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Synthesis and evaluation of 4,4′,6,6′-tetrasubstituted binaphtholphosphate dirhodium(II) complexes as catalysts in enantioselective carbonyl ylide formation–cycloaddition reactions

David M. Hodgson,[a,*] Deborah A. Selden[a] and Alexander G. Dossetter[b]

[a]*Dyson Perrins Laboratory, Department of Chemistry, University of Oxford, South Parks Road, Oxford OX1 3QY, UK*
[b]*AstraZeneca, Mereside, Alderley Park, Macclesfield, Cheshire SK10 4TG, UK*

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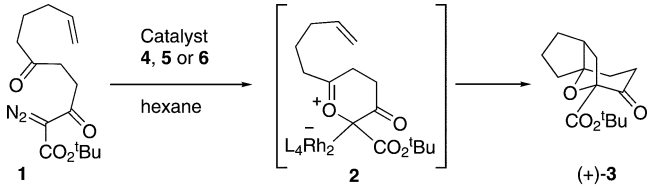
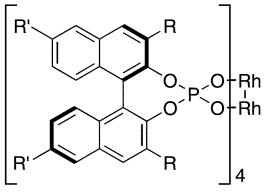
Abstract—The synthesis of tetrakis[4,4′,6,6′-tetrasubstituted-1,1′-bi-2-naphtholphosphate]dirhodium(II) complexes, and their use as catalysts in the enantioselective tandem carbonyl ylide formation–intramolecular 1,3-dipolar cycloaddition of an unsaturated 2-diazo-3,6-diketoester, generating cycloadduct in up to 86% ee, is described.

1. Introduction

Compared with enantioselective Diels–Alder and hetero Diels–Alder processes, enantioselective 1,3-dipolar cycloadditions are relatively underdeveloped.[1] Nevertheless, the latter reaction class holds considerable potential for the asymmetric synthesis of heterocycles.[2] Studies by Padwa et al. established Rh(II)-catalysed tandem carbonyl ylide formation–1,3-dipolar cycloaddition of diazocarbonyl compounds as an excellent method for the synthesis of oxapolycycles (e.g. Scheme 1).[3–7] Catalytic enantioselective processes involving ylides from diazo compounds are an emerging field in asymmetric synthesis.[8,9] A variety of chiral, non-racemic dirhodium carboxylates and carboxamidates have been extensively examined as asymmetric catalysts in a number of diazocarbonyl transformations.[4,10] However, our previous investigations have revealed that rhodium phosphate catalysts can be superior to these more commonly utilised complexes: we observed enantioselectivities of up to 92% in tandem carbonyl ylide formation–cycloadditions using the didodecylbinaphthol phosphate catalyst Rh_2[(*R*)-DDBNP]$_4$ **5** in saturated hydrocarbon solvents (Scheme 1).[11,12]

The cascade reactions discussed above are of interest because of the rapid generation of molecular complexity,[3] and because of the demands which it places upon the catalyst. Efficient decomposition of the diazo precursor and the formation of a catalyst-associated ylide (e.g. **2**)[8] from the resulting metallocarbene are required if highly enantioenriched cycloadduct is to be produced. The enantioselectivity levels obtained in these cycloadditions, as the structure of the catalyst is varied in an organised manner, is of importance in providing insight into the nature of the enantiodiscrimination process. Substitution at various positions on the binaphthyl





4 R = R' = H, Rh_2[(*R*)-BNP]$_4$, 25 °C, 65% y, 64% *ee*
5 R = H, R' = $C_{12}H_{25}$, Rh_2[(*R*)-DDBNP]$_4$, –15 °C, 66% y, 90% *ee*
6 R = Me, R' = H, Rh_2[(*R*)-DMBNP]$_4$, no reaction in hexane

Scheme 1.

* Corresponding author. Tel.: +44-1865-275697; fax: +44-1865-275674; e-mail: david.hodgson@chem.ox.ac.uk

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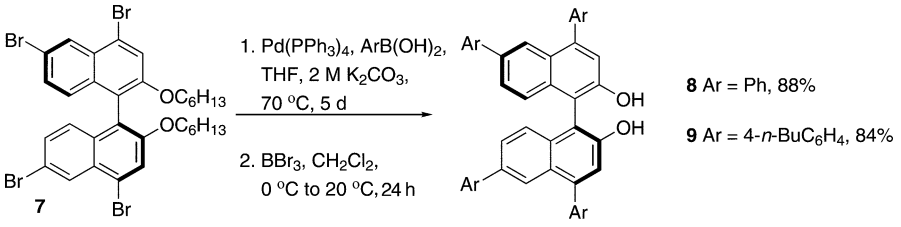


Scheme 2.

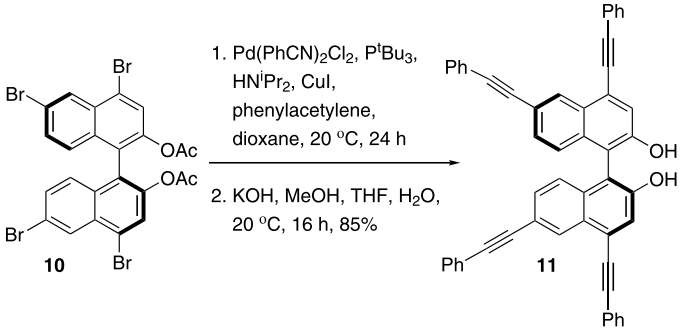
framework has often been used to alter asymmetric induction with catalysts containing binaphthyl ligands.[13] With regard to rhodium phosphate catalysts previously studied, for those containing DDBNP and the unsubstituted BNP ligands (Scheme 1), the main difference is the complete solubility in saturated hydrocarbon solvents imparted to $Rh_2[(R)\text{-DDBNP}]_4$ **5** compared with $Rh_2[(R)\text{-BNP}]_4$ **4** (the latter having originally been prepared by Pirrung[14]). There appears to be little, if any, influence on ee due to the dodecyl substituents in $Rh_2[(R)\text{-DDBNP}]_4$ **5** either by electronically reducing the electrophilic nature of the catalyst, or altering intra-planar (binaphthyl) torsion angles.[11,15] In contrast to substitution at the 6,6′-positions (and simultaneous substitution at the 6,6′- and 5,5′-positions found in bis-steroidal binaphthol phosphate catalysts),[11] even minimal substitution at the 3,3′-positions resulted in a considerable loss of enantiocontrol: reaction of $Rh_2[(R)\text{-DMBNP}]_4$ **6** with α-diazo-β-ketoester **1** led to no cycloadduct in hexane and a low ee (7%) of (+)-**3** in CH_2Cl_2, [65 and 67% ees were observed in CH_2Cl_2 using $Rh_2[(R)\text{-BNP}]_4$ **4** and $Rh_2[(R)\text{-DDBNP}]_4$ **5** respectively; see Ref. 11]. The loss of enantiocontrol with $Rh_2[(R)\text{-DMBNP}]_4$ could possibly be due to steric congestion at the axial binding sites on the dirhodium core, which (in CH_2Cl_2) might also facilitate catalyst release to give the free ylide for cycloaddition. With the primary aim of further probing of the effects of structural variation of the binaphthol core on enantioselectivity in the above transformation, whilst also expanding the pool of differently substituted rhodium phosphate catalysts (and binaphthols) available for other asymmetric transformations (especially of diazo compounds),[4,10] we report here the first synthesis of rhodium phosphate catalysts bearing substitution in the 4,4′-positions and their use in enantioselective tandem carbonyl ylide formation–intramolecular 1,3-dipolar cycloaddition of 2-diazo-3,6-diketoester **1**.

2. Results and discussion

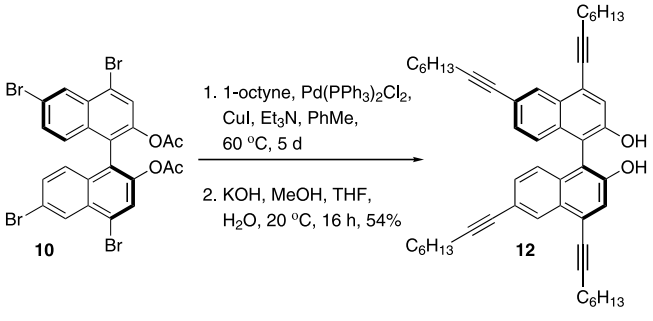
2.1. Catalyst syntheses

Pu et al.[16,17] have reported a range of 4,4′,6,6′-tetrasubstituted binaphthols in the synthesis of optically active dendrimers to be used in enantioselective fluorescence sensors, and as catalysts for the asymmetric reaction of diethylzinc with aldehydes. Chow et al.[18] have reported oligomers of 1,1′-bi-2-naphthol linked by an acetylene spacer between the 4- and 4′-carbon atoms, in order to investigate their chiroptical properties. Chan[19] has introduced perfluoroalkyl chains at the 4,4′- and 6,6′-positions of 1,1′-bi-2-naphthol in order to form a titanium catalyst for the asymmetric addition of diethylzinc to aldehydes in a fluorous biphasic system, allowing the catalyst to be recycled.

