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Synthesis of modified binol-phosphoramidites☆

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ABSTRACT

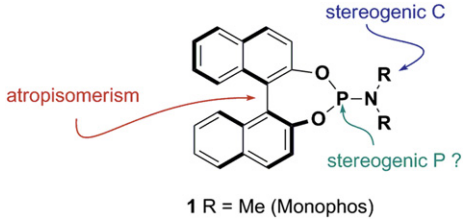
A number of chiral phosphoramidite ligands containing electronically different *N*-heterocycles at the 3,3′-positions of the binol scaffold were synthesized. The nucleophilicity of the pendant heterocycles correlated with the propensity of the P(III) centre to undergo aerobic oxidation to P(V). Due to an unexpected Staudinger-type reaction between the product phosphoramidites, the order in which the individual synthetic transformations were conducted was found to be important. The synthesis of a phosphoramidite ligand containing flanking groups at the 3,3′-positions of the binol scaffold in addition to a stereogenic phosphorus atom was also undertaken.

1. Introduction

Chiral binol-phosphoramidites have become a privileged ligand-set in the field of asymmetric catalysis (Fig. 1).[1] Although they were first introduced by Feringa as enantio-differentiating chiral shift reagents,[2] the utility of these compounds to serve as stereochemically defined monodentate ligands ensured their rapid adoption for the generation of asymmetric metal complexes.[3] This general strategy has been highly successful with binol-phosphoramidite containing metal catalysts realizing high levels of enantiocontrol over a wide-range of transformations including hydrogenations,[4] conjugate additions,[5–7] hydrovinylations[8,9] and cycloadditions.[10] Possessing a highly modular framework, binol-phosphoramidites are amenable to large-scale synthesis, automated synthesis and in many instances,[11] are commercially available.

The ability of binol-phosphoramidite ligands to influence the stereochemical course of a reaction results from the interplay of several factors (Fig. 1). Firstly, the axially chiral 1,1′-binaphthyl backbone provides a chiral cavity in which the phosphorus atom is located. Increasing the steric bulk at the flanking positions on the binol scaffold enhances this effect and 3,3′-disubstituted binol analogues are commonly employed.

A second element of chirality that can be conveniently incorporated into binol-phosphoramidite ligands are additional stereogenic centres on the amine unit. This results in the formation



1 R = Me (Monophos)

Fig. 1. Sources of chirality in binol-phosphoramidites.

of diastereomers and there are reports of binol-phosphoramidites containing either matched or mismatched stereogenic elements, which greatly affect the observed level of stereoinduction.[12] There have also been reports of transformations that require primary amines containing a matched stereocentre in which the hydrogen atom attached to the amine is involved in a secondary interaction, that is, crucial for high levels of selectivity.[13]

The third factor that influences the stereochemical course of a reaction involving phosphoramidite ligands is the nature of the complex formed between the chiral phosphoramidite and the metal centre (Fig. 2). The generated complexes can be homoleptic, with two identical phosphoramidite ligands bound to the metal centre, or heteroleptic, containing two non-identical phosphoramidite ligands.[14] The monodentate nature of phosphoramidites allows a new mode of catalyst optimization in which mixed ligand systems can generate more reactive catalysts.[14] Indeed, hetero-ligand binding involving one chiral binol-phosphoramidite ligand paired with an achiral ligand has been disclosed as a new paradigm in asymmetric catalysis.[15]

The final element of chirality, that is, available in this class of ligands is the stereogenicity of the phosphorus atom (Fig. 1). X-ray

☆ Binol=2,2′-dihydroxy-1,1′-binaphthyl.

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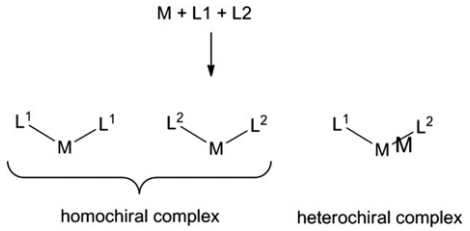


Fig. 2. Modes of phosphoramidite–metal complexation.

crystallographic analysis of several binol-phosphoramidites have revealed that (in the solid state at least) the molecules are not C_2-symmetric, and that the phosphorus atom adopts a pseudo-tetrahedral geometry.[9,16] Unlike nitrogen, the lone pair on phosphorus does not undergo inversion at room temperature.[17,18] When a binaphthol scaffold comprising two non-identical ring systems is employed in phosphoramidite generation, the phosphorus atom constitutes a stereogenic centre. While interest in *P*-stereogenic ligands is burgeoning,[19] to date there are only a handful of examples of binol-phosphoramidites possessing a stereogenic centre at phosphorus.[20,21] At the outset of this work, there were no examples of phosphoramidite ligands bearing a stereogenic phosphorus centre and flanking substituents at the 3,3′-positions.

Recently, we set ourselves the goal of synthesizing chiral phosphoramidite ligands containing additional *N*-heterocycles at the 3,3′-positions of the binol scaffold.[22] We reasoned that such an arrangement may allow for new binding modes and facilitate more efficient catalyst design by allowing the incorporation of under-utilized metals. Additionally, we anticipated that appending heteroatoms to the phosphoramidite backbone may generate an intramolecular mimic of a tethered hetero-ligand type catalyst. Finally, we became fascinated with the possibility of generating a phosphoramidite ligand bearing chelating substituents at the 3,3′-positions, which also incorporated a stereogenic phosphorus atom. This article describes in detail our synthetic rationale, full results, and extends to include the synthesis of some novel heterocycle-containing binol based phosphoramidites, and *P*-stereogenic phosphoramidites (Fig. 3).

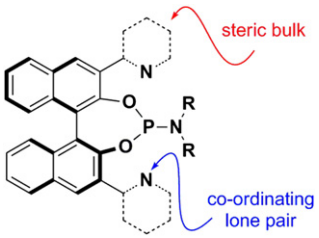


Fig. 3. Targeted 3,3′-*N*-heterocycle binol-phosphoramidite.

2. Results and discussion

Our initial efforts focused on the construction of the 3,3′-bipyridyl-1,1′-binaphth-2-ol based phosphoramidites. In analogy to the logic of Snieckus[23] and Goa,[24] we anticipated that the introduction of pyridine at the flanking positions of the binol scaffold would serve our purpose well—it would introduce steric bulk and a chelating group, without the complications associated with the introduction of further stereogenic centres.

The strategy of appending nitrogen containing heterocycles to the binol scaffold has already been used to good effect in several asymmetric transformations, such as the addition of diethylzinc and the addition of acetylides to aromatic and aliphatic aldehydes.[23,25–27] Appending such a heterocycle to a phosphoramidite molecule finds only a single precedent. Hoppe and co-workers reported the synthesis compound **2**, which was used as a control during the ^{31}P NMR investigations of a related biphenyl compound (Fig. 4).[28] At the outset of this research program, the synthesis of the symmetrically substituted bis-nitrogen heterocycle containing phosphoramidites had not been reported.

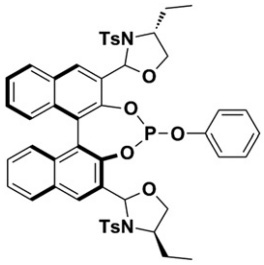
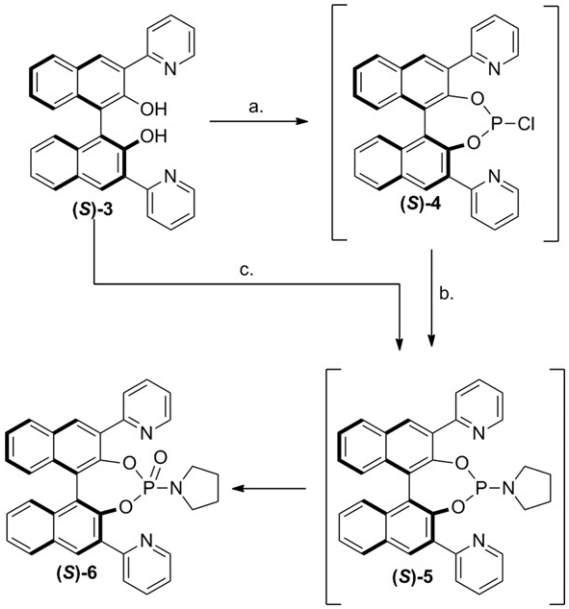


Fig. 4. Compound **2**.

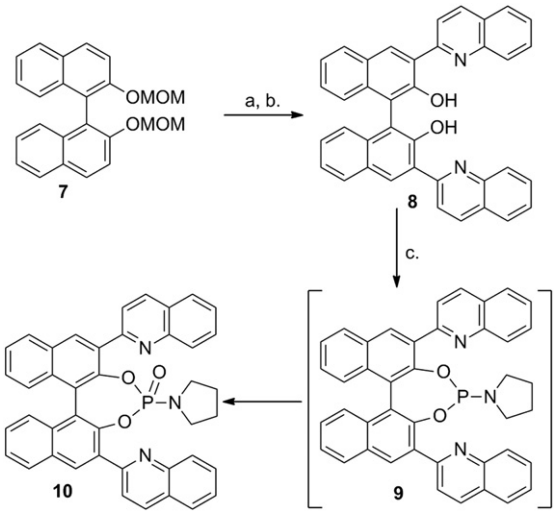
To begin, we employed the fast, efficient and highly flexible route to substituted binol motifs that had been uncovered in our laboratory to generate the 3,3′-dipyridyl-2,2′-dihydroxy-1,1′-binaphthyl (**3**).[29] This process allowed access to both racemic and single-enantiomer binol scaffolds in readiness for conversion into the corresponding phosphoramidites.

The standard method for the introduction of the phosphoramidite unit onto a binol scaffold involves reaction with PCl_3 and to give the intermediate chlorophosphite followed by reaction with the desired amine. To avoid complications inherent with appending a chiral (matched or mismatched) amine, we employed pyrrolidine. As such, binol **3** was treated with PCl_3 at elevated temperature and then with an excess of pyrrolidine (Scheme 1). Disappointingly, the product of the reaction proved to be the oxidized phosphoramidate **6**. We presumed that this product arose either from aerobic oxidation of the desired phosphoramidite **5** during isolation, or from oxidation of the intermediate chlorophosphite **4**.[30] As an alternative synthetic route, Feringa has reported the direct displacement reaction between binol and a phosphorustriamide to give the corresponding phosphoramidite directly.[2] Accordingly, the 2,2′-



Scheme 1. Reagents and conditions: a. PCl_3, PhMe Δ; b. pyrrolidine 68%; c. $P(C_4H_8N)_3$, PhMe, Δ, 76%.

bispyridyl binol **3** was treated with excess pyrrolidinylphosphortriamide, but again the reaction returned exclusively the oxidized product **6**. The non-involvement of a chlorophosphoramidite intermediate in this second approach strongly suggested that the desired phosphoramidite **5** was formed but underwent oxidation when exposed to the atmosphere during isolation. To ensure that this propensity towards oxidation was not specific to pyridine, the synthesis of bis-quinolinyl binol phosphoramidite **9** was attempted (Scheme 2).



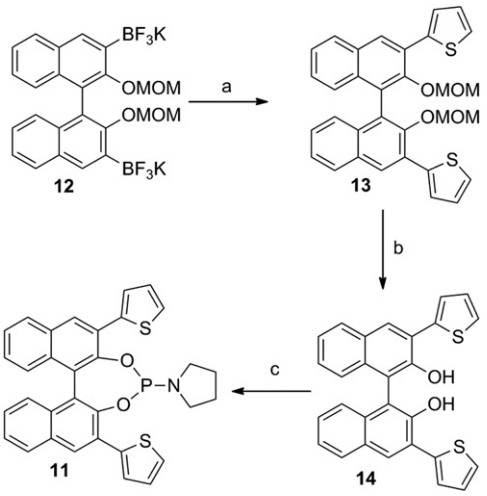
Scheme 2. Reagents and conditions: a. *n*-BuLi, quinoline, THF, −78 °C, then MnO_2; b. HCl, MeOH 78%; c. PCl_3, PhMe Δ, then pyrrolidine 74%.

Compound **7** was transformed into the phosphoramidite precursor **8** by directed lithiation, reaction with quinoline, and cleavage of the MOM protecting groups. As before, attempted phosphoramidite formation using this electronically similar but sterically different bis-quinoline compound **8**, gave the oxidized phosphoramidate **10** as the sole reaction product.

Given that other 3,3′-bisaryl phosphoramidites have been synthesized using a similar strategy and are both chromatographically and air stable,[31,32] the propensity of compounds **6** and **10** to undergo oxidation must be due to the proximity of the pyridine lone pair to the phosphorus centre. It is known that the phosphorus atom in phosphoramidites can function as a π-acceptor. Studies using ironcarbonyl–phosphoramidite complexes have previously been performed to quantify this binding mode. To confirm this supposition, we sought to replace nucleophilic pyridine unit with a non-nucleophilic heterocycle containing with a lone pair. Based on the relative nucleophilicity measurements of Mayr,[33,34] we elected to synthesize the bis-thienyl binol based phosphoramidite **11** (Scheme 3).

In the event, the bis-trifluoroboronate **12**[29] underwent smooth microwave-assisted coupling to 2-bromothiophene as shown in Scheme 3. Removal of the MOM units gave **14**. Conversion into the phosphoramidite **11** was accomplished in the standard fashion and gave the desired product in high yield. The oxidized product P(V) compound was not observed in the reaction mixture. As expected, compound **11** proved inert towards aerobic oxidation, remaining unchanged after standing in air for 2 days.

While the stability of **11** highlighted the importance of the pendant heterocycle in the unwanted oxidation reaction, our primary goal remained the synthesis of chiral phosphoramidite ligands with additional nitrogen containing heterocycles. Although the exact mechanism of the *N*-heterocycle facilitated phosphorus oxidation is not known, we anticipated that the propensity towards oxidation could be attenuated by employing a less nucleophilic



Scheme 3. Reagents and conditions: a. 2-bromothiophene, $Pd(PPh_3)_4$, K_2CO_3, DMF/H_2O, MW 150 °C, 89%; b. HCl, MeOH, 99%; c. PCl_3, PhMe, Δ, then pyrrolidine 79%.

nitrogen heterocycle. For that reason, we turned our attention to the 3,3′-triazolyl substituted compounds (Fig. 5).

Introduction of a triazole unit at the flanking position of the binol scaffold would accomplish the same aims as previously set-

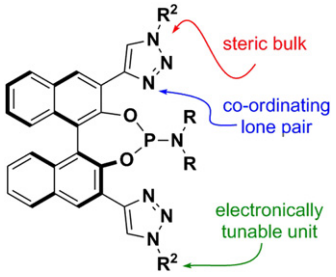
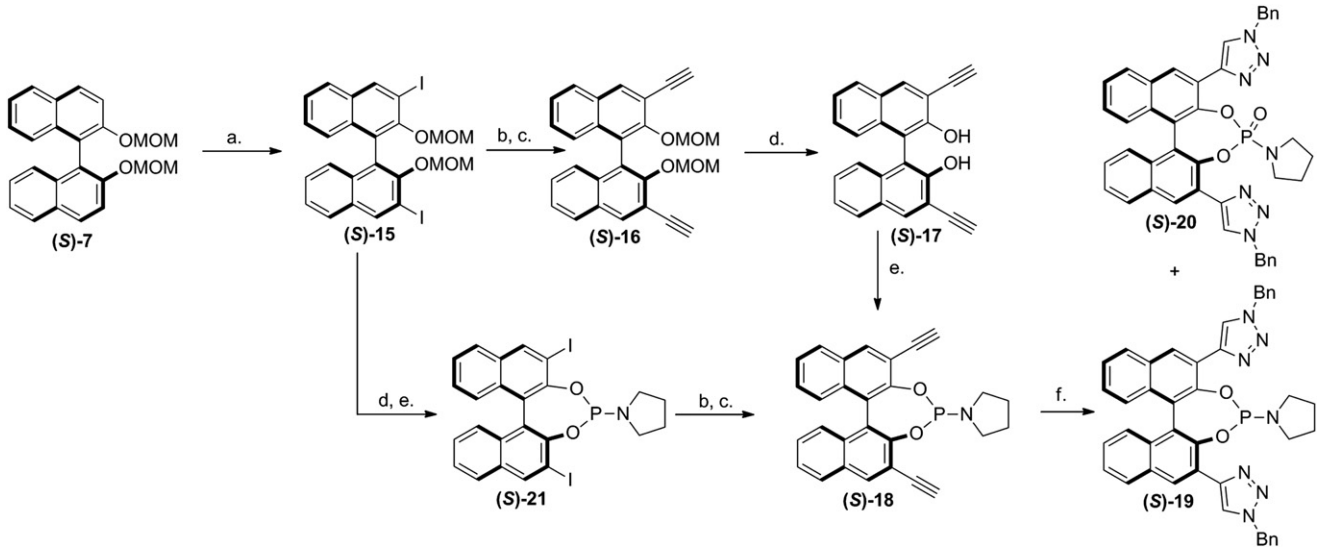


Fig. 5. Targeted 3,3′-triazolyl binol phosphoramidite.

out; it would introduce both a sterically bulky group and an additional chelating group. The electronic properties of the triazole could be tuned by a judicious choice of the R^2 unit, attenuating or enhancing the nucleophilicity of the parent heterocycle. Due to their ease of formation via azide–alkyne 'click' cycloadditions,[35] triazoles have been commonly used as linking groups that allow access to a wide range of chemical diversity.[36–39] We planned to use the bis-acetylene substituted phosphoramidite **18** as the alkyne coupling partner for a series of click reactions with azides possessing differing electronic properties (Scheme 4).

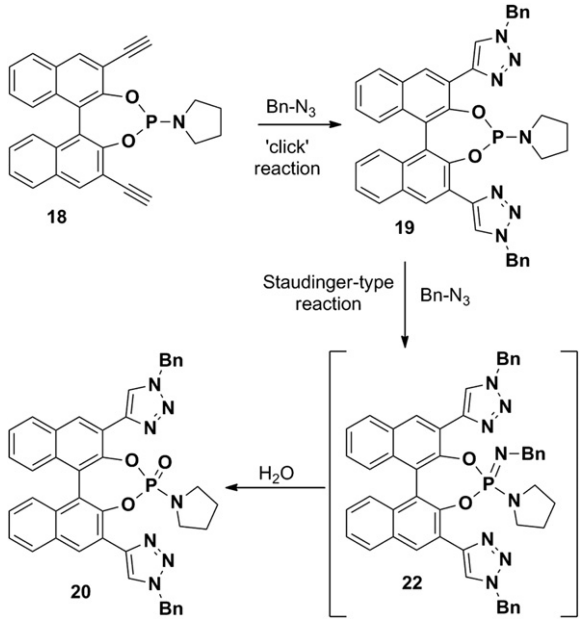
The required bis-acetylene compound **18** was generated using a Sonogashira based strategy. As shown in Scheme 4, 3,3′-diiodo-2,2′-bismethoxymethoxy-1,1′-binaphthyl **15** was generated from **7** via a directed lithiation–iodine quench. Compound **15** subsequently underwent smooth palladium-catalysed cross-coupling with trimethylsilylacetylene, followed by silyl cleavage to give the desired terminal acetylene **16**. The phosphoramidite unit was installed under standard conditions and compound **18** displayed no tendency towards oxidation. Indeed compound **18** could also be obtained by initial formation of the 3,3′-diiodophosphoramidite **21**, followed by Sonogashira coupling, which exposed the phosphorus centre to the action of copper(I) with no deleterious effects. After some experimentation, conditions to effect a copper catalysed Huisgen 1,3-dipolar cycloaddition of **18** with benzyl azide were uncovered. This delivered the desired phosphoramidite **19** in low yield along with the oxidized compound **20**. The isolation of



Scheme 4. Reagents and conditions: a. *n*-BuLi, quinoline, THF, −78 °C, I_2, 78%; b. TMSCCH, $Pd(PPh_3)_4$, CuI, NEt_3, THF, 97%; c. K_2CO_3, MeOH, 98%; d. HCl, MeOH, 91%; e. PCl_3, PhMe Δ, then pyrrolidine 69%; f. BnN_3, CuI, *i*-Pr_2NEt, CH_3CN, 17% (*S*)-**19**, 77% (*S*)-**20**.

