Synthesis and application of bulky phosphoramidites: highly effective monophosphorus ligands for asymmetric hydrosilylation of styrenes†

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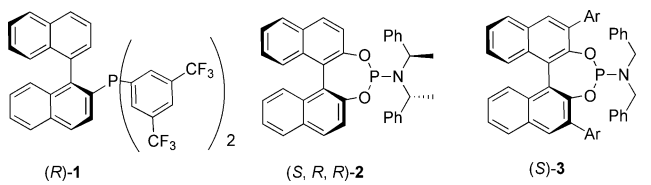
A series of bulky monodentate phosphoramidite ligands were synthesized from chiral 3,3′-diaryl substituted BINOL derivatives and achiral or dendritic amines in good yields. Asymmetric hydrosilylation of styrenes with trichlorosilane in the presence of palladium complexes of these bulky ligands gave chiral silanes in high yields with excellent activity and productivity. Oxidation of these chiral silanes with hydrogen peroxide gave the corresponding chiral secondary alcohols in up to 96% ee.

Introduction

The asymmetric catalytic functionalization of alkenes has been recognized as one of the most powerful tools for the construction of chiral units.[1] In particular, the Pd-catalyzed asymmetric hydrosilylation of alkenes with trichlorosilane is one important example of hydrometallation reactions that display excellent regioselectivities and enantioselectivities for a variety of aryl- and alkyl-substituted terminal olefins.[2–4] The resulting chiral organosilanes can be converted into chiral alcohols *via* a Tamao oxidation with complete retention of configuration at the carbon center.[5] In this hydrosilylation reaction, a monophosphane–palladium combination has proven to be a necessary requirement for achieving high catalytic activity and enantioselectivity.[2a] Thus far, a number of chiral monophosphorus ligands have been developed for such reactions.[1–4] However, only a few of them have displayed high efficiency with respect to both reactivity and enantioselectivity. Among them, the most efficient ligands include Hayashi's MOP ligands[2] (such as ligand **1** shown in Fig. 1) based on an axially chiral biaryl scaffold and Johannsen's MOPF ligands[4a,4b] based on a planar chiral ferrocene scaffold. Therefore, it is still desirable to develop highly effective and easily available chiral monophosphorus ligands for Pd-catalyzed hydrosilylation.



(*R*)-**1** (*S*, *R*, *R*)-**2** (*S*)-**3**

Fig. 1 Binaphthol-based monophosphane and phosphoramidite ligands.

Monodentate chiral phosphoramidite ligands have recently attracted considerable attention because of their excellent performance, relatively simple synthesis from readily available building materials and good stability.[6] In 2002, Johannsen and co-workers firstly applied chiral phosphoramidite **2** to the Pd-catalyzed asymmetric reaction of styrenes, which afforded the chiral alcohols upon oxidation in up to 99% ee.[3a] Subsequently, Zhou *et al.* developed a novel class of chiral monophosphoramidite ligand containing a 1,1′-spirobiindane scaffold[7] and demonstrated that these ligands were highly efficient for the Pd-catalyzed asymmetric hydrosilylation of styrenes affording high yields with excellent enantioselectivities (up to 99.1% ee).[3b] It was noted that the chiral side chains in these ligands played a dominant role in enantioselection in this reaction. In contrast, much lower reactivity and enantioselectivity were observed with similar ligands lacking the additional chirality on the side chain.[3]

Recently, we reported a series of chiral dendritic phosphoramidites by attaching dendritic wedges on the nitrogen atom.[8] It was found that these ligands exhibited unprecedented enhancement of enantioselectivity in the Rh-catalyzed asymmetric hydrogenation of olefins. As indicated by the reaction mechanism, Pd intermediates bearing only one phosphorus ligand have proven to be the real catalytically active species.[2a,2c] It is thus reasonable to expect that our sterically demanding dendritic phosphoramidites without additional chiral elements in the side chain will be effective in this reaction. In addition, most recently, de Vries *et al.* reported that an iridium(I) complex containing a single phosphoramidite ligand could induce an efficient asymmetric hydrogenation.[9] It demonstrated that the steric properties of the substituents in the 3,3′-positions of the chiral diol backbone played a very important role in achieving high reactivity and enantioselectivity. As an extension of our research and inspired by de Vries's work, we report here the synthesis and application of a new kind of bulky phosphoramidite ligand (such as **3** in Fig. 1) based on a 1,1-binaphthyl backbone with substituents in the 3,3′-positions and/or dendritic wedges attached on the nitrogen atom of the ligand for the Pd-catalyzed asymmetric hydrosilylation reaction of styrenes.

