DOI: 10.1002/adsc.200800366

A New Class of 3′-Sulfonyl BINAPHOS Ligands: Modulation of Activity and Selectivity in Asymmetric Palladium-Catalysed Hydrophosphorylation of Styrene

Katalin Barta,[a] Giancarlo Franciò,[a] Walter Leitner,[a,*] Guy C. Lloyd-Jones,[b,*] and Ian R. Shepperson[b]

[a] Institut für Technische und Makromolekulare Chemie, RWTH Aachen, Worringerweg 1, 52074 Aachen, Germany
[b] School of Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS, UK
Fax: (+44)-(0)117-929-8611; e-mail: guy.lloyd-jones@bristol.ac.uk

Received: June 12, 2008; Published online: August 21, 2008

Abstract: Palladium-catalysed monophosphorylation of (*R*)-2,2′-bisperfluoroalkanesulfonates of BINOL ($R^F = CF_3$ or C_4F_9) by a diaryl phosphinate [$Ar_2P(O)H$] followed by phosphine oxide reduction (Cl_3SiH) then lithium diisopropylamide-mediated anionic thia-Fries rearrangement furnishes enantiomerically-pure (*R*)-2′-diarylphosphino-2′-hydroxy-3′-perfluoralkanesulfonyl-1,1′-binaphthalenes [(*R*)-**8ab** and (*R*)-**8g–j**], which can be further diversified by Grignard reagent (RMgX)-mediated CF_3-displacement [→(*R*)-**8c–f**]. Coupling of (*R*)-**8a–j** with (*S*)-1,1′-binaphthalene-2,2′-dioxychlorophosphine (*S*)-**9** generates 3′-sulfonyl BINAPHOS ligands (*R*,*S*)-**10a–j** in good yields (43–82%). These new ligands are of utlility in the asymmetric hydrophosphonylation of styrene (**1**) by 4,4,5,5-tetramethyl-1,3,2-dioxaphospholane 2-oxide (**2**), for which a combination of the chiral ligands with either [Pd(Cp)(allyl)] or $[Pd(allyl)(MeCN)_2]^+/NaCH(CO_2Me)_2$ proves to be a convenient and active pre-catalyst system. A combination of an electron-rich phosphine moiety and an electron-deficient 3′-sulfone moiety provides the best enantioselectivity to date for this process, affording the branched 2-phenethenephosphonate, (−)-*iso*-**3**, in up to 74% *ee* with ligand (*R,S*)-**10i**, where Ar = *p*-anisyl and the 3′-SO_2R group is triflone.

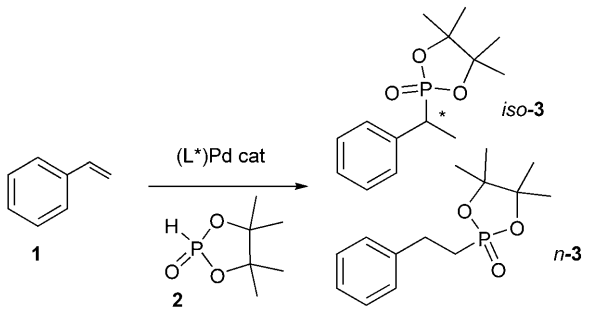
Keywords: asymmetric catalysis; BINOL; hydrophosphination; palladium; phosphines; phosphites

Introduction

The relatively inert nature of many organophosphorus compounds and their structural similarity to biologically important phosphate esters has given rise to their wide-spread application as antibacterial, antiviral, antibiotic, and pesticidal agents. A broad variety of such compounds has been synthesised[1] but only a minority of them in enantiomerically pure form. In particular, arenephosphonates have shown biological activity both as Ca^{2+} antagonists[2] and as cyclooxygenase inhibitors.[3] The majority of routes to generate non-racemic arenephosphonates have involved enantioselective hydrogenation of α,β-unsaturated phosphonates with rhodium-,[4] iridium-,[5] and ruthenium-based[6] catalysts. Whilst these methods have established the requisite chirality with very high selectivity, other strategies in which the C–P bond is installed as part of the asymmetric catalytic process have been less well studied and developed. A catalytic process that is able to generate enantiomerically pure arenephosphonates *directly* by the addition of hydrogen phosphonates across the double bond of styrenes and derivatives will be of significant utility. Whilst promising results for asymmetric hydrophosphination reactions have been reported,[7] the selectivity and generality of such processes lag substantially behind the other, much more extensively explored, asymmetric transition metal-catalysed H–X additions such as hydroamination,[8] hydrosilylation,[9] and hydroboration.[10]

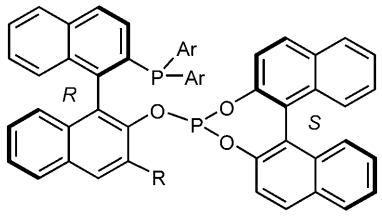
The first example of palladium-catalysed hydrophosphorylation of aryl-olefins was described by Tanaka et al. who discovered that using a bulky pinacol phosphonate reagent made it possible to (racemically) hydrophosphorylate styrene (**1**) with promising regioselectivity for the branched (chiral) arenephosphonate product *iso*-**3** (*iso*-**3**: *n*-**3** = 55:45) (Scheme 1).[11]

It was subsequently found that bidentate chiral ligands enable high levels of regioselectivity (*iso*-**3**:*n*-**3** = 91:9) and moderate levels of enantioselectivity in



Scheme 1. Palladium-catalysed reaction of styrene (**1**) with pinacol phosphonate reagent **2** to generate the 'branched' *sec*-phenethyl phosphonate (*iso*-**3**) and the 'linear' phenethyl phosphonate (*n*-**3**) hydrophosphorylation products. With appropriate chiral ligand(s) L*, *iso*-**3** can be generated in up to 72.5% *ee* with good regioselectivity (*iso*-**3**:*n*-**3** ≤ 94/6). The absolute configuration of *iso*-**3** has not yet been assigned.

the hydrophosphorylation of vinylarenes.[12] A wide range of ligands were examined, with catalysts systems generated *in situ* by reaction of the ligand with [Pd(Cp)(allyl)] (Cp = cyclopentadienyl), which triggers reductive elimination of allyl-Cp and generates the active catalyst ([LPd(0)]). Nozaki's 'BINAPHOS' ligand [(*R*,*S*)-**4a**][13] was identified as the most promising, 93/7 *iso*-**3**/*n*-**3**; 56% *ee* being attained at 70 °C.[12]



(*R*,*S*)-**4a**, R = H, Ar = Ph
(*R*,*S*)-**4b**, R = H, Ar = -C_6H_{5-n}-X_n
(*R*,*S*)-**4c**, R = Ph, Ar = Ph

More recently, Xu and Han reported that by using a bulky, electron-deficient 'Josiphos' type ligand, *iso*-**3** is generated in high regioselectivity (*iso*-**3**:*n*-**3** = 94:6) and good enantioselectivity (72.5% *ee*) under optimised conditions.[14]

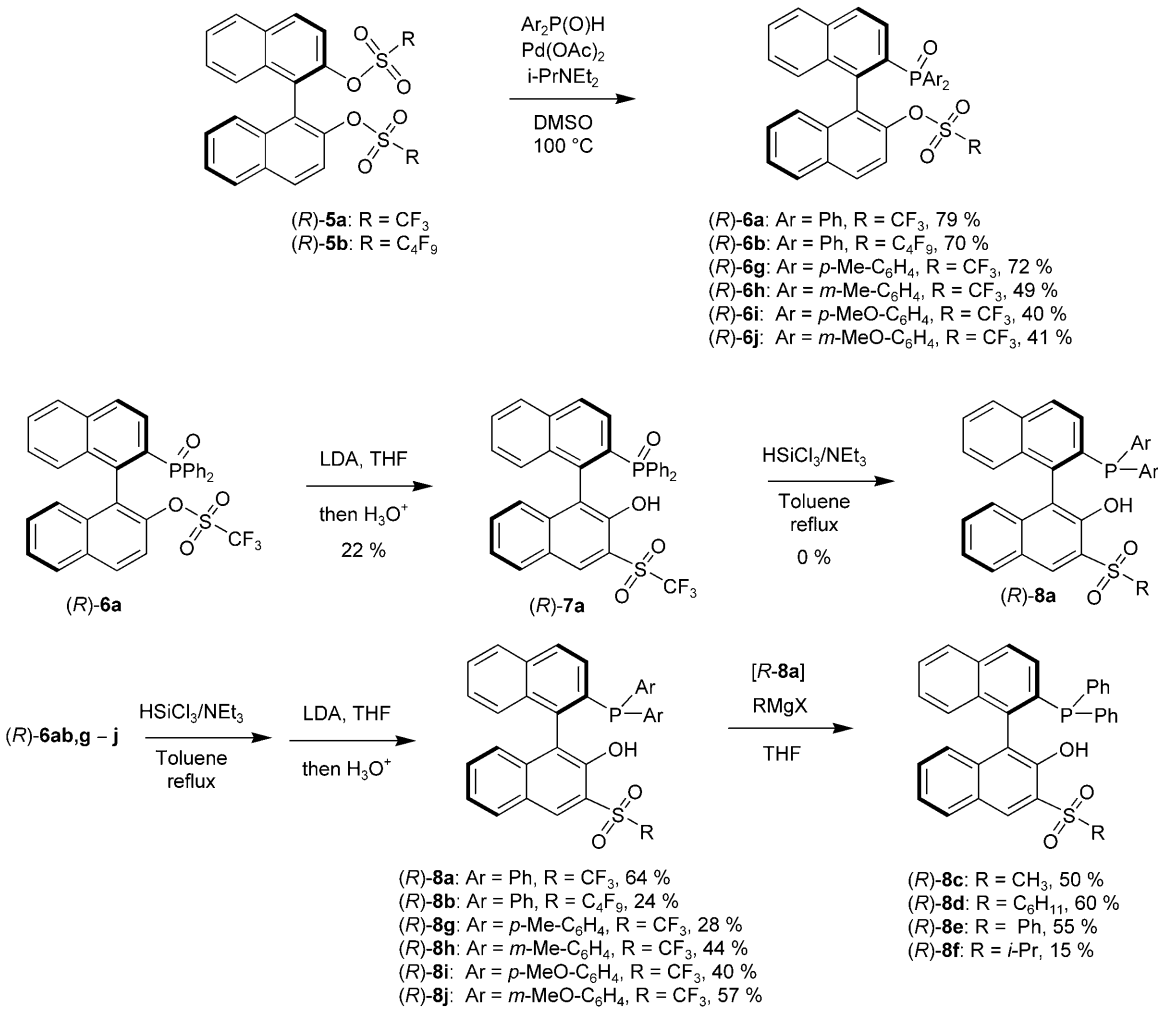
The phosphine-phosphite ligand (*R*,*S*)-**4a** [(*R*,*S*)-BINAPHOS] incorporating two axially chiral 2,2′-binaphthalene moieties, was developed by Nozaki for use in asymmetric rhodium-catalysed hydroformylation. The (*R*,*S*)-diastereoisomer was found to induce substantially greater enantioselectivity than the (*R*,*R*)-diastereoisomer with the configuration of the product being mainly dependent on the chirality of the binaphthalene-phosphine moiety, rather than the BINOL-derived phosphite.[13] The same diastereoisomer also proved to be an excellent ligand for Pd-catalysed alkene/CO copolymerisation[15] and, with fluorinated side chains, for asymmetric rhodium-catalysed alkene hydrogenation in supercritical carbon dioxide ($scCO_2$).[16] Later, it was shown that higher regioselectivity towards the branched aldehyde in the hydroformylation of styrenes could be achieved using (*R*,*S*)-BINAPHOS derivatives having substituted phenyl groups on the phosphine moiety [(*R*,*S*)-**4b**; X = 3-$(CH_2)_2(CF_2)_6F$,[17a] and 3-Me, 3-MeO, 3-*i*-PrO, 3,5-$(MeO)_2$, 4-Me, 4-MeO, 3-$(C_6F_{13})(CH_2)_2$-C_6H_4-[17b]] and that the presence of a perfluoroalkyl chain permits use of $scCO_2$ as solvent.[16,17a] Modification of the phosphine-bearing binaphthalene skeleton of BINAPHOS by addition of a phenyl group in the 3′ position [(*R*,*S*)-**4c**] also has a significant effect on the enantioselectivity in the Rh-catalysed hydrogenation of dehydroamino acids.[18] It was suggested that this arises from an increased rigidity of the ligand backbone.