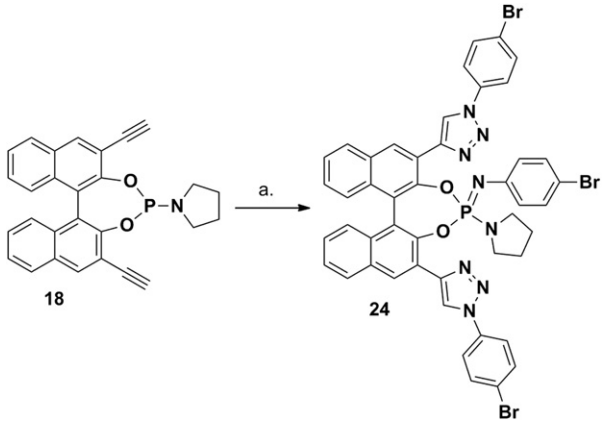
compound **19** represented the first synthesis of a 3,3′-bis-*N*-heterocycle substituted binol-phosphoramidite.

The increased oxidative stability of compound **19** relative to the bis-pyridyl compound **5** was exemplified by the fact that phosphoramidite **19** could be stirred in air for over an hour with only 10% conversion into the corresponding phosphoramidite **20**. Given this relatively slow rate of aerobic oxidation, we hypothesised that the large amount of oxidized product isolated from the reaction mixture must reflect another oxidative process (Scheme 5). The triazolyl phosphoramidite **19** was either more susceptible to Cu(I) catalysed oxidation than the parent phosphoramidite **18**, or compound **19** engaged in a Staudinger-type reaction with excess azide to generate a phosphonimidate **22**, which upon hydrolysis would give the oxidized compound **20**.



Scheme 5. Possible non-aerobic oxidation pathway.

Instructively, when compound **18** was subjected to the Cu(I) 'click' conditions in the presence of excess *p*-bromophenyl azide, the phosphonimidate **24** was isolated in high yield (Scheme 6). This provided compelling support for the Staudinger-type pathway.



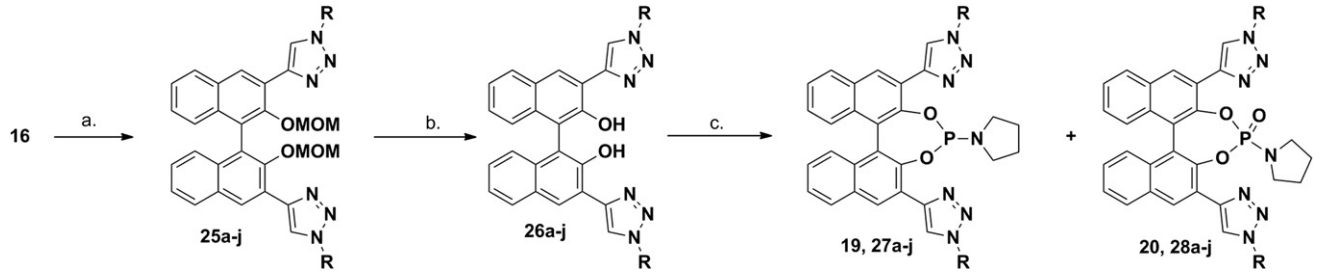
Scheme 6. Reagents and conditions: a. *p*-$BrPhN_3$, CuI, *i*-Pr_2NEt, CH_3CN, 82%.

When just 1 equiv of *p*-bromophenyl azide was employed in the reaction, the slow 'click' reaction between the alkyne **18** and the electron deficient azide rendered the Staudinger-type reaction competitive and **24** was still observed in the reaction mixture. This outcome prompted us to change the order in which the reactions were carried out to avoid the interaction between azide and phosphoramidite.

As detailed in Scheme 7, the bis-alkyne **16** was subjected to a series of 'click' reactions to install the triazole unit giving **25a**–**f**. The alcohol protecting groups were removed and the diols **26a**–**j** were treated with PCl_3 and pyrrolidine to give the corresponding phosphoramidites **27a**–**f** and phosphoramidates **28a**–**f**.

Our supposition that a Staudinger-type reaction contributed to the formation of compound **20** is supported by the data in Table 2. Forming the heterocycle before the incorporation of phosphorus (entry 2 vs entry 1) greatly decreased the relative proportion of P(V) in the product mixture, from 82% to 52%. This latter value is a more accurate reflection of the aerobic stability of the compound **19**. The oxidized product **20** provided crystals suitable for X-ray analysis, which enabled unambiguous confirmation of the structure of the 1,4-triazole moiety (Fig. 6).

In order to probe the relationship between the nucleophilicity of the *N*-heterocycle and the relative ease of aerobic oxidation, a range of electronically different azides were employed. Phenyl azide behaved in a similar manner to benzyl azide (entry 3) returning



Scheme 7. Reagents and conditions: a. RN_3, CuI, *i*-Pr_2NEt, CH_3CN, 89% (**25a**), 94% (**25b**), 99% (**25c**), 92% (**25d**), 96% (**25e**), 87% (**25f**); b. HCl, MeOH, 91% (**26a**), 78% (**26b**), 92% (**26c**), 97% (**26d**), 92% (**26e**), 96% (**26f**); c. PCl_3, PhMe Δ, then pyrrolidine, see Table 1.

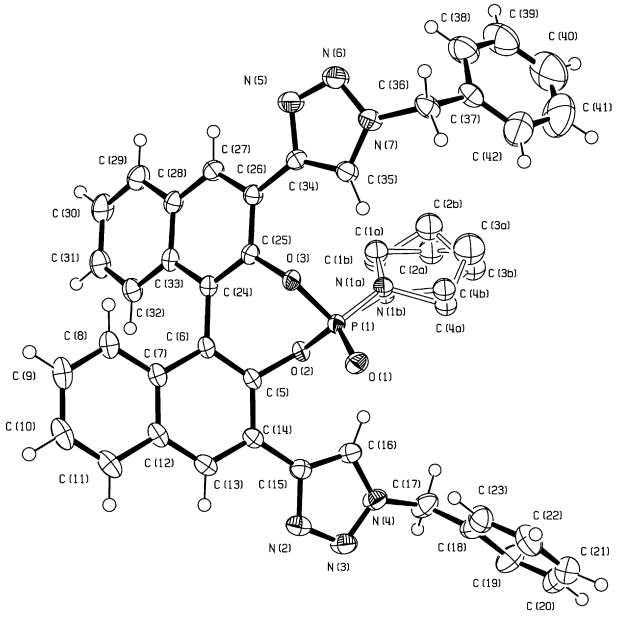


Fig. 6. X-ray structure of **19**.

greater than 40% of the undesired oxidation product **28a**. Employing a more electron-rich azide to generate a more nucleophilic triazole unit, lead to an increased proportion of oxidized product (entry 4). Employing increasingly electron-poor azides (entries 5–8) gave a smooth gradient of decreasing phosphorus oxidation. In this regard, the pentafluorophenyl compound (entry 9) gave the most satisfactory results, giving exclusively the phosphoramidite **27f** in high yield.

The ability of the flanking heterocycle to affect the nucleophilicity of the triazole nitrogen was evidenced by the chemical shift of the alcohol proton in the precursor diols **26a**–**f**. As shown in Table 1, the more nucleophilic nitrogen atoms at the flanking positions were able to engage in intramolecular H-bonding with the alcohol group of binol and shift the corresponding resonance to lower field. This trend may be a useful diagnostic tool for assessing the likely stability of possible 3,3′-*N*-heterocycle containing binol-phosphoramidite ligands.

In line with several other reported phosphoramidites, the acetylenic compound **18** (see Scheme 4) used to form the triazole units does not exhibit C_2-symmetry in the solution phase. The ^1H NMR spectrum for this compound displayed individual resonances for the two terminal alkyne protons, which were well separated. The seven-membered ring must therefore be in conformation that situates the two alkynes in different chemical environments, with one being positioned closer to the pyrrolidine ring (Fig. 7).

Quantum mechanical calculations at the HF/6-31G* level of theory support this picture, suggesting the lowest energy conformation of the molecule as depicted in Fig. 8. It is noteworthy that there are only two signals for the alkyne hydrogens, suggesting that a single ring-conformation is present. A fast inversion of the phosphorus lone pair would produce an intermediate conformer in which the pyrrolidine ring would be positioned equidistant to the two acetylenic protons, giving rise to additional signals in the ^1H NMR spectrum. It is interesting to note the unusual implications that such an inversion would have on the molecule. Inverting the lone pair would lead to a different ring conformation, but the phosphorus atom is neither a stereogenic nor pseudo-stereogenic centre. Attempts to obtain crystals of **18** suitable for X-ray analysis have so far proved fruitless, with all phosphoramidites generated in this work existing as powders.

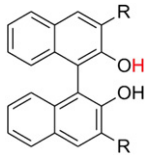
We anticipated that we could use the conformational preference of the system to generate a *P*-stereogenic binol-phosphoramidite. If the two ring systems of the binol unit were non-identical, then the phosphorus atom would constitute a stereogenic centre (see Fig. 1). In that case, inversion of the phosphorus lone pair would generate diastereomers. Reetz has demonstrated that the stereogenicity of the phosphorus atom can influence the behaviour of phosphoramidite ligands, but to date, *P*-stereogenic phosphoramidites with only a single flanking group have been reported.[20,21] We set out to generate a binol-phosphoramidite ligand containing flanking

Table 1
Relative proportion of phosphorus oxidation.

Entry	Compound	R	Isolated yield of P(III) product (%)[a]	Isolated yield of P(V) product (%) [a]	Proportion of oxidation (%)
1	**20**	Benzyl	17[b]	77[b]	82[b]
2	**20**	Benzyl	36	40	52
3	**27a**, **28a**	Phenyl	32	24	43
4	**27b**, **28b**	4-Methoxyphenyl	24	54	68
5	**27c**, **28c**	4-Bromophenyl	66	28	30
6	**27d**, **28d**	4-Fluorophenyl	68	17	20
7	**27e**, **28e**	2,4,5-Trichlorophenyl	59	10	14
8	**27f**	Pentafluorophenyl	89	0	0

[a] After chromatography.
[b] Synthesised as shown in Scheme 5.

Table 2
Chemical shift of alcohol protons.



Entry	Compound	R	OH shift (ppm)
1	**3**	Pyridyl	14.50[a]
2	**8**	Quinolyl	15.17[a]
3	**20**	Benzyl triazolyl	8.95[a]
4	**26a**	Phenyl triazolyl	9.54[a]
5	**26b**	4-Methoxyphenyl triazolyl	9.60[a]
6	**26c**	4-Bromophenyl triazolyl	9.74[b]
7	**26d**	4-Fluorophenyl triazolyl	9.47[b]
8	**26e**	2,4,5-Trichlorophenyl triazolyl	9.47[a]
9	**26f**	Pentafluoro-phenyl triazolyl	7.79[a]
10	**14**	Thiophenyl	5.54[a]

[a] Spectrum measured in $CDCl_3$.
[b] Spectrum measured in DMSO-d_6.

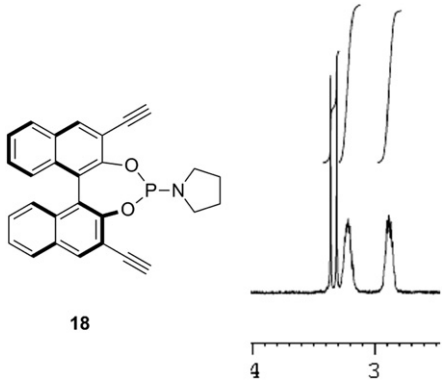


Fig. 7. Acetylenic ^{1}H NMR signals for **18**.

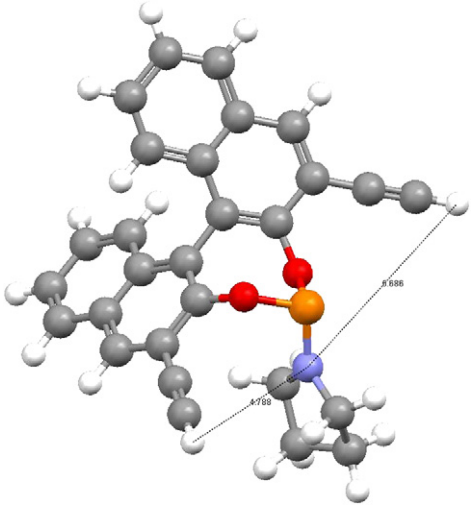


Fig. 8. Calculated lowest energy conformer of **18**.

groups at both the 3 and 3′ positions on the binol ring in addition to a stereogenic phosphorus centre.

To that end, (*S*)-binol **29** was transformed into the brominated monopivalate **30** according to the method of Reider and co-workers.[40] Due to the C_2-symmetry of the starting diol this procedure can only return a single product. Ester hydrolysis and installation of MOM protecting/directing groups gave compound **32**.[41] Negeshi cross-coupling with dimethylzinc furnished compound **33**, which possessed a single biaryl configuration, but which contained non-identical naphthol rings. In analogy to the previously described synthesis of the parent compound **18**, compound **33** was subjected to an *ortho*-lithiation, iodination, alkynation sequence to give compound **35**. Removal of the MOM protecting groups under acidic conditions revealed the diol **36**, and set the scene for installation of the *P*-seterogenic centre. Binol **36** was treated with PCl_3 and pyrrolidine to furnish phosphoramidites **37a** and **37b**, which contained a single biaryl configuration, a single seven-membered ring conformation, and either the (*R*) or (*S*) configuration at the newly stereogenic phosphorus atom. The generation of these diastereomers is plainly visible in the ^{1}H NMR spectrum of the product mixture (Fig. 9), where both the acetylenic and methyl protons give rise to two sets of signals. Frustratingly, compounds **37a** and **37b** were not chromatographically separable (by FC or HPLC) and so the stereogenicity at phosphorus for each compound could not be identified. The generation of more readily separable diastereomers will be pursued in the next phase of the project (Scheme 8).

3. Conclusions

This work details our successful synthesis of chiral phosphoramidite ligands containing *N*-heterocycles at the 3,3′-positions of the binol scaffold. During the course of the study, we observed a correlation between the nucleophilicity of the pendant heterocycles and the propensity of the P(III) centre to undergo aerobic oxidation to P(V). This unwanted oxidation narrows the scope of *N*-heterocycles that can be employed as additional chelating groups on binol based phosphoramidite ligands. Whilst the synthetic sequence used to access the desired ligands is straightforward, the order in which the individual steps are conducted was found to be important. The product phosphoramidites were observed to engage in a Staudinger-type reaction with azides, providing an additional pathway to the undesired P(V) products. This unwanted reaction necessitated late-stage introduction of the phosphorus centre. Using that strategy, a series of triazole containing compounds with electronically different substituents were generated and the pentafluorophenyl compound **27f** was identified as the most stable member of the family.

Taking advantage of the lack of C_2-symmetry in binol based phosphoramidites, the synthesis of a *P*-stereogenic phosphoramidite was undertaken. A single-enantiomer binol scaffold with non-identical ring systems was employed to generate diastereomeric phosphoramidites. To the best of our knowledge, this is the first report of a phosphoramidite ligand containing flanking groups at the 3,3′-positions of the binol scaffold in addition to a stereogenic phosphorus atom.

The ability of 3,3′-triazolyl substituted binol-phosphoramidites to serve as nucleophilic catalysts and ligands for chiral metal complex formation is currently under investigation in our laboratory.

4. Experimental section

4.1. General

All reactions were conducted under an inert atmosphere (nitrogen or argon) in oven-dried glassware. Dichloromethane was freshly distilled from CaH_2 and tetrahydrofuran was freshly distilled from sodium/benzophenone. Acetonitrile, methanol and toluene were obtained from a PureSolv MD Solvent Purification System. All other solvents and reagents were used as received from commercial sources with recrystallization or distillation performed

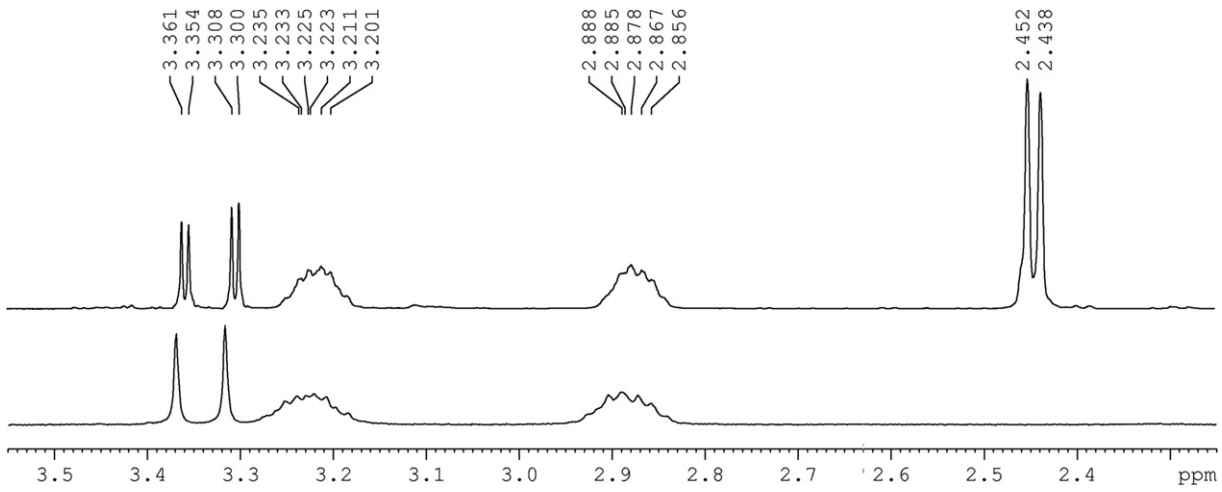
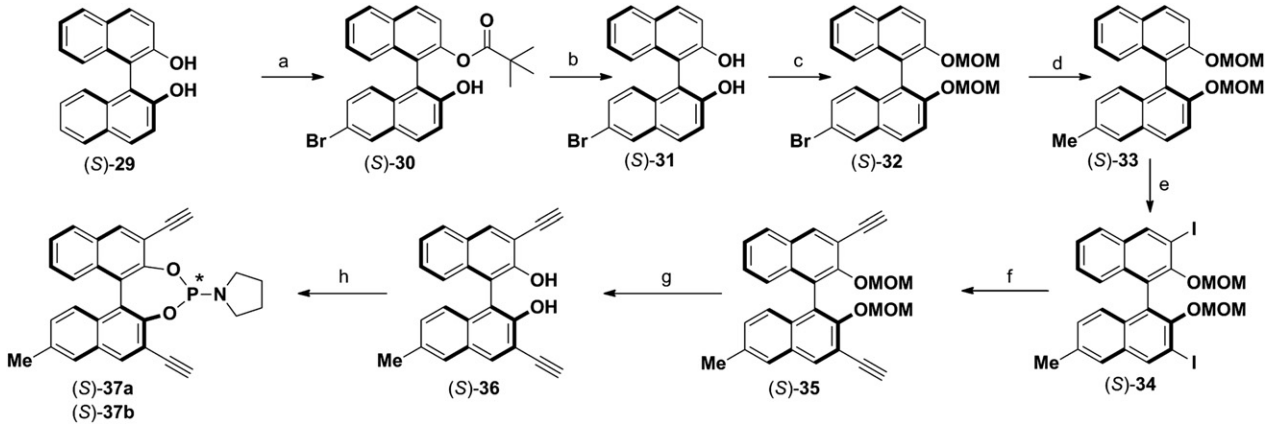


Fig. 9. Acetylenic and methyl ^{1}H NMR signals for compounds **18** (bottom spectrum), **37a** and **37b** (top spectrum).



