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Chiral fluorous phosphorus ligands based on the binaphthyl skeleton: synthesis and applications in asymmetric catalysis

Jerôme Bayardon,[a] Marco Cavazzini,[b] David Maillard,[a] Gianluca Pozzi,[b,*] Silvio Quici[b] and Denis Sinou[a,*]

[a]*Laboratoire de Synthèse Asymétrique, associé au CNRS, CPE Lyon, Université Claude Bernard Lyon 1, 43, boulevard du 11 novembre 1918, 69622 Villeurbanne Cedex, France*
[b]*CNR-Istituto di Scienze e Tecnologie Molecolari, via C. Golgi 19, 20133 Milano, Italy*

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Abstract—Two enantiopure fluorous phosphines have been conveniently synthesized by combining palladium-catalyzed coupling reactions of easily available binaphthyl building-blocks with the introduction of fluorous ponytails onto aromatic compounds via ether bond formation. These new fluorous chiral phosphines have been tested as ligands in metal-catalyzed asymmetric transformations, the best results being obtained in the palladium-catalyzed asymmetric allylic substitution of 1,3-diphenyl-2-propenyl acetate affording the products of up to 87% e.e.

1. Introduction

Homogeneous organometallic asymmetric catalysis is now a powerful tool for the preparation of a large number of non-racemic chiral compounds.[1] However, the separation of the usually costly and sometimes toxic catalyst from the product(s) of the reaction is still problematic. In order to solve this problem, the use of novel reaction media such as supercritical fluids,[2] ionic liquids,[3] and liquid biphasic systems[4] is now thoroughly investigated. These new media not only offer the possibility of cleaner technology, but can also promote new selectivities.

Following the pioneering work of Horváth and Rábai on fluorous biphase systems,[5] various homochiral fluorous organometallic complexes have been reported in the last few years for use in asymmetric catalysis in liquid-liquid fluorous solvent/organic solvent systems, or even under homogeneous conditions in partly fluorinated solvents such as benzotrifluoride. Literature examples include epoxidation of alkenes in the presence of fluorous chiral salen manganese complexes,[6] hydrolytic kinetic resolution of terminal epoxides using fluorous chiral Co(salen) complexes,[7] asymmetric alkylation of aldehydes with fluorous BINOL titanium alkoxides,[8] reduction of ketones via hydrogen transfer reactions in the presence of iridium complexes of fluorous diimines and diamines,[9] ruthenium-catalyzed hydrogenation of dimethyl itaconate,[10] Heck reactions,[11] and palladium-catalyzed alkylations of allylic acetates.[12]

Enantiopure 2-(diphenylphosphino)-2′-alkoxy-1,1′-binaphthyls (MOPs) are useful ligands for several metal-catalyzed asymmetric transformations.[13] We have recently described the synthesis and some possible applications in catalysis of MOP analogues characterized by the presence of different fluorous ponytails in selected positions on the MOP scaffold.[12a,b] Promising results were obtained in the palladium-catalyzed asymmetric alkylation of 1,3-diphenylprop-2-enyl acetate, for which ligand (*R*)-**1** (Fig. 1) afforded enantioselectivities up to 87%.[12a] We report here a more complete investigation concerning this ligand and the extension of the methodology for the introduction of fluorous ponytails successfully applied in the case of (*R*)-**1** to the preparation of the fluorous BINAP analogue (*R*)-**2** (Fig. 1).

* Corresponding author. Tel.: 33 (0) 4 72 44 81 83; fax: 33 (0) 4 78 89 89 14; e-mail: sinou@univ-lyon1.fr

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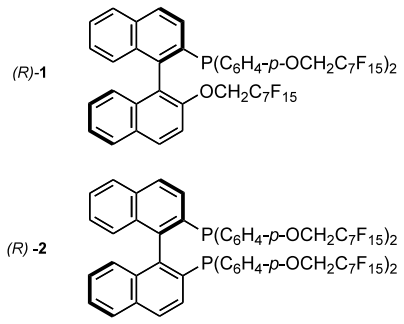
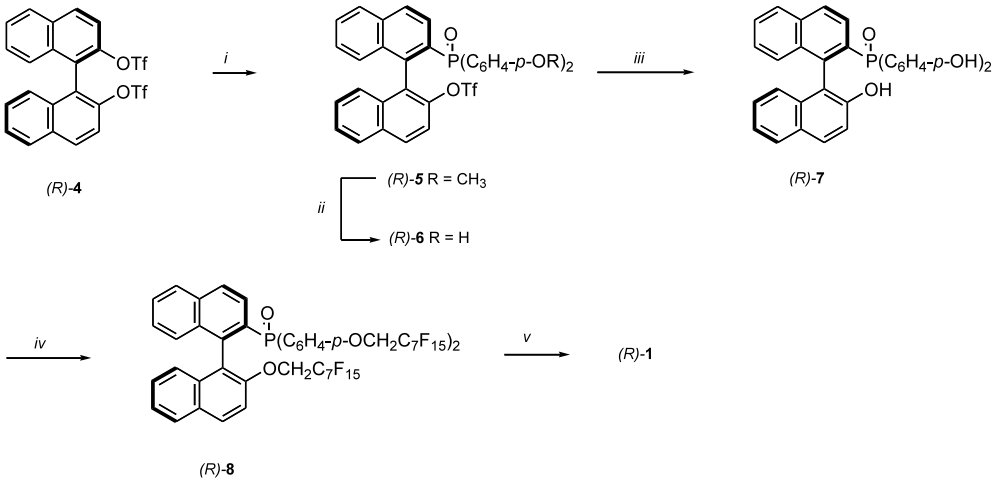


Figure 1.

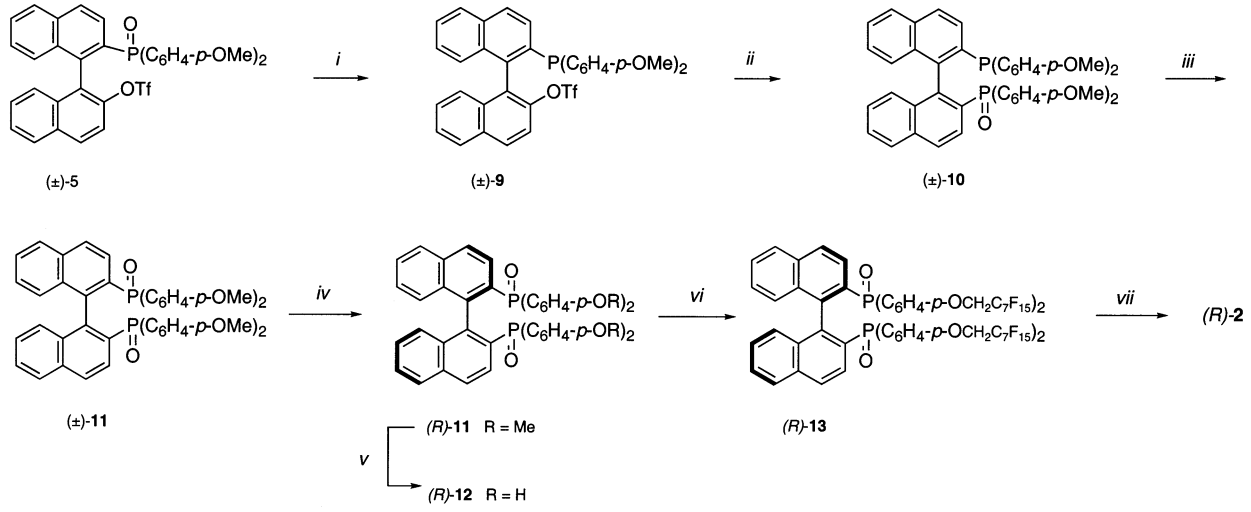
2. Results and discussion

The fluorous chiral phosphorus ligands (*R*)-**1** and (*R*)-**2**, analogues of MOP and BINAP, respectively, were prepared according to the multi-step procedures shown in Schemes 1 and 2. In both cases, the required fluorous ponytails were introduced through *O*-alkylation of preformed polyhydroxy chiral phosphines, according to a methodology developed by us in the achiral series.[14] This approach is particularly convenient due to its simplicity and flexibility. When applied to the preparation of 1,1′-binaphthyl-based phosphorus ligands, it also offers a wider choice of possible locations for the fluorous ponytails, which can be inserted both onto the binaphthyl moiety and onto the other phosphorus substituents.

