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New ferrocenyl P,S and S,S ligands for asymmetric catalysis

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Abstract—Various new chiral ferrocenyl phosphine-thioethers and thiophosphine-thioethers with planar chirality only have been efficiently synthesized with good overall yields (39–43%) in enantiomerically pure form by a nine-step sequence involving the introduction of the planar chirality by Kagan's acetal method. These new P,S and S,S ligands have been successfully used in the palladium-catalyzed asymmetric allylic substitution reaction (ee up to 93%).

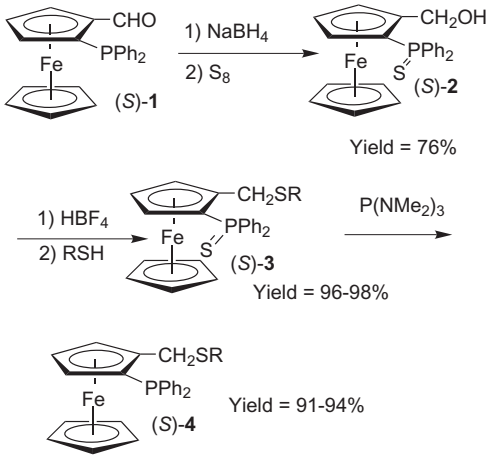
1. Introduction

Over 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. However, whereas numerous ligands bearing various combinations of heteroelements (in particular, P–P, P–N, or N–N ligands) have been extensively studied, sulfur-containing ligands have been much less involved in homogenous asymmetric catalysis[2] despite their rich coordination chemistry.[3] Meanwhile, very efficient systems for asymmetric catalysis,[4] using P–S ligands, have been recently disclosed. Herein, we report new P,S and S,S ligands, namely chiral ferrocenyl phosphine-thioethers and thiophosphine-thioethers with planar chirality only. These new compounds associate planar chirality of ferrocenes and sulfur atoms, potentially asymmetric after complexation. Furthermore, these ligands are 1,2-disubstituted ferrocenes, which are amongst the most successful ligands in asymmetric catalysis.[5] The synthesis of these novel ligands, in an enantiomerically pure form, will be described below. The catalytic potential of these ligands has been examined in the asymmetric allylic substitution reaction.

2. Results and discussion

2.1. Synthesis of ligands

Our target molecules were ligands **3** and **4** (Scheme 1). Some examples of the direct transformation of ferrocenyl alcohols into the corresponding thiothers can be found in the literature.[6] As a result we thought that compounds **3** could be obtained from alcohol **2** with a protected phosphino group (Scheme 1). Furthermore, Kagan et al. already reported a very efficient synthesis of the enantiomerically pure aldehyde (***S***)-**1**.[7] By reduction with sodium borohydride followed by sulfuration of the free phosphine, we obtained, with good yields, enantiomerically pure (***S***)-**2** from (***S***)-**1**.



Scheme 1.

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The conversion of α-ferrocenylalcohols into the corresponding thioethers is commonly carried out by reacting alcohols and thiols in the presence of a catalytic amount of acid (typically acetic acid or trifluoroacetic acid) over several hours of heating.[6] In the case of (*S*)-**2**, which is a hindered primary alcohol, this kind of reaction did not seem very promising to us. As a result, we wanted to test harsher conditions, that is, to run the reaction via a carbocation.[8] α-Ferrocenyl carbocations are known to be rather stable. Some of them have already been isolated[9] and the X-ray diffraction of a few of them has even been disclosed.[10] In some cases, the carbocation salts are stable enough to be successfully involved in further syntheses.[9b–d,f,11] We decided to use a concentrated solution of HBF_4 in ether as originally reported by Cais, to generate the carbocation. However, all our attempts to isolate and purify carbocation salts were unsuccessful. Nevertheless, by rapidly adding the thiol to the carbocation solution and after an optimization of solvents, temperature, amount of thiol and reaction times, we found excellent reaction conditions to synthesize various new thioethers from (*S*)-**2** (Table 1). In fact, for the six alkyl and arylthiols that we tried, the isolated yields were over 95% after only 2 min of reaction. The desulfuration of thioethers (*S*)-**3** to yield phosphine-thioethers (*S*)-**4** was achieved with high efficiency using tris(dimethylamino)phosphine in refluxing toluene (Table 1).

Table 1. Synthesis of compounds **3** and **4**

Entry	R	**3** (yield, %)[a]	**4** (yield, %)[b]
1	*t*-Bu	**3a** (97)	**4a** (93)
2	*i*-Pr	**3b** (97)	**4b** (93)
3	Et	**3c** (95)	**4c** (91)
4	Cy	**3d** (98)	**4d** (93)
5	$PhCH_2$	**3e** (96)	**4e** (93)
6	Ph	**3f** (98)	**4f** (95)

[a] Yields are given after purification and are based on the initial alcohol **2**.
[b] Yields are given after purification and are based on the initial compound **3**.

