NITROGEN HETEROCYCLES VIA PHOSPHORUS BASED ALLENE INTERMEDIATES AND [Cu]-CATALYZED RING EXPANSION/ HYDROARYLATION OF 3-DIENYLINDOLES

A THESIS

SUBMITTED FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

BY

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Dedicated to

Tatayya-Nanamma
Amma-Nanna
And
Kumari

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STATEMENT

I hereby declare that the matter embodied in this thesis is the result of investigations carried out by me in the School of Chemistry, University of Hyderabad, Hyderabad, under the supervision of Prof. K. C. Kumara Swamy.

In keeping with the general practice of reporting scientific observations, due acknowledgements have been made wherever the work described is based on the findings of other investigators.

Hyderabad

August 2014

Gangadhararao Golime

CERTIFICATE

This is to certify that the work described in this thesis entitled *“Nitrogen Heterocycles via Phosphorus Based Allene Intermediates and [Cu]-Catalyzed Ring expansion/ Hydroarylation of 3-Dienylindoles”* has been carried out by Mr. Gangadhararao Golime, under my supervision and the same has not been submitted elsewhere for any degree.

Hyderabad

August 2014

Prof. K. C. Kumara Swamy

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Gangadhararao Golime

LIST OF PUBLICATIONS

1. Unusual nitrogen based heterocycles via allenic intermediates from the reaction of propargyl alcohols with P(III) substrates
   G. Gangadhararao and K. C. Kumara Swamy.
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2. Allenylphosphine oxides as simple scaffolds for phosphinoylindoles and phosphinoylisocoumarins
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   Beilstein J. Org. Chem. **2014,** *10,* 996.

3. Cyclodiphosph(III)azane chemistry- Ylides from the reaction of $[(RNH)P\text{-}N(t\text{-}Bu)]_2$ [R = *t*-Bu, *i*-Pr] with dimethyl maleate and chiral ansa-type derivatives from reaction of $[ClP\text{-}N(t\text{-}Bu)]_2$ with a substituted BINOL
   K. C. Kumara Swamy, **G. Gangadhararao**, Venu Srinivas, N. N. Bhuvan Kumar, E. Balaraman and Manab Chakravarty.
   Inorg. Chim. Acta **2011**, *372*, 374.

4. The Phospha-Michael addition product $\{(t\text{-}BuNH)P(\mu\text{-}N\text{-}t\text{-}Bu)_2P(=N\text{-}t\text{-}Bu)\text{-}C(=CH_2)CH(p\text{-}CH_3O\text{-}C_6H_4)\ P(O)[(OCH_2C(CH_3)_2CH_2O)]\}$
   G. Gangadhararao and Venu Srinivas.
   Acta Cryst. **2011**, *E67*, o1212.

5. Exploring organic reactions using simple cyclodiphosphazanes
   K. C. Kumara Swamy, **G. Gangadhararao**, R. Rama Suresh, N. N. Bhuvan Kumar and Manab Chakravarty.
   J. Organomet. Chem. **2010**, *695*, 1042.

6. Cyclodiphosphazanes as synthetic probes: P-C/P-N bond formation from the reaction with functionalized propargyl alcohols and *N*-hydroxy substrates
   G. Gangadhararao and K. C. Kumara Swamy (*submitted*)

7. Copper-catalyzed aerobic oxidative ring-expansion/ hydroarylation reactions of 3-dienylindoles: A Novel approach to cyclopenta[c]quinolines
   G. Gangadhararao, Anasuyamma Uruvakilli and K. C. Kumara Swamy (*to be communicated*)

8. Synthesis of phosphorus based quinolines *via* base catalyzed intermolecular cyclization reactions of allenylphosphonates with *N*-(2-formylphenyl)benzamide
G. Gangadhararao and K. C. Kumara Swamy (*to be communicated*)

9. Synthesis of chiral bis-phosphonylated allenylphosphine oxides from propargyl alcohols
G. Gangadhararao and K. C. Kumara Swamy (*to be communicated*)

Posters presented in symposia

1. Cyclodiphosphazanes as probes for organic transformations
G. Gangadhararao and K. C. Kumara Swamy.
MTIC-XIV, School of Chemistry, University of Hyderabad, Hyderabad, INDIA, Dec-**2011**.

2. Cyclodiphosphazanes as synthetic probes to explore organic reactions
G. Gangadhararao and K. C. Kumara Swamy.
Chemfest-2013 (annual inhouse symposium), School of Chemistry, University of Hyderabad, Feb-**2013** (**Poster & Oral Presentation**).

Synopsis

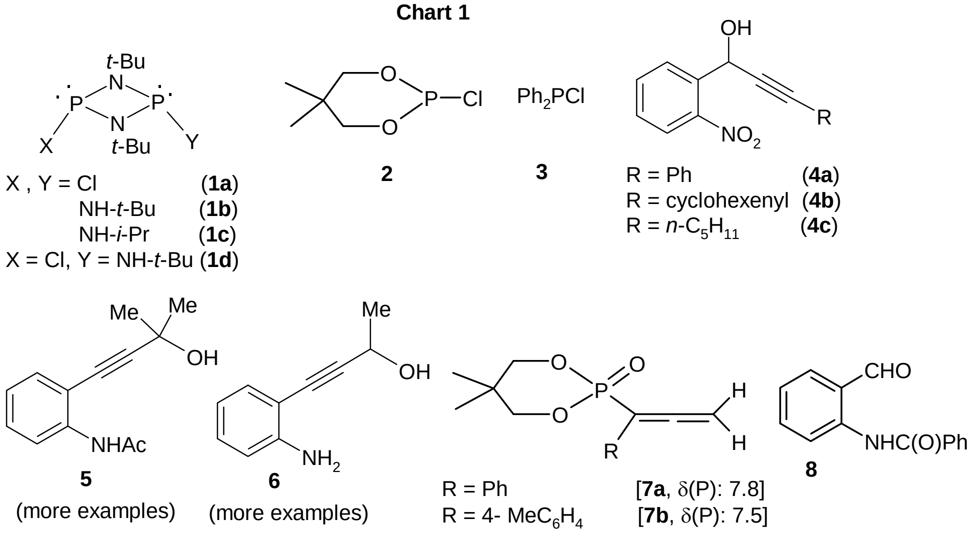
This thesis is divided into two parts: **Part-A** and **Part-B**. **Part-A** deals with the reactions of various P^{III} compounds with functionalized propargyl alcohols that lead to phosphorus based carbo-/hetero-cycles *via in situ* generated allene intermediates. This part also describes intermolecular cyclization/ nucleophilic addition reactions of allenylphosphonates/ allenylphosphine oxides with various nucleophiles. In **Part-B**, reactions of substituted indoles with tertiary propargyl alcohols that afford novel cyclopenta[c]quinolines *via* oxidative dehydrogenation/ring expansion and 3-indenylindoles *via* Friedel-Crafts hydroarylation are discussed.

Each part is subdivided into three chapters: (a) Introduction (literature survey), (b) Results and Discussion and (c) Experimental Section. The compounds synthesized in the present study are, in general, characterized by mp, IR and NMR (^{1}H, ^{13}C & ^{31}P) techniques followed by HRMS or elemental analyses in conjunction with LC-MS. X-ray structure determination is undertaken wherever required. Summary as well as references are given at the end of each part.

PART-A

In Chapter 1, a review of literature on aspects relevant to this part is presented. In Chapter 2, the results obtained on these aspects are discussed while in Chapter 3, the experimental details are described. The precursors used in the present study are shown in Chart 1 [*Note*: The numbering of compounds given here is different from that in the main part of the thesis]. Many more similar precursors which are not listed here are discussed in the thesis in detail. They are prepared by methodologies available (with modifications where necessary) in the literature.

Chart 1

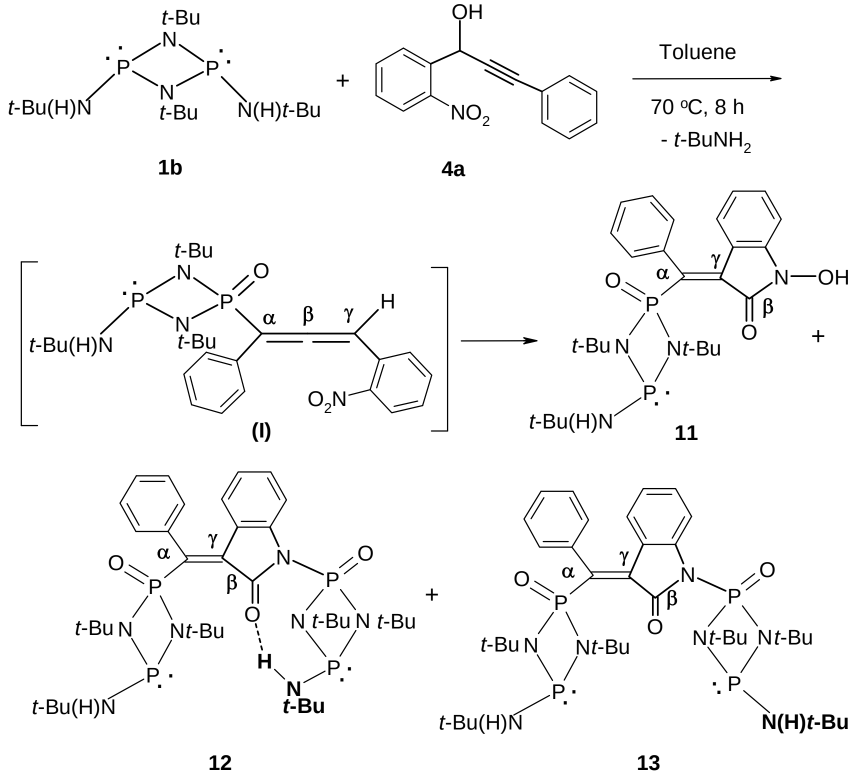


Representative precursors

(i) Reactivity of P^{III} precursors with *o*-nitro functionalized propargyl alcohols and *N*-hydroxy substrates- Synthesis of phosphono- or phosphorus-free heterocycles

Treatment of cyclodiphosphazane $[(t\text{-BuNH})P(\mu\text{-N-}t\text{-Bu})]_2$ (**1b**) with the propargyl alcohol **4a** led to the cyclodiphosphazane based *N*-hydroxy indolinone **11** as the major product and bis**(**cyclodiphosphazanyl)-indolinones **12** and **13** as minor products (Scheme 1). The yields of the bis(cyclophosphazanyl) products **12-13** could be enhanced by increasing the stoichiometry of the cyclophosphazane **1b**. These compounds were formed by substitution of -NH*t*-Bu group by propargyloxy group. The resulting intermediate, by *pseudo*-Claisen type rearrangement, afforded cyclodiphosphazane based allene (**I**) that further underwent cyclization utilizing the -NO_2 functionality in a rather complicated reaction pathway. The structures of compounds **12** and **13** are proven by X-ray crystallography (Figure 1). The difference in the structures of **12** and **13** is related to 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**.

Scheme 1



Stoichiometry used (**1b: 4a**): 1.2:1	**11** (34%)	**12+13** (18%) [+ other products]	
Stoichiometry used (**1b: 4a**): 2:1	**11** (<15%)	**12** (36%)	**13** (28%)

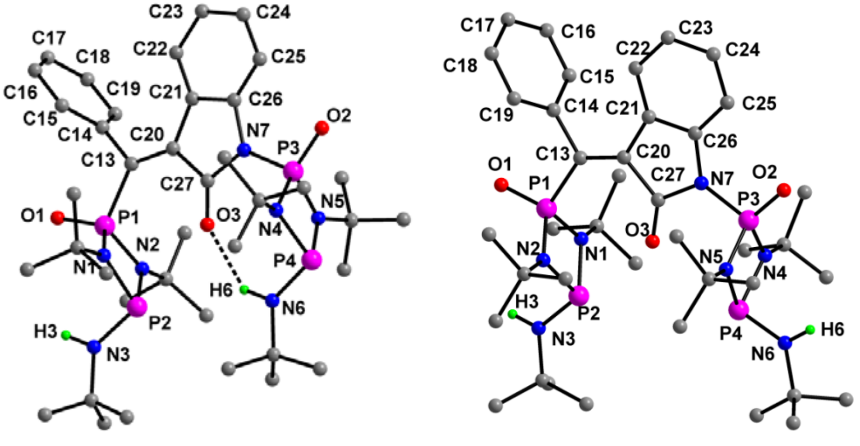
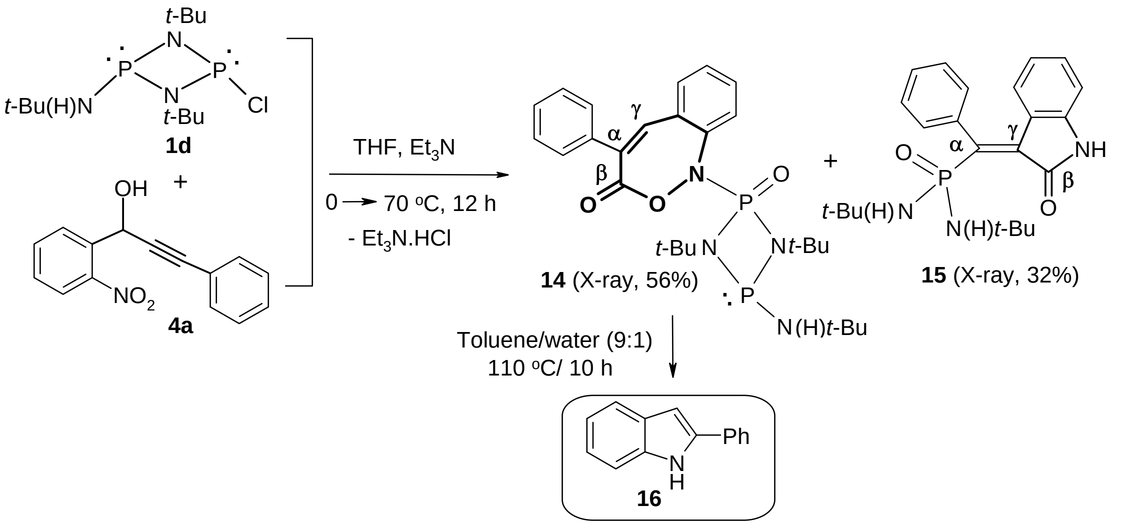


Figure 1. Molecular structures of compounds **12** and **13**

Surprised by the above result, we then performed the reaction by using the monochloro-cyclodiphosphazane [(*t*-BuNH)P(*μ*-N-*t*-Bu)$_2$P-Cl] (**1d**) and the same propargyl alcohol **4a**. Here the major products were the unusual phosphazane connected oxa-aza-benzocycloheptenone **14** and indolinone **15** (Scheme 2). Additionally, removal of phosphorus from **14** led to the phosphorus-free 2-phenyl indole **16**. The structures of compounds **14** and **15** were confirmed by X-ray crystallography (Figure 2).

Scheme 2



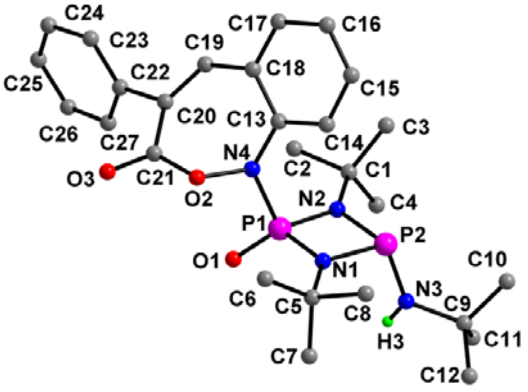
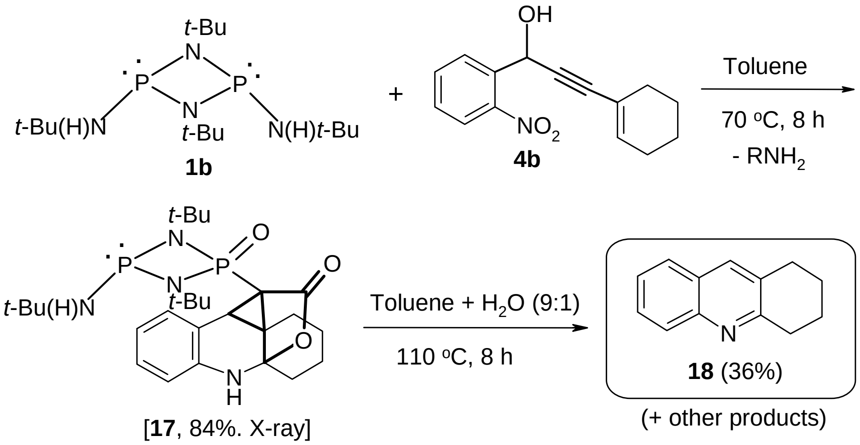


Figure 2. Molecular structure of compound **14**

In the next reaction, we treated the cyclodiphosphazane **1b** with cyclohexenyl precursor **4b** (instead of the phenyl precursor **4a**). A new (bizarre looking!) polycycle **17** fused with ***cyclopropane ring*** (Scheme 3) was obtained. This reaction is also assumed to proceed *via in situ* generated allene intermediate. Interestingly, **17** could be dephosphonylated in the presence of water to lead to tetrahydroacridine **18**. The structure of compound **17** was confirmed by X-ray crystallography (Figure 3). Compound **18** was characterized by NMR spectroscopy and HRMS.

Scheme 3



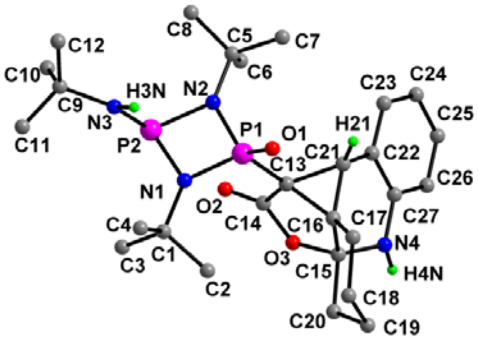
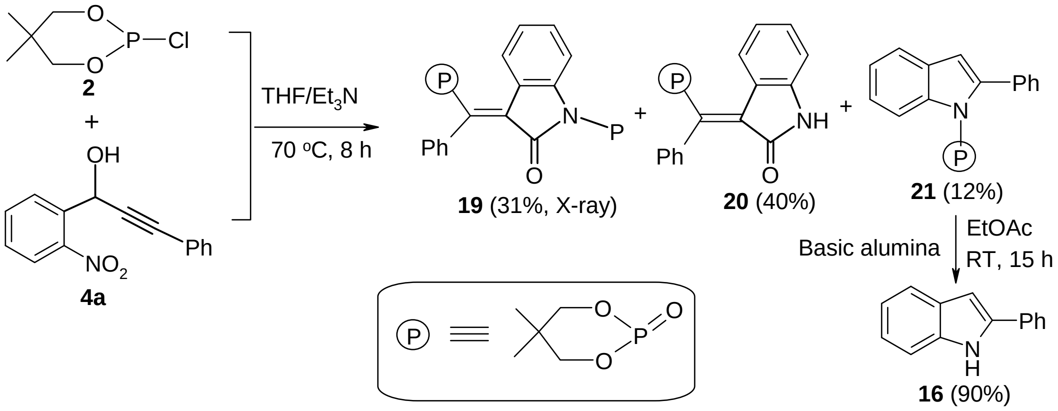


Figure 3. Molecular structure of compound **17**

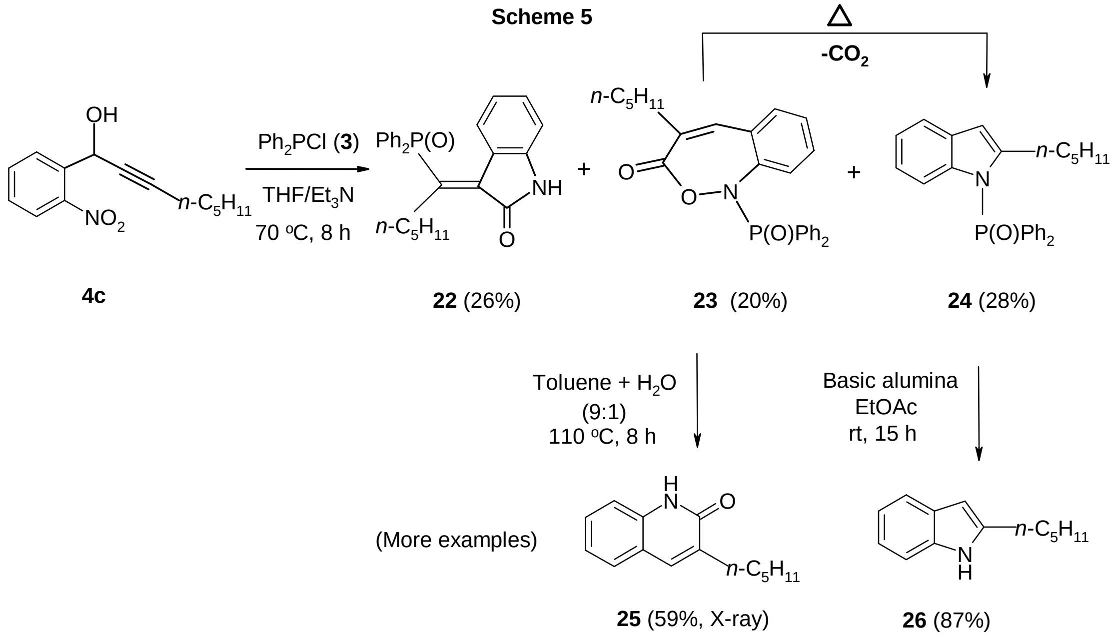
In an extension of the above chemistry, we have treated the P^{III}-Cl precursor **2** with propargyl alcohol **4a**. Here phosphono-indolinones **19-20** and indole **21** are obtained **(**Scheme 4). These products are analogous to compounds shown in Schemes 1-2. However, the more important result of this part is that we can obtain the phosphorus-free indole **16** in excellent yield upon dephosphorylation of **21**.

Scheme 4



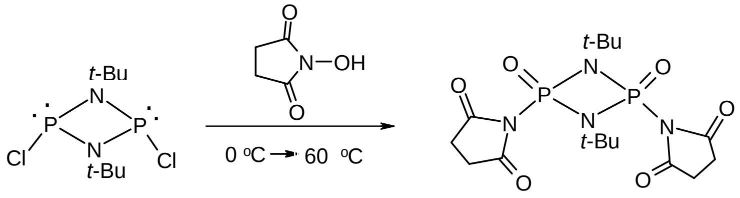
In the reaction of Ph_2PCl (**3**) and propargyl alcohol **4c**, we obtained three different products in good yield (combined): indolinone **22**, oxa-aza-benzocycloheptenone **23** (similar to **14**) and indole **24** (Scheme 5). Decarboxylation of compound **23** upon melting might have led to P-N-connected indole **24**. The elimination of CO_2 was established in the case of **23** by recording the ^{31}P NMR spectra before and after melting (with bubbling) and also by recording TGA. More interestingly, dephosphorylation of compounds **23** (X-ray) and **24** led to the phosphorus-free quinolinone **25** (X-ray) and indole **26** respectively.

Scheme 5



In the reaction leading to compounds **12-13** shown in Scheme 1, 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 **12-13**. In order to conclusively establish that products **12-13** result from such a reaction, we treated cyclodiphosphazane $[ClP\text{-}N(t\text{-}Bu)]_2$ (**1a**) with *N*-hydroxy-succinimide. This reaction afforded the novel rearranged product **27** (Scheme 6). It is formed by the substitution of a chloro group by the *N*-hydroxyl reactant, followed by Arbuzov-type rearrangement. Compound **27** (X-ray) is the major product, but the other isomer is also present as a minor product. Many analogous products have also been described.

Scheme 6



1a

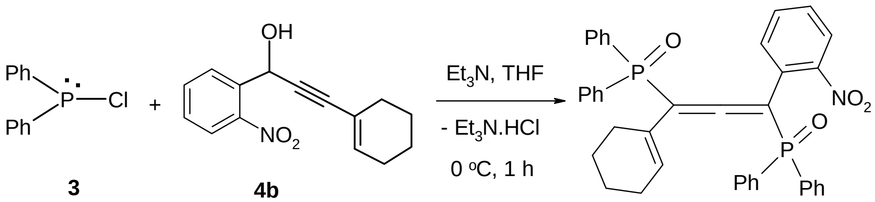
[**27**, δ(P): -17.3, 74%, X-ray]

(Similarly 5-more examples)

(ii) Synthesis of bisphosphonylated allenylphosphine oxides

As shown in Scheme 5, the reaction of Ph_2PCl (**3**) with *o*-nitro functionalized propargyl alcohol **4c** at 70 °C led to the unexpected phosphono-heterocycles **22-24**. When we performed the reaction by using 2:1 molar stoichiometry of **3** and propargyl alcohol **4b** (Scheme 7), the allenyl-(bis)phosphine oxide (**28**) was obtained in excellent yield. Compound **28** crystallized in a chiral space group $P2_12_12_1$ revealing an illustrative example of 'spontaneous resolution'. More interesting is the fact that for compound **28**, we were able to determine the X-ray structures of both the enantiomers (*R* and *S*). Solid state CD spectra also confirm this result. Such a phenomenon is observed for the first time in allene chemistry.

Scheme 7



3 **4b**

(2:1 stoichiometry)

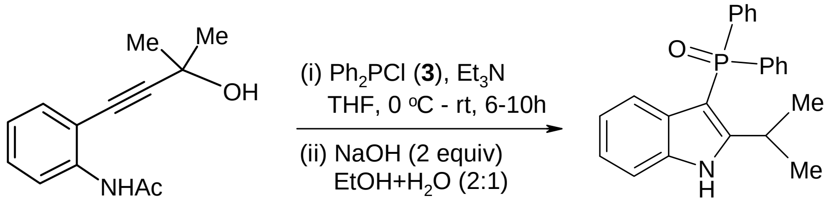
[**28**, δ(P) 25.9, 27.1; 94%, X-ray]

(more examples)

(iii) Reactivity of P^{III} compounds with *o*-amido/ amino functionalized propargyl alcohols- Synthesis of phosphono-indoles

In the earlier reactions, we used *o*-nitro functionalized propargyl alcohols in order to get the phosphono heterocycles. In continuation of such a study, we also used propargyl alcohols bearing an *o*-amido functionality. Thus, treatment of Ph_2PCl (**3**) with propargyl alcohol **5** in the presence of triethylamine, followed by aq. NaOH work up afforded the phosphono indole **29** (Scheme 8). This reaction most likely proceeded through aq. NaOH mediated deprotection followed by cyclization. This one-pot method furnished the desired phosphinoyl-indole **29** in good yield.

Scheme 8



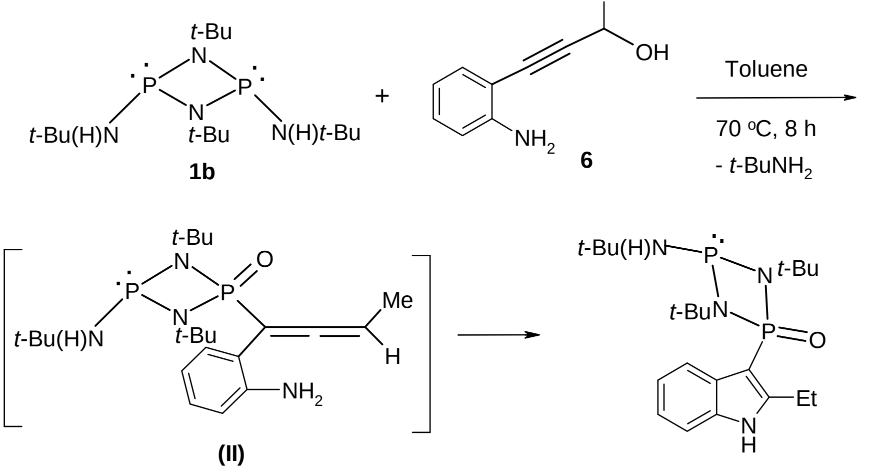
5

[**29**, δ(P): 24.3; 80%]

(Similarly 12-more examples)

In continuation of the above studies, treatment of cyclodiphosphazane **1b** with *o*-amino functionalized propargyl alcohol **6** led to cyclodiphosphazane based indole **30** in excellent yield (Scheme 9). Here, the cyclodiphosphazane reacted with the propargyl alcohol forming the cyclodiphosphazane based allene intermediate **II** that underwent intramolecular cyclization using -NH$_2$ functionality.

Scheme 9



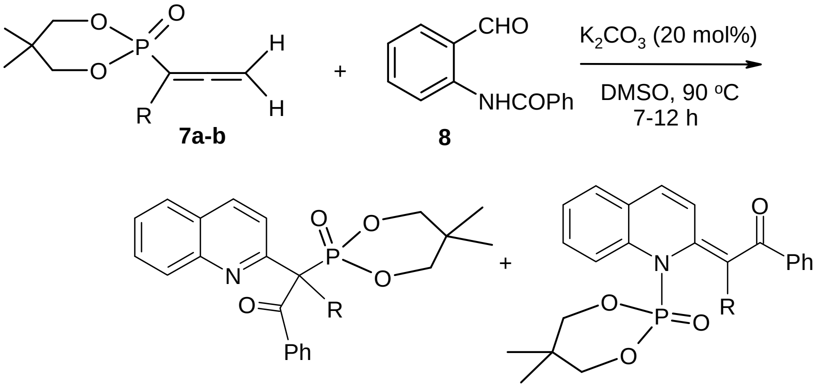
[**30**, δ(P): 17.5, 82.6; 88%]

(Similarly 3-more examples)

(iv) Base catalyzed intermolecular cyclization reactions of allenylphosphonates with *N*-(2-formylphenyl)benzamide (Synthesis of phosphono-quinolines)

The reaction of allenylphosphonates **7a-b** with *N*-(2-formylphenyl)benzamide **8** in the presence K_2CO_3 (as base) leads to phosphono-quinolines and *N*-phosphorylated quinolines [**31-34**] (Scheme 10). At high temperature, the phosphono-quinolines undergo isomerization to *N*-phosphorylated quinolines. A possible pathway for this reaction involves intermolecular cyclization followed by dehydration and rearrangement. The structure of compound **31** was confirmed by X-ray crystallography.

Scheme 10

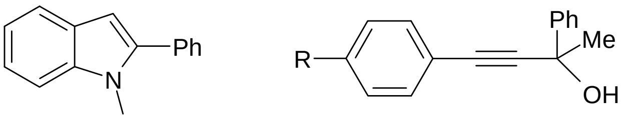


R = Ph, [**31**, δ(P): 12.2; 43%, X-ray] + [**32**, δ(P): -13.8; 45%]
R = 4-Me-C_6H_4, [**33**, δ(P): 12.3; 43%] + [**34**, δ(P): -13.8; 46%]

(Similarly 4-more examples)

PART-B

Chapter 4 deals with a brief review of literature on indoles, propargyl alcohols and the relevant [Cu]-catalyzed reactions. Chapter 5 describes the results obtained in the present study on these aspects. Chapter 6 is the experimental section for this part. The main precursors are **9** and **10a-b**. Important results of this part are outlined below.



9

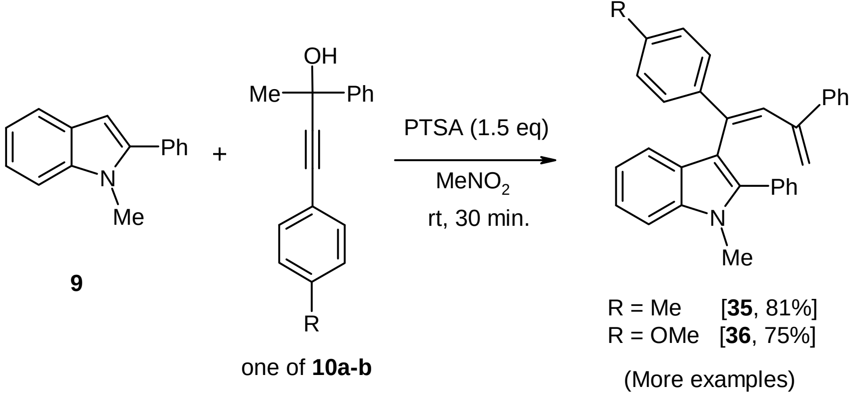
R = Me (**10a**)
R = OMe (**10b**)

Representative precursors

(i) Synthesis of 3-dienylindoles from 2-substituted N-methylindoles and propargyl alcohols under Brønsted acid mediation

The 3-dienylindoles **35-36** (Scheme 11) have been utilized in the present study for a novel ring expansion reaction as described later. They have been prepared by treating *N*-methyl-2-phenylindole **9** with one of tertiary propargyl alcohols **10a-b** in the presence of PTSA. Formation of these 3-dienylindoles is explained through a Brønsted acid mediated dehydration followed by a competitive Friedel-Crafts alkenylation leading to the allene derivative, which undergoes isomerization. The structure of compound **36** is confirmed by X-ray crystallography.

Scheme 11

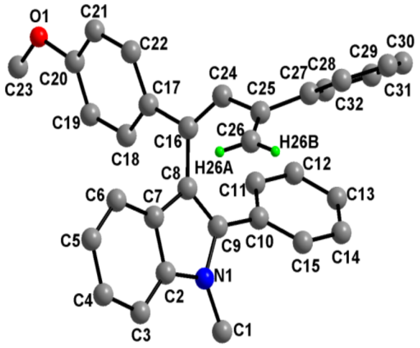


9

one of **10a-b**

R = Me [**35**, 81%]
R = OMe [**36**, 75%]

(More examples)

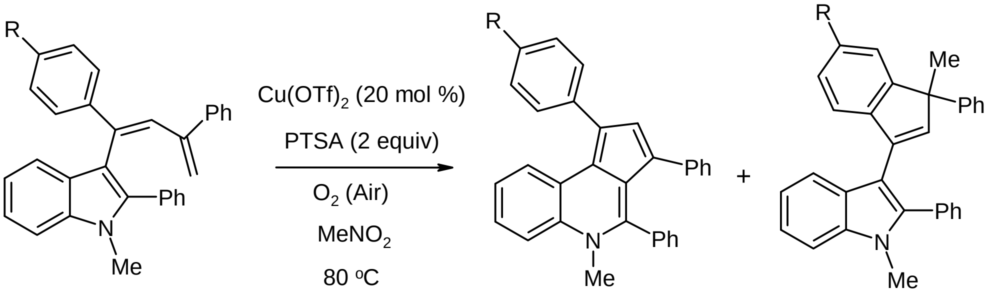


Compound **36**

(ii) Cyclopenta[c]quinolines/ 3-indenylindoles from 3-dienylindoles *via* copper catalysis

Treatment of 3-dienylindoles **35-36** with Cu(OTf)$_2$ in nitromethane afforded the cyclopenta[c]quinolines [**37**, **39**] and 3-indenylindoles [**38**, **40**] as shown in Scheme 12. The combined yields were good to excellent in both the cases. To our knowledge, the ring expansion leading to **37**/**39** is unprecedented. This novel reaction may be rationalized by copper catalyzed aerobic oxidative dehydrogenation/ ring expansion. 3-Indenylindoles [**38/40**] are most likely generated by a simple intramolecular hydroarylation of the allene intermediate, an isomer of the 3-dienylindole, in the presence of traces of trifluoromethanesulfonic acid (TfOH). The structures of compounds **38** and **39** were confirmed by X-ray crystallography (Figure 4).

Scheme 12



R = Me (**35**)
R = OMe (**36**)

R = Me [**37**, 61%] + [**38**, 26%]
R = OMe [**39**, 53%] + [**40**, 30%]
(Similarly 9 more examples)

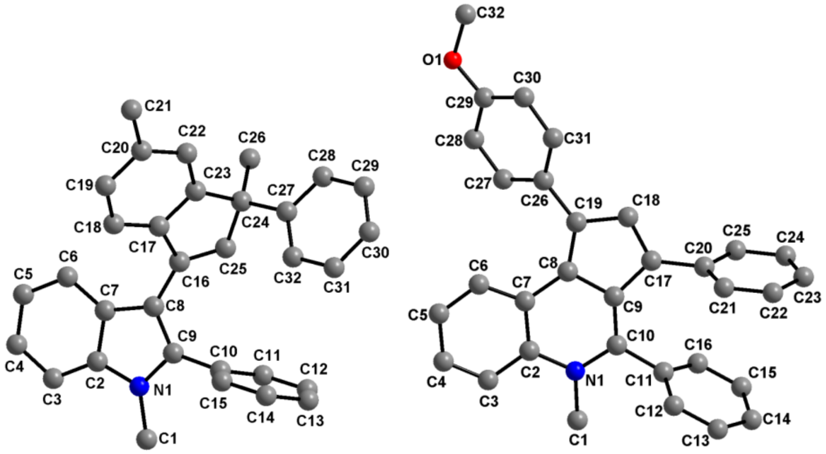
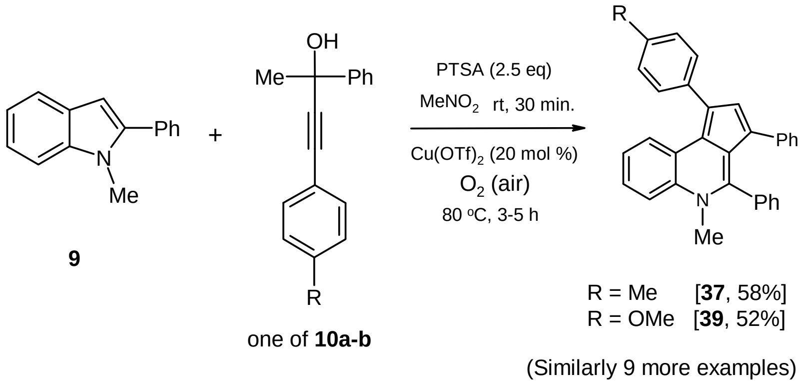


Figure 4. Molecular structures of compounds **38** and **39**.

(iii) One-pot synthesis of ring-expansion products [e.g., 37, 39] from *N*-methyl,2-phenylindole and tertiary propargyl alcohols

Based on the above Schemes 11 and 12, we intended to develop a one-pot method in order to obtain the cyclopenta[c]quinolines. This objective was successful and cyclopenta[c]quinolines **37, 39** have been synthesized in moderate to good yields (Scheme 13) starting from indole **9** and one of tertiary propargylic alcohols **10a** or **10b** in the presence PTSA/Cu(OTf)$_2$ in nitromethane. In this one-pot method, the overall yield of cyclopenta[c]quinolines was slightly higher than the stepwise method.

Scheme 13



9

one of **10a-b**

R = Me [**37**, 58%]
R = OMe [**39**, 52%]

(Similarly 9 more examples)

PART-A

NITROGEN HETEROCYCLES VIA PHOSPHORUS BASED ALLENE INTERMEDIATES

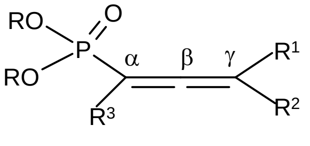
Chapter 1

INTRODUCTION

1.1 General Introduction: Allenes

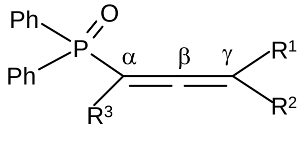
Allenes, by virtue of cumulative double bonds that facilitate reactions with diverse classes of substrates, are versatile synthons for numerous organic structural motifs.[1,2] They are also found in many natural products,[3] pharmaceuticals[4] and molecular materials.[5] For a long time, allenes were considered as highly unstable, which retarded the development of the chemistry of allenes. However, over the last decade, allenes have attained a prominent position in organic transformations like cyclization/cycloisomerization, cycloaddition and nucleophilic addition *via* base or metal-catalyzed reactions.[6] In particular, cyclization reaction of allenes has emerged as a valuable tool in developing different methods leading to various carbo-/hetero-cyclics.[7]

Allenes possessing $–P(O)(OR)_2$ or $–P(O)(Ph)_2$ group as a substituent are called as allenylphosphonates (phosphorylated allenes) (**I**) or allenylphosphine oxides (**II**), respectively. Many of these are stable solids, and can be handled more conveniently when compared to non-phosphorylated allenes. The presence of these groups is quite useful in interpreting the reaction pathways by means of ^{31}P NMR.[8] In many cases, the electron withdrawing nature of the phosphorus moiety leads to products with better regioselectivity. In the following sections, a brief literature survey on the preparation and utility of allenylphosphonates/ allenylphosphine oxides and related allenes will be presented. Wherever possible, comparison will be made between the reactivity of phosphorus-based allenes and other allenes.



I

Allenylphosphonate



II

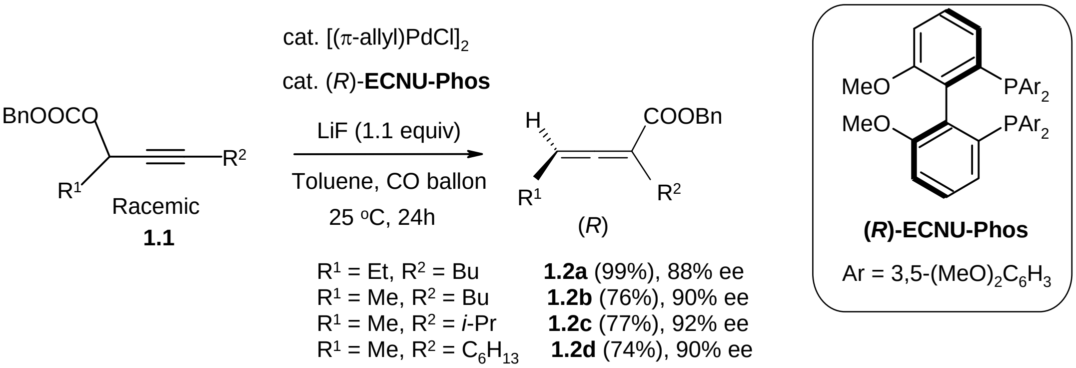
Allenylphosphine oxide

1.2 Synthesis of allenes/ allenylphosphonates/ allenylphosphine oxides

Umpteen number of methods are available for the synthesis of nonphosphorylated allenes in the literature.[9] The most commonly employed method for the synthesis of a variety of functionalized allenes is the Wittig reaction of phosphonium ylides and ketenes.[9a-h] Another reaction to obtain a wide range of optically active allenes from corresponding propargyl alcohols and hydrazine as a nucleophile is the Mitsunobu reaction.[10] Many of these are discussed in the book 'Modern Allene Chemistry' by Krause and Hashmi.[1a] Other relevant methods for the synthesis of allenes are briefly outlined below.

Ma and co-workers discovered the first catalytic asymmetric carbonylation of racemic propargylic carbonates **1.1** to optically active 2,3-allenoates **1.2a-d** at 1 atm CO at room temperature with a chiral ligand (Scheme 1.1).[11] For the first time, highly enantioselective synthesis of chiral allenes from the readily available racemic propargylic carbonates has been accomplished.

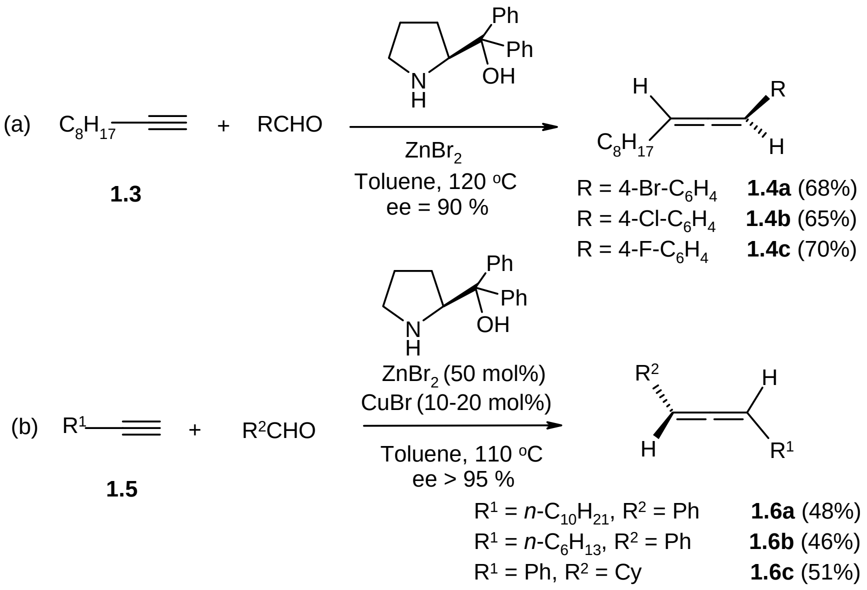
Scheme 1.1



Recently, Periasamy's group reported the synthesis of chiral allenes **1.4a-c** with excellent enantioselectivities from the reaction of terminal alkyne **1.3**, aldehydes and chiral secondary amines.[12a] The reaction is promoted by zinc halide and involves sequential chirality transfer *via* an intramolecular hydride shift from the *in situ* generated propargyl amine intermediate to produce chiral allene in a single pot operation (Scheme 1.2a). Very recently, Ma and co-workers also developed a new bimetallic asymmetric approach for the synthesis of simple axially chiral allenes from terminal alkynes **1.5**, substituted aldehydes and an inexpensive secondary chiral amine

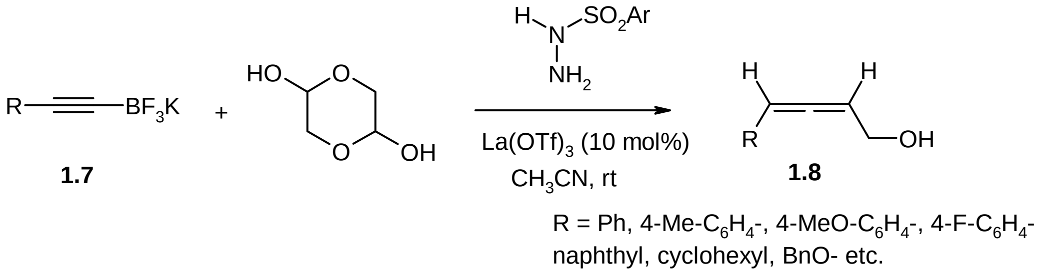
(Scheme 1.2b).[12b] This one pot method has broad substrate scope and provides axially chiral allenes **1.6a-c** with excellent enantioselectivity.

Scheme 1.2



Thomson and co-workers reported an efficient $La(OTf)_3$ catalyzed one pot synthesis of allenes **1.8** by sulfonylhydrazine mediated coupling of hydroxy aldehydes/ ketones with alkynyl trifluoroborate salts **1.7**.[13] The reaction involves the formation of sulfonylhydrazone that reacts with alkynyltrifluoroborate to give transient propargylic hydrazide species which upon degradation *via* monoalkyldiazine produces the allene (Scheme 1.3).

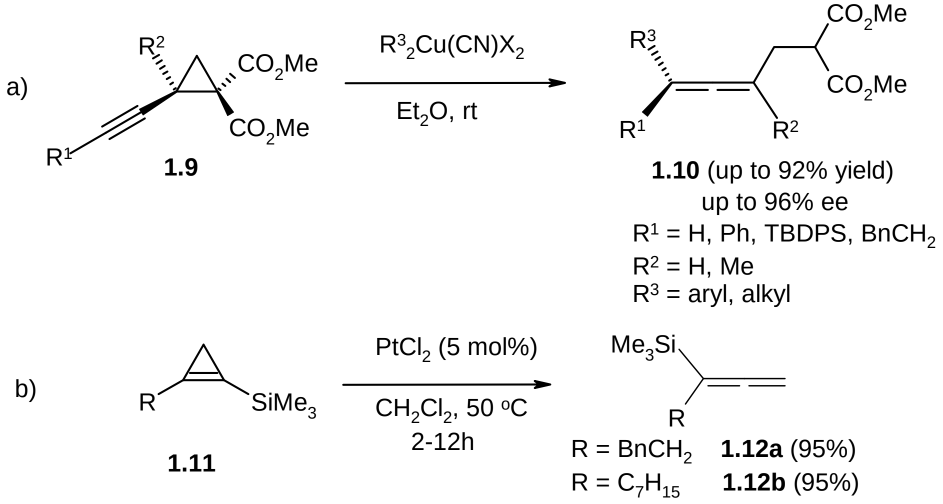
Scheme 1.3



R = Ph, 4-Me-C_6H_4-, 4-MeO-C_6H_4-, 4-F-C_6H_4-
naphthyl, cyclohexyl, BnO- etc.

In the year 2010, Charette and co-workers described a method for the synthesis of highly substituted enantio-enriched allenes **1.10** by the S_N2 addition of organocuprate reagents on 1,1-cyclopropane diesters **1.9** (Scheme 1.4a).[14a] Later, Lee and co-workers also developed an efficient platinum-catalyzed rearrangement of silylated cyclopropenes **1.11** to the corresponding allenes **1.12a-b** in good yields (Scheme 1.4b).[14b]

Scheme 1.4

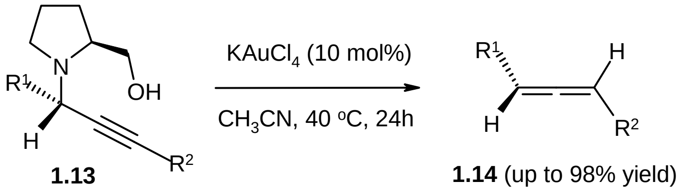


1.10 (up to 92% yield)
up to 96% ee
R^1 = H, Ph, TBDPS, $BnCH_2$
R^2 = H, Me
R^3 = aryl, alkyl

R = $BnCH_2$ **1.12a** (95%)
R = C_7H_{15} **1.12b** (95%)

The first gold-catalyzed synthesis of axially chiral allenes **1.14** from chiral propargylamines **1.13** has been reported by Che, Wong and co-workers.[15] This reaction involves the gold(I)-catalyzed intramolecular hydride transfer of chiral propargyl amines as shown by deuterium-labeling experiments. It affords the desired chiral allenes in good yields and excellent enantioselectivities (Scheme 1.5).

Scheme 1.5

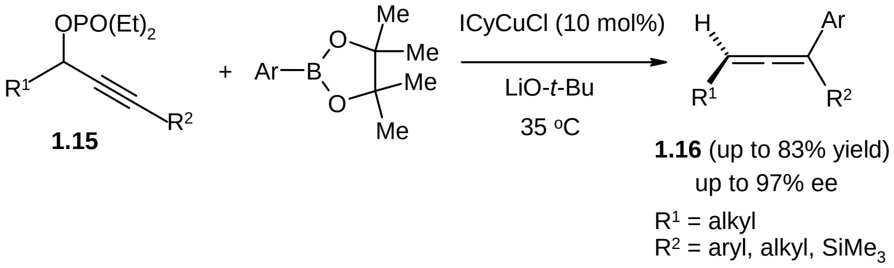


1.13
99% ee

1.14 (up to 98% yield)
up to 97% ee
R^1 = aryl, cyclohexyl
R^2 = aryl, cyclohexynyl

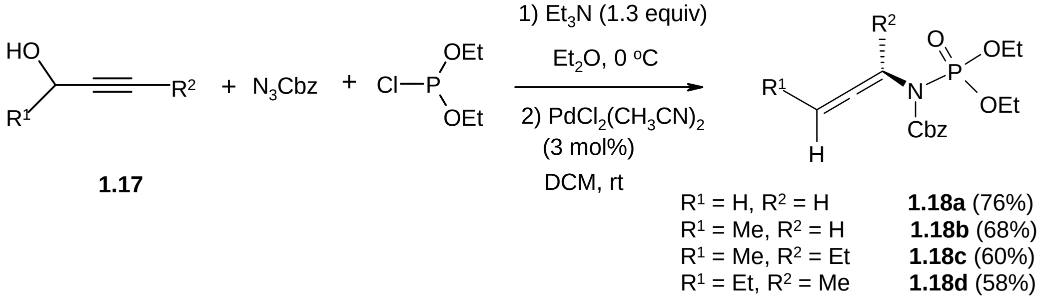
Recently Lalic and co-workers developed a new method for the synthesis of chiral allenes of type **1.16** by copper-catalyzed alkylation and arylation of propargylic phosphates **1.15** using organoboron nucleophiles (Scheme 1.6).[16a] The reaction took place at room temperature with high chirality transfer and regioselectivity. Later, Miura's group reported the reaction of polyfluoroarenes with propargyl phosphates producing the polyfluoroarene substituted allenes by using copper catalysis.[16b]

Scheme 1.6



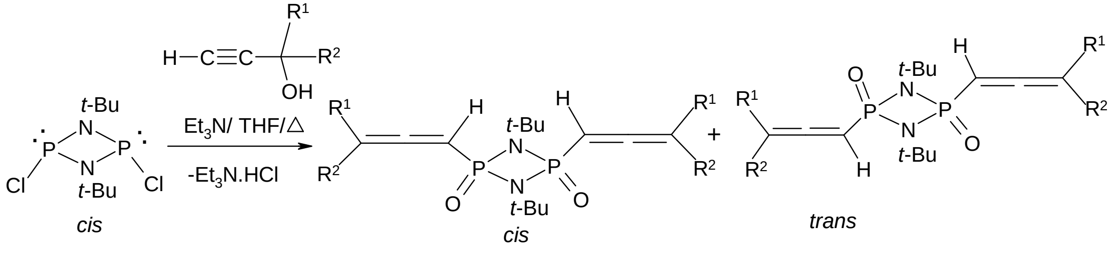
A straight-forward application of a [3,3]-rearrangement for the synthesis of allenamides under palladium catalysis is demonstrated by Mapp and co-workers.[17] Easily accessible propargyl alcohols **1.17**, a chlorophosphite and an organic azide are combined to provide propargylic phosphorimidates, which, in the presence of catalytic palladium(II), rearrange to highly functionalized allenamides **1.8a-d** (Scheme 1.7).

Scheme 1.7



Synthesis of allenylphosphonates/allenylphosphine oxides is generally accomplished by the treatment of trivalent phosphorus chlorides X_2PCl with the propargyl alcohols.[18] Similarly, *cis* and *trans* forms of allenylphosphoramidates **1.23a-b** and **1.24a-b** based on a cycodiphosph(V)azane skeleton are readily obtained by treating the well-known cyclodiphosphazane [ClP(μ-N-*t*Bu)]$_2$ (**1.22**) with substituted propargylic alcohols in the presence of triethylamine (Scheme 1.8).[19]

Scheme 1.8



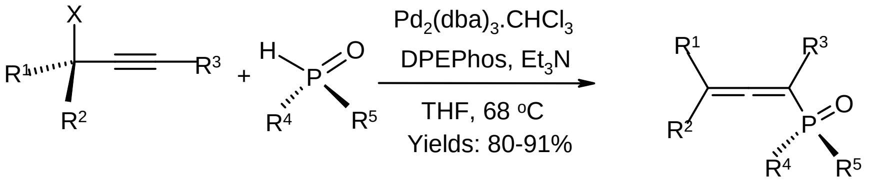
1.19

R¹ = R² = H **1.20a** (75%)
R¹ = R² = Me **1.20b** (60%)

R¹ = R² = Me **1.21a** (15%)
R¹ = Me, R² = Et **1.21b** (15%)

Recently, Stawinski and co-workers reported a novel method for the construction of allenylphosphonates **1.26a-d** and related compounds. The reaction involves a Pd(0)/DPEPhos-[bis(2-phenylphosphinophenyl)ether-] catalyzed coupling of propargyl chlorides or carbonates **1.25** with *H*-phosphonate diesters or their analogues (Scheme 1.9).[20] The reaction permits stereoselective and stereospecific construction of an allenic moiety with complete transfer of chiral center to axial chirality and retention of configuration at the phosphorus center.

Scheme 1.9



1.22
X = Cl or carbonate

R¹ = R² = R³ = H, R⁴ = R⁵ = OEt (**1.23a**)
R¹ = R³ = H, R² = *n*-C_5H_{11}, R⁴ = R⁵ = OEt (**1.23b**)
R¹ = R² = R³ = Me, R⁴ = R⁵ = OEt (**1.23c**)
R¹ = R² = R³ = H, R⁴ = Me, R⁵ = OEt (**1.23d**)

1.3 Allenes/ allenylphosphonates/ allenylphosphine oxides in organic synthesis

Allenes have hybrid character of an olefin and acetylene and can involve in transition metal catalyzed, base catalyzed, Brønsted acid catalyzed, organo-catalyzed as well as non-catalytic reactions. In the following sections, selected cyclization and addition reactions of allenes that are relevant to our work will be presented.

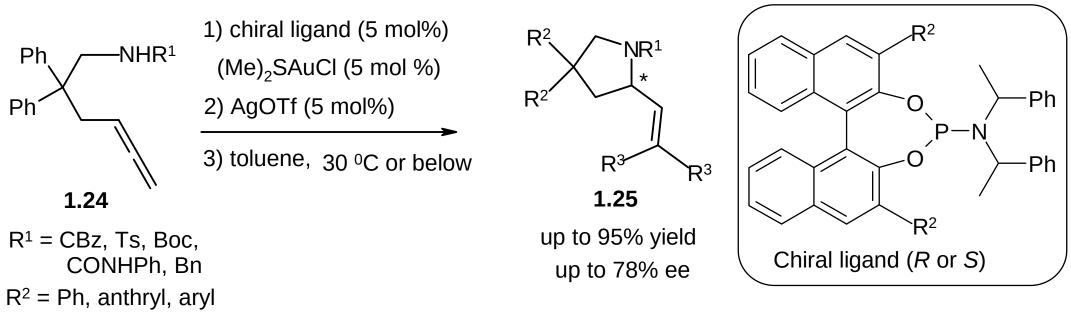
1.31 Cyclization reactions of allenylphosphonates or related allenes

Due to the presence of cumulative π electron system, allenes can undergo cyclization reactions *via* metal or non-metal mediation leading to various carbo-/heterocycles like furans, pyrans, pyrroles, pyridines, chromans, chromenes, pyrazoles, pyrazolines, thiophenes, benzapine, indolines, benzofurans, isochromenes, indenes, indolo-pyranones or pyrroles. These can be intra- or inter-molecular cyclizations as discussed below.

1.311 Intramolecular cyclization reactions

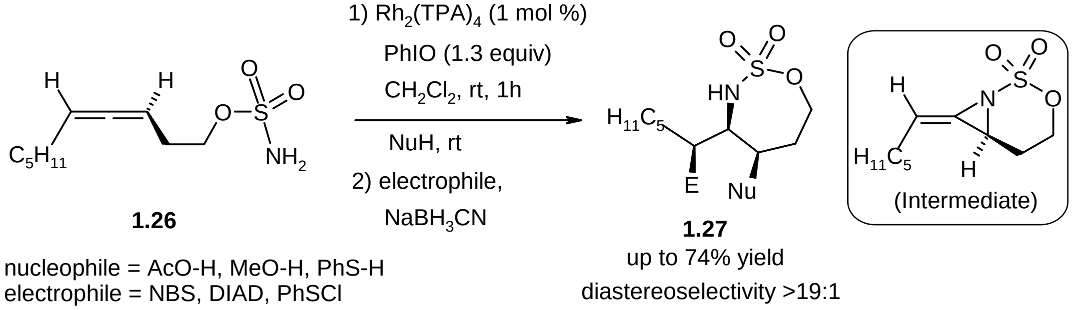
Allenes bearing a pro-nucleophile (nitrogen, oxygen, sulfur or carbon) can be cyclized intramolecularly on treatment with a wide variety of transition metal catalysts and reagents to produce biologically important heterocycles with various ring sizes. Thus, very recently, gold-catalyzed asymmetric intramolecular hydroamination of allenes by a series of mononuclear gold(I) complexes in combination with silver salts was studied by Michon and Agbossou-Niedercorn.[21] The resulting gold(I) complexes were combined with selected silver salts to afford efficient catalysts for cyclization of allenes **1.24** at room temperature or below. Thus substituted tetrahydropyrrolidine derivatives **1.25** with good conversions and enantioselectivities (Scheme 1.10) were synthesized.

Scheme 1.10



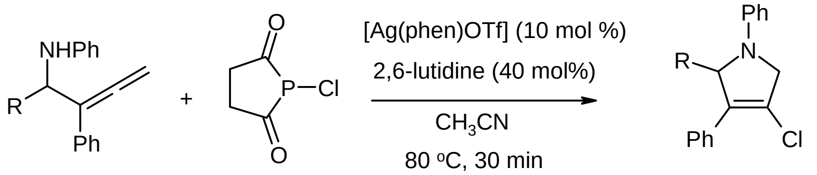
Schomaker and co-workers have described rhodium catalyzed transformation of allenes to aminated stereo-triads under mild conditions.[22] This reaction involves intramolecular cyclization of sulfomoyl allenes **1.26** that lead to a strained bicyclic methylene aziridine. This intermediate upon treatment with nucleophile followed by electrophile in the presence of reductant affords the desired products **1.27** in good yields (Scheme 1.11).

Scheme 1.11



Matsubara and Sai developed silver-catalyzed intramolecular chloroamination of allenes **1.28** with *N*-chlorosuccinimide using 2,6-lutidine as a base.[23] This process proceeds under mild conditions and can tolerate a variety of functional groups such as keto, ester, cyano, halogen, acetal or silyl ether. The *in situ* generated chloroamination intermediate can be easily transformed into functionalized 3-pyrroline and pyrrole derivatives **1.29a-c** (Scheme 1.12).

Scheme 1.12

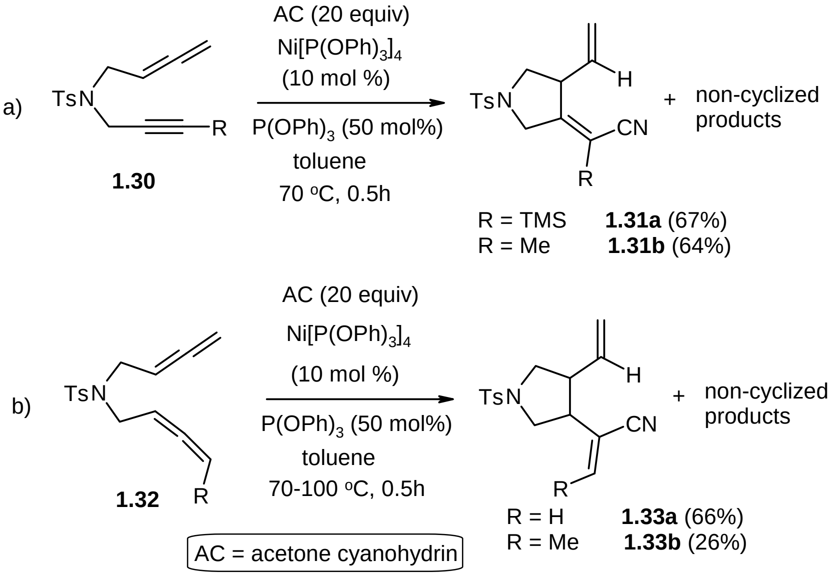


1.28

R = 4-CO_2Me-C_6H_4 **1.29a** (82%)
R = 4-CN-C_6H_4 **1.29b** (91%)
R = 4-Br-C_6H_4 **1.29c** (76%)

Very recently, the carbocyanative intramolecular cyclization of allene-ynes **1.30** and bis-allenes **1.32** under nickel catalysis was reported by Arai and co-workers.[24] This reaction involves regioselective hydro-nickelation of allene followed by intramolecular cyclization *via* carbometalation and subsequent reductive elimination of nickel leading to the *N*-tosylated pyrrolidine derivatives **1.31a-b** or **1.33a-b** (Scheme 1.13).

Scheme 1.13



1.30

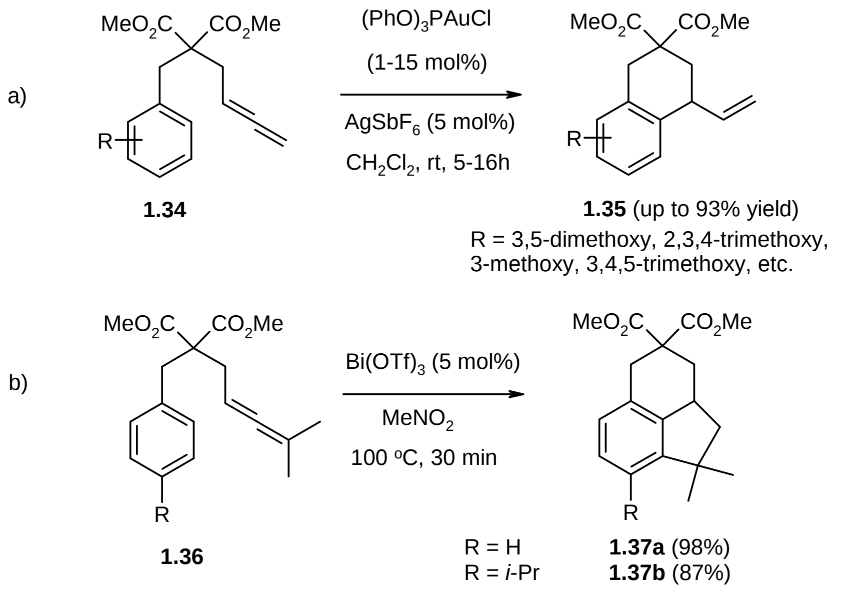
R = TMS **1.31a** (67%)
R = Me **1.31b** (64%)

1.32

R = H **1.33a** (66%)
R = Me **1.33b** (26%)

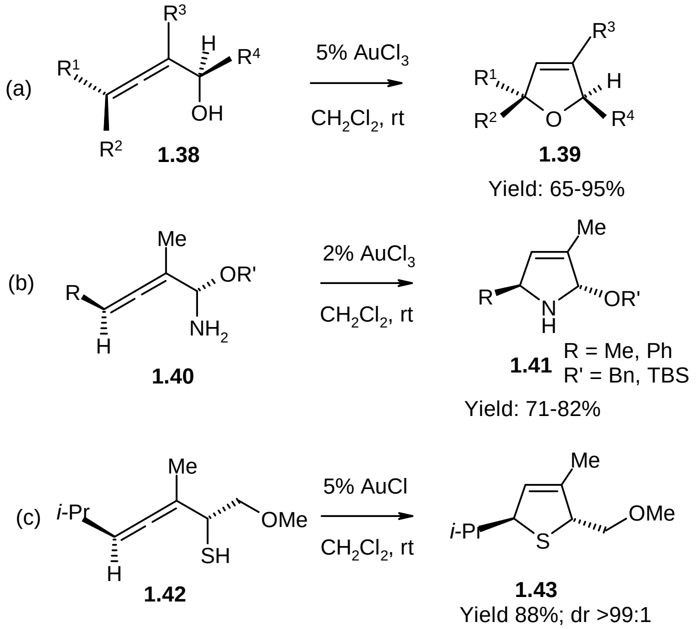
Gagne and Tarselli reported gold catalyzed intramolecular hydroarylation of allenes **1.34** producing vinyl-substituted benzocycles **1.35** in good to excellent yields (Scheme 1.14a).[25] Later, Dunach and co-workers reported the cycloisomerization reaction of aryl allenes **1.36** under bismuth catalysis. This reaction also proceeds *via* intramolecular hydroarylation reaction of allenes under mild conditions producing fused polycycles **1.37a-b** (Scheme 1.14b).[26] In both the reactions hydroarylation takes place at room temperature itself.

Scheme 1.14



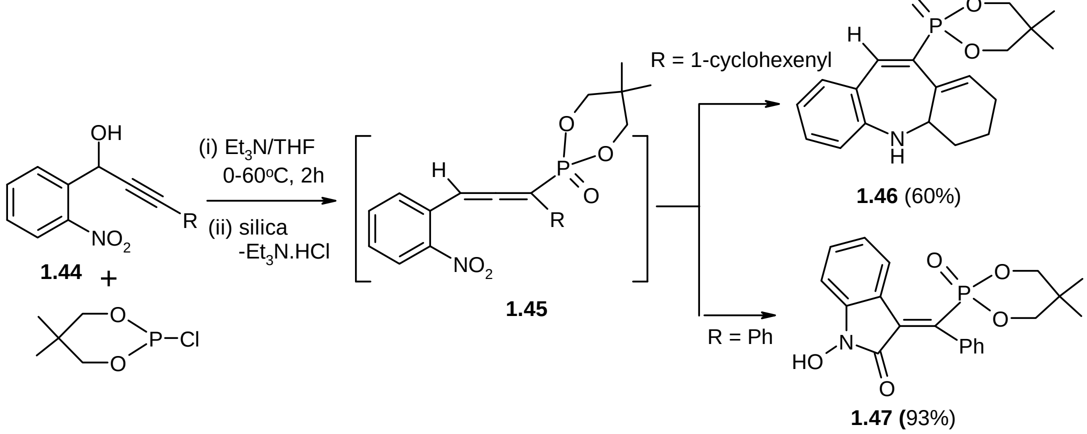
Krause and co-workers have discovered a mild and efficient method for the electrophilic intramolecular cyclization of highly functionalized α-hydroxyallenes **1.38** to the corresponding 2,5-dihydrofurans **1.39** by using gold(III) catalysis (Scheme 1.15a).[27a] This method is also applicable to various alkyl or alkenyl substituted allenes furnishing the dihydrofurans in excellent yields with complete chirality transfer. The same group reported the cycloisomerization of various α-aminoallenes **1.40** to pyrrolines **1.41** with complete axis-to-center chirality transfer in excellent diastereoselectivity by using the gold(III) catalysis (Scheme 1.15b).[27b] The first gold catalyzed carbon-sulfur bond formation by stereoselective cycloisomerization of α-thioallenes **1.42** to 2,5-dihydrothiophenes **1.43** was also reported by the same group (Scheme 1.15c).[27c]

Scheme 1.15



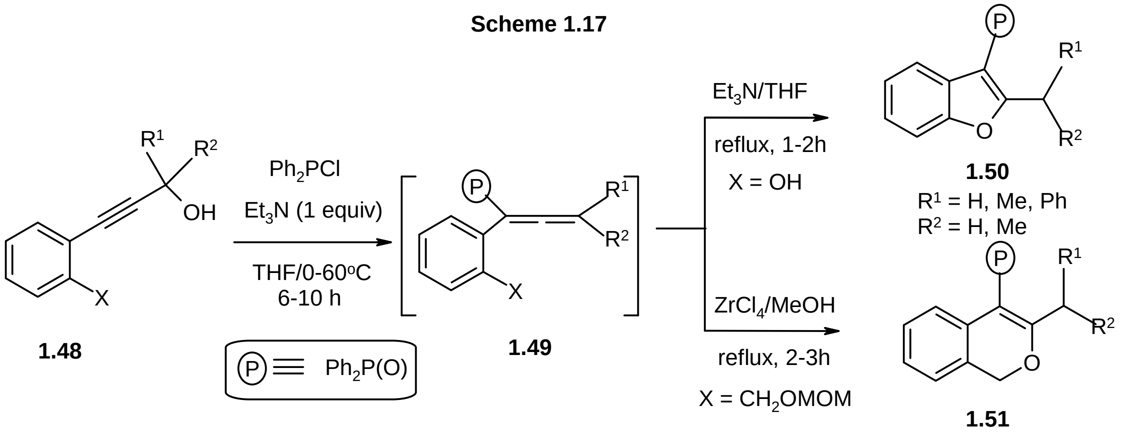
A facile and efficient synthesis of phosphono-heterocycles and polycyclics has been discovered from our laboratory by using functionalized propargyl alcohols.[28] Thus the reaction of *o*-nitro functionalized propargyl alcohols **1.44** with $(RO)_2PCl$ in the presence of a base leads to the allene intermediate **1.45** which further undergoes a dramatic intramolecular cyclization followed by CO_2 elimination to yield novel phosphono benzazepine/ indoline derivatives. If the terminal substituent on the propargyl alcohol is cyclohexenyl group, the product is (tetrahydro)dibenzazepine **1.46** whereas with the phenyl substituent, the product is phosphono-*N*-hydroxyindolinone **1.47** (Scheme 1.16).

Scheme 1.16



In addition to the above, the nucleophilic intramolecular cyclizations of allenylphosphine oxides **1.49**, which are assumed to be intermediates from propargyl alcohols **1.48**, leading to phosphorus based benzofurans **1.50** and isochromenes **1.51,** have been reported from our laboratory.[29] The final products were formed from the *in situ* generated allene intermediate which underwent intramolecular cyclization in the presence of Et_3N and $ZrCl_4$ (Scheme 1.17). Synthesis of phosphorus based indenes and indenones by using alkylidene and aldehyde groups as nucleophiles or functional groups was also reported in the same paper.

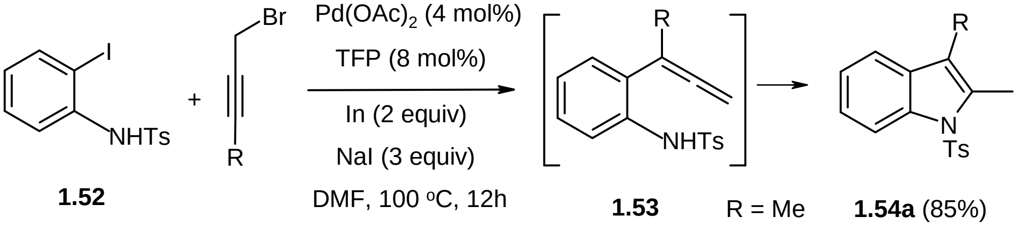
Scheme 1.17



$R^1 = R^2 =$ H, Me

Very recently, Ma and Zhu reported a sequential one-pot method for the efficient synthesis of polysubstituted indoles **1.54a-d** starting from readily available 2-iodoanilines **1.52** and propargyl bromides that involved the intermediacy of allenes **1.53** (Scheme 1.18).[30] This coupling and cyclization reaction proceeds *via* palladium(0)-catalyzed carbon-carbon bond formation followed by cycloisomerization. The *in situ* generated allene intermediate is cyclized intramolecularly.

Scheme 1.18



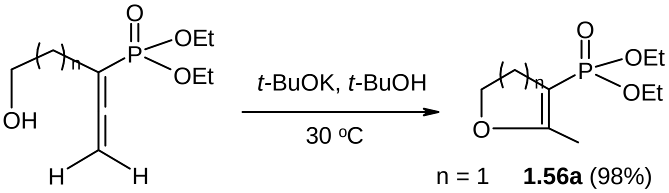
1.52

1.53

R = Me **1.54a** (85%)
R = H **1.54b** (54%)
R = allyl **1.54c** (77%)
R = Ph **1.54d** (65%)

Mukai *et al* developed a method for the construction of various oxacycles *via* base catalyzed endo-mode cyclization of allenes.[31] Thus allenes **1.55** substituted with phosphonate group and hydroxyl function at C1-position underwent an *endo* type ring closing reaction to give five- to eight-membered oxacycles **1.56a-d** in good yields (Scheme 1.19). This method worked well for allenes having –PO(Ph)$_2$, -SOPh and -SO$_2$Ph groups also.

Scheme 1.19



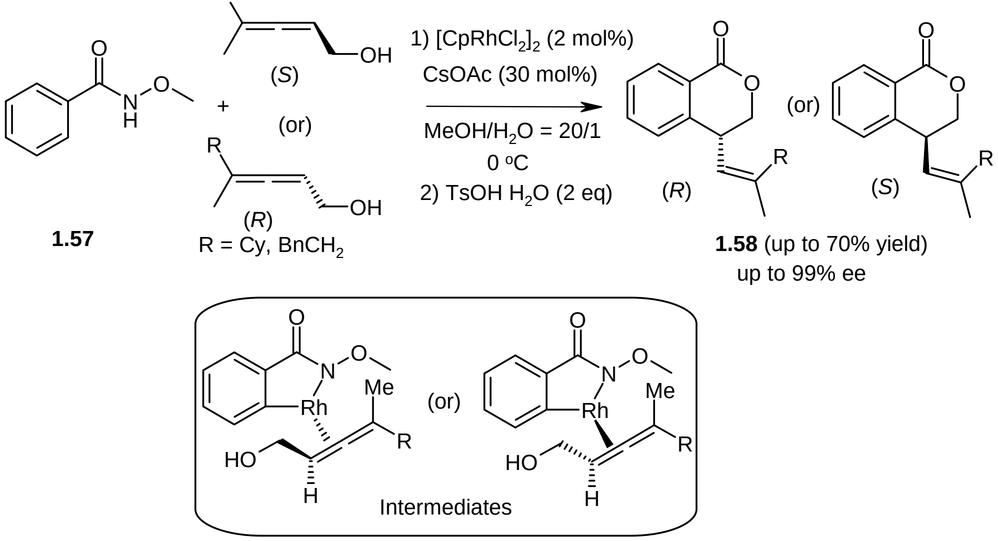
1.55

n = 1 **1.56a** (98%)
= 2 **1.56b** (71%)
= 3 **1.56c** (94%)
= 4 **1.56d** (75%)

1.312 Intermolecular cyclization reactions

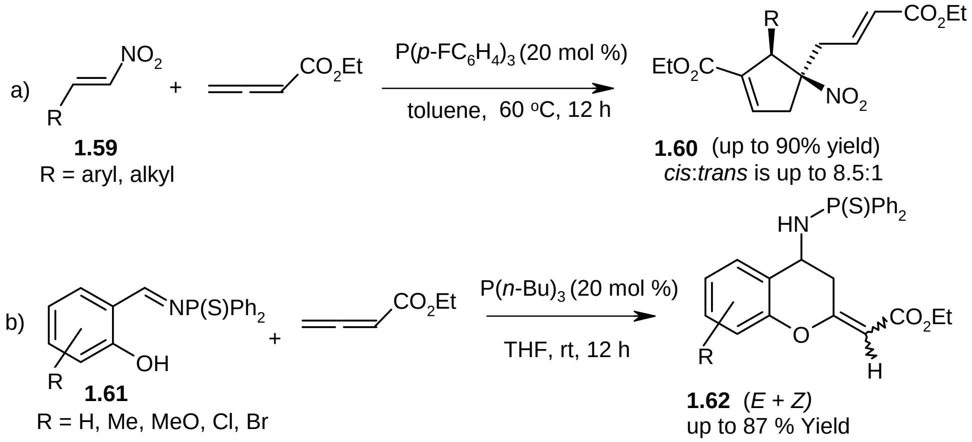
Phosphine or base catalyzed/ promoted reaction of allenes with substrates containing both nucleophilic (OH, NH, SH etc) and electrophilic centers (carbonyl or imine or activated alkene) can lead to carbo- or hetero-cycles. Very recently, Ma and co-workers developed a Rh(III)-catalyzed hydroarylation reaction of allenes with *N*-methoxybenzamide **1.57** under very mild conditions to obtain optically active lactones **1.58** with highly efficient axial chirality transfer (Scheme 1.20).[32] This reaction proceeds *via* C-H bond functionalization followed by allene insertion.

Scheme 1.20



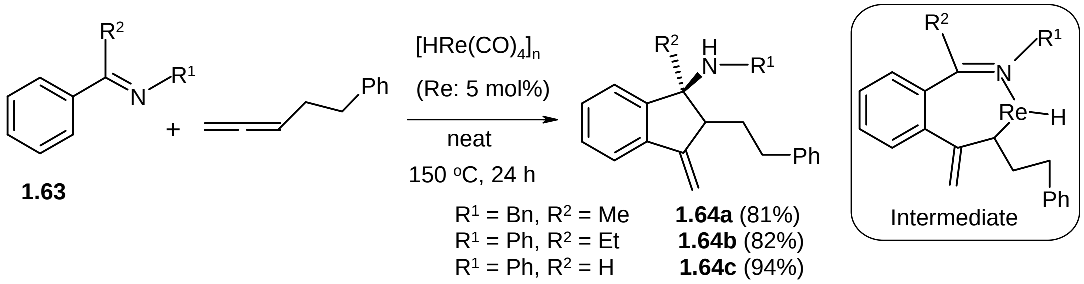
Recently, Shi and co-workers reported a novel phosphine catalyzed tandem reaction between allenoates and nitroalkenes **1.59** that led to highly functionalized cyclopentene derivatives **1.60** (Scheme 1.21a).[33a] This reaction offers a new approach for the synthesis of cyclopentanoid natural products. The same group developed a new route for biologically active chromans **1.62** by the reaction of salicyl-*N*-thiophosphinyl imines **1.61** or salicylaldehydes with allenoate under phosphine catalysis (Scheme 1.21b).[33b]

Scheme 1.21



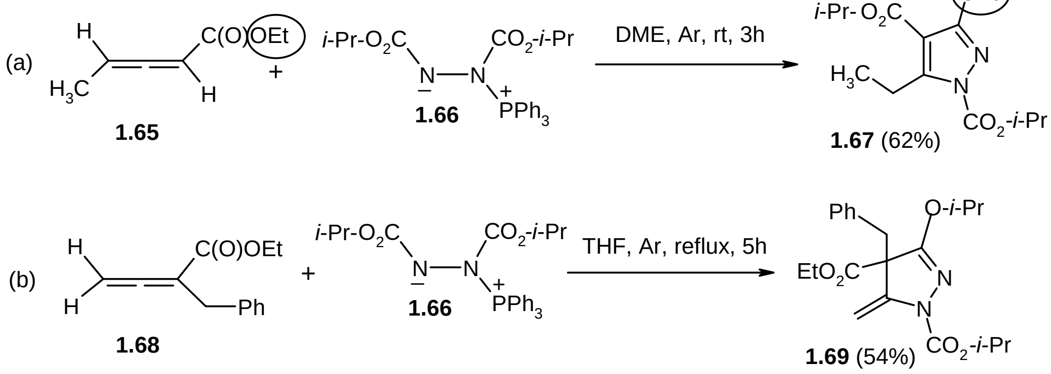
Kuninobu and Takai reported the diastereoselective synthesis of aminoindane derivatives **1.64a-c** by the reaction of aromatic imines **1.63** with an allene by rhenium catalysis.[34] This reaction proceeds *via* the intermolecular insertion of allene into a C-H bond of aromatic compounds followed by successive intramolecular nucleophilic cyclization (Scheme 1.22).

Scheme 1.22



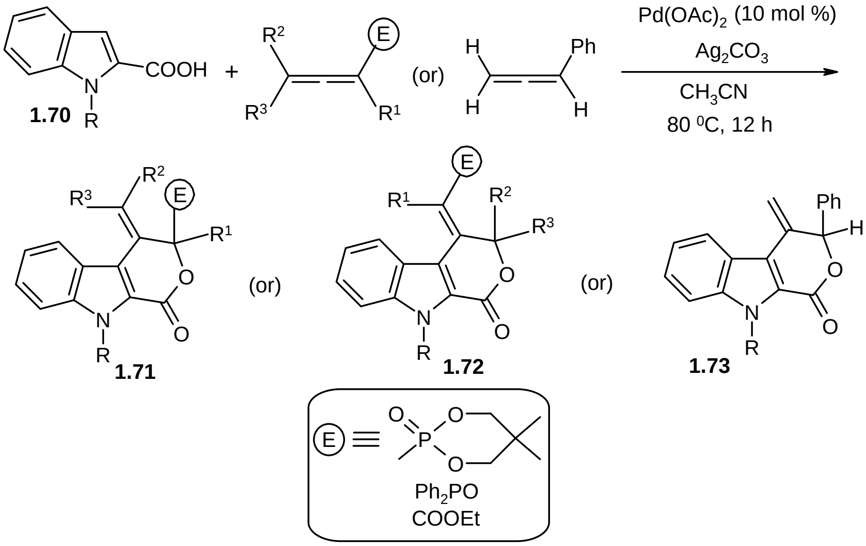
Nair and co-workers discovered a new method for the synthesis of highly functionalized pyrazolines and fully substituted pyrazoles by triphenylphosphine mediated reaction of dialkyl azodicarboxylates with allenic esters.[35a] When they treated allene **1.65** with the *in situ* generated Morrison-Brunn-Huisgen betaine **1.66** in DME at room temperature, substituted pyrazole derivative **1.67** was obtained in good yields (Scheme 1.23a). This reaction took place *via* a novel rearrangement involving the nitrogen-carbon migration of the carboalkoxy group. When they treated *α*-substituted allene **1.68** with the zwitterion **1.66**, functionalized pyrazoline **1.69** was obtained (Scheme 1.23b). Similarly, optically active pyrazolidine derivatives were synthesized by using copper and palladium catalyzed one-pot tandem addition-cyclization reaction of allenes with organic halides and dibenzyl azodicarboxylate.[35b]

Scheme 1.23



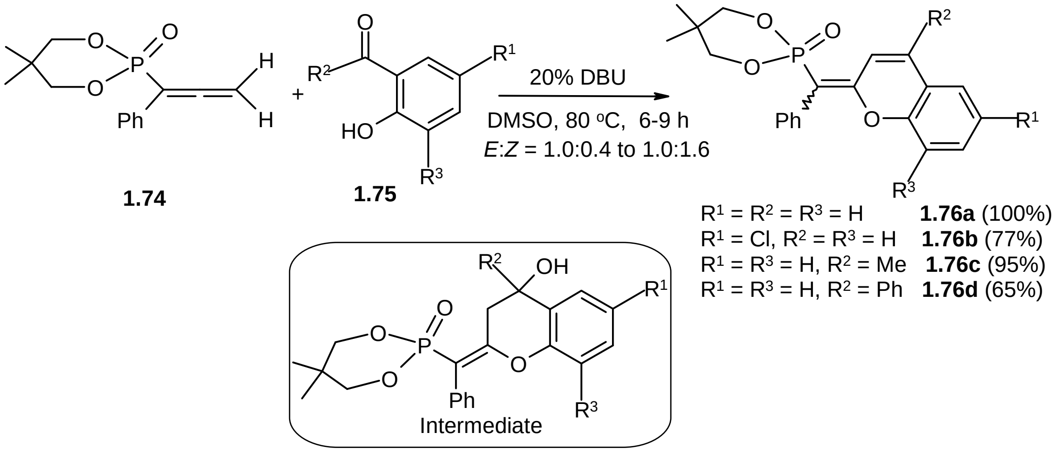
Very recently, a highly efficient approach to indolo[2,3-*c*]pyrane1-one derivatives through the Pd-catalyzed regioselective annulation of allenes with indole-2-carboxylic acid derivatives *via* C-H functionalization was reported from our laboratory (Scheme 1.24).[36] This reaction involves the palladium catalyzed oxidative annulation of allenes *via* direct C-H functionalization of indole-2-carboxylic acids **1.70** at the C-3 position affording the desired indolo pyranones **1.71-1.73** in moderate to good yields. In another report from our research group, several phosphono heterocycles were obtained by Pd-catalyzed coupling reactions of allenylphosphonates with aryl iodides, iodophenols, or 2-iodobenzoic acid.[8a]

Scheme 1.24



Base catalyzed cyclization of allenylphosphonates with salicylaldehydes or hydroxyaceto-/benzo-phenones leading to phosphono-chromenes has also been reported from our laboratory.[37] Thus, phosphorylated allene **1.74** reacted with salicylaldehydes or hydroxyaceto-/benzophenones **1.75** in the presence of DBU (20 mol%) to give phosphono-chromenes **1.76a-d** in good yields with an *E*/*Z* ratio up to 1.0:0.4 (Scheme 1.25). This reaction involves a nucleophilic attack of phenoxide ion at the *β*-position of allene followed by the cyclization to lead to a hydroxy derivative that undergoes dehydration to afford **1.76a-d**.

Scheme 1.25

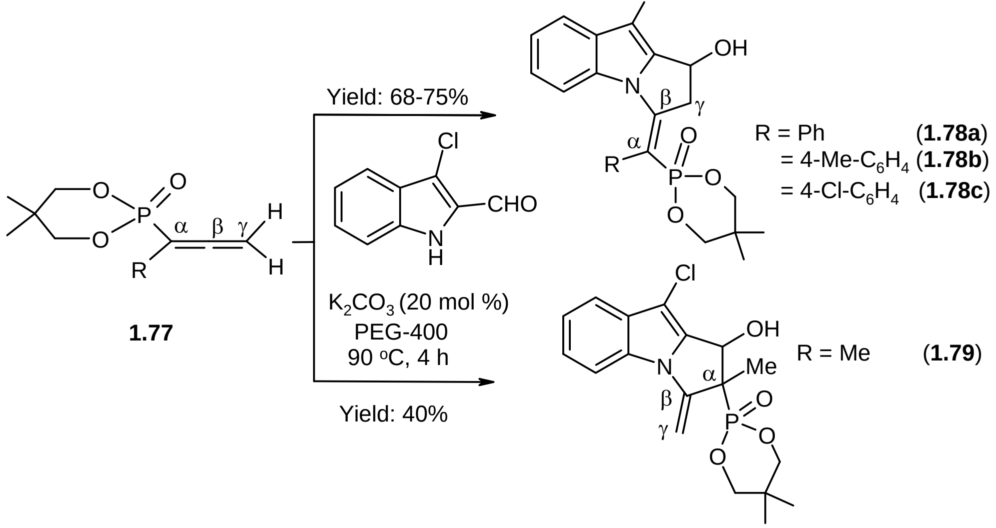


1.74 1.75

$R^1 = R^2 = R^3 = H$ **1.76a** (100%)
$R^1 = Cl, R^2 = R^3 = H$ **1.76b** (77%)
$R^1 = R^3 = H, R^2 = Me$ **1.76c** (95%)
$R^1 = R^3 = H, R^2 = Ph$ **1.76d** (65%)

Similar to the above, pyrrolo[1,2-a]indoles were also synthesized from our laboratory *via* base catalyzed domino cyclization of activated allenes with 3-chloro-2-formylindole in the environmentally friendly PEG-400 medium.[38] Thus α-aryl substituted allenylphosphonates **1.77** were treated with 3-chloro-2-formylindoles to give the (β,γ)-cyclized products **1.78a-c**, while the α-methyl substituted allenylphosphonate resulted in the (β,α)-cyclized product **1.79** (Scheme 1.26). The structure of the product depends on the type of substituent present on the allene. Allenes containing a sulfonyl group ($ArSO_2$-) in place of phosphoryl group provided a result similar to that of allenylphosphonates.

Scheme 1.26



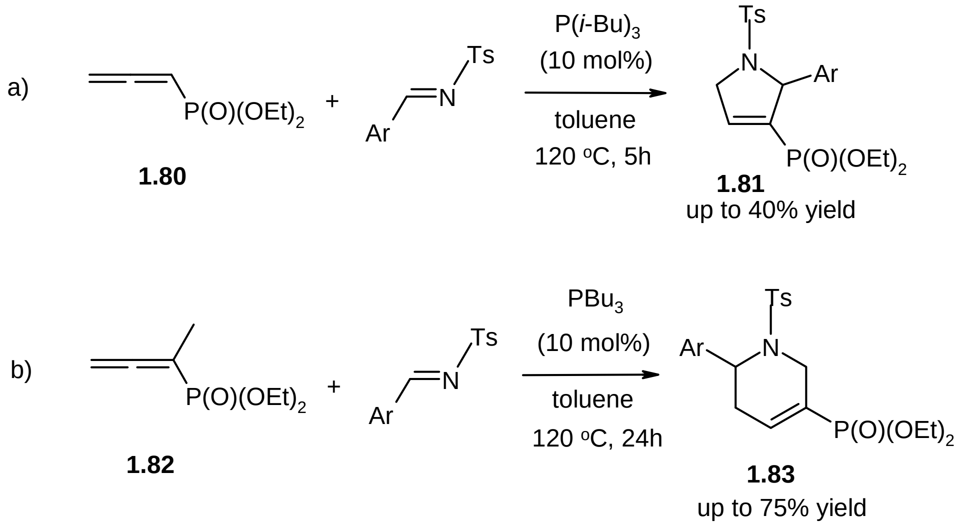
1.77

R = Ph (**1.78a**)
= 4-Me-C_6H_4 (**1.78b**)
= 4-Cl-C_6H_4 (**1.78c**)

R = Me (**1.79**)

Marinetti and co-workers investigated the phosphine-catalyzed annulations reactions of allenylphosphonates (Scheme 1.27a).[39] Formation of phosphorus based pyrrolines **1.81** has been explained by intermolecular cyclization of allenylphosphonate **1.80** with imines in the presence of P(*i*-Bu)$_3$. Similarly, tetrahydropyridines **1.83** were synthesized from α-methyl substituted allenylphosphonate **1.82** by using PBu$_3$ (Scheme 1.27b).

Scheme 1.27

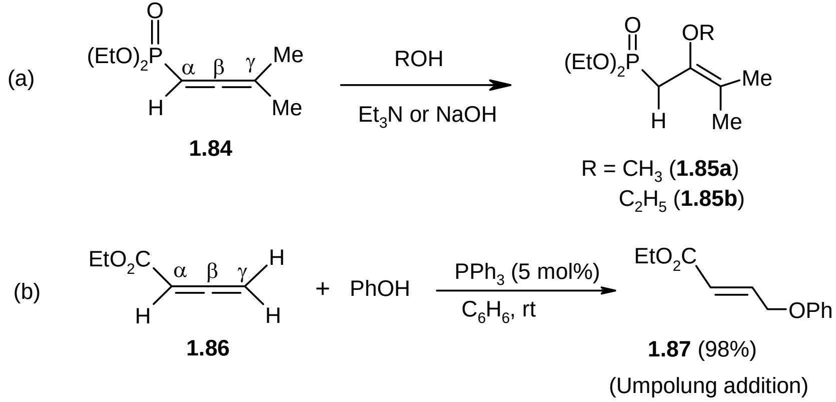


1.32 Nucleophilic addition reactions

Allenes are susceptible for nucleophilic addition reactions which are prominent synthetic tools for heterocyclic rings and many functionalized molecules.[40] Since allene is an unsaturated hydrocarbon having two cumulative double bonds, the incoming nucleophile can attack any one of the three sp^2 carbon atoms. If one of the substituents on allene is an electron withdrawing group (e.g., ester or phosphonate), nucleophile attacks at *β*–carbon of allene with very limited exceptions.[41] Simple addition reactions of allenylphosphonates with nucleophiles like alcohols, phenols, amines or thiols leading to vinyl-or allyl-phosphonates have been reported.

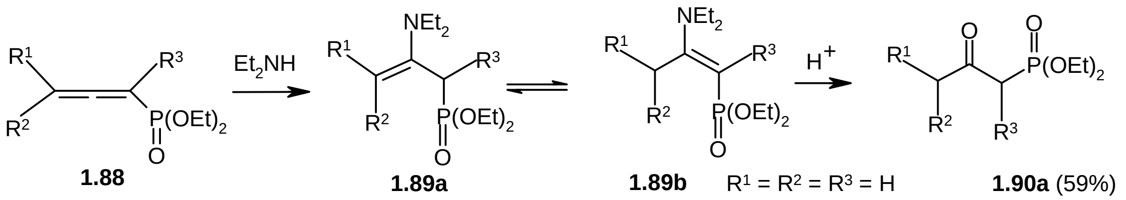
The reaction of alcohols with allenylphosphonate **1.84** in the presence of NaOH or triethylamine as a base leads to the addition products enol ethers **1.85a-b**, which are formed by the nuclophilic addition at the *β*-carbon of the allene (Scheme 1.28a).[42] In contrast to this, phenol attacks the *γ*-carbon of allenyl ester **1.86** under phosphine catalyzed reactions and produces umpolung addition product **1.87** in 98% yield (Scheme 1.28b).[43]

Scheme 1.28



Nucleophilic addition of diethylamine takes place at the *β*-carbon of the allenylphosphonates **1.88** and produces enamines **1.89a** and **1.89b** that are in equilibrium with each other. These enamines upon subsequent acid hydrolysis lead to the *β*-ketophosphonates **1.90a-d** (Scheme 1.29).[44]

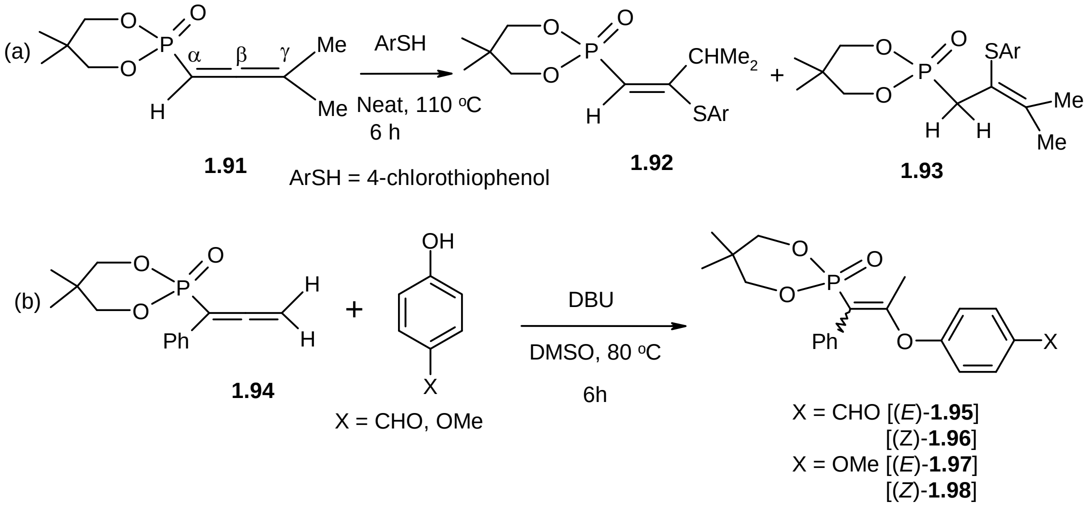
Scheme 1.29



$R^1 = R^2 = R^3 = H$ **1.90a** (59%)
$R^1 = H, R^2 = Me, R^3 = H$ **1.90b** (71%)
$R^1 = R^2 = Me, R^3 = H$ **1.90c** (78%)
$R^1 = R^2 = H, R^3 = Me$ **1.90d** (68%)

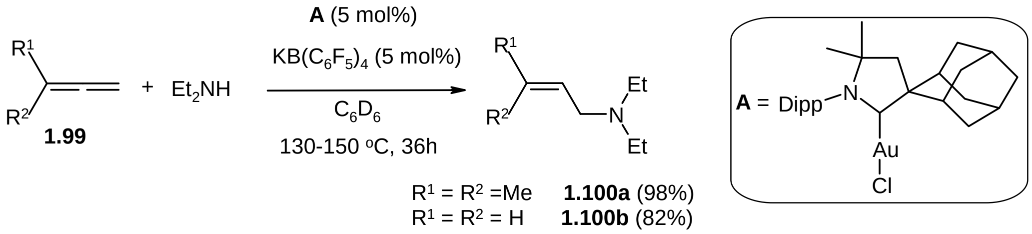
Nucleophilic addition reactions of allenylphosphonate **1.91** with various thiophenols under neat conditions lead to vinyl- and allyl-phosphonates **1.92** and **1.93** (Scheme 1.30a).[45] Similarly, vinyl-phosphonates **1.95-1.98** were prepared by nucleophilic addition of substituted phenols at the *β*-carbon of the allenylphosphonate **1.94** in the presence of base (Scheme 1.30b).[37] The addition of nucleobases to allenylphosphonates, developed from our group, also represents a new route to *β*–amino phosphonates.[46]

Scheme 1.30



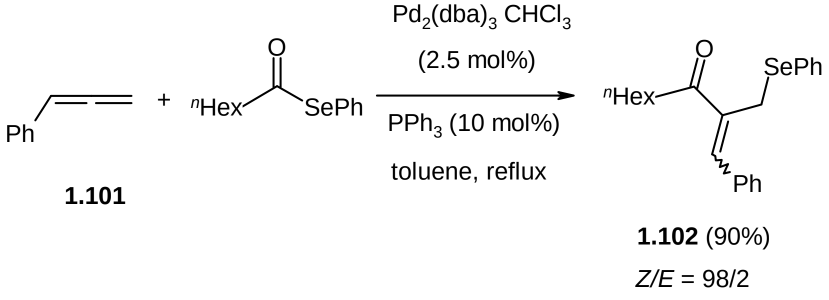
Bertrand and co-workers reported gold-catalyzed intermolecular Markovnikov addition or hydroamination of allenes with nontertiary amines.[47] A cationic gold(I) complex promoted the addition diethylamine to the less substituted terminus of allenes **1.99** producing allylic amines **1.100a-b** in good to excellent yields (Scheme 1.31).

Scheme 1.31



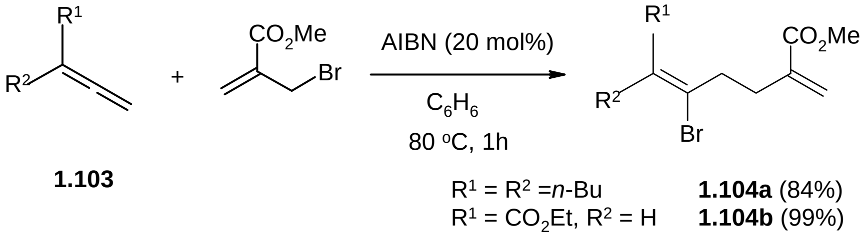
Selenoacylation of allenes leading to allyl selenides catalyzed by palladium has been reported by Fuziwara, Kambe and co-workers.[48] Thus 1,2-addition of selenol esters onto allene **1.101** proceeded with excellent regioselectivity and high stereoselectivity in the presence of Pd(0)-PPh_3 catalytic system, producing functionalized allyl selenides **1.102** (Scheme 1.32). Addition of acyl group took place at the inner carbon and SePh group entered the terminal carbon.

Scheme 1.32



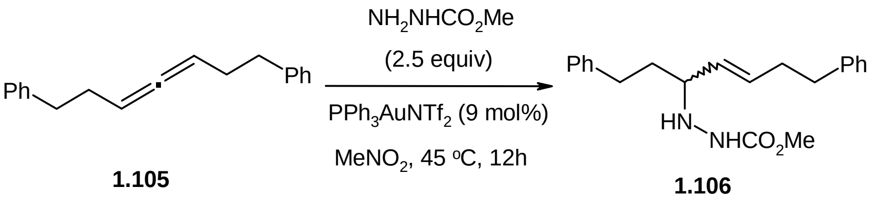
Ryu and co-workers have discovered a regioselective radical bromoallylation of allenes **1.103** with allyl bromides to obtain 5-bromo-substituted 1,5-dienes **1.104a-b** in the presence of AIBN as a radical initiator.[49] This reaction proceeded through the addition of bromine radical onto the central carbon of allenes generating a stable allyl radical, which underwent addition/*β*-fragmentation with allyl bromides (Scheme 1.33). The introduction of -CO_2Me group to the *β*-position of allyl bromide accelerated the addition reaction.

Scheme 1.33



Toste and co-workers reported the first example of intermolecular hydroamination of allenes by using gold catalysis.[50] The nucleophilic addition of N-N linked hydrazide on allene **1.105** in the presence of $Ph_3PAuNTf_2$ led to the α- or γ-addition product **1.106** (Scheme 1.34).

Scheme 1.34



1.105

1.106

> 95% conversion

Thus the above survey highlights the potential of allenic substrates in cyclization/ cyclo-isomerization/ addition reactions. Our objective was to utilize allene intermediates for the synthesis of phosphorus based carbo-/hetero-cycles as discussed in the next chapter.

OBJECTIVES OF THE PRESENT WORK - PART A

The main goal of this part of the present work is to explore the synthesis of various phosphorus based nitrogen heterocycles *via* intermediacy of allenes. Specifically, the objectives were

(i) To synthesize functionalized allenylphosphonates/ allenylphosphine oxides using propargyl alcohols and various P^{III}-Cl precursors,

(ii) To study the intramolecular cyclization reactions of *in situ* generated phosphorus-based allenes leading to various nitrogen heterocycles,

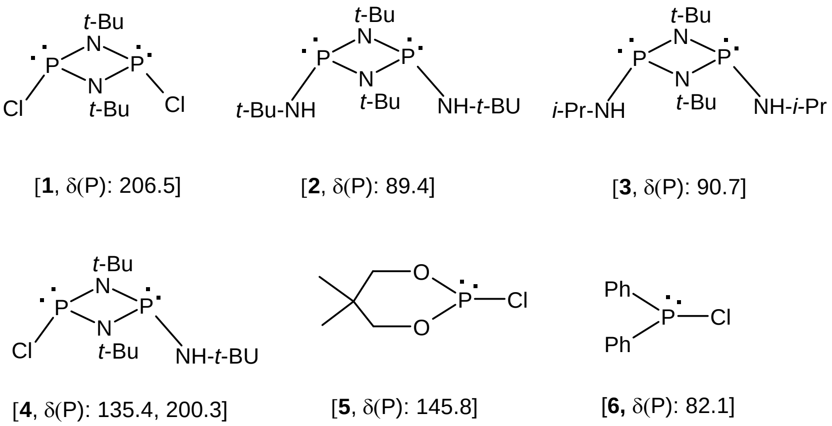
(iii) To investigate the base-catalyzed intermolecular cyclization and isomerization reactions of allenylphosphonates/ allenylphosphine oxides and

(iv) To study the nucleophilic addition/cyclization reactions allenylphosphonates/ allenylphosphine oxides.

RESULTS AND DISCUSSION

The P^{III} precursors $[ClP(\mu\text{-}N\text{-}t\text{-}Bu)]_2$ (**1**),[51] $[(t\text{-}BuNH)P(\mu\text{-}N\text{-}t\text{-}Bu)]_2$ (**2**),[52] $[(i\text{-}PrNH)P(\mu\text{-}N\text{-}t\text{-}Bu)]_2$ (**3**),[52c] $[(t\text{-}BuNH)P(\mu\text{-}N\text{-}t\text{-}Bu)_2P\text{-}Cl]$ (**4**),[53] $(OCH_2CMe_2CH_2O)PCl$ (**5**)[54] and Ph_2PCl (**6**) used in the present study are shown in Chart 1. The precursor **3** was prepared by using a literature procedure.[52a] These P^{III}-Cl compounds are sensitive to moisture but can be handled under inert atmosphere.

