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MOP-phosphonites: A novel ligand class for asymmetric catalysis†

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Chiral phosphonite ligands (S,R_b)-**5a**, (S,S_b)-**5b**, (R,R_b)-**6a** and (R,S_b)-**6b** are introduced, comprising a MOP-type backbone with a binol-based binaphthyl group bound to the phosphorus. Their reaction with $[Pd(\eta^3\text{-}C_4H_7)Cl]_2$ affords η^3-methallylpalladium chloride complexes **7a/b** and **8a/b** which have been isolated and structurally characterised. Solid-state and solution studies indicate subtle differences in their coordination behaviour, which ultimately affects their efficacy in the asymmetric hydrosilylation of styrene.

Introduction

Chiral monophosphorus ligands have attracted considerable attention as their transition metal complexes have been found to be valuable catalysts in a variety of organic transformations.[1] Binaphthyl-derived phosphorus ligands based on phosphine,[2] phosphoramidite[3] and phosphonite[4] architectures (Chart 1) have all demonstrated their effectiveness in asymmetric catalysis.

Primary phosphines have a reputation for being difficult compounds to work with owing to their perceived high reactivity towards oxygen.[5] Hence, they are somewhat under-represented as synthons in synthetic chemistry, despite the two P–H bonds being easily functionalised. A few examples of user-friendly, air-stable primary phosphines have however been reported,[6] and we were the first to describe enantiopure analogues;[7] we subsequently published a DFT-based model to help rationalise this stability.[8] We also recently described how air-stable, chiral primary phosphines (S)-**1** and (R)-**2** could form novel

phosphiranes with unusually high oxidative and thermal stability.[9] We were therefore keen to establish whether we could transform (S)-**1** and (R)-**2** into their dichlorophosphines, and ultimately access MOP/XuPhos-type hybrids (Chart 1), or whether their resistance to oxidation would render them unreactive to halogen sources. This work focuses on the synthesis and characterisation of a novel MOP-phosphonite ligand class. The coordination chemistry of their methallylpalladium complexes is described and we have therefore investigated their potential as asymmetric ligands in the catalytic hydrosilylation of styrene.

Results and discussion

Four MOP-phosphonite ligand derivatives have each been synthesised in a straightforward two-step, one-pot reaction approach. The ligands differ in the substituent on the 2′-position of the MOP-backbone (H or OMe) and in the stereochemistry of the affiliated hydroxyl compound ((R)- or (S)-binol). By comparing the two pairs of diastereomeric compounds with each other, we were able to elucidate the effect of the second stereocentre.

Following the synthetic method of Weferling,[10,11] (S)-**1** and (R)-**2** were treated with phosphorus pentachloride to give the dichlorophosphines (S)-**3** and (R)-**4** in quantitative conversion. Subsequent addition of (R)-binol under basic conditions afforded the MOP-phosphonite hybrids (S,R_b)-**5a** and (R,R_b)-**6a** as white solids (Scheme 1). Their diastereomers (S,S_b)-**5b** and (R,S_b)-**6b** were afforded from reactions with (S)-binol, again in high yield.

The ^{31}P NMR spectroscopic data for the phosphonites are as expected, showing characteristic resonances ($\delta = 177.4$ ppm for (S,R_b)-**5a**; 177.8 ppm for (R,R_b)-**6a**; 175.7 ppm for (S,S_b)-**5b**; 177.9 for (R,S_b)-**6b**). Notably, all the ligands could conveniently be handled in air; in common reagent grade solvents no hydrolysis products were found after 24 h.[12] We next studied the coordination chemistry of the phosphonites; reaction of two equivalents of the pertinent ligand with $[Pd(\eta^3\text{-}C_4H_7)Cl]_2$ resulted in the rapid, quantitative formation of **7a**, **7b**, **8a** and **8b** (Scheme 2) as shown by NMR, HRMS and X-ray crystallography.
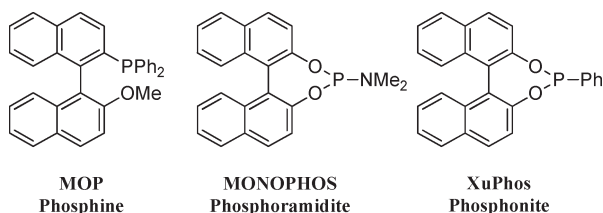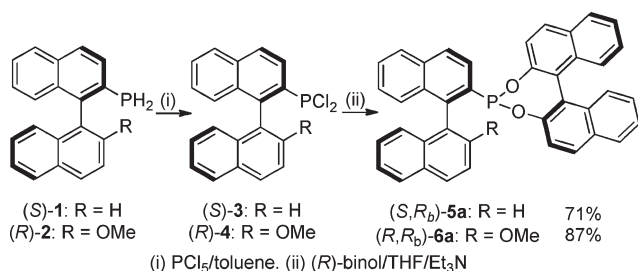

Chart 1 Established classes of binaphthyl monophosphorus ligands.

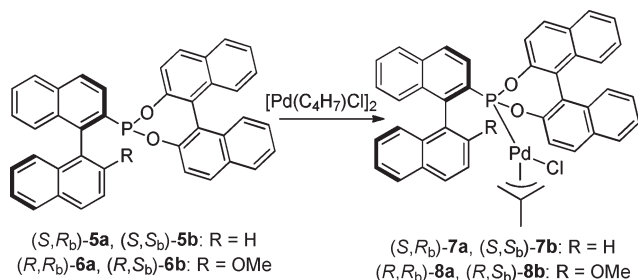MOP Phosphine

MONOPHOS Phosphoramidite

XuPhos Phosphonite

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Scheme 1 The synthesis of phosphonites (S,R_b)-**5a** and (R,R_b)-**6a**.

(S,R_b)-**5a**, (S,S_b)-**5b**: R = H
(R,R_b)-**6a**, (R,S_b)-**6b**: R = OMe

(S,R_b)-**7a**, (S,S_b)-**7b**: R = H
(R,R_b)-**8a**, (R,S_b)-**8b**: R = OMe

Scheme 2 The synthesis of the complexes **7a**, **7b**, **8a** and **8b**.

In all four complexes the X-ray crystal structure reveals the methyl group on the allyl fragment points towards the binol component of the ligand (see Fig. 1–4). The torsion angles of the two binaphthyl fragments present are significantly different from each other. The unstrained MOP portion preserves an almost right angle while the torsion of the binol moiety is enforced by the bonding of both oxygen atoms to the phosphorus, and thus appears acutely angled. The ligands coordinate *via* the phosphorus donor atom in an expected monodentate manner to form a pseudo-square-planar configuration around the palladium. Pd–P bond lengths are similar in all complexes (2.2354(7) to 2.2542(8) Å) and are found to be shorter than for the two MOP-phosphine allylpalladium complexes previously reported (2.3098(9)

and 2.328(1) Å);[13] however, shortened Pd–P bond lengths are anticipated for phosphonite complexes due to their stronger π-acceptor character.[14] Pd–C bond lengths show the dominant *trans* effect of the P-ligand relative to the chloride; the bonds *trans* to the phosphorus are about 0.1 Å longer compared to the bonds in the *cis* position. In all complexes the position of the palladium centre is face-to-face with the lower naphthyl moiety of the MOP fragment of the ligand. However, the exact position of the methallylpalladium moiety is somewhat diverse. When the phosphonite consists of a (R)-binol fragment (**7a/8a**), the palladium is situated towards the back of the lower naphtyl ring (Fig. 1 and Fig. 3); in **7b/8b**, as a consequence of the opposite binol stereochemistry, the metal is instead located above the front of this group (Fig. 2 and Fig. 4). The distance of the palladium atom from the naphthyl group ranges from 3.0653(1) Å in **7a** to 3.4458(1) in **8b**.
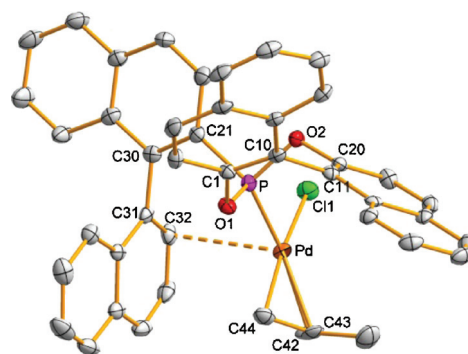

Fig. 2 View of the molecular structure of **7b**. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Pd–P 2.2354(7), Pd–Cl(1) 2.3730(8), Pd–C(44) 2.078(3), Pd–C(42) 2.198(3), C(42)–C(43) 1.387(4), C(43)–C(44) 1.409(4), Pd···C(32) 3.1412(1); P–Pd–Cl(1) 94.51(3), P–Pd–C(44) 96.49(9), Cl(1)–Pd–C(42) 101.71(9), C(42)–Pd–C(44) 67.31(13), C(21)–C(30)–C(31)–C(32) −90.5(4), C(1)–C(10)–C(11)–C(20) 52.1(4).
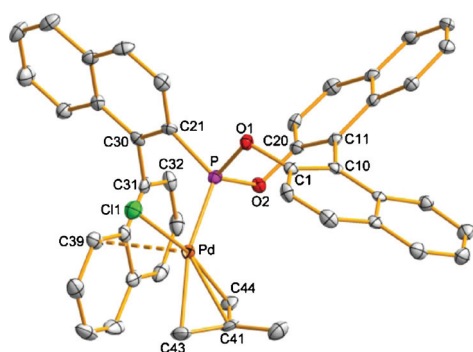

Fig. 1 Molecular structure of **7a** with 50% probability displacement ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Pd–P 2.2476(7), Pd–Cl(1) 2.3854(7), Pd–C(44) 2.093(2), Pd–C(43) 2.206(2), C(41)–C(43) 1.384(4), C(41)–C(44) 1.415(4), Pd···C(39) 3.0653(1); P–Pd–Cl(1) 93.67(2), P–Pd–C(44) 98.23(9), Cl(1)–Pd–C(43) 101.60(7), C(43)–Pd–C(44) 66.68(11), C(21)–C(30)–C(31)–C(32) −101.2(3), C(1)–C(10)–C(11)–C(20) −51.2(3).

