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Tetrahedron: Asymmetry
Tetrahedron: *Asymmetry* 15 (2004) 2621–2631

Synthesis of chiral monodentate binaphthophosphepine ligands and their application in asymmetric hydrogenations

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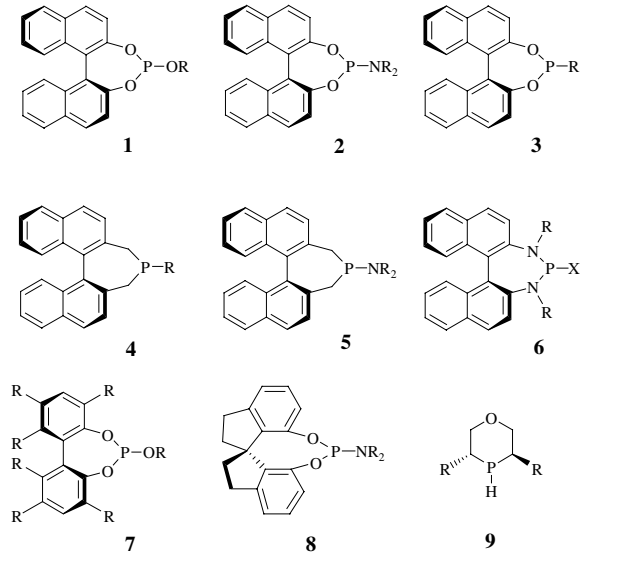
Received 1 June 2004; accepted 1 July 2004

Abstract—A general synthesis of chiral monodentate 4,5-dihydro-3*H*-dinaphthophosphepines **4** and a detailed study of the catalytic performance of the resulting ligands **4a**–**n** in benchmark hydrogenation reactions is presented. Hydrogenation of methyl α-acetamidocinnamate **11** and methyl α-acetamidoacrylate **13** proceeded with enantioselectivities up to 95% and 94%, respectively. The best enantioselectivity for the rhodium-catalyzed hydrogenation of dimethyl itaconate **15** was 88%.

1. Introduction

Transition metal-catalyzed asymmetric reactions offer an efficient and elegant possibility for the synthesis of enantiomerically pure compounds.[1] Among the different transition metal-catalyzed enantioselective reactions, hydrogenations of olefins, imines and ketones have been used extensively over the last two decades and are likely to provide the most important accesses to pharmaceutical intermediates.[2] In general, optically active bidentate phosphine ligands have been viewed as essential in order to achieve high selectivities and excellent control in a number of catalytic asymmetric hydrogenation reactions.[3]

However more recently, based on the important discovery by Reetz and co-workers (phosphites **1**),[4] Feringa et al. (phosphoramidites **2**),[5] Pringle et al. (phosphonites **3**)[6] monodentate ligands have become increasingly important for various catalytic asymmetric hydrogenations.[7] A selection of monodentate ligands that have recently been obtained (2002–2004) is presented in Scheme 1. To date, phosphites and phosphoramidites with a 2,2′-binaphthol core have attracted considerable interest.[8] Furthermore, biphenyl-based monodentate ligands



Scheme 1. Selection of recent chiral monodentate phosphorus containing ligands.

7 were introduced by Chen and Xiao[9] and Ojima et al.[10] Recently, Zhou et al.[11] also developed a monophosphoramidite ligand named SIPHOS **8** containing a 1,1′-spirobiindane-7,7′-diol backbone.

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doi:10.1016/j.tetasy.2004.07.022

Apart from phosphites and phosphoramidites, monodentate phosphine ligands are also of interest due to their often increased stability against hydrolysis and easier purification when compared to the corresponding P–O ligands. An interesting example of a monodentate secondary phosphine **9**,[12] which gives excellent enantioselectivities in the Rh-catalyzed hydrogenation of itaconates, has been reported by Helmchen et al.

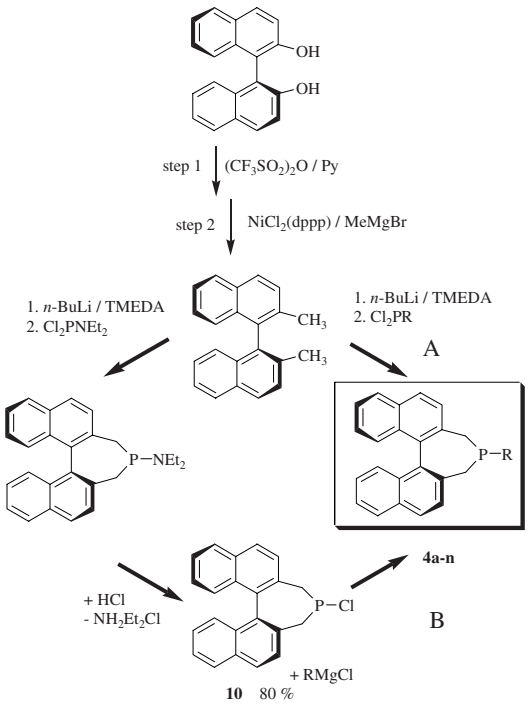
Similar to the 2,2′-binaphthol core, the corresponding carba analogue (2,2′-bismethylenbinaphthyl) proved to be a structural unit, which induces high stereoselectivity in asymmetric hydrogenations.[13] Therefore, Gladiali et al.,[14] Chi and Zhang[15] and ourselves[16] introduced independently new monodentate phosphines based on a 4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]phosphepine **4**.

In previous communications we briefly described the synthesis of ligands **4**[16] and **5**[17] and their use in different benchmark hydrogenation reactions. Herein, we report a full account of our work on the synthesis and characterization of 14 monodentate ligands of this type and their application in the hydrogenation of dehydroamino acid methyl esters and dimethyl itaconate.

2. Results and discussion

Our general synthesis of the different 4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]phosphepine ligands **4** started from enantiomerically pure 2,2′-binaphthol, which is available on a large scale and is relatively inexpensive. Esterification with trifluoromethanesulfonic acid anhydride in the presence of pyridine gave the corresponding diester in 99% yield. Subsequent nickel-catalyzed Grignard reaction with methyl magnesium bromide in diethyl ether leads to enantiomerically pure (ee >99%) 2,2′-dimethylbinaphthyl in 95% yield.

As shown in Scheme 2, two synthetic routes were used to prepare 14 different 4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]phosphepine ligands **4** from homochiral 2,2′-dimethylbinaphthyl. The first synthesis involved the double metallation of 2,2′-dimethylbinaphthyl with *n*-butyl lithium in the presence of TMEDA (tetramethylethylenediamine) and quenching with commercially available dichlorophosphines gave ligands **4a** (P-ethyl), **4c** (P-*tert* butyl) and **4d** (P-phenyl) in 60–83% yield. On the other hand double metallation, quenching with diethylaminodichloro-phosphine and subsequent reaction with HCl gave the corresponding chlorophosphepine **10** in 80% yield. It is interesting to note that this chlorophosphepine is a valuable building block for the synthesis of a variety of substituted 4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]phosphepines by simple Grignard reaction. Hence, ligands **4b** (P-isopropyl), and **4e**–**n** (P-aryl) were prepared without optimization in 62–76% yield. In general, the Grignard reagents were prepared from commercially available alkyl or aryl halides and 1.2 equiv of magnesium turnings. In the case of the 3,5-di-*t*-butyl-1-bromobenzene and 2-bromonaphthalene, the preparation of the Grignard solution caused some problems because of the sterically demanding substituents. Hence, ligand **4h** (3,5-(*t*-Bu)$_2$–C$_6$H$_3$–P) gave a somewhat lower yield (50%) and **4l** (P-2-naphthyl) was obtained with a lower purity. Advantageously, monodentate phosphepines **4b**, **4c** and **4e** (4-CH$_3$O–C$_6$H$_4$–P) can be purified by simple crystallization from toluene or toluene/methanol.



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

All ligands were characterized by NMR, IR, mass spectroscopy and elemental analysis. In addition, the structure of the isopropyl-substituted **4b** and the 4-methoxyphenyl-substituted **4e** phosphepine ligands were confirmed by X-ray crystallography (Figs. 1 and 2).[18]

As expected in both compounds **4b** and **4e**, the phosphorus atom is arranged in a trigonal pyramidal structure.

