Regioselective Alkylation Reactions of Enamines Derived from Phosphane Oxides − Synthesis of Phosphorus Substituted Enamino Esters, δ-Amino-phosphonates, Pyridone Derivatives and Pyrroles

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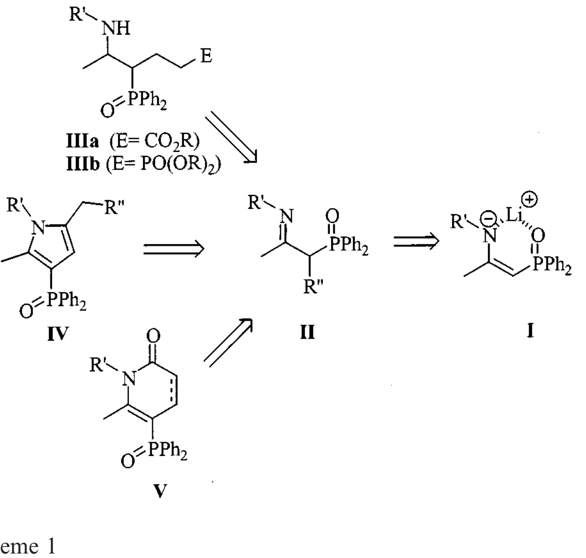
α-Substituted (2-iminoalkyl)phosphane oxides were obtained from the azaenolates of imines or enamines and alkyl halides. The functionalized imines or enamines thus obtained were used for the synthesis of δ-amino esters, δ-amino phosphonates and heterocycles such as 3,4-dihydropyridin-2-ones, 2-pyridones and pyrroles containing a phosphinyl substituent.

Introduction

Enamines have attracted a great deal of attention in recent years because of their range of applications,[1] and enamines stabilized through conjugation with an electron-withdrawing group have also been extensively used as versatile key intermediates in organic synthesis.[2,3] In particular, metaloenamines,[4] carbanions derived from enamines or enolizable imines, are useful substrates for the regio- and stereoselective carbon−carbon bond formation reaction with alkylating agents.[5] We are interested in the design of new nitrogen-containing acyclic and cyclic derivatives bearing a phosphane oxide moiety. This substituent could regulate important biological functions and increase the biological activity of these compounds, in a similar way to that reported for other pharmaceuticals,[6] and has recently been used for the design of organic solids.[7] In this context, we have described the synthesis of three-,[8] five-[9] and six-membered[10] phosphorus-substituted nitrogen heterocycles from enamines and imines derived from phosphazenes or phosphane oxides. β-Functionalized enamines derived from phosphane oxides and phosphonates are also used as synthetic intermediates in the synthesis of acyclic derivatives such as α,β-unsaturated imines[11a] allylamines,[11b,11c] 1-azadienes derived from γ-amino esters,[11d] and β-amino-functionalized compounds,[11e] as well as of phosphorus-containing heterocycles.[12] Continuing with our interest in the chemistry of new phosphorus-substituted compounds, we report here an easy and regioselective synthesis of α-substituted (2-iminoalkyl)phosphane oxides (**II**) from *N*-metalated β-posphinylenamines (**I**) (Scheme 1). These α-functionalized β-imines (**II**) are a versatile tool for the formation of δ-amino esters (**IIIa**; E = CO_2R) or δ-amino phosphonates [**IIIb**; E = $PO(OR)_2$] and for the construction of phosphorus-containing five and six-membered heterocycles such as pyrroles (**IV**) and 2-pyridone derivatives (**V**).



Scheme 1

Results and Discussion

Reaction of *N*-metalated β-Phosphinylenamines with Alkyl Halides

N-metalated enamines have recently been prepared from aziridines,[13] although they used to be obtained by treatment of primary or secondary enamines or enolizable imines with bases. Simple imines will deprotonate regioselectively on the less substituted side, forming an azaenolate,[4,5] which can then be alkylated. But in our case, the presence

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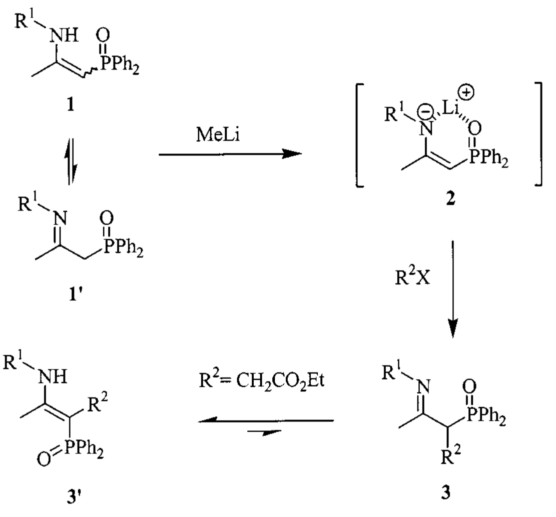
of an excellent anion stabilizing group such as phosphane oxide could control the deprotonation at the internal carbon. Enamines and imines derived from phosphane oxides **1/1′** were easily prepared by addition of achiral and chiral amines to allenes.[11c] In the case of *N*-aliphatic derivatives, these compounds were obtained as mixures of *E*- and *Z*-enamines, while in the case of *N*-aromatic compounds, they were obtained as mixtures of β-imino (major) and β-enamino (minor) phosphane oxides. The deprotonation of functionalized enamines and/or imines **1/1′** with methyllithium in THF (*N*-aromatic enamines/imines were metalated at 0 °C whereas *N*-aliphatic enamines were metalated at lower temperatures) gave the azaenolates **2**, which were then alkylated with alkyl halides (Scheme 2). Mixtures of β-imino and β-enamino phosphane oxides could be used without separation for this metalation as the reaction with both enamino or imino derivatives gave lithium enamides (lithium azaenolates). After aqueous workup, the α-substituted imine **3a** (see Table 1, entry 2) was obtained in moderate to good yields, and in a regioselective fashion, when ethyl bromide was used. Compounds **3** were characterized on the basis of their spectroscopic data. Thus, the ^{31}P NMR spectrum of compound **3a** showed an absorption at $\delta_P = 30.9$. Likewise, the ^{1}H and ^{13}C NMR spectra gave a multiplet for the methine proton at $\delta_H = 3.44$ and a well resolved doublet at $\delta_C = 55.0$ with a coupling constant of $^1J_{PC} = 62.9$ Hz for the carbon atom directly bonded to the phosphinyl moiety.



Scheme 2. Reaction of *N*-metalated β-phosphinyl enamines with alkyl halides

The scope of the reaction was not limited to simple alkyl halides (ethyl bromide), given that functionalized alkyl halides such as allyl or propargyl halides, ethyl 3-bromopropionate or diethyl (2-bromoethyl)phosphonate also reacted with aza-enolates **2** to give the α,α-difunctionalized imines **3** (see Table 1, entries 3−11), while the use of ethyl bromoacetate afforded the *E* isomer of the tautomeric β-enamine **3′** (see Table 1, entry 1). This methodology, used for the preparation of α-functionalized β-imines **3**, can also be extended to chiral β-phosphinylenamines when chiral *N*-(α-methylbenzyl)enamine derivatives were used (see Table 1, entries 6−8).

