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## Chiral Phosphinoferrocenyl Calixarenes.

Andrii Karpus,<sup>1,2,3</sup> Oleksandr Yesypenko,<sup>4</sup> Vyacheslav Boiko,<sup>4</sup> Rinaldo Poli,<sup>1,2,5</sup> Jean-Claude Daran,<sup>1,2</sup> Zoia Voitenko,<sup>3\*</sup> Vitaly Kalchenko,<sup>4\*</sup> Eric Manoury<sup>1,2\*</sup>

<sup>1</sup> Université Toulouse III - Paul Sabatier, 118 route de Narbonne 31062 Toulouse Cedex 9

<sup>2</sup> Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne,  
31077 Toulouse cedex 4, [eric.manoury@lcc-toulouse.fr](mailto:eric.manoury@lcc-toulouse.fr)

<sup>3</sup> Taras Shevchenko National University of Kyiv, 64/13 Volodymyrska st.,  
Kiev, 01033, Kyiv, Ukraine, [z.voitenko@ukr.net](mailto:z.voitenko@ukr.net)

<sup>4</sup> Institute of Organic Chemistry NAS of Ukraine, Murmanska st. 5,  
Kyiv, Ukraine, 02660, [vik@ioch.kiev.ua](mailto:vik@ioch.kiev.ua)

<sup>5</sup> Institut Universitaire de France, 103, bd Saint-Michel, 75005 Paris, France

**Abstract:** By the Mitsunobu alkylation of 4-*tert*-butyltetrahydroxycalix[4]arene with (S)-(2-diphenylthiophosphinoferrocenyl)methanol, followed by desulfuration of the thiophosphine unit by tris-(dimethylamino)phosphine, enantiomerically pure calixarene mono- or diferrocenyldiphosphine ligands were synthesized in high yields. The calixarene ferrocenylphosphine ligands exhibited good catalytic activity but low atropoenantioselectivity in the asymmetric Suzuki-Miyaura coupling reaction of 1-naphthaleneboronic acid and 1-bromo-2-methylnaphthalene. However, the diferrocenyldiphosphine ligand displayed good catalytic activity and enantioselectivity (*ee* up to 86%) in the asymmetric Tsuji-Trost allylic alkylation of 1,3-diphenylprop-2-enyl acetate by dimethylmalonate.

### Introduction

Calixarenes are fascinating macrocyclic molecules that have raised great interest in supramolecular chemistry in the last decades.<sup>1</sup> The synthetic versatility of calixarenes and their ability to form host-guest supramolecular complexes allow using calixarene derivatives in numerous applications, such as in biomedicine,<sup>2</sup> nanoscience,<sup>3</sup> sensors,<sup>4</sup> etc. Catalysis has also been one important application of calixarenes<sup>5</sup> and quite efficient catalytic systems based on

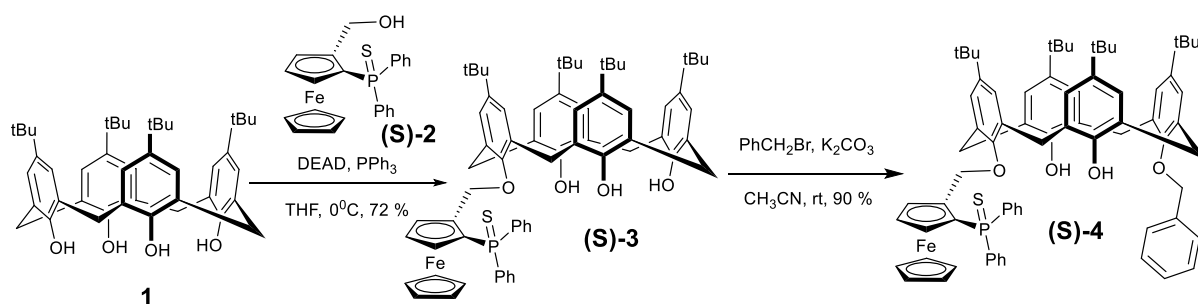
calixarenes have been developed.<sup>6</sup> However calixarenes have been much less used in asymmetric catalysis.<sup>7</sup> On the other hand, chiral ferrocenyl ligands are privileged ligands<sup>8</sup> for asymmetric catalysis.