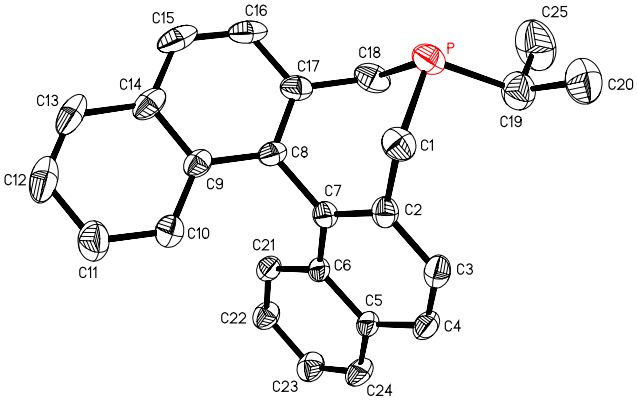


Figure 1. ORTEP plot of compound **4b**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 30% probability.

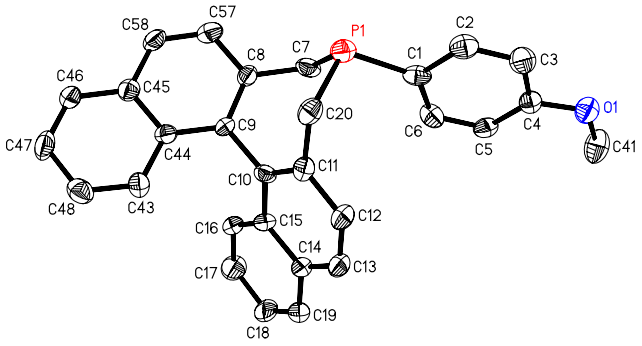


Figure 2. ORTEP plot of compound **4e**. Only one of the both symmetry-independent molecules of the asymmetric unit is depicted. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 30% probability.

Table 1. Selected bond lengths [Å] and angles [°] of **4b** and **4e**

Ligand **4b**		Ligand **4e**[a]	
P–C1	1.871(3)	P1–C20	1.861(6)
		(P2–C40)	1.867(7)
P–C18	1.867(4)	P1–C7	1.839(6)
		(P2–C27)	1.842(6)
P–C19	1.845(4)	P1–C1	1.829(7)
		(P2–C21)	1.819(6)
C19–P–C18	100.4(2)	C1–P1–C7	102.2(3)
		(C21–P2–C27)	104.3(3)
C19–P–C1	100.6(2)	C1–P1–C20	104.1(3)
		(C21–P2–C40)	101.1(3)
C18–P–C1	98.38(15)	C7–P1–C20	99.2(3)
		(C27–P2–C40)	98.5(3)

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

Selected bond lengths and angles are shown in Table 1. The exocyclic P–C bond (**4b**: P–C19; **4e**: P1–C1) is slightly shorter in both molecules then the P–C bonds in the phosphepine ring.

^{1}H and ^{13}C NMR spectra of ligands **4** show the non-equivalence of the methylene groups and both naphthalene ring systems of the 1,1′-binaphthalene-2,2′-bis(methylene) backbone. Two ^{13}C doublets for the CH_2 groups are observed were different P–C coupling constants. For the diastereotopic CH_2 protons, in general, four sets of double doublets are displayed in the ^{1}H NMR spectra due to geminal $^{1}H,^{1}H$ and $^{31}P,^{1}H$ couplings. The ^{31}P spectra of **4a**–**n** show a signal in the range of $\delta = -3$ to +28.

With a number of chiral monodentate ligands in hand, we were interested in their catalytic behaviour. As model reactions, the asymmetric hydrogenation of methyl (*Z*)-α-acetamidocinnamate **11** (Table 2), methyl α-acetamidoacrylate **13** (Table 3) and dimethyl itaconate **15** (Table 4) were studied at ambient pressure. All these reactions are generally accepted as typical benchmark tests for chiral ligands.

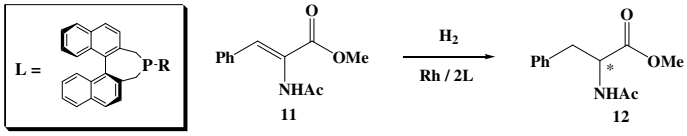
Initial hydrogenation experiments with methyl α-acetamidocinnamate **11** as substrate were carried out using different solvents. The best results were obtained in toluene, ethyl acetate or a mixture of toluene/SDS (sodium dodecylsulfonate) as the reaction medium. Thus, these solvents were tested with most of the prepared ligands **4a**–**n**. Selected results of this study are shown in Table 2. As a pre-catalyst, a mixture of 1 mol% $[Rh(COD)_2]BF_4$ and 2 mol% of the respective ligand was used. In order to compare catalyst activities, the time necessary for achieving 50% conversion (*t*/2) was measured.

Although toluene is an unusual solvent for asymmetric hydrogenation reactions of α-amino acid precursors, when applying P-aryl substituted 4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]phosphepines **4d**–**n** as ligands, enantioselectivities between 70% and 90% ee were observed. Interestingly, the addition of the tenside SDS led in most cases to a slight increase (5–10%) in the enantioselectivity (Table 2, compare entries 4–5, 9–10, 14–15, 18–19).[19] The reason for this effect is still unclear. Notably, the catalyst activity in ethyl acetate is significantly higher when compared to toluene because of the formation of arene complexes in the latter case (Table 2, entry 6 vs 7; 20 vs 21).[20] Thus, it is possible to decrease the catalyst concentration by one order of magnitude without a significant change of selectivity. Notably, the substituents on the phenyl group displayed a significant influence on the hydrogenation activity. While electron-withdrawing substituents decrease the activity (vide supra), electron-donating groups increase it. In toluene, high catalyst activities were obtained using the simple alkyl-substituted ligands **4a** and **4b**, as well as the 4-methoxyphenyl-substituted ligand **4e** and the 3,5-(*t*-Bu)$_2$-phenyl-substituted ligand **4h** (TOF = 1.000–3.000 h^{-1} at 50% conversion).

A comparison of the structures of ligands **4** demonstrated the necessity of a P-aryl group for obtaining good enantioselectivity. Hence, alkyl-substituted phosphepine ligands only gave disappointing enantioselectivities (<50%) in the model reaction. Interestingly, both the substitution of the electron-donating (OMe) as well as the electron-withdrawing substituents (F, CF_3) at the 4-position of the phenyl group resulted in a decrease in enantioselectivity (Table 2, entries 4, 6, 8, 16). Similar substitutions at the 2-position of the phenyl group also led to a slight decrease in the enantioselectivity (Table 2, entries 13, 14, 18). When using bulky substituents at the 3- and 5-position (**4h**), a further increase of the enantioselectivity above 95% ee was not observed (Table 2, entry 11).

Next, the asymmetric hydrogenation of methyl α-acetamidoacrylate **13** was investigated in more detail. Again the influence of different solvents and ligands studied. Only the best results for the respective ligands are shown in Table 3. In general, the ee's were significantly lower when compared to the hydrogenation of methyl α-acetamidocinnamate **11**. For example the alkyl-substituted derivatives **4a**–**c** gave 5–20% ee (Table 3, entries 1–3) while the phenyl-substituted ligand **4d** led only to 67% ee (Table 3, entry 4). The influence of different substituents on the phenyl group can not be rationalized easily. The best enantioselectivity (94% ee) was obtained in the

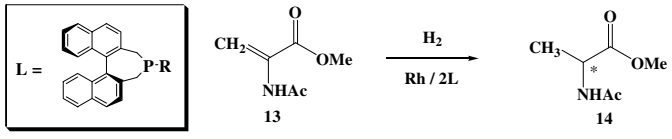
Table 2. Asymmetric hydrogenation of methyl α-acetamidocinnamate **11**



Entry	Ligand	R =	Solvent	*t*/2 [min]	Conversion %	Ee % (*R*)
1[a]	**4a**	Et	Toluene	6	>99	47
2[a]	**4b**	*i*-Pr	Toluene	4	>99	50
3[a]	**4c**	*t*-Bu	Toluene	31	>99	20
4[a]	**4d**	Ph	Toluene	50	>99	90
5[b]	**4d**	Ph	Toluene + SDS	33	>99	**95**
6[a]	**4e**	4-CH_3O–C_6H_4	Toluene	2	>99	74
7[a]	**4e**	4-CH_3O–C_6H_4	Ethyl acetate	4	>99	88
8[a]	**4f**	4-CF_3–C_6H_4	Toluene	36	>99	82
9[a]	**4g**	3,5-$(CH_3)_2$–C_6H_3	Toluene	17	>99	67
10[b]	**4g**	3,5-$(CH_3)_2$–C_6H_3	Toluene + SDS	15	>99	81
11[a]	**4h**	3,5-(*t*-Bu)$_2$–C_6H_3	Toluene	2	>99	**95**
12[b]	**4h**	3,5-(*t*-Bu)$_2$–C_6H_3	Toluene + SDS	2	>99	**95**
13[a]	**4i**	2-CH_3O–C_6H_4	Toluene	59	>99	64
14[a]	**4j**	2-F–C_6H_4	Toluene	13	>99	87
15[b]	**4j**	2-F–C_6H_4	Toluene + SDS	53	>99	91
16[a]	**4k**	4-F–C_6H_4	Toluene	160	>99	73
17[b]	**4k**	4-F–C_6H_4	Toluene + SDS	126	>99	86
18[a]	**4l**	2-Naphthyl	Toluene	22	>99	88
19[b]	**4l**	2-Naphthyl	Toluene + SDS	50	>99	**94**
20[a]	**4m**	3-CH_3O–C_6H_4	Toluene	36	>99	83
21[a]	**4m**	3-CH_3O–C_6H_4	Ethyl acetate	5	>99	88
22[a]	**4n**	3,4-$(CH_3O)_2$–C_6H_3	Toluene	—	>99	**93**

[a] Reaction conditions: 1.0 mmol substrate; 0.01 mmol $[Rh(COD)_2]BF_4$; cat.:ligand = 1:2; 15 mL solvent; 25 °C, 1 bar H_2.
[b] Reaction conditions like [a] + 0.2 mmol SDS.