Reaction of *N*-metalated β-Phosphinylenamines with Ethyl Chloroformate: *N*- vs. C_α-Acylation

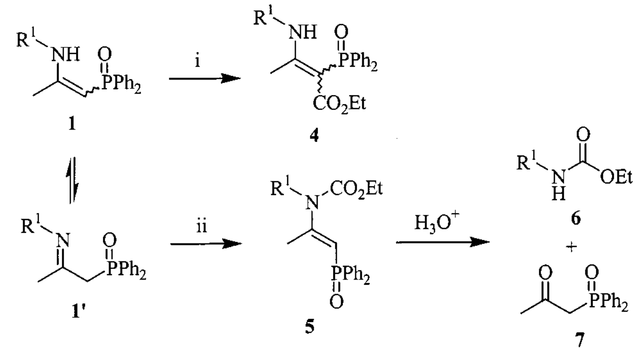
The acylation of enamines gives access to a wide variety of acyclic and cyclic derivatives.[2b] Enamines are ambident nucleophilic reagents (*N* vs. C_α) and the course of the acylation reaction is often critically dependent upon the type of enamine used, on the substituent present in the two reagents and on the experimental conditions.[14] The regioselective C_α-acylation of *N*-tolyl-functionalized phosphane oxides (R^1 = *p*-CH_3-Ph) **1/1′** was accomplished using methyllithium as the base followed by the addition of ethyl chloroformate, at 0 °C, and the (α-phosphinyl-β-enamino)-ester **4** was obtained as a mixture of the *Z*- and *E*-isomers (see Table 1, entry 12). However, when the acylation reac-

Table 1. α-Functionalized imines and enamines **3**−**5** obtained

Entry	Compound	R^1	R^2	Yield (%)[a]	M.p. (°C)
1	**3′**	*p*-CH_3-Ph	CH_2-CO_2Et	79	176−177
2	**3a**	*p*-CH_3-Ph	Et	82	174−175
3	**3b**	*p*-CH_3-Ph	$CH_2-CH=CH_2$	81	121−122
4	**3c**	*p*-CH_3-Ph	$CH_2-CH_2-PO(OEt)_2$	73	132−133
5	**3d**	*p*-CH_3-Ph	$CH_2-C\equiv CH$	81[b]	119−120
6	**3e**	(*S*)-Ph−CH−CH_3	$CH_2-CH_2-CO_2Et$	84[b]	Oil
7	**3f**	(*S*)-Ph−CH−CH_3	$CH_2-CH_2-PO(OEt)_2$	78[b]	Oil
8	**3g**	(*S*)-Ph−CH−CH_3	$CH_2-C\equiv CH$	84	Oil
9	**3h**	Ph_2CH	$CH_2-CH_2-CO_2Et$	84	106−107
10	**3i**	Ph_2CH	$CH_2-CH_2-PO(OEt)_2$	68	124−125
11	**3j**	Ph_2CH	$CH_2-C\equiv CH$	91	113−114
12	**4**	*p*-CH_3-Ph	-	83[c]	122−123
13	**5a**	*p*-CH_3-Ph	-	69	115−116
14	**5b**	(*S*)-Ph−CH−CH_3	-	74	122−123
15	**5c**	(*R*)-Ph−CH−CH_3	-	74	122−123
16	**5d**	(±)-Ph−CH−CH_3	-	74	106−107

[a] Yield obtained from enamines and/or imines **1/1′**. − [b] Obtained as a 1:1 mixture of (*S*,*R*) and (*S*,*S*) diastereoisomers. − [c] Obtained as a 1:1 mixture of *Z* and *E* isomers.

tion of achiral (R^1 = *p*-CH_3-Ph, *rac*-Ph−CH−CH_3) and chiral [R^1 = (*R*)-, (*S*)-Ph−CH−CH_3] compounds **1**/**1′** was carried out at low temperature (−78 °C), only the (*E*)-*N*-acylated β-enaminophosphane oxides **5a**−**d** were isolated (see Table 1, entries 13−16). Compounds **5** were characterized on the basis of their spectroscopic data and a crystal structure determination for **5b**. Acid hydrolysis of **5a** led to the formation of ethyl *N*-tolylcarbamate **6** and β-ketophosphane oxide **7** (see Scheme 3).



i) 1. MeLi, 0 °C. 2. $ClCO_2Et$, 0 °C to r.t.
ii) 1. MeLi, -78 °C. 2. $ClCO_2Et$, -78 °C to r.t.

Scheme 3. Reaction of *N*-metalated β-phosphinyl enamines with ethyl chloroformate

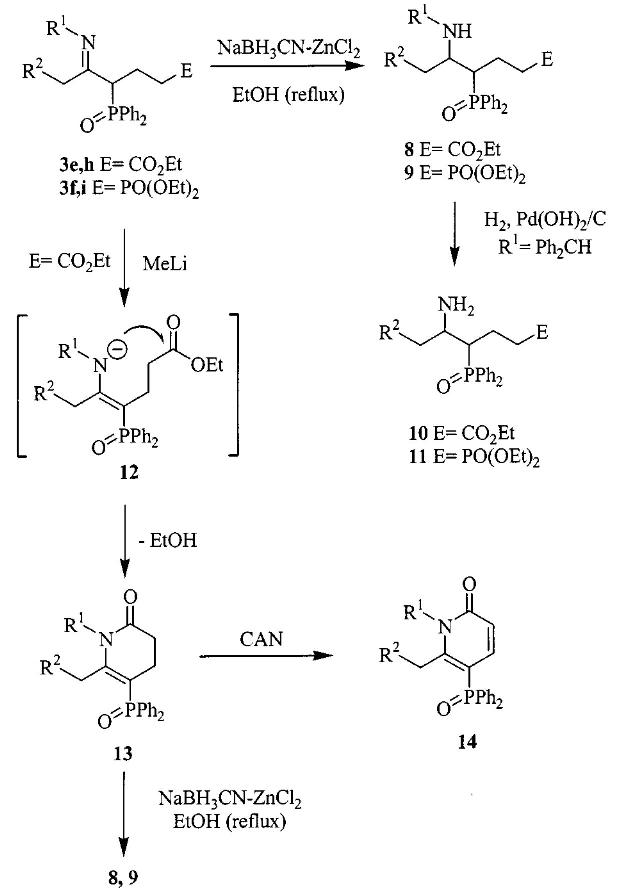
Reduction of Functionalized Imines 3c,e,f,h,i: Synthesis of the δ-Amino Esters 8,10 and δ-Amino Phosphonates 9,11