Chart 1

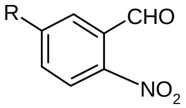


[**1**, δ(P): 206.5] [**2**, δ(P): 89.4] [**3**, δ(P): 90.7]

[**4**, δ(P): 135.4, 200.3] [**5**, δ(P): 145.8] [**6**, δ(P): 82.1]

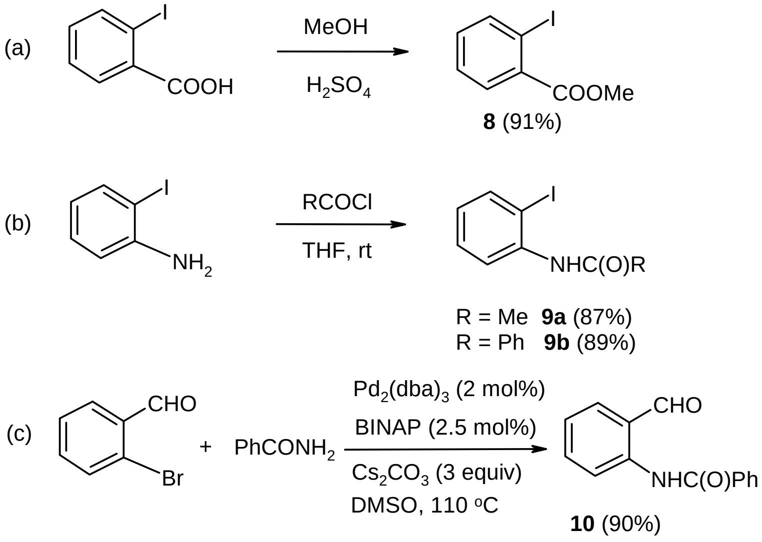
2.1 Synthesis of substituted haloarenes 7-9 and *N*-(2-formylphenyl)benzamide 10

5-Halo-2-nitrobenzaldehydes **7a-b** were prepared by following a literature method *via* nitration of corresponding benzaldehyde with potassium nitrate using sulfuric acid as the solvent.[55] The iodoarene **8**[56] was synthesized by esterification of 2-iodobenzoic acid in methanol in the presence of catalytic amount of sulfuric acid (Scheme 1a). 2-Substituted iodobenzenamides **9a-b**[57] were synthesized by treating 2-iodoaniline with the corresponding acid chlorides in THF (Scheme 1b). *N*-(2-Formylphenyl)benzamide **10**[58] was prepared by using a literature procedure *via* palladium catalyzed amidation (Scheme 1c).[59]



R = Cl, **7a**
R = Br, **7b**

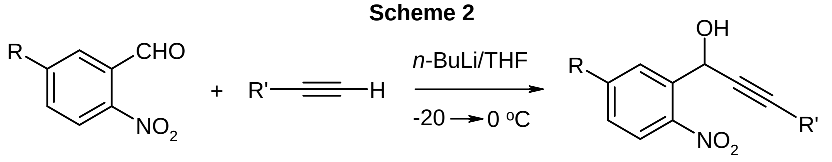
Scheme 1



2.2 Synthesis of functionalized propargylic precursors 11a-m and 12-15

The nitro-group containing propargylic alcohols **11a-m** were prepared by modifying a literature method (Scheme 2).[28,60] In this reaction, initially, *n*-BuLi forms lithium acetylide using the terminal (acetylinic) proton. This acetylide adds across the carbonyl carbon to form the -OLi salt which upon treatment with aqueous NH_4Cl affords the corresponding propargyl alcohol. Among these propargyl alcohols, compounds **11h-j** and **11l-m** are new. They have been characterized by IR [υ(C≡C) ~2223 and υ(OH) ~ 3410 (br) cm^{-1}] and NMR [^1H, ^{13}C] spectroscopic techniques. Various functionalized propargyl alcohols **12-15** were also obtained by following a standard method *via* Sonogashira coupling (Scheme 3).[61] Among these propargyl alcohols, **12**[62], **13**[63] and **14a-b**[64] are known. Compounds **14c**, **15b-c** and **15e-m** are new. They have been characterized by IR [υ(C≡C) ~2220 and υ(OH) ~ 3342 (br) cm^{-1}] and ^1H/ ^{13}C NMR spectroscopic techniques. They are stable viscous brown colored liquids.

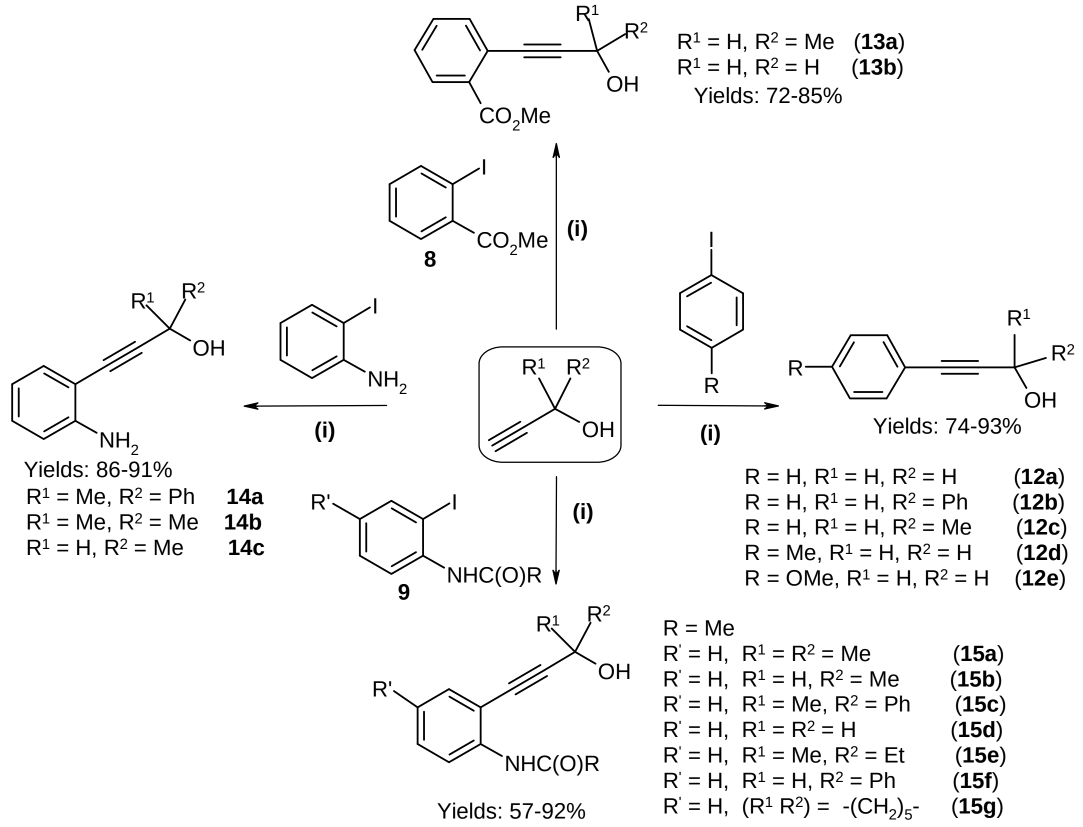
Scheme 2



Yields: 73-91%

R = H, R' = Ph (**11a**)
R = H, R' = $SiMe_3$ (**11b**)
R = H, R' = cyclohexenyl (**11c**)
R = H, R' = n-C_5H_{11} (**11d**)
R = H, R' = 4-Me-C_6H_4 (**11e**)
R = Cl, R' = Ph (**11f**)
R = Cl, R' = cyclohexenyl (**11g**)
R = Cl, R' = n-C_5H_{11} (**11h**)
R = Cl, R' = 4-Me-C_6H_4 (**11i**)
R = Br, R' = Ph (**11j**)
R = Br, R' = cyclohexenyl (**11k**)
R = Br, R' = n-C_5H_{11} (**11l**)
R = Br, R' = 4-Me-C_6H_4 (**11m**)

Scheme 3



R^1 = H, R^2 = Me (**13a**)
R^1 = H, R^2 = H (**13b**)
Yields: 72-85%

Yields: 86-91%
R^1 = Me, R^2 = Ph **14a**
R^1 = Me, R^2 = Me **14b**
R^1 = H, R^2 = Me **14c**

Yields: 74-93%

R = H, R^1 = H, R^2 = H (**12a**)
R = H, R^1 = H, R^2 = Ph (**12b**)
R = H, R^1 = H, R^2 = Me (**12c**)
R = Me, R^1 = H, R^2 = H (**12d**)
R = OMe, R^1 = H, R^2 = H (**12e**)

Yields: 57-92%

R = Me
R' = H, R^1 = R^2 = Me (**15a**)
R' = H, R^1 = H, R^2 = Me (**15b**)
R' = H, R^1 = Me, R^2 = Ph (**15c**)
R' = H, R^1 = R^2 = H (**15d**)
R' = H, R^1 = Me, R^2 = Et (**15e**)
R' = H, R^1 = H, R^2 = Ph (**15f**)
R' = H, (R^1 R^2) = -$(CH_2)_5$- (**15g**)
R' = Me, R^1 = R^2 = H (**15h**)
R' = Me, R^1 = H, R^2 = Me (**15i**)
R' = Me, R^1 = H, R^2 = Ph (**15j**)
R' = Me, R^1 = Me, R^2 = Me (**15k**)
R' = Me, R^1 = Me, R^2 = Ph (**15l**)
R = Ph, R' = R^1 = H, R^2 = Me (**15m**)

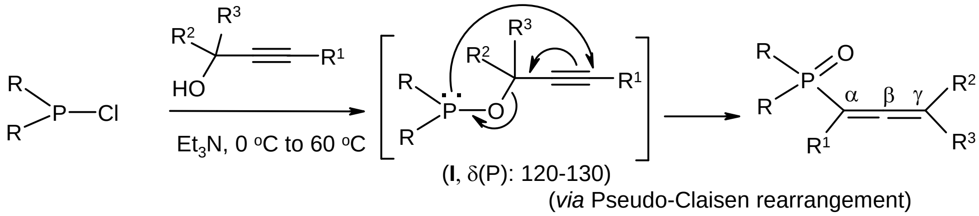
(i) Conditions: $PdCl_2(PPh_3)_2$/CuI/Et_3N/CH_3CN/rt/4-6h

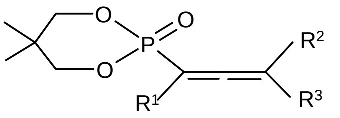
2.3 Reactivity of P^{III} precursors with propargyl alcohols

2.31 Synthesis of functionalized allenylphosphonates 16-17 and allenylphosphine oxides 18-20

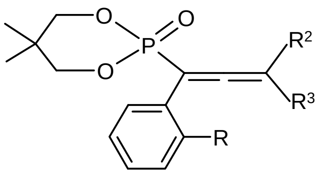
Allenylphosphonates **16a-k/ 17a-c** and allenylphosphine oxides **18-19/ 20a-d** are prepared by following a method previously reported from our laboratory (Scheme 4).[19,65] The reaction involves the reaction of P^{III}-Cl precursor with the appropriate propargyl alcohol in the presence of triethylamine leading to the allenylphosphonates/ allenylphosphine oxides *via* a *pseudo*-Claisen rearrangement of the initially formed P^{III} intermediate (**I**). Among these, **16a-c**[37], **18**[66], **19**[63] are known. Allenes **16d-k**, **17a-c**, and **20a-d** are new. These allenes are quite stable in the solid state in air for a day, and can be preserved for a few months at low temperature (4 ^{o}C) under an inert atmosphere. In the IR spectra, they show a characteristic strong band at 1920-1965 cm^{-1} due to ν_{asym}(C=C=C).[67] The ^{31}P NMR spectra of allenylphosphonates **16a-k** and **17a-c** show a peak in the range δ 5-9, whereas allenylphosphine oxides **18-19** and **20a-d** show a peak in the range δ 27-35. In the ^{13}C NMR spectra, the α-carbon (to phosphorus) appears as a doublet at δ 94-100 [^{1}J(P-C) ~ 185.0 Hz] for **16a-k** and **17a-c** whereas it is at δ 98-105 [^{1}J(P-C) ~ 100 Hz] for **20a-d**. The PC=*C* signal for all these compounds appears as a doublet in the region δ 208-214 [^{2}J(P-C) ~ 6.0-8.0 Hz]. Since this protocol is fairly well-known, it is not elaborated here.

Scheme 4

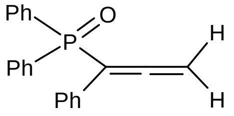




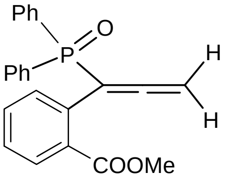
R^1 = Ph, R^2 = R^3 = H [**16a**, δ(P): 6.6; 72%]
R^1 = 4-Me-C_6H_4, R^2 = R^3 = H [**16b**, δ(P): 7.8; 80%]
R^1 = 4-MeO-C_6H_4, R^2 = R^3 = H [**16c**, δ(P): 7.5; 79%]
R^1 = Ph, R^2 = Me, R^3 = H [**16d**, δ(P): 8.2; 72%]
R^1 = 4-MeO-C_6H_4, R^2 = Me, R^3 = H [**16e**, δ(P): 8.6; 78%]
R^1 = Ph, R^2 = Ph, R^3 = H [**16f**, δ(P): 6.1; 73%]
R^1 = 4-MeO-C_6H_4, R^2 = Ph, R^3 = H [**16g**, δ(P): 6.5; 81%]
R^1 = Ph, R^2 = 4-Cl-C_6H_4, R^3 = H [**16h**, δ(P): 5.8; 92%]
R^1 = Ph, R^2 = 4-Br-C_6H_4, R^3 = H [**16i**, δ(P): 5.7; 86%]
R^1 = Ph, R^2 = 2-Br-C_6H_4, R^3 = H [**16j**, δ(P): 5.7; 83%]
R^1 = Ph, R^2 = 4-Me-C_6H_4, R^3 = Me [**16k**, δ(P): 7.2; 82%]



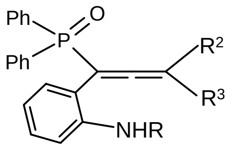
R = NHC(O)Me
R^2 = Me, R^3 = Ph [**17a**, δ(P): 9.0; 72%]
R = NHC(O)Ph
R^2 = Me, R^3 = Ph [**17b**, δ(P): 8.7; 64%]
R = CO_2Me
R^2 = Me, R^3 = H [**17c**, δ(P): 8.3; 83%]



[**18**, δ(P): 30.2; 78%]



[**19**, δ(P): 27.7; 83%]



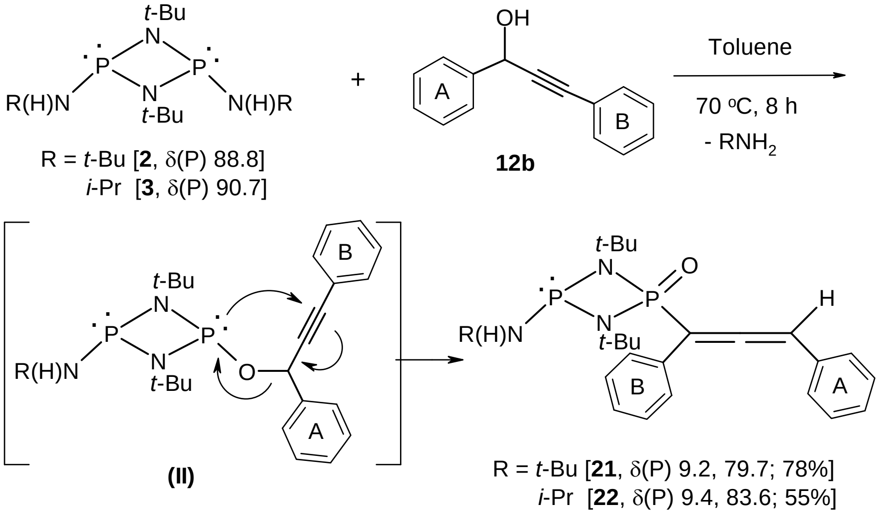
R = -C(O)Me
R^2 = R^3 = Me [**20a**, δ(P): 35.2; 87%]
R^2 = H, R^3 = Me [**20b**, δ(P): 34.1; 78%]
R^2 = Me, R^3 = Ph [**20c**, δ(P): 34.5; 92%]
R = -C(O)Ph
R^2 = H, R^3 = Me [**20d**, δ(P): 34.3; 75%]

2.32 Reactivity of P^{III} compounds with *o*-nitro functionalized propargyl alcohols and *N*-hydroxy substrates

2.321 Synthesis of phosphorus based indolinones, oxa-aza-benzocycloheptenones, fused polycyclics, phosphorus-free indoles, quinolinones and tetrahydroacridine

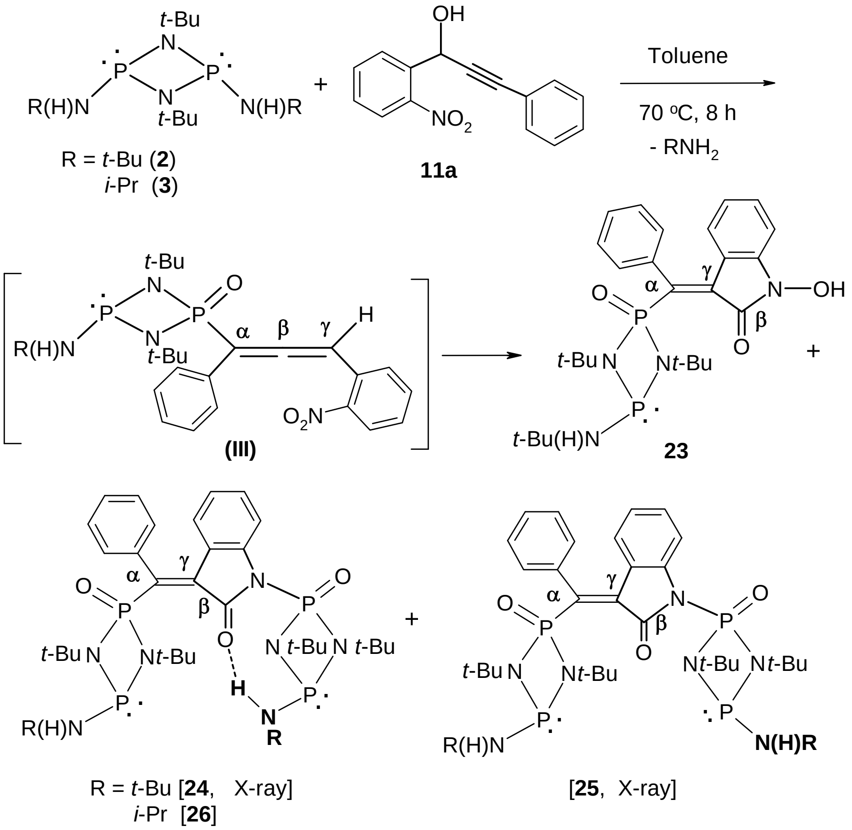
Initially, we started the reaction of cyclodiphosphazanes **2-3** with aryl substituted propargyl alcohol **12b**[68] that led to cyclodiphosphazane based allenes **21** and **22** (Scheme 5). The ^{31}P NMR spectra showed two signals each, one at tetracoordinate region and the other at tricoordinate region, as expected. The presence of the allenic group was readily inferred from IR [1912-1929 cm^{-1}] and ^{13}C NMR [δ(C=*C*=C) ~ 216] spectra. The P-C carbon appeared 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 **II**.

Scheme 5



What is perhaps interesting is that, in the above reaction, if we provide an *o*-NO_2 group on the phenyl ring (A), we end up in the uncommon cyclodiphosphazane based heterocycles. Thus treatment of [(*t*-BuNH)P(*μ*-N-*t*-Bu)]$_2$ (**2**) with the propargyl alcohol **11a** leads to the cyclodiphosphazanyl-indolinones **23** and **24-25**. The yields of the bis(cyclophosphazanyl) products **24-25** can be enhanced by increasing the stoichiometry of the cyclophosphazane **2** (Scheme 6). The yields given in Scheme 6 are after isolation from column chromatography. In the reaction mixture (^{31}P NMR), these are slightly higher. NMR (^{1}H, ^{13}C and ^{31}P), IR and HRMS data confirm the identity of **23**.[28] Additional proof comes from the single crystal X-ray structural characterization of **24**·1.5H_2O and **25** (Figure 1). The difference in the structures of **24** and **25** lies in 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 only in **24**. Use of the isopropylamino substrate **3** afforded mainly product **26**. A structure similar to **24** is assigned based on the similarity in the ^{1}H NMR spectra between the two compounds. To our knowledge, reactions such as these are unprecedented.

Scheme 6



<u>**Yields of isolated products 23-26 (see text for details)**</u>

Stoichiometry used (**2: 11a**): 1.2:1	**23** (34%)	**24+25** (18%) [+ other products]	
Stoichiometry used (**2: 11a**): 2:1	**23** (<15%)	**24** (36%)	**25** (28%)
Stoichiometry used (**3: 11a**): 2:1	**26** (33%) [+ other hydrolyzed products]		

Notable features in the structures of **23-26** are (i) the unusual ***change of position of the β-carbon*** in the intermediate **III** and the final products **23-26** suggesting a new rerrangement, (ii) the transfer of an oxygen atom from the –NO_2 group to a carbon in the five-membered ring, and (iii) an novel rearrangement from P^{III}-O-N to (O)P^{V}–N[69] (for **24-26**).

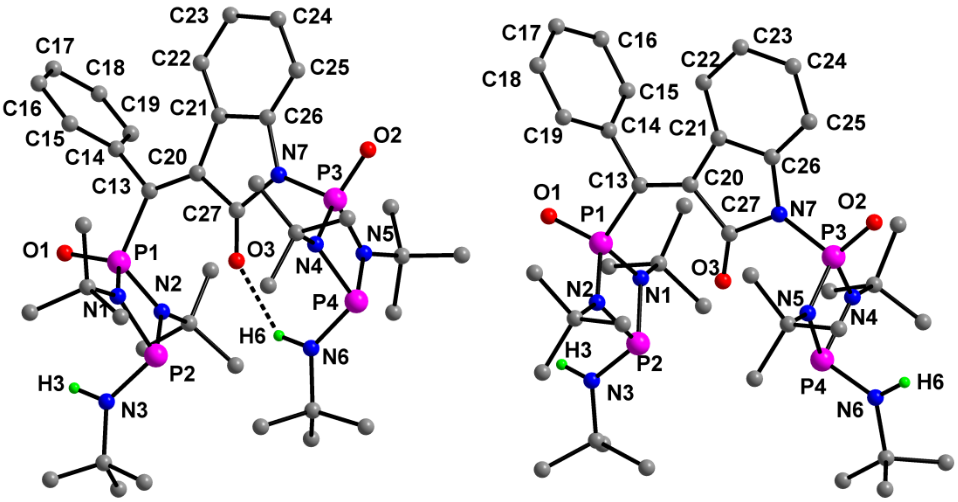
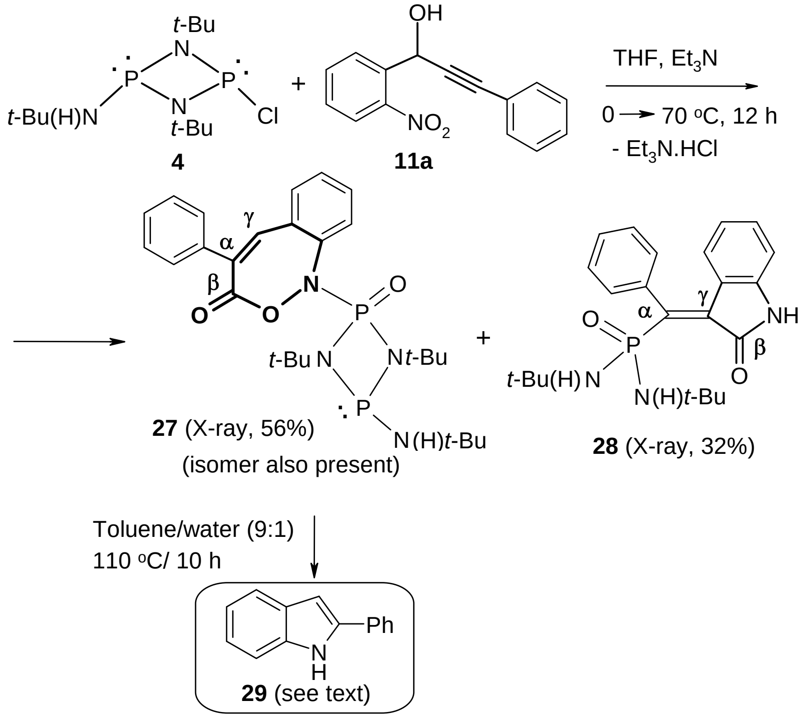


Figure 1. Left: Molecular structure of compound **24**·1.5H_2O. Only selected atoms are labeled. Hydrogen atoms (except NH) and the water molecules are omitted for clarity. Selected bond distances: C13-C20 distance 1.375(6) (Å). Hydrogen bonding interactions: N6-H6…O3 0.98(5), 2.21(5), 3.055(5) Å, 144(4)°. **Right**: Molecular structure of compound **25.** Hydrogen atoms (except NH) are omitted for clarity. C13-C20 distance is 1.363(4) (Å).

Surprised by the intricacies involved in the above reaction, we probed the reaction further by using the monochloro-cyclodiphosphazane [(*t*-BuNH)P(*μ*-N-*t*-Bu)$_2$P-Cl] (**4**). It may be noted that a simple replacement of –Cl by the propargyloxy group followed by rearrangement should have afforded the same compounds **24-25**. However, **24-25** were only the minor products and the major products were the unsuspected and unusual phosphazane connected cyclic products **27** and **28** (Scheme 7). The molar stoichiometry used was 1.2:1 [**4**:**11a**]. Compound **27** is fairly stable but in $CDCl_3$ solution exhibits two sets of signals [ca 7:3 ratio] in both ^1H 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 **27**, although the crystals obtained showed two sets of signals corresponding to two isomers [$^{31}P/^1H$ NMR]. The ^{31}P NMR spectrum exhibited signals at δ 73.1 and 3.0 with J = 6.7 Hz [I set:] and 74.1 and –0.7 with J = 12.2 Hz [II set]. We were able to isolate 2-phenyl-indole **29 (**ca 48%) from the hydrolysis/dephosphorylation as well as CO_2 elimination from compound **27** (Scheme

7). The reaction is significant in the sense that a new (perhaps bizarre) route to 2-substituted indoles has been uncovered.

Scheme 7



Compound **28** (cf. Scheme 7) was isolated in 32% yield. The ^{31}P NMR spectrum exhibited a single peak at δ(P) 11.1, suggesting the cleavage of cyclodiphosphazane ring. The presence of P-C bond is confirmed by a doublet at δ 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 7.

Further confirmation of the structures **27** and **28** is provided by single crystal X-ray structures (Figures 2 and 3). The novel seven-membered ring in **27** 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 **11a** has been altered. *While there are three intervening carbon atoms between the two aryl groups in the precursor **11a**, only two intervening carbon atoms are present in the product **27**.* To our knowledge, such a reaction is unprecedented.

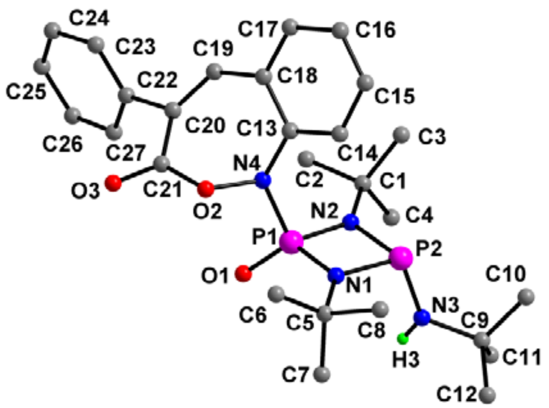


Figure 2. Molecular structure of compound **27.**$PhCH_3$. Solvent molecule and hydrogen atoms (except NH) are omitted for clarity. Selected bond distances (Å): N4-O2 1.447(4), O2-C21 1.370(5), C21-C20 1.484(6), C20-C19 1.340(6), C19-C18 1.449(6), C18-C13 1.424(6), C13-N4 1.428(5). N3-H3 O1^{i}…0.76(5), 2.47(5), 3.195(5), 160(6). Symm. equiv.:(i) 1-x, -y, 1-z.

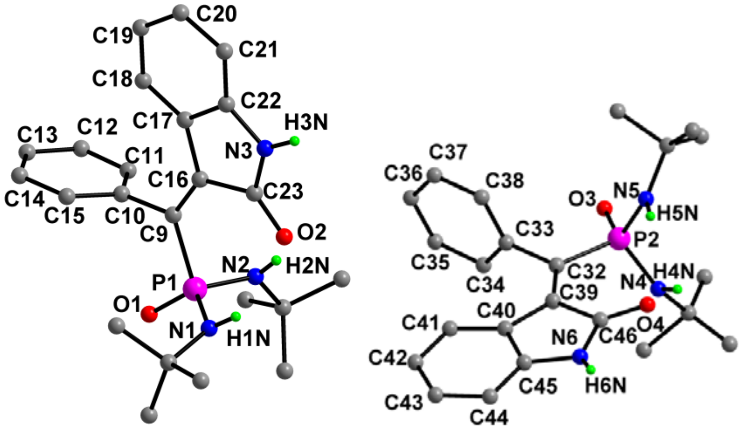
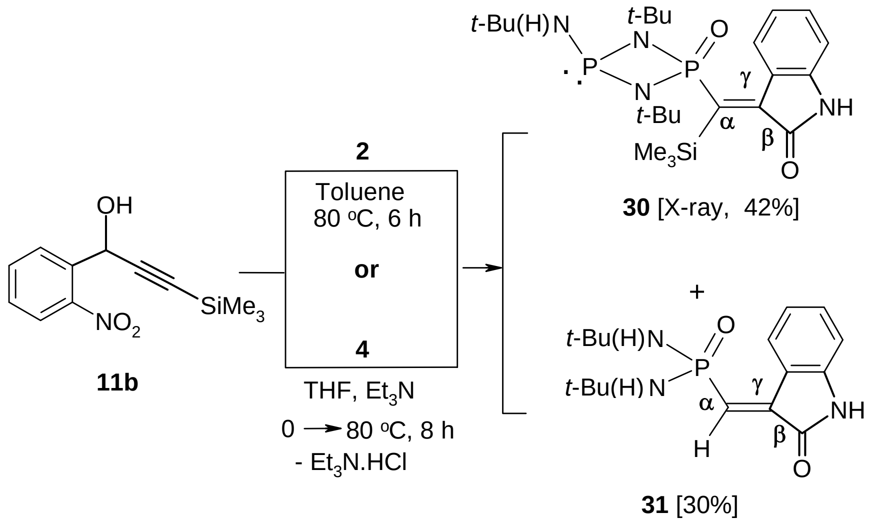


Figure 3. Molecular structure of compound **28**; Hydrogen atoms (except NH) are omitted for clarity. Both the molecules in the asymmetric unit are shown. Selected bond distances (Å): P1-C1 1.852(4), C9-C16 1.355(4), P2-C32 1.835(4), C32-C39 1.356(5). H-bond parameters (Å, Å, Å, ^{o}): N6-H6N…O1 0.75(5), 2.06(5), 2.798(4), 169(6); N5-H5N-O4 0.77(5,) 2.33(5), 2.977(5), 142(5); N4-H4N…O4 0.785(19), 2.38(3), 2.897(4), 124(4); N1-H1N…O2 0.78(5), 2.19(5), 2.834(5), 141(5); N2-H2N…O2 0.72(5), 2.49(5), 3.039(5), 134(6); N3-H3N…O3^{i} 0.84(5), 1.92(5), 2.762(4), 175(5). Symm. equiv: (i) x, 1+y, z.

Use of the propargyl alcohol $Me_3SiC{\equiv}CCH(OH)(2\text{-}NO_2C_6H_4)$ (**11b**),[68b] which has a $-SiMe_3$ group in place of a phenyl group in $PhC{\equiv}CCH(OH)(2\text{-}NO_2C_6H_4)$ (**11a**) resulted in the formation of cyclophosphazanyl-indolinones **30-31**. Either of the two substrates **2** or **4** can be used in this reaction (Scheme 8). The molar stoichiometry used was ~1.2:1 [**2** or **4**:**11b**]. Product **31** arises due to hydrolysis, most likely on the silica gel column. The structure of **30** is proven by X-ray crystallography (Figure 4). The principal difference in structure between these two compounds (**30-31**) and **28** lies in the relative disposition of phosphorus and the newly formed indolinone ring, as revealed by the X-ray structure. While in **28**, the phosphorus and C=O are *cis* with respect to the intervening double bond, they are *trans* in **30** and **31**.

Scheme 8



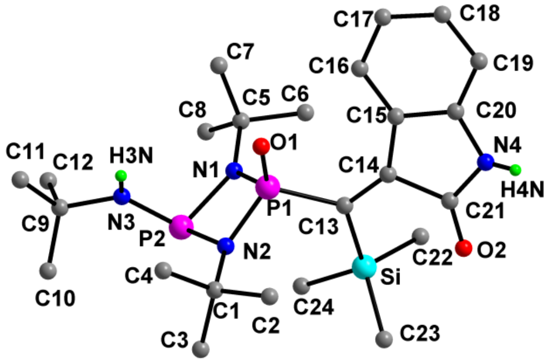
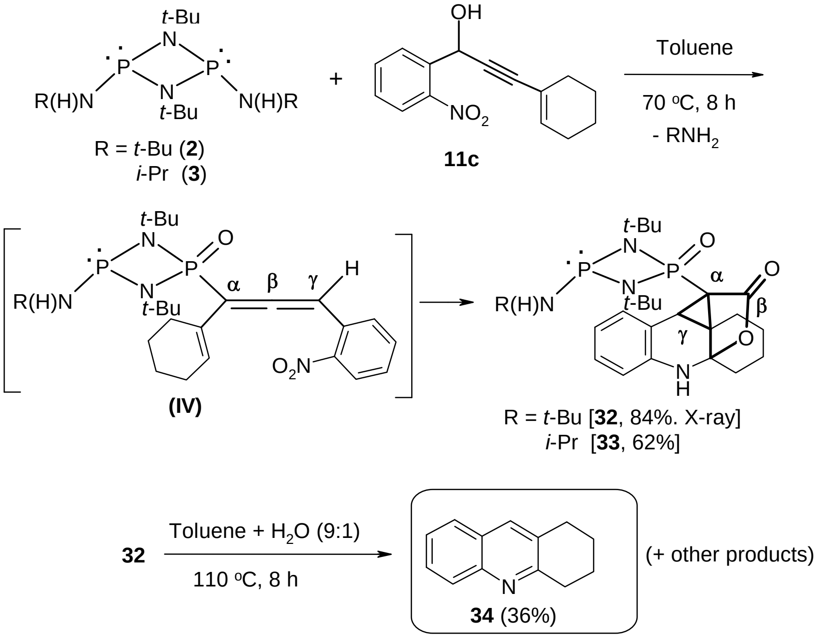


Figure 4. Molecular structure of compound $\mathbf{30}\cdot H_2O$. Hydrogen atoms (except NH) and water molecule are omitted for clarity. Selected bond distances (Å): Si-C13 1.954(5), C13-C14 1.351(6).

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 **11a** with a cyclohexenyl moiety in the precursor **11c**, the fused polycyclics **32-33** with a ***cyclopropane ring*** can be readily isolated (Scheme 9). The ^{31}P NMR spectra of **32-33** show two signals each at δ (74.3, 10.3) and (78.9, 10.2), respectively. These values are close to that for **21-22**. However, in the ^{13}C NMR spectra, the P-*C* carbon appears at δ ~38 [^{1}J(P-C) ~ 140-143 Hz] and δ(*C*=O) is around 171 ppm. These are quite different from that of the phosphoramidyl-allenes **21-22**. Fortunately, we were successful in obtaining the X-ray crystal structure of **32** that shows the novel structure. The three membered rings comprise [C13, C16, C21] and [C40, C43, C48] 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 (Figure 5). Based on the reaction shown in Scheme 6, compounds **32-33** are likely to be formed *via* cyclodiphosphazane based allene intermediate (**IV**) that further undergoes cyclization using the $-NO_2$ functionality. Treatment of the same propargyl alcohol **11c** with the cyclodiphosphazane [(*t*-BuNH)P(μ-N-*t*-Bu)$_2$P-Cl] (**4**) in the presence of Et_3N also led to the product **32**. Interestingly, compound **32** in the presence of water could be dephosphonylated to lead to tetrahydroacridine **34** (NMR and HRMS evidence;[70] it has two less carbon atoms than **32)** along with other products!

Scheme 9



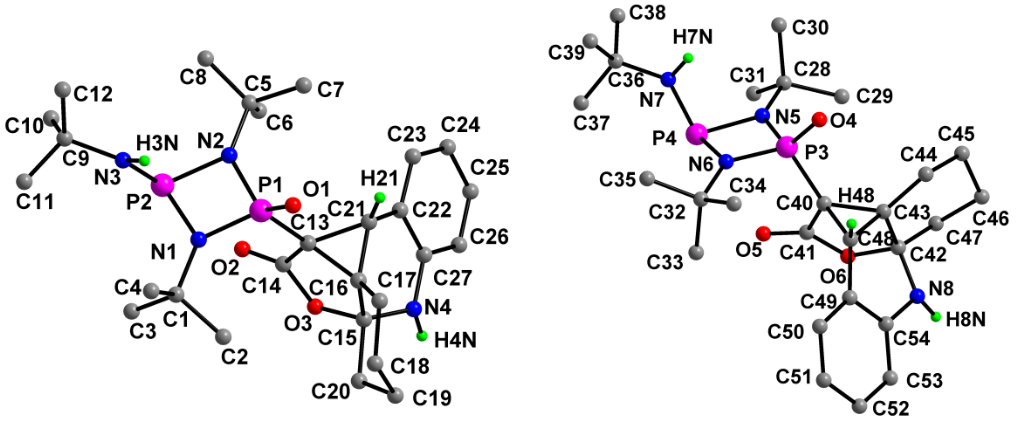
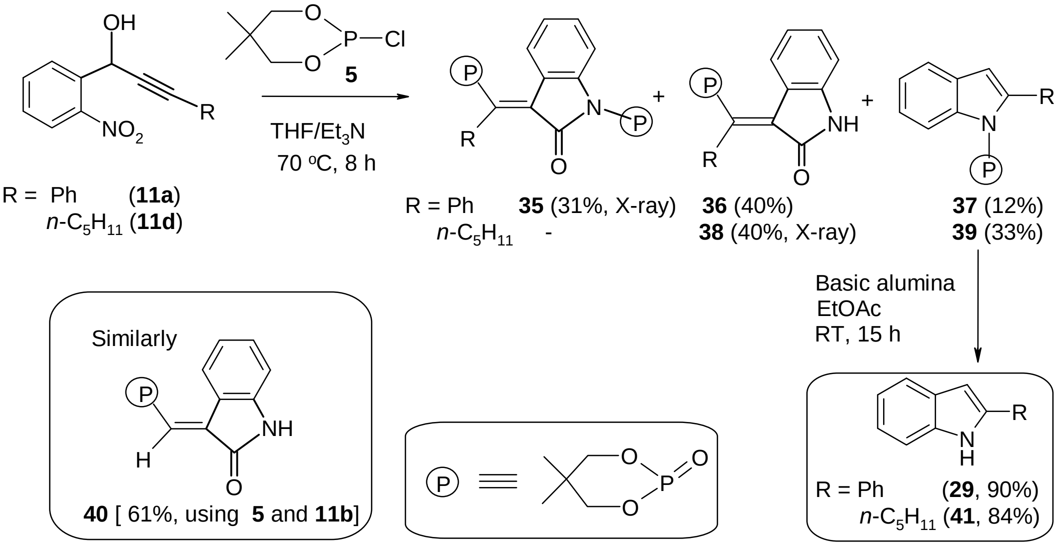


Figure 5. Molecular structure of compound **32**·1/2H$_2$O; both the molecules in the asymmetric unit are shown. Hydrogen atoms (except NH) and the solvent molecule are omitted for clarity. Selected bond distances (Å): P1-C13 1.820(5), C13-C16 1.533(8), C13-C21 1.547(6), C16-C21 1.496(7). P3-C40 1.811(5), C40-C43 1.532(7), C40-C48 1.545(8), C48-C43 1.473(7). H-bond parameters: O7-H7E…O1^{i} 0.898(19), 2.12(3), 2.976(5), 159(7),; O7-H7D…O4^{ii} 0.908(19), 2.13(3), 3.021(7), 168(9); N3-H3N…O6 0.98(6), 2.42(6), 3.344(6), 156(4); N4-H4N…O4 0.91(5), 2.02(5), 2.929(5), 177(5); N7-H7N…O3^{iv} 0.97(4), 2.48(4), 3.400(5), 159(5); N8-H8N…O1 0.94(5), 1.97(5), 2.898(6), 170(4).. Symm. equiv (not shown in the picture): (i) 1-x, 1-y, -z; (ii) 1+x, y, z; (iii) x, 1+y, z, (iv) x, -1+y, z,

We then proceeded to see if products similar to those using cyclodiphosphazanes are obtained if we use other P^{III} precursors like $(OCH_2CMe_2CH_2O)PCl$ (**5**)[54] and Ph_2PCl (**6**). In the reaction shown in Scheme 10, while the product **35** (X-ray, Figure 6) is similar to **24-26** obtained by using the cyclodiphosphazanes **2-3**, the second product **36** isolated after column chromatography is the P-N bond cleaved product from **35** and is similar to **28**. Using the propargyl alcohol **11d**, we could isolate analogous product **38** (X-ray, Figure 6). Although we did not isolate the product **37** in our earlier attempts, we could do so after isolating **39** (and realizing that we missed it). The product **40** obtained using the silyl substituted propargyl alcohol **11b** (Scheme 10) is close in structure to compound **31**. However, the more important result of this part was that we could obtain the phosphorus-free indole **29** or **41** starting from **37** or **39**, respectively.

Scheme 10



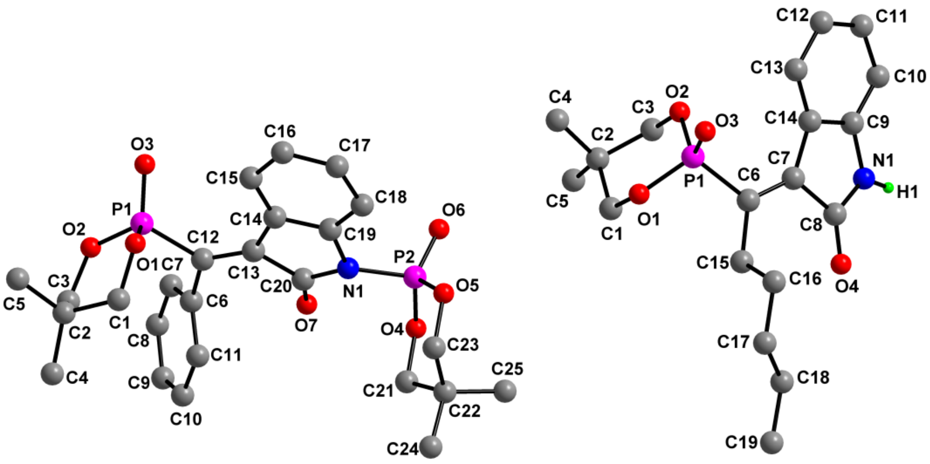
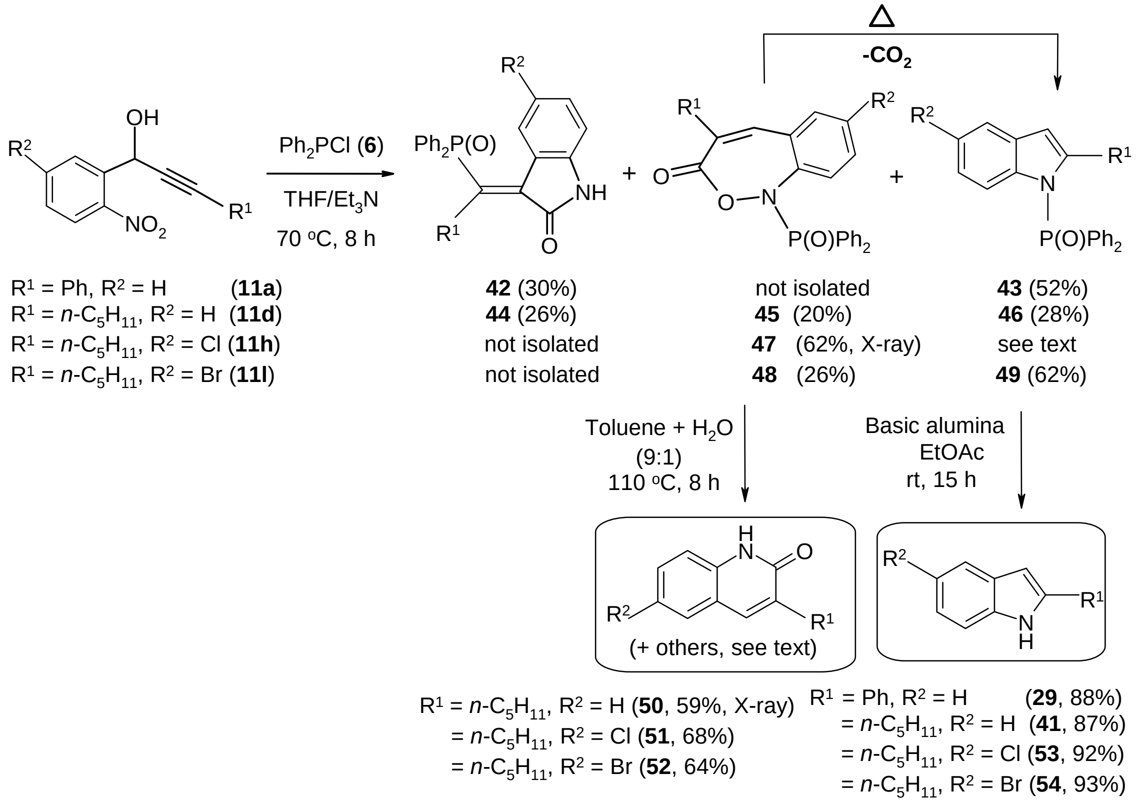


Figure 6. **Left:** Molecular structure of **35** (Hydrogen atoms are omitted for clarity). P1-C12 1.825(2), P2-N1 1.693(2), C12-C13 1.347(3) Å. **Right:** Molecular structure of **38** (Hydrogen atoms are omitted for clarity). P1-C6 1.812(3), C6-C7 1.363(4), N1...O3' 2.862(3) Å.

In the reactions using Ph_2PCl (**6**) shown in Scheme 11, products **42** and **44** are similar to **30**. Compounds **45**, **47** (X-ray, see Figure 7), and **48** are similar to **27**. Analogous compound with R^1 = Ph and R^2 = H, because of the facile decarboxylation to **43**, could not be isolated. These compounds, during chromatography or upon melting, eliminated CO_2 to lead to *N*-substituted indoles **43, 46** or **49**. In the case of R^1 = *n*-C_5H_{11} and R^2 = Cl, we could isolate a similar species [δ(P) 26.6 and HRMS (ESI) 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 **45** by recording the ^{31}P NMR spectra before and after melting (with bubbling) and also by recording TGA (Figure 8).

Scheme 11



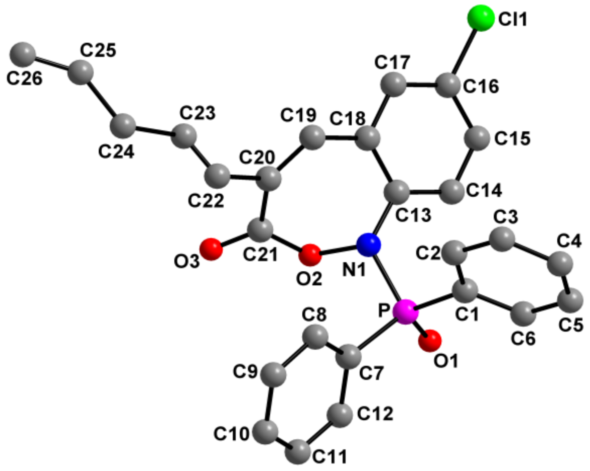


Figure 7. Molecular structure of **47** (Hydrogen atoms are omitted for clarity). P-N1 1.698(3), P-C1 1.779(4), P-C7 1.786(4), C13-N1 1.404(5), N1-O2 1.456(4), C21-O2 1.366(6), C20-C21 1.473(7), C19-C20 1.326(7), C18-C19 1.460(6) Å.

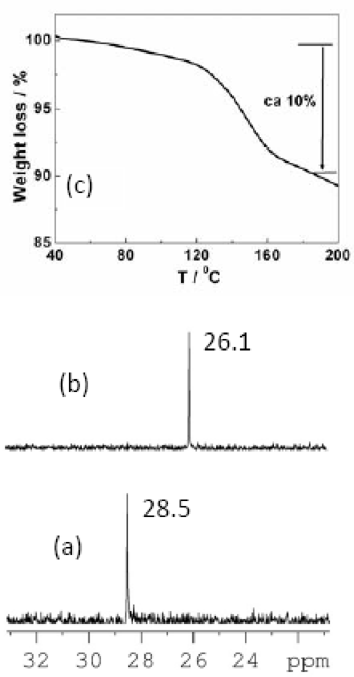


Figure 8. (a) Compound **45**, (b) Compound **45** upon melting and keeping the temperature at 120 °C for 2h (converted to **46** and (c) TGA of compound **45** showing weight loss corresponding to the elimination of CO_2 to lead to **46**.

Compounds **45**, **47**, and **48** could be dephosphonylated readily by treating them with toluene/water mixture (cf. Scheme 11 above) to the ***quinolinones*** **50-52**. Although indoles of the type **46/49** (ca 15%) were also present alongside, we could easily isolate quinolinones **50-52**. We could get the single crystal X-ray structure of one of these (**50**; Figure 9) to confirm their identity.[71] We are rather puzzled by this observation because in addition to the removal of phosphonate group, there is elimination of oxygen in these cases. Formation of phosphorus-free indoles **29**, **41**, **53** and **54** occurs *via* base hydrolysis and the reaction, as mentioned above, offers a new way to generate 2-substituted indoles.

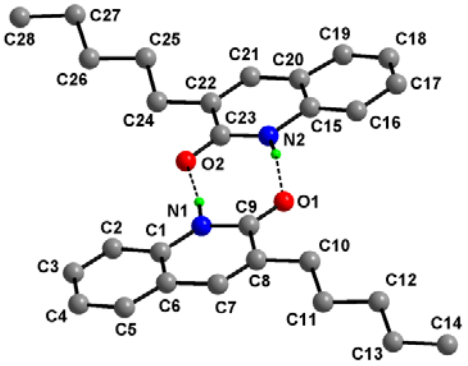
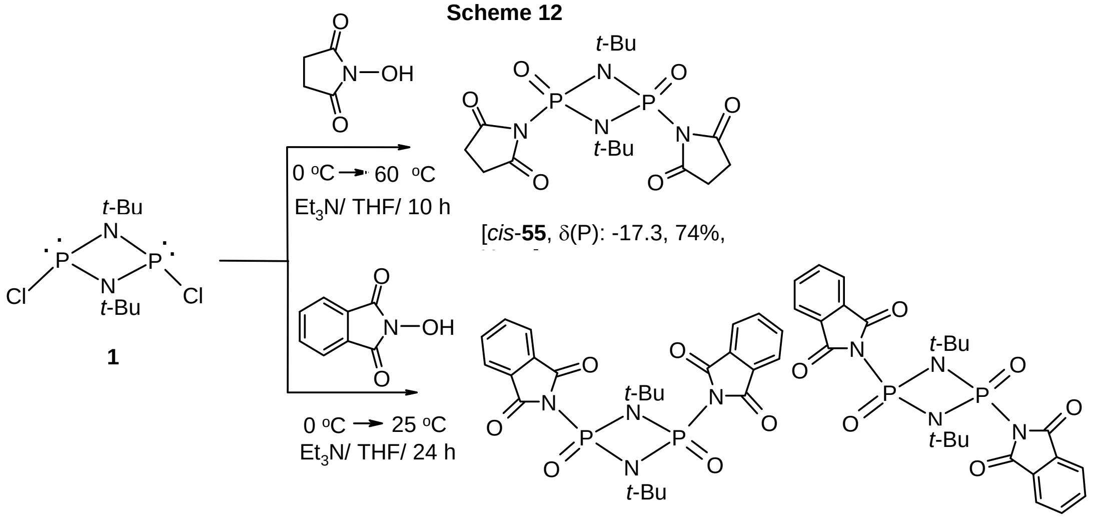


Figure 9. Molecular structure of **50**. (Hydrogen atoms (except NH) are omitted for clarity). Two molecules are present in the asymmetric unit, only one is shown. H-bond distances (Å): N1…O2 2.779(11), N2…O1 2.819(11), N3…O4 2.776(14), N4…O3 2.815(15).

2.322 Reactivity of P^{III} compounds towards N-hydroxysubstrates

In the formation of compounds **23-26** shown in Scheme 6, it can be inferred that the reaction of the –OH group of the *N*-hydroxy moiety in **23** with an additional cyclodiphosphazane molecule must have led to the P-N bonded compounds **24-26**. Since, to our knowledge, such reactions are never reported in cyclodiphosphazane chemistry before, and in order to conclusively establish that products **24-26** result from such a reaction, we treated cyclodiphosphazane [ClP-N(*t*-Bu)]$_2$ (**1**) with *N*-hydroxy-succinimide and *N*-hydroxy-phthalimide. These reactions afforded the novel rearranged products *cis*-**55**, *cis*-**56** and *trans*-**56** (Scheme 12). These compounds are formed by the substitution of a chloro group by the *N*-hydroxyl reactant, followed by rearrangement. Interestingly in the reaction using *N*-hydroxy-succinimide, prior to isolation, the reaction mixture showed substantial amounts of a partially (one side) rearranged product [δ(P): 124.6, -9.1, ^2J(PP) = 12.0 Hz] vindicating our assertion. At the end, compounds *cis*-**55** and *trans*-**56** are the major products, but the other isomer is present in each case in minor quantities (≤15%). We were able to isolate the isomer *cis*-**56** in the case of *N*-hydroxy-phthalimide. The ^{31}P NMR spectra of *cis*-**55**, *cis*-**56** and *trans*-**56** show signals at -17.3, -17.4 and -20.4, respectively. The major difference in the structures is that the diposition of the two P=O groups [*cis* or *trans*] (Figure 10; although the quality of data for *trans*-**56** was poor, the structure could be refined readily).

Scheme 12



[*cis*-**55**, δ(P): -17.3, 74%,

[*cis*-**56**, δ(P): -17.4, 14%, X-ray] [*trans*-**56**, δ(P): -20.4, 82%, X-ray]

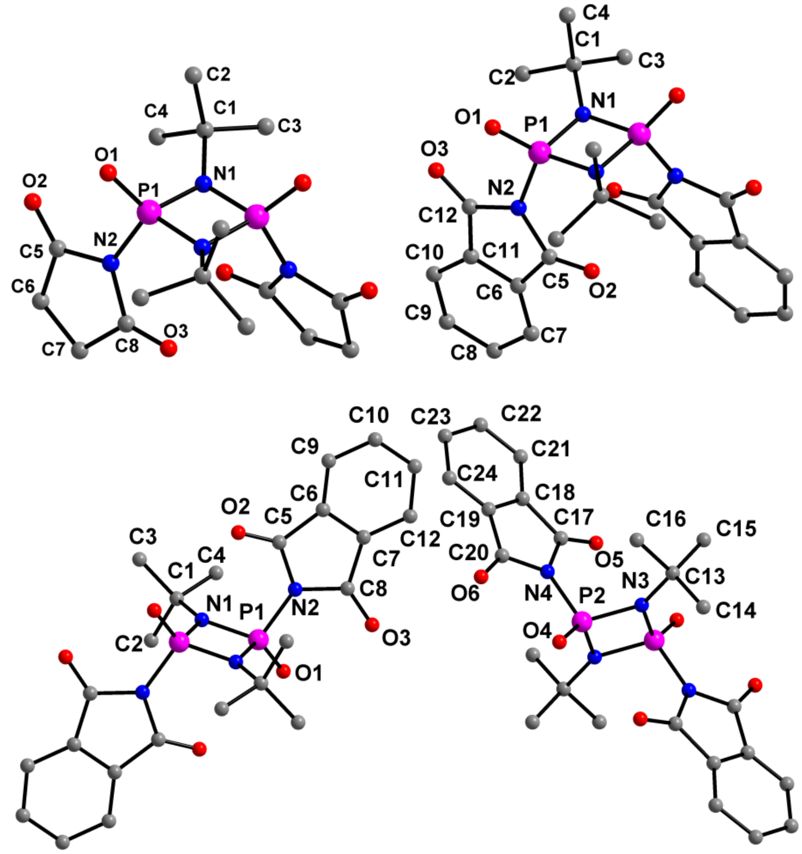
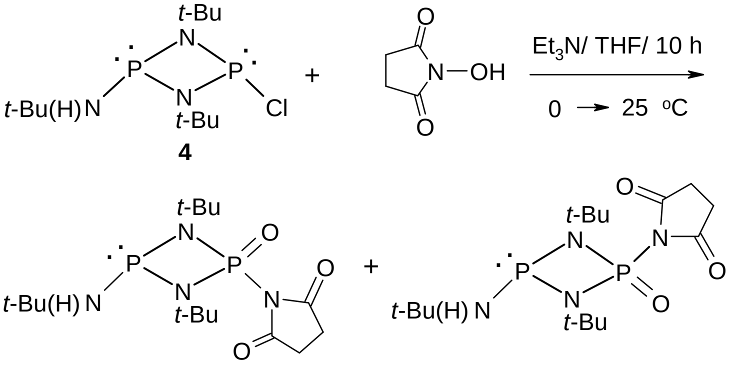


Figure 10. Molecular structures of compounds *cis*-**55**, *cis*-**56** and *trans*-**56**. Hydrogen atoms are omitted for clarity. **Top Left**: *Cis*-**55**. **Top Right**: *Cis*-**56**. One identical half molecule present in the asymmetric unit in *cis*-**55** and *cis*-**56**. **Bottom:** *Trans*-**56**·1/2CH_2Cl_2. Hydrogen atoms and the solvent are omitted for clarity. Two essentially identical half molecules in the asymmetric unit are present in *trans*-**56**·1/2CH_2Cl_2.

In an effort to probe whether there is any special preference for either of the isomers, *cis* or *trans*, we treated the chloro-substrate [(*t*-BuNH)P(μ-N-*t*-Bu)$_2$P-Cl] (**4**) with *N*-hydroxy succinimide. Here we could isolate both the rearranged products *cis*-**57** and *trans*-**57** (Scheme 13; *cis* and *trans* with respect exocyclic P-N bonds) in yields of 70% and 19% respectively. The ^{31}P NMR spectra of *cis*-**57** and *trans*-**57** show two signals each at δ [-10.5, 90.4] and [-11.2, 73.3], respectively which suuggest that the two isomers are readily distinguishable in the P^{III} region. Compound *cis*-**57** shows intra-molecular hydrogen bonding between N(3)H and C(13)=O(2) (Figure 11); this feature could be a driving force for the predominance of isomer with this configuration.

Scheme 13



cis-**57** [δ(P): -10.5, 90.4; 70%]
(X-ray)

trans-**57** [δ(P): -11.2, 73.3; 19%]

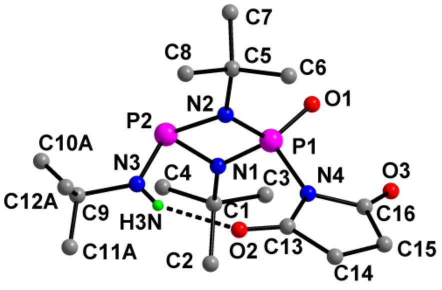
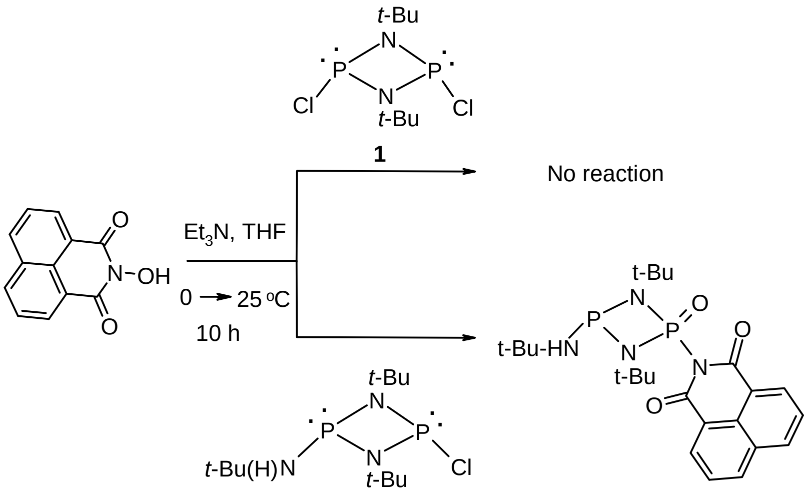


Figure 11. Molecular structure of compound *cis*-**57.** For the disordered *t*-butyl group at C13; only one position for the methyl groups is shown. Hydrogen atoms (except NH) are omitted for clarity. Selected bond distances (Å): N3-H3N…O2 0.80(4) 2.17(4) 2.902(4) Å, 154(4)°.

We then treated *N*-hydroxy-1,8-naphthalimide with cyclodiphosphazane [ClP-N(*t*-Bu)]$_2$ (**1**) also, but we could not effect the reaction under these conditions. However, the cyclodiphosphazane [(*t*-BuNH)P(μ-N-*t*-Bu)$_2$P-Cl] (**4**) afforded *cis*-**58** shown in Scheme 14. The IR spectrum of *cis*-**58** shows the ν(NH) band at 3279 cm^{-1}. The ^{31}P NMR spectrum exhibits two signals at δ -8.9 and 82.1 [^2J(PP) < 3 Hz] as expected. The ^{1}H NMR spectrum of *cis*-**58** shows the *t*-BuN*H* peak at δ 6.70. It may be noted that the *t*-BuN*H* peak for *cis*-**57** [δ 5.15] is much downifed compared to that for *trans*-**57** [δ 3.44]. On this basis, we have assigned a *cis*- stereochemistry for compound **58**. The assignment of *cis*-stereochemistry for **58** is also consistent with the fact that analogous reaction of **4** with *N*-hydroxysuccinimide led to *cis*-**57** as the major product. The observation that **1** failed react, but **4** reacted with *N*-hydroxy-1,8-naphthalimide may have to do with electronic factors. We have not probed this aspect further.

Scheme 14

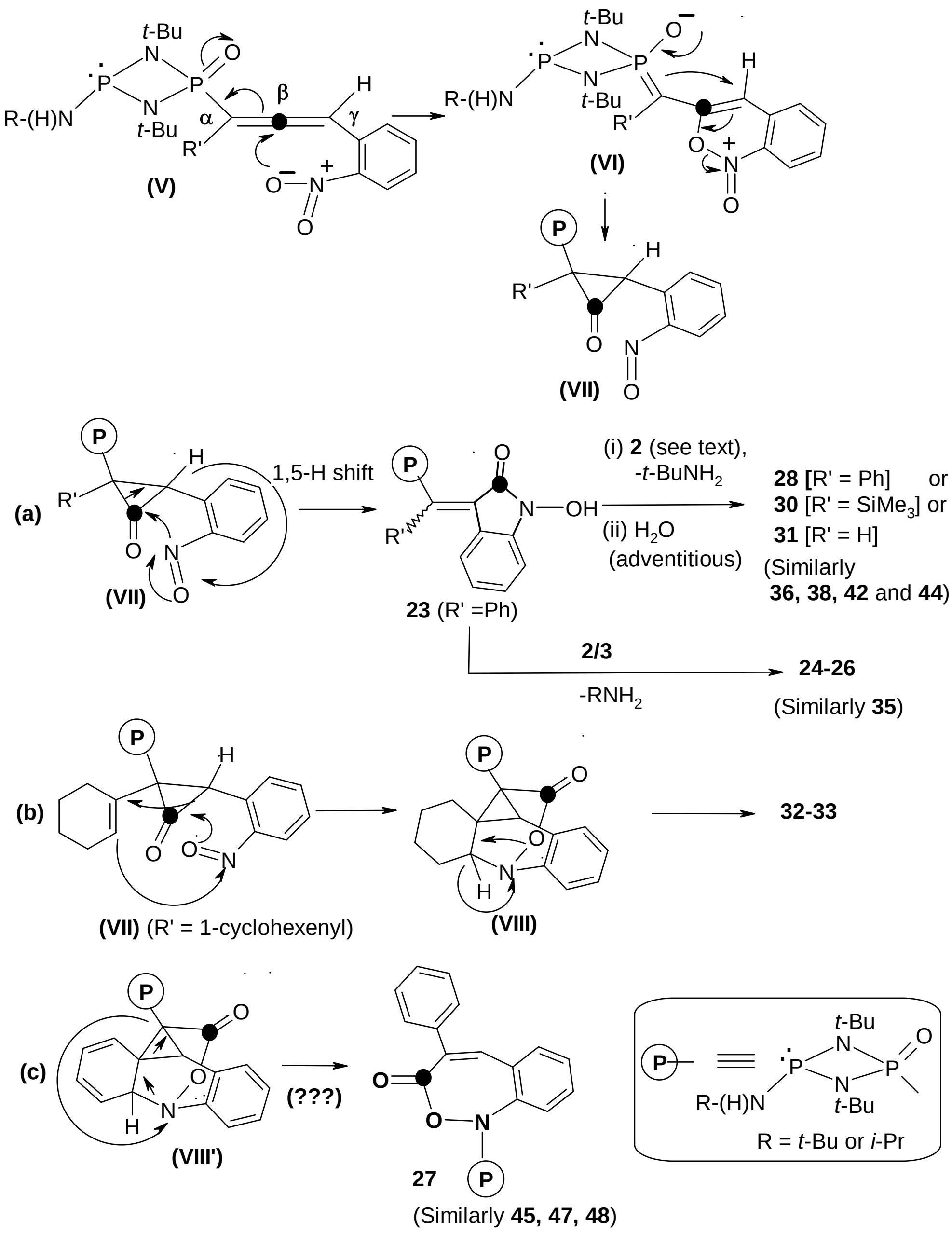


[*cis*-**58**, δ(P) -8.9, 82.1; 68%]

2.323 Mechanistic pathways

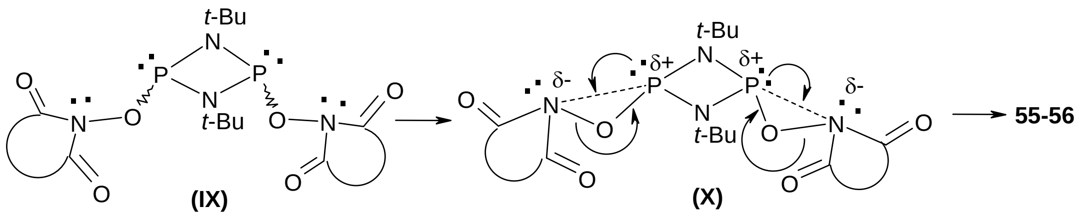
As discussed above in Scheme 5 (compounds **21-22**), the normal reaction of a propargyl alcohol with cyclodiphosphazane (or a P$^{\mathrm{III}}$-Cl precursor) is expected to lead to the cyclophosphazanyl-allenic intermediate **V** (Scheme 15). However, what is to be noticed in the structures of **23-26, 28** and **30-31** is that in the final products, ***what was originally the β-carbon, is now at a position γ- to the phosphorus***. This observation needs an explanation. Since in most cases, the nucleophilic attack takes place at the *β*-carbon of the allene,[36-38] the oxygen end of the –NO_2 group attacks the *β*-carbon to lead to the cyclic species **VI**, facilitated by the phosphoryl group. In the next step, rearrangement leads to species (**VII**). Formation of the five-membered ring can then be envisioned to lead to the cyclophosphazanyl-*N*-hydroxy product **23**. Compounds **24-26** result from the further reaction of this intermediate **23** with the respective cyclodiphosphazane (Scheme 15a) 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 **55-58**. Hydrolysis of such a species by adventitious moisture (or during the column chromatography) may then lead to facile formation of cyclophosphazanyl-indolinone (**30**) or the ring opened products **28/31**. Formation of the bizarre looking products **32-33** may also be rationalized by appropriate bond-movements from **VII** (R' = 1-cyclohexenyl; Scheme 15b). The cleavage of N-O bond from the intermediate **VIII** would lead to the products **32-33**.[72] Formation of **34** from **32** requires elimination of two molecules of CO in addition to the phosphorus moiety. The seven-membered ring compound **27** looks odd, but we presume that intermediate (**VIII'**; Scheme 15c) may again be involved, but at the moment we need to admit that the suggested pathway is still speculative. However, the interesting part is the isolation of the analogous compounds **45, 47** and **48** and thermal conversion of **45** to the 2-substituted indole **46** by elimination of CO_2 (cf. Scheme 11 above) which also suggests an alternative pathway for these reactions. The substituted indoles **43**, **46** and **49** are formed in a similar manner. For the observation that only one end of the cyclodiphosphazane is reactive, it is possible that the electronic effect induced by the P(V) center due to the shrinking of the P(V)-N(ring) bond may be responsible (*vide infra*).

Scheme 15



As regards the formation of products **55-58**, involvement of intermediates **IX-X** may be invoked (Scheme 16). Rearrangement of the three-membered ring containing phosphonium betaine (**X**) will lead to compounds **55-56** (similarly, compounds **57** and *cis*-**58**). It may be noted that the phosphonium intermediate resulting from **X** has some resemblance to the one proposed in Arbuzov rearrangement. However, no additional reagent similar to alkyl halide is used in our rearrangement. Formation of *cis* or *trans* isomer may have to do with the relative disposition of the substituents in the P^{III} intermediate **IX**.

Scheme 16



2.324 Brief comments on the structural aspects

The P-N bond distances and selected angles in the compounds studied by X-ray crystallography are tabulated in Table 1. As can be readily seen, P^{III}-N(ring) distances are always longer than the P(V)-N(ring) distances. However, ***exocyclic P^{V}-N distances are longer than the corresponding P^{III}-N distances*** in all the cyclodiphosphazane derivatives. This feature suggests a competition for the bonding electrons. The endocyclic N-P^{III}-N angle is, in general, smaller than that of endocyclic N-P^{V}-N angle probably because of (i) the lone pair of electrons on P^{III} tries to occupy more space, and (ii) the greater contribution from ~sp^3 hybridization at the P^{V} center. This feature could have forced the P^{III}-N(ring) distance longer. The P^{V}-N exocyclic distances are comparable to the apical P-N bonds in pentacoordinate phosphoranes[73] and are somewhat shorter than the expected P-N (single) bond distances based on Schomaker-Stevenson empirical expression [1.77 Å].[74] In the ring cleaved product **28**, though, the P^{V}-N distances are short and are in the range 1.59-1.63Å, which is clearly shorter than the accepted P-N single bond length.[74] The ring nitrogen atoms are essentially planar with the sum of the bond angles at nitrogen close to 360°. The four-membered P_2N_2 ring in compounds **55-56** are planar, but in other cases deviations do occur, with the maximum deviation of ca 0.08 Å from the mean plane in compound **24**. In this compound, apart from the intramolecular N-H…O hydrogen bond shown in Figure 1, the both the phosphoryl oxygen atoms are engaged in H-bonding interactions with water; additional intermolecular interactions involving the remaining N-H and water molecules also exist. In the case of its isomer **25**, though, only weak intermolecular hydrogen bonding involving N3-H3…O1 and N6-H6…O2 are found; the carbonyl oxygen does not have any hydrogen bonding partner (Figure 12). In compound **30**.H_2O, the water molecule is engaged in four-fold H-bonding to both the N-H groups as well as two P=O's of different molecules as shown in Figure 13; the carbonyl oxygen O2 does not have a hydrogen bonding partner. In **28**, there is a weak intermolecular H-bond involving N-H and P=O. Although there are both intra and intermolecular hydrogen bonding involving the NH, P=O and C=O, they do not affect the geometry significantly. In the case of **32**.1/2H_2O, the two molecules in the asymmetric unit (Figure 5) primarily differ in H-bonding interactions, with the C=O still not having H-bonding partner.

Table 1. Comparison of P-N bond parameters in the structures reported in this work.

	P(V)-N(ring)	PIII-N(ring)	P(V)-N(exo)	PIII-N(exo)	N-P(V)-N (ring)	N-PIII-P (ring)
24.1.5H_2O	1.649(4), 1.634(4), 1.635(4), 1.628(4)	1.757(4), 1.755(4), 1.760(3), 1.755(3)	1.712(3)	1.649(4), 1.646(3	86.10(19) 86.28(18)	79.30(18) 78.79(16)
25	1.644(3), 1.642(3), 1.634(3), 1.631(3)	1.750(3), 1.763(3), 1.769(3), 1.752(3)	1.716(3)	1.663(3), 1.646(3)	85.58(13) 86.60(13)	78.91(12) 78.97(12)
27.$PhCH_3$	1.652(4), 1.639(3)	1.736(4), 1.736(4)	1.697(3),	1.642(4)	85.32(17)	79.54(16)
28			1.626(4), 1.635(5), 1.617(5), 1.589(5)		-	-
30.H_2O	1.639(4), 1.645(3)	1.754(3), 1.759(4)		1.634(5)	85.59(18)	78.83(16)

32.1/2H_2O	1.649(4), 1.649(5), 1.643(5), 1.639(4),	1.743(5), 1.760(4), 1.752(4), 1.767(5)		1.662(5), 1.654(5),	85.2(2) 86.0(2)	79.1(2) 79.0(2)
Cis-**55**	1.667(2), 1.650(2)	1.705(2).			85.45(9)	-
Cis-**56**	1.673(2), 1.655(2)		1.706(2)		85.30(9)	
Trans-**56.**1/2CH_2Cl_2	1.643(6), 1.672(6), 1.679(7), 1.670(7),	1.708(7), 1.713(7)			84.5(3) 86.1(4)	
cis-**57**	1.626(3), 1.631(3),	1.750(3), 1.747(3),	1.738(3),	1.638(3).	86.49(15)	79.33(14)

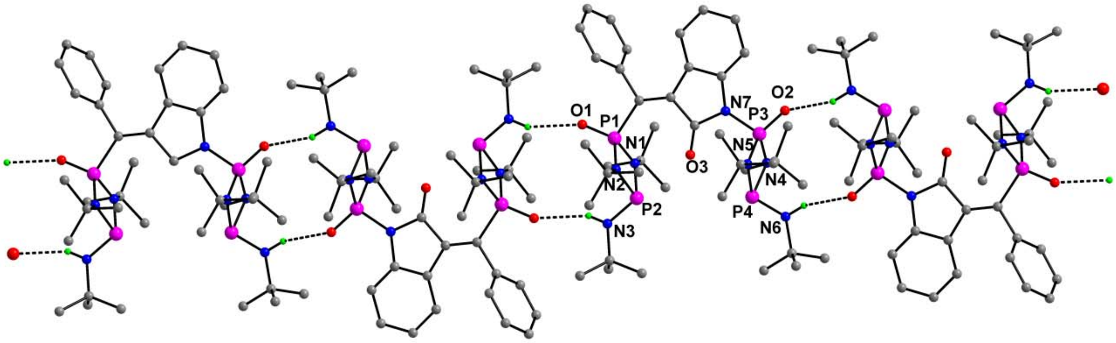


Figure 12. Weak hydrogen bonding in **25**. H-bond parameters (Å, Å, Å, °): N3-H3…O1^{i} 0.88(4), 2.48(4), 3.299(4), 156(3). N6-H6…O2^{ii} 0.92(4), 2.69(4), 3.536(4), 153(3). Symmetry codes: (i) 1-x, 1-y, 1-z, (ii) 2-x, 2-y, -z.

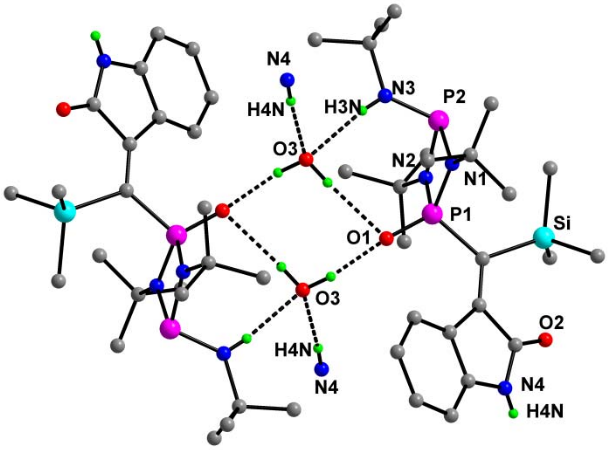


Figure 13. Weak hydrogen bonding in compound **30**.H_2O. H-bond parameters (Å, Å, Å, °): O3-H3D…O1^{i} 0.89(5), 1.94(5), 2.820(5), 171(5), O3-H3E…O1^{ii} 0.86(6), 2.35(6), 3.197(6), 169(6), N3-H3N…O3^{iii} 0.77(4), 2.43(4), 3.173(6), 162(5), N4-H4N^{iv}…O3 0.76(5), 2.37(5), 3.128(6), 172(6). Symmetry codes: (i) 1-x, -y, 1-z, (ii) x, y, 1+z (iii) x, y, -1+z, (iv) x, 0.5-y, -0.5+z.

2.325 Overall summary and possible implications

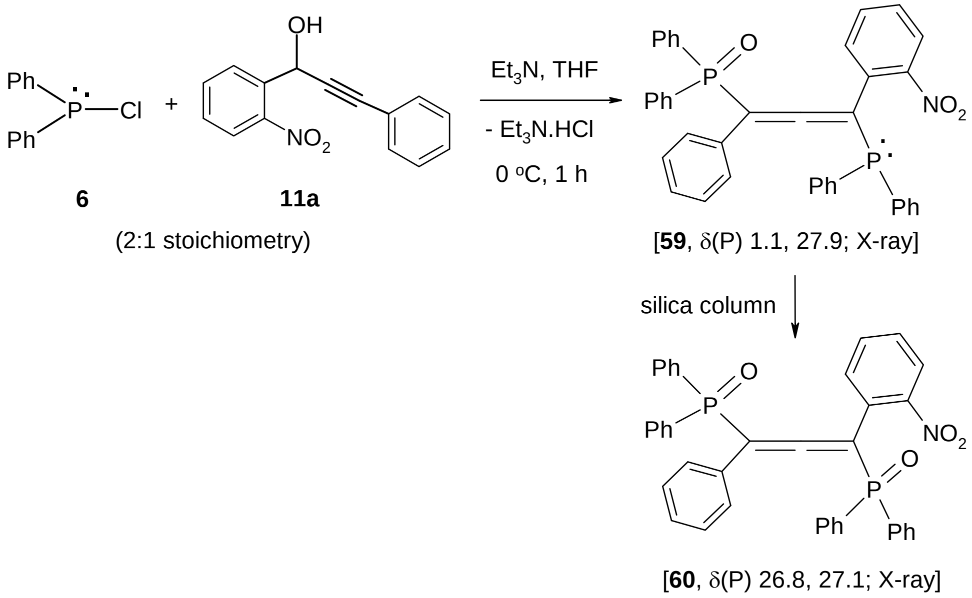
We have presented here several new and previously unpredicted outcomes in the reactions of the cyclodiphosphazanes with functionalized propargyl alcohols. While in the present work we focused on utilizing cyclodiphosphazanes, the results could act as a lead to utilizing a host of other P^{III} precursors. A demonstrative set of indolinones and 2-substituted indoles using $(OCH_2CMe_2CH_2)PCl$ and Ph_2PCl is also presented. The main advantage of the cyclodiphosphazane substrates **1-4**, 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 **27** or **32-33**, 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 [**29**, **41**, **53-54**], tetrahydroacridine [**34**] and quinolinones [**50-52**]. The present work, to our knowledge, represents new ways of generating such heterocycles.

2.33 Synthesis of bisphosphonylated allenylphosphine oxides

2.331 Reactions of Ph_2PCl (6) with o-nitro functionalized propargyl alcohols

As shown in Scheme 11, the reaction of chlorodiphenylphosphine [Ph_2PCl (**6**)] with *o*-nitro functionalized propargyl alcohols (**11a** or **11d**) at 70 ^oC led to the unexpected phosphono heterocycles (**42-46**). We performed the same reaction at 0 ^oC for 1h, but by using 2:1 molar stoichiometry of **6** and **11a** (Scheme 17). The reaction mixture after work up was subjected to column chromatography using silica gel resulted in a product that showed two doublets at δ 1.1 and 27.9 in the ^{31}P NMR spectrum. This observation suggested that there are two phosphorus moieties in the compound. In the IR spectrum, the presence of a sharp band at 1931cm^{-1} suggested allenic moiety. Fortunately, we could obtain the single crystal X-ray structure for this product (Figure 14). This compound is allene **59**, containing one phosphinoyl group at α position and one phosphine group at γ position. We could not get good $^1H/^{13}C$ NMR spectra for this compound, because of non-phosphorus impurities. The solution of this compound in $CDCl_3$ was initially colorless, but after one hour turned to pale green, and finally after 6h, became dark green. Surprised by this observation, we recorded ^{31}P NMR spectra again. Two doublets at δ(P) 26.8 and 27.1 (J = 13.0 Hz) suggested that it was no more compound **59**. This new the compound (**60**) was purified to obtain a colorless solid that showed ^{31}P NMR spectrum indentical to the green solution. In the IR spectrum, a sharp band at 1934 cm^{-1} clearly showed the presence of allenic moiety. Similarly ^{13}C NMR spectrum also showed the allenic peak at δ 210.0. These data are consistent with the oxidation at the phosphine end. Finally, the structure of compound **60** is proven by X-ray crystallography (Figure 14). Thus compound **59** upon exposure to air was oxidized to **60**. Interestingly, both the compounds **59** and **60** crystallized in the chiral space group $P2_12_12_1$ but showed absolute configurations of *R* and *S* respectively (Figure 15). This aspect is quite interesting since such 'spontaneous resolution' by crystallization is an important topic by itself.[75] The origin of the green color is not yet ascertained.

Scheme 17



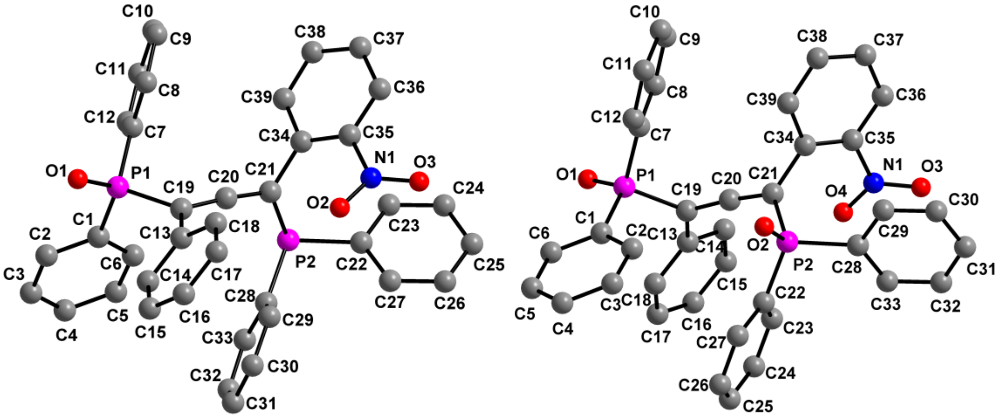


Figure 14. **Left:** Molecular structure of compound **59**. Selected bond parameters: P1-O1 1.472(2), P1-C19 1.825(3), C19-C13 1.495(4), C19-C20 1.322(4), C20-C21 1.293(4), C21-C34 1.488(4), C21-P2 1.861(3) (Å). **Right:** Molecular structure of compound **60**. Selected bond parameters: P1-O1 1.474(3), P1-C19 1.821(4), C19-C13 1.492(5), C19-C20 1.319(6), C20-C21 1.300(6), C21-C34 1.495(5), C21-P2 1.834(4), P2-O2 1.483(3) (Å). Hydrogen atoms are omitted for clarity in both the drawings.

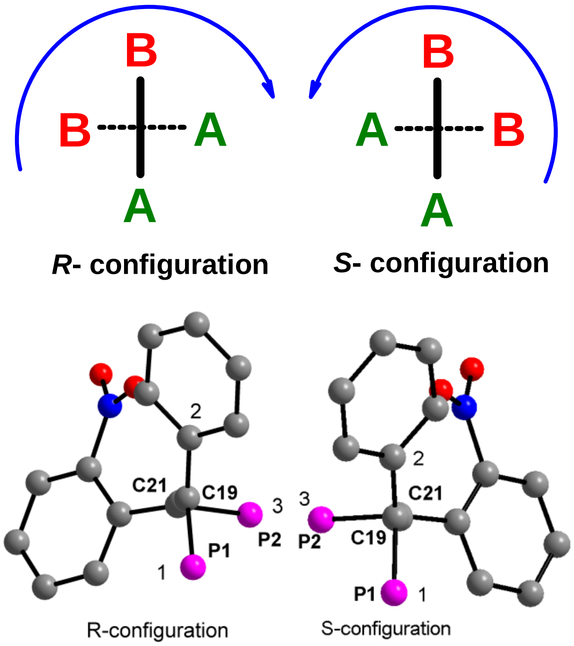
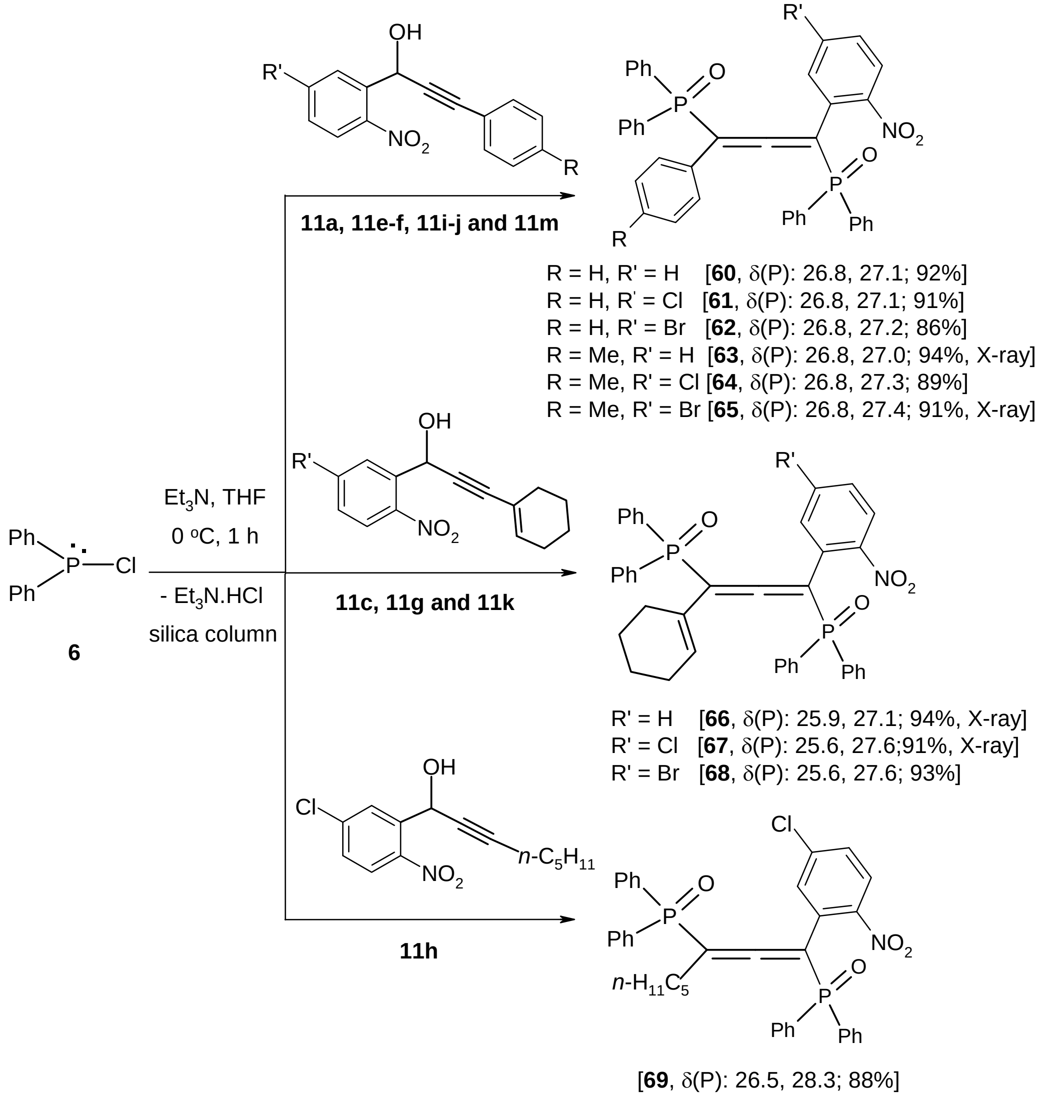


Figure 15. A diagram showing the (*R*)-configuration for compound **59** and (*S*)-configuration for **60**. ***Note:*** The view taken is along the C=C=C axis. The numbers 1, 2 and 3 on the structures show the ordering of atoms for deciphering the configuration.

Because of the ‘spontaneous resolution’ of enantiomeric allene by crystallization in the above case, we became interested in this topic and synthesized some more derivatives. In addition, substitution of allenic CH by a phosphorus moiety is not kown in the literature. Thus, we treated various *o*-nitro functionalized propargyl alcohols **11a**, **11c**, **11e-11k** and **11m** with Ph_2PCl (**6**) [Scheme 18]. As a result, allenyl-(bis)phosphine oxides (**60-69**) were obtained after column chromatography. In all the cases the yields were good to excellent. In the IR spectra, these compounds showed a characteristic strong band at 1907-1940 cm^{-1} due to ν_{asym}(C=C=C). The ^{31}P NMR spectra of allenyl(bis)phosphine oxides **(60-69)** showed two doublets in the region of δ 25.6-26.8 and 27.0-28.3 (J ~ 13.0 Hz), which indicated that the two phosphorus atoms were tetracoordinated. In the ^{13}C NMR spectra, the α-carbons attached to phosphorus appeared as doublet of doublets at δ 100-107 [^{1}J(P-C) ~ 88.0-97.0 Hz, ^{3}J(P-C) ~ 8.0-14.0 Hz]. The allenic signals for all these compounds appeared as triplets at δ 209-211 [^{2}J(P-C) ~ 6.0 Hz], as expected. All these data are consistent with the structures shown in Scheme 18. Further confirmation of the structures of **63, 65 and 66-67** is provided by single crystal X-ray structures (Figures 16-18). Among these structures, **63** and **66** crystallized in the chiral space group *P*$2_12_12_1$ again revealing illustrative examples of ‘spontaneous resolution’. More interesting is the fact that for compound 66, we were able to isolate both the enantiomers (*R* and *S*) for which details are given below.

Scheme 18



R = H, R' = H [**60**, δ(P): 26.8, 27.1; 92%]
R = H, R' = Cl [**61**, δ(P): 26.8, 27.1; 91%]
R = H, R' = Br [**62**, δ(P): 26.8, 27.2; 86%]
R = Me, R' = H [**63**, δ(P): 26.8, 27.0; 94%, X-ray]
R = Me, R' = Cl [**64**, δ(P): 26.8, 27.3; 89%]
R = Me, R' = Br [**65**, δ(P): 26.8, 27.4; 91%, X-ray]

R' = H [**66**, δ(P): 25.9, 27.1; 94%, X-ray]
R' = Cl [**67**, δ(P): 25.6, 27.6;91%, X-ray]
R' = Br [**68**, δ(P): 25.6, 27.6; 93%]

[**69**, δ(P): 26.5, 28.3; 88%]

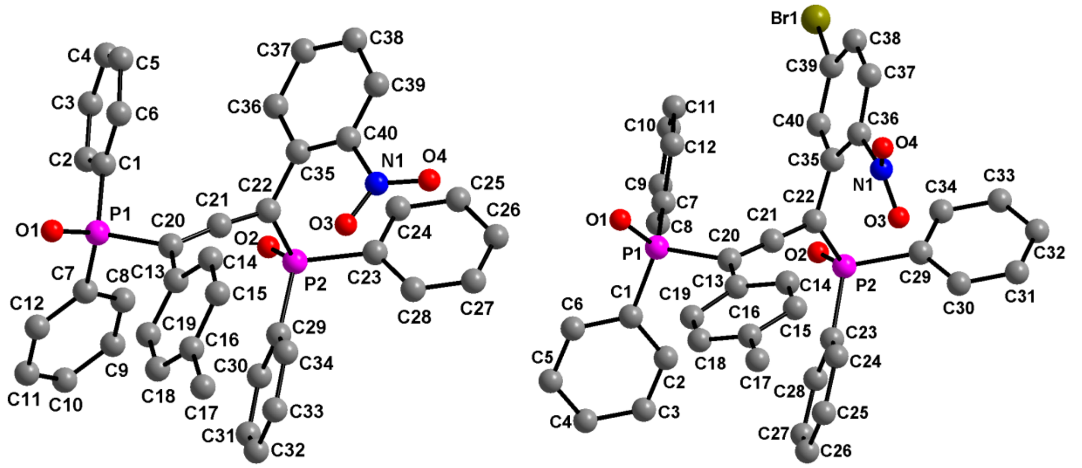


Figure 16. **Left:** Molecular structure of compound **63**. Hydrogen atoms are omitted for clarity. Selected bond parameters: P1-O1 1.468(4), P1-C20 1.806(6), C20-C13 1.463(8), C20-C21 1.322(8), C21-C22 1.278(8), C22-C35 1.478(8), C22-P2 1.829(6), P2-O2 1.467(4) (Å). **Right:** Molecular structure of compound **65**. Selected bond parameters: P1-O1 1.488(4), P1-C20 1.828(5), C20-C13 1.481(7), C20-C21 1.307(7), C21-C22 1.305(6), C22-C35 1.483(6), C22-P2 1.828(5), P2-O2 1.482(3) (Å).

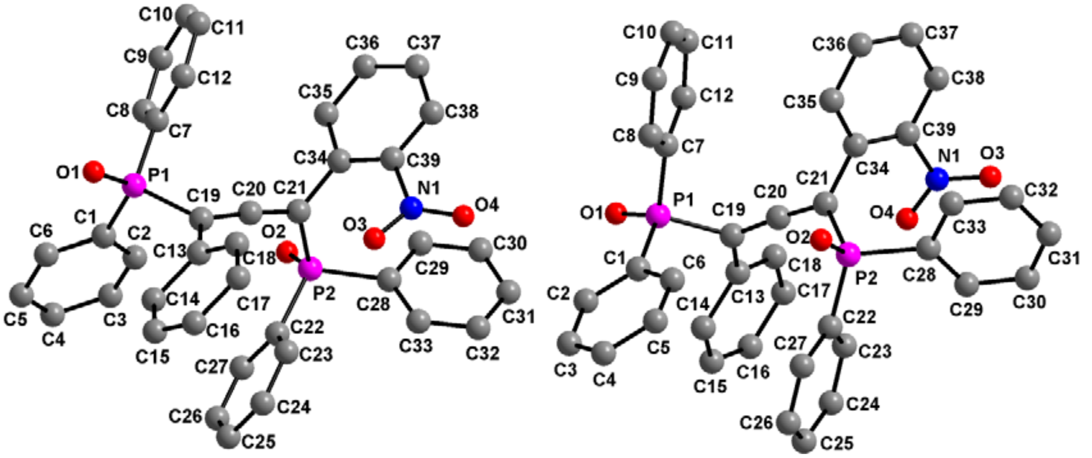


Figure 17. Molecular structures for compounds (a) (*R*)-**66** (*b*) (*S*)-**66**. Hydrogen atoms are omitted for clarity. Selected bond parameters with esd's in parentheses follow. **Compound (*R*)-66:** P1-O1 1.475(3), P1-C19 1.823(4), C19-C13 1.487(5), C19-C20 1.307(5), C20-C21 1.301(5), C21-C34 1.480(5), C21-P2 1.824(4), P2-O2 1.476(3) (Å). **Compound (*S*)-66**: P1-O1 1.472(2), P1-C19 1.818(3), C19-C13 1.493(4), C19-C20 1.300(4), C20-C21 1.295(5), C21-C34 1.484(4), C21-P2 1.821(3), P2-O2 1.473(2) (Å).

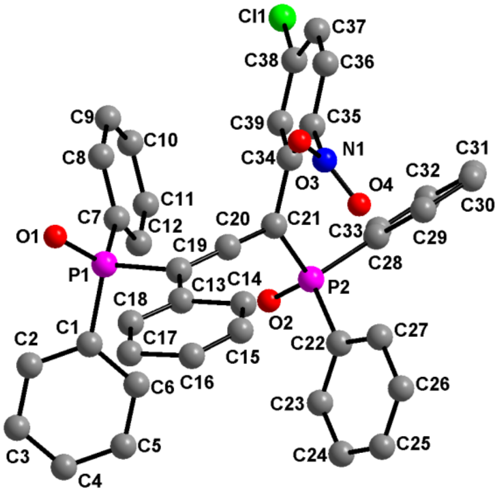


Figure 18. Molecular structure of compound **67**. Hydrogen atoms are omitted for clarity. Selected bond parameters with esd's in parentheses: P1-O1 1.4779(19), P1-C19 1.828(3), C19-C13 1.493(4), C19-C20 1.309(3), C20-C21 1.306(3), C21-C34 1.492(3), C21-P2 1.831(3), P2-O2 1.4713(19) (Å).

The presence of sterically bulky *o*-nitro functionality may be responsible for the separation of axially chiral entntiomers. In the case of compound **66**, fortunately, we could obtain the CD spectra for both the *R* and *S* enantiomers (Figure 19) as shown in Figure 20. We are not able to get significant optical rotation in solution. We are exploring this aspect further.

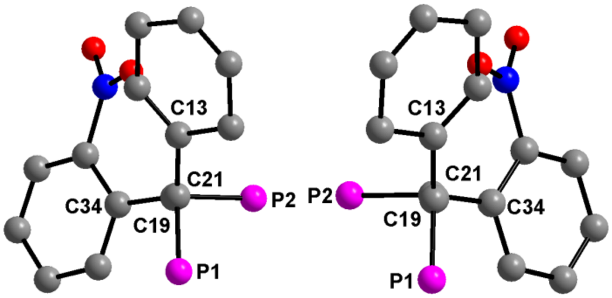


Figure 19. A picture showing the *R* (left) and *S* (right) configurations in the two different crystals of **66**.

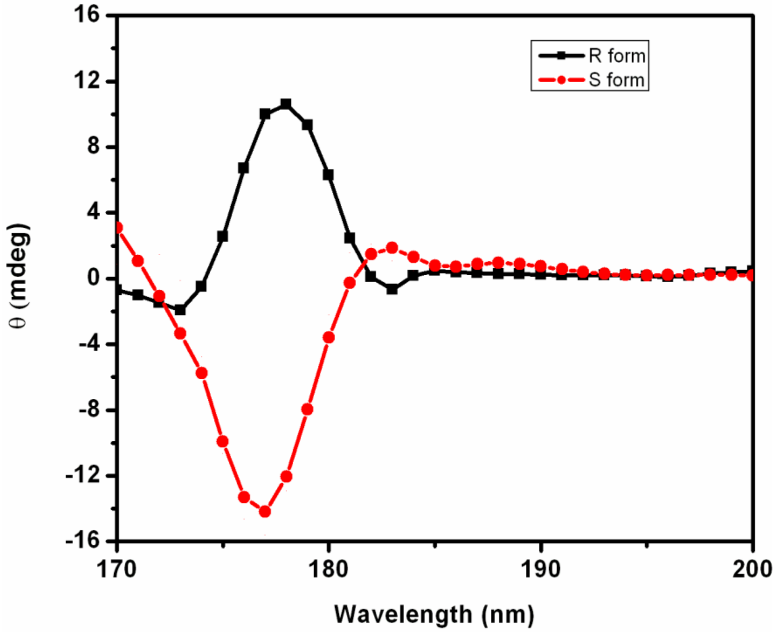
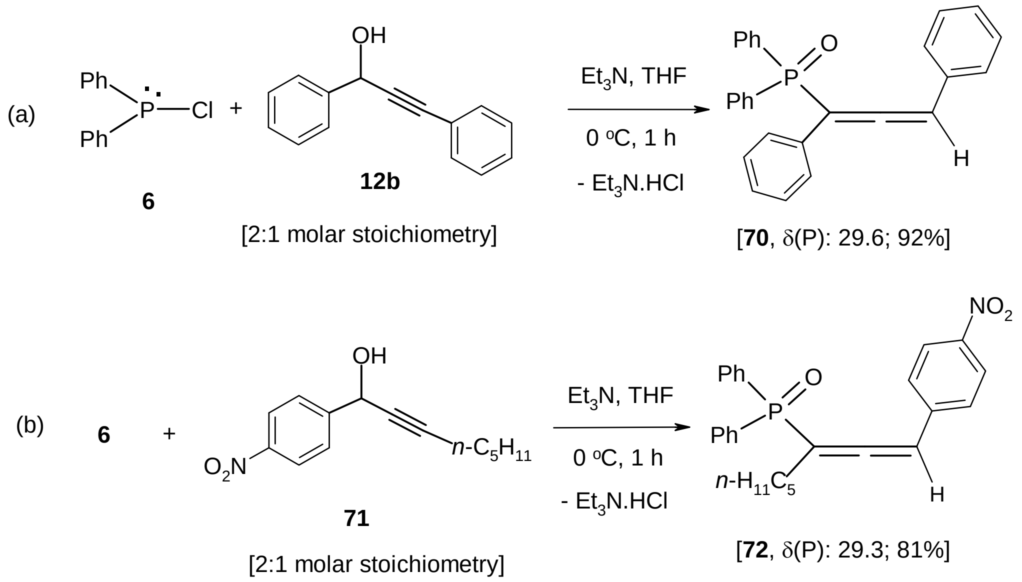


Figure 20. CD spectra of *R* and *S* forms of crystals of **66**

2.332 Reactions of Ph_2PCl with 12b and p-nitro propargyl alcohol 71

The bis-phosphinoylated allenes of the type described above are not reported so far in the literature. Hence we wanted to check whether the NO_2 group on propargyl alcohol is playing a role for the formation of bis-phosphinoylated allenes or not. To test this, we treated propargyl alcohol **12b** with two mol equivalents of Ph_2PCl (**6**) and obtained a product that exhibited only one signal in the ^{31}P NMR spectrum (Scheme 19a). IR, NMR (^{1}H and ^{13}C) and HRMS spectra confirmed that the product is allenylphosphine oxide **70**. Thus, for the above reaction, -NO_2 group is necessary for the bis-phosphinoylation. We also needed to check if propargyl alcohols bearing NO_2 functionality at *para*-position will undergo bis-phosphinoylation or not. But a similar 2:1 stoichiometric reaction of Ph_2PCl (**6**) with propargyl alcohol **71** resulted only in the allenylphosphine oxide **72** [IR, NMR and HRMS] (Scheme 19b). From these control experiments, it may is concluded that NO_2 functionality at *ortho*-position is required for the formation of bis-phosphinoylated allenes.