Table 3. Asymmetric hydrogenation of methyl α-acetamidoacrylate **13**

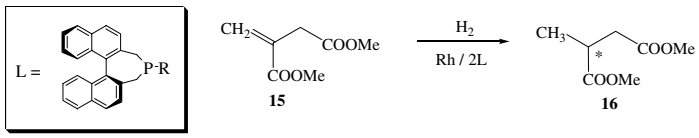


Entry	Ligand	R =	Solvent	*t*/2 [min]	Conversion %	Ee % (*R*)
1[a]	**4a**	Et	Toluene	6	>99	5
2[a]	**4b**	*i*-Pr	Toluene	4	>99	20
3[a]	**4c**	*t*-Bu	Toluene	—	99	15 (*S*)
4[a]	**4d**	Ph	Toluene	18	>99	67
5[a]	**4e**	4-CH_3O–C_6H_4	Ethyl acetate	2	>99	51
6[a]	**4f**	4-CF_3–C_6H_4	Ethyl acetate	2	>99	57
7[a]	**4g**	3,5-$(CH_3)_2$–C_6H_3	Ethyl acetate	2	>99	43
8[a]	**4h**	3,5-(*t*-Bu)$_2$–C_6H_3	Toluene	1	>99	**94**
9[b]	**4i**	2-CH_3O–C_6H_4	Toluene	58	>99	55
10[a]	**4j**	2-F–C_6H_4	Toluene	7	>99	76
11[b]	**4j**	2-F–C_6H_4	Toluene + SDS	20	>99	84
12[a]	**4k**	4-F–C_6H_4	Toluene	95	>99	49
13[b]	**4k**	4-F–C_6H_4	Toluene + SDS	106	>99	73
14[a]	**4l**	2-Naphthyl	Toluene	34	97	64
15[b]	**4l**	2-Naphthyl	Toluene + SDS	33	97	75
16[a]	**4m**	3-CH_3O–C_6H_4	Toluene	16	>99	75
17[b]	**4m**	3-CH_3O–C_6H_4	Toluene + SDS	17	>99	86
18[a]	**4n**	3,4-$(CH_3O)_2$–C_6H_3	Ethyl acetate	—	98	56

[a] Reaction conditions: 1.0 mmol substrate; 0.01 mmol $[Rh(COD)_2]BF_4$; cat.:ligand = 1:2; 15 mL solvent; 25 °C, 1 bar H_2.
[b] Reaction conditions like [a] + 0.2 mmol SDS.

presence of **4h** with bulky *tert*-butyl groups at the 3- and 5-position of the phenyl ring (Table 3, entry 8). Comparably high selectivities (84–86% ee) were also obtained with the 2-fluorophenyl- and 3-methoxyphenyl-substituted ligands **4j** and **4m** (Table 3, entries 11 and 17). With regard to activity, similar trends were observed

Table 4. Asymmetric hydrogenation of dimethyl itaconate **15**



Entry	Ligand	R =	Solvent	*t*/2 [min]	Conversion %	Ee % (*S*)
1[a]	**4a**	Et	Toluene	180	>99	54
2[a]	**4b**	*i*-Pr	Dichloromethane	—	>99	65
3[a]	**4c**	*t*-Bu	Dichloromethane	—	98	62
4[a]	**4d**	Ph	Dichloromethane	56	>99	**86**
5[a]	**4e**	4-CH_3O–C_6H_4	Ethyl acetate	6	>99	79
6	**4e**	4-CH_3O–C_6H_4	Dichloromethane	—	>99	**86**
7[a]	**4f**	4-CF_3–C_6H_4	Ethyl acetate	14	>99	63
8[a]	**4g**	3,5-$(CH_3)_2$–C_6H_3	Ethyl acetate	26	>99	67
9[a]	**4h**	3,5-(*t*-Bu)$_2$–C_6H_3	Dichloromethane	16	>99	83
10[a]	**4i**	2-CH_3O–C_6H_4	Dichloromethane	—	7	22
11[a]	**4j**	2-F–C_6H_4	Dichloromethane	16	86	77
12[a]	**4k**	4-F–C_6H_4	Ethyl acetate	13	>99	65
13[a]	**4l**	2-Naphthyl	Dichloromethane	34	29	70
14[a]	**4m**	3-CH_3O–C_6H_4	Dichloromethane	—	>99	**88**
15[a]	**4n**	3,4-$(CH_3O)_2$–C_6H_3	Dichloromethane	—	32	66

[a] Reaction conditions: 0.5 mmol substrate; 0.005 mmol $[Rh(COD)_2]BF_4$; cat.:ligand=1:2; 7.5 mL solvent; 25 °C, 1 bar H_2.

when compared to the hydrogenation of methyl α-acetamidocinnamate **11**. Hence, good catalyst activity (TOF = 1.000–6.000 h^{-1} at 50% conversion) was seen with ligands **4a**, **4b**, **4e**–**h** and **4j**. Pleasingly, **4h**, which showed the best enantioselectivity induces also the highest activity.

Initially, the asymmetric hydrogenation of dimethyl itaconate **15** proved to be the most difficult test reaction (Table 4). Here, in toluene and toluene/SDS, a significantly lower catalyst activity was observed (compare entry 1 in Tables 2–4). In addition, in most cases lower enantioselectivities were observed. Surprisingly, the highest observed enantioselectivity was when using toluene as the solvent for ligand **4a** (Table 4, entry 1).

However, by changing the solvent to dichloromethane or ethyl acetate moderate to good enantioselectivities were obtained. For example, the phenyl- and *p*-methoxy-phenyl-substituted derivatives **4d** and **4e** gave 86% ee.

The best selectivity (88% ee) seen was by applying **4m** as ligand.

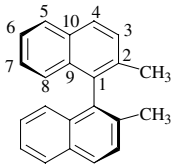
3. Conclusion

In conclusion, the synthesis and characterization of 14 different enantiomerically pure monodentate dinaphtho-phosphepine ligands **4** has been described in detail. Several members of this class are presented here for the first time. In general, this class of chiral ligands is easily available in 3–5 steps from commercially available 2,2′-binaphthol on 10 g scale. By using the corresponding chlorodinaphtho-phosphepine **10**, a toolbox of chiral ligands can be synthesized in one step. Aryl-substituted dinaphthophosphepine ligands **4d**–**n** led to good enantioselectivities in various rhodium-catalyzed hydrogenations. Hence, reactions of methyl α-acetamidocinnamate **11** proceeded up to 95% ee and for methyl α-acetamidoacrylate **13** up to 94% ee, while the best enantioselectivity for the hydrogenation of dimethyl itaconate **15** obtained was 88%.

4. Experimental

^1H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker spectrometer ARX 400 (^1H: 400.13 MHz, ^{13}C: 100.6 MHz, ^{31}P: 162.0 MHz). The calibration of ^1H and ^{13}C spectra was carried out on solvent signals [$\delta(CDCl_3)$ = 7.27 and 77.0; $\delta(C_6D_6)$ = 7.15 and 128.0; $\delta(CD_3COCD_3)$ = 2.05 and 29.8]. The ^{31}P chemical shifts are referenced to 85% H_3PO_4. The ^1H and ^{13}C NMR signals were assigned by DEPT and two-dimensional ^1H,^1H COSY and ^1H,^{13}C correlation spectra. The differentiation between the signals of both nonequivalent naphthalenes, if possible, and the assignment of these rings to the CH_2 and CH_2' groups, respectively, were based on long-range correlation (HMBC) and ^1H,^1H NOESY spectra recorded for compounds **4c** and **4d**. Mass spectra were recorded on an AMD 402 spectrometer. Elemental analyses were performed in a Leco CHNS-932. 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 experiments were carried out under an argon atmosphere. Enantiomerically pure 2,2′-dimethylbinaphthyl was obtained in 92% overall yield from enantiomerically pure 2,2′-binaphthol via esterification with trifluoromethanesulfonic acid anhydride in pyridine and subsequent Ni-catalyzed Grignard reaction with MeMgBr.

