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A convenient approach to λ5-phosphinines via interaction of phosphorylated 3-pyrrolidinocrotonitrile with 2-bromoacetophenones

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Abstract—The alkylation of 2-(diphenylphosphino)-3-pyrrolidin-1-ylbut-2-enenitrile with a set of bromoacetophenones has been studied. Cyclization of the phosphonium salts into 6-cyano-3-hydroxy-3-aryl-1,1-diphenyl-5-pyrrolidin-1-yl-1,2,3,4-tetrahydrophosphininium bromides under heating in the presence of catalytic amount of a base is discussed. Starting both from the acyclic and the cyclic phosphonium salts, new types of λ5-phosphinines have been synthesized.

1. Introduction

The phosphorus-containing heterocycles are a less numerous and less accessible class of compounds in comparison with the classical nitrogen or sulfur heterocycles.[1] However, interest in this class of compounds, especially toward the ones with an endocyclic P–C bond, has increased due to their recent use in a wide variety of areas such as model objects in fundamental research,[2] as ligands for new catalysts,[3] for modifying properties of materials,[4] and as important building blocks for drug discovery.[5]

Among the most important representatives of the phosphorus containing heterocycles λ3- and λ5-phosphinines should be noted.[6] These two classes differ in the coordination state of the phosphorus atom and confer marked difference in their chemical properties. For example, unlike λ5-phosphinines, λ3-phosphinines are air-sensitive compounds and their handling requires special laboratory equipment and synthetic procedures. At the same time the majority of the methods for synthesis of λ5-phosphinines is based on oxidation of λ3-phosphinines so that even λ5-phosphinines are fairly inaccessible compounds with limited practical use. Synthetic approaches to λ5-phosphinines circumventing the formation of λ3-phosphinines would certainly solve many above-mentioned problems.

There are few such methods depicted in Figure 1.

The first synthesis of phosphinine comprises double alkylation of potassium phosphide with 1,5-bishalogen derivative **II** followed by oxidation (Way 1).[7a] Later use of unsaturated derivatives, acetylenes **IV**,[7b,c] in the reaction with primary phosphines allowed circumvention of the oxidation stage, an umpolung approach of the reaction was also studied utilizing dihalogenophosphines (Way 2).[7d] In both cases, λ5-phosphinines are formed in the course of 4-methoxy-1,4-dihydrophosphinine rearrangement. Another synthetic approach to λ5-phosphinines is based on the recyclization of phosphapyrillium salt **IX** followed by reduction with $SiHCl_3$ (Way 3).[7e] All these approaches are either multistep syntheses with low total yields or include steps with unstable, highly reactive or fairly inaccessible compounds.

Recently we have found a convenient approach to λ5-phosphinines based on the reaction of phosphonium salt **XI**, a 1,5-bisnucleophile, with the 1,1-biselectrophile, DMFDMA. In this work we describe that phosphines of type **X** can act as 1,4-bisnucleophiles with 1,2-biselectrophilic bromoacetophenones.

2. Results and discussion

The lack of a convenient synthetic procedure for preparation of phosphine **1** prompted us to optimize an available procedure. The procedure developed for preparation of the starting phosphine **1** does not require reducing the corresponding

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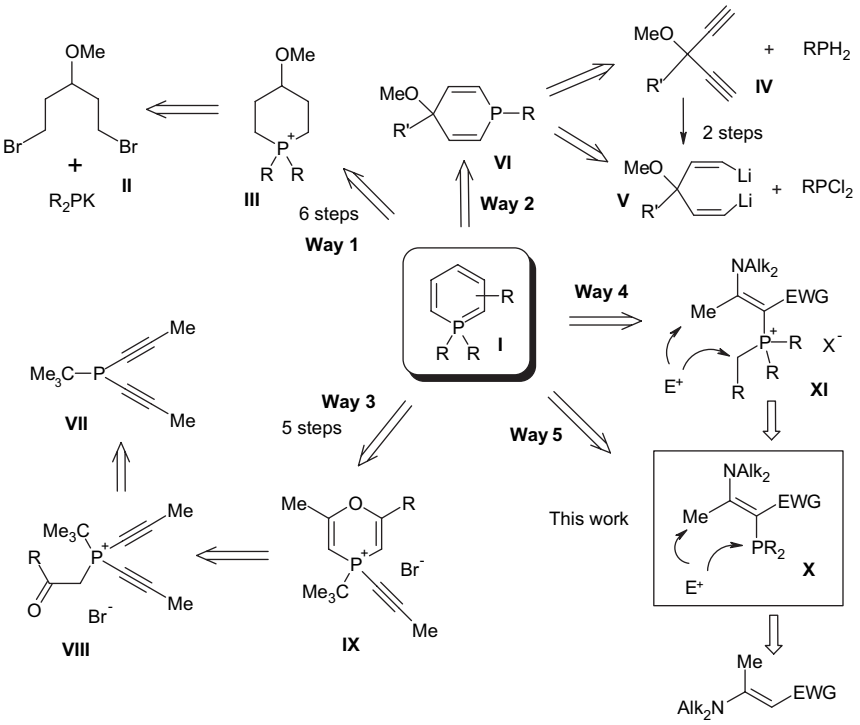
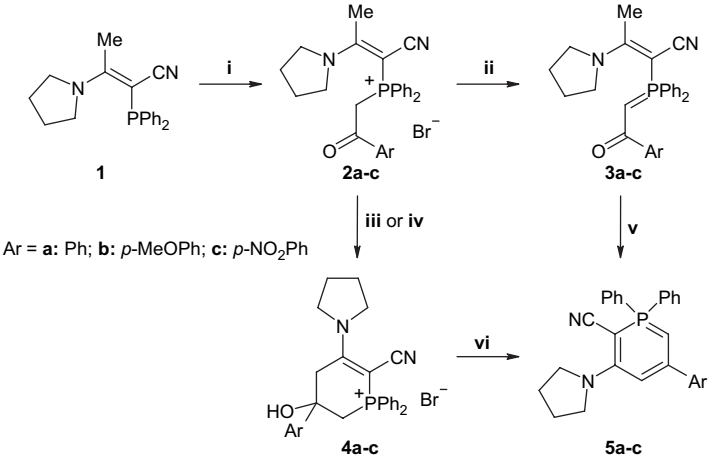


Figure 1. Available methods for synthesis of λ^5-phosphinines circumventing the formation of λ^3-phosphinines.

phosphine selenide.[8a] We have found that neat phosphine **1** prepared by direct phosphorylation of pyrrolidinocrotononitrile[8] is quite stable and could be recrystallized from ethanol. The procedure allows us to prepare it in gram scale batches.

Alkylation of phosphines with alkyl halogens bearing an electron–acceptor group is known to be a quite complicated process that in many cases does not lead to phosphonium salts.[9] Fortunately, in our case phosphine **1** reacts with bromoacetophenones in benzene affording phosphonium salts **2a**–**c** in high yield. Moreover, the phosphonium salts precipitate leaving admixture in the solution (Scheme 1).

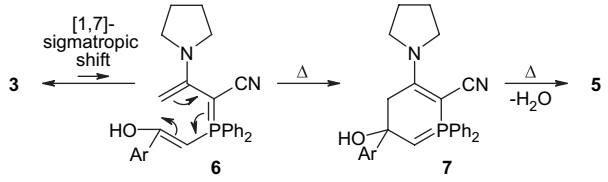
Our main objective was to cyclize the phosphonium salts **2a**–**c** into the corresponding phosphinines **5a**–**c**. It is well known that the phosphonium salts of type **2** are easily converted into stabilized phosphorane ylides.[10] Indeed, bases such as aqueous sodium carbonate or triethylamine transformed the phosphonium salts into stabilized ylides **3a**–**c**. Compounds of type **3a**–**c** bearing a carbon atom instead of a phosphorus atom are known to cyclize into benzene derivatives upon treatment with bases.[11] In the case of compounds **3a**–**c** due to conjugation with the ylide, the electrophilicity of carbonyl group is markedly decreased compared to the carbon analogues. Various attempts to cyclize these compounds at elevated temperature with and without triethylamine lead to pronounced resinification of the reaction mixtures that contain 10–15% of phosphinines **5** as judged from ^{31}P NMR and HPLC–MS spectra. Ylides **3** behave likewise upon treatment with strong bases such as DBU in DMF (100 °C) and LDA in



Scheme 1. Reagents and conditions: (i) $ArCOCH_2Br$, benzene, 7–10 h; (ii) CH_2Cl_2, 1 equiv base; (iii) benzene, 80 °C, 0.1 equiv base; (iv) benzene, 80 °C, 0.1 equiv **6**; (v) 150 °C, 0.03 Torr; (vi) DMF, microwave, 220 °C, 5 min.

