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Convenient method for the synthesis of *C*-phosphorylated *N*-arylformamidines

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ABSTRACT

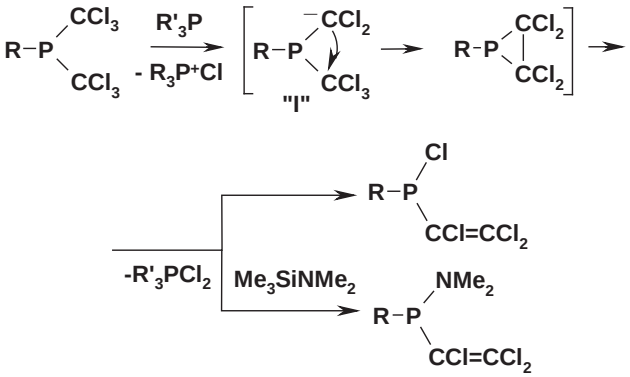
C-Phosphorylated (P^V) arylformamidines have been prepared by the reaction of *N*-arylamidotrichloromethyl derivatives of phosphorus, thiophosphorus, and selenophosphorus acids with secondary amines. Dependence of the reaction on the nature of chalcogene, electronic and steric factors has been studied. By reduction of *N*-arylformamidinophosphonoselenides the corresponding *C*-phosphorylated (P^{III}) arylformamidines have been synthesized.

1. Introduction

C-phosphorylated formamidines are the subject of systematic study due to their multiple functionality that makes them useful both as building blocks and as ligands. Quite often they are called as phosphaguanidines because of structural similarity to guanidines. Methods for their synthesis are not numerous. With few exceptions these compounds have been synthesized by addition of either P(III)H or P(V)H compounds to carbodiimides usually under basic catalysis. It was shown that primary and secondary phosphines add to carbodiimides affording phospha(III)guanidines.[1] Thus, diethyl sodium phosphite readily adds to diphenyl- and to dibutylcarbodiimides; magnesium salts can be used as well.[2] Also in this reaction silylated phosphites can be applied.[3] An addition of *N*-monoarylphosphoramidous esters to carbodiimides also was exploited.[3] Such compounds as *C*-phosphorylated imidoyl chlorides[4] and *C*-phosphorylated derivatives of thioformimidic acid[5] undergo nucleophilic substitution with amines to give *C*-phosphorylated formamidines. There is an exotic approach based on addition of amines to 1-aza-3-phosphaallenes.[6] Another quite attractive method is a direct phosphorylation of formamidines with phosphorus tribromide followed by aminolysis resulting in dialkylamino derivatives of *C*-phosphorylated formamidines in 25–30% yields.[7] *C*-phosphorylated formamidines bearing a single NH functionality that can be converted to the corresponding amidinate anions are used in the synthesis of metal functionalized complexes.[8] This set of methods for the synthesis of *C*-phosphorylated formamidines testifies to their synthetic feasibility, but does not offer a general and convenient approach, so that the need for new convenient methods remains high.

2. Results and discussion

The proposed method was inspired by the property of bis(trichloromethyl)organylphosphines to undergo the rearrangement induced by triorganylphosphines as dechlorinating agents into perchlorovinylchlorophosphines or their amino derivatives in a tricomponent reaction (Scheme 1).[9]



Scheme 1. Proposed mechanism.

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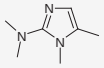
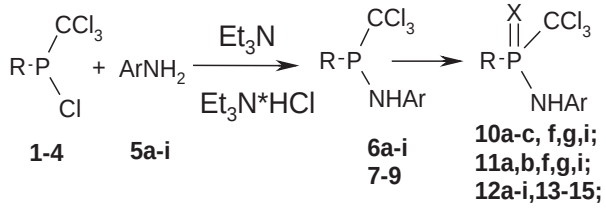
One can expect that in the intermediate 'I' change of the carbanion ($^{-}CCl_2$) for an amide anion ($R'N^{-}$) would lead to the formation of an imidoyl chloride group instead of the perchlorovinyl group. Moreover, use of an amine can further lead to phosphorylated amidines.

To this end, by the reaction of chlorophosphines **1** with arylamines **5** a set of previously unknown phosphonites **6** and phosphinites **7**–**9** has been prepared. They are crystalline low melting compounds (Table 1, Scheme 2).

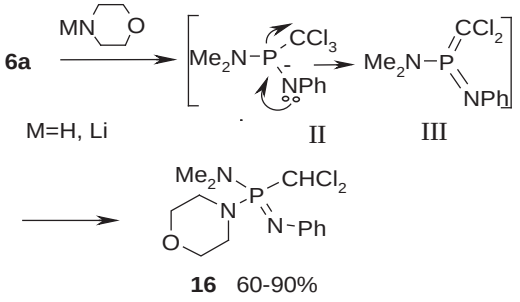
Table 1
The list of substituents for Schemes 2, 4, and 8

Entry	R	Ar	X
1, **6a**, **10a**, **17a**	Me_2N	Ph	O
2, **7**, **13**, **20**, **28**		Ph	Se
3, **8**, **14**, **21**, **29**	*t*-Bu	Ph	Se
4, **9**, **15**, **22**, **30**	1-Ad	Ph	Se
6b, **10b**, **17b**	Me_2N	$C_6H_4CH_3$-*p*	O
6c, **10c**, **17c**	Me_2N	$C_6H_4OCH_3$-*p*	O
6f, **10f**, **17f**	Me_2N	$C_6H_4CF_3$-*m*	O
6g, **10g**, **17g**	Me_2N	$C_6H_4CF_3$-*p*	O
6i, **17i**	Me_2N	Naphth-1-yl	O
11a, **18a**	Me_2N	Ph	S
18b	Me_2N	$C_6H_4CH_3$-*p*	S
11f, **18f**	Me_2N	$C_6H_4CF_3$-*m*	S
11g, **18g**	Me_2N	$C_6H_4CF_3$-*p*	S
18i	Me_2N	Naphth-1-yl	S
5a, **12a**, **19a**, **27a**	Me_2N	Ph	Se
5b, **12b**, **19b**, **27b**	Me_2N	$C_6H_4CH_3$-*p*	Se
5c, **12c**, **19c**, **27c**	Me_2N	$C_6H_4OCH_3$-*p*	Se
5d, **6d**, **12d**, **19d**, **27d**	Me_2N	$C_6H_4OCH_3$-*m*	Se
5e, **6e**, **12e**, **19e**	Me_2N	$C_6H_4NMe_2$-*m*	Se
5f, **12f**, **19f**, **27f**	Me_2N	$C_6H_4CF_3$-*m*	Se
5g, **12g**, **19g**, **27g**	Me_2N	$C_6H_4CF_3$-*p*	Se
5h, **6h**, **12h**, **19h**	Me_2N	C_6H_4Br-*m*	Se
5i, **12i**, **19i**, **27i**	Me_2N	Naphth-1-yl	Se



Scheme 2. Synthesis of the starting materials **10**–**15**.

Compounds like **6**–**9** but bearing Alk group instead of Ar are known to be unstable and are easily transformed into dichloromethyl-*N*-alkylimino-P(Cl)phosphonates.[10] In contrast to this, compounds **6**–**9** are much more stable and they do not change in inert atmosphere at room temperature during a few days, and at temperature below 0 °C they can be stored for a prolonged



Scheme 3. Reaction of P(III) compounds with amines.

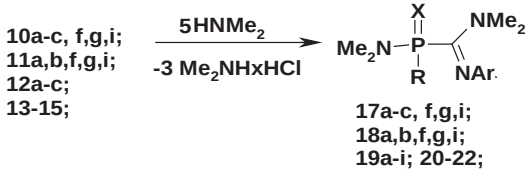
period of time. At the same time their chemical behavior is alike and they tend to form pentavalent phosphorus compounds. For example, the reaction of compound **6a** with morpholine at 60 °C or with lithium morpholide at −60 °C leads to iminophosphonate **16**, but not to the expected *C*-phosphorylated formamidine (Scheme 3).

Most probably amide anion '**II**' stabilizes itself not by nucleophilic attack at the trichloromethyl group, but by more energetically favorable process of shifting negative charge on the phosphorus atom followed by β-decomposition of the formed P anion to a highly reactive σ^3,λ^5-iminomethylenephosphorane '**III**', which upon quick aminolysis afforded iminophosphonate **16**.

Since such a pathway of stabilization of the amide anion is impossible for the pentavalent compounds having tetrahedral phosphorus atoms it would be logical to assume that in similar reactions *C*-phosphorylated amidines would be formed.

As preliminary investigations have shown this mode of the reaction is indeed possible for trichloromethyl derivatives of pentavalent phosphorus bearing an arylamide group at the phosphorus atom with relatively labile hydrogen atom. Due to these properties compounds of this type react with dialkylamines affording *C*-phosphorylated formamidines. To study the reaction in detail and elucidate factors influencing it we have synthesized previously unknown *N*-arylamidotrichloromethylphosphine oxides **10**, -sulfides **11**, -selenides **12**–**15**, the last compounds as a potential source of trivalent *C*-phosphorylated formamidines (Scheme 2).

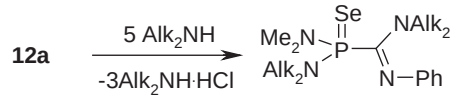
Experimental studies have shown that all compounds **10**–**15** without exception react with dimethylamine in an excess of the amine in the molar ratio 1:5 giving *C*-phosphorylated formamidines **17**–**22** and three equivalents of dimethylamine hydrochloride (Scheme 4).



Scheme 4. Synthesis of phosphorylated formamidines.

It has been found by ^{31}P NMR spectroscopic data that the higher the electronegativity of the chalcogene atom 'X' the easier the reaction proceeds, forming a series P═Se<P═S<P═O. Thus, the reaction runs to completion as follows for **17a**,**18a**,**19a** at 15 °C at 1 h, 5 h and 20 h, respectively. The same time is required for the formation of compounds **17a**,**f**; **18f**; **19a**–**e**, thus confirming that the presence of electron-donating (CH_3–, CH_3O–, Me_2N–) groups at the benzene ring of the anilide group does not influence significantly the relative rate of the reaction. At the same time presence of electron-accepting substituents (Br–, CF_3–), particularly at the *para* position markedly slows the reaction. For example, formation of phosphonates **17f**, **17g** completes in 6 h and 24 h, respectively; thiophosphonates **18f**, **18g**—in 30 h and 5×24 h; selenophosphonates **19f**, **19g**, **19h**,—in 7×24 h, 18×24 h and 5×24 h, respectively. As one would expect, elevating the temperature markedly enhances the rate of the reaction, for example, formation of compound **19g** at 50 °C completes in 2 h, while at 15 °C it requires 18 days.

It has been established that the relative rate of the reaction depends on the nature of the dialkylamine. Thus, the rate increases in the following order: morpholine<dimethylamine<piperidine (Scheme 5). Thus, the reaction of selenophosphonate **12a** with morpholine, dimethylamine, and piperidine at 15 °C completes in 100 h, 20 h, and 1 h, affording compounds **23**, **19**, and **24**, respectively. The observed difference in relative rates of the reaction is due to nucleophilicity of the amines, as addition of strong bases such as Et_3N, *i*-Pr_2EtN does not influence the rate of the reaction.



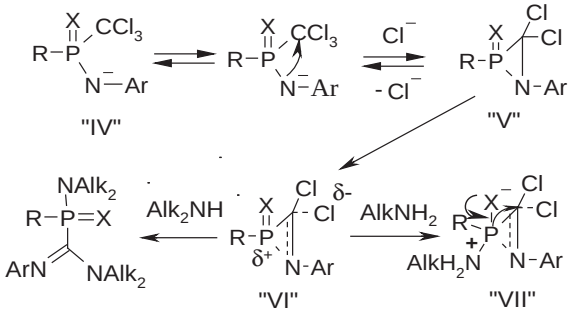
Alk_2N= Me_2N (**19a**); $O(CH_2CH_2)_2N$ (**23**);$(CH_2)_5N$ (**24**)

Scheme 5. Influence of amines.

While introduction into compounds of type **6** instead of a dialkylamino group a sterically hindered and less electron-donating group such as *tert*-butyl, adamantyl group (compounds **8**, **9**) increases their reactivity, an electron-donating and sterically small group such as an imidazolyl group (compound **7**) decreases the reactivity of these compounds. Thus, the reaction of selenophosphinates **13**–**15** with dimethylamine completes at 15 °C in 2 h for **14**, **15** and 3×24 h for **13** leading to *C*-phosphorylated formamidines.