Scheme 8. Reagents and conditions: a. Ref. 41; b. K_2CO_3, MeOH, 89%; c. NaH, MOMCl, THF, 74%; d. $Pd(PPh_3)_4$, Me_2Zn, THF Δ, 88%; e. *n*-BuLi, I_2, THF, −78 °C, 49%; f. TMSCCH, $Pd(PPh_3)_4$, CuI, NEt_3, THF, then K_2CO_3, MeOH, 98%; g. HCl, MeOH, 96%; h. PCl_3, PhMe Δ, then pyrrolidine 62%.

as required. Melting points were determined using a Stanford Research Systems Optimelt automated melting point system. Infrared spectra were acquired on a Shimadzu FTIR-8400S or Bruker Alpha-E ATR spectrometer as a solution between sodium chloride plates, as a KBr disk or neat. Absorption maxima are expressed in wavenumbers (cm^{-1}). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE DPX300, or Bruker DPX400 spectrometer (^{1}H frequencies 300, 400 MHz; ^{13}C frequencies 75 and 100 MHz, respectively). ^{1}H chemical shifts are expressed as parts per million (ppm) with residual chloroform (δ 7.26) as reference and are reported as chemical shift (δ_H); relative integral; multiplicity (s=singlet, br=broad, d=doublet, t=triplet, dd=doublet of doublets, dt=doublet of triplets, q=quartet, m=multiplet); and coupling constants (*J*) reported in hertz. ^{13}C NMR chemical shifts are expressed as parts per million (ppm) with residual chloroform (δ 77.1) as internal reference and are reported as chemical shift (δ_C); multiplicity (assigned from DEPT experiments). ^{31}P NMR and ^{19}F NMR chemical shifts are expressed as parts per million (ppm) using residual chloroform (δ 7.26, ^{1}H NMR) as an external reference. High resolution mass spectra were recorded on a Bruker ApexII Fourier Transform Ion Cyclotron Resonance mass spectrometer with a 7.0 T magnet, fitted with an off-axis Analytica electrospray source. Phenyl azide, benzyl azide, 4-methoxyphenyl azide, 4-bromophenyl azide, 4-fluorophenyl azide, 2,4,5-trichlorophenyl azide and pentafluorophenyl azide were prepared according to literature procedures. 2,2′-Bismethoxymethoxy-1,1′-binaphthyl was prepared as previously reported.[29] 6-bromo-2,2′-bismethoxymethoxy-1,1′-binaphthyl was prepared according to a published procedure.

4.2. (*S*)-3,3′-Di(2-pyridyl)-1,1′-binaphthyl-2,2′-diyl 1-pyrrolidylphosphonate (6)

Phosphorus trichloride (0.39 mL, 4.5 mmol) was added to a stirred solution of 3,3′-di(2-pyridyl)-2,2′-dihydroxy-1,1′-binaphthyl **3** (100 mg, 2.27×10^{-4} mol) in toluene (10 mL) and the reaction mixture was heated under gentle reflux for 8 h. The mixture was cooled to 0 °C and pyrrolidine (1.1 mL, 13 mmol) added slowly. The mixture was stirred at 0 °C for 15 min and then heated to 50 °C for 5 h. The reaction mixture was allowed to cool to room temperature then partitioned between saturated aqueous ammonium chloride (80 mL) and dichloromethane (80 mL). The aqueous phase was extracted with dichloromethane (3×30 mL) and the combined organic phases were washed with saturated aqueous ammonium chloride (20 mL), water (20 mL) and were dried over anhydrous sodium sulfate. The solvent was evaporated and the residues were subjected to flash column chromatography (ethyl acetate/hexanes: 1/5) to give compound **6** as a colourless solid (86 mg, 68%); mp>230 °C; IR (neat) ν_{max}/cm^{-1} 2925, 1728, 1293, 1201, 975; ^{1}H NMR (300 MHz, $CDCl_3$) 8.56 (1H, s), 8.51 (1H, s), 8.43–8.47 (2H, m), 8.23–8.29 (2H, m), 7.82–8.01 (4H, m), 7.13–7.42 (8H, m), 2.66–3.41 (4H, m), 0.92–1.29 (4H, m); ^{13}C NMR (75 MHz, $CDCl_3$) 159.9, 156.4, 149.7, 149.1, 145.0 (d, $^2J_{C-P}$ 9.8), 144.5 (d, $^2J_{C-P}$

7.3), 136.6, 134.5, 131.1, 130.9, 129.9, 129.6, 128.8, 128.8, 128.3, 128.0, 127.7, 126.4, 126.2, 125.5, 125.1, 125.0, 124.4, 124.2, 124.0, 122.9, 122.8, 122.6, 122.0, 121.1, 119.4, 116.7, 47.4 (2C, CH_2, d, $^2J_{C-P}$ 5.1), 26.1 (2C, CH_2, d, $^3J_{C-P}$ 10.3); ^{31}P NMR (121 MHz, $CDCl_3$) 12.14; MS (ESI) *m*/*e* (relative intensity) 578 (MNa^+, 12), 556 (MH^+, 100), 486 (4); HRMS (ESI) calcd (M^+) 555.1712, obsd 555.1710.

4.3. 3,3′-Di(2-quinolyl)-2,2′-dihydroxy-1,1′-binaphthyl (8)[23]

A solution of **7** (493 mg, 1.32 mmol) in THF (15 mL) was cooled to −78 °C and a solution of *n*-butyllithium in hexanes (2.01 M; 3.28 mL, 6.59 mmol) was added. The solution was stirred for 30 min, then allowed to warm to room temperature and stirred for a further 2 h. Quinoline (785 μL, 6.62 mmol) was added and the resulting mixture was stirred for 15 h before being poured onto saturated aqueous ammonium chloride (100 mL) and extracted with dichloromethane (3×50 mL). The combined organic extracts were washed with water (100 mL) then dried over anhydrous sodium sulfate and the solvent evaporated. The residue was taken up in dichloromethane (15 mL) and manganese(IV) oxide (2.30 g, 26.5 mmol) was added. The mixture was stirred vigorously under air for 20 h, then filtered through a pad of silica, eluting with dichloromethane. The filtrate was concentrated and the residue was subjected to flash column chromatography (ethyl acetate/hexanes: 3/20) to give a yellow oil, which was triturated with methanol (5 mL) to give 3,3′-di(2-quinolyl)-2,2′-bismethoxymethoxy-1,1′-binaphthyl (647 mg, 78%) as a colourless powder; mp>340 °C (decomposes); R_f 0.15 (ethyl acetate/hexanes: 3/20); IR (neat) ν_{max}/cm^{-1} 2954, 1596, 1502, 1195, 967, 833, 792; ^{1}H NMR (300 MHz; $CDCl_3$) 8.54 (2H, s), 8.33 (2H, d, *J* 8.2), 8.22 (2H, d, *J* 9.3), 8.14 (2H, d, *J* 8.2), 8.03 (2H, d, *J* 8.2), 7.86 (2H, d, *J* 7.8), 7.77 (2H, ddd, *J* 1.2, 7.2, 9.3), 7.57 (2H, dd, *J* 7.4, 7.2) 7.46 (2H, ddd, *J* 2.5, 6.6, 9.9) 7.34–7.38 (4H, m), 4.63 (2H, d, *J* 6.5), 4.55 (2H, d, *J* 6.5), 2.48 (6H, s); ^{13}C NMR (75 MHz; $CDCl_3$) 157.4 (C), 151.2 (C), 148.5 (C), 135.7 (CH), 135.7 (C), 134.5 (C), 134.5 (C), 132.0 (C), 131.0 (C), 129.7 (CH), 129.6 (CH), 128.7 (CH), 127.5 (C), 127.1 (C), 127.1 (C), 126.6 (CH), 126.3 (CH), 125.4 (CH), 123.4 (C) 99.4 (CH_2), 56.2 (CH_3); MS (ESI) *m*/*e* (relative intensity) 629 (13), 651 (100); HRMS (ESI) obsd 651.2241 (MNa^+) calcd 651.2254. The 3,3′-di(2-quinolyl)-2,2′-bismethoxymethoxy-1,1′-binaphthyl intermediate (200 mg, 3.18×10^{-4} mol) was taken up in dichloromethane (10 mL) and methanol (15 mL). Hydrochloric acid (10 M; 1.0 mL, 10 mmol) was added and the solution was stirred for 2 h. The mixture was then neutralized by the addition of excess sodium bicarbonate then poured onto water (100 mL). The resulting mixture was extracted with dichloromethane (3×50 mL) and the combined organic extracts were washed with water (100 mL), dried over anhydrous sodium sulfate and the solvent was evaporated. The residue was taken up in a minimum of warm dichloromethane and pentane was added to precipitate the product. Compound **8** (156 mg, 91%) was collected on the sinter as a yellow powder; IR (neat) ν_{max}/cm^{-1} 3055, 1508, 1204, 820, 745; ^{1}H NMR (200 MHz, $CDCl_3$) 15.17 (2H, br), 8.72 (2H, s), 8.37 (2H, d, *J* 9.0), 8.41 (2H, d, *J* 9.0), 7.83–8.01 (4H, m), 7.66 (2H, ddd, *J* 7.0, 6.1, 1.2), 7.57 (2H, ddd, *J* 7.0, 6.1, 1.1), 7.24–7.37 (4H, m); ^{13}C NMR (200 MHz, $CDCl_3$) 157.8, 154.8, 144.0, 138.7, 135.0, 131.5, 129.2, 128.8, 127.0, 127.8, 127.3, 127.1, 126.6, 126.5, 124.0, 123.0, 120.8, 118.7, 117.8.

4.4. 3,3′-Di-(2-quinolyl)-1,1′-binaphthyl-2,2′-diyl 1-pyrrolidylphosphonate (10)

To a solution of **8** (50 mg, 9.3×10^{-4} mol) in *m*-dichlorobenzene (5 mL) was added phosphorus trichloride (81 μL, 9.2×10^{-4} mol). The reaction mixture was heated under reflux for 15 h. The mixture was then cooled to 0 °C and pyrrolidine (350 μL, 4.26 mmol) added. The mixture was allowed to warm to room temperature with stirring over 1 h, and was then poured onto saturated aqueous ammonium chloride (40 mL). The resulting mixture was extracted with dichloromethane (3×20 mL). The combined organic phases were washed with saturated aqueous ammonium chloride (40 mL), water (40 mL), were dried over anhydrous sodium sulfate and the solvent was evaporated. The residue was subjected to flash column chromatography (ethyl acetate/hexanes: 1/4) to give **10** (44 mg, 74%) as a colourless powder; mp>180 °C (decomposes); R_f 0.26 (ethyl acetate/hexanes: 1/4); IR (neat) ν_{max}/cm^{-1} 2923, 1596, 1503, 1297, 1199; ^{1}H NMR (300 MHz; $CDCl_3$) 8.70 (1H, s), 8.49 (1H, s), 8.45 (1H, d, *J* 7.0), 8.31 (1H, d, *J* 6.8), 8.28 (1H, d, *J* 6.8), 8.23 (1H, d, *J* 6.3), 8.22 (1H, d, *J* 6.3), 8.21 (1H, d, *J* 7.0), 8.11 (1H, d, *J* 6.5), 8.07 (1H, d, *J* 6.5), 7.90 (1H, d, *J* 6.3), 7.87 (1H, d, *J* 6.3), 7.78 (1H, ddd, *J* 9.0, 6.0, 1.3), 7.74 (1H, ddd, *J* 9.0, 6.0, 1.3), 7.51–7.62 (4H, m), 7.46 (1H, d, *J* 7.0), 7.33–7.39 (3H, m), 2.47–2.53 (2H, m), 2.24–2.29 (2H, m), 1.33–1.38 (2H, m), 1.13–1.18 (2H, m); ^{13}C NMR (75 MHz; $CDCl_3$) 156.1 (C), 155.3 (C), 148.6 (C), 148.5 (C), 145.4 (d, $^2J_{C-P}$ 11.9), 144.8 (d, $^2J_{C-P}$ 10.5), 136.3 (CH), 136.2 (CH), 133.5 (C), 133.5 (C), 133.1 (CH), 133.1 (CH), 132.9 (C), 132.8 (CH), 129.8 (CH), 129.8 (CH), 129.6 (CH), 129.6 (CH), 129.6 (CH), 129.2 (CH), 127.9 (CH), 127.8 (CH), 127.6 (C), 127.5 (CH), 127.4 (C), 127.2 (CH), 127.2 (CH), 126.9 (CH), 126.7 (CH), 126.2 (CH), 126.2 (CH), 123.9 (CH), 123.8 (CH), 123.2 (C), 123.2 (C), 122.5 (C), 47.4 (2C, CH_2, d, $^2J_{C-P}$ 4.9), 25.9 (2C, CH_2, d, $^3J_{C-P}$ 9.8); ^{31}P NMR (121 MHz; $CDCl_3$) 23.7; MS (ESI) *m*/*e* (relative intensity) 656 (100), 1333 (57); HRMS (ESI) obsd 656.2097 (MH^+) calcd 656.2098.

4.5. 3,3′-3,3′-Bis-(potassium trifluoroboronato)-2,2′-bismethoxymethoxy-1,1′-binaphthyl (12)

A solution of **7** (243 mg, 6.49×10^{-4} mol, 1.00 equiv) in dry THF (18 mL) was cooled to −78 °C and *n*-butyllithium (2.45 M in hexanes; 790 μL, 1.95 mmol) was added. The mixture was stirred for 15 min, then allowed to warm to room temperature and stirred for a further hour. The resulting suspension was re-cooled to −78 °C and triisopropyl borate (750 μL, 1.07 mmol) was added. The mixture was stirred for 15 h, allowing to warm slowly to room temperature. Saturated aqueous ammonium chloride (7.0 mL), then dichloromethane (10 mL) and water (2 mL) were added and the organic and aqueous phases separated. The aqueous phase was extracted with dichloromethane (2×20 mL) and the organics phases were combined. The solvent was removed in vacuo and the residue was taken up in methanol (17 mL). Potassium hydrogendifluoride (254 mg, 3.25 mmol) and water (3.5 mL) were added, and the mixture stirred for 3 h. The resulting suspension was cooled to 4 °C and after a further 2 h the precipitate was collected on a sinter, washed with a cold ether to remove traces of coloured impurities and dried in vacuo to give compound **12** as a colourless solid (345 mg, 91%); mp>290 °C (decomposes); IR (KBr) ν_{max}/cm^{-1} 3055, 1108, 980, 906; ^{1}H NMR (300 MHz; DMSO-d_6) 8.01 (2H, s), 7.79 (2H, d, *J* 7.9), 7.25 (2H,dd, *J* 6.9, 6.9), 7.07 (2H, ddd, *J* 8.4, 6.6, 0.9), 6.95 (2H, d, *J* 8.4), 4.85 (2H, d, *J* 19.4), 4.83 (2H, d, *J* 19.4), 2.26 (6H, s); ^{13}C NMR (75 MHz; DMSO-d_6) 157.0 (C), 134.2 (C), 133.9 (C), 131.0 (CH), 128.0 (CH), 126.6 (CH), 125.6 (C), 124.6 (CH), 124.3 (CH), 123.7 (CH_2), 98.2 (CH_2), 55.5 (CH_3).

4.6. 3,3′-Di(2-thiophenyl)-2,2′-bismethoxymethoxy-1,1′-binaphthyl (13)

To a mixture of 2-bromothiophene (154 μL, 1.59 mmol), tetrakistriphenylphosphinepalladium(0) (30 mg, 2.6×10^{-4} mol) and **12** (300 mg, 4.61×10^{-4} mol, 1.00 equiv) in DMF (4.5 mL) was added a solution of potassium carbonate (420 mg, 4.24 mmol) in water (4.5 mL). The mixture was irradiated in a sealed microwave reactor tube at 150 W, 150 °C for a period of 15 min. After cooling to room temperature, the mixture was poured onto water (60 mL) and extracted with dichloromethane (3×40 mL). The combined organic phases were dried over anhydrous sodium sulfate and the solvent was evaporated. The residue was subjected to flash column

chromatography (ethyl acetate/hexanes: 1/20) to give **13** (221 mg, 89%) as a colourless powder. R_f 0.19 (ethyl acetate/hexanes: 1/5); IR (neat) ν_{max}/cm^{-1} 2924, 1245, 1159, 978, 751, 700; ^1H NMR (300 MHz; $CDCl_3$) 8.17 (2H, s), 7.89 (2H, d, *J* 7.5), 7.64 (2H, dd, *J* 2.5, 1.0), 7.39–7.45 (4H, m), 7.21–7.31 (2H, m), 7.14 (2H, dd, *J* 4.8, 3.3), 4.64 (2H, d, *J* 6.0), 4.46 (2H, d, *J* 6.0), 2.48 (6H, s); ^{13}C NMR (75 MHz; $CDCl_3$) 150.5 (C), 140.0, 133.7, 131.0, 129.7, 128.6, 128.1, 127.6, 127.1, 126.9, 126.7, 126.6, 126.4, 125.6, 98.6 (CH_2), 56.4 (CH_3); MS (ESI) *m*/*e* (relative intensity) 539 (MH^+, 100), 444 (24), 359 (42), 258 (72).

4.7. 3,3′-Di(2-thiophenyl)-2,2′-dihydroxy-1,1′-binaphthyl (14)

To a solution of **13** (200 mg, 3.71×10^{-4} mol, 1.00 equiv) in dichloromethane (5 mL) and methanol (15 mL) then hydrochloric acid (10 M; 1.0 mL, 10 mmol) was added. The mixture was stirred for 15 h before being poured onto saturated aqueous sodium hydrogen carbonate (50 mL). The mixture was extracted with dichloromethane (3×30 mL), the combined organic phases were dried over anhydrous sodium sulfate and the solvent was evaporated. The residue was subjected to flash column chromatography (ethyl acetate/hexanes: 1/5), which gave **14** (165 mg, 99%) as a colourless powder. R_f 0.19 (ethyl acetate/hexanes: 1/5); IR (neat) ν_{max}/cm^{-1} 2919, 1455, 1230, 1084, 714, 619; ^1H NMR (300 MHz; $CDCl_3$) 8.26 (2H, s), 7.86 (2H, d, *J* 7.5), 7.63 (2H, dd, *J* 5.6, 1.6), 7.28–7.36 (4H, m), 7.22 (2H, dd, *J* 2.5, 1.0), 7.19 (2H, dd,), 7.05–7.11 (4H, m), 5.54 (2H, br s); ^{13}C NMR (75 MHz; $CDCl_3$) 149.8, 139.0, 132.7, 129.8, 129.5, 126.8, 127.9, 127.7, 127.2, 126.3, 124.8, 124.2, 123.6, 112.2.

4.8. 3,3′-Di(2-thiophenyl)-2,2′-diyl-1-pyrrolidylphosphonite (11)

To a solution of **14** (100 mg, 2.22×10^{-4} mol) in toluene (5 mL) was added phosphorus trichloride (200 μL, 2.29 mmol). The reaction mixture was heated under reflux for 4 h. The mixture was cooled to 0 °C and pyrrolidine (1.90 mL, 23.2 mmol) was added. The mixture was stirred, warming to room temperature over 1 h and was then poured onto saturated aqueous ammonium chloride (40 mL). The resulting mixture was extracted with dichloromethane (3×20 mL). The combined organic phases were washed with saturated aqueous ammonium chloride (50 mL), water (50 mL), dried over anhydrous sodium sulfate and the solvent was evaporated. The residue was subjected to flash column chromatography (ethyl acetate/hexanes: 1/4), which gave **11** (96 mg, 79%) as a colourless powder. Mp>150 °C (decomposes); R_f 0.70 (ethyl acetate/hexanes: 1/1); IR (neat) ν_{max}/cm^{-1} 2962, 1499, 1456, 1230, 716; ^1H NMR (300 MHz; $CDCl_3$) 8.30 (1H, s), 8.22 (1H, s), 7.93 (2H, d, *J* 8.4), 7.71 (1H, dd, *J* 3.6, 0.9), 7.69 (1H, dd, *J* 3.6, 0.9), 7.37–7.44 (4H, m), 7.21–7.33 (4H, m), 7.13–7.17 (2H, m), 2.77–2.83 (2H, m), 2.67–2.75 (2H, m), 1.39–1.48 (2H, m); ^{13}C NMR (75 MHz; $CDCl_3$) 147.5 (C), 146.7 (C), 139.8 (C), 139.3 (C), 132.4 (C), 132.3 (C), 131.2 (C), 130.8 (C), 128.5, 128.5, 128.3, 128.0, 127.4, 127.4, 127.4, 127.1, 127.0, 126.9, 126.7, 126.7, 126.6, 126.3, 126.3, 126.2, 125.4, 125.4, 125.2, 124.5, 45.5 (2C, CH_2, d, $^2J_{C-P}$ 15.8), 25.8 (2C, CH_2, d, $^3J_{C-P}$ 4.5); ^{31}P NMR (121 MHz; $CDCl_3$) 151.7; MS (ESI) *m*/*e* (relative intensity) 550 (100), 479 (32); HRMS (ESI) obsd 550.1062 (MH^+) calcd 550.1059.

