Pergamon

Tetrahedron: *Asymmetry* 13 (2002) 1449–1456

TETRAHEDRON: *ASYMMETRY*

Chiral perfluorous analogues of MOP. Synthesis and applications in catalysis

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Received 8 July 2002; accepted 11 July 2002

Abstract—Chiral perfluoroalkyl- and tris(perfluoroalkyl)silyl-derivatized analogues of the ligand MOP, having a fluorine content of 55.65 and 56.88%, respectively, have been prepared starting from optically active 6,6′-dibromo-2,2′-diethoxy-1,1′-binaphthyl. These ligands have been used in the palladium-catalyzed asymmetric substitution of 1,3-diphenylprop-2-enyl acetate with dimethyl malonate affording chiral products with e.e. of up to 37%.

1. Introduction

There is growing interest in the use of non-standard solvents such as fluorinated materials in organometallic reactions, because these new media can offer the possibility of cleaner technology for the chemical industry, and can also promote a change in the selectivity of a reaction. In the case of catalytic reactions in a fluorous-organic biphase (FBS), the fluorous catalyst is soluble in the fluorous phase, while the reactants and products are preferentially soluble in the organic phase, allowing easy separation at the end of the reaction.[1]

However, despite the growing number of articles on the chemistry of fluorous materials, only a few chiral perfluorous ligands have been prepared and applied in organometallic catalysis. Literature examples include the epoxidation of alkenes using perfluorus chiral salen manganese complexes,[2] asymmetric alkylation of aldehydes with perfluorous BINOL titanium alkoxides,[3] hydrogen transfer reaction using iridium complexes of perfluorous diimines and diamines,[4] hydrolytic kinetic resolution of terminal epoxides in the presence of fluorous chiral Co(salen) complexes,[5] and more recently hydrogenation[6] and Heck reactions[7] using perfluorous chiral BINAP complexes with rhodium and palladium, respectively. Although chiral phosphorous-based ligands are extensively used in catalytic reactions, the synthesis of perfluorinated analogues of such ligands and their applications in asymmetric organometallic catalysis are scarce.[6–8]

We have recently described the synthesis of a chiral perfluorous analogue of the ligand 2-(diphenylphosphino)-2′-alkoxy-1,1′-binaphthyl (MOP)[9] bearing three fluorous tails, and its application as a ligand in the palladium-catalyzed asymmetric allylic alkylation of 1,3-diphenylprop-2-enyl acetate, affording chiral products with up to 87% e.e.[10] The recent results concerning the synthesis of perfluorous analogues of BINAP prompted us to investigate the synthesis of two new analogues of MOP, bearing perfluorinated alkyl chains on the naphthyl ring, and to conduct a preliminary investigation into their applications as ligands in asymmetric catalysis. The results are described herein.

2. Results and discussion

We prepared two perfluorous analogues of MOP, **9** and **16**, bearing perfluoroalkyl- and tris(perfluoroalkyl)silyl chains on the naphthyl ring, respectively. The chiral (*R*)-Rf-MOP **9** was prepared by the way shown in Scheme 1.

(*R*)-6,6′-Dibromo-2,2′-diethoxy-1,1′-binaphthyl, **2** was prepared in 73% yield from (*R*)-2,2′-diethoxy-1,1′-binaphthyl **1** by bromination with bromine in CH_2Cl_2,

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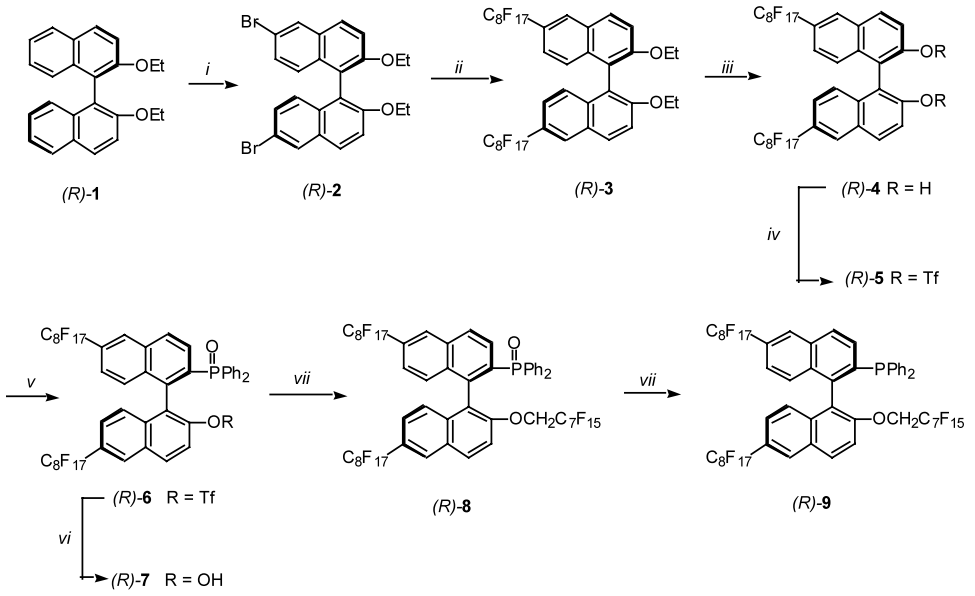
PII: S0957-4166(02)00375-0

