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Chiral Calixarenes

Chiral Phosphinoferrocenyl-Calixarenes

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Abstract: The Mitsunobu alkylation of 4-*tert*-butylcalix[4]arene with (*S*)-(2-diphenylthiophosphinoferrocenyl)methanol followed by desulfuration of the thiophosphine unit using tris(dimethylamino)phosphine afforded enantiomerically pure calixarene mono- and di(ferrocenylphosphine) ligands in high yields. The calixarene mono(ferrocenylphosphine) ligands exhibited good catalytic activity but low atropoenantioselectivity when used in the asymmetric Suzuki–Miyaura coupling reaction of 1-naphthaleneboronic acid and 1-bromo-2-methylnaphthalene. However, the di(ferrocenylphosphine) ligand displayed both good catalytic activity and enantioselectivity (*ee* values up to 86 %) when employed in the asymmetric Tsuji–Trost allylic alkylation of 1,3-diphenylprop-2-enyl acetate with dimethyl malonate.

Introduction

Calixarenes are fascinating macrocyclic molecules that have increased the interest in supramolecular chemistry over the past decades.[1] The synthetic versatility of calixarenes and their ability to form host–guest supramolecular complexes allow for the use of calixarene derivatives in numerous applications, such as biomedicine,[2] nanoscience,[3] and sensors.[4] Catalysis is another important application of calixarenes,[5] and efficient catalytic systems based on calixarenes have been developed.[6] However, calixarenes have seldomly been used for asymmetric catalysis.[7] On the other hand, chiral ferrocenyl units are privileged ligands[8] for asymmetric catalysis.

Herein, we present the synthesis of ferrocene-containing enantiomerically pure calixarene derivatives and the first investigation of their use as catalysts in the asymmetric Suzuki–Miyaura coupling and Tsuji–Trost allylic alkylation reactions. Indeed, some calixarenes that contain ferrocenyl moieties have already been described,[9] but to the best of our knowledge, none in an enantiomerically pure form and rarely for catalysis.[7i]

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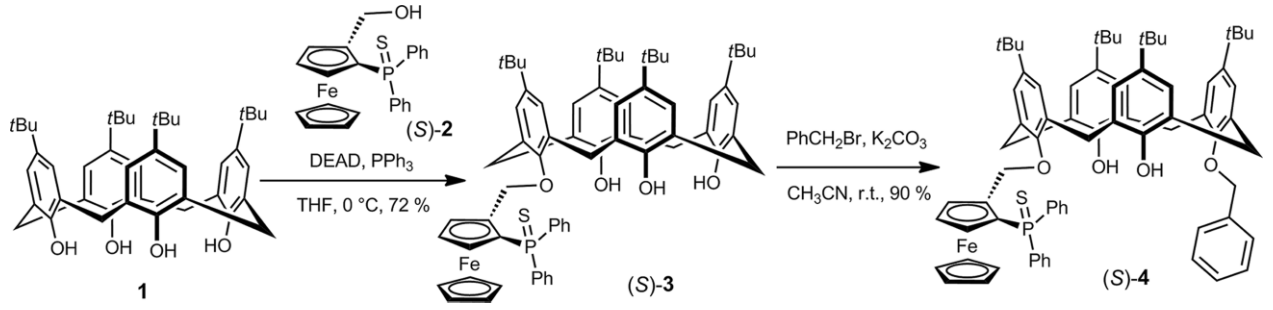
Results and Discussion

Upon activation by tetrafluoroboric acid, (*S*)-(2-diphenylthiophosphinoferrocenyl)methanol [(*S*)-**2**] can successfully alkylate various nucleophiles,[10,11] including alcohols.[12] However, this method failed when 4-*tert*-butylcalix[4]arene (**1**) was used as the nucleophile. In this case, (thiophosphinoferrocenyl)methanol [(*S*)-**2**] decomposed under the reaction conditions without the formation of any of the desired ferrocene-containing calixarene.

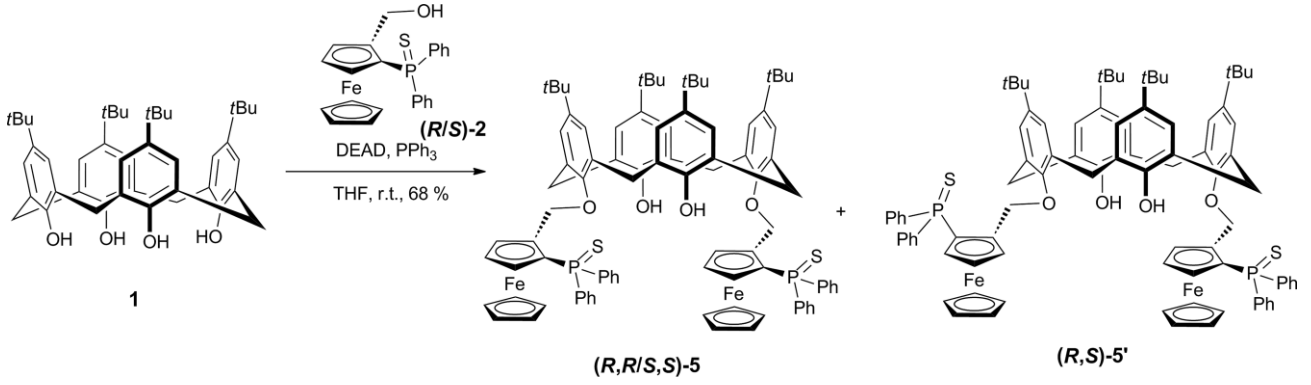
We then decided to use milder conditions to activate phenol **1**. Using classical Mitsunobu reaction conditions [i.e., PPh_3 and diethyl azodicarboxylate (DEAD)], which have been successfully applied to the selective *O*-alkylation of calix[4]arenes,[13] we were able to synthesize monosubstituted (*S*)-**3** selectively in 72 % yield by using 4-*tert*-butylcalix[4]arene (**1**) in tetrahydrofuran (THF) at 0 °C (Scheme 1). The subsequent alkylation of calixarene (*S*)-**3** with benzyl bromide in acetonitrile under basic conditions at room temperature exclusively yielded distally disubstituted compound (*S*)-**4** (Scheme 1). This type of regioselectivity, which is commonly explained by the intramolecular hydrogen-bonding interactions between the OH groups at the lower rim of the macrocycle, is typical of monosubstituted calixarenes.[13]

When the Mitsunobu condensation of calixarene **1** with ferrocenylmethanol (*S*)-**2** was carried out at room temp., instead of at 0 °C, distal di(thiophosphinoferrocenyl) calixarene (*S*,*S*)-**5** (Scheme 2) was formed in good yield after 35 h. A similar distal substitution has been observed in the alkylation of calixarenes under Mitsunobu conditions.[13]

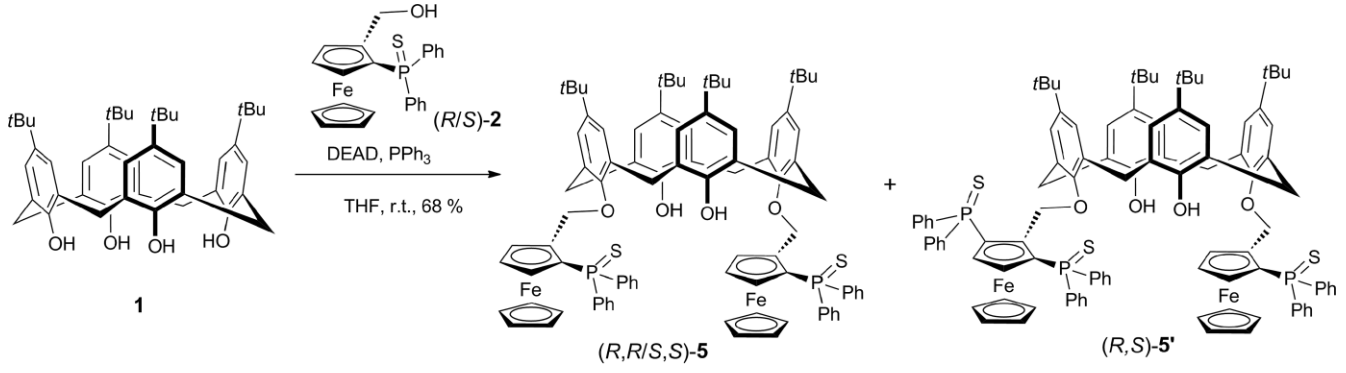
To determine whether any erosion in the enantiomeric purity of the ferrocene occurs during the synthesis of (*S*,*S*)-**5**, we carried out a reaction between **1** and racemic **2**, instead of enantiomerically pure (*S*)-**2**, under the same conditions (Scheme 3). Two inseparable diasteroisomers in a 1:1 ratio resulted from this reaction, and only a small number of ^{31}P and ^{1}H NMR signals of the resulting *meso* diastereoisomer (*R*,*S*)-**5′** could be identi-



Scheme 1. Synthesis of calixarene monothiophosphines (*S*)-**3** and (*S*)-**4**.



