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# Unusual nitrogen based heterocycles via allenic intermediates from the reaction of propargyl alcohols with P(III) substrates

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ABSTRACT

The apparently simple reaction of the P(III) precursors [(RNH)P(μ-N-*t*-Bu)$_2$**PY**] (**Y**=NH-*t*-Bu, Cl), ($OCH_2CMe_2CH_2O$)PCl, and $Ph_2PCl$ with functionalized propargyl alcohols is examined. In most cases, the final products are not the expected allenes but several previously unpredicted structural motifs, such as substituted oxazabenzocycloheptenones, indolinones, and fused heterocycles as revealed by X-ray crystallography. Mechanistic aspects of these novel reactions, as well as possible utility and the structural chemistry of the products are also discussed. The P–C or P–N bond cleavage of many of these compounds led to phosphorus-free 2-substituted indoles, quinolinones, and tetrahydroacridine.



## 1. Introduction

The reaction of propargyl alcohols R′C≡$CCH_2OH$ with $R_2P$(III)–Cl compounds constitutes a facile route to allenylphosphonates/allenylphosphine oxides $R_2P(O)C(R')=C=CH_2$ via a *pseudo*-Claisen rearrangement of the initially formed P(III) compounds $R_2P(OCH_2C{\equiv}CR')$.[1] A large number of synthetically useful phosphorus (and analogous sulfur) based allenes (cf. compound **1**, Scheme 1a), can be conveniently synthesized by this method.[1d] Allenes, including these allenylphosphonates, are valuable synthons and hence their synthesis and reactivity are currently a prime area of research activity.[2–5] In a recent study, we revealed that reactions similar to that shown in Scheme 1 led to rather previously unsuspected and unexpected products [e.g., **2** in Scheme 1b, after the elimination of a molecule of $CO_2$] by using functionalized propargylic alcohols.[6a] Alkylidene substituted propargyl alcohols led to another class of derivatives, the phosphono-indenes (e.g., **3**, Scheme 1c).[6b]

Cyclodiphosphazanes [**XP**(μ-NR)$_2$**PY**] (**4**) [R=*t*-Bu or Ph] constitute a well-known class of simple ring systems with two reactive phosphorus(III) centers.[7] In a significant number of their reactions, the substitution reactions of the P-X/P–Y bond and the oxidative addition/coordinating ability of the phosphorus have been profitably engaged to analyze 'intermediates' proposed in organic transformations involving P(III) species as one of the components,[8] and to generate a diverse range of coordination complexes.[9] The nucleophilicity of P(III) center in cyclodiphosph(III)azanes towards alkenes, alkynes, allenylphosphonates, and azo compounds has also been employed in isolating the products analogous to the proposed intermediates in the well-known Mitsunobu reaction as well as 'umpolung addition' via phosphine activation of alkynes.[8c,10] In the reaction with allenylphosphonates, we have also reported rather unusual 'spontaneous resolution' in which both the enantiomers were separated by crystallization.[11] The steric protection offered by the two ring N-*t*-Bu groups, amenability of the system to be monitored by $^{31}$P NMR, and in most cases, good crystallinity of the products makes these compounds as wonderful precursors to probe organic reactions. Thus we wanted to explore reactions with nitro-functionalized propargyl alcohols (cf. Scheme 2) further in an effort to unravel the details of the new reaction shown in Scheme 1b. The results include the structural characterization of previously unsuspected class of products, and unusual ways of forming phosphorus-free 2-substituted indoles,[12] quinolinones, and tetrahydroacridine.

## 2. Results and discussion

We shall first discuss the reaction of cyclophosphazane precursors **4a**–**d** (Chart 1) with propargyl alcohols. For generalization, we then deal with the corresponding results using the P(III) precursors **5** and **6**. Hydrolysis/thermal decarboxylation that leads to phosphorus-free quinolinones, 2-substituted indoles, and

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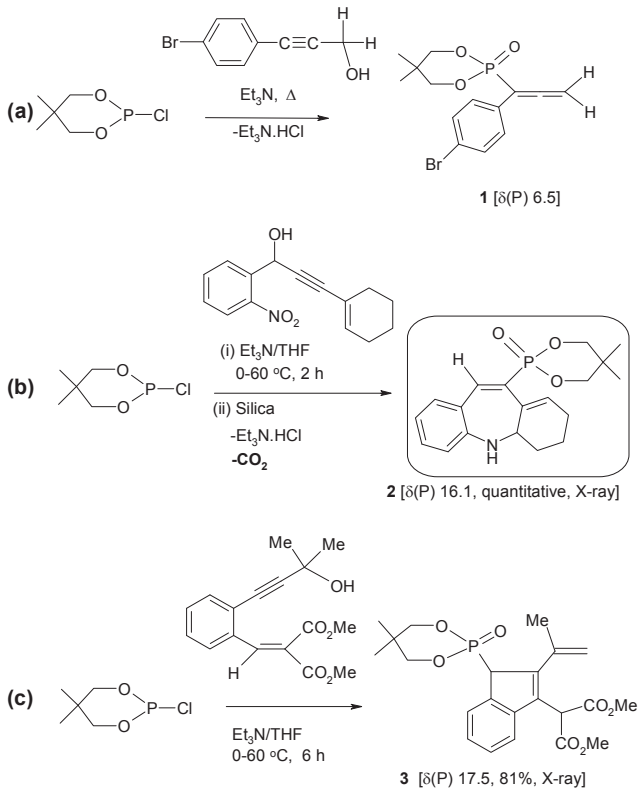
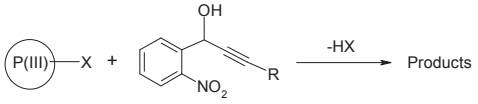



**Scheme 1.** Reaction of P(III)–Cl precursors with propargyl alcohols leading to (a) allene **1**, (b) benzepin **2**, or (c) phosphono indene **3**.




**Scheme 2.** Schematic representation of the reactions studied in this work.

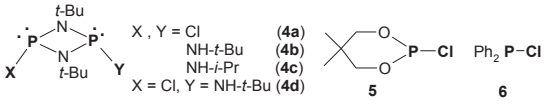
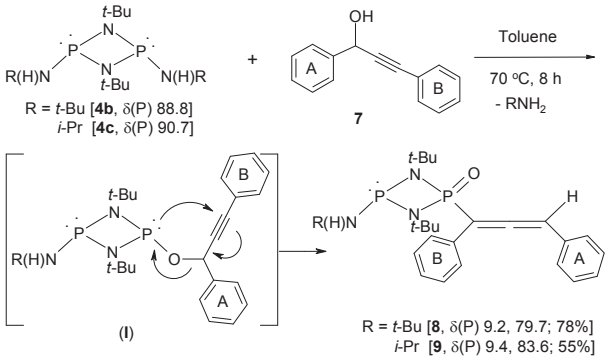



**Chart 1.**

tetrahydroacridine is also described as appropriate. Mechanistic features are briefly discussed at the end.

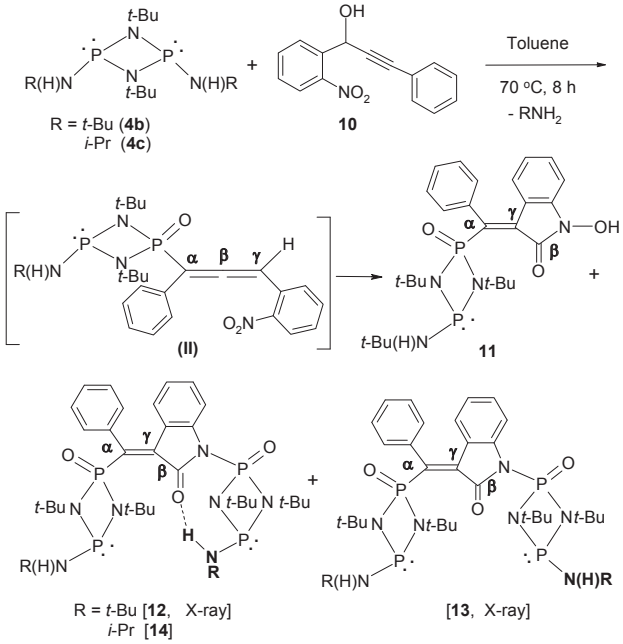
## 2.1. Reactivity of [(RNH)P(μ-N-*t*-Bu)]$_2$ [R=*t*-Bu (4b), *i*-Pr (4c)] and [(*t*-BuNH)P(μ-N-*t*-Bu)$_2$P–Cl] (4d) with functionalized propargyl alcohols

Initially, we started the reaction of cyclodiphosphazanes **4b**,**c**[8c,d] with aryl substituted propargyl alcohol[13] **7** that led to cyclodiphosphazane based allenes **8** and **9**[14] (Scheme 3). These are formed by the attack of OH of the propargyl alcohol on cyclodiphosphazane followed by rearrangement. The $^{31}$P NMR shows two signals, one at tetracoordinate region and the other at tricoordinate region, as expected. The presence of the allenic group is readily inferred from IR [1912–1929 cm$^{-1}$] and $^{13}$C NMR [δ(C=*C*=C)~216] spectra. The P–C carbon appears at δ 107.5–107.7 [$^{1}J$(P–C)~138–139 Hz]. It may be noted that a simple substitution would lead to the product of type **I**.




**Scheme 3.** Formation of allenes **8** and **9** from **4b**,**c**.

What is perhaps interesting is that, in the above reaction, if the phenyl ring (A) has *o*-NO$_2$ group, it produces the uncommon cyclodiphosphazane based heterocycles. Thus treatment of [(*t*-BuNH)P(μ-N-*t*-Bu)]$_2$ (**4b**) with the propargyl alcohol **10** leads to the cyclodiphosphazanyl-indolinones **11** and **12**,**13**. The yields of the bis(cyclophosphazanyl) products **12**,**13** can be enhanced by increasing the stoichiometry of the cyclophosphazane **4b** (Scheme 4). The yields given in Scheme 4 are from the isolation by column chromatography. NMR ($^{1}$H, $^{13}$C, and $^{31}$P), IR, and HRMS data confirm the identity of **11**.[6a] Additional proof comes from the single crystal X-ray structural characterization of **12**·1.5H$_2$O and **13** [Figs. S1 and S2, Supplementary data]. The difference in the structures of **12** and **13** stems from the *trans* or *cis* disposition of the P(O)/PNH(*t*-Bu) groups on one of the cyclophosphazanyl residues, and consequently, the intramolecular NH···O type H-bonding in **12**. This feature could have affected the δ(*C*=O) in **12** in comparison to compound **13**. The reaction of isopropylamino substrate **4c** with the same propargyl alcohol in 2:1 molar stoichiometry ratio mainly




**Yields of isolated products 11-14 (see text for details)**

Stoichiometry used (**4b**: **10**): 1.2:1 **11** (34%) **12+13** (18%) [+ other products]

Stoichiometry used (**4b**: **10**): 2:1 **11** (<15%) **12** (36%) **13** (28%)

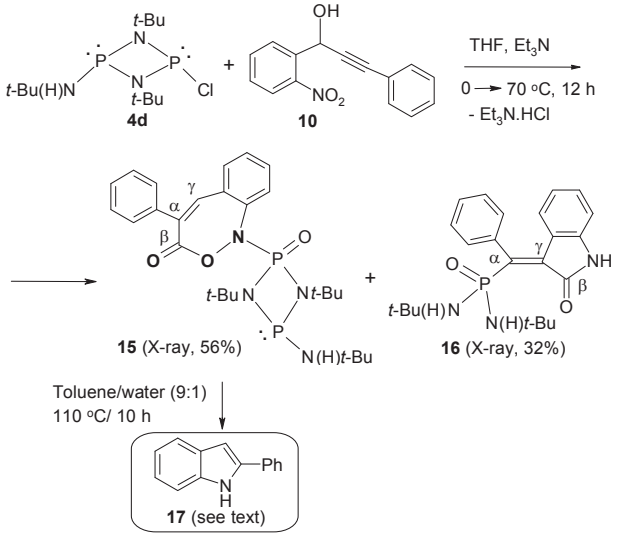
Stoichiometry used (**4c**: **10**): 2:1 **14** (33%) [+ other hydrolyzed products]

**Scheme 4.** Formation of *N*-hydroxyindolinone **11** and indolinones **12**–**14** from **4b**,**c**.

afforded bis(cyclophosphazanyl)indolinone **14**, a compound with a structure similar to **12**. This assignment is based on the similarity in the $^{1}$H NMR spectra between the two compounds. We did not isolate any mono(cyclophosphazanyl) product that is similar to compound **11**. This observation may be related to higher reactivity of the precursor **4c**.

