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Synthesis and asymmetric catalytic application of chiral imidazolium–phosphines derived from (1*R*,2*R*)-*trans*-diaminocyclohexane

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Abstract

Reaction between a chiral imidazole–amine precursor derived from (1*R*,2*R*)-*trans*-diaminocyclohexane and P^1Cl (where $P^1 = PPh_2$, $P(1,3,5\text{-}Me_3C_6H_3)_2$, P(2,2′-*O*,*O*′-(1,1′-biphenyl), P((*R*)-(2,2′-*O*,*O*′-(1,1′-binaphthyl))) and P((*S*)-(2,2′-*O*,*O*′-(1,1′-binaphthyl)))) followed by RX (where R = ^{n}Pr, ^{i}Pr, $CHPh_2$, X = Br; R = ^{i}Pr, X = I), respectively, gives a selection of chiral imidazolium–phosphine compounds. Deprotonation of the imidazolium salt gives the corresponding NHC–P ligands that can be used in metal-mediated asymmetric catalytic applications. Catalytic reactions show that NHC–P ligands give a significantly greater rate of reaction for a palladium catalysed allylic substitution reaction in comparison to analogous di-NHC or NHC–imine ligands and that NHC–P hybrids are also effective for iridium catalysed transfer hydrogenation.

Keywords: Imidazolium salts; *N*-Heterocyclic carbenes; Catalysis; Allylic substitution; Transfer hydrogenation

1. Introduction

The application of *N*-heterocyclic carbene (NHC) ligands represents one of the most important developments in the field of metal-mediated catalysis over recent years and valuable contributions have been made to a diversity of reactions [1]. Commonly, NHC's have been described as alternatives to tertiary phosphines because of their similar electronic properties as ligands, although differences are apparent, particularly with respect to the much poorer π-acidity of NHC ligands [2–5]. Furthermore, the distinct structural differences of NHC compared to phosphines offer the possibility of modified or new reactivity, and the opportunity of novel structural motifs for asymmetric chemistry. The potential of chiral NHC for asymmetric catalytic applications has recently begun to be realised [6,7], however, the development and use of chiral NHC's still remains largely underdeveloped.

We have been interested in developing chiral hybrid NHC ligands principally derived from (1*R*,2*R*)-*trans*-diaminocyclohexane (Fig. 1) and have prepared new classes of chiral NHC based ligands, structurally characterised their metal complexes, and investigated applications to asymmetric catalysis. However, we have found that the ligand classes shown in Fig. 1 generally give slow rates for reactions that require a formal change in the oxidation state of the metal [8,9]. As many useful reactions encompass oxidative addition/reductive elimination steps we wished to prepare new ligands that would increase the rate of reaction. We assumed that one reason for the slow reaction rates is charge build-up during reductive elimination that cannot be relieved by the weakly π-acidic NHC or imine ligand moieties. We therefore instigated a short study to investigate the synthesis and application of NHC–phosphine hybrid ligands where it was anticipated that the phosphine moiety would provide some π-acidity

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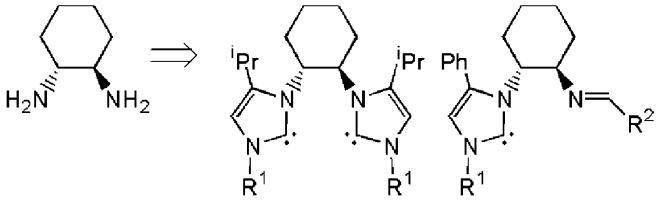


Fig. 1. Chiral diNHC and NHC–imine ligands.

consequently increasing the rate of reaction, and potentially, give a further structural modification inducing good enantioselectivity.

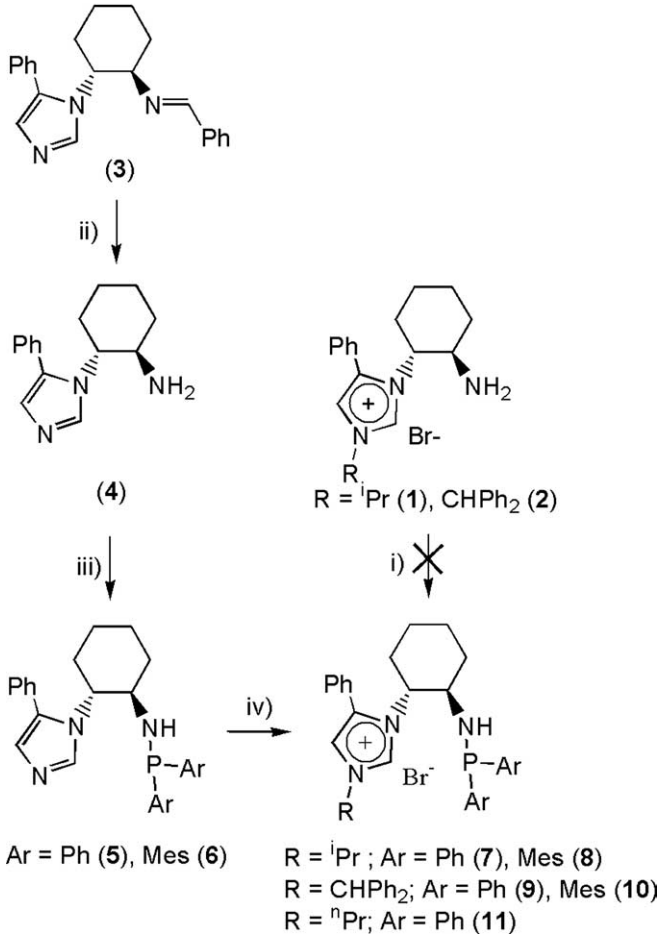
To date the number of reported NHC–phosphine hybrids is limited [10–17], however, chiral derivatives have been prepared and in two cases excellent ee's have been obtained for rhodium [11] and iridium [10] asymmetric hydrogenation reactions.

2. Results and discussion

2.1. Ligand synthesis

We wished to prepare a small library of chiral imidazolium–phosphine compounds that could serve as precursors to chelating NHC–P ligands. In previous work, we described the synthesis of the imidazolium salts **1** and **2** (Scheme 1) that we envisaged would be useful building blocks to a range of hybrid chiral ligands via functionalisation of the amine moiety [8,9]. Initial investigation focused on reactions between **1** or **2** and 1 equiv. of chlorodiarylphosphines and NEt_3; a strategy that has previously been used with success for the synthesis of analogous bisphosphines derived from *trans*-1,2-diaminocyclohexane [18,19]. However, we found that reaction was very solvent dependent and as judged by $^{31}P\{^1H\}$ NMR spectroscopy several phosphine containing species resulted. Unambiguous identification of the target product was not possible and separation using recrystallisation or column chromatography was unsuccessful. We assumed that the presence or proximity of the imidazolium salt was detrimental to the target reaction and therefore decided to attempt an alternative strategy where the phosphine moiety is introduced prior to imidazolium salt formation. Compound **3** shown in Scheme 1 has been described previously [9] and hydrolysis gives the imidazole–amine **4**. Reaction between **4** and 1 equiv. of Ar_2PCl (where Ar = Ph and 1,3,5-$Me_3C_6H_3$(Mes)) and NEt_3 gives the imidazole–aminophosphines **5** and **6** in good yield. Characterising data is consistent with the proposed formulations including a single signal in the $^{31}P\{^1H\}$ NMR spectrum at δ 34.7 and 20.2 ppm for **5** and **6**, respectively, that is similar to those observed for reported Ar_2PNR compounds [18].

Imidazolium salt formation is compatible with the phosphine functionality and reaction between **5** or **6** and hydrocarbylbromides, RBr (where R = ^{i}Pr, $CHPh_2$, ^{n}Pr) gives the corresponding imidazolium–aminophosphines **7**–**11**

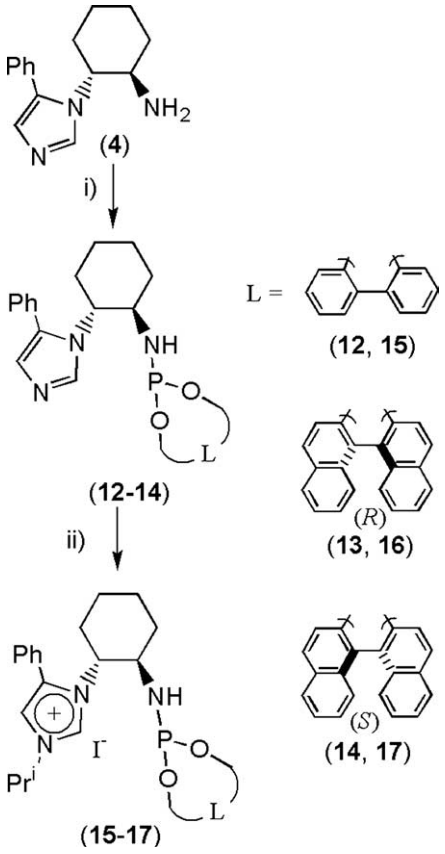


Scheme 1. (i) $ClPAr_2$, Et_3N, C_6H_6, 25 °C; (ii) HCl(aq); (iii) $ClPAr_2$, Et_3N, C_6H_6, 25 °C; (iv) RBr, MeCN, 50 °C.

