Design of P-Chirogenic Aminophosphine-Phosphinite (AMPP*) Ligands at both Phosphorus Centers: Origin of Enantioselectivities in Pd-Catalyzed Allylic Reactions

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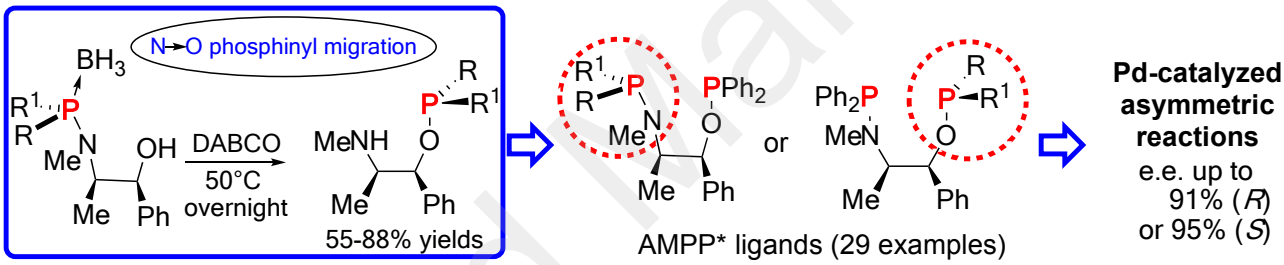


ABSTRACT

We have recently patented an unprecedented stereospecific N→O phosphinyl migration process which transforms P-chirogenic aminophosphines into phosphinites. A fine design of aminophosphine phosphinite ligands (AMPP*) derived from ephedrine and bearing a P-chirogenic center either at the aminophosphine or phosphinite moiety, was performed. The synthesis of AMPP* ligands with P-chirogenic aminophosphine moiety was based on the well-established stereospecific reaction of oxazaphospholidine-borane with organolithium

reagents, followed by trapping with a chlorophosphine and borane decomplexation. Concurrently, the preparation of AMPP* ligands with P-chirogenic phosphinite moiety were performed by N→O phosphinyl migration of aminophosphines borane by heating at 50 °C with DABCO, and then reaction with chlorophosphines. AMPP* ligands were studied in palladium-catalyzed asymmetric allylic alkylations, leading to enantioselectivities from 91% (*R*) to 95% e.e. (*S*). X-ray crystallographic data for relevant Pd-AMPP* complexes and computer modeling explained the origin of the enantioselectivities based on MO interactions of most stable conformers with nucleophiles.

KEYWORDS

P-Chirogenic ligands / Asymmetric catalysis / Palladium / Allylic substitution / Aminophosphine-phosphinites / Phosphorus rearrangement/ DFT-computation

1. INTRODUCTION

The chirality in phosphines used in enantioselective metal-catalyzed or organocatalyzed reactions has overwhelmingly been located on the carbon skeleton.[1-3] If the efficiency of P-chirogenic ligands is also documented,[4] the design of chiral ligands at the phosphorus centers has largely been neglected due to the lack of versatile methods to

efficiently design series of catalysts and to obtain their enantiopure stereoisomers. Although the use of P-chirogenic compounds in organocatalyzed asymmetric reactions is also known for several decades,[3] their applications also recently increased significantly.[5] Consequently and unsurprisingly, the design of P-chirogenic compounds (and not only phosphines) is still a very active research area for the development of enantioselective catalyzed reactions. So far, the stereoselective synthesis of P-chirogenic organophosphorus compounds was usually achieved by P-C bond formation. This was done using a limited number of P-chirogenic tetracoordinated building blocks, such as *t*-butylmethylphosphine-borane, secondary phosphine-oxide or phosphinous-borane derivatives.[4]

Chiral aminophosphine phosphinites (AMPP) such as **1**-**8**, represent a large family of readily available bidendate ligands in asymmetric catalysis (Chart 1).[6] These ligands are obtained from the reaction between two equivalents of Ph_2PCl or $(c\text{-pent})_2PCl$ with commercially available amino alcohols such as ephedrine, threoninol,[7a] prolinol,[7b] valinol,[7c] propranolol,[7d] 1,2-diphenyl aminoethanol,[7e,f] 2-indoline-methanol[7g,h] or azabicyclo[2.2.1]hept-3-ylmethanol.[7i] AMPP ligands **2**-**8** are excellent for the asymmetric hydrovinylation of cyclohexadiene,[7a] [2+2+2] cycloaddition,[7b,c] hydrogenation of C=C[7d-f,i] or

C=O,[7g,h] respectively. Enantioselectivities up to 99% e.e. using Ni-, Co- or Rh-based complexes have been reached.

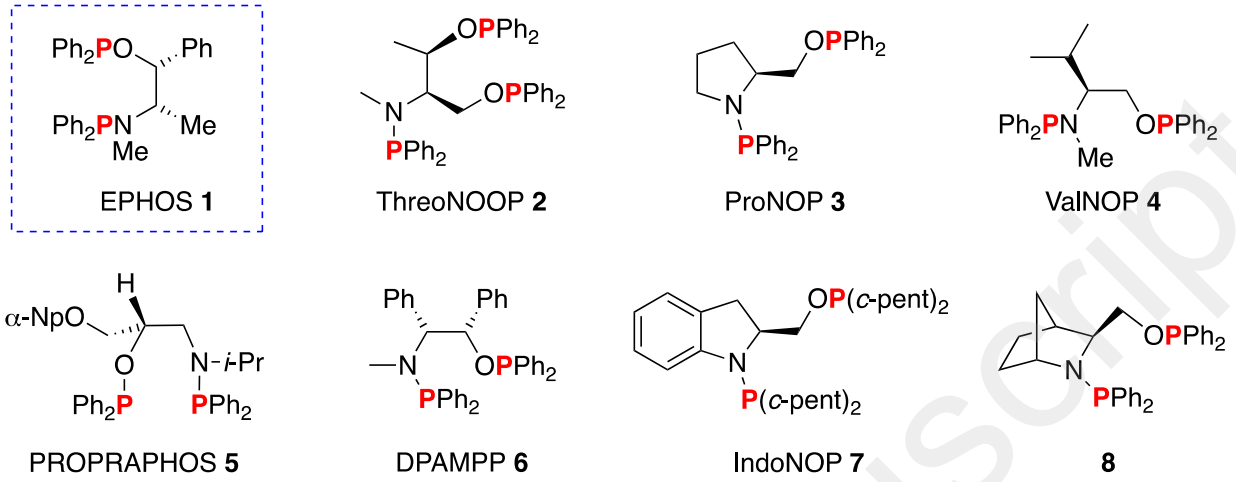
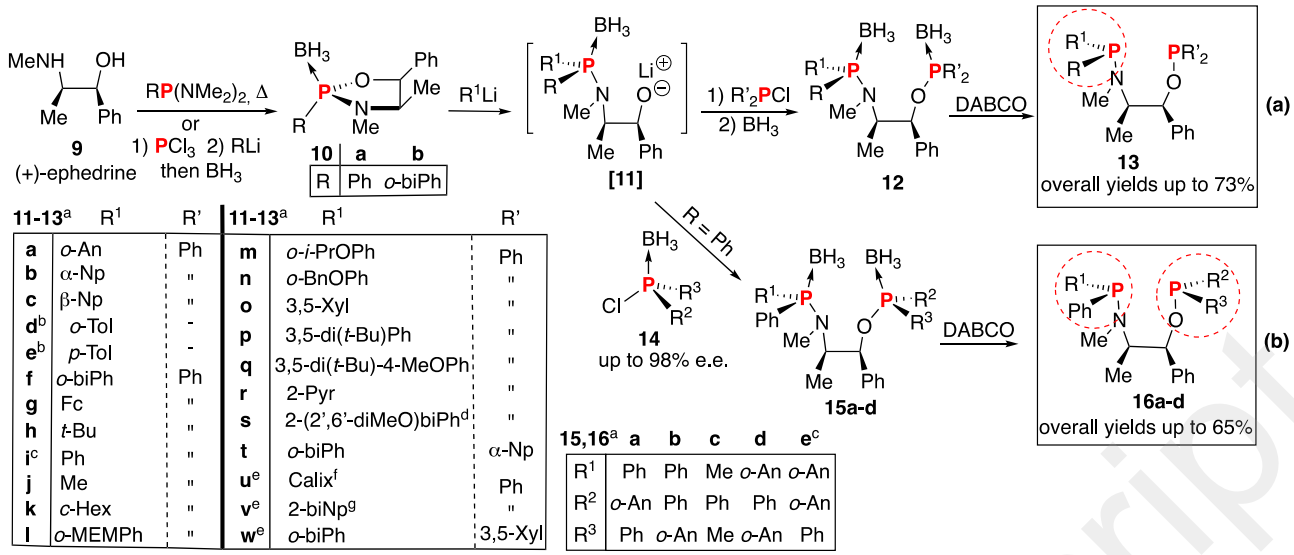


Chart 1. Representative Chiral Aminophosphine-Phosphinite (AMPP) ligands

The EPHOS ligand **1** derived from (-)-ephedrine, described in pioneering works by B. Petit and G. Buono,[8a] led to moderate enantioselectivities in asymmetric hydrogenation,[8b] hydroformylation,[8c,d] hydrosilylation[8e] and allylation[8f] catalyzed by Pt-, Rh- or Pd-complexes, respectively. During the past decade, we and Vogt group have independently described the synthesis of two series of modified EPHOS ligands **13** and **16** with P-chirogenic phosphorus centers (Scheme 1).[9,10]

Scheme 1. Stereoselective Synthesis of Modified EPHOS with P-chirogenic P-Centers



11-13[a]	R^1	R'	11-13[a]	R^1	R'
a	*o*-An	Ph	**m**	*o*-*i*-PrOPh	Ph
b	α-Np	"	**n**	*o*-BnOPh	"
c	β-Np	"	**o**	3,5-Xyl	"
d[b]	*o*-Tol	-	**p**	3,5-di(*t*-Bu)Ph	"
e[b]	*p*-Tol	-	**q**	3,5-di(*t*-Bu)-4-MeOPh	"
f	*o*-biPh	Ph	**r**	2-Pyr	"
g	Fc	"	**s**	2-(2',6'-diMeO)biPh[d]	"
h	*t*-Bu	"	**t**	*o*-biPh	α-Np
i[c]	Ph	"	**u**[e]	Calix[f]	Ph
j	Me	"	**v**[e]	2-biNp[g]	"
k	*c*-Hex	"	**w**[e]	*o*-biPh	3,5-Xyl
l	*o*-MEMPh	"			

15,16[a]	**a**	**b**	**c**	**d**	**e**[c]
R^1	Ph	Ph	Me	*o*-An	*o*-An
R^2	*o*-An	Ph	Ph	Ph	*o*-An
R^3	Ph	*o*-An	Me	*o*-An	Ph

[a] R= Ph. [b] Only for **11.** [c] R= *o*-biPh. [d] 2-[2',6'-$(MeO)_2C_6H_3$]C_6H_4
[e] Prepared from (-)-ephedrine. [f] Calix[4]arenyl. [g] 1,1'-Binapht-2-yl

So far, a large series of P-chirogenic modified EPHOS ligands **13** (AMPP*) has been synthesized from the oxazaphospholidine-borane (-)- or (+)-**10**. They were derived from (+)- or (-)-ephedrine **9** based on a well-established methodology (Scheme 1).[9,10] Thus, the borane complex (-)-**10** reacted with organolithium reagents (R^1Li) to afford the lithium salts **[11]** by a ring opening reaction upon P-O bond cleavage. The salts **[11]** were successively trapped with a chlorophosphine R'_2PCl then with borane to produce the AMPP*-diborane complexes **12**, and then isolated as air-stable and storable compounds (Scheme 1a). The free AMPP* **13** finally obtained after borane decomplexation of their corresponding diborane complexes **12** with DABCO, yielded up to 73% from ephedrine (Scheme 1a). This methodology permitted to synthesize numerous P-chirogenic AMPP* ligands **13** with R^1 = alkyl, cycloalkyl, aryl, bisaryl, heteroaryl or ferrocenyl and R' = phenyl-, α-naphtyl- or 3,5-

xylyl-substituents on the aminophosphine and phosphinite moieties, respectively (Scheme 1a).[9,10] Similarly, the AMPP* ligands **13u-w** bearing *o*-biphenyl, calix[4]arenyl and 1,1'-binaphth-2-yl substituents on the P-chirogenic aminophosphine moiety were prepared using the same methodology, but starting from (-)-ephedrine **9** (Scheme 2 and Supporting Information, SI).[9c] For instance of their efficiency in asymmetric catalysis, the rhodium(I) complex with the P-chirogenic AMPP* **13a** ligand bearing an *o*-anisyl group on the aminophosphine moiety (*i.e.* R^1 = *o*-An), efficiently promoted the asymmetric hydrogenation of dehydrophenylalanine with 99% e.e.[9a] When the ring opened products **[11]** reacted with P-chirogenic chlorophosphine-boranes **14**, the resulting AMPP*-diboranes **15** were obtained with inversion of configuration at the phosphorus atom. After decomplexation by DABCO, the free P-chirogenic ligands **16** were diastereoselectively obtained with the chirality located on either the phosphinite or both aminophosphine and phosphinite moieties (Scheme 1b).[9a,b]

However, the design of the phosphinite moiety in AMPP* **16** based on this methodology is limited. This is because the reaction of the products **[11]** with P-chirogenic chlorophosphine-boranes **14** bearing other substituents R^2, R^3 than *o*-anisyl, phenyl or methyl group was proven to be difficult (Scheme 1b). In this case, the reaction of the secondary alkoxide salts **[11]** with the chlorophosphine-boranes **14** led to epimeric AMPP*

mixtures **16** with low yields due to the poor reactivity and the racemization of **14** in the medium (Scheme 1b).[11]

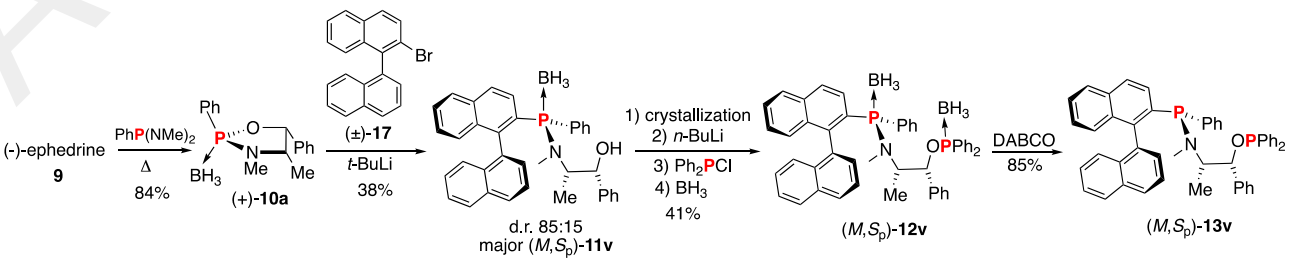
We have recently discovered an unexpected stereospecific intramolecular rearrangement of free P(III)-chirogenic aminophosphine {$R^1R^2PN(R)$-OH} derived from chiral 1,2-aminoalcohols into their corresponding phosphinites {R^1R^2PO-NH(R)}.[12] This rearrangement obtained by stereospecific N→O phosphinyl migration, has been used for the synthesis of AMPP* ligands **20** bearing a P-chirogenic phosphinite moiety. As proof of the method efficiency, the stereoselective synthesis of four epimers of the *o*-biphenyl containing AMPP* ligands **13f,i** and **20f,i**, was herein reported with (R_p)- or (S_p)-configuration either on aminophosphine or phosphinite moieties. Finally, the P-chirogenic AMPP* ligands **13** and **20** has been investigated in asymmetric palladium-catalyzed allylic reactions and the resulting enantioselectivities (*R* or *S*), based on the P-chirality in the metal-sphere of coordination, were explained by DFT computations.

2. RESULTS AND DISCUSSION

Due to the atropoisomery of the binaphtyl substituent, the preparation of the AMPP* **13v** warrants a particular attention (Scheme 2). The synthesis was achieved by reacting oxazaphospholidine-borane (+)-**10a** (prepared from (-)-ephedrine) with the 1,1'-binaphth-2-

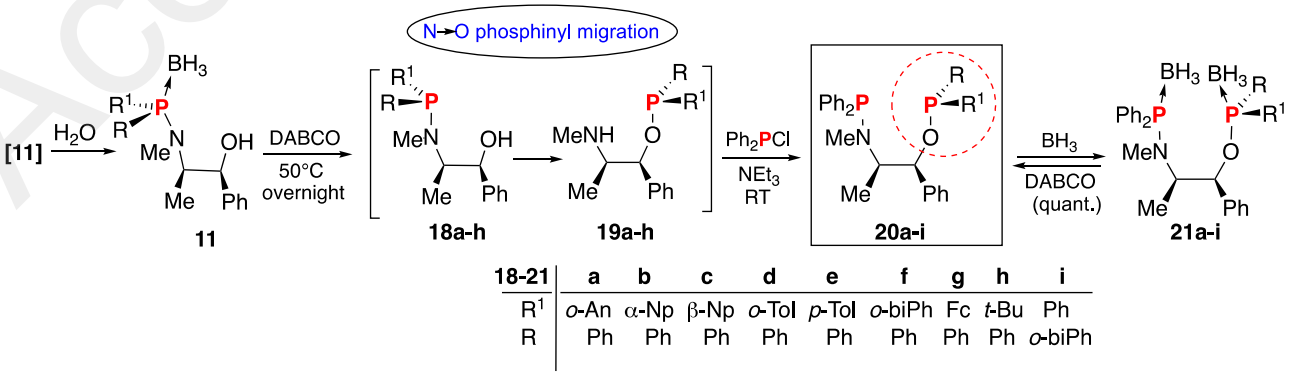
yllithium reagent (prepared by a metal-halide exchange of (±)-2-bromobinaphtyl **17** with *t*-BuLi), at -78°C in THF (Scheme 2). The aminophosphine-borane **11v** was obtained in 38% yield as a mixture of stereoisomers in 85:15 ratio. The major isomer of **11v** was isolated by crystallisation in ethyl acetate and its structure was established by X-ray diffraction. This latter showed that the absolute configuration at the phosphorus center was S_p when the atropoisomeric binaphtyl moiety was *M* (see SI). The diastereoselectivity was explained by the dynamic resolution of the binaphtyllithium reagent during the reaction with the oxazaphospholidine-borane (+)-**10a** leading to the ring-opened product **11v** (Scheme 2).[13] The aminophosphine-borane (*M*,S_p)-**11v** was then deprotonated with *n*-BuLi at -78°C, to afford the corresponding alkoxide salt **[11v]** which was trapped with Ph_2PCl then with borane to form the AMPP*-diborane complex **12v** in 41% yield. The free diastereomerically pure AMPP* (*M*,S_p)-**13v** was isolated in 85% yield after decomplexation of the diborane complex **12v** upon heating with DABCO in toluene at 50 °C overnight, and purification on a neutral alumina column.

Scheme 2. Synthesis of P-chirogenic binaphtyl-AMPP* (*M*,S_p)-13v



Concurrently, the synthesis of AMPP* derivatives with the chirality located on the phosphinite moiety was achieved according to Scheme 3. The aminophosphine-boranes **11**, resulting from the hydrolysis of their alkoxide salts **[11]**, afforded the P-chirogenic aminophosphines **18** upon heating at 50°C in toluene overnight with two equivalents of DABCO. The aminophosphine **18** then led to the P-chirogenic phosphinite **19** by intramolecular S_N2-like substitution resulting in N→O phosphinyl migration.[12] This new rearrangement could also be achieved with 0.5 equivalent of DABCO. It proceeded with complete retention of configuration at the P-atom and was easily monitored by ^{31}P NMR. The decomplexation of the aminophosphine-borane complex **11** into free aminophosphine **18**, followed by the rearrangement into their corresponding phosphinites **19**, exhibited the disappearance and appearance of characteristic signals at ≈ +70, 50 and 110 ppm, respectively (Scheme 3).

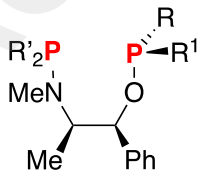
Scheme 3. Synthesis of AMPP*s from Aminophosphines *via* N→O Phosphinyl Migration



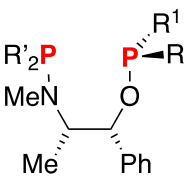
18-21	a	b	c	d	e	f	g	h	i
R^1	*o*-An	α-Np	β-Np	*o*-Tol	*p*-Tol	*o*-biPh	Fc	*t*-Bu	Ph
R	Ph	Ph	Ph	Ph	Ph	Ph	Ph	Ph	*o*-biPh

The phosphinites **19** could be isolated either under a P-free form or after complexation with borane. They were directly used without purification for the synthesis of the AMPP* **20** bearing a P-chirogenic phosphinite moiety. They reacted with the chlorodiphenylphosphine in presence of triethylamine at room temperature (Scheme 3). The free AMPP* ligands **20** were isolated from the reaction medium, but they were usually complexed by borane-dimethylsulfide and then stored as diborane complexes **21** (Scheme 3). The P-chirogenic AMPP* **20** were obtained as free ligands directly usable in asymmetric catalysis, in contrast with the synthetic method reported in Scheme 1. AMPP* **20** , their ^{31}P NMR chemical shifts and their diborane complexes **21**, are reported in Table 1.