In this communication, we present the synthesis and the first catalytical tests in the asymmetric Suzuki-Miyaura coupling reaction or the Tsuji-Trost allylic alkylation of ferrocene-containing chiral enantiomerically pure calixarene derivatives. Indeed, some calixarenes bearing ferrocenyl moieties have already been described<sup>9</sup> but, to the best of our knowledge, none in an enantiomerically pure form. In addition, they were very rarely used for catalysis.<sup>7i</sup>

## Results and discussion

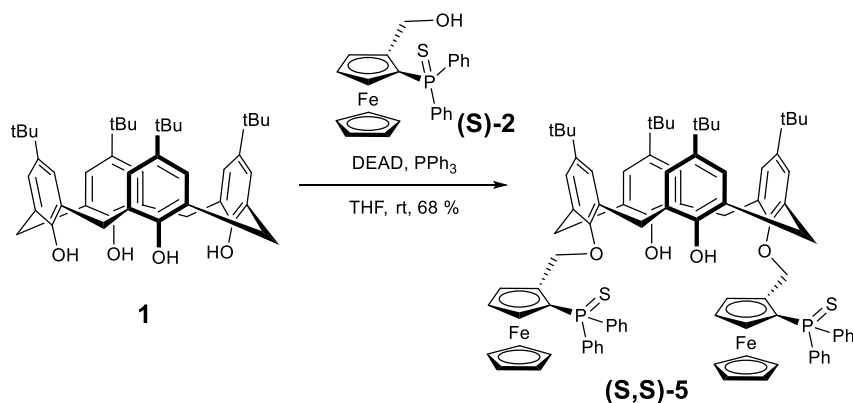
(S)-(2-diphenylthiophosphinoferrocenyl)methanol **2**, after activation by tetrafluoroboric acid, successfully alkylates various nucleophiles<sup>10,11</sup> including alcohols.<sup>12</sup> However, this methodology failed completely with 4-*tert*-butyltetrahydroxycalix[4]arene **1** as the nucleophile: thiophosphinoferrocenylmethanol (**S**)-**2** was completely decomposed under these conditions without formation of any of the desired ferrocene-containing calixarenes.

We then decided to use milder conditions to activate phenol **1**. Using classical Mitsunobu reaction conditions ( PPh<sub>3</sub>, diethyl azodicarboxylate (DEAD) ), which have been successfully applied to the selective O-alkylation of calix[4]arenes,<sup>13</sup> we were able to synthesize selectively the monosubstituted compound (**S**)-**3** from 4-*tert*-butylcalix[4]arene **1** in THF at 0°C with 72% yield (Scheme 1). Subsequent alkylation of calixarene (**S**)-**3** using benzyl bromide under basic conditions in acetonitrile at room temperature was totally selective yielding exclusively the distally disubstituted compound (**S**)-**4** (see scheme 1). This kind of regioselectivity is usual in monosubstituted calixarenes and is usually explained by interplaying of the intramolecular hydrogen bonds between the OH groups at the lower rim of the macrocycle.<sup>13</sup>



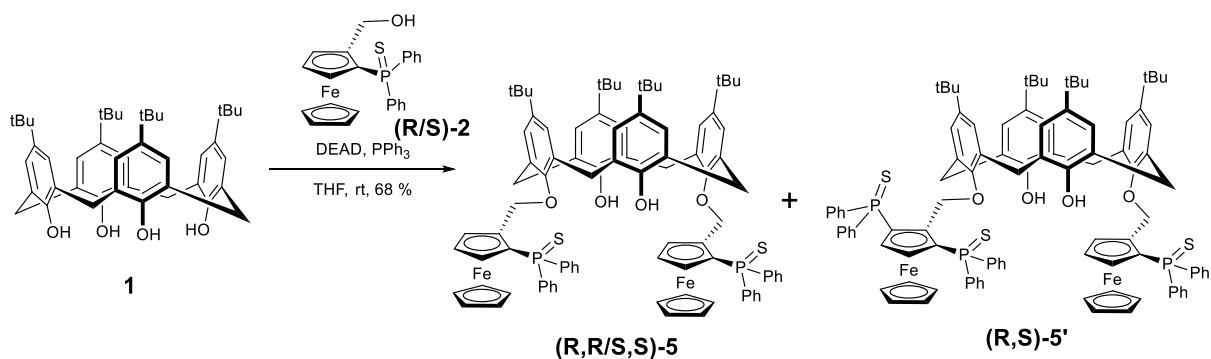
Scheme 1. Synthesis of calixarene monothiophosphines (**S**)-**3** and (**S**)-**4**.