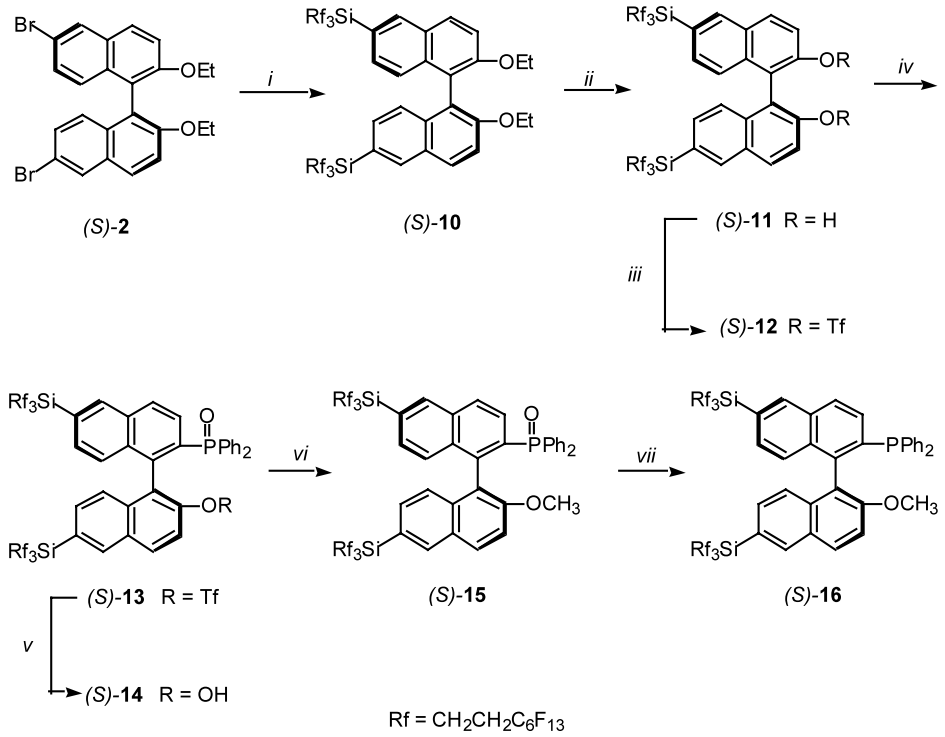


Scheme 1. *Reagents and conditions*: (i) Br_2, CH_2Cl_2;[11] (ii) $C_8F_{17}I$, Cu, DMSO, 120°C; (iii) BBr_3, CH_2Cl_2, 0°C; (iv) Tf_2O, C_5H_5N, $CH_2Cl_2/C_6H_5CF_3$, 0°C; (v) $HPO(C_6H_5)_2$, $EtN(i\text{-}Pr)_2$, $Pd(OAc)_2$, dppb, DMSO; (vi) LiOH, H_2O, THF; (vii) $C_7F_{15}CH_2OSO_2C_4F_9$, Cs_2CO_3, DMF, 100°C; (viii) $HSiCl_3$, Et_3N, toluene.

according to the method of Dong et al.[11] The copper-mediated perfluoroalkylation of dibromonaphthyl derivative **2** with perfluorooctyl iodide was performed in DMSO at 120°C to give (*R*)-6,6′-diperfluorooctyl-2,2′-diethoxy-1,1′-binaphthyl **3** in 76% yield after column chromatography. Subsequent cleavage of the ethoxy group of perfluoro derivative **3** with BBr_3 in CH_2Cl_2 afforded the perfluoroalkylated (*R*)-binaphthol **4** in 85% yield. It is noteworthy that the direct copper-mediated perfluoroalkylation of (*R*)-6,6′-dibromo-1,1′-naphthyl-2,2′-diol, obtained by bromination of (*R*)-binaphthol,[12] gave the expected compound **4**, but in low chemical yield (<35%). The perfluoroalkylated binaphthol **4** was treated with triflic anhydride in the presence of pyridine in a mixture of $CH_2Cl_2/C_5H_5CF_3$ to give the perfluorous bistriflate **5** in 86% yield. The monophosphinylation of compound **5** was effected by condensation with diphenylphosphonic acid in DMSO at 100°C in the presence of a catalytic amount of $Pd(OAc)_2$, dppb, and $EtN(i\text{-}Pr)_2$,[13] giving the perfluorophosphine oxide **6** in 61% yield. Hydrolysis of the remaining triflate group with aqueous lithium hydroxide in a THF–water mixture led to (*R*)-2-diphenylphosphinyl-2′-hydroxy-6,6′-diperfluorooctyl-1,1′-binaphthyl **7** in 85% yield. Another fluorous ponytail was introduced by reaction of the free hydroxy group of compound **7** with 1*H*,1*H*-perfluorooctyl-1-ol perfluorobutanesulfonate in DMF at 100°C in the presence of Cs_2CO_3. Phosphine oxide **8** was obtained in 88% yield after flash-chromatography. Reduction of this phosphine oxide **8** with $HSiCl_3$ in refluxing toluene afforded enantiopure perfluorous (*R*)-Rf-MOP **9**, having 55.65% fluorine content, in 90% yield.

The chiral (*S*)-Rf_3Si-MOP **9** was prepared by the way shown in Scheme 2. Lithiation of (*S*)-6,6′-dibromo-2,2′-diethoxy-1,1′-binaphthyl **2** with *n*-BuLi at −78°C, followed by reaction with $(C_6F_{13}CH_2CH_2)_3SiBr$,[14] afforded (*S*)-6,6′-bis[tris(1*H*,1*H*,2*H*,2*H*-perfluorooctyl) silyl]-2,2′-diethoxy-1,1′-binaphthyl **10** in 34% yield. The ethoxy group of compound **10** was removed with BBr_3 in CH_2Cl_2 to give (*S*)-6,6′-bis[tris(1*H*,1*H*,2*H*,2*H*-perfluoro octyl)silyl]-1,1′-binaphthyl-2,2′-diol **11** in 85% yield. Treatment of the perfluoroalkylated binaphthol **11** with triflic anhydride in the presence of pyridine in CH_2Cl_2 gave the chiral perfluorous bistriflate **12** in 87% yield. Palladium-catalyzed condensation of compound **12** with diphenylphosphonic acid in DMSO at 100°C in the presence of $Pd(OAc)_2$, dppb, and $EtN(i\text{-}Pr)_2$,[13] then gave the chiral perfluorophosphine oxide **13** in 70% yield. The remaining triflate group was hydrolyzed with aqueous lithium hydroxide in a THF–water mixture to afford (*S*)-6,6′-bis[tris(tris(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)silyl]-2-(diphenylphosphinyl)-2′-hydroxy-1,1′-binaphthyl **14** in 81% yield. Reaction of hydroxyphosphine **14** with CH_3I in acetone in the presence of potassium carbonate gave (*S*)-6,6′-bis[tris(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)silyl]-2-diphenylphosphinyl-2′-methoxy-1,1′-binaphthyl **15** in 84% yield. Finally, reduction of this phosphine oxide **15** with $HSiCl_3$ in boiling toluene afforded pure perfluorous (*S*)-Rf_3Si–MOP **16**, having 56.88% fluorine content, in 91% yield.

Palladium complexes of enantiopure 2-(diphenylphosphino)-2′-alkoxy-1,1′-binaphthyls (MOPs) catalyze several asymmetric transformations,[9] and we have recently shown that a light fluorous MOP, with a fluorine content of 52.4% was an efficient ligand in the alkylation of 1,3-diphenylprop-2-enyl acetate, with e.e. of up to 87% being obtained when methyl malonate was used as the nucleophile.[10] We decided therefore to investigate the performance of the new fluorous MOPs (*R*)-**9** and (*S*)-**16** as ligand in the same reaction.