Scheme 19



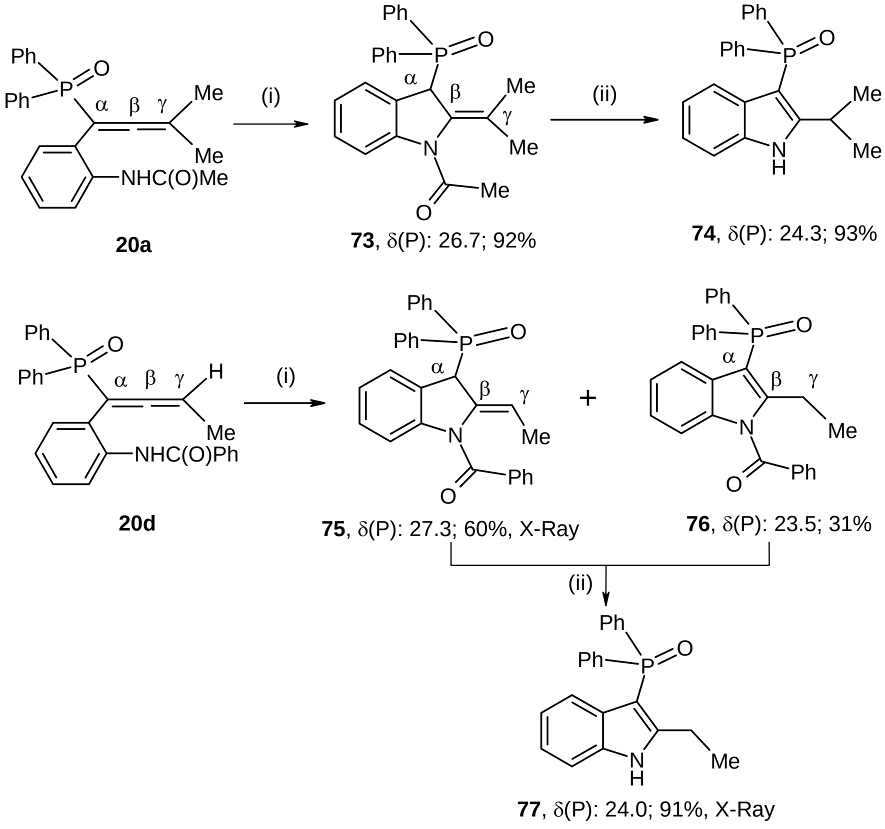
2.34 Reactivity of P^{III} compounds with *o*-amido or *o*-amino functionalized propargyl alcohols (Synthesis of phosphorus based indoles)

2.341 Synthesis of phosphinoyl indoles

As discussed earlier, the reactions using *o*-nitro functionalized propargyl alcohols led to various unexpected nitrogen heterocycles. If we use propargyl alcohols bearing an *o*-amido or amino functionality will it lead to another type of nitrogen heterocycle? To answer this question, we prepared allenylphosphine oxides **20a-d** (Scheme 4). Initially we chose allenes **20a** and **20d** to achieve intramolecular cyclization. These were treated with 0.5 mol equivalent of base (K_3PO_4) since the substrates contained active hydrogen. This reaction afforded the *N*-substituted phosphinoyl-indoles **73** and **75-76**. Essentially a single isomer **73** (a dihydroindole), in which the N-*H* proton moves only to the α-carbon resulting in an exocyclic double bond, was formed (Scheme 20). The presence of a doublet for P*C*H carbon at *δ* 48.3 with a low ^1J(P-C) value of 62.0 Hz revealed that phosphorus moiety is attached to an sp^3 hybridized carbon. On the other hand, in the reaction using the =CHMe allene **20d,** two isomers in which the N-*H* proton moved to either the α-carbon (**75**) or the γ-carbon (**76**), were obtained. These two isomers could be readily distinguished by the corresponding δ and ^1J values for the P-*C* carbon [for **75**, δ 47.3 and J = 62.0 Hz; for

76, δ 106.5 and *J* = 120.0 Hz].[36] Overall, the yields of the isolated products were excellent in both the cases. The structure of compound **75** was further confirmed by X-ray crystallography (Figure 21). The *C*=*C*HMe distance of 1.317(2) Å clearly indicated a double bond between these two carbon atoms. The other stereoisomer in which the methyl group is *trans* to the nitrogen was not observed. Interestingly though, the deprotection of acyl/ benzoyl group on nitrogen in compounds **73** or **75-76** in aq. NaOH afforded the 2,3-disubstituted NH-indoles **74** or **77**, respectively, in excellent yields. The NH band (3156 cm^{-1}) in the IR spectrum and a doublet for P*C* carbon at δ 98.4 [^{1}J(PC) = 128.0 Hz] revealed the identity of compound **77**. Its structure was further confirmed by X-ray crystallography (Figure 22).

Scheme 20



20a

73, δ(P): 26.7; 92%

74, δ(P): 24.3; 93%

20d

75, δ(P): 27.3; 60%, X-Ray

76, δ(P): 23.5; 31%

77, δ(P): 24.0; 91%, X-Ray

Conditions: (i) K_3PO_4 (0.5 equiv), THF, 80 °C, 12 h
(ii) NaOH (2 equiv), EtOH+H_2O (4:1), 80 °C, 8 h

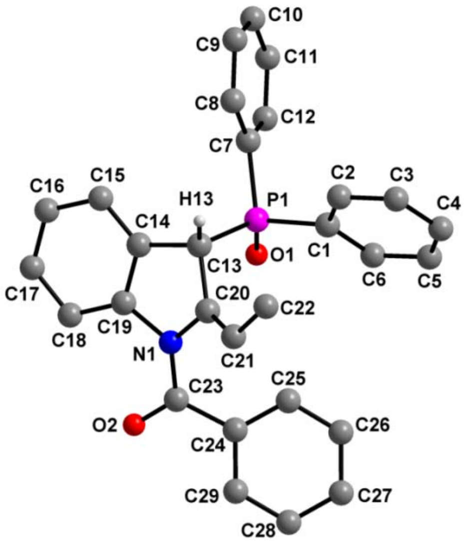


Figure 21. Molecular structure of compound **75**. Hydrogen atoms (except PCH) are omitted for clarity. Selected bond distances (Å): P1-C13 1.8402(15), C13-C20 1.5161(19), C13-C14 1.512(2), C20-N1 1.4508(18), C20-C21 1.317(2).

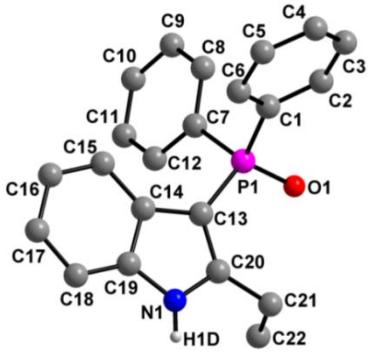
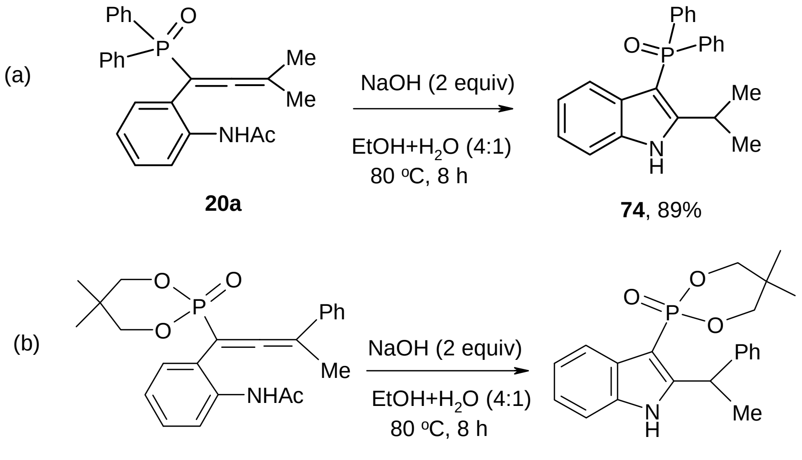


Figure 22. Molecular structure of compound **77**. Hydrogen atoms (except NH) are omitted for clarity. Selected bond distances (Å): P1-C13 1.771(2), C13-C20 1.385(3), C13-C14 1.450(3), C20-N1 1.360(3), C20-C21 1.489(3).

Subsequently, we used aq. NaOH as the base instead of K_3PO_4 (cf. condition (ii) in Scheme 20) to perform reaction on allene **20a**. To our delight, only phosphinoyl-NH-indole **74** was the sole product with not even traces of **73** (Scheme 21a). Similarly, allenylphosphonate **17a** in the presence of aq. NaOH afforded the corresponding phosphinoyl indole (**78**) in good yield (Scheme 21b). This showed that a strong base like sodium hydroxide effectively performed both deprotection and cyclization in a single step.

Scheme 21



20a

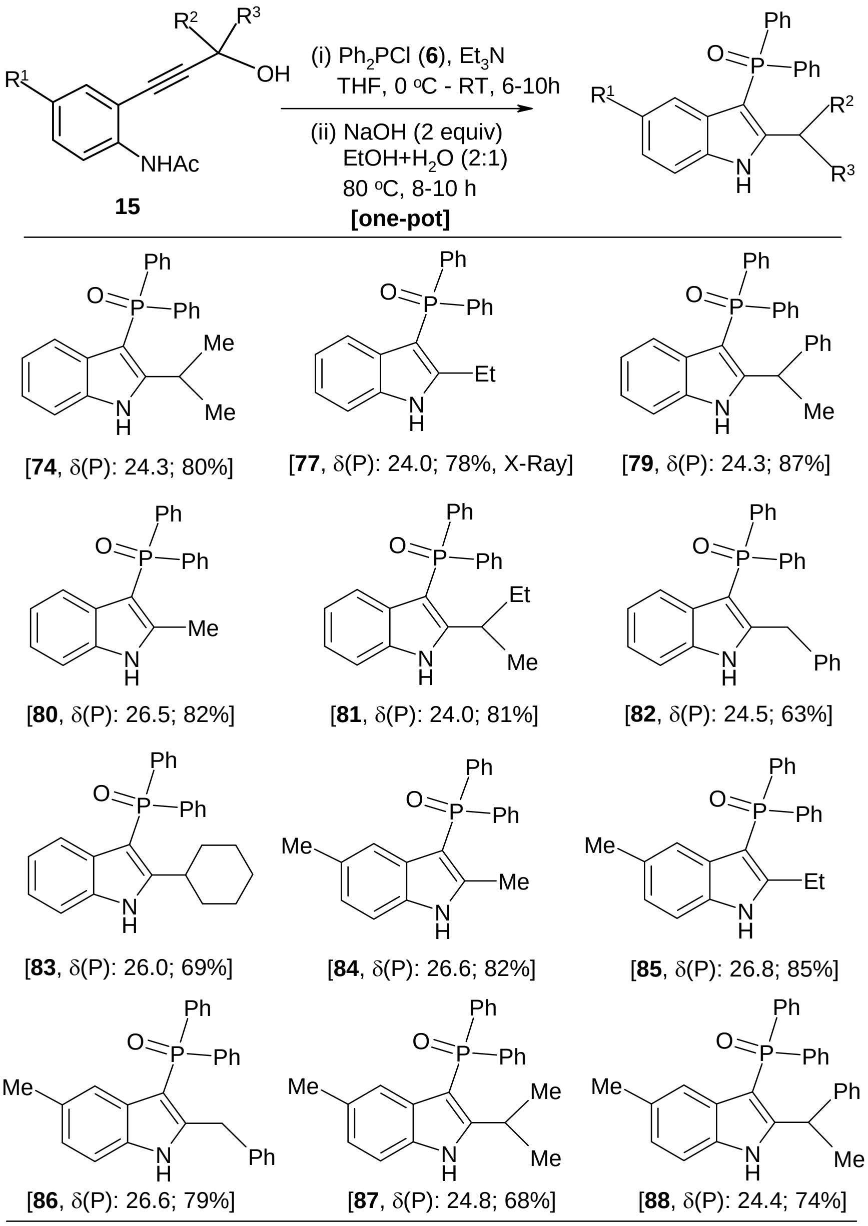
74, 89%

[**17a**, δ(P): 9.0;72%]

[**78**, δ(P): 16.5; 83%]

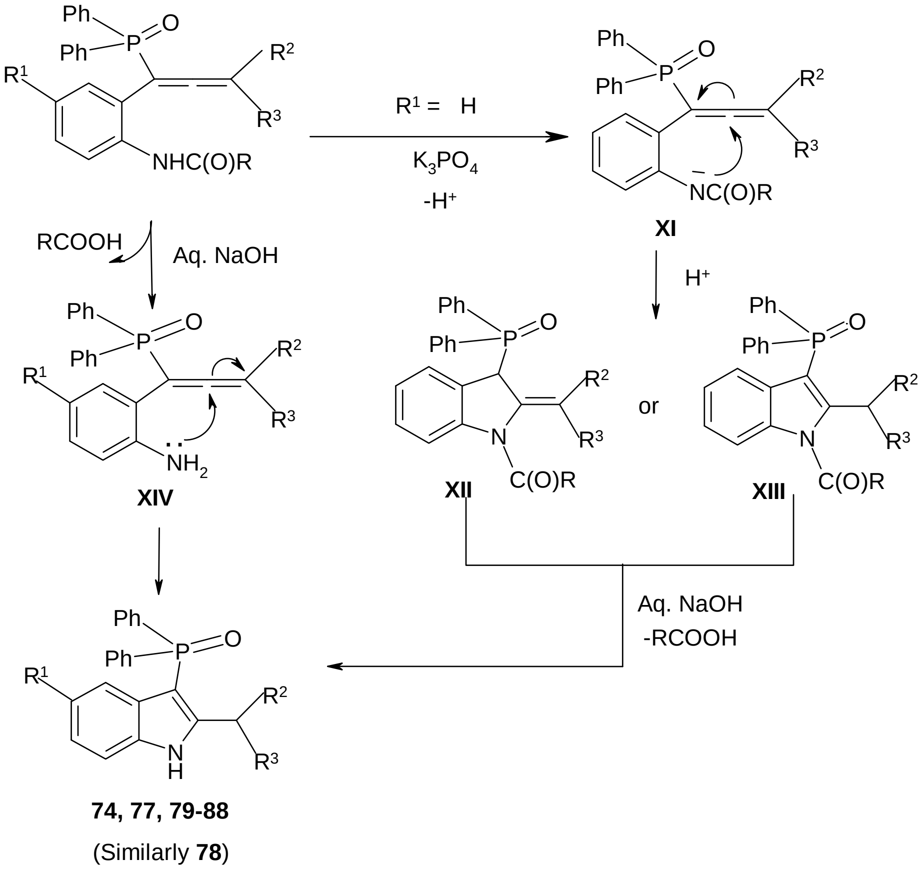
With the above conditions in hand, we then performed the reaction *in one-pot* starting from propargyl alcohol **15a** without isolating the intermediate allenylphosphine oxide **20a**. Gratifyingly, the method furnished the desired product **74** in 80 % yield. Inspired by this, functionalized propargyl alcohols **15b-l** were also subjected to the same one pot condition (Scheme 22). This one-pot strategy furnished the desired phosphinoyl-indoles **77**, **79-88** in good to excellent yields without any difficulty in isolation.

Scheme 22



A plausible pathway for the formation of phosphinoyl-indoles **74** and **77-88** is shown in Scheme 23. As discussed in Scheme 4, the normal reaction of propargyl alcohol with Ph_2PCl **(6)** is expected to lead to the allenylphosphine oxide.[18,65] We believe that there is only a subtle difference between the use of K_3PO_4 and aq. NaOH. K_3PO_4 abstracts the NH proton from allenylphosphine oxide leading to intermediate (**XI**) which is followed by attack of nitrogen lone pair on the ***β***-carbon[38,76] of allene forming addition product (X**II**) or (X**III**). This upon treatment with aq. NaOH leads to the deacylated/debenzoylated phosphinoyl indoles. In the one pot reaction, though, the *in situ* generated allenylphosphine oxide first undergoes deacylation[77] /debenzoylation with aq. NaOH resulting in $-NH_2$ functionalized allene (X**IV**). The lone pair on nitrogen will then attack the ***β***-carbon of the allene intramolecularly leading to phosphinoyl indoles **74** or **77-88**.

Scheme 23

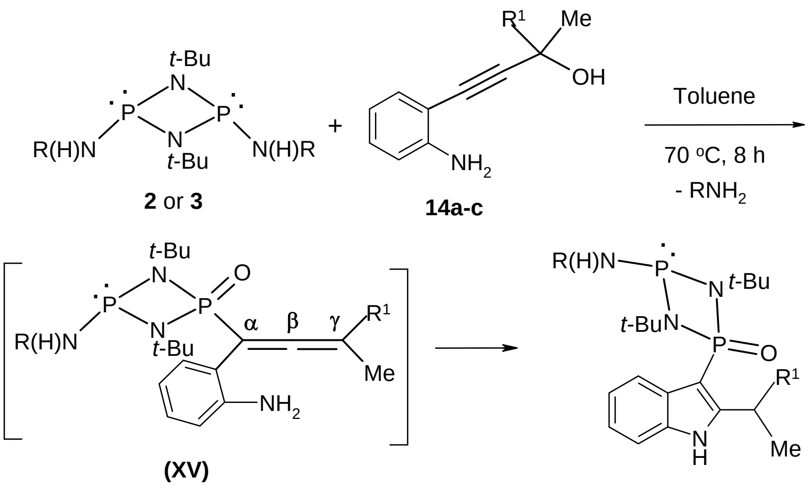


Thus a fairly simple route to phosphinoyl-indoles starting from functionalized propargyl alcohols *via* allenyl phosphine oxide is developed. The reaction involves base (K_2CO_3) mediated cyclization of allenylphosphine oxides, and deprotection in the presence aq.NaOH. We also developed a one-pot method for the synthesis of *NH*-free phosphinoyl indoles from propargyl alcohols. This reaction proceeds through aq. NaOH mediated deprotection followed by cyclization.

2.342 Synthesis of cyclodiphosphazanyl indoles

In continuation of the above work, we have also treated the cyclodiphosphazanes [(RNH)P(μ-N-*t*-Bu)]$_2$ [R = *t*-Bu (**2**), *i*-Pr (**3**)] with the aryl substituted propargyl alcohol **14a** possessing *o*-amino group. This led to cyclodiphosphazane based substituted indoles **89** and **90** shown in Scheme 24. These compounds are formed essentially as single products, but the solubility in organic solvents is rather poor. Here, the cyclodiphosphazane reacts with the propargyl alcohol forming the cyclodiphosphazane based allene intermediate **XV** that undergoes cyclization by the attack of -NH$_2$ functionality on the β-carbon of the allene leading to the substituted cyclodiphosphazane based indole. The IR spectra of **89** and **90** show the expected ν(NH) band in the region 3353-3381 cm^{-1}. In the ^{1}H NMR spectrum of **89**, the *t*-BuN*H* and indole -N*H* peaks appear at δ 3.32 and 8.28, respectively. The corresponding signals for **90** appear at δ 3.01 and 8.50, respectively. The ^{31}P NMR spectra of **89** shows two doublets at δ 10.7 and 78.0 with ^2J(PP) of 10.0 Hz. In the case of **90**, the broad signals appear at δ 10.5 and 82.7. In the ^{13}C NMR spectra, the ^1J(P-C) value of 172.0 Hz [δ(C) ~102] for **89**-**90** suggests that the corresponding phosphorus is connected to an sp^2 carbon.[52b] All these data are consistent with the structures shown in Scheme 24. Compounds **91** and **92** are prepared similarly by using the cyclodiphosphazane (**2**) and propargyl alcohols **14b** and **14c**, respectively. The structure in the case of compound **89** is further confirmed by single crystal X-ray diffraction (Figure 23). Although the quality of X-ray data is only moderate, complete refinement can be effected and the formation of the P-C bond as well as the indole ring can be clearly seen. Of the two isomers possible, the one in which indolyl group on one phosphorus is *trans* to the -NHR group on the second phosphorus is the product that is formed in the reaction.

Scheme 24



R = *t*-Bu, R^1 = Ph [**89**, δ(P): 10.7, 78.0; 92%, X-ray]
R = *i*-Pr, R^1 = Ph [**90**, δ(P): 10.5, 82.7; 81%]
R = *t*-Bu, R^1 = Me [**91**, δ(P): 13.5, 78.5; 90%]
R = *t*-Bu, R^1 = H [**92**, δ(P): 17.5, 82.6; 88%]

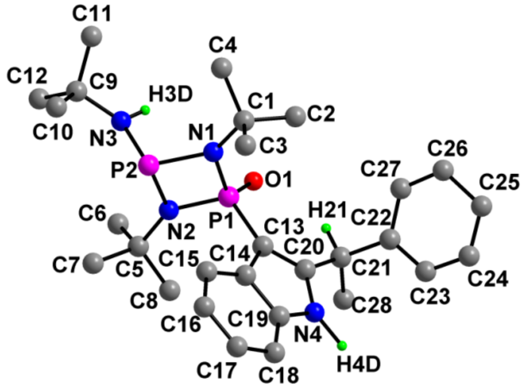


Figure 23. Molecular structure of compound **89**. Hydrogen atoms (except NH and CH) are omitted for clarity. Selected bond parameters: P1-C13 1.766(9), C13-C14 1.462(11), C13-C20 1.351(12), C20-C21 1.525(13), C20-N4 1.384(11) (Å).

Thus we have developed a straightforward route to cyclophosphazane based indoles starting from *ortho* amino functionalized propargyl alcohols *via* an allene intermediate. We have isolated these indoles directly from the reaction mixture without performing column chromatography.

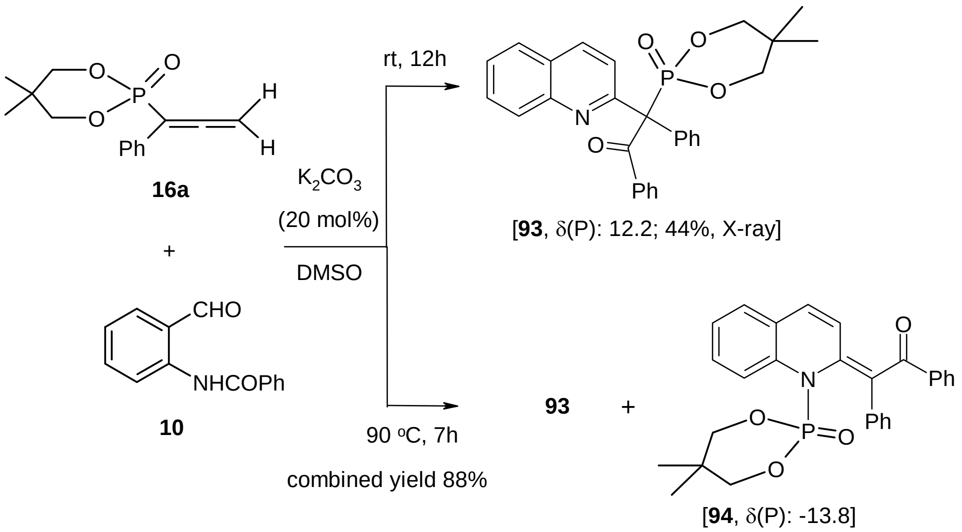
2.4 Base catalyzed intermolecular cyclization reactions of allenylphosphonates/ allenylphosphine oxides with *N*-(2-formylphenyl)benzamide

The reaction of allenylphosphonates with *N*-(2-formylphenyl)benzamide in the presence of base can lead to a variety of phosphono-quinolines by utilizing the -NHCOPh and –CHO functionalities on the latter. This section deals with base catalyzed intermolecular cyclization of allenylphosphonates/allenylphosphine oxides with *N*-(2-formylphenyl)benzamide. We used allenylphosphonate **16a** as a model substrate for the standardization of experimental conditions, because the products could be characterized more readily.

2.41 Reaction of substituted allenylphosphonates 16a-i with N-(2-formylphenyl)benzamide

First, we treated the allenylphosphonate **16a** with *N*-(2-formylphenyl)benzamide (**10**) in the presence of K_2CO_3 in DMSO at room temperature (Scheme 25) and obtained phosphono-quinoline **93** in 44% yield. This compound exhibits a peak at δ 12.2 in ^{31}P NMR spectrum. In the ^{13}C NMR spectrum a peak at δ 74.2 is seen, indicating that the phosphorus is attached to sp^3 carbon atom. However, to know the exact structure, we needed X-ray crystallography (Figure 24). When the reaction is conducted at 90 ^{o}C, compound **93** and the *N*-phosphorylated quinoline **94** are obtained with the combined yield of the isolated products being 88% (Scheme 25; see below for details). The δ(P) value of -13.8 for compound **94** is much upfiled to that for **93** (*vide supra*) which indicates that the phosphorus atom in **94** is linked to nitrogen.[78] Consistent with this, the P*C* signal was absent in ^{13}C NMR spectrum. IR, NMR (^{1}H, ^{13}C and ^{31}P) and HRMS data are consistent with the proposed structure for **94**.

Scheme 25



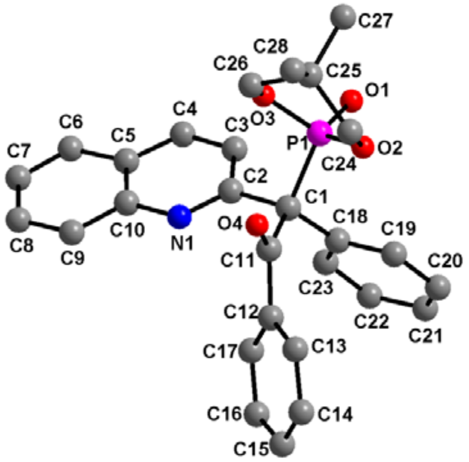


Figure 24. Molecular structure of compound **93**. Hydrogen atoms are omitted for clarity. Selected bond parameters: N1-C2 1.311(3), C2-C3 1.411(3), C3-C4 1.352(3), C2-C1 1.533(3), C1-P1 1.867(2), C1-C11 1.543(3), C1-C18 1.542(3) (Å).

To check the effect of bases and solvents on the yields of compounds **93** and **94**, different reaction conditions are employed. The results are summarized in the Table 2. It is found that this reaction leads exclusively to quinolines **93** and **94** (1:1 ratio) [^{31}P NMR evidence] using K_2CO_3 (20 mol%)/DMSO (Table 2, entry 1). Reducing the amount of base to 10 mol% lowers the combined yield to 75% (entry 2). In the absence of base, reaction does not proceed (entry 3). Use of other bases like K_3PO_4, Cs_2CO_3,

$NaHCO_3$ and NaOAc also gives good yields based on the ^{31}P NMR spectra of the reaction mixtures (entries 4-7). Triphenylphosphine is ineffective and 1,8-diazabicycloundec-7-ene (DBU) or 4-dimethylaminopyridine (DMAP) gives low yield (entries 8-11). Other solvents like toluene, 1,2-dichloroethane, dimethoxyethane, DMF, DMA, dioxane, acetonitrile, PEG-400, THF and ethanol (entries 12-21) in place of DMSO do not improve the yield. Among these, entry 1 is the best reaction condition for this transformation. Hence the optimal reaction conditions are as follows: K_2CO_3 (20 mol%) under nitrogen atmosphere in DMSO at 90 ^{o}C.

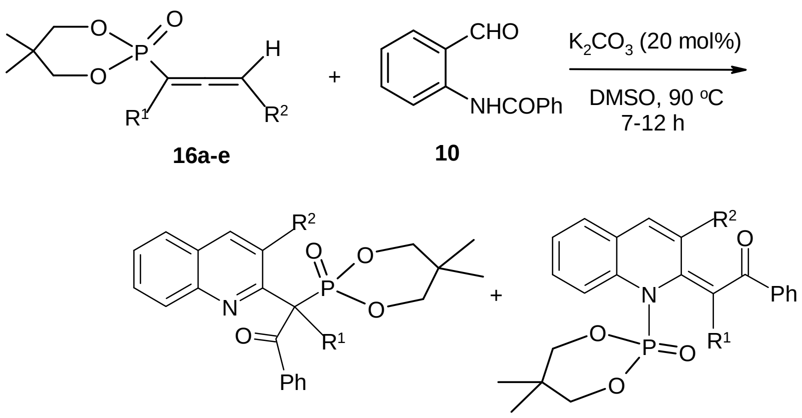
Having the above reaction conditions in hand, we then treated various allenylphosphonates (**16a-e**) with *N*-(2-formylphenyl)benzamide (**10**) that led to the desired phosphono- and *N*-phosphorylated quinolines **93-101** (Scheme 26). The combined yields of the isolated products in all the cases are good to excellent. In the case of allenylphosphonate **16e** as the substrate, the reaction afforded only **101** in 79% yield. ^{31}P NMR spectra show signals in the range δ 10.0-12.5 for phosphono-quinolines and δ -13.7– -14.4 for *N*-phosphorylated-quinolines, respectively. In the ^{13}C NMR spectra, the P-*C* carbon appears in the range at δ ~74 [^{1}J(P-C) ~ 127-134 Hz] for phosphono-quinolines. It should be mentioned here that in the reaction leading products **99** and **100**, we also isolated another product **102** (benzoyl group eliminated) in 10% yield. The ^{31}P NMR signal for this compound was observed at δ 17.1. The presence of a doublet for P*C*H carbon at *δ* 52.0 (using DEPT) with a ^{1}J(P-C) value of 140.0 Hz suggests that phosphorus moiety is attached to an sp^3 hybridized carbon.[36]

Table 2. Effect of base and solvent on the yields of compounds **93** and **94** from the reaction of allene **16a** with *N*-(2-formylphenyl)benzamide[a]

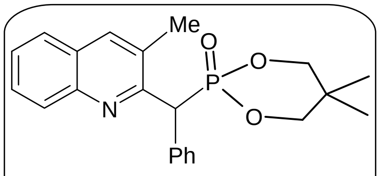
Entry	base	solvent	time (h)	Yield (%) (**93**:**94**)[b]
1	K_2CO_3	DMSO	8	98 (1.0:1.0)
2[c]	K_2CO_3	DMSO	12	75 (1.0:0.8)
3[d]	-	DMSO	12	N.R
4	K_3PO_4	DMSO	12	96 (1.0:0.9)
5	Cs_2CO_3	DMSO	12	75 (1.0:0.8)
6	$NaHCO_3$	DMSO	12	95 (1.0:0.7)
7	NaOAc	DMSO	12	94 (1.0:0.6)
8[e]	PPh_3	DMSO	7	N.R
9	DBU	DMSO	7	45 (1.0:1.1)
10[e]	DABCO	DMSO	7	N.R
11	DMAP	DMSO	7	70 (1.0:0.4)
12	K_2CO_3	toluene	12	10 (1.0:0.0)
13[e]	K_2CO_3	dichloroethane	12	N.R
14	K_2CO_3	DME	12	65 (1.0:0.3)
15	K_2CO_3	DMF	7	90 (1.0:0.7)
16	K_2CO_3	DMA	7	88 (1.0:1.2)
17	K_2CO_3	dioxane	7	50 (1.0:0.5)
18	K_2CO_3	acetonitrile	10	75 (1.0:0.4)
19	K_2CO_3	PEG-400	12	45 (1.0:0.0)
20	K_2CO_3	THF	7	25 (1.0:0.0)
21	K_2CO_3	ethanol	7	35 (1.0:0.0)

[a] Reaction conditions: **16a** (1.0 equiv), **10** (1.0 equiv), base (0.2 equiv) and solvent (1.0 mL) at 90 °C (oil bath) under nitrogen unless otherwise noted. [b] Yields are based on ^{31}P NMR spectra of the reaction mixtures. [c] K_2CO_3 (0.1 equiv) used. [d] No catalyst was used. [e] Allenylphosphonate **16a** completely recovered.

Scheme 26



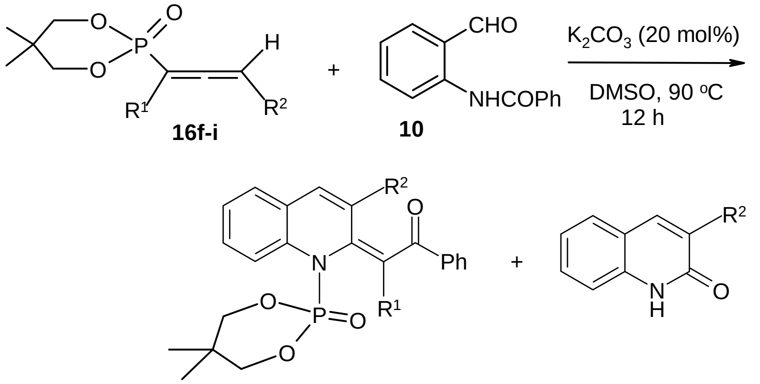
R^1 = Ph, R^2 = H	[**93**, δ(P): 12.2; 43%]	+	[**94**, δ(P): -13.8; 45%]
R^1 = 4-Me-C_6H_4, R^2 = H	[**95**, δ(P): 12.3; 43%]	+	[**96**, δ(P): -13.8; 46%]
R^1 = 4-MeO-C_6H_4, R^2 = H	[**97**, δ(P): 12.5; 31%]	+	[**98**, δ(P): -13.7; 59%]
R^1 = Ph, R^2 = Me	[**99**, δ(P): 10.1; 22%]	+	[**100**, δ(P): -14.4; 57%]
R^1 = 4-MeO-C_6H_4, R^2 = Me	-	+	[**101**, δ(P): -14.2; 79%]



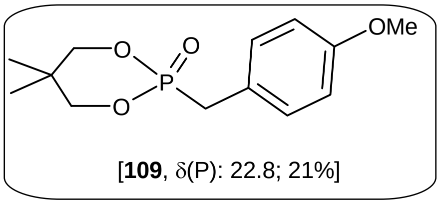
[**102**, δ(P): 17.1; 10%]

When we performed the reaction of allenylphosphonates **16f-i** with *N*-(2-formylphenyl)benzamide (**10**) under the above conditions, we obtained the corresponding *N*-phosphorylated quinolines **103** and **105-106** along with phosphorus free quinolinones **104**, **107-108** in good (combined) yields (Scheme 27). IR spectra of the compounds **104** and **107-108** show the ν(NH) band in the region 3304-3457 cm^{-1} and ^1H NMR spectra show N*H* signals in the region at δ ~12.0. In the ^{13}C NMR spectra, δ(*C*O) is in the range 161.3-163.2. All these data are consistent with the proposed structures of **104** and **107-108** as shown in Scheme 27. Since these are new types of reactions, confirmation of the structures in the case of **104** and **107** was done by single crystal X-ray diffraction (Figure 25). However, it may be noted that compounds **104**[79] and **108**[80] are known, but were prepared by different routes. Compound **107** is new. Another point to be noted is that in the reaction using allenylphosphonate **16g**, along with the products **104** and **105**, we also isolated compound **109** in 21% yield. This compound shows a signal at δ 22.8 in the ^{31}P NMR spectrum. IR, NMR (^{1}H and ^{13}C) and HRMS data are consistent with the structure shown.

Scheme 27



R^1 = Ph, R^2 = Ph [**103**, δ(P): -15.0; 48%] + [**104**, 21%, X-ray]
R^1 = 4-MeO-C_6H_4, R^2 = Ph [**105**, δ(P): -15.0; 45%] + [**104**, 27%]
R^1 = Ph, R^2 = 4-Cl-C_6H_4 [**106**, δ(P): -14.7; 41%] + [**107**, 36%, X-ray]
R^1 = Ph, R^2 = 4-Br-C_6H_4 - + [**108**, 39%]



[**109**, δ(P): 22.8; 21%]

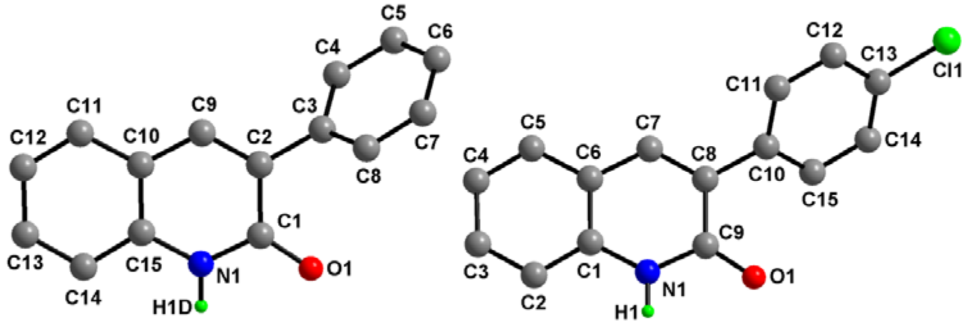
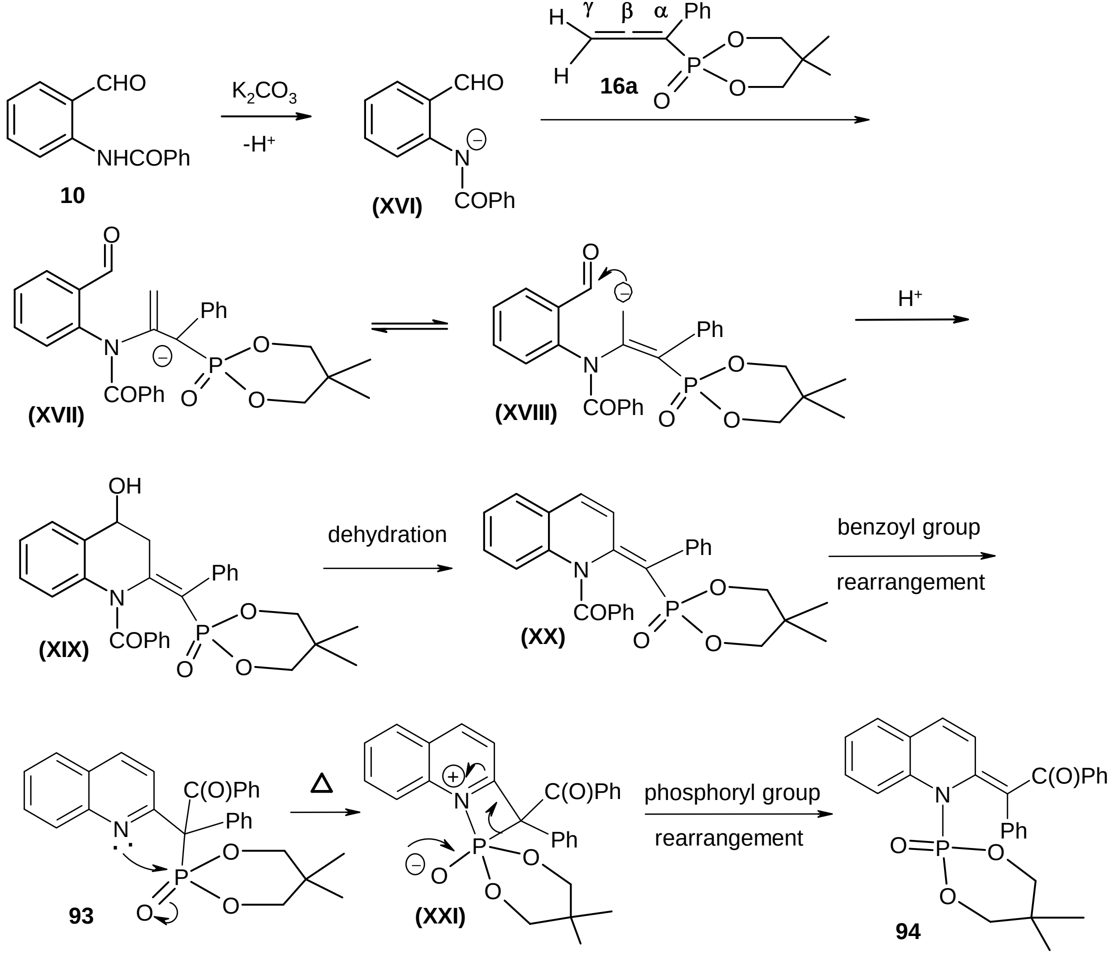


Figure 25. **Left:** Molecular structure of compound **104**. Hydrogen atoms omitted for clarity. Selected bond parameters: N1-H1D 0.892(18), N1-C1 1.3648(18), C1-O1 1.2380(17), C1-C2 1.4673(19), C2-C9 1.3489(19), C2-C3 1.482(2) (Å). **Right:** Molecular structure of compound **107**. Selected bond parameters: N1-H1 0.89(2), N1-C9 1.364(2), C9-O1 1.235(2), C9-C8 1.462(2), C8-C7 1.346(3), C8-C10 1.482(2), C13-Cl1 1.735(2) (Å).

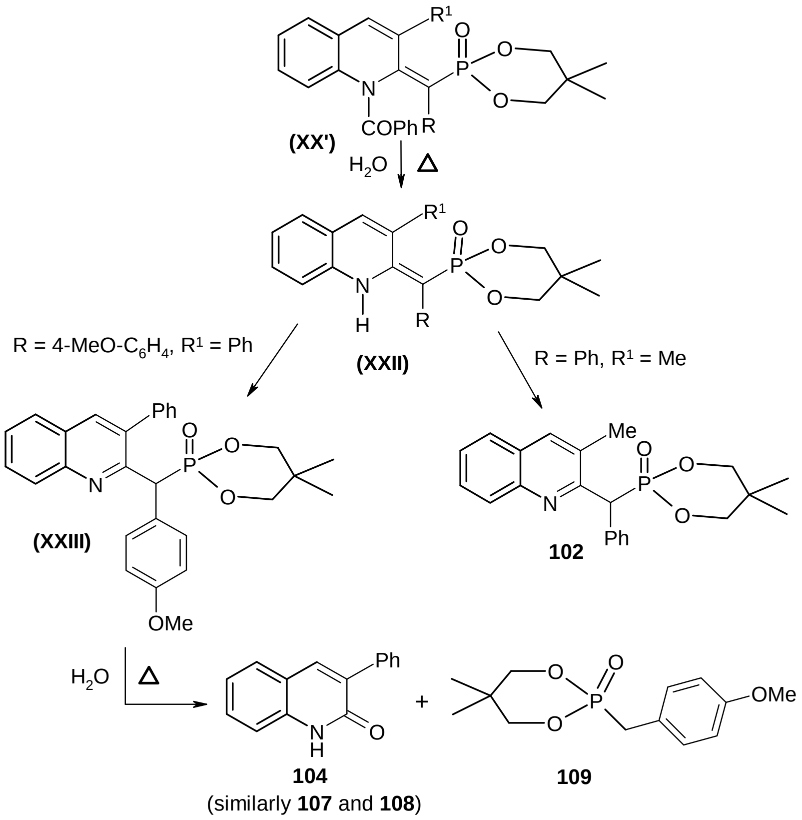
A plausible pathway for the formation of phosphono- and *N*-phosphorylated quinolines **93** and **94** is shown in Scheme 28. Initially, the base abstracts proton from *N*-(2-formylphenyl)benzamide (**10**) and generates aza-anionic intermediate **XVI** which reacts with allenylphosphonate **16a** at *β*- position[37] to give **XVII**. Species **XVII** is in equilibrium with X**VIII**. Intermediate **XVIII** undergoes intramolecular aldol reaction followed by proton abstraction to afford **XIX**, which upon dehydration leads to the intermediate **XX**.[37] Benzoyl group in the intermediate **XX** undergoes 1,3-migration to afford **93**. Upon heating the nitrogen may attack the phosphoryl phosphorus to form the four-membered intermediate **XXI**. This is followed by phosphoryl group rearrangement leading to product **94**.

Scheme 28



Formation of compound **102** can be explained *via* intermediate **XX’** (R = Ph, R^1 = Me, Scheme 29) that is similar to **XX** (cf. Scheme 28). In the presence of liberated H_2O, **XX’** leads to **XXII** after benzoyl group elimination, which then undergoes isomerization to product **102**. Formation of phosphorus-free quinolinone **104** and anisyl phosphonate **109** looks odd, but we presume that intermediate **XXIII** that is analogous to compound **102** may be involved. Compounds **107** and **108** are formed in a similar manner.

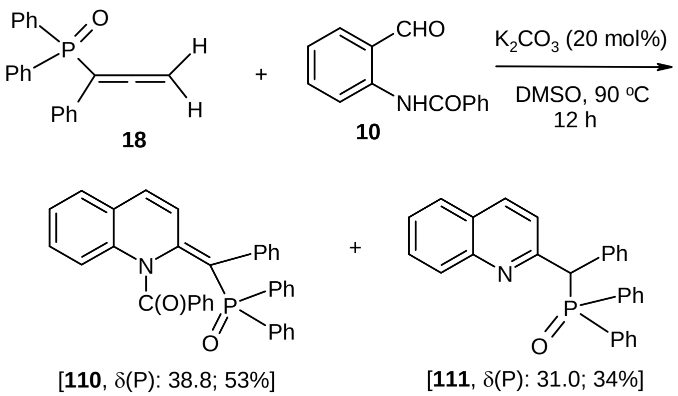
Scheme 29



2.42 *Reaction of allenylphosphine oxide 18 with N-(2-formylphenyl)benzamide*

In the reaction of allenylphosphine oxide **18** with *N*-(2-formylphenyl)benzamide, the isolated products **110** and **111** (Scheme 30) are different from those using allenylphosphonates (Schemes 25-27). The combined yield of the products is good. The ^{31}P NMR signals for the compounds **110** and **111** appear at δ 38.8 and 31.0 respectively which indicate that the phosphorus atoms are attached to carbon. In the ^1H NMR spectrum of compound **111**, a doublet at δ 5.4 [J = 8.8 Hz] shows the presence of P*CH* moiety. The δ(*C*O) for **110** is at δ 199.5. The P*C* signal for compound **110** appears at δ 132.2 [^1J(PC) = 98.0 Hz] and that for compound **111** appears at δ 57.1 [^1J(PC) = 63.0 Hz], as expected.[63] The corresponding P*C*H carbon appears at δ 57.0 (using DEPT). It may be noted that compound **110** is analogous to species **XX** and compound **111** is analogous to product **102**. Hence these results are also consistent with mechanistic pathway presented above.

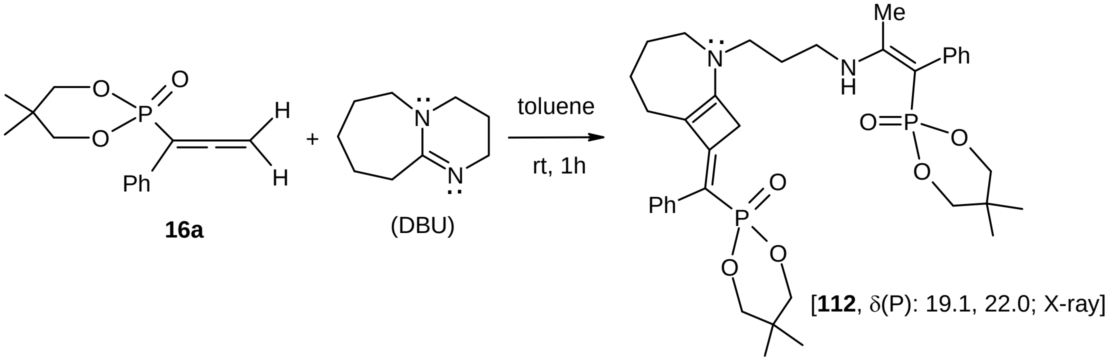
Scheme 30



2.43 Reaction of allenylphosphonate 16a with DBU

In the reaction shown in Table 2, entry 9, we used DBU as a base and the yield of the products was low. We were a bit curious because of our previous results while using DBU[81] and hence treated allenylphosphonate **16a** with DBU in toluene (Scheme 31). Interestingly, the ^{31}P NMR spectrum of crude mixture showed peaks at δ 17.7, 19.0, 22.1 and 22.5. We tried to separate the products by column chromatography, and in this process obtained a very small quantity of crystalline **112** [δ(P) 19.1 and 22.0], good ^{1}H and ^{13}C NMR spectra could not be obtained. Since the crystals were suitable for X-ray diffraction, we obtained the structure which is shown in Figure 26.

Scheme 31



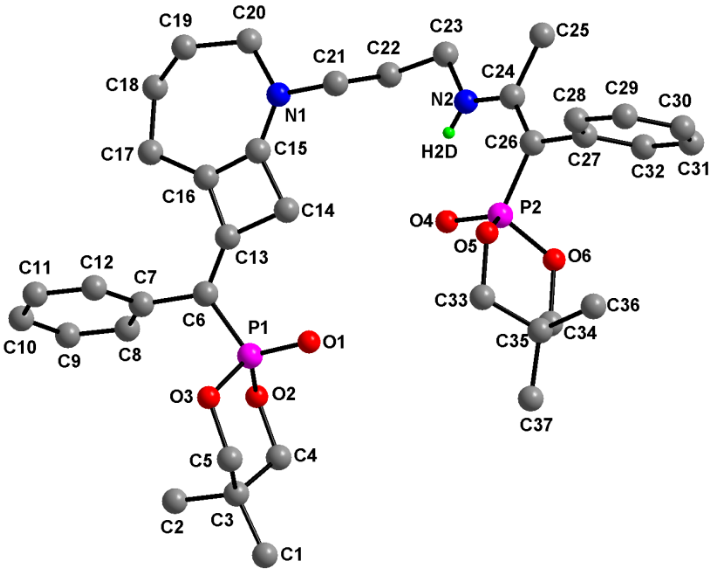
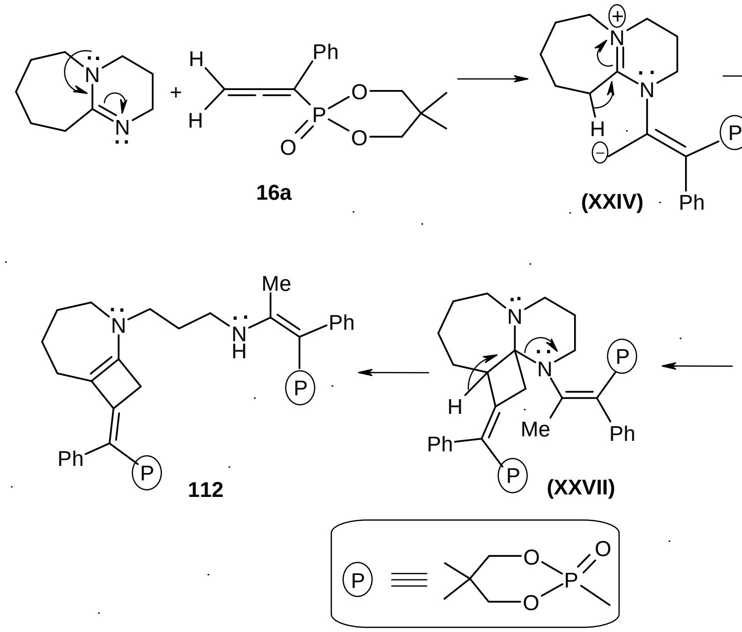


Figure 26. Molecular structure of compound **112·*n*-C$_5$H$_{12}$**. Hydrogen atoms (except NH) and solvent molecule are omitted for clarity. Selected bond parameters: P1-C6 1.736(6), C6-C13 1.351(9), C13-C14 1.536(8), C14-C15 1.498(9), C13-C16 1.432(9), C15-C16 1.387(9), C15-N1 1.328(8), N1-C21 1.465(8), C21-C22 1.507(9), C22-C23 1.515(9), C23-N2 1.469(8), N2-C24 1.337(8), C24-C25 1.503(9), C24-C26 1.380(9), C26-P2 1.745(6) (Å).

The formation of compound **112** is explained by the initial attack of DBU on *β*-carbon of allene[37] that may lead to an intermediate **XXIV**, which is further neutralized by subsequent elimination of proton may produce intermediate **XXV** (Scheme 32). Later, the lone pair on nitrogen may initiate the reaction further with another allenylphosphonate **16a**, which will lead to ionic intermediate **XXVI**. Intermediate

XXVI undergoes cyclization to produce **XXVII**. Subsequent breaking of C-N bond coupled with proton capture by nitrogen may finally lead to **112**. Some of these intermediates can be stabilized by the presence of the phosphory (P=O) group.

Scheme 32

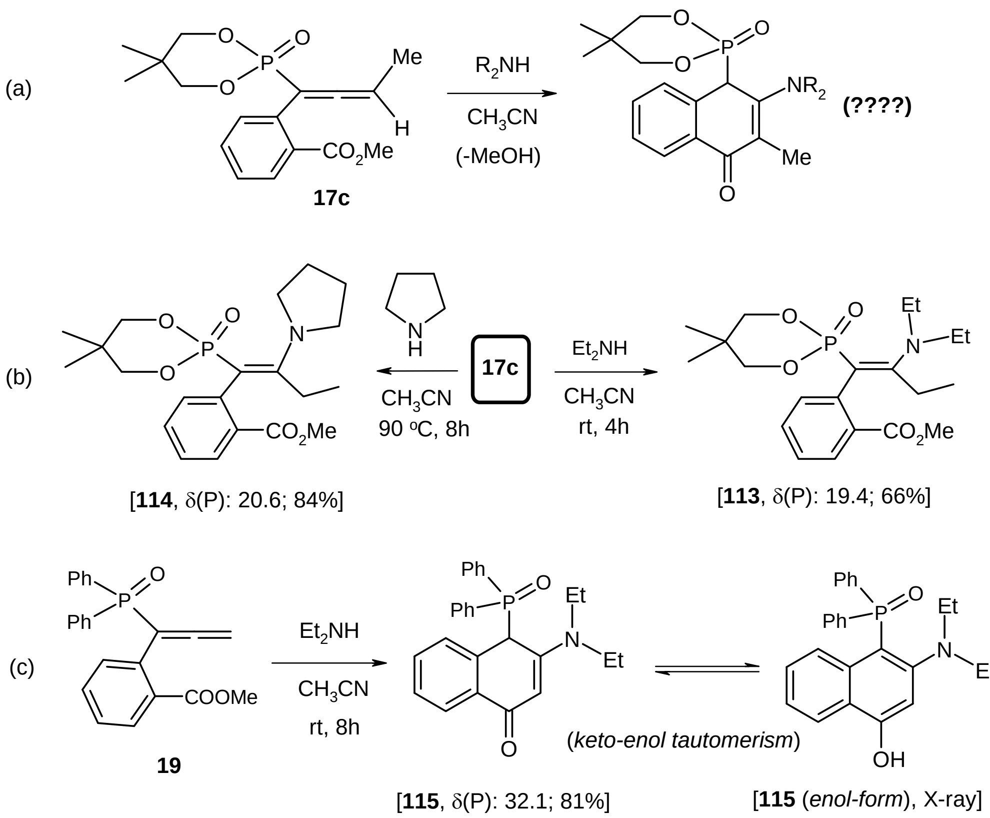


2.5 Nucleophilic addition/cyclization reactions of allenylphosphonates or allenylphosphine oxides

2.51 Reaction of secondary amines with functionalized allenylphosphonate (17c)/ allenylphosphine oxide (19)

In earlier reactions we have synthesized various phosphono-heterocycles via *in situ* generated allene intermediate using internal *o*-functionality (Schemes 6-11 and 20-22). As an extension, we wanted to use an external nucleophile for cyclization of allenylphosphonate bearing an *o*-functionality like CO_2Me (Scheme 33a). For this reason, we treated allenylphosphonate (**17c)** with secondary amines like diethylamine and pyrrolidine (Scheme 33b). However, in both the cases we obtained only (β,γ) addition products **113** and **114** [^{1}H, ^{13}C/^{31}P NMR; IR, HRMS]. Since similar addition products are reported in the literature (including that from our laboratory),[37,46] we wanted to check the reaction using a more stable allene like **19** with no substituents at the γ-position. Gratifyingly, this reaction was successful [Scheme 33c]. Efforts are still on the way to generalize this reaction with other secondary amines.

Scheme 33



Absence of C(O)OCH_3 proton signal in the ^1H NMR spectrum suggested that the cyclization had taken place. The presence of doublet for PC*H* at δ 4.98 (^2J = 20.8 Hz) in the ^1H NMR spectrum and a doublet for P*C*H carbon at δ 48.9 [^1J(PC) = 49.0 Hz] in the ^{13}C NMR spectrum revealed that the phosphorus is attached to sp^3 hybridized (*C*H) carbon.[63] The δ(*C*O) signal was observed at 182.4 ppm, showing the presence of carbonyl moiety. All these data are consistent with the structure **115** (*keto-form*) proposed in Scheme 33c. The IR (KBr) spectrum for a crystal, though, shows the absence of carbonyl band. Single crystal X-ray data confirmed the *enol-form* for compound **115** (Figure 27). Further work regarding this type of cyclization is in progress in our laboratory.

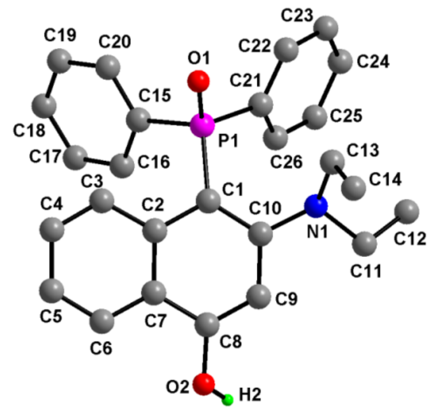
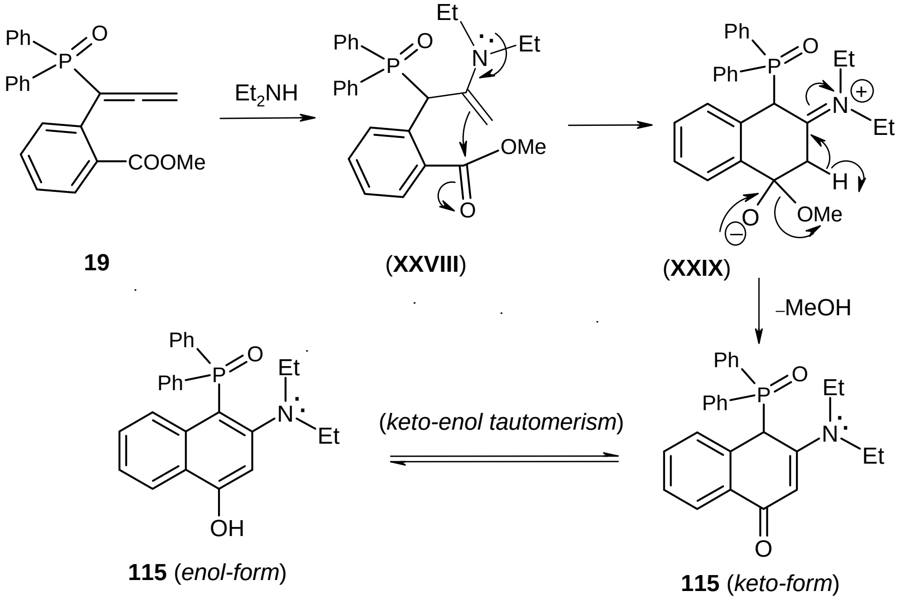


Figure 27. Molecular structure of compound **115** (*enol-form*). Hydrogen atoms (except OH) are omitted. Selected bond parameters: P1-C1 1.788(5), C1-C10 1.394(7), C10-N1 1.412(7), C10-C9 1.416(7), C9-C8 1.353(7), C8-O2 1.347(6), O2-H2 0.82 (Å).

A possible pathway for the formation of compound **115** (*keto* or *enol* form) as shown in Scheme 34. Initially, the addition of Et_2NH on *β*-carbon of allene may lead to (*β,α*) addition product (intermediate) **XXVIII**.[46] Later, the lone pair of electrons on nitrogen may initiate the cyclization to lead to intermediate **XXIX** that undergoes elimination of MeOH to produce compound **115** (*keto* or *enol* form).

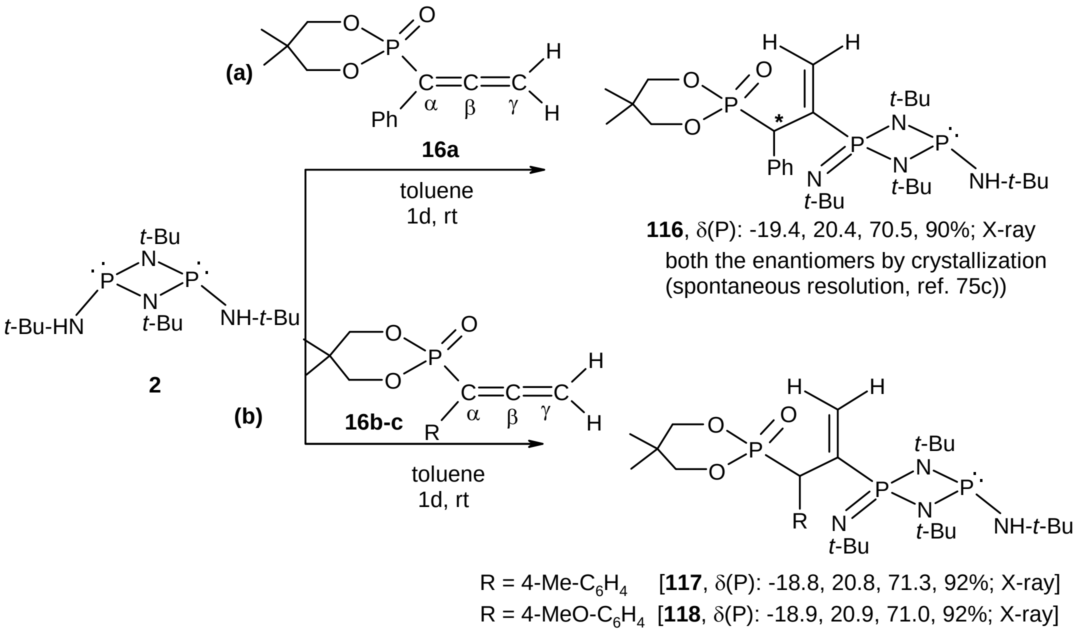
Scheme 34



2.52 Oxidative addition of cyclodiphosphazanes with allenylphosphonates/allenylphosphine oxide/ dimethyl maleate

In an earlier work from our laboratory it was shown that allenylphosphonates react with the cyclodiphosphazane $[(t\text{-BuNH})P(\mu\text{-N-}t\text{-Bu})]_2$ (**2**) leading to species that have structures close to that shown in Scheme 33b.[75c] Thus both the enantiomers of the product $[(t\text{-Bu-HN})P(\mu\text{-N-}t\text{-Bu})_2P(\text{=N-}t\text{-Bu})C(\text{=}CH_2)\text{-}CH(Ph)\text{-}P(O)(OCH_2CMe_2CH_2O)]$ (**116**) were isolated from the reaction of **2** with the allene **16a** (Scheme 35a). The identity of the two enantiomers [separated by spontaneous resolution by crystallization] was confirmed by X-ray crystallography as well as solid state CD spectra of the crystals. Since resolution of enantiomers without using chiral auxiliaries was one of the interests in our group [also see section 5.33 above],[75c] in the present work, the reaction of the *p*-tolyl substituted allene $(OCH_2CMe_2CH_2O)P(O)C(C_6H_4\text{-4-Me})\text{=C=}CH_2$ (**16b**) with $[(t\text{-BuNH})P(\mu\text{-N-}t\text{-Bu})]_2$ (**2**) was performed (Scheme 35b). We did obtain the expected new product $[(t\text{-BuNH})P(\mu\text{-N-}t\text{-Bu})_2P(\text{=N-}t\text{-Bu})\text{-}C(\text{=}CH_2)CH(C_6H_4\text{-4-Me})\text{-}P(O)(OCH_2CMe_2CH_2O)]$ (**117**), but it crystallized as a racemic mixture (Figure 28). Similarly compound **118** was prepared by using respective allenylphosphonate with cyclophosphazane **2**. In contrast to our hope [on the basis of the results on compound **116**], compound **118** crystallized as a racemic mixture (Figure 29). Hence this system was not pursued further. Nevertheless, the results clearly show that the initial attack of the P^{III} species occurs at the central carbon of the allene, which lead to (*β,α*) addition products.

Scheme 35



116, δ(P): -19.4, 20.4, 70.5, 90%; X-ray
both the enantiomers by crystallization
(spontaneous resolution, ref. 75c))

R = 4-Me-C_6H_4 [**117**, δ(P): -18.8, 20.8, 71.3, 92%; X-ray]
R = 4-MeO-C_6H_4 [**118**, δ(P): -18.9, 20.9, 71.0, 92%; X-ray]

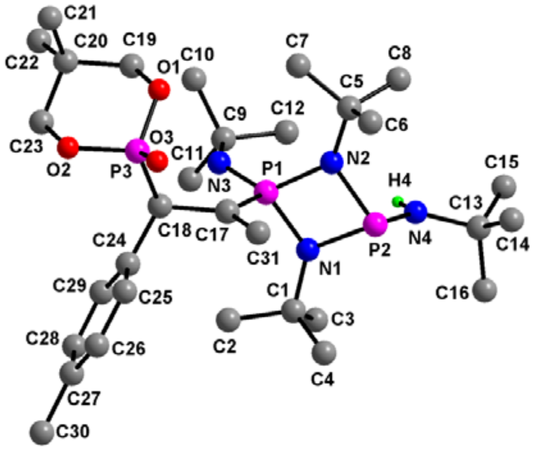


Figure 28. Molecular structure of compound **117**. Hydrogen atoms (except NH) are omitted for clarity. Selected bond parameters: P3-C18 1.814(3), C18-C17 1.536(4), C17-C31 1.317(4), C17-P1 1.828(3), P1-N3 1.540(2), N4-H4 0.86(4) (Å).

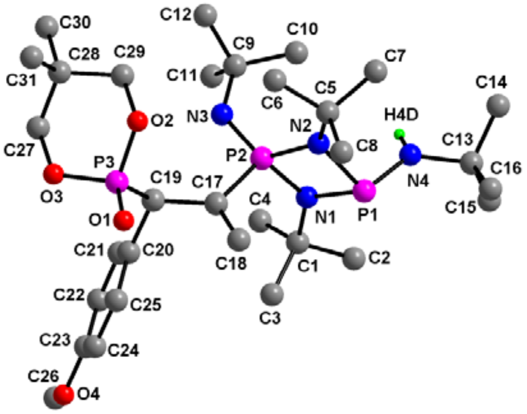
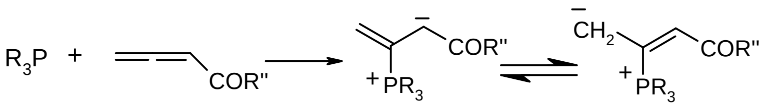


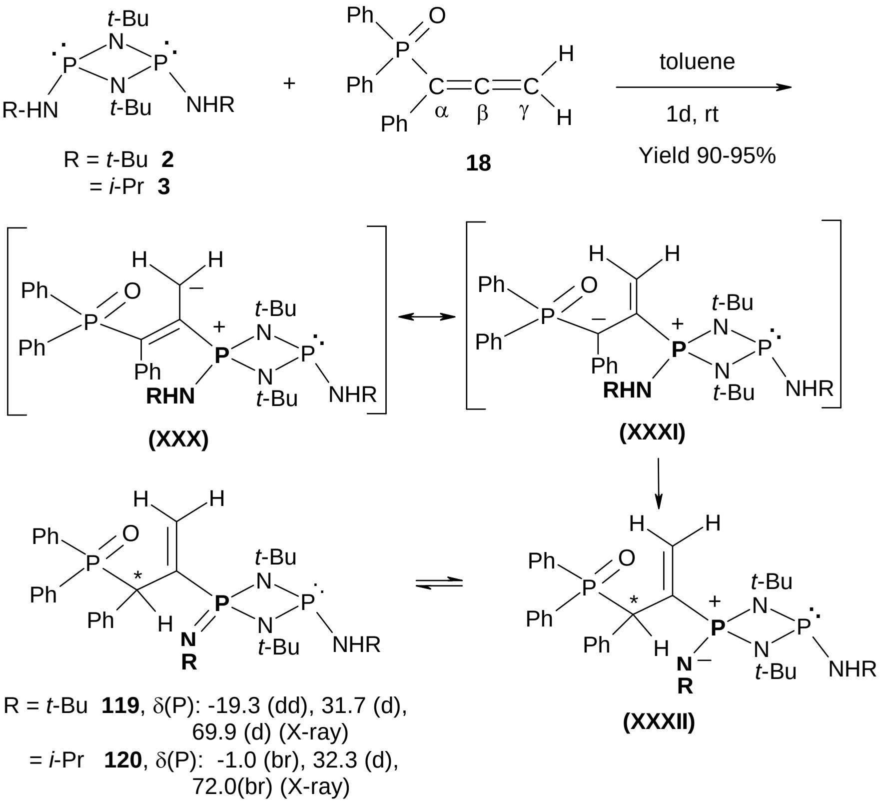
Figure 29. Molecular structure of compound **118**. Hydrogen atoms (except NH) are omitted for clarity. Selected bond parameters: P3-C19 1.808(2), C19-C17 1.530(3), C17-C18 1.323(3), C17-P2 1.827(2), P2-N3 1.5457(17), N4-H4D 0.84(3) (Å).

The basic premise for conducting the above reacions was to isolate compounds that are analogous to those proposed in the phosphine catalyzed reactions of allenes/alkynes as shown in Scheme 36.[43a,82] Hence we have also performed the reaction of cyclodiphosphazanes **2-3** with the allenylphosphine oxide **18**. The reaction afforded compound **119** or **120** (Scheme 37) as essentially a single product by the attack of P^{III} center on the *β*-carbon atom of the allenylphosphine oxide. Compound **119** exhibits three signals in the ^{31}P NMR spectrum at δ -19.3 [dd, $^{2,3}J$(PP) = 24.9, 8.3 Hz *P*=N-*t*-Bu], 31.7 [d, *J*(PP) = 24.9 Hz, Ph$_2$*P*(O)-] and 69.9 [d, *J*(PP) = 8.3 Hz; *P*^{III}-NH-*t*-Bu] as expected. However, the ^{31}P NMR signals corresponding to the cyclodiphosphazane ring of compound **120** showed broad signals at δ 72.0 and -1.0, although the signal for –Ph$_2$***P***(O) at δ 32.3 (d) was sharp. This behavior (broad peaks in the ^{31}P NMR spectrum) is probably due to the more pronounced amino-imino (**XXX-XXXI**) tautomerism or phosphinimine (**XXXI**)- phosphinium salt (**XXXII**) equilibrium in compound **120** compared to compound **119**. However, we have not studied this aspect in detail. The structures of compounds **119** and **120** are proven by X-ray crystallography (Figure 30).

Scheme 36



Scheme 37



Formation of **119** entails the generation of a chiral center. We have earlier pointed out in an analogous case that it is possible to observe spontaneous resolution by crystallization.[75c] Indeed, the samples that we checked crystallized in the chiral space group *Pca2(1)* with (*S*)-chirality at the (Ph)(H)***C***-P carbon center. However, unlike in the earlier example, the other enantiomer of **119** could not be separated although the solid state CD spectrum suggested that it may also be present in the bulk. In contrast to this, compound **120** crystallized in the centrosymmetric space group $P\bar{1}$.

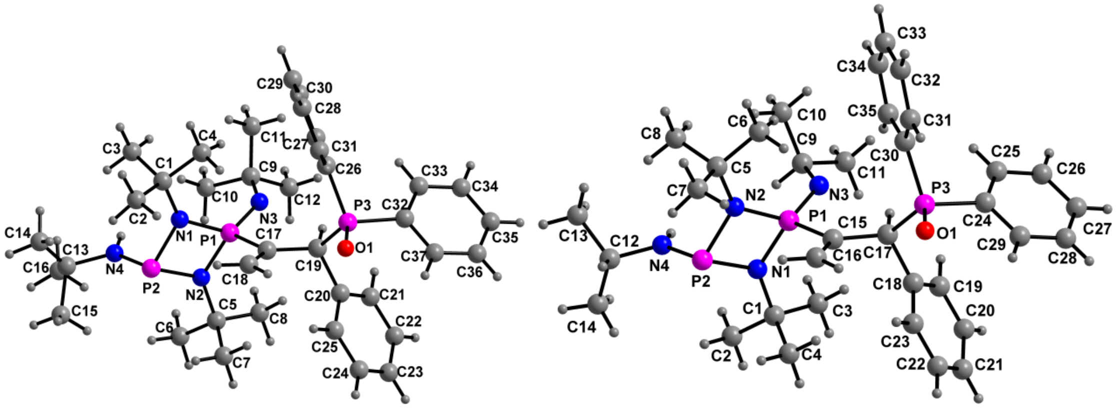
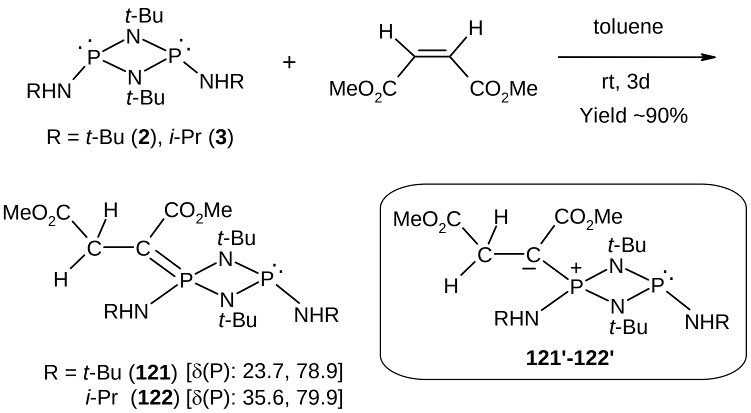


Figure 30. Molecular structures of compounds **119-120**; for **119**, only one position each for C14-C16 is shown. Hydrogen bonding interactions in compound **120** (Å, Å, Å, °): N(4)-H(4D)...O(1) 0.80, 2.35, 3.102(3), 156.9; symm. equiv: x, -1+y, z.

In another set of reactions, and in continuation of the above idea, we treated **2-3** with dimethyl maleate and obtained the stable ylides **121-122**. Among these two ylides, **121** was already synthesized by my colleague (Scheme 38).[83] The IR spectrum of **122** showed the ν(NH) band at 3426 cm^{-1}. The ^{31}P NMR signal for **122** appeared at δ 35.6 and 79.9, with negligible ^{2}J(PP) value. In the ^{13}C NMR spectrum, the P-*C* carbon appears at δ 44 with a large ^{1}J(P-C) of 182.5 Hz. Notably, the ^{13}C NMR chemical shift value is not in the typical alkenic region perhaps because the formal double bond is with phosphorus. The corresponding ^{1}J(P-C) values [involving the cyclophosphazane phosphorus] in compounds **119-120** are in the range 149-160 Hz at δ(C) 142-145. On the basis of our previous studies, it is expected that the ^{1}J(P-C) values involving an sp^2 carbon will be significantly higher than that involving a sp^3 carbon.[52b-c] Observation of a doublet at δ 2.69 with integrated intensity corresponding to two protons and with a ^{3}J(P-H) value of 14.4 Hz in the ^{1}H NMR spectra reveals a P=CCH_2 group. All these data are consistent with the structure **122** shown in Scheme 38, but there could be contribution from the phosphonium salt structures **121'-122'**. In any case, these are clearly ***different from the phosphinimine structures*** observed in the case of **119-120**. It must also be noted that such ylidic structures were ***not proposed in the mechanism for Morita-Baylis-Hillman reaction,***[84] ***but may be involved in specific cases***. Further confirmation of the structure of **122** is provided by single crystal X-ray structure as shown in Figure

31. The shorter P1-C15 distance [1.718 Å] and the longer P1-N3 distance [1.616 Å] in **122** when compared to the corresponding distances in **119-120** clearly demonstrate that in compound **122**, the P1-C15 bond is formally a double bond and the P1-N3 bond is formally a single bond. The presence of intramolecular hydrogen bond between N3 and a carbonyl oxygen atom in **122** (Figure 31) is another proof for the structure as given in Scheme 38.

Scheme 38



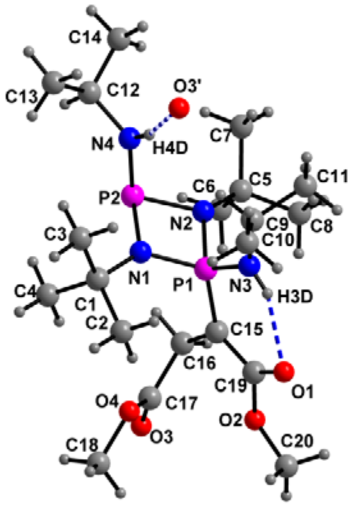


Figure 31. Molecular structure of compound **122**; all the non-hydrogen atoms are labeled. Some of the *t*-butyl carbon atoms are disordered. Selected bond distances (Å): P1-N1 1.6604(18), P1-N2 1.6636(18), P1-N3 1.6164(19), P1-C15 1.718(2), C15-C16 1.513(3), N4-H4D 0.83(3). Hydrogen bond parameters in compound **122** (Å, Å, Å, ^{o}): N4-H4D**…**O3’ 0.83(3), 2.27(3) 3.067(3), 161(2); N3-H3D**…**O1 0.80(3), 2.01(3), 2.718(2), 147(3). Symm equiv: 0.5-x, 0.5+y, z.

SUMMARY – PART A

1) The reaction of cyclodiphosphazanes with aryl substituted propargyl alcohols possessing *o*-nitro group leads to cyclodiphosphazanyl indolinones, oxa-aza-benzocycloheptenone and polycycles rather than the expected cyclodiphosphazane based allenes. A demonstrative set of indolinones, oxa-aza-benzocycloheptenones and 2-substituted indoles using Ph_2PCl and $(OCH_2CMe_2CH_2)PCl$ is also presented. In some cases, dephosphorylation occurs, leading to phosphorus-free indoles, quinolinones and tetrahydroacridine. Many of these reactions are unprecedented. We have synthesized novel P-N bonded compounds using cyclodiphosphazanes and *N*-hydroxy substrates. This reaction involves a novel P^{III}-O-N → P^{V}(O)-N rearrangement.
2) Treatment of Ph_2PCl with *o*-nitro functionalized propargyl alcohols in 2:1 molar stoichiometry produces bis-phosphinyoylallenes. Some of these compounds undergo ‘spontaneous resolution’ by crystallization. For one set of enantiomeric system, crystal structures as well as the solid state CD spectra for both the *R* and *S* enantiomers vindicating a case of spontaneous resolution are presented.
3) A fairly simple route to phosphinoyl-indoles starting from *o*-amido functionalized propargyl alcohols *via* allenyl phosphine oxide is developed. A one-pot method for the synthesis of *NH*-free phosphinoyl indoles from propargyl alcohols is demonstrated. This reaction proceeds through NaOH mediated deprotection followed by cyclization. In addition, we have also discovered a straight-forward route to cyclophosphazane based indoles *via* an allene intermediate, starting from *ortho* amino functionalized propargyl alcohols.
4) The reaction of *N*-(2-formylphenyl)benzamide with allenylphosphonates in the presence K_2CO_3 leads to a variety of phosphono-quinolines and *N*-phosphorylated quinolines. At high temperature, phosphono-quinolines isomerize to *N*-phosphorylated quinolines. In the case of γ-substituted allenylphosphonates, along with P-N-bonded compounds, phosphorus-free quinolinones are also formed *via* a hydrolytic pathway.

5) We have given the structural proof for the attack of P^{III} center at the β-carbon of allenylphosphonates/ allenylphosphine oxides. The NH proton of P-NH-*t*-Bu group migrates to α- or γ-carbon of the allene resulting in the formation of phosphinimines with different structures. These results are significant since similar species are proposed (but not isolated) in phosphine catalyzed reactions of unsaturated organic systems.

EXPERIMENTAL SECTION

General: Chemicals and solvents were procured from Aldrich/ Fluka or local manufacturers. Further purification was done according to standard procedures wherever required.[85]All operations, unless otherwise specified, were carried out under dry nitrogen atmosphere using standard vacuum line techniques.[86]

Melting point: Melting points were determined using a SUPERFIT hot stage apparatus and are uncorrected.

Elemental analyses: Elemental analyses were carried out on a Perkin-Elmer 240C CHN or Thermo Finnigan EA1112 CHNS analyzer.

Infrared spectroscopy: IR spectra were recorded on a JASCO FT/IR 5300 spectrophotometer.

NMR spectroscopy: ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded using 5 mm tubes on a Bruker 400 MHz NMR spectrometer [field strengths: 400, 100,162 MHz respectively] in $CDCl_3$ solution (unless specified otherwise) with shifts referenced to $SiMe_4$ (^{1}H, ^{13}C: $\delta = 0$) and ext. 85% H_3PO_4 (^{31}P: $\delta = 0$) respectively. All J values are in Hz.

LC-MS, GC-MS and HRMS: LC-MS or GC-MS equipment were used to record mass spectra for isolated compounds where appropriate. LC-MS data were obtained using electrospray ionization (positive mode) on a C-18 column. GC-MS data were obtained on EI mode using ZB-1 column. Mass spectra were recorded using HRMS (ESI-TOF analyzer) equipment.

The P^{III}-Cl precursors $[ClP(\mu\text{-N-}t\text{-Bu})]_2$ (**1**)[51], $[(t\text{-BuNH})P(\mu\text{-N-}t\text{-Bu})]_2$ (**2**)[52], $[(i\text{-PrNH})P(\mu\text{-N-}t\text{-Bu})]_2$ (**3**)[52c], $[(t\text{-BuNH})P(\mu\text{-N-}t\text{-Bu})_2P\text{-Cl}]$ (**4**)[53] and $(OCH_2CMe_2CH_2O)PCl$ (**5**)[54], were prepared by well known methods. Chlorodiphenylphosphine (Ph_2PCl) (**6**), procured from Aldrich, was distilled prior to use. Precursors 5-halo-2-nitrobenzaldehydes **7a-b**,[55] iodoarene **8**,[56] 2-substituted iodobenzenamides **9a-b**[57] and *N*-(2-formylphenyl)benzamide **10**[58] were prepared by standard literature methods.

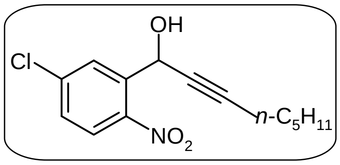
3.1 Preparation of propargylic precursors 11a-m and 12-15

Aryl substituted propargyl alcohols **11a-m** were prepared by following the literature method with slight modification.[28,60] Propargyl alcohols **12-15** were synthesized by Sonogashira coupling reaction of aryl halides with respective terminal propargyl alcohols according to the literature procedure.[61]

3.11 Synthesis of propargyl alcohols 11a-m

Among these propargylic alcohols **11h-j** and **11l-m** are new. A literature procedure[28] was followed by using 1-heptyne (1.49 mL, 11.32 mmol) and 5-chloro-2-nitro-benzaldehyde[55] (1.5 g, 8.08 mmol).

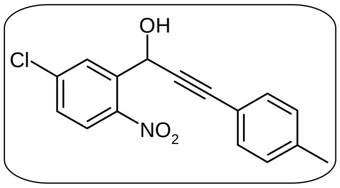
Compound 11h



Yield:	2.0 g (88%, gummy liquid).
IR (neat):	3414, 3101, 2959, 2926, 2855, 2225, 1611, 1573, 1523, 1468, 1342, 1293, 1178, 1140, 1107, 1074, 1014, 893 cm^{-1}.
^{1}H NMR:	δ 7.95-7.41 (m, 3H, Ar-*H*), 6.01 (s, 1H, C*H*OH), 3.27 (br, 1H, O*H*), 2.23 (t, 2H, CH_2), 1.51-1.27 (m, 6H, CH_2), 0.88 (t, 3H, CH_2CH_3).
^{13}C NMR:	δ 146.1, 140.2, 138.2, 129.3, 129.0, 126.5 (Ar-*C*), 88.7 (*C*≡C), 77.4 (C≡*C*), 60.9 (*C*HOH), 31.0, 28.0, 22.2 and 18.7 (CH_2), 14.0 (CH_3).
LC-MS:	*m/z* 282 [M]$^+$.

Anal. Calcd. for $C_{14}H_{16}ClNO_3$: C, 59.68; H, 5.72; N, 4.97. Found: C, 59.76; H, 5.69; N, 5.07.

Compound 11i



4-Ethynyl toluene (0.79 mL, 6.25 mmol) and 5-chloro-2-nitro-benzaldehyde[55] (1.05 g, 5.68 mmol) were used.

Yield: 1.49 g (87%, brown solid).

Mp: 70–72 °C.

IR (KBr): 3260, 2964, 2921, 2866, 2219, 1605, 1573, 1523, 1353, 1288, 1178, 1112, 1079, 1041, 981, 877 cm^{-1}.

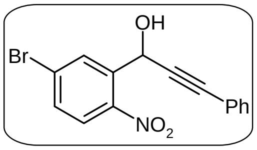
^{1}H NMR: δ 8.01 (dd→t, 1H, Ar-*H*), 7.94 (dd, *J* = 8.8 Hz, *J* = 2.4 Hz, 1H, Ar-*H*), 7.46-7.10 (m, 5H, Ar-*H*), 6.26 (d, *J* = 2.4 Hz, 1H, C*H*OH), 3.54 (br, 1H, O*H*), 2.34 (s, 3H, C*H*$_3$).

^{13}C NMR: δ 146.0, 140.3, 139.2, 137.7, 131.8, 129.3, 129.2, 129.1, 126.6, 118.6 (Ar-*C*), 87.3 (*C*≡C), 85.4 (C≡*C*), 61.3 (*C*HOH), 21.5 (*C*H$_3$).

LC-MS: *m/z* 302 [M]$^+$.

Anal. Calcd. for $C_{16}H_{12}ClNO_3$: C, 63.69; H, 4.01; N, 4.64. Found: C, 63.58; H, 4.07; N, 4.58.

Compound 11j



Phenylacetylene (0.42 mL, 3.8 mmol) and 5-bromo-2-nitrobenzaldehyde[55] (0.8 g, 3.48 mmol) were used.

Yield: 1.04 g (90%, yellow solid).

Mp: 68–70 °C.

IR (KBr): 3222, 2953, 2926, 2849, 2219, 1605, 1562, 1518, 1348, 1293, 1173, 1074, 1036, 975, 899 cm^{-1}.

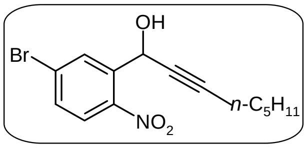
^{1}H NMR: δ 8.17 (d, *J* = 1.6 Hz, 1H, Ar-*H*), 7.87 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 7.62 (dd, *J* = 8.8 Hz, *J* = 2.0 Hz, 1H, Ar-*H*), 7.44-7.27 (m, 5H, Ar-*H*), 6.26 (s, 1H, C*H*OH), 3.46 (br, 1H, O*H*).

^{13}C NMR: δ 146.6, 137.5, 132.4, 132.3, 131.9, 129.0, 128.9, 128.4, 126.6, 121.7 (Ar-*C*), 87.1 (*C*≡C), 86.1 (C≡*C*), 61.2 (*C*HOH).

LC-MS: *m/z* 332 [M]$^+$.

Anal. Calcd. for $C_{15}H_{10}BrNO_3$: C, 54.24; H, 3.03; N, 4.22. Found: C, 54.32; H, 3.09; N, 4.28.

Compound 11l



1-Heptyne (0.52 mL, 3.95 mmol) and 5-bromo-2-nitrobenzaldehyde (0.83 g, 3.59 mmol) were used.

Yield: 0.96 g (82%, brown liquid).

IR (neat): 3441, 2953, 2926, 2855, 2225, 1638, 1600, 1573, 1529, 1468, 1353, 1288, 1178, 1090, 1068, 1013, 871 cm^{-1}.

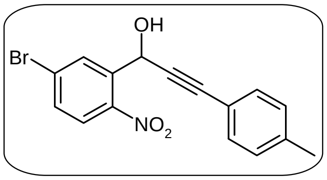
^{1}H NMR: δ 8.12-7.58 (m, 3H, Ar-*H*), 6.01 (s, 1H, C*H*OH), 3.27 (br, 1H, O*H*), 2.22 (t, 2H, CH_2), 1.54-1.29 (m, 6H, CH_2), 0.90 (t, 3H, CH$_2$CH_3).

^{13}C NMR: δ 146.6 (Ar-*C*), 138.1, 132.3, 132.1, 128.7, 126.5, 88.7 (*C*≡C), 77.4 (C≡*C*), 60.8 (*C*HOH), 31.0, 28.0, 22.2 and 18.7 (*C*H$_2$), 14.0 (*C*H$_3$).

LC-MS: *m/z* 326 [M]$^+$.

Anal. Calcd. for $C_{14}H_{16}BrNO_3$: C, 51.55; H, 4.94; N, 4.29. Found: C, 51.65; H, 4.91; N,4.21.

Compound 11m



4-Ethynyl toluene (0.49 mL, 3.83 mmol) and 5-bromo-2-nitrobenzaldehyde (0.80 g, 3.48 mmol) were used.

Yield: 1.03 g (86%, brown solid).

Mp: 76–78 °C.

IR (KBr): 3266, 2964, 2915, 2860, 2219, 1600, 1562, 1523, 1348, 1293, 1173, 1079, 1041, 970, 860 cm^{-1}.

^{1}H NMR: δ 8.17 (d, *J* = 1.6 Hz, 1H, Ar-*H*), 7.86 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 7.62 (dd, *J* = 8.8 Hz, *J* = 2.0 Hz, 1H, Ar-*H*), 7.34-7.10 (m, 4H, Ar-*H*), 6.25 (s, 1H, C*H*OH), 3.42 (br, 1H, O*H*), 2.35 (s, 3H, CH_3).

^{13}C NMR: δ 146.6, 139.3, 137.6, 132.3, 131.8, 129.1, 128.8, 126.6, 118.6 (Ar-*C*), 87.4 (*C*≡C), 85.4 (C≡*C*), 61.3 (*C*HOH), 21.6 (*C*H$_3$).

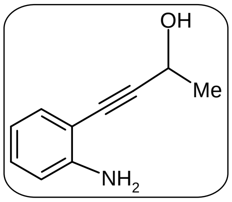
LC-MS: *m/z* 346 $[M]^+$.

Anal. Calcd. for $C_{16}H_{12}BrNO_3$: C, 55.51; H, 3.49; N, 4.05. Found: C, 55.62; H, 3.45; N, 4.12.

3.12 Synthesis of propargyl alcohols 12-15

Among these propargylic alcohols **14c** and **15b-c** and **15e-m** are new. A literature procedure was used here.[61] 2-Iodoaniline (1.50 g, 6.80 mmol) and but-3-yn-2-ol (0.64 mL, 8.22 mmol) were used.

Compound 14c



Yield: 1.36 g (91%, gummy liquid).

IR (neat): 3359, 2980, 2931, 2219, 1616, 1490, 1457, 1364, 1314, 1161, 1101, 1079, 1029, 936, 744 cm^{-1}.

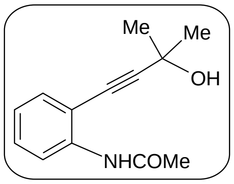
^{1}H NMR: δ 7.27-6.66 (m, 4H, Ar-*H*), 4.78 (qrt, 1H, C*H*CH$_3$), 4.19 (br, 2H, N*H*$_2$), 3.41 (br, 1H, O*H*), 1.55 (d, *J* = 6.4 Hz, 3H, CHC*H*$_3$).

^{13}C NMR: δ 147.8, 132.2, 129.7, 118.0, 114.5, 107.4 (Ar-*C*), 96.7 (*C*≡C), 80.5 (C≡*C*), 58.7 (*C*H(CH$_3$)$_2$), 24.6 (CH*C*H$_3$).

LC-MS: *m/z* 162 $[M+1]^+$.

Anal. Calcd. for $C_{10}H_{11}NO$: C, 74.51; H, 6.88; N, 8.69. Found: C, 74.43; H, 6.75; N, 8.61.

Compound 15a



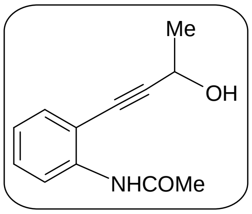
In a round bottomed flask (50 mL) equipped with *N*-(2-iodophenyl)acetamide (**9a**)[57] (0.8 g, 3.06 mmol), $Pd(PPh_3)_2Cl_2$ (0.05 g, 0.08 mmol), CuI (0.03 g, 0.15 mmol) and acetonitrile (20 mL), was added 2-methyl-3-butyne-2-ol (0.33 mL, 3.37 mmol) and

Et_3N (1.71 mL, 12.25 mmol). The mixture was stirred at room temperature for 6-8 h. Upon completion of the reaction (TLC), the mixture was filtered, the solid residue washed with EtOAc and washings added to the filtrate. The combined solution was concentrated under reduced pressure. The oily material obtained was subjected to column chromatography (ethyl acetate-hexane (1:4) to afford the desired product (**15a**). Propargyl alcohols **15b—15m** were prepared by using the same experimental procedure.

Yield: 0.60 g (90%, light yellow solid).

The spectral data are in accordance with the literature report.[87a]

Compound 15b



N-(2-Iodophenyl)acetamide (1.0 g, 3.80 mmol) was used as the starting material.

Yield: 0.94 g (94%, brown gummy liquid).

IR (neat): 3320, 2981, 2926, 2871, 2224, 1671, 1583, 1523, 1446, 1364, 1299, 1118, 1096, 1030, 931, 860 cm^{-1}.

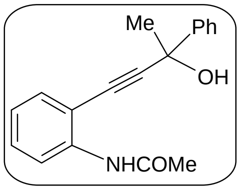
^{1}H NMR: δ 8.21 (s, 1H, N*H*), 8.04 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.22 (d, *J* = 7.6 Hz, 1H, Ar-*H*), 7.11 (t, 1H, Ar-*H*), 6.88 (t, 1H, Ar-*H*), 5.15 (br s, 1H, O*H*), 4.71 (qrt, 1H, C*H*CH_3), 2.06 (s, 3H, COCH_3), 1.47 (d, *J* = 6.4 Hz, 3H, CHCH_3).

^{13}C NMR: δ 169.5 (*C*=O), 138.6, 131.6, 129.2, 123.8, 120.4, 112.7 (Ar-*C*), 98.6 (*C*≡C), 78.9 (C≡*C*), 77.6 (*C*HCH_3), 58.2 (CO*C*H_3), 24.3 (CH*C*H_3).

LC-MS: *m/z* 204 $[M+1]^+$.

Anal. Calcd. for $C_{12}H_{13}NO_2$: C, 70.92; H, 6.45; N, 6.89. Found: C, 70.85; H, 6.53; N, 6.76.

Compound 15c



N-(2-Iodophenyl)acetamide (2.0 g, 7.66 mmol) was used as the starting material.

Yield: 1.91 g (89%, brown solid).

Mp: 94–96 ^{o}C.

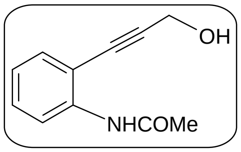
IR (KBr): 3342, 3255, 2986, 2926, 2175, 1633, 1540, 1423, 1375, 1304, 1096, 1052, 899, 762 cm^{-1}.

^{1}H NMR: δ 8.26 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 7.88 (br s, 1H, N*H*), 7.71 (d, *J* = 7.2 Hz, 2H, Ar-*H*), 7.41-7.25 (m, 5H, Ar-*H*), 7.02 (t, 1H, Ar-*H*), 3.78 (br s, 1H, O*H*), 1.95 and 1.91 (2 s, 6H, CH_3 + COCH_3).

^{13}C NMR: δ 168.8 (*C*=O), 145.6, 139.2, 131.6, 129.9, 128.6, 128.4, 127.9, 124.9, 124.8, 123.5, 119.6 (Ar-*C*), 100.6 (*C*≡C), 79.8 (C≡*C*), 70.2 (*C*OH), 33.1 and 24.6 (2 s, *C*H$_3$ + CO*C*H$_3$).

HRMS (ESI): Calcd. for $C_{18}H_{17}NO_2$ (M^+ + Na): *m/z* 302.1157. Found: 302.1156.

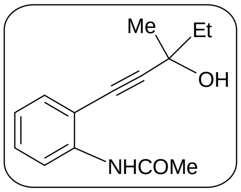
Compound 15d



Yield: 0.54 g (92%, light yellow solid; *N*-(2-iodophenyl)acetamide (0.8 g, 3.06 mmol) was used as the starting material.

The spectral data are in accordance with the literature report.[87b]

Compound 15e



N-(2-Iodophenyl)acetamide (0.8 g, 3.06 mmol) was used as the starting material.

Yield: 0.63 g (89%, brown gummy liquid).

IR (neat): 3381, 3293, 2975, 2932, 2225, 1677, 1578, 1518, 1447, 1381, 1310, 1156, 1003, 762 cm^{-1}.

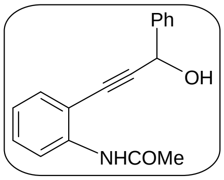
^{1}H NMR: δ 8.28 (d, *J* = 7.6 Hz, 1H, Ar-*H*), 7.99 (br s, 1H, N*H*), 7.34 (d, *J* = 6.8 Hz, 1H, Ar-*H*), 7.28-7.24 (m, 1H, Ar-*H*), 6.99 (t, 1H, Ar-*H*), 3.16 (br s, 1H, O*H*), 2.16 (s, 3H, COCH_3), 1.85-1.78 (m, 2H, CH_2CH$_3$), 1.60 (s, 3H, CCH_3), 1.12 (t, 3H, CH$_2$CH_3).

^{13}C NMR: δ 168.6 (*C*=O), 138.9, 131.6, 129.6, 123.5, 119.6, 111.8 (Ar-*C*), 100.4 (*C*≡C), 78.6 (C≡*C*), 69.2 (*C*OH), 36.6 (*C*H$_3$), 29.5 (*C*H$_2$CH$_3$), 24.7 (CO*C*H$_3$), 9.3 (CH$_2$*C*H$_3$).

LC-MS: *m/z* 232 [M+1]$^+$.

Anal. Calcd. for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41; N, 6.06. Found: C, 72.83; H,7.36; N, 6.15.

Compound 15f



N-(2-Iodophenyl)acetamide (0.8 g, 3.06 mmol) was used as the starting material.

Yield: 0.46 g (57%, brown solid).

Mp: 92–94 °C.

IR (KBr): 3337, 3254, 3052, 3030, 2203, 1633, 1573, 1529, 1447, 1299, 1184, 1025, 970, 767 cm^{-1}.

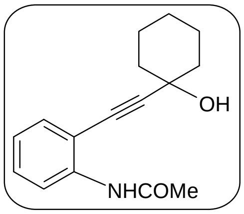
^{1}H NMR: δ 8.27 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 7.85 (s, 1H, N*H*), 7.59 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 7.42-7.33 (m, 4H, Ar-*H*), 7.30 (d, *J* = 7.6 Hz, 1H, Ar-*H*), 7.01 (t, 1H, Ar-*H*), 5.73 (s, 1H, C*H*OH), 3.69 (br s, 1H, O*H*), 1.98 (s, 3H, COCH_3).

^{13}C NMR: δ 168.8 (*C*=O), 140.9, 139.2, 131.7, 130.0, 128.9, 128.6, 126.4, 123.5, 119.7, 111.4 (Ar-*C*), 96.8 (*C*≡C), 81.7 (C≡*C*), 64.9 (*C*HOH), 24.6 (CO*C*H$_3$).

LC-MS: *m/z* 266 [M+1]$^+$.

Anal. Calcd. for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.85; H, 5.65; N, 5.32.

Compound 15g



N-(2-Iodophenyl)acetamide (0.8 g, 3.06 mmol) was used as the starting material.

Yield: 0.67 g (85%, brown solid).

Mp: 110–112 °C.

IR (KBr): 3408, 3381, 2948, 2926, 2860, 2214, 1676, 1578, 1528, 1451, 1309, 1265, 1161, 1068, 964, 755 cm^{-1}.

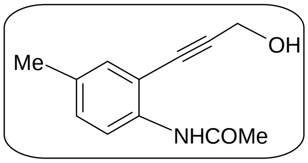
^{1}H NMR: δ 8.27 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 8.02 (br s, 1H, N*H*), 7.33 (d, *J* = 7.6 Hz, 1H, Ar-*H*), 7.27-7.23 (m, 1H, Ar-H), 6.98 (t, 1H, Ar-*H*), 3.49 (br s, 1H, O*H*), 2.15 (s, 3H, COC*H*$_3$), 2.03 (d, *J* = 9.6 Hz, 2H, cyclohexyl-*H*), 1.77-1.58 (m, 7H, cyclohexyl-*H*), 1.30 (br s, 1H, cyclohexyl-*H*).

^{13}C NMR: δ 168.6 (*C*=O), 138.8, 131.5, 129.5, 123.5, 119.6, 111.9 (Ar-*C*), 100.6 (*C*≡C), 79.4 (C≡*C*), 69.1 (*C*OH), 40.0, 25.1, 24.7 and 23.5 (*C*H$_2$+CO*C*H$_3$).

LC-MS: *m/z* 258 $[M+1]^+$.

Anal. Calcd. for $C_{16}H_{19}NO_2$: C, 74.68; H, 7.44; N, 5.44. Found: C, 74.57; H,7.51; N, 5.36.

Compound 15h



N-(2-Iodo-4-methylphenyl)acetamide[88] (0.5 g, 1.82 mmol) was used as the starting material.

Yield: 0.28 g (75%, brown solid).

Mp: 104–106 °C.

IR (KBr): 3332, 2921, 2855, 2247, 1671, 1589, 1518, 1458, 1414, 1315, 1129, 1030, 893, 827 cm^{-1}.

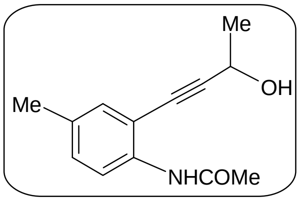
^{1}H NMR: δ 8.07-8.00 (m, 2H, N*H*+Ar-*H*), 7.12 (s, 1H, Ar-*H*), 7.04 (t, 1H, Ar-*H*), 4.50 (d, *J* = 3.2 Hz, 2H, CH_2OH), 4.04 (br s, 1H, O*H*), 2.20 and 2.14 (2 s, 6H, Ar-CH_3 + COCH_3).

^{13}C NMR: δ 169.2 (*C*=O), 136.3, 133.4, 132.1, 130.3, 120.2, 112.3 (Ar-*C*), 94.3 (*C*≡C), 80.8 (C≡*C*), 51.1 (*C*H$_2$), 24.5 (CO*C*H$_3$), 20.6 (Ar-*C*H$_3$).

LC-MS: *m/z* 204 [M+1]$^+$.

Anal. Calcd. for $C_{12}H_{13}NO_2$: C, 70.92; H, 6.45; N, 6.89. Found: C, 70.85; H,6.52; N, 6.81.

Compound 15i



N-(2-Iodo-4-methylphenyl)acetamide[88] (0.6 g, 2.18 mmol) was used as the starting material.

Yield: 0.44 g (92%, brown gummy liquid).

IR (neat): 3359, 3271, 2975, 2926, 2855, 2219, 1633, 1578, 1529, 1403, 1364, 1310, 1107, 1041, 970, 811 cm^{-1}.

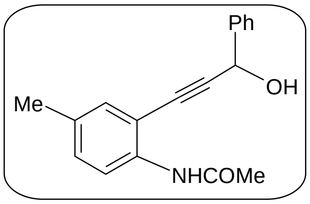
^{1}H NMR: δ 8.05 (s, 1H, N*H*), 8.02 (d, *J* = 5.6 Hz, 1H, Ar-*H*), 7.11 (s, 1H, Ar-*H*), 7.02 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 4.76 (qrt, 1H, C*H*CH$_3$), 4.20 (br s, 1H, O*H*), 2.20 and 2.13 (2 s, 6H, Ar-CH_3 + COCH_3), 1.54 (d, *J* = 6.8 Hz, 3H, CHCH_3).

^{13}C NMR: δ 169.0 (*C*=O), 136.3, 133.3, 131.9, 130.2, 120.1, 112.2 (Ar-*C*), 98.2 (*C*≡C), 79.2 (C≡*C*), 58.4 (*C*HOH), 24.5, 24.4 and 20.6 (3 s, *C*H$_3$).

LC-MS: *m/z* 218 [M+1]$^+$.

Anal. Calcd. for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96; N, 6.45. Found: C, 71.96; H, 7.02; N, 6.38.

Compound 15j



N-(2-Iodo-4-methylphenyl)acetamide (0.6 g, 2.18 mmol) was used as the starting material.

Yield: 0.52 g (85%, brown gummy liquid).

IR (neat): 3386, 3293, 3030, 2921, 2230, 1666, 1595, 1518, 1452, 1370, 1304, 1134, 1030, 822, 701 cm^{-1}.

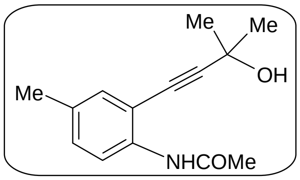
^{1}H NMR: δ 8.08 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 7.84 (s, 1H, N*H*), 7.58 (d, *J* = 7.2 Hz, 1H, Ar-*H*), 7.40-7.33 (m, 3H, Ar-*H*), 7.17 (s, 1H, Ar-*H*), 7.05 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 5.71 (s, 1H, C*H*OH), 4.22 (br s, 1H, O*H*), 2.24 and 1.95 (2 s, 6H, Ar-CH_3 + COCH_3).

^{13}C NMR: δ 168.9 (*C*=O), 141.0, 136.7, 133.2, 131.9, 130.6, 128.8, 128.5, 126.4, 119.9, 111.7 (Ar-*C*), 96.4 (*C*≡C), 81.8 (C≡*C*), 64.8 (*C*HOH), 24.4 (CO*C*H$_3$), 20.6 (Ar-*C*H$_3$).

LC-MS: *m/z* 280 [M+1]$^+$.

Anal. Calcd. for $C_{18}H_{17}NO_2$: C, 77.40; H, 6.13; N, 5.01. Found: C, 77.32; H, 6.07; N, 5.12.

Compound 15k



N-(2-Iodo-4-methylphenyl)acetamide (0.49 g, 1.78 mmol) was used as the starting material.

Yield: 0.37 g (90%, brown solid).

Mp: 100–102 °C.

IR (KBr): 3386, 3364, 2981, 2926, 2194, 1682, 1600, 1518, 1458, 1403, 1310, 1173, 1140, 964, 877, 827 cm^{-1}.

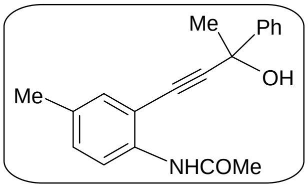
^{1}H NMR: δ 8.06 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 7.96 (br s, 1H, N*H*), 7.10 (s, 1H, Ar-*H*), 7.01 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 3.96 (br s, 1H, O*H*), 2.20 and 2.19 (2 s, 6H, Ar-CH_3 + COCH_3), 1.62 (s, 6H, C(CH_3)$_2$).

^{13}C NMR: δ 168.7 (*C*=O), 136.4, 133.1, 131.7, 130.1, 119.9, 112.1 (Ar-*C*), 101.2 (*C*≡C), 77.4 (C≡*C*), 65.4 (*C*OH), 31.5 (C*C*H$_3$), 24.5 and 20.6 (2 s, *C*H$_3$).