THF (−78 °C) so that it is impossible to separate the target product in pure form.

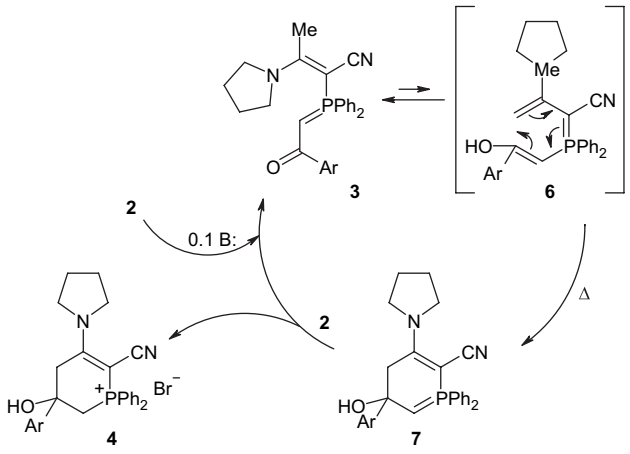
Analysis of MS spectrum (of ylide **3a**) revealed the presence of a peak that can be ascribed to phosphinine **5a** (M=420). Thus, it was logical to assume that under analogous conditions ylides **3** could be transformed into phosphinines **5**. Indeed, heating ylides **3** neat at 150 °C in vacuo (0.03 Torr) for 5 min afforded the corresponding phosphinines **5** in moderate yields (33–35%). It should be noted that except for phosphinines **5**, in the course of the reaction the phosphineoxide of phosphorylated enamine **1**[8b] is formed, most probably via thermal intermolecular Wittig reaction as judged by ^{31}P NMR and HPLC–MS spectra. Thus, we conclude that ylides **3** undergo thermal cyclization leading to cyclic ylides **7** followed by dehydration thus affording the final phosphinines **5** (Scheme 2).



Scheme 2.

Searching to improve yields we tested other procedures. Thus, heating for 10 h at a temperature of 100 °C ylide **3a** in DMF with 3 equiv of trimethylchlorosilane followed by treatment with water[12] afforded 2-(diphenylphosphoryl)-1-phenylethanone[13] in 81% yield. Under analogous conditions the phosphonium salt **2a** gave only 63% 2-(diphenylphosphoryl)-1-phenylethanone. As cleavage of aminophosphonium salts is well known in the case of the salts bearing enamine residue, that is, vinylogous amines, one can assume that cleavage proceeds analogously.[14] At the same time boiling salts **2** in the presence of catalytic amounts of bases such as triethylamine or Hunig's base afforded cyclic phosphonium salts **4** (Scheme 1). It should be noted that the reaction was run in nonpolar solvents such as benzene or toluene where both the starting salts **2** and the resulting cyclic salts **4** are very poorly soluble. In the course of the reaction organic by-products remain in solution so that it is very easy to separate the target products. Monitoring the reaction was conducted by taking ^{31}P NMR spectra of the precipitate periodically. Taking into account the fact that upon treatment with a base, salts **2** are converted into ylides **3** that thermally cyclize into the phosphinines as well as the fact that both the starting and the targeted phosphonium salts are in precipitate in the course of the reaction one can assume that this transformation proceeds via ylide **3**.

The following mechanistic pathway was proposed to rationalize the reaction (Scheme 3). The reaction starts with partial transformation of salt **2** into ylide **3** upon treatment of a base. Ylide **3** undergoes [1,7]-sigmatropic H-shift affording cyclic ylide **7** as in the case of the flash vacuum pyrolysis described above. We have already mentioned that thermal cyclization of ylide **3** in a solution failed probably due to low stability of the intermediate cyclic ylide **7**. In this case ylide **7**, a strong base, removes a proton from the acyclic salt **2** turning it into the final cyclic phosphonium salt **4** and liberating ylide **3** so that the whole cycle can be repeated (Scheme 3). Additional proof supporting the mechanism is the fact that the reaction proceeds analogously when the corresponding ylide (0.1 equiv) is used instead of an organic base (0.1 equiv).

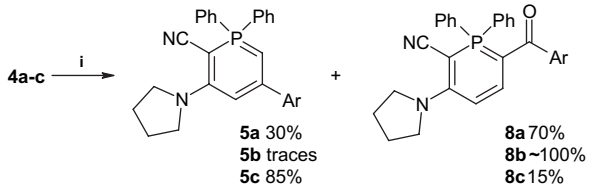


Scheme 3.

The most obvious approach to λ^5-phosphinines is by dehydration and dehydrohalogenation of phosphonium salts **4a–c**. This simple looking transformation was very difficult to accomplish. The reaction in pyridine using thionyl chloride proceeds with considerable resinification of the reaction mixture. As in the case of ylide **3** treatment of these salts with strong bases such as LDA, DBU, dimsyl sodium or a methanol–water solution of potassium hydroxide resulted in a mixture of products containing predominantly the phosphineoxide of enamine **1** as judged by ^{31}P NMR and HPLC–MS spectra.[8b]

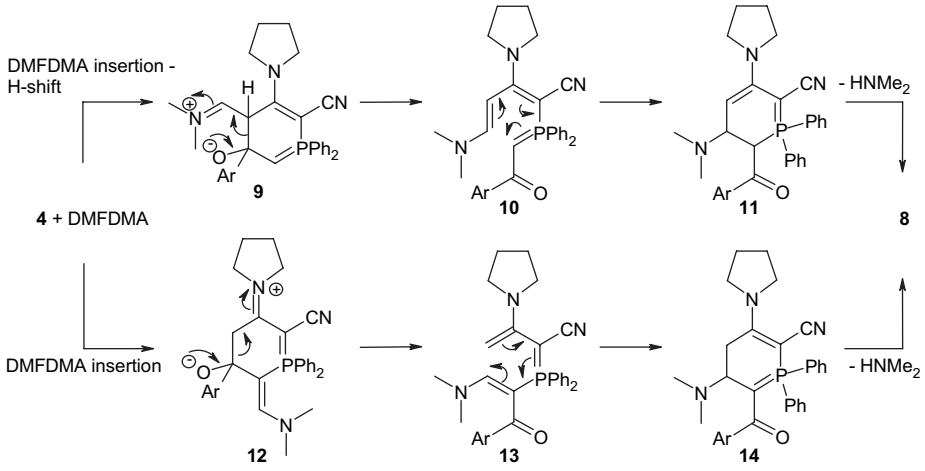
As the cyclic phosphonium salts **4a–c** are high melting compounds, flash vacuum pyrolysis requires high temperatures so that under these conditions we failed to obtain any individual compound. However, under microwave irradiation at 220 °C the salt **4**a was transformed into the corresponding phosphinine **5a**.

Quite unexpected results were obtained in the reaction of the cyclic phosphonium salts with DMFDMA as a base. Thus, heating the phosphonium salts **4** in DMFDMA results in a mixture of phosphinines **5** and **8** in various ratios (Scheme 4).



Ar = **a:** Ph; **b:** *p*-MeOPh; **c:** *p*-NO_2Ph

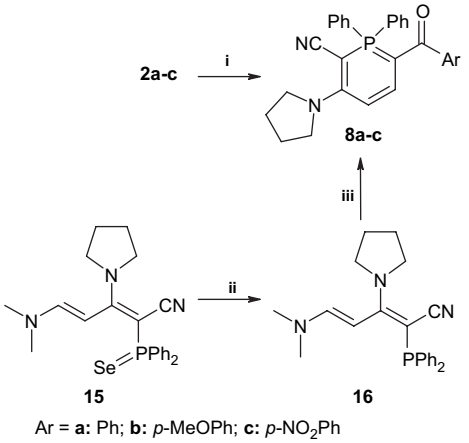
Scheme 4. Reagents and conditions: (i) DMFDMA, 110 °C, 2 h. Ratios of compounds **5** and **8** are given based on chromato-mass spectrometry data of the reaction mixtures.



Scheme 5.

Formation of phosphinines **5** proceeds via dehydrogenation and dehydrohalogenation of the starting phosphonium salts. At the same time synthesis of phosphinines **8** could be rationalized by the following scheme (Scheme 5). DMFDMA can react at both CH_2 groups of the cyclic phosphonium salts **4** affording intermediates **9** or **12**. Both these intermediates could undergo opening of the cycle giving acyclic ylides **10** or **13**, further cyclization followed by elimination of dimethylamine in both cases lead to the final phosphinines **8**.[8a]

We have synthesized compound **8** by an alternative method,[8a] namely the reaction of the phosphonium salts **2a–c** with DMFDMA under heating. It should be noted that these λ^5-phosphinines could be prepared under milder conditions. Thus, phosphine **16** prepared from its selenide **15**[8a] by the reaction with $P(NMe_2)_3$ was treated in situ with bromoacetophenones at room temperature affording λ^5-phosphinines **8a–c**. The cyclization proceeds spontaneously followed by elimination of dimethylamine (Scheme 6).