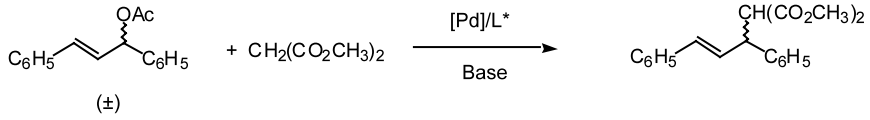


Scheme 2. *Reagents and conditions*: (i) $C_8F_{17}I$, Cu, DMSO, 120°C; (ii) BBr_3, CH_2Cl_2, 0°C; (iii) Tf_2O, C_5H_5N, $CH_2Cl_2/C_6H_5CF_3$, 0°C; (iv) $HPO(C_6H_5)_2$, $EtN(i\text{-}Pr)_2$, $Pd(OAc)_2$, dppb, DMSO; (v) LiOH, H_2O, THF; (vi) $C_7F_{15}CH_2OSO_2C_4F_9$, Cs_2CO_3, DMF, 100°C; (vii) $HSiCl_3$, Et_3N, toluene.

We determine first the partition coefficients for these two new ligands between FC-72 and two organic solvents: THF and toluene. For ligand (*R*)-**9**, the values are 0.25 and 0.69, and for ligand (*S*)-**16** 0.69 and 4.29, respectively. As expected, these new ligands show a certain affinity for THF and toluene, which is probably due to their relatively low fluorine content, and also to the aromatic backbone. However, we used these ligands in palladium-catalyzed allylic alkylation, expecting that they could be re-used by the application of light fluorous techniques.[15]

The preliminary results obtained are summarized in Table 1. The reaction of 1,3-diphenylprop-2-enyl ace-

Table 1. Asymmetric allylic alkylation of 1,3-diphenylprop-2-enyl acetate with dimethyl malonate



Entry	Ligand	Base	Solvent	*T* (°C)	Time (h)	Conversion (%)[a]	E.e. (%) [a](Config.)[b]
1	(*R*)-**9**	BSA + KOAc	BTF[c]	50	27	12	14 (*R*)
2		BSA + KOAc	THF[d]	50	20	0	–
3		NaH	THF[d]	25	20	32	28 (*R*)
4		NaH	THF[c]	50	3	100	32 (*R*)
5			THF[e]	50	16	20	37 (*R*)
6	(*S*)-**16**	BSA + KOAc	BTF[d]	50	16	11	26 (*R*)
7		BSA + KOAc	BTF[c]	50	64	40	20 (*R*)
8		NaH	THF	25	1	20	–
9		NaH	THF[c]	25	1	57	5 (*R*)
10		NaH	THF	50	24	100	7 (*R*)
11		NaH	BTF[c]	25	24	40	24 (*R*)
12		NaH	BTF	50	24	76	22 (*R*)

[a] Determined by HPLC analysis (column Chiralpak AD 0.46×25 cm).
[b] Determined by comparison with an authentic sample.
[c] The complex was prepared at 50°C.
[d] The complex was prepared at 25°C.
[e] Recycling of the catalyst.

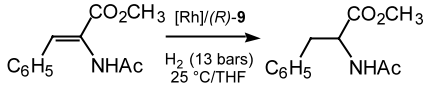
tate with dimethyl malonate using MOP (*R*)-**9** (8 mol%) and $[Pd(C_3H_5)Cl]_2$ (2 mol%) was performed in the presence of bis(trimethylsilyl)acetamide (BSA, 2 equiv.) and potassium acetate (0.1 equiv.) in benzotrifluoride at 50°C for 27 h; however the conversion was only 12%, and the e.e. was 14% (Table 1, entry 1). When the reaction was conducted in THF under exactly the same conditions, no conversion was observed at all (Table 1, entry 2). Using sodiated dimethyl malonate (formed from dimethyl malonate and NaH in THF) as the nucleophile, 32% conversion was obtained at room temperature, with an enantioselectivity of 28% (Table 1, entry 3); complete conversion was obtained after 3 h when the reaction was performed at 50°C, the enantioselectivity being 32% (Table 1, entry 4). In this latter case, recycling of the catalyst was attempted. The solution was cooled and extracted with fluorous solvent FC-72 (2×3 mL); evaporation of the solvent gave a residue that was used in another alkylation reaction giving conversion of only 24%, but with enantioselectivity of 37% (Table 1, entry 5). A ^{31}P NMR spectrum of the organic phase showed a broad signal at δ 28.3 ppm corresponding to the palladium complex, indicating that a large quantity of perfluorous complex had leached into the organic phase, due probably to the low fluorine content of the phosphine. It is to be noted that the use of D-100/toluene as the solvent gave no reaction at all.

We then used ligand (*S*)-**16** in this alkylation reaction. Again low conversion was obtained using the methyl malonate in the presence of BSA and KOAc in benzotrifluoride, even at 50°C, with enantioselectivity up to 26% (Table 1, entries 6 and 7). When NaH was used as the base, higher conversions were obtained in THF as the solvent; however, the conversion was quantitative only when the reaction was performed at 50°C, as well as the formation of the complex, the enantioselectivity being unfortunately very low (e.e. up to 7%) (Table 1, entry 10). The same trends were observed when benzotrifluoride was used as the solvent, enantioselectivity of 24% being obtained (Table 1, entries 11 and 12).

It is of note that the two ligands, although they are 'enantiomers' gave the same configuration for the alkylated product. One reason could be the bulkiness of the $-Si(CH_2CH_2C_6F_{13})_3$ residue, which could change the structure of the intermediate π-allyl complex.

The perfluorous ligand (*R*)-**9** was also used in two other reactions. Reduction of α-acetamidocinnamic acid methyl ester was performed in THF at room temperature under hydrogen (13 bar pressure) using the rhodium complex prepared from $[Rh(COD)_2]BF_4$ (1% mol) and (*R*)-**9** (2.2% mol) (Eq. (1)); complete conversion was observed after 40 h, the enantioselectivity being 14%. Complete conversion was also obtained using a ratio [Rh]/[(*R*)-**9**] = 1/1.2, with an enantioselectivity of 14%.

Hydroformylation of styrene was also performed in toluene at 80°C under 80 bar pressure ($H_2/CO = 1/1$), using the complex obtained by mixing $[Rh(acac)(CO)_2]$ (1% mol) and (*R*)-**9** (3% mol). (Eq. (2)). After 24 h, complete conversion was observed, with the formation of the *iso* isomer as the sole product with an enantioselectivity of 5%.



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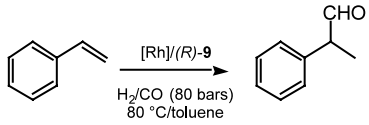

(2)

3. Conclusion

In conclusion, we have prepared two perfluorous analogues of MOP, bearing three perfluoroalkylchains for one ligand (two of them being on the naphthyl ring) and two (trisperfluoroalkyl)silyl chain for the second. Palladium-catalyzed alkylation of 1,3-diphenylprop-2-enyl acetate with dimethyl malonate occurred, although with low enantioselectivity. Work is actually in progress in order to understand the reasons for this lower enantioselectivity and to prepare other perfluorous MOP analogues.

