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P-chirogenic phosphines. MOP/diPAMP hybrids, their oxide crystal structures, reduction studies and alternative syntheses

Lee J. Higham *,[1], Eoin F. Clarke, Helge Müller-Bunz, Declan G. Gilheany *

Chemistry Department, Conway Institute of Biomolecular and Biomedical Sciences, The Centre for Synthesis and Chemical Biology, University College Dublin, Belfield, Dublin 4, Ireland

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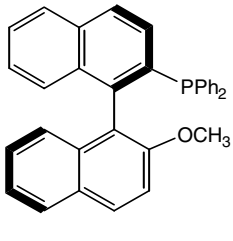
Abstract

The novel P-chirogenic anisylphenylMOP derivatives (*R*,*R*) and (*R*,*S*)-2-(anisylphenylphosphino)-2′-methoxy-1,1′-binaphthyl (**10a** and **b**) have been synthesized and their corresponding oxides characterised by X-ray crystallography. The results of a parallel screening regimen with various reducing agents highlight the sensitivity of the tertiary phosphine oxides to epimerisation and, interestingly, reveal that the P=O, O–CH_3 and P–C_6H_5 bonds can all be cleaved selectively depending on the reducing agents employed. An alternative synthesis was provided by direct coupling of the secondary phosphine with (*R*)-methoxytriflate **4**, which led to the isolation of the optically pure P-chirogenic phosphines via their borane adducts. A brief study of the coordination chemistry of **10a** with different rhodium precursors, relevant to the catalytic asymmetric addition of boronic acids to aldehydes is also reported.

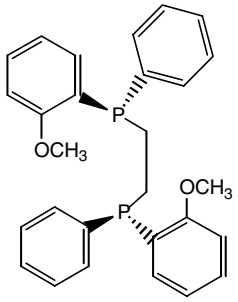
Keywords: Monophosphine; Asymmetric; Chirogenic; Synthesis and characterisation

1. Introduction

Hayashi's MOP ligand, built around the binaphthyl backbone, has been highly successful in a variety of asymmetric transformations [1]. In certain cases it is desirable to improve still further its propensity for chiral induction [2]. One potential method of achieving this is to incorporate additional chirality at the phosphorus centre. In a recent study, Lipkowitz et al. [3] have shown the potential of such an approach when they demonstrated that, in most cases in their best catalysts, the regions of maximum stereoinduction by the ligands were near the site of the chemistry. For the particular case of phosphorus ligands, Crépy and Imamoto, in a recent review [4] provide many examples where the use of P-chirogenic phosphorus ligands is superior to those with chirality located in the ligand backbone. They surmised that this was because of the potentially more inefficient secondary transfer of chirality from the ligand backbone compared to that from P-chirality. P-chirogenic ligands are not necessarily better per se at a given catalytic procedure, but manipulation of the phosphorus in this manner provides a powerful tool in the search for improved enantioselection.



(*R*)-**MOP**



(*R*,*R*)-**diPAMP**

* Corresponding authors. Tel.: +35317162316; fax: +35317162308.
E-mail addresses: leehigham@eircom.net (L.J. Higham), declan.gilheany@ucd.ie (D.G. Gilheany).
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Our choice of substituents on the phosphorus was guided by our desire to prepare a hybrid MOP/DiPAMP monophosphine, in view of the acknowledged success of the latter P-chirogenic bisphosphine [5]. Hence we report here our successful synthesis of the chiral-at-phosphorus, diastereomeric monophosphines (*R*,*R*) and (*R*,*S*)-2-(anisylphenylphosphino)-2′-methoxy-1,1′-binaphthyl; the anisylphenylMOPs **10a** and **b**.

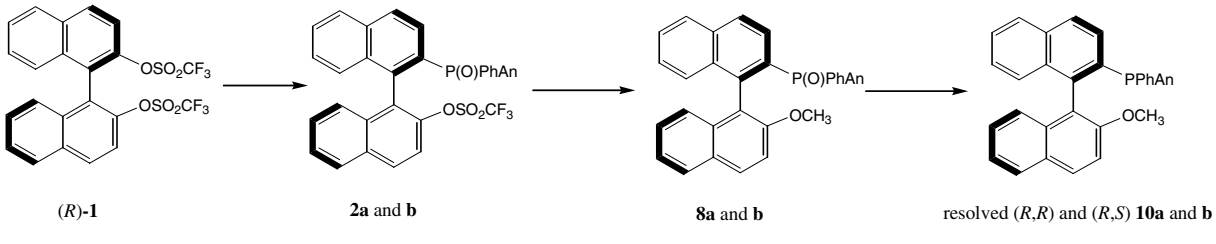
2. Results and discussion

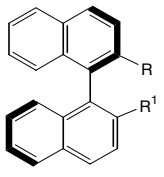
The standard route to MOP ligands involves the coupling of a single diphenylphosphine oxide unit to (*R*) or (*S*)-2,2′-bis(trifluoromethanesulfonyloxy)-1,1′-binaphthyl, followed by treatment with sodium hydroxide, methyl iodide/potassium carbonate and finally trichlorosilane/triethylamine reduction to yield the phosphine [6]. We prepared the diastereomeric anisylphenylMOP oxides **8** following this route (Scheme 1) using anisylphenylphosphine oxide via, in turn, phosphinyloxy triflates **2** and alcohols **3**. Frustratingly we found that **8a** and **b** could not be separated. However we were able to separate the triflates **2a** and **b** by column chromatography and take these through, via the alcohols **3a** and **b**, to the optically pure oxides **8a** and **b**. Recrystallisation of **8a** and **b** gave crystals suitable for an X-ray crystallographic study and the structures are given for comparison in Fig. 1. The pertinent bond lengths and angles are collected in Table 1, and the crystallographic parameters are summarised in Table 2.