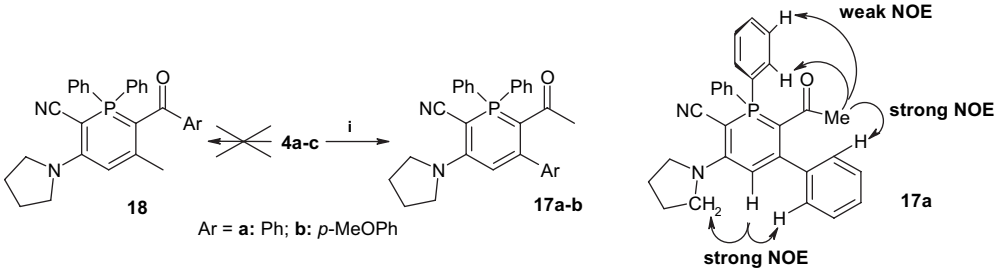
Scheme 6. Reagents and conditions: (i) DMFDMA, 110 °C; (ii) benzene, $P(NMe_2)_3$; (iii) benzene, $ArCOCH_2Br$.

Use of Ac_2O in the presence of AcONa leads to the phosphinines **17a–c** being acylated at the 6-position of the phosphinine heterocycle (Scheme 7). The reaction proceeds in low yields; moreover phosphinine **17c** was only obtained in trace amounts.

It should be noted that in this case unstable ylide **7** formed at the first stage undergoes acylation at the ylidic carbon atom followed by dehydration. Alternative compounds of type **18** that can be formed by the recyclization mechanism given for DMFDMA could not be ruled out. Nevertheless, no evidence for their formation was found. Moreover, the structure of phosphinine **17** was confirmed by NOE experiment (Scheme 7).

3. Conclusion

In conclusion, we have found a convenient and simple method for the synthesis of different derivatives of λ^5-



Scheme 7. Reagents and conditions: (i) Ac_2O, AcONa, 140 °C.

phosphinines. The starting materials are readily available enamines and bromoacetophenones. It was shown that the phosphonium salts prepared by alkylation of 2-(diphenylphosphino)-3-pyrrolidin-1-ylbut-2-enenitrile with bromoacetophenones gave stabilized ylides upon treatment with an equimolar amount of a base, but their treatment with catalytic amounts of a base leads to the cyclic phosphonium salts. Reaction conditions for transformation of the ylides and the cyclic phosphonium salts into the corresponding 5-aryl-2-cyano-3-pyrrolidin-1-yl-1λ^5-phosphinines have been found. In addition, it was found that dehydration of the cyclic phosphonium salts with DMFDMA was accompanied with formylation and recyclization and the dehydration with Ac_2O in the presence of AcONa was accompanied with acylation at the 6-position of the phosphinine heterocycle. Plausible mechanisms of these transformations were discussed.

4. Experimental

4.1. General

All procedures with compounds sensitive to hydrolysis and oxidation were carried out in an atmosphere of dry argon. All solvents were purified and dried by standard methods. ^{1}H and ^{31}P NMR spectra were recorded on a Varian VXR-300 spectrometer: ^{1}H (300 MHz), C_6D_6, $CDCl_3$ or DMSO-d_6 as solvents with TMS as an internal standard; ^{31}P (121 MHz) with 85% H_3PO_4 as an external standard, for all compounds phosphorus spectra were recorded in the same solvent that was used for recording ^{1}H NMR. NOE correlations and ^{13}C NMR spectra were recorded on a Bruker Avance DRX 500 spectrometer (500 MHz and 100 MHz, respectively) with C_6D_6, $CDCl_3$, and DMSO-d_6 as solvents with TMS as an internal standard. IR spectra were recorded on a Nexus-470 spectrometer for samples in KBr discs. LC/MS (APCI MS) spectra were recorded using chromatography/mass spectrometric system, Agilent 1100/DAD/MSD VL G1965a instrument and 'HEWLETT-PACKARD' HP GC/MS 5890/5972 instrument (EI, 70 eV) by GC inlet. Mass spectra were obtained on a VG 70-70EQ, VG ANALYTICAL (FAB) for phosphonium salts or a MX-1321 instrument (EI, 70 eV) by direct inlet for other substances. Column chromatography was performed on silica gel (63–200 mesh, Merck). Silica gel Merck $60F_{254}$ plates were used for TLC. Microwave irradiation experiments were performed using Emrys Creator EXP. Microanalyses were performed in the Microanalytical Laboratory of the Institute of Organic Chemistry, National Academy of Sciences of Ukraine. Melting points are uncorrected. Yields refer to pure isolated products.

4.1.1. 2-(Diphenylphosphino)-3-pyrrolidin-1-ylbut-2-enenitrile (1). To a stirred solution of Ph_2PCl (3.24 g, 14.7 mmol) in dichloromethane (30 mL) under dry argon, a solution of enamine **1** (2 g, 14.7 mmol) and Et_3N (1.93 g, 19 mmol) in dichloromethane (20 mL) was added dropwise. After 7 h the reaction mixture was washed with water (30 mL). The organic layer was separated, dried (Na_2SO_4), and evaporated in vacuo. The residue was crystallized from *i*-PrOH; white solid (2.82 g, 60%); mp 115–116 °C; [found: C 74.95; H 6.62; N 8.69; P 9.60. $C_{20}H_{21}N_2P$ requires: C 74.98; H 6.61; N 8.74; P 9.67%]; δ_P −10.2; δ_H (C_6D_6) 7.83 (4H, dd, $^3J_{HH}$ 7.5 Hz, $^3J_{PH}$ 7.5 Hz, PPh_2), 7.09–7.25 (6H, m, PPh_2), 3.04 (4H, br m, NCH_2), 2.02 (3H, s, CH_3), 1.03 (4H, br m, CH_2); δ_C (C_6D_6) 164.5 ($^2J_{CP}$ 40.6 Hz, C(3)), 139.0 ($^1J_{CP}$ 8.2 Hz, PPh_2), 133.4 ($^2J_{CP}$ 20.2 Hz, PPh_2), 128.7 (PPh_2), 128.7 ($^3J_{CP}$ 5.1 Hz, PPh_2), 121.6 ($^2J_{CP}$ 3.8 Hz, CN), 68.3 ($^1J_{CP}$ 11 Hz, C(2)), 50.9 (NCH_2), 25.1 (CH_2), 20.8 (C(4)); *m*/*z* (EI): 320 (M^+, 100), 243 (18), 212 (61), 183 (30), 108 (58), 70 (14), 42 (20%).

4.2. General procedure for acyclic phosphonium salts

Procedure A. To a stirred solution of phosphine **1** (0.5 g, 1.6 mmol) in benzene (10 mL) under dry argon, a solution of an appropriate bromoacetophenone (1.7 mmol) was added. After 4 days the precipitated solid was collected by filtration and washed with benzene (20 mL) or acetone (20 mL) for **2c**.

4.2.1. (1-Cyano-2-pyrrolidin-1-ylprop-1-enyl)(2-oxo-2-phenylethyl)diphenylphosphonium bromide (2a). Procedure A was applied; off-white solid (0.63 g, 77%); mp 195–196 °C (benzene); [found: C 64.70; H 5.39; Br 15.29; N 5.43; P 6.01. $C_{28}H_{28}BrN_2OP$ requires: C 64.75; H 5.43; Br 15.38; N 5.39; P 5.96%]; ν_{max} (KBr): 3052, 3014, 2875, 2786, 2179, 1675, 1542, 1436, 1403, 1346, 1263, 1145, 1106, 991, 862, 763, 688, 549 cm^{-1}; δ_P 23.2; δ_H ($CDCl_3$) 8.30 (2H, d, $^3J_{HH}$ 7.5 Hz, Ph), 7.85–7.95 (4H, m, PPh_2), 7.54–7.73 (7H, m, PPh_2 (6H), Ph (1H)), 7.46 (2H, t, $^3J_{HH}$ 7.5 Hz, Ph), 5.57 (2H, d, $^2J_{PH}$ 13.5 Hz, PCH_2), 4.06 (2H, br m, NCH_2), 3.77 (2H, br m, NCH_2), 2.25 (3H, s, CH_3), 2.22 (2H, br m, CH_2), 2.05 (2H, br m, CH_2); δ_C ($CDCl_3$) 191.2 ($^2J_{CP}$ 6.4 Hz, CO); 169.2 ($^2J_{CP}$ 15.5 Hz, C(2)), 135.5 ($^3J_{CP}$ 4.8 Hz, Ph), 134.5 ($^4J_{CP}$ 4 Hz, PPh_2), 133.9 (Ph), 133.4 ($^3J_{CP}$ 10.5 Hz, PPh_2), 132.6 ($^4J_{CP}$ 3 Hz, Ph), 130.7 (Ph), 130.0 ($^2J_{CP}$ 13.0 Hz, PPh_2), 120.6 ($^1J_{CP}$ 90.6 Hz, PPh_2), 118.6 ($^2J_{CP}$ 11.9 Hz, CN), 54.5 (NCH_2), 53.2 (NCH_2), 49.7 ($^1J_{CP}$ 125.8 Hz, C(1)), 39.7 ($^1J_{CP}$ 61.9 Hz, PCH_2), 25.7 (CH_2), 24.8 (CH_2), 24.6 ($^3J_{CP}$ 4.2 Hz, C(3)); *m*/*z* (FAB): 439 (M^+, 100%).