4. Experimental

4.1. General

Solvents were purified by standard methods and dried if necessary. All commercially available reagents were used as received. All reactions were monitored by TLC (TLC plates GF_{254} Merck); detection was effected by UV absorbance. Reactions involving organometallic catalysis were carried out in Schlenk tube under an inert atmosphere. Column chromatography was performed on silica gel 60 (230–240 mesh, Merck). Optical rotations were recorded using a Perkin–Elmer 241 polarimeter. NMR spectra were recorded with Bruker AMX 300 spectrometer and referenced as following: ^1H (300 MHz), internal $SiMe_4$ at δ 0.00 ppm, ^{13}C (75 MHz), internal $CDCl_3$ at δ 77.23 ppm, ^{19}F (282 MHz), external $CFCl_3$ at δ 0.00 ppm, and ^{31}P (121 MHz), external 85% H_3PO_4 at δ 0.00 ppm.

The following compounds were prepared according to literature procedure: (*S*)- and (*R*)-6,6′-dibromo-2,2′-diethoxy-1,1′-binaphthyl,[11] bromotris(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)silane,[14a] and 1*H*,1*H*-perfluorooctyl-1-ol perfluorobutanesulfonate $C_7F_{15}CH_2OSO_2C_4F_9$.[16]

4.2. (*R*)-2,2′-Diethoxy-6,6′-diperfluorooctyl-1,1′-binaphthyl, 3

A mixture of (*R*)-6,6′-dibromo-2,2′-diethoxybinaphthyl **2**[11] (1.8 g, 3.56 mmol), $C_8F_{17}I$ (4.86 g, 8.9 mmol), and activated copper powder (1.36 g, 21.4 mmol) in anhydrous DMSO (30 mL) was heated to 120°C for 60 h under nitrogen. The mixture was cooled to 0°C, and

hydrolyzed with water (10 mL). The solid was filtered and washed with diethyl ether. The aqueous phase was extracted with diethyl ether (3×20 mL) and the organic phase was dried over Na_2SO_4. Evaporation of the solvent gave a residue that was purified by flash-chromatography on silica gel, using petroleum ether/ethyl acetate (20:1) as the eluent, to give the perfluoro derivative **3** (3.2 g, 76%). White solid; mp 54–55°C; $R_f=0.45$ (petroleum ether/ethyl acetate 20:1); $[\alpha]_D^{25}=+29.5$ (*c* 0.2, Et_2O). ^1H NMR ($CDCl_3$): δ 1.06 (t, $J=7.0$ Hz, 6H, CH_3), 4.10 (m, 4H, CH_2), 7.21 (d, $J=9.0$ Hz, 2H, Ar-H), 7.34 (dd, $J=9.0$, 2.0 Hz, 2H, Ar-H), 7.51 (d, $J=9.0$ Hz, 2H, Ar-H), 8.05 (d, $J=9.0$ Hz, 2H, Ar-H), 8.14 (d, $J=2.0$ Hz, 2H, Ar-H); ^{13}C NMR ($CDCl_3$): δ 15.1, 65.2, 116.5, 119.7, 123.3, 126.3, 128.2, 131.0, 135.8, 156.4; ^{19}F NMR ($CDCl_3$): δ −126.9 (s, 4F, CF_2), −123.4 (s, 4F, CF_2), −122.6 (s, 4F, CF_2), −122.2 (s, 4F, CF_2), −121.9 (bs, 8F, CF_2), −110.60 (t, $^3J_{F,F}=13.8$ Hz, 4F, CF_2Ar), −81.6 (t, $^3J_{F,F}=9.0$ Hz, 6F, CF_3). Anal. calcd for $C_{40}H_{20}O_2F_{34}$ (1178.53): C, 40.74; H, 1.71; found: C, 40.40; H, 1.65%.

4.3. (*S*)-6,6′-Bis[tris(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)silyl]-2,2′-diethoxy-1,1′-binaphthyl, 10

To a solution of (*S*)-6,6′-dibromo-2,2′-diethoxy-1,1′-binaphthyl **2** (1 g, 2 mmol) in THF (10 mL) under argon was slowly added at −78°C a 1.7 M solution of *n*-BuLi in hexane (4 mL, 6.8 mmol). After stirring for 1 h at −78°C, the solution was added on bromotris(1*H*,1*H*,2*H*,2*H*-perfluorooctyl) silane (5.8 g, 5.05 mmol) dissolved in diethyl ether (40 mL). After stirring for 1.5 h, a saturated aqueous solution of NH_4Cl (40 mL) was added, the solvent was evaporated and CH_2Cl_2 (80 mL) was added. The organic phase was extracted with perfluorosolvent FC-72 (3×20 mL), and the perfluorous phases were dried over sodium sulfate. Evaporation of the solvent gave a residue that was purified by flash-chromatography on silica gel, using petroleum ether/ethyl acetate (20:1) as the eluent, to give compound **10** (1.46 g, 34%). Oil; $R_f=0.35$ (petroleum ether/ethyl acetate 20:1); $[\alpha]_D^{25}=-17.0$ (*c* 1, $C_6H_5CF_3$); ^1H NMR ($CDCl_3$): δ 1.04 (t, $J=7.0$ Hz, 6H, CH_3), 1.15–1.25 (m, 12H, CH_2Si), 2.02–2.20 (m, 12H, CH_2CF_2), 4.08 (q, $J=7.0$ Hz, 4H, CH_2O), 7.17–7.24 (m, 4H, Ar-H), 7.48 (d, $J=9.0$ Hz, 2H, Ar-H), 7.96 (s, 2H, Ar-H), 8.0 (d, $J=9.0$, 2H, Ar-H); ^{13}C NMR ($CDCl_3$): δ 1.6, 14.7, 25.6, 65.0, 115.9, 119.7, 125.9, 125.8, 128.8, 129.1, 129.8, 135.0, 135.4, 155.5, 110.3–120.7; ^{19}F NMR ($CDCl_3$) δ −126.9 (m, 12F, CF_2), −123.8 (m, 12F, CF_2), −123.6 (m, 12F, CF_2), −122.6 (m, 12F, CF_2), −116.6 (m, 12F, CF_2), −81.5 (t, $^3J_{F,F}=10.5$ Hz, CF_3). Anal. calcd for $C_{72}H_{44}O_2F_{78}Si_2$ (2479.20): C, 34.88; H, 1.79; found: C, 34.35; H, 1.61%.