4.9. (*S*)-3,3′-Diiodo-2,2′-bismethoxymethoxy-1,1′-binaphthyl (15)[23]

To a stirred solution of **7** (754 mg, 2.01 mmol) in dry THF (20 mL) at −78 °C was added a solution of *n*-butyllithium (2.52 M in hexanes; 4.00 mL, 10.1 mmol) and the reaction mixture was stirred for 1 h. The mixture was then allowed to warm to room temperature and stirred for a further 4 h. The reaction mixture was re-cooled to −78 °C and a solution of iodine (2.00 g, 7.89 mmol) in THF (10 mL) was added. The reaction mixture was stirred for 1 h then allowed to warm slowly to room temperature and stirred overnight. Saturated aqueous ammonium chloride (40 mL) and water (20 mL) were added and the organic and aqueous phases separated. The aqueous phase was extracted with dichloromethane (2×30 mL) and the combined organic phases were then washed with aqueous sodium sulfite (10% w/v; 30 mL), brine (10 mL), were dried over anhydrous sodium sulfate, and the solvent was evaporated. The residue was subjected to flash column chromatography (ethyl acetate/hexanes: 1/15), which gave **15** (981 mg, 78%) as a colourless powder. R_f 0.26 (ethyl acetate/hexanes: 1/15); $[\alpha]_D^{20}$ −7.4 (*c* 1.0, THF); IR ν_{max} (neat)/cm^{-1} 2967, 2869, 1201, 1068, 905, 813, 726; ^1H NMR (300 MHz, $CDCl_3$) 8.54 (2H, s), 7.77 (2H, d, *J* 8.1), 7.17–7.45 (6H, m) 4.81 (2H, d, *J* 5.5), 4.69 (2H, d, *J* 5.5), 2.60 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) 152.9, 140.7, 134.5, 132.9, 127.8, 127.4, 127.2, 126.9, 126.5, 100.1, 93.2, 57.2; MS (ESI) *m*/*e* (relative intensity) 627 (MH^+, 100), 612 (10), 583 (7).

4.10. (*S*)-3,3′-Diethynyl-2,2′-bismethoxymethoxy-1,1′-binaphthyl (16)[42]

To a stirred solution of 15 (500 mg, 9.29×10^{-4} mol) in a mixture of freshly distilled triethylamine/THF: 1/1 (10 mL) was added tetrakistriphenylphosphinepalladium(0) (54 mg, 4.7×10^{-5} mol), copper(I) iodide (9.0 mg, 4.7×10^{-5} mol) and trimethylsilylacetylene (0.53 mL, 3.7 mmol). The mixture was stirred for 15 h before being diluted with ether (50 mL) and filtered through Celite, eluting with ether (50 mL). The solvent was removed in vacuo and the residue was subjected to flash **c**olumn chromatography (ethyl acetate/hexanes: 3/100) to give 3,3′-bistrimethylsilylethynyl-2,2′-bismethoxymethoxy-1,1′-binaphthyl (435 mg, 97%) as a colourless foam. Mp 170 °C; R_f 0.35 (ethyl acetate/hexanes: 3/100); $[\alpha]_D^{20}$ −34 (*c* 1.0, THF); IR ν_{max} (neat)/cm^{-1} 2960, 2154, 1488, 1246, 1158, 1070, 976, 844, 753; ^1H NMR (300 MHz, $CDCl_3$) 8.15 (2H, s), 7.80 (2H, d, *J* 6.0) 7.39 (2H, dd, *J* 6.0, 6.5), 7.26 (2H, dd, *J* 6.0, 6.5), 7.16 (2H, d, *J* 6.5), 5.17 (2H, d, *J* 5.5), 4.86 (2H, d, *J* 5.5), 2.44 (6H, s), 0.26 (18H, s); ^{13}C NMR (75 MHz, $CDCl_3$) 153.5, 135.0, 134.0130.3, 127.6, 127.4, 126.7, 125.9, 125.6, 117.6, 102.0, 99.2, 98.8, 56.1, 0.1; MS (APCI) *m*/*e* (relative intensity) 953 (100), 849 (71), 821 (36), 809 (30), 535 (16), 463 (27), 433 (17), 379 (11); HRMS (APCI) calcd for $C_{34}H_{39}O_4Si_2$ (MH^+) 567.2381, found 567.2387. The 3,3′-bistrimethylsilylethynyl-2,2′-bismethoxymethoxy-1,1′-binaphthyl intermediate (200 mg, 3.53×10^{-4} mol) in dichloromethane (2 mL) and methanol (20 mL) was added potassium carbonate (2.0 g, 15 mmol). The resulting suspension was stirred vigorously for 2 h. The mixture was filtered and the filtrate partitioned between dichloromethane (20 mL) and water (20 mL). The aqueous layer was extracted with dichloromethane (3×20 mL) and the combined organic phases were washed with saturated aqueous ammonium chloride (20 mL), water (20 mL), were dried over anhydrous sodium sulfate and the solvent was evaporated. The residue was subjected to flash column chromatography (ethyl acetate/hexanes: 1/20), which gave **16** (116 mg, 98%) as a colourless solid. R_f 0.35 (ethyl acetate/hexanes: 1/10); $[\alpha]_D^{20}$ −83 (*c* 1.0, THF); IR ν_{max} (neat)/cm^{-1} 3280, 2925, 2100, 1617, 1490, 1425, 1392, 1353, 1240, 1156, 1064, 917, 751; ^1H NMR (300 MHz, $CDCl_3$) 8.20 (2H, s), 7.82–7.84 (2H, m), 7.41–7.44 (2H, m), 7.29–7.32 (2H, m), 7.19–7.21 (2H, m), 5.08 (2H, d, *J* 6.0), 4.89 (2H, d, *J* 6.0), 3.33 (2H, s), 2.53 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) 153.4 (C), 135.4 (CH), 134.1 (C), 130.2 (C), 127.7 (CH), 127.6 (CH), 126.6 (CH), 125.9 (C), 125.7 (CH), 116.4 (C), 99.0 (CH2), 81.7 (C), 80.7 (CH), 56.2 (CH3); MS (ESI) *m*/*e* (relative intensity) 422 (MH^+, 36), 391 (100). HRMS (APCI) calcd for $C_{28}H_{23}O_4$ (MH^+) 423.1591, found 423.1594.

4.11. (*S*)-3,3′-Diethynyl-2,2′-dihydroxy-1,1′-binaphthyl (17)

Hydrochloric acid (10 M; 0.5 mL, 5 mmol) was added to a solution of **16** (200 mg, 4.19×10^{-4} mol) in dichloromethane (2 mL) and

methanol (20 mL). The resulting mixture was stirred for 5 h before being partitioned between dichloromethane (20 mL) and water (20 mL). The aqueous layer was extracted with dichloromethane (3×10 mL) and the combined organic phases were washed with saturated aqueous sodium hydrogen carbonate (2×10 mL) and water (10 mL). The organic phase was then dried over anhydrous sodium sulfate and the solvent was evaporated. The residue was subjected to flash column chromatography (ethyl acetate/hexanes: 1/20) to give **17** (127 mg, 91%) as a colourless solid. Mp>270 °C (decomposes); R_f 0.22 (ethyl acetate/hexanes: 1/20); $[\alpha]_D^{20}$ −83 (*c* 1.0, THF); IR ν_{max} (neat)/cm^{-1} 3050, 2159, 1718, 1496, 1427, 1010, 952; ^{1}H NMR (200 MHz, $CDCl_3$) 8.17 (2H, s), 7.83 (2H, dd, *J* 9.0, 1.5) 7.41–7.25 (4H, m), 7.11 (2H, dd, *J* 9.0, 1.0), 5.45 (2H, s), 3.53 (2H, s); ^{13}C NMR (50 MHz, $CDCl_3$) 151.4, 134.6, 134.1, 128.7, 128.4, 128.4, 124.8, 124.6, 113.4, 111.1, 84.0, 78.9; MS (APCI) *m*/*e* (relative intensity) 335 (MH^+, 42), 292 (49), 168 (95), 199 (100); HRMS (APCI) calcd for $C_{24}H_{15}O_2$ (MH^+) 335.1067, found 335.1065.

4.12. (*S*)-3,3′-Diethynyl-1,1′-binaphthyl-2,2′-diyl 1-pyrrolidylphosphonite (18)

Phosphorus trichloride (520 μL, 6.0 mmol, 20 equiv) was added to a stirred solution of **17** (100 mg, 2.99×10^{-4} mol) in toluene (5 mL) and the reaction mixture was heated under gentle reflux for 8 h. The mixture was cooled to 0 °C and pyrrolidine (1.5 mL, 18 mmol) added slowly. The mixture was stirred at 0 °C for 15 m and was then heated to 50 °C for 5 h. After cooling to room temperature the reaction mixture was partitioned between saturated aqueous ammonium chloride (80 mL) and dichloromethane (80 mL). The aqueous phase was extracted with dichloromethane (3×30 mL) and the combined organic phases were washed with saturated aqueous ammonium chloride (20 mL), water (20 mL), were dried over anhydrous sodium sulfate and then the solvent was evaporated. Flash column chromatography (ethyl acetate/hexanes: 1/5) gave **18** (89 mg, 69%) as a colourless solid. Mp 120 °C (decomposes); R_f 0.28 (ethyl acetate/hexanes: 1/5); $[\alpha]_D^{20}$ −17 (*c* 1.0, THF); ν_{max} (neat)/cm^{-1} 2965, 2878, 2365, 1488, 1414, 1080, 753, 690; ^{1}H NMR (300 MHz, $CDCl_3$) 8.20 (1H, s), 8.15 (1H, s), 7.87 (2H, d, *J* 9.0), 7.39–7.45 (2H, m), 7.23–7.32 (4H, m), 3.37 (1H, s), 3.31 (1H, s), 3.18–3.24 (2H, m), 2.86–2.90 (2H, m), 1.68–1.77 (4H, m); ^{13}C NMR (75 MHz, $CDCl_3$) 150.5 (d, $^2J_{C-P}$ 3.8), 149.7 (C), 135.1 (CH), 134.7 (CH), 132.8 (C), 132.7 (C), 130.6 (C), 130.0 (C), 128.3 (CH), 128.3 (CH), 127.2 (CH), 127.2 (CH), 126.9 (CH), 126.9 (CH), 125.5 (CH), 125.3 (CH), 124.4 (CH, d, $^3J_{C-P}$ 5.3), 123.3 (C, d, $^3J_{C-P}$ 1.8), 45.6 (2C, CH_2, d, $^2J_{C-P}$ 15.2), 25.9 (2C, CH_2, d, $^3J_{C-P}$ 4.6); ^{31}P NMR (121 MHz, $CDCl_3$) 154.2; MS (APCI) *m*/*e* (relative intensity) 434 (MH^+, 5), 395 (14), 365 (7), 347 (12), 334 (26), 316 (100), 300 (22); HRMS (ESI) calcd for $C_{28}H_{21}NO_2P$ (MH^+) 433.1232, found 433.1231.

4.13. (*S*)-3,3′-Diiodo-1,1′-binaphthyl-2,2′-diyl 1-pyrrolidylphosphonite (21)

To a solution of **15** (208 mg, 3.32×10^{-4} mol) in methanol/dichloromethane: 1/1 (10 mL) was added hydrochloric acid (10 M; 0.50 mL, 5.0 mmol). The mixture was stirred overnight and then water (20 mL) was added. The resulting mixture was extracted with dichloromethane (3×20 mL), the combined organic phases dried over anhydrous sodium sulfate and the solvent removed in vacuo. Flash column chromatography (ethyl acetate/hexanes: 1/5) gave (*S*)-3,3′-diiodo-2,2′-dihydroxy-1,1′-binaphthyl[43] (167 mg, 88%) as a colourless solid; R_f 0.22 (ethyl acetate/hexanes: 1/10); mp 311–314 °C; $[\alpha]_D^{20}$ −98 (*c* 1.0, THF); ν_{max} (KBr)/cm^{-1} 3483, 1565, 1355, 1177, 1141; ^{1}H NMR (300 MHz, $CDCl_3$) 8.52 (2H, s), 7.80 (2H, d, *J* 8.3), 7.31–7.41 (4H, m), 7.07 (2H, d, *J* 8.2), 5.44 (2H, s); ^{13}C NMR (75 MHz, $CDCl_3$) 150.0, 140.2, 133.1, 130.6, 127.8, 127.1, 124.6, 124.3, 112.5, 86.5; MS (ESI) *m*/*e* (relative intensity) 539 (MH^+, 100), 413 (17).

Phosphorus trichloride (0.65 mL, 7.4 mmol) was added to a stirred solution of 3,3′-diiodo-2,2′-dihydroxy-1,1′-binaphthyl (200 mg, 3.72×10^{-4} mol) in toluene (10 mL) and the reaction mixture was heated under gentle reflux for 8 h. The mixture was cooled to 0 °C and pyrrolidine (1.8 mL, 22 mmol) added slowly. The mixture was stirred at 0 °C for 15 min and was then heated to 50 °C for 5 h. After cooling to room temperature, the mixture was partitioned between saturated aqueous ammonium chloride (80 mL) and dichloromethane (80 mL). The aqueous phase was extracted with dichloromethane (3×30 mL) and the combined organic phases were washed with saturated aqueous ammonium chloride (30 mL) then water (30 mL). The organic phase was dried over anhydrous sodium sulfate and the solvent was evaporated. The residue was subjected to flash column chromatography (ethyl acetate/hexanes: 1/5), which gave **21** (147 mg, 62%) as a colourless solid. Mp 160 °C (decomposes); R_f 0.28 (ethyl acetate/hexanes: 1/5); $[\alpha]_D^{20}$ −7.4 (*c* 1.0, THF) ν_{max} (neat)/cm^{-1} 2890, 1498, 1457, 1276, 990; ^{1}H NMR (300 MHz, $CDCl_3$) 8.72 (1H, s), 8.75 (1H, s), 8.01 (1H, d, *J* 8.5), 8.00 (1H, d, *J* 8.5) 7.45–7.51 (2H, m) 7.30–7.38 (2H, m), 7.13 (1H, d, *J* 8.8), 7.05 (1H, d, *J* 8.8), 3.16–3.19 (2H, m), 2.79–2.82 (2H, m), 1.69–1.75 (4H, m); ^{13}C NMR (75 MHz, $CDCl_3$) 147.8, 147.7, 139.6, 139.6, 132.2, 131.7, 131.6, 131.5, 127.7, 127.6, 127.1, 125.9, 125.8, 125.5, 123.8, 121.8, 92.2, 45.5 (2C, CH_2, d, $^2J_{C-P}$ 15.1) 25.3 (2C, CH_2, d, $^3J_{C-P}$ 5.5); ^{31}P NMR (121 MHz, $CDCl_3$) 151.5; MS (ESI) *m*/*e* (relative intensity) 654 (MH^+,100), 528 (4), 400 (2); HRMS (APCI) calcd for $C_{24}H_{18}I_2NO_2P$ (M^+) 636.9165, found 636.9162.

4.14. (*S*)-3,3′-Di(1-benzyl-1,2,3-triazol-4-yl)-1,1′-binaphthyl-2,2′-diyl 1-pyrrolidylphosphonite (19) and (*S*)-3,3′-di(1-benzyl-1,2,3-triazol-4-yl)-1,1′-binaphthyl-2,2′-diyl 1-pyrrolidylphosphonate (20)

Compound **18** (65 mg, 1.5×10^{-4} mol) was dissolved in acetonitrile (2 mL). Benzyl azide (93 μL, 7.5×10^{-4} mol) and Hünig's base (1.05 mL, 6.00 mmol) were added and the mixture was stirred for 5 min. Copper (I) iodide (57 mg, 3.0×10^{-4} mol) was added and the mixture was then stirred for 2 h. Ether (10 mL) was added to precipitate inorganic salts prior to exposing the mixture to air. The ether layer was filtered and the reaction flask washed with dichloromethane (3×10 mL), the combined organics were filtered and combined with the ether layer. The resulting solution was washed with water (2×10 mL) then dried over anhydrous sodium sulfate and the solvent was evaporated. Flash column chromatography (ethyl acetate/hexanes: 1/1) gave **19** (18 mg, 17%) as a colourless solid. Mp 120 °C (decomposes); R_f 0.25 (ethyl acetate/hexanes: 1/5); $[\alpha]_D^{20}$ −8.3 (*c* 0.4, THF); ν_{max} (neat)/cm^{-1} 2946, 2869, 1498, 1456, 1323, 1233, 1077, 1051, 830, 717; ^{1}H NMR (300 MHz, $CDCl_3$) 8.95 (1H, s), 8.87 (1H, s) 8.10 (1H, s), 7.99–8.03 (2H, m), 7.81 (1H, s) 7.26–7.44 (16H, m), 5.69 (1H, d, *J* 15.0), 5.62 (1H, d, *J* 14.2), 5.56 (1H, d, *J* 14.2), 5.48 (1H, d, *J* 15.0), 2.36–2.40 (4H, m), 1.14–1.20 (4H, m); ^{13}C NMR (75 MHz, $CDCl_3$) 146.8 (d, $^2J_{C-P}$ 11.3), 146.1, 144.1, 143.7, 135.0, 134.7, 132.6, 132.4, 131.3, 130.8, 129.3, 129.2, 129.0, 128.9, 128.9, 128.8, 128.4, 128.4, 128.0, 127.9, 126.8, 126.6, 125.5, 125.3, 124.8, 123.8, 123.8, 123.2, 123.0, 123.0, 122.9, 122.9, 54.5, 54.4, 45.2 (2C, CH_2, d, $^2J_{C-P}$ 16.1), 25.6 (2C, CH_2, d, $^3J_{C-P}$ 4.3); ^{31}P NMR (121 MHz, $CDCl_3$) 148.98; MS (ESI) *m*/*e* (relative intensity) 738 (MK^+, 41), 722 (MNa^+, 54), 700 (MH^+, 100), 661 (62), 579 (20); HRMS (ESI) calcd for $C_{42}H_{35}N_7O_2P$ (MH^+) 700.2584, found 700.2571; and **20** (83 mg, 77%) as a colourless solid. Mp 140 °C (decomposes); R_f 0.11 (ethyl acetate/hexanes: 1/5); $[\alpha]_D^{20}$ −16 (*c* 0.4, THF); ν_{max} (neat)/cm^{-1} 2920, 2851, 2362, 1498, 1456, 1233, 1083, 950, 717; ^{1}H NMR (300 MHz, $CDCl_3$) 8.95 (1H, s), 8.94 (1H, s) 8.84 (1H, s), 8.36 (1H, s), 8.21 (1H, s), 8.04 (1H, d, *J* 8.1), 8.02 (1H, d, *J* 8.1), 7.44–7.51 (2H, m), 7.19–7.37 (12H, m), 5.70 (1H, d, *J* 15.0), 5.68 (1H, d, *J* 14.7), 5.53–5.59 (2H, m), 2.36–2.44 (4H, m), 1.20–1.31 (4H, m); ^{13}C NMR (75 MHz, $CDCl_3$) 144.5 (C, d, $^2J_{C-P}$ 11.3), 143.9 (C, d, $^2J_{C-P}$

10.4), 143.2 (C), 143.1 (C), 135.3, 135.1, 132.3, 131.8, 130.4, 129.6, 129.4, 129.3, 129.0, 128.9, 128.6, 127.5, 127.3, 127.1, 126.7, 126.5, 124.5, 123.7, 123.4, 123.4 (C, d, $^3J_{C-P}$ 2.5), 123.1 (C, d, $^3J_{C-P}$ 2.9), 123.0 (C, d, $^3J_{C-P}$ 2.2), 122.3 (C, d, $^3J_{C-P}$ 1.8), (CH_2), 54.6 (CH_2), 54.3 (CH_2), 47.8 (2C, CH_2, d, $^2J_{C-P}$ 4.6), 26.3 (2C, CH_2, d, $^3J_{C-P}$ 9.5); ^{31}P NMR (121 MHz, $CDCl_3$) 11.4; MS (ESI) *m*/*e* (relative intensity) 752 (MK^+, 100), 738 (MNa^+, 66), 716 (MH^+, 86); HRMS (ESI) calcd for $C_{42}H_{35}N_7O_3P$ (MH^+) 715.2534, found 715.2512.