Notable features in the structures of **11**–**14** are (i) the unusual *change of position of the β-carbon* in the intermediate **II** and the final products **11**–**14** suggesting a new rearrangement, (ii) the transfer of an oxygen atom from the $-NO_2$ group to a carbon in the five-membered ring, and (iii) a rearrangement from P(III)–O–N to (O)P(V)–N[15] (for **12**–**14**).

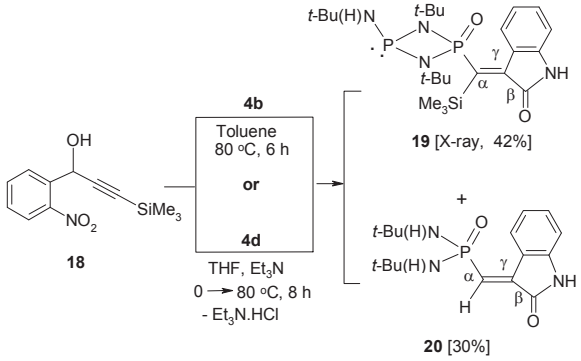
Surprised by the intricacies involved in the above reaction, we probed the reaction further by using the monochlorocyclodiphosphazane **4d**.[8a] It may be noted that a simple replacement of –Cl by the propargyloxy group followed by rearrangement should have afforded the same compounds **12**,**13**. However, **12**,**13** were only the minor products and the major products were the unsuspected and unusual phosphazane connected cyclic products **15** and **16** (Scheme 5). The molar stoichiometry used was 1.2:1 [**4d**:**10**]. Compound **15** is fairly stable but in $CDCl_3$ solution exhibits two sets of signals [ca. 7:3 ratio] in both $^{1}$H and $^{31}$P NMR spectra, suggesting an isomerization process [*cis*⇔-*trans* of P(O) and P(NH-*t*-Bu) groups]. It was not possible to distinguish these two isomers by TLC, but fortunately we could obtain the crystal structure of one isomer of **15**. This crystal also exhibited isomerization in solution [$CDCl_3$; $^{31}$P/$^{1}$H NMR]. The $^{31}$P NMR spectrum shows major signals at $\delta$ 73.1 and 3.0. It is interesting to note that we were able to isolate 2-phenyl-indole **17** (ca. 48%) from the hydrolysis/dephosphorylation of compound **15**. The reaction is significant because a new (perhaps bizarre) route to 2-substituted indoles has been uncovered.




**Scheme 5.** Formation of oxa-aza-benzocycloheptenone **15**, indolinone **16** and 2-phenyl-indole from **4d**.

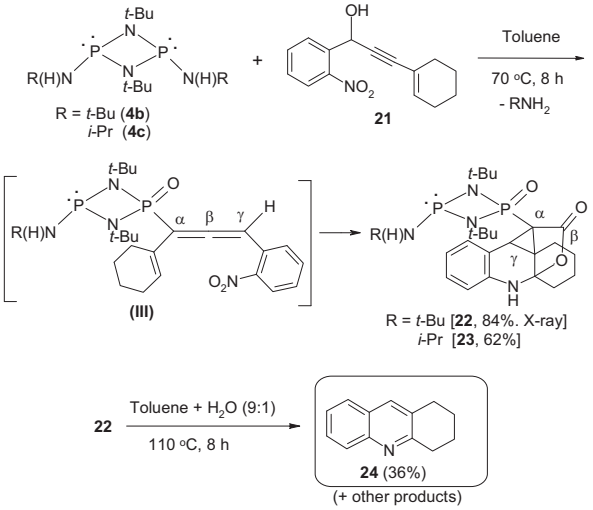
Compound **16** (cf. Scheme 5) was isolated in 32% yield. The $^{31}$P NMR spectrum exhibited a single peak at $\delta$(P) 11.1, suggesting the cleavage of cyclodiphosphazane ring. The presence of P–C bond is confirmed by a doublet at $\delta$ 154.2 [$^{1}J$(P–C)=126.0 Hz] in the $^{13}$C NMR spectrum. A carbonyl resonance at 168.7 is also clearly discernible in the spectrum. All these data are consistent with the structures shown in Scheme 5. Further confirmation of the structures **15** and **16** is provided by single crystal X-ray structures [Figs. S3 and S4, Supplementary data]. The novel seven-membered ring in **15** comprises the atoms N4, C13, C18, C19, C20, C21, and O2. A careful perusal of the structure reveals that the position of the carbon atoms at the C≡C site of **10** has been altered. While there are three intervening carbon atoms between the two-aryl groups in the precursor **10**, only two intervening carbon atoms are present in the product **15**.

Use of the propargyl alcohol $Me_3SiC{\equiv}CCH(OH)(2\text{-}NO_2C_6H_4)$ (**18**),[13b] which has a $-SiMe_3$ group in place of a phenyl group in $PhC{\equiv}CCH(OH)(2\text{-}NO_2C_6H_4)$ (**10**) resulted in the formation of cyclophosphazanyl-indolinones **19**,**20**. Either of the two substrates **4b** or **4d** can be used in this reaction (Scheme 6). The molar stoichiometry used was ~1.2:1 [**4b** or **4d**:**18**]. The production of **20** is most likely caused by the hydrolysis on the silica gel column. The structure of **19** is proven by X-ray crystallography [Fig. S5, Supplementary data]. The principal difference in structure between these two compounds (**19**,**20**) and **16** lies in the relative disposition of phosphorus and the newly formed indolinone ring, as revealed by the X-ray structure. While in **16**, the phosphorus and C=O are *cis* with respect to the intervening double bond, they are *trans* in **19** and **20**. Steric factors involving the $-SiMe_3$ (or Ph) group may be responsible for this difference.




**Scheme 6.** Formation of phosphorus-based indolinones **19** and **20**.

Keeping the $-NO_2$ group intact, subtle changes in the precursor propargyl alcohol do bring in another novel species. Thus, by replacing the phenyl group in **10** with a cyclohexenyl moiety in the precursor **21**, the fused polycycles **22**,**23** with a *cyclopropane ring* can be readily isolated (Scheme 7). The $^{31}$P NMR spectra of **22**,**23**

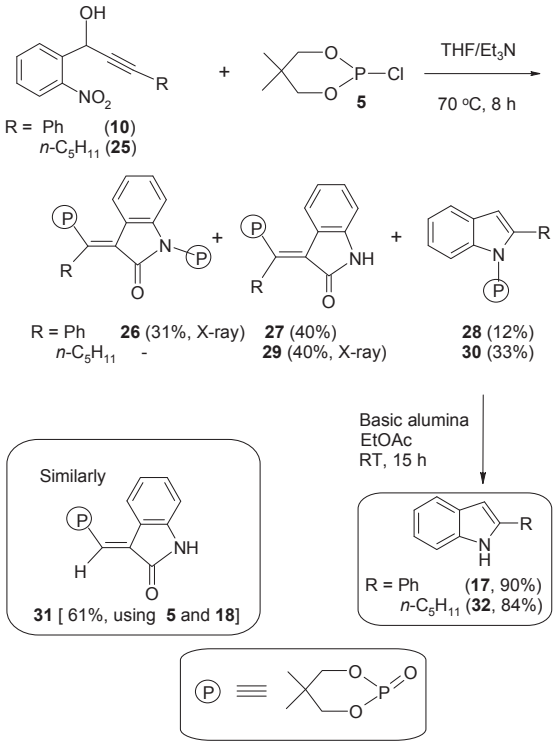



**Scheme 7.** Formation of fused polycycles **22**,**23** from **4b**,**c** and propargyl alcohol **21**.

show two signals each at $\delta$ 74.3, 10.3 and 78.9, 10.2, respectively; these values are close to that for **8** and **9**. However, in the $^{13}C$ NMR spectra, the P–*C* carbon appears at $\delta \sim 38$ [$^1J$(P–C) ~ 140–143 Hz] and $\delta$(*C*=O) around 171, which are quite different from that of the phosphoramidyl-allenes **8** and **9**. Fortunately, we were successful in obtaining the X-ray crystal structure of **22** that shows the novel structure. The three membered rings comprise [C13, C16, C21] and [C40, C43, C48] atoms in the two molecules present in the asymmetric unit. The nitrogen [N4/N8] from the precursor is part of a six-membered ring with both the oxygen atoms of the nitro group transferred to a carbon [Fig. S6, Supplementary data]. Based on the reaction shown in Scheme 1, compounds **22** and **23** are likely to be formed via cyclodiphosphazane based allene intermediate (**III**) that further undergoes cyclization using the $-NO_2$ functionality. Treatment of the same propargyl alcohol **21** with the cyclodiphosphazane **4d** in the presence of $Et_3N$ also led to the product **22**. Interestingly, compound **22** could be dephosphonylated to tetrahydroacridine **24** (NMR and HRMS evidence[16]) and other products in the presence of water.

### 2.2. Reactions of propargylic alcohol with the P(III) precursors ($OCH_2CMe_2CH_2O$)PCl (5) and $Ph_2PCl$ (6)

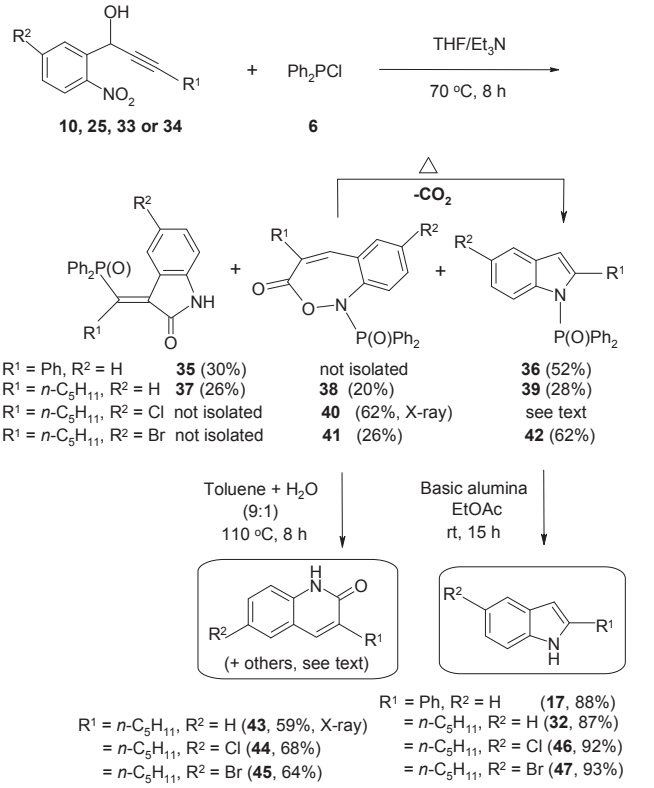
As an extension to the above studies, we wanted to explore similar reactions by using other P(III) precursors like **5** and **6**. In the reaction shown in Scheme 8, while the product **26** (X-ray, Fig. S7) is similar to **12**–**14** obtained by using the cyclodiphosphazanes **4b**,**c**, the second product **27** isolated after column chromatography is the P–N bond cleaved product from **26** and is analogous to **16**. Using the propargyl alcohol **25**, we could isolate analogous product **29** (X-ray, Fig. S8). Although we did not isolate the product **28** in our earlier attempts, we could do so after isolating **30**[17] (and realizing that we missed it). The product **31** from the silyl substituted propargyl alcohol **18** is close in structure to compound **20**. The assignment of *trans*-stereochemistry to **31** is based on a NOESY experiment. However, the more important result of this part was




**Scheme 8.** Formation of fused phosphono-indolinones/indoles **26**–**31** and phosphorus-free indoles **17** and **32**.

that we could obtain the phosphorus-free indole **17** or **32** starting from **28** or **30**, respectively.