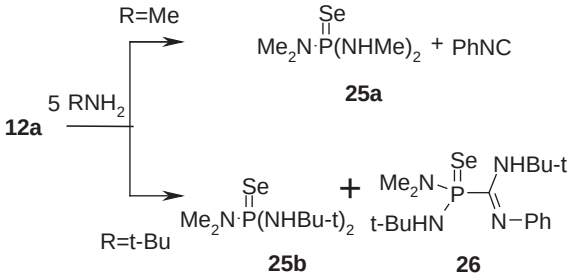
Based on the data on the influence of electronic and steric factors on the reaction rate one can assume that the reaction of trichloromethylphosphonates **10**–**15** with dialkylamines starts at first with deprotonation of the anilide group affording an amide anion. This assumption was confirmed by a complex decomposition of compound **10a** upon treatment with triethylamine in methylene chloride affording benzoisonitrile that was separated as an individual compound. Under these conditions compound **12a** does not react with Et_3N. It is obvious that the higher electronegativity of the chalcogene 'X', the quicker deprotonation would occur. Localization of negative charge on the nitrogen atom would facilitate its attack at the carbon atom of trichloromethyl group resulting in formation of *gem*-dichlorophosphaaziridine. A similar pathway for formation of dichloroaziridines under treatment of bases is known for compounds having HN–C–CCl_3 fragment.[11]

In contrast, delocalization of the negative charge would hamper formation of phosphaaziridine 'V' as a limiting stage. Accordingly, the time of the reaction would be longer for compounds containing electron-accepting substituents (R′=–CF_3, –Br) at the benzene ring of the anilide group. Aminolysis of the intermediate 'V' having tetrahedral composition probably proceeds via transition state 'VI' like the one postulated for acyclic *gem*-dichloroaziridines[12], that correlates with our results. While such factors, steric overcrowdness of the ligands (R=*t*-Bu, Ad) at the phosphorus atom facilitate formation of 'VI', electron-donating ligands (R=NMe_2, imidazolyl) due to delocalization of positive charge hamper the aminolysis stage (Scheme 6).



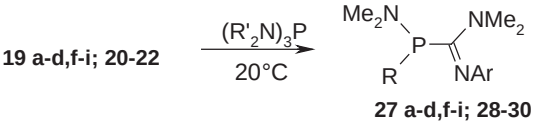
Scheme 6. Proposed mechanism.

It also can be assumed that the interaction of 'VI' with an amine proceeds not only as a synchronous cleavage of the P–N bond, but also can proceed via intermediate 'VII' that has a phosphorane structure and in which cleavage of P–C bond leads to benzoisonitrile. Indeed, the reaction of phosphonate **10a** with methylamine and *tert*-butylamine affords different products (Scheme 7). A small volume of methylamine probably facilitates the reaction along pathway 'V'–'VII' affording *N*,*N*-dimethyl-bis(*N*′-methyl)triamidophosphate **25a** and benzoisonitrile. In the case of *tert*-butylamine formation of phosphorane 'VII' is sterically hindered so that another pathway 'V'–'VI' is realized resulting in phosphorylated amidine **26** and admixture of phosphate **25b** (11%).



Scheme 7. Reaction with primary amines.

Among various types of *C*-phosphorylated arylformamidines the derivatives of trivalent phosphorus with dialkylamide group are the least studied. The only *N*,*N*-dimethyl-*N*-*p*-tolylformamidinotetramethyldiamidophosphonite[7] is described that upon distillation undergoes intramolecular condensation eliminating dimethylamine and forming 2,3-bis(dimethylamino)-5-methyl-1,3-benzazaphosphole in 36% yield. To this end we studied a possibility of preparing *C*-phosphorylated (P^{III}) formamidines and we have found that they can be easily prepared by reduction of selenophosphonates **19**–**22** with tris(*N*,*N*-dialkylamido)phosphites in high yields (Scheme 8).



Scheme 8. Synthesis of *C*-phosphorylated P(III) arylformamidines.

Compounds **27**–**30** are liquids or low-melting crystalline compounds; their composition was proved by a set of physico-chemical methods. Chemical behavior of these compounds will be presented in the future.

Thus, the method developed is a general one and allows preparation of *C*-phosphorylated (P^{III} and P^{V}) arylformamidines.

3. Experimental section

3.1. General methods

All procedures with air and moisture sensitive compounds were performed under an atmosphere of dry argon in flame-dried glassware. Solvents were purified and dried by standard methods. Melting points were determined with an electrothermal capillary melting point apparatus. ^1H spectra were recorded on a Bruker Avance DRX 500 (500.13 MHz) or Varian VXR-300 (299.94 MHz) spectrometer. ^{13}C NMR spectra were recorded on a Bruker Avance DRX 500 (125.75 MHz) spectrometer. ^{31}P NMR spectra were recorded on a Varian VXR-300 (80.95 MHz) spectrometer. Chemical shifts (δ) are reported in parts per million downfield relative to internal TMS (for ^1H, ^{13}C) and external 85% H_3PO_4 (for ^{31}P). Chromatography was performed on silica gel Gerudan SI60. Elemental analyses were performed at the Microanalytical laboratory of the Institute of the Organic Chemistry National Academy of Sciences of Ukraine.

3.2. General procedure for the synthesis of compounds 6. (Compound 6b as an example)

3.2.1. N,N-Dimethyl-N′-(4-methylphenyl)-P-(trichloromethyl)-phosphonous diamide ***6b***. To a solution of *N*,*N*-dimethyl-*P*-(trichloromethyl)phosphonamidous chloride (4.57 g, 20 mmol) in benzene (6 mL), freezed to 0+5 °C was added a solution of *p*-toluidine (2.25 g, 21 mmol) and triethylamine (2.12 g, 21 mmol) in pyridine (20 mL). The reaction mixture was stirred at 18 °C for 20 h monitoring by ^{31}P NMR, upon completion the solvents were evaporated under reduced pressure (keeping temperature below 35–40 °C), the residue was extracted with ether (60 mL), the precipitate obtained was filtered off and the filtrate evaporated in vacuum. The crude product was crystallized from pentane to afford **6b** 4.55 g (76%) as a white solid, mp 41–42 °C; ^{1}H NMR ^{1}H NMR (500 MHz, C_6D_6) δ 7.09 (2H, d, *J*=8.5 Hz, Ar), 7.02 (2H, d, *J*=8.5 Hz, Ar), 5.16 (1H, d, *J*=15.0 Hz, NH), 2.90 (6H, d, *J*=9.0 Hz, NMe_2), 2.30 (3H, s, Me); ^{13}C NMR (125 MHz, C_6D_6) δ 142.4 (d, *J*=2.5 Hz), 140.8 (d, *J*=19.0 Hz), 140.1 (d, *J*=11.4 Hz), 123.6, 123.3 (d, *J*=15.0 Hz), 103.7 (d, *J*=87.0 Hz), 37.9 (d, *J*=18.0 Hz); ^{31}P NMR (81 MHz, C_6D_6) δ 75.7. [Found: C, 40.27; N, 9.31; P, 10.03. $C_{10}H_{14}Cl_3N_2P$ requires C, 40.09; N, 9.35; P, 10.34].

3.2.2. N,N-Dimethyl-N′-phenyl-P-(trichloromethyl)phosphonous diamide ***6a***. Yield 64%, mp 67–68 °C; (pentane); ^{1}H NMR (500 MHz, C_6D_6) δ 7.07 (2H, t, *J*=8.0 Hz, *m*-Ph), 6.90 (2H, d, *J*=7.5 Hz, *o*-Ph), 6.79 (1H, t, *J*=7.0 Hz, *p*-Ph), 4.88 (1H, d, *J*=7.5 Hz, NH), 2.46 (6H, d, *J*=9.0 Hz, NMe_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.3 (d, *J*=20.9 Hz), 129.5, 121.0 (d, *J*=4.0 Hz), 117.4 (d, *J*=13.0 Hz), 104.3 (d, *J*=86.0 Hz), 37.7 (d, *J*=18.0 Hz); ^{31}P NMR (81 MHz, C_6D_6) δ 76.0. [Found: C, 37.53; N, 9.90; P, 10.72. $C_9H_{12}Cl_3N_2P$ requires C, 37.86; N, 9.81; P, 10.85].

3.2.3. N′-(4-Methoxyphenyl)-N,N-dimethyl-P-(trichloromethyl)-phosphonous diamide ***6c***. Yield 75%, mp 45–46 °C; (pentane); ^{1}H NMR (500 MHz, C_6D_6) δ 6.86 (2H, d, *J*=8.5 Hz, Ar), 6.70 (2H, d, *J*=8.5 Hz, Ar), 4.73 (1H, d, *J*=8.5 Hz, NH), 3.33 (3H, s, MeO), 2.49 (6H, d, *J*=8.5 Hz, NMe_2); ^{13}C NMR (125 MHz, C_6D_6) δ 155.0, 137.3 (d, *J*=20.0 Hz), 119.4 (d, *J*=13.0 Hz), 114.9, 104.6 (d, *J*=89.0 Hz), 55.0, 37.8 (d, *J*=18.0 Hz); ^{31}P NMR (81 MHz, C_6D_6) δ 76.6. [Found: C, 37.82; N, 8.64; P, 9.95. $C_{10}H_{14}Cl_3N_2OP$ requires C, 38.06; N, 8.88; P, 9.82].

3.2.4. N′-(3-Methoxyphenyl)-N,N-dimethyl-P-(trichloromethyl)-phosphonous diamide ***6d***. Yield 92%, 140–145 °C/0.05 Torr; ^{1}H NMR (500 MHz, C_6D_6) δ 7.02 (1H, dd, *J*=8.0 Hz, 5H–Ar), 6.71 (1H, s, 2H–Ar), 6.59 (1H, d, *J*=8.5 Hz, Ar), 6.40 (1H, d, *J*=8.5 Hz, Ar), 4.94 (1H, d, *J*=8.5 Hz, NH), 3.33 (3H, s, MeO), 2.46 (6H, d, *J*=9.0 Hz, NMe_2); ^{13}C NMR (125 MHz, C_6D_6) δ 161.2, 145.63 (d, *J*=21.4 Hz), 130.28, 104.21 (d, *J*=42.8 Hz), 103.73 (d, *J*=13.8 Hz), 106.46, 110.01 (d, *J*=12.8 Hz), 54.6, 37.8 (d, *J*=17.6 Hz); ^{31}P NMR (81 MHz, C_6D_6) δ 74.4. [Found: C, 37.96; N, 8.84; P, 9.92. $C_{10}H_{14}Cl_3N_2OP$ requires C, 38.06; N, 8.88; P, 9.82].

3.2.5. N′-[3-(Dimethylamino)phenyl]-N,N-dimethyl-P-(trichloromethyl)phosphonous diamide ***6e***. Yield 80%, mp 75–76 °C; (pentane); ^{1}H NMR (500 MHz, C_6D_6) δ 7.11 (1H, dd, *J*=8.0 Hz, 5H–Ar), 6.48–6.52 (2H, m, Ar), 6.24–6.28 (2H, dd, *J*=2.4, 8.7 Hz), 4.97 (1H, d, *J*=8.7 Hz, NH), 2.53 (6H, s, NMe_2), 2.45 (6H, d, *J*=8.5 Hz, $PNMe_2$); ^{13}C NMR (125 MHz, C_6D_6) δ 151.9, 145.1 (d, *J*=20.1 Hz), 130.1, 106.3 (d, *J*=12.8 Hz), 106.2, 104.6 (d, *J*=86.8 Hz), 40.0, 37.8 (d, *J*=18.9 Hz); ^{31}P NMR (81 MHz, C_6D_6) δ 74.0. [Found: C, 40.11; N, 12.87; P, 9.35. $C_{11}H_{17}Cl_3N_3P$ requires C, 40.21; N, 12.79; P, 9.43].

