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Regioselective functionalisation of nitrobenzene and benzonitrile derivatives via nucleophilic aromatic substitution of hydrogen by phosphorus-stabilized carbanions

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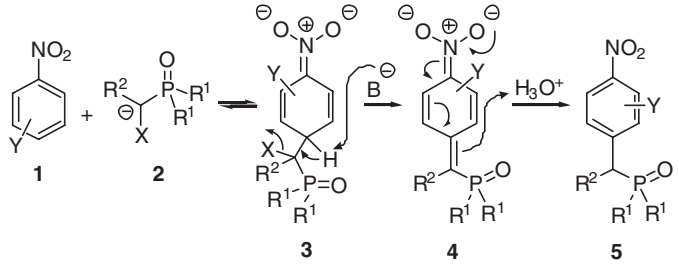
Abstract—The synthesis of *P*-benzylic products by reaction of anions stabilised by *N*-phosphorylphosphazenyl, *N*-methoxycarbonylphosphazenyl, phosphine borane complex, and phosphine oxide groups by displacement of hydrogen of a variety of electron-deficient benzene derivatives is described. Lithium phosphazenes were the most suitable nucleophiles for the substitution of hydrogen in nitrobenzene and some *ortho*-, *meta*-, and *para*- substituted nitrobenzenes. Lithiated phosphine borane complexes produced efficiently the substitution of the hydrogen at the *para* position of a cyano group in cyanobenzenes, whereas the anion of ethyldiphenylphosphine oxide lead to complex mixtures with all electrophiles assayed. The method reported here represents a convenient alternative to the vicarious nucleophilic substitution for the synthesis of benzylic phosphorus derivatives using phosphorus-stabilised anions that do not bear a leaving group at the carbanionic centre.

1. Introduction

The direct functionalisation of electron-deficient arenes via nucleophilic replacement of hydrogen is a process of great interest both in the academia and in the industry.[1] The introduction of a *P*-alkyl substituent into an aromatic system is particularly attractive owing to the possibility of using benzylic phosphorus derivatives into olefination reactions. The end products would be stilbenes, a compound class that have shown important biomedical properties.[2] Nucleophilic aromatic substitution of hydrogen, S_NAr^H, by phosphorus-stabilised carbanions has been achieved exclusively via vicarious nucleophilic substitution (VNS),[3] and only on nitrobenzenes. The VNS method requires that the nucleophile also contains a nucleofugal group (X) at the reactive centre. Attack of the carbanion **2** formed by deprotonation of the corresponding organophosphorus compound to the nitroarene **1** leads to a Meisenheimer complex **3**, which is in equilibrium with the starting reagents (Scheme 1). This σ-adduct undergoes β-elimination of HX promoted by a second equivalent of base. The resulting nitronate intermediate **4** provides the substituted arene **5** upon work-up.[4]

The organophosphorus reagents used in VNS reactions include chloromethyldiphenylphosphine oxide,[5] dimethyl



Scheme 1.

Keywords: Phosphazenes; Phosphine-boron complexes; Nucleophilic aromatic substitution; Carbanions; Cyano group.
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α-chlorobenzylphosphonate,[5a] and 2-(1,3-dithianyl)triphenylphosphonium chloride.[6] Phosphorus ylides derived from (halomethyl)triphenylphosphonium halides (halide = Cl, Br) failed to give VNS products in the reaction with nitrobenzene.[5c] Interestingly, Lawrence and co-workers showed that the vicarious nucleophilic substitution products formed in the reaction of the anion of chloromethyldiphenylphosphine oxide with a series of substituted nitrobenzenes can be transformed into stilbenes in a one-pot process.[5b,c]

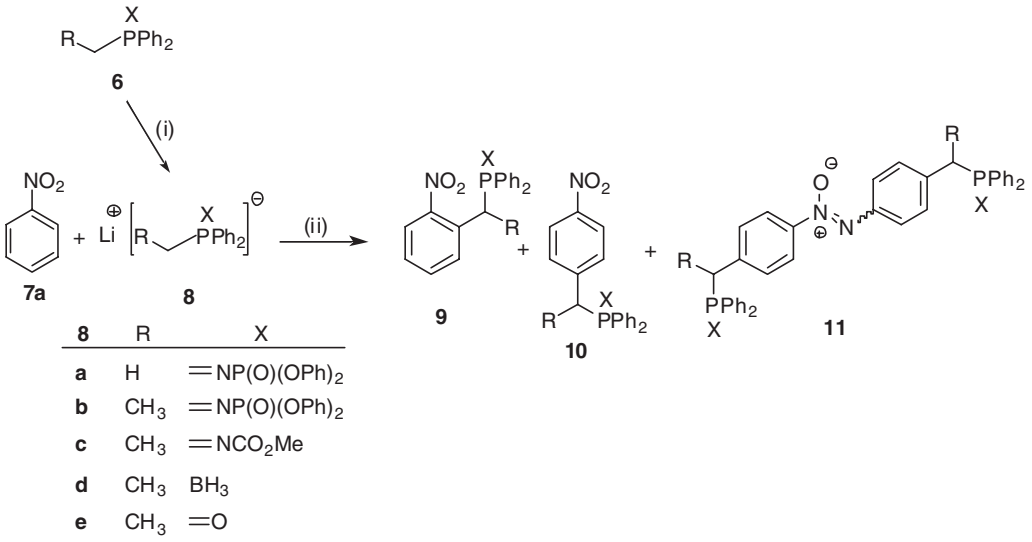
The introduction into an aromatic ring of alkyl side chains bearing phosphorus-containing functional groups through the VNS protocol shows two important limitations. On the one hand, the nucleophile must bear an auxiliary leaving group at the carbanionic centre. On the other, only nitrobenzenes have been used as electrophiles.

We have recently reported a new method for the direct introduction of alkylphosphorus substituents into nitro- and cyano-benzenes, with high yield and regioselectivity, through nucleophilic aromatic substitution of hydrogen without the requirement of a nucleofuge at the α position with respect to the phosphorus atom.[7] Generally, aromatization occurred spontaneously in the reaction medium or during work-up. In some cases the use of an external oxidant such as DDQ proved to be beneficial for increasing the yield of S_NAr^H products. Here we wish to report the full details of this investigation showing the scope of the methodology. We have evaluated the feasibility of α-lithiated *N*-phosphorylphosphazenes, *N*-methoxycarbonylphosphazenes, phosphine borane complexes, and phosphine oxides, as nucleophiles for the S_NAr^H reactions. The influence of the substituents for activating the aromatic nucleus and the different reactivity of primary and secondary carbanions are also discussed.

2. Results and discussion

2.1. Functionalisation of nitrobenzene and benzonitrile derivatives via S_NAr^H

We initially chose lithiated phosphazenes bearing electron-withdrawing groups at the nitrogen atom **8a–c** as nucleophiles for the reaction with nitrobenzene **7a** based on our experience on the synthetic applications of these anions,[8] which includes their utilisation in olefination reactions.[9] The carbanions **8a–c**, generated through metalation of phosphazenes **6a–c** with LiBu^n, were allowed to react with **7a** at low temperature in THF (Scheme 2). The results obtained are collected in Table 1 (entries 1–3). High conversions were observed for **8b–c**. The major products isolated consisted of compounds **9** and **10** resulting from the hydrogen substitution at the *ortho* and *para* position to the nitro group, respectively. The later is generated in higher yield except for lithium phosphazene **8a**. This carbanion affords equimolecular amounts of both regiosiomers, albeit in very low yield. The poor performance of the reaction of **8a** with nitrobenzene can be ascribed to



Scheme 2. Reagents and conditions: (i) for **6a–c** and **6e** LiBu^n (1 equiv), THF, HMPA (6 equiv), −30 °C, 30 min; for **6d** LiBu^s (1 equiv), THF, HMPA (6 equiv), −90 °C, 30 min; (ii) 1 equiv of **7a**, THF, −90 °C, 12 h.

Table 1. Distribution of products (%) in the reaction of phosphorus-stabilised anions **8a–e** with nitrobenzene

Entry	Nucleophile	R	X	Conversion	S_NAr^{Ha}	**9**[b]	**10**[b]	**11**[b]
1	**8a**	H	=NP(O)(OPh)$_2$	18	100	9 (**a**)	9 (**a**)	
2	**8b**	CH_3	=NP(O)(OPh)$_2$	84	77	11 (**b**)	54 (**b**)	19 (**a**)
3	**8c**	CH_3	=NCO_2Me	76	55	10 (**c**)	32 (**c**)	10 (**b**)
4	**8d**	CH_3	BH_3	58	83	3 (**d**)	45 (**d**)	10 (**c**)
5	**8e**	CH_3	=O	94	20		19 (**e**)	<1% (**d**)

[a] Referred to the % of conversion.
[b] Crude yield.

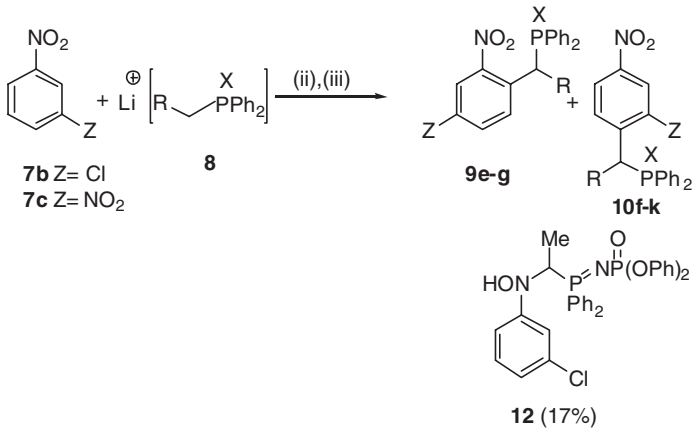
the lower nucleophilicity of the primary carbanion as compared with anions **8b–c**. This behaviour has been noted previously in lithiated *N*-phosphoryl[8e] and *N*-methoxycarbonylphosphazenes.[8c,10]

Besides S_NAr^H products, variable amounts of azoxy derivatives **11** were obtained in the reactions of **8b** and **8c** (Scheme 2, Table 1). Arylation of carbanions via S_NAr reactions with nitroarenes might be complicated by electron-transfer processes as well as the attack of the carbanion to the nitro function.[11] Azoxy compounds have been described[12] as decomposition products of nitroso derivatives formed by reduction of the NO_2 moiety. The formation of compounds **11** suggests that the reaction proceeds in part via a mechanism involving radical-anion species. Addition to the reaction medium of DDQ as an external oxidant did not improved the yield of S_NAr^H products. On the other hand, in absence of the strongly coordinating cosolvent HMPA the yields of **9** and **10** decreased significantly.[7]

We were also interested in studying the feasibility of lithium ethyldiphenylphosphine borane complex **8d** as nucleophiles in S_NAr^H reactions with nitrobenzene **7a**. The BH_3 moiety of phosphine borane complexes has a double function. It enhances the acidity of the protons adjacent to the phosphorus and protects the heteroatom from oxidation.[13] The BH_3 group can be removed in several ways (e.g., heating with triethylamine, DABCO, fluoroboric acid, etc.)[14] and the resulting phosphine can be further transformed. Lithium ethyldiphenylphosphine borane complex **8d** reacted with **7a** in a similar manner to the phosphazenyl carbanions **8b–c**. Although in this case the conversion was slightly lower, the yield of S_NAr^H products and the selectivity in favour of the *para* isomer increased notably (Table 1, entry 4).

We next attempted the reaction between lithiated phosphine oxide **8e** and nitrobenzene **7a** under the same reaction conditions used with phosphazenyl anions **8a–c**. The ^1H and ^{31}P NMR spectra of the crude mixture showed that the conversion was high. However, a complex mixture of products was formed in which compound **10e** represents only a 19% (Table 1, entry 5). After column chromatography (eluent ethyl acetate/hexane 5:1) the azoxy derivative **11d** could be identified although only traces of this compound are present in the crude mixture (Table 1, entry 5). The structures of **10e** and **11d** were confirmed by comparison of their ^1H and ^{31}P NMR data with the products obtained in the acid hydrolysis of **10b** and **11b**, respectively.

3-Chloronitrobenzene **7b** and 1,3-dinitrobenzene **7c** were also reacted with carbanions **8a–e**. The results obtained are shown in Scheme 3 and Table 2. As can be observed in Table 2, the higher electrophilicity of the nitroarenes **7b–c** as compared with nitrobenzene **7a** produced an increase in the yield of S_NAr^H products. Furthermore, although several regioisomers might be formed, the products of substitution at the *para* position with respect to the nitro group **10f–k** were obtained with high (entries 1, 3 and 4) or total regioselectivity (entries 2, 5 and 6). No displacement of halogen was observed in any case. Except for **8a**, the reactions performed well in the absence of coordinating cosolvents. However, the efficient replacement of hydrogen in **7b–c** by anions **8b–d** required the use of DDQ as external oxidant. Otherwise, byproducts arising from nucleophilic



Scheme 3. Reagents and conditions: (ii) $ArNO_2$ 1 equiv, THF, −90 °C, 12 h; (iii) DDQ 1.2 equiv, −90 °C, 15 min then 1 h at room temperature.

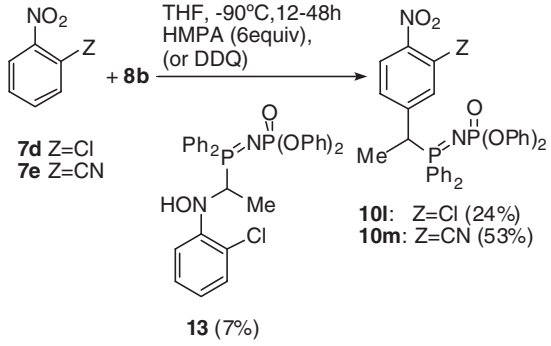
Table 2. Distribution of products (%) in the reaction of anions **8a–e** with **7b** and **7c**

Entry	Nucleophile	R	X	Z	Conversion	**9**[a]	**10**[a]
1	**8a**	H	$=NP(O)(OPh)_2$	Cl	46[b]	5 (**e**)	41 (**f**)
2	**8b**	CH_3	$=NP(O)(OPh)_2$	Cl	62[c]		62 (**g**)
3	**8c**	CH_3	$=NCO_2Me$	Cl	87	8 (**f**)	79 (**h**)
4	**8e**	CH_3	$=O$	Cl	72	7 (**g**)	34 (**i**)
5	**8b**	CH_3	$=NP(O)(OPh)_2$	NO_2	79		79 (**j**)
6	**8d**	CH_3	BH_3	NO_2	54		54 (**k**)

[a] Crude yield.
[b] Metalation in the presence of 6 equiv of HMPA; absence of DDQ.
[c] In the absence of DDQ compound **12** was also formed in 17% yield.

attack to the nitro group are detected. For example, in the reaction of **8b** with *m*-chloronitrobenzene in the absence of DDQ the hydroxylamine **12** was formed in 17% yield. By contrast, the presence of the oxidizing agent in the reaction of the primary carbanion **8a** with *m*-chloronitrobenzene **2c** inhibits almost completely the S_NAr^H process. The lithiated phosphine oxide **8e** proved to be the less efficient nucleophile in terms of substitution products. Either in the presence or absence of DDQ a complex mixture of products was obtained. Compounds **9g/10i** were obtained in a yield of 41% in a ratio of 1:5 (entry 4). From the comparison of Tables 1 and 2 it can be concluded that the regiochemistry is mainly controlled by steric factors. Nevertheless, some electronic effects are also operative, which would explain the higher ratios of *para*:*ortho* products generated in the reactions of lithium phosphine borane complex **8d** as compared with the corresponding phosphazenes (cf. **10d/9d** 10:1 vs **10b/9b** 5:1 and **10c/9c** 3:1).