Scheme 2. Synthesis of calixarene dithiophosphine (*S*,*S*)-**5**.



Scheme 3. Synthesis of the mixture of calixarene dithiophosphines **5** and **5′**.

fied (see Supporting Information). These signals are absent from the spectrum of (*S*,*S*)-**5**, which proves that (*S*,*S*)-**5** is diastereoisomerically and, therefore, enantiomerically pure. We also concluded that no erosion in the enantiomeric purity of the ferrocene occurs during the synthesis of (*S*,*S*)-**3**, which is carried out under milder conditions (at 0 °C instead of room temp.).

Single crystals suitable for X-ray diffraction analysis were obtained by the slow evaporation of acetonitrile solutions of compounds (*S*)-**3** and (*S*,*S*)-**5**. A molecular view of compound (*S*)-**3** is shown in Figure 1. As observed in related calixarenes that are substituted with ferrocenyl moieties,[14] the calixarene of (*S*)-**3** has an irregular cone conformation with a dihedral angle between the two distal phenyl rings that contain a hydroxyl group of 77.5(5)°. The dihedral angle between the other two distal phenyl rings, which contain a hydroxyl and ferrocenyl group, is 55.0(2)°. Within the ferrocenyl moiety, the two cyclopentadienyl (Cp) rings are nearly parallel with a dihedral angle of 3.2(3)°, and the substituted Cp ring is nearly coplanar with the bisecting plane of the calixarene ring (defined by the O-1, C-111, C-311, and O-3 atoms) having a dihedral angle of 11.61(4)°. As expected, intramolecular O–H···O hydrogen bonds between the hydroxyl groups are present in the crystals of compound (*S*)-**3** (Table 1).

In the crystal structure of compound (*S*,*S*)-**5**, there are two roughly identical molecules within the asymmetric unit, but only one of them is represented in Figure 2. The poor quality

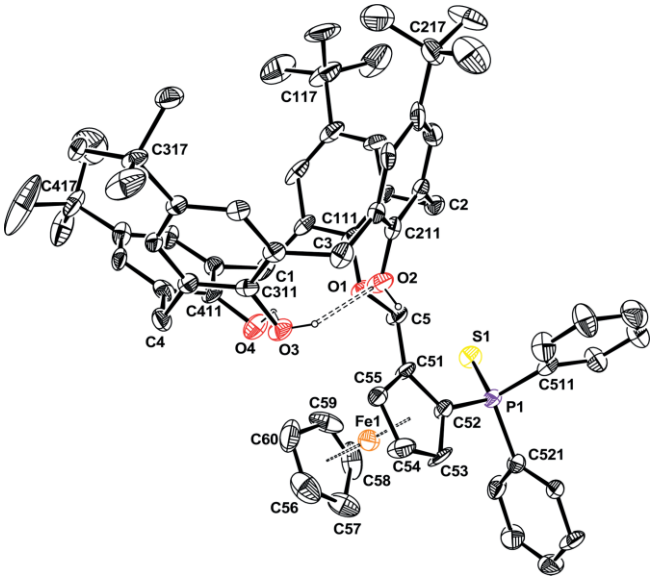


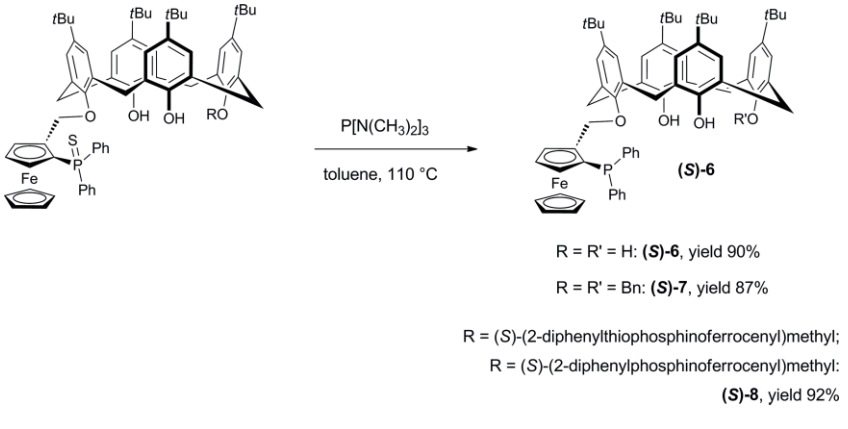
Figure 1. Ortep view of (*S*)-**3** with the atom labeling scheme. Ellipsoids are drawn at the 30 % probability level. The H atoms attached to the C atoms have been omitted for the sake of clarity. Hydrogen bonds between the hydroxyl groups are represented as a dashed line.

Table 1. Intramolecular O–H···O hydrogen bonds [Å] between the hydroxyl groups in the crystal of (*S*)-**3**.

D–H···A	D–H	H···A	D···A	D–H···A
O-3–H-3···O-2	0.82	1.99	2.672(11)	139.8
O-4–H-4···O-3	0.82	2.04	2.654(11)	131.7

of the data does not allow a detailed discussion of the bonding parameters, but it clearly proves the molecular structure, which confirms the spectral analyses. The distances between the O atoms suggest the presence of hydrogen bonding.

Thiophosphino calixarenes **3**–**5** could then be efficiently deprotected by treatment with $P(NMe_2)_3$[10–12] to yield new enantiomerically pure phosphine ferrocenyl ligands **6**–**8**, respectively (Scheme 4).



Scheme 4. Desulfuration of thiophosphines.

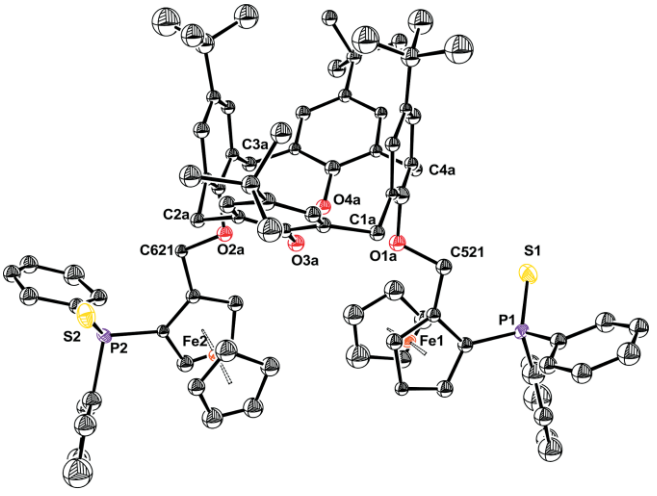


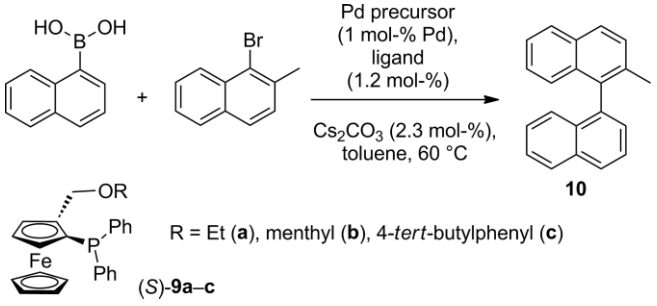
Figure 2. Ortep view of compound (*S*,*S*)-**5** with the atom labeling scheme. Ellipsoids are drawn at the 30 % probability level. H atoms attached to the C atoms have been omitted for the sake of clarity.