The required ligands were synthesised by analogy with the work of Pu.[16,17] Firstly, the synthesis of the 4,4′,6,6′-tetraphenyl-1,1′-bi-2-naphthol **8**[17] was undertaken (Scheme 2); the analogous 4-*n*-butylphenyl-substituted binaphthol **9** was also synthesised as the alkyl chains might provide increased hexane solubility and so allow the catalyst to function well at a range of temperatures in the reaction solvent of choice. Pu[16] has also reported the introduction of substituted phenylacetylenes around binaphthol, and it was envisaged that preparation of the 4,4′,6,6′-tetra(2-phenylethynyl)-1,1′-bi-2-naphthol **11** and 4,4′,6,6,′-tetraoctynyl-1,1′-bi-2-naphthol **12** (Schemes 3 and 4), followed by hydrogenation of the triple bonds to the alkanes would produce ligands with flexible 2-phenylethyl substituents or C_8-alkyl chains, respectively, at the four positions. The latter would provide a direct analogue to $Rh_2[(R)\text{-DDBNP}]_4$ with additional 4,4′-substitution.



Scheme 3.



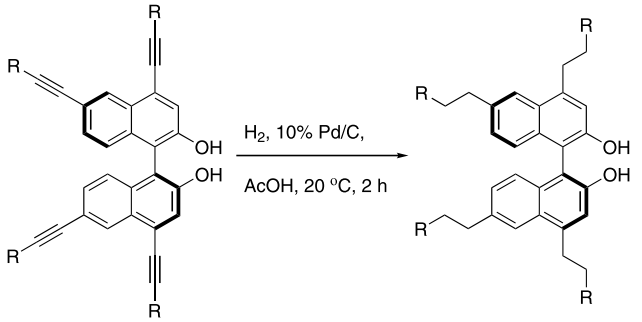
Scheme 4.

The 4,4′,6,6′-tetraphenyl and 4,4′,6,6′-tetra(4-*n*-butylphenyl)-1,1′-bi-2-naphthols **8** and **9** were prepared from readily accessible *O*,*O*-dihexyl-4,4′,6,6′-tetrabromo-1,1′-bi-2-naphthol **7**[17] via a Suzuki coupling with the appropriate aryl boronic acid, followed by deprotection of the crude reaction mixture with BBr_3 in CH_2Cl_2, which gave the substituted binaphthols **8** and **9** in 88% yield (lit.,[17] 80%) and 84% yield, respectively, over two steps (Scheme 2).

The 4,4′,6,6′-tetra(2-phenylethynyl)-1,1′-bi-2-naphthol **11** was prepared using the method of Fu et al.[20] for the coupling of deactivated aryl halides with terminal acetylenes (Scheme 3). The *O*,*O*-diacetyl-4,4′,6,6′-tetrabromo-1,1′-bi-2-naphthol **10**[16] (obtained via Pu's strategy) and phenylacetylene were treated with $Pd(PhCN)_2Cl_2$, CuI, $^tBu_3P$ and $^iPr_2NH$ in 1,4-dioxane at 25°C for 24 h, and the crude reaction mixture then treated with KOH to afford the tetrasubstituted binaphthol **11** in 85% yield after column chromatography. Pu's reported method[16] for the coupling of aryl acetylenes with **10**, using $Pd(PPh_3)_4$, CuI and Et_3N in refluxing THF, gave only moderate yields (up to 42%) in our hands.

Preparation of the 4,4′,6,6′-tetraoctynyl-1,1′-bi-2-naphthol **12** was achieved using a modification of Chow's[18] procedure; treatment of *O*,*O*-diacetyl-4,4′,6,6′-tetrabromo-1,1′-bi-2-naphthol **10**[16] with 1-octyne, CuI, $Pd(PPh_3)_2Cl_2$ and Et_3N in toluene at 60°C for 5 days, followed by removal of the *O*-acetyl groups as above, yielded 56% of the tetrasubstituted product **12** after chromatography (Scheme 4).

The triple bonds in both **11** and **12** were then reduced by catalytic hydrogenation in acetic acid over 10% Pd/C at atmospheric pressure, as reported by Azzena et al.[21] for the reduction of a diaryl-substituted triple bond. After 2 h an 80% yield of 4,4′,6,6′-tetra(2-phenylethyl)-1,1′-bi-2-naphthol **13** and a 95% yield of 4,4′,6,6′-tetraoctyl-1,1′-bi-2-naphthol **14** could be obtained (Scheme 5).

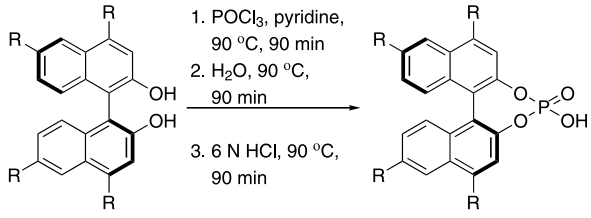


11 R = Ph
12 R = C_6H_{13}

13 R = Ph, 87%
14 R = C_6H_{13}, 95%

Scheme 5.

The phosphates of the substituted binaphthols **8**, **9**, **13** and **14** were prepared by treating the binaphthols with $POCl_3$ in pyridine at 90°C for 90 min, addition of water and heating for a further 90 min, then removal of the solvent and treatment of the residue with 6 N HCl at 90°C for 90 min; this protocol afforded the phosphates **15**–**18** as off-white powders in 64–90% yield (Scheme 6). These harsh conditions, compared with those used in the formation of 6,6′-didodecyl-1,1′-bi-2-naphthol,[11] (stirring with $POCl_3$ in pyridine at 20°C for 2 h, followed by pouring into water and filtration of the product) were necessary to ensure proper formation of the phosphate and full hydrolysis of the intermediate phosphoryl chloride.

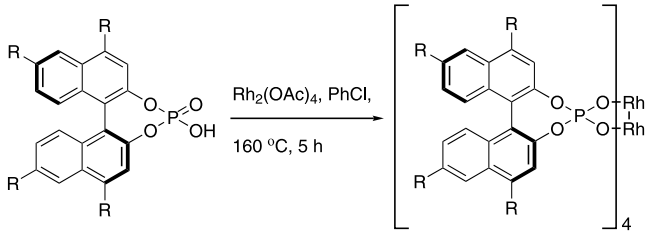


8 R = Ph
9 R = 4-*n*-BuC_6H_4
13 R = $PhCH_2CH_2$
14 R = C_8H_{17}

15 R = Ph, 91%
16 R = 4-*n*-BuC_6H_4, 82%
17 R = $PhCH_2CH_2$, 90%
18 R = C_8H_{17}, 64%

Scheme 6.

Ligand exchange using phosphates **15**–**18** was carried out with $Rh_2(OAc)_4$ using Callot's procedure.[22] This method favours the forward reaction by azeotropic removal of the displaced acetic acid from the reaction mixture by constant distillation and replacement of the solvent, and is therefore an efficient technique for the introduction of bulky ligands. Heating of a mixture of the ligand and $Rh_2(OAc)_4$ in chlorobenzene at $\sim$160°C for 5 h followed by isolation of the blue–green complexes by column chromatography gave the desired catalysts **19**–**22** in 31–43% yields (Scheme 7)



15 R = Ph
16 R = 4-*n*-BuC_6H_4
17 R = $PhCH_2CH_2$
18 R = C_8H_{17}

19 R = Ph, 43%
20 R = 4-*n*-BuC_6H_4, 31%
21 R = $PhCH_2CH_2$, 37%
22 R = C_8H_{17}, 35%

Scheme 7.

The 4,4′,6,6′-tetra(2-phenylethynyl)-1,1′-bi-2-naphthol **11** was converted to the phosphate using the method described above, and a ligand exchange reaction carried out. This gave an inseparable mixture of two partially ligand-exchanged products $(Rh_2(OAc)_{4-n}L_n,\ 1 \le n \le 3)$.