2.2. Allylic substitution

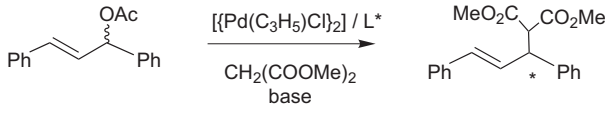
We then decided to explore the palladium-catalyzed asymmetric allylic substitution as a preliminary evaluation of the catalytic properties of these chiral ligands.[12] The reaction of 1,3-diphenylprop-2-enylacetate **9** with the anion of dimethyl malonate in the presence of $[Pd(C_3H_5)Cl]_2$ (1 mol %) and chiral ligand (*S*)-**4** was tested under various conditions. After the optimization of solvent, temperature, base, and amount of ligand, we found good conditions to carry out the reaction with the different ligands **4** (Table 2). While the five ligands with alkyl R groups gave similar results in terms of yields and enantiomeric excesses (around 80%), **4f** with a phenyl group gave slightly better yields but much better enantiomeric excess (93%) reaching almost the level of the best ligands P,S used in this reaction (Scheme 2).[4f–j]

We also tried ligands (*S*)-**3** in the same reaction (see Table 3). These potential S,S ligands proved to be again

Table 2. Asymmetric allylic substitution reaction of 1,3-diphenylprop-2-enylacetate with the anion of dimethyl malonate using different ligands (*S*)-**4**[a]

Entry	Ligand	Yield[b] (%)	ee[c] (%)
1	(*S*)-**4a**	93	80
2	(*S*)-**4b**	94	81
3	(*S*)-**4c**	96	83
4	(*S*)-**4d**	93	80
5	(*S*)-**4e**	95	78
6	(*S*)-**4f**	97	93

[a] Reaction run with 0.5 mmol of *rac*-1,3-diphenylprop-2-enyl acetate, 1 mmol of dimethylmalonate, 1 mmol of BSA, a catalytic amount of LiOAc, 0.02 mmol of ligand (4 mol %), and 0.02 mol of palladium (4 mol % as $[PdCl(allyl)]_2$) in 3 mL of dichloromethane at rt during 2 h.
[b] Isolated yield.
[c] (*R*)-configuration, determined by ^1H NMR using Eu-(+)-$(hfc)_3$ as chiral chemical shift reagent.



Scheme 2.

efficient ligands giving very good yields and enantioselectivities [up to 93% for (*S*)-**3a**]. The effects of the different alkyl and aryl substituents on the sulfur atom for ligands (*S*)-**3** are rather low for both yields and enantiomeric excesses in contrast to ligands (*S*)-**4**, the best results being obtained with the most hindered (*S*)-**3a**. Furthermore, the direction of the enantioselectivities is reversed using ligands (*S*)-**4** instead of ligands (*S*)-**3** with the same backbone. These differences might be due to chelate ring size effects [from six-membered chelate rings with ligands (*S*)-**4** to seven-membered chelate rings with ligands (*S*)-**3**] as already reported, but to a lesser extent, for P,N[13] or P,P ligands.[14] Anyway, the level of enantioselectivity using ligands (*S*)-**3** are amongst the best in the allylic substitution reaction using S,S ligands[4d,15] and are, to our knowledge, the best with thiophosphines.[15e,16]

Table 3. Asymmetric allylic substitution reaction of 1,3-diphenylprop-2-enylacetate with the anion of dimethyl malonate using different ligands (*S*)-**3**[a]

Entry	Ligand	Yield[b] (%)	ee[c] (%)
1	(*S*)-**3a**	90	93
2	(*S*)-**3b**	91	88
3	(*S*)-**3c**	97	90
4	(*S*)-**3d**	90	87
5	(*S*)-**3e**	88	91
6	(*S*)-**3f**	93	88

[a] Reaction run with 0.5 mmol of *rac*-1,3-diphenylprop-2-enyl acetate, 1 mmol of dimethylmalonate, 1 mmol of BSA, a catalytic amount of LiOAc, 0.02 mmol of ligand (4 mol %), and 0.02 mol of palladium (4 mol % as $[PdCl(allyl)]_2$) in 3 mL of dichloromethane at rt during 2 h.
[b] Isolated yield.
[c] (*S*)-configuration, determined by ^1H NMR using Eu-(+)-$(hfc)_3$ as chiral chemical shift reagent.

3. Conclusion

We have described a new and efficient synthesis of various chiral ferrocenyl phosphine-thioethers (*S*)-**4** and thiophosphine-thioethers (*S*)-**3** in enantiomerically pure form using Kagan's method to control planar chirality. The synthesis is again highly efficient with global yields in the range 39–43% from commercially available ferrocenecarboxaldehyde after nine steps. The synthesis is versatile, so thioethers (*S*)-**4** and (*S*)-**3** with different R groups attached to the sulfur atom can be easily obtained. Efforts are currently being aimed at extending the methodology to synthesize new compounds with other R groups.

The preliminary tests of the catalytic properties of ligands (*S*)-**4** and (*S*)-**3** in the asymmetric allylic substitution reaction proved to be successful with high activities and good enantioselectivities (up to 93% ee with ligands **4f** and **3a**). Further studies to develop the coordination chemistry of these ligands and to use them in other catalytic reactions are currently in progress in our laboratory.

4. Experimental

4.1. General

All of the reactions were carried out in the absence of air using standard Schlenk techniques and vacuum-line manipulations. The tetrafluoroboric acid solution and the different thiols were used as commercial samples. All solvents were dried before use. Thin layer chromatography was carried out on Merck Kieselgel 60 F_{254} precoated silica gel plates. Preparative flash chromatography was performed on Merck Kieselgel. Instrumentation: Bruker AM250 and AMX 400 (^{1}H, ^{13}C, and ^{3}1P NMR).