A variety of reducing agents, such as hydrogen in the presence of metal catalysts,[15,16] and simple or modified hydrides,[15,17] have been developed for the conversion of imine group into amines. In our case, reduction of the imino C=N double bond of functionalized imines **3c**,**e**,**f**,**h**,**i** was achieved when these derivatives were treated with sodium cyanoborohydride in the presence of a Lewis acid such as zinc chloride. Reduction of the previously prepared achiral and chiral imines **3** with $NaBH_3CN/ZnCl_2$ in EtOH at reflux for 12−24 hours led to the formation of the δ-amino esters **8a**,**b** (E = CO_2Et, Table 2, entries 1, 2) or δ-amino phosphonates **9a**−**c** [E = $PO(OEt)_2$, Table 2, entries 4−6] (see Scheme 4) containing a phosphane oxide group in the γ-position. They were obtained as mixtures of two diastereomers. From a preparative point of view, it is of interest that the synthesis of the δ-amino esters **8** and phosphonates **9** does not require the isolation and purification of the imines **3**, and the former can be obtained in one pot from the phosphane oxides **1**/**1′** after alkylation, evaporation of the solvent and reduction with the hydride (Table 2, entries 1−3,5,6). Spectroscopic data support the structure of compounds **8** and **9**. The ^{13}C NMR spectra of products **8** and **9** show the presence of a new signal at δ = 48−50 belonging to the C−N bond and the absence of the typical signal for the C=N group (in the range of δ = 150−170). The selective removal of the benzhydryl group of *N*-substituted δ-amino esters **8b** and phosphonates **9b** was achieved by catalytic hydrogenation [$Pd(OH)_2/C$], affording functionalized primary amines derived from δ-amino esters **10** and phosphonates **11** (Table 2, entries 7,8). δ-Amino phosphonates are constituents of phosphapeptide antibiotics such as Plumbeomicin[18a] or Rhizocticin[18b] and have

Table 2. Secondary and primary amines **8**, **9**, **10**, **11** and pyridone derivatives **13**, **14** obtained

Entry	Compound	R^1	R^2	Yield (%)	M.p. (°C)
1	**8a**	(*S*)-Ph−CH−CH_3	H	86,[a] 81[b]	Oil
2	**8b**	Ph_2CH	H	91,[a] 84[b]	Oil
3	**8c**	*p*-CH_3−Ph	H	62,[b] 64[c]	104−105
4	**9a**	(*S*)-Ph−CH−CH_3	H	87[a]	Oil
5	**9b**	Ph_2CH	H	85,[a] 80[b]	Oil
6	**9c**	*p*-CH_3−Ph	H	77,[a] 70[b]	108−109
7	**10**	H	H	89[d]	Oil
8	**11**	H	H	85[e]	Oil
9	**13a**	*p*-CH_3−Ph	H	83[b]	146−147
10	**13b**	*p*-CH_3O−Ph	CH_3	78[b]	159−160
11	**13c**	(*S*)-Ph−CH−CH_3	H	80,[a] 79[b]	142−143
12	**13d**	Ph_2CH	H	81,[a] 77[b]	101−102
13	**14**	*p*-CH_3O−Ph	CH_3	69[f]	162−163

[a] Yield obtained from imines **3**. − [b] Yield obtained from enamines and/or imines **1**/**1′**. − [c] Yield obtained from dihydropyridone **13a**. − [d] Yield obtained by deprotection of imine **8b**. − [e] Yield obtained by deprotection of imine **9b**. − [f] Yield obtained from dihydropyridone **13b**.



Scheme 4. Cyclization and reduction of α-substituted (2-iminoalkyl)phosphane oxides

proved to be potent antagonists of *N*-methyl-D-aspartic acid (NMDA) displaying anticonvulsant activity.[18c−18h]

Cyclization of Imines 3e,3h: Synthesis of the Phosphinylated 2-Pyridone Derivatives 13 and 14

The imines derived from ethyl 3-bromopropionate (**3e** and **3h**) can be used for the construction of six-membered heterocycles containing a phosphinyl substituent in the 5-position of the heterocyclic system. Thus, the compounds **3e** and **3h** (E = CO_2Et) were cyclocondensed with methyllithium as the base to give the achiral and chiral 5-phosphinylated 3,4-dihydropyridin-2-ones **13c** and **13d** in excellent yields (Table 2, entries 11,12). Likewise, the phosphinylated 3,4-dihydropyridin-2-ones **13a−d** were directly prepared from the phosphane oxides **1/1′**, a base (methyllithium) and ethyl bromopropionate (Table 2, entries 9−12). Compounds **13** were characterized on the basis of their spectroscopic data. Thus, the ^{31}P NMR of compound **13a** showed an absorption at $\delta_P = 31.5$, while the ^1H NMR spectrum showed multiplet signals for the CH_2 groups ($\delta_H = 2.14$, $\delta_H = 2.56$) and the ^{13}C NMR spectrum gave three well-resolved doublets at $\delta_C = 23.8$ ($^3J_{PC} = 11.2$ Hz) for one methylene carbon, at $\delta_C = 31.2$ ($^2J_{PC} = 7.5$ Hz) for two methylene carbons, and at $\delta_C = 105.4$ ($^1J_{PC} = 109.5$ Hz) for the carbon atom directly bonded to the phosphinyl moiety of **13a**. As far as we know, this strategy leads to the first examples of 3,4-dihydropyridin-2-ones **13** containing phosphinyl substituents in the ring system. The formation of heterocycles **13** can be explained by a cyclization reaction of the aza-enolates **12** derived from imines **3** (E = CO_2Et) followed by the loss of ethanol (Scheme 4).

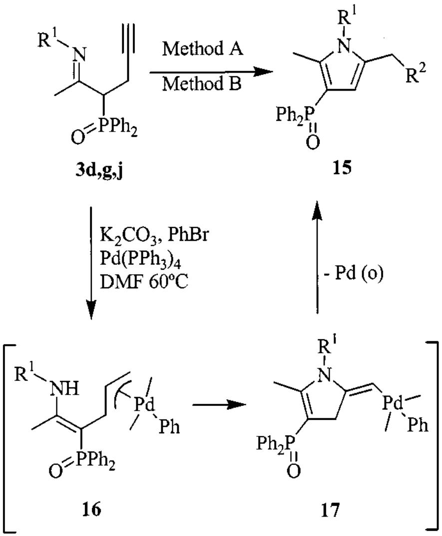
Reduction of the previously prepared 3,4-dihydropyridin-2-one **13a** (R^1 = *p*-CH_3−Ph) with $NaBH_3CN/ZnCl_2$ in refluxing EtOH led to the formation of the δ-amino ester **8c** (E = CO_2Et, R^1 = *p*-CH_3−Ph, Table 2, entry 3) containing a phosphane oxide group in the γ-position, while the oxidation of the phosphinylated 3,4-dihydropyridin-2-one **13b** (R^1 = *p*-CH_3O−Ph) with cerium(IV) ammonium nitrate (CAN) in acetonitrile gave 2-pyridone **(14)** (see Scheme 4, Table 2, entry 13). A solid-phase approach to 3,4-dihydropyridin-2-ones has been reported recently.[19a] These heterocycles are potential calcium channel modulators[19b] and have been used for the synthesis of peptides[19c] and alkaloids,[19d−19f] while the pyridin-2-one substructure is found in many biologically active natural and synthetic compounds that possess medicinal properties.[20,21] During the preparation of this manuscript, a synthesis of 2-pyridones with a phosphane oxide substituent for the design of organic solids was reported.[7]

Palladium-Catalyzed Cyclization Reaction of the α-Propargyl β-Imino Phosphane Oxides 3d,g,j: Synthesis of the Phosphinylated Pyrroles 15 and 18