The preparation of enantiopure fluorous phosphine (*R*)-**1** was successfully accomplished by a five-step procedure (Scheme 1). Bis(4-methoxyphenyl)phosphine oxide **3** was obtained in 70% yield by reaction of (4-methoxy-benzene)magnesium bromide with *N*,*N*-



Scheme 1. *Reagents and conditions*: (i) $(4\text{-MeOC}_6\text{H}_4)_2\text{POH}$ (**3**), $Pd(OAc)_2$, dppb, $(i\text{-Pr})_2NEt$, DMSO, 120°C, 12 h; (ii) BBr_3, CH_2Cl_2, 0°C, 2 h; (iii) aqueous NaOH 3 M, MeOH/dioxane 2:1, 25°C, 24 h; (iv) $C_7F_{15}CH_2OSO_2C_4F_9$, Cs_2CO_3, DMF, 100°C, 8 h; (v) $HSiCl_3$, toluene, 110°C, 3 h.



Scheme 2. *Reagents and conditions*: (i) $HSiCl_3$, toluene, 110°C, 8 h; (ii) $(4\text{MeO-C}_6\text{H}_4)_2\text{POH}$ (**3**), $Pd(OAc)_2$, dppb, DMSO, $(i\text{-Pr})_2NEt$, 120°C, 24 h; (iii) H_2O_2 10%, acetone, rt, 8 h; (iv) (2*R*,3*R*)-2,3-di-*O*,*O*-benzoyltartaric acid, toluene, $CHCl_3$, AcOEt; (v) BBr_3, CH_2Cl_2, 0°C to rt, 24 h; (vi) $C_7F_{15}CH_2OSO_2C_4F_9$, Cs_2CO_3, DMF, 120°C, 24 h; (vii) $HSiCl_3$, xylene, 125°C, 48 h.

diethyl-phosphoramidous dichloride Cl_2PNEt_2 at −10°C followed by acidic hydrolysis at −10°C, according to a one-pot procedure based on similar methods reported in the literature.[15] The condensation of the bis(trifluoromethanesulfonate) of binaphthol (*R*)-**4** with phosphine oxide **3** in the presence of 10 mol% $Pd(OAc)_2$ and 10 mol% of 1,4-bis(diphenylphosphino) butane (or dppb) in DMSO at 120°C[16] afforded compound (*R*)-**5**, resulting from a monophosphinylation reaction, in 96% yield. Subsequent cleavage of the methyl group of the phosphinyl derivative (*R*)-**5** with BBr_3 in CH_2Cl_2 at 0°C[17] led to the dihydroxy derivative (*R*)-**6** in quantitative yield after recrystallization from diethyl ether. Hydrolysis of the remaining triflate group with aqueous sodium hydroxide in a methanol/dioxane mixture converted compound (*R*)-**6** into (*R*)-2-[bis(4-hydroxyphenyl) phosphinyl]-2′-hydroxy-1,1′-binaphthyl (*R*)-**7** in 92% yield. Reaction of binaphthyl derivative (*R*)-**7** with 1*H*,1*H*-pentadecafluorooctan-1-ol nonafluorobutane sulfonate in DMF at 100°C in the presence of caesium carbonate[14] allowed the introduction of three fluorous ponytails; phosphine oxide (*R*)-**8** was obtained in 70% yield after simple flash chromatography. Finally reduction of phosphine oxide (*R*)-**8** with trichlorosilane in boiling toluene[18] afforded the corresponding pure fluorous MOP (*R*)-**1** (having 52.4% fluorine content) in 91% yield.

Gladiali et al. described the preparation of 2-diphenylphosphino-2′-diphenylphosphinyl-1,1′-binaphthalene (BINAPO) through two subsequent palladium-catalyzed coupling reaction.[19] Their findings and the good results obtained in the synthesis of (*R*)-**1** led us to investigate the synthetic route to fluorous phosphine BINAP (*R*)-**2** described in Scheme 2. The racemic monophosphinyl derivative (±)-**5**, obtained from the bistriflate of racemic binaphthol as described above for the (*R*)-enantiomer, was converted into the diarylphosphino triflate (±)-**9** in 74% yield by reduction with trichlorosilane in boiling toluene.[18] This allowed a further palladium-catalyzed coupling reaction between phosphine (±)-**9** and bis(4-methoxyphenyl)phosphine oxide **3** to proceed at 120°C in dry DMSO using $Pd(OAc)_2$/dppb as the catalyst.[16] The diarylphosphinodiarylphosphinyl derivative (±)-**10** obtained in 41% yield, was readily oxidized to the racemic diphosphine oxide (±)-**11** in 96% yield in the presence of H_2O_2. Reaction of racemic (±)-**11** with (2*R*,3*R*)-2,3-di-*O*,*O*-benzoyltartaric acid afforded a solid that was dissolved in $CHCl_3$ and washed several times with NaOH to give enantiopure (*R*)-**11** in 74% yield. A similar procedure has been previously described for the resolution of closely related diphosphine oxides.[20] Cleavage of the four methyl groups of the diphosphine oxide (*R*)-**12** was performed as above with BBr_3 in CH_2Cl_2 at 0°C[17] to afford the tetrahydroxy-binaphthyl derivative (*R*)-**11** in 95% yield. Four fluorous ponytails were then introduced by reaction of (*R*)-**12** with 1*H*,1*H*-pentadecafluorooctan-1-ol nonafluorobutanesulfonate in DMF at 120°C in the presence of cesium carbonate;[14] diphosphine oxide (*R*)-**13** was obtained in 42% yield after column chromatography. Reduction of phosphine oxide (*R*)-**13** with trichlorosilane in boiling xylene,[18] a procedure currently employed for the reduction of enantiomerically pure BINAPOs,[20] afforded the corresponding pure fluorous BINAP (*R*)-**2** in 48% yield.

In order to check the enantiomeric purity of compound (*R*)-**13**, the corresponding racemic form (±)-**13** was also prepared from (±)-**11** according to the above-mentioned procedure. Comparative ^{1}H NMR titration experiments involving (±)-**13** and (*R*)-**13** were then performed (Fig. 2). In the presence of increasing amounts of (2*R*,3*R*)-2,3-di-*O*,*O*-benzoyltartaric acid as resolving agent, remarkable splitting of the doublet at δ 6.69 ppm and of the broad triplet at δ 6.89 ppm were observed for

