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P-Chirogenic Phosphines Supported by Calix[4]arene: New Insight into Palladium-Catalyzed Asymmetric Allylic Substitution

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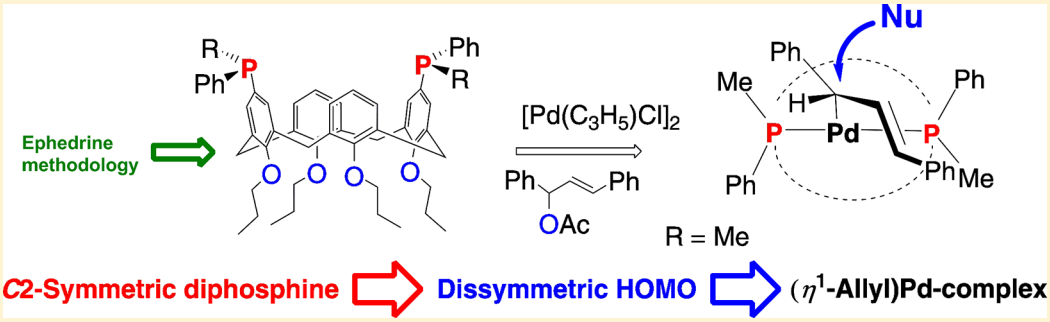
Supporting Information



ABSTRACT: The first P-chirogenic mono- and diphosphine ligands supported on the upper rim of a calix[4]arene moiety were synthesized using the ephedrine methodology. The lithiated calix[4]arene mono- and dianions both react with the oxazaphospholidine−borane, prepared from ephedrine, to afford regio- and stereoselectively the corresponding calix[4]arenyl aminophosphine−boranes, by cleavage of the heterocyclic ring at the P−O bond position. Subsequent reactions with HCl and then organolithium reagent and finally decomplexation with DABCO lead to the corresponding calix[4]arenyl mono- or diphosphines. Both enantiomers of the calix[4]arenyl phosphines were obtained either by using (+)- or (−)-ephedrine or by changing the addition order of the organolithium reagents during the synthesis. The enantiomeric excesses of the phosphines were determined either by HPLC on a chiral column of their borane complexes or by ^{31}P NMR in the presence of a chiral palladium complex. The absolute configurations of the mono- and diphosphinocalix[4]arenes were assigned by X-ray analysis of their crystalline borane complexes. The P-chirogenic calix[4]arenyl phosphines were tested for asymmetric palladium-catalyzed allylic substitution of (*E*)-1,3-diphenylprop-2-en-1-yl acetate, by dimethyl malonate or benzylamine. When the bis-methylphenylphosphino calix[4]arene was used, the allylic products were obtained with 82% and 79% ee, respectively. In both cases, the use of a diphosphine affords better results than using 2 equivalents of monophosphine. Despite the C_2 symmetry of the P-chirogenic diphosphine calix[4]arene ligand, computer modeling of the corresponding Pd(allyl) complex shows a clear dissymmetry of the LUMO, which is in good agreement with a complexed η^1-allyl moiety and with the regio- and enantioselectivity of the Pd-catalyzed allylations.

INTRODUCTION

Chiral phosphorus ligands play a central role in transition-metal-catalyzed asymmetric reactions, and these processes are now commonly used for the enantioselective synthesis of chiral substances, including those that are industrially commercialized.[1,2] Recently, among the numerous types of reported chiral ligands described, phosphines bearing the chirality on the P center (P-chirogenic) have received a growing interest, due to the development of efficient methods for their stereoselective synthesis.[3] The interest in these ligands is due to the P-chirality that is positioned in close proximity to the reaction center, which favors a more sterically and electronically defined architecture about the metal atom.[4,5] So far, many P-chirogenic ligands allow high enantioselectivities in catalyzed asymmetric reactions with various C−Y (Y = H, C, N, B) bond formation.[6−8]

Over the past decades, calix[4]arene-containing phosphine ligands have led to an extremely rich coordination chemistry and have been extensively studied in transition-metal catalysis.[9,10] The use of a phosphorus ligand containing a calix[4]arene moiety in catalysis has been more recently recognized for its potential applications and has already been evaluated in olefin hydroformylation,[11] oligomerization and polymerization reactions,[12] hydrogenation,[13] carbon−carbon bond forming reactions,[14] and allylic alkylation.[15] So far, many

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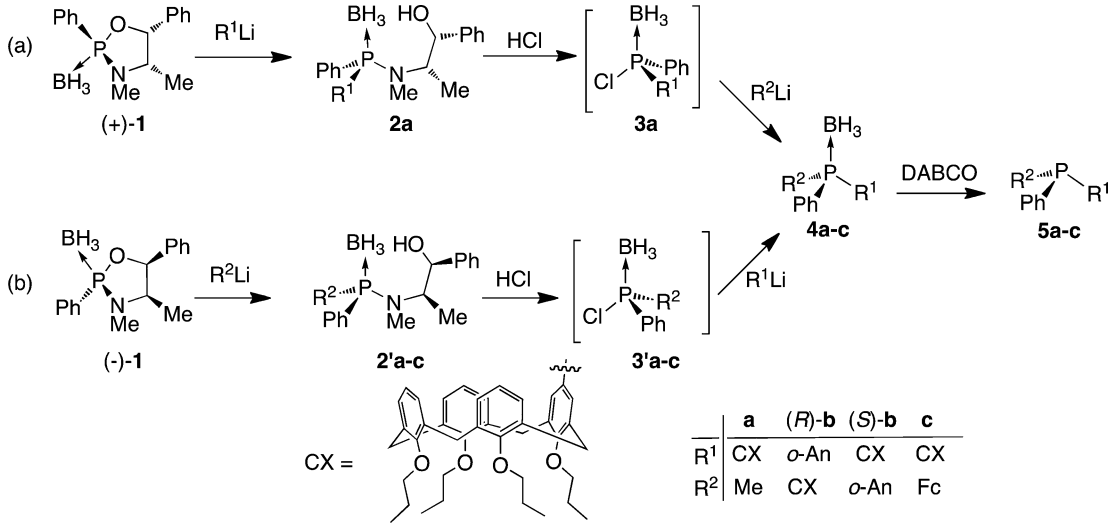
Scheme 1. Synthesis of the P-Chirogenic Calix[4]arenyl Monophosphines 5



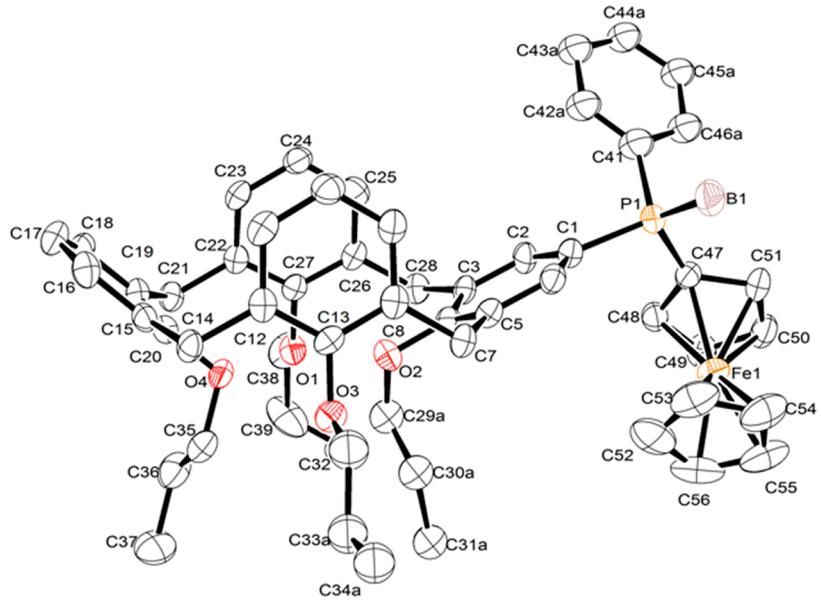


Figure 1. ORTEP[19] view of the P-chirogenic monophosphine borane (*S*)-**4c**. Thermal ellipsoids are shown at the 50% probability level. The hydrogen and disordered atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): P1−B1 = 1.909(7), P1−C1 = 1.803(5), P1−C41 = 1.827(6), P1−C47 = 1.806(6); C1−P1−C47 = 105.3(2), C1−P1−C41 = 104.9(3), C47−P1−C41 = 105.0(3), C1−P1−B1 = 114.9(3), C47−P1−B1 = 115.2(3), C41−P1−B1 = 110.5(3).

chiral organophosphorus ligands derived from calix[4]arene are known,[9−15] but only few asymmetric catalysis have been described.[13] Recently, we reported the first synthesis of a P-chirogenic AMP*P ligand with a calix[4]arenyl substituent on the aminophosphine moiety and its uses in rhodium-catalyzed asymmetric hydrogenation reactions.[16a] The preparation of chiral calix[4]arene-based phosphorus ligands is of continuing interest, and we report the first stereoselective synthesis of P-chirogenic mono- and diphosphines supported on the upper rim of a calix[4]arene moiety and their use as ligands in palladium-catalyzed asymmetric allylic substitution.

RESULTS AND DISCUSSION

The P-chirogenic calix[4]arenyl monophosphines **5a−c** have been synthesized according to the methodology starting from the (+)- or (−)-oxazaphospholidine borane complex **1**, prepared respectively from (−)- or (+)-ephedrine (Scheme 1).[17]

The reaction of the complex (+)-**1** with (25,26,27,28-tetrapropoxycalix[4]aren-5-yl)lithium[16b] as the R^1Li reagent stereospecifically affords the aminophosphine−borane **2a** (R^1 = CX) in 84% yield, by P−O bond cleavage and retention at the P center (Scheme 1a). Evidence for the stereochemistry of the ring-opening reaction has been provided by an X-ray structure determination of the previously described P-chirogenic calix[4]-arenyl aminophosphine−phosphinite (AMPP*) ligand, derived from **2a**.[16] After acidolysis of the aminophosphine−borane **2a** with dry HCl, the resulting chlorophosphine−borane **3a** reacted with organolithium reagents to provide the corresponding P-chirogenic monophosphine−boranes (*S*)-**4a−c** with yields ranging from 46 to 62% (Scheme 1a). The enantiomeric excesses of the phosphine−boranes **4a−c** were determined by HPLC on a chiral column, with 99% and 84% ee, respectively.

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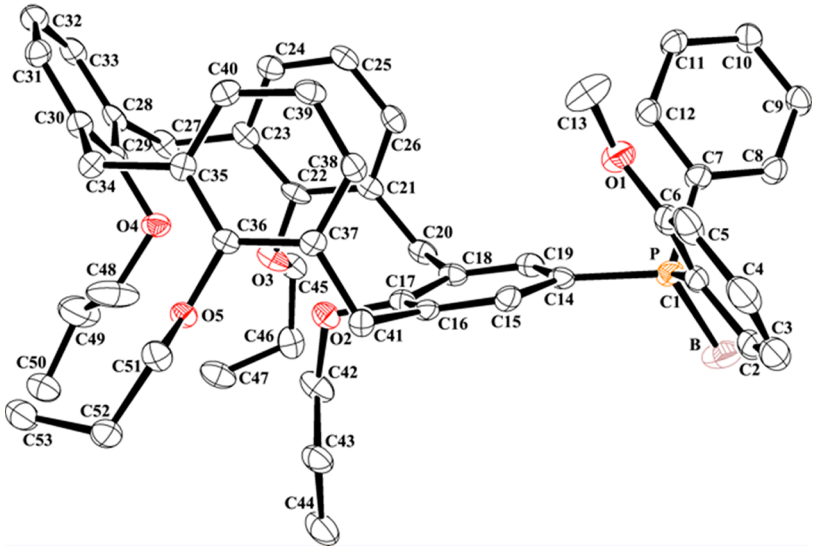
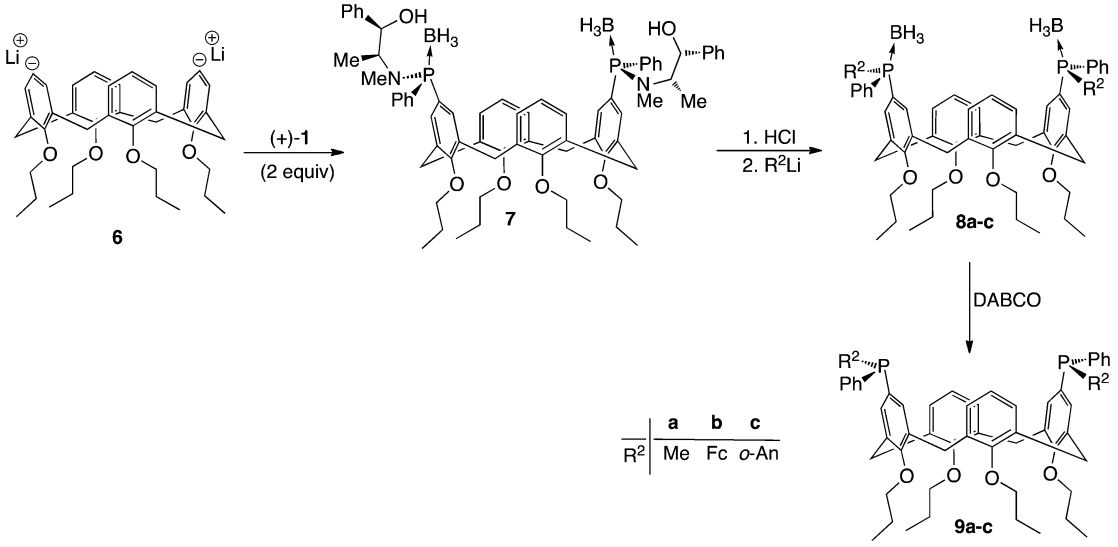


Figure 2. ORTEP[19] view of the P-chirogenic phosphine−borane (*R*)-**4b**. Thermal ellipsoids are shown at the 30% probability level. The hydrogen and disordered atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): C1−P1 = 1.808(3), C7−P1 = 1.820(3), C14−P1 = 1.812(3), P1−B1 = 1.893(4); C1−P1−C14 = 107.95(14), C1−P1−C7 = 108.84 (15), C14−P1−C7 = 106.12(14), C1−P1−B1 = 109.5(2), C14−P1−B1 = 113.0(2), C7−P1−B1 = 111.23(17).