(Scheme 1). In comparison to **5** and **6** the chemical shift of the $^{31}P\{^1H\}$ NMR spectra for **7**–**11** are not significantly different and in addition to signals attributable to the hydrocarbyl fragment in the ^1H NMR spectrum a signal at ca. 10 ppm is observed that is characteristic of an NC(*H*)N imidazolium proton.

Compounds **7**–**11** are hygroscopic yellow powders that in air decompose within minutes as judged by several new signals in the $^{31}P\{^1H\}$ NMR spectrum generally consistent with oxidation.

Using similar methodology for **5**–**11** the imidazole–phosphoramidates **12**–**14** were prepared in good yield, which can then be converted to imidazolium salt derivatives **15**–**17** as shown in Scheme 2. Phosphoramidates have been the focus of much attention and used very successfully in several metal-mediated catalytic reactions [20–25]. The three phosphite precursors shown in Scheme 2 were chosen partly to investigate the relative influence of chiral moieties in addition to those derived from 1,2-*trans*-diaminocyclohexane. *R* and *S*-binaphthol derived phosphoramidates have been shown to be very effective ligands for a range of asymmetric catalytic reactions and coupled with use of an achiral biphenyl derivative,

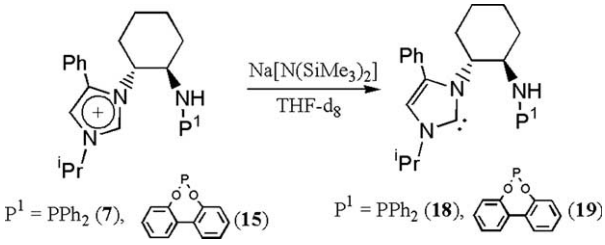


Scheme 2. (i) $ClPO_2L$, Et_3N, C_6H_6, 25 °C, (ii) $CH(CH_3)_2I$, 1,4-dioxane, 60 °C.

collectively some insight may be provided into the geometric elements of our ligands that affect catalysis. Furthermore, phosphoramidates are far less prone to oxidation that aminophosphines and can be handled in air.

Comparison between the NMR data of diastereoisomers **13** and **14** or **16** and **17** indicates that the phosphoramidate is independent of the imidazole and imidazolium moieties, respectively. For example the $^{31}P\{^1H\}$ NMR signals of **13**, **14**, **16** and **17** are observed at δ 149.5, 149.3, 150.0 and 150.4 ppm, respectively, and the ^1H NMR signals attributed to the imidazolium moieties of **16** and **17** are essentially identical.

For purposes of catalytic screening we wished to generate NHC–P ligands in situ and therefore investigated the deprotonation of representative imidazolium salts **7** and **15** on an NMR tube scale. Reaction between **7** or **15** and 1 equiv. of $Na[N(SiMe_3)_2]$ in THF-d_8 (Eq. (1)) gave quantitatively the corresponding NHC compounds **18** and **19**, respectively, as judged by ^1H, ^{13}C and ^{31}P NMR spectroscopy. Characteristic signals attributed to carbene N*C*N carbons in the $^{13}C\{^1H\}$ NMR spectra are observed at δ 212.7 and 216.2 ppm and imidazolium NC(*H*)N proton signals are absent in ^1H NMR spectra. In the absence of air compounds **18** and **19** are stable indefinitely at room temperature.

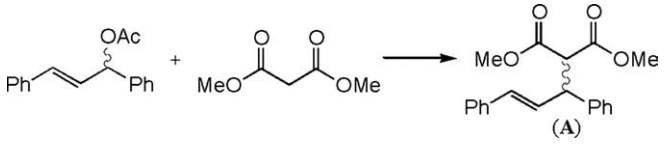


(1)

2.2. Catalysis

We have previously investigated the palladium catalysed allylic substitution reaction between (*E*)-1,3-diphenylprop-3-en-1-yl acetate and dimethylmalonate using chiral di-NHC and NHC–imine ligands and although in some cases an excellent enantiomeric excess (ee) could be obtained for the NHC–imine derivatives (up to 92% ee), the rate of reaction was somewhat disappointing [9]. Typically reactions required 15 h at 50 °C and the use of NaH as a base. Table 1 shows results of an analogous reaction using ligands **7**–**11** and **15**–**17**. The data in Table 1 shows that in this unoptimised study, using the NHC–phosphine ligands, the rate of reaction is significantly increased, even at 0 °C (entries 2 and 5), and that a weaker base can be used. The yield is more sensitive to variation of the phosphine moiety than the imidazolium *N*-substituent. Within 5 h yields of **A** are essentially quantitative for the ligands **7**, **9** and **11** (entries 2, 5 and 7) that contain a PPh_2 moiety whereas for ligands **8** and **10** (entries 3 and 6) containing a $P(Mes)_2$ moiety, reaction is incomplete. Furthermore, comparing entries 2 and 11 at 0 °C, the aminophosphine gives a greater rate

Table 1
Asymmetric allylic substitution between (*E*)-1,3-diphenylprop-3-en-1-yl acetate and dimethylmalonate[a]



Entry	Ligand	Temp (°C)	Yield (%)[b]	ee (%)[c]
1	**7**	25	98	38 (*S*)
2	**7**	0	98	45 (*S*)
3	**8**	25	70	17 (*S*)
4	**9**	25	98	12 (*S*)
5	**9**	0	98	22 (*S*)
6	**10**	25	64	8 (*S*)
7	**11**	25	98	24 (*S*)
8	**15**	25	97	17 (*S*)
9	**16**	25	95	11 (*R*)
10	**17**	25	86	42 (*S*)
11	**17**	0	0	

[a] 2.5 mol% $[Pd(n^3\text{-}C_3H_5)Cl]_2$, 5 mol% ligand, (*E*)-1,3-diphenylprop-3-en-1-yl acetate, 3.0 equiv. of dimethylmalonate, 2.9 equiv. of BSA, 0.02 equiv. of KOAc, CH_2Cl_2, 5 h.
[b] Determined from isolation of pure product by flash chromatography.
[c] Measured by ^1H NMR (270 MHz) with (+)-Eu(hfc)$_3$.

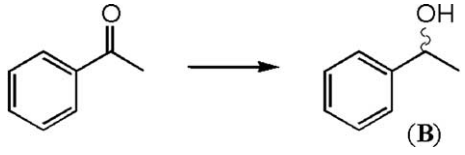
than a corresponding phosphoramidate **17**, although phosphoramidates **15** and **16** (entries 8 and 9) give near quantitative yield for **A** at 25 °C.

However, with respect to the ee values, the ligands in this study give disappointing results, the highest being ca. 42% *S*-**A** for ligands **7** and **17** (entries 2 and 10). The data corroborate the trend observed in previous work using NHC–imines where it was found that increasing steric bulk of the imine substituents significantly reduced the proportion of the *S* enantiomer. [9] Entry 9 shows that using a (*R*)-binaphthol derived phosphoramidate causes a switch in the preferred stereochemistry of the product from *S* to *R*, however using the analogous (*S*)-binaphthylphosphoramidate does not proportionally increase the quantity of *S* product.

Notwithstanding the disappointing ee's obtained for the allylic substitution reaction the significantly improved rates indicated that investigation into an alternative reaction was warranted. NHC ligands have previously been investigated for catalytic hydrogenation using both dihydrogen [26–28] and transfer hydrogenation methods [29–32], however, asymmetric examples are rare. Excellent enantioselectivities have been observed for direct hydrogenation [10,11,33,34] but transfer hydrogenation has received far less attention, the only reported example giving a max ee of 53% for reduction of acetophenone derivatives [13].

Table 2 contains data from iridium catalysed transfer hydrogenation of acetophenone using ligands **7**–**11** and **15**–**17**. The rates of reaction are similar to those reported for other iridium–NHC catalysts and in this context the presence of the phosphorus atom appears not to be advantageous. Furthermore, it can be seen that in contrast to the allylic substitution reaction the phosphoramidates give a greater rate of reaction than the aminophosphines (e.g., entry 1 vs. 11). However, in common with the allylic substitution reaction the $P(Mes)_2$ derivatives **8** and **10** (entries 3 and 7) give poorer yields that the PPh_2 derivatives **7**, **9** and **11** after the same length of time (entries 1, 5 and 9). The ee values are again not impressive and in general are similar to those obtained for the only other study on asymmetric transfer hydrogenation using NHC ligands [13]. Reactions were analysed after 1 and 5 h to determine if the ee is dependent on the reaction time as a consequence of potential racemisation of the product alcohol. Comparison of the 1 and 5 h samples does not indicate that there is any significant change in the ee as a function of time. In all reactions *R*-**B** is the predominant enantiomer except for ligand **16** (entries 13 and 14) that contains a phosphoramidate moiety derived from *R*-binaphthol, which favours *S*-**B**. In comparison ligand **17** that incorporates a *S*-binaphthyl moiety does slightly enhance the proportion of *R*-**B** (entries 15 and 16) in comparison to the related achiral biphenylphosphoramidate **15** (entries 11 and 12), however overall the enantiomeric ratio is considered quite insensitive to the imidazolium-*N* and phosphine substituents, respectively.

