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Pinene-Derived Monodentate Phosphoramidites for Asymmetric Hydrogenation

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Phosphoramidite ligands based on pinene-derived chiral amines have been prepared by a straightforward procedure in good yields. The key step of the synthetic protocol is a stereoselective hydrogenation of annulated pinene–pyridine derivatives leading to (diastereoisomeric) secondary amines that were separated and treated with different chlorophosphites to yield the envisaged phosphoramidites. The absolute configurations of the ligands were assigned on the basis of NMR analyses and corroborated by X-ray diffraction analysis of a borane adduct of a typical ligand. The new ligands were employed in the asymmetric hydrogenation of imines and olefins. The iridium-catalyzed hydrogenation of imines provided up to 81 % *ee*, whereas in the rhodium-catalyzed hydrogenation of functionalized olefins enantioselectivities of up to 99 % *ee* were achieved. In this particular application, the different chiral elements of the ligand structure led to synergistic effects and the enantioselectivity is dominated by the chiral diol moiety.

Introduction

Transition-metal-catalyzed asymmetric transformations using chiral ligands belong to the most efficient procedures for the construction of enantiopure/enriched compounds.[1,2] In this field, the development of novel chiral ligands is important for new applications and challenging substrates. Among chiral ligands, phosphorus auxiliaries are of the utmost importance and have been extensively investigated over the past few decades.[3,4] Phosphoramidites have evolved to become a very efficient and versatile class of ligands and have been successfully used in a variety of asymmetric transformations, including hydrogenation reactions.[5–7] Their modular and simple synthesis from a diol, a (secondary) amine, and phosphorus trichloride has allowed for the creation of phosphoramidite libraries.[6a] Thus, the combination of a chiral diol [(1,1′-binaphthalene)-2,2′-diol (BINOL) in most cases] and a chiral amine component offers additional potential for exploiting the cooperative effects of the different chiral elements and hence for additional control over enantiodiscrimination/selectivity in asymmetric catalysis.[6] The chiral information in the amine moiety of the ligand can be of "synthetic" or "natural" origin.

Chiral ligands and auxiliaries synthesized from starting materials from the chiral pool have a long tradition and have found numerous applications.[2,8] Many of these chiral starting materials possess multiple stereogenic centers, which can allow a stereoselective construction of the desired ligand and result in synergistic effects in catalysis.[8,9] Among natural products, α-pinene is an attractive candidate for ligand synthesis as it is inexpensive, commercially available in both enantiomeric forms with high optical purity, and can be easily tailored by (diastereoselective) functionalizations.[9,10] The incorporation of the pinene moiety into chiral ligands has been exploited in the past. Ligands possessing N-, O-, and/or P-donor atoms have been de-

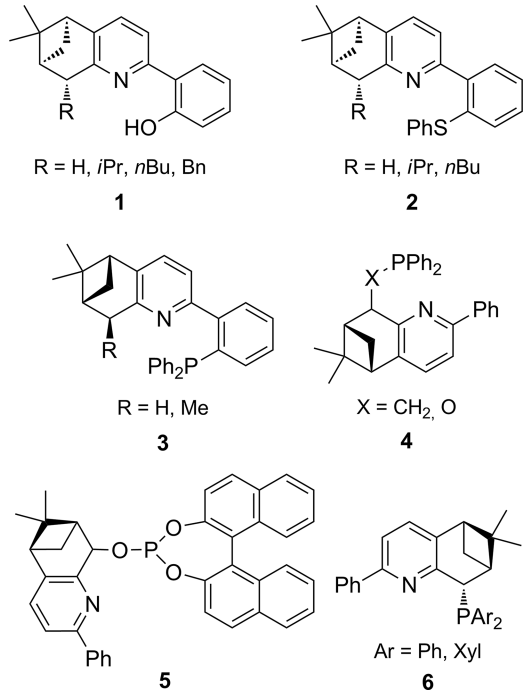

Figure 1. Examples of *N*,*O*-, *N*,*S*-, and *N*,*P*-ligands based on a pinene–pyridine framework.[12–14]

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scribed and employed in various catalytic transformations.[11] In particular, bidentate *N*,*O*- (**1**),[12] *N*,*S*- (**2**),[13] and *N*,*P*- (**3**–**6**)[14] -ligands containing an annulated pyridine ring have been reported in the last decade (Figure 1).

Differing from all the approaches exploited up to now, we envisaged utilising α-pinene to prepare chiral secondary amines and to use them as novel building blocks for the synthesis of phosphoramidite ligands. Herein we report the synthesis of a series of such monodentate phosphoramidites containing multiple chiral centers and different substituents in close spatial proximity to the phosphorus donor atom. The underlying amines were obtained by a stereoselective hydrogenation of annulated pinene–pyridine derivatives as the key synthetic step. The ligands were employed in the asymmetric hydrogenation of functionalized olefins (Rh-catalyzed) and imines (Ir-catalyzed), and the steric influence of the ligand substituents was evaluated as well as the interplay of the different chirality elements.

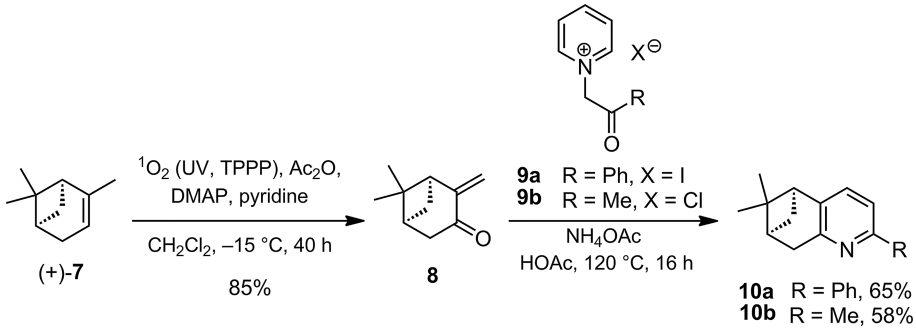
Results and Discussion

Ligand Synthesis

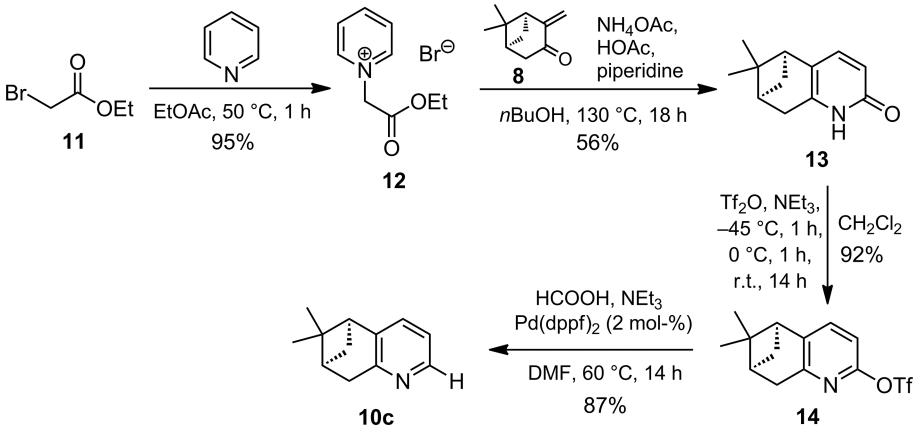
Enantiopure (1*R*,5*R*)-(+)-α-pinene (**7**) was used as the common starting material for the synthesis of all ligands **L1**–**L13**. Compound **7** was reacted in a photolysis apparatus with singlet oxygen in the presence of acetic anhydride and pyridine to give pinocarvone (**8**) in 85% yield.[15] In parallel, the pyridinium salts **9a** and **9b** were prepared by treating pyridine with chloroacetone or acetophenone and iodine, respectively.[16] The pyridinium salts **9a** and **9b** were subjected to Kröhnke annulation with pinocarvone (**8**) and ammonium acetate to give the pinene–pyridines **10a** and **10b** substituted at the 2-position of the pyridine ring with Me and Ph, respectively, in yields of 58–65% (Scheme 1).[17,18]

The unsubstituted pinene–pyridine **10c** (with R = H) is not directly accessible by simple Kröhnke annulation and was synthesized following the reaction sequence shown in Scheme 2.[19] First, the pyridinium salt **12** was prepared from pyridine and ethyl 2-bromoacetate (**11**) and then treated with pinocarvone (**8**) to give the pyridone **13**. The latter compound was aromatized to the triflate derivative **14** and finally the triflate group was substituted by a hydrogen atom to give the unsubstituted pinene–pyridine **10c** in an overall yield of 43% (Scheme 2).

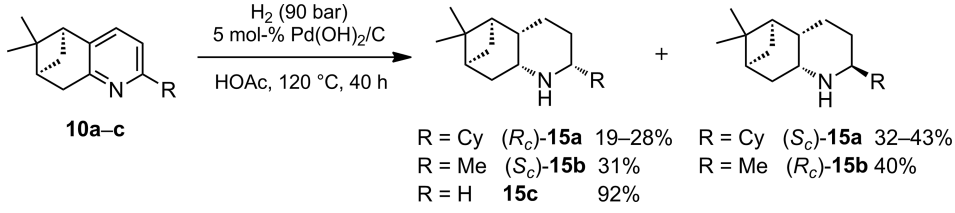
The pinene–pyridines **10a**–**c** were then hydrogenated to the desired pinene–piperidines. This is the key step of the synthesis because three new stereocenters are generated within this transformation and up to eight stereoisomers can be formed. Several heterogeneous hydrogenation catalysts were tested by using Ph-pinene–pyridine **10a** as the substrate.



Scheme 1. Synthesis of pinene–pyridines by ene reaction and subsequent Kröhnke annulation.



Scheme 2. Synthesis of **10c**.



Scheme 3. Hydrogenation of pinene–pyridines and the resulting diastereomers.

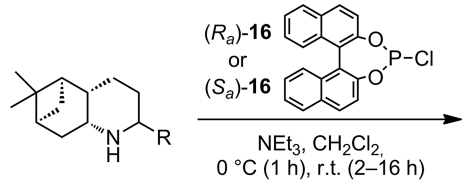
The first attempts using Rh/C, Rh/Al_2O_3, Pt/C, PtO_2, or Raney Ni (5 mol-%, 120 bar H_2, 120 °C) did not lead to the desired product, but to the reduction of the phenyl substituent to a cyclohexyl group. Even when HBF_4 or HOAc were added as acidic co-catalysts, the reduction of the pyridine ring did not occur. Finally, the use of Ru/C or $Pd(OH)_2/C$ in glacial acetic acid resulted in the successful conversion of Ph-pinene–pyridine **10a** into the fully hydrogenated product Cy-pinene–piperidine **15a** as a mixture of two stereoisomers in ratios of 70:30 and 55:45, respectively (Scheme 3).[20] The diastereomeric mixture could be separated either by column chromatography or by fractional precipitation of the HCl adduct from HOAc/diethyl ether to give (S_c)- and (R_c)-**15a** in yields of up to 43 and 28%, respectively.

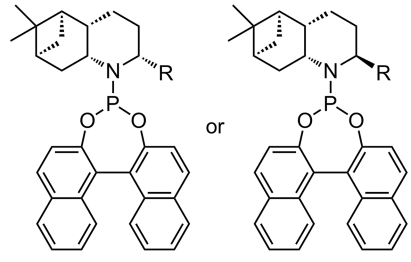
The structures of the hydrogenation products were assigned by NMR (NOESY) spectroscopy. From the optimized geometries of all eight possible stereoisomers (DFT calculations: M062X/def2-TZVP), proton distances relevant for establishing the stereochemistry were identified. The measured NOE interactions match the structures of the two diastereomers that differ only in the configuration at the 2-position of the heterocycle (see the Supporting Information). Interestingly, the hydrogen atoms have been preferentially delivered to the apparently more hindered face of the pyridine ring leading to the less-crowded product.

Following the same protocol, Me-pinene–pyridine **10b** was hydrogenated to the corresponding pinene–piperidine **15b** by using $Pd(OH)_2/C$ in HOAc (Scheme 3). Again, just two stereoisomers were obtained in a ratio of 60:40, which were successfully separated by column chromatography and (S_c)-**15b** and (R_c)-**15b** were isolated in yields of 31 and 40%, respectively. NMR spectroscopic analysis indicated that the stereoisomers obtained are epimers at C-2 and possess the same configurations at the remaining chiral centers as Cy-pinene–piperidines **15a**. It is important to note that the change in CIP priority between the Me- and Cy-substituted backbones leads to a different nomenclature with respect to the (R_c) or (S_c) configuration at the chiral center at the 2-position, although the relative spatial arrangements are identical (Scheme 3).

As expected, under the same conditions as above, the hydrogenation of H-pinene–pyridine **10c** led to only a single stereoisomer of **15c** in 92% yield. The configurations at the bridging carbons are identical to those of the pinene–piperidines **15a** and **15b**.[21]

The successfully synthesized secondary amines **15a**–**c** were then used for the synthesis of the envisaged phosphoramidite ligands. The pinene–piperidines were dissolved in CH_2Cl_2 in the presence of NEt_3, the solution was cooled to 0 °C, and a solution of (R_a)- or (S_a)-BINOL-PCl (**16**)[22] in CH_2Cl_2 was added dropwise over 15 min. After 1 h at 0 °C, the reaction mixture was allowed to warm to room temperature and then stirred for 2–16 h to allow full conversion of the chlorophosphite **16**. After filtration through a pad of basic alumina, the ligands **L1**–**L10** were obtained in moderate to good yields (49–87%; Scheme 4).[23]





Ligand	R	Yield	Geometry
(S_a), **L1**	H	84%	-
(R_a), **L2**	H	87%	-
(S_cS_a), **L3**	Me	69%	**A**
(S_cR_a), **L4**	Me	84%	**A**
(R_cS_a), **L5**	Me	62%	**B**
(R_cR_a), **L6**	Me	59%	**B**
(S_cS_a), **L7**	Cy	62%	**B**
(S_cR_a), **L8**	Cy	70%	**B**
(R_cS_a), **L9**	Cy	49%	**A**
(R_cR_a), **L10**	Cy	78%	**A**

Scheme 4. Synthesis of pinene-derived phosphoramidites.