Scheme 2. Synthesis of the P-Chirogenic Calix[4]arene Diphosphines 9a−c



However, an analytically pure sample of the P-chirogenic calix[4]arenyl phosphine−borane (*S*)-**4c** has been obtained as single crystals by slow diffusion of methanol into dichloromethane, and its structure was established by X-ray analysis (Figure 1). The crystallographic unit cell of the crystal contains two independent molecules with similar conformations. Thus, the X-ray structure of **4c** shows the calix[4]arene moiety with a flattened cone conformation, due to the presence of the propoxy groups in the lower rim, and the ferrocenyl substituent outside of the cavity. In addition, the structure proves the absolute configuration (*S*) of the phosphorus atom, which is in good agreement with the stereochemistry with inversion of configuration previously established for the acidolysis with HCl of aminophosphine−borane derivatives and for the stereoselective synthesis of P-chirogenic phosphine−boranes.[17,18]

It is worth noting that the synthesis of the phosphine−borane enantiomers **4** can also be achieved from the starting complex (−)-**1**, derived from (+)-ephedrine, by inverting the introduction order of the lithium reagents during the synthesis (Scheme 1b). Thus, subsequent reactions of the (−)-oxazaphospholidine−borane complex **1** with the *o*-anisyllithium reagent, acidolysis with HCl, and then trapping of the resulting chlorophosphine **3′b** (R^2 = *o*-An) with (calix[4]arenyl)lithium (R^1= CX) affords the phosphine−borane (*R*)-**4b** in 60% yield and with 99% ee (Scheme 1b). The enantiomeric phosphine−borane (*R*)-**4b** was thus obtained using this second strategy, but starting from the complex (+)-**1**, derived from (−)-ephedrine (Scheme 1a). A single crystal of (*R*)-**4b** has been obtained, and its structure was established by X-ray analysis.

This structure exhibits a flattened cone conformation for the calix[4]arene ring, notably due to the presence of the phosphine−borane moiety on the upper ring, and the *R* absolute configuration is established for the P center (Figure 2).

Finally, the decomplexation of phosphine−boranes **4a−c** was achieved with retention of configuration on the phosphorus atom, upon heating with the 1,4-diazabicyclo[2.2.2]octane

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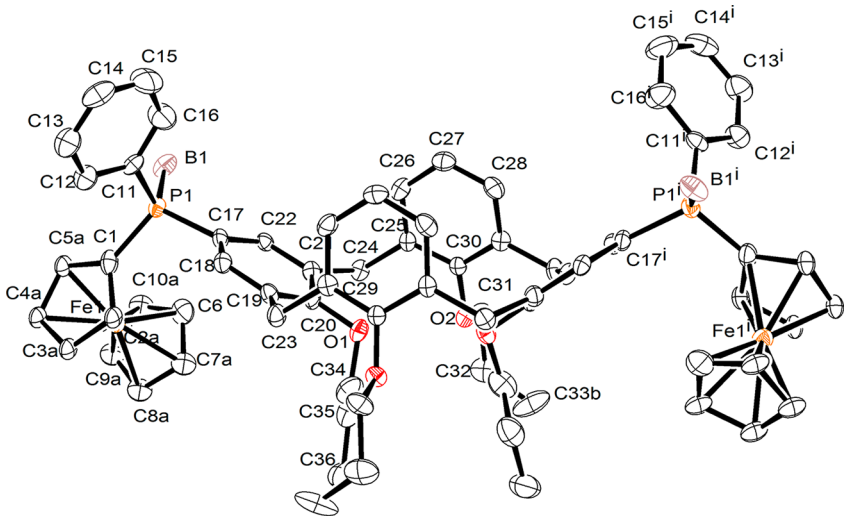
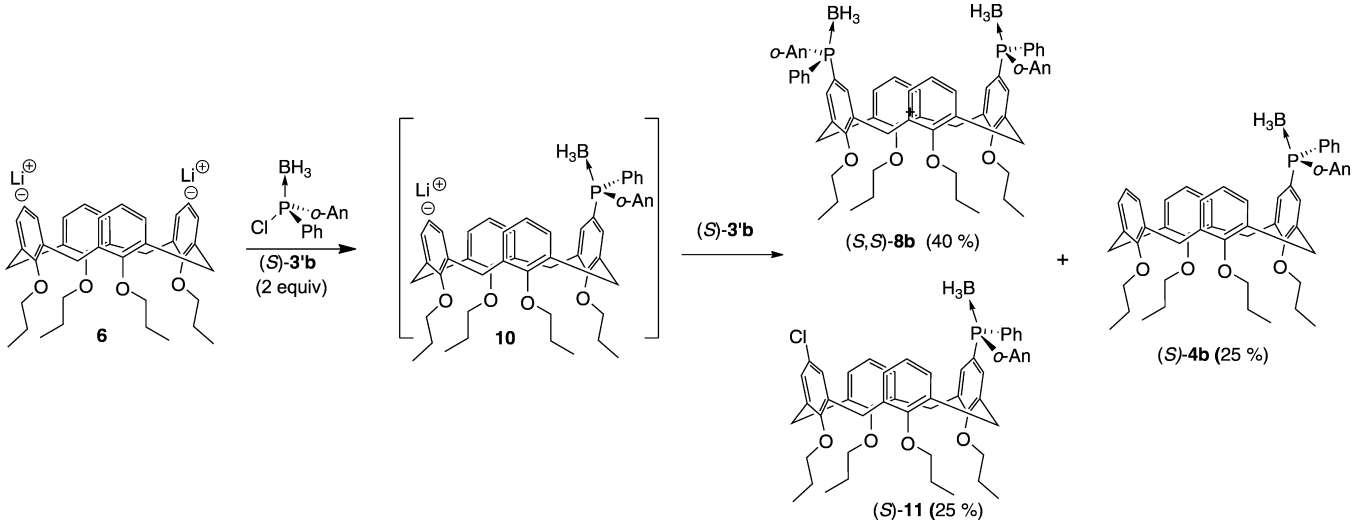


Figure 3. ORTEP[19] representation of P-chirogenic diphosphine−diborane (*S,S*)-**8c**. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): P1−B1 = 1.914(5), C11−P1 = 1.831(4), C1−P1 = 1.799(5), C17−P1 = 1.818(4); C1−P1−C17 = 104.9(2), C17−P1−C11 = 103.8(2), C1−P1−B1 = 114.9(2), C17−P1−B1 = 115.2(2), C11−P1−B1 = 111.0(2).

Scheme 3. Synthesis of the P-Chirogenic Calix[4]arene Diphosphine (*S,S*)-8b from the Chlorophosphine−Borane (*S*)-3′b



(DABCO) in toluene at 50 °C. After a short filtration on neutral alumina free uncoordinated P-chirogenic monophosphines **5a−c** were obtained in yields >97% (Scheme 1).

Concurrently, the synthesis of P-chirogenic diphosphines **9a−c** supported on the upper rim of a calix[4]arene moiety was achieved according to a similar methodology as described above for the monophosphines **5**, but using the calix[4]arene dilithium reagent **6** (Scheme 2).

Thus, the reaction of the (25,26,27,28-tetrapropoxycalix[4]-arene)dilithium reagent **6** with 2 equiv of the starting complex (+)-**1** leads to the bis(aminophosphine)−borane product **7** in 73% yield, from ring opening of the heterocycle at the P−O bond. After acidolysis of compound **7** with dry HCl in toluene, the resulting bis(chlorophosphine)−borane intermediate reacts with 2 equivalents of organolithium reagents to afford the corresponding P-chirogenic diphosphine diboranes **8a−c** in 43−46% isolated yields. Crystals of diphosphine−diborane **8c** suitable for X-ray structure analysis have been obtained from methanol, and the X-ray structure is depicted in Figure 3. Compound **8c** crystallizes with two half molecules in its unit cell, showing a clear C_2 symmetry. Thus, the diphosphine−diborane **8c** crystallizes in the noncentrosymmetric C_2 space group, establishing the *S,S* absolute configuration for the P center, supported by refinement of the Flack parameter.[20]

The P-chirogenic diphosphine−diborane **8b** was also synthesized according to a second strategy, which consists of reacting 2 equiv of the chlorophosphine−borane (*S*)-**3′b** (R^2 = *o*-An), previously prepared from (−)-**1**, with the (25,26,27,28-tetrapropoxycalix[4]arene)dilithium reagent **6** (Schemes 2 and 3). However, in this case the diphosphine−diborane **8b** was obtained with a lower yield with respect to the former synthetic route (40%). This is, in fact, due to the formation of byproducts such as the monophosphine−borane (*S*)-**4b** (25%) and the 17-chlorocalix[4]arene phosphine−borane (*S*)-**11** (25%) (Scheme 3). The formation of these compounds is explained either by the protonation of the unreacted monanion **10** derived from the monophosphine−borane or by metal−halogen exchange with the chlorophosphine−borane **3′b** (Scheme 3). We previously described the reaction of a bulky organolithium reagent with the chlorophosphine−borane **3′b**, to prepare the

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corresponding P-chirogenic phosphide−borane lithium salt, by metal halide exchange.[3,17] The structure of the 17-chlorocalix[4]arene phosphine−borane (*S*)-**11** was confirmed by X-ray analysis, after extracting crystals issued from a recrystallization in a mixture of methanol and dichloromethane (Figure 4).

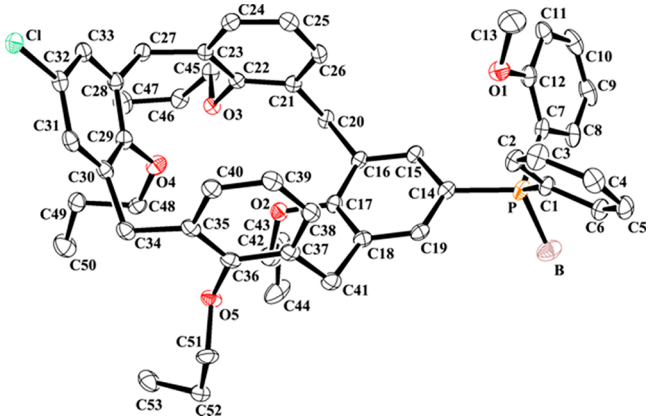
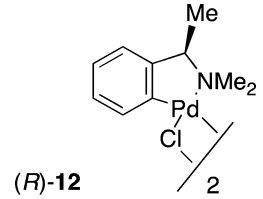


Figure 4. ORTEP[19] representation of the 17-chloro-5-*o*-anisylphenyl-{25,26,27,28-tetrapropoxy calix[4]arene}phosphine−borane (*S*)-**11**. Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths (Å) and angles (deg): C1−P = 1.819(2), C7−P = 1.812(3), C14−P = 1.818(3), P−B = 1.851(4); C7−P−C14 = 107.91(14), C7−P−C1 = 108.81(1), C14−P−C1 = 106.37(14), C7−P−B = 110.55(19), C14−P−B = 112.23(19), C1−P−B = 110.81(17).

Finally, the free P-chirogenic diphosphines **9a−c** were obtained in excellent yields after decomplexation of their borane complexes with DABCO in toluene at 50 °C, followed by filtration on neutral alumina. The enantiomeric excesses of the diphosphines **9a−c** were determined by ^{31}P NMR in the presence of the chiral palladium complex (*R*)-**12** (Figure 5).[21]



(*R*)-**12**

Figure 5. Structure of the chiral palladium NMR reagent used to check the enantiomeric purity of the calix[4]arene diphosphines **9a−c**.

All of these diphosphines were obtained with enantioselectivities superior to 98% ee, except in the case of the diphosphine **9c**, bearing a ferrocenyl substituent on the phosphorus center (87% ee).

The use of P-chirogenic mono- and diphosphines **5a−c** (and **9a−c**) as chiral ligands was evaluated in the palladium-catalyzed asymmetric allylic alkylation of dimethyl malonate and benzylamine by (*E*)-(±)-1,3-diphenylprop-2-en-1-yl acetate (**13**). The results are summarized in Tables 1 and 2, respectively.