We recently developed an LDA-mediated rearrangement of aryl perfluoroalkanesulfonates, which are converted at −78 °C in THF into 1-hydroxy-2-(perfluoroalkyl)aryl sulfones, after aqueous acidic work-up.[19] We have applied this 'anionic-thia Fries rearrangement'[20] in the synthesis of enantiomerically pure 3,3′-perfluoralkylsulfonyl-2,2′-dihydroxy-1,1′-binaphthelenes [3,3′-$(SO_2R^F)_2$-BINOLs] by way of a double rearrangement of BINOL bis-triflate (*R*)-**5a**.[21] These 3,3′-$(SO_2R^F)_2$-BINOLs have proven outstanding as catalysts for the indium-mediated asymmetric allylation of hydrazones (up to 99% *ee*), in contrast to their non-perfluorinated analogues.

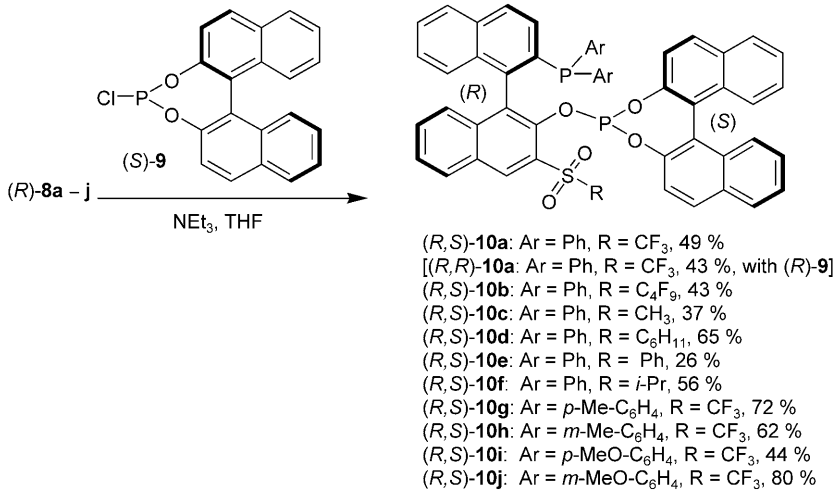
Herein, we report on the application of the anionic-thia Fries rearrangement in the synthesis of a series of 3′-sulfonyl BINAPHOS ligands. We have used the rearrangement to install a perfluoralkyl sulfone at the 3′-position of the naphthyl ring, with subsequent Grignard-mediated CF_3-displacement allowing further diversification. Unexpectedly, the diphenylphosphino moiety was found to substantially enhance the efficiency of the anionic-thia Fries rearrangement on the adjacent binaphthalene ring. We have also explored the effect of modification of the diphenylphosphino moiety in the parent 3′-trifluoromethanesulfonyl BINAPHOS ligand. These variations are shown to have substantial influence on the activity and selectivity of the resultant palladium complexes in asymmetric hydrophosphination of styrene.

Results and Discussion

The overall synthetic procedures developed to prepare the BINAPHOS ligands are outlined in Scheme 2 and Scheme 3. Palladium-catalysed monophosphorylation of 2,2′-bis-trifluoromethanesulfonyloxy-1,1′-binaphthalene [bis-triflate, (*R*)-**5a**] was carried out in high yield using the method of Hayashi.[22] Rearrangement of the trifluoromethanesulfonyloxy



Scheme 2. Synthetic route developed for the preparation of 3′-sulfonyl-bearing BINAPHOS precursors (*R*)-**8a–j**. See Experimental Section for full details.



Scheme 3. Coupling of 3′-sulfonyl-bearing BINAPHOS precursors *R*-**8a–j** (Scheme 2) with *S*-1,1′-binaphthalene-2,2′-dioxychlorophosphine (*S*-**9**), in the presence of NEt_3, to generate (*R*,*S*)-**10a–j**. The analogous procedure starting from *R*-**8a** but using *R*-**9** furnished (*R*,*R*)-**11a**, the diastereoisomer of (*R*,*S*)-**10a** in 43% yield. Selected NMR data for (*R*,*S*)-**10a–j** and (*R*,*R*)-**10a** are presented in Table 1.

group in the presence of the phosphine oxide proceeded in low yield (22%) to give (*R*)-**7a**. But all attempts to reduce the phosphine oxide (*R*)-**7a** to the corresponding phosphine (*R*)-**8a** failed, presumably because of the high reactivity of the phenolic OH group on the adjacent ring. However, reversing the sequence such that the phosphine oxide was reduced with Cl_3SiH first, without the trifluoromethanesulfonyloxy group being reduced or inhibiting reduction, and then the rearrangement conducted on the phosphine proceeded well. Moreover, the two steps could be successfully conducted without need for purification of the intermediate phosphine and furnished (*R*)-**8a** in 64% overall yield from (*R*)-**6a** (Scheme 2). Using the same strategy and starting from 2,2′-bisnonafluorobutanesulfonyloxy-1,1′-binaphthalene [(*R*)-**5b**], monophosphorylation followed by reduction gave the corresponding phosphine,[23] which underwent rearrangement to the 3′-perfluorobutanesulfone (*R*)-**8b** in overall 24% yield. The nucleofugacity of the trifluoromethyl moiety was exploited by reacting (*R*)-**8a** (unprotected) with an excess of Grignard reagent[24] (R = Me, *c*-Hex, Ph, *i*-Pr) to give a range of alkylsulfones (*R*)-**8cd/f** and a phenylsulfone (*R*)-**8e**. In addition, by use of aryl secondary phosphine oxides [$Ar_2P(O)H$] in place of $Ph_2P(O)H$ in the palladium-catalysed mono-phosphorylation step, four analogues [(*R*)-**8g–j**)] of (*R*)-**8a** were prepared from (*R*)-**5a**, *via* (*R*)-**6g–j**.

With the requisite 2′-hydroxy-3′-sulfonyl-2-diarylphosphine building blocks (*R*)-**8a–j** in hand, the BINAPHOS systems (*R,S*)-**10a–j**, in which modulation of the sulfone and phosphine moieties engenders differing steric and electronic properties, were readily generated by reaction with *S*-1,1′-binaphthalene-2,2′-dioxychlorophosphine [(*S*)-**9**][25] in the presence of NEt_3 (Scheme 3).

As elucidated in prior work on transition metal-catalysed reactions employing BINAPHOS, the isomer with opposite configurations at the two binaphthalene moieties (*R,S or S,R*), is the 'matched' diastereoisomer for hydroformylation (Rh), hydrogenation (Rh) and alkene-CO copolymerisation (Pd).[13,15,16] Since this may not be the case for hydrophosphorylation, we also prepared (*R,R*)-**10a** from (*R*)-**8a**, by an identical route, but employing *R*-1,1′-binaphthalene-2,2′-dioxychlorophosphine [(*R*)-**9**]. Selected NMR data for ligands **10a–j** are summarised in Table 1. Most of the ^{31}P chemical shifts are in the regions expected by comparison with the parent BINAPHOS ligands, (*R,S*)-**4a** and (*R,R*)-**4a**[13] the only exception being the chemical shift of the phosphite nucleus of (*R,R*)-**10a**, which is shifted 10 ppm to higher field than that in (*R,R*)-**4a**.[13] In addition to the coupling exhibited between the two ^{31}P nuclei, the three ^{19}F nuclei of the trifluoromethylsulfonyl group in (*R,S*)-**10a** also couple 'through-space'[26] to both the phosphine and the phosphite ^{31}P nuclei ($J = 7.7$, 2.3 Hz). This additional J_{PF} coupling makes extraction of J_{PP} troublesome and similar couplings are observed in the diarylphosphino derivatives (*R,S*)-**10g–j**. In contrast, the analogous coupling between the trifluoromethylsulfonyl group and the phosphite is absent in the (*R,R*)-**10a** diastereomer, with only a moderate coupling (4.5 Hz) observed with the, apparently more remote, phosphine. These data are indicative of substantially different

Table 1. Selected $^{31}P\{^1H\}$ NMR data (121 MHz, $CDCl_3$) for ligands **10a–j**.