4.4. (*R*)-6,6′-Diperfluorooctyl-1,1′-binaphthyl-2,2′-diol, 4

A solution of BBr_3 in CH_2Cl_2 (1 M, 8.8 mmol, 8.8 mL) was slowly added at 0°C to a solution of phosphane **3** (2.6 g, 2.2 mmol) in CH_2Cl_2 (50 mL) under argon. After stirring for 20 h at room temperature, the solution was slowly poured into cold water (100 mL). The aqueous phase was extracted with ethyl acetate (3×60 mL), and the combined organic phases were dried over Na_2SO_4. Evaporation of the solvent gave a solid (2.4 g, 97%) which could be used directly for the next step. The solid could also be purified by flash-chromatography on silica gel, using petroleum ether/ethyl acetate (5:1) as the eluent. White solid; mp 124–126°C. $R_f=0.4$ (petroleum ether/ethyl acetate 5:1); $[\alpha]_D^{25}=-16.9$ (*c* 0.5, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 5.44 (s, 2H, OH), 7.21 (d, $J=9.0$ Hz, 2H, Ar-H), 7.44 (dd, $J=9.0$, 1.8 Hz, 2H, Ar-H), 7.49 (d, $J=9.0$ Hz, 2H, Ar-H), 8.09 (d, $J=9.0$ Hz, 2H, Ar-H), 8.17 (d, $J=1.8$ Hz, 2H, Ar-H); ^{13}C NMR ($CDCl_3$): δ 110.9, 119.7, 120.4, 125.1, 128.7, 133.1, 135.4, 155.1; ^{19}F NMR ($CDCl_3$): δ −126.8 (s, 2F, CF_2), −126.7 (s, 2F, CF_2), −123.3 (bs, 4F, CF_2), −122.5 (bs, 8F, CF_2), −122.0 (bs, 8F, CF_2), −110.6 (t, $^3J_{F,F}=13.8$ Hz, 4F, CF_2Ar), −81.4 (t, $^3J_{F,F}=9.6$ Hz, 6F, CF_3). Anal. calcd for $C_{36}H_{12}O_2F_{34}$ (1122.43): C, 38.52; H, 1.08; found: C, 38.76; H, 0.81%.

4.5. (*S*)-6,6′-Bis[tris(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)silyl]-1,1′- binaphthyl-2,2′-diol, 11

Starting from compound **10** (1.5 g, 0.6 mmol), and using the same procedure than for the preparation of compound **4**, compound **11** was obtained (1.28 g, 87%). Oil; $R_f=0.46$ (petroleum ether/ethyl acetate 7:1); $[\alpha]_D^{25}=+13.5$ (*c* 0.6, FC-72); ^1H NMR ($CDCl_3$): δ 1.09–1.28 (m, 12H, CH_2Si), 2.03–2.09 (m, 12H, CH_2CF_2), 5.16 (s, 2H, OH), 7.22 (d, $J=8.0$ Hz, 2H, Ar-H), 7.30 (d, $J=8.0$ Hz, 2H, Ar-H), 7.47 (d, $J=9.0$ Hz, 2H, Ar-H), 8.00 (s, 2H, Ar-H), 8.04 (d, $J=9.0$ Hz, 2H, Ar-H). These values are in agreement with the literature.[17]

4.6. (*R*)-2,2′-Bis(trifluoromethanesulfonyloxy)-6,6′-diperfluorooctyl-1,1′-binaphthyl, 5

To a solution of perfluorobinaphthyl derivative **4** (1.12 g, 1 mmol) in CH_2Cl_2 (20 mL) and trifluoromethylbenzene (10 mL) cooled at 0°C was added pyridine (243 μL, 3 mmol) and then during 30 min triflic anhydride (421 μL, 2.5 mmol). After stirring the mixture for 12 h, the solvents were evaporated and the residue was dissolved in ethyl acetate (50 mL). The organic phase was washed with a 5% aqueous solution of HCl (30 mL), an aqueous solution of $NaHCO_3$ (30 mL), an aqueous solution of NaCl (30 mL) and dried over Na_2SO_4. Evaporation of the solvent gave a residue that was purified by flash-chromatography on silica gel, using petroleum ether/ethyl acetate (40:1) as the eluent, to give the bistriflate **5** (1.2 g, 86%). Oil; $R_f=0.22$ (petroleum ether/ethyl acetate 40:1); $[\alpha]_D^{25}=-51.3$ (*c* 0.3, AcOEt); ^1H NMR ($CDCl_3$): δ 7.37 (d, $J=9.0$ Hz, 2H, Ar-H), 7.57 (dd, $J=9.0$, 2.0 Hz, 2H, Ar-H), 7.76 (d, $J=9.0$ Hz, 2H, Ar-H), 8.29 (d, $J=9.0$ Hz, 2H, Ar-H), 8.31 (d, $J=2.0$ Hz, 2H, Ar-H); ^{13}C NMR ($CDCl_3$): δ 116.3, 120.6, 121.3, 123.5, 125.4, 127.7, 128.7, 131.7, 133.7, 134.0, 147.3; ^{19}F NMR ($CDCl_3$): δ −126.9 (s, 4F, CF_2), −123.5 (s, 4F, CF_2), −122.6 (bs, 8F, CF_2), −122.3 (s, 4F, CF_2), −121.9 (s, 4F, CF_2), −111.4 (t, $^3J_{F,F}=13.9$ Hz, 4F, CF_2Ar), −81.6 (t, $^3J_{F,F}=9.5$ Hz, 6F, CF_3CF_2), −75.2 (s, 6F, CF_3SO_2). Anal. calcd for $C_{38}H_{10}O_6F_{40}S_2$ (1386.53): C, 32.90; H, 0.73; found: C, 32.81; H, 0.86%.

4.7. (*S*)-2,2′-Bis(trifluoromethanesulfonyloxy)-6,6′-bis-[tris(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)silyl]-1,1′-binaphthyl, 12

The same procedure used for the synthesis of **5** was applied starting from compound **11** (1.4 g, 0.60 mmol) to give bistriflate **12** (1.41 g, 87%). Oil; R_f= 0.5 (petroleum ether/ethyl acetate 10:1); $[\alpha]_D^{25}$= + 29.8 (*c* 0.5, Et_2O); ^1H NMR ($CDCl_3$): δ 1.14–1.20 (m, 12H, CH_2Si), 1.94–2.10 (m, 12H, CH_2CF_2), 7.29–7.37 (m, 4H, Ar-H), 7.62 (d, J=9 Hz, 2H, Ar-H), 8.05 (s, 2H, Ar-H), 8.13 (d, J=9 Hz, 2H, Ar-H); ^{19}F NMR ($CDCl_3$): δ −126.7 (m, 12F, CF_2), −123.8 (m, 12F, CF_2), −123.5 (m, 12F, CF_2), −122.5 (m, 12F, CF_2), −116.4 (m, 12F, CF_2), −81.4 (t, $^3J_{F,F}$=10.9 Hz, 18F, CF_3), −75.2 (s, 6F, OSO_2CF_3). Anal. calcd for $C_{70}H_{34}O_6F_8Si_2S_2$ (2687.20): C, 31.29; H, 1.28; found: C, 30.95; H, 1.22%.