For ligand **L2**, synthesized from H-pinene–piperidine **15c** and (R_a)-BINOL-PCl, single crystals of the borane adduct suitable for X-ray analysis were obtained from diethyl ether by slow evaporation at room temperature (Figure 2).

In the solid state, the piperidine ring exhibits a chair conformation and the pinene moiety adopts a half-chair con-

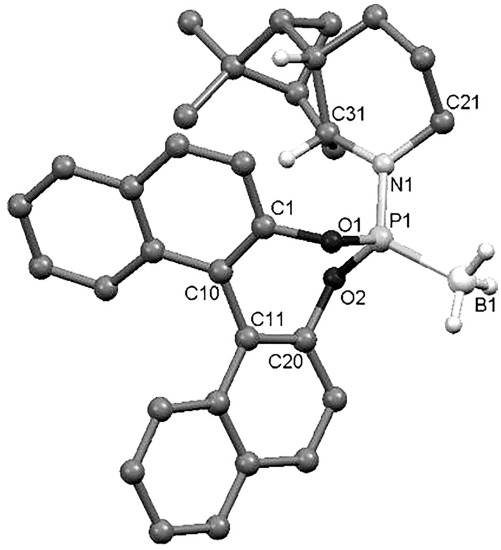


Figure 2. Structure of **L2**·BH_3 in the solid state as determined by X-ray diffraction analysis.

formation. The P1–N1 bond length of 1.6165 Å is relatively short (Table 1) and the P1–O1 and P1–O2 bond lengths of 1.6310 and 1.6145 Å differ slightly, which is rather unusual for BINOL-based ligands (Table 1). The dihedral angle of C1–C10–C11–C20 in the binaphthyl unit is relatively small (–47.98°), but is still within the expected range (Table 2). The phosphorus atom shows a nearly perfect tetrahedral geometry (sum of angles 655.55°) whereas the nitrogen atom shows a nearly perfect trigonal-planar geometry (sum of angles 359.70°) and hence has a high degree of sp^2-hybridized character (Table 2). The pinene fragment of the ligand shows a relatively large spatial distance to the phosphorus atom and in particular to the lone pair of the phosphorus atom (here coordinated by borane).

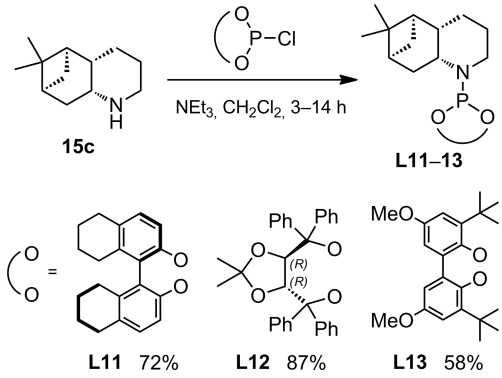
Table 1. Selected bond lengths [Å] in **L2**·BH_3.

P1–N1	1.6165	P1–O2	1.6145
P1–O1	1.6310	P1–B1	1.8886

Table 2. Selected bond angles [°] in **L2**·BH_3.

P1–N1–C31	124.09	O1–P1–B1	108.21
P1–N1–C21	119.30	O2–P1–B1	116.80
C21–N1–C31	116.31	N1–P1–B1	117.19
O1–P1–O2	99.97	N1–P1–O2	99.93
O1–P1–N1	113.45	C1–C10–C11–C20	–47.98

Then the diol moiety was varied by using the pinene–piperidine **15c** as the common amine. The chloro phosphites of (R_a)-H_8-BINOL, (*R*,*R*)-TADDOL, and of a tropoisomeric biphenol (generated in situ) were treated with **15c** following the procedure described above. The envisaged ligands **L11**–**L13** were obtained in yields of 58–87% (Scheme 5). The $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$, room temp.) of **L13** shows two peaks at δ = 144.4 and 150.6 ppm in a ratio of 87:13. The ^{31}P-^{31}P EXSY NMR measurements confirmed that the two peaks are in exchange, which indicates the presence in solution of interconverting isomers most probably differing in the conformation of the tropoisomeric biphenol unit. Consequently, separation was not feasible.

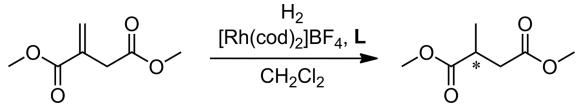


Scheme 5. Synthesis of phosphoramidites possessing different diol moieties.

Application in Asymmetric Hydrogenation

Ligands **L1**–**L13** were used in the rhodium-catalyzed asymmetric hydrogenation of functionalized olefins using dimethyl itaconate as a benchmark substrate. The catalysts were prepared in situ from $[Rh(cod)_2]BF_4$ and the phosphoramidite ligands with a Rh/P ratio of 1:2.05. The results are shown in Table 3.

Table 3. Asymmetric hydrogenation of dimethyl itaconate.[a]



Entry	Ligand	R	Diol	Geometry[b]	Conv.[c] [%]	*ee*[d] [%]
1	**L1**	H	(S_a)	–	>99	72 (*S*)
2	**L2**	H	(R_a)	–	>99	95 (*R*)
3	**L3**	(S_c)-Me	(S_a)	**A**	>99	24 (*S*)
4	**L4**	(S_c)-Me	(R_a)	**A**	>99	33 (*R*)
5	**L5**	(R_c)-Me	(S_a)	**B**	>99	16 (*S*)
6	**L6**	(R_c)-Me	(R_a)	**B**	>99	7 (*R*)
7	**L7**	(S_c)-Cy	(S_a)	**B**	>99	24 (*S*)
8	**L8**	(S_c)-Cy	(R_a)	**B**	>99	2 (*S*)
9	**L9**	(R_c)-Cy	(S_a)	**A**	>99	49 (*S*)
10	**L10**	(R_c)-Cy	(R_a)	**A**	>99	16 (*R*)
11	**L11**	H	(R_a)	–	>99	77 (*R*)
12	**L12**	H	(*R*,*R*)	–	>99	11 (*S*)
13	**L13**	H		–	>99	4 (*R*)
14[e]	**L2**	H	(R_a)	–	99	95 (*R*)
15[e,f]	**L2**	H	(R_a)	–	>99	83 (*R*)
16[g]	**L2**	H	(R_a)	–	98	94 (*R*)
17[h]	**L2**	H	(R_a)	–	98	95 (*R*)

[a] Substrate: 3 mmol, substrate/Rh/L = 1000:1:2.05, CH_2Cl_2: 2 mL, $p(H_2)$ = 40 bar, room temp., t = 16 h. [b] In analogy to Scheme 4. [c] Determined by GC. [d] Determined by chiral GC. [e] t = 1 h. [f] In MeOH. [g] Substrate/Rh = 10000:1. [h] $p(H_2)$ = 10 bar, t = 1 h.

All the ligands formed active Rh catalysts for this transformation and full conversion was achieved with all the catalyst systems under the standard conditions. The enantio-

selectivity was very strongly dependent on the amine moiety of the ligand, with the axial chirality at the diol moiety having a dominating steering effect determining in most cases the preferred configuration of the product formed. Cooperative effects between the pinene skeleton and the BINOL moiety were observed for ligands **L1** and **L2** based on the 2-unsubstituted amine **15c**. While a moderate enantioselectivity of 72% *ee* (*S*) was obtained with **L1** (Table 3, entry 1), the matched diastereomer **L2** led to 95% *ee* of the opposite enantiomer (*R*) (entry 2).

Surprisingly, the additional steric bulk caused by substituents at the 2-position of the pinene–piperidine moiety in **L3**–**L10** had a very negative influence on the enantioselectivity regardless of the configuration of the stereocenter. Considering the spatial orientation of the respective substituents, the ligands with geometry **A** gave higher *ee* values than the ligands with geometry **B** (Table 3, entries 3–10).

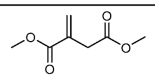
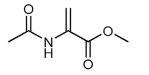
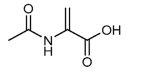
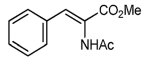
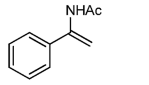
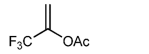
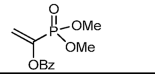
The three ligands **L11**–**L13** based on the most promising amine moiety **15c** did not lead to improved results. In particular, **L11** bearing (R_a)-H_8-BINOL gave a lower *ee* than the related (R_a)-BINOL-based **L2** (77 vs. 95% *ee*, respectively), and almost racemic products were obtained with (*R*,*R*)-TADDOL and the biphenol-based ligands **L12** and **L13** (Table 3, entries 11–13).

The activity and productivity of the Rh/**L2** system were investigated further. At a 0.1 mol-% catalyst loading, full conversion was achieved within 1 h corresponding to a TOF of ≥1000 h^{-1} (Table 3, entry 14). Almost full conversion (TON 9800) at the same level of enantioselectivity could be obtained by reducing the catalyst loading to 0.01 mol-% (Table 3, entry 16). When MeOH was used as the reaction solvent, the enantioselectivity was slightly reduced (Table 3, entry 15).[24] A reduced hydrogen pressure of 10 bar did not affect the enantioselectivity (Table 3, entry 17).

The substrate scope was explored by using the isolated catalyst complex [Rh(cod)(**L2**)$_2$]BF_4 prepared from [Rh(cod)acac], HBF_4·Et_2O, and **L2**.[25] The results of the substrate screening are summarized in Table 4.

The asymmetric hydrogenation using [Rh(cod)(**L2**)$_2$]BF_4 led to full conversion for all the substrates tested. In the case of dimethyl itaconate, the use of the isolated catalyst gave the same enantioselectivity as the in situ generated catalyst (Table 3, entry 2 vs. Table 4, entry 1). Methyl 2-acetamidoacrylate was hydrogenated with 95% *ee* (*S*) (Table 4, entry 2), whereas a slightly lower enantiomeric excess of 88% (*S*) was achieved with the corresponding free acid 2-acetamidoacrylic acid (Table 4, entry 3). The enantioselectivity obtained in this hydrogenation might be negatively affected by the use of MeOH as solvent, which is necessary due to solubility constraints of the substrate in CH_2Cl_2. In the hydrogenation of methyl (*Z*)-acetamidocinnamate, an enantiomeric excess of 96% (*S*) was achieved (Table 4, entry 4), whereas a lower enantioselectivity of 49% *ee* (*S*) was obtained for *N*-(1-phenylvinyl)acetamide (Table 4, entry 5). Using 1-trifluoromethylvinyl acetate as substrate, a good enantiomeric excess of 95% (*S*) was again obtained (Table 4, entry 6). Finally, a high enantioselectivity of 99% (*S*) was achieved in the hydrogenation of 1-(dimethoxyphosphoryl)vinyl benzoate by using 1 mol-% of the catalyst (Table 4, entry 7). To the best of our knowledge this is the highest enantioselectivity ever reported for this substrate using monodentate ligands.

Table 4. Rhodium-catalyzed asymmetric hydrogenation of prochiral olefins using [Rh(cod)(**L2**)$_2$]BF_4.[a]

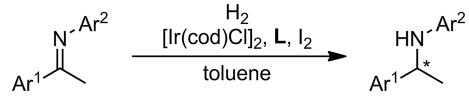
Entry	Substrate	cv[b] [%]	*ee*[c] [%]
1		>99	95 (*R*)
2		>99	95 (*S*)
3[d]		>99	88 (*S*)
4		>99	96 (*S*)
5		>99	49 (*S*)
6		>99	95 (*S*)
7[e]		>99	99 (*S*)

[a] Substrate: 1.5 mmol, substrate/Rh = 1000:1, CH_2Cl_2: 2 mL, $p(H_2)$ = 20 bar, room temp., t = 14 h. [b] Determined by ^{1}H NMR spectroscopy. [c] Determined by chiral GC or HPLC. [d] In MeOH. [e] Substrate/Rh = 100:1.

Next, the Ir-catalyzed hydrogenation of prochiral imines was investigated by using the phosphoramidites **L1** and **L2**. The catalytic systems were generated in situ from [Ir(cod)Cl]$_2$ and the respective ligand in an iridium/phosphorus ratio of 1:2.1. Iodine (5 mol-%) was used as an activator. The results are summarized in Table 5. In the hydrogenation of *N*-(1-phenylethylidene)aniline, full conversion was obtained with both ligands. While **L2** led to the (*S*) enantiomer with 70% *ee*, the use of **L1** gave a higher *ee* of 74% of the opposite enantiomer (*R*) (Table 5, entries 1 and 2). Thus, in contrast to the Rh-catalyzed olefin hydrogenation reaction, the two diastereomers **L1** and **L2** led to similar levels of enantioselectivity and, again, the enantiodiscrimination is largely dominated by the configuration of the BINOL moiety.