Entry	Ligand	δ_P Ar_3P	δ_P $(ArO)_3P$	$J_{PP'}$ [Hz]	J_{FP} [Hz]
1	(*R,S*)-**4a**[a]	−13.3	146.2	29.0	–[b]
2	(*R,R*)-**4a**[a]	−12.7	145.8	9.2	–[b]
3	(*R,S*)-**10a**	−12.4[c]	142.5[c]	–[d]	7.7, 2.3
4	(*R,R*)-**10a**	−13.2	136.5	24.4	4.5[e]
5	(*R,S*)-**10b**	−12.7[c]	142.0	10.2	10.2,[f] 2.8,[f] 10.2,[g] 10.2 [g]
6	(*R,S*)-**10c**	−13.7	141.5	14.9	–[b]
7	(*R,S*)-**10d**	−13.3	141.6	29.8	–[b]
8	(*R,S*)-**10e**	−13.3	142.3	33.5	–[b]
9	(*R,S*)-**10f**	−12.7	142.3	18.6	–[b]
10	(*R,S*)-**10g**	−13.6[c]	142.5[c]	–[d]	8.4, 2.0
11	(*R,S*)-**10h**	−11.7[c]	140.5[c]	–[d]	7.5, 2.0
12	(*R,S*)-**10i**	−14.6[c]	141.1[c]	–[d]	9.7, 2.2
13	(*R,S*)-**10j**	−10.7[c]	140.5[c]	–[d]	6.5, 2.2

[a] Data for parent BINAPHOS ligands (*R,S*)-**4a** and (*R,R*)-**4a** taken from ref.[13], acquired at 109 MHz, $CDCl_3$.
[b] No J_{PF} feasible due to lack of CF_3SO_2 moiety.
[c] Chemical shift is midpoint of multiplet, see Experimental Section for multiplet width.
[d] J_{PP} unresolved.
[e] Coupling observed to phosphine only.
[f] Coupling of phosphite to diastereotopic fluorine nuclei in CF_2 group.
[g] Coupling of phosphine to diastereotopic fluorine nuclei in CF_2 group.

Table 2. Palladium-catalysed hydrophosphorylation of styrene (**1**) by pinacol phosphonate **2** to generate the 'branched' *sec*-phenethyl phosphonate (*iso*-**3**) and the 'linear' phenethyl phosphonate (*n*-**3**) hydrophosphorylation products (Scheme 1), using {L + [Pd(allyl)(Cp)]} as the *in situ* catalyst precursor.[a]

Entry	Ligand (L)	Conversion **2** [%][b]	*iso*-**3**/*n*-**3**[c]	*ee* of *iso*-**3** [%][c,d]
1	(*R*,*S*)-**4a**	99	89:11	42 (−)
2	(*R*,*S*)-**10a**	87	88:12	63 (−)
3[e]	(*R*,*S*)-**10a**	**28**	**88:12**	**72** (−)
4	(*R*,*S*)-**10c**	42	86:14	42 (−)
5	(*R*,*S*)-**10d**	16	88:12	34 (−)
6	(*R*,*S*)-**10e**	88	86:14	52 (−)
7	(*R*,*S*)-**10f**	69	69:31	28 (−)

[a] *Reaction conditions:* [Pd(allyl)(Cp)] = 5 mol%, L 5 mol%, styrene (**1**) 200 mol%, 1,4-dioxane, 100 °C, 35 h.
[b] Based on $^{31}P\{^{1}H\}$ NMR analysis of reaction mixture.
[c] Analysed by chiral HPLC (AD-H – 0.5 mL min^{-1} 95:5 heptane:ethanol, UV detection: 209 nm, 20 °C, t_1 = 27.8 min t_2 = 37.9 min.
[d] (−) and (+) indicates sign of optical rotation of major isomer of *iso*-**3** at the sodium D-line.
[e] Reaction conducted at 70 °C, 48 h.

spatial dispositions of the phosphine and phosphite moieties in the two diastereomers (*R*,*S*)- and (*R*,*R*)-**10a**.

The new Ph_2P-based 3′-sulfonyl BINAPHOS ligands (*R*,*S*)-**10a–f** were tested in the hydrophosphorylation of styrene (**1**) by pinacol phosphonate **2** (Scheme 1) using [Pd(allyl)(Cp)] as catalyst precursor under previously described conditions, so as to allow comparison (entries 2–7) with the results[12] obtained using the parent BINAPHOS (*R*,*S*)-**4a** ligand,[13] (entry 1, Table 2).

All of the ligands tested were able to generate active Pd hydrophosphorylation catalysts (Table 1, entries 2–7) and the presence and electronic/steric nature of the sulfone moiety was found to strongly modulate the catalyst activity and enantioselectivity. In contrast, the regioselectivity (*iso*-**3**/*n*-**3**) was essentially unaffected, except for ligand (*R*,*S*)-**10f** (entry 7) where the sulfone bears an isopropyl group. High conversions (87-88%) were obtained with the sulfones bearing electron-withdrawing CF_3 and Ph groups (entries 2 and 6), whereas catalyst activity was reduced somewhat by alkyl groups (Me, *c*-Hex, *i*-Pr, entries 4, 5 and 7). The presence of the electron-withdrawing CF_3 and Ph groups (entries 2 and 6) had a beneficial effect on the enantioselectivity, this being somewhat better than for the BINAPHOS ligand (*R*,*S*)-**4a** (42% *ee*, entry 1). Reducing the temperature from 100 °C to 70 °C had a beneficial effect on the enantioselectivity with the trifluoromethylsulfonyl ligand (*R*,*S*)-**10a**, increasing the *ee* of *iso*-**3** from 63 to 72%, with identical regioselectivity. The catalyst activity, however, was substantially reduced at lower temperature (entries 2 and 3). Based on this primary screening of the effect of sulfone, we chose to concentrate on the trifluoromethanesulfonyl systems (*R*,*S*)-**10a** and (*R*,*S*)-**g–j**.

The volatile and air-sensitive complex [Pd(allyl)(Cp)] is rather inconvenient to handle, and an alternative palladium catalyst precursor was sought. Since the [Pd(allyl)(Cp)] acts as a Pd(0) precursor by way of phosphine-phospite ligand-induced allyl-Cp reductive elimination, the readily prepared and air-stable $[(Pd(allyl)(CH_3CN)_2]^+$ cation was chosen for its ability to undergo rapid and quantitative alkylation by simple stabilised carbanions. Indeed, addition of one equivalent of sodium dimethylmalonate to the pre-ligated allyl cation allowed the reaction to run to completion in only 18 h instead of the 35 h required at the same palladium loading with [Pd(allyl)(Cp)] as pre-catalyst. The $[(Pd(allyl)(CH_3CN)_2]^+$ cation pre-catalyst system also induced good, albeit slightly reduced, selectivity for (−)-*iso*-**3**, (compare Table 3 entry 1 with Table 2 entry 2).

The (*R*,*S*)- and the (*R*,*R*)-diastereoisomers of the 3′-trifluoromethanesulfonyl-bearing BINAPHOS ligand **10a** gave very similar activity and regioselectivity. However, the (*R*,*R*)-diastereoisomer, which is the 'mis-matched' pairing of configurations for Rh-catalysed hydroformylation,[13] gave slightly higher enantioselectivity (Table 3 entries 1 and 2). Since the sense

Table 3. Palladium-catalysed hydrophosphorylation of styrene (**1**) by pinacol phosphonate **2** to generate the 'branched' *sec*-phenethyl phosphonate (*iso*-**3**) and the 'linear' phenethyl phosphonate (*n*-**3**) hydrophosphorylation products (Scheme 1), using $\{L + [Pd(allyl)(MeCN)_2][OTf] + [NaCH(CO_2Me)_2]\}$ as the *in situ* catalyst precursor.[a]

Entry	Ligand (L)	Conversion **2** [%][b]	*iso*-**3**/*n*-**3**[c]	*ee* of *iso*-**3**/%[c,d]
1	(*R*,*S*)-**10a**	94	84:16	61 (–)
2	(*R*,*R*)-**10a**	99	82:18	72 (–)
3[e]	(*R*,*S*)-**10a**	10	82:18	68 (–)
4	(*R*,*S*)-**10b**	96	87:13	62 (–)
5[e]	(*R*,*S*)-**10b**	5	87:13	66 (–)
6	(*R*,*S*)-**10g**	98	80:20	71 (–)
7	(*R*,*S*)-**10h**	99	89:11	72 (–)
8	(*R*,*S*)-**10i**	**99**	**76:24**	**74** (–)
9	(*R*,*S*)-**10j**	99	81:19	63 (–)

[a] *Reaction conditions:* $[Pd(allyl)(MeCN)_2][OTf]$, $[NaCH(CO_2Me)_2]$ and L, 5 mol%, styrene (**1**) 200 mol%, 1,4-dioxane, 100 °C, 18 h.
[b] Based on $^{31}P\{^{1}H\}$ NMR analysis of reaction mixture.
[c] Analysed by chiral HPLC (AD-H - 0.5 mL min^{-1} 95:5 heptane : ethanol, UV detection: 209 nm, 20 °C, t_1 = 27.8 min t_2 = 37.9 min.
[d] (–) and (+) indicates sign of optical rotation of major isomer of *iso*-**3** at the sodium D-line.
[e] Reaction conducted at 70 °C, 48 h.

of asymmetric induction, favouring (−)-*iso*-**3**, is identical for both diastereomers of **10a**, it is evident that, as with Rh-catalysed hydroformylation,[13] the configuration of the binaphthalene that bears the phosphine dominates in terms of enantiocontrol. Reducing the temperature of the reaction from 100 °C to 70 °C had an adverse effect on the activity of this system and afforded a less marked enhancement of enantioselectivity (entries 1 and 3); a similar effect was observed with the perfluorobutylsulfone ligand (*R,S*)-**10b** (entries 4 and 5), which offered no advantage over the trifluoromethanesulfonyl ligand (*R,S*)-**10a** and is less readily synthesised (Scheme 2 and Scheme 3).