LC-MS: *m/z* 232 [M+1]$^+$.

Anal. Calcd. for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41; N, 6.06. Found: C, 72.61; H,7.36; N, 6.13.

Compound 15l



N-(2-Iodo-4-methylphenyl)acetamide[88] (0.4 g, 1.45 mmol) was used as the starting material.

Yield: 0.40 g (93%, brown gummy liquid).

IR (neat): 3375, 3299, 3030, 2975, 2926, 2219, 1677, 1595, 1447, 1370, 1304, 1184, 1140, 822, 762 cm^{-1}.

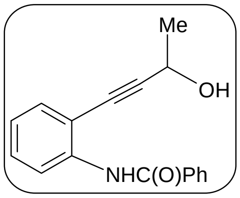
^{1}H NMR: δ 8.09 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 7.83 (br s, 1H, N*H*), 7.70 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 7.37 (dd→t, 1H, Ar-*H*), 7.32-7.29 (m, 1H, Ar-*H*), 7.19 (s, 1H, Ar-*H*), 7.05 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 4.06 (br s, 1H, O*H*), 2.25 and 1.93 (2 s, 6H, Ar-CH_3 + COCH_3), 1.89 (s, 3H, CCH_3).

^{13}C NMR: δ 168.7 (*C*=O), 145.8, 136.7, 133.1, 131.8, 130.5, 128.5, 127.8, 124.8, 119.8, 111.7 (Ar-*C*), 100.2 (*C*≡C), 79.9 (C≡*C*), 70.1 (*C*HOH), 33.2, 24.4 and 20.6 (3 s, *C*H$_3$).

LC-MS: *m/z* 294 [M+1]$^+$.

Anal. Calcd. for $C_{19}H_{19}NO_2$: C, 77.79; H, 6.53; N, 4.77. Found: C, 77.82; H, 6.61; N, 4.68.

Compound 15m



N-(2-iodophenyl)benzamide[89] (1.0 g, 3.10 mmol) was used as the staring material.

Yield: 0.90 g (90%, brown solid).

Mp: 84–86 °C.

IR (KBr): 3386, 3063, 2975, 2926, 2860, 2218, 1666, 1578, 1523, 1446, 1304, 1260, 1107, 1030, 937, 794 cm^{-1}.

^{1}H NMR: δ 8.75 (s, 1H, N*H*), 8.46 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 7.84 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 7.42-7.23 (m, 5H, Ar-*H*), 6.96 (t, 1H, Ar-*H*), 4.80 (qrt, 1H, C*H*CH_3), 4.03 (br s, 1H, O*H*), 1.54 (d, *J* = 6.8 Hz, 3H, CHCH_3).

^{13}C NMR: δ 165.3 (*C*=O), 138.8, 134.1, 132.0, 131.4, 129.6, 128.7, 127.0, 123.5, 119.1, 111.9 (Ar-*C*), 99.5 (*C*≡C), 78.7 (C≡*C*), 58.3 (*C*HCH_3), 24.3 (*C*H_3).

LC-MS: *m/z* 266 $[M+1]^+$.

Anal. Calcd. for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.85; H, 5.62; N, 5.37.

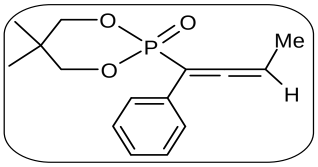
3.2 Preparation of allenylphosphonates [16a-k, 17a-c] and allenylphosphine oxides [18-20]

3.21 Synthesis of allenylphosphonates [16a-k, 17a-c]

Allenylphosphonates **16a-k** and **17a-c** were synthesized according to literature procedure.[18-19,65] Among these, allenes **16d-k** and **17a-c** are new. Spectroscopic and analytical data for these compounds are given below.

Compound 16d

Propargyl alcohol **12c**[62] (0.46 g, 3.15 mmol) and $(OCH_2CMe_2CH_2O)PCl$ (**5**)[54] (0.43 mL, 3.15 mmol) were used. Purification was done by column chromatography using ethyl acetate/hexane (1:2) mixture as the eluent.



Yield: 0.63 g (72%, white solid).

Mp: 140–144 °C.

IR (KBr): 3063, 2972, 2888, 1934, 1597, 1479, 1371, 1263, 1053 cm^{-1}.

^{1}H NMR: δ 7.60-7.27 (m, 5H, Ar-*H*), 5.77-5.76 (m, 1H), 4.00-3.95 (m, 4H), 1.92-1.88 (m, 3H), 1.30 and 0.89 (2s, 6H).

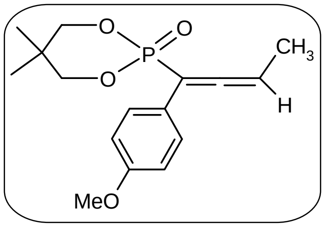
^{13}C NMR: δ 210.5 (C=*C*=C), 131.7 (d, *J* = 4.0 Hz), 131.6, 128.7, 127.8, 127.7, 127.6 Ar-*C*), 94.9 (d, *J* = 182.0 Hz, P*C*), 77.2, 76.9, 32.5 (d, *J* = 6.0 Hz), 21.9, 20.7, 13.3 (d, *J* = 6.0 Hz).

^{31}P NMR: δ 8.22.

LC-MS: *m/z* 279 [M+1]$^{+}$.

Anal. Calcd for $C_{15}H_{19}O_3P$: C, 64.74; H, 6.88. Found: C, 64.86; H, 6.95.

Compound 16e



4-(4-Methoxyphenyl)but-3-yn-2-ol[90] (1.63 g, 9.26 mmol) was used.

Yield: 2.23 g (78%, yellow solid).

Mp: 80–83 °C.

IR (KBr): 3063, 2975, 2930, 2834, 1946, 1609, 1576, 1510, 1466, 1368, 1290, 1260, 1059, 1011, 947, 839 cm^{-1}.

^{1}H NMR: δ 7.51 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 6.87 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 5.76-5.71 (m, 1H), 4.00-3.90 (m, 4H, OC*H*$_2$), 3.79 (s, 3H, OC*H*$_3$), 1.89-1.86 (dd→t, 3H, C*H*$_3$), 1.29 and 0.87 (2 s, 6H, C*H*$_3$).

^{13}C NMR: δ 209.5 (d, ^{2}J(P-C) = 4.2 Hz, PC*C*C), 159.0, 128.6, 128.5, 123.3, 123.2, 113.8 (Ar-*C*), 94.0 (d, ^{1}J(P-C) = 181.1 Hz, P*C*), 89.6 (d, ^{3}J (P-C) = 15.0

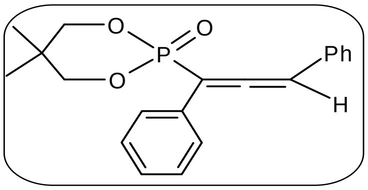
Hz, PCC*C*), 77.4 and 76.8 (O*C*H$_2$), 54.9 (O*C*H$_3$), 32.2 (d, ^3J(P-C)= 6.8 Hz, *C*(CH$_3$)$_2$), 21.6 and 20.3 (*C*H$_3$), 13.1 (d, ^4J(P-C) = 6.7 Hz, *C*H$_3$).

^{31}P NMR: δ 8.63.

LC-MS: *m/z* 307 [M-1]$^+$.

Anal. Calcd for $C_{16}H_{21}O_4P$: C, 62.33; H, 6.87. Found: C, 62.45; H, 6.75.

Compound 16f



Propargyl alcohol **12b**[91] (1.0 g, 4.81 mmol) was used.

Yield: 1.19 g (73 %, white solid).

Mp: 179–182 °C.

IR (KBr): 3057, 2969, 2888, 1931, 1597, 1489, 1460, 1372, 1265, 1055 cm^{-1}.

^{1}H NMR: δ 7.71-7.27 (m, 10H), 6.82 (d, *J* =12.4 Hz, 1H), 4.11-3.86 (m, 4H), 1.29 and 0.77 (2s, 6H).

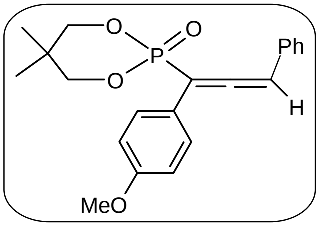
^{13}C NMR: δ 211.8, 99.9 (d, *J* = 179.0 Hz), 98.5 (d, *J* = 15.0 Hz), 77.1, 76.8, 32.5 (d, *J* =7.0 Hz), 22.0, 20.5.

^{31}P NMR: δ 6.09.

LC-MS: *m/z* 341 [M+1]$^+$.

Anal. Calcd for $C_{20}H_{21}O_3P$: C, 70.58; H, 6.22. Found: C, 70.41; H, 6.18.

Compound 16g



3-(4-Methoxyphenyl)-1-phenylprop-2-yn-1-ol[92] (1.99 g, 8.36 mmol) was used.

Yield: 2.5 g (81%, yellow solid).

Mp: 110–113 °C.

IR (KBr): 3034, 2959, 2838, 1931, 1607, 1510, 1460, 1267, 1182, 1055, 1005, 837 cm^{-1}.

^{1}H NMR: δ 7.62 (d, *J* =8.4 Hz, 2H, Ar-*H*), 7.39-7.27 (m, 5H, Ar-*H*), 6.89 (d, *J* =8.4 Hz, 2H, Ar-*H*), 6.79 (d, ^{3}*J*(P-H) = 12.4 Hz, 1H), 4.11-3.83 (m, 4H, OCH_2), 3.81 (s, 3H, OCH_3), 1.29 and 0.76 (2 s, 6H, CH_3).

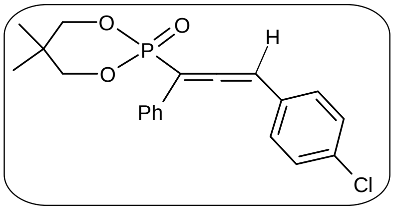
^{13}C NMR: δ 211.1 (d, ^{2}*J*(P-C) = 4.0 Hz, PC*C*C), 159.7, 131.8, 131.7, 129.1_4, 129.0_7, 129.0, 128.3, 127.3, 122.6, 122.5, 114.4 (Ar-*C*), 99.3 (d, ^{1}*J*(P-C) = 177.7 Hz, P*C*), 98.4 (d, ^{3}*J*(P-C)= 15.3 Hz, PCC*C*), 77.7 and 77.0 (O*C*H_2), 55.3(O*C*H_3), 32.5 (d, ^{3}*J*(P-C)= 6.9 Hz, *C*$(CH_3)_2$), 21.9, 20.4 (*C*H_3).

^{31}P NMR: δ 6.46.

LC-MS: *m/z* 371 $[M+1]^+$.

Anal. Cacld for $C_{21}H_{23}O_4P$: C, 68.10; H, 6.26. Found: C, 68.26; H, 6.15.

Compound 16h



1-(4-Chlorophenyl)-3-phenylprop-2-yn-1-ol[93] (5.69 g, 23.4 mmol) was used.

Yield: 8.12 g (92 %, white solid).

Mp: 148–150 °C.

IR (KBr): 3056, 2976, 2892, 1929, 1491, 1373, 1399, 1267, 1057, 1005, 841 cm^{-1}.

^{1}H NMR: δ 7.66 (d, *J* =7.6 Hz, 2H, Ar-*H*), 7.38-7.27 (m, 7H, Ar-*H*), 6.77 (d, *J* =12.8 Hz, 1H, C*H*), 4.06-3.88 (m, 4H, OCH_2), 1.28 and 0.81 (2 s, 6H, CH_3).

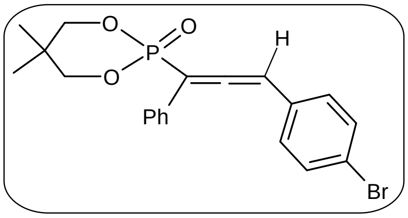
^{13}C NMR: δ 211.6 (C=*C*=C), 133.9, 130.3, 130.2, 129.9_3, 129.8_5, 129.2, 128.8, 128.4, 127.7, 127.6 (Ar-*C*), 100.3 (d, ^{1}*J* (P-C) = 178.0 Hz, P*C*), 97.4 (d, ^{3}*J*(P-C)= 15.2 Hz, PCC*C*), 77.4 and 77.3 (O*C*H_2), 32.4 (d, ^{3} *J*(P-C)= 7.0 Hz, *C*$(CH_3)_2$), 21.8 and 20.5 (*C*H_3).

^{31}P NMR: δ 5.81.

LC-MS: *m/z* 375 $[M+1]^+$.

Anal. Cacld for $C_{20}H_{20}ClO_3P$: C, 64.09; H, 5.38. Found: C, 64.21; H, 5.32.

Compound 16i

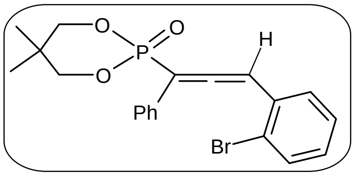


1-(4-Bromophenyl)-3-phenylprop-2-yn-1-ol[93] (1.22 g, 4.26 mmol) was used.

Yield:	1.53 g (86%, white solid).
Mp:	110–114 °C.
IR (KBr):	2978, 2946, 1929, 1480, 1445, 1399, 1275, 1173, 1059, 1009, 851 cm^{-1}.
^{1}H NMR:	δ 7.65 (d, *J* =7.2 Hz, 2H, Ar-*H*), 7.46 (d, *J* =8.0 Hz, 2H, Ar-*H*), 7.34-7.22 (m, 5H, Ar-*H*), 6.75 (d, *J* =12.8 Hz, 1H, C*H*), 4.07-3.86 (m, 4H, OCH_2), 1.26 and 0.79 (2 s, 6H, CH_3).
^{13}C NMR:	δ 211.7 (C=*C*=C), 132.3, 130.5$_3$, 130.4$_5$, 130.4, 130.3, 129.0, 128.8, 128.5, 127.8$_3$, 127.7$_8$, 122.2 (Ar-*C*), 100.5 (d, ^1J (P-C) = 178.0 Hz, P*C*), 97.6 (d, ^3J(P-C)= 15.2 Hz, PCC*C*), 77.5 and 77.4 (O*C*H$_2$), 32.6 (d, ^3J (P-C)= 7.0 Hz, *C*(CH$_3$)$_2$), 21.9 and 20.7 (*C*H$_3$).
^{31}P NMR:	δ 5.71.
LC-MS:	*m/z* 419 [M+1]$^+$.

Anal. Cacld for $C_{20}H_{20}BrO_3P$: C, 57.30; H, 4.81. Found: C, 57.21; H, 4.73.

Compound 16j



1-(Bromophenyl)-3-phenylprop-2-yn-1-ol[93] (0.49 g, 1.71 mmol) was used.

Yield:	0.59 g (83%, white solid).
Mp:	160–162 °C.
IR (KBr):	3057, 2969, 2888, 1929, 1589, 1470, 1372, 1269, 1182, 1057, 833 cm^{-1}.
^{1}H NMR:	δ 7.70 (d, *J* =4.0 Hz, 2H, Ar-*H*), 7.60 (d, *J* =4.0 Hz, 1H, Ar-*H*), 7.51-7.14 (m, 7H, Ar-*H*), 4.09-3.94 (m, 4H, OCH_2), 1.30 and 0.81 (2 s, 6H, CH_3).

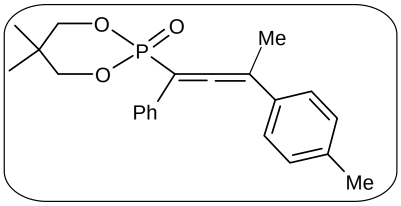
^{13}C NMR: δ 212.2 (C=*C*=C), 133.4, 131.4, 131.3, 130.2$_4$, 130.1$_7$, 129.7, 129.2, 129.0, 128.5, 128.4, 128.0, 127.9, 127.8, 127.3, 122.9 (Ar-*C*), 100.2 (d, ^1J(P-C) = 178.0 Hz, P*C*), 97.5 (d, ^3J(P-C)= 15.0 Hz, PCC*C*), 77.7 and 77.6 (O*C*H$_2$), 32.6 (d, ^3J (P-C)= 7.0 Hz, *C*(CH$_3$)$_2$), 22.0 and 20.6 (*C*H$_3$).

^{31}P NMR: δ 5.67.

LC-MS: *m/z* 419 [M+1]$^+$.

Anal. Cacld for $C_{20}H_{20}BrO_3P$: C, 57.30; H, 4.81. Found: C, 57.41; H, 4.75.

Compound 16k



4-Phenyl-2-*p*-tolylbut-3-yn-2-ol[94] (6.97 g, 29.5 mmol) was used.

Yield: 8.91 g (82 %, white solid).

Mp: 92–94 °C.

IR (KBr): 2971, 2926, 2874, 1925, 1595, 1512, 1493, 1372, 1273, 1055, 1007, 916 cm^{-1}.

^{1}H NMR: δ 7.68 (d, *J* =7.6 Hz, 2H, Ar-*H*), 7.38-7.27 (m, 5H, Ar-*H*), 7.19 (d, *J* =8.0 Hz, 1H, Ar-*H*), 4.03-3.82 (m, 4H, OC*H*$_2$), 2.36 (1 s, 3H, Ar-C*H*$_3$), 2.30 (d, *J* = 6.4 Hz, 3H, C*H*$_3$), 1.27 and 0.71 (2 s, 6H, C*H*$_3$).

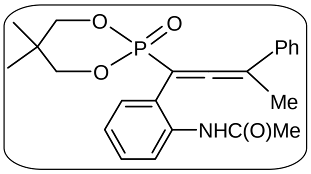
^{13}C NMR: δ 211.5 (C=*C*=C), 131.5 (d, *J* =10.0 Hz), 131.2 (d, *J* =7.5 Hz), 129.5, 128.7, 127.9, 127.6$_4$ 127.5$_8$, 125.9 (Ar-*C*), 105.1 (d, ^3J(P-C)= 15.7 Hz, PCC*C*), 97.6 (d, ^1J(P-C) = 181.2 Hz, P*C*), 77.4 and 77.3 (O*C*H$_2$), 32.3 (d, ^3J(P-C)= 6.0 Hz, *C*(CH$_3$)$_2$), 21.9, 21.1 and 20.4 (*C*H$_3$), 16.3 (d, ^3J(P-C)= 6.0 Hz) (*C*H$_3$).

^{31}P NMR: δ 7.20.

LC-MS: *m/z* 369 [M+1]$^+$.

Anal. Cacld for $C_{22}H_{25}O_3P$: C, 71.72; H, 6.84. Found: C, 71.65; H, 6.91.

Compound 17a



Propargyl alcohol **15c** (0.35 g, 1.25 mmol) was used.

Yield: 0.37 g (72%, white solid).

Mp: 80–82 °C.

IR (KBr): 3277, 3058, 2964, 2932, 2921, 1945, 1688, 1578, 1523, 1436, 1370, 1249, 1052, 1003, 844 cm^{-1}.

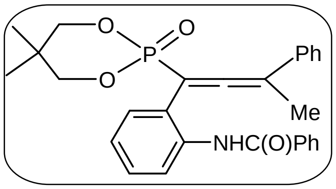
^{1}H NMR: δ 9.55 (br s, 1H, N*H*), 8.02 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 7.46-7.28 (m, 7H, Ar-*H*), 7.12 (t, 1H, Ar-*H*), 4.08-3.86 (m, 4H, CH_2), 2.25 (d, *J* = 6.8 Hz, 3H, CH_3), 2.16 (s, 3H, COCH_3), 1.23 and 0.78 (2 s, 6H, CH_3).

^{13}C NMR: δ 211.8 (PC*C*C), 169.2 (*C*=O), 136.6, 134.1 (d, *J* = 6.0 Hz), 132.9, 132.2, 132.1, 130.4 (d, *J* = 6.0 Hz), 129.4, 129.0, 128.6, 128.5, 128.4, 126.1, 124.8, 124.4, 123.9 (d, *J* = 7.0 Hz) (Ar-*C*), 103.4 (d, *J* = 15.0 Hz PCC*C*), 94.6 (d, *J* = 182.0 Hz, P*C*), 77.4 and 77.3 (2 s, *C*H$_2$), 32.5 (d, *J* = 7.0 Hz, *C*(CH$_3$)$_2$), 24.3, 21.8 and 20.6 (3 s, *C*H$_3$), 16.9 (d, *J* = 7.0 Hz, *C*H$_3$).

^{31}P NMR: δ 9.01.

HRMS (ESI) Calcd. for $C_{23}H_{26}NO_4P$ (M$^+$ + Na): 434.1497. Found: 434.1494.

Compound 17b



N-(2-(3-hydroxy-3-phenylbut-1-ynyl)phenyl)benzamide (0.40 g, 1.17 mmol) was used.

Yield: 0.36 g (64%, light yellow solid).

Mp: 96–98 °C.

IR (KBr): 3277, 3058, 2970, 2926, 1940, 1671, 1584, 1529, 1441, 1310, 1255, 1052, 1008, 833 cm^{-1}.

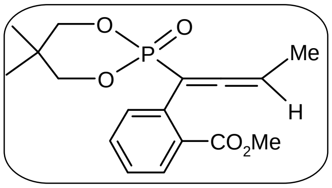
^{1}H NMR: δ 10.29 (br s, 1H, N*H*), 8.15 (2 d, *J* = 2.0 Hz, 2H, Ar-*H*), 8.09 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.57-7.18 (m, 11H, Ar-*H*), 4.11-3.89 (m, 4H, CH_2), 2.17 (d, *J* = 6.4 Hz, 3H, CH_3), 1.25 and 0.78 (2 s, 6H, CH_3).

^{13}C NMR: δ 211.2 (PC*C*C), 165.8 (*C*=O), 136.8, 134.5, 133.8, (d, *J* = 7.0 Hz), 131.7, 130.4 (d, *J* = 4.0 Hz), 129.3, 128.8, 128.6, 128.2, 127.7, 126.0, 125.6, 125.2, 125.1, 125.0 (d, *J* = 6.0 Hz) (Ar-*C*), 103.2 (d, *J* = 16.0 Hz PCC*C*), 94.2 (d, *J* = 182.0 Hz, P*C*), 77.5 and 77.4 (2 s *C*H_2), 32.4 (d, *J* = 6.0 Hz, *C*$(CH_3)_2$), 21.8 and 20.5 (2 s, *C*H_3), 16.7 (d, *J* = 6.0 Hz *C*H_3).

^{31}P NMR: δ 8.69.

HRMS (ESI) Calcd. for $C_{28}H_{28}NO_4P$ ($M^+ + H$): 474.1835. Found: 474.1839.

Compound 17c



Propargyl alcohol **13a**[63] (0.82 g, 4.04 mmol) was used.

Yield: 1.12 g (83%, white solid).

Mp: 110–112 °C.

IR (KBr): 2976, 1950, 1723, 1597, 1574, 1474, 1443, 1256, 1190, 1136, 1063, 1011, 986 cm^{-1}.

^{1}H NMR: δ 7.73-7.70 (m, 2H, Ar-*H*), 7.44 (dd→t, 1H, Ar-*H*), 7.33 (dd→t, 1H, Ar-*H*), 5.53-5.48 (m, 1H, C*H*), 4.22-3.79 (m, 7H, OCH_2+CH_3), 1.76 (dd→t, 3H, CH_3), 1.19 and 0.83 (2 s, 6H, CH_3).

^{13}C NMR: δ 210.9 (C=*C*=C), 168.1 (*C*=O), 132.7 (d, *J* =9.0 Hz), 131.5, 131.0$_3$, 130.9$_6$, 130.5, 130.2, 127.7 (Ar-*C*), 93.5 (d, ^{1}*J*(P-C) = 186.0 Hz, P*C*), 88.5 (d, ^{3}*J*(P-C)= 15.0 Hz, PCC*C*), 76.9 and 76.7 (O*C*H_2), 52.2 (*C*H_3), 32.4 (d, ^{3}*J*(P-C)= 7.0 Hz, *C*$(CH_3)_2$), 21.9 and 20.6 (*C*H_3), 12.1 (d, ^{3}*J*(P-C)= 7.0 Hz, *C*H_3).

^{31}P NMR: δ 8.33.

LC-MS: *m/z* 337 $[M+1]^+$.

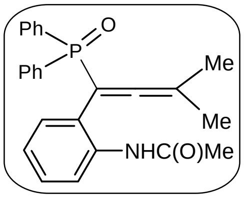
Anal. Cacld. for $C_{17}H_{21}O_5P$: C, 60.71; H, 6.29. Found: C, 60.85; H, 6.21.

3.22 Synthesis of allenylphosphine oxides 18, 19 and 20a-d

Allenylphosphine oxides **18**,[66] **19**[63] and **20a-d** were synthesized according to literature procedures using Ph_2PCl (**6**) and the corresponding propargyl alcohol.[18-19] Among these, allenes **20a-d** are new.

Compound 20a

Propargyl alcohol **15a** (0.52 g, 2.41 mmol) was used.



Yield: 0.85 g (87%, white solid).

Mp: 120–122 °C.

IR (KBr): 3315, 3255, 3184, 2992, 2921, 1956, 1688, 1616, 1589, 1556, 1479, 1447, 1381, 1310, 1162, 1112, 767 cm^{-1}.

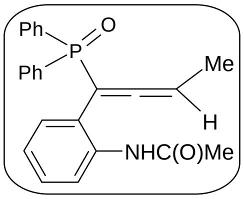
^{1}H NMR: δ 10.87 (s, 1H, N*H*), 7.92 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.73-7.39 (m, 10H, Ar-*H*), 7.17 (t, 1H, Ar-*H*), 7.10 (d, *J* = 7.6 Hz, 1H, Ar-*H*), 6.95 (t, 1H, Ar-*H*), 2.24 (s, 3H, COC*H*$_3$), 1.42 (d, *J* = 6.0 Hz, 6H, C*H*$_3$).

^{13}C NMR: δ 211.7 (PC*C*C), 169.1 (*C*=O), 136.9, 132.0, 131.8, 131.4, 131.3, 130.3, 128.6, 128.4, 128.2, 125.7, 124.3, 124.0 (Ar-*C*), 97.8 (d, *J* = 13.0 Hz PCC*C*), 97.6 (d, *J* = 100.0 Hz, P*C*), 24.2 (CO*C*H$_3$), 18.9 (d, *J* = 4.0 Hz *C*H$_3$).

^{31}P NMR: δ 35.19.

HRMS (ESI) Calcd. for $C_{25}H_{24}NO_2P$ (M^+ + H): 402.1624. Found: 402.1625.

Compound 20b



Propargyl alcohol **15b** (0.40 g, 1.97 mmol) was used.

Yield: 0.59 g (78%, pale yellow solid).

Mp: 114–116 °C.

IR (KBr): 3441, 3238, 3052, 1945, 1688, 1611, 1584, 1540, 1479, 1436, 1370, 1304, 1271, 1162, 1118, 1101, 1068, 762 cm^{-1}.

^{1}H NMR: δ 10.84 (s, 1H, N*H*), 7.95 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.79-7.43 (m, 10H, Ar-*H*), 7.23 (t, 1H, Ar-*H*), 7.11 (d, *J* = 7.6 Hz, 1H, Ar-*H*), 6.98 (t, 1H, Ar-*H*), 5.14 (qrt, 1H, C*H*CH$_3$), 2.27 (s, 3H, COC*H*$_3$), 1.47 (dd, *J* = 7.6 Hz, *J* = 6.4 Hz, 3H, CHC*H*$_3$).

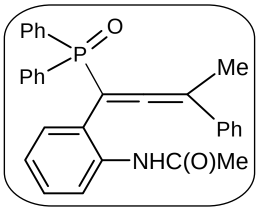
^{13}C NMR: δ 213.0 (d, *J* = 7.9 Hz, PC*C*C), 169.3 (*C*=O), 137.1, 132.3 (d, *J* = 5.6 Hz), 131.8$_3$, 131.7$_9$, 131.7, 131.6, 131.5, 131.0, 130.4, 129.9, 129.0, 128.6, 128.4, 128.2, 125.1, 124.5, 124.3 (Ar-*C*), 99.4 (d, *J* = 99.5 Hz P*C*), 87.6 (d, *J* = 12.5 Hz, PCC*C*H), 24.4 (CO*C*H$_3$), 12.8 (d, *J* = 5.6 Hz CH*C*H$_3$).

^{31}P NMR: δ 34.07.

LC-MS: *m/z* 388 [M+1]$^{+}$.

Anal. Calcd. for $C_{24}H_{22}NO_2P$: C, 74.41; H, 5.72; N, 3.62. Found: C, 74.32; H, 5.62; N, 3.75.

Compound 20c



Propargyl alcohol **15c** (0.70 g, 2.51 mmol) was used.

Yield: 1.07 g (92%, brown gummy liquid).

IR (neat): 3457, 3249, 3052, 2920, 1934, 1687, 1578, 1539, 1435, 1369, 1298, 1161, 1123, 755 cm^{-1}.

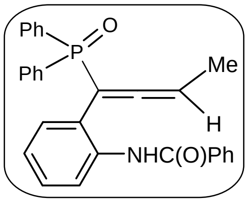
^{1}H NMR: δ 10.80 (s, 1H, N*H*), 7.97 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.76-7.23 (m, 15H, Ar-*H*), 7.12 (d, *J* = 7.6 Hz, 1H, Ar-*H*), 7.01 (t, 1H, Ar-*H*), 2.28 (s, 3H, COC*H*$_3$), 1.85 (d, *J* = 6.0 Hz, 3H, C*H*$_3$).

^{13}C NMR: δ 213.5 (d, *J* = 6.0 Hz, PC*C*C), 169.2 (*C*=O), 137.0, 134.2 (d, *J* = 6.0 Hz), 132.6 (d, *J* = 3.0 Hz), 131.5, 131.4, 131.3, 131.0, 130.7, 129.9, 129.0, 128.8, 128.5, 128.4, 128.3, 127.9, 125.8, 125.1 (d, *J* = 4.0 Hz), 124.6 (d, *J* = 8.0 Hz) (Ar-*C*), 103.4 (d, *J* = 13.0 Hz PCC*C*), 101.5 (d, *J* = 98.0 Hz, P*C*), 24.3 (CO*C*H_3), 16.2 (d, *J* = 5.0 Hz *C*H_3).

^{31}P NMR: δ 34.45.

HRMS (ESI) Calcd. for $C_{30}H_{26}NO_2P$ (M + H)$^+$: 464.1780. Found: 464.1778.

Compound 20d



Propargyl alcohol **15m** (0.37 g, 1.40 mmol) was used.

Yield: 0.47 g (75%, white solid).

Mp: 172–174 ^{o}C.

IR (KBr): 3227, 3058, 1940, 1666, 1605, 1578, 1534, 1436, 1310, 1173, 1118, 1101, 767 cm^{-1}.

^{1}H NMR: δ 11.36 (s, 1H, N*H*), 8.35-8.33 (m, 2H, Ar-*H*), 7.97 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.80-7.41 (m, 13H, Ar-*H*), 7.31 (t, 1H, Ar-*H*), 7.11 (d, *J* = 7.6 Hz, 1H, Ar-*H*), 7.03 (t, 1H, Ar-*H*), 5.12 (m, 1H, C*H*CH_3), 1.42 (dd, *J* = 7.2 Hz, *J* = 4.4 Hz 3H, CHC*H*$_3$).

^{13}C NMR: δ 212.0 (d, *J* = 8.2 Hz, PC*C*C), 166.0 (*C*=O), 137.3, 134.7, 132.3 (d, *J* = 11.0 Hz), 131.8, 131.7, 131.6_1, 131.5_6, 131.4, 130.7, 130.3, 129.6, 129.1, 128.9, 128.8, 128.5, 128.4, 128.0, 127.4, 126.3, 126.0, 125.0 (Ar-*C*), 98.8 (d, *J* = 100.9 Hz, P*C*), 87.5 (d, *J* = 12.7 Hz, PCC*C*H), 12.8 (d, *J* = 5.4 Hz CH*C*H_3).

^{31}P NMR: δ 34.28.

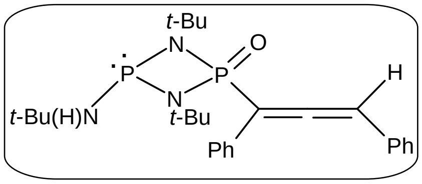
LC-MS: *m/z* 450 [M+1]$^+$.

Anal.Calcd. for $C_{29}H_{24}NO_2P$: C, 77.49; H, 5.38; N, 3.12. Found: C, 77.58; H, 5.32; N, 3.21.

3.3 Synthesis of phosphorus containing and phosphorus free *N*-heterocycles

3.31 Synthesis of cyclodiphosphazane based allenes [(t-BuNH)P(μ-N-t-Bu)$_2$P(=O)-C(Ph)=C=CH(Ph)] (21) and [(i-PrNH)P(μ-N-t-Bu)$_2$P(=O)-C(Ph)=C=CH(Ph)] (22)

Compound 21



In a round bottomed flask (RBF), [(*t*-BuNH)P(*μ*-N-*t*-Bu)]$_2$ (**2**)[52] (0.365 g, 1.05 mmol) and propargyl alcohol **12b**[62] (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 product **21** was purified by column chromatography using (EtOAc/ hexane (1:2)) as the eluent.

Yield: 0.395 g (78%, white solid); $R_f = 0.55$ (EtOAc/ hexane; 1:2).

Mp: 174–178 °C.

IR (KBr): 3441, 3252, 3059, 2967, 2866, 1929, 1597, 1495, 1458, 1364, 1221, 1138, 1076, 1034, 1001, 932, 907, 882, 816 cm^{-1}.

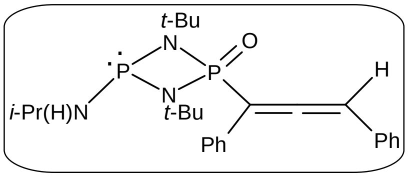
^{1}H NMR: δ 7.60-7.22 (m, 10H), 6.66 (d, *J* = 11.2 Hz, 1H), 3.30 (d, *J* = 7.2 Hz, 1H), 1.34, 1.31 (2 s, 27H).

^{13}C NMR: δ 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: δ 79.73 (d, *J* = 11.0 Hz), 9.21 (d, *J* = 11.0 Hz).

HRMS (ESI): Calcd. for $C_{27}H_{39}N_3OP_2$ ($M^+ + H$): *m/z* 484.2647. Found: 484.2646.

Compound 22



The procedure was similar to that for compound **21** using cyclodiphosphazane [(*i*-PrNH)P(*μ*-N-*t*-Bu]$_2$ (**3**) [δ(P) 90.7; 0.509 g, 1.59 mmol] and propargyl alcohol **12b**

(0.33 g, 1.59 mmol). The reaction time was 8 h. The eluent for column chromatography was EtOAc/ hexane (1:3).

Yield: 0.413 g (55%, white solid); $R_f = 0.32$ (EtOAc/ hexane; 1:3).

Mp: 154–156 ^{o}C.

IR (KBr): 3244, 2959, 2920, 2871, 1912, 1594, 1490, 1452, 1414, 1359, 1260, 1233, 1216, 1134, 1074, 926, 888, 816 cm^{-1}.

^{1}H NMR: δ 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 (2 s, 18H), 1.20 (d, *J* = 6.4 Hz, 6H).

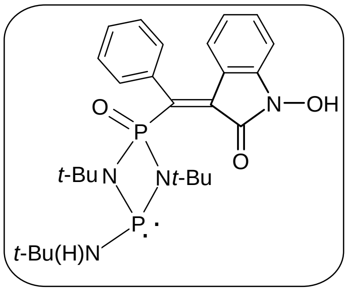
^{13}C NMR: δ 216.1, 134.4, 134.3, 132.8, 132.7, 128.8, 128.6, 127.9, 127.6, 107.5 (d, *J* ~ 139.0 Hz), 96.9 (d, *J* ~ 13.0 Hz), 52.8 (d, *J* ~ 5.0 Hz), 45.1 (d, *J* = 29.0 Hz), 31.3, 26.5.

^{31}P NMR: δ 83.64, 9.42

HRMS (ESI): Calcd. for $C_{26}H_{37}N_3OP_2$ (M^+ + H): *m/z* 470.2491. Found: 470.2491.

3.32 *Synthesis of cyclodiphosphazane based indolinones [(t-BuNH)P(µ-N-t-Bu)$_2$P(O)-C(Ph)=C{-C$_6$H$_4$-N(OH)-C(=O)-}] (23), isomers of [(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)] (24 and 25) and [(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)] (26)*

Compound 23



The procedure was similar to that for compound **21** using [(*t*-BuNH)P(*µ*-N-*t*-Bu)]$_2$ (**2**)[52] [0.73 g, 2.1 mmol] and propargyl alcohol **11a**[28] (0.44 g, 1.74 mmol). The reaction was conducted at 70 ^{0}C for 8 h; eluent for column chromatography was EtOAc/ hexane (2:1).

Yield: 0.316 g (34%, yellow solid); $R_f = 0.33$ (EtOAc/ hexane; 2:1).

Mp: 226–228 °C.

IR (KBr): 3470, 3289, 3138, 3081, 3029, 2967, 1705, 1699, 1616, 1557, 1466, 1362, 1325, 1213, 1082, 1032, 997, 889, 831 cm^{-1}.

^{1}H NMR: δ 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 (2 s, 27H).

^{13}C NMR: δ 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.

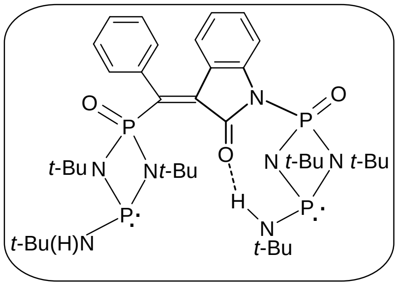
^{31}P NMR: δ 81.92 (d, J = 12.0 Hz), 6.23 (d, J = 12.0 Hz).

HRMS (ESI): Calcd. for $C_{27}H_{38}N_4O_3P_2$ (M^+ + H): *m/z* 529.2498. Found: 529.2499.

Compounds 24 and 25

The procedure was the same as that for **21**, using [(*t*-BuNH)P(*μ*-N-*t*-Bu)]$_2$ (**2**) (0.80 g, 2.29 mmol) and propargyl alcohol **11a** (0.29 g, 1.15 mmol); reaction time was 8 h and the eluent for column chromatography was EtOAc/ hexane (1:1). Compound **24** eluted first, followed by isomer **25**.

Compound 24



Yield: 0.333 g (36%, yellow solid); R_f = 0.5 (EtOAc/ hexane; 1:1).

Mp: 214–216 °C.

IR (KBr): 3501, 3316, 3212, 2971, 1728, 1638, 1595, 1458, 1364, 1308, 1211, 1082, 1034, 961, 885 cm^{-1}.

^{1}H NMR: δ 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 (4 s, 54H).

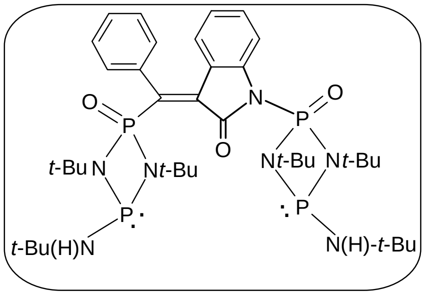
^{13}C NMR: δ 166.2, 151.2 (d, *J* ~ 121.8 Hz), 144.1, 141.9, 141.8, 136.4, 130.9, 129.1, 129.0, 128.9, 128.2, 125.5, 124.3, 124.2, 122.7, 116.2, 53.2 (d, *J* ~ 9.0 Hz), 52.6 (d, *J* ~ 6.0 Hz), 51.9, 51.8, 33.2 (d, *J* = 7.5 Hz), 32.6 (d, *J* = 3.6 Hz), 32.0 (d, *J* = 4.3 Hz), 31.1 (d, *J* = 4.3 Hz), 29.8.

^{31}P NMR: δ 85.22 (d, *J* = 14.0 Hz), 85.06, 9.06 (d, *J* = 14.0 Hz), -5.18.

HRMS (ESI): Calcd. for $C_{39}H_{65}N_7O_3P_4$ (M^+ + Na): *m/z* 826.3997. Found: 826.3989.

X-ray structure was determined for this isomer.

Compound 25



Yield: 0.259 g (28%, yellow solid); R_f = 0.46 (EtOAc/ hexane; 1:1).

Mp: 204–206 °C.

IR (KBr): 3410, 3246, 2967, 2926, 2855, 1699, 1632, 1547, 1464, 1385, 1366, 1312, 1269, 1221, 1146, 1080, 1038, 1009, 918, 893 cm^{-1}.

^{1}H NMR: δ 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 (4 s, 54H).

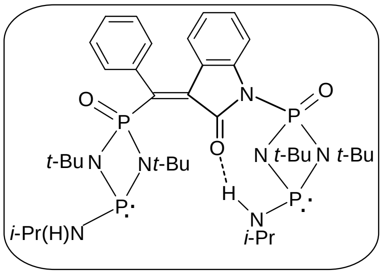
^{13}C NMR: δ 166.2, 151.1 (d, *J* ~ 121.7 Hz), 144.1, 141.8$_2$, 141.8$_1$, 139.4, 136.4, 131.0, 129.0, 128.9, 128.2, 125.5, 124.3, 124.1, 123.7, 122.7, 116.2, 53.2 (d, *J* ~ 9.1 Hz), 52.6 (d, *J* ~ 6.0 Hz), 51.8 (d, *J* ~ 15.4 Hz), 50.9, 33.2 (d, *J* = 7.4 Hz), 32.6 (d, *J* = 8.0 Hz), 32.0, 31.8 (d, *J* = 4.3 Hz), 31.1, 29.8.

^{31}P NMR: δ 83.8 (br), 73.42 (br), 6.31 (d, *J* = 11.0 Hz), -5.73 (d, *J* = 6.5 Hz).

HRMS (ESI): Calcd. for $C_{39}H_{65}N_7O_3P_4$ (M^+ + Na): *m/z* 826.3997. Found: 826.3997.

X-ray structure was determined for this isomer also.

Compound 26



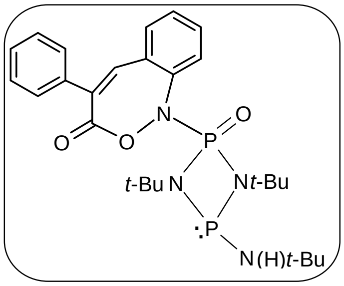
The procedure was similar to that for compound **21** using [(*i*-PrNH)P(μ-N-*t*-Bu]$_2$ (**3**)[52c] [δ(P) 90.7; 1.33 g, 4.14 mmol] and propargyl alcohol **11a** (0.52 g, 2.07 mmol). The reaction was conducted at 70 ^{0}C for 8 h and the eluent for column chromatography was EtOAc/ hexane (1:2).

Yield:	0.523 g (33%, yellow solid); $R_f = 0.54$ (EtOAc/ hexane; 1:2).
Mp:	234–238 ^{o}C.
IR (KBr):	3326, 2964, 2920, 1720, 1594, 1451, 1369, 1221, 1166, 1134, 1073, 887, 805 cm^{-1}.
^{1}H NMR:	δ 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 (6 s, 48H).
^{13}C NMR:	δ 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:	δ 89.10, 85.45, 6.84, -4.20.
HRMS (ESI):	Calcd. for $C_{37}H_{61}N_7O_3P_4$ (M^+ + H): *m/z* 776.3865. Found: 776.3865.

3.33 Synthesis of (t-BuNH)P(μ-N-t-Bu)$_2$P(O)N[-o-C$_6$H$_4$-C(H)=C(Ph)-C(O)-O-] (27), [(t-BuNH)$_2$P(O)-C(Ph)=C{-C$_6$H$_4$-NH-C(=O)-}] (28), and the indole 29

An oven dried 25 mL round-bottomed flask was charged with propargyl alcohol **11a** (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 ^{0}C for 5 min. To this, [(*t*-BuNH)P(μ-N-*t*-Bu)$_2$P-Cl] (**4**)[53] (0.369 g, 1.18 mmol) dissolved in dry THF (5 mL) was added drop-wise at 0 ^{o}C over a period of 15 min, and then the mixture allowed to warm to rt followed by heating at 70 ^{0}C for 12 h with continuous stirring. After cooling, filtration followed by removal of the solvent and purification by column chromatography (acetone/ hexane; 1:9) afforded product **27** followed by **28**. Although we could get an X-ray structure of the major product **27** (crystallization from ethyl acetate + chloroform), this compound underwent degradation/isomerization in solution and hence spectra for the pure isomer could not be obtained.

Compound 27



Yield: 0.292 g (56%, pale yellow solid); $R_f = 0.5$ (acetone/ hexane; 1:9).

Mp: 164–166 ^{o}C.

IR (KBr): 3424, 2970, 2931, 2854, 1731, 1462, 1369, 1276, 1216, 1084, 1040, 958, 887 cm^{-1}.

^{1}H NMR: δ 8.10-7.27 (m, 10H), 3.07 (d, J = 6.4 Hz, 1H), 1.34, 1.33, 1.24 (3 s, 27H), additional peaks at δ 8.07-7.25, 3.42 (d), 1.56, 1.54, 0.95 were also seen.

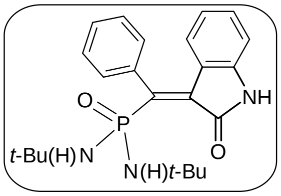
^{13}C NMR: δ 171.4, 142.0, 138.3, 135.5, 133.0, 132.8, 130.8, 130.2, 128.9, 128.6, 128.3, 127.7, 126.8, 125.3, 53.2, 52.0, 32.9, 31.8, 31.1; additional peaks at δ 172.3, 141.1, 138.3, 136.5, 135.1, 133.0, 132.1, 130.8, 129.0, 128.3, 127.5, 121.8, 52.2, 52.0, 32.8, 31.7, 31.0 were also seen due to isomerization/transformation.

^{31}P NMR: δ 73.07 (d, J = 6.8 Hz), 3.01 (d, J = 6.8 Hz), 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): Calcd. for $C_{27}H_{38}N_4O_3P_2$ (M^+ + Na): m/z 551.2317. Found: 551.2317.

X-ray structure was determined for this compound.

Compound 28



Yield: 0.129 g (32%, yellow solid); $R_f = 0.27$ (acetone/ hexane; 1:9).

Mp: 230–234 °C.

IR (KBr): 3351, 3065, 2965, 2816, 1699, 1616, 1466, 1383, 1331, 1217, 1011, 837, 748 cm^{-1}.

^1H NMR: δ 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).

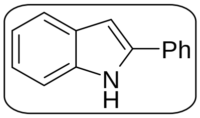
^{13}C NMR: δ 168.7, 154.2 (d, *J* ~ 126.0 Hz), 142.3, 138.8_2, 138.8, 132.6, 132.5, 129.9, 128.8, 127.9, 125.0, 123.3, 123.2, 121.6, 110.3, 51.9, 32.3, 32.2.

^{31}P NMR: δ 11.11.

HRMS (ESI): Calcd. for $C_{23}H_{30}N_3O_2P$ (M^+ + Na): *m/z* 434.1974. Found 434.1974.

X-ray structure was determined for this compound.

Compound 29

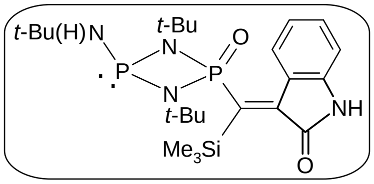


When compound **27** (0.18 g) was heated with toluene-water (9:1) mixture at 110 °C/ 12 h, the indole derivative **29** could be isolated (0.031 g, ca 48 %); R_f = 0.53 (EtOAc/ hexane 1:9). It is a known compound[95] and is commercially available.

3.34 Synthesis of [(t-BuNH)P(μ-N-t-Bu)$_2$P(O)-C(SiMe$_3$)=C{-C$_6$H$_4$-NH-C(=O)-}] (30) and [(t-BuNH)$_2$P(O)-CH=C{-C$_6$H$_4$-NH-C(=O)-}] (31)

The procedure was similar to that for compound **21** using [(*t*-BuNH)P(*μ*-N-*t*-Bu)]$_2$ (**2**) [0.56 g, 1.61 mmol] and propargyl alcohol **11b** (0.34 g, 1.34 mmol). The reaction time was 6 h at 80 °C and the eluent was EtOAc/ hexane (1:2) to obtain solids **30** (eluted first) and **31**.

Compound 30



Yield: 0.289 g (42%, yellow solid); R_f = 0.58 (EtOAc/ hexane; 1:2).

Mp: 242–246 °C.

IR (KBr): 3431, 2965, 2856, 1718, 1609, 1459, 1371, 1247, 1205, 1071, 890, 843 cm^{-1}.

^1H NMR: δ 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 (2 s, 27H), 0.43 (s, 9H).

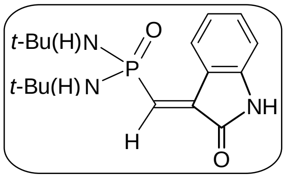
^{13}C NMR: δ 168.7 (d, ^3J(P-C) = 31.0 Hz), 155.0 (d, J ~ 90.0 Hz), 150.8, 143.7, 131.9, 131.4, 123.2, 122.2, 109.6, 52.9 (d, J ~ 4.0 Hz), 52.4 (d, J ~ 15.0 Hz), 33.0 (d, J = 9.0 Hz), 31.4_6, 31.5_4 (d, J = 10.0 Hz), 4.5.

^{31}P NMR: δ 92.87 (d, J(P-P) = 12.0 Hz), 24.50 (d, J = 12.0 Hz).

HRMS (ESI): Calcd. for $C_{24}H_{42}N_4O_2P_2Si$ (M^+ + H): m/z 509.2631. Found 509.2629.

X-ray structure was determined for this compound.

Compound 31



Yield: 0.136 g (30%, yellow solid); R_f = 0.38 (EtOAc/ hexane; 1:2).

Mp: 118–120 °C.

IR (KBr): 3265, 2970, 2926, 2876, 1718, 1614, 1528, 1467, 1391, 1366, 1293, 1260, 1221, 1090, 1046, 1013, 920, 838 cm^{-1}.

^1H NMR: δ 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).

^{13}C NMR: δ 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.

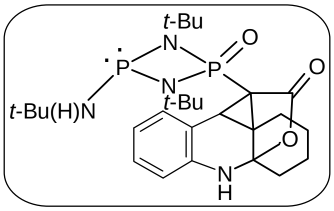
^{31}P NMR: δ 9.32.

HRMS (ESI): Calcd .for $C_{17}H_{26}N_3O_2P$ (M^+ + H): m/z 336.1842. Found: 336.1840.

3.35 Synthesis of [(t-BuNH)P(μ-N-t-Bu)$_2$P(O){C$_{15}$H$_{14}$NO$_2$}] (32) and [(i-PrNH)P(μ-N-t-Bu)$_2$P(O){C$_{15}$H$_{14}$NO$_2$}] (33) and the tetrahydroacridine (34)

Cyclodiphosphazane [(*t*-BuNH)P(*μ*-N-*t*-Bu)]$_2$ (**2**) (0.338 g, 0.97 mmol) was added to propargyl alcohol **11c**^{28} (0.25 g, 0.97 mmol) and dry toluene (5 mL) was added at rt. The solution was then maintained at 70 ^{0}C with stirring for 8 h. After cooling, the crude product was purified by column chromatography (EtOAc/ hexane; 2:3) affording **32** as a pure white solid. This was crystallized from ethyl acetate.

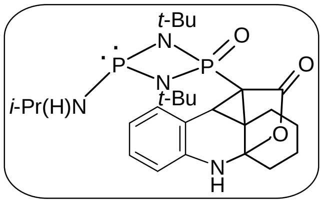
Compound 32



Yield:	0.434 g (84%, white solid); R$_f$ = 0.35 (EtOAc/ hexane; 2:3).
Mp:	202–206 ^{o}C.
IR (KBr):	3337, 3245, 2975, 2928, 2857, 2631, 1757, 1618, 1543, 1491, 1368, 1209, 1140, 1078, 885, 762 cm^{-1}.
^{1}H NMR:	δ 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 (3 s, 27H).
^{13}C NMR:	δ 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:	δ 74.31 (slightly broad), 10.28 (d, *J* ~ 5.2 Hz).
HRMS (ESI):	Calcd. for $C_{27}H_{42}N_4O_3P_2$ (M^+ + Na): *m/z* 555.2630. Found: 555.2630.

X-ray structure was determined for this compound.

Compound 33



The procedure was similar to that for compound **32** using [(*i*-PrNH)P(μ-N-*t*-Bu]$_2$ (**3**) [δ(P) 90.7; 0.329 g, 1.03 mmol] and propargyl alcohol **11c**[28] (0.22 g, 0.86 mmol). The reaction time was 8 h and the eluent for column chromatography was EtOAc/ hexane (1:2).

Yield: 0.276 g (62%, white solid); $R_f = 0.49$ (EtOAc/ hexane; 1:2).

Mp: 192–196 °C.

IR (KBr): 3343, 3241, 3117, 2969, 2930, 2863, 1757, 1616, 1491, 1399, 1366, 1262, 1209, 1132, 1076, 1015, 986, 887, 760 cm^{-1}.

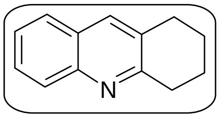
^{1}H NMR: δ 7.40 (d, *J* = 6.8 Hz, 1H), 7.10 (dd, 1H), 6.83 (dd, 1H), 6.62 (d, *J* = 8.0 Hz, 1H), 4.37 (s, 1H), 3.53 (s, 1H), 3.04-2.85 (m, 3H), 2.22-1.67 (m, 7H), 1.48, 1.43 (2 s, 18H), 1.19, 1.17 (2 s, 6H).

^{13}C NMR: δ 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: δ 78.90, 10.22 (*P*(O)-C).

HRMS (ESI): Calcd. for $C_{26}H_{40}N_4O_3P_2$ (M$^+$ + H): *m/z* 519.2655. Found: 519.2654.

Compound 34



When compound **32** (0.25 g) was heated with toluene-water (9:1) mixture at 110 °C / 12 h, tetrahydroacridine **34** could be isolated (0.031 g, ca 36%). It is a known compound;[70] ^{1}H and ^{13}C NMR spectra were identical to that reported before. HRMS (ESI): Calcd. for $C_{13}H_{13}N$ (M$^+$ + H): 184.1127. Found: 184.1124.

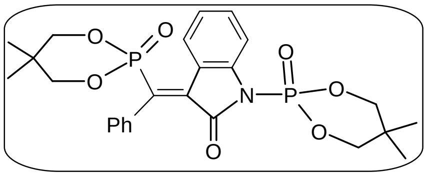
3.36 Synthesis of phosphorus-containing heterocycles 35-40 and phosphorus free indoles 29/ 41

Compounds 35-37 (and 29)

The procedure was same as that for compound **27** using P(III)-Cl precursor **5**[54] (0.681 mL, 4.93 mmol), propargyl alcohol **11a** (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 **35** + **36** (total

71%) along with **37** (ca 12%). Using EtOAc/ hexane (2:3) mixture as the eluent, we isolated compounds **35** (eluted last), **36** (eluted second) and **37** (eluted first).

Compound 35



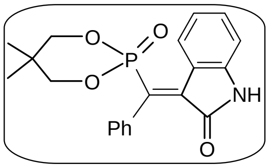
Yield:	0.381 g (31%, yellow solid); R_f = 0.22 (EtOAc/ hexane; 2:3).
Mp:	196–198 °C.
IR (KBr):	2965, 1728, 1601, 1466, 1408, 1262, 1061, 1019, 799 cm^{-1}.
^{1}H NMR:	δ 8.56 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.45-7.27 (m, 6H), 7.17 (t, 1H), 4.31-3.52 (m, 8H), 1.36, 1.24, 0.83, 0.74 (4 s, 12H).
^{13}C NMR:	δ 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:	δ 3.47, -14.69.

LC-MS: *m/z* 518 [M+1]$^+$.

Anal. Calcd. for $C_{25}H_{29}NO_7P_2$: C, 58.03; H, 5.65; N, 2.71. Found: C, 58.12; H, 5.61; N 2.65.

X-ray structure was determined for this compound.

Compound 36



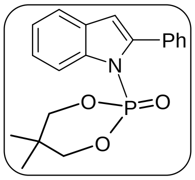
Yield:	0.35 g (40%, yellow solid); R_f = 0.44 (EtOAc/ hexane; 2:3).
Mp:	172–174 °C.
IR (KBr):	3238, 2981, 2964, 2926, 1726, 1622, 1468, 1392, 1337, 1227, 1200, 1052, 1014, 986, 953 cm^{-1}.
^{1}H NMR:	δ 8.47 (d, *J* = 8.0 Hz, 1H), 8.17 (s, 1H), 7.42-7.23 (m, 6H), 7.02 (t, 1H), 6.65 (d, *J* = 7.6 Hz, 1H), 3.90-3.56 (m, 4H), 1.21 (s, 3H), 0.74 (s, 3H).

^{13}C NMR: δ 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: δ 4.19.

HRMS (ESI): Calcd. for $C_{20}H_{20}NO_4P$ ($M^+ + H$): *m/z* 370.1209. Found: 370.1210.

Compound 37 and its conversion to compound 29



Yield: 0.108 g (12%, white solid); R_f = 0.59 (EtOAc/ hexane; 2:3).

Mp: 78–80 °C.

IR (KBr): 3063, 2959, 2926, 2855, 1655, 1523, 1463, 1370, 1299, 1271, 1129, 1052, 1014, 855 cm^{-1}.

^{1}H NMR: δ 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, OCH_2), 1.26, 0.61 (2 s, 6H, CH_3).

^{13}C NMR: δ 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: δ -10.68.

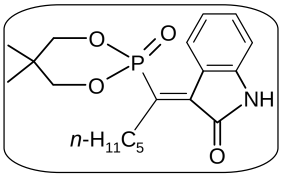
HRMS (ESI): calcd for $C_{19}H_{20}NO_3P$ ($M^+ + Na$): *m/z* 364.1079. Found: 364.1076.

Passing compound **37** (0.10 g, 0.29 mmol) through a basic alumina column afforded the indole **29** (0.0512 g, 90%). It is a known compound (see above).[95]

Compounds 38-39

The procedure was similar to that for compound **27** using P(III)-Cl precursor **5** (0.314 mL, 2.27 mmol), propargyl alcohol **11d**[60] (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 EtOAc/ hexane (2:3) to obtain solids **38** (eluted second) and **39** (eluted first).

Compound 38



Yield: 0.159 g (40%, yellow solid); $R_f = 0.4$ (h EtOAc/ exane; 2:3).

Mp: 170–172 °C.

IR (KBr): 3278, 2963, 2932, 1711, 1622, 1470, 1260, 1057, 1015, 797 cm^{-1}.

^1H NMR: δ 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).

^{13}C NMR: δ 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.

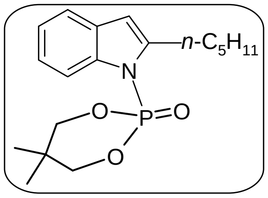
^{31}P NMR: δ 11.13.

LC-MS: *m/z* 362 $[M-1]^+$.

Anal. Calcd. for $C_{19}H_{26}NO_4P$: C, 62.80; H, 7.21; N, 3.85. Found: C, 62.71; H, 7.18; N, 3.91.

HRMS (ESI): Calcd. for $C_{19}H_{26}NO_4P$ (M^+ + H): *m/z* 364.1678. Found: 364.1676.

Compound 39



Yield: 0.121 g (33%, white solid); $R_f = 0.6$ (EtOAc/ hexane; 2:3).

Mp: 68–70 °C.

IR (KBr): 2959, 2932, 1586, 1564, 1454, 1375, 1302, 1155, 1123, 1057, 1009, 947 cm^{-1}.

^1H NMR: δ 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).

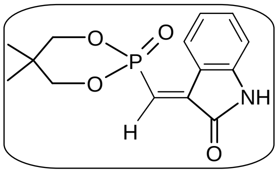
^{13}C NMR: δ 143.2$_2$, 143.1$_6$, 138.2, 138.1, 130.9, 130.7, 129.1, 128.3, 123.1, 122.3, 120.2, 113.4, 107.0$_5$, 106.9$_6$, 78.1 (d, J = 6.6 Hz), 32.4 (d, J = 5.6 Hz), 31.7, 28.6, 28.1, 22.6, 22.0, 20.7, 14.1.

^{31}P NMR: δ -8.87.

LC-MS: m/z 336 $[M+1]^+$.

Anal. Calcd. for $C_{18}H_{26}NO_3P$: C, 64.46; H, 7.81; N, 4.18. Found: C, 64.58; H, 7.76; N, 4.25.

Compound 40



This product was obtained by adapting the same procedure as that for compound **27** by using P(III)-Cl precursor **5** (0.532 mL, 3.85 mmol), propargyl alcohol **11b** (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 [ethyl acetate/ hexane (3:2)].

Yield: 0.327 g (61%, white solid); R_f = 0.3 (EtOAc/ hexane; 3:2).

Mp: 296–298 °C.

IR (KBr): 3160, 3106, 3054, 3019, 2965, 2897, 1651, 1561, 1497, 1476, 1429, 1372, 1240, 1155, 1134, 1076, 1020, 947 cm^{-1}.

^{1}H NMR: δ 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 (2 s, 6H).

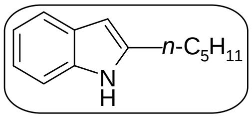
^{13}C NMR: δ 163.1, 151.8 (d, J = 8.4 Hz), 140.1, 133.0, 129.7, 123.3, 120.9, 119.1, 119.0, 115.6, 77.8 (d, J = 6.9 Hz) 32.9 (d, J = 9.0 Hz), 22.5, 21.2.

^{31}P NMR: δ 6.06.

LC-MS m/z 292 $[M-1]^+$.

Anal. Calcd. for $C_{14}H_{16}NO_4P$: C, 57.34; H, 5.50; N, 4.78. Found: C, 57.19; H, 5.56; N, 4.68.

Compound 41



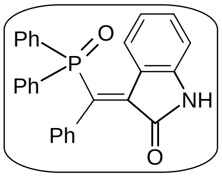
Passing compound **39** (0.11 g, 0.33 mmol) through a basic alumina column afforded the indole **41** as a white solid. Yield: 0.052 g (84%); $R_f = 0.54$ (EtOAc/ hexane; 1:9). It is a known compound.[95]

3.37 Synthesis of phosphorus-containing heterocycles (42-49), quinolinones (50-52) and 2-substituted indoles (29, 41, 53-54)

Compounds 42 and 43

The procedure was similar to that for compound **27** using Ph_2PCl (**6**) (0.396 mL, 2.21 mmol), propargyl alcohol **11a** (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 EtOAc/ hexane (2:3) to obtain compounds **42** (eluted second) and **43** (eluted first).

Compound 42



Yield: 0.235 g (30%, yellow solid); $R_f = 0.36$ (EtOAc/ hexane; 2:3).

Mp: 224–226 °C.

IR (KBr): 3134, 3068, 2921, 2849, 1715, 1616, 1468, 1436, 1326, 1211, 1151, 1118, 921 cm^{-1}.

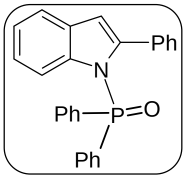
^1H NMR: δ 8.36 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 8.03 (br s, 1H, N*H*), 7.60-6.62 (m, 18H, Ar-*H*).

^{13}C NMR: δ 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: δ 30.67.

HRMS (ESI): Calcd. for $C_{27}H_{20}NO_2P$ (M^+ + H): *m/z* 422.1311. Found: 422.1309.

Compound 43



Yield: 0.376 g (52%, brown gummy liquid); $R_f = 0.59$ (EtOAc/ hexane 2:3).

IR (neat): 3058, 2926, 2849, 1594, 1436, 1310, 1255, 1222, 1123, 1074, 1008, 811 cm^{-1}.

^1H NMR: δ 7.61-6.97 (m, 19H, Ar-*H*), 6.64 (d, $J = 4.0$ Hz, 1H, Ar-*H*).

^{13}C NMR: δ 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.

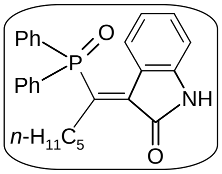
^{31}P NMR: δ 23.83.

HRMS (ESI): Calcd. for $C_{26}H_{20}NOP$ ($M^+ + H$): *m/z* 394.1362. Found: 394.1360.

Compounds 44-46

The procedure was similar to that for compound **27** using Ph_2PCl (**6**) (0.381 mL, 2.12 mmol), propargyl alcohol **11d** (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 EtOAc/ hexane (2:3) to obtain compounds **44** (eluted last), **45** (eluted second) and **46** (eluted first).

Compound 44



Yield: 0.112 g (26%, brown gummy liquid); $R_f = 0.33$ (EtOAc/ hexane; 2:3).

IR (neat): 3346, 3072, 2928, 2859, 1713, 1622, 1470, 1435, 1327, 1173, 1105, 1022, 752 cm^{-1}.

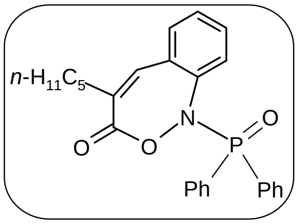
^1H NMR: δ 8.27 (d, $J = 8.0$ Hz, 1H), 7.82 (br s, 1H), 7.78-6.68 (m, 13H), 2.90 (br, 2H), 1.43-0.86 (m, 6H), 0.71 (t, 3H).

^{13}C NMR: δ 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: δ 33.61.

HRMS (ESI): Calcd. for $C_{26}H_{26}NO_2P$ ($M^+ + H$): *m/z* 416.1780. Found: 416.1774.

Compound 45



Yield: 0.083 g (20%, white solid); $R_f = 0.5$ (EtOAc/ hexane; 2:3).

Mp: 98–100 °C (bubbling).

IR (KBr): 3052, 2959, 2921, 2855, 1726, 1622, 1589, 1436, 1216, 1195, 1118, 1063, 975, 762 cm^{-1}.

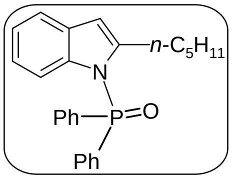
^1H NMR: δ 8.07-7.19 (m, 14H), 7.11 (s, 1H), 2.69-2.24 (m, 2H), 1.36 (br s, 6H), 0.94 (t, 3H).

^{13}C NMR: δ 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: δ 28.52.

HRMS (ESI): Calcd. for $C_{26}H_{26}NO_3P$ (M^+ + H): *m/z* 432.1729. Found: 432.1722.

Compound 46



Yield: 0.108 g (28%, brown gummy liquid); $R_f = 0.67$ (EtOAc/ hexane 2:3).

IR (neat): 3054, 2928, 2857, 1583, 1453, 1229, 1125, 1053, 729 cm^{-1}.

^1H NMR: δ 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).

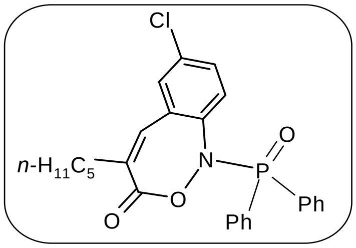
^{13}C NMR: δ 146.4, 139.6, 132.9, 132.4, 132.1, 132.0, 131.1, 130.9, 129.0, 128.9, 121.9, 121.6, 119.8, 114.3, 106.9_4, 106.8_8, 31.4, 29.7, 28.5, 22.4, 14.0.

^{31}P NMR: δ 26.11.

LC-MS *m/z* 388 $[M+1]^+$.

Anal. Calcd. for $C_{25}H_{26}NOP$: C, 77.50; H, 6.76; N, 3.62. Found: C, 77.65; H, 6.72; N, 3.71.

Compound 47



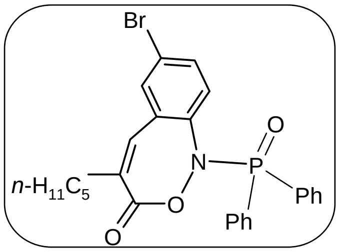
The procedure was similar to that for compound **27** using Ph_2PCl (**6**) (0.474 mL, 2.64 mmol), propargyl alcohol **11h** (0.62 g, 2.20 mmol) and NEt_3 (0.368 mL, 2.64 mmol). The reaction time was 4 h at 70 °C and the eluent was EtOAc/ hexane (2:3) to obtain compound **47** as a white crystalline solid.

Yield:	0.632 g (62%, white solid); $R_f = 0.43$ (EtOAc/ hexane; 2:3).
Mp:	142–144 °C (bubbling).
IR (KBr):	2953, 2915, 2871, 2844, 1737, 1479, 1441, 1370, 1216, 1118, 888 cm^{-1}.
^1H NMR:	δ 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).
^{13}C NMR:	δ 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:	δ 28.65.
HRMS (ESI):	Calcd. for $C_{26}H_{25}ClNO_3P$ ($M^+ + H$ and $M^+ + H + 2$): *m/z* 466.1340 and 468.1340. Found: 466.1337 and 468.1287.

Compounds 48-49

The procedure was similar to that for compound **27** using Ph_2PCl (**6**) (0.269 mL, 1.50 mmol), propargyl alcohol **11l** (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 EtOAc/ hexane (2:3) to obtain compounds **48** (eluted second), **49** (eluted first).

Compound 48



Yield: 0.294 g (26%, white solid); R_f = 0.5 (EtOAc/ hexane; 2:3).

Mp: 148–150 °C (bubbling).

IR (KBr): 3058, 2953, 2921, 2855, 1742, 1611, 1595, 1474, 1436, 1364, 1222, 1123, 1058, 992, 882 cm^{-1}.

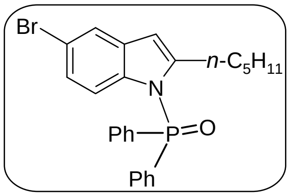
^{1}H NMR: δ 8.03-7.76 (m, 4H), 7.62-7.29 (m, 9H), 7.01 (s, 1H), 2.69-2.24 (m, 2H), 1.38-1.32 (m, 6H), 0.93 (t, 3H) (traces of solvent ethyl acetate could not be removed because it got converted to **42**).

^{13}C NMR: δ 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: δ 28.83.

HRMS (ESI): Calcd. for $C_{26}H_{25}BrNO_3P$ (M^+ + H and M^+ + H +2): *m/z* 510.0834 and 512.0834. Found: 510.0831 and 512.0815.

Compound 49



Yield: 0.637 g (62%, green gummy liquid); R_f = 0.59 (EtOAc/ hexane; 2:3).

IR (neat): 2959, 2926, 2844, 1589, 1436, 1271, 1227, 1123 cm^{-1}.

^{1}H NMR: δ 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 (1 s, 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*$_3$).

^{13}C NMR: δ 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.

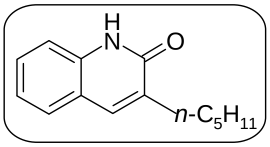
^{31}P NMR: δ 26.51.

HRMS (ESI): Calcd. for $C_{25}H_{25}BrNOP$ (M^+ + H and M^+ + H + 2): *m/z* 466.0936 and 468.0936. Found: 466.0936 and 468.0919.

Compounds 50-51

In a round bottomed flask equipped with 0.18 g (0.42 mmol) of phosphono-heterocycle **45**, toluene-water mixture (2 mL; 9:1 v/v) was added and the contents heated with stirring at 110 ^{0}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 (EtOAc/ hexane; 1:9) affording **50**. Compounds **51-52** were prepared similarly.

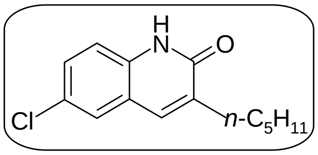
Compound 50



Yield: 0.054 g (59%); R_f = 0.55 (EtOAc/ hexane; 1:9); It is a known compound.[96] HRMS and X-ray structure were not reported for this compound. HRMS (ESI): Calcd. for $C_{14}H_{17}NO$ (M^+ + H): *m/z* 216.1389. Found: 216.1389.

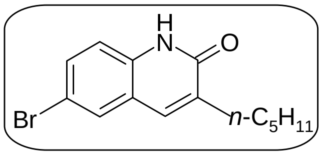
X-ray structure was determined for this compound.

Compound 51



Yield:	0.042 g (68%, white solid); By using 0.116 g, (0.25 mmol) of phosphono heterocycle **47**. R_f = 0.46 (EtOAc/ hexane; 1:9).
Mp:	158–160 ^{o}C.
IR (KBr):	3156, 2992, 2959, 2926, 2855, 1666, 1573, 1479, 1414, 1370, 1216, 1079, 942 cm^{-1}.
^{1}H NMR:	δ 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(C*H*$_2$)), 1.72-1.65 (m, 2H, C*H*$_2$), 1.42-1.39 (m, 4H, C*H*$_2$), 0.93 (t, 3H, C*H*$_3$).
^{13}C NMR:	δ 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):	Calcd. for $C_{14}H_{16}ClNO$ (M^+ + H and M^+ + H + 2): *m/z* 250.0999 and 252.0999. Found: 250.1000 and 252.0963.

Compound 52



Yield: 0.085 g [64%, by using 0.23 g, (0.47mmol) of phosphono heterocycle **48**, white solid]; $R_f = 0.53$ (EtOAc/ hexane; 1:9).

Mp: 148–150 °C.

IR (KBr): 3151, 2959, 2915, 2849, 1666, 1616, 1573, 1474, 1414, 1370, 1255, 1205, 1063, 932 cm^{-1}.

^{1}H NMR: δ 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).

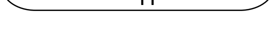
^{13}C NMR: δ 163.8 (*C*=O), 136.2, 135.9, 135.3, 132.2, 129.5, 121.9, 117.1, 115.0, 31.7, 30.3, 28.0, 22.6, 14.1.

HRMS (ESI): Calcd. for $C_{14}H_{16}BrNO$ (M^+ + H and M^+ + H + 2): *m/z* 294.0494 and 296.0494. Found: 294.0494 and 296.0477.

Compounds 29, 41, 53 and 54

In a round bottomed flask equipped with 0.20 g (0.51 mmol) of phosphonoindole **43,** 1.0 g of basic alumina, 3 mL of ethyl acetate was 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 (EtOAc/ hexane; 1:9) affording **29** as a white solid (known compound;[95] also see above). Yield: 0.086 g (88%). Compound **41** was prepared by passing **46** through alumina column using ethyl acetate/hexane (1:4). Yield: 0.084 g [87%; using 0.28 g (0.52 mmol) of phosphono-indole **46**].

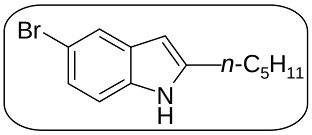
Compound 53



The phosphorus precursor (similar to **46**) [δ(P) 26.56] of **53** could be isolated in only 95% purity, but **53** could be readily obtained from this by passing through a basic alumina column.

Yield:	0.065 g [92%, by using 0.134 g (0.32 mmol) of corresponding phosphono indole pale yellow solid]; $R_f = 0.71$ (EtOAc/ hexane; 1:9).
Mp:	40–42 °C.
IR (KBr):	3403, 2932, 2849, 1463, 1447, 1408, 1085, 871 cm^{-1}.
^{1}H NMR:	δ 7.89 (br s, 1H, N*H*), 7.50 (1 s, 1H, Ar-*H*), 7.20-7.06 (m, 2H, Ar-*H*), 6.20 (1 s, 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).
^{13}C NMR:	δ 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):	Calcd. for $C_{13}H_{16}ClN$ (M^+ + H and M^+ + H +2): *m/z* 222.1050 and 224.1050. Found: 222.1046 and 224.1013.

Compound 54



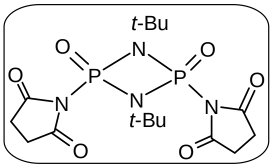
This was isolated by passing a solution of **49** in ethylacetate-hexane (1:9) through basic alumina column.

Yield:	0.159 g (93%, pale yellow solid); By using 0.3 g (0.64 mmol) of phosphono indole **49**. $R_f = 0.67$ (EtOAc/ hexane; 1:9).
Mp:	46–48 °C.
IR (KBr):	3397, 2959, 2921, 2849, 1567, 1452, 1408, 1315, 1260, 1052, , 877 cm^{-1}.
^{1}H NMR:	δ 7.86 (br s, 1H, N*H*), 7.68 (1 s, 1H, Ar-*H*), 7.23-7.12 (m, 2H, Ar-*H*), 6.20 (1 s, 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).
^{13}C NMR:	δ 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):	Calcd. for $C_{13}H_{16}BrN$ (M^+ + H and M^+ + H +2): *m/z* 266.0545 and 268.0545. Found: 266.0545 and 268.0525.

3.4 Synthesis of phosphorus-nitrogen bonded compounds 55-58

3.41 Synthesis of cis-{[-C(=O)-CH$_2$-CH$_2$-C(=O)-]-N-P(=O)-N-t-Bu}$_2$(cis-55) and cis- and trans-{[-C(=O)-C$_6$H$_4$-C(=O)-]-N-P(=O)-N-t-Bu}$_2$ (cis-56 and trans-56)

Compound cis-55



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 ^{0}C for 5 min, and then [ClP-N(*t*-Bu)]$_2$ (**1**)[51] (0.985 g, 3.58 mmol) dissolved in THF (20 mL) was added drop-wise at 0 ^{0}C (20 min). The mixture was warmed to rt (25 ^{o}C) and then heated with stirring at 60 ^{0}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 ***cis*-55** settled down at the bottom of the flask. This compound was crystallized from ethyl acetate-chloroform mixture (1:2).

Yield:	1.14 g (74%, white solid); R$_f$ = 0.48 (EtOAc/ hexane; 1:3).
Mp:	210–214 ^{o}C.
IR (KBr):	2984, 1734, 1476, 1431, 1373, 1281, 1223, 1111, 1047, 1020, 995, 943, 910, 824 cm^{-1}.
^{1}H NMR:	δ 2.77 (s, 8H), 1.46 (s, 18H).
^{13}C NMR:	δ 175.8, 58.3, 30.1, 29.8.
^{31}P NMR:	δ -17.34.

HRMS (ESI): Calcd. for $C_{16}H_{26}N_4O_6P_2$ (M$^+$ + H): *m/z* 433.1407. Found: 433.1407.

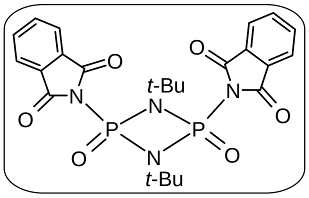
X-ray structure was determined for this compound.

Compounds cis-56 and trans-56

To a solution of N-hydroxy phthalimide (0.494 g, 3.02 mmol) and NEt$_3$ (0.46 mL, 3.33 mmol) in THF (20 mL) was added [ClP-N(*t*-Bu)]$_2$ (**1**)[51] (0.417 g, 1.51 mmol) dissolved in THF (10 mL) drop-wise at 0 ^{o}C over a period of 15 min. Then the contents were brought to room temperature and stirred for 24 h. After removal of amine hydrochloride (filtration) and solvent, the crude product was purified by column chromatography

(EtOAc/ hexane 2:3) to afford cis-56 followed by *trans*-**56**. *Cis*-**56** was crystallized from ethyl acetate and *trans*-**56** was crystallized from dichloromethane**.**

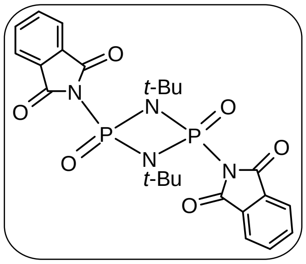
Compound cis-56



Yield:	0.115 g (14%, white solid).
Mp:	248–250 °C.
IR (KBr):	3090, 3047, 2970, 2871, 1781, 1737, 1600, 1468, 1364, 1293, 1255, 1167, 1085, 1003, 904, 866 cm^{-1}.
^{1}H NMR:	δ 7.90-7.88 (m, 4H), 7.84-7.82 (m, 4H), 1.52 (s, 18H).
^{13}C NMR:	δ 166.6, 135.3, 132.2, 124.3, 58.0, 30.1.
^{31}P NMR:	δ -17.40.
HRMS (ESI):	Calcd. for $C_{24}H_{26}N_4O_6P_2$ (M$^+$ + H): *m/z* 529.1407. Found: 529.1407.

X-ray structure was determined for this compound.

Compound trans-56



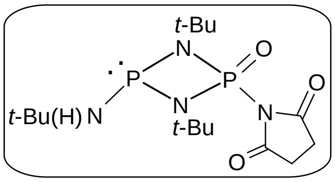
Yield:	0.651 g (82%, white solid).
Mp:	250–252 °C.
IR (KBr):	3083, 2976, 2928, 1794, 1748, 1717, 1645, 1599, 1468, 1373, 1300, 1265, 1192, 1148, 1051, 1015, 916 cm^{-1}.
^{1}H NMR:	δ 8.04-8.02 (m, 4H), 7.88-7.86 (m, 4H), 1.39 (s, 18H).
^{13}C NMR:	δ 166.2, 135.5, 132.3, 124.7, 56.8, 30.0.
^{31}P NMR:	δ -20.36.
HRMS (ESI):	Calcd. for $C_{24}H_{26}N_4O_6P_2$ (M$^+$ + H): *m/z* 529.1407. Found: 529.1406.

X-ray structure was determined for this compound.

3.42 Synthesis of cis- and trans- [(t-BuNH)P(μ-N-t-Bu)$_2$P(=O)-N{-C(=O)-CH$_2$-CH$_2$-C(=O)-}] (cis-57 and trans-57)

The procedure was similar to that for compounds **56** using [(*t*-BuNH)P(*μ*-N-*t*-Bu)$_2$P-Cl] (**4**)[53] [0.65 g, 2.09 mmol] and *N*-hydroxysuccinimide (0.24 g, 2.09 mmol). After removing solvent, the residue was purified by column chromatography (EtOAc/ hexane; 1:1) to afford pure *cis*-**57** followed by *trans*-**57**.

Compound cis-57



Yield: 0.572 g (70%, white solid).

Mp: 212–216 °C.

IR (KBr): 3308, 2971, 2934, 2872, 1771, 1721, 1466, 1427, 1395, 1366, 1296, 1213, 1121, 1086, 1034, 1007, 930, 887, 853 cm^{-1}.

^{1}H NMR: δ 5.15 (d, J = 6.8 Hz, 1H), 2.73 (s, 4H), 1.30 (s, 27H).

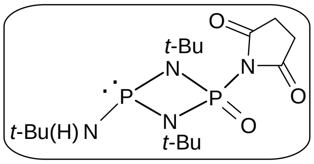
^{13}C NMR: δ 176.7, 53.4 (d, J ~ 8.0 Hz), 51.3 (d, J ~ 17.0 Hz), 32.6 (d, J = 10.0 Hz), 31.0, 29.5 (d, J = 4.0 Hz).

^{31}P NMR: δ 90.41, -10.47.

HRMS (ESI): Calcd. for $C_{16}H_{32}N_4O_3P_2$ (M^+ + H): *m/z* 391.2029. Found: 391.2028.

X-ray structure was determined for this compound.

Compound trans-57



Yield: 0.151 g (19%, white solid).

Mp: 152–254 °C.

IR (KBr): 3306, 2973, 2922, 2853, 1740, 1709, 1644, 1470, 1439, 1370, 1292, 1215, 1103, 999, 918, 885, 851 cm^{-1}.

^{1}H NMR: δ 3.44 (d, J = 4.8 Hz, 1H), 2.70 (s, 4H), 1.33, 1.30 (2 s, 27H).

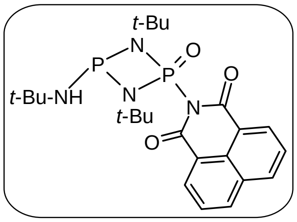
^{13}C NMR: δ 172.3, 53.1 (d, *J* ~ 6.0 Hz), 52.1 (d, *J* ~ 16.0 Hz), 32.7 (d, *J* = 9.0 Hz), 31.0, 25.5.

^{31}P NMR: δ 73.30 (d, *J* = 6.4 Hz), -11.15 (d, *J* = 6.4 Hz).

HRMS (ESI): Calcd. for $C_{16}H_{32}N_4O_3P_2$ (M^+ + H): *m/z* 391.2029. Found: 391.2028.

3.43 Synthesis of cis [(t-BuNH)P(μ-N-t-Bu)$_2$P(=O)-N{-C(=O)-C$_{10}$H$_6$-C(=O)-}] (cis-58)

Procedure was similar to that for **56** using cyclodiphosphazane [(*t*-BuNH)P(*μ*-N-*t*-Bu)$_2$P-Cl] (**4**) [0.35 g, 1.12 mmol], *N*-hydroxy-1,8-naphthalimide (0.239 g, 1.12 mmol) and NEt_3 (0.16 mL, 1.12 mmol). The product was isolated by column chromatography (EtOAc/ hexane; 1:1) as a pale yellow solid *cis*-**58**.



Yield: 0.375 g (68%, pale yellow solid).

Mp: 178–182 °C.

IR (KBr): 3279, 2969, 2928, 2866, 1676, 1632, 1588, 1559, 1510, 1468, 1372, 1316, 1208, 1142, 1092, 1038, 1011, 943, 880, 762 cm^{-1}.

^{1}H NMR: δ 8.66 (d, *J* = 7.6 Hz, 1H, Ar-*H*), 8.59 (d, *J* = 7.2 Hz, 1H, Ar-*H*), 8.28 (d, *J* = 3.2 Hz, 1H, Ar-*H*), 8.26 (d, *J* = 3.2 Hz, 1H, Ar-*H*), 7.82 (t, 1H, Ar-*H*), 7.74 (t, 1H, Ar-*H*), 6.66 (d, *J* = 7.6 Hz, 1H, *t*-BuN*H*), 1.41 and 1.37 (2 s, 27H, C(C*H*$_3$)$_3$).

^{13}C NMR: δ 173.0 (*C*=O), 166.7 (d, *J* = 7.6 Hz, (*C*=O)-H-N), 135.4, 134.6, 132.7, 131.6, 131.1, 130.1, 127.8, 127.1, 123.8, 119.1$_3$, 119.1, (Ar-*C*), 53.2 (d, ^{2}*J*(P-C) ~ 8.0 Hz, *C*(CH$_3$)$_3$), 51.9 (d, ^{2}*J*(P-C) ~ 18.0 Hz, *C*(CH$_3$)$_3$), 32.2 (d, ^{3}*J*(P-C) = 11.0 Hz, C(*C*H$_3$)$_3$), 31.2 (1 s, C(*C*H$_3$)$_3$).

^{31}P NMR: δ 82.10 (1 s, 1P, (*P*-NH*t*-Bu), -8.93 (1 s, 1P, *P*-N).

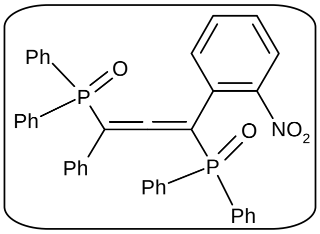
HRMS (ESI): Calcd. for $C_{24}H_{34}N_4O_3P_2$ (M^+ + H): *m/z* 489.2185. Found: 489.2184.

3.5 Reactions of Ph$_2$PCl (6) with *o*-nitro functionalized propargyl alcohols

3.51 Synthesis of bisphosphorylated allenylphosphine oxides [60-69]

An oven dried 25 mL round-bottomed flask was charged with propargyl alcohol **11a**^{28} (0.34 g, 1.36 mmol), NEt$_3$ (0.4 mL, 2.85 mmol) and dry THF (5 mL). The mixture was stirred at 0 ^{0}C for 5 min. To this, chlorodiphenylphosphine (**6**) (0.51 mL, 2.85 mmol) dissolved in dry THF (5 mL) was added drop-wise at 0 ^{o}C over a period of 15 min. Then the mixture was stirred at 0 ^{0}C for 1-2 h. Filtration followed by removal of the solvent and purification by column chromatography (hexane/ethyl acetate; 2:1) afforded **60**. Similarly, compounds **61-69** were prepared.

Compound 60



Yield: 0.797 g (92%, white solid).

Mp: 176–178 ^{o}C.

IR (KBr): 3057, 2924, 2853, 1935, 1738, 1593, 1526, 1435, 1346, 1198, 1117, 750 cm^{-1}.

^{1}H NMR: δ 7.99-7.94 (m, 2H, Ar-*H*), 7.90 (dd, *J* = 7.6, 2.0 Hz, 1H, Ar-*H*), 7.58-7.19 (m, 25H, Ar-*H*), 6.77 (d, *J* = 7.2 Hz, 1H, Ar-*H*).

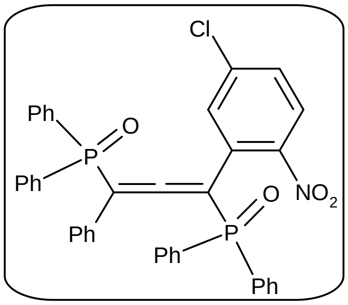
^{13}C NMR: δ 210.4 (C=*C*=C), 148.0, 132.9, 132.6, 132.5, 132.4, 132.2, 131.9, 131.7, 131.6, 130.9, 130.6, 130.3, 130.0, 129.3, 129.0, 128.8, 128.6, 128.5, 128.4, 128.2, 126.0, 124.8 (Ar-*C*), 104.9 (dd, ^1J(P-C) = 90.0 Hz, ^3J(P-C) = 12.9 Hz, P-*C*), 102.0 (dd, ^1J(P-C) = 90.7 Hz, ^3J(P-C) = 14.9 Hz, P-*C*).

^{31}P NMR: δ 27.10 (d, *J* = 12.8 Hz), 26.83 (d, *J* = 12.8 Hz).

LC-MS: *m/z* 638 [M+1]$^+$.

Anal. Calcd. for $C_{39}H_{29}NO_4P_2$: C, 73.47; H, 4.58; N, 2.20. Found: C, 73.65; H, 4.51; N, 2.28.

Compound 61



Propargyl alcohol **11f**[78] (0.31 g, 1.06 mmol) was used.

Yield: 0.653 g (91%, white solid).

Mp: 164–166 °C.

IR (KBr): 3052, 2926, 2855, 1940, 1600, 1529, 1441, 1337, 1200, 1112, 948 cm^{-1}.

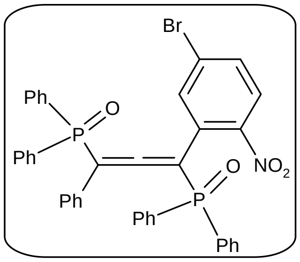
^{1}H NMR: δ 7.96-7.91 (m, 2H, Ar-*H*), 7.80 (d, *J* = 8.8 Hz, 1H, Ar-*H*), 7.59-7.19 (m, 24H, Ar-*H*), 6.50 (1 s, 1H, Ar-*H*).

^{13}C NMR: δ 210.0 (t, *J* ~ 6.0 Hz, C=*C*=C), 146.1, 139.2, 132.7, 132.5, 132.4, 132.3, 132.2, 132.1, 132.0, 131.6, 131.5, 129.3, 128.9, 128.8, 128.7, 128.6, 128.4, 128.3, 127.8, 126.0 (Ar-*C*), 105.5 (dd, ^1J(P-C) = 88.0 Hz, ^3J(P-C) = 13.0 Hz, P-*C*), 101.4 (dd, ^1J(P-C) = 91.0 Hz, ^3J(P-C) = 14.0 Hz, P-*C*).

^{31}P NMR: δ 27.14 (d, *J* = 13.5 Hz), 26.80 (d, *J* = 13.5 Hz).

HRMS (ESI): Calcd. for $C_{39}H_{28}ClNO_4P_2$ (M^+ + H and M^+ + H +2): *m/z* 672.1261 and 674.1261. Found: 672.1260 and 674.1245.

Compound 62



Propargyl alcohol **11j** (0.32 g, 0.96 mmol) was used.

Yield: 0.595 g (86%, white solid).

Mp: 158–160 °C.

IR (KBr): 3052, 2926, 2849, 1934, 1595, 1562, 1529, 1436, 1347, 1205, 1118, 1074, 926 cm^{-1}.

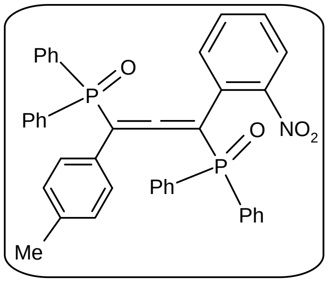
^{1}H NMR: δ 7.95-7.90 (m, 2H, Ar-*H*), 7.74 (d, *J* = 8.8 Hz, 1H, Ar-*H*), 7.60-7.20 (m, 24H, Ar-*H*), 6.70 (1 s, 1H, Ar-*H*).

^{13}C NMR: δ 210.1 (t, *J* ~ 6.0 Hz, C=*C*=C), 146.7, 135.1, 132.7, 132.6, 132.5, 132.4, 132.3, 132.2, 132.1, 131.9, 131.7_0, 131.6_6, 131.6, 131.4, 131.3, 130.9, 130.6, 130.3, 130.0_8, 130.0_5, 129.8_2, 129.7_7, 129.7, 129.0_1, 128.9_8, 128.9, 128.7_9, 128.7_5, 128.7, 128.5, 128.3, 127.9, 127.7, 126.1 (Ar-*C*), 105.6 (dd, ^1J(P-C) = 90.0 Hz, ^3J(P-C) = 12.5 Hz, P-*C*), 101.3 (dd, ^1J(P-C) = 91.5 Hz, ^3J(P-C) = 13.5 Hz, P-*C*).

^{31}P NMR: δ 27.23 (d, *J* = 13.0 Hz), 26.83 (d, *J* = 13.0 Hz).

HRMS (ESI): Calcd. for $C_{39}H_{28}BrNO_4P_2$ (M^+ + H and M^+ + H +2): *m/z* 716.0756 and 718.0756. Found: 716.0777 and 718.0766.

Compound 63



Propargyl alcohol **11e** (0.31 g, 1.16 mmol) was used.

Yield: 0.711 g (94%, white solid).

Mp: 190–192 °C.

IR (KBr): 3052, 2997, 2953, 2915, 1934, 1600, 1573, 1523, 1436, 1348, 1195, 1123, 997, 904 cm^{-1}.

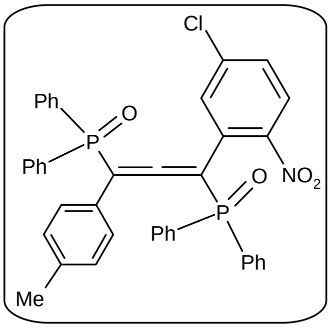
^{1}H NMR: δ 7.99-7.94 (m, 2H, Ar-*H*), 7.87 (dd, *J* = 6.8 Hz, *J* = 2.4 Hz, 1H, Ar-*H*), 7.60-7.01 (m, 24H, Ar-*H*), 6.83 (d, *J* = 6.8 Hz, 1H, Ar-*H*), 2.29 (s, 3H, CH_3).

^{13}C NMR: δ 210.5 (t, *J* = 6.0 Hz, C=*C*=C), 148.1, 138.4, 132.8, 132.6, 132.5, 132.4, 132.2, 132.1, 131.8, 131.7, 131.6, 131.0_3, 130.9_7, 130.8, 130.4, 129.4, 129.2, 128.8, 128.7_1, 128.6_6, 128.5_9, 128.5_5, 128.3, 128.2, 126.8, 126.1, 124.7 (Ar-*C*), 104.9 (dd, ^1J(P-C) = 95.0 Hz, ^3J(P-C) = 8.0 Hz, P-*C*), 101.8 (dd, ^1J(P-C) = 97.5 Hz, ^3J(P-C) = 9.5 Hz, P-*C*), 21.3 (*C*H_3).

^{31}P NMR: δ 27.01 and 26.84 (AB quartet, *J* ~ 13.0 Hz).

HRMS (ESI): Calcd. for $C_{40}H_{31}NO_4P_2$ (M^+ + H): *m/z* 652.1807. Found: 652.1804.

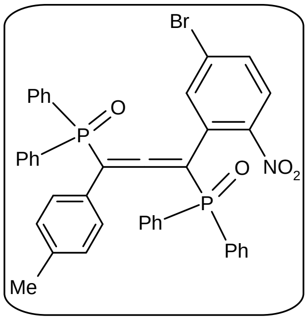
Compound 64



Propargyl alcohol **11i** (0.35 g, 1.16 mmol) was used.

Yield:	0.713 g (89%, white solid).
Mp:	180–182 °C.
IR (KBr):	3058, 2926, 2849, 1918, 1600, 1556, 1523, 1436, 1342, 1195, 1112, 937 cm^{-1}.
^{1}H NMR:	δ 7.94-7.89 (m, 2H, Ar-*H*), 7.75 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 7.56-7.00 (m, 23H, Ar-*H*), 6.55 (1 s, 1H, Ar-*H*), 2.24 (1 s, 3H, CH_3).
^{13}C NMR:	δ 210.0 (t, *J* ~ 6.0 Hz, C=*C*=C), 146.1, 139.0, 138.5, 132.5, 132.3, 132.2_4, 132.1_5, 132.0, 131.9, 131.7, 131.5, 131.4, 131.2, 130.7, 130.5, 130.2, 129.3, 129.2, 128.9, 128.7, 128.5, 128.3, 128.2, 127.7, 126.4, 125.9 (Ar-*C*), 105.3 (dd, ^1J(P-C) = 90.0 Hz, ^3J(P-C) = 12.0 Hz, P-*C*), 101.0 (dd, ^1J(P-C) = 93.0 Hz, ^3J(P-C) = 13.0 Hz, P-*C*), 21.1 (PhCH_3).
^{31}P NMR:	δ 27.25 (d, *J* ~ 13.0 Hz), 26.76 (d, *J* ~ 13.0 Hz).
HRMS (ESI):	Calcd. for $C_{40}H_{30}ClNO_4P_2$ (M^+ + Na and M^+ + Na +2): *m/z* 708.1237 and 710.1237. Found: 708.1236 and 710.1219.

Compound 65



Propargyl alcohol **11m** (0.30 g, 0.86 mmol) was used.

Yield: 0.577 g (91%, white solid).

Mp: 184–186 °C.

IR (KBr): 3052, 2921, 2855 1912, 1595, 1556, 1523, 1436, 1348, 1200, 1118, 932 cm^{-1}.

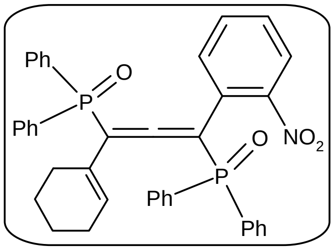
^{1}H NMR: δ 7.91-7.02 (m, 26H, Ar-*H*), 6.74 (1 s, 1H, Ar-*H*), 2.24 (1 s, 3H, CH_3).

^{13}C NMR: δ 210.0 (t, *J* ~ 6.0 Hz, C=*C*=C), 146.6, 138.5, 134.9, 132.5, 132.3_4, 132.2_5, 132.2, 132.0, 131.9, 131.7, 131.5, 131.4, 131.3, 130.7, 130.5, 130.2, 130.0, 129.3, 128.9, 128.7, 128.6, 128.3, 128.2, 127.8, 127.5, 126.4, 125.9 (Ar-*C*), 105.3 (dd, ^1J(P-C) = 90.0 Hz, ^3J(P-C) = 12.0 Hz, P-*C*), 100.9 (dd, ^1J(P-C) = 93.5 Hz, ^3J(P-C) = 12.5 Hz, P-*C*), 21.1 (Ph*C*H_3).

^{31}P NMR: δ 27.41 (d, *J* = 13.1 Hz), 26.79 (d, *J* = 13.1 Hz).

HRMS (ESI): Calcd. for $C_{40}H_{30}BrNO_4P_2$ (M^+ + Na and M^+ + Na +2); *m/z* 752.0731 and 754.0731. Found: 752.0733 and 754.0723.

Compound 66



Propargyl alcohol **11c** [28] (0.45 g, 1.75 mmol) was used.

Yield: 1.061 g (94%, white solid).

Mp: 180–182 °C.

IR (KBr): 3052, 2921, 2855, 1918, 1611, 1573, 1529, 1479, 1436, 1342, 1195, 1118, 997 cm^{-1}.

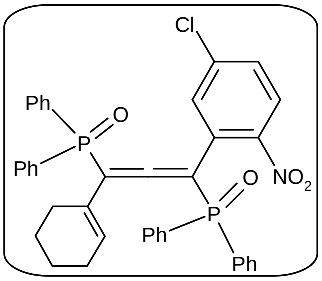
^{1}H NMR: δ 8.02-7.97 (m, 2H, Ar-*H*), 7.85 (d, *J* = 7.6 Hz, 1H, Ar-*H*), 7.67-7.29 (m, 20H, Ar-*H*), 6.77 (d, *J* = 7.2 Hz, 1H, Ar-*H*), 5.76 (br s, 1H, =C*H*), 1.94-1.89 (m, 4H, CH_2), 1.55-1.45 (m, 4H, CH_2).

^{13}C NMR: δ 210.1 (t, *J* ~ 6.0 Hz, C=*C*=C), 148.0, 132.6, 132.5_1, 132.4_7, 132.4, 132.3, 132.2, 131.9, 131.8, 131.7, 131.6, 131.5, 131.4, 131.3, 130.8, 129.7, 128.9, 128.5, 128.4, 128.2, 128.1, 127.8, 126.4, 124.5 (Ar-*C*), 106.3 (dd, ${}^1J$(P-C) = 90.5 Hz, ${}^3J$(P-C) = 11.5 Hz, P-*C*), 101.8 (dd, ${}^1J$(P-C) = 95.0 Hz, ${}^3J$(P-C) = 13.0 Hz, P-*C*), 28.4, 25.9, 22.6 and 21.4 (*C*H_2).

^{31}P NMR: δ 27.12 (d, *J* = 13.8 Hz), 25.93 (d, *J* = 13.8 Hz).

HRMS (ESI): Calcd. for $C_{39}H_{33}NO_4P_2$ (M^+ + H): *m/z* 642.1964. Found 642.1964.

Compound 67



Propargyl alcohol **11g**[28] (0.36 g, 1.22 mmol) was used.

Yield: 0.752 g (91%, white solid).

Mp: 148–150 °C.

IR (KBr): 3058, 2926, 2860, 1907, 1595, 1562, 1534, 1441, 1342, 1195, 1112, 932 cm^{-1}.

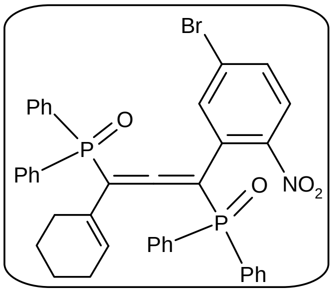
^{1}H NMR: δ 7.99-7.94 (m, 2H, Ar-*H*), 7.76 (d, *J* = 8.8 Hz, 1H, Ar-*H*), 7.64-7.30 (m, 19H, Ar-*H*), 6.49 (1 s, 1H, Ar-*H*), 5.84 (br s, 1H, =C*H*), 1.93 (br, 4H, CH_2), 1.55-1.45 (m, 4H, CH_2).

^{13}C NMR: δ 209.7 (t, *J* ~ 6.0 Hz, C=*C*=C), 146.1, 139.0, 132.6, 132.4, 132.3, 132.2_4, 132.1_5, 132.1, 132.0, 131.9, 131.7, 131.6, 131.4, 131.3_2, 131.2_8, 131.0, 130.5, 129.5, 129.1, 128.7, 128.6_7, 128.6_5, 128.5_9, 128.5_5, 128.5, 128.4, 128.3, 128.2, 127.6_3, 127.5_8, 127.5, 125.9 (Ar-*C*), 107.1 (dd, ${}^1J$(P-C) = 90.0 Hz, ${}^3J$(P-C) = 11.2 Hz, P-*C*), 101.2 (dd, ${}^1J$(P-C) = 95.5 Hz, ${}^3J$(P-C) = 12.5 Hz, P-*C*), 28.5, 26.1, 22.7 and 21.5 (*C*H_2).

^{31}P NMR: δ 27.55 (d, *J* = 13.4 Hz), 25.59 (d, *J* = 13.4 Hz).

HRMS (ESI): Calcd. for $C_{39}H_{32}ClNO_4P_2$ (M^+ + Na and M^+ + Na +2): *m/z* 698.1393 and 700.1393. Found: 698.1391 and 700.1373.

Compound 68



Propargyl alcohol **11k** (0.22 g, 0.65 mmol) was used.

Yield: 0.433 g (93%, white solid).

Mp: 188–190 °C.

IR (KBr): 3052, 2926, 2855, 1912, 1595, 1562, 1534, 1436, 1353, 1205, 1123, 932 cm^{-1}.

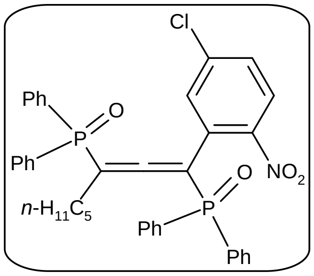
^{1}H NMR: δ 7.99-7.94 (m, 2H, Ar-*H*), 7.70-7.31 (m, 20H, Ar-*H*), 6.69 (1 s, 1H, Ar-*H*), 5.85 (br s, 1H, =C*H*), 1.93 (br, 4H, CH_2), 1.55-1.46 (m, 4H, CH_2).