4.1. (*S*)-2,2′-Dimethylbinaphthyl



Yield: 95%. ^{1}H NMR (400 MHz, acetone-d_6): δ = 2.01 (s, 6H, CH_3); 6.97 (d″q″, $J_{7,8}$ = 8.5 Hz, 3× J = 1.2 Hz, 2H, H-8); 7.22 (ddd, $J_{7,8}$ = 8.5 Hz, $J_{6,7}$ = 6.6 Hz, $J_{5,7}$ = 1.2 Hz, 2H, H-7); 7.41 (ddd, $J_{5,6}$ = 8.3 Hz, $J_{6,7}$ = 6.6 Hz, $J_{6,8}$ = 1.2 Hz, 2H, H-6); 7.57 (d, $J_{3,4}$ = 8.5 Hz, 2H, H-3); 7.95 (br d, 2H, H-4,5). ^{13}C NMR (100.6 MHz, acetone-d_6): δ = 20.1 (CH_3); 125.9 (C-6); 126.0 (C-8); 127.0 (C-7); 128.5, 129.1 (C-4,5); 129.5 (C-3), 133.4, 133.6 (C-9,10); 134.9 (C-1); 135.8 (C-2). IR (Nujol, KBr): 3045w, 2953s, 2857s, 1617w, 1594w, 1506w, 1463s, 1421w, 1378m, 1352w, 1261w, 1221w, 1158w, 1143w, 1028w, 958w, 898w, 863w, 810s, 796m, 783m, 775m, 742s, 720m, 662w, 621m, 574w, 483w, 416m. MS (ESI): *m*/*z* (%) = 282 ([M$^+$], 100); 267 ([M$^+$−Me], 50); 252 ([M$^+$−2Me], 27); 239 (12); 133 (25); 126 (15); 69 (8); 58 (7); 28 (13). Anal. Calcd for $C_{22}H_{18}$ (%): C, 93.57; H, 6.43. Found: C, 93.22; H, 6.58. $[\alpha]_D^{23} = +14.5$ (*c* 1, toluene).

4.2. General procedure for the synthesis of 4

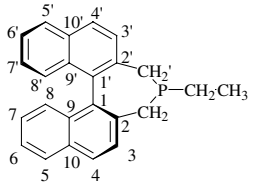
Procedure A: Metallation[15] of enantiomerically pure 2,2′-dimethyl-binaphthyl with *n*-BuLi/TMEDA afforded the crystalline dilithio species in 70–80% yield. Starting from 12 mmol dilithium salt of homochiral 2,2′-dimethylbinaphthyl in 35 mL hexane, 13.6 mmol phenyl dichlorophosphine in 15 mL hexane was added at 0 °C. After 2 h refluxing, the reaction mixture was quenched with water/toluene. The organic layer was separated and dried over $MgSO_4$. Ligand **4** was purified by column chromatography in toluene or crystallized from toluene/methanol.

Procedure B: Starting from 30 mmol of the dilithium salt of 2,2′-dimethyl-1,1′-binaphthyl in 100 mL hexane, 34 mmol Cl_2PNEt_2 in 30 mL hexane was added at 0 °C (30–45 min). After 2 h refluxing, the hexane was removed and 100 mL toluene added. LiCl was filtrated under inert conditions and washed with 50 mL toluene. The toluene was then removed from the filtrate. The yellow solid compound was suspended in 200 mL cyclohexane. HCl was bubbled through the stirred suspension for 1 h at 0 °C and then argon for an additional hour through the reaction mixture. The precipitate was removed by filtration to give a clear yellow solution. Rotation of the filtrate gave the corresponding chlorophosphine **10** (light yellow foam) in 80% yield.

Compound **10** (6.2 mmol) was dissolved in 20 mL THF. The corresponding Grignard solution (1.1 equiv) prepared from Mg and aryl or alkylhalides in THF was added during 30 min. After 2 h refluxing, the reaction mixture was quenched with water/toluene. The organic layer was separated and dried over $MgSO_4$. Ligand **4** was purified by column chromatography in toluene or crystallized from toluene/methanol.

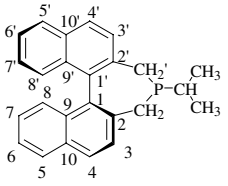
Compounds **4a**, **4c** and **4d** were synthesized by procedure A, ligands **4b** and **4e**–**n** by procedure B.

4.2.1. 4-Ethyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]-phosphepine 4a.



Yield: 74%. ^{1}H NMR (400 MHz, C_6D_6): δ = 0.93 (dt, 3H, $J_{P,H}$ = 15.2 Hz, $J_{H,H}$ = 7.6 Hz, CH_3); 1.08–1.15 (m, 2H, CH_2CH_3); 1.98 (dd, 1H, $J_{H,H}$ = 11.7 Hz, $J_{P,H}$ = 4.0 Hz, CH_2(a)); 2.18 (dd, 1H, $J_{H,H}$ = 14.3 Hz, $J_{P,H}$ = 6.4 Hz, CH'_2(a)); 2.54 (dd, 1H, $J_{P,H}$ = 8.2 Hz, CH'_2(b)); 2.55 (dd, 1H, $J_{P,H}$ = 17.2 Hz, CH_2(b)); 6.95–7.01 (m, 2H, H-7,7′); 7.01 (d, 1H, H-8); 7.16–7.22 (m, 2H, H-6,6′); 7.39–7.46 (2d, 1dd, 3H, H-3,3′,8′); 7.69–7.76 (4d, 4H, H-4,4′,5,5′). ^{13}C NMR (100.6 MHz, C_6D_6): δ = 10.1 (d, J = 16.2 Hz, CH_3); 19.0 (d, J = 17.2 Hz, CH_2CH_3); 29.1 (d, J = 22.0 Hz, CH_2); 32.5 (d, J = 18.0 Hz, CH_2); 125.17, 125.2 (C-6,6′); 126.3, 126.4 (C-7,7′); 127.07, 127.15 (C-8,8′); 127.4 (d, C-3); 127.6–128.6 (C-3′,4,4′,5,5′); 132.8–133.9 (C-1,1′,2,2′,9,9′,10,10′). ^{31}P NMR (162 MHz, C_6D_6): δ = 8.5. IR (Nujol): 2953s, 2843s, 1618w, 1591w, 1507m, 1457s, 1422w, 1377m, 1247w, 1224w, 1160w, 1144w, 1063w, 1025m, 993w, 958w, 935m, 864m, 828s, 821s, 804s, 775m, 747s, 676m, 658w, 634w, 620w, 566m, 520m. MS (ESI): *m*/*z* (%) = 340 ([M$^+$], 100); 311 ([M$^+$−Et], 47); 276 (23); 265 (63); 252 (7); 183 (12); 170 (14); 138 (21); 91 (2); 75 (1); 63 (2); 41 (2). HRMS calcd for $C_{24}H_{21}P$: 340.13809. Found: 340.13792. $[\alpha]_D^{23} = +301$ (*c* 1, toluene).

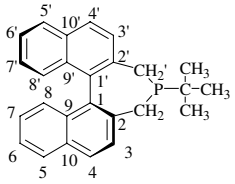
4.2.2. 4-*i*-Propyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]-phosphepine 4b.