It was also a goal of ours to prepare quantities of the potentially useful methoxy triflate **4**, which is more suited to our parallel synthesis work in that it would allow the rapid screening of coupling reactions with a number of chiral racemic secondary phosphine oxides/phosphines. The reported route [7] to compound **4**, is via the mono-methylation of resolved binol (we have recently improved this resolution [8]), to give the methoxy alcohol **5**, followed by treatment with trifluoromethanesulfonic anhydride. We encountered problems in following this because we often found small quantities of the dimethoxy compound **6**, which was tedious to remove. A more convenient procedure was to instead prepare the monotriflate alcohol **7** [9] from resolved binol and the mild triflating reagent *N*-phenyl trifluoromethanesulfonimide. Treating **7** with methyl iodide and sodium hydroxide routinely afforded **4** in good yield.

For the synthesis of the anisylphenylMOP phosphines, our first approach was to investigate the reduction of a 50:50 mixture of the diastereomeric phosphine oxides **8**. Our studies revealed that the reductions gave products that are highly dependent on the reducing agent employed Scheme 2. Thus, upon treatment of the mixture **8** with lithium aluminium hydride in THF we found that reduction took place accompanied by cleavage of the phenyl group. The ^{31}P NMR spectrum was consistent with the formation of the racemic secondary phosphines (*R*,*R*) and (*R*,*S*)-anisylMOP **9a** and **b**, on account of the chemical shifts and doublet splittings observed for both peaks in the ^{31}P–^{1}H coupled spectrum (δ −47.3 ppm, $^{1}J_{P-H}$ = 219.5 Hz; δ −47.7 ppm, $^{1}J_{P-H}$ = 218.6 Hz) and the parent ion in the mass spectrum, which indicated the phenyl group was cleaved. The two distinct resonances indicate that epimerisation does not occur at room temperature in the absence of acid. Work-ups involving the addition of aqueous acid to the reaction solution cause the signals to broaden, indicative of acid-catalysed epimerisation. The formation of **9a** and **b** should allow for unusual MOP derivatives to be prepared by hydrophosphination of unsaturated compounds across the reactive P–H bond.

In contrast, when hexachlorodisilane in acetonitrile was used to reduce the phosphine oxide functionality, we observed only cleavage of the ether methyl–oxygen bond, to produce the phosphine oxide alcohols **3a** and





2: R=AnPhP(O), R^1=OSO_2CF_3
3: R=AnPhP(O), R^1=OH
4: R=OSO_2CF_3, R^1=OCH_3
5: R=OH, R^1=OCH_3
6: R=OCH_3, R^1=OCH_3
7: R=OSO_2CF_3, R^1=OH

Scheme 1. Planned synthetic route to (*R*,*R*) and (*R*,*S*) anisylphenylMOP (**10a** and **b**).

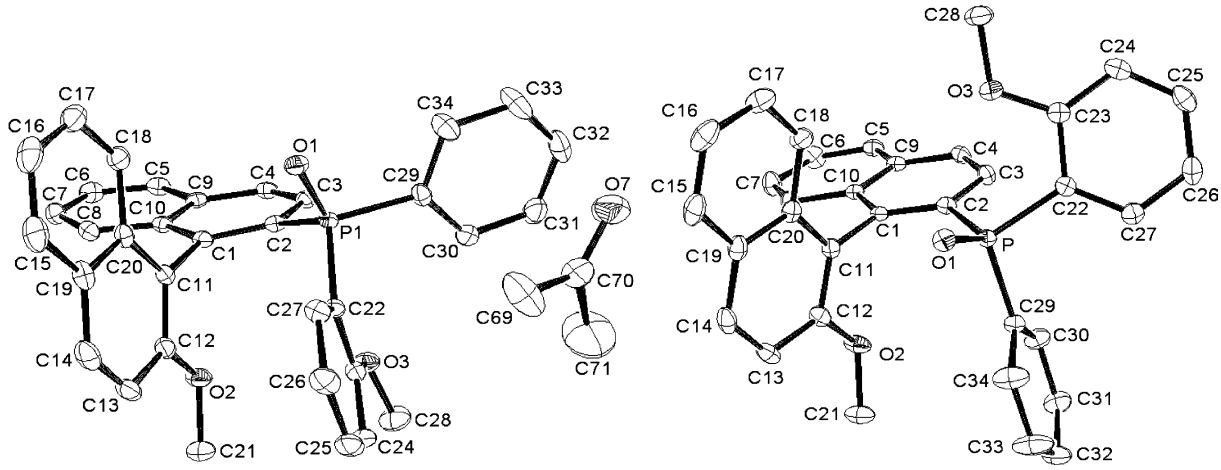


Fig. 1. The crystal structures of (*R*,*R*)-and (*R*,*S*)-anisylphenylMOP oxides **8a** and **b**.