Fig. 3 View of the molecular structure of **8a**. Hydrogen atoms and cocrystallised solvent have been omitted for clarity. Selected bond distances (Å) and angles (deg): Pd–P 2.2363(8), Pd–Cl(1) 2.3755(10), Pd–C(42) 2.104(4), Pd–C(44) 2.185(4), C(42)–C(43) 1.415(6), C(43)–C(44) 1.381(7), Pd···C(32) 3.4018(1); P–Pd–Cl(1) 93.29(3), P–Pd–C(42) 98.24(12), Cl–Pd–C(44) 101.41(16), C(42)–Pd–C(44) 67.08(19), C(21)–C(30)–C(31)–C(40) −98.0(4), C(1)–C(10)–C(11)–C(20) −52.1(4).
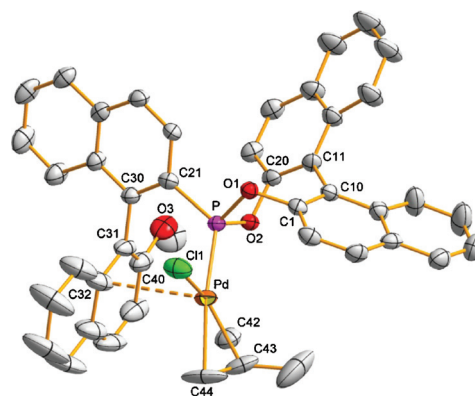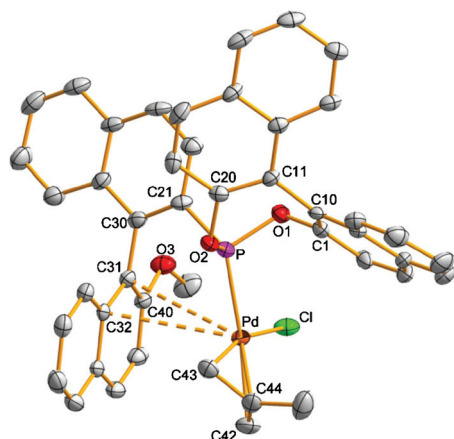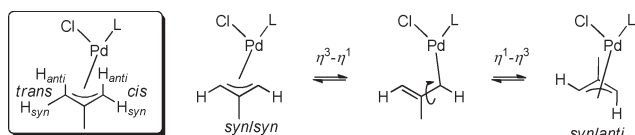
Fig. 4 View of the molecular structure of **8b**. Hydrogen atoms and cocrystallised solvent have been omitted for clarity. Selected bond distances (Å) and angles (deg): Pd–P 2.2542(8), Pd–Cl 2.3675(7), Pd–C (43) 2.101(3), Pd–C(42) 2.177(3), C(42)–C(44) 1.402(5), C(43)–C(44) 1.412(4), Pd···C(31) 3.4458(1), Pd···C(32) 3.4793(0); P–Pd–Cl 98.46 (3), P–Pd–C(43) 96.80(8), Cl–Pd–C(42) 97.23(9), C(42)–Pd–C(43) 67.39(12), C(21)–C(30)–C(31)–C(40) −98.9(3), C(1)–C(10)–C(11)–C (20) 53.8(4).

The NMR spectra of complexes **7a** and **8a** show the presence of two isomers in a 97/3 and 93/7 ratio, respectively, which can be rationalised by a rotation of the allyl moiety. NOE contacts between each pair of *syn* and *anti* protons and between the *syn* allyl protons and the central methyl group, in addition to allyl proton–phosphorus coupling, allowed for a complete NMR assignment of the allyl signals (Table S2†). The protons *trans* to the phosphorus ligand are deshielded and show coupling with ^{31}P whereas the *cis* protons are observed as singlets at higher field.[15] The ^{13}C chemical shifts for the atoms in terminal allyl positions are consistent with those reported for similar complexes:[16] 77–79 ppm ($^2J_{CP} \approx 46$ Hz) for the allyl carbons *trans* to the P-donor, and 56–59 ppm ($^2J_{CP} \approx 5$ Hz) for the *cis* allyl carbons. The phase-sensitive NOESY spectrum of **8a** shows exchange peaks due to interconversion of the two isomers (see Fig. S2†). Quantitative analysis of the peak integrals yielded exchange rate constant values of $k_{AB} \approx 0.12$ s^{-1} and $k_{BA} \approx 1.5$ s^{-1} at room temperature.

The selective *syn*/*anti* exchange of the allyl protons *cis* to the phosphorus is caused by the well-known η^3–η^1–η^3 mechanism (Scheme 3); the protons in the *trans* position exchange *syn*/*syn* and *anti*/*anti*, while the *cis* protons exchange *syn*/*anti* due to the selective opening of the allyl ligand.[16,17] The selectivity of the process is due to the stronger *trans* effect of the P-donor ligand compared to the chloro ligand. An apparent allyl rotation mechanism which is often observed in N-donor ligands requires a *syn*/*syn* and *anti*/*anti* exchange for both *cis* and *trans* allyl protons

Table 1 Selected ^{13}C NMR data (δ in ppm) for ligands **6a** and **6b** and their palladium complexes **8a**, **8b**, **9a** and **9b** (CD$_2$Cl$_2$, 21 °C)

Carbon	6a	8a[a]	9a[b]	6b	8b	9b[b]
1′	118.9	118.8	104.6/n.d.[c]	119.0	118.2	103.4/104.5
2′	156.6	156.4	157.2/159.0	154.9	156.2	156.6/154.8
3′	112.8	113.1	114.9/114.5	113.0	113.5	115.3/115.9
4′	130.8	131.0	134.6/134.6	130.7	129.7	134.9/134.3
9′	134.5	134.2	131.5/131.4	135.0	135.5	132.7/133.7
10′	128.2	127.0	128.4/128.4	128.3	128.2	129.3/130.0

[a] Major isomer. [b] Two isomers were observed due to allyl rotation. [c] No distinctive assignment due to signal overlap and peak broadening.

and can be ruled out here.[18] Note that conversely for complexes **7b** and **8b**, we observe only a single isomer in each case.

MOP ligands can display unexpected bonding characteristics upon metal complexation, using their aromatic backbone to co-ordinate to a vacant metal site, as shown by several groups who observed binding in a chelating P,C-σ-donor or P,C-π-olefin bidentate fashion.[13b,16,19,20] When the chloride counterions of complexes **8a** and **8b** were exchanged for the non-coordinating BArF anion to give complexes **9a** and **9b**, the C1′ carbon shifted by −14.3 (**9a**) or −15.6/−14.5 ppm (for the two isomers of **9b**) to lower frequency compared to the free ligand, indicative of greater sp^3 character. The chemical shift of the C2′ carbon remains almost unchanged (Table 1).

In agreement with studies made by Pregosin and co-workers[20b] we therefore propose a weak η^1 binding mode of the lower naphthyl ring *via* the C-1′ carbon (Fig. 5, left). The downfield shifts of 3.8 ppm in **9a** and 4.2/3.6 ppm in **9b** for the C-4′ carbon also suggests it carries some of the associated positive charge of the cation, again matching the aforementioned work. A section of the ^{13}C–^{1}H HMBC spectrum of **9b** showing the indirect resonances of the C1′ and C2′ carbons is given (Fig. 5, right).

The catalytic activity of the newly prepared ligands was tested in the asymmetric hydrosilylation of styrene.[21] The catalysts were generated *in situ* from allylpalladium chloride dimer and the appropriate phosphonite. We chose a ligand to palladium ratio of 1 : 1 to form the catalyst precursors as the methallylpalladium complexes **7a/b** and **8a/b** had been obtained in this way (*vide supra*). We found that the activity of the catalyst was predominantly dependent on the substituent in the 2′-position of the

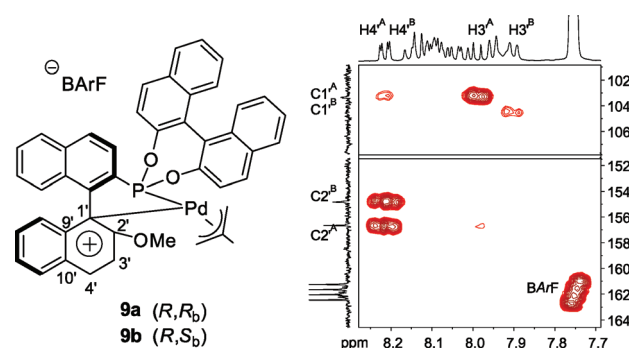**Scheme 3** *Syn*/*anti* exchange mechanism in allyl palladium complexes.

