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A Highly Diastereoselective Route to Dinaphtho[*c*,*e*][1,2]oxaphosphinines and Their Application as Ligands in Homogeneous Catalysis

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Dedicated to Henri B. Kagan on the occasion of his 80th birthday

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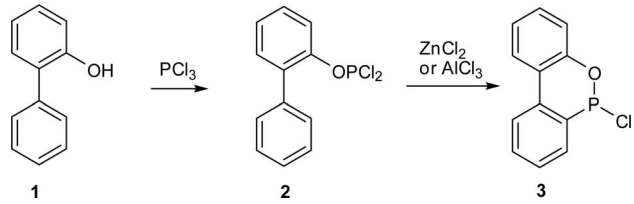
A new and facile method for the synthesis of 6*H*-dinaphtho[*c*,*e*][1,2]oxaphosphinines starting from dinaphthol (BINOL) is described. The ring-opening of an intermediary dinaphtho[2,1-*b*;1′,2′-*d*]furan proceeds with extremely high diastereoselectivity and forms the thermodynamically most stable product. The stereochemistry was elucidated by ^{31}P NMR spectroscopy and X-ray structural analysis. Epimerization at the stereogenic P-centre did not take place. DFT calculations were performed to determine the dihedral angles of several dinaphtho[*c*,*e*][1,2]oxaphosphinines and to explain the observed loss of stereochemistry during the total synthesis from the starting enantiopure BINOL. The synthetic potential of 6-chloro-6*H*-dinaphtho[*c*,*e*][1,2]oxaphosphinine was corroborated in its reactions with phenols to afford the corresponding phosphonites. These were successfully applied as ligands in the Rh-catalysed hydroformylation of three terminal olefins.

Introduction

Heterocyclic phosphanes play a central role as ligands in homogeneous catalysis. In particular, chiral phosphanes have seen widespread applications in asymmetric catalysis with "soft" metals such as Rh, Pd, Ru or Ir.[1] Interestingly, on reviewing heterocyclic phosphanes of different ring size,[2] chiral six-membered phosphanes containing a second heteroatom have only been rarely used as ligands.[3,4] This is astonishing, because several methods for the preparation of the corresponding achiral compounds are described in the literature.[5] Of considerable interest are 1,2-oxaphosphinines. Dibenzo[*c*,*e*][1,2]oxaphosphinines, investigated by the Keglevich group,[6] for example, are useful substrates for Pd- and Ni-catalysed arylations.[7] These heterocycles have also been used as ligands in the Ni-catalysed hydrocyanation of butadienes[8] and in the regioselective Rh-catalysed hydroformylation of olefins.[9] Moreover, they were employed as additives to enhance the thermal stability of polymers.[10]

Surprisingly, synthetic approaches to fused 1,2-oxaphosphinines are rare. The cyclization of biphenyl-2-yl phosphorodichloridite (**2**) in the presence of a Lewis acid, for example, gives 6-chlorodibenzo[*c*,*e*][1,2]oxaphosphinine (**3**), containing a stereogenic phosphorus centre (Scheme 1). For the cyclization step, Chernyshev and co-workers employed $AlCl_3$ in heptane at reflux.[11] Later on, Pastor et al. suggested a one-pot synthesis involving cyclization of **1** in PCl_3 with $ZnCl_2$ as catalyst at high temperature.[12,13] The chloro compound **3**[6–12] represents an interesting starting material for subsequent substitution reactions on the trivalent phosphorus.



Scheme 1. Lewis-acid-mediated approach for the synthesis of the *P*-chlorodibenzo[*c*,*e*][1,2]oxaphosphinine **3** (according to Chernyshev and Pastor).

Inspired by these results and as part of our ongoing studies concerned with the synthesis of chiral P-ligands,[14] we became interested in the synthesis of sterically more hindered compounds such as the binaphthyl[1,2]oxaphosphinines **7** (Scheme 2). These compounds each contain two ele-

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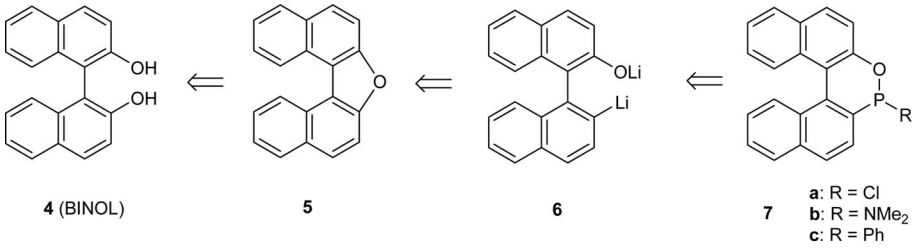


Scheme 2. Retrosynthetic approach for the synthesis of dinaphtho[*c*,*e*][1,2]oxaphosphinines **7**.

ments of chirality (stereogenic P-centre and atropoisomery of the biaryl unit) and should therefore exist as diastereomers. During the synthesis, provided that the rotation barrier is high enough, a stereodifferentiating effect of the atropoisomeric backbone on the formation of the chirogenic phosphorus can be expected. Interestingly, up to now the 6*H*-dinaphtho[*c*,*e*][1,2]oxaphosphinine structure has been mentioned in the literature only once. Regnat and Kleiner claimed the synthesis of **7a** by a modification of the procedure of Pastor[12] at 200–245 °C.[15] Unfortunately, the product was only sketchily characterized. Recently, Heinicke et al. published an analogue synthesis of this compound but without any experimental data.[16]

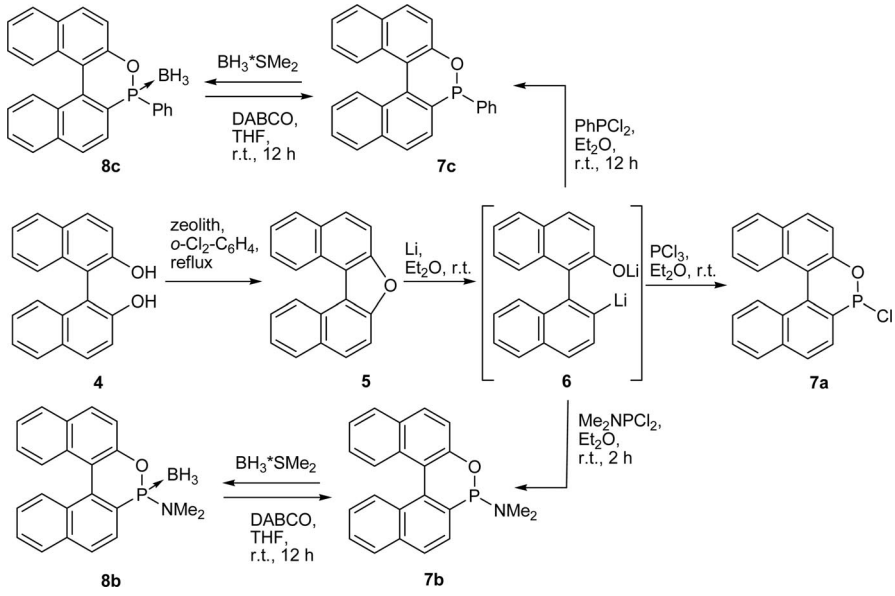
Our envisaged alternative strategy is shown in Scheme 2. Retrosynthetically, compounds of type **7** can be traced back to dinaphthol (BINOL, **4**).

By the methods of Kadyrov and Heinicke[17] or of Sartori,[18] *rac*-BINOL can be converted into dinaphtho[2,1-*b*;1′,2′-*d*]furan (**5**). We assumed that dilithiation of **5** could open the furan ring as already shown in a related protocol with benzofuran[17] and should thus afford the dilithiated compound **6**. Upon in situ treatment of this intermediate with $RPCl_2$ (R = Ph, NR'_2 or Cl) the desired products **7** should be available by ring-closure. In turn compounds **7a** and **7b** might serve as starting materials for P–O or P–C coupling reactions with the aim of producing new heterocyclic phosphorus ligands for metal catalysis.

Results and Discussion

a) Synthesis

As starting material, dinaphtho[2,1-*b*;1′,2′-*d*]furan (**5**) was prepared from *rac*-BINOL (**4**) by a modification of the procedure of Sartori and co-workers (Scheme 3).[18] We found that the cheap and commercially available HY Zeolith CBV400 (Zeolyst International) could also be used for the pyrolytic dehydration of BINOL in place of the originally suggested Zeolite HSZ 360 (Tosoh). The target product **5** was obtained in good yield (90%) in *o*-dichlorobenzene at reflux. The selective cleavage of one C–O bond in the naphtho-fused furan ring after 2 days in diethyl ether at room temperature, in analogy with Heinicke's procedure,[17] afforded the dilithium salt **6**, which represents the pivotal intermediate for all subsequent transformations. Treatment with PCl_3, for example, afforded 6-chloro-6*H*-dinaphtho[*c*,*e*][1,2]oxaphosphinine (**7a**) in good yield (85%). Remarkably, only a single stereoisomer was produced in this

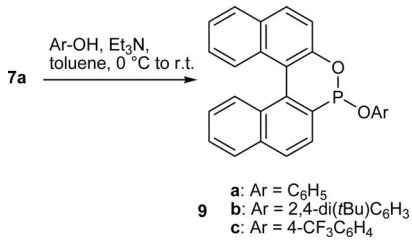


Scheme 3. Synthesis of 6*H*-dinaphtho[*c*,*e*][1,2]oxaphosphinines of type **7**.

reaction, as shown by ^{31}P NMR spectroscopy (δ = 131.7 ppm). The amido derivative **7b** was synthesized in a similar one-pot manner: treatment of **6** with Cl_2PNMe_2[19] closed the six-membered ring and gave 6-dimethylamino-6*H*-dinaphtho[*c*,*e*][1,2]oxaphosphinine (**7b**). In this reaction, too, only a single diastereoisomer was produced (^{31}P NMR, δ = 92.6 ppm). The compound was isolated and purified via the borane adduct **8b**, with final treatment with 1,4-diazabicyclo[2,2,2]octane (DABCO) releasing the oxaphosphinine **7b**. In contrast with the findings of Keglevich,[6] removal of the borane group occurred even at room temperature. Cyclization with $PhPCl_2$ afforded 6-phenyl-6*H*-dinaphtho[*c*,*e*][1,2]oxaphosphinine (**7c**, ^{31}P NMR, δ = 92.0 ppm).