It was concluded that the rigidity of the phenylacetylenic substituents makes the approach of the ligands to the dirhodium core too hindered to form the complex with four binaphtholphosphate ligands around the core. However, hydrogenation of the triple bonds of **11** to **12** introduced greater flexibility into the ligand and therefore probably reduced hindrance to formation of the desired rhodium complex **21** from **17**.

2.2. Cycloaddition reactions

The *tert*-butyl ester cycloaddition substrate **1**[11] had previously afforded the highest ee with Rh_2[(*R*)-DDBNP]$_4$ **5** (Scheme 1), and was therefore used as a standard for the experiments. Initial reaction conditions for the catalysts were standardised to 20°C with CH_2Cl_2 and hexane as solvents; if solubility in hexane allowed, the reaction temperature was systematically reduced with the aim of improving ee.

In CH_2Cl_2, the tetraphenyl-substituted catalyst **19** appeared to decompose in solution after 2 h and addition of more catalyst to the mixture did not restart the reaction, which was stopped after 112 h since no further consumption of starting ester **1** was observed (Table 1, entry 1). Catalyst **19** was totally insoluble in hexane and decomposed the substrate extremely slowly: after 112 h, the yield of cycloadduct **3** was barely detectable and so no ee determination was possible (Table 1, entry 2). Although catalyst **19** was soluble in $PhCF_3$,[9] its reactivity was found to be relatively poor (Table 1, entry 3); this appears inconsistent with the results below, as good catalyst activity usually correlated with good solubility. Interestingly, the opposite cycloadduct enantiomer (+)-**3** was favoured with catalyst **19** compared with related catalysts having the same absolute stereochemistry in this and previous work.

In contrast, the tetra(*p*-*n*-butylphenyl)-substituted complex **20** was found to be much more soluble and active than **19**, although in CH_2Cl_2 at 25°C catalyst **20** appeared to become inactive as no further substrate consumption was observed after 23 h; a low yield and moderate ee were achieved (Table 1, entry 4). At 25°C in hexane the catalyst was soluble and very active, the substrate **1** being consumed within 30 min, and the cycloadduct **3** was obtained in an acceptable yield and good ee (63%) (Table 1, entry 5). Unfortunately, however, at 0°C the catalyst was no longer soluble; although some reaction was seen by TLC, the catalyst appeared to become inactive after a short period, and no cycloadduct was isolated from the reaction mixture (Table 1, entry 6). It appears that the *n*-butyl substituents do not increase the hexane solubility enough to keep the catalyst in solution below room temperature, although the increase in solubility over the tetraphenylbinaphtholphosphate catalyst **19** is significant.

The tetra(2-phenylethyl)-substituted catalyst **21** was insoluble in hexane, producing a poor yield and ee of cycloadduct **3** (Table 1, entry 7). However, the results were much more promising in CH_2Cl_2, and the ready solubility of **21** in CH_2Cl_2 and the high activity of the catalyst suggested that catalyst activity would be observed below ambient temperature. Reducing the reaction temperature from 25 to 0°C gave a small increase in ee from 54 to 66% with no diminution in yield of **3** (Table 1, entries 8 and 9). Further reduction of the temperature to −20°C, however, appeared to shut down the catalytic activity of **21** despite its solubility, as indicated by incomplete consumption of the substrate and the loss of the green catalyst colour. No cycloadduct was isolated from this latter reaction (Table 1, entry 10).

Table 1. Effect of catalysts **19**–**22** on the cycloaddition of ester **1**

Entry	Catalyst	Solvent	T (°C)	Time (h)	Yield (%)[a]	Ee (%)[b]
1	**19**	CH_2Cl_2	20	112[c]	20	5
2	**19**	Hexane	20	112	Trace	–
3	**19**	$PhCF_3$	20	22.5	35	11
4	**20**	CH_2Cl_2	20	23.5[c]	35	−50
5	**20**	Hexane	20	0.5	48	−63
6	**20**	Hexane	0	29[c]	0	–
7	**21**	Hexane	20	2.5	24	−37
8	**21**	CH_2Cl_2	20	5 min	48	−54
9	**21**	CH_2Cl_2	0	1.5	47	−66
10	**21**	CH_2Cl_2	−20	24[c]	0	–
11	**22**	CH_2Cl_2	20	5 min	86	−70
12	**22**	CH_2Cl_2	0	25 min	75	−76
13	**22**	CH_2Cl_2	−15	1	64	−79
14	**22**	CH_2Cl_2	−30	7[c]	32	−78
15	**22**	Hexane	20	5 min	76	−82
16	**22**	Hexane	0	10 min	72	−80
17	**22**	Hexane	−15	0.5	75	−86
18	**22**	Hexane	−30	7	49	−85

[a] Isolated yield of cycloadduct **3**.
[b] Ees determined by chiral GC (CP Chirasil Dex-CD or SGE Cydex-β, 140°C isotherm, 0.7 ml min^{-1}, 2 mg ml^{-1}). Negative values correspond to enrichment in (−)-cycloadduct **3**.
[c] No further consumption of substrate **1** apparent by TLC.

The tetraoctyl-substituted catalyst **22** was fully soluble in both CH_2Cl_2 and hexane, and extremely active as catalyst in both solvents, decomposing the substrate **1** at room temperature within 5 min to give cycloadduct **3** in 86% yield (70% ee) and 76% yield (82% ee), respectively. (Table 1, entries 11 and 15). The high activity of catalyst **22**, together with the good yields and promising ees obtained for **3**, suggested that lower temperature reactions would be feasible and might provide further improvement in ee. In CH_2Cl_2, it was possible to reduce the reaction temperature to −15°C with some reduction in yield but an increase in ee of **3** to 79% (Table 1, entries 12 and 13). However, carrying out the reaction at −30°C led to extremely slow decomposition of the substrate, with no apparent change after 7 h; the yield of **3** dropped to 39% and the ee showed no increase over that obtained at −15°C (Table 1, entry 14). To date these are the highest ees obtained for this substrate in CH_2Cl_2 (cf. Rh_2[(*R*)-DDBNP]$_4$, in CH_2Cl_2 at 0°C, 47% yield, 72% ee of **3**), and could expand the substrate scope for the reaction, where solubility in hexane had previously been limiting.

With catalyst **22** in hexane, it was possible to reduce the reaction temperature to −30°C; a progressive reduction in reaction rate and yield of **3** was observed with decrease in temperature, and no significant increase in ee was observed (82% ee at 20°C to 85% ee at −30°C; Table 1, entries 15–18). The asymmetric induction observed at 20°C with this catalyst **22** and Rh_2[(*R*)-DDBNP]$_4$ **5** is identical; however the stronger temperature dependence of the ee of **3** observed with Rh_2[(*R*)-DDBNP]$_4$ **5** allows a 90% ee to be achieved with **5** at −15°C.[11]

The results obtained with the new complexes described herein show that substitution at the 4,4′-sites of the binaphthol scaffold appear not to influence the asymmetric induction observed with substrate **1**; this contrasts with the severe erosion observed with Rh_2[(*R*)-DMBNP]$_4$ **6**, and provides a similar reaction profile to Rh_2[(*R*)-DDBNP]$_4$ **5**. The improved solubility of the catalysts lead to more reliable results compared with Rh_2[(*R*)-BNP]$_4$ **4** in hexane, and additionally the tetraoctyl-substituted catalyst **22** provides the best ees obtained in this type of system using a phosphate catalyst in CH_2Cl_2 thus far. This latter is important since not all cycloaddition substrates will be soluble, and hence undergo reaction, in hydrocarbon solvents. Further studies into the scope of these catalysts with other cycloaddition substrates will be reported in due course.