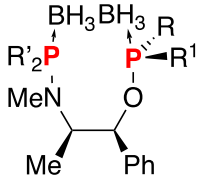
Table 1. Synthesis of AMPP* and Diborane Complexes with P-chirogenic Phosphinite Moieties



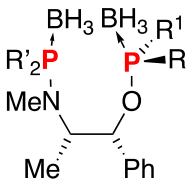
20a-i



(S_P)-**20a,b**



21a-i



(S_P)-**21a,b**

entry	ephedrine **9**	AMPP* **20** R^1	R	R'	AMPP*$(BH_3)_2$[a] **21**

						$\delta^{31}P^b$		yield (%)[c]
1	(+)	(R_p)-**20a**	*o*-An	Ph	Ph	+64.4 +100.5	(R_p)-**21a**	68
2	(-)	(S_p)-**20a**	*o*-An	"	"	+64.9 +100.1	(S_p)-**21a**	65
3	(+)	(R_p)-**20b**	α-Np	"	"	+65.0 +107.1	(R_p)-**21b**	63
4	(-)	(S_p)-**20b**	α-Np	"	"	+64.7 +107.4	(S_p)-**21b**	61
5	(+)	(R_p)-**20c**	β-Np	"	"	+64.8 +110.5	(R_p)-**21c**	81
6	(+)	(R_p)-**20d**	*o*-Tol	"	"	+64.7 +104.7	(R_p)-**21d**	65
7	(+)	(R_p)-**20e**	*p*-Tol	"	"	+64.5 +112.5	(R_p)-**21e**	67
8	(+)	(R_p)-**20f**	*o*-biPh	"	"	+64.9 +101.9	(R_p)-**21f**	67
9	(+)	(R_p)-**20g**	Fc	"	"	+64.7 +105.5	(R_p)-**21g**	68
10	(+)	(S_p)-**20h**	*t*-Bu	"	"	+66.4 +129.4	(S_p)-**21h**	59
11	(+)	(S_p)-**20i**	Ph	*o*-biPh	"	+65.1 +104.8	(S_p)-**21i**	58

[a] Isolated yield from aminophosphine-borane **11**. [b] δ in ppm. [c] Diastereoselectivity (> 99%) checked by NMR.

The *o*-anisyl-aminophosphine-borane **11a** (R^1 = *o*-An, R = Ph), prepared from (+)-ephedrine, afforded the *o*-anisylphosphinite **19a** upon heating at 50°C overnight with two equivalents of DABCO in toluene. It reacted with Ph_2PCl in presence of NEt_3 to provide the free AMPP* (R_p)-**20a** (Table 1, entry 1). The AMPP* (S_p)-**20a** was similarly synthesized

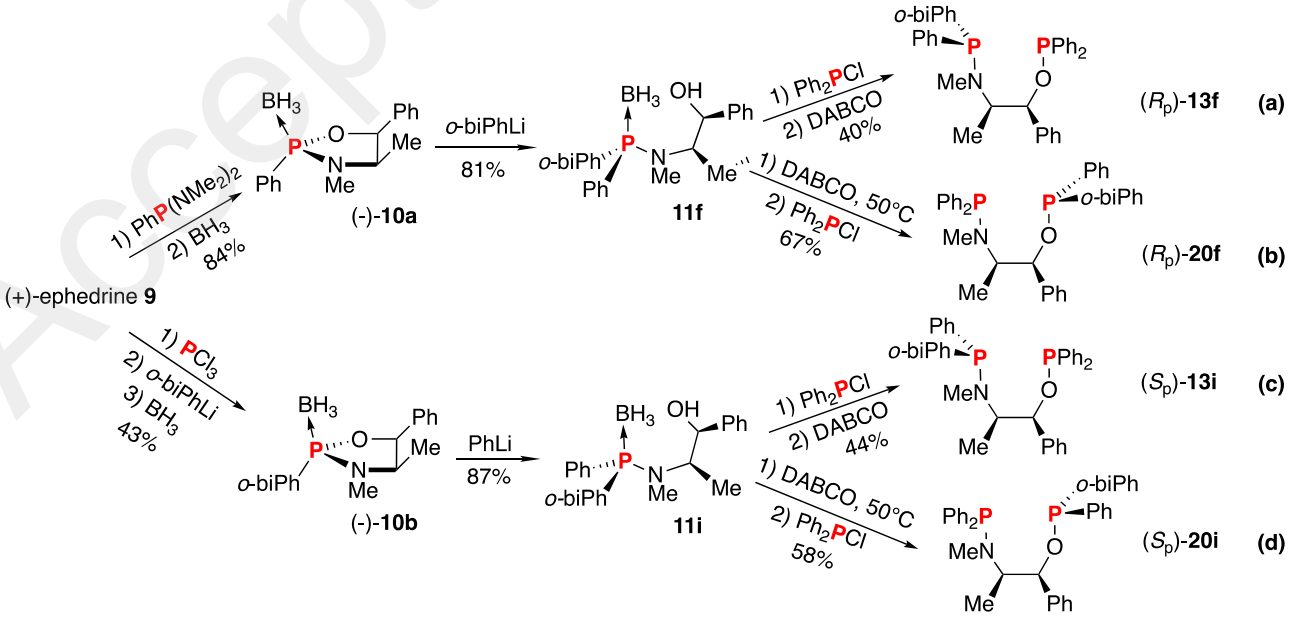
from (-)-ephedrine **9** (entry 2). These AMPP* were characterized by their ^{31}P NMR chemical shifts at ~ +64 and +100 ppm, corresponding to their trivalent aminophosphine and phosphinite moieties. They were isolated after addition of BH_3.DMS as diborane complexes (R_p)- or (S_p)-**21a** in 68 or 65% yield, respectively (entries 1, 2). The diastereoselectivity (> 99%) was checked by NMR analysis of the free AMPP* **20a** and its diborane complex **21a**. The free P-chirogenic ligands **20a** could be recovered by borane decomplexation of **21a** with DABCO (Scheme 3). In addition, the α- or β-naphtyl-, *o*- or *p*-tolyl-, *o*-biphenyl-, ferrocenyl- and *t*-butylphenylphosphinites **19b-i** were obtained from the rearrangement of their corresponding aminophosphine-boranes **11b-i** previously prepared from (+)-ephedrine **9**. Finally, the reaction of the phosphinite-boranes **19b-i** with Ph_2PCl in presence of NEt_3 and then complexation with BH_3.DMS, led to the AMPP*-diborane complexes **21b-i** in yields up to 81% (entries 3-11).

The X-ray crystal structures of eight AMPP*-diborane complexes **21a-h** have been solved. Their absolute configurations are reported in SI (Figures S8 to S16). Consequently, as the borane complexation and decomplexation proceed with retention of configuration at the P-atom, the resulting stereochemistry of the AMPP* **20** from aminophosphine-borane **11** is consistent with the retention during the N→O phosphinyl migration step (Scheme 3). The ORTEP views of all AMPP*-diborane complexes **12**, **15** or **21** exhibited similar aspects

of unfolded conformations of the chain, flattened geometries for the amino groups, and *anti* orientation of the P–B bonds with P1-B1-P2-B2 dihedral angles up to 165° (Figures S4 to S16, SI).

The efficiency of the method was demonstrated by the stereoselective synthesis of all (R_p)- and (S_p)-epimers of the free *o*-biphenyl-containing AMPP* ligands **13f,i** and **20f,i**, bearing a P-chirogenic center either at the aminophosphine or phosphinite moiety. These epimers were prepared from the oxazaphospholidine-borane complexes (-)-**10a** and (-)-**10b** derived from (+)-ephedrine **9** (Scheme 4). The latter complex (-)-**10b** was prepared in a diastereomerically pure form according to a modified litterature procedure.[14,15] It uses successive reactions of (+)-ephedrine **9** with PCl_3, then with *o*-biphenyllithium reagent and finally with BH_3·DMS for complexation (Scheme 4).

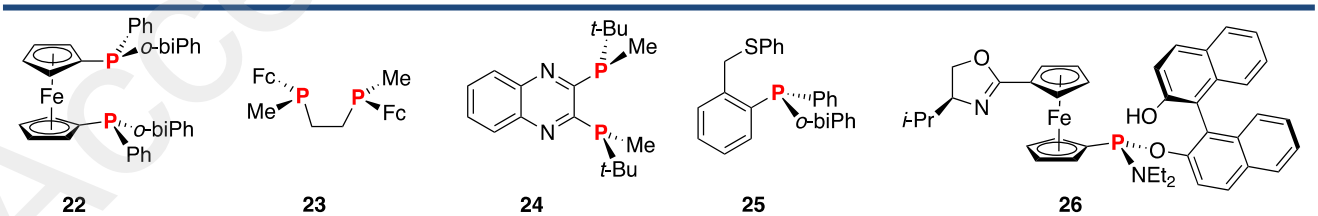
Scheme 4. Diastereodivergent Synthesis of P-chirogenic AMPP* bearing an *o*-biphenyl Group



Oxazaphospholidine complex (+)-**10a** reaction with the *o*-biphenyllithium reagent led first to the (R_p)-aminophosphine-borane **11f** in 81% yield (Scheme 4). This latter was reacted with Ph_2PCl either directly followed by decomplexation, or after rearrangement upon heating with DABCO to afford the free P-chirogenic AMPP* (R_P)-**13f** or (R_P)-**20f** in 40% and 67% yields, respectively (Scheme 4a,b). The X-ray structures of the diborane complexes (R_p)-**12f** and (R_p)-**21f** of the AMPP* (R_P)-**13f** and (R_p)-**20f**, are showed in Figures S4 and S14 (SI). Concurrently, the oxazaphospholidine complex (-)-**10b** reacted with the phenyllithium reagent to form the (S_p)-aminophosphine-borane **11i** with a yield of 87% (Scheme 4). The reaction of **11i** with Ph_2PCl followed by decomplexation, or after rearrangement upon heating with DABCO, led to the free AMPP* (S_P)-**13i** and (S_P)-**20i** with respective yield of 44% and 58% (Scheme 4c,d). Figure S6 (SI) shows the X-ray structure of the borane complexes (S_p)-**12i** of P-chirogenic AMPP* (S_p)-**13i**, bearing an epimeric *o*-biphenyl-aminophosphine moiety in relation to (R_P)-**13f**.

The P-chirogenic AMPP* ligands bearing P-chirogenic aminophosphine **13** or phosphinite moieties **20** were studied in palladium-catalyzed allylic reactions of dimethyl malonate and benzylamine (*vide infra*). The palladium-catalyzed asymmetric allylic

alkylation led to many elegant applications in organic synthesis and the fine design of efficient chiral ligands is still topical.[16,17] This asymmetric catalysis proceeds by nucleophilic attacks to the π-allylic moiety formed upon complexation to palladium, which led Trost group to develop efficient pocket-shaped ligands supported by a chiral 1,2-diamine bridge.[16] Although P-chirogenic ligands, such as **22** to **26**, led also to highly enantioselective allylic catalyzed allylation with e.e.> 95%,[18-22] the design of phosphines at the P-centers for this reaction was rarely performed and few structural elements allowed the prediction of their stereoselectivity (Chart 2). This outcome could be explained by a limited level of understanding of the influence of chirality located on the P-atoms on the environment of the π-allylic moiety. Given the homochirality of the twenty nine P-chirogenic AMPP* **13** and **20** synthesized herein, they were investigated in Pd-catalyzed allylic alkylation reactions. This was to determine the relationship between their structure and the enantioselectivity (*R*) or (*S*) obtained.



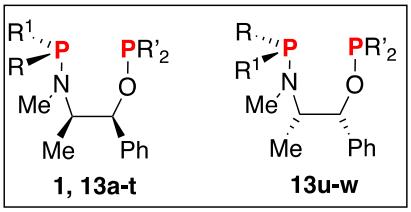
22 **23** **24** **25** **26**

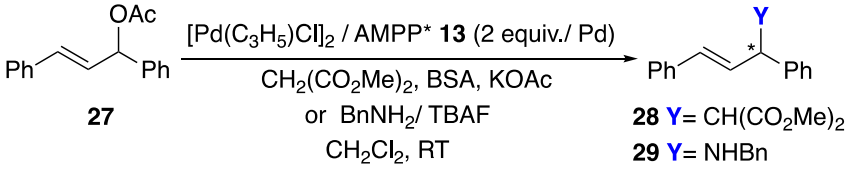
Chart 2. Representative P-chirogenic Phosphorus Ligands used in Pd-catalyzed Asymmetric Allylic Alkylation

The allylation reaction of dimethyl malonate was first examined with the allylic substrate **27**, using 1-2 mol% of $[Pd(C_3H_5)Cl]_2$ and 2-4 mol% of AMPP* **13** or **21** as *in situ* generated catalyst, in the presence of 2 equiv. of *N,O*-bis(trimethylsilyl)acetamide (BSA) in dichloromethane, and a catalytic amount of potassium acetate as base (Tables 2 and 3). According to the AMPP* used, the reactions were usually completed within 1 to 48 h at room temperature to afford the mono allylated malonate **28**, in isolated yields up to 92% (Table 2). The dependence of the reaction conditions on the allylation showed a moderate effect on the enantioselectivity (see SI).

The catalyzed allylic substitution of the (*E*)-1,3-diphenylprop-2-en-1-yl acetate **27** by palladium AMPP* complexes, was also investigated using benzylamine as the nucleophile. The reactions were performed at room temperature in dichloromethane, using TBAF as base, affording the corresponding allylated benzylamine **29** in 7 h. The results on the catalyzed asymmetric allylations using the P-chirogenic AMPP* **13** and **21** are respectively summarized in Tables 2 and 3.

Table 2. Asymmetric Allylation of Dimethylmalonate and Benzylamine Catalyzed by Palladium Complexes of AMPP*13





entry	P-chirogenic AMPP* ligand **13**				product **28**			product **29**		
		R^1	R	R'	Yield (%)[a,b]	ee (%)[c]	abs. conf.	Yield (%)[a,d]	ee (%)[c]	abs. conf.
1	EPHOS **1**	Ph	Ph	Ph	-	42[e]	(*S*)	90	27	(*R*)
2	(R_p)-**13a**	*o*-An	Ph	Ph	90	62	"	86	33	"
3	(R_p)-**13b**	α-Np	"	"	87	44	"	-[f]	-	-
4	(R_p)-**13c**	β-Np	"	"	74	38	"	"	"	"
5	(R_p)-**13f**	*o*-biPh	"	"	92	82	"	89	80	(*R*)
6	(R_p)-**13g**	Fc	"	"	83	70	"	91	56	(*R*)
7	(S_p)-**13h**	*t*-Bu	"	"	83	41	(*R*)	-	-	-
8	(S_p)-**13i**	Ph	*o*-biPh	"	91	91	(*R*)	89	95	(*S*)
9	(S_p)-**13j**	Me	"	"	88	41	(*S*)	-[f]	-	-
10	(S_p)-**13k**	*c*-Hex	"	"	66	61	"	"	"	"
11	(R_p)-**13l**	*o*-MEMPh	"	"	86	55	"	"	"	"
12	(R_p)-**13m**	*o*-*i*-PrOPh	"	"	70	36	"	"	"	"
13	(R_p)-**13n**	*o*-BnOPh	"	"	70	34	"	"	"	"
14	(R_p)-**13o**	3,5-Xyl	"	"	74	8	"	"	"	"
15	(R_p)-**13p**	3,5-di(*t*-Bu)Ph	"	"	82	38	"	"	"	"
16	(R_p)-**13q**	3,5-di(*t*-Bu)-4-MeOPh	"	"	74	39	"	"	"	"
17	(R_p)-**13r**	2-Pyr	"	"	71	43	"	"	"	"
18	(R_p)-**13s**	2-(2',6'-diMeO)biPh	"	"	86	28	(*R*)	"	"	"
19	(R_p)-**13t**	*o*-biPh	"	α-Np	82	70	"	"	"	"
20	(S_p)-**13u**[g]	Calix	"	Ph	87	27	"	"	"	"
21	(M,S_p)-**13v**[g]	2-biNp	"	Ph	84	81	"	"	"	"
22	(S_p)-**13w**[g]	*o*-biPh	"	3,5-Xyl	84	85	"	"	"	"

[a] Reactions were carried out in CH_2Cl_2 ([**27**] = 0.3 M) with 1-2 mol% of $[Pd(C_3H_5)Cl]_2$ and 2-4 mol% of AMPP* **13**, 2 equiv. of dimethyl malonate or benzylamine as nucleophile, 2 equiv. of *N,O*-bis(trimethylsilyl)acetamide (BSA) and a catalytic amount of KOAc (10 mol%) or 2 equiv. of TBAF as base, respectively. [b] The reaction was performed to completion in 1 to 48 h. [c] Determined by HPLC on chiral column. [d] Reaction time 7 h. [e] Reference 8f. [f] Test not realized. [g] Prepared from (-)-ephedrine **9**.

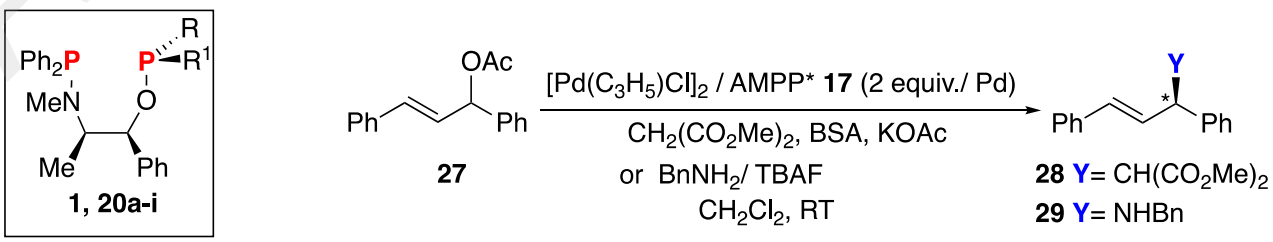
EPHOS ligand **1** (R^1, R, R' = Ph) bearing achiral aminophosphine and phosphinite moieties used in the Pd-catalyzed asymmetric allylation of malonate and benzylamine, exhibited moderate enantioselectivities of 42%[8f] and 27% e.e. for products (*S*)-**28** and (*R*)-**29**, respectively (Table 2, entry 1). In contrast, the enantioselectivities of the catalyzed reactions exhibited a strong substituent-dependence of the P-chirogenic EPHOS ligands **13**, as the allylated products **28** and **29** with (*S*)- or (*R*)-configurations were obtained with enantioselectivities up to 95% (entry 8). However, when the AMPP* ligands **13** derived from (+)-ephedrine bore R^1 = *o*-An, α-Np, β-Np, Fc, Me, *c*-Hex, *o*-MEMPh, *o*-*i*-PrOPh, *o*-BnOPh, 3,5-Xyl, 3,5-di(*t*-Bu)Ph, 3,5-di(*t*-Bu)-4-MeOPh or 2-Pyr on the aminophosphine moiety, the allylated methyl malonate (*S*)-**28** were obtained with 8-70% e.e. (entries 2-4, 6, 9-17). In the case of AMPP* **13u** linked at the upper-rim to a calix[4]arene unit, the catalyzed allylic alkylation also led to a low enantioselectivity (27% e.e.; entry 20). On the

other hand, when the catalyzed allylation was performed with the AMPP* **13h** or **13s** prepared from (+)-ephedrine **9** and bearing *t*-butyl or 2-(2',6'-dimethoxy)biphenyl as R^1 substituent, the observed enantioselectivities were reversed and (*R*)-**28** was obtained with 41 and 28% e.e., respectively (entries 7, 18). When the aminophosphine arm of the AMPP* ligands **13** bore a binaphtyl or a biphenyl substituent, the enantioselectivities were strikingly enhanced. Thus, the binaphtyl AMPP* (M,S_p)-**13v**, derived from (-)-ephedrine **9**, was used in the palladium-catalyzed asymmetric allylation of the dimethyl malonate, the product (*R*)-**28** was obtained with 81% e.e. (entry 21). Using the ligand AMPP* **13f** derived from (+)-ephedrine **9** and bearing an *o*-biphenyl as R^1 substituent, the palladium catalysed reaction afforded the allylated malonate derivative (*S*)-**28** with 82% e.e. (entry 5). Surprisingly, when the phenyl- of diphenylphosphinite moiety of AMPP* **13f** was replaced by a α-naphtyl- or a 3,5-xylyl- group, the corresponding AMPP* **13t** and **13w** exhibited a modest change of the enantioselectivities. This was because the asymmetric catalyzed allylation were achieved with 70% and 85% *vs* 82% e.e., respectively (entries 5, 19 and 22). Interestingly, the AMPP* (S_p)-**13i** derived from (+)-ephedrine **9** and bearing an *o*-biphenyl substituent at the aminophosphine moiety as R group, led to the allylated product (*R*)-**28** with 91% e.e. (entry 8). In this latter case, the product **28** was obtained with a reversed absolute configuration upon using the epimeric *o*-biphenyl AMPP* ligand (R_p)-**13f**. This

illustrates the key importance of the P-chirality at the aminophosphine moiety on the enantioselectivity of the catalytic transformation (82% e.e. (*S*) *vs* 91% e.e. (*R*); entries 5 and 8).[23]

The AMPP* ligands **13a** and **13g** bearing *o*-anisyl or ferrocenyl as R^1 substituents at the aminophosphine moiety, also enhanced the enantioselectivity with respect to EPHOS **1** (Table 2, entry 1), for the Pd-catalyzed allylation using benzylamine. In these case, the product (*R*)-**29** was obtained with 33 and 56% e.e., respectively (entries 2 and 6). The epimeric AMPP* ligands (R_p)-**13f** and (S_p)-**13i** bearing an *o*-biphenyl group either as R^1 or R on the aminophosphine moiety, remarkably, led to the allylated benzylamine **29** with an opposite absolute configuration and with e.e. up to 95% (entries 5 and 8).[23] Results obtained for the catalyzed allylation of dimethyl malonate and benzylamine using palladium complexes derived from AMPP* **20** bearing a P-chirogenic phosphinite moiety, are reported in Table 3.