This product was also purified by column chromatography as its borane adduct **8c**. Removal of the BH_3 group with DABCO gave **7c** as a colorless foam.[20] We were pleased to see that this six-membered heterocycle is stable towards epimerization even at reflux in toluene for 24 h.

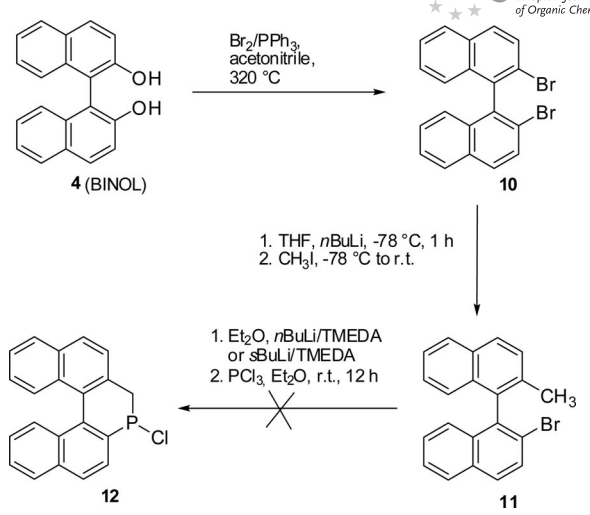
The chloro compound **7a** is a valuable building block for the synthesis of phosphonites through P–O coupling reactions (Scheme 4). We found that **7a** can be used in reactions with phenols without prior purification. Treatment with phenol in the presence of triethylamine in toluene as solvent, for example, afforded the *P*-phenoxy-substituted 1,2-oxaphosphinine **9a**. Alternatively, analogous phosphonites such as **9b** or **9c** could be easily prepared by this methodology (Scheme 4). Compounds **9a**–**c** were obtained in 57–75% yields without optimization of the reaction conditions. The formation of single diastereoisomers was in all cases confirmed by ^{31}P NMR spectroscopy (**9a**: δ = 125.5; **9b**: δ = 122.7; **9c**: δ = 125.3 ppm). It should be noted that the products exhibit the opposite net configuration at phosphorus to that of **7a**, due to the S_N2 mechanism of the reaction (vide infra).[21]



Scheme 4. Synthesis of phosphonites on treatment of 6-chloro-6*H*-dinaphtho[*c*,*e*][1,2]oxaphosphinine (**7a**) with phenols.

The success of the new methodology prompted us also to test it in the synthesis of an analogue phosphinane, as shown in Scheme 5. In the first step, racemic BINOL was converted into the binaphthyl dibromide **10** by a method of Takaya and Noyori.[22] Selective monolithiation and subsequent alkylation with methyl iodide afforded 2′-bromo-2-methyl-[1,1′]binaphthalenyl (**11**) in a yield of 97%.

Unfortunately, all attempts to achieve in situ ring-closure via the corresponding intermediate dilithio salt with PCl_3 or Cl_2PNMe_2 failed.[23] Prolongation of the reaction time,



Scheme 5. Attempt to synthesize dinaphtho[*c*,*e*][1,2]phosphepine chloride **12**.

using *s*BuLi/TMEDA and temperature elevation did not afford **12**. The reason for this difference in behaviour from that of the oxygen-containing analogue is currently unclear.

b) Structure Elucidation

In order to obtain evidence for the stereochemical structures of the products, the isolated 6-phenyl-6*H*-dinaphtho[*c*,*e*][1,2]oxaphosphinine–borane complex **8c** was investi-

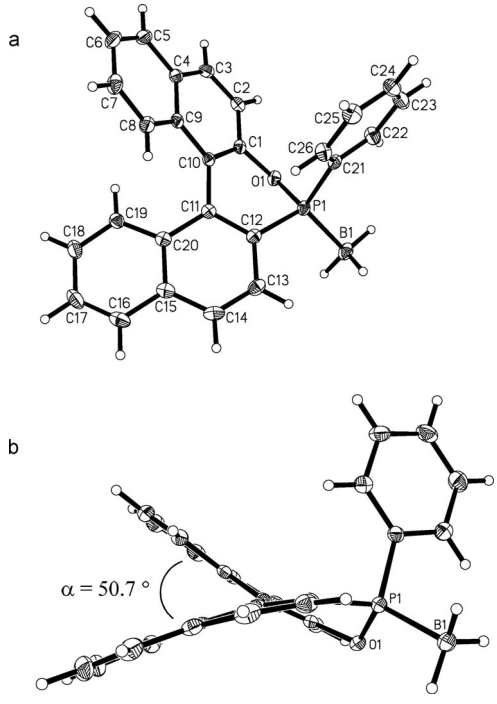


Figure 1. ORTEP diagram of the 6-phenyl-6*H*-dinaphtho[*c*,*e*][1,2]-oxaphosphinine–borane complex **8c**. The thermal ellipsoids correspond to 30% probability; **a**: top view, **b**: side view.

gated by X-ray crystallography (Figure 1). Suitable crystals were obtained by slow crystallization from a toluene/heptane mixture.

As shown in Figure 1 (b), the deviation of the binaphthalene backbone from planarity is considerable. The angle between the planes defined by C1–C10 and by C11–C20 is 50.7°. As a result of this out-of-plane arrangement two stereochemical faces are created, with the *P*-phenyl group accommodated in the less hindered space. This corresponds to the extremely high diastereoselection noted in the reaction between the prochiral $PhPCl_2$ and the intermediate chiral dilithio salt **6**.

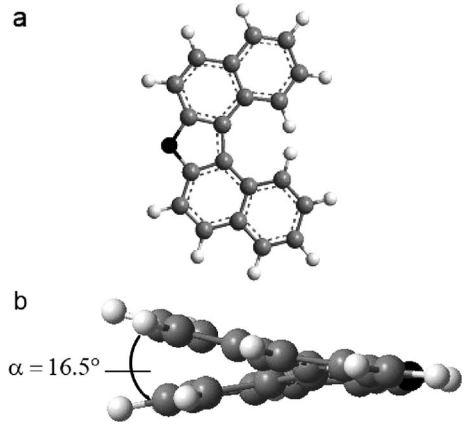
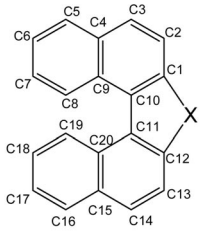


Figure 2. B3LYP/6–31G(d)-optimized structure of dinaphtho[*c*,*e*]furan (**5**); **a**: top view, **b**: side view.

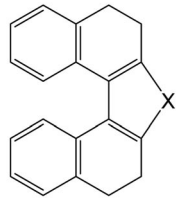
c) Discussion of Diastereofacial Selection

The perfect diastereoselectivity found for the 1,2-oxaphosphinines prompted us to examine whether the original atropoisomery of the starting BINOL can be restored over the whole reaction sequence. Because experiments with enantiopure BINOL did not lead to enantioenrichment in the final 1,2-oxaphosphinines we considered the stereochemical structures of the intermediary dinaphtho[2,1-*b*;1′,2′-*d*]furan (**5**) and the 1,2-oxaphosphinine–borane complex **8c** in more detail. Unfortunately, though, we failed to obtain crystals suitable for X-ray crystallography from the former compound,[24] so we performed DFT calculations on **5** at the B3LYP/6–31G(d) level, including ZPE corrections. As would be expected, the binaphthyl units in the 1,2-oxaphosphinine **8c** are much more twisted [compare X-ray analysis, in which the torsional angles are $\phi_{C1–C10–C11–C12}$ = 38.0(2)°; $\phi_{C9–C10–C11–C20}$ = 45.7(2)°] than in **5** ($\phi_{C1–C10–C11–C12}$ = 4.64°; $\phi_{C9–C10–C11–C20}$ = 13.48°; Figure 2 and Table 1, Entry 1).[25] The computed epimerization barrier of **5** via a planar (C_{2v}) dinaphthofuran structure is 1.6 kcal mol^{-1}, which indicates a very facile process. This in turn means that the structure of dinaphtho[*c*,*e*]furan easily loses axial chirality induced by the dinaphtho backbone. *Therefore it is not possible under these conditions to convert optically pure BINOL into optically pure compounds of type* **7** via **5**.

As can be seen above, the rather planar structure of the tetrahydrofuran ring in 1,2-oxaphosphinine **5** does not permit a large dihedral angle of the two fused binaphthyl units. In order to identify crucial effects on the degree of distortion, the related compounds **5b**–**h** were included in the calculations (Table 1).



5, **5b–f**



5g, **h**

As would be expected, the angle C9–C10–C11–C20 is smallest in **5**, which corresponds to a large angle of C8–X–C19 (X = O). The long distance between C8–C19 indicates only weak repulsive interactions between the two naphthyl rings, which are important forces for deviation from planarity. With increasing size of the heteroatom X and ring size, respectively, the degree of distortion increases in the order: O < N < S < P < As < CH=CH. Substituents at the

Table 1. B3LYP/6–31G(d)-optimized structural parameters; angles in [°] and distances in [Å].