3. Experimental

3.1. General methods

All reactions requiring anhydrous conditions were conducted in flame-dried apparatus under an atmosphere of argon. Syringes and needles for the transfer of reagents were dried at 140°C and allowed to cool in a dessicator over self-indicating SiO_2 before use. Ethers were distilled from sodium/benzophenone, (chlorinated) hydrocarbons and Et_3N from CaH_2. Reactions were monitored by TLC by using commercially available aluminium-backed plates, pre-coated with a 0.20 mm layer of silica containing a fluorescent indicator (Merck). Column chromatography was carried out on Kieselgel 60 (40–63 μm). Petrol refers to the fraction with bp 30–40°C. [α] values are recorded between 21.5 and 24.5°C and are given in 10^{-1} deg cm^2 g^{-1}. IR spectra were recorded as KBr discs unless stated otherwise. Peak intensities are specified as strong (s), medium (m) or weak (w). ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker AC200, a Varian Gemini 200, a Bruker DPX400, a Bruker DQX400, or a Bruker AMX500. Spectra were taken in $CDCl_3$ unless otherwise stated; chemical shifts are reported relative to $CHCl_3$ [$\delta_H = 7.27$, δ_C (central line of t) = 77.0], or externally referenced to 85% H_3PO_4 in H_2O for ^{31}P spectra. *J* values are reported to the nearest hertz (Hz). COSY and HMQC experiments were used to aid spectral assignment. Mass spectra were obtained by the EPSRC National Mass Spectrometry Service Centre at the University of Swansea by using a Micromass Quattro II low-resolution triple quadrupole mass spectrometer, or, for accurate masses, by using a Finnigan MAT900 XLT high-resolution double-focusing mass spectrometer with tandem ion trap, or an Applied Biosystems Voyager MALDI-TOF mass spectrometer with linear and reflection analysers; or by the mass spectrometry service of the Dyson Perrins Laboratory by using an Open Linx Micromasss Platform 1 (ESI or APCI) or, for accurate masses, using a Waters 2790-Micromass LCT electrospray ionisation mass spectrometer calibrated relative to poly-DL-alanine with leucine enkephalin as the internal lock mass. Chiral gas chromatography was carried out using a CE instruments Trace GC (Thermoquest) machine with a CP Chirasil Dex-CD column, or a SGE Cydex-β column.

3.2. (*S*)-4,4′,6,6′-Tetra(4-*n*-butylphenyl)-1,1′-bi-2-naphthol 9

A solution of (*S*)-4,4′,6,6′-tetrabromo-*O*,*O*-dihexyl-1,1′-bi-2-naphthol **7**[17] (2.00 g, 2.60 mmol), in degassed THF (52 ml) was added via cannula to a mixture of 4-*n*-butylbenzeneboronic acid (2.04 g, 11.4 mmol, 4.4 equiv.) and $Pd(PPh_3)_4$ (260 mg, 0.220 mmol, 2 mol% per Br), followed by K_2CO_3 (32 ml, 2 M in H_2O). The mixture was heated to 70°C with vigorous stirring for 5 days. After cooling to rt, the mixture was poured into 1:1 EtOAc:H_2O (200 ml) and the layers separated; the aqueous layer was extracted with EtOAc (50 ml), and the combined organic layers washed with brine, dried ($MgSO_4$), filtered through a pad of silica and concentrated in vacuo. The residue was dissolved in CH_2Cl_2 (60 ml), cooled to 0°C, and treated with BBr_3 (7.80 ml, 1 M in CH_2Cl_2, 7.80 mmol). After stirring at 25°C for 24 h, the mixture was diluted with CH_2Cl_2 (50 ml) and H_2O (20 ml) added. The layers were separated, the aqueous layer extracted with CH_2Cl_2 (30 ml), and the combined organic layers washed with brine (30 ml), dried ($MgSO_4$) and concentrated in vacuo. Purification of the residue by column chromatography (6:1 petrol:Et_2O) yielded the title compound as a pale yellow foam (1.78 g, 2.19 mmol, 84% over two steps): R_f (3:1 petrol:Et_2O) 0.4; $[\alpha]_D$ +68.9 (*c* 1, $CHCl_3$); mp 75°C; ν_{max}

(cm^{-1}) 3253 (w, br), 2955 (s), 2928 (s), 2856 (m), 1588 (s), 1497 (m), 1456 (w), 1377 (m), 1326 (w), 1182 (m), 1145 (s), 1019 (w), 946 (m), 820 (m); δ_H (400 MHz) 0.92 (6H, t, *J* 7, 2×CH_3), 1.01 (6H, t, *J* 7, 2×CH_3), 1.39 (4H, q, *J* 7, 2×CH_3CH_2), 1.49 (4H, q, *J* 7, 2×CH_3CH_2), 1.62 (4H, quin, *J* 7, 2×$CH_3CH_2CH_2$), 1.75 (4H, quin, *J* 7, 2×$CH_3CH_2CH_2$), 2.68 (4H, t, *J* 7, 2×^{n}PrCH$_2$), 2.78 (4H, t, *J* 7, 2×^{n}PrCH$_2$), 5.22 (2H, s, 2×OH), 7.24 (4H, d, *J* 14, 2×*m*-H of C(4 and 4′)Ar), 7.40 (4H, d, *J* 14, 2×*m*-H of C(6 and 6′)Ar), 7.42 (2H, s, C(3 and 3′)H), 7.44 (2H, d, *J* 9, C(8 and 8′)H), 7.49 (4H, d, *J* 14, 2×*o*-H of C(4 and 4′)Ar), 7.58 (4H, d, *J* 14, 2×*o*-H of C(6 and 6′)Ar), 7.63 (2H, dd, *J* 9,2, C(7 and 7′)H), 8.21 (2H, d, *J* 2, C(5 and 5′)H); δ_C (100 MHz) 14.0, 14.1, 22.4, 22.6, 33.4, 33.6, 35.2, 35.5, 110.1, 115.0, 119.0, 124.6, 125.2, 127.0, 127.2, 127.6, 128.3, 129.4, 129.8, 129.9, 133.0, 136.8, 137.1, 138.5, 142.0, 142.5, 144.2, 152.2; *m*/*z* (ESI–) 813 ([M–H]$^-$, 15%), 255 (100); calcd for $C_{60}H_{61}O_2$ ([M–H]$^-$) 813.4672, found 813.4660.

3.3. (*S*)-4,4′,6,6′-Tetra(2-phenylethynyl)-1,1′-bi-2-naphthol 11

To a mixture of (*S*)-*O*,*O*-diacetyl-4,4′,6,6′-tetrabromo-1,1′-bi-2-naphthol **10**[16] (0.800 g, 1.17 mmol), CuI (18 mg, 0.088 mmol, 0.075 equiv.) and $Pd(PhCN)_2Cl_2$ (54 mg, 0.13 mmol, 3 mol% per Br) were added 1,4-dioxane (5 ml), ^{i}Pr$_2$NH (790 μl, 5.5 mmol, 4.7 equiv.), ^{t}Bu$_3$P (1.17 ml, 0.25 M solution in 1,4-dioxane, 0.280 mmol, 0.24 equiv.) and phenylacetylene (600 μl, 5.54 mmol, 4.75 equiv.). After stirring at 20°C for 24 h, the mixture was diluted with EtOAc (20 ml), filtered through silica, and concentrated in vacuo. The residue was dissolved in a mixture of THF (115 ml), MeOH (48 ml) and H_2O (24 ml) and treated with KOH (4.40 g) at 20°C for 24 h before being diluted with petrol (100 ml) and neutralised with 2N HCl. The layers were separated, and the organic layer was washed successively with brine (30 ml), satd aq. $NaHCO_3$ (30 ml), and brine (30 ml), then dried ($MgSO_4$) and concentrated in vacuo. Purification of the residue by column chromatography (3:1 petrol:Et_2O) gave the title compound as an orange solid (0.683 g, 0.997 mmol, 85%): R_f (1:1 Et_2O:petrol) 0.4; $[\alpha]_D$ +137.5 (*c* 1, $CHCl_3$); mp 148°C; ν_{max} (cm^{-1}) 3509 (br), 1572 (m), 1490 (w), 1385 (w), 1141 (w), 752 (s), 688 (s); δ_H (400 MHz) 5.39 (2H, br s, 2×OH), 7.18 (2H, d, *J* 9, C(8 and 8′)H), 7.35 (6H, m, *p*-H of C(4 and 4′)CCPh and *m*-H of C(6 and 6′)CCPh), 7.43-7.47 (6H, m, *m*-H of C(4 and 4′)CCPh and *p*-H of C(6 and 6′)CCPh), 7.50 (2H, dd, *J* 9, 2, C(7 and 7′)H), 7.59 (4H, dd, *J* 5, 1, *o*-H of C(6 and 6′)CCPh), 7.67 (2H, s, C(3 and 3′)H), 7.75 (4H, dd, *J* 5, 2, *o*-H of C(4 and 4′)CCPh), 8.66 (2H, s, C(5 and 5′)H); δ_C (100 MHz) 86.2, 87.3, 89.6, 90.3, 96.2, 111.8, 119.9, 122.3, 122.8, 123.2, 124.5, 124.6, 128.3, 128.5, 128.9, 129.1, 130.2, 130.9, 131.7, 131.9, 132.7, 152.7, 172.4; *m*/*z* (ESI–) 685 ([M–H]$^-$, 100%); calcd for $C_{52}H_{29}O_2$ ([M–H]$^-$) 685.2168, found 685.2189.