Ligands (*R,S*)-**10g–j**, bearing *para* or *meta* substituents on the aryl rings of the phosphine moiety, provided enhanced reactivity and selectivity as compared to the diphenylphosphino system (*R,S*)-**10a**, (entries 6–9). Of note is the *para*-methoxy ligand (*R,S*)-**10i**, which provides quantitative conversion in less that 18 h at 100 °C and gave 74% *ee* (−) *iso*-**3** (entry 8). Within experimental error, this equals the highest enantioselectivity to date when compared with the value of 72.5% *ee iso*-**3** (80 °C, 90 h) reported by Xu and Han when employing a hindered Josiphos ligand.[14]

Conclusions

The BINAPHOS ligand [(*R*, *S*)-**4a**] of Nozaki[13] has been successfully modified in the 3′ position by way of an anionic thia-Fries rearrangement of perfluoroalkanesulfonates (CF_3 and C_4F_9) to afford perfluoroalkyl sulfones. Using the method of Steensma,[24] the CF_3 group of the trfluoromethylsulfone is readily substituted by Grignard reagents, without requirement for protection of the hydroxy group, allowing rapid access to a diverse range of BINAPHOS precurors. Ligands (*R,S*)-**10a**, **b** and (*R,R*)-**10a** which bear electron-withdrawing perfluoroalkyl groups on the 3′-sulfone moiety increase the enantioselectivity and activity of the system in the palladium-catalysed hydrophosphorylation of styrene (Scheme 1) as compared to the standard BINAPHOS ligand (*R,S*)-**4a**. Electron-donating alkyl substituents have a negative impact on both activity and selectivity. In contrast, adding electron-donating substituents to the *meta*- or *para*-positions of the non-naphthyl phosphine aryl rings (Ar_2P-Nap) has a beneficial effect on the enantioselectivity, affording (−)-*iso*-**3** in up to 74% *ee*, the highest value reported to date. In contrast to earlier uses of BINAPHOS, where the (*R,R*)-pairing of configurations is 'mis-matched', for the Pd-catalysed hydrophosphorylation of styrene this diastereomer is 'matched' and gives slightly enhanced asymmetric induction, again yielding (−)-*iso*-**3** as the major isomer. This is indicative that it is the configuration of the phosphine-bearing binaphathlene that is the major control element and that the BINOL could, in principle, be replaced by a tropoisomeric biphenol system. These results reinforce the concept that chiral phosphine-phosphite ligands are promising structures for the development of a highly efficient asymmetric hydrophosphorylation reaction of vinylarenes and that perfluoroalkylsulfone substituents offer unique opportunities for the modulation of the electronic and steric properties of aryl rings in ligand design.[21,27]

Experimental Section

General

Reactions were carried out under an inert atmosphere of nitrogen using solvents that had been dried using a nitrogen-pressurised alumina-column drying system from Anhydrous Engineering. Thin layer chromatography (TLC) was performed on silica gel Whatman-60F glass plates, and components were visualised by illumination with UV light (254 nm) or by staining with slightly acidic (H_2SO_4) potassium permanganate solution. Preparative (flash) chromatography was performed using E. Merck silica gel 60 (230–400 mesh). Analytical (chiral) HPLC was performed using a Chiralcel AD-H column, flow rate of eluant = 0.5 mL min^{-1} (95:5, heptane:ethanol), UV detection: 209 nm, 20 °C, retention time of enantiomers of *iso*-**3**: t_1 = 27.8 min t_2 = 37.9 min (configurations not assigned). NMR spectra were recorded in $CDCl_3$ on a Jeol 300 and 400 MHz spectrometers. ^{13}C and ^{31}P NMR was recorded using broad-band proton decoupling {^{1}H}. For ^{1}H NMR, chemical shifts are reported in δ relative to TMS (0.00 ppm); for ^{13}C NMR, chemical shifts are reported in δ relative to $CDCl_3$ (77.0 ppm); for ^{31}P NMR and ^{19}F NMR, chemical shifts are internally referenced and reported in δ relative to CCl_3F (0.00 ppm) and 85% H_3PO_4 (0.00 ppm). In most cases the ^{13}C{^{1}H} spectra exhibited dense populations of C_{Ar}-H and C_{Ar} signals in the aromatic region of the spectrum, made complex by diastereotopicity, C-F and C-P coupling. These spectra could not be reliably interpreted without access to ^{19}F/^{31}P decoupling. In appropriate cases, selected ^{13}C{^{1}H} signals are reported. Optical rotations were recorded on a JASCO-CIP-370 polarimeter. Low-resolution (MS) and high-resolution (HR-MS) mass spectra were obtained using positive ion FAB (FAB$^+$), chemical (CI$^+$), electron impact (EI) or electrospray (ESI) ionisation methods, as indicated, and were obtained at the Mass Spectrometry Laboratory at the University of Bristol School of Chemistry. Melting points were determined without correction.

(*R*)-2-[Di(*p*-tolyl)phosphinooxide]-2′-(trifluoromethanesulfonyloxy)-1,1′-binaphthalene (*R*)-6g

Prepared in 72% yield employing the same procedure as for (*R*)-**6j** (see below) but using (*p*-tolyl)$_2$P(O)H; mp 94–96 °C; $[\alpha]_D^{21}$: +10 (*c* 0.6, dichloromethane); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.30 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 7.00–7.07 (m, 4H), 7.15–7.20 (m , 2H), 7.38- 7.28 (m, 7H), 7.45–7.41 (m, 1H), 7.57–7.53 (m, 1H), 7.76–7.71 (m, 1H), 7.82 (d, *J* =

8.3 Hz, 1 H), 7.94–7.89 (m, 2 H), 8.01 (dd, $J = 8.6$, 2.0 Hz, 1 H); $^{13}C\{^1H\}$ NMR (72 MHz, $CDCl_3$, selected peaks): $\delta =$ 21.6 (s, 2 × CH_3), 118 .1 (q, $J = 321$ Hz, CF_3); $^{31}P\{^1H\}$ NMR (121 MHz, , $CDCl_3$): $\delta = 29.3$ {s, [ArP(O)(*p*-tolyl)$_2$]}; $^{19}F\{^1H\}$ NMR (282 MHz, $CDCl_3$): $\delta = -74.9$ (s, CF_3); IR: $\nu_{max} = 2925$, 1737, 1601, 1501, 1415, 1207, 1137, 1114, 1098, 1061 cm^{-1}; MS (CI^+): $m/z = 631$ $(M+H)^+$, 499, 481, 406; HR-MS (CI^+): $m/z = 631.1304$, calcd. for $(M+H)^+$: 631.1320.

(*R*)-2-[Di(*m*-tolyl)phosphinooxide)-2′-(trifluoromethanesulfonyloxy)-1,1′-binaphthalene (*R*)-6h

Prepared in 49% yield employing the same procedure as for (*R*)-**6j** but using (*m*-tolyl)$_2$P(O)H; mp 84–86 °C; $[\alpha]_D^{22}$: +17 (*c* 0.6, dichloromethane); ^1H NMR (400 MHz, $CDCl_3$): $\delta =$ 2.21 (s, 3 H), 2.21 (s, 3 H), 7.04 (d, $J = 8.4$ Hz, 1 H), 7.08–7.34 (m, 13 H), 7.43 (t, $J = 7.3$ Hz, 1 H), 7.56 (t, $J = 7.3$ Hz, 1 H), 7.75–7.70 (m, 1 H), 7.95–7.83, (m, 3 H), 8.01 (dd, $J = 8.6$, 2.0 Hz); $^{13}C\{^1H\}$ NMR (72 MHz, $CDCl_3$, selected peaks): $\delta =$ 21.4 (s, 2×CH_3), 118.2 (q, $J = 320$ Hz, CF_3); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta = 29.3$ {s, [ArP(O)(*m*-tolyl)$_2$]}; $^{19}F\{^1H\}$ NMR (282 MHz, $CDCl_3$): $\delta = -74.8$ (s, CF_3); IR: $\nu_{max} = 3053$, 1925, 2854, 1739, 1583, 1415, 1248, 1198, 1137, 1114, 1087, 955, 940 cm^{-1}; MS (CI^+): $m/z = 631$ $(M+H)^+$, 531, 481, 406; HR-MS (CI^+): $m/z = 631.1339$, calcd. for $(M+H)^+$: 631.1320.

(*R*)-2-[di(*p*-anisyl)phosphinooxide]-2′-(trifluoromethanesulfonyloxy)-1,1′-binaphthalene (*R*)-6i[28]

Prepared in 40% yield employing the same procedure as for (*R*)-**6j** but using (*p*-anisyl)$_2$P(O)H and was spectroscopically identical (^1H, $^{31}P\{^1H\}$, and $^{19}F\{^1H\}$ NMR) to the compound reported by Pozzi and Sinou.[28]

(*R*)-2-[Di(3-anisyl)phosphinooxide]-2′-(trifluoromethanesulfonyloxy)-1,1′-binaphthalene (*R*)-6j[29]

(*R*)-**5a** (3.18 g, 5.78 mmol), (*m*-anisyl)$_2$P(O)H (3.03 g, 11.56 mmol), $Pd(OAc)_2$ (0.13 g, 0.58 mmol), DPPB (0.25 g, 0.58 mmol), and *N,N*-diisopropylethylamine (3.03 mL, 17.34 mmol) were dissolved in degassed DMSO (10 mL) and heated to 120 °C overnight. The reaction mixture was then cooled to room temperature and quenched with water. The reaction was extracted three times with diethyl ether and washed with 10% HCl and brine. The organic phase was dried over magnesium sulfate and the solvent evaporated to give the crude product. This was purified by column chromatography with 100% ethyl acetate on silica to give the product as white friable solid; yield: 1.58 g (41%); mp 86–90 °C; $[\alpha]_D^{24}$: +22 (*c* 1, dichloromethane). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 3.61$ (s, 3 H), 3.66 (s, 3 H), 6.82–7.23 (m, 13 H), 7.27–7.34 (m, 1 H), 7.35–7.44 (m, 2 H), 7.55 (t, $J =$ 7.5 Hz, 3 H), 8.00 (dd, $J = 8.6$, 2.2 Hz, 1 H); $^{13}C\{^1H\}$ NMR (72 MHz, $CDCl_3$, selected peaks): $\delta = 55.3$ (s, OMe), 55.3 (s, OMe); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta = 28.5$ [s, ArP(O)(*m*-anisyl)$_2$]; $^{19}F\{^1H\}$ NMR (282 MHz, $CDCl_3$): $\delta =$ −74.9 (s, CF_3); IR: $\nu_{max} = 3059$, 2935, 1589, 1576, 1483, 1414, 1248, 1203, 1137, 1039 cm^{-1}; MS (CI^+): m/z = 662 $(M+H)^+$, 512, 469, 315; HR-MS (CI^+): $m/z = 663.1215$, calcd. for $(M+H)^+$: 663.1218.