Table 1
Bond distances (Å) and angles (°) for (*R*,*R*) and (*R*,*S*) anisylphenylMOP oxides (**8a** and **b**)

	8a · acetone	**8b**
Bond lengths (Å)		
P(1)–O(1)	1.4890(10)	1.4842(10)
P(1)–C(2)	1.8138(13)	1.8200(13)
P(1)–C(22)	1.8050(13)	1.8117(14)
P(1)–C(29)	1.8167(13)	1.8088(14)
C(12)–O(2)	1.3653(17)	1.3665(18)
C(23)–O(3)	1.3613(17)	1.3541(18)
O(2)–C(21)	1.4258(18)	1.4317(17)
O(3)–C(28)	1.4260(18)	1.4289(18)
Bond angles (°)		
O(1)–P(1)–C(2)	110.62(6)	117.51(6)
O(1)–P(1)–C(22)	109.40(6)	113.58(6)
O(1)–P(1)–C(29)	109.58 (6)	110.59(6)
C(12)–O(2)–C(21)	118.68(12)	118.44(11)
C(23)–O(3)–C(28)	117.70(12)	118.14(12)

b. Reduction to phosphine could be achieved with the mild reducing agent phenylsilane, which has been used successfully in the past to reduce P-chirogenic groups whilst retaining the optical integrity of the compound [10]. In a test study, neat phenylsilane slowly reduced a diastereomeric mixture of the oxides to the phosphines **10a** and **b**, over 3 days at 80 °C. However when the reaction was carried out on an optically pure sample, epimerisation occurred even when the reduction was still incomplete. Finally, when **8a** was treated overnight with trichlorosilane (10 mole equivalents) in benzene at room temperature, full reduction to phosphine occurred but there was still significant epimerisation (18%).

As a result of the difficulties associated with the reduction of the phosphine oxides, we sought an alternative route to the optically pure phosphines **10a** and **b**. We noted that they were separable (with difficulty) by chromatography and so we adapted the general Merck procedure of coupling secondary phosphines to aryl triflates [11] by reacting (*R*)-methoxy triflate **4** with racemic anisylphenylphosphine [12] Scheme 3.

In the coupling step, we noted an asymmetric induction effect in favour of one of the phosphines **10a/b** (~60/40) in the ^{31}P NMR spectra. The reaction proceeds reasonably cleanly and pure **10a** could be easily obtained by column chromatography (ethyl acetate:pentane, 50:1). The isolation of **10b** by this route was more problematic and therefore we opted instead to convert diastereomeric mixtures of **10a** and **b** to the corresponding boranes (see Section 4). The separation of the boranes is more facile and was accomplished by column chromatography (ethyl acetate:cyclohexane, 1:19). The subsequent deprotection step was sensitive to the reaction conditions; for instance epimerisation occurred at 50 °C overnight with diethylamine as the base. However, using trifluoromethanesulphonic acid in a procedure similar to that of McKinstry and Livinghouse [13], deprotection of both **11a** and **b** occurred without loss of optical integrity to give **10a** and **b**.

In order to assign the configuration of **10a** and **b**, oxidation of the phosphines with hydrogen peroxide – a reaction known to proceed with retention [14] – was carried out. We found that **10a** was oxidized cleanly (in *d*-chloroform at room temperature) by this reagent to the oxide **8b** (*R*,*S*) and hence, according to convention, **10a** has the corresponding *R*,*R* configuration. In other words **10a** is related to **8b** by a process of oxidation with retention of configuration [15].

The rhodium coordination chemistry of the anisylphenylMOPs was briefly investigated by reacting **10a** with $[Rh_2Cl_2(CO)_4]$ in dichloromethane at room temperature, and the product was found to be *cis*-[RhCl(CO)(**10a**-anisylphenylMOP)] **12a** by ^{31}P NMR and mass spectroscopy. In addition, and as a prelude to our catalytic studies on the rhodium-catalysed addition of boronic acids to aldehydes [2a] (Scheme 4), we reacted a diastereomeric mixture (1:1) of **10a** and **b** with $[Rh(acac)(C_2H_4)_2]$ (1:1, Rh:P) in an attempt to form [Rh(acac)(**10**)] complexes. We found two major products in the ^{31}P NMR spectrum in d-chloroform; two

Table 2
Crystal data for (*R*,*R*) and (*R*,*S*) anisylphenylMOP oxides (**8a** and **b**)

Crystal	[**8a**] · acetone	[**8b**]
Formula	$C_{34}H_{27}O_3P \cdot C_3H_6O$	$C_{34}H_{27}O_3P$
Colour, habit	Colourless block	Colourless block
Temperature (K)	100(2)	100(2)
λ of Mo Kα radiation	0.71073	0.71073
Formula weight	572.60	514.53
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1$	$P2_12_12_1$
Unit cell dimensions		
a (Å)	12.5476(11)	8.0294(7)
b (Å)	15.7599(14)	16.4643(14)
c (Å)	15.8394(14)	19.7512(17)
α (°)	90.00	90.00
β (°)	108.5100(10)	90.00
γ (°)	90.00	90.00
Volume (Å^3)	2970.2(5)	2611.1(4)
Z	4	4
Density (calculated) (mg/m^3)	1.281	1.309
Absorption coefficient (mm^{-1})	0.133	0.140
Crystal size (mm^3)	$0.70 \times 0.70 \times 0.50$	$0.60 \times 0.50 \times 0.50$
Reflections collected	51 368	22 518
Independent reflections (R_{int})	14 014 (0.0237)	6184 (0.0209)
Absorption correction	Multiscan	Multiscan
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.034	1.061
Final R indices [$I>2\sigma(I)$]	$R_1 = 0.0337$ $wR_2 = 0.0838$	$R_1 = 0.0345$ $wR_2 = 0.0875$
R indices (all data)	$R_1 = 0.0355$ $wR_2 = 0.0851$	$R_1 = 0.0351$ $wR_2 = 0.0881$

broad overlapping doublets (δ 47.3 ppm, $^1J_{Rh-P} \sim 189$ Hz; δ 45.7 ppm, $^1J_{Rh-P} \sim 182$ Hz) tentatively assigned to [Rh(acac)(**10a/b**)], together with some minor resonances characteristic of Rh complexes of a higher oxidation state. The coordination chemistry of MOP itself has come under scrutiny recently as it ligates in unusual modes to a number of palladium centres [16]. It is noteworthy that there is no reaction of **10a** with [Rh(acac)(η^4-cod)] as the rhodium precursor, implying these MOP ligands do not bind strongly enough to displace the bidentate cyclooctadiene ligand from the metal center. The nature of the rhodium precursors and the resultant phosphine complexes have been shown to be critical in the asymmetric addition of phenylboronic acid to 2-cyclohexenone [17]. The ramifications of the coordination chemistry with regard to the catalysis and the catalytic results themselves will be the subject of a forthcoming report.