3.4. (*S*)-4,4′,6,6′-Tetraoctynyl-1,1′-bi-2-naphthol 12

To a mixture of (*S*)-*O*,*O*-diacetyl-4,4′,6,6′-tetrabromo-1,1′-bi-2-naphthol **10**[16] (2.18 g, 3.18 mmol), CuI (144 mg, 0.74 mmol, 6 mol% per Br) and $Pd(PPh_3)_2Cl_2$ (446 mg, 0.640 mmol, 5 mol% per Br) were added toluene (26 ml), Et_3N (4.89 ml) and 1-octyne (2.13 ml, 14.4 mmol, 4.5 equiv.), and the resulting mixture heated to 60°C. After 5 days, the mixture was cooled to rt, filtered through a short pad of silica, diluted with EtOAc, washed with 2N HCl (100 ml) and brine (50 ml), and dried ($MgSO_4$). The solution was concentrated in vacuo, and the residue dissolved in THF (300 ml), MeOH (130 ml) and H_2O (65 ml) and treated with KOH (12.0 g) at 20°C for 18 h. The mixture was then diluted with petrol, and neutralised with 2N HCl. The layers were separated and the aqueous portion extracted with petrol (3×150 ml); the organics were washed with brine (100 ml), satd aq. $NaHCO_3$ (2×100 ml) and brine (100 ml), dried ($MgSO_4$), and concentrated in vacuo. Purification by column chromatography (two columns: 3:1 petrol:Et_2O followed by 2:1 petrol:CH_2Cl_2→100% CH_2Cl_2, gradient elution) gave an orange oil (1.24 g, 1.72 mmol, 54%): R_f (3:1 petrol:Et_2O) 0.1; $[\alpha]_D$ +78.9 (*c* 1, $CHCl_3$); ν_{max} (thin film, cm^{-1}) 3467 (w), 2955 (m), 2930 (s), 2857 (m), 2223 (w), 1581 (m), 1377 (m), 1138 (m); δ_H (400 MHz) 0.92 (6H, t, *J* 8, C(4 and 4′)CCC$_5$H$_{10}$CH_3), 0.96 (6H, t, *J* 8, C(6 and 6′)CCC$_5$H$_{10}$CH_3), 1.37–1.30 (8H, m, C(4 and 4′)CCC$_3$H$_6$CH_2CH_2CH$_3$), 1.45–1.37 (8H, m, C(6 and 6′)CCC$_3$H$_6$CH_2CH_2CH$_3$), 1.53–1.44 (4H, m, C(4 and 4′)CCC$_2$H$_4$CH_2C$_3$H$_7$), 1.62–1.54 (4H, m, C(6 and 6′)CCC$_2$H$_4$CH_2C$_3$H$_7$), 1.69–1.61 (4H, m, C(4 and 4′)CCCH$_2$CH_2C$_4$H$_9$), 1.80–1.71 (4H, m, C(6 and 6′)CCCH$_2$CH_2C$_4$H$_9$), 2.45 (4H, t, *J* 8, C(4 and 4′)CCCH_2C$_5$H$_{11}$), 2.63 (4H, t, *J* 8, C(6 and 6′)CCCH_2C$_5$H$_{11}$), 5.04 (2H, br s, 2×OH), 7.02 (2H, d, *J* 9, C(8 and 8′)H), 7.30 (2H, dd, *J* 2, 9, C(7 and 7′)H), 7.48 (2H, s, C(3 and 3′)H), 8.42 (2H, d, *J* 2, C(5 and 5′)H); δ_C (100 MHz) 14.0, 14.1, 14.3, 19.5, 19.8, 22.5, 22.6, 23.9, 25.5, 28.5, 28.6, 28.7, 30.2, 31.3, 31.4, 37.5, 55.1, 67.9, 77.7, 80.8, 91.0, 97.6, 110.9, 120.3, 121.3, 121.7, 124.3, 125.1, 129.4, 130.0, 130.8, 132.3, 152.3; *m*/*z* (ESI–) 717 ([M–H]$^-$, 100%); calcd for $C_{52}H_{61}O_2$ ([M–H]$^-$) 717.4672, found 717.4680.

3.5. (*S*)-4,4′,6,6′-Tetra(2-phenylethyl)-1,1′-bi-2-naphthol 13

(*S*)-4,4′,6,6′-Tetra(2-phenylethynyl)-1,1′-bi-2-naphthol **11** (230 mg, 0.336 mmol) was dissolved in AcOH (7.5 ml) in a 50 ml conical flask under argon. 10% Pd/C (64 mg) was added without stirring, and the mixture purged with Ar (3×) and H_2 (3×). The mixture was stirred under a balloon of H_2. After 2 h (monitoring by TLC, 3:2 petrol:Et_2O), the reaction mixture was purged with Ar (3×) and filtered through Celite®. The filtrate was diluted with H_2O (10 ml), and extracted with CH_2Cl_2 (20 ml). The organic layer was washed with H_2O (10 ml), satd aq. $NaHCO_3$ (2×10 ml) and brine (10 ml), dried ($MgSO_4$) and concentrated in vacuo. Purification of the residue by column chromatography (3:1 petrol:Et_2O) yielded the title compound as a yellow foam (207 mg, 0.295 mmol, 87%): R_f (3:2 petrol:Et_2O) 0.4; $[\alpha]_D$ +15.0 (*c* 1, $CHCl_3$); mp 44°C; ν_{max} (cm^{-1}) 3508 (br), 3024 (m), 2921 (m), 1599 (s), 1495 (m), 1452 (m), 1384 (m), 1175 (m), 1139 (s), 749 (m), 698 (s); δ_H (400 MHz) 2.98–3.03 (4H, m, C(6 and 6′)CH$_2$CH_2Ph), 3.03–

3.19 (8H, m, C(6 and 6′)CH_2CH$_2$Ph and C(4 and 4′)CH$_2$CH_2Ph), 3.37–3.49 (4H, m, C(4 and 4′)CH_2CH$_2$Ph), 4.95 (2H, br s, 2×OH), 7.15 (2H, d, *J* 9, C(8 and 8′)H), 7.18–7.26 (10H, m, ArH), 7.26–7.34 (10H, m, ArH), 7.39 (4H, t, *J* 7, 4×*p*-H of CH$_2$CH$_2$Ph), 7.83 (2H, s, C(3 and 3′)H); δ_C (100 MHz) 35.0, 36.6, 37.9, 38.0, 109.3, 117.5, 123.1, 125.2, 125.8, 126.0, 126.2, 128.0, 128.3, 128.4, 128.5, 128.5, 132.4, 137.2, 141.2, 141.6, 141.8, 151.8; *m*/*z* (ESI–) 701 ([M–H]$^-$, 40%), 255 (100); calcd for $C_{52}H_{45}O_2$ ([M–H]$^-$) 701.3420, found 701.3440.