	C9–C10–C11–C20	C7–C10–C11–C18	C1–C10–C11–C12	C1–C10–C11–C12[a]	C8–C19	C8–X–C19
5 (X = O)	13.48	18.94	4.64		3.37	41.07
5b (X = N–H)	15.91	22.14	5.21	5.40	3.30	40.37
5b′(X = N–Me)	16.63	23.04	5.58		3.28	40.02
5c (X = S)	22.26	30.94	10.43	10.80	3.10	35.21
5c′ (X = S–O)	25.32	33.10	14.30		3.10	35.08
5c′′ (X = S^+–Me, BF_4^-)	23.98	32.19	14.19		3.09	35.24
5d (X = P–Ph)	26.39	35.09	14.71	13.60	3.05	34.48
5e (X = As–PH)	27.14	36.46	16.97	15.30	3.02	33.55
5f (X = CH=CH)	29.73	41.78	20.50	19.70	2.96	34.46
5g (X = O)	16.74	30.08	2.07	1.90	3.34	41.35
5h (X = N–H)	15.79	28.72	1.88	2.10	3.40	41.85

[a] The X-ray data were taken from ref.[24]

heteroatom X also contribute to the widening of this decisive angle (compounds **5b′**, **5c′**, **5c′′**). Partial saturation of the binaphthyl ring (compounds **5g**, **5h**) has only a slight effect.

As outlined above, dinaphtho[*c*,*e*][1.2]oxaphosphinines each have two elements of chirality – the stereogenic axis and the stereogenic centre at phosphorus – so two diastereomeric pairs of enantiomers are possible (Figure 3).

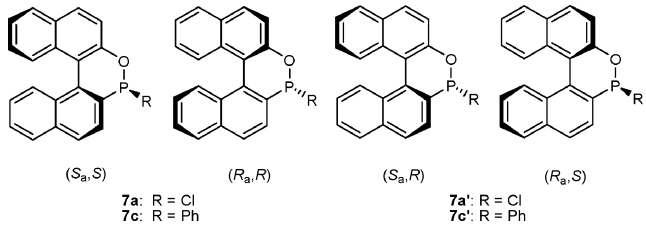


Figure 3. Four stereoisomers of *P*-substituted dinaphtho[*c*,*e*][1.2]-oxaphosphinines.

Our ^{31}P NMR and X-ray investigations showed that exclusively one of the two possible pairs of diastereomers – namely (*S*a,*S*/*R*a,*R*) – was formed in the reaction.

B3LYP density functional calculations were performed in order to compare the stabilities of both diastereomers and to confirm the possibility of epimerisation.

Table 2 shows that the B3LYP/6–31G(d)-optimized structural parameters for **8c** agree well with those determined by X-ray analysis. Further optimization at the B3LYP/6–311+G(d,p) level had only marginal changes on structural parameters. Detailed comparison reveals that BH_3 coordination does not significantly change the structural parameters of the unprotected phosphonite. On the basis of this agreement, we have also computed the structures of diastereomers **7a** and **7c**; these data are likewise listed in Table 2. The change in substituent from phenyl to chloride does not affect the structural parameters.

The computed relative energies in Table 3 give clear evidence that diastereomer **7a** with the chloro substituent is more stable than **7a′**. The large energy difference of ca. 7 kcal mol^{-1} explains why **7a** is the only diastereomer found. For diasteromers with phenyl as P-substituent, the energy difference is smaller, but also significant, and explains why **7c** is either the major (> 97%, at B3LYP) or the only (at MP2) isomer observed experimentally.

Table 3. Computed total electronic (E_{tot} [au]) and relative (ΔE_{rel} [kcal mol^{-1}]) energies for both diastereomers of **7a** and **7c** (**7a′** and **7c′** correspond to the other diastereomers, which were not formed).

	E_{tot} (**7a**)	E_{tot} (**7a′**)	ΔE_{rel} [kcal mol^{-1}]
B3LYP/6–31G(d)[a]	–1646.18766	–1646.17672	6.87
B3LYP/6–311+G(d.p)[b]	–1646.44328	–1646.43206	7.04
MP2/6–311+G(d.p)[b]	–1642.89007	–1642.87815	7.48
	E_{tot} (**7c**)	E_{tot} (**7c′**)	
B3LYP/6–31G(d)[a]	–1417.61270	–1417.60934	2.11
B3LYP/6–311+G(d.p)[b]	–1417.89693	–1417.89352	2.14
MP2/6–311+G(d.p)[b]	–1414.22768	–1414.22005	4.79

[a] From full optimization. [b] From single-point energy calculation.

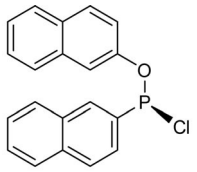
Apart from these energy differences, we also noted differences in bond lengths and bond angles around the P1 centre. For example, the more stable diasteromers (**7a**, **7c**) have shorter P1–O1 and P1–C12 interatomic distances than the less stable diasteromers (**7a′**, **7c′**), and the bond angles around the P1 centres in **7a** and **7c** are larger than those in **7a′** and **7c′**. To aid understanding of these geometric and

Table 2. B3LYP/6–31G*-optimized bond parameters (Å for distances and degrees for angles) of compounds **8c**, **7a** and **7c** (**7a′** and **7c′** correspond to the diastereomers not formed) and comparison with the experimentally measured data for **8c**.

Compound	**8c** (X-ray)	**8c**	**7a** (**7a′**)	**7c** (**7c′**)[a]
P1–O1	1.6287(12)	1.6713	1.7028 (1.7192)	1.6665 (1.6992)
P1–B1	1.895(2)	1.9193		
P1–C21 (or P1–Cl)	1.808(2)	1.8269	1.8505 (1.8380)	2.1442 (2.0997)
P1–C12	1.799(2)	1.8129	1.8309 (1.8469)	1.8180 (1.8424)
O1–C1	1.404(2)	1.3820	1.3748 (1.3761)	1.3824 (1.3837)
C1–C10	1.381(2)	1.3939	1.3949 (1.3956)	1.3928 (1.3942)
C10–C11	1.491(2)	1.4883	1.4862 (1.4924)	1.4820 (1.4928)
C11–C12	1.396(2)	1.4000	1.3998 (1.3967)	1.3997 (1.3967)
O1–P1–C12	100.49(7)	98.92	97.00 (94.74)	97.74 (95.64)
P1–O1–C1	115.31(10)	116.99	118.14 (111.95)	120.85 (111.30)
O1–C1–C10	120.25(14)	121.38	121.53 (120.84)	121.16 (120.86)
C1–C10–C11	119.24(15)	118.63	118.47 (118.10)	118.56 (118.13)
C10–C11–C12	118.59(14)	119.14	118.92 (118.81)	118.84 (118.90)
C11–C12–P1	116.92(12)	118.35	119.85 (116.46)	120.92 (115.62)
C21–P1–O1	105.24(7)	105.80	103.17 (97.48)	102.32 (97.71)
C21–P1–C12	109.89(9)	108.50	104.20 (100.80)	102.08 (100.04)
C21–P1–B1	113.64(9)	114.90		
C1–C10–C11–C12	38.0(2)	36.67	36.98 (–38.04)	35.31 (–37.97)
O1–C1–C10–C11	–8.7(2)	–8.75	–7.69 (10.51)	–8.63 (10.91)
C10–C11–C12–P1	–15.0(2)	–14.30	–16.28 (6.39)	–17.05 (5.99)
C1–O1–P1–C12	54.32(12)	51.73	50.59 (63.42)	45.50 (63.84)

[a] Replace C21 by Cl (compare Figure 1).

energy differences, we computed the structure of chloro(naphthalen-2-yl)(naphthalen-2-yloxy)phosphane (**7a-2H**) as a strain-free molecule with the same stereocentre as **7a**; this compound can be regarded as the hydrogenation product produced by breaking the C10–C11 bond between two naphthyl units in **7a**.



7a-2H

The comparison revealed that the bond lengths at the P1 centre in **7a** are closer to those (P1–O1 1.6712 Å; P1–Cl1 2.1427 Å; P1–C12 1.6263 Å; P1–O1–C1 119.91) in **7a-2H** than to those in **7a′**. These data provide evidence that **7a′** is more strained than **7a**, as indicated especially by the large difference in the P1–O1–C1 bond angles (111.30° vs. 120.85°). This reasonably explains the stability of **7a** over **7a′**, and also the experimental findings of **7a** as the only diastereomer.

