Available online at www.sciencedirect.com
SCIENCE DIRECT
Journal of Organometallic Chemistry 691 (2006) 2297–2310
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Synthesis and catalytic applications of new chiral ferrocenyl P,O ligands

Nuno Mateus [1], Lucie Routaboul, Jean-Claude Daran, Eric Manoury *

Laboratoire de Chimie de Coordination, CNRS, 205 route de Narbonne, F-31077 Toulouse Cedex, France

Received 3 October 2005; received in revised form 22 November 2005; accepted 22 November 2005
Available online 18 January 2006

Abstract

A new method to synthesize both enantiomers of 2-diphenylphosphino-ferrocenecarboxaldehyde with the phosphine group protected as a thiophosphine group was developed. These aldehydes react with 1,2 or 1,3 diols to give, in good yields, new chiral phosphine-acetals. For unsymmetrical (*R*)-1,3-butanediol, the new asymmetrical acetalic carbon is asymmetric and its configuration was completely controlled by the chirality of the diol. These new P,O ligands were tested in the palladium-catalyzed asymmetric allylic substitution of 1,3-diphenylprop-2-enylacetate. Good yields and enantioselectivities up to 77% were observed. The catalytic performances of two diastereoisomeric ligands with opposite configurations in planar chirality only proved to be significantly different, showing a strong influence of both planar and central chiralities.

Keywords: Ferrocene; Chiral ligands; P,O ligands; Phosphine; Dioxane; Dioxolane; Asymmetric catalysis; Allylic substitution

1. Introduction

In the last three decades, asymmetric catalysis has attracted much interest because of its huge importance in synthetic organic chemistry [1]. The design of new chiral catalysts is essential for exploring new catalytic asymmetric reactions and for improving existing reactions in terms of selectivities, especially enantioselectivities but also of activities, robustness, convenience, etc. Numerous ligands bearing various combinations of heteroelements [1] (P,P; P,N; N,N; P,S [2] etc. ligands) have been extensively studied. However, P,O ligands despite their rich coordination chemistry [3,4] and a growing importance in catalysis [3,5] are still rather scarcely used in asymmetric catalysis [6,7]. As a part of our continuous interest in ferrocene chemistry [8], we became interested in developing new ferrocenyl phosphine-acetals P,O ligands. A wide range of such ligands can be potentially obtained taking into account the large number of 1,2 or 1,3-diols which can be easily obtained in an enantiomerically pure form. Furthermore, these ligands belong to the 1,2 disubstituted ferrocene family which has produced some of the most successful ligands used in asymmetric catalysis [9].

The synthesis of these novel ligands, in an enantiomerically pure form, will be described in this report. The catalytic behavior of these ligands has been examined for the asymmetric allylic substitution reaction.

2. Results and discussion

2.1. Synthesis

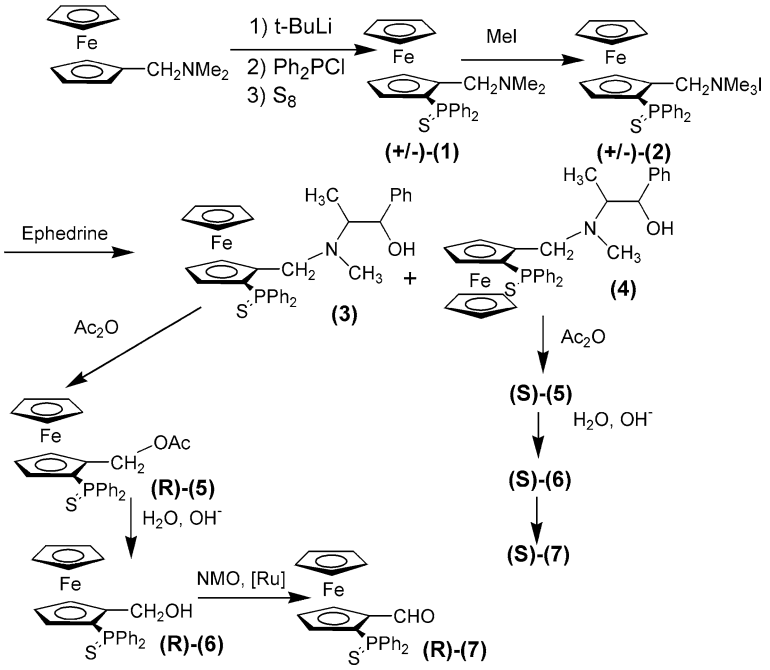
In order to obtain our target ligands (**10**) or (**11**) (see Scheme 2), we need an easy access of both enantiomers of 2-diphenylphosphino-ferrocenecarboxaldehyde. Although the (*S*) enantiomer can be easily synthesized by a method developed by Kagan et al. [10], no convenient synthesis is available, to the best of our knowledge, for the (*R*)-enantiomer. We imagined a synthetic route via the oxidation of a corresponding alcohol as a protected form to avoid the phosphine oxidation during the aldehyde synthesis step. We decided to try to obtain both enantiomers of alcohols (**6**) (see Scheme 1) by extending the method successfully

* Corresponding author. Tel.: +33 5 61 33 31 73; fax: +33 5 61 55 30 03.
E-mail address: manoury@lcc-toulouse.fr (E. Manoury).
[1] Present address: Leverhulme Centre for Innovative Catalysis, University of Liverpool, L69 7ZD Liverpool, UK.

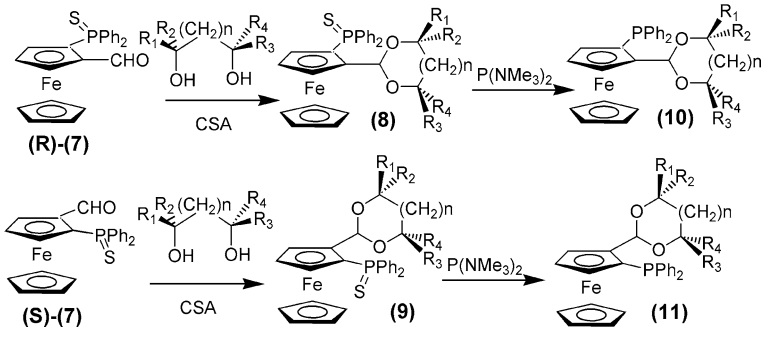
0022-328X/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2005.11.053

developed by Weissensteiner et al. for the resolution of 2-bromodimethylaminomethylferrocene and of 2-iododimethylaminomethyl ferrocene with ephedrine as a chiral auxiliary [11]. Racemic 2-(diphenylthiophosphino) dimethylaminomethylferrocene (**1**) was obtained very efficiently by a published procedure [12]. The reaction of iodomethane with (**1**) yielded the ammonium salt (**2**) quantitatively. The displacement of trimethylamine by ephedrine was carried out and the two diasteroisomers (**3**) and (**4**) of opposite planar chirality were obtained in high yields in a 1/1 ratio (see Scheme 1). Flash chromatography on silicagel allowed an efficient separation of both diastereoisomers. The planar chirality of both diastereoisomers (**3**) and (**4**) was determined by X-ray diffraction (see below). The transformation of ferrocenylmethylamines into corresponding acetoxymethyl ferrocenes by action of acetic anhydride is a well-established reaction. We also followed this approach by limiting both reaction times and temperature, and we found very efficient conditions for the synthesis of the enantiomerically pure acetate (**5**) from (**3**) or (**4**) (95% yield). A straightforward saponification of (**5**) yielded both enantiomerically pure (*R*)-(**6**) or (*S*)-(**6**) in high yields. We unsuccessfully tested several oxidation methods (with manganese dioxide [13], with Dess-Martin reagent [14] and in Swern conditions [15]) known to allow an efficient oxidation of primary alcohols into the corresponding aldehydes. Finally, aldehyde (**7**) could be efficiently synthesized following a procedure developed by Sharpless et al. using NMO as oxidant and a ruthenium catalyst [16].

The synthesis of cyclic acetals was successfully carried out for the 1,2 diols as well as for 1,3 diols (see Table 1) in toluene in presence of a catalytic amount of the organic acid, camphorsulfonic acid (CSA) with continuous removal of water by distillation [17]. In the case of compound (**8a**), the new acetalic carbon (carbon 1 of the 1,3-dioxolane ring) is asymmetric. However, the acetalization reaction yields one single diastereoisomer. The molecular structure was determined by X-ray diffraction on a single crystal (see Sec-



Scheme 1.



Scheme 2.

Table 1
Synthesis of cyclic acetals

Entry	Diol	Product	Yield[a] (%)
1	(*R*)-1,3-butanediol	(**8a**)	66
2	(*R*)-1,3-butanediol	(**9a**)	75
3	(1*R*,3*R*)-1,3-pentanediol	(**8b**)	63
4	(1*R*,3*R*)-1,3-pentanediol	(**9b**)	67
5	(1*R*,2*R*)-1,2-butanediol	(**8c**)	72
6	(1*R*,2*R*)-1,2-butanediol	(**9c**)	76

[a] Isolated yield.

tion 2.2). The configuration on carbon 1 was determined to be *S* (see Fig. 4). As shown in Fig. 2, the dioxolane has a perfect chair conformation. The configuration on carbon 1 is easily explained by the preferred equatorial position of the methyl group and essentially of the huge ferrocenyl group. Similarly, and for the same reasons, the new asymmetric carbon 1 of the dioxolane ring in (**9a**) was proved to have a *S* configuration (see Fig. 7) as shown by the molecular structure determined by X-ray diffraction.

Finally, ligands (**10**) and (**11**) were obtained by desulfurization of the corresponding thiophosphines (**8**) or (**9**) using $P(NMe_2)_3$ [8g].

2.2. Crystal structures

Molecular views of the nine compounds (**1**), (**3**), (**4**), (**8a**), (**8b**), (**8c**), (**9a**), (**9b**) and (**9c**) with atom labelling schemes are shown in Figs. 1–9. The bond lengths and angles in all compounds are within expected ranges.

In compound (+/−)-**1**, the dimethylamino moiety is *exo* with respect to the Cp ring and the N atom is nearly located in the bisecting plane passing through C2 and the middle of C4–C5 bond as showed by the torsion angles C1–C2–C21–N1 and C3–C2–C21–N1 of −79.5(2)° and 100.5(2)°. The S atom is displaced *endo* towards the Fe atom by 1.293(4) Å from the Cp ring. The two Cp rings are nearly eclipsed with a twist angle of 4.9° and they are slightly bent with a dihedral angle of 6.04(9)°.

In both the ephedrine derivatives (**3**) and (**4**), the S atom is displaced *endo* towards the Fe atom by

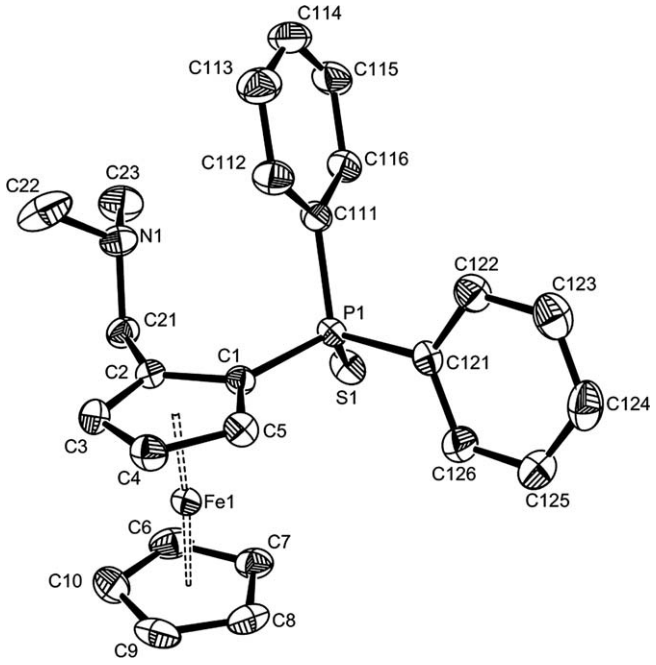


Fig. 1. Molecular view of (+/−)-**1** with atom labelling. Ellipsoids represent 50% probability. H atoms have been omitted for clarity.