3.6. (*S*)-4,4′,6,6′-Tetraoctyl-1,1′-bi-2-naphthol 14

(*S*)-4,4′,6,6′-Tetraoctynyl-1,1′-bi-2-naphthol **12** (198 mg, 0.276 mmol) was dissolved in AcOH (6.5 ml) in a 25 ml conical flask under Ar. 10% Pd/C (53 mg) was added without stirring and the mixture purged with Ar (3×) and then H_2 (3×). The mixture was then stirred at rt under a balloon of H_2. After 2 h (monitoring by TLC, 10% Et$_2$O:petrol), the mixture was purged with Ar (3×), diluted with CH_2Cl_2, and filtered through Celite®. The filtrate was washed with water (2×10 ml), satd aq. NaHCO$_3$ (3×10 ml), and brine (10 ml) then dried (MgSO$_4$) and concentrated in vacuo to yield a yellow oil requiring no further purification (195 mg, 0.266 mmol, 95%): R_f (10% Et$_2$O:petrol) 0.1; $[\alpha]_D$ +16.3 (*c* 1, CHCl$_3$); ν_{max} (thin film, cm^{-1}) 3531 (m), 2955 (m), 2925 (s), 2854 (s), 1599 (m), 1466 (w), 1386 (w), 1175 (w), 1141 (w), 881 (w), 824 (w), 722 (w); δ_H (400 MHz) 0.91 (6H, t, *J* 7, C(4 and 4′)C$_7$H$_{14}$CH_3), 0.95 (6H, t, *J* 7, C(6 and 6′)C$_7$H$_{14}$CH_3), 1.45–1.25 (24H, m, C(4, 4′, 6 and 6′)C$_3$H$_6$C$_4$$H_8CH_3$), 1.47 (4H, quin, *J* 7, C(4 and 4′)C$_2$H$_4$CH_2C$_5$H$_{11}$), 1.58 (4H, quin, *J* 7, C(6 and 6′)C$_2$H$_4$CH_2C$_5$H$_{11}$), 1.71 (4H, quin, *J* 7, C(4 and 4′)CH$_2$CH_2C$_6$H$_{13}$), 1.90 (4H, quin, *J* 8, C(6 and 6′)CH$_2$CH_2C$_6$H$_{13}$), 2.77 (4H, t, *J* 8, C(4 and 4′)CH_2C$_7$H$_{15}$), 3.16 (4H, t, *J* 8, C(6 and 6′)CH_2C$_7$H$_{15}$), 4.98 (2H, br s, 2×OH), 7.16 (4H, AB t, *J* 10, C(7 and 7′)H and C(8 and 8′)H), 7.25 (2H, s, C(5 and 5′)H), 7.87 (2H, s, C(3 and 3′)H); δ_C (100 MHz) 14.1, 14.1, 22.7, 22.7, 29.3, 29.3, 29.4, 29.5, 29.6, 29.7, 29.9, 30.4, 31.9, 32.0, 33.1, 36.2, 109.1, 117.3, 122.9, 125.0, 128.2, 128.3, 132.3, 138.1, 142.2, 151.7; *m*/*z* (ESI–) 734 ([M–H]$^-$, 25%), 622 ([M–octyl]$^-$, 10), 509 ([M–(2 octyl)]$^-$, 10), 397 ([M–(3 octyl)]$^-$, 10), 367 ([M/2]$^-$, 10), 283 ([M–(4 octyl)]$^-$, 10), 255 ([M/2–octyl]$^-$, 20); calcd for $C_{52}H_{77}O_2$ [M–H]$^-$ 733.5924, found 733.5940.

3.7. (*S*)-4,4′,6,6′-Tetraphenyl-1,1′-bi-2-naphthol phosphate 15

(*S*)-4,4′,6,6′-Tetraphenyl-1,1′-bi-2-naphthol **8**[17] (325 mg, 0.551 mmol) was dissolved in pyridine (4 ml) and treated with POCl$_3$ (76 μl, 0.81 mmol, 1.5 equiv.), then heated to 90°C. After 2.5 h, the mixture was cooled to rt; H_2O (28 μl) was added and the mixture reheated to 90°C. After 90 min, the pyridine was removed by distillation and 6N HCl (7 ml) was added to the residue, which was then heated at reflux. After 90 min the mixture was cooled and the precipitate collected by suction filtration, washing with 2N HCl then EtOH. The precipitate was dried under high vacuum to yield the title compound as a pale grey powder (327 mg, 0.502 mmol, 91%): $[\alpha]_D$ +76.5 (*c* 0.33, CHCl$_3$); mp 240°C (dec.); ν_{max} (cm^{-1}) 3420 (br), 3056 (w), 1488 (s), 1086 (m), 1025 (m), 961 (s), 758 (s), 699 (s); δ_H (400 MHz, DMSO-d_6) 4.30 (1H, br s, OH), 7.37 (2H, d, *J* 8, C(8 and 8′)H), 7.48 (8H, t, *J* 8, *m*-H of C(4, 4′, 6 and 6′)Ph), 7.57 (2H, s, C(3 and 3′)H), 7.57–7.63 (4H, m, ArH), 7.66 (4H, d, *J* 8, *o*-H of Ph), 7.71 (4H, dd, *J* 8, 2, *o*-H of Ph), 7.80 (2H, dd, *J* 8, 2, C(7 and 7′)H), 8.16 (2H, s, C(5 and 5′)H); δ_C (100 MHz, DMSO-d_6); 121.6, 123.8, 124.4, 126.8, 127.1, 127.5, 127.7, 128.4, 128.6, 129.0, 129.6, 129.8, 129.9, 130.0, 130.8, 132.6, 137.8, 139.8, 140.6, 143.3, 149.2; δ_P (160 MHz, DMSO-d_6) 3.6 (s); *m*/*z* (ESI–) 651 ([M–H]$^-$, 100%); calcd for $C_{44}H_{28}O_4P$ ([M–H]$^-$) 651.1725, found 651.1741.

3.8. (*S*)-4,4′,6,6′-Tetra(4-*n*-butylphenyl)-1,1′-bi-2-naphthol phosphate 16

Following the procedure for **15**, using (*S*)-4,4′,6,6′-tetra(4-*n*-butylphenyl)-1,1′-bi-2-naphthol **9** (357 mg, 0.439 mmol) and POCl$_3$ (61 μl, 0.65 mmol), the title compound was obtained as a pale yellow solid (316 mg, 0.361 mmol, 82%): $[\alpha]_D$ +82.4 (*c* 1, CHCl$_3$); mp (EtOH) 175°C; ν_{max} (cm^{-1}) 3437 (br), 2953 (m), 2927 (s), 2855 (m), 1490 (w), 1182 (m), 1084 (m), 1019 (m), 960 (s), 820 (m); δ_H (400 MHz) 0.95 (12H, 2×t, *J* 8, ArC$_3$H$_6$CH_3), 1.31–1.47 (8H, m, ArC$_2$H$_4$CH_2CH$_3$), 1.58–1.69 (8H, m, ArCH$_2$CH_2C$_2$H$_5$), 2.55 (8H, t, *J* 8, ArCH_2C$_3$H$_7$), 7.24 (8H, dd, *J* 8, 2, ArH *o*- to ^{n}Bu), 7.50 (8H, dd, *J* 8, 2, ArH *m*- to ^{n}Bu), 7.55 (2H, s, C(3 and 3′)H), 7.59 (2H, dd, *J* 8, 2, C(7 and 7′)H), 7.67 (2H, d, *J* 8, C(8 and 8′)H), 8.25 (2H, d, *J* 2, C(5 and 5′)H); δ_C (100 MHz) 14.0, 14.0, 22.4, 22.5, 33.5, 33.6, 35.3, 35.4, 124.1, 124.2, 124.7, 125.0, 125.9, 126.6, 127.2, 127.6, 128.1, 128.5, 128.9, 129.3, 130.0, 130.4, 135.9, 136.6, 137.9, 138.1, 141.6, 142.2, 142.3, 142.7; δ_P (160 MHz) 4.6 (s); *m*/*z* (EI+) 876 (M$^+$, 15%), 277 (38), 79 (70); calcd for $C_{60}H_{61}O_4P$ (M$^+$) 876.4307, found 876.4298.

3.9. (*S*)-4,4′,6,6′-Tetra(2-phenylethyl)-1,1′-bi-2-naphthol phosphate 17

Following the procedure for **15**, using (*S*)-4,4′,6,6′-tetra(2-phenylethyl)-1,1′-bi-2-naphthol **13** (0.531 g, 0.757 mmol) and POCl$_3$ (104 μl, 1.11 mmol), the title compound was obtained as an off-white powder (0.520 g, 0.682 mmol, 90%): $[\alpha]_D$ +104 (*c* 1, CHCl$_3$); mp 140–142°C (dec.); ν_{max} (cm^{-1}) 3024 (w), 2920 (w), 1589 (w), 1496 (w), 1452 (w), 1340 (w), 1256 (m), 1103 (m), 1036 (s), 966 (m), 923 (w), 882 (w), 818 (w), 751 (w), 699 (m); δ_H (400 MHz) 2.96–3.20 (12H, m, C(4, 4′, 6 and 6′)CH$_2$CH_2Ph and C(6 and 6′)CH_2CH$_2$Ph), 3.29–3.49 (4H, m, C(4 and 4′)CH_2CH$_2$Ph), 7.10–7.40 (24H, m, C(7 and 7′)H, C(8 and 8′)H and ArH of C(4, 4′, 6 and 6′)C$_2$H$_4$*Ph*), 7.42 (2H, s, C(3 and 3′)H), 7.82 (2H, s, C(5 and 5′)H); δ_C (100 MHz) 34.9, 36.4, 37.7, 38.1, 119.7, 120.2, 123.0, 126.0, 126.2, 127.7, 128.1, 128.4, 128.5, 128.5, 128.6, 130.4, 138.9, 141.1, 141.3, 141.5; δ_P (160 MHz) 5.7 (s); *m*/*z* (ESI–) 763 ([M–H]$^-$, 100%); calcd for $C_{52}H_{44}O_4P$ ([M–H]$^-$) 763.2977, found 763.3016.