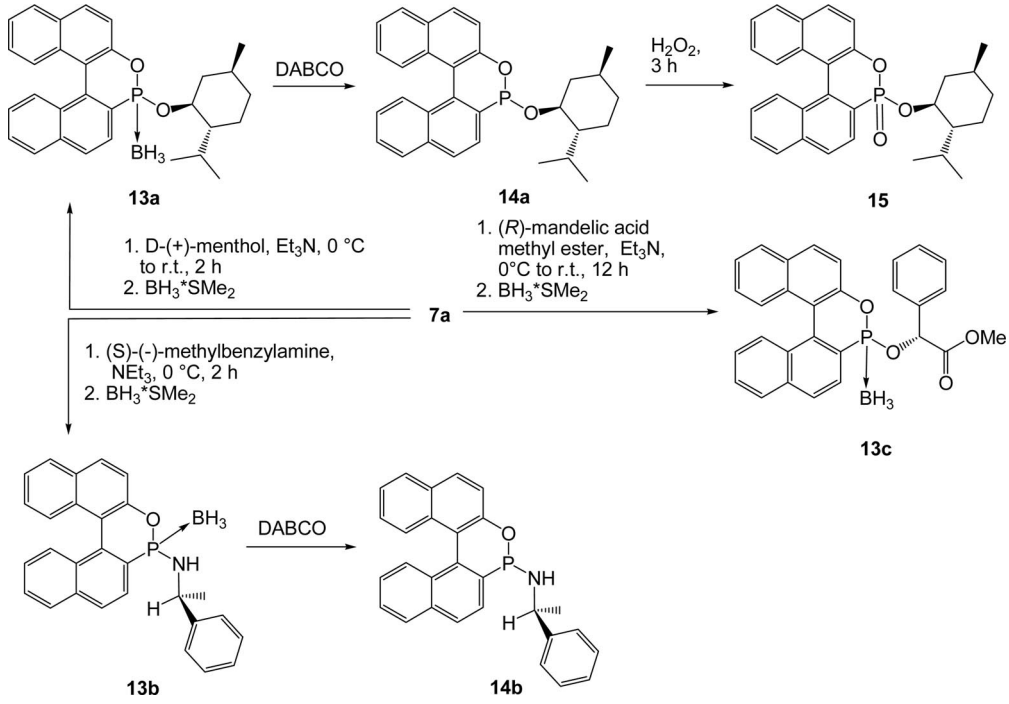
d) Trials of Resolution

As pointed out above, the stereoselective synthesis of enantiopure *P*-substituted dinaphtho[*c*,*e*][1.2]oxaphosphinines starting from enantiopure BINOL is not possible, due to the low epimerization barrier of the intermediate binaphthofuran **5**. We therefore considered the resolution of racemic *P*-substituted dinaphtho[*c*,*e*][1.2]oxaphosphinines via corresponding diastereomeric esters and amides, respectively. Our synthetic trials began with the 6-chloro compound **7a** and are summarized in Scheme 6.

Thus, treatment with (+)-menthol in the presence of triethylamine afforded the corresponding menthyl ester **14a**. The product was isolated and purified by column chromatography as its borane adduct adduct **13a**. As expected, two diastereomers were produced in this reaction and were characterized by ^{31}P NMR spectroscopy (δ = 167.4 and 168.1 ppm). In contrast with Keglevich's observations,[6] the borane group was partially lost even at room temperature. Complete removal of the BH_3 group was achieved by treatment of **13a** with 1,4-diazabicyclo[2.2.2]-octane (DABCO) to give **14a**. Unfortunately, neither phosphonite **14a** nor its borane product **13a** were crystalline, so the originally intended separation by crystallization could not be applied.

Therefore, in the next step **14a** was converted into the corresponding *P*-oxide **15** by treatment with hydrogen peroxide (30%).[26] The diastereomeric mixture of crystalline oxaphosphinine *P*-oxide **15** obtained from *n*-pentane could be successfully subjected to X-ray crystallography.

The solid-state structure of **15** is depicted in Figure 4. The asymmetric unit contains the enantiomeric pair [(*S*a,*R*) and (*R*a,*S*)]. This fact is additional evidence of the (*S*a,*S*) and (*R*a,*R*) configuration of the starting 6-chloro-6*H*-dinaphtho[*c*,*e*][1,2]oxaphosphinine (**7a**), suggested above on the basis of NMR results and DFT calculations. As would be expected for reactions of phosphorus chloride with nucleophiles, under S_N2 conditions inversion of the configuration at the stereogenic phosphorus centre takes place. The subsequent oxidation should not affect the chirogenic phosphorus.



Scheme 6. Synthesis of *P*-chiral substituted 6*H*-dinaphtho[*c*,*e*][1,2]oxaphosphinines.

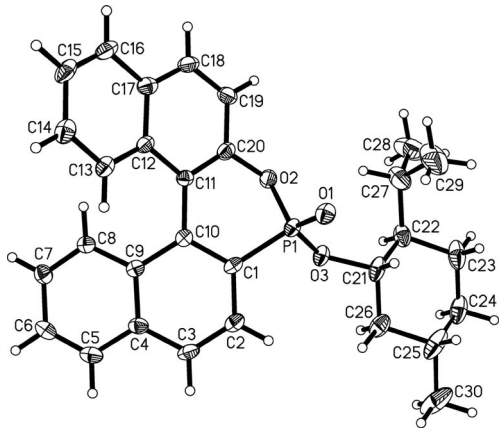


Figure 4. ORTEP diagram of 6-{[(1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl]oxy}-6*H*-dinaphtho[*c*,*e*][1,2]oxaphosphinine *P*-oxide (**15**). The thermal ellipsoids correspond to 30% probability. Only one of the two molecules of the asymmetric unit is depicted.

Alternatively, the (*R*)-mandelic acid ester and the corresponding (*S*)-(–)-α-methylbenzylamide were prepared. Both borane adducts **13b** and **13c** were isolated as amorphous solids. With compound **13b**, BH_3 removal with DABCO delivered the amidophosphinite **14b**.

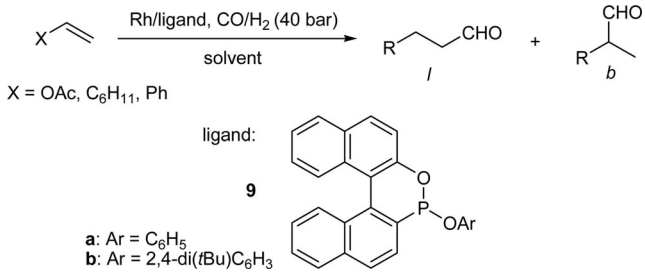
Unfortunately all attempts to separate the diastereomers by fractional crystallization or preparative chromatography failed. The most promising attempted resolution, by repeated crystallization of oxide **15** from pentane, gave rise only to final diastereomeric enrichment in a ratio of 100:67.

e) Dinaphtho[*c*,*e*][1,2]oxaphosphinines as Ligands in Rh-Catalysed Hydroformylation

Rhodium-catalysed hydroformylation is one of the most important processes in industrial homogeneous catalysis[27] and was therefore chosen to test the capabilities of dinaphtho[*c*,*e*][1,2]oxaphosphinines **9a** and **9b** to act as ancillary ligands. As benchmark substrates vinyl acetate, oct-1-ene and styrene were chosen. The catalytic reactions were carried out in 5 mL of solvent, at temperatures of 60, 80 and 100 °C under 50 bar of syngas pressure (CO/H_2 ratio 1:1) for 3 hours. The catalyst was prepared in situ from $Rh(acac)(CO)_2$ (acac = acetyl acetonate) by treatment with 2.6 equivalents of ligand in toluene or propylene carbonate (PC) as solvent.

As clearly shown in Table 4, the phosphonites **9a** and **9b** provide highly active hydroformylation catalysts in toluene as solvent. Superior results were achieved in the reaction with vinyl acetate at 60 °C (high regioselectivity with a *b*/*l* ratio exceeding 90, run 1), although the regioselectivity was significantly lowered at higher temperature (*b*/*l* ratio 35:1 at 80 °C, run 2). The hydroformylation of oct-1-ene proceeded preferably at higher temperatures (100 °C) but at the expense of the formation of the desired terminal aldehyde

Table 4. Rh-catalysed hydroformylation of terminal alkenes.[a]



Run	Ligand of type **9**	Substrate	Solvent	*T* [°C]	Conv.[b] [%]	Yield [%]	*b*:*l*[b]
1	**a**	vinyl acetate	toluene	60	100	95	>90:1
2	**a**	vinyl acetate	toluene	80	100	98	35:1
3	**a**	vinyl acetate	PC	60	75	100	12:1
4	**a**	vinyl acetate	PC	80	100	100	12:1
5	**a**	oct-1-ene	toluene	80	98	75	1:1
6	**a**	oct-1-ene	toluene	100	97	90	1:1.6
7	**a**	oct-1-ene	PC	80	95	92	1:1.5
8	**a**	oct-1-ene	PC	100	99	82	1:1.8
9	**a**	styrene	toluene	60	2	99	5:1
10	**a**	styrene	toluene	80	99	98	3:1
11	**a**	styrene	toluene	100	99	98	3:1
12	**a**	styrene	PC	80	100	100	1.3:1
13	**a**	styrene	PC	100	100	100	1:1
14	**b**	vinyl acetate	toluene	80	100	100	7:1
15	**b**	oct-1-ene	toluene	80	100	83	1:1.5
16	**b**	styrene	toluene	80	100	100	4:1

[a] Reaction conditions: substrate/$Rhacac(CO)_2$/ligand = 2800:1:2.6; 50 bar CO/H_2 (ratio 1:1), in 5 mL of solvent, 3 h. [b] Determined by GC.

(runs 5 and 6). In general only moderate *l*/*b* ratios were obtained. Excellent yields were also noted with styrene as substrate at temperatures equal to or higher than 80 °C (runs 10, 11). Interestingly, the use of the more sterically hindered *tert*-butyl-substituted ligand **9b** did not increase the formation of linear aldehydes (runs 14–16).

The effect of the commonly used solvent toluene was compared with that of propylene carbonate (PC).[28] Application of this "green" solvent lowered the production of branched aldehydes. Particularly remarkable is the formation of considerable amounts of 3-acetoxypropanal from vinyl acetate (runs 3 and 4) and of phenylbutanal from styrene (runs 12 and 13); both substrates usually direct the hydroformylation in favour of the branched product. The effect is not significant with oct-1-ene as substrate.

Summary and Conclusions

A new methodology for the one-pot synthesis of 6*H*-dinaphtho[*c*,*e*][1,2]oxaphosphinines from easily available starting materials has been developed. The synthesis was based on the selective ring-opening reaction of dinaphtho[2,1-*b*;1′,2′-*d*]furan (**5**) with lithium, followed by cyclization of the resulting C,O-dilithio salt **6** with trivalent dichlorophosphorus compounds. The reactions occurred highly diastereoselectively and yielded only single diastereomers. The structures of the 6-phenyl-6*H*-dinaphtho[*c*,*e*][1,2]oxaphosphinine–borane complex **8c** and of 6-{[(1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl]oxy}-6*H*-dinaphtho[*c*,*e*][1,2]oxaphosphinine *P*-oxide (**15**) were determined by X-ray crystallography. Chemical calculations were applied to explain the extremely high diastereoselectivities found in the formation of chiral dinaphtho[*c*,*e*][1,2]oxaphosphinines. The synthetic potential of 6-chloro-6*H*-dinaphtho[*c*,*e*][1,2]oxaphosphinine (**7a**) was corroborated in its reactions with phenols. Unfortunately, all trial attempts to prepare enantiopure compounds through the formation of diasteromeric esters or amides failed.