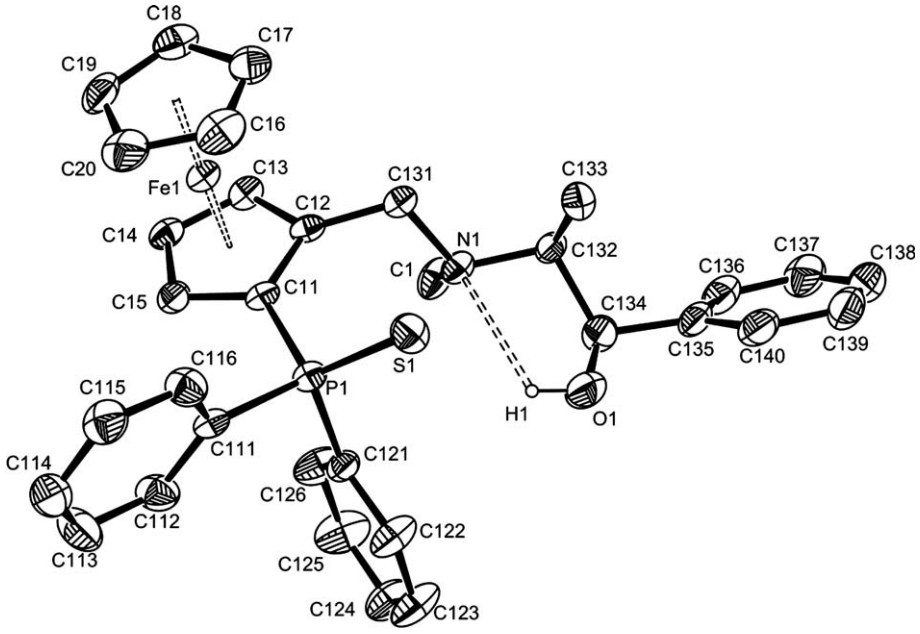


Fig. 2. Molecular view of (R_p)-(**3**) with atom labelling. Ellipsoids represent 50% probability. H atoms not involved in hydrogen bonding have been omitted for clarity.

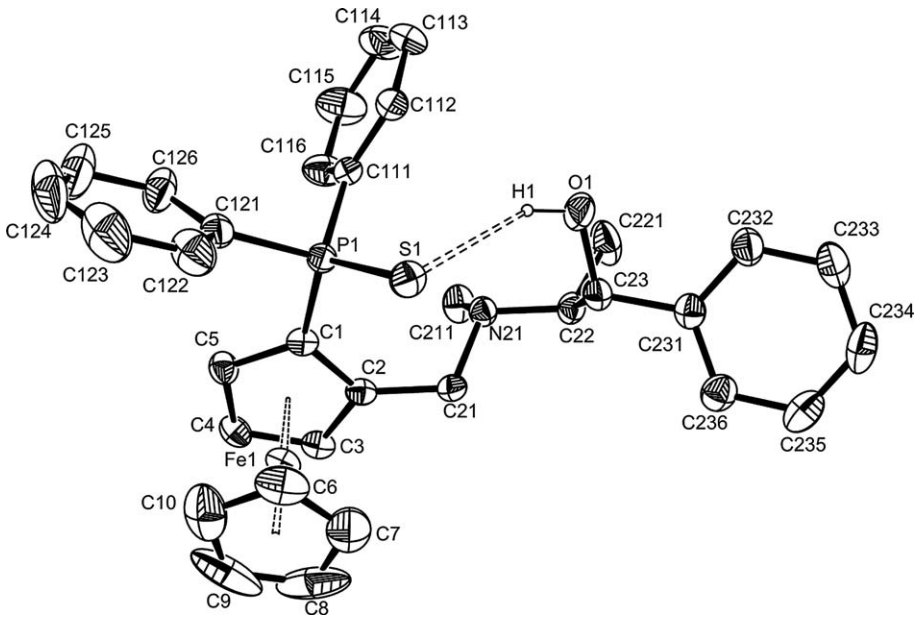


Fig. 3. Molecular view of (S_p)-(**4**) with atom labelling. Ellipsoids represent 50% probability. H atoms not involved in hydrogen bonding have been omitted for clarity.

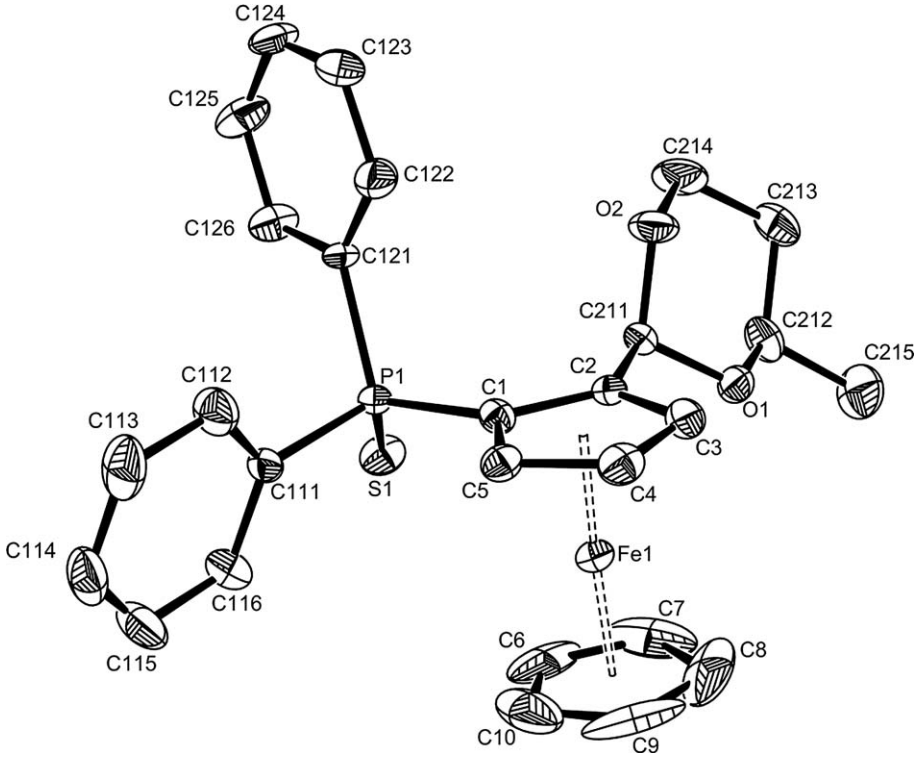


Fig. 4. Molecular view of (*1S,3R,R*$_p$)-**8a** with atom labelling. Ellipsoids represent 50% probability. H atoms have been omitted for clarity.

0.766(6) Å [1.146(6) Å] and 1.261(5) Å for (**3**) and (**4**), respectively, whereas the nitrogen atom is *exo* with respect to the Cp ring by 1.249(5) and 1.230(4) Å for (**3**) and (**4**), respectively. The Cp rings are nearly parallel with a dihedral angle of 0.6(2)° [2.1(2)° for molecule 2] and 3.5(2)° for (**3**) and (**4**), respectively, and they are nearly eclipsed with a twist angle of 2.4° [11.9°] and 5.6°, respectively.

It is worth pointing out that in compound (**3**), a hydrogen bond occurs between the H atom of the hydroxyl group and the nitrogen atom [O–H = 0.85(1) Å, H–N = 2.54(4) Å, O–N = 2.903(3) Å, O–H–N = 107(3)°] whereas in compound (**4**) the hydrogen bond is established with the sulfur atom [O–H = 0.85(1) Å, H–S = 2.639(2) Å, O–S = 3.348(2) Å, O–H–S = 147(2)°] resulting in a different conformation for the ephedrine moiety.

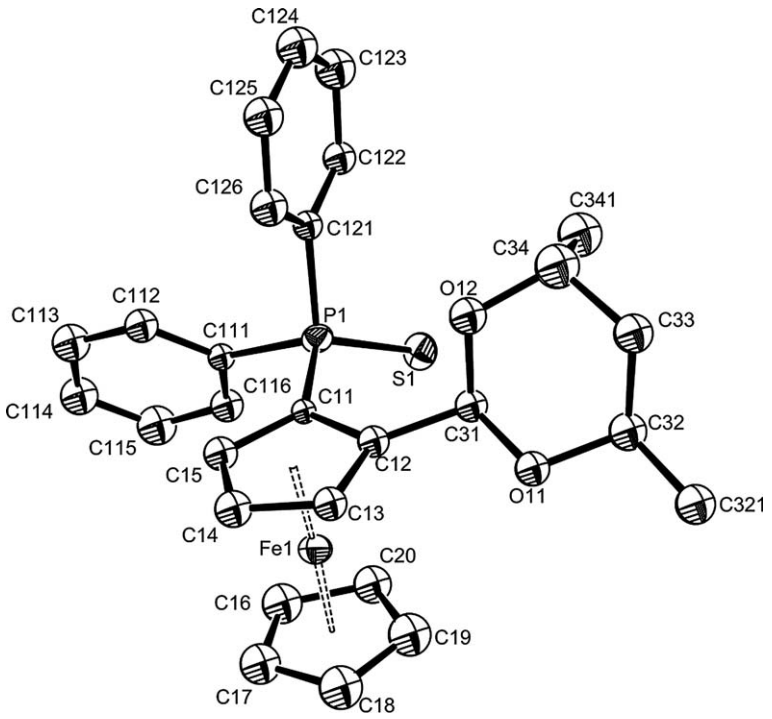


Fig. 5. Molecular view of (*3R*,*5R*,R_p)-**8b** with atom labelling. Ellipsoids represent 50% probability. H atoms have been omitted for clarity.

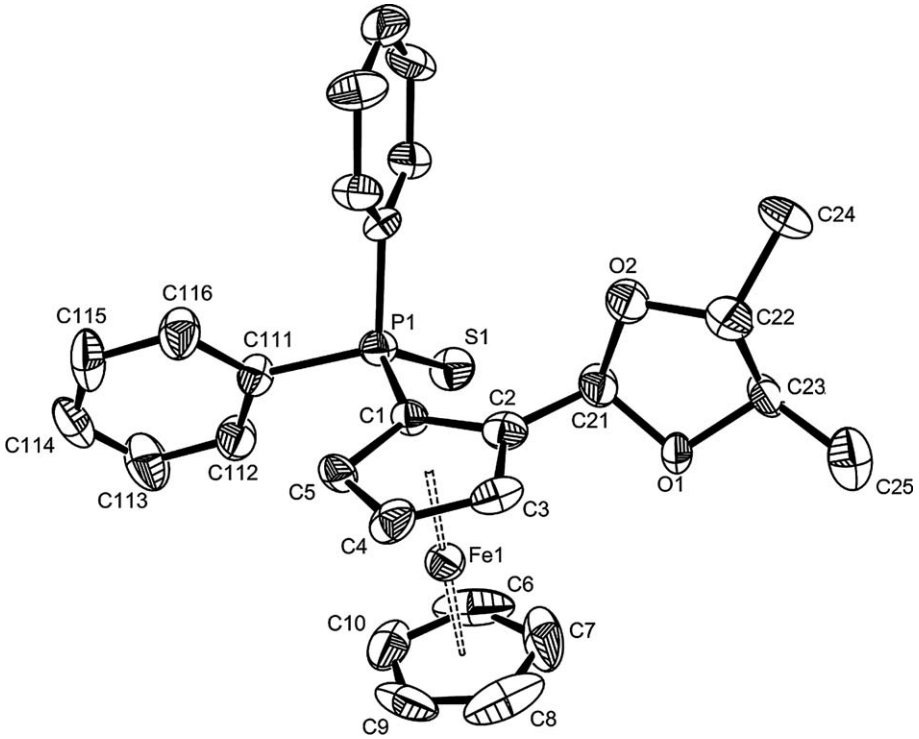


Fig. 6. Molecular view of (*3R*,*4R*,R_p)-**8c** with atom labelling scheme. Ellipsoids represent 50% probability. H atoms have been omitted for clarity.