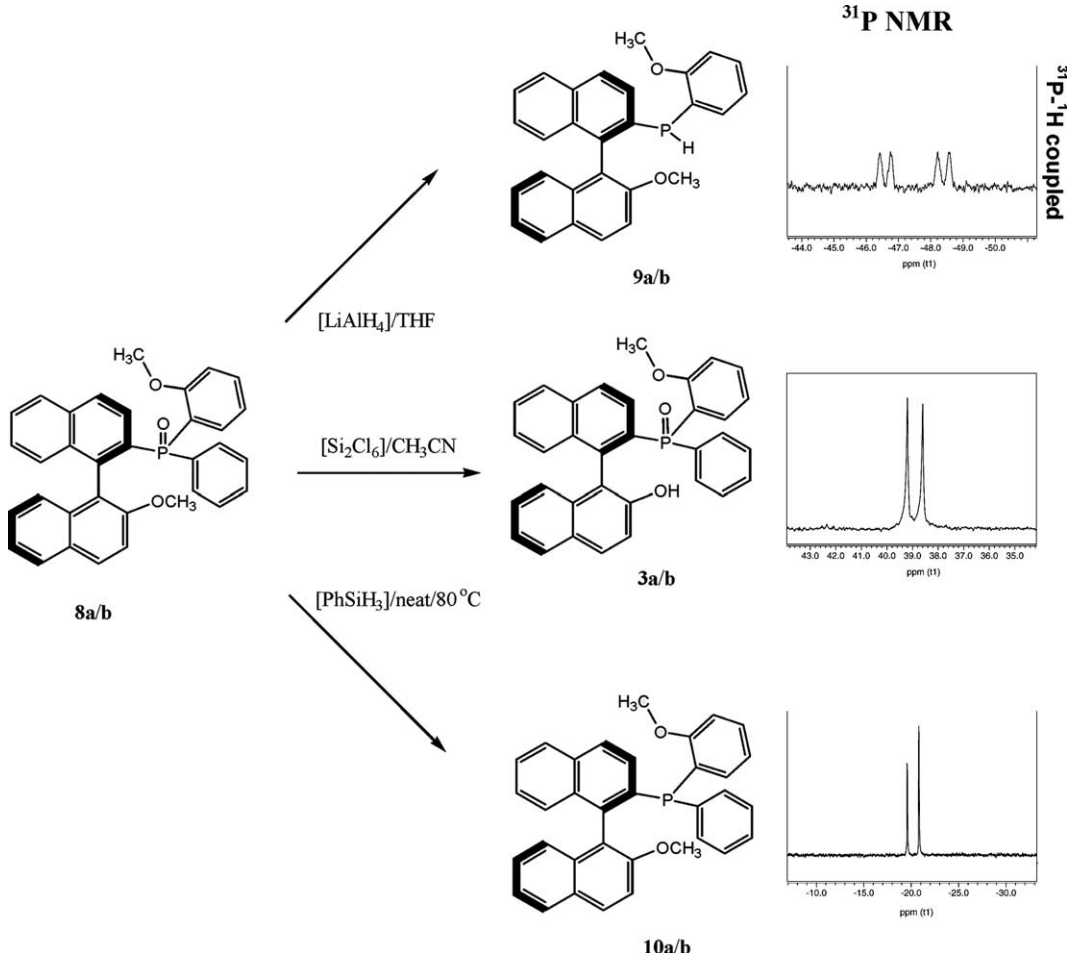
3. Conclusion

Two diastereomeric anisylphenylMOP oxides (**8a** and **b**) have been prepared and characterized. A variety of reducing agents were employed on them and the reactions demonstrate that the chemistry is highly reagent-specific, the highlight being the formation of a secondary anisylnaphthylphosphine when lithium aluminium hydride was used as the reductant. In an alternative approach we reacted anisylphenylphosphine with the methoxy triflate intermediate **4**, which we synthesized by an improved route to that reported. From the diastereomeric mixture we prepared the corresponding boranes **11a** and **b**, and following separation by column chromatography and deprotection, we isolated the optically pure diastereomeric phosphines **10a** and **b**. The coordination chemistry with rhodium was explored with a view to utilizing the complexes in the asymmetric addition of boronic acids to aldehydes.