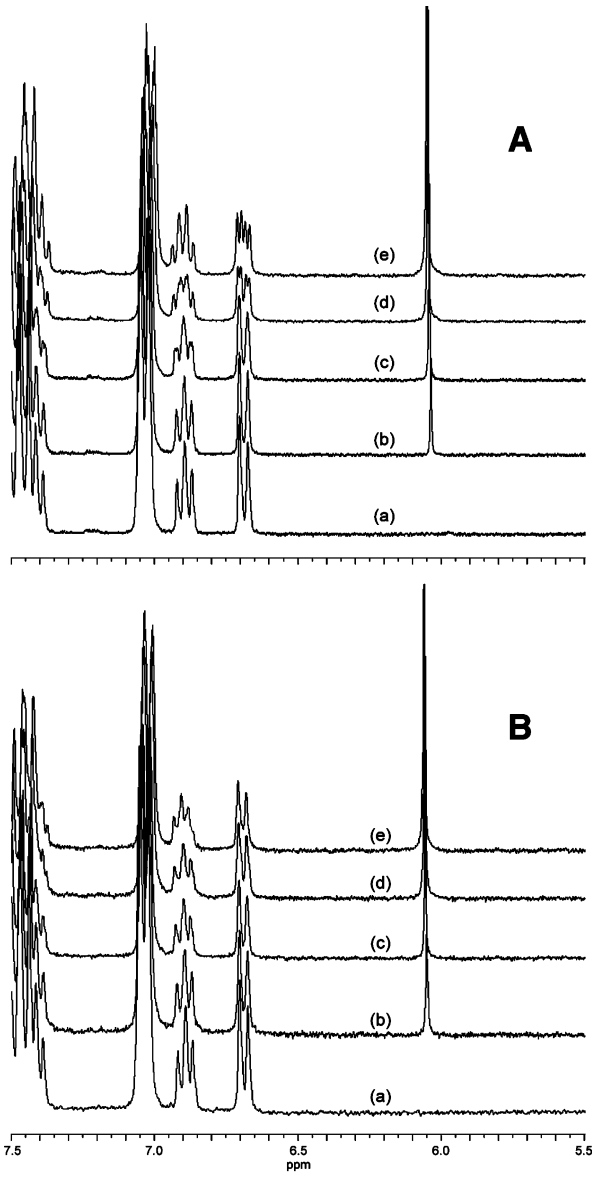


Figure 2. ^{1}H NMR spectra of (±)-**13** (5.8 μmol, A) and (*R*)-**13** (5.8 μmol, B) in the presence of increasing amount of (2*R*,3*R*)-2,3-di-*O*,*O*-benzoyltartaric acid: (a) no addition; (b) 2.2 μmol; (c) 3.3 μmol; (d) 4.4 μmol; (e) 6.6 μmol; solvent: acetone-d_6 (0.75 ml).

(±)-**13**, whereas multiplicity of those signals remained unchanged in the case of (*R*)-**13**, thus showing that the enantiomeric purity of the latter was at least 95%.

Another synthetic way was also studied in order to circumvent the resolution step in the synthesis of (*R*)-**13**. Reduction of (*R*)-**5** with $HSiCl_3$ in toluene at 110°C afforded (*R*)-**9** in 88% yield. Condensation of bis(4-methoxyphenyl)phosphine oxide **13** with phosphine (*R*)-**9** gave compound (*R*)-**10** in 46% yield, that was quantitatively oxidized to the diphosphine oxide (*R*)-**13**. Unfortunately, some racemization occurred during this sequence, since the specific rotation of the obtained compound was $[\alpha]_D^{20}$ +21.6 (*c* 1, $CHCl_3$), lower than the value obtained using the resolution sequence: $[\alpha]_D^{20}$ +107.6 (*c* 1, $CHCl_3$).

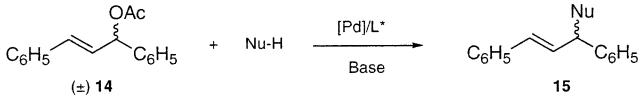
In order to use phosphines (*R*)-**1** and (*R*)-**2** as ligands in organometallic catalysis in a two-phase system organic solvent/fluorous solvent, the partition coefficients between FC-72 (perfluoromethylcyclohexane) and various organic solvents were determined. For phosphine (*R*)-**1** with a fluorine content of 52.4%, the values for CH_2Cl_2, toluene, CH_3OH, and CH_3CN, were 0.20, 0.23, 7.42, and 11.05, respectively. For phosphine (*R*)-**2** with a fluorine content of 51.5%, the values for toluene, ethanol, and acetonitrile, were 0.08, 3.1, and 1.8, respectively. This affinity of the two fluorous phosphines for organic solvent is probably due to their relatively low fluorine content and also to the presence of an aromatic backbone.

The new fluorous ligands were tested at first under homogeneous conditions in the palladium-catalyzed asymmetric allylic alkylation of 1,3-diphenylprop-2-enyl acetate **14** with various nucleophiles using standard solvents (Table 1). The reaction of racemic acetate **14** with dimethyl malonate catalyzed by $[Pd(C_3H_5)Cl]_2$ (2 mol%) in the presence of ligand (*R*)-**1** (8 mol%), bis(trimethylsilyl)acetamide (BSA, 2 equiv.) and potassium acetate (10.1 equiv.) proceeded quantitatively in benzotrifluoride at 25°C to give, after 35 h, the corresponding alkylated product **15** with 81% e.e. (Table 1, entry 2); this value is quite close to that obtained (88% e.e.) using toluene as the solvent (Table 1, entry 1). It is noteworthy that the original non-fluorous MOP gave the alkylated product in 95% yield and 99% e.e. using toluene as the solvent.[21]

Reaction of **14** with various substituted dimethyl malonate gave lower chemical yields. Dimethyl methylmalonate gave the expected alkylated product with 7% yield only and 77% e.e. at room temperature, whereas performing the reaction at 50°C increased the yield to 69% after 48 h, but lowered the e.e. to 44% e.e. (Table 1, entries 4 and 5). Diethyl acetamidomalonate also gave the alkylated product in very low yield at room temperature (9%), the yield increasing to 67% when the reaction was performed at 50°C, the enantioselectivity being 85% (Table 1, entries 6 and 7). A quantitative chemical yield was obtained when acetylacetone was used as the nucleophile, the enantioselectivity being as high as 81% (Table 1, entry 3). Amines were also used as nucleophiles in this reaction; morpholine gave only 10% conversion with a very low enantioselectivity (7% e.e.), when benzylamine gave no reaction at all (Table 1, entries 8 and 9).

The fluorous nature of the catalyst allowed its quick and effective separation from reaction mixtures, as

Table 1. Asymmetric alkylation of 1,3-diphenylprop-2-enyl acetate (**14**) using various nucleophiles



Entry	Ligand	Nu-H	Solvent	*T* (°C)	Time (h)	Conversion (%)[a]	E.e. (%)[a] (Config.)[b]
1	(*R*)-**7**	$CH_2(CO_2Me)_2$[c]	$C_6H_5CH_3$	25	25	88	87 (*R*)
2	(*R*)-**7**	$CH_2(CO_2Me)_2$[c]	$C_6H_5CF_3$	25	36	<99 (88)	81 (*R*)
3	(*R*)-**7**	$CH_2(COCH_3)_2$[c]	$C_6H_5CF_3$	25	1	100	85 (*R*)
4	(*R*)-**7**	$MeCH(CO_2Me)_2$[c]	$C_6H_5CF_3$	25	48	7	77 (*S*)
5	(*R*)-**7**	$MeCH(CO_2Me)_2$[c]	$C_6H_5CF_3$	50	48	69	44 (*S*)
6	(*R*)-**7**	$AcNHCH(CO_2Me)_2$[c]	$C_6H_5CF_3$	25	21	9	n.d.[e]
7	(*R*)-**7**	$AcNHCH(CO_2Me)_2$[c]	$C_6H_5CF_3$	50	25	67	85 (*S*)
8	(*R*)-**7**	Morpholine[c]	$C_6H_5CF_3$	50	44	10	7
9	(*R*)-**7**	Benzylamine[c]	$C_6H_5CF_3$	50	24	0	–
10	(*R*)-**13**	$CH_2(CO_2Me)_2$[c]	$C_6H_5CF_3$	50	23	12	14 (*R*)
11	(*R*)-**13**	$CH_2(CO_2Me)_2$[d]	THF	50	3	100	32 (*R*)
11bis	(*R*)-**13**	$CH_2(CO_2Me)_2$[d]	THF	50	16	20	37 (*R*)
12	(*R*)-**13**	$CH_2(CO_2Me)_2$[d]	D-100[f]/CH_3CN	50	160	20	25 (*R*)