Results and discussion

Firstly, a series of 1,1′-binaphthol derivatives (*S*)-**4** were synthesized according to the published methods.[10] The resulting diols were refluxed with trichlorophosphine in the presence of a catalytic amount of N-methyl-2-pyrrolidinone (NMP)[11], followed

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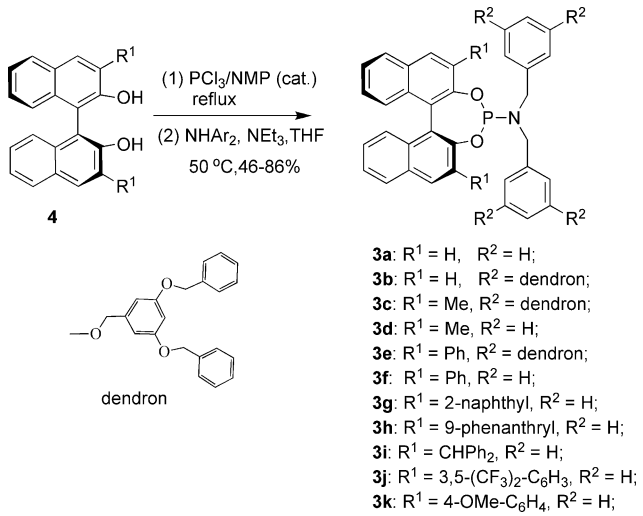
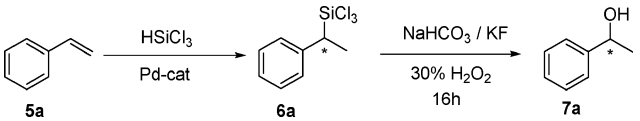
by reaction with a dendritic secondary amine[8] or dibenzylamine at 50 °C, providing the desired phosphoramidites **3a**–**3k** in 46–86% yields (Scheme 1). All these chiral ligands were well characterized by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy as well as MALDI-TOF or high-resolution mass spectrometry. All the results were consistent with the compounds synthesized. The target ligands obtained with this method possess modular properties, thus allowing fine-tuning of their steric and electronic characteristics.



Scheme 1 Synthesis of bulky binaphthol-based chiral phosphoramidites.

With these ligands in hand, we first investigated the steric effect on catalytic properties by choosing the asymmetric hydrosilylation of styrene **5a** as the standard reaction. The reaction was carried out without additional organic solvents at 0 °C in the presence of 0.25 mol% catalyst generated *in situ* by the mixing of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ and the chiral phosphoramidite at room temperature. As shown in Table 1, in the cases with a ligand : Pd ratio of 2 : 1, it was found that both the reactivities and enantioselectivities were strongly dependent on the substituents in the 3,3′-positions of the binaphthyl backbone as well as the dendritic wedges on the nitrogen atom of the ligand. As expected, the most simple ligand **3a** afforded low conversion (20%) in 8 h. The oxidation of the resulting silane **6a** under Tamao conditions provided alcohol **7a** in only 11% ee with an (*R*) configuration (entry 1).[3a] Surprisingly, the dendritic ligand **3b** bearing sterically demanding substituents on the nitrogen atom provided even lower conversion and racemic product (entry 3). Introducing methyl groups into the 3,3′-positions of **3b** to afford ligand **3c** enhanced the reactivity significantly (entry 5). It was interesting to note that ligand **3d** with only the methyl substituents resulted in moderate enantioselectivity, but with opposite configuration as compared to **3c** (entry 7 *vs*. entry 5). When we replaced the methyl groups with bulky phenyl groups, to our delight, much higher enantioselectivities and reactivities were achieved (entries 9 and 11). Unlike ligands **3c** and **3d**, both **3e** and **3f** gave the chiral alcohols with the same configuration upon oxidation. Furthermore, the dendritic ligand **3e** exhibited better enantioselectivity than ligand **3f** (88% *vs*. 76% ee, entries 9 and 11), indicating the synergistic effect of the combination of aryl substituents in the 3,3′-positions and dendritic wedges on the nitrogen atom of the ligand. However, when the ligand : palladium (L : Pd) ratio was reduced to 1 : 1, both ligands **3e** and **3f** exhibited similar high enantioselectivities (entries 10 and 12).