The catalytic efficiency of chiral calixarene mono(ferrocenylphosphine) ligands (*S*)-**6** and (*S*)-**7** was examined in a palladium-catalyzed Suzuki–Miyaura cross-coupling reaction, and that of the di(ferrocenylphosphine) ligand (*S*,*S*)-**8** was assessed in the Tsuji–Trost allylic substitution reaction.

The asymmetric version of the well-known palladium-catalyzed Suzuki–Miyaura cross-coupling reaction has only been developed in the last fifteen years and is still challenging, as no reports of privileged ligands with a broad substrate scope have emerged.[15] If efficient catalytic systems for the Suzuki–Miyaura cross-coupling reaction with calixarene-based ligands have previously been developed,[6f,6h,16] an asymmetric version has not yet been published. To determine whether the calixarene macrocyclic frame can influence the coupling reaction of 1-naphthaleneboronic acid and 1-bromo-2-methylnaphthalene, we compared the reactions that included the addition of ligands (*S*)-**6** and (*S*)-**7** to that of the model diphenylphosphino ferrocenes (*S*)-**9a**–(*S*)-**9c** (Table 2).[12] When bis(dibenzylideneacetone)palladium(0) [$Pd(dba)_2$] was used as the palladium precursor and the reaction was carried out at 60 °C, the catalytic

systems based on ligands (*S*)-**6** and (*S*)-**7** were sluggish compared with the those that contained ligands (*S*)-**9a**–(*S*)-**9b** (Table 2). However, when the allylpalladium chloride dimer was used, full conversion and good yields of the coupling products were obtained after 24 h (Table 2). The enantiomeric excess values of 2-methyl-1,1′-binaphthalene (**10**), however, were very low [less than 5 % for (*S*)-**6** and (*S*)-**7**)]. The values for (*S*)-**6** and (*S*)-**7** were lower than those obtained by using the other phosphine-ether ligands based on the same chiral scaffold (*S*)-**9a**–(*S*)-**9c**, and even lower than **9c**, which is a better model of ligands **6** and **7** in terms of its stereoelectronic properties because it contains a 4-*tert*-butylphenyl substituent (Table 2).[12] Contrary to expectations, the free hydroxy groups on the lower rim of the calixarene ligands do not have a positive effect on the catalysis of the reaction because of the formation of hydrogen bonds with the incoming boronic acids. Possibly, these OH groups could enter the palladium coordination sphere and give several coordination complexes to result in an overall lowering of the enantioselectivity.

Table 2. Suzuki–Miyaura coupling reactions.[a]

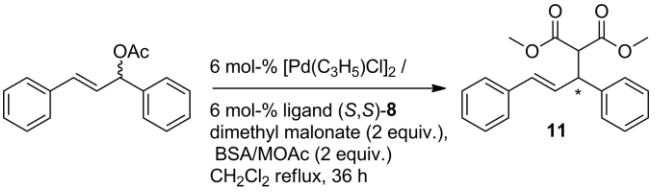


Entry	Ligand	Palladium precursor	Yield [%][b]	% *ee*
1[b]	**6**	$Pd(dba)_2$	<5	–
2[b]	**7**	$Pd(dba)_2$	<5	–
3[b]	**6**	$[Pd(Cl)(allyl)]_2$	66	<5 %
4[b]	**7**	$[Pd(Cl)(allyl)]_2$	100	<5 %
5[c]	**9a**	$Pd(dba)_2$	100	12
6[c]	**9b**	$Pd(dba)_2$	99	26
7[c,d]	**9b**	$Pd(dba)_2$	75	37
8[b]	**9c**	$[Pd(Cl)(allyl)]_2$	82	34 %

[a] Reagent and conditions: ligand (0.012 mmol, 1.2 mol-%), palladium precursor (1.1 mol-% of palladium), 1-naphthaleneboronic acid (1.2 mmol), cesium carbonate (2.3 mol-%), and 1-bromo-2-methylnaphthalene (1.00 mmol) in toluene (10 mL) at 60 °C for 24 h. [b] From this work. [c] See ref.[12]. [d] Reaction was carried out at 40 °C.

We have also employed ligand (*S*,*S*)-**8** in the asymmetric allylic alkylation of 1,3-diphenylprop-2-enyl acetate with dimethyl malonate (Table 3).[17] Full conversion and good yields of malonate **11** were obtained regardless of the acetate salt used with the *N*,*O*-bis(trimethylsilyl)acetamide (BSA) probase. However, the enantiomeric excess value of the product strongly depended on the alkaline cation of the acetate, and the best enantioselectivity was obtained with the potassium cation (Table 3, Entry 3). To the best of our knowledge, this 86 % *ee* is the best result obtained for an asymmetric allylic substitution with a calixarene-based ligand.[7i,18] In the presence of the potassium cation, we propose that the dimethyl malonate anion interacts more strongly with the two hydroxyl groups of ligand (*S*,*S*)-**8** to selectively direct the nucleophile towards one carbon atom of the π-allyl intermediate. This hypothesis is further supported by the addition of the K^+-specific complexing agent 18-crown-6 crown ether to the reaction mixture, which resulted in a drop in the *ee* value of the product (Table 3, Entry 4).

Table 3. Asymmetric allylic alkylation in presence of the diphosphine ligand (*S*,*S*)-**8**.



Entry	Base	Yield [%][a]	% *ee*
1	CH_3COOLi/BSA	86	14
2	CH_3COONa/BSA	76	25
3	CH_3COOK/BSA	75	86
4	CH_3COOK/BSA [+ 18-crown-6 (1.2 equiv.)]	86	32
5	CH_3COOCs/BSA	88	71

[a] Isolated yield with full conversion.

Conclusions

We have described the synthesis of three enantiomerically pure phosphinoferrocenyl-substituted calixarene ligands. These compounds are the first calixarene derivatives that contain planar chiral ferrocenyl moieties. We have carried out preliminary catalytic studies with these ligands in the asymmetric Suzuki–Miyaura coupling reaction and the asymmetric Tsuji–Trost reaction. Although the resulting enantioselectivities of the Suzuki–Miyaura reaction were disappointing, interesting enantiomeric excess values (*ee* values up to 86 %) were obtained by using ligand (*S*,*S*)-**8** in the asymmetric allylic alkylation reaction. An investigation of the coordination of ligands **6**–**8** is now necessary to explore the potential of these ligands in asymmetric catalysis, especially for ligand (*S*,*S*)-**8**, which displays a large bite angle.[19,20]

Experimental Section

General Methods: All reactions were carried out under argon by using standard Schlenk techniques. Solvents were carefully dried by conventional methods and distilled under argon before use. 4-*tert*-Butyl-calix[4]arene (**1**)[21] and (*S*)-(2-diphenylthiophosphinoferrocenyl)methanol [(*S*)-**2**][22] were synthesized according to literature procedures. $[Pd(C_3H_5)Cl]_2$ was purchased from Strem Chemicals and used as received. The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopic data were recorded with a Bruker Avance 500 FT-NMR spectrometer. The resonances were calibrated relative to the residual solvent peaks and are reported with positive values downfield from TMS. The ^1H and ^{13}C NMR signal assignments for all of the characterized compounds were made by using COSY, heteronuclear single quantum correlation (HSQC), and HMBC 2D experiments. HRMS data were obtained from dichloromethane solutions of the samples, and

the HRMS was performed on a Xevo G2 Q TOF spectrometer by electrospray ionization.