Two of the diastereomeric phosphonites were examined as ligands for the regioselective Rh-catalysed hydroformylation of terminal olefins. Three benchmark substrates were successfully converted with excellent rates in toluene as solvent. It was found that propylene carbonate (PC), as an alternative, "green" solvent, increases the formation of linear aldehydes. Unfortunately, in preliminary trials of the Ni-catalysed hydrocyanation of styrene poor activity was noted.[29]

Experimental Section

General: All reagents, unless otherwise mentioned, were purchased from commercial sources and used without additional purification. Solvents were dried and freshly distilled under argon before use. All reactions involving phosphanes were performed under dry argon with use of standard Schlenk techniques. Thin-layer chromatography was performed on pre-coated TLC plates (silica gel 60 F_{254}, Merck). Flash chromatography was carried out with silica gel 60 (230–400 mesh ASTM). NMR spectra were recorded with Bruker ARX 300 and AVANCE 500 spectrometers. Chemical shifts of ^{1}H, ^{13}C, ^{31}P and ^{19}F NMR spectra are reported in parts per million (ppm). The solvent peak was used as internal standard for ^{1}H and ^{13}C NMR spectra. Chemical shifts of ^{31}P NMR spectra are referred to H_3PO_4 as external standard. Chemical shifts of ^{19}F NMR spectra are reported relative to $CFCl_3$ as external standard. Elemental analyses were performed with a LEGO CHNS-932 instrument. Mass spectra were obtained with an AMD 402/3 spectrometer. HRMS analysis was carried out with a high-resolution magnetic-sector spectrometer.

Computational Details: All structures were optimized at the B3LYP/6–31G(d) level of density functional theory and characterized as energy minimum structures on the potential energy surface at the same level. Single-point energy calculations were carried out at the B3LYP/6–311+G(d,p) and MP2/6–311+G(d,p) levels on the B3LYP/6–31G(d)-optimized structures. For comparison of the stabilities of two diastereomers the relative energies at the B3LYP/6–311+G(d,p) and MP2/6–311+G(d,p) levels were used. All calculations were performed with the aid of the Gaussian 03 program.[30]

X-ray Crystallographic Study of 8c and 15: Data were collected with a STOE IPDS diffractometer with use of graphite-monochromated Mo-K_α radiation. The structures were solved by direct methods (SHELXS-97)[31] and refined by full-matrix, least-squares techniques on F^2 (SHELXL-97). XP (Bruker AXS) was used for graphical representations.

CCDC-754721 (for **8c**) and -754722 (for **15**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal Data for 6-Phenyl-6*H*-dinaphtho[*c*,*e*][1,2]oxaphosphinine–Borane Complex 8c: $C_{26}H_{20}BOP$, M_r = 390.20, triclinic, space group $P\bar{1}$, a = 9.797(2), b = 10.776(2), c = 11.669(2) Å, α = 73.24(3), β = 66.67(3), γ = 65.46(3)°, V = 1017.6(4) Å^3, Z = 2, $\rho_{calcd.}$ = 1.273 g cm^{-3}, μ = 0.149 mm^{-1}, T = 200 K, $2\theta_{max}$ = 52°, 3700 independent reflections, of which 2609 were observed [$I > 2\sigma(I)$], final R indices [$I > 2\sigma(I)$]: R_1 = 0.0342, wR_2 = 0.0760, R indices (all data): R_1 = 0.0557, wR_2 = 0.0814, 274 parameters, largest diff. peak and hole 0.231/–0.241 e·Å^{-3}.

Crystal Data for 6-{[(1*S*,2*R*,5*S*)-2-Isopropyl-5-methylcyclohexyl]-oxy}-6*H*-dinaphtho[*c*,*e*][1,2]oxaphosphinine *P*-Oxide (15): $C_{30}H_{31}O_3P$, M_r = 470.52, monoclinic, space group $P2_1$, a = 11.2826(6), b = 16.4347(6), c = 14.0591(8) Å, β = 104.056(4)°, V = 2528.9(2) Å^3, Z = 4, $\rho_{calcd.}$ = 1.236 g cm^{-3}, μ = 0.138 mm^{-1}, T = 200 K, $2\theta_{max}$ = 58.36°, 13635 independent reflections, of which 8635 were observed [$I > 2\sigma(I)$], final R indices [$I > 2\sigma(I)$]: R_1 = 0.0332, wR_2 = 0.0630, R indices (all data): R_1 = 0.0582, wR_2 = 0.0666, 613 parameters, largest diff. peak and hole 0.222/–0.331 e·Å^{-3}.

Dinaphtho[2,1-*b*;1′,2′-*d*]furan (5): The compound was prepared by a modification of the procedure of Sartori et al.[18] A mixture of *rac*-BINOL (2.00 g, 6.99 mmol) and Zeolith CBV400 (Zeolyst International, 1.10 g) in *o*-dichlorobenzene (15 mL) was heated at reflux for 5 h with stirring. After cooling to room temperature, the resulting pale-brown suspension was filtered off and the yellow solution was evaporated. The residue was purified by chromatography through a short column (silica gel, *n*-hexane/AcOEt 2:1, R_f = 0.65) to give **5** (1.69 g, 90%) as colourless crystals. M.p. 155–156 °C (ref.[17a] 153–155 °C; ref.[18] 154–155.5 °C). ^{1}H NMR (250.1 MHz, $CDCl_3$, cf. ref.[17a]): δ = 7.35–7.42 (m, 2 H), 7.51–7.58 (m, 2 H), 7.61 (d, J = 9 Hz, 2 H), 7.73 (d, J = 9 Hz, 2 H), 7.86 (d, J = 9 Hz, 2 H), 8.95 (d, J = 9 Hz, 2 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, cf. ref.[17a]): δ = 113.1, 119.9, 124.8, 126.1, 126.6, 128.7, 129.1, 129.9, 131.7, 154.7 ppm.

6-Chloro-6*H*-dinaphtho[*c*,*e*][1,2]oxaphosphinine (7a): Lithium (0.054 g, 7.7 mmol) was added to a solution of dinaphtho[2,1-*b*;1′,2′-*d*]furan (**5**, 0.537 g, 2.00 mmol) in diethyl ether (30 mL) and the reaction mixture was stirred for 48 h at room temperature. The resulting red-brown suspension was filtered and the solution was added dropwise at 0 °C to a solution of PCl_3 (0.288 g, 2.10 mmol) in diethyl ether (10 mL). The reaction mixture was stirred for 2 h at room temperature and the solvent was then evaporated under reduced pressure. The residue was transferred into toluene (10 mL), and the solution was filtered through a short column of celite to give 6-chloro-6*H*-dinaphtho[*c*,*e*][1,2]oxaphosphinine (**6**) as a light yellow foam (0.57 g, 85%). ^{1}H NMR (300 Hz, $CDCl_3$): δ = 7.17–7.28 (m, 3 H, Ar), 7.34–7.69 (m, 5 H, Ar), 7.75–7.98 (m, 4 H, Ar) ppm. ^{13}C NMR (125 Hz, $CDCl_3$): δ = 119.0, 120.5, 124.8, 125.6, 126.2, 126.5, 127.7, 128.0, 128.4, 128.7, 128.8, 128.9, 129.0, 131.2, 131.4, 131.6, 136.4, 149.5 (d, J = 6.5 Hz, q, C–O) ppm. ^{31}P NMR (121 Hz, $CDCl_3$): δ = 131.7 ppm. MS (CI, isobutane): *m*/*z* (%) = 299 (43) [M – Cl], 271 (100), 207 (39).

6-Dimethylamino-6*H*-dinaphtho[*c*,*e*][1,2]oxaphosphinine (7b): DABCO (1,4-diazabicyclo[2,2,2]octane, 0.083 g, 0.74 mmol) was added to a solution of 6-dimethylamino-6*H*-dinaphtho[*c*,*e*][1,2]oxaphosphinine–borane complex **8b** (0.20 g, 0.56 mmol) in THF (15 mL). The mixture was stirred at room temperature for 11 h (progress of the reaction was monitored by ^{31}P NMR). The solvent was evaporated and the product was purified on a short column of celite (toluene) to give pure compound **7c** (131 mg, 68%) as a colourless oil. ^{1}H NMR (300 Hz, $CDCl_3$): δ = 2.88 (s, 3 H, CH_3), 2.93 (s, 3 H, CH_3), 7.05–7.28 (m, 4 H, Ar), 7.34–7.52 (m, 4 H, Ar), 7.78–8.01 (m, 4 H, Ar) ppm. ^{13}C NMR (125 Hz, $CDCl_3$): δ = 120.1, 120.2, 125.4, 125.6, 126.3, 126.4, 126.6, 127.1, 128.2, 128.6, 128.8, 128.9, 129.4, 129.6, 130.4 (q), 131.5 (q), 131.5 (q), 131.9, 134.9 (q), 135.9 (q), 139.3 (q), 151.2 (q) ppm. ^{31}P NMR (121 Hz, $CDCl_3$): δ = 92.6 ppm.