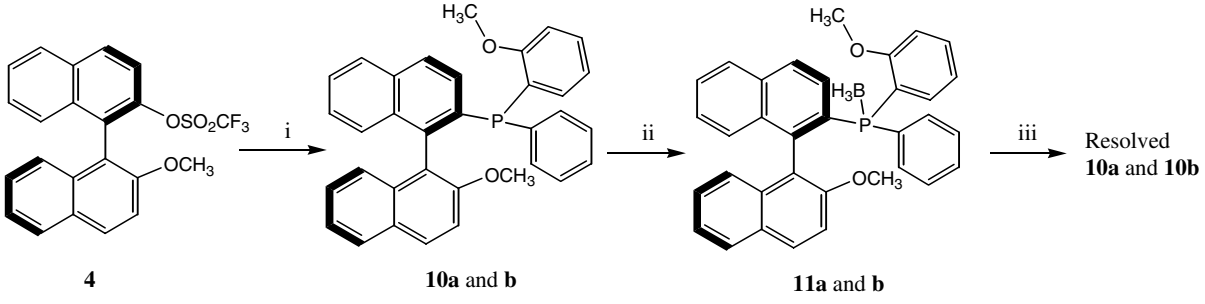
4. Experimental

4.1. General methods

All operations were carried out under a N_2 atmosphere using standard Schlenk-line techniques. Solvents were dried according to standard procedures [18] although DMF and DMSO were purchased in an anhydrous state from Aldrich and purged with N_2 before use. Bis(diphenylphosphino)butane (dppb), [1,2-bis(diphenylphosphino)ethane]dichloronickel(II), borane–THF complex (1.0 M in THF), diazabicyclo[2.2.2]octane (DABCO), *N*,*N*-diisopropylethylamine, hexachlorodisilane, lithium aluminium hydride (1.0 M solution in THF), methyl iodide, palladium(II) acetate, phenylsi-



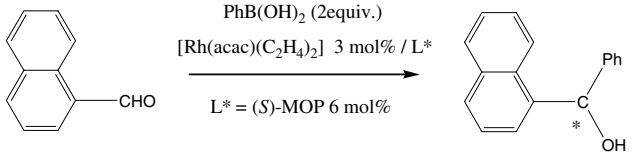
Scheme 2. The reduction of the phosphine oxides **8a** and **b** with a variety of reagents.



i). $[NiCl_2(dppe)]$/DMSO/AnPhPH/100 °C ii). BH_3.THF iii). Column separation of diastereomers then treat with CF_3SO_2H/-5 °C

Scheme 3. Actual synthetic route to (*R*,*R*) and (*R*,*S*) anisylphenylMOP (**10a** and **b**).

lane, *N*-phenyl trifluoromethanesulfonimide, trichlorosilane, triethylamine, trifluoromethanesulfonic acid and trifluoromethanesulfonic anhydride were purchased from Aldrich. Silica gel 60 (0.040–0.063 mm) was purchased from Merck. Anisylphenylphosphine was prepared according to the literature method [12]. $[Rh_2Cl_2(CO)_4]$ [19], $[Rh(acac)(C_2H_4)_2]$ [20] and [Rh(acac)(η^4-cod)] [21] were prepared according to the known procedures. The d-chloroform was purged with N_2 and stored over molecular sieves. The NMR spectra were recorded at 25 °C on a Varian Unity 300 MHz spectrometer with chemical shifts relative to tetramethylsilane for ^1H and ^{13}C spectra and 85% H_3PO_4 for ^{31}P spectra. IR spectra (KBr) were recorded on a Mattson Instruments Galaxy Series FTIR3000 spectrophotometer. Elemental analyses and mass spectra were carried out at UCD. Melting point measurements were carried out on a Reichert thermovar instrument.



Scheme 4. The catalytic asymmetric addition of phenylboronic acid to naphthaldehyde.

4.2. Synthesis of anisylphenylphosphine oxide

Anisylphenylphosphine oxide was synthesized by simple air oxidation of the neat phosphine (2 g, 8.6 mmol) over 2 weeks in the fume cupboard. Over this time the oily solid which formed was broken-up with a spatula to prevent the formation of a crust, which otherwise traps secondary phosphine underneath. Using these conditions we observed no over-oxidation to the P(V) acid. Yield was quantitative. ^{31}P NMR (121 MHz, $CDCl_3$): δ 18.89 ppm ($^1J_{P-H}$ = 500.1 Hz).

4.3. Synthesis of (R,R) and (R,S)-2-(anisylphenylphosphinyl)-2′-((trifluoromethanesulfonyl)oxy)-1,1′-binaphthyl (**2a** and **b**)

A mixture of (*R*)-2,2′-bis(trifluoromethanesulfonyloxy)-1,1′-binaphthyl **1** (2.72 g, 4.94 mmol), anisylphenylphosphine oxide (2.31 g, 9.95 mmol), palladium diacetate (56.0 mg, 0.249 mmol), 1,4-bis(diphenylphosphino)butane (dppb) (106.0 mg, 0.249 mmol), and anhydrous diisopropylethylamine (2.56 g, 19.8 mmol) in dry degassed dimethylsulfoxide (30 cm^3) were heated at 100–110 °C for 16 h. After this time TLC analysis (ethyl acetate/hexane 1:1) indicated that the binaphthyl triflate reactant had been consumed. The mixture had changed from its initial deep red colour to a dark brown. After cooling to room temperature, the mixture was concentrated under reduced pressure to yield a brown residue, which was diluted with ethyl acetate (250 cm^3). The resultant pink precipitate was filtered and recrystallised from ethyl acetate to give 0.906 g of white crystals (60% based on one diastereomer) of **2b**. The remaining solution of crude product was washed with water (2 × 150 cm^3) and dried over magnesium sulphate. The mixture was filtered and concentrated under reduced pressure, yielding a light brown solid (3.24 g). This crude mixture was chromatographed on silica gel (pentane:ethyl acetate, 2:1) to yield 0.88 g (58% based on one diastereomer) of **2a**.