4.8. (*R*)-6,6′-Diperfluorooctyl-2-diphenylphosphinyl-2′-(trifluoromethanesulfonyloxy)-1,1′-binaphthyl, 6

A solution of bistriflate **5** (308 mg, 0.22 mmol), $Pd(OAc)_2$ (2.5 mg, 11 μmol), 1,4-bis(diphenylphosphino)butane (4.8 mg, 11 μmol), diphenylphosphine oxide (89 mg, 0.44 mmol), and diisopropylethylamine (154 μL, 0.88 mmol) in anhydrous dimethylsulfoxide (10 mL) under argon was warmed to 100°C for 12 h. After cooling and hydrolysis with water (10 mL), the aqueous phase was extracted with ethyl acetate (4×10 mL). The organic phase was washed with water (20 mL), dried over Na_2SO_4. Evaporation of the solvent gave a residue that was purified by flash-chromatography on silica gel, using petroleum ether/ethyl acetate (3:1) as the eluent, to give compound **6** (196 mg, 61%). White solid; mp 71–73°C. R_f=0.46 (petroleum ether/ethyl acetate 3:1), $[\alpha]_D^{25}$=+3.7 (*c* 0.2, AcOEt); ^1H NMR ($CDCl_3$): δ 6.92 (d, J=8.8 Hz, 1H, Ar-H), 7.16–7.40 (m, 9H, Ar-H), 7.47–7.61 (m, 5H, Ar-H), 7.68 (dd, $J_{H,P}$=11.5 Hz, $J_{H,H}$=8.6 Hz, 1H, Ar-H), 8.12 (d, J=9.0 Hz, 1H, Ar-H), 8.14 (dd, $J_{H,P}$=8.6 Hz, $J_{H,H}$=1.9 Hz, 1H, Ar-H), 8.16 (bs, 1H, Ar-H), 8.25 (bs, 1H, Ar-H); ^{31}P NMR ($CDCl_3$): δ 28.8 (s); ^{19}F NMR ($CDCl_3$): δ −126.6 (s, 4F, CF_2), −123.2 (s, 4F, CF_2), −122.2 (bs, 10F, CF_2), −121.6 (bs, 6F, CF_2), −111.2 (t, $^3J_{F,F}$=14.3 Hz, 2F, CF_2Ar), −110.8 (t, $^3J_{F,F}$=14.3 Hz, 2F, CF_2Ar), −81.2 (t, $^3J_{F,F}$=10.4 Hz, 6F, CF_3CF_2), −75.4 (s, 3F, CF_3SO_2). Anal. calcd for $C_{49}H_{20}O_4F_{37}PS$ (1438.64): C, 40.89; H, 1.40; found: C, 40.59; H, 1.14%.

4.9. (*S*)-6,6′-Bis[tris(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)silyl]-2-diphenylphosphinyl-2′-(trifluoromethanesulfonyloxy)-1,1′-binaphthyl, 13

The same procedure used for the synthesis of 6 was applied starting from compound **12** (400 mg, 0.15 mmol) to give compound **13** (290 mg, 70%). Oil; R_f= 0.38 (petroleum ether/ethyl acetate 5:1); $[\alpha]_D^{25}$=+3.5 (*c* 0.3, Et_2O); ^1H NMR ($CDCl_3$): δ 1.17–1.26 (m, 12H, CH_2Si), 1.98–2.09 (m, 12H, CH_2CF_2), 7.17–7.57 (m, 15H, Ar-H), 7.66 (dd, J=11.5, 8.7 Hz, 1H, Ar-H), 8.00–8.08 (m, 4H, Ar-H); ^{13}C NMR ($CDCl_3$) δ 0.12, 23.9, 125.7, 126.5, 126.7, 126.8, 127.4, 128.0, 128.5, 129.0, 129.9, 130.0, 130.1, 130.4, 130.5, 130.6, 130.9, 131.0, 131.6, 132.0, 132.4, 132.6, 132.7, 133.3, 133.7, 135.7, 135.8, 145.1, 108.8–118.6; ^{31}P NMR ($CDCl_3$): δ 29.3 (s); ^{19}F NMR ($CDCl_3$): δ −126.8 (m, 12F, CF_2), −123.8 (m, 12F, CF_2), −123.5 (m, 12F, CF_2), −122.6 (m 12F, CF_2), −166.5 (m, 12F, CF_2), −81.5 (t, $^3J_{F,F}$= 10.9 Hz, 18F, CF_2CF_3), −75.7 (s, 3F, OSO_2CF_3). Anal. calcd for $C_{81}H_{44}F_{81}O_4PSSi_2$ (2739.32): C, 35.52; H, 1.62; found: C, 35.93; H, 2.01%.

4.10. (*R*)-6,6′-Diperfluorooctyl-2-diphenylphosphinyl-2′-hydroxy-1,1′-binaphthyl, 7

To a solution of compound **6** (743 mg, 0.52 mmol) in THF (10 mL) was added a saturated aqueous solution of LiOH (10 mL). After stirring for 15 h, the solution was acidified to pH 2 using aqueous hydrochloric acid (32%). The aqueous phase was extracted with ethyl acetate (2×10 mL), the organic phase was washed with water (3×5 mL), and dried over Na_2SO_4. Evaporation of the solvent gave a residue that was purified by flash-chromatography on silica gel, using petroleum ether/ethyl acetate (3:1) as the eluent, to give compound **7** (573 mg, 85%). White solid; mp 102–104°C; R_f=0.25 (petroleum ether/ethyl acetate 3:1); $[\alpha]_D^{25}$=−39.5 (*c* 0.2, AcOEt); ^1H NMR ($CDCl_3$): δ 6.44 (d, J=8.8 Hz, 1H, Ar-H), 6.71–6.84 (m, 3H, Ar-H), 7.03 (d, J=8.7 Hz, 1H, Ar-H), 7.17–7.26 (m, 3H, Ar-H), 7.38 (d, J=9.2 Hz, 1H, Ar-H), 7.47–7.64 (m, 5H, Ar-H), 7.78 (d, J=9.0 Hz, 1H, Ar-H), 7.80 (bs, 1H, Ar-H), 7.87–7.93 (m, 2H, Ar-H), 8.05 (dd, $J_{H,P}$=2.1 Hz, $J_{H,H}$=8.7 Hz, 1H, Ar-H), 8.22 (bs, 1H, Ar-H), 9.52 (bs, 1H, OH); ^{31}P NMR ($CDCl_3$): δ 31.9 (s); ^{19}F NMR ($CDCl_3$): δ −126.6 (s, 4F, CF_2), −123.1 (s, 4F, CF_2), −122.3 (bs, 8F, CF_2), −121.9 (s, 2F, CF_2), −121.6 (bs, 6F, CF_2), −111.1 (t, $^3J_{F,F}$=14.3 Hz, 2F, CF_2Ar), −110.4 (t, $^3J_{F,F}$=14.9 Hz, 2F, CF_2Ar), −81.18 (t, $^3J_{F,F}$=9.2 Hz, 6F, CF_3). Anal. calcd for $C_{48}H_{21}O_2F_{34}P$ (1306.61): C, 44.10; H, 1.62; found: C, 44.18; H, 1.87%.