Fig. 5 Left: Proposed binding mode in **9a/b** using ^{13}C NMR data. Right: Section of the ^{13}C–^{1}H HMBC spectrum of **9b** with key C1′/H3′ and C2′/H4′ data shown; two isomers of **9b** (labelled A, B) are present.

Table 2 The palladium-catalyzed asymmetric hydrosilylation of styrene

	L^a	Time	Conv.^{b}	ee^c
1	**5a**	6 h	94%^{d}	7% (R)
2	**5b**	4 h	95%^{d}	80% (R)
3	**6a**	16 h	100%	55% (S)
4	**6b**	16 h	100%	79% (R)

^{a} The catalyst was generated *in situ* from the ligand (0.25 mol%) and [Pd(allyl)Cl]$_2$ (0.125 mol%), and reacted with styrene (10.0 mmol) and trichlorosilane (12.0 mmol). ^{b} Determined by ^{1}H NMR spectroscopy. ^{c} Determined by chiral HPLC; absolute configuration assigned by comparing the retention times to literature data.[23] ^{d} Complete conversion after additional 2 h reaction time.

ligand: H-MOP derivatives **5a/b** showed a higher activity (>94% conversion after 6 h) than their corresponding OMe-MOP derivatives **6a/b** (completed after 16 h, Table 2). In contrast, the selectivity was mostly determined by the configuration of the adherent binol group. Enantioselectivities of 80 and 79% were achieved with the (S)-binol derivatives **5b** and **6b**, while (R)-binol compounds **5a** and **6a** gave lower *ee* values. In previous studies H-MOP ligands have been found to be more selective in this transformation than their OMe-MOP counterparts,[2a] hence our results for **5a** (H-MOP derivative, low *ee*) and **6b** (OMe-MOP derivative, high *ee*) were somewhat surprising. Solid-state analysis of an H-MOP allylpalladium phosphine complex,[13b] found to be very selective in the same catalytic reaction,[22] shows a similar P/Pd environment to that found in the H-MOP complex **7b**. In contrast, the palladium atom in **7a** is located more towards the back of the lower naphthyl ring. Thus the subtle differences in the position of the palladium atom relative to the MOP fragment in the catalytically active species could be crucial in determining the reaction enantioselectivity, again emphasising that we are comparing pairs of diastereomers in this study; an examination of the wider implications of these results is now underway.

Conclusions

In summary, we have demonstrated that the air-stable primary phosphines (S)-**1** and (R)-**2** readily form their dichlorophosphine counterparts, which react as electrophiles with enantiopure binol to give novel chiral phosphonites. We have characterised each ligand as its methallylpalladium complex by NMR and X-ray crystallography, which together with detailed NMR experiments on related cationic complexes indicate the subtly different metal environment in each case and the P,C ligation of **9a/b**. In the hydrosilylation of styrene, enantioselectivities of 80% were achieved in reactions that have not yet been optimised.

Experimental

General

All air- and/or water-sensitive reactions were performed under an N$_2$ atmosphere using standard Schlenk line techniques. THF and CH$_2$Cl$_2$ were dried over Na/benzophenone and CaH$_2$ respectively, and distilled prior to use. Toluene (Acros) was purchased in an anhydrous state and stored over molecular sieves. The preparations of (S)-**1** and (R)-**2** were carried out using literature procedures.[7] All other chemicals were used as received without further purification. Flash chromatography was performed on silica gel from Fluorochem (silica gel, 40–63u, 60A, LC301). Thin-layer-chromatography was performed on Merck aluminium-based plates with silica gel and fluorescent indicator 254 nm. For indicating, UV light or KMnO$_4$ solution (1.0 g KMnO$_4$, 6.7 g K$_2$CO$_3$, 0.1 g NaOH, 100 mL H$_2$O) was used. Melting points were determined in open glass capillary tubes on a Stuart SMP3 melting point apparatus. Optical rotation values were determined on an Optical Activity Polaar 2001 device. ^{1}H NMR, ^{11}B{^{1}H} NMR, ^{13}C{^{1}H} NMR, ^{19}F NMR, and ^{31}P{^{1}H} NMR spectra were recorded on a JEOL Lambda 500 (^{1}H 500.16 MHz) or JEOL ECS-400 (^{1}H 399.78 MHz) spectrometer at room temperature (21 °C) if not otherwise stated, using the indicated solvent as internal reference. Two-dimensional NMR experiments (COSY, NOESY, HSQC, HMBC) were used for the assignment of proton and carbon resonances, the numbering scheme is given in Fig. S1†. Full range NOESY spectra were acquired with 512 × 1024 data points and a spectral width of 9.0 ppm; mixing times were chosen between 10 and 500 ms. For the measurement of exchange rate constants in **8a**, the proton resonances of the methoxy group were used. Peak volumes were determined manually from the NOESY spectrum using MestReNova 6, and the rate constants were calculated with an estimated error of 10% using EXSYCalc.[24] Mass spectrometry was carried out by the EPSRC National Mass Spectrometry Service Centre, Swansea. Analytical high performance liquid chromatography (HPLC) was performed on a Varian Pro Star HPLC equipped with a variable wavelength detector.

Synthesis of (S,R$_b$)-[1,1′-binaphthalene]-2,2′-diyl [1,1′-binaphthalen]-2-ylphosphonite (5a)

PCl$_5$ (458 mg, 2.20 mmol) was dissolved in toluene (8 mL). (S)-**1** (286 mg, 1.00 mmol) was added and the reaction mixture was left to stir for 45 min. The volatiles were removed *in vacuo* to give (S)-**3** (^{31}P{^{1}H} NMR, CDCl$_3$: δ = 157.1 ppm) as a yellow oil. THF (8 mL), NEt$_3$ (448 mg, 0.64 mL, 4.40 mmol) and (R)-binol (286 mg, 1.00 mmol) were subsequently added and the solution was left to stir overnight. The volatiles were removed *in vacuo* and the crude product was filtered through a plug of silica in toluene. The title product was obtained after removal of the solvent as a white solid. Yield: 404 mg (71%). MP: 158 °C. $[\alpha]_D^{20}$ = +238° (c = 1.0 mg mL^{-1}, CHCl$_3$). IR (neat): ν 3055.4, 2981.3, 1588.6, 1505.9, 1462.5, 1362.2, 1326.4, 1228.2, 1203.1, 1154.9, 1070.0, 949.2, 869.5, 818.8, 782.0, 747.7, 629.4 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, 500 MHz): δ (ppm) 8.06 (d, $^3J_{HH}$ = 8.3 Hz, 1H, H4′), 8.01 (d, $^3J_{HH}$ = 8.3 Hz, 1H, ArH), 7.95–7.91 (m, 3H, H14/ArH), 7.88 (d, $^3J_{HH}$ = 8.2 Hz, 1H, ArH), 7.84 (dd, $^3J_{HH}$ = 7.0 Hz, $^5J_{HP}$ = 1.0 Hz, 1H, H2′), 7.73 (d, $^3J_{HH}$ = 8.7 Hz, 1H, H14′), 7.69 (dd, $^3J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 7.0 Hz, 1H, H3′), 7.61 (d, $^3J_{HH}$ = 8.6 Hz, 1H, H4), 7.56–7.52, (m, 2H, ArH), 7.49–7.40 (m, 4H, H13/ArH), 7.38–7.31 (m, 5H, H3/ArH), 7.30–7.24 (m, 3H, H3/ArH), 6.91 (d, $^3J_{HH}$ = 8.7 Hz, 1H, H13′). ^{13}C{^{1}H} NMR

(CD$_2$Cl$_2$, 126 MHz): δ (ppm) 150.2 (d, $^2J_{CP}$ = 2.4 Hz, $C$12), 149.0 (d, $^2J_{CP}$ = 6.1 Hz, $C$12′), 145.0 (d, $^2J_{CP}$ = 37.2 Hz, $C$1), 136.2 (d, $^1J_{CP}$ = 38.9 Hz, $C$2), 135.0, 134.8 (d, J_{CP} = 10.0 Hz), 133.5, 133.3 (d, J_{CP} = 2.1 Hz), 133.0 (d, J_{CP} = 4.7 Hz), 132.9 (d, J_{CP} = 1.5 Hz), 132.8 (d, J_{CP} = 1.0 Hz), 131.7, 131.2, 130.9 (d, $^4J_{CP}$ = 5.8 Hz, $C$2′), 130.6 ($C$14), 129.6 (d, $^4J_{CP}$ = 0.7 Hz, $C$14′), 129.1 ($C$4′), 128.5, 128.4, 128.3, 128.2, 127.7, 127.1 ($C$4), 127.0 (d, J_{CP} = 2.8 Hz), 126.8, 126.7, 126.6, 126.6, 126.5, 126.3, 126.3, 126.2, 125.0, 124.9 ($C$3′), 124.9, 124.7 (d, $^3J_{CP}$ = 5.7 Hz, $C$11), 124.2 (d, $^2J_{CP}$ = 2.7 Hz, $C$3), 123.8 (d, $^3J_{CP}$ = 2.6 Hz, $C$11′), 122.2 ($C$13′), 121.5 (d, $^3J_{CP}$ = 1.4 Hz, $C$13). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 202 MHz): δ (ppm) 177.4. HRMS (m/z, ESI$^+$, MeOH): found 585.1605, calcd for [M + H$_2$O]$^+$ 585.1614.