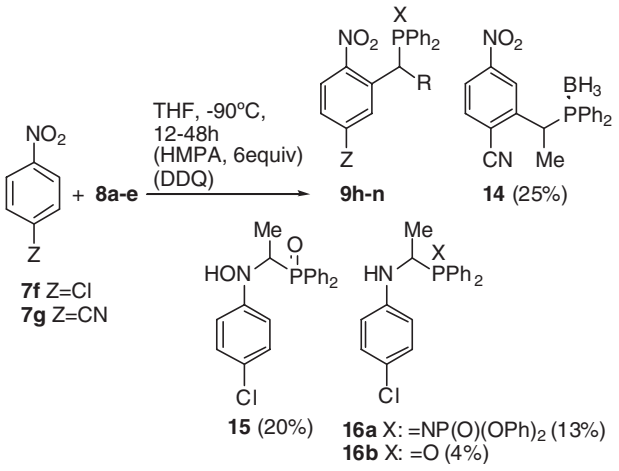
Replacement of hydrogen in *ortho* substituted nitrobenzenes such as *o*-chloronitrobenzene **7d** and *o*-nitrobenzonitrile **7e** by reaction with anion **8b** proceed with some problems. Substitution occurs exclusively at the *para* position to the nitro group to give the nitrobenzylphosphazenes **10l** and **10m**, respectively (Scheme 4). The yields of **10l** were low and the hydroxylamine **13** was persistently formed even when the external oxidizing agent DDQ was used. On the other hand, compound **10m** could be obtained in reasonable yield only when the addition of *o*-nitrobenzonitrile **7e** was carried out in the presence of HMPA. On the light of these results no further assays of these nitroarenes with the other nucleophiles were performed.



Scheme 4. The stoichiometry phosphorylphosphazene/LiBu^n/nitroarene used was 1:1:1 for **7d** and 1:2.5:2.5 for **7e**.

The reactivity of anions **8a–e** towards the *p*-substitued systems 4-chloro- and 4-cyanonitrobenzene was also evaluated. The substituents of these nitroarenes represent a good test of the efficiency of the process. Besides the expected S_NAr^H reactions alternative pathways are possible. Among others, it might occur the displacement of some substituent of the aromatic system,[15] the addition to the CN function,[16] and the competition between the CN and NO_2 groups for directing the nucleophilic attack to the aromatic nucleus.

Lithium phosphazenes **8a–c** react with **7f** and **7g** in THF at −90 °C to give exclusively products of replacement of hydrogen at the *ortho* position with respect to the nitro group **9h,i,k,l,m** (Scheme 5 and Table 3). The reaction conditions required some optimization to obtain the best yields of nitrobenzylphosphazenes **9**. Thus, good yields of **9k** are obtained when the reaction is effected in the presence of HMPA (entry 4). In the absence of coordinating solvent compound **9k** was formed only in 26% yield.[17] The increased reactivity of **8a** induced by the cosolvent may be assigned to the well known deaggregating effect of HMPA.[18] The yield of **9m** increased slightly (from 75 to 81%, entry 6) when the rearomatisation was forced by addition of DDQ to the reaction mixture. Likewise, the use of DDQ in the reaction of **8b** with *para*-chloronitrobenzene **7f** was necessary for the clean formation of **9i**, otherwise the amine **16a** arising from the attack of the nucleophile to the nitro group is also isolated in 13% yield (entry 2). The reaction of the primary carbanion **8a** with **7f** proceeds with low yield and the addition of HMPA promotes the generation of a number of byproducts without increasing the amount of **9h** obtained.



Scheme 5. The stoichiometry used was phosphorous compound **6a–c**, **6e**/LiBu^n/nitroarene 1:1:1 for **7f** and 1:2.5:2.5 for **7g**. Metalation of phosphine borane to give **8d** was performed with LiBu^s and the stoichiometry used was **6d**/LiBu^s/**7g** 1:1.5:1.2.

Once again, the lithium phosphine oxide **8e** was the less efficient nucleophile for S_NAr^H processes. The reaction of **8e** with 4-chloronitrobenzene in the presence of DDQ gives a complex mixture of products, with compound **9j** being obtained in only 27% yield (entry 3). Purification by column chromatography allowed to identify also the hydroxylamine **15** and the amine **16b** formed as byproducts. When 4-cyanonitrobenzene was used as electrophile no products of hydrogen substitution could be unambiguously detected.

The reaction of lithium phosphine borane complex **8d** with *p*-cyanonitrobenzene was remarkable. No evidences of displacement of cyanide or nucleophilic addition to the cyano group were observed. Only products of aromatic hydrogen substitution were detected. The conversion was only of 37%. A 63% of the starting phosphine borane complex remained unreacted even when the metalation was performed in presence of HMPA and DDQ was added as external oxidizing agent prior to the aqueous work-up. However, the most important feature of this reaction concerns its regioselectivity. The reaction products consisted of a mixture of the regioisomers **9n** and **14** in a ratio of

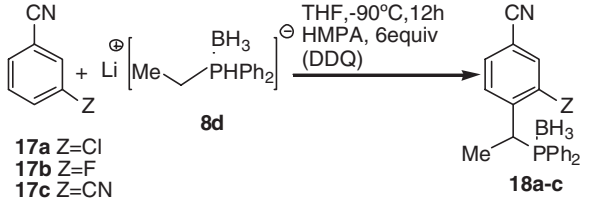
Table 3. Compounds **9h–n** obtained in the reaction of anions **8a–e** with **7f** and **7g**

Entry	Nucleophile	R	X	Z	Yield (%) **9**
1	**8a**	H	$=NP(O)P(OPh)_2$	Cl	28 (**h**)
2	**8b**	CH_3	$=NP(O)P(OPh)_2$	Cl	53 (**i**)[a,b]
3	**8e**	CH_3	$=O$	Cl	27 (**j**)[a,c]
4	**8a**	H	$=NP(O)P(OPh)_2$	CN	64 (**k**)[d]
5	**8b**	CH_3	$=NP(O)P(OPh)_2$	CN	81 (**l**)
6	**8c**	CH_3	$=NCO_2Me$	CN	81 (**m**)[a]
7	**8d**	CH_3	BH_3	CN	12 (**n**)[e,f]

[a] Addition of DDQ (1.2 equiv).
[b] In absence of DDQ a 13% of compound **16a** was also obtained.
[c] Also obtained 20% of compound **15** and 4% of compound **16b**.
[d] Metalation in the presence of 6 equiv of HMPA.
[e] Metalation in the presence of HMPA (6 equiv) and addition of DDQ (1.2 equiv).
[f] Also obtained 25% of compound **14**.

1:2 (Scheme 5, Table 3 entry 7). This means that both the nitro and the cyano groups compete for directing the attack of the incoming nucleophile, with the later being more potent than the nitro function by a factor of 2. Selective replacement of hydrogen in *p*-nitrobenzonitrile using Grignard reagents as nucleophiles has been reported.[19] The presence of the CN group did not improve the efficiency of the substitution compared to the nitrobenzene itself. In other cases, a cyano substituent on a nitroarene makes difficult or prevents to attain the desired products of nucleophilic aromatic substitution of hydrogen.[20] As far as we know this is the first time that such competing effect between a nitro and a cyano group in a S_NAr^H reaction on a phenyl ring is observed.[19,21,22] Hydrogen displacement via VNS reactions of 1-naphthonitrile has been described.[23] We are not aware of S_NAr^H of organolithium reagents with benzonitriles.[24]

These results prompted us to study the reactivity of lithium phosphine borane complex **8d** with a variety of other substituted cyanoarenes. 3-Chlorobenzonitrile **17a**, 3-fluoro benzonitrile **17b**, and 1,3-dicyanobenzene **17c** reacted with **8d** to give exclusively the products of hydrogen substitution at the *para* position to the CN group **18a–c** (Scheme 6, Table 4). The same conditions described for the reaction with **7g** were used, except that the use of the external oxidising agent DDQ was necessary for obtaining high yield of **18a**. Otherwise, the major compound formed is the cyclohexadiene derivative resulting from the [1,6] addition to the aromatic ring (Table 4, entries 1 and 2).[25] The reaction of the fluorinated nitrile **17b** proceeds in a disappointing 25% yield in absence of DDQ and the addition of the oxidant proved to be detrimental for the process (entries 3 and 4). It is worth nothing, however, that no displacement of fluorine was observed in spite of the known high rate of fluorine substitution in fluoroarenes. The higher activation of the aromatic system provided by



Scheme 6. The metalation of phosphine borane was achieved with Bu^{s}Li. Stoichiometry phosphine borane/LiBu^s/benzonitrile 1:1.2:1.2.

the two cyano groups present in **17c** allowed to perform the reaction of this electrophile with **8d** in absence of DDQ affording **18c** in high yield (entry 5).

Table 4. Compounds **18** obtained in the reaction of anion **8d** with cyanoarenes **17a–c**

Entry	**17**	Z	**18**	Yield (%)
1	**a**	Cl	**a**	21
2	**a**[a]	Cl	**a**	64
3	**b**	F	**b**	25
4	**b**[a]	F	**b**	17
5	**c**	CN	**c**	87

[a] Addition of DDQ (1.2 equiv).

2.2. Structural characterization

The structural identification of S_NAr^H products **9**, **10**, **14** and **18** was straightforward based on the correlations observed in the 2D HMBC spectra between the benzylic protons and the carbons of the aromatic system.

For the products of the reaction of **8a–d** with nitrobenzene, the P–C*H* protons of *ortho* regioisomers (**9a–d**) correlate with two quaternary carbons and one methine carbon *meta* with respect to the nitro group. In the *para* isomers (**10a–d**) the benzylic protons show only two correlations corresponding to the C_{ipso} and the two adjacent isochronous CH carbons. From the analysis of the NMR data a rule merged that can be applied to the identification of the substitution pattern: in the ^{1}H NMR spectra the benzylic protons of the *ortho* isomers appear notably deshielded as compared with the *para* derivatives ($\Delta\delta$ (P–C*H*)$_{(ortho-para)} \approx 1$ ppm), whereas the opposite occurs for the corresponding methine carbon in the ^{13}C NMR spectra ($\Delta\delta$ (P–*C*H)$_{(para-ortho)} \approx 7$ ppm).

For compounds **9e–g** and **10f–k**, the P–C*H* protons show correlations with two quaternary carbons and one methine carbon. This fact implies that products of nucleophilic attack at position 2 of the nitroarenes were not formed and that nitrocompounds **10j** and **10k** are the exclusive S_NAr products of the reaction between 1,3-dinitrobenzene and anions **8b** and **8d**, respectively. Substitution products of attack *ortho*, **9e–g**, and *para* to the nitro group of 3-chloronitrobenzene, **10f–i**, give rise to the same set of correlations for the benzylic protons. They can be easily distinguished based on the chemical shifts of the C_{ipso} carbons bonded to the chlorine atom and the nitro group,

the later inducing a much larger downfield shift ($\Delta\delta^{C_{ipso}}$ (NO_2–Cl) ≈ 16 ppm). Similarly, the exclusive replacement of hydrogen at the *ortho* position respect to the nitro group in the reaction of carbanions **8a–c** and nitroarenes **7f–g** was deduced from the correlations observed in the 2D *g*HMBC spectra between the benzylic proton and the C_{ipso} carbon bonded to the nitro group. In all cases, this carbon appears in the ^{13}C NMR spectra as the most downfield signal.

The structural characterization of the new functionalized benzonitriles **18a–c** was realized following the same procedure described for the nitrobenzyl derivatives. The ^{31}P NMR spectra of the products resulting from the hydrogen displacement by lithium phosphine borane complex **8e** are characterized by a very pronounced deshielding of the phosphrus signal respect to the starting phosphine borane complex **6e** ($\Delta\delta_P \approx 7$ ppm). As expected, very broad ^{31}P NMR signals were observed for compounds containing the phosphine borane moiety owing to the combined effect of fast relaxation and unresolved couplings produced by the quadrupolar nuclei $^{10/11}B$.[26]

Compounds **9n** and **14** were isolated by column chromatography (eluent ethyl acetate/hexane 1:5) and characterised by their spectroscopic data. The 2D HMBC spectra provided the proton–carbon connectivity for identifying the position of entering of the nucleophile. The benzylic proton of **14** (δ_H 4.52 ppm, dc, $^3J_{HH}=7.3$ Hz, $^2J_{PH}=15.3$ Hz) correlates with two high field quaternary carbons at δ_C 115.91 ppm (d, $^4J_{PC}=1.5$ Hz) and 118.54 ppm (d, $^3J_{PC}=5.1$ Hz), assigned to the CN and *ipso*-carbon linked to the CN group, respectively. For compound **9n** the replacement of the hydrogen *ortho* to the nitro group is evidenced by the correlation of the P–C*H* proton (δ_H 5.02 ppm, dq, $^3J_{HH}=$ 7.3 Hz, $^2J_{PH}=15.8$ Hz) with the quaternary carbon bonded to the NO_2 group (δ_C 151.21 ppm, d, $^3J_{PC}=5.7$ Hz).

The redox products **11** exhibited the same pattern of carbon–proton correlations found in the precursors **10** with duplicate signals. Thus, the ^{31}P NMR spectrum of **11a** shows two set of signals of very close chemical shifts corresponding to both phosphazene moieties present in this compound. Molecular weight determinations via mass spectrometry supports the assignment made.

Finally, the structure of hydroxylamines **12**, **13** and **15** and the anilines **16a–b** was deduced from the analysis of the mass spectrum, IR and ^1H, ^{31}P, ^{13}C, DEPT, 2D *g*HMQC, and 2D *g*HMBC NMR spectra. Focusing in compound **12**, the molecular weight of 602 is in agreement with the formula $C_{32}H_{29}ClN_2O_4P$. Relevant spectroscopic data of this compound are the O–H stretching absorption in the IR spectrum at 3456 cm^{-1} and the chemical shift of the methine carbon linked to the phosphorus ($\delta_C=63.52$ ppm, d, $^1J_{PC}=85.6$ Hz). This chemical shift indicates that this carbon must be also bonded to a second heteroatom of moderate electronegativity, that is, nitrogen.

3. Conclusions

Non-functionalised carbanions stabilised by *N*-phosphorylphosphazenyl, *N*-methoxycarbonylphosphazenyl, phosphine borane complex, and phosphine oxide groups were used as nucleophiles in reactions of aromatic substitution of hydrogen with a variety of electron-deficient benzene derivatives. The process is strongly influenced by the nature of both the phosphorus functionality linked to the carbanion and the substituents present in the aromatic system. The results obtained indicate that lithium phosphazenes are suitable nucleophiles for the direct preparation of benzyl phosphorus derivatives via S_NAr^H reactions with *ortho*-, *meta*- and *para*-substituted nitrobenzenes. The substituents used were Cl, NO_2, and CN. The new synthetic method provides nitrobenzylphosphazenes in moderate to good yield (range from 24 to 81%) and with high regioselectivity. Products of substitution of hydrogen at the *para* position to the nitro group are predominantly or exclusively formed. Contrary to the VNS protocol, in this case the existence of a nucleofuge at the carbanion centre is not necessary. The reactions of primary anions proceed in lower yields most probably due to the lower nucleophilicity as compared with secondary anions. Generally, higher yields are obtained when the reaction is performed in the presence of HMPA. In some cases, the use of an external oxidising agent such as DDQ to help the departure of hydride ion with subsequent aromatization improved the efficiency of the process. The addition of DDQ to the reactions of **8b** with chloro-substituted nitrobenzenes prevents the formation of byproducts arising from the nucleophilic attack to the nitro group. By contrast, the reactions of the anion of ethyldiphenylphosphine oxide with nitroarenes lead to complex mixtures of compounds, in which S_NAr^H products are detected only in minor amounts.

Lithium phosphine borane complex **8d** is less efficient than phosphazenyl anions in S_NAr^H reactions with nitroarenes. However, it proved to be a good nucleophile for the replacement of hydrogen of benzonitriles such as 3-chlorobenzonitrile, 3-fluorobenzonitrile, and 1,3-dicyanobenzene. Only products of substitution *para* to the CN group were formed in yields of 25–87%. The use of DDQ increased notably the yield of the reaction of **8d** with 3-chlorobenzonitrile, whereas left almost unaffected the reaction with 3-fluorobenzonitrile. In the reaction with *p*-nitrobenzonitrile the replacement of hydrogen took place at *ortho* positions to both activating groups, NO_2 and CN, with the later being produced predominantly.