In the reactions using $Ph_2PCl$ (**6**) shown in Scheme 9, products **35** and **37** are similar to **19**. Compounds **38**, **40** (X-ray, see Figs. 1, 2 and




**Scheme 9.** Formation of phosphinoyl indolinones/indoles/oxa-aza-benzocycloheptenones [**35**–**42**] and phosphorus-free quinolinones/indoles [**17**, **32**, **43**–**47**].

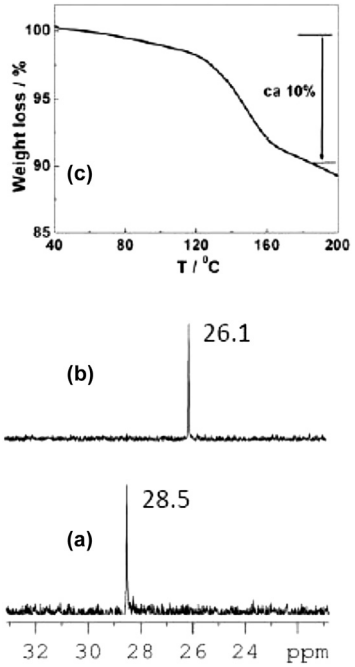



**Fig. 1.** (a) Compound **38**, (b) compound **38** upon melting and keeping the temperature at 120 °C for 2 h converted to **39**, and (c) TGA of compound **38** showing weight loss corresponding to the elimination of $CO_2$ to lead to **39**.

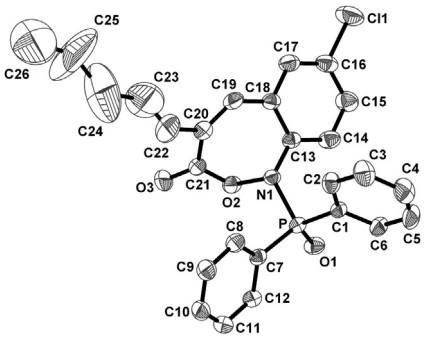



**Fig. 2.** ORTEP of compound **40** (hydrogen atoms are omitted for clarity).

S9) and **41** are similar to **15**. Analogous compounds with $R^1$=Ph and $R^2$=H could not be isolated because of the facile decarboxylation to **36**. Elimination of $CO_2$ from **38**, **40**, and **41** leads to *N*-substituted indoles **36**, **39**, and **42**, respectively, during chromatography or upon melting. In the case of $R^1$=*n*-$C_5H_{11}$ and $R^2$=Cl, we could isolate a similar species [$\delta$(P) 26.6 and HRMS: calcd for $C_{25}H_{25}ClNOP$ ($M^+$+H and $M^+$+H+2) 422.1441 and 424.1441; found 422.1440 and 424.1413] only in 95% purity. The elimination of $CO_2$ was established in the case of **38** by recording the $^{31}P$ NMR spectra before and after melting (with bubbling) and also by recording TGA (Fig. 1).

Compounds **38**, **40**, and **41** could be readily dephosphonylated to the quinolinones **43**–**45** by treating them with toluene/water mixture (cf. Scheme 9 above). Although indoles of the type **39**/**42** (ca. 15%) were also present alongside, we could easily isolate quinolinones **43**–**45**. We could get the single crystal X-ray structure of one of these (**43**; Fig. 3 and S10) to confirm their identity.[18] We are rather puzzled by this observation because in these cases there is elimination of oxygen in addition to the removal of phosphonate group. Formation of phosphorus-free indoles **17**, **32**, **46**, and **47** occurs via base hydrolysis. The reaction, as mentioned above, offers a new way to generate 2-substituted indoles.

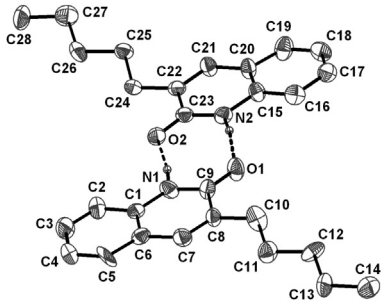
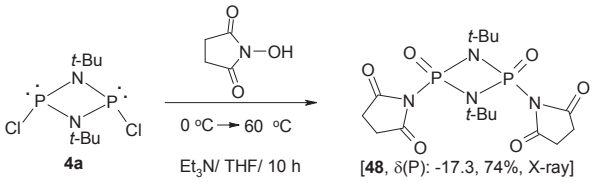



**Fig. 3.** ORTEP of compound **43**. There are two dimers present in the asymmetric unit, one set is shown here. Hydrogen atoms (except NH) are omitted for clarity.

## 2.3. Reactivity of 4a towards *N*-hydroxy-succinimide

In the reaction leading to compounds **12**–**14** shown in Scheme 4, it can be inferred that the reaction of the –OH group of the *N*-hydroxy moiety in **11** with an additional cyclodiphosphazane molecule must have led to the P–N bonded compounds **12**–**14**. To our knowledge, such reactions have never been reported in cyclodiphosphazane chemistry and in order to conclusively establish that products **12**–**14** result from such a reaction, we treated cyclodiphosphazane **4a** with *N*-hydroxy-succinimide. This reaction afforded the novel rearranged product **48** (Scheme 10). It is formed by the substitution of a chloro group by the *N*-hydroxyl reactant, followed by P–O–N to P(O)N rearrangement. The reaction mixture

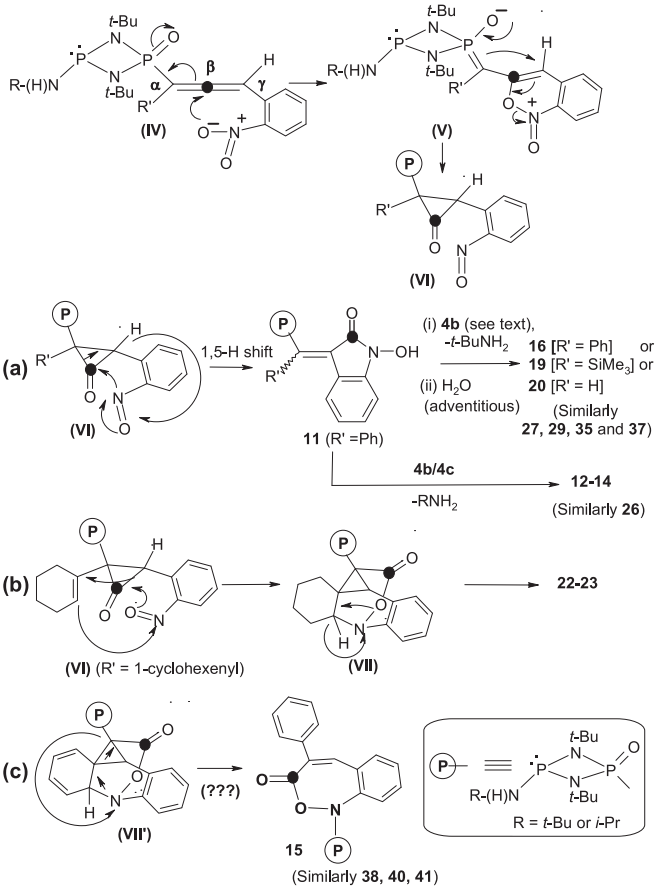



**Scheme 10.** Reaction of *N*-hydroxy succinimide with **4a** leading to P–N substituted product **48**.

initially showed substantial amounts of a partially (one side) rearranged product [$\delta$(P): 124.6, –9.1, $^2J$(PP)=12.0 Hz] vindicating our assertion that rearrangement takes place after substitution. At the end, compound **48** (X-ray, Fig. S11) is the major product, but the other isomer is also present in minor quantities (<15%).

## 2.4. Mechanistic pathways

As discussed above in Scheme 3 (compounds **8** and **9**), the normal reaction of a propargyl alcohol with cyclodiphosphazane (or a P(III)–Cl precursor) is expected to lead to the cyclophosphazanyl-allenic intermediate **IV** (Scheme 11). The β-carbon (relative to the phosphorus) in **IV** is the γ-carbon in the structures of **11**–**14**, **16**, and **19**,**20**.[19] This observation needs an explanation. Since in most cases, the nucleophilic attack takes place at the β-carbon of the allene,[20] the oxygen end of the $-NO_2$ group attacks the β-carbon to lead to the cyclic zwitterionic intermediate **V**, facilitated by the phosphoryl group. In the next step, rearrangement leads to species (**VI**). Formation of the five-membered ring can then be envisioned to lead to the cyclophosphazanyl-*N*-




**Scheme 11.** Possible pathways for the formation of the new *N*-heterocycles presented in this work [cf. Schemes 3–9].

hydroxy product **11**. The stereochemistry at the newly formed double bond may be a result of steric factors involving the R′ group. Compounds **12**–**14** result from the further reaction of this intermediate **11** with the respective cyclodiphosphazane (Scheme 11a) that also involves P(III)–O–N to P(V)(O)–N rearrangement. Proof for the latter rearrangement has been provided in this work by the structural characterization of **48**. Hydrolysis of such a species by adventitious moisture (or during the column chromatography) may then lead to facile formation of cyclophosphazanyl-indolinone (**19**) or the ring-opened products **16**/**20**. Formation of the fused heterocycles **22** and **23** may also be rationalized by appropriate bond-movements from **VI** (R′=1-cyclohexenyl; Scheme 11b). The breaking of N–O bond from the intermediate **VII** would lead to the products **22** and **23**.[21] Formation of **24** from **22** requires elimination of two molecules of CO in addition to the phosphorus moiety. The seven-membered ring compound **15** looks odd, but we presume that intermediate (**VII**′; Scheme 11c) may again be involved. At the moment we need to admit that the suggested pathway is still speculative. The isolation of the analogous compounds **38**, **40**, and **41** and thermal conversion of **38** to the 2-substituted indole **39** by elimination of $CO_2$ (cf. Scheme 9 above) also suggests an alternative pathway for these reactions. The substituted indoles **36**, **39**, and **42** are formed in a similar manner. Finally, the electronic effect induced by the P(V) center due to the shrinking of the P(V)–N(ring) bond may be responsible for the observation that only one end of the cyclodiphosphazane is reactive.

## 3. Conclusions

We have presented several new and previously unpredicted outcomes in the reactions of the cyclodiphosphazanes with functionalized propargyl alcohols. A set of indolinones and 2-substituted indoles were also prepared from the reaction of the precursors ($OCH_2CMe_2CH_2$)PCl (**5**) and $Ph_2PCl$ (**6**) with nitro-functionalized propargyl alcohols. The main advantage of the cyclodiphosphazane substrates **4a**–**d**, apart from their ready accessibility and use as $^{31}P$ NMR probes, is that the products tend to be crystalline solids readily amenable for structure determination thus assisting us to delineate intricate pathways in these apparently simple reactions. For example, it is known that in the activity of several high-energy materials (e.g., TNT) the oxygen of the $-NO_2$ group ultimately leaves as $CO_2$, but the detailed reaction chemistry is not obvious. Looking at the structures, such as **15** or **22**–**23**, we could perhaps get an idea of the involvement of unusual intermediates. We have also examined ways by which the current reaction may be put to practical use, for example, by complete removal of phosphorus-moiety. This has led to the isolation phosphorus-free indoles [**17**, **32**, **46** and **47**], tetrahydroacridine [**24**] and quinolinones [**43**–**45**]. Thus the present work illustrates new ways of generating such heterocycles.