In the six acetal derivatives (**8a**), (**8b**), (**8c**), (**9a**), (**9b**) and (**9c**), the chirality of the diols used for the synthesis appears to be retained in the final products.

In compounds (**8a**), (**8b**), (**9a**) and (**9b**) the dioxane rings have a chair conformation with the out of plane atoms being away from the mean plane by −0.627(4) Å and 0.661(7) Å (**8a**), −0.668(9) Å [−0.60(1) Å] and 0.58(1) Å [0.655(9) Å] (**8b**), −0.679(3) Å and 0.624(4) (**9a**) and −0.560(7) Å and 0.653(3) Å (**9b**). In compound (**8a**) and (**9a**), the methyl and the ferrocene moiety are both in

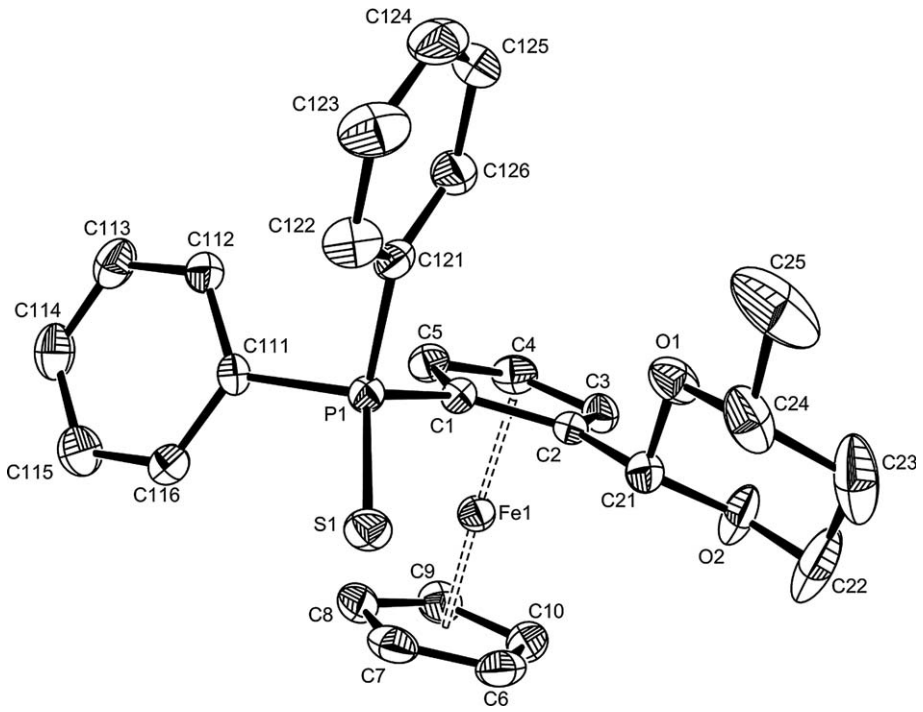


Fig. 7. Molecular view of (*1S*,*3R*,S_p)-**9a** with atom labelling scheme. Ellipsoids represent 50% probability. H atoms have been omitted for clarity.

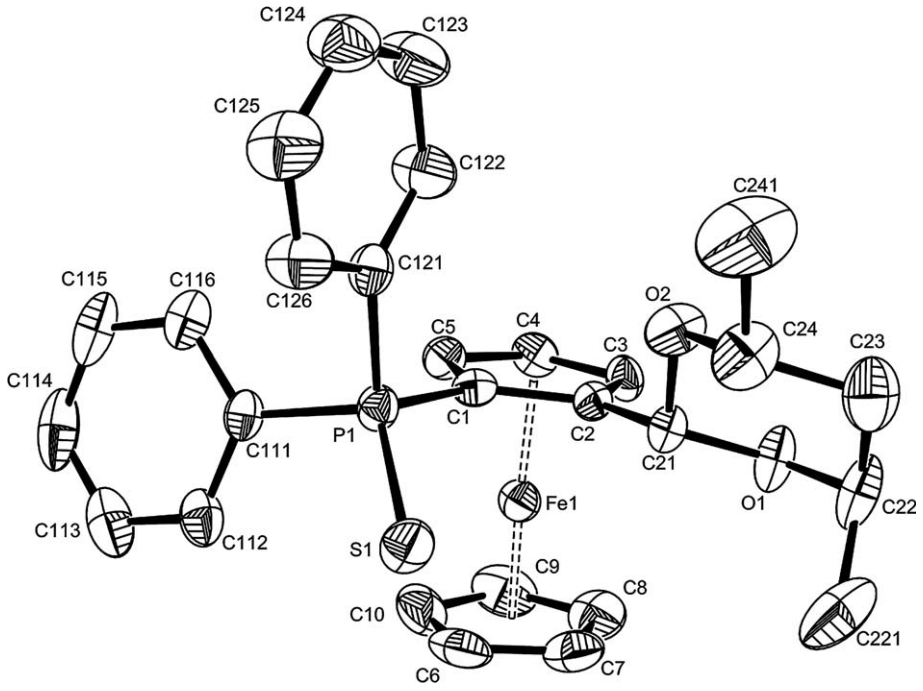


Fig. 8. Molecular view of (*3R*,*5R*,S_p)-**9b** with atom labelling scheme. Ellipsoids represent 50% probability. H atoms have been omitted for clarity.

equatorial position whereas in (**8b**) and (**9b**) the presence of two methyls results in one being equatorial and the other axial. These dioxane rings are twisted with respect to the Cp ring to which they are attached by 68.8(1)° (**8a**), 54.3(3)° [62.3(3)°] (**8b**), 42.03(9)° (**9a**) and 43.8(2)° (**9b**). In (**8a**), the methyl substituent on the dioxane ring is oriented *endo* towards the Fe atom whereas in (**9a**) it is oriented *exo*. In compounds (**8a**), (**9a**) and (**9b**) the Cp rings are nearly eclipsed with twist angles of 9.4°, 3.9° and 5.1°, respectively, whereas in compound (**8b**), the Cp rings have intermediate conformation between eclipsed and staggered with twist angles of 22.9° [17.2]. The Cp rings for all compounds are roughly parallel and the S atoms are always *endo* towards the iron atom.

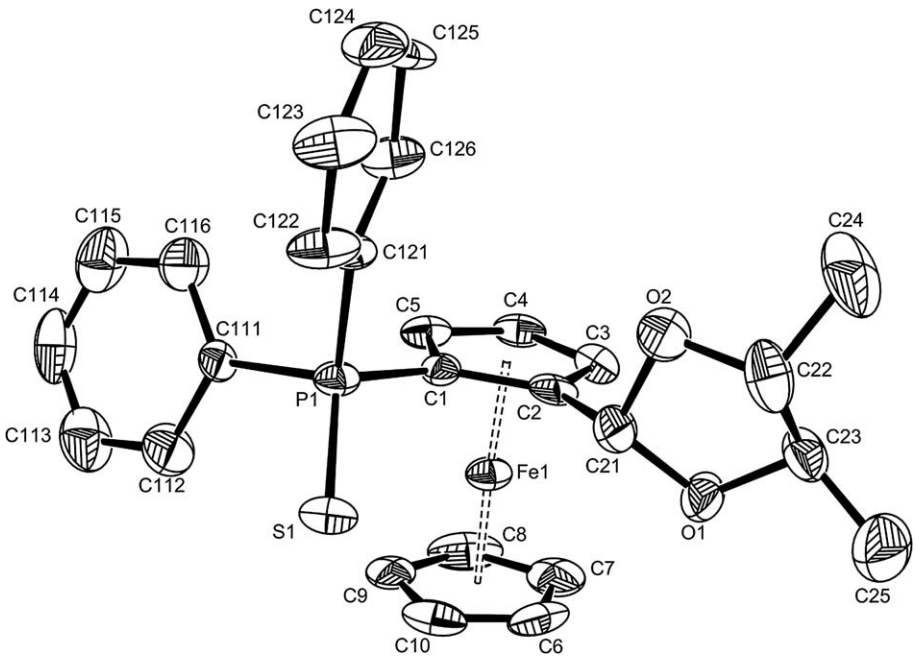
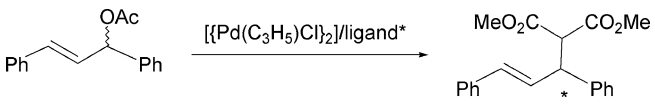


Fig. 9. Molecular view of (*3R,4R,S*$_p$)-**9c** with atom labelling scheme. Ellipsoids represent 50% probability. H atoms have been omitted for clarity.

In compounds (**8c**) and (**9c**), the dioxolane ring has an half-chair conformation with the atoms C21–O1–O2–C22 being roughly in a plane (largest deviation being −0.038(5) and 0.153(4) Å, respectively) and the C23 atom being out of the mean plane by 0.61(1) and 0.44(1) Å for (**8c**) and (**9c**), respectively. These planes are twisted with respect to the Cp ring where they are attached by 81.1(3)° and 72.0(2)° for (**8c**) and (**9c**), respectively. In (**8c**) and (**9c**) the Cp rings have a conformation between eclipsed and staggered with twist angles of 20.2° and 16.2°, respectively, whereas they are roughly parallel to each other with dihedral angle of 2.8(4)° and 3.5(2)°. The two methyl groups attached to the dioxolane rings are *trans*.

2.3. Catalytic studies

Because some P,O ligands already proved to be good ligands for the palladium-catalyzed asymmetric allylic substitution [7], we then decided to explore this reaction as a preliminary evaluation of the catalytic properties of these chiral ligands [18]. The reaction of 1,3-diphenylprop-2-enyl-acetate with the anion of dimethyl malonate in the presence of $[Pd(C_3H_5)Cl]_2$ (1 mol%) and various chiral ligands (**10**) and (**11**) was tested under classical conditions (see Scheme 3). The results are summarized in Table 2.



Scheme 3.

For every ligand studied, good catalytic activities were observed. The main purpose of this preliminary studies was to compare the two members of each pair of diastereoisomeric ligands (**10**) and (**11**) built up from the same chiral diol or, in other words, to compare the influence of planar chirality of the ferrocene moiety, different in (**10**) and (**11**), with the influence of the central chirality from the diol. For ligands (**10a**) and (**11a**), the difference in enantio-selectivities observed with the matched ((**11a**), ee = 53%) and the mismatched diastereoisomer ((**10a**), ee = −8%) is high, indicating that both elements of chirality have a strong influence on the stereochemical outcome of the catalytic reaction. This effect is even more pronounced for ligands (**10c**) and (**11c**) (Table 2, entries 5 and 6). In the case of ligands (**10b**) and (**11b**), the elements of chirality from (1*R*,3*R*)-1,3-pentanediol have a much stronger influence than planar chirality on enantio-selectivity (Table 2, entries

Table 2
Aymmetric allylic substitution with P,O ligands (**10**) and (**11**)

Entry	Ligand	Yield[a] (%)	ee[b] (%)	Configuration
1	(1*S*,3*R*,*R*$_p$)-**10a**	90	8	*R*
2	(1*S*,3*R*,*S*$_p$)-**11a**	94	53	*S*
3	(3*R*,5*R*,*R*$_p$)-**10b**	89	41	*S*
4	(3*R*,5*R*,*S*$_p$)-**11b**	93	64	*S*
5	(3*R*,4*R*,*R*$_p$)-**10c**	95	18	*S*
6	(3*R*,4*R*,*S*$_p$)-**11c**	97	77	*R*

Reactions run with 0.5 mmol of *rac*-1,3-diphenylprop-2-enyl acetate, 1 mmol of dimethylmalonate, 1 mmol of BSA and a catalytic amount of base, 0.015 mol of $[PdCl(allyl)]_2$ and 0.03 mol of ligand in 20 mL of dichloromethane at RT during 16 h.

