Synthesis of 1,1,6,6-tetramethylphosphajulolidine †

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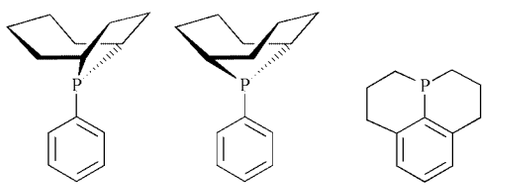
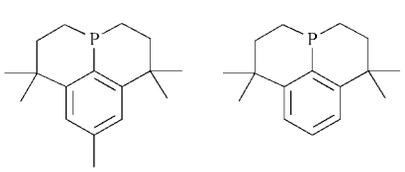
The fused tricyclic dialkyl(phenyl)phosphine, 1,1,6,6-tetramethylphosphajulolidine **11**, has been synthesised on a large scale with a view to verifying a computationally derived theory of ligand influence upon the catalytic alkoxycarbonylation of propyne.

Triphenylphosphine complexes of palladium(II) acetate are well known to catalyse the alkoxycarbonylation of propyne to methacrylate esters.[1] Recent studies have shown that this reaction is more effectively catalysed by analogous palladium complexes of phenylphosphabicyclononanes (PPBNs), and that the 4,2,1-PPBN isomer (**1a**) produces a significantly more active



(1a) **(1b)** **(1c)**

catalyst than the 3,3,1-PPBN isomer (**1b**).[2] These observations prompted a closer investigation of the co-ordination properties of these strained bridgehead cyclic alkanediyl(phenyl)-phosphines. In addition, structural data obtained from these studies have allowed us to undertake detailed quantum mechanical calculations in order to help further understand these ligand-derived influences upon catalytic activity.[3] These calculations indicate one of the most significant differences in the electronic structure of the two PPBN isomers to be the ellipticity of the P–C *ipso* bond between the phosphorus and the aryl substituent and that this increases in the series PPh_3 < 3,3,1-PPBN < 4,2,1-PPBN. Bond ellipticity has been interpreted as an indication of π-character, which in this case arises as a result of the phenyl ring being restricted in both rotation and conformation relative to the aliphatic cycle due to intramolecular interactions. The ellipticity of this bond is maximised by tethering the alkyl substituents to the *ortho* carbons of the aromatic ring as for example in 2,3,6,7-tetrahydro-1*H*,5*H*-benzo[*ij*]phosphinolizine (**1c**). A related phosphajulolidine



10 **11**

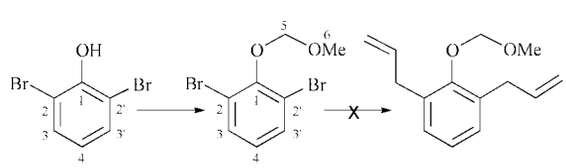
† The IUPAC name for phosphajulolidine is 2,3,6,7-tetrahydro-1*H*,5*H*-benzo[*ij*]phosphinolizine.

derivative (**10**) is known in the literature,[4] which was prepared by a multistep synthesis; the overall yield was extremely low, starting from dimethyl(phenyl)phosphine oxide, these authors prepared 120 mg by this method. This synthetic methodology is inadequate, however, for the preparation of the quantities of related phosphines that would be required for a detailed study of their properties in catalysis. Our present study is designed to test whether the apparent increase in π-bond character may help explain the relative differences between the PPBN ligand systems, hence developing a deeper understanding of ligand influences upon catalytic reactions involving phenylphosphines in this context. In order to enable this study, new, more accessible routes to appropriate phosphajulolidines are required. Detailed here are the synthetic methods adopted in attempting to arrive at the target ligand and the synthesis of an analogue, 1,1,6,6-tetramethylphosphajulolidine (**11**), which has been shown by further calculations to retain the optimised properties of the original target ligand.

Results and discussion

Several methods for the synthesis of the novel ligand 2,3,6,7-tetrahydro-1*H*,5*H*-benzo[*ij*]phosphinolizine (**1c**) were attempted (Schemes 1–4).

Route 1 (Scheme 1)



1 **2** **3**

Scheme 1

The first approach involved the Grignard promoted cross-coupling of aryl bromide groups with allyl bromide. The synthesis of 2,6-dibromophenoxy(methoxy)methane (**2**) required the use of a Soxhlet extractor containing heat-activated molecular sieves, which force the reaction to completion by absorption of the methanol by-product. The molecular sieves could not be placed directly in the reaction vessel as the protecting group is cleaved in their presence.

The preparation of 2,6-diallylphenoxy(methoxy)methane (**3**), *via* an adaptation of a previously reported Ni(dppp)Cl_2 [dppp = 1,3-bis(diphenylphosphino)propane] catalysed Grignard cross-coupling reaction,[5] failed. The only isolable product proved to

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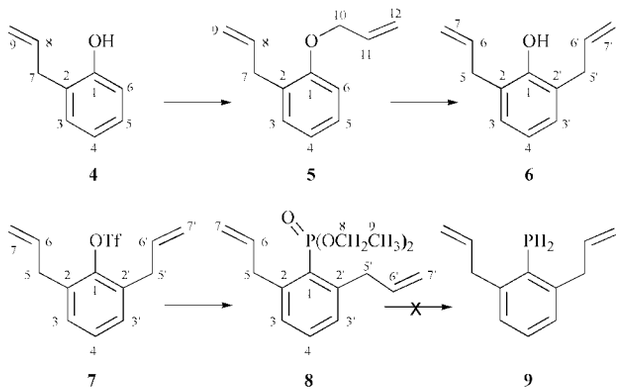
be the deprotected alcohol **1** along with unreacted starting material **2**. An alternative method *via* the *in situ* lithiation of the 2 and 6 positions on **2**, followed by direct reaction with allyl bromide yielded only **1**, again resulting in cleavage of the protecting group.

Route 2 (Scheme 2)



Scheme 2

The second approach sought to make use of the Claisen rearrangement. The preparations of 2-allylphenyl allyl ether **5** and 2,6-diallylphenol **6** were adapted from literature procedures.[6] The synthesis of **5** was found to be far cleaner when the reaction mixture was heated in a nitrogen atmosphere. The reaction was monitored by ^{1}H NMR spectroscopy and shown to be complete after 8 hours by the loss of the allyl bromide multiplet signal at δ 6.05 ppm ($BrCH_2CHCH_2$) coincident with the enlarging of the already present allyl multiplet (CCH_2-$CHCH_2$) by the allyl ether resonance (OCH_2CHCH_2) at δ 5.99–5.84 ppm.

The Claisen rearrangement to **6** required neat **5** to be strongly heated (≥200 °C) and was again cleaner when heated under a nitrogen atmosphere. The optimum heating time was 8 hours after which polymeric impurities started to form. Any unreacted **5** was removed by vacuum distillation leaving the alcohol **6** as a pale yellow oil, identified by its simple ^{1}H NMR spectrum in the aromatic region; which contained a doublet at δ 7.07 ppm corresponding to the *meta* protons ($H^{3,3'}$) and a triplet at δ 6.88 ppm corresponding to the *para* proton (H^4).