4.15. 3,3′-Bis(1-(*p*-bromophenyl)-1*H*-1,2,3-triazol-4-yl)-1,1′-binaphthyl-2,2′-diyl *N*-*p*-bromophenylpyrrolidylphosphonimidate (24)

To a solution of **18** (35 mg, 8.1×10^{-5} mol) in acetonitrile (3 mL) was added *p*-bromophenyl azide (80 mg, 4.04×10^{-4} mol) and Hünig's base (0.60 mL, 3.4 mmol). The mixture was stirred for 5 min. Copper (I) iodide (30 mg, 1.57×10^{-4} mol) was added and the mixture was stirred for a further 15 h. The reaction mixture was partitioned between ethyl acetate (20 mL) and saturated aqueous ammonium chloride (100 mL). The aqueous layer was extracted with ethyl acetate (2×20 mL) and the combined organic layers were washed with saturated aqueous ammonium chloride (50 mL), water (50 mL), were dried over anhydrous sodium sulfate and then the solvent was evaporated. Flash column chromatography (ethyl acetate/hexanes: 1/4) gave **25** (66 mg, 82%) as a colourless powder. R_f 0.40 (ethyl acetate/hexanes: 3/10); IR (neat) ν_{max}/cm^{-1} 2924, 2855, 1497, 1088, 826; ^{1}H NMR (300 MHz; $CDCl_3$) 9.01 (1H, s), 8.89 (1H, s), 8.79 (1H, s), 8.53 (1H, s), 8.12 (1H, d, *J* 9.1), 8.08 (1H, d, *J* 9.1), 7.64–7.69 (4H, m), 7.52–7.60 (6H, m), 7.33–7.42 (4H, m), 7.04 (2H, d, *J* 8.4), 7.03 (2H, d, *J* 8.4) 6.53 (2H, d, *J* 8.4) 6.53 (2H, d, *J* 8.4), 2.60–2.68 (2H, m), 2.50–2.58 (2H, m), 1.40–1.48 (4H, m); ^{13}C NMR (75 MHz; $CDCl_3$) 145.8 (d, $^2J_{C-P}$ 3.8), 144.3, 144.2, 143.5, 136.1, 135.8, 133.3, 133.1, 132.4, 132.0, 131.9, 131.8, 131.7, 131.5, 130.9, 129.3, 129.2, 129.0, 128.0, 127.7, 127.4, 127.1, 127.1, 126.7, 126.4, 125.4, 125.2, 123.2 (d, $^3J_{C-P}$ 3.0), 122.8, 122.6 (d, $^3J_{C-P}$ 3.0), 122.4, 122.3, 122.0 (d, $^3J_{C-P}$ 2.6), 121.6, 121.2, 112.3, 48.4 (2C, CH_2, d, $^2J_{C-P}$ 4.2), 26.2 (2C, CH_2, d, $^3J_{C-P}$ 9.6); ^{31}P NMR (121 MHz; $CDCl_3$) 4.3; MS (ESI) *m*/*e* (relative intensity) 997 (38), 998 (16), 999 (95), 1000 (47), 1001 (100), 1002 (46), 1003 (41), 1004 (21), 1889 (36); HRMS (ESI) obsd 1000.9985 (MH^+) calcd 1000.9968.

4.16. 3,3′-Bis(1-phenyl-1*H*-1,2,3-triazol-4-yl)-2,2′-bismethoxymethoxy-1,1′-binaphthyl (25a)

To a solution of **16** (50 mg, 1.5×10^{-4} mol) in acetonitrile (5 mL) was added phenyl azide (45 mg, 3.8×10^{-4} mol) and Hünig's base (1.05 mL, 6.00 mmol). The mixture was stirred for 5 min and then copper (I) iodide (28 mg, 1.5×10^{-4} mol) was added and the mixture was stirred for a further 2 h. The reaction mixture was partitioned between dichloromethane (20 mL) and water (20 mL). The aqueous layer was extracted with dichloromethane (3×10 mL) and the combined organic layers were washed with water (2×10 mL), dried over anhydrous sodium sulfate and the solvent was evaporated. Flash column chromatography (ethyl acetate/hexanes: 1/1) gave **25a** (79 mg, 89%) as a colourless solid. Mp 201–205 °C; R_f 0.20 (ethyl acetate/hexanes: 2/5); IR (neat) ν_{max}/cm^{-1} 2951, 1599, 1502, 1236, 976; ^{1}H NMR (300 MHz; $CDCl_3$) 9.06 (1H, s), 8.82 (1H, s), 8.07 (1H, s), 7.84 (1H, dd, *J* 5.5, 1.0), 7.83 (1H, dd, *J* 5.5, 1.0), 7.42–7.57 (4H, m), 7.28–7.38 (2H, m), 4.67 (2H, d, *J* 4.5), 4.33 (2H, d, *J* 4.5), 2.72 (6H, s); ^{13}C NMR (75 MHz; $CDCl_3$) 149.9 (C), 144.1 (C), 137.2 (C), 133.9 (CH), 131.1 (C), 129.9 (4C, CH), 128.9 (CH), 128.8 (CH), 128.8 (C), 127.3 (CH), 126.1 (CH), 125.9 (CH), 125.9 (C), 124.1 (C), 121.4 (CH), 120.5 (4C, CH), 98.9 (CH_2), 57.2 (CH_3); MS (ESI) *m*/*e* (relative intensity) 661 (38), 683 (100); HRMS (ESI) obsd 661.25734 (MH^+) calcd 661.2558, obsd 683.2391 (MNa^+) calcd 683.2377.

4.17. 3,3′-Bis(1-(*p*-methoxyphenyl)-1*H*-1,2,3-triazol-4-yl)-2,2′-bismethoxymethoxy-1,1′-binaphthyl (25b)

To a solution of **16** (250 mg, 5.92×10^{-4} mol) in acetonitrile (10 mL) was added *p*-anisoyl azide (220 mg, 1.48 mmol) and Hünig's base (2.00 mL, 11.5 mmol). The mixture was stirred for 5 min. Copper (I) iodide (113 mg, 5.92×10^{-4} mol) was added and the mixture was then stirred for 15 h. The reaction mixture was partitioned between dichloromethane (20 mL) and saturated aqueous ammonium chloride (20 mL). The aqueous layer was extracted with dichloromethane (2×20 mL) and the combined organic phases were washed with saturated aqueous ammonium chloride (50 mL), water (50 mL), were dried over anhydrous sodium sulfate and the solvent was evaporated. Flash column chromatography (ethyl acetate/hexanes: 1/1) gave **25b** (401 mg, 94%) as a colourless powder. Mp 220–222 °C; R_f 0.16 (ethyl acetate/hexanes: 1/1); IR (neat) ν_{max}/cm^{-1} 2929, 1517, 1253, 1161, 1040, 975; ^{1}H NMR (300 MHz; $CDCl_3$) 9.01 (2H, s), 8.76 (2H, s), 8.07 (2H, d, *J* 8.1), 7.73 (4H, d, *J* 9.0), 7.48 (2H, ddd, *J* 8.1, 5.7, 2.4), 7.28–7.39 (4H, m), 7.04 (4H, d, *J* 9.0), 4.63 (2H, d, *J* 4.8), 4.40 (2H, d, *J* 4.8), 3.82 (6H, s), 2.67 (6H, s); ^{13}C NMR (75 MHz; $CDCl_3$) 159.8 (C), 149.8 (C), 143.8 (C), 133.8 (CH), 131.0 (C), 130.6 (C), 128.8 (CH), 128.6 (CH), 127.2 (CH), 126.0 (CH), 125.8 (CH), 125.7 (CH), 124.2 (C), 122.1 (2C, CH), 121.5 (CH), 114.8 (2C, CH), 98.7 (CH_2), 57.0 (CH_3), 55.6 (CH_3); MS (ESI) *m*/*e* (relative intensity) 721 (71), 743 (100), 1463 (31); HRMS (ESI) obsd 71.2771 (MH^+) calcd 721.2769.

4.18. 3,3′-Bis(1-(*p*-bromophenyl)-1*H*-1,2,3-triazol-4-yl)-2,2′-bismethoxymethoxy-1,1′-binaphthyl (25c)

To a solution of **16** (300 mg, 7.10×10^{-4} mol) in acetonitrile (20 mL) was added *p*-bromophenyl azide (350 mg, 1.77 mmol) and Hünig's base (5.00 mL, 28.7 mmol). The mixture was stirred for 5 min. Copper (I) iodide (135 mg, 7.09×10^{-4} mol) was then added and the mixture was stirred for an additional 15 h. The reaction mixture was partitioned between dichloromethane (20 mL) and saturated aqueous ammonium chloride (20 mL). The aqueous layer was extracted with dichloromethane (2×20 mL). The combined organics were washed with water (100 mL) and dried over anhydrous sodium sulfate. The solvent volume was reduced to give a slurry, which was adsorbed onto silica and the remaining solvent removed in vacuo. A short silica column eluting with ethyl acetate/hexanes: 1/4 removed unreacted material and excess azide and then the silica was subjected to Soxhlet extraction (toluene). The solvent was removed in vacuo to give **25c** as a tan-coloured powder (577 mg, 99%) as a colourless powder. Mp 205–210 °C (partial decomposition); R_f 0.17 (ethyl acetate/hexanes: 2/5); IR (neat) ν_{max}/cm^{-1} 2924, 1497, 1276, 1040, 973; ^{1}H NMR (400 MHz; $CDCl_3$) 9.06 (2H, s), 8.81 (2H, s), 8.08 (2H, d, J), 7.74 (2H, d, *J* 8.0), 7.73 (2H, d, *J* 8.0), 7.51 (2H, ddd, *J* 8.0, 8.0, 1.0), 7.35 (2H, ddd, *J* 8.0, 8.0, 1.0), 4.65 (2H, d, *J* 5.5), 4.41 (2H, d, *J* 5.5), 2.73 (6H, s); ^{13}C NMR (100 MHz; $CDCl_3$) 149.8 (C), 144.2 (C), 136.1 (C), 133.8 (C), 133.0 (CH), 131.0 (C), 128.8 (CH), 128.8 (CH), 127.4 (C), 125.9 (CH), 125.8 (CH), 125.7 (CH), 123.8 (C), 122.3 (C), 121.8 (CH), 121.1 (CH), 98.8 (CH_2), 57.1 (CH_3); MS (ESI) *m*/*e* (relative intensity) 764 (49), 839 (60), 841 (100), 843 (44), 1656 (33), 1658 (41), 1659 (33); HRMS (ESI) obsd 819.0732 (MNa^+) calcd 819.0748.

4.19. 3,3′-Bis(1-(*p*-fluorophenyl)-1*H*-1,2,3-triazol-4-yl)-2,2′-bismethoxymethoxy-1,1′-binaphthyl (25d)

To a solution of **16** (50 mg, 1.2×10^{-4} mol) in acetonitrile (2.0 mL) was added *p*-fluorophenyl azide (80 mg, 5.8×10^{-4} mol) and Hünig's base (0.40 mL, 2.3 mmol). The mixture was stirred for 5 min. Copper (I) iodide (22 mg, 1.2×10^{-4} mol) was added and the mixture was stirred for a further 5 h. The reaction mixture was partitioned between dichloromethane (20 mL) and saturated aqueous ammonium

chloride (20 mL). The aqueous layer was extracted with dichloromethane (2×20 mL) and the combined organic layers were washed with saturated aqueous ammonium chloride (50 mL), water (50 mL), were dried over anhydrous sodium sulfate and the solvent was evaporated. The residue was triturated with ether (10 mL) to remove excess *p*-fluorophenyl azide, which gave **25d** (76 mg, 92%) as a colourless powder. Mp 241–243 °C; R_f 0.6 (ethyl acetate/hexanes: 3/7); IR (neat) ν_{max}/cm^{-1} 2197, 1514, 1232, 919, 815; ^1H NMR (300 MHz; $CDCl_3$) 9.05 (2H, s), 8.77 (2H, s), 8.07 (2H, d, *J* 8.0), 7.78–7.81 (4H, m), 7.50 (2H, ddd, *J* 8.0, 6.8, 1.2), 7.34 (2H, ddd, *J* 7.6, 6.4, 1.2), 7.30 (2H, d, *J* 8.4), 7.22–7.27 (2H, m), 4.64 (2H, d, *J* 5.2), 4.41 (2H, d, *J* 5.2), 2.72 (6H, s); ^{13}C NMR (75 MHz; $CDCl_3$) 162.6 (CF, d, $^1J_{C-F}$ 249), 149.9 (C), 144.3 (C), 134.0 (CH), 133.6 (C, d, $^4J_{C-F}$ 3.0), 131.2 (C), 129.0 (CH), 128.9 (CH), 127.5 (CH), 126.1 (CH), 126.0 (CH), 125.9 (C), 124.1 (C), 122.5 (CH, d, $^3J_{C-F}$ 8.6), 121.6 (CH), 116.9 (CH, d, $^2J_{C-F}$ 23), 98.9 (CH_2), 57.3 (CH_3); ^{19}F NMR (282 MHz; $CDCl_3$) −112.63 (2F, m); MS (ESI) *m*/*e* (relative intensity) 696 (22), 719 (100); HRMS (ESI) obsd 697.2373 (MH^+) calcd 697.2369.

4.20. 3,3′-Bis(1-(2,4,5-trichlorophenyl)-1*H*-1,2,3-triazol-4-yl)-2,2′-bismethoxymethoxy-1,1′-binaphthyl (25e)

To a solution of **16** (50 mg, 1.2×10^{-4} mol) in acetonitrile (2.0 mL) was added 2,4,5-trichlorophenyl azide (132 mg, 5.93×10^{-4} mol) and Hünig's base (0.40 mL, 2.3 mmol). The mixture was stirred for 5 min. Copper (I) iodide (22 mg, 1.2×10^{-4} mol) was then added and the mixture was stirred for 5 h. The reaction mixture was then partitioned between dichloromethane (20 mL) and saturated aqueous ammonium chloride (20 mL). The aqueous layer was extracted with dichloromethane (2×20 mL) and the combined organic phases were washed with saturated aqueous ammonium chloride (50 mL), water (50 mL), were dried over anhydrous sodium sulfate and the solvent was removed in vacuo. The residue was triturated with ether (10 mL) to remove excess 2,4,5-trichlorophenyl azide to give **25e** (98 mg, 96%) as a colourless powder. Mp>330 °C (decomposes); R_f 0.34 (ethyl acetate/hexanes: 1/5); IR (neat) ν_{max}/cm^{-1} 1651, 999, 969, 921; ^1H NMR (500 MHz; $CDCl_3$) 9.03 (2H, s), 8.77 (2H, s), 8.06 (2H, d, *J* 8.0), 7.87 (2H, s), 7.71 (2H, s), 7.50 (2H, ddd, *J* 8.0, 7.0, 1.2), 7.35 (2H, ddd, *J* 8.0, 7.0, 1.2), 7.30 (2H, d, *J* 8.0), 4.63 (2H, d, *J* 5.0), 4.40 (2H, d, *J* 5.0), 2.66 (6H, s); ^{13}C NMR (125 MHz; $CDCl_3$) 150.0 (C), 143.8 (C), 134.8 (CH), 134.2 (C), 134.1 (C), 132.6 (C), 132.0 (C), 131.1 (C), 129.1 (CH), 129.0 (2C, CH), 127.5 (CH), 127.3 (C), 126.2 (CH), 126.0 (CH), 125.9 (C), 125.1 (CH), 123.8 (C), 98.8 (CH_2), 57.1 (CH_2); MS (ESI) *m*/*e* (relative intensity) 865 (57), 866 (34), 867 (100), 868 (47), 869 (96), 870 (42), 871 (48), 872 (18), 873 (14); HRMS (ESI) obsd 867.0182 (MH^+) calcd 800.0195.

4.21. 3,3′-Bis(1-(pentafluorophenyl)-1*H*-1,2,3-triazol-4-yl)-2,2′-bismethoxymethoxy-1,1′-binaphthyl (25f)

To a solution of **16** (100 mg, 2.31×10^{-4} mol) in acetonitrile (7 mL) was added pentafluorophenyl azide (200 mg, 9.57×10^{-4} mol) and Hünig's base (1.60 mL, 9.19 mmol) were added and the mixture was stirred for 5 min. Copper (I) iodide (22 mg, 1.6×10^{-4} mol) was added and the mixture was stirred for 15 h. The reaction mixture was partitioned between dichloromethane (20 mL) and water (20 mL). The aqueous layer was extracted with dichloromethane (3×10 mL) and the combined organic layers were washed with water (2×20 mL), dried over anhydrous sodium sulfate and the solvent was evaporated. Flash column chromatography (ethyl acetate/hexanes: 3/20) gave **25f** (160 mg, 87%) as a colourless solid. Mp 205–207 °C (partial decomposition); R_f 0.54 (ethyl acetate/hexanes: 1/5); IR (neat) ν_{max}/cm^{-1} 2940, 1533, 1150, 991, 730; ^1H NMR (400 MHz; $CDCl_3$) 9.06 (2H, s), 8.67 (2H, s), 8.08 (2H, d, *J* 9.2), 7.50 (2H, ddd, *J* 9.2, 8.3, 1.1), 7.36 (2H, ddd, *J* 9.2, 8.3, 1.1), 7.31 (2H, d, *J* 8.3), 4.61 (2H, d, *J* 5.0), 4.43 (2H, d, *J* 5.0), 2.72 (6H, s); ^{13}C NMR (100 MHz; $CDCl_3$) 150.0 (C), 143.9 (C), 144.5 (4CF, dm, $^1J_{C-F}$ 269), 137.8 (2CF, dm, $^1J_{C-F}$ 259), 134.1 (CH), 130.1 (C), 129.2 (CH), 129.0 (CH), 127.7 (CH), 126.0 (CH), 125.7 (CH), 125.6 (C), 123.3 (C), 113.1 (2C, m) 98.8 (CH_2), 57.0 (CH_3); ^{19}F NMR (282 MHz; $CDCl_3$) −145.9 (2F, dd, *J* 27.4, 9.6), −150.5 (1F, t, *J* 21.8), −159.8 (4F, dddd, *J* 27.4, 21.8, 14.7, 10.5); MS (ESI) *m*/*e* (relative intensity) 841 (27), 863 (100); HRMS (ESI) obsd 863.1444 (MNa^+) calcd 863.1435.