## 4. Experimental section

### 4.1. General

All synthesis and manipulations were performed under nitrogen atmosphere unless stated otherwise. Chemicals/solvents were purified as required using standard procedures,[22] unless otherwise noted. $^1H$, $^{13}C$, and $^{31}P$ NMR spectra ($^1H$ 400 MHz, $^{13}C$ 100 MHz, and $^{31}P$ 162 MHz) were recorded using a $CDCl_3$ solution (unless stated otherwise) with shifts referenced to $SiMe_4$ ($\delta$=0) or 85% $H_3PO_4$ ($\delta$=0). Melting points were determined by using a hot stage melting point apparatus and were uncorrected. IR spectra were recorded on an FT-IR spectrophotometer. Elemental analyses were carried out on a Perkin–Elmer 240C CHN or Thermo-Finnigan EA1112 CHNS analyzer from School of Chemistry, University of Hyderabad. Mass spectra were recorded using LC/MS and HRMS (ESI-TOF analyzer) equipment.

Cyclodiphosphazane precursors [ClP(μ-N-*t*-Bu)]$_2$,[23] (**4a**), [(RNH)P(μ-N-*t*-Bu)]$_2$ [R=*t*-Bu (**4b**),[8c] *i*-Pr (**4c**),[8d] [(*t*-BuNH)P(μ-N-*t*-Bu)$_2$PCl] (**4d**),[8a] and propargyl alcohols[13] **7**, **10**, **18**, **21**, **25**, **33**, and **34** were prepared by known synthetic routes.

### 4.2. Synthesis of cyclodiphosphazane based allenes 8,9 and enamine 9a

*4.2.1. [(t-BuNH)P(μ-N-t-Bu)$_2$P(=O)–C(Ph)=C=CH(Ph)] **8**.* In a round bottomed flask (RBF), [(*t*-BuNH)P(μ-N-*t*-Bu)]$_2$ (**4b**) (0.365 g, 1.05 mmol), and propargyl alcohol **7** (0.218 g, 1.05 mmol) were dissolved in dry toluene (6 mL), and the mixture was heated with stirring at 70 °C for 8 h. After the completion of the reaction (TLC), solvent was removed under reduced pressure. The crude product was purified by column chromatography (hexane/EtOAc) affording **8** as a white crystalline solid. Yield 0.395 g (78%); mp 174–178 °C; $R_f$ (30% EtOAc/hexane) 0.55; $\nu_{max}$ (KBr) 3441, 3252, 3059, 2967, 2866, 1929, 1597, 1495, 1458, 1364, 1221, 1138, 1076, 1034, 1001, 932, 907, 882, 816 cm$^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 7.60–7.22 (m, 10H), 6.66 (d, *J*=11.2 Hz, 1H), 3.30 (d, *J*=7.2 Hz, 1H), 1.34, 1.31 (2s, 27H); $\delta_C$ (100 MHz, $CDCl_3$) 216.2, 134.4$_3$, 134.3$_5$, 132.8$_3$, 132.7$_6$, 128.7, 128.5, 127.8, 127.5$_0$, 127.4$_6$, 107.7 (d, *J*=138.0 Hz), 96.7 (d, *J*=13.0 Hz), 52.8 (d, *J*=4.0 Hz), 52.0 (d, *J*=14.0 Hz), 32.8 (d, *J*=9.0 Hz), 31.4 (d, *J*=5.0 Hz); $^{31}P$ NMR (162 MHz, $CDCl_3$) 79.73 (d, *J*=11.0 Hz), 9.21 (d, *J*=11.0 Hz); HRMS (ESI): [M$^+$+H], found 484.2646. $C_{27}H_{39}N_3OP_2$ requires 484.2647.

*4.2.2. [(i-PrNH)P(μ-N-t-Bu)$_2$P(=O)–C(Ph)=C=CH(Ph)] **9** and the by-product [(i-PrNH)P(μ-N-t-Bu)$_2$P(=O)–C(Ph)=C(NH(i-Pr)–CH$_2$Ph] **9a**.* The procedure was similar to that for compound **8** using cyclodiphosphazane [(*i*-PrNH)P(μ-N-*t*-Bu]$_2$ (**4c**) [$\delta$(P) 90.7; 0.509 g, 1.59 mmol] and propargyl alcohol **7** (0.33 g, 1.59 mmol). The reaction time was 8 h. The eluent for column chromatography was hexane/EtOAc. Compound **9a** as a minor product was also isolated subsequently (see later for characterization data) along with compound **9**. Yield 0.413 g (55%); mp 154–156 °C; $R_f$ (30% EtOAc/hexane) 0.32; $\nu_{max}$ (KBr) 3244, 2959, 2920, 2871, 1912, 1594, 1490, 1452, 1414, 1359, 1260, 1233, 1216, 1134, 1074, 926, 888, 816 cm$^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 7.60–7.21 (m, 10H), 6.66 (d, *J*=11.6 Hz, 1H), 3.55 (br, 1H), 3.02 (br, 1H), 1.33, 1.30 (2s, 18H), 1.20 (d, *J*=6.4 Hz, 6H); $\delta_C$ (100 MHz, $CDCl_3$) 216.1, 134.4, 134.3, 132.8, 132.7, 128.8, 128.6, 127.9, 127.6, 107.5 (d, *J*=139.0 Hz), 96.9 (d, *J*=13.0 Hz), 52.8 (d, *J*=5.0 Hz), 45.1 (d, *J*=29.0 Hz), 31.3, 26.5; $^{31}P$ NMR (162 MHz, $CDCl_3$) 83.64, 9.42; HRMS (ESI): [M$^+$+H], found 470.2491. $C_{26}H_{37}N_3OP_2$ requires 470.2491.

Compound **9a** was also isolated along with **9**. Yield 0.286 g (34%); mp 102–104 °C; $R_f$ (30% EtOAc/hexane) 0.64; $\nu_{max}$ (KBr) 3375, 3216, 3117, 2970, 2920, 2865, 1605, 1590, 1495, 1462, 1414, 1358, 1342, 1212, 1188, 1112, 1069, 1035, 973, 939, 889 cm$^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 9.06 (d, *J*=9.2 Hz, 1H), 7.30–7.05 (m, 10H), 3.60 (1s, 2H), 3.51–3.33 (br, 2H), 2.79 (t, 1H), 1.24 (s, 18H), 1.15 (d, *J*=6.4 Hz, 6H), 1.07 (d, *J*=6.4 Hz, 6H); $\delta_C$ (100 MHz, $CDCl_3$) 158.3 (d, *J*=12.0 Hz), 139.7, 139.6, 139.2, 130.6, 128.4, 127.7, 127.6, 125.9, 125.3, 94.4 (d, *J*=146.0 Hz), 52.2 (d, *J*=5.0 Hz), 44.7 (d, *J*=31.0 Hz), 44.5, 36.1 (d, *J*=13.0 Hz), 31.0 (t), 26.5 (d, *J*=4.0 Hz), 24.7; $^{31}P$ NMR (162 MHz, $CDCl_3$) 85.54 (*P*–NH*i*-Pr), 28.77 (*P*–C); HRMS (ESI): [M$^+$+H], found 529.3222. $C_{29}H_{46}N_4OP_2$ requires 529.3226.

### 4.3. Synthesis of cyclophosphazane containing and phosphorus free *N*-heterocycles [11–17], [19,20], [22–24]

*4.3.1. [(t-BuNH)P(μ-N-t-Bu)$_2$P(O)–C(Ph)=C{–C$_6$H$_4$–N(OH)–C(=O)–}] **11**.* The procedure was similar to that for compound **8** using

[(*t*-BuNH)P(μ-N-*t*-Bu)]$_2$ (**4b**) [0.73 g, 2.1 mmol] and propargyl alcohol **10** (0.44 g, 1.74 mmol). The reaction was conducted at 70 °C for 8 h. Eluent for column chromatography was hexane/EtOAc (1:2). Yellow solid; yield (after isolation) 0.316 g (34%); mp 226–228 °C; $R_f$ (70% EtOAc/hexane) 0.33; $\nu_{max}$ (KBr) 3470, 3289, 3138, 3081, 3029, 2967, 1705, 1699, 1616, 1557, 1466, 1362, 1325, 1213, 1082, 1032, 997, 889, 831 cm$^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 8.80 (s, 1H), 7.47–7.32 (m, 5H), 7.09 (dd, 1H), 6.88 (d, *J*=7.6 Hz, 1H), 6.55 (dd, 1H), 5.45 (d, *J*=8.0 Hz, 1H), 3.62 (d, *J*=2.4 Hz), 1.38, 1.37 (2s, 27H); $\delta_C$ (100 MHz, $CDCl_3$) 166.8, 152.9 (d, *J*=121.0 Hz), 142.6, 141.5, 135.9, 130.4, 128.9, 128.8, 128.2, 126.0, 123.9, 123.8, 121.6, 109.8, 52.5 (d, *J*=7.0 Hz), 52.0 (d, *J*=15.0 Hz), 33.0 (d, *J*=9.0 Hz), 31.8; $^{31}$P NMR (162 MHz, $CDCl_3$) 81.92 (d, *J*=12.0 Hz), 6.23 (d, *J*=12.0 Hz); HRMS (ESI): [M$^+$+H], found 529.2499. $C_{27}H_{38}N_4O_3P_2$ requires 529.2498.

*4.3.2. [(t-BuNH)P(μ-N-t-Bu)$_2$P(O){–N–C$_6$H$_4$–C(C=O)=C(Ph)–}–P(O)(μ-N-t-Bu)$_2$P(t-BuNH)] **12** and **13**.* The procedure was the same as that for **8**, using [(*t*-BuNH)P(μ-N-*t*-Bu)]$_2$ (**4b**) (0.80 g, 2.29 mmol) and propargyl alcohol **10** (0.29 g, 1.15 mmol); reaction time was 8 h and the eluent for column chromatography was hexane/EtOAc (1:1). Compound **12** was eluted firstly and followed by isomer **13**.

*Compound* **12**. Yellow solid; yield 0.333 g (36%); mp 214–216 °C; $R_f$ (50% EtOAc/hexane) 0.5; $\nu_{max}$ (KBr) 3501, 3316, 3212, 2971, 1728, 1638, 1595, 1458, 1364, 1308, 1211, 1082, 1034, 961, 885 cm$^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 8.37 (d, *J*=8.4 Hz, 1H), 7.45 (m, 3H), 7.30 (m, 2H), 7.13 (~dd, 1H), 6.59 (~dd, 1H), 5.44 (d, *J*=8.0 Hz, 1H), 5.40 (d, *J*=7.6 Hz, 1H), 3.68 (s, 1H), 1.46, 1.38, 1.36, 1.32 (4s, 54H); $\delta_C$ (100 MHz, $CDCl_3$) 166.2, 151.2 (d, *J*=121.8 Hz), 144.1, 141.9, 141.8, 136.4, 130.9, 129.1, 129.0, 128.9, 128.2, 125.5, 124.3, 124.2, 122.7, 116.2, 53.2 (d, *J*=9.0 Hz), 52.6 (d, *J*=6.0 Hz), 51.9, 51.8, 33.2 (d, *J*=7.5 Hz), 32.6 (d, *J*=3.6 Hz), 32.0 (d, *J*=4.3 Hz), 31.1 (d, *J*=4.3 Hz), 29.8; $^{31}$P NMR (162 MHz, $CDCl_3$) 85.22 (d, *J*=14.0 Hz), 85.06, 9.06 (d, *J*=14.0 Hz), –5.18; HRMS (ESI): [M$^+$+Na], found 826.3989. $C_{39}H_{65}N_7O_3P_4$ requires 826.3997. X-ray structure was determined for this isomer.