Table 2
Asymmetric transfer hydrogenation of benzophenone in isopropanol[a]



Entry	Ligand	Time (h)	Conversion (%)[b]	ee (%)[b]
1	**7**	1	70	18 (*R*)
2	**7**	5	93	15 (*R*)
3	**8**	1	46	15 (*R*)
4	**8**	5	74	13 (*R*)
5	**9**	1	68	34 (*R*)
6	**9**	5	89	31 (*R*)
7	**10**	1	44	21 (*R*)
8	**10**	5	68	21 (*R*)
9	**11**	1	72	16 (*R*)
10	**11**	5	90	11 (*R*)
11	**15**	1	84	15 (*R*)
12	**15**	5	95	12 (*R*)
13	**16**	1	87	26 (*S*)
14	**16**	5	94	20 (*S*)
15	**17**	1	86	37 (*R*)
16	**17**	5	96	34 (*R*)

[a] 0.25 mol% $[Ir(COD)Cl]_2$, 0.5 mol% ligand, 2.5 mol% KOH, acetophenone, $(CH_3)_2CHOH$, 80 °C.
[b] Determined by GC.

3. Conclusions

We have shown that NHC–P ligands are effective as ancillary ligands for an allylic substitution and a transfer hydrogenation reaction. Comparison with previous work indicates that the presence of the phosphine moiety increases the rate of the allylic substitution reaction with respect to related di-NHC and NHC–imine ligands. A possible reason for the increase in rate is the potential for the phosphine donor to act as a π-acid relieving charge build-up at the palladium atom. Other mechanisms to relieve charge build-up, such as widening of the C_{NHC}–Pd–P angle or dissociation of an ancillary ligand donor to give a 3-coordinate complex, are restricted by the constrained geometry of the palladacycle and because the ligand is chelating. Although the ee's reported for the two reactions investigated are to say the least modest, successful elaboration of the imidazole–amine **4** allows a wider array of ligands to be prepared than previously available from the corresponding imidazolium–amines. It is therefore envisaged that a more diverse library of chiral NHC-based ancillary ligands will therefore become available for screening studies.

4. Experimental

4.1. General procedures

All manipulations were performed under argon using standard Schlenk techniques unless stated otherwise. All

solvents were distilled under dinitrogen from a drying agent prior to use: calcium hydride (dichloromethane and acetonitrile), sodium benzophenone ketyl (diether ether, petroleum ether (40–60 °C) and tetrahydrofuran), or sodium (benzene). Reagents were purchased from Aldrich, Acros or Lancaster and used as supplied, except triethylamine, chlorodiphenylphosphine, 1-bromopropane, 2-bromopropane, 2-iodopropane and bromodiphenylmethane. Triethylamine was dried over calcium hydride and distilled under argon. Chlorodiphenylphosphine was distilled under reduced pressure. 1-Bromopropane, 2-bromopropane and 2-iodopropane were dried over $MgSO_4$ and fractionally distilled under argon. Bromodiphenylphosphine was sublimed under reduced pressure. Compounds **1**–**3** [9], chlorodimesitylphosphine, chlorobiphenylphosphite, and (*R*) and (*S*)-chlorobinaphthylphosphite, were prepared using literature procedures [35,36] NMR spectra were recorded at probe temperature on a Brüker AMX-300 (^{1}H, 300 MHz; ^{13}C, 75.5 MHz; ^{31}P, 121.5 MHz), Brüker AV-500 (^{1}H, 500 MHz; ^{13}C, 125 MHz; ^{31}P, 202.4 MHz), Jeol EX 270 (^{1}H, 270 MHz; ^{13}C, 67.9 MHz; ^{31}P, 109.4 MHz), or a Jeol ECX 400 (^{1}H, 400 MHz; ^{13}C, 100.5 MHz; ^{31}P, 161.8 MHz), respectively. Chemical shifts are described in parts per million downfield shift from $SiMe_4$ and are reported consecutively as position (δ_H, δ_C or δ_P), relative integral, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sext = sextet, sep = septet, m = multiplet, dd = doublet of doublet, br = broad, v = virtual), coupling constant (*J*/Hz) and assignment. Proton NMR spectra were referenced to the chemical shift of residual proton signals ($CHCl_3$ δ 7.27, C_6D_5H δ 7.16, $CDHCl_2$ δ 5.3, C_4D_7HO δ 3.58 and CD_2HCN δ 1.94). Carbon spectra were referenced to a ^{13}C resonance of the solvent ($CDCl_3$ δ77.16, C_6D_6 δ 128.06, CD_2Cl_2 δ 54.0, C_4D_8O δ 67.6 and CD_3CN δ 118.26). ^{13}C HSQC, PENDANT and Gradient HMBC experiments were performed using standard Brüker pulse sequences. Chemical ionisation (CI+), and Fast Atom Bombardmant (FAB+) mass spectra were recorded on a Micromass Autospec spectrometer, using 3-nitrobenzyl alcohol as the matrix. Electrospray (ES) mass spectra were recorded on a Micromass LCT using dichloromethane as the mobile phase. Major fragments were given as percentages of the base peak intensity (100%). Elemental Analyses were performed at the University of Manchester.

4.2. Synthesis of 1*R*-amino-2*R*-(5-phenylimidazolyl)-cyclohexane ($C(H)N^{H2}$) (**4**)

A mixture of 1*R*-(benzylidene-amino)-2*R*-(5-phenylimidazolyl)-cyclohexane, **3** (0.5 g, 1.5 mmol) and hydrochloric acid (10 mL, 1 M) was stirred at 25 °C for 2 h, filtered and the filtrate washed with CH_2Cl_2 (2 × 10 mL). The aqueous solution was cooled to 5 °C and an aqueous solution of sodium hydroxide (12 mL, 1 M) added drop wise to pH 9–11. The resulting cloudy precipitate was extracted with diethyl ether (2 × 10 mL) and the combined ether layers washed with water (10 mL), dried over $MgSO_4$ and filtered. Removal of the volatiles under reduced pressure gave **4** as a yellow solid. Yield: 0.33 g, 92%. MS (CI+): *m*/*z* 242 (100%) $[M + H]^+$. MS (HRCI+): Calc. for $C_{15}H_{20}N_3$: 242.1657. Found: 242.1662. ^{1}H NMR (chloroform-d_1, 270 MHz) 1.02–1.88 (8H, m, $^{c\text{-hex}}CH_2$), 2.02 (2H, m, NH_2), 3.04 (1H, m, $^{c\text{-hex}}CHN_{amine}$), 3.69 (1H, m, $^{c\text{-hex}}CHN^{imid}$), 7.06 (1H, s, $^{imid}NCHC$), 7.42 (5H, m, ^{Ph}CH), 7.69 (1H, s, $^{imid}NCHN$). $^{13}C\{^1H\}$ NMR (chloroform-d_1, 67.9 MHz) 24.6, 25.4, 34.1, 34.6 ($^{c\text{-hex}}CH_2$), 55.9 ($^{c\text{-hex}}CHN^{amine}$), 61.9 ($^{c\text{-hex}}CHN_{imid}$), 127.6 (N*C*HC), 128.0, 128.7, 129.4 (^{Ph}CH), 130.0 (^{imid}C(Ph)N), 133.9 ($^{Ph}C_{ipso}$), 134.7 (N*C*HN).

4.3. Synthesis of $C(H)N^{(H)PPh2}$ (**5**)

To a stirred solution of **4** (72 mg, 0.30 mmol) in benzene (3 mL) at 25 °C was added triethylamine (42 μL, 0.30 mmol) and chlorodiphenylphosphine (54 μL, 0.30 mmol). The resulting solution was stirred for 2 h to give a white precipitate. The mixture was filtered and the volatiles removed from the filtrate under reduced pressure to give **5** as a pale yellow solid. Yield: 109 mg, 85%. MS (FAB+): *m*/*z* 426 (61%) $[M + H]^+$, 442 (100%) $[M + H + O]^+$. MS (HRFAB+): Calc. for $C_{27}H_{29}N_3P$: 426.2099. Found: 426.2102. ^{1}H NMR (benzene-d_6, 270 MHz) δ 0.82 (3H, m, $^{c\text{-hex}}CH_2$), 1.30 (3H, m, $^{c\text{-hex}}CH_2$), 1.62 (1H, m, N*H*), 1.83 (2H, m, $^{c\text{-hex}}CH_2$), 3.06 (1H, m, $^{c\text{-hex}}CHN_{phos}$), 3.69 (1H, m, $^{c\text{-hex}}CHN_{imid}$), 6.95–7.32 (15H, m, ^{Ph}CH), 7.36 (1H, s, $^{imid}NCHC$), 7.76 (1H, s, $^{imid}NCHN$). $^{13}C\{^1H\}$ NMR (benzene-d_6, 67.9 MHz) δ 25.1, 25.4, 35.1 ($^{c\text{-hex}}CH_2$), 36.8 (d, $^3J_{P-C} = 4.8$, $^{c\text{-hex}}CH_2$), 60.8 (d, $^3J_{P-C} = 4.8$, $^{c\text{-hex}}CHN_{imid}$), 61.8 (d, $^2J_{P-C} = 27.7$, $^{c\text{-hex}}CHN_{phos}$), 127.4 (N*C*HC), 127.9, 128.1, 128.4, 128.6, 128.9 (^{Ph}CH), 128.8 (^{imid}C(Ph)N), 129.8 (^{Ph}CH), 131.0 (d, $^2J_{P-C} = 20.8$, ^{PPh}CH), 131.5 (^{Ph}CH), 131.6 (d, $^2J_{P-C} = 20.8$, ^{PPh}CH), 133.7 ($^{Ph}C_{ipso}$), 135.9 (br, N*C*HN), 143.3 (d, $^1J_{P-C} = 57.5$, $^{PPh}C_{ipso}$), 143.9 (d, $^1J_{P-C} = 63.1$, $^{PPh}C_{ipso}$). $^{31}P\{1H\}$ NMR (benzene-d_6, 109.4 MHz) δ 34.7 (s, $NPPh_2$).