4.2. Synthesis of (*S*)-2

4.2.1. (*S*)-2-(Diphenylthiophosphinoferrocenyl)methanol (*S*)-2. In a Schlenk tube, under argon, 1.5 g of (*S*)-2-diphenylphosphinoferrocenecarboxaldehyde (*S*)-**1** (3.77 mmol) was dissolved in 100 mL of deoxygenated methanol. A 25 mL solution of NaOH (2 mol L^{-1}) in water containing 1.1 g of $NaBH_4$ (29 mmol, 30 equiv) was added by cannula at 0 °C. The solution was then stirred for 24 h at rt. The reaction mixture was then partially evaporated using a high vacuum pump. The solution was then extracted, under argon, by three portions of dichloromethane. The organic phase was transferred by cannula on sodium sulfate in a Schlenk tube. After 30 min of stirring, sodium sulfate was filtered. The solution was then evaporated under high vacuum. The residue was dissolved in 80 mL of dichloromethane and 665 mg of sulfur added. The solution was heated to reflux for 2 h. After cooling back to rt, the solvent was evaporated and the crude materials purified by flash chromatography on silica gel with a pentane/ether mixture (1/1, v/v) as eluent to yield 1.24 g of (*S*)-2-(diphenylthiophosphinoferrocenyl)methanol (*S*)-**4** as an orange solid (76%). The ^{1}H, ^{13}C and ^{31}P NMR data were similar to those published in Ref. 17 for racemic **2**. $[\alpha]_D = +6.7$ (*c* 0.5, $CHCl_3$) MS (DCI, NH_3) *m*/*e*: 433 (M+1, 100%).

4.3. General procedure for the synthesis of thioethers 3 from alcohol 2

In a Schlenk tube, 100 mg of (*S*)-2-thiodiphenylphosphino-(hydroxymethyl)ferrocene (*S*)-**2** (0.23 mmol) was dissolved in 2 mL of dry dichloromethane. Hundred microliters of a 54% solution of fluoroboric acid in ether (0.724 mmol) was then added. After 1 min stirring, 0.78 mL of *tert*-butylthiol was added. After 1 min of stirring, the crude materials were filtered on silica gel with ether as an eluent. After evaporation of the solvent, a yellow oil was obtained, which was extracted in pentane to yield, after evaporation, 113 mg of (*S*)-**5a** (yield = 97%) as a yellow solid.

4.3.1. (*S*)-2-Thiodiphenylphosphino-(*tert*-butylthiomethyl)ferrocene (*S*)-3a. ^{1}H NMR (δ (ppm), $CDCl_3$): 7.85–7.8 (2H, m: PPh_2); 7.7–7.6 (2H, m: PPh_2); 7.55–7.45 (4H, m: PPh_2); 7.4–7.35 (2H, m: PPh_2); 4.64 (1H, m: subst Cp); 4.37 (5H, s: Cp); 4.29 (1H, m: subst Cp); 3.99 (1H, d (AB), $J = 12.7$ Hz: CH_2); 3.96 (1H, d (AB), $J = 12.7$ Hz: CH_2); 3.71 (1H, m: subst Cp); 1.18 (9H, s: CH_3). ^{13}C NMR (δ (ppm), $CDCl_3$): 134.8 (d, $J_{PC} = 87.2$ Hz: quat PPh_2); 133.9 (d, $J_{PC} = 86.0$ Hz: quat PPh_2); 132.7 (d, $J_{PC} = 10.7$ Hz: PPh_2); 132.5 (d, $J_{PC} = 10.8$ Hz: PPh_2); 131.7 (d, $J_{PC} = 2.9$ Hz: PPh_2); 131.6 (d, $J_{PC} = 2.9$ Hz: PPh_2); 128.6 (d, $J_{PC} = 7.8$ Hz: PPh_2); 128.4 (d, $J_{PC} = 7.6$ Hz: PPh_2); 90.1 (d, $J_{PC} = 12.1$ Hz: quat Cp); 74.7 (d, $J_{PC} = 12.7$ Hz: subst Cp); 74.4 (d, $J_{PC} = 95.4$ Hz: quat Cp); 73.8 (d, $J_{PC} = 9.3$ Hz: subst Cp); 71.4 (s: Cp); 69.5 (d, $J_{PC} = 10.4$ Hz: subst Cp); 43.1 ($C(CH_3)_3$); 31.2 (CH_3); 26.7 (CH_2). ^{31}P NMR (δ (ppm), $CDCl_3$): 44.5. $[\alpha]_D = +76.0$ (*c* 0.5, $CHCl_3$) MS (DCI, CH_4) *m*/*e*: 504 (M, 43%), 415 (M−S*t*Bu, 100%). Mp: 185 °C (dec). Anal. Calcd for $C_{27}H_{29}FePS_2$: C, 64.29; H, 5.79. Found: C, 63.68; H, 5.53.