Yield: 81%. ^{1}H NMR (400 MHz, C_6D_6): δ = 0.79 (dd, 3H, $J_{P,H}$ = 13.9 Hz, $J_{H,H}$ = 7.0 Hz, CH_3); 1.06 (dd, 3H, $J_{P,H}$ = 14.8 Hz, $J_{H,H}$ = 7.0 Hz, CH_3); 1.29 (m, 1H, CH); 2.12 (dd, 1H, $J_{H,H}$ = 11.5 Hz, $J_{P,H}$ = 4.0 Hz, CH_2(a)); 2.43 (dd, 1H, $J_{H,H}$ = 14.5 Hz, $J_{P,H}$ = 6.8 Hz, CH'_2(a)); 2.53 (dd, 1H, $J_{P,H}$ = 8.1 Hz, CH'_2(b)); 2.63 (dd, 1H, $J_{P,H}$ = 17.3 Hz, CH_2(b)); 6.95–7.01 (m, 2H, H-7,7′); 7.10 (d, 1H, H-8); 7.17–7.22 (m, 2H, H-6,6′); 7.39–7.48 (2d, 1dd, 3H, H-3,3′,8′); 7.68–7.76 (4d, 4H, H-4,4′,5,5′); ^{13}C NMR (100.6 MHz, C_6D_6): δ = 18.9 (d, J = 17.2 Hz, CH_3); 20.1 (d, J = 18.1 Hz, CH_3); 24.8 (d, J = 15.3 Hz, CH); 28.2 (d, J = 24.8 Hz, CH_2); 31.8

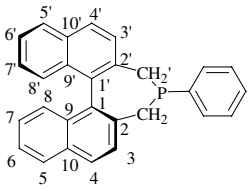
(d, $J = 20.0$ Hz, CH_2); 125.2 (C-6,6′); 126.3, 126.4 (C-7,7′), 127.1, 127.2 (C-8,8′); 127.6 (C-3), 127.7–128.6 (C-3′,4,4′,5,5′); 132.8–134.4 (C-1,1′,2,2′,9,9′,10,10′). ^{31}P NMR (162 MHz, C_6D_6): $\delta = 21.8$. IR (Nujol): 2945s, 2851s, 1616w, 1589w, 1507w, 1463s, 1419w, 1378s, 1329w, 1248w, 1224w, 1187w, 1144w, 1025w, 948w, 938w, 864m, 831m, 824m, 750m, 673w, 658w, 628w, 566w, 520w. MS (ESI): *m/z* (%) = 354 ([M^+], 86); 311 ([M^+-Pr], 100); 283 (35); 265 (63); 183 (11); 138 (14); 91 (5); 57 (2); 43 (13). Anal. Calcd for $C_{25}H_{23}P$ (%): C, 84.72; H, 6.54; P, 8.74. Found: C, 84.43; H, 6.49; P, 8.69. $[\alpha]_D^{24} = +218$ (*c* 0.5, toluene).

4.2.3. 4-*t*-Butyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]phosphepine 4c.



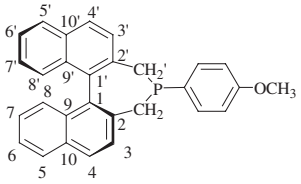
Yield: 60%. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.94$ (d, 9H, $J = 11.9$ Hz, CH_3); 2.54–2.66 (m, 4H, CH_2); 6.96 (d, 1H, H-8), 7.01–7.13 (m, 3H, H-7,7′,8′); 7.23–7.30 (m, 2H, H-6,6′); 7.33 (d, 1H); 7.50 (dd, 1H), (H-3,3′); 7.72–7.78 (m, 4H, H-4,4′,5,5′). ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 27.2$ (d, $J = 23.8$ Hz, CH_2); 27.3 (d, $J = 23.8$ Hz, CH_2); 28.3 (d, $J = 13.3$ Hz, CH_3); 29.3 (d, $J = 20.0$ Hz, $C(CH_3)_3$); 124.7, 124.8 (C-6,6′); 125.7, 125.8 (C-7,7′); 126.6, 126.8 (C-8,8′); 127.4 (d, C-3); 127.6 (C-4′); 128.0, 128.2, 128.3 (C-4,5,5′); 129.0 (C-3′); 132.2 (d, C-1′); 132.05, 132.15, 132.5, 133.1 (C-9,9′,10,10′); 132.8 (C-1); 134.5 (C-2′); 134.9 (C-2). ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = 29.8$. IR (Nujol): 2935s, 2860s, 1615w, 1591w, 1507w, 1458s, 1420w, 1377m, 1359m, 1331w, 1248m, 1225w, 1206w, 1173m, 1143w, 1063w, 1026w, 963w, 948w, 933m, 868m, 832s, 812w, 791w, 773w, 750s, 739w, 674m, 621m, 567w, 521m. MS (ESI): *m/z* (%) = 368 ([M^+], 57); 311 ([M^+-Bu], 100); 283 (20); 265 (61); 183 (4); 138 (5); 91 (1); 57 (4); 41 (4). Anal. Calcd for $C_{26}H_{25}P$ (%): C, 84.75; H, 6.84; P, 8.41. Found: C, 84.21; H, 6.70; P, 8.34. $[\alpha]_D^{24} = +304$ (*c* 0.5, toluene).

4.2.4. 4-Phenyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]-phosphepine 4d.



Yield: 83%. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.66$ (dd, 1H, $J_{H,H} = 14.3$ Hz, $J_{P,H} = 4.8$ Hz, CH_2(a)); 2.77 (dd, 1H, $J_{P,H} = 11.3$ Hz, CH_2(b)); 2.82 (dd, 1H, $J_{H,H} = 11.5$ Hz, $J_{P,H} = 3.0$ Hz, CH_2'(a)); 2.91 (dd, 1H, $J_{P,H} = 14.3$ Hz, CH_2'(b)); 6.81 (d, 1H, H-3′); 7.11–7.22 (m, 9H, H-7,7′,8,8′, Ph); 7.30–7.36 (m, 2H, H-6,6′); 7.57 (dd, 1H), 7.61 (d, 1H), (H-3,4′); 7.79 (d, 1H, H-5′); 7.83–7.86 (2d, 2H, H-4,5′). ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 30.3$ (d, $J = 16.2$ Hz, CH_2); 32.2 (d, $J = 22.0$ Hz, CH_2'); 124.8, 125.0 (C-6,6′); 125.8, 125.9 (C-7,7′); 126.6, 126.7 (C-8,8′); 127.4 (d, C-3); 127.5 (C-4′); 128.0 (C-3′); 128.1–128.7 (C-4,5,5′, *m*-Ph, *p*-Ph); 131.6 (d, *o*-Ph); 132.2 (d, C-1′); 131.9, 132.3, 132.7, 132.8 (C-9,9′,10,10′); 133.5 (d, C-2′); 133.7 (d, C-1); 134.3 (C-2); 137.5 (d, *i*-Ph). ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = 7.8$. IR (Nujol): 2948s, 2870s, 1616w, 1590w, 1507w, 1463s, 1377s, 1248w, 1159w, 1101w, 1063w, 1025m, 934m, 864m, 827s, 749s, 695m, 669w, 657w, 620w, 566w, 520w. MS (ESI): *m/z* (%) = 388 ([M^+], 100); 282 ([$M^+-P-C_6H_5$], 20); 265 (20); 194 (5); 155 (10); 91 (3); 39 (1). Anal. Calcd for $C_{28}H_{21}P$ (%): C, 86.58; H, 5.45; P, 7.79. Found: C, 85.99; H, 5.47; P, 8.03. $[\alpha]_D^{23} = -27$ (*c* 0.5, toluene).

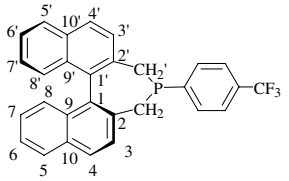
4.2.5. 4-(4-Methoxy)-phenyl-4,5-dihydro-3*H*-dinaphtho-[2,1-*c*;1′,2′-*e*]phosphepine 4e.



Yield: 76%. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.68$ (dd, 1H, $J_{H,H} = 14.5$ Hz, $J_{P,H} = 4.2$ Hz, CH_2(a)); 2.87 (dd, 1H, $J_{P,H} = 11.0$ Hz, CH_2(b)); 2.92–3.00 (dq, 2H, $J_{H,H} = 12.0$ Hz, $J_{P,H} = 14.8$ Hz, $J_{P,H} = 2.2$ Hz, CH_2'); 3.82 (s, 3H, CH_3O); 6.84 (m, 2H, *m*-PC_6H_4); 6.95 (d, 1H, H-3′); 7.17 (m, 2H, *o*-PC_6H_4); 7.23–7.28 (m, 3H), 7.31 (d, 1H), (H-7,7′,8,8′); 7.42–7.46 (m, 2H, H-6,6′); 7.66 (dd, 1H, H-3′); 7.77 (d, 1H, H-4′); 7.91–7.96 (3d, 3H, H-4,5,5′). ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 30.7$ (d, $J = 13.5$ Hz, CH_2); 32.6 (d, $J = 20.0$ Hz, CH_2'); 55.2 (CH_3O); 113.9 (d, *m*-PC_6H_4); 124.9, 125.0 (C-6,6′); 125.8, 125.9 (C-7,7′); 126.7, 126.7 (C-8,8′); 127.3 (d, C-3); 127.4 (C-4′); 128.17, 128.25, 128.35, 128.41 (C-3′,4,5,5′); 132.0–132.9 (C-1′,9,9′,10,10′); 133.4 (C-2′); 133.6 (d, C-1); 133.7 (d, *o*-PC_6H_4); 134.3 (C-2); 160.6 (*p*-PC_6H_4). ^{31}P NMR (162 MHz, CD_2Cl_2): $\delta = 5.7$. IR (Nujol): 2945s, 2865s, 1591m, 1567w, 1497m, 1464s, 1377s, 1281m, 1246m, 1176m, 1092w, 1023m, 960w, 933w, 865w, 822m, 808m, 755m, 729m, 695w, 671w, 621w, 600w, 567w, 526w. MS (ESI): *m/z* (%) = 418 ([M^+], 100); 335 ([$M^+-MeOPh$], 45); 265 (30); 235 (15); 169 (100); 147 (63); 119 (30); 69 (70); 44 (17). Anal. Calcd for $C_{29}H_{23}PO$ (%): C, 83.20; H, 5.51; P, 7.41. Found: C, 82.78; H, 5.58; P, 7.59. $[\alpha]_D^{23} = -35$ (*c* 0.01, toluene).