4.4. Synthesis of $C(H)N^{(H)PMes2}$ (**6**)

To a stirred solution of **4** (72 mg, 0.30 mmol) in benzene (3 mL) at 25 °C was added triethylamine (42 μL, 0.30 mmol) and chlorodimesitylphosphine (91 mg, 0.30 mmol). The resulting solution was stirred for 5 h to give a white precipitate. Workup as for **5** gives **6** as a pale yellow solid. Yield: 136 mg, 89%. MS (FAB+): *m*/*z* 510 (76%) $[M + H]^+$, 526 (100%) $[M + H + O]^+$. MS (HRFAB+): Calc. for $C_{33}H_{41}N_3P$: 510.3038. Found: 510.3048. ^{1}H NMR (benzene-d_6, 270 MHz) δ 0.61–2.62 (8H, m, $^{c\text{-hex}}CH_2$), 1.26 (1H, m, N*H*), 2.07 (3H, s, $^{p\text{-Mes}}CH_3$), 2.10 (3H, s, $^{o\text{-Mes}}H_3$), 2.27 (6H, s, $^{o\text{-Mes}}CH_3$), 2.30 (6H, s, $^{o\text{-Mes}}CH_3$), 3.07 (1H, m, $^{c\text{-hex}}CHN_{phos}$), 3.70 (1H, m, $^{c\text{-hex}}CHN_{imid}$), 6.52–6.72 (4H, m, $^{m\text{-Mes}}CH$), 7.00–7.14 (5H, m, ^{Ph}CH), 7.24 (1H, s, $^{imid}NCHC$), 7.50 (1H, s, $^{imid}NCHN$). $^{13}C\{^1H\}$ NMR (benzene-d_6, 67.9 MHz) δ 22.3 ($^{Mes}CH_3$), 22.5 (d, $^3J_{P-C} = 4.1$, $^{Mes}CH_3$), 22.8

($^{Mes}CH_3$), 23.1 (d, $^3J_{P-C} = 4.1$, $^{Mes}CH_3$), 24.6, 25.5 ($^{c\text{-hex}}CH_2$), 33.8 (d, $^3J_{P-C} = 5.5$, $^{c\text{-hex}}CH_2$), 34.4 ($^{c\text{-hex}}CH_2$), 60.6 (d, $^2J_{P-C} = 25.9$, $^{c\text{-hex}}CHN_{phos}$), 61.1 (br, $^{c\text{-hex}}CHN_{imid}$), 127.8 (N*C*HC), 128.7, 129.8, 130.1, 130.4, 130.6 ($^{aromatic}CH$), 131.0 (^{imid}C(Ph)N), 133.8 ($^{Ph}C_{ipso}$), 135.2 (br, N*C*HN), 136.6 ($^{Mes}C_{ipso}$), 136.7 (d, $^2J_{P-C} = 24.9$, $^{Mes}C_{ipso}$), 137.6 (d, $^2J_{P-C} = 23.8$, $^{Mes}C_{ipso}$), 136.9 ($^{Mes}C_{ipso}$), 140.4 (d, $^1J_{P-C} = 43.5$, $^{PMes}C_{ipso}$), 140.7 (d, $^1J_{P-C} = 44.6$, $^{PMes}C_{ipso}$). $^{31}P\{1H\}$ NMR (benzene-d_6, 121.50 MHz) δ 20.2 (s, N*P*Mes$_2$).

4.5. Synthesis of [^{iPr}C(H)N$^{(H)PPh2}$][Br] (7)

In an ampoule sealed with a Teflon stopcock an acetonitrile solution (3 mL) of **5** (85 mg, 0.20 mmol) and 2-bromopropane (20 μL, 0.21 mmol) was stirred at 50 °C for 72 h. The solution was reduced in volume to ca. 0.5 mL under reduced pressure and added dropwise to benzene (10 mL) to give an off white precipitate that was filtered, washed with benzene (2 × 5 mL) and dried under reduced pressure to give **7** as a pale yellow solid. Yield: 90 mg, 82%. MS (FAB+): *m*/*z* 468 (100%) $[M - Br]^+$. MS (HRFAB+): Calc. for $C_{30}H_{35}N_3P$: 468.2569. Found: 468.2580. ^1H NMR (acetonitrile-d_3, 300 MHz) δ 1.12–2.21 (8H, m, $^{c\text{-hex}}CH_2$), 1.53 (3H, d, $^3J_{H-H} = 6.7$, CH(CH_3)$_2$), 1.54 (3H, d, $^3J_{H-H} = 6.7$, CH_3), 3.31 (1H, m, N*H*), 3.80 (1H, m, $^{c\text{-hex}}CHN_{phos}$), 4.10 (1H, m, $^{c\text{-hex}}CHN_{imid}$), 4.65 (1H, vsep, $^3J_{H-H} = 6.7$, C*H*(CH$_3$)$_2$), 7.09–7.58 (15H, m, ^{Ph}CH), 7.46 (1H, s, $^{imid}NCHC$), 10.06 (1H, s, $^{imid}NCHN$). $^{13}C\{^1H\}$ NMR (acetonitrile-d_3, 75.5 MHz) δ 22.9, 23.1 ($^{c\text{-hex}}CH_2$), 25.5, 25.6 (*C*H$_3$), 34.7 ($^{c\text{-hex}}CH_2$), 36.9 (d, $^3J_{P-C} = 4.1$, $^{c\text{-hex}}CH_2$), 54.2 (*C*H(CH$_3$)$_2$), 61.5 (d, $^2J_{P-C} = 29.8$, $^{c\text{-hex}}CHN_{phos}$), 64.9 (d, $^3J_{P-C} = 6.2$, $^{c\text{-hex}}CHN_{imid}$), 118.7 (N*C*HC), 126.6 (^{imid}C(Ph)N), 129.0, 129.1, 129.3, 129.5, 129.9, 130.0 (^{Ph}CH), 130.9 (d, $^2J_{P-C} = 24.9$, ^{Ph}CH), 131.0 (^{Ph}CH), 131.2 (d, $^2J_{P-C} = 24.2$, ^{Ph}CH), 135.7 (br, N*C*HN), 136.4 ($^{Ph}C_{ipso}$), 144.0 (d, $^1J_{P-C} = 64.5$, $^{PPh}C_{ipso}$), 144.2 (d, $^1J_{P-C} = 71.4$, $^{PPh}C_{ipso}$). $^{31}P\{1H\}$ NMR (acetonitrile-d_3, 121.5 MHz) δ 37.7 (s, N*P*Ph$_2$). Anal. Calc. for; $C_{30}H_{35}N_3BrP$; C, 65.69; H, 6.43; N, 7.66. Found: C, 65.41; H, 6.30; N, 7.56%.

4.6. Synthesis of [^{iPr}C(H)N$^{(H)PMes2}$][Br] (8)

In an ampoule sealed with a Teflon stopcock a mixture of acetonitrile (3 mL), **6** (102 mg, 0.20 mmol) and 2-bromopropane (20 μL, 0.21 mmol) was stirred at 50 °C for 72 h. Workup as for **7** gives **8** as a pale yellow solid. Yield: 95 mg, 75%. MS (FAB+): *m*/*z* 552 (100%) $[M - Br]^+$. MS (HRFAB+): Calc. for $C_{36}H_{47}N_3P$: 552.3508. Found: 552.3519. ^1H NMR (acetonitrile-d_3, 300 MHz) δ 0.98–2.58 (8H, m, $^{c\text{-hex}}CH_2$), 1.57 (3 H, d, $^3J_{H-H} = 6.6$, CH(CH_3)$_2$), 1.58 (3 H, d, $^3J_{H-H} = 6.6$, CH_3), 2.13 (3 H, s, $^{o\text{-Mes}}H_3$), 2.15 (3H, s, $^{o\text{-Mes}}H_3$), 2.32 (6H, s, $^{o\text{-Mes}}CH_3$), 2.35 (6H, s, $^{o\text{-Mes}}CH_3$), 3.36 (1H, m, N*H*), 3.76 (1H, m, $^{c\text{-hex}}CHN_{phos}$), 4.09 (1H, m, $^{c\text{-hex}}CHN_{imid}$), 4.68 (1H, vsep, $^3J_{H-H} = 6.6$, C*H*(CH$_3$)$_2$), 6.56–6.82 (4H, m, $^{m\text{-Mes}}CH$), 7.11–7.30 (5H, m, ^{Ph}CH), 7.39 (1H, s, $^{imid}NCHC$), 10.14 (1H, s, $^{imid}NCHN$). $^{13}C\{^1H\}$ NMR (acetonitrile-d_3, 75.5 MHz) δ 21.9, 22.5 ($^{Mes}CH_3$), 22.8 (d, $^3J_{P-C} = 4.4$, $^{Mes}CH_3$), 23.1 (d, $^3J_{P-C} = 4.4$, $^{Mes}CH_3$), 23.2, 23.4 ($^{c\text{-hex}}CH_2$), 25.9, 26.0 (*C*H$_3$), 35.2 (d, $^3J_{P-C} = 5.27$, $^{c\text{-hex}}CH_2$), 36.1 ($^{c\text{-hex}}CH_2$), 55.0 (*C*H(CH$_3$)$_2$), 62.0 (d, $^2J_{P-C} = 28.2$, $^{c\text{-hex}}CHN_{phos}$), 65.6 (d, $^3J_{P-C} = 5.9$, $^{c\text{-hex}}CHN_{imid}$), 120.2 (N*C*HC), 126.4 (^{imid}C(Ph)N), 129.3, 129.7, 129.8, 130.1, 131.3 ($^{aromatic}CH$), 134.5 (br, N*C*HN), 135.1 ($^{Ph}C_{ipso}$), 137.0 (d, $^2J_{P-C} = 23.6$, $^{Mes}C_{ipso}$), 137.3 (d, $^2J_{P-C} = 23.8$, $^{Mes}C_{ipso}$), 137.7, 138.0 ($^{Mes}C_{ipso}$), 141.8.0 (d, $^1J_{P-C} = 48.7$, $^{PMes}C_{ipso}$), 142.5 (d, $^1J_{P-C} = 50.0$, $^{PMes}C_{ipso}$). $^{31}P\{1H\}$ NMR (acetonitrile-d_3, 121.5 MHz) δ 23.4 (s, N*P*Mes$_2$). Anal. Calc. for $C_{36}H_{47}N_3BrP$: C, 68.34; H, 7.49; N, 6.64. Found: C, 68.53; H, 7.61; N, 6.47%.