Aromatic hydrocarbons are very important building blocks in organic synthesis. They are low-cost readily available reagents, which utility depends on the ability of performing the functionalisation of C_{Ar}–H bonds in a regioselective manner. The synthesis here described represents a convenient route for accessing to nitrobenzylphosphazenes and cyanobenzylphosphine borane complexes via S_NAr^H reactions. The method developed allows the regioselective installation of a phosphaalkyl moiety into an electron-deficient aromatic ring providing a substitution pattern generally not accessible through electrophilic aromatic substitution or directed *ortho* metalation processes.[27] The use of non-functionalised phosphorus-stabilised carbanions opens a pathway alternative to VNS reactions for introducing organophosphorus moieties into π-deficient arenes. Both phosphorus functional groups can be further transformed into a variety of other functions with retention

or elimination of the phosphorus atom by known procedures.

4. Experimental

4.1. General

All reactions were carried out under an atmosphere of nitrogen using dried glassware. Solvents were distilled before use. THF was dried with sodium and distilled under nitrogen. Commercial starting materials were purchased from Aldrich. Liquids, except LiBu^n and LiBu^s, were distilled prior use. TLC was performed on Merck plates with aluminium backing and silica gel 60 F_{254}. For column chromatography silica gel 60 (40–63 μm) from Scharlau was used.

Melting points were recorded on a Büchi B-540 apparatus and are uncorrected. Infrared spectra were obtained in KBr pellets using a Mattson Genesis II FT spectrometer. Mass spectra were determined by APCI (Atmospheric Pressure Chemical Ionization) on a Hewlett-Packard 1100. Microanalysis were performed on a Perkin-Elmer 2400. NMR spectra were measured on a Bruker 300DPX and Bruker Avance 500 spectrometers. Chemical shifts are referred to internal tetramethylsilane for ^{1}H, the deuterated solvent for ^{13}C, and to external 85% H_3PO_4 for ^{31}P. 2D NMR correlation spectra (HMQC and HMBC) were acquired using standard Bruker software and processing routines.

4.2. General procedure for the reaction of phosphorus-stabilised carbanions and electron-deficient aromatic compounds

Phosphazenes **6a–c** were readily synthesised through the Staudinger reaction of commercial methyl and ethyldiphenylphosphine with the corresponding azide.[8c,e,28] Phosphine borane complex **6d** was prepared by complexation of ethyldiphenylphosphine with $BH_3\cdot THF$.[25]

Anions **8a–c** and **8e** were prepared by adding a solution of LiBu^n (0.3–0.8 mL of a 1.6 M solution in hexane, 0.5–1.25 mmol) to a solution of 0.5 mmol of the appropriate phosphorus compound **6a–c** or **6e** in THF (25 mL) at −30 °C. The metalation of the phosphine borane complex (0.5 mmol) to give **8d** was achieved with LiBu^s (0.4–0.5 mL of a 1.3 M solution in cyclohexane) also at −90 °C. In some cases, 0.5 mL (3 mmol) of the co-ordinating agent HMPA was also added.

After 30 min of metalation, the temperature was lowered at −90 °C and the corresponding aromatic compound **7a–g/17a–c** (0.5, 0.6 or 1.25 mmol) was added. The reaction mixture was stirred for 12–48 h at this temperature, monitoring the reaction progress by ^{31}P NMR. Addition of water (25 mL) followed by extraction with ethyl acetate (3×15 mL) and solvent evaporation under vacuum afforded a crude product, which was purified by column chromatography using a mixture of ethyl acetate/hexane or, in the case of **18c**, by precipitation from diethyl ether.

Treatment with external oxidizing agent. Before the hydrolytic work-up, 137 mg (0.6 mmol) of DDQ were added to the reaction crude at −90 °C. The mixture was then stirred for an additional hour at room temperature and processed as it is describe above.

4.2.1. 2-{1-[(*P*,*P*-Diphenyl)(*N*-diphenylphosphoryl)phosphazenyl]methyl}nitrobenzene (9a). Eluent: ethyl acetate/hexane 3:1. Oil. Yield: 9%. IR (KBr pellets, neat), ν (cm^{-1}): 1261, 1199. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 4.61 (d, $^2J_{PH}$=14.6 Hz, 2H), 7.08 (m, 2H, H^{ar}), 7.22 (m, 10H, H^{ar}), 7.37 (m, 4H, H^{ar}), 7.46 (m, 2H, H^{ar}), 7.56 (m, 6H, H^{ar}), 7.73 (m, 1H^{ar}), 7.96 (m, 1H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 32.99 (dd, $^1J_{PC}$=60.4 Hz, $^3J_{PC}$=1.7 Hz), 120.58 (d, $^3J_{PC}$=5.1 Hz), 123.77 (d, $^5J_{PC}$=1.2 Hz), 125.02 (d, $^4J_{PC}$=2.4 Hz), 126.37 (d, $^2J_{PC}$=8.7 Hz), 127.64 (dd, $^1J_{PC}$=104.8 Hz, $^3J_{PC}$=5.4 Hz), 128.08 (d, $^4J_{PC}$=3.3 Hz), 128.67 (d, $^3J_{PC}$=12.9 Hz), 129.18 (d, $^4J_{PC}$=0.9 Hz), 131.72 (d, $^2J_{PC}$=10.5 Hz), 132.62 (d, $^4J_{PC}$=2.7 Hz), 133.35 (d, $^5J_{PC}$=3.0 Hz), 134.56 (d, $^3J_{PC}$=4.8 Hz), 148.33 (d, $^3J_{PC}$=5.7 Hz), 152.18 (d, $^2J_{PC}$=7.8 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): −7.13 (d, $^2J_{PP}$=31.2 Hz), 17.22 (d, $^2J_{PP}$=31.2 Hz). Anal. Calcd for $C_{31}H_{26}N_2O_5P_2$ (568.51): C, 65.49; H, 4.57; N, 4.93. Found: C, 66.44; H, 4.56; N, 4.90. MS *m*/*z* (%): 569 (100).

4.2.2. 2-{1-[(*P*,*P*-Diphenyl)(*N*-diphenylphosphoryl)-phosphazenyl]ethyl}nitrobenzene (9b). Eluent: ethyl acetate/hexane 3:1. Oil. Yield: 11%. IR (KBr pellets, neat), ν (cm^{-1}): 1260, 1091, 1022. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 1.69 (dd, $^3J_{HH}$=7.1 Hz, $^3J_{PH}$=17.4 Hz, 3H), 4.92 (dquintet, $^3J_{HH}$=$^2J_{PH}$=7.1 Hz, $^4J_{PH}$=3.2 Hz, 1H), 7.15 (m, 6H, H^{ar}), 7.26 (m, 9H, H^{ar}), 7.55 (m, 6H, H^{ar}), 7.99 (m, 3H, H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 15.45 (d, $^2J_{PC}$=3.6 Hz), 34.01 (dd, $^1J_{PC}$=69.4 Hz, $^3J_{PC}$=3.3 Hz), 120.41 (d, $^3J_{PC}$=5.1 Hz), 120.70 (d, $^3J_{PC}$=4.8 Hz), 123.73 (d, $^5J_{PC}$=1.2 Hz), 123.83 (d, $^5J_{PC}$=1.2 Hz), 124.43 (d, $^4J_{PC}$=1.8 Hz), 127.52 (d, $^1J_{PC}$=96.7 Hz), 128.19 (d, $^1J_{PC}$=103.9 Hz), 128.22 (d, $^3J_{PC}$=12.6 Hz), 128.85 (d, $^4J_{PC}$=0.8 Hz), 129.09 (d, $^3J_{PC}$=12.3 Hz), 129.24 (d, $^4J_{PC}$=0.9 Hz), 129.28 (d, $^4J_{PC}$=0.6 Hz), 131.10 (d, $^2J_{PC}$=10.1 Hz), 131.46 (d, $^3J_{PC}$=4.8 Hz), 132.05 (d, $^2J_{PC}$=9.9 Hz), 132.06 (d, $^4J_{PC}$=3.0 Hz), 132.13 (d, $^2J_{PC}$=5.4 Hz), 132.68 (d, $^5J_{PC}$=3.0 Hz), 133.27 (d, $^4J_{PC}$=2.7 Hz), 148.82 (d, $^3J_{PC}$=6.6 Hz), 152.39 (d, $^2J_{PC}$=7.8 Hz), 152.41 (d, $^2J_{PC}$=8.1 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): −10.42 (d, $^2J_{PP}$=34.5 Hz), 17.85 (d, $^2J_{PP}$=34.5 Hz). Anal. Calcd for $C_{32}H_{28}N_2O_5P_2$ (582.53): C, 65.98; H, 4.84; N, 4.81. Found: C, 66.21; H, 4.83; N, 4.82. MS *m*/*z* (%): 583 (100).

4.2.3. 2-{1-[(*P*,*P*-Diphenyl)(*N*-methoxycarbonyl)-phosphazenyl]ethyl}nitrobenzene (9c). Eluent: ethyl acetate/hexane 5:1.Oil. Yield: 10%. IR (KBr pellets, neat), ν (cm^{-1}): 1732, 1657, 1260, 1092, 1019. ^{1}H NMR (300.13 MHz, $CDCl_3$): 1.76 (dd, $^3J_{HH}$=7.2 Hz, $^3J_{PH}$=16.3 Hz, 3H), 3.63 (s, 3H), 4.50 (dq, $^3J_{HH}$=7.2 Hz, $^2J_{PH}$=11.2 Hz, 1H), 7.19–7.44 (m, 8H^{ar}), 7.57–7.72 (m, 4H^{ar}), 7.90–8.01 (m, 2H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 16.48 (d, $^2J_{PC}$=3.0 Hz), 33.04 (d, $^1J_{PC}$=69.7 Hz), 52.72 (d, $^4J_{PC}$=3.6 Hz), 124.48 (d, $^4J_{PC}$=1.8 Hz), 125.94 (d, $^1J_{PC}$=88.3 Hz), 126.76 (d, $^1J_{PC}$=94.9 Hz), 127.99 (d, $^5J_{PC}$=2.4 Hz), 128.31 (d, $^3J_{PC}$=12.0 Hz), 129.00

(d, $^{3}J_{PC}$=11.4 Hz), 131.37 (d, $^{3}J_{PC}$=4.2 Hz), 131.60 (d, $^{2}J_{PC}$=9.0 Hz), 132.06 (d, $^{4}J_{PC}$=3.0 Hz), 132.44 (d, $^{2}J_{PC}$=5.4 Hz), 132.62 (d, $^{2}J_{PC}$=8.4 Hz), 132.65 (d, $^{4}J_{PC}$=3.6 Hz), 132.88 (d, $^{4}J_{PC}$=2.4 Hz), 149.87 (d, $^{3}J_{PC}$=6.6 Hz), 162.46 (d, $^{2}J_{PC}$=1.2 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 27.32. Anal. Calcd for $C_{22}H_{21}N_2O_4P$ (408.39): C, 64.70; H, 5.18; N, 6.86. Found: C, 64.66; H, 5.17; N, 6.91. MS *m/z* (%): 409 (100), 352 (45).

4.2.4. 2-[1-(*P*,*P*-Diphenylphosphynylborane)ethyl]nitrobenzene (9d). Eluent: ethyl acetate/hexane 1:3, then 1:20. Oil. Yield: 3%. IR (KBr pellets, neat), ν (cm^{-1}): 2385, 1260, 1106, 1063, 1027. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 1.63 (dd, $^{3}J_{HH}$=7.3 Hz, $^{3}J_{PH}$=15.8 Hz, 3H), 5.1 (dq, $^{3}J_{HH}$=7.3 Hz, $^{2}J_{PH}$=16.5 Hz, 1H), 7.19 (m, 4H^{ar}), 7.34 (m, 1H^{ar}), 7.48 (m, 2H^{ar}), 7.65 (m, 5H^{ar}), 8.01 (m, 3H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 16.61 (d, $^{2}J_{PC}$=3.6 Hz), 30.21 (d, $^{1}J_{PC}$=31.8 Hz), 124.46 (d, $^{4}J_{PC}$=1.5 Hz), 126.75 (d, $^{1}J_{PC}$=53.2 Hz), 127.56 (d, $^{1}J_{PC}$=53.5 Hz), 127.79 (d, $^{5}J_{PC}$=2.4 Hz), 128.33 (d, $^{3}J_{PC}$=9.6 Hz), 129.08 (d, $^{3}J_{PC}$=9.9 Hz), 131.08 (d, $^{4}J_{PC}$=1.8 Hz), 131.3 (d, $^{3}J_{PC}$=3.9 Hz), 131.81 (d, $^{4}J_{PC}$=2.4 Hz), 132.13 (d, $^{2}J_{PC}$=8.4 Hz), 132.73 (d, $^{4}J_{PC}$=2.1 Hz), 133.12 (d, $^{2}J_{PC}$=8.7 Hz), 133.63, 149.2 (d, $^{3}J_{PC}$=5.7 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 27.82. Anal. Calcd for $C_{20}H_{21}BNO_2P$ (349.18): C, 68.80; H, 6.06; N, 4.01. Found: C, 68.77; H, 6.03; N, 4.10. MS *m/z* (%): 352 (100).

4.2.5. 3-Chloro-2-{1-[(*P*,*P*-diphenyl)(*N*-diphenylphosphoryl)phosphazenyl]methyl}nitrobenzene (9e). Eluent: ethyl acetate/hexane 2:1. Oil. Yield: 5%. IR (KBr pellets, neat), ν (cm^{-1}): 1260, 1094, 1020. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 4.57 (d, $^{2}J_{PH}$=14.1 Hz, 2H), 7.10–7.60 (m, 21H, H^{ar}), 7.72 (m, 1H^{ar}), 7.92 (dd, $^{3}J_{HH}$=8.5 Hz, $^{4}J_{PH}$=2.4 Hz, 1H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 32.48 (dd, $^{1}J_{PC}$=59.8 Hz, $^{3}J_{PC}$=1.5 Hz), 120.59 (d, $^{3}J_{PC}$=5.1 Hz), 123.89 (d, $^{5}J_{PC}$=1.2 Hz), 124.82 (d, $^{2}J_{PC}$=9.3 Hz), 125.00 (d, $^{3}J_{PC}$=2.4 Hz), 127.40 (dd, $^{1}J_{PC}$=105.4 Hz, $^{3}J_{PC}$=5.4 Hz), 128.81 (d, $^{3}J_{PC}$=12.9 Hz), 129.22 (d, $^{4}J_{PC}$=0.9 Hz), 131.71 (d, $^{2}J_{PC}$=10.5 Hz), 132.81 (d, $^{4}J_{PC}$=3.0 Hz), 133.36 (d, $^{4}J_{PC}$=3.3 Hz), 133.92 (d, $^{5}J_{PC}$=3.6 Hz), 135.76 (d, $^{3}J_{PC}$=4.5 Hz), 148.52 (d, $^{3}J_{PC}$=5.7 Hz), 152.06 (d, $^{2}J_{PC}$=7.5 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): −6.51 (d, $^{2}J_{PP}$=31.8 Hz), 17.55 (d, $^{2}J_{PP}$=31.8 Hz). Anal. Calcd for $C_{31}H_{25}ClN_2O_5P_2$ (602.95): C, 61.65; H, 4.18; N, 4.65. Found: C, 61.71; H, 4.19; N, 4.65. MS *m/z* (%): 603 (100).

4.2.6. 5-Chloro-2-{1-[(*P*,*P*-diphenyl)(*N*-methoxycarbonyl)phosphazenyl]ethyl}nitrobenzene (9f) and 3-chloro-4-{1-[(*P*,*P*-diphenyl)(*N*-methoxycarbonyl)-phosphazenyl]ethyl}nitrobenzene (10h). Solid isolated as a 16:1 mixture after column chromatography using ethyl acetate/hexane 2:1 as eluent. Mp 141–145 °C. IR (KBr), ν (cm^{-1}): 1639, 1303, 1112.