3.2.6. N,N-Dimethyl-P-(trichloromethyl)-N′-[3-(trifluoromethyl)-phenyl]phosphonous diamide ***6f***. Yield 96%; mp 35–36 °C (Et_2O); ^{1}H NMR (500 MHz, C_6D_6) δ 7.17 (1H, s, 2H–Ar), 6.97 (1H, d, J=7.5 Hz, Ar), 6.83–7.00 (2H, m, Ar), 4.89 (1H, d, *J*=7.5 Hz, NH), 2.39 (6H, d, *J*=8.0 Hz, NMe_2); ^{13}C NMR (125 MHz, C_6D_6) δ 145.0 (d, *J*=21.4 Hz), 131.8 (q, *J*=31.4 Hz), 129.9, 124.6 (q, *J*=273.0 Hz), 117.4 (d, *J*=5.0 Hz), 113.8 (dq, *J*=3.8, 11.3 Hz), 103.53 (d, *J*=86.8 Hz), 120.0 (d, *J*=12.8 Hz), 37.8 (d, *J*=17.6 Hz); ^{31}P NMR (81 MHz, C_6D_6) δ 73.3; ^{19}F NMR (81 MHz, C_6D_6) δ −62.7. [Found: C, 33.69; N, 7.88; P, 8.90. $C_{10}H_{11}Cl_3F_3N_2P$ requires C, 33.97; N, 7.92; P, 8.76].

3.2.7. N,N-Dimethyl-P-(trichloromethyl)-N′-[4-(trifluoromethyl)-phenyl]phosphonous diamide ***6g***. Yield 93%, mp 49–50 °C (pentane); ^{1}H NMR (500 MHz, C_6D_6) δ 7.26 (2H, d, *J*=8.5 Hz, 3,5-H–Ar), 6.65 (2H, d, *J*=7. 0 Hz, 2,6-H–Ar), 4.95 (1H, d, *J*=7.0 Hz, NH), 2.43 (6H, d, *J*=8.5 Hz, NMe_2); ^{13}C NMR (125 MHz, C_6D_6) δ 147.5 (d, *J*=21.4 Hz), 126.7 (d, *J*=3.8 Hz), 125.1 (q, *J*=270.0 Hz), 122.6 (q, *J*=31.4 Hz), 116.6 (d, *J*=12.8 Hz), 103.5 (d, *J*=87.0 Hz), 37.5 (d, *J*=19.0 Hz); ^{31}P NMR (81 MHz, C_6D_6) δ 72.5. [Found: C, 33.73; N, 7.85; P, 8.87. $C_{10}H_{11}Cl_3F_3N_2P$ requires C, 33.97; N, 7.92; P, 8.76].

3.2.8. N′-(3-Bromophenyl)-N,N-dimethyl-P-(trichloromethyl)-phosphonous diamide ***6h***. Yield 96%, mp 57–58 °C (pentane); ^{1}H NMR (500 MHz, C_6D_6) δ 7.06 (1H, d, *J*=7.5 Hz, Ar), 6.89 (1H, d, *J*=7.5 Hz, Ar), 6.65–6.71 (2H, m, Ar), 4.76 (1H, br d, *J*=7.5 Hz, NH), 2.73 (6H, d, *J*=9.0 Hz, NMe_2); ^{13}C NMR (125 MHz, C_6D_6) δ 145.9 (d, *J*=21.4 Hz), 130.7, 123.9 (d, *J*=2.5 Hz), 123.3, 120.3 (d, *J*=12.8 Hz), 115.6 (d, *J*=15.1 Hz), 103.7 (d, *J*=85.5 Hz), 37.8 (d, *J*=18.9 Hz); ^{31}P NMR (81 MHz, C_6D_6) δ 73.4. [Found: C, 29.90; N, 7.63; P, 8.14. $C_9H_{11}BrCl_3N_2P$ requires C, 29.66; N, 7.69; P, 8.50].

3.2.9. N,N-Dimethyl-N′-(1-naphthyl)-P-(trichloromethyl)phosphonous diamide ***6i***. Yield 63%, mp 67–68 °C(pentane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (1H, d, *J*=8.1 Hz, Ar); 7.15–7.30 (5H, m, Ar), 7.05 (1H, d, *J*=7.5 Hz, Ar), 5.59 (1H, d, *J*=7.5 Hz, NH), 2.50 (6H, d, *J*=8.7 Hz, NMe_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 37.7 (d, *J*=18.9 Hz), 104.5 (d, *J*=88.0 Hz), 113.4 (d, *J*=26.4 Hz), 120.6, 122.1, 125.8, 126.1, 126.2, 126.5 (d, *J*=5.0 Hz), 129.0, 134.8, 139.8 (d, *J*=18.9 Hz); ^{31}P NMR (81 MHz, $CDCl_3$) δ 80.7. [Found: C, 46.21; N, 8.56; P, 9.15. $C_{13}H_{14}Cl_3N_2P$ requires C, 46.53; N, 8.35; P, 9.23].

3.2.10. P-[2-(Dimethylamino)-1-methyl-1H-imidazol-5-yl]-N-phenyl-P-(trichloromethyl)phosphinous amide ***7***. Yield 68%, mp 62–63 °C(Et_2O); ^{1}H NMR (500 MHz, C_6D_6) δ 7.62 (1H, s, Im), 7.26 (2H, d, *J*=7.5 Hz, Ph), 7.12 (2H, t, *J*=7.5 Hz, Ph), 6.81 (1H, t, *J*=7.5 Hz, Ph), 6.09 (1H, d, *J*=12.0 Hz, NH), 3.15 (3H, s, NMe), 2.48 (6H, s, NMe_2); ^{13}C NMR (125 MHz, C_6D_6) δ 157.4 (d, *J*=7.5 Hz), 145.2 (d, *J*=22.6 Hz), 134.4, 129.3, 122.9 (d, *J*=4.0 Hz), 121.1, 117.4 (d, *J*=12.6 Hz), 102.5 (d, *J*=69.2 Hz), 42.3, 31.6 (d, *J*=13.8 Hz); ^{31}P NMR (81 MHz, C_6D_6) δ 34.6. [Found: C, 44.08; N, 14.64; P, 8.11. $C_{14}H_{18}Cl_3N_4P$ requires C, 44.29; N, 14.76; P, 8.16].

Compound **8** was not separated individually; it was in solution transformed into selenide **14**.

3.2.11. P-(tert-Butyl)-N-phenyl-P-(trichloromethyl)phosphinoselenoic amide ***14***. To *tert*-butyl(trichloromethyl)phosphinous chloride (3.0 g, 12.5 mmol) a solution of aniline (1.20 g, 13.0 mmol) in pyridine (25 mL), NaI (2.8 g, 19 mmol), and then selenium (1.0 g, 12.5 mmol) was added. The reaction mixture was stirred at 5 °C for 30 min, then at 15 °C for 48 h. Pyridine was removed in vacuum (at 32–35 °C) and the solid residue was extracted with CH_2Cl_2 and degassed water. The organic layer was separated, evaporated in vacuum and the residue was treated with activated charcoal in Et_2O (30 mL). The ethereal solution was concentrated in vacuum, the residue was crystallized from pentane (25 mL) to give **14** (2.5 g, 57%) as a light yellow solid; mp 92–94 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (2H, d, *J*=8.5 Hz, Ph), 7.34 (2H, d, *J*=8.5 Hz, Ph), 7.30 (1H, dd, *J*=8.0 Hz), 5.30 (1H, br s, NH), 1.63 (9H, d, *J*=18.3 Hz, *t*-Bu); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.1 (d, *J*=5.0 Hz), 128.7, 124.9, 124.8

(d, J=3.8 Hz), 98.5 (d, J=12.6 Hz), 43.0 (d, J=46.5 Hz), 28.2; ^{31}P NMR (81 MHz, pyridine) δ 100.7. [Found: C, 35.32; N, 3.78; P, 8.27. $C_{11}H_{15}Cl_3NPSe$ requires C, 35.00; N, 3.71; P, 8.20].

Compound **9** was not separated individually; it was in solution transformed into selenide **15**.

The procedure analogous to 1**4** was applied.

*3.2.12. P-(1-adamantyl)-N-phenyl-P-(trichloromethyl)phosphinoselenoic amide **15**.* Yield 68%, mp 177–178 °C(hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (2H, d, J=7.5 Hz, Ph), 7.28 (2H, t, J=7.5 Hz, Ph), 7.13 (1H, t, J=7.5 Hz, Ph), 5.30 (1H, s, NH), 2.38 (6H, br s, Ad), 2.15 (3H, br s, Ad), 1.77 (6H, br s, Ad); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.3 (d, J=5.0 Hz), 128.6, 124.7, 98.6 (d, J=11.3 Hz), 46.5 (d, J=47.8 Hz), 38.0, 36.2, 28.8 (d, J=11.3 Hz); ^{31}P NMR (81 MHz, $CDCl_3$) δ 96.7. [Found: C, 44.65; N, 2.98; P, 6.76. $C_{17}H_{21}Cl_3NPSe$ requires C, 44.81; N, 3.07; P, 6.80].

*3.2.13. P-[2-(Dimethylamino)-1-methyl-1H-imidazol-5-yl]-N-phenyl-P-(trichloromethyl)phosphinoselenoic amide **13**.* Yield 79%, mp 150–151 °C (Et_2O); H NMR (500 MHz, $CDCl_3$) δ 7.53 (1H, s, Im), 7.21 (2H, dd, J=7.5 Hz, 3,5-Ph), 7.10 (1H, d, J=8.0 Hz, 4-Ph), 7.04 (2H, dd, J=7.5 Hz, 2,6-Ph), 5.80 (1H, d, J=6.5 Hz, NH), 3.80 (3H, s, NMe), 2.80 (6H, s, NMe_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.3 (d, J=15.0 Hz), 141.3 (d, J=13.8 Hz), 138.4, 129.1, 124.2, 122.6 (d, J=6.3 Hz), 113.3 (d, J=129.5 Hz), 97.2 (d, J=60.4 Hz), 42.7, 33.3; ^{31}P NMR (81 MHz, C_6D_6) δ 50.6. [Found: C, 35.32; N, 12.53; P, 6.86. $C_{13}H_{16}Cl_3N_4PSe$ requires C, 35.12; N, 12.60; P, 6.97].

3.3. General procedure for the synthesis of 10a,b,c,f,g (with 10c as an example)

To a solution of **6c** (0.91 g, 3 mmol) in pyridine (3 mL) cooled to 0+5 °C was added 20% solution of hydrogen peroxide (0.5 mL). The reaction mixture was stirred at 20 °C for 1 h. The solvents were removed in vacuum, the residue washed with water (2×1 mL) and crude solid product crystallized from acetonitrile to give **10c** (0.91 g, 96%) as a fine white solid.

*3.3.1. N,N-Dimethyl-N′-phenyl-P-(trichloromethyl)phosphonic diamide **10a**.* Yield 98%, mp 126–127 °C(hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (2H, m, *m*-Ph), 7.20 (2H, d, J=7.5 Hz, *o*-Ph), 7.05 (1H, t, J=7.5 Hz, *p*-Ph), 5.31 (1H, d, J=15.0 Hz, NH), 2.92 (6H, d, J=9.0 Hz, NMe_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.5, 129.3 (d, J=26.0 Hz), 119.4 (d, J=5.0 Hz), 93.5 (d, J=141.0 Hz), 38.6 (d, J=4.0 Hz); ^{31}P NMR (81 MHz, $CDCl_3$) δ 13.3. [Found: C, 35.47; N, 9.45; P, 10.13. $C_9H_{12}Cl_3N_2OP$ requires C, 35.85; N, 9.29; P, 10.27].

*3.3.2. N,N-Dimethyl-N′-(4-methylphenyl)-P-(trichloromethyl)-phosphonic diamide **10b**.* Yield 59%, 153–154 °C(acetonitrile); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (2H, d, J=8.0 Hz, Ar), 7.24 (2H, d, J=8.5 Hz, Ar), 5.56 (1H, d, J=15.0 Hz, NH), 2.96 (6H, d, J=9.0 Hz, NMe_2) 1.71 (3H, s, Me–Ar); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.6, 132.8, 130.0, 119.6 (d, J=6.3 Hz), 93.6 (d, J=137.1 Hz), 38.6 (d, J=2.5 Hz), 20.7; ^{31}P NMR (81 MHz, $CDCl_3$) δ 13.80. [Found: C, 37.90; N, 8.95; P, 10.04. $C_{10}H_{14}Cl_3N_2OP$ requires C, 38.06; N, 8.88; P, 9.82].