Table 1 The Pd-catalyzed asymmetric hydrosilylation of styrene: steric effect and ligand screening[a]



Entry	Ligand	**3**/Pd	Temp./°C	Conv. to **6a** (%)[b]	Ee of **7a** (%)[c]
1	**3a**	2	0	20	11 (*R*)
2	**3a**	1	0	46	4 (*R*)
3	**3b**	2	0	16	Racemic
4	**3b**	1	0	30	5 (*S*)
5	**3c**	2	0	>95	43 (*R*)
6	**3c**	1	0	>95	36 (*R*)
7	**3d**	2	0	>95	38 (*S*)
8	**3d**	1	0	>95	8 (*R*)
9	**3e**	2	0	>95	88 (*S*)
10	**3e**	1	0	>95	86 (*S*)
11[d]	**3f**	2	0	>95	76 (*S*)
12[d]	**3f**	1	0	>95	85 (*S*)
13	**3f**	1	–20	>95	92 (*S*)
14	**3g**	1	–20	>95	82 (*S*)
15	**3h**	1	–20	50 (>95)[e]	94 (96)[e] (*S*)
16	**3i**	1	–20	>95	80 (*S*)
17	**3j**	1	–20	>95	82 (*S*)
18	**3k**	1	–20	>95	96 (*S*)

[a] The reactions were conducted with **5a** : $HSiCl_3$: $[PdCl(\eta^3\text{-}C_3H_5)]_2$: **3** = 1 : 1.2 : 0.00125 : 0.0025, solvent free, 8 h. [b] Conversion determined by ^{1}H NMR spectroscopy. [c] Ee values determined by GC analysis with chiral column, and absolute configuration determined by optical rotation. [d] Reaction time is 6 h. [e] Data in brackets were obtained upon prolonged reaction time (16 h).

Given the excellent performance of the catalyst with **3f**, we intended to further explore the influence of the aryl substituents on the reactivity and enantioselectivity in the asymmetric hydrosilylation of **5a**. As compared to **3f**, ligand **3g** bearing 2-naphthyl substituents showed lower enantioselectivity (entry 13 *vs*. entry 14). However, further increasing the bulkiness of the aryl substituents (ligand **3h**) led to high enantioselectivity, albeit with reduced reactivity (entry 15). A comparison of selectivity between ligand **3i** and **3d** revealed that the steric properties of the substituents did play an important role in selectivity (entry 16 *vs*. entry 8). In addition, the electronic effect of the substituents was also observed. Ligand **3j** with electron-deficient aryl substituents gave lower enantioselectivity (entry 17). In contrast, an electron-rich aryl substituent (**3k**) was beneficial for the enantioselectivity (entry 18). Therefore, ligand **3k** was found to be the best choice of ligand for this asymmetric hydrosilylation reaction in terms of the reactivity and enantioselectivity.

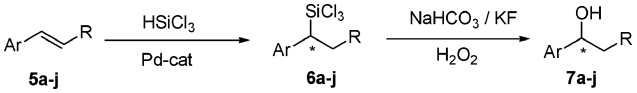
Next, we focused on the examination of reaction parameters, and the results are collected in Table 2. The effect of the L : Pd ratio was first investigated. Generally, a L : Pd ratio of 2 : 1 was applied in most of the reported catalytic systems.[2–4] In our cases, it was interesting to note that higher enantioselectivity was observed upon changing the L : Pd ratio from 2 : 1 to 1 : 1 (entries 11 and 12 in Table 1, and entries 1 and 2 in Table 2). When the L : Pd ratio was further reduced to 0.5 : 1, complete conversion could be achieved but with much lower enantioselectivity together with the appearance of Pd black (entry 3). In contrast, the complex

Table 2 The Pd-catalyzed asymmetric hydrosilylation of styrene using phosphoramidite **3k**: reaction conditions optimization[a]