3.10. (*S*)-4,4′,6,6′-Tetraoctyl-1,1′-bi-2-naphthol phosphate 18

Following the procedure for **15**, using (*S*)-4,4′,6,6′-tetraoctyl-1,1′-bi-2-naphthol **14** (265 mg, 0.361 mmol) and $POCl_3$ (49 μl, 0.52 mmol), and isolating the product by extraction into CH_2Cl_2 (2×10 ml). The organic layer was washed with 2N HCl (2×10 ml), dried over $MgSO_4$, and concentrated in vacuo to give a viscous brown oil. On treatment with MeOH (5 ml), a beige solid was precipitated, collected by filtration and dried under high vacuum to yield the title compound (183 mg, 0.230 mmol, 64%): $[\alpha]_D$ +119 (*c* 1, $CHCl_3$); mp 62–63°C; ν_{max} (cm^{-1}) 2922 (s), 2850 (s), 1588 (w), 1466 (w), 1374 (w), 1346 (w), 1262 (w), 1215 (w), 1111 (w), 1036 (m), 968 (w), 912 (w), 884 (w), 818 (w); δ_H (400 MHz) 0.90 (6H, t, *J* 7, C(6 and 6′)$C_7H_{14}CH_3$), 0.93 (6H, t, *J* 7, C(4 and 4′)$C_7H_{14}CH_3$), 1.50–1.18 (40 H, m, C(4, 4′, 6 and 6′)$C_2H_4C_5H_{10}CH_3$), 1.74 (8H, t, *J* 7, C(4, 4′, 6 and 6′)$CH_2CH_2C_6H_{13}$), 2.81 (4H, t, *J* 7, C(6 and 6′)$CH_2C_7H_{15}$), 2.85–2.95 and 2.98–3.12 (4H, 2×m, C(4 and 4′)$CH_2C_7H_{15}$), 7.14 (2H, d, *J* 8, C(7 and 7′)H), 7.40 (2H, d, *J* 8, C(8 and 8′)H), 7.43 (2H, s, C(3 and 3′)H), 7.82 (2H, s, C(5 and 5′)H), 8.58 (1H, br s, OH); δ_C (100 MHz) 14.1, 22.7, 29.3, 29.4, 29.5, 29.5, 29.7, 29.9, 30.2, 30.4, 31.5, 31.9, 32.9, 36.2, 89.0, 119.8, 120.7, 122.6, 126.4, 127.1, 128.0, 130.3, 131.3, 139.3, 141.5, 141.6, 146.7, 146.8; δ_P (160 MHz) 4.3 (s); *m*/*z* (ESI−) 795 ($[M-H]^-$, 100%), 683 ([M−octyl]$^-$, 15), 571 ([M−(2 octyl)]$^-$, 5); calcd for $C_{52}H_{76}O_4P$ ($[M-H]^-$) 795.5481, found 795.5494.

3.11. Tetrakis[(*S*)-4,4′,6,6′-tetraphenyl-1,1′-bi-2-naphthol phosphate] dirhodium(II) 19

$Rh_2(OAc)_4$ (25 mg, 0.050 mmol) and (*S*)-4,4′,6,6′-tetraphenyl-1,1′-bi-2-naphthol phosphate **15** (262 mg, 0.402 mmol, 8 equiv.) were placed in a round-bottomed flask fitted with a short-path distillation apparatus. Chlorobenzene (7 ml) was added and the mixture heated to 150–160°C, replacing the chlorobenzene in 5 ml aliquots as it distilled off (ca 15–20 ml/h). After 5 h, the remaining solvent was removed by distillation and the residue purified by column chromatography (50→70% CH_2Cl_2:petrol, gradient elution). The blue fractions were concentrated in vacuo and the residue further purified by column chromatography (60% CH_2Cl_2:petrol) to yield a blue–green solid (61 mg, 0.0217 mmol, 43%): $[\alpha]_D$ +215 (*c* 1, $CHCl_3$); ν_{max} (cm^{-1}) 1569 (w), 1489 (w), 1362 (w), 1212 (w), 1153 (w), 1059 (s), 974 (w), 895 (w), 758 (w), 698 (m), 544 (w); δ_H (400 MHz) 7.10 (8H, d, *J* 7, C(3 and 3′)H), 7.29–7.39 (24H, m, ArH), 7.39–7.47 (24H, m, ArH), 7.50 (8H, d, *J* 8, C(8 and 8′)H), 7.52–7.70 (32H, m, ArH), 7.72 (8H, d, *J* 8, C(7 and 7′)H), 8.21 (8H, d, *J* 2, C(5 and 5′)H); δ_C (100 MHz) 110.4, 119.2, 123.2, 124.2, 124.3, 124.4, 124.8, 125.3, 125.8, 127.1, 127.2, 127.3, 127.3, 127.5, 127.9, 128.1, 128.3, 128.6, 128.8, 129.2, 130.0, 130.1, 132.1, 133.2, 137.0, 137.8, 139.3, 139.5, 139.8, 141.0, 141.0, 142.6, 144.2, 147.7, 152.3; δ_P (160 MHz) 17.5 (s); *m*/*z* (MALDI+) 2813 (M^+); isotope peak match obtained for M^+.

3.12. Tetrakis[(*S*)-4,4′,6,6′-tetra(4-*n*-butylphenyl)-1,1′-bi-2-naphthol phosphate]dirhodium(II) 20

Following the procedure for **19**, using $Rh_2(OAc)_4$ (14 mg, 0.028 mmol) and (*S*)-4,4′,6,6′-tetra(4-*n*-butylphenyl)-1,1′-bi-2-naphthol phosphate **16** (182 mg, 0.208 mmol): after 6 h, the residue was purified by column chromatography (25% CH_2Cl_2:petrol); the blue fractions were concentrated and the residue further purified by column chromatography (5→25% CH_2Cl_2:petrol, gradient elution) to yield a pale green solid (32 mg, 8.60 μmol, 31%): $[\alpha]_D$ +219 (*c* 1, $CHCl_3$); ν_{max} (cm^{-1}) 3432 (br, w), 2953 (m), 2926 (m), 2855 (m), 1059 (s), 975 (w), 896 (w), 819 (w), 543 (w); δ_H (400 MHz) 0.91 (24H, t, *J* 7, 8×Me), 0.97 (24H, t, *J* 7, 8×Me), 1.25–1.48 (32H, m, 16×CH_2Me), 1.59 (16H, q, *J* 7, 8×CH_2Et), 1.60–1.70 (16H, m, 8×CH_2Et), 2.50–2.63 (16H, m, 8×CH_2Pr), 2.63–2.71 (16H, m, 8×CH_2Pr), 6.87–7.11 (16H, m, *o*-H of C(6 and 6′)Ar), 7.12–7.31 (24H, m, *m*-H of C(6 and 6′)Ar and C(3 and 3′)H), 7.33–7.48 (8H, m, C(8 and 8′)H), 7.49–7.59 (32H, m, *o*- and *p*-H of C(4 and 4′)Ar), 7.59–7.80 (8H, m, C(7 and 7′)H), 8.12–8.31 (8H, m, C(5 and 5′)H); δ_C (100 MHz) 13.8, 22.3, 33.4, 33.5, 35.3, 124.1, 125.4, 127.0, 127.1, 127.4, 127.9, 128.1, 128.7, 129.7, 129.9, 130.2, 132.0, 136.6, 136.8, 137.4, 138.3, 141.9, 143.1, 151.1; δ_P (160 MHz) 17.4 (s); *m*/*z* (MALDI) 3709 (M^+, 100%), 2835 ($[M-L]^+$, 10), 1956 ($[M-2L]^+$, 10); isotope peak match obtained for M^+.