4.2.2. (1-Cyano-2-pyrrolidin-1-ylprop-1-enyl)[2-(4-methoxyphenyl)-2-oxoethyl]diphenylphosphonium bromide (2b). Procedure A was applied; white solid (0.6 g, 68%); mp 193–195 °C (benzene); [found: C 63.48; H 5.45; Br 14.65; N 5.11; P 5.68. $C_{29}H_{30}BrN_2O_2P$ requires: C 63.39; H 5.50; Br 14.54; N 5.10; P 5.64%]; δ_P 28.4; δ_H ($CDCl_3$) 8.34 (2H, d, $^3J_{HH}$ 7.8 Hz, *p*-MeOPh), 7.85–7.95 (4H, m, PPh_2), 7.55–7.74 (6H, m, PPh_2), 6.94 (2H, d, $^3J_{HH}$ 7.8 Hz, *p*-MeOPh), 5.45 (2H, d, $^2J_{PH}$ 14 Hz, PCH_2), 4.06 (2H, br m, NCH_2), 3.84 (3H, s, OCH_3), 3.79 (2H, br m, NCH_2), 2.27 (3H, s, CH_3), 2.15 (2H, br m, CH_2), 2.05 (2H, br m, CH_2); δ_C ($CDCl_3$) 190.2 ($^2J_{CP}$ 6.3 Hz, CO), 169.2 ($^2J_{CP}$ 15.1 Hz, C(2)), 164.8 (*p*-MeOPh), 134.4 ($^4J_{CP}$ 3.8 Hz, PPh_2), 133.4 ($^3J_{CP}$ 11.3 Hz, PPh_2), 132.5 (*p*-MeOPh), 130.0 ($^2J_{CP}$ 12.6 Hz, PPh_2), 128.7 ($^3J_{CP}$ 5 Hz, *p*-MeOPh), 120.8 ($^1J_{CP}$ 90.5 Hz, PPh_2), 118.6 ($^2J_{CP}$ 11.3 Hz, CN), 114.2 (*p*-MeOPh), 55.7 (OCH_3), 54.5 (NCH_2), 53.2 (NCH_2), 50.0 ($^1J_{CP}$ 124.5 Hz, C(1)), 39.3 ($^1J_{CP}$ 61.6 Hz, PCH_2), 25.7 (CH_2), 24.9 (CH_2), 24.5 ($^3J_{CP}$ 4 Hz, C(3)); *m*/*z* (FAB): 469 (M^+, 100%).

4.2.3. (1-Cyano-2-pyrrolidin-1-ylprop-1-enyl)[2-(4-nitrophenyl)-2-oxoethyl]diphenylphosphonium bromide (2c). Procedure A was applied; pale yellow solid (0.57 g, 63%); mp 195–197 °C (acetone); [found: C 59.57; H 4.81; Br 14.22; N 7.43; P 5.51. $C_{28}H_{27}BrN_3O_3P$ requires: C 59.59; H 4.82; Br 14.16; N 7.44; P 5.49%]; δ_P 22.9; δ_H ($CDCl_3$) 8.59 (2H, d, $^3J_{HH}$ 8.1 Hz, *p*-NO_2Ph), 8.25 (2H, d, $^3J_{HH}$ 8.1 Hz, *p*-NO_2Ph), 7.88–7.99 (4H, m, PPh_2), 7.61–7.73 (6H, m, PPh_2), 5.82 (2H, d, $^2J_{PH}$ 13.2 Hz, PCH_2), 4.10 (2H, br m, NCH_2), 3.76 (2H, br m, NCH_2), 2.25 (3H, s, CH_3), 2.22 (2H, br m, CH_2), 2.06 (2H, br m, CH_2); δ_C ($CDCl_3$) 191.3 ($^2J_{CP}$ 5.5 Hz, CO), 168.8 ($^2J_{CP}$ 15.4 Hz, C(2)), 150.7 (*p*-NO_2Ph), 139.8 ($^3J_{CP}$ 5.3 Hz, *p*-NO_2Ph), 134.7 ($^4J_{CP}$ 3.3 Hz, PPh_2), 133.4 ($^3J_{CP}$ 11.3 Hz, PPh_2), 131.1 (*p*-NO_2Ph), 130.1 ($^2J_{CP}$ 13.5 Hz, PPh_2), 123.8 (*p*-NO_2Ph), 120.1 ($^1J_{CP}$ 90.6 Hz, PPh_2), 118.4 ($^2J_{CP}$ 11.7 Hz, CN), 54.5 (NCH_2), 53.2 (NCH_2), 49.5 ($^1J_{CP}$ 126.2 Hz, C(1)), 40.3 ($^1J_{CP}$ 62.0 Hz, PCH_2), 25.7 (CH_2), 24.8 (CH_2), 24.5 ($^3J_{CP}$ 4.2 Hz, C(3)); *m*/*z* (FAB): 484 (M^+, 100%).

4.3. General procedures for cyclic phosphonium salts

Procedure A. To a stirred suspension of phosphonium salts **2a–c** (1 mmol) in benzene (15 mL) Et_3N (0.01 g, 0.1 mmol) was added, and the reaction mixture was heated under reflux with stirring for 10 h. After cooling, precipitated solid was collected by filtration and washed with benzene (20 mL).

Procedure B. To a stirred suspension of phosphonium salt **2a** (0.52 g, 1 mmol) in benzene (15 mL) ylide **3a** (0.04 g, 0.1 mmol) was added, and the reaction mixture was refluxed with stirring for 10 h. After cooling, the precipitated solid was collected by filtration and washed with benzene (20 mL).

4.3.1. 6-Cyano-3-hydroxy-1,1,3-triphenyl-5-pyrrolidin-1-yl-1,2,3,4-tetrahydrophosphininium bromide (4a). Procedure A was applied; white solid (0.42 g, 80%); procedure B was applied (0.46 g, 88%); mp 218–220 °C (benzene); [found: C 64.71; H 5.39; Br 15.35; N 5.41; P 6.02. $C_{28}H_{28}BrN_2OP$ requires: C 64.75; H 5.43; Br 15.38; N 5.39; P 5.96%]; ν_{max} (KBr): 3135 (b), 3064, 2977, 2912, 2175, 1537, 1436, 1342, 1112, 1062, 943, 856, 744, 705, 520 cm^{-1}; δ_P 20.6; δ_H (DMSO-d_6) 7.95–8.06 (2H, m, PPh_2), 7.59–7.90 (10H, m, PPh_2 (8H), Ph (2H)), 7.30–7.45 (3H, m, Ph), 6.28 (1H, s, OH), 4.11–4.23 (1H, m, C(2)H_2), 3.94–4.06 (1H, m, C(2)H_2), 3.59–3.79 (4H, br m, NCH_2), 3.51 (1H, d, $^2J_{HH}$ 16.5 Hz, C(4)H_2), 3.05 (1H, d, $^2J_{HH}$ 16.5 Hz, C(4)H_2), 1.81–2.09 (4H, br m, CH_2CH_2); δ_C (DMSO-d_6) 165.7 ($^2J_{CP}$ 15.1 Hz, C(5)), 146.2 ($^3J_{CP}$ 11.3 Hz, Ph), 133.9 (PPh_2), 133.2 and 132.9 ($^3J_{CP}$ 10.5 Hz, PPh_2), 129.3 and 129.1 ($^2J_{CP}$ 12.6 Hz, PPh_2), 128.0 (Ph), 127.5 (Ph), 125.0 (Ph), 122.5 and 122.1 ($^1J_{CP}$ 90.6 Hz, PPh_2), 118.5 ($^2J_{CP}$ 6.3 Hz, CN), 71.1 ($^2J_{CP}$ 6.3 Hz, C(2)), 52.4 (NCH_2), 51.7 (NCH_2), 45.6 ($^1J_{CP}$ 110.3 Hz, C(6)), 43.3 (C(4)), 31.4 ($^1J_{CP}$ 4.2 Hz, C(2)), 25.8 (CH_2), 24.1 (CH_2); *m*/*z* (FAB): 439 (M^+, 100%); *m*/*z* (EI): 420 (M^+-H_2O, 12), 235 (17), 85 (70), 83 (100), 47 (28%).