Table 3. Asymmetric Allylation of Dimethylmalonate and Benzylamine Catalyzed Palladium Complexes of AMPP* 20



entry	P-chirogenic AMPP* ligand **20**			product (*S*)-**28**		product (*R*)-**29**	
		R^1	R	Yield (%)[a,b]	ee (%)[c]	Yield (%)[a,b]	ee (%)[c]
1	EPHOS **1**	Ph	Ph	-	42[d]	90	27
2	(R_p)-**20a**	*o*-An	Ph	71	43	87	47
4	(R_p)-**20b**	α-Np	"	92	34	85	44
5	(R_p)-**20c**	β-Np	"	83	13	87	14
6	(R_p)-**20d**	*o*-Tol	"	87	37	91	27
7	(R_p)-**20f**	*o*-biPh	"	85	50	85	70
8	(R_p)-**20g**	Fc	"	64	47	89	56
9	(S_p)-**20i**	Ph	*o*-biPh	85	14	85	34

[a] Reactions were carried out in dichloromethane ([**27**] = 0.3 M) with 2 mol% of $[Pd(C_3H_5)Cl]_2$ and 4 mol% of AMPP* **20**, 2 equiv. of dimethyl malonate or benzylamine as nucleophile, 2 equiv. of *N*,*O*-bis(trimethylsilyl)acetamide (BSA) and a catalytic amount of KOAc (10 mol%) or 2 equiv. of TBAF as base, respectively. [b] The reaction was performed at room temperature to completion in 7 h. [c] Determined by HPLC on chiral column. [d] Reference 8f.

The allylated products **28** and **29** were obtained with moderate enantioselectivities up to 70% e.e. (Table 3). The P-chirogenic phosphinite substituents of the AMPP* ligands **20** in this catalyzed allylic reaction, did not show significant effect on the stereoselectivity. The products (*S*)-**28** and (*R*)-**29** were obtained with low to moderate enantioselectivities of 13-56% e.e., compared to 27-42% for the EPHOS **1** (Table 3, entries 1-6 and 8). This was after changing the R^1 substituents of AMPP* **20** by *o*-anisyl, α-naphtyl, β-naphtyl, *o*-tolyl or

ferrocenyl. However, when R^1 = *o*-biphenyl, the enantioselectivities obtained for the products (*S*)-**28** and (*R*)-**29** reached 50 and 70% e.e., respectively (entry 7). When R is an *o*-biphenyl, lower enantioselectivities up to 34% e.e. were obtained using the ligand (S_p)-**20i** compared to epimer (R_p)-**20f** (entry 9 *vs* entry 7). Results in Tables 2 and 3 show that the enantioselectivities in the palladium catalyzed asymmetric allylic reactions was considerably increased with the AMPP* **13** bearing a P-chirogenic aminophosphine moiety, even if the best asymmetric induction was obtained with the *o*-biphenyl-containing AMPP* ligand **20f**.

From a mechanistic standpoint, the P-chirogenic AMPP* ligands **13** and **20** were useful to improve the understanding of the enantioselectivity (*R* or *S*) in the asymmetric catalyzed allylations by comparing the structural modifications of the ligands at the aminophosphine or phosphinite-arms. X-ray structures of the AMPP*.$PdCl_2$ complexes **30**, **31** and **32**, prepared by ligand exchange of the dichlorobis(acetonitrile)palladium with the P-chirogenic AMPP* (R_p)-**13f**, (R_p)-**13g** and (R_p)-**20b**, respectively, are shown Figure 1 and in SI.

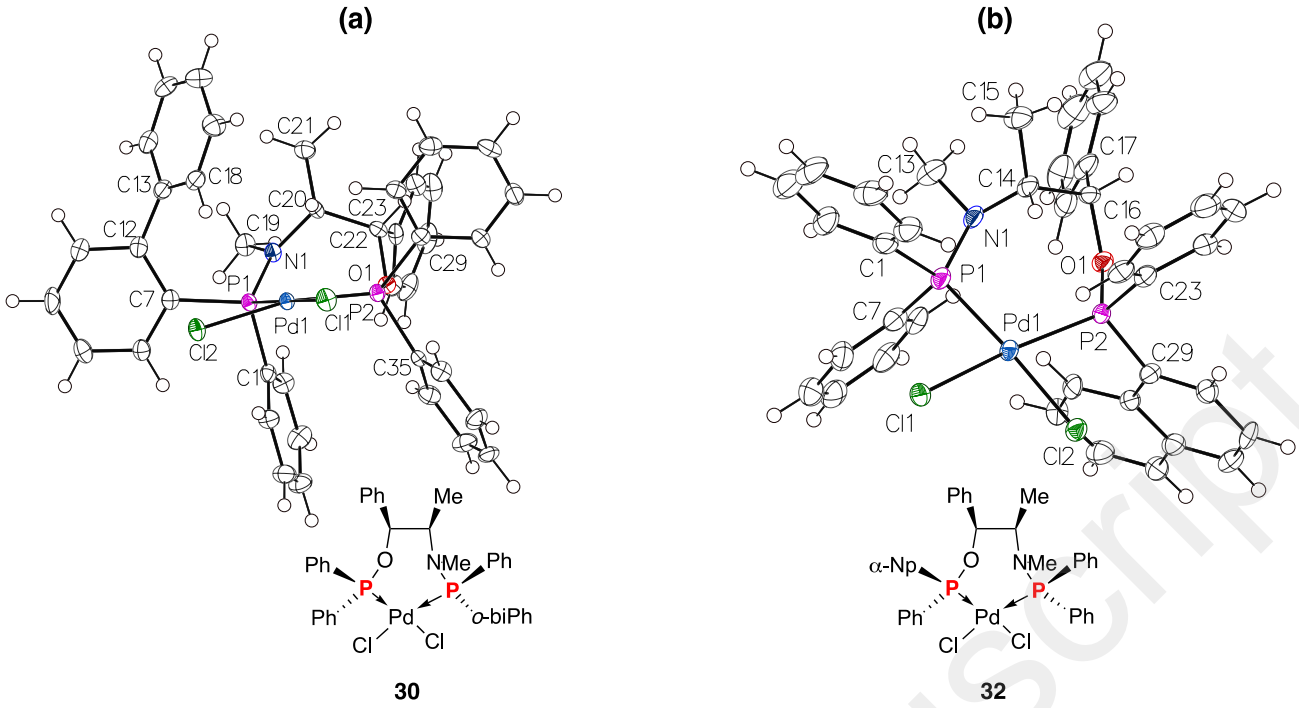


Figure 1. ORTEP view of palladium complexes [Pd(**13f**)Cl_2] **30** and [Pd(**20b**)Cl_2] **32** showing thermal ellipsoids at 50% probability level. Selected mean bond lengths (Å), angles (°) and dihedral angles (°). Complex **30**: Pd1-P1 = 2.2579(12); Pd1-P2 = 2.2330(12); Pd1-Cl1 2.3329(12); Pd1-Cl2 = 2.3591(12); P2-Pd1-P1 = 93.34(4); Pd1-P1-C7-C12 = -98.4(4); O1-P2-P1-N1 = -36.28(19); C7-C12-C13-C18 = -51.5(7); P1-C7-C12-C13 = -6.5(7). Complex **32**: Pd1-P1 = 2.2582(17); Pd1-P2 = 2.2430(15); Pd1-Cl1 2.3404(15); Pd1-Cl2 = 2.3570(16); P2-Pd1-P1 = 100.16(6); O1-P2-P1-N1 = -18.1539(9); Pd1-P2-C29-C38 = 69.2 (6); P2-C29-C38-C37 = -3.126(1).

The seven-membered ring in $PdCl_2$-complexes **30-32** adopted a boat-like geometry, with a slight distorsion O1-P2-P1-N1 of -36° and -18°, respectively. This was explained by the

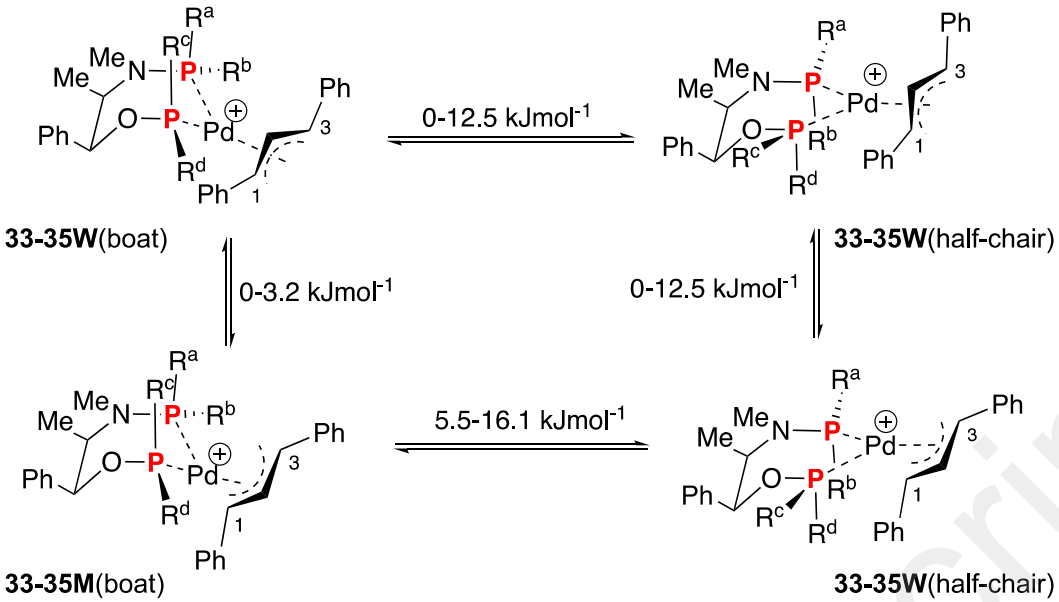
required equatorial positions of the methyl and phenyl substituents of the ephedrine chain (here, *cis*-positioning). A shorter phosphinite-Pd bond was also noted with the Pd1-P2 and Pd1-P1 bond lenghts measured between 2.23-2.25Å and 2.26-2.27Å, respectively (Figure 1 and SI). Very similar structures have already been observed in case of rhodium or ruthenium complexes with AMPP derived from ephedrine.[9b,c,24]Here, the structure of the $PdCl_2$-complex **30** prepared with the ligand (R_p)-**13f** interestingly showed the *o*-biphenyl substituent of the aminophosphine moiety placed perpendicular to the palladium square (*i.e.* P1P2PdCl_2) with a dihedral angle Pd1-P1-C7-C8 of 103.5(4)° (Figure 1a). In addition, the biphenyl group adopted a staggered conformation with a dihedral angle C7-C12-C13-C14 of -46.1(5)°. This could explain the strong influence of the ligand (R_p)-**13f** in the palladium sphere of coordination and consequently the high enantioselectivities observed in allylic reactions (Figure 1a; Table 2, entry 5: e.e. up to 82%), By contrast, the α-naphtyl substituent in the $PdCl_2$-complex **32**, located in back area of the Pd-sphere of coordination, might explain the moderate asymmetric induction resulting from ligand (R_p)-**20b** (Figure 1b; Table 3, entry 2: e.e. up to 44%).

The origin of the observed enantioselectivity (*i.e. R* or *S*) has been addressed by DFT computations, notably for the π-allylpalladium complexes **33**-**35** derived from the AMPP* ligands (R_p)-**13f**, (S_p)-**13i** and (R_p)-**20f**, respectively (Schemes 5, 6; Table 4 and SI). These

ligands were derived from (+)-ephedrine and bearing a P-chirogenic *o*-biphenyl-aminophosphine or -phosphinite moiety, led to catalyzed allylations with enantioselectivities up to 91% (*R*) or 95% (*S*) (Table 2, entries 5, 8; Table 3, entry 7).

π-Allylpalladium complexes **33-35** geometry was optimized considering the boat conformation of the seven-membered ring observed in the X-ray structure of $PdCl_2$-complexes **30-32**. This included changing the two chlorides by the π-allyl ligand (PhCCCPh). Both preferred M- or W- orientations of the π-allyl moiety coordinated onto the palladium (II), were investigated (see Figures S22-S76, SI). The half-chair conformation in complexes **33-35** were also examined because the biphenyl substituent at the axial position to the Pd-square plane in complexes **34** and **35**, could induce steric hindrance (R^a or R^c = *o*-biPh, Scheme 5). In total four starting conformations were optimized for the π-allyl complexes **33-35**, named **33-35M**- or **33-35W** (boat or half-chair). A maximal energy differences between all these species of 16.1 $KJmol^{-1}$ was observed (Scheme 5, Table S61, SI).

Scheme 5. Geometry Optimization of the π-Allylpalladium-AMPP* Complexes 33-35



AMPP*	Pd complex	R^a	R^b	R^c	R^d
(R_p)-**13f**	**33**	Ph	*o*-biPh	Ph	Ph
(S_p)-**13i**	**34**	*o*-biPh	Ph	Ph	Ph
(R_p)-**20f**	**35**	Ph	Ph	*o*-biPh	Ph

The optimized structures of complexes **33-35** in the ground state, selected bond lenghts, energies, electronic affinities (Fukui function), representation of HOMO/LUMOs and their contributions at C1 and C3 positions of the π-allyl group, are detailled in SI. As the Pd-complexes **34-35** adopted chair or half-chair conformations more or less twisted, for clarity purposes they were denoted as **34-35** (boat or half-chair). A selection of key data from Tables S61, S65 to S76, is reported in Table 4. Among all these optimized structures, the π-allyl Pd-complexes **33W**(boat), **33M**(boat), **34M**(boat), **34W**(boat), **34W**(half-chair), **35M**(boat), **35W**(half-chair) and **35W**(boat) exhibited the lowest calculated total energies with differences not exceeding 3.2 KJmol^{-1} (Tables 4 and SI). The observed enantioselectivity provided from the nucleophilic attack on either the C1 or C3 of the π-allyl

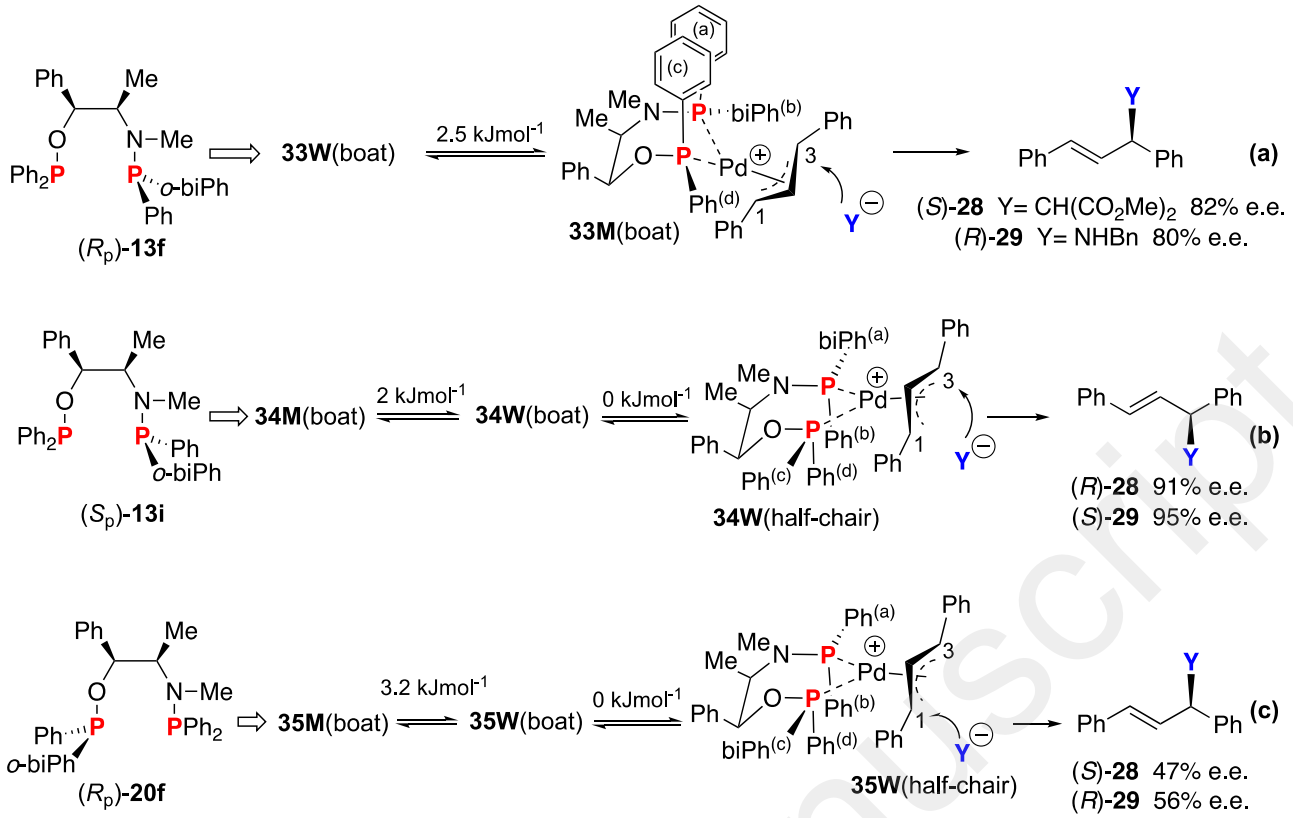
complexed moiety. The Pd-C3 bond, *trans* to the phosphinite moiety in the Pd-square planar center was most commonly longer than the Pd-C1 bonds and was observed in similar X-ray structures of the ProNOP ligand **2**.[25] However, computations showed that the Pd-C1 and Pd-C3 bond lenghts also depend on the Pd-complex conformation (Table 4). Even if the electroaffinity values of the C1 and C3 atoms in all π-allyl complexes **33**-**35** are of unequal value, the enantioselectivity of the allylation is much better explained by molecular orbital (MO) than electrostatic interactions between the nucleophile and the π-allyl moiety (Table 4; see detail Table S61 to S76, SI).[26]

Table 4. Data Selection of the Optimized Structures of Complexes 33-35 (DFT).

entr	complex	Relative total energy		Selected bond length		LUMO rel. atomic cont.	
			Δ(KJ mol⁻	Pd-C3	Pd-C1	C3 (%)	C1 (%)
1	**33M**(boat)	-65202.8789	2.5	2.36703	2.27063	13.79	10.71
2	**33W**(boat)	-65202.9047	0	2.33082	2.28902	12.25	11.90
3	**34M**(boat)	-65202.6722	2.0	2.24787	2.35432	9.06	16.52
4	**34W**(boat)	-65202.6928	0	2.35003	2.26769	12.73	11.89
5	**34W**(half-chair)	-65202.6928	0	2.34958	2.26783	15.93	9.81
6	**35M**(boat)	-65202.7893	3.2	2.27871	2.37415	10.94	13.84
7	**35W**(boat)	-65202.8227	0	2.27178	2.32581	10.63	13.71
8	**35W**(half-chair)	-65202.8227	0	2.27193	2.32565	10.64	13.71

The most stable Pd-complexes **33M** and **33W**, derived from AMPP* ligand (R_p)-**13f**, were in boat conformation and in equilibrium from each other with an energy difference of 2.5 KJmol^{-1}. This was due to the changing M- or W-shape of the π-allyl group (Scheme 6a; Table 4, entries 1 and 2). In this case, the enantioselectivity was explained by a favored nucleophilic attack at the C3 position of the complex **33M**(boat), leading to the products (*S*)-**28** or (*R*)-**29** respectively after reaction with malonate or benzyl amine (Scheme 6a). This selectivity was possible by a longer Pd-C3 bond length and a larger LUMO relative atomic contribution at the C3 position of the π-allyl group, higher in **33M**(boat) than **33W**(boat). This allows the favored interaction with the nucleophile and consequently the cleavage of the Pd-C3 bond to enantioselectively afford the corresponding allylated product (Table 4, entries 1 and 2).

Scheme 6. Computed Stereochemical Course of Pd-Catalyzed Allylations using AMPP* Ligands (R_p)-13f, (S_p)-13i or (R_p)-20f.



In contrast, the computed structures for the Pd-complex derived of the AMPP* ligand (S_p)-**13i** indicated three species **34M**(boat), **34W**(boat) and **34W**(half-chair) with lower energy difference by 2 KJ.mol^{-1} (Table 4, entries 3, 4 and 5). The complex **34** could also be in half-chair conformation (*i.e.* **34W**(half-chair)), due to steric hindrance of the biphenyl substituent when it is in axial position with regard to the Pd-square as in boat form (Scheme 5, R^a = biPh, $R^{b,c,d}$ = Ph). The observed enantioselectivities of the products (*R*)-**28** and (*S*)-**29** were again explained by a favored nucleophilic attack at the C3 position of the complexes **34W**(half-chair) or **34W**(boat). This was due to their longer Pd-C3 bonds and higher LUMO contributions at their C3 positions *i.e* 2.35 Å, 15.93% and 12.73%, respectively (Scheme

6b, Table 4, entries 4 and 5). However, the computed Pd-C1 bond length and the LUMO contribution for the complex **34M**(boat) were higher at the C1 than C3 position of the π-allyl group, *i.e.* 2.35 Å and 16.52% *vs* 2.25 Å and 9.06% (Table 4, entry 3). In this case the enantioselectivity was explained by a nucleophilic attack at the C1-position of the π-allyl group. It is noteworthy that all stereochemical course from the three lower stable π-allyl Pd-complexes **34** resulted in the same enantioselectivities, justifying the obtained high enantiomeric excesses up to 95% using the ligand (S_p)-**13i** (Scheme 6b).

Finally, the more stable optimized complexes **35** derived from AMPP* ligand (R_p)-**20f** were either in boat or in half-chair conformation and with a π-allyl group in both M- or W-shape (Scheme 6c; Table 4, entries 6, 7 and 8). All these species were in equilibrium from each other with an energy difference of 3.2 KJ.mol^{-1}. The modest enantioselectivity was explained by a nucleophilic attack at the C1 position of the complexes **35W**(boat) or **35W**(half-chair), but also in a lesser extent of **35M** (boat) which led to reverse enantiomers (*R*)-**28** or (*S*)-**29**. This was due in all case to their longer Pd-C1 than Pd-C3 bonds and their higher LUMO contributions at the C1 rather than C3 position, *i.e.* 2.37 Å and 13.84%, 2.33 Å and 13.71% *vs* 2.27 Å and 10.63%, respectively (Scheme 6b, Table 4, entries 6, 7 and 8).