(*R*)-2-(Diphenylphosphino)-2′-hydroxy-3′-trifluoromethanesulfonyl-1,1′-binaphthalene (*R*)-8a

To a stirred solution of (*R*)-**6a**[22] (3.50 g, 5.81 mmol), and triethylamine (5.32 mL, 40.69 mmol) in degassed toluene (75 mL) at room temperature was added trichlorosilane (2.93 mL, 29.05) dropwise. The reaction was then heated to reflux and monitored by ^{31}P NMR until the signal from the substrate (12.7 ppm) had disappeared (*ca.* 5 h). The reaction was then quenched with a saturated solution of sodium hydrogen carbonate, dried over anhydrous magnesium sulfate and filtered through Celite (washing through with diethyl ether). The solvent was removed under vacuum and the residue re-dissolved in anhydrous THF (20 mL). This solution was then added dropwise to a solution of LDA [diisopropylamine (0.87 mL, 6.38 mmol) dissolved in THF (20 mL), cooled to −78 °C] and then *n*-butyllithium (2.47 mL, 6.38 mmol) was added at −78 °C, then stirred for 1 h, cooled to −78 °C, resulting in a bright yellow solution that then darkened to near-black. The reaction was allowed to warm to room temperature over 2 h, quenched with 10% HCl solution and extracted three times with dichloromethane. The organic phase was washed with HCl and brine solution before drying over magnesium sulfate, filtering and removing the solvent under vacuum. The residue was purified by column chromatography on silica gel (30% ethyl acetate, 70% hexane) to give the product as an off-white friable solid; 2.18 g (64% yield after 2 steps); mp 182 °C (dec.); $[\alpha]_D^{20}$: −36.2 (*c* 1.82, dichloromethane). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 6.93$ (d, $J = 8.6$ Hz, 1 H), 7.09–7.03 (m 1 H), 7.54–7.13 (m, 16 H), 7.98–7.91 (m, 3 H), 8.63 (s, 1 H); $^{13}C\{^1H\}$ NMR (72 MHz, $CDCl_3$, selected peaks): $\delta = 120.1$ (q, $J =$ 326.5, CF_3); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta = -12.2$ (q, $J = 2.7$ Hz, $ArPPh_2$); $^{19}F\{^1H\}$ NMR (282 MHz, $CDCl_3$): $\delta =$ −78.2 (d, $J = 2.7$ Hz, 3 F); IR: $\nu_{max} = 3429$, 3053, 2538, 1621, 1288, 1203, 1149, 1115, 1070, 1008 cm^{-1}; MS (CI^+): $m/z =$ 587 $(M+H)^+$, 575, 508, 453; HR-MS (CI^+): m/z = 587.1040, calcd. for $(M+H)^+$: 587.1058.

(*R*)-2-(Diphenylphosphino)-2′-hydroxy-3′-perfluorobutanesulfonyl-1,1′-binaphthalene (*R*)-8b

As for (*R*)-**8a**, but starting from perfluorobutanesulfonate (*R*)-**6b**[23] gave (*R*)-**8b**; yield: 24%; mp 76 °C (dec.); $[\alpha]_D^{20}$: +12 (*c* 0.9, dichloromethane). ^1H NMR: $\delta = 6.97$ (d, $J =$ 8.7 Hz, 1 H), 7.06–7.55 (m, 17 H), 7.92–8.01 (m, 3 H), 8.61 (s, 1 H); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta = -12.4$ (s, $ArPPh_2$); $^{19}F\{^1H\}$ NMR (282 MHz, $CDCl_3$): $\delta = -80.5$ (t, $J =$ 9.8 Hz, 3F), −111.3 (m, 2F), 120.7 (m, 2F), 125.7 (m, 2F); IR: $\nu_{max} = 3430$, 3057, 1288, 1203, 1149, 1115, 1070, 1008 cm^{-1}; MS (EI^+): $m/z = 736$ (M^+), 719, 550, 517; HR-MS (EI^+): $m/z = 736.0883$, calcd. for $(M)^+$: 736.0908.

(*R*)-2-(Diphenylphosphino)-2′-hydroxy-3′-methanesulfonyl-1,1′-binaphthalene (*R*)-8c

(*R*)-**8a** (0.3 g, 0.51 mmol) was dissolved in degassed THF (5 mL) and cooled to 0 °C. Methylmagnesium bromide solution (2.96 M in THF, 1.04 mL, 3.08 mmol) was added dropwise and the reaction left to stir overnight. The reaction was quenched with 10% HCl solution and extracted 3 times with diethyl ether. The organic phase was washed with HCl solution and brine before drying over magnesium sulfate. After

filtration, the solvent was removed under vacuum and the residue purified by column chromatography on silica gel (30% diethyl ether, 70% hexane) to afford (*R*)-**8c** as a white friable solid; yield: 0.25 g (46%); mp 126 °C (dec.); $[\alpha]_D^{20}$: +21 (*c* 0.9, dichloromethane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.96 (s, 3H), 7.52–6.93 (m, 18H), 7.96–7.89 (m, 3H), 8.54 (s, 1H); ^{13}C{^{1}H} NMR (72 MHz, $CDCl_3$, selected peaks): δ = 44.2 (s, CH_3); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = −12.2 (s, $ArPPh_2$); IR: ν_{max} = 3320, 3052, 2925, 2519, 1621, 1585, 1432, 1291, 1117, 1010 cm^{-1}; MS (CI$^+$): *m/z* = 533 $(M+H)^+$, 513, 453; HR-MS (CI$^+$): m/z = 533.1331, calcd. for $(M+H)^+$: 533.1340.

(*R*)-2-(diphenylphosphino)-2′-hydroxy-3′-cyclohexanesulfonyl-1,1′-binaphthalene (*R*)-8d

Using an identical procedure to that employed for (*R*)-**8c**, but with *c*-HexMgCl in place of MeMgBr gave (*R*)-**8d**; yield: 60%; mp 110 °C (dec.); $[\alpha]_D^{20}$: +6 (*c* 2.17, dichloromethane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.83–2.11 (m, 10H), 2.96 (tt, *J* = 8.8 Hz, 3.3 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 7.08–7.39 (m, 15H), 7.50 (t, *J* = 7.0 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.87–7.95 (m, 3H), 8.42 (1H, s), 8.49 (s, 1H); ^{13}C NMR (72 MHz, $CDCl_3$, selected peaks): δ = 64.9 (s, C-SO_2Ar); ^{31}P NMR (121 MHz, $CDCl_3$): δ = −12.6 (s, $ArPPh_2$); IR: ν_{max} = 3673, 3054, 2931, 2855, 1621, 1451, 1295, 1113 cm^{-1}; MS (CI$^+$): *m/z* = 601 $(M+H)^+$, 533, 470, 454; HR-MS (CI$^+$): m/z = 601.1947 calcd. for $(M+H)^+$: 601.1966.

(*R*)-2-(Diphenylphosphino)-2′-hydroxy-3′-benzenesulfonyl-1,1′-binaphthalene (*R*)-8e

Using an identical procedure to that employed for (*R*)-**8c**, but with PhMgCl in place of MeMgBr gave (*R*)-**8e**; yield: 55%; M. p. 86 °C (dec.); $[\alpha]_D^{20}$: +20 (*c* 1.71, dichloromethane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.95 (d, *J* = 8.7 Hz, 1H), 7.00–7.56 (m, 20H), 7.92–7.85 (m, 4H), 8.44 (s, 1H), 8.53 (s, 1H); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = −12.5 (s, $ArPPh_2$); IR: ν_{max} = 3663, 3321, 3054, 2854, 1739, 1621, 1584, 1497, 1432, 1366, 1288, 1216, 1132, 1086 cm^{-1}; MS (CI$^+$): *m/z* = 595 $[MH]^+$, 577, 517, 453; HR-MS (CI$^+$): *m/z* = 595.1492, calcd. for $(M+H)^+$: 595.1497.

(*R*)-2-(Diphenylphosphino)-2′-hydroxy-3′-isopropylsulfonyl-1,1′-binaphthalene (*R*)-8f

Using an identical procedure to that employed for (*R*)-**8c**, but with *i*-PrMgCl in place of MeMgBr gave (*R*)-**8f**; yield: 15%; mp 132 °C (dec.); $[\alpha]_D^{20}$: +9 (*c* 1.93, dichloromethane); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.24–1.27 (m, 3H), 1.27–1.29 (m, 3H), 3.04–3.22 (m, 1H), 7.01 (d, *J* = 8.6 Hz, 1H), 7.05–7.16 (m, 2H), 7.16–7.44 (m, 12H), 7.46–7.59 (m, 1H), 7.83–8.04 (m, 3H), 8.39 (s, 1H), 8.47 (s, 1H); ^{13}C{^{1}H} NMR (72 MHz, $CDCl_3$, selected peaks); δ = 15.0 (s, CH_3), 15.3 (s, CH_3), 56.9 [s, $CH(CH_3)_2$]; ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = −12.6 (s, $ArPPh_2$); IR: ν_{max} = 3286, 3016, 2971, 1738, 1622, 1366, 1229, 1217 cm^{-1}; MS (CI$^+$): *m/z* = 561 $(M+H)^+$, 533, 453; HR-MS (CI$^+$): *m/z* = 561.1650, calcd. for $(M+H)^+$: 561.1653.

(*R*)-2-[Di(*p*-tolyl)phosphino]-2′-hydroxy-3′-trifluoromethanesulfonyl-1,1′-binaphthalene (*R*)-8g

As for (*R*)-**8a**, but starting from (*R*)-**6g** gave (*R*)-**8g**; yield: 28%; mp 112 °C (dec.); $[\alpha]_D^{19}$: −44 (*c* 0.5, dichloromethane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.29 (s, 3H), 2.34 (s, 3H), 6.87–7.04 (m, 3H), 7.05–7.20 (m, 5H), 7.23–7.58 (m, 7H), 7.47–7.56 (m, 1H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.97 (d, *J* = 8.2 Hz, 1H), 8.63 (s, 1H); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = −13.4 [q, *J* = 2.7 Hz, $ArP(p\text{-tolyl})_2$]; ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): δ = −78.2 (d, *J* = 2.7 Hz, CF_3); IR: ν_{max} = 3061, 2920, 1707, 1601, 1578,1556,1501, 1450, 1356, 1204, 1114, 1084, 1005 cm^{-1}; MS (EI$^+$): *m/z* = 614 $(M)^+$, 498, 481, 400; HR-MS (EI): *m/z* = 614.1280, calcd. for (M^+): 614.1292.

(*R*)-2-[Di(*m*-tolyl)phosphino]-2′-hydroxy-3′-trifluoromethanesulfonyl-1,1′-binaphthalene (*R*)-8h

As for (*R*)-**8a**, but starting from (*R*)-**6h** gave (*R*)-**8h**; yield: 44%; mp 93 °C (dec.); $[\alpha]_D^{19}$: 33 (*c* 0.5, dichloromethane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.17 (s, 3H), 2.28 (s, 3H), 6.78–6.94 (m, 3H), 6.97–7.56 (m, 13H), 7.93 (d, *J* = 8.4 Hz, 2H), 7.97 (d, *J* = 8.2 Hz, 1H), 8.32 (s, 1H); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = −11.6 [q, *J* = 2.7 Hz, $ArP(m\text{-tolyl})_2$]; ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): δ = −78.1 (d, *J* = 2.7 Hz, CF_3); IR: ν_{max} = 3453, 2921, 1708, 1617, 1578, 1450, 1356, 1204, 1113, 1082, 1006 cm^{-1}; MS (EI$^+$): *m/z* = 614 $(M)^+$, 597, 481, 465, 400; HR-MS (EI): *m/z* = 614.1278, calcd. for (M^+): 614.1292.