When the Mitsunobu condensation of calixarene **1** with ferrocenylmethanol (**S**)-**2** was carried out at RT instead of 0 °C, the distal bi-thiophosphinoferrocenyl calixarene (**S,S**)-**5** (see Scheme 2) was formed in good yields after 35 h. Similar distal substitution has been observed for alkylation of hydroxycalixarenes in Mitsunobu conditions.<sup>13</sup>



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

To check whether any erosion of the ferrocene enantiomeric purity 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. Two inseparable diastereoisomers were found in the reaction mixture in a 1/1 ratio. A few <sup>31</sup>P and <sup>1</sup>H NMR signals of the meso diastereoisomer (**R,S**)-**5'** could be identified (see supplementary materials). These signals are absent from the spectrums of (**S,S**)-**5**, proving that the latter is diastereoisomerically pure and therefore also enantiomerically pure. We therefore suppose that no erosion of the ferrocene enantiomeric purity occurs also during the synthesis of (**S,S**)-**3**, which is carried out under milder conditions (0°C instead of RT).



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

Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of acetonitrile solutions of compounds **(S)**-**3** and **(S,S)**-**5**. A molecular view of compound **(S)**-**3** is represented in Figure 1. As observed in related calixarenes substituted with ferrocenyl moieties,<sup>14</sup> the calixarene in **(S)**-**3** has an irregular cone conformation with a dihedral angle between the two distal phenyl rings bearing a hydroxyl group of  $77.5(5)^\circ$  whereas the dihedral angle between the other two distal phenyl rings, bearing respectively a hydroxyl and the ferrocenyl group, is  $55.0(2)^\circ$ . Within the ferrocenyl moiety, the two Cp rings are nearly parallel with a dihedral angle of  $3.2(3)^\circ$  and the substituted Cp ring is nearly coplanar with the bisecting plane of the calixarene ring (defined by the O1, C111, C311 and O3 atoms) with a dihedral angle of  $11.61(4)^\circ$ . As expected, intramolecular O-H $\cdots$ O hydrogen bonds between the hydroxyl groups are present in the crystals of compound **(S)**-**3** (see Table 1).

Table 1. Intramolecular O-H $\cdots$ O hydrogen bonding between the hydroxyl groups in the crystal of **(S)**-**3**.

<i>D</i> — <i>H</i> $\cdots$ <i>A</i>	<i>D</i> — <i>H</i>	<i>H</i> $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> — <i>H</i> $\cdots$ <i>A</i>
O3—H3 $\cdots$ O2	0.82	1.99	2.672 (11)	139.8
O4—H4 $\cdots$ O3	0.82	2.04	2.654 (11)	131.7