3. CONCLUSION

We have developed an important series of chiral aminophosphine-phosphinite ligands bearing a chirality at the phosphorus atom of the aminophosphine or phosphinite moiety (AMPP*). Until now the design of AMPP* with a P-chirogenic phosphinite center has been poorly investigated. We synthetized this series with the ephedrine methodology used in stereoselective synthesis of P-chirogenic phosphines. The synthesis of AMPP* ligands with P-chirogenic aminophosphine moieties is based on the stereospecific ring opening of an oxazaphospholidine-borane by reaction with organolithium reagents, trapping the aminophosphine-borane intermediates with a chlorophosphine and borane decomplexation. A broader design of AMPP* ligands notably on phosphinite center was achieved thank to an unprecedented stereospecific N→O phosphinyl migration process recently developed in our group. When the aminophosphine-boranes were heated at 50°C in the presence of DABCO, P-chirogenic phosphinites were obtained by N→O phosphinyl migration. Their reaction with chlorophosphines led then to the corresponding free AMPP* with P-chirogenic phosphinite moiety. Synthesis efficiency was demonstrated by the stereoselective synthesis of the four epimers of the *o*-biphenyl containing AMPP* ligands, with (*S*)- or (*R*)- absolute configuration at the P-centers. Twenty nine AMPP* including eight with a P-chirogenic phosphinite moiety were investigated in palladium-catalyzed

asymmetric allylic reactions. The enantioselectivities varied from 91% (*R*) to 95% e.e. (*S*), according to the spatial position of the P-substituents in the palladium sphere of coordination. The best asymmetric inductions were obtained with AMPP* bearing P-chirogenic aminophosphine moieties. The (*S*)- or (*R*)-enantioselectivity depends on the absolute configuration at the phosphorus atom. X-ray crystallographic data for relevant Pd-AMPP* complexes and computer modeling explained enantioselectivities origin, based on MO interactions of the most stable conformers with nucleophiles. The selectivity provided from the nucleophilic attack at the C3 or C1 position of the complexed π-allyl group. It was favorized by the interaction of the nucleophile with the LUMO having the larger contribution in one of those positions, and also by the cleavage of the corresponding longer Pd-C3 or Pd-C1 bond.

To conclude, this methodology to prepare P-chirogenic modified EPHOS ligands derived from ephedrine, opens up further possibilities for optimizing and predict enantioselectivities in asymmetric catalyzed processes by designing AMPP* derived from aminoalcohols.

4. EXPERIMENTAL SECTION

4.1. General Information. All reactions were carried out using standard Schlenk techniques under an inert atmosphere, unless stated otherwise. Dichloromethane, toluene,

pentane, THF and diethylether were dried using a MBRAUN SPS 800. Chromatographic grade hexane and isopropanol for HPLC were used without further purification. Commercially available methyllithium, *s*-butyllithium, *t*-butyllithium, chlorodiphenylphosphine, phosphorus trichloride, N-methylmorpholine, 1-bromonaphtalene, 2-bromonaphtalene, 2-bromobiphenyl and bromocyclohexane were used without purification, whereas 2-bromoanisole was distillated before use. EPHOS **1** and AMPP* **13a-c**, **13f-h**, **13j-l**, **13u** and their corresponding diborane complexes **12** were synthesized according to literature procedures.[9a,b,10a] The 2-benzyloxy-[27a] and 2-isopropoxybromobenzene[27b] were prepared from 2-bromophenol according to reported procedures. The 4-bromo-2,6-bis(*t*-butyl)anisole was synthesized from 4-bromo-2,6-bis(*t*-butyl)phenol, according to a modified procedure using K_2CO_3 as base.[27c] The bromo-2,6-dimethoxybiphenyl has been prepared and generously provided by Dr F. Leroux (LIMA-Strasbourg).[28] Thin layer chromatography was performed on silica chromagel (60 µm F_{254}) and exposed by UV, potassium permanganate or iodine treatment. Flash chromatography was carried out with the indicated solvents using silica gel 60 (60AAC, 35-70 µm). HPLC analyses were performed on a chromatograph equipped with a UV detector at λ = 210 and 254 nm. The ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectra were recorded on 600, 500, 400 or 300 MHz spectrometers at ambient temperature, using tetramethylsilane (TMS) as internal

reference for ^{1}H and ^{13}C spectra, and phosphoric acid (85%) as external reference for ^{31}P NMR. Data were reported as s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br.s = broad signal, coupling constant(s) in Hertz. Infrared spectra were recorded on FT-IR instrument and the data are given in cm^{-1}. Melting points were measured on a Kofler melting points apparatus. Optical rotation values were determined at 20 °C on a polarimeter at 589 nm (sodium lamp). The mass spectra and accurate mass measurements (HRMS) were performed under (ESI) conditions with a micro Q-TOF detector or Orbitrap detector, or in the MALDI/TOF reflectron mode using dithranol as a matrix. Elemental analyses were performed with a precision superior to 0.3% on a CHNS-O instrument apparatus.

Crystal Structure Determination. All experimental data procedure and refinement are detailed in the part B of the Supplementary Information (SI) for each compound. Data CCDC-1982667, 1982668, 1982669, 1982665, 1982666, 1982663, 1982664, 1982661, 1982662, 1982659, 1982660, 1982656, 1982657, 1982658, 1982652, 1982653, 1982654, 1982650 and 1982651 for compounds (R_p)-**11e**, (R_p)-**11h**, (M,S_p)-**11v**, R_p)-**12f**, (R_p)-**12g**, (S_p)-**12i**, (S_p)-**15e**, (S_p)-**21a**, (S_p)-**21b**, (R_p)-**21c**, (R_p)- **21d**, (S_p)-**21d**, (R_p)-**21e**, (R_p)-**21f**, (R_p)-**21g**, (S_p)-**21h**, **30**, **31** and **32**, respectively 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

Computational Details All density functional theory (DFT) calculations were performed with Gaussian 16 and were detailed in the Supplementary Information (part C, SI). The DFT ground state calculations were carried out using the B3LYP/genecp method. A 6-31g (d, p) basis set was used for C, H, N and O atoms. VDZ (valence double ζ) with SBKJC effective core potentials was used for P and Pd atoms.

4.2. Synthesis of the oxazaphospholidine-2-borane complexes 10.

4.2.1. (2S,4R,5S)-3,4-Dimethyl-2,5-diphenyl-1,3,2-oxazaphospholidine-2-borane (-)- and (+)-**10a**. These starting compounds were prepared from bis(dimethylamino)phenylphosphine and (+)- and (-)-ephedrine **9**, respectively, according to a methodology already described.[9,15]

4.2.2. (2S,4R,5S)-3,4-Dimethyl-2-biphenyl-5-phenyl-1,3,2-oxazaphospholidine-2-borane (-)-**10b**. This compound was prepared from 2-chloro-1,3,2-oxazaphospholidine according to a modified procedure using *o*-biphenyllithium as reagent.[14,15] To a solution of 2-chloro-1,3,2-oxazaphospholidine (1 mmol) previously prepared by reaction of PCl_3 with the (+)-ephedrine **9** and *N*-methylmorpholine, was added at -78 °C a solution of *o*-biphenyllithium in diethyl ether (0.7 mmol). After stirring overnight, borane-dimethylsulfide (1.1 mmol) was added and the mixture was stirred under argon for 6 h. After hydrolysis, the organic phase

was successively extracted with ethyl acetate, dried over $MgSO_4$ and filtered. The solvent was removed under vacuum and the residue was purified by chromatography on silica gel using a mixture of petroleum ether/dichloromethane (1:1) as eluent. The oxazaphospholidine-borane complex (-)-**10b** was recrystallized from a mixture of methanol/dichloromethane. 0.16 g, 43% yield; White crystals; Mp = 155 °C; R_f = 0.53 (petroleum ether/dichloromethane 1/1); $[\alpha]_D^{20}$ = -12.8 (c 0.3, $CHCl_3$). ^1H NMR (300 MHz, CD_2Cl_2): δ -0.18-1.24 (m, 3H), 0.50 (d, J = 6.5 Hz, 3H), 2.32 (d, J = 10.2 Hz, 3H), 3.21-3.33 (m, 1H), 4.56 (dd, J = 6.0, 2.3 Hz, 1H), 7.02-7.06 (m, 2H), 7.14-7.22 (m, 4H), 7.26 (br.s, 5H), 7.30-7.43 (m, 2H), 7.77 (ddd, J = 11.8, 7.4, 1.2 Hz, 1H). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ 132.5 (br.s). Anal. calcd for $C_{22}H_{25}BNOP$: C 73.15, H 6.98, N 3.88; found C 73.02, H 7.03, N 3.98.

4.3. Synthesis of aminophosphine-boranes 11.

4.3.1. Preparation of aryllithium reagents by metal/halide exchange. To a solution of bromoaryl derivatives (2 M) in THF was added 1 equivalent of *s*-butyllithium at 0 °C or 2 equivalents of *t*-butyllithium at -78 °C. After the formation of a white precipitate, the mixture was stirred at 0 °C for 1 h (or at -78 °C in the second case). The organolithium reagent was dissolved with a minimum of dry THF before use.

4.3.2. Preparation of ferrocenyllithium reagent by ferrocene deprotonation. A 50 mL three-necked flask equipped with a magnetic stirrer under an argon atmosphere was charged with ferrocene (0.74 g, 4 mmol) and THF (10 mL). At 0 °C, *t*-BuLi (2.75 mL, 1.6 M in hexane, 4.4 mmol) was added dropwise, and the reaction mixture was stirred at 0 °C for 1 h, before use.

4.3.3. Synthesis of aminophosphine-boranes **11***: General procedure.* In a 50 mL three-necked flask, equipped with a magnetic stirrer and an argon inlet, 5 mmol of the oxazaphospholidine borane complex **10** were dissolved in 5 mL of anhydrous THF. The mixture was cooled at – 78 °C and 2 equiv. (10 mmol) of the organolithium reagent were slowly added. The resulting mixture was stirred and warmed to RT until the starting material was completely consumed, and hydrolyzed at 0 °C with 2 mL of water. The THF was removed under reduced pressure and the aqueous layer was extracted several times with dichloromethane. The combined organic phases were dried over $MgSO_4$ and the solvent was removed. The residue was purified by chromatography on a column of silica gel, using a mixture of toluene/AcOEt as eluent, to afford aminophosphine-boranes **11**. The aminophosphine-boranes **11** were typically recrystallized using a mixture of hexane/isopropanol (7:3).

4.3.4. The *o-anisyl-*,[11b] *α-naphtyl-*,[11b,29] *β-naphtyl-*,[11b,29b] *o-tolyl-*,[30,31] *p-tolyl-*,[31] *o-biphenyl-*,[11b,29,30] *ferrocenyl-*,[11b,14,30] *t-butyl-*,[11b,32] *methyl-*,[10,11b] *cyclohexyl-*,[11b] *o-[(2-methoxyethoxy)methoxy]phenyl-*,[9b] *o-isopropoxyphenyl-*,[31] *3,5-xylyl-*,[15] *3,5-di-t-butylphenyl-*,[33] *2-(2',6'-dimethoxy)biphenyl-*,[34] *calix[4]arenyl-*,[9c] *aminophosphines* **11a-h**, **11j-m**, **11o**, **11p**, **11u**, respectively, were prepared from the appropriate oxazaphospholidine-borane complex (+)- *or* (-)-**10a** *or* (-)-**10b**, according to the described procedure. These compounds exhibited satisfactory analytical and spectrochemical data in agreement with the literature.

4.3.5. (R_p)-(-)-N-[(1R,2S)-2-Hydroxy-1-methyl-2-phenylethyl], N-methylamino(phenyl-p-tolyl) phosphine-borane **11e**.[31] This compound was synthesized by reaction of oxazaphospholidine-borane complex (-)-**10a** with *p*-tolyllithium reagent. Colorless crystals (1.64 g, 87% yield). X-ray quality crystals were grown by slow evaporation of hexane. The structure and the data were reported in the SI; R_f = 0.25 (toluene/ethyl acetate 9:1); $[\alpha]_D^{20}$ = -44.3 (c 0.5, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.20-2.00 (m, 3H), 1.26 (d, J = 6.7 Hz, 3H), 1.89 (br.s, 1H), 2.41 (s, 3H), 2.49 (d, J = 7.8 Hz, 3H), 4.25-4.39 (m, 1H), 4.83 (d, J = 6.6 Hz, 1H), 7.14-7.20 (m, 2H), 7.25-7.44 (m, 8H), 7.47-7.53 (m, 4H). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ 13.5 (d, J = 1.2 Hz), 21.5, 30.4 (d, J = 3.7 Hz), 58.1 (d, J = 10.1 Hz), 78.7 (d, J = 6.1 Hz), 126.8, 127.6 (d, J = 61.7 Hz), 127.9, 128.3 (d, J = 10.7 Hz), 128.5, 129.2

(d, J = 10.2 Hz), 130.6 (d, J = 2.3 Hz), 130.9 (d, J = 68.3 Hz), 132.0 (d, J = 10.5 Hz), 132.5 (d, J = 10.6 Hz), 141.5 (d, J = 2.3 Hz), 142.5. $^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$): δ +69.8-70.2 (m). HRMS (ESI/Q-TOF) calcd for $C_{23}H_{29}BNOPNa$ $[M+Na]^+$: 400.19720; found: 400.19738. Anal. calcd for $C_{23}H_{29}BNOP$: C 73.22, H 7.75, N 3.71; found C 73.10, H 7.73, N 3.62.

4.3.6. (S_p)-(+)-N-[(1R,2S)-2-Hydroxy-1-methyl-2-phenylethyl], N-methylamino(o-biphenyl) phenylphosphine-borane **11i**. This compound was synthesized by reaction of oxazaphospholidine-borane complex (-)-**10b** with phenyllithium reagent. White solid (1.91 g, 87% yield); Mp = 56-58 °C; R_f = 0.45 (CH_2Cl_2); $[\alpha]_D^{20}$ = +9.9 (c 0.6, $CHCl_3$). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 0.52-1.82 (m, 3H), 0.85 (d, J = 6.9 Hz, 3H), 2.43 (d, J = 8.0 Hz, 3H), 4.17-4.22 (m, 1H), 4.52-4.53 (m, 1H), 7.02-7.07 (m, 1H), 7.13-7.17 (m, 3H), 7.23-7.30 (m, 4H), 7.33-7.45 (m, 8H), 7.48-7.54 (m, 3H). $^{13}C\{^{1}H\}$ NMR (125.8 MHz, CD_2Cl_2): δ 11.4, 30.8 (d, J = 5.0 Hz), 57.8 (d, J = 10.0 Hz), 78.1 (d, J = 7.7 Hz), 126.4, 126.9, 127.0, 127.5, 127.7 (d, J = 9.8 Hz), 128.3, 128.4 (d, J = 65.6 Hz), 130.1, 130.3 (d, J = 2.1 Hz), 130.3 (d, J = 2.1 Hz), 130.6 (d, J = 2.2 Hz), 131.3 (d, J = 52.9 Hz), 132.3 (d, J = 9.8 Hz), 132.6 (d, J = 8.8 Hz), 133.7 (d, J = 9.8 Hz), 141.3 (d, J = 2.7 Hz), 143.0, 146.7 (d, J = 9.6 Hz). $^{31}P\{^{1}H\}$ NMR (121.5 MHz, CD_2Cl_2): δ +70.7 (br.s). FTIR (neat): ν_{max} 3448, 2961, 2897, 2388, 1643, 1604,

1535, 1493, 1446, 1157, 1064, 998, 951, 912, 886, 751, 697, 636 cm^{-1}. HRMS (ESI/Q-TOF) calcd for $C_{28}H_{31}BNOPNa$ $[M+Na]^+$: 462.2129; found: 462.2120.

4.3.7. (R_p)-N-[(1R,2S)-2-Hydroxy-1-methyl-2-phenylethyl], N-(methylamino)phenyl(2-pyridyl) phosphine-borane **11r**. This compound was synthesized by reaction of oxazaphospholidine-borane complex (-)-**10a** with 2-pyridinyllithium reagent. ^1H NMR (300 MHz, $CDCl_3$): δ 0.40-1.70 (m, 3H), 1.18 (d, J = 6.8 Hz, 3H), 2.64 (d, J = 8.5 Hz, 3H), 3.04-3.06 (m, 1H), 4.10-4.20 (m, 1H), 4.82 (dd, J = 5.2, 5.0 Hz, 1H), 7.16-7.17 (m, 2H), 7.28-7.48 (m, 9H), 7.76-7.85 (m, 1H), 7.95-8.03 (m, 1H), 8.79 (d, J = 3.3 Hz, 1H). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 13.7 (d, J = 1.6 Hz), 31.1, 58.4 (d, J = 6.7 Hz), 78.2 (d, J = 5.9 Hz), 124.9 (d, J = 2.4 Hz), 126.9, 128.2 (d, J = 42.0 Hz), 128.5, 128.6, 129.2 (d, J = 26.0 Hz), 130.3 (d, J = 72.0 Hz), 131.0 (d, J = 2.2 Hz), 132.3 (d, J = 7.2 Hz), 136.3 (d, J = 9.4 Hz), 142.4, 149.9 (d, J = 12.6 Hz), 156.5 (d, J = 73.2 Hz). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ +69.6 (br.s). Anal. calcd for $C_{21}H_{26}BN_2OP$: C 69.25, H 7.20, N 7.69; found C 69.14, H 7.25, N 7.95.

4.3.8. (M,S_p)-(+)-N-[(1S,2R)-2-(Hydroxy-1-methyl-2-phenylethyl)], N-methylamino-2-(1,1'-binaphtyl)phenylphosphine-borane **11v**. To a solution of (2*R*,4*S*,5*R*)-3,4-dimethyl-2,5-diphenyl-1,3,2-oxazaphospholidine-2-borane (+)-**10a** (1.0 g, 3.5 mmol) in THF (6 mL) was added at -78 °C 1,1'-binapht-2-yllithium. It was previously prepared by slow addition at -78

°C of *t*-butyllithium (1.9 M in hexane, 7.4 mL, 14 mmol) to a solution of (±)-2-bromo-1,1'-binaphtyl **17** (2.3 g, 7 mmol) in Et_2O (3.5 mL) and stirring at this temperature during one hour. The reaction mixture was stirred overnight until it reached room temperature, and 20 mL of water was added. The aqueous phase was extracted with CH_2Cl_2 (3 x 20 mL). The organic extracts were dried over anhydrous $MgSO_4$ and the solvent was evaporated. The crude product was purified by chromatography on silica gel using CH_2Cl_2 as eluent to give the aminophosphine-borane **11v** as a mixture of diastereoisomers in 85:15 ratio. Recrystallization in ethyl acetate afforded the titled compound as only one diastereoisomer. The X-ray structure and the data were reported in the SI. White solid (0.72 g, 38% yield). R_f = 0.41 (CH_2Cl_2); $[\alpha]_D^{20}$ = +18.0 (c 0.3, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.40-1.38 (m, 3H), 0.46 (d, J = 7.1 Hz, 3H), 2.56 (d, J = 7.7 Hz, 3H), 3.71-3.74 (m, 1H), 4.86-4.87 (m, 1H), 7.02 (d, J = 8.4 Hz, 1H), 7.12-7.27 (m, 10H), 7.35-7.43 (m, 4H), 7.52 (t, J = 7.5 Hz, 1H), 7.57-7.62 (m, 3H), 7.82-7.85 (m, 2H), 7.91-7.92 (m, 2H). ^{13}C{1H} NMR (125.8 MHz), $CDCl_3$): δ 9.7 (d, J = 5.5 Hz), 32.6 (d, J = 3.5 Hz), 57.9 (d, J = 9.4 Hz), 78.9, 125.1, 125.5, 125.6, 125.7, 126.7, 126.9, 127.1, 127.5 (d, J = 9.8 Hz), 127.6, 127.8, 127.9, 128.1, 128.2, 128.5, 129.3 (d, J = 10.7 Hz), 129.8, 130.3 (d, J = 2.0 Hz), 131.9 (d, J = 9.8 Hz), 133.2, 133.4, 133.7, 134.0 (d, J = 9.7 Hz), 134.1, 134.2 (d, J = 7.2 Hz), 134.8 (d, J = 4.0 Hz), 142.6, 144.2 (d, J = 9.9 Hz). ^{31}P{^{1}H} NMR (202.5 MHz), $CDCl_3$): δ +71.7 (br.s). FTIR

(neat): ν_{max} 3520, 3078, 2830, 2380, 2365, 1450, 1437, 1385, 1367, 1163, 1106, 1062, 1022, 998, 883, 822 cm^{-1}. HRMS (ESI/Q-TOF) calcd for $C_{36}H_{35}BNOPNa$ $[M+Na]^+$: 562.2448; found: 562.2446.

4.4. Synthesis of the AMPP*-diboranes 12a-w with P-chirogenic aminophosphine moieties.

4.4.1. Typical procedures: AMPP*-diborane complexes **12** were obtained either according to a one-pot procedure from the oxazaphospholidine-2-borane **10** (Method A), or by deprotonation of the isolated aminophosphine-borane **11** (Method B).