The scope of the Ir/**L1**/I_2 system was evaluated for a series of acyclic imines containing additional functional groups. In comparison with *N*-(1-phenylethylidene)aniline, an increased steric demand around the C=N bond, either at the carbon (Ar^1 = *o*-tolyl) or the nitrogen (Ar^2 = 2-naphthyl), led to slightly reduced enantioselectivity (Table 5, entries 3 and 4). When both groups were present in the substrate, a significantly lower conversion was also obtained (Table 5, entry 5). Electron-withdrawing fluoro or chloro substituents at the *para* position of Ar^1 led to lower enantiomeric excesses of 65 and 55% (Table 5, entries 6 and

Table 5. Ir-catalyzed asymmetric hydrogenation of acyclic imines.[a]



Entry	Ligand	Ar^1	Ar^2	Conv.[b] [%]	*ee*[c] [%]
1	**L1**	Ph	Ph	>99	74 (*R*)
2	**L2**	Ph	Ph	>99	70 (*S*)
3	**L1**	Ph	2-MeC_6H_4	>99	72 (–)
4	**L1**	2-naphthyl	Ph	92	63 (–)
5	**L1**	2-naphthyl	2-MeC_6H_4	77	60 (–)
6	**L1**	4-FC_6H_4	Ph	96	65 (–)
7	**L1**	Ph	4-$MeOC_6H_4$	65	81 (+)
8	**L1**	2-naphthyl	4-$MeOC_6H_4$	<10	–
9	**L1**	4-$MeOC_6H_4$	4-$MeOC_6H_4$	>99	63 (+)
10	**L1**	4-ClC_6H_4	Ph	>99	55 (–)
11	**L1**	4-ClC_6H_4	4-$MeOC_6H_4$	>99	63 (+)

[a] Substrate: 0.5 mmol, substrate/Ir/L/I_2 = 100:1:2.1:5, toluene: 2 mL, $p(H_2)$ = 40 bar, room temp., t = 14 h. [b] Determined by GC or ^{1}H NMR spectroscopy. [c] Determined by chiral GC or chiral HPLC.

10), whereas an electron-donating *p*-methoxy substituent in Ar^2 resulted in an increased enantioselectivity of 81% *ee* (+) with a reduced conversion of 65% (Table 5, entry 7). The reactivity of the substrate dramatically decreased when both the 2-naphthyl group (Ar^1) and the *p*-methoxyphenyl (Ar^2) were present (Table 5, entry 8). In contrast, *p*-methoxy substituents in both Ar^1 and Ar^2 led to full conversion and a moderate enantiomeric excess of 63% (+) (Table 5, entry 9). The combination of an electron-donating *p*-methoxy substituent in Ar^2 and an electron-withdrawing chloro substituent in Ar^1 again resulted in full conversion and 63% *ee* (+) (Table 5, entry 11).

Conclusions

Chiral secondary amines derived from pinene have been synthesized and used as novel building blocks for the preparation of a small library of monodentate phosphoramidites, which has been evaluated in the asymmetric hydrogenation of prochiral olefins and imines. The underlying amine components were synthesized from enantiopure α-pinene by a Schenk–ene reaction followed by Kröhnke annulation and subsequent hydrogenation of the pyridine ring as the key step of the synthetic protocol. The hydrogenation of the annulated pyridines bearing H, Me, or Ph at C-2 was catalyzed by $Pd(OH)_2$/C (or Ru/C) and proceeded stereoselectively at the two carbon atoms at the ring junctures, whereas the chirality at C-2 was not controlled. Thus, the chirality embedded in the pinene scaffold is effective in directing the stereochemistry of the hydrogenation reaction. The resulting Me- and Cy-substituted diastereomers were easily separated either by column chromatography or crystallization of the hydrochloride derivatives. The structures of the novel pinene–piperidines were elucidated by means of NMR spectroscopy (NOESY) and confirmed in the solid state by X-ray diffraction analysis.

The pinene–piperidines were then treated with different diols to give 13 structurally different phosphoramidite ligands, which were evaluated in asymmetric catalysis. In the rhodium-catalyzed asymmetric hydrogenation of differently functionalized olefins, **L2** comprising the most simple piperidine derivative and the (R_a)-BINOL moiety proved to be the most efficient ligand leading to high enantiomeric excesses of up to 99%, a TOF of ≥1000 h^{-1}, and a TON of 9800. The diastereomeric counterpart **L1** bearing the (S_a)-BINOL gave the highest enantioselectivities in the iridium-catalyzed asymmetric hydrogenation of acyclic imines with *ee* values of up to 81%.

This investigation has shown that α-pinene is a useful chiral starting material for the synthesis of phosphoramidites with multiple stereogenic centers and the right combination of different chiral and structural elements has provided two valuable ligands for metal-catalyzed asymmetric hydrogenation reactions.

Experimental Section

General: All reactions and manipulations were performed using standard Schlenk techniques or in a glovebox under argon. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded with Bruker AV 600 (600, 150, and 243 MHz, respectively), AV 400 (400, 100, and 162 MHz, respectively), and Bruker AV 300 (300, 75, and 121 MHz, respectively) spectrometers. The chemical shifts are referenced to residual solvent peaks (^{1}H, ^{13}C NMR) or H_3PO_4 85% as external standard (^{31}P NMR). Mass spectra were recorded with a Finnigan MAT 8200 (MS + HRMS-EI) or Bruker FTICR-Apex III (HRMS-ESI) spectrometer. Optical rotations were measured with a Jasco P-1020 polarimeter. The concentrations used for measuring specific rotations are given as g per 100 mL. CH_2Cl_2, toluene, and *n*-pentane were dried with alumina and molecular sieves with a solvent purification system from Innovative Technology. THF, diethyl ether, and NEt_3 were distilled from KOH and dried with molecular sieves. PCl_3 was freshly distilled. $CDCl_3$, CD_2Cl_2, and C_6D_6 were degassed through freeze–pump–thaw cycles and stored over molecular sieves. All solvents and compounds were stored over molecular sieves under argon. The following compounds were synthesized according to literature procedures: (R_a)- and (S_a)-BINOL-PCl (**16**),[22] (*R*)-H_8-BINOL-PCl,[26] (*R*,*R*)-TADDOL-PCl,[27] 1-(2-oxo-2-phenylethyl)pyridinium iodide (**9a**),[16b] 1-(2-oxopropyl)pyridinium chloride (**9b**),[16c] 1-(2-ethoxy-2-oxoethyl)pyridinium bromide (**12**),[19a] (1*S*,9*S*)-10,10-dimethyl-5-phenyl-6-azatricyclo[7.1.1.$0^{2,7}$]undeca-2,4,6-triene (**10a**).[17c] Silica gel (SiO_2 60, 0.04–0.063 mm, 230–400 mesh) and basic alumina (Al_2O_3 90 basic, pH 8.5–10.5, 0.063–0.2 mm) were purchased from Roth. All other chemicals were purchased from Sigma–Aldrich, ABCR, TCI, or AlfaAesar and used as received.

General Procedure for the Synthesis of Ligands: The pinene–piperidine derivatives **15a**–**c** (1.0 equiv.) were dissolved in CH_2Cl_2 (10 mL). The solution was cooled to 0 °C and triethylamine (3.0 equiv.) was added. After 10 min a solution of the chlorophosphite **16** (1.0 equiv.) in CH_2Cl_2 (5 mL) was added dropwise during 15 min. The reaction mixture was stirred at 0 °C for 30 min and for a further 5 h at room temperature. The solvent was removed under reduced pressure and the residue redissolved in THF (8 mL). The solution was filtered through a pad of basic alumina and rinsed with THF (8 mL). Removal of the solvent under reduced pressure yielded the desired product as a white powder.

General Procedure for the Catalytic Hydrogenation of Dimethyl Itaconate Using in situ Generated Catalysts: A solution of the respective ligand (6.15 μmol, 2.05 equiv.) in CH_2Cl_2 (1 mL) was added to a solution of $[Rh(cod)_2]BF_4$ (1.22 mg, 3.0 μmol, 1.0 equiv.) in CH_2Cl_2 (1 mL). The mixture was stirred for 15 min at room temperature and then transferred under argon to a 10 mL stainless-steel autoclave equipped with a glass inlet and magnetic stirring bar and charged with dimethyl itaconate (474.5 mg, 3.0 mmol, 1.000 equiv.). After stirring for 10 min, the autoclave was pressurized with hydrogen and the mixture stirred for 14 h at room temperature. Further details and modifications of the conditions are given in Table 3. After carefully releasing the pressure, the reaction mixture was filtered through a short plug of silica and analyzed by NMR spectroscopy and chiral GC.

General Procedure for the Catalytic Hydrogenation of C=C Double Bonds Using $[Rh(cod)(L2)_2]BF_4$: A solution of $[Rh(cod)(\mathbf{L2})_2]BF_4$ (1.9 mg, 1.5 μmol, 1.0 equiv.) in CH_2Cl_2 or MeOH (1 mL) was transferred under argon to a 10 mL stainless-steel autoclave equipped with a glass inlet, a magnetic stirring bar and containing the desired substrate (1.5 mmol, 1.000 equiv.). After stirring for 10 min, the autoclave was pressurized with hydrogen and the mixture stirred for the indicated time at room temperature. Further details and modifications of the conditions are given in Table 4. After carefully releasing the pressure, the reaction mixture was filtered through a short plug of silica and analyzed by NMR spectroscopy and chiral GC or HPLC. The absolute configurations of the hydrogenation products were assigned by comparison of their signs of optical rotation with those reported in the literature.

General Procedure for the Catalytic Hydrogenation of C=N Double Bonds: A solution of the ligand (10.5 μmol, 2.1 equiv.) in toluene (1 mL) was added to a solution of $[Ir(cod)Cl]_2$ (1.68 mg, 2.5 μmol, 0.5 equiv.) in toluene (1 mL). The mixture was stirred for 15 min at room temperature and then added to the substrate (0.5 mmol, 100 equiv.) and iodine (6.4 mg, 25 μmol, 5.0 equiv.). After stirring for 10 min the solution was transferred under argon to a 10 mL stainless-steel autoclave, equipped with a glass inlet and a magnetic stirring bar. The autoclave was pressurized with hydrogen and the mixture stirred for 14 h at room temperature. Further details are given in Table 5. After carefully releasing the pressure, all the volatiles were removed under reduced pressure. The residue was analyzed by NMR spectroscopy and in the case of incomplete conversion purified by column chromatography. The enantiomeric excess was determined by chiral GC or HPLC.

(1*S*,5*S*)-6,6-Dimethyl-2-methylenebicyclo[3.1.1]heptan-3-one (8): In a photolysis apparatus (DEMA, UV apparatus 13/11, 300 mL total volume), (1*R*,5*R*)-(+)-α-pinene (**7**; 15.9 mL, 100 mmol, 1.0 equiv.) was dissolved in CH_2Cl_2 (130 mL). Acetic acid anhydride (14.2 mL, 150 mmol, 1.5 equiv.), pyridine (12.9 mL, 160 mmol, 1.6 equiv.), 4-(dimethylamino)pyridine (DMAP; 245 mg, 2.0 mmol, 0.02 equiv.), and 5,10,15,20-tetraphenyl-21*H*,23*H*-porphyrin (123 mg, 0.2 mmol, 0.002 equiv.) were added. The UV apparatus was equipped with a reflux condenser with a drying tube ($CaCl_2$) at the top. The reaction vessel was cooled to –10 °C by a cryostat. The deep-purple reaction mixture was stirred for 10 min and a slow stream of pressurized air was purged through the reaction mixture under vigorous stirring from the bottom of the reaction vessel to give small bubbles. The Hg lamp (Philips HPK 125) of the UV apparatus, which was cooled by a cryostat at –15 °C, was switched on and the reaction mixture stirred at the maximal rate (1200 rpm) for 40 h. When full conversion was achieved (TLC monitoring, pentane/ethyl acetate, 9:1), the Hg lamp and the pressurized air were switched off and the reaction mixture stirred at 5 °C for another 14 h. The yellow solution was diluted with CH_2Cl_2 (250 mL) and washed carefully with a saturated aqueous $NaHCO_3$ solution (3 × 150 mL) until the aqueous phase stayed basic. Then the organic phase was washed with 10% aqueous hydrochloric acid (2 × 75 mL) until the aqueous phase stayed acidic. Finally, the organic phase was washed with a saturated aqueous $CuSO_4$ solution (75 mL) and NaCl solution (150 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure keeping the temperature below 30 °C to prevent polymerization of the product. The brown oily residue was distilled under vacuum (5 mbar) by using a Vigreux column to give the product as a colorless liquid, yield 12.7 g (84.6 mmol, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.77 (s, 3 H, CH_3), 1.25 (d, $J_{H,H}$ = 10.4 Hz, 1 H, CH_2), 1.33 (s, 3 H, CH_3), 2.17 (m, 1 H, CH), 2.48 (m, 1 H, CH_2), 2.59–2.69 (m, 2 H, CH_2), 2.74 (t, $J_{H,H}$ = 6.0 Hz, 1 H, CH), 4.97 (d, $J_{H,H}$ = 1.7 Hz, 1 H, C=CH_2), 5.90 (d, $J_{H,H}$ = 1.7 Hz, 1 H, C=CH_2) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 21.4 (CH_3), 25.9 (CH_3), 32.3 (CH_2), 38.5 (CH), 40.7 (C_q), 42.4 (CH_2), 48.1 (CH), 117.2 (CH_2), 149.0 (C_q), 199.6 (C=O) ppm. The analytical data are in accordance with the literature.[15a,19a]

(1*S*,9*S*)-5,10,10-Trimethyl-6-azatricyclo[7.1.1.0^{2,7}]undeca-2,4,6-triene (10b): 1-(2-Oxopropyl)pyridinium chloride (**9b**; 10.43 g, 60.8 mmol, 1.5 equiv.) was dissolved in glacial acetic acid. Ammonium acetate (40.0 g, 520 mmol, 12.8 equiv.) was added and the mixture was heated to 130 °C and stirred until it became clear. Then (1*S*,5*S*)-6,6-dimethyl-2-methylenebicyclo[3.1.1]heptan-3-one (**8**; 6.1 g, 40.5 mmol, 1.0 equiv.) was added and the brownish reaction mixture was heated at reflux for 16 h. After cooling to room temperature, the brown solution was diluted with water (100 mL) and basified by the addition of a 15 M sodium hydroxide solution. The aqueous phase was extracted with ethyl acetate (4 × 100 mL) and the combined organic extracts were diluted with CH_2Cl_2 (500 mL). The organic layers were washed with water (3 × 100 mL) and brine (100 mL), and dried with Na_2SO_4. The solvent was removed under reduced pressure to give a brownish residue which was subjected to column chromatography (pentane/ethyl acetate, 2:1, R_f = 0.38). The product was obtained as a light-yellow liquid, yield 4.38 g (23.4 mmol, 58%). $[\alpha]_D^{28}$ = 57.0 (c = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.62 (s, 3 H, CH_3), 1.23 (d, $J_{H,H}$ = 9.3 Hz, 1 H, CH_2), 1.37 (s, 3 H, CH_3), 2.40 (tt, $J_{H,H}$ = 6.0, $J_{H,H}$ = 2.9 Hz, 1 H, CH), 2.49 (s, 3 H, CH_3), 2.60–2.71 (m, 1 H, CH, 1 H, CH_2), 3.06 (d, $J_{H,H}$ = 2.8 Hz, 2 H, CH_2), 6.80 (d, $J_{H,H}$ = 7.6 Hz, 1 H, Ar), 7.07 (d, $J_{H,H}$ = 7.6 Hz, 1 H, Ar) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 21.1 (CH_3), 24.0 (CH_3), 25.9 (CH_3), 32.0 (CH_2), 36.4 (CH_2), 39.3 (C_q), 40.1 (CH), 46.0 (CH), 119.4 (CH, Ar), 133.2 (CH, Ar), 138.4 (C_q, Ar), 154.8 (C_q, Ar), 155.8 (C_q, Ar) ppm. MS (EI): *m*/*z* (%) = 186 (24), 172 (38), 158 (17), 157 (11), 146 (15), 145 (15), 144 (100), 143 (27), 132 (10), 131 (12), 77 (11). HRMS (ESI): calcd. for $C_{13}H_{18}N^+$ $[M + H]^+$ 188.14338; found 188.14346.