*Compound* **13**. Yellow solid; yield 0.259 g (28%); mp 204–206 °C; $R_f$ (50% EtOAc/hexane) 0.46; $\nu_{max}$ (KBr) 3410, 3246, 2967, 2926, 2855, 1699, 1632, 1547, 1464, 1385, 1366, 1312, 1269, 1221, 1146, 1080, 1038, 1009, 918, 893 cm$^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 8.20 (d, *J*=8.0 Hz, 1H), 7.42 (m, 3H), 7.28 (m, 2H), 7.13 (~dd, 1H), 6.57 (~dd, 1H), 5.50 (d, *J*=7.6 Hz, 1H), 3.38 (br, 1H), 3.09 (d, *J*=3.6 Hz, 1H), 1.38, 1.36, 1.34, 1.32 (4s, 54H); $\delta_C$ (100 MHz, $CDCl_3$) 166.2, 151.1 (d, *J*=121.7 Hz), 144.1, 141.8$_2$, 141.8$_1$, 139.4, 136.4, 131.0, 129.0, 128.9, 128.2, 125.5, 124.3, 124.1, 123.7, 122.7, 116.2, 53.2 (d, *J*=9.1 Hz), 52.6 (d, *J*=6.0 Hz), 51.8 (d, *J*=15.4 Hz), 50.9, 33.2 (d, *J*=7.4 Hz), 32.6 (d, *J*=8.0 Hz), 32.0, 31.8 (d, *J*=4.3 Hz), 31.1, 29.8; $^{31}$P NMR (162 MHz, $CDCl_3$) 83.8 (br), 73.42 (br), 6.31 (d, *J*=11.0 Hz), –5.73 (d, *J*=6.5 Hz); HRMS (ESI): [M$^+$+Na], found 826.3997. $C_{39}H_{65}N_7O_3P_4$ requires 826.3997. X-ray structure was determined for this isomer also.

*4.3.3. [(i-PrNH)P(μ-N-t-Bu)$_2$P(O){–N–C$_6$H$_4$–C(C=O)=C(Ph)–}–P(O)(μ-N-t-Bu)$_2$P(i-PrNH)] **14**.* The procedure was similar to that for compound **8** using [(*i*-PrNH)P(μ-N-*t*-Bu)]$_2$ (**4c**) [δ(P) 90.7; 1.33 g, 4.14 mmol] and propargyl alcohol **10** (0.52 g, 2.07 mmol). The reaction was conducted at 70 °C for 8 h and the eluent for column chromatography was hexane/EtOAc (2:1). Yellow solid; yield 0.523 g (33%); mp 234–238 °C; $R_f$ (30% EtOAc/hexane) 0.54; $\nu_{max}$ (KBr) 3326, 2964, 2920, 1720, 1594, 1451, 1369, 1221, 1166, 1134, 1073, 887, 805 cm$^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 8.34 (d, *J*=8.4 Hz, 1H), 7.48–7.29 (m, 5H), 7.14 (~dd, 1H), 6.60 (~dd, 1H), 5.50 (m, 2H), 3.58 (br, 3H), 1.37, 1.35, 1.34, 1.32 1.23, 1.21 (6s, 48H); $\delta_C$ (100 MHz, $CDCl_3$) 166.3, 151.5 (d, *J*=122.0 Hz), 144.0$_8$, 144.0$_5$, 141.7, 141.6, 136.0, 131.1, 129.1, 128.6, 128.2, 125.5, 124.1, 123.9, 122.8, 115.9, 53.2 (d, *J*=9.0 Hz), 52.5 (d, *J*=6.0 Hz), 46.1, 45.7, 31.9, 31.0, 26.7, 26.5; $^{31}$P NMR (162 MHz, $CDCl_3$) 89.10, 85.45, 6.84, –4.20; HRMS (ESI): [M$^+$+H], found 776.3865. $C_{37}H_{61}N_7O_3P_4$ requires 776.3865.

*4.3.4. (t-BuNH)P(μ-N-t-Bu)$_2$P(O)N[–o–C$_6$H$_4$–C(H)=C(Ph)–C(O)–O–] **15**, [(t-BuNH)$_2$P(O)–C(Ph)=C{–C$_6$H$_4$–NH–C(=O)–}] **16**, and the indole **17**.* An oven dried 25 mL round-bottomed flask was charged with propargyl alcohol **10** (0.25 g, 0.99 mmol), $NEt_3$ (0.17 mL, 1.18 mmol), and dry THF (5 mL). The mixture was stirred at 0 °C for 5 min. To this, [(*t*-BuNH)P(μ-N-*t*-Bu)$_2$P–Cl] (**4d**) (0.369 g, 1.18 mmol) dissolved in dry THF (5 mL) was added drop-wise at 0 °C over a period of 15 min, and then the mixture allowed to warm to rt followed by heating at 70 °C for 12 h with continuous stirring. Filtration followed by removal of the solvent and purification by column chromatography (hexane/acetone; 9:1) afforded product **15** followed by **16**. Although we could get an X-ray structure of the major product **15** (crystallization from ethyl acetate+chloroform), this compound underwent degradation/isomerization in solution and hence spectra for the pure isomer could not be obtained.

*Compound* **15**. Pale yellow solid; yield 0.292 g (56%); mp 164–166 °C; $R_f$ (10% acetone/hexane) 0.5; $\nu_{max}$ (KBr) 3424, 2970, 2931, 2854, 1731, 1462, 1369, 1276, 1216, 1084, 1040, 958, 887 cm$^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 8.10–7.27 (m, 10H), 3.07 (d, *J*=6.4 Hz, 1H), 1.34, 1.33, 1.24 (3s, 27H), additional peaks at δ 8.07–7.25, 3.42 (d), 1.56, 1.54, 0.95 were also seen; $\delta_C$ (100 MHz, $CDCl_3$) 171.4, 142.0, 138.3, 135.5, 133.0, 132.8, 130.8, 130.2, 128.9, 128.6, 128.3, 127.7, 126.8, 125.3, 53.2, 52.0, 32.9, 31.8, 31.1 additional peaks at δ 172.3, 141.1, 138.3, 136.5, 135.1, 133.0, 132.1, 130.8, 129.0, 128.3, 127.5, 121.8, 52.2, 52.0, 32.8, 31.7, 31.0 were also seen due to isomerization/transformation; $^{31}$P NMR (162 MHz, $CDCl_3$) 73.07 (d, *J*=6.8 Hz), 3.01 (d, *J*=6.8 Hz) and peaks at δ 74.14 (d, *J*=11.6 Hz), –0.66 (d, *J*=11.6 Hz) were also observed (for the other isomer in solution); HRMS (ESI): [M$^+$+Na], found 551.2317. $C_{27}H_{38}N_4O_3P_2$ requires 551.2317.

*Compound* **16**. Yellow solid; yield 0.129 g (32%); mp 230–234 °C; $R_f$ (10% acetone/hexane) 0.27; $\nu_{max}$ (KBr) 3351, 3065, 2965, 2816, 1699, 1616, 1466, 1383, 1331, 1217, 1011, 837, 748 cm$^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 9.87 (s, 1H), 7.42–7.27 (m, 5H), 7.03 (dd, 1H), 6.65 (d, *J*=7.6 Hz, 1H), 6.55 (dd, 1H), 5.78 (d, *J*=7.6 Hz, 1H), 4.09 (d, *J*=7.2 Hz, 2H), 1.36 (s, 18H); $\delta_C$ (100 MHz, $CDCl_3$): 168.7, 154.2 (d, *J*=126.0 Hz), 142.3, 138.8$_2$, 138.8, 132.6, 132.5, 129.9, 128.8, 127.9, 125.0, 123.3, 123.2, 121.6, 110.3, 51.9, 32.3, 32.2; $^{31}$P NMR (162 MHz, $CDCl_3$) 11.11; HRMS (ESI): [M$^+$+Na], found 434.1974. $C_{23}H_{30}N_3O_2P$ requires 434.1974. X-ray structure was determined for this compound. *Note*: When compound **15** (0.18 g) was heated with toluene/water (9:1) mixture at 110 °C/12 h, the indole derivative **17** could be isolated (0.031 g, ca. 48%). $R_f$ (10% EtOAc/hexane) 0.53. It is a known compound.[24] The $^1$H/$^{13}$C NMR spectra were identical to that for the commercially available (Aldrich) sample.

*4.3.5. [(t-BuNH)P(μ-N-t-Bu)$_2$P(O)–C(SiMe$_3$)=C{–C$_6$H$_4$–NH–C(=O)–}] **19** and [(t-BuNH)$_2$P(O)–CH=C{–C$_6$H$_4$–NH–C(=O)–}] **20**.* The procedure was similar to that for compound **8** using [(*t*-BuNH)P(μ-N-*t*-Bu)]$_2$ (**4b**) [0.56 g, 1.61 mmol] and propargyl alcohol **18** (0.34 g, 1.34 mmol). The reaction time was 6 h at 80 °C and the eluent was hexane/EtOAc (2:1) to obtain solids **19** (eluted first) and **20**.

*Compound* **19**. Yellow solid; yield 0.289 g (42%); mp 242–246 °C; $R_f$ (30% EtOAc/hexane) 0.58; $\nu_{max}$ (KBr) 3431, 2965, 2856, 1718, 1609, 1459, 1371, 1247, 1205, 1071, 890, 843 cm$^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 9.06 (d, *J*=8.0 Hz, 1H), 7.76 (s, 1H), 7.23 (dd, 1H), 7.02 (dd, 1H), 6.76 (d, *J*=7.2 Hz, 1H), 3.50 (d, *J*=5.6 Hz, 1H), 1.40, 1.38 (2s, 27H), 0.43 (s, 9H); $\delta_C$ (100 MHz, $CDCl_3$): 168.7 (d, $^3J$(P–C)=31.0 Hz), 155.0 (d, *J*=90.0 Hz), 150.8, 143.7, 131.9, 131.4, 123.2, 122.2, 109.6, 52.9 (d, *J*=4.0 Hz), 52.4 (d, *J*=15.0 Hz), 33.0 (d, *J*=9.0 Hz), 31.5$_4$, 31.4$_6$ (d, *J*=10.0 Hz), 4.5; $^{31}$P NMR (162 MHz, $CDCl_3$) 92.87 (d, *J*(P–P)=12.0 Hz), 24.50 (d, *J*=12.0 Hz); HRMS (ESI): [M$^+$+H], found

509.2629. $C_{24}H_{42}N_4O_2P_2Si$ requires 509.2631. X-ray structure was determined for this compound.

*Compound* **20**. Yellow solid; yield 0.136 g (30%); mp 118–120 °C; $R_f$ (30% EtOAc/hexane) 0.38; $\nu_{max}$ (KBr) 3265, 2970, 2926, 2876, 1718, 1614, 1528, 1467, 1391, 1366, 1293, 1260, 1221, 1090, 1046, 1013, 920, 838 $cm^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 8.81 (d, *J*=8.0 Hz, 1H), 8.16 (s, 1H), 7.25–6.81 (m, 3H), 6.82 (d, *J*=12.8 Hz, 1H), 2.55 (d, *J*=9.2 Hz, 2H), 1.35 (s, 18H); $\delta_C$ (100 MHz, $CDCl_3$) 169.0 (d, *J*=22.0 Hz), 142.6, 137.6$_4$, 137.5$_9$, 131.4, 130.4 (d, *J*=147.0 Hz), 129.5, 123.0, 121.1, 121.0, 109.8, 52.0, 32.1; $^{31}$P NMR (162 MHz, $CDCl_3$) 9.32; HRMS (ESI): [$M^+$+H], found 336.1840. $C_{17}H_{26}N_3O_2P$ requires 336.1842.