Synthesis of 5,11,17,23-Tetra-*tert*-butyl-25-(*S*)-(2-diphenylthiophosphinoferrocenyl)methoxy-26,27,28-calix[4]arene [(*S*)-3]: In a Schlenk tube under argon, a mixture of 4-*tert*-butylcalix[4]arene (**1**, 0.308 mmol), triphenylphosphine (0.496 mmol), and (*S*)-(2-diphenylthiophosphinoferrocenyl)methanol [(*S*)-**2**, 0.694 mmol] was dissolved in THF (48 mL) and then cooled in an ice bath. At this temperature, diethyl diazodicarboxylate (40 % in toluene, 0.659 mmol) was added dropwise. The resulting mixture was stirred at room temperature for 24 h, and the solvent was removed in vacuo. Purification by flash chromatography on a silica gel column (EtOAc/hexanes, 1:20) gave (*S*)-**3** (72 % yield) as an orange solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.17 (s, 1 H, OH), 9.55 (s, 1 H, OH), 9.33 (s, 1 H, OH), 7.91 (m, 2 H, Ar), 7.78 (m, 2 H, Ar), 7.56 (m, 3 H, Ar), 7.3–6.9 (m, 11 H, Ar), 5.76 (br. s, 1 H, subst Cp), 5.49 [d (AB system), J = 11.6 Hz, 1 H, CH_2], 5.32 [d (AB system), J = 11.6 Hz, 1 H, CH_2], 4.70 [d (AB system), J = 12.6 Hz, 1 H, CH_2], 4.66 (br. s, 1 H, subst Cp), 4.47 (s, 5 H, Cp), 4.35 [d (AB system), J = 13.5 Hz, 1 H, CH_2], 4.20 [d (AB system), J = 13.7 Hz, 1 H, CH_2], 3.94 (br. s, 1 H, subst Cp), 3.51 (m, 4 H, 4H CH_2), 2.97 [d (AB system), J = 13.5 Hz, 1 H, CH_2], 1.25 (s, 27 H, *t*Bu), 1.19 (s, 9 H, *t*Bu) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 148.9 (s, quat Ar *C*-OH), 148.8 (s, quat Ar *C*-OCH_2), 148.0 (s, quat Ar *C*-OH + quat Ar *C*-*t*Bu), 147.6 (s, quat Ar *C*-OH), 143.7 (s, quat Ar *C*-*t*Bu), 143.1 (s, quat Ar *C*-*t*Bu), 142.9 (s, quat Ar *C*-*t*Bu), 134.2 (d, J = 86.5 Hz, quat Ar PPh_2), 134.0 (s, quat Ar *C*-CH_2), 133.2 (d, J = 86.0 Hz, quat Ar PPh_2), 132.6 (s, quat Ar *C*-CH_2), 132.1 (d, J = 10.9 Hz, CH Ar PPh_2), 131.8 (d, J = 10.6 Hz, CH Ar PPh_2), 131.4 (d, J = 2.7 Hz, CH Ar PPh_2), 131.1 (d, J = 2.8 Hz, CH Ar PPh_2), 129.2 (s, quat Ar *C*-CH_2), 128.7 (s, quat Ar *C*-CH_2), 128.4 (d, J = 12.5 Hz, CH Ar PPh_2), 128.1 (d, J = 12.4 Hz, CH Ar PPh_2), 127.7 (s, quat Ar *C*-CH_2), 127.5 (s, quat Ar *C*-CH_2), 127.4 (s, quat Ar *C*-CH_2), 126.75 (s, quat Ar *C*-CH_2 or Ar *C*H), 126.74 (s, quat Ar *C*-CH_2 or Ar *C*H), 126.1 (s, Ar *C*H), 125.8 (s, 2C Ar *C*H), 125.61 (s, Ar *C*H), 125.55 (s, 2C Ar *C*H), 125.49 (s, Ar *C*H), 83.5 (d, J = 12.0 Hz, quat Cp), 74.70 (d, J = 8.9 Hz, subst Cp), 74.66 (d, J = 12.1 Hz, subst Cp), 74.0 (s, CH_2), 71.2 (s, Cp), 73.8 (d, J = 94.8 Hz, quat Cp), 70.7 (d, J = 10.2 Hz, subst Cp), 34.21 (*C*-CH_3), 34.04 (*C*-CH_3), 33.92 (*C*-CH_3), 33.90 (*C*-CH_3), 33.15 (s, CH_2), 33.10 (s, CH_2), 32.10 (s, CH_2), 31.59 (s, CH_3), 31.56 (s, CH_3), 31.49 (s, CH_3), 31.45 (s, CH_2), 31.2 (s, CH_3) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 40.9 ppm. HRMS (ESI–): calcd. for $C_{67}H_{75}FeO_4PS$ [M – H] 1061.4397; found 1061.4397. $[\alpha]_D^{20}$ = +28.8 ($CHCl_3$, c = 0.5).

Synthesis of 5,11,17,23-Tetra-*tert*-butyl-25-(*S*)-(2-diphenylthiophosphinoferrocenyl)methoxy-27-benzyloxy-26,28-calix[4]arene [(*S*)-4]: To a mixture of 5,11,17,23-tetra-*tert*-butyl-25-(*S*)-(2-diphenylthiophosphinoferrocenyl)methoxy-26,27,28-calix[4]arene [(*S*)-**3**, 0.100 mmol] and potassium carbonate (0.500 mmol) in dry acetonitrile (10 mL) in a Schlenk tube at room temperature under argon was added benzyl bromide (0.250 mmol) dropwise. The resulting mixture was stirred at room temperature for 12 h and then diluted with HCl (2 M). The resulting mixture was extracted with CH_2Cl_2. The organic phase was washed with distilled water (2 × 15 mL) and brine and then dried with Na_2SO_4. The solvent was removed in vacuo, and the crude product was purified by flash chromatography on a silica gel column (EtOAc/hexanes, 1:25), to give (*S*)-**4** (90 % yield) as an orange solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83 (m, 2 H, Ar), 7.72 (m, 2 H, Ar), 7.62 (m, 4 H, Ar), 7.47 (m, 6 H, ArH), 7.34 (m, 4 H, Ar OH), 7.15 (br. s, 1 H, OH), 7.14 (br. s, 1 H, Ar), 7.12 (d, J = 2.2 Hz, 1 H, Ar), 7.10 (d, J = 2.2 Hz, 1 H, Ar), 7.03 (d, J = 2.2 Hz, 1 H, Ar), 6.79 (br. s, 1 H, Ar), 6.77 (br. s, 1 H, Ar), 6.75 (br. s, 1 H, Ar), 6.68 (d, J = 2.1 Hz, 1 H, Ar), 5.63 [d (AB system), J = 12.4 Hz, 1 H, CH_2], 5.46 (br. s, 1 H, subst Cp), 5.07 [dd (AB system), J = 11.4 Hz, 2 H, Ph*C*H_2O], 4.52 [d (AB system), J = 12.8 Hz, 1 H, CH_2], 4.52 [d (AB system), J = 12.9 Hz, 1 H, CH_2], 4.44 (m, 5 H, Cp + 1 H, CH_2), 4.58 (d, 1 H, CH_2), 4.40 [d (AB system), J = 13.6 Hz, 1 H, CH_2], 4.35 (br. s, 1 H, subst Cp), 4.00 [d (AB system), J = 13.1 Hz, 1 H, CH_2], 3.79 (br. s, 1 H, subst Cp), 3.45 [d (AB system), J = 13.6 Hz, 1 H, CH_2], 3.36 [d (AB system), J = 13.1 Hz, 1 H, CH_2], 3.34 [d (AB system), J = 13.1 Hz, 1 H, CH_2], 3.08 [d (AB system), J = 13.4 Hz, 1 H, CH_2], 1.36 (s, 9 H, *t*Bu), 1.34 (s, 9 H, *t*Bu), 0.93 (s, 9 H, *t*Bu), 0.92 (s, 9 H, *t*Bu) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 150.9 (s, quat Ar *C*-CH_2), 150.8 (s, quat Ar *C*-CH_2), 149.9 (s, quat Ar *C*-OCH_2), 149.5 (s, quat Ar *C*-OH), 147.0 (s, quat Ar *C*-*t*Bu), 146.9 (s, quat Ar *C*-*t*Bu), 141.4 (s, quat Ar *C*-*t*Bu), 141.3 (s, quat Ar *C*-*t*Bu), 137.3 (s, quat Ar *C*-OCH_2), 134.5 (d, J = 86.5 Hz, quat Ar PPh_2), 133.4 (d, J = 86.0 Hz, quat Ar PPh_2), 132.6 (s, quat Ar *C*-CH_2), 132.4 (s, quat Ar *C*-CH_2), 132.2 (s, quat Ar *C*-CH_2), 132.1 (s, quat Ar *C*-CH_2), 132.08 (s, Ar *C*H), 131.97 (s, Ar *C*H), 131.77 (s, Ar *C*H), 131.66 (s, Ar *C*H), 131.25 (d, J = 2.9 Hz, CH Ar PPh_2), 131.18 (d, J = 2.9 Hz, CH Ar PPh_2), 128.62 (s, Ar *C*H), 128.4 (d, J = 12.6 Hz, CH Ar PPh_2), 128.1 (d, J = 12.3 Hz, CH Ar PPh_2), 127.9 (s, Ar *C*H), 127.83 (s, quat Ar *C*-CH_2), 127.80 (s, quat Ar *C*-CH_2), 127.76 (s, Ar *C*H), 127.62 (s, quat Ar *C*-CH_2), 127.53 (s, quat Ar *C*-CH_2), 125.6 (s, Ar *C*H), 125.5 (s, Ar *C*H), 125.3 (s, Ar *C*H), 125.2 (s, Ar *C*H), 125.1 (s, Ar *C*H), 125.0 (s, Ar *C*H), 124.9 (s, Ar *C*H), 124.8 (s, Ar *C*H), 88.9 (d, J = 11.6 Hz, quat Cp), 78.2 (s, PhCH_2O), 74.2 (d, J = 12.1 Hz, subst Cp), 73.5 (d, J = 95.2 Hz, quat Cp), 72.7 (s, CH_2), 72.1 (d, J = 9.0 Hz, subst Cp), 71.1 (s, 5 C, CH Cp), 69.4 (d, J = 10.2 Hz, subst Cp), 33.90 (*C*-CH_3), 33.86 (*C*-CH_3), 33.84 (*C*-CH_3), 31.77 (s, CH_3), 31.75 (s, CH_3 + CH_2), 33.65 (s, CH_2), 31.48 (s, CH_2), 31.24 (s, CH_2), 30.97 (s, CH_3) ppm. ^{31}P NMR (400 MHz, $CDCl_3$): δ = 41.5 ppm. HRMS (ESI+): calcd. for $C_{74}H_{81}FeO_4PS$ $[M]^+$ 1152.4943; found 1152.4923. $[\alpha]_D^{20}$ = +15.4 ($CHCl_3$, c = 0.6).