Entry	**3k**/Pd	Sub./cat.	Temp./°C	Time	Ee of **7a** (%)[b]
1	2	400	–20	8 h	93
2	1	400	–20	8 h	96
3	0.5	400	–20	8 h	78
4	4	400	–20	8 h	—[c]
5[d]	1	400	–20	8 h	87
6[e]	1	400	–20	8 h	93
7[f]	1	400	–20	8 h	94
8	1	1000	r.t.	20 min	77
9	1	1000	0	20 min	92
10	1	1000	–20	8 h	93
11	1	5000	0	12 h	90
12	1	10 000	0	72 h	81

[a] The reactions were conducted with **5a** : $HSiCl_3$: $[PdCl(\eta^3\text{-}C_3H_5)]_2$: **3k** = 1 : 1.2 : 0.00125 : 0.0025, solvent free. [b] Complete conversions were obtained in all cases; ee values were determined by GC analysis with chiral column. [c] No reaction determined by ^1H NMR spectroscopy. [d] $Pd(acac)_2$ as metal precursor. [e] CH_2Cl_2 as solvent. [f] 4 equiv of $HSiCl_3$ to styrene.

Table 3 Catalytic asymmetric hydrosilylation of styrene derivatives catalyzed by Pd–**3k**[a]



Entry	Substrate (Ar, R)	Temp./°C	Time/h	Ee of **7** (%)[b]
1	**5a** (Ar = C_6H_5; R = H)	–20	8	96 (*S*)
2	**5b** (Ar = 2-Me-C_6H_4; R = H)	–20	16	80 (*S*)
3	**5c** (Ar = 4-Me-C_6H_4; R = H)	–20	16	93 (*S*)
4	**5d** (Ar = 4-OMe-C_6H_4; R = H)	–20	16	89 (*S*)
5	**5e** (Ar = 4-Br-C_6H_4; R = H)	–20	16	89 (*S*)
6	**5f** (Ar = 3-Br-C_6H_4; R = H)	–20	16	90 (*S*)
7	**5g** (Ar = 4-Cl-C_6H_4; R = H)	–20	16	91 (*S*)
8	**5h** (Ar = 4-CF_3-C_6H_4; R = H)	r.t.	24	87 (*S*)
9	**5i** (Ar = 3-CF_3-C_6H_4; R = H)	–20	16	87 (*S*)
10	**5j** (Ar = C_6H_5; R = Me)	r.t.	24	94 (*S*)

[a] The reactions were conducted with **5** : $HSiCl_3$: $[PdCl(\eta^3\text{-}C_3H_5)]_2$: **3k** = 1 : 1.2 : 0.00125 : 0.0025, solvent free. [b] Complete conversions were obtained in all cases; ee values were determined by GC analysis with chiral column.

obtained from a L : Pd ratio of 4 : 1 was found to be an inactive catalyst (entry 4). Although similar L : Pd ratio effects were reported by Johannsen and co-workers for the same reaction, they found that the reaction became more problematic when approaching a L : Pd ratio of 1 : 1 or less than 1 : 1.[4b]

In addition to the L : Pd ratio, other parameters such as metal precursor, solvent, reaction temperature and substrate/catalyst (S/C) ratio were also studied. It was found that catalyst prepared from the neutral complex $[Pd(acac)_2]$ was less selective than that from $[PdCl(C_3H_5)]_2$ under otherwise identical conditions (entry 5). When the reaction was carried out in CH_2Cl_2, slightly low enantioselectivity was observed (entry 6). Similar results with excess amount of $HSiCl_3$ were observed (entry 7). Notably, this reaction was found to be highly sensitive to the reaction temperature. The asymmetric hydrosilylation of **5a** proceeded very fast at room temperature, but rather low enantioselectivity was observed (entry 8). Most importantly, excellent reactivity and enantioselectivity were achieved at low temperature even under much lower catalyst loading (entries 2, 9 and 10), affording a TOF number of at least 3000 h^{-1}. When the S/C ratio was further increased to 10 000, the reaction still proceeded smoothly to give complete conversion to the product upon prolonged reaction time, but at the expense of reduced enantioselectivity (entry 12). This result clearly demonstrated that the catalyst obtained from the bulky phosphoramidite **3k** with a L : Pd ratio of 1 : 1 was highly stable.