Synthesis of (S,S_b)-[1,1′-binaphthalene]-2,2′-diyl [1,1′-binaphthalen]-2-ylphosphonite (5b)

The same procedure was followed as for **5a**, except for using (S)-binol as the nucleophile. The title product was obtained as a white solid after removal of the solvent. Yield: 527 mg (93%). MP: 197 °C. [α]$_D^{20}$ = −264° (c = 1.0 mg mL^{-1}, CHCl$_3$). IR (neat): ν 3060.6, 2981.3, 1588.6, 1506.5, 1466.0, 1366.0, 1330.0, 1262.7, 1232.0, 1204.0, 1141.6, 1141.6, 1072.2, 951.6, 869.5, 822.7, 789.4, 753.7, 684.6, 630.2 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, 500 MHz): δ (ppm) 8.04 (d, $^3J_{HH}$ = 8.2 Hz, 1H, $H$4′), 7.99–7.89 (m, 4H, $H$14′/ArH), 7.88 (d, $^3J_{HH}$ = 8.2 Hz, 1H, $H$5), 7.78 (d, $^3J_{HH}$ = 8.7 Hz, 1H, $H$14), 7.68 (dd, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 7.0 Hz, 1H, $H$3′), 7.63 (dd, $^3J_{HH}$ = 7.0 Hz, $^5J_{HP}$ = 1.2 Hz, 1H, $H$2′), 7.61 (d, $^3J_{HH}$ = 8.6 Hz, 1H, $H$4), 7.55 (ddd, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 5.5 Hz, $^4J_{HH}$ = 2.5 Hz, 1H, $H$6), 7.53–7.36 (m, 7H, $H$13′/ArH), 7.35–7.28 (m, 3H, $H$7/$H$8/ArH), 7.23–7.21 (m, 3H, $H$3/ArH), 6.90 (d, $^3J_{HH}$ = 8.7 Hz, 1H, $H$13). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 126 MHz): δ (ppm) 150.1 (d, $^2J_{CP}$ = 1.9 Hz, $C$12′), 148.9 (d, $^2J_{CP}$ = 5.7 Hz, $C$12), 145.4 (d, $^2J_{CP}$ = 37.0 Hz, $C$1), 136.5 (d, $^1J_{CP}$ = 40.4 Hz, $C$2), 135.0 (d, J_{CP} = 7.9 Hz), 134.1 (d, J_{CP} = 2.9 Hz), 133.5, 133.0 (d, J_{CP} = 4.3 Hz), 132.9, 132.8, 131.6, 131.4, 131.2, 130.6 ($C$14′), 129.6 ($C$14), 129.4 ($C$2′), 128.7 ($C$4′), 128.5, 128.4, 128.4, 128.1 ($C$5), 127.8, 127.4 (d, J_{CP} = 2.6 Hz), 127.1 ($C$4), 127.0, 126.9, 126.8, 126.6, 126.5, 126.4, 126.2, 126.1, 125.9, 125.1 ($C$3′), 124.9, 124.8 ($C$11′), 124.3 (d, $^2J_{CP}$ = 2.6 Hz, $C$3), 123.6 ($C$11), 122.5 ($C$13), 121.4 ($C$13′). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 202 MHz): δ (ppm) 175.7. HRMS (m/z, EI$^+$): found: = 567.1514, calcd for [M − H]$^+$ 567.1508.

Synthesis of (R,R_b)-[1,1′-binaphthalene]-2,2′-diyl (2′-methoxy-[1,1′-binaphthalen]-2-yl)phosphonite (6a)

PCl$_5$ (458 mg, 2.20 mmol) was dissolved in toluene (8 mL). (R)-**2** (316 mg, 1.00 mmol) was added and the reaction mixture was left to stir for 45 min. The volatiles were removed *in vacuo* to give (R)-**4** (^{31}P{^{1}H} NMR, CDCl$_3$: δ = 159.1 ppm) as a yellow solid. THF (8 mL), NEt$_3$ (448 mg, 0.64 mL, 4.40 mmol) and (R)-binol (286 mg, 1.00 mmol) were added subsequently and the solution was left to stir overnight. The volatiles were removed *in vacuo* and the crude product was dissolved in toluene and filtered through a plug of silica. The title product was obtained after removal of the solvent as a white solid. Yield: 523 mg,

(87%). MP: >270 °C. [α]$_D^{20}$ = +444° (c = 1.0 mg mL^{-1}, CHCl$_3$). IR (neat): ν 2981.2, 1619.8, 1590.0, 1507.0, 1461.8, 1431.0, 1327.7, 1228.2, 1149.5, 1078.1, 947.3, 866.6, 820.5, 799.5, 746.7, 686.7, 630.3 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, 500 MHz): δ (ppm) 8.09 (d, $^3J_{HH}$ = 9.1 Hz, 1H, $H$4′), 7.94–7.90 (m, 4H, $H$5′/$H$14/$H$15′/ArH), 7.89 (d, $^3J_{HH}$ = 8.2 Hz, 1H, $H$5), 7.72 (d, $^3J_{HH}$ = 8.8 Hz, 1H, $H$14′), 7.59 (d, $^3J_{HH}$ = 8.5 Hz, 1H, $H$4), 7.55 (ddd, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 5.7 Hz, $^4J_{HH}$ = 2.1 Hz, 1H, $H$6), 7.53 (d, $^3J_{HH}$ = 9.1 Hz, 1H, $H$3′), 7.47 (ddd, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 6.8 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, ArH), 7.44–7.40 (m, 3H, $H$13/ArH), 7.38 (ddd, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 6.8 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, ArH), 7.36–7.24 (m, 6H, ArH), 7.23 (dd, $^3J_{HH}$ = 8.5 Hz, $^3J_{HP}$ = 1.4 Hz, 1H, $H$3), 7.02 (d, $^3J_{HH}$ = 8.5 Hz, 1H, ArH), 6.93 (d, $^3J_{HH}$ = 8.8 Hz, 1H, $H$13′), 3.99 (s, 3H, OCH_3). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 126 MHz): δ (ppm) 156.6 (d, $^4J_{CP}$ = 3.5 Hz, $C$2′), 150.3 (d, $^2J_{CP}$ = 2.5 Hz, $C$12), 154.9 (d, $^2J_{CP}$ = 5.8 Hz, $C$12′), 141.8 (d, $^2J_{CP}$ = 37.5 Hz, $C$1), 136.3 (d, $^1J_{CP}$ = 37.7 Hz, $C$2), 135.3, 134.5 (d, $^4J_{CP}$ = 2.9 Hz, $C$9′), 132.9, 132.8, 132.7 (d, J_{CP} = 1.0 Hz), 131.6 (d, J_{CP} = 0.9 Hz), 131.4, 131.2, 130.8 ($C$4′), 130.5 ($C$5′), 129.5 ($C$14′), 128.7, 128.5, 128.5, 128.3 ($C$5), 128.2 ($C$10′), 128.1, 127.7, 127.1, 126.8, 126.7 ($C$4), 126.6, 126.5, 126.4 (d, J_{CP} = 2.6 Hz), 126.2, 126.1, 125.2, 124.9, 124.8, 124.5 (d, $^2J_{CP}$ = 2.0 Hz, $C$3), 123.8, 122.7 ($C$13), 121.6 ($C$13′), 118.9 (d, $^3J_{CP}$ = 10.2 Hz, $C$1′), 112.8 ($C$3′), 56.2 (s, OCH_3). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 202 MHz): δ (ppm) 177.8. HRMS (m/z, ESI$^+$, CH$_2$Cl$_2$): found 599.1767, calcd for [M + H]$^+$ 599.1771.

