CYCLOADDITION/ CYCLIZATION REACTIONS OF ALLENYLPHOSPHONATES/ RELATED ALLENES AND PALLADIUM-CATALYZED DIARYLATION OF ALKYNES

A THESIS

SUBMITTED FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

By

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INDIA

SEPTEMBER 2011

Dedicated to

Umma-Uppa

Saji, Shemi, Sani, Bicha

And

Seenu

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PART B

PALLADIUM-CATALYZED DIARYLATION OF ALKYNES

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

September 2011

K. V. Sajna

CERTIFICATE

This is to certify that the work described in this thesis entitled "*Cycloaddition/ Cyclization Reactions of Allenylphosphonates/ Related Allenes and Palladium-Catalyzed Diarylation of Alkynes*" has been carried out by Miss. K. V. Sajna, under my supervision and the same has not been submitted elsewhere for any degree.

Hyderabad

September 2011

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LIST OF PUBLICATIONS

1. Cycloaddition Reactions of Allenylphosphonates and Related Allenes with Dialkyl Acetylenedicarboxylates, 1,3-Diphenylisobenzofuran and Anthracene
K. V. Sajna, Ramesh Kotikalapudi, Manab Chakravarty, N. N. Bhuvan Kumar and K. C. Kumara Swamy*
J. Org. Chem. **2011**, *76*, 920.

2. Efficient Palladium-Catalyzed Double Arylation of Phosphonoalkynes and Diarylalkynes in Water: Use of a Dinuclear Palladium(I) Catalyst
K. V. Sajna, Venu Srinivas and K. C. Kumara Swamy*****
Adv. Synth. Catal. **2010**, *352*, 3069.

3. To stay as allene or go further? Synthesis of novel phosphono-heterocycles and polycyclics *via* propargyl alcohols
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4. Allenylphosphonates-Useful Precursors of Pyrazoles and 1,2,3-Triazoles
Manab Chakravarty, N. N. Bhuvan Kumar, **K. V. Sajna**, K. C. Kumara Swamy*
Eur. J. Org. Chem. **2008**, 4500.

5. Diversity Oriented Synthesis of Novel Polycyclics, Benzofurans, and 3-*H*-Isochromans *via* Allenylphosphonates and Allenylphosphine oxides
K. V. Sajna and K. C. Kumara Swamy* (*manuscript under preparation*)

6. Synthesis of Novel Polysubstituted Pyrroles and Pyrazines *via* vinyl azides: Utility in Horner-Wadsworth-Emmons Reaction
K. V. Sajna and K. C. Kumara Swamy* (*manuscript under preparation*)

7. $Zn(OTf)_2$ catalyzed addition-cyclization reaction of allenylphosphine oxides with propargyl alcohol-Unexpected formation of 2,5-dimethylenetetra-hydrofurans and 2-substituted furans.
Venu Srinivas, **K. V. Sajna** and K. C. Kumara Swamy*****
Tetrahedron Lett. **2011**, *Article in Press* (10.1016/j.tetlet.2011.08.020)

8. Catalyst-free and Catalyzed Addition of P(O)-H Bonds to Allenyl/Alkynyl Phosphonates and Phosphane Oxides: Use of a Robust, Recoverable Dinuclear Palladium(I) Catalyst
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9. Allenylphosphonates with 1,3,2-dioxaphosphorinane ring: Synthesis, Structures and Stability
N. N. Bhuvan Kumar, Manab Chakravarty, N. Satish Kumar, **K. V. Sajna** and K. C. Kumara Swamy*
J. Chem. Sci., **2009**, *121*, 23.

Papers presented in symposia

1. Cycloaddition Reactions of Allenylphosphonates and Related allenes with DMAD/DEAD, 1,3-Diphenylisobenzofuran and Anthracene.
   K. V. Sajna, Ramesh Kotikalapudi and K. C. Kumara Swamy*
   6th J-NOST Conference, University of Hyderabad, Hyderabad. INDIA, January 28-31, **2011**.

2. Cycloaddition Reactions Involving Allenylphosphonates and Allenylphosphine Oxides.
   K. V. Sajna and K. C. Kumara Swamy*
   Chemfest-2011, School of Chemistry, University of Hyderabad, February, **2011**.
   (Oral and poster presentation)

3. Allenylphosphonates as Useful Precursors in Cycloaddition and Cyclization Reactions.
   K. Ramesh, **K. V. Sajna**, N. N. Bhuvan Kumar, Manab Chakravarty and K. C. Kumara Swamy*
   11th National Symposium in Chemistry, NCL Pune, INDIA, February 6-8, **2009**.

4. Organophosphorus chemistry-Probing traditional organic reactions.
   K. C. Kumara Swamy*, Venu Srinivas, K. V. Sajna, and K. Ramesh
   National Symposium on Frontiers in Main Group and Organometallic Chemistry (NSFMOC),
   November 20, **2010** (Department of Inorganic and Physical Chemistry, IISc, Bangalore)

Synopsis

This thesis is divided into two parts: **Part-A** and **Part-B**. **Part-A** deals with (i) phosphorus containing polycyclic and heterocyclic derivatives synthesized *via* allenes and (ii) cycloaddition reactions of allenylphosphonates. The reactivity of allenylphosphonates is compared with that of allenylphosphine oxides/ ester allenes as appropriate. **Part-B** comprises three component coupling reaction of phosphorus-based alkynes, iodoarenes and arylboronic acids by using the novel Pd-catalyst $[(OCH_2CMe_2CH_2O)P\text{-}S\text{-}Pd(PPh_3)]_2$ under environmental friendly conditions; this reaction has been extended to diarylalkynes. The efficacy of this dinuclear Pd-catalyst is compared with that of traditional palladium catalysts [$Pd(OAc)_2$ and $Pd(PPh_3)_4$] in Suzuki and Sonogashira coupling reactions.

Each part is subdivided into three chapters: (a) Introduction (literature survey), (b) Results and Discussion and (c) Experimental Section. The compounds obtained in the present study are, in general, characterized by mp, IR and NMR (^1H, ^{13}C & ^{31}P) techniques followed by elemental analyses and mass spectra (LC-MS). Wherever feasible, X-ray structure determination is undertaken. Summary as well as references are compiled 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 presented. Important results of this part are outlined here. The precursors used in the present study are shown in Charts 1 and 2 [*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

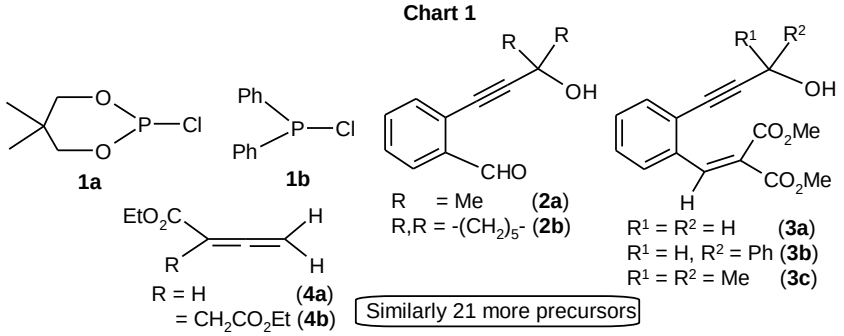
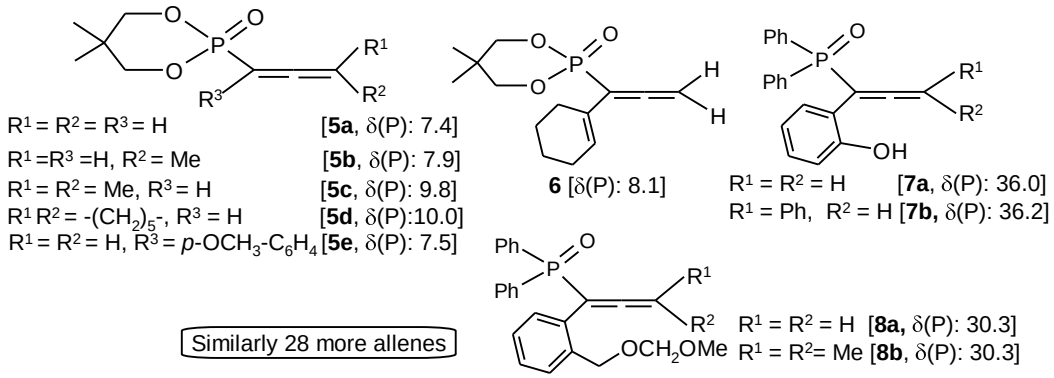


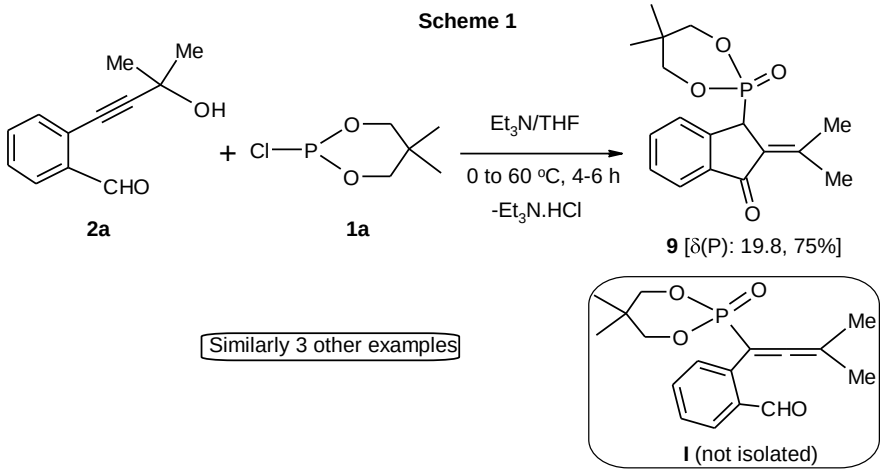
Chart 2



(i) Synthesis of novel phosphorus-based polycyclics

In an attempt to synthesize aldehyde functionalized allenes of type **I** from the reaction of propargyl alcohol **2a** with the P^{III}-Cl precursor **1a** (Scheme 1), surprisingly, we isolated a novel phosphono-indanone derivative **9** rather than the expected allene **I**. The structure of this compound was confirmed by single crystal X-ray crystallography (Fig. 1). The reaction of Ph_2PCl (**1b**) with propargyl alcohol **2a** led to an analogous product. Similar products were obtained by using propargyl alcohol **2b** also. To our knowledge, reactions of this type are unprecedented.

Scheme 1



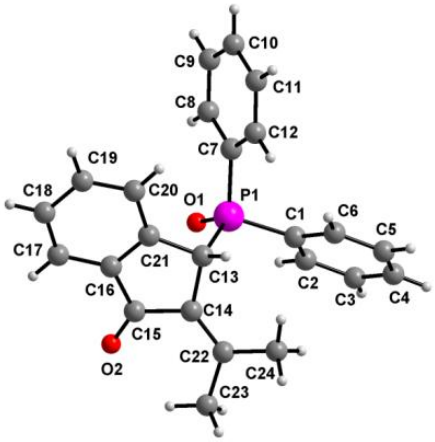
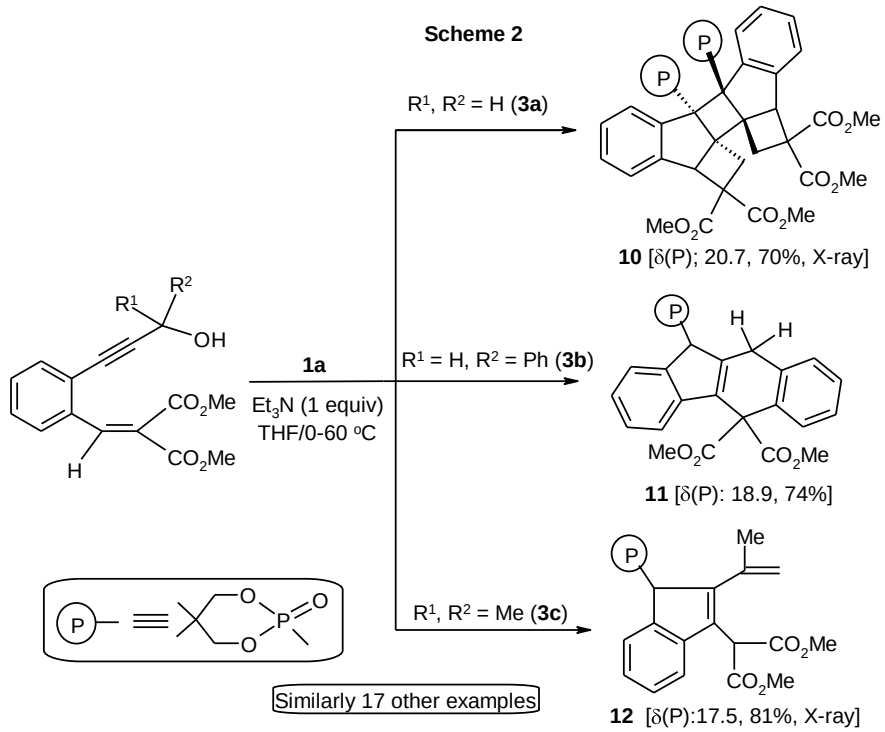


Figure 1. Molecular structure of compound **9**

Encouraged by the above promising result, we focused our attention on the propargyl alcohols **3a-c** that contain alkylidene group in place of the –CHO functionality. Thus, the reaction of **1a** with alcohol **3a** furnished the unexpected polycyclic product **10**, which was entirely different from expected allene. It constitutes a rare brand of 3-fused cyclobutane ring system formed from two molecules each of propargylic residue and phosphorus containing moiety (Scheme 2, Fig. 2, left). In a similar way, the reaction of a P^{III}-Cl precursor **1a** with phenyl substituted propargyl alcohol 2-(CH=C(CO_2Me)$_2$)C_6H_4C≡CCH(Ph)OH (**3b**) or dialkyl substituted propargyl alcohol 2-(CH=C(CO_2Me)$_2$)C_6H_4C≡CCMe_2OH (**3c**) delivered two entirely different products, phosphono-tetracycle **11** or indene **12**, respectively, in good yields. Thus, formation of three distinct varieties of products **10-12** was demonstrated in the reaction of **1a** with the propargyl alcohols (**3a, 3b** or **3c**). The structures of the compounds **10** (Fig. 2, left), and **12** (Fig. 2, right) were confirmed by single crystal X-ray crystallography. Phosphine oxide-based derivatives were also obtained by employing the precursor **1b** in similar reactions.



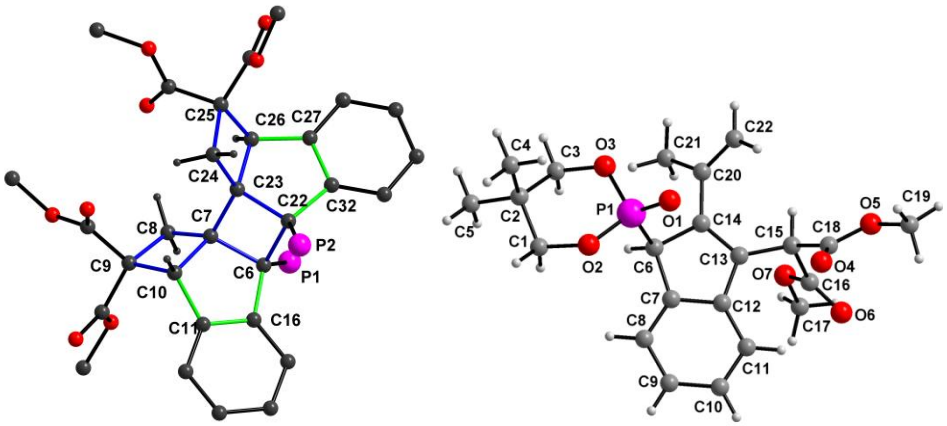


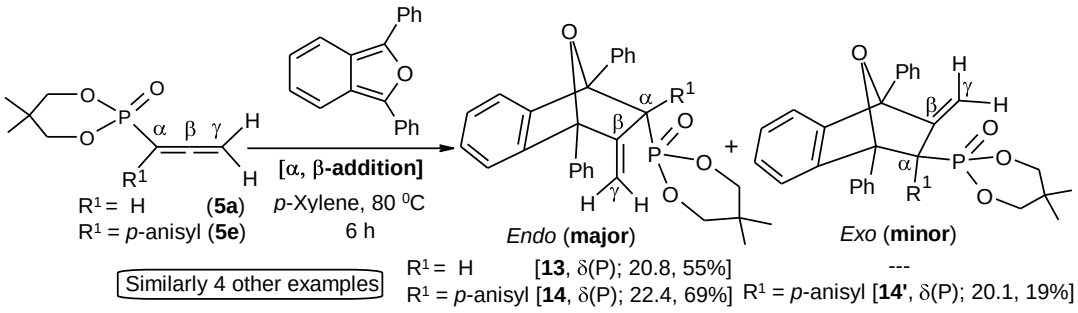
Figure 2. Molecular structures of compounds **10**.CH_2Cl_2 and **12**.

(ii) Cycloaddition reactions of allenes

Allenes, by virtue of their reactive and cumulative double bonds, are excellent partners for both [2+2] and [4+2] cycloaddition reactions. Hence we explored the reactivity of the allenes towards the cycloaddition reaction with the dienes 1,3-diphenylisobenzofuran and anthracene under thermal activation. We also describe the reaction of **6** with the dienophile dimethyl acetylenedicarboxylate (DMAD). The cycloaddition reaction of allene $(OCH_2CMe_2CH_2O)(O)PC(H)=C=CH_2$ (**5a**) with 1,3-diphenylisobenzofuran in *p*-xylene at 80 ^oC afforded preferentially *endo*-[4+2] adduct **13** *via* [α,β] attack (Scheme 3). Other α-substituted allenes behaved in a similar

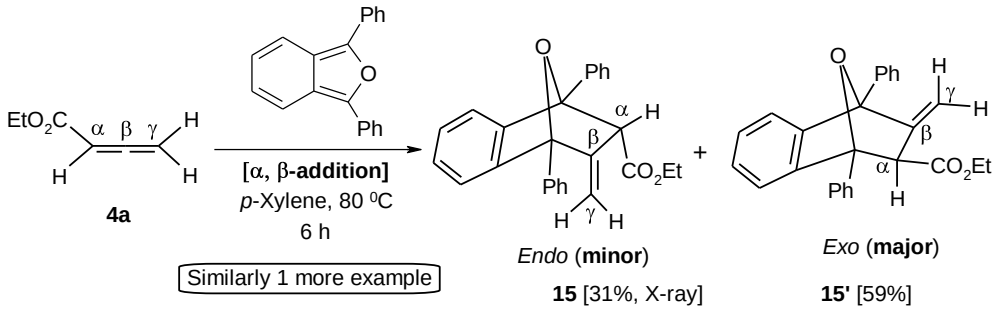
manner. In one case (reaction of allene **5e** with IBF), X-ray structures were obtained for both *endo* and *exo* isomers [**14** and **14'**].

Scheme 3



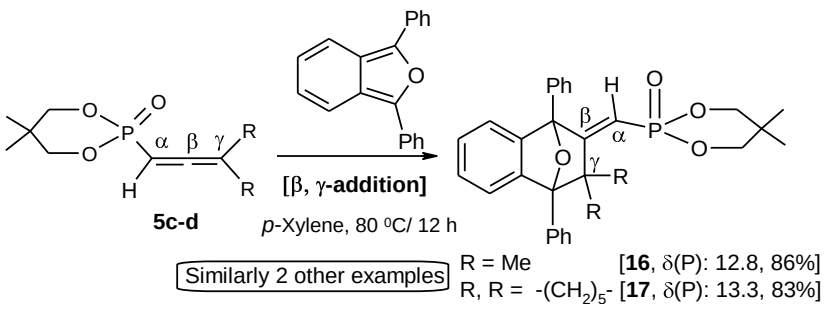
In order to compare the above reactions with that of non-phosphorylated allenes, we carried out thermal cycloaddition reactions using the allene $(EtO_2C)C(H)=C=CH_2$ (**4a**) under the above conditions (Scheme 4). Although the *endo* isomer was the major product in the case of phosphorus-based allenes, there appeared to be a reversal in the reactions using allenoate **4a** that lead to the products **15-15'** in which the *exo*-(with respect to CO_2Et group) isomer **15'** was the major product.

Scheme 4



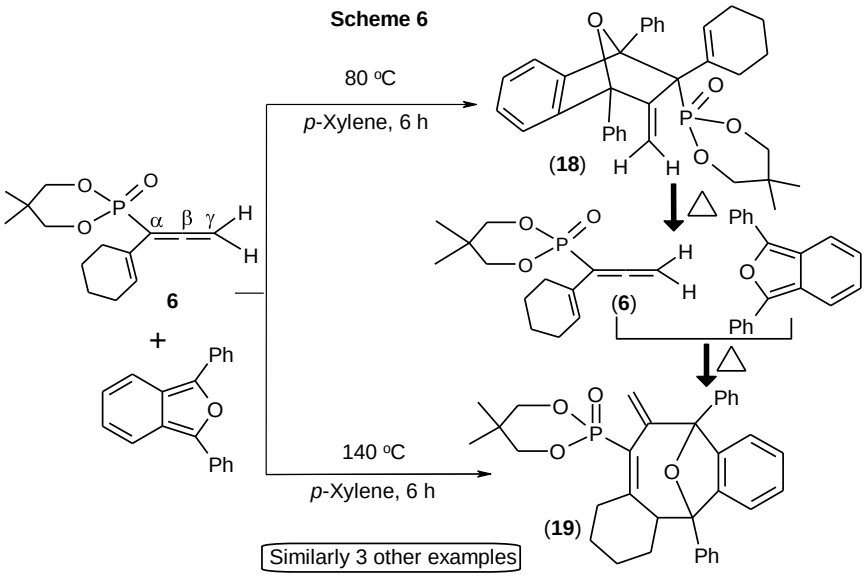
After studying the nature of cycloaddition reactions of α-substituted allenes we turned our attention to γ-dialkylsubstituted allenes. Thus we treated phosphorus-based allenes **5c-d** with IBF. Surprisingly, the addition occurred regio-selectively at the (β,γ) carbon-carbon double bond of allenes leading to vinylphosphonates **16-17** (Scheme 5). The corresponding allenylphosphine oxide precursors behaved similarly.

Scheme 5



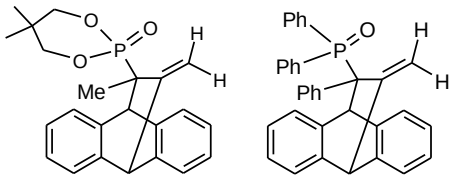
An interesting result was observed in the cycloaddition reaction of α-vinyl substituted allene **6** with IBF. When the reaction was carried out at 80 ^{o}C, it ended up mostly in the [4+2] cycloaddition product **18** (Scheme 6) along with only a minor quantity of compound **19** (<20 % based on ^{31}P NMR) whereas at 140 ^{o}C, [4+4] cycloadduct **19** was the predominant product. It is very likely that the above reaction occurs *via retro* Diels-Alder reaction followed by [4+4] cycloaddition as shown in Scheme 6. The thermal conversion of compound **18** to **19** was also demonstrated by a ^{31}P NMR spectroscopic study.

Scheme 6



Thermal [4+2] cycloaddition of allenes (dienophiles) with anthracene (diene) worked well although it took a longer time and higher temperature than that required in the case of 1,3-diphenylisobenzofuran. As far as the site of attack on allene is concerned, anthracene reacted in a manner similar to IBF (Chart 3).

Chart 3



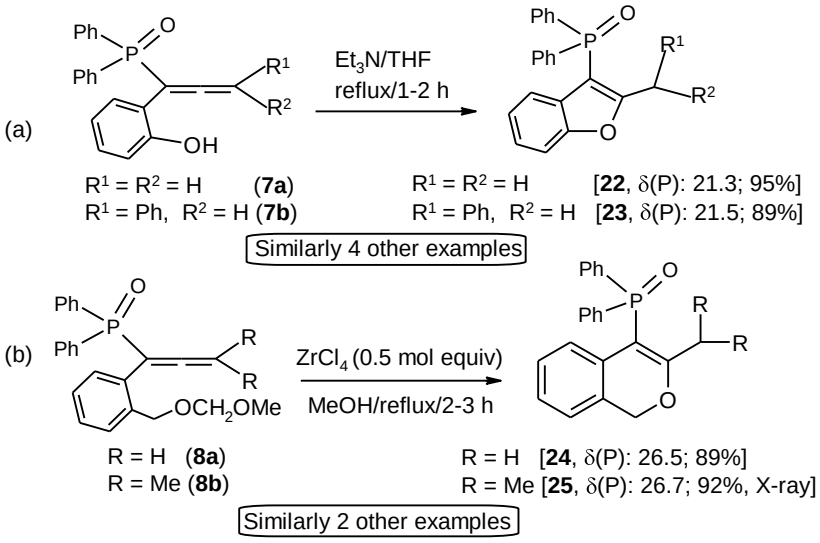
20 (67%) **21** (64%)

(iii) Nucleophilic addition-cyclization reactions of allenes 7a-b and 8a-b-Synthesis of 1,2-disubstituted benzofuran and isochromene derivatives

While investigating the nucleophilic reactions of functionalized allenes, a variety of 2,3-substituted benzofuran derivatives **22-23** have been obtained by an intramolecular cyclization reaction of allenes [$Ph_2P(O)(2\text{-}OHC_6H_4)C{=}C{=}CR^1R^2$] (**7a-**

b) comprising a 2-hydroxy phenyl moiety at the α-position (Scheme 7a). Inspired by this result, we made an attempt to deprotect MOM-containing allenes **8a-b** by using a catalytic amount of Lewis-acid $ZrCl_4$ but unexpectedly, a deprotection followed by intamolecular nucleophilic-addition cyclization had taken place leading to isochromene derivatives **24-25** (Scheme 7b). The scope of the reaction was extended by preparing more of these types of products.

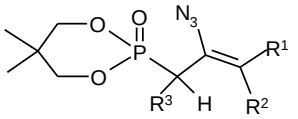
Scheme 7



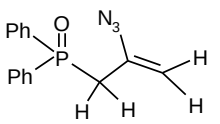
(iv) Synthesis and utility of nitrogen containing heterocycles

Vinyl azides are excellent precursors for the synthesis of nitrogen containing heterocyclics. Hence we synthesized some of the vinyl azides **26-28** by following procedure developed in our laboratory which involves treatment of allenylphosphonates/ allenylphosphine oxides with Me_3SiN_3 in DMF or NaN_3 in *t*-BuOH-H_2O mixture at room temperature (Chart 4). These azides are further utilized in the cyclization reactions with ethyl acetoacetate in methanol as solvent and $Mn(OAc)_3.2H_2O$ as catalyst to obtain polysubstituted pyrroles **29-30**. Later on we were successful in obtaining these pyrroles in one pot route starting from allenes **5a** or **5b** (without isolating azide) in good to excellent yields under photochemical conditions (Scheme 8). We explored this reaction further by using allenylphosphine oxides and various 1,3-dicabonyls (ethyl-4-chloro acetoacetate and acetyl acetone). The allene **4a** also afforded tetrasubstituted pyrroles **31-33** in good yields under the optimized reaction conditions (Chart 5).

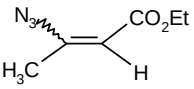
Chart 4



$R^1 = R^2 = R^3 = H$ [**26a**, δ(P): 19.8; 88%]
$R^1 = R^3 = H$, $R^2 = Me$ [**26b**, δ(P): 19.8; 50%]
$R^1 = R^2 = Me$, $R^3 = H$ [**26c**, δ(P): 21.2; 80%]



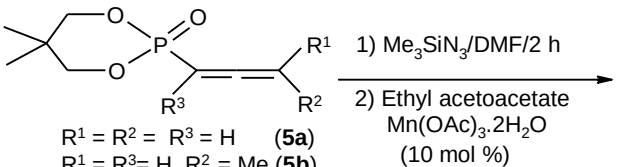
27 [δ(P): 28.1; 89%]



28 [90%]

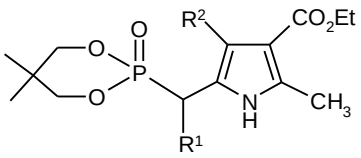
Similarly 3 other precursors

Scheme 8



$R^1 = R^2 = R^3 = H$ (**5a**)
$R^1 = R^3 = H$, $R^2 = Me$ (**5b**)

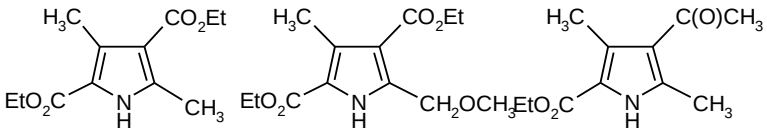
1) Me_3SiN_3/DMF/2 h
2) Ethyl acetoacetate
$Mn(OAc)_3.2H_2O$
(10 mol %)
AcOH (2 eqiv)
MeOH, hυ, 4 h



$R^1 = R^2 = H$ [**29**, δ(P): 20.0; 80%, X-ray]
$R^1 = H$, $R^2 = Me$ [**30**, δ(P): 21.3; 81%]

Similarly 12 other examples

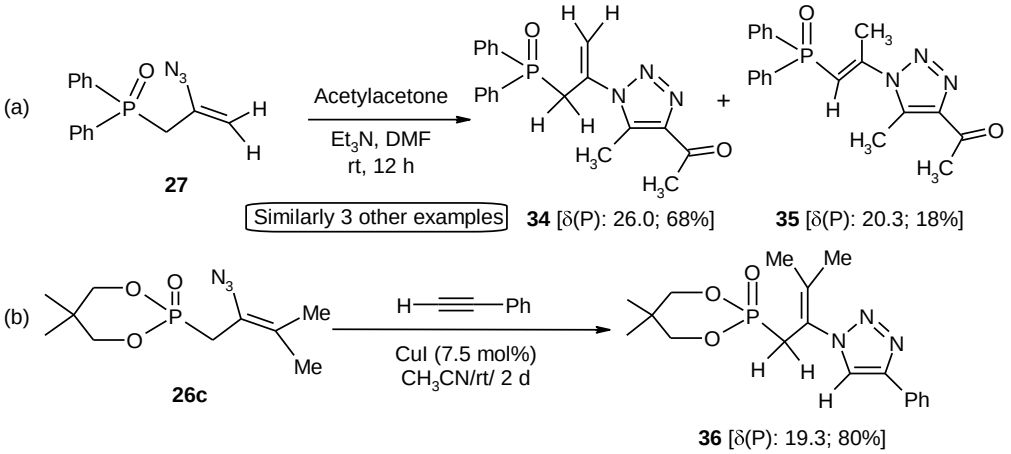
Chart 5



31 (75%) **32** (72%) **33** (71%, X-ray)

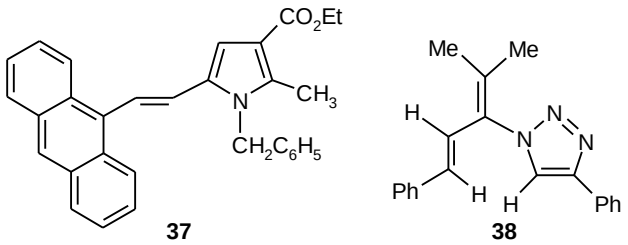
We further checked the reactivity of vinyl azides in 1,3-dipolar addition reactions with acetyl acetone as well as phenyl acetylene (Scheme 9). Interestingly, the reaction of azide **27** with acetyl acetone by using triethylamine afforded the novel 1,2,3-triazoles **34-35**. The product **35** is formed *via* proton migration from α-CH_2 (to phosphorus) of compound **34**. The reaction of vinyl azide **26c** with phenyl acetylene in the presence of CuI in acetonitrile as solvent led to phosphono-1,2,3-triazole **36** stereo-selectively in high yield (Scheme 9b).

Scheme 9



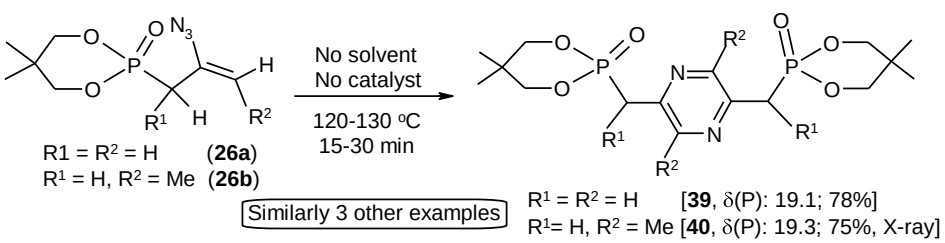
We have also demonstrated the utility of the newly synthesized phosphorus-based nitrogen heterocycles (pyrroles and 1,2,3-triazoles) in Horner-Wadsworth-Emmons (HWE) reaction. Thus, this method provides a convenient access to diverse phosphorus-free nitrogen heterocycles (Chart 6). Other examples are also discussed in the thesis.

Chart 6



An unprecedented route for 1,4-pyrazines **39-40** has been recognized while studying the thermal stability of vinyl azides **26a-b**. The solid material resulting upon heating phosphorus-based vinyl azides above its melting point under neat condition (no solvent, no catalyst) was pyrazines (Scheme 10) and not the expected azirines. Phosphine oxide-based vinyl azides were also led to the similar types of pyrazines under similar reaction conditions. The nitrogen gas evolution in this reaction was corroborated by thermo-gravimetric analysis (TGA) experiment.

Scheme 10



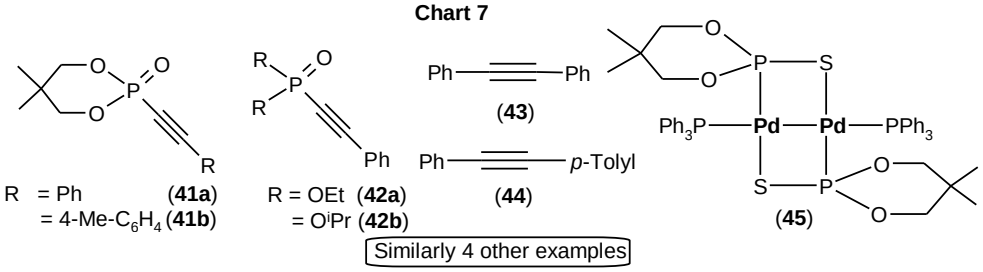
PART-B

Chapter 4 focuses mainly on literature survey on coupling reactions of phosphonoalkynes and other alkynes. Chapter 5 describes the results obtained in the present study on these aspects. Chapter 6 is the experimental section for this part. Important results of this part are outlined below.

(i) Synthesis of phosphorus-based alkynes/diarylalkynes and the dinuclear Pd(I) catalyst

The phosphonate/phosphine oxide precursors **41-42** (selected examples) and diarylalkynes **43-44** used for the present study were prepared by literature methods (Chart 7). The dinuclear Pd(I) catalyst $[(OCH_2CMe_2CH_2O)P\text{-}S\text{-}Pd(PPh_3)]_2$ **45** was prepared by following a method reported recently from our laboratory.

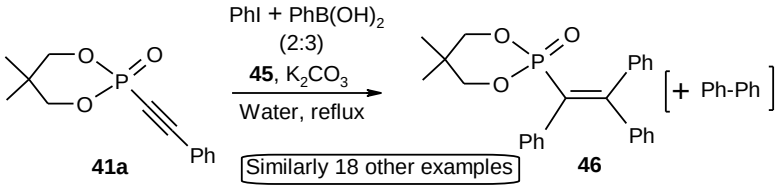
Chart 7



(ii) Synthesis of symmetrically diarylated vinylphosphonates and vinylphosphine oxides

When phosphonoalkyne **41a** treated with iodobenzene and phenylboronic acid in the presence of catalyst **45** in water medium at 100 °C for 0.5 h by using K_2CO_3 as the base, tetrasubstituted vinylphosphonate **46** was formed quantitatively (Scheme 11). Under optimized conditions, we have conducted the reactions of a variety of substituted phosphorus-based alkynes with different iodoarenes and arylboronic acids to form symmetrically diarylated vinylphosphonates. Despite the heterogeneous nature of the components used, the reaction works well in aqueous medium affording the phosphonate products in yields that are essentially quantitative with the only minor limitation being the formation of the biaryls. From the X-ray structures of compounds (not shown here), it is clear that the incoming aryl groups from both aryl iodide and arylboronic acid add *cis* to alkynes.

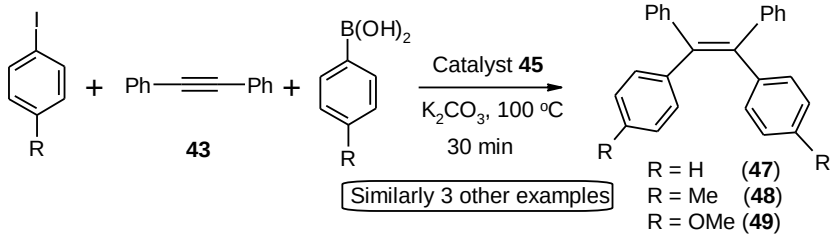
Scheme 11



(iii) Synthesis of symmetrically diarylated alkynes

In order to prove the efficacy of this novel route, we have extended the methodology to include the disubstituted alkyne **43** (or **44**) and obtained the tetrasubstituted alkenes **47**-**49** by double arylation (Scheme 12). In these cases also, compounds **47**-**49** were the sole arylated products.

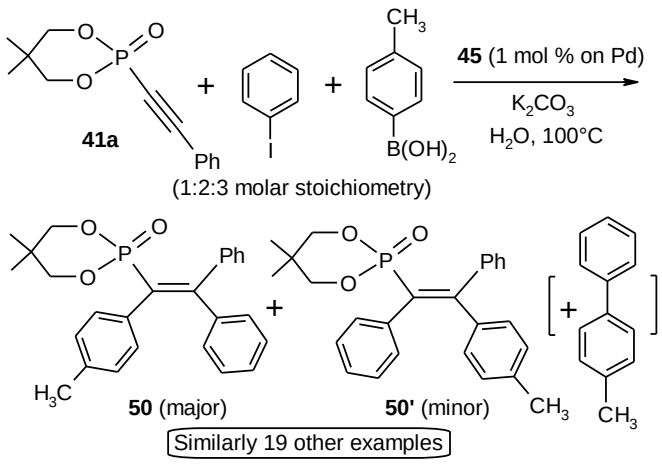
Scheme 12



(iv) Synthesis of unsymmetrically diarylated vinylphosphonates

After synthesizing the symmetrically doubly arylated vinylphosphonates and alkenes, we ventured into preparing unsymmetrically double arylated products (**50**-**50'**) by using the above methodology (Scheme 13). The yield (^{31}P NMR) was again quantitative with the incoming aryl groups *cis* to each other. In most cases, the isomer with the aryl moiety from the boronic acid entering the position *geminal* to the phosphorus was dominant and the other isomer was the minor product.

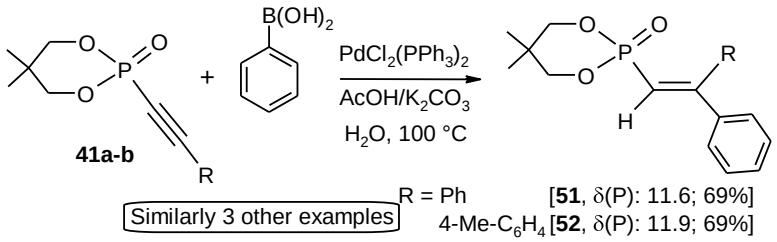
Scheme 13



(v) Synthesis of monoarylated vinylphosphonates

After obtaining various diarylated vinylphosphonates, we synthesized monoarylated vinylphosphonates **51-52** by the reaction of phosphorus-based alkynes **41a-b** with phenylboronic acid in the presence of $PdCl_2(PPh_3)_2$/AcOH/K_2CO_3 system in H_2O at 100 ^oC (Scheme 14). Due to the ready availability of various substituted arylboronic acids our method is preferred over the literature method which involves $NaBPh_4$ as the aryl source.

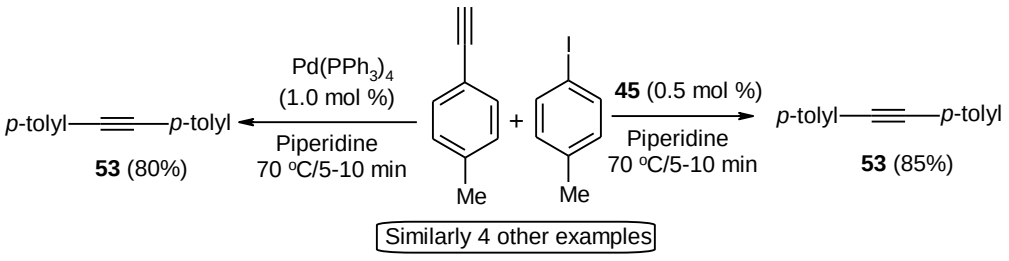
Scheme 14



(vi) Use of dinuclear palladium(I) catalyst 45 in various coupling reactions-A comparative study

To explore the efficacy of our dinuclear palladium(I)-catalyst **45**, we have performed a few well known coupling reactions and compared these with the traditional palladium [$Pd(OAc)_2$ and $Pd(PPh_3)_4$] catalyzed reactions (Scheme 15). The results suggest that our catalyst is at least as active as or better than the other catalysts under the similar conditions. The added advantage in the case of catalyst **45** is its stability to air.

Scheme 15



PART-A

CYCLOADDITION/ CYCLIZATION REACTIONS OF ALLENYLPHOSPHONATES AND RELATED ALLENES

Chapter 1

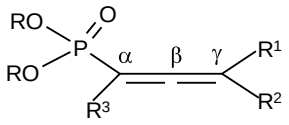
INTRODUCTION

1.1 General Introduction: Allenes

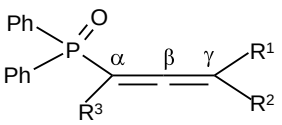
Allenes have always fascinated chemists because of the intriguing features of the cumulative diene function such as the higher reactivity compared to simple alkenes and alkynes.[1] For a long period, allenes had been considered more as chemical curiosities and unstable unsaturated moieties than as reliable partners in chemical reactions which retarded the development of their synthetic applications. However, over the last twenty years, allene chemistry has become increasingly popular.[1, 2]

During the last 10-15 years, numerous new reactions of allenes have been developed and some of them have been successfully applied for the efficient synthesis of natural products.[2] Due to the presence of two cumulative C=C bonds in allenes, there are issues of regio-selectivity (which C=C bond reacts and in which direction addition occurs) and stereo-selectivity. For example, when there is a nucleophilic functionality in the allene, cyclizations afford the products with very high regio- and stereo-selectivity.[1k] Moreover, with diverse and appropriate substituents, allenes can be utilized as versatile starting materials to develop sequential reactions either in the presence or in the absence of catalysts, affording an efficient method for preparation of synthetically and biologically important molecules.[3]

Allenes having $-P(O)(OR)_2$ or $-P(O)(Ph)_2$ as a substituent are called as allenylphosphonates (phosphorylated allenes) (**I**) or allenylphosphine oxides (**II**), respectively. Many of these allenes are stable solids, and can be handled easily when compared to other allenes. The presence of phosphorus moiety may provide regioselective products in cyclization reactions.[4] In the following sections, a brief literature survey on the preparation and utility of allenes/ allenylphosphonates/ allenylphosphine oxides will be presented. Wherever possible, comparison will be made between the reactivity of phosphorus-based allenes and other allenes.



I
Allenylphosphonate



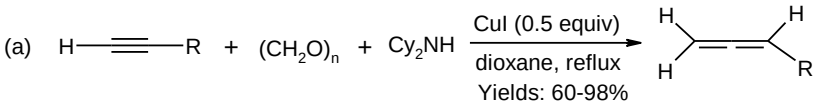
II
Allenylphosphine oxide

1.2 Synthesis of allenes/allenylphosphonates/allenylphosphine oxides

Several methods are available for the synthesis of non-phosphorylated allenes in the literature.[5] A most commonly employed method for the synthesis of a variety of functionalized allenes, including allenyl esters, ketones, lactones and lactams, is the Wittig reaction of phosphonium ylides and ketenes.[5a-h, k-n] Another general class of reaction to access allenes is 1,2-elimination of two groups from a vinyl precursor.[5i, j, n] These are elegantly discussed in the book 'Modern Allene Chemistry' by Krause and Hashmi.[2a] Some of the other relevant methods for synthesis of allenes are outlined below.