NMR data for **9f**. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 1.67 (dd, $^{3}J_{HH}$=7.3 Hz, $^{3}J_{PH}$=16.1 Hz, 3H), 3.56 (s, 3H), 4.95 (dq, $^{3}J_{HH}$=7.3 Hz, $^{2}J_{PH}$=11.7 Hz), 7.18–8.11 (m, 13H, H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 16.33 (d, $^{2}J_{PC}$=3.3 Hz), 32.59 (d, $^{1}J_{PC}$=68.8 Hz), 52.76, 124.47 (d, $^{3}J_{PC}$=1.8 Hz), 128.48 (d, $^{3}J_{PC}$=11.7 Hz), 129.02 (d, $^{3}J_{PC}$=11.7 Hz), 130.87 (d, $^{2}J_{PC}$=5.4 Hz), 131.65, 132.31 (d, $^{3}J_{PC}$=3.0 Hz), 132.64 (d, $^{2}J_{PC}$=8.7 Hz), 132.86 (d, $^{4}J_{PC}$=3.6 Hz), 133.82 (d, $^{5}J_{PC}$=3.0 Hz), 149.58 (d, $^{3}J_{PC}$=6.6 Hz), 162.36 (d, $^{2}J_{PC}$=1.5 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 27.28.

NMR data for **10h**. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 1.64 (dd, $^{3}J_{HH}$=7.3 Hz, $^{3}J_{PH}$=16.1 Hz, 3H), 3.60 (s, 3H), 4.56 (dq, $^{3}J_{HH}$=7.3 Hz, $^{2}J_{PH}$=11.3 Hz, 1H), 7.18–8.11 (m, 13H, H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 16.23 (d, $^{2}J_{PC}$=3.6 Hz), 35.29 (d, $^{1}J_{PC}$=70.6 Hz), 52.84 (d, $^{4}J_{PC}$=3.9 Hz), 121.67 (d, $^{4}J_{PC}$=2.4 Hz), 123.98 (d, $^{4}J_{PC}$=2.1 Hz), 125.77 (d, $^{1}J_{PC}$=88.3 Hz), 126.41 (d, $^{1}J_{PC}$=95.2 Hz), 128.32 (d, $^{3}J_{PC}$=12.0 Hz), 129.08 (d, $^{3}J_{PC}$=11.7 Hz), 131.53 (d, $^{4}J_{PC}$=3.6 Hz), 131.81 (d, $^{2}J_{PC}$=9.0 Hz), 132.39 (d, $^{3}J_{PC}$=2.7 Hz), 132.56 (d, $^{2}J_{PC}$=9.0 Hz), 132.82 (d, $^{4}J_{PC}$=3.0 Hz), 135.04 (d, $^{3}J_{PC}$=7.5 Hz), 143.02 (d, $^{2}J_{PC}$=4.8 Hz), 146.97 (d, $^{5}J_{PC}$=3.0 Hz), 162.41 (d, $^{2}J_{PC}$=1.5 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 26.68.

4.2.7. 5-Chloro-2-[1-(*P*,*P*-diphenylphosphinoyl)ethyl]-nitrobenzene (9g) and 3-chloro-4-[1-(*P*,*P*-diphenylphosphinoyl)ethyl]nitrobenzene (10i). Solid isolated as a 9:1 mixture after column chromatography using ethyl acetate/hexane 2:1 as eluent. Mp 164–168 °C. IR (KBr), ν (cm^{-1}): 1183, 1119, 1022.

NMR data for **9g**. 1.58 (dd, $^{3}J_{HH}$=7.3 Hz, $^{3}J_{PH}$=15.3 Hz, 3H), 4.6 (quintet, $^{3}J_{HH}$=$^{2}J_{PH}$=7.3 Hz, 1H), 7.19–8.27 (m, 13H, H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 15.61 (d, $^{2}J_{PC}$=3.6 Hz), 33.90 (d, $^{1}J_{PC}$=66.1 Hz), 124.39 (d, $^{4}J_{PC}$=1.2 Hz), 128.41 (d, $^{3}J_{PC}$=12.0 Hz), 128.92 (d, $^{3}J_{PC}$=11.4 Hz), 130.36 (d, $^{2}J_{PC}$=9.0 Hz), 130.79 (d, $^{5}J_{PC}$=0.6 Hz), 130.67 (d, $^{1}J_{PC}$=97.3 Hz), 131.77 (d, $^{4}J_{PC}$=2.4 Hz), 132.42 (d, $^{3}J_{PC}$=4.8 Hz), 133.11 (d, $^{4}J_{PC}$=2.4 Hz), 133.33 (d, $^{2}J_{PC}$=2.4 Hz), 149.28 (d, $^{3}J_{PC}$=7.8 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 33.79.

NMR data for **10i**. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 1.54 (dd, $^{3}J_{HH}$=6.9 Hz, $^{3}J_{PH}$=15.3 Hz, 3H), 4.36 (quintet, $^{3}J_{HH}$=$^{2}J_{PH}$=6.9 Hz, 1H), 7.19–8.27 (m, 13H, H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 15.30 (d, $^{2}J_{PC}$=3.0 Hz), 36.11 (d, $^{1}J_{PC}$=66.7 Hz), 121.92 (d, $^{4}J_{PC}$=1.8 Hz), 124.09 (d, $^{4}J_{PC}$=1.8 Hz), 128.30 (d, $^{3}J_{PC}$=12.0 Hz), 128.94 (d, $^{3}J_{PC}$=12.0 Hz), 130.51 (d, $^{2}J_{PC}$=9.6 Hz), 130.86 (d, $^{1}J_{PC}$=97.3 Hz), 131.09 (d, $^{2}J_{PC}$=9.0 Hz), 131.13 (d, $^{3}J_{PC}$=3.0 Hz), 131.89 (d, $^{4}J_{PC}$=3.0 Hz), 132.21 (d, $^{4}J_{PC}$=2.7 Hz), 134.29 (d, $^{3}J_{PC}$=8.1 Hz), 144.32 (d, $^{2}J_{PC}$=4.2 Hz), 146.74 (d, $^{5}J_{PC}$=2.4 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 33.73.

4.2.8. 4-Chloro-2-{1-[(*P*,*P*-diphenyl)(*N*-diphenylphosphoryl)phosphazenyl]methyl}nitrobenzene (9h). Eluent: ethyl acetate/hexane 1:1. Oil. Yield: 28%. IR (KBr pellets, neat), ν (cm^{-1}): 1261, 1095, 1022. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 4.62 (d, $^{2}J_{PH}$=14.5 Hz, 2H), 7.08 (m, 2H, H^{ar}), 7.31 (m, 13H, H^{ar}), 7.55 (m, 6H, H^{ar}), 7.71 (d, $^{3}J_{HH}$=8.9 Hz, 1H^{ar}), 8.1 (m, 1H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 32.99 (dd, $^{1}J_{PC}$=59.5 Hz, $^{3}J_{PC}$=1.5 Hz), 120.54 (d, $^{3}J_{PC}$=4.8 Hz), 123.82 (d, $^{5}J_{PC}$=1.2 Hz), 126.45 (d, $^{4}J_{PC}$=2.4 Hz), 127.35 (dd, $^{1}J_{PC}$=105.1 Hz, $^{3}J_{PC}$=4.8 Hz), 128.39 ($^{5}J_{PC}$=3.2 Hz), 128.67 (d, $^{2}J_{PC}$=9.0 Hz),

128.77 (d, $^3J_{PC}$=13.2 Hz), 129.19 (d, $^4J_{PC}$=0.8 Hz), 131.71 (d, $^2J_{PC}$=10.8 Hz), 132.79 (d, $^4J_{PC}$=3.0 Hz), 134.24 (d, $^3J_{PC}$=4.8 Hz), 139.84 (d, $^4J_{PC}$=3.6 Hz), 146.57 (d, $^3J_{PC}$=5.4 Hz), 152.15 (d, $^2J_{PC}$=7.8 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): −7.08 (d, $^2J_{PP}$= 31.2 Hz), 16.87 (d, $^2J_{PP}$=31.2 Hz). Anal. Calcd for $C_{31}H_{25}ClN_2O_5P_2$ (602.95): C, 61.75; H, 4.18; N, 4.65. Found: C, 61.70; H, 4.21; N, 4.66. MS *m/z* (%): 603 (100).

4.2.9. 4-Chloro-2-{1-[(*P*,*P*-diphenyl)(*N*-diphenylphosphoryl)phosphazenyl]ethyl}nitrobenzene (9i). Eluent: ethyl acetate/hexane 1.5:1. Oil. Yield: 53%. IR (KBr pellets, neat), ν (cm^{-1}): 1261, 1095, 1022. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 1.66 (dd, $^3J_{HH}$=7 Hz, $^3J_{PH}$=17.7 Hz, 3H, H-8), 5.01 (dquintet, $^3J_{HH}$=$^2J_{PH}$=7.3 Hz, $^4J_{PH}$=1.7 Hz, 1H, H-7), 6.92–7.40 (m, 15H^{ar}), 7.46–7.71 (m, 5H^{ar}), 7.93–8.08 (m, 2H^{ar}), 8.17 (dd, $^4J_{HH}$=$^4J_{PH}$=2.1 Hz, 1H^{ar}, H-3). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 15.24 (d, $^2J_{PC}$= 3.3 Hz), 34.04 (dd, $^1J_{PC}$=67.9 Hz, $^3J_{PC}$=2.9 Hz), 120.45 (d, $^3J_{PC}$=5.1 Hz), 120.68 (d, $^3J_{PC}$=5.1 Hz), 123.74 (d, $^5J_{PC}$=1.2 Hz), 123.86 (d, $^5J_{PC}$=1.2 Hz), 125.94 (d, $^4J_{PC}$=1.8 Hz), 127.08 (d, $^1J_{PC}$=96.9 Hz), 127.91 (dd, $^1J_{PC}$=105.6 Hz, $^3J_{PC}$=5.3 Hz), 128.23, 128.42 (d, $^3J_{PC}$=12.9 Hz), 129.22 (d, $^3J_{PC}$=12.6 Hz), 129.29 (d, $^4J_{PC}$=0.8 Hz), 130.99 (d, $^2J_{PC}$=10.5 Hz), 131.56 (d, $^3J_{PC}$=4.8 Hz), 132.06 (d, $^2J_{PC}$=10.2 Hz), 132.01 (d, $^4J_{PC}$=3.0 Hz), 132.87 (d, $^4J_{PC}$=3.0 Hz), 134.37 (d, $^2J_{PC}$=5.7 Hz), 139.84 (d, $^4J_{PC}$=3.0 Hz), 147.06 (d, $^3J_{PC}$= 6.6 Hz), 152.38 (d, $^2J_{PC}$=7.8 Hz), 152.45 (d, $^2J_{PC}$= 7.8 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): −9.24 (d, $^2J_{PP}$=37.9 Hz), 18.65 (d, $^2J_{PP}$=37.9 Hz). Anal. Calcd for $C_{32}H_{27}ClN_2O_5P_2$ (616.98): C, 62.30; H, 4.41; N, 4.54. Found: C, 62.22; H, 4.37; N, 4.50. MS *m/z* (%): 617 (100).

4.2.10. 4-Chloro-2-[1-(*P*,*P*-diphenylphosphinoyl)ethyl]-nitrobenzene (9j). Eluent: ethyl acetate/hexane 7:1. Oil. Yield: 27%. IR (KBr pellets, neat), ν (cm^{-1}): 1550, 1177. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 1.62 (dd, $^3J_{HH}$= 7.3 Hz, $^3J_{PH}$=15.3 Hz, 3H), 4.73 (quintet, $^3J_{HH}$=$^2J_{PH}$= 7.3 Hz, 1H), 7.26 (m, 3H, H^{ar}), 7.50 (m, 7H, H^{ar}), 7.96 (m, 2H, H^{ar}), 8.1 (m, 1H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 15.49 (d, $^2J_{PC}$=3.3 Hz), 34.20 (d, $^1J_{PC}$=65.2 Hz), 125.87 (d, $^4J_{PC}$=1.5 Hz), 127.84 (d, $^5J_{PC}$=2.1 Hz), 128.37 (d, $^3J_{PC}$=11.7 Hz), 128.95 (d, $^3J_{PC}$=11.7 Hz), 130.43 (d, $^2J_{PC}$=9.0 Hz), 131.13 (d, $^3J_{PC}$=4.5 Hz), 131.18 (d, $^2J_{PC}$= 8.7 Hz), 131.74 (d, $^4J_{PC}$=2.7 Hz), 132.22 (d, $^4J_{PC}$= 2.7 Hz), 135.81 (d, $^2J_{PC}$=4.8 Hz), 139.59 (d, $^4J_{PC}$= 2.4 Hz), 147.21 (d, $^3J_{PC}$=6.6 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 32.74. Anal. Calcd for $C_{20}H_{17}NO_3P$ (385.79): C, 62.27; H, 4.44; N, 3.63. Found: C, 62.19; H, 4.46; N, 3.59. MS *m/z* (%): 477 (100).

4.2.11. 3-{1-[(*P*,*P*-Diphenyl)(*N*-diphenylphosphoryl)-phosphazenyl]methyl}-4-nitrobenzonitrile (9k).[17] Eluent: ethyl acetate/hexane 2:1. Oil. Yield: 64%. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 4.59 (d, $^2J_{PH}$=14.5 Hz, 2H), 7.07 (m, 2H, H^{ar}), 7.19 (m, 4H, H^{ar}), 7.25 (m, 5H, H^{ar}), 7.42 (m, 4H, H^{ar}), 7.57 (m, 6H, H^{ar}), 7.79 (d, $^3J_{HH}$=8.9 Hz, 1H^{ar}), 8.26 (t, $^4J_{HH}$=$^4J_{PH}$=1.6 Hz, 1H^{ar}). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): −5.86 (d, $^2J_{PP}$= 31.1 Hz), 17.58 (d, $^2J_{PP}$=31.1 Hz).

4.2.12. 3-{1-[(*P*,*P*-Diphenyl)(*N*-diphenylphosphoryl)phosphazenyl]ethyl}-4-nitrobenzonitrile (9l).[17] Eluent: ethyl acetate/hexane 1:1. Oil. Yield: 81%. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 1.64 (dd, $^3J_{HH}$=7.3 Hz, $^3J_{PH}$=17.2 Hz, 3H), 4.83 (dquintet, $^3J_{HH}$=$^2J_{PH}$=7.3 Hz, $^4J_{PH}$=2.6 Hz, 1H), 7.12 (m, 7H, H^{ar}), 7.32 (m, 8H, H^{ar}), 7.63 (m, 5H, H^{ar}), 8.00 (m, 2H, H^{ar}), 8.32 (s, 1H^{ar}). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): −7.65 (d, $^2J_{PP}$=35.6 Hz), 19.65 (d, $^2J_{PP}$=35.6 Hz).

4.2.13. 3-{1-[(*P*,*P*-Diphenyl)(*N*-methoxycarbonyl)phosphazenyl]ethyl}-4-nitrobenzonitrile (9m). Eluent: ethyl acetate/hexane 1.5:1. Oil. Yield: 81%. IR (KBr pellets, neat), ν (cm^{-1}): 2233, 1637, 1261, 1090, 1023. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 1.71 (dd, $^3J_{HH}$=7.3 Hz, $^3J_{PH}$=15.9 Hz, 3H), 3.58 (s, 3H), 5.1 (dq, $^3J_{HH}$=7.3 Hz, $^2J_{PH}$=12.6 Hz, 1H), 7.36 (m, 2H, H^{ar}), 7.48 (m, 3H, H^{ar}), 7.64 (m, 4H, H^{ar}), 7.81 (m, 4H, H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 16.31 (d, $^2J_{PC}$=3.0 Hz), 32.48 (d, $^1J_{PC}$= 66.1 Hz), 52.94 (d, $^4J_{PC}$=3.9 Hz), 116.33 (d, $^4J_{PC}$= 2.7 Hz), 116.51, 124.18 (d, $^1J_{PC}$=94.3 Hz), 125.15 (d, $^4J_{PC}$=2.1 Hz), 125.77 (d, $^1J_{PC}$=94.6 Hz), 128.75 (d, $^3J_{PC}$=12.0 Hz), 129.11 (d, $^3J_{PC}$=12.0 Hz), 131.64 (d, $^5J_{PC}$=2.4 Hz), 131.87 (d, $^2J_{PC}$=9.3 Hz), 132.66 (d, $^4J_{PC}$=3.0 Hz), 132.92 (d, $^2J_{PC}$=9.0 Hz), 133.27 (d, $^4J_{PC}$=3.0 Hz), 133.82 (d, $^2J_{PC}$=5.1 Hz), 134.96 (d, $^3J_{PC}$= 4.2 Hz), 151.69 (d, $^3J_{PC}$=6.6 Hz), 162.53 (d, $^2J_{PC}$= 1.8 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 27.07. Anal. Calcd for $C_{23}H_{20}N_3O_4P$(433.39): C, 63.74; H, 4.65; N, 9.69. MS, m/z (%): 434 (100), 377 (20).