^{13}C NMR: δ 209.7 (t, *J* ~ 6.0 Hz, C=*C*=C), 146.7, 134.9, 132.5, 132.3, 132.2, 132.1_2, 132.0_6, 132.0, 131.9, 131.8, 131.6, 131.5_4, 131.4_8, 131.4, 131.3, 131.2, 130.9, 130.4, 129.4, 128.7, 128.6, 128.5_3, 128.4_9, 128.3, 128.2, 127.5, 127.4, 125.9 (Ar-*C*), 107.0 (dd, ^1J(P-C) = 90.0 Hz, ^3J(P-C) = 11.0 Hz, P-*C*), 101.0 (dd, ^1J(P-C) = 95.5 Hz, ^3J(P-C) = 12.5 Hz, P-*C*), 28.5, 26.0, 22.6 and 21.4 (CH_2).

^{31}P NMR: δ 27.58 (d, *J* = 13.4 Hz), 25.64 (d, *J* = 13.4 Hz).

HRMS (ESI): Calcd. for $C_{39}H_{32}BrNO_4P_2$ (M^+ + Na and M^+ + Na +2): *m/z* 742.0888 and 744.0888. Found: 742.0889 and 744.0880.

Compound 69



Propargyl alcohol **11h** (0.45 g, 1.61 mmol) was used.

Yield: 0.946 g (88%, white solid).

Mp: 124–126 °C.

IR (KBr): 3063, 2959, 2926, 2849, 1934, 1595, 1567, 1523, 1468, 1436, 1353, 1195, 1129, 1003, 937 cm^{-1}.

^{1}H NMR: δ 8.04-7.99 (m, 2H, Ar-*H*), 7.80 (d, *J* = 8.8 Hz, 1H, Ar-*H*), 7.67-7.30 (m, 19H, Ar-*H*), 6.86 (1 s, 1H, Ar-*H*), 2.08-2.01 (m, 2H, CH_2), 1.27-1.07 (m, 6H, CH_2), 0.78 (t, 3H, CH_3).

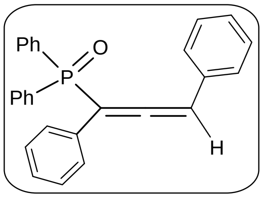
^{13}C NMR: δ 209.0 (t, *J* ~ 6.0 Hz, C=*C*=C), 146.6, 139.1, 132.7, 132.6, 132.5, 132.4, 132.2_2, 132.2_0, 132.1_4, 132.1_1, 131.9, 131.8, 131.7, 131.6, 131.5, 131.4, 131.2, 130.8, 130.5, 130.3, 130.1, 129.4, 129.1, 128.8, 128.7, 128.5, 128.4, 126.0 (Ar-*C*), 102.8 (dd, ^1J(P-C) = 90.5 Hz, ^3J(P-C) = 10.5 Hz, P-*C*), 100.1 (dd, ^1J(P-C) = 97.0 Hz, ^3J(P-C) = 13.0 Hz, P-*C*), 31.7, 28.7, 28.3 and 22.2 (*C*H_2), 13.9 (*C*H_3).

^{31}P NMR: δ 28.27 (d, *J* = 13.8 Hz), 26.53 (d, *J* = 13.8 Hz).

HRMS (ESI): Calcd. for $C_{38}H_{34}ClNO_4P_2$ (M^+ + Na and M^+ + Na +2): *m/z* 688.1550 and 690.1550. Found: 688.1551 and 690.1533.

3.52 Synthesis of allenylphosphine oxides 70 and 72

Compound 70



This compound was prepared by following a procedure similar to that for **60** using propargyl alcohol **12b** (0.35 g, 1.70 mmol).

Yield: 0.613 g (92%, white solid).

Mp: 146–148 °C.

IR (KBr): 3085, 3052, 3030, 1923, 1655, 1595, 1490, 1436, 1381, 1118, 1074, 926, 827 cm^{-1}.

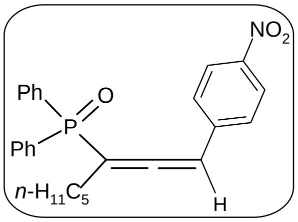
^{1}H NMR: δ 7.83-7.70 (m, 6H, Ar-*H*), 7.46-7.12 (m, 14H, Ar-*H*), 6.30 (d, *J* = 10.8 Hz, 1H, C*H*).

^{13}C NMR: δ 212.9 (d, ^2J(P-C) = 5.0 Hz, C=*C*=C), 132.9, 132.5, 131.9, 131.8, 131.7, 131.6, 131.5, 128.7_0, 128.6_8, 128.3_2, 128.2_7, 128.2, 128.1, 127.9, 127.8, 126.9 (Ar-*C*), 105.4 (d, ^1J(P-C) = 98.0 Hz, P*C*), 98.4 (d, ^3J(P-C) = 13.0 Hz, *C*H).

^{31}P NMR: δ 29.64.

HRMS (ESI): Calcd. for $C_{27}H_{21}OP$ (M^+ + H): *m/z* 393.1409. Found 393.1410.

Compound 72



This compound was prepared by following a procedure similar to that for **60** using propargyl alcohol **71** (0.25 g, 0.99 mmol).

Yield: 0.346 g (81%, yellow liquid).

IR (neat): 3058, 2959, 2932, 2860, 1929, 1595, 1512, 1436, 1342, 1195, 1118, 866 cm^{-1}.

^{1}H NMR: δ 8.10 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 7.79-7.65 (m, 4H, Ar-*H*), 7.55-7.31 (m, 6H, Ar-*H*), 7.18 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 6.17 (d, *J* = 10.4 Hz, 1H, C*H*), 2.50-2.36 (m, 2H, CH_2), 1.59-1.51 (m, 2H, CH_2), 1.33-1.21 (m, 4H, CH_2), 0.80 (t, 3H, CH_3).

^{13}C NMR: δ 209.8 (^2J(P-C) = 6.0 Hz, C=*C*=C), 146.8, 140.1, 132.3, 132.1, 132.0, 131.6, 131.5, 131.4, 131.3, 130.9, 130.5, 128.6, 128.5, 128.4, 128.3, 127.0, 124.0 (Ar-*C*), 104.6 (d, ^1J(P-C) = 95.0 Hz, P*C*), 96.1 (d, ^3J(P-C) = 13.0 Hz, *C*H), 31.3, 28.0$_9$, 28.0$_6$ and 22.3 (CH_2), 13.9 (CH_3).

^{31}P NMR: δ 29.27.

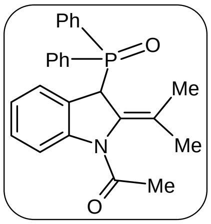
HRMS (ESI): Calcd. for $C_{26}H_{26}NO_3P$ (M^+ + Na): *m/z* 454.1548. Found: 454.1549.

3.6 Synthesis of phosphorus based indoles [73-92]

3.61 Synthesis of N-protected phosphinoyl indoles 73 and 75-76

A mixture of *N*-acylated allenylphosphine oxide **20a** (0.48 g, 1.19 mmol), K_3PO_4 (0.13 g, 0.59 mmol) and tetrahydrofuran (10 mL) was stirred at 80 °C for 12 h. After completion of the reaction (TLC), the solvent was removed under reduced pressure. Purification the resulting product by column chromatography (hexane: ethyl acetate 1:1) afforded the desired product **73**. Compounds **75-76** were isolated using same method using the same molar quantity of *N*-benzoylated allenylphosphine oxide **20d.**

Compound 73



Yield: 0.44 g (92%, white solid).

Mp: 218–220 °C.

IR (KBr): 3052, 2980, 2931, 1660, 1588, 1468, 1435, 1369, 1336, 1287, 1194, 1117, 871 cm^{-1}.

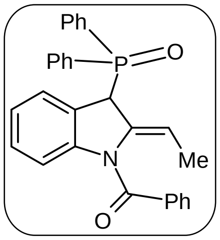
^{1}H NMR: δ 7.85-7.18 (m, 12H, Ar-*H*), 6.85 (t, 1H, Ar-*H*), 6.30 (br s, 1H, Ar-*H*), 4.73 (d, *J* = 16.4 Hz, 1H, PC*H*), 2.01 (br s, 3H, C*H*$_3$), 1.64 (d, *J* = 5.2 Hz, 3H, C*H*$_3$), 1.54 (br s, 3H, C*H*$_3$).

^{13}C NMR: δ 169.6 (*C*O), 145.0 (d, *J* = 3.0 Hz), 132.5, 132.3$_3$, 132.2$_5$, 131.5$_4$, 131.4$_5$, 128.6, 128.5, 128.3, 128.2, 126.3, 124.3, 124.0, 118.3, 48.3 (d, *J* = 62.0 Hz, P*C*H), 22.2 (*C*H$_3$), 21.5 and 20.5 (*C*H$_3$).

^{31}P NMR: δ 26.69.

HRMS (ESI): Calcd. for $C_{25}H_{24}NO_2P$ (M$^+$ + H): *m/z* 402.1624. Found: 402.1627.

Compound 75



Yield: 0.12 g [60%, by using 0.20 g (0.44 mmol) of allene **20d**, white solid]; R_f = 0.55 (hexane/EtOAc 1:1).

Mp: 184–186 °C.

IR (KBr): 3052, 2937, 1682, 1616, 1589, 1578, 1474, 1436, 1386, 1315, 1293, 1205, 1118, 932 cm^{-1}.

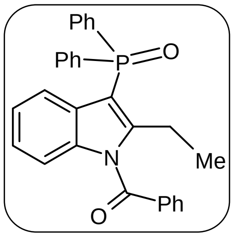
^{1}H NMR: δ 7.87-7.28 (m, 16H, Ar-*H*), 7.11 (t, 1H, Ar-*H*), 6.80 (t, 1H, Ar-*H*), 6.44 (d, *J* = 7.2 Hz, 1H, Ar-*H*), 5.37 (m, 1H, C*H*), 4.86 (d, *J* = 14.4 Hz, 1H, PC*H*), 1.36 (dd, *J* = 12.0 Hz, 1.6 Hz, 3H, CH_3).

^{13}C NMR: δ 168.5 (*C*O), 136.5 (d, *J* = 9.0 Hz), 144.7 (d, *J* = 4.0 Hz), 135.9, 132.7, 132.4, 132.3, 132.1, 131.9, 131.8, 131.2, 130.9, 129.7, 128.8, 128.6_9, 128.6_5, 128.6, 128.5, 128.2, 125.3 (d, *J* = 6.0 Hz), 125.0 (d, *J* = 3.0 Hz), 123.5, 116.0 (d, *J* = 9.0 Hz), 116.4, 47.3 (d, *J* = 62.0 Hz, P*C*H), 13.4 (d, *J* = 2.0 Hz, CH_3).

^{31}P NMR: δ 27.31.

HRMS (ESI): Calcd. for $C_{29}H_{24}NO_2P$ (M^+ + Na): *m/z* 472.1443. Found: 472.1443.

Compound 76



Yield: 0.06 g [31%, by using 0.20 g (0.44 mmol) of allene **20d** white solid]; R_f = 0.45 (hexane/EtOAc 1:1).

Mp: 168–170 °C.

IR (KBr): 3052, 2964, 2926, 2855, 1699, 1595, 1523, 1452, 1353, 1310, 1266, 1189, 1118, 1074, 975 cm^{-1}.

^{1}H NMR: δ 7.81-7.47 (m, 15H, Ar-*H*), 6.99 (t, 1H, Ar-*H*), 6.92-6.89 (m, 2H, Ar-*H*), 6.70 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 3.18 (qrt, 2H, CH_2), 1.01 (t, 3H, CH_3).

^{13}C NMR: δ 169.9 (*C*O), 153.4 (d, *J* = 18.0 Hz), 137.2 (d, *J* = 11.0 Hz), 134.5, 134.4, 134.0, 133.5, 132.1, 132.0, 131.9, 130.5, 129.2, 128.8, 128.7, 123.2, 122.6, 121.0, 113.4, 106.5 (d, *J* = 120.0 Hz), 20.2 (CH_2), 14.9 (CH_3).

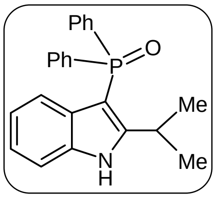
^{31}P NMR: δ 23.45.

HRMS (ESI): Calcd. for $C_{29}H_{24}NO_2P$ (M^+ + Na): *m/z* 472.1443. Found: 472.1446.

3.62 *Synthesis of NH-phosphinoyl indoles 74 and 77 by deprotection of compounds 73 and 75-76*

In a 50 mL round bottomed flask, *N*-acylated phosphinoyl indole **73** (0.25 g, 0.62 mmol) and NaOH (0.05 g, 1.24 mmol), were dissolved in ethanol-water mixture (v/v 4:1) (20 mL)), and the contents were heated with stirring at 80 °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; 1:1) affording **74** as a white solid. Simlarly compound **77** was obtained from the isomeric mixture **75+76**.

Compound 74



Yield: 0.21 g (93%, white solid).

Mp: 242–244 °C.

IR (KBr): 3161, 3068, 2970, 2865, 1490, 1457, 1435, 1293, 1156, 1117, 1101, 744 cm^{-1}.

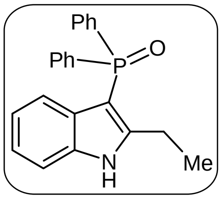
^{1}H NMR: δ 10.21 (br s, 1H, N*H*), 7.77-7.40 (m, 10H, Ar-*H*), 7.29 (d, *J* = 7.6 Hz, 1H, Ar-*H*), 7.02 (t, 1H, Ar-*H*), 6.82 (t, 1H, Ar-*H*), 6.54 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 3.90 (m, 1H, C*H*), 1.19 (d, *J* = 6.4 Hz, 6H, CH_3).

^{13}C NMR: δ 156.0 (d, *J* = 17.0 Hz), 136.3 (d, *J* = 12.0 Hz), 135.5, 134.5, 132.0, 131.9, 131.7, 129.3 (d, *J* = 12.0 Hz), 128.6, 128.5, 121.6, 120.5, 120.1, 111.3, 97.7 (d, *J* = 129.0 Hz, P*C*), 26.6 (*C*H), 22.5 (CH_3).

^{31}P NMR: δ 24.30.

HRMS (ESI): Calcd. for $C_{23}H_{22}NOP$ (M^{+} + H): *m/z* 360.1518. Found: 360.1515.

Compound 77



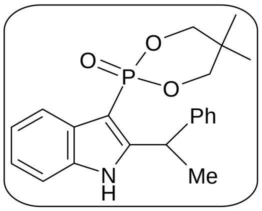
N-benzoylated phosphinoyl indole mixture of **75** + **76** (0.15 g, 0.34 mmol) was used.

Yield:	0.11 g (91%, white solid).
Mp:	214–218 °C.
IR (KBr):	3156, 3085, 3036, 2975, 2932, 1622, 1578, 1534, 1490, 1463, 1436, 1293, 1331, 1162, 1112, 1101, 1084, 756 cm^{-1}.
^{1}H NMR:	δ 10.63 (br s, 1H, N*H*), 7.78-7.40 (m, 10H, Ar-*H*), 7.26 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 7.01 (t, 1H, Ar-*H*), 6.81 (t, 1H, Ar-*H*), 6.56 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 2.88 (qrt, 2H, CH_2), 1.06 (t, 3H, CH_2CH_3).
^{13}C NMR:	δ 152.0 (d, *J* = 17.0 Hz), 136.3 (d, *J* = 12.0 Hz), 135.4, 134.4, 131.9, 131.8, 131.7, 129.6 (d, *J* = 13.0 Hz), 128.6, 128.5, 121.5, 120.5, 120.0, 111.3, 98.4 (d, *J* = 128.0 Hz, P*C*), 21.2 (*C*H_2), 14.3 (*C*H_3).
^{31}P NMR:	δ 23.95.
HRMS (ESI):	Calcd. for $C_{22}H_{20}NOP$ (M^+ + H): *m/z* 346.1632. Found: 346.1634.

3.63 Synthesis of NH-phosphono-indole 78 from allenylphosphonate 17a

In a 25 mL round bottomed flask, allenylphosphonate **17a** (0.25 g, 0.62 mmol) and NaOH (0.05 g, 1.23 mmol), were dissolved in ethanol-water mixture (v/v 4:1) (20 mL)), and the contents were heated with stirring at 80 °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; 2:1) affording **78**.

Compound 78



Yield:	0.19 g (83%, white solid).
Mp:	184–186 °C.
IR (KBr):	3162, 3129, 3090, 2964, 2871, 1578, 1496, 1458, 1436, 1299, 1249, 1222, 1118, 1058, 1014, 948 cm^{-1}.

^{1}H NMR: δ 10.08 (s, 1H, N*H*), 7.84-7.14 (m, 9H, Ar-*H*), 4.97 (qrt, 1H, C*H*), 4.23-3.55 (m, 4H, CH_2), 1.53 (d, *J* = 7.2 Hz, 1H, CH_3), 1.15 and 0.96 (2 s, 6H, CH_3).

^{13}C NMR: δ 152.3 (d, *J* = 26.0 Hz), 143.0, 136.2 (d, *J* = 14.0 Hz), 128.4 (d, *J* = 13.0 Hz), 127.5, 126.7, 122.4, 121.4, 120.1, 111.8, 94.0 (d, *J* = 215.0 Hz), 75.7 and 75.5 (CH$_2$), 37.6 (*C*H), 32.5 (C(CH$_3$)$_2$), 21.9, 21.6 and 20.7 (3 s, CH$_3$).

^{31}P NMR: δ 16.50.

HRMS (ESI): Calcd. for $C_{21}H_{24}NO_3P$ (M^+ + H): *m/z* 370.1573. Found: 370.1570.

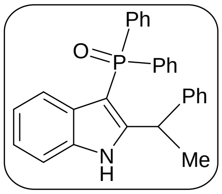
3.64 One pot synthesis of phosphinoyl indoles 74, 77 and 79-88

To an oven dried round bottomed flask (50 mL) was added *N*-acylated propargyl alcohol **15a**[87a] (0.33 g, 1.52 mmol), Et$_3$N (0.25 mL, 1.82 mmol) and tetrahydrofuran (10 mL) under N$_2$ atmosphere. To this was added Ph$_2$PCl (**6**) (0.33 mL, 1.82 mmol) dissolved in 5 mL of tetrahydrofuran drop-wise at 0 °C during 15 min; the contents were brought to rt and stirred for 6-10 h. After formation of the allene (TLC), NaOH (0.08 g, 2.04 mmol) and ethanol-water mixture (v/v 2:1) (15 mL) were added and then the mixture was stirred further at 80 °C for 8-10 h. After completion of the reaction (TLC), the solvent was removed under reduced pressure. The residue was dissolved in ethyl acetate (20 mL), washed with water (2x10 mL) and then with brine (10 mL). The organic part was dried over anh. Na$_2$SO$_4$ and the solvent removed under reduced pressure. Purification by column chromatography (hexane: ethyl acetate 1:1) afforded the desired product **74** as a white solid; Yield: 0.44 g, (80%). Anlaytical data are given above. Similarly compounds **77** and **79-88** were prepared.

Compound 77

Yield: 0.41 g [78%; using 0.31 g, (1.53 mmol) of propargyl alcohol **15b**, white solid]. Anlaytical data are given above.

Compound 79



Propargyl alcohol **15c** (0.2 g, 0.72 mmol) was used.

Yield: 0.26 g (87%, white solid).

Mp: 238–240 °C.

IR (KBr): 3167, 3068, 2986, 2942, 1479, 1458, 1436, 1288, 1162, 1123, 1074, 745 cm^{-1}.

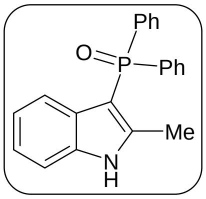
^{1}H NMR: δ 9.48 (s, 1H, N*H*), 7.80-7.14 (m, 16H, Ar-*H*), 7.01 (t, 1H, Ar-*H*), 6.83 (t, 1H, Ar-*H*), 6.58 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 5.37 (qrt, 1H, C*H*), 1.64 (d, *J* = 7.2 Hz, 3H, CH_3).

^{13}C NMR: δ 153.5 (d, *J* = 17.0 Hz), 143.0, 136.1 (d, *J* = 11.0 Hz), 135.3 (d, *J* = 9.0 Hz), 134.2 (d, *J* = 9.0 Hz), 132.0, 131.9, 131.8, 131.7, 129.3 (d, *J* = 12.0 Hz), 128.6_0, 128.5_5, 128.4, 127.7, 126.6, 122.0, 120.8, 120.5, 111.3, 99.3 (d, *J* = 126.0 Hz, P*C*), 36.5 (*C*H), 20.4 (CH_3).

^{31}P NMR: δ 24.25.

HRMS (ESI): Calcd. for $C_{28}H_{24}NOP$ (M^+ + H): *m/z* 422.1675. Found: 422.1679.

Compound 80



Propargyl alcohol **15d**[87b] (0.37 g, 1.95 mmol) was used

Yield: 0.53 g (82%, white solid).

Mp: 272–274 °C.

IR (KBr): 3156, 3052, 2920, 2838, 1534, 1484, 1440, 1347, 1287, 1150, 1123, 1073, 810 cm^{-1}.

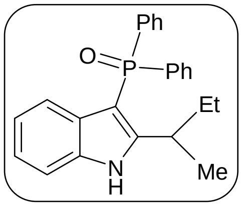
^{1}H NMR ($CDCl_3$+CD_3OD): δ 11.03 (br s, 1H, N*H*), 7.66-7.23 (m, 11H, Ar-*H*), 6.97 (t, 1H, Ar-*H*), 6.76 (t, 1H, Ar-*H*), 6.52 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 2.25 (d, *J* = 1.2 Hz, 3H, CH_3).

^{13}C NMR ($CDCl_3$+CD_3OD): δ 145.8 (d, *J* = 18.0 Hz), 136.0 (d, *J* = 12.0 Hz), 134.2, 133.2, 131.8, 131.6, 131.5, 129.5 (d, *J* = 13.0 Hz), 128.6, 128.5, 121.5, 120.4, 119.5, 111.0, 97.8 (d, *J* = 131.0 Hz, P*C*), 13.4 (*C*H_3).

^{31}P NMR ($CDCl_3$+CD_3OD): δ 26.51.

HRMS (ESI): Calcd. for $C_{21}H_{18}NOP$ (M^+ + H): *m/z* 332.1205. Found: 332.1200.

Compound 81



Propargyl alcohol **15e** (0.69 g, 2.99 mmol) was used.

Yield: 0.91 g (81%, white solid).

Mp: 258–260 °C.

IR (KBr): 3145, 3074, 2964, 2871, 1479, 1435, 1331, 1293, 1166, 1117, 750 cm^{-1}.

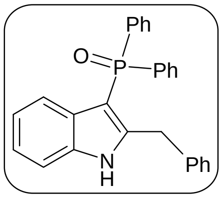
^{1}H NMR: δ 9.70 (s, 1H, N*H*), 7.78-7.30 (m, 11H, Ar-*H*), 7.05 (t, 1H, Ar-*H*), 6.84 (t, 1H, Ar-*H*), 6.60 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 3.74-3.69 (m, 1H, C*H*), 1.66-1.55 (m, 2H, CH_2), 1.21 (d, *J* = 7.2 Hz, 3H, CH_3), 0.68 (t, 3H, CH_2CH_3).

^{13}C NMR: δ 155.1 (d, *J* = 18.0 Hz), 136.4 (d, *J* = 11.0 Hz), 135.7 (d, *J* = 14.0 Hz), 134.6 (d, *J* = 15.0 Hz), 132.0, 131.9, 131.6, 129.3 (d, *J* = 12.0 Hz), 128.6, 128.5, 128.4_4, 128.4_0, 121.6, 120.5, 120.3, 111.2, 99.1 (d, *J* = 129.0 Hz, P*C*), 33.1 (*C*H), 29.9 (*C*H_2), 20.6 and 12.1 (2 s, *C*H_3).

^{31}P NMR: δ 23.95.

HRMS (ESI): Calcd. for $C_{24}H_{24}NOP$ (M^+ + H): *m/z* 374.1675. Found: 374.1678.

Compound 82



Propargyl alcohol **15f** (0.27 g, 1.02 mmol) was used.

Yield: 0.26 g (63%, white solid).

Mp: 192–194 °C.

IR (KBr): 3145, 3074, 2926, 2778, 1518, 1485, 1430, 1299, 1151, 1096, 1063, 745 cm^{-1}.

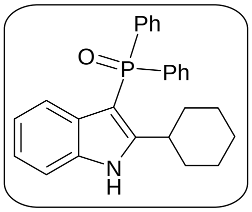
^1H NMR: δ 9.16 (s, 1H, N*H*), 7.77-7.14 (m, 16H, Ar-*H*), 7.05 (t, 1H, Ar-*H*), 6.86 (t, 1H, Ar-*H*), 6.65 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 4.43 (s, 2H, CH_2).

^{13}C NMR: δ 148.5 (d, *J* = 17.0 Hz), 138.4, 136.5 (d, *J* = 12.0 Hz), 135.1, 134.1, 131.9, 131.8, 131.6, 129.4 (d, *J* = 13.0 Hz), 129.0, 128.6. 128.4_2, 128.3_6, 126.3, 121.7, 120.5, 120.1, 111.5, 99.3 (d, *J* = 128.0 Hz, P*C*), 33.5 (*C*H_2).

^{31}P NMR: δ 24.49.

HRMS (ESI): Calcd. for $C_{27}H_{22}NOP$ (M^+ + H): *m/z* 408.1518. Found: 408.1519.

Compound 83



Propargyl alcohol **15g** (0.50 g, 1.94 mmol) was used.

Yield: 0.54 g (69%, white solid).

Mp: 268–270 °C.

IR (KBr): 3167, 3117, 2980, 2931, 2849, 1484, 1430, 1287, 1156, 1101, 744 cm^{-1}.

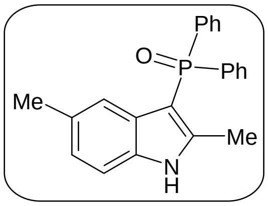
^1H NMR ($CDCl_3$+CD_3OD): δ 10.76 (br s, 1H, N*H*), 7.67-7.35 (m, 10H, Ar-*H*), 7.30 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 6.98 (t, 1H, Ar-*H*), 6.77 (t, 1H, Ar-*H*), 6.68 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 2.76 (m, 1H, C*H*), 1.64-0.90 (m, 10H, CH_2).

^{13}C NMR ($CDCl_3$+CD_3OD): δ 154.3 (d, *J* = 19.0 Hz), 136.2 (d, *J* = 11.0 Hz), 134.6, 133.5, 132.3, 131.7, 131.6, 129.1 (d, *J* = 12.0 Hz), 128.5, 128.4, 121.5, 120.3, 120.1, 111.1, 96.8 (d, *J* = 131.0 Hz, P*C*), 36.4 (*C*H), 32.6, 26.1 and 25.6 (*C*H_2).

^{31}P NMR ($CDCl_3$+CD_3OD): δ 26.02.

HRMS (ESI): Calcd. for $C_{26}H_{26}NOP$ (M^+ + H): *m/z* 400.1831. Found: 400.1834.

Compound 84



Propargyl alcohol **15h** (0.25 g, 1.22 mmol) was used.

Yield: 0.35 g (82%, white solid).

Mp: 264–266 °C.

IR (KBr): 3118, 3074, 3014, 2970, 2921, 2849, 1589, 1523, 1479, 1430, 1315, 1189, 1145, 1101, 1068, 805 cm^{-1}.

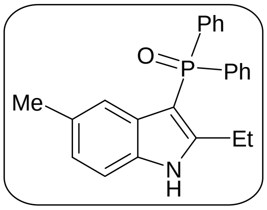
^{1}H NMR (CDCl$_3$+CD$_3$OD): δ 10.96 (br s, 1H, N*H*), 7.72-7.42 (m, 10H, Ar-*H*), 7.17 (d, *J* = 7.6 Hz, 1H, Ar-*H*), 6.85 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 6.36 (s, 1H, Ar-*H*), 2.24 and 2.13 (2 s, 6H, C*H*$_3$).

^{13}C NMR (CDCl$_3$+CD$_3$OD): δ 145.7 (d, *J* = 19.0 Hz), 134.3 (d, *J* = 8.0 Hz), 133.3, 131.7, 131.6, 129.9 (d, *J* = 12.0 Hz), 129.5, 128.6, 128.4, 122.9, 119.4, 110.7, 97.3 (d, *J* = 131.0 Hz, P*C*), 21.3 and 13.5 (2 s, *C*H$_3$).

^{31}P NMR (CDCl$_3$+CD$_3$OD): δ 26.55.

HRMS (ESI): Calcd. for $C_{22}H_{20}NOP$ (M^+ + H): *m/z* 346.1362. Found: 346.1359.

Compound 85



Propargyl alcohol **15i** (0.43 g, 1.96 mmol) was used.

Yield: 0.60 g (85%, white solid).

Mp: 252–254 °C.

IR (KBr): 3118, 3068, 3014, 2970, 2932, 1578, 1523, 1436, 1310, 1178, 1156, 805 cm^{-1}.

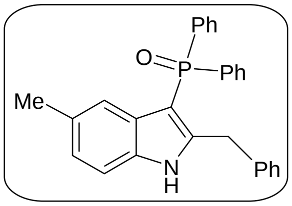
^{1}H NMR (CDCl$_3$+CD$_3$OD): δ 10.97 (br s, 1H, N*H*), 7.67-7.35 (m, 10H, Ar-*H*), 7.16 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 6.80 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 6.28 (s, 1H, Ar-*H*), 2.70 (qrt, 2H, C*H*$_2$), 2.06 (s, 3H, C*H*$_3$), 1.03 (t, 3H, C*H*$_3$).

^{13}C NMR ($CDCl_3$+CD_3OD): δ 151.6 (d, *J* = 18.0 Hz), 134.6 (d, *J* = 8.0 Hz), 134.5, 133.4, 131.7, 131.6, 129.7 (d, *J* = 12.0 Hz), 129.4, 128.5, 128.3, 122.9, 119.5, 110.8, 96.4 (d, *J* = 131.0 Hz, P*C*), 21.3 (*C*H_3), 20.9 (*C*H_2), 13.8 (*C*H_3).

^{31}P NMR ($CDCl_3$+CD_3OD): δ 26.80.

HRMS (ESI): Calcd. for $C_{23}H_{22}NOP$ (M^+ + H): *m/z* 360.1518. Found: 360.1522.

Compound 86



Propargyl alcohol **15j** (0.45 g, 1.61 mmol) was used.

Yield: 0.54 g (79%, white solid).

Mp: 230–232 °C.

IR (KBr): 3112, 3058, 2921, 2866, 1584, 1529, 1452, 1436, 1315, 1162, 1123, 1101, 800 cm^{-1}.

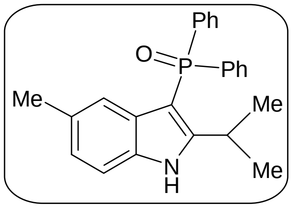
^{1}H NMR ($CDCl_3$+CD_3OD): δ 10.38 (br s, 1H, N*H*), 7.70-7.38 (m, 10H, Ar-*H*), 7.16 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 7.11-7.03 (m, 5H, Ar-*H*), 6.86 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 6.39 (s, 1H, Ar-*H*), 4.21 (s, 2H, C*H*$_2$), 2.13 (s, 3H, C*H*$_3$).

^{13}C NMR ($CDCl_3$+CD_3OD): δ 147.9 (d, *J* = 17.0 Hz), 138.1, 134.6 (d, *J* = 12.0 Hz), 134.4, 133.3, 131.8, 131.7, 129.8, 129.6 (d, *J* = 12.0 Hz), 128.7, 128.5, 128.4, 128.3, 126.3, 123.4, 119.8, 110.9, 98.3 (d, *J* = 130.0 Hz, P*C*), 33.3 (*C*H_2), 21.3 (*C*H_3).

^{31}P NMR ($CDCl_3$+CD_3OD): δ 26.63.

HRMS (ESI): Calcd. for $C_{28}H_{24}NOP$ (M^+ + H): *m/z* 422.1675. Found: 422.1677.

Compound 87



Propargyl alcohol **15k** (0.36 g, 1.56 mmol) was used.

Yield: 0.40 g (68%, white solid).

Mp: 248–250 ^{o}C.

IR (KBr): 3288, 3047, 2959, 2915, 1512, 1436, 1304, 1184, 1112, 701 cm^{-1}.

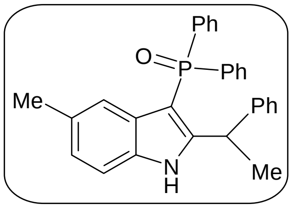
^{1}H NMR: δ 9.83 (br s, 1H, N*H*), 7.83-7.29 (m, 10H, Ar-*H*), 7.19 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 6.86 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 6.33 (s, 1H, Ar-*H*), 3.79 (m, 1H, C*H*), 2.13 (s, 3H, CH_3), 1.18 (d, *J* = 6.8 Hz, 6H, CH_3).

^{13}C NMR: δ 155.7 (d, *J* = 18.0 Hz), 135.7, 134.6 (d, *J* = 9.0 Hz), 134.4, 132.0, 131.9, 131.5, 129.7 (d, *J* = 17.0 Hz), 128.5, 128.4, 123.0, 120.1, 110.8, 97.3 (d, *J* = 128.0 Hz, P*C*), 26.7 (*C*H), 22.5 and 21.6 (*C*H$_3$).

^{31}P NMR: δ 24.78.

HRMS (ESI): Calcd. for $C_{24}H_{24}NOP$ (M^{+} + H): *m/z* 374.1675. Found: 374.1678.

Compound 88



Propargyl alcohol **15l** (0.39 g, 1.32 mmol) was used.

Yield: 0.42 g (74%, pale yellow solid).

Mp: 212–214 ^{o}C.

IR (KBr): 3128, 3047, 2970, 2921, 1584, 1436, 1321, 1189, 1151, 1118, 1074, 805 cm^{-1}.

^{1}H NMR: δ 9.48 (s, 1H, N*H*), 7.79-7.10 (m, 16H, Ar-*H*), 6.84 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 6.35 (s, 1H, Ar-*H*), 5.23 (qrt, 1H, C*H*), 2.13 (s, 3H, CH_3), 1.61 (d, *J* = 7.2 Hz, 3H, CH_3).

^{13}C NMR: δ 153.2 (d, *J* = 18.0 Hz), 143.4, 135.3 (d, *J* = 27.0 Hz), 134.7 (d, *J* = 12.0 Hz), 134.2 (d, *J* = 27.0 Hz), 132.0, 131.9$_4$, 131.9$_1$, 131.6, 131.5, 129.6 (d, *J* = 13.0 Hz), 128.5, 128.4, 128.3, 127.6, 126.2, 123.2, 120.1, 111.1, 98.1 (d, *J* = 128.0 Hz, P*C*), 36.7 (*C*H), 21.5 and 20.3 (2 s, *C*H$_3$).

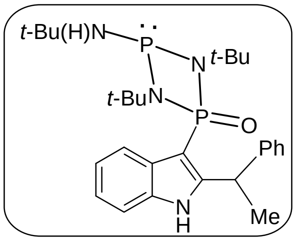
^{31}P NMR: δ 24.44.

HRMS (ESI): Calcd. for $C_{29}H_{26}NOP$ (M^{+} + H): *m/z* 436.1831. Found: 436.1832.

3.65 Synthesis of cyclodiphosphazanyl indoles 89-92

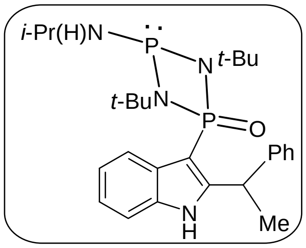
To a round bottomed flask (25 mL) equipped with cyclodiphosphazane [(*t*-BuNH)P(μ-N-*t*-Bu)]$_2$ (**2**)[52] [0.73 g, 2.1 mmol] and propargyl alcohol (**14a**)[64] (0.50 g, 2.1 mmol), was added dry toluene (8 mL). The mixture was stirred 80 °C for 4-5 h, cooled to room temperature upon which a white solid material settled down. This was then filtered and washed with diethyl ether (3 x 10 mL) to afford pure 2-(1-phenyl-ethyl),3-[(*t*-Bu)NH)P(μ-N-*t*-Bu)$_2$P(O)]-indole **89** as a white solid. Compounds **90-92** were prepared by following the same procedure.

Compound 89



Yield:	0.99 g (92%, white solid).
Mp:	252–256 °C.
IR (KBr):	3353, 3162, 3123, 3079, 2964, 2866, 1425, 1364, 1194, 1123, 1074, 888, 838 cm^{-1}.
^{1}H NMR:	δ 8.28 (1 s, 1H, N*H*), 7.67-7.12 (m, 9H, Ar-*H*), 5.88 (qrt, 1H, C*H*-CH$_3$), 3.32 (d, *J* = 7.6 Hz, 1H, N*H*-*t*-Bu), 1.74 (d, *J* = 7.6 Hz, 3H, CH-C*H*$_3$), 1.38 (d, *J* = 0.8 Hz, 9H, C(C*H*$_3$)$_3$), 1.26 and 1.14 (2 s, 18H, C(C*H*$_3$)$_3$).
^{13}C NMR:	δ 153.1 (d, ^{2}*J*(P-C) ~ 25.0 Hz, PC*C*-NH), 144.0, 135.7, 135.6, 129.1, 129.0, 128.6, 127.9, 126.5, 121.8, 120.6, 120.5, 120.4, 110.8, (Ar-*C*), 102.1 (d, ^{1}*J*(P-C) ~ 172.0 Hz, P-*C*), 52.6 (d, ^{2}*J*(P-C) ~ 5.0 Hz, *C*(CH$_3$)$_3$), 51.9 (d, ^{2}*J*(P-C) ~ 15.0 Hz, *C*(CH$_3$)$_3$), 35.9 (`1 s, *C*H-CH$_3$), 32.9 (d, ^{3}*J*(P-C) = 10.0 Hz, C(*C*H$_3$)$_3$), 31.3 (d, ^{3}*J*(P-C) = 5.0 Hz, C(*C*H$_3$)$_3$), 20.5 (1 s, CH-*C*H$_3$).
^{31}P NMR:	δ 77.97 (d, ^{2}*J*(P-P) = 10.0 Hz, (*P*-NH*t*-Bu), 10.67 (d, ^{2}*J*(P-P) = 10.0 Hz, *P*-C).
HRMS (ESI):	Calcd. for $C_{28}H_{42}N_4OP_2$ (M$^+$ + H): *m/z* 513.2913. Found: 513.2912.

Compound 90



Precursors **3**[52c] (0.42 g, 1.31 mmol) and **14a** (0.31 g, 1.31 mmol) were used.

Yield: 0.529 g (81%, white solid).

Mp: 264–268 °C.

IR (KBr): 3381, 3167, 3123, 3090, 3024, 2968, 2926, 2871, 1528, 1456, 1433, 1391, 1363, 1293, 1197, 1133, 1070, 891, 802 cm^{-1}.

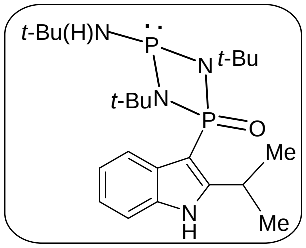
^{1}H NMR: δ 8.50 (1 s, 1H, N*H*), 7.66-7.12 (m, 9H, Ar-*H*), 5.91 (qrt, 1H, C*H*-CH$_3$), 3.65 (br, 1H, NH-C*H*(CH$_3$)$_2$), 3.01 (br, 1H, N*H*-*i*-Pr), 1.75 (d, J = 7.2 Hz, 3H, CH-C*H*$_3$), 1.24-1.22 (m, 6H, NH-CH(C*H*$_3$)$_2$), 1.25 and 1.14 (2 s, 18H, C(C*H*$_3$)$_3$).

^{13}C NMR: δ 153.4 (d, ^2J(P-C) ~ 25.0 Hz, PC*C*-NH), 144.1, 135.9, 135.7, 129.1, 128.9, 128.5, 128.3, 127.9, 126.4, 121.7, 120.6, 120.5, 120.3, 110.9 (Ar-*C*), 101.6 (d, ^1J(P-C) ~ 172.0 Hz, P-*C*), 52.5 (*C*(CH$_3$)$_3$), 44.9 (1 s, NH-*C*H(CH$_3$)$_2$), 35.9 (1 s, *C*H-CH$_3$), 31.2 (1 s, C(*C*H$_3$)$_3$), 26.5 (1 s, NH-CH(*C*H$_3$)$_2$), 20.6 (1 s, CH-*C*H$_3$).

^{31}P NMR: δ 82.67 (br, *P*-NH-*i*-Pr), 10.48 (br, 1P, *P*-C).

HRMS (ESI): Calcd. for $C_{27}H_{40}N_4OP_2$ (M$^+$ + H): *m/z* 499.2756. Found: 499.2757.

Compound 91



Precursors **2** (0.64 g, 1.83 mmol) and **14b**[64] (0.32 g, 1.83 mmol) were used.

Yield: 0.74 g (90%, white solid).

Mp: 296–298 °C.

IR (KBr): 3359, 3140, 2970, 2860, 1485, 1458, 1430, 1359, 1288, 1211, 1129, 1058, 1030, 992, 878 cm^{-1}.

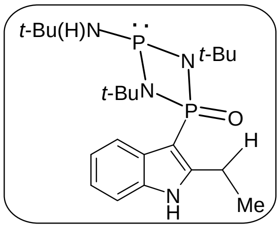
^{1}H NMR (CDCl$_3$+CD$_3$OD): δ 7.78 (br, 1H, N*H*), 7.60-7.10 (m, 4H, Ar-*H*), 4.37 (m, 1H, C*H*(CH$_3$)$_2$, 3.51 (br, 1H, N*H*-*t*-Bu), 1.40 (1 s, 9H, C(C*H*$_3$)$_3$), 1.35, (1 s, 6H, CH(C*H*$_3$)$_2$), 1.19 (1 s, 18H, C(C*H*$_3$)$_3$).

^{13}C NMR (CDCl$_3$+CD$_3$OD): δ 155.7 (d, ^2J(P-C) ~ 27.0 Hz, PC*C*-NH), 135.8, 128.3, 120.9, 119.5, 119.4, 110.3 (Ar-*C*), 98.0 (d, ^1J(P-C) ~ 176.0 Hz, P-*C*), 52.0 (d, ^2J(P-C) ~ 6.0 Hz, *C*(CH$_3$)$_3$), 51.0 (d, ^2J(P-C) ~ 14.0 Hz, *C*(CH$_3$)$_3$), 32.0 (d, ^3J(P-C) = 10.0 Hz, C(*C*H$_3$)$_3$), 30.4 (1 s C(*C*H$_3$)$_3$), 26.8 (1 s, *C*H(CH$_3$)$_2$, 25.0 and 21.3 (2 s, CH(*C*H$_3$)$_2$).

^{31}P NMR (CDCl$_3$+CD$_3$OD): δ 78.52 (d, ^2J(P-P) = 9.5 Hz, (*P*-NH*t*-Bu), 13.48 (d, ^2J(P-P) = 9.5 Hz, *P*-C).

HRMS (ESI): Calcd. for $C_{23}H_{40}N_4OP_2$ (M^+ + Na): *m/z* 473.2575. Found: 473.2577.

Compound 92



Precursors **2** (0.32 g, 0.91 mmol) and **14c** (0.15 g, 0.91 mmol) were used.

Yield: 0.35 g (88%, white solid).

Mp: 278–280 °C.

IR (KBr): 3359, 3090, 2964, 1458, 1436, 1364, 1288, 1195, 1129, 1063, 992, 888 cm^{-1}.

^{1}H NMR (CDCl$_3$+CD$_3$OD): δ 7.75 (1 s, 1H, N*H*), 7.60-7.07 (m, 4H, Ar-*H*), 4.09 (d, *J* = 7.6 Hz, 1H, N*H*-*t*-Bu), 3.22 (qrt, 2H, C*H*$_2$CH$_3$), 1.40 (s, 9H, C(C*H*$_3$)$_3$), 1.35 (t, 3H, CH$_2$C*H*$_3$), 1.19 (1 s, 18H, C(C*H*$_3$)$_3$).

^{13}C NMR (CDCl$_3$+CD$_3$OD): δ 151.5 (d, ^2J(P-C) ~ 25.0 Hz, PC*C*-NH), 135.5, 128.5, 128.3, 120.7, 119.2, 119.0, 110.0 (Ar-*C*), 98.4 (d, ^1J(P-C) ~ 177.0 Hz, P-*C*), 51.8 (d, ^2J(P-C) ~ 7.0 Hz, *C*(CH$_3$)$_3$), 50.8 (d, ^2J(P-C) ~ 15.0 Hz, *C*(CH$_3$)$_3$), 31.6 (d, ^3J(P-C) = 10.0 Hz, C(*C*H$_3$)$_3$), 30.0 (d, ^3J(P-C) = 5.0 Hz, C(*C*H$_3$)$_3$), 19.7 (1 s, *C*H$_2$CH$_3$), 12.7 (1 s, CH$_2$*C*H$_3$).

^{31}P NMR ($CDCl_3$+CD_3OD): δ 82.6 (d, ^2J(P-P) = 9.2 Hz, (*P*-NH*t*-Bu), 17.5 (d, ^2J(P-P) = 9.2 Hz, *P*-C).

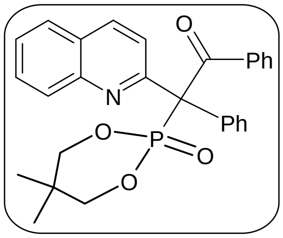
HRMS (ESI): Calcd. for $C_{22}H_{38}N_4OP_2$ (M^+ + H): *m/z* 437.2600. Found: 437.2601.

3.7 Synthesis of phosphorus based quinolines and phosphorus free quinolinones

3.71 Synthesis of phosphono- or N-phosphorylated quinolines [93-102]

To a solution of *N*-(2-formylphenyl)benzamide (**10**)^{58} (0.1 g, 0.44 mmol) and allenylphosphonate **16a**^{37} (0.116 g, 0.44 mmol) in DMSO (3 mL) was added K_2CO_3 (0.01 g, 0.09 mmol) and the mixture heated with stirring at 90 °C for 8 h. The contents were washed with water and extracted with ethyl acetate (2 x 20 mL). The solvent was removed under reduced pressure and purification by column chromatography (hexane/ethyl acetate; 2:1) afforded **93** (eluted second) and **94** (eluted first). Other compounds **95-102** were prepared similarly.

Compound 93



Yield: 0.089 g (43%, white solid).

Mp: 198–200 °C.

IR (KBr): 3052, 2959, 2921, 1710, 1677, 1595, 1496, 1425, 1249, 1063, 1019, 805 cm^{-1}.

^{1}H NMR: δ 8.16 (br s, 2H, Ar-*H*), 7.93 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 7.82 (dd, *J* = 8.4 Hz, *J* = 0.8 Hz, 1H, Ar-*H*), 7.68-7.51 (m, 6H, Ar-*H*), 7.31-7.20 (m, 4H, Ar-*H*), 7.06 (dd→t, 2H, Ar-*H*), 4.42-3.86 (m, 4H, OCH_2), 1.28 and 0.83 (2 s, 6H, CH_3).

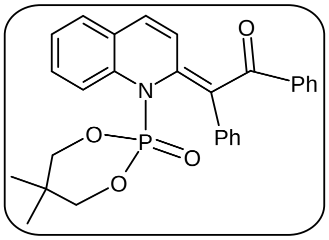
^{13}C NMR: δ 199.0 (d, *J* = 6.0 Hz, *C*O), 156.4 (d, *J* = 6.0 Hz), 147.4, 137.3 (d, *J* = 4.0 Hz), 136.0, 135.6 (d, *J* = 7.0 Hz), 131.5, 130.4, 130.3, 129.6, 129.4, 128.3, 127.8, 127.5_4, 127.4_8, 127.1, 123.8 (Ar-*C*), 78.2 and 77.4 (2 d, *J* =

8.0 Hz, OCH$_2$), 74.2 (d, J = 134.0 Hz, PC), 32.9 (d, J = 10.0 Hz, C(CH$_3$)$_2$), 22.8 and 21.0 (2 s, CH$_3$).

^{31}P NMR: δ 12.17.

HRMS (ESI): Calcd. for $C_{28}H_{26}NO_4P$ (M^+ + H): *m/z* 472.1678. Found: 472.1677.

Compound 94



Yield: 0.093 g (45%, white solid).

Mp: 192–194 °C.

IR (KBr): 2953, 2921, 2849, 1732, 1463, 1375, 1255, 1090, 1047, 1014, 805 cm^{-1}.

^{1}H NMR: δ 8.16 (dd→t, 2H, Ar-*H*), 7.83 (d, J = 8.0 Hz, 1H, Ar-*H*), 7.72 (t, 1H, Ar-*H*), 7.57-7.46 (m, 4H, Ar-*H*), 7.27-7.16 (m, 8H, Ar-*H*), 3.91-3.41 (m, 4H, OC*H*$_2$), 1.08 and 0.64 (2 s, 6H, C*H*$_3$).

^{13}C NMR: δ 158.8 (CO), 147.9, 146.2 (d, J = 9.0 Hz), 138.3, 136.3, 134.7, 130.7, 130.3, 130.2, 130.1, 129.4, 129.0, 128.2, 128.0, 127.8, 127.4, 127.2, 126.6, 123.8 (Ar-C), 77.8 (d, J = 7.0 Hz, OCH$_2$), 31.8 (d, J = 6.0 Hz, C(CH$_3$)$_2$), 21.8 and 20.0 (2 s, CH$_3$).

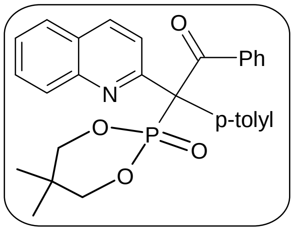
^{31}P NMR: δ -13.76.

HRMS (ESI): Calcd. for $C_{28}H_{26}NO_4P$ (M^+ + H): *m/z* 472.1678. Found: 472.1677.

Compounds 95 and 96

N-(2-formylphenyl)benzamide (**10**) (0.1 g, 0.44 mmol) and allenylphosphonate **16b**[37] (0.124 g, 0.44 mmol) were used.

Compound 95



Yield: 0.092 g (43%, white solid).

Mp: 192–194 °C.

IR (KBr): 3052, 2973, 2913, 1676, 1597, 1501, 1464, 1427, 1341, 1260, 1063, 1020, 997, 801 cm^{-1}.

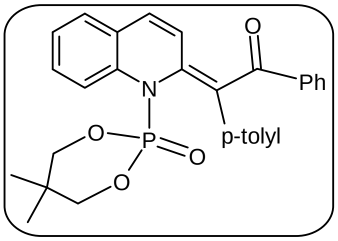
^1H NMR: δ 8.16-8.10 (m, 2H, Ar-*H*), 7.93 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 7.81 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.64 (t, 1H, Ar-*H*), 7.57-7.51 (m, 5H, Ar-*H*), 7.23 (t, 1H, Ar-*H*), 7.12-7.06 (m, 4H, Ar-*H*), 4.42-3.86 (m, 4H, OCH_2), 2.30 (s, 3H, Ar-CH_3), 1.25 and 0.83 (2 s, 6H, CH_3).

^{13}C NMR: δ 198.8 (d, *J* = 6.0 Hz, *C*O), 156.6 (d, *J* = 6.0 Hz), 147.3, 137.5, 137.3 (d, *J* = 5.0 Hz), 135.9, 132.4 (d, *J* = 7.0 Hz), 131.5, 130.4, 130.2_2, 130.1_7, 129.6, 129.4, 129.0, 127.5, 127.4, 127.0, 123.7 (Ar-*C*), 78.0 and 77.3 (2 d, *J* = 8.0 Hz, OCH_2), 73.9 (d, *J* = 133.0 Hz, P*C*), 32.9 (d, *J* = 10.0 Hz, $C(CH_3)_2$), 22.8 and 21.1 (2 s, Ar-CH_3+CH_3).

^{31}P NMR: δ 12.31.

HRMS (ESI): Calcd. for $C_{29}H_{28}NO_4P$ (M^+ + H): *m/z* 486.1835. Found: 486.1834.

Compound 96



Yield: 0.099 g (46%, white solid).

Mp: 138–140 °C.

IR (KBr): 3057, 2961, 2920, 2855, 1595, 1501, 1424, 1373, 1308, 1182, 1049, 1009, 988, 851 cm^{-1}.

^1H NMR: δ 8.16 (dd→t, 2H, Ar-*H*), 7.83 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 7.71 (t, 1H, Ar-*H*), 7.56-7.47 (m, 4H, Ar-*H*), 7.27-6.94 (m, 7H, Ar-*H*), 3.90-3.39 (m, 4H, OCH_2), 2.25 (s, 3H, Ar-CH_3), 1.07 and 0.63 (2 s, 6H, CH_3).

^{13}C NMR: δ 159.0 (*C*O), 147.7, 145.8 (d, *J* = 9.0 Hz), 137.2, 136.4, 135.2, 134.8, 130.6, 130.1, 129.4_3, 129.3_6, 129.0, 128.9, 128.0, 127.8, 127.2, 126.5, 123.8 (Ar-*C*), 77.8 (d, *J* = 7.0 Hz, OCH_2), 31.8 (d, *J* = 6.0 Hz, $C(CH_3)_2$), 21.8, 21.3 and 20.0 (3 s, CH_3).

^{31}P NMR: δ -13.76.

LC-MS: *m/z* 486 [M+1]$^+$.

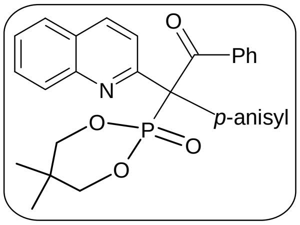
Anal. Cacld for $C_{29}H_{28}NO_4P$: C, 71.74; H, 5.81; N, 2.88. Found: C, 71.85; H, 5.75; N, 2.96.

HRMS (ESI): Calcd. for $C_{29}H_{28}NO_4P$ (M^+ + H): *m/z* 486.1835. Found: 486.1834.

Compounds 97 and 98

N-(2-formylphenyl)benzamide (**10**) (0.103 g, 0.46 mmol) and allenylphosphonate **16c**[37] (0.134 g, 0.46 mmol) were used.

Compound 97



Yield: 0.071 g (31%, white solid).

Mp: 150–152 °C.

IR (KBr): 3057, 2926, 2855, 1678, 1597, 1512, 1464, 1426, 1373, 1258, 1188, 1071, 1019, 920, 812 cm^{-1}.

^{1}H NMR: δ 8.15-8.07 (m, 2H, Ar-*H*), 7.95 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.80 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.68-7.52 (m, 6H, Ar-*H*), 7.25 (t, 1H, Ar-*H*), 7.10-6.83 (m, 4H, Ar-*H*), 4.39-3.87 (m, 4H, OCH_2), 3.77 (s, 3H, OCH_3), 1.24 and 0.83 (2 s, 6H, CH_3).

^{13}C NMR: δ 198.8 (d, *J* = 6.0 Hz, *C*O), 159.0, 156.5 (d, *J* = 6.0 Hz), 147.4, 137.2 (d, *J* = 4.0 Hz), 136.0, 131.7_0, 131.6_5, 131.6, 130.5, 129.7, 129.5, 127.6, 127.4, 127.3, 127.1, 123.7, 113.7 (Ar-*C*), 78.0 and 77.3 (2 d, *J* = 8.0 Hz, O*C*H_2), 73.4 (d, *J* = 134.0 Hz, P*C*), 55.3 (*C*H_3), 33.0 (d, *J* = 9.0 Hz, *C*$(CH_3)_2$), 22.8 and 21.1 (2 s, *C*H_3).

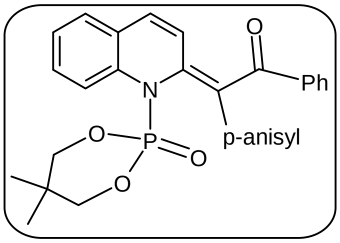
^{31}P NMR: δ 12.53.

LC-MS: *m/z* 502 [M+1]$^+$.

Anal. Cacld for $C_{29}H_{28}NO_5P$: C, 69.45; H, 5.63; N, 2.79. Found: C, 69.36; H, 5.68; N, 2.71.

HRMS (ESI): Calcd. for $C_{29}H_{28}NO_5P$ (M^+ + H): *m/z* 502.1784. Found: 502.1783.

Compound 98



Yield:	0.135 g (59%, white solid).
Mp:	158–160 °C.
IR (KBr):	2922, 2845, 1645, 1597, 1510, 1302, 1250, 1175, 1080, 1051, 1007, 972, 864 cm^{-1}.
^{1}H NMR:	δ 8.16 (dd→t, 2H, Ar-*H*), 7.82 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.72 (t, 1H, Ar-*H*), 7.55-7.47 (m, 4H, Ar-*H*), 7.27-6.67 (m, 7H, Ar-*H*), 3.88 (d, *J* = 10.4 Hz, 2H, OCH_2), 3.73 (s, 3H, OCH_3), 3.47-3.39 (m, 2H, OCH_2), 1.07 and 0.63 (2 s, 6H, CH_3).
^{13}C NMR:	δ 159.1 (*C*O), 158.8, 147.8, 145.5 (d, *J* = 10.0 Hz), 136.3, 134.9, 131.9, 131.4, 130.5, 130.1, 129.9, 129.8, 129.4, 128.9, 128.1, 127.8, 127.2, 126.5, 123.8, 113.7 (Ar-*C*), 77.8 (d, *J* = 7.0 Hz, O*C*H$_2$), 55.2 (s, O*C*H$_3$), 31.8 (d, *J* = 6.0 Hz, *C*(CH$_3$)$_2$), 21.8 and 20.0 (2 s, *C*H$_3$).
^{31}P NMR:	δ -13.66.
LC-MS:	*m/z* 502 [M+1]$^+$.

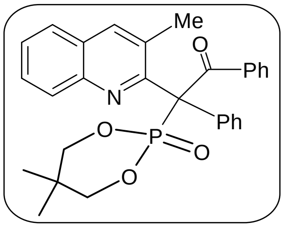
Anal. Cacld for $C_{29}H_{28}NO_5P$: C, 69.45; H, 5.63; N, 2.79. Found: C, 69.58; H, 5.56; N, 2.86.

HRMS (ESI): Calcd. for $C_{29}H_{28}NO_5P$ (M$^+$ + H): *m/z* 502.1784. Found: 502.1783.

Compounds 99 and 100

N-(2-formylphenyl)benzamide (**10**) (0.07 g, 0.31 mmol) and allenylphosphonate **16d** (0.09 g, 0.31 mmol) were used.

Compound 99



Yield: 0.033 g (22%, white solid).

Mp: 200–202 °C.

IR (KBr): 3068, 2959, 2926, 2888, 1693, 1600, 1496, 1441, 1381, 1255, 1205, 1074, 997, 811 cm^{-1}.

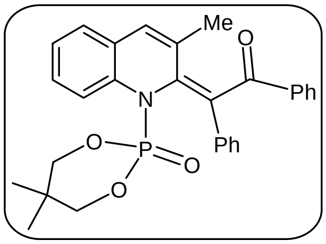
^{1}H NMR: δ 8.29 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 7.86 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 7.76-7.70 (m, 4H, Ar-*H*), 7.63-7.24 (m, 6H, Ar-*H*), 7.05 (dd→t, 2H, Ar-*H*), 6.66 (s, 1H, Ar-*H*), 4.10-3.92 (m, 4H, OCH_2), 1.78, 1.16 and 0.70 (3 s, 9H, CH_3).

^{13}C NMR: δ 195.5 (d, *J* = 3.0 Hz, *C*O), 158.8 (d, *J* = 7.0 Hz), 149.8, 145.4, 138.8, 138.4, 137.9, 135.8, 134.6, 131.8, 131.5, 131.4, 131.1, 130.8, 130.3, 129.6, 129.2, 128.8, 128.4, 128.1, 127.8, 127.6, 127.3, 126.8 (Ar-*C*), 77.4 and 76.1 (2 s, OCH_2), 74.5 (d, *J* = 127.0 Hz, P*C*), 32.9 (d, *J* = 9.0 Hz, $C(CH_3)_2$), 22.6, 21.3 and 20.0 (3 s, CH_3).

^{31}P NMR: δ 10.09.

HRMS (ESI): Calcd. for $C_{29}H_{28}NO_4P$ (M^+ + H): *m/z* 486.1835. Found: 486.1833.

Compound 100



Yield: 0.086 g (57%, white solid).

Mp: 208–210 °C.

IR (KBr): 3052, 2970, 2920, 2887, 1632, 1599, 1490, 1446, 1320, 1205, 1150, 1112, 1051, 1008, 854 cm^{-1}.

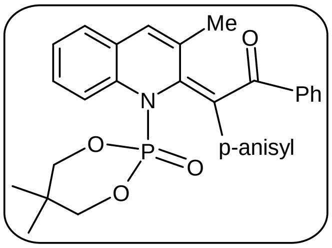
^{1}H NMR: δ 8.19 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 7.97 (s, 1H, Ar-*H*), 7.78 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 7.68 (dd→t, 1H, Ar-*H*), 7.56-7.51 (m, 3H, Ar-*H*), 7.29-7.10 (m, 8H, Ar-*H*), 3.44 (br, 4H, OCH_2), 2.42, 1.01 and 0.50 (3 s, 9H, CH_3).

^{13}C NMR: δ 158.9 (*C*O), 146.4, 145.8 (d, *J* = 9.0 Hz), 136.7, 136.6, 134.1, 132.0, 130.4, 130.3, 129.2, 129.0, 128.7_4, 128.6_7, 128.6, 128.1_0, 128.0_5, 127.3, 127.1, 126.5 (Ar-*C*), 77.7 (br, O*C*H$_2$), 31.7 (d, *J* = 6.0 Hz, *C*(CH$_3$)$_2$), 21.7, 19.7 and 19.3 (3 s, *C*H$_3$).

^{31}P NMR: δ -14.44.

HRMS (ESI): Calcd. for $C_{29}H_{28}NO_4P$ (M^+ + H): *m/z* 486.1835. Found: 486.1837.

Compound 101



N-(2-formylphenyl)benzamide (**10**) (0.05 g, 0.22 mmol) and allenylphosphonate **16e** (0.07 g, 0.22 mmol) were used.

Yield: 0.093 g (79%, white solid).

Mp: 128–130 °C.

IR (KBr): 3063, 2964, 2926, 2893, 1605, 1512, 1447, 1403, 1304, 1249, 1184, 1047, 1003, 970, 849 cm^{-1}.

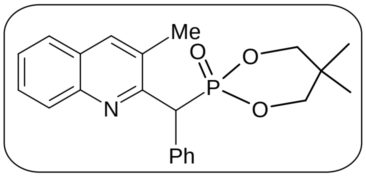
^{1}H NMR: δ 8.19 (d, *J* = 8.8 Hz, 1H, Ar-*H*), 7.96 (s, 1H, Ar-*H*), 7.76 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.67 (t, 1H, Ar-*H*), 7.58-7.50 (m, 3H, Ar-*H*), 7.29-6.63 (m, 7H, Ar-*H*), 4.00-2.91 (m, 7H, OC*H*$_3$+OC*H*$_2$), 2.40 (s, 3H, C*H*$_3$), 1.00 and 0.49 (2 s, 6H, *CH*$_3$).

^{13}C NMR: δ 159.1 (*C*O), 158.7, 146.3, 144.9 (d, *J* = 10.0 Hz), 136.6, 134.3, 131.9, 131.4, 130.3, 130.1, 129.0, 128.7, 128.5, 128.3, 128.2, 128.1, 127.1, 126.5, 113.5 (Ar-*C*), 77.7 (br, O*C*H$_2$), 55.1 (s, O*C*H$_3$), 31.7 (d, *J* = 6.0 Hz, *C*(CH$_3$)$_2$), 21.6, 19.7 and 19.2 (3 s, *C*H$_3$).

^{31}P NMR: δ -14.24.

HRMS (ESI): Calcd. for $C_{30}H_{30}NO_5P$ (M^+ + H): *m/z* 516.1941. Found: 516.1943.

Compound 102



This compound was isolated along with compounds **99** and **100** It was eluted last by using hexane- ethyl acetate (2:1) mixture.

Yield: 0.012 g (10%, white solid).

Mp: 182–184 °C.

IR (KBr): 3052, 2953, 2921, 2849, 1644, 1595, 1562, 1490, 1447, 1375, 1249, 1079, 1063, 1008, 833 cm^{-1}.

^{1}H NMR: δ 8.17 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 7.87 (s, 1H, Ar-*H*), 7.72 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.67 (t, 1H, Ar-*H*), 7.54-7.49 (m, 3H, Ar-*H*), 7.30-7.23 (m, 3H, Ar-*H*), 5.20 (d, *J* = 24.8 Hz, 1H, PC*H*), 4.36-3.78 (m, 4H, OCH_2), 2.38 (s, 3H, Ar-CH_3), 1.09 and 0.71 (2 s, 6H, CH_3).

^{13}C NMR: δ 156.7 (d, *J* = 7.0 Hz), 146.1, 137.0, 134.4 (d, *J* = 8.0 Hz), 130.3, 130.2_4, 130.1_8, 130.1, 129.1, 128.7, 128.4_7, 128.4_5, 127.7, 127.5_1, 127.4_8, 126.9, 126.6 (Ar-*C*), 76.7 and 76.0 (2 d, *J* = 7.0 Hz, OCH_2), 52.0 (d, *J* = 140.0 Hz, P*C*H), 32.7 (d, *J* = 8.0 Hz, $C(CH_3)_2$), 22.2, 21.1 and 19.5 (3 s, Ar-CH_3+CH_3).

^{31}P NMR: δ 17.07.

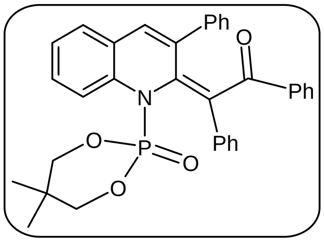
HRMS (ESI): Calcd. for $C_{22}H_{24}NO_3P$ (M^+ + H): *m/z* 382.1573. Found: 382.1572.

3.72 Synthesis of N-phosphorylated quinolines or phosphorus free quinolinones [103-108] and anisyl phosphonate 109

Compounds 103 and104

Proecedure was similar to that for **93/94**. *N*-(2-formylphenyl)benzamide (**10**) (0.1 g, 0.44 mmol) and allenylphosphonate **16f** (0.15 g, 0.44 mmol) were used. The eluent was hexane/EtOAc (2:1) to obtain solids **103** (eluted second) and **104** (eluted first).

Compound 103



Yield: 0.117 g (48%, white solid).

Mp: 156–158 °C.

IR (KBr): 3052, 2959, 2921, 2855, 1721, 1655, 1463, 1370, 1310, 1178, 1047, 997, 860 cm^{-1}.

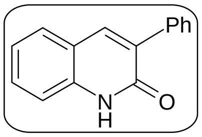
^{1}H NMR: δ 8.26 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 8.08 (s, 1H, Ar-*H*), 7.87 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.77 (t, 1H, Ar-*H*), 7.60 (t, 1H, Ar-*H*), 7.37-7.18 (m, 10H, Ar-*H*), 6.93 (t, 1H, Ar-*H*), 6.87-6.70 (m, 4H, Ar-*H*), 4.16-3.32 (br m, 4H, OCH_2), 1.08 and 0.61 (2 s, 6H, CH_3).

^{13}C NMR: δ 157.7 (*C*O), 146.9, 146.1 (d, *J* = 8.0 Hz), 139.0, 136.9 (d, *J* = 6.0 Hz), 133.8, 130.2, 130.1, 129.5, 129.3_4, 129.2_6, 129.1, 128.4, 128.3, 127.9, 127.5, 127.4, 127.0, 126.6 (Ar-*C*), 77.8 (d, *J* = 7.0 Hz, O*C*H$_2$), 31.9 (d, *J* = 5.0 Hz, *C*(CH$_3$)$_2$), 21.7 and 19.9 (2 s, *C*H$_3$).

^{31}P NMR: δ -15.02.

HRMS (ESI): Calcd. for $C_{34}H_{30}NO_4P$ ($M^+ + H$): *m/z* 548.1991. Found: 548.1988.

Compound 104



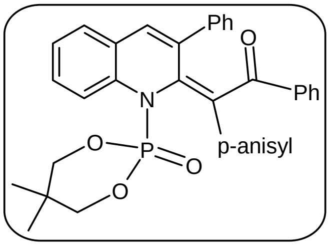
Yield: 0.021 g (21%, white solid).

The spectral data are in accordance with the literature report.[97]

Compounds 105

Proecedure was similar to that for **93/94**. *N*-(2-formylphenyl)benzamide (**10**) (0.08 g, 0.36 mmol) and allenylphosphonate **16g** (0.13 g, 0.36 mmol) were used. The eluent was hexane/EtOAc (2:1) to obtain solids **104** (eluted first; 0.021 g, 27%, white solid, see above)) and **105** (eluted second).

Compound 105



Yield: 0.093 g (45%, white solid).

Mp: 150–152 °C.

IR (KBr): 3052, 2970, 2915, 2855, 1649, 1605, 1518, 1403, 1299, 1249, 1173, 1074, 1041, 1014, 997, 844 cm^{-1}.

^{1}H NMR: δ 8.26 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 8.08 (s, 1H, Ar-*H*), 7.87 (d, *J* = 7.6 Hz, 1H, Ar-*H*), 7.76 (t, 1H, Ar-*H*), 7.59 (t, 1H, Ar-*H*), 7.37-7.21 (m, 10H, Ar-*H*), 6.64-6.39 (m, 4H, Ar-*H*), 4.13-3.31 (m, 7H, OCH_3+OCH_2), 1.07 and 0.59 (2 s, 6H, CH_3).

^{13}CNMR: δ 158.2 (*C*O), 157.8, 146.8, 145.3 (d, *J* = 8.0 Hz), 139.1, 136.9, 136.8, 133.9, 131.3, 130.1, 129.5, 129.3, 129.1, 129.0, 128.0, 127.9, 127.5$_2$, 127.4$_5$, 126.9, 113.0 (Ar-*C*), 77.7 (d, *J* = 7.0 Hz, OCH_2), 55.1 (s, OCH_3), 31.9 (d, *J* = 6.0 Hz, $C(CH_3)_2$), 21.7 and 19.9 (2 s, CH_3).

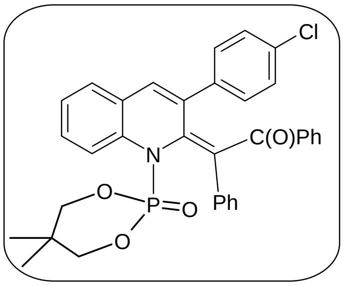
^{31}P NMR: δ -14.96.

HRMS (ESI): Calcd. for $C_{35}H_{32}NO_5P$ (M^+ + H): *m/z* 578.2097. Found: 578.2095.

Compounds 106 and107

Procedure was similar to that for compounds **93/94**. *N*-(2-formylphenyl)benzamide (**10**) (0.18 g, 0.8 mmol) and allenylphosphonate **16h** (0.3 g, 0.8 mmol) were used. The eluent was hexane/EtOAc (2:1) to obtain solids **106** (eluted second) and **107** (eluted first).

Compound 106



Yield: 0.191 g (41%, white solid).

Mp: 234–236 °C.

IR (KBr): 3063, 2964, 2882, 1643, 1490, 1408, 1358, 1303, 1183, 1051, 991, 832 cm^{-1}.

^{1}H NMR: δ 8.27 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 8.03 (s, 1H, Ar-*H*), 7.87 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.78 (t, 1H, Ar-*H*), 7.60 (t, 1H, Ar-*H*), 7.40-7.19 (m, 9H, Ar-

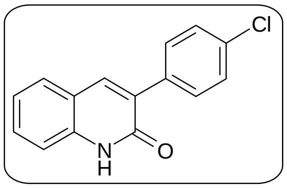
H), 6.96-6.85 (m, 3H, Ar-*H*), 6.67 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 4.15-3.24 (m, 4H, OCH_2), 1.08 and 0.64 (2 s, 6H, CH_3).

^{13}C NMR: δ 157.4 (*C*O), 146.9, 146.4 (d, *J* = 8.0 Hz), 138.0, 137.6, 137.1, 136.9, 135.7, 133.9, 133.6, 131.1, 131.0, 130.7, 130.2, 129.7, 129.2, 129.1, 128.6, 128.5, 128.0, 127.9, 127.5, 127.4, 127.1, 126.7, 121.8 (Ar-*C*), 77.8 (d, *J* = 7.0 Hz, O*C*H_2), 31.9 (d, *J* = 6.0 Hz, *C*(CH_3)$_2$), 21.7 and 19.9 (2 s, *C*H_3).

^{31}P NMR: δ -14.65.

HRMS (ESI): Calcd. for $C_{34}H_{29}ClNO_4P$ (M^+ + Na and M^+ + Na +2): *m/z* 604.1421 and 606.1421. Found: 604.1425 and 606.1403.

Compound 107



Yield: 0.073 g (36%, white solid).

Mp: 246–248 °C.

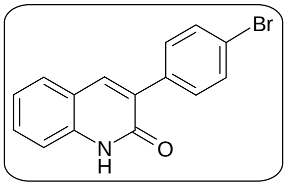
IR (KBr): 3457, 3150, 3013, 2948, 2893, 2854, 1660, 1567, 1495, 1419, 1238, 1079, 1013, 816 cm^{-1}.

^{1}H NMR: δ 11.99 (s, 1H, N*H*), 8.14 (s, 1H, Ar-*H*), 7.81 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 7.72 (d, *J* = 7.6 Hz, 1H, Ar-*H*), 7.50-7.47 (m, 3H, Ar-*H*), 7.33 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.19 (t, *J* = 7.6 Hz, 1H, Ar-*H*).

^{13}C NMR: δ 161.3 (*C*O), 138.9, 138.3, 135.5, 133.0, 130.9, 130.5, 128.7, 128.4, 122.4, 119.9, 115.2.

HRMS (ESI): Calcd. for $C_{15}H_{10}ClNO$ (M^+ + Na and M^+ + Na +2): *m/z* 278.0349 and 280.0349. Found: 278.0349 and 280.0316.

Compound 108

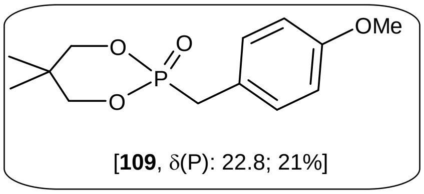


Procedure was similar to that for compounds **93/94**. *N*-(2-formylphenyl)benzamide (**10**) (0.17 g, 0.75 mmol) and allenylphosphonate **16i** (0.34 g, 0.75 mmol) were used. This compound was isolated by using hexane- ethyl acetate (2:1) mixture as the eluent.

Yield: 0.087 g (39%, white solid).

The spectral data are in accordance with the literature report.[98]

Compound 109



[**109**, δ(P): 22.8; 21%]

Procedure was similar to that for compounds **93/94**. This compound was isolated along with compounds **104** and **105**. It was eluted last by using hexane- ethyl acetate (2:1) mixture.

Yield: 0.02 g (21%, white solid).

Mp: 104–106 °C.

IR (KBr): 2964, 2926, 2838, 1666, 1605, 1512, 1468, 1255, 1178, 1063, 1014, 866 cm^{-1}.

^{1}H NMR: δ 7.20 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 6.84 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 4.19-4.15 (m, 2H, OCH_2), 3.78 (s, OCH_3), 3.76-3.64 (m, 2H, OCH_2), 3.30 (d, *J* = 21.6 Hz, 2H, PCH_2), 0.92 and 0.82 (2 s, 6H, CH_3).

^{13}C NMR: δ 158.7 (d, *J* = 3.0 Hz), 130.9 (d, *J* = 6.0 Hz), 122.8 (d, *J* = 10.0 Hz), 114.1 (d, *J* = 2.0 Hz) (Ar-*C*), 75.1 (d, *J* = 6.0 Hz, OCH_2), 55.3 (s, OCH_3), 32.5 (br, $C(CH_3)_2$), 31.8 (d, *J* = 143.0 Hz, PCH_2), 21.4 (s, CH_3).

^{31}P NMR: δ 22.78.

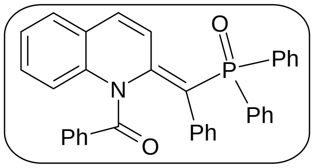
HRMS (ESI): Calcd. for $C_{13}H_{19}O_4P$ (M^+ + H): *m/z* 271.1100. Found: 271.1100.

3.73 Synthesis of phosphinoyl quinolines 110-111 and DBU ring cleaved product 112

Compounds 110 and 111

Procedure was similar to that for compounds **93/94**. *N*-(2-formylphenyl)benzamide (**10**) (0.074 g, 0.33 mmol) and allenylphosphine oxide **18**[66] (0.104 g, 0.33 mmol) were used. Eluent for column chromatography was hexane-ethyl acetate (2:1) mixture.

Compound 110

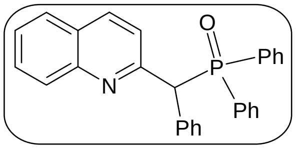


Yield:	0.091 g (53%, white solid).
Mp:	78–80 °C.
IR (KBr):	3057, 2924, 1715, 1674, 1593, 1497, 1437, 1308, 1229, 1179, 1105, 1022, 843 cm^{-1}.
^{1}H NMR:	δ 8.07-8.02 (m, 2H, Ar-*H*), 7.83-7.64 (m, 6H, Ar-*H*), 7.59-7.34 (m, 8H, Ar-*H*), 7.28-7.15 (m, 8H, Ar-*H*), 7.03-6.99 (m, 2H, Ar-*H*).
^{13}C NMR:	δ 199.5 (*C*O), 156.7, 147.0, 137.3, 135.8, 134.5, 134.0, 133.9, 133.8, 132.2 (d, *J* = 98.0 Hz, P*C*), 131.7, 131.2, 131.1, 130.3, 129.4, 129.2, 127.9, 127.6, 127.5, 127.4, 127.3, 126.9, 126.8, 123.5 (Ar-*C*).
^{31}P NMR:	δ 38.79.
LC-MS:	*m/z* 524 [M+1]$^+$.

Anal. Cacld for $C_{35}H_{26}NO_2P$: C, 80.29; H, 5.01; N, 2.68. Found: C, 80.11; H, 5.12; N, 2.58.

HRMS (ESI): Calcd. for $C_{35}H_{26}NO_2P$ (M^+ + Na): *m/z* 546.1599. Found: 546.1599.

Compound 111



Yield:	0.058 g (34%, white solid).
Mp:	202–204 °C.
IR (KBr):	3061, 2920, 2853, 1709, 1595, 1491, 1435, 1360, 1271, 1181, 1117, 1071, 866 cm^{-1}.

^{1}H NMR: δ 8.16 (d, *J* = 8.8 Hz, 1H, Ar-*H*), 8.06 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 7.89 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 7.79-7.63 (m, 8H, Ar-*H*), 7.47-7.39 (m, 2H, Ar-*H*), 7.36-7.19 (m, 8H, Ar-*H*), 5.39 (d, *J* = 8.8 Hz, 1H, PC*H*).

^{13}C NMR: δ 157.6, 147.7, 136.9, 131.6, 131.5, 131.4, 131.3, 130.2, 130.1, 129.4, 128.9, 128.7, 128.4$_1$, 128.3$_6$, 128.3, 128.2, 127.6, 127.4, 127.1, 126.4, 122.3 (Ar-*C*), 57.1 (d, *J* = 63.0 Hz, P*C*H).

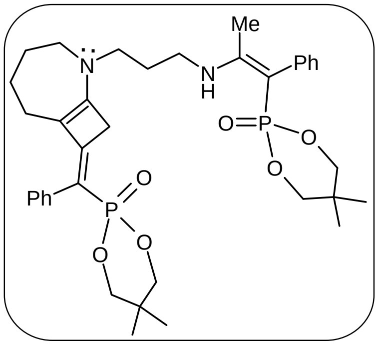
^{31}P NMR: δ 30.99.

LC-MS: *m/z* 420 [M+1]$^+$.

Anal. Cacld for $C_{28}H_{22}NOP$: C, 80.18; H, 5.29; N, 3.34. Found: C, 80.26; H, 5.23; N, 3.41.

HRMS (ESI): Calcd. for $C_{28}H_{22}NOP$ (M^+ + Na): *m/z* 442.1337. Found: 442.1337.

Compound 112



Allenylphosphonate **16a** (0.204 g, 0.77 mmol) was dissolved in dry toluene (3 mL). To this was added DBU (0.06 mL, 0.39 mmol) and the mixture was stirred at room temperature for 1 h. Then the solution was concentrated *in vacuo* (to ca 1 mL), to this was added 1 mL of *n*-pentane and cooled at -4 °C to obtain crystals of **112**. X-ray structure was determined for this compound, but we could not get good NMR spectra.

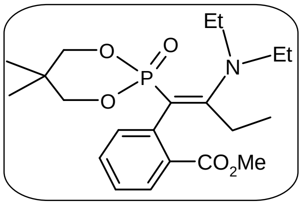
3.8 Nucleophilic addition/ cyclization reaction of allenylphosphonate 17c or allenylphosphine oxide 19

3.81 Synthesis of β-amino phosphonates 113 and 114

An oven dried 25 mL round-bottomed flask was charged with allenylphosphonate **17c** (0.2 g, 0.59 mmol) and diethyl amine (0.19 mL, 1.78 mmol) in. acetonitrile (4 mL). The mixture was stirred rt for 4h. After completion of the reaction

(TLC), the solvent was removed under reduced pressure. Purification by column chromatography (hexane: ethyl acetate 2:1) afforded the desired product **113**.

Compound 113



Yield: 0.162 g (66%, yellow liquid).

IR (neat): 3054, 2963, 2926, 2872, 1724, 1600, 1542, 1473, 1374, 1290, 1250, 1065 cm^{-1}.

^{1}H NMR: δ 7.81 (dd→t, 1H, Ar-*H*), 7.37-7.19 (m, 3H, Ar-*H*), 4.04-4.01 (m, 2H, OC*H*$_2$), 3.84 (s, 3H, OC*H*$_3$), 3.52-2.73 (m, 8H, OC*H*$_2$+C*H*$_2$), 1.23 (t, 3H, C*H*$_3$), 0.85 (t, 6H, C*H*$_3$), 0.81 and 0.50 (2 s, 6H, C*H*$_3$).

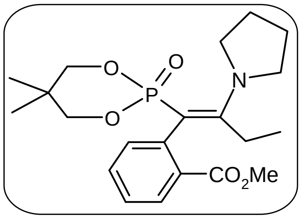
^{13}C NMR: δ 168.8 (*C*O), 166.3 (d, *J* =25.0 Hz), 140.9, 134.5, 133.0, 131.3, 130.3, 126.4 (Ar-*C*), 97.0 (d, ^1J(P-C) = 206.0 Hz, P*C*), 74.7 and 74.3 (O*C*H$_2$), 52.0 (*C*H$_3$), 44.1 (*C*H$_2$), 32.1 (*C*(CH$_3$)$_2$), 26.0, 21.6, 21.1, 14.0 and 13.7 (5 s, *C*H$_2$+*C*H$_3$).

^{31}P NMR: δ 19.37.

LC-MS: *m/z* 410 [M+1]$^+$.

Anal. Cacld for $C_{21}H_{32}NO_5P$: C, 61.60; H, 7.88; N, 3.42. Found: C, 61.72; H, 7.82; N, 3.51.

Compound 114



This compound was prepared by following a route similar to that for compound **113**.using allene **17c** (0.15 g, 0.45 mmol) and pyrrolidine (0 04 mL, 1.34 mmol). Reaction was conducted at 80 °C for 8h.

Yield: 0.153 g (84%, white solid).

Mp: 102–104 °C.

IR (KBr): 2965, 2878, 1726, 1603, 1541, 1478, 1399, 1279, 1128, 1059, 1007, 914 cm^{-1}.

^{1}H NMR: δ 7.56 (d, *J* =7.6 Hz, 1H, Ar-*H*), 7.21-7.10 (m, 3H, Ar-*H*), 3.92-3.85 (m, 2H, OCH_2), 3.72 (s, 3H, OCH_3), 3.38-3.33 (m, 2H, OCH_2), 3.00-2.74 (m, 6H, NCH_2+CH_2), 1.54-1.49 (m, 4H, CH_2), 1.17 (t, 3H, CH_3), 0.72 and 0.39 (2 s, 6H, CH_3).

^{13}C NMR: δ 169.0 (*C*O), 163.6 (d, *J* =26.0 Hz), 139.7 (d, *J* =7.0 Hz), 135.5_0, 135.4_5, 134.0, 133.9, 129.9, 129.0, 125.9 (Ar-*C*), 89.1 (d, ^1J(P-C) = 210.0 Hz, P*C*), 74.3 and 74.2 (OCH_2), 51.6 (CH_3), 49.9 (CH_2), 31.8 (d, *J* =5.0 Hz, $C(CH_3)_2$), 25.9 (CH_3), 25.2 (CH_2), 21.4, 20.9 and 13.7 (3 s, CH_3).

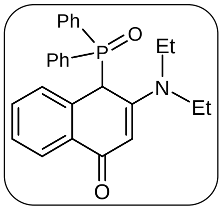
^{31}P NMR: δ 20.61.

LC-MS: *m/z* 406 $[M-1]^+$.

Anal. Cacld for $C_{21}H_{30}NO_5P$: C, 61.90; H, 7.42; N, 3.44. Found: C, 61.76; H, 7.52; N, 3.36.

3.82 Synthesis of phosphinoyl naphthalenone 115

Procedure was similar to that for compound **113** using allenylphosphine oxide **19**[63] (1.0 g, 2.67 mmol) and diethylamine (0 56 mL, 5.34 mmol). Reaction time was 8h at rt (25 °C).



Yield: 0.90 g (81%, white solid).

Mp: 140–144 °C.

IR (KBr): 3052, 2970, 1616, 1589, 1545, 1381, 1260, 1140, 762 cm^{-1}.

^{1}H NMR: δ 7.81 (d, *J* =7.2 Hz, 1H, Ar-*H*), 7.60-7.10 (m, 13H, Ar-*H*), 5.51 (s, 1H, C*H*), 4.98 (d, *J* =20.8 Hz, 1H, PC*H*), 3.98-2.87 (m, 4H, NCH_2), 1.16 (t, 6H, CH_3).

^{13}C NMR: δ 182.4 (*C*O), 158.2 (d, *J* =4.0 Hz), 133.9 (d, *J* =4.0 Hz), 133.1 (d, *J* =6.0 Hz), 132.6_4, 132.5_5, 132.1, 131.3, 131.2, 130.7, 129.7, 129.6, 128.3, 128.2, 128.0, 127.9, 127.8, 127.3, 126.3, 125.5 (Ar-*C*), 100.0 (*C*H), 48.9 (d, *J* =49.0 Hz, P*C*H), 45.3 (*C*H_2), 14.3 and 11.6 (2 br s, *C*H_3).

^{31}P NMR: δ 32.06.

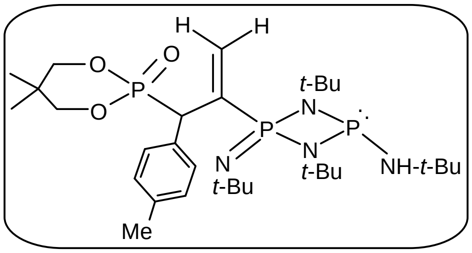
LC-MS: *m/z* 416 $[M+1]^+$.

Anal. Cacld for $C_{26}H_{26}NO_2P$: C, 75.16; H, 6.31; N, 3.37. Found: C, 75.31; H, 6.26; N, 3.45.

3.9 Nucleophilic addition reactions of cyclodiphosphazanes with allenylphosphonates/ allenylphosphine oxide/ dimethyl maleate

3.91 Synthesis of [(t-BuNH)P(μ-N-t-Bu)$_2$P(=N-t-Bu)-C(=CH$_2$)CH(R)-P(O)(OCH$_2$CMe$_2$CH$_2$O) R = 4-Me-C$_6$H$_4$ (117), 4-MeO-C$_6$H$_4$ (118)]

Compound 117



Cyclodiphosphazane **2**[52] (0.484 g, 1.38 mmol) and allenylphosphonate **16b**[37] (0 386 g, 1.38 mmol) were dissolved in dry toluene (8 mL), and the mixture was stirred at rt for 1 d. The solution was concentrated *in vacuo* (to ca 3 mL) and cooled for 1 d at -4 °C to obtain crystals of **117**. Similarly, compound **118** was prepared.

Yield: 0.804 g (92%, white solid).

Mp: 178–180 °C.

IR (KBr): 3335, 2970, 2901, 2629, 2550, 2262, 1819, 1606, 1512, 1473, 1361, 1280, 1215, 1062 cm^{-1}.

^{1}H NMR: δ 7.42 (d, ^{3}*J*(H-H) = 7.6 Hz, 2H, Ar-*H*), 7.04 (d, ^{3}*J*(H-H) = 8.0 Hz, 2H, Ar-*H*), 6.79 (d, ^{3}*J*(P-H) ~ 51.6 Hz, 1H, = CH$_A$*H*$_B$, *trans* to P), 6.01 (dd, ^{3}*J*(P-H) ~ 11.6 Hz, ^{2}*J*(P-H) ~ 14.8 Hz, 1H, P(O)C*H*), 5.75 (dd, ^{3}*J*(P-H) ~ 26.8 Hz, ^{4}*J*(P-H) = 3.6 Hz, 1H, =C*H*$_A$H$_B$, *cis* to P), 4.35–3.80 (m, 4H, OCH_2), 2.67 (d, ^2J(P-H) = 8.0 Hz, 1H, N*H*), 2.28 (1s, 3H, Ar-CH_3), 1.40, 1.39, 1.27, 1.17 and 0.89 (5s, 42H, $C(CH_3)_2$+$C(CH_3)_3$).

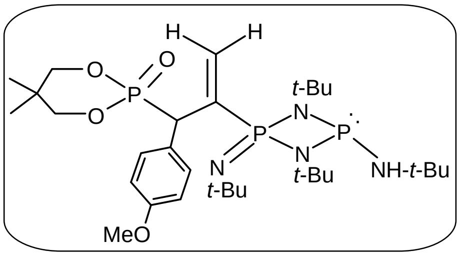
^{13}C NMR: δ 143.5 (d, ^1J(P-C) = 163.0 Hz, P*C*=CH$_2$), 136.5, 133.0 (d, ^2J(P-C) ~ 7.4 Hz), 130.0, 129.0, 128.9 and 128.2 (Ar-*C* + PC=*C*H$_2$), 76.5$_2$ and 76.4$_6$ (2s, O*C*H$_2$), 52.6 (d, ^2J(P-C) = 8.1 Hz, *C*(CH$_3$)$_3$), 52.2 (dd→t, ^2J(P-C) ~ 9.5 Hz, *C*(CH$_3$)$_3$), 51.4 (d, ^2J(P-C) = 14.6 Hz, *C*(CH$_3$)$_3$), 41.1 (dd, ^1J(P-C) ~ 125.0 Hz, ^2J(P-C) = 4.6 Hz, P(O)*C*(Ar)), 34.5 (d, ^3J(P-C) = 12.0 Hz, C(*C*H$_3$)$_3$), 32.9 (d, ^3J(P-C) ~ 9.6 Hz, C(*C*H$_3$)$_3$), 32.4 (d, ^3J(P-C) = 6.3 Hz, C(*C*H$_3$)$_3$), 31.1 (d, ^3J(P-C) = 24.3 Hz, C(*C*H$_3$)$_3$), 22.0 (Ar-*C*H$_3$), 21.1 and 20.9 (2s, C(*C*H$_3$)$_2$).

^{31}P NMR: δ 71.3 (d, ^3J(P-P) ~ 6.4 Hz), 20.8 (d, ^2J(P-P) ~ 35.2 Hz), -18.71 (dd, ^3J(P-P) ~ 6.4 Hz, ^2J(P-P) ~ 35.2 Hz).

LC-MS: *m/z* 627 $[M+1]^+$.

X-ray structure was determined for this compound.

Compound 118



Precursors **2** (0.561 g, 1.61 mmol) and **16c**[37](0 474 g, 1.61 mmol) were used.

Yield: 0.956 g (92%, white solid).

Mp: 150–154 °C.

IR (KBr): 3337, 2967, 2897, 1615, 1584, 1510, 1464, 1364, 1281, 1209, 1063, 1028, 885 cm^{-1}.

^{1}H NMR: δ 7.47 (d, ^3J(H-H) = 8.0 Hz, 2H, Ar-*H*), 6.81 (d, ^3J(H-H) = 8.4 Hz, 2H, Ar-*H*), 6.76 (d, ^3J(P-H) ~ 52.4 Hz, 1H, =CH_AH_B *trans* to P), 6.00 (dd, ^3J(P-H) ~ 15.2 Hz, ^2J(P-H) ~ 18.0 Hz, 1H, P(O)C*H*), 5.76 (d, ^3J(P-H) ~ 28.8 Hz, 1H, =CH_AH_B *cis* to P), 4.36-3.82 (m, 4H, OCH_2), 3.78 (s, 3H, Ar-OCH_3), 2.69 (d, ^2J(P-H) = 7.6 Hz, 1H, N*H*), 1.37, 1.29, 1.18, 1.08 and 0.83 (5 s, 42H, $C(CH_3)_2$+$C(CH_3)_3$).

^{13}C NMR: δ 143.6 (d, ^{1}J(P-C) = 159.0 Hz, P*C*=CH$_2$), 158.7 (d, ^{2}J(P-C) ~ 6.4 Hz, Ar-*C* + PC=*C*H$_2$), 131.1$_2$, 131.0$_5$, 128.1, 113.5 (Ar-*C*), 76.4$_2$ and 76.3$_8$ (2 s, O*C*H$_2$), 55.1 (Ar-O*C*H$_3$), 52.5 (d, ^{2}J(P-C) = 7.7 Hz, *C*(CH$_3$)$_3$), 52.3 (d, ^{2}J(P-C) ~ 8.8 Hz, *C*(CH$_3$)$_3$), 51.3 (d, ^{2}J(P-C) = 14.5 Hz, *C*(CH$_3$)$_3$), 40.7 (d, ^{1}J(P-C) ~ 125.4 Hz, P(O)*C*(Ar)), 34.4 (d, ^{3}J(P-C) = 11.2 Hz, C(*C*H$_3$)$_3$), 32.8 (d, ^{3}J(P-C) ~ 9.2 Hz, C(*C*H$_3$)$_3$), 32.3 (d, ^{3}J(P-C) = 6.0 Hz, C(*C*H$_3$)$_3$), 31.1 (d, ^{3}J(P-C) = 23.4 Hz, C(*C*H$_3$)$_3$), 21.9 and 20.8 (2s, C(*C*H$_3$)$_2$).

^{31}P NMR: δ 70.99 (br d, ^{2}J(P-P) ~ 6.7 Hz), 20.91 (d, ^{3}J(P-P) ~ 35.8 Hz), -18.90 (dd, ^{3}J(P-P) ~ 35.8 Hz, ^{2}J(P-P) ~ 6.7 Hz).

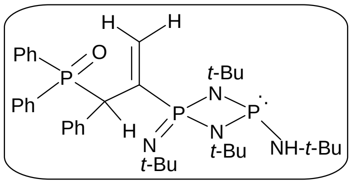
LC-MS: *m/z* 643 [M+1]$^+$.

Anal. Calcd. For $C_{31}H_{57}N_4O_4P_3$: C, 57.93; H, 8.94; N, 8.72. Found: C, 57.79; H, 8.98; N, 8.82.

X-ray structure was determined for this compound.

3.92 Synthesis of [(t-BuNH)P(μ-N-t-Bu)$_2$P(=N-t-Bu)-C(=CH$_2$)CH(Ph)-P(O)Ph$_2$ (119) and [(i-PrNH)P(μ-N-t-Bu)$_2$P(=N-i-Pr)-C(=CH$_2$)CH(Ph)-P(O)Ph$_2$ (120)

Compound 119



This compound was prepared by following a procedure similar to that for compound **117** using **2** (0.20 g, 0.57 mmol) and allenylphosphine oxide **18**[66] (0.18 g, 0.57 mmol).

Yield: 0.347 g (91%, white solid).

Mp: 188–190 °C.

IR (KBr): 3358, 2963, 2712, 1887, 1597, 1366, 1308, 1030, 887, 693 cm^{-1}.

^{1}H NMR: δ 8.16-7.00 (m, 16H, Ar-*H* + =CH$_A$*H*$_B$ *trans* to P*)*, 6.16 (dd, ^{3}J(P-H) ~ 4.8 Hz, ^{2}J(P-H) ~ 13.1 Hz, 1H, P(O)C*H*), 5.73 (d, ^{3}J(P-H) ~ 27.6 Hz, 1H, =C*H*$_A$H$_B$ *cis* to P), 2.57 (d, ^{2}J(P-H) = 6.8 Hz, 1H, N*H*), 1.46, 1.23, 0.94 and 0.80 (4 s,36H, C(C*H*$_3$)$_3$).

^{13}C NMR: δ 144.5 (d, ^{1}J(P-C) = 159.9 Hz, P*C*=CH$_2$), 136.2 (d, ^{2}J(P-C) ~ 11.2 Hz, (Ar-*C* + PC=*C*H$_2$), 134.4, 133.1, 132.2, 132.1, 131.3, 130.8, 130.8, 130.5, 129.1, 128.4, 128.3, 127.7, 127.6, 126.4 (Ar-*C*), 52.2 (d, ^{2}J(P-C) ~ 6.5 Hz, *C*(CH$_3$)$_3$), 51.4 (d, ^{2}J(P-C) = 14.6 Hz, *C*(CH$_3$)$_3$), 47.3 (d, ^{1}J(P-C) ~ 63.4 Hz, P(O)*C*(Ph)), 34.4 (d, ^{3}J(P-C) = 10.9 Hz, C(*C*H$_3$)$_3$), 32.7 (d, ^{3}J(P-C) = 9.5 Hz, C(*C*H$_3$)$_3$), 31.1 (d, ^{3}J(P-C) = 17.2 Hz, C(*C*H$_3$)$_3$).

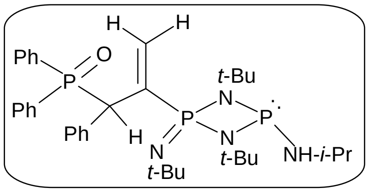
^{31}P NMR: δ 69.9 (d, ^{2}J(P^{III}-P^{V}) ~ 8.3 Hz), 31.8 (d, ^{3}J(P-P) ~ 24.9 Hz), -19.3 (dd, ^{3}J(P-P) ~ 24.9 Hz, ^{2}J(P^{III}-P^{V}) ~ 8.3 Hz).

LC-MS: *m/z* 665 [M+1]$^{+}$.

Anal. Calcd. for $C_{37}H_{55}N_4OP_3$: C, 66.85; H, 8.34; N, 8.25. Found: C, 66.75; H, 8.30; N, 8.51.

X-ray structure was determined for this compound.

Compound 120



This compound was prepared by following the procedure for compound **117** by using 1.12 mmol of **3**.[52c]

Yield: 0.625 g (88%, white solid).

Mp: 86–88 °C.

IR (KBr): 3437, 3256, 3059, 2965, 2866, 1597, 1493, 1439, 1366, 1206, 1028, 873 cm^{-1}.

^{1}H NMR: δ 8.22-7.02 (m, 16H, Ar-*H*+=CH$_A$*H*$_B$ *trans* to P*)*, 6.21 (dd, ^{2}J(P-H) ~ 13.2 Hz, ^{3}J(P-H) ~ 6.0 Hz, 1H, P(O)C*H*), 5.80 (d, ^{3}J(P-H) ~ 26.4 Hz, 1H, =C*H*$_A$H$_B$ *cis* to P), 3.64-3.47 (br, 2H, NC*H*(CH$_3$)$_2$), 2.01 (d, ^{2}J(P-H) = 8.4 Hz, 1H, N*H*), 1.31 (d, ^{2}J(H-H) = 6.0 Hz, 3H, CHC*H*$_3$), 1.21 (d, ^{2}J(H-H) = 6.0 Hz, 3H, CHC*H*$_3$), 1.13 (d, ^{2}J(H-H) = 6.4 Hz, 3H, CHC*H*$_3$), 1.10 (d, ^{2}J(H-H) = 6.4 Hz, 3H, CHC*H*$_3$), 0.87 and 0.74 (2 s,18H, C(C*H*$_3$)$_3$).

^{13}C NMR: δ 142.5 (d, ^{1}J(P-C) = 149.1 Hz, P*C*=CH$_2$), 136.3 (2 d, ^{2}J(P-C) ~ 13.1 Hz, Ar-*C* + PC=*C*H$_2$), 136.2, 134.2, 133.2, 133.1, 132.3, 132.2, 131.3, 130.9, 130.8, 130.5, 128.4, 128.2, 127.8, 127.6, 126.5 (Ar-*C*), 51.8 (d, ^2J(P-C) = 8.5 Hz, *C*(CH$_3$)$_3$), 46.5 (d, ^1J(P-C) ~ 63.0 Hz, P(O)*C*(Ph)), 44.4 (d, ^2J(P-C) = 7.2 Hz, *C*(CH$_3$)$_3$), 31.0 and 30.7 (2 s, C(*C*H$_3$)$_3$), 28.3 (d, ^3J(P-C) = 8.0 Hz, NCH(*C*H$_3$)$_2$), 28.2 (d, ^3J(P-C) = 6.2 Hz, NCH(*C*H$_3$)$_2$), 26.6 and 26.2 (2 s, =NCH(*C*H$_3$)$_2$).

^{31}P NMR: δ 71.9 (br, *P*-N), 32.0 (d, ^3J(P-P) ~ 24.5 Hz, *P*=O), -1.0 (br, *P*=N).

LC-MS: *m/z* 638 [M+1]$^+$.

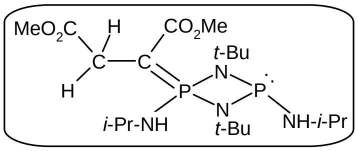
Anal. Calcd. for C$_{35}$H$_{51}$N$_4$OP$_3$: C, 66.02; H, 8.07; N, 8.80. Found: C, 66.12; H, 8.15; N, 8.69.

X-ray structure was determined for this compound.

3.93 Synthesis of (t-Bu-NH)P(μ-N-t-Bu)$_2$P(NH-t-Bu)=C(CO$_2$Me)CH$_2$(CO$_2$Me) (121) and (i-Pr-NH)P(μ-N-t-Bu)$_2$P(NH-i-Pr)=C(CO$_2$Me)CH$_2$(CO$_2$Me) (122)

Compound **121** is known.[83]

Compound 122



To a solution of [(*i*-PrNH)PN-*t*-Bu]$_2$ (**3**)[52c] [δ(P) 90.7; 0.315 g, 0.98 mmol] in toluene (15 mL), dimethyl maleate (0.283 g, 0.98 mmol) was added *via* syringe at room temperature, the mixture was stirred for 1 d and the solution concentrated *in vacuo* (*ca* 1.5 mL) and kept at -4 °C for 24 h to obtain the crystals of **122**.

Yield: 0.406 g (89%, white solid).

Mp: 132–136 °C.

IR (KBr): 33426, 3337, 3100, 2978, 2878, 2288, 2060, 1728, 1609, 1410, 1339, 1277, 1132, 1094, 889 cm^{-1}.

^{1}H NMR: δ 8.23-8.17 (m, 1H, =P-N*H*), 3.61 and 3.49 (2s, 6H, OC*H*$_3$), 3.52-3.18 (br, 2H, NC*H*(CH$_3$)$_2$), 2.69 (d, ^3J(H-H) = 14.4 Hz, 2H, PCC*H*$_2$), 2.23 (m, 1H, N*H*), 1.38-1.14 (m, 30H, (C(C*H*$_3$)$_2$+C(C*H*$_3$)$_3$).

^{13}C NMR: δ 174.9 (d, ^3J(P-C) = 9.2 Hz, PCCH$_2$-*C*(O)), 171.8 (d, ^2J(P-C) = 31.4 Hz, PC-*C*(O)), 52.8 (d, ^2J(P-C) ~ 8.4 Hz, *C*(CH$_3$)$_3$), 49.9 and 51.2 (2s,

$\mathrm{O}\mathit{C}\mathrm{H_3}$), 44.4 and 44.7 (2s, N-$\mathit{C}\mathrm{H(CH_3)_2}$), 43.7 (d, ^1J(P-C) ~ 182.5 Hz, P*C*), 41.5 (s, $\mathrm{PC}\mathit{C}\mathrm{H_2}$), 31.4 (d, ^3J(P-C) ~ 14.2 Hz, $\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$), 30.9 (br, $\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$), 26.4 (d, ^3J(P-C) = 4.6 Hz, $\mathrm{NCH(}\mathit{C}\mathrm{H_3)_2}$), 25.6 (d, ^3J(P-C) ~ 4.6 Hz, $\mathrm{NCH(}\mathit{C}\mathrm{H_3)_2}$).

^{31}P NMR: δ 79.9 (1s, 1P, NH-*P*), 35.6 (1s, 1P, C=*P*).

LC-MS: *m/z* 465 $[\mathrm{M+1}]^+$.

Anal. Calcd. for $C_{20}H_{42}N_4O_4P_2$: C, 51.71; H, 9.11; N, 12.06. Found: C, 51.62; H, 9.18; N, 12.15.

X-ray structure was determined for this compound.