Synthesis of (R,S_b)-[1,1′-binaphthalene]-2,2′-diyl (2′-methoxy-[1,1′-binaphthalen]-2-yl)phosphonite (6b)

The same procedure was followed as for **6a**, except for using (S)-binol as the nucleophile. The title product was obtained as a white solid after removal of the solvent. Yield: 430 mg (72%). MP: 231 °C (decomposition). [α]$_D^{20}$ = −310° (c = 1.0 mg mL^{-1}, CHCl$_3$). IR (neat): ν 2980.8, 1620.1, 1590.2, 1506.3, 1462.7, 1431.5, 1329.8, 1230.2, 1203.4, 1146.0, 1070.1, 949.5, 867.8, 820.8, 789.7, 747.2, 684.7, 628.8 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, 500 MHz): δ (ppm) 8.09 (d, $^3J_{HH}$ = 9.1 Hz, 1H, $H$4′), 7.97 (d, $^3J_{HH}$ = 8.8 Hz, 1H, $H$14′), 7.93–7.90 (m, 3H, $H$15/$H$5′/$H$15′), 7.88 (d, $^3J_{HH}$ = 8.2 Hz, 1H, $H$5), 7.76 (d, $^3J_{HH}$ = 8.7 Hz, 1H, $H$14), 7.60 (d, $^3J_{HH}$ = 8.6 Hz, 1H, $H$4), 7.54 (dd, $^3J_{HH}$ = 8.0 Hz, $^{3/4}J_{HH}$ = 4.0 Hz, 1H, $H$6′), 7.52 (d, $^3J_{HH}$ = 8.8 Hz, 1H, $H$13′), 7.51 (d, $^3J_{HH}$ = 9.1 Hz, 1H, $H$3′), 7.46 (ddd, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 6.8 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, $H$16), 7.42–7.35 (m, 4H, $H$18/ArH), 7.32 (d, $^3J_{HH}$ = 4.0 Hz, 2H, $H$7′/$H$8′), 7.30 (ddd, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 6.8 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, $H$17), 7.23–7.18 (m, 4H, $H$3/ArH), 6.87 (d, $^3J_{HH}$ = 8.7 Hz, 1H, $H$13), 3.89 (s, 3H, OCH_3). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 101 MHz): δ (ppm) 154.9 (d, $^4J_{CP}$ = 2.9 Hz, $C$2′), 150.2 (d, $^2J_{CP}$ = 2.3 Hz, $C$12′), 149.0 (d, $^2J_{CP}$ = 5.9 Hz, $C$12), 141.9 (d, $^2J_{CP}$ = 39.2 Hz, $C$1), 136.4 (d, $^1J_{CP}$ = 38.3 Hz, $C$2), 135.3, 135.0 ($C$9′), 132.8, 132.7, 132.7, 131.6, 131.1, 130.7 ($C$4′), 130.5 ($C$14′), 129.5 ($C$14), 128.8, 128.4 ($C$15), 128.4 ($C$15′), 128.3 ($C$5′), 128.3 ($C$10′), 128.2 ($C$5), 127.7, 126.9 ($C$4), 126.8, 126.7, 126.6, 126.5, 126.4 (d, J_{CP} = 2.1 Hz), 126.2, 126.1, 125.5, 124.9, 124.8 ($C$16), 124.6 (d, J_{CP} = 2.5 Hz), 123.7, 123.6 (d, J_{CP} = 2.5 Hz), 122.5 ($C$13), 121.5 ($C$13′), 119.0 (d, $^3J_{CP}$ = 10.3 Hz, $C$1′),

113.0 (*C*3′), 56.4 (s, O*C*H$_3$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 202 MHz): δ (ppm) 177.9. HRMS (*m/z*, ESI$^+$, CH$_2$Cl$_2$): found 599.1766, calcd for [M + H]$^+$ 599.1771.

Synthesis of [Pd(5a)(η^3-C$_4$H$_7$)Cl] (7a)

[Pd(η^3-C$_4$H$_7$)Cl]$_2$ (7 mg, 18 μmol) and **5a** (20 mg, 35 μmol) were dissolved in CH$_2$Cl$_2$ (1 mL) and stirred for 10 min. The intended complex was formed quantitatively. Slow diffusion of diethyl ether into the reaction mixture yielded colorless crystals overnight, which were suitable for X-ray diffraction analysis. Yield: 25 mg (92%). MP: >270 °C. IR (neat): ν 3052.0, 1587.6, 1505.8, 1460.0, 1432.9, 1360.3, 1322.4, 1220.7, 1067.8, 977.3, 942.2, 871.8, 838.4, 810.2, 759.4, 706.9, 677.2, 634.3, 596.8 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, 500 MHz): δ (ppm) isomer A (97%), 7.97 (d, $^3J_{HH}$ = 8.1 Hz, 1H, *H*4′), 7.94–7.90 (m, 4H, *H*14/*H*5/*H*15/*H*15′), 7.89–7.85 (m, 2H, *H*2–/*H*5′), 7.84–7.80 (m, 2H, *H*13/*H*4), 7.78 (d, $^3J_{HH}$ = 8.9 Hz, 1H, *H*14′), 7.72 (dd, $^3J_{HH}$ = 8.6 Hz, $^3J_{HP}$ = 5.5 Hz, 1H, *H*3), 7.69 (dd, $^3J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 7.2 Hz, 1H, *H*3′), 7.58–7.55 (m, 1H, Ar*H*), 7.53–7.43 (m, 5H, *H*6′/Ar*H*), 7.39–7.27 (m, 5H, Ar*H*), 7.18–7.13 (m, 2H, *H*13′/Ar*H*), 3.75 (dd, $^3J_{HP}$ = 9.9 Hz, $^4J_{HH}$ = 2.5 Hz, 1H, allyl-*H*t$_{syn}$), 2.56 (s, 1H, allyl-*H*c$_{syn}$), 1.57 (d, $^3J_{HP}$ = 14.1 Hz, 1H, allyl-*H*t$_{anti}$), 1.00 (s, 3H, allyl-C*H*$_3$), 0.83 (s, 1H, allyl-*H*c$_{anti}$); isomer B (3%), 8.00–6.99 (m, 23H, Ar*H*), 6.92 (m, 1H, Ar*H*), 6.87 (m, 1H, Ar*H*), 3.96 (d, $^3J_{HP}$ = 6.8 Hz, 1H, allyl-*H*t$_{syn}$), 2.96 (m, 1H, allyl-*H*c$_{syn}$), 2.64 (d, $^3J_{HP}$ = 12.3 Hz, 1H, allyl-*H*t$_{anti}$), 1.53 (m, 1H, allyl-*H*c$_{anti}$), 1.42 (s, 3H, allyl-C*H*$_3$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 126 MHz): δ (ppm) isomer A (97%), 149.1 (d, $^2J_{CP}$ = 5.3 Hz, *C*12), 148.6 (d, $^2J_{CP}$ = 13.2 Hz, *C*12′), 144.7 (d, $^2J_{CP}$ = 27.2 Hz, *C*1), 135.2, 134.7 (d, $^1J_{CP}$ = 9.3 Hz, *C*2), 133.5, 133.4, 133.3, 133.1, 132.6 (d, J_{CP} = 1.4 Hz), 132.2 (d, J_{CP} = 1.9 Hz), 131.9 (d, J_{CP} = 1.3 Hz), 131.5 (d, J_{CP} = 1.3 Hz), 131.1 (*C*2′), 131.0 (d, J_{CP} = 28.6 Hz, allyl-*C*), 130.7 (d, $^4J_{CP}$ = 1.1 Hz, *C*14), 130.2 (d, $^4J_{CP}$ = 1.4 Hz, *C*14′), 129.7, 129.2 (*C*4′), 128.6, 128.5, 128.3, 128.2, 128.2, 127.7 (d, $^3J_{CP}$ = 5.2 Hz, *C*4), 127.3, 127.1, 127.1, 127.0 (d, J_{CP} = 2.3 Hz), 126.9, 126.8, 126.7, 126.6, 126.4, 125.5, 125.4, 125.2 (*C*3′), 124.9 (d, $^2J_{CP}$ = 2.8 Hz, *C*3), 124.2 (d, $^3J_{CP}$ = 3.8 Hz, *C*11), 123.7 (d, $^3J_{CP}$ = 2.9 Hz, *C*11′), 122.4 (d, $^3J_{CP}$ = 2.4 Hz, *C*13), 120.4 (*C*13′), 76.8 (d, $^2J_{CP}$ = 45.3 Hz, allyl-*C*t), 56.1 (d, $^2J_{CP}$ = 5.8 Hz, allyl-*C*c), 22.4 (allyl-*C*H$_3$); signals of isomer B could not be observed. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 202 MHz): δ (ppm) isomer A (97%), 173.4; isomer B (3%), 175.7. HRMS (*m/z*, ESI$^+$, MeOH): found 727.1178, calcd for [M − Cl]$^+$ 727.1176.

Synthesis of [Pd(5b)(η^3-C$_4$H$_7$)Cl] (7b)

The same procedure was followed as for **7a**. Yield: 23 mg (83%). MP: >270 °C. IR (neat): ν 3047.7, 1585.8, 1505.6, 1461.1, 1434.2, 1360.9, 1322.9, 1269.3, 1222.1, 1161.0, 1121.5, 1068.7, 1027.5, 977.3, 943.4, 877.1, 839.5, 803.3, 757.5, 729.6, 687.3, 634.8, 598.0, 557.6 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, 500 MHz): δ (ppm) 8.13 (d, $^3J_{HH}$ = 7.0 Hz, 1H, *H*2′), 7.98–7.86 (m, 7H, *H*4′/*H*15/*H*5′/*H*14′/*H*5/*H*15′/*H*13′), 7.83 (d, $^3J_{HH}$ = 8.8 Hz, 1H, *H*14), 7.74 (d, $^3J_{HH}$ = 8.7 Hz, 1H, *H*4), 7.69 (dd, $^3J_{HH}$ = 8.7 Hz, $^3J_{HH}$ = 7.0 Hz, 1H, *H*3′), 7.60–7.57 (m, 1H, Ar*H*), 7.53–7.40 (m, 7H, *H*3/Ar*H*), 7.36–7.23 (m, 5H, Ar*H*), 7.00 (d, $^3J_{HH}$ = 8.7