6-Phenyl-6*H*-dinaphtho[*c*,*e*][1,2]oxaphosphinine (7c): DABCO (1,4-diazabicyclo[2,2,2]octane, 0.04 g, 0.35 mmol) was added to a solution of 6-phenyl-6*H*-dinaphtho[*c*,*e*][1,2]oxaphosphinine–borane complex **8c** (0.10 g, 0.26 mmol) in THF (10 mL). The mixture was stirred at room temperature for 12 h (the progress of the reaction was monitored by ^{31}P NMR). The solvent was evaporated and the product was purified on a short column of celite (toluene) to give pure compound **7c** (60 mg, 60%) as a colourless foam. ^{1}H NMR (300 Hz, $CDCl_3$): δ = 6.88–7.01 (m, 3 H, Ar), 7.08–7.30 (m, 6 H, Ar), 7.37–7.51 (m, 3 H, Ar), 7.56–7.65 (m, 2 H, Ar), 7.76–7.97 (m, 3 H, Ar) ppm. ^{13}C NMR (125 Hz, $CDCl_3$): δ = 120.2 (q, d, J = 6 Hz), 120.4, 124.1, 125.5, 125.6, 126.8, 127.6, 127.8, 127.9, 128.1, 128.4, 128.6, 129.6, 130.0, 130.2 (q), 130.6 (q), 130.6 (q), 131.1 (q), 131.5, 131.8, 134.2 (q), 134.4 (q), 135.3 (q), 136.4 (q), 136.8 (q), 153.2 (d, J = 9.4 Hz, q, C–O) ppm. ^{31}P NMR (121 Hz, $CDCl_3$): δ = 92.0 ppm.

6-Dimethylamino-6*H*-dinaphtho[*c*,*e*][1,2]oxaphosphinine–Borane Complex 8b: Lithium (0.054 g, 7.70 mmol) was added to a solution of dinaphtho[2,1-*b*;1′,2′-*d*]furan (**5**, 0.537 g, 2.00 mmol) in diethyl ether (30 mL). The resulting red-brown suspension was stirred for 48 h at room temperature. The mixture was added dropwise at 0 °C to a solution of Me_2NPCl_2 (prepared by the procedure of Nöth and Vetter,[19] 0.150 g, 2.10 mmol) in diethyl ether (10 mL). The reaction mixture was stirred at room temperature for 2 h, a solution of BH_3·Me_2S (2 M in toluene, 2.60 mmol, 1.30 mL) was then added, and the resulting solution was stirred for a further 2 h at room temperature. The solvent was evaporated, and the residue was dried under vacuum. The product **8b** (light yellow solid) was purified by column chromatography (silica gel, toluene/*n*-heptane 1:1, R_f = 0.2); yield 0.51 g (71%). ^{1}H NMR (300 Hz, $CDCl_3$): δ = 1.17 (br. m, 3 H, BH_3), 2.33 (s, 3 H, CH_3), 2.37 (s, 3 H, CH_3), 7.01–7.28 (m, 4 H, Ar), 7.33–7.54 (m, 4 H, Ar), 7.78–8.01 (m, 4 H, Ar) ppm. ^{13}C NMR (125 Hz, $CDCl_3$): δ = 120.2 (q, d, J = 10.5 Hz), 120.3, 125.5, 125.7, 126.3, 126.5, 126.7, 127.1, 128.3, 128.6, 128.8, 128.9, 129.4, 129.6, 130.3 (q), 131.3 (q), 131.5 (q), 131.9, 134.9 (q), 135.9 (q), 138.2 (q), 150.1 (d, J = 12.9 Hz, q, C–O) ppm. ^{31}P NMR (121 Hz, $CDCl_3$): δ = 94.7 (br. m) ppm. MS (EI, 70 eV): *m*/*z* (%) = 343 (55) $[M – BH_3]^+$, 299 (100) $[M – BH_3 – NMe_2]^+$. $C_{22}H_{21}BNOP$ (M = 357.19): calcd. C 74.00, H 5.93, N 3.92, P 8.67; found C 75.00, H 6.12, N 2.73, P 8.01.

6-Phenyl-6*H*-dinaphtho[*c*,*e*][1,2]oxaphosphinine–Borane Complex 8c: A suspension of lithium (0.10 g, 14.3 mmol) was added to a solution of dinaphtho[2,1-*b*:1′,2′-*d*]furan (**5**, 1.00 g, 3.73 mmol) in diethyl ether (60 mL). The resulting red-brown suspension was stirred for 48 h at room temperature. The solution was then added dropwise at 0 °C to a solution of $PhPCl_2$ (0.51 mL, 3.76 mmol) in diethyl ether (30 mL). The reaction mixture was stirred at room temperature for 12 h, a solution of BH_3·Me_2S (2 M in toluene, 2.5 mL, 4.96 mmol) was added, and the resulting solution was stirred for an additional 3 h at room temperature. The solvent was evaporated, and the residue was dried under vacuum. The crude product was purified by column chromatography (silica gel, toluene/*n*-heptane 1:2; R_f = 0.3). Compound **8c** was isolated as a white solid (1.15 g, 80%). ^{1}H NMR (300 Hz, $CDCl_3$): δ = 1.18 (br. m, 3 H, BH_3), 7.02–7.36 (m, 5 H, Ar), 7.39–7.46 (m, 3 H, Ar), 7.50–7.58 (m, 2 H, Ar), 7.68–7.73 (m, 2 H, Ar), 7.94–8.07 (m, 3 H, Ar) ppm. ^{13}C NMR (125 Hz, $CDCl_3$): δ = 120.1, 120.5, 120.6, 125.5, 126.3, 126.6, 127.0, 127.2, 127.3, 128.5, 128.7, 128.8, 128.9, 129.0, 129.2, 129.6, 129.8, 130.3, 130.4, 131.3, 131.7, 131.8, 132.0, 132.7, 134.3, 136.5, 136.6, 150.3 (d, J = 14.1 Hz, q, C–O) ppm. ^{31}P NMR (121 Hz, $CDCl_3$): δ = 98.4 (br. d, J = 62 Hz) ppm. MS (EI, 70 eV): *m*/*z* (%) = 376 (100) $[M – BH_3]^+$, 297 (60), 252 (50) $[C_{20}H_{12}]^+$, 149 (10). MS (CI, isobutane): *m*/*z* (%) = 389 (40) [M – H], 377 (90) $[M – BH_2]$, 299 (100) $[M – BH_3 – Ph]$. HRMS (EI) calcd. for $C_{26}H_{20}OBP$ $[M – BH_3]^+$ 376.1012; found 376.1017.

6-Phenoxy-6*H*-dinaphtho[*c*,*e*][1,2]oxaphosphinine (9a): A mixture of phenol (0.071 g, 0.75 mmol) and triethylamine (0.114 g, 0.157 mL, 1.123 mmol), dissolved in toluene (8 mL), was added dropwise at 0 °C to a stirred solution of 6-chloro-6*H*-dinaphtho[*c*,*e*][1,2]oxaphosphinine (**7a**, 0.250 g, 0.75 mmol) in toluene (8 mL). The reaction mixture was allowed to warm to room temperature, stirred for 12 h and then filtered. The solvent was evaporated in vacuo and the residue was purified by column chromatography (silica gel, toluene; R_f = 0.93) to give **9a** (0.179 g, 61%). ^{1}H NMR (250.1 MHz, $CDCl_3$): δ = 6.54–6.64 (m, 1 H, arom. H), 6.79 (d, J = 8.7 Hz, 2 H, arom. H), 6.84–7.37 (m, 8 H, arom. H), 7.48 (d, J = 8.1 Hz, 2 H, arom. H), 7.63 (d, J = 8.7 Hz, 1 H, arom. H), 7.75–7.95 (m, 3 H, arom. H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 118.9 (q), 119.8, 120.2, 121.2 (q), 123.7, 124.5, 125.5, 125.6, 126.3, 126.4, 127.2, 127.4, 128.1–128.3 (2 × arom. C), 128.4, 128.7, 129.3–129.4 (2 × arom. C), 130.0 (q), 130.2 (q), 130.5, 133.4 (q), 133.6 (q), 135.8 (q), 149.2 (q), 155.3 (q) ppm. ^{31}P NMR (125 Hz, $CDCl_3$): δ = 125.5 ppm. MS (EI, 70 eV): *m*/*z* (%) = 392 (28) $[M]^+$, 299 (100) $[M – OC_6H_4]^+$, 252 (33).

6-[2,4-Bis(*tert*-butyl)phenoxy]-6*H*-dinaphtho[*c*,*e*][1,2]oxaphosphinine (9b): A mixture of 2,4-bis(*tert*-butyl)phenol (0.155 g, 0.75 mmol) and triethylamine (0.114 g, 0.157 mL, 1.123 mmol), dissolved in toluene (10 mL), was added dropwise at 0 °C to a stirred solution of the 6-chlorooxaphosphinine **7a** (0.250 g, 0.75 mmol) in toluene (8 mL). The reaction mixture was allowed to warm to room temperature, stirred overnight at ambient temperature and then fil-

tered. The solvent was evaporated in vacuo and the residue was purified by column chromatography (silica gel, toluene; R_f = 0.94) to give **9b** (0.226 g, 57%). ^{1}H NMR (250.1 MHz, $CDCl_3$): δ = 1.18 (s, 9 H, CH_3), 1.27 (d, J = 30 Hz, 9 H, CH_3), 6.85–7.98 (m, 15 H, arom. H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 25.9 (CH_3), 31.5 (CH_3), 33.3 (q), 33.6 (q), 114.5 (q), 114.8, 116.4 (q), 118.0, 118.5 (q), 122.5, 123.1, 122.4.3–128.0, 129.4 (q), 129.9, 131.1 (q), 131.7 (q), 134.3 (q), 136.7 (q), 141.7 (q), 150.8 (q), 151.4 (q) ppm. ^{31}P NMR (125 Hz, $CDCl_3$): δ = 122.7 ppm. MS (EI, 70 eV): m/z (%) = 504 (18) $[M]^+$, 299 (100) $[M - (O\text{-}2,4\text{-}t\text{BuPh})]^+$, 252 (22).