(8*S*,10*S*)-10,10-Dimethyl-6-azatricyclo[7.1.1.0^{2,7}]undeca-2,4,6-triene (10c): Formic acid (1.0 mL, 26.0 mmol, 2.5 equiv.) was added dropwise to a solution of (5*S*,7*S*)-5,6,7,8-tetrahydro-6,6-dimethyl-5,7-methanoquinolin-2-yl trifluoromethanesulfonate (**14**; 3.32 g, 10.3 mmol, 1.0 equiv.), $Pd(OAc)_2$ (47 mg, 0.21 mmol, 0.02 equiv.), 1,1′-bis(diphenylphosphanyl)ferrocene (233 mg, 0.42 mmol, 0.04 equiv.), and triethylamine (4.3 mL, 31.0 mmol, 3.0 equiv.) in DMF (40 mL). The reaction mixture was stirred overnight at 60 °C. After cooling to room temperature, the reaction mixture was quenched by the addition of water (20 mL) and extracted with diethyl ether (4 × 50 mL). The combined organic extracts were washed with brine (50 mL) and dried with Na_2SO_4. The solvent was removed under reduced pressure and the brownish-orange resi-

due subjected to column chromatography (pentane/ethyl acetate, 4:1 to 1:1, R_f = 0.37) to give the product as a colorless liquid, yield 1.56 g (9.0 mmol, 87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.62 (s, 3 H, CH_3), 1.25 (d, $J_{H,H}$ = 9.5 Hz, 1 H, CH_2), 1.39 (s, 3 H, CH_3), 2.35 (m, 1 H, CH), 2.66 (dt, $J_{H,H}$ = 9.4, $J_{H,H}$ = 5.6 Hz, 1 H, CH_2), 2.73 (t, $J_{H,H}$ = 5.7 Hz, 1 H, CH), 3.10 (d, $J_{H,H}$ = 2.5 Hz, 2 H, CH_2), 6.95 (m, 1 H, Ar), 7.16 (m, 1 H, Ar), 8.33 (m, 1 H, Ar) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 21.1 (CH_3), 25.9 (CH_3), 31.8 (CH_2), 36.3 (CH_2), 39.3 (C_q), 40.1 (CH), 46.3 (CH), 120.2 (CH, Ar), 132.7 (CH, Ar), 141.7 (C_q, Ar), 146.5 (CH, Ar), 156.7 (C_q, Ar) ppm. The analytical data are in accordance with the literature.[19c]

(5*S*,7*S*)-5,6,7,8-Tetrahydro-6,6-dimethyl-5,7-methanoquinolin-2(1*H*)-one (13): Ammonium acetate (74.0 g, 960 mmol, 10.0 equiv.) and 1-(2-ethoxy-2-oxoethyl)pyridinium bromide (**12**; 26.0 g, 105.6 mmol, 1.1 equiv.) were suspended in dry *n*-butanol. (1*S*,5*S*)-6,6-Dimethyl-2-methylenebicyclo[3.1.1]heptan-3-one (**8**; 14.4 g, 96.0 mmol, 1.0 equiv.) and piperidine (1.9 mL, 19.2 mmol, 0.2 equiv.) were added sequentially to the yellow solution. The resulting red solution was heated at reflux for 2 h and glacial acetic acid (11.0 mL, 192.0 mmol, 2.0 equiv.) was added. The reaction mixture was then heated at reflux for 18 h at 140 °C. After cooling to room temperature the mixture was neutralized by the addition of a 2 M aqueous sodium hydroxide solution and extracted with ethyl acetate (4 × 100 mL). The combined organic layers were washed with brine (100 mL) and dried with Na_2SO_4. The solvent was removed under reduced pressure and the brownish residue subjected to column chromatography (pentane/diethyl ether/acetone/methanol, 45:30:22:3, R_f = 0.22) to yield the product as a colorless solid, yield 10.23 g (54.1 mmol, 56%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.70 (s, 3 H, CH_3), 1.26 (d, $J_{H,H}$ = 9.4 Hz, 1 H, CH_2), 1.37 (s, 3 H, CH_3), 2.28 (m, 1 H, CH), 2.57 (t, $J_{H,H}$ = 5.6 Hz, 1 H, CH), 2.63 (dt, $J_{H,H}$ = 9.5, $J_{H,H}$ = 5.5 Hz, 1 H, CH_2), 2.95 (m, 2 H, CH_2), 6.33 (d, $J_{H,H}$ = 8.9 Hz, 1 H, Ar), 7.15 (d, $J_{H,H}$ = 8.9 Hz, 1 H, Ar), 14.02 (br. s, 1 H, NH) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 21.0 (CH_3), 25.9 (CH_3), 31.4 (CH_2), 32.7 (CH_2), 39.4 (CH), 40.2 (C_q), 44.1 (CH), 114.8 (CH, Ar), 124.8 (C_q, Ar), 141.2 (CH, Ar), 142.3 (C_q, Ar), 165.6 (C=O) ppm. The analytical data are in accordance with the literature.[19a,19b]

(5*S*,7*S*)-5,6,7,8-Tetrahydro-6,6-dimethyl-5,7-methanoquinolin-2-yl Trifluoromethanesulfonate (14): Triethylamine (9.0 mL, 64.8 mmol, 1.2 equiv.) was added to a solution of (5*S*,7*S*)-5,6,7,8-tetrahydro-6,6-dimethyl-5,7-methanoquinolin-2(1*H*)-one (**13**; 10.2 g, 54.0 mmol, 1.0 equiv.) in CH_2Cl_2 (200 mL) and the solution was cooled to –45 °C. Trifluoromethanesulfonic acid anhydride (13.6 mL, 81.0 mmol, 1.5 equiv.) was added dropwise during 30 min leading to a deep-red solution. After stirring at –45 °C for 1 h, the solution turned brownish and then was allowed to slowly warm to room temperature. The reaction mixture was stirred overnight and then quenched by the addition of water (20 mL) and an aqueous $NaHCO_3$ solution (100 mL, 2 M). The mixture was extracted with CH_2Cl_2 (3 × 100 mL) and the combined organic extracts washed with brine (100 mL) and dried with Na_2SO_4. The solvent was removed under reduced pressure and the residue subjected to column chromatography (pentane/ethyl acetate, 19:1, R_f = 0.42) to give the product as a light-yellow oil, yield 15.89 g (49.5 mmol, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.64 (s, 3 H, CH_3), 1.27 (d, $J_{H,H}$ = 9.9 Hz, 1 H, CH_2), 1.42 (s, 3 H, CH_3), 2.38 (m, 1 H, CH), 2.71 (dt, $J_{H,H}$ = 9.7, $J_{H,H}$ = 5.6 Hz, 1 H, CH_2), 2.83 (t, $J_{H,H}$ = 5.6 Hz, 1 H, CH), 3.08 (d, $J_{H,H}$ = 2.7 Hz, 2 H, CH_2), 6.86 (d, $J_{H,H}$ = 8.0 Hz, 1 H, Ar), 7.37 (d, $J_{H,H}$ = 8.0 Hz, 1 H, Ar) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 20.2 (CH_3), 24.8 (CH_3), 30.6 (CH_2), 35.1 (CH_2), 38.3 (C_q), 38.7 (CH), 44.7 (CH), 110.3 (CH, Ar), 136.1 (CH, Ar), 142.0 (C_q, Ar), 152.8 (C_q, Ar), 156.1 (C_q, Ar) ppm. The analytical data are in accordance with the literature.[19a]

(1*R*,2*S*,7*R*,9*S*)-5-Cyclohexyl-10,10-dimethyl-6-azatricyclo-[7.1.1.0^{2,7}]undecane (15a): The pinene–pyridine derivative **10a** (4.99 g, 20.0 mmol, 1.0 equiv.) and dry $Pd(OH)_2$/C (702 mg, 1.0 mmol, 20% Pd, 0.05 equiv.) were placed in a 75 mL stainless-steel autoclave with a glass inlet and stirring bar under argon. Glacial acetic acid (30 mL) was added and the autoclave pressurized with 90 bar hydrogen. The reaction mixture was stirred at 120 °C under isobaric conditions for 3 d. After cooling to room temperature the pressure was released and the reaction mixture filtered through a pad of Celite. Concentrated hydrochloric acid (5 mL) was added to the light-yellow solution and the mixture stirred for 1 h. The following section gives two alternatives for the purification and isolation of the two diastereomeric products of the reaction.

Method A: Diethyl ether (15 mL) was added dropwise to the acidic solution to give a colorless precipitate [(R_c)-**15a**H$^+$Cl$^-$] which was collected by filtration and dried under high vacuum. The addition of an additional amount of ether (15–20 mL) led to the precipitation of a mixture of the two diastereomers, which was also collected. The mother liquor, containing predominantly the (S_c)-diastereomer, was concentrated to a volume of about 8–10 mL. Slow addition of small portions of diethyl ether (5 mL each) again resulted in the precipitation of diastereomeric mixtures and finally in the precipitation of pure (S_c)-**15a**H$^+$Cl$^-$, which was collected by filtration and dried under high vacuum to give a colorless powder. To improve the yield, the diastereomeric mixtures obtained were redissolved in glacial acetic acid and subjected to the same process as described above. To obtain the desired amines, the hydrochloride adducts were suspended in diethyl ether (30 mL) and saturated aqueous Na_2CO_3 solution (20 mL) and stirred overnight. Extraction with diethyl ether (3 × 30 mL), drying over Na_2SO_4, and removal of the solvent gave the products as light-yellow liquids that slowly crystallized upon standing.

Method B: All the volatiles were removed under reduced pressure. Diethyl ether (30 mL) and a saturated aqueous Na_2CO_3 solution (30 mL) were added to the residual colorless powder. The suspension was stirred overnight at room temperature. The aqueous phase was extracted with diethyl ether (3 × 30 mL) and the combined organic layers washed with brine (20 mL) and dried with Na_2SO_4. The solvent was removed under reduced pressure to give a light-yellow liquid (5.16 g, 19.7 mmol, 99%), which was subjected to column chromatography (basic alumina, pentane/ethyl acetate, 9:1). Both diastereomers were collected after removal of the solvent under reduced pressure as colorless liquids that slowly crystallized upon standing.

(2*S*,4a*S*,5*R*,7*S*,8a*R*)-2-Cyclohexyl-6,6-dimethyldecahydro-5,7-methanoquinoline [(S_c)-15a]: Yield method A: 1.66 g (6.35 mmol, 32%); method B: 2.25 g (8.6 mmol, 43%). $[a]_D^{28}$ = 29.0 (c = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, C_6D_6): δ = 0.92–1.08 (m, 2 H, CH_2), 1.09–1.24 (m, 3 H, CH_3, 5 H, CH_2, 1 H, CH), 1.28–1.38 (m, 3 H, CH_3, 1 H, CH_2), 1.53 (m, 1 H, CH_2), 1.58–1.80 (m, 6 H, CH_2), 1.87–2.01 (m, 1 H, CH_2, 3 H, CH), 2.23–2.35 (m, 2 H, CH_2), 2.39 (dt, $J_{H,H}$ = 9.1, $J_{H,H}$ 5.2 Hz, 1 H, CH), 3.10 (dt, $J_{H,H}$ = 9.5, $J_{H,H}$ = 4.8 Hz, 1 H, CH) ppm. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ = 22.6 (CH_3), 24.1 (CH_2), 26.9 (CH_2), 27.0 (CH_2), 27.1 (CH_2), 27.3 (CH_2), 28.4 (CH_3), 28.8 (CH_2), 29.1 (CH_2), 31.5 (CH_2), 36.1 (CH_2), 39.4 (C_q), 41.6 (CH), 43.9 (CH), 45.2 (CH), 47.0 (CH), 48.3 (CH), 58.3 (CH) ppm. MS (EI): *m*/*z* (%) = 179 (13), 178 (100), 82 (27), 67 (12), 55 (14), 41 (17). HRMS (ESI): calcd. for $C_{18}H_{32}N^+$ [M + H]$^+$ 262.25293; found 262.25241.