Synthesis of 5,11,17,23-Tetra-*tert*-butyl-25,27-bis[(*S*)-(2-diphenylthiophosphinoferrocenyl)methoxy]-26,28-calix[4]arene [(*S*,*S*)-5]: In a Schlenk tube under argon, a mixture of 4-*tert*-butylcalix[4]-arene (**1**, 0.308 mmol), triphenylphosphine (0.992 mmol), and (*S*)-(2-diphenylthiophosphinoferrocenyl)methanol [(*S*)-**2**, 0.992 mmol] was dissolved in THF (48 mL) and then cooled in an ice bath. At this temperature, diethyl diazodicarboxylate (40 % in toluene, 1.317 mmol) was added dropwise. The resulting mixture was stirred at room temperature for 35 h, and the solvent was then removed in vacuo. The crude product was purified by flash chromatography on a silica gel column (EtOAc/hexanes, 1:15) to give (*S*)-**5** (68 % yield) as an orange solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (dd, 4 H, Ar), 7.64 (dd, 4 H, Ar), 7.51 (m, 6 H, Ar), 7.32 (m, 6 H, Ar), 7.14 (d, J = 2.5 Hz, 2 H, Ar), 7.01 (d, J = 2.2 Hz, 2 H, Ar), 6.94 (br. s, 2 H, OH), 6.66 (d, J = 2.2 Hz, 2 H, Ar), 6.60 (d, J = 2.3 Hz, 2 H, Ar), 5.53 [m, 2 H, subst Cp + (AB system), J = 11.9 Hz, 2 H, CH_2], 4.64 [d (AB system), J = 12.4 Hz, 2 H, CH_2], 4.52 (m, 10 H, Cp + 2 H, CH_2), 4.44 (m, 2 H, subst Cp), 3.92 [d (AB system), J = 13.1 Hz, 2 H, CH_2], 3.80 (m, 2 H, subst Cp), 3.45 [d (AB system), J = 13.1 Hz, 2 H, CH_2], 3.02 [d (AB system), J = 13.1 Hz, 2 H, CH_2], 1.35 (s, 18 H, *t*Bu), 0.85 (s, 18 H, *t*Bu) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 150.7 (s, quat Ar *C*-CH_2), 149.6 (s, quat Ar *C*-OH), 146.8 (s, quat Ar *C*-*t*Bu), 141.3 (s, quat Ar *C*-*t*Bu), 134.3 (d, J = 86.4 Hz, quat Ar PPh_2), 133.3 (d, J = 85.4 Hz, quat Ar PPh_2), 132.11 (s, quat Ar *C*-CH_2), 132.11 (s, CH Ar PPh_2), 131.99 (s, CH Ar PPh_2), 131.91 (s, CH Ar PPh_2), 131.67 (d, J = 10.8 Hz, CH Ar PPh_2), 131.3 (d, J = 2.7 Hz, CH Ar PPh_2), 128.45 (d, J = 12.2 Hz, CH Ar PPh_2), 128.1 (d, J = 12.2 Hz, CH Ar PPh_2), 127.96 (s, quat Ar *C*-CH_2), 127.75 (s, CH Ar PPh_2), 125.25 (s, quat Ar *C*-CH_2), 125.19 (s, CH Ar), 124.9 (s, CH Ar), 88.84 (d, J = 11.5 Hz, quat Cp), 74.2 (d, J = 12.3 Hz, subst Cp), 74.07 (d, J = 94.9 Hz, subst Cp *C*-PPh_2), 72.82 (s, CH_2), 72.57 (d, J = 9.1 Hz, subst Cp), 71.22 (s, Cp), 71.16 (s, subst Cp), 69.21 (d, J = 9.9 Hz, subst Cp), 33.84 (*C*-CH_3), 33.78 (*C*-CH_3),

31.77 (s, CH_3), 31.45 (s, CH_2), 30.99 (s, CH_2), 30.90 (s, CH_3) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 41.3 ppm. HRMS (ESI–): calcd. for $C_{90}H_{93}Fe_2O_4P_2S_2$ [M – H] 1475.4689; found 1475.4765. $[\alpha]_D^{20}$ = +15.0 ($CHCl_3$, *c* = 0.5).