[a] Isolated yield after quantitative conversion.

[b] (*R*) determined by ^{1}H NMR using Eu-(+)-(hfc)$_3$ as chiral chemical shift reagent.

3 and 4). These preliminary experiments are not sufficient to rationalize the observed enantio-selectivities and complementary investigations are now in progress. In addition, it is worth pointing out that, with ligand (**11c**), for instance, the catalytic system has already achieved a promising level of enantioselectivity (ee = 77%) before any attempts at optimization (solvent, temperature, base, ligand/metal ratio, etc.).

2.4. Conclusion

We have developed a straightforward synthesis of new chiral ferrocenyl phosphine-acetals P,O ligands. These ligands could be obtained with the two possible planar chiralities (*R* or *S* configuration), so the two possible diastereoisomers from the same diol are available for catalytic evaluations. These new P,O ligands were successfully used in the palladium-catalyzed asymmetric allylic substitution of 1,3-diphenylprop-2-enylacetate. A significant level of enantio-selectivity (up to 77%) was achieved. For each pair of diastereoisomeric ligands with opposite planar chirality, only the observed enantio-selectivities were significantly different, showing a strong mutual influence of planar and central chiralities on the catalytic systems.

Further studies in order to develop the coordination chemistry of these ligands to other metals and to use them in other catalytic reactions are currently in progress in our laboratory.

3. Experimental

3.1. General

All solvents were dried before use. Thin layer chromatography was carried out on Merck Kieselgel 60F254 precoated silicagel plates. Preparative flash chromatography was performed on Merck Kieselgel. Instrumentation: Bruker AM250 and AMX 400 (^{1}H, ^{13}C, and ^{3}1P NMR). Elemental analyses were performed by the Service d'Analyse du Laboratoire de Chimie de Coordination, Toulouse (France).

3.1.1. Synthesis of 2-(diphenylthiophosphino)-dimethylaminomethylferrocene ((+/−)-1)

The 2-(diphenylthiophosphino)dimethylaminomethylferrocene was synthesized according to Ref. [12a] and was sulfurized as described below.

In a Schlenk tube, under argon, 4 g of crude 2-(diphenylthiophosphino)dimethylaminomethylferrocene (0.47 mmol) was dissolved in 100 mL of dichloromethane. 1.7 g of sulfur (53 mmol) was then added and the solution was heated to reflux for 2 h. The crude products were separated by flash chromatography on silicagel with pentane then ether as eluent to yield 0.89 g of an yellow solid (Yield = 91% from dimethylaminomethylferrocene).The physical data were similar to those published in Ref. [12b].

3.1.2. Synthesis of (2-diphenylthiophosphinoferrocenyl)-trimethylammonium iodide (2)

In an Erlenmeyer flask, 8 g (17.4) of 2-(diphenylthiophosphino)dimethylaminomethylferrocene (**1**) was dissolved in 150 ml of ether. 10 ml (161 mmol) of iodomethane was added. The reaction mixture was stirred 1 h at RT. An abundant yellow solid precipitated. The yellow solid was filtered in a sintered glass funnel, washed with ether and dried to yield 9.9 g of yellow solid (95%).

^{1}H NMR (δ (ppm), $CDCl_3$): 7.80 (2H, m, PPh_2); 7.67 (2H, m, PPh_2); 7.5–7.3 (6H, m, PPh_2); 5.83 (1H, d, AB syst, $J = 13.0$ Hz, CH_2); 5.36 (1H, d, AB syst, $J = 13.0$ Hz, CH_2); 5.23 (1H, m, subst Cp); 4.61 (1H, m, subst Cp); 4.28 (5H, s, Cp); 4.11 (1H, m, subst Cp); 2.98 (9H, s, CH_3). ^{13}C NMR (δ (ppm), $CDCl_3$): 133.7 ($J_{PC} = 84.4$ Hz, quat PPh_2); 132.09 ($J_{PC} = 87.4$ Hz, quat PPh_2); 132.08 ($J_{PC} = 2.8$ Hz, PPh_2); 131.93 ($J_{PC} = 10.8$ Hz, PPh_2); 131.93 ($J_{PC} = 2.5$ Hz, PPh_2); 131.5 ($J_{PC} = 10.2$ Hz, PPh_2); 128.9 ($J_{PC} = 12.3$ Hz, PPh_2); 128.3 ($J_{PC} = 12.6$ Hz, PPh_2); 78.9 ($J_{PC} = 8.5$ Hz, quat Cp); 76.9 ($J_{PC} = 12.5$ Hz, subst Cp); 76.5 ($J_{PC} = 11.3$ Hz, subst Cp); 73.9 ($J_{PC} = 92.2$ Hz, quat Cp); 72.8 ($J_{PC} = 10.8$ Hz, subst Cp); 72.2 (Cp); 63.9 (CH_2); 52.6 (NCH_3). ^{31}P NMR (δ (ppm), $CDCl_3$): 40.4. MS (FAB^+) *m/e*: 474 (M cation, 18%),, 415 (M(cation-NMe_3), 100%).

3.1.3. Synthesis of N-(2-diphenylthiophosphinoferrocenylmethyl) ephedrine (3) and (4)

In a round-bottomed flask, 10 g of (2-diphenylthiophosphinoferrocenyl)trimethylammonium iodide (16.6 mmol) and 10 g of ephedrine (61 mmol) were dissolved in 350 mL of dry toluene. The solution was heated to reflux with stirring for 3 h. After cooling to RT, potassium carbonate was added. The reaction mixture was filtered on paper and the solvents were evaporated. The crude products were purified by flash chromatography on silicagel by using a pentane/ether mixture (1/1, v/v) as eluent to yield 4.70 g (97%) of each diastereoisomer as a yellow solid.

First diastereoisomer (R_{fc})-(**3**): ^{1}H NMR (δ (ppm), $CDCl_3$): 7.9–7.8 (2H, m, PPh_2); 7.8–7.7 (2H, m, PPh_2); 7.6–7.4 (6H, m, PPh_2); 7.25–7.15 (3H, m, PPh_2); 7.0–6.95 (2H, m, PPh_2); 4.64 (1H, d(AB), $J = 12.4$ Hz, CH_2); 4.61 (1H, d, $J = 3.8$ Hz, C*H*–Ph); 4.52 (1H, m, Cp subst); 4.32 (5H, s, Cp); 4.31 (1H, m, Cp subst); 3.76 (1H, m, Cp subst); 3.37 (1H, br s, OH); 3.27 (1H, d(AB), $J = 12.4$ Hz, CH_2); 2.84 (1H, qd, $J = 6.9$ and 3.8 Hz, C*H*–CH_3); 1.63 (3H, s, N–CH_3); 0.72 (3H, d, $J = 6.9$ Hz, CH-C*H*$_3$). ^{13}C NMR (δ (ppm), $CDCl_3$): 142.9 (quat Ph); 135.1 ($J_{P-C} = 87.6$ Hz, quat Ph); 134.1 ($J_{P-C} = 85.6$ Hz, quat Ph); 132.5 ($J_{P-C} = 10.7$ Hz, Ph); 132.4 ($J_{P-C} = 10.5$ Hz, Ph) ;131.6 ($J_{P-C} = 3.0$ Hz, 2 Ph); 128.6 ($J_{P-C} = 12.5$ Hz, Ph); 128.4 ($J_{P-C} = 12.3$ Hz, Ph); 127.9 (Ph); 126.9 (Ph); 126.8 (Ph); 90.3 ($J_{P-C} = 11.7$ Hz, Cp quat); 76.2 ($J_{P-C} = 9.8$ Hz, Cp subst); 75.6 ($J_{P-C} = 12.4$ Hz, Cp subst); 74.5 (*C*H–Ph); 74.2 ($J_{P-C} = 95.6$ Hz, Cp quat); 71.2(Cp); 69.3 ($J_{P-C} = 10.3$ Hz, Cp subst); 64.1 (*C*H–CH_3); 55.5 (CH_2); 37.4 (N–

CH_3); 9.3 (CH–CH_3). ^{31}P NMR (δ (ppm), $CDCl_3$): 44.1. $[\alpha]_D = -6.5$ ($CHCl_3$, $c = 0.5$) MS (DCI, NH_3) *m/e*: 580 (M+1, 100%). Anal. Found: C, 68.25; H, 5.98; N, 2.22%. $C_{34}H_{36}FeNOPS$. Calc.: C, 68.38; H, 5.92; N, 2.42.

Second diastereoisomer (S_{fc})-(***4***): ^1H NMR (δ (ppm), $CDCl_3$): 7.9–7.8 (2H, m, PPh_2); 7.8–7.7 (2H, m, PPh_2); 7.5–7.4 (6H, m, PPh_2); 7.32–7.25 (2H, m, PPh_2); 7.24–7.18 (3H, m, PPh_2); 4.6–4.5 (3H, m, 1H CH_2 1H CHPh + 1H subst Cp); 4.35 (5H, s, Cp); 4.31 (1H, m, Cp subst); 3.73 (1H, m, Cp subst); 3.30 (1H, d(AB), $J = 12.9$ Hz, CH_2); 3.20 (1H, br s, OH); 2.55 (1H, qd, $J = 6.9$ and 3.0 Hz, C*H*-CH_3); 1.93 (3H, s, N–CH_3); 0.84 (3H, d, $J = 6.9$ Hz, CH-CH_3). ^{13}C NMR (δ (ppm), $CDCl_3$): 143.2 (quat Ph); 134.8 ($J_{P-C} = 87.6$ Hz, quat Ph); 134.0 ($J_{P-C} = 85.9$ Hz, quat Ph); 132.5 ($J_{P-C} = 10.9$ Hz : Ph); 132.4 ($J_{P-C} = 10.8$ Hz, Ph); 131.6 ($J_{P-C} = 3.6$ Hz, 2 Ph); 128.5 ($J_{P-C} = 12.5$ Hz, Ph); 128.4 ($J_{P-C} = 12.3$ Hz, Ph); 128.2 (Ph); 126.9 (Ph); 126.4 (Ph); 90.7 ($J_{P-C} = 12.1$ Hz, Cp quat); 75.9 ($J_{P-C} = 9.8$ Hz, Cp subst); 75.7 ($J_{P-C} = 12.7$ Hz, Cp subst); 74.6 ($J_{P-C} = 95.4$ Hz, Cp quat); 73.9 (*C*H-Ph); 71.2(Cp); 69.1 ($J_{P-C} = 10.5$ Hz, Cp subst); 65.7 (*C*H-CH_3); 52.9 (CH_2); 39.4 (N–CH_3); 9.3 (CH-*C*H_3). ^{31}P NMR (δ (ppm), $CDCl_3$): 44.6. $[\alpha]_D = -60.8$ ($CHCl_3$, $c = 0.5$) MS (DCI, NH_3) *m/e*: 580 (M+1, 100%). Anal. Found: C, 67.93; H, 5.89; N, 2.18%. $C_{34}H_{36}FeNOPS$. Calc.: C, 68.38; H, 5.92; N, 2.42.

*3.1.4. Synthesis of (R)-(2-diphenylthiophosphino-ferrocenyl)(acetoxy)-methane (**5**)*

In a schlenk tube, 2.2 g of *N*-(2-diphenylthiophosphinoferrocenylmethyl)ephedrine (**3**) (3.8 mmol) was dissolved in 100 mL of acetic anhydride (1.06 mmol) under argon. The solution was stirred for 16 h at 120 °C. After cooling to RT and removal of the solvent with a high vacuum pump, the crude products were filtered over silicagel with a pentane/ether mixture (1/1, v/v) to yield 1.60 g of *R*-(**5**) as an orange solid (Yield = 95%).