4.3.1. (R,R)-AnPhMOP(O)OSO_2CF_3 (**2a**)

$[\alpha]_D$ = 35.0 (c 0.43, $CHCl_3$); IR (KBr, cm^{-1}) 3060, 2937, 2839, 1589, 1478, 1432, 1209, 1140; ^{1}H (300 MHz, $CDCl_3$) δ 7.97–7.84 (m, 4H, Ar*H*), 7.70–7.15 (m, 14H, Ar*H*), 7.05 (m, 1H, Ar*H*), 6.97–6.81 (m, 2H, Ar*H*), 3.55 (s, 3H, OCH_3); ^{13}C (75 MHz, $CDCl_3$) δ 160.7–110.9 (multiple signals, Ar*C* and *C*F_3), 54.9 (O*C*H_3); ^{31}P (121 MHz, $CDCl_3$) δ 30.78; *m*/*z* (% intensity): $[MH]^+$ 633.0 (100); HRMS Calc. for $[MH]^+$ ($C_{34}H_{25}O_5F_3SP$): 633.1112, Found: 633.1117%.

4.3.2. (R,S)-AnPhMOP(O)OSO_2CF_3 (**2b**)

m.p. 285–289 °C; $[\alpha]_D$ = 59.0 (c 0.40, $CHCl_3$); (Found: C, 64.72; H, 4.00. $C_{34}H_{24}F_3O_5PS$ requires C, 64.55; H, 3.82%.); IR (KBr, cm^{-1}) 3066, 2940, 2839, 1589, 1477, 1401, 1214, 1154; ^{1}H (300 MHz, $CDCl_3$) δ 7.97–7.79 (m, 4H, Ar*H*), 7.66–7.52 (m, 4H, Ar*H*), 7.42–7.08 (m, 10H, Ar*H*), 6.95 (m, 1H, Ar*H*), 6.71–6.65 (m, 2H, Ar*H*), 3.51 (s, 3H, OCH_3); ^{13}C (75 MHz, $CDCl_3$) δ 159.9–110.7 (multiple signals, Ar*C* and *C*F_3), 55.0 (O*C*H_3); ^{31}P (121 MHz, $CDCl_3$) δ 30.46; *m*/*z* (% intensity): [MH$^+$] 633.1 (100); HRMS Calc. for $[MH]^+$ ($C_{34}H_{25}O_5F_3SP$) 633.1112. Found: 633.1101%.

4.4. Synthesis of (R,R) and (R,S)-2-(anisylphenylphosphinyl)-2′-hydroxy-1,1′-binaphthyl (**3a** and **b**). Both diastereomers are prepared in the same manner

To a solution of AnPhMOP(O)OSO_2CF_3 (300 mg, 0.474 mmol) in a 2:1 mixture of 1,4-dioxane and methanol (15 cm^3) was added 3N aqueous sodium hydroxide (0.51 cm^3, 1.54 mmol) at room temperature. The yellow solution was stirred for 2 days. The mixture was then acidified by the addition of conc. HCl until the pH had reached around 1.5. The now clear solution was extracted with dichloromethane (3 × 10 cm^3), dried over magnesium sulphate, and concentrated under reduced pressure to yield an off-white solid (220 mg, 93%).

4.4.1. (R,R)-AnPhMOP(O)OH (**3a**)

m.p. 247–252 °C; $[\alpha]_D$ = −111.7 (c 0.30, $CHCl_3$); IR (KBr, cm^{-1}) 3058, 2955, 2850, 2360, 1589, 1434, 1275, 1133; ^{1}H (300 MHz, $CDCl_3$) δ 8.05–7.98 (m, 1H, Ar*H*), 7.93–7.88 (m, 2H, Ar*H*), 7.60–7.08 (m, 12H, Ar*H*), 7.09–6.94 (m, 2H, Ar*H*), 6.80–6.74 (m, 1H, Ar*H*), 6.64–6.58 (m, 3H, Ar*H*), 3.74 (s, 3H, OCH_3); ^{13}C (75 MHz, $CDCl_3$) δ 160.3, 153.7, 140.6–111.1 (multiple signals, Ar*C*), 55.2 (O*C*H_3); ^{31}P (121 MHz, $CDCl_3$) δ 35.90; m.p. 247–252 °C; *m*/*z* (% intensity): $[MH]^+$ 501.2 (100); HRMS Calc. for $[MH]^+$ ($C_{33}H_{26}O_3P$) 501.1620. Found: 501.1626%.

4.4.2. (R,S)-AnPhMOP(O)OH (**3b**)

m.p. 242–246 °C; $[\alpha]_D$ = 55.0 (c 0.30, $CHCl_3$); IR (KBr, cm^{-1}) 3053, 2932, 2853, 2360, 1590, 1435, 1274, 1130, 748, 694; ^{1}H (300 MHz, $CDCl_3$) δ 8.03–7.87 (m, 4H, Ar*H*), 7.61–7.04 (m, 14H, Ar*H*), 6.91–6.75 (m, 2H, Ar*H*), 6.41–6.36 (m, 2H, Ar*H*), 6.07–6.02 (m, 1H, Ar*H*), 3.46 (s, 3H, OCH_3); ^{13}C (75 MHz, $CDCl_3$) δ 158.5, 153.5, 139.7, 109.2 (multiple signals, Ar*C*), 54.2 (O*C*H_3); ^{31}P (121 MHz,$CDCl_3$) δ 35.49; *m*/*z* (% inten-

sity): $[MH]^+$ 501.2 (100); HRMS Calc. for $[MH]^+$ ($C_{33}H_{26}O_3P$) 501.1620. Found: 501.1618%.