The palladium-catalyzed allylation of carbon, oxygen or nitrogen nucleophiles is widely recognized as one of the most powerful synthetic tools for the construction of carbon−carbon, carbon−oxygen or carbon−nitrogen bonds from allenes[22] or propargyl derivatives.[23] Similarly, electrophile-mediated cyclization is an efficient route to nitrogen-containing heterocycles,[24] and palladium-mediated cyclizations are particularly attractive in this sense especially when allene[25] or propargyl[26] systems are used as the π-components. For this reason, we envisaged that achiral and chiral propargylic-substituted β-imines derived from the phosphane oxides **3d,g,j** could be used for the synthesis of phosphinylated pyrroles by Pd^0- and Pd^{II}-catalyzed regioselective heterocyclization reactions. Thus, treating the β-imines derived from the phosphane oxides **3d,g,j** with bromobenzene, catalytic amounts of $Pd(PPh_3)_4$ and K_2CO_3 in DMF at 60 °C, and aqueous workup (Scheme 5, method A), led to the formation of the achiral and chiral pyrroles **15a−c** (R^2 = Ph) in moderate yields and in a regioselective fashion (see Table 3, entries 1−3). The spectroscopic data and mass spectrometry were in agreement with the proposed structure for pyrroles **15**. In the ^1H NMR spectrum of pyrrole **15a** the signal for the methine proton appears at $\delta_H = 5.70$ with a coupling constant of $^3J_{PH} = 3.8$ Hz, while the ^{13}C NMR spectrum of this compound shows a signal at $\delta_C = 107.9$ ($^1J_{PC} = 128.9$ Hz) for the carbon atom directly bonded to the phosphinyl moiety (C-3), as well as doublets at $\delta_C = 110.4$ ($^2J_{PC} = 13.1$ Hz) and at $\delta_C = 137.1$ ($^2J_{PC} = 16.6$ Hz) and a singlet at $\delta_C = 138.4$, for the heterocyclic carbon atoms C-4, C-2 and C-5, respectively. The formation of these heterocycles may be supposed to proceed by generation of the σ-vinylpalladium complexes **17** via an intramolecular regioselective *trans* addition of the enamino NH to the palladium-allyl system **16**.[25] The reductive elimination of Pd^0 and isomerization would afford the pyrroles **15** (Scheme 5).

This process can be extended to the preparation of pyrroles **15d,e,f** (R^2 = H) by treating the β-imines derived from phosphane oxides **3d,j,g** with catalytic amounts of $Pd(OAc)_2$ and K_2CO_3 in DMF at 60 °C and aqueous workup (Scheme 5, method B; Table 3, entries 4−6). Alternatively, the phosphinylated pyrroles **15** were prepared in a one-pot reaction from β-enamines and/or imines **1/1′** and propargyl bromide, when the crude adducts **3d,j** were directly treated with bromobenzene, without their prior isolation, catalytic amounts of $Pd(PPh_3)_4$ and K_2CO_3 in DMF (R^2 = Ph) or catalytic amounts of $Pd(OAc)_2$ and K_2CO_3 in DMF (R^2 = H) and aqueous workup (Table 3, entries 1,2,4). Pyrrole ring systems are important in organic chemistry because they constitute the skeleton of natural products such as alkaloids, and some antibiotics and polymers.[27]

In conclusion, the synthesis described in this paper provides an efficient and easy access to α-functionalized β-imines substituted with a phosphane oxide group, making use of readily available starting materials. These functionalized imines can serve as intermediates in the synthesis of acyclic compounds such as δ-amino esters and δ-amino phosphonates, as well as of new nitrogen heterocycle compounds such as 5-phosphinylated-3,4-dihydropyridin-2-ones or 2-pyri-



Method A: K_2CO_3, PhBr, $Pd(PPh_3)_4$, DMF 60°C
Method B: K_2CO_3, $Pd(OAc)_2$, DMF 60°C

Scheme 5. Palladium-catalyzed cyclization reaction of α-propargyl (2-iminoalkyl)phosphane oxides

Table 3. Pyrroles obtained

Entry	Compound	R¹	R²	Yield (%)	M.p. (°C)
1	**15a**	*p*-CH_3−Ph	Ph	70,[a] 65[b]	131−132
2	**15b**	Ph_2CH	Ph	76,[a] 72[b]	142−143
3	**15c**	(*S*)-Ph−CH−CH_3	Ph	74[a]	105−106
4	**15d**	*p*-CH_3−Ph	H	69,[a] 63[b]	153−154
5	**15e**	Ph_2CH	H	73[a]	165−166
6	**15f**	(*S*)-Ph−CH−CH_3	H	78[a]	121−122

[a] Yield obtained from propargyl imines **3**. − [a] Yield obtained from enamines and/or imines **1/1′**.

dones as well as 3-phosphinylated-pyrroles, in a stepwise fashion or in a one-pot reaction.

Experimental Section

General: Chemicals were purchased from Aldrich. Solvents for extraction and chromatography were technical grade. All solvents used in reactions were freshly distilled from appropriate drying agents before use. All other reagents were recrystallized or distilled as necessary. All reactions were performed under an atmosphere of dry nitrogen. Analytical TLC was performed with Merck silica gel 60 F_{254} plates. Visualization was accomplished by UV light. Flash chromatography was carried out using Merck silica gel 60 (230−400 mesh ASTM). Melting points were determined with an Electrothermal IA9100 Digital Melting Point Apparatus and are uncorrected. ^{1}H (300 MHz), ^{13}C (75 MHz) and ^{31}P NMR (120 MHz) spectra were recorded on a Varian VXR 300 MHz spectrometer using $CDCl_3$ solutions with TMS as an internal reference (δ = 0.00) for ^{1}H and ^{13}C NMR spectra and 85% phosphoric acid (δ = 0.0) for ^{31}P NMR spectra. Chemical shifts (δ) are reported in ppm. Coupling constants (*J*) are reported in Hertz. Low-resolution mass spectra (MS) were obtained at 50−70 eV by electron impact (EIMS) on a Hewlett Packard 5971 or 5973 spectrometer, or by chemical ionization (CI) on a Hewlett Packard 1100MSD. Data are reported in the form *m*/*z* (intensity relative to base = 100). Infrared spectra (IR) were recorded on a Nicolet IRFT Magna 550 spectrometer, and were obtained as solids in KBr or as neat oils. Peaks are reported in cm^{-1}. Elemental analyses were performed in a LECO CHNS-932 apparatus. $[\alpha]_D^{20}$ measurements were taken on a Perkin−Elmer 341 polarimeter using a Na/HaI lamp. Enamines and/or imines **1/1′** were synthesized according to literature procedures.[11c]

General Procedure for the Alkylation of Imines and/or Enamines 1/1′ Derived from Phosphane Oxides: To a solution of aromatic enamine/imine **1/1′** at −78 °C or a solution of aliphatic enamine **1** at 0 °C (both 5 mmol) in THF (15 mL) was added a 1.6 M methyllithium solution in diethyl ether (5 mmol). The mixture was allowed to stir at this temperature for 1 h. A solution of alkyl halide (6 mmol) in THF (5 mL) was then added at the same temperature. After the mixture was allowed to warm to room temp., the reaction mixture was stirred at this temperature until TLC indicated the disappearance of the enamine and/or imine **1/1′**. The mixture was then diluted with water (50 mL) and extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layers were washed with water, dried over $MgSO_4$ and concentrated under vacuum. The crude residue was purified by flash column chromatography eluting with AcOEt/hexanes (3:1).