4.4.1.1. From oxazaphospholidine borane **10** (Method A). To a solution of 3,4-dimethyl-5-phenyl-1,3,2-oxazaphospholidine-2-borane **10** (3.5 mmol) in THF (6 mL) was slowly added at -78 °C the organolithium reagent (7 mmol). The temperature reaction was slowly warmed to 0 °C and the solution was stirred until the starting material was completely consumed. Chlorophosphine R'_2PCl (7 mmol; R' = Ph, α-Np or 3,5-Xyl) was added and the mixture was stirred for 2 h. Borane-dimethylsulfide complex (2.7 mL, 28 mmol) was slowly added at 0 °C and the reaction mixture was stirred overnight until the solution reached room temperature. Water (20 mL) was added and the aqueous phase was extracted with CH_2Cl_2 (3 x 20 mL). The organic extracts were dried over anhydrous $MgSO_4$ and the

solvent was evaporated. The crude product was purified by chromatography on silica gel and, in some cases, by recrystallization to afford the desired AMPP*-diboranes **12**.

4.4.1.2. From aminophosphine-borane **11** (Method B). To a solution of aminophosphine-borane **11** (0.5 mmol) in THF (1 mL) was slowly added at -78 °C *n*-BuLi (0.6 mmol). After stirring during one hour at -78 °C, chlorophosphine R'_2PCl (1.1 mmol) was added and the resulting mixture was stirred until the solution reached room temperature (~ 5 h). Borane-dimethylsulfide complex (4 mmol) was added at 0 °C and the solution was stirred overnight before hydrolysis with water (10 mL). The work-up is similar as described above.

4.4.2. The *EPHOS*-[8] and the *AMPP*-diborane complexes* **12a-c**,[9a,b] **12f-h**,[9b] **12j**,[9a,b,10] **12k**, **12l**,[9b] **12u**[9c] and **15e**,[9a] were synthetized as described in literature.

4.4.3. (S_p)-(-)-N-[(1R,2S)-2-(Diphenylphosphinito-borane)-1-methyl-2-phenylethyl], N-methyl amino(o-biphenyl)phenylphosphine-borane **12i**. The synthesis of **12i** was achieved using the method A (as described above) by reaction of the complex (-)-**10b** (1.26 g, 3.5 mmol) in THF (6 mL) at -78 °C with phenyllithium (1.8 M in dibutylether, 3.9 mL, 7 mmol). The ring opening product **[11i]** was then trapped by Ph_2PCl. The purification was achieved by chromatography on silica gel using petroleum ether/CH_2Cl_2 1:1 as eluent and recrystallization in hexane/dichloromethane to give the AMPP*-diborane **12i** as a white solid (1.16 g, 52% yield). X-ray quality crystals were grown by slow evaporation of a

mixture of CH_2Cl_2 and hexane. The structure and the data were reported in the SI. R_f = 0.62 (petroleum ether/CH_2Cl_2 1:1); Mp = 206-208 °C; $[\alpha]_D^{20}$ = -52.2 (c 0.4, $CHCl_3$). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 0.56-1.73 (m, 6H), 1.03 (d, J = 6.6 Hz, 3H), 2.19 (d, J = 7.7 Hz, 3H), 4.69-4.77 (m, 1H), 5.42 (t, J = 9.1 Hz, 1H), 6.27 (ddd, J = 12.2, 2.1, 1.2 Hz, 1H), 6.89-6.96 (m, 4H), 7.07-7.24 (m, 8H), 7.32-7.42 (m, 9H), 7.48-7.56 (m, 5H), 7.73-7.78 (m, 2H). ^{13}C{^{1}H} NMR (125.8 MHz, CD_2Cl_2): δ 15.2, 29.2 (d, J = 4.9 Hz), 57.2 (dd, J = 10.0, 8.9 Hz), 83.5 (dd, J = 10.4, 2.7 Hz), 126.8, 126.9, 127.1 (d, J = 9.5 Hz), 127.4 (d, J = 10.1 Hz), 127.7, 127.9, 128.0, 128.3, 128.5 (d, J = 10.7 Hz), 128.7, 129.0, 129.0 (d, J = 54.1 Hz), 130.0, 130.1 (d, J = 2.4 Hz), 130.5 (d, J = 1.8 Hz), 131.0 (d, J = 10.7 Hz), 131.4 (d, J = 1.8 Hz), 131.5, 131.6, 131.7 (d, J = 1.8 Hz), 132.0 (d, J = 59.4 Hz), 132.3 (d, J = 8.9 Hz), 132.5 (d, J = 10.1 Hz), 132.8, 132.9 (d, J = 7.7 Hz), 138.4, 140.5 (d, J = 2.6 Hz), 146.4 (d, J = 11.0 Hz). ^{31}P{^{1}H} NMR (202.5 MHz, CD_2Cl_2): δ +69.7-70.0 (m), +106.5-106.9 (m). FTIR (neat): ν_{max} 3054, 2933, 2393, 2353, 1457, 1437, 1220, 1159, 1135, 1115, 1066, 1011, 974, 892, 864, 760, 738, 715 cm^{-1}. HRMS (ESI/Q-TOF) calcd for $C_{40}H_{43}B_2P_2NONa$ $[M+Na]^+$: 660.2911; found: 660.2896. Anal. calcd for $C_{40}H_{43}B_2P_2NO$: C 75.38, H 6.80, N 2.20; found: C 75.03, H 6.92, N 2.29.

4.4.4. (R_p)-(-)-N-[(1R,2S)-2-(Diphenylphosphinito-borane)-1-methyl-2-phenylethyl], N-methyl amino(2-isopropoxyphenyl)phenylphosphine-borane **12m**. The synthesis of **12m**

was achieved using the method A (as described above), by reaction of the complex (-)-**10a** (1.0 g, 3.5 mmol) with the 2-*i*-propyloxyphenyllithium previously prepared from 1-bromo-2-*i*-propyloxybenzene (1.5 g, 7 mmol) in THF (3.5 mL) and *s*-BuLi (1.4 M in cyclohexane, 5.0 mL, 7 mmol). The ring opening product **[11m]** was then trapped by Ph_2PCl. The purification was achieved by column chromatography on silica gel using petroleum ether/toluene (1:1) as eluent. White crystals (1.06 g, 54% yield). R_f = 0.10 (petroleum ether/toluene 1:1); Mp = 172-174 °C; $[\alpha]_D^{20}$ = -50.7 (c 1.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.33-1.61 (m, 6H), 0.68 (d, J = 6.2 Hz, 3H), 0.78 (d, J = 6.2 Hz, 3H), 1.25 (d, J = 6.2 Hz, 3H), 2.37 (d, J = 7.8 Hz, 3H), 4.27 (hept, J = 6.2 Hz, 1H), 4.52-4.59 (m, 1H), 5.32 (t, J = 8.8 Hz, 1H), 6.50 (2d, J = 7.7 Hz, 2H), 6.69 (dd, J = 4.2, 2.3 Hz, 1H), 6.90-6.95 (m, 3H), 7.00-7.44 (m, 15H), 7.61-7.67 (m, 2H), 7.80 (ddd, J = 1.5, 7.6, 13.8 Hz, 1H). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 16.1, 20.6, 21.1, 29.8 (d, J = 5.1 Hz), 57.5 (dd, J = 8.3, 11.3 Hz), 69.0, 83.5 (dd, J = 2.9, 11.5 Hz), 111.7 (d, J = 4.1 Hz), 118.1 (d, J = 54.2 Hz), 120.1 (d, J = 10.8 Hz), 127.6 (d, J = 11.2 Hz), 127.8 (d, J = 10.6 Hz), 128.1, 128.3, 128.5 (d, J = 10.6 Hz), 128.8, 129.3 (d, J = 2.1 Hz), 130.2 (d, J = 11.2 Hz), 131.1 (d, J = 11.3 Hz), 131.3 (d, J = 2.0 Hz), 131.6 (d, J = 11.7 Hz), 131.7 (d, J = 2.0 Hz), 132.2 (d, J = 7.8 Hz), 132.3 (d, J = 76.4 Hz), 132.9, 133.2 (d, J = 1.5 Hz), 136.1 (d, J = 14.1 Hz), 138.1, 158.6. ^{31}P{^{1}H} NMR (161.9 MHz, $CDCl_3$): δ +68.3 (br.s), +106.4 (br.s). FTIR (neat): ν_{max} 3080-3010, 2978-2819, 2391, 2378, 2346,

1587, 1572, 1471, 1456, 1437, 1383, 1372, 1275, 1244, 1222, 1164, 1132, 1113, 1061, 1013, 983, 952, 890, 865, 768, 752, 735, 714, 694 cm^{-1}. HRMS (ESI/Q-TOF) calcd for $C_{37}H_{44}B_2NO_2P_2$ $[M-H]^+$: 618.3033; found 618.3043. Anal. calcd for $C_{37}H_{45}B_2NO_2P_2$: C 71.75, H 7.32, N 2.26; found C 72.02, H 7.56, N 2.32.

4.4.5. (R_p)-(-)-N-[(1R,2S)-2-(Diphenylphosphinito-borane)-1-methyl-2-phenylethyl], N-methyl amino(2-benzyloxyphenyl)phenylphosphine-borane **12n**. The synthesis of **12n** was achieved using the method A (as described above), by reaction of the complex (-)-**10a** (1.0 g, 3.5 mmol) with the 2-benzyloxyphenyllithium reagent, previously prepared using 2-benzyloxybromobenzene (1.8 g, 7 mmol) in THF (3.5 mL) and *s*-BuLi (1.4 M in cyclohexane, 5.0 mL, 7 mmol). The ring opening product **[11n]** was then trapped by Ph_2PCl. The purification was achieved by column chromatography on silica gel using petroleum ether/toluene (1:1) as eluent. White crystals (1.05 g, 45% yield). R_f = 0.10 (petroleum ether/toluene 1:1); Mp = 140-142 °C; $[\alpha]_D^{20}$ = -36.5 (c 1.9, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 0.20-1.60 (m, 6H), 1.22 (d, J = 6.6 Hz, 3H), 2.27 (d, J = 7.8 Hz, 3H), 4.45-4.60 (m, 1H), 4.69 (s, 2H), 5.27 (t, J = 9.2 Hz, 1H), 6.53 (dd, J = 7.4, 11.7 Hz, 2H), 6.63 (d, J = 6.9 Hz, 2H), 6.85-7.41 (m, 22H), 7.60-7.80 (m, 3H). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 15.9, 29.8 (d, J = 4.5 Hz), 57.5 (br.s), 70.1, 83.4 (d, J = 9.8 Hz), 112.3 (d, J = 4.5 Hz), 118.2, 118.9, 121.2 (d, J = 11.3 Hz), 126.8, 127.6, 127.8, 128.0 (d, J = 9.1 Hz), 128.2,

128.3, 128.5 (d, J = 10.6 Hz), 128.8, 129.6 (d, J = 2.0 Hz), 130.4 (d, J = 10.6 Hz), 131.0, 131.2, 131.3 (d, J = 2.0 Hz), 131.5, 131.7, 132.0, 132.2 (d, J = 8.3 Hz), 132.9, 133.5, 135.8, 136.0 (d, J = 13.6 Hz), 138.0, 159.9. $^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$): δ +68.7 (br.s), +106.7 (br.s). FTIR (neat): v_{max} 3083-3040, 2976-2854, 2344, 2299, 1570, 1546, 1465, 1437, 1363, 1250, 1223, 1130, 1115, 1066, 1043, 999, 973,922, 914, 860, 831, 740, 714, 694 cm^{-1}. HRMS (ESI/Q-TOF) calcd for $C_{41}H_{46}B_2P_2NO_2$ $[M+H]^+$: 668.3190; found: 668.3195.

4.4.6. (R_p)-(-)-N-[(1R,2S)-2-(Diphenylphosphinito-borane)-1-methyl-2-phenylethyl], N-methyl amino(3,5-dimethylphenyl)phenylphosphine-borane **12o**. The synthesis of **12o** was achieved using the method A (as described above), by reaction of the complex (-)-**10a** (1.0 g, 3.5 mmol) with the 3,5-dimethylphenyllithium reagent previously prepared using 1-bromo-3,5-dimethylbenzene (0.95 mL, 7 mmol) in THF (3.5 mL) and *s*-BuLi (1.4 M in cyclohexane, 5.0 mL, 7 mmol). The ring opening product **[11o]** was then trapped by Ph_2PCl. The purification was achieved by column chromatography on silica gel using petroleum ether/toluene (7:3) as eluent. White crystals (0.62 g, 30% yield). R_f = 0.10 (petroleum ether/toluene 7:3); Mp = 168-170 °C; $[\alpha]_D^{20}$ = -78.8 (c 1.0, CH_2Cl_2). ^1H NMR (500 MHz, $CDCl_3$): δ 0.50-1.81 (m, 6H), 1.37 (d, J = 6.2 Hz, 3H), 2.32 (s, 6H), 2.33 (d, J = 8.5 Hz, 3H), 4.58-4.64 (m, 1H), 5.40 (t, J = 9.2 Hz, 3H), 6.64-6.68 (m, 2H), 7.09-7.17 (m,

10H), 7.26-7.40 (m, 6H), 7.47-7.54 (m, 3H), 7.73-7.77 (m, 2H). $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$): δ 16.3, 21.4, 29.4 (d, J = 4.5 Hz), 57.3 (dd, J = 11.2, 8.8 Hz), 83.3 (dd, J = 9.0, 2.5 Hz), 127.8 (d, J = 10.6 Hz), 127.9 (d, J = 11.1 Hz), 128.2, 128.5 (d, J = 9.2 Hz), 128.6, 128.7, 129.8 (d, J = 34.2 Hz), 130.1 (d, J = 10.3 Hz), 130.2 (d, J = 1.9 Hz), 130.4 (d, J = 20.4 Hz), 131.0 (d, J = 11.2 Hz), 131.3 (d, J = 2.2 Hz), 131.6, 131.7, 131.8 (d, J = 9.8 Hz), 132.1 (d, J = 6.5 Hz), 132.7, 133.0 (d, J = 1.6 Hz), 137.9, 138.1 (d, J = 5.9 Hz). $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$): δ +71.2 (br.s), +106.8 (br.s). FTIR (neat): ν_{max} 3062-2817, 2394-2249, 1454, 1436, 1222, 1161, 1128, 1108, 1063, 1011, 1000, 991, 958, 894, 864, 855, 769, 761, 753, 736, 712, 691 cm^{-1}. HRMS (ESI/Q-TOF) calcd for $C_{36}H_{42}B_2NOP_2$ $[M-H]^+$: 588.2928; found 588.2934. Anal. calcd for $C_{36}H_{43}B_2NOP_2$: C 73.37, H 7.35, N 2.38; found: C 73.26, H 7.46, N 2.43.

4.4.7. (R_p)-(-)-N-[(1R,2S)-2-(Diphenylphosphinito-borane)-1-methyl-2-phenylethyl], N-methyl amino(3,5-di-t-butylphenyl)phenylphosphine-borane **12p**. The synthesis of **12p** was achieved using the method A (as described above), by reaction of the complex (-)-**10a** (1.0 g, 3.5 mmol) with the 3,5-di-*t*-butylphenyllithium previously prepared from 1-bromo-3,5-di-*t*-butylbenzene (1.9 g, 7 mmol) in THF (3.5 mL) and *t*-BuLi (1.9 M in hexane, 7.4 mL, 14 mmol). The ring opening product **[11p]** was then trapped by Ph_2PCl. The purification was achieved by column chromatography on silica gel using petroleum ether/CH_2Cl_2 (2:1) as

eluent. White solid (1.67 g, 71% yield). R_f = 0.68 (petroleum ether/CH_2Cl_2 2:1); $[\alpha]_D^{20}$ = -63.4 (c 0.4, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 0.59-1.52 (m, 6H), 1.30 (s, 18H), 1.42 (d, J = 6.7 Hz, 3H), 2.30 (d, J = 7.5 Hz, 3H), 4.66-4.72 (m, 1H), 5.42 (t, J = 9.6 Hz, 1H), 6.67-6.71 (m, 2H), 7.08-7.20 (m, 7H), 7.28-7.36 (m, 4H), 7.40-7.42 (m, 4H), 7.48-7.54 (m, 4H), 7.75-7.78 (m, 2H). $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$): δ 16.1, 29.3 (d, J = 4.4 Hz), 31.3, 35.0, 57.4 (t, J = 9.7 Hz), 83.2 (d, J = 7.3 Hz), 124.9, 126.8 (d, J = 11.9 Hz), 127.8, 127.9 (d, J = 1.2 Hz), 128.2, 128.4, 128.5 (d, J = 10.8 Hz), 128.8, 129.3 (d, J = 58.6 Hz), 130.1 (d, J = 70.6 Hz), 130.2, 131.1 (d, J = 11.0 Hz), 131.3, 131.6-131.7 (m), 131.8, 132.2 (d, J = 8.8 Hz), 132.8, 138.2, 150.7 (d, J = 9.6 Hz). $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$): δ +72.6 (br.s), +106.9 (br.s). FTIR (neat): ν_{max} 3070-2810, 2391, 2375, 2339, 1585, 1573, 1473, 1435, 1242, 1163, 1153, 1100, 1088, 999, 965, 873, 797 cm^{-1}. HRMS (ESI/Q-TOF) calcd for $C_{42}H_{55}B_2NOP_2Na$ $[M+Na]^+$: 696.3854; found: 696.3834.

4.4.8. (R_p)-(-)-N-[(1R,2S)-2-(Diphenylphosphinito-borane)-1-methyl-2-phenylethyl], N-methyl amino(3,5-di-t-butyl-4-methoxyphenyl)phenylphosphine-borane **12q**. The synthesis of **12q** was achieved using the method A (as described above), by reaction of the complex (-)-**10a** (1.0 g, 3.5 mmol) with the 3,5-di-*t*-butyl-4-methoxyphenyllithium previously prepared from bromo-3,5-di(*t*-butyl)-4-methoxybenzene (2.1 g, 7 mmol) in THF (3.5 mL) and *s*-BuLi (1.4 M in hexane, 5.0 mL, 7 mmol). The ring opening product **[11q]** was then trapped by

Ph_2PCl. The purification was performed by column chromatography on silica gel using petroleum ether/toluene (7:3) as eluent. White solid (0.49 g, 20% yield). R_f = 0.10 (petroleum ether/toluene 7:3); Mp = 166-168 °C; $[\alpha]_D^{20}$ = -75.3 (c 1.1, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 0.48-1.78 (m, 6H), 1.37 (s, 18H), 1.39 (d, J = 6.8 Hz, 3H), 2.28 (d, J = 8.0 Hz, 3H), 3.72 (s, 3H), 4.62-4.69 (m, 1H), 5.39 (t, J = 9.4 Hz, 1H), 6.64-6.68 (m, 2H), 7.06-7.18 (m, 7H), 7.27-7.34 (m, 4H), 7.38-7.43 (m, 4H), 7.47-7.54 (m, 3H), 7.73-7.77 (m, 2H). $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$): δ 16.2, 29.2 (d, J = 4.7 Hz), 31.9, 36.0, 57.3 (dd, J = 11.1, 9.4 Hz), 64.3, 83.3 (dd, J = 8.7, 2.5 Hz), 123.5 (d, J = 61.9 Hz), 127.8 (d, J = 9.9 Hz), 128.2, 128.4, 128.6 (d, J = 9.9 Hz), 128.7, 130.1 (d, J = 71.8 Hz), 130.2 (d, J = 2.2 Hz), 131.1 (d, J = 11.1 Hz), 131.2 (d, J = 12.1 Hz), 131.4 (d, J = 1.9 Hz), 131.6-131.7 (m), 132.1 (d, J = 10.2 Hz), 132.7, 138.1, 143.7 (d, J = 10.4 Hz), 161.9 (d, J = 2.5 Hz). $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$): δ +71.6 (br.s), +106.9 (br.s). FTIR (neat): ν_{max} 3059-3008, 2981-2869, 2375, 2344, 1455, 1437, 1410, 1395, 1264, 1230, 1144, 1118, 1065, 1011, 999, 972, 962, 893, 870, 768, 758, 739, 714, 698, 690 cm^{-1}. HRMS (ESI/Q-TOF) calcd for $C_{43}H_{56}B_2P_2NO_2$ $[M-H]^+$: 702.3972; found 702.3979. Anal. calcd for $C_{43}H_{57}B_2NO_2P_2$: C 73.41, H 8.17, N 1.99; found: C 73.72, H 8.16, N 2.09.

4.4.9. (R_p)-(-)-N-[(1R,2S)-2-(Diphenylphosphinito-borane)-1-methyl-2-phenylethyl], N-(methyl amino)phenyl(2-pyridyl)phosphine-borane **12r**. The synthesis of **12r** was achieved

using the method A (as described above), by reaction of the complex (-)-**10a** (1.0 g, 3.5 mmol) previously prepared from 2-bromopyridine (1.1 g, 7 mmol) and *s*-BuLi (1.4 M in cyclohexane, 5.0 mL, 7 mmol). The ring opening product **[11r]** was then trapped by Ph_2PCl. The purification was performed by column chromatography on silica gel using toluene as eluent. White crystals (1.06 g, 54% yield). R_f = 0.15 (toluene); Mp = 178-180 °C; $[\alpha]_D^{20}$ = -40.2 (c 1.1, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 0.20-1.60 (m, 6H), 1.32 (d, J = 6.5 Hz, 3H), 2.49 (d, J = 7.3 Hz, 3H), 4.56-4.65 (m, 1H), 5.42 (t, J = 9.3 Hz, 1H), 6.52-6.59 (m, 2H), 7.00-7.50 (m, 18H), 7.74-7.85 (m, 3H), 7.98-8.00 (m, 1H), 8.73-8.74 (m, 1H). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 16.3, 29.8 (d, J = 5.0 Hz), 57.5 (dd, J = 10.7, 8.7 Hz), 83.2 (dd, J = 7.3, 2.5 Hz), 124.9 (d, J = 2.0 Hz), 128.0, 128.1 (d, J = 4.2 Hz), 128.2, 128.3, 128.6 (d, J = 5.4 Hz), 128.6, 129.0, 129.1 (d, J = 26.5 Hz), 129.9 (d, J = 75.8 Hz), 130.6 (d, J = 2.5 Hz), 131.2 (d, J = 11.3 Hz), 131.5 (d, J = 2.4 Hz), 131.7, 131.8 (d, J = 2.5 Hz), 131.9 (d, J = 38.7 Hz), 132.7 (d, J = 51.9 Hz), 136.1 (d, J = 9.4 Hz), 138.2, 150.0 (d, J = 12.7 Hz). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 72.1 (br.s), 106.6 (br.s). FTIR (neat): ν_{max} 3061-2934, 2387, 2345, 1455, 1437, 1421, 1133, 1113, 1062, 1010, 977, 895, 739, 721, 691 cm^{-1}. Anal. calcd for $C_{33}H_{38}B_2N_2OP_2$: C 70.50, H 6.81, N 4.98; found: C 70.60, H 6.94, N 5.20.