In the first case, the alkylation of malonate was performed in the presence of an (allyl)palladium complex generated *in situ* from [Pd(η^3-C_3H_5)Cl]$_2$ (1 mol %) and monophosphine **5a** (4 mol %) or diphosphines **9a−c** (2 mol %) (Scheme 4). The nucleophile was generated from dimethyl malonate in the presence of a base (*N*,*O*-bis(trimethylsilyl)acetamide (BSA) or

Table 1. Results of Pd-Catalyzed Allylation of Dimethyl Malonate in the Presence of P-Chirogenic Mono- and Diphosphines 5a and 9a−c[a]

entry	ligand	base	solvent	conversn (%)[b]	ee (%)[c,d]
1	(*S*)-**5a**	BSA/KOAc	CH_2Cl_2	100	5
2	(*S*,*S*)-**9a**	BSA/KOAc	CH_2Cl_2	100	70
3	(*S*,*S*)-**9b**	BSA/KOAc	CH_2Cl_2	100	16
4[e]	(*S*,*S*)-**9c**	BSA/KOAc	CH_2Cl_2	100	40
5	(*S*,*S*)-**9a**	BSA/LiOAc	CH_2Cl_2	100	69
6	(*S*,*S*)-**9a**	BSA/NaOAc	CH_2Cl_2	100	69
7[f]	(*S*,*S*)-**9a**	BSA/KOAc	CH_2Cl_2	100	73
8[f]	(*S*,*S*)-**9a**	*n*-BuLi	THF	100	82

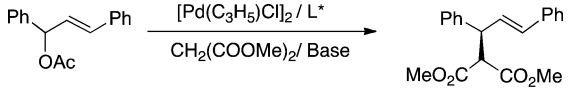
[a]Reaction conditions: 0.008 mmol of [Pd(η^3-C_3H_5)Cl]$_2$, 0.016 mmol of ligand **9a−c** (or 0.032 mmol **5a**), 0.8 mmol of (*E*)-(±)-1,3-diphenylprop-2-en-1-yl acetate (**13**), 1.6 mmol of dimethyl malonate, and 1.6 mmol of base (and a catalytic amount of acetate if necessary) in 6 mL of dry solvent. Reaction times: 1−20 h. [b]Conversion was determined by ^{1}H NMR of the crude mixture. [c]Determined by HPLC with a Chiralpak AD column. [d]*S* absolute configuration. [e]Ligand **9c** with 84% ee was used. [f]The reaction was performed at 0 °C.

Table 2. Results of Pd-Catalyzed Allylation of Benzylamine in the Presence of P-Chirogenic Mono- and Diphosphines 5a,b and 9a,b[a]

entry	ligand	conversn (%)[b]	ee (%)[c,d]
1	(*S*)-**5a**	100	24
2[e]	(*S*)-**5b**	100	76
3	(*S*)-**5b**	100	58
4	(*S*,*S*)-**9b**	100	0
5	(*S*,*S*)-**9a**	100	75
6[e]	(*S*,*S*)-**9a**	100	79

[a]Reaction conditions: 0.005 mmol of [Pd(η^3-C_3H_5)Cl]$_2$, 0.012 mmol of ligand **9a,b** or 0.024 mmol of ligand **5a,b**, 0.5 mmol of (*E*)-(±)-1,3-diphenylprop-2-en-1-yl acetate (**13**), and 1.45 mmol of benzylamine in 6 mL of dry CH_2Cl_2. Reaction times: 19−48 h. [b]Conversion was determined by ^{1}H NMR of the crude mixture. [c]Determined by HPLC with a Chiralcel OD-H column. [d]*R* absolute configuration. [e]Reaction performed at 0 °C.

Scheme 4. Pd-Catalyzed Allylation of Dimethyl Malonate in the Presence of P-Chirogenic Calix[4]arene Phosphines 5a and 9a−c



13 (*S*)-**14**

n-BuLi). With reaction times ranging from 1 to 20 h at room temperature or 0 °C, full conversions were obtained for all phosphine ligands. The chemoselectivity toward the malonate derivative **14** was excellent for all runs, and no isomerized *cis* product was observed in the crude reaction mixture. The use of the P-chirogenic mono- and diphosphines **5a** and **9b,c** and BSA/KOAc as base leads to the (*S*)-alkylated product **14** in dichloromethane with modest enantioselectivities: i.e., 5−40% ee (Table 1, entries 1, 3, and 4). Conversely, when the reaction was performed with the calix[4]arene diphosphine **9a** under the same conditions, higher asymmetric induction was obtained (70% ee; Table 1, entry 2). When the mixtures BSA/LiOAc and BSA/NaOAc were used for the base of the catalysis, the diphosphine **9a** afforded similar enantioselectivities (69% ee,

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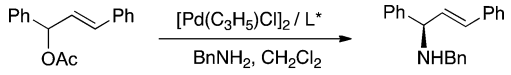
Table 1, entries 5 and 6). In the case where the reaction was carried out at 0 °C with BSA/KOAc as the base in dichloromethane, a slight increase of the ee value was observed (73% ee, Table 1, entry 7). Finally, the best result was obtained when the catalyzed reaction was performed in the presence of diphosphine **9a** as ligand, with *n*-BuLi as base in THF at 0 °C, leading to the (*S*)-alkylated malonate **14** with 82% ee (Table 1, entry 8).

In the case of the allylation of the benzylamine, the reaction was performed in the presence of an (allyl)palladium complex generated *in situ* from $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (1 mol %) and monophosphine **5a** (4.8 mol %) or diphosphines **9a**–**c** (2.4 mol %) (Scheme 5).

Scheme 5. Pd-Catalyzed Allylation of Benzylamine in the Presence of P-Chirogenic Mono- and Diphosphines 5a–c and 9a–c



13 (*R*)-**15**

All calix[4]arene mono- and diphosphine ligands carry out the allylation with excellent conversions to give products with the *R* configuration (Scheme 5; Table 2). As observed using dimethyl malonate, the chemoselectivity of the reaction was excellent and no isomerized *cis* product was formed during the reaction. Initial experiments were carried out using the P-chirogenic monophosphines **5a,b** with a 2.4/1 ligand/palladium ratio in dichloromethane. When the catalysis was achieved in the presence of the P-chirogenic monophosphine (*S*)-**5a**, the reaction required 48 h to be complete and the allylated amine (*R*)-**15** was obtained with 24% ee (Table 2, entry 1). In the presence of the monophosphine ligand (*S*)-**5b**, the asymmetric induction reaches 58% ee, but when the reaction temperature decreased to 0 °C, the enantiomeric excesses grow up to 76% ee (Table 2, entries 2 and 3). On the other hand, surprisingly, when the reaction was performed in dichloromethane in the presence of P-chirogenic diphosphines (*S,S*)-**9b**, the allylated amine **15** was unexpectedly obtained in racemic form (Table 2, entry 4). In contrast, the use of the calix[4]arene diphosphine (*S,S*)-**9a** under the same conditions afforded the product (*R*)-**15** with 75% ee (Table 2, entry 5). Finally, when catalysis with the diphosphine (*S,S*)-**9a** was carried out at 0 °C, the asymmetric induction reached 79% ee (Table 2, entry 6).

In order to provide an explanation for the enantioselectivity of the catalyzed allylation affording the products (*S*)-**14** and (*R*)-**15** from dimethyl malonate and benzylamine, respectively, computer modelings were examined in the case of the calix[4]arenediphosphine **9a**. This is exemplified in Figure 6, showing the HOMO and LUMO of the calix[4]arenyl-diphosphine (*S,S*)-**9a**/Pd(allyl) complex, for which an optimized geometry was computed.

Surprisingly, despite the C_2 symmetry of the calix[4]arene diphosphine ligand **9a**, the two molecular orbitals show a high-level dissymmetry of the complexed allyl moiety (Figure 6). The dissymmetry of the molecular orbitals is induced by the complexation of the diphenylpropenyl group in a W conformation and with an inclination with respect to the median plane crossing via the palladium and the two phosphorus atoms. As the Pd–C bonds with the allyl moiety are 2.156, 2.925, and 3.810 Å, respectively, the structure is

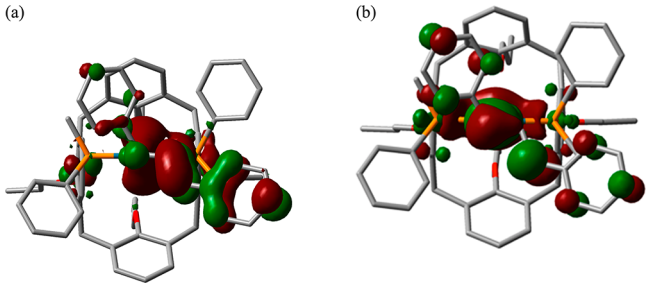
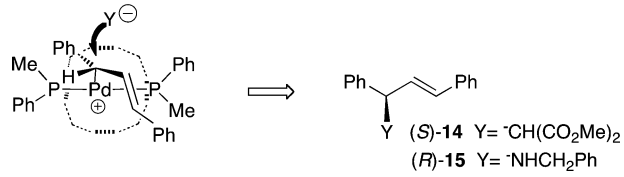


Figure 6. Drawings of the HOMO (a) and LUMO (b) of the calix[4]arenyl-diphosphine (*S,S*)-**9a**/Pd(allyl) complex.

finally in good agreement with a complexed η^1-allyl moiety to the Pd center. Although the η^3 bonding mode is expected, a few Pd complexes containing η^1-allyl ligands have been described in the literature and their stabilization was notably explained by the presence of a rigid ligand environment in the sphere of coordination.[22] Consequently, the nucleophilic attack occurs more favorably on the allylic carbon linked to the palladium, which shows a very large atomic contribution to the LUMO precisely at this carbon atom. This regioselectivity of the nucleophilic attack explains the formation of products **14** and **15** with *S* and *R* configurations, respectively, whether the reagent is dimethyl malonate or benzylamine (Scheme 6).

Scheme 6. Stereochemical Nucleophilic Approach of the Pd-Catalyzed Allylation in the Presence of P-Chirogenic Diphosphine 9a



CONCLUSION

The first synthesis of P-chirogenic mono- and diphosphine ligands located on the upper rim of a calix[4]arene moiety was achieved in three steps starting from the (+)- or (−)-oxazaphospholidine–borane complex **1**, derived from ephedrine. These ligands were tested with standard Pd-catalyzed asymmetric allylic substitutions of racemic (*E*)-1,3-diphenylprop-2-en-1-yl acetate with dimethyl malonate and benzylamine. The reaction of (*E*)-1,3-diphenylprop-2-en-1-yl acetate with dimethyl malonate catalyzed by $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ and diphosphine **9** resulted in high enantioselectivity (82% ee) using *n*-BuLi as base. In the case of the allylic amination of (*E*)-1,3-diphenylprop-2-en-1-yl acetate with benzylamine the *N*-benzyl-1,3-diphenyl-2-propenylamine **15** was obtained in high yields and with asymmetric inductions up to 79% ee using the mono- or diphosphines derived from calix[4]arenes **5a** and **9a**. Computer modeling of the calix[4]arenyl diphosphine (*S,S*)-**9a**/Pd(allyl) complex indicates a clear dissymmetry of both the HOMO and LUMO, in good agreement with a complexed η^1-allyl moiety. The dissymmetry of the LUMO is particularly determinant in the regio- and enantioselectivity with respect to attack by the C- or N-nucleophiles. The complexation of substrate to this palladium complex explains why the C_2 symmetry of the P-chirogenic calixarene diphosphine plays a

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key role in the enantioselectivity of these Pd-catalyzed allylations.