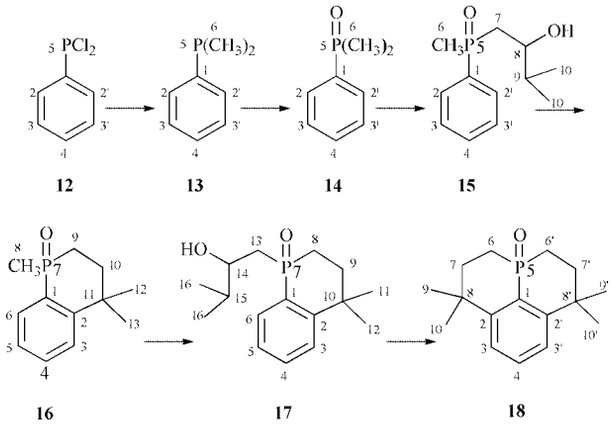
The reaction of **6** with trifluoromethanesulfonic (triflic) anhydride was performed in the presence of pyridine to prevent the acid catalysed formation of bright purple polymerisation products. The ^{1}H NMR spectrum of the product, 2,6-diallylphenyl triflate **7**, was largely unchanged from **6**, however, its IR spectrum confirmed the presence of the triflate group by (ν_{C-F} 1210, 1120 cm^{-1}, $\nu_{S=O}$ 1080 cm^{-1}).

Diethyl 2,6-diallylphenylphosphonate (**8**) was prepared from **7** and freshly prepared sodium diethylphosphonite by reflux in THF. The desired compound was obtained after purification by vacuum distillation, in moderate yield. A singlet was observed in the ^{31}P NMR spectrum at δ −8.5 ppm. The ^{1}H NMR spectrum was similar to that of **7** except for the additional signals of the ethoxy groups. The IR spectrum confirmed the presence of the phosphonate group ($\nu_{P=O}$ 1090 cm^{-1}, ν_{P-O} 1020 cm^{-1}).

All attempts to reduce **8** using a variety of reducing agents including lithium tetrahydridoaluminate, dichloroalane[7] and trimethylsilane[8] at reaction temperatures ranging from −78 to 75 °C failed. Most attempts did not yield any phosphorus-containing products, probably due to cleavage of the P–Ph bond yielding phosphine (PH_3).

Route 3 (Scheme 3)

This approach sought to improve upon the previously reported low yield synthesis of a similar compound 1,1,6,6,8-pentamethylphosphajulolidine (**10**).[4] Chen and co-workers attributed



Scheme 3

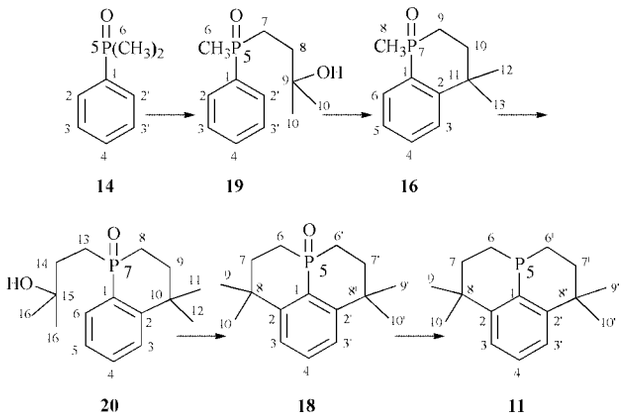
the poor yield of **10** to an unexpected *ipso* ring closure to form a spiro conjugated carbonium ion during the synthesis, which is strongly favoured and leads to the formation of an undesired product containing a *meta* methyl group as opposed to the required *para* methyl group.[4] To negate this, the *para* methyl group was omitted from the starting material leading to a new target molecule 1,1,6,6-tetramethylphosphajulolidine (**11**). Calculations predicted that the additional methyl groups would not have any significant effect on the desired electronic influences of the target ligand.[9]

This route is based upon dimethyl(phenyl)phosphine oxide (**14**), a readily prepared starting material. Deprotonation of **14** at the methyl group followed by addition of isobutyraldehyde yielded 1-[(methyl)phenylphosphinoyl]-3-methylbutan-2-ol (**15**) as a pale yellow oil. The ^{31}P NMR spectrum showed a singlet at δ 37.6 ppm and a small signal corresponding to approximately 5% of the starting material **14** at δ 31.2 ppm. Due to the combination of phosphorus–proton coupling and the presence of diastereomers, the ^{1}H NMR spectrum of **15** was complicated but compared well with the literature description.[4] A vast excess of polyphosphoric acid (62 × 10^3 mol%) was used to dehydrate and annulate **15**; ^{31}P NMR spectroscopy showed the reaction to be complete after heating at 120 °C for 5 days. Work-up gave the 1,2,3,4-tetrahydrophosphinoline oxide (**16**) as a dark brown oil in low yield. The integrated ^{31}P NMR spectrum of **16** contained a minor signal (5%) corresponding to the alcohol **15** and a singlet at δ 26.3 that corresponded to the desired product. The ^{1}H NMR spectrum gave good agreement with the literature description.[4]

Compound **16** was selectively deprotonated by butyllithium at the 8-methyl position and subsequent addition of isobutyraldehyde yielded 1-(2-hydroxy-3-methylbutyl)-4,4-dimethyl-1,2,3,4-tetrahydrophosphinoline oxide (**17**) as a dark brown oil in excellent yield. Compound **17** was reasonably pure by ^{31}P NMR spectroscopy with a singlet at δ 33.6 ppm and a minor (10%) signal at δ 41.0 ppm and could not be readily purified. The ^{1}H NMR spectrum was broad and uninformative due to a series of overlapping multiplets arising from the combination of phosphorus coupling and the presence of a statistical mixture of diastereomers. The brown oil **17** was added to polyphosphoric acid and heated at 120 °C for 6 days yielding a black oil, 62% of which was identified, by the presence of a singlet at δ 22.5 ppm in the ^{31}P NMR spectrum, to be 1,1,6,6-tetramethylphosphajulolidine oxide (**18**). Subsequent dissolution in dichloromethane and filtration yielded (1.12 g, 4.26 mmol, 2.2% overall yield from **12**) a dark brown oil after removal of solvent, no improvement in the ^{31}P NMR spectrum was observed.

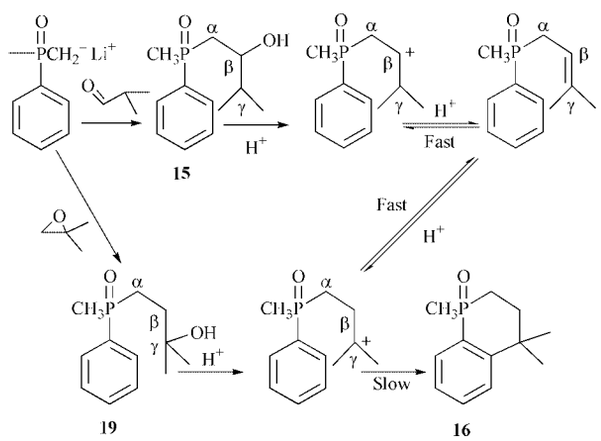
Reduction of the oxide **18** with trichlorosilane yielded a pale brown oil; the ^{31}P NMR spectrum consisted of a large number of peaks none of which corresponded to the chemical shift of the previously reported analogue 1,1,6,6,8-pentamethylphosphajulolidine (**10**).[4]

Route 4 (Scheme 4)



Scheme 4

Previous studies on dehydration and annulation reactions of closely related alkyl(diphenyl)phosphine oxides have highlighted the need for forcing conditions for these reactions.[10] Under mild conditions the dehydration of alcohols similar to **15** and **17** leads to the formation of allyl or vinyl substituents (Scheme 5). To overcome the deactivating effect of the



Scheme 5

phosphinoyl group on the phenyl ring, polyphosphoric acid and high temperatures were required. One possible way to improve upon the low yield of **11** previously obtained[4] is to facilitate the dehydration of both **15** and **17**, hence limiting the time the reagents are exposed to such forcing conditions. This can be achieved by the synthesis of more reactive isomers of **15** and **17** which have the alcohol in the more electron rich γ-position as opposed to the β-position (Scheme 5). The synthesis was repeated as previously described except that after deprotonation of **14**, isobutylene oxide was added as opposed to isobutyraldehyde (Scheme 5). This modification yielded 1-[(methyl)phenylphosphinoyl]-3-methylbutan-3-ol (**19**), with the hydroxy group now in the γ-position, as a pale yellow oil (Scheme 5). ^{31}P NMR spectroscopy revealed a minor product (17%) at δ 42.9 ppm which was later identified as the disubstituted, bis(3-hydroxy-3-methylbutyl)phenylphosphine oxide, any efforts to increase the yield of this fortuitous by-product failed leading to further unwanted impurities; the main signal corresponding to **19** was a singlet at δ 37.9 ppm. The IR confirmed the presence of the alcohol group ν_{CO-H} 3350, ν_{CO-H} 1380, 1360, ν_{C-OH} 1210 cm^{-1}.