6-(4-Trifluoromethylphenoxy)-6*H*-dinaphtho[*c*,*e*][1,2]oxaphosphinine (9c): A mixture of 4-(trifluoromethyl)phenol (0.15 g, 0.90 mmol) and triethylamine (0.11 g, 0.15 mL, 1.07 mmol), dissolved in toluene (10 mL), was added dropwise at 0 °C to a stirred solution of 6-chloro-6*H*-dinaphtho[*c*,*e*][1,2]oxaphosphinine (**7a**, 0.300 g, 0.90 mmol) in toluene (10 mL). The reaction mixture was allowed to warm to room temperature, stirred for 12 h and then filtered. The solvent was evaporated in vacuo and the residue was purified by column chromatography [silica gel, toluene/*n*-heptane (1:1); R_f = 0.85] to give **9c** (0.370 g, 75%) as a colourless oil. ^{1}H NMR (500 Hz, $CDCl_3$): δ = 6.75 (d, J = 8.7 Hz, 1 H, Ar), 7.03–7.45 (m, 9 H, Ar), 7.57 (d, J = 8.7 Hz, 1 H, Ar), 7.72–7.94 (m, 5 H, Ar) ppm. ^{13}C NMR (125 Hz, $CDCl_3$): δ = 119.8 (d, J = 7.7 Hz, C-2), 120.4 (m, 2 × C_o, $PhCF_3$), 124.8, 125.4, 125.8, 126.3, 126.5, 126.6, 126.8 (m, 2 × C_m, $PhCF_3$), 127.1, 127.2, 127.5, 128.2, 128.3, 128.3, 128.5, 128.5, 128.7, 129.1, 130.7, 130.9, 131.3, 135.9, 149.2 (d, J = 5.5 Hz, C–O), 157.9 (C_{ipso}, $PhCF_3$) ppm. ^{19}F NMR (125 Hz, $CDCl_3$): δ = –61.9 ppm. ^{31}P NMR (125 Hz, $CDCl_3$): δ = 125.3 ppm. MS (EI, 70 eV): m/z (%) = 460 (10) $[M]^+$, 299 (40) $[C_{20}H_{12}OP]^+$, 270 (11) $[C_{20}H_{14}O]^+$, 252 (13) $[C_{20}H_{12}]^+$, 162 (100) $[C_7H_5F_3O]^+$, 143 (60) $[C_7H_3F_3]^+$, 112 (28). HRMS (EI): $C_{27}H_{16}O_2F_3P$ = 460.0818 (found:) $[M]^+$; 460.0834 (calcd.) $[M]^+$.

2,2′-Dibromo-[1,1′]binaphthalenyl (10): The synthesis of 2,2′-dibromo-[1,1′]binaphthalenyl (**10**) was carried out by the procedure of Takaya and Noyori.[22] The crude product was purified by column chromatography (silica gel, *n*-hexane/EtOAc 4:1; R_f = 0.77); yield: 39% (ref.[21] yield 45%).

2′-Bromo-2-methyl-[1,1′]binaphthalenyl (11): A solution of *n*BuLi (1.6 M, 1.630 mmol, 1.02 mL) was added dropwise at –78 °C to a solution of 2,2′-dibromo-[1,1′]binaphthalenyl (**10**, 0.67 g, 1.625 mmol) in THF (15 mL). The reaction mixture was stirred at a temperature interval from –78 °C to –60 °C for 1 h. The solution was then cooled down to –78 °C and methyl iodide (0.23 g, 1.625 mmol) was added dropwise. The solution was stirred at the temperature interval from –78 °C to –60 °C for an additional 1 h. After warming to room temperature, the reaction mixture was poured into ice-cold water (50 mL) and extracted with diethyl ether (3 × 20 mL). The combined organic layers were dried with Na_2SO_4 and the solvents were removed in vacuo to give pure compound **11** as colourless crystals (0.55 g, 97%). R_f = 0.9; *n*-hexane/EtOAc 4:1; m.p. 123–124 °C. ^{1}H NMR (250.1 MHz, $CDCl_3$): δ = 1.99 (s, 3 H, CH_3), 6.92–7.03 (m, 2 H, arom. H), 7.12–7.20 (m, 2 H, arom. H), 7.27–7.45 (m, 3 H, arom. H), 7.73 (s, 2 H, arom. H), 7.80–7.85 (m, 3 H, arom. H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 20.5, 123.3, 125.4, 125.7, 126.6–126.8, 127.5, 128.4–128.8, 129.0, 129.6, 130.5, 132.5, 132.7, 132.9, 134.2, 134.9, 135.5, 137.7 ppm. MS (EI, 70 eV): m/z (%) = 348 (69) $[M + 1]^+$, 347 (13) $[M]^+$, 346 (69) $[M - 1]^+$, 267 (100) $[M - Br]^+$, 252 (95) $[M - Br - CH_3]^+$.

6-[(1*S*,2*R*,5*S*)-Menthyloxy]-6*H*-dinaphtho[*c*,*e*][1,2]oxaphosphinine–Borane Complex 13a (Diastereomeric Mixture): A mixture of (+)-menthol (0.15 g, 0.95 mmol) and triethylamine (0.15 mL, 1.80 mmol), dissolved in toluene (8 mL), was added dropwise at 0 °C to a stirred solution of 6-chloro-6*H*-dinaphtho[*c*,*e*][1,2]oxaphosphinine (**7a**, 0.30 g, 0.90 mmol) in toluene (20 mL). The reaction mixture was allowed to warm to room temperature and stirred for 2 h. A solution of $BH_3{\cdot}Me_2S$ (2 M in toluene, 1.20 mmol, 0.6 mL) was then added and the resulting solution was stirred overnight at room temperature. The solvent was evaporated, and the residue was purified by column chromatography (silica gel, toluene/*n*-heptane 1:1; R_f = 0.55) to give compound **13a** (mixture of the two diastereomers in a ratio of 1:1) as a white solid (0.199 g, 47%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.75–1.75 (m, 19 H, menthyl, BH_3), 2.15–2.45 (m, 2 H, menthyl, $H_{6'}$), 4.60 (ddd, J = 20.7, J = 10.4, J = 5.8 Hz, 1 H, 1′-H), 7.04–7.12 (m, 2 H, arom. H), 7.13–7.26 (m, 4 H, arom. H), 7.30–7.42 (m, 3 H, arom. H), 7.45–7.52 (m, 2 H, arom. H), 7.64 (ddd, J = 8.7, J = 8.7, J = 5.4 Hz, 1 H, H), 7.79–7.89 (m, 3 H, arom. H) 7.93–7.99 (m, 1 H, arom. H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.0 ($CHMeCH_3$), 16.1 ($CHMeCH_3$), 21.4 ($CHMeCH_3$), 21.5 ($CHMeCH_3$), 21.9 (C-5′), 22.5 (C-5′), 23.2 (C-3′), 25.8 (C-5′-CH_3), 26.3 (C-5′-CH_3), 32.0 (C-2′-CH), 32.1 (C-2′-CH), 34.4 (C-4′), 34.5 (C-4′), 43.7 (C-6′), 44.0 (C-6′), 49.1 (m, C-2′), 82.0 (d, $J_{C,P}$ = 3 Hz, CH–O), 82.2 (d, $J_{C,P}$ = 3 Hz, CH–O), 120.4 (m, C–P), 125.5, 125.7, 126.4, 126.5, 127.6, 128.1, 128.6, 128.9, 129.4, 129.8, 129.9, 129.9, 130.0, 131.6, 131.8, 134.5, 134.6, 134.7, 134.7, 136.2, 138.3, 146.8 (m, C–O) ppm. ^{31}P NMR (125 MHz, $CDCl_3$): δ = 139.1 (br. s) ppm. MS (EI, 70 eV): m/z (%) = 468 (3) $[M]^+$, 454 $[M - BH_3]^+$, 316 (100) $[M - C_{10}H_{18}]^+$, 297 (49), 268 (19) $[C_{20}H_{12}O]^+$, 252 (80) $[C_{20}H_{12}]^+$, 239 (17), 138 (5) $[C_{10}H_{18}]^+$.

6-[(*S*)-α-Methyl-benzylamino]-6*H*-dinaphtho[*c*,*e*][1,2]oxaphosphinine–Borane Complex 13b (Diastereomeric Mixture): A mixture of (*S*)-(–)-α-methyl-benzylamine (0.084 mL, 0.66 mmol) and triethylamine (0.07 mL, 0.60 mmol), dissolved in toluene (8 mL), was added dropwise at 0 °C to a stirred solution of 6-chloro-6*H*-dinaphtho[*c*,*e*][1,2]oxaphosphinine (**7a**, 0.20 g, 0.60 mmol) in toluene (10 mL). The reaction mixture was allowed to warm to room temperature and stirred for 2 h. A solution of $BH_3{\cdot}Me_2S$ (2 M in toluene, 0.80 mmol, 0.4 mL) was then added and the resulting solution was stirred for an additional 2 h at room temperature. The solvent was evaporated, and the residue was purified by column chromatography (silica gel, toluene/*n*-heptane 1:1; R_f = 0.15) to give **13b** (mixture of two diastereomers in a ratio of 1:1 as a white solid, 0.133 g, 51%). ^{1}H NMR (250 Hz, $CDCl_3$): δ = 0.51–1.49 (br. m, BH_3), 0.92 (d, J = 7 Hz, 3 H, CH_3), 1.07 (d, J = 7 Hz, 3 H, CH_3), 3.21–3.69 (m, 2 H, NH), 3.94 (m, 1 H, CH), 4.18 (m, 1 H, CH), 6.45 (d, 1 H, Ar), 6.75–7.98 (m, 11 H, Ar) ppm. ^{13}C NMR (125 Hz, $CDCl_3$): δ = 24.2 (CH_3), 26.2 (CH_3), 52.3 (CH), 53.1 (CH), 117.5, 120.4, 123.3, 147.7–121.2, 129.7, 131.0, 131.5, 143.2 (q), 144.2 (q), 147.6 (q), 148.7 (q), 151.0 (q) ppm. ^{31}P NMR (121 Hz, $CDCl_3$): δ = 83.5 (br. m), 111.1 (br. m) ppm. MS (EI, 70 eV): m/z (%) = 420 (32) $[M - BH_3]^+$, 299 (100) $[M - BH_3 - MeBnN]^+$.