EXPERIMENTAL SECTION

General Procedures. All reactions were carried out under an argon atmosphere in dried glassware with magnetic stirring. Solvents were dried prior to use. Tetrahydrofurane (THF) and toluene were distilled from sodium/benzophenone and stored under argon. Dichloromethane (CH_2Cl_2) was distilled from CaH_2. Hexane and propan-2-ol for HPLC were of chromatographic grade and were used without further purification. *sec*-Butyllithium (1.4 M in cyclohexane), *tert*-butyllithium (1.6 M in pentane), methyllithium (1.6 M in Et_2O), 1,4-diazabicyclo[2.2.2]octane (DABCO), ferrocene, 2-bromoanisole, $BH_3.SMe_2$, and (*R*)-(+)-1-phenylethylamine were purchased from Aldrich, Acros, or Alfa Aesar and used as received. (+)- and (−)-ephedrine were purchased from Aldrich and dried by an azeotropic shift of toluene on a rotary evaporator. $[PdCl(\eta^3\text{-}C_3H_5)]_2$ was purchased from Strem. 5-Bromo-25,26,27,28-tetrapropoxycalix[4]arene and 5,17-dibromo-25,26,27,28-tetrapropoxycalix[4]arene[10a] were prepared according to literature procedures. (2*R*,4*S*,5*R*)-(+)-3,4-dimethyl-2,5-diphenyl-1,3,2-oxazaphospholidine-2-borane (**1**) and its enantiomer (2*S*,4*R*,5*S*)-(−)-**1** were prepared from the appropriate (−)- or (+)-ephedrine, as previously described.[18] (S_p)-(+)-*N*-methyl-*N*-[(1*S*,2*R*)(1-hydroxy-2-methyl-1-phenyl-2-propyl)]aminomethylphenyl phosphine−borane **2′a**, (R_p)-(+)-*N*-methyl-*N*-[(1*S*,2*R*)(1-hydroxy-2-methyl-1-phenyl-2-propyl)]amino-*o*-anisylphenylphosphine−borane (**2′b**) and (R_p)-(+)-*N*-methyl-*N*-[(1*S*,2*R*)(1-hydroxy-2-methyl-1-phenyl-2-propyl)]-aminoferrocenylphosphine−borane (**2′c**) were prepared from (+)-ephedrine according to the published procedure.[18] (*R*)-(+)-di-μ-chlorobis[2[1-(dimethylamino)ethyl]phenyl-*C*,*N*]dipalladium (**12**) was prepared from (*R*)-(+)-1-phenylethylamine according to literature procedures.[21] The toluene/HCl solution was obtained by bubbling HCl gas, and the resulting solution was titrated before use. Reactions were monitored by thin-layer chromatography (TLC) using 0.25 mm E. Merck precoated silica gel plates. Visualization was accomplished with UV light and/or appropriate staining reagents. Flash chromatography was performed with the indicated solvents using silica gel 60 (particle size 35−70 μm; Acros) or aluminum oxide 90 standardized (Merck). NMR spectra (^1H, ^{13}C and ^{31}P) were recorded on Bruker 500 MHz Avance DRX, 300 MHz Avance, and 600 MHz Avance II spectrometers at ambient temperature. Data are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br s = broad singlet; integration, coupling constant(s) in Hz. Melting points were measured on a Kofler bench melting point apparatus and are uncorrected. Optical rotation values were determined at 25 °C on a Perkin-Elmer 341 polarimeter, using a 10 cm quartz vessel. Mass spectral analyses were performed on the Bruker Daltonics microTOF-Q apparatus at Burgundy University.

Crystal Structure Determination. Diffraction data were collected on a Nonius Kappa CCD or Nonius Kappa APEX II diffractometer equipped with a nitrogen jet stream low-temperature system (Oxford Cryosystems). The X-ray source was graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) from a sealed tube. The lattice parameters were obtained by a least-squares fit to the optimized setting angles of the entire set of collected reflections. No significant temperature drift was observed during the data collections. Data were reduced by using DENZO[23] software without applying absorption corrections; the missing absorption corrections were partially compensated by the data scaling procedure in the data reduction. The structures were solved by direct methods using the SIR92[24] program. Refinements were carried out by full-matrix least squares on F^2 using the SHELXL97[25] program on the complete set of reflections. Absolute configurations of all compounds were determined reliably from anomalous scattering, using the Flack method.[20]

Computations. The optimization was calculated with Gaussian 09,[26] at the Université de Sherbrooke's Mammouth supercomputer, supported by the Réseau Québécois de Calcul de Haute Performance. DFT[27−30] was calculated by the B3LYP[31−33] method with specific basis sets assigned for different atom types. C, H, O, and P were described by 3-21G*;[34−39] palladium was described by SBKJC ECP and VDZ.[40−43]

Synthesis of the Aminophosphine−Boranes 2 and 7. *(Sp)-(−)-N-Methyl[(1S,2R)(2-hydroxy-1-phenyl)ethyl]amino{25,26,27,28-tetrapropoxycalix[4]arene}phenylphosphine−Borane (**2a**).* A solution of *sec*-butyllithium (1.4 M in hexane, 1.8 mL, 2.5 mmol) was added under argon at −78 °C to a solution of 5-bromo-25,26,27,28-tetrapropoxycalix[4]arene (1.5 g, 2.2 mmol) in THF (3 mL). After 45 min, the mixture was added slowly to a solution of (+)-oxazaphospholidine−borane **1** (0.7 g, 2.5 mmol) in THF (3 mL). The reaction mixture was warmed to room temperature. When the starting complex **1** was totally consumed (TLC), the mixture was hydrolyzed with water and then extracted with CH_2Cl_2. The organic layers were dried with anhydrous $MgSO_4$, and the solvent was removed. The residue was purified by column chromatography on silica gel using toluene/ethyl acetate 9/1 as eluent to afford the aminophosphine− borane **2a**, which was recrystallized with methanol (1.62 g, yield 84%): white solid; mp 106−109 °C. R_f = 0.20 (AcOEt/toluene 1/9). $[\alpha]_D^{25}$ = −8.0 (*c* 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.30−6.93 (m, 10H, CH_{arom}), 6.75−6.50 (m, 8H, CH_{arom}), 6.17 (m, 3H, CH_{arom}), 4.56 (d, 1H, *J* = 5.1 Hz, *CH*O), 4.34 (AX system, 4H, *J* = 13.1, 12.9 Hz, ArCH_2Ar), 3.95 (m, 5H, $CHCH_3$ and CH_2O), 3.64 (m, 4H, CH_2O, OPr), 3.11 (AX system, 4H, *J* = 13.5, 12.6 Hz, ArCH_2Ar), 1.97 (m, 4H, CH_2CH_3, OPr), 1.83 (m, 4H, CH_2CH_3, OPr), 1.52 (d, 3H, *J* = 7.2 Hz, CH_3N), 1.10 (d, 3H, *J* = 6.9 Hz, CH_3CH), 1.02 (m, 6H, CH_3, OPr), 0.86 (m, 6H, CH_3, OPr). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 157.7 (d, *J* = 3.0 Hz, C_{arom}), 157.1 (d, *J* = 18.0 Hz, C_{arom}), 155.6 (s, C_{arom}), 142.6 (s, C_{arom}), 137.9 (s, C_{arom}), 136.5 (d, *J* = 5.3 Hz, C_{arom}), 136.3 (d, *J* = 12.8 Hz, C_{arom}), 134.4 (d, *J* = 12.8 Hz, C_{arom}), 134.2 (d, *J* = 12.8 Hz, C_{arom}), 133.8 (d, *J* = 15.8 Hz, C_{arom}), 132.4 (d, *J* = 12.8 Hz, CH_{arom}), 132.3 (d, *J* = 10.5 Hz, CH_{arom}), 131.7 (d, *J* = 9.8 Hz, CH_{arom}), 130.5 (d, *J* = 32.4 Hz, CH_{arom}), 130.1 (d, *J* = 32.4 Hz, CH_{arom}), 129.1 (s, CH_{arom}), 128.8 (d, *J* = 7.5 Hz, CH_{arom}), 128.7 (s, CH_{arom}), 128.3 (d, *J* = 4.5 Hz, CH_{arom}), 128.0 (d, *J* = 10.6 Hz, CH_{arom}), 127.6 (d, *J* = 9.8 Hz, CH_{arom}), 126.3 (s, CH_{arom}), 125.3 (s, CH_{arom}), 122.7 (s, CH_{arom}), 122.3 (d, *J* = 5.3 Hz, CH_{arom}), 78.6 (d, *J* = 3.8 Hz, *C*HO), 77.5 (s, CH_2O, OPr), 77.4 (s, CH_2O, OPr), 76.7 (s, CH_2O, OPr), 76.6 (s, CH_2O, OPr), 58.0 (d, *J* = 10.6 Hz, $CHCH_3$), 30.9 (s, ArCH_2Ar), 30.8 (s, ArCH_2Ar), 28.0 (d, *J* = 3.8 Hz, CH_3N), 23.5 (s, CH_2CH_3, OPr), 23.1 (s, CH_2CH_3, OPr), 23.0 (s, CH_2CH_3, OPr), 13.0 (d, *J* = 3.8 Hz, CH_3CH), 10.7 (s, CH_3, OPr), 10.6 (s, CH_3, OPr), 10.2 (s, CH_3, OPr), 10.0 (s, CH_3, OPr). ^{31}P NMR ($CDCl_3$, 121 MHz): δ +69.5. HRMS (ESI-Q-TOF): calcd for $C_{56}H_{69}BNO_5PNa$ $[M + Na]^+$ 900.49078, found 900.49334. Anal. Calcd for $C_{56}H_{69}BNO_5P$ (877.95): C, 76.61; H, 7.92; N, 1.60. Found: C, 76.91; H, 7.62; N, 1.69.

*(Sp,Sp)-5,17-Bis[(−)-N-methyl[(1S,2R)(2-hydroxy-1-phenyl)ethyl]-amino]{25,26,27,28-tetrapropoxycalix[4]arene}-diphenylphosphine−Diborane (**7**).* This compound was prepared according to a procedure similar to that for **2a**, using 5,17-dibromo-25,26,27,28-tetrapropoxycalix[4]arene (3.3 g, 4.1 mmol) and *sec*-butyllithium (1.4 M in hexane, 9.7 mL, 13.5 mmol) to generate the corresponding (25,26,27,28-tetrapropoxycalix[4]arene-5,17-yl)-dilithium reagent and (+)-oxazaphospholidine−borane **1** (2.4 g, 8.3 mmol): yield 3.48 g, 73%; white solid; mp 236−238 °C. R_f = 0.26 (AcOEt/toluene 1/9). $[\alpha]_D^{25}$ = −33.0 (*c* 1, $CHCl_3$). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.41−7.09 (m, 26H, CH_{arom}), 6.12 (t, 2H, *J* = 7.5 Hz, CH_{arom}), 5.90 (d, 4H, *J* = 7.8 Hz, CH_{arom}), 4.80 (d, 2H, *J* = 3.9 Hz, *CH*O), 4.34 (AX system, 6H, *J* = 13.5 Hz, ArCH_2Ar and $CHCH_3$), 4.00 (t, 4H, *J* = 8.1 Hz, CH_2O, OPr), 3.54 (t, 4H, *J* = 6.6 Hz, CH_2O, OPr), 3.05 (AX system, 4H, *J* = 14.4 Hz, ArCH_2Ar), 2.46 (d, 6H, *J* = 7.8 Hz, CH_3N), 1.87 (m, 4H, CH_2CH_3, OPr), 1.76 (m, 4H, CH_2CH_3, OPr), 1.24 (d, 6H, *J* = 6.6 Hz, CH_3CH), 1.00 (t, 6H, *J* = 7.3 Hz, CH_3, OPr), 0.84 (t, 6H, *J* = 7.5 Hz, CH_3, OPr). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 160.8 (d, *J* = 2.2 Hz, C_{arom}), 155.2 (s, C_{arom}), 142.7 (s, C_{arom}), 137.4 (d, *J* = 11.4 Hz, C_{arom}), 137.2 (d, *J* = 10.6 Hz, C_{arom}), 133.6 (d, *J* = 12.4 Hz, CH_{arom}), 133.4 (d, *J* = 11.0 Hz, CH_{arom}), 132.7 (d, *J* = 3.5 Hz, C_{arom}), 132.6 (d, *J* = 10.2 Hz, CH_{arom}), 131.8 (s, C_{arom}), 130.8 (s, C_{arom}), 130.6 (d, *J* = 2.3 Hz, CH_{arom}), 128.7 (s, CH_{arom}), 128.3 (d, *J* = 10.4 Hz, CH_{arom}), 128.0 (s, CH_{arom}), 127.4 (d, *J* = 5.0 Hz, CH_{arom}),

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126.9 (s, CH_{arom}), 123.5 (s, C_{arom}), 122.6 (s, C_{arom}), 122.3 (s, CH_{arom}), 78.9 (d, J = 8.2 Hz, CHO), 77.2 (s, CH_2O, OPr), 76.7 (s, CH_2O, OPr), 64.5 (s, $CHCH_3$), 31.5 (br.s, $ArCH_2Ar$), 30.5 (d, J = 3.8 Hz, CH_3N), 23.5 (s, CH_2CH_3, OPr), 23.2 (s, CH_2CH_3, OPr), 13.6 (s, CH_3CH), 10.9 (s, CH_3, OPr), 9.8 (s, CH_3, OPr). ^{31}P NMR ($CDCl_3$, 121 MHz): δ +69.8. HRMS (ESI-Q-TOF): calcd for $C_{72}H_{90}B_2O_6P_2N_2Na$ $[M + Na]^+$ 1185.6352, found 1185.6376. Anal. Calcd for $C_{72}H_{90}B_2O_6P_2N_2$ + CH_3OH (1195.12): C, 73.36; H, 7.93; N, 2.34. Found: C, 73.59; H, 8.18; N, 2.43.