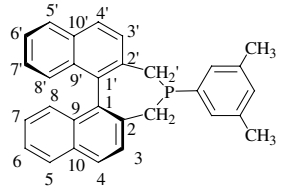
4.2.6. 4-(4-Trifluoromethyl)-phenyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]phosphepine 4f.

Yield: 70%. ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 2.83$ (dd, 1H, $J_{H,H} = 17.2$ Hz, $J_{P,H} = 3.5$ Hz, CH_2'(a)); 2.86 (d, 2H,



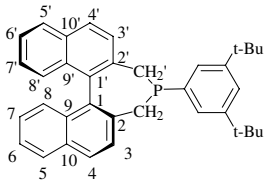
$J_{P,H}$ = 8.3 Hz, CH_2); 3.14 (dd, 1H, $J_{P,H}$ = 11.5 Hz, CH'_2(b)); 6.92 (d, 1H, H-3′); 7.15–7.25 (m, 6H, H-7,7′,8,8′, *o*-PC_6H_4); 7.36–7.45 (m, 2H, H-6,6′); 7.55 (d, 2H, *m*-PC_6H_4); 7.67–7.72 (2d, 2H, H-3,4′); 7.85–8.00 (3d, 3H, H-4,5,5′). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ = 30.5 (d, J = 18.1 Hz, CH_2); 32.0 (d, J = 24.0 Hz, CH'_2); 116.0 (q, CF_3); 125.3, 125.6 (C-6,6′); 126.2, 126.3 (C-7,7′); 126.8, 126.9 (C-8,8′); 127.5 (C-3); 127.8 (C-4′); 128.1, 128.5, 128.7, 128.8 (C-3′,4,5,5′); 130.2 (q, *p*-PC_6H_4); 131.7 (d, *o*-PC_6H_4); 132.2–133.6 (C-1,1′,2′,9,9′,10,10′); 134.2 (C-2); 143.9 (d, *i*-PC_6H_4). ^{31}P NMR (162 MHz, CD_2Cl_2): δ = 8.2. IR (Nujol): 2958s, 2830s, 1607m, 1592w, 1507m, 1463s, 1395m, 1377m, 1324s, 1249w, 1224w, 1168s, 1131s, 1060s, 1015m, 958m, 935m, 865m, 822s, 803m, 750s, 696m, 670w, 658w, 620w, 597w, 566w, 521w, 503w. MS (ESI): *m*/*z* (%) = 456 ([M^+], 100); 437 ([M^+−F], 2); 276 (16); 265 (27); 228 (6); 183 (3); 155 (7); 132 (5); 107 (3); 91 (2); 43 (1). HRMS calcd for $C_{29}H_{20}PF_3$: 456.12549. Found: 456.12298. $[\alpha]_D^{23} = -34.3$ (*c* 0.01, toluene).

4.2.7. 4-(3,5-Dimethyl)-phenyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]phosphepine 4g.



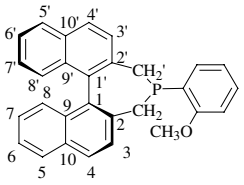
Yield: 83%. ^{1}H NMR 400 MHz, CD_2Cl_2): δ = 2.15 (s, 6H, CH_3); 2.81 (d, 2H, $J_{P,H}$ = 8.2 Hz, CH_2); 2.86 (dd, 1H, $J_{H,H}$ = 11.5 Hz, $J_{P,H}$ = 3.0 Hz, CH'_2(a)); 3.05 (dd, 1H, $J_{P,H}$ = 16.8 Hz, CH'_2(b)); 6.90 (d, 2H, *o*-PC_6H_3); 6.97 (d, 1H, *p*-PC_6H_3); 7.00 (d, 1H, H-3′); 7.18–7.28 (m, 4H, H-7,7′,8,8′); 7.39–7.47 (m, 2H, H-6,6′); 7.69 (dd, 1H); 7.76 (d, 1H), (H-3,4′); 7.90–8.00 (3d, 3H, H-4,5,5′). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ = 21.3 (d, J = 3.0 Hz); 30.8 (d, J = 17.2 Hz, CH_2); 32.1 (d, J = 23.0 Hz, CH'_2); 125.1, 125.3 (C-6,6′); 126.1, 126.2 (C-7,7′); 126.8, 126.9 (C-8,8′); 127.6 (d, C-3); 127.7 (C-4′); 128.4–128.6 (C-3,4,5,5′); 129.3 (d, *o*-PC_6H_3); 130.5 (*p*-PC_6H_3); 132.3–133.2 (C-1′,9,9′,10,10′); 134.0 (d, C-1); 134.3, 134.7 (C-2,2′); 137.9 (d, *i*-PC_6H_3); 138.0 (*m*-PC_6H_3). ^{31}P NMR (162 MHz, CD_2Cl_2): δ = 7.8. IR (Nujol): 2948s, 2870s, 1616w, 1590w, 1507w, 1463s, 1377s, 1248w, 1159w, 1101w, 1063w, 1025m, 934m, 864m, 827s, 749s, 695m, 669w, 657w, 620w, 566w, 520w. MS (ESI): *m*/*z* (%) = 388 ([M^+], 100); 282 ([M^+−P−C_6H_5], 20); 265 (20); 194 (5); 155 (10); 91 (3); 39 (1). HRMS calcd for $C_{30}H_{25}P$: 416.16940. Found: 416.16273. Optical rotation: $[\alpha]_D^{26} = +12$ (*c* 0.5, toluene).

4.2.8. 4-(3,5-Di-*t*-butyl)-phenyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]phosphepine 4h.



Yield: 61%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26 (m, 18H, CH_3); 2.73 (dd, 1H, $J_{H,H}$ = 14.3 Hz, $J_{P,H}$ = 4.5 Hz, CH_2(a)); 2.88 (dd, $J_{P,H}$ = 11.3 Hz, CH_2(b)); 2.91–3.00 (m, 2H, CH'_2); 7.02 (d, 1H, H-3′); 7.11 (2d, 2H, H-8,8′); 7.21–7.31 (m, 4H, H-7,7′, *o*-PC_6H_3); 7.38–7.44 (m, 3H, H-6,6′, *p*-PC_6H_3); 7.66 (dd, 1H), 7.76 (d, 1H), (H-3,4′); 7.88–7.95 (3d, 3H, H-4,5,5′). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 31.0 (d, J = 21.0 Hz, CH_2); 31.4 (CH_3); 32.1 (d, J = 21.0 Hz, CH'_2); 35.0 (*C*Me_3); 121.4 (*p*-PC_6H_3); 124.8, 125.0 (C-6,6′); 125.8, 125.9 (C-7,7′); 126.4 (d, *o*-PC_6H_3); 126.6, 126.7 (C-8,8′); 127.4 (d, C-3); 127.4 (d, C-4′); 128.1, 128.2, 128.4, 128.5 (C-3′,4,5,5′); 132.0, 132.3, 132.8, 132.9 (C-9,9′,10,10′); 132.1 (d, C-1′); 133.6 (d, C-1); 133.7 (C-2′); 134.6 (C-2); 135.5 (*i*-PC_6H_4); 150.9 (*m*-PC_6H_3). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 8.0. IR (Nujol): 2968s, 2874s, 1595w, 1563w, 1507w, 1462s, 1377m, 1364m, 1248w, 1217w, 1146w, 1027w, 932w, 864w, 810m, 741m, 705w, 660w, 622w, 566w, 543w. MS (ESI): *m*/*z* (%) = 500 ([M^+], 100); 444 ([M^+−Bu], 6); 387 ([M^+−2Bu], 1); 311 (2); 265 (10); 183 (1); 141 (1); 91 (1); 57 (6). HRMS calcd for $C_{36}H_{37}P$: 500.65274. Found: 500.65029. $[\alpha]_D^{26} = +48$ (*c* 0.5, toluene).