Synthesis of (4-*tert*-Butylphenyl) (*S*)-[(2-Diphenylthiophosphinoferrocenyl)methyl] Oxide: In a Schlenk tube under argon, a mixture of 4-*tert*-butylphenol (0.616 mmol), triphenylphosphine (0.992 mmol), and (*S*)-(2-diphenylthiophosphinoferrocenyl)methanol (0.308 mmol) was dissolved in THF (48 mL) and then cooled in an ice bath. At this temperature, diethyl diazodicarboxylate (40 % in toluene, 1.317 mmol) was added dropwise, and the resulting mixture was stirred at room temperature for 12 h. The solvent was removed in vacuo, and the crude product was purified by flash chromatography on a silica gel column (EtOAc/hexanes, 1:10) to give the product (82 % yield) as an orange solid. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.85 (m, 2 H, PPh_2), 7.66 (m, 2 H, PPh_2), 7.49 (m, 2 H, PPh_2), 7.34 (m, 4 H, PPh_2), 7.21 (m, 2 H, *O*-C_6H_4-*p*-*t*Bu), 6.64 (m, 2 H, *O*-C_6H_4-*p*-*t*Bu), 5.05 [d (AB system), *J* = 11.1 Hz, 1 H, CH_2], 5.02 [d (AB system), *J* = 11.1 Hz, 1 H, CH_2], 4.75 (br. s, 1 H, subst Cp), 4.40 (br. s, 1 H, subst Cp), 4.39 (s, 5 H, unsubst Cp), 3.95 (br. s, 1 H, subst Cp), 1.29 [s, 9 H, $C(CH_3)_3$] ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 159.3 (quat Ar *C*-O-CH_2), 143.2 (quat Ar *C*-O-*t*Bu), 133.8 (d, $^1J_{C,P}$ = 19.4 Hz, quat Ar *C*-P), 132.2 (d, $^3J_{C,P}$ = 10.8 Hz, PhH), 132.0 (d, $^3J_{C,P}$ = 10.7 Hz, PhH), 131.3 (d, $^4J_{C,P}$ = 2.9 Hz, PhH), 131.1 (d, $^4J_{C,P}$ = 2.9 Hz, PhH), 128.2 (d, $^2J_{C,P}$ = 11.2 Hz, PhH), 128.0 (d, $^2J_{C,P}$ = 11.2 Hz, PhH), 125.9 (ArH), 114.1 (ArH), 87.5 (d, *J* = 11.7 Hz, quat Cp), 75.11 (d, *J* = 12.6 Hz, subst Cp), 73.78 (d, *J* = 9.2 Hz, subst Cp), 70.8 (s, Cp), 75.0 (d, *J* = 94.6 Hz, quat Cp), 69.7 (d, *J* = 10.4 Hz, subst Cp), 64.7 (s, CH_2), 34.0 [*C*(CH_3)$_3$], 31.5 [C(*C*H_3)$_3$] ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 41.7 ppm. HRMS (ESI–): calcd. for $C_{33}H_{33}FeOPSNa$ [M + Na] 587.1237; found 587.1245 (25 %); calcd. for $C_{23}H_{20}FePS$ [M – (OAr)] 415.0373; found 415.0378 (100 %). $[\alpha]_D^{20}$ = +36.1 ($CHCl_3$, *c* = 0.4).

General Procedure of Desulfuration of the Thiophosphines: In a Schlenk tube, the thiophosphine derivative (0.115 mmol) was dissolved in toluene (5 mL) along with tris(dimethylamino)phosphine (0.2 mL) under argon. The resulting solution was heated at reflux overnight. After the mixture was cooled to room temp., the solvent was removed in vacuo. The crude product was purified by flash chromatography under argon on a silica gel column (CH_2Cl_2) to give the product as an orange solid.

5,11,17,23-Tetra-*tert*-butyl-25-(*S*)-(2-diphenylphosphinoferrocenyl)methoxy-26,27,28-calix[4]arene [(*S*)-6]: (90 % yield). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.50 (m, 2 H, Ar), 7.36 (m, 3 H, 2 OH, Ar), 7.30 (m, 2 H, Ar), 7.26 (m, 1 H, Ar), 7.18 (m, 2 H, Ar), 7.15 (m, 1 H, Ar), 7.10 (m, 1 H, Ar), 7.08 (m, 1 H, Ar), 7.05 (m, 1 H, Ar), 7.00 (m, 3 H, Ar), 7.00 (br. s, 1 H, OH), 6.87 (m, 1 H, Ar), 6.77 (m, 2 H, Ar), 4.69 [d (AB system), *J* = 14.6 Hz, 1 H, CH_2], 4.62 (m, 2 H, CH_2), 4.58 (m, 1 H, subst Cp), 4.31 [td (AB system), *J* = 12.6 Hz, 3 H, CH_2], 4.23 (m, 2 H, CH_2), 3.94 (s, 5 H, Cp), 3.66 [d (AB system), *J* = 14.5 Hz, 2 H, CH_2], 3.65 [d (AB system), *J* = 14.4 Hz, 1 H, CH_2], 3.61 (br. s, 1 H, subst Cp), 1.42 (s, 9 H, *t*Bu), 1.39 (s, 9 H, *t*Bu), 1.29 (s, 9 H, *t*Bu), 1.17 (s, 9 H, *t*Bu) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 154.8 (s, quat Ar *C*-OH), 147.08 (s, quat Ar *C*-OCH_2), 147.05 (s, quat Ar *C*-OH + quat Ar *C*-*t*Bu), 147.6 (s, quat Ar *C*-OH), 146.5 (s, quat Ar *C*-*t*Bu), 146.2 (s, quat Ar *C*-*t*Bu), 145.9 (s, quat Ar *C*-*t*Bu), 144.4 (s, Ar *C*H), 138.9 (d, *J* = 8.8 Hz, quat Ar PPh_2), 137.4 (d, *J* = 8.8 Hz, quat Ar PPh_2), 135.3 (s, Ar *C*H), 135.1 (s, Ar *C*H), 134.9 (d, *J* = 3.7 Hz, CH Ar PPh_2), 134.8 (d, *J* = 3.7 Hz, CH Ar PPh_2), 133.3 (s, quat Ar *C*-CH_2), 133.28 (s, Ar CH), 133.22 (s, quat Ar *C*-CH_2), 132.94 (s, quat Ar *C*-CH_2), 132.91 (s, quat Ar *C*-CH_2), 131.8 (s, CH Ar), 131.6 (s, CH Ar), 130.4 (d, *J* = 2.9 Hz, quat Ar), 131.4 (d, *J* = 2.9 Hz, quat Ar), 129.02 (s, CH Ar), 128.1 (s, CH Ar), 128.0 (s, CH Ar), 127. 8 (s, Ar *C*H), 127.7 (s, Ar *C*H), 127.1 (s, CH Ar), 126.3 (s, CH Ar), 126.25 (s, CH Ar), 126.12 (s, CH Ar), 125.8 (s, CH Ar), 125.6 (s, CH Ar), 125.5 (s, CH Ar), 89.00 (d, *J* = 24.2 Hz, quat Cp), 72.4 (d, *J* = 3.7 Hz, subst Cp), 71.3 (d, *J* = 3.7 Hz, subst Cp), 70.9 (d, *J* = 11.2 Hz, CH_2), 70.7 (s, subst Cp), 69.7 (s, subst Cp), 69.6 (s, Cp), 34.4 (*C*-CH_3), 34.3 (*C*-CH_3), 34.2 (s, CH_2), 34.0 (s, CH_2), 33.6 (s, CH_2), 31.7 (s, CH_3), 31.6 (s, CH_3), 31.5 (s, CH_3) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = –22.2 ppm.