4.3.2. (*S*)-2-Thiodiphenylphosphino-(isopropylthiomethyl)ferrocene (*S*)-3b. Yellow solid. ^{1}H NMR (δ (ppm), $CDCl_3$): 7.85–7.8 (2H, m: PPh_2); 7.75–7.65 (2H, m: PPh_2); 7.55–7.35 (6H, m: PPh_2); 4.61 (1H, m: subst Cp); 4.34 (5H, s: Cp); 4.31 (1H, m: subst Cp); 4.07 (1H, d (AB), $J = 13.6$ Hz: CH_2); 3.91 (1H, d (AB), $J = 13.6$ Hz: CH_2); 3.77 (1H, m: subst Cp); 2.70 (1H, hept, $J = 6.7$ Hz: CH); 1.09 (3H, d, $J = 6.7$ Hz: CH_3); 1.08 (3H, d, $J = 6.7$ Hz: CH_3). ^{13}C NMR (δ (ppm), $CDCl_3$): 134.9 (d, $J_{PC} = 87.3$ Hz: quat PPh_2); 133.9 (d, $J_{PC} = 86.3$ Hz: quat PPh_2); 132.53 (d, $J_{PC} = 10.7$ Hz: PPh_2); 132.50 (d, $J_{PC} = 10.6$ Hz: PPh_2); 131.7 (d, $J_{PC} = 2.8$ Hz: PPh_2); 131.6 (d, $J_{PC} = 2.9$ Hz: PPh_2); 128.6 (d, $J_{PC} = 11.9$ Hz: PPh_2); 128.4 (d, $J_{PC} = 11.9$ Hz: PPh_2); 90.6 (d, $J_{PC} = 12.1$ Hz: quat Cp); 74.9 (d, $J_{PC} = 12.7$ Hz: subst Cp); 73.953 (d, $J_{PC} = 95.3$ Hz: quat Cp); 73.950 (d, $J_{PC} = 9.3$ Hz: subst Cp); 71.3 (s: Cp); 69.5 (d, $J_{PC} = 10.4$ Hz: subst Cp); 35.7 (CH); 29.2 (CH_2); 23.8 (s: CH_3); 23.6 (s: CH_3). ^{31}P NMR (δ (ppm), $CDCl_3$): 44.5. $[\alpha]_D = +25.6$ (*c* 0.5, $CHCl_3$). MS (DCI, NH_3) *m*/*e*: 491 (M+1, 27%), 415 (M−S*i*Pr,

100%). Mp: 152 °C. Anal. Calcd for $C_{26}H_{27}FePS_2$: C, 63.67; H, 5.55. Found: C, 63.42; H, 5.30.

4.3.3. (*S*)-2-Thiodiphenylphosphino-(ethylthiomethyl)-ferrocene (*S*)-3c. Yellow solid. ^{1}H NMR (δ (ppm), $CDCl_3$): 7.85–7.8 (2H, m: PPh_2); 7.7–7.65 (2H, m: PPh_2); 7.55–7.45 (4H, m: PPh_2); 7.4–7.35 (2H, m: PPh_2); 4.62 (1H, m: subst Cp); 4.34 (5H, s: Cp); 4.32 (1H, m: subst Cp); 4.09 (1H, d (AB), $J = 13.7$ Hz: CH_2-Cp); 3.87 (1H, d (AB), $J = 13.7$ Hz: CH_2-Cp); 3.78 (1H, m: subst Cp); 2.34 (2H, q, $J = 7.4$ Hz: CH_2CH_3); 1.08 (3H, t, $J = 7.4$ Hz: CH_3). ^{13}C NMR (δ (ppm), $CDCl_3$): 134.9 (d, $J_{PC} = 87.2$ Hz: quat PPh_2); 133.9 (d, $J_{PC} = 86.1$ Hz: quat PPh_2); 132.53 (d, $J_{PC} = 10.8$ Hz: PPh_2); 132.47 (d, $J_{PC} = 10.7$ Hz: PPh_2); 131.68 (d, $J_{PC} = 3.0$ Hz: PPh_2); 131.63 (d, $J_{PC} = 3.0$ Hz: PPh_2); 128.5 (d, $J_{PC} = 11.2$ Hz: PPh_2); 128.4 (d, $J_{PC} = 11.1$ Hz: PPh_2); 90.5 (d, $J_{PC} = 12.0$ Hz: quat Cp); 74.9 (d, $J_{PC} = 12.6$ Hz: subst Cp); 74.01 (d, $J_{PC} = 9.3$ Hz: subst Cp); 74.00 (d, $J_{PC} = 95.3$ Hz: quat Cp); 71.3 (s: Cp); 69.5 (d, $J_{PC} = 10.4$ Hz: subst Cp); 30.3 (CH_2-Cp); 26.9 (CH_2CH_3); 15.1 (CH_3). ^{31}P NMR (δ (ppm), $CDCl_3$): 44.4. $[\alpha]_D = +44.5$ (c 0.5, $CHCl_3$). MS (DCI, NH_3) m/e: 477 (M+1, 43%), 415 (M−SEt, 100%). Mp: 134 °C. Anal. Calcd for $C_{25}H_{25}FePS_2$: C, 63.02; H, 5.29. Found: C, 62.65; H, 5.25.