[a] Determined by HPLC analysis (column Chiralpak AD 0.46×25 cm).
[b] Determined by comparison with an authentic sample.
[c] Base: *N*,*O*-bis-(trimethylsilyl)acetamide (BSA)
[d] Base: NaH
[e] Not determined
[f] A mixture of perfluorooctanes

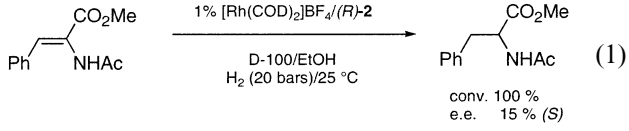
shown in the case of the alkylation of **14** with dimethyl malonate when toluene was used as the solvent. A simple liquid-liquid extraction of the organic phase with FC-72 (2×5 ml) led to the complete removal of the fluorous palladium complex, as revealed by the absence of phosphine resonances in the ^{1}H NMR of the crude product. However, the recovered fluorous solution did not show any catalytic activity when tested in a second run. A similar behavior was previously observed in the allylation of benzaldehyde catalyzed by platinum complexes of achiral light fluorous phosphines.[22]

The catalytic alkylation of racemic acetate **14** with dimethyl malonate using (*R*)-**2** as the ligand was also performed. The conversion (12%) and the enantioselectivity (14% e.e.) were low when the reaction was carried out in benzotrifluoride at 50°C in the presence of BSA as the base (Table 1, entry 10). Although no reaction occurred when the reaction was performed in THF in the presence of BSA, the conversion was quantitative after 3 h when the reaction was run in the presence of NaH, the enantioselectivity being rather low (32% e.e.) (Table 1, entry 11). In this latter experiment, the fluorous catalyst was separated by liquid-liquid extraction of the reaction mixture using FC-72 as the solvent. The recovered catalyst gave a lower conversion after 16 h (20%), but the enantioselectivity was the same (Table 1, entry 11bis). Finally the use of (*R*)-**2** as a ligand in a fluorous biphasic system perfluorooctane/CH_3CN at 50°C gave a very low conversion (20%) after 160 h, with an enantioselectivity up to 25% (Table 1, entry 12).

It was reported that $Pd(OAc)_2$/BINAP catalyzed the asymmetric Heck reaction between 2,3-dihydrofuran and aryl triflates at 40°C to give the corresponding 2-aryl-2,3-dihydrofuran in 91% e.e.;[23] a fluorous chiral BINAP analogue recently used by Nakamura and coworkers afforded enantioselectivity up to 93% for the same reaction.[11] It was obviously interesting to compare the new BINAP analogue (*R*)-**2** to these literature examples. The reaction was thus carried out in benzotrifluoride, in the presence of $Pd(OAc)_2$ (3 mol%) associated with (*R*)-**2** (7 mol%). The results are summarized in Table 2.

The reaction was quantitative using 4-chlorophenyl triflate (Table 2, entry 2), 2-(4-chlorophenyl)-2,3-dihydrofuran being formed with a very high selectivity (97%) and 68% enantioselectivity. These results compare favorably to those obtained using the parent BINAP ligand in the same solvent (yield 67%, selectivity 92%, e.e. 76%), but the observed e.e. was lower than that achieved using a fluorous BINAP ligand bearing fluorous ponytails in the 6,6′-positions of the binaphthyl moiety (yield 59%, selectivity 88%, e.e. 90%).[11] Condensation of phenyl triflate with dihydrofuran occurred with a lower reaction rate (only 56% conversion after 138 h) (Table 2, entry 1), but with a high regioselectivity (95%) and the same enantioselectivity (68% e.e.). The reaction between naphthyl triflate and dihydrofuran gave the condensation product with a lower regioselectivity (only 74% of 2-naphthyl-2,3-dihydrofuran) and also a lower enantioselectivity (14% e.e.) (Table 2, entry 4). As expected, condensation of dihydrofuran with 4-methoxyphenyl triflate gave a very low conversion (11%) (Table 2, entry 3). We also tried to react dihydrofuran and 4-chlorophenyl triflate in a toluene/FC-72 biphasic system; unfortunately no reaction occurred after 72 h.

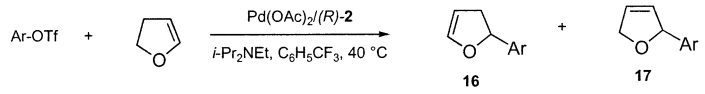
Finally, fluorous BINAP (*R*)-**2** was tested as a ligand in two other standard catalytic reactions. Reduction of α-acetamidocinnamic acid methyl ester (Eq. (1)) was performed in THF at room temperature under hydrogen (13 bar pressure) using the rhodium complex prepared from $[Rh(COD)_2]BF_4$ (1 mol%) and (*R*)-**2** (2.2 or 1.2 mol%) at 50°C for 1 h; complete conversion was observed after 18h, the enantioselectivity being 15 and 16% using 2.2 and 1.2% ligand, respectively.



(1)

Hydroboration of styrene, followed by oxidation, was also performed (Eq. (2)). Reaction of catechol borane with styrene in the presence of $[Rh(COD)_2]BF_4$ (1

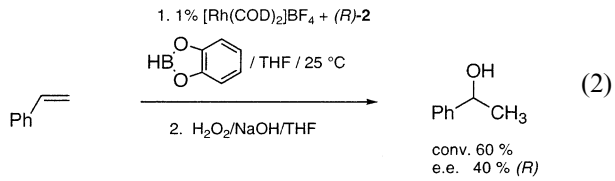
Table 2. Asymmetric Heck reaction of 2,3-dihydrofuran with various aryl triflates



Entry	Ar-OTf	Solvent	Time (h)	Conversion (%)[a]	Ratio **16**/**17**[a]	E.e. of **16** (%)[b] (config)[c]
1	C_6H_5OTf	$C_6H_5CF_3$	138	56	95/5	68 (*R*)
2	4-Cl-C_6H_4OTf	$C_6H_5CF_3$	89	100	97/3	54 (*R*)
3	4-CH_3O-C_6H_4OTf	$C_6H_5CF_3$	118	11	–	–
4	1-Naphthyl	$C_6H_5CF_3$	120	96	74/26	14[d]
5	4-Cl-C_6H_4OTf	$C_6H_5CH_3$/FC-72 (1/1)	72	0	–	–

[a] Determined by GC analysis (column Quadrex 30m×0.25 mm).
[b] Determined by GC analysis (Ar = C_6H_5 and 4-Cl-C_6H_4) (column Cydex B 25m×0.25 mm) and HPLC analysis (Ar = naphthyl) (column Chiralpak AD 0.46×25 cm).
[c] Determined by comparison of the specific rotation with literature data.
[d] Not determined.

mol%) and (*R*)-**2** (1 mol%) in THF at room temperature for 18 h, followed by oxidation with hydrogen peroxide in the presence of sodium hydroxide, gave 60% conversion in a 86/14 mixture of 1-phenylethanol and 2-phenylethanol, the enantioselectivity for 1-phenylethanol being 40% (*R*). Extraction of the fluorous rhodium catalyst before oxidation using FC-72 gave a catalyst solution having a very low activity (16% conversion after 24 h).



(2)

3. Conclusion

Despite the growing interest for chiral fluorous ligands, only a few examples of chiral fluorous phosphines have been reported in the literature. We have now devised an effective approach to the synthesis of fluorous analogues of two versatile ligands such as MOP and BINAP, combining palladium-catalyzed coupling reactions of easily available binaphthyl building-blocks with the introduction of fluorous ponytails onto aromatic compounds via ether bond formation.