4.7. Synthesis of [$^{CH(Ph)2}$C(H)N$^{(H)PPh2}$][Br] (9)

In an ampoule sealed with a Teflon stopcock an acetonitrile solution (3 mL) of **5** (85 mg, 0.20 mmol) and bromodiphenylmethane (52 mg, 0.21 mmol) was stirred at 50 °C for 72 h. Workup as for **7** gives **9** as a yellow solid. Yield: 106 mg, 79%. MS (FAB+): *m*/*z* 592 (100%) $[M - Br]^+$. MS (HRFAB+): Calc. for $C_{40}H_{39}N_3P$: 592.2882. Found: 592.2874. ^1H NMR (acetonitrile-d_3, 300 MHz) δ 0.95–2.28 (8H, m, $^{c\text{-hex}}CH_2$), 3.37 (1H, m, N*H*), 3.59 (1H, m, $^{c\text{-hex}}CHN_{phos}$), 4.14 (1H, m, $^{c\text{-hex}}CHN_{imid}$), 6.72–7.87 (25H, m, ^{Ph}CH), 6.97 (1H, s, C*H*(C$_6$H$_5$)$_2$), 7.64 (1H, s, $^{imid}NCHC$), 9.97 (1H, s, $^{imid}NCHN$). $^{13}C\{^1H\}$ NMR (acetonitrile-d_3, 75.5 MHz) δ 23.0, 23.3, 34.9 ($^{c\text{-hex}}CH_2$), 37.1 (d, $^3J_{P-C} = 4.1$, $^{c\text{-hex}}CH_2$), 61.7 (*C*HPh$_2$), 63.1 (d, $^2J_{P-C} = 28.5$, $^{c\text{-hex}}CHN_{phos}$), 65.2 (d, $^3J_{P-C} = 6.0$, $^{c\text{-hex}}CHN_{imid}$), 117.3 (N*C*HC), 125.9 (^{imid}C(Ph)N), 127.6, 127.7, 128.6, 128.9, 129.0, 129.1, 129.3, 129.5, 130.1, 130.5, 130.7, 130.8, 131.0 (^{Ph}CH), 131.2 (d, $^2J_{P-C} = 24.8$, ^{Ph}CH), 131.4 (d, $^2J_{P-C} = 24.5$, ^{Ph}CH), 135.6 ($^{Ph}C_{ipso}$), 135.9 (br, N*C*HN), 136.3, 136.9 ($^{Ph}C_{ipso}$), 144.4 (d, $^1J_{P-C} = 59.8$, $^{PPh}C_{ipso}$), 144.6 (d, $^1J_{P-C} = 68.4$, $^{PPh}C_{ipso}$). $^{31}P\{1H\}$ NMR (acetonitrile-d_3, 121.5 MHz) δ 37.9 (s, N*P*Ph$_2$). Anal. Calc. for $C_{40}H_{39}N_3BrP$: C, 71.42; H, 5.84; N, 6.25. Found: C, 71.63; H, 5.79; N, 6.37%.

4.8. Synthesis of [$^{CH(Ph)2}$C(H)N$^{(H)PMes2}$] [Br] (10)

In an ampoule sealed with a Teflon stopcock a mixture of acetonitrile (3 mL), **6** (85 mg, 0.20 mmol) and bromodiphenylmethane (52 mg, 0.21 mmol) was stirred at 50 °C for 72 h. Workup as for **7** gives **10** as a yellow solid. Yield: 109 mg, 72%. MS (FAB+): *m*/*z* 676 (100%) $[M - Br]^+$. MS (HRFAB+): Calc. for $C_{46}H_{51}N_3P$: 676.3821. Found: 676.3824. ^1H NMR (acetonitrile-d_3, 300 MHz) δ 0.92–2.63 (8H, m, $^{c\text{-hex}}CH_2$), 2.20 (3H, s, $^{o\text{-Mes}}H_3$), 2.23 (3H, s, $^{o\text{-Mes}}H_3$), 2.46 (6H, s, $^{o\text{-Mes}}CH_3$), 2.48 (6H, s, $^{o\text{-Mes}}CH_3$), 3.10 (1H, m, N*H*), 3.67 (1H, m, $^{c\text{-hex}}CHN_{phos}$), 4.05 (1H, m, $^{c\text{-hex}}CHN_{imid}$), 6.68–7.78 (19H, m, ^{Ph}CH), 6.91 (1H, s, C*H*(C$_6$H$_5$)$_2$), 7.35 (1H, s, $^{imid}NCHC$), 10.09 (1H, s, $^{imid}NCHN$). $^{13}C\{^1H\}$ NMR (acetonitrile-d_3, 75.5 MHz) δ

21.1, 21.6 ($^{Mes}CH_3$), 22.0 (d, $^3J_{P-C} = 4.3$, $^{Mes}CH_3$), 22.5 (d, $^3J_{P-C} = 4.2$, $^{Mes}CH_3$), 22.9, 23.1 ($^{c\text{-hex}}CH_2$), 34.9 (d, $^3J_{P-C} = 4.9$, $^{c\text{-hex}}CH_2$), 35.7 ($^{c\text{-hex}}CH_2$), 61.3 ($CHPh_2$), 63.8 (d, $^2J_{P-C} = 26.1$, $^{c\text{-hex}}CHN_{phos}$), 66.0 (d, $^3J_{P-C} = 5.0$, $^{c\text{-hex}}CHN_{imid}$), 119.5 (NCHC), 125.1 ($^{imid}C$(Ph)N), 128.7, 128.9, 129.0, 129.3, 129.4, 129.7, 129.8, 130.1, 131.3, 131.4, 131.6 ($^{aromatic}CH$), 134.5 (br, NCHN), 135.8, 136.5 ($^{aromatic}C_{ipso}$), 137.1 (d, $^2J_{P-C} = 24.67$, $^{aromatic}C_{ipso}$), 137.5 (d, $^2J_{P-C} = 24.3$, $^{aromatic}C_{ipso}$), 137.7 ($^{aromatic}C_{ipso}$), 141.8 (d, $^1J_{P-C} = 45.5$, $^{PMes}C_{ipso}$), 142.5 (d, $^1J_{P-C} = 48.3$, $^{PMes}C_{ipso}$). $^{31}P\{1H\}$ NMR (acetonitrile-d_3, 121.5 MHz) δ 23.6 (s, $NPMes_2$). Anal. Calc. for $C_{30}H_{33}N_3BrP$: C, 73.00; H, 6.79; N, 5.55. Found: C, 73.15; H, 6.91; N, 5.50%.