4.3.4. (*S*)-2-Thiodiphenylphosphino-(cyclohexylthiomethyl)ferrocene (*S*)-3d. Yellow solid. ^{1}H NMR (δ (ppm), $CDCl_3$): 7.85–7.78 (2H, m: PPh_2); 7.72–7.63 (2H, m: PPh_2); 7.55–7.35 (6H, m: PPh_2); 4.61 (1H, m: subst Cp); 4.34 (5H, s: Cp); 4.31 (1H, m: subst Cp); 4.05 (1H, d (AB), $J = 13.6$ Hz: CH_2-Cp); 3.93 (1H, d (AB), $J = 13.6$ Hz: CH_2-Cp); 3.76 (1H, m: subst Cp); 2.46 (1H, m: CH); 1.8–1.65 (4H, m: Cy); 1.2–1.1 (6H, m: Cy). ^{13}C NMR (δ (ppm), $CDCl_3$): 135.1 (d, $J_{PC} = 87.3$ Hz: quat PPh_2); 134.0 (d, $J_{PC} = 86.1$ Hz: quat PPh_2); 132.54 (d, $J_{PC} = 10.8$ Hz: PPh_2); 132.48 (d, $J_{PC} = 10.7$ Hz: PPh_2); 131.7 (d, $J_{PC} = 2.9$ Hz: PPh_2); 131.6 (d, $J_{PC} = 2.9$ Hz: PPh_2); 128.6 (d, $J_{PC} = 12.9$ Hz: PPh_2); 128.4 (d, $J_{PC} = 12.6$ Hz: PPh_2); 90.9 (d, $J_{PC} = 12.1$ Hz: quat Cp); 74.9 (d, $J_{PC} = 12.6$ Hz: subst Cp); 74.0 (d, $J_{PC} = 9.4$ Hz: subst Cp); 73.8 (d, $J_{PC} = 95.4$ Hz: quat Cp); 71.3 (s: Cp); 69.5 (d, $J_{PC} = 10.4$ Hz: subst Cp); 44.1 (CH); 34.0 (Cy); 33.7 (Cy); 28.6 (CH_2-Cp); 26.42 (Cy); 26.36 (Cy); 26.2 (Cy). ^{31}P NMR (δ (ppm), $CDCl_3$): 44.5. $[\alpha]_D = -77.6$ (c 0.5, $CHCl_3$). MS (DCI, NH_3) m/e: 531 (M, 7%), 415 (M−SCy, 100%). Mp: 151 °C. Anal. Calcd for $C_{29}H_{31}FePS_2$: C, 65.70; H, 5.89. Found: C, 65.47; H, 5.57.

4.3.5. (*S*)-2-Thiodiphenylphosphino-(benzylthiomethyl)-ferrocene (*S*)-3e. Yellow solid. ^{1}H NMR (δ (ppm), $CDCl_3$): 7.9–7.8 (2H, m: PPh_2); 7.75–7.65 (2H, m: PPh_2); 7.55–7.35 (6H, m: PPh_2); 7.32–7.2 (5H, m: SCH_2Ph); 4.52 (1H, m: subst Cp); 4.33 (1H, m: subst Cp); 4.32 (5H, s: Cp); 4.14 (1H, d (AB), $J = 13.6$ Hz: CH_2Cp); 3.81 (1H, m: subst Cp); 3.77 (1H, d (AB), $J = 13.6$ Hz: CH_2Cp); 3.57 (1H, d, AB, $J = 13.2$ Hz, CH_2Ph); 3.55 (1H, d, AB, $J = 13.2$ Hz, CH_2Ph). ^{13}C NMR (δ (ppm), $CDCl_3$): 133.9 (s, quat CH_2Ph); 135.1 (d, $J_{PC} = 87.2$ Hz: quat PPh_2); 134.0 (d, $J_{PC} = 86.1$ Hz: quat PPh_2); 132.54 (d, $J_{PC} = 10.8$ Hz: PPh_2); 132.51 (d, $J_{PC} = 10.7$ Hz: PPh_2); 131.67 (d, $J_{PC} = 3$ Hz: PPh_2); 131.62 (d, $J_{PC} = 3$ Hz: PPh_2); 129.3 (s: CH_2Ph); 128.8 (s: CH_2Ph); 128.6 (d, $J_{PC} = 12.8$ Hz: PPh_2); 128.4 (d, $J_{PC} = 12.6$ Hz: PPh_2); 127.2 (s: CH_2Ph); 90.2 (d, $J_{PC} = 12.0$ Hz: quat Cp); 75.0 (d, $J_{PC} = 12.6$ Hz: subst Cp); 74.06 (d, $J_{PC} = 9.4$ Hz: subst Cp); 74.04 (d, $J_{PC} = 95.3$ Hz: quat Cp); 71.3 (s: Cp); 69.5 (d, $J_{PC} = 10.4$ Hz: subst Cp); 37.5 (s: CH_2Ph); 30.5 (s: CH_2Cp). ^{31}P NMR (δ (ppm), $CDCl_3$): 44.3. $[\alpha]_D = -17.1$ (c 0.5, $CHCl_3$) MS (DCI, NH_3) m/e: 539 (M+1, 100%), 415 (M−SCH_2Ph, 62%). Mp: 154 °C. Anal. Calcd for $C_{30}H_{27}FePS_2$: C, 66.91; H, 5.05. Found: C, 66.70; H, 4.79.

4.3.6. (*S*)-2-Thiodiphenylphosphino-(phenylthiomethyl)-ferrocene (*S*)-3f. Yellow solid. ^{1}H NMR (δ (ppm), $CDCl_3$): 7.85–7.8 (2H, m: PPh_2); 7.7–7.65 (2H, m: PPh_2); 7.55–7.4 (6H, m: PPh_2); 7.3–7.15 (5H, m: SPh); 4.56 (1H, m: subst Cp); 4.42 (1H, d (AB), $J = 13.7$ Hz: CH_2); 4.35 (1H, d (AB), $J = 13.7$ Hz: CH_2); 4.34 (5H, s: Cp); 4.29 (1H, m: subst Cp); 3.80 (1H, m: subst Cp). ^{13}C NMR (δ (ppm), $CDCl_3$): 137.3 (s, quat SPh); 134.9 (d, $J_{PC} = 87.3$ Hz: quat PPh_2); 133.8 (d, $J_{PC} = 86.2$ Hz: quat PPh_2); 132.5 (d, $J_{PC} = 11.1$ Hz: 2 C PPh_2); 131.7 (s: 2C PPh_2); 130.1 (s: SPh); 129.1 (s: SPh); 128.7 (d, $J_{PC} = 12.6$ Hz: PPh_2); 128.5 (d, $J_{PC} = 12.4$ Hz: PPh_2); 126.4 (s: SPh); 89.3 (d, $J_{PC} = 11.8$ Hz: quat Cp); 75.0 (d, $J_{PC} = 12.4$ Hz: subst Cp); 74.4 (d, $J_{PC} = 95.1$ Hz: quat Cp); 74.1 (d, $J_{PC} = 9.1$ Hz: subst Cp); 71.4 (s: Cp); 69.6 (d, $J_{PC} = 10.3$ Hz: subst Cp); 33.3 (s: CH_2). ^{31}P NMR (δ (ppm), $CDCl_3$): 44.3. $[\alpha]_D = -39.0$ (c 0.5, $CHCl_3$) MS (DCI, NH_3) m/e: 525 (M+1, 100%), 415 (M−SPh, 80%). Mp: 143 °C. Anal. Calcd for $C_{29}H_{25}FePS_2$: C, 66.41; H, 4.80. Found: C, 66.14; H, 4.70.