Ethyl 3-(Diphenylphosphinyl)-4-(*p*-tolylamino)pent-3-enoate (3′): Synthesized according to the general procedure with ethyl bromoacetate (0.67 mL, 6 mmol), affording 1.71 g (79%) of **3′** as a white solid. M.p.: 176−177 °C. − ^{1}H NMR: δ = 7.63−7.15 (m, 14 H), 3.92 (m, 1 H), 3.77 (m, 1 H), 3.37 (d, $^2J_{HH}$ = 17.0 Hz, 1 H), 2.77 (d, $^2J_{HH}$ = 17.0 Hz, 1 H), 2.30 (s, 3 H), 1.67 (s, 1 H), 1.43 (s, 3 H), 1.11−1.02 (m, 3 H). − ^{13}C NMR: δ = 170.0, 154.8 (d, $^2J_{PC}$ = 17.6 Hz), 138.6−128.2 (m), 103.8 (d, $^1J_{PC}$ = 126.4 Hz), 60.4, 41.1, 21.2, 15.3, 14.0. − ^{31}P NMR: δ = 24.6. − IR (KBr): ṽ = 2992, 1739, 1616 cm^{-1}. − MS: *m*/*z* (%) = 433 (24) [M$^+$]. − $C_{26}H_{28}NO_3P$ (433.48): calcd. C 72.04, H 6.51, N 3.23; found C 71.97, H 6.48, N 3.19.

[2-(Diphenylphosphinyl)-1-methylbutylidene]-*p*-tolylamine (3a): Synthesized according to the general procedure with ethyl iodide (0.48 mL, 6 mmol), affording 1.53 g (82%) of **3a** as a white solid. M.p.: 174−175 °C. − ^{1}H NMR: δ = 7.91−6.04 (m, 14 H), 3.44 (m, 1 H), 2.20 (s, 3 H), 1.78 (s, 3 H), 1.76 (m, 2 H), 0.96 (t, $^3J_{HH}$ = 7.5 Hz, 3 H). − ^{13}C NMR: δ = 168.9, 147.8−118.7 (m), 55.0 (d, $^1J_{PC}$ = 62.9 Hz), 20.7, 19.2, 18.2, 12.7 (d, $^3J_{PC}$ = 5.1 Hz). − ^{31}P NMR: δ = 30.9. − IR (KBr): ṽ = 2959, 1634, 1450 cm^{-1}. − MS: *m*/*z* (%) = 375 (60) [M$^+$]. − $C_{24}H_{26}NOP$ (375.45): calcd. C 76.78, H 6.98, N 3.73; found C 76.69, H 6.93, N 3.78.

General Procedure for the *C*- and *N*-acylation of Enamines and/or Imines 1/1′ Derived from Phosphane Oxides: A 1.6 M methyllithium solution in diethyl ether (5 mmol) was added to a solution of enamine and/or imine **1/1′**derived from phosphane oxide (5 mmol) in THF (15 mL) at 0 °C (for *C*-acylation) or −78 °C (for *N*-acylation). The mixture was allowed to stir at this temperature for 1 h. A solution of ethyl chloroformate 0.57 mL (6 mmol) in THF (5 mL) was then added at the same temperature. After the mixture was allowed to warm to room temp., the reaction mixture was stirred until TLC indicated the disappearance of the enamine and/or imine **1/1′**. The mixture was then diluted with water (50 mL) and extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layers were washed with water, dried over $MgSO_4$ and concentrated under vacuum. The crude residue was purified by flash column chromatography eluting with AcOEt/hexanes (1:4) in the case of *C*-acylation or precipitated from diethyl ether and recrystallized from hexanes/dichloromethane in the case of *N*-acylation.

Ethyl 2-(Diphenylphosphinyl)-3-*p*-tolylaminobut-2-enoate (4): Synthesized according to the general procedure with the corresponding enamine/imine **1/1′** (5 mmol), affording 1.74 g (83%) of a mixture of isomers **4** (*E*/*Z* = 1:1) as a white solid. M.p.: 122−123 °C. − ^{1}H NMR: δ = 12.50 (s, 1 H), 7.86−6.99 (m, 14 H), 3.81−3.69 (m, 2 H), 2.48 (s, 3 H), 2.34 and 2.33 (s, 3 H), 0.76 and 0.61 (2 t, $^{3}J_{HH}$ = 7.3 Hz and $^{3}J_{HH}$ = 7.3 Hz, 3 H). − ^{13}C NMR: δ = 173.0 and 171.2 (2 d, $^{2}J_{PC}$ = 4.0 Hz and $^{2}J_{PC}$ = 13.6 Hz), 169.9 and 167.4 (2 d, $^{2}J_{PC}$ = 11.1 Hz and $^{2}J_{PC}$ = 12.1 Hz), 137.6−126.0 (m), 85.6 and 81.2 (2 d, $^{1}J_{PC}$ = 123.7 Hz and $^{1}J_{PC}$ = 112.3 Hz), 59.3, 58.8, 20.9, 20.2 and 19.3 (d, $^{3}J_{PC}$ = 8.0 Hz and $^{3}J_{PC}$ = 3.5 Hz), 13.8, 13.3. − ^{31}P NMR: δ = 42.2, 31.0. − IR (KBr): ṽ = 2924, 1690, 1608 cm^{-1}. − MS: *m*/*z* (%) = 419 (46) [M^{+}]. − $C_{25}H_{26}NO_3P$ (419.46): calcd. C 71.59, H 6.25, N 3.34; found C 71.50, H 6.20, N 3.38.

Ethyl [2-(Diphenylphosphinyl)-1-methylvinyl]-*p*-tolylcarbamate (5a): Synthesized according to the general procedure with the corresponding enamine/imine **1/1′** (5 mmol), affording 1.44 g (69%) of **5a** as a white solid. M.p.: 115−116 °C. − ^{1}H NMR: δ = 7.71−6.92 (m, 14 H), 6.00 (d, $^{2}J_{PH}$ = 19.2 Hz, 1 H), 4.11 (q, $^{3}J_{HH}$ = 7.2 Hz, 2 H), 2.27 (s, 3 H), 2.12 (d, $^{4}J_{PH}$ = 1.5 Hz, 3 H), 1.13 (t, $^{3}J_{HH}$ = 7.2 Hz, 3 H). − ^{13}C NMR: δ = 155.1 (d, $^{2}J_{PC}$ = 10.6 Hz), 153.2, 136.9−126.6 (m), 111.2 (d, $^{1}J_{PC}$ = 108.3 Hz), 61.4, 20.2 (d, $^{3}J_{PC}$ = 4.0 Hz), 19.6, 13.5. − ^{31}P NMR: δ = 22.4. − IR (KBr): ṽ = 2919, 1705, 1620 cm^{-1}. − MS: *m*/*z* (%) = 419 (44) [M^{+}]. − $C_{25}H_{26}NO_3P$ (419.46): calcd. C 71.59, H 6.25, N 3.34; found C 71.67, H 6.21, N 3.30

General Procedure for the Synthesis of δ-Amino Esters 8 and δ-Amino Phosphonates 9: To a suspension of $ZnCl_2$ (0.68 g, 5 mmol) in EtOH (10 mL) was added $NaBH_3CN$ (0.63 g, 10 mmol). After 10 min. stirring a solution of δ-imino ester or δ-iminophosphonate **3** (5 mmol) in EtOH (10 mL) was added. The reaction mixture was stirred and refluxed until TLC indicated the disappearance of the imine **3** (12−24 h). The mixture was then concentrated under vacuum, washed with NaOH (0.1 M, 50 mL) and extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layers were washed with water, dried over $MgSO_4$ and concentrated under vacuum. The crude residue was purified by flash column chromatography eluting with AcOEt/hexanes (4:1).