4.4.10. (R_p)-(-)-N-[(1R,2S)-2-(Diphenylphosphinito-borane)-1-methyl-2-phenylethyl], N-methyl amino-2-(2',6'-dimethoxy-1,1'-biphenyl)phenylphosphine-borane **12s**. The synthesis of **12s** was achieved using the method A (as described above), by reaction of the complex (-)-**10a** (1.0 g, 3.5 mmol) with the 2',6'-dimethoxy-1,1'-biphenyllithium previously prepared from 2-bromo-2',6'-dimethoxy-1,1'-biphenyl (2.1 g, 7 mmol) in THF (3.5 mL) and *t*-BuLi (1.9 M in hexane, 7.4 mL, 14 mmol). The ring opening product **[11s]** was then trapped by Ph_2PCl. The purification was achieved by column chromatography on silica gel using petroleum ether/CH_2Cl_2 (2:1) as eluent. White solid (1.00 g, 41% yield). R_f = 0.47 (petroleum ether/CH_2Cl_2 2:1); $[\alpha]_D^{20}$ = -23.3 (c 0.3, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 0.20-1.69 (m, 6H), 1.33 (d, J = 6.1 Hz, 3H), 2.49 (d, J = 7.6 Hz, 3H), 3.38 (s, 3H), 3.64 (s, 3H), 4.28-4.34 (m, 1H), 5.37-5.40 (m, 1H), 6.23 (d, J = 8.1 Hz, 1H), 6.38 (d, J = 8.1 Hz, 1H), 6.90-7.00 (m, 7H), 7.08-7.17 (m, 7H), 7.24-7.32 (m, 4H), 7.38-7.54 (m, 5H), 7.71-7.75 (m, 2H). $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$): δ 14.8, 30.4 (d, J = 2.4 Hz), 54.8, 55.1, 57.3 (t, J = 9.2 Hz), 83.8 (dd, J = 2.9, 6.4 Hz), 103.0 (d, J = 17.4 Hz), 117.8 (d, J = 3.2 Hz), 126.5 (d, J = 9.2 Hz), 127.3 (d, J = 10.3 Hz), 127.7, 127.8 (d, J = 10.3 Hz), 128.2, 128.3, 128.5 (d, J = 10.3 Hz), 129.3, 129.8 (d, J = 2.0 Hz), 130.5 (d, J = 59.0 Hz), 130.6 (d, J = 1.8 Hz), 131.1 (d, J = 11.6 Hz), 131.3 (d, J = 1.8 Hz), 131.5, 131.6 (2s), 131.7, 131.8, 132.1 (d, J = 28.5 Hz), 132.7 (d, J = 36.2 Hz), 133.2 (d, J = 8.8 Hz), 133.9 (d, J = 7.8 Hz), 138.0, 140.0

(d, J = 12.0 Hz), 157.6, 157.8. $^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$): δ +72.1 (br.s), +106.0-106.2 (m). FTIR (neat): ν_{max} 3075-2820, 2380, 2369, 2337, 1583, 1476, 1436, 1242, 1164, 1100, 1086, 998, 963, 870, 795, 738, 718 cm^{-1}. HRMS (ESI/Q-TOF) calcd for $C_{42}H_{47}B_2P_2NO_3Na$ $[M+Na]^+$: 720.3144; found: 720.3109.

4.4.11. (R_p)-(-)-N-[(1R,2S)-(2-(Di-α-naphtylphosphinito-borane)-1-methyl-2-phenylethyl], N-methylamino(o-biphenyl)phenylphosphine-borane **12t**. The synthesis of the **12t** was achieved using the method A (as described above) by reaction of the complex (-)-**10a** (1.0 g, 3.5 mmol) with the 1,1'-biphenyllithium previously prepared from 2-bromo-1,1'-biphenyl (1.3 mL, 7 mmol) in THF (3.5 mL) and *s*-BuLi (1.4 M in cyclohexane, 5.0 mL, 7 mmol). The ring opening product **[11t]** was then trapped by α-Np_2PCl. The purification was achieved by column chromatography on silica gel using petroleum ether/CH_2Cl_2 (2:1) as eluent. White solid (1.65 g, 64% yield). R_f = 0.27 (petroleum ether/ CH_2Cl_2, 2:1); $[\alpha]_D^{20}$ -93.2 (c 0.3, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 0.50-1.82 (m, 6H), 1.37 (d, J = 6.9 Hz, 3H), 2.45 (d, J = 6.9 Hz, 3H), 4.55-4.58 (m, 1H), 5.47 (t, J = 8.2 Hz, 1H), 6.39 (t, J = 7.7 Hz, 2H), 6.53 (t, J = 7.4 Hz, 1H), 6.83-6.87 (m, 6H), 6.98-7.08 (m, 7H), 7.16-7.27 (m, 4H), 7.35-7.38 (m, 2H), 7.41-7.44 (m, 2H), 7.57 (d, J = 8.3 Hz), 7.65-7.75 (m, 3H), 7.80 (d, J = 8.3 Hz, 1H), 7.94 (d, J = 8.3 Hz, 1H), 8.01 (d, J = 7.8 Hz, 1H), 8.11 (dd, J = 15.6, 6.4 Hz, 1H), 8.38 (ddd, J = 13.0, 7.2, 1.0 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$): δ 15.8 (d, J = 1.6 Hz),

29.9 (d, *J* = 3.1 Hz), 57.7 (t, *J* = 10.2 Hz), 82.9 (dd, *J* = 4.9, 3.0 Hz), 124.2 (d, *J* = 15.8 Hz), 124.9 (d, *J* = 9.5 Hz), 125.7, 125.9 (d, *J* = 6.3 Hz), 126.0, 126.1, 126.4 (d, *J* = 10.1 Hz), 126.8, 126.9, 127.0, 127.5 (d, *J* = 10.8 Hz), 127.9, 128.4 (d, *J* = 51.2 Hz), 128.5, 128.8 (d, *J* = 4.2 Hz), 128.9, 129.3 (d, *J* = 9.5 Hz), 129.8 (d, *J* = 1.8 Hz), 129.9, 130.3 (d, *J* = 1.8 Hz), 130.8 (d, *J* = 62.4 Hz), 131.7 (d, *J* = 8.9 Hz), 131.8, 131.9, 132.1 (d, *J* = 11.3 Hz), 132.3 (d, *J* = 3.6 Hz), 132.7, 132.8 (d, *J* = 2.6 Hz), 132.9, 133.2-133.3 (m), 133.6 (d, *J* = 8.2 Hz), 133.6 (d, *J* = 8.2 Hz), 134.5, 134.6, 136.4, 140.7 (d, *J* = 2.7 Hz), 147.0 (d, *J* = 9.5 Hz). $^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$): δ +71.3 (br.s), +106.5 (br.s). FTIR (neat): ν_{max} 3057-2807, 2393, 2375, 2345, 1579, 1475, 1437, 1242, 1163, 1099, 1086, 999, 965, 871, 798 cm^{-1}. HRMS (ESI/Q-TOF) calcd for $C_{48}H_{47}B_2NOP_2Na$ $[M+Na]^+$: 760.3211; found: 760.3226.

4.4.12. (M,S_p)-(+)-N-[(1S,2R)-2-(Diphenylphosphinito-borane)-1-methyl-2-phenylethyl], N-methylamino-2-(1,1'-binaphtyl)phenylphosphine-borane **12v**. The synthesis of **12v** was achieved using the method B (as described above) by reaction of the aminophosphine-borane **11v** (0.30 g, 0.56 mmol) with *n*-BuLi (1.6 M in hexane (0.42 mL, 0.67 mmol), then with Ph_2PCl (0.20 mL, 1.12 mmol) and borane-dimethyl sulfide (0.42 mL, 4.48 mmol). The purification was achieved by chromatography on silica gel using petroleum ether/CH_2Cl_2 (1:1) as eluent to afford AMPP*-diborane **12v** as a white solid (0.17 g, 41% yield). R_f = 0.33 (petroleum ether/CH_2Cl_2 1:1); $[\alpha]_D^{20}$ = +10.6 (c 0.8, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ

0.19-1.20 (m, 6H), 1.14 (d, *J* = 6.4 Hz, 3H), 2.55 (d, *J* = 7.4 Hz), 4.15-4.22 (m, 1H), 5.36 (t, *J* = 9.1 Hz, 1H), 6.81-6.93 (m, 9H), 7.02-7.09 (m, 6H), 7.14-7.25 (m, 6H), 7.38-7.41 (m, 1H), 7.43-7.52 (m, 4H), 7.64-7.70 (m, 4H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.89-7.92 (m, 2H). $^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$): δ 14.4, 31.2 (d, *J* = 1.5 Hz), 57.6 (t, *J* = 9.0 Hz), 83.7 (dd, *J* = 5.5, 2.9 Hz), 124.6, 125.6, 125.8, 126.6, 127.0, 127.2 (d, *J* = 9.6 Hz), 127.5 (d, *J* = 2.9 Hz), 127.6, 127.7, 127.8, 127.9 (d, *J* = 5.0 Hz), 128.1, 128.2, 128.5 (d, *J* = 2.7 Hz), 128.6, 128.7 (d, *J* = 11.2 Hz), 129.1, 129.8 (d, *J* = 2.3 Hz), 131.0, 131.1, 131.3 (d, *J* = 1.8 Hz), 131.4, 131.5, 131.6 (2s), 131.7 (d, *J* = 15.6 Hz), 132.1 (d, *J* = 9.2 Hz), 132.3, 132.6, 133.1, 133.6, 133.9 (d, *J* = 9.6 Hz), 134.0 (d, *J* = 1.6 Hz), 134.6 (d, *J* = 4.3 Hz), 137.9, 143.7 (d, *J* = 10.6 Hz); $^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$): δ +73.4 (br.s), +106.0 (br.s). FTIR (neat): ν_{max} 3073-2820, 2390, 2372, 2342, 1580, 1571, 1470, 1435, 1240, 1160, 1151, 1101, 1090, 997, 963, 870, 795, 740, 721 cm^{-1}. HRMS (ESI/Q-TOF) calcd for $C_{48}H_{45}BNOP_2$ $[M\text{-}BH_3+H]^+$: 724.3097; found 724.3064.

4.4.13. (S_p)-(+)-N-[(1S,2R)-2-[Bis(3,5-dimethylphenyl)phosphinito-borane]-1-methyl-2-phenylethyl], N-methylamino(o-biphenyl)phenylphosphine-borane **12w**. This compound was synthesized using the method A (as described above) by reaction of the complex (+)-**10a** (1.0 g, 3.5 mmol) prepared from (-)-ephedrine **9**, with the *o*-biphenyllithium reagent previously prepared from 2-bromo-1,1'-biphenyl (1.2 mL, 7 mmol) in THF (3.5 mL) and *s*-

BuLi (1.4 M in cyclohexane, 5 mL, 7 mmol). The ring-opening product **[11w]** was then trapped with chloro-bis(3,5-dimethylphenyl)phosphine $(3,5\text{-Xyl})_2PCl$ (1.9 g, 7 mmol). The purification was achieved by chromatography on silica gel using petroleum ether/CH_2Cl_2 (2:1) as eluent to afford the AMPP*-diborane **12w** as a white sticky solid (1.02 g, 42% yield); R_f = 0.24 (petroleum ether/CH_2Cl_2 2:1); $[\alpha]_D^{20}$ = +85.5 (c 0.3, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 0.50-1.52 (m, 6H), 1.26 (d, J = 6.8 Hz, 3H), 2.05 (s, 6H), 2.37 (s, 6H), 2.44 (d, J = 6.5 Hz, 3H), 4.44-4.50 (m, 1H), 5.21 (t, J = 9.2 Hz, 1H), 6.74 (d, J = 9.5 Hz, 2H), 6.82-6.85 (m, 3H), 6.90-7.18 (m, 14H), 7.31 (d, J = 5.5 Hz, 2H), 7.36-7.40 (m, 1H), 7.44-7.52 (m, 3H). $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$): δ 15.2 (d, J = 1.9 Hz), 21.0, 21.4, 30.0 (d, J = 3.5 Hz), 57.8 (dd, J = 9.9, 8.4 Hz), 82.8 (dd, J = 4.2, 3.1 Hz), 115.8, 120.8, 126.9, 127.0 (2s), 127.5, 127.6 (d, J = 10.9 Hz), 128.1, 128.2, 128.6 (d, J = 11.4 Hz), 129.0 (d, J = 62.0 Hz), 129.1 (d, J = 11.3 Hz), 129.9, 130.3 (d, J = 1.5 Hz), 130.9 (d, J = 62.5 Hz), 131.5, 131.9, 132.0, 132.4, 132.8 (d, J = 8.1 Hz), 133.0 (d, J = 2.5 Hz), 133.3 (d, J = 9.1 Hz), 133.4 (d, J = 2.0 Hz), 137.3 (d, J = 11.3 Hz), 138.0 (d, J = 11.9 Hz), 138.1, 140.8 (d, J = 2.5 Hz), 147.0 (d, J = 8.7 Hz). $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$): δ +71.1 (br.s), +107.4 (br.s). IR (neat): ν_{max} 3067-2817, 2389, 2370, 2346, 1580, 1473, 1436, 1241, 1162, 1153, 1099, 998, 965, 870, 797 cm^{-1}. HRMS (ESI/Q-TOF) calcd for $C_{44}H_{51}B_2NOP_2$ $[M+Na]^+$: 716.3524; found: 716.3534.

4.5. Typical procedure for the decomplexation of aminophosphine-phosphinite-diboranes 12. A solution of aminophosphine-phosphinite-diborane **12** (1 mmol) and DABCO (4 mmol) in toluene (3 mL) was heated at 50°C with an oil bath and was stirred under argon overnight. After removing the solvent under vacuum, the residue was purified by chromatography on neutral aluminium-oxide using a mixture of petroleum ether/ethyl acetate (4:1) or toluene as eluent, to afford the free AMPP* **13**.

4.5.1. The EPHOS **1**[9a] and the free *o-anisyl-*,[9a] *α-naphtyl-*,[9a] *β-naphtyl-*,[9a] *o-biphenyl-*,[9b] *ferrocenyl-*,[9b] *t-butyl-*,[9a] *methyl-*,[9a,10a] *cyclohexyl-*,[9b] *o-[(2-methoxyethoxy)methoxy]phenyl-*,[9b] *calixarenyl-*[9c] AMPP* ligands **13a-c**, **13f-h**, **13j-l** and **13u**, respectively, were prepared and characterized according to described procedures.

4.5.2. (S_p)-(-)-N-[(1R,2S)-2-(Diphenylphosphinito)-1-methyl-2-phenyl]ethyl], N-methyl amino(o-biphenyl)phenylphosphine **13i**. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ +60.2, +108.7.

4.5.3. (R_p)-N-[(1R,2S)-2-(Diphenylphosphinito)-1-methyl-2-phenylethyl], N-methylamino(2-isopropoxyphenyl)phenylphosphine **13m**. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ +54.7, +111.7.

4.5.4. (R_p)-N-[(1R,2S)-2-(Diphenylphosphinito)-1-methyl-2-phenylethyl], N-methylamino(2-benzyloxyphenyl)phenylphosphine **13n**. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ +53.1, +111.1.

4.5.5. (R_p)-N-[(1R,2S)-2-(Diphenylphosphinito)-1-methyl-2-phenylethyl], N-methylamino (3,5-dimethylphenyl)phenylphosphine **13o**. $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$): δ +61.4, +110.6.

4.5.6. (R_p)-N-[(1R,2S)-2-(Diphenylphosphinito)-1-methyl-2-phenylethyl], N-methylamino(3,5-di-t-butylphenyl)phenylphosphine **13p**. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ +68.6, +110.4.

4.5.7. (R_p)-N-[(1R,2S)-2-(Diphenylphosphinito)-1-methyl-2-phenylethyl], N-methylamino (3,5-di-t-butyl-4-methoxyphenyl)phenylphosphine **13q**. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ +67.8, +111.5.

4.5.8. (R_p)-N-[(1R,2S)-2-(Diphenylphosphinito)-1-methyl-2-phenylethyl], N-(methylamino) phenyl(2-pyridyl)phosphine **13r**. $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$): δ +61.3, +111.8.

4.5.9. (R_p)-N-[(1R,2S)-2-(Diphenylphosphinito)-1-methyl-2-phenylethyl], N-methylamino-2-(2',6'-dimethoxy-1,1'-biphenyl)phenylphosphine **13s**. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ +56.5, +110.1.

4.5.10. (R_p)-N-[(1R,2S)-(2-(Di-α-naphtylphosphinito)-1-methyl-2-phenylethyl], N-methylamino (o-biphenyl)phenylphosphine **13t**. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ +56.0, +97.2.

4.5.11. (M,S_p)-(+)-N-[(1S,2R)-2-(Diphenylphosphinito)-1-methyl-2-phenylethyl], N-methylamino-2-(1,1'-binaphtyl)phenylphosphine **13v**. $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$): δ +53.8, +109.9.

4.5.12. (S_p)-N-[(1S,2R)-2-Bis(3,5-dimethylphenyl)phosphinito]-1-methyl-2-phenylethyl], N-methyl amino(o-biphenyl)phenylphosphine-borane **13w**. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ +56.0, +114.0.

4.6. AMPP*-diborane (*1S*$_p$, *2R*$_p$)-15e bearing P-chirogenic aminophosphine and phosphinite moieties. (S_p)-(+)-*N-{(1S, 2R)-2-[(R_p)-o-Anisylphenylphosphinito-borane]-1-methyl-2-phenylethyl}, N-methylamino-o-anisylphenylphosphine-borane* ***15e***.

This compound was synthesized from (-)-ephedrine **9** according to the described procedure.[9a] Suitable colorless crystals for X-ray structure were obtained by slow evaporation of CH_2Cl_2. Crystallographic data and structure of (*1S*$_p$, *2R*$_p$)-**15e** were reported in SI.

4.7. Synthesis of AMPP*-diborane 21a-i with a P-chirogenic phosphinite moieties.

4.7.1. Typical procedure.[12] To a solution of the aminophosphine-borane **11** (1 mmol) in toluene (3 mL) was added 0.6 mmol (2.0 mmol for **11** with R^1 = alkyl) of DABCO. The solution was heated at 50°C with an oil bath and was stirred overnight. Chlorodiphenylphosphine (2 mmol) and triethylamine (5 mmol) were added at room temperature. The solution was stirred for 4 h before addition of BH_3.DMS (8 mmol) at 0 °C and the mixture was again stirred for 4 h. After hydrolysis, the aqueous phase was extracted with dichloromethane and the organic phase was washed with saturated NaCl solution, dried over $MgSO_4$ and evaporated. The residue was purified by chromatography on silica gel with toluene as eluent to afford the AMPP*$(BH_3)_2$ **21** which was recrystallized in a mixture of hexane/CH_2Cl_2.

4.7.2. (S_p)-(+)-N-[(1S,2R)-2-(o-Anisylphenylphosphinito-borane)-1-methyl-2-phenylethyl], N-methylaminodiphenylphosphine-borane **21a**. This compound was synthesized from *(S_p)-(+)-N-[(1S,2R)-2-hydroxy-1-methyl-2-phenylethyl], N-methylamino(o-anisyl)phenyl phosphine-borane* **11a** previously prepared from (-)-ephedrine **9**.[11b] X-ray quality crystals were grown by slow evaporation of CH_2Cl_2; The structure and the data were reported in the SI. White crystalline needles (0.38 g, 65% yield); R_f = 0.60 (toluene); Mp = 155 °C. $[\alpha]_D^{20}$ = +68.8 (c 0.6, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.34-1.45 (m, 6H), 1.26 (d, J = 6.6 Hz, 3H), 2.21 (d, J = 7.6 Hz, 3H), 3.47 (s, 3H), 4.47-4.57 (m, 1H), 5.33 (t, J = 9.4 Hz, 1H), 6.51-

6.58 (m, 2H), 6.77 (dd, *J* = 8.2, 4.6 Hz, 1H), 6.95-7.09 (m, 8H), 7.10-7.15 (m, 1H), 7.16-7.34 (m, 7H), 7.35-7.50 (m, 4H), 7.80 (ddd, *J* = 11.9, 7.0, 1.7 Hz, 1H). $^{13}C\{^{1}H\}$ NMR: (125.8 MHz, $CDCl_3$): δ 16.0, 29.4 (d, *J* = 4.5 Hz), 55.5, 57.6 (dd, *J* = 11.1, 8.6 Hz), 82.4 (dd, *J* = 8.9, 2.5 Hz), 111.8 (d, *J* = 5.2 Hz), 120.2 (d, *J* = 70.2 Hz), 120.8 (d, *J* = 10.5 Hz), 127.4 (d, *J* = 10.9 Hz), 128.0 (d, *J* = 10.9 Hz), 128.1, 128.3 (d, *J* = 8.4 Hz), 128.4, 128.7, 129.7 (d, *J* = 71.7 Hz), 130.3 (d, *J* = 2.4 Hz), 130.6 (d, *J* = 2.2 Hz), 130.7 (d, *J* = 57.3 Hz), 131.0, 131.7 (d, *J* = 10.5 Hz), 132.5 (d, *J* = 10.2 Hz), 132.6 (d, *J* = 62.4 Hz), 133.3 (d, *J* = 9.3 Hz), 133.9 (d, *J* = 2.0 Hz), 138.4, 160.9 (d, *J* = 4.4 Hz). $^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$): δ +71.1 (br.s), +105.3 (br.s). HRMS (ESI/Q-TOF) calcd for $C_{35}H_{41}B_2NO_2P_2Na$ $[M+Na]^+$: 614.27026; found 614.26804. Anal. calcd for $C_{35}H_{41}B_2NO_2P_2$: C 71.10, H 6.99, N 2.37; found: C 70.76, H 7.02, N 2.46.