(2*R*,4a*S*,5*R*,7*S*,8a*R*)-2-Cyclohexyl-6,6-dimethyldecahydro-5,7-methanoquinoline [(*R*$_c$)-15a]: Yield method A: 1.48 g (5.7 mmol, 28%); method B: 1.00 g (3.82 mmol, 19%). $[\alpha]_D^{28}$ = 41.2 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.83 (s, 3 H, CH_3), 0.85–0.95 (m, 3 H, CH_2), 1.05–1.40 (m, 6 H, CH_2, 1 H, CH), 1.22 (s, 3 H, CH_3), 1.44–1.52 (m, 1 H, CH_2), 1.65–1.70 (m, 2 H, CH_2), 1.71–1.79 (m, 2 H CH_2, 1 H, CH), 1.82–1.91 (m, 2 H, CH_2, 1 H, CH), 1.94–1.99 (m, 1 H, CH), 2.04–2.11 (m, 1 H, CH_2), 2.32 (ddt, $J_{H,H}$ = 14.0, $J_{H,H}$ = 9.2, $J_{H,H}$ = 2.0 Hz, 1 H, CH_2), 2.59 (q, $J_{H,H}$ = 8.8 Hz, 1 H, CH), 3.15 (dt, $J_{H,H}$ = 8.7, $J_{H,H}$ = 1.5 Hz, 1 H, CH) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 20.5 (CH_3), 24.3 (CH_2), 25.7 (CH_2), 26.2 (CH_2), 26.3 (CH_2), 26.4 (CH_3), 26.6 (CH_2), 26.7 (CH_2), 29.4 (CH_2), 30.3 (CH_2), 36.2 (CH_2), 38.8 (CH), 39.2 (C_q), 41.0 (CH), 42.1 (CH), 42.6 (CH), 46.7 (CH), 57.4 (CH) ppm. MS (EI): *m*/*z* (%) = 179 (43), 178 (100), 165 (20), 133 (11), 119 (16), 108 (10), 107 (11), 105 (12), 93 (22), 91 (23), 83 (12), 82 (63), 81 (18), 80 (15), 79 (22), 77 (8), 69 (10), 67 (24), 55 (36), 41 (39). HRMS (ESI): calcd. for $C_{18}H_{32}N^+$ $[M + H]^+$ 262.25293; found 262.25250.

(4a*S*,5*R*,7*S*,8a*R*)-2,6,6-Trimethyldecahydro-5,7-methanoquinoline (15b): The pinene–pyridine derivative **10b** (1.87 g, 10.0 mmol, 1.0 equiv.) and dry $Pd(OH)_2$/C (351 mg, 0.5 mmol, 20% Pd, 0.05 equiv.) were placed in a 75 mL stainless-steel autoclave with a glass inlet and stirring bar under argon. Glacial acetic acid (30 mL) was added and the autoclave pressurized with 90 bar hydrogen. The reaction mixture was stirred at 120 °C under isobaric conditions for 3 d. After cooling to room temperature the pressure was released and the reaction mixture filtered through a pad of Celite. Concentrated hydrochloric acid (5 mL) was added to the light-yellow solution and the mixture stirred for 1 h. All the volatiles were removed under reduced pressure. To the residual colorless powder was added ether (30 mL) and a saturated aqueous sodium carbonate solution (20 mL). The suspension was stirred overnight at room temperature. The aqueous phase was extracted with diethyl ether (3× 30 mL) and the combined organic layers washed with brine (20 mL) and dried with sodium sulfate. The solvent was removed under reduced pressure to give a light-yellow liquid (1.86 g, 9.6 mmol, 96%), which was subjected to column chromatography (silica, toluene/ethanol, 6:1). Both diastereomers could be collected as colorless liquids from the observed fractions after removal of the solvent under reduced pressure.

(2*R*,4a*S*,5*R*,7*S*,8a*R*)-2,6,6-Trimethyldecahydro-5,7-methanoquinoline [(*R*$_c$)-15b]: Yield 770.1 mg (3.98 mmol, 40%). $[\alpha]_D^{28}$ = 49.2 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.07 (s, 3 H, CH_3), 1.11 (d, $J_{H,H}$ = 6.4 Hz, 3 H, CH_3), 1.15 (m, 1 H, CH), 1.18 (s, 3 H, CH_3), 1.21 (m, 1 H, CH_2), 1.32 (m, 1 H, CH_2), 1.51–1.63 (m, 2 H, CH_2), 1.76–1.92 (m, 1 H, CH_2, 2 H, CH), 2.01 (m, 1 H, CH_2), 2.25 (m, 1 H, CH_2), 2.37 (m, 1 H, CH_2), 2.78 (m, 1 H, CH), 3.30 (dt, $J_{H,H}$ = 10.0, $J_{H,H}$ = 6.0 Hz, 1 H, CH) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 22.5 (CH_2), 22.8 (CH_3), 24.1 (CH_3), 27.9 (CH_3), 30.1 (CH_2), 30.9 (CH_2), 34.8 (CH_2), 39.0 (C_q), 40.8 (CH), 41.8 (CH), 46.4 (CH), 48.1 (CH), 48.2 (CH) ppm. MS (EI): *m*/*z* (%) = 192 (12), 190 (50), 155 (41), 151 (18), 146 (27), 137 (21), 136 (18), 124 (16), 122 (20), 121 (18), 111 (22), 109 (40), 108 (17), 107 (18), 99 (90), 98 (49), 97 (21), 95 (22), 91 (23), 83 (100), 81 (25), 80 (11), 79 (24), 77 (29), 71 (20), 70 (80), 69 (37), 67 (20), 65 (14). HRMS (ESI): calcd. for $C_{13}H_{24}N^+$ $[M + H]^+$ 194.19033; found 194.19029.

(2*S*,4a*S*,5*R*,7*S*,8a*R*)-2,6,6-Trimethyldecahydro-5,7-methanoquinoline [(*S*$_c$)-15b]: Yield 599.3 mg (3.10 mmol, 31%). $[\alpha]_D^{28}$ = 22.3 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.83 (s, 3 H, CH_3), 0.95 (m, 1 H, CH_2), 1.09 (d, $J_{H,H}$ = 6.5 Hz, 3 H, CH_3), 1.20 (s, 3 H, CH_3), 1.24–1.44 (m, 4 H, CH_2), 1.68 (dt, $J_{H,H}$ = 5.7, $J_{H,H}$ = 1.6 Hz, 1 H, CH), 1,81–1.99 (m, 1 H, CH_2, 2 H, CH), 2.10 (m, 1 H, CH_2), 2.36 (m, 1 H, CH_2), 3.12 (m, 1 H, CH), 3.21 (dt, $J_{H,H}$ = 9.0, $J_{H,H}$ = 1.8 Hz, 1 H, CH) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 20.4 (CH_3), 21.9 (CH_3), 24.4 (CH_2), 26.1 (CH_2), 26.4 (CH_3), 30.3 (CH_2), 36.1 (CH_2), 38.8 (CH), 39.1 (C_q), 40.9 (CH), 41.6 (CH), 46.7 (CH), 47.2 (CH) ppm. MS (EI): *m*/*z* (%) = 192 (12), 190 (56), 174 (13), 164 (24), 148 (25), 146 (12), 139 (18), 138 (17), 136 (12), 134 (27), 133 (20), 132 (15), 131 (24), 124 (12), 120 (25), 119 (14), 117 (18), 108 (15), 107 (18), 106 (17), 105 (30), 96 (12), 95 (13), 94 (18), 93 (28), 92 (13), 91 (49), 86 (100), 82 (12), 81 (19), 80 (15), 79 (42), 78 (13), 77 (39), 69 (20), 67 (32), 65 (16). HRMS (ESI): calcd. for $C_{13}H_{24}N^+$ $[M + H]^+$ 194.19033; found 194.19022.

(1*R*,2*S*,7*R*,9*S*)-10,10-Dimethyl-6-azatricyclo[7.1.1.0^{2,7}]undecane (15c): The pinene–pyridine derivative **10c** (3.47 g, 20.0 mmol, 1.0 equiv.) and dry $Pd(OH)_2$/C (702 mg, 1.0 mmol, 20% Pd, 0.05 equiv.) were placed in a 75 mL stainless-steel autoclave with a glass inlet and stirring bar under argon. Glacial acetic acid (30 mL) was added and the autoclave pressurized with 90 bar hydrogen. The reaction mixture was stirred at 120 °C under isobaric conditions for 3 d. After cooling to room temperature the pressure was released and the reaction mixture filtered through a pad of Celite. Concentrated hydrochloric acid (5 mL) was added to the light-yellow solution and the mixture stirred for 1 h. The solution was concentrated to a volume of 5 mL and diethyl ether (15 mL) was added to give a colorless precipitate. The precipitate was collected by filtration, washed with diethyl ether, and dried under high vacuum. Diethyl ether (30 mL) and a saturated aqueous sodium carbonate solution (20 mL) were added to the residual colorless powder. The suspension was stirred for 3 h at room temperature and extracted with diethyl ether (3× 30 mL). The combined organic extracts were washed with brine (20 mL) and dried with sodium sulfate. The solvent was removed under reduced pressure to give the product as a colorless liquid, yield 3.31 g (18.46 mmol, 92%). $[\alpha]_D^{28}$ = –20.2 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.78 (s, 3 H, CH_3), 1.14 (s, 3 H, CH_3), 1.19 (m, 1 H, CH_2), 1.26 (d, $J_{H,H}$ = 10.0 Hz, 1 H, CH_2), 1.29–1.49 (m, 3 H, CH_2, 1 H, NH), 1.58–1.70 (m, 1 H, CH_2, 1 H, CH), 1.81 (m, 1 H, CH), 1.93 (m, 1 H, CH), 2.06 (m, 1 H, CH_2), 2.33 (ddt, $J_{H,H}$ = 14.2, $J_{H,H}$ = 9.5, $J_{H,H}$ = 2.2 Hz, 1 H, CH_2), 2.71 (ddd, *J* = 12.7, *J* = 9.2, $J_{H,H}$ = 4.3 Hz, 1 H, CH_2), 2.92 (m, 1 H, CH_2, 1 H, CH) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 20.5 (CH_3), 21.0 (CH_2), 22.9 (CH_2), 26.4 (CH_3), 26.7 (CH_2), 36.2 (CH_2), 37.4 (CH), 39.3 (C_q), 40.9 (CH), 42.7 (CH_2), 47.1 (CH), 48.4 (CH) ppm. MS (EI): *m*/*z* (%) = 110 (10), 83 (100), 82 (24), 68 (16), 41 (16). HRMS (ESI): calcd. for $C_{12}H_{22}N^+$ $[M + H]^+$ 180.17468; found 180.17470.

(4a*S*,5*R*,7*S*,8a*R*)-1-[(11b*S*)-Dinaphtho(2,1-*d*:1′,2′-*f*)[1,3,2]dioxaphosphepin-4-yl]-6,6-dimethyldecahydro-5,7-methanoquinoline (L1): Compound **L1** was synthesized following the general procedure for ligand synthesis starting from (1*R*,2*S*,7*R*,9*S*)-10,10-dimethyl-6-azatricyclo[7.1.1.0^{2,7}]undecane (**15c**; 2.0 mmol, 1.0 equiv.) and (11b*S*)-4-chlorodinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepine [(S_a)-**16**; 2.0 mmol, 1.0 equiv.]. The product was obtained as a colorless solid, yield 831.2 mg (1.684 mmol, 84%). $[\alpha]_D^{28}$ = 356.8 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.87 (s, 3 H, CH_3), 1.22 (s, 3 H, CH_3), 1.32–1.61 (m, 5 H, CH_2), 1.80 (m, 1 H, CH), 1.93 (m, 1 H, CH), 2.12–2.37 (m, 3 H, CH_2, 1 H, CH), 2.78 (m, 2 H, CH_2), 4.22 (m, 1 H, CH), 7.16–7.52 (m, 8 H, Ar), 7.84–7.97 (m, 4 H, Ar) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 21.6 (CH_3), 23.5 (CH_2), 25.2 (CH_2), 27.7 (CH_3), 29.9 (CH_2), 34.9 (d, $J_{C,P}$ = 12.0 Hz, CH_2), 35.3 (d, $J_{C,P}$ = 5.2 Hz, CH), 39.1 (C_q), 39.2 (d, $J_{C,P}$ = 2.7 Hz, CH_2), 41.4 (CH), 48.2 (d, $J_{C,P}$ = 32.2 Hz, CH), 48.4 (CH), 122.0 (d, $J_{C,P}$ = 2.0 Hz, C_q, Ar), 122.2 (d, $J_{C,P}$ = 1.3 Hz, CH,

Ar), 122.3 (CH, Ar), 124.0 (d, $J_{C,P}$ = 5.1 Hz, C_q, Ar), 124.4 (CH, Ar), 124.6 (CH, Ar), 125.9 (CH, Ar), 126.0 (CH, Ar), 127.0 (2 CH, Ar), 128.1 (CH, Ar), 128.3 (CH, Ar), 129.5 (CH, Ar), 130.2 (CH, Ar), 130.5 (C_q, Ar), 131.3 (C_q, Ar), 132.7 (C_q, Ar), 132.8 (d, $J_{C,P}$ = 1.1 Hz, C_q, Ar), 149.7 (C_q, Ar), 150.0 (d, $J_{C,P}$ = 6.9 Hz, C_q, Ar) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 146.9 ppm. MS (EI): *m*/*z* (%) = 279 (32), 205 (16), 179 (14), 178 (81), 167 (63), 150 (16), 149 (92), 138 (13), 113 (14), 112 (17), 111 (78), 110 (20), 109 (10), 96 (42), 91 (11), 84 (19), 83 (100), 82 (52), 81 (14), 79 (12). HRMS (ESI): calcd. for $C_{32}H_{32}NO_2P^+$ $[M]^+$ 493.21707; found 493.21743.