Preparation of Monophosphine− and Diphosphine−Boranes 4a−c and 8a−c (Route a). *(S)-(−)-Methylphenyl{25,26,27,28-tetrapropoxycalix[4]arene}phosphine−borane (**4a**).* In a 50 mL two-necked flask equipped with a magnetic stirrer, an argon inlet, and a rubber septum was introduced the aminophosphine− borane **2a** (0.53 g, 0.6 mmol). A solution of HCl in toluene (0.4 M, 15 mL, 6 mmol) was added with stirring at room temperature, without previous dissolution of **2a**. After 2 h, the acidolysis completion was controlled by TLC, and the precipitate of ephedrine hydrochloride was filtered off with a Millipore 4 μm filter. The excess HCl was removed by several vacuum/argon cycles. The 5-(chlorophenylphosphino borane)-25,26,27,28-tetrapropoxycalix[4]arene obtained was used without further purification (^{31}P NMR ($CDCl_3$, 121 MHz): δ +93.6). Methyllithium (1.6 M in Et_2O, 1.12 mL, 1.8 mmol) was added dropwise at −78 °C to the vigorously stirred toluene solution of the chlorophosphine−borane **3a**. The reaction mixture was warmed to room temperature. After 2 h, the mixture was hydrolyzed with water and then extracted with CH_2Cl_2. The organic layers were dried with anhydrous $MgSO_4$, and the solvent was removed. The residue was purified by column chromatography on silica gel using hexane/ethyl acetate 95/5 as eluent to afford compound **4a**, which was recrystallized with methanol (0.38 g, yield 84%): white solid; mp 124−126 °C. R_f = 0.32 (AcOEt/hexane 5/95). $[\alpha]_D^{25}$ = −30.0 (c 0.8, $CHCl_3$) for 99% ee. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.41−7.29 (m, 5H, CH_{arom}), 6.84−6.39 (m, 11H, CH_{arom}), 4.38 (AX system, 4H, J = 13.2 Hz, $ArCH_2Ar$), 3.84 (m, 4H, CH_2O, OPr), 3.74 (m, 4H, CH_2O, OPr), 3.11 (AX system, 4H, J = 13.2 Hz, $ArCH_2Ar$), 1.86 (m, 8H, CH_2CH_3, OPr), 1.38 (d, 3H, J = 2.6 Hz, CH_3P), 0.94 (m, 12H, CH_3, OPr). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 158.8 (d, J = 11.3 Hz, C_{arom}), 159.6 (s, C_{arom}), 156.1 (d, J = 13.8 Hz, C_{arom}), 135.6 (d, J = 6.6 Hz, C_{arom}), 135.1 (d, J = 12.7 Hz, C_{arom}), 134.9 (s, C_{arom}), 134.6 (d, J = 8.9 Hz, C_{arom}), 132.0 (d, J = 9.4 Hz, CH_{arom}), 131.8 (s, CH_{arom}), 131.6 (d, J = 3.3 Hz, CH_{arom}), 131.5 (s, CH_{arom}), 130.6 (d, J = 2.3 Hz, CH_{arom}), 128.6 (d, J = 4.0 Hz, CH_{arom}), 128.5 (s, CH_{arom}), 128.2 (d, J = 13.0 Hz, CH_{arom}), 128.0 (d, J = 24.0 Hz, CH_{arom}), 122.3 (d, J = 1.1 Hz, CH_{arom}), 122.1 (s, CH_{arom}), 77.1 (s, CH_2O, OPr), 77.0 (s, CH_2O, OPr), 76.7 (s, CH_2O, OPr), 76.6 (s, CH_2O, OPr), 31.0 (s, $ArCH_2Ar$), 30.9 (s, $ArCH_2Ar$), 30.8 (s, $ArCH_2Ar$), 30.7 (s, $ArCH_2Ar$), 23.4 (s, CH_2CH_3, OPr), 23.3 (s, CH_2CH_3, OPr), 23.1 (s, CH_2CH_3, OPr), 13.0 (d, J = 44.9 Hz, CH_3P), 10.5 (s, CH_3, OPr), 10.4 (s, CH_3, OPr), 10.2 (s, CH_3, OPr). ^{31}P NMR ($CDCl_3$, 121 MHz): δ +9.0. HRMS (ESI-Q-TOF): calcd for $C_{47}H_{58}BO_4PNa$ $[M + Na]^+$ 751.4066, found 751.4068. Anal. Calcd for $C_{47}H_{58}BO_4P$ (728.75): C, 77.46; H, 8.02. Found: C, 77.33; H, 8.09.

The enantiomeric excess of **4a** was determined by HPLC analysis on a Lux 5 μ cellulose-2 column, hexane/i-PrOH 99/1, 1 mL/min, 40 °C, λ 254 nm, $t_R(R)$ = 27.7 min, $t_R(S)$ = 34.6 min.

*(S)-(+)-(o-Anisylphenyl{25,26,27,28-tetrapropoxycalix[4]arene}-phosphine−Borane (**4b**).* In a two-necked flask equipped with a magnetic stirrer and an argon inlet, 1.8 mL (1.4 M in hexane, 2.8 mmol) of *sec*-butyllithium was added. The mixture was cooled to 0 °C, and 0.3 mL (2.8 mmol) of 2-bromoanisole was slowly added with a syringe while stirring. After the formation of a white precipitate, the mixture was stirred for 1 h at 0 °C. The organolithium reagent was dissolved with a minimum amount of dry THF before use. After 1 h, the o-anisyllithium was added at −78 °C to a toluene solution of the chlorophosphine−borane **3a** (1 mmol), previously prepared as described above. The resulting mixture was progressively warmed to room temperature and stirred for 2 h. After hydrolysis, the aqueous layer was extracted two times with dichloromethane. The organic layers were dried over anhydrous $MgSO_4$, and the solvent was removed. The residue was purified by column chromatography on silica gel using a petroleum ether/ethyl acetate 8/2 mixture as eluent (0.56 g, yield 62%): white crystals; mp 213−215 °C. $[\alpha]_D^{25}$ = +33.0 (c 1, $CHCl_3$) for 98% ee. R_f = 0.60 (petroleum ether/AcOEt 8/2). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.59 (m, 5H, CH_{arom}), 7.26 (m, 2H, CH_{arom}), 7.04 (m, 2H, CH_{arom}), 6.93 (t, 1H, J = 5.2 Hz, CH_{arom}), 6,78 (m, 3H, CH_{arom}), 6.59 (t, 1H, J = 5.3 Hz, CH_{arom}), 6.38 (m, 4H, CH_{arom}), 6.28 (m, 2H, CH_{arom}), 4.37 (AX system, 4H, J = 13.3, 5.8 Hz, $ArCH_2Ar$), 3.83 (dd, 4H, J = 15.6, 5.8 Hz, CH_2O, OPr), 3.71 (m, 4H, CH_2O, OPr), 3.39 (s, 1H, CH_3O), 3.06 (AX system, 4H, J = 17.0, 13.3 Hz, $ArCH_2Ar$), 1.87 (m, 8H, J = 7.3 Hz, CH_2CH_3, OPr), 0.95 (t, 6H, J = 7.5 Hz, CH_3, OPr), 0.88 (t, 6H, J = 7.5 Hz, CH_3, OPr). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 161.3 (d, J = 2.2 Hz, C_{arom}), 156.8 (d, J = 14.8 Hz, C_{arom}), 155.9 (s, C_{arom}), 135.9 (s, C_{arom}), 135.6 (d, J = 9.7 Hz, C_{arom}), 134.6 (d, J = 12.1 Hz, CH_{arom}), 134.5 (d, J = 11.0 Hz, CH_{arom}), 133.9 (s, CH_{arom}), 133.7 (d, J = 10.2 Hz, CH_{arom}), 133.5 (s, CH_{arom}), 133.4 (s, CH_{arom}), 132.6 (d, J = 2.2 Hz, CH_{arom}), 130.1 (s, CH_{arom}), 128.4 (s, CH_{arom}), 128.1 (d, J = 10.4 Hz, CH_{arom}), 127.8 (d, J = 4.4 Hz, CH_{arom}), 122.1 (s, CH_{arom}), 120.9 (s, C_{arom}), 120.8 (s, CH_{arom}), 120.5 (s, CH_{arom}), 77.2 (s, CH_2O, OPr), 76.8 (s, CH_2O, OPr), 76.8 (s, CH_2O, OPr), 76.7 (s, CH_2O, OPr), 55.1 (s, CH_3O), 30.9 (s, $ArCH_2Ar$), 30.9 (s, $ArCH_2Ar$), 30.8 (s, $ArCH_2Ar$), 30.8 (s, $ArCH_2Ar$), 23.3 (s, CH_2CH_3, OPr), 23.3 (s, CH_2CH_3, OPr), 23.2 (s, CH_2CH_3, OPr), 23.1 (s, CH_2CH_3, OPr), 10.4 (s, CH_3, OPr), 10.1 (s, CH_3, OPr); ^{31}P NMR ($CDCl_3$, 121 MHz): δ +17.1. HRMS (ESI-Q-TOF): calcd for $C_{53}H_{62}BNaO_5P$ $[M + Na]^+$ 843.43201, found 843.42947. Anal. Calcd for $C_{53}H_{62}BO_5P$ (820.85): C, 77.55; H, 7.61. Found: C, 77.30; H, 7.53.

The enantiomeric excess of **4b** was determined by HPLC analysis on a Lux 5 μ cellulose-2 column, hexane/i-PrOH 99/1; 1 mL/min, 40 °C, λ 254 nm, $t_R(R)$ = 15.6 min, $t_R(S)$ = 19.3 min.

*(S)-(−)-Ferrocenylphenyl{25,26,27,28-tetrapropoxycalix[4]arene}-phosphine−Borane (**4c**).* In a 50 mL two-necked flask equipped with a magnetic stirrer and an argon inlet was added 1.37 mL of *tert*-butyllithium (1.6 M in pentane, 2.2 mmol) with stirring at 0 °C to a solution of ferrocene (0.465 g, 2.5 mmol) in 8 mL of THF. After 1 h, the ferrocenyllithium reagent was added at −78 °C to a toluene solution of the chlorophosphine−borane **3a** (1.05 mmol), previously prepared as described above. The resulting mixture was progressively warmed to room temperature and stirred for 2 h. After hydrolysis with water, the aqueous phase was extracted several times with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$, and the solvents were removed. The residue was purified by chromatography on silica gel using diethyl ether/petroleum ether 5/95 as eluent, to afford compound **4c** in 46% yield (0.43 g): orange solid; mp 97−99 °C. R_f = 0.32 (Et_2O/petroleum ether 5/95). $[\alpha]_D^{25}$ = −2.7 (c 0.4, $CHCl_3$) for 93% ee. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.40−7.25 (m, 5H, CH_{arom}), 6.90 (m, 2H, CH_{arom}), 6.76 (m, 2H, CH_{arom}), 6.63 (m, 1H, CH_{arom}), 6.49−6.28 (m, 6H, CH_{arom}), 4.36 (AX system, 6H, $ArCH_2Ar$ and Fc), 4.27 (m, 1H, Fc), 4.18 (m, 1H, Fc), 4.00 (s, 5H, Fc), 3.78 (m, 8H, CH_2O, OPr), 3.10 (AX system, 4H, $ArCH_2Ar$), 1.85 (m, 8H, CH_2CH_3, OPr), 0.90 (m, 12H, CH_3, OPr). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.3 (d, J = 2.5 Hz, C_{arom}), 156.8 (s, C_{arom}), 156.0 (d, J = 2.6 Hz, C_{arom}), 135.7 (d, J = 11.2 Hz, C_{arom}), 135.5 (d, J = 3.5 Hz, C_{arom}), 134.7 (d, J = 4.5 Hz, C_{arom}), 133.9 (s, C_{arom}), 133.1 (d, J = 4.8 Hz, CH_{arom}), 133.0 (d, J = 5.8 Hz, CH_{arom}), 132.5 (d, J = 9.6 Hz, CH_{arom}), 131.7 (s, C_{arom}), 130.4 (d, J = 2.8 Hz, CH_{arom}), 128.4 (d, J = 5.3 Hz, CH_{arom}), 128.2 (d, J = 4.5 Hz, CH_{arom}), 128.1 (d, J = 1.7 Hz, CH_{arom}), 127.8 (d, J = 2.6 Hz, CH_{arom}), 122.3 (br.s, CH_{arom}), 122.1 (s, CH_{arom}), 76.9 (s, CH_2O, OPr), 76.8 (s, CH_2O, OPr), 76.7 (s, CH_2O, OPr), 72.4 (d, J = 10.3 Hz, Fc), 72.5 (d, J = 9.3 Hz, Fc), 71.6 (d, J = 7.5 Hz, Fc), 71.3 (d, J = 7.6 Hz, Fc), 70.2 (d, J = 70.9 Hz, Fc), 69.6 (br.s, Fc), 30.9 (s, $ArCH_2Ar$), 30.8 (s, $ArCH_2Ar$), 23.3 (s, CH_2CH_3, OPr), 23.2 (s, CH_2CH_3, OPr), 10.4 (s, CH_3, OPr), 10.2 (s, CH_3, OPr). ^{31}P NMR ($CDCl_3$, 121 MHz): δ +15.0. HRMS (ESI-Q-TOF) calcd for $C_{56}H_{64}BFeO_4P$ $[M]^+$ 898.3990, found 898.3993. Anal. Calcd for $C_{56}H_{64}BFeO_4P$ (898.75): C, 74.84; H, 7.18. Found: C, 74.53; H, 7.14.

The enantiomeric excess of **4c** was determined by HPLC analysis on a Lux 5 μ cellulose-2 column, hexane/i-PrOH 98/2, 1 mL/min, 40 °C, λ 254 nm, $t_R(S)$ = 8.7 min, $t_R(R)$ = 10.9 min.