4.4. General procedure for the desulfuration of thiophosphines

4.4.1. (*S*)-2-Diphenylphosphino-(*tert*-butylthiomethyl)ferrocene (*S*)-4a. In a Schlenk tube, 100 mg of (*S*)-2-thiodiphenylphosphino-(*tert*-butylthiomethyl)ferrocene (***S*)-3a** (0.23 mmol) was dissolved in 5 mL of toluene with 0.2 mL of tris-(dimethylamino)phosphine (5 equiv). The solution was kept at reflux overnight. After cooling back to rt, the solution was evaporated on vacuum line. The crude materials were purified, under argon, by flash chromatography on silica gel using dichloromethane as an eluent. Eighty-seven milligrams of pure (***S*)-4a** was obtained as a yellow solid (93% yield). ^{1}H NMR (δ (ppm), $CDCl_3$): 7.65–7.55 (2H, m: PPh_2); 7.45–7.35 (3H, m: PPh_2); 7.3–7.2 (5H, m: PPh_2); 4.56 (1H, m: subst Cp); 4.29 (1H, br t, $J = 2.4$ Hz: subst Cp); 4.06 (5H, s: Cp); 3.80 (1H, d (AB), $J = 12.4$ Hz: CH_2); 3.76 (1H, m: subst Cp); 3.63 (1H, dd (ABX), $J_{HH} = 12.4$ Hz, $J_{PH} = 2.3$ Hz: CH_2); 1.26 (9H, s: CH_3). ^{13}C NMR (δ (ppm), $CDCl_3$): 140.2 (d, $J_{PC} = 9.0$ Hz: quat PPh_2); 138.0 (d, $J_{PC} = 8.3$ Hz: quat PPh_2); 135.6 (d, $J_{PC} = 21.1$ Hz: PPh_2); 132.9 (d, $J_{PC} = 17.7$ Hz: PPh_2); 129.6 (s: PPh_2); 128.6 (d, $J_{PC} = 7.9$ Hz: PPh_2); 128.3 (d, $J_{PC} = 5.9$ Hz: PPh_2); 128.1 (s: PPh_2); 91.1 (d, $J_{PC} = 25.4$ Hz: quat Cp); 76.0 (d, $J_{PC} = 6.7$ Hz: quat

Cp); 71.7 (d, $J_{PC} = 3.7$ Hz: subst Cp); 71.5 (d, $J_{PC} = 4.0$ Hz: subst Cp); 70.2 (s: Cp); 69.8 (s: subst Cp); 43.0 ($C(CH_3)_3$); 31.2 (CH_3); 27.4 (d, $J_{PC} = 12.5$ Hz: CH_2). ^{31}P NMR (δ (ppm), $CDCl_3$): −20.8. $[\alpha]_D = -197$ (c 0.5, $CHCl_3$). Anal. Calcd for $C_{27}H_{29}FePS$: C, 68.65; H, 6.19. Found: C, 68.75; H, 6.10.

4.4.2. (*S*)-2-Diphenylphosphino-(isopropylthiomethyl)ferrocene (*S*)-4b. Yellow oil. ^{1}H NMR (δ (ppm), $CDCl_3$): 7.6–7.55 (2H, m: PPh_2); 7.45–7.4 (3H, m: PPh_2); 7.25–7.2 (5H, m: PPh_2); 4.52 (1H, m: subst Cp); 4.30 (1H, m: subst Cp); 4.02 (5H, s: Cp); 3.81 (1H, m: subst Cp); 3.77 (1H, d (AB), $J = 13.4$ Hz: CH_2); 3.69 (1H, ddd (ABX), $J_{HH} = 13.4$ Hz, $J_{PH} = 2.2$ Hz: CH_2); 2.73 (1H, hept, $J = 6.7$ Hz: CH); 1.16 (3H, d, $J = 6.7$ Hz: CH_3); 1.12 (3H, d, $J = 6.7$ Hz: CH_3). ^{13}C NMR (δ (ppm), $CDCl_3$): 140.3 (d, $J_{PC} = 8.5$ Hz: quat PPh_2); 138.0 (d, $J_{PC} = 8.1$ Hz: quat PPh_2); 135.6 (d, $J_{PC} = 21.3$ Hz: PPh_2); 132.8 (d, $J_{PC} = 17.7$ Hz: PPh_2); 129.6 (s: PPh_2); 128.5 (d, $J_{PC} = 7.9$ Hz: PPh_2); 128.3 (d, $J_{PC} = 6.0$ Hz: PPh_2); 128.1 (s: PPh_2); 91.6 (d, $J_{PC} = 25.8$ Hz: quat Cp); 75.9 (d, $J_{PC} = 7.5$ Hz: quat Cp); 71.9 (d, $J_{PC} = 3.8$ Hz: subst Cp); 71.7 (d, $J_{PC} = 4.1$ Hz: subst Cp); 70.2 (s: Cp); 69.8 (s: subst Cp); 45.2 (CH); 24.3 (d, $J_{PC} = 3.8$ Hz: CH_2); 22.5 (CH_3); 21.9 (CH_3). ^{31}P NMR (δ (ppm), $CDCl_3$): −21.0. $[\alpha]_D = -282$ (c 0.5, $CHCl_3$). Anal. Calcd for $C_{26}H_{27}FePS$: C, 68.13; H, 5.94. Found: C, 67.94; H, 5.86.