4.3.2. 6-Cyano-3-hydroxy-3-(4-methoxyphenyl)-1,1-diphenyl-5-pyrrolidin-1-yl-1,2,3,4-tetrahydrophosphininium bromide (4b). Procedure A was applied; white solid (0.4 g, 74%); mp 223–225 °C (benzene); [found: C 63.40; H 5.48; Br 14.60; N 5.11; P 5.61. $C_{29}H_{30}BrN_2O_2P$ requires: C 63.39; H 5.50; Br 14.54; N 5.10; P 5.64%]; δ_P 21.6; δ_H (DMSO-d_6) 7.95–8.06 (2H, m, PPh_2), 7.67–7.88 (8H, m, PPh_2), 7.53 (2H, d, $^3J_{HH}$ 9 Hz, *p*-MeOPh), 6.95 (2H, d, $^3J_{HH}$ 9 Hz, *p*-MeOPh), 6.20 (1H, s, OH), 4.10–4.22 (1H, m, C(2)H_2), 3.95–4.07 (1H, m, C(2)H_2), 3.75 (3H, s, OCH_3), 3.56–3.73 (4H, br m, NCH_2), 3.43 (1H, d, $^2J_{HH}$ 16.5 Hz, C(4)H_2), 3.01 (1H, d, $^2J_{HH}$ 16.2 Hz, C(4)H_2), 1.82–2.09 (4H, br m, CH_2CH_2); δ_C (DMSO-d_6) 166.3 ($^2J_{CP}$ 15.1 Hz, C(5)), 159.2 (*p*-MeOPh), 138.9 ($^3J_{CP}$ 11.3 Hz, *p*-MeOPh), 134.5 and 134.1 (PPh_2), 133.7 and 133.4 ($^3J_{CP}$ 11.3 Hz, PPh_2), 130.0 and 129.7 ($^2J_{CP}$ 12.6 Hz, PPh_2), 126.8 (*p*-MeOPh), 123.1 and 122.6 ($^1J_{CP}$ 91.8 Hz, PPh_2), 119.1 ($^2J_{CP}$ 6.3 Hz, CN), 114.0 (*p*-MeOPh), 71.4 ($^2J_{CP}$ 6.3 Hz, C(3)), 55.7 (OCH_3), 53.0 (NCH_2), 52.3 (NCH_2), 46.0 ($^1J_{CP}$ 117 Hz, C(6)), 44.2 ($^3J_{CP}$ 2.5 Hz, C(4)), 32.0 ($^1J_{CP}$ 51.6 Hz, C(2)), 25.7 (CH_2), 24.7 (CH_2); *m*/*z* (FAB): 469 (M^+, 100%).

4.3.3. 6-Cyano-3-hydroxy-3-(4-nitrophenyl)-1,1-diphenyl-5-pyrrolidin-1-yl-1,2,3,4-tetrahydrophosphininium bromide (4c). Procedure A was applied; pale yellow solid (0.38 g, 68%); mp 230–233 °C (benzene); [found: C 59.65; H 4.84; Br 14.20; N 7.48; P 5.40. $C_{28}H_{27}BrN_3O_3P$ requires: C 59.59; H 4.82; Br 14.16; N 7.44; P 5.49%]; δ_P 17.7; δ_H (DMSO-d_6) 8.27 (2H, d, $^3J_{HH}$ 9 Hz, *p*-NO_2Ph), 7.68–8.10 (12H, m, PPh_2 (10H), *p*-NO_2Ph (2H)), 6.62 (1H, s, OH), 4.10–4.22 (1H, m, C(2)H_2), 3.93–4.05 (1H, m, C(2)H_2), 3.6–3.83 (4H, br m, NCH_2), 3.57 (1H, d, $^2J_{HH}$ 16.5 Hz, C(4)H_2), 3.11 (1H, d, $^2J_{HH}$=17.7 Hz, C(4)H_2), 1.81–2.08 (4H, br m, CH_2CH_2); δ_C (DMSO-d_6) 165.6 ($^2J_{CP}$ 15.1 Hz, C(2)), 153.7 ($^3J_{CP}$ 6.3 Hz, *p*-NO_2Ph), 147.5 (*p*-NO_2Ph), 134.6 and 134.2 ($^4J_{CP}$ 2.5 Hz, PPh_2), 133.8 and 133.5 ($^3J_{CP}$ 11.3 Hz, PPh_2), 130.0 and 129.8 ($^2J_{CP}$ 12.6 Hz, PPh_2), 127.3 (*p*-NO_2Ph), 123.9 (*p*-NO_2Ph), 122.8 and 122.4 ($^1J_{CP}$ 93.1 Hz, PPh_2), 119.0 ($^2J_{CP}$ 7.5 Hz, CN), 71.8 ($^2J_{CP}$ 6.3 Hz, C(3)), 53.0 (NCH_2), 52.4 (NCH_2), 46.0 ($^1J_{CP}$ 115.7 Hz, C(6)), 43.2 ($^3J_{CP}$ 2.5 Hz, C(4)), 31.5 ($^1J_{CP}$ 54.1 Hz, C(2)), 25.8 (CH_2), 24.6 (CH_2); *m*/*z* (FAB): 484 (M^+, 100%).

4.4. General procedure for ylides 3

To a solution of phosphonium salts **2a–c** (1 mmol) in dichloromethane (15 mL) a 10% aqueous Na_2CO_3 (15 mL) was added, and the reaction mixture was stirred for 5 min. The organic layer was separated, dried (Na_2SO_4), and evaporated in vacuo.

4.4.1. 2-[(2-Oxo-2-phenylethylidene)(diphenyl)phosphoranyl]-3-pyrrolidin-1-ylbut-2-enenitrile (3a). Yellow solid (0.19 g, 43%); mp 124–127 °C (CH_2Cl_2); [found: C 76.73; H 6.20; N 6.35; P 6.98. $C_{28}H_{27}N_2OP$ requires: C 76.69; H 6.21; N 6.39; P 7.06%]; ν_{max} (KBr): 3054, 2958, 2923, 2171, 1602, 1582, 1525, 1436, 1407, 1390, 1346, 1249, 1168, 1105, 1027, 873, 750, 694, 549, 514 cm^{-1}; δ_P 16.8; δ_H ($CDCl_3$) 7.85–7.95 (6H, m, PPh_2 (6H), Ph (2H)), 7.45–7.59 (6H, m, PPh_2), 7.32–7.40 (3H, m, Ph), 4.26 (1H, d, $^2J_{PH}$ 24.6 Hz, PCH), 3.92 (2H, br m, NCH_2), 3.59 (2H, br m, NCH_2), 2.26 (3H, s, CH_3), 1.99 (4H, br m, CH_2); δ_C ($CDCl_3$) 184.3 ($^2J_{CP}$ 3.8 Hz, CO), 168.3 ($^2J_{CP}$ 11.3 Hz, C(3)), 142.2 ($^3J_{CP}$ 16.3 Hz, Ph), 132.7 ($^3J_{CP}$ 10.1 Hz,

PPh_2), 131.9 ($^4J_{CP}$ 2.5 Hz, PPh_2), 132.6 (Ph), 128.8 ($^2J_{CP}$ 13.8 Hz, PPh_2), 128.1 ($^1J_{CP}$ 84.3 Hz, PPh_2), 127.8 (Ph), 126.8 (Ph), 120.8 ($^2J_{CP}$ 10.1 Hz, CN), 57.0 ($^1J_{CP}$ 117 Hz, C(2)), 53.3 ($^1J_{CP}$ 114.4 Hz, PCH), 51.5 (NCH_2), 52.9 (NCH_2), 25.7 (CH_2), 24.9 (CH_2), 22.0 ($^3J_{CP}$ 5 Hz, C(4)); *m/z* (FAB): 439 (MH^+, 100), 421 (8), 337 (11), 201 (13), 154 (17), 136 (13), 77 (8%).