6-[(*S*)-Methoxycarbonyl-phenylmethoxy]-6*H*-dinaphtho[*c*,*e*][1,2]oxaphosphinine–Borane Complex 13c (Diastereomeric Mixture): A mixture of methyl (*R*)-mandelate (0.15 g, 0.90 mmol) and triethylamine (0.11 g, 0.15 mL, 1.07 mmol), dissolved in toluene (10 mL), was added dropwise at 0 °C to a stirred solution of 6-chloro-6*H*-dinaphtho[*c*,*e*][1,2]oxaphosphinine (**7a**, 0.300 g, 0.90 mmol) in toluene (10 mL). The reaction mixture was allowed to warm to room temperature and stirred for 12 h. A solution of $BH_3{\cdot}Me_2S$ (2 M in toluene, 2.60 mmol, 4 mL) was then added and the resulting solution was stirred overnight at room temperature. The solvent was evaporated, and the residue was purified by column chromatography (silica gel, toluene/*n*-heptane 1:1; R_f = 0.85) to give **13c** (mixture of two diastereomers in a ratio of 1:1 as a white solid, 0.2 g, 40%). ^{1}H NMR (500 Hz, $CDCl_3$): δ = 1.09 (br. m, BH_3), 3.44 (s, 3

H, OCH_3), 3.57 (s, 3 H, OCH_3), 5.66 (d, J = 9.5 Hz, 1 H, CHPh), 5.90 (d, J = 9.8 Hz, 1 H, CHPh), 6.82–7.36 (m, 7 H, Ar), 7.44–7.69 (m, 4 H, Ar), 7.83–8.14 (m, 4 H, Ar) ppm. ^{13}C NMR (125 Hz, $CDCl_3$): δ = 52.6 (OCH$_3$), 52.7 (OCH$_3$), 77.0 (d, J = 4 Hz, CHPh), 78.0 (d, J = 6 Hz, CHPh), 118.3 (q), 119.2 (d, J = 3.7 Hz, C-2), 119.9 (d, J = 3.7 Hz, C-2), 125.2, 125.3, 125.4, 125.8, 126.0, 126.1, 126.1, 126.8, 126.8, 127.3, 127.4, 128.3, 128.3, 128.4, 128.4, 128.5, 128.6, 128.9, 129.0, 129.3, 129.3, 129.5, 129.6, 130.9, 131.1, 131.2, 131.3, 134.4, 136.2 (d, J = 2 Hz, C–P), 136.3 (d, J = 2 Hz, C–P), 147.1 (C_{Ar}–O), 168.5 (COOMe), 168.6 (COOMe) ppm. ^{31}P NMR (125 Hz, $CDCl_3$): δ = 118.5 (br. s), 120.5 (br. s) ppm. MS (EI, 70 eV): m/z (%) = 478 (3) $[M]^+$, 464 (72) $[M - BH_3]^+$, 315 (100) $[M - BH_3 - C_9H_9O_2]^+$, 299 (100).

6-[(*S*)-α-Methyl-benzylamino]-6*H*-dinaphtho[*c*,*e*][1,2]oxaphosphinine (14b, Diastereomeric Mixture): The compound was prepared by a literature procedure by treatment of 6-[(1*S*,2*R*,5*S*)-menthyloxy]-6*H*-dinaphtho[*c*,*e*][1,2]oxaphosphinine–borane complex **13b** with DABCO (1,4-diazabicyclo[2,2,2]octane).[20] ^{31}P NMR (125 MHz, $CDCl_3$): δ = 76.4 and 76.8 ppm (mixture of two diastereomers in a ratio of 1:1).

6-[(1*S*,2*R*,5*S*)-Menthyloxy]-6*H*-dinaphtho[*c*,*e*][1,2]oxaphosphinine (14a, Diastereomeric Mixture): 6-[(1*S*,2*R*,5*S*)-Menthyloxy]-6*H*-dinaphtho[*c*,*e*][1,2]oxaphosphinine (**14a**) was prepared by treatment of 6-[(1*S*,2*R*,5*S*)-menthyloxy]-6*H*-dinaphtho[*c*,*e*][1,2]oxaphosphinine–borane complex (**13a**) with DABCO (1,4-diazabicyclo[2,2,2]octane) in toluene.[32] ^{31}P NMR (125 MHz, $CDCl_3$): δ = 167.4 and δ = 168.1 ppm (two diastereomers in a ratio of 1:1).

6-{[(1*S*,2*R*,5*S*)-2-Isopropyl-5-methylcyclohexyl]oxy}-6*H*-dinaphtho-[*c*,*e*][1,2]oxaphosphinine *P*-Oxide (15, Diastereomeric Mixture): A mixture of (+)-menthol (0.175 g, 0.0011 mol) and triethylamine (0.114 g, 0.157 mL, 0.001123 mol), dissolved in toluene (8 mL), was added dropwise at 0 °C to a stirred solution of 6-chloro-6*H*-dinaphtho[*c*,*e*][1,2]oxaphosphinine (**7a**, 0.350 g, 0.00104 mol) in toluene (20 mL). The reaction mixture was allowed to warm to room temperature and stirred for 3 h. A solution of hydrogen peroxide (30%, 1 mL) was added to the reaction mixture at 0 °C. The resulting biphasic system was vigorously stirred for 3 h at room temperature. The organic layer was separated, washed with water (10 mL) and dried with Na_2SO_4. The solvent was removed in vacuo and the residue was purified by column chromatography (silica gel, toluene/*n*-heptane 1:1) to give compound **15** (mixture of two diastereomers in a ratio of 1:1) as a white solid. It was crystallized from *n*-pentane (0.34 g, 70%), to give a mixture of two diastereomers in a ratio of 100:67. R_f = 0.85 (CH_2Cl_2/MeOH 98:2), 0.4 (CH_2Cl_2). ^{1}H NMR (500 Hz, $CDCl_3$): δ = 0.78–1.70 (m, 16 H, menthyl), 1.20 (br. m, BH_3), 2.15–2.57 (m, 2 H, menthyl), 4.00–4.09 (m, 1 H, CH–O), 4.60–4.78 (m, 1 H, CH–O), 7.16–7.27 (m, 2 H, Ar), 7.33–7.61 (m, 5 H, Ar), 7.73–7.98 (m, 5 H, Ar) ppm. ^{13}C NMR (125 Hz, $CDCl_3$): δ = 14.1, 15.7, 20.9, 21.0, 21.1, 22.0, 22.3, 22.8 (C-3′), 22.9 (C-3′), 25.7, 25.9, 31.6, 31.7, 34.0 (C-4′), 34.1 (C-4′), 43.1 (C-6′), 43.5 (C-6′), 48.4 (d, J = 10 Hz, C-2′), 48.5 (d, J = 10 Hz, C-2′), 79.7 (d, J = 7.5 Hz, C-1′), 80.1 (d, J = 7.5 Hz, C-1′), 119.8, 119.9, 119.9, 123.5, 123.7, 123.9, 124.0, 124.4, 125.1, 125.9, 127.6, 127.7, 127.8, 128.3, 128.3, 128.5, 128.6, 128.9, 129.7, 129.9, 131.4, 135.4 (C–P), 135.5 (C–P), 147.3 (d, J = 5 Hz, C_{Ar}–O), 147.5 (d, J = 5 Hz, C_{Ar}–O) ppm. ^{31}P NMR (125 Hz, $CDCl_3$): δ = 11.2 (P=O), 11.5 (P=O) ppm. MS (EI, 70 eV): m/z (%) = 470 (14) $[M]^+$, 332 (14.2) $[M - C_{10}H_{18}]^+$, 313 (21), 266 (17), 138 (11) $[C_{10}H_{18}]^+$.

General Procedure for Hydroformylation: A Schlenk flask (25 mL) containing a magnetic stirring bar was charged with ligand (0.01 mmol), Rh(acac)$(CO)_2$ (1.00 mg, 0.0038 mmol) and solvent (5 mL). The mixture was stirred for 60 min and then the substrate (10.8 mmol) was added. The yellow reaction mixture was transferred under argon to a Parr autoclave (25 mL). The autoclave was purged three times with syngas and subsequently charged with syngas (CO/H_2 1:1, 50 atm). The autoclave was warmed up to 80 °C and the reaction was started by stirring. After 3 h, the autoclave was cooled and the gases were carefully released in a well-ventilated hood. The reaction mixture was analysed by GC to determine level of conversion and regioselectivity.

General Procedure for Hydrocyanation: A Schlenk flask (10 mL) was charged with ligand (0.20 mmol), $[Ni(cod)_2]$ (0.050 mmol) and toluene (1 mL). The dark orange solution was stirred for 60 min at room temperature. A solution of styrene (2.0 mmol) in toluene (1 mL) was then added, followed by acetone cyanohydrin (1.5 mmol). The reaction mixture was then stirred for 25 h at 60 °C. After cooling to room temperature, the homogeneous mixture was filtered and analysed by GC to determine the level of conversion and regioselectivity.

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