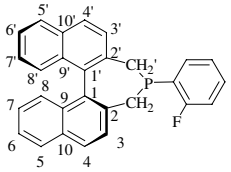
4.2.9. 4-(2-Methoxy)-phenyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]phosphepine 4i.



Yield: 62%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.75 (dd, 1H, $J_{H,H}$ = 14.0 Hz, $J_{P,H}$ = 13.3 Hz, CH_2(a)); 2.83 (dd, 1H $J_{H,H}$ = 11.5 Hz, $J_{P,H}$ = 2.4 Hz, CH'_2(a)); 3.03 (dd, 2H, $J_{H,H}$ = 10.8 Hz, CH'_2(b)); 3.20 (dd, 1H, $J_{P,H}$ = 2.4 Hz, CH_2(b)); 3.94 (s, 3H, CH_3O); 6.87 (d, 1H, H-3); 6.90–6.96 (m, 2H, *m*-, *m*′-PC_6H_4); 7.20–7.34 (m, 6H, H-7,7′,8,8′, *o*′-, *p*-PC_6H_4); 7.39–7.45 (m, 2H, H-6,6′); 7.65 (d, 1H), 7.71 (dd, 1H), (H-3,4′); 7.83–7.93 (3d, 3H, H-4,5,5′). ^{13}C NMR (100.6 MHz, $CDCl_3$), (not all signals are given): δ = 28.9 (d, J = 13.3 Hz, CH_2); 29.2 (d, J = 19.2 Hz, CH_2); 55.6 (CH_3O); 110.0 (*m*-PC_6H_4); 120.8 (*m*′-PC_6H_4); 124.9, 125.0 (C-6,6′); 125.7, 125.9 (C-7,7′); 126.6, 126.7 (C-8,8′); 132.1 (d, C-1′); 132.7 (d, C-2′); 133.9 (d, C-1); 134.3 (C-2); 160.2 (d, *o*-PC_6H_4). ^{31}P NMR (162 MHz, $CDCl_3$): δ = −2.32. IR (Nujol): 3050s, 2726w, 1591w, 1570w, 1507w, 1459s, 1430m, 1377m, 1239m, 1175w, 1161w, 1021m, 935w, 866w, 827m, 809m, 747s. MS (ESI): *m*/*z* (%) = 418 ([M^+], 100); 403 (4); 387 (6); 311 (2); 281

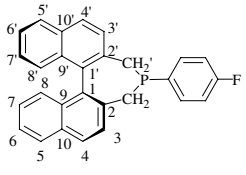
(39); 265 (44); 209 (8); 141 (14); 91 (18). HRMS calcd for $C_{29}H_{23}OP$: 418.14865. Found: 418.14840. $[\alpha]_D^{25} = -189$ (*c* 0.5, toluene).

4.2.10. 4-(2-Fluoro)-phenyl-4,5-dihydro-3*H*-dinaphtho-[2,1-*c*;1′,2′-*e*]phosphepine 4j.



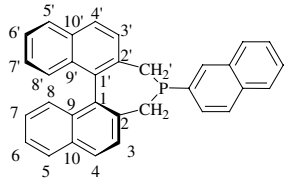
Yield: 67%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.82 ('t', 1H, $J_{H,H}$ = 14.5 Hz, $J_{P,H}$ = 14.2 Hz, CH_2'(a)); 2.87 (dd, 1H, $J_{H,H}$ = 11.5 Hz, $J_{P,H}$ = 2.5 Hz, CH_2(a)); 3.09 (dd, 1H, $J_{P,H}$ = 16.7 Hz, CH_2(b)); 3.13 (dd, 1H, $J_{P,H}$ = 4.5 Hz, CH_2'(b)); 6.95–7.00 (m, 3H, H-3′, *o*′-, *m*′-PC_6H_4); 7.08–7.18 (m, 1H, *m*-PC_6H_4); 7.20–7.34 (m, 5H, H-7,7′,8,8′, *p*-PC_6H_4); 7.44–7.50 (m, 2H, H-6,6′); 7.69 (d, 1H), 7.71 (dd, 1H), (H-3,4′); 7.90 (d, 1H), 7.99 (2d, 2H), (H-4,5,5′). ^{13}C NMR (100.6 MHz, $CDCl_3$), (not all signals are given): δ = 29.2 (dd, $J_{P,C}$ = 16.2 Hz, $J_{F,C}$ = 2.8 Hz, CH_2); 29.8 (dd, $J_{P,C}$ = 22.5 Hz, $J_{F,C}$ = 2.5 Hz, CH_2'); 115.1 (d, *m*-PC_6H_4); 124.1 (d, *m*′-PC_6H_4); 124.8, 125.1 (C-6,6′); 125.8, 125.9 (C-7,7′); 126.6, 126.7 (C-8,8′); 127.3 (d, $J_{P,C}$ = 2.0 Hz); 127.5 (C-4′); 128.1–128.4 (C-3′,4,5,5′); 130.1 (d, *p*-PC_6H_4); 131.2 (dd, *o*′-PC_6H_4); 132.5 (d, C-1′); 132.9 (d, C-2′); 133.8 (C-2); 133.8 (d, C-1); 163.3 (dd, *o*-PC_6H_4). ^{31}P NMR (162 MHz, $CDCl_3$): δ = −3.2 (d, $J_{P,F}$ = 34.5 Hz). IR (Nujol): 2668w, 1909w, 1710w, 1591w, 1507w, 1467s, 1377m, 1260w, 1213w, 1160w, 1072w, 1024w, 935w, 864w, 822m, 751m, 673w, 566w, 520w. MS (ESI): *m*/*z* (%) = 406 ([M^+], 100); 311 (2); 279 (12); 265 (27); 183 (4); 141 (4); 96 (2); 75 (3). HRMS calcd for $C_{28}H_{20}PF$: 406.12454. Found: 406.12466. $[\alpha]_D^{23} = -157$ (*c* 0.5, toluene).

4.2.11. 4-(4-Fluoro)-phenyl-4,5-dihydro-3*H*-dinaphtho-[2,1-*c*;1′,2′-*e*]phosphepine 4k.



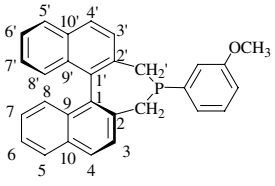
Yield: 45%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.71 (dd, 1H, $J_{H,H}$ = 14.3 Hz, $J_{P,H}$ = 4.8 Hz, CH_2(a)); 2.87–2.94 (m, 2H, CH_2'(a), CH_2(b)); 3.02 (dd, 1H, $J_{H,H}$ = 16.6 Hz, $J_{P,H}$ = 11.7 Hz, CH_2'(b)); 6.94 (d, 1H, H-3′); 7.04 (m, 2H, *m*-PC_6H_4); 7.21–7.35 (m, 6H, H-7,7′,8,8′, *o*-PC_6H_4); 7.45–7.51 (m, 2H, H-6,6′); 7.70 (dd, 1H), 7.79 (d, 1H), (H-3,4′); 7.93–8.01 (m, 3H, H-4,5,5′). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 30.6 (d, J = 15.3 Hz, CH_2); 32.5 (d, J = 22.0 Hz, CH_2'); 115.3 (dd, $J_{F,C}$ = 21.0 Hz, $J_{P,C}$ = 6.6 Hz, *m*-PC_6H_4); 124.9, 125.1 (C-6,6′); 125.9, 126.0 (C-7,7′); 126.6 (C-8,8′); 127.3 (d, C-3); 127.6 (C-4′); 127.9 (C-3′); 128.2, 128.3, 128.4 (C-4,5,5′); 131.9, 132.3, 132.8, 132.8 (C-9,9′,10,10′); 132.2 (d, C-1′); 133.2 (C-2′); 133.6 (d, C-1); 133.8 (dd, $J_{P,C}$ = 20.0 Hz, $J_{F,C}$ = 7.6 Hz, *o*-PC_6H_4); 134.0 (C-2); 134.7 (d, $J_{P,C}$ = 83.9 Hz, *i*-PC_6H_4); 163.4 (d, $J_{F,C}$ = 249 Hz, *p*-PC_6H_4). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 5.1 (d, $J_{P,F}$ = 2.8 Hz). IR (Nujol): 3046w, 1588m, 1507w, 1495s, 1462m, 1377w, 1234m, 1160w, 1092w, 1026w, 935w, 865w, 822m, 751m, 671w, 566w, 513w. MS (ESI): *m*/*z* (%) = 406 ([M^+], 100); 311 (2); 279 (12); 265 (27); 183 (4); 141 (4); 96 (2); 75 (3). HRMS calcd for $C_{28}H_{20}PF$: 406.12867. Found: 406.12866. $[\alpha]_D^{23} = -16$ (*c* 0.5, toluene).