4.9. Synthesis of $[^{nPr}C(H)N^{(H)PPh2}][Br]$ (11)

In an ampoule sealed with a Teflon stopcock an acetonitrile solution (3 mL) of **5** (85 mg, 0.20 mmol) and 1-bromopropane (20 μL, 0.21 mmol) was stirred at 50 °C for 72 h. Workup as for **7** gives **11** as a pale yellow solid. Yield: 92 mg, 84%. MS (FAB+): *m/z* 468 (100%) $[M - Br]^+$. MS (HRFAB+): Calc. for $C_{30}H_{35}N_3P$: 468.2569. Found: 468.2566. ^1H NMR (acetonitrile-d_3, 270 MHz) δ 0.94 (3H, t, $^3J_{H-H} = 7.3$, CH_2CH_3), 1.14–2.33 (8H, m, $^{c\text{-hex}}CH_2$), 1.90 (2H, sex, $^3J_{H-H} = 7.3$, CH_2CH_3), 3.27 (1H, m, NH), 3.67 (1H, m, $^{c\text{-hex}}CHN_{phos}$), 4.10 (1H, m, $^{c\text{-hex}}CHN_{imid}$), 4.13 (2H, t, $^3J_{H-H} = 7.3$, NCH_2CH_2), 7.11–7.68 (15H, m, ^{Ph}CH), 7.38 (1H, s, $^{imid}NCHC$), 9.93 (1H, s, $^{imid}NCHN$). $^{13}C\{^1H\}$ NMR (acetonitrile-d_3, 67.9 MHz) δ 11.5 (CH_2CH_3), 24.5 (CH_2CH_3), 26.0, 26.2, 35.4 ($^{c\text{-hex}}CH_2$), 37.6 (d, $^3J_{P-C} = 4.0$, $^{c\text{-hex}}CH_2$), 52.6 (NCH_2CH_2), 62.6 (d, $^2J_{P-C} = 27.1$, $^{c\text{-hex}}CHN_{phos}$), 65.3 (d, $^3J_{P-C} = 5.4$, $^{c\text{-hex}}CHN_{imid}$), 120.8 (NCHC), 127.2 ($^{imid}C$(Ph)N), 129.1, 129.4, 129.5, 129.7, 130.0, 130.5, 131.3 (^{Ph}CH), 131.6 (d, $^2J_{P-C} = 23.4$, ^{Ph}CH) 131.9 (d, $^2J_{P-C} = 23.3$, ^{Ph}CH), 137.2 ($^{Ph}C_{ipso}$), 137.4 (br, NCHN), 143.2 (d, $^1J_{P-C} = 66.1$, $^{PPh}C_{ipso}$), 143.5 (d, $^1J_{P-C} = 73.5$, $^{PPh}C_{ipso}$). $^{31}P\{1H\}$ NMR (acetonitrile-d_3, 109.4 MHz) δ 34.3 (s, $NPPh_2$). Anal. Calc. for $C_{30}H_{35}N_3BrP$: C, 65.69; H, 6.43; N, 7.66. Found: C, 65.39; H, 6.35; N, 7.51%.

4.10. Synthesis of $C(H)N^{(H)PO2BiPh}$ (12)

To a stirred solution of **4** (48 mg, 0.20 mmol) in benzene (2 mL) at 25 °C was added triethylamine (28 μL, 0.20 mmol) and chlorobiphenylphosphite (50 mg, 0.20 mmol). The resulting solution was stirred for 5 h giving a white precipitate. The mixture was filtered and the volatiles removed from the filtrate under reduced pressure to give **12** as a yellow solid. Yield: 71 mg, 78%. MS (FAB+): *m/z* 456 (100%) $[M + H]^+$. MS (HRFAB+): Calc. for $C_{27}H_{27}N_3O_2P$: 456.1841. Found: 456.1826. ^1H NMR (benzene-d_6, 270 MHz) δ 0.43 (1H, m, $^{c\text{-hex}}CH_2$), 0.85 (2H, m, $^{c\text{-hex}}CH_2$), 1.31 (3H, m, $^{c\text{-hex}}CH_2$), 1.78 (2H, m, $^{c\text{-hex}}CH_2$), 2.79 (1H, m, NH), 3.12 (1H, m, $^{c\text{-hex}}CHN_{phos}$), 3.48 (1H, m, $^{c\text{-hex}}CHN_{imid}$), 7.01–7.49 (13H, m, ^{Ph}CH), 7.53 (1H, s, $^{imid}NCHC$), 7.73 (1H, s, $^{imid}NCHN$). $^{13}C\{^1H\}$ NMR (benzene-d_6, 67.9 MHz) δ 25.0, 25.2, 34.5 ($^{c\text{-hex}}CH_2$), 36.1 (d, $^3J_{P-C} = 4.1$, $^{c\text{-hex}}CH_2$), 55.4 (d, $^2J_{P-C} = 25.9$, $^{c\text{-hex}}CHN_{phos}$), 60.7 (br, $^{c\text{-hex}}CHN_{imid}$), 122.6, 122.8, 124.7, 125.0 (^{BiPh}CH), 127.9 (NCHC), 128.6, 128.8, 129.0, 129.5.1, 129.7, 129.9, 130.1 ($^{aromatic}CH$), 131.7 (^{imid}C(Ph)N), 132.1 (d, $^3J_{P-C} = 3.12$, $^{BiPh}C_{ipso}$), 132.2 (d, $^3J_{P-C} = 3.24$, $^{BiPh}C_{ipso}$), 133.9 ($^{Ph}C_{ipso}$), 135.9 (NCHN), 150.4 (d, $^2J_{P-C} = 5.1$, $^{O2BiPh}C_{ipso}$), 150.9 (d, $^2J_{P-C} = 4.1$, $^{O2BiPh}C_{ipso}$). $^{31}P\{1H\}$ NMR (benzene-d_6, 109.4 MHz) δ 148.9 (s, NPO_2BiPh).

4.11. Synthesis of $C(H)N^{(H)PO2Binap(R)}$ (13)

To a stirred solution of **4** (48 mg, 0.20 mmol) in benzene (2 mL) at 25 °C was added triethylamine (28 μL, 0.20 mmol) and (*R*)-chlorobinaphthylphosphite (70 mg, 0.20 mmol). Workup as for **12** gives **13** as a yellow solid. Yield: 86 mg, 77%. MS (FAB+): *m/z* 556 (100%) $[M + H]^+$. MS (HRFAB+): Calc. for $C_{35}H_{31}N_3O_2P$: 556.2154. Found: 556.2168. ^1H NMR (benzene-d_6, 270 MHz) δ 0.36 (1H, m, $^{c\text{-hex}}CH_2$), 0.71 (1H, m, $^{c\text{-hex}}CH_2$), 0.89 (1H, m, $^{c\text{-hex}}CH_2$), 1.27 (3H, m, $^{c\text{-hex}}CH_2$), 1.66 (1H, m, $^{c\text{-hex}}CH_2$), 1.78 (1H, m, $^{c\text{-hex}}CH_2$), 2.75 (1H, m, NH), 3.02 (1H, m, $^{c\text{-hex}}CHN_{phos}$), 3.40 (1H, m, $^{c\text{-hex}}CHN_{imid}$), 6.90–7.71 (17H, m, $^{aromatic}CH$), 7.33 (1H, s, $^{imid}NCHC$), 7.67 (1H, s, $^{imid}NCHN$). $^{13}C\{^1H\}$ NMR (benzene-d_6, 75.5 MHz) δ 25.1, 25.2, 34.4 ($^{c\text{-hex}}CH_2$), 35.8 (d, $^3J_{P-C} = 2.7$, $^{c\text{-hex}}CH_2$), 55.8 (d, $^2J_{P-C} = 27.1$, $^{c\text{-hex}}CHN_{phos}$), 61.0 (br, $^{c\text{-hex}}CHN_{imid}$), 122.5, 123.0 ($^{aromatic}CH$), 124.5, 124.6 ($^{BiNap}C$), 124.9, 125.0, 126.4, 126.5, 127.2, 127.4 ($^{aromatic}CH$), 127.8 (NCHC), 127.9, 128.2, 128.5, 128.7, 128.8, 129.6, 130.2 ($^{aromatic}CH$), 130.9 (^{imid}C(Ph)N), 131.4, 131.9 ($^{BiNap}C$), 133.2, 133.3 ($^{BiNap}C_{ipso}$), 134.3 ($^{Ph}C_{ipso}$), 135.6 (br, NCHN), 147.8 (d, $^2J_{P-C} = 3.4$, $^{O2BiNap}C_{ipso}$), 150.1 ($^{O2BiNap}C_{ipso}$). $^{31}P\{1H\}$ NMR (benzene-d_6, 109.4 MHz) δ 149.5 (s, $NPO_2BiNap(R)$).

4.12. Synthesis of $C(H)N^{(H)PO2Binap(S)}$ (14)

To a stirred solution of **4** (48 mg, 0.20 mmol) in benzene (2 mL) at 25 °C was added triethylamine (28 μL, 0.20 mmol) and (*S*)-chlorobinaphthylphosphite (70 mg, 0.20 mmol). The resulting solution was stirred for 5 h giving a white precipitate. Workup as for **12** gave **14** as a yellow solid. Yield: 91 mg, 82%. MS (FAB+): *m/z* 556 (100%) $[M + H]^+$. MS (HRFAB+): Calc. for $C_{35}H_{31}N_3O_2P$: 556.2154. Found: 556.2171. ^1H NMR (benzene-d_6, 300 MHz) δ 0.51–1.85 (8H, m, $^{c\text{-hex}}CH_2$), 3.15 (2H, m, $NH + {}^{c\text{-hex}}CHN_{phos}$), 3.52 (1H, m, $^{c\text{-hex}}CHN_{imid}$), 6.89–7.71 (17H, m, $^{aromatic}CH$), 7.40 (1H, s, $^{imid}NCHC$), 7.66 (1H, s, $^{imid}NCHN$). $^{13}C\{^1H\}$ NMR (benzene-d_6, 75.5 MHz) δ 24.9, 25.1, 34.8 ($^{c\text{-hex}}CH_2$), 37.0 (d, $^3J_{P-C} = 2.7$, $^{c\text{-hex}}CH_2$), 55.1 (d, $^2J_{P-C} = 22.1$, $^{c\text{-hex}}CHN_{phos}$), 60.6 (br, $^{c\text{-hex}}CHN_{imid}$), 122.2, 123.2 ($^{aromatic}CH$), 123.9, 124.5 ($^{BiNap}C$), 124.9, 125.0, 126.4, 126.5, 127.2, 127.3 ($^{aromatic}CH$), 127.7 (NCHC), 128.5, 128.7, 128.8, 128.9, 129.9, 130.0, 130.7 ($^{aromatic}CH$), 131.3 ($^{BiNap}C$), 131.4 (^{imid}C(Ph)N),

131.9 ($^{BiNap}C$), 133.2, 133.3 ($^{BiNap}C_{ipso}$), 133.4 ($^{Ph}C_{ipso}$), 136.4 (br, NCHN), 148.5 (d, $^{2}J_{P-C} = 4.8$, $^{O2BiPh}C_{ipso}$), 150.1 (d, $^{2}J_{P-C} = 1.3$, $^{O2BiPh}C_{ipso}$). ^{31}P{1H} NMR (benzene-d_6, 121.5 MHz) δ 149.8 (br, NPO$_2$BiNap(S)).