Ethyl 5-(Benzhydrylamino)-4-(diphenylphosphinyl)hexanoate (8b): Synthesized according to the general procedure with δ-iminoester **3h** (2.62 g, 5 mmol), affording 2.39 g (91%) of a mixture of diastereoisomers **8b** (*de* = 50%) as a pale yellow oil. R_f = 0.08 (AcOEt). − ^{1}H NMR: δ = 7.80−7.00 (m, 20 H), 4.84 and 4.76 (s, 1 H), 4.04−3.89 (m, 3 H), 3.05−2.94 (m, 1 H), 2.76 and 2.49 (m, 1 H), 2.22−2.00 (m, 4 H), 1.17−1.09 (m, 6 H). − ^{13}C NMR: δ = 172.7 and 172.4, 144.2−126.1 (m), 64.0, 63.3, 59.8, 49.5, 49.1, 41.3 and 38.8 (2 d, $^{1}J_{PC}$ = 69.5 Hz and $^{1}J_{PC}$ = 68.9 Hz), 32.9 and 32.3 (2 d, $^{3}J_{PC}$ = 8.6 Hz and $^{3}J_{PC}$ = 7.6 Hz), 19.1, 17.8, 18.9 and 17.8 (2 d, $^{3}J_{PC}$ = 10.9 Hz and $^{3}J_{PC}$ = 8.9 Hz), 13.8. − ^{31}P NMR: δ = 35.9 and 33.0. − IR (film): ṽ = 2979, 1733, 1447 cm^{-1}. − MS: *m*/*z* (%) = 526 (100) [M^{+} + 1]. − $C_{33}H_{36}NO_3P$ (525.63): calcd. C 75.41, H 6.90, N 2.66; found C 75.35, H 6.84, N 2.67.

Diethyl [4-(Benzhydrylamino)-3-(diphenylphosphinyl)pentyl]phosphonate (9b): Synthesized according to the general procedure with δ-iminophosphonate **3i** (2.94 g, 5 mmol), affording 2.50 g (85%) of a mixture of diastereoisomers **9b** (*de* = 50%) as a pale yellow oil. R_f = 0.10 (AcOEt). − ^{1}H NMR: δ = 7.81−7.00 (m, 20 H), 4.82 and 4.75 (s, 1 H), 4.02−3.74 (m, 5 H), 3.07−2.98 (m, 1 H), 2.51 and 2.16 (m, 1 H), 2.16−1.90 (m, 2 H), 1.65−1.53 (m, 2 H), 1.23−1.05 (m, 9 H). − ^{13}C NMR: δ = 144.5−126.4 (m), 64.5, 63.5, 61.6, 61.4, 50.1, 49.5, 43.0 and 44.9 (2 dd, $^{1}J_{PC}$ = 69.5 Hz, $^{3}J_{PC}$ = 14.1 Hz and $^{1}J_{PC}$ = 67.5 Hz, $^{3}J_{PC}$ = 12.1 Hz), 25.1 and 24.8 (2 dd, $^{1}J_{PC}$ = 139.0 Hz, $^{3}J_{PC}$ = 8.1 Hz and $^{1}J_{PC}$ = 139.0 Hz, $^{3}J_{PC}$ = 7.1 Hz), 19.3, 19.1, 17.2, 17.1, 16.3, 16.1. − ^{31}P NMR: δ = 31.4, 28.9, 30.7, 30.1. − IR (film): ṽ = 2985, 1699, 1435 cm^{-1}. − MS: *m*/*z* (%) = 590 (100) [M^{+} + 1]. − $C_{34}H_{41}NO_4P_2$ (589.65): calcd. C 69.26, H 7.01, N 2.38; found C 69.20, H 6.97, N 2.42.

The δ-amino esters **8a−c** and δ-amino phosphonates **9b,c** can also be obtained in a one-pot reaction: To a solution of aromatic enamine/imine **1/1′** at −78 °C or a solution of aliphatic enamine **1** at 0 °C (each 5 mmol) in THF (15 mL) was added a 1.6 M methyllithium solution in diethyl ether (5 mmol). The mixture was allowed to stir at this temperature for 1 h. A solution of alkyl halide (6 mmol) in THF (5 mL) was then added at the same temperature. After the mixture was allowed to warm to room temp., it was stirred for 12 h. The resulting solution was then concentrated under vacuum, diluted with EtOH (15 mL) and a previously prepared solution of $NaBH_3CN$ and $ZnCl_2$ in EtOH (10 mL) was then added. The mixture was stirred and refluxed for 24 h. and then was concentrated under vacuum, washed with NaOH (0.1 M, 50 mL) and extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layers were washed with water, dried over $MgSO_4$ and concentrated under vacuum. The crude residue was purified by flash column chromatography eluting with AcOEt/hexanes (4:1 or 1:4) to afford 1.88 g (81%) of **8a**, 2.20 g (84%) of **8b**, 1.39 g (62%) of **8c**, 2.51 g (85%) of **9b** or 1.79 g (70%) of **9c**.

General Procedure for the Synthesis of the Primary δ-Amino esters 10 and the Primary δ-Amino Phosphonates 11: A solution of δ-amino ester **8b** or δ-amino phosphonate **9b** (5 mmol) and $Pd(OH)_2$/C 20% (0.35 g, 0.5 mmol) in EtOH (15 mL) was stirred under a hydrogen atmosphere (80 psi) until TLC indicated the disappearance of the starting material (3−4 days). The mixture was then filtered through celite, washed with a 10% aqueous solution of citric acid (50 mL) and extracted with AcOEt (3 × 25 mL). The combined organic layers were washed with water, dried over $MgSO_4$ and concentrated under vacuum.