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*(S,S)-(−)-5,17-Bis[(methylphenylphosphinoborane)]{25,26,27,28-tetrapropoxycalix[4]arene} (**8a**).* In a 50 mL two-necked flask equipped with a magnetic stirrer, an argon inlet, and a rubber septum was introduced the bis(aminophosphine)−borane **7** (2.5 g, 2.15 mmol). A solution of HCl in toluene (0.32 M, 81 mL, 25.8 mmol) was added with stirring at room temperature, without previous dissolution of **7**. After 2 h, the acidolysis completion was controlled by TLC, and the precipitate of ephedrine hydrochloride was filtered off with a Millipore 4 μm filter. The excess HCl was removed by several vacuum/argon cycles. The 5,17-(bischlorophenylphosphinoborane)-25,26,27,28-tetrapropoxycalix[4]arene obtained was used without further purification (^{31}P NMR ($CDCl_3$, 121 MHz): δ +92.5). Methyllithium (1.6 M in Et_2O, 17.9 mL, 10.7 mmol) was added dropwise at −78 °C to the vigorously stirred toluene solution of the bis(chlorophosphine)−borane intermediate. The reaction mixture was warmed to room temperature. After 2 h, the mixture was hydrolyzed with water and then extracted with CH_2Cl_2. The organic layers were dried with anhydrous $MgSO_4$, and the solvent was removed. The residue was purified by column chromatography on silica gel using dichloromethane/petroleum ether 2/8 as eluent (0.85 g, yield 46%): white solid; mp 192−194 °C. R_f = 0.54 (CH_2Cl_2/petroleum ether 2/8). $[\alpha]_D^{25}$ = −0.8 (*c* 0.4, $CHCl_3$) for 98% ee. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.65−7.52 (m, 4H, C*H*$_{arom}$), 7.37−7.19 (m, 10H, C*H*$_{arom}$), 6.17 (t, 2H, *J* = 7.6 Hz, C*H*$_{arom}$), 5.9 (d, 4H, *J* = 7.8 Hz, C*H*$_{arom}$), 5.93 (m, 4H, C*H*$_{arom}$), 4.35 (AX system, 4H, *J* = 13.4 Hz, ArC*H*$_2$Ar), 4.00 (m, 4H, C*H*$_2$O, OPr), 3.57 (t, 4H, *J* = 6.7 Hz, C*H*$_2$O, OPr), 3.09 (AX system, 4H, *J* = 13.4 Hz, ArC*H*$_2$Ar), 1.82 (m, 14H, C*H*$_2$CH$_3$ and CH$_3$P), 1.00 (t, 6H, *J* = 7.5 Hz, C*H*$_3$, OPr), 0.83 (t, 6H, *J* = 7.5 Hz, C*H*$_3$, OPr). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 155.1 (s, *C*$_{arom}$), 137.7 (d, *J* = 11.3 Hz, *C*$_{arom}$), 132.5 (br.s, *C*H$_{arom}$), 131.5 (d, *J* = 9.2 Hz, *C*H$_{arom}$), 130.8 (s, *C*H$_{arom}$), 128.7 (d, *J* = 9.9 Hz, *C*H$_{arom}$), 127.5 (s, *C*H$_{arom}$), 122.3 (s, *C*H$_{arom}$), 121.6 (s, *C*$_{arom}$), 77.1 (s, *C*H$_2$O, OPr), 76.7 (s, *C*H$_2$O, OPr), 30.9 (s, ArCH$_2$Ar), 23.5 (s, *C*H$_2$CH$_3$, OPr), 23.1 (s, *C*H$_2$CH$_3$, OPr), 12.4 (d, *J* = 60.7 Hz, *C*H$_3$P), 10.8 (s, *C*H$_3$, OPr), 9.8 (s, *C*H$_3$, OPr). ^{31}P NMR ($CDCl_3$, 121 MHz): δ +8.5. HRMS (ESI-Q-TOF): calcd for $C_{54}H_{68}B_2O_4P_2Na$ $[M + Na]^+$ 887.46712, found 887.46590. Anal. Calcd for $C_{54}H_{68}B_2O_4P_2 + CH_3OH$ (896.74): C, 73.67; H, 8.09. Found: C, 74.04; H, 8.37.

*(S,S)-(−)-5,17-Bis[(o-anisylphenylphosphinoborane)]-{25,26,27,28-tetrapropoxycalix[4]arene} (**8b**).* This compound was prepared from bis(aminophosphine)−borane **7** (1.7 g, 1.45 mmol) according to a procedure similar to that for **8a**, using *o*-anisyllithium in place of methyllithium. The *o*-anisyllithium was previously prepared by metal−halide exchange of 2-bromoanisole (1.20 g, 6 mmol) with *sec*-butyllithium (1.4 M in cyclohexane, 4.3 mL, 6 mmol). After workup, the residue was purified by column chromatography on silica gel using a petroleum ether/ethyl acetate 8/2 mixture as eluent (1.09 g, yield 68%): white crystals; mp 169−171 °C. $[\alpha]_D^{25}$ = −24.5 (*c* 1, $CHCl_3$) for 95% ee. R_f = 0.30 (petroleum ether/AcOEt 8/2). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.62 (m, 4H, C*H*$_{arom}$), 7.40 (m, 12H, C*H*$_{arom}$), 7.26 (dd, 2H, *J* = 8.8, 2.2 Hz, C*H*$_{arom}$), 6.98 (t, 2H, *J* = 7.2 Hz, C*H*$_{arom}$), 6.88 (m, 2H, C*H*$_{arom}$), 6.17 (t, 2H, *J* = 7.5 Hz, C*H*$_{arom}$), 5.98 (t, 4H, *J* = 7.4 Hz, C*H*$_{arom}$), 4.35 (AX system, 4H, *J* = 13.3 Hz, ArC*H*$_2$Ar), 3.99 (m, 4H, C*H*$_2$O, OPr), 3.55 (m, 10H, C*H*$_2$O and C*H*$_3$O), 3.04 (AX system, 4H, *J* = 13.3, 7.4 Hz, ArC*H*$_2$Ar), 1.78 (m, 4H, *J* = 13.3, 7.4 Hz, C*H*$_2$CH$_3$, OPr), 0.99 (t, 6H, *J* = 7.4 Hz, C*H*$_3$, OPr) 0.82 (t, 6H, *J* = 7.4 Hz, C*H*$_3$, OPr). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 161.4 (d, *J* = 13.2 Hz, *C*$_{arom}$), 160.4 (d, *J* = 4.2 Hz, *C*$_{arom}$), 155.1 (s, *C*$_{arom}$), 137.4 (s, *C*$_{arom}$), 137.2 (d, *J* = 9.7 Hz, *C*H$_{arom}$), 133.6 (d, *J* = 11.1 Hz, *C*H$_{arom}$), 132.9 (s, *C*H$_{arom}$), 132.8 (d, *J* = 6.4 Hz, *C*H$_{arom}$), 132.7 (s, *C*H$_{arom}$), 132.7 (d, *J* = 10.6 Hz, *C*H$_{arom}$), 130.5 (d, *J* = 13.2 Hz, *C*H$_{arom}$), 128.3 (d, *J* = 4.7 Hz, *C*H$_{arom}$), 128.2 (s, *C*H$_{arom}$), 127.4 (s, *C*H$_{arom}$), 121.9 (s, *C*H$_{arom}$), 121.1 (s, *C*H$_{arom}$), 120.7 (s, *C*H$_{arom}$), 118.1 (s, *C*$_{arom}$), 111.6 (d, *J* = 2.2 Hz, *C*H$_{arom}$), 111.5 (s, *C*H$_{arom}$), 77.2 (s, *C*H$_2$O, OPr), 76.8 (s, *C*H$_2$O, OPr), 76.4 (s, *C*H$_2$, OPr), 55.3 (s, *C*H$_3$O), 30.9 (s, ArCH$_2$Ar), 23.5 (s, *C*H$_2$CH$_3$, OPr), 23.1 (s, *C*H$_2$CH$_3$, OPr), 10.8 (s, *C*H$_3$, OPr), 9.8 (s, *C*H$_3$, OPr). ^{31}P NMR ($CDCl_3$, 121 MHz): δ +17.3. HRMS (ESI-Q-TOF): calcd for $C_{66}H_{76}B_2NaO_6P_2$ $[M + Na]^+$ 1071.51955, found 1071.51431. Anal. Calcd for $C_{66}H_{76}B_2O_6P_2$ (1048.89): C, 75.58; H, 7.30. Found: C, 75.35; H, 7.26.

*(S,S)-(−)-5,17-Bis[(ferrocenylphenylphosphinoborane)]-{25,26,27,28-tetrapropoxycalix[4]arene} (**8c**).* This compound was prepared from bis(aminophosphine)−borane **7** (1.7 g, 1.45 mmol) according to a procedure similar to that for **8a**, using ferrocenyllithium in place of the methyllithium. The ferrocenyllithium was previously prepared by deprotonation of ferrocene (1.35 g, 7.3 mmol) with *tert*-butyllithium (1.6 M in pentane, 4.6 mL, 7.3 mmol). After workup, the residue was purified by column chromatography on silica gel using a petroleum ether/ethyl acetate 9/1 mixture as eluent (0.80 g, yield 46%): orange solid; mp 154−156 °C. R_f = 0.33 (AcOEt/petroleum ether 1/9). $[\alpha]_D^{25}$ = −8.4 (*c* 0.4, $CHCl_3$) for 84% ee. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.49 (m, 4H, C*H*$_{arom}$), 7.40−7.25 (m, 10H, C*H*$_{arom}$), 6.14 (t, 2H, *J* = 7.6 Hz, C*H*$_{arom}$), 5.95 (m, 4H, C*H*$_{arom}$), 4.46 (AX system, 8H, ArC*H*$_2$Ar and Fc), 4.38 (m, 2H, Fc), 4.34 (m, 2H, Fc), 4.09 (s, 10H, Fc), 4.01 (t, 4H, *J* = 8.2 Hz, C*H*$_2$O, OPr), 3.85 (t, 4H, *J* = 6.7 Hz, C*H*$_2$O, OPr), 3.08 (AX system, 4H, ArC*H*$_2$Ar), 1.86 (m, 4H, C*H*$_2$CH$_3$, OPr), 1.76 (m, 4H, C*H*$_2$CH$_3$, OPr), 0.99 (t, 6H, *J* = 7.3 Hz, C*H*$_3$, OPr), 0.82 (t, 6H, *J* = 7.5 Hz, C*H*$_3$, OPr). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 160.7 (d, *J* = 1.9 Hz, *C*$_{arom}$), 155.1 (s, *C*$_{arom}$), 137.5 (d, *J* = 4.8 Hz, *C*$_{arom}$), 137.3 (d, *J* = 4.9 Hz, *C*$_{arom}$), 133.7 (d, *J* = 9.9 Hz, *C*H$_{arom}$), 133.2 (s, *C*$_{arom}$), 132.4 (d, *J* = 12.6 Hz, *C*H$_{arom}$), 132.2 (s, *C*$_{arom}$), 130.5 (s, *C*H$_{arom}$), 128.3 (d, *J* = 10.0 Hz, *C*H$_{arom}$), 127.5 (d, *J* = 8.6 Hz, *C*H$_{arom}$), 123.3 (s, *C*$_{arom}$), 122.4 (s, *C*$_{arom}$), 122.1 (s, *C*H$_{arom}$), 77.1 (s, *C*H$_2$O, OPr), 76.6 (s, *C*H$_2$O, OPr), 73.4 (d, *J* = 11.6 Hz, Fc), 72.1 (d, *J* = 7.9 Hz, Fc), 71.8 (d, *J* = 7.2 Hz, Fc), 71.7 (d, *J* = 7.6 Hz, Fc), 69.8 (s, Fc), 69.6 (d, *J* = 68.5 Hz, Fc), 30.9 (br.s, ArCH$_2$Ar), 23.5 (s, CH$_2$CH$_3$, OPr), 23.1 (s, CH$_2$CH$_3$, OPr), 10.8 (s, CH$_3$, OPr), 9.8 (s, CH$_3$, OPr). ^{31}P NMR ($CDCl_3$, 121 MHz): δ +14.5. HRMS (ESI-Q-TOF): calcd for $C_{72}H_{80}B_2Fe_2O_4P_2$ $[M]^+$ 1204.44113, found 1204.43551. Anal. Calcd for $C_{72}H_{80}B_2Fe_2O_4P_2 + CH_3OH$ (1236.72): C, 70.90; H, 6.85. Found: C, 70.71; H, 7.13.

Preparation of Monophosphine− and Diphosphine−Boranes (*R*)-4b and (*S,S*)-8b (Route b). *(R)-(−)-(o-Anisylphenyl-{25,26,27,28-tetrapropoxycalix[4]arene}phosphine−Borane (**4b**).* In a 50 mL two-necked flask equipped with a magnetic stirrer, an argon inlet, and a rubber septum was dissolved 0.67 g (1 mmol) of 5-bromo-25,26,27,28-tetra-*n*-propoxycalix[4]arene in 3 mL of THF. After the solution was cooled to −78 °C 0.81 mL (1.31 M in cyclohexane, 1.1 mmol) of *sec*-butyllithium was added drop by drop with stirring. After 5 min, a toluene solution containing 1.1 mmol of (*S*)-*o*-anisylchlorophenylphosphine−borane **3′b** (prepared according to the literature procedure[18]), was slowly added at −78 °C and the reaction mixture was stirred for 1 h. After hydrolysis, the aqueous layer was extracted two times with dichloromethane. The organic layers were dried over anhydrous $MgSO_4$, and the solvent was removed. The residue was purified by column chromatography on silica gel using a petroleum ether/ethyl acetate 8/2 mixture as eluent. Yield: 60%. The analysis of (*R*)-**4b** was similar to that already described above for its enantiomer (*S*)-**4b**.