Recently Ma and co-workers developed a one-step method for converting terminal alkynes to terminal allenes **1.1a-d** in high yields by using CuI, paraformaldehyde, and dicyclohexylamine (Scheme 1.1a).[6a-b] However, this reaction is limited to the use of paraformaldehyde. The same group overcame this problem by using the easily available aldehydes (beyond paraformaldehyde) and terminal alkynes in the presence of cost-effective ZnI_2 and morpholine [6c] affording 1,3-disubstituted allenes **1.2a-d** (Scheme 1.1b).

Scheme 1.1

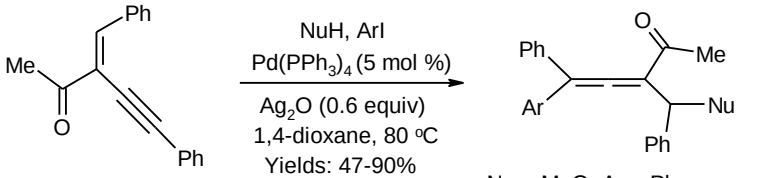


R = $CH_3(CH_2)_7$ (**1.1a**)
= $CH_3(CH_2)_9$ (**1.1b**)
= *p*-Cl-C_6H_4 (**1.1c**)
= *p*-$O_2NC_6H_4CH_2OCH_2$ (**1.1d**)

R = $CH_3(CH_2)_7$, R' = Ph (**1.2a**)
R = $CH_3(CH_2)_7$, R' = *p*-ClC_6H_4 (**1.2b**)
R = *p*-$O_2NC_6H_4CH_2O(CH_2)_2$, R' = Ph (**1.2c**)
R = *p*-$O_2NC_6H_4CH_2O(CH_2)_2$, R' = *i*-Pr (**1.2d**)

Xiao and Zhang reported the first example of Pd(0) catalyzed three-component domino reactions of electron-deficient enynes, nucleophiles and aryl halides that lead to multifunctionalized tetrasubstituted allenes **1.3** (Scheme 1.2).[7] A variety of functionalities such as alkoxy, carboxyl, carbonyl and nitro groups were tolerated, providing opportunities for further elaboration of the functional groups on the allene skeleton.

Scheme 1.2

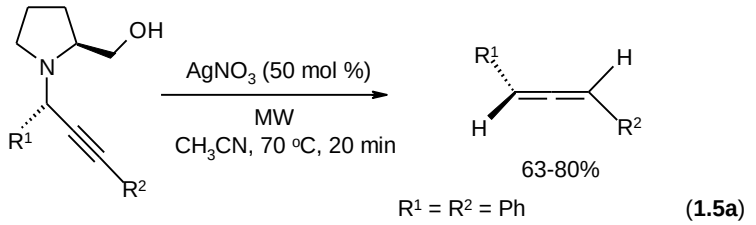


Nu = MeO, Ar = Ph (**1.3a**)
Nu = BnO, Ar = Ph (**1.3b**)
Nu = $PhCH_2CH_2O$, Ar = Ph (**1.3c**)
Nu = MeO, Ar = 4-$MeOC_6H_4$ (**1.3d**)
Nu = MeO, Ar = 4-$NO_2C_6H_4$ (**1.3e**)

Che and co-workers reported silver(I)-mediated reaction of optically active propargyl amines to form a wide range of axially chiral allenes in excellent yields with enantiomeric excess values of 96-99%.[8] This protocol allows the synthesis of a variety of 1,3-diarylallenes having different aryl moieties from the corresponding propargyl amines in a stereospecific manner. They also investigated microwave (MW) assisted

silver(I)-mediated transformation of propargyl amines **1.4** to allenes **1.5a-e**, with a considerably shorter reaction time (Scheme 1.3).

Scheme 1.3



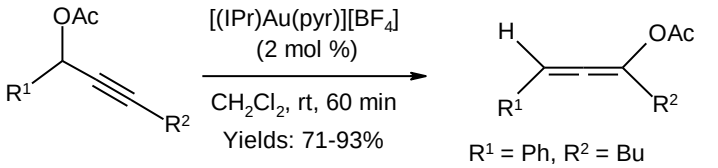
1.4

63-80%

$R^1 = R^2 = Ph$ (**1.5a**)
$R^1 = t$-Bu, $R^2 = Ph$ (**1.5b**)
R^1 = cyclohexyl, $R^2 = Ph$ (**1.5c**)
$R^1 = n$-Bu, $R^2 = Ph$ (**1.5d**)
$R^1 = -(CH_2)_2Ph$, $R^2 = n$-hexyl (**1.5e**)

Nolan *et al*. explored a synthetic route to substituted allenes **1.7a-e** from propargylic acetates **1.6** catalyzed by cationic gold(I) complex [(IPrAu(pyr)][BF_4] generated *in situ* from the air and moisture stable precatalyst [(IPr)AuOH] and ammonium or pyridinium salt (Scheme 1.4).[9] Various aryl and alkyl substituted allenes were synthesized by this method.

Scheme 1.4



1.6

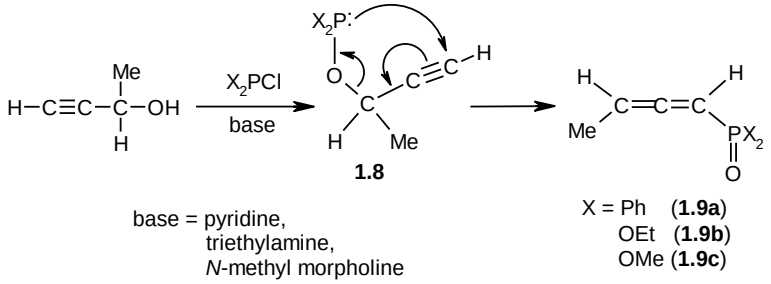
$R^1 = Ph$, $R^2 = Bu$ (**1.7a**)
$R^1 = 2\text{-}MeC_6H_4$, $R^2 = Bu$ (**1.7b**)
$R^1 = 4\text{-}MeC_6H_4$, $R^2 = Bu$ (**1.7c**)
$R^1 = 4\text{-}FC_6H_4$, $R^2 = Bu$ (**1.7d**)
$R^1 = Ph$, $R^2 = -(CH_2)_2Br$ (**1.7e**)

IPr = *N*, *N'*-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene

A general and easy procedure for the synthesis of allenylphosphonates/ allenylphosphine oxides was established by the treatment of trivalent phosphorus chlorides [X_2PCl, X = OMe, OEt, Ph] with the propargyl alcohol [e.g. Me(H)C(OH)C≡CH] in the presence of a base [pyridine, triethylamine or *N*-methyl morpholine] in a suitable solvent like THF, ether or toluene.[10a-d] The P(III) intermediate

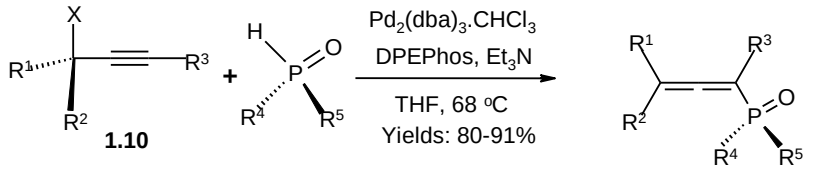
1.8 undergoes a *pseudo*-Claisen type rearrangement, usually at ambient temperature or below, to afford allenylphosphonates/ allenylphosphine oxides **1.9a-c** (Scheme 1.5). A variety of cyclodiphosphazane[10e] and pentaerythritol[10f] containing allenes were also synthesized by using this methodology in our laboratory.

Scheme 1.5



Stawinski and co-workers has been reported a novel method for the construction of allenylphosphonates **1.11** and related compounds which involves a Pd(0)/DPEPhos-[bis(2-phenylphosphinophenyl)ether-] catalyzed coupling of propargyl chlorides **1.10a** or carbonates **1.10b** with *H*-phosphonate diesters or their analogues (Scheme 1.6).[11] The reaction represents a new means for the formation of the P-C bond and 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 1.6



X = Cl (**1.10a)** or a carbonate (**1.10b**)

$R^1 = R^2 = R^3 = H$, $R^4 = R^5 = OEt$ (**1.11a**)
$R^1 = R^3 = H$, $R^2 = n\text{-}C_5H_{11}$, $R^4 = R^5 = OEt$ (**1.11b**)
$R^1 = R^2 = R^3 = Me$, $R^4 = R^5 = OEt$ (**1.11c**)
$R^1 = R^2 = R^3 = H$, $R^4 = Me$, $R^5 = OEt$ (**1.11d**)
$R^1 = H$, $R^2 = Me$, $R^3 = Ph$, $R^4 = R^5 = OEt$ (**1.11e**)

1.3 Reactions of allenes/allenylphosphonates/allenylphosphine oxides

Allenes can undergo transition-metal catalyzed, base-catalyzed and organo-catalyzed reactions affording a variety of molecules having pharmaceutical and biological significance. In the following sections selected cycloaddition and cyclization reactions of allenes that are relevant to our work will be presented.

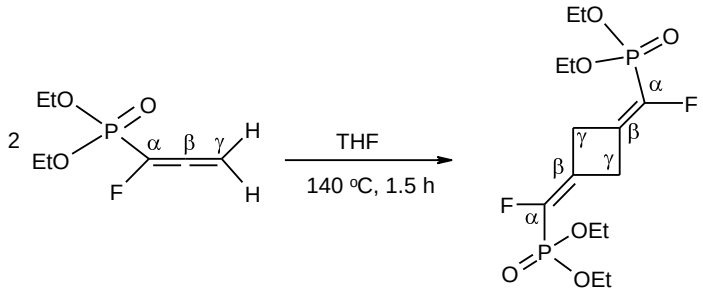
1.31 Cycloaddition reactions involving allenylphosphonates or related allenes

Allenes are excellent partners for both [2+2] and [4+2] cycloaddition reactions.[12] This pathway provides an atom economical approach to a diverse range of products, and hence is attractive from the synthetic chemist's point of view. These reactions can be inter- and intra-molecular cycloadditions as discussed below.

1.311 Intermolecular cycloaddition reactions

[2+2] Cycloaddition reactions between an allene and an alkene are well established and constitute a powerful method for the synthesis of methylenecyclobutane derivatives.[13] An allene can undergo [2+2] cycloaddition with itself or with another partner (e.g. R'C≡CR') leading to a range of cyclobutanes/cyclobutenes, with the nature of the product depending on the electronic and/or steric requirements. For example, heating of α-fluoroallenylphosphonate **1.12** in a sealed tube furnished the tail-to-tail dimer **1.13** exclusively at the β,γ-position (Scheme 1.7).[14] The bulky phosphorus substituent on the allene moiety allowed rotation in the bisallyl diradical intermediate yielding the corresponding dimer **1.13**.

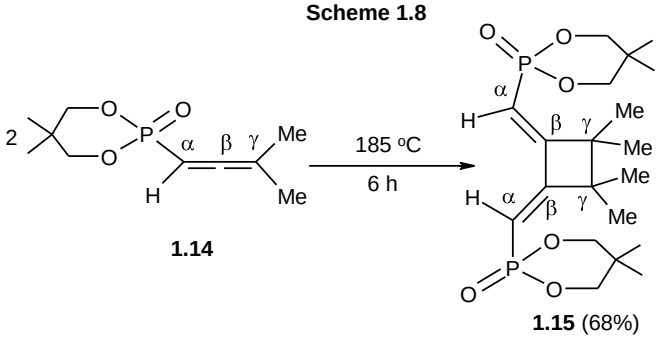
Scheme 1.7



1.12 **1.13** (73%)

In contrast to the above, a head-to-head [2+2] dimerization of allene **1.14** involving the β,γ-position under thermal conditions has been reported from our laboratory.[10f] The cycloadduct **1.15** was formed exclusively with the defined stereochemistry as shown in Scheme 1.8 *via* a concerted diradical mechanism.

Scheme 1.8

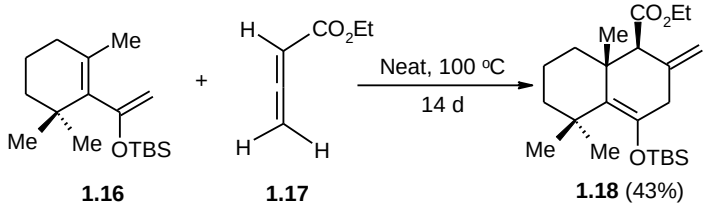


1.14

1.15 (68%)

Allenes can also act as dienophiles in [4+2] cycloadditions.[15] Jung and co-workers reported [4+2] cycloaddition reaction of hindered diene **1.16** and ester allene **1.17** (Scheme 1.9).[16] This synthetic methodology had been used as a key step for the total synthesis of (±)-hedychenone,[16a] (±)-hedychilactone B,[16b] and (±)-kellermanoldione.[16c]

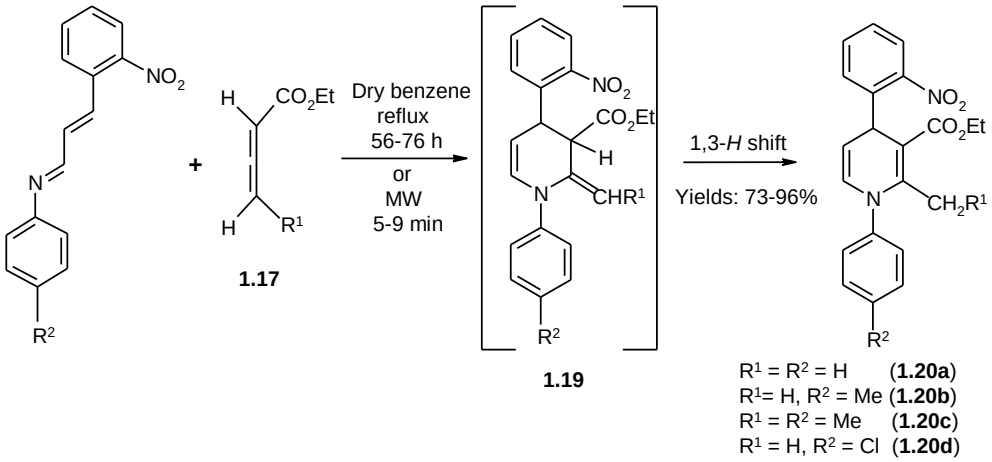
Scheme 1.9



1.16 **1.17** **1.18** (43%)

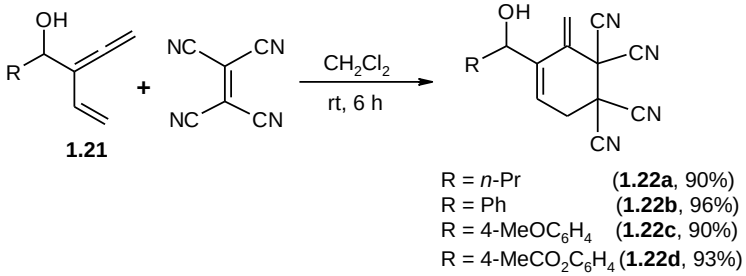
Ishar *et al.* investigated the thermally assisted [4+2] cycloaddition of 1,4-diaryl-1-aza-1,3-butadienes with allenic esters **1.17** leading to cycloadducts **1.19**, which after a 1,3-*H* shift afforded substituted unsymmetrical 2-alkyl-1,4-diaryl-3-ethoxycarbonyl-1,4-dihydropyridines **1.20a-d** in high yields (Scheme 1.10).[17] They were also successful in obtaining the same products under microwave (MW) irradiation with much shortened reaction time (5-9 min).

Scheme 1.10



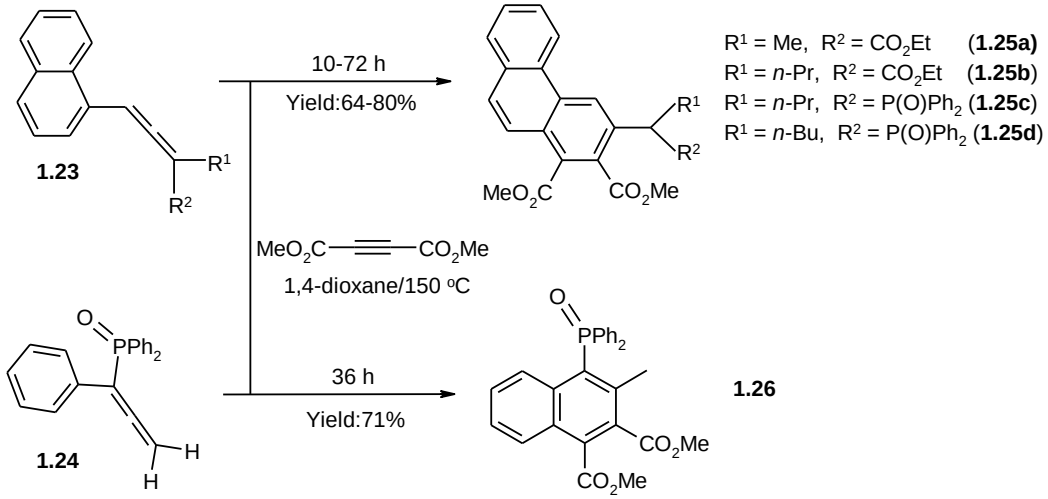
Allene precursors with an additional multiple bond [e.g. ene-allenes] can act as dienes.[18] Very recently, Lee and co-workers investigated the Diels-Alder reaction of vinyl allenols **1.21** with tetracyanoethylene to give cyclohexenylmethyl alcohols **1.22** having an *exo* methylene moiety[18a] (Scheme 1.11). This [4+2] cycloaddition reaction proceeded smoothly under mild reaction conditions (room temperature) to afford the products in excellent yields. Dienophiles like *N*-methylmaleimide, maleic anhydride and dimethyl maleate were also employed in this reaction.

Scheme 1.11



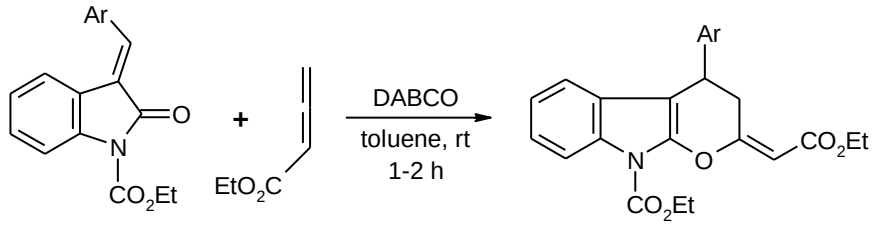
Only two reports of cycloaddition in which C=C double bond of an aryl group and the conjugated C=C bond of an allene together incorporated as a 1,3-diene unit are available in the literature.[19] In one of these, Ma and co-workers observed an intermolecular [4+2] cycloaddition reaction of 1-aryl-1,2-allenes **1.23** or **1.24** with dimethyl acetylenedicarboxylate ($Me_2OC{\equiv}CCO_2Me$, DMAD) affording phenanthrenes **1.25a-d** or naphthalene **1.26** respectively (Scheme 1.12).[19b]

Scheme 1.12



A DABCO (1,4-diazabicyclo[2.2.2]octane) catalyzed [4+2] cycloaddition of arylidenoxindole **1.27** and allenoate **1.17** was developed by Wang and co-workers.[20] This reaction provided a new route to dihydropyran-fused indoles **1.28a-d** in good yields with excellent regio- and diastereo-selectivity (Scheme 1.13). It represents the first example of a formal [4+2] cycloaddition, wherein allenoates act as surrogates of a 1,2-dipole.

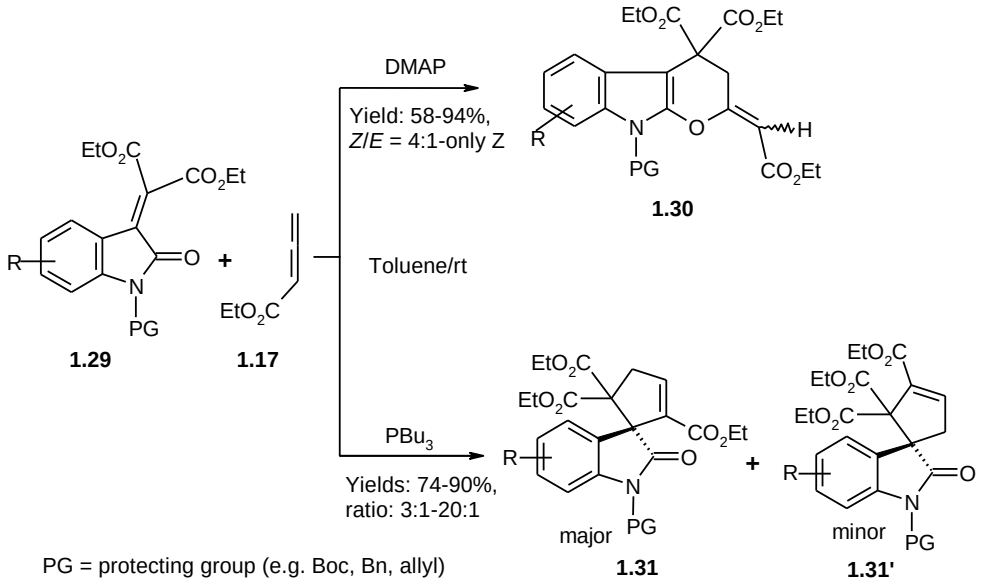
Scheme 1.13



A novel nitrogen-containing Lewis base catalyzed highly stereoselective [4+2] cycloaddition of isatin derived α,β-unsaturated diester **1.29** with α-allenic ester **1.17** furnishing the corresponding cyclic adducts **1.30** in good to excellent yields under mild conditions has been disclosed by Shi *et al.* (Scheme 1.14).[21] In contrast to this, by employing tributylphosphine as the catalyst, the analogous reaction led to the

spirocyclic products **1.31-1.31'** in good yields *via* highly regioselective [3+2] cycloaddition (Scheme 1.14).[21] Thus, it is interesting to note that subtle changes in the reaction conditions gave rise to the different products.

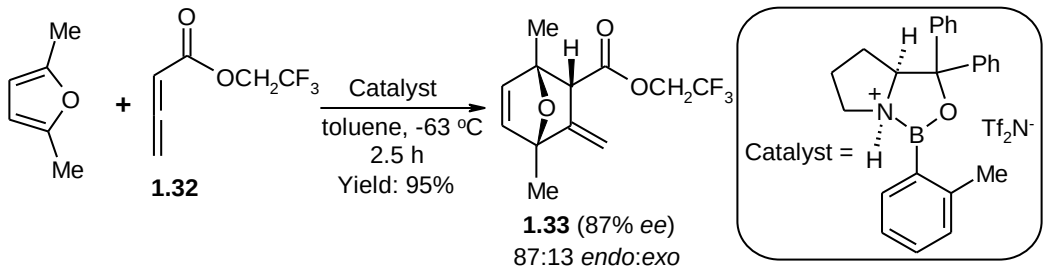
Scheme 1.14



1.29 **1.17** **1.30** **1.31** **1.31'**

Corey and co-workers reported a catalytic asymmetric Diels-Alder route for the synthesis of (-)-laurenditerpenol.[22] The product **1.33** required for the synthesis of (-)-laurenditerpenol was obtained by organocatalyzed [4+2] cycloaddition of 1,5-dimethylfuran with allenic ester **1.32** (Scheme 1.15).

Scheme 1.15



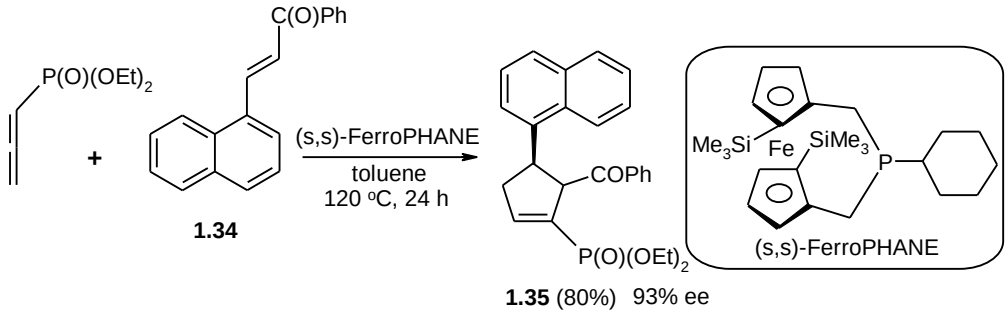
1.32

1.33 (87% *ee*)
87:13 *endo*:*exo*

Variations like phosphine catalyzed [3+2] cycloadditions can pave the pathway to novel five-membered cyclic compounds also.[23] For example, the planar chiral 2-

phospha[3]ferrocenophane has been employed by Marinetti *et al*. as an efficient nucleophilic organocatalyst for the enantioselective synthesis of cyclopentenylphosphonate **1.35**, through [3+2] cyclizations between diethyl allenylphosphonate and α,β-unsaturated ketones **1.34** (Scheme 1.16).[23g] The enantiomeric excess in this case was 93%.

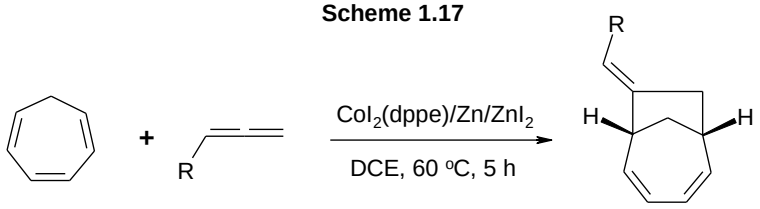
Scheme 1.16



1.35 (80%) 93% ee

Recently, a cobalt catalyzed [6π+2π] cycloaddition between cycloheptatriene with allenes has been investigated by Buono *et al.* to obtain **1.36a-d** [24](Scheme 1.17). Cobalt salts were found to promote this transformation efficiently and also allowed for both regioselectivity and *E*/*Z* selectivity control.

Scheme 1.17



Only *E*-isomer

R = Ph (**1.36a**, 85%)
R = 4-MeC$_6$H$_4$ (**1.36b**, 75%)
R = 4-MeOC$_6$H$_4$ (**1.36c**, 76%)
R = CH$_2$Ph (**1.36d**, 82%)

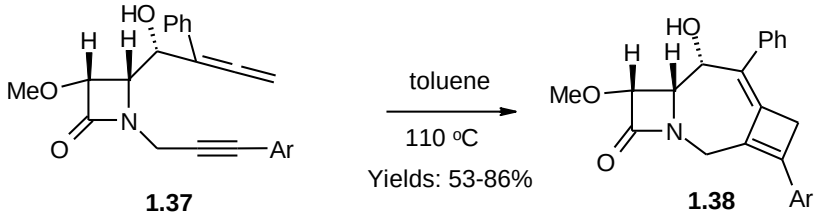
1.312 Intramolecular cycloaddition reactions

The intramolecular thermal cycloaddition reaction of allenenes and allenynes is well documented and constitutes an interesting opportunity to prepare polycyclic compounds, mainly methylenecyclobutane derivatives. In general, the regioselectivity

of the cycloaddition depends on the steric nature of the substituents attached to the allene or alkene/alkyne moieties, providing the corresponding proximal or distal adducts. From a mechanistic point of view, the transition-metal catalyzed[25] reactions usually proceed through a series of metallacyclic intermediates formed through oxidative cyclization and carbometalation steps. A final reductive elimination process affords the corresponding cycloadducts and regenerates the metal catalyst.[26] In addition to transition-metal catalyzed cycloaddition reactions, microwave assisted cyclization offers opportunities for accelerating the sluggish reactions or for providing alternative pathways.[27]

A thermal methodology for the expeditious preparation of structurally novel strained tricyclic β-lactams containing a cyclobutene ring **1.38** *via* [2+2] intramolecular cycloaddition of allene **1.37** has been developed by Alcaide and co-workers (Scheme 1.18).[28] This is the first example accounting for the intramolecular double [2+2] cycloaddition resulting in a tricyclic β-lactam.

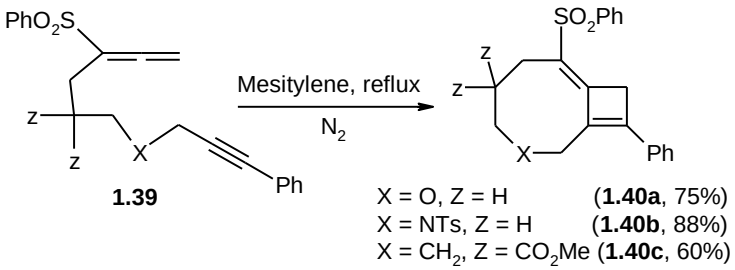
Scheme 1.18



1.37 **1.38**

A simple method for synthesis of bicyclo[6.2.0]deca-1,8-dienes **1.40a-c** has been developed by Mukai *et al.* by heating under reflux (in mesitylene) a solution of allenynes **1.39** possessing a phenylsulfonyl functionality on the allenyl group (Scheme 1.19).[29] This method offers a new route for bicyclo[6.2.0]deca-1,8-dienes.

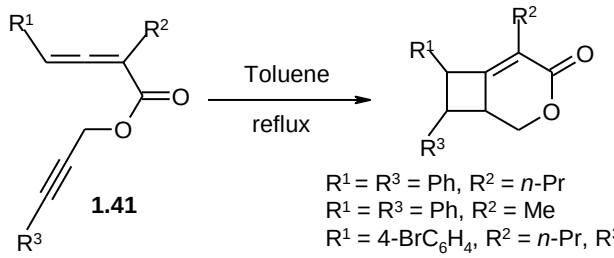
Scheme 1.19



X = O, Z = H (**1.40a**, 75%)
X = NTs, Z = H (**1.40b**, 88%)
X = CH_2, Z = CO_2Me (**1.40c**, 60%)

Jiang and Ma investigated a [2+2]-cycloaddition reaction of propargylic 2,3-allenoates **1.41** for the efficient formation of 3-oxabicyclo[4.2.0]octa-1(8),5-dien-4-ones **1.42a-e** under thermal conditions[30] (Scheme 1.20). These products contain the biologically important 5,6-dihydropyran-2-one and cyclobutadiene units.

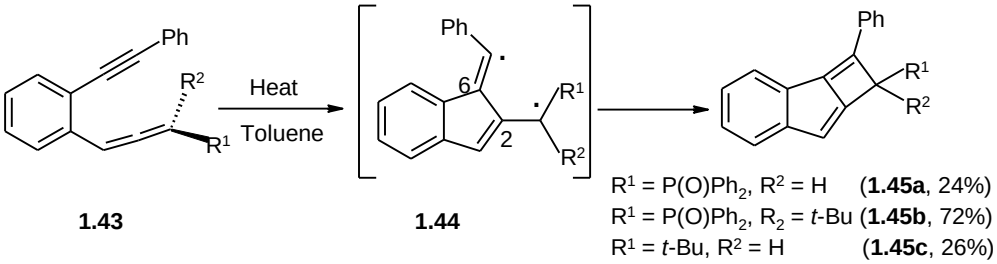
Scheme 1.20



$R^1 = R^3 = Ph$, $R^2 = n$-Pr (**1.42a**, 65%)
$R^1 = R^3 = Ph$, $R^2 = Me$ (**1.42b**, 82%)
$R^1 = 4\text{-}BrC_6H_4$, $R^2 = n$-Pr, $R^3 = Ph$ (**1.42c**, 61%)
$R^1 = Ph$, $R^2 = n$-Pr, $R^3 = TMS$ (**1.42d**, 74%)
$R^1 = Ph$, $R^2 = Bn$, $R^3 = TMS$ (**1.42e**, 70%)

A new set of enyne-allenes **1.43** were structurally designed by Schmittel *et al*. and employed in thermal [2+2] cyclization to form the products **1.45a-c** (Scheme 1.21).[31] The mechanism of their transformation to [2+2] cycloadducts was established by trapping experiments and DFT computations. These results suggest a stepwise pathway involving the reversible formation of the C2–C6 diradical intermediate **1.44**.

Scheme 1.21

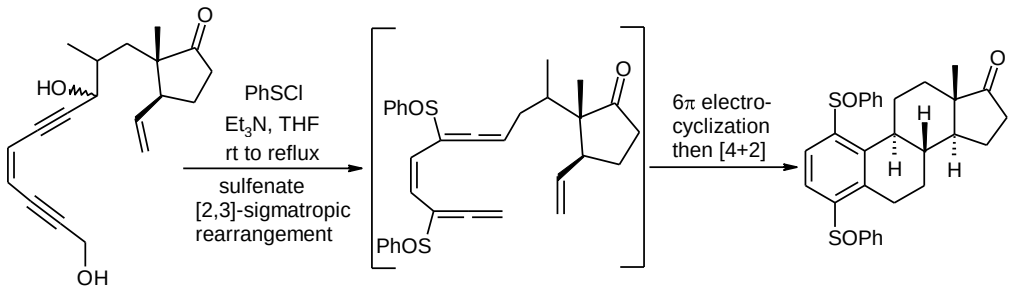


1.43 **1.44**

$R^1 = P(O)Ph_2$, $R^2 = H$ (**1.45a**, 24%)
$R^1 = P(O)Ph_2$, $R_2 = t$-Bu (**1.45b**, 72%)
$R^1 = t$-Bu, $R^2 = H$ (**1.45c**, 26%)

A one-pot construction of perhydrophenanthrene **1.48** from an acyclic substrate **1.46** was achieved by Mukai and Kitagaki *via* a sequential pericyclic reaction, which involved the *in situ* generation of ene-diallene species **1.47** (Scheme 1.22).[32] The resulting perhydrophenanthrene derivative was successfully converted into (±)-estrone.

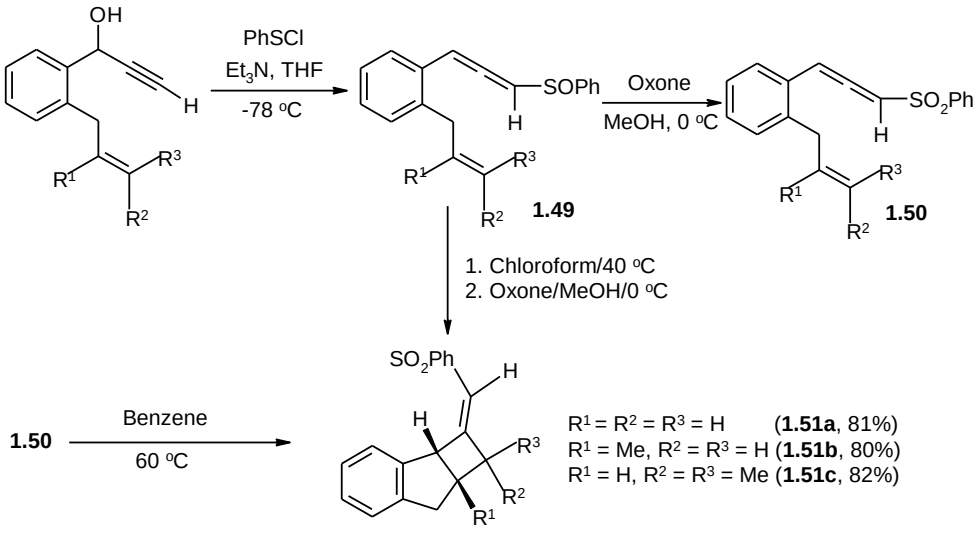
Scheme 1.22



1.46 **1.47** **1.48** (32%)

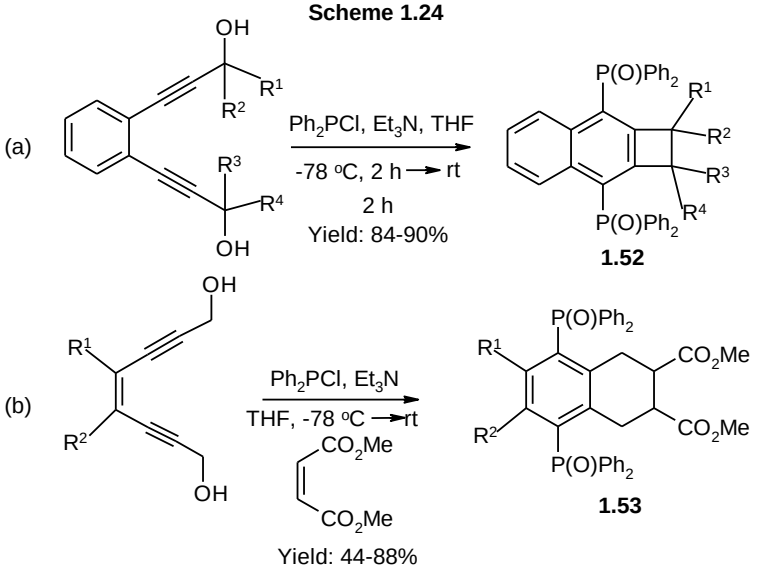
Various phenylsulfonyl allene derivatives comprising double bonds connected to the γ-position **1.50** were prepared by Padwa *et al*.[33] These substrates underwent a highly regio- and stereo-specific thermal [2+2] cycloaddition across the nonactivated cumulene double bond to form **1.51a-c** in excellent yields (Scheme 1.23). They also obtained the same products **1.51a-c** by warming the sulfoxide allene **1.49** in chloroform at 40 ^{o}C and subsequent oxidation with oxone.

Scheme 1.23



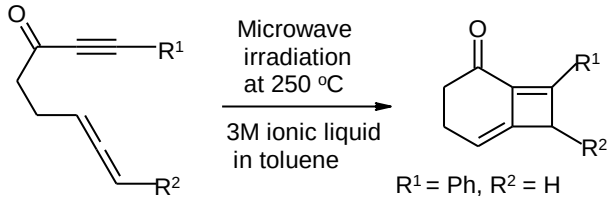
Mukai and co-workers have shown that benzene-bis(phosphinylallenes), derived from benzene-bis(propargyl alcohols) and Ph_2PCl, underwent an intramolecular [2+2] cycloaddition leading to the naphtho[*b*]cyclobutene derivatives **1.52** (Scheme 1.24a).[34] On the other hand, ethylene-bis(phosphinylallenes) afforded the [4+2] cycloadducts instead of the [2+2] cycloadducts **1.53** (Scheme 1.24b). Thus, the reaction pathway is controlled by the proper choice of propargyl alcohol moiety.

Scheme 1.24



Brummond and Chen discovered a microwave-assisted [2+2] cycloaddition reaction of an alkynyl allene **1.54** that provides bicyclomethylenecyclobutenes **1.55a-d** in good to excellent yields (Scheme 1.25).[35] The scope of this reaction was investigated by subjecting alkynyl allenes possessing a wide range of substituents and functionalities to the optimized formal cycloaddition reaction conditions.

Scheme 1.25

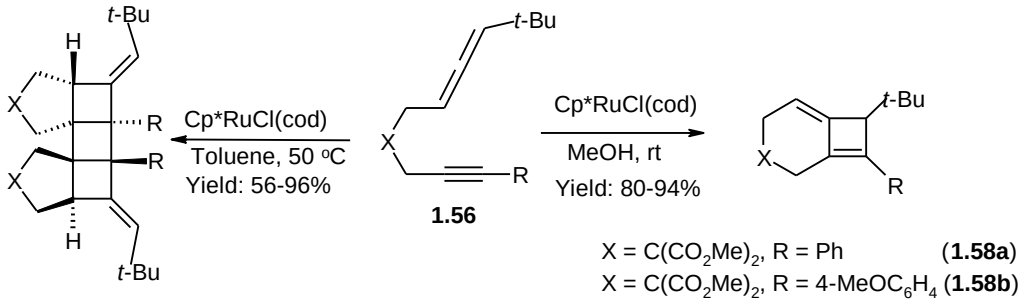


1.54

R^1 = Ph, R^2 = H (**1.55a**, 68%)
R^1 = 1-cyclohexene, R^2 = H (**1.55b**, 77%)
R^1 = C_4H_9, R^2 = H (**1.55c**, 33%)
R^1 = Ph, R^2 = Me (**1.55d**, 66%)

Sato and co-workers reported a Ru-catalyzed cyclodimerization of allenynes **1.56** to give a pentacyclic compound **1.57a-c** in toluene, whereas, a [2+2] cycloaddition of the same substrate is observed in methanol to give various bicyclo[4.2.0]octa-1(8),5-diene derivatives **1.58a-c** (Scheme 1.26).[36] Thus, the authors observed a dramatic change in reaction pathway of cyclization allenynes depending on the nature of the solvent employed. They also established that the [2+2] cycloaddition was catalyzed by a cationic ruthenium complex generated *in situ* from Cp*RuCl(cod) [chloro(1,5-cyclooctadiene)(pentamethylcyclopentadienyl)ruthenium] and methanol.

Scheme 1.26



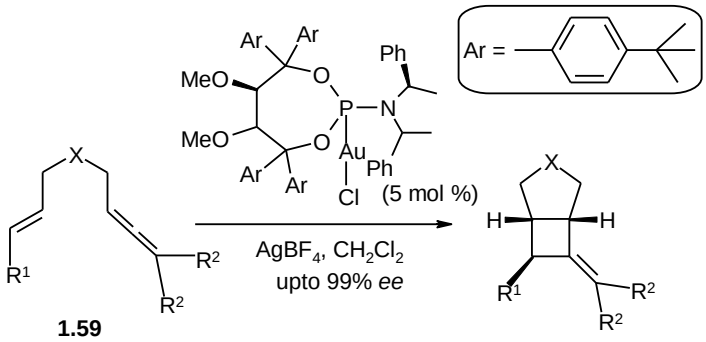
1.56

X = $C(CO_2Me)_2$, R = Me (**1.57a**)
X = $C(CO_2Me)_2$, R = Ph (**1.57b**)
X = NTs, R = Me (**1.57c**)

X = $C(CO_2Me)_2$, R = Ph (**1.58a**)
X = $C(CO_2Me)_2$, R = 4-$MeOC_6H_4$ (**1.58b**)
X = NTs, R = Me (**1.58c**)

A powerful phosphoramidite gold catalyst has been developed by Furstner *et al*. for intramolecular [2+2] cycloaddition of allenenes **1.59** to give compounds **1.60a-e** [37] (Scheme 1.27). By using this catalyst, even the *N*-tosyl derivatives showed excellent optical purity of 95% ee.

Scheme 1.27

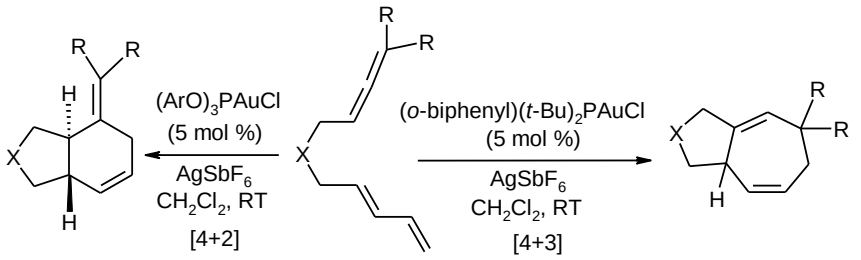


1.59

X = $C(CO_2Me)_2$, R^1 = Ph, R^2 = Me (**1.60a**, 91%)
X = $C(CO_2Bn)_2$, R^1 = Ph, R^2 = Me (**1.60b**, 98%)
X = NTs, R^1 = Ph, R^2 = Me (**1.60c**, 52%)
X = $C(CO_2Me)_2$, R^1 = 4-$MeOC_6H_4$, R^2 = Me (**1.60d**, 94%)
X = $C(CO_2Me)_2$, R^1 = Ph, R^2, R^2 = cyclohexyl (**1.60e**, 93%)

Toste and co-workers demonstrated a high selective intramolecular [4+2] and [4+3] cycloaddition reaction of allene-dienes **1.61** by gold(I)-catalysis.[38] The product selectivity in this gold(I)-catalyzed reaction is modulated to the [4+2] cycloadduct side **1.62a-c** by the use of arylphosphitegold(I) complexes whereas in favor of [4+3] adduct side **1.63a-c** by using di-*tert*-butylbiphenylphosphinegold(I) [38a] (Scheme 1.28). The same group achieved an enantioselectivity of up to 99% *ee* of [4+2]-cycloadduct **1.62a** by the use of suitable chiral phosphoramiditegold(I) complexes as catalysts.[38b]

Scheme 1.28



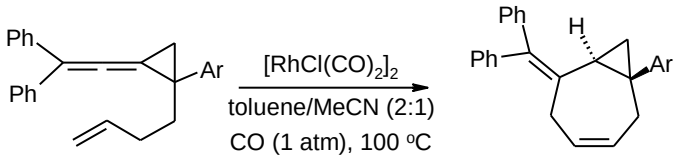
(Ar = 2, 4-di-tert-butylphenyl) **1.61**

R = Me, X = $C(CO_2Me)_2$ (**1.62a**, 89%)
R = Me, X = NTs (**1.62b**, 83%)
R,R = cyclohexyl, X = $C(CO_2Me)_2$ (**1.62c**, 81%)

R = Me, X = $C(CO_2Me)_2$ (**1.63a**, 85%)
R = Me, X = NTs (**1.63b**, 83%)
R,R = cyclohexyl, X = $C(CO_2Me)_2$ (**1.63c**, 81%)

Recently, an efficient catalytic system for the intramolecular ene reaction of allene and alkene of diarylvinylidenecyclopropanes **1.64** to compounds **1.65** has been established by Shi *et al*. (Scheme 1.29).[39] This reaction was achieved by using $[RhCl(CO)_2]_2$ as the catalyst in co-solvents of toluene and acetonitrile. Acetonitrile was found to play a crucial role in controlling the reaction towards the formation of bicyclo[5.1.0]octylene derivatives **1.65**. This catalytic system without using acetonitrile was found to result in intramolecular [2+2] cycloaddition adducts.