Hz, 1H, *H*13), 4.16 (dd, $^3J_{HP}$ = 10.2 Hz, $^4J_{HH}$ = 2.8 Hz, 1H, allyl-*H*t$_{syn}$), 2.56 (d, $^3J_{HP}$ = 14.8 Hz, 1H, allyl-*H*t$_{anti}$), 2.31 (s, 1H, allyl-*H*c$_{syn}$), 0.93 (s, 3H, allyl-C*H*$_3$), 0.50 (s, 1H, allyl-*H*c$_{anti}$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 126 MHz): δ (ppm) 149.1 (d, $^2J_{CP}$ = 5.3 Hz, *C*12′), 148.4 (d, $^2J_{CP}$ = 13.1 Hz, *C*12), 145.1 (d, $^2J_{CP}$ = 29.7 Hz, *C*1), 135.5, 134.5 (d, $^1J_{CP}$ = 9.4 Hz, *C*2), 134.3, 133.6 (d, J_{CP} = 4.7 Hz), 133.5 d, J_{CP} = 4.4 Hz), 133.3, 132.6 (d, J_{CP} = 1.4 Hz), 132.1, 131.8 (d, J_{CP} = 0.9 Hz), 131.6, 131.5 (d, $^4J_{CP}$ = 1.0 Hz, *C*2′), 130.8 (d, J_{CP} = 28.5 Hz, allyl-*C*), 130.7 (*C*14′), 130.2 (d, $^4J_{CP}$ = 1.4 Hz, *C*14), 128.6, 128.5, 128.5, 128.3, 128.1, 128.1 (*C*4′), 127.6 (d, $^3J_{CP}$ = 4.9 Hz, *C*4), 127.3, 127.2, 127.1, 127.0, 126.6, 126.6, 126.5, 126.3, 126.3, 126.2 (*C*3′), 125.5, 125.4, 124.5 (*C*3), 124.1 (d, $^3J_{CP}$ = 4.2 Hz, *C*11′), 123.5 (d, $^3J_{CP}$ = 2.6 Hz, *C*11), 122.5 (d, $^3J_{CP}$ = 2.3 Hz, *C*13′), 121.1 (d, $^3J_{CP}$ = 0.8 Hz, *C*13), 77.8 (d, $^2J_{CP}$ = 46.5 Hz, allyl-*C*t), 57.6 (d, $^2J_{CP}$ = 5.3 Hz, allyl-*C*c), 22.5 (allyl-*C*H$_3$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 202 MHz): δ (ppm) 172.1. HRMS (*m/z*, ESI$^+$, MeOH): found 725.1177, calcd for [M − Cl]$^+$ 725.1176.

Synthesis of [Pd(6a)(η^3-C$_4$H$_7$)Cl] (8a)

The same procedure was followed as for **7a**. Yield: 26 mg (91%). MP: >270 °C. IR (neat): ν 3065.2, 1620.2, 1589.0, 1507.6, 1463.0, 1431.3, 1327.7, 1247.8, 1223.0, 1194.2, 1151.8, 1068.9, 1021.8, 943.5, 873.9, 839.0, 807.0, 743.7, 677.2, 637.2, 597.2, 597.8, 560.2 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, 500 MHz): δ (ppm) isomer A (93%), 7.98 (d, $^3J_{HH}$ = 9.1 Hz, 1H, *H*4′), 7.93 (dd, $^3J_{HH}$ = 8.9 Hz, $^4J_{HP}$ = 0.9 Hz, 1H, *H*13), 7.91–7.86 (m, 4H, *H*14/*H*5/*H*15/*H*15′), 7.78–7.73 (m, 2H, *H*5′/*H*4), 7.72 (d, $^3J_{HH}$ = 8.9 Hz, 1H, *H*14′), 7.63 (dd, $^3J_{HH}$ = 8.6 Hz, $^3J_{HP}$ = 5.4 Hz, 1H, *H*3), 7.55 (ddd, $^3J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 6.8 Hz, $^4J_{HH}$ = 1.1 Hz, 1H, Ar*H*), 7.50 (d, $^3J_{HH}$ = 9.1 Hz, 1H, *H*3′), 7.47–7.24 (m, 10H, Ar*H*/*H*6′), 7.19 (d, $^3J_{HH}$ = 8.9 Hz, $^4J_{HP}$ = 1.0 Hz, 1H, *H*13′), 7.14 (d, $^3J_{HH}$ = 8.4 Hz, 1H, Ar*H*), 3.97 (s, 3H, O*C*H$_3$), 3.73 (dd, $^3J_{HP}$ = 10.0 Hz, $^4J_{HH}$ = 3.0 Hz, 1H, allyl-*H*t$_{syn}$), 2.60 (m, 1H, allyl-*H*c$_{syn}$), 1.63 (d, $^3J_{HP}$ = 14.1 Hz, 1H, allyl-*H*t$_{anti}$), 0.92 (s, 3H, allyl-C*H*$_3$), 0.85 (m, 1H, allyl-*H*c$_{anti}$); isomer B (7%), 8.05 (d, $^3J_{HH}$ = 9.1 Hz, 1H, *H*4′), 7.99–7.10 (m, 20H, Ar*H*), 7.07–7.02 (m, 1H, Ar*H*), 6.97 (d, $^3J_{HH}$ = 8.9 Hz, 1H, *H*13′), 6.74 (d, $^3J_{HH}$ = 8.5 Hz, 1H, Ar*H*), 4.12 (s, 3H, O*C*H$_3$), 3.87 (m, 1H, allyl-*H*t$_{syn}$), 3.18 (m, 1H, allyl-*H*c$_{syn}$), 1.94 (d, $^3J_{HP}$ = 13.0 Hz, 1H, allyl-*H*t$_{anti}$), 1.70 (s, 3H, allyl-C*H*$_3$), 1.35 (m, 1H, allyl-*H*c$_{anti}$). ^{13}C {^{1}H} NMR (CD$_2$Cl$_2$, 126 MHz): δ (ppm) isomer A (93%), 156.4 (*C*2′), 149.3 (d, $^2J_{CP}$ = 5.3 Hz, *C*12), 149.1 (d, $^2J_{CP}$ = 12.9 Hz, *C*12′), 141.5 (d, $^2J_{CP}$ = 27.0 Hz, *C*1), 135.5 (d, $^1J_{CP}$ = 1.4 Hz, *C*2), 134.2 (*C*9′), 133.2 (d, J_{CP} = 7.1 Hz), 133.2 (d, J_{CP} = 8.1 Hz), 132.4 (d, J_{CP} = 1.3 Hz), 132.1 (d, J_{CP} = 1.4 Hz), 131.8 (d, J_{CP} = 8.1 Hz), 131.6 (d, J_{CP} = 1.1 Hz), 131.3 (d, $^2J_{CP}$ = 28.8 Hz, allyl-*C*), 131.0 (*C*4′), 130.5 (d, $^4J_{CP}$ = 1.1 Hz, *C*14), 130.1 (d, $^4J_{CP}$ = 1.3 Hz, *C*14′), 128.6, 128.5, 128.4, 128.4, 128.3, 128.2 (*C*6), 128.0, 127.5 (d, $^3J_{CP}$ = 5.3 Hz, *C*4), 127.0 (*C*10′), 127.0, 126.9 (*C*5′), 126.7, 126.4, 126.3 (d, J_{CP} = 2.3 Hz), 126.2 (*C*8), 125.4, 125.3, 125.0 (d, $^2J_{CP}$ = 2.7 Hz, *C*3), 124.5 (*C*6′), 124.4 (d, $^3J_{CP}$ = 3.8 Hz, *C*11), 123.7 (d, $^3J_{CP}$ = 3.0 Hz, *C*11′), 122.9 (d, $^3J_{CP}$ = 2.4 Hz, *C*13), 121.5 (*C*13′), 118.8 (d, $^3J_{CP}$ = 9.5 Hz, *C*1′), 113.1 (*C*3′), 77.3 (d, $^2J_{CP}$ = 44.9 Hz, allyl-*C*t), 56.2 (O*C*H$_3$), 56.1 (d, $^2J_{CP}$ = 5.3 Hz, allyl-*C*c), 22.5 (allyl-*C*H$_3$); signals of isomer B could not be observed. ^{31}P{^{1}H} NMR

(CD$_2$Cl$_2$, 202 MHz): δ (ppm) isomer A (93%), 173.6; isomer B (7%) 175.6. HRMS (*m/z*, ESI$^+$, MeOH): found 755.1301, calcd for [M − Cl]$^+$ 755.1296.