4.2.14. 3-[1-(*P*,*P*-Diphenylphosphynylborane)ethyl]-4-nitrobenzonitrile (9n). Eluent: ethyl acetate/hexane 1:5. Oil. Yield: 12%. IR (KBr pellets, neat), ν (cm^{-1}): 2384, 2298, 1261, 1097, 1021. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 1.65 (dd, $^3J_{HH}$=7.3 Hz, $^3J_{PH}$=15.5 Hz, 3H), 5.02 (dq, $^3J_{HH}$=7.3 Hz, $^2J_{PH}$=15.8 Hz, 1H), 7.27 (m, 5H, H^{ar}), 7.65 (m, 4H, H^{ar}), 7.98 (m, 2H, H^{ar}), 8.20 (m, 1H^{ar}), 8.38 (d, $^3J_{HH}$= 8.9 Hz, 1H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 16.42 (d, $^2J_{PC}$=3.0 Hz), 30.38 (d, $^1J_{PC}$=30.3 Hz), 116.49 (d, $^4J_{PC}$=2.4 Hz), 116.54, 124.22, 124.95 (d, $^5J_{PC}$=1.5 Hz), 125.72 (d, $^1J_{PC}$=53.8 Hz), 126.77 (d, $^1J_{PC}$=53.2 Hz), 128.70 (d, $^3J_{PC}$=9.9 Hz), 129.24 (d, $^3J_{PC}$=9.9 Hz), 131.31 (d, $^4J_{PC}$=2.4 Hz), 131.55 (d, $^4J_{PC}$=2.4 Hz), 132.1 (d, $^2J_{PC}$= 9.0 Hz), 133.08 (d, $^2J_{PC}$=8.7 Hz), 135.24, 135.29 (d, $^3J_{PC}$= 3.9 Hz), 151.21 (d, $^3J_{PC}$=5.7 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 28.15. Anal. Calcd for $C_{21}H_{20}BN_2O_2P$ (374.19): C, 67.41; H, 5.39; N, 7.49. Found: C, 67.35; H, 5.40; N, 7.53. MS *m/z* (%): 373 (100), 129 (90).

4.2.15. 4-{1-[(*P*,*P*-Diphenyl)(*N*-diphenylphosphoryl)-phosphazenyl]methyl}nitrobenzene (10a). Eluent: ethyl acetate/hexane 3:1. Oil. Yield: 9%. IR (KBr pellets, neat), ν (cm^{-1}): 1261, 1095. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 4.02 (d, $^2J_{PH}$=13.7 Hz, 2H), 7.17 (m, 2H, H^{ar}), 7.46 (m, 4H, H^{ar}), 7.62 (m, 6H, H^{ar}), 7.88 (m, 2H, H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 36.57 (dd, $^1J_{PC}$=60.7 Hz, $^3J_{PC}$=1.2 Hz), 120.56 (d, $^3J_{PC}$=4.8 Hz), 123.12 (d, $^4J_{PC}$= 3.0 Hz), 123.85 (d, $^5J_{PC}$=1.2 Hz), 127.96 (dd, $^1J_{PC}$= 105.1 Hz, $^3J_{PC}$=6.0 Hz), 128.86 (d, $^3J_{PC}$=12.9 Hz), 129.15 (d, $^4J_{PC}$=0.6 Hz), 131.29 (d, $^3J_{PC}$=4.8 Hz), 131.64 (d, $^2J_{PC}$=10.2 Hz), 132.79 (d, $^4J_{PC}$=3.0 Hz), 137.88 (d, $^2J_{PC}$=8.4 Hz), 146.87 (d, $^5J_{PC}$=3.9 Hz),

152.04 (d, $^{2}J_{PC}$=7.8 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): −6.31 (d, $^{2}J_{PP}$=31.2 Hz), 16.51 (d, $^{2}J_{PP}$=31.2 Hz). Anal. Calcd for $C_{31}H_{26}N_2O_5P_2$ (568.51): C, 65.49; H, 4.57; N, 4.93. Found: C, 66.50; H, 4.55; N, 4.94. MS *m/z* (%): 569 (100).

4.2.16. 4-{1-[(*P*,*P*-Diphenyl)(*N*-diphenylphosphoryl)-phosphazenyl]ethyl}nitrobenzene (10b). Eluent: ethyl acetate/hexane 3:1. Oil. Yield: 54%. IR (KBr pellets, neat), ν (cm^{-1}): 1522, 1487, 1200, 1108, 1024. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 1.64 (dd, $^{3}J_{HH}$=7.2 Hz, $^{3}J_{PH}$=17.6 Hz, 3H), 4.04 (m, 1H), 7.03–7.66 (m, 22H^{ar}), 7.82–7.92 (m, 2H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 15.11 (d, $^{2}J_{PC}$=2.4 Hz), 40.70 (dd, $^{1}J_{PC}$=66.1 Hz, $^{3}J_{PC}$=3.0 Hz), 120.46 (d, $^{3}J_{PC}$=5.4 Hz), 120.62 (d, $^{3}J_{PC}$=5.1 Hz), 122.98 (d, $^{4}J_{PC}$=2.7 Hz), 123.81 (d, $^{5}J_{PC}$=1.2 Hz), 123.86 (d, $^{5}J_{PC}$=1.2 Hz), 126.92 (dd, $^{1}J_{PC}$=97.6 Hz, $^{3}J_{PC}$=2.7 Hz), 128.51 (d, $^{3}J_{PC}$=12.6 Hz), 128.97 (d, $^{3}J_{PC}$=12.3 Hz), 129.22 (d, $^{4}J_{PC}$=0.9 Hz), 129.25 (d, $^{4}J_{PC}$=0.6 Hz), 130.32 (d, $^{3}J_{PC}$=5.1 Hz), 131.57 (d, $^{2}J_{PC}$=10.2 Hz), 132.21 (d, $^{2}J_{PC}$=9.9 Hz), 132.38 (d, $^{4}J_{PC}$=3.0 Hz), 132.78 (d, $^{4}J_{PC}$=3.0 Hz), 144.15 (d, $^{2}J_{PC}$=6.3 Hz), 146.83 (d, $^{5}J_{PC}$=3.3 Hz), 152.29 (d, $^{2}J_{PC}$=7.8 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): −9.51 (d, $^{2}J_{PP}$=34.5 Hz), 18.36 (d, $^{2}J_{PP}$=34.5 Hz). Anal. Calcd for $C_{32}H_{28}N_2O_5P_2$ (582.53): C, 65.98; H, 4.84; N, 4.81. Found: C, 66.15; H, 4.80; N, 4.79. MS *m/z* (%): 583 (100), 284 (20).

4.2.17. 4-{1-[(*P*,*P*-Diphenyl)(*N*-methoxycarbonyl)-phosphazenyl]ethyl}nitrobenzene (10c). Eluent: ethyl acetate/hexane 5:1. Oil. Yield: 32%. IR (KBr pellets, neat), ν (cm^{-1}): 1732, 1657, 1260, 1092, 1019. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ (ppm): 1.61 (dd, $^{3}J_{HH}$=7.3 Hz, $^{3}J_{PH}$=16.7 Hz, 3H), 3.58 (s, 3H), 4.67 (dq, $^{3}J_{HH}$=7.3 Hz, $^{2}J_{PH}$=15.8 Hz, 1H), 7.13 (dd, $^{3}J_{HH}$=8.8 Hz, $^{4}J_{PH}$=2.0 Hz, 2H^{ar}), 7.41–7.70 (m, 8H^{ar}), 7.73–7.82 (m, 2H^{ar}), 8.03 (d, $^{3}J_{HH}$=8.8 Hz, 2H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 15.42 (d, $^{2}J_{PC}$=2.1 Hz), 37.18 (d, $^{1}J_{PC}$=57.2 Hz), 52.69 (d, $^{4}J_{PC}$=3.8 Hz), 122.96 (d, $^{4}J_{PC}$=2.4 Hz), 123.66 (d, $^{1}J_{PC}$=99.6 Hz), 125.17 (d, $^{1}J_{PC}$=93.4 Hz), 128.41 (d, $^{3}J_{PC}$=11.9 Hz), 128.49 (d, $^{3}J_{PC}$=11.9 Hz), 129.87 (d, $^{3}J_{PC}$=4.8 Hz), 132.49 (d, $^{4}J_{PC}$=3.0 Hz), 132.63 (d, $^{2}J_{PC}$=9.2 Hz), 132.83 (d, $^{4}J_{PC}$=3.0 Hz), 133.19 (d, $^{2}J_{PC}$=8.6 Hz), 144.22 (d, $^{2}J_{PC}$=5.4 Hz), 144.21 (d, $^{5}J_{PC}$=3.5 Hz), 162.63 (d, $^{2}J_{PC}$=2.4 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 29.19. Anal. Calcd for $C_{22}H_{21}N_2O_4P$ (408.39): C, 64.70; H, 5.18; N, 6.86. Found: C, 64.75; H, 5.16; N, 6.93. MS *m/z* (%): 409 (100), 120 (20).

4.2.18. 4-[1-(*P*,*P*-Diphenylphosphynylborane)ethyl]nitrobenzene (10d). Eluent: ethyl acetate/hexane 1:3. Oil. Yield: 45%. IR (KBr pellets, neat), ν (cm^{-1}): 2365, 1261, 1097, 1025. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 1.62 (d, $^{3}J_{HH}$=7.3 Hz, $^{3}J_{PH}$=15.8 Hz, 3H), 3.98 (dq, $^{3}J_{HH}$=7.3 Hz, $^{2}J_{PH}$=14.5 Hz, 1H), 7.28 (m, 4H^{ar}), 7.43 (m, 3H^{ar}), 7.58 (m, 3H^{ar}), 7.93 (m, 2H^{ar}), 8.01 (m, 2H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 16.06 (d, $^{2}J_{PC}$=2.7 Hz), 37.5 (d, $^{1}J_{PC}$=29.7 Hz), 122.93 (d, $^{4}J_{PC}$=2.1 Hz), 126.86 (d, $^{1}J_{PC}$=52.6 Hz), 127.56 (d, $^{1}J_{PC}$=53.2 Hz), 128.51 (d, $^{3}J_{PC}$=9.9 Hz), 129.04 (d, $^{3}J_{PC}$=9.6 Hz), 130.08 (d, $^{3}J_{PC}$=4.5 Hz), 131.42 (d, $^{4}J_{PC}$=2.7 Hz), 131.78 (d, $^{4}J_{PC}$=2.4 Hz), 132.59 (d, $^{2}J_{PC}$=8.7 Hz), 132.94 (d, $^{2}J_{PC}$=8.4 Hz), 145.75 (d, $^{2}J_{PC}$=0.9 Hz), 146.89 (d, $^{5}J_{PC}$=3 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 26.65. Anal. Calcd for $C_{20}H_{21}BNO_2P$ (349.18): C, 68.80; H, 6.06; N, 4.01. Found: C, 68.78; H, 6.10; N, 3.98. MS *m/z* (%): 352 (100), 346 (60).

4.2.19. 4-[1-(*P*,*P*-Diphenylphosphinoyl)ethyl]nitrobencene (10e). Eluent: ethyl acetate/hexane 5:1. Solid. Yield: 19%. Mp 208–210 °C. IR (KBr), ν (cm^{-1}): 1173, 1109. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 1.61 (dd, $^{3}J_{HH}$=7.3 Hz, $^{3}J_{PH}$=15.7 Hz, 3H), 3.75 (quintet, $^{3}J_{HH}$=$^{2}J_{PH}$=7.3 Hz, 1H), 7.26–7.36 (m, 2H^{ar}), 7.38–7.46 (m, 3H^{ar}), 7.47–7.63 (m, 5H^{ar}), 7.93 (m, 2H^{ar}), 8.05 (m, 2H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 15.26 (d, $^{2}J_{PC}$=3.0 Hz), 41.05 (d, $^{1}J_{PC}$=65.2 Hz), 123.30 (d, $^{4}J_{PC}$=1.8 Hz), 128.34 (d, $^{3}J_{PC}$=11.7 Hz), 128.85 (d, $^{3}J_{PC}$=11.4 Hz), 129.91 (d, $^{3}J_{PC}$=5.4 Hz), 130.78 (d, $^{2}J_{PC}$=8.7 Hz), 130.92 (d, $^{1}J_{PC}$=96.1 Hz), 131.19 (d, $^{2}J_{PC}$=8.7 Hz), 131.32 (d, $^{1}J_{PC}$=98.5 Hz), 131.75 (d, $^{4}J_{PC}$=2.7 Hz), 132.08 (d, $^{4}J_{PC}$=3.0 Hz), 145.95 (d, $^{2}J_{PC}$=5.4 Hz), 146.79 (d, $^{5}J_{PC}$=2.7 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 33.17. Anal. Calcd for $C_{20}H_{18}NO_3P$ (351.34): C, 61.54; H, 5.16; N, 3.99. Found: C, 61.79; H, 5.14; N, 4.02. MS *m/z* (%): 352 (100).

4.2.20. 3-Chloro-4-{1-[(*P*,*P*-diphenyl)(*N*-diphenylphosphoryl)phosphazenyl]methyl}nitrobenzene (10f). Eluent: ethyl acetate/hexane 2:1. Oil. Yield: 41%. IR (KBr pellets, neat), ν (cm^{-1}): 1262, 1096, 1023. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 4.23 (d, $^{2}J_{PH}$=14.6 Hz, 2H), 7.18 (m, 8H, H^{ar}), 7.42 (m, 5H, H^{ar}), 7.60 (m, 7H, H^{ar}), 7.87 (m, 2H, H^{ar}), 7.97 (d, $^{3}J_{HH}$=2.4 Hz, 1H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 33.50 (dd, $^{1}J_{PC}$=61.9 Hz, $^{3}J_{PC}$=1.8 Hz), 120.58 (d, $^{3}J_{PC}$=4.8 Hz), 121.52 (d, $^{4}J_{PC}$=3.0 Hz), 123.97 (d, $^{5}J_{PC}$=1.2 Hz), 124.05 (d, $^{4}J_{PC}$=3.0 Hz), 127.71 (dd, $^{1}J_{PC}$=105.1 Hz, $^{3}J_{PC}$=5.4 Hz), 128.77 (d, $^{3}J_{PC}$=12.6 Hz), 129.27 (d, $^{4}J_{PC}$=1.2 Hz), 131.76 (d, $^{2}J_{PC}$=10.8 Hz), 132.93 (d, $^{4}J_{PC}$=3.0 Hz), 133.39 (d, $^{3}J_{PC}$=4.2 Hz), 135.10 (d, $^{2}J_{PC}$=6.6 Hz), 136.42 (d, $^{3}J_{PC}$=8.4 Hz), 147.07 (d, $^{5}J_{PC}$=3.6 Hz), 152.03 (d, $^{2}J_{PC}$=7.2 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): −6.44 (d, $^{2}J_{PP}$=31.2 Hz), 16.36 (d, $^{2}J_{PP}$=31.2 Hz). Anal. Calcd for $C_{31}H_{25}ClN_2O_5P_2$ (602.95): C, 61.65; H, 4.18; N, 4.65. Found: C, 61.73; H, 4.18; N, 4.67. MS *m/z* (%): 603 (100).