*3.3.3. N′-(4-Methoxyphenyl)-N,N-dimethyl-P-(trichloromethyl)-phosphonic diamide **10c**.* Yield 96%, mp 158–159 °C (acetonitrile); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (2H, d, J=8.5 Hz, Ar), 6.80 (2H, d, J=8.5 Hz, Ar), 5.28 (1H, d, J=15.0 Hz, NH), 3.75 (3H, s, MeO), 2.37 (6H, d, J=9.0 Hz, NMe_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.1, 130.8, 121.9 (d, J=6.0 Hz), 114.8, 93.6 (d, J=137.0 Hz), 55.5, 38.6 (d, J=4.0 Hz); ^{31}P NMR (81 MHz, $CDCl_3$) δ 14.5. [Found: C, 36.08; N, 8.62; P, 9.45. $C_{10}H_{14}Cl_3N_2O_2P$ requires C, 36.23; N, 8.45; P, 9.34].

*3.3.4. N,N-Dimethyl-P-(trichloromethyl)-N′-[3-(trifluoromethyl)-phenyl] phosphonic diamide **10f**.* Yield 77%, oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29–7.44 (4H, m, Ar), 5.59 (1H, d, J=11.5 Hz, NH), 2.93 (6H, d, J=9.3 Hz, NMe_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.6, 131.6 (q, J=32.7 Hz), 129.9, 123.8 (q, J=273.0 Hz), 122.5 (d, J=3.8 Hz), 119.5 (d, J=3.8 Hz), 116.22 (q, J=3.8 Hz), 93.2 (d, J=139.6 Hz), 38.5 (d, J=2.5 Hz); ^{31}P NMR (81 MHz, $CDCl_3$) δ 12.9; ^{19}F NMR (81 MHz, C_6D_6) δ −63.2. [Found: C, 32.37; N, 7.52; P, 8.52. $C_{10}H_{11}Cl_3F_3N_2OP$ requires C, 32.50; N, 7.58; P, 8.38].

*3.3.5. N,N-Dimethyl-P-(trichloromethyl)-N′-[4-(trifluoromethyl)-phenylphosphonic diamide **10g**.* Yield 71%, mp 123–124 °C (pentane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (2H, d, J=8.5 Hz, 3,5-H–Ar), 7.28 (2H, d, J=8.5 Hz, 2,6-H–Ar), 6.36 (1H, d, J=16.0 Hz, NH), 2.91 (6H, d, J=9.0 Hz, NMe_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.2, 126.5 (q, J=3.8 Hz), 124.9 (q, J=32.7 Hz), 124.2 (q, J=271.6 Hz), 118.9 (d, J=7.5 Hz), 93.1 (d, J=139.6 Hz), 38.5 (d, J=2.5 Hz); ^{31}P (81 MHz, $CDCl_3$) δ 13.1. [Found: C, 32.35; N, 7.48; P, 8.44. $C_{10}H_{11}Cl_3F_3N_2OP$ requires C, 32.50; N, 7.58; P, 8.38].

3.4. General procedure for the synthesis of 11a,f,g (with 11g as an example)

To a solution of **6a** (1.1 g, 3 mmol) in pyridine (3 mL) was added fine-crushed sulfur (0.096 mmol). The reaction mixture was stirred at 16 °C for three days monitoring by ^{31}P NMR. Pyridine was removed in vacuum; the residual crude product was crystallized from pentane to give **11g** (0.91, 78%) as a yellow solid.

*3.4.1. N,N-Dimethyl-N′-phenyl-P-(trichloromethyl)phosphonothioic diamide **11a**.* Yield 81%, 93–94 °C (hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (2H, t, J=8.0 Hz, *m*-Ph), 7.05–7.09 (3H, m, *o*-Ph, *p*-Ph), 5.13 (1H, d, J=12.0 Hz, NH), 3.06 (6H, d, J=7.5 Hz, NMe_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.5, 129.5, 123.1, 119.4 (d, J=7.0 Hz), 98.4 (d, J=87.0 Hz), 39.6 (d, J=4.0 Hz); ^{31}P NMR (81 MHz, $CDCl_3$) δ 65.6. [Found: C, 34.26; N, 8.95; P, 9.48$C_9H_{12}Cl_3N_2PS$ requires C, 34.04; N, 8.82; P, 9.75].

*3.4.2. N,N-Dimethyl-P-(trichloromethyl)-N′-[3-(trifluoromethyl)-phenyl]phosphonothioic diamide **11f**.* Yield 64%, 80–81 °C (pentane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (1H, dd, J=7.5 Hz, 5H–Ar), 7.31–7.33 (3H, m, Ar), 5.19 (1H, d, J=11.0 Hz, NH), 3.07 (6H, d, J=10.5 Hz, NMe_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.3, 131.9 (q, J=32.7 Hz), 130.0, 123.8 (q, J=276.7 Hz), 122.1 (d, J=5.0 Hz), 119.7 (d, J=3.8 Hz), 116.0 (d, J=3.8 Hz), 38.0 (d, J=89.3 Hz), 39.5 (d, J=3.8 Hz); ^{31}P NMR (81 MHz, $CDCl_3$) δ 68.7. [Found: C, 31.44; N, 7.18; P, 7.94. $C_{10}H_{11}Cl_3F_3N_2PS$ requires C, 31.15; N, 7.26; P, 8.03].

*3.4.3. N,N-Dimethyl-P-(trichloromethyl)-N′-[4-(trifluoromethyl)-phenyl]phosphonothioic diamide **11g**.* Yield 78%, mp 78–79 °C (pentane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.6 (2H, d, J=8.0 Hz, 3,5-H–Ar), 7.2 (2H, d, J=8.0 Hz, 2,6-H–Ar), 5.40 (1H, d, J=12.0 Hz, NH), 3.08 (6H, d, J=10.5 Hz, NMe_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.0, 126.7 (q, J=3.8 Hz), 124.9 (d, J=32.3 Hz), 124.2 (q, J=271.6 Hz), 118.6 (d, J=6.3 Hz), 97.93 (d, J=89.3 Hz), 39.5 (d, J=3.8 Hz); ^{31}P NMR (81 MHz, $CDCl_3$) δ 65.5; ^{19}F NMR (81 MHz, C_6D_6) δ −62.6. [Found: C, 31.48; N, 7.17; P, 7.90. $C_{10}H_{11}Cl_3F_3N_2PS$ requires C, 31.15; N, 7.26; P, 8.03].

3.5. General procedure for the synthesis of 12a–i, (with 12a as an example)

To a solution of **6a** (1.43 g, 5 mmol) in pyridine (6 mL) was added selenium (0.6 g, 7.5 mmol). The reaction mixture was stirred at 20 °C for 15 h monitoring by ^{31}P NMR. Pyridine was removed in vacuum, the residue was dissolved in CH_2Cl_2 (20 mL) (ether for **6d**, **6h**), the solution obtained was refined with charcoal, which was then filtered off and the filtrate evaporated. The residual crude product was crystallized from acetonitrile to give **12a** (1.67 g, 92%) as a white solid; mp 115–116 °C.

3.5.1. N,N-Dimethyl-N′-phenyl-P-(trichloromethyl)phosphonoselenoic diamide ***12a***. Yield 98%, 115–116 °C (acetonitrile); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (2H, t, J=7.50 Hz, *m*-Ph), 7.06–7.10 (3H, m, *o*-Ph, *p*-Ph), 5.15 (1H, d, J=11.5 Hz, NH), 3.09 (6H, d, J=10.5 Hz, NMe_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.6, 129.5, 123.2, 119.4 (d, J=8.0 Hz), 98.7 (d, J=65.0 Hz), 39.8 (d, J=4.0 Hz); ^{31}P NMR (81 MHz, $CDCl_3$) δ 70.3. [Found: C, 29.34; N, 7.53; P, 8.76. $C_9H_{12}Cl_3N_2PSe$ requires C, 29.66; N, 7.69; P, 8.50].

3.5.2. N,N-Dimethyl-N′-(4-methylphenyl)-P-(trichloromethyl)-phosphonoselenoic diamide ***12b***. Yield 94%, 117–118 °C (Et_2O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.1 (4H, m, Ar), 5.44 (1H, d, J=10.0 Hz, NH), 3.09 (6H, d, J=10.5 Hz, NMe_2), 2.30 (3H, s, Me); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.9, 132.9, 130.0, 119.8 (d, J=2.5 Hz), 98.8 (d, J=66.7 Hz), 39.7 (d, J=3.8 Hz), 20.8; ^{31}P NMR (81 MHz, $CDCl_3$) δ 73.1. [Found: C, 31.85; N, 7.44; P, 7.96. $C_{10}H_{14}Cl_3N_2PSe$ requires C, 31.73; N, 7.40; P, 8.18].

3.5.3. N′-(4-Methoxyphenyl)-N,N-dimethyl-P-(trichloromethyl)-phosphonoselenoic diamide ***12c***. Yield 82%, 113–114 °C (Et_2O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.0 (4H, m, Ar), 5.02 (1H, d, J=10.0 Hz, NH), 3.79 (3H, s, MeO), 3.10 (6H, d, J=10.5 Hz, NMe_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.2, 131.3, 122.2 (d, J=3.8 Hz), 114.7, 98.8 (d, J=65.4 Hz), 55.6, 39.9 (d, J=3.8 Hz); ^{31}P NMR (81 MHz, Py) δ 74.5. [Found: C, 30.15; N, 7.01; P, 8.03. $C_{10}H_{14}Cl_3N_2OPSe$ requires C, 30.44; N, 7.10; P, 7.85].

3.5.4. N′-(3-Methoxyphenyl)-N,N-dimethyl-P-(trichloromethyl)-phosphonoselenoic diamide ***12d***. Yield 86%, bp 155–160 °C/0.05 Torr; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (1H, dd, J=8.0 Hz, 5H–Ar), 6.68 (1H, s, 2H–Ar), 6.61–6.65 (2H, m, Ar), 5.1 (1H, d, J=9.0 Hz, NH), 3.8 (3H, s, MeO), 3.09 (6H, d, J=10.8 Hz, NMe_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.54, 139.8, 111.8 (d, J=6.3 Hz), 108.5, 105.6 (d, J=6.3 Hz), 98.7 (d, J=65.4 Hz), 55.4, 39.8 (d, J=3.8 Hz); ^{31}P NMR (81 MHz, $CDCl_3$) δ 68.8. [Found: C, 30.13; N, 7.05; P, 8.10. $C_{10}H_{14}Cl_3N_2OPSe$ requires C, 30.44; N, 7.10; P, 7.85].

3.5.5. N′-[3-(Dimethylamino)phenyl]-N,N-dimethyl-P-(trichloromethyl)phosphonoselenoic diamide ***12e***. Yield 87%, 118–119 °C (hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (1H, dd, J=8.0 Hz, 5H–Ar), 6.53–6.48 (3H, m, Ar), 5.04 (1H, d, J=11.5 Hz, NH), 3.09 (6H, d, J=26.4 Hz, $PNMe_2$), 2.95 (6H, s, NMe_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.5, 139.4, 129.9, 107.6, 107.4 (d, J=6.3 Hz), 103.4 (d, J=6.3 Hz), 98.8 (d, J=65.4 Hz), 40.5, 39.9 (d, J=3.8 Hz); ^{31}P NMR (81 MHz, $CDCl_3$) δ 69.8. [Found: C, 32.30; N, 10.23; P, 7.54. $C_{11}H_{17}Cl_3N_3PSe$ requires C, 32.42; N, 10.31; P, 7.60].

3.5.6. N,N-Dimethyl-P-(trichloromethyl)-N′-[3-(trifluoromethyl)-phenyl]phosphonoselenoic diamide ***12f***. Yield 74%, 92–93 °C (pentane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (1H, dd, J=8.0 Hz, 5H–Ar), 7.30–7.33 (3H, m, Ar), 5.32 (1H, d, J=10.5 Hz, NH), 3.09 (6H, d, J=11.0 Hz, NMe_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.4, 131.8 (q, J=32.7 Hz), 130.0, 123.8 (q, J=271.6 Hz), 122.3 (d, J=6.3 Hz), 119.8 (q, J=3.8 Hz), 116.2 (q, J=3.8 Hz), 39.8 (d, J=3.8 Hz); ^{31}P NMR (81 MHz, $CDCl_3$) δ 69.4; ^{19}F NMR (81 MHz, $CDCl_3$) δ −63.0. [Found: C, 28.05; N, 6.40; P, 7.27. $C_{10}H_{11}Cl_3F_3N_2PSe$ requires C, 27.77; N, 6.48; P, 7.16].