Synthesis of [Pd(6b)(η^3-C$_4$H$_7$)Cl] (8b)

The same procedure was followed as for **7a**. Yield: 23 mg (80%). MP: >270 °C. IR (neat): ν 3066.0, 1619.1, 1587.6, 1506.6, 1463.6, 1429.5, 1323.0, 1276.0, 1226.1, 1199.8, 1155.9, 1117.7, 1070.1, 1028.0, 946.1, 867.4, 833.3, 814.2, 751.9, 706.2, 686.6, 634.8, 606.6, 560.1 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, 500 MHz): δ (ppm) 8.02 (d, $^3J_{HH}$ = 9.1 Hz, 1H, *H*4′), 8.00–7.97 (m, 2H, *H*15/*H*13′), 7.94 (d, $^3J_{HH}$ = 8.9 Hz, 1H, *H*14′), 7.91 (d, $^3J_{HH}$ = 8.1 Hz, 1H, *H*5), 7.89 (d, $^3J_{HH}$ = 8.2 Hz, 1H, *H*15′), 7.86 (d, $^3J_{HH}$ = 8.7 Hz, 1H, *H*14), 7.83 (d, $^3J_{HH}$ = 8.2 Hz, 1H, *H*5′), 7.65 (d, $^3J_{HH}$ = 8.7 Hz, 1H, *H*4), 7.59 (ddd, $^3J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 6.6 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, *H*6), 7.54–7.51 (m, 1H, *H*16), 7.49 (d, $^3J_{HH}$ = 9.1 Hz, 1H, *H*3′), 7.46–7.39 (m, 3H, Ar*H*/*H*16′), 7.37–7.27 (m, 7H, Ar*H*/*H*17/*H*7′/*H*6′/*H*3/*H*7/*H*18′), 7.25–7.22 (m, 1H, *H*17′), 7.00 (d, $^3J_{HH}$ = 8.7 Hz, 1H, *H*13), 4.07 (dd, $^3J_{HP}$ = 9.9 Hz, $^4J_{HH}$ = 3.8 Hz, 1H, allyl-*H*t$_{syn}$), 3.87 (s, 3H, OC*H*$_3$), 2.35 (s, 1H, allyl-*H*c$_{syn}$), 2.24 (d, $^3J_{HP}$ = 13.6 Hz, 1H, allyl-*H*t$_{anti}$), 0.84 (s, 3H, allyl-C*H*$_3$), 0.32 (s, 1H, allyl-*H*c$_{anti}$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 126 MHz): δ (ppm) 156.2 (*C*2′), 149.2 (d, $^2J_{CP}$ = 5.3 Hz, *C*12′), 148.5 (d, $^2J_{CP}$ = 12.4 Hz, *C*12), 142.6 (d, $^2J_{CP}$ = 29.8 Hz, *C*1), 135.6 (d, $^1J_{CP}$ = 1.3 Hz, *C*2), 135.5 (d, $^4J_{CP}$ = 0.9 Hz, *C*9′), 134.0 (d, J_{CP} = 9.2 Hz), 133.1 (d, J_{CP} = 9.8 Hz), 132.7 (d, J_{CP} = 1.5 Hz), 132.1 (d, J_{CP} = 1.9 Hz), 131.8 (d, J_{CP} = 1.3 Hz), 131.6 (d, J_{CP} = 1.3 Hz), 131.3 (d, $^2J_{CP}$ = 26.3 Hz, allyl-*C*), 130.5 (d, $^4J_{CP}$ = 0.9 Hz, *C*14′), 130.1 (d, $^4J_{CP}$ = 1.3 Hz, *C*14), 129.7 (*C*4′), 128.5 (*C*15), 128.5 (*C*15′), 128.5 (*C*6), 128.3 (*C*5), 128.2 (*C*10′), 128.0 (*C*5′), 127.3 (d, $^3J_{CP}$ = 4.7 Hz, *C*4), 127.0, 127.0, 126.9, 126.8, 126.6, 126.6, 126.2 (*C*17′), 125.5 (*C*16), 125.3 (*C*16′), 125.3, 125.1 (d, $^2J_{CP}$ = 1.4 Hz, *C*3), 124.1 (d, $^3J_{CP}$ = 3.8 Hz, *C*11′), 123.5, 123.4 (d, $^3J_{CP}$ = 2.8 Hz, *C*11), 123.1 (d, $^3J_{CP}$ = 2.4 Hz, *C*13′), 121.4 (*C*13), 118.2 (d, $^3J_{CP}$ = 10.5 Hz, *C*1′), 113.5 (*C*3′), 79.3 (d, $^2J_{CP}$ = 46.1 Hz, allyl-*C*t), 59.0 (d, $^2J_{CP}$ = 4.5 Hz, allyl-*C*c), 56.0 (OC*H*$_3$), 22.3 (allyl-C*H*$_3$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 202 MHz): δ (ppm) 174.4. HRMS (*m/z*, ESI$^+$, MeOH): found 755.1280, calcd for [M − Cl]$^+$ 755.1296.

Synthesis of [Pd(6a)(η^3-C$_4$H$_7$)]BArF (9a)

Sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (33.4 mg, 37.7 μmol) and **8a** (30.0 mg, 37.7 μmol) were dissolved in CH$_2$Cl$_2$ (2 mL) and stirred for 30 min. The reaction mixture was filtered through a layer of celite and the solvent removed *in vacuo*; the intended product was obtained as a yellow solid. Yield: 48.9 mg (80%). IR (neat): ν 1612.4, 1588.2, 1506.9, 1464.1, 1353.8, 1273.2, 1220.7, 1116.5, 953.5, 882.6, 836.8, 813.3, 746.2, 711.9, 681.4, 638.0, 599.2 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, 500 MHz): δ (ppm) isomer A,B, 8.27–7.23 (m, 2H, *H*4′^{B}/*H*4′^{A}), 8.14–7.98 (m, 10H, *H*5′/*H*14/*H*15′/*H*15/*H*14′), 7.93–7.89 (m, 3H, *H*5′/*H*3′^{B}), 7.86–7.80 (m, 3H, *H*3′^{A}/*H*4), 7.74 (br s, 16H, *o*-BArF), 7.63–7.51 (m, 18H, *H*6′/*H*16/*H*16′/*H*6/Ar*H*/*p*-BArF), 7.48–7.38 (m, 10H, *H*13/Ar*H*), 7.26–7.19 (m, 4H, *H*7/Ar*H*), 7.13–7.02 (m, 4H, *H*13′/*H*3), 6.06 (d, $^3J_{HH}$ = 8.3

Hz, 2H, *H*8), 4.06 (s, OC*H*$_3$^{B}), 4.00 (s, OC*H*$_3$^{A}), 3.16 (br d, $^3J_{HP}$ = 10.7 Hz, allyl-*H*t$_{anti}$^{B}), 3.03 (s, allyl-*H*c$_{syn}$^{B}), 2.99 (s, allyl-*H*c$_{syn}$^{A}), 2.90 (d, $^3J_{HP}$ = 13.2 Hz, allyl-*H*t$_{anti}$^{A}), 2.43 (br d, $^3J_{HP}$ = 8.2 Hz, allyl-*H*t$_{syn}$^{A}), 2.39 (s, allyl-*H*c$_{anti}$^{A}), 2.34 (br s, allyl-*H*t$_{syn}$^{B}), 2.22 (s, allyl-*H*c$_{anti}$^{B}), 1.58 (s, allyl-C*H*$_3$), 1.30 (s, allyl-C*H*$_3$^{B}); A : B ratio from integration of C*H*$_3$ signals: 52 : 48. ^{11}B NMR (CD$_2$Cl$_2$, 160 MHz): δ (ppm) −7.6. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 101 MHz): δ (ppm) isomer A,B, 161.8 (q, $^1J_{CB}$ = 40.8 Hz, *ipso*-BArF), 159.0 (*C*2′^{B}), 157.2 (*C*2′^{A}), 148.1 (d, $^3J_{CP}$ = 10.1 Hz, *C*11′^{B}), 148.0 (d, $^3J_{CP}$ = 11.0 Hz, *C*11′^{A}), 147.1 (d, $^3J_{CP}$ = 7.7 Hz, *C*11), 142.1 (d, $^2J_{CP}$ = 41.7 Hz, *C*1^B), 141.9 (d, $^2J_{CP}$ = 41.7 Hz, *C*1^A), 137.9 (d, $^2J_{CP}$ = 9.5 Hz, allyl-*C*^{A}), 137.0 (*C*2), 134.8 (*o*-BArF), 134.6 (*C*4′), 132.8, 132.5, 132.1, 132.0, 131.7, 131.6 (*C*14), 131.5 (*C*9′^{A}), 131.4 (*C*9′^{B}), 131.4 (*C*14′), 130.9, 130.8, 130.4, 130.3 (*C*4), 130.1 (*C*5′), 130.0, 129.8, 129.4, 128.9 (qq, $^2J_{CF}$ = 31.2 Hz, $^4J_{CF}$ = 2.8 Hz, *m*-BArF), 128.8, 128.4 (*C*10′), 127.5, 127.4, 127.3, 127.1, 127.0, 126.9, 126.5, 126.4, 126.3, 126.0, 125.0, 124.8, 124.7 (q, $^1J_{CF}$ = 273.2 Hz, *C*F$_3$), 124.1, 124.0 (d, J_{CP} = 3.4 Hz), 123.8, 123.7, 123.3, 122.5, 122.3, 120.7 (*C*3), 120.6 (*C*13′), 120.3 (*C*13), 120.1, 117.5 (septet, $^3J_{CF}$ = 4.0 Hz, *p*-BArF), 114.9 (*C*3′^{A}), 114.5 (*C*3′^{B}), 104.6 (*C*1′^{A}), 99.6 (d, $^2J_{CP}$ = 40.1 Hz, allyl-*C*t^A), 57.5 (OC*H*$_3$^{B}), 57.4 (OC*H*$_3$^{A}), 53.2 (allyl-*C*c^A), 22.4 (allyl-C*H*$_3$^{A}), 21.6 (allyl-C*H*$_3$^{B}); not all signals could be observed due to peak broadening and overlap. ^{19}F NMR (CD$_2$Cl$_2$, 471 MHz): δ (ppm) −62.7. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 202 MHz): δ (ppm) isomer A, 177.5; isomer B, 178.0. HRMS (*m/z*, ESI$^+$, MeCN): found 757.1287, calcd for [M]$^+$ 757.1281.