4.2.21. 3-Chloro-4-{1-[(*P*,*P*-diphenyl)(*N*-diphenylphosphoryl)phosphazenyl]ethyl}nitrobenzene (10g). Eluent: ethyl acetate/hexane 2:1. Oil. Yield: 62%. IR (KBr pellets, neat), ν (cm^{-1}): 1262, 1096, 1023. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 1.63 (dd, $^{3}J_{HH}$=7.3 Hz, $^{3}J_{PH}$=17.4 Hz, 3H), 4.47 (dquintet, $^{3}J_{HH}$=$^{2}J_{PH}$=7.3 Hz, $^{4}J_{PH}$=3.1 Hz, 1H), 6.92–7.42 (m, 14H, H^{ar}), 7.57 (m, 6H, H^{ar}), 8.01 (m, 3H, H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 15.33 (d, $^{2}J_{PC}$=3.3 Hz), 36.2 (dd, $^{1}J_{PC}$=70.3 Hz, $^{3}J_{PC}$=3.6 Hz), 120.39 (d, $^{3}J_{PC}$=5.4 Hz), 120.46 (d, $^{3}J_{PC}$=5.1 Hz), 121.92 (d, $^{4}J_{PC}$=2.7 Hz), 123.80 (d, $^{4}J_{PC}$=1.8 Hz), 123.91 (d, $^{5}J_{PC}$=0.9 Hz), 124.05 (d, $^{5}J_{PC}$=1.2 Hz), 127.31 (d, $^{1}J_{PC}$=96.4 Hz), 127.87 (dd, $^{1}J_{PC}$=104.5 Hz, $^{3}J_{PC}$=4.2 Hz), 128.26 (d, $^{3}J_{PC}$=12.8 Hz), 129.22 (d, $^{3}J_{PC}$=12.3 Hz), 129.36 (d, $^{4}J_{PC}$=0.9 Hz), 129.38 (d, $^{4}J_{PC}$=0.9 Hz), 131.31 (d, $^{2}J_{PC}$=10.8 Hz), 131.46 (d, $^{3}J_{PC}$=4.5 Hz), 132.00 (d, $^{2}J_{PC}$=9.9 Hz), 132.48 (d, $^{4}J_{PC}$=3.3 Hz), 132.91 (d, $^{4}J_{PC}$=3.0 Hz), 134.63 (d, $^{2}J_{PC}$=

7.8 Hz), 142.48 (d, $^3J_{PC}$=5.4 Hz), 146.85 (d, $^5J_{PC}$=3.0 Hz), 152.25 (d, $^2J_{PC}$=7.8 Hz), 152.28 (d, $^2J_{PC}$=7.8 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): −9.09 (d, $^2J_{PP}$= 35.6 Hz), 18.29 (d, $^2J_{PP}$=35.6 Hz). Anal. Calcd for $C_{32}H_{27}ClN_2O_5P_2$ (616.98): C, 62.30; H, 4.41; N, 4.54. Found: C, 62.21; H, 4.36; N, 4.45. MS *m/z* (%): 617 (100).

4.2.22. 1-{1-[(*P*,*P*-Diphenyl)(*N*-diphenylphosphoryl)phosphazenyl]ethyl}-2,4-dinitrobenzene (10j). Eluent: ethyl acetate/hexane 2:1. Oil. Yield: 79%. IR (KBr pellets, neat), ν (cm^{-1}): 1261, 1094, 1022. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 1.74 (dd, $^3J_{HH}$=7.3 Hz, $^3J_{PH}$=17.8 Hz, 3H), 4.99 (dquintet, $^3J_{HH}$=$^2J_{PH}$=7.3 Hz, $^4J_{PH}$=2.4 Hz, 1H), 7.27 (m, 12H, H^{ar}), 7.66 (m, 6H, H^{ar}), 7.96 (m, 2H, H^{ar}), 8.23 (d, J_{HH}= 1.2 Hz, 2H, H^{ar}), 8.44 (t, J_{HH}=1.2 Hz, 1H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 15.47 (d, $^2J_{PC}$=3.7 Hz), 34.82 (dd, $^1J_{PC}$=67.5 Hz, $^3J_{PC}$=3.7 Hz), 119.66 (d, $^4J_{PC}$= 2.1 Hz), 120.34 (d, $^3J_{PC}$=5.4 Hz), 120.69 (d, $^3J_{PC}$=5.1 Hz), 123.99 (d, $^5J_{PC}$=1.2 Hz), 124.13 (d, $^5J_{PC}$=1.5 Hz), 126.99 (d, $^4J_{PC}$=2.0 Hz), 127.46 (d, $^1J_{PC}$=105.1 Hz), 127.52 (d, $^1J_{PC}$=105.4 Hz), 128.67 (d, $^3J_{PC}$=12.9 Hz), 129.33 (d, $^3J_{PC}$=12.6 Hz), 129.38 (d, $^4J_{PC}$=0.9 Hz), 129.42 (d, $^4J_{PC}$=0.6 Hz), 130.90 (d, $^2J_{PC}$=10.5 Hz), 131.99 (d, $^2J_{PC}$= 9.9 Hz), 132.66 (d, $^4J_{PC}$=3.0 Hz), 133.11 (d, $^4J_{PC}$=3.0 Hz), 133.29 (d, $^3J_{PC}$=4.5 Hz), 139.15 (d, $^2J_{PC}$=5.4 Hz), 146.34 (d, $^5J_{PC}$=2.7 Hz), 148.68 (d, $^3J_{PC}$=6.9 Hz), 152.21 (d, $^2J_{PC}$=7.8 Hz), 152.22 (d, $^2J_{PC}$=7.8 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): −9.20 (d, $^2J_{PP}$=35.6 Hz), 18.03 (d, $^2J_{PP}$=35.6 Hz). Anal. Calcd for $C_{32}H_{27}N_3O_7P_2$ (627.53): C, 61.25; H, 4.34; N, 6.70. Found: C, 61.37; H, 4.34; N, 6.69. MS *m/z* (%): 628 (100).

4.2.23. 1-[1-(*P*,*P*-Diphenylphosphynylborane)ethyl]-2,4-dinitrobenzene (10k). Eluent: ethyl acetate/hexane 1:7. Oil. Yield: 54%. IR (KBr pellets, neat), ν (cm^{-1}): 2326, 1261, 1105, 1065, 1027. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 1.67 (dd, $^3J_{HH}$=7.1 Hz, $^3J_{PH}$=15.6 Hz, 3H), 5.18 (dq, $^3J_{HH}$=7.1 Hz, $^2J_{PH}$=16.0 Hz, 1H), 7.25 (m, 4H, H^{ar}), 7.38 (m, 1H^{ar}), 7.61 (m, 3H, H^{ar}), 8.01 (m, 2H, H^{ar}), 8.19 (dd, $^3J_{HH}$=8.7 Hz, $^4J_{PH}$=1.7 Hz, 1H^{ar}), 8.44 (dd, $^3J_{HH}$=8.7 Hz, $^4J_{HH}$=2.4 Hz, 1H^{ar}), 8.5 (d, $^4J_{HH}$=2.4 Hz, 1H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 16.59 (d, $^2J_{PC}$=3.0 Hz), 30.97 (d, $^1J_{PC}$=30.3 Hz), 119.80 (d, $^4J_{PC}$=1.5 Hz), 125.79 (d, $^1J_{PC}$=54.1 Hz), 126.54 (d, $^4J_{PC}$=2.1 Hz), 126.65 (d, $^1J_{PC}$=53.2 Hz), 128.77 (d, $^3J_{PC}$=9.9 Hz), 129.31 (d, $^3J_{PC}$= 9.9 Hz), 131.73 (d, $^4J_{PC}$=2.7 Hz), 132.07 (d, $^2J_{PC}$=8.7 Hz), 132.24 (d, $^4J_{PC}$=2.7 Hz), 132.94 (d, $^3J_{PC}$=3.6 Hz), 133.06 (d, $^2J_{PC}$=8.7 Hz), 140.87, 146.39 (d, $^5J_{PC}$=2.7 Hz), 149.05 (d, $^3J_{PC}$=5.7 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 28.85. Anal. Calcd for $C_{20}H_{20}BN_2O_4P$ (394.17): C, 60.94; H, 5.11; N, 7.11. Found: C, 60.91; H, 5.12; N, 7.16. MS *m/z* (%): 393 (100).

4.2.24. 2-Chloro-4-{1-[(*P*,*P*-diphenyl)(*N*-diphenylphosphoryl)phosphazenyl]ethyl}nitrobenzene (10l). Eluent: ethyl acetate/hexane 2:1. Oil. Yield: 24%. IR (KBr pellets, neat), ν (cm^{-1}): 1261, 1094. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 1.60 (dd, $^3J_{HH}$=7.3 Hz, $^3J_{PH}$=17.7 Hz, 3H), 4.00 (ddq, $^3J_{HH}$=7.3 Hz, $^2J_{PH}$=10.6 Hz, $^4J_{PH}$=1.4 Hz, 1H), 7.05–7.64 (m, 21H^{ar}), 7.85 (m, 2H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 14.91 (d, $^2J_{PC}$=2.4 Hz), 40.38 (dd, $^1J_{PC}$=65.5 Hz, $^3J_{PC}$=2.7 Hz), 120.48 (d, $^3J_{PC}$= 5.1 Hz), 120.60 (d, $^3J_{PC}$=5.1 Hz), 123.87 (d, $^4J_{PC}$=1.2 Hz), 123.90 (d, $^4J_{PC}$=1.5 Hz), 125.14 (d, $^4J_{PC}$=2.4 Hz), 126.38 (dd, $^1J_{PC}$=98.5 Hz, $^3J_{PC}$=2.7 Hz), 126.50 (d, $^4J_{PC}$= 2.7 Hz), 127.53 (dd, $^1J_{PC}$=103.3 Hz, $^3J_{PC}$=4.5 Hz), 128.66 (d, $^3J_{PC}$=5.1 Hz), 128.67 (d, $^3J_{PC}$=12.6 Hz), 129.02 (d, $^3J_{PC}$=12.3 Hz), 129.25 (d, $^4J_{PC}$=0.9 Hz), 129.28 (d, $^4J_{PC}$=0.9 Hz), 131.51 (d, $^2J_{PC}$=10.2 Hz), 132.26 (d, $^2J_{PC}$= 9.9 Hz), 132.59 (d, $^4J_{PC}$=3.0 Hz), 132.66 (d, $^3J_{PC}$=5.4 Hz), 132.95 (d, $^4J_{PC}$=3.0 Hz), 143.14 (d, $^2J_{PC}$=6 Hz), 146.37 (d, $^5J_{PC}$=3.6 Hz), 152.23 (d, $^2J_{PC}$=7.8 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): −8.32 (d, $^2J_{PP}$=35.6 Hz), 19.39 (d, $^2J_{PP}$=35.6 Hz). Anal. Calcd for $C_{32}H_{27}ClN_2O_5P_2$ (616.98): C, 62.30; H, 4.41; N, 4.54. Found: C, 62.39; H, 4.37; N, 4.50. MS *m/z* (%): 617 (20).

4.2.25. 5-{1-[(*P*,*P*-Diphenyl)(*N*-diphenylphosphoryl)-phosphazenyl]ethyl}-2-nitrobenzonitrile (10m). Eluent: ethyl acetate/hexane 4:1. Oil. Yield: 53%. IR (KBr pellets, neat), ν (cm^{-1}): 2245, 1261, 1096, 1024. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 1.64 (dd, $^3J_{HH}$=7.3 Hz, $^3J_{PH}$=17.3 Hz, 3H), 4.13 (quintet, $^3J_{HH}$=$^2J_{PH}$=7.3 Hz, 1H), 7.25 (m, 8H, H^{ar}), 6.38 (m, 5H, H^{ar}), 7.57 (m, 5H, H^{ar}), 7.69 (m, 2H, H^{ar}), 7.85 (m, 2H, H^{ar}), 7.99 (d, $^3J_{HH}$=8.8 Hz, 1H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 14.82 (d, $^2J_{PC}$=2.2 Hz), 40.5 (dd, $^1J_{PC}$=63.7 Hz, $^3J_{PC}$=2.7 Hz), 107.07 (d, $^4J_{PC}$=2.4 Hz), 114.58, 120.45 (d, $^3J_{PC}$=5.1 Hz), 120.54 (d, $^3J_{PC}$=5.1 Hz), 124.00 (d, $^5J_{PC}$=1.2 Hz), 125.11 (d, $^4J_{PC}$=2.4 Hz), 125.68 (dd, $^1J_{PC}$=100.2 Hz, $^3J_{PC}$= 3.8 Hz), 127.31 (dd, $^1J_{PC}$=102.7 Hz, $^3J_{PC}$=4.2 Hz), 128.91 (d, $^4J_{PC}$=12.9 Hz), 129.16 (d, $^3J_{PC}$=12.6 Hz), 129.27 (d, $^4J_{PC}$=0.9 Hz), 129.32 (d, $^5J_{PC}$=0.8 Hz), 131.40 (d, $^2J_{PC}$=10.5 Hz), 132.27 (d, $^2J_{PC}$=9.9 Hz), 132.91 (d, $^4J_{PC}$=3.0 Hz), 133.26 (d, $^4J_{PC}$=3.0 Hz), 134.90 (d, $^3J_{PC}$=4.8 Hz), 135.85 (d, $^3J_{PC}$=5.1 Hz), 144.55 (d, $^2J_{PC}$=6.0 Hz), 146.90 (d, $^5J_{PC}$=3.3 Hz), 152.09 (d, $^2J_{PC}$=7.8 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): −8.09 (d, $^2J_{PP}$=35.6 Hz), 19.3 (d, $^2J_{PP}$=35.6 Hz). Anal. Calcd for $C_{33}H_{27}N_3O_5P_2$ (607.53): C, 65.24; H, 4.47; N, 6.91. Found: C, 65.29; H, 4.50; N, 6.99. MS *m/z* (%): 608 (100).