The new phosphines (*R*)-**1** and (*R*)-**2** have been tested as ligands in selected metal-catalyzed asymmetric transformations and the most promising results have been obtained in the case of the allylic alkylation of 1,3-diphenyl-2-propenyl acetate (±)-**14** with several nucleophiles catalyzed by $[Pd(C_3H_5)Cl]_2$ in the presence of the MOP analogue (*R*)-**1**. This ligand proved to be superior to other previously reported chiral phosphines bearing fluorous ponytails in the 6,6′-positions of the binaphthyl scaffold,[12b] showing both higher enantioselectivity and catalytic activity. Good results were also obtained in the asymmetric Heck reaction between 2,3-dihydrofuran and aryl triflates catalyzed by $Pd(OAc)_2$/(*R*)-**2**, but preliminary attempts at using this fluorous BINAP analogue as rhodium ligand for the hydrogenation of α-acetamidocinnamic acid methyl ester and for the hydroboration/oxidation of styrene were less satisfactory. It appears that in these cases the introduction of fluorous ponytails has a negative effect on the level of enantioselection, possibly due to steric effects arising from mutual interaction of the perfluoroalkyl chains. Indeed electronic effects cannot be the determining factor as the interposition of aryl rings and -OCH_2- insulating spacers effectively shields the phosphorous atoms from the electron withdrawing effect of the perfluoroalkyl chains.[14]

None of the ligands here studied contained enough fluorine to be used with success in an FB system, but they did have enough fluorine to separate them quickly from the product using liquid-liquid extraction with perfluorocarbons, as already shown in the case of similar light fluorous catalytic systems.

4. Experimental

4.1. General

Solvents were purified by standard methods and dried if necessary. All commercial available reagents were used as received. All reactions were monitored by TLC (TLC plates GF_{254} Merck); detection was effected by UV absorbance. Air- and moisture-sensitive reactions were performed under usual inert atmosphere techniques. Reactions involving organometallic catalysis were carried out in a 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 procedures: (*R*)-1,1′-bis(2-naphthol)bis(trifluoromethanesulfonate) (*R*)-**4**,[16] and 1*H*,1*H*-pentadecafluorooctyl-1-ol nonafluorobutanesulfonate $C_7F_{15}CH_2OSO_2C_4F_9$.[14]

4.2. Bis(4-methoxyphenyl)phosphine oxide, 3

A solution of (4-methoxyphenyl)magnesium bromide was prepared by slow addition (1 h) of 4-bromoanisole (11 ml, 86 mmol) in THF (30 ml) to a slurry of magnesium turnings (2.3 g, 95 mmol) in THF (5 ml). The mixture was stirred 1 h at reflux and then cooled to rt. The upper liquid layer was transferred into a flame-dried flask placed in a cooling bath at −15°C. Neat Cl_2PNEt_2 (5 ml, 34.4 mmol) was carefully added while maintaining the solution temperature lower than −10°C (**Caution**!). After 5 min, the cooling bath was removed and the viscous reaction mixture was stirred 1 h before being cooled again to −10°C. Aqueous 37% HCl (10 ml) was slowly added under stirring (**Caution**!), the mixture was warmed up to rt, stirred for 1 h and finally treated with H_2O (50 ml). The mixture was then extracted with CH_2Cl_2 (3×50 ml), and the combined organic phases were dried over Na_2SO_4. Evaporation of the solvent under reduced pressure afforded a yellow crude product that was purified by crystallization from acetone/Et_2O to give compound **3** (6.3 g, 70%). White solid, physical data in full agreement with those reported in the literature.[24]

4.3. (*R*)-2-[Bis(4-methoxyphenyl)phosphinyl]-2′-[(trifluoromethanesulfonyl)oxy]-1,1′-binaphthyl, (*R*)-5

To a mixture of bistriflate (*R*)-**4** (550 mg, 1 mmol), bis(4-methoxyphenyl)phosphine oxide **3** (1.05 g, 4 mmol), $Pd(OAc)_2$ (22 mg, 0.1 mmol), and 1,4-bis-(diphenylphosphino)butane (43 mg, 0.1 mmol), were added dry DMSO (5 ml) and (i-Pr)$_2$NEt (0.68 ml, 4 mmol). After being stirred at 120°C for 12 h, the solution was cooled to rt, and diluted with AcOEt (50

ml). The organic solution was washed with water (10× 20 ml), and dried over Na_2SO_4. Evaporation of the solvent under reduced pressure gave a residue that was purified by flash chromatography on silica gel using CH_2Cl_2/MeOH (98/2) as the eluent, and then a second flash chromatography using AcOEt as the eluent to give compound (*R*)-**5** (636 mg, 96%). White solid; mp 80–81°C; R_f = 0.6 (AcOEt); $[\alpha]_D^{20}$ = +66.2 (*c* 0.7, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.76 (s, 3H, CH_3), 3.77 (s, 3H, CH_3), 6.66 (dd, *J* = 8.8, 2.3 Hz, 2H, $H_{arom.}$), 6.76 (dd, *J* = 8.8, 2.3 Hz, 2H, $H_{arom.}$), 6.99 (d, *J* = 8.5 Hz, 1H, $H_{arom.}$), 7.10 (d, *J* = 8.5 Hz, 1H, $H_{arom.}$), 7.17 (bt, *J* = 7.2 Hz, 2H, $H_{arom.}$), 7.25-7.36 (m, 6H, $H_{arom.}$), 7.42 (bt, *J* = 7.2 Hz, 1H, $H_{arom.}$), 7.55 (bt, *J* = 7.2 Hz, 1H, $H_{arom.}$), 7.71–7.94 (m, 3H, $H_{arom.}$), 8.00 (dd, *J* = 8.8, 2.3 Hz, 1H, $H_{arom.}$); ^{31}P NMR (76 MHz, $CDCl_3$): δ 28.6 (s); ^{19}F NMR (122 MHz, $CDCl_3$): δ −75.4 (s). Anal. calcd for $C_{35}H_{26}F_3O_6PS$ (662.62): C, 63.44; H, 3.96; found: C, 63.01; H, 3.84.

4.4. (*R*)-2-[Bis(4-hydroxyphenyl)phosphinyl]-2′-[(trifluoromethanesulfonyl)oxy]-1,1′-binaphthyl, (*R*)-6

Triflate (*R*)-**5** (1.8 g, 2.72 mmol) was dissolved in dry CH_2Cl_2 (40 ml) and the solution was cooled to 0°C. A 1 M solution of BBr_3 in CH_2Cl_2 (16.3 ml, 16.3 mmol) was added dropwise in 5 min, and the solution was stirred at 0°C for 2 h. After warming up the solution to 5°C, water (15 ml) was slowly added. The organic layer was separated, diluted with AcOEt (15 ml), and washed several times with H_2O (4×10 ml). After removal of the organic solvent, the residue was recrystallized from Et_2O to give compound (*R*)-**6** (1.7 g, 99%). White solid; mp 176–180°C; R_f = 0.4 (CH_2Cl_2/CH_3OH 98:2); ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.49 (dd, *J* = 11.0, 2.4 Hz, 2H, $H_{arom.}$), 6.55 (dd, *J* = 11.0, 2.4 Hz, 2H, $H_{arom.}$), 6.85 (d, *J* = 8.5 Hz, 1H, $H_{arom.}$), 6.98–7.10 (m, 6H, $H_{arom.}$), 7.19–7.25 (m, 2H, $H_{arom.}$), 7.32 (bt, *J* = 7.6 Hz, 1H, $H_{arom.}$), 7.48 (bt, *J* = 7.6 Hz, 1H, $H_{arom.}$), 7.61 (dd, *J* = 11.6, 8.5 Hz, 1H, $H_{arom.}$), 7.72 (d, *J* = 8.2 Hz, 1H, $H_{arom.}$), 7.82 (d, *J* = 8.2 Hz, 1H, $H_{arom.}$), 7.89 (d, *J* = 8.2 Hz, 1H, $H_{arom.}$), 7.96 (dd, *J* = 8.5, 2.4 Hz, 1H, $H_{arom.}$); ^{31}P NMR (76 MHz, $CDCl_3$): δ 33.2 (s); ^{19}F NMR (122 MHz, $CDCl_3$): δ −75.7 (s). Anal. calcd for $C_{33}H_{22}F_3O_6PS$ (634.57): C, 62.46; H, 3.49; found: C, 62.93; H, 3.69.