5,11,17,23-Tetra-*tert*-butyl-25-(*S*)-(2-diphenylphosphinoferrocenyl)methoxy-27-benzyloxy-26,28-calix[4]arene [(*S*)-7]: (87 % yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.69 (m, 2 H, Ar), 7.55 (m, 3 H, Ar), 7.4 (m, 6 H, ArH, 2 OH), 7.14 (m, 8 H, ArH), 7.03 (m, 2 H, Ar), 6.77 (m, 3 H, Ar), 6.70 (br. s, 1 H, Ar), 5.23 (br. s, 1 H, subst Cp), 5.17 [d (AB system), *J* = 11.8 Hz, 1 H, CH_2], 5.06 [dd (AB system), *J* = 11.4 Hz, 2 H, PhCH_2O], 4.52 [d (AB system), *J* = 12.8 Hz, 1 H, CH_2], 4.52 [d (AB system), *J* = 12.9 Hz, 1 H, CH_2], 4.40 (br. s, 1 H, subst Cp), 4.38 (d, *J* = 13.5 Hz, 2 H, CH_2), 4.36 (br. s, 1 H, subst Cp), 4.19 (s, 5 H, Cp), 4.16 [d (AB system), *J* = 13.3 Hz, 1 H, CH_2], 3.43 [d (AB system), *J* = 13.6 Hz, 1 H, CH_2], 3.36 [d (AB system), *J* = 13.8 Hz, 1 H, CH_2], 3.34 [d (AB system), *J* = 13.8 Hz, 1 H, CH_2], 3.14 [d (AB system), *J* = 13.2 Hz, 1 H, CH_2], 1.35 (s, 9 H, *t*Bu), 1.33 (s, 9 H, *t*Bu), 0.94 (s, 9 H, *t*Bu), 0.92 (s, 9 H, *t*Bu) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 150.9 (s, quat Ar *C*-CH_2), 150.8 (s, quat Ar *C*-CH_2), 149.9 (s, quat Ar *C*-OCH_2), 149.8 (s, quat Ar *C*-OH), 146.9 (s, quat Ar *C*-*t*Bu), 146.8 (s, quat Ar *C*-*t*Bu), 141.3 (s, quat Ar *C*-*t*Bu), 141.2 (s, quat Ar *C*-*t*Bu), 137.2 (s, quat Ar *C*-OCH_2), 134.9 (d, *J* = 20.5 Hz, quat Ar PPh_2), 132.4 (d, *J* = 24.3 Hz, quat Ar PPh_2), 129.2 (s, quat Ar *C*-CH_2), 129.1 (s, quat Ar *C*-CH_2), 128.9 (s, quat Ar *C*-CH_2), 128.6 (s, Ar *C*H), 128.3 (s, Ar *C*H), 128.2 (s, Ar *C*H), 128.1 (s, Ar *C*H), 127.92 (s, Ar *C*H), 127.89 (s, Ar *C*H), 127.85 (s, quat Ar *C*-CH_2), 127.78 (s, quat Ar *C*-CH_2), 127.77 (s, Ar *C*H), 127.59 (s, quat Ar *C*-CH_2), 127.43 (s, quat Ar *C*-CH_2), 125.5 (s, Ar *C*H), 125.46 (s, Ar *C*H), 125.3 (s, Ar *C*H), 125.2 (s, Ar *C*H), 125.05 (s, Ar *C*H), 125.02 (s, Ar *C*H), 124.99 (s, Ar *C*H), 124.86 (s, Ar *C*H), 89.68 (d, *J* = 22.7 Hz, quat Cp), 78.3 (s, Ph*C*H_2O), 73.5 (d, *J* = 12.5 Hz, subst Cp), 70.95 (d, *J* = 3.7 Hz, quat Cp), 70.2 (d, *J* = 3.7 Hz, subst Cp), 70.0 (s, 5 C, CH Cp), 69.7 (subst Cp), 69.6 (s, CH_2), 53.4 (CH_2), 33.90 (*C*-CH_3), 33.86 (*C*-CH_3), 33.83 (*C*-CH_3), 31.77 (s, CH_3), 31.75 (s, CH_3 + CH_2), 31.50 (s, CH_2), 31.48 (s, CH_2), 31.24 (s, CH_2), 30.98 (s, CH_3), 30.96 (s, CH_3) ppm. ^{31}P NMR (400 MHz, $CDCl_3$): δ = –23.0 ppm.

5,11,17,23-Tetra-*tert*-butyl-25,27-bis[(*S*)-(2-diphenylphosphinoferrocenyl)methoxy]-26,28-calix[4]arene [(*S*,*S*)-8]: (92 % yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.56 (m, 4 H, Ar), 7.40 (m, 6 H, Ar), 7.22–7.06 (m, 12 H, Ar), 7.00 (d, *J* = 2.2 Hz, 2 H, Ar), 6.97 (br. s, 2 H, OH), 6.69 (d, *J* = 2.2 Hz, 2 H, Ar), 6.62 (d, *J* = 2.2 Hz, 2 H, Ar), 5.25 (br. s, 2 H, subst Cp), 5.49 [d (AB system), *J* = 11.9 Hz, 2 H, CH_2], 4.62 [d (AB system), *J* = 11.3 Hz, 2 H, CH_2], 4.55 [d (AB system), *J* = 12.6 Hz, 2 H, CH_2], 4.39 (m, 2 H, subst Cp), 4.24 (s, 10 H, Cp), 4.05 [d (AB system), *J* = 13.1 Hz, 2 H, CH_2], 3.77 (m, 2 H, subst Cp), 3.42 [d (AB system), *J* = 13.0 Hz, 2 H, CH_2], 3.07 [d (AB system), *J* = 13.2 Hz, 2 H, CH_2], 1.35 (s, 18 H, *t*Bu), 0.86 (s, 18 H, *t*Bu) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 150.8 (s, quat Ar *C*-OCH_2), 149.9 (s, quat Ar *C*-OH), 146.7 (s, quat Ar *C*-*t*Bu), 141.1 (s, quat Ar *C*-*t*Bu), 139.1 (d, *J* = 9.8 Hz, quat Ar PPh_2), 137.1 (d, *J* = 9.2 Hz, quat Ar PPh_2), 135.1 (s, Ar *C*H), 134.9 (s, Ar *C*H), 132.23 (s, quat Ar *C*-CH_2), 132.21 (s, Ar CH), 132.03 (s, quat Ar *C*-CH_2), 132.01 (s, quat Ar *C*-CH_2), 129.1 (s, CH Ar), 128.7 (d, *J* = 86.0 Hz, quat Ar PPh_2), 128.24 (d, *J* = 9.8 Hz, CH Ar PPh_2), 128.17 (d, *J* = 11.4 Hz, CH Ar PPh_2), 127.9 (s, s, quat Ar *C*-CH_2), 127.7 (d, *J* = 22.8 Hz, CH Ar PPh_2), 125.29 (s, Ar *C*H), 125.18 (s, quat Ar *C*-CH_2), 124.98 (s, Ar *C*H), 124.89 (s, Ar *C*H), 89.47 (d, *J* = 23.2 Hz, quat Cp), 74.63 (d, *J* = 7.4 Hz, subst Cp), 73.72 (s, CH_2), 73.60 (s, CH_2), 71.08 (d, *J* = 3.4 Hz, subst Cp), 70.91 (d, *J* = 3.5 Hz, subst Cp), 70.06 (s, Cp), 69.66 (s, subst Cp), 33.82 (*C*-CH_3), 33.78 (*C*-

CH_3), 31.77 (s, CH_3), 31.62 (s, CH_2), 31.23 (s, CH_2), 30.92 (s, CH_3) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = –23.0 ppm.

(4-*tert*-Butylphenyl) [(2-Diphenylphosphinoferrocenyl)methyl] Oxide [(*S*)-9c]: (93 % yield). In a Schlenk tube, thiophosphine (0.115 mmol) was dissolved in toluene (5 mL) along with tris(dimethylamino)phosphine (0.2 mL) under argon. The resulting mixture was heated at reflux overnight. After the mixture was cooled to room temp., the solvent was removed in vacuo. The crude product was purified by flash chromatography under argon on a silica gel column (CH_2Cl_2), to give (*S*)-**9c** (93 % yield) as an orange solid. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.61 (m, 2 H, PPh_2), 7.40 (m, 8 H, PPh_2), 7.24 (m, 2 H, O-C_6H_4-*p*-*t*Bu), 6.71 (m, 2 H, O-C_6H_4-*p*-*t*Bu), 4.98 [dd (AB system), *J* = 10.6 Hz, *J* = 2.1 Hz, 1 H, CH_2], 4.92 [d (AB system), *J* = 10.6 Hz, 1 H, CH_2], 4.65 (br. s, 1 H, subst Cp), 4.37 (br. s, 1 H, subst Cp), 4.11 (s, 5 H, unsubst Cp), 3.86 (br. s, 1 H, subst Cp), 1.31 [s, 9 H, $C(CH_3)_3$] ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 156.6 (quat Ar *C*-O-CH_2), 143.2 (quat Ar *C*-O-*t*Bu), 139.8 (d, $^1J_{C,P}$ = 9.5 Hz, quat Ar *C*-P), 137.5 (d, $^1J_{C,P}$ = 9.5 Hz, quat Ar *C*-P), 135.2 (d, $^2J_{C,P}$ = 21.1 Hz, PhH), 133.8 (d, $^3J_{C,P}$ = 19.4 Hz, PhH), 132.3 (d, $^3J_{C,P}$ = 17.7 Hz, PhH), 126.0 (ArH), 114.1 (ArH), 88.5 (d, *J* = 23.9 Hz, quat Cp), 72.0 (d, *J* = 17.4 Hz, subst Cp), 72.1 (d, *J* = 17.2 Hz, subst Cp), 69.7 (s, Cp), 65.5 (d, *J* = 10.5 Hz, quat Cp), 55.8 (s, CH_2), 34.0 [*C*$(CH_3)_3$], 31.5 [C$(CH_3)_3$] ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = –22.5 ppm.