3.5.7. N,N-Dimethyl-P-(trichloromethyl)-N′-[4-(trifluoromethyl)-phenyl] phosphonoselenoic diamide ***12g***. Yield 85%, mp 108–109 °C (Et_2O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (2H, d, J=8.4 Hz, 3,5-H–Ar), 7.18 (2H, d, J=8.4 Hz, 2,6-H–Ar), 5.37 (1H, d, J=11.1 Hz, NH), 3.10 (6H, d, J=10.8 Hz, NMe_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.1 (d, J=1.3 Hz), 126.7 (q, J=4.0 Hz), 124.2 (q, J=272.0 Hz), 125.0 (q, J=33.0 Hz), 118.8 (d, J=63.0 Hz), 98.3 (d, J=67.0 Hz), 39.8; ^{31}P NMR (81 MHz, $CDCl_3$) δ 63.4; ^{19}F NMR (81 MHz, C_6D_6) δ −62.5. [Found: C, 28.00; N, 6.42; P, 7.32. $C_{10}H_{11}Cl_3F_3N_2PSe$ requires C, 27.77; N, 6.48; P, 7.16].

3.5.8. N′-(3-Bromophenyl)-N,N-dimethyl-P-(trichloromethyl)-phosphonoselenoic diamide ***12h***. Yield 79%, 94–95 °C (pentane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15–7.24 (3H, m, Ar), 7.06 (1H, d, J=7.0 Hz, Ar), 5.17 (1H, d, J=10.5 Hz, NH), 3.08 (6H, d, J=10.5 Hz, NMe_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.1, 130.7, 126.3, 123.0, 122.4 (d, J=6.3 Hz), 117.9 (d, J=6. 3), 98.5 (d, J=66.6 Hz), 39.8 (d, J=3.8 Hz); ^{31}P NMR (81 MHz, $CDCl_3$) δ 69.3. [Found: 24.22; N, 6.40; P, 7.14. $C_9H_{11}BrCl_3N_2PSe$ requires C, 24.38; N, 6.32; P, 6.99].

3.5.9. N,N-Dimethyl-N′-(1-naphthalenyl)-P-(trichloromethyl)-phosphonoselenoic diamide ***12i***. Yield 81%, mp 160–161 °C (acetonitrile); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87–7.90 (2H, m, Ar), 7.41–7.65 (5H, m, Ar), 5.71 (1H, d, J=7.5 Hz, NH), 3.10 (6H, d, J=7.5 Hz, NMe_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.4, 133.8, 129.0, 127.0 (d, J=8.0 Hz), 126.4 (d, J=28.0 Hz), 124.3, 120.0, 116.6 (d, J=5.0 Hz), 99.6 (d, J=88.0 Hz), 40.0 (d, J=4.0 Hz); ^{31}P NMR (81 MHz $CDCl_3$) δ 70.9. [Found: C, 37.31; N, 6.85; P, 7.69. $C_{13}H_{14}Cl_3N_2PSe$ requires C, 37.66; N, 6.76; P, 7.47].

3.5.10. P-(Dichloromethyl)-N,N-dimethyl-P-morpholin-4-yl-N′-phenylphosphonimidic diamide ***16***.

3.5.10.1. Method A. A solution of **6a** (300 mg, 1 mmol) in morpholine (2.5 mL) was heated at 60 °C for three days with stirring. The reaction mixture was concentrated in vacuum and the residue was treated with hot pentane (20 mL) to give **16** precipitating under cooling (180 mg, 55%) as white solid; mp 86–87 °C.

3.5.10.2. Method B. At −45 °C a solution of **6a** (1.5 g, 5.15 mmol) in morpholine (2.5 mL) and THF (10 mL) was added dropwise over 10 min to a solution of lithium morpholide [prepared using *n*-BuLi (2.5 M pentane solution, 5.15 mmol) and morpholine (0.7 mL, 7.6 mmol)] in THF (10 mL). The reaction mixture was stirred at −45 °C for 15 min, then allowed to warm to 20 °C and stirring was kept for 2 h. The solvents were removed in vacuum and the residue was treated with hot hexane (2×50 mL), the precipitate was filtered off, the filtrate was concentrated to 10 mL to give **16** precipitating under cooling (1.15 g, 67%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.13 (2H, dd, J=7.5 Hz, Ph), 6.74–6.78 (3H, m, Ph), 3.64–3.75 (4H, m, OCH_2), 3.27–3.33 (4H, m, NCH_2), 2.84 (6H, d, J=9.6 Hz, Me_2NP); ^{31}P NMR (81 MHz, $CHCl_3$) δ 10.8. MS (EI, 70 eV): m/z (%)=338 (100) $[M+H]^+$.

3.6. General procedure for the synthesis of 17, 18, 19a–i, 20–24 (with 19b as an example)

Compound **12b** (3.0 g, 10 mmol) was dissolved in dimethylamine (10.5 mL, 150 mmol) and the reaction mixture was stirred at 20 °C for 15 h. Dimethylamine was removed under reduced pressure. The residue was extracted with ether (3×40 mL), after evaporation of the ether the crude product was crystallized from pentane to afford **19b** 3.34 g (93%) as a white solid. For compounds **23** and **24** morpholine and piperidine were used, respectively.

3.6.1. 1,1-Bis(dimethylamino)-N,N-dimethyl-N′-phenylphosphine carboximidamide oxide ***17a***. Yield 90%, mp 56–57 °C (pentane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (2H, t, J=7.5 Hz, *m*-Ph), 6.89 (1H, t, J=7.5 Hz, *p*-Ph), 6.72 (2H, d, J=7.5 Hz, *o*-Ph), 2.90 (6H, s, NMe_2), 2.64 (12H, d, J=9.0 Hz, NMe_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.9 (d, J=190.0 Hz), 150.5 (d, J=20.0 Hz), 121.2, 120.2, 40.5 and 36.4 (d, J=2.5 Hz); ^{31}P NMR (81 MHz, $CDCl_3$) δ 23.6. [Found: C, 55.21; N, 19.92; P, 10.95. $C_{13}H_{23}N_4OP$ requires C, 55.31; N, 19.84; P, 10.97].

3.6.2. 1,1-Bis(dimethylamino)-N,N-dimethyl-N′-(4-methyl-phenyl)-phosphinecarboximidamide oxide ***17b***. Yield 92%, mp 61–62 °C (pentane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 (2H, d, J=8.0 Hz, Ar),

6.62 (2H, d, J=8.0 Hz, Ar), 2.87 (s, 6H, NMe_2), 2.67 (s, 3H, Me), 2.64 (d, 12H, J=9.5 Hz, NMe_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.5 (d, J=192.4 Hz), 147.8 (d, J=21.4 Hz), 130.4, 128.9, 120.1, 40.5, and 36.4 (d, J=4.0 Hz), 20.7; ^{31}P NMR (81 MHz, $CDCl_3$) δ 23.7. [Found: C, 56.90; N, 18.85; P, 10.57. $C_{14}H_{25}N_4OP$ requires C, 56.74; N, 18.91; P, 10.45].

3.6.3. 1,1-Bis(dimethylamino)-N,N-Dimethyl-N′-(4-methoxy-phenyl)phosphinecarboximidamide oxide ***17c***. Yield 92%, mp 41–42 °C (pentane); ^1H NMR (500 MHz, $CDCl_3$) δ 6.76 (2H, d, J=9.0 Hz, Ar), 6.65 (2H, d, J=9.0 Hz, Ar), 3.75 (3H, s, MeO), 2.86 (6H, s, NMe_2), 2.63 (12H, d, J=9.6 Hz, NMe_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.2, 151.7 (d, J=193.7 Hz), 143.5 (d, J=22.6 Hz), 120.8, 113.4, 55.0, 40.1, 36.0; ^{31}P NMR (81 MHz, $CDCl_3$) δ 23.6. [Found: C, 53.62; N, 17.75; P, 10.20. $C_{14}H_{25}N_4O_2P$ requires C, 53.83; N, 17.94; P, 9.92].

3.6.4. 1,1-Bis(dimethylamino)-N,N-dimethyl-N′-[3-(trifluoromethyl)phenyl]phosphinecarboximidamide oxide ***17f***. Yield 86%; oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.24 (1H, dd, J=7.5 Hz, 5H–Ar), 7.05 (1H, d, J=7.0 Hz, Ar), 6.87 (1H, s, 2H–Ar), 6.81 (1H, d, J=7.0 Hz, Ar), 2.88 (6H, s, NMe_2), 2.54 (12H, d, J=9.5 Hz, $PNMe_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.5 (d, J=183.6 Hz), 150.9 (d, J=20.1 Hz), 128.8, 130.7 (q, J=32.7 Hz), 124.2 (q, J=273.0 Hz), 123.4, 117.5 (q, J=7.5 Hz), 116.7 (q, J=7.5 Hz), 40.1 (d, J=3.8 Hz), 36.2 (d, J=5.0 Hz); ^{31}P NMR (81 MHz, $CDCl_3$) δ 21.3. [Found: C, 47.88; N, 16.14; P, 9.13. $C_{14}H_{22}F_3N_4OP$ requires C, 48.00; N, 15.99; P, 8.84].

3.6.5. 1,1-Bis(dimethylamino)-N,N-dimethyl-N′-[4-(trifluoromethyl)phenyl]phosphinecarboximidamide oxide ***17g***. Yield 96%; oil; ^1H NMR (300 MHz, $CDCl_3$) δ 7.46 (2H, d, J=8.4 Hz, 3,5-H–Ar), 6.77 (2H, d, J=8.1 Hz, 2,6-H–Ar), 2.96 (6H, s, NMe_2), 2.62 (12H, d, J=9.6 Hz, $PNMe_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.5 (d, J=19.0 Hz), 151.9 (d, J=183.6 Hz), J=270.4 Hz), 124.2 (q, 124.9, 122.0 (q, J=32.7 Hz), 119.6, 39.8, 35.5; ^{31}P NMR (81 MHz, $CDCl_3$) δ 22.2; ^{19}F NMR (81 MHz, C_6D_6) δ −62.1. [Found: C, 47.86; N, 16.13; P, 9.08. $C_{14}H_{22}F_3N_4OP$ requires C, 48.00; N, 15.99; P, 8.84].

3.6.6. 1,1-Bis(dimethylamino)-N,N-dimethyl-N′-1-naphthalenyl phosphinecarboximidamide oxide ***17i***. Yield 94%; mp 93–94 °C (hexane); ^1H NMR (500 MHz, $CDCl_3$) δ 7.93 (1H, d, J=8.0 Hz, Ar), 7.71 (1H, d, J=7.0 Hz, Ar), 7.37 (3H, m, Ar), 7.28 (1H, t, J=7.5 Hz, Ar); 6.59 (1H, d, J=7.0 Hz, Ar), 2.82 (6H, s, NMe_2), 2.61(12H, d, J=9.5 Hz, $PNMe_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.0 (d, J=190.0 Hz), 147.3 (d, J=20.1 Hz), 134.1, 127.8, 127.3, 125.8, 125.7, 125.0, 124.4, 121.1, 113.3, 40.3, 36.4; ^{31}P NMR (81 MHz, $CDCl_3$) δ 23.3. [Found: C, 61.60; N, 16.74; P, 9.06. $C_{17}H_{25}N_4OP$ requires C, 61.43; N, 16.86; P, 9.32].

3.6.7. 1,1-Bis(dimethylamino)-N,N-dimethyl-N′-phenylphosphinecarboximidamide sulfide ***18a***. Yield 93%, mp 44–45 °C (pentane); ^1H NMR (500 MHz, $CDCl_3$) δ 7.22 (2H, dd, J=7.5 Hz, 3,5-Ph), 6.89 (1H, t, J=7.5 Hz, Ph), 6.76 (2H, d, J=7.5 Hz, 2,6-Ph), 2.88 (6H, s, Me_2N), 2.76 (12H, d, J=12.0 Hz, Me_2NP); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.3 (d, J=162.2 Hz), 150.3 (d, J=20.1 Hz), 128.4, 121.3, 120.3, 41.1 (d, J=2.5 Hz), 36.4 (d, J=3.8 Hz); ^{31}P NMR (81 MHz, $CDCl_3$) δ 69.0. [Found: C, 52.70; N, 18.63; P, 10.12. $C_{13}H_{23}N_4PS$ requires C, 52.33; N, 18.78; P, 10.38].