4.4.3. (*S*)-2-Diphenylphosphino-(ethylthiomethyl)ferrocene (*S*)-4c. Yellow oil. ^{1}H NMR (δ (ppm), $CDCl_3$): 7.65–7.55 (2H, m: PPh_2); 7.45–7.35 (3H, m: PPh_2); 7.3–7.15 (5H, m: PPh_2); 4.53 (1H, m: subst Cp); 4.32 (1H, br t, $J = 2.5$ Hz: subst Cp); 4.02 (5H, s: Cp); 3.83 (1H, m: subst Cp); 3.74 (2H, d, $J_{H\text{-}P} = 1.2$ Hz: CH_2Cp); 2.5–2.3 (2H, m: CH_2CH_3); 1.14 (3H, t, $J = 7.4$ Hz: CH_3). ^{13}C NMR (δ (ppm), $CDCl_3$): 140.3 (d, $J_{PC} = 8.4$ Hz: quat PPh_2); 138.1 (d, $J_{PC} = 8.0$ Hz: quat PPh_2); 135.6 (d, $J_{PC} = 21.3$ Hz: PPh_2); 132.8 (d, $J_{PC} = 17.7$ Hz: PPh_2); 129.6 (s: PPh_2); 128.6 (d, $J_{PC} = 8.0$ Hz: PPh_2); 128.3 (d, $J_{PC} = 6.0$ Hz: PPh_2); 128.1 (s: PPh_2); 91.6 (d, $J_{PC} = 26.0$ Hz: quat Cp); 75.9 (d, $J_{PC} = 7.5$ Hz: quat Cp); 71.9 (d, $J_{PC} = 3.8$ Hz: subst Cp); 71.8 (d, $J_{PC} = 4.1$ Hz: subst Cp); 70.2 (s: Cp); 69.9 (s: subst Cp); 30.9 (d, $J_{PC} = 11.6$ Hz: CH_2); 26.8 (CH_2CH_3); 15.0 (CH_3). ^{31}P NMR (δ (ppm), $CDCl_3$): −21.5. $[\alpha]_D = -261$ (c 0.5, $CHCl_3$). Anal. Calcd for $C_{25}H_{25}FePS$: C, 67.57; H, 5.67. Found: C, 67.58; H, 5.67.

4.4.4. (*S*)-2-Diphenylphosphino-(cyclohexylthiomethyl)-ferrocene (*S*)-4d. Yellow oil. ^{1}H NMR (δ (ppm), $CDCl_3$): 7.63–7.56 (2H, m: Ar); 7.43–7.39 (3H, m: Ar); 7.29–7.19 (5H, m: Ar); 4.54 (1H, m: subst Cp); 4.32 (1H, t, $J = 2.5$ Hz: subst Cp); 4.02 (5H, s: Cp); 3.81 (1H, m: subst Cp); 3.80 (1H, d (AB), $J = 13.5$ Hz: CH_2Cp); 3.72 (1H, dd (ABX), $J = 13.5$ Hz and $J_{PH} = 2.2$ Hz: CH_2Cp); 2.47 (1H, m: CH); 1.83 (2H, m: Cy); 1.67 (2H, m: Cy); 1.3–1.05 (6H, m: Cy). ^{13}C NMR (δ (ppm), $CDCl_3$): 140.5 (d, $J_{PC} = 8.5$ Hz: quat Ar); 138.1 (d, $J_{PC} = 8.0$ Hz: quat Ar); 135.6 (d, $J_{PC} = 21.3$ Hz: Ar); 132.7 (d, $J_{PC} = 17.6$ Hz: Ar); 129.6 (s: Ar); 128.5 (d, $J_{PC} = 7.5$ Hz: Ar); 128.3 (d, $J_{PC} = 5.9$ Hz: Ar); 128.1 (s: Ar); 92.0 (d, $J_{PC} = 26.1$ Hz: quat Cp); 75.8 (d, $J_{PC} = 7.4$ Hz: quat Cp); 71.9 (d, $J_{PC} = 3.9$ Hz: subst Cp); 71.7 (d, $J_{PC} = 4.1$ Hz: subst Cp); 70.2 (s: Cp); 69.9 (s: subst Cp); 44.0 (s: CH); 34.0 (s: Cy); 33.7 (s: Cy); 29.3 (s: CH_2Cp); 26.44 (s: Cy); 26.41 (s: Cy); 26.1 (s: Cy). ^{31}P NMR (δ (ppm), $CDCl_3$): −21.5. $[\alpha]_D = -166$ (c 0.6, $CHCl_3$). Anal. Calcd for $C_{29}H_{31}FePS$: C, 69.88; H, 6.27. Found: C, 70.16; H, 6.21.