(4a*S*,5*R*,7*S*,8a*R*)-1-[(11b*R*)-Dinaphtho(2,1-*d*:1′,2′-*f*)[1,3,2]dioxaphosphepin-4-yl]-6,6-dimethyldecahydro-5,7-methanoquinoline (L2): Compound **L2** was synthesized following the general procedure for ligand synthesis starting from (1*R*,2*S*,7*R*,9*S*)-10,10-dimethyl-6-azatricyclo[7.1.1.0^{2,7}]undecane (**15c**; 2.0 mmol, 1.0 equiv.) and (11b*R*)-4-chlorodinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepine [(R_a)-**16**; 2.0 mmol, 1.0 equiv.]. The product was obtained as a colorless solid, yield 860.8 mg (1.744 mmol, 87%). $[\alpha]_D^{28}$ = –266.9 (*c* = 0.5, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.21 (br. s, 3 H, CH_3), 1.03 (s, 3 H, CH_3), 1.10 (d, *J* = 10.0 Hz, 1 H, CH_2), 1.35–1.79 (m, 5 H, CH_2, 2 H, CH), 2.04–2.19 (m, 2 H, CH_2, 1 H, CH), 2.51 (m, 1 H, CH_2), 3.20 (m, 1 H, CH_2), 4.01 (m, 1 H, CH), 7.12–7.20 (m, 2 H, Ar), 7.26–7.40 (m, 5 H, Ar), 7.44–7.49 (m, 1 H, Ar), 7.79–7.91 (m, 4 H, Ar) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 21.1 (CH_3), 26.1 (CH_2), 26.4 (CH_2), 28.4 (CH_3), 31.6 (CH_2), 34.2 (d, $J_{C,P}$ = 3.5 Hz, CH), 37.3 (d, $J_{C,P}$ = 2.3 Hz, CH_2), 38.2 (C_q), 39.9 (d, $J_{C,P}$ = 25.9 Hz, CH_2), 41.6 (CH), 46.2 (d, $J_{C,P}$ = 15.9 Hz, CH) 48.9 (CH), 122.0 (CH, Ar), 122.2 (d, $J_{C,P}$ = 1.2 Hz, CH, Ar), 122.4 (d, $J_{C,P}$ = 2.0 Hz, C_q, Ar), 124.0 (d, $J_{C,P}$ = 4.9 Hz, C_q, Ar), 124.4 (CH, Ar), 124.7 (CH, Ar), 125.9 (CH, Ar), 126.0 (CH, Ar), 126.8 (CH, Ar), 127.0 (CH, Ar), 128.2 (CH, Ar), 128.3 (CH, Ar), 129.7 (CH, Ar), 130.2 (CH, Ar), 130.8 (C_q, Ar), 131.3 (C_q, Ar), 132.8 (C_q, Ar), 132.9 (C_q, Ar), 149.8 (C_q, Ar), 149.9 (C_q, Ar) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 148.3 ppm. MS (EI): *m*/*z* (%) = 279 (60), 167 (89), 150 (29), 149 (100), 113 (26), 112 (18), 111 (11), 104 (11), 83 (56), 71 (44), 70 (48). HRMS (ESI): calcd. for $C_{32}H_{32}NO_2P^+$ $[M]^+$ 493.21707; found 493.21774.

(2*S*,4a*S*,5*R*,7*S*,8a*R*)-1-[(11b*S*)-Dinaphtho(2,1-*d*:1′,2′-*f*)[1,3,2]dioxaphosphepin-4-yl]-2,6,6-trimethyldecahydro-5,7-methanoquinoline (L3): Compound **L3** was synthesized following the general procedure for ligand synthesis starting from (2*S*,4a*S*,5*R*,7*S*,8a*R*)-2,6,6-trimethyldecahydro-5,7-methanoquinoline [(S_c)-**15b**; 1.0 mmol, 1.0 equiv.] and (11b*S*)-4-chlorodinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepine [(S_a)-**16**; 1.0 mmol, 1.0 equiv.]. The product was obtained as a colorless solid, yield 350.8 mg (0.691 mmol, 69%). $[\alpha]_D^{28}$ = 342.5 (*c* = 0.5, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.72 (s, 3 H, CH_3), 0.78–0.91 (m, 2 H), 1.13 (d, $J_{H,H}$ = 6.6 Hz, 3 H, CH_3), 1.20 (s, 3 H, CH_3), 1.22–1.30 (m, 1 H), 1.55 (dq, *J* = 12.8, *J* = 4.0 Hz, 1 H), 1.67–1.78 (m, 2 H), 1.82–1.89 (m, 1 H), 1.94–2.03 (m, 2 H), 2.17–2.28 (m, 2 H), 3.54 (m, 1 H), 3.92 (m, 1 H), 7.16–7.28 (m, 3 H, Ar), 7.34–7.40 (m, 3 H, Ar), 7.44 (d, $J_{H,H}$ = 6.4 Hz, 1 H, Ar), 7.46 (d, $J_{H,H}$ = 6.4 Hz, 1 H, Ar), 7.88 (m, 3 H, Ar), 7.94 (d, $J_{H,H}$ = 8.8 Hz, 1 H, Ar) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 20.6 (CH_3), 21.5 (d, $J_{C,P}$ = 6.2 Hz, CH_3), 24.8 (CH_2), 26.0 (d, $J_{C,P}$ = 9.7 Hz, CH_2), 26.4 (CH_3), 29.2 (d, $J_{C,P}$ = 34.4 Hz, CH_2), 30.8 (CH_2), 38.8 (CH), 40.0 (d, $J_{C,P}$ = 2.6 Hz, C_q), 41.4 (CH), 45.5 (CH), 45.7 (CH), 47.2 (CH), 121.3 (d, $J_{C,P}$ = 2.8 Hz, C_q, Ar), 122.4 (d, $J_{C,P}$ = 1.8 Hz, CH, Ar), 122.8 (CH, Ar), 124.0 (d, $J_{C,P}$ = 5.5 Hz, C_q, Ar), 124.2 (CH, Ar), 124.6 (CH, Ar), 125.7 (CH, Ar), 125.9 (CH, Ar), 127.1 (CH, Ar), 127.2 (CH, Ar), 128.1 (CH, Ar), 128.3 (CH, Ar), 129.2 (CH, Ar), 130.3 (CH, Ar), 130.4 (C_q, Ar), 131.3 (C_q, Ar), 132.8 (C_q, Ar), 132.9 (d, $J_{C,P}$ = 1.5 Hz, C_q, Ar), 149.9 (C_q, Ar), 150.3 (d, $J_{C,P}$ = 9.5 Hz, C_q, Ar) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 143.9 ppm. MS (EI): *m*/*z* (%) = 279 (11), 191 (17), 176 (13), 167 (20), 149 (60), 148 (10), 97 (100), 82 (35). HRMS (ESI): calcd. for $C_{33}H_{34}NO_2P^+$ $[M]^+$ 507.23217; found 507.23247.

(2*S*,4a*S*,5*R*,7*S*,8a*R*)-1-[(11b*R*)-Dinaphtho(2,1-*d*:1′,2′-*f*)[1,3,2]dioxaphosphepin-4-yl]-2,6,6-trimethyldecahydro-5,7-methanoquinoline (L4): Compound **L4** was synthesized following the general procedure for ligand synthesis starting from (2*S*,4a*S*,5*R*,7*S*,8a*R*)-2,6,6-trimethyldecahydro-5,7-methanoquinoline [(S_c)-**15b**; 1.0 mmol, 1.0 equiv.] and (11b*R*)-4-chlorodinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepine [(R_a)-**16**; 1.0 mmol, 1.0 equiv.]. The product was obtained as a colorless solid, yield 425.4 mg (0.838 mmol, 84%). $[\alpha]_D^{28}$ = –267.8 (*c* = 0.5, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.72–0.98 (m, 2 H), 1.00–1.38 (m, 9 H), 1.43–1.88 (m, 6 H), 1.95–2.19 (m, 3 H), 3.30 (m, 1 H), 3.89 (m, 1 H), 7.17–7.39 (m, 6 H, Ar), 7.44 (d, $J_{H,H}$ = 8.7 Hz, 1 H, Ar), 7.50 (d, $J_{H,H}$ = 8.7 Hz, 1 H, Ar), 7.85–7.96 (m, 4 H, Ar) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 20.3 (CH_3), 20.8 (d, $J_{C,P}$ = 7.7 Hz, CH_2), 21.6 (d, $J_{C,P}$ = 19.8 Hz, CH_3), 26.1 (CH_2), 27.2 (CH_3), 39.0 (m, CH_2), 40.3 (C_q), 41.2 (2 CH), 45.8 (CH), 45.9 (CH), 47.8 (m, CH), 48.1 (m, CH_2), 121.6 (C_q, Ar), 122.4 (d, $J_{C,P}$ = 1.8 Hz, CH, Ar), 122.5 (CH, Ar), 124.1 (d, $J_{C,P}$ = 5.7 Hz, C_q, Ar), 124.2 (CH, Ar), 124.6 (CH, Ar), 125.8 (CH, Ar), 125.9 (CH, Ar), 127.0 (CH, Ar), 127.1 (CH, Ar), 128.1 (CH, Ar), 128.2 (CH, Ar), 129.5 (CH, Ar), 130.2 (CH, Ar), 130.4 (C_q, Ar), 131.3 (C_q, Ar), 132.8 (d, $J_{C,P}$ = 1.7 Hz, C_q, Ar), 132.9 (C_q, Ar), 150.2 (C_q, Ar), 150.5 (d, $J_{C,P}$ = 6.0 Hz, C_q, Ar) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 145.5 (br. s) ppm. MS (EI): *m*/*z* (%) = 411 (10), 279 (15), 268 (12), 191 (11), 176 (10), 167 (30), 149 (81), 98 (12), 97 (100), 83 (11), 82 (66), 81 (10). HRMS (ESI): calcd. for $C_{33}H_{34}NO_2P^+$ $[M]^+$ 507.23217; found 507.23231.

(2*R*,4a*S*,5*R*,7*S*,8a*R*)-1-[(11b*S*)-Dinaphtho(2,1-*d*:1′,2′-*f*)[1,3,2]dioxaphosphepin-4-yl]-2,6,6-trimethyldecahydro-5,7-methanoquinoline (L5): Compound **L5** was synthesized following the general procedure for ligand synthesis starting from (2*R*,4a*S*,5*R*,7*S*,8a*R*)-2,6,6-trimethyldecahydro-5,7-methanoquinoline [(R_c)-**15b**; 1.0 mmol, 1.0 equiv.] and (11b*S*)-4-chlorodinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepine [(S_a)-**16**; 1.0 mmol, 1.0 equiv.]. The product was obtained as a colorless solid, yield 316.7 mg (0.624 mmol, 62%). $[\alpha]_D^{28}$ = 305.8 (*c* = 0.5, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.78–0.89 (m, 1 H), 1.07 (s, 3 H, CH_3), 1.09 (s, 3 H, CH_3), 1.14–1.28 (m, 2 H), 1.32 (d, $J_{H,H}$ = 7.1 Hz, 3 H, CH_3), 1.40 (m, 1 H), 1.56 (m, 1 H), 1.69 (m, 2 H), 1.80 (m, 1 H), 1.90–2.09 (m, 3 H), 3.64 (m, 1 H), 3.99 (m, 1 H), 7.19–7.44 (m, 7 H, Ar), 7.53 (d, $J_{H,H}$ = 8.7 Hz, 1 H, Ar), 7.84–7.92 (m, 3 H, Ar), 7.95 (d, $J_{H,H}$ = 8.8 Hz, 1 H, Ar) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 20.5 (CH_2), 22.2 (d, $J_{C,P}$ = 4.0 Hz, CH_3), 23.5 (CH_3), 24.7 (CH_2), 28.7 (CH_3), 31.9 (d, $J_{C,P}$ = 3.0 Hz, CH_2), 33.6 (CH_2), 39.4 (CH), 40.4 (C_q), 41.5 (CH), 45.1 (d, $J_{C,P}$ = 3.0 Hz, CH), 46.1 (d, $J_{C,P}$ = 43.5 Hz, CH), 47.1 (CH), 121.7 (d, $J_{C,P}$ = 1.9 Hz, C_q, Ar), 122.1 (CH, Ar), 122.2 (d, $J_{C,P}$ = 1.4 Hz, CH, Ar), 124.0 (d, $J_{C,P}$ = 5.1 Hz, C_q, Ar), 124.3 (CH, Ar), 124.6 (CH, Ar), 125.9 (CH, Ar), 126.0 (CH, Ar), 126.9 (CH, Ar), 127.0 (CH, Ar), 128.1 (CH, Ar), 128.3 (CH, Ar), 129.3 (CH, Ar), 130.2 (CH, Ar), 130.6 (C_q, Ar), 131.3 (C_q, Ar), 132.7 (C_q, Ar), 132.8 (d, $J_{C,P}$ = 1.3 Hz, C_q, Ar), 149.8 (C_q, Ar), 150.2 (d, $J_{C,P}$ = 5.0 Hz, C_q, Ar) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 149.9 ppm. MS (EI): *m*/*z* (%) = 412 (23), 411 (88), 316 (11), 315 (44), 268 (33), 252 (10), 167 (16), 149 (47), 124 (14), 110 (11), 97 (100), 82 (45). HRMS (ESI): calcd. for $C_{33}H_{34}NO_2P^+$ $[M]^+$ 507.23217; found 507.23213.