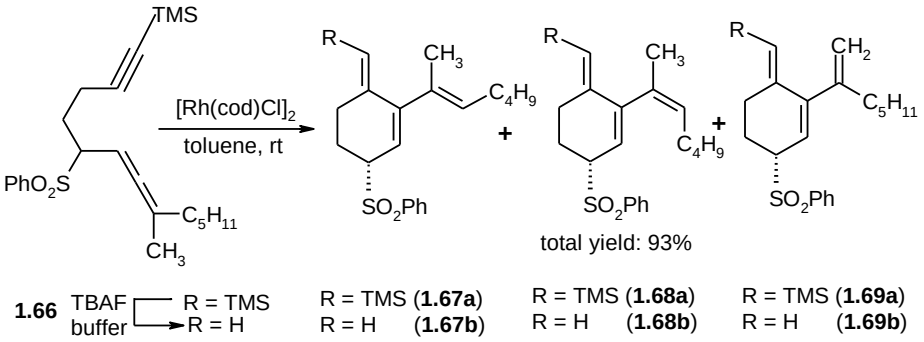
Scheme 1.29



1.64 **1.65**

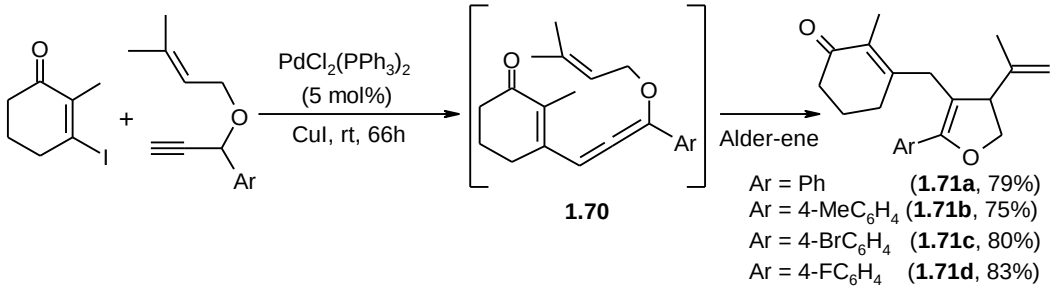
A rhodium catalyzed intramolecular Alder-ene reaction of allene-ynes **1.66** has been demonstrated by Brummond and McCabe.[40] This allenyl substitution pattern gave three cross-conjugated triene products **1.67a-b**, **1.68a-b** and **1.69a-b** (Scheme 1.30). The selectivity of this transformation is controlled by reaction temperature, solvent and catalyst.

Scheme 1.30



An interesting sequential reaction involving Pd-catalyzed coupling, propargyl-allenyl isomerization, and Alder-ene cycloaddition is reported by Huang and co-workers (Scheme 1.31).[41] They describe a facile synthetic route to not-so-readily available 2,3-dihydrofurans **1.71a-d** from electron-deficient vinyl or aromatic halides and 1-aryl-prop-2-ynyl 3′-methylbut-2′-enyl ethers *via* intermediate **1.70** (Scheme 1.31).

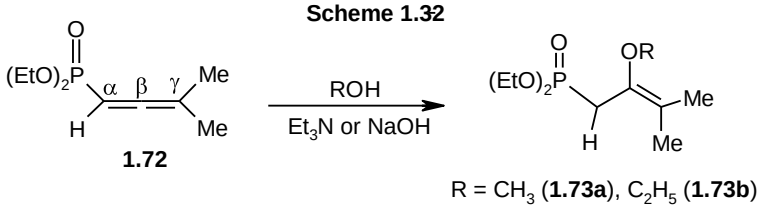
Scheme 1.31



1.32 Nucleophilic addition and cyclization reactions of allenes

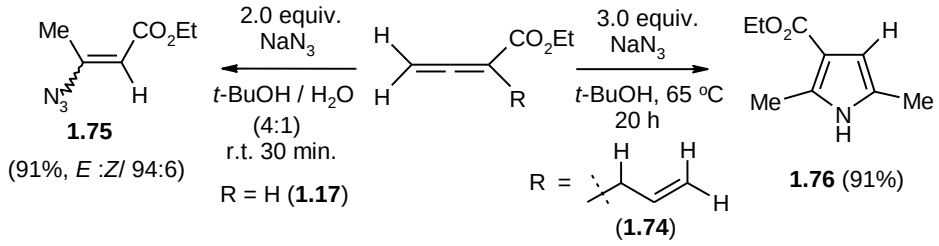
Nucleophilic addition forms an important class of reactions allowing the conversion of C=C moiety into a range of important functional groups. Since allene is an unsaturated hydrocarbon having two cumulative double bonds, the incoming nucleophile can attack any one of the three carbon atoms. If one of the substituents on the allene is electron-withdrawing (e.g. ester or phosphonate), the nucleophile attacks at central carbon atom with only very limited exceptions.[42] Allenylphosphonate **1.72** reacts with alcohols in the presence of NaOH or triethylamine to produce allylphosphonates **1.73a-b** (Scheme 1.32).[43]

Scheme 1.32



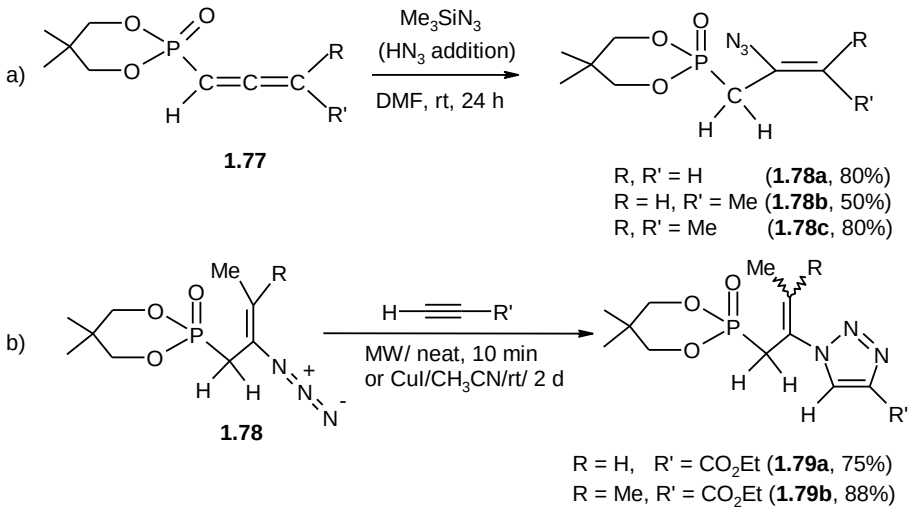
Zhang and co-workers described the nucleophilic addition of sodium azide to 1,2-allenyl ester **1.17** to form vinyl azide **1.75** in good yield with excellent regio- and stereo-selectivity. Interestingly, the use of 1-allyllic 1,2-allenyl ester **1.74** in this reaction led to the pyrrole **1.76** *via* domino cyclization and aromatization process (Scheme 1.33).[44] This reaction represents a novel route to substituted pyrroles.

Scheme 1.33



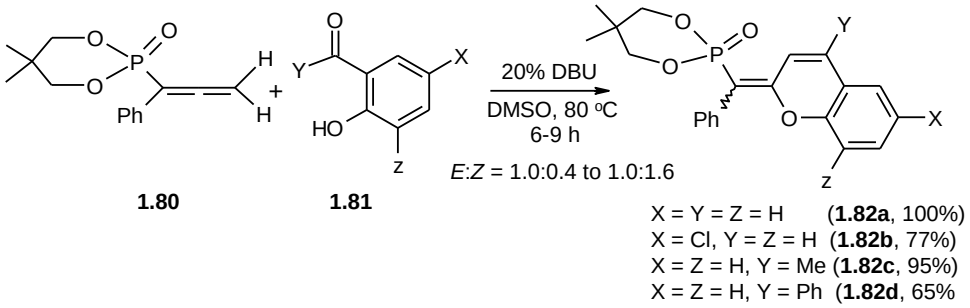
A straightforward method for the synthesis of phosphorus based vinyl azides **1.78a-c** regioselectively by the reaction of allenylphosphonates **1.77** with trimethylsilyl azide at ambient temperature has been reported from our laboratory (Scheme 1.34a).[45] These azides underwent 1,3-dipolar cycloaddition with activated acetylenes to give the 1,2,3-triazoles in good yields (Scheme 1.34b).

Scheme 1.34



A DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) catalyzed cyclization reaction of allenylphosphonates with salicylaldehydes or hydroxyaceto-/benzophenones leading to phosphono-chromenes has been reported from our laboratory.[46] Allene **1.80** reacted with salicylaldehydes or hydroxyaceto-/benzophenones (**1.81**) in the presence of DBU (20 mol%) in DMSO as the solvent leading to phosphono-chromenes **1.82a-d** in good yields with an *E*/*Z* ratio up to 1.0:0.4 (Scheme 1.35). This reaction involves a nucleophilic attack of phenoxide ion at the β-position of allene followed by the cyclization.

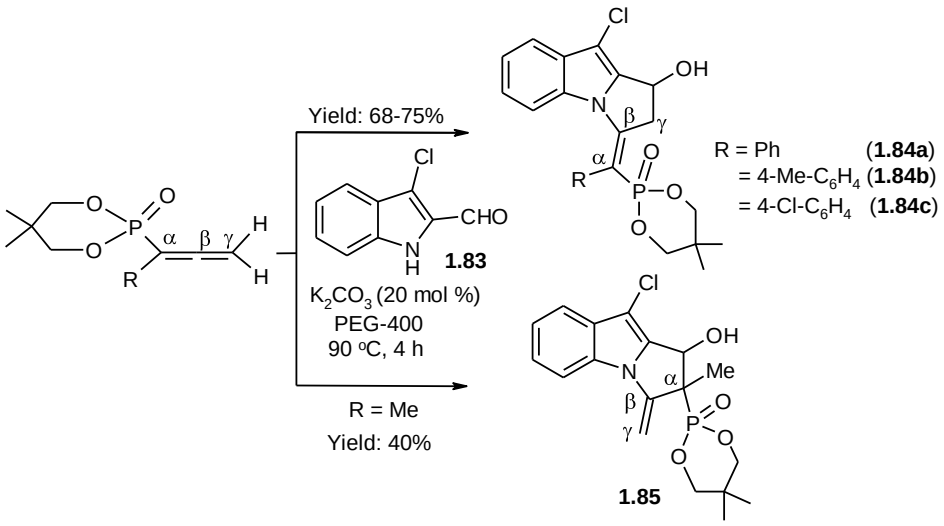
Scheme 1.35



In continuation of the above type of reactions, pyrrolo[1,2-a]indoles **1.84**-**1.85** were generated *via* base catalyzed domino cyclization of activated allenes with 3-chloro-2-formylindole **1.83** in PEG-400 medium.[47] An α-aryl substituted

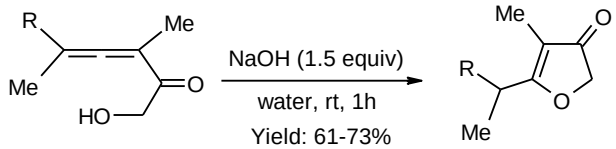
allenylphosphonates treated with 3-chloro-2-formylindoles gave the (β,γ)-cyclized product **1.84a-c**, while the α-methyl substituted allenylphosphonate resulted in the (β,α)-cyclized product **1.85** (Scheme 1.36). Thus the structure of the product depends on the type of substituent present on allene used. The allene containing a sulfonyl group ($ArSO_2$-) in place of phosphoryl group gave a result similar to that of allenylphosphonates.

Scheme 1.36



Very recently, Krause and Poonoth described a novel method for the synthesis of 3(2*H*)-furanones **1.87a-d** by cycloisomerization of allenic hydroxyketones **1.86** with aqueous NaOH (Scheme 1.37).[48] This transformation is achieved in water and in the absence of any expensive metal catalyst.

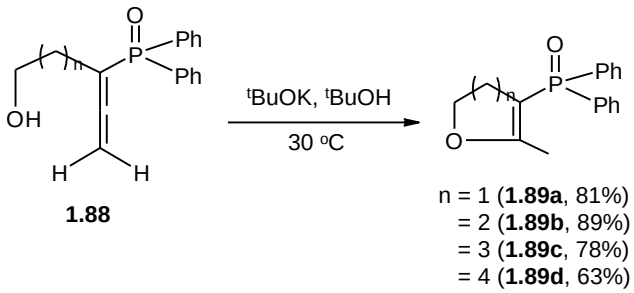
Scheme 1.37



A reliable and efficient method for constructing five- to eight-membered oxacycles has been developed by Mukai and co-workers.[49] Allenes **1.88** with both a

phosphine oxide group and a suitable hydroxyalkyl side chain at the α-position underwent an endo mode ring-closing reaction to give five- to eight-membered oxacycles **1.89a-d** in good yields (Scheme 1.38). This method also worked well for allenes having -$PO(OEt)_2$, -SOPh and -SO_2Ph groups.

Scheme 1.38

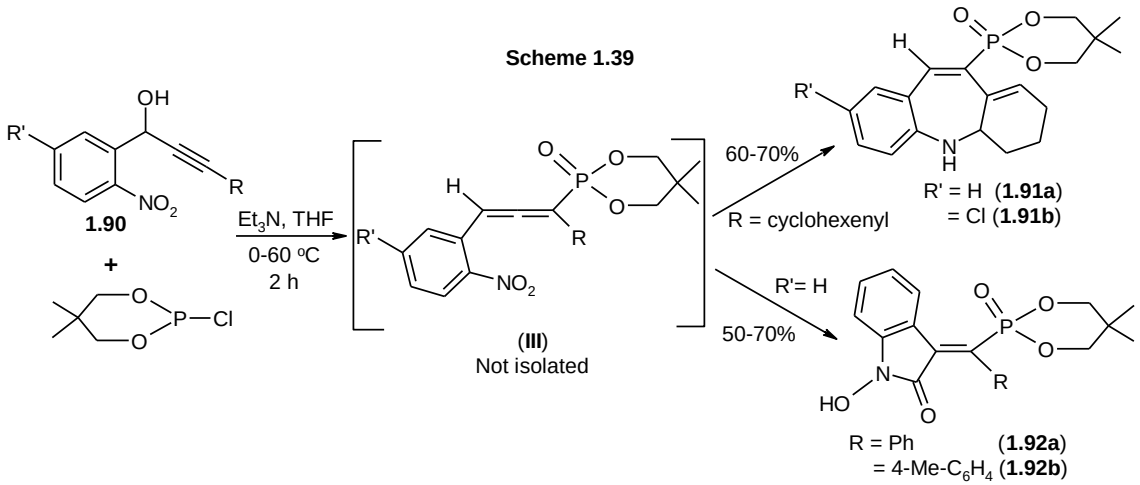


1.88

n = 1 (**1.89a**, 81%)
= 2 (**1.89b**, 89%)
= 3 (**1.89c**, 78%)
= 4 (**1.89d**, 63%)

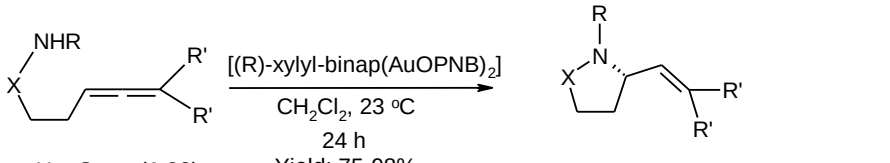
A facile and efficient formation of novel phosphono-(tetrahydro)dibenzazepines and *N*-hydroxyindolinones was explored very recently in our laboratory.[50] This is the traditional pathway for the synthesis of allene (**III**), which involves the treatment of functionalized propargyl alcohols **1.90** with P(III)-Cl precursor in the presence of a base (Scheme 1.39). Use of cyclohexenyl substituted propargyl alcohol resulted in the formation of tetrahydrodibenzazepine derivatives **1.91**, whereas phenyl substitution led to *N*-hydroxyindolinones **1.92**.

Scheme 1.39



Toste and co-workers developed a method to access a series of chiral vinyl isoxolidines, oxazines, and differentially protected pyrazolidines by the enantioselective gold(I)-catalysis.[51] Intramolecular hydroaminations and hydroalkoxylations of allenes with hydroxylamines (**1.93**) and hydrazines (**1.94**) led to products **1.95a-c** and **1.96a-c** respectively (Scheme 1.40). Chiral biarylphosphinegold(I) complexes are suitable catalysts for the enantioselective addition of nitrogen nucleophiles to allenes.

Scheme 1.40



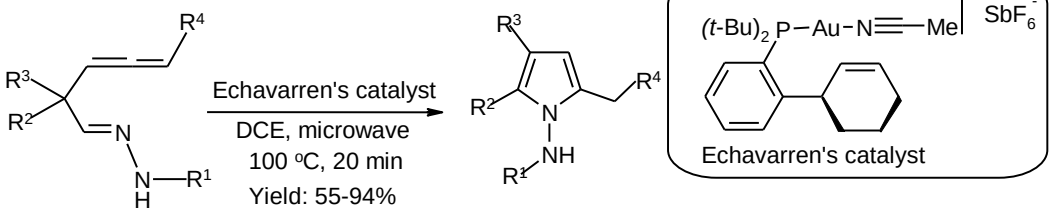
X = O (**1.93**)
X = NBoc (**1.94**)

Boc = *t*-butoxycarbonyl
Mts = 2-mesitylsulfonyl

X = O, R = Boc, R' = Me (**1.95a**)
X = O, R = Boc, R',R' = -$(CH_2)_4$- (**1.95b**)
X = O, R = Boc, R',R' = -$(CH_2)_5$- (**1.95c**)
X = NBoc, R = Mts, R' = Me (**1.96a**)
X = NBoc, R = Mts, R',R' = -$(CH_2)_4$- (**1.96b**)
X = NBoc, R = Mts, R',R' = -$(CH_2)_5$- (**1.96c**)

An efficient access to multisubstituted *N*-aminopyrroles, *via* a gold(I)-catalyzed cycloisomerization of β-allenylhydrazones is developed by Fenterbank *et al*.[52] This reaction involves an intramolecular nitrogen nucleophilic attack at the central carbon atom of the allene **1.97** under microwave conditions and affords **1.98a-e** (Scheme 1.41**)**. This protocol is effective for a broad range of *N*-substituted precursors and works even when either alkyl or aryl group is at the terminal allenyl carbon atom.

Scheme 1.41

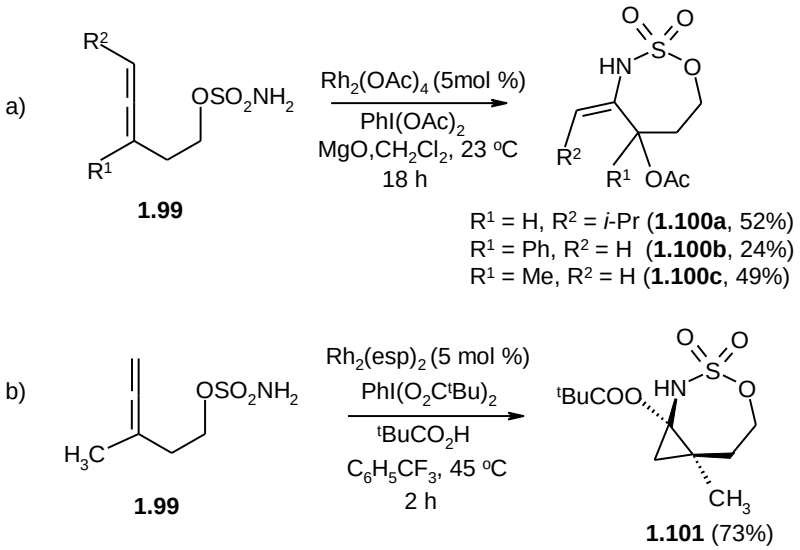


1.97

R^1 = Ts, R^2 = R^3 = R^4 = Me (**1.98a**)
R^1 = Ts, R^2 = R^3 = Me, R^4 = Ph (**1.98b**)
R^1 = Ts, R^2 = R^3 = Ph, R^4 = Me (**1.98c**)
R^1 = Ts, R^2 = C_2H_5, R^3 = R^4 = Me (**1.98d**)
R^1 = Ts, R^2 = Ph, R^3 = R^4 = Me (**1.98e**)

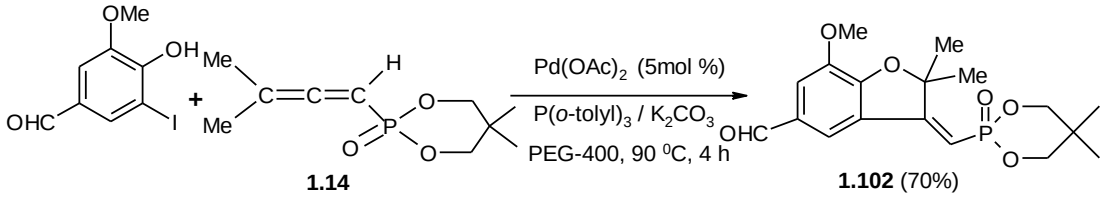
Recently, a rhodium(II)-mediated intramolecular amination of allenyl sulfamate was reported by Robertson *et al.*[53] This reaction involves participation of the sulfamate functionality of allenes (**1.99**) to form products of the type **1.100a-c** (Scheme 1.42a). It provides opportunity for compelling new synthetic methodology when combined with substitution by functionalized nucleophiles. Intramolecular amination of the same type of allenyl sulfamate substrate **1.99** was used by Blakey and Stoll as a synthetic approach to highly substituted aminocyclopropane **1.101** (Scheme 1.42b).[54]

Scheme 1.42



From our research group, Pd-catalyzed coupling reactions of allenylphosphonates with aryl iodides, iodophenols, iodobenzoic acid were investigated.[4d] Recently, a modified procedure leading to regioselective aldehyde-functionalized benzofurans from allenylphosphonates and substituted iodophenols in PEG-400 as the solvent has also been reported by our group.[55] Allenylphosphonate **1.14** reacted with 5-iodovanilin in the presence of $Pd(OAc)_2/P(o\text{-tolyl})_3$ and K_2CO_3 to give the corresponding phosphono-benzofuran **1.102** in good yield (Scheme 1.43).

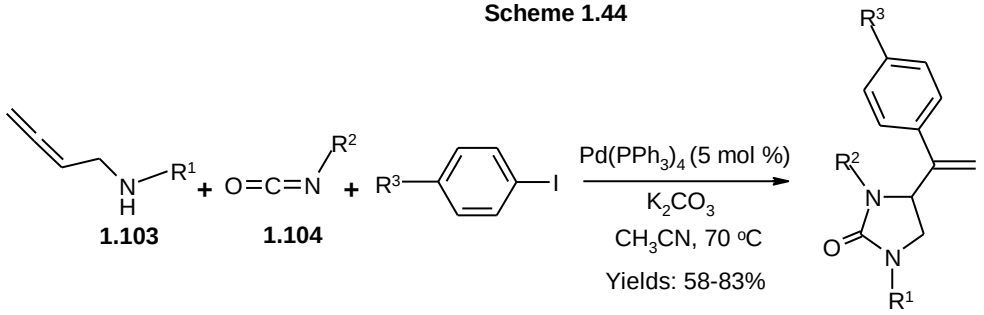
Scheme 1.43



1.14 **1.102** (70%)

Ma *et al.* demonstrated an interesting three-component cascade reaction of 2,3-allenyl amines (**1.103**) with isocyanates (**1.104**) and organic halides which provides an elegant methodology for the synthesis of polysubstituted imidazolidinones **1.105a-d** (Scheme 1.44).[56] This method offers several advantages such as good functional-group tolerance, mild reaction conditions, high yields, and easily accessible starting materials, which is of board interest for medicinal chemistry. In this transformation, one C-C bond and two C-N bonds are simultaneously formed with the cleavage of two π bonds.

Scheme 1.44

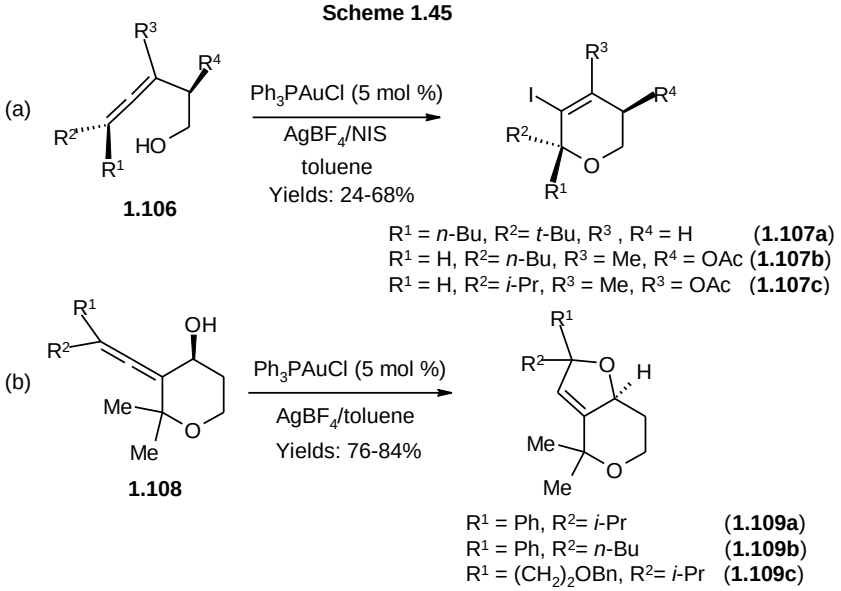


1.103 **1.104**

R^1 = PMB, R^2= Ph, R^3 = H (**1.105a**)
R^1 = *n*-Bu, R^2= Ph, R^3 = Me (**1.105b**)
R^1 = Bn, R^2= 4-$MeOC_6H_4$, R^3 = Me (**1.105c**)
R^1 = Bn, R^2= 4-$NO_2C_6H_4$, R^3 = Me (**1.105d**)

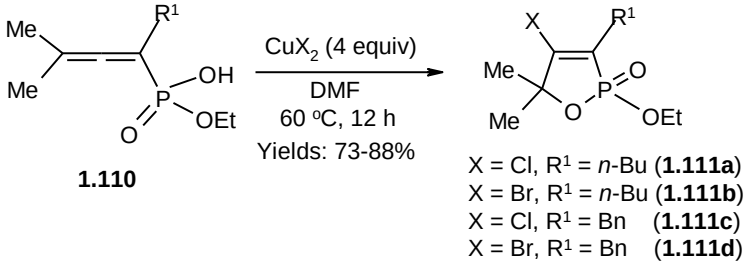
Krause and Gockel developed an efficient and stereoselective access to iodinated dihydropyrans (**1.107a-d**) in good yields from β-hydroxyallenes (**1.106**) by gold catalyzed cyclization (Scheme 1.45a).[57] Subsequent functionalization by palladium-catalyzed cross-coupling opened an access to α-hydroxyallenes. These compounds (**1.108**) were further converted to furopyrans **1.109a-d** *via* a second gold-catalyzed cyclization (Scheme 1.45b). Thus, the synthesis of the desired furopyrans involved a gold/palladium/gold-catalyzed cyclization/cross-coupling sequence.

Scheme 1.45



Ma and co-workers utilized a CuX_2 [X= Cl or Br] mediated halolactonization of monoesters of 1,2-allenyl phosphonic acids (**1.110**) under mild condition for differently substituted allenic substrates giving the 4-halo-2,5-dihydro[1,2]oxaphosphole 2-oxides **1.111a-d** in good yields (Scheme 1.46).[58] The authors reported that this method provides a very useful synthetic strategy for the construction of relatively more complex phosphorus containing compounds and a possibility for finding potentially bioactive hits in medicinal chemistry.

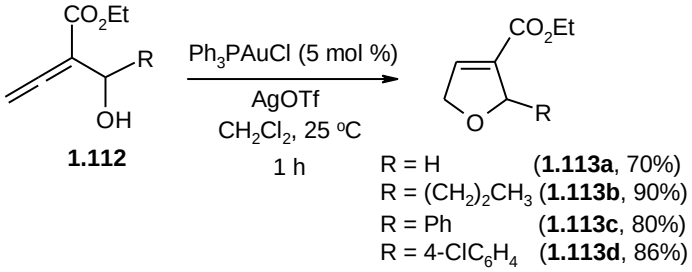
Scheme 1.46



An efficient synthetic route to 2-alkyl- and aryl-3-ethoxycarbonyl-2,5-dihydrofurans **1.113a-d** through gold-catalyzed intramolecular hydroalkoxylation of hydroxyallenes **1.112** by a 5-*endo* mode (Scheme 1.47) was reported by Lee *et al.*[59]

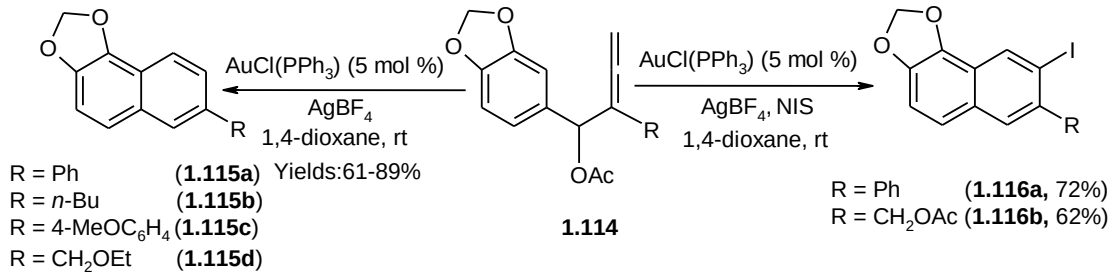
This method paves a way to a wide range of functionalized 2,5-dihydrofuran derivatives.

Scheme 1.47



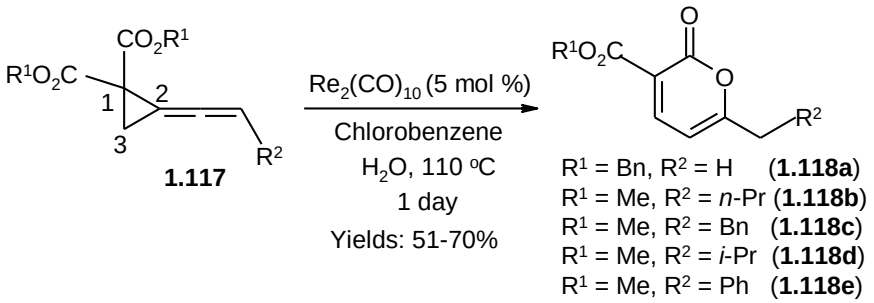
An effective synthetic strategy to generate substituted naphthalene **1.115a-d** and iodonaphthalene **1.116a-b** derivatives has been developed by Ma and co-workers through an intramolecular *C*-alkylation of 1-aryl buta-2,3-dienyl acetate **1.114** catalyzed by employing AuCl(PPh_3) (Scheme 1.48).[60] The substituent loading capability of both the aromatic ring and the allene moiety made it possible to introduce various substituents at different positions on the naphthalene skeleton.

Scheme 1.48



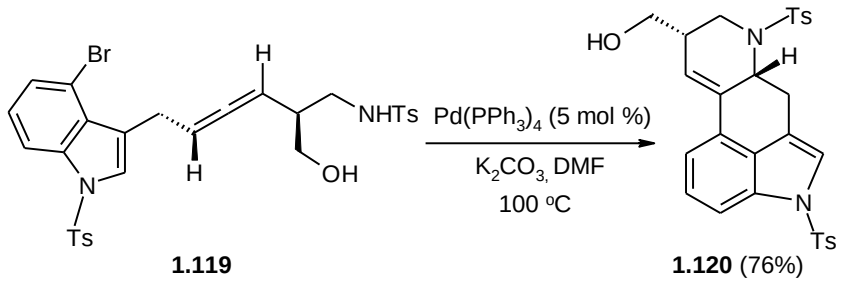
Shi and Wu reported an interesting ring-opening reaction of vinylidenecyclopropane diesters **1.117** through a highly regioselective carbon–carbon bond cleavage pathway catalyzed by $Re_2(CO)_{10}$ to produce 2*H*-pyran-2-one (**1.118a-e**) derivatives in moderate to good yields (Scheme 1.49).[61] The presence of two electron-withdrawing groups at the geminal position of cyclopropane ring significantly facilitates C–C bond cleavage, which exclusively takes place at C1–C2, leading to the tandem ring-opening reaction.

Scheme 1.49



Ohno *et al.* reported total synthesis of the biologically important indole alkaloids (+)-lysergol, (+)-isolysergol and (+)-lysergic acid.[62] A key step employed in this total synthesis is the domino Pd(0) catalyzed cyclization of substituted allene bearing amino and bromoindolyl groups **1.119** to form **1.120** (Scheme 1.50).

Scheme 1.50



Apart from the above, three other developments are worth mentioning but not directly relevant to the thesis and hence are not elaborated further.

(i) Fu and Sun have described an asymmetric γ-sulfenylation of allenoates in the presence of TangPhos (a bisphosphine) as the catalyst.[63]

(ii) Hammond and co-workers investigated the reactivity of alkynylenolates in the reactions of allenic ketones and vinyl ketone.[64] They found that use of tetrabutylammonium fluoride or KOH/K_2CO_3 as a base led to different types of Michael addition products.

(iii) A $FeCl_3/PdCl_2$ co-catalyzed protocol involving coupling cyclization of 2,3-allenoates with allylic bromides leading to β-allylic substituted butenolides was reported by Ma and co-workers.[65]

OBJECTIVES OF THE PRESENT WORK - PART A

The main objective of this part of the present work is to develop allenylphosphonate chemistry. Specifically, it is intended to explore the following:

(i) Synthesis of new functionalized allenylphosphonates using a variety of propargyl alcohols and a suitable P^{III}-Cl precursor,

(ii) To explore the reactivity of phosphorus-based and related allenes in the cycloaddition reactions with 1,5-diphenylisobenzofuran and anthracene,

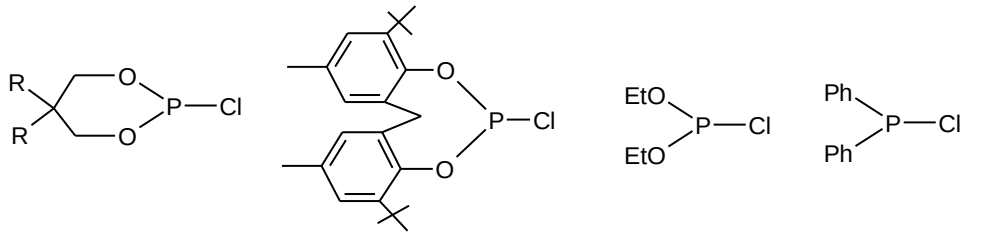
(iii) To investigate base or Lewis acid-catalyzed intramolecular cyclization reactions of allenylphosphine oxides and

(iv) To study the reactivity of phosphorus-based vinyl azides in the formation of nitrogen-heterocycles.

RESULTS AND DISCUSSION

The P^{III}-Cl precursors $(OCH_2CR_2CH_2O)PCl$ [R = Me (**1a**)[66a], Et (**1b**)[66b]], $CH_2[6\text{-}t\text{-Bu-4-Me-}C_6H_2O]_2PCl$ (**1c**),[67] $(EtO)_2PCl$ (**1d**)[68] and Ph_2PCl (**1e**) used in the present study are shown in Chart 1. All these compounds are hydrolytically unstable, but can be handled under normal inert atmosphere conditions.

Chart 1



R = Me [**1a**, δ(P): 145.8]
= Et [**1b**, δ(P): 148.2]

1c [δ(P): 153.7]

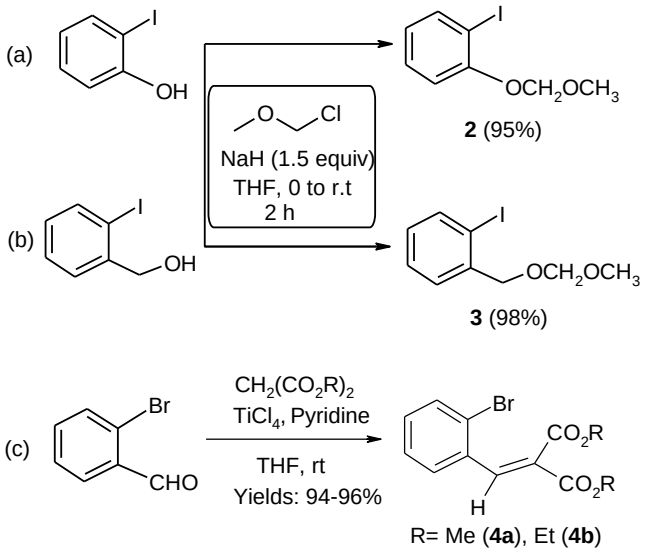
1d [δ(P): 145.8]

1e [δ(P): 82.1]

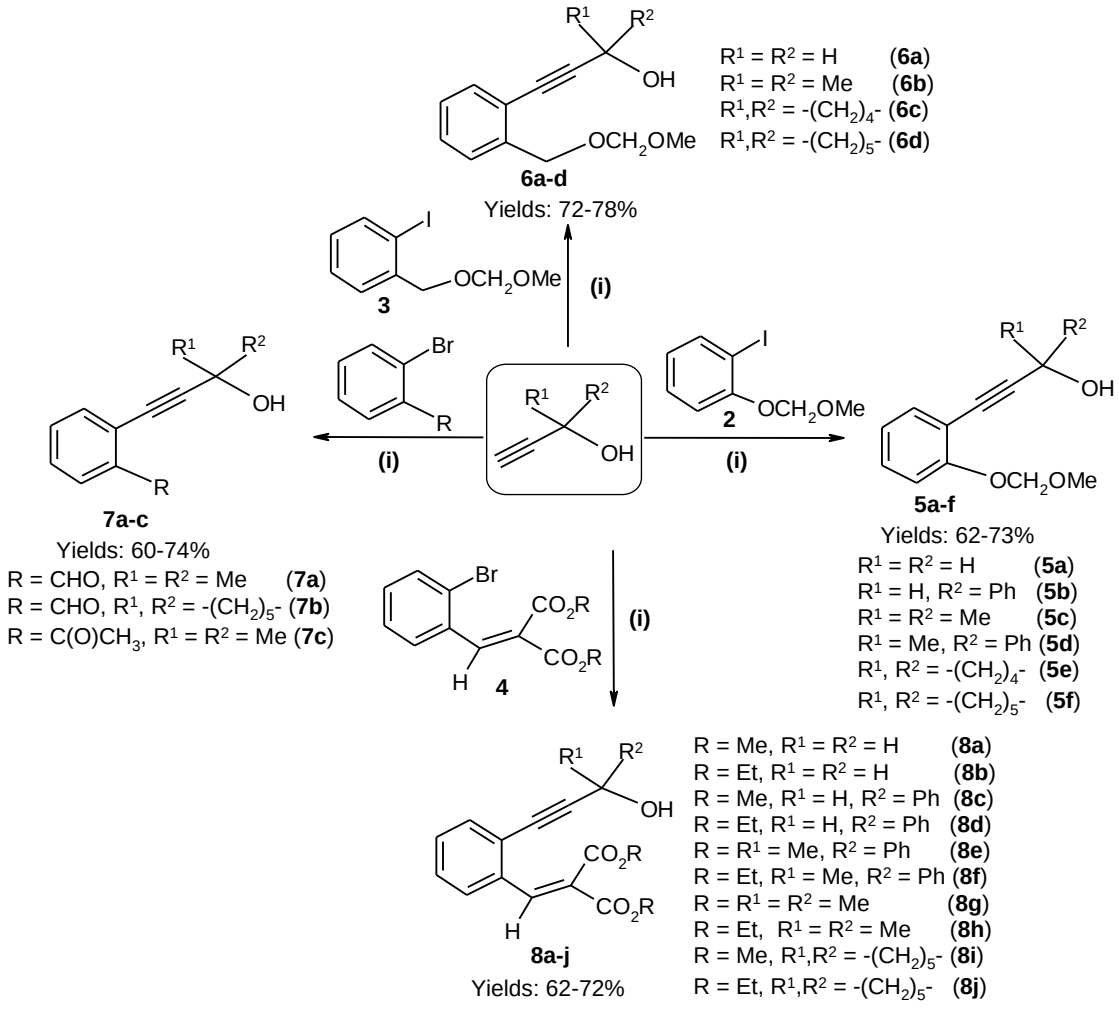
2.1 Synthesis of substituted haloarenes 2-4, propargylic precursors 5-8 and ester allenes 9a-b

The iodoarenes **2**[69a] and **3**[69b] required for the synthesis of propargyl alcohols are prepared by treating the corresponding alcohols with chloromethyl methyl ether in the presence of sodium hydride (NaH) in THF (Scheme 1). 2-(2-Bromo-benzylidene)-malonic acid dimethyl (diethyl) esters **4a** and **4b** are prepared according to a literature procedure (Scheme 1).[70] Various functionalized propargyl alcohols **5-8** were also obtained by following a standard method *via* Sonogashira coupling (Scheme 2).[71] Among these propargyl alcohols, only **5c**,[72] **7a**,[71a] and **8b**[73] are known; compounds **5a-b**, **5d-f**, **6a-d**, **7b-c**, **8a**, and **8c-j** are new. They can be characterized readily by IR [υ(C≡C) ~1600 and υ(OH) ~ 3400 (br) cm^{-1}] and NMR [^1H, ^{13}C] spectroscopic techniques. They are stable viscous liquids. Ester allenes (2,3-allenoates) **9a-b** were synthesized by following known procedures.[74]

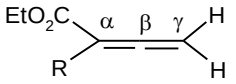
Scheme 1



Scheme 2



(i) Conditions: $PdCl_2(PPh_3)_2$/ CuI/ Et_3N/ CH_3CN/ 70 ^oC/ 4-6 h



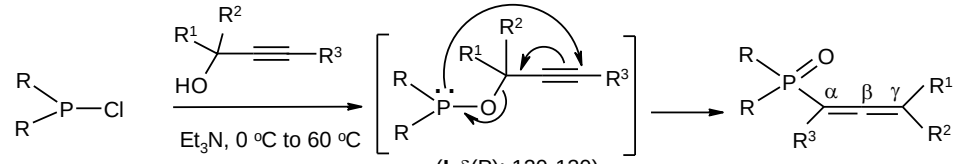
R = H (**9a**)
= CH_2CO_2Et (**9b**)

2.2 Reactions of P^{III}-Cl compounds with propargyl alcohols

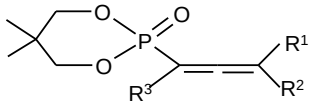
2.21 Synthesis of functionalized allenylphosphonates [10a-j, 11a-d] and allenylphosphine oxides [12a-h, 13a-f, 14a-d]

Allenylphosphonates **10a-j/ 11a-d** and allenylphosphine oxides **12a-h/ 13a-f/ 14a-d** are prepared by a method previously reported from our laboratory which involves the reaction of P^{III}-Cl precursor with the appropriate propargyl alcohol in the presence of triethylamine (Scheme 3).[10] Among these, allenes **10f**, **11a-d**, **12g**, **13a-f**, **14a-d** are new. These allenes are fairly stable in the solid state in air for a day, but can be preserved for a few months at low temperature (4 ^oC) under an inert atmosphere. In the IR spectra, they show a characteristic strong band at 1920-1975 cm^{-1} due to ν_{asym}(C=C=C).[75] The ^{31}P NMR spectra of allenylphosphonates **10a-j** show a peak at δ ~12, whereas allenylphosphine oxides **12a-h**, **13a-f** and **14a-d** exhibit a peak in the range δ 24-31. The ^{31}P NMR chemical shifts of cyclohexenyl substituted allenes **11a-c** appear up-field to that for the allene **11d**, most likely due to the effect of the ring at phosphorus.[76] Allenes **11a-d** exhibit a signal in the region of δ ~ 6.24-6.48 due to the cyclohexenyl =C*H* proton in the ^1H NMR spectra. In the ^{13}C NMR spectra, the *α*-carbon (to phosphorus) appears as a doublet at δ ~ 92.0 for **10a-j** and **11a-d** with ^1J(P-C) ~ 183.0 Hz and at δ 95-100 for **12a-h**/ **13a-f**/ **14a-d**, all with ^1J(P-C) ~ 103 Hz. The PC=*C* signal for all these compounds appears as a doublet in the region δ 206-214 [^2J(P-C) ~ 6.0-7.0 Hz]. However, the observed coupling constants [*J*(P-H) or *J*(P-C)] of allenylphosphine oxides **12a-h**-**14a-d** are lower than those observed for allenylphosphonates **10a-j**-**11a-d**. Formation of these allenylphosphonates/ allenylphosphine oxides occurs *via* a *pseudo*-Claisen rearrangement of the intermediate P(III) precursor as shown in Scheme 3.[10] Since this aspect is fairly well-known, it is not elaborated here.