Ethyl 5-Amino-4-(diphenylphosphinyl)hexanoate (10): Synthesized according to the general procedure with a mixture of δ-amino esters **8b** (2.56 g, 5 mmol), affording 1.60 g (89%) of a mixture of diastereoisomers **10** (*de* = 50%) as a pale yellow oil. R_f = 0.09 (AcOEt). − ^{1}H NMR: δ = 7.82−7.11 (m, 10 H), 5.92 and 5.81 (s, 2 H), 4.08−3.87 (m, 2 H), 2.47−1.43 (m, 6 H), 1.35−1.10 (m, 3 H), 1.01 and 0.98 (2 d, $^{3}J_{HH}$ = 6.4 Hz and $^{3}J_{HH}$ = 6.4 Hz, 3 H). − ^{13}C NMR: δ = 173.7, 171.3, 133.2−126.0 (m), 60.3, 48.3, 47.4, 39.5 and 37.3 (2 d, $^{1}J_{PC}$ = 71.0 Hz and $^{1}J_{PC}$ = 71.0 Hz), 31.5 and 30.6 (2 d, $^{3}J_{PC}$ = 12.1 Hz and $^{3}J_{PC}$ = 11.9), 23.8 and 23.4 (2 d, $^{3}J_{PC}$ = 16.3 Hz and $^{3}J_{PC}$ = 11.9), 21.4, 21.3, 14.1. − ^{31}P NMR: δ = 32.7, 32.3. − IR (film): ṽ = 3051, 1725, 1672 cm^{-1}. − MS: *m*/*z* (%) = 360 (100) [M^{+} + 1]. − $C_{20}H_{26}NO_3P$ (359.40): calcd. C 66.84, H 7.29, N 3.90; found C 66.75, H 7.33, N 3.87.

Diethyl [4-Amino-3-(diphenylphosphinyl)pentyl]phosphonate (11): Synthesized according to the general procedure with the mixture of δ-amino phosphonates **9b** (2.95 g, 5 mmol), affording 1.80 g (85%) of a mixture of diastereoisomers **11** (*de* = 50%) as a pale yellow oil. R_f = 0.05 (AcOEt). − ^{1}H NMR: δ = 7.79−7.10 (m, 12 H), 4.05−3.82 (m, 4 H), 2.42−2.15 (m, 1 H), 2.17−1.42 (m, 5 H), 1.27−1.08 (m, 9 H). − ^{13}C NMR: δ = 132.3−126.0 (m), 61.7, 61.6, 56.3 and 55.7 (2 dd, $^{1}J_{PC}$ = 55.4 Hz, $^{3}J_{PC}$ = 10.6 Hz and $^{1}J_{PC}$ =

55.4 Hz, $^3J_{PC}$ = 11.0 Hz), 47.3, 47.2, 29.7, 29.6, 23.9 and 22.8 (2 dd, $^1J_{PC}$ = 142.5 Hz, $^3J_{PC}$ = 8.5 Hz and $^1J_{PC}$ = 142.6 Hz, $^3J_{PC}$ = 6.9 Hz), 20.1, 20.0, 16.4, 16.3. − ^{31}P NMR: δ = 31.5, 30.1, 31.4, 29.1. − IR (film): ṽ = 2984, 1693, 1486 cm^{-1}. − MS: *m/z* (%) = 424 (100) [M$^+$ + 1]. − $C_{21}H_{31}NO_4P_2$ (423.43): calcd. C 59.57, H 7.38, N 3.31; found C 59.49, H 7.34, N 3.29.

General Procedure for the Synthesis of the *N*-aryl Dihydropyridones 13a and 13b: To a −78 °C solution of aromatic enamine/imine **1/1′**(5 mmol) in THF (15 mL) was added a 1.6 M methyllithium solution in diethyl ether. The mixture was allowed to stir at this temperature for 1 h. and a solution of ethyl 3-bromopropionate (0.48 mL, 6 mmol) in THF (5 mL) was then added. After the mixture was allowed to warm to room temp., the reaction mixture was stirred until TLC indicated the disappearance of the aromatic imine/enamine **1/1′**. The mixture was then diluted with water (50 mL) and extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layers were washed with water, dried over $MgSO_4$ and concentrated under vacuum. The crude residue was purified by crystallization from diethyl ether.

5-(Diphenylphosphinyl)-6-methyl-1-*p*-tolyl-3,4-dihydro-1*H*-pyridin-2-one (13a). Synthesized according to the general procedure withthe corresponding enamine/imine **1/1′** (5 mmol), affording 1.66 g (83%) of **13a** as a white solid. M.p.: 146−147 °C. − ^{1}H NMR: δ = 7.85−7.03 (m, 14 H), 2.56 (m, 2 H), 2.30 (s, 3 H), 2.14 (m, 2 H), 1.86 (s, 3 H). − ^{13}C NMR: δ = 170.2, 150.9 (d, $^2J_{PC}$ = 15.5 Hz), 132.8−128.5 (m), 105.4 (d, $^1J_{PC}$ = 109.5 Hz), 31.2 (d, $^2J_{PC}$ = 7.5 Hz), 23.8 (d, $^3J_{PC}$ = 11.2 Hz), 21.0, 19.8 (d, $^3J_{PC}$ = 5.0 Hz). − ^{31}P NMR: δ = 31.5. − IR (KBr): ṽ = 3061, 1694, 1620 cm^{-1}. − MS: *m/z* (%) = 401 (80) [M$^+$]. − $C_{25}H_{24}NO_2P$: calcd. C 74.80, H 6.03, N 3.49; found C 73.75, H 5.99, N 3.47.

General Procedure for the Synthesis of *N*-alkyl Dihydropyridones 13c and 13d: To a solution of imine **3e** or **3h** (5 mmol) in THF (15 mL) at 0 °C was added a 1.6 M methyllithium solution in diethyl ether (5 mmol). The mixture was allowed to stir at this temperature for 1 h. After the mixture was allowed to warm to room temp. it was stirred until TLC indicated the disappearance of **3e** or **3h**. The mixture was then diluted with water (50 mL) and extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layers were washed with water, dried over $MgSO_4$ and concentrated under vacuum. The crude residue was purified by crystallization from diethyl ether.

5-(Diphenylphosphinyl)-6-methyl-1-[1-(*S*)-phenylethyl]-3,4-dihydro-1*H*-pyridin-2-one (13c): Synthesized according to the general procedure with imine **3e** (2.31 g, 5 mmol), affording 1.65 g (80%) of **13c** as a white solid. M.p.: 142−143 °C. − $[\alpha]_D^{20}$ = −13.1 (*c* = 1.09, CH_2Cl_2). − ^{1}H NMR: δ = 7.74−7.09 (m, 15 H), 5.45 (q, $^3J_{HH}$ = 6.6 Hz, 1 H), 2.45 (m, 2 H), 2.05 (m, 2 H), 1.95 (s, 3 H), 1.91 (d $^3J_{HH}$ = 6.6 Hz, 3 H). − ^{13}C NMR: δ = 170.3, 151.5 (d, $^2J_{PC}$ = 16.1 Hz), 133.2−126.1 (m), 109.1 (d, $^1J_{PC}$ = 108.8 Hz), 60.3, 32.0 (d, $^2J_{PC}$ = 7.2 Hz), 23.2 (d, $^3J_{PC}$ = 11.1 Hz), 19.8, 13.7. − ^{31}P NMR: δ = 30.9. − IR (KBr): ṽ = 3033, 1700, 1632 cm^{-1}. − MS: *m/z* (%) = 416 (100) [M$^+$ + 1]. − $C_{26}H_{26}NO_2P$ (415.47): calcd. C 75.16, H 6.31, N 3.37; found C 73.25, H 6.29, N 3.34.