To understand the high efficiency of the bulky ligand, we then investigated the coordination of the phosphoramidite with palladium precursors by using ^{31}P NMR spectroscopy. It was found that the addition of one equivalent of **3f** to $[PdCl(\eta^3\text{-}C_3H_5)]_2$ led to the complete disappearance of the ^{31}P NMR signal of the free ligand at 141.4 ppm and the appearance of a single peak at 143.2 ppm. If another equivalent of **3f** was added, the peak at 143.2 ppm was retained and another peak at 141.5 ppm appeared, which was temporarily assigned to the excess free ligand. In contrast, the complex obtained from the less sterically bulky ligand **3a** provided much different ^{31}P NMR spectra. In the case of a **3a** : Pd ratio of 1 : 1, two peaks at 145.3 and 144.6 ppm were observed. When the L : Pd ratio changed from 1 : 1 to 2 : 1, completely different peaks at 159.4, 144.6 and 117.0 ppm were presented. These results suggest that introducing aryl groups into the 3,3′-positions of the binaphthyl backbone of the ligand can influence the coordination mode of palladium with the phosphoramidite. The ability to provide a vacant coordination site for the olefin substrate during the catalytic reaction by the bulky ligand **3f** might be responsible for its excellent catalytic performance. However, further study is still required to confirm if the catalyst precursor contains only one **3f** ligand per Pd ion.[9,12]

To further demonstrate the efficacy of the bulky ligands, we decided to investigate the applications of the Pd complex of **3k** in the asymmetric hydrosilylation of a variety of styrene derivatives (Table 3). In general, most of the substituted styrenes were efficiently hydrosilylated with good enantioselectivities and conversions within 16 h at –20 °C. The hydrosilylation of a 2-substituted styrene derivative resulted in the lowest enantioselectivity (entry 2). High enantioselectivities were observed for all the 3- and 4-substituted substrates (entries 3–9). It was noted that the positioning of the electron-withdrawing CF_3 group on the aromatic ring showed significant effect on the reactivity. The hydrosilylation of 4-trifluoromethylstyrene **5h** could be completed at room temperature in 24 h, while the reaction with 3-trifluoromethylstyrene **5i** proceeded fast at –20 °C. In addition, β-methyl-substituted styrene **5j** is another exception, with a prolonged reaction time at room temperature (entry 10).

Conclusions

In summary, we have developed a new type of bulky monodentate phosphoramidite ligand prepared from chiral 3,3′-diaryl substituted BINOL derivatives and achiral or dendritic amines. These bulky ligands were successfully applied in the Pd-catalyzed asymmetric hydrosilylation of styrenes, providing the chiral silanes with excellent activity and productivity, which are much higher than those obtained from all the reported phosphoramidite ligands and most of the other monodentate phosphorus ligands.[2–5] Oxidation of these chiral silanes with hydrogen peroxide gave the corresponding chiral secondary alcohols in good to high

enantioselectivities (up to 96% ee). These bulky ligands are modular, allowing fine-tuning of their steric and electronic characteristics, and further applications to other asymmetric reactions are under way in our laboratory.

Experimental

General

Unless otherwise noted, all experiments were carried out under an inert atmosphere of dry nitrogen by using standard Schlenk-type techniques, or performed in a nitrogen-filled glovebox. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra were recorded on a Bruker Model Avance DMX 300 or 400 Spectrometer (^{1}H 300 MHz, ^{13}C 75 MHz and ^{31}P 121 MHz, respectively). Chemical shifts (δ) are given in ppm and are referenced to residual solvent or TMS peaks (^{1}H and ^{13}C NMR), or to an external standard (85% H_3PO_4, ^{31}P NMR). MALDI-TOF mass spectra were obtained on a BIFLEX III instrument with α-cyano-4-hydroxycinnamic acid (CCA) as the matrix. High resolution mass spectra [HRMS (ESI)] were obtained on a Bruker Moder Apex-Qe-FTMS. Optical rotations were measured with PerkinElmer 341 polarimeter. All enantiomeric excess values were obtained from GC analysis with a Chrompack CHIR-L-VAL column. All solvents were dried using standard published methods, and were distilled under a nitrogen atmosphere before use. All other chemicals were used as received from Aldrich or Acros without further purification. Chiral 1,1-binaphthol derivatives **4**[10] and chiral dendritic ligands **3b**–**3c**[8] were synthesized according to the published methods.