The preparation of polyphosphoric acid and dehydration of **19** were carried out under nitrogen, which produced a pale yellow mixture as opposed to the dark brown mixture previously obtained (route 3). The dehydration and annulation of the more reactive structural isomer **19** to form the previously prepared fused bicyclic **16** required only 15 hours heating at 120 °C compared to the 5 days necessary for the original alcohol **15**. Neutralisation of the polyphosphoric acid with NaOH before extraction greatly increased the isolated yield of the yellow oil. The ^{31}P NMR spectrum was a singlet at δ 26.3 ppm. The annulation was shown to have occurred by the production of 4 aromatic signals in the ^{1}H NMR spectrum and by the loss of the C–O–H signals and monosubstituted aromatic overtone pattern from the IR spectrum.

1-(3-Hydroxy-3-methylbutyl)-4,4-dimethyl-1,2,3,4-tetrahydrophosphinoline oxide (**20**), with the hydroxy group in the γ-position, was prepared by deprotonation of **16** and addition of isobutylene oxide yielding a light brown oil. The singlet at δ 31.7 ppm in the ^{31}P NMR spectrum showed the product to be essentially pure. The presence of the alcohol was again confirmed by IR spectroscopy ν_{max} 3350 (O–H stretch), 1370 (CO–H bend), 1360 (CO–H bend), 1200 (C–OH bend) cm^{-1}.

1,1,6,6-Tetramethylphosphajulolidine oxide **18** was obtained after heating the bicyclic alcohol **20** in polyphosphoric acid at 120 °C for 15 hours under nitrogen. Once again the polyphosphoric acid was neutralised before work-up, which yielded 29 g of a dark brown oil. Purification by chromatography yielded **18** as a golden yellow powder. After several purifications *via* the same method, the total yield obtained was 23.42 g, 48.1%. The ^{31}P NMR spectrum (s, δ_P 18.5 ppm) confirmed the absence of any P-containing impurities. The aromatic region of the ^{1}H NMR spectrum was simplified to a triplet corresponding to H$^{3,3'}$ at δ 7.31 ppm and a doublet corresponding to H^4 at δ 7.24 ppm, the methyl groups 9,9′ and 10,10′ give rise to two singlets one at δ 1.45 ppm and one at δ 1.27 ppm. The loss of the alcohol group was confirmed by IR spectroscopy.

The reduction of the oxide **18** was achieved by reflux in benzene with trichlorosilane for 24 hours; work-up afforded a pale brown oil which was purified by extraction into methanol followed by filtration. The resultant yellow solution readily yielded 1,1,6,6-tetramethylphosphajulolidine (**11**) as a low melting, oily, yellow solid upon evaporation (14.04 g, 0.057 mol, 13% overall yield from **12**). The ^{31}P NMR spectrum was a singlet at δ −61.0. The ^{1}H NMR spectrum is similar to that of the oxide **18** except for a general upfield shift. The aromatic triplet assigned to the *para* hydrogen shifts from δ 7.31 to 7.05 ppm effectively changing positions with the doublet assigned to the *meta* hydrogens which shifts from δ 7.24 to 7.15 ppm. The methyl protons become equivalent forming a singlet δ 1.25 ppm. The complicated multiplets attributed to the methylene protons become much more clearly resolved into the characteristic pattern of an AA′BB′X system (where X = P). The carbon DEPT spectrum is again largely unchanged from that of the oxide **18** except that the aromatic *ipso* carbon bonded directly to phosphorus is shifted downfield from δ 123.5 to 127.1 ppm and the $^1J_{P-C}$ to C^1 decreases from 90 to 10 Hz. Also of note is the fact that the methyl carbons remain inequivalent giving rise to a singlet at δ 30.7 ppm, and a doublet $^1J_{P-C}$ 10 Hz at δ 28.45 ppm, despite the equivalency of the methyl protons. The phosphorus splitting of the aliphatic phosphorus bound carbons C^6 decreases from 60 to 10 Hz. The success of the reduction is also confirmed by the loss of the P=O absorption in the IR spectrum.

Conclusion

Theoretical calculations have predicted that a crucial factor in the catalysis of the alkoxycarbonylation of propyne by complexes of dialkyl(phenyl)phosphines, is the phosphorus to *ipso* carbon bond ellipticity. A ligand, which maximises this property, 1,1,6,6-tetramethylphosphajulolidine (**11**), has been synthesised *via* an improvement of a previously reported low yield synthesis of an analogue **10** on a scale large enough (14.04 g) to

test this theory experimentally. Studies of the co-ordination behaviour of this ligand and the properties of its transition metal complexes are underway, and will be discussed in future papers.

Experimental

All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk and cannula techniques or in a conventional nitrogen filled glove box. All solvents were refluxed under nitrogen over sodium–benzophenone and distilled immediately prior to use with the exception of dichloromethane, which was dried over CaH_2, and toluene, which was dried over sodium, both under reflux. Light petroleum had boiling point 40–60 °C.

All NMR data are quoted in δ (ppm). The ^{31}P-{^1H} NMR spectra (referenced to 85% H_3PO_4, δ 0 ppm) were collected on a JEOL FX90Q spectrometer operating at 36.2 MHz; ^1H (400.13 MHz) and ^{13}C-{^1H} (100 MHz) spectra were recorded on a Bruker DPX400 as a solution in $CDCl_3$ unless otherwise stated and referenced to $SiMe_4$. Relative intensities in the ^{31}P NMR spectra were confirmed by increasing the pulse delay until the ratio of integrals was constant (*ca*. 10 s). All IR data were collected from thin films (CsI plates) on a Perkin-Elmer 783 spectrometer and are quoted in cm^{-1}. The numbering systems applied to the structures in Schemes 1–5, which are not consistent with standard IUPAC systems, are simply intended to clarify the assignment of NMR signals.

All chemicals were obtained commercially and used as received unless otherwise stated, with the exceptions of allylmagnesium bromide and methylmagnesium chloride, which were prepared from allyl bromide and methyl chloride using standard Grignard techniques. Dimethyl(phenyl)phosphine (**13**) was prepared from dichloro(phenyl)phosphine (**12**) and methylmagnesium chloride,[11] yielding an air sensitive, colourless oil with the characteristic strong odour.

The oxidation of **13** with hydrogen peroxide yielded the air stable dimethyl(phenyl)phosphine oxide **14**, as an odourless, colourless oil. δ_P: 31.9. δ_H: 7.75 (2H, dd, $J_{(H-H)}$ 9.9 and 12.1 Hz, $H^{3,3'}$), 7.42 (3H, m, $H^{2,2'}$ + H^4), 7.11 (s, CH_3Cl), 1.65 (6H, d, $J_{(H-H)}$ 3.0 Hz, H^6). ν_{max}: 3400 (br, m, H_2O), 3050 (w, Ar-H), 2900 (w, C-H_3), 2850 (w, C-H_3), 1650 (br, H_2O bend), 1590 (w, Ar C=C), 1480 (w, CH_3 asym), 1440 (m, Ar-P), 1420 (w, CH_3 sym), 1300 (m), 1170 (s, P=O), 1160 (s, CH_3 rock), 1070 (m, Ar), 1010 (w, P-Ar), 750 (s, P-C). MS (APCI): *m*/*z* 155.0 (M^+ + H, 100%).