3.10 X-ray crystallography

A suitable crystal was mounted on a glass fiber (for **24**$\cdot 1.5H_2O$, **25, 27**$\cdot$PhCH$_3$, **28**, **30**$\cdot H_2O$, **32**$\cdot 1/2H_2O$, **35**, **38**, **47**, **50**, *cis*-**55**, *cis*-**56**, *trans*-**56**$\cdot 1/2CH_2Cl_2$, *cis*-**57**, **59**, **60**, **63**, **65**$\cdot 2CHCl_3$, (*R*)-**66**, (*S*)-**66**, **67**, **75**, **77**, **89**, **93**, **104**, **107**, **112**$\cdot$***n*-C$_5$H$_{12}$**, **115**, **117**, **118**, **119**, **120** and **122**) and X-ray data were collected at 293 K on a Bruker AXS-SMART or on an OXFORD diffractometer using Mo-K_α radiation (λ = 0.71073 Å). Structures were solved and refined using standard methods.[99] Absorption corrections were done using SADABS program, where applicable. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were fixed by geometry or located by a Difference Fourier and refined isotropically. Some of the methyl carbon atoms of the *t*-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 **50**. Specifically, in the structures of compounds **24**, and **28**, disorder is found at the *t*-butyl carbons attached to C9 and (N4, C24, C28) respectively. Crystal data are summarized in Table 3a-i.

Table 3a. Crystal data for compounds **24**·1.5H_2O, **25**, **27**·$PhCH_3$ and **28**[a]

Compound	**24**·1.5H_2O	**25**	**27**·$PhCH_3$	**28**
CCDC no.	927541	927542	927543	927544
Emp. formula	$C_{39}H_{68}N_7O_{4.5}P_4$	$C_{39}H_{65}N_7O_3P_4$	$C_{34}H_{46}N_4O_3P_2$	$C_{23}H_{30}N_3O_2P$
Formula weight	830.88	803.86	620.69	411.47
Crystal system	Monoclinic	Triclinic	Orthorhombic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$	*P*bca	$P\bar{1}$
a /Å	15.4582(7)	12.5852(6)	16.5803(10)	9.0147(6)
b /Å	13.8327(9)	13.1691(6)	16.9445(14)	15.4480(6)
c /Å	26.5063(14)	15.2915(7)	25.294(2)	17.8261(11)
α/deg	90	73.274(4)	90	98.656(4)
β/deg	122.642(3)	84.181(4)	90	95.555(5)
γ/deg	90	68.371(4)	90	98.978(4)
V /Å^3	4772.6(5)	2256.19(18)	7106.1(9)	2405.6(2)
Z	4	2	8	4
D_{calc} /g cm^{-3}]	1.156	1.183	1.160	1.136
μ /mm^{-1}	0.202	0.210	0.159	0.136
F(000)	1788	864	2656	880
Data/ restraints/ parameters	6860/7/531	7657/0/502	6090/10/400	8370/3/552
S	0.917	1.040	0.990	1.057
R1 [I>2σ(I)]	0.0657	0.0592	0.0789	0.0789
wR2 [all data]	0.1753	0.1512	0.1972	0.2062
Max./min. residual electron dens. [eÅ^{-3}]	0.604/-0.384	0.557/-0.370	0.778/-0.298	0.520/-0.463

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma wF_o^4]^{0.5}$

Table 3b. Crystal data for compounds **30**·H_2O, **32**·1/2H_2O, **35** and **38**[a]

Compound	**30**·H_2O	**32**·1/2H_2O	**35**	**38**
CCDC no.	927545	927546	935222	935223
Emp. formula	$C_{24}H_{44}N_4O_3P_2Si$	$C_{27}H_{43}N_4O_{3.5}P_2$	$C_{25}H_{29}NO_7P_2$	$C_{19}H_{26}NO_4P$
Formula weight	526.66	541.59	517.43	363.38
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P2_1/c$
a /Å	15.3487(19)	10.5313(8)	14.8591(6)	10.7416(11)
b /Å	9.8290(5)	16.6140(13)	10.9574(5)	10.7810(9)
c /Å	20.556(2)	18.4226(13)	16.3655(7)	17.0232(14)
α/deg	90	106.365(7)	90	90
β/deg	110.653(14)	96.757(6)	107.239(4)	103.470(9)
γ/deg	90	101.564(7)	90	90
V /Å^3	2901.8(5)	2977.5(4)	2544.89(18)	1917.2(3)
Z	4	4	4	4
D_{calc} /g cm^{-3}]	1.206	1.208	1.350	1.259
μ /mm^{-1}	0.222	0.181	0.216	0.166
F(000)	1136	1164	1088	776
Data/ restraints/ parameters	5057/0/331	9869/3/694	4465/0/ 320	3367.0/233
S	0.814	0.746	1.053	1.030
R1 [I>2σ(I)]	0.0692	0.0668	0.0459	0.0580
wR2 [all data]	0.0806	0.0855	0.1179	0.1413
Max./min. residual electron dens. [eÅ^{-3}]	0.263/-0.320	0.295/-0.246	0.265/ -0.266	0.444/ -0.303

[a] $R1 = \Sigma||F_O| - |F_C||/\Sigma|F_O|$ and $wR2 = [\Sigma w(F_O^2-F_C^2)^2/\Sigma wF_O^4]^{0.5}$

Table 3c. Crystal data for compounds **47**, **50**, *cis*-**55** and *cis*-**56**[a]

Compound	**47**	**50**	*cis*-**55**	*cis*-**56**
CCDC no.	966228	966229	927547	927548
Emp. formula	$C_{26}H_{25}ClNO_3P$	$C_{14}H_{17}NO$	$C_{16}H_{26}N_4O_6P_2$	$C_{24}H_{26}N_4O_6P_2$
Formula weight	465.89	215.30	432.35	528.43
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$P\bar{1}$	$C2/c$	$C2/c$
a /Å	27.797(7)	11.0340(16)	17.2960(13)	21.035(4)
b /Å	16.4138(15)	12.493(3)	8.0022(4)	10.233(2)
c /Å	15.143(4)	19.617(5)	17.8356(13)	15.523(3)
α/deg	90	88.024(19)	90	90
β/deg	133.53(4)	76.769(17)	120.694(10)	128.87(3)
γ/deg	90	68.061(17)	90	90
V /Å^3	5009.6(18)	2437.8(9)	2122.7(2)	2601.4(9)
Z	8	8	4	4
D_{calc} /g cm^{-3}]	1.235	1.173	1.353	1.349
μ /mm^{-1}	0.243	0.073	0.244	0.213
F(000)	1952	928	912	1104
Data/ restraints/ parameters	4407/5/289	8563/4/594	1872/0/130	2294/0/166
S	1.075	0.721	1.062	1.037
R1 [I>2σ(I)]	0.0786	0.1072	0.0397	0.0411
wR2 [all data]	0.2306	0.2024	0.1065	0.1091
Max./min. residual electron dens. [eÅ^{-3}]	0.464/-0.456	0.268/-0.192	0.291/-0.258	0.249/-0.269

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma wF_o^4]^{0.5}$

Table 3d. Crystal data for compounds *trans*-**56**·1/2CH_2Cl_2, *cis*-**57**, **59** and **60**[a]

Compound	*trans*-**56**·1/2CH_2Cl_2	*cis*-**57**	**59**[b]	**60**[c]
CCDC no.	927549	927550	-	-
Emp. formula	$C_{25}H_{28}N_4O_6P_2Cl2$	$C_{16}H_{32}N_4O_3P_2$	$C_{39}H_{29}NO_3P_2$	$C_{39}H_{29}NO_4P_2$
Formula weight	613.35	390.40	621.57	637.57
Crystal system	Triclinic	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P\bar{1}$	$P2_1/c$	$P2_12_12_1$	$P2_12_12_1$
a /Å	7.9645(14)	18.116(4)	11.2790(6)	11.2810(5)
b /Å	9.0060(12)	10.276(2)	16.1962(8)	16.1001(8)
c /Å	22.375(3)	11.554(2)	17.5843(9)	17.7437(7)
α/deg	95.477(11)	90	90	90
β/deg	93.033(13)	90.29(3)	90	90
γ/deg	113.752(15)	90	90	90
V /Å^3	1454.9(4)	2150.7(7)	3212.2(3)	3222.7(2)
Z	2	4	4	4
D_{calc} /g cm^{-3}]	1.400	1.206	1.285	1.314
μ /mm^{-1}	0.379	0.223	0.175	0.178
F(000)	636	840	1296	1328
Data/ restraints/ parameters	5019/0/359	3629/0/262	5347/0/406	5547/0/415
S	1.067	1.094	1.042	0.964
R1 [I>2σ(I)]	0.1331	0.0740	0.0421	0.0586
wR2 [all data]	0.2994	0.1505	0.1054	0.0989
Max./min. residual electron dens. [eÅ^{-3}]	0.476/-0.503	0.689/-0.284	0.770/-0.165	0.300/ -0.202

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma wF_o^4]^{0.5}$

[b] Flack parameter: -0.03(9)

[c] Flack parameter: -0.09(12)

Table 3e. Crystal data for compounds **63**, **65**·2CHCl$_3$, (*R*)-**66** and (*S*)-**66**[a]

Compound	**63**[b]	**65**·2CHCl$_3$	(*R*)-**66**[c]	(*S*)-**66**[d]
Emp. formula	$C_{40}H_{31}NO_4P_2$	$C_{42}H_{32}BrCl_6NO_4P_2$	$C_{39}H_{33}NO_4P_2$	$C_{39}H_{33}NO_4P_2$
Formula weight	651.60	969.24	641.60	641.60
Crystal system	Orthorhombic	Triclinic	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P\bar{1}$	$P2_12_12_1$	$P2_12_12_1$
a /Å	11.1755(11)	11.5145(7)	11.3350(6)	11.3101(10)
b /Å	15.950(2)	13.3968(8)	17.7472(12)	17.7378(17)
c /Å	18.117(2)	14.6374(9)	16.1457(8)	16.0426(14)
α/deg	90	86.833(5)	90	90
β/deg	90	75.632(5)	90	90
γ/deg	90	87.590(5)	90	90
V /Å^3	3229.3(7)	2183.0(2)	3247.9(3)	3218.4(5)
Z	4	2	4	4
D_{calc} /g cm^{-3}]	1.340	1.475	1.312	1.324
μ /mm^{-1}	0.179	1.424	0.177	0.179
F(000)	1360	980	1344	1344
Data/ restraints/ parameters	5200/0/425	7681/0/507	5525/0/415	5523/0/415
S	1.043	1.063	1.033	1.040
R1 [I>2σ(I)]	0.0765	0.0729	0.0564	0.0487
wR2 [all data]	0.1258	0.2028	0.1529	0.1275
Max./min. residual electron dens. [eÅ^{-3}]	0.291/-0.272	1.212/-0.905	0.640/-0.334	0.488/ -0.281

[a] $R1 = \Sigma||F_O| - |F_C||/\Sigma|F_O|$ and $wR2 = [\Sigma w(F_O^2-F_C^2)^2/\Sigma wF_O^4]^{0.5}$

[b] Flack parameter: -0.03(16)

[c] Flack parameter: -0.13(12)

[d] Flack parameter: -0.27(11)

Table 3f. Crystal data for compounds **67**, **75**, **77** and **89**[a]

Compound	**67**	**75**	**77**	**89**
CCDC no.	-	981067	981068	1016234
Emp. formula	$C_{39}H_{33}ClNO_4P_2$	$C_{29}H_{24}NO_2P$	$C_{22}H_{20}NOP$	$C_{28}H_{42}N_4OP_2$
Formula weight	677.05	449.46	345.36	512.60
Crystal system	Triclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	*Pccn*	$P2_1/c$
a /Å	9.7782(6)	9.9427(15)	11.2497(6)	13.4400(19)
b /Å	12.6735(7)	16.894(3)	21.1287(9)	17.383(2)
c /Å	15.2180(9)	14.819(2)	15.2880(6)	13.2418(17)
α/deg	72.422(5)	90	90	90
β/deg	88.076(5)	109.195(2)	90	104.546(13)
γ/deg	69.077(5)	90	90	90
V /Å^3	1673.42(17)	2350.8(6)	3633.8(3)	2994.5(7)
Z	2	4	8	4
D_{calc} /g cm^{-3}]	1.344	1.270	1.263	1.137
μ /mm^{-1}	0.253	0.143	0.160	0.171
$F(000)$	706	944	1456	1104
Data/ restraints/ parameters	5885/0/424	4141/0/299	3205/0/231	4580/1/332
S	1.061	1.074	1.085	1.011
R1 [I>2σ(I)]	0.0534	0.0408	0.0430	0.1372
wR2 [all data]	0.1409	0.1101	0.1076	0.2844
Max./min. residual electron dens. [eÅ^{-3}]	0.408/-0.462	0.181/-0.315	0.339/-0.296	0.804/ -0.339

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma wF_o^4]^{0.5}$

Table 3g. Crystal data for compounds **93**, **104**, **107** and **112·*n*-C_5H_{12}**[a]

Compound	**93**	**104**	**107**	**112·*n*-C_5H_{12}**
Emp. formula	$C_{28}H_{26}NO_4P$	$C_{15}H_{11}NO$	$C_{55}H_{10}ClNO$	$C_{42}H_{62}N_2O_6P_2$
Formula weight	471.47	221.25	255.69	752.88
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$C2/c$	$C2/c$	$P\bar{1}$
a /Å	12.282(3)	17.8590(16)	17.482(4)	9.7795(10)
b /Å	8.9370(18)	5.8124(4)	5.9043(13)	12.6937(13)
c /Å	22.179(4)	21.742(2)	23.251(5)	17.1610(17)
α/deg	90	90	90	101.547(2)
β/deg	92.60(3)	106.101(10)	100.505(3)	102.290(2)
γ/deg	90	90	90	110.168(2)
V /Å^3	2431.9(8)	2168.3(3)	2359.7(9)	1864.9(3)
Z	4	8	8	2
D_{calc} /g cm^{-3}]	1.288	1.355	1.439	1.341
μ /mm^{-1}	0.148	0.085	0.308	0.169
F(000)	992	928	1056	812
Data/ restraints/ parameters	4288/0/309	1902/0/158	2057/0/167	6514/4/479
S	1.156	1.044	1.068	1.161
R1 [I>2σ(I)]	0.0573	0.0409	0.0479	0.1260
wR2 [all data]	0.1269	0.1042	0.1212	0.2846
Max./min. residual electron dens. [eÅ^{-3}]	0.401/-0.282	0.155/-0.170	0.251/-0.331	1.163/-0.207

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma wF_o^4]^{0.5}$

Table 3h. Crystal data for compounds **115**, **117**, **118** and **119**[a]

Compound	**115**[b]	**117**	**118**
CCDC no.	-	749652	-
Emp. formula	$C_{28}H_{30}NO_3P$	$C_{31}H_{57}N_4O_3P_3$	$C_{31}H_{57}N_4O_4P_3$
Formula weight	459.50	626.72	642.72
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	*C*c	$P\bar{1}$	$P\bar{1}$
a /Å	25.538(3)	10.3463(7)	13.8603(9)
b /Å	12.4575(8)	10.7424(7)	15.7746(10)
c /Å	16.7582(13)	16.4625(11)	16.2606(11)
α/deg	90	87.232(2)	88.0040(10)
β/deg	111.076(10)	89.947(3)	84.9490(10)
γ/deg	90	82.1340(10)	87.6000(10)
V /Å^3	4974.8(7)	1810.3(2)	3536.6(4)
Z	8	2	4
D_{calc} /g cm^{-3}]	1.227	1.150	1.207
μ /mm^{-1}	0.140	0.199	0.207
F(000)	1952	680	1392
Data/ restraints/ parameters	5803/2/608	7113/ 0/ 389	12397/0/795
S	1.025	1.079	1.012
R1 [I>2σ(I)]	0.0601	0.0684	0.0487
wR2 [all data]	0.1016	0.1672	0.1195
Max./min. residual electron dens. [eÅ^{-3}]	0.258/-0.222	0.694/ -0.366	0.536/-0.280

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma wF_o^4]^{0.5}$

[b] Flack parameter: 0.06(13)

Table 3i. Crystal data for compounds **119**, **120** and **122**[a]

Compound	**119**[b]	**120**	**122**
CCDC no.	797416	797417	797419
Emp. formula	$C_{37}H_{55}N_4OP_3$	$C_{35}H_{51}N_4OP_3$	$C_{20}H_{42}N_4O_4P_2$
Formula weight	664.76	636.71	464.52
Crystal system	Orthorhombic	Triclinic	Orthorhombic
Space group	*Pca2(1)*	$P\bar{1}$	*Pbca*
a /Å	18.099(2)	9.515(2)	10.354(1)
b /Å	10.038(1)	10.152(2)	18.366(2)
c /Å	20.933(2)	19.544(3)	27.289(3)
α/deg	90	79.155(2)	90
β/deg	90	89.058(2)	90
γ/deg	90	87.047(2)	90
V /Å^3	3803.1(6)	1851.7(5)	5189.5(8)
Z	4	2	8
D_{calc} /g cm^{-3}]	1.161	1.142	1.189
μ /mm^{-1}	0.189	0.192	0.198
F(000)	1432	684	2016
Data/ restraints/ parameters	6685/ 7/ 446	6496 /0/ 398	4563/ 0/ 291
S	1.053	1.044	1.198
R1 [I>2σ(I)]	0.0301	0.0543	0.0510
wR2 [all data]	0.0779	0.1401	0.1085
Max./min. residual electron dens. [eÅ^{-3}]	0.289 / -0.192	0.457/ -0.191	0.557/ -0.278

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma wF_o^4]^{0.5}$

[b] Flack parameter: 0.06(8)

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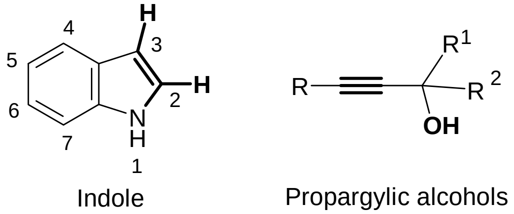
PART-B

[Cu]-CATALYZED RING EXPANSION/ HYDROARYLATION OF 3-DIENYLINDOLES

INTRODUCTION

4.1 General Introduction- Indoles, Propargyl Alcohols and [Cu]-Catalysis

Indoles and their derivatives are important core structures present in numerous natural products and pharmaceuticals.[1] The well-known amino acid tryptophan is based on an indole skeleton and is the precursor for the neurotransmitter serotonin.[2] For this reason, the synthesis as well as reactivity of indoles is currently a prime area of research activity. An important feature of this system is that the C-H bonds at C-2 and C-3 can be readily functionalized.[3] This was the motivation for our interest in this ring system as the substrate. Propargylic alcohols, the other class of reactants for our study, are extremely versatile synthetic precursors in organic synthesis due to the presence of dual functionalities, the –OH and the alkyne.[4] Catalytic [or noncatalytic] coupling of indoles with propargylic alcohols is expected to lead to synthetically and pharmaceutically valuable targets. For such transformations, [Cu]-catalysis is an important avenue. Thus, in the following sections, a brief survey of literature on the reactivity of propargylic alcohols, with some of them involving indoles, as well as [Cu]-catalysis, is presented.



Indole Propargylic alcohols

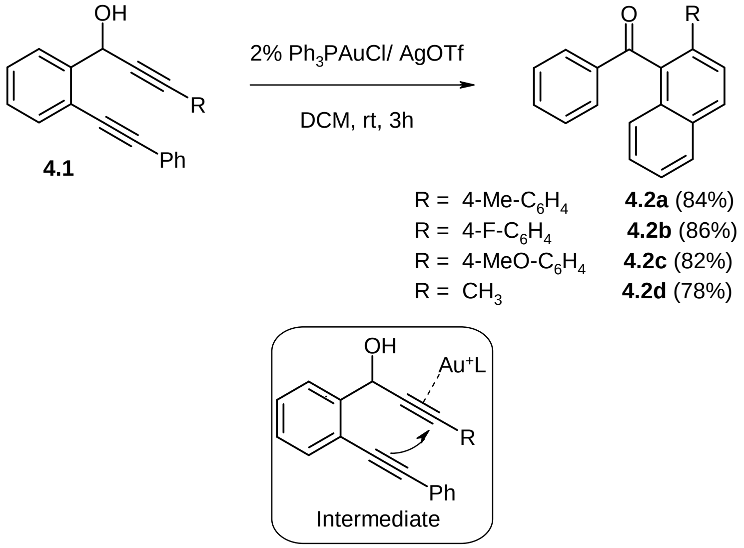
4.2 Organic transformations involving propargyl alcohols

Due to dual functionalities, propargyl alcohols undergo metalation on electrophilic alkyne or protonation on alcoholic group and cycloisomerization which leads to various carbo-/hetero-cycles. These reactions involve one or more of Friedel-Crafts alkylation, isomerization, cyclization, addition or substitution leading to a variety of heterocycles like furans, pyrroles, thiophenes, quinolines, pyrans, oxazines, pyridines, isochromans, indenes, thiazoles and triazoles. In the following subsection, selected reactions of propargyl alcohols from the literature that are relevant to our work are discussed.

4.21 Cyclization/cycloisomerization

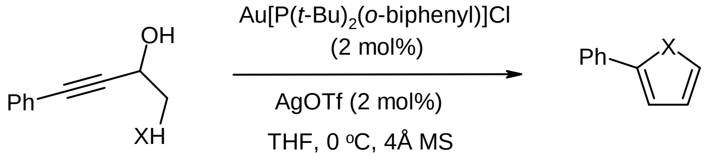
Liu and Lian described an efficient gold-catalyzed cyclization of 1,6-diyne-4-en-3-ol **4.1** to give naphthyl ketones and their derivatives **4.2a-d** (Scheme 4.1).[5] This cyclization is assumed to proceed *via* an OH-chelated Au(I)-π alkyne species, which subsequently triggers the cyclization by a 6-endo-dig attack of the second alkyne group. This type of cyclization is applicable to diverse propargyl alcohols as substrates.

Scheme 4.1



Aponick *et al* developed an efficient gold-catalyzed dehydrative cyclization of heteroatom-substituted propargyl alcohols **4.3** that afforded aromatic heterocycles **4.4a-c** (Scheme 4.2).[6] The conversion took place in minutes with low catalyst loading and at low temperature.

Scheme 4.2

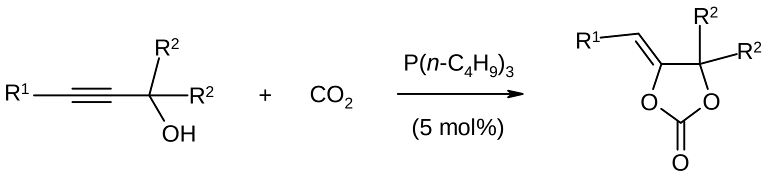


4.3

X = O **4.4a** (93%)
X = NTs **4.4b** (89%)
X = S **4.4c** (90%)

Ikariya and co-workers developed stereoselective synthesis of α-alkylidene cyclic carbonates *via* carboxylative cyclization of propargyl alcohols.[7] Thus a phosphine catalyzed carboxylative cyclization of propargyl alcohols **4.5** in supercritical carbon dioxide afforded the α-alkylidene-1,3-dioxolan-2-ones **4.6a-d** (Scheme 4.3). Internal propargyl alcohols gave *Z*-alkylidene cyclic carbonates exclusively due to the formation of a putative P(*n*-C_4H_9)$_3$-CO_2 adduct as a key intermediate.

Scheme 4.3

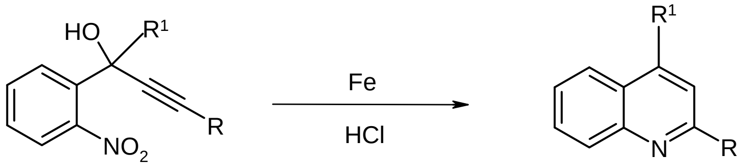


4.5

R^1 = H, R^2 = Me **4.6a** (99%)
R^1 = Ph, R^2 = Me **4.6b** (76%)
R^1 = 4-O_2N-C_6H_4, R^2 = Me **4.6c** (77%)
R^1 = Ph, R^2 = -(CH$_2$)$_5$- **4.6d** (74%)

Deshong and Sandelier discovered a facile synthesis of substituted quinolines *via* reductive cyclization of *o*-nitrophenyl propargyl alcohols.[8] This method involved the reduction of secondary and tertiary propargyl alcohols **4.7** possessing *o*-nitro group followed by acid catalyzed Meyer-Schuster rearrangement producing 2-substituted or 2,4-disubstituted quinolines **4.8a-c** (Scheme 4.4). Tertiary propargyl alcohols gave better yields than secondary propargyl alcohols in this reaction.

Scheme 4.4



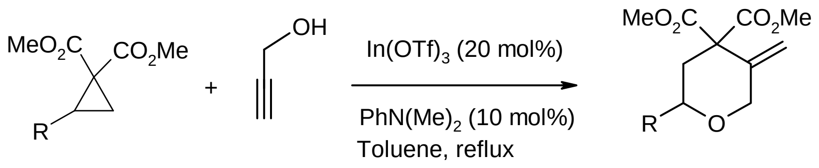
4.7

R = n-C_4H_9, R^1 = Me **4.8a** (95%)
R = Ph, R^1 = Me **4.8b** (82%)
R = Ph, R^1 = H **4.8c** (64%)

4.22 Nucleophilic addition/cyclization

Kerr and co-workers described one-pot synthesis of tetrahydropyrans from propargyl alcohols and 1,1-cyclopropane diesters.[9] This method involves ring-opening of 1,1-cyclopropanediesters **4.9** by the hydroxyl group of a propargyl alcohol that sets up a subsequent Conia-ene cyclization under Lewis acid catalysis to lead to substituted tetrahydropyrans **4.10a-c** in high yields (Scheme 4.5).

Scheme 4.5

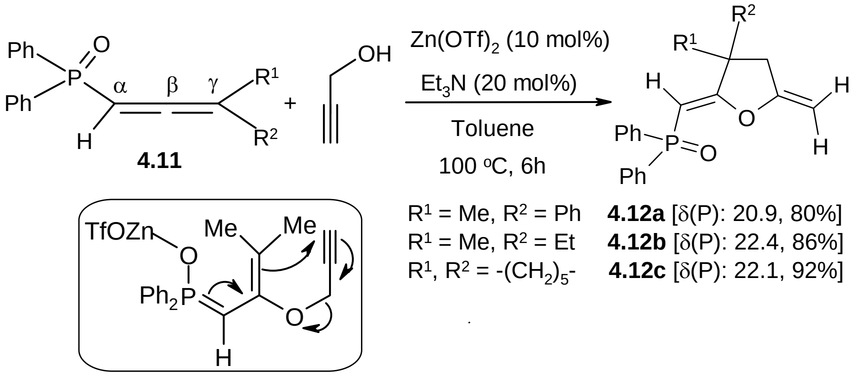


4.9

R = Ph **4.10a** (88%)
R = 4-Br-C_6H_4 **4.10b** (61%)
R = 4-MeO_2C-C_6H_4 **4.10c** (60%)

Recently, our research group reported the synthesis of 2,5-dimethylenetetrahydrofurans and 2-substituted furans from propargyl alcohols by using zinc triflate.[10] The reaction proceeded through nucleophilic addition of propargyl alcohol to the allenylphosphine oxide **4.11** followed by cyclization in the presence of zinc triflate/triethylamine combination resulting in 2,5-dimethylenetetrahydrofurans **4.12a-c** (Scheme 4.6).

Scheme 4.6

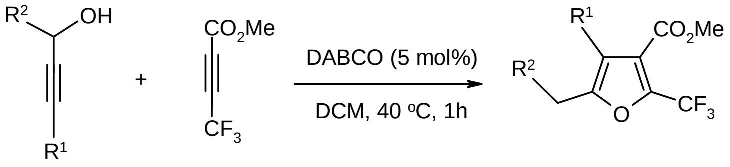


4.11

R^1 = Me, R^2 = Ph **4.12a** [δ(P): 20.9, 80%]
R^1 = Me, R^2 = Et **4.12b** [δ(P): 22.4, 86%]
R^1, R^2 = -$(CH_2)_5$- **4.12c** [δ(P): 22.1, 92%]

Synthesis of trifluoromethylated furans **4.14a-c** from propargyl alcohols **4.13** and methyl 2-perfluoroalkynoate catalyzed by DABCO was reported by Shi, Wan and co-workers (Scheme 4.7).[11] The established allene-enol and control experiments indicated that the reaction involved a Michael addition and Claisen rearrangement/cyclization process under mild conditions.

Scheme 4.7

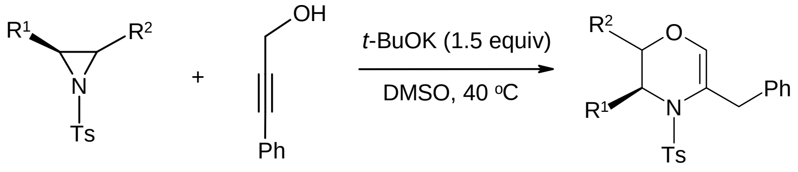


4.13

R^1 = Ph, R^2 = Ph **4.14a** (98%)
R^1 = Ph, R^2 = 4-MeO-C_6H_4 **4.14b** (72%)
R^1 = 4-Cl-C_6H_4, R^2 = Ph **4.14c** (89%)

Xiao and Zhou described a potassium *tert*-butoxide promoted tandem ring opening or closing reactions of *N*-tosyl aziridines and arylpropargyl alcohols.[12] This new reaction furnished the desired dihydro-oxazine derivatives **4.16a-c** from *N*-tosyl aziridines **4.15** and aryl substituted propargyl alcohols in moderate to good yields (Scheme 4.8).

Scheme 4.8



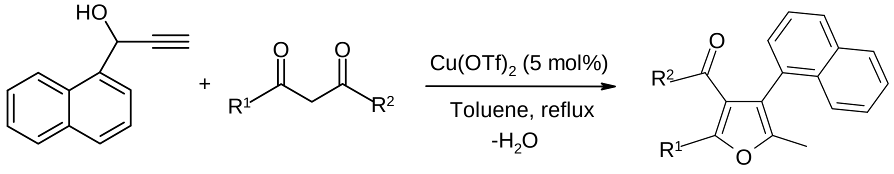
4.15

R^1 = *i*-Pr, R^2 = H **4.16a** (69%)
R^1 = Me, R^2 = H **4.16b** (65%)
R^1 = Bn, R^2 = H **4.16c** (22%)

4.23 Nucleophilic substitution/ cyclization

Zhan and co-workers described a one-pot approach to substituted furans through copper catalysis.[13] Tandem sequential propargylation of 1,3-dicarbonyl compounds with propargyl alcohol **4.17** followed by cycloisomerization in the presence of $Cu(OTf)_2$ provided the substituted furan derivatives **4.18a-b** (Scheme 4.9). The conversion took less reaction time (within hours) under mild conditions.

Scheme 4.9

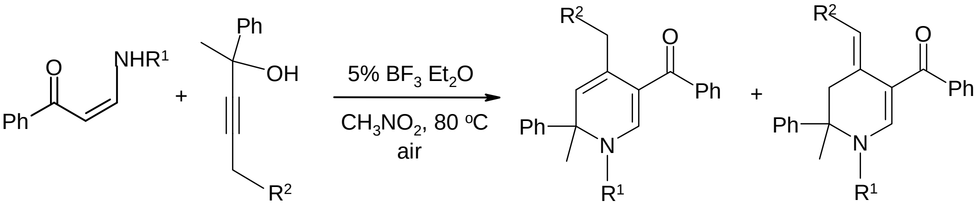


4.17

$R^1 = R^2$ = Me **4.18a** (76%)
$R^1 = R^2$ = Ph **4.18b** (81%)

Recently, Li and co-workers reported the synthesis of multisubstituted 1,2-dyhydropyridines **4.21a-c** and **4.22a-c** by Lewis acid-catalyzed cyclization of enaminones **4.19** with propargylic alcohols **4.20** (Scheme 4.10).[14] Aryl and alkyl substituents on both enaminones and propargyl alcohols were compatible in the cascade reactions furnishing the desired 1,2-dihydropyridine and its isomers in good yields under mild conditions.

Scheme 4.10

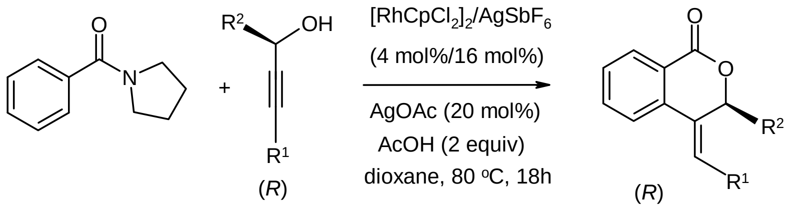


4.19 **4.20**

R^1 = Ph, R^2 = $(CH_2)_2CH_3$ **4.21a** (21%) + **4.22a** (39%)
R^1 = Ph, R^2 = CH_2Ph **4.21b** (35%) + **4.22b** (31%)
R^1 = 4-O_2N-C_6H_4, R^2 = CH_2Ph **4.21c** (21%) + **4.22c** (33%)

Wang *et al* reported the coupling of benzamides with propargyl alcohols *via* hydroarylation-lactonization.[15] The reaction proceeded through Rh(III)-catalyzed C-H activation followed by annulation of 1-benzoylpyrrolidine with propargyl alcohol **4.23** affording highly enantio-enriched (4-benzylidene)isochroman-1-ones **4.24a-c** (Scheme 4.11).

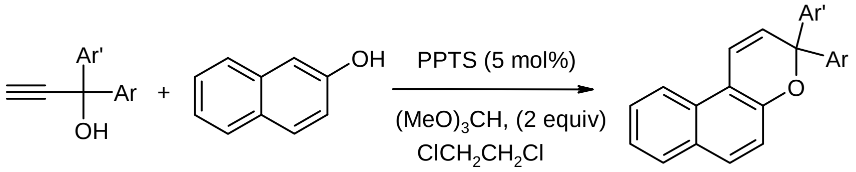
Scheme 4.11



4.23 R^1 = Ph, R^2 = Me **4.24a** (86%) (ee 97.3)
R^1 = 4-MeO-C_6H_4, R^2 = Me **4.24b** (85%) (ee 95.7)
R^1 = 4-Br-C_6H_4, R^2 = Ph **4.24c** (77%) (ee 97.7)

Carreira and Zhao developed a facile one–pot method for photochromic pyrans *via* PPTS catalysis (Scheme 4.12).[16] Thus synthesis of photochromic pyrans **4.26a-b**, including [3*H*]naphtha[2,1-b]pyrans, [2*H*]naphtho[1,2-*b*]pyrans, indeno-fused naphtho[1,2-*b*]pyrans and heteroannulated pyrans from the reaction of propargyl alcohol **4.25** and naphthol or phenol derivatives in the presence of PPTS (5 mol%) and (MeO)3CH (2 equiv) was achieved in excellent yields.

Scheme 4.12

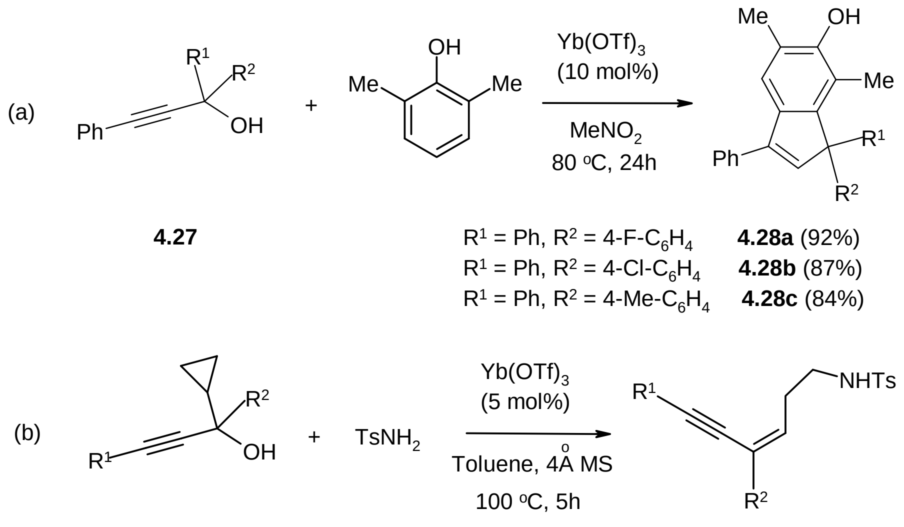


4.25

Ar = Ar' = Ph **4.26a** (92%)
Ar = Ar' = 4-OMe-C$_6$H$_4$ **4.26b** (96%)

Recently, Hong Chan and co-workers reported a new synthetic route to bioactive indenols and their derivatives by ytterbium(III) triflate catalyzed tandem Friedel-Crafts alkylation or hydroarylation of propargylic alcohols **4.27** with phenols (Scheme 4.13a).[17a] This reaction gave excellent yields and regioselectivity under mild conditions. It offers a straight forward and convenient one step route to indenols **4.28a-c**. The same group also reported the synthesis of conjugated enynes **4.30a-c** by ytterbium(III) triflate catalyzed amination or ring opening of substituted 1-cyclopropylprop-2-yn-1-ols **4.29** with sulfonamides (Scheme 4.13b).[17b] Moderate to good yields were obtained with decent regioselectivity under mild conditions.

Scheme 4.13



4.27

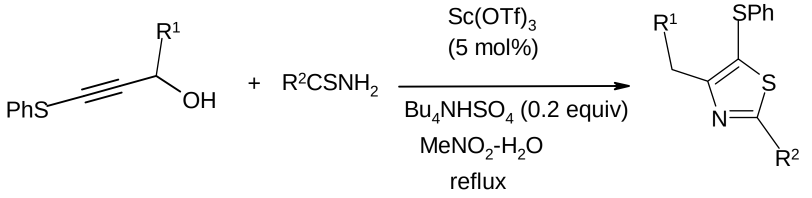
R^1 = Ph, R^2 = 4-F-C$_6$H$_4$ **4.28a** (92%)
R^1 = Ph, R^2 = 4-Cl-C$_6$H$_4$ **4.28b** (87%)
R^1 = Ph, R^2 = 4-Me-C$_6$H$_4$ **4.28c** (84%)

4.29

R^1 = Ph, R^2 = 4-F-C$_6$H$_4$ **4.30a** (70%)
R^1 = Ph, R^2 = 4-Cl-C$_6$H$_4$ **4.30b** (67%)
R^1 = 4-Me-C$_6$H$_4$, R^2 = 4-MeO-C$_6$H$_4$ **4.30c** (56%)

Yoshimatsu et al reported regioselective synthesis of multifunctionalized thiazoles and selenazoles **4.32a-c** in high yields using the catalytic system scandium triflate-nitromethane-H_2O in the presence of Bu_4NHSO_4 (Scheme 4.14).[18] This is a new type of regioselective cycloaddition reaction of the 3-sulphanyl or 3-selanylpropargyl alcohols **4.31** having thioamide or selenamide.

Scheme 4.14

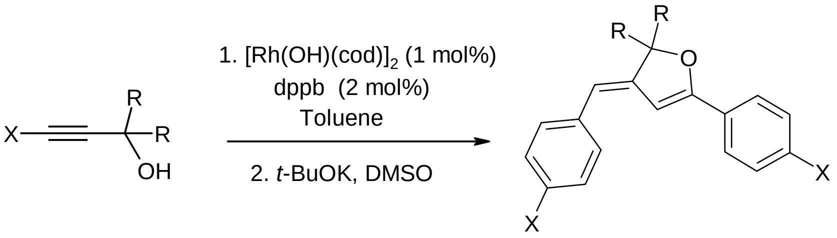


4.31

R^1 = Ph, R^2 = Ph **4.32a** (50%)
R^1 = 4-Cl-C_6H_4, R^2 = Ph **4.32b** (50%)
R^1 = 4-MeO-C_6H_4, R^2 = Me **4.32c** (84%)

Miura and co-workers synthesized fluorescent dihydrofurans derivatives from *γ*-arylated *tert*-propargyl alcohols.[19] Thus 1,1-disubstituted 3-aryl-2-propyn-1-ols **4.33** underwent regio- and stereo-selective homocoupling with the liberation of a ketone through *β*-carbon elimination to give 2-hydroxymethyl-(*E*)-enynes, which on cyclization led to the desired dihydrofuran derivatives **4.34a-d** (Scheme 4.15). These products exhibit intense fluorescence in the solid state.

Scheme 4.15

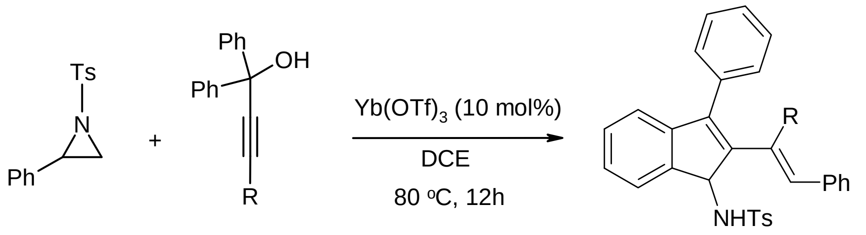


4.33

X = H, R = Ph **4.34a** (80%)
X = OMe, R = Ph **4.34b** (74%)
X = H, R = Me **4.34c** (72%)
X = Cl, R = Me **4.34d** (70%)

Wang and Lu reported a new methodology for the synthesis of functionalized indenes from aziridines and propargyl alcohols.[20] This reaction proceeds *via* Lewis acid catalyzed cascade reaction of aziridines **4.35** and propargyl alcohols to give indene derivatives **4.36a-c** (Scheme 4.16). This methodology offers a great potential for the synthesis of biologically active indene derivatives and related polycyclic compounds.

Scheme 4.16

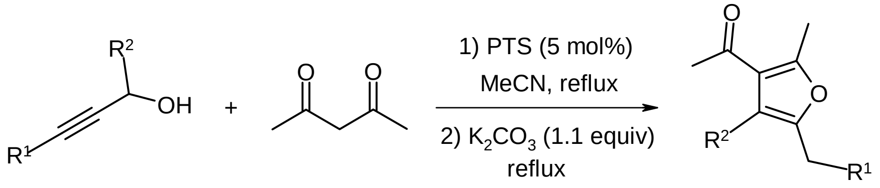


4.35

R = Ph **4.36a** (63%)
R = 4-Me-C_6H_4 **4.36b** (54%)
R = n-C_4H_9 **4.36c** (41%)

Sanz *et al* described propargylation of 1,3-dicarbonyl derivatives by using Brønsted acid catalysis.[21] Thus *p*-toluenesulfonic acid catalyzed direct substitution of the hydroxyl group in propargyl alcohols **4.37** with 1,3-dicarbonyl compounds led to the propargylation or allenylation depending on the nature of the alkynol, which further cyclized to a range of polysubstituted furans **4.38a-b** in one pot (Scheme 4.17). Reactions could be performed in air in normal solvents with water being the only side product.

Scheme 4.17



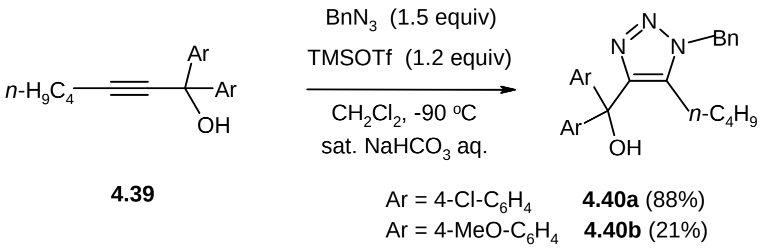
4.37

$R^1 = R^2$ = Ph **4.38a** (70%)
R^1 = n-C_4H_9, R^2 = Ph **4.38b** (52%)

4.24 Cycloaddition

Tanimoto and co-workers reported the regioselective rapid cycloaddition reaction of azide with alkyne functionality of propargyl alcohol **4.39** generated in acid media to produce highly substituted 1*H*-1,2,3-triazole **4.40a-b** (Scheme 4.18).[22] Along with these triazoles, various three-component coupling reactions were also demonstrated, and the presence of allenyl aminodiazonium intermediates were indicated. Most of the reactions were completed within 5 min at rt or below.

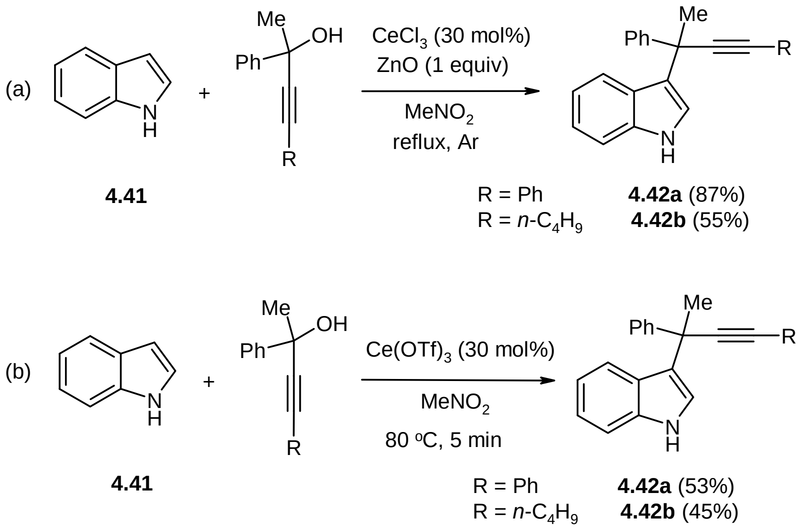
Scheme 4.18



4.3 Reactions of propargyl alcohols with indoles

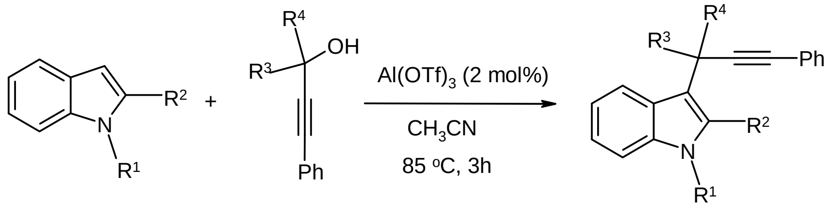
In the year 2010, Silveira et al described a convenient method for the preparation of 3-propargyl indoles **4.42a-b** by C3-selective propargylation of indole **4.41**, catalyzed by anhydrous cerium(III) chloride (Scheme 4.19a).[23a] Similarly, the same research group developed another simple route for 3-propargyl indoles **4.42a-b** catalyzed by cerium(III) triflate by using same starting precursors (Scheme 4.19b).[23b] In these two methods, the conversion took place within a short time of less than an hour.

Scheme 4.19



Bezuidenhoudt and co-workers developed an efficient method for the propargylation of secondary or tertiary propargyl alcohols with indoles using environmentally benign conditions.[24] In this method, $Al(OTf)_3$ was found to be a highly effective and reusable Lewis acid catalyst for the direct nucleophilic substitution of the -OH of propargylic alcohols by indoles **4.43**, providing 3-substituted propargylated products **4.44a-d** in excellent yields and high selectivities (Scheme 4.20).

Scheme 4.20

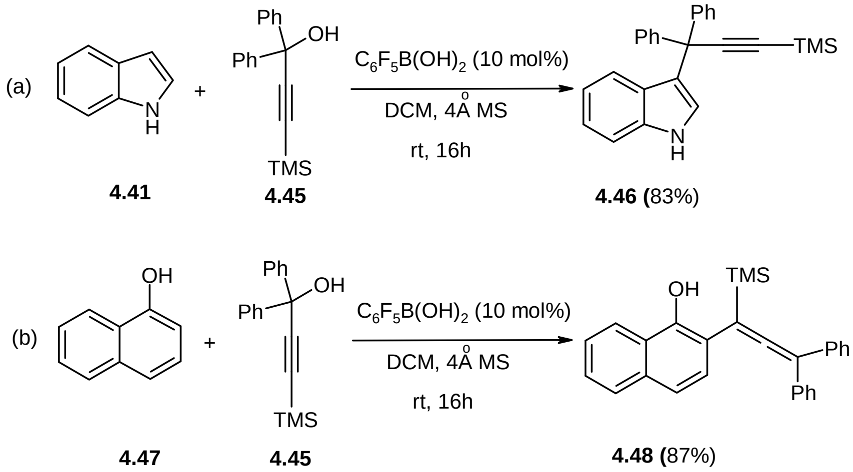


4.43

R^1 = Me, R^2 = H, R^3 = Me, R^4 = Ph **4.44a** (90%)
R^1 = H, R^2 = Me, R^3 = Me, R^4 = Ph **4.44b** (89%)
R^1 = Me, R^2 = H, R^3 = H, R^4 = Ph **4.44c** (90%)
R^1 = H, R^2 = H, R^3 = Me, R^4 = Me **4.44d** (54%)

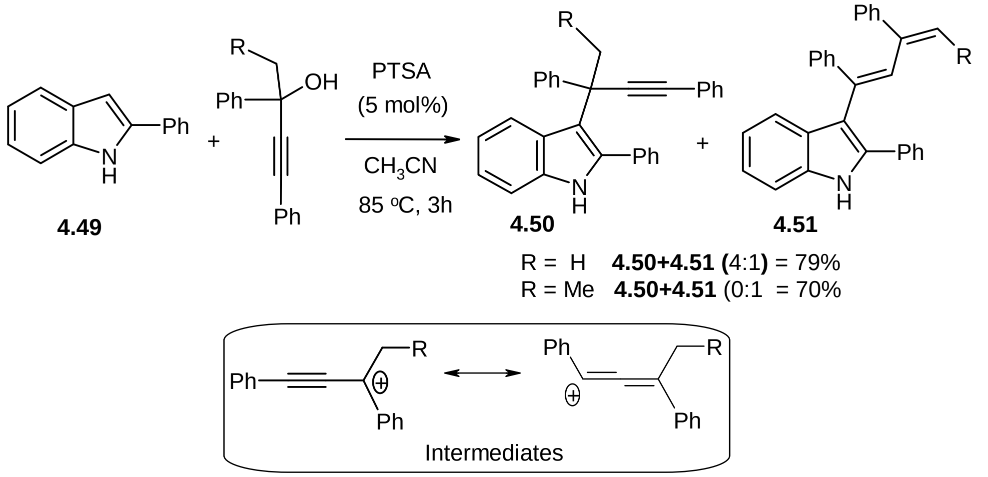
McCubbin and co-workers described a method for the propargylation or allenylation of aryl and heteroaryl nucleophiles with propargyl alcohols.[25] The direct nucleophilic substitution reaction of tertiary propargylic alcohol with indole **4.45** using catalytic aryl boronic acid led to the 3-propargylated indole **4.46** (Scheme 4.21a). Under the same experimental conditions, the reaction of propargyl alcohol with naphthol **4.47** involved Friedel-Crafts allenylation leading to allene **4.48** (Scheme 4.21b).

Scheme 4.21



Sanz *et al* reported Brønsted acid catalyzed Friedel-Crafts alkylation/allenylation of indoles with tertiary propargyl alcohols.[26] Both the alkyne and the butadiene products were observed. In the first case, the reaction proceeded through elimination of water molecule followed by direct alkylation leading to the 3-propargylated indole **4.50**. In the second case, the generated carbocation after elimination of H_2O underwent rearrangement followed by allenylation with indole **4.49** affording the allene that isomerized to the 3-dienylindole **4.51** (Scheme 4.22).

Scheme 4.22

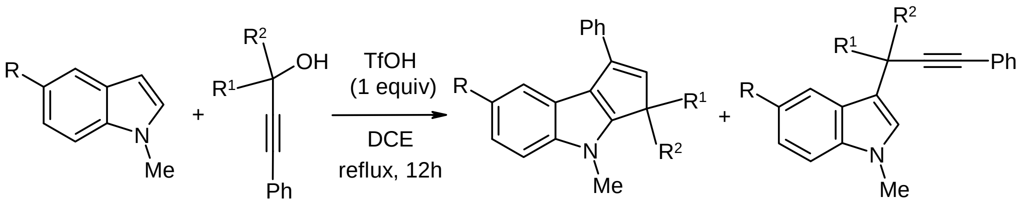


4.49 **4.50** **4.51**

R = H **4.50+4.51 (**4:1**)** = 79%
R = Me **4.50+4.51** (0:1 = 70%

Wang and co-workers developed a method for the construction of 3,4-dihydrocyclopenta[b]indoles from propargyl alcohols and indoles under Brønsted acid mediation (Scheme 4.23).[27] The formation of 3,4-dihydrocyclopenta[b]indoles **4.53a-b** was rationalized by a Brønsted acid mediated competitive allenylation of propargyl alcohols with indoles **4.52** leading to the allene which further underwent hydroarylation.

Scheme 4.23

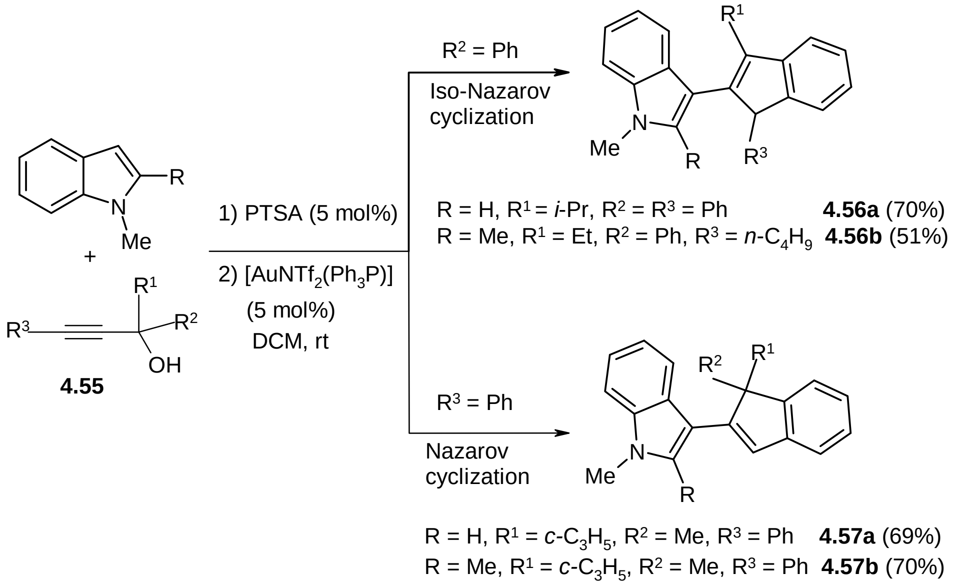


4.52 **4.53** **4.54**

R = H, $R^1 = R^2$ = Ph **4.53a** (58%)
R = NO_2, R^1 = Me, R^2 = Et **4.53b** (38%)
R = NO_2, R^1 = H, R^2 = Ph **4.54** (61%)

Sanz *et al* developed an efficient one-pot synthesis of 3-indenylindoles and their derivatives **4.56a-b** or **4.57a-b** by using *p*-toluenesulfonic acid catalyzed propargylation of indoles with tertiary propargyl alcohols **4.55** followed by gold-catalyzed 1,2-migration (Scheme 4.24).[28] Depending on the substituents at the propargylic and terminal positions of the starting 3-propargylindoles, two different reaction pathways may be operating, an iso-Nazarov (cf. compound **4.56**) or a Nazarov-type pentadienyl cyclization (cf. compound **4.57**).

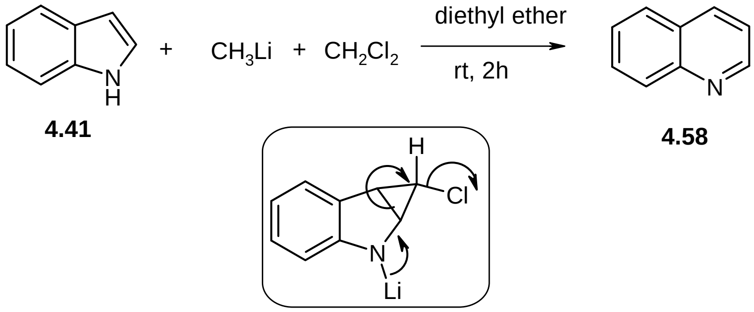
Scheme 4.24



4.4 Ring-expansion reactions of indoles

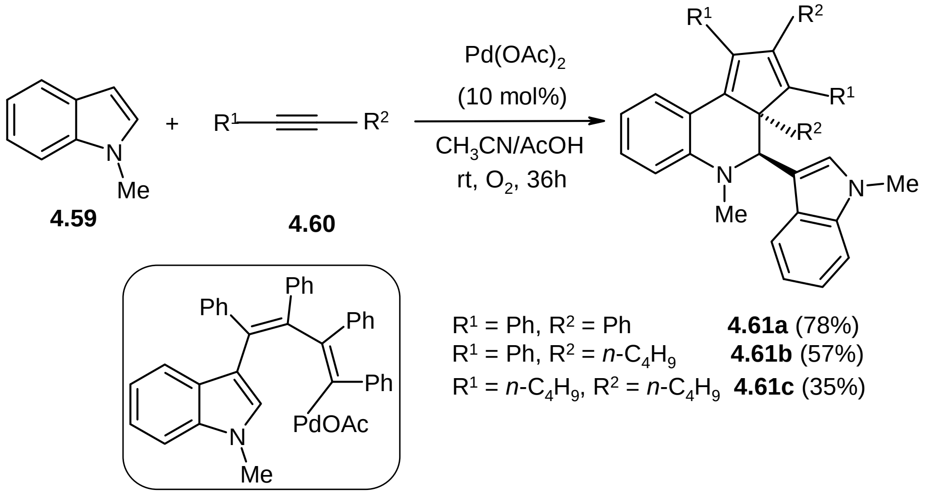
The first ring-expansion reaction of indole was reported by Closs and Schwartz in 1961.[29] The reaction proceeds through the chlorocarbene (formed from dichloromethane), which reacts with indole **4.41**. The final result is ring-expansion leading to quinoline **4.58** (Scheme 4.25).

Scheme 4.25



Recently, Jiao and co-workers described the first palladium-catalyzed, highly selective ring-expansion reaction of readily available indole **4.59** with various substituted internal alkynes **4.60** leading to polysubstituted tetrahydroquinolines **4.61a-c** under mild conditions (Scheme 4.26).[30] This kind of transformation involves dual C-H bond activation, one C-C bond cleavage, five new C-C bond formation, and uniquely, ring-expansion of the indole through a rearrangement pathway.

Scheme 4.26



R^1 = Ph, R^2 = Ph **4.61a** (78%)
R^1 = Ph, R^2 = n-C_4H_9 **4.61b** (57%)
R^1 = n-C_4H_9, R^2 = n-C_4H_9 **4.61c** (35%)

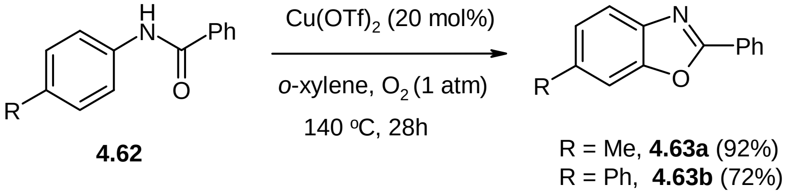
Thus, very few reports regarding the ring expansion reaction of indoles are available in the literature. The involvement of propargyl alcohols in the ring-expansion of indoles is a topic that is not explored so far.

4.5 [Cu]-catalyzed oxidative dehydrogenation/coupling

The construction of C-C and C-heteroatom bonds using copper-mediated reactions has found widespread use in numerous synthetic applications.[31-33] The versatility of copper results from the readily accessible oxidation states of 0 to +3. Oxidation utilizing oxygen or air has been employed safely in numerous commodity chemicals in both continuous and batch processes.[34] Recently, numerous reports of C-C or C-X bond formation *via* copper catalyzed oxidative dehydrogenation using molecular oxygen as oxidant have appeared.[35] Most copper salts are economical, less toxic compared to palladium and are more amenable to greener conditions.[36] Some of the recent methods on oxidative dehydrogenation relevant to our work are described herein.

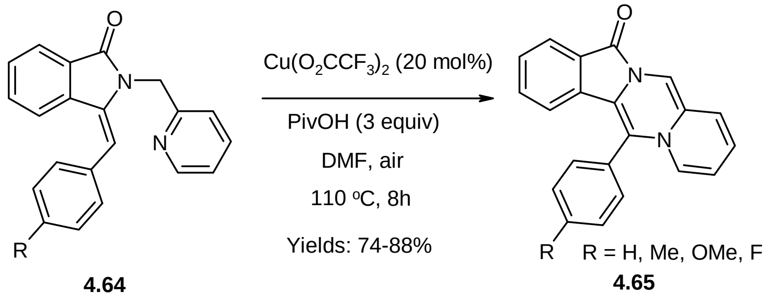
Nagasawa and Ueda developed a convenient route to 2-aryl benzoxazoles **4.63a-b** through [Cu]-catalyzed intramolecular oxidative C-O coupling of benzanilides **4.62** with high regioselectivity in the presence of molecular oxygen (Scheme 4.27).[35d] This method furnished benzoxazoles from inexpensive starting materials.

Scheme 4.27



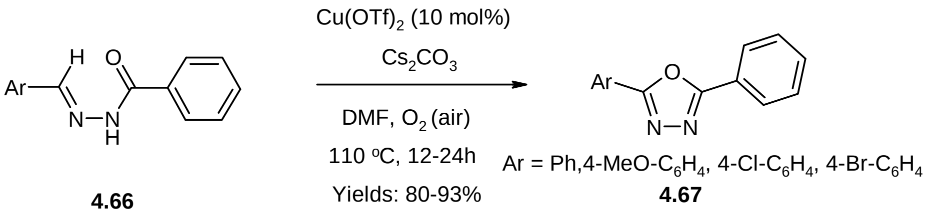
Fu and co-workers found a useful strategy for the construction of *N*-heterocycles **4.65a-d** *via* copper-catalyzed aerobic oxidative intramolecular alkene C-H amination of substituted 3-benzylidene-2-pyridin-2-ylmethyl-2,3-dihydro-isoindol-1-ones **4.64** (Scheme 4.28).[37] This protocol utilized an inexpensive and readily available copper catalyst.

Scheme 4.28



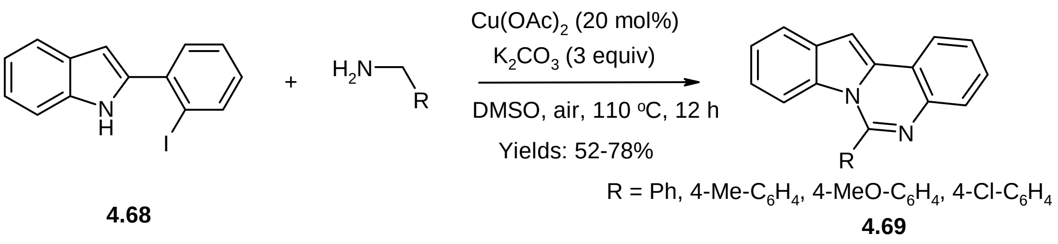
Patel and co-workers developed a catalytic method for the synthesis of 2,5-disubstituted [1,3,4]-oxadiazoles **4.67a-d** *via* imine C-H functionalization of *N*-benzylidenebenzohydrazide **4.66** by using catalytic copper triflate with air as the oxidant (Scheme 4.29).[38] The cyclization proceeds through deprotonation/metalation at the imine sp^2 C-H bond followed by the reductive elimination and C-O bond formation leading to the 2,5-disubstituted 1,3,4-oxadiazoles.

Scheme 4.29



Zhang and co-workers developed a simple and efficient method for indolo[1,2-*c*]-quinazoline derivatives **4.69a-d** by using readily available 2-(2-halophenyl)-1H-indoles **4.68** and arylmethanamines (Scheme 4.30).[39] This one-pot reaction proceeds *via* copper-catalyzed sequential Ullmann *N*-arylation followed by aerobic oxidative C-H amination.

Scheme 4.30



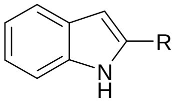
OBJECTIVES OF THE PRESENT WORK - PART B

The main objective of this part of the present work was to explore the reactivity of indoles with propargyl alcohols and possible ring-expansion or hydroarylation reactions of 3-dienylindoles *via* copper catalysis. Assuming that the reaction would be successful, it was envisaged to develop one-pot method for the ring-expansion products starting from indoles and propargyl alcohols under Brønsted acid mediation in conjunction with copper catalysis.

RESULTS AND DISCUSSION

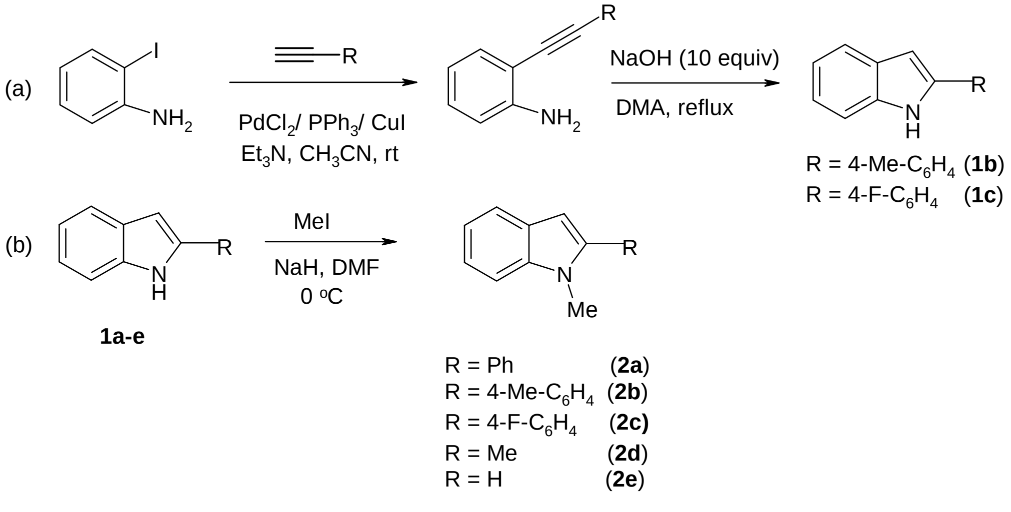
5.1 Synthesis of 2-substituted indoles 1a-e and 2a-e

Among the basic indole precursors utilized in the present study, **1a** and **1d-e** are commercially available. Precursors **1b-c** are prepared according to a literature method.[40] Thus, Sonogashira cross coupling of 2-iodoaniline with 1-ethynyl toluene or 1-ethynyl-4-fluorobenzene and subsequent treatment with NaOH in dimethyl acetamide gives the 2-substituted indoles **1b-c** in good yields (Scheme 1a).[40b] *N*-methyl 2-substituted indoles **2a-e** are prepared by using the corresponding *N*H-indoles **1a-e** and methyl iodide in the presence of NaH in DMF (Scheme 1b).[40b,41] All the compounds **1a-e** and **2a-e** are known.



R = Ph (**1a**), 4-Me-C_6H_4 (**1b**), 4-F-C_6H_4 (**1c**), Me (**1d**), H (**1e**)

Scheme 1



R = 4-Me-C_6H_4 (**1b**)
R = 4-F-C_6H_4 (**1c**)

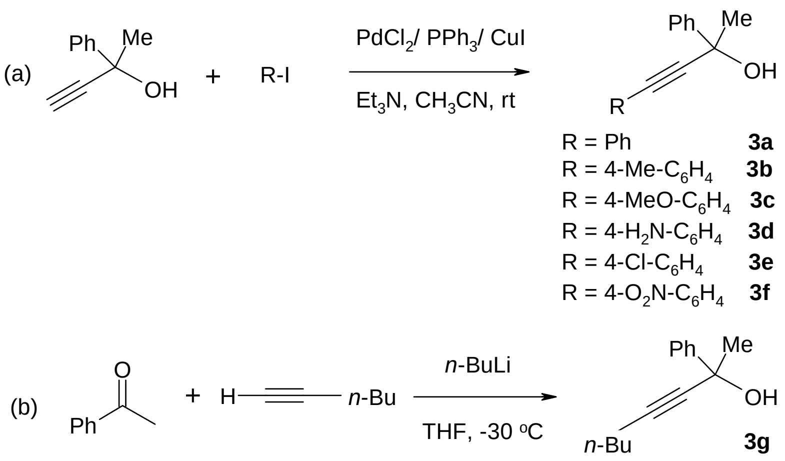
1a-e

R = Ph (**2a**)
R = 4-Me-C_6H_4 (**2b**)
R = 4-F-C_6H_4 (**2c**)
R = Me (**2d**)
R = H (**2e**)

5.2 Synthesis of propargyl alcohols (3a-g)

For the synthesis of propargyl alcohols, a number of methods are available in the literature. These include (a) Sonogashira cross coupling reaction of terminal propargyl alcohols and aromatic iodides,[42a] (b) tetrabutylammonium fluoride (TBAF)-catalyzed addition of substituted trialkylsilylalkynes to aldehydes and ketones,[42b] and (c) catalytic asymmetric alkynylation of aldehydes promoted by $InBr_3$/BINOL complex and Cy_2NMe.[42c] We have followed the Sonogashira cross coupling for the synthesis of propargyl alcohols **3a-f** (Scheme 2a).[14,43] The propargyl alcohol **3g**[44] was prepared by the reaction of 1-hexynyl lithium with acetophenone in THF (Scheme 2b).[4c] Among these, compounds **3d-f** are new. The identities of all these compounds are ascertained by means of IR and NMR data.

Scheme 2

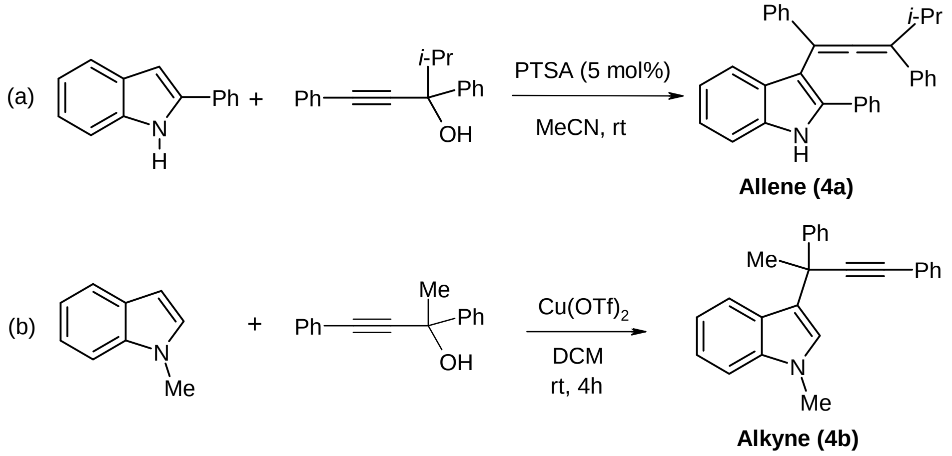


5.3 Reactivity of 2-substituted indoles with tertiary propargyl alcohols

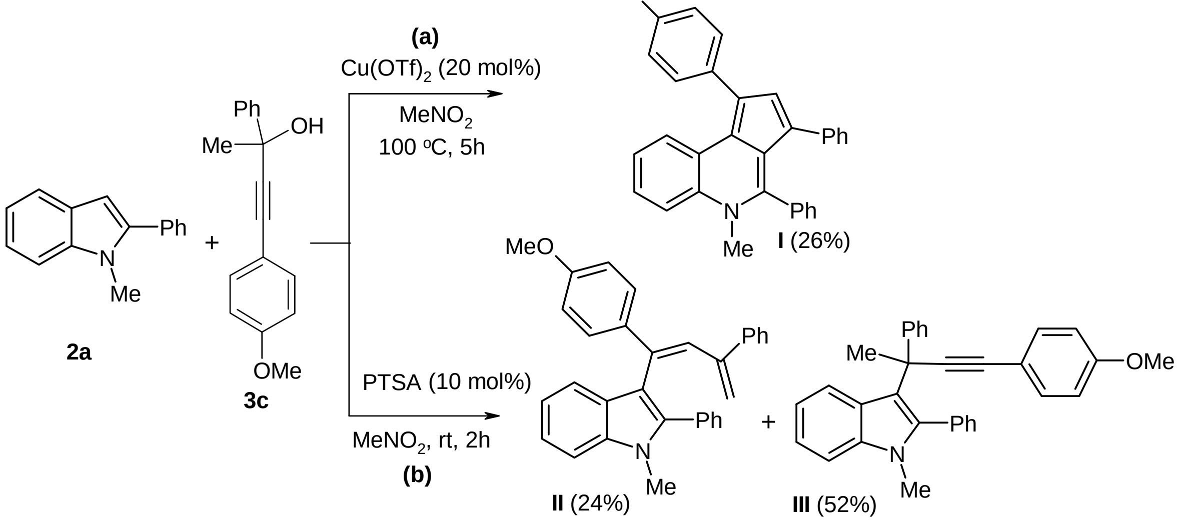
As a part of our ongoing studies on allene/alkyne chemistry by using functionalized propargyl alcohols,[4b-c,45] we also wanted to synthesize indole based allenes/alkynes. It is reported that several tertiary propargyl alcohols, after elimination of water, lead to allenes (e.g., **4a**) or alkynes (e.g., **4b**) in the presence of *p*-toluenesulfonic acid (PTSA),[26] but only to alkynes in the presence of $Cu(OTf)_2$ (Scheme 3).[27] Some of these products have been utilized elegantly for further derivatization to 1,3-butadienes or other fused heterocycles.[28,46] When we tried a similar reaction using 1-methyl-2-phenylindole (**2a**) and propargylic alcohol **3c** using $Cu(OTf)_2/MeNO_2$ under reflux conditions, surprisingly, we isolated one pure compound (**I**) which exhibited only ***two methyl signals*** in the ^1H NMR spectrum (Scheme 4a; see later for full details). It can be noted that for a compound similar to allene **4a** or alkyne

4b, ***three methyl signals* [O*Me,* N*Me,* =C*Me*(Ph)]** are expected. As is discussed in the following sections, our product **I** is different from any type of product[26-27] reported by earlier workers and hence we proceeded to investigate this reaction further. Thus, the same reaction was conducted in nitromethane using the Brønsted acid PTSA. In this case, however, we isolated two products that were shown to be 3-dienylindole (**II**) and 3-propargylindole (**III**; Scheme 4b, discussed later in detail). It should be noted that in the literature, diene of type **II** was obtained only in one case, and in low yields (16%).[26b] Species **II** also shows only *two methyl* signals similar to **I**. For this reason, we surmised that **I** must have formed *via* diene **II** and therefore proceeded to optimize the conditions for obtaining better yields of the diene **II**. This is what is discussed in the next section using different substrates. Systematic (Hindu/Arabic) compound numbers will be given in that section.

Scheme 3



Scheme 4



5.4 Synthesis of 3-dienyl- and 3-propargyl-indoles (5-17) under Brønsted acid mediation

After several trials, gratifyingly, *N*H-indole **1a** upon treating with propargyl alcohol **3a** in the presence of PTSA (1.5 equiv) at rt for 30 min in nitromethane as a solvent, led to the expected Friedel-Crafts alkenylated 3-dienylindole **5** in 91% yield (Table 1, entry 1). Similarly, when *N*-methyl-2-phenylindole **2a** was treated with **3a**, smooth conversion to 3-dienylindole **6** in excellent yield (Table 1, entry 2) could be effected. The high yield of **5** and **6** encouraged us to study the 3-dienylindole formation in detail. Thus we conducted the reactions of substituted indoles (**2a-d**) with tertiary propargyl alcohols (**3a-f**) (Scheme 5) and obtained other 3-dienylindoles **7-14**. Details on these reactions are summarized in Table 1. All these compounds show two characteristic singlets in the region δ 4.9-5.3 in the ^{1}H NMR for the olefinic protons of the =CH_2 group. The corresponding carbon (=CH$_2$) appears around δ ~116 (using DEPT). The structure of compound **8** is proven by X-ray crystallography (Figure 1).

Scheme 5

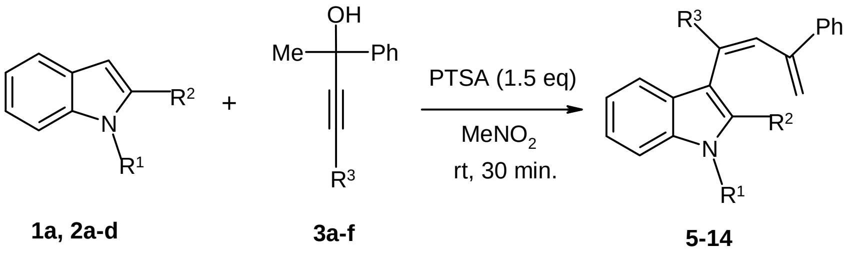


Table 1. Synthesis of 3-dienylindoles **5-14** from 1,2-substituted indoles and propargyl alcohols[a]

Entry	R^1/R^2 (indole)	R^3 (propargyl alcohol)	Product	Yield (%)[b]
1	H/Ph (**1a**)	Ph (**3a**)	**5**	91
2	Me/Ph (**2a**)	Ph (**3a**)	**6**	83
3	Me/Ph (**2a**)	*p*-MeC_6H_4 (**3b**)	**7**	81
4	Me/Ph (**2a**),	*p*-$OMeC_6H_4$ (**3c**)	**8**	75
5	Me/Ph (**2a**)	*p*-$NH_2C_6H_4$ (**3d**)	**9**	44
6	Me/Ph (**2a**)	*p*-ClC_6H_4 (**3e**)	**10**	87
7	Me/Ph (**2a**)	*p*-$NO_2C_6H_4$ (**3f**)	**11**	86
8	Me/*p*-MeC_6H_4 (**2b**)	Ph (**3a**)	**12**	82
9	Me/*p*-FC_6H_4 (**2c**)	Ph (**3a**)	**13**	79
10	Me/Me (**2d**)	*p*-$NO_2C_6H_4$ (**3f**)	**14**	66

[a] Reaction conditions: **1a** or **2a-d** (1 equiv), **3a-f** (1.1 equiv), PTSA (1.5 equiv) and $MeNO_2$ (4.0 mL) at rt for 30 min in air. [b] Isolated yields.

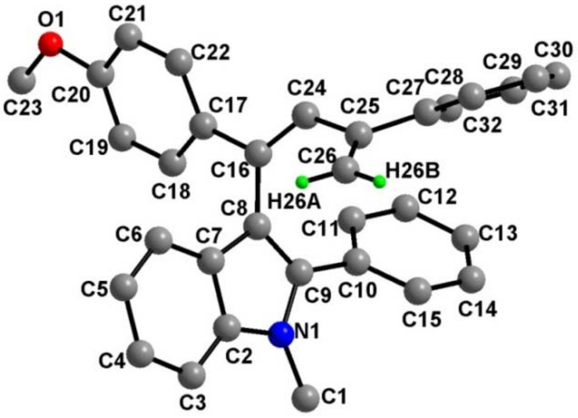
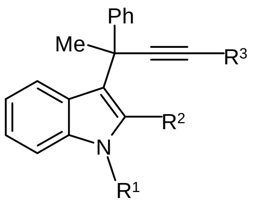


Figure 1. Molecular structure of compound **8**. Hydrogen atoms (except $=CH_2$) are omitted for clarity. Selected bond parameters: N1-C9 1.390(3), C9-C8 1.372(3), C8-C16 1.481(2), C16-C17 1.484(3), C16-C24 1.334(3), C24-C25 1.473(3), C25-C26 1.322(3), C25-C27 1.484(3) (Å).

It is clear from Table 1 that when propargyl alcohols bearing electron-donating groups are used as substrates, moderate to good yields of 3-dienylindoles are obtained (entries 3-5). Those with electron-withdrawing groups gave better or excellent yields of the corresponding products (entries 6-7). *N*-methyl-2-arylindoles with either electron-donating or electron-withdrawing group gave good yields (entries 8-9). When 2-alkyl indole **2d** was used as the substrate, the yield of 3-dienylindole was only moderate (entry 10).

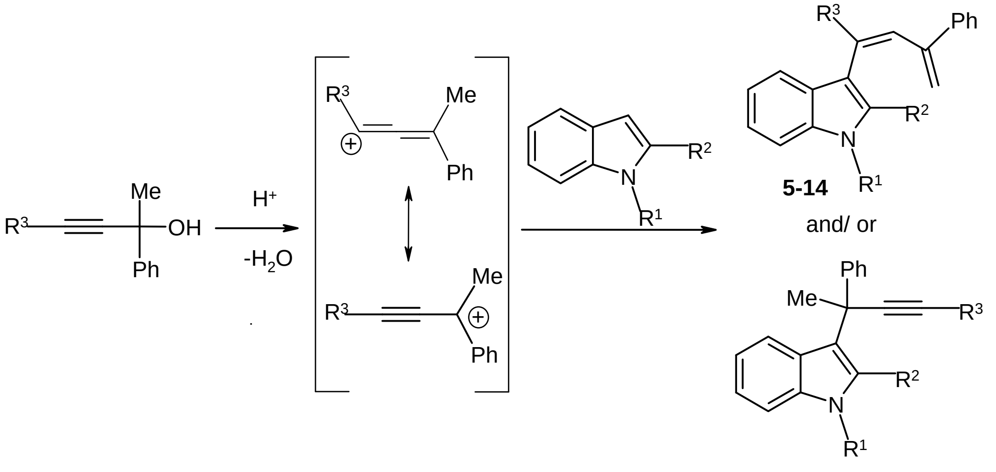
In the above reaction, in three cases [**2a+3c**, **2a +3d**, **2d +3f**] we have isolated the 3-propargylated indoles **15-17** also. In other cases also we did observe such products but could not isolate them, because of the low yield (<10%). In the IR spectra, a band at ~2230 cm^{-1} clearly shows the presence of an alkyne moiety in **15-17**. The number of methyl signals in the ^{1}H NMR matches with that present in the starting materials. In the ^{13}C NMR spectra, the expected alkyne carbons appear at δ 81-83 and 94-102.



R^1 = Me, R^2 = Ph, R^3 = 4-MeO-C_6H_4 **15** (13%)
R^1 = Me, R^2 = Ph, R^3 = 4-H_2N-C_6H_4 **16** (47%)
R^1 = Me, R^2 = Me, R^3 = 4-O_2N-C_6H_4 **17** (19%)

Formation of 3-dienylindoles **5-14** can be explained by a Brønsted acid mediated competitive allenylation reaction leading to the allene derivative which undergoes isomerization (Scheme 6).[26b] Formation of the 3-propargylated indoles **15-17** is explained by direct nucleophilic substitution reaction (Scheme 6).[26c]

Scheme 6



15-17

5.5 Ring-expansion chemistry of indoles

After having the 3-dienylindoles synthesized **5-14** in hand, the next task was to accomplish the dehydrogenative/oxidative ring-expansion reaction leading to substituted cyclopenta[c]quinolines of the type **III** shown in Scheme 4, since such a ring expansion is unprecedented in the literature. To date, only few reports regarding the ring-expansion reactions of indoles are available.[29,47] Recently, Jiao and co-workers reported the first example of cyclopentadienyl fused tetrahydroquinoline derivatives through palladium-catalyzed ring-expansion reaction of indoles with alkynes.[48] To the best of our knowledge, copper-catalyzed aerobic oxidative ring-expansion reactions are not reported so far. The results are described below.

5.51 $Cu(OTf)_2$ catalyzed synthesis of cyclopenta[c]quinolines and 3-indenylindoles from 3-dienylindoles 5-14

For this part, *N*-methyl-3-dienylindole **6** was chosen as a model substrate for optimization studies (Scheme 7). In an initial attempt we treated **6** with $Cu(OTf)_2$ (20 mol %) in nitromethane at 100 ^{o}C for 8h in open air. This reaction resulted the desired quinoline **18** (43%) together with hydroarylated product **19** (37%) [Table 2, entry 1]. When the reaction was performed at rt, product **18** was not detected, and only **19** (24%) could be obtained (Table 2, entry 2); rest of the material was starting compound. To our delight, though, when the reaction was performed at 80 ^{o}C for 5h, **18** could be obtained 55 % yield along with **19** (33 % yield; Table 2, entry 3). When pure O_2 was used as an oxidant instead of air, there was no significant change in the yield (Table 2, entry 4). Under nitrogen atmosphere, **18** and **19** were obtained in (1:1) ratio (combined yield 82%; Table 2, entry 5). Control reaction confirmed that the reaction did not proceed in the absence of copper catalyst (Table 2, entry 6). $Cu(OAc)_2$ as a catalyst produced only traces of **18** and **19** (Table 2, entry 7). Other catalysts like $CuBr_2$, $Cu(SO_4)_2.5H_2O$ and $Pd(OAc)_2$ did not work for this transformation (Table 2, entries 8-10), but use of $Zn(OTf)_2$ afforded 25% of **18** and 40% of **19** (Table 2, entry 11). Surprisingly, the hydroarylated product **19** was obtained in 82 % yield in the presence TfOH (Table 2, entry 13). Thus it appears that traces of triflic acid liberated from $Cu(OTf)_2$ is responsible for the formation of **19**. The yield of the ring-expansion product **18** did not improve by using solvents like MeCN, 1,2-dichloroethane, toluene and DMF in place of $MeNO_2$ (Table 2, entries 14-17). Thus nitromethane was proved to be an efficient reaction medium. The yield of **18** was further increased to 64% by using PTSA as an additive (Table 2, entry 20). The expected products were not even detected by using oxidants like TBHP, *p*-benzoquinone and $K_2S_2O_8$ in place of air. Accordingly, the optimal reaction conditions are as follows: $Cu(OTf)_2$ (20 mol %), PTSA (2 equiv), under open atmosphere in $MeNO_2$ at 80 ^{o}C.

Scheme 7

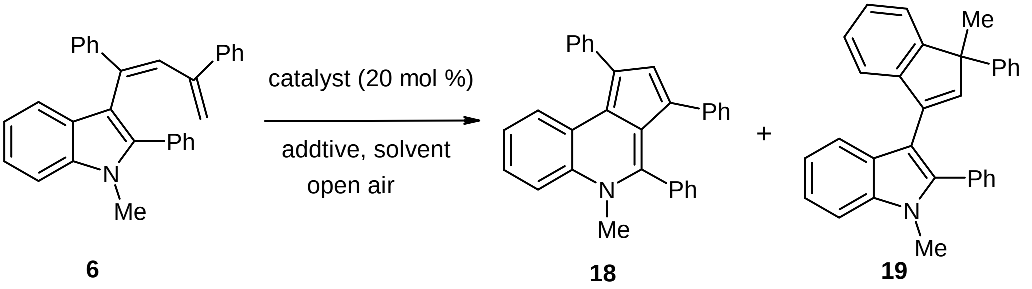


Table-2. Optimization Studies for the Ring-expansion/Hydroarylation Reaction of 3-Dienylindole **6**[a]

Entry	catalyst	additive	solvent	temp(°C) /time (h)	Yield(%)[b]	
					18	**19**
1	$Cu(OTf)_2$	-	$MeNO_2$	100/8	43	37
2[c]	$Cu(OTf)_2$	-	$MeNO_2$	rt/12	n.d.	24
3	$Cu(OTf)_2$	-	$MeNO_2$	80/5	55	33
4[d]	$Cu(OTf)_2$	-	$MeNO_2$	80/5	56	34
5[e]	$Cu(OTf)_2$	-	$MeNO_2$	80/5	42	40
6[f]	-	-	$MeNO_2$	80/15	n.d	n.d
7	$Cu(OAc)_2$	-	$MeNO_2$	80/15	trace	trace
8	$Cu(Br)_2$	-	$MeNO_2$	80/12	n.d	n.d
9	$Cu(SO_4)_2.5H_2O$	-	$MeNO_2$	80/12	n.d	n.d
10	$Pd(OAc)_2$	-	$MeNO_2$	80/8	n.d	trace
11	$Zn(OTf)_2$	-	$MeNO_2$	80/5	25	40
12	AgOTf	-	$MeNO_2$	80/4	31	45
13	TfOH	-	$MeNO_2$	80/8	n.d	82
14	$Cu(OTf)_2$	-	CH_3CN	80/5	trace	68
15	$Cu(OTf)_2$	-	DCE	80/4	30	28

16	$Cu(OTf)_2$	-	toluene	80/4	n.d	35
17	$Cu(OTf)_2$	-	DMF	80/4	26	57
18	$Cu(OTf)_2$	AcOH	$MeNO_2$	80/5	28	40
19	$Cu(OTf)_2$	pivOH	$MeNO_2$	80/5	23	34
20	$Cu(OTf)_2$	PTSA	$MeNO_2$	80/5	64	22
21	$Cu(OTf)_2$	TFA	$MeNO_2$	80/5	47	35

[a]Reaction conditions: **6** (0.3 mmol), catalyst (0.06 mmol), additive (2 equiv) and solvent (2.0 mL) at the specified temperature and time in air unless otherwise noted. [b]Isolated yields. [c]3-dienylindole was recovered in 52% yield. [d]in air. [e]under nitrogen. [f]3-dienylindole was completely recovered.

Having the optimal reaction conditions in hand, we examined a spectrum of substituted 3-dienylindoles to explore the generality of this novel reaction (Scheme 8). A range of differently substituted 3-dienylindoles with electron-donating or electron-withdrawing groups were tolerated and gave moderate to good yields of the corresponding ring expansion products, the cyclopenta[c]quinolines (**18, 20, 22, 24, 25, 27-29** and **31**), along with hydroarylated compounds, indenyl indoles (**19**, **21**, **23, 26** and **30**) (Table 3, entries 1-9). The latter compounds, indenyl indoles, were isolated only in five cases because of the closeness in R_f values with the quinolines. The combined yield of the products in all the cases was good to excellent (> 80%) with the 3-dienyl indole being completely consumed. As regards characterization, the two products, cyclopenta[c]quinolines and indenyl indoles exhibit different number of methyl signals in ^1H and ^{13}C NMR spectra. In the mass spectra, the cyclopenta[c]quinoline shows two hydrogen atoms less than that for indenyl indole. The structures of compounds **21** and **22** are confirmed by X-ray crystallography (Figures 2 and 3).

Scheme 8

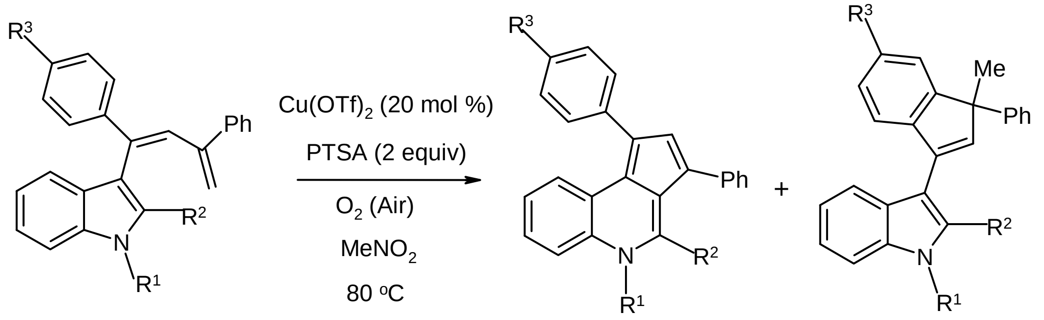
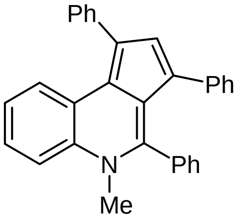
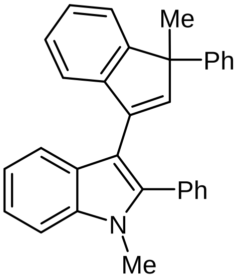
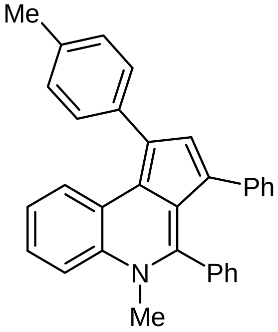
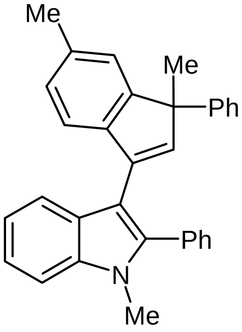
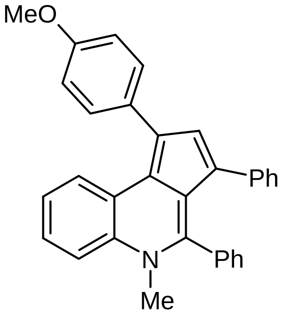
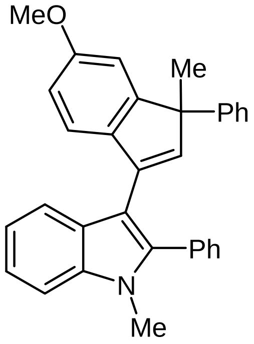
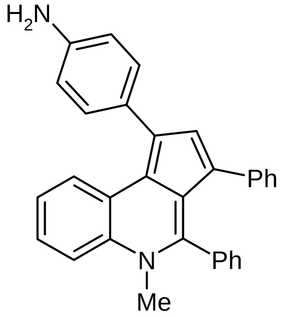
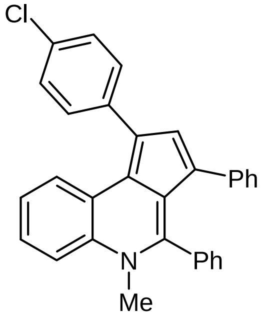
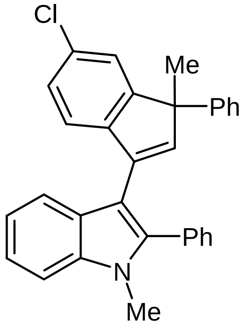
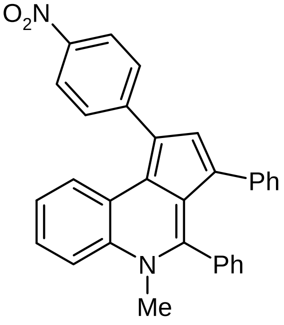
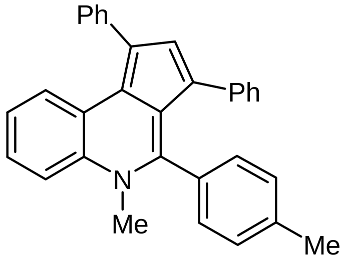
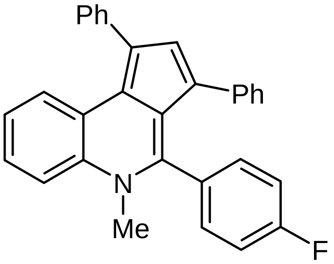
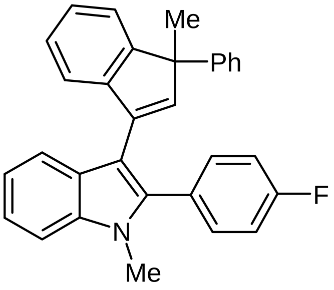
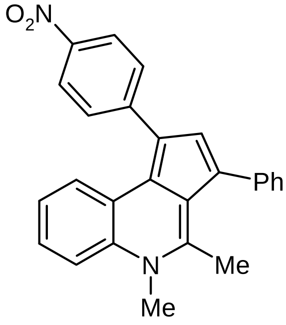


Table-3. Cu(OTf)$_2$ Catalyzed Ring-expansion/Hydroarylation of 3-Dienylindoles (**6-14**)^a

Entry	Substrate	6-membered ring derivative (Yield)^b	5-membered derivative (Yield)^b
1	**6**	 **18** (64%)	 **19** (22%)
2	**7**	 **20** (61%)	 **21** (26%)

3	**8**	 **22** (53%)	 **23** (30%)
4	**9**	 **24** (47%)	Not isolated
5	**10**	 **25** (63%)	 **26** (28%)
6	**11**	 **27** (74%)	Not isolated

7	**12**	 **28** (56%)	Not isolated
8	**13**	 **29** (59%)	 **30** (32%)
9	**14**	 **31** (70%)	Not isolated

[a] Reaction conditions: diene (1 equiv), Cu(OTf)$_2$ (20 mol %), PTSA (2 equiv) and MeNO$_2$ (4.0 mL) at 80 °C for 5h, in air. [b] Isolated yields.

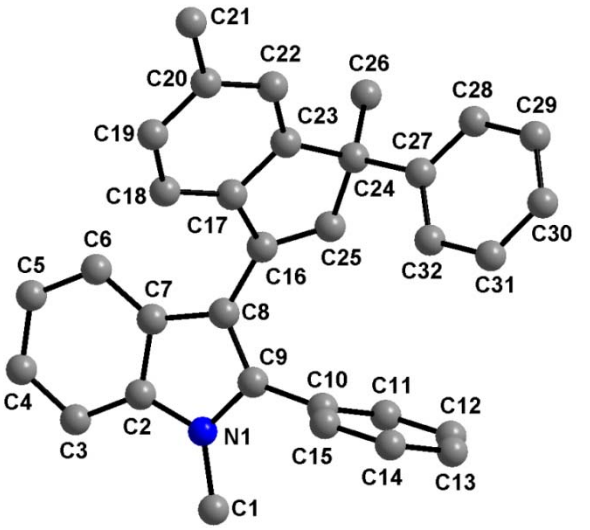


Figure 2. Molecular structure of compound **21**. Hydrogen atoms omitted for clarity. Selected bond parameters: N1-C9 1.384(4), C9-C8 1.365(4), C8-C16 1.468(4), C16-C17 1.475(4), C16-C25 1.328(4), C25-C24 1.515(4), C24-C23 1.514(4), C24-C26 1.540(4), C24-C27 1.522(4) (Å).

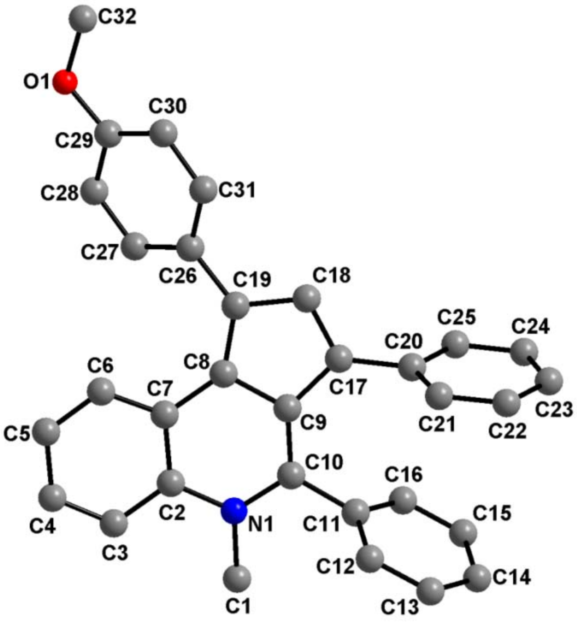
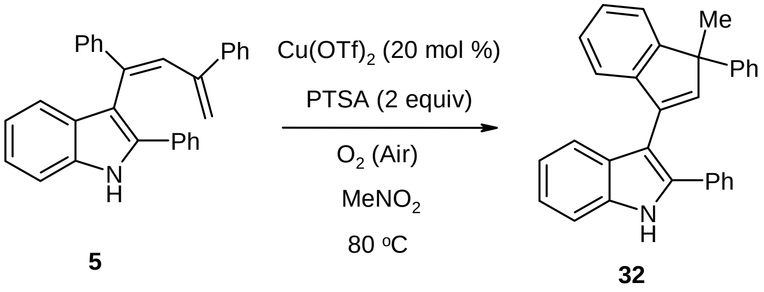


Figure 3. Molecular structure of compound **22**. Hydrogen atoms omitted for clarity. Selected bond parameters: N1-C10 1.364(2), C9-C10 1.370(2), C8-C9 1.449(2), C9-C17 1.437(2), C17-C20 1.472(2), C17-C18 1.364(2), C18-C19 1.428(2), C8-C19 1.383(2), C19-C26 1.468(2) (Å).

When the 3-dienylindole **5** with the NH group intact was used as a substrate, only the five membered ring compound **32** was isolated as the major product (Scheme 9). In the reaction mixture other expected ring expansion product was present only in traces. This may be the reason why the previous workers did not obtain the ring expansion product.

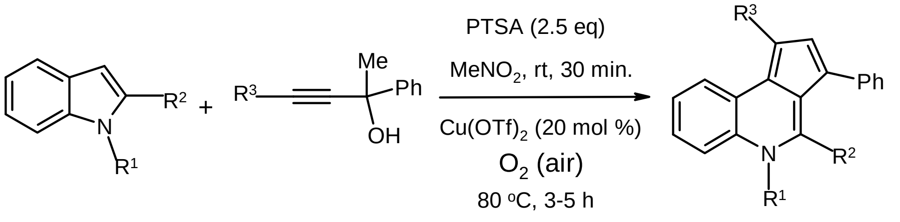
Scheme 9



5.52 One pot synthesis of cyclopenta[c]quinolines from the reaction of indoles with propargyl alcohols under Brønsted acid mediation followed by Cu(OTf)$_2$ catalysis

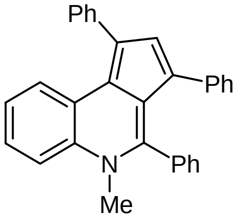
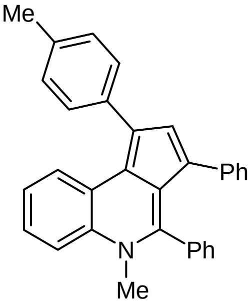
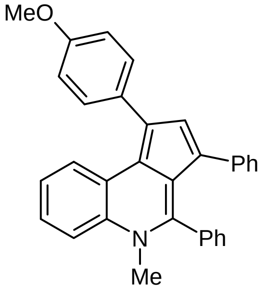
Instead of isolating the 3-dienylindole intermediates, it is more useful if one can get the cyclopenta[c]quinolines in one pot (cf. Scheme 10) by using the optimized conditions mentioned in Tables 1 and 3. Indeed we were able to obtain the desired product **18** in 65 % yield (Table 4, entry 1) in one pot by starting with **2a** and **3a**. Inspired by this, the scope of the one-pot reaction was extended to various alkyl or aryl substituted indoles and propargyl alcohols to afford the cyclopenta[c]quinolines **20**, **22**, **24**, **31** and **33-43** (Table 4, entries 2-16). Electron withdrawing groups on propargyl alcohols furnished better yields when compared to those containing electron donating groups. Alkyl chain containing propargyl alcohol **3g** also led to good yields of the products (e.g., **33** and **42**). The use of alkyl substituent on indole **2d** led to the ring-expansion products **31** and **43** in moderate yields. In this one-pot method also, we did observe trace amounts of 3-indenylindoles but they did not affect the isolation of the desired cyclopenta[c]quinolines. All these ring-expansion products are in dark red in color, while 3-indenylindoles are colorless. Thus the two types of products are readily distinguishable.