(*R*)-2-[Di(*p*-anisyl)phosphino]-2′-hydroxy-3′-trifluoromethanesulfonyl-1,1′-binaphthalene (*R*)-8i

As for (*R*)-**8a**, but starting from (*R*)-**6i** gave (*R*)-**8i**; yield: 40%; mp 120 °C (dec.); $[\alpha]_D^{19}$: 56 (*c* 0.5, dichloromethane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.65 (s, 3H), 3.71 (s, 3H), 6.64–6.90 (m, 4H), 6.94 (d, *J* = 8.4 Hz, 1H), 7.05–7.61 (m, 11H), 7.87–8.05 (m, 3H), 8.66 (s, 1H); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = −14.7 [q, *J* = 2.7 Hz, $ArP(p\text{-anisyl})_2$]; ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): δ = −78.1 (d, *J* = 2.7 Hz, CF_3); IR: ν_{max} = 3439, 3015, 1739, 1621, 1593, 1497, 1365, 1283, 1245, 1204, 1176, 1115, 1094 cm^{-1}; MS (CI$^+$): m/z = 647 $(M+H)^+$, 595, 539, 431; HR-MS (CI): m/z = 647.1259, calcd. for $(M+H^+)$: 647.1269.

(*R*)-2-[Di(*m*-anisyl)phosphino]-2′-hydroxy-3′-trifluoromethanesulfonyl-1,1′-binaphthalene (*R*)-8j

As for (*R*)-**8a**, but starting from (*R*)-**6j** gave (*R*)-**8j**; yield: 57%; mp 80 °C (dec.); $[\alpha]_D^{19}$: 33 (*c* 0.5, dichloromethane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.64 (s, 3H), 3.71 (s, 3H), 6.56–6.64 (m, 1H), 6.65–6.89 (m, 4H), 6.94 (d, *J* = 8.4 Hz, 1H), 7.04–7.63 (m, 10H), 7.88–8.05 (m, 3H), 8.66 (s, 1H); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = −10.5 [q, *J* = 2.7 Hz, $ArP(m\text{-anisyl})_2$]; ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): δ = −78.1 (d, *J* = 2.7 Hz, CF_3); IR: ν_{max} = 3428, 3059, 2939,2836, 1705, 1620, 1575, 1481, 1462, 1421, 1352, 1286, 1203, 1151, 1115, 1040 cm^{-1}; MS (CI$^+$): *m/z* = 647 $(M+H)^+$, 646, 629, 514, 497, 400; HR-MS (EI): *m/z* = 646.1176, calcd. for (M^+): 646.1191.

(*R,S*)-2′-Trifluoromethanesulfonyl-BINAPHOS (*R,S*)-10a

(*R*)-**8a** (0.33 g, 0.56 mmol) and (*S*)-**9**[25] (0.4 g , 1.24 mmol) were dissolved in THF (3 mL) and cooled to 0 °C. Triethylamine (0.23 mL, 1.78 mL) was then added drop-wise at such a rate that the yellow colour which appeared on addition of each drop had disappeared before the next drop was added. After complete addition, the mixture was stirred for 2 h, allowed to warm to room temperature, filtered through Celite and the solvent evaporated. The residue was purified by column chromatography (50% dichloromethane, 50% hexane) on silica-gel to give (*R,S*)-**10a** as a white friable solid; yield: 0.25 g (49%; mp 174 °C (dec.); $[\alpha]_D^{21}$: +139 (*c* 1.5, dichloromethane); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.66 (d, *J* = 8.8 Hz, 1H), 6.08–6.25 (m, 2H), 6.64 (t, *J* = 7.5 Hz, 1H), 6.71 (t, *J* = 7.1 Hz, 1H), 6.76–6.87 (m, 2H), 6.95–7.15 (m, 3H), 7.14–7.60 (m, 14H), 7.65 (d, *J* = 8.8 Hz, 1H), 7.69–7.77 (m, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.88 (d, *J* = 8.8 Hz, 1H), 7.91–8.00 (m, 2H), 8.06 (d, *J* = 8.1 Hz, 1H), 8.12 (d, *J* = 8.1 Hz, 1H), 8.96 (s, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, selected peaks): δ = 120.18 (q, *J* = 327 Hz, CF_3); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = −12.3–12.6 (m, 1P, $ArPPh_2$) 142.4–142.5 [m, 1P, $(ArO)_2POAr'$]; ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): δ = −76.2 (dd, *J* = 7.7, 2.3 Hz, CF_3); IR: ν_{max} = 3053, 2960, 1618, 1576, 1367, 1208, 1154, 1119, 1070, 941 cm^{-1}; MS (ESI$^+$): *m/z* = 923 $(M+Na)^+$, 901 $(M+H)^+$, 641, 569, 467; HR-MS (ESI$^+$): *m/z* = 901.1579, calcd. for $(M+H)^+$: 901.1554.

(*R,R*)-2′-Trifluoromethanesulfonyl-BINAPHOS (*R,R*)-10a

(*R*)-**8a** was reacted with (*R*)-**9**[25] following an identical procedure to that employed for (*R,S*)-**10a** to give the diatereomeric ligand (*R,R*)-**10a**; yield: 43%; mp 183 °C (dec.); $[\alpha]_D^{21}$: 96 (*c* 1.2, dichloromethane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.57 6.50 (d, *J* = 9.0, 1H), 6.55 (d, *J* = 8.6 Hz, 1H), 6.81–7.55 (m, 22H), 7.66 (d, *J* = 8.8 Hz, 1H), 7.73 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.78–7.93 (m, 3H), 7.98 (d, *J* = 8.2 Hz, 2H), 8.18 (d, *J* = 8.6 Hz, 1H), 8.95 (s, 1H); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = −13.2 (dq, *J* = 24.4, 4.5 Hz, 1P, $ArPPh_2$), 136.5 [d, *J* = 24.4, 1P, $(ArO)_2POAr'$)]; ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): δ = −75.8 (dd, *J* = 4.5 Hz, CF_3); IR: ν_{max} = 3053, 2960, 1618, 1576, 1367, 1208, 1154 cm^{-1}; MS (ESI$^+$): *m/z* = 901 $(M+H)^+$, 641, 569, 467; HR-MS (ESI$^+$): *m/z* = 901.1563, calcd. for $(M+H)^+$: 901.1554.

(*R,S*)-2′-Perfluorobutanesulfonyl-BINAPHOS (*R,S*)-10b

(*R*)-**8b** was reacted with (*S*)-**9** following an identical procedure to that employed for (*R,S*)-**10a** to give (*R,S*)-**10b**; yield: 43%; mp 146 °C (dec.); $[\alpha]_D^{22}$: +120 (*c* 0.6, dichloromethane, 22 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.68 (d, *J* = 8.8 Hz, 1H), 6.07–6.31 (m, 2H), 6.64 (t, *J* = 7.5 Hz, 1H), 6.70–6.88 (m, 4H), 6.92–7.05 (m, 2H), 7.05–7.14 (m, 1H), 7.16–7.54 (m, 13H), 7.65 (d, *J* = 8.8 Hz, 1H), 7.69–7.84 (m, 3H), 7.96–8.10 (m, 4H), 8.95 (s, 1H); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = −12.6–12.8 (m, 1P, $ArPPh_2$), 142.0 [td, *J* = 10.2, 2.8 Hz, 1P, $(ArO)_2POAr'$)]; ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): δ = −125.6–125.8 (m, 2F, CF_AF_B), −120.3–120.8 (m, 2F, (m, 2 F, CF_AF_B), −108.2–111.8 (m, 2F, (m, 2 F, CF_AF_B), −80.4 (t, *J* = 9.7 Hz, 3F, CF_3); IR: ν_{max} = 3058, 2962, 1620, 1579, 1465, 1437, 1350, 1234, 1171, 1138, 1116, 1028, 965 cm^{-1}; MS (ESI$^+$): *m/z* = 1083 $(M+HO_2)^+$, 791, 775, 753, 301; HR-MS (ESI$^+$): *m/z* = 1083.1368, calcd. for $(M+HO_2)^+$: 1083.1357.

(*R,S*)-2′-Methanesulfonyl-BINAPHOS (*R,S*)-10c

(*R*)-**8c** was reacted with (*S*)-**9** following an identical procedure to that employed for (*R,S*)-**10a** to give (*R,S*)-**10c**; yield: 37%; mp 168 °C (dec.); $[\alpha]_D^{22}$: +155 (*c* 1.1, dichloromethane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.03 (s, 3H), 5.99 (d, *J* = 8.8 Hz, 1H), 6.33 (t, *J* = 7.5 Hz, 2H), 6.63 (t, *J* = 7.3 Hz, 1H), 6.79 (t, *J* = 6.8 Hz, 2H), 6.85–7.55 (m, 18H), 7.63–7.85 (m, 4H), 7.92 (d, *J* = 8.1 Hz, 1H), 8.01 (dd, *J* = 8.2, 3.1 Hz, 2H), 8.12 (d, *J* = 8.4 Hz, 1H), 8.80 (s, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, selected peaks): δ = 43.52 (s, CH_3); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = −13.7 (d, *J* = 14.9 Hz, 1P, $ArPPh_2$), 141.5 [d, *J* = 14.9 Hz, 1P, $(ArO)_2POAr'$)]; IR: ν_{max} = 3054, 2927, 1618, 1581, 1500, 1309, 1200, 1135, 1069, 938 cm^{-1}; MS (ESI$^+$): *m/z* = 869 $(M+Na)^+$, 847 $(M+H)^+$, 653, 571, 547, 515; HR-MS (ESI$^+$): *m/z* = 869.1680, calcd. for $(M+Na)^+$: 869.1656.