Preparations

2,6-Dibromophenoxy(methoxy)methane (2). 2,6-Dibromophenol (5 g, 19.8 mmol) and toluene-*p*-sulfonic acid (20 mg) were placed in a 500 ml flask equipped with a Soxhlet extractor charged with heat-activated molecular sieves. Dimethoxymethane (6.04 g, 39.7 mmol) in chloroform (200 ml) was added to the solution and refluxed for 5 days under a nitrogen atmosphere, during which time the molecular sieves were exchanged for freshly activated sieves approximately every 12 hours. The solvent was removed yielding a colourless oil (4 g, 13.5 mmol). δ_H: 7.45 (2H, d, $J_{(H-H)}$ 8.9 Hz, $H^{3,3'}$), 6.81 (1H, t, $J_{(H-H)}$ 9.2 Hz, H^4), 5.12 (2H, s, O-CH_2-), 3.64 (3H, s, -O-CH_3). $\delta_{C\,+\,DEPT}$: 150.6 (C_4, C^1), 131.8 (CH, $C^{3,3'}$), 125.4 (CH, C^4), 115.1 (C_4, $C^{2,2'}$), 98.6 (CH_2, C^5), 57.4 (CH_3, C^6). MS (EI): *m*/*z* 296.0 (M^+, 80%).

Allyl 2-allylphenyl ether (5). A round bottomed flask equipped with a reflux condenser was charged with potassium carbonate (20.6 g, 0.149 mol), 2-allylphenol (20 g, 19.46 ml, 0.149 mol), allyl bromide (13 ml, 18.02 g, 0.149 mol) and acetone (40 ml) and the resultant mixture refluxed for 8 hours. After cooling, the reaction was washed with water (150 ml) and the aqueous phase separated and extracted with diethyl ether (3 × 10 ml). The combined organic phases were washed with sodium hydroxide (2 M, 50 ml) and dried over potassium carbonate. The mixture was filtered and the solvent was removed yielding a pale yellow oil (20.2 g, 0.116 mol, 77%). δ_H: 7.15–7.03 (2H, m, H^5 + H^6), 6.81 (1H, t, $J_{(H-H)}$ 7.5 Hz, H^4), 6.75 (1H, d, $J_{(H-H)}$ 8.1 Hz, H^3), 5.99–5.84 (2H, m, H^8 + H^{11}), 5.30 (1H, dd, $J_{(H-H)}$ 19.0 and 2.1 Hz, H^{12}-*cis*), 5.15 (1H, dd, $J_{(H-H)}$ 11.2 and 2.3 Hz, H^{12}-*trans*), 4.99 (2H, dd + dd, $J_{(H-H)}$ 20.1, 9.9 and 1.1 Hz, H^9-*cis* + *trans*), 4.45 (2H, d, $J_{(H-H)}$ 6.3 Hz, H^{10}), 3.34 (2H, d, $J_{(H-H)}$ 6.2 Hz, H^7). $\delta_{C\,+\,DEPT}$: 156.7 (C_4, C^1), 137.4 (CH, C^6), 134.0 (CH, C^5), 130.9 (CH, C^3), 129.4 (C_4, C^2), 127.7 (CH, C^4), 121.1 (CH, C^8), 116.9 (CH_2, C^9), 115.8 (CH_2, C^{12}), 112.1 (CH, C^{11}), 69.1 (CH_2, C^7), 35.6 (CH_2, C^{10}).

2,6-Diallylphenol (6). Neat **5** (20.2 g, 0.12 mol) was heated (200 °C) under a nitrogen atmosphere for 8 hours. The product was distilled under vacuum (0.05 mmHg) at 50 °C to remove unreacted **5**, leaving **6** as a pale yellow oil (17.84 g, 0.10 mol, 88.3%). δ_H: 7.07 (2H, d, $J_{(H-H)}$ 8.3 Hz, $H^{3,3'}$), 6.88 (1H, t, $J_{(H-H)}$ 7.5 Hz, H^4), 6.11–6.00 (2H, m, $H^{6,6'}$), 5.22 (2H, dt, $J_{(H-H)}$ 1.6 and 3.3 Hz, $H^{7,7'}$-*cis*), 5.17 (2H, d, $J_{(H-H)}$ 1.6 Hz, $H^{7,7'}$-*trans*) 3.42 (4H, d, $J_{(H-H)}$ 5.2 Hz, $H^{5,5'}$).

2,6-Diallylphenyl triflate (7), method i. Trifluoromethanesulfonic anhydride (2.55 ml, 4.27 g, 15 mmol) was added *via* syringe to an ice-cool solution of **6** (2.64 g, 15 mmol) in dichloromethane (10 ml) resulting in an intensely purple coloured oil, which gave broad and uninformative NMR data.

2,6-Diallylphenyl triflate (7), method ii. Trifluoromethanesulfonic anhydride (13.71 ml, 22.99 g, 81.49 mmol) was added to an ice-cool solution of pyridine (13.18 ml, 12.89 g, 162.9 mmol) and **6** (14.2 g, 81.49 mmol) in dichloromethane (300 ml). The solution was allowed to stir for 16 hours before the reaction was washed with water (2 × 300 ml), hydrochloric acid (0.1 M, 2 × 300 ml) and sodium carbonate (0.1 M, 2 × 300 ml). The solvent was removed and the residue distilled under vacuum (0.05 mmHg) at 55 °C to yield a colourless oil (18.46 g, 60.26 mmol, 73.9%). δ_H: 7.20 (1H, t, $J_{(H-H)}$ 7.3 Hz, H^4), 7.12 (2H, d, $J_{(H-H)}$ 8.1 Hz, $H^{3,3'}$), 5.89–5.77 (2H, m, $H^{6,6'}$), 5.15 (2H, d, $J_{(H-H)}$ 5.2 Hz, $H^{7,7'}$-*cis*), 5.12 (2H, s, $H^{7,7'}$-*trans*), 3.45 (4H, d, $J_{(H-H)}$ 6.8 Hz, $H^{5,5'}$). δ_C: 145.5 (C^1), 135.4 (C^4), 134.2 ($C^{3,3'}$), 129.9 ($C^{6,6'}$), 128.8 ($C^{2,2'}$), 117.8 ($C^{7,7'}$), 34.8 ($C^{5,5'}$). ν_{max}/cm^{-1} 3060 (w, Ar-H), 2960 (m, CH_2), 2900 (m, CH_2), 1640 (m, Ar C=C), 1400 (s, Ar C=C), 1210 (s, CF_3), 1120 (s, CF_3), 1080 (m, S=O).

Diethyl 2,6-diallylphenylphosphonate (8). Sodium diethyl phosphonite was prepared *in situ*: a mixture of diethyl phosphonate (8.54 ml, 9.15 g, 66 mmol) and sodium (1.68 g, 72.94 mmol) in THF (250 ml) was stirred for 16 hours, followed by 2 hours under reflux to dissolve the unreacted sodium. The reaction was shown to be complete by ^{31}P NMR δ_P (D_2O): 150.