4.11. (*S*)-6,6′-Bis[tris(tris(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)silyl]-2-diphenylphosphinyl-2′-hydroxy-1,1′-binaphthyl, 14

The same preceding procedure was applied starting from compound **13** (850 mg, 0.31 mmol) to give compound **14** (655 mg, 81%). Oil; R_f=0.32 (petroleum ether/ethyl acetate 5:1); $[\alpha]_D^{25}$=+36.5 (*c* 0.2, Et_2O); ^1H NMR ($CDCl_3$): δ 1.11–1.20 (m, 12H, CH_2Si), 1.99–2.08 (m, 12H, CH_2CF_2), 6.49 (d, J=8.5 Hz, 1H, Ar-H), 6.70–6.73 (m, 3H, Ar-H), 6.89 (d, J=8.5 Hz, 1H, Ar-H), 7.10–7.30 (m, 4H, Ar-H), 7.45–7.72 (m, 7H, Ar-H), 7.86–8.02 (m, 4H, Ar-H), 9.36 (s, 1H, OH); ^{31}P NMR ($CDCl_3$): δ 31.9 (s); ^{19}F NMR ($CDCl_3$): δ −126.8 (m, 12F, CF_2), −123.8 (m, 12F, CF_2), −123.6 (m, 12F, CF_2), −122.6 (m, 12F, CF_2), −116.5 (m, 12F, CF_2), −81.6 (t, $^3J_{F,F}$=10.9 Hz, 18F, CF_3). Anal. calcd for $C_{80}H_{45}O_2F_{78}PSi_2$ (2607.27): C, 36.85; H, 1.74; found: C, 36.68; H, 1.76%.

4.12. (*R*)-6,6′-Diperfluorooctyl-2-diphenylphosphinyl-2′-(1*H*,1*H*-perfluorooctyloxy)-1,1′-binaphthyl, 8

A mixture of hydroxyphosphane oxide **7** (480 mg, 0.37 mmol), butaflate $C_7F_{15}CH_2OSO_2C_4F_9$ (500 mg, 0.74 mmol) and Cs_2CO_3 (240 mg, 0.74 mmol) in DMF (10 mL) was stirred at 100°C under nitrogen for 15 h. The suspension was cooled to room temperature and poured into H_2O (5 mL). The aqueous solution was extracted with Et_2O (3×10 mL), the combined organic phases were washed with an saturated aqueous solution of NaCl (10 mL) and dried over Na_2SO_4. Evaporation of the solvent gave a residue that was purified by flash-chromatography on silica gel, using diethyl ether/ petroleum ether (2:3) as the eluent, to give compound **8** (552 mg, 88%). White solid; mp 54–56°C; $R_f=0.34$ (diethyl ether/ petroleum ether 2:3); $[\alpha]_D^{25}=+15.1$ (*c* 0.2, Et_2O); ^1H NMR ($CDCl_3$): δ 4.54 (dt, $J_{H,F}=12.3$ Hz, $J_{H,H}=12.3$ Hz, 1H, Ar-H), 4.68 (dt, $J_{H,F}=12.3$ Hz, $J_{H,H}=12.3$ Hz, 1H, Ar-H), 6.67 (d, $J=8.9$ Hz, 1H, Ar-H), 6.97 (d, $J=9.0$ Hz, 1H, Ar-H), 7.10–7.16 (m, 2H, Ar-H), 7.23–7.34 (m, 7H, Ar-H), 7.41–7.52 (m, 4H, Ar-H), 7.65 (dd, $J_{H,P}=11.7$ Hz, $J_{H,H}=8.7$ Hz, 1H, Ar-H), 7.99–8.07 (m, 3H, Ar-H), 8.21 (bs, 1H, Ar-H); ^{31}P NMR ($CDCl_3$): δ 28.3 (s); ^{19}F NMR ($CDCl_3$): δ −126.7–126.5 (m, 6F, CF_2), −124.0 (bs, 2F, CF_2), −123.3 (bs, 6F, CF_2), −122.8 (bs, 4F, CF_2), −122.3 (bs, 10F, CF_2), −121.8–121.5 (m, 6F, CF_2), −119.7 (bs, 2F, CF_2CH_2), −111.2 (t, $^3J_{F,F}=14.3$ Hz, 2F, CF_2), −110.5 (t, $^3J_{F,F}=14.3$ Hz, 2F, CF_2), −81.4 (t, $^3J_{F,F}=10.3$ Hz, 3F, CF_3), −81.3 (t, $^3J_{F,F}=10.3$ Hz, 3F, CF_3), −81.2 (t, $^3J_{F,F}=10.3$ Hz, 3F, CF_3). Anal. calcd for $C_{56}H_{22}O_2F_{49}P$ (1688.06): C, 39.81; H, 1.31; found: C, 39.86; H, 1.50%.

4.13. (*S*)-6,6′-Bis[tris(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)silyl]-2-diphenylphosphinyl-2′-methoxy-1,1′-binaphthyl, 15

A mixture of perfluorocompound 14 (620 mg, 0.24 mmol), K_2CO_3 (132 mg, 0.95 mmol), and CH_3I (0.06 mL, 0.95 mmol) in acetone (10 mL) was heated at reflux under argon for 3 h. Filtration of the mixture, followed by evaporation of the solvent gave a residue that was purified by flash-chromatography on silica gel, using petroleum ether/ethyl acetate (2:1) as the eluent, to give compound **15** (521 mg, 84%). Oil; $R_f=0.68$ (petroleum ether/ethyl acetate 2:1); $[\alpha]_D^{25}=-3.1$ (*c* 0.3, Et_2O); ^1H NMR ($CDCl_3$): δ 1.21–1.30 (m, 12H, CH_2Si), 2.06–2.13 (m, 12H, CH_2CF_2), 3.68 (s, 3H, OCH_3), 6.90 (d, $J=8.5$ Hz, 1H, Ar-H), 7.07 (d, $J=8.5$ Hz, 1H, Ar-H), 7.17–7.33 (m, 8H, Ar-H), 7.40–7.52 (m, 4H, Ar-H), 7.81–7.86 (m, 2H, Ar-H), 7.94 (dd, $J=11.3$, 8.7 Hz, 1H, Ar-H), 8.05–8.10 (m, 2H, Ar-H); ^{13}C NMR ($CDCl_3$): δ 0.2, 24.2, 54.2, 123.8, 124.4, 126.1, 126.2, 126.3, 126.5, 126.7, 127.8, 128.6, 129.6, 130.0, 130.2, 130.3, 130.5, 131.0, 131.1, 131.3, 132.4, 132.5, 132.8, 133.0, 133.7, 134.0, 139.2, 139.5, 155.0, 109.0–118.0; ^{31}P NMR ($CDCl_3$): δ 29.0 (s); ^{19}F NMR ($CDCl_3$): δ −127.0 (m, 12F, CF_2), −123.9 (m, 12F, CF_2), −123.6 (m, 12F, CF_2), −122.7 (m, 12F, CF_2), −116.6 (m, 12F, CF_2), −81.8 (t, $^3J_{F,F}=10.9$ Hz, 18F, CF_3). Anal. calcd for $C_{81}H_{47}O_2F_{78}PSi_2$ (2621.29): C, 37.12; H, 1.81; found: C, 36.94; H, 1.72%.