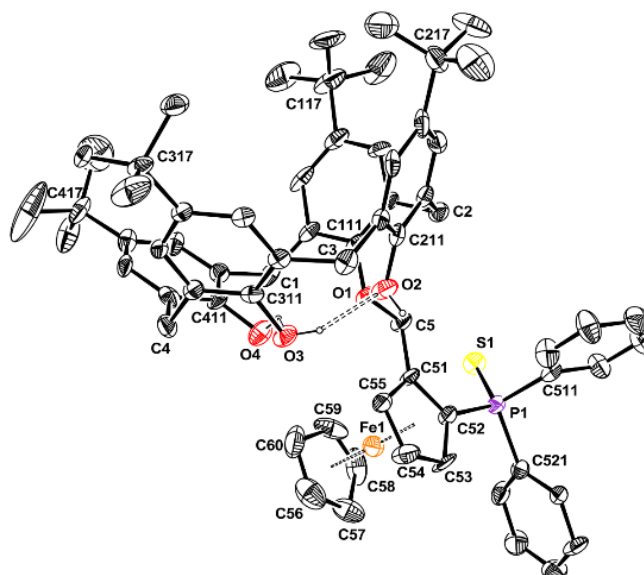


Figure 1. Ortep view of compound **(S)**-**3** with the atom labeling scheme. Ellipsoids are drawn at the 30% probability level. The H atoms attached to carbon atoms have been omitted for the sake of clarity. Hydrogen bonds between the hydroxyl groups are represented as dashed line.

In the crystal structure of compound (**S,S**)-**5** there are two roughly identical molecules within the asymmetric unit, only one of them being represented in Figure 2. The poor quality of the data does not allow detailed discussion of the bonding parameters but clearly proves the molecular structure, confirming the spectral analyses. The distances between the O atoms suggest the presence of H-bonding.

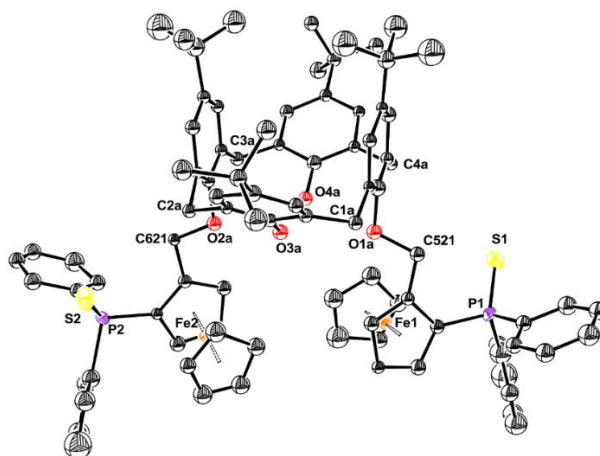
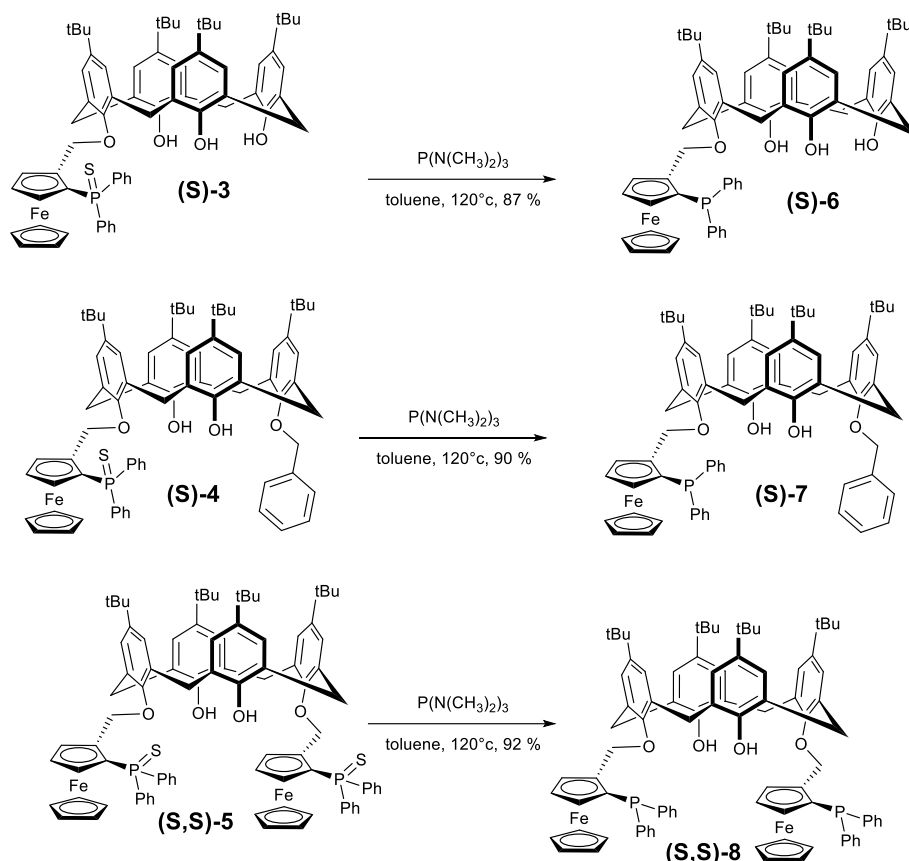


Figure 2 . Ortep view of compound (**S,S**)-**5** with the atom labeling scheme. Ellipsoids are drawn at the 30% probability level. H atoms attached have been omitted for the sake of clarity.