THF (250 ml) was added followed by **7** (18.46 g, 60.2 mmol) and the mixture was heated under reflux for 2 hours. The solvent was removed and the resultant yellow oil was left sealed under a nitrogen atmosphere for 5 days whereupon it turned bright purple. The purple oil was heated under reflux in chloroform yielding a yellow solution and an insoluble white precipitate. The yellow solution was filtered and the solvent was removed yielding a red oil, which was distilled under vacuum (0.05 mmHg) yielding 6 fractions. The sixth fraction, a yellow oil (8.49 g, 28.8 mmol, 47.9%) collected at 110–114 °C, contained the desired product. δ_P: −8.5. δ_H: 7.11 (3H, s accidental equivalence, $H^{3,3'}$ + H^4), 5.99–5.83 (2H, m, $H^{6,6'}$), 4.99 (4H, dd, $J_{(H-H)}$ 7.8 and 10.3 Hz, $H^{7,7'}$), 4.12 (4H, quartet, $J_{(H-H)}$ 6.5 Hz, H^8), 3.54 (4H, d, $J_{(H-H)}$ 8.2 Hz, $H^{5,5'}$), 1.25 (6H, t, $J_{(H-H)}$ 7.6 Hz, H^9). δ_C: 147.4 (C^1), 136.8 (C^4), 132.9 ($C^{2,2'}$), 128.9 ($C^{3,3'}$), 125.8 (C^8), 116.6 ($C^{7,7'}$), 65.0 ($C^{5,5'}$), 35.0 (C^8), 16.5 (C^9). ν_{max}/cm^{-1} 3350 (br, w), 3050 (m, Ar-H), 2950 (s, C-H_2), 2900 (m, C-H_3), 2985 (w, C-H_3), 1640 (m, Ar C=C), 1410 (m, Ar C=C), 1260 (s), 1090 (br, s, P=O), 1020 (br, s, P-OR).

Attempted synthesis of 2,6-diallylphenylphosphine (9), method i. A degassed 3 necked flask equipped with a dropping funnel and condenser was charged with lithium aluminium hydride (0.78 g, 20.5 mmol) and diethyl ether (20 ml), cooled in ice and then **8** (3.01 g, 10.22 mmol) in diethyl ether (40 ml) was added *via* the dropping funnel. The resultant grey mixture was left to stir for 16 hours at room temperature, cooled in ice and hydrolysed with water (0.78 ml), aqueous sodium hydroxide (15% wt, 0.78 ml) and water (2.34 ml) to produce a clear solution and a white precipitate. The strongly smelling solution was filtered and the solvent removed yielding a colourless oil which gave no ^{31}P NMR signal and was shown to be **6**. δ_H (360 MHz): 7.07 (2H, d, $J_{(H-H)}$ 8.3 Hz, $H^{3,3'}$), 6.88 (1H, t, $J_{(H-H)}$ 7.5 Hz, H^4), 6.11–6.00 (2H, m, $H^{6,6'}$), 5.22 (2H, dt, $J_{(H-H)}$ 1.6 and 3.3 Hz, $H^{7,7'}$-*cis*), 5.17 (2H, d, $J_{(H-H)}$ 1.6 Hz, $H^{7,7'}$-*trans*), 3.42 (4H, d, $J_{(H-H)}$ 5.2 Hz, $H^{5,5'}$).

Attempted synthesis of 2,6-diallylphenylphosphine (9), method ii. Lithium aluminium hydride (0.11 g, 2.9 mmol) in diethyl ether (5 ml) was added to an ice-cooled solution of aluminium trichloride (1.14 g, 8.5 mmol) in diethyl ether (5 ml). The resultant suspension was allowed to warm to room temperature with stirring for 16 hours. Compound **8** (1 g, 3.4 mmol) in diethyl ether (10 ml) was added to the ice-cooled mixture, which was allowed to warm to room temperature with stirring for 1 hour. The resultant mixture was heated under reflux in a sonic bath for 4 hours, cooled in ice and hydrolysed with water (10 ml). The aqueous phase was separated, washed with diethyl ether (20 ml) and the combined organic phases were dried over magnesium sulfate, filtered and the solvent was removed, yielding a colourless oil. δ_P: −13.7 singlet in ^{1}H coupled ^{31}P NMR.

Attempted synthesis of 2,6-diallylphenylphosphine (9), method iii. Trimethylchlorosilane (3.49 ml, 2.99 g, 27.49 mmol) in THF (5 ml) was added to a mixture of lithium aluminium hydride (1.05 g, 27.66 mmol) in THF (10 ml) at −78 °C (dry ice–acetone) and allowed to warm to room temperature with stirring for 3 hours. Compound **8** (2.96 g, 10.05 mmol) in THF (15 ml) was added to the cooled (−30 °C) mixture, which was allowed to warm to room temperature and stirred for a further 42 hours. The resultant mixture was ice-cooled, hydrolysed with water (20 ml) and sodium hydroxide (1 M, 5 ml); diethyl ether (15 ml) was added to aid partition, the aqueous phase was separated and washed with diethyl ether (15 ml). The combined organic phases were dried over magnesium sulfate, filtered and the solvent was removed yielding a viscous oil. δ_P: weak primary phosphine signal −113.2.

1-[(Methyl)phenylphosphinoyl]-3-methylbutan-2-ol (15). Butyllithium (2 M, 87.9 ml, 0.176 mol) in hexane was added to an ice-cooled solution of **14** (24.41 g, 0.188 mol) in THF (300 ml) producing an orange solution, which was stirred for 1 hour. The reaction was cooled to −78 °C (dry ice–acetone), freshly distilled (62 °C) isobutyraldehyde (11.42 g, 0.158 mol) in THF (15 ml) was added and the solution allowed to warm to room temperature with stirring for 15 hours. The reaction was quenched with aqueous ammonium chloride (500 ml) and the aqueous phase separated and washed with dichloromethane (2 × 200 ml). The combined organic phases were dried over magnesium sulfate, filtered and the solvent removed yielding a yellow oil (37.1 g, 0.017 mol, 110%). δ_P: 37.6 (**15**), 31.2 (**14**, 5%). δ_H: 7.74 (1H, dd, $J_{(H-H)}$ 11.0 and 20.9 Hz, $H^{3,3'}$), 7.43 (3H, m, $H^{2,2'}$ + H^4), 2.26–1.85 (2H, m, H^7), 1.65 (3H, d, $J_{(P-H)}$ 11.1 Hz, H^6), 1.89–1.65 (1H, m, H^8), 1.02–0.78 (7H, m, H^{10} + H^9). δ_{C+DEPT}: 134.0 (CR_4, d, $J_{(P-C)}$ 100 Hz, C^1), 132.1 (CH, s, C^4), 130.5 (CH, d, $J_{(P-C)}$ 10 Hz, $C^{3,3'}$), 129.1 (CH, d, $J_{(P-C)}$ 10 Hz, $C^{2,2'}$), 71.3 (CH, d, $J_{(P-C)}$ 70 Hz, C^8), 35.9 (CH_2, d, $J_{(P-C)}$ 20 Hz, C^7), 35.2 (CH, d, $J_{(P-C)}$ 10 Hz, C^9), 18.4 (CH_3, d, $J_{(P-C)}$ 10 Hz, C^{10}), 17.8 (CH_3, d, $J_{(P-C)}$ 10 Hz, C^{11}), 16.6 (CH_3, d, $J_{(P-C)}$ 70 Hz, C^6). ν_{max}/cm^{-1}: 3300 (br, s, O-H), 3050 (m, Ar-H), 2950 (s, C-H_2), 2900 (s, C-H_3), 2850 (s, C-H_3), 1960, 1900, 1825, 1775 (w, monosubstituted aromatic overtone pattern), 1660 (m, br, H_2O bend), 1590 (m, Ar C=C), 1460 (s, CH_3 asym + CH_2 scissor), 1440 (s, Ar-P), 1410 (s, CH_3 sym), 1380 (s, CO-H), 1340 (s, CO-H), 1300 (m), 1230 (s, C-OH), 1170 (s, P=O), 1160 (s, CH_3 rock), 1060 (w, Ar), 1100 (w, P-Ar), 750 (s, P-C). MS (APCI): *m*/*z* 227.1 (M + H^+, 100%), 140.4 (5), 125.0 (5).