3.13. Tetrakis[(*S*)-4,4′,6,6′-tetra(2-phenylethyl)-1,1′-bi-2-naphtholphosphate] dirhodium(II) 21

Following the procedure for **19**, using $Rh_2(OAc)_4$ (24 mg, 0.054 mmol) and (*S*)-4,4′,6,6′-tetra(2-phenylethyl)-1,1′-bi-2-naphthol phosphate **17** (250 mg, 0.327 mmol): after 5 h, the residue was purified by column chromatography (CH_2Cl_2). The green fractions were concentrated in vacuo and purified by column chromatography (2:1 CH_2Cl_2:petrol) to yield the title compound as a pale olive green solid (67 mg, 0.0205 mmol, 37%): $[\alpha]_D$ −14.8 (*c* 1, $CHCl_3$); ν_{max} (cm^{-1}) 2923 (w), 1452 (w), 1061 (s), 697 (w); δ_H (400 MHz) 2.83–2.92 (16H, m, C(4 and 4′)CH_2CH_2Ph), 3.00–3.09 (16H, m, C(6 and 6′)CH_2CH_2Ph), 3.09–3.19 (16H, m, C(6 and 6′)CH_2CH_2Ph), 3.21–3.32 (16H, m, C(4 and 4′)CH_2CH_2Ph), 7.01 (16H, dd, *J* 8, 2, ArH of C(4, 4′, 6 and 6′)C_2H_4Ph), 7.08–7.26 (56H, m, C(7 and 7′)H and ArH of C(4, 4′, 6 and 6′)C_2H_4Ph), 7.26–7.34 (16H, m, ArH of C(4, 4′, 6 and 6′)C_2H_4Ph), 7.40 (8H, d, *J* 10, C(8 and 8′)H), 7.55 (8H, s, C(3 and 3′)H), 7.80 (8H, s, C(5 and 5′)H); δ_C (100 MHz) 34.4, 36.0, 37.8, 38.2, 119.9, 120.9, 122.8, 125.6, 126.0, 127.4, 128.1, 128.3, 128.4, 128.6, 130.3, 131.4, 139.4, 140.6, 141.5, 141.7; δ_P (160 MHz) 20.3 (s); *m*/*z* (FAB+) 3285 ($[M+Na]^+$, 35%), 3262 ($[M+H]^+$, 62), 664 (100); MALDI isotope peak match obtained for M^+.

3.14. Tetrakis[(*S*)- 4,4′,6,6′-tetraoctyl-1,1′-bi-2-naphthol phosphate] dirhodium(II) 22

Following the procedure for **19**, using $Rh_2(OAc)_4$ (15 mg, 0.031 mmol) and (*S*)-4,4′,6,6′-tetraoctyl-1,1′-bi-2-

naphthol phosphate **18** (183 mg, 0.230 mmol): after 5 h, the residue was purified by column chromatography (25% CH_2Cl_2:petrol) to give a blue–green oil (31 mg, 9.14 μmol, 35%): R_f 0.4 (20% CH_2Cl_2:petrol); $[\alpha]_D$ −6.9 (*c* 1, $CHCl_3$); ν_{max} (cm^{-1}) 3441.6 (br), 2924.4 (m), 2853.2 (m), 2361.2 (w), 1591.8 (w), 1460.3 (w), 1345.9 (w), 1208.1 (w), 1062.1 (s), 969.5 (w); δ_H (400 MHz) 0.81 (24H, t, *J* 7, C(4 and 4′)$C_7H_{14}CH_3$), 0.92 (24H, t, *J* 7, C(6 and 6′)$C_7H_{14}CH_3$), 0.98–1.09 (16H, m, C(4 and 4′)$C_6H_{12}CH_2CH_3$), 1.09–1.20 (16H, m, C(6 and 6′)$C_6H_{12}CH_2CH_3$), 1.20–1.48 (128H, m, C(4, 4′, 6 and 6′)$C_2H_4C_4H_8CH_2CH_3$), 1.62 (16H, q, *J* 7, C(4 and 4′)$CH_2CH_2C_6H_{13}$), 1.71 (16H, q, *J* 7, C(6 and 6′)$CH_2CH_2C_6H_{13}$), 2.80 (16H, t, *J* 7, C(6 and 6′)$CH_2C_7H_{15}$), 2.91 and 3.04 (16H, 2×t, *J* 7, C(4 and 4′)$CH_2C_7H_{15}$), 7.13 (8H, d, *J* 9, C(7 and 7′)H), 7.49 (8H, d, *J* 9, C(8 and 8′)H), 7.53 (8H, s, C(3 and 3′)H), 7.82 (8H, s, C(5 and 5′)H); δ_C (126 MHz) 14.1, 14.1, 22.6, 22.7, 29.1, 29.2, 29.3, 29.4, 29.5, 29.6, 29.8, 31.4, 31.7, 31.9, 32.5, 36.2, 119.7, 120.6, 122.6, 127.1, 128.2, 130.5, 131.3, 139.3, 141.7, 147.0; δ_P (160 MHz) 22.0 (s); *m*/*z* (MALDI) 3390 ($M^{+\bullet}$, 100%); isotope peak match obtained for M^+.

3.15. General procedure for cycloaddition reactions

The diazo compound **1** (40 mg, 0.143 mmol) was dissolved in the chosen solvent (10 mg ml^{-1}) and the mixture degassed by bubbling Ar through the solution for 5 min. Rh^{II} catalyst **19**–**22** (1 mol%) was added and the reaction monitored by TLC. On complete consumption of the starting material, the reaction mixture was concentrated in vacuo and the residue purified by column chromatography (6:1 petrol:Et_2O) to give the cycloadduct **3**[11] with the yields and ees indicated in Table 1.

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References

1. *Cycloaddition Reactions in Organic Synthesis*; Kobayashi, S.; Jørgensen, K. A., Eds.; Wiley-VCH: Weinheim, 2002.
2. *Synthetic Applications of 1,3-Dipolar Cycloaddition Chemistry Toward Heterocycles and Natural Products*; Padwa, A.; Pearson, W. H., Eds.; John Wiley & Sons: New York, 2002. For a recent example, see: Longmire, J. M.; Wang, B.; Zhang, X. *J. Am. Chem. Soc.* **2002**, *124*, 13400–13401.
3. Padwa, A.; Weingarten, M. D. *Chem. Rev.* **1996**, *96*, 223–269.
4. Doyle, M. P.; McKervey, M. A.; Ye, T. *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds*; John Wiley & Sons: New York, 1998; Chapter 7.
5. Clark, J. S. *Nitrogen, Oxygen and Sulfur Ylide Chemistry*; Oxford University Press: Oxford, 2002.
6. Mehta, G.; Muthusamy, S. *Tetrahedron* **2002**, *58*, 9477–9504.
7. For a recent application, see: Hodgson, D. M.; Avery, T. D.; Donohue, A. C. *Org. Lett.* **2002**, *4*, 1809–1811.
8. Hodgson, D. M.; Pierard, F. Y. T. M.; Stupple, P. A. *Chem. Soc. Rev.* **2001**, *30*, 50–61.
9. Kitagaki, S.; Hashimoto, S. *J. Synth. Org. Chem. Jpn.* **2001**, *59*, 1157–1169.
10. Hodgson, D. M.; Stupple, P. A.; Forbes, D. C. In *Rodd's Chemistry of Carbon Compounds*, *Topical Volume*, *Asymmetric Catalysis*; Sainsbury, M., Ed.; Elsevier: Oxford, 2001; pp. 65–99.
11. Hodgson, D. M.; Stupple, P. A.; Pierard, F. Y. T. M.; Labande, A. H.; Johnstone, C. *Chem. Eur. J.* **2001**, *7*, 4465–4476.
12. (a) Hodgson, D. M.; Labande, A. H.; Glen, R.; Redgrave, A. J. *Tetrahedron: Asymmetry* **2003**, *14*, 921–924; (b) Hodgson, D. M.; Labande, A. H. L.; Pierard, F. Y. T. M.; Expósito Castro, M. Á. *J. Org. Chem.* **2003**, *68*, 6153–6159.
13. Pu, L.; Yu, H.-B. *Chem. Rev.* **2001**, *101*, 757–824.
14. Pirrung, M. C.; Zhang, J. *Tetrahedron Lett.* **1992**, *33*, 5987–5990.
15. Hodgson, D. M.; Petroliagi, M. *Tetrahedron: Asymmetry* **2001**, *12*, 877–881.
16. Hu, Q.-S.; Pugh, V.; Sabat, M.; Pu, L. *J. Org. Chem.* **1999**, *64*, 7528–7536.
17. Gong, L.-Z.; Hu, Q.-S.; Pu, L. *J. Org. Chem.* **2001**, *66*, 2358–2367.
18. Chow, H.-F.; Wan, C.-W. *J. Org. Chem.* **2001**, *66*, 5042–5047.
19. Tian, Y.; Chan, K. S. *Tetrahedron Lett.* **2000**, *41*, 8813–8816.
20. Hundertmark, T.; Littke, A. F.; Buchwald, S. L.; Fu, G. C. *Org. Lett.* **2000**, *2*, 1729–1731.
21. Azzena, U.; Melloni, G.; Pisano, L. *J. Chem. Soc., Perkin Trans. 1* **1995**, 261–266.
22. Callot, H. J.; Metz, F. *Tetrahedron* **1985**, *41*, 4495–4501.