4.13. Synthesis of [$^{iPr}C(H)N^{(H)PO2BiPh}$][I] (15)

In an ampoule sealed with a Teflon stopcock a 1,4-dioxane solution (2 mL) of **12** (68 mg, 0.15 mmol) and 2-iodopropane (20 μL, 0.20 mmol) was stirred at 60 °C for 72 h, giving a yellow precipitate. Removal of the volatiles under reduced pressure gave an yellow solid that was dissolved in CH_2Cl_2 (0.5 mL) and added drop wise to benzene (10 mL) to give an off white precipitate that was filtered, washed with benzene (2 × 5 mL) and dried under reduced pressure to give **15** as an off white solid. Yield: 73 mg, 78%. MS (FAB+): m/z 498 (100%) $[M + I]^+$. MS (HRFAB+): Calc. for $C_{30}H_{33}N_3O_2P$: 498.2310. Found: 498.2316. ^{1}H NMR (dichloromethane-d_2, 400 MHz) δ 1.16–2.12 (8H, m, $^{c\text{-hex}}CH_2$), 1.66 (3H, d, $^{3}J_{H-H} = 6.7$, CH(CH_3)$_2$), 1.69 (3H, d, $^{3}J_{H-H} = 6.7$, CH(CH_3)$_2$), 2.18 (1H, m, NH), 3.72–4.18 (2H, m, $^{c\text{-hex}}CHN_{phos}$ + $^{c\text{-hex}}CHN_{imid}$), 4.87 (1H, vsep, $^{3}J_{H-H} = 6.7$ Hz, CH(CH$_3$)$_2$), 6.94 (1H, m, ^{BiPh}CH), 7.01 (1H, m, ^{BiPh}CH), 7.21–7.50 (11H, m, $^{aromatic}CH$), 7.33 (1H, s, ^{imid}NCHC), 10.52 (1H, s, ^{imid}NCHN). ^{13}C{^{1}H} NMR (dichloromethane-d_2, 100.5 MHz) δ 23.4, 23.8 (CH$_3$), 24.9, 25.4, 32.7, 36.4 ($^{c\text{-hex}}CH_2$), 54.5 (CH(CH$_3$)$_2$), 55.4 (d, $^{2}J_{P-C} = 16.8$, $^{c\text{-hex}}CHN_{phos}$), 65.4 (br, $^{c\text{-hex}}CHN_{imid}$), 117.6 (NCHC), 121.9, 122.5, 125.5, 126.2 (^{BiPh}CH), 128.7, 129.6, 129.7, 129.8, 130.2, 130.7, 131.0 ($^{aromatic}CH$), 131.4 (^{imid}C(Ph)N), 131.8, 131.9 ($^{BiPh}C_{ipso}$), 136.1 (NCHN), 136.7 ($^{Ph}C_{ipso}$), 149.4 (d, $^{2}J_{P-C} = 3.8$, $^{O2BiPh}C_{ipso}$), 150.9 (br, $^{O2BiPh}C_{ipso}$). ^{31}P{1H} NMR (dichloromethane-d_2, 161.8 MHz) δ 148.7 (br, NPO$_2$BiPh). Anal. Calc. for $C_{30}H_{33}N_3O_2IP$: C, 57.61; H, 5.32; N, 6.72. Found: C, 57.83; H, 5.30; N, 6.37%.

4.14. Synthesis of [$^{iPr}C(H)N^{(H)PO2Binap(R)}$][I] (16)

In an ampoule sealed with a Teflon stopcock a 1,4-dioxane solution (2 mL) of **13** (83 mg, 0.15 mmol) and 2-iodopropane (20 μL, 0.20 mmol) was stirred at 60 °C for 72 h, giving an off white precipitate. The mixture was filtered, and the residue washed with 1,4-dioxane (2 × 5 mL) and dried under reduced pressure to give **16** as an off white solid. Yield: 90 mg, 83%. MS (FAB+): m/z 598 (100%) $[M - I]^+$. MS (HRFAB+): Calc. for $C_{38}H_{37}N_3O_2P$: 598.2623. Found: 598.2625. ^{1}H NMR (dichloromethane-d_2, 300 MHz) δ 1.06–2.76 (8H, m, $^{c\text{-hex}}CH_2$), 1.70 (3H, d, $^{3}J_{H-H} = 6.8$, CH(CH_3)$_2$), 1.73 (3H, d, $^{3}J_{H-H} = 6.8$, CH(CH_3)$_2$), 2.84 (1H, m, NH), 3.76 (1H, m, $^{c\text{-hex}}CHN_{phos}$), 4.11 (1H, m, $^{c\text{-hex}}CHN_{imid}$), 5.00 (1H, vsep, $^{3}J_{H-H} = 6.8$ Hz, CH(CH$_3$)$_2$), 7.05–7.46 (13H, m, $^{aromatic}CH$), 7.38 (1H, s, ^{imid}NCHC), 7.81–8.10 (4H, m, $^{aromatic}CH$), 10.86 (1H, s, ^{imid}NCHN). ^{13}C{^{1}H} NMR (dichloromethane-d_2, 75.5 MHz) δ 23.4, 24.0 ($^{c\text{-hex}}CH_2$), 24.9, 25.5 (CH$_3$), 33.2, 36.4 ($^{c\text{-hex}}CH_2$), 55.7 (d, $^{2}J_{P-C} = 26.3$, $^{c\text{-hex}}CHN_{phos}$), 65.4 (br, $^{c\text{-hex}}CHN_{imid}$), 67.5 ($C$H(CH$_3$)$_2$), 116.9 (N$C$HC), 121.6, 122.9 ($^{aromatic}CH$), 124.0, 124.5 ($^{BiNap}C$), 125.5, 125.6, 126.7, 126.9, 127.0, 127.2 ($^{aromatic}CH$), 128.9 (^{imid}C(Ph)N), 129.0, 129.7, 130.2, 130.3, 130.7, 130.9, 131.0 ($^{aromatic}CH$), 131.6, 131.9 ($^{BiNap}C$), 133.1 ($^{BiNap}C_{ipso}$), 133.2 (d, $^{3}J_{P-C} = 1.3$, $^{BiNap}C_{ipso}$), 136.3 (br, NCHN), 137.3 ($^{Ph}C_{ipso}$), 146.9 (d, $^{2}J_{P-C} = 4.8$, $^{O2BiNap}C_{ipso}$), 149.3 (d, $^{2}J_{P-C} = 2.0$, $^{O2BiNap}C_{ipso}$). ^{31}P{1H} NMR (dichloromethane-d_2, 121.5 MHz) δ 150.0 (s, NPO$_2$BiNap). Anal. Calc. for $C_{38}H_{37}N_3O_2IP$: C, 62.90; H, 5.14; N, 5.79. Found: C, 62.84; H, 5.29; N, 5.65%.

4.15. Synthesis of [$^{iPr}C(H)N^{(H)PO2Binap(S)}$][I] (17)

In an ampoule sealed with a Teflon stopcock a 1,4-dioxane solution (2 mL) of **14** (83 mg, 0.15 mmol) and 2-iodopropane (20 μL, 0.20 mmol) was stirred at 60 °C for 72 h, giving an off white precipitate. Workup as for **16** gives **17** as an off white solid. Yield: 93 mg, 85%. MS (FAB+): m/z 598 (100%) $[M + I]^+$. MS (HRFAB+): Calc. for $C_{38}H_{37}N_3O_2P$: 598.2623. Found: 598.2618. ^{1}H NMR (dichloromethane-d_2, 300 MHz) δ 1.08–2.79 (8H, m, $^{c\text{-hex}}CH_2$), 1.72 (3H, d, $^{3}J_{H-H} = 6.8$, CH(CH_3)$_2$), 1.75 (3H, d, $^{3}J_{H-H} = 6.8$, CH(CH_3)$_2$), 3.26 (1H, m, NH), 3.83 (1H, m, $^{c\text{-hex}}CHN_{phos}$), 4.17 (1H, m, $^{c\text{-hex}}CHN_{imid}$), 5.03 (1H, vsep, $^{3}J_{H-H} = 6.8$ Hz, CH(CH$_3$)$_2$), 7.10–8.0 (17H, m, $^{aromatic}CH$), 7.46 (1H, s, ^{imid}NCHC), 10.94 (1H, s, ^{imid}NCHN). ^{13}C{^{1}H} NMR (dichloromethane-d_2, 75.5 MHz) δ 23.2, 23.9 ($^{c\text{-hex}}CH_2$), 24.7, 25.2 (CH$_3$), 33.1, 36.2 ($^{c\text{-hex}}CH_2$), 55.3 (d, $^{2}J_{P-C} = 29.4$, $^{c\text{-hex}}CHN_{phos}$), 65.1 (br, $^{c\text{-hex}}CHN_{imid}$), 66.9 ($C$H(CH$_3$)$_2$), 117.1 (N$C$HC), 121.8, 122.7 ($^{aromatic}CH$), 124.2, 124.8 ($^{BiNap}C$) 125.4, 125.6, 126.7, 126.8, 127.0, 127.2, ($^{aromatic}CH$), 128.9 ($^{imidazolium}C$(Ph)N), 129.1, 129.5, 129.8, 130.1, 130.3, 130.5, 130.9, ($^{aromatic}CH$), 133.5, 133.7 ($^{BiNap}C_{ipso}$), 136.6 (NCHN), 137.7 ($^{Ph}C_{ipso}$), 147.9 (d, $^{2}J_{P-C} = 4.3$, $^{O2BiNap}C_{ipso}$), 150.8 (d, $^{2}J_{P-C} = 2.0$, $^{O2BiNap}C_{ipso}$). ^{31}P{1H} NMR (dichloromethane-d_2, 121.5 MHz) δ 150.4 (s, NPO$_2$BiNap). Anal. Calc. for $C_{38}H_{37}N_3O_2IP$: C, 62.90; H, 5.14; N, 5.79. Found: C, 62.82; H, 5.34; N, 5.70%.