General procedure for the preparation of chiral bulky phosphoramidite ligands 3d–3k

Under a nitrogen atmosphere, a drop of NMP was added to a warm solution (60 °C) of (*S*)-**4** and trichlorophosphine (10 mL). After refluxing for 5 h, azeotropic distillation of the residue with anhydrous toluene (5 mL) gave the intermediate chlorophosphite in quantitative yield.[11] Then, to a solution of dibenzylamine or dendritic amine (0.35 mmol) and Et_3N (0.1 mL, 0.7 mmol) in THF (10 mL) at 0 °C was added dropwise a solution of the above chlorophosphite (0.35 mmol) in THF (20 mL). The resulting mixture was stirred at 50 °C overnight. The precipitate of Et_3NHCl was filtered over a pad of celite. After the solvent was removed under reduced pressure, the residue was purified by flash column chromatography to give the product **3** as a white foam.

3d. 67% yield; $[\alpha]_D^{20}$ = +255.2 (*c* 0.2, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.08 (s, 3H), 2.69 (s, 3H), 3.50 (t, J = 12.5 Hz, 2H), 4.21 (AB system, J = 7.9 Hz, 1H), 4.25 (AB system, J = 7.9 Hz, 1H), 7.04–7.13 (m, 2H), 7.17–7.33 (m, 14H), 7.58 (s, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.80 (d, J = 8.0 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.4, 17.7, 48.1, 48.4, 122.1, 124.1, 124.2, 124.4, 124.8, 124.9, 125.1, 127.0, 127.0, 127.2, 127.3, 127.5, 128.3, 129.1, 129.4, 129.7, 130.2, 130.5, 131.3, 131.4, 131.7, 137.5, 148.4, 149.0, 149.1. ^{31}P NMR (122 MHz, $CDCl_3$): δ = 139.8. HRMS (ESI) for $C_{36}H_{30}O_2NP$, $[M + H]^+$: calcd. 540.20924, found 540.20894.

3e. 58% yield; $[\alpha]_D^{20}$ = +139.0 (*c* 0.1, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.21–3.33 (m, 2H), 3.29–3.32 (m, 2H), 4.49 (s, 8H), 4.81 (s, 16H), 5.93 (d, J = 1.8 Hz, 4H), 6.15 (s, 2H), 6.42 (d, J = 2.0 Hz, 4H), 6.48 (d, J = 2.0 Hz, 8H), 6.94 (t, J = 7.3 Hz, 1H), 7.15–7.453 (m, 51H), 7.61 (d, J = 7.6 Hz, 2H), 7.77 (d, J = 7.3 Hz, 2H), 7.86 (d, J = 8.5 Hz, 2H), 7.91 (s, 1H), 7.99 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 50.8, 51.0, 70.0, 70.1, 100.8, 101.8, 106.7, 107.8, 124.3, 125.2, 125.5, 126.3, 127.0, 127.2, 127.3, 127.7, 127.8, 128.1, 128.2, 128.4, 128.7, 130.3, 130.3, 131.1, 131.4, 132.5, 132.7, 134.4, 135.1, 137.0, 137.3, 137.9, 138.2, 139.4, 141.3, 141.3, 147.3, 147.3, 159.5, 160.2. ^{31}P NMR (122 MHz, $CDCl_3$): δ = 143.6. MS (MALDI-TOF): m/z for $C_{130}H_{106}O_{14}NP$: calcd 1937.2. found 1934.7.

3f. 51% yield; $[\alpha]_D^{20}$ = +312.7 (*c* 0.1, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.22 (AB system, J = 7.58 Hz, 1H), 3.26 (AB system, J = 7.58 Hz, 1H), 3.74 (AB system, J = 8.57 Hz, 1H), 3.78 (AB system, J = 8.57 Hz, 1H), 6.63 (d, J = 6.4 Hz, 4H), 6.97–7.04 (m, 6H), 7.25–7.32 (m, 2H), 7.38–7.54 (m, 10H), 7.75 (dd, J_1 = 7.6 Hz, J_2 = 0.7 Hz, 2H), 7.81 (dd, J_1 = 7.9 Hz, J_2 = 0.8 Hz, 2H), 7.91 (d, J = 8.0 Hz, 1H), 7.98 (d, J = 7.9 Hz, 2H), 8.05 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 49.4, 49.7, 124.1, 125.3, 125.6, 126.4, 126.5, 126.9, 127.4, 127.4, 127.9, 128.0, 128.3, 128.3, 128.5, 128.7, 128.8, 130.5, 130.7, 130.9, 131.1, 131.6, 132.7, 134.8, 135.6, 137.8, 137.8, 138.4, 138.7, 147.3, 147.6, 147.7. ^{31}P NMR (122 MHz, $CDCl_3$): δ = 141.4. HRMS (ESI) for $C_{46}H_{34}O_2NP$, $[M + H]^+$: calcd. 664.24054, found 664.24086.