4.5. (*R*)-2-[Bis(4-hydroxyphenyl)phosphinyl]-2′-hydroxy-1,1′-binaphthyl, (*R*)-7

Compound (*R*)-**6** (1.63 g, 2.57 mmol) was dissolved in a mixture of dioxane/MeOH 2:1 (13 ml). Aqueous NaOH 3 M (10 ml) was added and the mixture was vigorously stirred for 24 h at rt. The pH of the solution was brought to 1 by addition of HCl 36% and the mixture was extracted with AcOEt (3×20 ml). The organic phase was dried over Na_2SO_4, and the solvent was evaporated under reduced pressure to give compound (*R*)-**7** as a grayish solid (1.19 g, 92%) that was directly used for the next step without further purification. Mp 229–230°C; $[\alpha]_D^{20}$ = +124.3 (*c* 0.5, MeOH); ^{1}H NMR (300 MHz, DMSO-d_6): δ 6.41 (dd, *J* = 8.7, 2.4 Hz, 2H, $H_{arom.}$), 6.61 (dd, *J* = 8.7, 2.4 Hz, 2H, $H_{arom.}$), 6.65 (d, *J* = 8.7 Hz, 1H, $H_{arom.}$), 6.95 (d, *J* = 8.7 Hz, 1H, $H_{arom.}$), 7.00-7.10 (m, 4H, OH, $H_{arom.}$), 7.16 (bt, *J* = 7.1 Hz, 2H, $H_{arom.}$), 7.22–7.32 (m, 3H, $H_{arom.}$), 7.53–7.62 (m, 3H, $H_{arom.}$), 7.90 (dd, *J* = 11.4, 2.7 Hz, 1H, $H_{arom.}$), 7.99 (d, *J* = 8.7 Hz, 1H, $H_{arom.}$), 8.08 (dd, *J* = 8.7, 2.0 Hz, 1H, $H_{arom.}$); ^{31}P NMR (76 MHz, DMSO-d_6): δ 28.8 (s).

4.6. (*R*)-2-{Bis[4-(1*H*,1*H*-pentadecafluorooctyloxy)-phenyl]phosphinyl}-2′-(1*H*,1*H*-perfluorooctyloxy)-1,1′-binaphthyl, (*R*)-8

To a solution of compound (*R*)-**7** (800 mg, 1.6 mmol) and $C_7F_{15}CH_2OSO_2C_4F_9$ (5.46 g, 8 mmol) in DMF previously warmed at 100°C was added Cs_2CO_3 (2.08 g, 6.4 mmol). The mixture was stirred at 100°C for 8 h. The solution was cooled at rt, poured into water (50 ml), and extracted with Et_2O (3×10 ml), and with CH_2Cl_2 (3×10 ml). The combined organic phases were dried over Na_2SO_4. Evaporation of the organic solvents gave a residue that was purified by flash chromatography on silica using petroleum ether/Et_2O (4:1) as the eluent to give fluorous compound (*R*)-**8** (1.85 g, 70%). Yellow solid; mp 64–66°C; R_f = 0.5 (petroleum ether/Et_2O 4:1); $[\alpha]_D^{20}$ = +60.0 (*c* 0.3, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.24–4.59 (m, 6H, CH_2), 6.56 (dd, *J* = 8.8, 2.1 Hz, 2H, $H_{arom.}$), 6.74 (dd, *J* = 8.8, 2.1 Hz, 2H, $H_{arom.}$), 6.79 (d, *J* = 8.5 Hz, 1H, $H_{arom.}$), 7.00–7.28 (m, 7H, $H_{arom.}$), 7.38 (dd, *J* = 11.4, 8.7 Hz, 2H, $H_{arom.}$), 7.52 (bt, *J* = 7.4 Hz, 1H, $H_{arom.}$), 7.63 (d, *J* = 8.1 Hz, 1H, $H_{arom.}$), 7.76 (dd, *J* = 9.0, 5.0 Hz, 1H, $H_{arom.}$), 7.81 (d, *J* = 8.1 Hz, 1H, $H_{arom.}$), 7.91 (d, *J* = 8.1 Hz, 1H, $H_{arom.}$), 7.98 (dd, *J* = 8.8, 2.1 Hz, 1H, $H_{arom.}$); ^{31}P NMR (76 MHz, $CDCl_3$): δ 28.8 (s); ^{19}F NMR (122 MHz, $CDCl_3$): δ −126.5, −123.8, −123.5, −123.1, −122.6, −122.3, −120.0, −119.7, −81.3, −81.2. Anal. calcd for $C_{56}H_{26}F_{45}O_4P$ (1648.70): C, 40.80; H, 1.59; found: C, 40.47; H, 1.64.

4.6.1. (*R*)-2-{Bis[4-(1*H*,1*H*-pentadecafluorooctyloxy)-phenyl]-phosphino}-2′-(1*H*,1*H*-pentadecafluorooctyl-oxy)-1,1′-binaphthyl, (*R*)-1

To an ice-cooled suspension of perfluorous phosphine oxide (*R*)-**8** (1.21 g, 0.73 mmol) in deareated toluene (15 ml) was added $HSiCl_3$ (0.37 ml, 3.67 mmol). The reaction was warmed to 110°C for 3 h under stirring. The solution was cooled to 0°C, diluted with deareated Et_2O (10 ml), and neutralized with a saturated aqueous solution of $NaHCO_3$ (15 ml). The suspension was filtered under nitrogen on a Celite plug that was washed with Et_2O (3×15 ml). The organic phase was dried over Na_2SO_4. Evaporation of the solvent under reduced pressure gave phosphine (*R*)-**1** (1.08 g, 91%). White solid; mp 48–49°C; R_f = 0.7 (petroleum ether/Et_2O 4:1); $[\alpha]_D^{20}$ = +23.1 (*c* 0.3, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.16 (dt, *J* = 24.6, 12.6 Hz, 2H, CH_2), 4.48 (dt, *J* = 13.1 Hz, 4H, CH_2), 6.72 (d, *J* = 8.4 Hz, 2H, $H_{arom.}$), 6.86–6.92 (m, 3H, $H_{arom.}$), 7.03 (dd, *J* = 8.5, 7.1 Hz, 2H, $H_{arom.}$), 7.06–7.12 (m, 1H, $H_{arom.}$), 7.17–7.35 (m, 6H, $H_{arom.}$), 7.41 (dd, *J* = 8.5, 3.0 Hz, 1H, $H_{arom.}$), 7.44–7.50 (m, 1H, $H_{arom.}$), 7.86–7.91 (m, 3H, $H_{arom.}$), 8.01 (d, *J* = 9.1 Hz, 1H, $H_{arom.}$); ^{31}P NMR (76

MHz, $CDCl_3$): δ −15.5 (s). Anal. calcd for $C_{56}H_{26}F_{45}O_3P$ (1632.70): C, 41.17; H, 1.61; found: C, 40.56; H, 1.53.