The thiophosphino calixarenes **3-5** could be efficiently deprotected by reaction with  $\text{P}(\text{NMe}_2)_3$ <sup>10,11,12</sup> yielding the new chiral and enantiomerically pure phosphine ferrocenyl ligands **6-8** (Scheme 4).



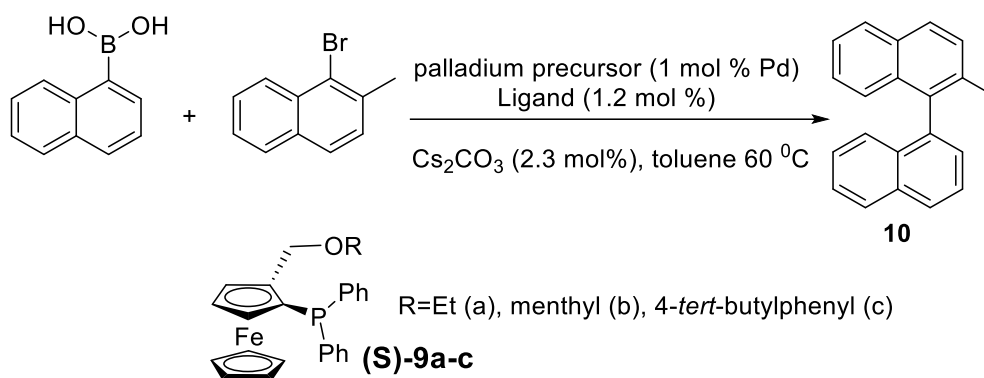
Scheme 4. Desulfuration of thiophosphines.

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

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 largely challenging since no privileged ligands with broad substrate range have emerged.<sup>15</sup> If efficient catalytic systems for Suzuki-Miyaura cross-coupling reaction with calixarene-based ligands have already been developed,<sup>6f,6h,16</sup> no asymmetric versions have been published yet to the best of our knowledge. To check whether the calixarene macrocyclic frame could influence the coupling reaction of 1-naphthaleneboronic acid and 1-bromo-2-methylnaphthalene, we compared **(S)-6** and **(S)-7** with modeling compound diphenylphosphino ferrocenes **(S)-9a-b** (see table 2).<sup>12</sup> Using bis(dibenzylideneacetone)palladium(0) (Pd(dba)<sub>2</sub>) as palladium precursor at 60 °C, the catalytic systems based on ligands **(S)-6** and **(S)-7** were very sluggish compared

with the similar system containing ligands (**S**)-**9a-b** (see table 2). However, using the allylpalladium chloride dimer, full conversion and good yields of the coupling products could be obtained after 24 h (see table 2) but the enantiomeric excesses of 2-methyl-1,1'-binaphthalene **10** were very low (less than 5%), lower than those obtained using other phosphine-ether ligands based on the same chiral scaffold (**S**)-**9a-c**, even **9c** bearing a 4-*t*-butylphenyl substituent, which is a better model of ligands **6** and **7** in terms of its stereoelectronic properties (see table 2).<sup>12</sup> Contrary to expectations, the free hydroxy groups in the lower rim of the ligands do not have positive effects on catalysis by establishing hydrogen bonds with the incoming boronic acids. Possibly, these OH groups could enter the palladium coordination sphere giving rise to several coordination complexes with an overall lowering of the enantioselectivity.

Table 2. Suzuki-Miyaura coupling reactions.