^1H NMR (δ (ppm), $CDCl_3$): 7.84–7.77 (2H, m, PPh_2); 7.67–7.61 (2H, m, PPh_2); 7.55–7.43 (4H, m, PPh_2); 7.41–7.36 (2H, m, PPh_2); 5.57 (1H, d, AB syst, $J = 11.8$ Hz, CH_2); 5.03 (1H, d, AB syst, $J = 11.8$ Hz, CH_2); 4.62 (1H, m, subst Cp); 4.37 (5H, s, Cp); 4.36 (1H, m, subst Cp); 3.83 (1H, m, subst Cp); 1.55 (3H, s, CH_3). ^{13}C NMR (δ (ppm), $CDCl_3$): 171.0 (CO); 135.3 ($J_{PC} = 87.6$ Hz, quat PPh_2); 133.6 ($J_{PC} = 86.0$ Hz, quat PPh_2); 132.4 ($J_{PC} = 10.9$ Hz, 2C PPh_2); 131.8 ($J_{PC} = 2.7$ Hz, PPh_2); 131.7 ($J_{PC} = 2.9$ Hz, PPh_2); 128.6 ($J_{PC} = 4.1$ Hz, PPh_2); 128.5 ($J_{PC} = 3.3$ Hz, PPh_2); 85.5 ($J_{PC} = 12.0$ Hz, quat Cp); 76.1 ($J_{PC} = 12.3$ Hz, subst Cp); 76.1 ($J_{PC} = 93.6$ Hz, quat Cp); 75.6 ($J_{PC} = 8.7$ Hz, subst Cp); 71.2 (Cp); 70.1 ($J_{PC} = 10.3$ Hz, subst Cp); 61.7 (CH_2); 20.8 (CH_3). ^{31}P NMR (δ (ppm), $CDCl_3$): 44.1. $[\alpha]_D = +23.0$ ($CHCl_3$, $c = 0.5$) MS (DCI, NH_3) *m/e*: 475 (M+1, 100%), 415 (M-OAc, 100%). Anal. Found: C, 63.24; H, 4.89%. $C_{25}H_{23}FeOPS$. Calc.: C, 63.28; H, 4.89.

*3.1.5. Synthesis of (R)-(2-diphenylthiophosphinoferrocenyl) methanol (**6**)*

In an Erlenmeyer flask, a solution of 2.5 g (5.27 mmol) of *R*-(**5**) in 420 mL of methanol was slowly poured into 170 mL of a sodium hydroxide solution in water (2 mol L^{-1}). The reaction mixture was vigorously stirred overnight. After evaporation of methanol, the reaction mixture was extracted with dichloromethane, washed with brine and dried on sodium sulfate. The crude product was then purified by flash chromatography on silicagel by using a pentane/ether mixture (1/1, v/v) as eluent to yield 2.17 g of *R*-(**6**) as a yellow solid (yield = 95%). The physical data were similar to those published in Refs. [8g,19].

*3.1.6. Synthesis of (R)-(2-diphenylthiophosphino)-ferrocenecarboxaldehyde (**7**)*

In a Schlenk tube, 100 mg of N-morpholine oxide (NMO) was heated at 90 °C under high vacuum for 3 h. After cooling to RT, 10 mL of dry acetone, 100 mg of alcohol *R*-(**6**) (0.23 mmol) and 10 mg of $[RuCl_2(PPh_3)_3]$ were successively introduced under argon. The reaction mixture was then stirred for 3 h at RT. After evaporation of the acetone, 20 mL of ether and 20 mL of a 2 N chlorhydric acid solution were added. The organic phase was washed with water and dried on sodium sulfate. The crude product was then purified by flash chromatography on silicagel by using a pentane/ether mixture (1/1, v/v) as eluent to yield 85 g of *R*-(**7**) (yield = 85%) as a red solid.

(*R*)-(***7***): ^1H NMR (δ (ppm), $CDCl_3$): 10.7 (CHO); 7.85–7.75 (2H, m, PPh_2); 7.7–7.3 (8H, m, PPh_2) ; 5.25 (1H, m, subst Cp); 4.71 (1H, m, subst Cp); 4.47 (5H, s, Cp); 4.09 (1H, td, $J = 2.6$ Hz and $J = 1.5$ Hz, subst Cp). ^{13}C NMR (δ (ppm), $CDCl_3$): 194.1 (CHO); 134.4 ($J_{PC} = 87.8$ Hz, quat PPh_2); 132.7 ($J_{PC} = 86.3$ Hz, quat PPh_2); 132.0 ($J_{PC} = 11.0$ Hz, PPh_2); 131.8 ($J_{PC} = 10.7$ Hz, PPh_2); 131.7 ($J_{PC} = 2.2$ Hz, PPh_2); 131.6 ($J_{PC} = 3.0$ Hz, PPh_2); 128.5 ($J_{PC} = 12.7$ Hz, PPh_2); 128.3 ($J_{PC} = 12.6$ Hz, PPh_2); 82.6 ($J_{PC} = 10.1$ Hz, quat Cp); 79.7 ($J_{PC} = 90.7$ Hz, quat Cp); 79.5 ($J_{PC} = 12.9$ Hz, subst Cp); 73.2 ($J_{PC} = 10.0$ Hz, subst Cp); 71.9 ($J_{PC} = 7.7$ Hz, subst Cp); 71.4 (Cp). ^{31}P NMR (δ (ppm), $CDCl_3$): 40.6. $[\alpha]_D = +433$ ($CHCl_3$, $c = 0.2$) MS (EI) *m/e*: 430 (M, 32%), 337 (53%), 49 (100%). Anal. Found: C, 62.51; H, 3.80%. $C_{23}H_{19}FeOPS$. Calc.: C, 64.20; H, 4.45.

3.2. Synthesis of the ligands

*3.2.1. General procedure for the preparation of acetals (**8**) and (**9**)*

Aldehyde (R_p)-**7** (117 mg, 0.27 mmol) was added to a round-bottomed flask equipped with a Dean-Stark apparatus. The system was purged with argon and the red solid was dissolved in 100 mL of dry toluene. (1*R*)-1,3-butanediol (36 mg, 0.4 mmol) and a catalytic amount of camphorsulphonic acid were then successively added to the reaction mixture. After heating for 2 h at 110 °C, the reaction mixture was cooled to room temperature and

diluted with 50 mL of dichloromethane. Anhydrous potassium carbonate was added and the mixture stirred for 1 h. After filtration through celite and evaporation of the solvents, the crude product was then purified by flash chromatography on silica gel with a pentane/ether mixture (10:1, v/v) as eluent to yield 91 mg (66%) of acetal as a yellow solid.

(*1S,3R,R*$_p$)-***8a*** (Yield = 66%): ^{1}H NMR ($CDCl_3$): δ 7.84 (2H, m, Ph); 7.63 (2H, m, Ph); 7.55–7.40 (4H, m, Ph), 7.37 (2H, m, Ph); 6.07 (1H, s, OC*H*O); 4.91 (1H, m, subst Cp); 4.36 (5H, s, Cp); 4.35 (1H, m, subst Cp); 3.91 (1H, m, CH); 3.80 (1H, m, subst Cp); 3.66 (1H, m, OCH_2); 3.61 (1H, m, OCH_2); 1.59 (1H, m, CH_2CH); 1.37 (1H, m, CH_2CH); 1.30 (3H, d, $J = 6.2$ Hz, CH_3). ^{13}C NMR ($CDCl_3$): δ 135.1 ($J = 88.6$ Hz, quat Ph); 133.7 ($J = 86.4$ Hz quat Ph); 132.3 ($J = 10.7$ Hz, Ph); 132.0 ($J = 10.9$ Hz, Ph); 131.2 ($J = 2.9$ Hz, Ph); 130.08 ($J = 3.0$ Hz, Ph); 128.0 ($J = 12.4$ Hz, Ph); 127.9 ($J = 12.7$ Hz, Ph); 97.8 (OCHO); 89.9 ($J = 11.2$ Hz, quat Cp); 74.9 ($J = 12.4$ Hz, subst Cp); 74.0 ($J = 94.6$ Hz, quat Cp); 73.1 (CH); 71.1 (Cp); 70.9 ($J = 8.8$ Hz, subst Cp); 69.5 ($J = 10.3$ Hz, subst Cp); 66.5 (O*C*H$_2$); 32.9 (*C*H$_2$CH); 22.0 (CH_3) ^{31}P NMR ($CDCl_3$): δ 42.6 $[\alpha]_D = -61.3$ ($CHCl_3$, $c = 0.3$). HR/MS (ES^+): 525.0701 (calc. M + Na: 525.0716).

(*1S,3R,S*$_p$)-***9a*** (Yield = 75%): ^{1}H NMR ($CDCl_3$): δ 7.84 (2H, m, Ph); 7.67 (2H, m, Ph); 7.46 (4H, m, Ph), 7.37 (2H, m, Ph); 6.22 (1H, s, OC*H*O); 4.86 (1H, m, subst Cp); 4.38 (5H, s, Cp); 4.33 (1H, m, subst Cp); 4.19 (1H, dd, $J = 11.3$ Hz and 4.8 Hz, OCH_2); 3.94 (1H, m, OCH_2); 3.91 (1H, m, CH); 3.72 (1H, m, subst Cp); 1.58 (1H, m, CH_2CH); 1.36 (1H, br d, $J = 14.9$ Hz, CH_2CH); 0.59 (3H, d, $J = 6.2$ Hz, CH_3). ^{13}C NMR ($CDCl_3$): δ 135.0 ($J = 89.0$ Hz, quat Ph); 133.6 ($J = 86.2$ Hz); 132.25 ($J = 10.7$ Hz, Ph); 132.18 ($J = 10.8$ Hz, Ph); 131.2 ($J = 2.9$ Hz, Ph); 130.8 ($J = 3.0$ Hz, Ph); 128.0 ($J = 12.3$ Hz, Ph); 127.8 ($J = 12.8$ Hz, Ph); 98.2 (OCHO); 89.6 ($J = 11.1$ Hz, quat Cp); 75.3 ($J = 12.1$ Hz, subst Cp); 74.0 ($J = 94.6$ Hz, quat Cp); 72.6 (CH); 71.0 (Cp); 70.6 ($J = 8.8$ Hz, subst Cp); 69.2 ($J = 10.3$ Hz, subst Cp); 67.2 (O*C*H$_2$); 33.0 (*C*H$_2$CH); 20.8 (CH_3) ^{31}P NMR ($CDCl_3$): δ 42.7 $[\alpha]_D = +8.6$ ($CHCl_3$, $c = 0.5$). HR/MS (ES^+): 525.0699 (calc. M + Na: 525.0716).

(*3R,5R,R*$_p$)-***8b*** (Yield = 63%): ^{1}H NMR ($CDCl_3$): δ 7.82 (2H, m, Ph); 7.66 (2H, m, Ph); 7.48 (4H, m, Ph), 7.38 (2H, m, Ph); 6.54 (1H, s, OC*H*O); 4.90 (1H, m, subst Cp); 4.42 (5H, s, Cp); 4.32 (1H, m, subst Cp); 4.15 (1H, m, CH); 3.93 (1H, m, CH); 3.61 (1H, m, subst Cp); 1.77 (1H, m, CH_2); 1.28 (3H, d, $J = 6.1$ Hz, CH_3); 1.25 (1H, m, CH_2); 0.98 (3H, d, $J = 7.0$ Hz, CH_3). ^{13}C NMR ($CDCl_3$): δ 134.6 ($J = 88.2$ Hz, quat Ph); 133.6 ($J = 85.9$ Hz quat Ph); 132.4 ($J = 10.8$ Hz, Ph); 132.1 ($J = 11.8$ Hz, Ph); 131.2 ($J = 2.9$ Hz, Ph); 130.9 ($J = 3.0$ Hz, Ph); 128.0 ($J = 12.4$ Hz, Ph); 127.8 ($J = 12.7$ Hz, Ph); 90.7 ($J = 11.8$ Hz, quat Cp); 90.5 (OCHO); 74.9 ($J = 12.2$ Hz, subst Cp); 74.2 ($J = 93.9$ Hz, quat Cp); 71.1 (Cp); 70.9 ($J = 8.8$ Hz, subst Cp); 69.3 ($J = 10.2$ Hz, subst Cp); 69.0 (CH); 68.0 (CH); 36.8 (CH_2); 22.1 (CH_3); 17.2 (CH_3). ^{31}P NMR ($CDCl_3$): δ 42.1 $[\alpha]_D = -32.2$ ($CHCl_3$, $c = 0.2$). HR/MS (ES^+): 539.0870 (calc. M + Na: 539.0873).