(*R,S*)-2′-Cyclohexanesulfonyl-BINAPHOS (*R,S*)-10d

(*R*)-**8d** was reacted with (*S*)-**9** following an identical procedure to that employed for (*R,S*)-**10a** to give (*R,S*)-**10d**; yield: 65%; mp 142 °C (dec.); $[\alpha]_D^{22}$: +170 (*c* 2.8, dichloromethane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.56–2.17 (m, 8H), 2.61 (m, 1H), 3.29–3.68 (m, 1H), 3.63–3.93 (m, 1H), 5.87 (d, *J* = 8.8 Hz, 1H), 6.34 (t, *J* = 6.8 Hz, 2H), 6.59–8.34 (m, 29H), 8.84 (s, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, selected peaks): δ = 14.32 (s, CH_2), 15.41 (s, CH_2), 25.39 (s, CH_2), 25.71 (s, CH_2), 34.77 (s, CH_2), 43.55 (s, CH); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = −13.3 (d, *J* = 29.8 Hz, 1P, $ArPPh_2$), 141.6 [d, *J* = 29.8 Hz, 1P, $(ArO)_2POAr'$)]; IR: ν_{max} = 3054, 292, 2856, 1710, 1618, 1579, 1503, 1463, 1433, 1308, 1191, 1069, 939 cm^{-1}; MS (ESI$^+$): *m/z* = 937 $(M+Na)^+$, 915 $(M+H)^+$, 301; HR-MS (ESI$^+$): *m/z* = 915.2478, calcd. for $(M+H)^+$: 915.2463.

(*R,S*)-2′-Benzenesulfonyl-BINAPHOS (*R,S*)-10e

(*R*)-**8e** was reacted with (*S*)-**9** following an identical procedure to that employed for (*R,S*)-**10a** to give (*R,S*)-**10e**; yield: 26%; mp 84 °C (dec.); $[\alpha]_D^{22}$: +170 (*c* 1.9, dichloromethane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.36 (t, *J* = 9.3 Hz, 2H), 6.53 (t, *J* = 7.0 Hz, 2H), 6.68 (d, *J* = 8.4 Hz, 1H), 6.76–7.09 (m, 9H), 7.09–7.55 (m, 14H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.82–8.12 (m, 7H), 8.99 (s, 1H); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = −13.3 (d, *J* = 33.5 Hz, 1P, $ArPPh_2$), 142.3 [d, *J* = 33.5 Hz, 1P, $(ArO)_2POAr'$)]; IR: ν_{max} = 3054, 2927, 1618, 1581, 1500, 1309, 1201, 1191, 1130, 1069, 938 cm^{-1}; MS (ESI$^+$): *m/z* = 931 $(M+Na)^+$ 931, 909 $(M+H)^+$, 308; HR-MS (ESI$^+$): *m/z* = 931.1820, calcd. for $(M+Na)^+$: 931.1813.

(*R,S*)-2′-(1″-Methylethane)sulfonyl-BINAPHOS (*R,S*)-10f

(*R*)-**8f** was reacted with (*S*)-**9** following an identical procedure to that employed for (*R,S*)-**10a** to give (*R,S*)-**10f**; yield:

56%; mp 122 °C (dec.); $[\alpha]_D^{22}$: +193 (*c* 1.9, dichloromethane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.19 (d, *J* = 6.6 Hz, 3H), 1.58 (d, *J* = 7.0 Hz, 3H), 3.53–3.66 (m, 1H), 6.10 (d, *J* = 8.8 Hz, 1H), 6.32 (t, *J* = 7.0 Hz, 2H), 6.62 (t, *J* = 7.3 Hz, 1H), 6.70–7.55 (m, 20H), 7.60–8.13 (m, 8H), 8.84 (s, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, selected peaks): δ = 14.23 (s, CH_3), 16.90 (s, CH_3), 53.52 (s, CH); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = −12.7 (d, *J* = 18.6 Hz, 1P, $ArPPh_2$), 142.3 [d, *J* = 18.6 Hz, 1P, $(ArO)_2POAr'$)]; IR: ν_{max} = 3054, 2927, 1618, 1581, 1500, 1309, 1201, 1191, 1130, 1069, 938 cm^{-1}; MS (ESI$^+$): *m/z* = 897 $(M+Na)^+$, 875 $(M+H)^+$, 575, 301; HR-MS (ESI$^+$): *m/z* = 897.2005, calcd. for $(M+Na)^+$: 897.1969.

(*R,S*)-2′-Trifluoromethanesulfonyl-[*P*(*p*-tolyl)$_2$]-BINAPHOS (*R,S*)-10g

(*R*)-**8h** was reacted with (*S*)-**9** following an identical procedure to that employed for (*R,S*)-**10a**, except that the silica gel column was eluted with 100% CH_2Cl_2, to give (*R,S*)-**10g**; yield: 72%; mp 128 °C (dec.); $[\alpha]_D^{22}$: +155 (*c* 1.6, dichloromethane); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.92 (s, 3H), 2.20 (s, 3H), 5.68 (d, *J* = 8.8 Hz, 1H), 5.98 (d, *J* = 7.7 Hz, 2H), 6.66 (t, *J* = 7.4 Hz, 2H), 6.71–6.90 (m, 5H), 7.10–7.60 (m, 11H), 7.63–7.78 (m, 3H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.89–8.04 (m, 3H), 8.06 (d, *J* = 8.1 Hz, 1H), 8.14 (d, *J* = 8.1 Hz, 1H), 8.98 (s, 1H); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = −13.5–13.7 (m, 1P, $ArPAr'_2$), 142.4–142.5 [m, 1P, $(ArO)_2POAr'$)]; ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): δ = −76.1 (dd, *J* = 8.4, 2.0 Hz, CF_3); IR: ν_{max} = 3055, 2920, 1618, 1576, 1497, 1366, 1203, 1154, 1118, 1070, 939 cm^{-1}; MS (ESI$^+$): *m/z* = 951 $(M+Na)^+$, 929 $(M+H)^+$ 929, 653, 597; HR-MS (ESI$^+$): *m/z* = 951.1694, calcd. for $(M+Na)^+$: 951.1681.

(*R,S*)-2′-Trifluoromethanesulfonyl-[*P*(*m*-tolyl)$_2$]-BINAPHOS (*R,S*)-10h

(*R*)-**8h** was reacted with (*S*)-**9** following an identical procedure to that employed for (*R,S*)-**10a**, except that the silica gel column was eluted with 100% CH_2Cl_2, to give (*R,S*)-**10h**; yield: 62%; mp 130 °C (dec.); $[\alpha]_D^{22}$: +142 (*c* 2.0, dichloromethane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.85 (s, 3H), 2.06 (s, 3H), 5.83–6.06 (m, 2H), 6.48–6.68 (m, 3H), 6.68–6.79 (m, 2H), 6.84 (d, *J* = 7.1 Hz, 1H), 6.87–6.99 (m, 2H), 7.08–7.56 (m, 11H), 7.67–7.77 (m, 2H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.90 (d, *J* = 9.0 Hz, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 8.04 (dd, *J* = 7.7, 5.7 Hz, 2H), 8.14 (d, *J* = 8.1 Hz, 2H), 9.00 (s, 1H); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = −11.6–11.9 (m, 1P, $ArPAr'_2$), 140.3–140.6 [m, 1P, $(ArO)_2POAr'$)]; ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): δ = −75.9 (dd, *J* = 7.5, 2.0 Hz, CF_3); IR: ν_{max} = 2923, 1738, 1575 1366, 1205, 1118, 1069, 939 cm^{-1}; MS (ESI$^+$): *m/z* = 929 $(M+H)^+$, 653, 597; HR-MS (ESI$^+$): *m/z* = 929.1884, calcd. for $(M+H)^+$: 929.1862.

(*R,S*)-2′-Trifluoromethanesulfonyl-[*P*(*p*-anisyl)$_2$]-BINAPHOS (*R,S*)-10i

(*R*)-**8h** was reacted with (*S*)-**9** following an identical procedure to that employed for (*R,S*)-**10a**, except that the silica gel column was eluted with 100% CH_2Cl_2, to give (*R,S*)-**10i**; yield: 44%; mp 198 °C (dec.); $[\alpha]_D^{22}$: +125 (*c* 1.5, dichloromethane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.49 (d, *J* = 0.9 Hz, 3H), 3.66 (d, *J* = 1.1 Hz, 3H), 5.81 (d, *J* = 8.8 Hz, 1H), 5.88–6.06 (m, 1H), 6.49 (d, *J* = 8.6 Hz, 2H), 6.53–6.67 (m, 3H), 6.68–6.81 (m, 2H), 7.09 (dd, *J* = 8.4, 7.1 Hz, 1H), 7.15–7.54 (m, 11H), 7.58 (d, *J* = 8.8 Hz, 1H), 7.63–7.75 (m, 2H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.86–8.07 (m, 4H), 8.11 (d, *J* = 8.2 Hz, 1H), 8.95 (s, 1H); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = −14.4–14.8 (m, 1P, $ArPAr'_2$), 141.0–141.2 [m, 1P, $(ArO)_2POAr'$)]; ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): δ = −76.1 (dd, *J* = 9.7, 2.2 Hz, CF_3); IR: ν_{max} = 3055, 1710, 1618, 1575, 1496, 1366, 1203, 1154, 1118 939 cm^{-1}; MS (ESI$^+$): *m/z* = 961 $(M+H)^+$, 753, 629, 497; HR-MS (ESI$^+$): *m/z* = 961.1783, calcd. for $(M+H)^+$: 961.1760.

(*R,S*)-2′-Trifluoromethanesulfonyl-[*P*(*m*-anisyl)$_2$]-BINAPHOS (*R,S*)-10j

(*R*)-**8g** was reacted with (*S*)-**9** following an identical procedure to that employed for (*R,S*)-**10a**, except that the silica gel column was eluted with 100% CH_2Cl_2, to give (*R,S*)-**10j**; yield: 80%; mp 150 °C (dec.); $[\alpha]_D^{22}$: +115 (*c* 2.5, dichloromethane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.19 (s, 3H), 3.56 (s, 3H), 5.99–6.09 (m, 1H), 6.12 (d, *J* = 8.8 Hz, 1H), 6.25–6.46 (m, 3H), 6.53 (t, *J* = 7.3 Hz, 1H), 6.60–6.77 (m, 3H), 6.88–7.02 (m, 1H), 7.04–7.15 (m, 1H), 7.17–7.57 (m, 11H), 7.67–7.80 (m, 2H), 7.84 (d, *J* = 8.6 Hz, 2H), 7.95 (d, *J* = 8.1 Hz, 1H), 8.05 (t, *J* = 8.3 Hz, 2H), 8.16 (d, *J* = 8.1 Hz, 1H), 9.01 (s, 1H); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = −10.6–10.9 (m, 1P, $ArPAr'_2$), 140.3–140.6 [m, 1P, $(ArO)_2POAr'$)]; ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): δ = −76.1 (dd, *J* = 6.5, 2.2 Hz, CF_3); IR: ν_{max} = 3053, 2935, 1618, 1586, 1572, 1366, 1203, 1155, 1118, 1069, 938 cm^{-1}; MS (ESI$^+$): *m/z* = 961 $(M+H)^+$, 685, 629, 497; HR-MS (ESI$^+$): *m/z* = 961.1178, calcd. for $(M+H)^+$: 961.1760.