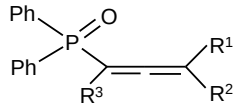
Scheme 3



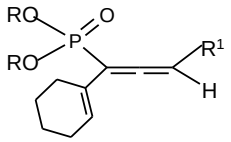
R,R = $OCH_2CMe_2CH_2O$ (**1a**)
R = Ph (**1e**)



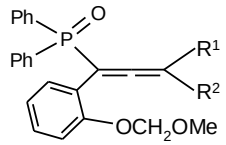
$R^1 = R^2 = R^3 = H$ [**10a**, δ(P): 7.4; 68%]
$R^1 = R^3 = H$, $R^2 = Me$ [**10b**, δ(P): 7.9; 64%]
$R^1 = R^2 = Me$, $R^3 = H$ [**10c**, δ(P): 9.8; 69%]
$R^1 R^2 = -(CH_2)_5-$, $R^3 = H$ [**10d**, δ(P):10.0; 86%]
$R^1 = R^2 = H$, $R^3 = Me$ [**10e**, δ(P): 12.2; 85%]
$R^1 = R^2 = H$, $R^3 = n$-Bu [**10f**, δ(P): 11.9; 76%]
$R^1 = R^2 = H$, $R^3 = Ph$ [**10g**, δ(P): 6.6; 70%]
$R^1 = R^2 = H$, $R^3 = p$-CH_3-C_6H_4 [**10h**, δ(P): 7.8; 81%]
$R^1 = R^2 = H$, $R^3 = p$-OCH_3-C_6H_4 [**10i**, δ(P): 7.5; 79%]
$R^1 = H$, $R^2 =$ -CH=CHMe, $R^3 = Ph$ [**10j**, δ(P): 6.7; 72%]



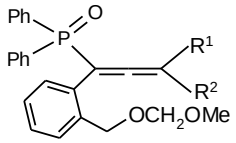
$R^1 = R^2 = R^3 = H$ [**12a**, δ(P): 24.6;69%]
$R^1 = H$, $R^2 = Me$, $R^3 = H$ [**12b**, δ(P): 25.1; 66%]
$R^1 = R^2 = Me$, $R^3 = H$ [**12c**, δ(P): 27.1; 73%]
R^1, $R^2 = -(CH_2)_5-$, $R^3 = H$ [**12d**, δ(P):26.5; 74%]
$R^1 = R^2 = H$, $R^3 = Me$ [**12e**, δ(P): 30.3; 68%]
$R^1 = R^2 = H$, $R^3 = Ph$ [**12f**, δ(P): 30.2; 69%]
$R^1 = R^2 = Me$, $R^3 = o$-$C_2H_3OC_6H_4$ [**12g**, δ(P): 30.2;78%]
$R^1 = R^3 = H$, $R^2 = Ph$ [**12h**, δ(P): 30.4; 65%]



$(R)_2 = -CH_2C(Me)_2CH_2-$, $R^1 = H$ [**11a**, δ(P): 8.1; 64%]
$(R)_2 = -CH_2C(Et)_2CH_2-$, $R^1 = H$ [**11b**, δ(P): 9.1; 60%]
$(R)_2 = -CH_2C(Me)_2CH_2-$, $R^1 = Ph$ [**11c**, δ(P): 6.8; 74%]
R = Et, $R^1 = H$ [**11d**, δ(P): 16.3; 65%]



$R^1 = R^2 = H$ [**13a**, δ(P): 27.9; 79%]
$R^1 = Ph$, $R^2 = H$ [**13b,** δ(P): 28.9; 80%]
$R^1 = R^2 = Me$ [**13c,** δ(P): 30.6; 84%]
$R^1 = Me$, $R^2 = Ph$ [**13d,** δ(P): 30.4; 85%]
$R^1 R^2 = -(CH_2)_4-$ [**13e,** δ(P): 31.1; 82%]
$R^1 R^2 = -(CH_2)_5-$ [**13f,** δ(P): 30.8; 82%]



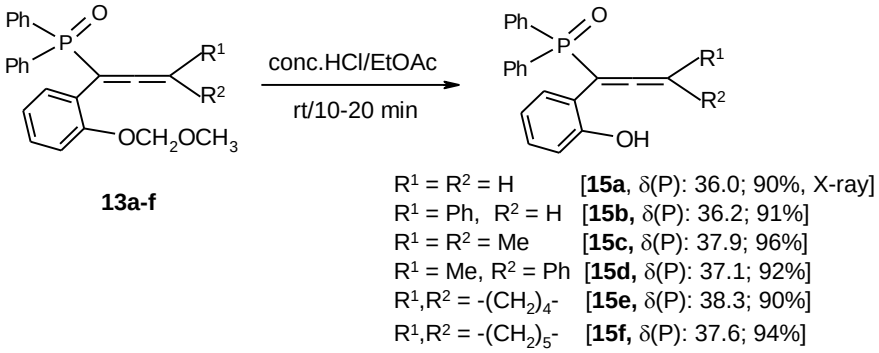
$R^1 = R^2 = H$ [**14a,** δ(P): 30.3; 79%]
$R^1 = R^2 = Me$ [**14b**, δ(P): 30.3; 81%]
$R^1, R^2 = -(CH_2)_4-$ [**14c**, δ(P): 31.1; 72%]
$R^1, R^2 = -(CH_2)_5-$ [**14d**, δ(P): 30.2; 75%]

2.22 Hydrolysis of the methoxymethyl (MOM)-protected allenes 13a-f: Formation of phenolic allenes 15a-f

In an effort to add additional functionalities on the allene substrates, we have utilized the MOM-protected allenes **13a-f**. Thus, upon treatment of allenes **13a-f** with an excess of conc. HCl at room temperature, allenes **15a-f** having a phenolic –OH group could be readily obtained (Scheme 4). These compounds are characterized by spectroscopic and analytical techniques. In the IR spectra, they show a broad band at 3057-3061 corresponding to the υ(OH) and a strong band at

1925-1956 cm^{-1} due to ν_{asym}(C=C=C) of allene moiety. In the ^{1}H NMR spectra, we clearly observe a broad peak at δ ~ 10.8 due to O*H* proton. The ^{13}C NMR spectra show a doublet at δ 97.8-104.3 with ^{1}J(P-C) ~ 100.8 Hz for α-PC signal. The β-carbon (to phosphorus) for these compounds also appears as a doublet at δ 209-214 [^{2}J(P-C) ~ 6.0-9.0 Hz]. In order to fully authenticate the multifunctional nature, one of these compounds (**15a**) was also characterized by single crystal X-ray crystallography (Fig. 1). The presence of –OH group is readily discerned by the participation of OH in the intramolecular H-bonding with the P=O acceptor.

Scheme 4



13a-f

$R^1 = R^2 = H$ [**15a**, δ(P): 36.0; 90%, X-ray]
R^1 = Ph, R^2 = H [**15b,** δ(P): 36.2; 91%]
$R^1 = R^2$ = Me [**15c,** δ(P): 37.9; 96%]
R^1 = Me, R^2 = Ph [**15d,** δ(P): 37.1; 92%]
R^1,R^2 = -$(CH_2)_4$- [**15e,** δ(P): 38.3; 90%]
R^1,R^2 = -$(CH_2)_5$- [**15f,** δ(P): 37.6; 94%]

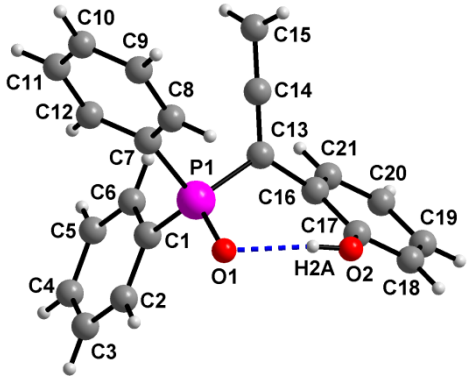
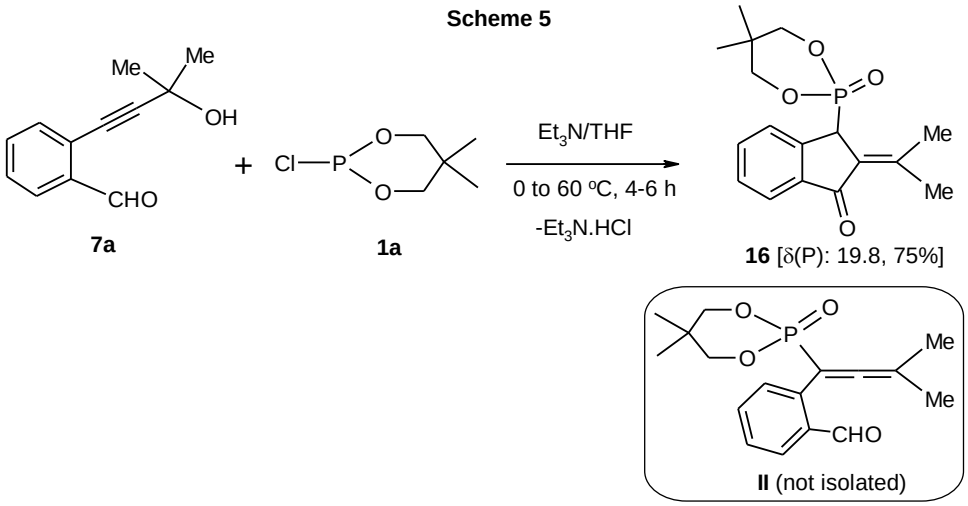


Figure 1. Molecular structure of compound **15a**. Two molecules are present in the asymmetric unit, but only one is shown for clarity. Selected bond lengths [Å] with esd's in parentheses: P1-C13 1.796(2), P2-C34 1.802(2), C13-C14 1.294(3), C14-C15 1.297(4), C34-C35 1.290(4), C35-C36 1.294(4). Intramolecular hydrogen bond parameters: O2–H2A…O1 0.81, 1.82, 2.619(3), 169.8°, O4-H4A…O3, 0.81, 1.82, 2.624(3), 169.1°.

2.23 Reaction of P^{III}-Cl compounds with aldehyde functionalized propargyl alcohols 7a-b- Formation of phosphono-indanone derivatives 16-19

Having synthesized a large number of allenes (cf. Scheme 3) we were interested in preparing the aldehyde functionalized allenes and utilize them further in cyclization reactions. Thus, we treated ($OCH_2CMe_2CH_2O$)PCl (**1a**) with the substituted propargyl alcohol **7a** (Scheme 5). But to our surprise, the reaction mixture showed a peak at 19.8 in the ^{31}P NMR spectrum instead of the one in the expected allene region (δ ~6.5-8.0 ppm). The IR spectrum of the isolated compound **16** did not exhibit any band in the region 1900-2000 cm^{-1} expected for the allene. The ^1H NMR spectrum showed a doublet at δ 4.56 with a *J*(P-H) of 23.2 Hz, which suggests the existence of PC*H* moiety. There are two singlets at δ 2.17 and 2.45 ascribable to =C(CH_3)$_2$ group. The ^{13}C NMR spectrum did not show any signal at δ 213-214 (absence of central carbon of allene) but there was a peak at δ 192.0 corresponding to a *C*=O group. Based on these, we surmised that this synthetic route afforded the ***unexpected cyclopentanone derivative*** **16** (Yield: 75%) instead of the expected allene **II**.

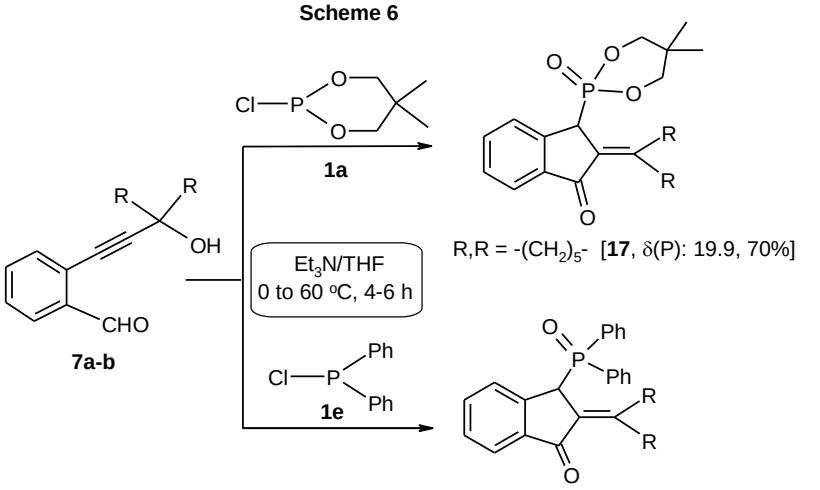
Scheme 5



After obtaining the above unexpected product **16**, we generalized the reaction by preparing more of this type of derivatives by the reaction of P^{III}-Cl precursors **1a** and **1e** with propargyl alcohols **7a-b**. The final compounds [**17-19**] were obtained in good yields (Scheme 6). All these products were well characterized by spectroscopic and analytical data. Some points about compound **16** are already mentioned above. In addition, they all show a band at 1680-1720 cm^{-1} in the IR

spectra due to the C=O stretch. In the ^{1}H NMR spectra a doublet in the region of δ 4.56- 5.06 is observed with a ^{2}J(P-H) of 23.2 Hz (for compounds **16-17**) or 17.2 Hz (for compounds **18-19**). The ^{13}C NMR spectra of **16-17** exhibit a characteristic doublet [^{1}J(P-C) ~ 136.9 Hz] for the P-C carbon at δ ~42.3. But in the case of compounds **18**-**19**, the doublet is observed in the downfield region [δ 47.7 and 47.1 respectively] with a lower coupling constant [62.5-62.7] as expected.[76] The structure of **18** is finally confirmed by X-ray crystallographic investigation (Fig. 2). The O2-C15 distance of 1.234(3) Å clearly shows the presence of C=O group. The C14-C22 distance of 1.337(4) Å shows that there is a double bond between these two atoms as depicted in the structural drawing (Scheme 6).

Scheme 6



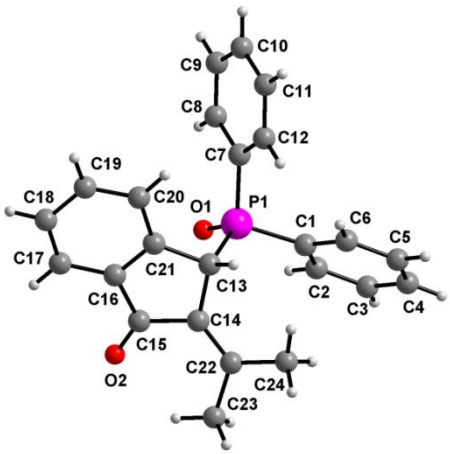
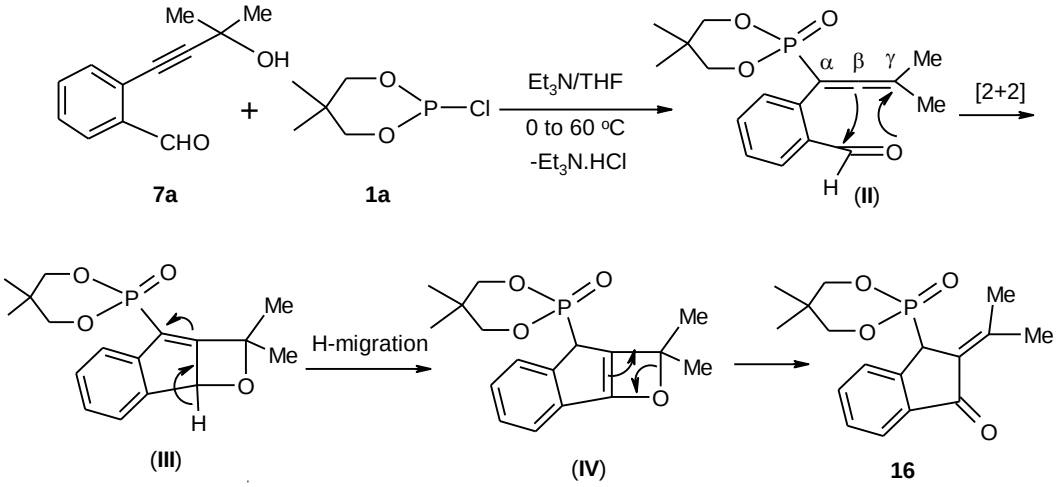


Figure 2. Molecular structure of compound **18**. Selected bond lengths [Å] with esd's in parentheses: P1-O1 1.4859(17), P1-C13 1.846(2), O2-C15 1.234(3), C13-C14 1.536(3), C14-C15 1.509(3), C14-C22 1.337(4), C15-C16 1.457(4).

The formation of unexpected phosphono-indanone derivatives **16-19** can be explained by the mechanism shown (for **16**) in Scheme 7. Initially formed allene intermediate **II** can undergo [2+2] cycloaddition leading to a polycyclic intermediate (**III**).[2a] H-migration in intermediate (**III**) then affords the allylphosphonate intermediate (**IV**). Finally, the four-membered ring can open up[77] to give the final product **16**. Isolation of allene **12g** from corresponding alcohol **7c** and Ph_2PCl (**1e**) under the same reaction condition provides proof for the existence of allene intermediate of the type **II**. In the presence of triethylamine, a nucleophilic attack of carbene formed from –CHO functionality of allene intermediate **II** is also possible; such a process can also lead to compound **16**.

Scheme 7

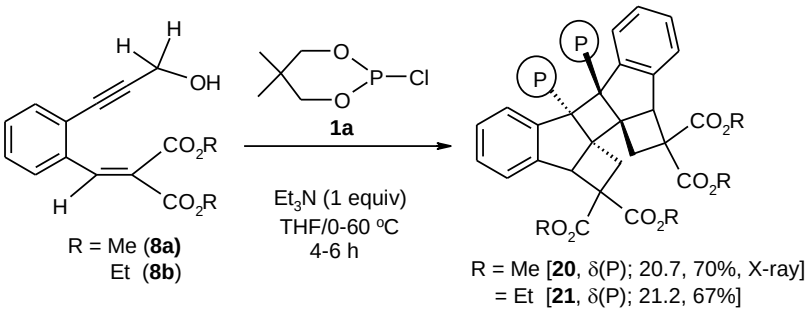


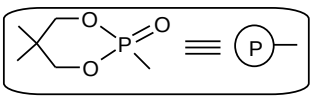
2.24 Reaction of P^{III}-Cl compounds with alkylidene functionalized propargyl alcohols 8a-j: Formation of fused polycyclics 20-32

Inspired by the above results, we focused our attention on the propargyl alcohols **8a-j** that contain an alkylidene group in place of the –CHO functionality. Thus, we treated **1a** with alcohol **8a** under the conditions employed for the synthesis of allenes. The ^{31}P NMR spectrum of corresponding reaction mixture showed a single peak at δ 20.7, which is again not in the region for the expected allene (cf. δ 6.6-7.5 for compounds **10g-j** in Scheme 3). In the ^{1}H NMR spectrum, two doublets in the region of δ 2.99 and 3.58 are observed with a *J*(H-H) of 14.8 Hz for each indicating the presence of an aliphatic CH_AH_B group. A singlet at δ 4.81 is present instead of expected peak at δ ~8.20 due to the alkylidene proton. Three signals at δ

33.0, 51.5 and 52.0 are seen in the ^{13}C NMR spectrum; the α-carbon appeared in the region of 63.5 with a ^{1}J(P-C) value 149.1 Hz. All these four signals give evidence for the presence of aliphatic carbons other than the ones at the 1,3,2-dioxaphosphorinane ring. There was no signal in the region δ 213-214 (central carbon of allene moiety). Hence, this compound (**20**) was subjected to single crystal X-ray crystallographic investigation. Very interestingly, this study revealed that it constitutes ***a rare brand of 3-fused cyclobutane ring system*** formed from two molecules each of propargylic residue and phosphorus containing moiety (Scheme 8 and Fig. 3). The three sets of carbon atoms [C6, C7, C23, C22], [C7, C8, C9, C10] and [C23, C24, C25, C26] constitute the three cyclobutane rings in the polycyclic frame work. Similarly, we synthesized compound **21** from the precursors **1a** and **8b**.

Scheme 8





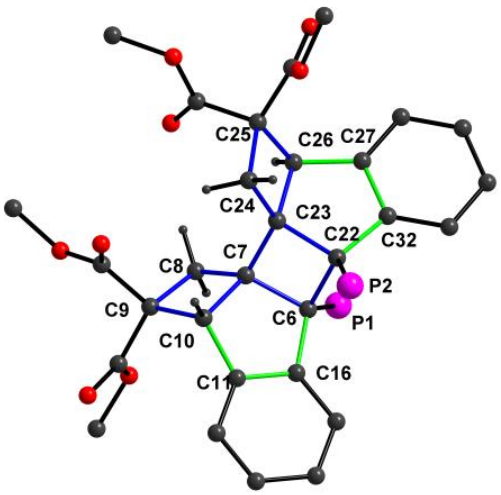
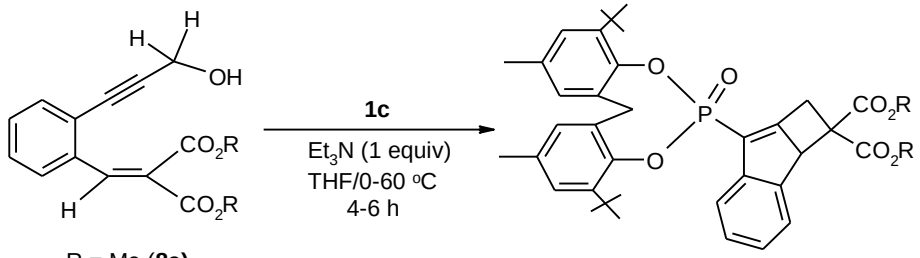


Figure 3. Molecular structure of compound **20**.CH_2Cl_2. Solvent molecule and hydrogen atoms are omitted for clarity. Only selected atoms are labeled. Selected bond lengths [Å] with esd's in parentheses: P(1)-C(6) 1.812(3), P(2)-C(22) 1.820(3), C(6)-C(7) 1.559(4), C(6)-C(22) 1.625(4), C(7)-C(8) 1.553(4), C(7)-C(10) 1.557(4), C(7)-C(23) 1.530(4), C(8)-C(9) 1.554(4), C(9)-C(10) 1.573(5), C(22)-C(23) 1.553(5), C(23)-C(24) 1.556(4), C(23)-C(26) 1.559(4), C(24)-C(25) 1.565(5), C(25)-C(26) 1.578(4).

In order to explore the chemistry further, we carried out the reaction of P^{III}-Cl precursor **1c** bearing a sterically encumbered aromatic entity, with the same alcohols **8a-b**. Surprisingly, this reaction afforded compounds **22-23** (Scheme 9) that can be considered as ***monomeric forms of* 20-21** shown above in Scheme 8. The ^{1}H NMR spectra showed signals in the region of δ 3.63-3.64 ascribable to a -C*H*$_2$ group and 3.85-4.08 and in the range δ 5.07-5.11 due to -C*H* moiety. The ^{13}C NMR spectra showed a signal at δ ~ 125.0 with a ^1J(P-C) of ~ 215.3 Hz clearly indicating the existence of vinylic carbon connected to phosphorus.[4m] These data are consistent with the structure shown in Scheme 9. The structure of compound **22** has been confirmed by single crystal X-ray crystallography (Fig. 4). The C(24)-C(34) distance of 1.349(5) Å establishes the existence of a double bond between these two atoms.

Scheme 9



R = Me (**8a)**
Et (**8b**)

R = Me [**22**, δ(P): 4.9, 70%, X-ray]
= Et [**23**, δ(P): 5.0, 68%]

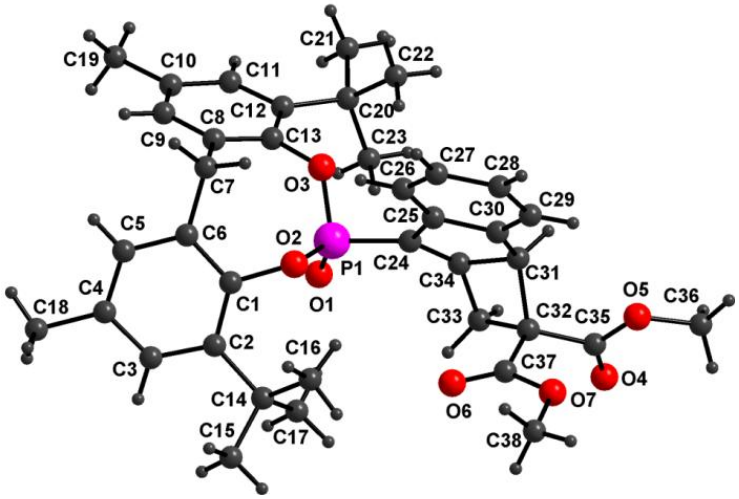
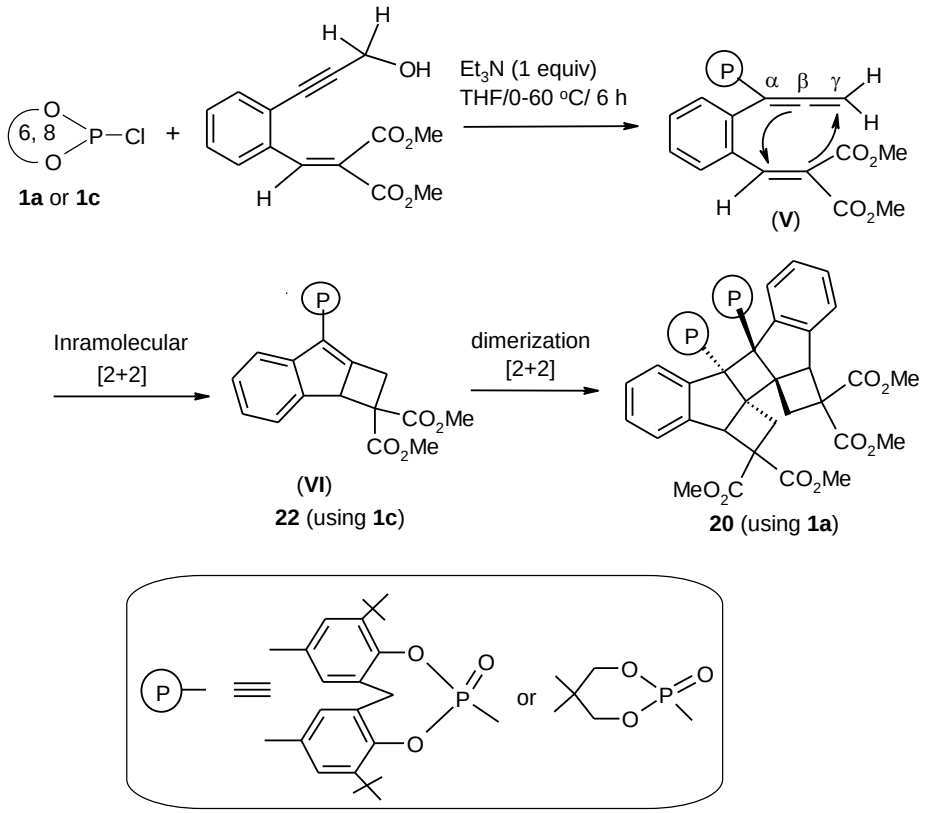


Figure 4. Molecular structure of compound **22**. Selected bond lengths [Å] with esd's in parentheses: P(1)-C(24) 1.764(4), C(24)-C(34) 1.349(5), C(31)-C(32) 1.596(5), C(31)-C(34) 1.483(5), C(32)-C(33) 1.572(6), C(32)-C(33) 1.572(6), C(33)-C(34) 1.501(5).

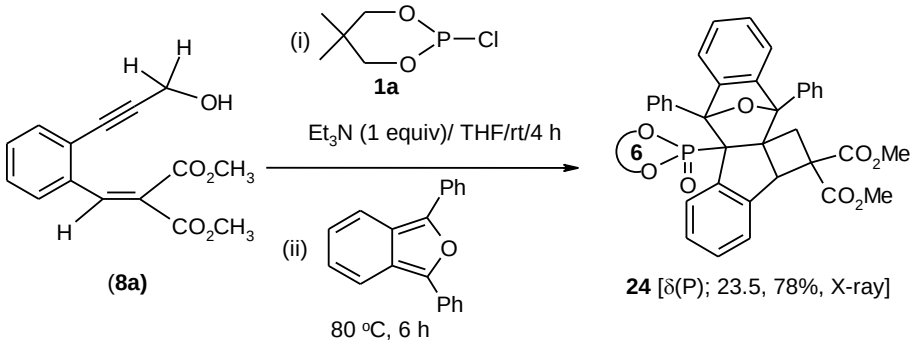
Formation of the above fused polycyclics can be explained by the pathway shown in Scheme 10. Initially, the reaction of alcohols **8a-b** with **1a** or **1c** leads to the allene intermediate **V**. This can undergo an intramolecular [2+2] cycloaddition[13] between β,γ-double bond and alkylidene moiety leading to the polycyclic intermediate **VI**. In the reaction using the precursor **1c** that is sterically encumbered, the reaction ends up at this stage (**VI** = **22-23**). When we used the relatively unrestrained **1a** as the precursor, a second intermolecular [2+2] cycloaddition between two molecules of the monomer **VI** (i.e. dimerization of **VI**) occurs to afford the products **20-21**.

Scheme 10



In none of the above cases, we were successful in isolating the allene. Hence we attempted trapping of allene intermediate by using the more reactive diene, 1,3-diphenylisobenzofuran (IBF). Thus we treated **1a** with alcohol **8a** at room temperature and after formation of the tricoordinated species [δ(P) 126.0, cf. Scheme 3], added 1,3-diphenylisobenzofuran and heated the mixture at 80 ^{o}C for 6 h. But, instead of trapping the allene, the monomeric form (cf. **VI**) underwent a [4+2] cycloaddition with 1,3-diphenylisobenzofuran resulting in compound **24** (Scheme 11). The existence of signals at δ 89.3 and 92.6 in ^{13}C NMR spectrum indicates the presence of Ph*C*O carbon atoms of the IBF residue.[4m] The structure of **24** has been confirmed by X-ray crystallographic analysis (Fig. 5).

Scheme 11



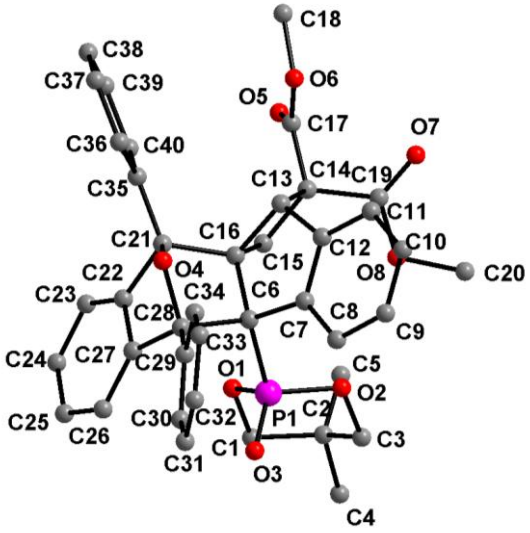
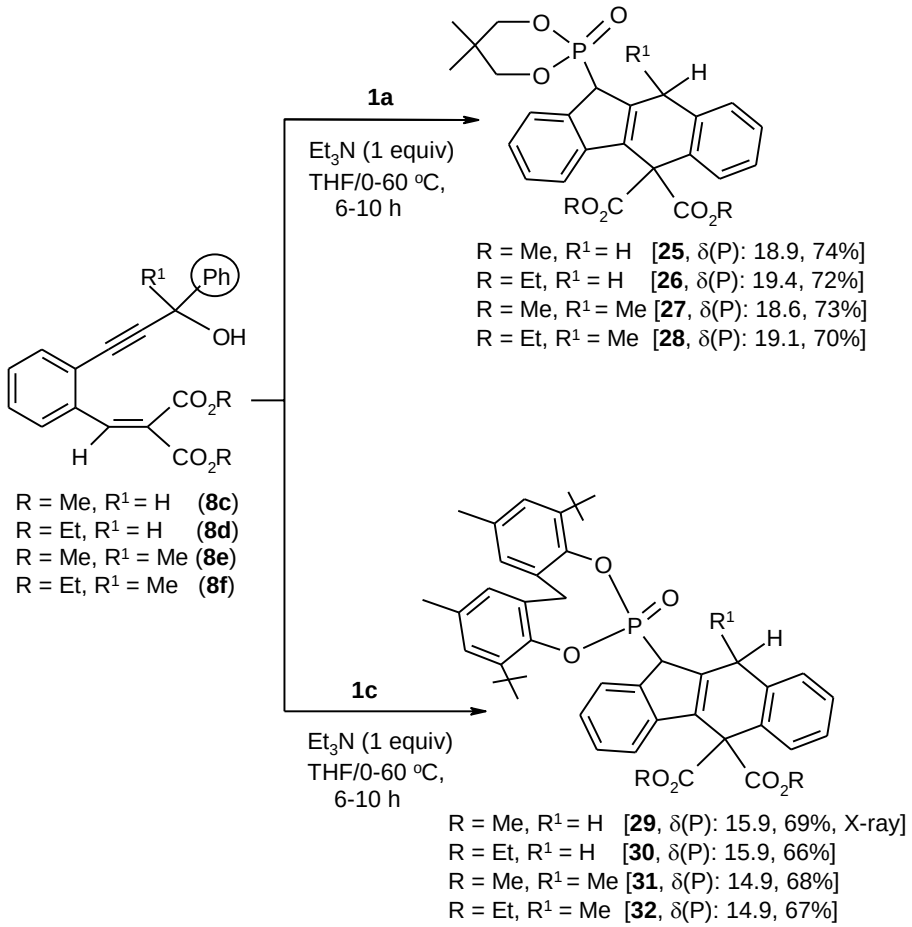


Figure 5. Molecular structure of compound **24**. Solvent molecule and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] with esd's in parentheses: P(1)-C(6) 1.829(2), C(6)-C16 1.588(3), C(6)-C(28) 1.626(4), C(13)-C(14) 1.574(4), C(13)-C(16) 1.557(3), C(14)-C(15) 1.550(4), C(15)-C(16) 1.539(4), C(16)-C(21) 1.564(3).

In an effort to explore the versatility of the above results, we carried out the reactions of P^{III}-Cl precursors **1a** and **1c** with various ***phenyl*** substituted propargyl alcohols **8c-f**. It may be noted that the main difference between these propargyl alcohols (**8c-f**) and the ones discussed above (**8a-b**) is the presence of a phenyl substituent in **8c-f** at the carbon bearing the –OH group. Interestingly, the final products obtained were the ***phosphono-tetracyclics 25-32 (Scheme 12) that have a structure entirely different from 20-21 or 22-23!*** The yields of these products are good to excellent. In the ^{31}P NMR spectra, for compounds **25-28**, a peak at δ 18.9-19.4 is observed whereas for compounds **29-32**, the signal appeared at δ 14.9-15.9.

The difference in these ^{31}P NMR chemical shifts is consistent with ring effects as discussed elsewhere.[76] The signal due to the PC*H* proton in compounds **25-28** is merged with C*H*(R^1) protons in the ^{1}H NMR; however, they are clearly seen in the case of compounds **29-32** [δ 4.63-5.11 (d); ^2J(P-H) ~29.5 Hz]. In the ^{13}C NMR spectra, the carbon attached to phosphorus is seen at δ 48.5-50.5 [^1J(P-C) ~ 130.7 Hz]. Therefore, it is concluded that the carbon to which phosphorus connected is a saturated one (sp^3 hybridized). [4m] A slightly higher value of ^1J(P-C) is observed in the case of tetracyclics **29-32** [~ 147.7 Hz]. Finally, the identity of one of these compounds (**29**) is proven by single crystal X-ray crystallography (Fig. 6). The molecular diagram clearly shows that phenyl group from propargyl alcohol has become a part of phosphono-tetracycle. The C(24)-C(36) distance of 1.512(3) Å confirms the presence of a single bond while C(28)-C(29) and C(27)-C(36) are newly formed single bonds.

Scheme 12



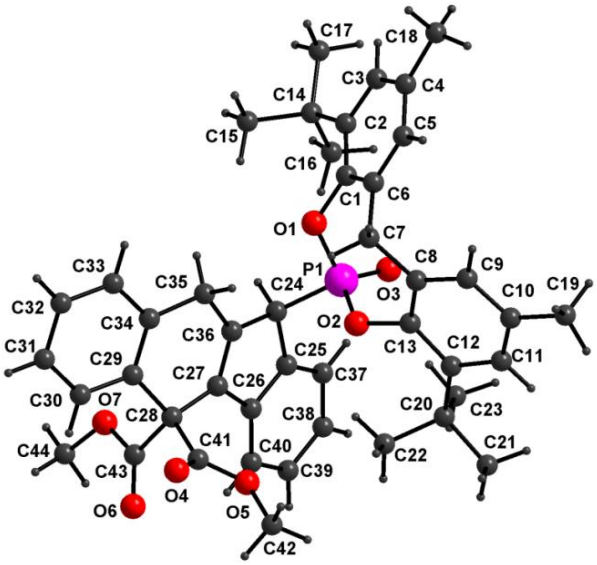
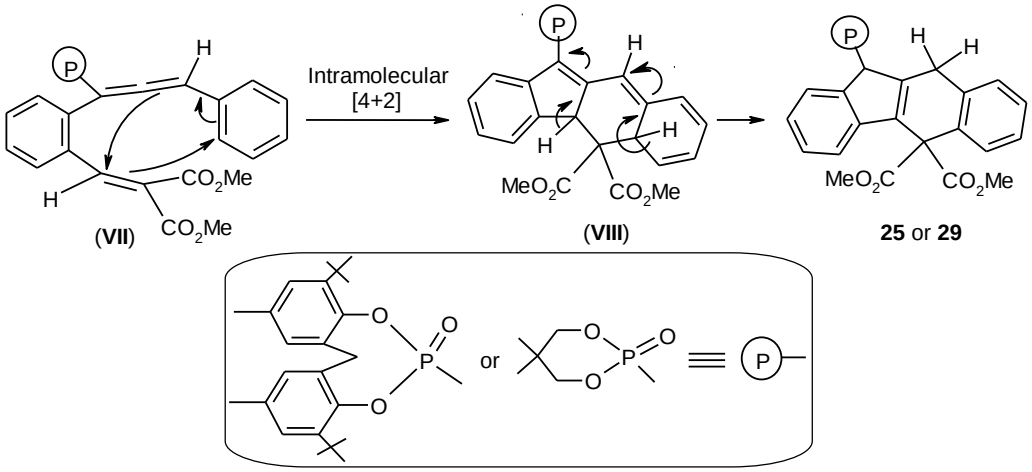


Figure 6. Molecular structure of compound **29**.2CH_3CN. Solvent molecules are omitted for clarity. Selected bond lengths [Å] with esd's in parentheses: P(1)-C(24) 1.804(2), C(24)-C(36) 1.512(3), C(27)-C(36) 1.343(3), C(27)-C(28) 1.517(3), C(28)-C(29) 1.534(3).

In the above reactions also, the first step is the formation allene intermediate **VII** (Scheme 13) that is similar to **V**. However, since the double bond of the phenyl group is also available in **VII**, a [4+2] cycloaddition between β,γ-double bond of allene plus an aryl double bond (together acting as the diene) and the alkylidene moiety (dienophile) results in the intermediate **VIII**. This is followed by aromatization *via* H-migration to lead to the final product **25**. Compounds **26-32** are also formed similarly.

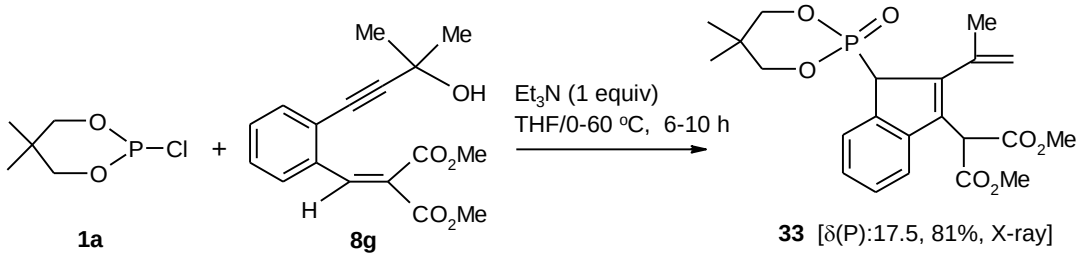
Scheme 13



2.25 Reaction of P^{III}-Cl compounds with dialkyl substituted propargyl alcohols 8g-i: Synthesis of phosphono-polycyclics 33-40 via ene reaction

As the reaction of **1a** or **1c** with propargyl alcohols **8a-b** resulted in fused polycyclics in a tandem manner, we thought that dialkyl substituted propargyl alcohols may also lead to new polycyclics. In order to explore this, we treated the P^{III}-Cl precursor **1a** with the propargyl alcohol **8g** (Scheme 14) by following the procedure similar to what is described above. The product **33** showed a peak at δ 17.3 in the ^{31}P NMR spectrum which is not in the allene region. A doublet at δ 4.51 (^2J(P-H) = 32.8 Hz) and two broad signals at δ 5.14 and 5.17 in the ^1H NMR spectrum can be assigned to =CH_2 and PC*H* protons respectively. A doublet observed at ó 50.4 [^1J(P-C) = 131.0 Hz] in the ^{13}C NMR spectrum suggests that the carbon attached to phosphorus is sp^3 hybridized.[76] The structure shown in Scheme 14 is consistent with these data as well as the elemental analyses and LC-MS data. The structure is proven by single crystal X-ray crystallographic studies. From the structural diagram (Fig. 7), it is clear that C6, C7, C12, C13, C14 carbon atoms make a new five-membered ring. The C20-C22 distance of 1.346(4) is in the C=C double bond region. We extended this work by using the propargyl alcohols **8h-j** to obtain products **34-36** (Scheme 15). Similar products **37-40** were formed when P^{III}-Cl precursor **1c** containing eight-membered ring (Chart 2) were used. All these compounds have been characterized by spectroscopic and analytical techniques.

Scheme 14



1a **8g** **33** [δ(P):17.5, 81%, X-ray]

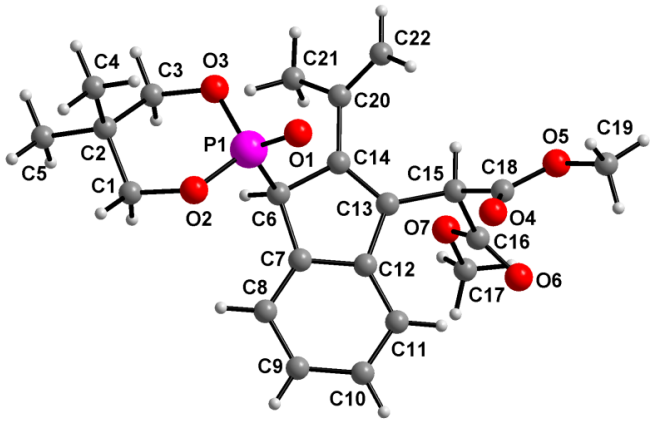


Figure 7. Molecular structure of compound **33**. Selected bond lengths [Å] with esd's in parentheses: P1-C6 1.819(2), C6-C14 1.518(3), C13-C15 1.510(3), C14-C20 1.485(4), C20-C21 1.480(4), C20-C22 1.346(4).