4.4.5. (*S*)-2-Diphenylphosphino-(benzylthiomethyl)ferrocene (*S*)-4e. Yellow oil. ^{1}H NMR (δ (ppm), $CDCl_3$): 7.63–7.59 (2H, m: Ar); 7.44–7.42 (3H, m: Ar); 7.33–7.23 (10H, m: Ar); 4.47 (1H, m: subst Cp); 4.32 (1H, t, $J = 2.4$ Hz: subst Cp); 4.01 (5H, s: Cp); 3.85 (1H, m: subst Cp): 3.72 (1H, dd (ABX), $J = 13.1$ Hz and $J_{HP} = 1.9$ Hz: CH_2Cp); 3.65 (1H, d (AB), $J = 13.1$ Hz: CH_2Cp); 3.61 (2H, s: CH_2Ph). ^{13}C NMR (δ (ppm), $CDCl_3$): 140.4 (d, $J_{PC} = 8.7$ Hz: quat Ph); 138.8 (s, PPh_2 quat Ph); 138.1 (d, $J_{PC} = 8.2$ Hz: quat Ph); 135.6 (d, $J_{PC} = 21.2$ Hz: Ph); 132.8 (d, $J_{PC} = 17.7$ Hz: Ph); 129.6 (s: Ph); 129.3 (s: Ph); 128.8 (s: Ph); 128.6 (d, $J_{PC} = 8.0$ Hz: Ph); 128.4 (d, $J_{PC} = 5.9$ Hz: Ph); 128.2 (s: Ph); 127.3 (s: Ph); 91.2 (d, $J_{PC} = 25.9$ Hz: quat Cp); 76.1 (d, $J_{PC} = 7.9$ Hz: quat Cp); 72.1 (d, $J_{PC} = 3.8$ Hz: subst Cp); 71.9 (d, $J_{PC} = 4.0$ Hz: subst Cp); 70.2 (s: Cp); 69.9 (s: subst Cp); 37.4 (s: CH_2Ph); 31.1 (d, $J_{PC} = 11.3$ Hz: CH_2Cp). ^{31}P NMR (δ (ppm), $CDCl_3$): −21.4. $[\alpha]_D = -167$ (c 0.5, $CHCl_3$). Anal. Calcd for $C_{30}H_{27}FePS$: C, 71.15; H, 5.37. Found: C, 70.90; H, 4.85.

4.4.6. (*S*)-2-Diphenylphosphino-(phenylthiomethyl)ferrocene (*S*)-4f. Yellow oil. ^{1}H NMR (δ (ppm), $CDCl_3$): 7.6–7.55 (2H, m: PPh_2); 7.45–7.4 (3H, m: PPh_2); 7.3–7.15 (10H, m: Ph); 4.53 (1H, m: subst Cp); 4.29 (1H, m: subst Cp); 4.17 (1H, d (AB), $J = 13.1$ Hz: CH_2); 4.09 (1H, dd (ABX), $J = 12.4$ and 2.1 Hz: CH_2); 4.05 (5H, s: Cp); 3.82 (1H, m: subst Cp). ^{13}C NMR (δ (ppm), $CDCl_3$): 140.1 (d, $J_{PC} = 8.7$ Hz: quat PPh_2); 137.9 (d, $J_{PC} = 8.1$ Hz: quat PPh_2); 137.5 (s: quat SPh); 135.5 (d, $J_{PC} = 21.2$ Hz: PPh_2); 132.8 (d, $J_{PC} = 17.7$ Hz: PPh_2); 130.1 (s: Ph); 129.6 (s: Ph); 129.2 (s: Ph); 128.6 (d, $J_{PC} = 7.9$ Hz: PPh_2); 128.4 (d, $J_{PC} = 5.9$ Hz: PPh_2); 128.2 (s: Ph); 126.5 (s: Ph); 90.3 (d, $J_{PC} = 25.5$ Hz: quat Cp); 76.3 (d, $J_{PC} = 7.7$ Hz: quat Cp); 72.0 (d, $J_{PC} = 3.6$ Hz: subst Cp); 71.8 (d, $J_{PC} = 3.8$ Hz: subst Cp); 70.3 (s: Cp); 70.0 (s: subst Cp); 34.2 (d, $J_{PC} = 12.3$ Hz: CH_2). ^{31}P NMR (δ (ppm), $CDCl_3$): −21.3. $[\alpha]_D = -138$ (c 0.5, $CHCl_3$). Anal. Calcd for $C_{29}H_{25}FePS$: C, 70.74; H, 5.12. Found: C, 69.95; H, 5.03.

4.5. General procedure for palladium-catalyzed allylic substitution

A mixture of ligand, 1,3-diphenylprop-2-enylacetate (0.126 g, 0.5 mmol) and $[(Pd(C_3H_5)Cl)]_2$ in dry solvent was stirred at room temperature. To the resulting solution were immediately added dimethyl malonate (0.12 mL, 1 mmol), potassium acetate, and BSA (0.07 mL, 1 mmol). The reaction was carried out at room temperature and monitored by TLC for the disap-

pearance of the acetate. After the reaction was complete, the resulting mixture was diluted with diethyl ether (5 mL) and quenched with a saturated aqueous solution of ammonium chloride (5 mL). The aqueous phase was extracted with Et_2O, the combined organics dried over magnesium sulfate, filtered, and evaporated. The conversion was calculated from the crude reaction mixture by ^1H NMR spectroscopy. Subsequent purification by chromatography on silica eluting with ethyl acetate/pentane (15/85) afforded the product as a white solid. The enantiomeric excess was determined by ^1H NMR using the chiral shift reagent $Eu(hfc)_3$.

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