4.2.26. 4,4′-Di{1-[(*P*,*P*-diphenyl)(*N*-diphenylphosphoryl)-phosphazenyl]ethyl}azoxybenzene (11a). Eluent: ethyl acetate/hexane 3:1. Oil. Yield: 19%. IR (KBr pellets, neat), ν (cm^{-1}): 1261, 1096, 1022. ^{1}H NMR (500.13 MHz, $CDCl_3$), δ (ppm): 1.66 (dd, $^3J_{HH}$=7.3 Hz, $^3J_{PH}$=17.5 Hz, 3H), 1.67 (dd, $^3J_{HH}$=7.1 Hz, $^3J_{PH}$= 17.8 Hz, 3H), 3.99 (m, 2H), 7.20 (m, 28H^{ar}), 7.42 (m, 6H^{ar}), 7.53 (m, 4H^{ar}), 7.63 (m, 2H^{ar}), 7.88 (m, 4H^{ar}), 7.95 (d, $^3J_{HH}$=8.5 Hz, 2H^{ar}), 8.05 (d, $^3J_{HH}$=8.5 Hz, 2H^{ar}). ^{13}C NMR (125.76 MHz, $CDCl_3$), δ (ppm): 15.22 (d, $^2J_{PC}$= 2.1 Hz), 15.31 (d, $^2J_{PC}$=1.7 Hz), 40.69 (dd, $^1J_{PC}$=66.9 Hz, $^3J_{PC}$=2.4 Hz), 40.95 (dd, $^1J_{PC}$=67.3 Hz, $^3J_{PC}$=2.4 Hz), 120.58 (d, $^3J_{PC}$=4.9 Hz), 120.61 (d, $^3J_{PC}$=4.9 Hz), 120.72 (d, $^3J_{PC}$=4.5 Hz), 120.77 ($^3J_{PC}$=4.9 Hz), 121.93 (d, $^4J_{PC}$= 2.1 Hz), 123.61, 123.69, 123.74, 125.35 (d, ^4J=2.2 Hz), 127.57 (d, $^1J_{PC}$=101.1 Hz), 127.94 (d, $^1J_{PC}$=116.9 Hz), 128.04 (d, $^1J_{PC}$=106.9 Hz), 128.27 (d, $^3J_{PC}$=12.4 Hz), 128.41 (d, $^3J_{PC}$=12.5 Hz), 128.80 (d, $^3J_{PC}$=10.1 Hz), 128.88 (d, $^3J_{PC}$=10.4 Hz), 129.17 (d, $^4J_{PC}$=1.3 Hz), 129.18 (d, $^4J_{PC}$=2.2 Hz), 129.79 (d, $^3J_{PC}$=5.2 Hz), 129.87 (d, $^3J_{PC}$=5.3 Hz), 131.84 (d, $^2J_{PC}$=10.0 Hz), 132.00 (d, $^2J_{PC}$=9.9 Hz), 132.10 (d, $^4J_{PC}$=2.0 Hz), 132.23 (d, $^4J_{PC}$=2.1 Hz), 132.30 (d, $^2J_{PC}$=10.1 Hz), 132.32

(d, $^{2}J_{PC}$=9.7 Hz), 132.44 (d, $^{4}J_{PC}$=2.4 Hz), 132.59 (d, $^{4}J_{PC}$=2.4 Hz), 138.25 (d, $^{2}J_{PC}$=6.5 Hz), 140.60 (d, $^{2}J_{PC}$=6.0 Hz), 142.92 (d, $^{5}J_{PC}$=3.5 Hz), 147.18 (d, $^{5}J_{PC}$=3.5 Hz), 152.47 (d, $^{2}J_{PC}$=8.7 Hz), 152.52 (d, $^{2}J_{PC}$=6.9 Hz), 152.54 (d, $^{2}J_{PC}$=8.7 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 18.83 (d, $^{2}J_{PP}$=33.4 Hz), 18.37 (d, $^{2}J_{PP}$=34.5 Hz), −9.43 (d, $^{2}J_{PP}$=33.4 Hz), −9.47 (d, $^{2}J_{PP}$=34.5 Hz). Anal. Calcd for $C_{64}H_{56}N_4O_7P_4$ (1116.56): C, 68.84; H, 5.01; N, 5.02. Found: C, 68.91; H, 5.05; N, 4.92. MS *m/z* (%): 1117 (37), 559 (100).

4.2.27. 4,4′-Di{1-[(*P*,*P*-diphenyl)(*N*-methoxycarbonyl)-phosphazenyl]ethyl}azoxybenzene (11b). Eluent: ethyl acetate/hexane 5:1. Oil. Yield: 10%. IR (KBr pellets, neat), ν (cm^{-1}): 1709, 1651, 1260, 1091, 1019. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 1.64 (dd, $^{3}J_{HH}$=7.3 Hz, $^{3}J_{PH}$=16.6 Hz, 3H), 1.65 (dd, $^{3}J_{HH}$=7.3 Hz, $^{3}J_{PH}$=16.6 Hz, 3H), 3.63 (s, 6H), 4.62 (dq, $^{3}J_{HH}$=7.3 Hz, $^{2}J_{PH}$=12.3 Hz, 1H), 4.67 (dq, $^{3}J_{HH}$=7.3 Hz, $^{2}J_{PH}$=12.3 Hz), 7.05 (m, 4H^{ar}), 7.43 (m, 4H^{ar}), 7.57 (m, 12H^{ar}), 7.79 (m, 4H^{ar}), 7.98 (d, $^{3}J_{HH}$=8.3 Hz, 2H^{ar}), 8.08 (d, $^{3}J_{HH}$=8.5 Hz, 2H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 15.44 (d, $^{2}J_{PC}$=2.0 Hz), 15.57 (d, $^{2}J_{PC}$=2.0 Hz), 37.14 (d, $^{1}J_{PC}$=57.7 Hz), 37.40 (d, $^{1}J_{PC}$=58.5 Hz), 52.76 (d, $^{4}J_{PC}$=3.9 Hz), 52.80 (d, $^{4}J_{PC}$=3.9 Hz), 121.91 (d, $^{4}J_{PC}$=2.4 Hz), 124.37 (d, $^{1}J_{PC}$=97.6 Hz), 124.89 (d, $^{1}J_{PC}$=95.8 Hz), 125.07 (d, $^{1}J_{PC}$=95.8 Hz), 125.18 (d, $^{1}J_{PC}$=94.9 Hz), 125.33 (d, $^{4}J_{PC}$=2.4 Hz), 128.26 (d, $^{3}J_{PC}$=11.7 Hz), 128.40 (d, $^{3}J_{PC}$=11.7 Hz), 128.49 (d, $^{3}J_{PC}$=12.0 Hz), 128.53 (d, $^{3}J_{PC}$=11.7 Hz), 129.58 (d, $^{3}J_{PC}$=4.8 Hz), 129.61 (d, $^{3}J_{PC}$=5.1 Hz), 132.37 (d, $^{4}J_{PC}$=2.7 Hz), 132.46 (d, $^{4}J_{PC}$=3.0 Hz), 132.55 (d, $^{4}J_{PC}$=3.0 Hz), 132.74 (d, $^{4}J_{PC}$=2.7 Hz), 132 99 (d, $^{2}J_{PC}$=9.0 Hz), 133.15 (d, $^{2}J_{PC}$=9.0 Hz), 133.27 (d, $^{2}J_{PC}$=8.7 Hz), 133.31 (d, $^{2}J_{PC}$=8.7 Hz), 138.31 (d, $^{2}J_{PC}$=5.4 Hz), 140.68, (d, $^{2}J_{PC}$=5.1 Hz), 142.93 (d, $^{5}J_{PC}$=3.6 Hz), 147.18 (d, $^{5}J_{PC}$=3.3 Hz), 162.91 (d, $^{2}J_{PC}$=2.4 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 29.59, 29.76. Anal. Calcd for $C_{44}H_{42}N_4O_5P_2$ (768.79): C, 68.74; H, 5.51; N, 7.29. Found: C, 68.69; H, 5.53; N, 7.33. MS *m/z* (%): 385 (100), 769 (37).

4.2.28. 4,4′-Di[1-(*P*,*P*-diphenylphosphynylborane)ethyl]-azoxybenzene (11c). Eluent: ethyl acetate/hexane 1:3. Oil. Yield: 10%. IR (KBr pellets, neat), ν (cm^{-1}): 2380, 1261, 1101, 1017. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 1.63 (dd, $^{3}J_{HH}$=7.3 Hz, $^{3}J_{PH}$=16.1 Hz, 3H), 1.64 (dd, $^{3}J_{HH}$=7.3 Hz, $^{3}J_{PH}$=16.1 Hz, 3H), 3.91 (dq, $^{3}J_{HH}$=7.3 Hz, $^{2}J_{PH}$=12.1 Hz, 1H), 3.95 (dq, $^{3}J_{HH}$=7.3 Hz, $^{2}J_{PH}$=12.1 Hz, 1H), 7.18 (dd, $^{3}J_{HH}$=8.5 Hz, $^{4}J_{PH}$=1.6 Hz, 2H^{ar}), 7.2 (dd, $^{3}J_{HH}$=8.5 Hz, $^{4}J_{PH}$=1.6 Hz, 2H^{ar}), 7.29 (m, 4H^{ar}), 7.41 (m, 4H^{ar}), 7.56 (m, 8H^{ar}), 7.92 (m, 4H^{ar}), 8.00 (d, $^{3}J_{HH}$=8.5 Hz, 2H^{ar}), 8.08 (d, $^{3}J_{HH}$=8.5 Hz, 2H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 16.17 (d, $^{2}J_{PC}$=3.3 Hz), 16.23 (d, $^{2}J_{PC}$=3 Hz), 37.31 (d, $^{1}J_{PC}$=30.3 Hz), 37.57 (d, $^{1}J_{PC}$=30 Hz), 121.73 (d, $^{4}J_{PC}$=2.1 Hz), 125.19 (d, $^{4}J_{PC}$=2.1 Hz), 127.35 (d, $^{1}J_{PC}$=52 Hz), 127.65 (d, $^{1}J_{PC}$=52 Hz), 127.79 (d, $^{1}J_{PC}$=53.5 Hz), 127.97 (d, $^{1}J_{PC}$=53.5 Hz), 128.27 (d, $^{3}J_{PC}$=8.7 Hz), 128.4 (d, $^{3}J_{PC}$=9 Hz), 128.86 (d, $^{3}J_{PC}$=9.6 Hz), 128.94 (d, $^{3}J_{PC}$=9.6 Hz), 129.55 (d, $^{3}J_{PC}$=5.4 Hz), 129.61 (d, $^{3}J_{PC}$=4.2 Hz), 131.07 (d, $^{4}J_{PC}$=2.4 Hz), 131.23 (d, $^{4}J_{PC}$=2.7 Hz), 131.46 (d, $^{4}J_{PC}$=2.7 Hz), 131.59 (d, $^{4}J_{PC}$=2.4 Hz), 132.72 (d, $^{2}J_{PC}$=8.4 Hz), 132.82 (d, $^{2}J_{PC}$=8.4 Hz), 132.97 (d, $^{2}J_{PC}$=8.2 Hz), 133.00 (d, $^{2}J_{PC}$=8.4 Hz), 139.84 (d, $^{2}J_{PC}$=1.8 Hz), 142.09 (d, $^{2}J_{PC}$=1.5 Hz), 142.78 (d, $^{5}J_{PC}$=3.3 Hz), 147.05 (d, $^{5}J_{PC}$=3.0 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 26.46. Anal. Calcd for $C_{40}H_{42}B_2N_2OP_2$ (650.35): C, 73.87; H, 6.51; N, 4.31. Found: C, 73.81; H, 6.54; N, 4.29. MS *m/z* (%): 634 (100), 673 (M+23, 20%).

4.2.29. 4,4′-Di[1-(*P*,*P*-diphenylphosphinoyl)ethyl]azoxybenzene (11d). Eluent: ethyl acetate/hexane 5:1. Solid. Mp 267–270 °C. IR (KBr), ν (cm^{-1}): 1261, 1098, 1025. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 1.62 (dd, $^{3}J_{HH}$=7.7 Hz, $^{3}J_{PH}$=15.8 Hz, 6H), 3.71 (m, 2H), 7.33 (m, 10H^{ar}), 7.54 (m, 10H^{ar}), 7.93 (m, 4H, H^{ar}), 8.03 (m, 2H^{ar}), 8.11 (m, 2H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 15.27 (d, $^{2}J_{PC}$=3.0 Hz), 15.39 (d, $^{2}J_{PC}$=3.0 Hz), 40.80 (d, $^{1}J_{PC}$=66.1 Hz), 41.06 (d, $^{1}J_{PC}$=66.7 Hz), 122.09 (d, $^{4}J_{PC}$=2.1 Hz), 125.57 (d, $^{4}J_{PC}$=1.5 Hz), 128.14 (d, $^{3}J_{PC}$=11.4 Hz), 128.25 (d, $^{3}J_{PC}$=11.7 Hz), 128.69 (d, $^{3}J_{PC}$=11.1 Hz), 128.77 (d, $^{3}J_{PC}$=11.1 Hz), 129.39 (d, J_{PC}=5.4 Hz), 129.46 (d, $^{3}J_{PC}$=5.1 Hz), 130.92 (d, $^{2}J_{PC}$=8.7 Hz), 131.04 (d, $^{2}J_{PC}$=9.0 Hz), 131.25 (d, $^{2}J_{PC}$=8.7 Hz), 131.30 (d, $^{2}J_{PC}$=8.4 Hz), 131.40 (d, $^{1}J_{PC}$=108.7 Hz), 131.46 (d, $^{4}J_{PC}$=2.7 Hz), 131.54 (d, $^{1}J_{PC}$=109.0 Hz), 131.59 (d, $^{4}J_{PC}$=3.0 Hz), 131.80 (d, $^{2}J_{PC}$=2.7 Hz), 131.92 (d, $^{4}J_{PC}$=3.0 Hz), 139.89 (d, $^{2}J_{PC}$=5.7 Hz), 142.19 (d, $^{2}J_{PC}$=5.4 Hz), 142.65 (d, $^{5}J_{PC}$=3.0 Hz), 146.94 (d, $^{5}J_{PC}$=3.0 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 33.65, 33.93. Anal. Calcd for $C_{40}H_{36}N_2O_3P_2$ (654.69): C, 73.38; H, 5.54; N, 4.28. Found: C, 72.98; H, 5.51; N, 4.31. MS *m/z* (%): 655 (100).

4.2.30. *N*-{1-[(*P*,*P*-Diphenyl)(*N*-diphenylphosphoryl)-phosphazenyl]ethyl}-3-chlorohydroxylamine (12). Eluent: ethyl acetate/hexane 2:1. Oil. Yield: 17%. IR (KBr pellets, neat), ν (cm^{-1}): 3456, 1260, 1094. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 1.25 (dd, $^{3}J_{HH}$=7.3 Hz, $^{3}J_{PH}$=14.0 Hz, 3H), 4.43 (dquintet, $^{3}J_{HH}$=$^{2}J_{PH}$=7.3 Hz, $^{4}J_{PH}$=0.6 Hz, 1H), 6.81–7.72 (m, 20H^{ar}), 7.78 (dd, $^{3}J_{HH}$=7.3 Hz, $^{3}J_{PH}$=8.2 Hz, 4H^{ar}), 10 (s, OH). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 8.99 (d, $^{2}J_{PC}$=4.2 Hz), 63.52 (d, $^{1}J_{PC}$=85.6 Hz), 115.98, 120.52 (d, $^{3}J_{PC}$=5.1 Hz), 120.91 (d, $^{3}J_{PC}$=4.8 Hz), 121.25, 123.43 (d, $^{1}J_{PC}$=94.8 Hz), 123.95 (d, $^{5}J_{PC}$=1.2 Hz), 124.14 (d, $^{5}J_{PC}$=1.2 Hz), 124.71 (d, $^{1}J_{PC}$=97.9 Hz), 128.82 (d, $^{3}J_{PC}$=12.6 Hz), 128.86 (d, $^{3}J_{PC}$=12.0 Hz), 129.12 (d, $^{4}J_{PC}$=0.6 Hz), 129.26 (d, $^{4}J_{PC}$=0.9 Hz), 129.49, 131.79 (d, $^{2}J_{PC}$=9.6 Hz), 132.31 (d, $^{2}J_{PC}$=10.5 Hz), 132.57 (d, $^{4}J_{PC}$=2.4 Hz), 132.60 (d, $^{4}J_{PC}$=2.7 Hz), 134.67, 151.85 (d, $^{2}J_{PC}$=7.5 Hz), 152.08 (d, $^{2}J_{PC}$=7.5 Hz), 152.68 (d, $^{3}J_{PC}$=13.2 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 16.25 (d, $^{2}J_{PP}$=35.6 Hz), −5.43 (d, $^{2}J_{PP}$=35.6 Hz). Anal. Calcd for $C_{32}H_{29}ClN_2O_4P_2$ (602.99): C, 63.74; H, 4.85; N, 4.65. Found: C, 63.71; H, 4.89; N, 4.67. MS *m/z* (%): 625 (M+23, 20%), 434 (100).

4.2.31. *N*-{1-[(*P*,*P*-Diphenyl)(*N*-diphenylphosphoryl)-phosphazenyl]ethyl}-2-chlorophenylhydroxylamine (13). Eluent: ethyl acetate/hexane 2:1. Oil. Yield: 7%. IR (KBr pellets, neat), ν (cm^{-1}): 3490, 1261, 1097. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 1.56 (dd, $^{3}J_{HH}$=7.0 Hz, $^{3}J_{PH}$=16.1 Hz, 3H), 2.8 (br, 1H, OH), 5.21 (dquintet, $^{3}J_{HH}$=$^{2}J_{PH}$=7.0 Hz, $^{4}J_{PH}$=0.7 Hz, 1H), 6.67 (d, $^{3}J_{HH}$=8.4 Hz, 1H^{ar}), 6.82–7.63 (m, 19H^{ar}), 7.73–8.00 (m, 4H^{ar}).