*(S,S)-(−)-5,17-Bis[(o-anisylphenylphosphinoborane)]-{25,26,27,28-tetrapropoxycalix[4]arene} (**8b**).* In a 50 mL two-necked flask equipped with a magnetic stirrer, an argon inlet, and a rubber septum was dissolved 0.8 g (1 mmol) of 5,17-dibromo-25,26,27,28-tetra-*n*-propoxycalix[4]arene in 5 mL of THF. After the solution was cooled to −78 °C 1.62 mL (1.31 M in cyclohexane, 2.2 mmol) of *sec*-butyllithium was added drop by drop with stirring. After 5 min, a toluene solution containing 2.2 mmol of (*S*)-*o*-anisylchlorophenylphosphine−borane **3′b** (prepared according to the literature procedure[18]) was slowly added at −78 °C, and the reaction mixture was stirred for 1 h. After hydrolysis, the aqueous layer was extracted two times with dichloromethane. The organic layers were dried over anhydrous $MgSO_4$, and the solvent was removed. The residue was purified by column chromatography on silica gel using a petroleum ether/ethyl acetate 8/2 mixture as eluent, to afford the calix[4]arene diphosphine (*S,S*)-**8b** in 40% yield (0.42 g), the monophosphine−borane (*R*)-**4b** (0.21 g, 25%), and the 17-chloro derivative **11** (0.21 g, 25%). The analyses of (*R*)-**4b** and (*S,S*)-**8b** were similar to those already described above.

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*(S)-(−)-17-Chloro-5-o-anisylphenyl{25,26,27,28-tetrapropoxycalix[4]arene}phosphine−Borane (**11**).* This was a byproduct obtained during the preparation of diphosphine−borane **8b** according to route b, described above: yield 0.21 g, 25%; white crystals; mp 223−225 °C. $[\alpha]_D^{25}$ = −27.0 (*c* 1, $CHCl_3$). R_f = 0.6 (petroleum ether/AcOEt 8/2). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.44 (m, 4H, CH_{arom}), 7.36 (m, 1H, CH_{arom}), 7.30 (m, 2H, CH_{arom}), 7.16 (dd, 1H, *J* = 11.0, 2.0 Hz, CH_{arom}), 7.09 (dd, 1H, *J* = 11.0, 2.0 Hz, CH_{arom}), 6.96 (m, 1H, CH_{arom}), 6.91 (dd, 2H, *J* = 9.6, 7.1 Hz, CH_{arom}), 6.78 (dd, 1H, *J* = 7.8, 3.7 Hz, CH_{arom}), 6.30 (m, 4H, CH_{arom}), 6.17 (m, 2H, CH_{arom}), 4.35 (dd, 4H, *J* = 13.2, 2.7 Hz, $ArCH_2Ar$), 3.87 (m, 4H, OCH_2, OPr), 3.64 (td, 4H, *J* = 7.0, 2.9 Hz, OCH_2, OPr), 3.39 (s, 3H, OCH_3), 3.04 (d, 4H, *J* = 13.2 Hz, $ArCH_2Ar$), 1.85 (m, 8H, CH_2CH_3, OPr), 0.95 (t, 6H, *J* = 7.4 Hz, CH_3, OPr), 0.8 (td, 6H, *J* = 7.4, 1.4 Hz, CH_3, OPr). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 161.4 (s, C_{arom}), 159.7 (d, *J* = 2.6 Hz, C_{arom}), 156.0 (s, C_{arom}), 155.6 (s, C_{arom}), 155.5 (s, C_{arom}), 137.9 (d, *J* = 4.9 Hz, C_{arom}), 136.5 (d, *J* = 4.7 Hz, C_{arom}), 136.3 (d, *J* = 4.7 Hz, C_{arom}), 135.8 (d, *J* = 11.2 Hz, C_{arom}), 133.7 (s, C_{arom}), 133.6 (s, C_{arom}), 133.5 (s, C_{arom}), 133.5 (d, *J* = 30.7 Hz, C_{arom}), 133.4 (s, C_{arom}), 133.2 (s, C_{arom}), 132.7 (s, C_{arom}), 130.4 (s, C_{arom}), 130.3 (d, *J* = 59.7 Hz, C_{arom}), 130.3 (s, C_{arom}), 128.2 (s, C_{arom}), 128.1 (d, *J* = 7.2 Hz, C_{arom}), 127.9 (s, C_{arom}), 127.7 (s, C_{arom}), 126.5 (s, C_{arom}), 122.3 (d, *J* = 1.9 Hz, C_{arom}), 121.6 (d, *J* = 11.2 Hz, C_{arom}), 121.1 (d, *J* = 63.0 Hz, C_{arom}), 117.9 (s, C_{arom}), 117.5 (s, C_{arom}), 111.4 (s, C_{arom}), 77.3 (s, CH_2O, OPr), 76.9 (s, CH_2O, OPr), 76.8 (s, CH_2O, OPr), 55.1 (s, OCH_3), 30.9 (s, $ArCH_2Ar$), 23.4 (s, CH_2CH_3, OPr), 23.3 (s, CH_2CH_3, OPr), 23.2 (s, CH_2CH_3, OPr), 23.0 (s, CH_2CH_3, OPr), 10.6 (s, CH_3, OPr), 10.6 (s, CH_3, OPr), 10.0 (s, CH_3, OPr) 9.9 (s, CH_3, OPr). ^{31}P NMR ($CDCl_3$, 121 MHz): δ +17.3. HRMS (ESI-Q-TOF): calcd for $C_{53}H_{61}BClNaO_5P$ $[M + Na]^+$ 877.39304, found 877.39045. Anal. Calcd for $C_{53}H_{61}BClO_5P$ (855.30): C, 74.43; H, 7.19. Found: C, 74.46; H, 7.30.

Preparation of Mono- and Diphosphines from Their Borane Complexes. *General Procedure.* In a 50 mL two-necked flask equipped with a magnetic stirrer and an argon inlet, 1 mmol of monophosphine−borane **4a−c** and 2 equiv of DABCO were dissolved in 2 mL of toluene (in the case of **8a−c** 4 equiv of DABCO were used). The reaction mixture was heated to 50 °C for 12 h. After it was cooled, the crude product was rapidly transferred via cannula into a column previously evacuated and filled with argon containing neutral alumina. The reaction solution was filtered using degassed dichloromethane as eluent. After removal of the solvent under vacuum/argon, the free phosphine was obtained in excellent yield.

*(S)-Methylphenyl{25,26,27,28-tetrapropoxycalix[4]arene}phosphine (**5a**):* yield 0.70 g, 98%; white solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.15−7.09 (m, 6H, CH_{arom}), 6.67−6.45 (m, 10H, CH_{arom}), 4.38 (AX system, 4H, *J* = 13.2 Hz, $ArCH_2Ar$), 3.77 (m, 8H, CH_2O, OPr), 3.06 (AX system, 4H, *J* = 14.4 Hz, $ArCH_2Ar$), 1.78 (m, 8H, CH_2CH_3, OPr), 1.29 (d, 3H, *J* = 3.0 Hz, CH_3P), 0.92 (m, 12H, CH_3, OPr). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 156.4 (s, C_{arom}), 155.3 (d, *J* = 12.8 Hz, C_{arom}), 134.1 (br.s, C_{arom}), 133.7 (d, *J* = 3.7 Hz, C_{arom}), 131.6 (d, *J* = 21.9 Hz, CH_{arom}), 131.1 (d, *J* = 17.4 Hz, CH_{arom}), 130.6 (d, *J* = 18.1 Hz, CH_{arom}), 127.1 (br.s, CH_{arom}), 126.7 (s, CH_{arom}), 122.0 (d, *J* = 3.0 Hz, CH_{arom}), 75.8 (s, CH_2O, OPr), 75.7 (s, CH_2O, OPr), 75.6 (s, CH_2O, OPr), 29.9 (s, $ArCH_2Ar$), 29.8 (s, $ArCH_2Ar$), 22.3 (s, CH_2CH_3, OPr), 22.2 (s, CH_2CH_3, OPr), 12.1 (d, *J* = 13.6 Hz, CH_3P), 9.3 (s, CH_3, OPr). ^{31}P NMR ($CDCl_3$, 121 MHz): δ −27.8.

*(S)-o-Anisylphenyl{25,26,27,28-tetrapropoxycalix[4]arene}phosphine (**5b**):* yield 0.79 g, 98%; white solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.16 (m, 2H, CH_{arom}), 6.71 (m, 6H, CH_{arom}), 6.53 (m, 1H, CH_{arom}), 6.34 (m, 6H, CH_{arom}), 4.35 (AX system, 4H, *J* = 13.2 Hz, $ArCH_2Ar$), 3.85 (m, 4H, CH_2O, OPr), 3.68 (m, 7H, CH_2O and CH_3O), 3.02 (AX system, 4H, *J* = 13.2, 10.4 Hz, $ArCH_2Ar$), 1.85 (m, 8H, CH_2CH_3, OPr), 0.91 (m, 12H, CH_3, OPr). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 160.0 (d, *J* = 14.8 Hz, C_{arom}), 156.4 (d, *J* = 73.8 Hz, C_{arom}), 154.9 (s, C_{arom}), 154.8 (s, C_{arom}), 136.8 (s, C_{arom}), 136.2 (s, C_{arom}), 136.1 (s, C_{arom}), 135.0 (s, CH_{arom}), 134.9 (d, *J* = 2.4 Hz, CH_{arom}), 134.8 (d, *J* = 2.7 Hz, CH_{arom}), 133.7 (s, CH_{arom}), 133.5 (s, CH_{arom}), 133.3 (s, CH_{arom}), 133.3 (s, CH_{arom}), 133.0 (d, *J* = 1.3 Hz, CH_{arom}), 132.5 (s, CH_{arom}), 132.5 (s, CH_{arom}), 132.2 (s, CH_{arom}), 129.1 (s, CH_{arom}), 128.0 (s, CH_{arom}), 127.4 (d, *J* = 5.2 Hz, CH_{arom}), 127.2 (s, CH_{arom}), 127.1 (s, CH_{arom}), 126.9 (s, CH_{arom}), 126.8 (s, CH_{arom}), 126.7 (s, CH_{arom}), 125.4 (d, *J* = 12.0 Hz, CH_{arom}), 124.3 (s, CH_{arom}), 121.0 (s, CH_{arom}), 120.9 (s, CH_{arom}), 120.9 (s, CH_{arom}), 119.9 (s, C_{arom}), 109.0 (s, CH_{arom}), 76.2 (s, CH_2O, OPr), 75.7 (s, CH_2O, OPr), 54.6 (s, CH_3O), 29.9 (s, $ArCH_2Ar$), 29.8 (s, $ArCH_2Ar$), 22.3 (s, CH_2CH_3, OPr), 22.2 (s, CH_2CH_3, OPr), 22.2 (s, CH_2CH_3, OPr), 22.1 (s, CH_2CH_3, OPr), 9.2 (s, CH_3, OPr), 9.1 (s, CH_3, OPr). ^{31}P NMR ($CDCl_3$, 121 MHz): δ −17.2.

*(S)-Ferrocenylphenyl{25,26,27,28-tetrapropoxycalix[4]arene}-phosphine (**5c**):* yield 0.86 g, 97%; orange solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.26−7.16 (m, 5H, CH_{arom}), 6.85−6.71 (m, 5H, CH_{arom}), 6.54−6.42 (m, 6H, CH_{arom}), 4.43 (AX system, 4H, $ArCH_2Ar$), 4.31 (t, 2H, *J* = 1.8 Hz, Fc), 4.07 (s, 5H, Fc), 4.04 (t, 1H, *J* = 1.8 Hz, Fc), 3.96 (t, 1H, *J* = 1.8 Hz, Fc), 3.92 (m, 4H, CH_2O, OPr), 3.80 (m, 4H, CH_2O, OPr), 3.14 (AX system, 4H, *J* = 13.2 Hz, $ArCH_2Ar$), 1.94 (m, 8H, CH_2CH_3, OPr), 0.98 (m, 8H, CH_3, OPr). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 157.6 (s, C_{arom}), 156.8 (s, C_{arom}), 156.1 (d, *J* = 4.5 Hz, C_{arom}), 140.2 (d, *J* = 9.8 Hz, C_{arom}), 135.5 (s, C_{arom}), 135.2 (d, *J* = 6.8 Hz, CH_{arom}), 135.1 (s, CH_{arom}), 134.7 (d, *J* = 4.5 Hz, CH_{arom}), 134.4 (d, *J* = 3.7 Hz, CH_{arom}), 134.3 (s, CH_{arom}), 133.9 (d, *J* = 12.1 Hz, CH_{arom}), 133.6 (s, CH_{arom}), 132.9 (d, *J* = 18.1 Hz, CH_{arom}), 130.2 (d, *J* = 6.0 Hz, CH_{arom}), 129.0 (s, CH_{arom}), 128.4 (br.s, CH_{arom}), 128.2 (s, CH_{arom}), 128.0 (br.s, CH_{arom}), 127.9 (s, CH_{arom}), 127.8 (s, CH_{arom}), 122.1 (s, CH_{arom}), 121.9 (s, CH_{arom}), 76.8 (s, CH_2O, OPr), 76.7 (s, CH_2O, OPr), 73.1 (d, *J* = 18.1 Hz, Fc), 72.1 (d, *J* = 11.3 Hz, Fc), 70.4 (d, *J* = 3.0 Hz, Fc), 70.3 (d, *J* = 4.5 Hz, Fc), 69.0 (br.s, Fc), 30.9 (br.s, $ArCH_2Ar$), 23.3 (br.s, CH_2CH_3, OPr), 23.2 (s, CH_2CH_3, OPr), 10.4 (s, CH_3, OPr), 10.3 (s, CH_3, OPr), 10.2 (s, CH_3, OPr). ^{31}P NMR ($CDCl_3$, 121 MHz): δ −17.1.