(2*R*,4a*S*,5*R*,7*S*,8a*R*)-1-[(11b*R*)-Dinaphtho(2,1-*d*:1′,2′-*f*)[1,3,2]dioxaphosphepin-4-yl]-2,6,6-trimethyldecahydro-5,7-methanoquinoline

(L6): Compound **L6** was synthesized following the general procedure for ligand synthesis starting from (2*R*,4a*S*,5*R*,7*S*,8a*R*)-2,6,6-trimethyldecahydro-5,7-methanoquinoline [(*R*$_c$)-**15b**; 1.0 mmol, 1.0 equiv.] and (11b*R*)-4-chlorodinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepine [(*R*$_a$)-**16**; 1.0 mmol, 1.0 equiv.]. The product was obtained as a colorless solid, yield 298.5 mg (0.588 mmol, 59%). $[\alpha]_D^{28}$ = –258.3 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.86 (m, 1 H), 1.11 (d, $J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 1.17 (s, 3 H, CH_3), 1.20–1.52 (m, 5 H), 1.72 (d, *J* = 10.2 Hz, 1 H), 1.83–2.08 (m, 5 H), 2.15 (m, 1 H), 2.32 (m, 1 H), 3.35 (m, 1 H), 4.35 (m, 1 H), 7.19–7.32 (m, 3 H, Ar), 7.36–7.44 (m, 4 H, Ar), 7.53 (d, $J_{H,H}$ = 8.8 Hz, 1 H, Ar), 7.85–7.93 (m, 3 H, Ar), 7.97 (d, $J_{H,H}$ = 8.8 Hz, 1 H, Ar) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 20.6 (CH_3), 21.8 (CH_2), 23.6 (CH_2), 25.6 (CH_3), 28.8 (CH_3), 31.2 (CH_2), 34.9 (CH_2), 39.9 (d, $J_{C,P}$ = 6.7 Hz, CH), 40.8 (C_q), 41.6 (CH), 44.5 (CH), 45.8 (d, $J_{C,P}$ = 45.4 Hz, CH), 47.6 (CH), 121.8 (d, $J_{C,P}$ = 2.0 Hz, C_q, Ar), 122.2 (CH, Ar), 122.4 (d, $J_{C,P}$ = 1.7 Hz, CH, Ar), 124.1 (d, $J_{C,P}$ = 5.0 Hz, C_q, Ar), 124.3 (CH, Ar), 124.7 (CH, Ar), 125.8 (CH, Ar), 125.9 (CH, Ar), 127.1 (2 CH, Ar), 128.2 (CH, Ar), 128.3 (CH, Ar), 129.4 (CH, Ar), 130.2 (CH, Ar), 130.5 (C_q, Ar), 131.3 (C_q, Ar), 132.7 (C_q, Ar), 132.8 (d, $J_{C,P}$ = 1.7 Hz, C_q, Ar), 149.9 (C_q, Ar), 150.3 (d, $J_{C,P}$ = 6.0 Hz, C_q, Ar) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 148.7 ppm. MS (EI): *m*/*z* (%) = 412 (17), 411 (64), 332 (29), 315 (34), 268 (53), 267 (13), 239 (26), 167 (12), 149 (36), 124 (18), 123 (14), 110 (12), 98 (12), 97 (100), 96 (11), 82 (65), 79 (10), 70 (20). HRMS (ESI): calcd. for $C_{33}H_{34}NO_2P^+$ $[M]^+$ 507.23217; found 507.23225.

(2*S*,4a*S*,5*R*,7*S*,8a*R*)-2-Cyclohexyl-1-[(11b*S*)-dinaphtho(2,1-*d*:1′,2′-*f*)-[1,3,2]dioxaphosphepin-4-yl]-6,6-dimethyldecahydro-5,7-methanoquinoline (L7): Compound **L7** was synthesized following the general procedure for ligand synthesis starting from (2*S*,4a*S*,5*R*,7*S*,8a*R*)-2-cyclohexyl-6,6-dimethyldecahydro-5,7-methanoquinoline [(*S*$_c$)-**15a**; 1.0 mmol, 1.0 equiv.] and (11b*S*)-4-chlorodinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepine [(*S*$_a$)-**16**; 1.0 mmol, 1.0 equiv.]. The product was obtained as a light-yellow solid, yield 358.1 mg (0.622 mmol, 62%). $[\alpha]_D^{28}$ = 200.7 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.80–1.98 (m, 6 H, CH_3, 15 H, CH_2, 4 H, CH), 2.03–2.46 (m, 3 H, CH_2), 3.26 (m, 1 H, CH), 3.53 (m, 1 H, CH), 7.09–7.48 (m, 8 H, Ar), 7.72–7.90 (m, 4 H, Ar) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 21.1 (CH_2), 23.2 (CH_3), 24.6 (CH_2), 26.4 (CH_2), 26.5 (2 CH_2), 27.7 (d, $J_{C,P}$ = 3.3 Hz, CH_2), 28.8 (CH_3), 30.6 (CH_2), 30.8 (CH_2), 32.3 (CH_2), 39.0 (d, $J_{C,P}$ = 7.4 Hz, CH), 39.6 (CH), 40.4 (C_q), 41.4 (CH), 44.9 (d, $J_{C,P}$ = 7.8 Hz, CH), 47.0 (CH), 56.9 (d, $J_{C,P}$ = 45.7 Hz, CH), 121.5 (d, $J_{C,P}$ = 4.8 Hz, C_q, Ar), 122.1 (CH, Ar), 122.4 (CH, Ar), 124.1 (d, $J_{C,P}$ = 5.1 Hz, C_q, Ar), 124.3 (CH, Ar), 124.6 (CH, Ar), 125.9 (2 CH, Ar), 126.9 (CH, Ar), 127.1 (CH, Ar), 128.0 (CH, Ar), 128.3 (CH, Ar), 129.3 (CH, Ar), 130.1 (CH, Ar), 130.5 (C_q, Ar), 131.3 (C_q, Ar), 132.7 (C_q, Ar), 132.8 (C_q, Ar), 149.8 (C_q, Ar), 150.4 (d, $J_{C,P}$ = 4.7 Hz, C_q, Ar) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 150.8 ppm. MS (EI): *m*/*z* (%) = 332.1 (36), 268.2 (30), 267.1 (14), 260.3 (10), 259.3 (42), 244.3 (13), 239.2 (23), 218.3 (12), 216.3 (11), 204.3 (52), 179.2 (27), 178.2 (100), 177.2 (34), 176.2 (40), 165.2 (21), 162.2 (15), 149.1 (22), 134.2 (13), 108.2 (13), 95.2 (14), 94.2 (10), 93.2 (12), 91.2 (14), 83.2 (14), 82.2 (57), 81.2 (18), 79.2 (17). HRMS (ESI): calcd. for $C_{38}H_{42}NO_2P^+$ $[M]^+$ 575.29477; found 575.29467.

(2*S*,4a*S*,5*R*,7*S*,8a*R*)-2-Cyclohexyl-1-[(11b*R*)-dinaphtho(2,1-*d*:1′,2′-*f*)[1,3,2]dioxaphosphepin-4-yl]-6,6-dimethyldecahydro-5,7-methanoquinoline (L8): Compound **L8** was synthesized following the general procedure for ligand synthesis starting from (2*S*,4a*S*,5*R*,7*S*,8a*R*)-2-cyclohexyl-6,6-dimethyldecahydro-5,7-methanoquinoline [(*S*$_c$)-**15a**; 1.0 mmol, 1.0 equiv.] and (11b*R*)-4-chlorodinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepine [(*R*$_a$)-**16**; 1.0 mmol, 1.0 equiv.]. The product was obtained as a colorless solid, yield 405.3 mg (0.704 mmol, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88–1.99 (m, 6 H, CH_3, 16 H, CH_2, 4 H, CH), 2.09–2.41 (m, 2 H, CH_2), 2.97 (m, 1 H, CH), 3.15 (m, 1 H, CH), 7.10–7.46 (m, 8 H, Ar), 7.76–7.91 (m, 4 H, Ar) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 21.0 (CH_2), 23.4 (CH_3), 25.4 (CH_2), 26.3 (CH_2), 26.5 (CH_2), 26.6 (CH_2), 27.4 (CH_2), 29.0 (CH_3), 30.5 (CH_2), 31.0 (CH_2), 32.7 (CH_2), 38.6 (d, $J_{C,P}$ = 4.9 Hz, CH), 40.0 (d, $J_{C,P}$ = 2.5 Hz, CH), 40.9 (C_q), 41.6 (CH), 45.3 (d, $J_{C,P}$ = 27.3 Hz, CH), 47.5 (CH), 55.4 (d, $J_{C,P}$ = 19.3 Hz, CH), 121.5 (C_q, Ar), 122.4 (CH, Ar), 122.5 (CH, Ar), 124.1 (C_q, Ar), 124.2 (CH, Ar), 124.6 (CH, Ar), 125.7 (CH, Ar), 125.9 (CH, Ar), 127.2 (2 CH, Ar), 128.1 (CH, Ar), 128.3 (CH, Ar), 129.1 (CH, Ar), 130.2 (CH, Ar), 130.4 (C_q, Ar), 131.3 (C_q, Ar), 132.8 (C_q, Ar), 132.9 (C_q, Ar), 149.4 (C_q, Ar), 150.0 (C_q, Ar) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 146.1 ppm. HRMS (ESI): calcd. for $C_{38}H_{43}NO_2P^+$ $[M + H]^+$ 576.30259; found 576.30291.

(2*R*,4a*S*,5*R*,7*S*,8a*R*)-2-Cyclohexyl-1-[(11b*S*)-dinaphtho(2,1-*d*:1′,2′-*f*)[1,3,2]dioxaphosphepin-4-yl]-6,6-dimethyldecahydro-5,7-methanoquinoline (L9): Compound **L9** was synthesized following the general procedure for ligand synthesis starting from (2*R*,4a*S*,5*R*,7*S*,8a*R*)-2-cyclohexyl-6,6-dimethyldecahydro-5,7-methanoquinoline [(*R*$_c$)-**15a**; 1.0 mmol, 1.0 equiv.] and (11b*S*)-4-chlorodinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepine [(*S*$_a$)-**16** (1.0 mmol, 1.0 equiv.]. The work-up by filtration through basic alumina was skipped due to decomposition. After removal of the solvent from the crude reaction mixture the product was obtained as a light-yellow solid, yield 283.2 mg (0.492 mmol, 49%). Purity: The ligand was prone to decomposition during the work-up procedure. The purity was about 85%, as estimated by ^{1}H NMR spectroscopy. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.26 (br. s, 3 H, CH_3), 0.78 (m, 2 H, CH_2), 0.94–1.27 (m, 6 H), 1.36–1.81 (m, 14 H), 1.93–2.10 (m, 3 H, CH_2), 2.81 (m, 1 H, CH), 3.79 (dq, *J* = 9.9, *J* = 5.3 Hz, 1 H, CH), 7.10–7.18 (m, 3 H, Ar), 7.24 (d, $J_{H,H}$ = 8.5 Hz, 1 H, Ar), 7.30 (m, 2 H, Ar), 7.41 (m, 2 H, Ar), 7.79–7.90 (m, 4 H, Ar) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 20.5 (CH_2), 25.5 (CH_3), 26.2 (CH_2), 26.4 (2 CH_2), 26.5 (CH_2), 26.8 (CH_3), 27.0 (CH_2), 30.4 (CH_2), 30.5 (d, $J_{C,P}$ = 1.4 Hz, CH_2), 32.4 (CH_2), 39.1 (CH), 39.3 (CH), 40.3 (C_q), 41.5 (CH), 46.8 (d, $J_{C,P}$ = 8.1 Hz, CH), 47.9 (CH), 56.9 (d, $J_{C,P}$ = 44.7 Hz, CH), 121.3 (C_q, Ar), 122.3 (CH, Ar), 123.1 (CH, Ar), 124.1 (C_q, Ar), 124.2 (CH, Ar), 124.5 (CH, Ar), 125.7 (CH, Ar), 125.9 (CH, Ar), 127.0 (CH, Ar), 127.1 (CH, Ar), 127.9 (CH, Ar), 128.2 (CH, Ar), 129.1 (CH, Ar), 130.3 (CH, Ar), 130.4 (C_q, Ar), 131.2 (C_q, Ar), 132.8 (C_q, Ar), 132.9 (d, $J_{C,P}$ = 1.4 Hz, C_q, Ar), 150.0 (C_q, Ar), 150.3 (C_q, Ar) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 149.1 (br.) ppm. MS (EI): *m*/*z* (%) = 259.3 (21), 255.3 (19), 220.3 (53), 205.2 (12), 200.2 (21), 179.2 (20), 178.2 (100), 177.2 (23), 176.2 (31), 149.1 (18), 93.2 (10), 91.2 (12), 83.2 (15), 82.2 (27), 81.2 (14), 79.2 (13). HRMS (ESI): calcd. for $C_{38}H_{42}NO_2P^+$ $[M]^+$ 575.29477; found 575.29456.

(2*R*,4a*S*,5*R*,7*S*,8a*R*)-2-Cyclohexyl-1-[(11b*R*)-dinaphtho(2,1-*d*:1′,2′-*f*)[1,3,2]dioxaphosphepin-4-yl]-6,6-dimethyldecahydro-5,7-methanoquinoline (L10): Compound **L10** was synthesized following the general procedure for ligand synthesis starting from (2*R*,4a*S*,5*R*,7*S*,8a*R*)-2-cyclohexyl-6,6-dimethyldecahydro-5,7-methanoquinoline [(*R*$_c$)-**15a**; 1.0 mmol, 1.0 equiv.] and (11b*R*)-4-chlorodinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepine [(*R*$_a$)-**16**; 1.0 mmol, 1.0 equiv.]. The product was obtained as a colorless solid, yield 448.5 mg (0.779 mmol, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.71–0.84 (m, 3 H, CH_3, 2 H, CH_2), 0.94–1.79 (m, 3 H, CH_3, 13 H, CH_2, 3 H, CH), 1.93 (m, 2 H, CH_2), 2.23 (m, 1 H, CH_2), 2.63 (m, 1 H, CH), 3.13 (m, 1 H, CH), 7.03–7.20 (m, 3 H, Ar), 7.25–7.45 (m, 5 H, Ar), 7.71–7.89 (m, 4 H, Ar) ppm. ^{13}C{^{1}H}

NMR (100 MHz, $CDCl_3$): δ = 20.6 (CH_2), 26.2 (2 CH_2), 26.3 (CH_3), 26.4 (CH_2), 26.5 (CH_2), 26.6 (CH_2), 28.6 (d, $J_{C,P}$ = 2.2 Hz, CH_2), 29.7 (CH_3), 30.5 (CH_2), 31.0 (CH_2), 38.6 (d, $J_{C,P}$ = 5.5 Hz, CH), 40.9 (CH), 41.3 (CH), 41.5 (C_q), 46.6 (CH), 47.5 (CH), 57.2 (d, $J_{C,P}$ = 11.8 Hz, CH), 122.4 (CH, Ar), 122.5 (CH, Ar), 122.6 (C_q, Ar), 124.2 (CH, Ar), 124.6 (CH, Ar), 125.7 (CH, Ar), 125.9 (CH, Ar), 126.9 (C_q, Ar), 127.0 (CH, Ar), 127.1 (CH, Ar), 128.0 (CH, Ar), 128.1 (d, $J_{C,P}$ = 22.1 Hz, C_q, Ar), 128.2 (CH, Ar), 129.3 (CH, Ar), 130.1 (CH, Ar), 130.3 (d, $J_{C,P}$ = 16.8 Hz, C_q, Ar), 131.3 (C_q, Ar), 132.8 (C_q, Ar), 149.4 (C_q, Ar), 149.9 (C_q, Ar) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 144.6 ppm. HRMS (ESI): calcd. for $C_{38}H_{43}NO_2P^+$ $[M + H]^+$ 576.30259; found 576.30284.