4.7. 2-[Bis(4-methoxyphenyl)phosphino]-2′-[(trifluoromethanesulfonyl)oxy]-1,1′-binaphthyl, 9

To a solution of racemic 2-[bis(4-methoxyphenyl)-phosphinyl] - 2′ - [(trifluoromethanesulfonyl)oxy] - 1,1′-binaphthyl **5** (3.54 g, 5.21 mmol) in deareated toluene (80 ml) cooled to 0°C was added $HSiCl_3$ (2.63 ml, 26.1 mmol). After being stirred for 8 h at 110°C, the solution was cooled to 0°C, neutralized with an aqueous solution of NaOH 30% (30 ml). The mixture was warmed to 40°C until two clear solutions were obtained. The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (2×10 ml), and diethyl ether (2×10 ml). The combined organic layers were dried over Na_2SO_4, and evaporated under reduced pressure. The obtained residue was purified by column chromatography on silica gel (eluent petroleum ether/diethyl ether 1:1) to give phosphine **9** (2.5 g, 74%). White solid; mp 76–78°C; R_f=0.5 (petroleum ether/Et_2O 1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.72 (s, 3H, CH_3), 3.80 (s, 3H, CH_3), 6.63 (d, J=8.3 Hz, 2H, $H_{arom.}$), 6.84–6.94 (m, 5H, $H_{arom.}$), 7.08 (bt, J=7.1 Hz, 1H, $H_{arom.}$), 7.12–7.21 (m, 3H, $H_{arom.}$), 7.27 (m, 1H, $H_{arom.}$), 7.41 (d, J=8.3 Hz, 1H, $H_{arom.}$), 7.40–7.52 (m, 2H, $H_{arom.}$), 7.52 (d, J=9.0 Hz, 1H, $H_{arom.}$), 7.87–7.94 (m, 3H, $H_{arom.}$), 8.00 (d, J=9.0 Hz, 1H, $H_{arom.}$); ^{31}P NMR (76 MHz, $CDCl_3$): δ −15.3 (s). Anal. calcd for $C_{35}H_{26}F_3O_5PS$ (646.62): C, 65.01; H, 4.05; found: C, 65.13; H, 4.35.

4.8. 2-[Bis(4-methoxyphenyl)phosphino]-2′-[bis(4-methoxyphenyl)phosphinyl]-1,1′-binaphthyl, 10

A mixture of compound **9** (2.5 g, 3.85 mmol), bis(4-methoxyphenyl)phosphine oxide **3** (3.03, 11.6 mmol), palladium acetate (86 mg, 0.385 mmol), 1,4-bis-(diphenylphosphino)butane (164 mg, 0.385 mmol), diisopropylethylamine (2 ml, 11.6 mmol), in dry DMSO (30 ml), was stirred at 120°C for 24 h. The solution was cooled to rt, diluted with ethyl acetate (80 ml), and washed with water (10×10 ml). The solvent was evaporated under reduced pressure to give a dark green residue that was purified by flash column chromatography on silica using ethyl acetate as the eluent to afford compound **10** (1.2 g, 41%). Pale yellow solid; mp 128–130°C; R_f=0.7 (AcOEt); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.71 (s, 6H, CH_3), 3.75 (s, 6H, CH_3), 6.54–6.59 (m, 5H, $H_{arom.}$), 6.64 (dd, J=8.8, 2.2 Hz, 2H, $H_{arom.}$), 6.72–6.88 (m, 6H, $H_{arom.}$), 6.97 (bt, J=7.0 Hz, 1H, $H_{arom.}$), 7.18 (dd, J=8.8, 6.4 Hz, 2H, $H_{arom.}$), 7.28–7.37 (m, 5H, $H_{arom.}$), 7.43 (dd, J=8.6, 11.0 Hz, 2H, $H_{arom.}$), 7.65–7.73 (m, 3H, $H_{arom.}$), 7.81 (d, J=8.1 Hz, 1H, $H_{arom.}$), 7.92 (dd, J=8.6, 2.3 Hz, 1H, $H_{arom.}$); ^{31}P NMR (76 MHz, $CDCl_3$): δ –17.7 (s), 27.7 (s). Anal. calcd for $C_{48}H_{40}O_5P_2$ (758.80): C, 75.98; H, 5.31; found: C, 76.05; H, 5.49.

4.9. (*R*)-2,2′-[Bis(4-methoxyphenyl)phosphinyl]-1,1′-binaphthyl, (*R*)-11

To a solution of compound **10** (1.2 g, 1.58 mmol) in acetone (10 ml) was added at rt H_2O_2 10% (0.81 ml). The mixture was stirred at rt for 8 h, then poured into water (10 ml), and extracted with CH_2Cl_2 (3×20 ml). The combined organic phases were dried over Na_2SO_4, and the solvent removed under reduced pressure to afford racemic compound **11** as a yellowish solid (1.18 mg, 96%). A solution of racemic compound **11** (1.18 g, 1.52 mmol), (2*R*,3*R*)-2,3-di-*O*,*O*-benzoyltartaric acid (0.572 g, 1.52 mmol), and toluene (0.14 g, 1.52 mmol), in $CHCl_3$ (5 ml) was heated at reflux until a homogeneous solution was obtained. Ethyl acetate (16 ml) was added dropwise at the refluxing temperature, and the mixture was allowed to stand at rt overnight to give a complex 1:1 of (*R*)-**11** and (*2R*,*3R*)-2,3-di-*O*,*O*-benzoyltartaric acid with $[\alpha]_D^{20}$=−34.2 (*c* 0.5, $CHCl_3$). No essential change in optical rotation was observed after further recrystallization. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.74 (s, 6H, CH_3), 3.72 (s, 6H, CH_3), 5.76 (s, 2H, CHO), 6.58–6.64 (m, 8H, $H_{arom.}$), 6.82 (d, J=8.5 Hz, 2H, $H_{arom.}$), 6.93 (bt, J=7.0 Hz, 2H, $H_{arom.}$), 7.12 (dd, J=11.4, 8.6 Hz, 4H, $H_{arom.}$), 7.23–7.41 (m, 12H, $H_{arom.}$), 7.49 (bt, J=7.4 Hz, 2H, $H_{arom.}$), 7.68–7.72 (m, 4H, $H_{arom.}$), 8.00 (d, J=7.4 Hz, 4H, $H_{arom.}$). This solid was dissolved in $CHCl_3$ (10 ml), and washed with a 1N NaOH solution (5×5 ml). Evaporation of the solvent gave (*R*)-**11** (433 mg, 74%) White solid; mp 150–152°C; $[\alpha]_D^{20}$=+107.6 (*c* 0.4, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.74 (s, 6H, CH_3), 3.78 (s, 6H, CH_3), 6.60 (dd, J=8.7, 2.1 Hz, 4H, $H_{arom.}$), 6.73 (d, J=8.3 Hz, 2H, $H_{arom.}$), 6.87 (dd, J=8.7, 2.1 Hz, 4H, $H_{arom.}$), 6.93 (m, 2H, $H_{arom.}$), 7.19 (dd, J=8.6, 6.4 Hz, 4H, $H_{arom.}$), 7.39 (m, 2H, $H_{arom.}$), 7.42 (dd, J=11.4, 8.6 Hz, 2H, $H_{arom.}$), 7.65 (dd, J=8.6, 6;4 Hz, 4H, $H_{arom.}$), 7.69 (d, J=8.1 Hz, 2H, $H_{arom.}$), 7.87 (dd, J=8.6, 2.1 Hz, 2H, $H_{arom.}$); ^{31}P NMR (76 MHz, CDCl3): δ 28.7 (s). Anal. calcd for $C_{48}H_{40}O_6P_2$ (774.80): C, 74.41; H, 5.20; found: C, 74.58; H, 5.17.