*(S,S)-5,17-Bis[(methylphenylphosphino)]{25,26,27,28-tetrapropoxycalix[4]arene} (**9a**):* yield 0.87 g, 97%; white solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.27−7.01 (m, 14H, CH_{arom}), 6.19 (t, 2H, *J* = 7.2 Hz, CH_{arom}), 6.07 (m, 4H, CH_{arom}), 4.34 (AX system, 4H, *J* = 13.2 Hz, $ArCH_2Ar$), 3.93 (m, 4H, CH_2O, OPr), 3.59 (t, 4H, *J* = 6.9 Hz, CH_2O, OPr), 3.03 (AX system, 4H, *J* = 13.5 Hz, $ArCH_2Ar$), 1.92−1.76 (m, 8H, CH_2CH_3), 1.57 (d, 6H, *J* = 3.3 Hz, CH_3P), 0.99 (t, 6H, *J* = 7.2 Hz, CH_3, OPr), 0.83 (t, 6H, *J* = 7.5 Hz, CH_3, OPr). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 158.6 (s, C_{arom}), 155.3 (s, C_{arom}), 137.9 (s, C_{arom}), 136.9 (d, *J* = 6.8 Hz, CH_{arom}), 136.8 (d, *J* = 7.5 Hz, CH_{arom}), 133.2 (d, *J* = 8.3 Hz, CH_{arom}), 131.6 (d, *J* = 18.1 Hz, CH_{arom}), 129.1 (s, CH_{arom}), 128.2 (s, CH_{arom}), 128.1 (s, CH_{arom}), 127.8 (s, CH_{arom}), 127.5 (d, *J* = 3.8 Hz, CH_{arom}), 125.3 (s, CH_{arom}), 122.1 (s, C_{arom}), 77.2 (s, CH_2O, OPr), 76.9 (s, CH_2O, OPr), 30.9 (s, $ArCH_2Ar$), 23.5 (s, CH_2CH_3, OPr), 23.1 (s, CH_2CH_3, OPr), 13.0 (d, *J* = 6.0 Hz, CH_3P), 10.8 (s, CH_3, OPr), 9.9 (s, CH_3, OPr). ^{31}P NMR ($CDCl_3$, 121 MHz): δ −28.0.

The enantiomeric excess of **9a** was determined by comparison with a racemic sample, by ^{31}P NMR in the presence of (+)-di-μ-chlorobis{2[1-(dimethylamino)ethyl]phenyl-*C*,*N*}dipalladium (**12**). ^{31}P NMR ($CDCl_3$, 121 MHz): δ +26.0.

*(S,S)-5,17-Bis[(o-anisylphenylphosphino)]{25,26,27,28-tetrapropoxycalix[4]arene} (**9b**):* yield 1.05 g, 98%; white solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.27 (m, 11H, CH_{arom}), 7.11−7.05 (m, 3H, CH_{arom}), 6.90−6.80 (m, 6H, CH_{arom}), 6.76−6.62 (m, 2H, CH_{arom}), 6.16 (t, 2H, *J* = 6.0 Hz, CH_{arom}), 6.03−5.95 (m, 4H, CH_{arom}), 4.32 (AX system, 4H, *J* = 12.0 Hz, $ArCH_2Ar$), 3.96 (t, 4H, *J* = 9.0 Hz, CH_2O, OPr), 3.71 (s, 6H, CH_3O), 3.51 (t, 4H, *J* = 6.0 Hz, CH_2O, OPr), 2.96 (AX system, 4H, *J* = 12.0 Hz, $ArCH_2Ar$), 1.89 (m, 4H, CH_2CH_3, OPr), 1.74 (m, 4H, CH_2CH_3, OPr), 0.98 (t, 6H, *J* = 9.0 Hz, CH_3, OPr), 0.82 (t, 6H, *J* = 9.0 Hz, CH_3, OPr). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 161.1 (d, *J* = 15.8 Hz, C_{arom}), 158.8 (s, C_{arom}), 155.1 (s, C_{arom}), 137.6 (d, *J* = 10.6 Hz, C_{arom}), 137.3 (d, *J* = 6.5 Hz, C_{arom}), 137.1 (d, *J* = 9.5 Hz, C_{arom}), 135.2 (d, *J* = 26.7 Hz, CH_{arom}), 134.7 (d, *J* = 15.8 Hz, CH_{arom}), 133.8 (s, CH_{arom}), 133.5 (d, *J* = 3.0 Hz, CH_{arom}), 132.9 (s, C_{arom}), 130.1 (s, CH_{arom}), 129.0 (s, CH_{arom}), 128.5 (d, *J* = 7.5 Hz, C_{arom}), 128.3 (br.s, CH_{arom}), 128.2 (d, *J* = 2.5 Hz, CH_{arom}), 127.4 (d, *J* = 6.2 Hz, CH_{arom}), 126.9 (d, *J* = 13.0 Hz, C_{arom}), 125.3 (s, CH_{arom}), 121.3 (d, *J* = 65.7 Hz, CH_{arom}), 110.1 (s, CH_{arom}), 76.9 (s, CH_2O, OPr), 76.4 (s, CH_2O, OPr), 55.6 (s, CH_3O), 30.8 (s, $ArCH_2Ar$), 23.4

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(s, CH_2CH_3, OPr), 23.1 (s, CH_2CH_3, OPr), 10.8 (s, CH_3, OPr), 9.8 (s, CH_3, OPr), ^{31}P NMR ($CDCl_3$, 121 MHz): δ −17.3.

The enantiomeric excess of **9b** was determined by comparison with a racemic sample, by ^{31}P NMR in the presence of (+)-di-μ-chlorobis{2[1-(dimethylamino)ethyl]phenyl-*C*,*N*}dipalladium (**12**). ^{31}P NMR ($CDCl_3$, 125 MHz): δ +31.5.

*(S,S)-5,17-Bis[(ferrocenylphenylphosphino)]{25,26,27,28-tetrapropoxycalix[4]arene} (**9c**):* yield 1.16 g, 99%; orange solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.38−7.13 (m, 14H, CH_{arom}), 6.27 (t, 2H, J = 7.8 Hz, CH_{arom}), 6.12 (t, 4H, J = 7.8 Hz, CH_{arom}), 4.23 (AX system, 8H, ArCH_2Ar and Fc), 4.27 (m, 2H, Fc), 4.18 (m, 2H, Fc), 4.15 (br.s, 10H, Fc), 4.05 (m, 4H, CH_2O, OPr), 3.64 (t, 4H, J = 6.6 Hz, CH_2O, OPr), 3.11 (AX system, 4H, J = 13.5 Hz, ArCH_2Ar), 2.01−1.93 (m, 4H, CH_2CH_3, OPr), 1.89−1.82 (m, 4H, CH_2CH_3, OPr), 1.08 (t, 6H, J = 7.2 Hz, CH_3, OPr), 0.92 (t, 6H, J = 7.5 Hz, CH_3, OPr). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 158.8 (s, C_{arom}), 155.1 (s, C_{arom}), 140.6 (d, J = 10.6 Hz, C_{arom}), 136.8 (d, J = 6.0 Hz, C_{arom}), 134.8 (d, J = 12.1 Hz, CH_{arom}), 134.5 (d, J = 8.3 Hz, CH_{arom}), 133.0 (br.s, CH_{arom}), 132.8 (s, CH_{arom}), 130.7 (d, J = 6.8 Hz, C_{arom}), 129.0 (s, CH_{arom}), 128.2 (s, CH_{arom}), 128.0 (s, CH_{arom}), 127.9 (d, J = 3.0 Hz, CH_{arom}), 127.4 (d, J = 3.8 Hz, CH_{arom}), 125.3 (s, CH_{arom}), 121.9 (s, CH_{arom}), 75.9 (s, CH_2O, OPr), 76.4 (s, CH_2O, OPr), 73.4 (d, J = 17.3 Hz, Fc), 72.2 (d, J = 11.3 Hz, Fc), 70.6 (d, J = 3.6 Hz, Fc), 70.4 (d, J = 5.1 Hz, Fc), 69.1 (br.s, Fc), 31.0 (s, ArCH_2Ar), 23.5 (s, CH_2CH_3, OPr), 23.1 (s, CH_2CH_3, OPr), 10.8 (s, CH_3, OPr), 9.9 (s, CH_3, OPr). ^{31}P NMR ($CDCl_3$, 121 MHz): δ −17.3.

The enantiomeric excess of **9c** was determined by comparison with a racemic sample, by ^{31}P NMR in the presence of (+)-di-μ-chlorobis{2[1-(dimethylamino)ethyl]phenyl-*C*,*N*}dipalladium (**12**). ^{31}P NMR ($CDCl_3$, 125 MHz): δ +32.7.

Typical Procedure for the Allylic Alkylation. A degassed solution of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (0.003 g, 0.008 mmol) and the ligand **9a−c** (0.016 mmol) (or 0.032 mmol of **5a**) in dichloromethane (2 mL) was stirred for 30 min. Subsequently, a solution of (*E*)-1,3-diphenylprop-2-en-1-yl acetate (0.202 g, 0.8 mmol) in dichloromethane (2 mL), dimethyl malonate (0.2 mL, 1.6 mmol), *N*,*O*-bis(trimethylsilyl)acetamide (0.4 mL, 1.6 mmol), and a pinch of KOAc were added. The reaction mixture was stirred at the desired temperature. After the desired reaction time, the reaction mixture was diluted with Et_2O and saturated aqueous NH_4Cl solution was added. The mixture was extracted with Et_2O, and the organic phases were dried over $MgSO_4$. The solvent was removed, and the conversion was measured by ^{1}H NMR. The enantiomeric excess was determined by HPLC on a chiral column (Chiralpak AD, hexane/*i*-PrOH 90/10, 0.5 mL/min, $t_R(R)$ = 21.5 min, $t_R(S)$ = 30.3 min), after purification by flash column chromatography on silica gel using petroleum ether/ethyl acetate 10/1 as eluent. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33−7.18 (m, 10H, CH_{arom}), 6.48 (d, 1H, J = 16.0 Hz, C*H*═), 6.33 (dd, 1H, J = 8.2, 16.0 Hz, C*H*═), 4.27 (dd, 1H, J = 8.2, 11.2 Hz, C*H*), 3.96 (d, 1H, J = 11.2 Hz, C*H*), 3.70 (s, 3H, CH_3), 3.52 (s, 3H, CH_3).

Typical Procedure for the Allylic Amination. A degassed solution of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (0.002 g, 0.005 mmol) and ligand **9a,b** (0.012 mmol) (or 0.024 mmol of ligand **5a,b**) in dichloromethane (2 mL) was stirred for 30 min. Subsequently, a solution of (*E*)-1,3-diphenylprop-2-en-1-yl acetate (0.125 g, 0.5 mmol) in dichloromethane (2 mL) and benzylamine (0.158 mL, 1.45 mmol) were added. The reaction mixture was stirred at the desired temperature. After the desired reaction time, the mixture was diluted with Et_2O and saturated aqueous NH_4Cl solution was added. The mixture was extracted with Et_2O, and the organic phases were dried over $MgSO_4$. The solvent was removed, and the conversion was measured by ^{1}H NMR. The enantiomeric excess was determined by HPLC on a chiral column (Chiralcel OD-H, hexane/*i*-PrOH 99/1, 0.5 mL/min, $t_R(R)$ = 40.2 min, $t_R(S)$ = 44.3 min), after purification by flash column chromatography on silica gel using *n*-hexane/ethyl acetate 8/2 as eluent. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.52−7.13 (m, 15H, CH_{arom}), 6.58 (d, 1H, J = 15.8 Hz, C*H*═), 6.32 (dd, 1H, J = 7.6, 15.8 Hz, C*H*═), 4.40 (d, 1H, J = 7.6 Hz, C*H*), 3.79 (d, 1H, J = 13.2 Hz, CH_2N), 3.77 (d, 1H, J = 13.2 Hz, CH_2N), 1.70 (s, 1H, *H*N).

■ ASSOCIATED CONTENT

Supporting Information

Figures giving NMR spectra and tables and CIF files giving crystallographic data for (*R*)-**4b**, (*S*)-**4c**, (*S*,*S*)-**8c**, and (*S*)-**11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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