4.2.12. 4-(2-Naphthyl)-4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]phosphepine 4l.



Yield: 80%. ^{1}H NMR (400 MHz, $CDCl_3$), (only signals for the CH_2 groups are given): δ = 2.87 (dd, 1H, $J_{H,H}$ = 14.5 Hz, $J_{P,H}$ = 4.8 Hz, CH_2'(a)); 2.96 (dd, 1H, $J_{P,H}$ = 11.8 Hz, CH_2'(b)); 3.07 (dd,, 1H, $J_{H,H}$ = 11.7 Hz, $J_{P,H}$ = 2.8 Hz, CH_2(a)); 3.13 (dd, 1H, $J_{P,H}$ = 16.1 Hz, CH_2(b)). ^{13}C NMR (100.6 MHz, $CDCl_3$), (not all signals are given): δ = 30.5 (d, J = 16.5 Hz, CH_2); 32.1 (d, J = 23.0 Hz, CH_2); 138.1 (d, 2-Naph). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 3.82. IR (Nujol): 2752w, 1916w, 1695w, 1591w, 1506m, 1462s, 1377m, 1338w, 1268w, 1218w, 1159w, 1025w, 932w, 862w, 811s, 742s, 681w, 660w, 636w, 476m. MS (ESI): *m*/*z* (%) = 438 ([M^+], 100); 309 ([M^+−naphth], 3); 265 (24); 157 (8); 141 (4); 132 (7). HRMS calcd for $C_{32}H_{23}P$: 438.15375. Found: 438.15349. $[\alpha]_D^{24} = -89$ (*c* 0.5, toluene).

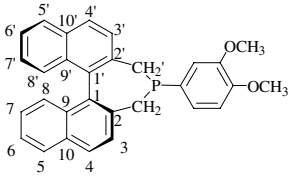
4.2.13. 4-(3-Methoxy)-phenyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]phosphepine 4m.



Yield: 61%. ^{1}H NMR (400 MHz, $CDCl_3$): 2.79 (dd, 1H, $J_{H,H}$ = 14.5 Hz, $J_{P,H}$ = 4.5 Hz, CH_2(a)); 2.89 (dd, 1H, $J_{P,H}$ = 11.6 Hz, CH_2(b)); 2.93 (dd, 1H, $J_{H,H}$ = 11.7 Hz, $J_{P,H}$ = 3.3 Hz, CH_2'(a)); 3.02 (dd, 1H, $J_{P,H}$ = 16.7 Hz, CH_2'(b)); 3.75 (s, 3H, CH_3O); 6.81–6.88 (m, 3H, *o*-, *o*′-, *p*-PC_6H_4); 6.99 (d, 1H, H-3′); 7.17–7.31 (m, 5H, H-7,7′,8,8′, *m*′-PC_6H_4); 7.39–7.46 (m, 2H, H-6,6′); 7.68 (d, 1H, H-3); 7.74 (d, 1H, H-4′); 7.87–7.95 (m, 3H, H-4,5,5′). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 30.5 (d, J = 15.4 Hz, CH_2); 32.1 (d, J = 21.0 Hz, CH_2'); 55.2 (CH_3O); 114.5 (*p*-PC_6H_4); 116.8 (d, *o*-PC_6H_4); 124.0 (d, *o*′-PC_6H_4); 124.9, 125.1 (C-6,6′); 125.8, 125.9 (C-7,7′); 126.6, 126.7 (C-8,8′); 127.3 (d, C-3); 127.4 (C-4′); 128.0–128.4 (C-3′,4,5,5′); 129.2 (d, *m*′-PC_6H_4); 131.9,

132.2, 132.8, 132.8 (C-9,9′,10,10′); 132.3 (d, C-1′); 133.6 (d, C-2′); 133.7 (d, C-1); 134.3 (C-2); 139.2 (d, *i*-PC_6H_4); 159.1 (d, *m*-PC_6H_4). ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = 7.8$. IR (KBr): 3049m, 3005 m, 2952 m, 2912 m, 2832 m, 1617 w, 1590 s, 1572 s, 1507 s, 1479 s, 1462 m, 1414 s, 1358 m, 1317 w, 1284 m, 1247 s, 1181 m, 1160 m, 1145 m, 1102 w, 1041 s, 992 m, 960 w, 934 m, 864 m, 814 s, 773 s, 748 s, 691 s, 658 m, 621 m, 565 m, 541 w, 520 m, 465 m, 417 m. MS (ESI): *m*/*z* (%) = 418 ([M^+], 100); 281 (6); 276 (30); 265 (31); 252 (5); 108 (5). HRMS calcd for $C_{29}H_{23}OP$: 418.14865. Found: 418.14343. $[\alpha]_D^{24} = -15$ (*c* 0.3, toluene).

4.2.14. 4-(3,4-Dimethoxy)-phenyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]phosphepine 4n.



Yield: 67%. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 2.68$ (dd, 1H, $J_{H,H} = 14.3$ Hz, $J_{P,H} = 4.5$ Hz, CH_2(a)); 2.89 (dd, 1H, $J_{P,H} = 11.7$ Hz, CH_2(b)); 2.96 (dq, 2H, $J_{H,H} = 11.7$ Hz, CH'_2); 3.73 (s, 3H, CH_3O); 3.90 (s, 3H, CH_3O); 6.70 (dd, 1H, *o*-PC_6H_3); 6.81 (d, 1H, *m*′-PC_6H_3); 6.89 (m, 1H, *o*′-PC_6H_3); 7.03 (d, 1H, H-3′); 7.17–7.32 (m, 4H, H-7,7′,8,8′); 7.40–7.47 (m, 2H, H-6,6′); 7.67 (dd, 1H, H-3); 7.80 (d, 1H, H-4′); 7.89–7.97 (3d, 3H, H-4,5,5′). ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 31.1$ (d, $J = 15.5$ Hz, CH_2); 32.7 (d, $J = 22.0$ Hz, CH_2); 55.8, 55.8 (2CH_3O); 110.9 (d, *m*′-PC_6H_3); 114.6 (d, *o*-PC_6H_3); 124.9, 125.0 (C-6, 6′); 125.6 (d, *o*′-PC_6H_3); 125.9, 125.9 (C-7,7′); 126.62, 126.65 (C-8, 8′); 127.3 (d, C-3); 127.4 (C-4); 128.0, 128.2, 128.4, 128.5 (C-3′,4,5,5′); 132.0, 132.3, 132.8, 132.8 (C-9, 9′,10,10′); 132.2 (d, C-1′); 133.5 (d, C-1); 133.6 (C-2′); 134.3 (C-2); 148.5 (d, *m*-PC_6H_3); 149.1 (*p*-PC_6H_3). ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = 6.0$. IR (KBr): 3056 m, 3002 m, 2955 m, 2835 m, 1592 s, 1506 s, 1463 s, 1441 s, 1397 m, 1359 w, 1329 m, 1254 s, 1231 s, 1176 s, 1144 m, 1124 s, 1027 s, 912 w, 867 w, 853 w, 814 m, 745 s, 683 w, 660 w, 622 w, 581 w, 544 w, 468 w, 419 m. MS (ESI): *m*/*z* (%) = 448 ([M^+], 100); 433 (7); 276 (17); 265 (19); 151 (15). HRMS calcd for $C_{30}H_{25}O_2P$: 448.15921. Found: 448.15980. $[\alpha]_D^{24} = -33.5$ (*c* 0.4, toluene).

Acknowledgements

The authors thank M. Heyken, H. Baudisch, Dr. W. Baumann, S. Buchholz and Dr. C. Fischer (all IfOK) for analytical and technical support. We also thank Prof. Dr. S. Gladiali (University di Sassari, Italy) for helpful discussions. Generous financial support of this project from the state Mecklenburg-Western Pomerania (Landesforschungsschwerpunkt), the Fonds der Chemischen Industrie, and the Bundesministerium für Bildung und Forschung (BMBF) is also gratefully acknowledged.

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