(*3R,5R,S*$_p$)-***9b*** (Yield = 67%): ^{1}H NMR ($CDCl_3$): δ 7.84 (2H, m, Ph); 7.68 (2H, m, Ph); 7.55–7.42 (4H, m, Ph), 7.37 (2H, m, Ph); 6.52 (1H, s, OC*H*O); 4.86 (1H, m, subst Cp); 4.40 (1H, m, subst Cp); 4.37 (5H, s, Cp); 4.33 (1H, m, subst Cp); 3.85 (1H, m, CH); 3.75 (1H, m, CH); 1.75 (1H, m, CH_2); 1.49 (3H, d, $J = 6.1$ Hz, CH_3); 1.25 (1H, m, CH_2); 0.59 (3H, d, $J = 6.2$ Hz, CH_3). ^{13}C NMR ($CDCl_3$): δ 135.0 ($J = 88.8$ Hz, quat Ph); 133.6 ($J = 86.1$ Hz quat Ph); 132.3 ($J = 7.1$ Hz, Ph); 132.2 ($J = 7.2$ Hz, Ph); 131.2 ($J = 2.9$ Hz, Ph); 130.8 ($J = 3.0$ Hz, Ph); 128.0 ($J = 2.3$ Hz, Ph); 127.8 ($J = 2.8$ Hz, Ph); 90.8 (OCHO); 89.8 ($J = 11.1$ Hz, quat Cp); 75.2 ($J = 12.2$ Hz, subst Cp); 74.4 ($J = 94.6$ Hz, quat Cp); 71.0 (Cp); 70.5 ($J = 8.8$ Hz, subst Cp); 69.2 ($J = 10.4$ Hz, subst Cp); 68.8 (CH); 67.7 (CH); 36.7 (CH_2); 21.0 (CH_3); 17.8 (CH_3). ^{31}P NMR ($CDCl_3$): δ 42.8 $[\alpha]_D = +25.4$ ($CHCl_3$, $c = 0.6$). HR/MS (ES^+): 539.0884 (calc. M + Na: 539.0873).

(*3R,4R,R*$_p$)-***8c*** (Yield = 72%): ^{1}H NMR ($CDCl_3$): δ 7.84 (2H, m, Ph); 7.67 (2H, m, Ph); 7.55–7.35 (6H, m, Ph), 6.53 (1H, s, OC*H*O); 4.80 (1H, m, subst Cp); 4.41 (5H, s, Cp); 4.36 (1H, m, subst Cp); 3.85 (1H, m, subst Cp); 3.59 (1H, m, CH); 3.45 (1H, m, CH); 1.32 (3H, d, $J = 6.0$ Hz, CH_3); 0.95 (3H, d, $J = 6.1$ Hz, CH_3). ^{13}C NMR ($CDCl_3$): δ 134.9 ($J = 78.0$ Hz, quat Ph); 133.6 ($J = 86.3$ Hz quat Ph); 132.3 ($J = 10.8$ Hz, Ph); 132.1 ($J = 10.9$ Hz, Ph); 131.2 ($J = 2.9$ Hz, Ph); 131.0 ($J = 3.0$ Hz, Ph); 127.98 ($J = 13.4$ Hz, Ph); 127.94 ($J = 12.7$ Hz, Ph); 99.0 (OCHO); 90.1 ($J = 11.2$ Hz, quat Cp); 79.4 (CH); 77.5 (CH); 75.5 ($J = 12.4$ Hz, subst Cp); 74.1 ($J = 93.8$ Hz, quat Cp); 71.1 ($J = 8.9$ Hz, subst Cp); 71.0 (Cp); 69.4 ($J = 10.4$ Hz, subst Cp); 17.1 (CH_3); 16.4 (CH_3). ^{31}P NMR ($CDCl_3$): δ 42.2 $[\alpha]_D = -94.9$ ($CHCl_3$, $c = 0.2$). HR/MS (ES^+): 525.0705 (calc. M + Na: 525.0716).

(*3R,4R,S*$_p$)-***9c*** (Yield = 76%): ^{1}H NMR ($CDCl_3$): δ 7.84 (2H, m, Ph); 7.66 (2H, m, Ph); 7.55–7.45 (4H, m, Ph), 7.38 (2H, m, Ph); 6.45 (1H, s, OC*H*O); 4.79 (1H, m, subst Cp); 4.40 (5H, s, Cp); 4.38 (1H, m, subst Cp); 3.87 (1H, m, subst Cp); 3.67 (1H, m, CH); 3.51 (1H, m, CH); 1.26 (3H, d, $J = 6.1$ Hz, CH_3); 1.06 (3H, d, $J = 6.0$ Hz, CH_3). ^{13}C NMR ($CDCl_3$): δ 135.0 ($J = 88.2$ Hz, quat Ph); 133.6 ($J = 86.4$ Hz quat Ph); 132.4 ($J = 10.8$ Hz, Ph); 132.2 ($J = 11.0$ Hz, Ph); 131.3 ($J = 2.9$ Hz, Ph); 131.0 ($J = 3.0$ Hz, Ph); 127.94 ($J = 12.4$ Hz, Ph); 127.92 ($J = 12.8$ Hz, Ph); 99.1 (OCHO); 89.9 ($J = 11.5$ Hz, quat Cp); 80.2 (CH); 78.7 (CH); 75.5 ($J = 12.4$ Hz, subst Cp); 74.9 ($J = 94.0$ Hz, quat Cp); 71.1 (Cp); 70.5 ($J = 8.5$ Hz, subst Cp); 69.6 ($J = 10.6$ Hz, subst Cp); 17.4 (CH_3); 16.9 (CH_3). ^{31}P NMR ($CDCl_3$): δ 42.4 $[\alpha]_D = +70.6$ ($CHCl_3$, $c = 0.2$). HR/MS (ES^+): 525.0708 (calc. M + Na: 525.0716).

3.2.2. General procedure for the desulfurization of the thiophosphines

In a Schlenk tube, 115 mg of **8a** (0.23 mmol) was dissolved in 5 mL of toluene with 0.2 mL of tris-(dimeth-

ylamino)phosphine (5 equiv.). The solution was heated to reflux overnight. After cooling to RT, the solvent was removed in vacuo. The crude product was then purified, under argon, by flash chromatography on silicagel by using dichloromethane as eluent. 87 mg of pure **10a** was obtained as a yellow solid (93% yield).

(*1S,3R,R*$_p$)-***10a*** (Yield = 96%): ^{1}H NMR ($CDCl_3$): δ 7.59 (2H, m, Ph); 7.40 (2H, m, Ph); 7.25–7.15 (6H, m, Ph); 5.56 (1H, s, OC*H*O); 4.72 (1H, m, subst Cp); 4.30 (1H, m, subst Cp); 4.09 (5H, s, Cp); 3.91 (2H, m, CH + 1H OCH_2); 3.72 (1H, m, subst Cp); 3.69 (1H, m, CH_2); 1.60 (1H, m, CH_2CH); 1.39 (1H, m, CH_2CH); 1.29 (3H, d, $J = 6.2$ Hz, CH_3). ^{13}C NMR ($CDCl_3$): δ 140.1 ($J = 9.4$ Hz, quat Ph); 137.8 ($J =$ 8.5 Hz, quat Ph); 135.2 ($J = 21.2$ Hz, Ph); 132.4 ($J =$ 17.7 Hz, Ph); 128.1 ($J = 7.8$ Hz, Ph); 127.7 ($J = 6.0$ Hz, Ph); 127.4 (Ph); 99.3 ($J = 9.2$ Hz, OCHO); 91.3 ($J = 21.0$ Hz, quat Cp); 74.9 ($J = 8.7$ Hz, quat Cp); 73.1 (CH); 71.6 ($J = 3.5$ Hz, subst Cp); 70.6 (Cp); 69.6 (subst Cp); 69.4 ($J = 3.7$ Hz, subst Cp); 66.8 (O*C*H_2); 32.9 (CH_2CH); 21.9 (CH_3) ^{31}P NMR ($CDCl_3$): δ −20.7.

(*1S,3R,S*$_p$)-***11a*** (Yield = 95%): ^{1}H NMR ($CDCl_3$): δ 7.58 (2H, m, Ph); 7.40 (3H, m, Ph); 7.25–7.15 (5H, m, Ph); 5.68 (1H, d, $J = 2.4$ Hz, OC*H*O); 4.71 (1H, m, subst Cp); 4.29 (1H, t, $J = 2.5$ Hz, subst Cp); 4.27 (1H, m, O*C*H_2); 4.10 (5H, s, Cp); 3.93 (1H, td, $J = 12.9$ Hz, $J = 2.6$ Hz, O*C*H_2); 3.71 (1H, m, subst Cp); 3.67 (1H, m, CH); 1.63 (1H, m, CH_2CH); 1.43 (1H, m, CH_2CH); 0.78 (3H, d, $J = 6.2$ Hz, CH_3). ^{13}C NMR ($CDCl_3$): δ 139.7 ($J = 8.8$ Hz, quat Ph); 137.3 ($J = 7.8$ Hz, quat Ph); 135.2 ($J = 26.8$ Hz, Ph); 132.6 ($J = 18.1$ Hz, Ph); 129.1 (Ph); 127.1 ($J = 7.8$ Hz, Ph); 127.6 ($J = 6.2$ Hz, Ph); 127.5 (Ph); 99.7 ($J = 9.9$ Hz, OCHO); 90.9 ($J = 21.2$ Hz, quat Cp); 74.9 ($J = 9.2$ Hz, quat Cp); 73.0 (CH); 71.7 ($J = 4.0$ Hz, subst Cp); 70.0 (Cp); 69.4 (subst Cp); 69.0 ($J = 3.7$ Hz, subst Cp); 67.2 (OCH_2); 32.9 (CH_2CH); 21.1 (CH_3) ^{31}P NMR ($CDCl_3$): δ −21.0.

(*3R,5R,R*$_p$)-***10b*** (Yield = 93%): ^{1}H NMR ($CDCl_3$): δ 7.57 (2H, m, Ph); 7.40 (3H, m, Ph); 7.24 (5H, m, Ph), 5.93 (1H, d, $J = 2.7$ Hz, OC*H*O); 4.76 (1H, m, subst Cp); 4.29 (1H, t, $J = 2.5$ Hz, subst Cp); 4.16–4.05 (2H, m, 2CH); 4.12 (5H, s, Cp); 3.63 (1H, m, subst Cp); 1.77 (1H, m, CH_2); 1.28 (3H, d, $J = 6.2$ Hz, CH_3); 1.26 (1H, m, CH_2); 1.10 (3H, d, $J = 7.0$ Hz, CH_3). ^{13}C NMR ($CDCl_3$): δ 139.6 ($J = 9.6$ Hz, quat Ph); 137.4 ($J = 8.8$ Hz quat Ph); 135.2 ($J = 20.9$ Hz, Ph); 132.7 ($J = 18.3$ Hz, Ph); 129.1 (Ph); 128.1 ($J = 7.7$ Hz, Ph); 127.7 ($J = 6.2$ Hz, Ph); 127.6 (Ph); 91.9 ($J = 10.8$ Hz, OCHO); 91.7 ($J = 20.6$ Hz, quat Cp); 74.9 ($J = 8.6$ Hz, quat Cp); 71.3 ($J = 4.4$ Hz, subst Cp); 70.0 (Cp); 69.5 (subst Cp); 69.2 ($J = 3.5$ Hz, subst Cp); 68.7 (CH); 68.1 (CH); 36.6 (CH_2); 22.1 (CH_3); 16.8 (CH_3). ^{31}P NMR ($CDCl_3$): δ −21.4.