Scheme 15

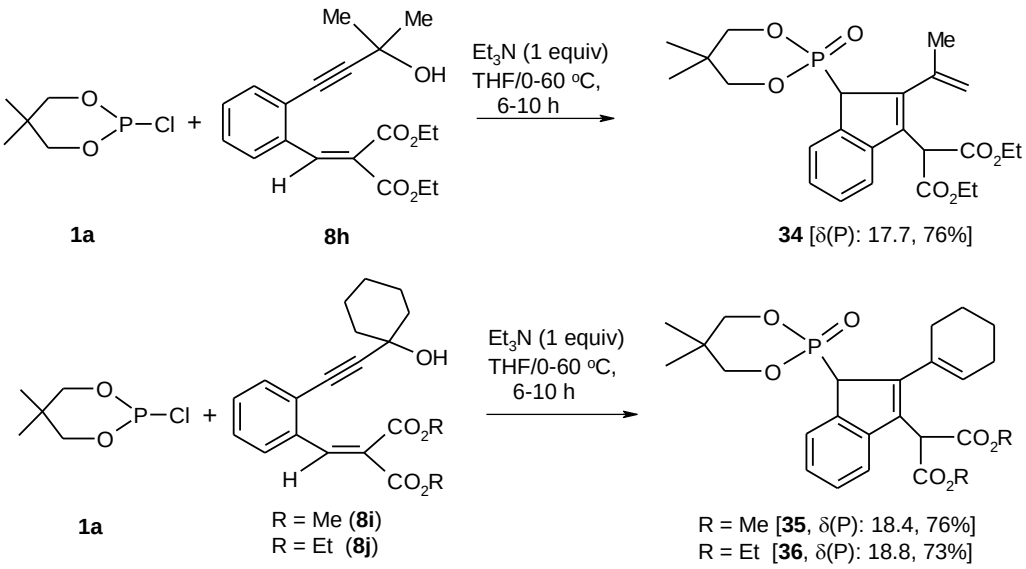
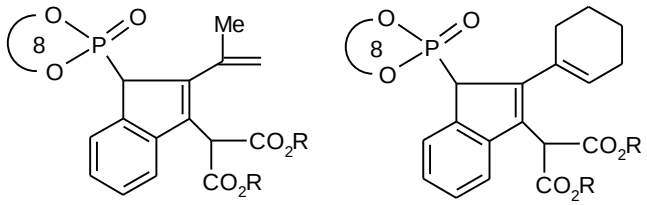


Chart 2



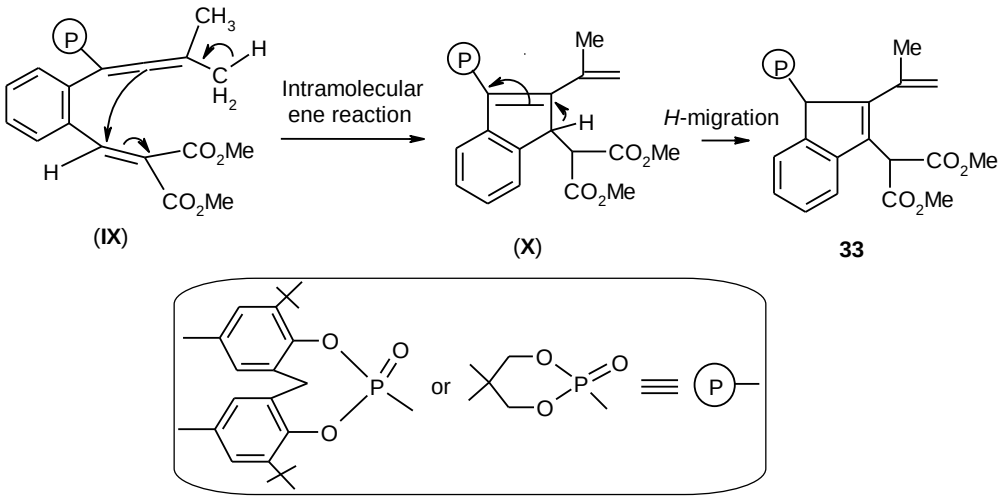
R = Me [**37**, δ(P): 15.9, 72%]
R = Et [**38**, δ(P): 15.9, 68%]

R = Me [**39**, δ(P): 16.4, 70%]
R = Et [**40**, δ(P): 16.5, 67%]

As discussed above, this cyclization reaction is also expected to proceed *via* an allene intermediate **IX** (Scheme 16) followed by an intramolecular-ene[41] reaction

leading to species **X** which on subsequent proton migration furnishes the final product **33**. Formation of products **34-40** can also be explained similarly.

Scheme 16



(**IX**) (**X**) **33**

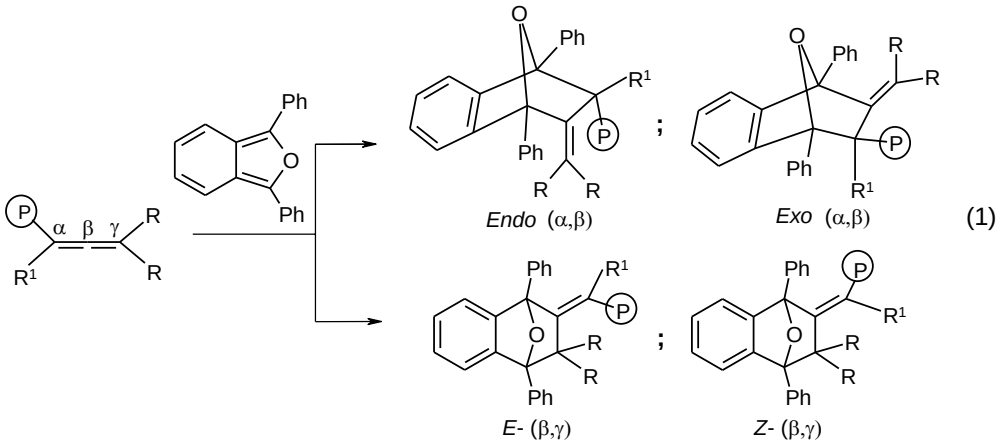
2.3 Cycloaddition reactions of allenes

Allenes can readily participate in many cyclization reactions due to their high reactivity compared to normal alkenes/alkynes.[12] The Diels-Alder cycloaddition of allenes provides an attractive approach to the synthesis of various cycloadducts that are useful building blocks of natural products.[16] Many of these reactions can be done under thermal,[10f, 17, 19] photochemical,[12k] or transition-metal catalyzed[37-38] conditions. In the following subsections, we discuss the reactivity of the allenes **9a-b**, **10a-j**, **11a-d**, **12a** and **12c-f** towards the cycloaddition reaction with the dienes 1,3-diphenylisobenzofuran and anthracene. We also describe the reaction of **11a** with the dienophile dimethyl acetylenedicarboxylate (DMAD) under thermal activation.

2.31 Reaction of allenes with 1,3-diphenylisobenzofuran (IBF)

Due to the aromatization of the six-membered ring during cycloaddition, 1,3-diphenylisobenzofuran (IBF) is a very reactive diene that readily undergoes [4+2] cycloaddition reaction with a wide range of dienophiles.[18] However, this feature has been utilized only to a very limited extent in allene chemistry.[11b, 11d] The cycloaddition can occur at (α,β) or (β,γ) positions of allene. In the case of (α,β) attack, *exo* or *endo* product can be formed, while for the (β,γ) attack, *Z* or *E* isomer

can be expected (equation 1). If additional functionalities exist, other products may also be expected. Hence we have explored the reaction of allenes **9a-b**, **10a-j, 11a-d** and **12c-d** with 1,3-diphenylisobenzofuran. The results are discussed below.



(1)

2.311 [4+2] Cycloaddition reaction of allenes 9a-b, 10a, and 10e-j with 1,3-diphenylisobenzofuran (IBF): Synthesis of α,β-cycloadducts 41-49

We started our experiment by heating a solution of allenylphosphonate **10a** and 1,3-diphenylisobenzofuran (IBF) in *p*-xylene at 80 ^{o}C for 6 h. The ^{31}P NMR spectrum of reaction mixture showed a major peak at δ 20.8 along with a minor peak at 18.5 (~9:1 ratio). We isolated the compound corresponding to δ 20.8. The ^{1}H NMR spectrum showed a doublet at δ 4.08 [^{2}J(P-H) = 18.0 Hz] ascribable to PC*H* proton. Two broad signals at δ 5.34 and 5.41 that may be assigned to =CH_2 protons are also observed. In the ^{13}C NMR spectrum, a doublet appeared at δ 47.9 (^{1}J(P-C) = 144.3 Hz) suggesting that the phosphorus is attached to a saturated carbon. These features are consistent with the cycloaddition occurring at (α,β) carbon-carbon double bond of allene **10a**. It can be readily recognized that two configurational isomers (*endo* and *exo*) are possible for this type of product **41** (i.e. excluding diastereomers due to chiral centers). The presence of isomers is readily ascertained by ^{31}P NMR spectroscopy [δ 20.8, 18.5; Δδ ~ 2.3]. But the spectroscopic analysis alone, however, will not clearly distinguish between the *endo* and the *exo* isomers. Based on what is described below for cycloadducts **44/46**, we assign the *endo* configuration for **41**. We then extended the cycloaddition reaction to allenes **10e-i** (Scheme 17). Details on the yields of both *endo* and *exo* isomers and δ(P) for the products **41-46** are given in Table 1. The structure of *endo* isomer is proven by

means of single crystal X-ray crystallographic analysis of product **44** (Fig. 8). The C6-C33 and C33-C34 bond distances of 1.539(2), 1.321(2) Å clearly reveal that IBF added across α,β- position of allenylphosphonate. In this *endo*-configuration, phosphoryl oxygen and IBF oxygen are *anti* to each other. In three cases [**43**/**43'**, **45**/**45'**, **46**/**46'**], we have been successful in isolating both of these isomers. Delightedly, X-ray structures could be obtained for both *endo* and *exo p*-anisyl substituted isomers **46** and **46'** (Fig. 9). This result also gives credence to the assignment of ^{31}P NMR chemical shifts for the *endo* and *exo* isomers.

Scheme 17

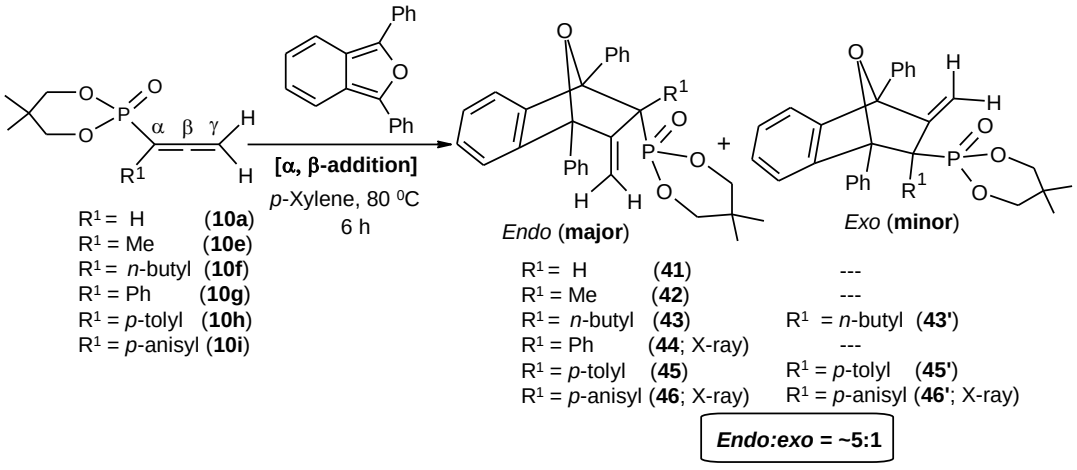


Table 1: Details on the yields of *endo* and *exo* isomers and ^{31}P NMR data for the products **41-46** (cf. Scheme 17).

Entry	Products		Yields (%) *endo:exo*	ó(P) *endo, exo*
	endo	*exo*		
1	**41**	-	55:0	20.8, -
2	**42**	-	81:0	26.2, -
3	**43**	**43'**	70:19	25.7, 22.1
4	**44**	-	84:0	22.1, -
5	**45**	**45'**	66:27	22.4, 20.1
6	**46**	**46'**	69:19	22.4, 20.1

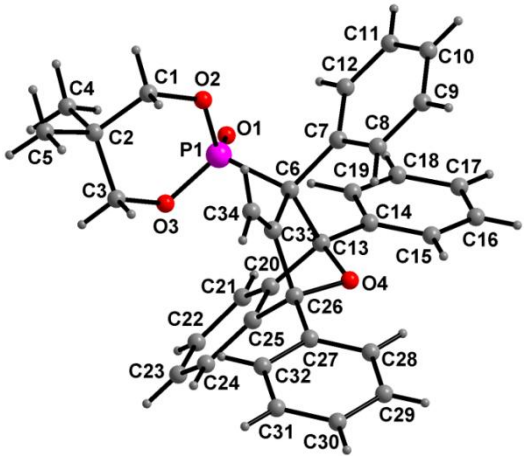


Figure 8. Molecular structure of compound **44**. Selected bond lengths [Å] with esd's in parentheses: P1-C6 1.8573(15), O4-C13 1.4521(17), O4-C26 1.4606(18), C6-C13 1.630(2), C6-C33 1.539(2), C26-C33 1.542(2), C33-C34 1.321(2).

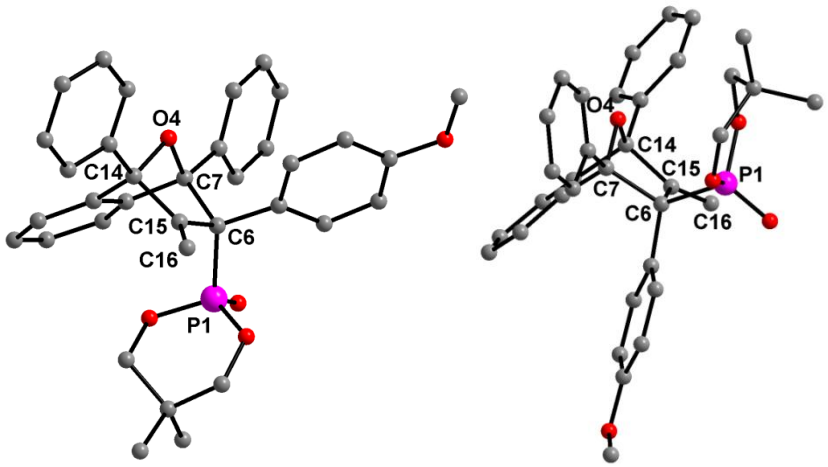


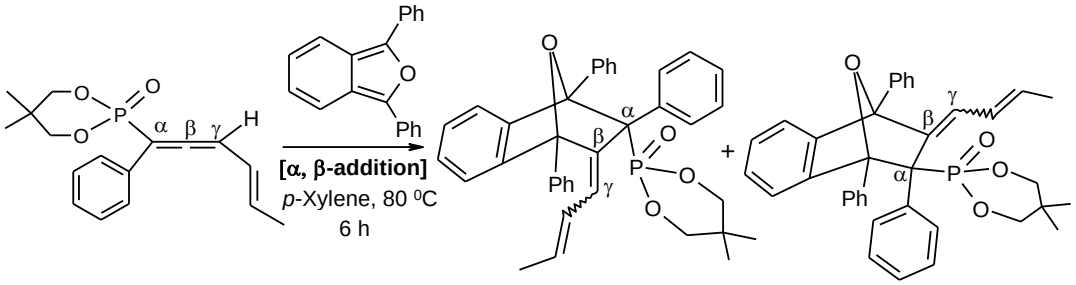
Figure 9. Molecular structure of **46**.CH_2Cl_2 [*endo*; left] and **46'** [*exo*; right] [4+2]-cycloaddition [Diels-Alder] products. For clarity, hydrogen atoms are omitted and only selected atoms are labeled. Selected distances with estimated standard deviations are given in parentheses. **46**: P1-C6 1.841(4), C6-C7 1.635(5), C6-C15 1.535(6), C14-C15 1.543(5), C15-C16 1.322(5). P1…O4 (non-bonded distance) 3.981(3) Å. **46'**: P1-C6 1.848(2), C6-C7 1.623(2), C6-C15 1.543(2), C14-C15 1.542(2), C15-C16 1.320(2), P1…O4 (non-bonded distance) 3.328(1) Å.

In the structures [see Fig. 9], the non-bonded P1…O4 distance between the bridgehead oxygen and the phosphorus in the *endo* [**46**] and *exo* [**46'**] isomers are, respectively, 3.981(3) Å and 3.328(1) Å and hence these isomers are easily distinguishable. Another interesting feature in these compounds is the unusually

long C6-C7 single bond distances of 1.635(5) and 1.623(2) Å. This may be because of steric repulsions involving two moderately bulky groups at C6. The *endo* preference had been rationalized earlier by invoking secondary orbital interactions (SOIs) but a recent paper suggests that closed shell interactions are involved.[78] This could explain the formation of *endo*-phosphonate products **41-46**. An e*ndo*-selective Diels-Alder reaction of diphenyl(1,2-propadienyl)phosphine oxide with cyclopentadiene has been reported by Scheufler and Maier.[79]

We then thought that the presence of a γ-vinyl group in the allene **10j** may lead to a different type of product. However, when we carried out the reaction using **10j**, the result was similar and the [4+2] adducts **47** and **47'** were isolated (Scheme 18). Thus the vinyl part remained intact. Here also, we were successful in isolating both the *endo* and the *exo* isomers. *Exo* is the favored configuration (*endo*:*exo* = 1:1.7) in this case. Hence, steric factors may be overriding the secondary orbital interactions in this case.[78-79]

Scheme 18

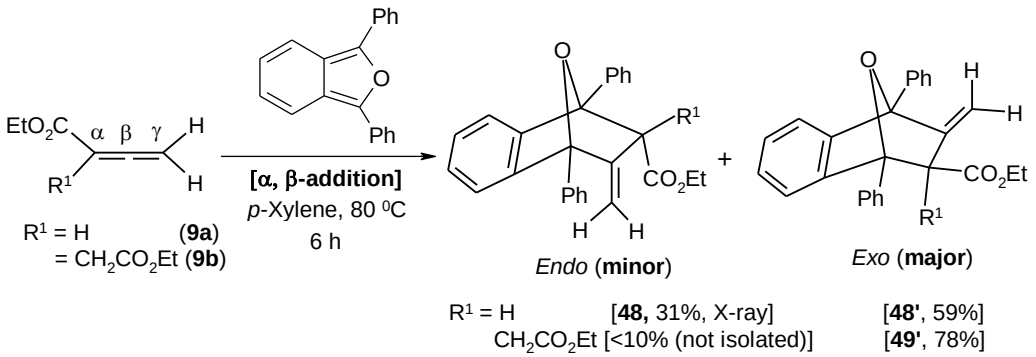


10j **47** [δ(P): 22.2, 32%] **47'** [δ(P): 19.5, 53%]

In continuation of above reactions, we were curious to know whether non-phosphorylated allenes (i.e. **9a-b**) also would undergo similar cycloaddition or not. Hence, we carried out thermal cycloaddition reactions of allenes **9a** and **9b** under the above conditions (Scheme 19). This reaction afforded adducts **48**/ **48'** and **49'**. The ^{1}H NMR spectra of these compounds showed two broad signals at δ ~ 5.21 and 5.36 due to =C*H*$_2$ protons. In the ^{13}C NMR spectra, two signals appeared at δ ~ 89.3 and 90.5 due to the Ph*C*O carbons of IBF-residue. X-ray structure of **48** confirms its identity (Fig. 10). The C1-C2, C2-C3 distances are (1.316(5) [C=C], 1.531(4) Å [C-C] respectively) in the range expected for *α, β*-cycloadduct. Although the *endo* isomer was the major product in the case of allenes **10a**, **10e-j**, there appeared to be a reversal in the reactions using allenoates **9a-b** that led to the products **48-49** in

which the *exo*-(with respect to CO_2Et group) isomer [**48'** or **49'**] was the major product. Thus the product ratio was ~2:3 in favor of *exo*, while for **25** the preferred product was again *exo* (i.e. **49'**). This feature is understandable since there is a slightly bulkier germinal $–CH_2CO_2Et$ group that could tilt the balance in favor of *exo*. *Exo*-selective [4+2] cycloaddition of allenoate **9a** with other dienes has also been noted by Jung and coworkers recently.[12h]

Scheme 19



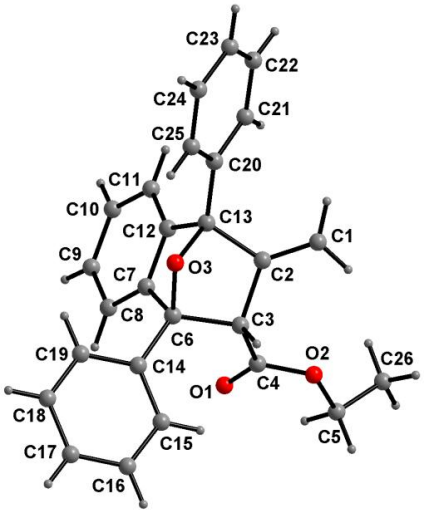


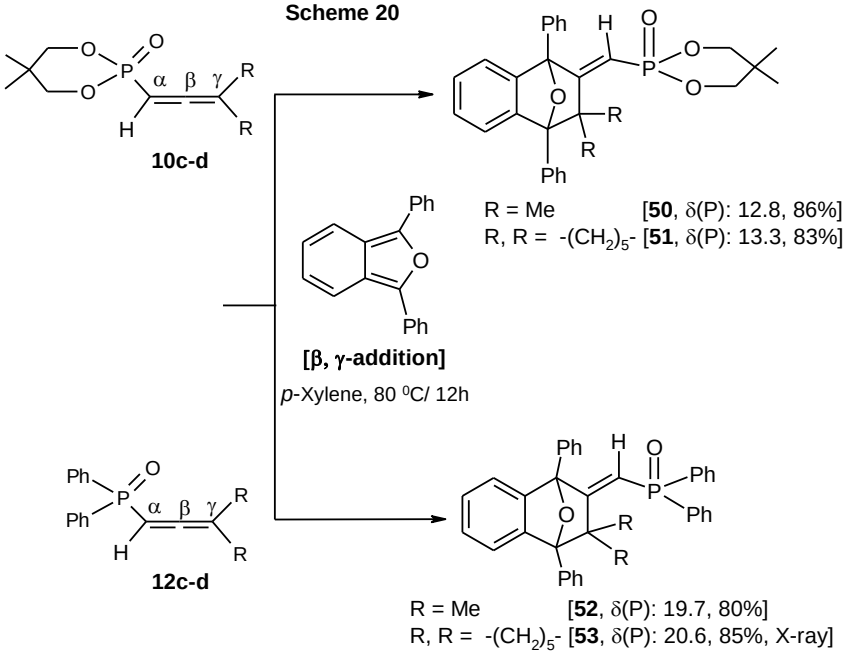
Figure 10. Molecular structure of compound **48**. Selected bond lengths [Å] with esd's in parentheses: O3-C6 1.467(4), O3-C13 1.456(4), C1-C2 1.316(5), C2-C3 1.531(4), C2-C13 1.528(5), C3-C4 1.495(5), C3-C6 1.551(4).

2.312 [4+2] Cycloaddition reactions of allenes 10c-d and 12c-d with 1,3-diphenylisobenzofuran: Formation of β,γ-cycloadducts 50-53

After studying the nature of cycloaddition reactions of α-substituted allenes we turned our attention to γ-dialkyl substituted allenes. Thus we treated phosphorus-

based allenes **10c-d** and **12c-d** with IBF. Surprisingly, the addition occurred regioselectively at the (β,γ) carbon-carbon double bond leading to **50-53** with *E*-selectivity (Scheme 20). The ^{31}P NMR spectra show a single peak at δ ~ 13.1 [compounds **50-51**] or δ ~ 20.2 [compounds **52-53**]. An olefinic proton with a ^{2}J(P-H) of ~ 11.7 Hz is seen in the ^{1}H NMR spectra for **50-51** at δ 5.58; the corresponding proton appeared at around δ 5.93 [^{2}J(P-H) ~ 20.4 Hz] for **52-53**. ^{13}C NMR spectra show the P-C carbon at δ ~ 105.0 [^{1}J(P-C) ~ 191.8 Hz] for **50-51** and at ~ δ 111.4 [^{1}J(P-C) of 102.3 Hz] for **52-53**. We have confirmed structure of **53** by X-ray crystallography (Fig. 11). The C13-C14 and C14-C15 distances [1.328(2), 1.530(2) Å respectively] [Å] clearly show that the former is a double bond while the latter is a single bond.

Scheme 20



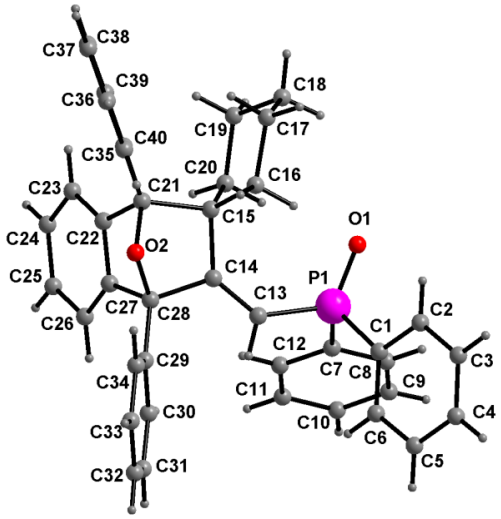


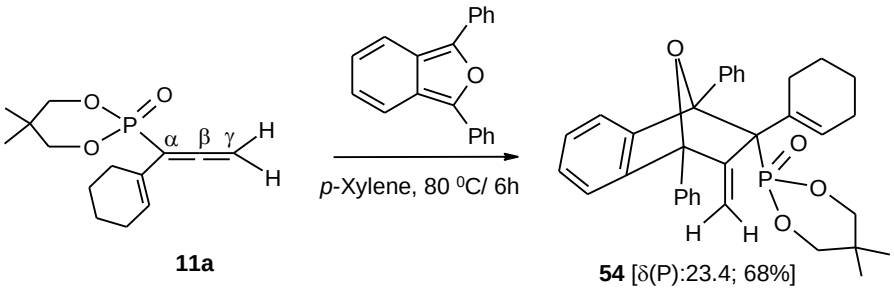
Figure 11. Molecular structure of compound **53**. Selected bond lengths [Å] with esd's in parentheses: P1-C13 1.7902(17), O2-C21 1.447(2), O2-C28 1.4384(19), C13-C14 1.328(2), C14-C15-1.530(2), C14-C28 1.540(2), C15-C21 1.613(2).

It may be expected that an electron withdrawing group [e.g. phosphonyl] on the dienophile will activate this center for [4+2] cycloaddition, but in the reactions of allenes **10c-d** and **12c-d** that have a terminal $=CR_2$ group, the cycloaddition occurs at the (β,γ) position, away from the phosphonyl group [cf. Scheme 20]. We do not have a ready explanation for this result, but it does not appear to be a steric effect. The electronegativity of the –Me group is slightly higher than that of hydrogen according to some calculations,[80] but to know whether this factor tilts the reaction in favor of (β,γ)-cycloaddition or not needs further investigations.

2.313 [4+4] Cycloaddition reactions of allenes 11a-d with 1,3-diphenylisobenzofuran: Formation of cycloadducts 54-58

So far, we discussed the [4+2] cycloaddition reactions of various allenes with IBF. In these reactions, allene acted as a dienophile. We were curious to know whether allenes can behave as dienes if we employ those containing a conjugated double bond at the α-position. Thus, we utilized the cyclohexenyl substituted allenes **11a-d** in thermally assisted cycloaddition reaction. We started our experiment by heating allene **11a** with IBF at 80 ^{o}C. In this case, the reaction ended up mostly in the [4+2] cycloaddition product **54** (Scheme 20) along with only a minor quantity of compound **55** (<20 % based on ^{31}P NMR). Thus, under these conditions, the α-cyclohexenyl double bond mostly remains intact.

Scheme 21

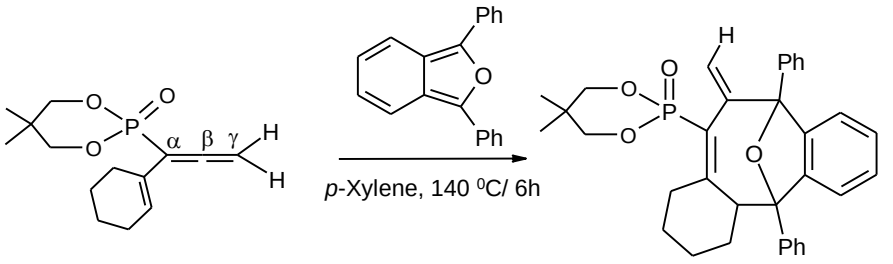


11a

54 [δ(P):23.4; 68%]

When the above reaction was carried out at higher temperature (140 ^{o}C/6 h), a ***rather unusual [4+4] cycloaddition product 55*** was the predominant product (Scheme 22). To our knowledge, such [4+4] cycloaddition involving allenes is rather rare.[81] In this cycloaddition, there may be a difference of opinion due to other possibilities like [4+2+2] or [2+2+2+2] addition. Even though [4+4] is not supposed to be thermally allowed, there is literature evidence for such a cycloaddition[81] and hence we treat it as [4+4] cycloaddition. As regards characterization of **55**, the ^{1}H NMR spectrum does not show a signal at δ 6.29 corresponding to =C*H* proton which indicates the participation of cyclohexenyl part of allene **11a** in the cycloaddition. Two doublets at δ 5.24 and 5.57 [^{2}J(H-H) ~ 2.4 Hz for both] due to =CH_2 protons is seen in the ^{1}H NMR spectrum. In the ^{13}C NMR spectrum, the carbon attached to phosphorus appeared at δ 120.7 with ^{1}J(P-C) = 166.6 Hz indicating P-*C* carbon is olefinic. These data, together with elemental analyses and LC-MS, are consistent with the structure as given in Scheme 21. Final confirmation is done by X-ray crystallography (Fig. 12). It is clear that both C6-C7 [1.348(3) Å] and C15-C16 [1.321(3) Å] are double bonds. The C12-C13 [1.549(3) Å] and C14-C15 [1.535(3) Å] bonds are newly formed. We synthesized three more such [4+4] adducts **56-58** from allenes **12b-d** under similar conditions (Table 2). X-ray structure of one of these compounds **57** is determined for further confirmation (Fig. 12).

Scheme 22



11a **55** [δ(P):13.4; 83%, X-ray]

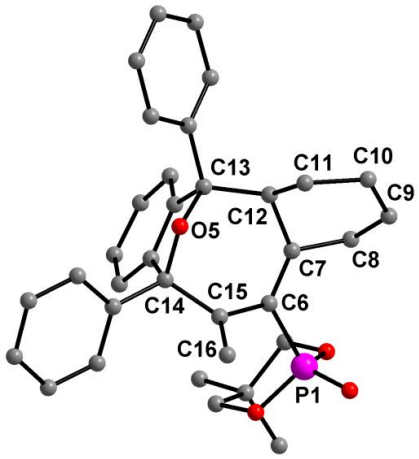
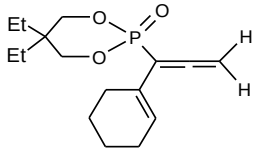
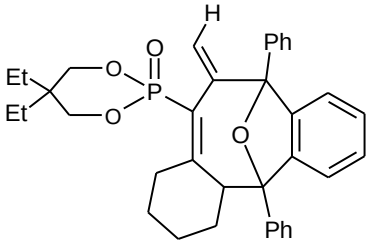
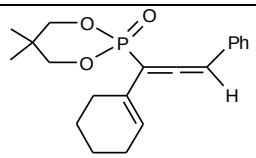
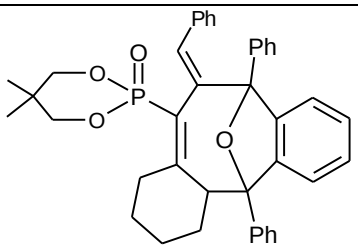
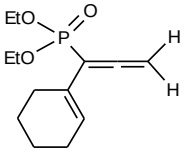
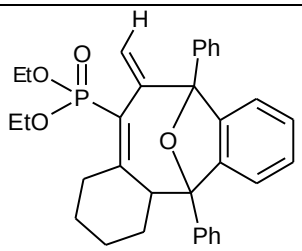


Figure 12. Molecular structure of [4+4]-cycloaddition product **55**. For clarity, hydrogen atoms are omitted and only selected atoms are labeled. Selected bond lengths [Å] with estimated standard deviations are given in parentheses. P1-C6 1.815(2), C6-C7 1.348(3), C6-C15 1.508(3), C7-C12 1.526(3), C12-C13 1.549(3), C14-C15 1.535(3), C15-C16 1.321(3).

Table 2: Scope of the [4+4] cycloaddition reaction depicted in Scheme 22[a]

Entry	allene	product	Yield[b]	δ(P)
1	 **11b**	 **56**	80	14.8

2	 **11c**	 **57** (X-ray)	82	10.3
3	 **11d**	 **58**	80	18.9

[a]Reaction conditions: allene (1.1 mmol), IBF (1.52 mmol) in *p*-Xylene (2 mL) at 140 [o]C for 6 h. [b]Isolated yields.

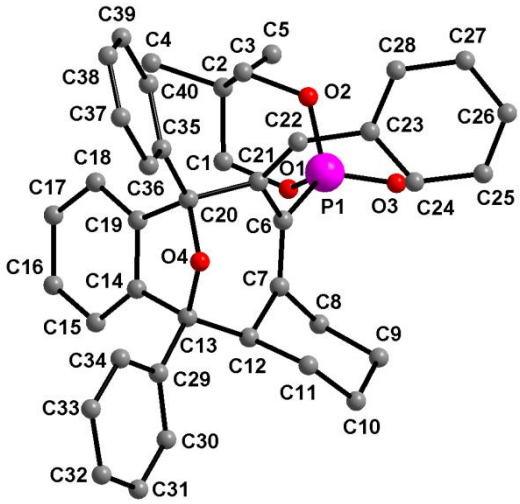


Figure 13. Molecular structure of [4+4]-cycloaddition product **57**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] with estimated standard deviations are given in parentheses. P1-C6 1.817(4), O4-C13 1.444(5), O4-C20 1.468(5), C6-C7 1.349(6), C6-C21 1.519(6), C7-C12 1.538(6), C12-C13 1.521(6), C13-C14 1.515(6), C19-C20 1.521(6), C20-C21 1.548(6), C21-C22 1.337(6).

It is very likely that the above reaction occurs *via retro* Diels-Alder reaction followed by [4+4] cycloaddition. In order to study the reaction pathway, a pure sample of **54** was heated at ca 140 [o]C/8 h, and monitored by recording ^{31}P NMR

spectrum in regular intervals (Fig. 14). When we checked the ^{31}P NMR spectrum after 10 min, a new signal at δ 8.1 was observed. This peak is due to allene **11a**. With the progress of reaction, there is regular consumption of allene **11a** with the formation of [4+4] adduct **55**. Finally, allene was fully converted to product **55**. During the course of heating of compound **54**, the characteristic yellow color of the isobenzofuran was also observed. Thus we conclude that this reaction involves a *retro* Diels-Alder reaction forming allene **11a** which undergoes a [4+4] cycloaddition with regenerated IBF at high temperature (Scheme 23).

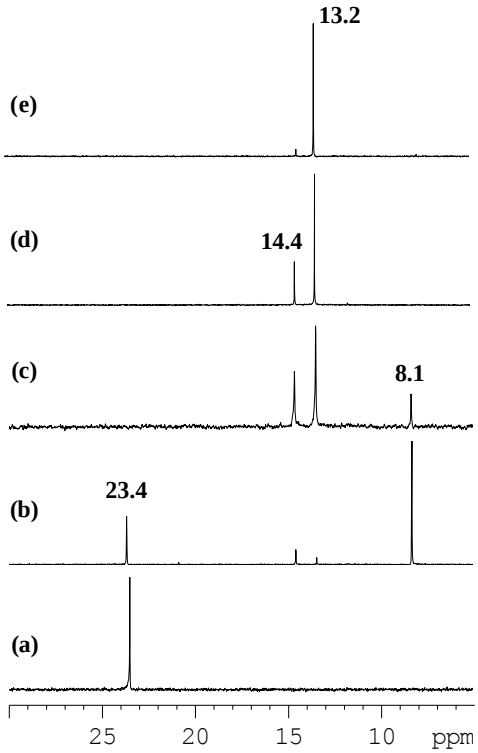
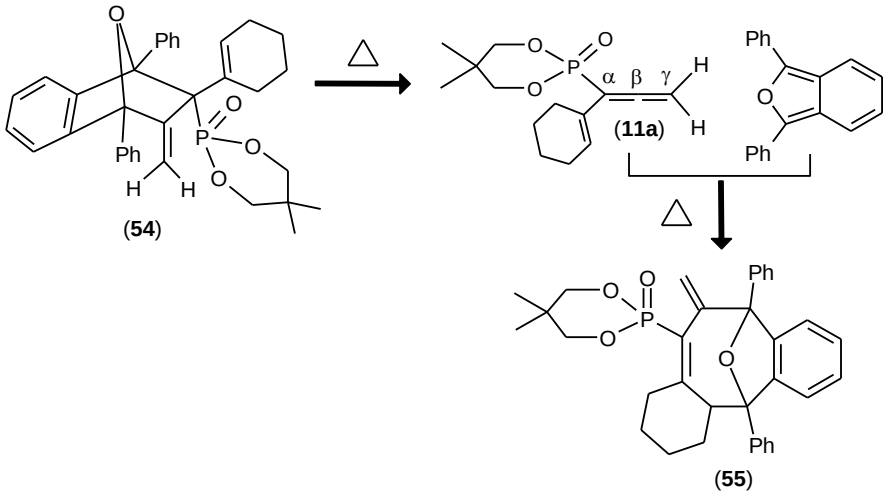


Figure 14. ^{31}P NMR spectra showing the conversion of [4+2] cycloaddition compound **54** [δ(P): 23.4] to [4+4] cycloaddition compound **55** [δ(P): 13.2] *via* allene precursor **11a** [δ(P): 8.1] at 140 ^{o}C in *p*-xylene: (a) after 10 min, (b) after 3 h, (c) after 5 h, (d) after 6 h, and (e) after 8 h.

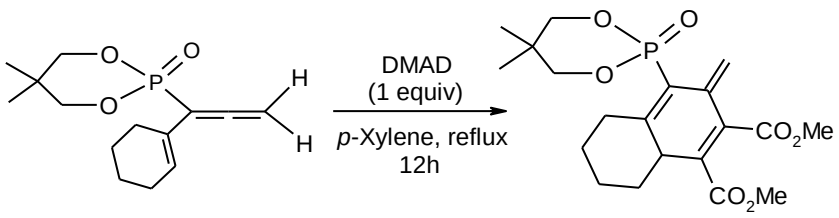
Scheme 23



2.32 Reaction of allene 11a with dimethyl acetylenedicarboxylate (DMAD): Synthesis of the [4+2] cycloadduct 59

We have also explored the cycloaddition reaction of the allene **11a** with $MeO_2CC{\equiv}CCO_2Me$ (DMAD). Here again, allene acted as a 1,3-diene and underwent a [4+2] cycloaddition with DMAD (dienophile) (Scheme 24). However, the aromatization of the newly formed ring did not occur.[82] The ^{1}H NMR spectrum of this compound shows two broad signals at δ 5.36 and 5.90 corresponding to =CH_2 protons; the double bond (C=C) at the carbon attached to phosphorus can be ascertained by the appearance of a signal at δ 116.9 with ^1J(P-C) = 172.6 Hz in the ^{13}C NMR spectrum.

Scheme 24



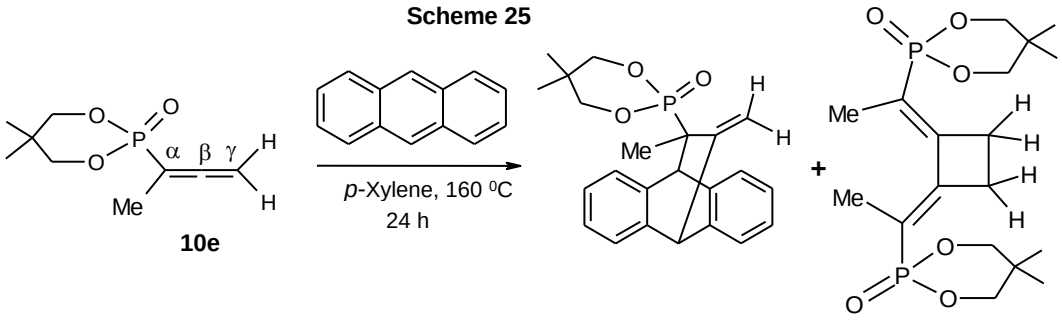
11a **59** [δ(P):11.0; 85%]

2.33 Reaction of allenes 10e-i, 12a, 12e and 12f with anthracene: Synthesis of [4+2] cycloadducts 60-69

Unlike the 1,3-diphenylisobenzofuran, it is known that anthracene as a diene has low reactivity in [4+2] cycloaddition reactions and to our knowledge, this diene has not been explored much in allene chemistry.[14, 83] In this context, we decided to

expand this area and hence utilized allenylphosphonates (**10e-i**) and allenylphosphine oxides (**12a**, **12e**, **12f**) as dienophiles. Thus, the reaction of allene **10e** with anthracene (Scheme 25) worked well although it took a longer time and higher temperature than that required in the case of 1,3-diphenylisobenzofuran. The ^{31}P NMR spectrum of this reaction mixture showed two peaks at δ 26.9 (compound **60**) and 15.0 (compound **61**) [4.5:1]. We were able to separate the both of these by column chromatography. The ^{1}H NMR spectrum of compound **60** showed two doublets at δ 5.09 and 5.37 with ^{2}J(H-H) ~ 4.8 Hz due to the terminal =CH_2 protons. The carbon directly connected to phosphorus (α-carbon) appeared at δ 46.0 [^{1}J(P-C) = 139.4 Hz]. This information led us to conclude that the cycloaddition occurred regioselectively at (α,β)-position. It is interesting to note that the minor compound **61** formed in this reaction is the β,γ-self dimerized product of allene **10e** as shown by spectroscopic, analytical and LC-MS data. In the ^{1}H NMR spectrum of this compound, there is a doublet at δ 1.97 [^{3}J(P-H) = 14.4 Hz] due to α-CH_3 protons. In the ^{13}C NMR spectrum, a signal at δ 116.8 [^{1}J(P-C) = 174.0 Hz] is seen due to the P*C* carbon. Finally, the X-ray structure of this compound has been determined (Figure 15). From the structure, it is clear that **61** is a self-dimerized [2+2] cycloaddition product of allene **10e**. The C8-C8' [1.497(3) Å] and C9-C9' [1.547(3) Å] are newly formed single bonds. Such a type of self-dimerized product has already been reported from our laboratory.[10e] It may be noted that this [2+2] addition takes place at the (β,γ)-position while the Diels-Alder cycloaddition leading to **60** preferentially takes place at (α,β)-position of the allene, evidently reflecting the different electronic requirement in the two types of cycloaddition reactions.

Scheme 25



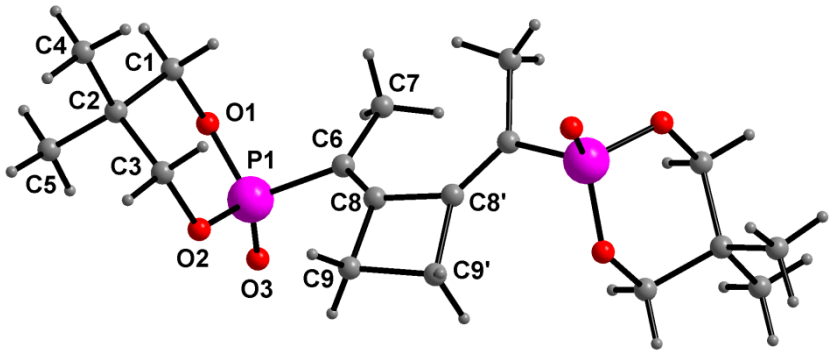
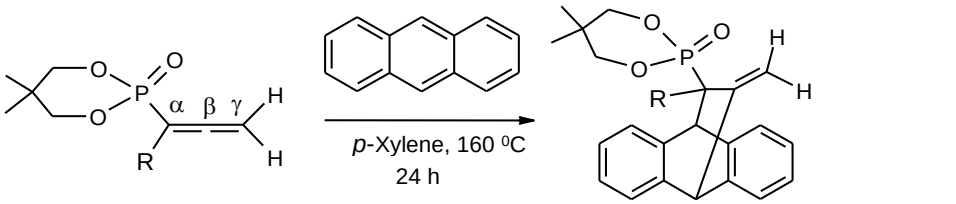


Figure 15. Molecular structure of compound **61**. Half molecule is present in the asymmetric unit. Selected bond lengths [Å] with esd's in parentheses: P1-C6 1.7897(14), C6-C8 1.332(2), C8-C8' 1.497(3), C9-C9' 1.547(3).