1,4,4-Trimethyl-1,2,3,4-tetrahydrophosphinoline oxide (16). Polyphosphoric acid was prepared by addition of phosphoric acid (642.08 ml, 5.57 mol), to phosphorus pentaoxide (1351.75 g, 9.52 mol) in a flask equipped with a mechanical stirrer, the solution reached 100 °C during mixing and was further heated to 120 °C for 1 hour. The crude oil of **15** (34.74 g, 0.15 mol) was added and the heating continued at 120 °C for 5 days. The hot mixture was poured into ice (1.5 l) allowed to cool, extracted with dichloromethane (4 × 500 ml) and the combined organic phases were washed with sodium hydrogen carbonate solution (1 M, 2 × 750 ml). The solvent was removed yielding a very dark brown oil (5.85 g, 0.022 mol, 13.5%). δ_P: 26.3 (**16**, 95%), 35.2 (**15**, 5%). δ_H: 7.75 (1H, dd, $J_{(H-H)}$ 7.0 and 11.8 Hz, H^5), 7.35 (2H, m, H^3 + H^4), 7.23 (1H, t, $J_{(H-H)}$ 6.8 Hz, H^6), 5.24 (CH_2Cl_2), 2.31–1.88 (2H, m, H^{10}), 1.55 (3H, quartet, $J_{(H-H)}$ 9.8 Hz, H^8), 1.35–1.01 (2H, m, H^9), 1.26 (6H, s, H^{12}). δ_C: 149.6 (d, $J_{(P-C)}$ 7 Hz, C^2), 130.9 (d, $J_{(P-C)}$ 2.4 Hz, C^4), 129.5 (d, $J_{(P-C)}$ 7.2 Hz, C^5), 128.7 (d, $J_{(P-C)}$ 10 Hz, C^1), 125.7 (d, $J_{(P-C)}$ 7 Hz, C^3), 34.5 (s, C^{11}), 33.9 (s, C^{10}), 30.0 (d, $J_{(P-C)}$ 7 Hz, $C^{12,13}$), 22.8 (d, $J_{(P-C)}$ 68 Hz, C^9), 16.7 (d, $J_{(P-C)}$ 50 Hz, C^8). ν_{max}/cm^{-1}: 3300 (br, m, O-H), 3050 (m, Ar-H), 2950 (s, C-H_2), 2900 (s, C-H_3), 2850 (m, C-H_3), 1640 (w, br, H_2O bend), 1590 (m, Ar C=C), 1480 (s, CH_3 asym + CH_2 scissor), 1430 (s, Ar-P), 1400 (s, CH_3 sym), 1300 (s), 1170 (s, P=O), 1150 (s, CH_3 rock), 1080 (m, Ar), 1000 (w, P-Ar), 750 (s, P-C). MS (APCI): *m*/*z* 417.6 ($2M^+$ + H, 100%), 209.3 (M^+ + H, 15).

1-(2-Hydroxy-3-methylbutyl)-4,4-dimethyl-1,2,3,4-tetrahydrophosphinoline oxide (17). Butyllithium solution (1.72 M, 20.98 ml, 36.1 mmol) in hexane was added dropwise to an ice-cold stirred solution of **16** (5.85 g, 28.1 mmol) in THF (50 ml). After 40 minutes freshly distilled (62 °C) isobutyraldehyde (4.84 g, 0.67 mmol) in THF (10 ml) was added and the dark brown solution allowed to warm to room temperature. Stirring was further continued for 1 hour before quenching with ammonium chloride solution (100 ml). The aqueous phase was separated and extracted with diethyl ether (2 × 50 ml). The combined organic phases were dried over magnesium sulfate, filtered and the solvent was removed yielding a dark brown oil (7.88 g, 28.1 mmol, 100%). δ_P: 41.0 (m, 10%), 33.6 (**17**, s, 90%). δ_H: 7.81 (1H, m, H^4), 7.25 (2H, m, $H^{5,6}$), 7.14 (1H, m, H^3), 2.67–2.25 (4H, m, $H^{9,14}$), 2.15–1.05 (5H, m, $H^{8,13,15}$), 1.33 (6H, s, $H^{11,12}$), 0.94 (6H, s, H^{16}). δ_{C+DEPT}: 150.2 (CR_4, C^2), 131.3 (CH, C^4), 131.1 (CH, C^5), 130.0 (CH, C^1), 125.9 (CH, C^3), 78.2 (CH, C^{14}), 34.5 (CH_3, C^{11}), 34.2 (CH, C^{15}), 33.7 (CH_3, C^{10}), 30.10 (CH_3, C^{16}), 27.8 (CH_2, d, $J_{(P-C)}$ 26.9 Hz, C^{13}), 27.5 (CH_3, C^{12}), 22.5 (CH_2, C^9), 20.50 (d, $J_{(P-C)}$ 66.2 Hz, C^8). ν_{max}/cm^{-1}: 3300 (br, s, O-H), 3050 (m, Ar-H), 2950 (s, C-H_2), 2900 (s, C-H_3), 2850 (s, C-H_3), 1720 (m, br, H_2O bend), 1590 (s, Ar C=C), 1460 (s, CH_3 asym + CH_2 scissor), 1430 (s, Ar-P), 1400 (s, CH_3 sym), 1380 (s, CO-H), 1340 (s, CO-H), 1260 (s), 1220 (s, C-OH), 1170 (s, P=O), 1150 (s, CH_3 rock), 1000 (s, P-Ar), 750 (s, P-C). MS (APCI): *m*/*z* 281.2 (100%).

Isobutylene oxide. A water aspirator connected to a mercury manometer was attached to a T-piece connected to a short length of hose open to air and the side arm of a Schlenk tube (the receiver flask for the reaction). A hose clamp was placed on the hose open to air to serve as a vacuum regulator, and a dip tube attached to the side arm of a second Schlenk tube (the reaction vessel) was placed in the receiver flask. The receiver flask was cooled to −78 °C (dry ice–acetone) and the reaction

vessel was charged with 1-chloro-2-methylpropan-2-ol (105.4 g, 0.97 mol) and cooled to −15 °C (ice–salt). An ice-cool solution of potassium hydroxide (95.2 g, 97 mmol) in water (100 ml) was added with vigorous stirring whilst the pressure was reduced to 500 mmHg by a water aspirator controlled by an air bleed. After 5 hours the vacuum was released and the product dried over calcium hydride for 15 hours before distilling (using the same method as above) to yield a colourless liquid (65 g, 90 mmol, 92%). δ_H: 2.52 (2H, s, CH_2), 1.34 (6H, s, $(CH_3)_2$). δ_C: 53.9 (CH_2), 53.5 (-C-(CH_3)$_2$), 22.1 ((CH_3)$_2$).