4.22. 3,3′-Bis(1-phenyl-1*H*-1,2,3-triazol-4-yl)-2,2′-dihydroxy-1,1′-binaphthyl (26a)

Hydrochloric acid (10 M; 0.50 mL, 5.0 mmol) was added to a solution of **25a** (70 mg, 1.06×10^{-4} mol) in acetone (10 mL). The mixture was stirred for 20 h, then neutralised by the addition of saturated aqueous sodium hydrogen carbonate (10 mL). The resulting mixture was partitioned between water (40 mL) and ethyl acetate (30 mL) and the aqueous layer was extracted with ethyl acetate (2×30 mL). The combined organic phases were washed with water (100 mL), dried over anhydrous sodium sulfate and reduced to a slurry, which was adsorbed onto silica and the remaining solvent removed in vacuo. Flash column chromatography (ethyl acetate/hexanes: 1/3) gave **26a** (55 mg, 91%) as a colourless powder. Mp decomposes above 280 °C; R_f 0.60 (ethyl acetate/hexanes: 1/1); IR (neat) ν_{max}/cm^{-1} 3286, 2954, 1596, 1355, 968, 756; ^1H NMR (500 MHz; DMSO-d_6) 9.87 (2H, br), 9.33 (2H, s), 8.75 (2H, s), 8.01 (6H, d, *J* 8.0), 7.66 (4H, d, *J* 7.5), 7.55 (2H, t, *J* 7.5), 7.33 (2H, m), 7.23 (2H, m), 6.98 (2H, d, *J* 8.0); ^{13}C NMR (125 MHz; $CDCl_3$) 145.5 (C), 136.6 (C), 133.7 (C), 130.0 (3C, CH), 130.0 (C), 129.0 (CH), 128.3 (CH), 126.6 (C), 124.3 (C), 121.6 (CH), 120.4 (3C, CH); MS (ESI) *m*/*e* (relative intensity) 573 (100), 574 (48); HRMS (ESI) obsd 573.2029 (MH^+) calcd 573.2039.

4.23. 3,3′-Bis(1-(*p*-methoxyphenyl)-1*H*-1,2,3-triazol-4-yl)-2,2′-dihydroxy-1,1′-binaphthyl (26b)

Hydrochloric acid (10 M; 1.0 mL, 20 mmol) added to a solution of **25b** (200 mg, 2.73×10^{-4} mol) in acetone (25 mL). The solution was stirred for 15 h, then neutralised with saturated aqueous sodium hydrogen carbonate (25 mL). The mixture was partitioned between water (50 mL) and ethyl acetate (40 mL) and the aqueous layer was extracted with ethyl acetate (2×40 mL). The combined organics were washed with water (100 mL) and dried over anhydrous sodium sulfate. The solvent volume was reduced to give a slurry, which was adsorbed onto silica and the remaining solvent removed in vacuo. A short silica column eluting with ethyl acetate/hexanes: 1/4 removed unreacted material and excess azide and then the silica was subjected to Soxhlet extraction (ethyl acetate). The solvent was removed in vacuo to give a tan-coloured powder. Trituration with ethyl acetate gave **26b** (135 mg, 78%) as a colourless powder. Mp 288–292 °C (partial decomposition); R_f 0.38 (ethyl acetate/hexanes: 1/1); IR (neat) ν_{max}/cm^{-1} 2939, 2851, 1518, 1257; ^1H NMR (300 MHz; $CDCl_3$) 9.59 (2H, s), 8.50 (2H, s), 8.49 (2H, s), 7.92 (2H, d, *J* 8.4), 7.75 (4H, d, *J* 9.0), 7.22–7.36 (6H, m), 7.07 (4H, d, *J* 9.0), 3.89 (6H, s); ^{13}C NMR (75 MHz; acetone-d_6) 161.2 (C), 152.4 (C), 147.6 (C), 135.1 (C), 131.3 (C), 129.5 (C), 129.1 (CH), 127.5 (CH), 127.4 (CH), 125.5 (CH), 124.4 (C), 123.1 (CH), 121.4 (CH), 118.8 (C), 117.4 (C), 115.8 (CH), 56.1 (CH_3); MS (ESI) *m*/*e* (relative intensity) 633 (58), 655 (100); HRMS (ESI) obsd 655.2060 (MH^+) calcd 655.2054.

4.24. 3,3′-Bis(1-(*p*-bromophenyl)-1*H*-1,2,3-triazol-4-yl)-2,2′-dihydroxy-1,1′-binaphthyl (26c)

Hydrochloric acid (10 M; 2.0 mL, 20 mmol) added to a solution of **25c** in acetone (50 mL). The solution was stirred for 20 h and then neutralised with saturated aqueous sodium hydrogen carbonate (50 mL). The mixture was partitioned between water (100 mL) and ethyl acetate (50 mL) and the aqueous layer was

extracted with ethyl acetate (2×50 mL). The combined organic layers were washed with water (100 mL). The resulting suspension was dried over anhydrous sodium sulfate and reduced to a slurry, which was adsorbed onto silica and the remaining solvent removed in vacuo. Flash column chromatography (ethyl acetate/hexanes: 1/3) gave **26c** (449 mg, 92%) as a tan-coloured powder. Mp>340 °C (decomposes); R_f 0.45 (ethyl acetate/hexanes: 1/1); IR (neat) ν_{max}/cm^{-1} 3303, 2957, 1438, 1191, 1059, 925; ^{1}H NMR (300 MHz; DMSO-d_6) 9.72 (2H, br), 9.32 (2H, s), 8.75 (2H, s), 8.02 (2H, d, *J* 8.0), 7.99 (4H, d, *J* 8.8), 7.85 (4H, d, *J* 8.8), 7.34 (2H, dd, *J* 8.3, 7.4), 7.24 (2H, dd, *J* 8.0, 7.4), 6.97 (2H, d, *J* 8.3); ^{13}C NMR (100 MHz; DMSO-d_6) 152.4, 151.0, 145.5, 135.8, 133.7, 132.9, 128.2, 126.8, 126.7, 124.2, 123.4, 122.4, 122.4, 121.7, 118.8, 115.9; MS (ESI) *m*/*e* (relative intensity) 731 (100), 1483 (27); HRMS (ESI) obsd 731.0216 (MH$^+$) calcd 731.0223.

4.25. 3,3′-Bis(1-(*p*-fluorophenyl)-1*H*-1,2,3-triazol-4-yl)-2,2′-dihydroxy-1,1′-binaphthyl (26d)

Hydrochloric acid (10 M; 1.0 mL, 10 mmol) was added to a solution of **25d** (76 mg, 1.1×10^{-4} mol) in acetone (20 mL). The solution was stirred for 4 h and then neutralised with excess sodium bicarbonate. The mixture was filtered, washing with dichloromethane (20 mL), and the filtrate was dried over anhydrous sodium sulfate. The solvent was removed in vacuo to give **26d** (70 mg, 97%) as a colourless solid. Mp 340–344 °C (partial decomposition); R_f 0.33 (ethyl acetate/hexanes: 3/7); IR (neat) ν_{max}/cm^{-1} 1349, 1237, 1054, 832; ^{1}H NMR (300 MHz; $CDCl_3$) 9.55 (2H, br s), 8.33 (2H, s), 8.15 (2H, s), 7.50–7.60 (6H, m), 6.97–7.08 (8H, m); ^{13}C NMR (75 MHz; $CDCl_3$) 162.4 (CF, d, J_{C-F} 249), 150.9 (C), 146.4 (C), 133.7, (C), 132.7 (C), 128.4 (CH), 128.4 (C), 127.1 (CH), 126.7 (CH), 124.3 (CH), 123.7 (CH), 122.2 (2C, CH, d, $^2J_{C-F}$ 8.3), 119.5 (CH), 117.1 (C), 116.6 (2C, CH, d, $^2J_{C-F}$ 23), 115.8 (C); ^{19}F NMR (282 MHz; $CDCl_3$) −111.97 (2F, m); MS (negative ESI) *m*/*e* (relative intensity) 607 (100, M−(H$^+$)), 608 (48, M−(H$^+$)), 1215 (42, 2M−(H$^+$)), 1216 (32, 2M−(H$^+$)); HRMS (ESI) obsd 609.1829 (MH$^+$) calcd 609.1845.

4.26. 3,3′-Bis(1-(2,4,5-trichlorophenyl)-1*H*-1,2,3-triazol-4-yl)-2,2′-dihydroxy-1,1′-binaphthyl (26e)

Hydrochloric acid (10 M; 1.0 mL, 10 mmol) was added to a solution of **25e** (80 mg, 92×10^{-4} mol) in acetone (100 mL). The solution was stirred for 4 h and was then neutralised with excess sodium bicarbonate. The mixture was filtered, eluting with dichloromethane (100 mL). The filtrate was dried over anhydrous sodium sulfate and the solvent was removed in vacuo to give **26e** (66 mg, 92%) as a colourless solid. Mp 265–268 °C; R_f 0.17 (ethyl acetate/hexanes: 1/5); IR (neat) ν_{max}/cm^{-1} 2923, 1711, 1471, 1400, 1092, 800; ^{1}H NMR (400 MHz; DMSO-d_6) 9.47 (2H, br s), 8.97 (2H, s), 8.87 (2H, s), 8.28 (2H, s), 8.27 (2H, s), 8.05 (2H, d, *J* 8.4), 7.34 (2H, ddd, *J* 8.4, 8.4, 1.2), 7.24 (2H, ddd, *J* 8.4, 8.4, 1.2), 6.94 (2H, d, *J* 8.4); ^{13}C NMR (100 MHz; $CDCl_3$) 151.0 (C), 143.9 (C), 134.2 (C), 133.9 (C), 133.7 (C), 131.7 (CH), 131.0 (C), 129.8 (CH), 128.5 (CH), 128.5 (C), 128.3 (C), 126.9 (CH), 126.7 (CH), 125.8 (CH), 124.0 (CH), 123.3 (CH); MS (ESI) *m*/*e* (relative intensity) 777 (49), 779 (100), 781 (80), 782 (51); HRMS (ESI) obsd 800.9492 (MNa$^+$) calcd 800.9489.

4.27. 3,3′-Bis(1-(pentafluorophenyl)-1*H*-1,2,3-triazol-4-yl)-2,2′-dihydroxy-1,1′-binaphthyl (26f)

Compound **25f** (160 mg, 2.02×10^{-4} mol) was dissolved in a mixture of dichloromethane (10 mL) and methanol (30 mL). Hydrochloric acid (10 M; 1.0 mL, 10 mmol) was added and the mixture was stirred for 15 h before being poured onto water (100 mL) and neutralised by addition of sodium hydrogen carbonate. The resulting suspension was extracted with dichloromethane (3×20 mL), the combined organic extracts washed with water (2×50 mL) and the solvent was evaporated. Flash column chromatography (ethyl acetate/hexanes: 3/20) gave **26f** (146 mg, 96%) as a colourless solid. Mp 205–207 °C; R_f 0.54 (ethyl acetate/hexanes: 1/5); IR (neat) ν_{max}/cm^{-1} 2940, 1533, 1150, 991, 730; ^{1}H NMR (400 MHz; $CDCl_3$) 9.06 (2H, s), 8.67 (2H, s), 8.08 (2H, d, *J* 9.2), 7.50 (2H, ddd, *J* 9.2, 8.3, 1.1), 7.36 (2H, ddd, *J* 9.2, 8.3, 1.1), 7.31 (2H, d, *J* 8.3), 4.61 (2H, d, *J* 5.0), 4.43 (2H, d, *J* 5.0), 2.72 (6H, s); ^{13}C NMR (100 MHz; $CDCl_3$) 150.0 (C), 143.9 (C), 144.5 (4CF, dm, $^1J_{C-F}$ 269), 137.8 (2CF, dm, $^2J_{C-F}$ 259), 134.1 (CH), 130.1 (C), 129.2 (CH), 129.0 (CH), 127.7 (CH), 126.0 (CH), 125.7 (CH), 125.6 (C), 123.3 (C), 113.1 (2C, m) 98.8 (CH_2), 57.0 (CH_3); ^{19}F NMR (282 MHz; $CDCl_3$) −145.7 (2F, dd, *J* 28.2, 9.3), −149.9 (1F, t, *J* 21.5), −159.5 (4F, dddd, J, 28.2, 21.5, 15.5, 10.9); MS (ESI) *m*/*e* (relative intensity) 841 (27), 863 (100); HRMS (ESI) obsd 863.1444 (MNa$^+$) calcd 863.1435.

4.28. 3,3′-Bis(1-phenyl-1*H*-1,2,3-triazol-4-yl)-1,1′-binaphthyl-2,2′-diyl 1-pyrrolidylphosphonite (27a) and 3,3′-bis(1-phenyl-1*H*-1,2,3-triazol-4-yl)-1,1′-binaphthyl-2,2′-diyl 1-pyrrolidylphosphonate (28a)

Phosphorus trichloride (100 μL, 1.15 mmol) was added to a stirred solution of **26a** (71 mg, 1.24×10^{-4} mol) in a 3:2 mixture of toluene/*m*-dichlorobenzene (5 mL). The reaction mixture was heated to 110 °C for 8 h. After cooling the mixture to 0 °C, pyrrolidine (400 μL, 4.87 mmol) was added slowly. The mixture was stirred at 0 °C for 15 min, then allowed to warm to room temperature and stirred for a further 1 h. The reaction mixture was partitioned between saturated aqueous ammonium chloride (50 mL) and dichloromethane (30 mL). The aqueous phase was extracted with dichloromethane (3×30 mL) and the combined organic layers were washed with saturated aqueous ammonium chloride (100 mL), brine (100 mL), then dried over anhydrous sodium sulfate and the solvent was evaporated. Flash column chromatography (ethyl acetate/hexanes: 2/3) gave **27a** (27 mg, 32%) as a colourless powder. Mp>150 °C (decomposes); R_f 0.76 (ethyl acetate/hexanes: 1/1); IR (neat) ν_{max}/cm^{-1} 3058, 2924, 1598, 1502, 1240, 1041; ^{1}H NMR (300 MHz; $CDCl_3$) 9.24 (1H, s), 9.06 (1H, s), 8.97 (1H, s), 8.78 (1H, s), 8.08 (2H, d, *J* 8.4), 7.81 (2H, dd, *J* 8.4, 1.5), 7.77 (2H, dd, *J* 8.4, 1.5), 7.44–7.61 (8H, m), 7.28–7.41 (4H, m), 2.82–2.89 (2H, m), 2.71–2.79 (2H, m), 1.39–1.52 (2H, m); ^{13}C NMR (75 MHz; $CDCl_3$) 147.0 (C, d, $^2J_{C-P}$ 4.6) 146.3 (C), 144.4 (C), 144.1 (C), 137.4 (C), 137.3 (C), 132.8 (CH), 132.6 (CH), 131.4 (C), 131.0 (C), 130.1 (2C, CH), 130.0 (2C, CH), 129.2 (2C, CH), 129.0 (CH), 128.9 (CH), 128.5 (CH), 128.4 (CH), 126.8 (2C, CH), 125.6 (CH), 125.4 (CH), 125.0 (C), 124.1 (C), 123.0 (C), 122.9 (C), 121.4 (CH), 121.0 (CH), 120.9 (CH), 120.7 (2C, CH), 120.6 (2C, CH), 45.7 (2C, CH_2, d, $^2J_{C-P}$ 15.9), 25.7 (2C, CH_2, d, $^3J_{C-P}$ 5.2); ^{31}P NMR (121 MHz; $CDCl_3$) 149.7; MS (ESI) *m*/*e* (relative intensity) 633 (66), 672 (100), 704 (51), 1365 (7); HRMS (ESI) obsd 672.2288 (MH$^+$) calcd 672.221, and the corresponding phosphoramidate **28a** (36 mg, 43%) as a colourless powder. Mp>170 °C (decomposes); R_f 0.68 (ethyl acetate/hexanes: 1/1); IR (neat) ν_{max}/cm^{-1} 2925, 1504, 1238, 1044, 756; ^{1}H NMR (400 MHz; $CDCl_3$) 9.12 (1H, s), 9.04 (1H, s), 8.89 (1H, s), 8.73 (1H, s), 8.11 (1H, d, *J* 8.5), 8.08 (1H, d, *J* 8.5), 7.86 (1H, dd, *J* 8.2, 2.1), 7.85 (1H, dd, *J* 8.2, 2.1), 7.45–7.60 (8H, m), 7.31–7.38 (4H, m), 2.70–2.88 (2H, m), 2.58–2.65 (2H, m), 1.41–1.52 (4H, m); ^{13}C NMR (100 MHz; $CDCl_3$) 144.2 (C, d, $^2J_{C-P}$ 10.5), 143.9 (C, d, $^2J_{C-P}$ 9.2), 143.2 (C), 143.1 (C), 137.4 (C), 136.7 (C), 132.3 (CH), 132.1 (CH), 131.7 (C), 131.6 (C), 130.8 (CH), 130.1 (2C, CH), 129.9 (2C, CH), 129.3 (CH), 129.2 (CH), 128.8 (CH), 127.5 (CH), 127.2 (CH), 127.2 (CH), 127.0 (CH), 126.6 (CH), 126.4 (CH), 123.0 (C), 123.0 (C), 122.9 (CH), 122.7 (C), 122.7 (C), 122.3 (CH), 122.0 (C), 122.0 (C), 121.5 (CH), 120.8 (2C, CH), 120.7 (2C, CH), 48.0 (2C, CH_2, d, $^2J_{C-P}$ 4.8), 26.2 (2C, CH_2, d, $^3J_{C-P}$ 9.7); ^{31}P NMR (121 MHz; $CDCl_3$) 11.9; MS (ESI) *m*/*e* (relative intensity) 688 (100), 710 (26); HRMS (ESI) obsd 688.2235 (MH$^+$) calcd 688.2221.

4.29. 3,3′-Bis(1-(*p*-methoxyphenyl)-1*H*-1,2,3-triazol-4-yl)-1,1′-binaphthyl-2,2′-diyl 1-pyrrolidylphosphonite (27b) and 3,3′-bis(1-(*p*-methoxyphenyl)-1*H*-1,2,3-triazol-4-yl)-1,1′-binaphthyl-2,2′-diyl 1-pyrrolidylphosphonate (28b)

Phosphorus trichloride (320 μL, 3.67 mmol) was added to a stirred solution of **26b** (230 mg, 3.64×10^{-4} mol) in a 3:2 mixture of toluene/*m*-dichlorobenzene (15 mL) and the reaction mixture was heated to 110 °C for 8 h. The mixture was cooled to 0 °C and pyrrolidine (1.20 mL, 14.6 mmol) was added slowly. The mixture was stirred at 0 °C for 15 min, then allowed to warm to room temperature and stirred for an additional 1 h. The reaction mixture was partitioned between saturated aqueous ammonium chloride (50 mL) and dichloromethane (30 mL). The aqueous phase was extracted with dichloromethane (3×30 mL) and the combined organic phases were washed with saturated aqueous ammonium chloride (100 mL), brine (100 mL), were dried over anhydrous sodium sulfate and the solvent was evaporated. Flash column chromatography (ethyl acetate/hexanes: 3/2) gave **27b** (64 mg, 24%) as a colourless powder. Mp>140 °C (decomposes); R_f 0.35 (ethyl acetate/hexanes: 3/2); IR (neat) ν_{max}/cm^{-1} 2967, 1519, 1261, 1035, 796; ^{1}H NMR (300 MHz; $CDCl_3$) 9.04 (1H, s), 8.95 (1H, s), 8.57 (1H, s), 8.36 (1H, s), 8.07 (2H, d, *J* 6.5) 7.65–7.71 (4H, m), 7.45–7.49 (2H, m), 7.27–7.39 (4H, m), 7.03–7.07 (4H, m), 3.87 (3H, m), 3.87 (3H, m), 2.82–2.91 (2H, m), 2.71–2.80 (2H, m), 1.42–1.49 (4H, m); ^{13}C NMR (75 MHz; $CDCl_3$) 160.1 (C), 160.0 (C), 147.0 (C, $^2J_{C-P}$ 4.1) 146.3 (C), 144.1 (C), 143.9 (C), 132.7 (CH), 132.6 (CH), 131.4 (C), 130.9 (C), 130.8 (C), 130.7 (C), 129.1 (2C, CH), 128.4 (CH), 128.3 (CH), 126.8 (CH), 126.8 (CH), 126.7 (2C, CH), 125.6 (CH), 125.4 (CH), 125.0 (C), 124.9 (C), 124.0 (C), 124.0 (C), 123.1 (C), 123.0 (C), 122.3 (2C, CH), 122.2 (2C, CH), 121.6 (CH), 121.2 (CH), 121.2 (CH), 115.1 (2C, CH), 115.0 (2C, CH), 55.8 (2C, CH_3), 45.6 (2C, CH_2, d, $^2J_{C-P}$ 16.8), 25.7 (2C, CH_2, d, $^3J_{C-P}$ 4.2); ^{31}P NMR (121 MHz; $CDCl_3$) 160.9; MS (ESI) *m*/*e* (relative intensity) 732 (100), 764 (44), 1485 (76); HRMS (ESI) obsd 732.2496 (MH^+) calcd 732.2429, and the corresponding phosphoramidate **28b** (147 mg, 54%) as a colourless powder. Mp>200 °C (decomposes); R_f 0.20 (ethyl acetate/hexanes: 3/2); IR (neat) ν_{max}/cm^{-1} 2930, 1517, 1253, 1041, 828; ^{1}H NMR (300 MHz; $CDCl_3$) 8.96 (1H, s), 8.94 (1H, s), 8.85 (1H, s), 8.63 (1H, s), 8.08 (1H, d, *J* 9.1), 8.07 (1H, d, *J* 9.1), 7.75 (1H, d, *J* 9.0), 7.72 (1H, d, *J* 9.0), 7.49–7.56 (2H, m), 7.22–7.34 (4H, m), 7.03 (2H, d, *J* 9.0), 3.87 (3H, s), 3.84 (3H, s), 2.65–2.73 (2H, m), 2.63–2.56 (2H, m), 1.38–1.49 (4H, m); ^{13}C NMR (75 MHz; $CDCl_3$) 160.2 (C), 159.9 (C), 144.2 (C, d, $^2J_{C-P}$ 11.7), 143.8 (C, d, $^2J_{C-P}$ 11.0), 143.0 (C), 142.9 (C), 132.2 (CH), 132.1 (CH) 131.6 (C), 131.6 (C), 130.9 (C), 130.6 (CH), 130.4 (C), 129.2 (CH), 129.2 (CH), 129.1 (CH), 127.4 (CH), 127.2 (2C, CH), 127.0 (CH), 126.6 (CH), 126.3 (CH), 123.1 (C, d, $^3J_{C-P}$ 3.8), 122.9 (C, d, $^3J_{C-P}$ 2.8), 122.8 (C, d, $^3J_{C-P}$ 3.1), 122.4 (CH), 122.3 (2C, CH), 122.3 (2C, CH), 122.0 (C, d, $^3J_{C-P}$ 2.1), 121.6 (CH), 115.1 (2C, CH), 114.9 (2C, CH), 55.8 (2C, CH_3), 48.1 (2C, CH_2, d, $^2J_{C-P}$ 4.7), 26.2 (2C, CH_2, d, $^3J_{C-P}$ 9.6); ^{31}P NMR (121 MHz; $CDCl_3$) 11.8; MS (ESI) *m*/*e* (relative intensity) 748 (100), 770 (77); HRMS (ESI) obsd 748.2430 (MH^+) calcd 748.2432.