*4.3.6. [(t-BuNH)P(μ-N-t-Bu)$_2$P(O){$C_{15}H_{14}NO_2$}]* ***22***. Compound **4b** (0.338 g, 0.97 mmol) and propargyl alcohol **21** (0.25 g, 0.97 mmol) were dissolved in dry toluene (5 mL) at rt. The resulting solution was heated with stirring at 70 °C for 8 h. The crude product was purified by column chromatography (hexane/EtOAc; 3:2) affording **22** as a pure white solid. This was crystallized from ethyl acetate. Yield 0.434 g (84%); mp 202–206 °C; $R_f$ (40% EtOAc/hexane) 0.35; $\nu_{max}$ (KBr) 3337, 3245, 2975, 2928, 2857, 2631, 1757, 1618, 1543, 1491, 1368, 1209, 1140, 1078, 885, 762 $cm^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 7.39 (d, *J*=7.6 Hz, 1H), 7.09 (~dd, 1H), 6.82 (~dd, 1H), 6.61 (d, *J*=7.6 Hz, 1H), 4.39 (s, 1H), 3.04 (d, *J*=3.6 Hz, 1H), 2.99–2.80 (m, 2H), 2.21–1.67 (m, 7H), 1.49, 1.44, 1.32 (3s, 27H); $\delta_C$ (100 MHz, $CDCl_3$) 171.1, 142.2$_9$, 142.2$_5$, 131.5, 128.9, 120.4, 117.3, 115.6, 91.0, 52.8 (d, *J*=4.0 Hz), 52.5 (d, *J*=4.0 Hz), 52.2 (d, *J*=7.0 Hz), 38.6 (d, *J*=141.0 Hz), 37.1, 35.1, 33.4, 32.6, 32.3, 24.3, 23.9, 22.3; $^{31}$P NMR (162 MHz, $CDCl_3$) 74.31 (slightly broad), 10.28 (d, *J*=5.2 Hz); HRMS (ESI): [$M^+$+Na], found 555.2630. $C_{27}H_{42}N_4O_3P_2$ requires 555.2630. X-ray structure was determined for this compound.

*4.3.7. [(i-PrNH)P(μ-N-t-Bu)$_2$P(O){$C_{15}H_{14}NO_2$}]* ***23*** *and the tetrahydroacridine* ***24***. The procedure was similar to that for compound **22** using [(*i*-PrNH)P(μ-N-*t*-Bu]$_2$ (**4c**) [δ(P) 90.7; 0.329 g, 1.03 mmol] and propargyl alcohol **21** (0.22 g, 0.86 mmol). The reaction time was 8 h and the eluent for column chromatography was hexane/EtOAc (2:1). White solid; yield 0.276 g (62%); mp 192–196 °C; $R_f$ (30% EtOAc/hexane) 0.49; $\nu_{max}$ (KBr) 3343, 3241, 3117, 2969, 2930, 2863, 1757, 1616, 1491, 1399, 1366, 1262, 1209, 1132, 1076, 1015, 986, 887, 760 $cm^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 7.40 (d, *J*=6.8 Hz, 1H), 7.10 (dd, 1H), 6.83 (dd, 1H), 6.62 (d, *J*=8.0 Hz, 1H), 4.37 (s, 1H), 3.53 (s, 1H), 3.04–2.85 (m, 3H), 2.22–1.67 (m, 7H), 1.48, 1.43 (2s, 18H), 1.19, 1.17 (2s, 6H); $\delta_C$ (100 MHz, $CDCl_3$) 171.1, 142.3, 131.6, 129.0, 120.5, 117.3, 115.6, 91.0, 52.8, 52.5, 44.9 (d, *J*=26.0 Hz), 38.3 (d, *J*=143.0 Hz), 37.2, 35.2, 33.3, 32.4, 32.2, 26.2, 24.4, 23.9, 22.3; $^{31}$P NMR (162 MHz, $CDCl_3$) 78.90, 10.22 (*P*(O)–C); HRMS (ESI): [$M^+$+H], found 519.2654. $C_{26}H_{40}N_4O_3P_2$ requires 519.2655. When compound **22** (0.25 g) was heated with toluene/water (9:1) mixture at 110 °C/12 h, tetrahydroacridine **24** could be isolated (0.031 g, ca. 36%). It is a known compound.[16a] The values of $\delta_H$ and $\delta_C$ were identical to that reported before (see Supplementary data). HRMS (ESI): [$M^+$+H], found 184.1124. $C_{13}H_{13}N$ requires 184.1127.

### 4.4. Synthesis of phosphorus containing and phosphorus free *N*-heterocycles [26–32], [35–47]

*4.4.1. Compounds* ***26***–***28*** *(and* ***17****).* The procedure was same as that for compound **15** using P(III)–Cl precursor **5**[25] (0.681 mL, 4.93 mmol), propargyl alcohol **10** (0.595 g, 2.35 mmol), and $NEt_3$ (0.687 mL, 4.93 mmol). The reaction time was 8 h at 70 °C. The reaction mixture showed **26**+**27** (total 71%) along with **28** (ca. 12%). Using hexane/EtOAc (3:2) mixture as the eluent, we isolated compounds **26** (eluted last), **27** (eluted second), and **28** (eluted first).

*Compound* **26**. Yellow solid; yield 0.381 g (31%); mp 196–198 °C; [found: C, 58.12; H, 5.61; N, 2.65. $C_{25}H_{29}NO_7P_2$ requires C, 58.03; H, 5.65; N, 2.71%].; $R_f$ (40% EtOAc/hexane) 0.22; $\nu_{max}$ (KBr) 2965, 1728, 1601, 1466, 1408, 1262, 1061, 1019, 799 $cm^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 8.56 (d, *J*=8.0 Hz, 1H), 7.73 (d, *J*=8.0 Hz, 1H), 7.45–7.27 (m, 6H), 7.17 (t, 1H), 4.31–3.52 (m, 8H), 1.36, 1.24, 0.83, 0.74 (4s, 12H); $\delta_C$ (100 MHz, $CDCl_3$) 167.8 (d, *J*=26.0 Hz), 141.8, 138.9 (d, *J*=167.0 Hz), 136.1, 135.6, 135.5, 132.5, 128.5, 128.3$_3$, 128.2$_6$, 128.2, 127.6, 124.0, 121.4, 121.3, 114.0, 79.4 (d, *J*=7.0 Hz), 77.3 (d, *J*=7.0 Hz), 32.4 (dd, *J*=7.0 Hz), 22.5, 22.0, 20.8, 20.4; $^{31}$P NMR (162 MHz, $CDCl_3$) 3.47, −14.69; LC/MS *m*/*z* 518 $[M+1]^+$.

*Compound* **27**. Yellow solid; yield 0.35 g (40%); mp 172–174 °C; $R_f$ (40% EtOAc/hexane) 0.44; $\nu_{max}$ (KBr) 3238, 2981, 2964, 2926, 1726, 1622, 1468, 1392, 1337, 1227, 1200, 1052, 1014, 986, 953 $cm^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 8.47 (d, *J*=8.0 Hz, 1H), 8.17 (s, 1H), 7.42–7.23 (m, 6H), 7.02 (t, 1H), 6.65 (d, *J*=7.6 Hz, 1H), 3.90–3.56 (m, 4H), 1.21 (s, 3H), 0.74 (s, 3H); $\delta_C$ (100 MHz, $CDCl_3$) 167.0 (d, *J*=25.0 Hz), 142.5, 137.9 (d, *J*=159.0 Hz), 137.0, 136.2, 136.1, 131.9, 128.4, 128.3$_3$, 128.2$_7$, 128.2, 128.0, 122.4, 120.5, 120.4, 109.7, 77.1 (d, *J*=7.0 Hz), 32.4 (d, *J*=7.0 Hz), 22.0, 20.9; $^{31}$P NMR (162 MHz, $CDCl_3$) 4.19; HRMS (ESI): [$M^+$+H], found 370.1210. $C_{20}H_{20}NO_4P$ requires 370.1209.

*Compound* **28**. White solid; yield 0.108 g (12%); mp 78–80 °C; $R_f$ (40% EtOAc/hexane) 0.59; $\nu_{max}$ (KBr) 3063, 2959, 2926, 2855, 1655, 1523, 1463, 1370, 1299, 1271, 1129, 1052, 1014, 855 $cm^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 7.87 (d, *J*=8.0 Hz, 1H, Ar–*H*), 7.72 (dd, 1H, Ar–*H*), 7.63 (d, *J*=7.6 Hz, 1H, Ar–*H*), 7.46–7.25 (m, 5H, Ar–*H*), 6.69 (d, *J*=3.2 Hz, 1H, Ar–*H*), 3.67–3.49 (m, 4H, O*CH*$_2$), 1.26, 0.61 (2s, 6H, *CH*$_3$); $\delta_C$ (100 MHz, $CDCl_3$) 141.8, 138.3, 133.0, 130.4, 129.2, 128.7, 128.2, 124.0, 122.7, 120.8, 114.2, 109.6, 77.8, 77.7, 31.9, 22.0, 20.1; $^{31}$P NMR (162 MHz, $CDCl_3$) −10.68; HRMS (ESI): [$M^+$+Na], found 364.1076. $C_{19}H_{20}NO_3P$ requires 364.1079. Passing this compound (0.10 g, 0.29 mmol) through a basic alumina column afforded the indole **17** (0.0512 g, 90%; see above[24]).

*4.4.2. Compounds* ***29*** *and* ***30****.* The procedure was similar to that for compound **15** using P(III)–Cl precursor **5** (0.314 mL, 2.27 mmol), propargyl alcohol **25** (0.268 g, 1.08 mmol), and $NEt_3$ (0.332 mL, 2.27 mmol) The reaction time was 6 h at 70 °C. The eluent was hexane/EtOAc (3:2) to obtain solids **29** (eluted second) and **30** (eluted first).

*Compound* **29**. Yellow solid; yield 0.159 g (40%); mp 170–172 °C; [found: C, 62.71; H, 7.18; N, 3.91. $C_{19}H_{26}NO_4P$ requires C, 62.80; H, 7.21; N, 3.85%]; $R_f$ (40% EtOAc/hexane) 0.4; $\nu_{max}$ (KBr) 3278, 2963, 2932, 1711, 1622, 1470, 1260, 1057, 1015, 797 $cm^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 8.64 (s, 1H), 8.31 (d, *J*=8.0 Hz, 1H), 7.24–6.95 (m, 2H), 6.78 (d, *J*=8.0 Hz, 1H), 4.28–3.86 (m, 4H), 3.32–3.23 (m, 2H), 1.66–1.23 (m, 6H), 1.15 (s, 3H), 1.05 (s, 3H), 0.90 (t, 3H); $\delta_C$ (100 MHz, $CDCl_3$) 168.7 (d, *J*=27.8 Hz), 141.6 (d, *J*=162.8 Hz), 141.3, 135.6, 135.5, 130.9, 127.3, 122.2, 120.9, 109.4, 76.0 (d, *J*=6.1 Hz), 32.6 (d, *J*=5.6 Hz), 32.2, 29.7 (d, *J*=77.3 Hz), 22.4, 21.7, 21.6, 14.1; $^{31}$P NMR (162 MHz, $CDCl_3$) 11.13; LC/MS *m*/*z* 362 $[M-1]^+$; HRMS (ESI): [$M^+$+H], found 364.1676. $C_{19}H_{26}NO_4P$ requires 364.1678.

*Compound* **30**. White solid; yield 0.121 g (33%); mp 68–70 °C; [found: C, 64.58; H, 7.76; N 4.25. $C_{18}H_{26}NO_3P$ requires C, 64.46; H, 7.81; N, 4.18%]; $R_f$ (40% EtOAc/hexane) 0.6; $\nu_{max}$ (KBr) 2959, 2932, 1586, 1564, 1454, 1375, 1302, 1155, 1123, 1057, 1009, 947 $cm^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 7.76 (d, *J*=8.4 Hz, 1H), 7.51 (d, *J*=7.2 Hz, 1H), 7.27–7.19 (m, 2H), 6.47 (d, *J*=3.2 Hz, 1H), 4.17–3.95 (m, 4H), 2.91 (t, 2H), 1.83–1.41 (m, 6H), 1.38 (s, 3H), 0.93 (t, 3H), 0.87 (s, 3H); $\delta_C$ (100 MHz, $CDCl_3$) 143.2$_2$, 143.1$_6$, 138.2, 138.1, 130.9, 130.7, 129.1, 128.3, 123.1, 122.3, 120.2, 113.4, 107.0$_5$, 106.9$_6$, 78.1 (d, *J*=6.6 Hz), 32.4 (d, *J*=5.6 Hz), 31.7, 28.6, 28.1, 22.6, 22.0, 20.7, 14.1; $^{31}$P NMR (162 MHz, $CDCl_3$) −8.87; LC/MS *m*/*z* 336 $[M+1]^+$.