3.6.8. 1,1-Bis(dimethylamino)-N,N-dimethyl-N′-(4-methylphe-nyl)-phosphinecarboximidamide sulfide ***18b***. Yield 83%, mp 67–68 °C (pentane); ^1H NMR (500 MHz, $CDCl_3$) δ 7.02 (2H, d, J=8.0 Hz, Ar), 6.67 (2H, d, J=8.0 Hz, Ar), 2.85 (6H, s, Me_2N), 2.76 (d, 12H, J=10.5 Hz, Me_2NP), 2.27 (3H, s, Me); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.3 (d, J=163.5 Hz), 147.7 (d, J=22.6 Hz), 130.6, 129.0, 120.3, 41.1 (d, J=4.0 Hz), 37.6 (d, J=1.3 Hz), 20.8; ^{31}P NMR (81 MHz, $CDCl_3$) δ 69.3. [Found: C, 54.05; N, 17.90; P, 9.57. $C_{14}H_{25}N_4PS$ requires C, 53.82; N, 17.93; P, 9.91].

3.6.9. 1,1-Bis(dimethylamino)-N,N-dimethyl-N′-[3-(trifluoromethyl)-phenyl]phosphinecarboximidamide sulfide ***18f***. Yield 95%, oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.30 (1H, dd, J=7.5 Hz, 5H–Ar), 7.12 (1H, d, J=7.5 Hz, Ar), 6.97 (1H, br s, 2H–Ar), 6.91 (1H, d, J=7.5 Hz, Ar), 2.91 (6H, s, NMe_2), 2.72 (12H, d, J=10.5 Hz, $PNMe_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.2 (d, J=154.7 Hz), 150.8 (d, J=20.0 Hz), 130.8 (q, J=31.4 Hz), 128.8, 124.2 (q, J=273.0 Hz), 123.5, 117.6 (q, J=4.0 Hz), 116.8 (q, J=4.0 Hz), 41.6, 37.5; ^{31}P NMR (81 MHz, $CDCl_3$) δ 67.0; ^{19}F NMR (81 MHz, $CDCl_3$) δ −62.9. [Found: C, 46.04; N, 15.18; P, 8.26. $C_{14}H_{22}F_3N_4PS$ requires C, 45.90; N, 15.29; P, 8.45].

3.6.10. 1,1-Bis(dimethylamino)-N,N-dimethyl-N′-[4-(trifluoromethyl)phenyl]phosphinecarboximidamide sulfide ***18g***. Yield 96%, oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.33 (2H, d, J=8.0 Hz, 3,5-H–Ar), 6.71 (2H, d, J=8.0 Hz, 2,6-H–Ar), 2.81 (s, 6H, NMe_2), 2.61 (12H, d, J=10.5 Hz, $PNMe_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.5 (d, J=19.0 Hz), 152.9 (d, J=154.7 Hz), 125.4 (q, J=4.0 Hz), 124.7 (q, J=27.0 Hz), 122.4 (q, J=33.0 Hz), 120.0, 40.8 (d, J=2.5 Hz), 37.3 (d, J=2.5 Hz); ^{31}P NMR (81 MHz, $CDCl_3$) δ 67.0; ^{19}F NMR (188 MHz, $CDCl_3$) δ −62.2. [Found: C, 46.10; N, 15.16; P, 8.21. $C_{14}H_{22}F_3N_4PS$ requires C, 45.90; N, 15.29; P, 8.45].

3.6.11. 1,1-Bis(dimethylamino)-N,N-dimethyl-N′-1-naphthalenyl phosphinecarboximidamide sulfide ***18i***. Yield 81%, 117–118 °C (pentane); ^1H NMR (500 MHz, $CDCl_3$) δ 8.01–8.03 (1H, m, Ar), 7.77–7.79 (1H, m, Ar), 7.43–7.45 (3H, m, Ar), 7.34 (1H, t, J=7.5 Hz, Ar), 6.70 (1H, d, J=7.0 Hz, Ar), 2.87 (s, 6H, NMe_2), 2.84 (12H, d, J=3.0 Hz, $PNMe_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.7 (d, J=161.0 Hz), 147.3 (d, J=20.0 Hz), 134.2, 127.9, 127.3, 126.0, 125.8, 125.2, 124.6, 121.2, 113.5, 40.8 (d, J=4.0 Hz), 37.8 (d, J=2.5 Hz); ^{31}P NMR (81 MHz, $CDCl_3$) δ 68.3. [Found: C, 58.36; N, 15.95; P, 9.00. $C_{17}H_{25}N_4PS$ requires C, 58.60; N, 16.08; P, 8.89].

3.6.12. 1,1-Bis(dimethylamino)-N,N-dimethyl-N′-phenylphosphinecarboximidamide selenide ***19a***. Yield 93%, 72–73 °C (hexane); ^1H NMR (500 MHz, $CDCl_3$) δ 7.22 (2H, dd, J=7.5 Hz, Ph), 6.89 (1H, t, J=7.50 Hz, Ph), 6.76 (2H, d, J=7.50 Hz, Ph), 2.87 (6H, s, Me_2N), 2.77 (12H, d, J=12.0 Hz, Me_2NP); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.8 (d, J=148 Hz), 150.0 (d, J=20.0 Hz), 128.4, 121.4, 120.3, 41.3 (d, J=2.5 Hz), 38.0; ^{31}P NMR (81 MHz, $CDCl_3$) δ 70.2. [Found: C, 45.40; N, 16.45; P, 8.77. $C_{13}H_{23}N_4PSe$ requires C, 45.22; N, 16.23; P, 8.97].

3.6.13. 1,1-Bis(dimethylamino)-N,N-dimethyl-N′-(4-methylphe-nyl)-phosphinecarboximidamide selenide ***19b***. Yield 92%; mp 85–86 °C (pentane); ^1H NMR (500 MHz, $CDCl_3$) δ 7.33 (2H, d, J=8.0 Hz, 2,6-Ar), 6.68 (2H, d, J=8.0 Hz, 3,5-Ar), 2.86 (6H, s, NMe_2), 2.81 (12H, d, J=11.0 Hz, NMe_2), 2.29 (3H, s, Me); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.8 (d, J=150.0 Hz), 147.4 (d, J=20.0 Hz), 130.8, 129.0, 120.3, 41.3 (d, J=3.8 Hz), 38.0, 20.8; ^{31}P NMR (81 MHz, $CDCl_3$) δ 66.9. [Found: C, 47.03; N, 15.65; P, 8.84. $C_{14}H_{25}N_4PSe$ requires C, 46.80; N, 15.59; P, 8.62].

3.6.14. 1,1-Bis(dimethylamino)-N′-(4-methoxyphenyl)-N,N-dimethylphosphinecarboximidamide selenide ***19c***. Yield 89%; bp 181–181/0.05 Torr, 69–70 °C (pentane); ^1H NMR (500 MHz, $CDCl_3$) δ 6.82–6.70 (4H, m, Ar), 3.73 (3H, s, MeO), 2.82 (6H, s, NMe_2), 2.76 (12H, d, J=10.5 Hz, NMe_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.7, 152.2 (d, J=151.0 Hz), 143.3 (d, J=34.0 Hz), 121.4, 113.8, 55.5, 41.2, 38.1; ^{31}P NMR (81 MHz, $CDCl_3$) δ 67.1. [Found: C, 44.53; N, 14.87; P, 8.32. $C_{14}H_{25}N_4OPSe$ requires C, 44.80; N, 14.93; P, 8.25].

3.6.15. 1,1-Bis(dimethylamino)-N′-(3-methoxyphenyl)-N,N-dimethylphosphinecarboximidamide selenide ***19d***. Yield 84%, 160–165 °C/0.05 Torr; ^1H NMR (500 MHz, $CDCl_3$) δ 7.10 (1H, dd, J=8.0 Hz, 5H–Ar), 6.45 (1H, m, Ar), 6.32–6.35 (2H, m, Ar), 3.77 (3H, s, MeO), 2.78 (12H, d, J=11.0 Hz, NMe_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.9, 151.8

(d, J=147.0 Hz), 151.4 (d, J=21.4 Hz), 113.1, 129.1, 106.9, 106.3, 55.4, 38.0 and 41.6 (d, J=2.5 Hz); ^{31}P NMR (81 MHz, $CDCl_3$) δ 65.70. [Found: C, 44.56; N, 14.85; P, 8.32. $C_{14}H_{25}N_4OPSe$ requires C, 44.80; N, 14.93; P, 8.25].

3.6.16. 1,1-Bis(dimethylamino)-N′-[3-(dimethylamino)phenyl]-N,N-dimethylphosphinecarboximidamide selenide ***19e***. Yield 83%, 99–100 °C (pentane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.05 (1H, dd, J=8.0 Hz, 5H–Ar), 6.29 (1H, m, Ar), 6.09–6.15 (2H, m, Ar), 2.89 (6H, s, NMe_2), 2.87 (6H, s, NMe_2), 2.77 (12H, d, J=11.0 Hz, $PNMe_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.2 (d, J=148.4 Hz), 151.1, 151.0 (d, J=21.4 Hz), 128.8, 109.1, 106.4, 105.1, 40.7, 38.1; ^{31}P NMR (81 MHz, $CDCl_3$) δ 65.8. [Found: C, 46.44; N, 18.13, P, 8.23. $C_{15}H_{28}N_5PSe$ requires C, 46.39; N, 18.03, P, 7.98].

3.6.17. 1,1-Bis(dimethylamino)-N,N-dimethyl-N′-[3-(trifluoromethyl)phenyl]phosphinecarboximidamide selenide ***19f***. Yield 92%, oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.92 (1H, s, 2H–Ar), 7.24 (1H, dd, J=8.0 Hz, 5H–Ar), 7.03 (1H, d, J=8.0 Hz, Ar), 6.85 (1H, d, J=8.0 Hz, Ar), 2.84 (s, 6H, NMe_2), 2.68 (12H, d, J=11.0 Hz, NMe_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.6 (d, J=146.0 Hz), 150.4 (d, J=19.0 Hz), 126.4 (q, J=272.0 Hz), 130.7 (q, J=31.4 Hz), 128.8, 123.4, 117.5 (d, J=3.8 Hz), 116.7 (d, J=3.8 Hz), 41.1, 37.9; ^{31}P NMR (81 MHz, $CDCl_3$) δ 64.0; ^{19}F NMR (188 MHz, $CDCl_3$) δ −63.0. [Found: C, 40.54; N, 13.71; P, 7.53. $C_{14}H_{22}F_3N_4PSe$ requires C, 40.69; N, 13.56; P, 7.49].

3.6.18. 1,1-Bis(dimethylamino)-N,N-dimethyl-N′-[4-(trifluoromethyl)phenyl]phosphinecarboximidamide selenide ***19g***. Yield 73%, 61–62 °C (pentane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (2H, d, J=8.0 Hz, 3,5-H–Ar), 6.82 (2H, d, J=8.0 Hz, 2,6-H–Ar), 2.93 (s, 6H, NMe_2), 2.76 (12H, d, J=11.0 Hz, $PNMe_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.3 (d, J=17.0 Hz), 152.3 (d, J=140.0 Hz), 125.6 (q, J=3.8 Hz), 124.7 (q, J=272.0 Hz), 122.8 (q, J=32.7 Hz), 120.1, 38.0, and 41.2 (d, J=2.5 Hz); ^{31}P NMR (81 MHz, $CDCl_3$) δ 64.2; ^{19}F NMR (188 MHz, $CDCl_3$) δ −62.8. [Found: C, 40.48; N, 13.72; P, 7.59. $C_{14}H_{22}F_3N_4PSe$ requires C, 40.69; N, 13.56; P, 7.49].