(*3R,5R,S*$_p$)-***11b*** (Yield = 93%): ^{1}H NMR ($CDCl_3$): δ 7.58 (2H, m, Ph); 7.40 (3H, m, Ph); 7.27–7.20 (5H, m, Ph), 5.99 (1H, d, $J = 2.4$ Hz, OC*H*O); 4.71 (1H, m, subst Cp); 4.44 (1H, m, CH); 4.28 (1H, t, $J = 2.4$ Hz, subst Cp); 4.10 (5H, s, Cp); 3.87 (1H, m, CH); 3.70 (1H, m, subst Cp); 1.80 (1H, m, CH_2); 1.50 (3H, d, $J = 7.0$ Hz, CH_3); 1.27 (1H, m, CH_2); 0.73 (3H, d, $J = 6.2$ Hz, CH_3). ^{13}C NMR ($CDCl_3$): δ 139.7 ($J = 8.8$ Hz, quat Ph); 137.4 ($J = 7.9$ Hz quat Ph); 135.2 ($J = 20.9$ Hz, Ph); 132.6 ($J = 18.2$ Hz, Ph); 129.1 (Ph); 128.1 ($J = 7.7$ Hz, Ph); 127.6 ($J = 6.3$ Hz, Ph); 127.5 (Ph); 92.3 ($J = 9.8$ Hz, OCHO); 91.0 ($J =$ 20.4 Hz, quat Cp); 75.1 ($J = 9.0$ Hz, quat Cp); 71.9 ($J = 3.4$ Hz, subst Cp); 69.9 (Cp); 69.3 (subst Cp); 69.0 (J = 3.7 Hz, subst Cp); 68.5 (CH); 67.8 (CH); 36.6 (CH_2); 21.2 (CH_3); 17.5 (CH_3). ^{31}P NMR ($CDCl_3$): δ −21.0.

(*3R,4R,R*$_p$)-***10c*** (Yield = 96%): ^{1}H NMR ($CDCl_3$): δ 7.57 (2H, m, Ph); 7.40 (3H, m, Ph); 7.23 (5H, m, Ph), 6.12 (1H, d, $J = 1.9$ Hz, OC*H*O); 4.64 (1H, m, subst Cp); 4.30 (1H, m, subst Cp); 4.14 (5H, s, Cp); 3.69 (1H, m, subst Cp); 3.63 (1H, m, CH); 3.49 (1H, m, CH); 1.15 (3H, d, $J = 6.0$ Hz, CH_3); 1.11 (3H, d, $J = 6.1$ Hz, CH_3). ^{13}C NMR ($CDCl_3$): δ 140.2 ($J = 10.4$ Hz, quat Ph); 137.8 ($J = 10.0$ Hz quat Ph); 135.2 ($J = 21.3$ Hz, Ph); 132.5 ($J = 18.1$ Hz, Ph); 129.1 (Ph); 128.1 ($J = 7.7$ Hz, Ph); 127.8 ($J = 6.0$ Hz, Ph); 127.5 (Ph); 101.0 ($J = 7.4$ Hz, OCHO); 90.4 ($J = 19.8$ Hz, quat Cp); 79.8 (CH); 78.0 (CH); 75.1 ($J = 12.0$ Hz, quat Cp); 72.2 ($J = 4.2$ Hz, subst Cp); 70.1 ($J = 3.7$ Hz, subst Cp); 70.0 (Cp); 69.6 (subst Cp); 16.9 (CH_3); 16.7 (CH_3). ^{31}P NMR ($CDCl_3$): δ −21.1.

(*3R,4R,S*$_p$)-***11c*** (Yield = 97%): ^{1}H NMR ($CDCl_3$): δ 7.59 (2H, m, Ph); 7.41 (3H, m, Ph); 7.23 (5H, m, Ph), 6.12 (1H, d, $J = 2.2$ Hz, OC*H*O); 4.66 (1H, m, subst Cp); 4.33 (1H, t, $J = 2$ Hz, subst Cp); 4.12 (5H, s, Cp); 3.73 (1H, m, subst Cp); 3.64 (1H, m, CH); 3.52 (1H, m, CH); 1.26 (3H, d, $J = 6.1$ Hz, CH_3); 1.14 (3H, d, $J = 6.1$ Hz, CH_3). ^{13}C NMR ($CDCl_3$): δ 140.4 ($J = 9.9$ Hz, quat Ph); 137.8 ($J = 9.2$ Hz quat Ph); 135.4 ($J = 21.5$ Hz, Ph); 132.4 ($J = 17.5$ Hz, Ph); 129.2 (Ph); 128.1 ($J = 7.8$ Hz, Ph); 127.8 ($J = 5.8$ Hz, Ph); 127.4 (Ph); 100.9 ($J = 8.6$ Hz, OCHO); 90.4 ($J = 19.7$ Hz, quat Cp); 80.6 (CH); 78.4 (CH); 75.3 ($J = 11.8$ Hz, quat Cp); 72.1 ($J = 4.2$ Hz, subst Cp); 70.0 (Cp); 69.9 (subst Cp); 69.4 ($J = 3.7$ Hz, subst Cp); 17.4 (CH_3); 16.7 (CH_3). ^{31}P NMR ($CDCl_3$): δ −21.0.

3.3. General procedure for palladium-catalyzed allylic substitution

A mixture of ligand **9** (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), potassium acetate and BSA (0.250 mL, 1 mmol) were then added to the resulting solution. The reaction was carried out at room temperature and monitored by TLC for disappearance of acetate. After complete reaction, 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 sulfate, filtered and the solvents evaporated. The conversion was calculated from the crude reaction mixture by ^{1}H NMR spectroscopy. Subsequent purification by chromatography on silica eluting with dichloromethane/pentane (1:1) afforded the product as colourless oil. The enantiomeric excess was

Table 3
Crystal data and structure refinement

Identification code	(+/−)-**(1)**	**3**	**4**	**8a**	**8b**	**8c**	**9a**	**9b**	**9c**
Empirical formula	C_{25} H_{26} Fe N P S	C_{66} H_{68} Fe_2 N_2 O_2 P_2 S_2	C_{33} H_{34} Fe N O P S	C_{27} H_{27} Fe O_2 P S	C_{28} H_{29} Fe O_2 P S	C_{27} H_{27} Fe O_2 P S	C_{27} H_{27} Fe O_2 P S	C_{28} H_{29} Fe O_2 P S	C_{27} H_{27} Fe O_2 P S
Formula weight	459.35	1158.98	579.49	502.37	516.39	502.37	502.37	516.39	502.37
Temperature (K)	293(2) K	180(2) K	160(2) K	180(2)	180(2)	180(2)	180(2)	180(2)	180(2)
Wavelength (Å)	0.71073 Å	0.71073 Å	0.71073 Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Orthorhombic	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_12_12_1$	$P2_12_12_1$	$P2_1$	$P2_12_12_1$	$P2_1$	$P2_12_12_1$	$P2_1$	$P2_1$
a (Å)	8.3085(12)	12.6524(8)	10.5269(7)	9.0520(8)	8.8718(17)	9.1705(15)	9.0578(7)	9.2967(9)	8.977(3)
b (Å	11.8545(17)	35.827(2)	12.2372(10)	11.2472(13)	15.184(3)	11.2379(14)	15.3064(16)	12.6384(13)	11.215(4)
c (Å)	12.6128(18)	12.7346(11)	22.677(2)	12.2179(10)	37.500(7)	12.426(3)	17.2544(14)	11.4338(11)	12.559(3)
α (°)	103.522(17)	90	90.0	90	90	90	90	90	90
β (°)	104.951(16)	90	90.0	109.577(9)	90	108.83(2)	90	104.368(8)	108.14(3)
γ (°)	106.548(17)	90	90.0	90	90	90	90	90	90
Volume (Å^3)	1085.3(3)	5772.6(7)	2921.2(4)	1172.0(2)	5051.5(17)	1212.1(3)	2392.2(4)	1301.4(2)	1201.6(6)
Z	2	4	4	2	8	2	4	2	2
D_{calc} (Mg/m^3)	1.406	1.334	1.318	1.424	1.358	1.376	1.395	1.318	1.388
Absorption coefficient (mm^{-1})	0.876	0.677	0.669	0.823	0.766	0.796	0.807	0.743	0.803
F(000)	480	2432	1216	524	2160	524	1048	540	524
Crystal size (mm^3)	$0.77 \times 0.75 \times 0.63$	$0.8 \times 0.64 \times 0.34$	$0.64 \times 0.64 \times 0.16$	$0.8 \times 0.44 \times 0.08$	$0.356 \times 0.139 \times 0.035$	$0.25 \times 0.25 \times 0.003$	$0.37 \times 0.33 \times 0.043$	$0.39 \times 0.266 \times 0.077$	$0.54 \times 0.46 \times 0.033$
Θ Range (°)	2.69–28.23	1.70–20.97	1.80–24.19	2.39–26.09	2.73–26.32	2.35–26.12	2.91–32.27	3.25–32.14	3.06–26.30
Reflections collected	13 139	25 012	23 736	11 586	38 888	12 064	25 635	13 376	8822
Independent reflections (R_{int})	4864 (0.0446)	6119 (0.0348)	4632 (0.0456)	4300 (0.0474)	10302 (0.2063)	4695 (0.1688)	7900 (0.0634)	6769 (0.0488)	4697 (0.0755)
Completeness (%)	90.7	99.3	99.1	92.3	99.8	98.3	95.2	93.9	99.8
Absorption correction	None	Empirical	Empirical	Multi-scan	Muli-scan	Multi-scan	Multi-scan	Multi-scan	Multi-scan
Max., min. transmission		0.7672, 0.3465	0.8523, 0.5326	1.0898, 0.5070	0.9295, 0.8568	0.9259 and 0.9035	0.9205, 0.7636	1.00, 0.679	0.9669, 0.7055
Refinement method	F^2	F^2	F^2	F^2	F^2	F^2	F^2	F^2	F^2
Data/restraints/parameters	4864/0/264	6119/0/697	4632/0/349	4300/1/290	10302/0/299	4695/1/291	7900/0/290	6769/1/300	4697/1/291
Goodness-of-fit on F^2	1.068	1.031	1.001	1.014	0.781	0.832	0.761	0.807	0.831
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0353$, $wR_2 = 0.0909$	$R_1 = 0.0215$, $wR_2 = 0.0536$	$R_1 = 0.0242$, $wR_2 = 0.0559$	$R_1 = 0.0347$, $wR_2 = 0.0868$	$R_1 = 0.0704$, $wR_2 = 0.0908$	$R_1 = 0.0530$, $wR_2 = 0.0759$	$R_1 = 0.0357$, $wR_2 = 0.0464$	$R_1 = 0.0383$, $wR_2 = 0.0650$	$R_1 = 0.0523$, $wR_2 = 0.0982$
R indices (all data)	$R_1 = 0.0423$, $wR_2 = 0.0987$	$R_1 = 0.0231$, $wR_2 = 0.0542$	$R_1 = 0.0282$, $wR_2 = 0.0570$	$R_1 = 0.0371$, $wR_2 = 0.0884$	$R_1 = 0.1996$, $wR_2 = 0.1249$	$R_1 = 0.1870$, $wR_2 = 0.1100$	$R_1 = 0.0800$, $wR_2 = 0.0518$	$R_1 = 0.0742$, $wR_2 = 0.0717$	$R_1 = 0.0886$, $wR_2 = 0.1113$
Absolute structure parameter		−0.009(9)	−0.020(11)	−0.025(13)	0.00(3)	−0.03(4)	−0.009(10)	0.028(12)	0.05(3)
Largest difference peak and hole (e Å^{-3})	0.352 and −0.436	0.291 and −0.139	0.164 and −0.180	0.631 and −0.709	0.389 and −0.370	0.711 and −1.617	0.255 and −0.286	0.340 and −0.296	0.518 and −0.445

determined by ^{1}H NMR spectroscopy using the chiral shift reagent (+) Eu(hfc)$_3$.