Synthesis of [Pd(6b)(η^3-C$_4$H$_7$)]BArF (9b)

The same procedure was followed as for **9a**; the intended product was obtained as a yellow solid. Yield: 54.0 mg (91%). IR (neat): ν 1612.1, 1588.9, 1506.1, 1463.5, 1353.6, 1273.0, 1219.8, 1116.1, 952.9, 882.4, 836.7, 811.4, 745.5, 711.9, 669.8, 638.6, 602.7 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, 500 MHz): δ (ppm) isomer A,B, 8.22 (d, $^3J_{HH}$ = 9.2 Hz, 1H, *H*4′^{A}), 8.21 (d, $^3J_{HH}$ = 9.2 Hz, 1H, *H*4′^{B}), 8.17–8.01 (m, 10H, *H*14/*H*14′/*H*5′/Ar*H*), 7.99 (d, $^3J_{HH}$ = 9.2 Hz, 1H, *H*3′^{A}), 7.96–7.89 (m, 5H, Ar*H*/*H*4/*H*3′^{B}), 7.76 (br s, 16H, *o*-BArF), 7.64–7.51 (m, 18H, Ar*H*/*p*-BArF), 7.49–7.35 (m, 12H, Ar*H*/*H*13^B/*H*13′^{A}/*H*13^A), 7.30–7.22 (m, 4H, Ar*H*/*H*7/*H*13′^{B}), 7.20 (dd, $^3J_{HH}$ = 8.5 Hz, $^3J_{HP}$ = 6.9 Hz, 1H, *H*3^A), 7.10 (dd, $^3J_{HH}$ = 8.5 Hz, $^3J_{HP}$ = 6.9 Hz, 1H, *H*3^B), 6.09 (br d, 1H, *H*8^B), 6.00 (d, $^3J_{HH}$ = 8.6 Hz, 1H, *H*8^A), 3.98 (s, OC*H*$_3$^{A}), 3.89 (s, OC*H*$_3$^{B}), 3.76 (d, $^3J_{HP}$ = 13.6 Hz, allyl-*H*t$_{anti}$^{A}), 3.00 (br d, allyl-*H*t$_{syn}$^{B}), 2.87 (s, allyl-*H*c$_{syn}$^{B}), 2.82 (s, allyl-*H*c$_{syn}$^{A}), 2.63 (d, $^3J_{HP}$ = 13.5 Hz, allyl-*H*t$_{anti}$^{B}), 2.32 (s, allyl-*H*c$_{anti}$^{A}), 2.20 (br s, allyl-*H*c$_{anti}$^{B}), 2.19 (d, allyl-*H*t$_{syn}$^{A}), 1.79 (br s, allyl-C*H*$_3$^{B}), 0.96 (s, allyl-C*H*$_3$^{A}); A : B ratio of 50 : 50 from integration of OMe resonances (signals of isomer B broadened). ^{11}B NMR (CD$_2$Cl$_2$, 128 MHz): δ (ppm) −7.6. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 126 MHz): δ (ppm) isomer A,B, 161.8 (q, $^1J_{CB}$ = 40.7 Hz, *ipso*-BArF), 156.6 (*C*2′^{A}), 154.8 (d, J_{CP} = 2.4 Hz, *C*2′^{B}), 148.3 (d, $^3J_{CP}$ = 13.5 Hz, *C*11^A), 148.3 (d, $^3J_{CP}$ = 13.3 Hz, *C*11^B), 147.2 (d, $^3J_{CP}$ = 7.1 Hz, *C*11′^{A}), 147.1 (d, $^3J_{CP}$ = 7.4 Hz, *C*11′^{B}), 142.4 (d, $^2J_{CP}$ = 43.5 Hz, *C*1^B), 142.2 (d, $^2J_{CP}$ = 41.3 Hz, *C*1^A), 138.9 (d, $^2J_{CP}$ = 10.4 Hz, allyl-*C*^{A}), 138.1 (d, J = 10.0 Hz, allyl-*C*^{B}), 137.1 (*C*2^B), 137.0 (*C*2^A), 134.9 (*C*4′^{A}),

134.9 (*o*-BArF), 134.3 (*C*4′B), 133.7 (*C*9′B), 132.8, 132.7 (*C*9′A) 132.1, 131.8, 131.7, 131.6, 131.5, 130.7 (d, $^3J_{CP}$ = 4.7 Hz, *C*4), 130.0 (*C*10′B), 129.8, 129.8, 129.7, 129.3 (*C*10′A), 128.9 (qq, $^2J_{CF}$ = 31.6 Hz, $^4J_{CF}$ = 2.9 Hz, *m*-BArF), 128.7, 128.6, 128.0, 127.6, 127.4, 127.4, 127.0, 127.0, 126.6, 126.5, 126.4, 125.1, 124.8, 124.7 (q, $^1J_{CF}$ = 272.3 Hz, *C*F$_3$), 124.3, 124.1, 123.7 (d, $^2J_{CP}$ = 1.4 Hz, *C*3^B), 123.7 (d, $^2J_{CP}$ = 1.4 Hz, *C*3^A), 123.0, 122.3, 122.1, 120.7 (d, $^3J_{CP}$ = 1.0 Hz, *C*13^B), 120.6 (d, $^3J_{CP}$ = 1.0 Hz, *C*13^A), 120.1 (d, $^3J_{CP}$ = 2.1 Hz, *C*13′A), 119.8 (*C*13′B), 117.5 (septet, $^3J_{CF}$ = 4.0 Hz, *p*-BArF), 115.9 (*C*3′B), 115.3 (*C*3′A), 104.5 (*C*1′B), 103.4 (*C*1′A), 99.5 (d, $^2J_{CP}$ = 41.1 Hz, allyl-*Ct*^{A}), 96.9 (br, allyl-*Ct*^{B}), 57.6 (O*C*H$_3$^{A}), 57.3 (O*C*H$_3$^{B}), 56.4 (allyl-*Cc*^{B}), 54.9 (allyl-*Cc*^{A}), 22.6 (allyl-*C*H$_3$^{B}), 21.5 (allyl-*C*H$_3$^{A}); not all signals could be observed due to peak broadening and overlap. ^{19}F NMR (CD$_2$Cl$_2$, 471 MHz): δ (ppm) −62.7. ^{31}P {^{1}H} NMR (CD$_2$Cl$_2$, 202 MHz): δ (ppm) isomer A, 178.9; isomer B, 179.1. HRMS (*m/z*, ESI$^+$, MeCN): found 757.1296, calcd for [M]$^+$ 757.1281.

Asymmetric palladium-catalyzed hydrosilylation of styrene

[Pd(η^3-C$_3$H$_4$)Cl]$_2$ (4.6 mg, 0.0125 mmol, 0.125 mol%), ligand (0.25 mol%) and styrene (1.2 mL, 1.0 g, 10.0 mmol) were stirred at room temperature for 20 min. Trichlorosilane (1.2 mL, 1.6 g, 12.0 mmol) was added and the reaction was stirred at room temperature for the appropriate time. The conversion of the reaction was followed by ^{1}H NMR spectroscopy. The product was purified by Kugelrohr distillation (reduced pressure, 150 °C).

Trichloro(1-phenylethyl)silane (400 mg, 1.67 mmol) was dissolved in MeOH (30 mL) and THF (30 mL). K$_2$CO$_3$ (1.40 g, 10.1 mmol), KF (600 mg, 10.3 mmol) and 35% H$_2$O$_2$ (1.8 mL) were added subsequently and left to stir overnight. The solution was filtered, water was added and the product was extracted with diethyl ether three times. The combined organic washings were dried over MgSO$_4$ and the crude product was purified by column chromatography on silica (hexane/ethyl acetate, 4 : 1, R_f = 0.20). The enantiomeric excess was measured by chiral HPLC (Column Daicel Chiralcel OD; flow rate: 0.5 mL min^{-1}; hexane/2-propanol, 95 : 5; retention times: (*R*) t_1 = 19.3 min, (*S*) t_2 = 22.3 min). The absolute configuration was assigned by comparing the retention times to literature data.[23]

Acknowledgements

Notes and references

1 Selected review articles: (*a*) F. Lagasse and H. B. Kagan, *Chem. Pharm. Bull.*, 2000, **48**, 315; (*b*) I. V. Komarov and A. Börner, *Angew. Chem., Int. Ed.*, 2001, **40**, 1197; (*c*) T. Jerphagnon, J.-L. Renaud and C. Bruneau, *Tetrahedron: Asymmetry*, 2004, **15**, 2101; (*d*) G. Erre, S. Enthaler, K. Junge, S. Gladiali and M. Beller, *Coord. Chem. Rev.*, 2008, **252**, 471;

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