4.4.2. 2-[[2-(4-Methoxyphenyl)-2-oxoethylidene](diphenyl)phosphoranyl]-3-pyrrolidin-1-ylbut-2-enenitrile (3b). Pale yellow solid (0.33 g, 70%); mp 114–116 °C (CH_2Cl_2); [found: C 74.34; H 6.20; N 5.93; P 6.65. $C_{29}H_{29}N_2O_2P$ requires: C 74.34; H 6.24; N 5.98; P 6.61%]; δ_P 16.6; δ_H ($CDCl_3$) 7.82–7.94 (6H, m, PPh_2 (4H), *p*-MeOPh (2H)), 7.41–7.52 (6H, m, PPh_2), 6.85 (2H, d, $^3J_{HH}$ 8.7 Hz, *p*-MeOPh), 4.21 (1H, d, $^2J_{PH}$ 24.3 Hz, PCH), 3.92 (2H, br m, NCH_2), 3.81 (3H, s, OCH_3), 3.52 (2H, br m, NCH_2), 2.23 (3H, s, CH_3), 1.98 (4H, br m, CH_2); δ_C ($CDCl_3$) 183.8 ($^2J_{CP}$ 3.8 Hz, CO), 168.3 ($^2J_{CP}$ 12.6 Hz, C(3)), 160.6 (*p*-MeOPh), 132.7 ($^3J_{CP}$ 8.8 Hz, PPh_2), 132.0 (*p*-MeOPh), 131.9 ($^4J_{CP}$ 2.5 Hz, PPh_2), 128.9 ($^1J_{CP}$ 94.3 Hz, PPh_2), 128.8 ($^2J_{CP}$ 12.6 Hz, PPh_2), 128.3 (*p*-MeOPh), 120.9 ($^2J_{CP}$ 8.8 Hz, CN), 112.9 (*p*-MeOPh), 57.3 ($^1J_{CP}$ 115.7 Hz, C(2)), 55.8 ($^1J_{CP}$ 122 Hz, PCH), 55.3 (OCH_3), 52.9 (NCH_2), 51.4 (NCH_2), 25.7 (CH_2), 25.0 (CH_2), 21.9 ($^3J_{CP}$ 5 Hz, C(3)); *m/z* (FAB): 469 (MH^+, 100), 337 (18), 201 (14), 154 (10), 136 (9), 135 (10%).

4.4.3. 2-[[2-(4-Nitrophenyl)-2-oxoethylidene](diphenyl)phosphoranyl]-3-pyrrolidin-1-ylbut-2-enenitrile (3c). Orange solid (0.25 g, 51%); mp 118–121 °C (CH_2Cl_2); [found: C 69.51; H 5.43; N 8.60; P 6.37. $C_{28}H_{26}N_3O_3P$ requires: C 69.56; H 5.42; N 8.69; P 6.41%]; δ_P 17.0; δ_H ($CDCl_3$) 8.18 (2H, d, $^3J_{HH}$ 8.4 Hz, *p*-NO_2Ph), 8.02 (2H, d, $^3J_{HH}$ 8.4 Hz, *p*-NO_2Ph), 7.84–7.95 (4H, m, PPh_2), 7.46–7.63 (6H, m, PPh_2), 4.35 (1H, d, $^2J_{PH}$ 23.1 Hz, PCH), 3.99 (2H, br m, NCH_2), 3.56 (2H, br m, NCH_2), 2.23 (3H, s, CH_3), 2.01 (4H, br m, CH_2); δ_C ($CDCl_3$) 181.2 ($^2J_{CP}$ 3.8 Hz, CO), 168.1 ($^2J_{CP}$ 13.8 Hz, C(3)), 148.2 ($^3J_{CP}$ 16.3 Hz, *p*-NO_2Ph), 148.1 (*p*-NO_2Ph), 132.7 ($^3J_{CP}$ 10.1 Hz, PPh_2), 132.3 ($^4J_{CP}$ 2.5 Hz, PPh_2), 129.0 ($^2J_{CP}$ 12.6 Hz, PPh_2), 128.0 ($^1J_{CP}$ 93.1 Hz, PPh_2), 127.7 (*p*-NO_2Ph), 123.1 (*p*-NO_2Ph), 120.4 ($^2J_{CP}$ 11.3 Hz, CN), 56.5 ($^1J_{CP}$ 117 Hz, C(2)), 56.4 ($^1J_{CP}$ 110.7 Hz, PCH), 53.0 (NCH_2), 51.6 (NCH_2), 25.8 (CH_2), 24.9 (CH_2), 22.3 ($^3J_{CP}$ 3.8 Hz, C(4)); *m/z* (FAB): 484 (MH^+, 95), 319 (47), 201 (100), 136 (21), 69 (30), 55 (45), 44 (33%).

4.5. General procedures for λ⁵-phosphinines 5

Procedure A. Finely powdered ylide **3** (0.5 mmol) was heated at 150 °C (0.03 Torr) approximately for 5 min (until gas evolution ceased from the melt). After cooling the residue was crystallized from MeOH.

Procedure B. The phosphonium salt **4a** (0.1 g, 0.19 mmol) was charged into an appropriate argon-flushed Smith microwave process vial and DMF (1.0 mL) was added. The vial was sealed with a Teflon septum and placed into the microwave cavity. After irradiation at 220 °C for 5 min and subsequent gas jet cooling to 40 °C the mixture was diluted with water (5 mL). The precipitated solid was collected by filtration and crystallized from MeOH.

4.5.1. 1,1,5-Triphenyl-3-pyrrolidin-1-yl-1λ⁵-phosphinine-2-carbonitrile (5a). Procedure A was applied; yellow solid (0.074 g, 35%); procedure B was applied (0.065 g, 81%); mp 175–176 °C (MeOH); [found: C 76.71; H 6.11; N 8.12; P 8.98. $C_{22}H_{21}N_2P$ requires: C 76.73; H 6.15; N 8.13; P 8.99%]; ν_{max} (KBr): 3055, 2968, 2945, 2870, 2159, 1527, 1502, 1477, 1436, 1373, 1346, 1330, 1109, 1099, 917, 870, 746, 736, 711, 694, 545, 514, 486 cm^{-1}; δ_P 16.4; δ_H ($CDCl_3$) 7.67–7.78 (4H, m, PPh_2), 7.45–7.61 (8H, m, Ph (2H), PPh_2 (6H)), 7.34 (3H, br m, Ph), 4.91 (1H, s, C(4)H), 4.33 (1H, d, $^2J_{PH}$ 18.6 Hz, C(6)H), 3.68 (4H, br m, NCH_2), 1.93 (4H, br m, CH_2); δ_C ($CDCl_3$) 156.3 ($^2J_{CP}$ 7.5 Hz, C(3)), 155.3 ($^2J_{CP}$ 11.3 Hz, C(5)), 144.8 ($^3J_{CP}$ 16.3 Hz, Ph), 132.0 ($^3J_{CP}$ 11.3 Hz, PPh_2), 131.7 ($^4J_{CP}$ 2.5 Hz, PPh_2), 131.4 ($^1J_{CP}$ 93.1 Hz, PPh_2), 128.7 ($^2J_{CP}$ 11.3 Hz, PPh_2), 128.4 (Ph), 128.2 (Ph), 127.0 (Ph), 123.9 ($^2J_{CP}$ 7.5 Hz, CN), 86.9 ($^3J_{CP}$ 8.8 Hz, C(4)), 61.3 ($^1J_{CP}$ 101.9 Hz, C(6)), 50.5 (NCH_2), 34.1 ($^1J_{CP}$ 118.2 Hz, C(2)), 25.7 (CH_2); *m/z* (EI): 420 (M^+, 32), 236 (48), 235 (100), 201 (15), 77 (11), 47 (6%).

4.5.2. 5-(4-Methoxyphenyl)-1,1-diphenyl-3-pyrrolidin-1-yl-1λ⁵-phosphinine-2-carbonitrile (5b). Procedure A was applied; yellow solid (0.077 g, 34%); mp 180–183 °C (MeOH); [found: C 77.28; H 6.03; N 6.22; P 6.93. $C_{29}H_{27}N_2OP$ requires: C 77.31; H 6.04; N 6.22; P 6.88%]; δ_P 16.3; δ_H ($CDCl_3$) 7.66–7.77 (4H, m, PPh_2), 7.43–7.58 (8H, m, *p*-MeOPh (2H), PPh_2 (6H)), 6.89 (2H, d, $^3J_{HH}$ 8.7 Hz, *p*-MeOPh), 4.90 (1H, s, C(4)H), 4.30 (1H, d, $^2J_{PH}$ 17.4 Hz, C(6)H), 3.82 (3H, s, OCH_3), 3.68 (4H, br m, NCH_2), 1.92 (4H, br m, CH_2); δ_C ($CDCl_3$) 159.9 (*p*-MeOPh), 155.3 ($^2J_{CP}$ 12.6 Hz, C(5)), 154.2 ($^2J_{CP}$ 6.3 Hz, C(3)), 137.1 ($^3J_{CP}$ 18.9 Hz, *p*-MeOPh), 132.0 ($^3J_{CP}$ 11.3 Hz, PPh_2), 131.7 (PPh_2), 131.4 ($^1J_{CP}$ 103.1 Hz, PPh_2), 128.7 ($^2J_{CP}$ 11.3 Hz, PPh_2), 128.1 (*p*-MeOPh), 124.0 ($^2J_{CP}$ 6.3 Hz, CN), 113.7 (*p*-MeOPh), 86.5 ($^3J_{CP}$ 8.8 Hz, C(4)), 61.7 ($^1J_{CP}$ 110.7 Hz, C(6)), 55.4 (OCH_3), 50.5 (NCH_2), 34.0 ($^1J_{CP}$ 115.7 Hz, C(2)), 25.7 (CH_2); *m/z* (EI): 450 (M^+, 44), 266 (22), 265 (100), 201 (11), 185 (15), 183 (7), 77 (12), 55 (6%).