^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 13.85 (d, $^2J_{PC}$= 2.7 Hz), 79.51 (dd, $^1J_{PC}$=81.4 Hz, $^3J_{PC}$=2.4 Hz), 115.89, 118.91, 120.67 (d, $^3J_{PC}$=5.1 Hz), 120.71 (d, $^3J_{PC}$=4.8 Hz), 122.55, 123.72 (d, $^4J_{PC}$=1.5 Hz), 123.78 (d, $^4J_{PC}$=1.2 Hz), 124.98 (d, $^1J_{PC}$=105.3 Hz), 125.07 (d, $^1J_{PC}$=105.6 Hz), 128.62 (d, $^3J_{PC}$=12.6 Hz), 128.82 (d, $^3J_{PC}$=12.6 Hz), 128.97, 129.05, 129.13 (d, $^4J_{PC}$=0.6 Hz), 12919 (d, $^4J_{PC}$=0.9 Hz), 132.1 (d, $^2J_{PC}$=10.5 Hz), 132.58 (d, $^4J_{PC}$=3 Hz), 132.79 (d, $^4J_{PC}$=3 Hz), 132.93 (d, $^2J_{PC}$= 9.9 Hz), 143.88, 152 (d, $^2J_{PC}$=7.2 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 15.82 (d, $^2J_{PP}$=33.4 Hz), −7.18 (d, $^2J_{PP}$=33.4 Hz). Anal. Calcd for $C_{32}H_{29}ClN_2O_4P_2$ (602.99): C, 63.74; H, 4.85; N, 4.65. Found: C, 63.69; H, 4.81; N, 4.70. MS *m*/*z* (%): 603 (79), 472 (100).

4.2.32. 2-[1-(*P*,*P*-Diphenylphosphynylborane)ethyl]-4-nitrobenzonitrile (14). Eluent: ethyl acetate/hexane 1:5. Oil. Yield: 25%. IR (KBr), ν (cm^{-1}): 2229, 1262, 1098, 1023. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 1.67 (dd, $^3J_{HH}$=7.3 Hz, $^3J_{PH}$=15.3 Hz, 3H), 4.52 (dq, $^3J_{HH}$= 7.3 Hz, $^2J_{PH}$=15.3 Hz, 1H), 7.27 (m, 2H, H^{ar}), 7.38 (m, 3H, H^{ar}), 7.62 (m, 4H, H^{ar}), 8.06 (m, 2H, H^{ar}), 8.14 (m, 1H^{ar}), 8.67 (m, 1H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 16.47 (d, $^2J_{PC}$=3.0 Hz), 35.53 (d, $^1J_{PC}$=29.7 Hz), 115.91 (d, $^4J_{PC}$=1.5 Hz), 118.54 (d, $^3J_{PC}$=5.1 Hz), 122.35 (d, $^5J_{PC}$=2.4 Hz), 124.64 (d, $^3J_{PC}$=3.3 Hz), 125.43 (d, $^1J_{PC}$=53.5 Hz), 126.59 (d, $^1J_{PC}$=53.2 Hz), 128.56 (d, $^3J_{PC}$=9.9 Hz), 129.31 (d, $^3J_{PC}$=9.9 Hz), 131.63 (d, $^4J_{PC}$=2.7 Hz), 132.29 (d, $^4J_{PC}$=2.7 Hz), 132.60 (d, $^2J_{PC}$= 8.7 Hz), 133.06 (d, $^4J_{PC}$=1.8 Hz), 133.19 (d, $^2J_{PC}$= 8.7 Hz), 144.50, 149.80 (d, $^4J_{PC}$=2.4 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 28.33. Anal. Calcd for $C_{21}H_{20}BN_2O_2P$ (374.19): C, 67.41; H, 5.39; N, 7.49. Found: C, 67.37; H, 5.37; N, 7.51. MS *m*/*z* (%): 374 (30), 148 (35).

4.2.33. *N*-(4-Chlorophenyl)-*N*-[1-(*P*,*P*-diphenylphosphinoyl)ethyl]hydroxylamine (15). Eluent: ethyl acetate/hexane 7:1. Oil. Yield: 20%. IR (KBr pellets, neat), ν (cm^{-1}): 3483, 1094, 799. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 1.31 (dd, $^3J_{HH}$=7.3 Hz, $^3J_{PH}$=15.4 Hz, 3H), 4.40 (quintet, $^3J_{HH}$=$^2J_{PH}$=7.3 Hz, 1H), 6.95 (d, $^3J_{HH}$=8.9 Hz, 2H^{ar}), 7.17 (d, $^3J_{HH}$=8.5 Hz, 2H^{ar}), 7.51 (m, 6H^{ar}), 7.86 (m, 4H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 7.86 (d, $^2J_{PC}$=3.0 Hz), 62.01 (d, $^1J_{PC}$=87.7 Hz), 117.43, 126.66, 128.58, 128.65 (d, $^3J_{PC}$=11.7 Hz), 128.75 (d, $^3J_{PC}$=11.4 Hz), 130.06 (d, $^1J_{PC}$= 94.6 Hz), 131.24 (d, $^2J_{PC}$=8.7 Hz), 132.08 (d, $^4J_{PC}$=2.1 Hz), 132.25 (d, $^4J_{PC}$=2.4 Hz), 149.64 (d, $^3J_{PC}$=12.3 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 34.46. Anal. Calcd for $C_{20}H_{19}ClNO_2P$ (371.80): C, 64.61; H, 5.15; N, 3.77. Found: C, 64.10; H, 5.17; N, 3.97. MS *m*/*z* (%): 394 (70), 201 (100).

4.2.34. *N*-{1-[(*P*,*P*-Diphenyl)(*N*-diphenylphosphoryl)-phosphazenyl]ethyl}-4-chloroaniline (16a). Eluent: ethyl acetate/hexane 1.5:1. Oil. Yield: 13%. IR (KBr pellets, neat), ν (cm^{-1}): 3420, 1261, 1094. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 1.47 (dd, $^3J_{HH}$=6.8 Hz, $^3J_{PH}$=15.8 Hz, 3H), 5.14 (dq, $^3J_{HH}$=6.8 Hz, $^2J_{PH}$=3.6 Hz, 1H), 6.56 (d, $^3J_{HH}$=8.6 Hz, 2H^{ar}), 6.91–7.62 (m, 18H^{ar}), 7.71 (dd, $^3J_{HH}$=7.1 Hz, $^3J_{PH}$=12.2 Hz, 2H^{ar}), 7.83 (dd, $^3J_{HH}$= 7.1 Hz, $^3J_{PH}$=12.2 Hz, 2H^{ar}), 7.92 (s, NH). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 14.03 (d, $^2J_{PC}$=3.0 Hz), 78.7 (d, $^1J_{PC}$=80.5 Hz, $^3J_{PC}$=1.8 Hz), 115.79, 120.65 (d, $^3J_{PC}$=5.1 Hz), 120.70 (d, $^3J_{PC}$=5.1 Hz), 120–133 (14C^{ar}), 146.52, 152.01 (d, $^2J_{PC}$=7.2 Hz), 152.15 (d, $^2J_{PC}$=8.1 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 16.01 (d, $^2J_{PP}$= 32.3 Hz), −7.15 (d, $^2J_{PP}$=32.3 Hz). Anal. Calcd for $C_{32}H_{29}ClN_2O_3P_2$ (586.99): C, 65.48; H, 4.98; N, 4.77. Found: C, 64.95; H, 4.76; N, 4.97. MS *m*/*z* (%): 586 (20), 284 (100).

4.2.35. *N*-[1-(*P*,*P*-Diphenylphosphinoyl)ethyl]-4-chloroaniline (16b). Eluent: ethyl acetate/hexane 7:1. Oil. Yield: 4%. IR (KBr pellets, neat), ν (cm^{-1}): 1092, 1023. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 1.34 (dd, $^3J_{HH}$=5.6 Hz, $^3J_{PH}$=14.5 Hz, 3H), 4.3 (m, 1H), 6.55 (d, $^3J_{HH}$=8.9 Hz, 2H^{ar}), 7.09 (d, $^3J_{HH}$=8.9 Hz, 2H^{ar}), 7.53 (m, 6H^{ar}), 7.81 (m, 4H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 14.09 (d, $^2J_{PC}$=2.4 Hz), 47.59 (d, $^1J_{PC}$=81.7 Hz), 114.64, 122.76, 128.72 (d, $^3J_{PC}$=11.7 Hz), 129.13, 130.14 (d, $^1J_{PC}$= 92.2 Hz), 131.20 (d, $^2J_{PC}$=8.7 Hz), 131.29 (d, $^2J_{PC}$= 8.7 Hz), 132.1 (d, $^4J_{PC}$=2.7 Hz), 132.21 (d, $^4J_{PC}$= 2.7 Hz), 144.76 (d, $^3J_{PC}$=10.2 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 33.32. Anal. Calcd for $C_{20}H_{19}ClNOP$ (355.80): C, 67.52; H, 5.38; N, 3.94. Found: C, 68.01; H, 5.35; N, 3.97. MS *m*/*z* (%): 378 (40), 203 (50).

4.2.36. 3-Chloro-4-[1-(*P*,*P*-diphenylphosphynylborane)-ethyl]benzonitrile (18a). Eluent: ethyl acetate/hexane 1:5. Oil. Yield: 64%. IR (KBr pellets, neat), ν (cm^{-1}): 2384, 2226, 1261, 1095. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 1.54 (dd, $^3J_{HH}$=7.3 Hz, $^3J_{PH}$=15.9 Hz, 3H), 4.63 (dq, $^3J_{HH}$=7.3 Hz, $^2J_{PH}$=16.1 Hz, 1H), 7.29 (m, 5H, H^{ar}), 7.45 (m, 1H^{ar}), 7.59 (m, 4H, H^{ar}), 7.92 (dd, $^3J_{HH}$=8.1 Hz, $^4J_{HH}$=1.7 Hz, 1H^{ar}), 8.01 (m, 2H, H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 16.49 (d, $^2J_{PC}$=3.3 Hz), 32.64 (d, $^1J_{PC}$=31.2 Hz), 112.12 (d, $^5J_{PC}$=2.7 Hz), 117.23, 126.68 (d, $^1J_{PC}$=53.2 Hz), 127.34 (d, $^1J_{PC}$=53.5 Hz), 128.24 (d, $^3J_{PC}$=9.9 Hz), 129.15 (d, $^3J_{PC}$=9.6 Hz), 130.23 (d, $^4J_{PC}$=2.1 Hz), 131.22 (d, $^4J_{PC}$=1.8 Hz), 131.27 (d, $^3J_{PC}$=3.21 Hz), 131.96 (d, $^4J_{PC}$=2.4 Hz), 132.23 (d, $^4J_{PC}$=1.8 Hz), 132.38 (d, $^2J_{PC}$=8.7 Hz), 133.09 (d, $^2J_{PC}$=8.7 Hz), 134.94 (d, $^3J_{PC}$=6.0 Hz), 142.38. ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 27.56. Anal. Calcd for $C_{21}H_{20}BClNP$ (363.63): C, 69.36; H, 5.54; N, 3.85. Found: C, 69.97; H, 5.51; N, 3.79. MS *m*/*z* (%): 364 (40), 221 (100).

4.2.37. 4-[1-(*P*,*P*-Diphenylphosphynylborane)ethyl]-3-fluorobenzonitrile (18b). Eluent: ethyl acetate/hexane 1:10. Oil. Yield 25%. IR (KBr pellets, neat), ν (cm^{-1}): 2391, 1261, 1097. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 1.57 (dd, $^3J_{HH}$=7.3 Hz, $^3J_{PH}$=15.7 Hz, 3H), 4.39 (dq, $^3J_{HH}$=7.3 Hz, $^2J_{PH}$=15.8 Hz, 1H), 7.07 (dd, $^4J_{HH}$= 1.5 Hz, $^3J_{FH}$=9.5 Hz, 1H^{ar}), 7.27 (m, 2H^{ar}), 7.42 (m, 4H^{ar}), 7.56 (m, 3H^{ar}), 7.74 (m, 1H^{ar}), 7.97 (m, 2H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 15.77 (d, $^2J_{PC}$= 3.3 Hz), 28.31 (dd, $^1J_{PC}$=31.5 Hz, $^3J_{FC}$=1.8 Hz), 112.04 (dd, $^5J_{PC}$=2.7 Hz, $^3J_{FC}$=10.1 Hz), 117.37 (dd, $^6J_{PC}$= 1.5 Hz, $^4J_{FC}$=2.7 Hz), 118.34 (dd, $^4J_{PC}$=2.1 Hz, $^2J_{FC}$= 27.0 Hz), 126.80 (d, $^1J_{PC}$=52.9 Hz), 127.87 (dd, $^4J_{PC}$= 2.4 Hz, $^4J_{FC}$=3.9 Hz), 128.30 (d, $^3J_{PC}$=9.9 Hz), 129.08 (d, $^3J_{PC}$=9.9 Hz), 131.39 (d, $^4J_{PC}$=2.4 Hz), 131.63 (t, $^3J_{PC}$=$^3J_{FC}$=3.3 Hz), 131.86 (d, $^4J_{PC}$=2.4 Hz), 132.01 (d, $^2J_{FC}$=14.1 Hz), 132.29 (dd, $^2J_{PC}$=8.7 Hz, $^6J_{FC}$= 1.2 Hz), 132.87 (d, $^2J_{PC}$=8.4 Hz), 159.23 (dd, $^3J_{PC}$= 5.1 Hz, $^1J_{FC}$=248.7 Hz). ^{31}P NMR (121.49 MHz, $CDCl_3$),

δ (ppm): 26.46. Anal. Calcd for $C_{21}H_{20}BFNP$ (347.18): C, 72.65; H, 5.81; N, 4.03. Found: C, 70.01; H, 5.79; N, 4.55. MS *m*/*z* (%): 370 (10), 344 (100).

4.2.38. 5-Cyano-2-[1-(*P*,*P*-diphenylphosphynylborane)-ethyl]benzonitrile (18c). Solid. Yield: 87%. Mp 172–174 °C. IR (KBr), ν (cm^{-1}): 2261, 2233, 1102. ^1H NMR (300.13 MHz, $CDCl_3$), δ (ppm): 1.62 (dd, $^3J_{HH}=7.3$ Hz, $^3J_{PH}=15.8$ Hz, 3H), 4.47 (dq, $^3J_{HH}=7.3$ Hz, $^2J_{PH}=15.4$ Hz, 1H), 7.31 (m, 4H, H^{ar}), 7.66 (m, 5H, H^{ar}), 7.90 (m, 1H^{ar}), 8.09 (m, 3H, H^{ar}). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 16.39 (d, $^2J_{PC}=3.6$ Hz), 35.73 (d, $^1J_{PC}=29.4$ Hz), 112.09 (d, $^5J_{PC}=2.4$ Hz), 114.48 (d, $^3J_{PC}=5.4$ Hz), 115.58 (d, $^4J_{PC}=1.8$ Hz), 116.41 (d, $^6J_{PC}=1.5$ Hz), 125.58 (d, $^1J_{PC}=54.1$ Hz), 126.46 (d, $^1J_{PC}=53.5$ Hz), 128.53 (d, $^3J_{PC}=9.6$ Hz), 129.34 (d, $^3J_{PC}=10.2$ Hz), 130.95 (d, $^3J_{PC}=3.0$ Hz), 131.72 (d, $^4J_{PC}=2.4$ Hz), 132.26 (d, $^4J_{PC}=2.4$ Hz), 132.52 (d, $^2J_{PC}=9.0$ Hz), 133.09 (d, $^2J_{PC}=9.0$ Hz), 135.20 (d, $^4J_{PC}=1.2$ Hz), 135.51 (d, $^4J_{PC}=1.8$ Hz), 147.54. ^{31}P NMR (121.49 MHz, $CDCl_3$), δ (ppm): 28.78. Anal. Calcd for $C_{22}H_{20}BN_2P$ (354.20): C, 74.60; H, 5.69; N, 7.91. Found: C, 74.58; H, 7.93; N, 7.85. MS *m*/*z* (%): 354 (80), 274 (100).

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