The scope of the above reaction was extended further by using different allenes **10f-i**. In all these cases, the (α,β)-carbon-carbon double bond of the allene preferentially acted as the dienophile affording the products **62-65** in good yields (Scheme 26). However, we did not observe any self-dimerized product(s) similar to **61**. The structure of one representative compound **63** has been confirmed by X-ray crystallography (Fig. 16). The C6-C13 and C13-C14 distances of 1.535(3) and 1.314(3) Å respectively, undoubtedly show the [4+2] cycloaddition [Diels-Alder (DA) reaction] between *9,10-position in anthracene* and *α,β-position* of the allene **10g**.

Scheme 26



R = *n*-butyl (**10f**)
Ph (**10g**)
p-tolyl (**10h**)
p-anisyl (**10i**)

R = *n*-butyl [**62**, δ(P): 26.1; 68%]
Ph [**63**, δ(P): 23.5; 70%, X-ray]
p-tolyl [**64**, δ(P): 23.8; 67%]
p-anisyl [**65**, δ(P): 24.0; 69%]

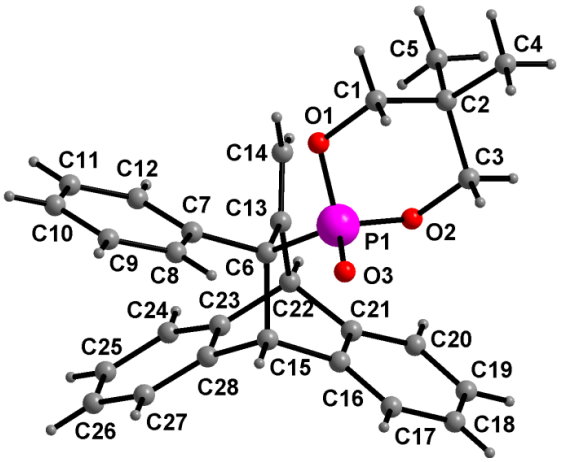
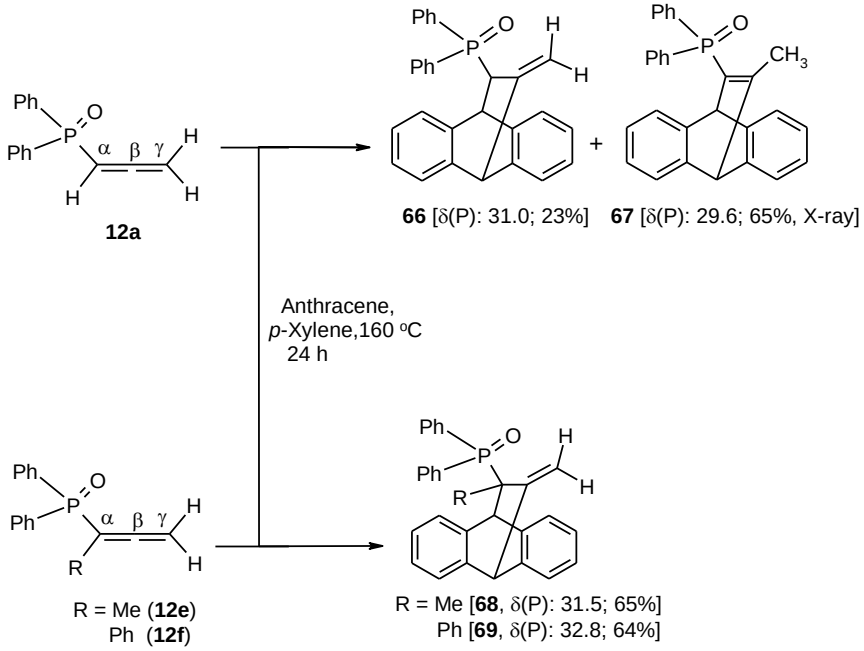


Figure 16. Molecular structure of compound **63**. Selected bond lengths [Å] with esd's in parentheses: P1-C6 1.836(2), C6-C13 1.535(3), C6-C15 1.596(3), C13-C14 1.314(3), C13-C22 1.528(3), C15-C16 1.513(3), C15-C28 1.519(3), C21-C22 1.514(3), C22-C23 1.512(3).

After exploring the cycloaddition reactions of allenylphosphonates with anthracene, for comparison, we also checked the reactivity of allenylphosphine oxides **12a**, **12e** and **12f** (Scheme 27). These thermal [4+2] cycloaddition reactions also resulted in the (α,β)-cycloaddition products **66-69** regioselectively. But in the reaction of allene **12a** with anthracene, surprisingly, the rearranged product **67** was obtained (65%) along with the expected product **66** (23%) [^{31}P NMR]. These two compounds can be distinguished very easily by NMR spectroscopy. The ^{31}P NMR spectrum of compound **66** shows a peak at δ 31.0 whereas **67** exhibited a peak at δ 29.6. A doublet of doublet at δ 3.72 with ^{2}J(P-H) = 16.8 Hz [^{3}J(H-H) ~ 2.4 Hz] due to PC*H* proton and two multiplets in the range of δ 4.98-5.00 and 5.13-5.15 due to =CH_2 protons are present in the ^{1}H NMR spectrum of compound **66**. In contrast, a doublet at δ 2.29 (^{4}J(P-H) = 2.8 Hz) appeared in the ^{1}H NMR spectrum of compound **67** which confirms the presence of CH_3 protons; the carbon directly attached to phosphorus appeared at 132.9 (^{1}J(P-C) = 105.1 Hz) in the ^{13}C NMR spectrum. Final structural confirmation for **67** was obtained from X-ray crystallography (Fig. 17).

Scheme 27



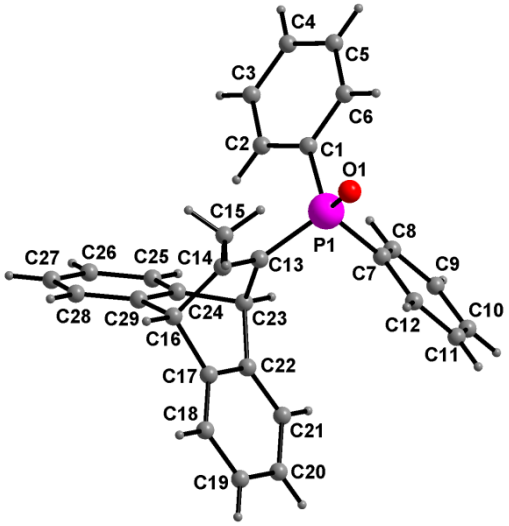


Figure 17. Molecular structure of compound **67**. Selected bond lengths [Å] with esd's in parentheses: P1-O1 1.4795(17), P1-C13 1.793(2), C13-C14 1.334(3), C14-C15 1.503(3), C13-C23 1.552(3), C14-C16 1.535(3).

Overall, the above results demonstrate that cycloaddition reactions of anthracene (as a diene) with allenes are consistent with those obtained with 1,3-diphenylisobenzofuran (diene) discussed in section 2.31. From these observations, we can also conclude that the reactivity of the allenylphosphonates is comparable to that of allenylphosphine oxides. More importantly, due to the presence of an electron withdrawing group (P=O) in the dienophile, the cycloaddition takes place at

the α,β-position of the respective allene in most of the cases except in the reaction of **10c-d** and **12c-d** with 1,3-diphenylisobenzofuran (IBF). In the latter case, β,γ-cycloaddition is observed. As far as reactivity of dienes is concerned, anthracene is a poor diene compared to 1,3-diphenylisobenzofuran towards thermal cycloaddition with phosphorus-based allenes.

2.4 Nucleophilic addition-cyclization reactions of allenes 14a-d and 15a-f

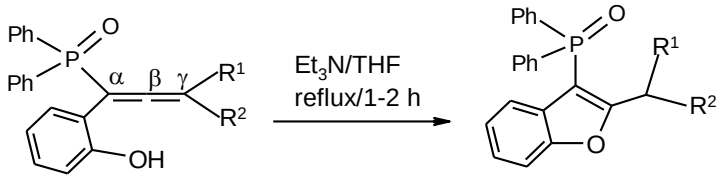
As discussed in Chapter 1, allenes can undergo cyclization reactions with nucleophiles having an additional functionality (e.g. -I, -Br, -CHO) to yield a diverse range of biologically important heterocycles.[42-43] These reactions can be accomplished by transition-metal, Lewis-acid or Lewis-base catalyzed conditions. Recently, our research group has reported the synthesis of furans,[84a] phosphono-benzofurans,[84b] chromenes[47] and oxindoles[48] from inexpensive allenes under Lewis-acid or transition-metal or base catalyzed conditions. In this section, we discuss the reactions in which the allene itself possesses –OH or -CH_2OMOM functionality; in the latter case the protective MOM group is cleaved during the reaction.

2.41 Cyclization reaction of allenes 8a-f possessing a 2-hydroxyphenol side group - Synthesis of 1,2-disubstituted benzofuran derivatives 70-75

Nucleophilic addition of phenols to allenylphosphonates in the presence of a base is already reported from our laboratory.[47, 84b] If the phenol contains an additional functionality at the *ortho* position (e.g. salicylaldehyde) then it can lead to cyclized products (i.e. chromans) with allenes. In the palladium catalyzed reactions of allenes with 2-iodophenols, after the first step, the phenolic –OH residue of aryl moiety reacts with the alkenic double bond to lead to benzofurans.[84b] In the reverse sense of it, allenes **15a-f** that have an additional internal phenolic –OH can undergo intramolecular cyclization to lead to benzofurans. By keeping these points in mind, we have utilized allenes **15a-f** comprising a 2-hydroxy-phenyl moiety at the α-position and with an intention to explore the intramolecular nucleophilic cyclization. Although allene **15a** did not react with triethylamine at room temperature, when the mixture was heated under reflux for 2 h, we succeeded in obtaining the expected benzofuran **70**. This reaction was clean and the product **70** was obtained in excellent yield (Scheme 28). This compound is known,[85] and the spectroscopic data is in consistent with that reported in the literature. However, the literature method[85] is

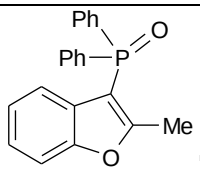
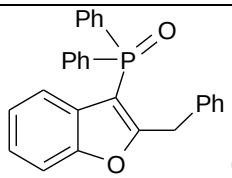
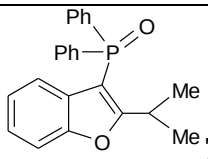
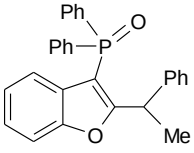
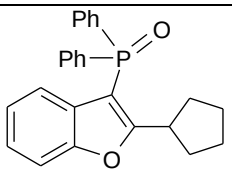
complicated and hence we decided to proceed further *via* our simple route by using various allenylphosphine oxides **15b-f** leading to **71-75** (Table 3). One of the products (**75**, Table 3, entry 6) is characterized by single crystal X-ray crystallography (Fig. 18). The newly formed five-membered furan ring comprises the atoms O2, C13, C14, C19 and C20. The phenolic proton could have moved to α-carbon also, but extended conjugation in compounds **70-75** is more favored.

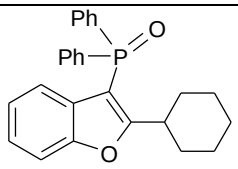
Scheme 28



15a-f **70-75**

Table 3: 2,3-Disubstituted benzofurans synthesized according to Scheme 28[a]

entry	allene	product	Yield[b]	δ(P)
1	**15a**	 **70**	95	21.3
2	**15b**	 **71**	89	21.5
3	**15c**	 **72**	90	21.5
4	**15d**	 **73**	93	21.6
5	**15e**	 **74**	88	21.7

6	**15f**	 **75** (X-ray)	90	21.2

[a]Reaction conditions: Allene (1.0 mol equiv.), Et_3N (1.0 mol equiv.), THF (2 mL), reflux for 1-2 h. [b]Isolated yield.

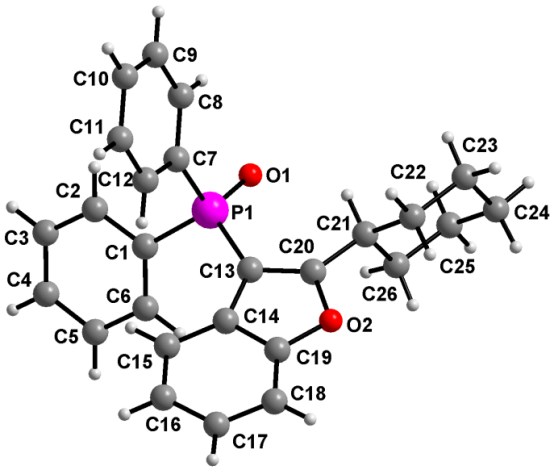


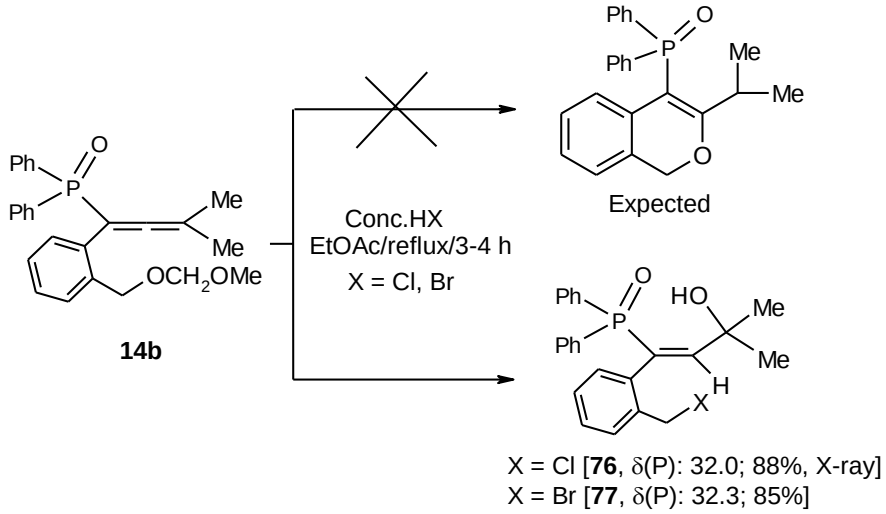
Figure 18. Molecular structure of compound **75**. Two molecules are present in the asymmetric unit, but only one is shown for clarity. Selected bond lengths [Å] with esd's in parentheses: P1-C13 1.782(3), O2-C20 1.379(3), C13-C20 1.357(4), C20-C21 1.477(4).

2.42 Attempted synthesis of 3,4-disubstituted isochromenes via MOM protected allenes 14a-d: Formation of non-cyclized products 76-77 and 3,4-disubstituted isochromenes 78-81

Inspired by above results, and in order to extend the nucleophilic reaction strategy, we chose MOM protected allenes **14a-d**. If the MOM part is deprotected by using HCl, there is a good chance for cyclization leading to 6-membered heterocycle. Hence, we attempted the deprotection of the MOM group containing allene **14b** in the presence of conc. HCl in EtOAc. There was no reaction at room temperature, but under reflux conditions (Scheme 29), we obtained the benzylic halide **76** which obviously is not the expected 6-membered heterocycle. The ^{1}H NMR spectrum of **76** shows two doublets at δ 3.70 and 4.07 with ^2J(H-H) = 11.5 Hz suggesting the presence of CH_2Cl protons (AB pattern). The olefinic carbon

connected to phosphorus appears at δ 128.5 with ^{1}J(P-C) of 106.5 Hz in the ^{13}C NMR spectrum. In the mass spectrum, peaks at m/z 413 and 411 in 1:3 ratio indicate the presence of chlorine atom. As a means for confirmation, compound **76** was subjected to single crystal X-ray crystallographic analysis (Fig. 19). The presence of the –OH group is readily discerned by the observation of H-bonding interaction of –OH group with the P=O acceptor. To check the consistency of this reaction, we also prepared the bromo substituted compound **77** in a similar manner by using conc. HBr (Scheme 29).

Scheme 29



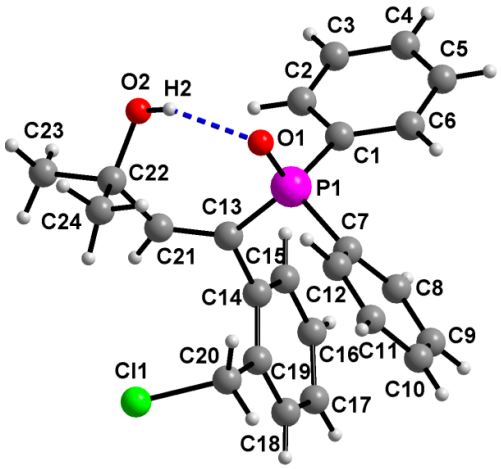
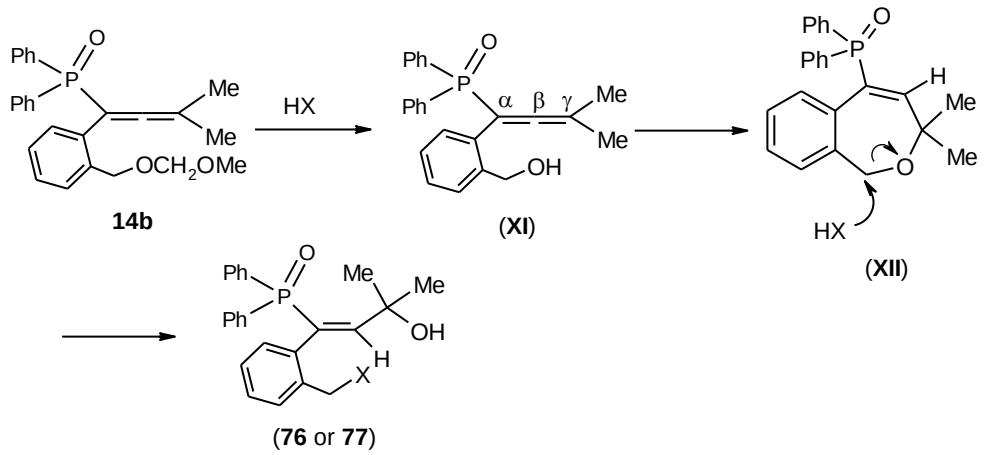


Figure 19. Molecular structure of compound **76**. Two molecules are present in the asymmetric unit. But only one molecule is shown for clarity. Selected bond lengths [Å] with esd's in parentheses: P1-C13 1.809(5), P2-C37 1.823(5), O2-C22 1.444(6), O4-C46 1.426(5), Cl1-C20 1.814(5), Cl2-C44 1.809(6), C13-C21 1.353(6), C37 C45 1.333(6), C21-C22 1.514(6), C22-C23 1.537(7), C22-C24 1.502(7), C45-C46 1.531(6), C46-C47 1.541(7), C46-C48 1.525(7). Intramolecular hydrogen bonding

parameters: O2-H2…O1 0.82, 1.95, 2.673(5), 146.7; O4-H4…O3 0.82, 1.87, 2.661(5), 162.6.

The unexpected formation of the products **76-77** can be explained by the speculative mechanism depicted in Scheme 30. Initially, the deprotection of MOM-allene **14b** can lead to the alcohol containing allene **XI**. Then, the benzylic -OH may attack at the γ-position of the allene part affording the 7-membered ring intermediate **XII**. This is followed by addition of HX [X = Cl or Br] at the *C*H_2O carbon of the 7-membered ring to open up the ring and furnish the product **76** or **77**. Perhaps the use of the strong Brönsted acid HX [X = Cl or Br] cleaves the 7-membered ring; use of a Lewis acid may deliver the 6- or 7-membered heterocycle (*vide infra*).

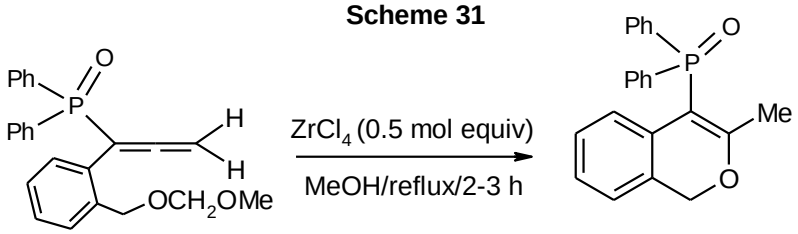
Scheme 30



Since our plan was to obtain the cyclized product and the use of strong Brönsted acid resulted in non-cyclized component, a Lewis acid is compulsory. Based on a literature report for the deprotection of MOM group leading to alcohols, we then made an attempt to deprotect allene **14a** by employing the Lewis-acid $ZrCl_4$.[86] Thus we treated allene **14a** with of $ZrCl_4$ [0.5 mole equiv] in methanol under reflux over a period of 2 h. To our surprise, this reaction ended up with nucleophilic addition-cyclization product **78** (Scheme 31) in one-step and there was no deprotected allene or the previously obtained product of the type **76**. Two singlets at δ 1.91 and 5.08 in the ^{1}H NMR spectrum indicate the presence of CH_3 and CH_2O protons. This observation suggests the migration of the alcoholic proton to the γ-position (but not to the α-position) of the allene. The Ph_2P(O)-*C* carbon appeared as a doublet at δ 104.9 with ^1J(P-C) of 113.9 Hz which is in the expected range. We

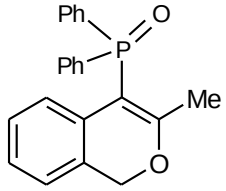
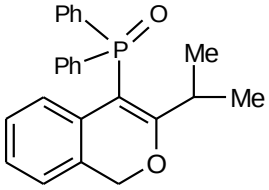
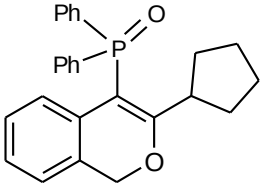
explored this reaction further by employing various γ-dialkyl substituted allenylphosphine oxides **14b-d** to obtain 3,4-disubstituted-1*H*-isochromenes **79-81** in excellent yields (Table 4). For further structural confirmation, one of these compounds (**79**, Table 4, entry 2) was subjected to single crystal X-ray crystallographic analysis (Fig. 20). The O2-C21 [1.370(3) Å] bond is newly formed and the C21-C22 distance [1.506(4) Å] is in the single bond range as expected.

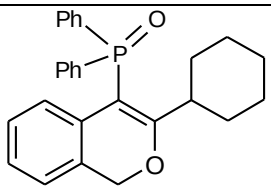
Scheme 31



14a **78**

Table 4: Isochromenes synthesized from allenylphosphine oxides **14a-d**[a]

entry	allene	product	Yield[b]	δ(P)
1	**14a**	 **78**	90	26.5
2	**14b**	 **79** (X-ray)	92	26.7
3	**14c**	 **80**	84	26.8

4	**14d**	 **81**	87	25.8

[a]Reaction conditions: Allene (1.0 mmol), $ZrCl_4$ (0.5 mol equiv.), MeOH (2 mL), reflux for 2-3 h. [b]Isolated yield.

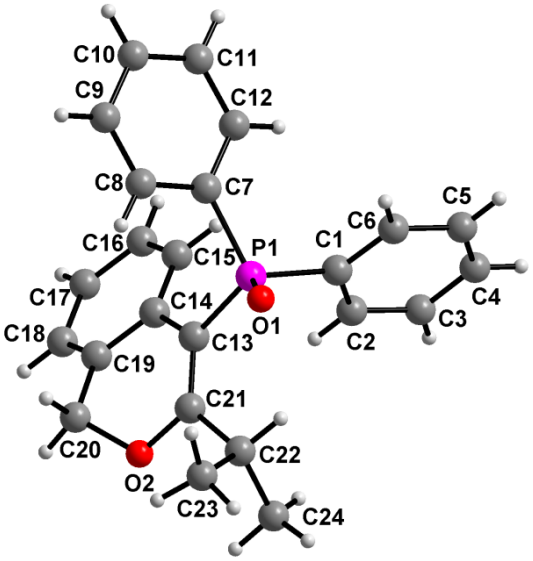


Figure 20. Molecular structure of compound **79**. Selected bond lengths [Å] with esd's in parentheses: P1-C13 1.799(3), O2-C21 1.370(3), C13-C21 1.349(4), C21-C22 1.506(4).

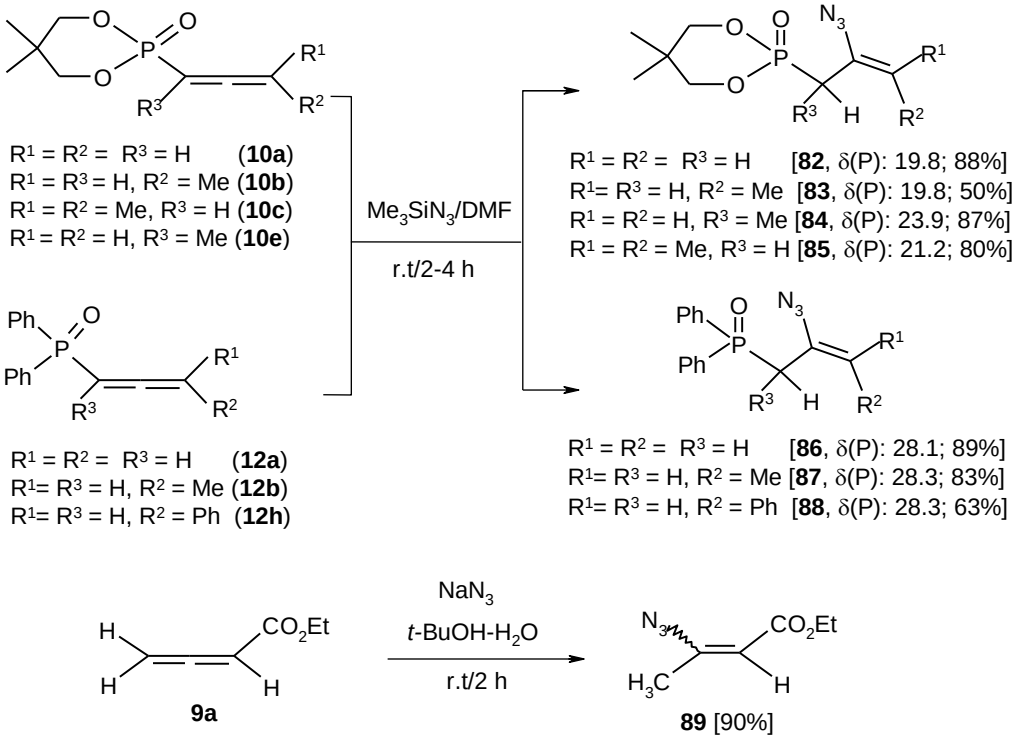
2.5 Synthesis and utility of nitrogen containing heterocycles prepared *via* allenes

2.51 Reaction of allenes 9a, 10a-c, 10e, 12a-c with Me_3SiN_3 or NaN_3: Synthesis of vinyl azides 82-89

As discussed in the Introduction (Chapter 1), vinyl azides are excellent precursors for the synthesis of nitrogen containing heterocyclics.[44-45, 52-55] Hence we became interested in the preparation of various phosphorus-based vinyl azides **82-88** (Scheme 32). They are obtained by following a procedure developed in our laboratory which involves treatment of allenylphosphonates/ allenylphosphine oxides with Me_3SiN_3 in DMF at room temperature (Scheme 32).[45] The vinyl azide **89** is prepared from ester allene **9a** by using a reported method.[44] Among these, **82**, **84** and **86-88** are new. These compounds (**82-89**) exhibit the $\nu(N_3)$ band at ~ 2100

cm^{-1}. A doublet at δ 2.74 (2H, ^{2}J(P-H) = 21.2 Hz) in the ^{1}H NMR and a doublet at δ 30.5 (d, ^{1}J(P-C) = 136.7 Hz) in the ^{13}C NMR, both characteristic of the PCH_2 group, are observed for compound **82**. In the case of azide **84**, a doublet of doublet is seen in the ^{1}H NMR spectrum at δ 1.43 (3H, ^{3}J(P-H) ~ 18.2 Hz, ^{3}J(H-H) ~ 7.0 Hz) for CHCH_3 protons. Vinyl azides **86-88** also show the expected spectroscopic pattern with lower *J* values in the ^{1}H/^{13}C NMR spectra.

Scheme 32



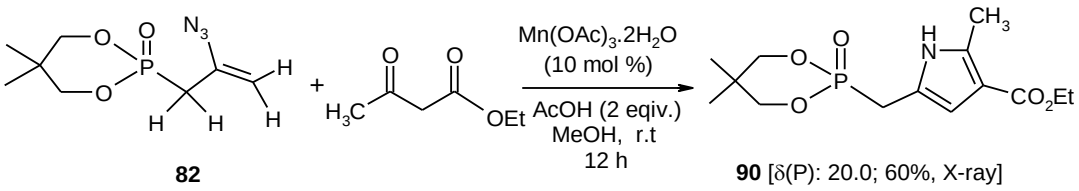
2.52 Reaction of allenes 10a-b, 10e, 12a-b with 1,3-dicarbonyl compounds via vinyl azides: Synthesis of 2-methylphosphonopyrroles/ 2-methylphosphine oxide pyrroles

Although there have been reports of many methods for the synthesis of pyrroles,[87] it is still challenging to prepare polysubstituted pyrroles with various substituents directly from the readily available building blocks. Recently, there are two reports in the synthetic preparation of pyrroles which involve vinyl azide and 1,3-dicarbonyl compounds as starting materials.[88] Since phosphonylated nitrogen heterocycles constitute an important class of compounds with significant biological potential,[89] new routes to them are still warranted. Only limited literature reports are available for the synthesis of phosphorus-based pyrroles. These cover only 2-

phosphonopyrroles [90] and 3-phosphonopyrroles[91] but a route to alkylphosphonopyrroles is not available so far. In this context, we planned the synthesis of phosphorus-based pyrroles from the corresponding vinyl azides.

Our experiment started by treating azide **82** with ethyl acetoacetate (EAA) and acetic acid in the presence of catalytic amount of $Mn(OAc)_3.2H_2O$ in methanol (Scheme 33).[88] Gratifyingly, we were successful in obtaining the expected ***alkylphosphono-pyrrole*** **90**. This reaction also worked well under photochemical conditions [λ = 254 nm] affording the final product **90** in excellent yield (90 %). The IR spectrum of this compound shows a band at 3248 cm^{-1} due to the NH stretch. A doublet at δ 3.23 [2H, ^2J(P-H) = 19.6 Hz] in the ^{1}H NMR and a doublet at δ 23.8 [^1J(P-C) = 136.8 Hz] in the ^{13}C NMR are observed due to P*CH*$_2$ group. In addition, a broad signal at δ 9.67 is present in the ^{1}H NMR spectrum due to N*H* proton. The strucure of **90** is confirmed by single crystal X-ray crystallography (Fig. 21). The newly formed pyrrole ring comprises the atoms N1, C7, C8, C9 and C10. The presence of the NH group is also revealed by its hydrogen-bonding interaction with the phosphoryl oxygen as shown in the Figure 22.

Scheme 33



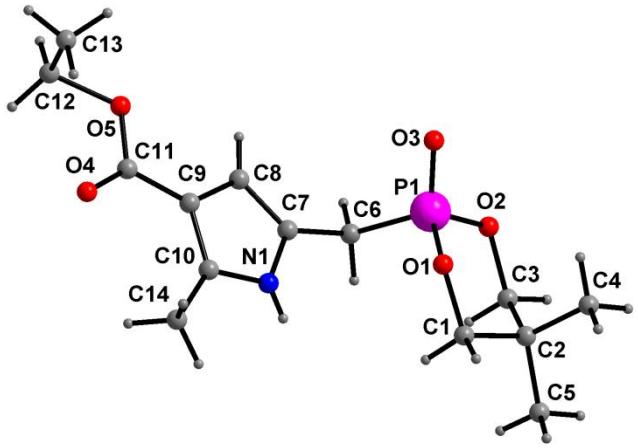


Figure 21. Molecular structure of compound **90**. Only one molecule is shown in the asymmetric unit. Selected bond lengths [Å] with esd's in parentheses: P(1)-C(6)

1.798(4), N(1)-C(7) 1.341(6), N(1)-C(10) 1.356(7), C(6)-C(7) 1.503(7), C(7)-C(8) 1.363(7), C(8)-C(9) 1.401(8), C(9)-C(10) 1.403(8).

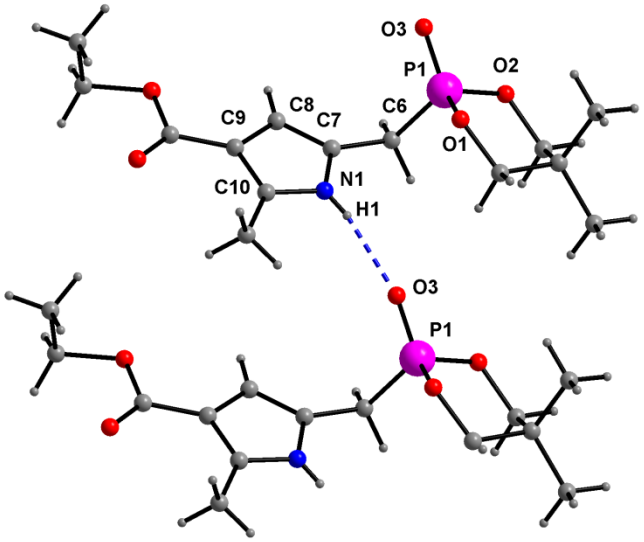
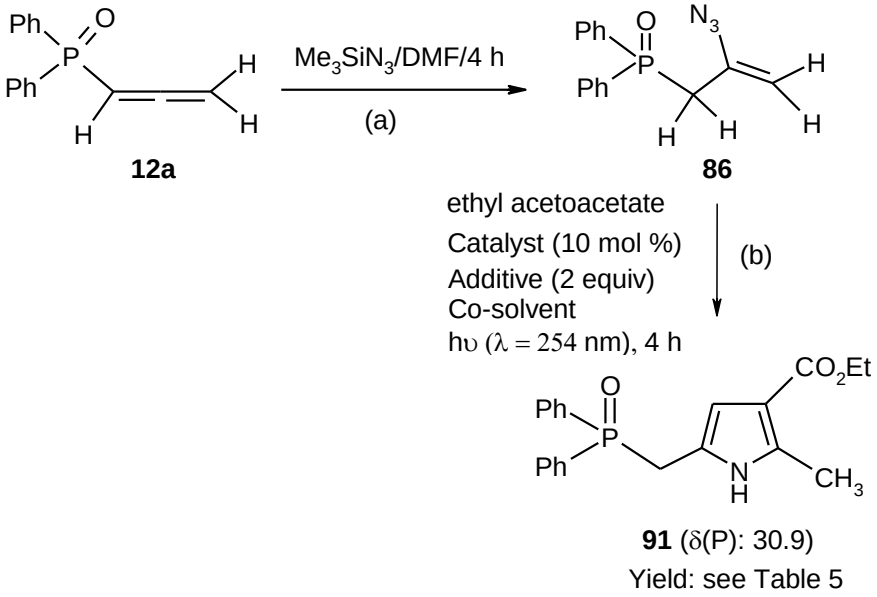


Figure 22. Drawing showing hydrogen bonding interactions in compound **90**: N(1)-H(1)…O(3) 0.74, 2.10, 2.833(5) Å 169.5°. Symmetry code: x, 1+y, z.

In order to perform the above reaction in one pot and also to maximize the yield of the product (under photochemical conditions), we have screened various co-solvents and additives. Optimization is done by taking the allene **12a** and ethyl acetoacetate (EAA) as model reactants for the synthesis of pyrrole **91** *via* azide **86** (Scheme 34). Formation of azide **86** is straightforward but needs a solvent like DMF; methanol does not work for this step. For the next step, we added methanol. There was no reaction in the absence of the catalyst [$Mn(OAc)_3.2H_2O$] or additive [acetic acid] (cf. Table 5, entries 1-2). However, in the presence of the catalyst and additive, the reaction occurred *smoothly to give product* **91** [entry 3] in *excellent yield*. Use of EtOH or *i*-PrOH lowered the yield and in fact there was no reaction in *t*-BuOH [entries 4-6]. DMF as a solvent was not effective for the second step [entry 7]. Trifluoroacetic acid or trifluoromethane sulfonic acid as an additive worked, but the yield was lower [entries 8-9]. PTSA was ineffective as an additive [entry 10]. Ceric ammonium nitrate (CAN) in place of [$Mn(OAc)_3.2H_2O$] also did not work [entry 11]. Thus, efforts towards the preparation of the pyrrole by employing the same solvent system (methanol or DMF) in two consecutive steps (cf. Scheme 34) failed. While DMF facilitates the azide formation, methanol is required for the

formation of pyrrole from azide. Hence, we carried out the first step in DMF and then a solution of ethyl acetoacetate, $Mn(OAc)_3.2H_2O$ and acetic acid in methanol was added to the crude azide under photochemical conditions to obtain pyrrole **91** in 88% yield.

Scheme 34



91 (δ(P): 30.9)
Yield: see Table 5

Table 5. Details on the conditions shown in Scheme 34(b)

Entry	Catalyst	Additive	Co-solvent (i.e. in addition to DMF)	Product yield **91** (%)[a]
1	-	Acetic acid	MeOH	n.r.
2	$Mn(OAc)_3.2H_2O$	-	MeOH	n.r.
3	$Mn(OAc)_3.2H_2O$	Acetic acid	MeOH	88
4	$Mn(OAc)_3.2H_2O$	Acetic acid	EtOH	65
5	$Mn(OAc)_3.2H_2O$	Acetic acid	^{i}PrOH	30
6	$Mn(OAc)_3.2H_2O$	Acetic acid	^{t}BuOH	n.r.
7	$Mn(OAc)_3.2H_2O$	Acetic acid	-	n.r.
8	$Mn(OAc)_3.2H_2O$	CF_3CO_2H	MeOH	46
9	$Mn(OAc)_3.2H_2O$	CF_3SO_3H	MeOH	10
10	$Mn(OAc)_3.2H_2O$	PTSA	MeOH	n.r.
11	CAN	Acetic acid	MeOH	n.r.

[a]Based on ^{31}P NMR analysis

After ascertaining that the above Mn-catalyzed reaction works, we explored the reactivity of other allenylphosphonates **10a**, **10b** and **10e** with three dicarbonyls (ethyl acetoacetate, ethyl-4-chloro acetoacetate and acetyl acetone) under the optimized conditions ($Mn(OAc)_3.2H_2O$/acetic acid/methanol/hυ) (Scheme 35). In all the cases, the reaction underwent smoothly to produce the substituted pyrrole derivatives **92-99** in good to excellent yields after isolation (Scheme 35, Table 6). However, in the reaction of the allenes **10a-b** and **10e** with ethyl-4-chloro acetoacetate, surprisingly, the –Cl atom was exchanged for the –OMe group in the products **94-96** (cf. Table 6, entries 4-6). This exchange substantiates the radical mechanism proposed in the literature for similar reactions.[88] Since the spectroscopic data for compounds **92-99**, are similar to that of compound **90**, they are not elaborated here. As a means for confirmation, the compound **97** was also characterized by single crystal X-ray crystallography (Fig. 23). Similar to compound **90**, N1, C7, C8, C9 and C10 form the pyrrole ring. The presence of NH group is established by its hydrogen-bonding interaction with the phosphoryl oxygen and is shown in Figure 24.

Scheme 35

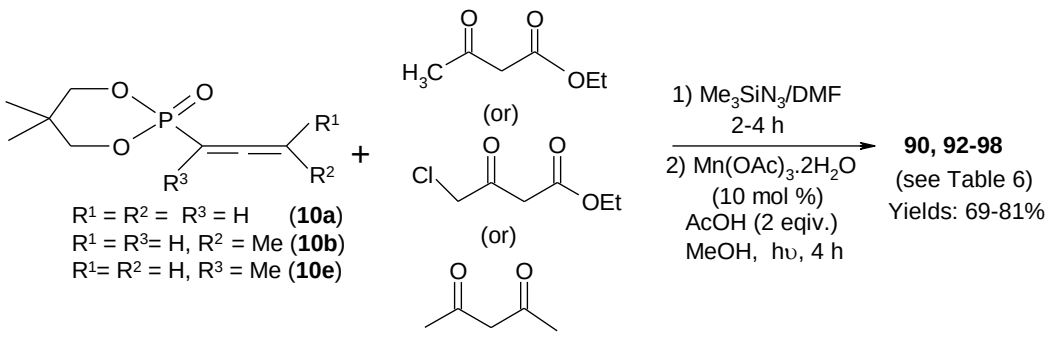
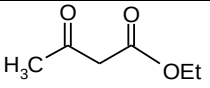
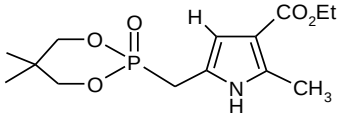
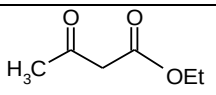
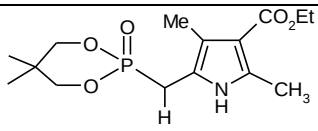
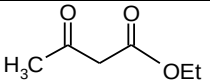
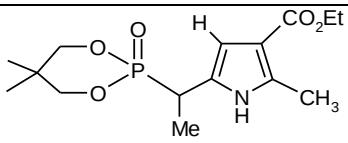
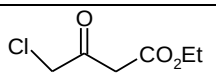
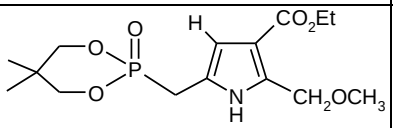
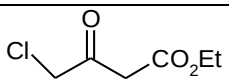
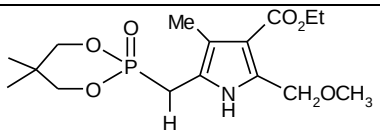
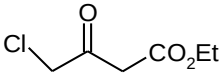
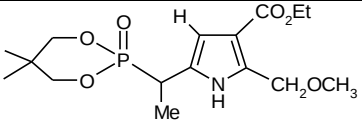
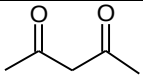
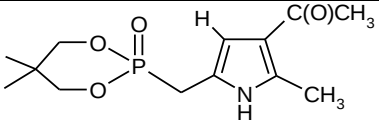
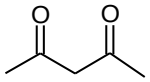
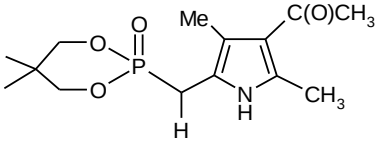
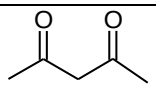
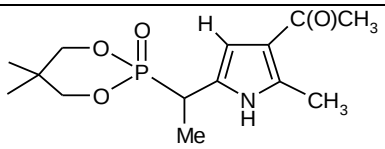


Table 6: Various pyrrole derivatives synthesized from allenes **10a-b** and **10e** with 1,3-dicarbonyls (cf. Scheme 35).

Entry	allene	1,3-dicarbonyl substrate	product	Yield[a]	δ(P)
1	**10a**		 **90** (X-ray)	80	20.0

2	**10b**		 **92**	81	21.3
3	**10e**		 **93**	79	24.7
4	**10a**		 **94**	78	20.5
5	**10b**		 **95**	69	21.3
6	**10e**		 **96**	77	24.8
7	**10a**		 **97** (X-ray)	72	20.4
8	**10b**		 **98**	72	21.3
9	**10e**		 **99**	71	25.1

[a]Isolated yield.

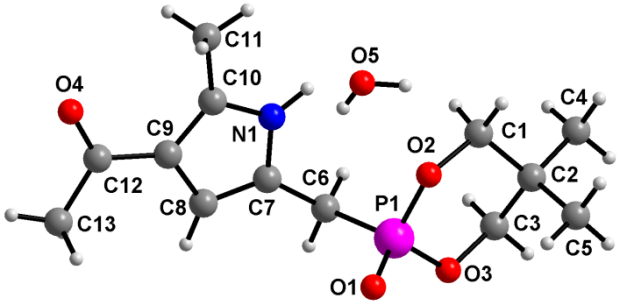


Figure 23. Molecular structure of compound **97**.H_2O. Selected bond lengths [Å] with esd's in parentheses: P1-C6 1.792(3), N1-C7 1.373(3), N1-C10 1.361(3), C6-C7 1.496(3), C7-C8 1.364(3), C8-C9 1.429(3), C9-C10 1.384(3).