4.5. Synthesis of (R)-2-((trifluoromethanesulfonyl)oxy)-2′-methoxy-1,1′-binaphthyl (**4**) from (**7**)

To a solution of (*R*)-2-((trifluoromethanesulfonyl)oxy)-2′-hydroxy-1,1′-binaphthyl (4.64 g, 11.1 mmol) in acetone (40 cm^3) was added potassium carbonate (2.30 g, 16.6 mmol) and methyl iodide (1.04 cm^3, 16.7 mmol). The mixture was stirred for 24 h by which time TLC analysis (silica, dichloromethane:pentane, 3:1) showed the reaction to be complete. After removal of solvent, 10% HCl was added until the pH of the solution was approximately 3. The product was extracted with ethyl acetate (2×75 cm^3), washed with water and brine, and dried over magnesium sulphate. Removal of solvent yielded a brown oil (4.85 g) which was recrystallised from ethanol/water to yield white needles (3.06 g, 64%). A further crop of crystals was recovered from the mother liquor after standing for a few days. m.p. 99–101 °C; ^1H (300 MHz, $CDCl_3$) δ 8.05 (m, 1H, Ar*H*), 8.02 (m, 1H, Ar*H*), 7.97 (m, 1H, Ar*H*), 7.88 (m, 1H, Ar*H*), 7.57–7.22 (m, 7H, Ar*H*), 7.00 (m, 1H, Ar*H*), 3.82 (s, 3H, OCH_3).

4.6. Synthesis of (R,R) and (R,S)-2-(anisylphenylphosphinyl)-2′-methoxy-1,1′-binaphthyl (**8a** and **b**). Both diastereomers are prepared in the same manner

To AnPhMOP(O)OH (**3a**) (480 mg, 0.960 mmol) and potassium carbonate (528 mg, 3.83 mmol) in anhydrous acetone (15 cm^3) was added methyl iodide (0.240 mL, 3.83 mmol). The mixture was refluxed overnight, and then cooled to room temperature, at which point some of the product precipitated out of solution. Dichloromethane (50 cm^3) was added to redissolve the precipitate and the solution was filtered through celite. Removal of the solvent *in vacuo* and recrystallisation from acetone yielded white crystals (520 mg, 75%).

4.6.1. (R,R)-AnPhMOP(O)OMe (**8a**)

m.p. 211–216 °C; $[\alpha]_D = -41.9$ (c 0.25, $CHCl_3$); IR (KBr, cm^{-1}) 3060, 2938, 2836, 2361, 1589, 1477, 1271, 1182, 1080, 732; ^1H (300 MHz, $CDCl_3$) δ 7.89 (m, 2H, Ar*H*), 7.80–7.74 (m, 1H, Ar*H*), 7.67–7.60 (m, 2H, Ar*H*), 7.51–7.45 (m, 3H, Ar*H*), 7.34–6.99 (m, 10H, Ar*H*), 6.86–6.77 (m, 2H, Ar*H*), 6.69–6.65 (m, 1H, Ar*H*), 3.57 (s, 3H, OCH_3), 3.44 (s, 3H, OCH_3); ^{13}C (126 MHz, $CDCl_3$) δ 160.7–111.0 (multiple P-coupled signals, Ar*C*), 56.0 (O*C*H_3), 55.2 (O*C*H_3); ^{31}P (121 MHz, $CDCl_3$) δ 26.9; *m/z* (% intensity): $[MH]^+$ 515.2 (100); HRMS Calc. for $[MH]^+$ ($C_{34}H_{28}O_3P$) 515.1776. Found: 515.1785%.

4.6.2. (R,S)-AnPhMOP(O)OMe (**8b**)

m.p. > 230 °C; $[\alpha]_D = 22.1$ (c 0.41, $CHCl_3$); IR (KBr, cm^{-1}) 2797, 2363, 1590, 1477, 1283, 1195, 803, 644; ^1H (300 MHz, $CDCl_3$) δ 7.90 (m, 2H, Ar*H*), 7.78–7.47 (m, 6H, Ar*H*), 7.31–7.10 (m, 9H, Ar*H*), 6.97 (m, 1H, Ar*H*), 6.73 (m, 1H, Ar*H*), 6.65 (m, 1H, Ar*H*), 6.40 (m, 1H, Ar*H*), 3.67 (s, 3H, OCH_3), 3.39 (s, 3H, OCH_3); ^{13}C (75 MHz, $CDCl_3$) δ 159.7–110.4 (multiple P-coupled signals, Ar*C*), 56.1 (O*C*H_3), 54.7 (O*C*H_3); ^{31}P (121 MHz, $CDCl_3$) δ 26.1; *m/z* (% intensity): $[MH]^+$ 515.2 (100); HRMS Calc. for $[MH]^+$ ($C_{34}H_{28}O_3P$) 515.1776. Found: 515.1765%.

4.7. Synthesis of (R,R) and (R,S)-2-(anisylphenylphosphino)-2′-methoxy-1,1′-binaphthyl (**10a** and **b**)

To a solution of $[NiCl_2(dppe)]$ (0.183 g, 0.347 mmol) in DMF (6.5 cm^3) was added anisylphenylphosphine (0.48 g, 2.08 mmol) via a syringe. After heating at 100 °C for 0.5 h, a solution of (*R*)-2-((trifluoromethanesulfonyl)oxy)-2′-methoxy-1,1′-binaphthyl (1.5 g, 3.47 mmol) and DABCO (1.56 g, 13.9 mmol) in DMF (10 cm^3) was added, causing an immediate colour change from red to green. After 1 h a further 0.48 g (2.08 mmol) of the secondary phosphine was added. The temperature was maintained at 100 °C for 2 days, after which a colour change to light brown was apparent. ^{31}P NMR of the solution at this point revealed that the major components (81% conversion by NMR) were the desired diastereomers **10a** and **b**.