3.6.19. N′-(3-Bromophenyl)-1,1-bis(dimethylamino)-N,N-dimethylphosphinecarboximidamide selenide ***19h***. Yield 90%, oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.95 (1H, dd, J=8.0 Hz, Ar), 6.87 (1H, d, J=7.5 Hz, Ar), 6.79 (1H, s, 2H–Ar), 6.57 (1H, d, J=7.0 Hz, Ar), 2.79 (6H, s, NMe_2), 2.63 (12H, d, J=11.0 Hz, $PNMe_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.2 (d, J=142.0 Hz), 151.4 (d, J=20.0 Hz), 129.7, 124.0, 123.0, 122.1, 119.0, 41.2 (d, J=3.8 Hz), 38.1; ^{31}P NMR (81 MHz, $CDCl_3$) δ 64.6. [Found: C, 36.75; N, 13.08; P, 7.63. $C_{13}H_{22}BrN_4PSe$ requires C, 36.81; N, 13.21; P, 7.30].

3.6.20. 1,1-Bis(dimethylamino)-N,N-dimethyl-N′-(1-naphthale-nyl)-phosphinecarboximidamide selenide ***19i***. Yield 98%, mp 108–110 °C (Et_2O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01–8.03 (1H, m, Ar), 7.77–7.79 (1H, m, Ar), 7.41–7.45 (3H, m, Ar), 7.30 (1H, t, J=8.0 Hz, Ar), 6.69 (1H, d, J=7.0 Hz, Ar), 2.86 (12H, d, J=10.5 Hz, $PNMe_2$), 2.85 (6H, s, NMe_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.1 (d, J=147.0 Hz), 146.9 (d, J=80.0 Hz), 124.2, 127.9, 127.4, 126.0, 125.2, 124.5, 113.5, 41.0 (d, J=3.0 Hz), 38.2 (d, J=3.0 Hz); ^{31}P NMR (81 MHz, $CDCl_3$) δ 65.8. [Found: C, 51.72; N, 14.15; P, 7.80. $C_{17}H_{25}N_4PSe$ requires C, 51.65; N, 14.17; P, 7.83].

3.6.21. N,N-Dimethyl-N′-phenyl-1-(dimethylamino)-1-[2-(dimethylamino)-1-methyl-1H-imidazol-5-yl]-phosphinecarboximidamide selenide ***20***. Yield 90%, oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (1H, s, Im), 7.12 (2H, t, J=7.50 Hz, Ph); 6.85 (2H, d, J=7.50 Hz, Ph), 6.76 (1H, t, J=7.50 Hz, p-Ph), 3.19 (3H, s, MeN), 2.57 (6H, s, Me_2NIm), 2.54 (6H, s, Me_2N), 2.22 (6H, d, J=9.50 Hz, Me_2NP); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.7 (d, J=13.0 Hz), 151.4 (d, J=138.0 Hz), 149.6 (d, J=21.0 Hz), 134.6 (d, J=15.0 Hz), 128.4, 121.7, 120.3, 118.9 (d, J=122.0 Hz), 42.3, 41.8 (d, J=4.0 Hz), 37.7 (d, J=3.0 Hz), 32.6; ^{31}P NMR (81 MHz, $CDCl_3$) δ 37.5. [Found: C, 48.08; N, 19.70; P, 7.60. $C_{17}H_{27}N_6PSe$ requires C, 48.00; N, 19.76; P, 7.28].

3.6.22. N,N-Dimethyl-N′-phenyl-1-(dimethylamino)-1-(tert-butyl)-phosphinecarboximidamide selenide ***21***. Yield 79%, mp 77–78 °C(pentane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (2H, dd, J=8.0 Hz, 3,5-Ph), 6.90 (1H, t, J=7.5 Hz, 4-Ph), 6.77 (2H, d, J=7.5 Hz, 2,6-Ph), 2.91 (6H, d, J=9.0 Hz, Me_2NP), 2.80 (6H, s, Me_2N), 1.41 (9H, d, J=18.0 Hz, t-Bu); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.9 (d, J=130.8 Hz), 149.5 (d, J=21.4 Hz), 128.5, 121.8, 120.3, 44.5 (d, J=58.0 Hz), 39.3, 39.2, 26.8; ^{31}P NMR (81 MHz, $CDCl_3$) δ 83.0. [Found: C, 50.22; N, 11.63; P, 8.98. $C_{15}H_{26}N_3PSe$ requires C, 50.28; N, 11.73; P, 8.64].

3.6.23. 1-(1-Adamantyl)-1-(dimethylamino)-N,N-dimethyl-N′-phenylphosphinecarboximidamide selenide ***22***. Yield 89%, 136–137 °C (pentane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (2H, dd, J=7.5 Hz, Ph), 6.90 (1H, t, J=7.5 Hz, Ph); 6.78 (2H, d, J=7.5 Hz, Ph), 2.92 (6H, d, J=9.0 Hz, Me_2NP), 2.80 (6H, s, Me_2N), 2.25 (6H, br s, Ad), 2.00 (3H, br s, Ad), 1.67(6H, br s, Ad); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.0 (d, J=128.3 Hz), 149.5 (d, J=20.1 Hz), 128.5, 121.8, 120.5, 47.5 (d, J=55.3 Hz), 41.0, 39.5, 36.8, 36.5, 28.4 (d, J=11.3 Hz); ^{31}P NMR (81 MHz, $CDCl_3$) δ 78.6. [Found: C, 57.60; N, 9.69; P, 7.00. $C_{21}H_{32}N_3PSe$ requires C, 57.79; N, 9.63; P, 7.10].

3.6.24. N,N-Dimethyl-P-(4-morpholinyl)-P-[4-morpholinyl(phenylimino)methyl]phosphinoselenoic amide ***23***. Yield 81%, 82–83 °C (pentane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (2H, t, J=7.5 Hz, Ph), 6.92 (1H, t, J=7.5 Hz, Ph), 6.73 (2H, d, J=7.5 Hz, Ph), 3.68–3.56 (8H, m, OCH_2), 3.41–3.44 (4H, m, NCH_2); 3.23–3.19 (2H, m, NCH_2), 3.08–3.12 (2H, m, NCH_2) 2.82 (6H, d, J=11.5 Hz, NCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.6 (d, J=151.0 Hz), 149.3 (d, J=21.4 Hz), 128.9, 122.8, 119.9, 67.2 (d, J=7.5 Hz), 66.2, 48.3, 46.5, 37.8 (d, J=2.5 Hz); ^{31}P NMR (81 MHz, $CDCl_3$) δ 66.1. [Found: C, 47.74; N, 13.15; P, 7.26. $C_{17}H_{27}N_4O_2PSe$ requires C, 47.56; N, 13.05; P, 7.21].

3.6.25. N,N-Dimethyl-P-[(phenylimino)-1-piperidinylmethyl]-P-(1-piperidinyl)phosphinoselenoic amide ***24***. Yield 89%, oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13 (2H, dd, J=7.5 Hz, Ph), 6.80 (1H, t, J=7.5 Hz, Ph), 6.66 (2H, d, J=7.5 Hz, Ph), 3.10–3.20 (8H, m, NCH_2); 2.70 (6H, d, J=11.5 Hz, NCH_3); 1.42–1.46 (m, 12H, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.6 (d, J=151.0 Hz), 149.9 (d, J=21.4 Hz), 128.3, 121.2, 119.5, 48.9, 46.5, 37.9, 25.9 (d, J=5.0 Hz), 24.9, 24.3, 23.6; ^{31}P NMR (81 MHz, $CDCl_3$) δ 67.5. [Found: C, 53.48; N, 13.14; P, 7.36. $C_{19}H_{31}N_4PSe$ requires C, 53.64; N, 13.17; P, 7.28].

3.6.26. Dimethylamino-bis(methylamino)phosphate ***25a***. A solution of **7a** (2.5 g, 7 mmol) in methylamine (10 mL) was stirred at 17 °C for 20 h. The methylamine was removed, the residue was treated with Et_2O (3×20 mL), the precipitate was filtered and the filtrate concentrated in vacuo along with isocyanobenzene evaporation. The residue was treated with hot pentane (30 mL). The precipitate (1.55 g) was filtered off and then distilled (bp 100–110 °C/10–12 Torr) to give **15** (500 mg, 34%) as white solid. ^{1}H NMR (300 MHz, DMSO) δ 4.34 (br s, 2H), 2.44 (d, 6H, J=13.0 Hz), 2.37 (dd, 6H, J=5.5 Hz; 14.0). ^{31}P NMR (81 MHz, pentane) δ 73.1. [Found: C, 22.35; N, 19.70; P, 14.53.$C_4H_{14}N_3PSe$ requires C, 22.44; N, 19.63; P, 14.47].

Solution of **10a** (0.5 g, 13 mmol) in *tert*-butylamine (7 mL) was stirred at 10 °C for 48 h. *tert*-Buthylamine was removed in vacuo, the residue was treated with Et_2O (2×20 mL), the precipitate was filtered. The filtrate was concentrated in vacuo, the residue was distilled (135 °C/0.05 Torr) to give distillate as a mixture of compounds **26** and **25b**. The distillate was treated with hot pentane (2×15 mL). The solution was refined with activated charcoal and

the filtrate was concentrated in vacuo. The residue was crystallized from pentane (25 mL). In 2 h the solid precipitating at 20 °C was filtered to give **25b** (0.23 g, 11%; δ ^{31}P (pentane) 51.93) as a yellow solid; mp 126–127 °C. The filtrate was concentrated in vacuo, the residue was distilled (130 °C/0.05 Torr) to give crude **26** (1.54 g). The distillate was crystallized from pentane (4 mL). The solid precipitating at −18 °C was filtered to give **26** (1.1 g, 41%; δ ^{31}P(pentane) 54.8) as a pale brown solid; mp 62–63 °C.

3.6.27. Dimethylamino-bis(tert-butylamino)selenophosphate ***25b***. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.61 (6H, d, J=13.5 Hz, Me_2N), 2.33 (2H, br s, NH), 1.38 (18H, s, *t*-Bu); ^{31}P NMR (81 MHz, $CDCl_3$) δ 52.5. [Found: C, 40.43; N, 14.15; P, 10.34. $C_{10}H_{26}N_3PSe$ requires C, 40.27; N, 14.09; P, 10.38].

3.6.28. 1-Dimethylamino-1-tert-butylamino N′-phenyl- N-(tert-butyl)phosphinecarboximidamide selenide ***26***. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (2H, t, J=7.5 Hz, Ph), 6.88–6.94 (3H, m, Ph), 6.43 (1H, br s,), 2.20 (1H, br s,), 2.52 (6H, d, J=13.5 Hz, Me_2N), 1.43 (9H, s, *t*-Bu), 1.13 (9H, s, *t*-Bu); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.1 (d, J=9.0 Hz), 146.4 (d, J=76.7 Hz), 128.8, 121.6, 121.4, 52.8, 52.5 (d, J=9.0 Hz), 36.3 (d, J=4.0 Hz), 31.0 (d, J=5.0 Hz), 28.3; ^{31}P NMR (81 MHz, $CDCl_3$) δ 55.5. [Found: C, 50.46; N, 14.01; P, 8.04. $C_{17}H_{31}N_4PSe$ requires C, 50.87; N, 13.96; P, 7.72].

3.7. General procedure for the synthesis of 27b–h, 29–30 (with 27b as an example)

To a solution of **19b** (1.08 g, 2 mmol) in benzene (2 mL) was added a solution of tris(morpholin-4-yl)phosphine (0.87 g, 0.003 mmol) in benzene (4 mL). In 10–15 min benzene was removed under reduced pressure and the residue was extracted with pentane (10 mL), the precipitate obtained was filtered off and the filtrate evaporated in vacuum. The residue was dissolved in pentane (3 mL), laid-down impurities were separated, residual solution was concentrated and the residue distilled (140–150 °C, 5×10^{-2} Torr) to give **27b** (0.55 g, 66%) as a colorless solid.

3.7.1. 1,1-Bis(dimethylamino)-N,N-dimethyl-N′-(4-methylphe-nyl)-phosphinecarboximidamide ***27b***. Yield 66%; mp 66–67 °C (pentane); ^{1}H NMR (300 MHz, C_6D_6) δ 6.98 (2H, d, J=8.0 Hz, Ar), 6.85 (2H, d, J=8.0 Hz, Ar), 2.73 (6H, s, NMe_2), 2.48 (12H, d, J=9.0 Hz, NMe_2), 2.19 (3H, s, Me); ^{13}C NMR (125 MHz, C_6D_6) δ 162.3 (d, J=26.4 Hz), 149.2 (d, J=2.5 Hz), 128.5, 128.3, 120.3 (d, J=2.5 Hz), 41.4 (d, J=16.3 Hz), 39.4 (d, J=8.0 Hz); ^{31}P NMR (81 MHz, C_6D_6) δ 96.6. [Found: C, 59.75; N, 20.06; P, 11.00. $C_{14}H_{25}N_4P$ requires C, 59.98; N, 19.98; P, 11.05].