4.30. 3,3′-Bis(1-(*p*-bromophenyl)-1*H*-1,2,3-triazol-4-yl)-1,1′-binaphthyl-2,2′-diyl 1-pyrrolidylphosphonite (27c) and 3,3′-bis(1-(*p*-bromophenyl)-1*H*-1,2,3-triazol-4-yl)-1,1′-binaphthyl-2,2′-diyl 1-pyrrolidylphosphonite (28c)

Phosphorus trichloride (60 μL, 70×10^{-4} mol, 10 equiv) was added to a stirring solution of **26c** (50 mg, 6.8×10^{-5} mol) in *m*-dichlorobenzene (5.0 mL) and the reaction mixture was heated to 110 °C for 8 h. The mixture was cooled to 0 °C and pyrrolidine (220 μL, 2.68 mmol) added slowly. The mixture was stirred at 0 °C for 15 min, then allowed to warm to room temperature and stirred for a further 1 h. The reaction mixture was partitioned between saturated aqueous ammonium chloride (30 mL) and dichloromethane (20 mL). The aqueous phase was extracted with dichloromethane (3×20 mL) and the combined organic phases were washed with saturated aqueous ammonium chloride (50 mL), brine (50 mL), were dried over anhydrous sodium sulfate and the solvent was evaporated. Flash column chromatography (ethyl acetate/hexanes: 1/1) gave **27c** (37 mg, 66%) as a colourless solid. R_f 0.23 (ethyl acetate/hexanes: 1/3); IR (neat) ν_{max}/cm^{-1} 3312, 2967, 1421, 1054, 905; ^{1}H NMR (300 MHz; $CDCl_3$) 9.27 (1H, s), 8.97 (1H, s), 8.91 (1H, s), 8.89 (1H, s), 8.23 (2H, d, *J* 6.8), 8.22 (2H, d, *J* 6.8), 7.99 (2H, d, *J* 8.7), 7.81–7.93 (6H, m), 7.51–7.58 (2H, m), 7.36–7.43 (2H, m), 7.20–7.27 (2H, m), 2.59–2.71 (2H, m), 2.71–2.80 (2H, m), 1.29–1.34 (4H, m); ^{31}P NMR (121 MHz; $CDCl_3$) 149.1; MS (ESI) *m*/*e* (relative intensity) 828 (44), 830 (100), 831 (40), 832 (57); HRMS (ESI) obsd 830.0502 (MH^+) calcd 830.0467 and the corresponding phosphoramidate **28c** (16 mg, 28%); R_f 0.16 (ethyl acetate/hexanes: 1/3); IR (neat) ν_{max}/cm^{-1} 2952, 1428, 1411, 1060; ^{1}H NMR (300 MHz; $CDCl_3$) 9.15 (1H, s), 9.09 (1H, s), 8.84 (1H, s), 8.79 (1H, s), 8.18 (1H, d, *J* 8.6), 8.11 (1H, d, *J* 8.6), 7.86–8.11 (2H, m), 7.59–7.65 (8H, m), 7.24–7.41 (4H, m), 2.73–2.89 (2H, m), 2.57–2.68 (2H, m), 1.31–1.47 (4H, m); ^{31}P NMR (121 MHz; $CDCl_3$) 11.8; MS (ESI) *m*/*e* (relative intensity) 844 (50), 846 (100), 847 (43), 848 (60); HRMS (ESI) obsd 846.0507 (MH^+) calcd 846.0416.

4.31. 3,3′-Bis(1-(*p*-fluorophenyl)-1*H*-1,2,3-triazol-4-yl)-1,1′-binaphthyl-2,2′-diyl 1-pyrrolidylphosphonite (27d) and 3,3′-bis(1-(*p*-fluorophenyl)-1*H*-1,2,3-triazol-4-yl)-1,1′-binaphthyl-2,2′-diyl 1-pyrrolidylphosphonite (28d)

Phosphorus trichloride (55 μL, 6.3 mmol) was added to a stirred solution of **27g** (40 mg, 63×10^{-5} mol) in toluene (3 mL) and the reaction mixture heated to 110 °C for 15 h. The mixture was cooled to 0 °C and pyrrolidine (0.20 mL, 2.4 mmol) was added slowly. The mixture was stirred at 0° C for 15 min, then allowed to warm to room temperature and stirred for a further 1 h. The reaction mixture was partitioned between saturated aqueous ammonium chloride (30 mL) and dichloromethane (10 mL). The aqueous phase was extracted with dichloromethane (3×10 mL) and the combined organic layers were washed with saturated aqueous ammonium chloride (50 mL), brine (50 mL), were dried over anhydrous sodium sulfate and the solvent was evaporated. Flash column chromatography (ethyl acetate/hexanes: 1/4) gave **22g** (31 mg, 68%) as a colourless powder. Mp 130 °C (decomposes); R_f 0.22 (ethyl acetate/hexanes: 1/4); ^{1}H NMR (300 MHz; $CDCl_3$) 9.04 (1H, s), 8.96 (1H, s), 8.62 (1H, s), 8.39 (1H, s), 8.08 (2H, d, *J* 8.0), 7.71–7.83 (4H, m), 7.46–7.51 (2H, m), 7.22–7.40 (10H, m), 2.80–2.87 (2H, m), 2.73–2.80 (2H, m), 1.43–1.49 (4H, m); ^{13}C NMR (75 MHz; $CDCl_3$) 162.6 (CF, d, $^1J_{C-F}$ 249.4), 162.5 (CF, d, $^1J_{C-F}$ 249.2), 146.9 (C, $^2J_{C-P}$ 4.1) 146.2 (C, $^2J_{C-P}$ 1.4), 144.4 (C), 144.2 (C), 133.6 (C, $^4J_{C-F}$ 3.2), 133.4 (C, $^4J_{C-F}$ 3.1), 132.7 (C, $^3J_{C-P}$ 6.8), 133.6 (C, $^3J_{C-P}$ 5.9), 131.3 (C), 130.9 (C), 129.1 (2C, CH), 128.5 (CH), 128.4 (CH), 126.8 (CH), 126.8 (CH), 125.6 (CH), 125.4 (CH), 124.9 (C), 124.8 (C), 124.0 (C, $^3J_{C-P}$ 2.1), 122.8 (C, $^3J_{C-P}$ 1.8), 122.7 (CH), 122.5 (2C, CH, d, $^3J_{C-F}$ 8.6), 122.5 (2C, CH, d, $^3J_{C-F}$ 8.6), 121.5 (CH), 121.1 (CH), 121.1 (CH), 117.0 (CH, $^2J_{C-F}$ 23.2), 116.9 (CH, $^2J_{C-F}$ 23.2), 45.6 (2C, CH_2, d, $^2J_{C-P}$ 15.9), 25.7 (2C, CH_2, d, $^3J_{C-P}$ 4.3); ^{31}P NMR (121 MHz; $CDCl_3$) 149.77; ^{19}F NMR (282 MHz; $CDCl_3$) −111.85 to −111.93 (1F, m), −111.85 to −111.93 (1F, m); MS (APCI) *m*/*e* (relative intensity) 708 (100), 709 (34); HRMS (ESI) obsd 708.1020 (MH^+) calcd 708.2089, and the corresponding phosphoramidate **24g** (8.0 mg, 17%) as a colourless powder. Mp 160 °C (decomposes); R_f 0.14 (ethyl acetate/hexanes: 1/3); ^{1}H NMR (300 MHz; $CDCl_3$) 9.06 (1H, s), 9.01 (1H, s), 8.88 (1H, s), 8.68 (1H, s), 8.09 (2H, d, *J* 8.1, 8.1), 7.80–7.89 (4H, m), 7.51–7.59 (2H, m), 7.21–7.41 (10H, m), 2.66–2.75 (2H, m), 2.56–2.64 (2H, m), 1.37–1.55 (4H, m); ^{13}C NMR (75 MHz; $CDCl_3$) 162.7 (CF, d, $^1J_{C-F}$ 249.6), 162.5 (CF, d, $^1J_{C-F}$ 250.6), 144.0 (C, d, $^2J_{C-P}$ 9.5), 143.8 (C, d, $^2J_{C-P}$ 9.8), 143.1 (C), 143.0 (C), 133.5 (C, d, $^4J_{C-F}$ 3.1), 133.1 (C, d, $^4J_{C-F}$

3.2), 132.1 (C, d, $^3J_{C-P}$ 1.4), 132.0 (C, d, $^3J_{C-P}$ 1.0), 131.6 (C, d, $^3J_{C-P}$ 1.5), 131.5 (C, d, $^3J_{C-P}$ 1.1), 130.6 (2C, CH), 129.2 (CH), 129.2 (CH), 127.5 (CH), 127.4 (CH), 127.1 (CH), 126.8 (CH), 126.6 (CH), 126.4 (CH), 122.6 (CH, d, $^3J_{C-F}$ 8.5), 122.4 (CH, d, $^3J_{C-F}$ 8.4), 122.2 (CH), 122.0 (C), 121.9 (C), 121.5 (CH), 117.0 (CH, d, $^2J_{C-F}$ 23.2), 116.9 (CH, d, $^2J_{C-F}$ 23.2), 48.0 (2C, CH_2, d, $^2J_{C-P}$ 5.1), 26.1 (2C, CH_2, d, $^3J_{C-P}$ 5.1); ^{31}P NMR (121 MHz; $CDCl_3$) 11.92; ^{19}F NMR (282 MHz; $CDCl_3$) −111.85 to −111.93 (1F, m), −112.77 to −112.84 (1F, m); MS (ESI) *m*/*e* (relative intensity) 724 (100), 725 (41); HRMS (ESI) obsd 724.2040 (MH^+) calcd 724.2038.

4.32. 3,3′-Bis(1-(2,4,5-trichlorophenyl)-1*H*-1,2,3-triazol-4-yl)-1,1′-binaphthyl-2,2′-diyl 1-pyrrolidylphosphonite (27e) and 3,3′-bis(1-(2,4,5-trichlorophenyl)-1*H*-1,2,3-triazol-4-yl)-1,1′-binaphthyl-2,2′-diyl 1-pyrrolidylphosphonate (28e)

Phosphorus trichloride (23 μL, 2.6 mmol) was added to a stirred solution of **26e** (20 mg, 2.6×10^{-5} mol) in toluene (2 mL) and the reaction mixture was heated to 110 °C for 15 h. The mixture was cooled to 0 °C and pyrrolidine (90 μL, 1.1 mmol) was added slowly. The mixture was stirred at 0 °C for 15 min, then allowed to warm to room temperature and stirred for an additional 1 h. The reaction mixture was partitioned between saturated aqueous ammonium chloride (30 mL) and dichloromethane (10 mL). The aqueous phase was extracted with dichloromethane (3×10 mL) and the combined organics were washed with saturated aqueous ammonium chloride (50 mL), brine (50 mL), were dried over anhydrous sodium sulfate and the solvent was evaporated. Flash column chromatography (ethyl acetate/hexanes: 3/17) gave **27e** (15 mg, 69%) as a colourless powder. Mp>140 °C (decomposes); R_f 0.87 (ethyl acetate/hexanes: 1/5); IR (neat) ν_{max}/cm^{-1} 2927, 1481, 1239, 1037, 823; ^{1}H NMR (300 MHz; $CDCl_3$) 9.04 (1H, s), 8.91 (1H, s), 8.66 (1H, s), 8.56 (1H, s), 8.08 (1H, d, *J* 8.1), 8.07 (1H, d, *J* 8.1), 7.98 (1H, s), 7.85 (1H, s), 7.73 (1H, s), 7.70 (1H, s), 7.49 (1H, ddd, *J* 8.0, 7.0, 1.0), 7.48 (1H, ddd, *J* 8.0, 6.8, 1.3), 7.39 (1H, d, *J* 8.3), 7.28–7.36 (3H, m), 2.85–2.81 (2H, m), 2.71–2.67 (2H, m), 1.43–1.48 (4H, m); ^{13}C NMR (75 MHz; $CDCl_3$) 146.8 (C, d, $^2J_{C-P}$ 3.7) 146.3 (C), 144.0 (C), 143.6 (C), 135.0 (C), 134.6 (C), 134.1 (C), 134.1 (C), 132.8 (C), 132.8 (C), 132.8 (C), 132.7 (C), 132.2 (CH), 132.1 (CH), 131.4 (C), 130.9 (C), 129.2 (2C, CH), 128.8 (CH), 128.7 (CH), 128.6 (2C, CH), 127.0 (2C, CH), 127.0 (C), 126.8 (CH), 126.8 (CH), 126.3 (C), 125.7 (CH), 125.6 (CH), 125.2 (C), 124.9 (C), 124.9 (C), 124.7 (CH, d, $^4J_{C-P}$ 4.1), 124.1 (CH, d, $^4J_{C-P}$ 2.1), 122.5 (2C, C), 45.8 (2C, CH_2, d, $^2J_{C-P}$ 16.1), 25.7 (2C, CH_2, d, $^3J_{C-P}$ 5.1); MS (ESI) *m*/*e* (relative intensity) 876 (47) 877 (20), 878 (100), 879 (44), 880 (88), 881 (40), 882 (11); HRMS (ESI) obsd 877.9797 (MH^+) calcd 877.9908, and the corresponding phosphoramidate **28e** (2.2 mg, 10%) as a colourless powder. Mp; 180 °C (decomposes); R_f 0.64 (ethyl acetate/hexanes: 1/5); IR (neat) ν_{max}/cm^{-1} 2927, 1481, 1086, 1038, 822, 730; ^{1}H NMR (300 MHz; $CDCl_3$) 9.06 (1H, s), 8.98 (1H, s), 8.93 (1H, s), 8.72 (1H, s), 8.11 (1H, d, *J* 7.5), 8.08 (1H, d, *J* 7.5), 7.95 (1H, s), 7.82 (1H, s), 7.45 (1H, s), 7.70 (1H, s), 7.50–7.59 (2H, m), 7.27–7.41 (3H, m), 2.60–2.81 (4H, m), 1.41–1.58 (4H, m); ^{13}C NMR (75 MHz; $CDCl_3$) 144.1 (C, d, $^2J_{C-P}$ 10.9) 143.7 (C, d, $^2J_{C-P}$ 9.1), 142.8 (C), 142.7 (C), 135.3 (C), 134.7 (C), 134.2 (C), 133.8 (C), 132.7 (C), 132.6 (C), 132.8 (C), 132.4 (C), 132.2 (CH), 132.2 (C), 132.0 (CH), 131.6 (2C, C), 130.6 (CH), 129.5 (CH), 129.3 (CH), 129.2 (CH), 128.9 (CH), 127.8 (CH), 127.7 (CH), 127.4 (CH), 127.4 (C), 127.1 (CH), 127.0 (C), 126.9 (CH), 126.7 (CH), 126.5 (CH), 125.9 (CH), 125.4 (CH), 123.0 (C, d, $^3J_{C-P}$ 2.1), 122.4 (C, d, $^3J_{C-P}$ 1.9), 122.3 (C, d, $^3J_{C-P}$ 2.3), 122.1 (C, d, $^3J_{C-P}$ 1.1), 48.0 (2C, CH_2, d, $^2J_{C-P}$ 5.2), 26.3 (2C, CH_2, d, $^3J_{C-P}$ 9.1); MS (ESI) *m*/*e* (relative intensity) 892 (53) 894 (100), 895 (40), 896 (89), 898 (46); HRMS (ESI) obsd 893.9783 (MH^+) calcd 893.9857.

4.33. 3,3′-Bis(1-(pentafluorophenyl)-1*H*-1,2,3-triazol-4-yl)-1,1′-binaphthyl-2,2′-diyl 1-pyrrolidylphosphonite (27f)

Compound **26f** (50 mg, 71×10^{-5} mol) was taken up in toluene (5 mL) and phosphorus trichloride (100 μL, 1.15 mmol) was added. The mixture was heated under reflux for 15 h. After cooling to room temperature, pyrrolidine (300 μL, 4.87 mmol) was added and the mixture was stirred for a further 1 h before being poured onto saturated aqueous ammonium chloride (10 mL). The resulting mixture was partitioned between water (50 mL) and dichloromethane (20 mL) and the aqueous layer was extracted with dichloromethane (2×15 mL). The combined organics were washed with saturated aqueous ammonium chloride (50 mL), water (50 mL) and then the solvent was evaporated. Flash column chromatography (ethyl acetate/hexanes: 1/10) gave **27f** (51 mg, 64 μmol, 89%) as a colourless solid. Mp>170 °C (decomposes); R_f 0.55 (ethyl acetate/hexanes: 1/5); IR (neat) ν_{max}/cm^{-1} 2929, 1535, 1521, 1233, 1053; 841 ^{1}H NMR (400 MHz; $CDCl_3$) 9.06 (1H, s), 9.04 (1H, s), 8.95 (1H, s), 8.49 (1H, s), 8.29 (1H, s) 8.08 (2H, d, *J* 8.5), 8.07 (2H, d J 8.5), 7.43–7.51 (2H, m), 7.30–7.40 (4H, m), 2.87–2.79 (2H, m), 2.66–2.73 (2H, m), 1.40–1.49 (4H, m); ^{13}C NMR (100 MHz; $CDCl_3$) 146.9 (C, d, $^2J_{C-P}$ 4.0) 146.3 (C), 144.3 (C), 143.9 (C), 132.9 (CH), 132.8 (CH), 131.3 (C), 130.9 (C), 129.2 (CH), 129.2 (CH), 128.9 (CH), 128.7 (CH), 127.2 (C), 127.2 (C), 126.8 (CH), 126.8 (CH), 125.8 (CH), 125.8 (CH), 125.6 (CH), 125.1 (C), 125.0 (C), 124.1 (CH), 122.1 (C), 122.0 (C), 113.1 (C), 113.1 (C), 45.8 (2C, CH_2, d, $^2J_{C-P}$ 15.5), 25.8 (2C, CH_2, d, $^3J_{C-P}$ 4.2); ^{19}F NMR (282 MHz; $CDCl_3$) −146.2 (1F, dd, *J* 10.3, 2.0), −146.3 (1F, dd, *J* 10.5, 2.0), −149.9 (1F, t, *J* 21.7), −150.8 (1F, t, *J* 21.7), −159.7 to −159.5 (4F, m); ^{31}P NMR (121 MHz; $CDCl_3$) 150.5; MS (ESI) *m*/*e* (relative intensity) 852 (100), 782 (37); HRMS (ESI) obsd 852.1322 (MH^+) calcd 852.1329.