4.10. (*R*)-2,2′-[Bis(4-hydroxyphenyl)phosphinyl]-1,1′-binaphthyl, (*R*)-12

A solution of phosphine oxide (*R*)-**11** (433 mg, 0.56 mmol) in dry CH_2Cl_2 (20 ml) was cooled at 0°C. A 1 M solution of BBr_3 in CH_2Cl_2 (5.6 ml, 5.6 mmol) was added, and the reaction mixture was stirred at 0°C for 1 h, and then at rt for 24 h. The solution was cooled to 5°C and CH_3OH (10 ml) was carefully added. After removal of the organic solvents, the residue was recrystallized from hot CH_3OH (10 ml) by adding cold water (5 ml) to give hydroxyphosphine oxide (*R*)-**12** (380 mg, 95%). White solid; mp >220°C; $[\alpha]_D^{20}$=+15.0 (*c* 0.5, CH_3OH); ^{1}H NMR (300 MHz, DMSO-d_6): δ 6.55 (d, J=8.6 Hz, 2H, $H_{arom.}$), 6.65–6.69 (m, 6H, $H_{arom.}$), 6.82 (bt, J=7.5 Hz, 2H, $H_{arom.}$), 7.13 (dd, J=11.5, 8.6 Hz, 4H, $H_{arom.}$), 7.31 (dd, J=11.5, 8.6 Hz, 2H, $H_{arom.}$), 7.38 (bt, J=7.5 Hz, 2H, $H_{arom.}$), 7.44 (dd, J=11.5, 8.6 Hz, 2H, $H_{arom.}$), 7.86–7.92 (m, 4H, $H_{arom.}$), 9.95 (s, 4H, OH); ^{31}P NMR (76 MHz, DMSO-d_6): δ 28.2 (s). Anal. calcd for $C_{44}H_{32}O_6P_2$ (718.69): C, 73.53; H, 4.49; found: C, 73.11; H, 4.40.

4.11. (*R*)-2,2′-[Bis(4-(1*H*,1*H*-pentadecafluorooctyloxy) phenyl)phosphinyl]-1,1′-binaphthyl, (*R*)-13

To a suspension of compound (*R*)-**12** (380 mg, 0.53 mmol) and $C_7F_{15}CH_2OSO_2C_4F_9$ (3.68 g, 5.4 mmol) in DMF (20 ml) warmed to 120°C was added Cs_2CO_3 (1.76 g, 5.4 mmol). The mixture was warmed at this temperature for 24 h, and then cooled to 0°C. A 10% aqueous HCl (20 ml) was carefully added, and the mixture was diluted with diethyl ether (40 ml), and washed several times with 10% HCl (2×20 ml), and water (10×10 ml). The aqueous phase was extracted one time with $CFCl_2CClF_2$ (10 ml). The combined organic and fluorous layers were dried over Na_2SO_4, and the solvents removed under reduced pressure to give a brown residue that was purified by column chromatography on silica (eluent CH_2Cl_2/AcOEt 1:1) to afford compound (*R*)-**13** (520 mg, 42%). Yellow solid; mp 128–130°C; R_f=0.5 (CH_2Cl_2/AcOEt 1:1); $[\alpha]_D^{20}$=+47.2 (*c* 0.7, $CFCl_2CClF_2$); ^{1}H NMR (300 MHz, acetone-d_6): δ 4.85 (bq, J=12.9 Hz, 8H, CH_2), 6.69 (d, J=8.3 Hz, 2H, $H_{arom.}$), 6.89 (t, J=7.4 Hz, 2H, $H_{arom.}$), 7.03–7.05 (m, 8H, $H_{arom.}$), 7.39–7.50 (m, 8H, $H_{arom.}$), 7.79 (dd, J=11.5, 8.8 Hz, 4H, $H_{arom.}$), 7.91–7.96 (m, 4H, $H_{arom.}$); ^{31}P NMR (76 MHz, d^6-acetone): δ 27.8 (s); ^{19}F NMR (122 MHz, acetone-d_6): δ −126.6, −123.5, −123.2, −122.4, −119.9, −119.7, −81.2 (t, J=4.2 Hz). Anal. calcd for $C_{76}H_{36}F_{60}O_6P_2$ (2246.98): C, 40.60; H, 1.61; found: C, 40.41; H, 1.52.

4.12. (*R*)-2,2′-[Bis(4-(1*H*,1*H*-pentadecafluorooctyloxy) phenyl)phosphino]-1,1′-binaphthyl, (*R*)-2

A mixture of phosphine oxide (*R*)-**13** (500 mg, 0.22 mmol), Et_3N (0.21 ml, 1.54 mmol), $HSiCl_3$ (0.11 ml, 1.11 mmol), in dry xylene (5 ml) was warmed at 125°C for 48 h under vigorous stirring. The solution was cooled at rt, and a 30% aqueous solution of NaOH (10 ml) was added carefully. The mixture was stirred at 60°C until the organic and aqueous layers became clear. CH_2Cl_2 (20 ml) was added, and the organic phase was separated. The aqueous phase was washed with $CFCl_2CClF_2$ (10 ml) and the organic and fluorous phases were dried over Na_2SO_4. Evaporation of the solvents under reduced pressure gave a residue that was purified by column chromatography on silica gel (eluent petroleum ether/CH_2Cl_2 4:1) to afford phosphine (*R*)-**2** (233 mg, 48%). White solid; mp 49–50°C; R_f=0.4 (petroleum ether/CH_2Cl_2 4:1), $[\alpha]_D^{20}$=+27.6 (*c* 0.4, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.36 (m, 8H, CH_2), 6.69 (bd, J=8.4 Hz, 8H, $H_{arom.}$), 6.81 (d, J=8.4 Hz, 1H, $H_{arom.}$), 6.94–7.01 (m, 5H, $H_{arom.}$), 7.37 (m, 2H, $H_{arom.}$), 7.86 (dd, J=12.4, 8.5 Hz, 4H, $H_{arom.}$); ^{31}P NMR (76 MHz, $CDCl_3$): δ −17.3 (s); ^{19}F NMR (122 MHz, $CDCl_3$): δ −126.6, −123.5, −123.2, −122.4, −120.0, −119.8, −81.2 (t, J=4.1 Hz). Anal. calcd for $C_{76}H_{36}F_{60}O_4P_2$ (2214.98): C, 41.21; H, 1.64; found: C, 41.19; H, 1.72.

4.13. Standard alkylation reaction

In a Schlenk tube, $[Pd(C_3H_5)Cl]_2$ (4.4 mg, 12 μmol) and the ligand (50 μmol) were dissolved in the solvent (3 ml). After stirring the mixture for 1 h at the desired temperature, a solution of racemic 1,3-diphenylprop-2-enyl acetate (**14**) (150 mg, 0.6 mmol) in the solvent (2 ml) was added. After 30 min, this solution was transferred to a Schlenk tube containing the nucleophile (1.2 mmol), *N*,*O*-bis-(trimethylsilyl)acetamid (244 mg, 1.2 mmol), and KOAc (5.9 mg, 60 μmol) in 4 ml of solvent. The reaction mixture was stirred at the desired temperature for the indicated time. After the indicated time, a 1 M solution of NaOH (8 ml) was added, and the product was extracted with AcOEt (10 ml). Evaporation of the solvent gave a residue; the conversion and enantiomeric excess were determined by HPLC analysis (column Chirapalk AD 0.46×25 cm).

4.14. Standard Heck reaction

In a Schlenk tube, $Pd(OAc)_2$ (4.1 mg, 18.4 μmol) and ligand (*R*)-**2** (92.4 mg, 41.7 μmol) were dissolved in trifluorotoluene (2 ml). After stirring for 15 min at 25°C, the solution was transferred to a Schlenk tube containing the aryl triflate (0.6 mmol). After stirring at 25°C for 10 min, dihydrofuran (215 mg, 7.0 mmol), and diisopropylethylamine (238 mg, 1.84 mmol) were added. The solution was stirred at 40°C for the indicated time. The solution was then cooled and diluted with diethyl ether (5 ml). The organic phase was separated and washed with a saturated aqueous solution of NaCl (5 ml), and water (5 ml). Evaporation of the solvent gave a residue that was purified by column chromatography on silica. The conversion was determined by GC using Quadrex OV1 (30 m×0.25 mm) as the column, and the e.e. was determined by GC using Cydex B (25 m×0.25 mm) for Ar=C_6H_5 and 4-Cl-C_6H_4, or HPLC using Chiralpak AD (25 cm×4.6 mm, hexane/*i*-PrOH 92.5/17.5 as the solvent) for Ar= naphthyl.

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