4.16. Synthesis of $^{iPr}C^{N(H)PPh2}$ (18)

To an NMR tube sealed with a Teflon stopcock was added **7** (60 mg, 0.11 mmol) and sodium bis(trimethylsilyl)amide (20 mg, 0.11 mmol). THF-d_8 (ca. 0.7 mL) was transferred via the gas phase to the tube cooled to −196 °C. On thawing the solution was allowed to warm to −84 °C, shaken for 5 min and allowed to warm to 25 °C . ^{1}H NMR (THF-d_8, 300 MHz) δ 0.73–2.13 (8H, m, $^{c\text{-hex}}CH_2$), 1.41 (3H, d, $^{3}J_{H-H} = 6.8$, CH(CH_3)$_2$), 1.42 (3H, d, $^{3}J_{H-H} = 6.8$, CH_3), 2.76 (1H, m, NH), 3.78 (1H, m, $^{c\text{-hex}}CHN_{phosphine}$), 3.93 (1H, m, $^{c\text{-hex}}CHN_{NHC}$), 4.45 (1H, vsep, $^{3}J_{H-H} = 6.8$, CH(CH$_3$)$_2$), 6.91 (1H, s, ^{NHC}NCHC), 6.84–7.47 (15H, m, ^{Ph}CH). ^{13}C{^{1}H} NMR (THF-d_8, 75.5 MHz) δ 24.6, 24.8 ($^{c\text{-hex}}CH_2$), 26.5, 26.6 (CH$_3$), 36.7 ($^{c\text{-hex}}CH_2$), 36.8 (d, $^{3}J_{P-C} = 8.3$, $^{c\text{-hex}}CH_2$), 53.3 (CH(CH$_3$)$_2$), 61.8 (d, $^{2}J_{P-C} = 24.9$, $^{c\text{-hex}}CHN_{phos}$),

63.4 (d, $^{3}J_{P-C} = 6.9$, $^{c\text{-hex}}CHN_{NHC}$), 115.6 (NCHC), 128.3 (^{NHC}C(Ph)N), 128.5, 128.6, 128.7, 129.2, 129.3, 129.6, 130.4 ($^{aromatic}CH$), 131.6 (d, $^{2}J_{P-C} = 4.7$, ^{PPh}CH), 131.0 (d, $^{2}J_{P-C} = 5.4$, ^{PPh}CH), 135.4 ($^{Ph}C_{ipso}$), 145.6 (d, $^{1}J_{P-C} = 14.5$, $^{PPh}C_{ipso}$), 145.8 (d, $^{1}J_{P-C} = 18.0$, $^{PPh}C_{ipso}$), 212.7 (NCN). $^{31}P\{1H\}$ NMR (THF-d_8, 121.5 MHz) δ 33.6 (s, $NPPh_2$).

4.17. Synthesis of $^{iPr}C^{N(H)PO2BiPh}$ (**19**)

To an NMR tube sealed with a Teflon stopcock was added **15** (g, mmol) and sodium bistrimethylsilylamide (g, mmol). THF-d_8 (ca. 0.7 mL) was transferred via the gas phase to the tube cooled to −196 °C and the sample treated as for **18**. ^{1}H NMR (THF-d_8, 300 MHz) δ 0.84–1.96 (8H, m, $^{c\text{-hex}}CH_2$), 1.59 (3H, d, $^{3}J_{H-H} = 6.7$, $CH(CH_3)_2$), 1.64 (3H, d, $^{3}J_{H-H} = 6.7$, $CH(CH_3)_2$), 2.74 (1H, m, NH), 3.62 (1H, m, $^{c\text{-hex}}CHN_{phosphine}$), 4.13 (1H, m, $^{c\text{-hex}}CHN_{NHC}$), 4.93 (1H, vsep, $^{3}J_{H-H} = 6.7$, $CH(CH_3)_2$), 6.81 (1H, m, ^{BiPh}CH), 6.92 (1H, m, ^{BiPh}CH), 7.12–8.04 (11H, m, ^{Ph}CH), 7.30 (1H, s, $^{NHC}NCHC$). $^{13}C\{^{1}H\}$ NMR (THF-d_8, 75.5 MHz) δ 23.2, 23.4 (CH_3), 25.7, 26.0, 29.5, 35.2 ($^{c\text{-hex}}CH_2$), 54.7 ($CH(CH_3)_2$), 55.5 (d, $^{2}J_{P-C} = 16.6$, $^{c\text{-hex}}CHN_{phosphine}$), 64.8 (br, $^{c\text{-hex}}CHN_{NHC}$), 114.3 (NCHC), 121.1, 121.8, 123.2, 123.6 (^{BiPh}CH), 129.2 (^{NHC}C(Ph)N), 126.5, 127.2, 130.1, 130.4, 130.8, 131.4, 131.9 ($^{aromatic}CH$), 132.1, 133.1 ($^{BiPh}C_{ipso}$), 137.9 ($^{Ph}C_{ipso}$), 151.2, 151.5 (br, $^{OBiPh}C_{ipso}$), 216.2 (NCN). $^{31}P\{1H\}$ NMR (THF-d_8, 121.5 MHz) δ 152.4 (s, NPO_2BiPh).

4.18. General procedure for asymmetric allylic substitution catalysis

To a THF solution (1 mL) of an imidazolium–phosphine (10 μmol) cooled to −84 °C was added dropwise a solution of sodium bis(trimetylsilyl)amide (2 mg, 11 μmol) in THF (1 mL). The solution was stirred for 10 min at −84 °C and subsequently added dropwise to a solution of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (1.8 mg, 5 μmol) in THF (1 mL) at −84 °C. The solution was stirred for 10 min at −84 °C, allowed to warm to 25 °C and stirred for a further 1 h. The volatiles were removed under reduced pressure and the solid dissolved in CH_2Cl_2 (1 mL) and added to a solution of (*E*)-1,3-diphenyl-3-acetoxyprop-1-ene (50 mg, 0.20 mmol, 1 equiv.), dimethyl malonate (69 μL, 0.60 mmol, 3 equiv.), bis(trimethylsilyl)acetamide (BSA) (143 μL, 0.58 mmol, 2.9 equiv.) and KOAc (0.2 mg, 4 μmol, 0.02 equiv.) in CH_2Cl_2 (1 mL). The resulting suspension was stirred at the required temperature for 5 h, diluted with Et_2O (4 mL), washed with ice-cold, saturated NH_4Cl solution (2 × 5 mL), dried over $MgSO_4$, filtered and the volatiles removed under reduced pressure. Purification of the crude product by flash chromatography (Et_2OAc:40–60 °C petrol, 1:12) gave methyl 2-methoxycarbonyl-3,5-diphenyl-4-pentenoate (**A**) as a colourless oil that solidified on standing. The enantiomeric ratio and absolute configuration were determined by ^{1}H NMR spectrum measured in the presence of Eu(hfc)$_3$ and comparison to the literature values [37].

4.19. General procedure for asymmetric transfer hydrogenation

To a THF solution (1 mL) of an imidazolium–phosphine (10 μmol) cooled to −84 °C was added dropwise a solution of sodium bis(trimetylsilyl)amide (2 mg, 11 μmol) in THF (1 mL). The solution was stirred for 10 min at −84 °C and subsequently added dropwise to a solution of $[Ir(COD)Cl]_2$ (3.4 mg, 5 μmol) in THF (1 mL) at −84 °C. The solution was stirred for 10 min at −84 °C, allowed to warm to 25 °C and stirred for a further 1 h. The volatiles were removed under reduced pressure and the solid dissolved in $(CH_3)_2CHOH$ (1 mL) and added to a stirred solution of acetophenone (235 μL, 2.0 mmol) and KOH (2.8 mg, 50 μmol) in $(CH_3)_2CHOH$ (4 mL) at 80 °C. The resulting solution was stirred at 80 °C for the required length of time. Intermittently aliquots were removed, diluted with CH_2Cl_2, run through a silica plug and analysed by chiral GC. GC conditions: Chiralsil-Dex CB, (25 m × 0.25 mm × 0.25 μm), 80 °C, 1 μL split injection (190 °C), FID detection (190 °C), Helium (15 psi). Absolute configuration was assigned by comparison to authenticated enantiomers of **B**.

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