4.14. (*R*)-6,6′-Diperfluorooctyl-2-diphenylphosphino-2′-(1*H*,1*H*-perfluorooctyloxy)-1,1′-binaphthyl, 9

$HSiCl_3$ (184 μL, 1.82 mmol) was cautiously added under argon at 0°C to a mixture of phosphane oxide **8** (770 mg, 0.46 mmol) and freshly distilled triethylamine (279 μL, 2 mmol) in dry toluene (10 mL). The mixture was warmed at 120°C for 6 h. After cooling to 5°C, the solution was treated with precooled, de-aerated 2N NaOH (15 mL). The aqueous phase was extracted with de-aerated Et_2O (3×5 mL), and the combined organic layers were washed with deaerated water (5 mL), and dried over Na_2SO_4. Evaporation of the solvent gave a residue that was purified by flash-chromatography on silica gel, using diethyl ether/petroleum ether (1:5) as the eluent, to give phosphane **9** (686 mg, 90%). White solid; mp 39–41°C: $R_f=0.76$ (diethyl ether/petroleum ether 1:5); $[\alpha]_D^{25}=+8.5$ (c 0.2, Et_2O); ^1H NMR ($CDCl_3$): δ 4.21 (dt, $J_{H,F}=12.2$ Hz, $J_{H,H}=12.2$ Hz, 1H, Ar-H), 4.36 (dt, $J_{H,P}=12.2$ Hz, $J_{H,H}=12.2$ Hz, 1H, Ar-H), 6.83 (d, $J=9.0$ Hz, 1H, Ar-H), 7.00 (t, $J=7.9$ Hz, 2H, Ar-H), 7.06–7.20 (m, 5H, Ar-H), 7.23–7.32 (m, 5H, Ar-H),7.36–7.41 (m, 2H, Ar-H), 7.51 (dd, $J_{H,H}=8.5$ Hz, $J_{H,P}=2.8$ Hz, 1H, Ar-H), 7.99 (d, $J=8.5$ Hz, 1H, Ar-H), 8.16 (d, $J=9.8$ Hz, 3H, Ar-H); ^{31}P NMR ($CDCl_3$): δ −11.2 (s); ^{19}F NMR ($CDCl_3$): δ −126.8–126.4 (m, 6F, CF_2), −123.9 (bs, 2F, CF_2), −123.5 to 123.1 (m, 6F, CF_2), −122.8 (bs, 4F, CF_2), −122.4 (bs, 10F, CF_2), −121.7 (bs, 6F, CF_2), −119.7 (bs, 1F, CF_2CH_2), −119.5 (bs, 1F, CF_2CH_2), −111.0 (t, $^3J_{F,F}=14.6$ Hz, 2F, CF_2), −110.5 (t, $^3J_{F,F}=14.6$ Hz, 2F, CF_2), −81.3 (t, $^3J_{F,F}=9.7$ Hz, 3F, CF_3), −81.2 (t, $^3J_{F,F}=9.7$ Hz, 3F, CF_3), −81.2 (t, $^3J_{F,F}=9,7$ Hz, 3F, CF_3). Anal. calcd for $C_{56}H_{22}OF_{49}P$ (1672.06): C, 40.19; H, 1.33; found: C, 40.24; H, 1.28%.

4.15. (*S*)-6,6′-Bis[tris(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)silyl]-2-diphenylphosphino-2′-methoxy-1,1′-binaphthyl, 16

The same preceding procedure was applied starting from compound **15** (547 mg, 0.21 mmol) to give phosphine **16** (495 mg, 91%). Oil; $R_f=0.82$ (petroleum ether/ ethyl acetate 10:1); $[\alpha]_D^{25}=-8.0$ (*c* 0.1, Et_2O); ^1H NMR ($CDCl_3$): δ 1.16–1.20 (m, 12H, CH_2Si), 2.04–2.09 (m, 12H, CH_2CF_2), 3.46 (s, 3H, OCH_3), 6.92–7.07 (m, 3H, Ar-H), 7.14–7.39 (m, 12H, Ar-H), 7.47 (dd, $J=11.5$, 8.5 Hz, 1H, Ar-H), 7.89–7.94 (m, 2H, Ar-H), 7.99–8.06 (m, 2H, Ar-H); ^{31}P NMR ($CDCl_3$): δ −12.2 (s); ^{19}F NMR ($CDCl_3$): δ −126.7 (m, 12F, CF_2), −123.7 (m, 12F, CF_2), −123.5 (m, 12F, CF_2), −122.5 (m, 12F, CF_2), −116.4 (m, 12F, CF_2), −81.4 (t, $^3J_{F,F}=10.9$ Hz, 18F, CF_3). HRMS (FAB) calcd for $C_{81}H_{48}OF_{78}PSi_2$ $[M+H]^+$ 2605.1735; found: 2605.1697.

4.16. Alkylation of 1,3-diphenylprop-2-enyl acetate

In a Schlenk tube, $[Pd(C_3H_5)Cl]_2$ (1.45 mg, 4 μmol) and the ligand (16 μmol) were dissolved in the solvent (3 mL). After stirring the mixture for 1 h at the desired temperature, a solution of 1,3-diphenylprop-2-enyl acetate (50 mg, 0.2 mmol) in the solvent (2 mL) was added.

After 30 min, this solution was transferred to a Schlenk tube containing the nucleophile (0.4 mmol) in 2 mL of solvent. The reaction mixture was stirred at the desired temperature for the indicated time. The conversion and enantiomeric excess were determined by HPLC analysis (column Chiralpak AD 0.46×25 cm).

Acknowledgements

This work was partially supported by a fellowship from the French Ministery of Education (D.M. and J.B.) and from Région Rhône-Alpes (J.D.K.).

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