The volatiles were removed *in vacuo* on a warm water bath and THF added (40 cm^3). The mixture was treated with an excess (20 cm^3, 20 mmol) of 1 M borane–THF complex to give the corresponding borane adducts. These were separated from the rest of the reaction mixture by employing a silica column with dichloromethane as eluent, followed by a second column to separate **10a** from **10b**. A sample second column (ethyl acetate:cyclohexane, 1:19) loaded with 253 mg of an approximate 1:1 mixture of the boranes yielded 52 mg (21%) of **10a** in the first fraction, a fraction containing a mixture of the boranes and a second fraction containing 63 mg (25%) of **10b**. The column procedure can be repeated on the middle fraction to give further quantities of both boranes.

4.7.1. (R,R)-AnPhMOP · BH_3 (**11a**)

^1H (300 MHz, $CDCl_3$) δ 7.90–6.59 (m, 21H, Ar*H*), 3.40 (s, 3H, OCH_3), 3.33 (s, 3H, OCH_3); ^{31}P (121 MHz, $CDCl_3$) δ 19.3.

4.7.2. (R,S)-AnPhMOP · BH_3 (**11b**)

^1H (300 MHz, $CDCl_3$) δ 7.90–6.62 (m, 21H, Ar*H*), 3.57 (s, 3H, OCH_3), 3.46 (s, 3H, OCH_3); ^{31}P (121 MHz, $CDCl_3$) δ 19.4.

10a from borane deprotection of **11a** (**10b** is produced in identical fashion from **11b**).

To a dichloromethane solution (1 cm^3) of **11a** (30 mg, 0.0586 mmol) on a sodium chloride/water bath, was added dropwise 10 equivalents of trifluoromethanesulphonic acid (88 mg, 0.586 mmol). Effervescence was observed, after which the cooling bath was removed. ^{31}P NMR showed that quantitative deprotection had taken place without epimerisation. The reaction was worked up by diluting with dichloromethane (2 cm^3) and adding degassed saturated sodium bicarbonate (2 cm^3). The solvent layers were separated and the aqueous phase extracted twice with dichloromethane (2×2 cm^3). The organic portions were combined and washed with degassed water, degassed brine and dried over magnesium sulphate. The solution was filtered and the solvent removed *in vacuo* to give **10a** (29.2 mg, 100% yield).

4.7.3. (R,R)-(+)-AnPhMOP (*10a*)

$[\alpha]_D = 83.5$ (c 0.82, $CHCl_3$); ^1H (300 MHz, $CDCl_3$) δ 7.96–7.80 (m, 4H, Ar*H*), 7.46–7.11 (m, 14H, Ar*H*), 6.81–6.62 (m, 3H, Ar*H*), 3.50 (s, 3H, OCH_3), 3.05 (s, 3H, OCH_3); ^{13}C (126 MHz, $CDCl_3$) δ 160.9–109.9 (multiple P-coupled signals, Ar*C*), 55.1 (OCH_3), 54.9 (OCH_3); ^{31}P (121 MHz, $CDCl_3$) δ −24.60; HRMS Calc. for $[MH]^+$ ($C_{34}H_{28}O_2P$) 499.1827. Found: 499.1811%.

4.7.4. (R,S)-(+)-AnPhMOP (*10b*)

$[\alpha]_D = 72.3$ (c 0.415, $CHCl_3$); ^1H (300 MHz, $CDCl_3$) δ 8.00–7.76 (m, 4H, Ar*H*), 7.50–6.96 (m, 12H, Ar*H*), 6.89–6.76 (m, 4H, Ar*H*), 3.59 (s, 3H, OCH_3), 3.46 (s, 3H, OCH_3); ^{13}C (126 MHz, $CDCl_3$) δ 161.1–110.0 (multiple P-coupled signals, Ar*C*), 55.8 (OCH_3), 55.4 (OCH_3); ^{31}P (121 MHz, $CDCl_3$) δ −22.65; HRMS Calc. for $[MH]^+$ ($C_{34}H_{28}O_2P$) 499.1827. Found: 499.1829%.

4.8. Synthesis of [RhCl(CO)((R,R)-AnPhMOP)] (*12a*)

To a solution of **10a** (26 mg, 0.052 mmol) in dichloromethane (10 cm^3) was added $[Rh_2Cl_2(CO)_4]$ (0.010 g, 0.026 mmol). The resulting orange solution was stirred for 0.5 h and then the volatiles were removed *in vacuo*. Further dichloromethane was added (10 cm^3), the solution stirred for 0.5 h again and the volatiles were removed once more to give an orange solid. The yield was quantitative. ^{31}P (121 MHz, $CDCl_3$) δ 47.1 ppm (d, $^1J_{P-Rh} = 159.3$ Hz). *m/z* 630 $[MH^+ - Cl]$; HRMS Calc. for $[MH^+ - Cl]$ ($C_{35}H_{28}O_3PRh$) 630.0831. Found: 630.0800%.

4.9. X-ray crystal structures of (R,R) and (R,S)-anisylphenylMOP oxides (*8a* and *b*)

X-ray diffraction experiments on **8a** and **b** were carried out at 100 K on a Bruker SMART diffractometer using Mo Kα X-radiation, $\alpha = 0.71073$ Å. It should be noted that there are two independent but identical molecules of **8a** and acetone in the unit cell. Crystal and refinement data are given in Table 2. Absorption corrections were based on equivalent reflections and structures refined against all F_o^2 data. In **8a**, the hydrogen atoms of the solvent acetone were added at calculated positions and refined using a riding model. All other hydrogens were located in the difference fourier map and allowed to refine freely including isotropic temperature factors. Anisotropic thermal parameters were refined for all non-hydrogen atoms. Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre [22].

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