Procedure for the Synthesis of 5-(Diphenylphosphinyl)-6-ethyl-1-(4-methoxyphenyl)-1*H*-pyridin-2-one (14): A solution of ceric ammonium nitrate (CAN) (8.22 g, 15 mmol) in water (50 mL) was added to a solution of *N*-aryl dihydropyridone **13b** (2.16 g, 5 mmol) in acetonitrile (30 mL) at 0 °C. The mixture was allowed to stir at this temperature for 1 h. and water (300 mL) was then added. The mixture was extracted with AcOEt (3 × 50 mL) and the organic layer was sequentially washed with a 20% aqueous solution of Na_2SO_3 (3 × 50 mL), a saturated solution of $KHCO_3$ (100 mL), a saturated solution of NaCl (100 mL) and water (100 mL). The combined organic layers were dried over $MgSO_4$ and concentrated under vacuum. The crude residue was purified by crystallization from diethyl ether, affording 1.48 g (69%) of **14** as a white solid. M.p.: 162−163 °C. − ^{1}H NMR: δ = 7.64−6.95 (m, 14 H), 6.86 (dd, $^3J_{PH}$ = 10.8 Hz, $^3J_{HH}$ = 9.5 Hz, 1 H), 6.32 (dd, $^4J_{PH}$ = 2.6 Hz $^3J_{HH}$ = 9.5 Hz, 1 H), 3.78 (s, 3 H), 2.82 (q, $^3J_{HH}$ = 7.2 Hz, 2 H), 0.64 (t, $^3J_{HH}$ = 7.2 Hz, 3 H). − ^{13}C NMR: δ = 162.0 (d, $^2J_{PC}$ = 15.1 Hz),159.7, 142.0 (d, $^2J_{PC}$ = 12.1 Hz), 133.4−114.1 (m), 117.0 (d, $^3J_{PC}$ = 12.0 Hz), 107.4 (d, $^1J_{PC}$ = 114.2 Hz), 55.5, 25.7, 13.1. − ^{31}P NMR: δ = 30.2. − IR (KBr): ṽ = 3012, 1694, 1629 cm^{-1}. − MS: *m/z* (%) = 430 (100) [M$^+$ + 1]. − $C_{26}H_{24}NO_3P$ (429.45): calcd. C 72.72, H 5.63, N 3.26; found C 72.81, H 5.60, N 3.28.

General Procedure for the Synthesis of Pyrroles 15. Procedure A: A solution of K_2CO_3 (3.46 g, 25 mmol), phenyl bromide (1.05 mL, 10 mmol), $Pd(PPh_3)_4$ (0.115 g, 0.1 mmol) and imine **3d,g,j** (5 mmol) in DMF (20 mL) was stirred at 60 °C until TLC indicated the disappearance of the starting material (6−12 h). The mixture was diluted with water (50 mL) and extracted with AcOEt (3 × 25 mL). The combined organic layers were washed with water (50 mL), dried over $MgSO_4$ and concentrated under vacuum. The crude residue was purified by flash column chromatography eluting with AcOEt/hexanes (3:1).

Procedure B: A solution of K_2CO_3 (3.46 g, 25 mmol), $Pd(OAc)_2$ (0.023 g, 0.1 mmol) and the imine **3d,g,j** (5 mmol) in DMF (20 mL) was stirred at 60 °C until TLC indicated the disappearance of the starting material (6−12 h). The mixture was then diluted with water (50 mL) and extracted with AcOEt (3 × 25 mL). The combined organic layers were washed with water (50 mL), dried over $MgSO_4$ and concentrated under vacuum. The crude residue was purified by flash column chromatography eluting with AcOEt/hexanes (1:3).

5-Benzyl-3-(diphenylphosphinyl)-2-methyl-1-*p*-tolyl-1*H*-pyrrole (15a): The general procedure A was followed using imine **3d** (1.93 g, 5 mmol), affording 1.61 g (70%) of **15a** as a white solid. M.p.: 131−132 °C. − ^{1}H NMR: δ = 7.75−6.74 (m, 19 H), 5.70 (d, $^3J_{PH}$ = 3.8 Hz, 1 H), 3.57 (s, 2 H), 2.31 (s, 3 H), 1.95 (s, 3 H). − ^{13}C NMR: δ = 138.4, 137.1 (d, $^2J_{PC}$ = 16.6 Hz), 135.7−127.8 (m), 110.4 (d, $^2J_{PC}$ = 13.1 Hz), 107.9 (d, $^1J_{PC}$ = 128.9 Hz), 32.7, 21.1, 14.0. − ^{31}P NMR: δ = 24.6. − IR (KBr): ṽ = 2919, 1507 cm^{-1}. − MS: *m/z* (%) = 461 (100) [M$^+$]. − $C_{31}H_{28}NOP$ (461.54): calcd. C 80.67, H 6.11, N 3.03; found C 80.74, H 6.08, N 3.07.

3-(Diphenylphosphinyl)-2,5-dimethyl-1-*p*-tolyl-1*H*-pyrrole (15d): The general procedure B was followed using imine **3d** (1.93 g, 5 mmol), affording 1.32 g (69%) of **15d** as a white solid. M.p.: 153−154 °C. − ^{1}H NMR: δ = 7.73−6.97 (m, 14 H), 5.56 (d, $^3J_{PH}$ = 3.7 Hz, 1 H), 2.34 (s, 3 H), 1.99 (s, 3 H), 1.77 (s, 3 H). − ^{13}C NMR: δ = 138.4, 137.0 (d, $^2J_{PC}$ = 17.1 Hz), 135.5−127.7 (m), 110.3 (d, $^2J_{PC}$ = 12.9 Hz), 107.7 (d, $^1J_{PC}$ = 138.4 Hz), 21.1, 12.7, 12.6. − ^{31}P NMR: δ = 24.7. − IR (KBr): ṽ = 3017, 1519 cm^{-1}. − MS: *m/z* (%) = 385 (75) [M$^+$]. − $C_{25}H_{24}NOP$ (385.44): calcd. C 77.90, H 6.28, N 3.63; found C 80.01, H 6.30, N 3.64.

X-ray Crystallography for 5b: Single-crystal X-ray diffraction experiments were carried out on a Enraf−Nonius CAD-4 diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.7173 Å). A prismatic crystal of dimensions 0.21 × 0.16 × 0.11 mm was used for data collection. Crystal data: orthorhombic (space group $P2_12_12_1$), *a* = 8.659(2), *b* = 10.673(2), *c* = 25.455(11) Å, *V* = 2352.5(12) Å^3,$\rho_{calcd.}$ = 1.224 g·cm^{-3}. Data collection was performed at 293 K, with $2\theta_{max}$ = 50° and θ−2θ scans. The total number of measured reflections was 4660, of which 4139 were independent with $I > 2\sigma(I)$. A Lorentzian polarization correction was applied using JANA98 software,[28] but no absorption correction (μ = 0.143 mm^{-1}). The structure was solved by direct methods, using the SIR97 program,[29] and was refined by full-matrix least-squares against $|F|^2$; all reflections were considered (SHELXL-97[30]). The total number of parameters was 284, and all H atoms were generated using geometrical criteria and refined isotropically. Final values for R indices: R_w(all) = 0.1269, R_w(obs) = 0.1083, R(all) = 0.0736 and R(obs) = 0.0391. Residual electron density: min. = −0.204 and max = 0.268.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-152699. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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