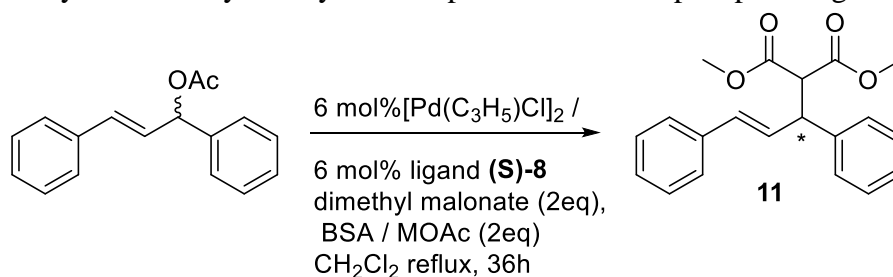
Entry	ligand	Palladium precursor	Yield, % <sup>a</sup>	ee, %
1 <sup>a</sup>	<b>6</b>	Pd(dba) <sub>2</sub>	<5%	-
2 <sup>a</sup>	<b>7</b>	Pd(dba) <sub>2</sub>	<5%	-
3 <sup>a</sup>	<b>6</b>	[Pd(Cl(allyl)) <sub>2</sub> ]	66	<5%
4 <sup>a</sup>	<b>7</b>	[Pd(Cl(allyl)) <sub>2</sub> ]	100	<5%
5 <sup>b</sup>	<b>9a</b>	Pd(dba) <sub>2</sub>	100	12
6 <sup>b</sup>	<b>9b</b>	Pd(dba) <sub>2</sub>	99	26
7 <sup>b,c</sup>	<b>9b</b>	Pd(dba) <sub>2</sub>	75	37
8 <sup>a</sup>	<b>9c</b>	[Pd(Cl(allyl)) <sub>2</sub> ]	82	34%

Reactions carried out with 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 %), 1-bromo-2-methylnaphthalene (1.00 mmol) in 10 mL of toluene at 60°C during 24h. <sup>a</sup>: from this work. <sup>b</sup>: reference 12, <sup>c</sup>: reaction carried out at 40°C.



We have also tested ligand **(S,S)**-**8** in the asymmetric allylic alkylation of 1,3-diphenylprop-2-enyl acetate by dimethylmalonate (see table 3).<sup>17</sup> Full conversion and good yields of malonate **11** could be obtained whatever the acetate salt used with the N,O-bis(trimethylsilyl)acetamide (BSA) probase. However, the enantiomeric excess of the product depended strongly on the acetate alkaline cation, the best enantioselectivity being obtained with potassium (table 3, entry 3). This 86% enantiomeric excess is, to the best of our knowledge, the best ones obtained in asymmetric allylic substitution using a calixarene-based ligand.<sup>71,18</sup> In the presence of the potassium cation, we can suppose that the dimethylmalonate anion interacts more strongly with the two hydroxyl groups of ligand **(S,S)**-**8**, directing the nucleophile more selectively toward one carbon of the  $\pi$ -allyl intermediate. This hypothesis is further supported by the fact that when the K<sup>+</sup>-specific complexing agent 18-crown-6 crown ether was added to the reaction mixture, the *ee* of the product dropped (table 3, entry 4).

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



Entry	Base	Isolated yield, % <sup>a</sup>	<i>ee</i> , %
1	CH <sub>3</sub> COOLi/BSA	86	14
2	CH <sub>3</sub> COONa/BSA	76	25
3	CH <sub>3</sub> COOK/BSA	75	86
4	CH <sub>3</sub> COOK/BSA (+ 1.2 eq of 18-Crown-6)	86	32
5	CH <sub>3</sub> COOCs/BSA	88	71

<sup>a</sup>: with full conversion.