3g. 47% yield; $[\alpha]_D^{20}$ = +128.0 (*c* 0.1, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.12 (AB system, J = 8.00 Hz, 1H), 3.16 (AB system, J = 8.00 Hz, 1H), 3.74 (AB system, J = 8.59 Hz, 1H), 3.78 (AB system, J = 8.59 Hz, 1H), 6.48 (d, J = 7.5 Hz, 4H), 6.64 (t, J = 7.5 Hz, 4H), 6.87 (t, J = 7.3 Hz, 2H), 7.29–7.35 (m, 2H), 7.40–7.50 (m, 4H), 7.52–7.58 (m, 4H), 7.89–8.04 (m, 10H), 8.08 (s, 1H), 8.18 (s, 1H), 8.23 (s, 1H), 8.26 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 48.7, 48.9, 123.9, 125.1, 125.4, 126.2, 126.3, 126.3, 126.6, 127.1, 127.4, 127.8, 127.8, 127.9, 128.2, 128.4, 128.4, 128.6, 128.7, 128.7, 128.8, 129.2, 130.8, 131.1, 131.4, 132.5, 132.7, 132.8, 132.9, 133.0, 133.5, 133.8, 134.5, 135.7, 136.0, 137.0, 137.0, 147.1, 147.4, 147.5. ^{31}P NMR (122 MHz, $CDCl_3$): δ = 141.3. HRMS (ESI) for $C_{54}H_{38}O_2NP$, $[M + H]^+$: calcd. 764.27184, found 764.27158.

3h. 67% yield; $[\alpha]_D^{20}$ = +63.4 (*c* 0.2, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.93–3.05 (m, 2H), 3.54 (AB system, J = 8.89 Hz, 1H), 3.58 (AB system, J = 8.89 Hz, 1H), 5.97 (d, J = 7.4 Hz, 1H), 6.02 (d, J = 7.5 Hz, 2H), 6.12 (d, J = 7.5 Hz, 1H), 6.30 (t, J = 7.6 Hz, 1H), 6.38 (t, J = 7.6 Hz, 3H), 6.68 (quart, J = 7.2 Hz, 2H), 7.42–8.16 (m, 24H), 8.75–8.89 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 48.8, 49.1, 122.6, 122.7, 122.9, 125.1, 125.5, 126.3, 126.4, 126.5, 126.7, 126.9, 127.0, 127.4, 127.6, 127.9, 128.4, 128.6, 128.6, 129.0, 130.3, 130.8, 131.5, 131.6, 133.1, 134.3, 136.9, 136.9, 148.2, 148.4, 148.6. ^{31}P NMR (122 MHz, $CDCl_3$): δ = 141.0. HRMS (ESI) for $C_{62}H_{42}O_2NP$, $[M + H]^+$: calcd. 864.30314, found 864.30467.

3i. 78% yield; $[\alpha]_D^{20}$ = −74.4 (*c* 0.5, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.50–3.55 (m, 2H), 4.17 (AB system, J = 8.00 Hz, 1H), 4.20 (AB system, J = 8.00 Hz, 1H), 5.73 (s, 1H), 6.31 (s, 1H), 6.66–6.69 (m, 2H), 7.05 (d, J = 7.9 Hz, 2H), 7.13–7.47 (m, 34H), 7.65 (d, J = 8.1 Hz, 1H), 7.74 (d, J = 8.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 51.1, 52.2, 123.0, 124.8, 126.0, 126.1, 126.6, 126.6, 127.1, 127.3, 128.5, 128.6, 128.6, 128.9, 129.0,

129.1, 129.5, 130.0, 130.4, 130.4, 130.5, 131.0, 132.2, 135.8, 136.7, 138.0, 143.2, 143.3, 143.6, 144.4, 148.3, 148.8, 148.9. ^{31}P NMR (122 MHz, $CDCl_3$): δ = 141.8. HRMS (ESI) for $C_{60}H_{46}O_2NP$, $[M + H]^+$: calcd. 844.33444, found 844.33416.