(4a*S*,5*R*,7*S*,8a*R*)-6,6-Dimethyl-1-[(11b*R*)-8,9,10,11,12,13,14,15-octahydrodinaphtho(2,1-*d*:1′,2′-*f*)[1,3,2]dioxaphosphepin-4-yl]decahydro-5,7-methanoquinoline (L11): Compound **L11** was synthesized following the general procedure for ligand synthesis starting from (1*R*,2*S*,7*R*,9*S*)-10,10-dimethyl-6-azatricyclo[7.1.1.$0^{2,7}$]undecane (**15c**; 1.0 mmol, 1.0 equiv.) and (11b*R*)-4-chloro-8,9,10,11,12,13,14,15-octahydrodinaphtho[2,1-*d*:1′,2′-*f*]-[1,3,2]dioxaphosphepine (1.0 mmol, 1.0 equiv.). The product was obtained as a colorless solid, yield 362.2 mg (0.722 mmol, 72%). $[\alpha]_D^{27}$ = –150.9 (c = 0.5, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.56 (s, 3 H, CH_3), 1.14 (s, 3 H, CH_3), 1.18 (m, 1 H, CH_2), 1.41–1.79 (m, 2 H, CH, 12 H, CH_2), 2.04–2.29 (m, 1 H, CH, 4 H, CH_2), 2.52–2.87 (m, 8 H, CH_2), 3.26 (m, 1 H, CH_2), 3.83 (m, 1 H, CH), 6.88 (m, 1 H, Ar), 7.00 (m, 3 H, Ar) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 21.7 (CH_3), 22.5 (CH_2), 22.6 (CH_2), 22.7 (CH_2), 22.8 (CH_2), 26.3 (CH_2), 26.5 (CH_2), 27.6 (CH_2), 27.8 (CH_2), 28.5 (CH_3), 29.0 (CH_2), 29.1 (CH_2), 31.7 (CH_2), 34.0 (CH), 37.3 (CH_2), 38.1 (C_q), 40.2 (d, $J_{C,P}$ = 36.1 Hz, CH_2), 41.5 (CH), 45.2 (d, $J_{C,P}$ = 6.3 Hz, CH), 49.0 (CH), 118.3 (CH, Ar), 118.6 (d, $J_{C,P}$ = 2.1 Hz, CH, Ar), 127.8 (d, $J_{C,P}$ = 1.3 Hz, C_q, Ar), 128.8 (CH, Ar), 129.1 (CH, Ar), 129.2 (d, $J_{C,P}$ = 4.4 Hz, C_q, Ar), 132.7 (C_q, Ar), 133.7 (d, $J_{C,P}$ = 1.0 Hz, C_q, Ar), 137.3 (C_q, Ar), 137.8 (d, $J_{C,P}$ = 1.3 Hz, C_q, Ar), 147.9 (d, $J_{C,P}$ = 3.2 Hz, C_q, Ar), 149.0 (C_q, Ar) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 140.9 ppm. MS (EI): *m*/*z* (%) = 355.2 (26), 354.2 (99), 233.1 (56), 210.2 (22), 211.2 (15), 208.2 (100). HRMS (ESI): calcd. for $C_{32}H_{41}NO_2P^+$ $[M + H]^+$ 502.28694; found 502.28629.

(4a*S*,5*R*,7*S*,8a*R*)-1-[(3a*R*,8a*R*)-2,2-Dimethyl-4,4,8,8-tetraphenyltetrahydro[1,3]dioxolo[4,5-*e*][1,3,2]dioxaphosphepin-6-yl]-6,6-dimethyldecahydro-5,7-methanoquinoline (L12): Compound **L12** was synthesized following the general procedure for ligand synthesis starting from (3a*R*,8a*R*)-6-chloro-2,2-dimethyl-4,4,8,8-tetraphenyltetrahydro[1,3]dioxolo[4,5-*e*][1,3,2]dioxaphosphepine (2.0 mmol, 1.0 equiv.) and (1*R*,2*S*,7*R*,9*S*)-10,10-dimethyl-6-azatricyclo[7.1.1.$0^{2,7}$]undecane (**15c**; 2.0 mmol, 1.0 equiv.). The product was obtained as a colorless solid, yield 1.172 g (1.740 mmol, 87%). $[\alpha]_D^{29}$ = –53.3 (c = 0.5, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.24 (s, 3 H, CH_3), 1.10 (s, 3 H, CH_3),1.26 (s, 3 H, CH_3), 1.29 (d, $J_{H,H}$ = 10.4 Hz, 1 H, CH_2), 1.33 (s, 3 H, CH_3), 1.52–1.70 (m, 4 H, CH_2), 1.80–1.93 (m, 2 H, CH, 1 H, CH_2), 2.19 (m, 1 H, CH_2), 2.32 (m, 1 H, CH, 1 H, CH_2), 2.98 (m, 1 H, CH_2), 3.40 (m, 1 H, CH_2), 4.52 (m, 1 H, CH), 4.73 (d, $J_{H,H}$ = 8.5 Hz, 1 H, CH), 5.17 (dd, $J_{H,H}$ = 8.5, $J_{H,P}$ = 3.2 Hz, 1 H, CH), 7.16–7.30 (m, 12 H, Ar), 7.44 (d, $J_{H,H}$ = 8.1 Hz, 2 H, Ar), 7.48 (d, $J_{H,H}$ = 8.1 Hz, 2 H, Ar), 7.61 (d, $J_{H,H}$ = 8.0 Hz, 2 H, Ar), 7.77 (d, $J_{H,H}$ = 8.1 Hz, 2 H, Ar) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 21.9 (CH_3), 25.1 (CH_2), 25.2 (CH_3), 26.3 (CH_2), 27.6 (CH_3), 28.3 (CH_3), 31.1 (CH_2), 34.9 (d, $J_{C,P}$ = 2.6 Hz, CH), 36.4 (d, $J_{C,P}$ = 7.3 Hz, CH_2), 38.7 (C_q), 40.4 (d, $J_{C,P}$ = 23.5 Hz, CH_2), 41.7 (CH), 45.8 (d, $J_{C,P}$ = 15.9 Hz, CH), 48.8 (CH), 81.2 (d, $J_{C,P}$ = 8.4 Hz, C_q), 81.3 (C_q), 82.4 (d, $J_{C,P}$ = 20.8 Hz, CH), 82.7 (d, $J_{C,P}$ = 3.7 Hz, CH), 111.3 (C_q), 126.8 (CH, Ar), 126.9 (CH, Ar), 127.0 (2 CH, Ar), 127.1 (5 CH, Ar), 127.3 (CH, Ar), 127.5 (2 CH, Ar), 127.6 (2 CH, Ar), 128.0 (2 CH, Ar), 128.7 (CH, Ar), 128.8 (CH, Ar), 129.1 (2 CH, Ar), 141.8 (C_q, Ar), 142.6 (d, $J_{C,P}$ = 1.2 Hz, C_q, Ar), 146.9 (d, $J_{C,P}$ = 1.3 Hz, C_q, Ar), 147.3 (C_q, Ar) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 138.7 ppm. MS (EI): *m*/*z* (%) = 577.3 (10), 478.3 (29), 420.2 (30), 242.1 (10), 238.1 (14), 237.1 (78), 236.1 (15), 208.1 (13), 207.1 (44), 180.1 (18), 179.1 (100), 178.1 (34), 167.1 (15), 165.1 (10), 105.1 (11). HRMS (ESI): calcd. for $C_{43}H_{49}NO_4P^+$ $[M + H]^+$ 674.33937; found 674.33862.

(4a*S*,5*R*,7*S*,8a*R*)-1-(4,8-Di-*tert*-butyl-2,10-dimethoxydibenzo[*d*,*f*]-[1,3,2]dioxaphosphepin-6-yl)-6,6-dimethyldecahydro-5,7-methanoquinoline (L13): Compound **L13** was synthesized following the general procedure for ligand synthesis from (1*R*,2*S*,7*R*,9*S*)-10,10-dimethyl-6-azatricyclo[7.1.1.$0^{2,7}$]undecane (**15c**; 2.0 mmol, 1.0 equiv.) and 4,8-di-*tert*-butyl-6-chloro-2,10-dimethoxydibenzo[*d*,*f*][1,3,2]dioxaphosphepine (2.0 mmol, 1.0 equiv., generated in situ). The product was obtained as a colorless solid, yield 653.9 mg (1.156 mmol, 58%). ^1H NMR (400 MHz, $CDCl_3$, major isomer): δ = 0.91 (s, 3 H, CH_3), 1.11–1.48 (m, 21 H CH_3, 5 H, CH_2), 1.69 (m, 1 H, CH_2, 1 H, CH), 1.89 (m, 1 H, CH), 2.10 (m, 3 H, CH_2), 2.41 (m, 1 H, CH), 2.60 (m, 1 H, CH), 2.88 (m, 1 H, CH_2), 3.73 (s, 3 H, OCH_3), 3.74 (s, 3 H, OCH_3), 6.60 (d, $J_{H,H}$ = 2.7 Hz, 1 H, Ar), 6.63 (d, $J_{H,H}$ = 3.0 Hz, 1 H, Ar), 6.88 (m, 2 H, Ar) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, major isomer): δ = 21.5 (CH_3), 24.5 (CH_2), 25.6 (CH_2), 27.4 (CH_3), 29.7 (CH_2), 30.7 (3 CH_3), 30.8 (3 CH_3), 31.0 (d, $J_{C,P}$ = 4.0 Hz, CH), 35.3 (C_q), 35.4 (C_q), 37.1 (d, $J_{C,P}$ = 7.1 Hz, CH_2), 39.2 (C_q), 41.3 (m, CH_2), 41.4 (m, CH), 41.5 (m, CH), 48.1 (CH), 55.6 (2 OCH_3), 112.2 (CH, Ar), 112.6 (CH, Ar), 114.0 (CH, Ar), 114.2 (CH, Ar), 133.3 (d, $J_{C,P}$ = 3.6 Hz, C_q, Ar), 133.6 (d, $J_{C,P}$ = 3.3 Hz, C_q, Ar), 142.1 (C_q, Ar), 142.4 (C_q, Ar), 143.1 (d, $J_{C,P}$ = 4.0 Hz, C_q, Ar), 144.2 (d, $J_{C,P}$ = 3.6 Hz, C_q, Ar), 154.8 (C_q, Ar), 154.9 (C_q, Ar) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 144.4 (major, 87%), 150.6 (minor, 13%) ppm.

[Rh(cod)(L2)$_2$]BF$_4$: A solution of HBF_4·diethyl ether (54%, 20.6 μL, 81.6 μmol, 1.02 equiv.) was added to a solution of [Rh(cod)(acac)] (24.8 mg, 80.0 μmol, 1.0 equiv.) in CH_2Cl_2 (5 mL) and the resulting yellow-orange solution stirred for 20 min at room temperature. A solution of (4a*S*,5*R*,7*S*,8a*R*)-1-[(11b*R*)-dinaphtho(2,1-*d*:1′,2′-*f*)[1,3,2]dioxaphosphepin-4-yl]-6,6-dimethyldecahydro-5,7-methanoquinoline (**L2**; 79.8 mg, 161.6 μmol, 2.02 equiv.) in CH_2Cl_2 (2 mL) was added and the solution stirred for 1.5 h at room temperature. All the volatiles were removed under reduced pressure, the residue was redissolved in CH_2Cl_2 (1 mL) and then added dropwise to vigorously stirred *n*-pentane (25 mL). A yellow precipitate formed. The supernatant was removed and the yellow solid washed with *n*-pentane (2× 10 mL) and diethyl ether (2× 10 mL). The solid was dried under vacuum (1× 10^{-3} mbar) to yield the desired Rh complex as a yellow-orange powder, yield 78.5 mg (61.1 μmol, 76%). ^1H NMR (400 MHz, $CDCl_3$): δ = –0.51 (br. s, 6 H, CH_3), 0.61 (s, 6 H, CH_3), 0.69–2.67 (m, 26 H, CH_2, 8 H, CH), 2.92 (m, 2 H, CH_2), 5.50–5.97 (m, 4 H, CH), 7.17–7.52 (m, 16 H, Ar), 7.84–8.12 (m, 8 H, Ar) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 140.4 (d, $J_{P,Rh}$ = 238.0 Hz) ppm. HRMS (ESI pos.): calcd. for $C_{72}H_{76}N_2O_4P_2Rh^+$ $[M – BF_4]^+$ 1197.43299; found 1197.43403.

CCDC-1038409 (for **L2**·BH_3) contains 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.

Supporting Information (see footnote on the first page of this article): ^1H, ^{13}C, and ^{31}P NMR spectra of all new key intermediates

and ligands, chiral GC and HPLC analyses of the catalytic reactions.

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