*4.4.3. Compound* ***31****.* This product was obtained by adapting the procedure same as that for compound **15** by using P(III)–Cl precursor **5** (0.532 mL, 3.85 mmol), propargyl alcohol **18** (0.458 g, 1.84 mmol), and $NEt_3$ (0.56 mL, 3.85 mmol). Reaction time was 8 h

at 70 °C. It was isolated by column chromatography [hexane/ethyl acetate (2:3)] as a white solid. Yield 0.327 g (61%); mp 296–298 °C; [found: C, 57.19; H, 5.56; N, 4.68. $C_{14}H_{16}NO_4P$ requires C, 57.34; H, 5.50; N, 4.78%]; $R_f$ (60% EtOAc/hexane) 0.3; $\nu_{max}$ (KBr) 3160, 3106, 3054, 3019, 2965, 2897, 1651, 1561, 1497, 1476, 1429, 1372, 1240, 1155, 1134, 1076, 1020, 947 $cm^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 11.73 (s, 1H), 8.76 (d, $J$=18.0 Hz, 1H), 7.71–7.27 (m, 4H), 4.76–4.12 (m, 4H), 1.39, 1.14 (2s, 6H); $\delta_C$ (125 MHz, $CDCl_3$) 163.1, 151.8 (d, $J$=8.4 Hz), 140.1, 133.0, 129.7, 123.3, 120.9, 119.1, 119.0, 115.6, 77.8 (d, $J$=6.9 Hz) 32.9 (d, $J$=9.0 Hz), 22.5, 21.2; $^{31}$P NMR (162 MHz, $CDCl_3$) 6.06; LC/MS $m/z$ 292 $[M-1]^+$.

*4.4.4. Compound **32**.* Passing compound **30** (0.11 g, 0.33 mmol) through a basic alumina column afforded the indole **32** as a white solid. $R_f$ (10% EtOAc/hexane) 0.54; yield: 0.052 g (84%). It is a known compound (see Supplementary data for NMR spectra).[24]

*4.4.5. Compounds **35** and **36**.* The procedure was similar to that for compound **15** using $Ph_2PCl$ (**6**) (0.396 mL, 2.21 mmol), propargyl alcohol **10** (0.47 g, 1.84 mmol), and $NEt_3$ (0.31 mL, 2.21 mmol). The reaction time was 4 h at 70 °C and the eluent was hexane/EtOAc (3:2) to obtain compounds **35** (eluted second) and **36** (eluted first).

*Compound* **35**. Yellow solid; yield 0.235 g (30%); mp 224–226 °C; $R_f$ (40% EtOAc/hexane) 0.36; $\nu_{max}$ (KBr) 3134, 3068, 2921, 2849, 1715, 1616, 1468, 1436, 1326, 1211, 1151, 1118, 921 $cm^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 8.36 (d, $J$=8.0 Hz, 1H, Ar–*H*), 8.03 (br s, 1H, N*H*), 7.60–6.62 (m, 18H, Ar–*H*); $\delta_C$ (100 MHz, $CDCl_3$) 166.9 (d, $J$=17.0 Hz, *C*=O), 143.5 (d, $^1J$(P–C)=84 Hz, P*C*), 142.5, 138.6, 137.5, 137.4, 132.2, 132.1, 132.0, 131.6, 131.4, 130.3, 129.9, 128.5, 128.3, 128.1, 128.0, 127.9, 127.0, 122.2, 120.6, 109.6; $^{31}$P NMR (162 MHz, $CDCl_3$) 30.67; HRMS (ESI): [$M^+$+H], found 422.1309. $C_{27}H_{20}NO_2P$ requires 422.1311.

*Compound* **36**. Brown colored gummy liquid; yield 0.376 g (52%); $R_f$ (40% EtOAc/hexane) 0.59; $\nu_{max}$ (neat) 3058, 2926, 2849, 1594, 1436, 1310, 1255, 1222, 1123, 1074, 1008, 811 $cm^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 7.61–6.97 (m, 19H, Ar–*H*), 6.64 (d, $J$=4.0 Hz, 1H, Ar–*H*); $\delta_C$ (100 MHz, $CDCl_3$) 144.1$_4$, 144.1$_0$, 140.7$_8$, 140.7$_5$, 133.4, 132.3$_8$, 132.3$_6$, 132.2, 132.1, 130.9, 130.6, 130.5, 130.0$_4$, 129.9$_8$, 128.6, 128.4$_4$, 128.3$_5$, 128.3, 127.6, 127.5, 123.1, 122.4, 120.5, 116.2, 110.9, 110.8; $^{31}$P NMR (162 MHz, $CDCl_3$) 23.83; HRMS (ESI): [$M^+$+H], found 394.1360. $C_{26}H_{20}NOP$ requires 394.1362.

*4.4.6. Compounds **37–39**.* The procedure was similar to that for compound **15** using $Ph_2PCl$ (**6**) (0.381 mL, 2.12 mmol), propargyl alcohol **25** (0.25 g, 1.01 mmol), and $NEt_3$ (0.311 mL, 2.12 mmol). The reaction time was 4 h at 70 °C and the eluent was hexane/EtOAc (3:2) to obtain compounds **37** (eluted last), **38** (eluted second), and **39** (eluted first).

*Compound* **37**. Brown colored gummy liquid; yield 0.112 g (26%); $R_f$ (40% EtOAc/hexane) 0.33; $\nu_{max}$ (neat) 3346, 3072, 2928, 2859, 1713, 1622, 1470, 1435, 1327, 1173, 1105, 1022, 752 $cm^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 8.27 (d, $J$=8.0 Hz, 1H), 7.82 (br s, 1H), 7.78–6.68 (m, 13H), 2.90 (br, 2H), 1.43–0.86 (m, 6H), 0.71 (t, 3H); $\delta_C$ (125 MHz, $CDCl_3$) 168.3 (d, $J$=18.8 Hz), 147.6 (d, $J$=81.3 Hz), 141.1, 137.0, 132.3$_4$, 132.3$_2$, 132.2$_3$, 132.1$_5$, 131.9, 131.1, 130.5, 129.3, 128.7, 128.6, 122.0, 121.3, 121.2, 116.2, 109.1, 32.0, 31.6 (d, $J$=7.5 Hz), 28.5, 21.9, 14.0; $^{31}$P NMR (162 MHz, $CDCl_3$) 33.61; HRMS (ESI): [$M^+$+H], found 416.1774. $C_{26}H_{26}NO_2P$ requires 416.1780.

*Compound* **38**. White solid; yield 0.083 g (20%); mp 98–100 °C (bubbling); $R_f$ (40% EtOAc/hexane) 0.5; $\nu_{max}$ (KBr) 3052, 2959, 2921, 2855, 1726, 1622, 1589, 1436, 1216, 1195, 1118, 1063, 975, 762 $cm^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 8.07–7.19 (m, 14H), 7.11 (s, 1H), 2.69–2.24 (m, 2H), 1.36 (br s, 6H), 0.94 (t, 3H); $\delta_C$ (125 MHz, $CDCl_3$) 171.0 (d, $J$=3.8 Hz), 140.2, 135.8, 135.5, 133.6$_3$, 133.5$_6$, 132.9, 132.8$_7$, 132.8$_5$, 132.6, 130.5, 132.4, 132.3, 130.7, 130.1, 130.0, 129.1, 128.9, 128.8, 128.7, 128.2, 124.9, 35.6, 31.7, 29.0, 22.6, 14.2; $^{31}$P NMR (162 MHz, $CDCl_3$) 28.52; HRMS (ESI): [$M^+$+H], found 432.1722. $C_{26}H_{26}NO_3P$ requires 432.1729.

*Compound* **39**. Brown gummy liquid; yield 0.108 g (28%); [found: C, 77.65; H, 6.72; N, 3.71. $C_{25}H_{26}NOP$ requires C, 77.50; H, 6.76; N, 3.62%]; $R_f$ (40% EtOAc/hexane) 0.67; $\nu_{max}$ (neat) 3054, 2928, 2857, 1583, 1453, 1229, 1125, 1053, 729 $cm^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 7.67–7.46 (m, 11H), 7.08 (t, 1H), 6.82 (t, 1H), 6.56 (d, $J$=8.4 Hz, 1H), 6.51 (s, 1H), 2.73 (t, 2H), 1.63–1.21 (m, 6H), 0.82 (t, 3H); $\delta_C$ (100 MHz, $CDCl_3$) 146.4, 139.6, 132.9, 132.4, 132.1, 132.0, 131.1, 130.9, 129.0, 128.9, 121.9, 121.6, 119.8, 114.3, 106.9$_4$, 106.8$_8$, 31.4, 29.7, 28.5, 22.4, 14.0; $^{31}$P NMR (162 MHz, $CDCl_3$) 26.11; LC/MS $m/z$ 388 $[M+1]^+$.

*4.4.7. Compound **40**.* The procedure was similar to that for compound **15** using $Ph_2PCl$ (**6**) (0.474 mL, 2.64 mmol), propargyl alcohol **33** (0.62 g, 2.20 mmol), and $NEt_3$ (0.368 mL, 2.64 mmol). The reaction time was 4 h at 70 °C and the eluent was hexane/EtOAc (3:2) to obtain compound **40** as a white crystalline solid. Yield 0.632 g (62%); mp 142–144 °C (bubbling); $R_f$ (40% EtOAc/hexane) 0.43; $\nu_{max}$ (KBr) 2953, 2915, 2871, 2844, 1737, 1479, 1441, 1370, 1216, 1118, 888 $cm^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 8.04–7.16 (m, 13H), 7.02 (s, 1H), 2.69–2.24 (m, 2H), 1.36–1.33 (m, 6H), 0.94 (t, 3H); $\delta_C$ (125 MHz, $CDCl_3$) 170.4 (d, $J$=5.0 Hz), 138.7, 137.1, 135.0$_4$, 134.9$_6$, 134.1, 133.8, 133.1, 133.0, 132.5, 132.4, 132.3, 132.2, 130.2, 129.9, 129.7, 128.9, 128.8, 128.6, 128.4, 126.1$_9$, 126.1$_6$, 35.5, 31.6, 28.8, 22.5, 14.1; $^{31}$P NMR (162 MHz, $CDCl_3$) 28.65; HRMS (ESI): [$M^+$+H and $M^+$+H+2], found 466.1337 and 468.1287. $C_{26}H_{25}ClNO_3P$ requires 466.1340 and 468.1340.

*4.4.8. Compounds **41** and **42**.* The procedure was similar to that for compound **15** using $Ph_2PCl$ (**6**) (0.269 mL, 1.50 mmol), propargyl alcohol **34** (0.407 g, 1.25 mmol), and $NEt_3$ (0.21 mL, 1.50 mmol). The reaction time was 4 h at 70 °C and the eluent was hexane/EtOAc (3:2) to obtain compounds **41** (eluted second), **42** (eluted first).

*Compound* **41**. White crystalline solid; yield 0.294 g (26%); mp 148–150 °C (bubbling); $R_f$ (40% EtOAc/hexane) 0.5; $\nu_{max}$ (KBr) 3058, 2953, 2921, 2855, 1742, 1611, 1595, 1474, 1436, 1364, 1222, 1123, 1058, 992, 882 $cm^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 8.03–7.76 (m, 4H), 7.62–7.29 (m, 9H), 7.01 (s, 1H), 2.69–2.24 (m, 2H), 1.38–1.32 (m, 6H), 0.93 (t, 3H); $\delta_C$ (100 MHz, $CDCl_3$) 170.4 (d, $J$=4.0 Hz), 139.2, 137.2, 135.3$_3$, 135.2$_5$, 134.0, 133.2, 133.1, 133.0, 132.6, 132.5, 132.4, 132.3, 132.2, 129.9, 129.7, 129.0, 128.8, 128.6, 128.4, 126.4$_2$, 126.3$_9$, 121.7, 35.5, 31.6, 28.8, 22.5, 14.1; $^{31}$P NMR (162 MHz, $CDCl_3$) 28.83; HRMS (ESI): [$M^+$+H and $M^+$+H+2], found 510.0831 and 512.0815. $C_{26}H_{25}BrNO_3P$ requires 510.0834 and 512.0834.