4.5.3. 5-(4-Nitrophenyl)-1,1-diphenyl-3-pyrrolidin-1-yl-1λ⁵-phosphinine-2-carbonitrile (5c). Procedure A was applied; red solid (0.077 g, 33%); mp 215–220 °C (MeOH); [found: C 72.27; H 5.19; N 9.08; P 6.67. $C_{28}H_{24}N_3O_2P$ requires: C 72.25; H 5.20; N 9.03; P 6.65%]; δ_P 16.5; δ_H ($CDCl_3$) 8.21 (2H, d, $^3J_{HH}$ 8.7 Hz, *p*-NO_2Ph), 7.63–7.77 (6H, m, *p*-NO_2Ph (2H), PPh_2 (4H)), 7.49–7.61 (6H, m, PPh_2), 4.84 (1H, s, C(4)H), 4.27 (1H, d, $^2J_{PH}$ 17.4 Hz, C(6)H), 3.69 (4H, br m, NCH_2), 1.95 (4H, br m, CH_2); δ_C ($CDCl_3$) 155.5 ($^2J_{CP}$ 12.6 Hz, C(5)), 153.6 ($^2J_{CP}$ 7.5 Hz, C(3)), 151.4 ($^3J_{CP}$ 17.6 Hz, *p*-NO_2Ph), 147.6 (*p*-NO_2Ph), 132.0 ($^3J_{CP}$ 10.1 Hz, PPh_2), 132.0 (PPh_2), 130.9 ($^1J_{CP}$ 91.8 Hz, PPh_2), 128.9 ($^2J_{CP}$ 12.6 Hz, PPh_2), 127.8 (*p*-NO_2Ph), 123.6 (*p*-NO_2Ph), 123.3 ($^2J_{CP}$ 7.5 Hz, CN), 86.9 ($^3J_{CP}$ 8.8 Hz, C(4)), 61.4 ($^1J_{CP}$ 103.1 Hz, C(6)), 50.6 (NCH_2), 35.0 ($^1J_{CP}$ 118.2 Hz, C(2)), 25.7 (CH_2); *m/z* (EI): 465 (M^+, 44), 281 (19), 280 (100), 234 (16), 201 (6), 185 (14), 183 (12), 55 (5%).

4.6. General procedures for λ⁵-phosphinines 8

Procedure A. A stirred suspension of phosphonium salts **2** (1 mmol) in DMFDMA (15 mL) was boiled at 110 °C for

8 h. After cooling the reaction mixture was poured into water (40 mL). The precipitated solid was collected and dried in vacuo. Then the solid was washed with boiling mixture of EtOAc/hexane (1:2) (60 mL).

Procedure B. To a suspension of dienamine **15** (0.5 g, 1.1 mmol) in benzene (15 mL) $P(NMe_2)_3$ (0.2 g, 1.2 mmol) was added, and the reaction mixture was boiled at 80 °C until complete dissolution. After cooling the corresponding alkyl halide (1.2 mmol) was added. After 1 h the reaction mixture was washed with water. The organic layer was separated, dried (Na_2SO_4), and evaporated in vacuo. The residue was washed with a boiling mixture of EtOAc/hexane (1:2) (60 mL).

4.6.1. 6-Benzoyl-1,1-diphenyl-3-pyrrolidin-1-yl-1λ^5-phosphinine-2-carbonitrile (8a). Procedure A was applied; yellow solid (0.30 g, 67%); procedure B was applied (0.36 g, 73%); mp 140–143 °C (EtOAc/hexane); [found: C 77.70; H 5.63; N 6.22; P 6.97. $C_{29}H_{25}N_2OP$ requires: C 77.66; H 5.62; N 6.25; P 6.91%]; ν_{max} (KBr): 3056, 2950, 2925, 2871, 2161, 1546, 1500, 1442, 1373, 1326, 1270, 1099, 728, 703, 509 cm^{-1}; δ_P 13.8; δ_H ($CDCl_3$) 7.85–7.95 (4H, m, PPh_2), 7.48–7.57 (8H, m, PPh_2 (6H), Ph (2H)), 7.35–7.40 (3H, m, Ph), 7.31 (1H, dd, $^3J_{HH}$ 9.3 Hz, $^3J_{PH}$ 33 Hz), 4.89 (1H, dd, $^3J_{HH}$ 10.2 Hz, $^4J_{PH}$ 1.5 Hz, C(4)H), 3.75 (4H, t, $^3J_{HH}$ 6.6 Hz, NCH_2), 1.94 (4H, m, $^3J_{HH}$ 6.6 Hz, CH_2); δ_C ($CDCl_3$) 190.9 ($^2J_{CP}$ 6.3 Hz, CO), 158.6 ($^2J_{CP}$ 10.1 Hz, C(3)), 142.8 ($^2J_{CP}$ 10.1 Hz, C(5)), 139.8 ($^3J_{CP}$ 7.5 Hz, Ph), 133.2 ($^3J_{CP}$ 11.3 Hz, PPh_2), 131.9 ($^4J_{CP}$ 2.5 Hz, PPh_2), 129.9 (Ph), 128.6 (Ph), 128.5 ($^2J_{CP}$ 13.8 Hz, PPh_2), 128.0 (Ph), 126.4 ($^1J_{CP}$ 95.6 Hz, PPh_2), 121.9 ($^2J_{CP}$ 6.3 Hz, CN), 94.4 ($^3J_{CP}$ 10.1 Hz, C(4)), 79.5 ($^1J_{CP}$ 99.4 Hz, C(6)), 51.0 (NCH_2), 44.4 ($^1J_{CP}$ 108.2 Hz, C(2)), 25.5 (CH_2); *m/z* (EI): 448 (M$^+$, 100), 263 (55), 235 (10), 185 (10), 183 (11), 105 (49), 77 (35), 45 (9), 44 (11%).

4.6.2. 6-(4-Methoxybenzoyl)-1,1-diphenyl-3-pyrrolidin-1-yl-1λ^5-phosphinine-2-carbonitrile (8b). Procedure A was applied; yellow solid (0.19 g, 40%); procedure B was applied (0.31 g, 59%); mp 178–180 °C (EtOAc/hexane); [found: C 75.35; H 5.69; N 5.80; P 6.54. $C_{30}H_{27}N_2O_2P$ requires: C 75.30; H 5.69; N 5.85; P 6.47%]; δ_P 13.9; δ_H ($CDCl_3$) 7.83–7.93 (4H, m, PPh_2), 7.45–7.57 (8H, m, PPh_2 (6H), *p*-MeOPh (2H)), 7.36 (1H, dd, $^3J_{HH}$ 10.2 Hz, $^3J_{PH}$ 33 Hz), 6.88 (2H, d, $^3J_{HH}$ 8.7 Hz, *p*-MeOPh), 5.02 (1H, dd, $^3J_{HH}$ 10.2 Hz, $^4J_{PH}$ 1.5 Hz, C(4)H), 3.82 (3H, s, OCH_3), 3.75 (4H, br m, NCH_2), 1.94 (4H, br m, CH_2); δ_C ($CDCl_3$) 190.9 ($^2J_{CP}$ 6.3 Hz, CO), 161.2 (*p*-MeOPh), 158.5 ($^2J_{CP}$ 8.8 Hz, C(3)), 142.9 ($^2J_{CP}$ 8.8 Hz, C(5)), 133.2 ($^3J_{CP}$ 11.3 Hz, PPh_2), 132.3 ($^3J_{CP}$ 10.1 Hz, *p*-MeOPh), 131.8 ($^4J_{CP}$ 2.5 Hz, PPh_2), 130.5 (*p*-MeOPh), 128.4 ($^2J_{CP}$ 12.6 Hz, PPh_2), 126.6 ($^1J_{CP}$ 95.6 Hz, PPh_2), 122.0 ($^2J_{CP}$ 6.3 Hz, CN), 113.3 (*p*-MeOPh), 94.0 ($^3J_{CP}$ 10.1 Hz, C(4)), 79.3 ($^1J_{CP}$ 100.6 Hz, C(6)), 55.4 (OCH_3), 51.0 (NCH_2), 44.4 ($^1J_{CP}$ 108.2 Hz, C(2)), 25.5 (CH_2); *m/z* (EI): 478 (M$^+$, 100), 293 (33), 265 (10), 185 (4), 183(5), 135 (51), 77 (13%).