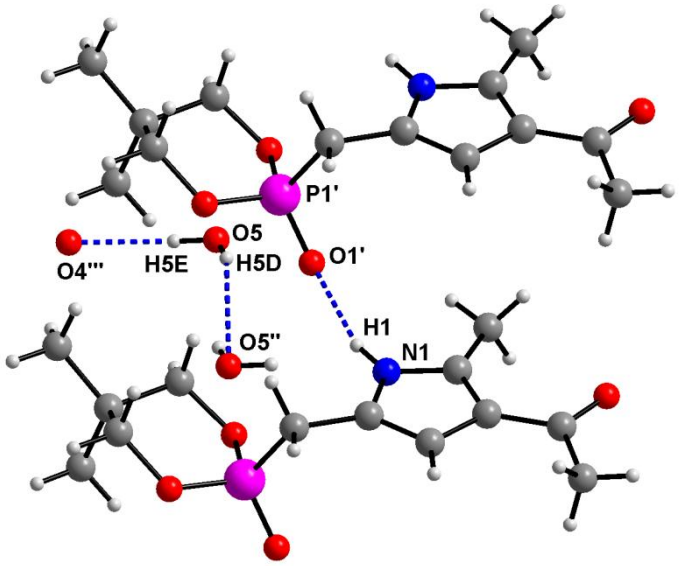
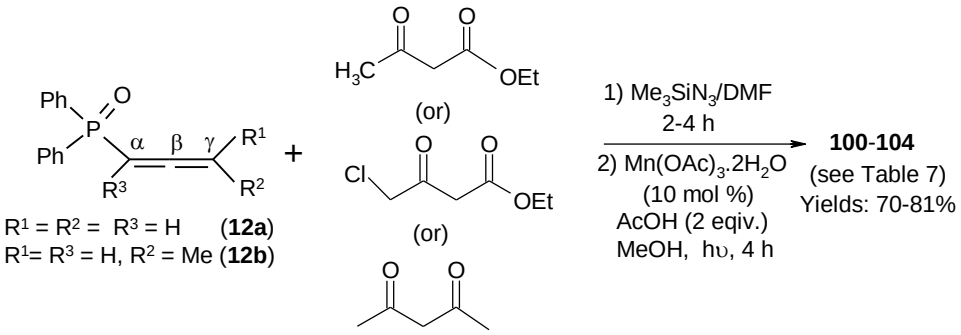


Figure 24. A schematic drawing showing the hydrogen bonding interactions in compound **97** (Å, °): N(1)-H(1)…O(1')^{i} 0.89, 1.95, 2.805(2) Å, 160.6°, O(5)-H(5D)…O(5")^{ii} 0.66(6), 2.38(6), 2.967(10) Å, 150(8)°, O(5)-H(5E)…O(4"')^{iii} 0.85, 2.02, 2.857(3) Å, 170.6°; Symmetry codes: (i) -1+x, y, z (ii) 1-x, 1-y, -z, (iii) x, 1+y, z.

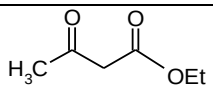
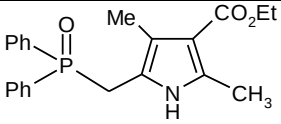
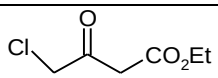
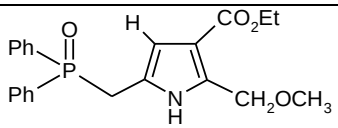
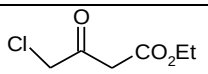
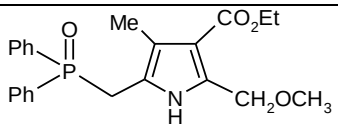
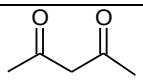
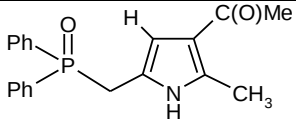
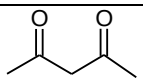
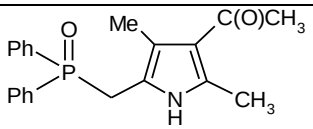
We then extended this work to allenylphosphine oxides **12a-b** and prepared the pyrroles **100-104** (Scheme 36, Table 7). The ^{31}P NMR spectra of these compounds show a peak at δ 30.5-33.0. A doublet in the range δ 3.62-4.16 [^{2}J(P-H) of ~ 12.4 Hz] in the ^{1}H NMR spectra, and a signal at ~ 29.5 [^{1}J(P-C) of ~ 68.9 Hz] in the ^{13}C NMR spectra are observed due to the P*CH* moiety. The N*H* proton is seen at δ ~ 9.90 in the ^{1}H NMR spectra.

Scheme 36



$R^1 = R^2 = R^3 = H$ (**12a**)
$R^1 = R^3 = H$, $R^2 = Me$ (**12b**)

Table 7: Synthesis of phosphine oxide-based pyrrole derivatives **100-104** using allenes **12a-b**, and 1,3-dicarbonyls (cf. Scheme 36).

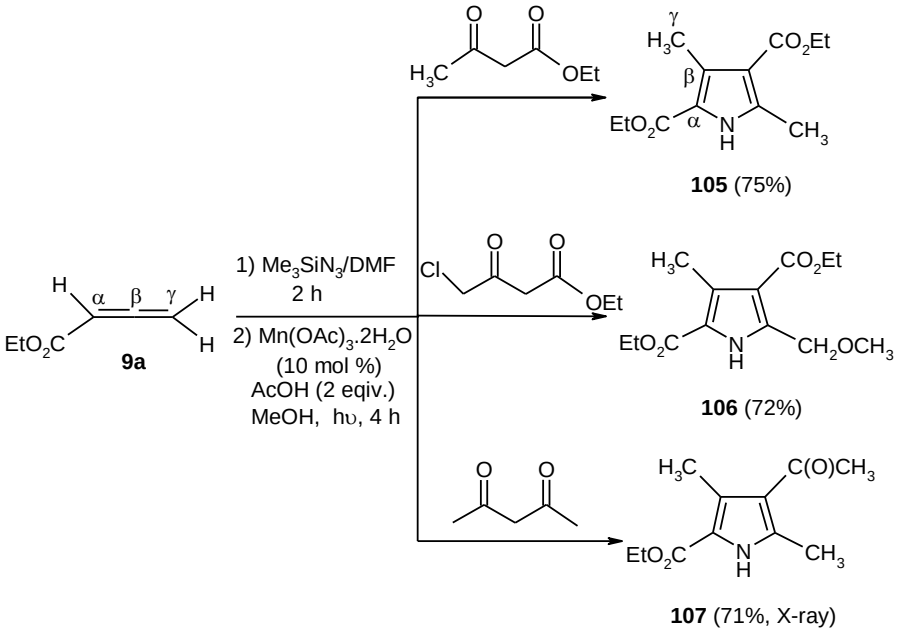
Entry	allene	1,3-dicarbonyl substrate	product	Yield[a]	δ(P)
1	**12b**		 **100**	81	30.8
2	**12a**		 **101**	80	30.5
3	**12b**		 **102**	77	30.8
4	**12a**		 **103**	70	33.0
5	**12b**		 **104**	73	32.0

[a]Isolated yields

2.53 Comparison of the reactivity of phosphorus-based allenes with ester allene CH_2=C=C(CO_2Et)H (9a): Synthesis of pyrroles 105-107

In the reaction of the *in situ* formed vinyl azide **89** with 1,3-dicarbonyls under the above reaction conditions resulted in the fully substituted pyrroles **105-107** (Scheme 37). It is clear that in the case of phosphorylated allenes, the β,γ-carbon atoms of allenes are involved in the pyrrole ring formation (Scheme 35 or 36) whereas in ester allene **9a**, α,β-carbons are participating (Scheme 37). The IR spectra of these compounds show a band at ~ 3289 cm^{-1} due to the NH stretch as expected. The characteristic signal corresponding to the NH proton appears at δ ~ 9.00 in the ^{1}H NMR spectra. Single crystal X-ray data was also collected for compound **107** (Fig. 25). This product exists in a dimeric form due to hydrogen-bonding interaction between NH and carbonyl oxygen of the ester group.

Scheme 37



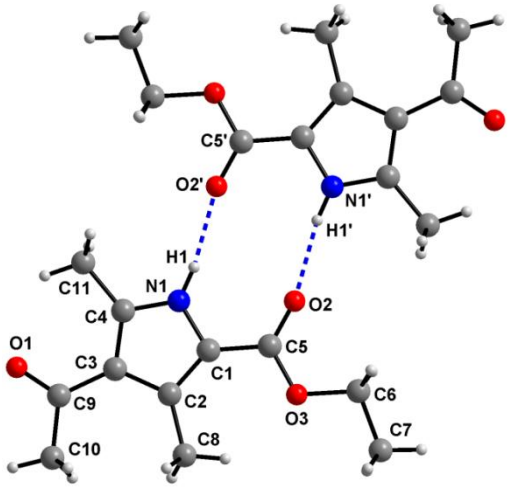
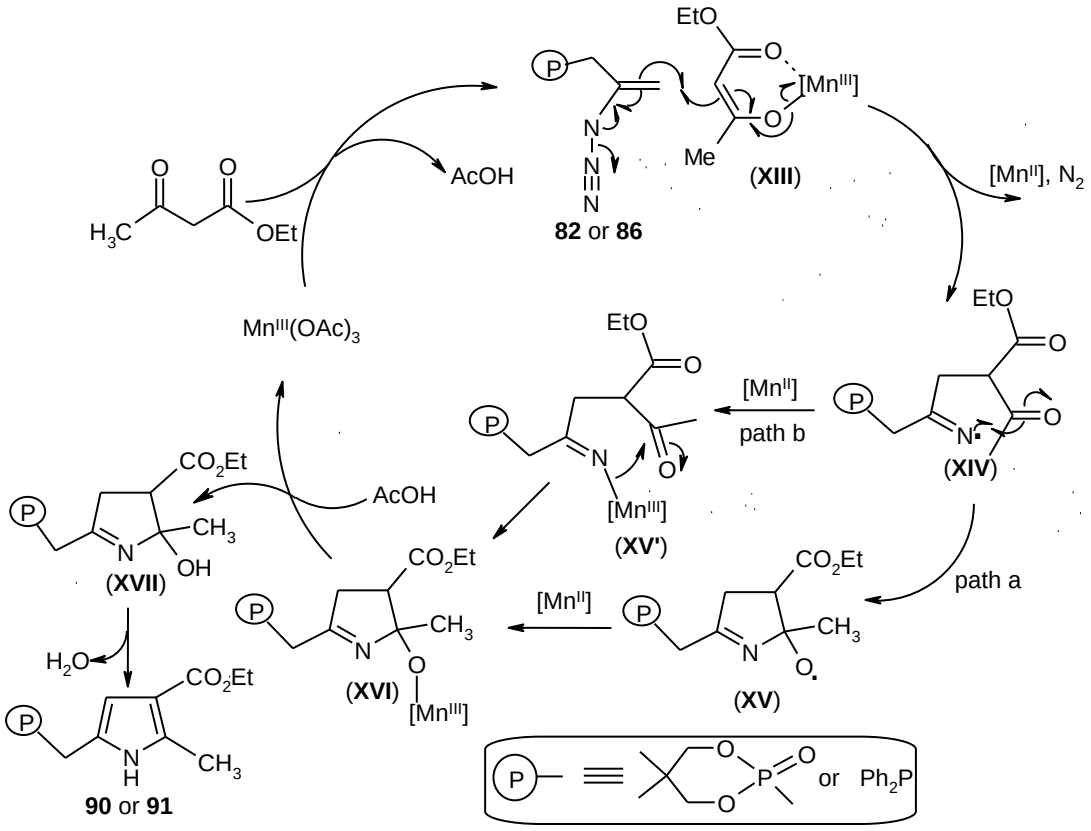


Figure 25. Dimeric structural unit of compound **107** due to the hydrogen bonding. Selected bond lengths [Å] with esd's in parentheses: N1-C1 1.370(3), N1-C4 1.332(3), C1-C2 1.380(3), C2-C3 1.423(3), C3 C4 1.395(3). Hydrogen bonding parameters: N(1)-H(1)…O(2') 0.87, 1.99, 2.852(3) Å, 171.0°. Symmetry code: 2-x, 1-y, 2-z.

We propose a free radical pathway for this Mn(III) catalyzed reaction based on a literature report on Mn(III) catalyzed reaction of vinyl azides with 1,3-dicarbonyl species.[88] Initially, addition of Mn(III) enolate (**XIII**) to vinyl azide occurs to form iminyl radical (**XIV**) with the release of Mn(II) species and dinitrogen (Scheme 38). This iminyl radical (**XIV**) undergoes an intramolecular addition to carbonyl group resulting in alkoxyl radical (**XV**). Reduction of this alkoxyl radical (**XV**) by Mn(II) species gives rise to Mn(III) alkoxide (**XVI**) [path a]. An alternate route is the reaction of iminyl radical (**XIV**) with Mn(II) species affording alkylideneiminomanganese(III) (**XV'**) [path b], which upon further nucleophilic attack on the carbonyl group leads to intermediate (**XVI**). Final steps involve the protonation of (**XVI**) with acetic acid leading to **XVII** followed by dehydration and proton shift to give pyrrole **90** or **99** along with regenerated Mn(III) species.

Scheme 38



2.54 Formation of triazoles from the reaction of vinyl azides with dicarbonyls or alkynes

2.541 Reaction of azides $Ph_2P(O)CH_2C(N_3)=CH_2$ (86) and $Ph_2P(O)CH_2C(N_3)=CH(Ph)$ (88) with dicarbonyls: Formation of triazoles 108-112

It is noteworthy that subtle changes in the reaction conditions can lead to different products. This phenomenon was observed when the azides and dicarbonyls were reacted in the presence of triethylamine, instead of Mn(III) as the catalyst. Thus the azide **86** upon treatment with acetyl acetone and two mole equivalents of triethylamine in DMF afforded the phosphorus-based fully substituted 1,2,3-triazoles **108** and **109** as shown in Scheme 39. The product **109** is formed *via* proton migration from α-CH_2 (to phosphorus) of compound **108**. These two products can be easily distinguished by spectroscopic data. In the ^{31}P NMR spectra, compounds **108** and **109** exhibit signals at δ 26.0 and 20.3, respectively. In the ^{1}H NMR spectra, the PCH_2 protons exhibit a doublet at δ 3.89 [^{2}J(P-H) = 12.8 Hz] for **108**, while the PC*H* proton is seen at δ 6.27 [^{2}J(P-H) = 17.6 Hz] for **109**. The ^{13}C NMR spectra also show distinct signals: at δ 37.4 [^{1}J(P-C) = 64.0 Hz] for **108** and at δ 120.3 [^{1}J(P-C) =

97.3 Hz] for **109** that are consistent with the corresponding carbon being sp^3 or sp^2 hybridize, respectively. These observations suggest the presence of P-CH_2 group in **108** and PCH= group in **109**. The reaction of **86** with ethyl acetoacetate or benzoyl acetone led mostly to the rearranged product (**110** or **111**; Table 8). As longer time (24 h) is required for this reaction, it is likely that the initial product with a PCH_2 group (similar to product **108**) might have rearranged leading to **110** or **111**. The azide $Ph_2P(O)CH_2C(N_3)=C(Ph)H$ (**88**) under these conditions afforded only compound **112** that has PCH_2 moiety.

Scheme 39

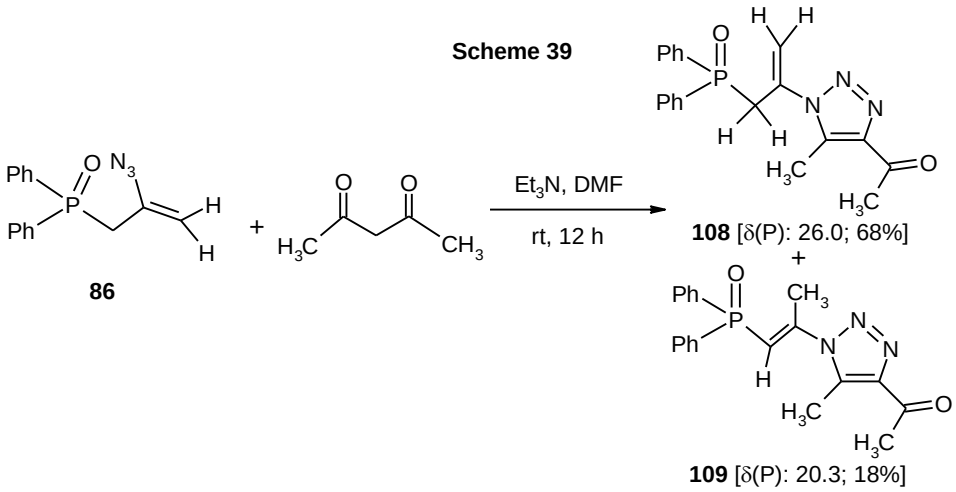
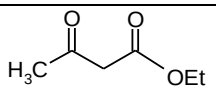
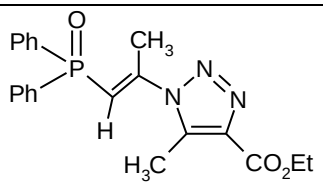
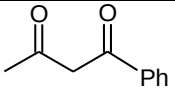
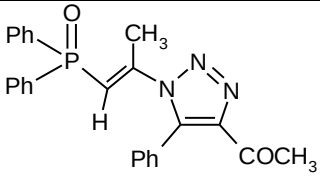
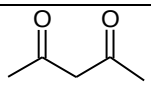
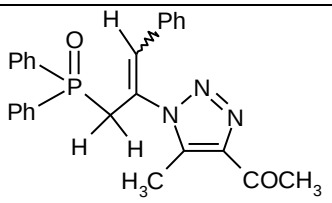


Table 8: Synthesis of phosphine oxide-based triazole derivatives **110-112** from azides **86** or **88** and 1,3-dicarbonyls (acetyl acetone, ethyl acetoacetate, benzoyl acetone).

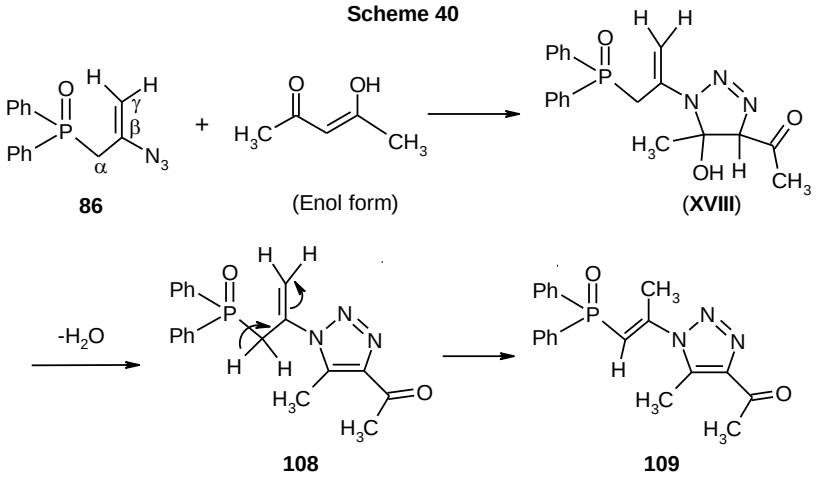
Entry	azide	1,3-dicarbonyl substrate	product	Yield[a]	δ(P)
1	**86**		 **110**	65	20.3
2	**86**		 **111**	68	20.0

3	**88**		 **112**	70	25.5

[a]Isolated yields

As far as the mechanism is concerned, the enol form of acetyl acetone can undergo a 1,3-dipolar addition with azide **86** leading to 1,2,3-triazoline intermediate (**XVIII**) which upon water elimination results in compound **108** (Scheme 40). [92] Proton migration from α-carbon of compound **108** resulted in product **109**. A detailed study on mechanism and generalization of this reaction is still in progress.

Scheme 40

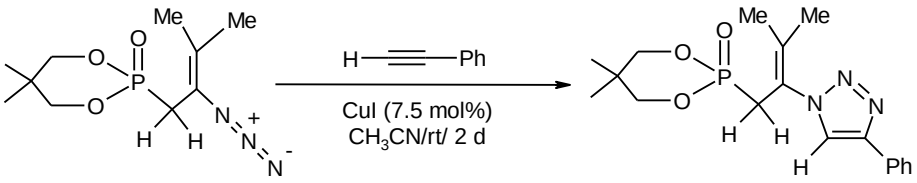


2.542 Reaction of azide $(OCH_2CMe_2CH_2O)P(O)CH_2C(N_3)=CMe_2$ (85) with phenyl acetylene: Synthesis of phosphono-1,2,3-triazole 113

Azides can undergo 1,3-dipolar cycloaddition with activated acetylenes to give 1,2,3-triazoles[93-94] and hence we reacted **85** with phenyl acetylene in the presence of CuI in acetonitrile as solvent (Scheme 41). We were successful in obtaining phosphono-1,2,3-triazole **113** stereoselectively in high yield. The ^{31}P NMR spectrum of product **113** showed a peak at δ 19.3. A doublet at δ 3.28 (^2J = 20.0 Hz) due to P*C*H_2 and a singlet at δ 7.98 due to the presence of =C*H* proton of the triazole ring were seen in the ^{1}H NMR spectrum. In the ^{13}C NMR spectrum, a doublet at δ 29.1 (^1J = 133.4 Hz) appeared due to P*C*H_2 carbon. The stereochemistry of this compound was established by comparison of the X-ray structure of a similar

compound reported from our laboratory.[45] For the same reason, this part of the work was not elaborated further.

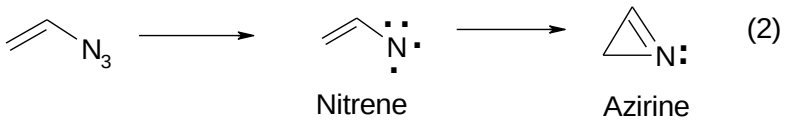
Scheme 41



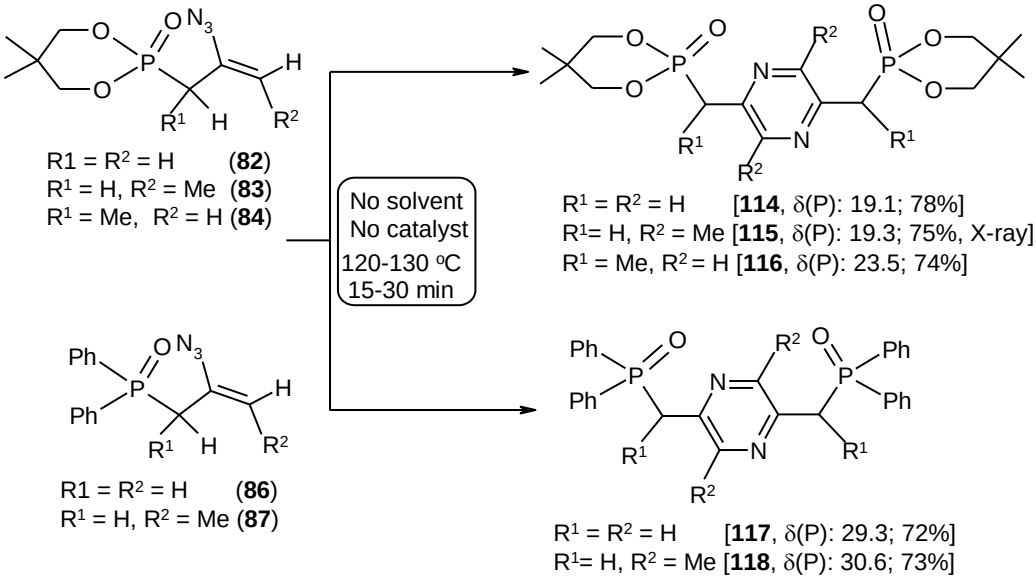
85 **113** [δ(P): 19.3; 80%]

2.55 Formation of phosphorus-based pyrazines 114-118 via vinyl azides

In this section, we focus our attention on the thermal stability of phosphorus-based vinyl azides. Usually, substituted vinyl azides under pyrolysis conditions yield azirines (cf. equation 2 below).[95] While checking the melting point of azide **82**, gas evolution at the melting region (of temperature) is observed. Upon further heating, gas evolution stops resulting in a solid material. In order to analyze the chemistry behind this, we heated *ca* 0.2 g of compound **82** above its melting point (15 min) to get a new solid material **114**. The ^{31}P NMR spectrum showed a single peak at δ 19.1. A doublet at δ 3.51 [^{2}J(P-H) = 20.8 Hz] in the ^{1}H NMR spectrum and the corresponding carbon at δ 32.2 [^{1}J(P-C) = 131.8 Hz] in the ^{13}C NMR spectrum indicated the presence of a P*C*H_2 group. The structure of this compound is ascertained conclusively by single crystal X-ray crystallography of a similar product **115** obtained from the azide **83** (Fig. 26). Thus, the resulting product upon heating phosphorus-based vinyl azides under neat condition (no solvent, no catalyst) was pyrazines (Scheme 42) ***and not azirines***. From Figure 26, it is clear that N1, C7, C8, N1A, C7A and C8A form the pyrazine ring. Even phosphine oxide-based azides **86-87** also led to pyrazines **117-118** under similar reaction conditions (Scheme 42).



Scheme 42



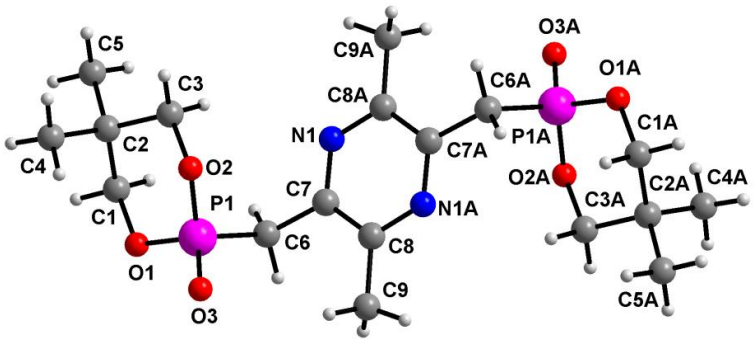
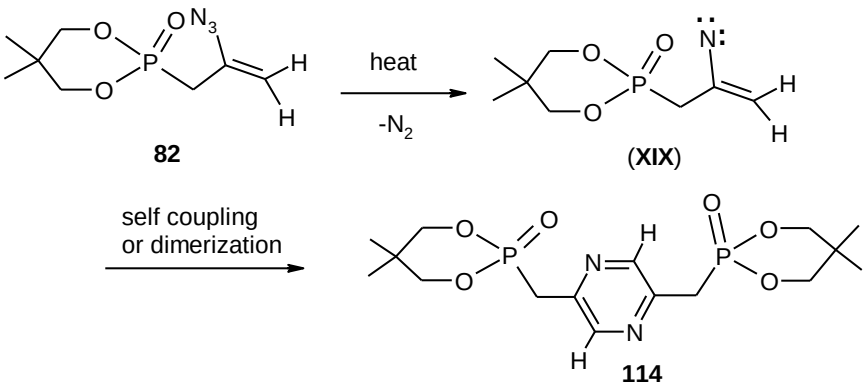


Figure 26. Molecular structure of compound **115**. Only a half molecule is present in the asymmetric unit. Full molecule is generated by growing. Selected bond lengths [Å] with esd's in parentheses: P1-C6 1.8028(19), N1-C8A 1.336(2), C6-C7 1.508(3), C7-C8 1.398(3), C8-C9 1.494(3).

The above pyrazines are likely to have formed *via* a radical mechanism as shown in Scheme 43. When the azide **82** was heated under neat conditions, N_2 molecule is eliminated to give the nitrene intermediate (**XIX**). The self dimerization of this intermediate leads to the pyrazine **114**. Formation of other pyrazines (**115-118**) is also explained *via* this pathway. An approximate weight loss of 10%, that is equal to loss of a nitrogen molecule from compound **86**, is observed in the TGA study (Fig. 27).

Scheme 43



82 (**XIX**) **114**

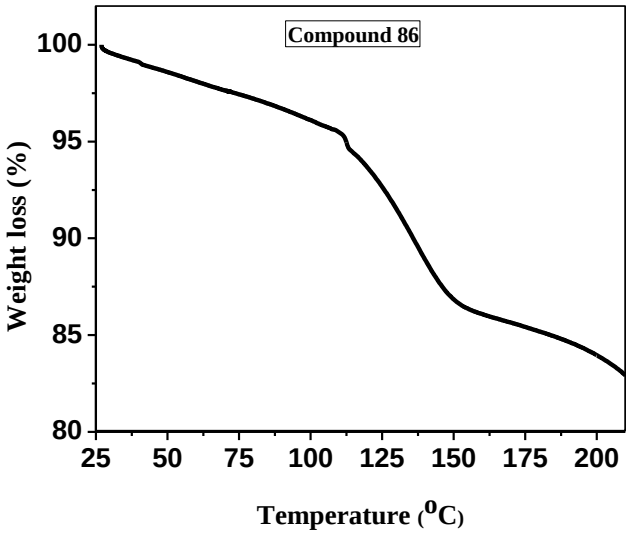


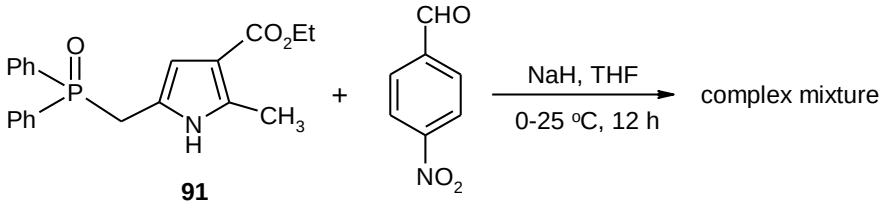
Figure 27. A drawing showing the TGA behavior of azide **86**.

2.56 Utility of phosphorus-based heterocycles in Horner-Wadsworth-Emmons (HWE) reaction: Synthesis pyrroles 119 (protected), 120-121, 123-124 and triazoles 125-128

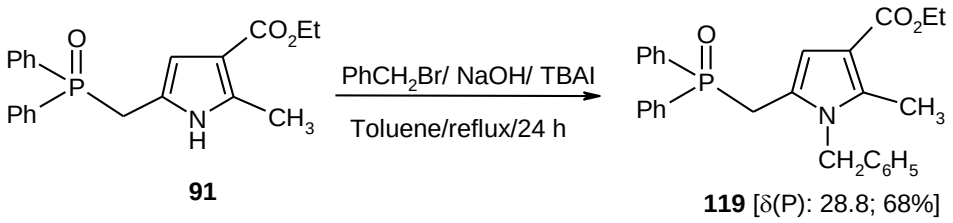
We were interested to see if at least some of the phosphorus-based heterocycles synthesized in the above sections (**2.52** and **2.53**) could be utilized further and in this direction, we felt that HWE reaction of these products possessing a PCH_2 group should be straightforward. In general, phosphinates or phosphonates having PCH_2 group undergo this reaction easily with aldehydes in the presence of suitable base to afford 1,3-butadiene.[45] Thus we treated phosphorus containing-pyrrole **91** with 4-nitrobenzaldehyde by using NaH as base in THF as solvent (Scheme 44). In this case, we could not isolate the expected product since the

reaction mixture was complex (TLC evidence). Hence we protected the pyrrole NH with CH_2Ph by using a known procedure [96] to afford compound **119** (Scheme 45). The newly formed protected compound **119** was characterized by spectroscopic and analytical data.

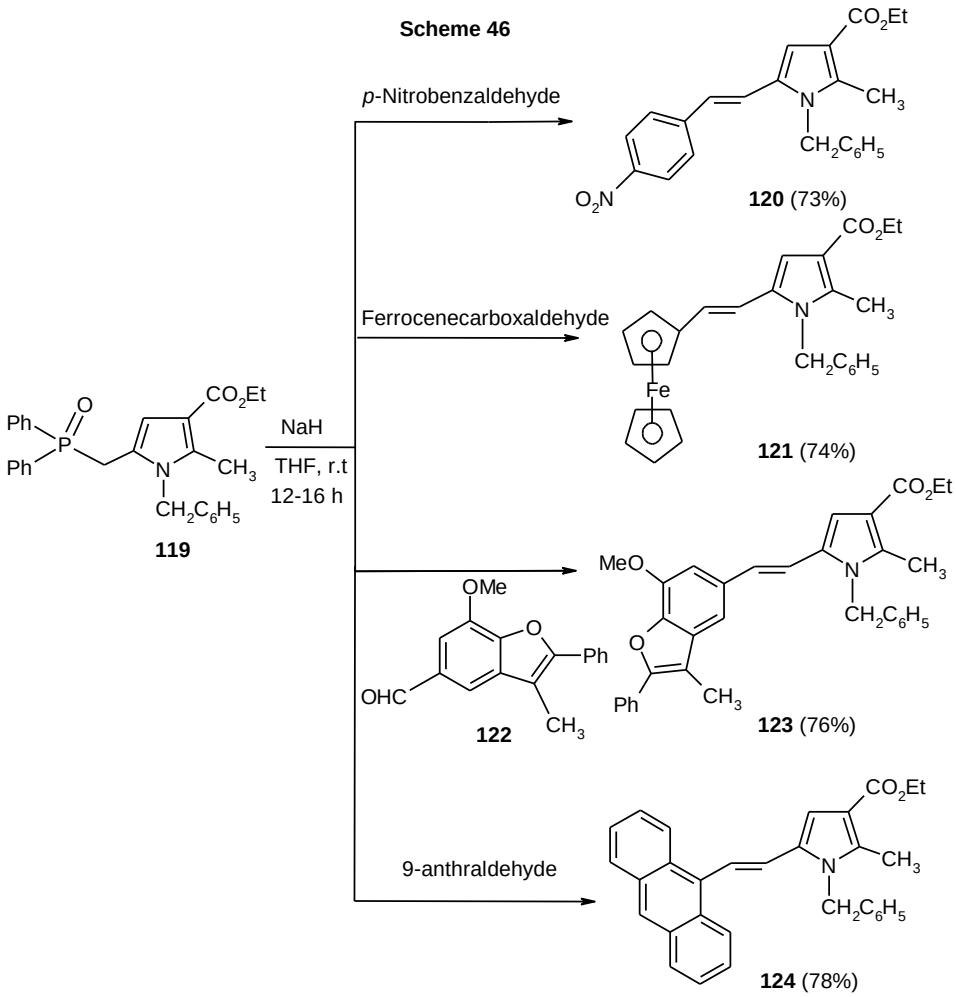
Scheme 44



Scheme 45



We have been able to perform the olefination of *N*-benzylated compound **119** using *p*-nitrobenzaldehyde by HWE reaction affording the product **120** in good yield (Scheme 46). Similarly, olefins **121, 123-124** were also prepared by treating compound **119** with ferrocene carboxaldehyde, compound **122**[58] and 9-anthraldehyde, respectively (Scheme 46). These compounds exhibit a band at ~ 1697 [ν(C=O)] and ~ 1598 [ν(C=C)] cm^{-1}. In the case of compounds **121** and **124** a doublet observed at δ 6.66 [^3J(H-H) = 15.8 Hz] and 7.72 [^3J(H-H) = 16.2 Hz] respectively in the ^{1}H NMR spectra suggests that the olefin is having a (*E*)-configuration. The structure of one of these compounds **124** is confirmed by X-ray crystallography (Fig. 28). Thus this reaction clearly shows one possible avenue for utililizing these phosphorus-based pyrroles.



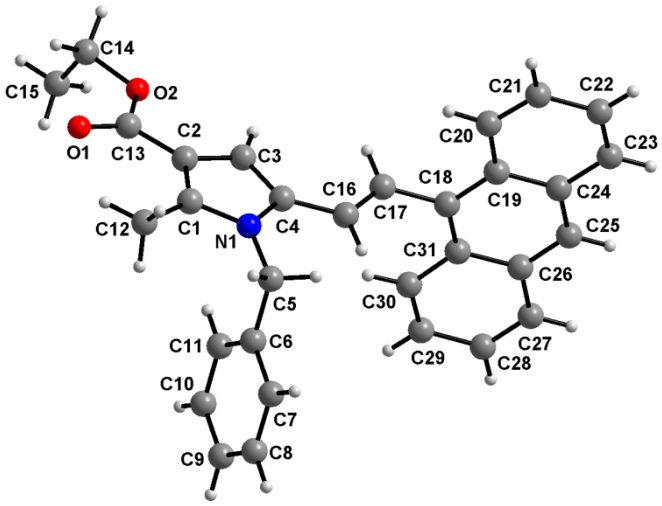
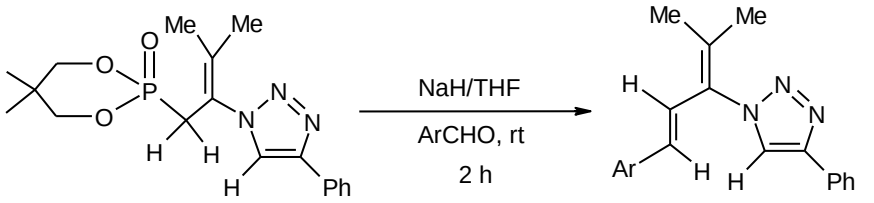


Figure 28. Molecular structure of compound **124**. Selected bond lengths [Å] with esd's in parentheses: C4-C16 1.453(6), C16-C17 1.263(6), C17-C18 1.485(7).

In the case of phosphonotriazole also, we were successful in getting the HWE products which are phosphorus-free 1,2,3-triazoles. Thus we treated substrate

113 with various aryl aldehydes under conditions discussed above to form triazoles **125-128** (Scheme 47). These compounds show a band at ~ 1611 cm^{-1}due to C=C stretch in the IR spectra. In the ^{1}H NMR spectra of these compounds a doublet at δ ~ 5.77 [^3J(H-H) = 16.0 Hz] due to =C*H* proton with a (*E*)-configuration is seen. Thus this approach opens up a convenient access to diverse phosphorus-free triazoles since three variables allene, acetylene and the aldehyde are available.

Scheme 47



113

Ar = Ph [**125**; 75%]
4-Me-C_6H_4 [**126**; 78%]
4-Cl-C_6H_4 [**127**; 75%]
4-MeO-C_6H_4 [**128**; 76%]

SUMMARY – PART A

1) The reaction of $(OCH_2CMe_2CH_2O)PCl$ (**1a**) or Ph_2PCl (**1e**) with aldehyde functionalized propargyl alcohols 2-$(CHO)C_6H_4C{\equiv}CCR_2OH$ (**7a-b)** leads to phosphono-indanones/ phosphine oxide indanones derivatives rather than the normally expected allenylphosphonates. The analogous reaction with alkylidene group containing propargyl alcohols 2-$(CH=C(CO_2R)_2)C_6H_4C{\equiv}CCR^1R^2OH$ (**8a-j)** proceed to give fused polycyclics which include compounds constituting a rare brand of three-fused cyclobutane ring system. An intramolecular [2+2] or [4+2] cycloaddition reaction is implicated in this process. When dialkyl substituted alkylidene-based propargyl alcohols [2-$(CH=C(CO_2R)_2)C_6H_4C{\equiv}CCR^1{}_2OH$] are employed in the same type of experiments, the resulting compounds are phosphono-polycyclics *via* an intramolecular ene reaction. Thus, different substituents on propargyl alcohols afford a variety of polycyclics; these reactions ***do not have precedence*** in the literature.

2) Cycloaddition reactions of allenylphosphonates $[(RO)_2P(O)(R^1)C=C=CR^2{}_2]$ with 1,3-diphenylisobenzofuran (IBF), dimethyl acetylenedicarboxylate (DMAD), and anthracene have been investigated and compared with those of allenoates $[(EtO_2C)RC=C=CH_2]$ and allenylphosphine oxides $[Ph_2P(O)(R^1)C=C=CR^2{}_2]$ in selected cases. The reaction of $=CH_2$ terminal allenylphosphonates with IBF afforded preferentially *endo*-[4+2] cycloaddition products and *via* [α,β] attack; the allenoate $(EtO_2C)RC=C=CH_2$ underwent *exo*-[4+2] cyclization. Under similar conditions, allenylphosphonates with a terminal $=CR_2$ group gave only [β,γ]-cycloaddition products. An ***unusual ring-opening*** of a [4+2] cycloaddition product to allene $(OCH_2CMe_2CH_2O)P(O)$(1-cyclohexenyl)$C=C=CH_2$ (**11a**) followed by ring-closing *via* [4+4] cycloaddition, as revealed by ^{31}P NMR spectroscopy, is reported. Reaction of cyclohexenyl substituted allene **11a** with DMAD resulted in a [4+2] adduct. Anthracene reacted in a manner similar to IBF, but the reactivity was low.

3) Allenes $[Ph_2P(O)(2\text{-}OHC_6H_4)C=C=CR^1R^2]$ comprising a 2-hydroxy phenyl moiety at the α-position undergo an intramolecular nucleophilic cyclization reaction leading to phosphorus-based benzofurans. Synthesis of ***phosphorus-***

based isochromenes was accomplished by deprotection followed by subsequent nucleophilic cyclization of allenes [$Ph_2P(O)(2\text{-}CH_2OCH_2OMeC_6H_4)C{=}C{=}CR_2$] by employing mild reaction conditions with $ZrCl_4$ as the Lewis acid.

4) A one pot synthetic route has been developed for 2-methylphosphonopyrroles/ 2-methylphosphine oxide-pyrroles starting from allene and 1,3-dicarbonyls by using $Mn(OAc)_3.2H_2O$ (catalyst)/ acetic acid (additive)/ methanol (solvent) combination under photochemical conditions. In the case of phosphorylated allenes, the β,γ-carbon atoms of allenes participate in the pyrrole ring formation whereas in ester allene α,β-carbon atoms are involved. In contrast to the reaction using $Mn(OAc)_3.2H_2O$, use of triethylamine in these reactions led to phosphorus-based ***1,2,3-triazoles*** (e.g. **108-112**). Thermolysis of phosphorus-based vinyl azides under solvent free, catalyst free conditions provides an entirely ***new route for the pyrazines*** (e.g. **114-118**).

5) The utility of newly synthesized phosphorus-based nitrogen heterocycles in Horner-Wadsworth-Emmons (HWE) reaction is demonstrated. This method provides a convenient access to diverse ***phosphorus-free nitrogen heterocycles***.

EXPERIMENTAL SECTION

General: Chemicals and solvents were procured from Aldrich/ Fluka or local manufacturers. Further purification was done according to standard procedures wherever required.[97]All operations, unless otherwise specified, were carried out under dry nitrogen atmosphere using standard vacuum line techniques.[98]

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 and GC-MS: 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.

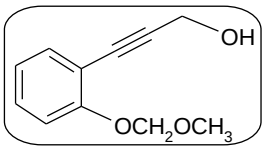
The P^{III}-Cl precursors $(OCH_2CR_2CH_2O)PCl$ [R = Me (**1a**)[66a], Et (**1b**)[66b]] were prepared by a well-known method involving the reaction of the corresponding diols with PCl_3 under neat conditions.[66] Other compounds CH_2[6-*t*-Bu-4-Me-$C_6H_2O]_2PCl$ **(1c)**[67] and $(EtO)_2PCl$ [**1d**, by treating $P(OEt)_3$ with PCl_3][68] were synthesized according to the reported procedures. Diphenylphosphine chloride Ph_2PCl (**1e**) was distilled prior to use.

3.1 Preparation of propargylic precursors 5a-f, 6a-d, 7a-c, 8a-j

1-Iodo-2-methoxymethoxy-benzene (**2**)[69a] and 1-iodo-2-methoxymethoxymethyl-benzene (**3**)[69b] were prepared by treating corresponding alcohols with chloromethyl methyl ether in the presence of sodium hydride (NaH) in THF.[69] 2-(2-Bromo-benzylidene)-malonic acid dimethyl (diethyl) esters **4a** and **4b** were prepared according to literature procedure.[70] The propargylic precursors **5a-f, 6a-d, 7a-c** and **8a-j** were synthesized by Sonogashira coupling reaction of respective iodo/bromo substrates with propargyl alcohols.[71-73] Among these propargyl alcohols, **5a-b**, **5d-f**, **6a-d**, **7b-c**, **8a**, and **8c-j** are new. General procedure for the synthesis of these compounds is given below.

General procedure for propargylic alcohols 5a-b, 5d-f, 6a-d, 7b-c, 8a and 8c-j: To a mixture of bromo or iodo compounds **2**, **3** or **4a-b** (1.0 mmol) and propargyl alcohol (1.2 mmol) in CH_3CN (20 mL) were added $PdCl_2(PPh_3)_2$ (0.02 mmol) and CuI (0.02 mmol) under nitrogen atmosphere. After the reaction mixture was stirred for 5 min at room temperature, triethylamine (4.0 equiv) was added *via* a syringe. The reaction mixture was then heated at 70 °C. The solvent was removed under reduced pressure to give the crude product, which was purified by column chromatography on silica gel using EtOAc-hexane mixture (*vide infra*) as eluent.

Compound 5a



This compound was prepared by using 1-iodo-2-methoxymethoxy-benzene (**2**) (0.82 g, 3.1 mmol) and propargyl alcohol (0.21 g, 3.7 mmol). It was isolated by using ethyl acetate-hexane (3:7) mixture as the eluent.