4.7.3. (R_p)-(+)-N-[(1R,2S)-2-(o-Anisylphenylphosphinito-borane)-1-methyl-2-phenylethyl], N-methylaminodiphenylphosphine-borane **21a**. This enantiomer was synthesized from *(R_p)-(+)-N-[(1R,2S)-2-hydroxy-1-methyl-2-phenylethyl], N-methylamino(o-anisyl)phenyl phosphine-borane* **11a** previously prepared from (+)-ephedrine **9**.[11b] (0.40 g, 68% yield). $^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$): δ +71.3 (br.s), +105.1 (br.s).

4.7.4. (S_p)-(+)-N-[(1S,2R)-2-(α-Naphtylphenylphosphinito-borane)-1-methyl-2-phenylethyl], N-methylaminodiphenylphosphine-borane **21b**. This compound was

synthesized from *(S_p)-(+)-N-[(1S,2R)-2-hydroxy-1-methyl-2-phenylethyl], N-methylamino(α-naphtyl)phenylphosphine-borane* **11c** previously prepared from (-)-ephedrine **9**.[11b,29] X-ray quality crystals were grown by slow evaporation of CH_2Cl_2. The structure and the data were reported in the SI. Colorless crystals (0.37 g, 61% yield); R_f = 0.60 (toluene); Mp = 198 °C. $[\alpha]_D^{20}$ = +48.9 (c 0.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.38-1.61 (m, 6H), 1.02 (d, J = 6.6 Hz, 3H), 2.19 (d, J = 7.6 Hz, 3H), 4.42-4.54 (m, 1H), 5.51 (t, J = 9.7 Hz, 1H), 6.56 (dd, J = 11.3, 7.8 Hz, 2H), 6.93-7.02 (m, 4H), 7.03- 7.21 (m, 8H), 7.22-7.45 (m, 8H), 7.49-7.54 (m, 1H), 7.77 (d, J = 8.2 Hz, 1H), 7.94 (d, J = 8.5 Hz, 2H), 8.31 (ddd, J = 14.8, 7.1, 0.7 Hz, 1H). ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ 16.0, 29.4 (d, J = 4.5 Hz), 57.5 (dd, J = 11.2, 7.7 Hz), 83.6 (dd, J = 8.9, 3.0 Hz), 124.7 (d, J = 13.5 Hz), 126.3, 126.8 (d, J = 5.0 Hz), 127.1, 127.7 (d, J = 63.7 Hz), 128.0 (d, J = 5.7 Hz), 128.1 (d, J = 6.1 Hz), 128.3, 128.4, 128.6, 128.9, 129.0, 129.7 (d, J = 71.6 Hz), 130.4 (d, J = 2.0 Hz), 130.9, 130.9 (d, J = 11.8 Hz), 131.1 (d, J = 1.7 Hz), 131.7 (d, J = 10.3 Hz), 132.3 (d, J = 6.4 Hz), 132.5 (d, J = 10.2 Hz), 133.0 (d, J = 63.3 Hz), 133.5 (d, J = 2.4 Hz), 133.8 (d, J = 7.6 Hz), 133.9, 134.0, 138.5. ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$): δ +71.3 (br.s), +110.0 (br.s). HRMS (ESI/Q-TOF) calcd for $C_{38}H_{41}B_2NOP_2Na$ $[M+Na]^+$: 634.27472; found: 634.27398. HRMS (ESI/Q-TOF) calcd for $C_{38}H_{42}B_2NOP_2$ $[M+H]^+$: 612.29278; found: 612.29213.

4.7.5. (R_p)-(+)-N-[(1R,2S)-2-(α-Naphtylphenylphosphinito-borane)-1-methyl-2-phenylethyl], N-methylaminodiphenylphosphine-borane **21b**. This enantiomer was synthesized from *(R_p)-(+)-N-[(1R,2S)-2-hydroxy-1-methyl-2-phenylethyl], N-methylamino(α-naphtyl)phenylphosphine-borane* **11c** previously prepared from (+)-ephedrine **9**.[11b,29] (0.39 g, 63% yield). $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$): δ +71.5 (br.s), +110.2 (br.s).

4.7.6. (R_p)-(-)-N-[(1R,2S)-2-(β-Naphtylphenylphosphinito-borane)-1-methyl-2-phenylethyl], N-methylaminodiphenylphosphine-borane **21c**. This compound was synthesized from *(R_p)-(-)-N-[(1R,2S)-2-hydroxy-1-methyl-2-phenylethyl], N-methylamino(β-naphtyl)phenylphosphine-borane* **11d** previously prepared from (+)-ephedrine **9**.[11b,29b] X-ray quality crystals were grown by slow evaporation of cyclohexane. The structure and the data were reported in the SI. Colorless crystals (0.49 g, 81% yield); R_f = 0.60 (toluene); Mp = 151 °C. $[\alpha]_D^{20}$ = -66.3 (c 0.6, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 0.38-1.81 (m, 6H), 1.35 (d, J = 6.5 Hz, 3H), 2.33 (d, J = 7.5 Hz, 3H), 4.58-4.74 (m, 1H), 5.46 (t, J = 9.4 Hz, 1H), 6.59-6.71 (m, 2H), 7.05-7.23 (m, 6H), 7.26-7.66 (m, 14H), 7.68-7.77 (m, 1H), 7.86-8.00 (m, 3H), 8.33 (d, J = 12.7 Hz, 1H). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 16.0, 29.4 (d, J = 4.5 Hz), 57.5 (dd, J = 11.2, 8.6 Hz), 83.6 (dd, J = 8.8, 3.0 Hz), 126.1 (d, J = 10.3 Hz), 126.9, 127.9 (d, J = 3.5 Hz), 128.0 (d, J = 2.8 Hz), 128.2 (d, J = 2.9 Hz), 128.3, 128.4 (d, J = 10.0 Hz), 128.4, 128.6, 128.8, 129.0, 129.2, 130.2 (d, J = 7.5 Hz), 130.4 (d, J = 2.2 Hz),

131.0, 131.2 (d, J = 2.1 Hz), 131.4 (d, J = 2.1 Hz), 131.5, 131.6 (d, J = 1.2 Hz), 131.8, 132.4, 132.5 (d, J = 10.3 Hz), 132.6 (d, J = 18.8 Hz), 132.8 (d, J = 12.6 Hz), 134.6 (d, J = 2.3 Hz), 138.1. $^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$): δ +71.1 (br.s), +107.2 (br.s). HRMS (ESI/Q-TOF) calcd for $C_{38}H_{41}B_2NOP_2Na$ $[M+Na]^+$: 634.27472; found: 634.27319.

4.7.7. (R_p)-(-)-N-[(1R,2S)-2-(Phenyl-o-tolylphosphinito-borane)-1-methyl-2-phenylethyl], N-methylaminodiphenylphosphine-borane **21d**. This compound was synthesized from *(R_p)-(-)-N-[(1R,2S)-2-hydroxy-1-methyl-2-phenylethyl], N-methylamino(phenyl-o-tolyl)phosphine-borane* **11d** previously prepared (+)-ephedrine **9**.[30,31] X-ray quality crystals were grown by slow evaporation of hexane. The structure and the data were reported in the SI. Colorless crystals (0.37 g, 65% yield); R_f = 0.60 (toluene); Mp = 190 °C. $[\alpha]_D^{20}$ = -59.3 (c 0.5, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.25-1.66 (m, 6H), 1.17 (d, J = 6.5 Hz, 3H), 2.07 (s, 3H), 2.23 (d, J = 7.6 Hz, 3H), 4.42-4.62 (m, 1H), 5.43 (t, J = 9.6 Hz, 1H), 6.50-6.60 (m, 2H), 6.95-7.24 (m, 12H), 7.27-7.51 (m, 9H), 8.04 (ddd, J = 12.5, 7.4, 1.4 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$): δ 16.2, 21.6 (d, J = 4.3 Hz), 29.4 (d, J = 4.6 Hz), 57.4 (dd, J = 11.2, 7.7 Hz), 83.1 (dd, J = 9.3, 2.8 Hz), 125.7 (d, J = 11.6 Hz), 127.9 (d, J = 3.1 Hz), 128.1 (d, J = 3.0 Hz), 128.3, 128.4 (d, J = 2.8 Hz), 128.7, 129.2 (d, J = 18.6 Hz), 130.2 (d, J = 6.8 Hz), 130.3 (d, J = 2.4 Hz), 130.6 (d, J = 51.9 Hz), 130.9, 131.0, 131.2 (d, J = 2.1 Hz), 131.7, 131.7 (d, J = 10.2 Hz), 132.1 (d, J = 2.3 Hz), 132.6 (d, J = 61.6 Hz), 132.5 (d, J

= 10.4 Hz), 132.9 (d, *J* = 14.2 Hz), 138.4, 141.5 (d, *J* = 8.8 Hz). $^{31}P\{^{1}H\}$ NMR: (121.5 MHz, $CDCl_3$): *δ* +70.9 (br.s), +109.3 (br.s). HRMS (ESI/Q-TOF) calcd for $C_{35}H_{41}B_2NOP_2Na$ $[M+Na]^+$: 598.27472; found: 598.27261. Anal. calcd for $C_{35}H_{41}B_2NOP_2$: C 73.07, H 7.18, N 2.43; found: C 72.70, H 7.28, N 2.62.

4.7.8. (S_p)-N-[(1S,2R)-2-(Phenyl-o-tolylphosphinito-borane)-1-methyl-2-phenylethyl], N-methyl aminodiphenylphosphine-borane **21d**. This compound was synthesized as described for *(R_p)-***21d** *(§ 4.7.7.)* starting from (-)-ephedrine **9**. X-ray quality crystals were grown by slow evaporation of hexane. The structure and the data were reported in the SI.

4.7.9. (R_p)-(-)-N-[(1R,2S)-2-(Phenyl-p-tolylphosphinito-borane)-1-methyl-2-phenylethyl], N-methylaminodiphenylphosphine-borane **21e**. This compound was synthesized from *(R_p)-(-)-N-[(1R,2S)-2-hydroxy-1-methyl-2-phenylethyl], N-methylamino(phenyl-p-tolyl)phosphine-borane* **11e** previously prepared from (+)-ephedrine **9**.[31] X-ray quality crystals were grown by slow evaporation of diethyl ether. The structure and the data were reported in the SI. Colorless crystals (0.39 g, 67% yield); R_f = 0.60 (toluene); Mp = 156 °C. $[\alpha]_D^{20}$ = -71.6 (c 0.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 0.30-1.68 (m, 6H), 1.25 (d, *J* = 6.5 Hz, 3H), 2.22 (d, *J* = 7.6 Hz, 3H), 2.32 (s, 3H), 4.46-4.55 (m, 1H), 5.30 (t, *J* = 9.4 Hz, 1H), 6.52-6.58 (m, 2H,), 6.97-7.11 (m, 7H), 7.15-7.24 (m, 6H), 7.28-7.35 (m, 4H), 7.37-7.42 (m, 1H), 7.43-7.49 (m, 2H), 7.51-7.56 (m, 2H). $^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$): *δ* 16.2,

21.6, 29.4 (d, J = 4.5 Hz), 57.4 (dd, J = 11.2, 8.0 Hz), 83.1 (dd, J = 9.0, 2.5 Hz), 127.8 (d, J = 10.3 Hz), 128.0 (d, J = 10.4 Hz), 128.2, 128.4 (d, J = 10.0 Hz), 128.4, 128.7, 129.3, 129.4 (d, J = 11.0 Hz), 129.7 (d, J = 71.5 Hz), 130.3 (d, J = 2.3 Hz), 130.7 (d, J = 57.8 Hz), 131.3 (d, J = 11.8 Hz), 131.2 (d, J = 11.9 Hz), 131.5 (d, J = 11.7 Hz), 131.7 (d, J = 10.2 Hz), 132.1 (d, J = 59.7 Hz), 132.5 (d, J = 10.2 Hz), 138.2, 142.2 (d, J = 3.0 Hz). $^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$): δ +71.0 (br.s), +107.0 (br.s). HRMS (ESI/Q-TOF) calcd for $C_{35}H_{41}B_2NOP_2Na$ $[M+Na]^+$: 598.27417; found: 598.27340. Anal. calcd for $C_{35}H_{41}B_2NOP_2$: C 73.07, H 7.18, N 2.43; found: C 72.70, H 7.28, N 2.52.

4.7.10. (R_p)-(-)-N-[(1R,2S)-2-(Phenyl-o-biphenylphosphinito-borane)-1-methyl-2-phenylethyl], N-methylamino-diphenylphosphine-borane **21f**. This compound was synthesized from *(R_p)-(-)-N-[(1R,2S)-2-hydroxy-1-methyl-2-phenylethyl], N-methylamino(phenyl-o-biphenyl)phosphine-borane* **11f** previously prepared from (+)-ephedrine **9**.[11b,29,30] X-ray quality crystals were grown by slow evaporation of CH_2Cl_2. The structure and the data were reported in the SI. White solid; (0.43 g, 67% yield); R_f = 0.57 (petroleum ether/dichloromethane 1:1); Mp = 217 °C. $[\alpha]_D^{20}$ = -5.9 (c 0.4, $CHCl_3$). ^{1}H NMR: (500 MHz, CD_2Cl_2): δ 0.48-1.52 (m, 6H), 1.29 (d, J = 5.7 Hz, 3H), 2.29 (d, J = 7.6 Hz, 3H), 4.51-4.54 (m, 1H), 5.54 (t, J = 9.9 Hz, 1H), 6.60-6.64 (m, 2H), 6.69-6.73 (m, 2H), 6.84-6.86 (m, 2H), 6.90-6.94 (m, 2H), 7.11-7.17 (m, 5H), 7.22-7.35 (m, 8H), 7.44-7.63 (m, 7H), 8.33

(dd, J = 13.1, 7.2 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (125.8 MHz, CD_2Cl_2): δ (ppm) 16.0, 29.2 (d, J = 4.5 Hz), 57.3 (dd, J = 10.9, 7.0 Hz), 83.6 (dd, J = 9.5, 3.3 Hz), 127.0 (d, J = 12.5 Hz), 127.1 (2s), 127.4 (d, J = 11.1 Hz), 128.0 (d, J = 10.2 Hz), 128.3, 128.4 (d, J = 9.9 Hz), 128.5, 128.7, 129.5, 129.8, 130.1 (d, J = 12.5 Hz), 130.2 (d, J = 3.7 Hz), 130.3 (d, J = 2.1 Hz), 130.5 (d, J = 24.5 Hz), 131.0 (d, J = 32.0 Hz), 131.1 (d, J = 2.1 Hz), 131.6 (d, J = 10.3 Hz), 131.7 (d, J = 2.2 Hz), 131.9 (d, J = 7.7 Hz), 132.5 (d, J = 10.3 Hz), 133.3 (d, J = 63.5 Hz), 133.5 (d, J = 18.0 Hz), 138.5, 140.3 (d, J = 3.0 Hz), 146.7 (d, J = 5.3 Hz). $^{31}P\{^{1}H\}$ NMR (202.5 MHz, CD_2Cl_2): δ +71.1 (br.s), +110.6 (br.s). IR (neat): ν_{max} 3057, 2982, 2393, 1458, 1436, 1225, 1160, 1132, 1112, 1062, 1009, 991, 965, 928, 895, 873, 758, 746, 735, 718, 697, 610 cm^{-1}. HRMS (ESI/Q-TOF) calcd for $C_{40}H_{43}B_2NOP_2Na$ $[M+Na]^+$: 660.2898; found: 660.2884. Anal. calcd for $C_{40}H_{43}B_2NOP_2$: C 75.38, H 6.80, N 2.20; found: C 75.05, H 6.80, N 2.20.

4.7.11. (R_p)-(+)-N-[(1R,2S)-2-Ferrocenylphenylphosphinito-borane)-1-methyl-2-phenylethyl], N-methylaminodiphenylphosphine-borane **21g**. This compound was synthesized from *(R_p)-(+)-N-[(1R,2S)-2-hydroxy-1-methyl-2-phenylethyl], N-methylamino(ferrocenylphenyl)phosphine-borane* **11g** previously prepared from (+)-ephedrine **9**.[11b,15,30] X-ray quality crystals were grown by slow evaporation of CH_2Cl_2. The structure and the data were reported in the SI. Orange crystals; (0.46 g, 68% yield); R_f =

0.60 (toluene); Mp = 150 °C. $[\alpha]_D^{20}$ = +9.8 (c 0.5, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 0.42-1.46 (m, 6H), 1.28 (d, J = 6.6 Hz, 3H), 2.19 (d, J = 7.6 Hz, 3H), 4.02 (s, 5H), 4.09 (m, 1H), 4.33 (m, 1H), 4.40 (m, 2H), 4.58 (m, 1H), 5.14 (t, J = 9.4 Hz, 1H), 6.52-6.58 (m, 2H), 6.95-7.05 (m, 5H), 7.07-7.18 (m, 3H), 7.15-7.17 (m, 1H), 7.19-7.24 (m, 2H), 7.29-7.33 (m, 2H), 7.36-7.40 (m, 1H), 7.42-7.49 (m, 4H). $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$): δ 15.9, 29.4 (d, J = 4.3 Hz), 57.9 (dd, J = 10.9, 8.1 Hz), 70.0, 71.1 (d, J = 9.6 Hz), 71.5 (d, J = 8.9 Hz), 72.1 (d, J = 7.7 Hz), 72.2 (d, J = 14.1 Hz), 72.6 (d, J = 85.3 Hz), 82.6 (dd, J = 8.6, 3.3 Hz), 125.3, 127.6 (d, J = 10.7 Hz), 128.0 (d, J = 10.6 Hz), 128.0, 128.1, 128.2, 128.4 (d, J = 10.0 Hz), 128.6, 128.9 (d, J = 29.0 Hz), 129.8 (d, J = 71.3 Hz), 130.3 (d, J =2.4 Hz), 130.7 (d, J = 57.9 Hz), 130.8, 131.1 (d, J = 1.8 Hz), 131.2 (d, J = 2.1 Hz), 131.3 (d, J = 11.2 Hz), 131.7 (d, J = 10.2 Hz), 131.9 (d, J = 61.7 Hz), 132.5 (d, J = 10.4 Hz), 138.3. $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$): δ +71.7 (br.s), +106.9 (br.s). HRMS (ESI/Q-TOF) calcd for $C_{38}H_{43}B_2FeNOP_2$ $[M]^+$: 669.2363 found: 669.2367. HRMS (ESI/Q-TOF) calcd for $C_{38}H_{43}B_2FeNOP_2Na$ $[M+Na]^+$: 692.2261; found: 692.2247. Anal. calcd for $C_{38}H_{43}B_2FeNOP_2$: C 68.21, H 6.48, N 2.09; found: C 68.00, H 6.49, N 2.11.

4.7.12. (S_p)-(-)-N-[(1R,2S)-2-t-Butylphenylphosphinito-borane)-1-methyl-2-phenylethyl], N-methyl aminodiphenylphosphine-borane **21h**. This compound was synthesized from *(S_p)-(+)-N-[(1R,2S)-2-hydroxy-1-methyl-2-phenylethyl], N-methylamino(t-*

butyl)phenylphosphine-borane **11h** previously prepared from (+)-ephedrine **9**.[11b,32] X-ray quality crystals were grown by slow evaporation of hexane. The structure and the data were reported in the SI. Colorless crystals; (0.32 g, 59% yield); R_f = 0.55 (toluene); Mp = 234 °C. $[\alpha]_D^{20}$ = -93.6 (c 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.25-1.77 (m, 6H), 1.13 (d, J = 14.6 Hz, 9H), 1.51 (d, J = 6.5 Hz, 3H), 2.23 (d, J = 7.5 Hz, 3H), 4.63-4.76 (m, 1H), 5.26 (t, J = 9.5 Hz, 1H), 6.53-6.63 (m, 2H), 6.96-7.62 (m, 18H). ^{13}C{^{1}H} NMR: (75.5 MHz, $CDCl_3$): δ 16.7, 24.4 (d, J = 2.9 Hz), 29.2 (d, J = 4.8 Hz), 32.5 (d, J = 44.7 Hz), 57.1 (dd, J = 11.1, 8.6 Hz), 82.4 (dd, J = 9.2, 5.1 Hz), 126.9 (d, J = 10.0 Hz), 128.0 (d, J = 10.8 Hz), 128.1, 128.3, 128.5 (d, J = 5.0 Hz), 128.7, 129.1, 129.3 (d, J = 6.8 Hz), 130.3 (d, J = 2,4 Hz), 130.4 (d, J = 19.2 Hz), 130.8 (d, J = 2.6 Hz), 131.1 (d, J = 2.1 Hz), 131.6 (d, J = 10.4 Hz), 132.5 (d, J = 10.1 Hz), 132.5 (d, J = 10.4 Hz), 138.2. ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ +71.1 (br.s), +125.5 (br.s). HRMS (ESI/Q-TOF) calcd for $C_{32}H_{43}B_2NOP_2Na$ $[M+Na]^+$: 564.28982; found: 664.28944. Anal. calcd for $C_{32}H_{43}B_2NOP_2$: C 71.01, H 8.01, N 2.59; found: C 70.92, H 8.39, N 2.65.