3j. 45% yield; $[\alpha]_D^{20}$ = +125.7 (*c* 0.2, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.16 (AB system, J = 9.24 Hz, 1H), 3.20 (AB system, J = 9.24 Hz, 1H), 3.77 (AB system, J = 8.93 Hz, 1H), 3.81 (AB system, J = 8.93 Hz, 1H), 6.66 (d, J = 7.0 Hz, 4H), 7.02–7.14 (m, 6H), 7.35–7.42 (m, 4H), 7.42–7.49 (m, 1H), 7.51–7.58 (m, 1H), 7.89 (s, 1H), 7.96–7.99 (m, 3H), 8.05 (d, J = 8.2 Hz, 1H), 8.13 (s, 3H), 8.30 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 48.3, 48.6, 121.4, 121.7, 123.8, 125.2, 125.7, 126.0, 126.9, 127.0, 127.2, 128.2, 128.6, 128.7, 130.0, 130.3, 130.5, 131.1, 131.2, 131.4, 131.5, 131.7, 131.9, 132.9, 133.1, 136.2, 136.3, 140.0, 140.2, 146.0, 146.3, 146.4. ^{31}P NMR (122 MHz, $CDCl_3$): δ = 142.2. HRMS (ESI) for $C_{50}H_{30}O_2F_{12}NP$, $[M + H]^+$: calcd. 936.19008, found 936.18996.

3k. 78% yield; $[\alpha]_D^{20}$ = +224 (*c* 0.1, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.25 (AB system, J = 7.89 Hz, 1H), 3.30 (AB system, J = 7.89 Hz, 1H), 3.82 (AB system, J = 8.64 Hz, 1H), 3.82 (AB system, J = 8.64 Hz, 1H), 3.90 (s, 3H), 3.92 (s, 3H), 6.68 (dd, J_1 = 7.6 Hz, J_2 = 1.5 Hz, 4H), 7.00–7.06 (m, 10H), 7.21–7.44 (m, 6H), 7.72 (t, J = 9.0 Hz, 4H), 7.88 (d, J = 8.2 Hz, 1H), 7.92–7.96 (m, 2H), 8.02 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 48.8, 49.1, 55.3, 55.4, 113.5, 113.9, 123.7, 124.9, 125.2, 125.8, 125.9, 126.6, 127.0, 127.9, 128.1, 128.4, 130.0, 130.0, 130.4, 130.7, 130.9, 131.1, 131.3, 131.4, 131.4, 132.1, 134.1, 134.8, 137.4, 137.4, 147.0, 147.3, 147.4, 159.2. ^{31}P NMR (122 MHz, $CDCl_3$): δ = 140.6. HRMS (ESI) for $C_{48}H_{38}O_2NP$, $[M + H]^+$: calcd. 724.26167, found 724.26153.

General procedure for the asymmetric hydrosilylation of alkenes

A dried Schlenk tube containing a stirring bar was charged with allylpalladium chloride dimer (1.5 mg, 0.0041 mmol), the corresponding phosphoramidite ligand **3** (0.0082 mmol) and styrene **5a** (341 mg, 3.28 mmol). After 20 min stirring at room temperature, trichlorosilane (0.66 mL, 6.56 mmol) was added at –20 °C. Conversion of the resulting silane was determined by ^{1}H NMR spectroscopy. The product was purified by distillation to yield 705 mg (90%) of **6a**.

General procedure for the oxidation of silanes

The silane **6a** (177 mg, 0.741 mmol), KF (258 mg, 4.446 mmol), $KHCO_3$ (445 mg, 4.446 mmol), MeOH (15 mL) and THF (15 mL) were transferred to a 50 mL flask. H_2O_2 (0.89 mL, 30%) was added, and the mixture was stirred for 16 h before quenching with 4 mL saturated $Na_2S_2O_3$ solution. After stirring for an additional 1 h, the reaction mixture was extracted with Et_2O (3 × 30 mL), and the combined organic phases were dried over $MgSO_4$, filtered and concentrated in a vacuum. The crude residue was purified by flash column chromatography on silica gel (pentane–ethyl acetate, 90 : 10), affording the chiral alcohol **7a** (76 mg, 99%) with 96% ee (*S*).

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