X-ray Analyses of 5,11,17,23-Tetra-*tert*-butyl-25-(*S*)-(2-diphenylthiophosphinoferrocenyl)methoxy-26,27,28-calix[4]arene [(*S*)-3] and 5,11,17,23-Tetra-*tert*-butyl-25,27-bis[(*S*)-(2-diphenylthiophosphinoferrocenyl)methoxy]-26,28-calix[4]arene [(*S,S*)-5]: Single crystals of (*S*)-**3** and (*S,S*)-**5** were mounted under inert perfluoropolyether on the tip of a loop and cooled in the cryostream of an Agilent Technologies GEMINI extra diffractometer with an EOS CCD detector. Data were collected by using monochromatic Mo-K_α radiation (λ = 0.71073 Å). The structure was solved by direct method (SIR97)[23] and refined by least-squares procedures on F^2 using the SHELXL-2013 program.[24] All H atoms attached to the C and O atoms were introduced at idealized positions and treated as riding on their parent atoms in the calculations. The crystal of (*S,S*)-**5** was poorly diffracting, and the data were only collected to 21° in θ. In the refinement of (*S,S*)-**5**, only heavy atoms were anisotropically refined. The drawings of the molecules were realized with the help of the ORTEP3 program.[25]Crystal data and refinement parameters are shown in Table 4.

Table 4. Crystal data and structure refinement for (*S*)-**3** and (*S,S*)-**5**.

	(*S*)-**3**	(*S,S*)-**5**
Empirical formula	$C_{67}H_{72}FeO_4PS$	$C_{90}H_{94}Fe_2O_4P_2S_2$
Formula mass	1060.12	1477.41
Temperature [K]	173(6)	173(2)
Wavelength [Å]	0.71073	0.71073
Crystal system	monoclinic	triclinic
Space group	$P2_1$	*P*1
a [Å]	12.6601(6)	14.7815(11)
b [Å]	16.3669(8)	16.9173(13)
c [Å]	14.1157(6)	20.6642(18)
α [°]	90	66.980(1)
β [°]	94.585(4)	89.966(7)
γ [°]	90	64.153(8)
Volume [Å^3]	2915.5(2)	4189.1(7)
Z	2	2
Density(calc) [Mg m^{-3}]	1.208	1.171
Abs. coefficient [mm^{-1}]	0.369	0.482
F(000)	1126	1560
Crystal size [mm]	0.2 × 0.2 × 0.07	0.1 × 0.08 × 0.07
θ range [°]	2.967–25.023	3.097–20.813
Reflections collected	27984	14645
Independent reflections (R_{int})	10254 (0.0805)	10884 (0.0991)
Completeness [%]	99.8	89.8
Absorption correction	multiscan	multiscan
Max./min. transmission	1.000 and 0.897	1.0 and 0.9612
Refinement method	F^2	F^2
Data/restraints/parameters	10254/4/671	10884/3/877
Goodness-of-fit on F^2	1.033	0.989
*R*1, *wR*2 [$I > 2\sigma(I)$]	0.0858, 0.1941	0.1096, 0.2539
*R*1, *wR*2 (all data)	0.1372, 0.2353	0.1688, 0.2993
Flack's parameter	0.026(16)	–0.03(5)
Residual density [e Å^{-3}]	0.867/–0.426	0.717/–0.497

CCDC 1415644 [for (*S*)-**3**] and 1451985 [for (*S,S*)-**5**] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

General Procedure for Asymmetric Suzuki–Miyaura Coupling Reaction: The ligand (0.012 mmol, 1.2 mol-%), $[Pd(C_3H_5)Cl]_2$ (1.8 mg, 0.005 mmol, 1.1 mol-%), 1-naphthaleneboronic acid (1.2 mmol), cesium carbonate (750 mg, 2.030 mmol, 2.3 mol-%), and 1-bromo-2-methylnaphthalene (1.00 mmol) were introduced, under an argon stream, into a Schlenk tube that contained toluene (10 mL). The reaction mixture was stirred at 60 °C for 24 h under Ar. The mixture was cooled to room temp., and then acidified water (1 mol L^{-1} HCl water solution) was added. The resulting mixture was extracted with diethyl ether, and the organic phase was then filtered through silica. The solvent was removed under reduced pressure to give the product. The enantiomeric excess value was determined by supercritical fluid chromatography (SFC)-HPLC [Chiralcel OJ column; CO_2/*i*PrOH, 9:1; flow rate: 4 mL min^{-1}]: t_R = 5.04 min (*R* isomer) and 8.68 min (*S* isomer).

General Procedure for Asymmetric Allylic Substitution: A mixture of calixarene ligand (*S,S*)-**8** (0.003 mmol), 1,3-diphenylprop-2-enyl acetate (0.126 g, 0.5 mmol), and $[Pd(C_3H_5)Cl]_2$ (5.3 mg, 0.0015 mmol) was dissolved in dry dichloromethane (20 mL). Dimethyl malonate (0.115 mL, 1 mmol), the acetate salt (1 mmol), and BSA (0.250 mL, 1 mmol) were then added to the resulting solution. The reaction was heated at reflux, and the progress of the reaction was monitored by TLC analysis. After 36 h, the mixture was quenched by the addition of a saturated aqueous solution of ammonium chloride (20 mL). The aqueous phase was extracted with dichloromethane, and the combined organic layers were dried with magnesium sulfate and filtered. The solvent was evaporated. The conversion was calculated by using the integration of signals of the ^1H NMR spectra for the crude reaction mixture. Subsequent purification by chromatography on silica (dichloromethane/pentane, 1:1) afforded the product as a colorless oil. The enantiomeric excess value was determined by ^1H NMR spectroscopy using the chiral shift reagent (+)-Eu(hfc)$_3$ [hfc = (heptafluoropropylhydroxymethylene)-camphorate].

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Keywords: Asymmetric catalysis · Calixarenes · Phosphorus · Cyclopentadienyl ligands · Alkylation

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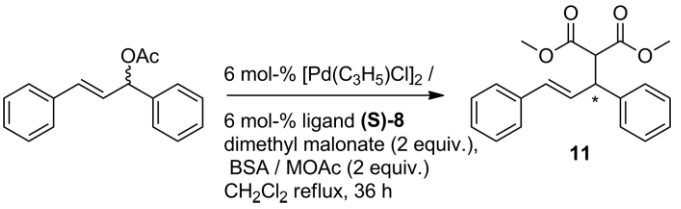

The Mitsunobu alkylation of 4-*tert*-butylcalix[4]arene and (*S*)-(2-diphenylthiophosphinoferrocenyl)methanol followed by desulfuration gave enantiomerically pure calixarene mono- and di(ferrocenylphosphine) ligands. These ligands have good catalytic activity, but the di(ferrocenylphosphine) ligand also showed good enantioselectivity (up to 86 % *ee*) in an asymmetric Tsuji–Trost allylic alkylation.

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