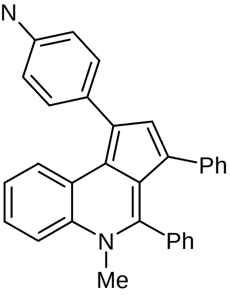
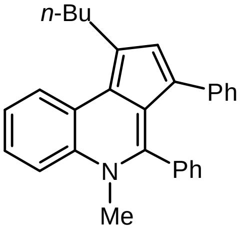
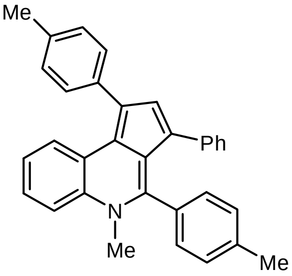
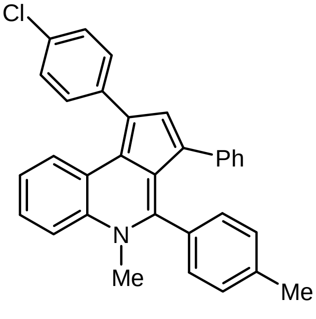
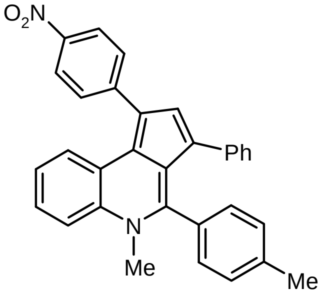
Scheme 10

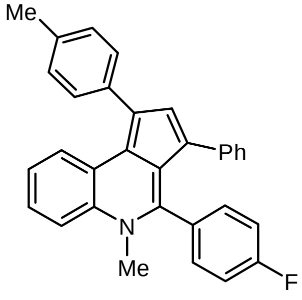
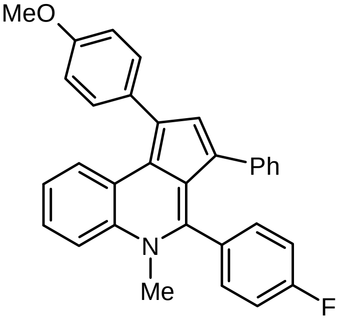
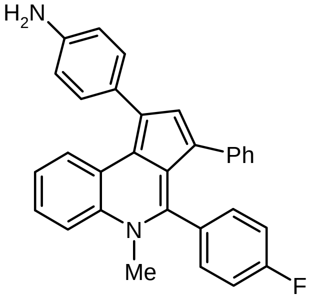
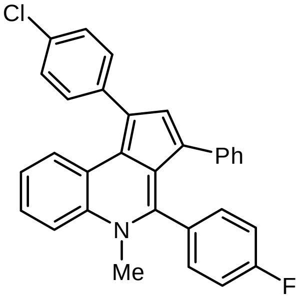
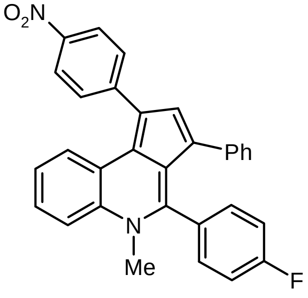


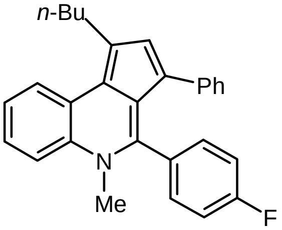
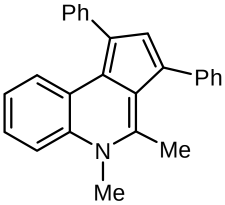
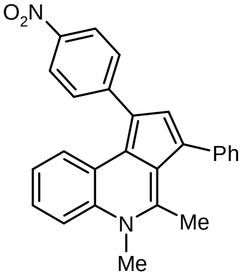
one of 2a-2d **one of 3a-3g** **18, 20, 22, 24, 31, 33-43**

Table 4. One-pot synthesis of cyclopenta[c]quinolines from *N*-methyl,2-substituted indoles **2a-d** and tertiary propargyl alcohols **3a-g**[a]

Entry	Substrates	cyclopenta[c]quinoline derivatives	Yield (%)[b]
1	**2a+3a**	 **18**	65
2	**2a+3b**	 **20**	58
3	**2a+3c**	 **22**	52

4	**2a+3d**	 **24**	34
5	**2a+3g**	 **33**	61
6	**2b+3b**	 **34**	53
7	**2b+3e**	 **35**	64
8	**2b+3f**	 **36**	72

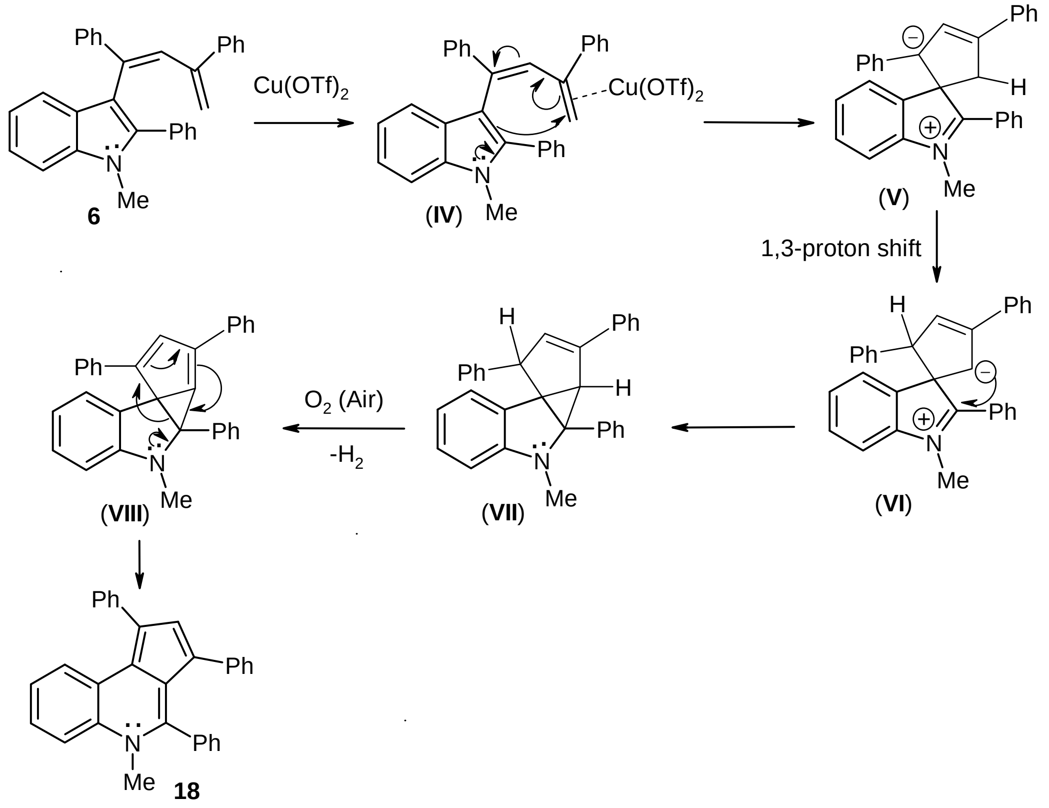
9	**2c+3b**	 **37**	56
10	**2c+3c**	 **38**	51
11	**2c+3d**	 **39**	38
12	**2c+3e**	 **40**	70
13	**2c+3f**	 **41**	75

14	**2c+3g**	 **42**	65
15	**2d+3a**	 **43**	43
16	**2d+3f**	 **31**	58

[a] Reaction conditions: **2** (1 equiv), **3** (1.1 equiv), PTSA (2.5 equiv), $Cu(OTf)_2$ (20 mol %), and $MeNO_2$ (4.0 mL) at 80 °C in air. [b] Isolated yields.

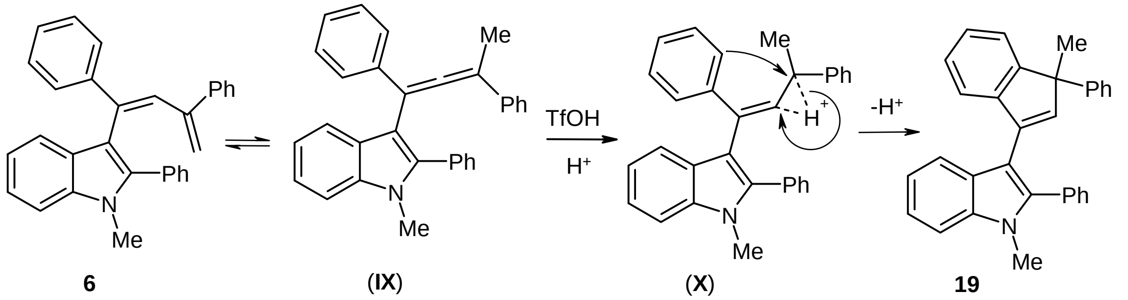
A possible pathway for the formation of cyclopenta[c]quinolines [e.g., **18**] is shown in Scheme 11. Initially, the $Cu(OTf)_2$ coordination in the intermediate **IV** may activate the terminal alkene part of diene.[49] Then the lone pair on nitrogen may facilitate the reaction and lead to the ionic spiro intermediate **V**. Subsequent 1,3-proton migration produces intermediate **VI**. This ionic intermediate **VI** may form the fused cyclopropane ring containing intermediate **VII**. Finally, this intermediate may undergo aerobic oxidation/ aromatization[37-39,50] and produce intermediate **VIII**. Subsequent selective rearrangement will lead to the highly conjugated cyclopenta[c]quinoline **18**.

Scheme 11



The formation of indenyl indoles (e.g., **19**) is rationalized by the initial attack of proton on isomeric allene intermediate (**IX**) of the 3-dienylindole (**6**) to lead to **X** as shown in Scheme 12. This assumption is based on the experimental observation that the yield of **19** from **6** can be maximized to 82% in the presence of triflic acid. While using Cu(OTf)$_2$, though, we assume that there are traces of triflic acid present in the medium. Intermediate **X** undergoes hydroarylation[17a,27,51] to produce the desired product **19**.

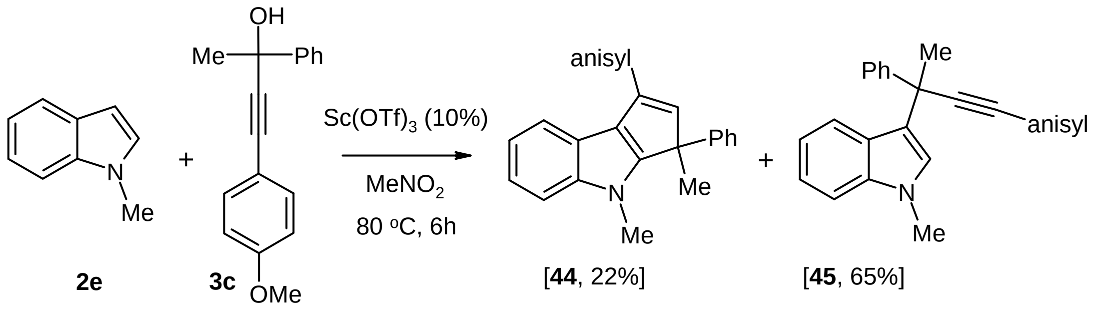
Scheme 12



5.6 Reaction of *N*-methyl indole (2e) with tertiary propargylic alcohol (3c) in the presence of Sc(OTf)$_3$

When 2-unsubstituted *N*-methylindole **2e** was treated with propargyl alcohol **3c** in nitromethane with Sc(OTf)$_3$ as the catalyst, we obtained 3,4-dihydrocyclopenta[b]indole **44** and 3-propargylated indole **45** in yields of 22% and 65% respectively (Scheme 13). Compound **44** is probably formed by the acid mediated Friedel-Crafts allenylation followed by hydroarylation/cyclization. The assignment of structure is based on NMR and HRMS data. Similar compounds are reported in the literature in the reaction of **2e** with substituted propargyl alcohols in the presence of triflic acid.[27] Compound **45** is also similar to some of the compounds described above. Hence this part is not elaborated here. The mechanism for the formation of **44** is similar to that shown in Scheme 12, except that more reactive C-2 position of the indole, rather than CH of the aromatic ring, is involved in cyclization of the allene intermediate. Compound **45** is formed *via* direct Friedel-Crafts alkylation as discussed above (cf. Scheme 6).

Scheme 13



2e **3c** [**44**, 22%] [**45**, 65%]

SUMMARY – PART B

1) Friedel-Crafts alkenylation and then isomerization reactions of indoles with propargyl alcohols under Brøunsted acid mediation have been developed. Thus the reaction of 2-substituted indoles with tertiary propargyl alcohols in the presence of PTSA/$MeNO_2$ selectively leads to the 3-dienylindoles *via* allene intermediate in good to excellent yields. Along with these, traces of 3-propargylated indoles were also formed and were isolated in some cases.

2) Synthesis of highly conjugated cyclopenta[c]quinolines and 3-indenylindoles *via* copper(II) triflate-catalysed aerobic oxidative ring–expansion/hydroarylation reactions of 3-dienylindoles is accomplished.

3) A new one-pot method for the synthesis of ring-expansion compounds starting from 2-substituted indoles and tertiary propargylic alcohols is also described. The reaction proceeds *via* Brønsted acid mediated Friedel-Crafts alkenylation, and then isomerization followed by copper(II) triflate-catalysed oxidative ring-expansion. This new ring-expansion chemistry is generalized by using the various aryl or alkyl substituted indoles and propargyl alcohols.

EXPERIMENTAL SECTION

Details of instruments, standards etc. are already given in Chapter 3.

The 2-substituted indoles **1a**, **1d** and **1e** are commercially available from Aldrich.

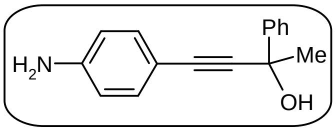
6.1 Preparation of 2-substituted indoles [1b, 1c, 2a-e] and propargylic precursors [3a-g]

2-*p*-tolyl-1*H*-indole **1b**[40a] and 2-(4-fluorophenyl)-1*H*-indole **1c**[40b-c] were prepared by following a literature procedure.[40b] *N*-methyl,2-substituted indoles **2a-e** were also synthesized in the presence MeI and NaH by using known procedure.[40b,41]

6.11 Synthesis of aryl substituted propargylic alcohols [3a-g]

Tertiary propargyl alcohols **3a-g** were prepared by Sonogashira cross coupling reaction of aromatic iodides with terminal acetylinic propargyl alcohols under palladium catalysis.[14,43] Among these, **3d-f** are new.

Compound 3d



In a round bottomed flask (50 mL) equipped with 4-iodoaniline (2.0 g, 9.13 mmol), $PdCl_2$ (0.05 g, 0.27 mmol), PPh_3 (0.14 g, 0.55 mmol) and CuI (0.10 g, 0.55 mmol) and acetonitrile (20 mL), was added 2-phenylbut-3-yn-2-ol (1.60 g, 10.9 mmol) and Et_3N (1.91 mL, 13.7 mmol). Then the reaction mixture was stirred at room temperature for 6 h and progress of the reaction monitored by TLC. Upon completion of the reaction, the crude mixture was filtered, the solid residue was washed with EtOAc, and washings added to the filtrate and the whole solution was concentrated under reduced pressure. Purification *via* column chromatography (ethyl acetate: hexane 1:4) yielded the desired 4-(4-aminophenyl)-2-phenylbut-3-yn-2-ol (**3d**).

Yield: 2.18 g (91%, orange solid).

Mp: 66–68 °C.

IR (KBr): 3375, 3227, 2975, 2219, 1605, 1266, 1058, 833, 707 cm^{-1}.

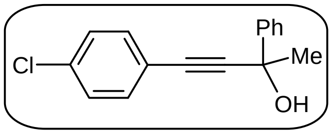
^{1}H NMR: δ 7.74 (d, *J* = 7.6 Hz, 2H), 7.41-7.37 (m, 2H), 7.33-7.27 (m, 3H), 6.60 (d, *J* = 8.0 Hz, 2H), 3.81 (s, 2H), 2.70 (s, 1H), 1.86 (s, 3H).

^{13}C NMR: δ 146.8, 146.1, 133.1, 128.3, 127.6, 125.1, 114.8, 112.0, 90.4, 85.5, 70.5, 33.5.

LC-MS: *m/z* 238 $[M+1]^+$.

Anal. Calcd. for $C_{16}H_{15}NO$: C, 80.98; H, 6.37; N, 5.90. Found: C, 80.78; H, 6.31; N, 5.76.

Compound 3e



Procedure was similar to that for compound **3d** using 1-chloro-4-iodobenzene (2.0 g, 8.39 mmol) and 2-phenylbut-3-yn-2-ol (1.47 g, 10.1 mmol).

Yield: 2.4 g (93%, orange solid)

Mp: 60–62 °C.

IR (KBr): 3375, 3058, 2981, 2230, 1589, 1398, 1085, 827, 762, 707 cm^{-1}.

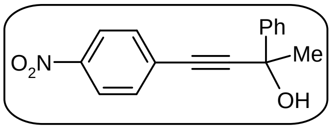
^{1}H NMR: δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.42-7.35 (m, 4H), 7.32-7.30 (m, 3H), 2.55 (qrt, 1H), 1.88 (s, 3H).

^{13}C NMR: δ 145.5, 134.6, 133.0, 128.7, 128.5, 127.9, 125.0, 121.1, 93.5, 83.8, 70.4, 33.3.

LC-MS: *m/z* 257 $[M+1]^+$.

Anal. Calcd. for $C_{16}H_{13}ClO$: C, 74.85; H, 5.10. Found: C, 74.68; H, 5.18.

Compound 3f



Procedure was similar to that for compound **3d** using 1-bromo-4-nitrobenzene (2.0 g, 9.9 mmol) and 2-phenylbut-3-yn-2-ol (1.74 g, 11.9 mmol).

Yield: 2.5 g (93%, orange solid)

Mp: 68–70 °C.

IR (KBr): 3567, 3096, 2992, 1595, 1348, 1096, 866, 773 cm^{-1}.

^{1}H NMR: δ 8.19 (d, J = 8.4 Hz, 2H), 7.70 (d, J = 7.6 Hz, 2H), 7.62 (d, J = 8.8 Hz, 2H), 7.44-7.40 (m, 2H), 7.35 (dd→t, 1H), 2.65 (qrt, 1H), 1.90 (s, 3H).

^{13}C NMR: δ 147.3, 144.9, 132.6, 129.5, 128.6, 128.1, 124.9, 123.6, 97.8, 83.0, 70.4, 33.0.

LC-MS: *m/z* 268 [M+1] +.

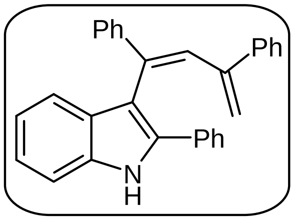
Anal. Calcd. for $C_{16}H_{13}NO_3$: C, 71.90; H, 4.90; N, 5.24. Found: C, 71.68; H, 4.97; N, 5.32.

6.2 Preparation of 3-dienylindoles [5-14] and 3-propargylated indoles [15-17]

6.21 Synthesis of 3-dienylindoles 5-14

An oven dried 25 mL round-bottomed flask was charged with 2-phenyl indole **1a** (0.2 g, 1.04 mmol), propargyl alcohol **3a** (0.25 g, 1.14 mmol), and PTSA (*p*-toluenesulfonic acid) (0.30 g, 1.55 mmol). To this was added nitromethane (4 mL) all at once and the mixture was stirred rt (25 °C) for 30 min. After completion of the reaction (TLC), the solvent was removed under reduced pressure. The residue was dissolved in ethyl acetate (20 mL), neutralized with aq. NaOH and then washed with water (2x10 mL) followed by brine solution (10 mL). The organic part was dried over anh. Na_2SO_4 and the solvent removed under reduced pressure. Purification by column chromatography (ethyl acetate: hexane 2:98) afforded the desired product **5**. Compounds **6-14** were prepared by using the same procedure. Subsequent to the elution of 3-dienylindoles [**8**, **9** and **14**], the 3-propargylated indoles **15-17** were separated using the same eluent.

Compound 5



This compound is known,[26a-b] but we could not find the spectroscopic data in the literature.

Yield: 0.374 g (91%, yellow liquid).

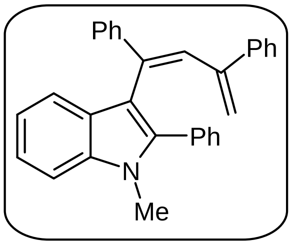
IR (neat): 3419, 3052, 3025, 1595, 1496, 1441, 1266, 1074, 1025, 904, 740 cm^{-1}.

^{1}H NMR: δ 8.02 (br 1H), 7.56 (d, *J* = 6.8 Hz, 2H), 7.51 (d, *J* = 7.2 Hz, 2H), 7.34-7.23 (m, 8H), 7.18 (t, 1H), 7.06-6.94 (m, 7H), 5.10 and 5.05 (2 s, 2H).

^{13}C NMR: δ 146.0, 142.3, 140.7, 136.5, 135.9, 135.3, 132.4, 130.4, 129.3, 128.5, 128.4, 127.5, 127.4, 127.2, 127.1, 127.0, 126.6, 126.4, 122.3, 120.4, 120.0, 117.1, 112.6, 110.6.

HRMS (ESI): Calcd. for $C_{30}H_{23}N$ (M^+ + H): *m/z* 398.1909. Found: 398.1905.

Compound 6



Procedure was similar to that for compound **5** using **2a** (0.30 g, 1.45 mmol) and **3a** (0.35 g, 1.59 mmol).

Yield: 0.493 g (83%, orange solid).

Mp: 180–182 °C.

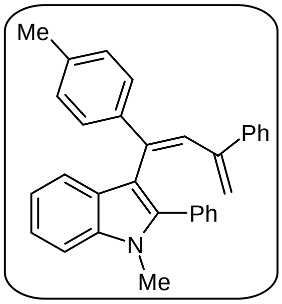
IR (KBr): 3047, 3014, 2937, 2915, 1600, 1567, 1485, 1458, 1436, 1370, 1326, 1227, 1151, 1014, 740 cm^{-1}.

^{1}H NMR: δ 7.56 (dd, *J* = 8.0 Hz, *J* = 1.0 Hz, 2H), 7.38-7.27 (m, 11H), 7.13-7.00 (m, 6H), 6.83 (s, 1H), 5.20 and 4.98 (2 s, 2H), 3.67 (s, 3H).

^{13}C NMR: δ 145.7, 143.1, 141.0, 138.7, 137.8, 136.9, 131.8, 130.3, 130.0, 128.2, 128.1, 127.7, 127.4, 127.3, 126.8, 126.4, 121.7, 120.5, 119.7, 115.8, 112.9, 109.4, 31.2.

HRMS (ESI): Calcd. for $C_{31}H_{25}N$ (M^+ + H): *m/z* 412.2066. Found: 412.2066.

Compound 7



This compound was prepared by following a route similar to that for **5** using **2a** (0.35 g, 1.68 mmol) and **3b** (0.44 g, 1.85 mmol).

Yield: 0.58 g (81%, orange solid).

Mp: 160–162 °C.

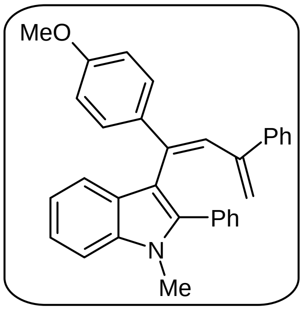
IR (KBr): 3041, 2926, 1600, 1567, 1468, 1364, 1332, 1184, 1145, 1014, 904, 811, 740 cm^{-1}.

^1H NMR: δ 7.48 (d, *J* = 8.0 Hz, 2H), 7.39-7.28 (m, 8H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.14-6.98 (m, 6H), 6.81 (s, 1H), 5.17 and 4.94 (2 s, 2H), 3.68 (s, 3H), 2.43 (s, 3H).

^{13}C NMR: δ 145.7, 141.0, 140.2, 138.6, 137.8, 137.2, 136.6, 131.8, 130.3, 129.2, 129.0, 128.3, 128.1, 127.6, 127.3, 127.1, 126.7, 126.4, 121.7, 120.5, 119.7, 115.5, 112.9, 109.3, 31.2, 21.2.

HRMS (ESI): Calcd. for $C_{32}H_{27}N$ ($M^+ + H$): *m/z* 426.2222. Found: 426.2220.

Compound 8



This compound was prepared by following a procedure similar to that for **5** using **2a** (0.3 g, 1.45 mmol) and **3c** (0.4 g, 1.59 mmol).

Yield: 0.478 g (75%, white solid).

Mp: 158–160 °C.

IR (KBr): 3052, 2992, 2942, 2833, 1600, 1507, 1468, 1359, 1255, 1184, 1047, 1014, 904, 833 cm^{-1}.

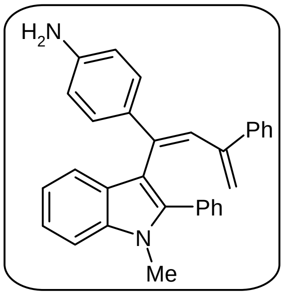
^{1}H NMR: δ 7.42 (d, *J* = 8.2 Hz, 2H), 7.32-7.22 (m, 8H), 7.05-7.00 (m, 4H), 6.90 (d, *J* = 7.2 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 6.64 (s, 1H), 5.07 and 4.83 (2 s, 2H), 3.81 (s, 3H), 3.61 (s, 3H).

^{13}C NMR: δ 159.1, 145.7, 141.1, 138.5, 137.8, 136.2, 135.6, 131.8, 130.3, 128.4, 128.3, 128.1, 127.6, 127.3, 126.7, 126.4, 121.7, 120.5, 119.7, 115.3, 113.6, 113.0, 109.3, 55.3, 31.2.

HRMS (ESI): Calcd. for $C_{32}H_{27}NO$ (M^+ + H): *m/z* 442.2172. Found: 442.2169.

X-ray structure has been determined for this compound.

Compound 9



Procedure was similar to that for compound **5** using **2a** (0.33 g, 1.59 mmol) and **3d** (0.41 g, 1.75 mmol).

Yield: 0.296 g (44%, pale yellow solid).

Mp: 190–192 °C.

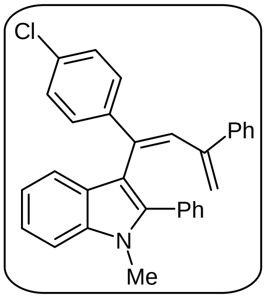
IR (KBr): 3441, 3359, 3030, 1633, 1507, 1468, 1288, 1178, 893, 822, 745 cm^{-1}.

^{1}H NMR: δ 7.36-7.27 (m, 10H), 7.09-7.04 (m, 4H), 6.95 (d, *J* = 7.6 Hz, 2H), 6.67 (s, 1H), 6.62 (d, *J* = 7.6 Hz, 2H), 5.09 and 4.85 (2 s, 2H), 3.67-3.65 (m, 5H).

^{13}C NMR: δ 145.9, 141.4, 138.5, 137.8, 136.5, 133.5, 131.9, 130.3, 128.4, 128.3, 128.0, 127.5, 127.3, 127.0, 126.6, 126.4, 121.6, 120.6, 119.6, 114.9, 113.1, 109.3, 31.2.

HRMS (ESI): Calcd. for $C_{31}H_{26}N_2$ (M^+ + H): *m/z* 427.2175. Found: 427.2174.

Compound 10



Procedure was similar to that for compound **5** using **2a** (0.28 g, 1.36 mmol) and **3e** (0.38 g, 1.49 mmol).

Yield: 0.525 g (87%, orange solid).

Mp: 164–166 °C.

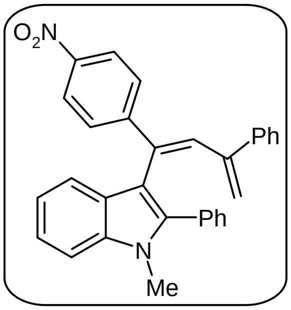
IR (KBr): 3052, 2942, 1611, 1490, 1364, 1310, 1227, 1156, 1090, 1014, 904, 838 cm^{-1}.

^1H NMR: δ 7.38-7.30 (m, 4H), 7.25-7.20 (m, 8H), 7.07-7.01 (m, 4H), 6.93-6.91 (m, 2H), 6.72 (s, 1H), 5.13 and 4.91 (2 s, 2H), 3.61 (s, 3H). (Additional peaks with low intensity are due to other isomer).

^{13}C NMR: δ 145.5, 141.6, 140.8, 138.8, 137.8, 135.8, 133.5, 133.4, 133.1, 132.2, 131.7, 131.0, 130.9, 130.3, 130.2, 129.9, 128.5, 128.3, 128.2, 127.9, 127.8, 127.6, 127.4, 126.9, 126.7, 126.4, 121.9, 120.4, 119.9, 116.2, 109.5, 31.2. (Additional peaks with low intensity are due to other isomer).

HRMS (ESI): Calcd. for $C_{31}H_{24}ClN$ (M^+ + H and M^+ + H + 2): *m/z* 446.1676 and 448.1676. Found: 446.1669 and 448.1653.

Compound 11



This compound was prepared by following a procedure similar to that for **5** using **2a** (0.25 g, 1.21 mmol) and **3f** (0.35 g, 1.33 mmol).

Yield: 0.472 g (86%, orange solid).

Mp: 166–168 °C.

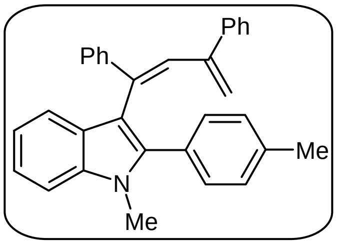
IR (KBr): 3052, 1584, 1512, 1474, 1348, 1107, 910, 855, 751 cm^{-1}.

^{1}H NMR: δ 8.09 (d, *J* = 7.2 Hz, 2H), 7.56 (d, *J* = 7.2 Hz, 2H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.28-7.26 (m, 7H), 7.11-7.02 (m, 6H), 6.93 (s, 1H), 5.29 and 5.11 (2 s, 2H), 3.66 (s, 3H).

^{13}C NMR: δ 149.8, 146.7, 145.2, 140.3, 139.1, 137.7, 135.2, 133.4, 131.3, 130.1, 128.3, 128.0, 127.8, 127.5, 127.4, 127.1, 126.4, 123.5, 122.1, 120.1, 117.5, 111.8, 109.6, 31.2.

HRMS (ESI): Calcd. for $C_{31}H_{24}N_2O_2$ (M^+ + Na): *m/z* 479.1736. Found: 479.1739.

Compound 12



This compound was prepared by following a procedure similar to that for **5** using **2b** (0.24 g, 1.07 mmol) and **3a** (0.26 g, 1.17 mmol).

Yield: 0.372 g (82%, pale yellow solid).

Mp: 152–154 °C.

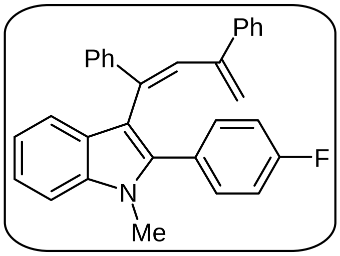
IR (KBr): 3047, 3014, 2910, 1600, 1496, 1468, 1370, 1332, 1019, 899, 822 cm^{-1}.

^{1}H NMR: δ 7.54 (d, *J* = 6.8 Hz, 2H), 7.36-7.24 (m, 6H), 7.18 (d, *J* = 7.6 Hz, 2H), 7.13-7.07 (m, 6H), 6.97 (d, *J* = 7.6 Hz, 2H), 6.78 (s, 1H), 5.18 and 4.94 (2 s, 2H), 3.65 (s, 3H), 2.36 (s, 3H).

^{13}C NMR: δ 145.6, 143.2, 140.9, 138.8, 137.7, 137.5, 137.0, 130.2, 130.0, 128.9, 128.3, 128.2, 127.3_2, 127.2_8, 126.7, 126.4, 121.6, 120.4, 119.6, 115.5, 112.6, 109.3, 31.1, 21.3.

HRMS (ESI): Calcd. for $C_{32}H_{27}N$ (M^+ + H): *m/z* 426.2222. Found: 426.2221.

Compound 13



Procedure was similar to that for compound **5** using **2c** (0.22 g, 0.98 mmol) and **3a** (0.24 g, 1.07 mmol).

Yield: 0.332 g (79%, pale yellow solid).

Mp: 180–182 °C.

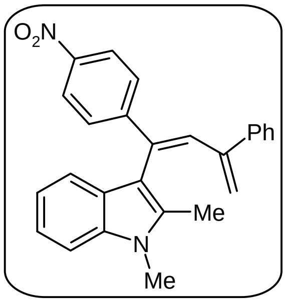
IR (KBr): 3052, 1605, 1551, 1468, 1337, 1227, 1162, 904, 849 cm^{-1}.

^{1}H NMR: δ 7.51-7.49 (m, 2H), 7.34-7.20 (m, 8H), 7.09-7.04 (m, 4H), 6.99-6.92 (m, 4H), 6.79 (d, *J* = 1.0 Hz, 1H), 5.18 and 4.92 (2 s, 2H), 3.61 (s, 3H).

^{13}C NMR: δ 162.5 (d, *J* = 246.0 Hz), 145.5, 143.0, 140.6, 137.7 (d, *J* = 16.0 Hz), 136.8, 132.0 (d, *J* = 9.0 Hz), 130.1, 128.3, 128.1, 127.8, 127.5, 127.4, 127.2, 126.9, 126.2, 121.9, 120.5, 119.8, 115.7, 115.2 (d, *J* = 21.0 Hz), 113.1, 109.4, 31.1.

HRMS (ESI): Calcd. for $C_{31}H_{24}FN$ ($M^+ + H$): *m/z* 430.1972. Found: 430.1970.

Compound 14



This compound was prepared by following a procedure similar to that for **5** using **2d** (0.19 g, 1.31 mmol) and **3f** (0.39 g, 1.44 mmol).

Yield: 0.341 g (66%, brown liquid).

IR (neat): 3058, 2926, 2855, 1600, 1507, 1474, 1342, 1107, 904, 855 cm^{-1}.

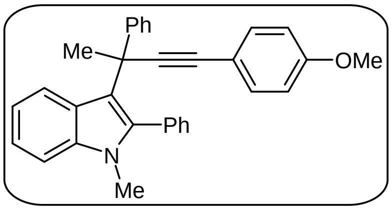
^{1}H NMR: δ 8.14 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.15 (s, 1H), 7.10-7.03 (m, 4H), 6.95-6.85 (m, 5H), 5.40 (s, 2H), 3.43 (s, 3H), 2.05 (s, 3H).

^{13}C NMR: δ 149.5, 147.0, 146.9, 140.0, 136.9, 135.5, 132.7, 129.0, 128.0, 127.2, 126.8, 126.6, 126.3, 123.6, 120.8, 119.9, 119.4, 119.3, 110.8, 108.4, 29.3, 11.4.

HRMS (ESI): Calcd. for $C_{26}H_{22}N_2O_2$ (M^+ + H): *m/z* 395.1760. Found: 395.1758.

6.22 Synthesis of 3-propargylindoles 15-17

Compound 15



Compound **15** was isolated after eluting compound **8**.

Yield: 0.083 g (13%, gummy liquid).

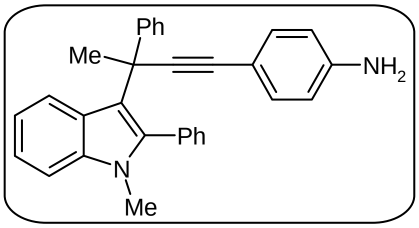
IR (neat): 3047, 2932, 2833, 1605, 1512, 1463, 1364, 1288, 1249, 1173, 1030, 827 cm^{-1}.

^{1}H NMR: δ 7.67-7.63 (m, 3H), 7.46 (br, 5H), 7.37-7.23 (m, 7H), 7.06 (t, 1H), 6.85 (d, *J* = 8.4 Hz, 2H), 3.83 (s, 3H), 3.45 (s, 3H), 1.81 (s, 3H).

^{13}C NMR: δ 159.0, 148.3, 137.5, 136.7, 134.0, 133.0, 131.6, 131.4, 128.4, 128.1, 128.0, 127.9, 126.7, 126.6, 126.1, 122.0, 121.6, 119.1, 116.3, 116.2, 113.6, 109.1, 94.6, 83.4, 55.3, 41.5, 33.3, 30.3.

HRMS (ESI): Calcd. for $C_{32}H_{27}NO$ (M^+ + Na): *m/z* 464.1991. Found: 464.1994.

Compound 16



Compound **16** was isolated after eluting compound **9**. It was isolated by using ethyl acetate-hexane (5:95) mixture as the eluent.

Yield: 0.317 g (47%, pale green solid).

Mp: 82–84 °C.

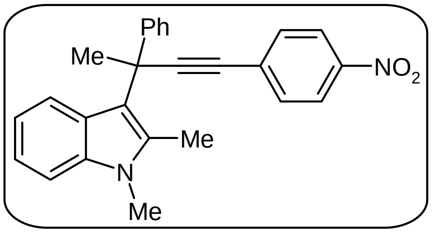
IR (KBr): 3458, 3370, 3047, 2937, 1616, 1512, 1468, 1370, 1173, 833 cm^{-1}.

^{1}H NMR: δ 7.65-7.62 (m, 3H), 7.43 (br, 5H), 7.35-7.18 (m, 7H), 7.05-7.02 (m, 1H), 6.56 (d, J = 8.4 Hz, 2H), 3.69 (br, 2H), 3.42 (s, 3H), 1.77 (s, 3H).

^{13}C NMR: δ 148.5, 146.0, 137.5, 136.8, 134.0, 132.8, 131.7, 131.4, 128.4, 128.0, 127.9, 126.8, 126.6, 126.0, 122.1, 121.5, 119.1, 116.4, 114.6, 113.7, 109.0, 93.7, 83.9, 41.5, 33.4, 30.2.

HRMS (ESI): Calcd. for $C_{31}H_{26}N_2$ (M^+ + H): *m/z* 427.2175. Found: 427.2178.

Compound 17



Compound **17** was isolated after eluting compound **14** by using the same eluent.

Yield: 0.098 g (19%, pale yellow solid).

Mp: 176–178 °C.

IR (KBr): 3079, 2981, 2937, 2230, 1600, 1529, 1447, 1337, 1178, 1151, 1112, 1025, 855 cm^{-1}.

^{1}H NMR: δ 8.18 (d, J = 8.8 Hz, 2H), 7.67 (d, J = 8.0 Hz, 1H), 7.61-7.58 (m, 4H), 7.37-7.27 (m, 4H), 7.19 (t, 1H), 7.05 (t, 1H), 3.68 (s, 3H), 2.35 (s, 3H), 2.31 (s, 3H).

^{13}C NMR: δ 147.5, 146.7, 136.5, 134.4, 132.3, 131.1, 128.4, 126.6, 126.5, 123.5, 120.5, 120.3, 119.2, 113.9, 109.0, 102.3, 81.8, 41.9, 32.2, 29.5, 12.0.

LC-MS: *m/z* 395 $[M+1]^+$.

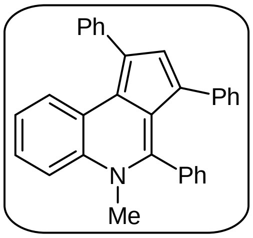
Anal. Calcd. for $C_{26}H_{22}N_2O_2$: C, 79.16; H, 5.62; N, 7.10. Found: C, 79.28; H, 5.65; N, 7.07.

6.3 Preparation of cyclopenta[c]quinolines and 3-indenylindoles 18-32

Compounds 18 and 19

To an oven dried round-bottomed flask (10 mL), diene **6** (0.248 g, 0.60 mmol), $Cu(OTf)_2$ (0.043 g, 0.12 mmol) and nitromethane (4 mL) were added. The mixture was stirred at 80 °C for 3-5 h in open air. After completion of the reaction (TLC), the solvent was removed under reduced pressure. The residue was dissolved in ethyl acetate (20 mL), neutralized with aq. NaOH solution and then washed with water (2x10 mL) followed by brine solution (10 mL). The organic part was dried over anh. Na_2SO_4 and the solvent removed under reduced pressure. Purification by column chromatography (ethyl acetate: hexane 1:9) afforded the desired products **18** and **19**. Compound 3-indenyl indole (**19**) eluted first. Similarly the remaining compounds **20-32** were prepared.

Compound 18



Yield: 0.158 g (64%, red solid).

Mp: 218–220 °C.

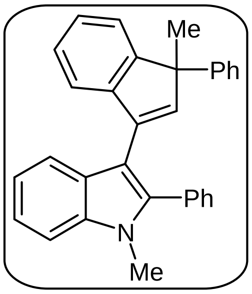
IR (KBr): 3052, 3013, 2920, 2822, 1599, 1578, 1534, 1462, 1364, 1320, 1238, 1112, 843 cm^{-1}.

^1H NMR: δ 8.41 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 7.2 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.47 (dd→t, 2H), 7.40-7.33 (m, 2H), 7.25-7.21 (m, 4H), 7.14-7.12 (m, 3H), 6.88 (br, 5H), 3.74 (s, 3H).

^{13}C NMR: δ 148.5, 140.4, 139.2, 133.7, 133.6, 133.1, 130.4, 129.7, 129.6, 129.2, 128.5, 127.9, 127.3, 126.9, 125.9, 124.7, 124.4, 124.2, 124.1, 124.0, 123.6, 119.8, 119.7, 116.6, 38.5.

HRMS (ESI): Calcd. for $C_{31}H_{23}N$ (M^+ + H): *m/z* 410.1909. Found: 410.1908.

Compound 19



Yield: 0.055 g (22%, white solid).

Mp: 164–166 °C.

IR (KBr): 3058, 2964, 2921, 1600, 1496, 1463, 1364, 1321, 1266, 1156, 1079, 1019, 751 cm^{-1}.

^{1}H NMR: δ 7.78 (d, *J* = 8.0 Hz, 1H), 7.55-7.52 (m, 3H), 7.46-7.43 (m, 4H), 7.32-7.27 (m, 7H), 7.23-7.21 (m, 3H), 6.39 (s, 1H), 3.84 (s, 3H), 1.84 (s, 3H).

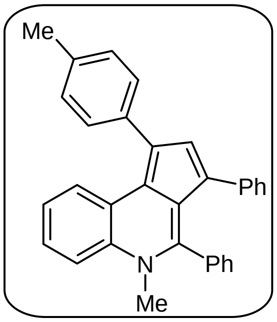
^{13}C NMR: δ 154.0, 145.4, 143.6, 143.4, 138.9, 137.5, 135.2, 132.0, 130.8, 129.4, 128.6, 128.3, 128.2, 128.0, 127.6, 126.4, 126.3, 126.2, 125.4, 122.5, 122.2, 121.7, 120.5, 119.9, 109.7, 109.1, 55.9, 31.2, 22.9.

HRMS (ESI): Calcd. for $C_{31}H_{25}N$ (M^+ + H): *m/z* 412.2066. Found: 412.2066.

Compounds 20 and 21

These compounds were prepared by following a procedure similar to that for **18** and **19** using **7** (0.392 g, 0.92 mmol).

Compound 20



Yield: 0.238 g (61%, red solid).

Mp: 224–226 °C.

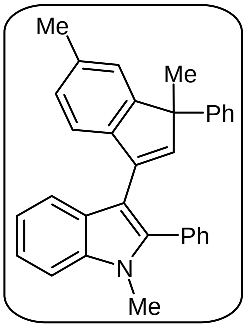
IR (KBr): 3046, 3014, 2915, 1605, 1578, 1512, 1463, 1364, 1326, 1238, 1107, 827 cm^{-1}.

^{1}H NMR: δ 8.44 (d, *J* = 8.0 Hz, 1H), 7.67-7.63 (m, 3H), 7.38 (dd→t, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.26-7.21 (m, 4H), 7.15-7.11 (m, 3H), 6.90-6.88 (m, 5H), 3.73 (s, 3H), 2.48 (s, 3H).

^{13}C NMR: δ 148.4, 139.2, 137.4, 135.5, 133.8, 133.6, 133.3, 130.4, 129.7, 129.4, 129.3, 129.2, 127.9, 127.2, 126.9, 124.6, 124.3, 124.1, 123.9, 123.6, 119.8, 119.5, 116.5, 38.4, 21.4.

HRMS (ESI): Calcd. for $C_{32}H_{25}N$ ($M^+ + H$): *m/z* 424.2066. Found: 424.2064.

Compound 21



Yield: 0.10 g (26%, white solid).

Mp: 192–194 °C.

IR (KBr): 3047, 2964, 2915, 1616, 1463, 1436, 1364, 1321, 1233, 1156, 1079, 1019, 816 cm^{-1}.

^{1}H NMR: δ 7.70 (d, *J* = 8.0 Hz, 1H), 7.49-7.46 (m, 3H), 7.41-7.34 (m, 4H), 7.27-7.20 (m, 6H), 7.05-6.95 (m, 3H), 6.23 (s, 1H), 3.79 (s, 3H), 2.34 (s, 3H), 1.55 (s, 3H).

^{13}C NMR: δ 154.3, 144.5, 143.7, 141.1, 138.9, 137.5, 135.1, 132.0, 130.9, 128.3, 128.2, 128.0, 127.6, 127.1, 126.3, 123.4, 122.1, 121.4, 120.6, 119.9, 109.6, 109.3, 55.7, 31.2, 23.0, 21.6.

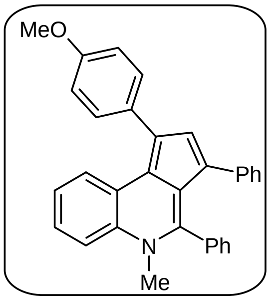
HRMS (ESI): Calcd. for $C_{32}H_{27}N$ ($M^+ + H$): *m/z* 426.2222. Found: 426.2223.

X-ray structure has been determined for this compound

Compounds 22 and 23

These compounds were prepared by following a procedure similar to that for **18** and **19** using **8** (0.25 g, 0.57 mmol).

Compound 22



Yield: 0.132 g (53 %, red solid).

Mp: 176–178 °C.

IR (KBr): 3063, 3013, 2926, 2822, 1610, 1578, 1506, 1440, 1369, 1282, 1243, 1156, 1024, 832 cm^{-1}.

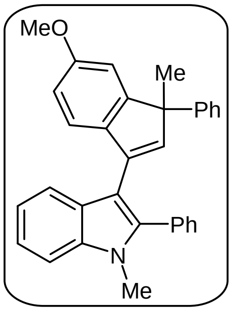
^{1}H NMR: δ 8.39 (d, *J* = 7.2 Hz, 1H), 7.66-7.63 (m, 3H), 7.37 (dd→t, 1H), 7.25-7.20 (m, 4H), 7.14-7.10 (m, 2H), 7.08 (s, 1H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.89-6.87 (m, 5H), 3.92 (s, 3H), 3.72 (s, 3H).

^{13}C NMR: δ 158.1, 148.4, 139.2, 133.8, 133.7, 133.3, 132.8, 130.6, 130.4, 129.7, 129.2, 127.9, 127.5, 127.2, 126.9, 126.5, 124.5, 124.1_1, 124.0_5, 123.9, 123.3, 119.7, 119.4, 116.5, 114.0, 55.4, 38.4.

HRMS (ESI): Calcd. for $C_{32}H_{25}NO$ (M^+ + H): *m/z* 440.2015. Found: 440.2015.

X-ray structure was determined for this compound

Compound 23



Yield: 0.075 g (30%, white solid).

Mp: 176–178 °C.

IR (KBr): 3058, 2964, 2921, 2827, 1600, 1463, 1436, 1364, 1288, 1238, 1178, 1079, 1019, 827 cm^{-1}.

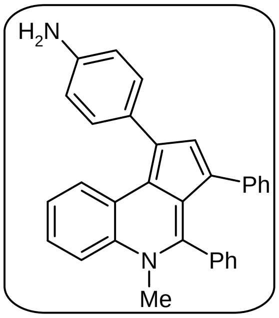
^{1}H NMR: δ 7.67 (d, *J* = 8.0 Hz, 1H), 7.47-7.43 (m, 3H), 7.38-7.31 (m, 4H), 7.22-7.17 (m, 6H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.77 (d, *J* = 2.0 Hz, 1H), 6.64 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 6.16 (s, 1H), 3.78 (s, 3H), 3.75 (s, 3H), 1.72 (s, 3H).

^{13}C NMR: δ 158.3, 155.8, 143.6, 143.4, 138.8, 137.5, 136.6, 134.7, 132.0, 130.8, 128.3, 128.2, 128.0, 127.6, 126.3, 126.2, 122.1, 120.5, 119.9, 111.3, 109.7, 109.4, 109.3, 55.8, 55.5, 31.3, 23.1.

HRMS (ESI): Calcd. for $C_{32}H_{27}NO$ ($M^+ + H$): *m/z* 442.2172. Found: 442.2170.

Compound 24

This compound was prepared by following a procedure similar to that for **18** and **19** using **9** (0.168 g, 0.39 mmol). The corresponding 3-indenyl indole could not be isolated.



Yield: 0.079 g (47%, brown solid).

Mp: 234–236 °C.

IR (KBr): 3436, 3359, 3052, 3019, 2921, 1600, 1573, 1512, 1370, 1277, 1249, 1184, 833 cm^{-1}.

^{1}H NMR: δ 8.34 (d, *J* = 7.6 Hz, 1H), 7.78 (br, 1H), 7.68-7.67 (m, 2H), 7.41-7.38 (m, 1H), 7.31 (dd→t, 1H), 7.21-7.15 (m, 4H), 7.12-7.05 (m, 3H), 6.86-6.80 (m, 6H), 3.73 (br, 5H).

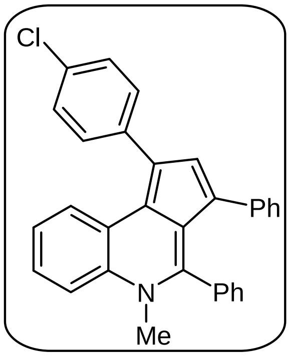
^{13}C NMR (500MHz): δ 153.5, 148.7, 139.0, 133.7, 133.5, 132.8, 130.8, 130.4, 129.7, 129.2, 127.9, 126.9, 125.0, 124.4, 124.2, 123.0, 120.1, 116.6, 38.5.

HRMS (ESI): Calcd. for $C_{31}H_{24}N_2$ ($M^+ + H$): *m/z* 425.2018. Found: 425.2021.

Compounds 25 and 26

These compounds were prepared by following a procedure similar to that for **18** and **19** using **10** (0.62 g, 1.39 mmol).

Compound 25



Yield: 0.387 g (63%, red solid).

Mp: 206–208 °C.

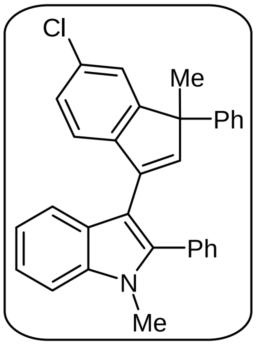
IR (KBr): 3047, 1611, 1584, 1512, 1463, 1397, 1370, 1244, 1090, 1003, 827 cm^{-1}.

^{1}H NMR: δ 8.42 (d, *J* = 8.0 Hz, 1H), 7.73-7.68 (m, 3H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.43 (dd→t, 1H), 7.32-7.23 (m, 4H), 7.18-7.13 (m, 3H), 6.95-6.91 (m, 5H), 3.75 (s, 3H).

^{13}C NMR: δ 148.7, 139.0, 138.9, 133.7, 133.4, 132.7, 131.5, 130.8, 130.3, 129.6, 129.3, 128.6, 127.9, 127.5, 126.9, 124.8, 124.2, 124.1, 124.0, 122.1, 119.9, 119.8, 116.7, 38.4.

HRMS (ESI): Calcd. for $C_{31}H_{22}ClN$ (M^+ + H and M^+ + H + 2): *m/z* 444.1520 and 446.1520. Found: 444.1517 and 446.1484.

Compound 26



Yield: 0.173 g (28%, white solid).

Mp: 188–190 °C.

IR (KBr): 3058, 3030, 2964, 2926, 2855, 1600, 1496, 1463, 1375, 1255, 1096, 1008, 833 cm^{-1}.

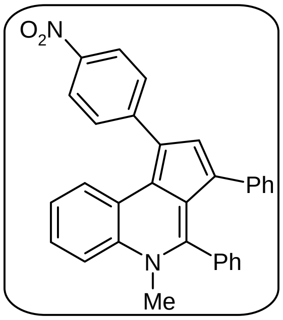
^{1}H NMR: δ 7.65 (d, *J* = 8.0 Hz, 1H), 7.49-7.43 (m, 4H), 7.41-7.32 (m, 3H), 7.25-7.17 (m, 7H), 7.07 (dd, *J* = 8.4 Hz, 2.0 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.32 (s, 1H), 3.79 (s, 3H), 1.75 (s, 3H).

^{13}C NMR: δ 155.8, 145.5, 142.5, 142.1, 139.0, 137.5, 134.7, 131.9, 131.3, 130.7, 129.4, 128.5, 128.4, 128.2, 128.0, 127.4, 127.1, 126.6$_2$, 126.5$_7$, 126.2, 123.1, 122.6, 122.3, 120.2, 120.1, 109.8, 108.6, 56.0, 31.3, 22.8.

HRMS (ESI): Calcd. for $C_{31}H_{24}ClN$ (M^+ + H and M^+ + H + 2): *m/z* 446.1676 and 448.1676. Found: 446.1682 and 448.1665.

Compound 27

This compound was prepared by following a procedure similar to that for **18** and **19** using **11** (0.372 g, 0.81 mmol). The corresponding 3-indenyl indole could not be isolated.



Yield: 0.274 g (74%, brown solid).

Mp: 206–208 °C.

IR (KBr): 3052, 2915, 1595, 1573, 1512, 1332, 1238, 1112, 855 cm^{-1}.

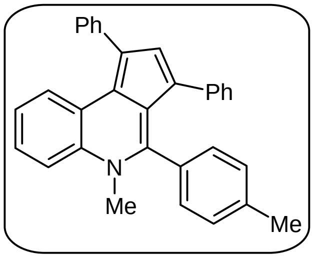
^{1}H NMR: δ 8.41 (d, *J* = 8.0 Hz, 1H), 8.27 (d, *J* = 8.8 Hz, 2H), 7.88 (d, *J* = 8.8 Hz, 2H), 7.75 (d, *J* = 8.8 Hz, 1H), 7.49-7.46 (m, 1H), 7.32 (dd→t, 1H), 7.25-7.21 (m, 3H), 7.17-7.12 (m, 3H), 6.94-6.85 (m, 5H), 3.80 (s, 3H).

^{13}C NMR: δ 149.3, 147.6, 145.4, 138.6, 133.8, 133.0, 132.0, 130.3, 129.5, 129.3, 128.3, 128.0, 127.0, 125.6, 124.5, 124.4, 124.0$_3$, 123.9$_5$, 123.8, 121.5, 120.9, 120.8, 117.1, 38.7.

HRMS (ESI): Calcd. for $C_{31}H_{22}N_2O_2$ (M^+ + H): *m/z* 455.1760. Found: 455.1759.

Compound 28

This compound was prepared by following a procedure similar to that for **18** and **19** using **12** (0.346 g, 0.81 mmol). The corresponding 3-indenyl indole could not be isolated.



Yield: 0.191 g (56%, red solid).

Mp: 160–162 °C.

IR (KBr): 3058, 2959, 2921, 2849, 1600, 1490, 1463, 1321, 1260, 1112, 1019, 822 cm^{-1}.

^{1}H NMR: δ 7.67-7.61 (m, 3H), 7.41-7.39 (m, 3H), 7.17 (br, 4H), 7.07-7.02 (m, 3H), 6.87-6.79 (m, 5H), 6.65 (s, 1H), 3.53 (s, 3H), 2.39 (s, 3H).

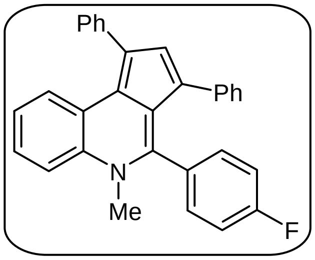
^{13}C NMR: δ 149.9, 146.6, 141.2, 138.5, 137.6, 136.1, 134.7, 130.9, 130.3, 129.5, 129.3, 129.0, 128.7, 128.3, 127.6, 127.4, 127.2, 125.0, 121.9, 120.6, 119.8, 113.1, 109.1, 31.4, 21.2.

HRMS (ESI): Calcd. for $C_{32}H_{25}N$ (M^{+} + H): *m/z* 424.2066. Found: 424.2066.

Compounds 29 and 30

These compounds were prepared by following a procedure similar to that for **18** and **19** using **13** (0.273 g, 0.64 mmol).

Compound 29



Yield: 0.159 g (59%, red solid).

Mp: 254–256 °C.

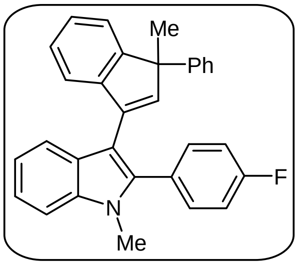
IR (KBr): 3052, 2921, 2849, 1710, 1595, 1578, 1501, 1463, 1222, 844 cm^{-1}.

^{1}H NMR: δ 8.44 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 7.2 Hz, 2H), 7.65 (d, *J* = 8.8 Hz, 1H), 7.52-7.49 (m, 2H), 7.42-7.36 (m, 2H), 7.26 (dd→t, 1H), 7.20-7.16 (m, 3H), 7.01-6.95 (m, 3H), 6.87 (d, *J* = 7.2 Hz, 2H), 6.84-6.80 (m, 2H), 3.73 (s, 3H).

^{13}C NMR: δ 163.2 (d, *J* = 248.0 Hz), 147.3, 140.3, 139.1, 133.7, 133.2, 132.3 (d, *J* = 8.0 Hz), 129.8, 129.5, 128.5, 127.1, 127.0, 126.0, 124.7, 124.4, 124.3, 124.2, 124.1, 123.7, 120.3, 119.6, 116.6, 115.0 (d, *J* = 22.0 Hz), 38.3.

HRMS (ESI): Calcd. for $C_{31}H_{22}FN$ (M^+ + H): *m/z* 428.1815. Found: 428.1814.

Compound 30



Yield: 0.086 g (32 %, white solid).

Mp: 158–160 °C.

IR (KBr): 3047, 2959, 1600, 1545, 1501, 1468, 1326, 1216, 1156, 1019, 844 cm^{-1}.

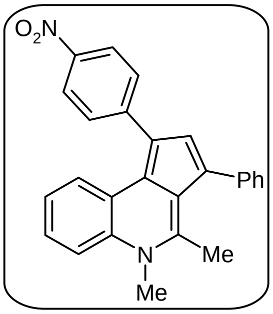
^{1}H NMR: δ 7.68 (d, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.43-7.34 (m, 3H), 7.27-7.23 (m, 7H), 7.21-7.13 (m, 3H), 7.09-7.05 (m, 2H), 6.28 (s, 1H), 3.77 (s, 3H), 1.77 (s, 3H).

^{13}C NMR: δ 162.6 (d, *J* = 247.0 Hz), 153.9, 145.5, 143.4 (d, *J* = 32.0 Hz), 137.6 (d, *J* = 31.0 Hz), 135.0, 132.5 (d, *J* = 8.0 Hz), 128.3, 128.0, 127.5, 126.4, 126.2, 125.5, 122.7, 122.3, 121.7, 120.5, 120.1, 115.3 (d, *J* = 21.0 Hz), 109.7, 109.4, 56.0, 31.2, 23.0.

HRMS (ESI): Calcd. for $C_{31}H_{24}FN$ (M^+ + H): *m/z* 430.1972. Found: 430.1971.

Compound 31

This compound was prepared by following a procedure similar to that for **18** and **19** using **14** (0.163 g, 0.41 mmol). The corresponding 3-indenyl indole could not be isolated.



Yield: 0.114 g (70%, red solid).

Mp: 154–156 °C.

IR (KBr): 3052, 2921, 2844, 1578, 1540, 1507, 1370, 1332, 1244, 1107, 855 cm^{-1}.

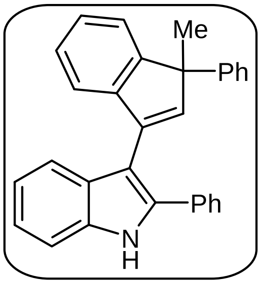
^{1}H NMR: δ 8.30 (d, *J* = 8.0 Hz, 1H), 8.25 (d, *J* = 8.0 Hz, 2H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.48-7.40 (m, 5H), 7.33 (dd→t, 1H), 7.24 (dd→t, 1H), 7.08 (s, 1H), 4.04 (s, 3H), 2.69 (s, 3H).

^{13}C NMR: δ 147.8, 147.5, 145.3, 140.1, 133.8, 131.8, 130.3, 129.3, 128.0, 127.4, 126.0, 125.4, 124.1, 123.9, 123.6, 120.9, 120.8, 120.5, 116.3, 35.7, 19.6.

HRMS (ESI): Calcd. for $C_{26}H_{20}N_2O_2$ (M^+ + H): *m/z* 393.1604. Found: 393.1606.

C***ompound 32***

This compound was prepared by following a procedure similar to that for **18** and **19** using **5** (0.34 g, 0.86 mmol). The corresponding cyclopenta[c]quinoline could not be isolated.



Yield: 0.241 g (71%, pale yellow solid).

Mp: 168–170 °C.

IR (KBr): 3414, 3052, 2964, 2921, 2860, 1595, 1490, 1441, 1321, 1222, 1025, 838, 740 cm^{-1}.

^{1}H NMR: δ 8.35 (br,s, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 7.6 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.33-7.23 (m, 8H), 7.20-

7.16 (m, 2H), 7.11 (t, 1H), 7.03 (d, *J* = 7.6 Hz, 1H), 6.57 (s, 1H), 1.89 (s, 3H).

^{13}C NMR: δ 154.0, 145.6, 143.3, 136.1, 135.2, 135.1, 132.8, 129.4, 128.7, 128.5, 127.8, 126.5, 126.3, 125.6, 122.7_9, 122.7_5, 121.9, 120.4, 120.3, 111.0, 108.5, 56.3, 23.0.

HRMS (ESI): Calcd. for $C_{30}H_{23}N$ ($M^+ + H$): *m/z* 398.1909. Found: 398.1910.

6.4 One pot synthesis of cyclopenta[c]quinolines [18, 20, 22, 24, 31, 33-43]

An oven dried 25 mL round-bottomed flask was charged with *N*-methyl-2-phenyl indole **2a** (0.1 g, 0.48 mmol), propargyl alcohol **3a** (0.12 g, 0.53 mmol), PTSA (*p*-toluenesulfonic acid) (0.138 g, 0.72 mmol) and nitromethane (4 mL). The mixture was stirred at rt for 30 min. and then $Cu(OTf)_2$ (0.035 g, 0.097 mmol) was added to the contents. The contents were stirred at 80 °C for 3-5 h in open air. After completion of the reaction (TLC), the solvent was removed under reduced pressure. The residue was dissolved in ethyl acetate (20 mL), neutralized with aq. NaOH solution and then washed with water (2x10 mL) followed by brine solution (10 mL). The organic part was dried over anh. Na_2SO_4 and the solvent removed under reduced pressure. Purification by column chromatography (ethyl acetate: hexane 1:9) afforded the desired product **18** (0.13 g, 65%). Similarly, compounds **20, 22, 24, 31**, **33-43** were prepared by using the same procedure.

Compound 20

Precursors **2a** (0.2 g, 0.97 mmol) and **3b** (0.25 g, 1.06 mmol) were used. Yield: 0.24 g (58%). Analytical data are given above.

Compound 22

Precursors **2a** (0.22 g, 1.06 mmol) and **3c** (0.29 g, 1.17 mmol) were used. Yield: 0.24 g (52%). Analytical data are given above.

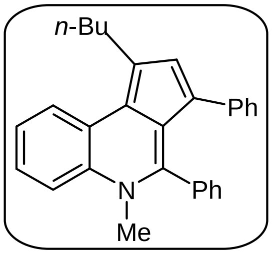
Compound 24

Precursors **2a** (0.25 g, 1.21 mmol) and **3d** (0.31 g, 1.33 mmol) were used. Yield: 0.18 g (34%). Analytical data are given above.

Compound 31

Precursors **2d** (0.18 g, 1.24 mmol) and **3f** (0.36 g, 1.36 mmol) were used. Yield: 0.283 g (58%). Analytical data are given above.

Compound 33



Precursors **2a** (0.2 g, 0.97 mmol) and **3g** (0.22 g, 1.06 mmol) were used.

Yield: 0.23 g (61%, red solid).

Mp: 128–130 °C.

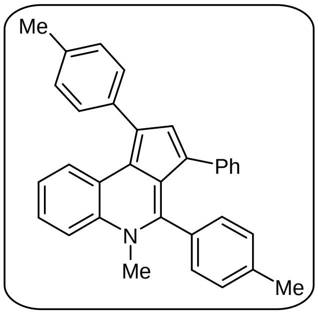
IR (neat): 3052, 2953, 2921, 2860, 1732, 1605, 1584, 1551, 1463, 1370, 1326, 1112, 745 cm^{-1}.

^{1}H NMR: δ 8.43 (d, *J* = 6.0 Hz, 1H), 7.65 (d, *J* = 6.8 Hz, 1H), 7.50 (t, 1H), 7.40 (t, 1H), 7.20-7.17 (m, 3H), 7.11-7.08 (m, 2H), 7.01 (s, 1H), 6.87-6.81 (m, 5H), 3.67 (s, 3H), 3.19 (t, 2H), 1.92-1.87 (m, 2H), 1.62-1.56 (m, 2H), 1.04 (t, 3H).

^{13}C NMR: δ 147.5, 139.6, 133.9, 133.7, 132.7, 130.4, 129.7, 129.0, 127.8, 126.8, 126.5, 125.4, 124.7, 124.3 124.1, 123.8, 123.6, 119.2_1, 119.1_6, 116.3, 38.2, 32.2, 30.2, 23.3 ,14.3.

HRMS (ESI): Calcd. for $C_{29}H_{27}N$ (M^+ + H): *m/z* 390.2222. Found: 390.2221.

Compound 34



Precursors **2b** (0.225 g, 1.02 mmol) and **3b** (0.264 g, 1.12 mmol) were used.

Yield: 0.237 g (53%, red solid).

Mp: 228–230 °C.

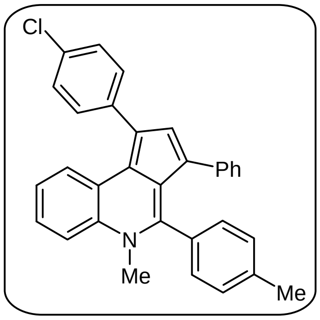
IR (KBr): 3047, 3014, 2910, 1605, 1578, 1540, 1501, 1397, 1326, 1244, 1178, 1112, 1008, 827 cm^{-1}.

^{1}H NMR: δ 8.42 (d, J = 8.0 Hz, 1H), 7.66-7.62 (m, 3H), 7.36 (dd→t, 1H), 7.29-7.20 (m, 3H), 7.09-7.07 (m, 3H), 6.91-6.83 (m, 7H), 3.76 (s, 3H), 2.46 (s, 3H), 2.29 (s, 3H).

^{13}C NMR: δ 148.7, 139.4, 139.2, 137.5, 135.4, 133.8, 133.0, 130.8, 130.3, 129.8, 129.4, 129.2, 128.5, 127.3, 126.8, 124.6, 124.5, 124.2, 123.9, 123.7, 123.5, 120.1, 119.4, 116.5, 38.4, 21.4, 21.3.

HRMS (ESI): Calcd. for $C_{33}H_{27}N$ (M^+ + H): *m/z* 438.2222. Found: 438.2222.

Compound 35



Precursors **2b** (0.25 g, 1.13 mmol) and **3e** (0.32 g, 1.24 mmol) were used.

Yield: 0.329 g (64%, red solid).

Mp: 216–218 °C.

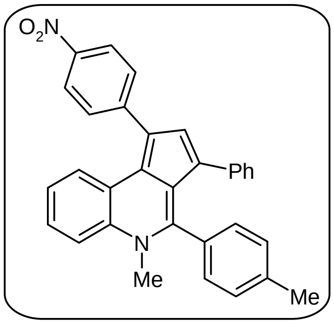
IR (KBr): 3041, 3025, 2921, 2855, 1611, 1573, 1540, 1507, 1392, 1370, 1249, 1085, 1014, 833 cm^{-1}.

^{1}H NMR: δ 8.34 (d, J = 4.4 Hz, 1H), 7.66-7.64 (m, 3H), 7.45-7.43 (m, 3H), 7.29 (dd→t, 1H), 7.08 (br, 3H), 6.91-6.82 (m, 7H), 3.82 (br s, 3H), 2.31 (s, 3H).

^{13}C NMR (500MHz): δ 149.2, 139.5, 139.0, 132.7, 132.2, 131.7, 131.1, 130.8, 130.4, 130.2, 129.7, 128.7, 128.6, 126.9, 124.2, 122.0, 120.0, 116.8, 38.6, 21.3.

HRMS (ESI): Calcd. for $C_{32}H_{24}ClN$ (M^+ + H and M^+ + H + 2): *m/z* 458.1676 and 460.1676. Found: 458.1675 and 460.1644.

Compound 36



Precursors **2b** (0.15 g, 0.68 mmol) and **3f** (0.20 g, 0.75 mmol) were used.

Yield: 0.232 g (72%, red solid).

Mp: 230–232 °C.

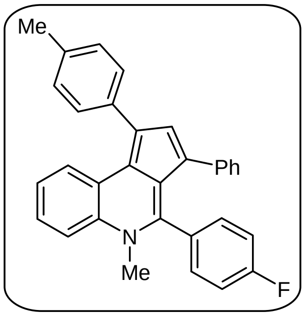
IR (KBr): 3074, 2970, 2921, 1589, 1573, 1540, 1244, 1189, 1107, 1014, 849 cm^{-1}.

^{1}H NMR: δ 8.39 (d, *J* = 8.4 Hz, 1H), 8.28 (d, *J* = 8.8 Hz, 2H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 8.8 Hz, 1H), 7.46 (t, 1H), 7.30 (dd→t, 1H), 7.11 (s, 1H), 7.06 (d, *J* = 7.6 Hz, 2H), 6.95-6.87 (m, 5H), 6.82 (d, *J* = 7.2 Hz, 2H), 3.83 (s, 3H), 2.29 (s, 3H).

^{13}C NMR: δ 149.7, 147.7, 145.4, 139.6, 138.7, 133.9, 131.8, 130.2, 129.6, 129.3, 128.6, 128.3, 126.9, 125.5, 124.3, 124.0$_4$, 123.9$_6$, 121.4, 121.1, 120.8, 117.1, 38.7, 21.3.

HRMS (ESI): Calcd. for $C_{32}H_{24}N_2O_2$ (M^+ + H): *m/z* 469.1917. Found: 469.1917.

Compound 37



Precursors **2c** (0.228 g, 1.01 mmol) and **3b** (0.263 g, 1.11 mmol) were used.

Yield: 0.251 g (56%, red solid).

Mp: 258–260 °C.

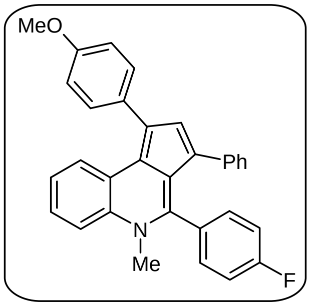
IR (KBr): 3063, 3019, 2942, 2921, 1611, 1578, 1507, 1370, 1216, 1003, 855 cm^{-1}.

^{1}H NMR: δ 8.44 (d, *J* = 8.4 Hz, 1H), 7.66-7.62 (m, 3H), 7.38 (t, 1H), 7.30 (d, *J* = 7.6 Hz, 2H), 7.27-7.17 (m, 3H), 7.12 (s, 1H), 6.98-6.93 (m, 3H), 6.85 (d, *J* = 6.8 Hz, 2H), 6.83-6.78 (m, 2H), 3.73 (s, 3H), 2.48 (s, 3H).

^{13}C NMR: δ 163.2 (d, *J* = 248.0 Hz), 147.2, 139.1, 137.3, 135.6, 133.7, 133.4, 132.3 (d, *J* = 8.0 Hz), 129.8, 129.7, 129.4, 129.3, 127.1, 127.0, 124.7, 124.5, 124.3_0, 124.2_6, 124.0, 123.8, 120.3, 119.4, 116.5, 115.0 (d, *J* = 22.0 Hz), 38.4, 21.4.

HRMS (ESI): Calcd. for $C_{32}H_{24}FN$ (M^+ + H): *m/z* 442.1972. Found: 442.1972.

Compound 38



Precursors **2c** (0.2 g, 0.89 mmol) and **3c** (0.25 g, 0.98 mmol) were used.

Yield: 0.208 g (51%, red solid).

Mp: 204–206 °C.

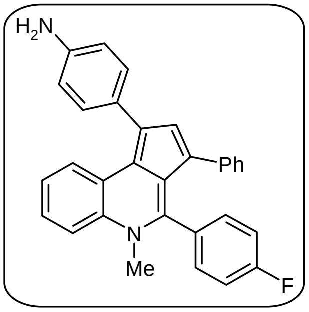
IR (KBr): 3068, 3025, 2921, 2827, 1616, 1584, 1507, 1364, 1288, 1249, 1167, 1036, 844 cm^{-1}.

^{1}H NMR: δ 8.44 (br, 1H), 7.65-7.64 (m, 3H), 7.27 (t, 1H), 7.19-7.16 (m, 3H), 7.09-7.07 (m, 3H), 6.97 (br, 3H), 6.87-6.79 (m, 4H), 3.95 (s, 3H), 3.71 (s, 3H).

^{13}C NMR: δ 163.2 (d, *J* = 248.0 Hz), 158.2, 147.1, 139.1, 133.8, 132.3 (d, *J* = 8.0 Hz), 130.4, 129.6, 126.9, 124.0, 119.3, 116.5, 115.0 (d, *J* = 22.0 Hz), 114.0, 55.3, 38.3.

HRMS (ESI): Calcd. for $C_{32}H_{24}FNO$ (M^+ + H): *m/z* 458.1921. Found: 458.1920.

Compound 39



Precursors **2c** (0.25 g, 1.11 mmol) and **3d** (0.29 g, 1.22 mmol) were used.

Yield: 0.186 g (38%, brown solid).

Mp: 220–222 °C.

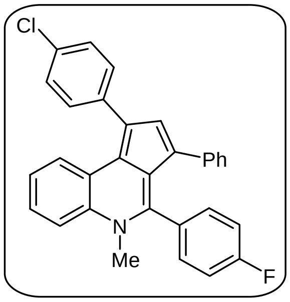
IR (KBr): 3353, 2926, 2855, 1595, 1501, 1463, 1436, 1277, 1222, 1173, 833 cm^{-1}.

^{1}H NMR: δ 8.38 (d, *J* = 5.2 Hz, 1H), 7.73 (br, 2H), 7.70-7.66 (m, 1H), 7.43-7.40 (m, 3H), 7.30 (dd→t, 1H), 7.23-7.18 (m, 2H), 7.08 (s, 1H), 6.98-6.94 (m, 4H), 6.86-6.79 (m, 5H), 3.76 (br s, 3H).

^{13}C NMR (500MHz): δ 163.3 (d, *J* = 248.0 Hz), 133.8, 133.1, 132.4 (d, *J* = 8.8 Hz), 131.0, 130.8, 130.5, 129.8, 129.6$_3$, 129.6$_0$, 128.8, 128.6, 127.0, 126.5, 124.9, 124.4, 122.9, 120.9, 116.6, 115.0 (d, *J* = 21.0 Hz), 114.1, 38.4.

HRMS (ESI): Calcd. for $C_{31}H_{23}FN_2$ (M^+ + H): *m/z* 443.1924. Found: 443.1923.

Compound 40



Precursors **2c** (0.2 g, 0.89 mmol) and **3e** (0.25 g, 0.98 mmol) were used.

Yield: 0.286 g (70%, red solid).

Mp: 230–232 °C.

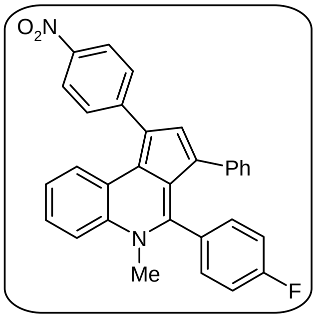
IR (KBr): 3063, 3019, 2926, 1605, 1573, 1501, 1463, 1397, 1364, 1216, 1090, 1008, 827 cm^{-1}.

^{1}H NMR: δ 8.38 (d, *J* = 8.0 Hz, 1H), 7.68-7.66 (m, 3H), 7.46-7.42 (m, 3H), 7.29 (t, 1H), 7.19-7.16 (m, 2H), 7.10 (s, 1H), 7.01-6.94 (m, 3H), 6.86-6.79 (m, 4H), 3.74 (s, 3H).

^{13}C NMR: δ 163.2 (d, *J* = 249.0 Hz), 147.5, 138.8 (d, *J* = 11.0 Hz), 133.7, 132.7, 132.3 (d, *J* = 8.0 Hz), 131.6, 130.7, 129.7, 129.4_1, 129.3_7, 128.7, 127.3, 127.0, 124.9, 124.4, 124.2, 124.0, 122.2, 120.3, 119.8, 116.7, 115.1 (d, *J* = 22.0 Hz), 38.4.

HRMS (ESI): Calcd. for $C_{31}H_{21}ClFN$ ($M^+ + H$): *m/z* 462.1426. Found: 462.1425.

Compound 41



Precursors **2c** (0.25 g, 1.11 mmol) and **3f** (0.326 g, 1.22 mmol) were used.

Yield: 0.393 g (75%, red solid).

Mp: 210–212 °C.

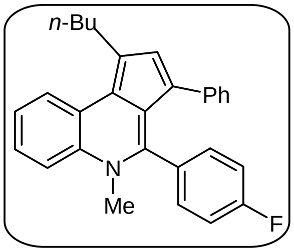
IR (KBr): 3058, 2921, 1595, 1573, 1501, 1370, 1332, 1233, 1112, 1008, 860 cm^{-1}.

^{1}H NMR: δ 8.38 (d, *J* = 8.4 Hz, 1H), 8.26 (d, *J* = 8.0 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 8.8 Hz, 1H), 7.47 (dd→t, 1H), 7.31 (dd→t, 1H), 7.20-7.12 (m, 3H), 7.01-6.94 (m, 3H), 6.85-6.80 (m, 4H), 3.81 (s, 3H).

^{13}C NMR: δ 163.3 (d, *J* = 249.0 Hz), 148.1, 147.5, 145.5, 138.5, 133.9, 132.3 (d, *J* = 8.0 Hz), 132.1, 129.7, 129.3, 129.1, 128.1, 127.1, 125.7, 124.7, 124.5, 124.0_6, 124.9_8, 123.8, 121.4, 121.2, 121.1, 117.1, 115.1 (d, *J* = 22.0 Hz), 38.7.

HRMS (ESI): Calcd. for $C_{31}H_{21}FN_2O_2$ ($M^+ + H$): *m/z* 473.1666. Found: 473.1664.

Compound 42



Precursors **2c** (0.213 g, 0.95 mmol) and **3g** (0.21 g, 1.04 mmol) were used.

Yield: 0.251 g (65%, red solid).

Mp: 136–138 °C.

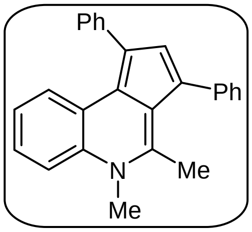
IR (KBr): 3052, 2942, 2926, 2860, 1600, 1578, 1551, 1512, 1468, 1375, 1321, 1222, 1156, 1096, 844 cm^{-1}.

^{1}H NMR: δ 8.41 (dd, J = 8.0 Hz, J = 1.2 Hz, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.52-7.48 (m, 1H), 7.42-7.38 (m, 1H), 7.15-7.12 (m, 2H), 7.01 (s, 1H), 6.95-6.89 (m, 3H), 6.82-6.74 (m, 4H), 3.67 (s, 3H), 3.18 (t, 2H), 1.91-1.85 (m, 2H), 1.61-1.55 (m, 2H), 1.03 (t, 3H).

^{13}C NMR: δ 163.2 (d, J = 248.0 Hz), 146.2, 139.6, 133.7, 132.9, 132.3 (d, J = 9.0 Hz), 130.0 (d, J = 4.0 Hz), 129.9, 126.9, 126.4, 125.4, 124.8, 124.4, 124.3, 124.1, 123.7, 119.8, 119.1, 116.3, 114.9 (d, J = 22.0 Hz), 38.2, 32.2, 30.1, 23.3, 14.3.

HRMS (ESI): Calcd. for $C_{29}H_{26}FN$ (M^+ + H): *m/z* 408.2128. Found: 408.2127.

Compound 43



Precursors **2d** (0.18 g, 1.24 mmol) and **3a** (0.30 g, 1.36 mmol) were used.

Yield: 0.185 g (43%, brown solid).

Mp: 178–180 °C.

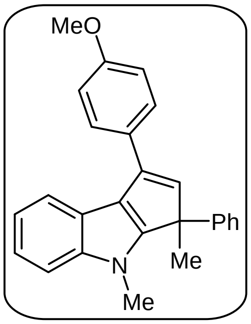
IR (KBr): 3063, 3014, 2932, 2849, 1578, 1545, 1507, 1474, 1370, 1326, 1244, 1123, 1052, 915, 833 cm^{-1}.

^{1}H NMR:	δ 8.39 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 7.2 Hz, 2H), 7.61-7.51 (m, 5H), 7.48-7.45 (m, 2H), 7.42-7.33 (m, 3H), 7.22 (dd→t, 1H), 7.18 (s, 1H), 3.91 (s, 3H), 2.67 (s, 3H).
^{13}C NMR:	δ 146.5, 140.7, 133.5, 132.8, 130.4, 129.6, 128.4, 127.8, 126.4, 125.9, 125.6, 124.4, 124.1, 123.6, 123.1, 119.8, 119.1, 115.8, 35.3, 19.5.
HRMS (ESI):	Calcd. for $C_{26}H_{21}N$ (M^+ + H): *m/z* 348.1753. Found: 348.1752.

6.5 Synthesis of 3,4-dihydrocyclopenta[b]indole 44 and 3-propargylated indole 45

To an oven dried round-bottomed flask (10 mL), indole **2e** (0.11 g, 0.87 mmol), alcohol **3c** (0.22 g, 0.87 mmol), $Sc(OTf)_3$ (0.04 g, 0.087 mmol) and nitromethane (3 mL) were added. The mixture was stirred at 80 °C (oil bath) for 6 h in open air. After completion of the reaction (TLC), the solvent was removed under reduced pressure. The residue was dissolved in ethyl acetate (20 mL), neutralized with aq. NaOH solution and washed with water (2x10 mL) followed by brine solution (10 mL). The organic part was dried over anh. Na_2SO_4 and the solvent removed under reduced pressure. Purification by column chromatography (hexane: ethyl acetate 9:1) afforded products **44** and **45**.

Compound 44

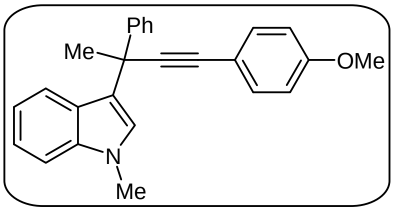


Yield:	0.071 g (22%, white solid).
Mp:	164–166 °C.
IR (KBr):	2921, 2849, 1605, 1512, 1452, 1249, 1173, 1025, 745 cm^{-1}.
^{1}H NMR:	δ 7.81 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.8 Hz, 2H), 7.35-7.31 (m, 1H), 7.28-7.27 (m, 3H), 7.25-7.16 (m, 4H), 7.02 (d, *J* = 8.8 Hz, 2H), 6.05 (s, 1H), 3.89 (s, 3H), 3.61 (s, 3H), 1.95 (s, 3H).

^{13}C NMR: δ 159.3, 156.4, 141.0, 140.7, 139.5, 135.3, 129.2, 128.7, 128.5, 126.8, 126.2, 121.6, 120.3, 119.8, 118.9, 114.0, 109.9, 55.5, 51.6, 30.8, 19.9.

HRMS (ESI): Calcd. for $C_{26}H_{23}NO$ ($M^+ + H$): *m/z* 366.1859. Found: 366.1858.

Compound 45



Yield: 0.206 g (65%, brown liquid)

IR (neat): 3052, 2981, 2932, 2833, 2362, 1600, 1507, 1463, 1370, 1326, 1249, 1173, 1025, 827 cm^{-1}.

^{1}H NMR: δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.41 (d, *J* = 8.8 Hz, 2H), 7.34-7.30 (m, 3H), 7.25-7.19 (m, 2H), 7.04 (s, 1H), 7.00 (t, 1H), 6.83 (d, *J* = 8.8 Hz, 2H), 3.81 and 3.79 (2 s, 6H), 2.13 (s, 3H).

^{13}C NMR: δ 159.2, 146.5, 137.9, 133.1, 128.2, 126.7, 126.4, 126.3, 121.6, 121.4, 120.4, 118.8, 116.2, 113.8, 109.2, 93.7, 82.8, 55.3, 39.9, 32.8, 31.2.

HRMS (ESI): Calcd. for $C_{26}H_{23}NO$ ($M^+ + H$): *m/z* 366.1859. Found: 366.1857.

6.6 X-ray crystallography

Data for **8, 21** and **22**were collected using Bruker AXS-SMART or on an OXFORD diffractometer as described in Chapter 3. Structures were solved and refined using standard methods.[52] Crystal data are summarized in Table 5.

Table 5. Crystallographic data for compounds **8, 21** and **22**[a]

Compound	**8**	**21**	**22**
Emp. formula	$C_{32}H_{27}NO$	$C_{32}H_{27}N$	$C_{32}H_{25}NO$
Formula weight	441.55	425.55	439.53
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	*Pbca*	$P2_1/c$
a /Å	12.1929(9)	14.3480(14)	11.4240(16)
b /Å	8.8550(7)	16.969(2)	9.4223(10)
c /Å	22.6406(17)	19.737(2)	21.475(3)
α/deg	90	90	90
β/deg	93.6150(10)	90	99.680(13)
γ/deg	90	90	90
V /Å^3	2439.6(3)	4805.5(9)	2278.6(5)
Z	4	8	4
Dcalc /g cm^{-3}]	1.202	1.176	1.281
μ /mm^{-1}	0.072	0.067	0.076
F(000)	936	1808	928
Data/ restraints/ parameters	4304/0/309	4218/0/301	4006/0/310
S	1.172	0.842	1.015
R1 [I>2σ(I)]	0.0610	0.0619	0.0427
wR2 [all data]	0.1373	0.0854	0.0973
Max./min. residual electron dens. [eÅ^{-3}]	0.190/-0.121	0.180/-0.206	0.176/-0.137

[a] $R1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$ and $wR2 = [\Sigma w(Fo^2-Fc^2)^2/\Sigma wFo^4]^{0.5}$

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A) Copies of $^{1}H/^{13}C$ NMR spectra for representative compounds