4.7.13. (S_p)-(-)-N-[(1R,2S), 2-(Phenyl-o-biphenylphosphinito-borane)-1-methyl-2-phenylethyl], N-methylamino-diphenylphosphine-borane **21i**. This compound was synthesized from *(S_p)-(+)-N-[(1R,2S)-2-hydroxy-1-methyl-2-phenylethyl], N-methylamino(phenyl-o-biphenyl)phosphine-borane* **11i** previously prepared from (+)-

ephedrine **9**. White solid; (0.37 g, 58% yield); R_f = 0.58 (petroleum ether/dichloromethane 1:1); Mp = 200-202 °C. $[\alpha]_D^{20}$ = -67.7 (c 0.4, $CHCl_3$). ^1H NMR: (500 MHz, CD_2Cl_2): δ 0.47-1.47 m, 6H), 1.25 (d, J = 6.6 Hz, 3H), 2.32 (d, J = 7.7 Hz, 3H), 4.57-4.65 (m, 1H), 5.52 (t, J = 8.9 Hz, 1H), 6.69-6.73 (m, 2H), 6.77-6.79 (m, 2H), 7.05-7.08 (m, 3H), 7.15-7.38 (m, 21H), 7.84 (ddd, J = 13.5, 7.8, 1.0 Hz, 1H). $^{13}C\{^1H\}$ NMR (125.8 MHz, CD_2Cl_2): δ 16.0, 29.3 (d, J = 4.5 Hz), 57.2 (dd, J = 11.4, 8.6 Hz), 83.5 (dd, J = 8.9, 2.5 Hz), 126.4 (d, J = 11.7 Hz), 127.0 (2s,), 127.9 (d, J = 10.9 Hz), 128.1 (d, J = 10.9 Hz,), 128.2, 128.4 (d, J = 10.1 Hz), 128.7, 129.2, 129.5, 129.6, 130.2 (d, J = 10.9 Hz), 130.3 (d, J = 48.4 Hz), 130.4 (d, J = 2.3 Hz), 130.6 (d, J = 2.3 Hz), 130.9 (d, J = 23.4 Hz), 131.1 (d, J = 1.6 Hz), 131.4 (d, J = 10.2 Hz), 131.4, 131.7 (d, J = 10.9 Hz), 132.5 (d, J = 10.2 Hz), 133.2 (d, J = 71.8 Hz), 133.9 (d, J = 17.2 Hz), 138.0, 140.2 (d, J = 2.5 Hz, 146.1 (d, J = 6.4 Hz). $^{31}P\{^1H\}$ NMR: (202.5 MHz, CD_2Cl_2): δ +71.2 (br.s), +107.7 (br.s). HRMS (ESI/Q-TOF) calcd for $C_{40}H_{44}B_2NOP_2$ $[M+H]^+$: 638.3092; found: 638.3091.

4.8. Typical procedure for the decomplexation of aminophosphine-phosphinite-diborane

21. A solution of aminophosphine-phosphinite-diborane **21** (1 mmol) and DABCO (4 mmol) in toluene (3 mL) was heated at 50°C with an oil bath and was stirred under argon overnight. After removing the solvent under vacuum, the residue was purified by

chromatography on neutral aluminium-oxide using a mixture of petroleum ether/ethyl acetate (4:1) or toluene as eluent, to afford the free AMPP* **20**.

4.8.1. (R_p)-N-[(1R,2S)-2-(o-Anisylphenylphosphinito)-1-methyl-2-phenylethyl], N-methylamino diphenylphosphine **20a**. 0.49 g, 87% yield; White sticky solid; R_f = 0.70 (petroleum ether/ethyl acetate 4:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.34 (d, J = 6.6 Hz, 3H), 2.13 (d, J = 3.0 Hz, 3H), 3.61 (s, 3H), 3.89-3.95 (m, 1H), 4.78 (t, J = 8.7 Hz, 1H), 6.56-6.59 (m, 2H), 6.72 (dd, J = 8.2, 4.6 Hz, 1H), 6.95-7.11 (m, 13H), 7.19-7.25 (m, 7H), 7.53 (ddd, J = 7.3, 4.2, 1.6 Hz, 1H). ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$): δ +64.9, +101.3.

4.8.2. (S_p)-N-[(1S,2R)-2-(o-Anisylphenylphosphinito)-1-methyl-2-phenylethyl], N-methylamino diphenylphosphine **20a**. 0.48 g, 85% yield; White sticky solid; R_f = 0.74 (petroleum ether/ethyl acetate 4:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.19 (d, J = 6.5 Hz, 3H), 2.10 (d, J = 3.1 Hz, 3H), 3.47 (s, 3H), 3.85-3.95 (m, 1H), 4.70 (t, J = 9.1 Hz, 1H), 6.57-6.60 (m, 2H), 6.77-6.80 (m, 1H), 6.99-7.20 (m, 13H), 7.23-7.32 (m, 7H), 7.43-7.52 (m, 1H). ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$): δ +65.2, +102.0.

4.8.3. (R_p)-N-[(1R,2S)-2-(α-Naphtylphenylphosphinito)-1-methyl-2-phenylethyl], N-methyl aminodiphenylphosphine **20b**. 0.53 g, 91% yield; White sticky solid; R_f = 0.70 (toluene). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.22 (d, J = 6.6 Hz, 3H), 2.10 (d, J = 3.0 Hz, 3H), 3.91-3.96 (m, 1H), 4.80 (t, J = 8.9 Hz, 1H), 6.56-6.59 (m, 2H), 6.97-7.21 (m, 16H), 7.30-

7.32 (m, 3H), 7.34-7.36 (m, 1H), 7.44-7.48 (m, 1H), 7.78 (dd, J = 17.5, 8.1 Hz, 2H), 7.92 (td, J = 7.2, 1.1 Hz, 1H), 8.18 (dd, J = 2.1, 8.4 Hz, 1H). $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$): δ +64.7, +107.4.

4.8.4. (S_p)-N-[(1S,2R)-2-(α-Naphtylphenylphosphinito)-1-methyl-2-phenylethyl], N-methyl aminodiphenylphosphine **20b**. $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$): δ +64.3, +108.4.

4.8.5. (R_p)-N-[(1R,2S)-2-(β-Naphtylphenylphosphinito)-1-methyl-2-phenylethyl], N-methyl aminodiphenylphosphine **20c**. 0.52 g, 89% yield; White sticky solid; R_f = 0.60 (toluene). ^1H NMR (500 MHz, $CDCl_3$): 1.28 (d, J = 6.6 Hz, 3H), 2.12 (d, J = 3.1 Hz, 3H), 3.89-3.99 (m, 1H), 4.76 (t, J = 8.9 Hz, 1H), 6.57-6.60 (m, 2H,), 6.95-6.99 (m, 2H), 7.05-7.20 (m, 13H), 7.29-7.32 (m, 2H), 7.42-7.44 (m, 3H), 7.70-7.80 (m, 4H), 8.06 (d, J = 9.9 Hz, 1H). $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$): δ +64.8, +110.5.

4.8.6. (R_p)-N-[(1R,2S)-2-(Phenyl-o-tolylphosphinito)-1-methyl-2-phenylethyl], N-methylamino diphenylphosphine **20d**. 0.51 g, 90% yield; White sticky solid; R_f = 0.65 (toluene). ^1H NMR (500 MHz, $CDCl_3$): δ 1.31 (d, J = 6.6 Hz, 3H), 2.13 (d, J = 3.1 Hz, 3H), 2.16 (s, 3H), 3.82-3.98 (m, 1H), 4.74 (t, J = 8.6 Hz, 1H), 6.57-6.60 (m, 2H), 6.98-7.21 (m, 21H), 7.71-7.73 (m, 1H). $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$): δ +64.7, +104.7.

4.8.7. (R_p)-N-[(1R,2S)-2-(Phenyl-p-tolylphosphinito)-1-methyl-2-phenylethyl], N-methylamino diphenylphosphine **20e**. $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$): δ +64.5, + 112.5.

4.8.8. (R_p)-N-[(1R,2S)-2-(Phenyl-o-biphenylphosphinito)-1-methyl-2-phenylethyl], N-methyl amino-diphenylphosphine **20f**. 0.66 g, 94% yield; White sticky solid; R_f = 0.75 (petroleum ether/ ethyl acetate 4:1). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.35 (d, J = 6.3 Hz, 3H), 2.19 (d, J = 3.2 Hz, 3H), 3.90-4.00 (m, 1H), 4.68 (t, J = 8.7 Hz, 1H), 6.65-6.70 (m, 2H), 6.98-7.03 (m, 2H), 7.07-7.15 (m, 4H), 7.16-7.27 (m, 12H), 7.28-7.35 (m, 6H), 7.42-7.52 (m, 2H), 7.90-8.00 (m, 1H). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2): δ +64.9, + 101.9.

4.8.9. (R_p)-(+)-N-[(1R,2S)-2-Ferrocenylphenylphosphinito)-1-methyl-2-phenylethyl], N-methyl aminodiphenylphosphine **20g**. 0.56 g, 88% yield; Orange sticky solid; R_f = 0.60 (toluene). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.27 (d, J = 6.7 Hz, 3H), 2.13 (d, J = 3.2 Hz, 3H), 3.67 (m, 1H), 3.74-3.85 (m, 1H), 4.00 (s, 5H), 4.19 (m, 1H), 4.29 (m, 1H), 4.36 (m, 1H), 4.71 (t, J = 9.0 Hz, 1H), 6.63-6.68 (m, 2H), 7.01-7.20 (m, 16H), 7.40-7.45 (m, 2H). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ +64.7 (s), +105.5 (s).

4.8.10. (S_p)-(-)-N-[(1R,2S)-2-t-Butylphenylphosphinito)-1-methyl-2-phenylethyl], N-methylamino diphenylphosphine **20h**. ^{1}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2): δ +66.4, + 129.4.

4.8.11. (S_p)-N-[(1R,2S)-2-(Phenyl-o-biphenylphosphinito)-1-methyl-2-phenylethyl], N-methyl aminodiphenylphosphine **20i**. 0.54 g, 88% yield; White sticky solid; R_f = 0.74 (petroleum ether/ethyl acetate 4:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.15 (d, J = 6.8 Hz, 3H), 2.05 (d, J = 4.0 Hz, 3H), 3.81-3.90 (m, 1H), 4.63 (t, J = 8.1 Hz, 1H), 6.52-6.57 (m, 2H),

6.81-6.85 (m, 2H), 6.96-7.21 (m, 24H), 7.58-7.62 (m, 1H). $^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$): δ +65.1, + 104.8.

4.9. Preparation of dichloropalladium-AMPP* complexes 30-32.

4.9.1. General procedure: In a Schlenck tube, under an argon atmosphere, 26.8 mg (0.104 mmol) of $Pd(CH_3CN)_2Cl_2$ and 2 mL of anhydrous dichloromethane were introduced. A solution of 0.104 mmol (1 equivalent) of decomplexed AMPP (R_p)-**13f**, (R_p)-**13g** or (R_p)-**20b** in 3 mL of dry dichloromethane was added. The mixture was then stirred at room temperature for 15 min. The solvents were evaporated under vaccuo and the crude solid was recrystallized using a mixture of CH_2Cl_2/toluene or toluene/hexane.

4.9.2. N-[(1R,2S)-(2-(Diphenylphosphinito)-1-methyl-2-phenylethyl], N-methylamino(o-biphenyl) phenylphosphine dichloropalladium complex **30**. Recrystallization in mixture of CH_2Cl_2/toluene; Colorless crystals; X-ray quality crystals were grown by slow evaporation of CH_2Cl_2. The structure and the data were reported in the SI. $[\alpha]_D^{20}$ = +214 (c 0.2, $CHCl_3$); Mp = 288 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.00 (d, J = 8.0 Hz, 3H), 1.92 (d, J = 7.2 Hz, 3H), 3.93 (br.s, 1H), 4.23-4.24 (m, 1H), 6.85 (dd, J = 14.2 Hz, 7.9 Hz, 1H), 6.96-6.98 (m, 2H), 7.15-7.35 (m, 8H), 7.46-7.73 (m, 14H), 7.92-7.96 (m, 2H), 8.14-8.56 (br.s, 2H). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, CD_2Cl_2): δ 12.8 (d, J = 6.0 Hz), 33.9 (d, J = 4.4 Hz), 59.0 (t, J = 9.9 Hz), 82.2 (d, J = 4.5 Hz), 126.4 (d, J = 11.2 Hz), 127.2, 127.7, 127.9 (d, J = 11.9 Hz),

128.2 (d, *J* = 9.8 Hz), 128.5, 128.6, 128.7, 129.6, 129.8 (d, *J* = 53.8 Hz), 130.7, 131.1 (d, *J* = 2.1 Hz), 131.6 (d, *J* = 45.4 Hz), 131.6 (d, *J* = 2.8 Hz), 131.7 (d, *J* = 2.1 Hz), 132.2 (d, *J* = 11.2 Hz), 133.0 (d, *J* = 2.1 Hz), 133.1 (d, *J* = 9.1 Hz), 134.4 (d, *J* = 10.2 Hz), 134.6 (d, *J* = 57.8 Hz), 134.9 (d, *J* = 12.7 Hz), 135.1, 142.8 (d, *J* = 9.3 Hz), 143.9 (d, *J* = 8.3 Hz). $^{31}P\{^{1}H\}$ NMR (161.9 MHz, CD_2Cl_2): δ +95.6 (d, *J* = 42.0 Hz), +106.2 (d, *J* = 42.0 Hz). FTIR (neat): ν_{max} 3054, 2991, 2891, 2835, 1480, 1463, 1444, 1434, 1382, 1376, 1230, 1207, 1182, 1158, 1134, 1101, 1084, 1072, 1029, 1018, 996, 944, 921, 896, 841, 833, 743, 732, 712, 689, 677, 653. Anal. calcd for $C_{40}H_{37}NOP_2Cl_2Pd$, H_2O: C 59.70, H 4.88, N 1.74; found: C 59.83, H 4.82, N 2.22.

4.9.3. (R_p)-N-[(1R,2S)-(2-(Diphenylphosphinito)-1-methyl-2-phenylethyl], N-methylamino ferrocenylphenylphosphine dichloropalladium complex **31**. Recrystallization in a mixture of toluene/hexane; orange crystals; X-ray quality crystals were grown by slow evaporation of CH_2Cl_2. The structure and the data were reported in the SI. $[\alpha]_D^{20}$ = -177 (c 0.5, $CHCl_3$); Mp = 250 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.81 (d, *J* = 6.8 Hz, 3H), 2.10 (d, *J* = 11.9 Hz, 3H), 3.85 (br.s, 1H), 4.03 (s, 5H), 4.53 (s, 1H), 4.70 (s, 2H), 5.40-5.51 (m, 2H), 6.56-6.58 (m, 2H), 7.00-7.19 (m, 7H), 7.42-7.63 (m, 7H), 8.27-8.33 (m, 4H). $^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$): δ 13.7 (d, *J* = 4.3 Hz), 29.6, 33.7 (d, *J* = 4.9 Hz), 53.4, 56.8, 71.2 (d, *J* = 11.8 Hz), 71.5, 72.4 (d, *J* = 67 Hz), 72.8 (d, *J* = 3.4 Hz), 79.3-79.4 (m), 79.7, 125.2, 127.5, 127.6,

127.7 (d, J = 4.8 Hz), 127.9, 128.5 (d, J = 11.6 Hz), 128.6 (d, J = 60.9 Hz), 131.4-131.5 (m), 132.0 (d, J = 2.8 Hz), 132.0 (d, J = 65.0 Hz), 132.9, 133.0, 133.2, 133.8, 134.5 (d, J = 54.4 Hz), 134.6 (d, J = 12.9 Hz), 134.8, 136.1 (d, J = 2.6 Hz). $^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$): δ +132.0 (d, J = 33.8 Hz), +87.4 (d, J = 33.8 Hz). FTIR (neat): ν_{max} 2963, 1481, 1258, 1081, 1012, 791, 688.

4.9.4. (R_p)-N-[(1R,2S)-2-(α-Naphtylphenylphosphinito)-1-methyl-2-phenylethyl], N-methylamino diphenylphosphine dichloropalladium complex **32**. X-ray quality crystals were grown by slow evaporation of CH_2Cl_2. The structure and the data were reported in the SI; Slighty yellow crystals. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.71 (d, J = 7.1 Hz, 3H), 1.78 (d, J = 9.7 Hz, 3H), 4.83-4.95 (m, 2H), 7.20-7.33 (m, 7H), 7.36-7.53 (m, 10H), 7.55-7.59 (m, 1H), 7.72-7.83 (m, 4H), 7.85-7.90 (m, 1H), 8.06-8.17 (m, 4H). $^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$): δ 14.0 (d, J = 2.8 Hz), 33.4 (d, J = 5.8 Hz), 56.3 (t, J = 8.3 Hz), 83.7 (t, J = 4.7 Hz), 124.2 (d, J = 14.4 Hz), 126.2, 126.7, 126.8, 127.0 (d, J = 8.4 Hz), 128.1, 128.2, 128.6 (d, J = 10.0 Hz), 128.6, 128.7 (d, J = 5.3 Hz), 129.1 (d, J = 75.5 Hz), 129.2, 130.0 (d, J = 56.1 Hz), 131.3 (d, J = 2.2 Hz), 131.6 (d, J = 2.5 Hz), 132.1 (d, J = 51.2 Hz), 132.6 (d, J = 9.1 Hz), 132.7 (d, J = 2.0 Hz), 132.9 (d, J = 2.6 Hz), 133.0 (d, J = 11.7 Hz), 133.3 (d, J = 10.4 Hz), 133.9 (d, J = 8.7 Hz), 134.9 (d, J = 12.8 Hz), 135.4 (d, J = 12.8 Hz), 135.4 (d, J = 12.8

Hz), 135.7 (d, J = 7.0 Hz). $^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$): δ +96.8 (d, J = 47.3 Hz), +116.3 (d, J = 47.3 Hz).

4.10. Allylic alkylation of (±)-1,3-diphenylpropenyl acetate 24 with dimethylmalonate or benzylamine.

4.10.1. General procedure: In a flask under argon atmosphere was introduced AMPP* ligand (0.02 or 0.04 mmol), $[Pd(C_3H_5)Cl]_2$ (0.01 or 0.02 mmol) and allylic acetate (1 mmol) in dry dichloromethane (3 mL). After stirring the solution for one hour at room temperature, dimethylmalonate or benzylamine (2 mmol) was added, followed by *N*,*O*-bis(trimethylsilyl)acetamide (2 mmol) and potassium acetate (10 mg) or TBAF (2 mmol), respectively. After complete reaction, the mixture was successively diluted with Et_2O (5 mL), washed with saturated NH_4Cl solution and extracted with Et_2O. The combinated organic layers were dried over $MgSO_4$ and filtered. The solvent was removed under vacuum to afford a residue which was purified by chromatography on silica gel using a mixture of petroleum ether/ethyl acetate (5:1) as eluent, to afford the allylated products **25** or **29** as colorless oils.

4.10.2. Procedure for oxidizable ligands: In the case of oxidizable ligand such as AMPP* **13j** (R^1 = Me), the purification after decomplexation of the ligand by short filtration on neutral alumina led to impure compound. The palladium catalyst was prepared according

to a one pot procedure. First, the AMPP*$(BH_3)_2$ and DABCO (4 equiv.) were heated at 50°C in toluene with an oil bath for 12 h. After removing the solvent under vacuum, the crude AMPP* ligand was then mixed with $[Pd(C_3H_5)Cl]_2$ in dichloromethane at room temperature for 20 min and the complex was used without further purification.

4.10.3. Dimethyl (1,3-diphenylallyl)malonate **28**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.44 (s, 3H), 3.63), 3.88 (d, J = 10.9 Hz, 1H), 4.19 (dd, J = 10.9, 8.5 Hz, 1H), 6.25 (dd, J = 15.8, 8.5 Hz, 1H), 6.41 (d, J = 15.8 Hz, 1H), 7.09-7.28 (m, 10H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 49.2, 52.5, 52.7, 57.7, 126.4, 127.2, 127.6, 127.9, 128.5, 128.7, 129.1, 131.9, 136.8, 140.2, 167.8, 168.2. The enantiomeric excess was determined by HPLC analysis on Chiralpack IA, 1.00 mL/min, hexane/isopropanol (9:1), t(*R*)= 8.5 min, t(*S*)= 10.4 min. The absolute configuration could also be determinated by comparison of the optical rotation to literature value: $[\alpha]_D^{25}$ = -22.4 (c 1.8, $CHCl_3$) for (*S*)-enantiomer.[35]

4.10.4. N-(1,3-Diphenylallyl),N-benzylamine **29**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.79-3.87 (m, 2H), 4.45 (d, J = 7.5 Hz, 1H), 6.38 (dd, J = 15.8, 7.5 Hz, 1H), 6.61 (d, J = 15.8 Hz, 1H), 7.21-7.26 (m, 1H), 7.28-7.34 (m, 4H), 7.36-7.42 (m, 8H), 7.44-7.51 (m, 2H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 51.4, 64.6, 126.4, 127.0, 127.3, 127.4, 127.5, 128.2, 128.5, 128.5, 128.7, 130.4, 132.7, 137.0, 140.5, 142.9. The enantiomeric excess was determined by

HPLC analysis on Lux 5μm cellulose-1, 0.5 mL/min, hexane/isopropanol (98:2), t(*R*)= 20.9 min, t(*S*) = 22.2 min.

ASSOCIATED CONTENT

Supporting Information

^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$ NMR spectra, X-ray structures with crystallographic data, HPLC chromatograms on chiral column, catalysis complementary results and computational calculations are reported in part A, B and C, respectively. This material is available free of charge via the internet at http://pubs.acs.org.

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