1-[(Methyl)phenylphosphinoyl]-3-methylbutan-3-ol (19). Butyllithium (2 M, 190.07 ml, 0.380 mol) in hexane was added to an ice-cooled solution of **13** (53.24 g, 0.345 mol) in THF (500 ml) producing an orange solution, which was stirred for 1 hour. The reaction was cooled to −78 °C (dry ice–acetone) before isobutylene oxide (24.90 g, 0.340 mol) in THF (50 ml) was added and the solution allowed to warm to room temperature with stirring for 15 hours. The reaction was quenched with aqueous ammonium chloride (500 ml) and the aqueous phase separated and washed with dichloromethane (2 × 250 ml). The combined organic phases were dried over magnesium sulfate, filtered and the solvent was removed yielding a yellow oil (65.93 g, 0.291 mol, 84.5%). δ_P: 42.9 (17%, disubstituted product), 37.9 (**19**, 83%). δ_H: 7.65 (2H, dd, $H^{3,3'}$), 7.42 (3H, m, $H^{2,2'}$ + H^4), 2.21–1.85 (2H, m, H^7), 1.65 (3H, d, $J_{(P-H)}$ 5.74 Hz, H^6), 1.75–1.58 (2H, m, H^8), 1.13 (6H, d, H^{10}). $\delta_{C\,+\,DEPT}$: 134.1 (CR_4, d, $J_{(P-C)}$ 10 Hz, C^1), 132.6 (CH, s, C^4), 130.9 (CH, d, $J_{(P-C)}$ 10 Hz, $C^{2,2'}$), 121.9 (CH, d, $J_{(P-C)}$ 10 Hz, $C^{3,3'}$), 69.8 (CR_4, d, $J_{(P-C)}$ 5 Hz, C^9), 35.3 (CH_2, d, $J_{(P-C)}$ 5 Hz, C^8), 26.0 (CH_2, d, $J_{(P-C)}$ 70 Hz, C^7), 16.1 (CH_3, d, $J_{(P-C)}$ 70 Hz, C^6). ν_{max}/cm^{-1}: 3350 (br, s, O-H), 3050 (m, Ar-H), 2950 (s, C-H_2), 2900 (s, C-H_3), 2850 (s, C-H_3), 1960, 1900, 1820, 1780 (w, monosubstituted aromatic overtone pattern), 1660 (m, br, H_2O bend), 1590 (m, Ar C=C), 1470 (m, CH_3 asym + CH_2 scissor), 1440 (s, Ar-P), 1410 (s, CH_3 sym), 1380 (s, CO-H), 1360 (s, CO-H), 1300 (s), 1210 (s, C-OH), 1170 (s, P=O), 1150 (s, CH_3 rock), 1070 (w, Ar), 1000 (w, P-Ar), 750 (s, P-C). MS (APCI): *m*/*z* 299.2 (100%), 227.1 (M^+ + H, 50), 209.1 (10).

1,4,4-Trimethyl-1,2,3,4-tetrahydrophosphinoline oxide (16). Due to the vast excess of reagents required, the reaction was split into two manageable halves. Polyphosphoric acid was prepared as above using phosphorus pentaoxide (1284 g, 9.04 mol) and phosphoric acid (609.9 ml, 3.65 mol). The crude oil of **19** (33 g, 0.146 mol) was added and the mixture heated at 120 °C for 15 hours, then poured into ice (2 l), allowed to cool and cautiously neutralised with sodium hydroxide pellets. The cloudy yellow mixture was extracted with dichloromethane (4 × 500 ml), the combined organic phases were washed with sodium hydrogen carbonate solution (1 M, 2 × 750 ml) and the solvent was removed yielding a brown oil. The total combined yield for these reactions was (47.79 g, 0.229 mol, 78.8%). δ_P: 26.3 (**16**). δ_H: 7.75 (1H, dd, $J_{(H-H)}$ 9.9 and 13.2 Hz, H^5), 7.35 (2H, m, H^3 + H^4), 7.24 (1H, t, H^6), 2.25 (1H, m, H^9), 2.03 (2H, m, H^{10}), 1.94 (1H, m, H^9), 1.65 (3H, d, $J_{(P-C)}$ 12.63 Hz, H^8), 1.25 (6H, d, $J_{(P-H)}$ 3.10 Hz, H^{12} + H^{13}). δ_C: 149.6 (d, $J_{(P-C)}$ 7 Hz, C^2), 130.9 (d, $J_{(P-C)}$ 2.4 Hz, C^4), 129.5 (d, $J_{(P-C)}$ 7.2 Hz, C^5), 128.7 (d, $J_{(P-C)}$ 10 Hz, C^1), 125.7 (d, $J_{(P-C)}$ 7 Hz, C^3), 34.5 (s, C^{11}), 33.9 (s, C^{10}), 30.0 (d, $J_{(P-C)}$ 7 Hz, $C^{12,13}$), 22.8 (d, $J_{(P-C)}$ 68 Hz, C^9), 16.7 (d, $J_{(P-C)}$ 50 Hz, C^8). ν_{max}/cm^{-1}: 3300 (br, m, O-H), 3050 (m, Ar-H), 2950 (s, C-H_2), 2900 (s, C-H_3), 2850 (m, C-H_3), 1640 (w, br, H_2O bend), 1590 (m, Ar C=C), 1480 (s, CH_3 asym + CH_2 scissor), 1430 (s, Ar-P), 1400 (s, CH_3 sym), 1300 (s), 1170 (s, P=O), 1150 (s, CH_3 rock), 1070 (m, Ar), 1000 (w, P-Ar), 750 (s, P-C). MS (APCI): *m*/*z* 417.6 ($2M^+$ + H, 100%), 209.3 (M^+ + H, 15).

1-(3-Hydroxy-3-methylbutyl)-4,4-dimethyl-1,2,3,4-tetrahydrophosphinoline oxide (20). Butyllithium solution (2.42 M, 113.5 ml, 0.275 mol) in hexane was added dropwise to an ice-cool solution of **16** (47.49 g, 0.229 mol) in THF (200 ml). The resultant mixture was stirred for 40 minutes before isobutylene oxide (38.1 g, 0.427 mmol) in THF (50 ml) was added and the brown solution allowed to warm to room temperature with stirring for 1 hour. The reaction was quenched with ammonium chloride solution (500 ml) and the aqueous phase was separated and extracted with diethyl ether (2 × 150 ml). The combined organic phases were dried over magnesium sulfate, filtered and the solvent was removed yielding a light brown oil (52.63 g, 0.188 mol, 82.1%). δ_P: 39.4 (5%), 37.5 (2%), 31.7 (**20**, 93%). δ_H: 7.75 (1H, m, H^4), 7.35 (2H, m, $H^{5,6}$), 7.14 (1H, d, $J_{(H-H)}$ 6.8 Hz, H^3), 2.32–2.05 (4H, m, $H^{9,14}$), 1.45–0.92 (4H, m, $H^{8,13}$), 1.34 (6H, s, $H^{11,12}$), 1.27 (6H, s, H^{16}). δ_C: 150.04 (C^2), 130.99 (C^4), 130.04 (d, $J_{(P-C)}$ 10 Hz, C^5), 126.39 (d, $J_{(P-C)}$ 110 Hz, C^1), 125.66 (d, $J_{(P-C)}$ 16.5 Hz, C^3), 68.57 (d, $J_{(P-C)}$ 10.7 Hz, C^{15}), 34.55 (C^{11}), 34.50 (d, $J_{(P-C)}$ 22.9 Hz, C^{14}), 33.83 (C^{10}), 30.10 (d, $J_{(P-C)}$ 19.5 Hz, C^{16}), 28.23 (d, $J_{(P-C)}$ 26.9 Hz, C^{13}), 27.98 (C^{12}), 24.82 (d, $J_{(P-C)}$ 69.9 Hz, C^9), 20.50 (d, $J_{(P-C)}$ 66.2 Hz, C^8). ν_{max}/cm^{-1}: 3350 (br, m, O-H), 3050 (m, Ar-H), 2950 (s, C-H_2), 2900 (s, C-H_3), 2850 (s, C-H_3), 1660 (w, br, H_2O bend), 1590 (m, Ar C=C), 1450 (s, CH_3 asym + CH_2 scissor), 1440 (s, Ar-P), 1400 (s, CH_3 sym), 1370 (s, CO-H), 1360 (s, CO-H), 1250 (s), 1200 (s, C-OH), 1170 (s, P=O), 1150 (s, CH_3 rock), 1070 (m, Ar), 1000 (m, P-Ar), 750 (s, P-C). MS (APCI): *m*/*z* 281.2 (M^+ + H, 100%).