PART A: Compounds 32, 35, 48, 52, 54, 63, 75, 79, 89, 95, 96 and 115

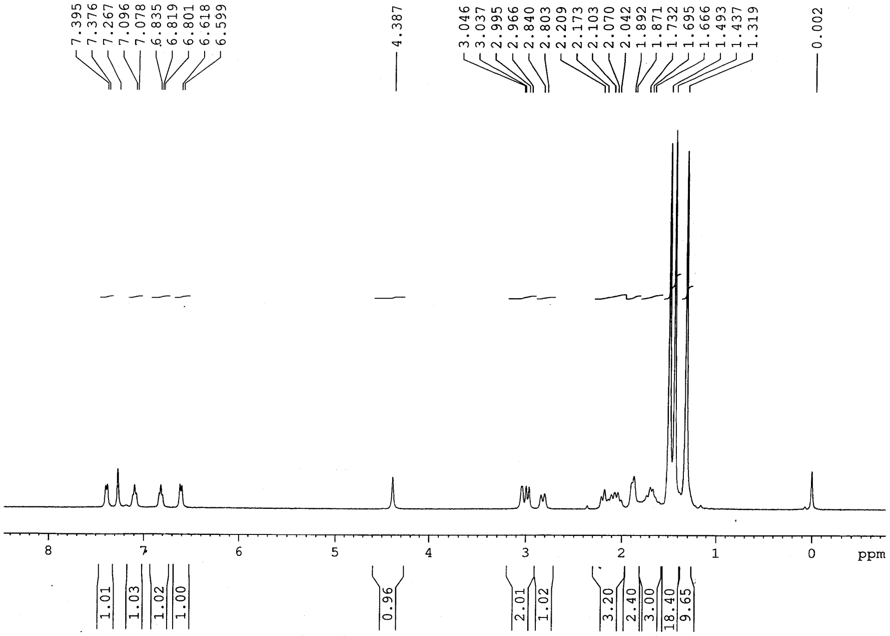


Figure A1. ^{1}H NMR spectrum of compound **32**

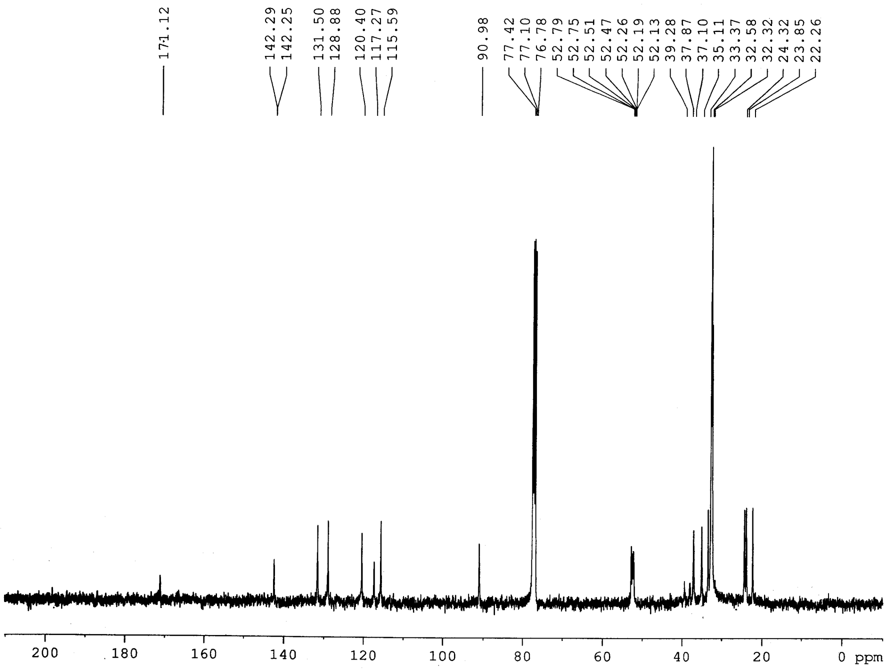


Figure A2. ^{13}C NMR spectrum of compound **32**

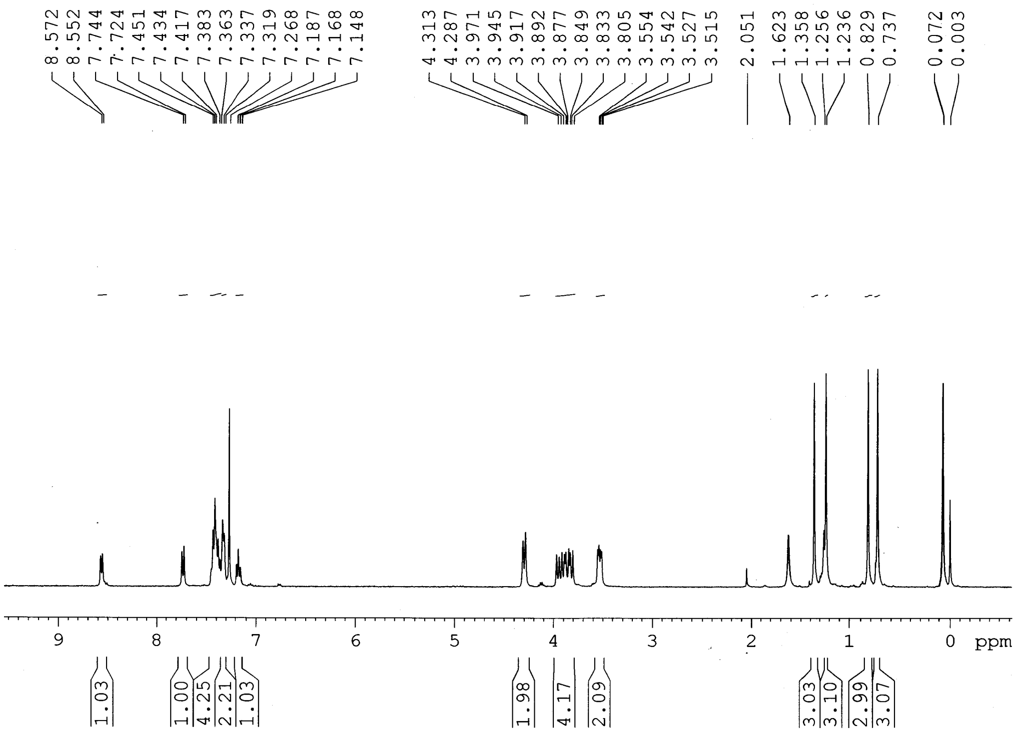


Figure A3. ^{1}H NMR spectrum of compound **35**

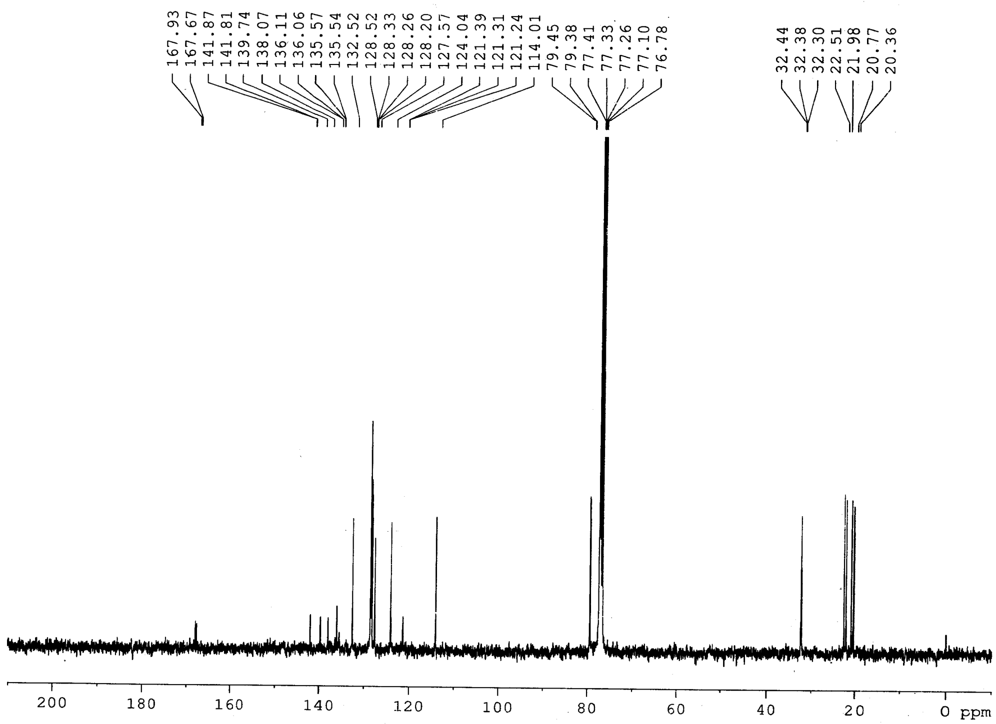


Figure A4. ^{13}C NMR spectrum of compound **35**

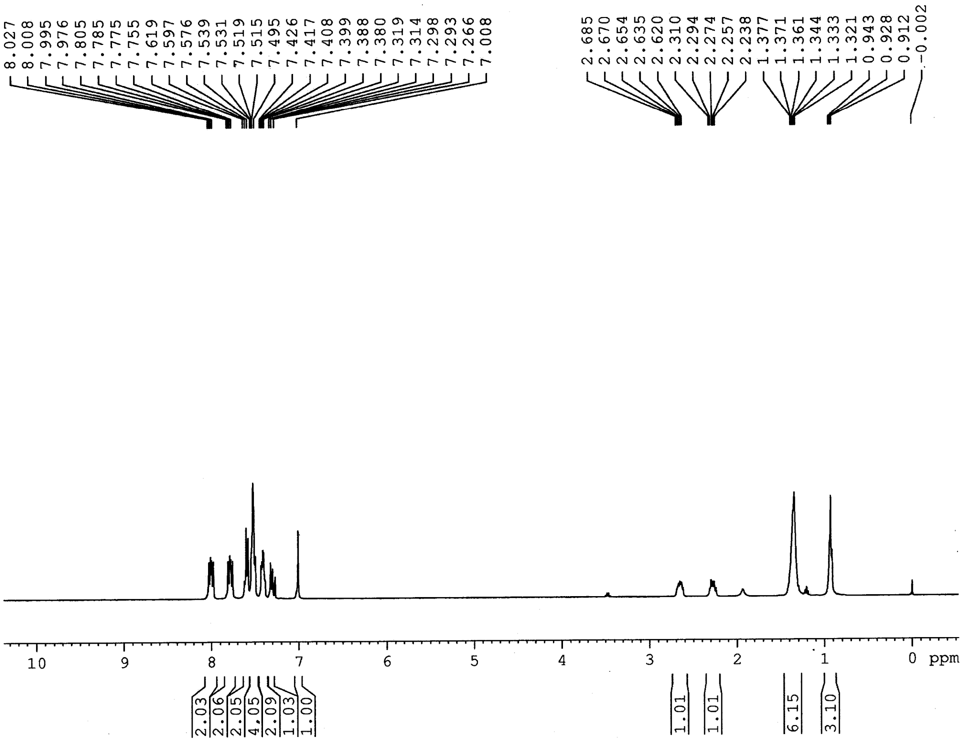


Figure A5. ^{1}H NMR spectrum of compound **48**

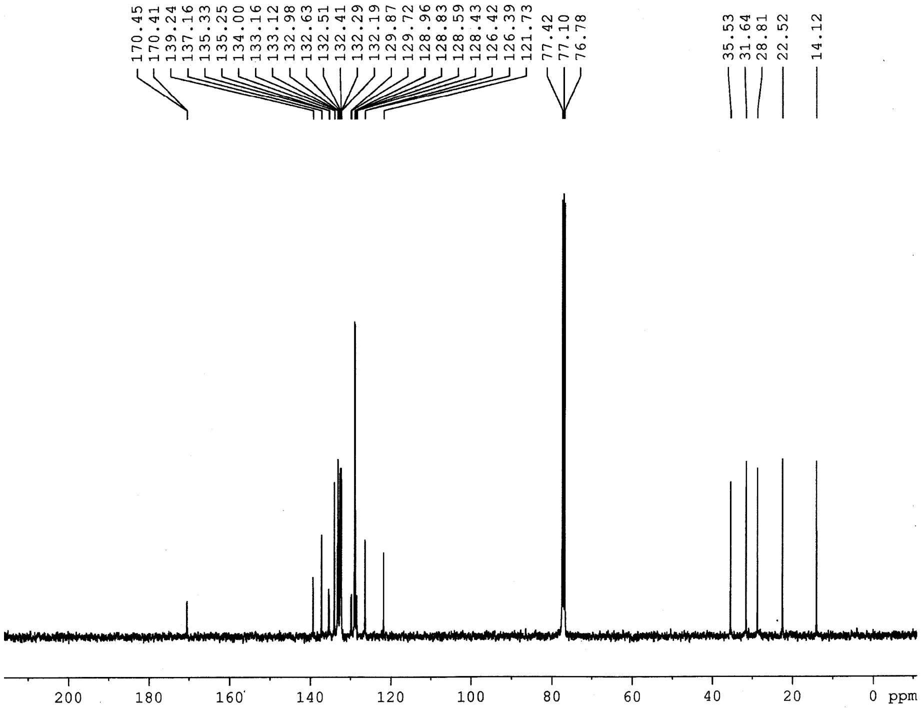


Figure A6. ^{13}C NMR spectrum of compound **48**

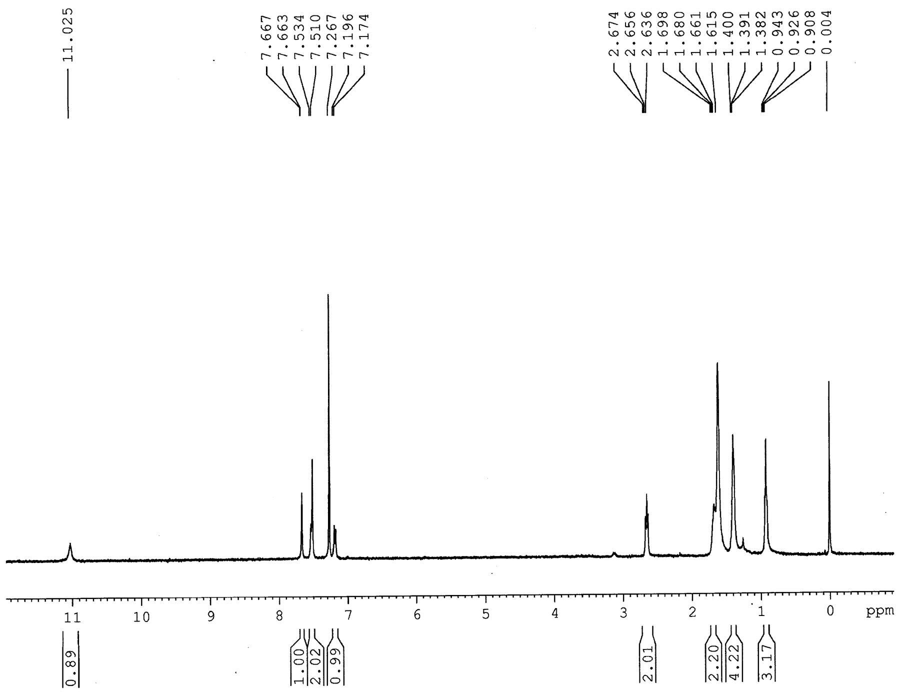


Figure A7. ^{1}H NMR spectrum of compound **52**

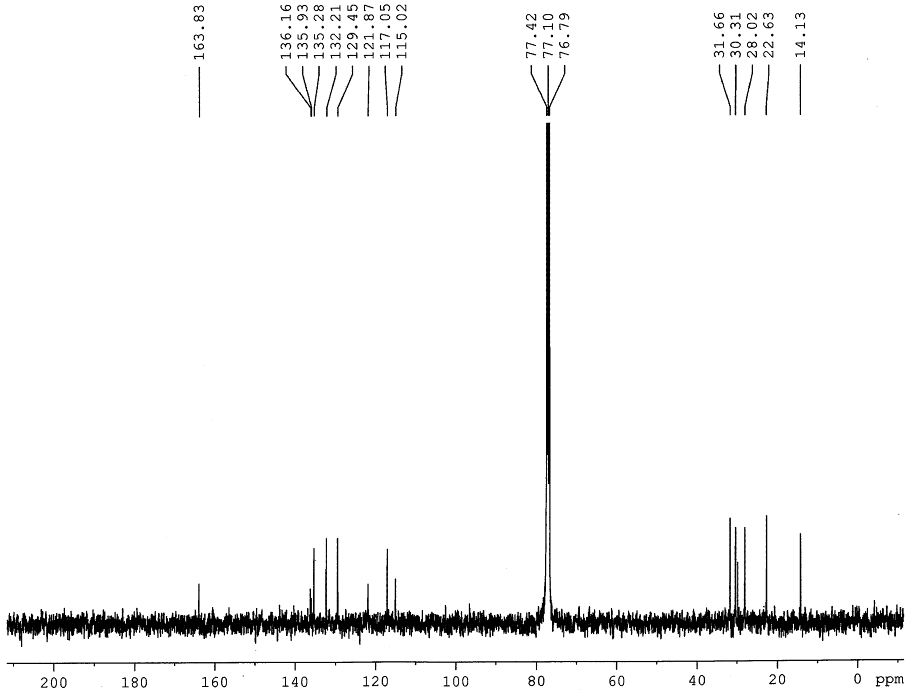


Figure A8. ^{13}C NMR spectrum of compound **52**

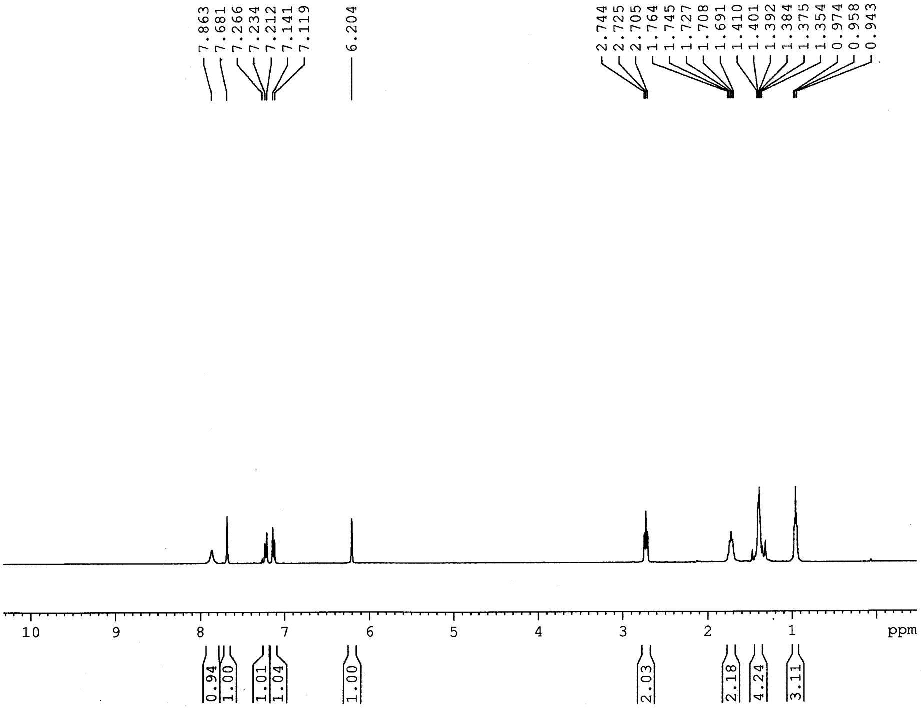


Figure A9. ^{1}H NMR spectrum of compound **54**

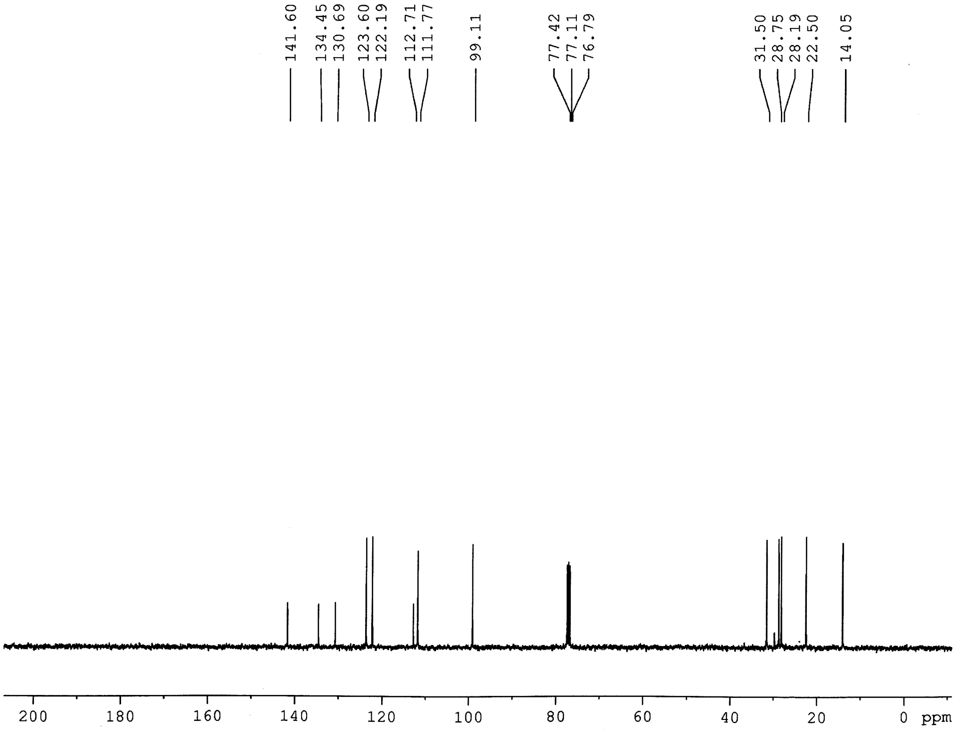


Figure A10. ^{13}C NMR spectrum of compound **54**

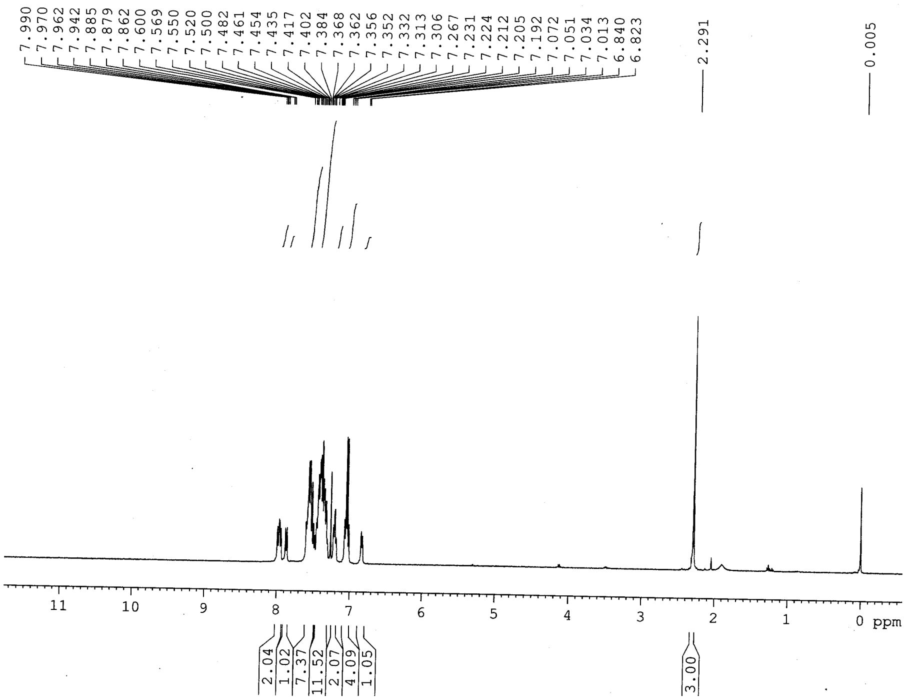


Figure A11. ^{1}H NMR spectrum of compound **63**

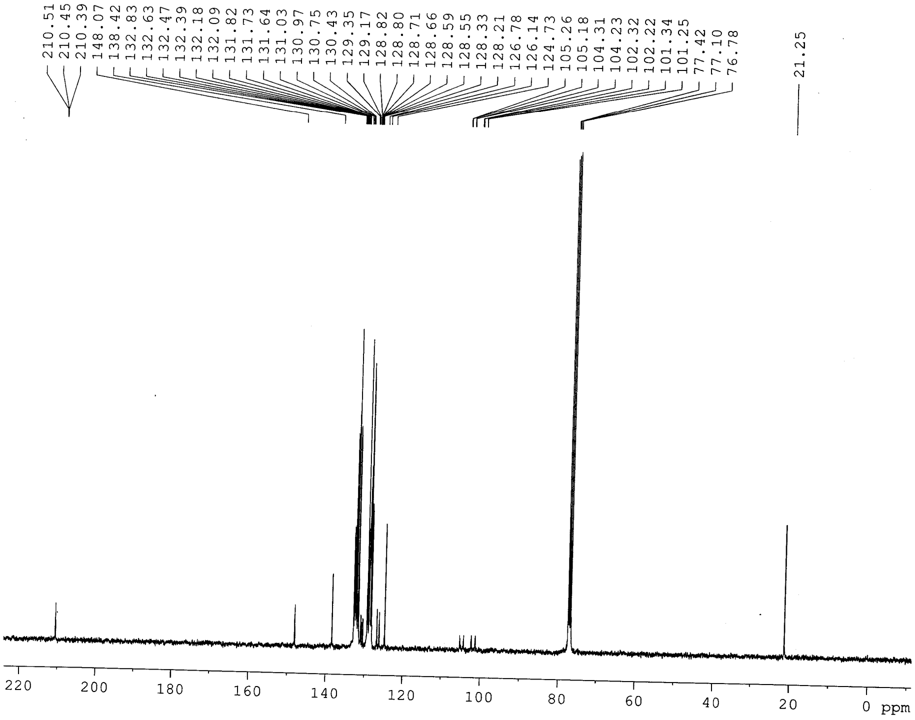


Figure A12. ^{13}C NMR spectrum of compound **63**

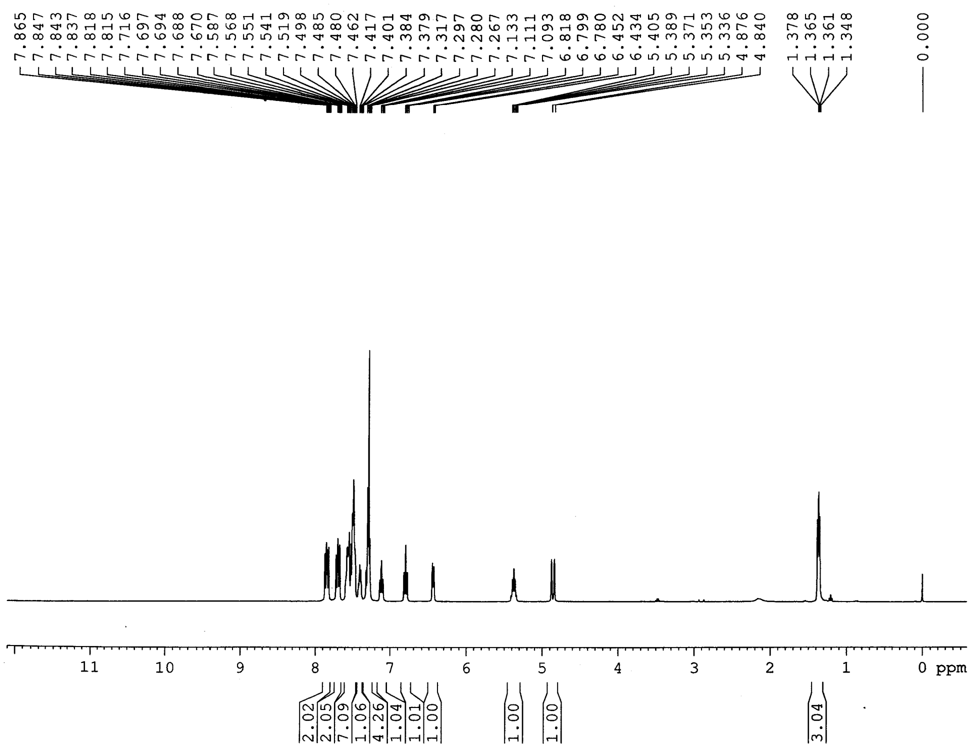


Figure A13. ^{1}H NMR spectrum of compound **75**

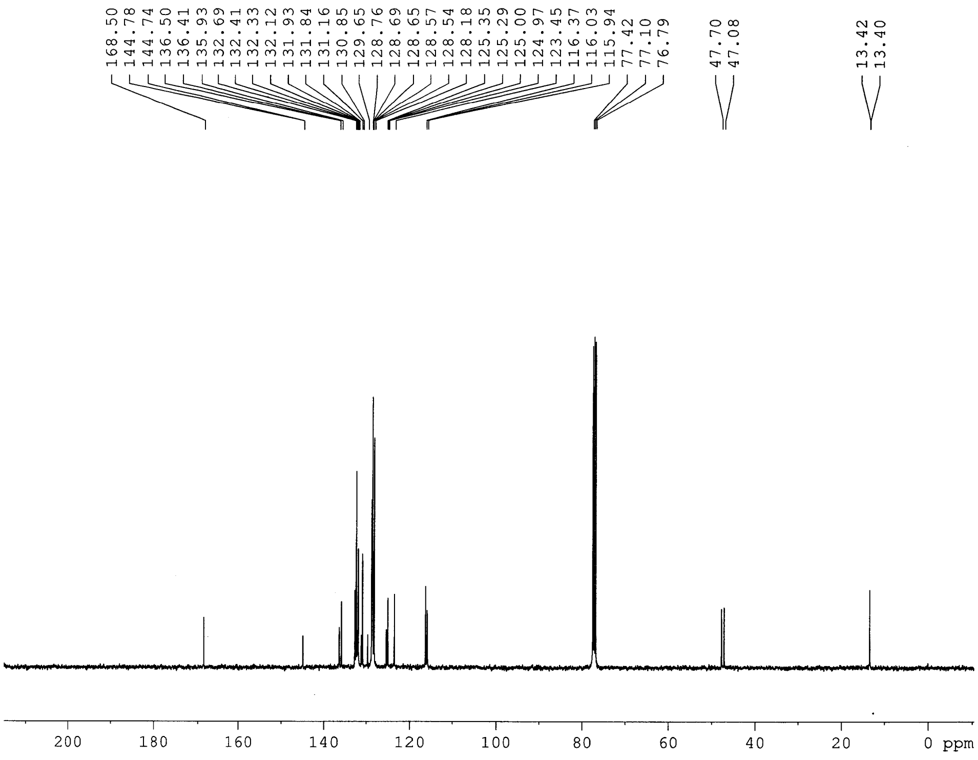


Figure A14. ^{13}C NMR spectrum of compound **75**

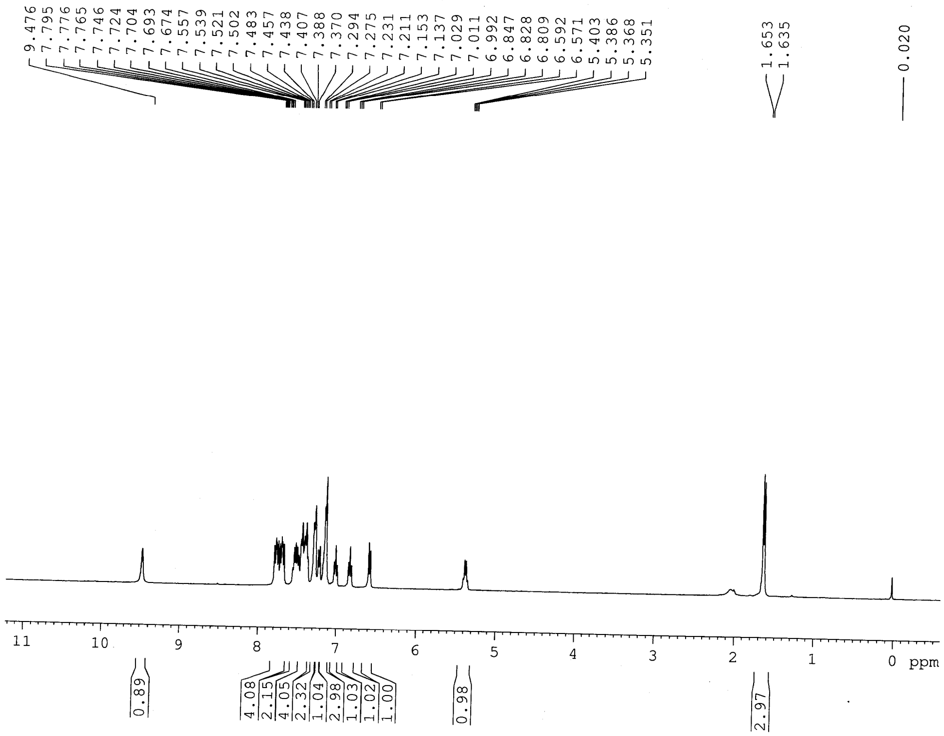


Figure A15. ^{1}H NMR spectrum of compound **79**

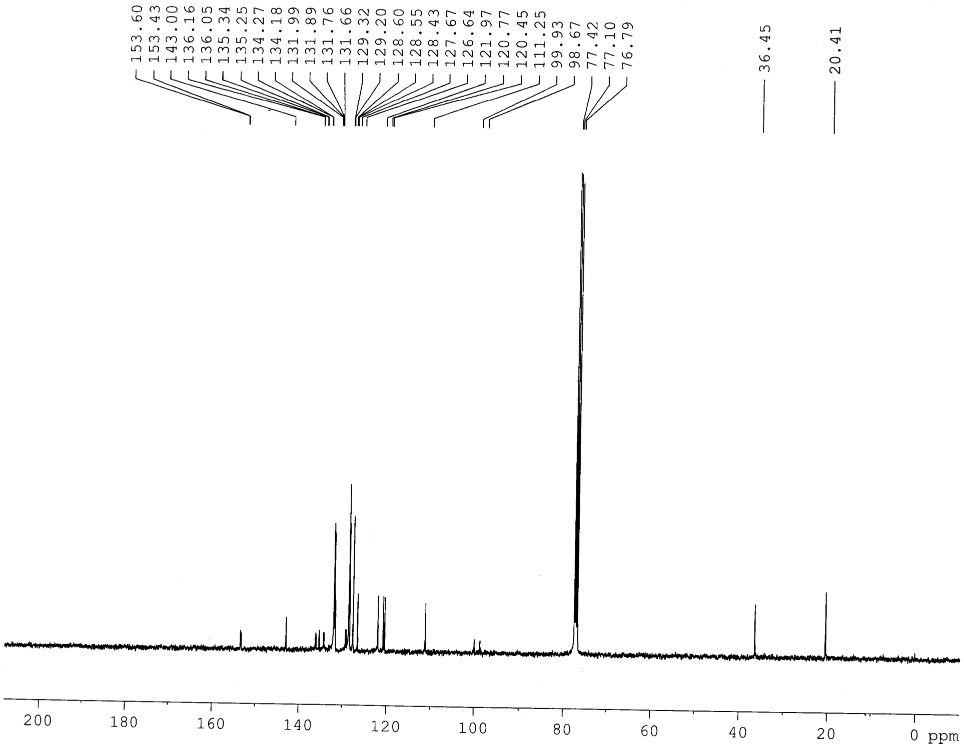


Figure A16. ^{13}C NMR spectrum of compound **79**

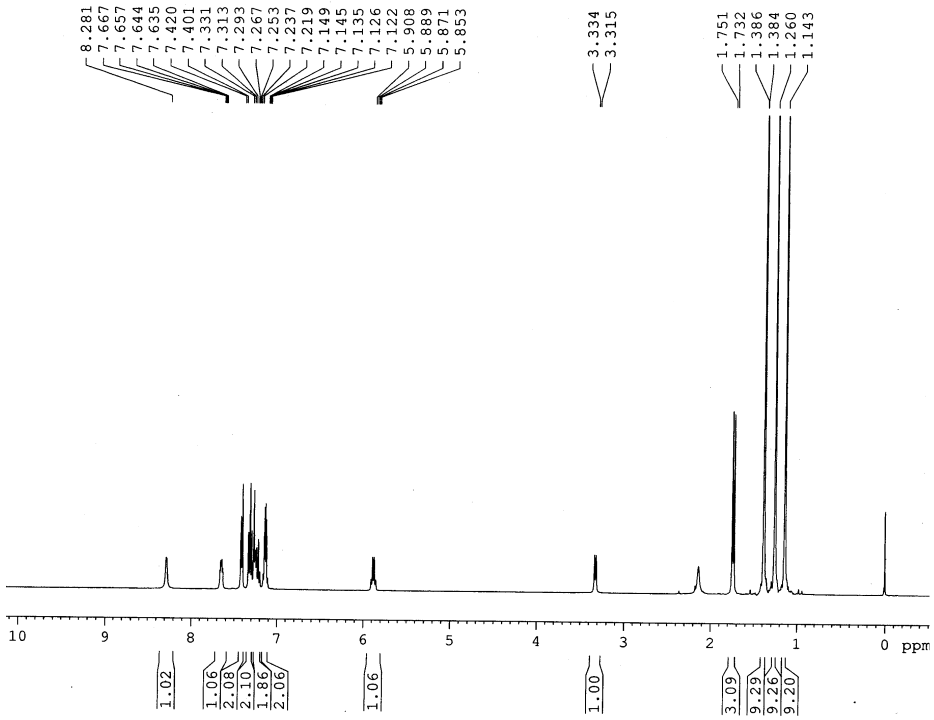


Figure A17. ^{1}H NMR spectrum of compound **89**

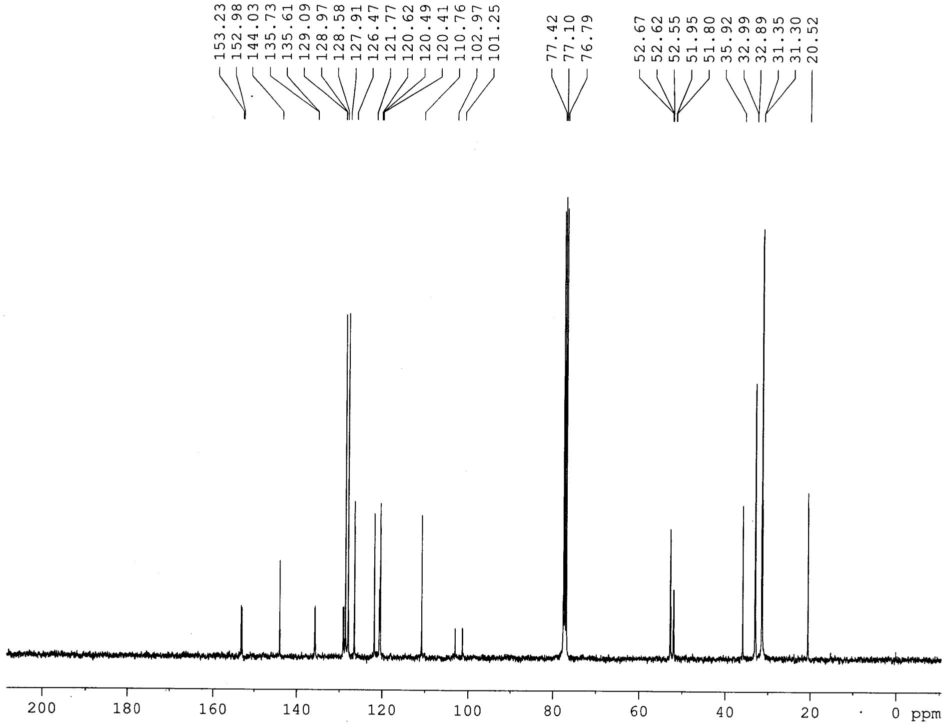


Figure A18. ^{13}C NMR spectrum of compound **89**

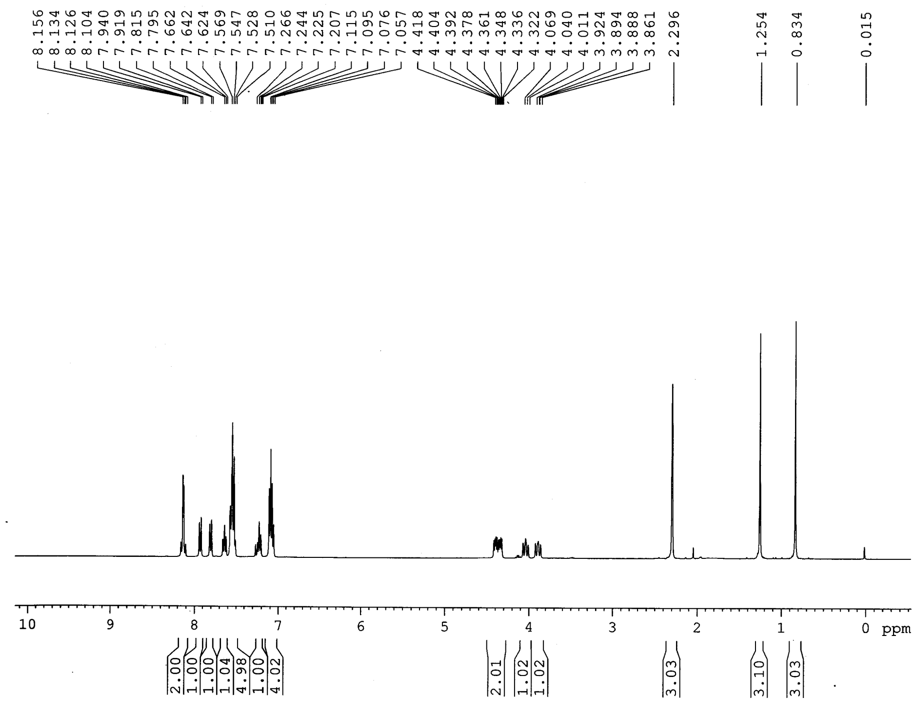


Figure A19. ^{1}H NMR spectrum of compound **95**

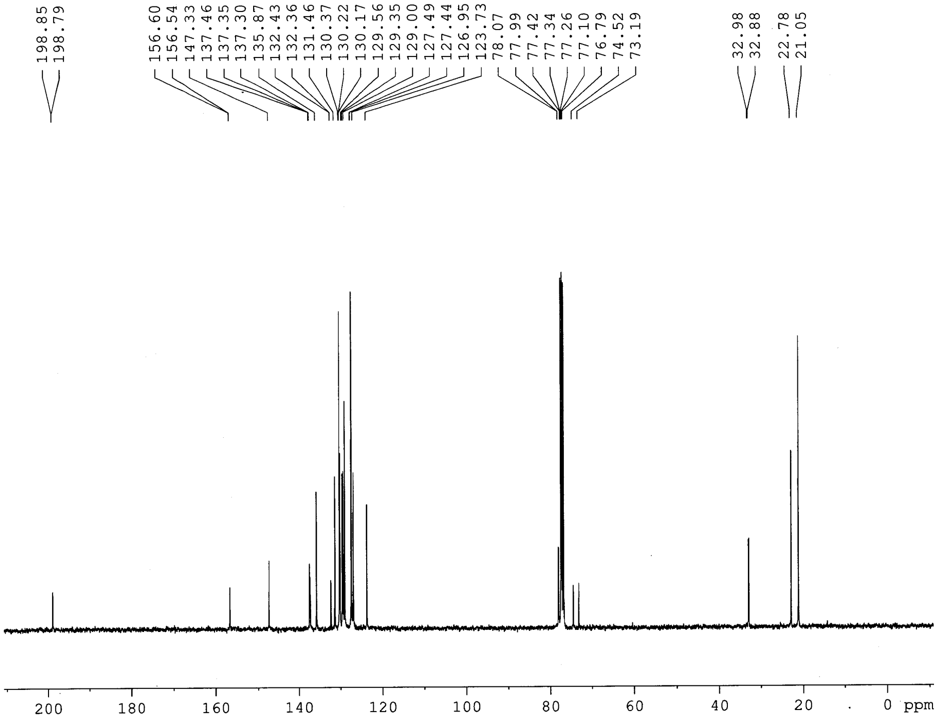


Figure A20. ^{13}C NMR spectrum of compound **95**

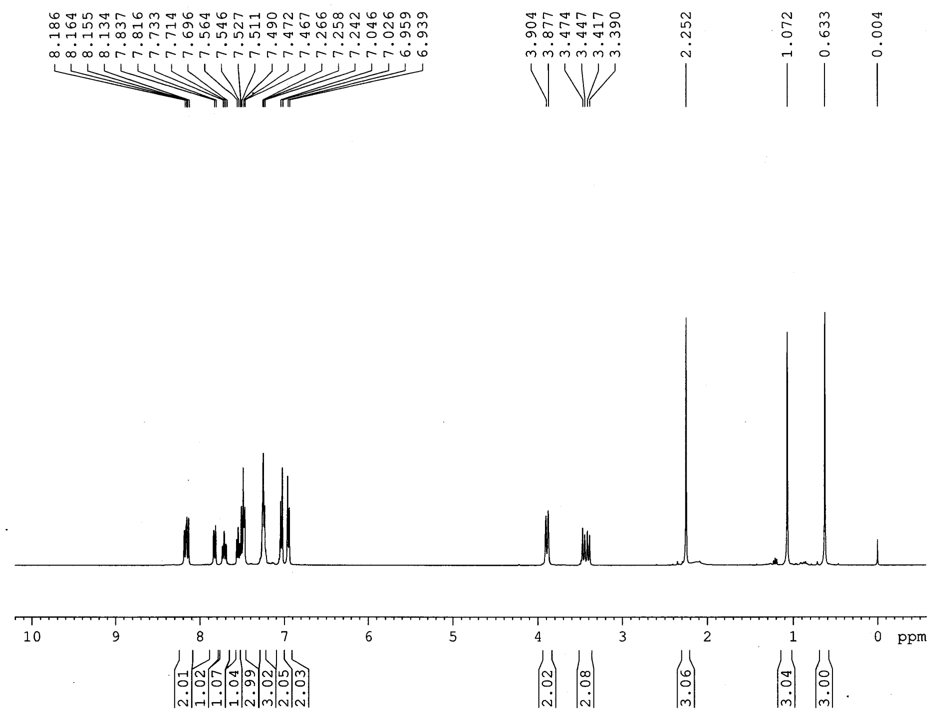


Figure A21. ^{1}H NMR spectrum of compound **96**

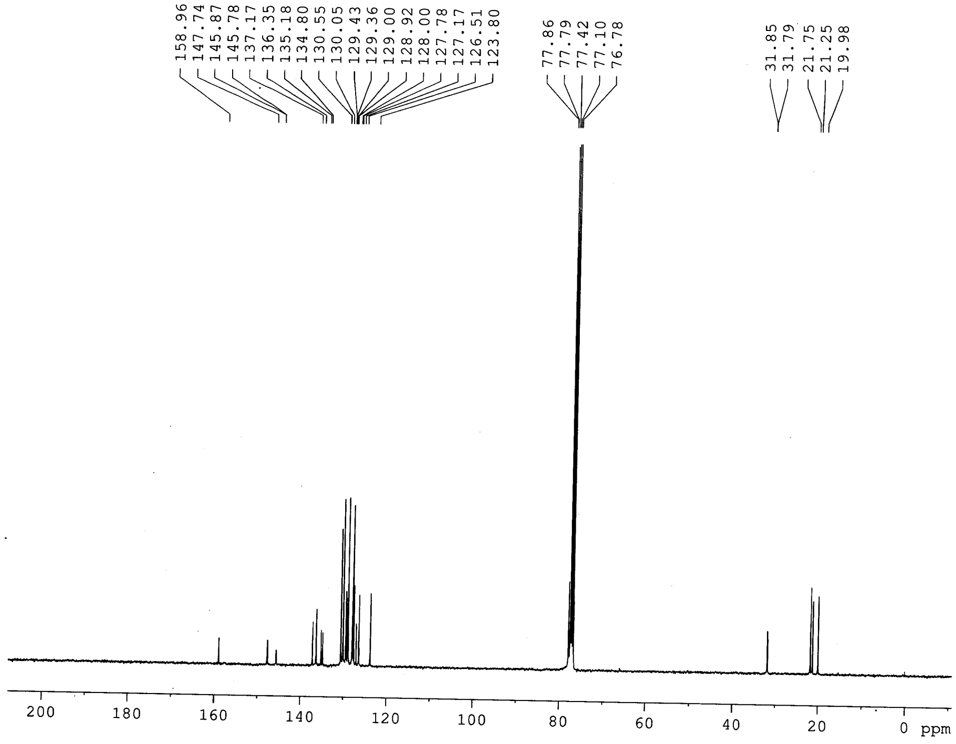


Figure A22. ^{13}C NMR spectrum of compound **96**

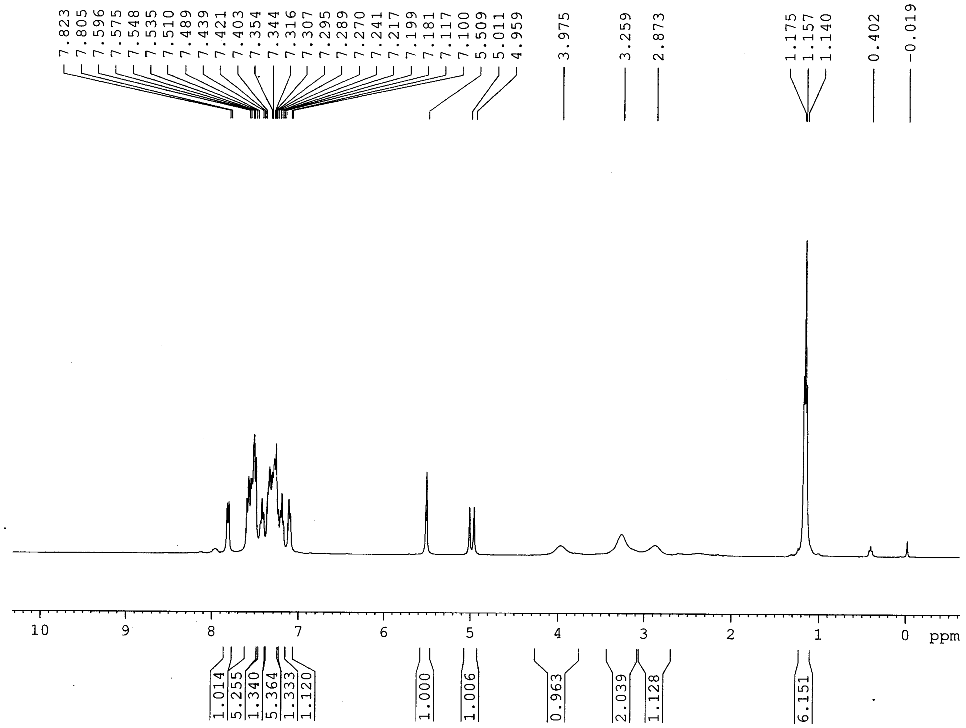


Figure A23. ^{1}H NMR spectrum of compound **115**

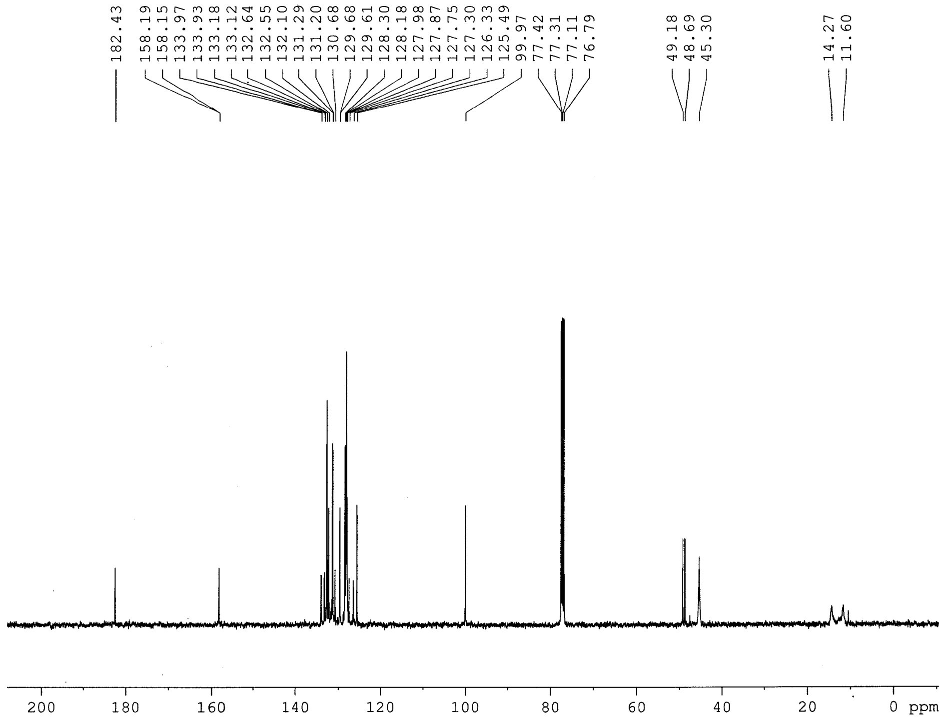


Figure A24. ^{13}C NMR spectrum of compound **115**

PART B: Compounds 11, 22, 23 and 42

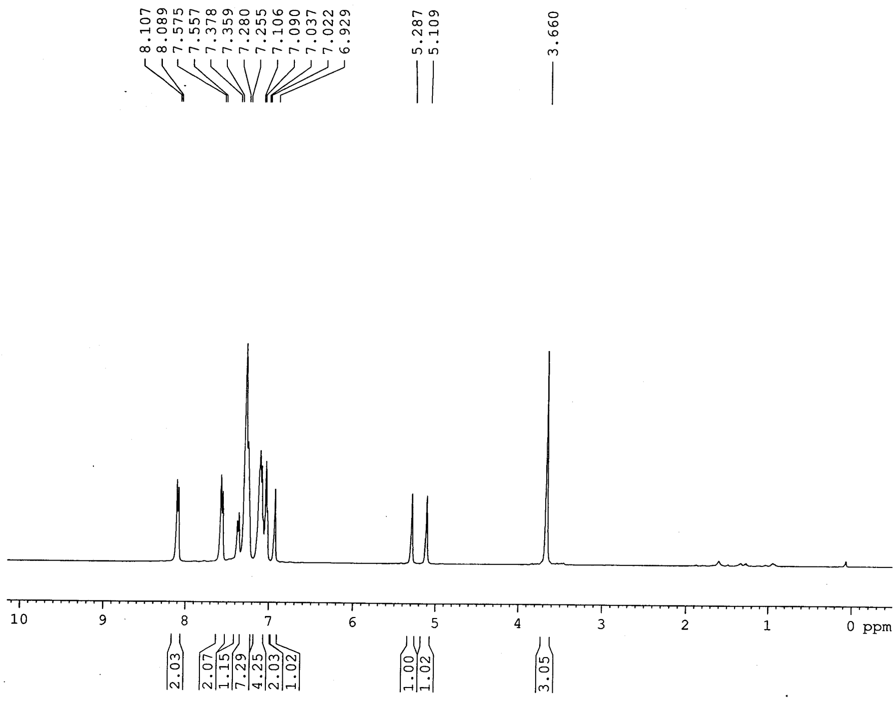


Figure A25. ^{1}H NMR spectrum of compound **11**

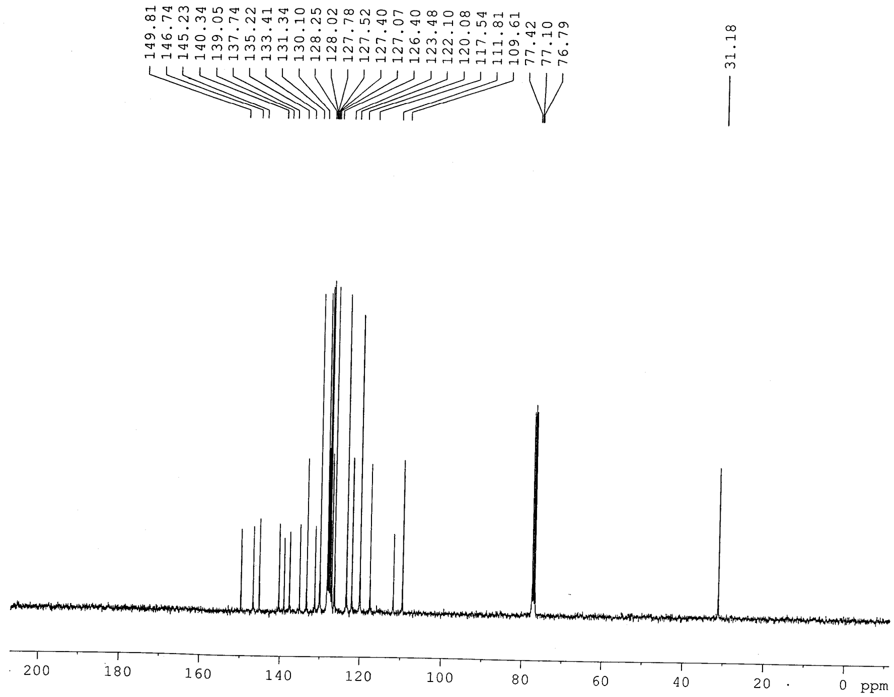


Figure A26. ^{13}C NMR spectrum of compound **11**

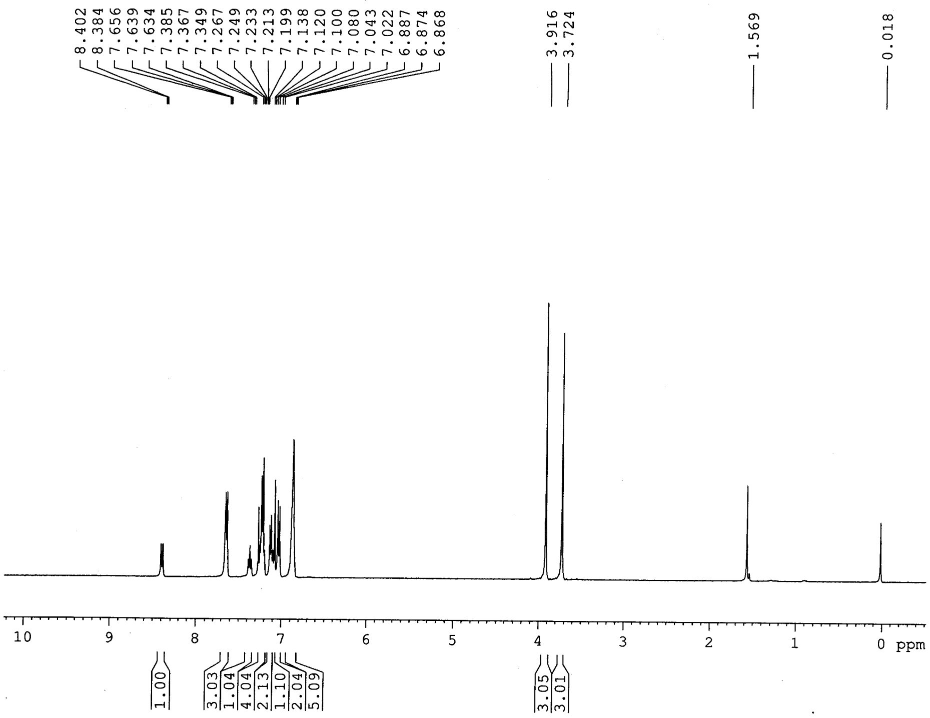


Figure A27. ^{1}H NMR spectrum of compound **22**

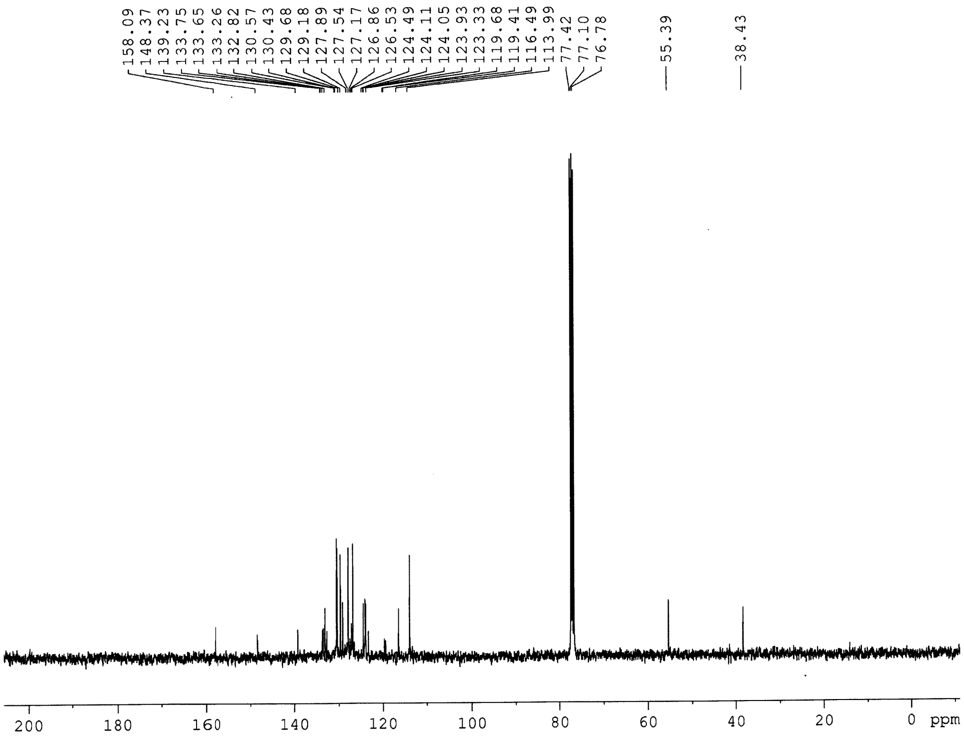


Figure A28. ^{13}C NMR spectrum of compound **22**

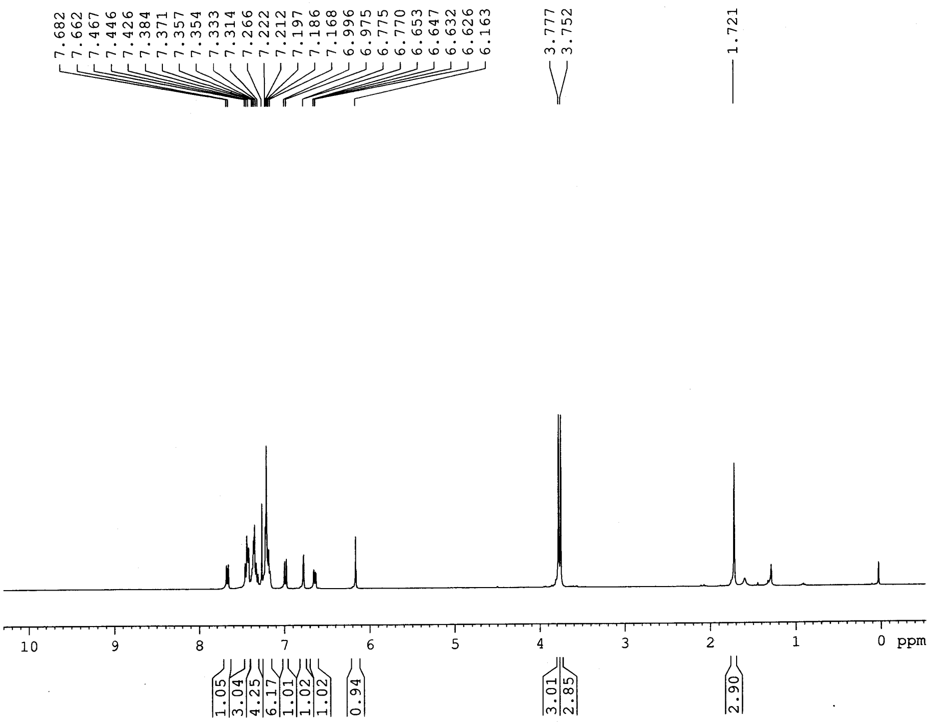


Figure A29. ^{1}H NMR spectrum of compound **23**

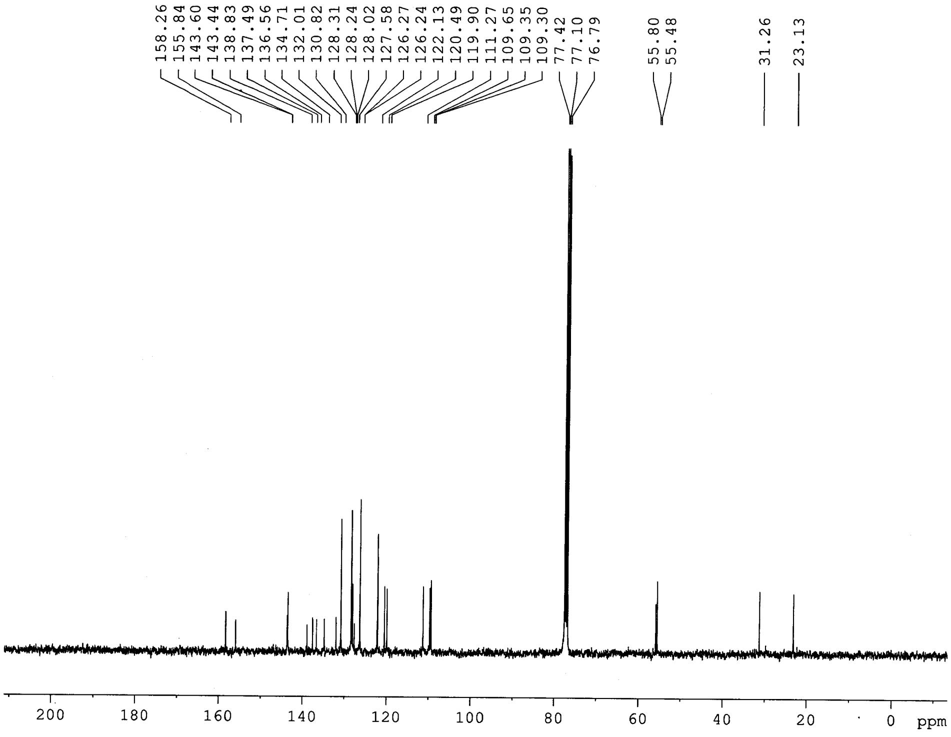


Figure A30. ^{13}C NMR spectrum of compound **23**

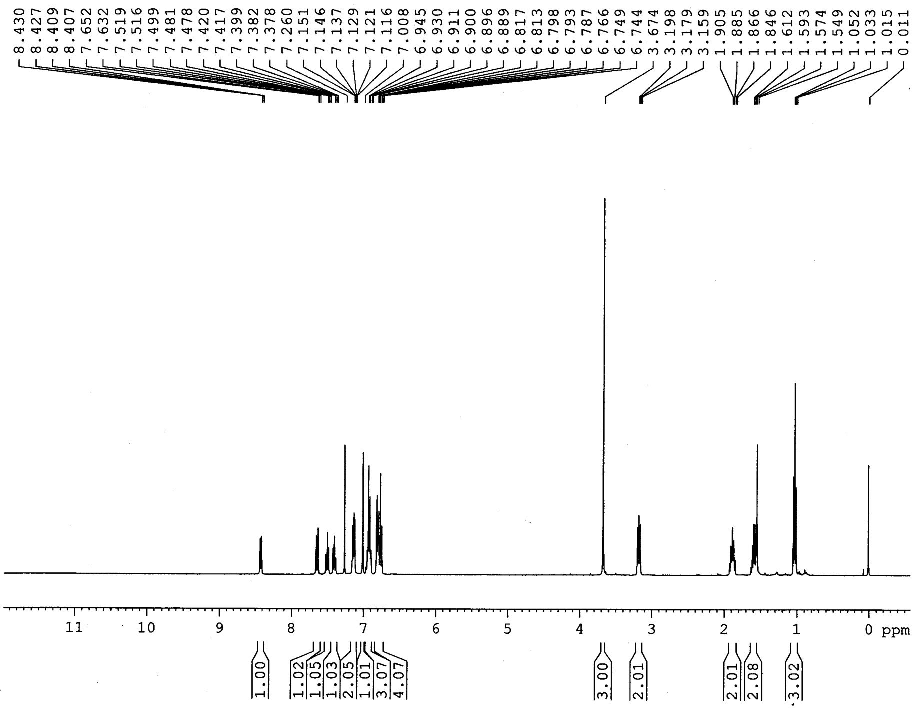


Figure A31. ^{1}H NMR spectrum of compound **42**

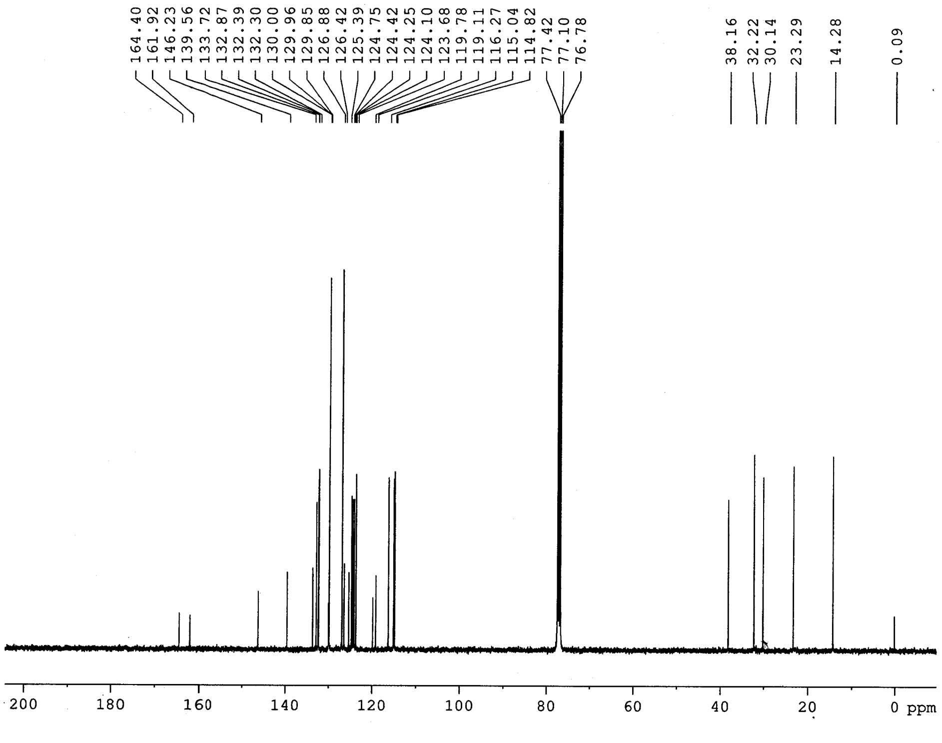


Figure A32. ^{13}C NMR spectrum of compound **42**

B) Publication numbers and atomic coordinates for X-ray structures reported in this thesis

I. Publication numbers for the published compounds

PART A: Compounds 24·1.5H_2O, 25, 27·$PhCH_3$, 28, 30·H_2O,
32·1/2H_2O, 35, 38, 47, 50 and *cis*-55 Publication no. 1
Compounds 75 and77 Publication no. 2
Compound 117 Publication no. 5
Compound 118 Publication no. 4
Compounds 119, 120 and122 Publication no. 3
(Contents, p. xi)

II. Selected atomic coordinates for compounds *cis*-56, *trans*-56·1/2CH_2Cl_2, *cis*-57, 59, 60, 63, 65·2$CHCl_3$, (*R*)-66, (*S*)-66, 67, 89, 93, 104, 107, 112·*n*-C_5H_{12} and 115 from PART A and for compounds, 8, 21 and 22 from PART B.

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for 4. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

PART A

Compound *cis*-56

Atom	x	y	z	U(eq)
P(1)	264(1)	9470(1)	1987(1)	44(1)
O(2)	-717(1)	6746(1)	1261(1)	56(1)
N(1)	641(1)	9476(1)	3310(1)	45(1)
O(1)	514(1)	10460(1)	1585(1)	61(1)
N(2)	390(1)	7956(1)	1652(1)	44(1)
C(5)	-77(1)	6794(2)	1430(2)	44(1)
O(3)	1619(1)	8354(2)	1984(1)	70(1)
C(12)	1101(1)	7604(2)	1773(2)	49(1)
C(6)	384(1)	5703(2)	1439(2)	46(1)
C(11)	1070(1)	6184(2)	1626(2)	48(1)
C(7)	209(2)	4389(2)	1309(2)	58(1)
C(10)	1618(1)	5360(2)	1683(2)	63(1)
C(8)	768(2)	3564(2)	1381(2)	71(1)
C(1)	1456(1)	9883(2)	4359(2)	59(1)
C(9)	1452(2)	4044(3)	1558(2)	73(1)
C(2)	2110(2)	9336(3)	4339(2)	90(1)
C(3)	1535(2)	9322(3)	5334(2)	80(1)
C(4)	1481(2)	11364(3)	4407(2)	97(1)

Compound *trans*-56

Atom	x	y	z	U(eq)

P(1)	4326(3)	40(2)	4499(1)	31(1)
O(1)	2556(7)	-851(7)	4146(3)	40(1)
O(2)	7928(10)	3289(9)	4846(3)	69(2)
O(3)	4435(9)	196(7)	3119(3)	49(2)
N(1)	4480(9)	903(7)	5193(3)	28(1)
N(2)	5734(9)	1470(8)	4092(3)	35(2)
C(1)	3555(11)	1909(10)	5475(4)	37(2)
C(2)	1829(15)	803(14)	5736(5)	63(3)
C(3)	4918(18)	3184(15)	5965(5)	76(4)
C(4)	3104(16)	2786(13)	4984(5)	60(3)
C(5)	7321(12)	2922(10)	4330(4)	39(2)
C(6)	7981(12)	3833(10)	3817(4)	36(2)
C(7)	6887(12)	2915(10)	3291(4)	35(2)
C(8)	5510(11)	1381(10)	3449(4)	36(2)
C(9)	9444(12)	5301(11)	3788(4)	44(2)
C(10)	9784(14)	5855(11)	3233(4)	49(2)
C(11)	8692(15)	4967(14)	2720(5)	65(3)
C(12)	7236(14)	3465(12)	2735(4)	53(3)
P(2)	1000(3)	265(3)	468(1)	36(1)
O(4)	1955(9)	-561(8)	768(3)	50(2)
O(5)	35(13)	3214(9)	273(3)	76(3)
O(6)	3100(12)	1812(9)	1755(3)	70(2)
N(3)	1259(10)	631(8)	-251(3)	37(2)
N(4)	1464(10)	2083(8)	903(3)	40(2)
C(13)	2920(14)	1377(13)	-582(5)	57(3)
C(15)	2573(19)	2529(16)	-970(6)	81(4)
C(14)	3171(19)	15(16)	-949(7)	82(4)
C(16)	4536(16)	2380(20)	-101(7)	98(5)
C(17)	951(13)	3329(10)	726(4)	42(2)
C(18)	1748(13)	4722(10)	1216(4)	40(2)
C(19)	2656(13)	4286(11)	1653(4)	45(2)
C(20)	2508(13)	2610(11)	1484(4)	43(2)
C(21)	1711(14)	6241(11)	1239(4)	50(2)
C(22)	2611(14)	7344(12)	1752(4)	51(2)
C(23)	3526(15)	6889(12)	2209(5)	54(3)
C(24)	3579(16)	5363(12)	2157(5)	57(3)
C(25)	773(17)	407(18)	2939(6)	82(4)
Cl(1)	1516(7)	2444(5)	3306(2)	108(1)
Cl(2)	-1456(6)	-366(8)	2623(2)	132(2)

Compound *cis*-57

Atom	x	y	z	U(eq)
P(1)	3163(1)	3694(1)	5581(1)	35(1)
P(2)	1927(1)	4832(1)	5516(1)	37(1)
N(4)	3694(2)	3658(3)	6838(2)	38(1)
N(1)	2310(2)	3314(3)	5852(2)	38(1)
N(2)	2866(2)	5176(3)	5378(2)	35(1)
O(1)	3586(2)	3035(3)	4687(2)	55(1)
N(3)	1681(2)	5501(4)	6741(3)	48(1)
O(2)	3081(2)	5181(3)	7939(3)	65(1)
C(13)	3612(2)	4510(4)	7787(3)	42(1)
C(5)	3225(2)	6270(4)	4764(3)	44(1)
C(1)	1959(2)	2092(4)	6250(3)	44(1)
C(14)	4274(2)	4401(4)	8553(4)	52(1)
O(3)	4463(2)	1919(4)	6446(3)	96(1)
C(9)	987(2)	6167(5)	7034(4)	57(1)
C(16)	4312(2)	2847(5)	7025(4)	55(1)
C(7)	3146(3)	6108(5)	3471(4)	75(2)
C(6)	4040(3)	6273(5)	5090(5)	85(2)
C(8)	2858(3)	7513(4)	5150(5)	85(2)
C(15)	4716(2)	3312(5)	8062(4)	66(1)
C(2)	1918(3)	2092(5)	7554(4)	79(2)
C(4)	1197(3)	2003(5)	5707(5)	75(2)
C(3)	2417(3)	953(4)	5826(5)	75(2)
C(10A)	432(8)	6040(20)	6134(16)	98(6)

C(11A)	961(12)	6480(30)	8250(17)	148(12)
C(12A)	1156(9)	7557(16)	7290(20)	111(7)
C(10B)	333(9)	5270(30)	6810(30)	165(11)
C(11B)	755(12)	5520(20)	8183(19)	127(9)
C(12B)	904(17)	7350(30)	6300(30)	260(20)

Compound 59

Atom	x	y	z	U(eq)
P(1)	4477(1)	10818(1)	8931(1)	33(1)
P(2)	1283(1)	8788(1)	9033(1)	36(1)
C(28)	2492(2)	8150(2)	8680(2)	36(1)
C(21)	1475(2)	9761(2)	8483(1)	32(1)
C(19)	3647(2)	10241(2)	8216(1)	32(1)
C(1)	5040(2)	10069(2)	9602(2)	38(1)
O(1)	5415(2)	11325(1)	8582(1)	47(1)
C(20)	2534(2)	10029(2)	8348(1)	32(1)
C(29)	2890(3)	8138(2)	7932(2)	45(1)
C(33)	3043(3)	7637(2)	9216(2)	53(1)
C(22)	-62(2)	8333(2)	8616(2)	37(1)
N(1)	-198(3)	9585(2)	7159(2)	58(1)
C(35)	-416(3)	10180(2)	7771(2)	44(1)
C(18)	3693(3)	10179(2)	6794(2)	57(1)
O(2)	821(2)	9438(2)	6982(1)	79(1)
C(34)	401(2)	10278(2)	8363(2)	35(1)
C(7)	3395(2)	11438(2)	9427(2)	37(1)
C(4)	5948(4)	8974(2)	10664(2)	62(1)
C(23)	-1139(3)	8580(2)	8927(2)	51(1)
C(13)	4247(2)	10029(2)	7484(2)	39(1)
C(30)	3796(3)	7628(2)	7718(2)	55(1)
C(39)	130(3)	10861(2)	8916(2)	45(1)
C(36)	-1468(3)	10623(2)	7746(2)	59(1)
C(12)	3092(3)	11325(2)	10188(2)	51(1)
C(26)	-1120(3)	7386(2)	7811(2)	64(1)
C(24)	-2193(3)	8238(3)	8674(2)	64(1)
C(10)	1738(3)	12461(3)	10112(3)	71(1)
C(8)	2872(3)	12084(2)	9028(2)	54(1)
C(38)	-895(3)	11326(2)	8888(2)	64(1)
C(3)	6647(3)	9558(3)	10354(2)	66(1)
C(5)	4781(4)	8921(2)	10459(2)	73(1)
C(37)	-1690(3)	11200(3)	8309(2)	67(1)
C(14)	5355(3)	9655(3)	7488(2)	64(1)
C(31)	4312(3)	7099(2)	8237(3)	66(1)
C(25)	-2181(3)	7637(3)	8122(2)	70(1)
C(17)	4245(5)	9953(3)	6118(2)	87(2)
O(3)	-1051(3)	9265(2)	6852(2)	89(1)
C(27)	-67(3)	7732(2)	8053(2)	48(1)
C(2)	6216(3)	10122(2)	9820(2)	53(1)
C(32)	3951(3)	7108(2)	8976(3)	69(1)
C(9)	2053(4)	12588(2)	9375(3)	72(1)
C(6)	4330(3)	9463(2)	9917(2)	59(1)
C(11)	2253(4)	11837(2)	10522(2)	70(1)
C(16)	5324(4)	9585(4)	6135(3)	101(2)
C(15)	5877(3)	9445(3)	6805(3)	89(2)

Compound 60

Atom	x	y	z	U(eq)
P(1)	473(1)	10793(1)	8972(1)	34(1)
P(2)	3651(1)	8755(1)	8968(1)	36(1)
C(19)	1280(4)	10215(3)	8253(2)	32(1)

O(1)	-470(3)	11299(2)	8625(1)	45(1)
O(2)	3709(3)	8868(2)	9796(1)	55(1)
C(22)	2429(4)	8133(3)	8655(2)	34(1)
C(20)	2400(4)	10015(3)	8367(2)	30(1)
C(35)	5354(4)	10187(3)	7782(2)	45(1)
C(21)	3475(4)	9748(3)	8476(2)	32(1)
C(23)	2071(4)	8088(3)	7911(2)	42(1)
C(1)	-83(4)	10045(3)	9641(2)	36(1)
C(7)	1582(3)	11424(3)	9437(2)	36(1)
C(14)	1201(5)	10134(3)	6849(2)	58(1)
C(34)	4557(4)	10268(3)	8358(2)	37(1)
C(13)	650(4)	9987(3)	7544(2)	36(1)
C(28)	5004(4)	8300(3)	8597(2)	37(1)
C(33)	5032(4)	7747(3)	8003(2)	49(1)
C(39)	4844(4)	10829(3)	8920(3)	52(1)
C(27)	1842(4)	7649(3)	9189(3)	53(1)
C(29)	6067(4)	8511(3)	8943(3)	52(1)
C(4)	-1001(5)	8941(3)	10686(3)	66(2)
C(36)	6401(4)	10631(3)	7750(3)	62(2)
C(12)	1920(4)	11324(3)	10182(2)	53(1)
C(2)	656(4)	9466(3)	9987(2)	53(1)
C(26)	903(4)	7136(3)	8961(4)	69(2)
N(1)	5120(5)	9604(3)	7155(2)	72(2)
C(30)	7118(4)	8180(4)	8709(3)	65(2)
C(6)	-1276(4)	10073(3)	9824(2)	50(1)
C(8)	2069(4)	12068(3)	9031(3)	57(1)
C(3)	188(5)	8917(3)	10505(2)	62(2)
C(32)	6107(5)	7406(3)	7772(3)	65(2)
C(18)	-437(4)	9600(3)	7569(2)	60(1)
C(17)	-993(5)	9356(4)	6912(3)	85(2)
C(24)	1141(5)	7580(3)	7699(3)	58(1)
O(4)	4089(4)	9454(3)	6981(2)	99(2)
C(9)	2898(5)	12597(4)	9342(3)	76(2)
C(16)	-458(6)	9490(4)	6234(3)	89(2)
O(3)	5955(4)	9302(3)	6804(2)	108(2)
C(37)	6660(4)	11175(4)	8307(3)	70(2)
C(31)	7138(5)	7631(4)	8127(3)	75(2)
C(25)	592(5)	7104(3)	8216(3)	66(2)
C(38)	5876(5)	11288(4)	8887(3)	71(2)
C(10)	3239(5)	12477(4)	10071(4)	73(2)
C(5)	-1736(5)	9508(4)	10345(3)	64(2)
C(15)	610(6)	9870(4)	6199(3)	73(2)
C(11)	2743(5)	11856(4)	10495(3)	74(2)

Compound 63

Atom	x	y	z	U(eq)
P(1)	655(1)	4180(1)	8977(1)	43(1)
P(2)	3788(1)	6237(1)	8929(1)	46(1)
O(1)	-295(3)	3659(2)	8655(2)	57(1)
C(21)	2563(6)	4976(4)	8349(3)	45(2)
O(2)	3896(4)	6078(2)	9724(2)	62(1)
C(23)	5115(5)	6726(4)	8561(3)	44(2)
C(13)	783(5)	4998(3)	7596(4)	45(2)
C(22)	3629(5)	5256(3)	8414(3)	39(2)
C(1)	1779(5)	3588(3)	9447(4)	46(2)
C(20)	1430(5)	4757(3)	8266(3)	40(2)
C(7)	102(5)	4936(3)	9607(3)	44(2)
C(29)	2539(5)	6859(4)	8677(4)	48(2)
C(35)	4732(5)	4789(4)	8233(4)	45(2)
C(12)	-1078(6)	4974(4)	9757(4)	57(2)
C(14)	1276(6)	4842(4)	6903(3)	59(2)
C(19)	-292(6)	5394(4)	7649(4)	60(2)
O(3)	4093(5)	5660(4)	6973(3)	96(2)
C(34)	2101(6)	6908(4)	7979(4)	59(2)
C(40)	5454(6)	4904(4)	7634(4)	56(2)

C(30)	2015(6)	7330(4)	9226(5)	65(2)
C(33)	1168(7)	7421(4)	7807(5)	73(2)
C(16)	-369(7)	5533(5)	6331(4)	67(2)
C(8)	851(6)	5482(4)	9969(4)	63(2)
C(10)	-759(8)	6082(4)	10599(5)	79(2)
C(2)	1921(7)	3610(4)	10189(4)	70(2)
C(15)	693(7)	5113(4)	6291(4)	67(2)
C(6)	2421(6)	3021(4)	9050(5)	77(2)
C(31)	1073(7)	7850(5)	9060(6)	92(3)
C(24)	6185(6)	6520(4)	8879(4)	62(2)
C(36)	5115(6)	4226(4)	8747(4)	60(2)
C(39)	6519(6)	4496(5)	7546(5)	68(2)
C(9)	427(8)	6052(4)	10462(4)	74(2)
N(1)	5147(7)	5487(4)	7058(4)	76(2)
C(11)	-1525(7)	5563(5)	10252(4)	75(2)
C(37)	6189(8)	3804(5)	8652(5)	89(3)
C(18)	-850(6)	5672(4)	7009(4)	71(2)
C(28)	5085(6)	7318(4)	8014(4)	59(2)
C(27)	6125(8)	7682(4)	7782(5)	78(2)
C(26)	7185(7)	7466(5)	8088(5)	83(3)
C(25)	7227(7)	6874(5)	8643(5)	79(2)
O(4)	5916(6)	5793(4)	6674(4)	120(2)
C(17)	-958(8)	5862(5)	5651(5)	121(3)
C(5)	3251(9)	2514(5)	9393(6)	102(3)
C(4)	3422(8)	2567(5)	10122(7)	98(4)
C(38)	6908(8)	3950(5)	8066(6)	93(3)
C(3)	2787(8)	3106(5)	10517(5)	91(3)
C(32)	662(7)	7898(5)	8360(7)	91(3)

Compound 65

Atom	x	y	z	U(eq)
P(1)	4261(1)	1701(1)	6788(1)	35(1)
Br(1)	4276(1)	6235(1)	9264(1)	57(1)
P(2)	2869(1)	2060(1)	10181(1)	27(1)
N(1)	148(4)	3649(4)	9078(4)	43(1)
Cl(2)	1368(5)	3950(3)	6479(2)	179(2)
Cl(6)	7440(3)	2712(4)	4905(3)	187(2)
C(35)	2276(4)	3767(3)	9134(3)	26(1)
Cl(5)	6641(4)	2198(6)	3405(4)	285(4)
O(3)	6(3)	2890(3)	9584(3)	52(1)
C(24)	1707(4)	409(4)	9758(4)	37(1)
O(4)	-556(4)	3958(4)	8629(4)	79(2)
C(36)	1211(4)	4233(4)	9024(4)	35(1)
Cl(3)	751(6)	2629(4)	5161(4)	217(2)
C(23)	2631(4)	751(4)	10099(3)	28(1)
C(22)	2503(4)	2669(3)	9135(3)	25(1)
C(19)	2021(6)	492(5)	6621(4)	51(2)
C(21)	2635(4)	2171(4)	8372(3)	30(1)
C(13)	1794(5)	1175(4)	7338(3)	34(1)
C(39)	3041(4)	5411(4)	9132(4)	35(1)
C(1)	4915(4)	471(4)	6872(4)	37(1)
C(40)	3198(4)	4379(4)	9190(3)	32(1)
C(28)	3438(5)	74(4)	10352(4)	37(1)
C(27)	3354(5)	-937(4)	10265(4)	48(2)
C(34)	2051(6)	3335(5)	11606(4)	51(2)
C(3)	5269(6)	-1026(5)	7753(4)	51(2)
C(14)	619(5)	1365(5)	7782(5)	55(2)
C(29)	1769(4)	2526(4)	11180(3)	32(1)
C(2)	4727(6)	-100(4)	7711(4)	46(1)
C(12)	4940(6)	3562(5)	7045(5)	56(2)
C(20)	2776(4)	1677(4)	7605(3)	31(1)
C(37)	1080(5)	5260(4)	8920(4)	43(1)
C(6)	5637(5)	78(5)	6059(4)	46(1)
C(4)	5997(6)	-1405(5)	6929(5)	57(2)
C(26)	2429(5)	-1267(4)	9930(5)	54(2)

C(38)	2013(5)	5855(4)	8965(4)	46(1)
C(32)	191(7)	3258(6)	12755(4)	65(2)
C(33)	1254(7)	3702(6)	12392(5)	69(2)
C(30)	688(5)	2076(5)	11554(4)	55(2)
C(8)	6017(6)	2252(5)	7665(5)	64(2)
C(7)	5135(5)	2558(4)	7213(4)	40(1)
C(5)	6179(6)	-860(5)	6100(5)	55(2)
C(15)	-306(6)	895(6)	7547(5)	66(2)
C(31)	-97(6)	2450(6)	12337(5)	70(2)
C(17)	-1093(8)	-204(7)	6524(7)	94(3)
C(25)	1615(5)	-612(4)	9683(5)	54(2)
C(18)	1091(6)	58(5)	6376(5)	61(2)
C(42)	6305(8)	2914(8)	4341(7)	100(3)
C(10)	6508(7)	3953(6)	7757(6)	76(2)
C(16)	-76(6)	253(5)	6811(5)	60(2)
C(41)	1855(10)	3253(8)	5489(7)	112(3)
C(9)	6696(8)	2954(7)	7929(6)	86(3)
Cl(4)	6218(7)	4058(5)	4039(8)	376(6)
C(11)	5637(8)	4257(5)	7312(6)	73(2)
Cl(1)	2574(6)	3944(5)	4538(3)	224(2)
O(2)	4103(3)	2281(3)	10226(2)	36(1)
O(1)	4164(4)	2007(3)	5816(3)	47(1)

Compound (*R*)-66

Atom	x	y	z	U(eq)
P(1)	2966(1)	1470(1)	8285(1)	33(1)
P(2)	6103(1)	1492(1)	6229(1)	35(1)
C(19)	3761(3)	764(2)	7685(2)	32(1)
O(1)	2024(2)	1120(2)	8785(2)	44(1)
C(22)	4880(3)	1183(2)	5605(2)	37(1)
O(2)	6175(2)	2317(2)	6330(2)	53(1)
C(23)	4556(3)	436(2)	5532(2)	44(1)
C(20)	4862(3)	881(2)	7480(2)	34(1)
C(13)	3133(3)	61(2)	7448(2)	37(1)
C(21)	5929(3)	1001(2)	7214(2)	34(1)
C(39)	7759(3)	264(3)	7659(3)	50(1)
N(1)	7514(4)	-366(3)	7073(3)	67(1)
C(7)	4061(3)	1933(2)	8922(2)	37(1)
C(34)	6997(3)	877(2)	7724(2)	38(1)
C(1)	2421(3)	2149(2)	7557(2)	39(1)
C(28)	7452(3)	1111(2)	5782(3)	44(1)
C(18)	3590(4)	-620(2)	7571(3)	48(1)
C(35)	7311(3)	1449(3)	8261(3)	57(1)
C(6)	1217(4)	2300(3)	7558(3)	57(1)
C(24)	3648(4)	220(3)	5019(2)	56(1)
C(4)	1466(6)	3164(3)	6450(3)	77(2)
C(33)	7490(4)	528(3)	5233(3)	55(1)
O(3)	6510(3)	-488(2)	6889(3)	98(2)
C(14)	1985(3)	150(2)	7021(3)	54(1)
C(12)	4626(4)	1499(3)	9511(3)	61(1)
C(2)	3132(4)	2515(3)	6995(3)	55(1)
C(29)	8499(3)	1471(3)	6005(3)	60(1)
C(25)	3045(4)	757(3)	4582(3)	65(1)
C(8)	4278(4)	2685(3)	8885(3)	56(1)
C(26)	3334(4)	1512(4)	4668(3)	72(2)
C(27)	4250(3)	1724(3)	5166(2)	50(1)
C(5)	748(4)	2804(3)	6986(4)	75(2)
C(38)	8828(4)	246(3)	8089(3)	68(1)
O(4)	8331(4)	-737(3)	6804(3)	108(2)
C(3)	2690(5)	3033(3)	6449(3)	69(1)
C(30)	9548(4)	1211(3)	5678(4)	71(2)
C(32)	8543(4)	283(3)	4906(4)	74(2)
C(10)	5646(5)	2579(4)	9988(3)	76(2)
C(17)	3039(5)	-1325(2)	7317(3)	67(1)
C(11)	5428(5)	1836(4)	10049(3)	80(2)

C(9)	5084(5)	2995(3)	9429(3)	73(1)
C(31)	9571(4)	645(4)	5128(4)	80(2)
C(36)	8361(4)	1408(4)	8719(3)	74(2)
C(37)	9096(4)	800(4)	8629(4)	80(2)
C(16)	1942(9)	-1200(4)	6893(8)	163(5)
C(15)	1422(5)	-584(4)	6802(6)	118(3)

Compound (*S*)-66

Atom	x	y	z	U(eq)
P(2)	3896(1)	1485(1)	6225(1)	34(1)
P(1)	7033(1)	1467(1)	8286(1)	32(1)
O(1)	7976(2)	1117(1)	8787(2)	44(1)
C(19)	6236(3)	762(2)	7685(2)	31(1)
C(22)	5115(3)	1183(2)	5603(2)	35(1)
O(2)	3820(2)	2308(1)	6331(2)	51(1)
C(20)	5141(3)	880(2)	7478(2)	33(1)
C(21)	4074(3)	993(2)	7213(2)	32(1)
C(39)	2244(3)	258(2)	7653(2)	46(1)
C(23)	5436(3)	433(2)	5529(2)	42(1)
C(28)	2552(3)	1105(2)	5778(2)	38(1)
C(13)	6871(3)	57(2)	7443(2)	36(1)
C(18)	6397(4)	-622(2)	7580(2)	48(1)
C(1)	7576(3)	2144(2)	7556(2)	39(1)
C(34)	2998(3)	872(2)	7725(2)	38(1)
C(7)	5940(3)	1927(2)	8916(2)	37(1)
C(35)	2690(3)	1437(2)	8263(2)	54(1)
C(6)	6857(4)	2518(2)	7001(2)	53(1)
C(12)	5362(4)	1499(2)	9505(2)	60(1)
C(2)	8786(3)	2288(2)	7545(3)	57(1)
C(4)	8524(5)	3157(3)	6445(3)	75(1)
C(33)	1496(3)	1452(2)	6001(3)	56(1)
C(29)	2517(3)	521(2)	5227(2)	50(1)
C(24)	6359(3)	224(2)	5017(2)	55(1)
C(27)	5740(3)	1721(2)	5164(2)	49(1)
C(25)	6960(4)	761(3)	4580(3)	63(1)
O(4)	3502(3)	-497(2)	6893(3)	97(1)
C(14)	8015(3)	147(2)	7021(3)	53(1)
C(5)	7311(5)	3032(2)	6453(3)	70(1)
C(8)	5725(4)	2692(2)	8884(3)	55(1)
C(30)	1459(4)	283(3)	4891(3)	70(1)
C(3)	9250(4)	2796(2)	6981(3)	71(1)
O(3)	1670(3)	-738(2)	6802(3)	104(1)
C(38)	1168(3)	237(3)	8093(3)	66(1)
C(32)	456(4)	1206(2)	5670(3)	69(1)
C(10)	4353(4)	2584(3)	9989(3)	75(1)
C(26)	6671(4)	1506(3)	4664(3)	67(1)
C(17)	6961(5)	-1328(2)	7320(3)	68(1)
C(31)	432(4)	634(3)	5121(4)	75(1)
C(9)	4927(4)	3004(3)	9426(3)	72(1)
C(11)	4576(4)	1829(3)	10050(3)	80(1)
C(37)	899(4)	801(3)	8633(3)	72(1)
C(36)	1634(4)	1399(3)	8718(3)	73(1)
C(16)	8050(8)	-1204(3)	6893(7)	173(5)
C(15)	8579(5)	-583(3)	6806(6)	124(3)
N(1)	2482(3)	-367(2)	7078(3)	65(1)

Compound 67

Atom	x	y	z	U(eq)

P(1)	6860(1)	9222(1)	2388(1)	38(1)
P(2)	11293(1)	5890(1)	2929(1)	39(1)
Cl(1)	10238(2)	6241(1)	-902(1)	98(1)
O(1)	5890(2)	10450(2)	1884(1)	49(1)
O(2)	10099(2)	5452(2)	3242(1)	52(1)
C(19)	8770(3)	9085(2)	2532(2)	38(1)
C(21)	10671(3)	7349(2)	2043(2)	37(1)
C(20)	9761(3)	8246(2)	2275(2)	39(1)
C(22)	12173(3)	6053(2)	3869(2)	43(1)
C(7)	6809(3)	8206(2)	1794(2)	41(1)
C(1)	6439(3)	8704(2)	3568(2)	40(1)
C(39)	10533(3)	6890(2)	585(2)	48(1)
C(28)	12640(3)	4912(2)	2407(2)	40(1)
C(34)	11008(3)	7481(2)	1062(2)	41(1)
C(13)	9117(3)	9918(2)	2923(2)	42(1)
N(1)	12321(3)	8830(3)	1040(2)	63(1)
C(33)	12394(3)	3918(2)	2371(2)	49(1)
C(29)	13878(3)	5101(3)	2039(2)	57(1)
C(6)	7464(3)	7793(3)	4238(2)	52(1)
C(18)	8086(3)	10758(3)	3169(2)	51(1)
C(35)	11759(3)	8192(2)	577(2)	49(1)
C(8)	6442(3)	8670(3)	853(2)	55(1)
O(4)	13127(3)	8271(3)	1738(2)	77(1)
C(32)	13384(4)	3113(3)	1992(2)	64(1)
C(12)	7075(3)	7016(3)	2232(2)	51(1)
C(23)	11672(4)	5729(3)	4739(2)	56(1)
C(38)	10837(4)	6995(3)	-324(2)	57(1)
C(9)	6347(4)	7952(3)	348(2)	68(1)
C(31)	14602(4)	3306(3)	1644(2)	66(1)
C(30)	14850(4)	4291(3)	1663(3)	70(1)
C(36)	12042(4)	8312(3)	-331(2)	63(1)
C(10)	6627(4)	6781(3)	786(3)	68(1)
C(37)	11590(4)	7696(3)	-777(2)	66(1)
C(2)	5077(3)	9270(3)	3807(2)	57(1)
C(5)	7125(4)	7475(3)	5141(2)	58(1)
C(26)	13989(4)	6504(3)	4538(3)	74(1)
C(4)	5771(4)	8043(3)	5375(2)	60(1)
O(3)	11947(4)	9895(3)	687(2)	110(1)
C(24)	12334(5)	5807(3)	5490(2)	74(1)
C(27)	13334(3)	6448(3)	3781(2)	57(1)
C(16)	9928(5)	11440(5)	3644(4)	120(2)
C(3)	4748(4)	8940(3)	4722(2)	68(1)
C(11)	6992(4)	6309(3)	1719(2)	64(1)
C(17)	8358(4)	11622(3)	3558(3)	65(1)
C(14)	10699(3)	9756(3)	3025(3)	71(1)
C(25)	13492(5)	6185(3)	5388(3)	79(1)
C(15)	10925(5)	10657(6)	3355(5)	158(3)

Compound 89

Atom	x	y	z	U(eq)
P(1)	1819(2)	6369(1)	8743(2)	36(1)
P(2)	2782(2)	5213(2)	8265(2)	43(1)
C(13)	1707(6)	6456(5)	10039(6)	29(2)
N(1)	1532(6)	5498(4)	8256(5)	41(2)
N(2)	3000(6)	6152(5)	8731(6)	44(2)
N(3)	2833(7)	5244(5)	7040(6)	51(2)
N(4)	1502(7)	6955(5)	11536(6)	45(2)
C(19)	2088(8)	6305(5)	11827(7)	44(3)
O(1)	1305(5)	7038(3)	8114(4)	44(2)
C(1)	620(8)	5026(6)	8144(8)	49(3)
C(22)	-492(8)	7574(5)	10062(9)	47(3)
C(9)	3271(9)	4706(7)	6444(9)	64(3)
C(20)	1264(7)	7029(5)	10461(7)	38(2)
C(23)	-787(8)	7709(7)	10950(9)	58(3)
C(18)	2490(8)	6001(7)	12815(7)	52(3)

C(14)	2249(7)	5971(5)	10904(7)	34(2)
C(8)	3920(10)	7223(7)	9777(11)	89(5)
C(16)	3181(9)	4987(7)	11982(9)	61(3)
C(5)	3961(8)	6591(7)	8991(9)	60(3)
C(2)	-305(9)	5518(7)	8093(10)	74(4)
C(21)	592(9)	7709(6)	9981(8)	51(3)
C(15)	2824(8)	5296(6)	11007(8)	49(3)
C(17)	3030(8)	5328(6)	12894(8)	54(3)
C(27)	-1242(13)	7330(7)	9176(11)	84(5)
C(3)	731(10)	4486(7)	9102(10)	83(4)
C(11)	2436(11)	4438(8)	5508(10)	91(5)
C(28)	1065(9)	8468(5)	10380(9)	62(3)
C(24)	-1755(10)	7584(7)	11029(12)	78(4)
C(4)	444(11)	4522(8)	7170(11)	105(6)
C(25)	-2494(12)	7329(9)	10174(17)	101(5)
C(6)	4129(12)	6968(9)	7992(12)	104(5)
C(7)	4861(9)	6031(8)	9413(12)	97(5)
C(10)	3733(14)	4031(9)	7100(11)	132(7)
C(12)	4081(11)	5143(9)	5999(10)	98(5)
C(26)	-2220(15)	7173(9)	9236(15)	105(6)

Compound 93

Atom	x	y	z	U(eq)
P(1)	2538(1)	2434(1)	136(1)	39(1)
O(2)	1472(1)	1514(2)	-13(1)	45(1)
O(4)	2201(2)	558(2)	1178(1)	56(1)
O(3)	3518(1)	1311(2)	111(1)	54(1)
O(1)	2650(1)	3703(2)	-267(1)	53(1)
N(1)	4096(2)	2770(2)	1599(1)	43(1)
C(1)	2510(2)	3114(3)	931(1)	37(1)
C(18)	1746(2)	4478(2)	963(1)	36(1)
C(2)	3694(2)	3486(3)	1123(1)	39(1)
C(11)	2107(2)	1848(3)	1339(1)	40(1)
C(4)	5343(2)	4800(3)	964(1)	50(1)
C(19)	672(2)	4348(3)	758(1)	45(1)
C(5)	5813(2)	4069(3)	1472(1)	48(1)
C(10)	5156(2)	3063(3)	1783(1)	47(1)
C(12)	1514(2)	2191(3)	1895(1)	42(1)
C(25)	2444(2)	-731(3)	-365(1)	51(1)
C(21)	279(2)	6815(3)	1091(1)	57(1)
C(17)	1803(2)	3314(3)	2302(1)	51(1)
C(23)	2072(2)	5808(3)	1238(1)	48(1)
C(20)	-60(2)	5504(3)	816(1)	53(1)
C(3)	4293(2)	4524(3)	791(1)	47(1)
C(22)	1337(2)	6967(3)	1299(1)	56(1)
C(13)	598(2)	1333(3)	1995(1)	56(1)
C(24)	1421(2)	-90(3)	-111(1)	49(1)
C(26)	3403(2)	-306(3)	52(1)	56(1)
C(6)	6897(2)	4319(4)	1688(2)	65(1)
C(14)	-24(3)	1616(4)	2479(2)	74(1)
C(16)	1177(3)	3570(4)	2794(1)	66(1)
C(9)	5584(3)	2358(3)	2309(1)	66(1)
C(15)	264(3)	2726(4)	2875(2)	73(1)
C(7)	7288(3)	3628(4)	2197(2)	81(1)
C(27)	2598(3)	-171(4)	-1005(1)	72(1)
C(28)	2330(3)	-2439(3)	-354(2)	76(1)
C(8)	6636(3)	2644(4)	2508(2)	82(1)

Compound 104

Atom	x	y	z	U(eq)
N(1)	390(1)	2481(2)	4693(1)	38(1)
C(2)	1534(1)	925(2)	5430(1)	34(1)
O(1)	934(1)	4457(2)	5602(1)	47(1)
C(3)	2156(1)	1060(2)	6043(1)	35(1)
C(15)	348(1)	695(2)	4268(1)	35(1)
C(9)	1486(1)	-870(2)	5027(1)	36(1)
C(11)	858(1)	-2874(3)	3996(1)	43(1)
C(1)	948(1)	2757(2)	5261(1)	36(1)
C(14)	-237(1)	631(3)	3691(1)	45(1)
C(10)	904(1)	-1063(2)	4429(1)	35(1)
C(4)	2291(1)	-765(3)	6471(1)	42(1)
C(5)	2886(1)	-682(3)	7034(1)	50(1)
C(8)	2645(1)	2963(3)	6194(1)	46(1)
C(13)	-270(1)	-1176(3)	3281(1)	51(1)
C(12)	279(1)	-2932(3)	3430(1)	50(1)
C(7)	3249(1)	3016(3)	6749(1)	55(1)
C(6)	3368(1)	1208(3)	7171(1)	54(1)

Compound 107

Atom	x	y	z	U(eq)
Cl(1)	3794(1)	926(1)	2600(1)	89(1)
N(1)	427(1)	2572(3)	-301(1)	41(1)
C(7)	1461(1)	-843(3)	-7(1)	40(1)
O(1)	884(1)	4426(2)	537(1)	50(1)
C(10)	2038(1)	968(3)	927(1)	38(1)
C(8)	1479(1)	908(3)	366(1)	37(1)
C(1)	418(1)	831(3)	-696(1)	39(1)
C(6)	937(1)	-960(3)	-554(1)	39(1)
C(2)	-102(1)	867(4)	-1226(1)	48(1)
C(11)	2121(1)	-904(3)	1289(1)	45(1)
C(9)	926(1)	2768(3)	221(1)	38(1)
C(12)	2657(1)	-914(4)	1809(1)	52(1)
C(4)	402(1)	-2708(4)	-1473(1)	57(1)
C(14)	3051(1)	2831(4)	1604(1)	58(1)
C(13)	3113(1)	965(4)	1956(1)	53(1)
C(5)	922(1)	-2737(4)	-955(1)	48(1)
C(15)	2504(1)	2841(4)	1092(1)	51(1)
C(3)	-106(1)	-901(4)	-1606(1)	56(1)

Compound 112

Atom	x	y	z	U(eq)
P(2)	4406(2)	3189(1)	1496(1)	19(1)
P(1)	-109(2)	1001(2)	-2744(1)	31(1)
O(4)	3591(5)	3207(4)	671(3)	25(1)
O(3)	-1583(5)	-188(4)	-3000(3)	27(1)
O(6)	5731(5)	2741(4)	1465(3)	24(1)
O(5)	3342(5)	2305(4)	1869(3)	23(1)
N(2)	4657(7)	5629(6)	1356(4)	26(1)
O(2)	583(5)	779(4)	-3490(3)	33(1)
C(24)	5311(7)	5569(6)	2101(4)	21(1)
N(1)	1091(7)	5624(5)	-697(4)	31(1)
C(13)	-196(7)	3110(6)	-2234(4)	24(2)

C(27)	6049(8)	4530(5)	3113(4)	22(1)
C(16)	-406(8)	4185(6)	-2130(4)	23(1)
C(3)	-636(7)	-1380(6)	-3879(4)	25(2)
C(26)	5278(7)	4544(6)	2270(4)	21(1)
C(15)	588(7)	4644(6)	-1321(4)	22(1)
C(12)	-3493(8)	1672(6)	-3557(4)	25(2)
C(7)	-2051(8)	1842(5)	-3616(4)	23(1)
C(14)	927(8)	3573(6)	-1348(4)	28(2)
C(19)	-470(20)	6466(12)	-1501(8)	173(11)
C(21)	2080(7)	5765(7)	124(4)	27(2)
C(6)	-770(8)	2087(6)	-2852(4)	26(2)
C(8)	-1834(8)	1804(6)	-4391(4)	30(2)
C(11)	-4662(8)	1492(6)	-4239(4)	29(2)
O(1)	985(8)	1234(5)	-1935(4)	70(2)
C(20)	822(8)	6668(6)	-798(5)	31(2)
C(25)	6097(8)	6718(6)	2788(4)	28(2)
C(4)	846(8)	-289(6)	-3646(5)	32(2)
C(29)	5945(9)	4216(7)	4442(5)	38(2)
C(10)	-4443(7)	1463(6)	-5003(4)	26(2)
C(35)	4366(9)	806(6)	1605(4)	32(2)
C(1)	-271(9)	-2466(6)	-3945(5)	34(2)
C(36)	5260(10)	1132(7)	2519(5)	38(2)
C(17)	-1317(8)	4660(6)	-2661(4)	26(2)
C(22)	3756(8)	6421(6)	255(4)	29(2)
C(9)	-3011(8)	1631(7)	-5077(5)	32(2)
C(28)	5251(8)	4292(6)	3684(4)	28(2)
C(32)	7571(8)	4681(7)	3335(5)	32(2)
C(33)	2941(9)	1057(6)	1510(5)	31(2)
C(2)	-1736(8)	-1487(6)	-4687(4)	29(2)
C(34)	5319(10)	1485(7)	1142(5)	37(2)
C(31)	8244(9)	4604(8)	4101(5)	45(2)
C(30)	7446(10)	4368(7)	4657(5)	41(2)
C(5)	-1344(9)	-1268(6)	-3165(5)	32(2)
C(37)	3861(12)	-516(7)	1177(6)	50(2)
C(18)	-902(12)	5915(7)	-2306(6)	61(3)
C(23)	4739(8)	6707(6)	1144(5)	31(2)
C(38)	478(11)	1514(8)	9785(7)	54(3)
C(39)	1640(20)	1452(16)	9498(10)	200(14)
C(42)	-1520(13)	671(11)	10826(10)	96(5)
C(40)	-410(20)	788(15)	10345(11)	188(12)
C(41)	-2580(20)	10(20)	11401(13)	171(9)

Compound 115

Atom	x	y	z	U(eq)
P(1)	3625(1)	3831(1)	3045(1)	41(1)
P(2)	1431(1)	8877(1)	1869(1)	43(1)
O(5)	492(4)	6154(6)	9149(5)	181(4)
O(4)	3651(2)	6798(3)	3002(4)	75(1)
O(1)	3750(2)	4847(3)	3549(2)	52(1)
C(2)	2484(2)	3821(4)	2107(3)	39(1)
C(28)	2572(2)	8817(4)	2177(3)	39(1)
C(41)	1328(2)	9005(4)	745(3)	43(1)
O(2)	1355(2)	1903(3)	1790(3)	67(1)
O(3)	1299(2)	9917(2)	2206(2)	51(1)
C(8)	1864(2)	2362(4)	2149(4)	45(2)
C(32)	3532(3)	8726(5)	2188(4)	57(2)
C(6)	1519(2)	3818(4)	1098(4)	52(2)
C(7)	1948(2)	3339(4)	1773(3)	42(1)
C(33)	3089(2)	8289(4)	2395(3)	46(1)
C(30)	2953(3)	10212(5)	1544(4)	58(2)
C(4)	2116(3)	5248(4)	1079(4)	54(2)
C(10)	2795(2)	2454(4)	3212(3)	44(1)
C(21)	4151(2)	2837(4)	3555(4)	43(1)
C(29)	2527(3)	9805(4)	1742(4)	51(2)
N(1)	3182(2)	2049(4)	3986(3)	60(1)

C(3)	2543(2)	4799(4)	1733(4)	46(1)
C(15)	3733(2)	3997(4)	2040(3)	47(1)
C(36)	2247(2)	7497(4)	2966(4)	44(1)
C(27)	2122(2)	8375(4)	2398(3)	42(1)
C(47)	909(2)	7882(4)	1839(4)	47(1)
C(34)	3165(3)	7303(4)	2855(4)	49(2)
C(9)	2263(3)	1954(4)	2855(4)	48(1)
C(48)	914(3)	6869(5)	1515(4)	61(2)
C(1)	2929(2)	3329(4)	2804(3)	39(1)
C(35)	2761(3)	6964(4)	3153(4)	51(2)
C(17)	3622(3)	3424(6)	621(4)	80(2)
N(2)	1875(2)	7158(4)	3353(3)	62(1)
C(42)	976(3)	9794(5)	292(4)	60(2)
C(25)	4579(3)	1117(5)	3587(5)	70(2)
C(45)	1463(3)	8413(5)	-521(4)	69(2)
C(16)	3494(3)	3305(5)	1352(4)	56(2)
C(24)	5051(3)	1465(5)	4262(5)	75(2)
C(31)	3465(3)	9681(5)	1765(4)	66(2)
C(46)	1572(3)	8313(4)	334(4)	56(2)
C(37)	1683(3)	7963(6)	3826(4)	71(2)
C(22)	4619(3)	3164(5)	4222(4)	61(2)
C(23)	5067(3)	2483(6)	4575(5)	81(2)
C(49)	484(3)	6162(5)	1431(5)	80(2)
C(51)	47(3)	7458(6)	2011(5)	82(2)
C(5)	1595(3)	4760(5)	755(4)	57(2)
C(43)	867(3)	9906(6)	-576(4)	79(2)
C(50)	59(3)	6460(6)	1688(5)	83(2)
C(13)	3380(3)	2787(6)	4696(4)	74(2)
C(44)	1112(3)	9221(6)	-982(4)	81(2)
C(11)	3107(3)	891(6)	4182(5)	105(3)
C(19)	4195(3)	4919(6)	1226(6)	85(2)
C(26)	4138(3)	1814(4)	3248(4)	54(2)
C(52)	477(3)	8170(5)	2089(4)	62(2)
C(20)	4088(3)	4793(5)	1982(4)	64(2)
C(18)	3962(4)	4239(7)	562(5)	90(3)
C(38)	2100(3)	8177(7)	4720(5)	114(3)
C(12)	3626(5)	337(8)	4657(7)	172(5)
O(6)	37(3)	7246(6)	8124(5)	140(2)
C(54)	161(5)	6866(9)	8896(8)	126(4)
C(55)	308(5)	6676(10)	7582(9)	165(5)
C(56)	15(6)	6971(12)	6751(10)	215(7)
C(53)	-113(5)	7525(10)	9383(7)	156(4)
C(14)	2962(3)	2988(7)	5134(5)	107(3)
C(39)	1940(4)	6103(7)	3738(7)	120(4)
C(40)	1569(9)	5362(13)	3458(11)	345(16)

PART B

Compound 8

Atom	x	y	z	U(eq)
C(17)	8959(2)	6816(2)	1205(1)	46(1)
C(16)	8046(2)	7085(2)	752(1)	45(1)
C(8)	7052(2)	7805(2)	970(1)	46(1)
C(25)	7241(2)	6744(2)	-292(1)	51(1)
C(24)	8116(2)	6697(2)	186(1)	51(1)
N(1)	5698(1)	9435(2)	1141(1)	60(1)
C(9)	6667(2)	9239(2)	858(1)	50(1)
C(2)	5472(2)	8125(3)	1436(1)	56(1)
C(7)	6302(2)	7084(2)	1338(1)	50(1)
C(27)	7513(2)	7423(2)	-864(1)	52(1)
O(1)	11570(1)	6052(2)	2447(1)	90(1)
C(6)	6242(2)	5636(3)	1577(1)	61(1)
C(18)	9108(2)	7732(2)	1696(1)	54(1)

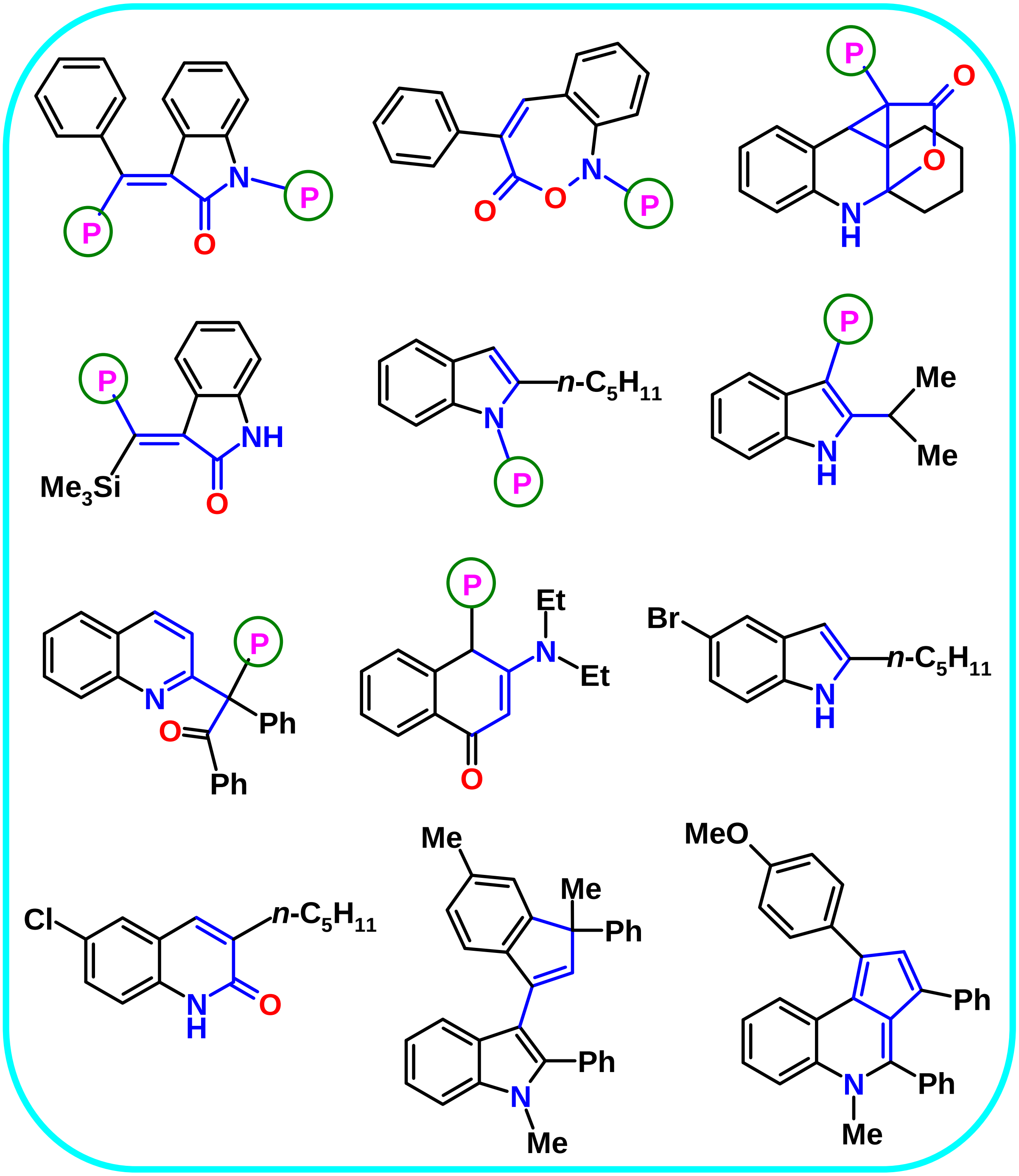
C(22)	9692(2)	5621(3)	1164(1)	64(1)
C(10)	7129(2)	10418(2)	491(1)	55(1)
C(19)	9971(2)	7534(3)	2117(1)	59(1)
C(20)	10695(2)	6368(3)	2055(1)	62(1)
C(11)	8245(2)	10737(3)	539(1)	68(1)
C(26)	6261(2)	6159(3)	-219(1)	67(1)
C(21)	10538(2)	5396(3)	1582(1)	75(1)
C(32)	7054(2)	6894(3)	-1401(1)	65(1)
C(15)	6482(2)	11216(2)	70(1)	68(1)
C(28)	8212(2)	8647(3)	-873(1)	68(1)
C(5)	5379(2)	5283(3)	1910(1)	77(1)
C(3)	4592(2)	7764(4)	1773(1)	75(1)
C(31)	7270(2)	7579(4)	-1924(1)	82(1)
C(4)	4567(2)	6339(4)	2006(1)	84(1)
C(30)	7952(3)	8801(4)	-1925(1)	93(1)
C(29)	8427(2)	9340(4)	-1402(1)	89(1)
C(14)	6929(3)	12285(3)	-283(1)	87(1)
C(12)	8691(2)	11803(3)	185(1)	87(1)
C(13)	8033(3)	12587(3)	-224(1)	96(1)
C(23)	11760(3)	7033(4)	2930(1)	110(1)
C(1)	5104(2)	10842(3)	1216(1)	85(1)

Compound 21

Atom	x	y	z	U(eq)
C(23)	2419(2)	2399(2)	5933(2)	35(1)
N(1)	-657(2)	3893(2)	7450(1)	44(1)
C(17)	1822(2)	3038(2)	6030(2)	31(1)
C(8)	299(2)	3290(2)	6718(2)	38(1)
C(27)	2686(2)	1366(2)	6826(2)	43(1)
C(25)	1158(2)	2016(2)	6602(2)	40(1)
C(24)	2030(2)	1676(2)	6282(2)	39(1)
C(10)	513(2)	3009(2)	7991(2)	38(1)
C(9)	66(2)	3358(2)	7386(2)	38(1)
C(2)	-891(2)	4178(2)	6823(2)	41(1)
C(16)	1042(2)	2775(2)	6460(2)	35(1)
C(7)	-297(2)	3809(2)	6346(2)	38(1)
C(20)	3439(2)	3198(2)	5272(2)	45(1)
C(18)	2035(2)	3759(2)	5751(2)	41(1)
C(6)	-387(2)	4006(2)	5664(2)	48(1)
C(3)	-1549(2)	4729(2)	6632(2)	55(1)
C(11)	211(2)	2315(2)	8268(2)	53(1)
C(19)	2848(2)	3829(2)	5371(2)	45(1)
C(28)	3257(2)	725(2)	6727(2)	63(1)
C(22)	3221(2)	2480(2)	5553(2)	45(1)
C(4)	-1604(2)	4920(2)	5962(2)	62(1)
C(12)	670(3)	1981(3)	8812(2)	63(1)
C(26)	1765(2)	1048(2)	5752(2)	59(1)
C(5)	-1041(2)	4562(2)	5481(2)	61(1)
C(13)	1419(3)	2356(3)	9092(2)	64(1)
C(15)	1281(2)	3381(2)	8276(2)	59(1)
C(32)	2744(2)	1728(3)	7447(2)	65(1)
C(21)	4328(2)	3300(3)	4863(2)	75(1)
C(29)	3857(3)	451(3)	7230(3)	83(2)
C(30)	3888(3)	816(3)	7834(3)	80(2)
C(14)	1727(3)	3045(3)	8825(2)	70(1)
C(31)	3337(3)	1457(3)	7954(2)	84(2)
C(1)	-1131(2)	4105(3)	8072(2)	75(2)

Compound 22

Atom	x	y	z	U(eq)
N(1)	4277(1)	6798(1)	402(1)	42(1)
O(1)	2383(1)	-2202(1)	1561(1)	63(1)
C(2)	4419(2)	6045(2)	969(1)	41(1)
C(10)	3404(2)	6456(2)	-90(1)	40(1)
C(7)	3748(2)	4810(2)	1020(1)	39(1)
C(8)	2989(2)	4291(2)	469(1)	39(1)
C(17)	1857(2)	4590(2)	-528(1)	42(1)
C(28)	3320(2)	-155(2)	1304(1)	45(1)
C(9)	2753(2)	5242(2)	-67(1)	39(1)
C(26)	2305(2)	1722(2)	665(1)	40(1)
C(27)	3331(2)	1135(2)	1011(1)	43(1)
C(19)	2318(2)	3075(2)	328(1)	40(1)
C(20)	1246(2)	5136(2)	-1139(1)	44(1)
C(11)	3183(2)	7463(2)	-629(1)	41(1)
C(3)	5203(2)	6543(2)	1493(1)	50(1)
C(6)	3826(2)	4203(2)	1618(1)	48(1)
C(29)	2285(2)	-937(2)	1253(1)	45(1)
C(31)	1281(2)	914(2)	621(1)	45(1)
C(30)	1260(2)	-396(2)	908(1)	48(1)
C(18)	1634(2)	3299(2)	-285(1)	45(1)
C(1)	5140(2)	7919(2)	338(1)	52(1)
C(16)	3419(2)	7091(2)	-1216(1)	46(1)
C(5)	4575(2)	4718(2)	2128(1)	56(1)
C(15)	3169(2)	8007(2)	-1714(1)	57(1)
C(12)	2701(2)	8780(2)	-550(1)	55(1)
C(4)	5283(2)	5877(2)	2061(1)	58(1)
C(21)	439(2)	6226(2)	-1165(1)	62(1)
C(13)	2451(2)	9692(2)	-1052(1)	64(1)
C(23)	35(2)	6157(3)	-2272(1)	78(1)
C(14)	2677(2)	9302(2)	-1634(1)	64(1)
C(25)	1429(2)	4544(2)	-1700(1)	59(1)
C(22)	-156(2)	6730(2)	-1723(1)	78(1)
C(32)	1407(2)	-3147(2)	1440(1)	74(1)
C(24)	829(2)	5066(3)	-2268(1)	75(1)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