4.34. (*S*)-6-Bromo-2,2′-dihydroxy-1,1′-binaphthyl (32)[40]

Compound **30** was prepared according to a published procedure[40] from **29** (1.00 g. 3.49 mmol). This intermediate pivalate ester was taken up in methanol (50 mL) and potassium carbonate (5.0 g, 36 mmol) added. The resulting mixture was stirred (3 h) then filtered, concentrated, and the concentrate partitioned between ethyl acetate (30 mL) and saturated aqueous ammonium chloride (100 mL). The aqueous phase was washed with ethyl acetate (2×20 mL) and the combined organic extracts were washed with water (100 mL), brine (100 mL), dried over anhydrous sodium sulfate and the solvent was evaporated. Flash column chromatography (ethyl acetate/hexanes: 3/7) gave **32** (1.15 g, 90% from 29) as a colourless solid. R_f 0.19 (ethyl acetate/hexanes: 1/5); IR (neat) ν_{max}/cm^{-1} 3404, 1590, 1496, 1142, 818; ^{1}H NMR ($CDCl_3$, 300 MHz) 7.99 (1H, d, *J* 1.8), 7.88 (1H, d, *J* 8.9), 7.84 (1H, d, *J* 8.0), 7.77 (1H, d, *J* 9.0), 7.27–7.33 (5H, m), 7.08 (1H, d, *J* 8.3), 7.00 (1H, d, *J* 8.9), 7.99 (1H, d, *J* 1.8), 5.43 (2H, br s); ^{13}C NMR (75 MHz, $CDCl_3$) 153.2 (C), 152.8 (C), 133.5 (C), 132.2 (C), 131.4 (C), 130.5 (CH), 130.5 (C), 130.3 (CH), 130.1 (CH), 129.4 (CH), 128.4 (CH), 127.5 (CH), 126.3 (CH), 124.2 (CH), 124.1 (CH), 119.1 (CH), 117.9 (CH), 117.7 (C), 111.9 (C), 110.8 (C).

4.35. (*S*)-6-Bromo-2,2′-bismethoxymethoxy-1,1′-binaphthyl (32)[41]

To a stirred suspension of sodium hydride (50% dispersion in mineral oil, 400 mg, 8.33 mmol) in THF (15 mL) at 0 °C was added a solution of (*S*)-**31** (500 mg, 1.37 mmol) in THF (15 mL). The solution was stirred at 0 °C for 1 h, then allowed to warm to room temperature and stirred for 5 h. The mixture was cooled to 0 °C and chloromethyl methyl ether (460 μL, 5.39 mmol) added. The solution was stirred for 15 h, allowing to warm to room temperature then quenched with aqueous potassium hydroxide (10%, 5 mL), followed by saturated aqueous ammonium chloride (20 mL). The reaction mixture was partitioned between ethyl acetate (20 mL) and water (100 mL). The aqueous layer was extracted with ethyl acetate (2×20 mL) and the combined organic layers were washed with saturated aqueous ammonium chloride (50 mL), water (50 mL), were dried over anhydrous sodium sulfate and then the

solvent was evaporated. Flash column chromatography (ethyl acetate/hexanes: 1/9) gave (*S*)-**32** (550 mg, 89%) as a colourless powder. R_f 0.31 (ethyl acetate/hexanes: 1/5); IR (neat) ν_{max}/cm^{-1} 2958, 1585, 1494, 1148, 1012, 923; ^1H NMR ($CDCl_3$, 300 MHz) 8.03 (1H, d, *J* 1.5), 7.96 (1H, d, *J* 9.0), 7.87 (1H, d, *J* 8.1), 7.86 (1H, d, *J* 9.0), 7.60 (1H, d, *J* 8.4), 7.57 (1H, d, *J* 8.7), 7.35 (1H, t, *J* 7.2), 7.21–7.29 (2H, m), 7.10 (1H, d, *J* 8.4), 7.03 (1H, d, *J* 9.0), 5.09 (1H, d, *J* 6.6), 5.08 (1H, d, *J* 6.6), 4.98 (1H, d, *J* 6.6), 3.15 (6H, s); ^{13}C NMR (50 MHz, $CDCl_3$) 153.0, 152.7, 133.9, 132.6, 131.0, 129.8, 129.74, 129.67, 129.6, 128.5, 128.0, 127.5, 126.5, 125.3, 124.2, 121.6, 120.5, 118.3, 117.9, 117.1, 95.2, 95.1, 55.9.

4.36. (*S*)-6-Methyl-2,2′-bismethoxymethoxy-1,1′-binaphthyl (33)

To a solution of (*S*)-**32** (350 mg, 7.72×10^{-4} mol) in THF (5 mL) was sequentially added tetrakistriphenylphosphine palladium(0) (90 mg, 7.8 10^{-4} mol) in THF (5 mL) and dimethylzinc (1.0 M in heptane; 2.32 mL, 2.32 mmol). The mixture was heated under reflux for 3 h, then cooled to room temperature and the reaction was quenched with methanol (10 mL). The mixture was poured onto water (100 mL) and the resulting mixture extracted with ethyl acetate (2×30 mL). The combined organic extracts were washed with water (100 mL) and concentrated. Flash column chromatography (ethyl acetate/hexanes: 7/100) gave **33** (263 mg, 88%) as a colourless glass; R_f 0.30 (ethyl acetate/hexanes: 1/10); $[\alpha]_D^{20}$ −58 (*c* 1.0, THF); IR (neat) ν_{max}/cm^{-1} 2956, 1238, 1148, 1032, 1015; ^1H NMR (300 MHz; $CDCl_3$) 7.95 (1H, d, *J* 6.9), 7.87 (1H, d, *J* 6.0), 7.86 (1H, d, *J* 6.9), 7.65 (1H, m), 7.58 (1H, d, *J* 6.6), 7.54 (1H, d, *J* 6.6), 7.35 (1H, ddd, *J* 6.0, 4.8, 0.9), 7.22 (1H, ddd, *J* 5.7, 4.8, 0.9), 7.17 (1H, d, *J* 6.3), 7.06–7.08 (2H, m), 5.08 (1H, d, *J* 5.1), 5.06 (1H, d, *J* 5.1), 4.98 (1H, d, *J* 5.1), 4.96 (1H, d, *J* 5.1), 3.16 (3H, s), 3.14 (3H, s), 2.46 (3H, s); ^{13}C NMR (75 MHz; $CDCl_3$) 152.8 (C), 152.2 (C), 134.2 (C), 133.7 (C), 132.3 (C), 130.3 (C), 130.0 (C), 129.4 (CH), 128.8 (CH), 128.7 (CH), 128.0 (CH), 127.0 (CH), 126.4 (CH), 125.7 (CH), 125.6 (CH), 124.2 (CH), 121.7 (C), 121.5 (C), 117.7 (CH), 117.6 (CH), 95.5 (CH_2), 95.4 (CH_2), 56.0 (CH_3), 55.9 (CH_3), 21.5 (CH_3); MS (ESI) *m*/*e* (relative intensity) 411 (100), 799 (11); HRMS (ESI) obsd 411.1567 (MNa^+) calcd 411.1567.

4.37. (*S*)-6-Methyl-3,3′-diiodo-2,2′-bismethoxymethoxy-1,1′-binaphthyl (34)

To a stirred solution of **33** (260 mg, 6.69×10^{-4} mol) in THF (7 mL) at −78 °C was added *n*-butyllithium (2.10 M in hexanes; 2.20 mL, 4.62 mmol) and the reaction mixture was stirred for 1 h, then allowed to warm to room temperature and stirred for a further 4 h. The reaction mixture was re-cooled to −78 °C and a solution of iodine (1.27 g, 5.00 mmol) in THF (5 mL) was added. The reaction mixture was stirred for 1 h, then allowed to warm slowly to room temperature and stirred overnight. The mixture was poured onto aqueous sodium sulfite (10% w/v; 100 mL) then extracted with ethyl acetate (2×20 mL). The combined organic phases were washed with brine (100 mL), dried over anhydrous sodium sulfate and the solvent was evaporated. Flash column chromatography (ethyl acetate/hexanes: 1/15) gave the **34** (208 mg, 49%) as a colourless glass; R_f 0.24 (ethyl acetate/hexanes: 1/15); $[\alpha]_D^{20}$ +4.8 (*c* 1.0, THF); IR (neat) ν_{max}/cm^{-1} 2924, 1161, 998, 959, 931; ^1H NMR (300 MHz; $CDCl_3$) 8.52 (1H, s), 8.43 (1H, s), 7.74 (1H, d, *J* 8.4), 7.51 (1H, m), 7.38 (1H, ddd, *J* 8.4, 7.3, 1.5), 7.26 (1H, ddd, *J* 8.4, 7.3, 1.5), 7.17 (1H, d, *J* 8.4), 7.04–7.13 (2H, m), 4.80 (1H, d, *J* 5.6), 4.79 (1H, d, *J* 5.6), 4.69 (1H, d, *J* 5.6), 4.69 (1H, d, *J* 5.6), 3.31 (1H, s), 2.62 (3H, s), 2.57 (3H, s), 2.43 (3H, s); ^{13}C NMR (75 MHz; $CDCl_3$) 152.2 (C), 151.5 (C), 140.0 (CH), 139.3 (CH), 135.6 (C), 133.9 (C), 132.5 (C), 132.2 (C), 132.1 (C), 129.5 (CH), 127.1 (CH), 126.8 (CH), 126.6 (CH), 126.4 (CH), 126.4 (C), 126.1 (C), 125.9 (CH), 125.7 (CH), 99.4 (CH_2), 92.6 (CI), 92.6 (CI), 56.5 (CH_3), 56.5 (CH_3), 21.5 (CH_3); MS (ESI) *m*/*e* (relative intensity) 663 (100), 1303 (7); HRMS (ESI) obsd 662.9497 (MNa^+) calcd 662.9500.

4.38. (*S*)-6-Methyl-3,3′-diethynyl-2,2′-bismethoxymethoxy-1,1′-binaphthyl (35)

A mixture of compound **34** (200 mg, 3.12×10^{-4} mol), tetrakistriphenylphosphinepalladium(0) (18 mg, 16×10^{-5} mol) and copper(I) iodide (3 mg, 1.6×10^{-5} mol) was taken up in THF/triethylamine: 2/1 (6 mL) and trimethylsilylacetylene (220 μL, 1.55 mmol) was added. The mixture was stirred for 4 h, then diluted with ether (20 mL) and filtered through a pad of silica, eluting with ether (20 mL). The solvent was evaporated and the residue was taken up in methanol (10 mL) and potassium carbonate (1.0 g) was added. The mixture was stirred for 2 h and was then poured onto water (100 mL). The resulting mixture was extracted with ethyl acetate (3×20 mL) and the combined organic extracts washed with water (100 mL), dried over anhydrous sodium sulfate and the solvent was evaporated. Flash column chromatography (ethyl acetate/hexanes: 1/10) gave the **35** (134 mg, 98%) as a colourless glass; R_f 0.32 (ethyl acetate/hexanes: 1/10); $[\alpha]_D^{20}$ +4.8 (*c* 1.0, THF); IR (neat) ν_{max}/cm^{-1} 3285, 2924, 1157, 974; ^1H NMR (300 MHz; $CDCl_3$) 8.17 (1H, s), 8.09 (1H, s), 7.80 (1H, d, *J* 8.4), 7.57 (1H, m), 7.39 (1H, ddd, *J* 8.4, 7.2, 1.6), 7.27 (1H, ddd, *J* 8.4, 7.2, 1.6), 7.20 (1H, d, *J* 8.4), 7.08–7.13 (2H, m), 5.06 (1H, d, *J* 6.3), 5.06 (1H, d, *J* 6.1), 4.88 (1H, d, *J* 6.3), 4.87 (1H, d, *J* 6.1), 3.31 (1H, s), 3.30 (1H, s), 2.56 (3H, s), 2.51 (3H, s), 2.43 (3H, s); ^{13}C NMR (75 MHz; $CDCl_3$) 153.4 (C), 152.8 (C), 135.3 (C), 135.2 (CH), 134.6 (CH), 134.1 (C), 132.3 (C), 130.4 (C), 130.2 (C), 129.9 (CH), 127.9 (CH), 127.6 (CH), 127.5 (C), 127.0 (C), 126.6 (CH), 126.6 (CH), 126.4 (CH), 126.0 (C), 125.6 (CH), 125.6 (CH), 116.4 (C), 116.3 (C), 98.9 (CH_2), 81.7 (CH), 81.5 (CH), 80.8 (CH), 80.7 (CH), 56.1 (CH_3), 56.1 (CH_3), 21.5 (CH_3); MS (ESI) *m*/*e* (relative intensity) 459 (100), 895 (46); HRMS (ESI) obsd 459.1565 (MNa^+) calcd 459.1567.

4.39. (*S*)-6-Methyl-3,3′-diethynyl-2,2′-dihydroxy-1,1′-binaphthyl (36)

To a solution of **35** (134 mg, 3.07×10^{-6} mol) in methanol (15 mL) was added hydrochloric acid (10 M; 1.0 mL, 10 mmol,) and the mixture was stirred for 4 h. The mixture was neutralised by addition of excess sodium bicarbonate then poured onto water (100 mL). The resulting mixture was extracted with ethyl acetate (3×20 mL) and the combined organic extracts were washed with water (100 mL), dried over anhydrous sodium sulfate and the solvent was evaporated. Flash column chromatography (ethyl acetate/hexanes: 3/25) gave **36** (103 mg, 96%) as a colourless glass; R_f 0.19 (ethyl acetate/hexanes: 1/20); $[\alpha]_D^{20}$ −74 (*c* 1.0, THF); IR (neat) ν_{max}/cm^{-1} 3285, 2924, 1240, 1157, 974; ^1H NMR (300 MHz; $CDCl_3$) 8.19 (1H, s), 8.10 (1H, s), 7.85 (1H, d, *J* 8.1), 7.84 (1H, d, *J* 8.1), 7.62 (1H, s), 7.37 (1H, ddd, *J* 8.1, 6.9, 1.3), 7.31 (1H, ddd, *J* 8.1, 6.6, 1.3), 7.14–7.18 (2H, m), 7.05 (1H, d, *J* 8.7), 5.72 (2H, br), 3.50 (2H, s), 2.46 (3H, s); ^{13}C NMR (75 MHz; $CDCl_3$) 151.4 (C), 150.9 (C), 134.5 (CH), 134.2 (C), 134.0 (C), 133.9 (CH), 132.2 (C), 130.7 (CH), 128.8 (C), 128.6 (C), 128.3 (2C, CH), 27.3 (CH), 124.8 (CH), 124.6 (CH), 124.5 (CH), 113.6 (C), 113.2 (C), 111.1 (C), 111.0 (C), 83.9 (2C, CH), 79.1 (C), 79.0 (C), 21.4 (CH_3); MS (ESI) *m*/*e* (relative intensity) 459 (100), 895 (46); HRMS (ESI) obsd 459.1565 (MNa^+) calcd 459.1567.

4.40. (S_a,*S*/R_p)-6-Methyl-3,3′-diethynyl-2,2′-diyl 1-pyrrolidylphosphonite (37a) and (S_a,*R*/S_p)-6-methyl-3,3′-diethynyl-2,2′-diyl 1-pyrrolidylphosphonite (37b)

Phosphorus trichloride (125 μL, 1.43×10^{-4} mol) was added to a stirred solution of **36** (50 mg, 1.4 mol) in toluene (5 mL) and the reaction mixture was heated under gentle reflux for 5 h. The mixture

was cooled to 0 °C and pyrrolidine (0.60 mL, 7.3 mmol) was added slowly. The mixture was stirred at 0 °C for 15 min, then allowed to warm to room temperature and stirred for a further 1 h. The reaction mixture was poured onto saturated aqueous ammonium chloride (80 mL) and the resulting mixture extracted with ethyl acetate (3×30 mL). The combined organic extracts were washed with saturated aqueous ammonium chloride (100 mL), water (100 mL), were dried over anhydrous sodium sulfate and the solvent was evaporated. Flash column chromatography (ethyl acetate/hexanes: 1/5) gave a 1:1 mixture of **37a** and **37b** (40 mg, 62%) as a colourless solid; mp decomposes>150 °C; R_f 0.32 (ethyl acetate/hexanes: 1/5); IR (neat) ν_{max}/cm^{-1} 2923, 2365, 1730, 1418, 1238, 1206, 1077, 869; ^{1}H NMR (300 MHz; $CDCl_3$) 8.20 (1H, s), 8.15 (1H, s), 8.11 (1H, s), 8.06 (1H, s), 7.86 (2H, d, *J* 8.4), 7.63 (2H, br s), 7.38–7.45 (2H, m), 7.19–7.34 (6H, m), 7.06–7.14 (4H, m), 3.37 (1H, s), 3.36 (1H, s), 3.31 (1H, s), 3.30 (1H, s), 3.18–3.25 (4H, m), 2.86–2.90 (4H, m), 2.45 (3H, s), 2.44 (3H, s), 1.68–1.77 (8H, m); ^{13}C NMR (100 MHz; $CDCl_3$) 150.5 (C, d, $^2J_{C-P}$ 4.0), 149.9 (C, d, $^2J_{C-P}$ 4.0), 149.7 (C, d, $^2J_{C-P}$ 2.0), 149.0 (C, d, $^2J_{C-P}$ 2.0), 135.2 (C), 135.0 (C), 135.0 (CH), 134.7 (CH), 134.6 (CH), 134.4 (CH), 134.0 (CH), 132.8 (C, d, $^3J_{C-P}$ 1.5), 132.7 (C, d, $^3J_{C-P}$ 0.5), 131.0 (C, d, $^3J_{C-P}$ 2.0), 130.9 (C, d, $^3J_{C-P}$ 0.5), 130.8 (C), 130.6 (C), 130.3 (C), 130.0 (C), 129.5 (CH), 129.5 (CH), 128.3 (CH), 128.2 (CH), 127.2 (CH), 127.2 (CH), 127.1 (CH), 127.1 (CH), 126.9 (CH), 126.9 (CH), 126.7 (CH), 126.7 (CH), 125.5 (CH), 125.3 (CH), 124.6 (C), 124.5 (C), 124.3 (C), 124.2 (C), 123.4 (C), 123.4 (C), 123.2 (C), 123.1 (C), 116.2 (C), 116.1 (C), 82.0 (CH), 81.8 (CH), 81.0 (CH), 80.8 (CH), 80.6 (CH), 80.5 (CH), 79.9 (CH), 45.7 (4C, d, $^2J_{C-P}$ 16.1), 25.9 (4C, d, $^3J_{C-P}$ 5.3), 21.5 (2C, CH_3); HRMS (ESI) obsd 448.1466 (MH^+) calcd 448.1461.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2011.11.020. These data include MOL files and InChiKeys of the most important compounds described in this article.

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