1,1,6,6-Tetramethyl-2,3,6,7-tetrahydro-1*H*,5*H*-benzo[*ij*]oxide (18). Polyphosphoric acid was prepared as above by the addition of phosphorus pentaoxide (1509.43 g, 10.63 mol) to phosphoric acid (85% wt, 1610.2 ml, 13.96 mol). The crude oil of the monocyclised alcohol **20** (35.56 g, 0.127 mol) was added and the mixture heated at 120 °C for 15 hours. The reaction was cooled and poured into ice (1.5 l), then cautiously neutralised with sodium hydroxide (10 M) before extraction with dichloromethane (4 × 250 ml). The combined organic phases were washed with sodium hydrogen carbonate solution (1 M, 2 × 250 ml) and the solvent was removed yielding a dark brown oil (17.02 g, 0.064 mol). The brown oil was purified on a silica gel column eluted with ethyl acetate–methanol 8 : 1. The first dark brown fraction contained a mixture of products and was reserved for further chromatography. Upon removal of solvent, the second yellow fraction yielded a golden yellow hygroscopic fibrous powder. The residual yellow fraction, which was removed with methanol, contained no **18** by ^{31}P NMR spectroscopy. After several repeat purifications the total yield of yellow powder **18** obtained was (23.42 g, 88.58 mol, 48.14%). δ_P: 18.5. δ_H: 7.31 (1H, t, $J_{(H-H)}$ 8.9 Hz, H^4), 7.24 (2H, m, $H^{3,3'}$), 2.63–2.45 (2H, m, $H^{7,7'}$), 2.35–2.29 (2H, m, $H^{6,6'}$), 2.17–1.85 (4H, 2 overlapping multiplets, $H^{6,6'}$ + $H^{7,7'}$), 1.45 (6H, s, $C^{9,9'}$), 1.27 (6H, s, $C^{10,10'}$) (confirmed by ^{1}H COSY NMR). $\delta_{C\,+\,DEPT}$: 151.1 (CR_4, d, $J_{(P-C)}$ 10 Hz, $C^{2,2'}$), 132.2 (CH, C^4), 125.4 (CH, d, $J_{(P-C)}$ 10 Hz, $C^{3,3'}$), 123.5 (CR_4, d, $J_{(P-C)}$ 90 Hz, C^1), 137.0 (CR_4, $C^{8,8'}$), 33.9 (CH_2, d, $J_{(P-C)}$ 10 Hz, $C^{7,7'}$), 32.8 (CH_3, d, $J_{(P-C)}$ 10 Hz, $C^{9,9'}$), 31.7 (CH_3, $C^{10,10'}$), 22.8 (CH_2, d, $J_{(P-C)}$ 60 Hz, $C^{6,6'}$). ν_{max}/cm^{-1}: 3350 (br, m, O-H), 3050 (m, Ar-H), 2950 (s, C-H_2), 2900 (s, C-H_3), 2850 (m, C-H_3), 2200 (m), 1700 (m, br, H_2O bend), 1580 (s, Ar C=C), 1460 (s, CH_3 asym + CH_2 scissor), 1440 (s, Ar-P), 1400 (s, CH_3 sym), 1260 (s), 1170 (s, P=O), 1150 (s, CH_3 rock), 1070 (m, Ar), 1000 (m, P-Ar), 750 (s, P-C). MS (APCI): *m*/*z* 263.3 (M^+ + H, 100%).

The previously attempted synthesis of **18** from the less reactive alcohol **17** (route 3) following the method described above, required a reaction time of 5 days and produced a black oil which contained a mixture of compounds by ^{31}P NMR. δ_P (360 MHz): 31.3 (**15**, s, 10%), 27.0 (**16**, s, 10%), 24.0 (s, 18%), 22.5 (**18**, 62%). Any attempts to isolate the desired product failed.

The attempted reduction of this black oil by the previously reported method,[4] also produced a mixture of products by

^{31}P NMR. δ_P (360 MHz): 23.5 (**18**, 4.7%), −39.4 (5.6%), −44.7 (2.8%), −48.7 (18%), −59.1 (34%), −62.4 (13%), −63.4 (11.3%), −65.5 (18.9%), −70.0 (2.8%), −72.1 (2.8%). The reported ^{31}P NMR shift for the close analogue **10** is δ −26.3.[4]

1,1,6,6-Tetramethyl-2,3,6,7-tetrahydro-1*H*,5*H*-benzo[*ij*]-phosphinolizine (11). Trichlorosilane (179 ml, 133.38 g, 0.98 mol) was added dropwise to an ice-cool solution of **18** (13.47 g, 0.05 mol) in benzene (400 ml) and heated under reflux for 24 hours. The resultant solution was cooled in ice, sodium hydroxide (25%, 1796 ml) was added cautiously producing a brown mixture, which was extracted with diethyl ether (2 × 100 ml). The combined organic phases were dried over magnesium sulfate, the solvent was removed and the resultant brown residue was warmed in methanol. The pale yellow mixture produced was filtered from the brown, insoluble, oily solid and the solvent was removed yielding a pale yellow, oily solid (8.34 g, 0.033 mol, 68%). The procedure was repeated yielding a further 5.70 g (0.023 mol) this gave a total yield for the synthesis of 14.04 g, 0.057 mol, 13%. δ_P: −61.0. δ_H: 7.15 (2H, d, $J_{(H-H)}$ 7.7 Hz, $H^{3,3'}$), 7.05 (1H, t, $J_{(H-H)}$ 6.6 Hz, H^4), 1.95 (2H, m, $H^{6,6'}$), 1.8 (2H, m, $H^{7,7'}$), 1.6 (2H, m, $H^{7,7'}$), 1.45 (2H, m, $H^{6,6'}$), 1.25 (12H, s, equivalent CH_3 groups). δ_{C+DEPT}: 147.3 (CR_4, d, $J_{(P-C)}$ 10 Hz $C^{2,2'}$), 132.9 (CR_4, d, $J_{(P-C)}$ 20 Hz, C^1), 127.1 (CH, s, C^4), 121.8 (CH, s, $C^{3,3'}$), 38.2 (CR_4, s, $C^{8,8'}$), 34.5 (CH_2, s, $C^{7,7'}$), 30.7 (CH_3, s, $C^{9,9'}$), 28.45 (CH_3, d, $J_{(P-C)}$ 10 Hz, $C^{10,10'}$), 18.53 (CH_2, d, $J_{(P-C)}$ 10 Hz, $C^{6,6'}$). ν_{max}/cm^{-1}: 3050 (w, Ar-H), 2950 (m, C-H_2), 2900 (m, C-H_3), 2850 (w, C-H_3), 1580 (w, Ar C=C), 1480 (m, CH_3 asym + CH_2 scissor), 1440 (m, Ar-P), 1400 (w, CH_3 sym), 1250 (s), 1150 (s, CH_3 rock), 1070 (s, Ar), 1000 (s, P-Ar), 750 (m, P-C). MS (APCI): *m*/*z* 247.2 (M^+ + H, 100%).

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