3.7.2. 1,1-Bis(dimethylamino)-N′-(4-methoxyphenyl)-N,N-dimethylphosphinecarboximidamide ***27c***. Yield 98%; mp 66–67 °C (benzene); ^{1}H NMR (500 MHz, C_6D_6) δ 6.88 (2H, d, J=9.0 Hz, Ar), 6.81 (2H, d, J=9.0 Hz, Ar), 3.40 (3H, s, MeO), 2.73 (6H, s, NMe_2), 2.50 (12H, d, J=9.0 Hz, NMe_2); ^{13}C NMR (125 MHz, C_6D_6) δ 162.6 (d, J=12.8 Hz), 153.7, 145.1, 121.1, 113.6, 54.8, 41.4 (d, J=16.4 Hz), 39.5 (d, J=7.5 Hz); ^{31}P NMR (81 MHz, C_6D_6) δ 96.7. [Found: C, 56.91; N, 18.73; P, 10.52. $C_{14}H_{25}N_4OP$ requires C, 56.74; N, 18.91; P, 10.45].

3.7.3. 1,1-Bis(dimethylamino)-N′-(3-methoxyphenyl)-N,N-dimethylphosphinecarboximidamide ***27d***. Yield 94%; oil; ^{1}H NMR (500 MHz, C_6D_6) δ 7.07 (1H, dd, J=8.0 Hz, 5H–Ar), 6.54–6.59 (2H, m, Ar), 6.46 (1H, d, J=8.0 Hz, Ar), 3.42 (3H, s, MeO), 2.72 (6H, s, NMe_2), 2.48 (12H, d, J=8.5 Hz, NMe_2); ^{13}C NMR (125 MHz, C_6D_6) δ 162.3 (d, J=12.8 Hz), 160.3, 153.2 (d, J=2.5 Hz), 128.6, 113.0, 106.2, 54.5, 41.5 (d, J=16.3 Hz), 39.4 (d, J=7.5 Hz); ^{31}P NMR (81 MHz, C_6D_6) δ 95.9. [Found: C, 56.94; N, 18.75; P, 10.48. $C_{14}H_{25}N_4OP$ requires C, 56.74; N, 18.91; P, 10.45].

3.7.4. 1,1-Bis(dimethylamino)-N,N-dimethyl-N′-[3-(trifluoromethyl)-phenyl]phosphinecarboximidamide ***27f***. Yield 97%, 22–24 (pentane); ^{1}H NMR (500 MHz, C_6D_6) δ 7.22 (1H, s, 2H–Ar), 6.92–6.97 (2H, m, Ar), 6.83 (1H, d, J=7.5 Hz, Ar), 2.68 (6H s, NMe_2), 2.28 (12H, d, J=8.7 Hz, NMe_2); ^{13}C NMR (125 MHz, C_6D_6) δ 125.2 (d, J=272.0 Hz), 163.1 (d, J=32.7 Hz), 152.2 (d, J=2.5 Hz), 130.0 (q, J=31.5 Hz), 128.1, 123.4, 116.6 (q, J=2.5 Hz), 115.2 (q, J=3.8 Hz), 41.3 (d, J=17.6 Hz), 39.1 (d, J=8.8 Hz); ^{31}P NMR (81 MHz, C_6D_6) δ 96.0; ^{19}F NMR (188 MHz, $CDCl_3$) δ −62.5. [Found: C, 50.24; N, 16.71; P, 9.38. $C_{14}H_{22}F_3N_4P$ requires C, 50.30; N, 16.76; P, 9.26].

3.7.5. 1,1-Bis(dimethylamino)-N,N-dimethyl-N′-[4-(trifluoromethyl)phenyl]phosphinecarboximidamide ***27g***. Yield 93%; bp 105–110 °C/0.05 Torr, mp 35–36 °C; ^{1}H NMR (500 MHz, C_6D_6) δ 7.36 (2H, d, J=9.0 Hz, 3,5-H–Ar), 6.67 (2H, d, J=8.0 Hz, 2,6-H–Ar), 2.67 (6H, s, NMe_2), 2.27 (12H, d, J=9.0 Hz, $PNMe_2$); ^{13}C NMR (125 MHz, C_6D_6) δ 162.8 (d, J=32.8 Hz), 154.8 (q, J=1.3 Hz), 125.6 (q, J=271.6 Hz), 124.8 (d, J=3.8 Hz), 120.1 (q, J=32.7 Hz), 119.8, 41.2 (d, J=17.6 Hz), 38.9 (d, J=7.5 Hz); ^{31}P NMR (81 MHz, C_6D_6) δ 96.2; ^{19}F NMR (188 MHz, $CDCl_3$) δ −61.0. [Found: C, 50.20; N, 16.75; P, 9.32. $C_{14}H_{22}F_3N_4P$ requires C, 50.30; N, 16.76; P, 9.26].

3.7.6. 1-(Dimethylamino)-1-(1,1-tert-butyl)-N,N-dimethyl-N′-phenylphosphinecarboximidamide ***29***. Yield 90%, 120–130 °C/0.05 Torr; ^{1}H NMR (500 MHz, C_6D_6) δ 7.16 (2H, dd, J=7.5 Hz, 3,5-Ph), 6.80–6.85 (3H, m, Ph); 2.64 (6H, d, J=7.5 Hz, Me_2NP), 2.45 (s, 6H, Me_2N), 1.38 (d, 9H, J=17.5 Hz, *t*-Bu); ^{13}C NMR (125 MHz, C_6D_6) δ 163.3 (d, J=5.0 Hz), 152.2 (d, J=2.5 Hz), 128.6, 120.8 (d, J=2.5 Hz), 120.6, 43.6 (d, J=14.0 Hz), 40.3 (d, J=11.3 Hz), 36.5 (d, J=16.3 Hz), 27.4 (d, J=15.0 Hz); ^{31}P NMR (81 MHz, C_6D_6) δ 80.6. [Found: C, 64.60; N, 15.07; P, 11.04. $C_{15}H_{26}N_3P$ requires C, 64.49; N, 15.04; P, 11.09].

3.7.7. 1-(1-Adamantyl)-1-(dimethylamino)-N,N-dimethyl-N′-phenylphosphinecarboximidamide ***30***. Yield 90%, 166–170 °C/0.05 (Torr); ^{1}H NMR (500 MHz, C_6D_6) 7.17 (2H, d, J=8.0 Hz, Ph), 6.85 (2H, d, J=8.0 Hz, Ph), 2.70 (6H, d, J=7.0 Hz, Me_2NP), 2.45 (6H, s, Me_2N), 2.33 (3H, d, J=11.0 Hz, Ad), 2.15 (3H, d, J=11.0 Hz, Ad), 2.00 (3H, s, Ad), 1.81 (3H, d, J=11.0 Hz, Ad), 1.74 (3H, d, J=11.0 Hz, Ad); ^{13}C NMR (125 MHz, C_6D_6) δ 163.1 (d, J=5.0 Hz), 158.2 (d, J=1.3 Hz), 129.2, 120.9, 120.6, 44.1 (d, J=15.0 Hz), 40.4 (d, J=16.3 Hz), 40.3 (d, J=10.0 Hz), 38.7 (d, J=12.8 Hz), 37.6, 29.0 (d, J=10.0 Hz); ^{31}P NMR (81 MHz, C_6D_6) δ 77.1. [Found: C, 70.33; N, 11.71, P, 8.47. $C_{21}H_{32}N_3P$ requires C, 70.56; N, 11.75, P, 8.66].

3.8. Procedure for the synthesis of 28

A solution of **20** (200 mg, 0.5 mmol) and hexamethylphosphorous triamide (220 mg, 1.3 mmol) in benzene (3 mL) was stirred at 90 °C for 15 min. The reaction mixture was concentrated in vacuo and the residue was distilled (110–125 °C/10–12 Torr) to give crude **28** as residual still, which was crystallized from pentane (3 mL) to give pure **28** (150 mg, 91%) as pale yellow oil.

3.8.1. 1-(Dimethylamino)-1-[2-(dimethylamino)-1-methyl-1H-imidazol-5-yl]-N,N-dimethyl-N′-phenylphosphinecarboximidamide ***28***. Yield 91%, oil; ^{1}H NMR (500 MHz, C_6D_6) δ 7.29 (1H, s, Im), 7.12 (2H, dd, J=7.5 Hz, 3,5-Ph), 6.85 (2H, d, J=7.5 Hz, 2,6-Ph), 6.76 (1H, t, J=7.5 Hz, 4-Ph), 3.19 (3H, s, NMe), 2.57 (6H, s, Me_2NIm), 2.54 (6H, s, Me_2N), 2.22 (6H, d, J=9.5 Hz, Me_2NP); ^{13}C NMR (125 MHz, C_6D_6) δ 160.5 (d, J=35.0 Hz), 156.8 (d, J=6.0 Hz), 151.6 (d, J=3.0 Hz), 134.3, 128.3, 124.0 (d, J=10.0 Hz), 120.5, 119.9, 42.7, 40.6 (d, J=18.0 Hz), 39.3 (d, J=16.0 Hz), 30.2 (d, J=11.0 Hz); ^{31}P NMR (81 MHz, C_6D_6) δ 32.1. [Found: C, 58.78; N, 24.30; P, 9.20. $C_{17}H_{27}N_6P$ requires C, 58.94; N, 24.26; P, 8.94].

3.9. General procedure for the synthesis of 27a, 27i

A solution of **19a** (1 g, 3 mmol) and hexabutylphosphorous triamide (1.32 g, 3.2 mmol) in benzene (6 mL) was stirred at 25 °C for 15 min. The reaction mixture was concentrated in vacuo and the residue was distilled (120–125 °C/5×10^{-2} Torr). The distillate was crystallized from pentane.

3.9.1. 1,1-Bis(dimethylamino)-N,N-dimethyl-N′-phenylphosphinecarboximidamide ***27a***. Yield 70%, 26–29 °C (pentane); ^{1}H NMR (500 MHz, C_6D_6) δ 7.10 (2H, t, J=7.5 Hz, Ph), 6.79 (2H, d, J=7.5 Hz, Ph), 6.73 (1H, t, J=7.0 Hz, Ph), 2.72 (6H, s, Me_2N), 2.44 (12H, d, J=9.0 Hz, Me_2NP); ^{13}C NMR (125 MHz, C_6D_6) δ 162, 2 (d, J=29.0 Hz), 151.8 (d, J=2.5 Hz), 120.4, 119.5, 41.5 (d, J=16.3 Hz), 39.5 (d, J=7.5 Hz); ^{31}P NMR (81 MHz, C_6D_6) δ 96.2. [Found: C, 58.63; N, 20.98, P, 11.67. $C_{13}H_{23}N_4P$ requires C, 58.63; N, 21.04, P, 11.63].

3.9.2. 1,1-Bis(dimethylamino)-N,N-dimethyl-N′-(1-naphthyl)phosphinecarboximidamide ***27i***. Yield 61%, mp 41–42 °C (pentane); ^{1}H NMR (500 MHz, C_6D_6) δ 8.35 (1H, d, J=8.0 Hz, Ar), 7.74 (1H, d, J=7.0 Hz, Ar), 7.32 (4H m, Ar), 6.80 (1H, d, J=6.0 Hz, Ar), 2.72 (s, 6H, NMe_2), 2.37 (12H, d, J=9.0 Hz, $PNMe_2$); ^{13}C NMR (125 MHz, C_6D_6) δ 162.8 (d, J=37.8 Hz), 148.6, 134.8, 128.1, 128.0, 127.8, 127.7, 127.6, 126.2, 125.6, 125.1, 124.3, 119.5, 113.6, 41.3 (d, J=16.0 Hz), 39.2 (d, J=9.0 Hz); ^{31}P NMR (81 MHz, C_6D_6) δ 96.0. [Found: C, 64.43; N, 17.76; P, 10.05. $C_{17}H_{25}N_4P$ requires C, 64.54; N, 17.71; P, 9.79].

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