## Conclusion

We have described the synthesis of three new chiral enantiomerically pure phosphinoferrocenyl calixarene ligands. To the best of our knowledge, these compounds are the first calixarene derivatives bearing planar chiral ferrocenyl moieties. We have carried out preliminary catalytic tests with these ligands in two asymmetric reactions: the asymmetric Suzuki-Miyaura coupling reaction and the asymmetric Tsuji-Trost reaction. Although the enantioselectivities observed in the Suzuki-Miyaura reaction were disappointing, interesting enantiomeric excesses (*ee* up to 86%) were obtained with ligand **(S,S)**-**8** in the asymmetric allylic alkylation. 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** that displays a large bite angle.<sup>19,20</sup>

## Experimental section

### General procedure for asymmetric Suzuki-Miyaura coupling reaction

In a typical procedure, the ligand (0.012 mmol, 1.2 mol %),  $[\text{Pd}(\text{C}_3\text{H}_5)\text{Cl}]_2$  (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 containing 10 mL of toluene. The reaction mixture was stirred at 60°C for 24 h under an Ar atmosphere. After cooling back to RT, acidified water was added to each collected samples. After extraction by diethylether, the organic phase was then filtered through silica and the solvent was evaporated under reduced pressure. The enantiomeric excess of the product was determined by SFC-HPLC with a Chiralcel OJ column (eluent:  $\text{CO}_2/\text{iPrOH}$  9/1: 4ml.min<sup>-1</sup>). Retention time: 5.04 min (R isomer), 8.68 (S isomer).

### General procedure for asymmetric allylic substitution

A mixture of the calixarene ligand (**S,S**)-**8** (0.003 mmol), 1,3-diphenylprop-2-enyl acetate (0.126 g, 0.5 mmol) and  $[\text{Pd}(\text{C}_3\text{H}_5)\text{Cl}]_2$  (5.3 mg, 0.0015 mmol) was dissolved in dry dichloromethane (20 mL). Dimethyl malonate (0.115 mL, 1 mmol), acetate salt (1mmol) and BSA (0.250 mL, 1 mmol) were then added to the resulting solution. The reaction was refluxed and monitored by TLC for substrate disappearance. After 36h, the mixture was quenched with a saturated aqueous solution of ammonium chloride (20 mL). The aqueous phase was extracted with dichloromethane, the combined organics were dried over magnesium sulphate, filtered and the solvents evaporated. The conversion was calculated by integration of signals in the <sup>1</sup>H NMR spectra of the crude reaction mixture. Subsequent purification by chromatography on silica eluting with dichloromethane/pentane (1:1) afforded the product as colourless oil. The enantiomeric excess was determined by <sup>1</sup>H NMR spectroscopy using the chiral shift reagent (+)  $\text{Eu}(\text{hfc})_3$ .

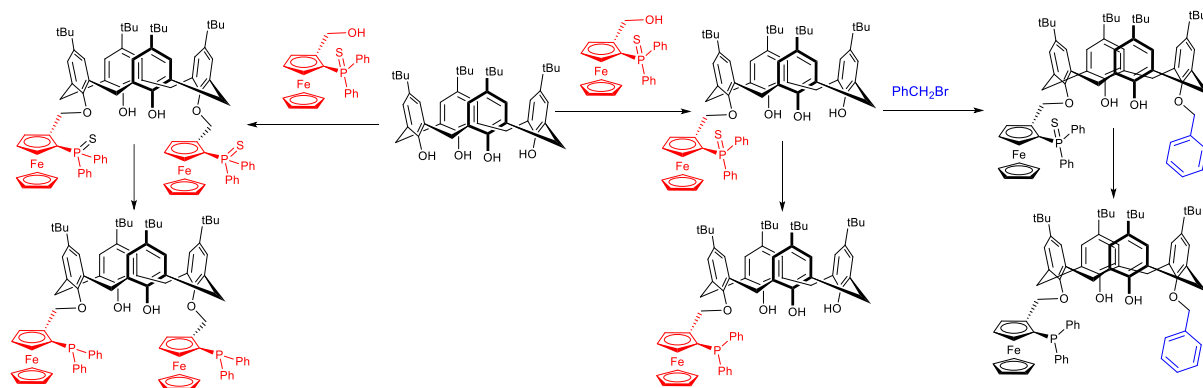
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## Graphical Abstract

### New Chiral Phosphinoferrocenyl Calixarenes

Andrii Karpus, Oleksandr Yesypenko, Vyacheslav Boiko, Rinaldo Poli, Jean-Claude Daran, Zoia Voitenko,\* Vitaly Kalchenko,<sup>4\*</sup> Eric Manoury\*



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