*Compound* **42**. Green gummy liquid; yield 0.637 g (62%); $R_f$ (40% EtOAc/hexane) 0.59; $\nu_{max}$ (neat) 2959, 2926, 2844, 1589, 1436, 1271, 1227, 1123 $cm^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 7.64–7.47 (m, 11H, Ar–*H*), 6.92 (d, $J$=8.8 Hz, 1H, Ar–*H*), 6.48 (d, $J$=8.8 Hz, 1H, Ar–*H*), 6.44 (1s, 1H, Ar–*H*), 2.66 (t, 2H, C*H*$_2$), 1.64–1.56 (m, 2H, C*H*$_2$), 1.20–1.16 (m, 4H, C*H*$_2$), 0.81 (t, 3H, C*H*$_3$); $\delta_C$ (100 MHz, $CDCl_3$) 147.8, 138.4, 133.2, 132.8, 132.7, 132.1, 132.0, 131.9, 130.6, 129.2, 129.0, 124.7, 122.4, 115.7, 115.1, 106.3, 106.2, 31.4, 29.7, 28.4, 22.4, 14.0; $^{31}$P NMR (162 MHz, $CDCl_3$) 26.51; HRMS (ESI): [$M^+$+H and $M^+$+H+2], found 466.0936 and 468.0919. $C_{25}H_{25}BrNOP$ requires 466.0936 and 468.0936.

*4.4.9. Compounds **43–45**.* In a round bottomed flask equipped with 0.18 g (0.42 mmol) of phosphono-heterocycle **38**, toluene/water mixture (2 mL; 9:1 v/v) was added and the content was heated with stirring at 110 °C for 8 h. After the completion of the reaction (TLC), the solvent was removed under reduced pressure. The crude product was purified by column chromatography (hexane/EtOAc; 9:1) affording **43**. Compounds **44** and **45** were prepared similarly.

*Compound* **43**. Yield 0.054 g (59%); $R_f$ (10% EtOAc/hexane) 0.55; It is a known compound.[18] HRMS and X-ray structure were not reported for this compound. HRMS (ESI): [$M^+$+H], found 216.1389.

$C_{14}H_{17}NO$ requires 216.1389. X-ray structure was determined for this compound.

*Compound* **44**. White solid; yield 0.042 g (68% using 0.116 g, (0.25 mmol) of phosphono heterocycle **40**); mp 158–160 °C; $R_f$ (10% EtOAc/hexane) 0.46; $\nu_{max}$ (KBr) 3156, 2992, 2959, 2926, 2855, 1666, 1573, 1479, 1414, 1370, 1216, 1079, 942 $cm^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 11.12 (br s, 1H, N*H*), 7.52 (s, 1H, Ar–*H*), 7.51 (d, *J*=2.4 Hz, 1H, Ar–*H*), 7.41–7.38 (m, 1H, Ar–*H*), 7.25 (d, *J*=8.4 Hz, 1H, Ar–*H*), 2.66 (t, 2H, CH($CH_2$)), 1.72–1.65 (m, 2H, $CH_2$), 1.42–1.39 (m, 4H, $CH_2$), 0.93 (t, 3H, $CH_3$); $\delta_C$ (100 MHz, $CDCl_3$) 164.2 (*C*=O), 135.9, 135.4, 129.5, 127.7, 126.3, 121.4, 117.0, 31.7, 30.3, 28.0, 22.6, 14.1; HRMS (ESI): [$M^+$+H and $M^+$+H+2], found 250.1000 and 252.0963. $C_{14}H_{16}ClNO$ requires 250.0999 and 252.0999.

*Compound* **45**. White solid; yield 0.085 g (64%; using 0.23 g (0.47 mmol) of phosphono heterocycle **41**); mp 148–150 °C; $R_f$ (10% EtOAc/hexane) 0.53; $\nu_{max}$ (KBr) 3151, 2959, 2915, 2849, 1666, 1616, 1573, 1474, 1414, 1370, 1255, 1205, 1063, 932 $cm^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 11.03 (br s, 1H, N*H*), 7.66 (s, 1H, Ar–*H*), 7.53–7.51 (m, 2H, Ar–*H*) 7.18 (d, *J*=8.8 Hz, 1H, Ar–*H*), 2.66 (t, 2H, $CH_2$), 1.70–1.62 (m, 2H, $CH_2$), 1.40–1.38 (m, 4H, $CH_2$), 0.93 (t, 3H, $CH_3$); $\delta_C$ (100 MHz, $CDCl_3$) 163.8 (*C*=O), 136.2, 135.9, 135.3, 132.2, 129.5, 121.9, 117.1, 115.0, 31.7, 30.3, 28.0, 22.6, 14.1; HRMS (ESI): [$M^+$+H and $M^+$+H+2], found 294.0494 and 296.0477. $C_{14}H_{16}BrNO$ requires 294.0494 and 296.0494.

*4.4.10. Compounds **17**, **32**, **46**, and **47**.* In a round bottomed flask equipped with 0.20 g (0.51 mmol) of phosphono indole **36**, 1 g of basic alumina and 3 mL of ethyl acetate were added. Then the mixture was stirred at rt for 15 h. After the completion of the reaction (TLC), the mixture was filtered and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (hexane/EtOAc; 9:1) affording **17** as a white solid (known compound;[24] also see above). Yield 0.086 g (88%). Compound **32** was prepared by passing **39** through alumina column using hexane/ethyl acetate (4:1). Yield 0.084 g [87%; using 0.28 g (0.52 mmol) of phosphono-indole **39**; also see above in 4.4.4].

*Compound* **46**. The phosphorus precursor (similar to **39**) [$\delta$(P) 26.56] of **46** could be isolated in only 95% purity, but **46** could be readily obtained from this by passing through a basic alumina column [hexane/ethyl acetate (9:1)]. Pale yellow solid; yield 0.065 g (92%; using 0.134 g (0.32 mmol) of corresponding phosphono indole); mp 40–42 °C; $R_f$ (10% EtOAc/hexane) 0.71; $\nu_{max}$ (KBr) 3403, 2932, 2849, 1463, 1447, 1408, 1085, 871 $cm^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 7.89 (br s, 1H, N*H*), 7.50 (1s, 1H, Ar–*H*), 7.20–7.06 (m, 2H, Ar–*H*), 6.20 (1s, 1H, Ar–*H*), 2.74 (t, 2H, $CH_2$), 1.76–1.71 (m, 2H, $CH_2$), 1.40–1.36 (m, 4H, $CH_2$), 0.93 (t, 3H, $CH_3$); $\delta_C$ (100 MHz, $CDCl_3$) 141.7, 134.2, 130.1, 125.2, 121.1, 119.2, 111.3, 99.3, 31.5, 28.8, 28.3, 22.5, 14.1; HRMS (ESI): [$M^+$+H and $M^+$+H+2], found 222.1046 and 224.1013. $C_{13}H_{16}ClN$ requires 222.1050 and 224.1050.

*Compound* **47**. This was isolated by passing a solution of **42** in hexane/ethylacetate(9:1) through basic alumina column. Pale yellow solid; yield 0.159 g (93%; using 0.3 g (0.64 mmol) of phosphono indole **42**); mp 46–48 °C; $R_f$ (10% EtOAc/hexane) 0.67; $\nu_{max}$ (KBr) 3397, 2959, 2921, 2849, 1567, 1452, 1408, 1315, 1260, 1052, 877 $cm^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 7.86 (br s, 1H, N*H*), 7.68 (1s, 1H, Ar–*H*), 7.23–7.12 (m, 2H, Ar–*H*), 6.20 (1s, 1H, Ar–*H*), 2.73 (t, 2H, $CH_2$), 1.76–1.69 (m, 2H, $CH_2$), 1.41–1.35 (m, 4H, $CH_2$), 0.96 (t, 3H, $CH_3$); $\delta_C$ (100 MHz, $CDCl_3$) 141.6, 134.5, 130.7, 123.6, 122.2, 112.7, 111.8, 99.1, 31.5, 28.8, 28.2, 22.5, 14.1; HRMS (ESI): [$M^+$+H and $M^+$+H+2], found 266.0545 and 268.0525. $C_{13}H_{16}BrN$ requires 266.0545 and 268.0545.

### 4.5. Synthesis of P–N connected compound 48

*4.5.1. {[–C(=O)–$CH_2$–$CH_2$–C(=O)–]–N–P(=O)–N-t-Bu}$_2$ **48**.* A solution of *N*-hydroxy succinimide (0.824 g, 7.16 mmol) and $NEt_3$ (1.0 mL, 7.16 mmol) in THF (20 mL) was stirred at 0 °C for 5 min, and then [ClP–N(*t*-Bu)]$_2$ (**4a**) (0.985 g, 3.58 mmol) dissolved in THF (20 mL) was added drop-wise at 0 °C (20 min). The mixture was warmed to rt (25 °C) and then heated with stirring at 60 °C for 10 h. The mixture was filtered and solvent was removed under reduced pressure. The residue was treated with ethyl acetate when white crystalline compound **48** settled down at the bottom of the flask. This compound was crystallized from ethyl acetate/chloroform mixture (1:2). Yield 1.14 g (74%); mp 210–214 °C; $R_f$ (25% EtOAc/hexane) 0.48; $\nu_{max}$ (KBr) 2984, 1734, 1476, 1431, 1373, 1281, 1223, 1111, 1047, 1020, 995, 943, 910, 824 $cm^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 2.77 (s, 8H), 1.46 (s, 18H); $\delta_C$ (100 MHz, $CDCl_3$) 175.8, 58.3, 30.1, 29.8; $^{31}P$ NMR (162 MHz, $CDCl_3$) −17.34; HRMS (ESI): ($M^+$+H), found 433.1407. $C_{16}H_{26}N_4O_6P_2$ requires 433.1407. X-ray structure was determined for this compound.

X-ray data for **9a**, **12**, **13**, **15**, **16**, **19**, **22**, **26**, **29**, **40**, **43**, and **48** were collected on Bruker AXS SMART or OXFORD diffractometer at 296 K using Mo-$K_\alpha$ ($\lambda$=0.71073 Å) radiation. The structures were solved by direct methods and refined by full matrix least-squares methods using standard procedures.[26] Absorption corrections were done using the *SADABS* program, where applicable. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were fixed by geometry or located by difference Fourier map; subsequently a riding model was used. Some of the methyl carbon atoms of the *tert*-butyl groups in these compounds have high thermal parameters, but these do not affect the overall structure around cyclophosphazane skeleton and hence we have not tried to model them rigorously. Data quality was moderate for **43**. Specifically, in the structures of compounds **12**, and **16**, disorder is found at the *tert*-butyl carbons attached to C9 and (N4, C24, C28) respectively. Crystallographic data as well as CCDC numbers are summarized in Table S1a–c for compounds **9a**, **12**, **13**, **15**, **16**, **19**, **22**, **26**, **29**, **40**, **43**, and **48** in the Supplementary data.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## Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2014.02.064.

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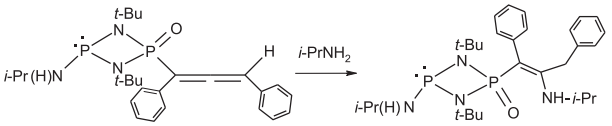
14. We wish to mention that, in addition to the cyclophosphazanyl-allene **9**, we have isolated another minor P–C bonded enamine product **9a** (ca. 34%; Fig. S12) resulting from the nucleophilic addition of liberated isopropylamine to the allene **9**. Such reactions have been reported by us before. See: Kumara Swamy, K. C.; Balaraman, E.; Satish Kumar, N. *Tetrahedron* **2006**, *62*, 10152




**9** [δ(P) 9.4, 83.6] **9a** [δ(P) 28.8, 85.5; 34%; X-ray] .

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