4.6.3. 6-(4-Nitrobenzoyl)-1,1-diphenyl-3-pyrrolidin-1-yl-1λ^5-phosphinine-2-carbonitrile (8c). Procedure A was applied; yellow solid (0.21 g, 43%); procedure B was applied (0.35 g, 65%); mp 225–226 °C (EtOAc/hexane); [found: C 70.57; H 4.94; N 8.46; P 6.25. $C_{29}H_{24}N_3O_3P$ requires: C 70.58; H 4.90; N 8.51; P 6.28%]; δ_P 13.0; δ_H ($CDCl_3$) 8.23 (2H, d, $^3J_{HH}$ 8.7 Hz, *p*-NO_2Ph), 7.85–7.95 (4H, m, PPh_2), 7.66 (2H, d, $^3J_{HH}$ 8.7 Hz, *p*-NO_2Ph), 7.45–7.62 (6H, m, PPh_2), 7.10 (1H, dd, $^3J_{HH}$ 10.5 Hz, $^3J_{PH}$ 32.4 Hz), 5.10 (1H, dd, $^3J_{HH}$ 10.5 Hz, $^4J_{PH}$ 1.5 Hz, C(4)H), 3.78 (4H, br m, NCH_2), 1.97 (4H, br m, CH_2); δ_C ($CDCl_3$) 188.0 ($^2J_{CP}$ 6.3 Hz, CO), 158.6 ($^2J_{CP}$ 10.1 Hz, C(3)), 148.4 (*p*-NO_2Ph), 146.0 ($^3J_{CP}$ 8.8 Hz, *p*-NO_2Ph), 141.3 ($^2J_{CP}$ 8.8 Hz, C(5)), 133.2 ($^3J_{CP}$ 11.3 Hz, PPh_2), 132.2 ($^4J_{CP}$ 2.5 Hz, PPh_2), 129.3 (*p*-NO_2Ph), 128.6 ($^2J_{CP}$ 12.6 Hz, PPh_2), 125.7 ($^1J_{CP}$ 96.8 Hz, PPh_2), 123.4 (*p*-NO_2Ph), 121.4 ($^2J_{CP}$ 5 Hz, CN), 95.9 ($^3J_{CP}$ 8.8 Hz, C(4)), 79.6 ($^1J_{CP}$ 99.4 Hz, C(6)), 51.1 (NCH_2), 44.8 ($^1J_{CP}$ 110.7 Hz, C(2)), 25.5 (CH_2); *m/z* (EI): 493 (M$^+$, 100), 308 (38), 201 (22), 185 (30), 183 (19), 150 (11), 104 (5), 77 (5%).

4.7. General procedures for λ^5-phosphinines 17

A stirred suspension of phosphonium salt **4** (1 mmol) and AcONa (0.25 g, 3 mmol) in Ac_2O (15 mL) was refluxed for 1 day (**17a**) or 2 days (**17b**). After cooling the reaction mixture was poured into water (50 mL). The precipitated solid was collected and dried in vacuo. The residue was subjected to flash chromatography over silica gel using EtOAc/cyclohexane 1:1 as an eluent affording **17**.

4.7.1. 6-Acetyl-1,1,5-triphenyl-3-pyrrolidin-1-yl-1λ^5-phosphinine-2-carbonitrile (17a). Yellow solid (0.09 g, 19%); mp 198–200 °C; [found: C 77.93; H 5.90; N 6.05; P 6.63. $C_{30}H_{27}N_2OP$ requires: C 77.90; H 5.88; N 6.06; P 6.70%]; R_f (EtOAc/hexane 1:1) 0.45; ν_{max} (KBr): 3052, 2956, 2923, 2865, 2169, 1521, 1477, 1438, 1361, 1294, 1182, 1099, 935, 750, 723, 545, 516, 476 cm^{-1}; δ_P 15.5; δ_H ($CDCl_3$) 7.85–7.95 (4H, m, PPh_2), 7.48–7.57 (6H, m, PPh_2), 7.38 (5H, br m, Ph), 4.96 (1H, s, C(4)H), 3.74 (4H, br m, NCH_2), 1.93 (4H, br m, CH_2), 1.41 (3H, s, $COCH_3$); δ_C ($CDCl_3$) 193.6 ($^2J_{CP}$ 5 Hz, CO), 157.4 ($^2J_{CP}$ 10.1 Hz, C(3)), 154.1 ($^2J_{CP}$ 12.6 Hz, C(5)), 144.1 ($^3J_{CP}$ 12.6 Hz, Ph), 132.9 ($^3J_{CP}$ 10.1 Hz, PPh_2), 131.5 ($^4J_{CP}$ 2.5 Hz, PPh_2), 128.4 (Ph), 128.3 ($^2J_{CP}$ 11.3 Hz, PPh_2), 128.3 (Ph), 128.2 (Ph), 127.8 ($^1J_{CP}$ 98.1 Hz, PPh_2), 122.2 ($^2J_{CP}$ 6.3 Hz, CN), 99.3 ($^3J_{CP}$ 7.5 Hz, C(4)), 81.1 ($^1J_{CP}$ 101.9 Hz, C(6)), 51.0 (NCH_2), 46.1 ($^1J_{CP}$ 106.9 Hz, C(2)), 29.1 ($^3J_{CP}$ 6.3 Hz, COCH_3), 25.5 (CH_2); *m/z* (EI): 462 (M$^+$, 47), 279 (18), 277 (100), 201 (13), 185 (6), 183 (9), 77 (6), 43 (15%).

4.7.2. 6-Acetyl-5-(4-methoxyphenyl)-1,1-diphenyl-3-pyrrolidin-1-yl-1λ^5-phosphinine-2-carbonitrile (17b). Yellow solid (0.09 g, 18%); mp 103–105 °C; [found: C 75.64; H 5.91; N 5.66; P 6.33. $C_{31}H_{29}N_2O_2P$ requires: C 75.59; H 5.93; N 5.69; P 6.29%]; R_f (EtOAc/hexane 1:1) 0.35; δ_P 16.0; δ_H ($CDCl_3$) 7.82–7.93 (4H, m, PPh_2), 7.48–7.57 (6H, m, PPh_2), 7.29 (2H, d, $^3J_{HH}$ 8.7 Hz, *p*-MeOPh), 6.91 (2H, d, $^3J_{HH}$ 8.7 Hz, *p*-MeOPh), 4.97 (1H, s, C(4)H), 3.84 (3H, s, OCH_3), 3.74 (4H, br m, NCH_2), 1.92 (4H, br m, CH_2), 1.46 (3H, s, $COCH_3$); δ_C ($CDCl_3$) 193.9 ($^2J_{CP}$ 5 Hz, CO), 159.8 (*p*-MeOPh), 157.4 ($^2J_{CP}$ 10.1 Hz, C(3)), 154.0 ($^2J_{CP}$ 12.6 Hz, C(5)), 136.5 ($^3J_{CP}$ 13.8 Hz, *p*-MeOPh), 132.8 ($^3J_{CP}$ 10.1 Hz, PPh_2), 131.5 ($^4J_{CP}$ 3.8 Hz, PPh_2), 129.5 (*p*-MeOPh), 128.3 ($^2J_{CP}$ 12.6 Hz, PPh_2), 127.8 ($^1J_{CP}$ 98.1 Hz, PPh_2), 122.3 ($^2J_{CP}$ 6.3 Hz, CN), 113.7 (*p*-MeOPh), 99.2 ($^3J_{CP}$ 7.5 Hz, C(4)), 81.0 ($^1J_{CP}$ 98.1 Hz, C(6)), 55.3

(OCH_3), 51.0 (NCH_2), 45.6 ($^1J_{CP}$ 104.4 Hz, C(2)), 29.2 ($^3J_{CP}$ 5 Hz, $COCH_3$), 25.5 (CH_2); *m/z* (EI): 492 (M^+, 5), 491 (33), 307 (100), 217 (23), 201 (34), 185 (3), 183 (9), 135 (8), 77 (20), 57 (32), 43 (39%).

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