Asymmetric Pd-Catalysed Hydrophosphorylation of Styrene

The following procedure, employing (*R,S*)-**10a** as ligand is typical. Styrene (0.16 mL, 1.4 mmol), pinacol phosphonate (0.12 g, 0.7 mmol), $[Pd(allyl)(CH_3CN)_2]$ OTf (0.013 g, 0.035 mmol), sodium dimethyl malonate (0.006 g, 0.038 mmol), (*R,S*)-**10a** (0.035 g, 0.038 mmol) were stirred in dry, degassed dioxane at reflux for 18 h. The reaction mixture was cooled to room temperature and a sample taken by microsyringe for was analysis by ^{31}P{^{1}H} NMR (121 MHz, dioxane, unlocked) to calculate the regioselectivity (41.2 ppm *n*-**3**, 41.0 ppm *iso*-**3**).[12] The sample was returned to the bulk reaction and the whole then added to a silica gel column and eluted with a mixture of isopropyl alcohol (10%) and hexane (90%). The purified products were then analysed by chiral HPLC to calculate the enantiomeric excess of *iso*-**3**. Chiralcel AD-H [0.5 mL min^{-1} 95:5 (heptane : ethanol) UV detection: 209 nm, 20 °C]: t_1 = 27.8 min t_2 = 37.9 min.

Acknowledgements

We thank the European Union (STRP 505167–1 LIGBANK) for generous support of this research collaboration.

References

[1] For a review see: S. C. Fields, *Tetrahedron* **1999**, *55*, 12237–12273.

[2] C. Bellucci, F. Gualtieri, S. Scapecchi, E. Teodori, R. Budriesi, A. Chiarini, *Farmaco* **1989**, *6*, 2281–2291.

[3] K. W. Jung, K. D. Janda, P. J. Sanfilippo, M. Wachter, *Biorg. Med. Chem. Lett.* **1996**, *6*, 2281–2282.

[4] M. Rubio, S Vargas, A. Suarez, E. Alvarez, A. Pizzano, *Chem. Eur. J.* **2007**, *13*, 1821–1833.

[5] N. S. Goulioukina, T. M. Dolgina, G. N. Bondarenko, I. P. Beletskaya, M. M. Ilyin, V. A. Davankov, A. Pfaltz, *Tetrahedron: Asymmetry* **2003**, *14*, 1397–1401.

[6] a) J.-C. Henry, D. Lavergne, V. Ratovelomanana-Vidal, J.-P. Genet, I. P. Beletskaya, T. M. Dolgina, *Tetrahedron Lett.* **1998**, *39*, 3473–3476; b) N. S. Goulioukina, T. M. Dolgina, I. P. Beletskaya, J.-C. Henry, D. Lavergne, V. Ratovelomanana-Vidal, J.-P Genet, *Tetrahedron: Asymmetry* **2001**, *12*, 319–327; c) N. S. Goulioukina, T. M. Dolgina, G. N. Bondarenko, I. P. Beletskaya, N. A. Bondarenko, J.-C Henry, D. Lavergne, V. Ratovelomanana-Vidal, J.-P. Genet, *Russ. J. Org. Chem.* **2002**, *38*, 573–587.

[7] a) I. Kovacik, D. K. Wicht, N. S. Grewal, D. S. Glueck, *Organometallics* **2000**, *19*, 950–953; b) A. D. Sadow, I. Haller, L. Fadini, A. Togni, *J. Am. Chem. Soc.* **2004**, *126*, 14704–14705; c) C. Scriban, I. Kovacik, D. S. Glueck, *Organometallics* **2005**, *24*, 4871–4874; d) A. D. Sadow, A. Togni, *J. Am. Chem. Soc.* **2005**, *127*, 17012–17024; e) N. Ajellal, C. M. Thomas, J.-F. Carpentier, *Adv. Synth. Catal.* **2006**, *348*, 1093–1100; f) N. F. Blank, J. R. Moncarz, T. J. Brunker, C. Scriban, B. J. Anderson, O. Amir, D. S. Glueck, L. N. Zakharov, J. A. Golen, C. D. Incarvito, A. L. Rheingold, *J. Am. Chem. Soc.* **2007**, *129*, 6847–6858.

[8] For reviews and accounts of transition metal-catalysed asymmetric hydroamination see: a) S. Hong, T. J. Marks, *Acc. Chem. Res.* **2004**, *37*, 673–686; b) K. C. Hultz, *Adv. Synth. Catal.* **2005**, *347*, 367–391; c) M. Beller, C. Breindl. M. Eichberger, C. G. Hartung, J. Seayad, O. R. Thiel, A. Tillack, H. Trauthwein, *Synlett* **2002**, 1579–1594; d) G. A. Molander, J. A. C. Romero, *Chem. Rev.* **2002**, *102*, 2161–2185.

[9] For recent reviews and accounts of transition metal-catalysed asymmetric hydrosilylation see: a) A. K. Roy, *Adv. Organometal. Chem.* **2008**, *55*, 1–59; b) O. Riant, N. Mostefai, J. Courmarcel, *Synthesis* **2004**, 2943–2958; c) T. Hayashi, *Acc. Chem. Res.* **2000**, *33*, 354–362; d) B. Bosnich, *Acc. Chem. Res.* **1998**, *31*, 667–674; e) K. A. Horn, *Chem. Rev.* **1995**, *95*, 1317–1350.

[10] For recent reviews and accounts of transition metal-catalysed asymmetric hydroboration see: a) A. M. Carroll, T. P. O'Sulivan, P. J. Guiry, *Adv. Synth. Catal.* **2005**, *347*, 609–631; b) C. M. Vogels, S. A. Westcott, *Curr. Org. Chem.* **2005**, *9*, 687–699; c) C. M. Crudden, D. Edwards, *Eur. J. Org. Chem.* **2003**, 4695–4712; d) ref.[8c]; e) I. P. Beletskaya, A. Pelter, *Tetrahedron* **1997**, *53*, 4957–5026.

[11] L.-B. Han, F. Mirzaei, C.-Q. Zhao, M. Tanaka, *J. Am. Chem. Soc.* **2000**, *122*, 5407–5408.

[12] a) M. O. Shulyupin, G. Franciò, I. P. Beletskaya, W. Leitner, *Adv. Synth. Catal.* **2005**, *347*, 667–672.

[13] K. Nozaki, N. Sakai, T. Nanno, T. Higashijima, S. Mano, T. Horiuchi, H. Takaya, *J. Am. Chem. Soc.* **1997**, *119*, 4413–4423.

[14] Q. Xu, L.-B. Han, *Org. Lett.* **2006**, *8*, 2099–2101.

[15] T. Fujita, K. Nakano, M. Yamashita, K. Nozaki, *J. Am. Chem. Soc.* **2006**, *128*, 1968–1975, and references cited therein.

[16] G. Franciò, K. Wittmann, W. Leitner, *J. Organomet. Chem.* **2001**, *621*, 130–142.

[17] a) G. Franciò, W. Leitner, *Chem. Commun.* **1999**, 1663–1664; b) K. Nozaki, T. Matsuo, F. Shibahara, T. Hiyama, *Adv. Synth. Catal.* **2001**, *343*, 61–63.

[18] Y. Yan, Y. Chi, X. Zhang, *Tetrahedron: Asymmetry* **2004**, *15*, 2173–2175.

[19] a) J. P. H. Charmant, A. M. Dyke, G. C. Lloyd-Jones, *Chem. Commun.* **2003**, 380–381; b) Z. Zhao, J. Messinger, U. Shöne, R. Wartchow, H. Butenshön, *Chem. Commun.* **2006**, 3007–3009.

[20] The mechanism of the reaction appears to involve generation of an aryl anion (rather than aryllithium) intermediate, see: A. M. Dyke, D. M. Gill, J. N. Harvey, A. J. Hester, G. C. Lloyd-Jones, M. P. Munoz, I. R. Shepperson, *Angew. Chem. Int. Ed.* **2008**, *47*, 5067–5070.

[21] a) R. Kargbo, Y. Takahashi, S. Bhor, G. R. Cook, G. C. Lloyd-Jones, I. R. Shepperson, *J. Am. Chem. Soc.* **2007**, *129*, 3846–3847; b) for an alternative highly enantioselective naphthyl-naphthyl coupling route to 3-sulfonyl BINOLs, see: X. Li, B. Hewgley, C. A. Mulrooney, J. Yang, M. C. Kozlowski, *J. Org. Chem.* **2003**, *68*, 5500–5511; c) for the preparation of 6,6′-bis(trifluoromethanesulfonyl)-1,1′-BINOL, see: O. Mouhtady, H. Gaspard-Iloughmane, A. Laporterie, C. Le Roux, *Tetrahedron Lett.* **2006**, *47*, 4125–4128.

[22] Y. Uozumi, A. Tanahashi, S.-Y. Lee, T. Hayashi, *J. Org. Chem.* **1993**, *58*, 1945–1948.

[23] P. N. M. Botman, O. David, A. Amore, J. Dinkelaar, M. T. Vlaar, K. Goubitz, J. Fraanje, H. Schenk, H. Hiemstra, J. H. van Maarseveen, *Angew. Chem. Int. Ed.* **2004**, *43*, 3471–3473.

[24] R. W. Steensma, S. Galabi, J. R. Tagat, S. W. McCombie, *Tetrahedron Lett.* **2001**, *42*, 2281–2283.

[25] G. Franciò, C. G. Arena, F. Faraone, C. Graiff, M. Lanfranchi, A. Tiripicchio, *Eur. J. Inorg. Chem.* **1999**, 1219–1227.

[26] M. Kruck, M. P. Muñoz, H. L. Bishop, C. G. Frost, C. J. Chapman, G. Kociok-Köhn, C. P. Butts, G. C. Lloyd-Jones, *Chem. Eur. J.* **2008**, *14*, in press; DOI 10.1002/chem.200800825.

[27] O. Mouhtady, H. Gaspard-Iloughmane, A. Laporterie, C. Le Roux, *Tetrahedron Lett.* **2006**, *47*, 4125–4128.

[28] J. Bayardon, M. Cavazzini, D. Maillard, G. Pozzi, S. Quici, D. Sinou, *Tetrahedron: Asymmetry* **2003**, *14*, 2215–2224.

[29] F Shibahara, K, Nozaki, T. Matsuo, T. Hiyama, *Biorg. Med. Chem. Lett.* **2002**, *12*, 1825–1827.