3.4. X-ray crystallographic study

A single crystal of each compound was mounted under inert perfluoropolyether at the tip of glass fibre and cooled in the cryostream of either the Oxford-Diffraction XCALIBUR CCD diffractometer for (**9a**), (**8b**), (**9b**) and (**9c**) or the Stoe IPDS diffractometer for (+/−)-(**1**), (**3**), (**4**), (**8a**) and (**8c**). Data were collected by using the monochromatic Mo Kα radiation ($\lambda = 0.71073$). The final unit cell parameters were obtained by the least-squares refinement of a large number of selected reflections. For all compounds, only statistical fluctuations were observed in the intensity monitors over the course of the data collections.

All structures were solved by direct methods (SIR97 [20]) and refined by least-squares procedures on F^2 with the SHELXL-97 program [21] using the integrated system WINGX(1.63) [22]. For all compounds, the H atoms attached to carbon atoms were introduced at calculated positions and treated as riding on their parent atoms [d(CH) = 0.96–0.98 Å] with a displacement parameter equal to 1.2 U_{eq} (C_6H_5, CH_2, OH) or 1.5 U_{eq} (CH_3) times that of the parent atom. Absolute configuration was confirmed by the refinement of the Flack's enantiopole parameter [23] and careful examination of the sensitive reflections. The molecular views were created with the help of ORTEP-III [24]. Crystal data and refinement parameters are shown in Table 3.

4. Supplementary material

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication Nos. CCDC 285551–285559. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

We gratefully acknowledge financial support from the Centre National de la Recherche Scientifique (CNRS). One of us (N.M.) thanks the European Community (Marie Curie Training Site Program, Contract Number HPMT-CT-2001-00398) for a financing his stay in Toulouse. We are also grateful to Dr. Guy Lavigne and Pr. Jianliang Xiao for coordinating Marie Curie Training Site placement of N. Mateus.

References

[1] (a) E.N. Jacobsen, A. Pfalz, H. Yamamoto, Comprehensive Asymmetric Catalysis, vols. 1–3, Springer, Berlin, 1999;
(b) I. Ojima, Catalytic Asymmetric Synthesis, Wiley–VCH, New York, 2000.

[2] A.M. Masdeu-Bulto, M. Dieguez, E. Martin, M. Gomez, Coord. Chem. Rev. 242 (2003) 159.

[3] A. Bader, E. Lindner, Coord. Chem. Rev. 108 (1991) 27.

[4] (a) E. Lindner, J. Dettinger, H.A. Mayer, H. Kühbauch, R. Fawzi, M. Steimann, Chem. Ber. 126 (1993) 1317;
(b) E. Lindner, J. Dettinger, R. Fawzi, M. Steimann, Chem. Ber. 126 (1993) 1347;
(c) A.M. Allgeier, E.T. Singewald, C.A. Mirkin, C.L. Stern, Organometallics 13 (1994) 2928;
(d) A.M. Allgeier, C.S. Slone, C.A. Mirkin, L.M. Liable-Sands, G.A. Yap, A.L. Rheingold, J. Am. Chem. Soc. 119 (1997) 5835;
(e) C. Andersson, J. Friedrich, M.H. Johansson, A. Oskarson, J. Mol. Struct. 479 (1999) 1;
(f) J.-F. Ma, Y. Kojima, Y. Yamamoto, J. Organomet. Chem. 616 (2000) 149;
(g) X. Bei, T. Uno, J. Norris, H.W. Turner, W.H. Weinberg, A.S. Guram, J.L. Petersen, J. Org. Chem. 64 (1999) 1840;
(h) X. Bei, H.W. Turner, W.H. Weinberg, A.S. Guram, J. Org. Chem. 64 (1999) 6797;
(i) R.C.J. Atkinson, V.C. Gibson, N.J. Long, A.J.P. White, D.J. Williams, Organometallics 23 (2004) 2744;
(j) J. Heinicke, M. Köhler, N. Peulecke, M.K. Kindermann, W. Keim, M. Köckerling, Organometallics 24 (2005) 344.

[5] (a) J.-F. Marcoux, S. Wagaw, S.L. Buchwald, J. Org. Chem. 62 (1997) 1568;
(b) B.H. Yang, S.L. Buchwald, J. Organomet. Chem. 576 (1999) 125;
(c) R. Weber, U. Englert, B. Ganter, W. Keim, M. Möthrath, Chem. Commun. (2000) 1419;
(d) E. Drent, R. van Dujk, R. van Ginkel, B. van Oort, R.I. Pugh, Chem. Commun. (2002) 964;
(e) W. Liu, J.M. Malinovski, M. Brookhart, Organometallics 21 (2002) 2836;
(f) L. Gonsalvi, H. Adams, G.S. Sunley, E. Ditzel, A. Haynes, J. Am. Chem. Soc. 124 (2002).

[6] (a) T. Hayashi, Acc. Chem. Rev. 33 (2000) 354;
(b) T. Hayashi, J.W. Han, A. Takeda, J. Tang, K. Nohmi, K. Mukaide, H. Tsuji, Y. Uozumi, Adv. Synth. Catal. 343 (2001) 279;
(c) J.W. Han, N. Tokunaga, T. Hayashi, J. Am. Chem. Soc. 123 (2001) 12915;
(d) F. Kakiuchi, P. Le Gendre, A. Yamada, H. Ohtaki, S. Murai, Tetrahedron Asym. 11 (2000) 2647;
(e) N. Nomura, J. Jin, H. Park, T.V. Rajanbabu, J. Am. Chem. Soc. 120 (1998) 459;
(f) T.V. Rajanbabu, N. Nomura, J. Jin, M. Nandi, H. Park, X. Sun, J. Org. Chem. 68 (2003) 8431;
(g) T.V. Rajanbabu, Chem. Rev. 103 (2003) 2845;
(h) A. Zhang, T.V. Rajanbabu, Org. Lett. 6 (2004) 1515;
(i) H. Huang, Z. Zheng, H. Luo, C. Bai, X. Hu, H. Chen, J. Org. Chem. 69 (2004) 2355.

[7] (a) Asymmetric alylic substitution: T. Hayashi, J. Organomet. Chem. 576 (1999) 195;
(b) T. Hayashi, M. Kawatsura, Y. Uozumi, J. Am. Chem. Soc. 120 (1998) 1681;
(c) M. Kawatsura, Y. Uozumi, M. Ogasawara, T. Hayashi, Tetrahedron 56 (2000) 2247;
(d) T. Okauchi, K. Fujita, T. Ohtaguro, S. Ohshima, T. Minami, Tetrahedron Asym. 11 (2000) 1397;
(e) H. Kodama, T. Taiji, T. Ohta, I. Furukawa, Tetrahedron Asym. 11 (2000) 4009;
(f) S.R. Gilbertson, P. Lan, Org. Lett. 3 (2001) 2237;
(g) W.-M. Dai, K.K.K. Yeung, J.-T. Liu, Y. Zhang, I.D. Williams, Org. Lett. 4 (2002) 1615;
(h) J. Clayden, P. Johnson, J.H. Pink, M. Helliwell, J. Org. Chem. 68 (2003) 8431;
(i) J. Clayden, L.W. Lai, M. Helliwell, Tetrahedron Asym. 12 (2001) 695;
(j) T. Mino, K. Kashiara, M. Yamashita, Tetrahedron Asym. 12 (2001) 287;

(k) M. Tollabi, E. Framery, C. Goux-Henry, D. Sinou, Tetrahedron Asym. 14 (2003) 3329;
(l) S. Gladiali, R. Taras, R.M. Ceder, M. Rocamora, G. Muller, X. Solans, M. Font-Bardia, Tetrahedron Asym. 14 (2004) 1477.

[8] (a) G. Iftime, C. Moreau-Bossuet, E. Manoury, G.G.A. Balavoine, J. Chem. Soc., Chem. Commun. (1996) 527;
(b) G. Iftime, J.-C. Daran, E. Manoury, G.G.A. Balavoine, Organometallics 15 (1996) 4808;
(c) G. Iftime, J.-C. Daran, E. Manoury, G.G.A. Balavoine, Angew. Chem. Int. Ed. 37 (1998) 1698;
(d) E. Manoury, J.S. Fossey, H. Ait-Haddou, J.-C. Daran, G.G.A. Balavoine, Organometallics 19 (2000) 3736;
(e) J. Chiffre, Y. Coppel, G.G.A. Balavoine, J.-C. Daran, E. Manoury, Organometallics 21 (2002) 4552;
(f) S. Mourgues, D. Serra, F. Lamy, S. Vincendeau, J.-C. Daran, E. Manoury, M. Gouygou, Eur. J. Inorg. Chem. (2003) 2820;
(g) L. Routaboul, S. Vincendeau, J.-C. Daran, E. Manoury, Tetrahedron Asym. 16 (2005) 2685.

[9] For recent overviews, see: (a) A. Togni, T. Hayashi, Ferrocenes, VCH, Weinheim, 1995;
(b) T.J. Colacot, Chem. Rev. 103 (2003) 3101;
(c) R.C.J. Atkinson, V.C. Gibson, N.J. Long, Chem. Soc. Rev. 33 (2004) 313.

[10] (a) O. Riant, O. Samuel, H.B. Kagan, J. Am. Chem. Soc. 115 (1993) 5835;
(b) O. Riant, O. Samuel, T. Flessner, S. Taudien, H.B. Kagan, J. Org. Chem. 62 (1997) 6733.

[11] L. Xiao, K. Mereiter, W. Weissensteiner, M. Wildham, Synthesis 8 (1999) 1354.

[12] (a) C. Marr, T. Hunt, J. Chem. Soc. C (1969) 1070;
(b) T. Hayashi, T. Mise, M. Fukushima, M. Kagotani, N. Nagashima, N. Hamada, A. Matsumoto, S. Kawakami, M. Konishi, K. Yamamoto, M. Kumada, Bull. Chem. Soc. Jpn. 53 (1980) 1138.

[13] J.D. Lou, Z.N. Xu, Tetrahedron Lett. 43 (2002) 6149.

[14] D.B. Desss, J.C. Martin, J. Org. Chem. 48 (1983) 4155.

[15] L. De Luca, G. Giacomelli, A. Porcheddu, J. Org. Chem. 66 (2001) 7907.

[16] K.B. Sharpless, K. Akashi, K. Oshima, Tetrahedron Lett. 29 (1976) 2503.

[17] J. Chiffre, F. Averseng, G.G.A. Balavoine, J.-C. Daran, G. Iftime, P.G. Lacroix, E. Manoury, K. Nakatani, Eur. J. Inorg. Chem. (2001) 2221.

[18] (a) B.M. Trost, D.L. van Vranken, Chem. Rev. 96 (1996) 395;
(b) A. Pfalz, H. Yamamoto, 834 of Ref. [1a].

[19] P. Stepnicka, I. Cisarova, New J. Chem. 26 (2002) 1389.

[20] A. Altomare, M.C. Burla, M. Camalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna, J. Appl. Cryst. 32 (1999) 115.

[21] G.M. Sheldrick, SHELXL97, Programs for Crystal Structure Analysis, Release 97-2, Institüt für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.

[22] L.J. Farrugia, J. Appl. Cryst. 32 (1999) 837.

[23] (a) H.D. Flack, Acta Crystallogr., Sect. A 39 (1983) 876;
(b) G. Bernardinelli, H.D. Flack, Acta Crystallogr., Sect. A 41 (1985) 500.

[24] (a) M.N. Burnett, C.K. Johnson, ORTEP-III-Report ORNL-6895, Oak Ridge National Laboratory, Oak Ridge, TN, 1996;
(b) L.J. Farrugia, J. Appl. Crystallogr. 30 (1997) 565.