Yield: 0.42 g (71%, brown oil).

IR (Neat): 3383, 2934, 1597, 1489, 1451, 1154 cm^{-1}.

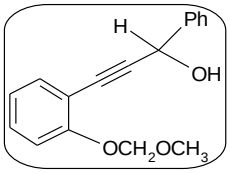
^1H NMR: δ 2.24 (br, 1H, O*H*), 3.52 (s, 3H, OCH_3), 4.54 (s, 2H, CH_2OH), 5.25 (s, 2H, OCH_2), 6.94-6.98 (m, 1H, Ar-*H*), 7.11-7.13 (m, 1H, Ar-*H*), 7.25-7.29 (m, 1H, Ar-*H*), 7.40-7.42 (m, 1H, Ar-*H*).

^{13}C NMR: δ 51.8, 56.3, 81.9, 91.3, 95.0, 113.0, 115.1, 121.9, 129.9, 133.7, 157.8.

LC-MS: *m/z* 193 $[M+1]^+$.

Anal. Calcd. for $C_{11}H_{12}O_3$: C, 68.74; H, 6.29. Found: C, 68.85; H, 6.38.

Compound 5b



This compound was prepared by using 1-iodo-2-methoxymethoxy-benzene (**2**) (0.73 g, 2.8 mmol) and 1-phenyl-prop-2-yn-1-ol (0.44 g, 3.3 mmol). It was isolated by using ethyl acetate-hexane (1:4) mixture as the eluent.

Yield: 0.48 g (65%, brown oil).

IR (Neat): 3400, 3065, 2928, 1597, 1489, 1447, 1154, 1001 cm^{-1}.

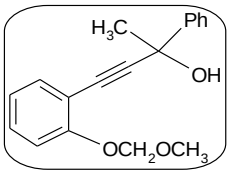
^{1}H NMR: δ 2.63 (br, 1H, O*H*), 3.50 (s, 3H, OCH_3), 5.25 (s, 2H, OCH_2), 5.74 (s, 1H, C*H*Ph), 6.96-7.00 (m, 1H, Ar-*H*), 7.12 (d, ^3J(H-H) = 8.4 Hz, 1H, Ar-*H*), 7.27-7.47 (m, 5H, Ar-*H*), 7.68-7.70 (m, 2H, Ar-*H*).

^{13}C NMR: δ 56.3, 65.2, 83.1, 92.8, 94.9, 113.0, 115.1, 121.8, 126.9, 128.4, 128.6, 130.0, 133.6, 140.8, 158.0.

LC-MS: *m/z* 269 $[M+1]^+$.

Anal. Calcd. for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01. Found: C, 76.21; H, 5.95.

Compound 5d



This compound was prepared by using 1-iodo-2-methoxymethoxy-benzene (**2**) (0.80 g, 3.0 mmol) and 2-phenyl-but-3-yn-2-ol (0.53 g, 3.6 mmol). It was isolated by using ethyl acetate-hexane (1:4) mixture as the eluent.

Yield: 0.58 g (68%, brown oil).

IR (Neat): 3428, 2928, 1597, 1489, 1451, 1154, 1080 cm^{-1}.

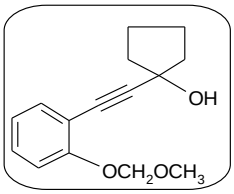
^{1}H NMR: δ 1.91 (s, 3H, CH_3), 2.70 (br, 1H, O*H*), 3.53 (s, 3H, OCH_3), 5.27 (s, 2H, OCH_2), 6.99-7.03 (m, 1H, Ar-*H*), 7.13 (d, ^3J(H-H) = 8.4 Hz, 1H, Ar-*H*), 7.29-7.49 (m, 5H, Ar-*H*), 7.82-7.84 (m, 2H, Ar-*H*).

^{13}C NMR: δ 33.3, 56.3, 70.6, 81.4, 94.9, 96.5, 113.2, 115.1, 121.8, 125.2, 127.7, 128.3, 129.8, 133.4, 145.9, 157.9.

LC-MS: *m/z* 283 $[M+1]^+$.

Anal. Calcd. for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.68; H, 6.35.

Compound 5e



This compound was prepared by using 1-iodo-2-methoxymethoxy-benzene (**2**) (0.92 g, 3.5 mmol) and 1-ethynyl-cyclopentanol (0.46 g, 4.2 mmol). It was isolated by using ethyl acetate-hexane (1:4) mixture as the eluent.

Yield: 0.53 g (62%, brown oil).

IR (Neat): 3418, 2959, 1491, 1198, 1154, 1078 cm^{-1}.

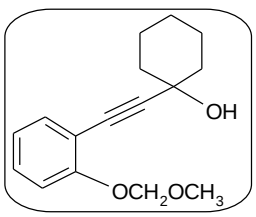
^{1}H NMR: δ 1.75-2.09 (m, 8H, cyclopentyl-*H*), 2.43 (br, 1H, O*H*), 3.53 (s, 3H, OCH_3), 5.24 (s, 2H, OCH_2), 6.93-6.97 (m, 1H, Ar-*H*), 7.08 (d, ^3J(H-H) = 8.4 Hz, 1H, Ar-*H*), 7.22-7.27 (m, 1H, Ar-*H*), 7.39 (d, ^3J(H-H) = 7.2 Hz, 1H, Ar-*H*).

^{13}C NMR: δ 23.5, 42.4, 42.5, 56.3, 75.0, 79.3, 95.1, 97.1, 113.7, 115.5, 121.9, 129.5, 133.5, 157.6.

LC-MS: *m/z* 245 $[M-1]^+$.

Anal. Calcd. for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37. Found: C, 73.26; H, 7.29.

Compound 5f



This compound was prepared by using 1-iodo-2-methoxymethoxy-benzene (**2**) (0.82 g, 6.1 mmol) and 1-ethynyl-cyclohexanol (0.91 g, 7.4 mmol). It was isolated by using ethyl acetate-hexane (1:4) mixture as the eluent.

Yield: 1.10 g (69%, brown oil).

IR (Neat): 3397, 2932, 1597, 1574, 1449, 1155 cm^{-1}.

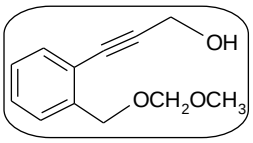
^{1}H NMR: δ 1.26-1.74 (m, 8H, cyclohexyl-*H*), 2.01-2.03 (m, 2H, cyclohexyl-*H*), 2.65 (br, 1H, O*H*), 3.51 (s, 3H, OCH_3), 5.24 (s, 2H, OCH_2), 6.93-6.97 (m, 1H, Ar-*H*), 7.07 (d, ^{3}J(H-H) = 8.4 Hz, 1H, Ar-*H*), 7.22-7.26 (m, 1H, Ar-*H*), 7.39 (d, ^{3}J(H-H) = 7.6 Hz, 1H, Ar-*H*).

^{13}C NMR: δ 23.4, 25.3, 40.1, 56.2, 69.3, 80.7, 94.9, 97.0, 113.6, 115.2, 121.8, 129.5, 133.4, 157.7.

LC-MS: *m/z* 261 $[M+1]^{+}$.

Anal. Calcd. for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.69; H, 7.82.

Compound 6a



This compound was prepared by using 1-iodo-2-methoxymethoxymethyl-benzene (**3**) (0.89 g, 3.1 mmol) and propargyl alcohol (0.21 g, 3.7 mmol). It was isolated by using ethyl acetate-hexane (1:4) mixture as the eluent.

Yield: 0.48 g (74%, brown oil).

IR (Neat): 3416, 2934, 1451, 1379, 1213, 1038 cm^{-1}.

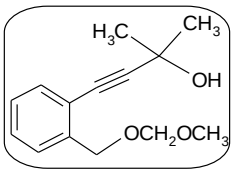
^{1}H NMR: δ 2.80 (br, 1H, O*H*), 3.45 (s, 3H, OCH_3), 4.52 (s, 2H, 2 CH_2OH), 4.76 and 4.78 (2 s, 4H, 2 OCH_2), 7.25-7.29 (m, 1H, Ar-*H*), 7.33-7.37 (m, 1H, Ar-*H*), 7.44-7.49 (m, 2H, Ar-*H*).

^{13}C NMR: δ 51.4, 55.4, 67.4, 83.2, 92.1, 95.7, 121.8, 127.6, 128.3, 128.7, 132.1, 139.5.

LC-MS: *m/z* 207 $[M+1]^{+}$.

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 69.75; H, 6.91.

Compound 6b



This compound was prepared by using 1-iodo-2-methoxymethoxymethyl-benzene (**3**) (0.59 g, 2.1 mmol) and 2-methyl-but-3-yn-2-ol (0.21 g, 2.5 mmol). It was isolated by using ethyl acetate-hexane (1:4) mixture as the eluent.

Yield: 0.38 g (76%, brown oil).

IR (Neat): 3414, 2982, 1601, 1377, 1150, 1049 cm^{-1}.

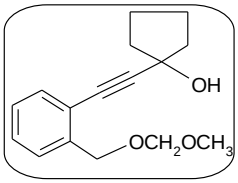
^1H NMR: δ 1.62 (s, 6H, 2 C*H*$_3$), 2.89 (br, 1H, O*H*), 3.44 (s, 3H, OC*H*$_3$), 4.74_6 and 4.74_8 (2 s, 4H, 2 OC*H*$_2$), 7.23-7.27 (m, 1H, Ar-*H*), 7.31-7.35 (m, 1H, Ar-*H*), 7.41-7.47 (m, 2H, Ar-*H*).

^{13}C NMR: δ 31.4, 55.4, 65.5, 67.1, 79.9, 95.6, 98.6, 122.0, 127.6, 128.5, 128.6, 131.9, 139.5.

LC-MS: *m/z* 235 $[M+1]^+$.

Anal. Calcd. for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.62; H, 7.83.

Compound 6c



This compound was prepared by using 1-iodo-2-methoxymethoxymethyl-benzene (**3**) (1.69 g, 6.1 mmol) and 1-ethynyl-cyclopentanol (0.80 g, 7.3 mmol). It was isolated by using ethyl acetate-hexane (1:4) mixture as the eluent.

Yield: 1.06 g (67%, brown oil).

IR (Neat): 3414, 2951, 1451, 1379, 1206, 1150, 1047 cm^{-1}.

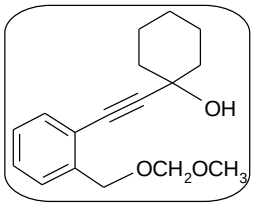
^1H NMR: δ 1.79-1.92 and 2.03-2.10 (2 m, 8H, cyclopentyl-*H*), 2.71 (br, 1H, O*H*), 3.45 (s, 3H, OC*H*$_3$), 4.76 and 4.77 (2 s, 4H, 2 OC*H*$_2$), 7.25-7.28 (m, 1H, Ar-*H*), 7.32-7.35 (m, 1H, Ar-*H*), 7.43-7.48 (m, 2H, Ar-*H*).

^{13}C NMR: δ 23.5, 42.5, 55.4, 67.3, 74.8, 80.9, 95.7, 97.7, 122.2, 127.5, 128.3_9, 128.4_3, 131.9, 139.6.

LC-MS: *m/z* 261 $[M+1]^+$.

Anal. Calcd. for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.69; H, 7.79.

Compound 6d



This compound was prepared by using 1-iodo-2-methoxymethoxymethyl-benzene (**3**) (1.05 g, 3.8 mmol) and 1-ethynyl-cyclohexanol (0.56 g, 4.5 mmol). It was isolated by using ethyl acetate-hexane (1:4) mixture as the eluent.

Yield: 1.75 g (72%, brown oil).

IR (Neat): 3412, 2934, 1601, 1449, 1150, 1049 cm^{-1}.

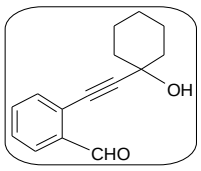
^{1}H NMR: δ 1.29-1.78 (m, 8H, cyclohexyl-*H*), 2.01-2.04 (m, 2H, cyclohexyl-*H*), 2.66 (br, 1H, O*H*), 3.44 (s, 3H, OCH_3), 4.75 and 4.77 (2 s, 4H, 2 OCH_2), 7.24-7.28 (m, 1H, Ar-*H*), 7.32-7.36 (m, 1H, Ar-*H*), 7.44-7.48 (m, 2H, Ar-*H*).

^{13}C NMR: δ 23.4, 25.3, 40.1, 55.4, 67.3, 69.1, 81.9, 95.7, 97.7, 122.1, 127.5, 128.3, 128.5, 132.1, 139.6.

LC-MS: *m/z* 275 $[M+1]^+$.

Anal. Calcd. for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08. Found: C, 74.29; H, 8.12.

Compound 7b



This compound was prepared by using 2-bromobenzaldehyde (1.59 g, 8.6 mmol) and 1-ethynyl-cyclohexanol (1.28 g, 10.2 mmol). It was isolated by using ethyl acetate-hexane (3:7) mixture as the eluent.

Yield: 1.29 g (66%, yellow oil).

IR (Neat): 3410, 2965, 1696, 1595, 1389, 1273, 1073 cm^{-1}.

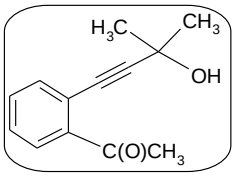
^{1}H NMR: δ 1.30-2.05 (m, 10H, cyclohexyl-*H*), 2.72 (br, 1H, O*H*), 7.41-7.52 (m, 3H, Ar-*H*), 7.87-7.89 (m, 1H, Ar-*H*), 10.50 (s, 1H, C*H*O).

^{13}C NMR: δ 23.4, 25.1, 39.9, 69.2, 79.9, 100.3, 126.5, 127.3, 128.6, 133.4, 133.8, 135.9, 191.8.

LC-MS: *m/z* 229 $[M+1]^+$.

Anal. Calcd. for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.85; H, 7.12.

Compound 7c



This compound was prepared by using 2-bromoacetophenone (1.48 g, 7.4 mmol) and 2-methyl-3-butyn-2-ol (0.75 g, 8.9 mmol). It was isolated by using ethyl acetate-hexane (3:7) mixture as the eluent.

Yield: 1.11 g (74%, yellow oil).

IR (Neat): 3430, 2982, 1682, 1593, 1360, 1163, 963 cm^{-1}.

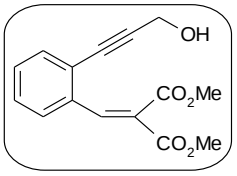
^1H NMR: δ 1.62 (s, 6H, $C(CH_3)_2$), 2.68 (s, 3H, $C(O)CH_3$), 3.19 (br, 1H, O*H*), 7.34-7.49 (m, 3H, Ar-*H*), 7.67-7.68 (m, 1H, Ar-*H*).

^{13}C NMR: δ 29.9, 31.2, 65.5, 81.1, 99.6, 121.3, 128.2, 128.7, 131.3, 134.0, 140.6, 200.6.

LC-MS: *m/z* 201 $[M-1]^+$.

Anal. Calcd. for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.09; H, 6.91.

Compound 8a



This compound was prepared by using 2-(2-bromo-benzylidene)-malonic acid dimethyl ester (**4a**) (1.22 g, 4.1 mmol) and prop-2-yn-1-ol (0.28 mL, 4.9 mmol) and purified by column chromatography using ethyl acetate-hexane (3:7) mixture as the eluent.

Yield: 0.69 g (62%, brown oil).

IR (Neat): 3437, 2953, 1732, 1632, 1435, 1372, 1221, 1069 cm^{-1}.

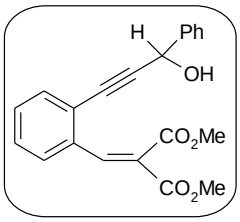
^1H NMR: δ 2.96 (br, 1H, CH_2OH), 3.76 and 3.84 (2 s, 6H, 2 CO_2CH_3), 4.52 (s, 2H, CH_2OH), 7.29-7.47 (m, 4H, Ar-*H*), 8.19 (s, 1H, $HC=C(CO_2CH_3)_2$).

^{13}C NMR: δ 51.4, 52.6, 52.8, 82.6, 94.4, 123.9, 126.9, 127.5, 128.5, 130.1, 132.8, 134.8, 141.9, 164.6, 166.8.

LC-MS: *m/z* 275 $[M+1]^+$.

Anal. Calcd. for $C_{15}H_{14}O_5$: C, 65.69; H, 5.15. Found: C, 65.58; H, 5.26.

Compound 8c



This compound was prepared by using 2-(2-bromo-benzylidene)-malonic acid dimethyl ester (**4a**) (1.71 g, 5.7 mmol) and 1-phenylprop-2-yn-1-ol (0.85 mL, 6.9 mmol) and purified by column chromatography using ethyl acetate-hexane (3:7) mixture as the eluent.

Yield: 1.30 g (65%, brown liquid).

IR (Neat): 3434, 2953, 2197, 1734, 1636, 1437, 1373, 1260, 1069 cm^{-1}.

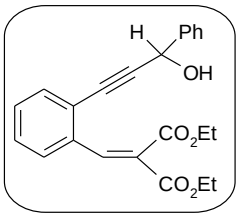
^{1}H NMR: δ 2.76 (br, 1H, O*H*), 3.80 and 3.85 (2 s, 6H, 2 CO_2CH_3), 5.75 (s, 1H, C*H*Ph(OH)), 7.33-7.39 and 7.41-7.45 (2 m, 6H, Ar-*H*), 7.54-7.56 and 7.64-7.66 (2 m, 3H, Ar-*H*), 8.26 (s, 1H, *H*C=C$(CO_2CH_3)_2$).

^{13}C NMR: δ 52.6, 52.8, 65.1, 83.8, 95.7, 123.7, 126.8, 127.1, 127.6, 128.5, 128.7, 130.0, 132.8, 135.1, 140.3, 141.7, 164.4, 166.7.

LC-MS: *m/z* 349 $[M-1]^+$.

Anal. Calcd. for $C_{21}H_{18}O_5$: C, 71.99; H, 5.18. Found: C, 71.85; H, 5.26.

Compound 8d



This compound was prepared by using 2-(2-bromo-benzylidene)-malonic acid diethyl ester (**4b**) (1.70 g, 5.2 mmol) and 1-phenylprop-2-yn-1-ol (0.77 mL, 6.2

mmol) and purified by column chromatography using ethyl acetate-hexane (3:7) mixture as the eluent.

Yield: 1.26 g (64%, brown liquid).

IR (Neat): 3432, 2984, 1728, 1630, 1449, 1377, 1252, 1067 cm^{-1}.

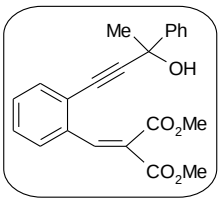
^1H NMR: δ 1.21 and 1.30 (2 t, ^3J(H-H) ~ 7.0 Hz, 6H, 2 $CO_2CH_2CH_3$), 2.94 (br, 1H, O*H*), 4.25-4.32 (m, 4H, 2 $CO_2CH_2CH_3$), 5.73 (s, 1H, C*H*Ph(OH)), 7.29-7.53 (m, 7H, Ar-*H*), 7.62-7.64 (m, 2H, Ar-*H*), 8.21 (s, 1H, *H*C=C$(CO_2Et)_2$).

^{13}C NMR: δ 13.8, 14.1, 61.7, 61.8, 65.1, 83.9, 95.6, 123.6, 126.8, 127.7, 127.9, 128.4, 128.6, 128.7, 129.9, 132.7, 135.2, 140.4, 141.0, 164.0, 166.3.

LC-MS: *m/z* 377 $[M-1]^+$.

Anal. Calcd. for $C_{23}H_{22}O_5$: C, 73.00; H, 5.86. Found: C, 73.12; H, 5.83.

Compound 8e



This compound was prepared by using 2-(2-bromo-benzylidene)-malonic acid dimethyl ester (**4a**) (0.98 g, 3.3 mmol) and 2-phenylbut-3-yn-2-ol (0.57 g, 3.9 mmol) and purified by column chromatography using ethyl acetate-hexane (3:7) mixture as the eluent.

Yield: 0.79 g (66%, brown liquid).

IR (Neat): 3488, 2976, 1970, 1728, 1626, 1433, 1370, 1229, 1069 cm^{-1}.

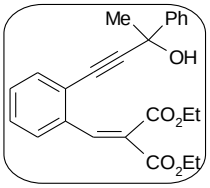
^1H NMR: δ 1.91 (s, 3H, CH_3), 2.82 (br, 1H, O*H*), 3.78 and 3.84 (2 s, 6H, 2 CO_2CH_3), 7.30-7.44 and 7.54-7.56 (2 m, 7H, Ar-*H*), 7.72-7.74 (m, 2H, Ar-*H*), 8.28 (s, 1H, *H*C=C$(CO_2CH_3)_2$).

^{13}C NMR: δ 33.3, 52.7, 52.8, 70.5, 82.2, 99.5, 123.8, 125.0, 126.9, 127.5, 127.8, 128.4, 128.7, 130.1, 132.6, 135.0, 141.7, 145.3, 164.3, 166.8.

LC-MS: *m/z* 363 $[M-1]^+$.

Anal. Calcd. for $C_{22}H_{20}O_5$: C, 72.51; H, 5.53. Found: C, 72.45; H, 5.56.

Compound 8f



This compound was prepared by using 2-(2-bromo-benzylidene)-malonic acid diethyl ester (**4b**) (0.99 g, 3.0 mmol) and 2-phenylbut-3-yn-2-ol (0.53 g, 3.6 mmol) and purified by column chromatography using ethyl acetate-hexane (3:7) mixture as the eluent.

Yield: 0.76 g (64%, brown liquid).

IR (Neat): 3441, 2984, 1730, 1632, 1449, 1377, 1252, 1067 cm^{-1}.

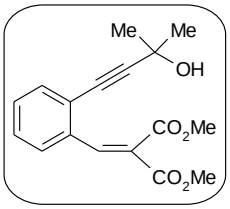
^{1}H NMR: δ 1.24 and 1.31 (2 t, ^{3}J(H-H) = 7.2 Hz, 6H, 2 $CO_2CH_2CH_3$), 1.92 (s, 3H, CH_3), 3.13 (br, 1H, O*H*), 4.27-4.32 (m, 4H, 2 $CO_2CH_2CH_3$), 7.30-7.42 and 7.49-7.55 (2 m, 7H, Ar-*H*), 7.74-7.76 (m, 2H, Ar-*H*), 8.26 (s, 1H, *H*C=C$(CO_2Et)_2$).

^{13}C NMR: δ 13.8, 14.1, 33.3, 61.7, 61.8, 70.4, 82.3, 99.4, 123.8, 125.0, 127.7, 127.8, 128.4, 128.5, 129.9, 132.5, 135.2, 140.9, 145.3, 164.0, 166.3.

LC-MS: *m/z* 393 $[M+1]^{+}$.

Anal. Calcd. for $C_{24}H_{24}O_5$: C, 73.45; H, 6.16. Found: C, 73.28; H, 6.25.

Compound 8g



This compound was prepared by using 2-(2-bromo-benzylidene)-malonic acid dimethyl ester (**4a**) (0.96 g, 3.2 mmol) and 2-methylbut-3-yn-2-ol (0.32 g, 3.8 mmol) and purified by column chromatography using ethyl acetate-hexane (3:7) mixture as the eluent.

Yield: 0.73 g (72%, yellow oil).

IR (Neat): 3441, 2984, 1732, 1628, 1437, 1368, 1258, 1069 cm^{-1}.

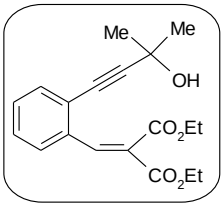
^{1}H NMR: δ 1.53 and 1.65 (2 s, 6H, C(C*H*$_3$)$_2$(OH)), 2.41 (br, 1H, C(CH$_3$)$_2$(O*H*)), 3.79 and 3.86 (2 s, 6H, 2 OC*H*$_3$), 7.27-7.48 (m, 4H, Ar-*H*), 8.23 (s, 1H, *H*C=C(CO$_2$CH$_3$)$_2$).

^{13}C NMR: δ 31.3, 52.7, 52.8, 65.5, 79.3, 101.1, 124.2, 126.4, 127.4, 128.4, 130.1, 132.4, 134.7, 141.9, 164.5, 166.8.

LC-MS: *m/z* 303 $[M+1]^+$.

Anal. Calcd. for $C_{17}H_{18}O_5$: C, 67.54; H, 6.00. Found: C, 67.55; H, 6.08.

Compound 8h



This compound was prepared by using 2-(2-bromo-benzylidene)-malonic acid diethyl ester (**4b**) (1.26 g, 4.0 mmol) and 2-methylbut-3-yn-2-ol (0.39 g, 4.6 mmol) and purified by column chromatography using ethyl acetate-hexane (3:7) mixture as the eluent.

Yield: 0.71 g (70%, yellow oil).

IR (Neat): 3434, 2980, 1732, 1630, 1470, 1377, 1250, 1065 cm^{-1}.

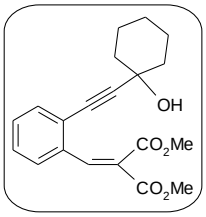
^{1}H NMR: δ 1.22 and 1.34 (2 t, ^{3}J(H-H) = 7.6 Hz, 6H, 2 OCH$_2$C*H*$_3$), 1.65 (s, 6H, C(C*H*$_3$)$_2$), 2.45 (br, 1H, C(CH$_3$)$_2$(O*H*)), 4.26-4.34 (m, 4H, 2 OC*H*$_2$CH$_3$), 7.26-7.34 (m, 2H, Ar-*H*), 7.45-7.47 (m, 2H, Ar-*H*), 8.18 (s, 1H, *H*C=C(CO$_2$Et)$_2$).

^{13}C NMR: δ 13.8, 14.2, 31.4, 61.7$_1$, 61.7$_4$, 65.6, 79.6, 100.8, 124.0, 127.4, 127.6, 128.3, 129.9, 132.4, 135.0, 140.9, 164.1, 166.4.

LC-MS: *m/z* 331 $[M+1]^+$.

Anal. Calcd. for $C_{19}H_{22}O_5$: C, 69.07; H, 6.71. Found: C, 69.21; H, 6.67.

Compound 8i



This compound was prepared by using 2-(2-bromo-benzylidene)-malonic acid dimethyl ester (**4a**) (1.50 g, 5.0 mmol) and 1-ethynyl-1-cyclohexanol (0.75 g, 6.0 mmol) and purified by column chromatography using ethyl acetate-hexane (3:7) mixture as the eluent.

Yield: 1.17 g (68%, yellow oil).

IR (Neat): 3470, 2938, 1732, 1628, 1437, 1373, 1256, 1069 cm^{-1}.

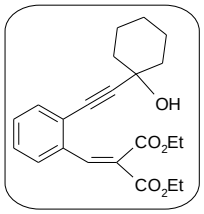
^{1}H NMR: δ 1.27 (br, 1H, cyclohexyl-*H*), 1.61-1.78 and 2.04-2.07 (2 m, 9H, cyclohexyl-*H*), 2.50 (br, 1H, O*H*), 3.79 and 3.84 (2 s, 6H, 2 OCH_3), 7.29-7.49 (m, 4H, Ar-*H*), 8.24 (s, 1H, *H*C=C$(CO_2CH_3)_2$).

^{13}C NMR: δ 23.4, 25.2, 39.9, 52.6, 52.9, 69.2, 81.6, 100.1, 124.4, 126.6, 127.4, 128.3, 130.1, 132.5, 134.7, 141.7, 164.4, 166.8.

LC-MS: *m/z* 342 $[M]^+$.

Anal. Calcd. for $C_{20}H_{22}O_5$: C, 70.16; H, 6.48. Found: C, 70.15; H, 6.58.

Compound 8j



This compound was prepared by using 2-(2-bromo-benzylidene)-malonic acid diethyl ester (**4b**) (1.18 g, 3.6 mmol) and 1-ethynyl-1-cyclohexanol (0.54 g, 4.3 mmol) and purified by column chromatography using ethyl acetate-hexane (3:7) mixture as the eluent.

Yield: 0.76 g (67%, yellow oil).

IR (Neat): 3461, 2936, 1730, 1632, 1449, 1379, 1254, 1065 cm^{-1}.

^{1}H NMR: δ 1.23 and 1.34 (2 t, ^{3}J(H-H) = 7.0 Hz, 6H, 2 OCH_2CH_3), 1.53-1.76 (m, 8H, cyclohexyl-*H*), 2.05 (br, 2H, cyclohexyl-*H*), 2.37 (br, 1H, O*H*), 4.26-4.33 (m, 4H, 2 OCH_2CH_3), 7.27-7.35 and 7.45-7.49 (2 m, 4H, Ar-*H*), 8.20 (s, 1H, *H*C=C$(CO_2Et)_2$).

^{13}C NMR: δ 13.9, 14.2, 23.4, 25.2, 39.9, 61.7, 69.2, 81.7, 99.8, 124.2, 127.5, 127.6, 128.3, 129.9, 132.5, 134.9, 140.9, 164.0, 166.4.

LC-MS: *m/z* 370 $[M]^+$.

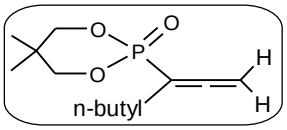
Anal. Calcd. for $C_{22}H_{26}O_5$: C, 71.33; H, 7.07. Found: C, 71.25; H, 7.18.

3.2 Reactions of P^{III}-Cl compounds with propargyl alcohols

3.21 General procedures for the synthesis of allenes 9a-b, allenylphosphonates [10a-j, 11a-d] and allenylphosphine oxides [12a-h, 13a-f, 14a-d]

The ester allenes **9a-b,** phosphorus-based allenes **10a-j, 11a-d, 12a-h, 13a-f** and **14a-d** were synthesized according to literature procedures.[10, 74] Among these, allenes **10f**, **11a-d**, **12g**, **13a-f** and **14a-d** are new. Spectroscopic and analytical data for these compounds are given below.

Compound 10f



This compound was prepared by using hept-2-yn-1-ol (1.09 g, 9.7 mmol) and ($OCH_2CMe_2CH_2O$)PCl (**1a**) (1.63 g, 9.7 mmol) in THF in the presence of triethylamine.[10,74] It was purified by using silica gel column chromatography [ethyl acetate-hexane (1:1)].

Yield: 1.80 g (76%).

Mp: 58−60 ^{o}C (white solid).

IR (KBr): 2965, 2928, 1942, 1472, 1258, 1047, 997cm^{-1}.

^{1}H NMR: δ 0.89 (t, ^{3}J(H-H) ~ 6.2 Hz, 3H, *n*-butyl-CH_3), 0.95 and 1.17 (2 s, 6H, C(CH_3)$_2$), 1.32-1.37 and 1.48-1.51 (m, 4H, *n*-butyl-CH_2), 2.16 (br, 2H, *n*-butyl-CH_2), 3.90-4.05 (m, 4H, OCH_2), 4.99 and 5.02 (2 s, 2H, =CH_2).

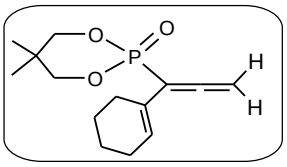
^{13}C NMR: δ 13.8, 21.0, 21.7, 22.1, 27.5 (d, ^{3}J(P-C) = 6.0 Hz), 30.0 (d, ^{2}J(P-C) = 6.4 Hz), 32.5 (d, ^{3}J(P-C) = 6.0 Hz, *C*(CH$_3$)$_2$), 76.7 (d, ^{3}J(P-C) = 6.5 Hz), 77.2 and 77.3 (2 d, ^{2}J(P-C) ~ 5.5 Hz, O*C*H$_2$), 91.9 (d, ^{1}J(P-C) = 182.3 Hz, P*C*), 211.5 (d, ^{2}J(P-C) = 6.2 Hz, PC*C*C).

^{31}P NMR: δ 11.9.

LC-MS: m/z 245 $[M+1]^{+}$.

Anal. Calcd. for $C_{12}H_{21}O_3P$: C, 59.00; H, 8.67. Found: C, 59.15; H, 8.59.

Compound 11a



This compound was prepared by using 3-cyclohex-1-enyl-prop-2-yn-1-ol[99] (3.00 g, 22.0 mmol) and **1a** (3.71 g, 22.0 mmol). It was purified by column chromatography [ethyl acetate-hexane (1:1)].

Yield: 3.80 g (64%).

M: 78−80 ^{o}C (white solid).

IR (KBr): 2961, 2934, 1921, 1474, 1262, 1059, 1011 cm^{-1}.

^{1}H NMR: δ 0.90 and 1.28 (2 s, 6H, C(C*H*$_3$)$_2$), 1.54-1.70 (m, 4H, cyclohexenyl C*H*$_2$), 2.08 and 2.14 (2 br s, 4H, cyclohexenyl C*H*$_2$), 3.99-4.01 (m, 4H, OC*H*$_2$), 5.18 and 5.21 (2 s, 2H, =C*H*$_2$), 6.29 (s, 1H, =C*H*).

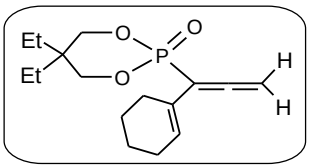
^{13}C NMR: δ 20.8, 21.7, 21.9, 22.6, 25.9, 27.1 (d, ^{3}J(P-C) = 8.1 Hz), 32.6 (d,^{3}J(P-C) = 7.1 Hz, *C*(CH$_3$)$_2$), 77.2, 77.3, 79.0 (d, ^{2}J(P-C) = 14.9 Hz,), 97.2 (d, ^{1}J(P-C) = 177.8 Hz, P*C*), 126.7 (d, ^{2}J(P-C) = 6.2 Hz), 128.9 (d, ^{3}J(P-C) = 4.5 Hz), 212.1 (d, ^{2}J(P-C) = 5.1 Hz, PC*C*C).

^{31}P NMR: δ 8.1.

LC-MS: m/z 269 [M+1]$^{+}$.

Anal. Calcd. for $C_{14}H_{21}O_3P$: C, 62.67; H, 7.89. Found: C, 62.85; H, 7.82.

Compound 11b



This compound was prepared by using 3-cyclohex-1-enyl-prop-2-yn-1-ol[99] (1.68 g, 12.3 mmol) and (OCH$_2$CEt$_2$CH$_2$O)PCl (**1b**) (2.43 g, 12.3 mmol). Purification was done by column chromatography [ethyl acetate-hexane (2:3)].

Yield: 2.19 g (60%).

Mp: 80-82 ^{o}C (white solid).

IR (KBr): 2940, 1929, 1464, 1260, 1080, 1034 cm^{-1}.

^{1}H NMR: δ 0.76-0.80 and 0.83-0.88 (2 m, 6H, 2 CH_2CH_3), 1.18-1.22 and 1.51-1.75 (2 m, 8H, 2 CH_2CH_3 + cyclohexenyl-*H*), 2.04 and 2.09 (br, 4H, cyclohexenyl CH_2), 3.92-4.07 (m, 4H, OCH_2), 5.15 and 5.18 (2 s, 2H, $=CH_2$), 6.24 (s, 1H, =C*H*).

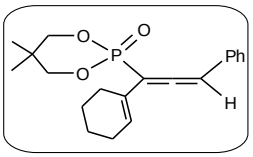
^{13}C NMR: δ 6.9, 7.2, 21.7, 22.0, 22.6, 23.1, 25.9, 27.0 (d, ^{3}J(P-C) = 8.2 Hz), 37.4 (d, ^{3}J(P-C) = 6.0 Hz, CEt_2), 74.6, 74.7, 78.8 (d, ^{2}J(P-C) = 14.9 Hz), 97.2 (d, ^{1}J(P-C) = 175.1 Hz, P*C*), 126.7 (d, ^{2}J(P-C) = 6.1 Hz), 128.8, 212.0 (d, ^{2}J(P-C) = 4.5 Hz, PC*C*C).

^{31}P NMR: δ 9.1.

LC-MS: m/z 297 $[M+1]^{+}$.

Anal. Calcd. for $C_{16}H_{25}O_3P$: C, 64.85; H, 8.50. Found: C, 64.72; H, 8.56.

Compound 11c



This allene was prepared by using 3-cyclohexenyl-1-(phenyl)prop-2-yn-1-ol[100] (0.90 g, 3.5 mmol) and **1a** (0.59 g, 3.5 mmol). It was purified by column chromatography [ethyl acetate-hexane (1:1)].

Yield: 0.90 g (74%).

Mp: 108−110 ^{o}C (white solid).

IR (KBr): 2948, 2917, 2830, 1919, 1599, 1456, 1260, 1061, 1013cm^{-1}.

^{1}H NMR: δ 0.75 and 1.27 (2 s, 6H, $C(CH_3)_2$), 1.59-1.67 (m, 4H, cyclohexenyl-*H*), 2.04 and 2.19 (m, 4H, cyclohexenyl-*H*), 3.80-4.09 (m, 4H, OCH_2), 6.47-6.48 (m, 1H, =C*H*), 6.65 (d, ^{4}J(P-H) = 3.1 Hz, 1H, =C*H*Ph), 7.25-7.28 (m, 2H, Ar-*H*), 7.32-7.37 (m, 3H, Ar-*H*).

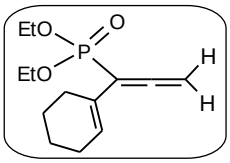
^{13}C NMR: δ 20.6, 21.8, 22.0, 22.6, 26.1, 27.3 (d, ^{3}J(P-C) = 8.0 Hz), 32.5 (d, ^{3}J(P-C) = 7.0 Hz, $C(CH_3)_2$), 76.9 (d, ^{2}J(P-C) = 6.7 Hz, OCH_2), 77.5 (d, ^{2}J(P-C) = 7.0 Hz, OCH_2), 98.2 (d, ^{3}J(P-C) = 15.0 Hz), 101.9 (d, ^{1}J(P-C) = 174.0 Hz, P*C*), 127.09, 127.11, 127.5 (d, ^{4}J(P-C) = 6.8 Hz), 128.0 (d, ^{3}J(P-C) = 1.5 Hz), 129.02, 129.03, 130.1, 132.4 (d, ^{2}J(P-C) = 8.2 Hz), 210.4 (d, ^{2}J(P-C) = 3.0 Hz, PC*C*C).

^{31}P NMR: δ 6.8.

LC-MS: m/z 345 $[M+1]^+$.

Anal. Calcd. for $C_{20}H_{25}O_3P$: C, 69.75; H, 7.32. Found: C, 69.85; H, 7.23.

Compound 11d



This allene was prepared from 3-cyclohex-1-enyl-prop-2-yn-1-ol[99] (0.64 g, 4.7 mmol) and $(EtO)_2PCl$ (**1d**) (0.74 g, 4.7 mmol). It was purified by column chromatography [ethyl acetate-hexane (1:2)].

Yield: 0.79 g (65%, brown oil).

IR (Neat): 2976, 2936, 1923, 1713, 1445, 1248, 1020 cm^{-1}.

1H NMR: δ 1.32-1.35 (m, 6H, 2 OCH_2CH_3), 1.58-1.69 (m, 4H, cyclohexenyl-*H*), 2.09 and 2.15 (2 br, 4H, cyclohexenyl-*H*), 4.10-4.18 (m, 4H, OCH_2), 5.14 and 5.17 (2 s, 2H, $=CH_2$), 6.27 (br, 1H, =C*H*).

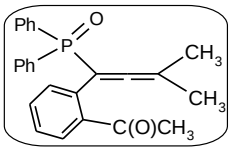
^{13}C NMR: δ 16.1_7, 16.2_4, 21.8, 22.7, 26.0, 27.3 (d, ^3J(P-C) = 8.2 Hz), 62.5_5, 62.6_1, 78.4 (d, ^2J(P-C) = 14.7 Hz), 98.8 (d, ^1J(P-C) = 182.9 Hz, P*C*), 127.2 (d, ^2J(P-C) = 6.0 Hz), 128.2 (d, ^3J(P-C) = 3.8 Hz), 213.0 (d, ^2J(P-C) = 4.4 Hz, PC*C*C).

^{31}P NMR: δ 16.3.

LC-MS: m/z 257 $[M+1]^+$.

Anal. Calcd. for $C_{13}H_{21}O_3P$: C, 60.93; H, 8.26. Found: C, 60.85; H, 8.21.

Compound 12g



This allene was prepared from propargyl alcohol **7c** (0.10 g, 0.5 mmol) and Ph_2PCl (**1e**) (0.11 g, 0.5 mmol). It was purified by column chromatography [ethyl acetate-hexane (3:2)].

Yield: 0.15 g (78%).

Mp: 142-144 ^oC (white solid).

IR (KBr): 3189, 1950, 1688, 1439, 1248, 1186, 1115 cm^{-1}.

^{1}H NMR: δ 1.43 and 1.45 (2 s, 6H, C(CH_3)$_2$), 2.53 (s, 3H, C(O)CH_3), 7.24-7.29 (m, 2H, Ar-*H*), 7.38-7.47 (m, 7H, Ar-*H*), 7.64-7.67 (m, 1H, Ar-*H*), 7.81-7.86 (m, 4H, Ar-*H*).

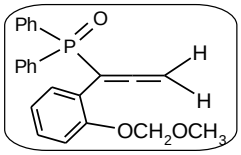
^{13}C NMR: δ 18.2, 18.3, 30.3, 97.5 (d, ^{1}J(P-C) = 102.7 Hz, P*C*), 99.1 (d, *J*(P-C) = 13.2 Hz, PC*C*), 127.2 (d, *J*(P-C) = 3.8 Hz), 128.1, 128.2, 130.4, 131.0$_8$ (d, *J*(P-C) = 88.9 Hz), 131.1$_2$ (d, *J*(P-C) = 88.6 Hz), 131.8, 131.9, 132.1, 132.2, 132.3, 133.1, 140.8 (d, *J*(P-C) = 5.3 Hz), 210.3 (d, ^{2}J(P-C) = 5.9 Hz, PC*C*).

^{31}P NMR: δ 30.2.

LC-MS: *m/z* 387 [M+1]$^{+}$.

Anal. Calcd. for $C_{25}H_{23}O_2P$: C, 77.70; H, 6.00. Found: C, 77.59; H, 6.12.

Compound 13a



This compound was prepared from propargyl alcohol **5a** (0.92 g, 4.8 mmol) and Ph_2PCl (**1e**) (1.06 g, 4.8 mmol). It was isolated by using ethyl acetate-hexane (3:2) mixture as the eluent.

Yield: 1.42 g (79%, gummy material).

IR (Neat): 2982, 1925, 1597, 1491, 1364, 1155 cm^{-1}.

^{1}H NMR: δ 3.33 (s, 3H, OCH_3), 4.79 and 4.82 (2 s, 2H, =CH_2), 4.92 (s, 2H, OCH_2), 6.91-6.95 (m, 1H, Ar-*H*), 7.06 (d, ^{3}J(H-H) = 8.0 Hz, 1H, Ar-*H*), 7.16-7.20 (m, 1H, Ar-*H*), 7.39-7.49 (m, 7H, Ar-*H*), 7.75-7.80 (m, 4H, Ar-*H*).

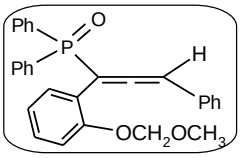
^{13}C NMR: δ 56.0, 76.5 (d, *J*(P-C) = 12.5 Hz), 94.5, 96.7 (d, ^{1}J(P-C) = 101.2 Hz, P*C*), 114.5, 121.7 (d, *J*(P-C) = 4.8 Hz), 121.9, 128.0, 128.1, 129.4, 130.8 (d, *J*(P-C) = 3.7 Hz), 131.5 (d, *J*(P-C) = 2.8 Hz), 131.7, 131.8, 133.0 (d, *J*(P-C) = 106.4 Hz), 154.7 (d, *J*(P-C) = 3.9 Hz), 214.1 (d, *J*(P-C) = 6.7 Hz).

^{31}P NMR: δ 27.9.

LC-MS: *m/z* 377 [M+1]$^{+}$.

Anal. Calcd. for $C_{23}H_{21}O_3P$: C, 73.39; H, 5.62. Found: C, 73.29; H, 5.68.

Compound 13b



This compound was prepared from propargyl alcohol **5b** (0.57 g, 2.2 mmol) and Ph_2PCl (**1e**) (0.47 g, 2.2 mmol). It was isolated by using ethyl acetate-hexane (3:2) mixture as the eluent.

Yield: 0.77 g (80%, gummy material).

IR (Neat): 3057, 1933, 1595, 1489, 1439, 1242, 1194, 1117 cm^{-1}.

^1H NMR: δ 3.23 (s, 3H, OC*H*$_3$), 4.93 (s, 2H, OC*H*$_2$), 6.17 (d, ^4J(P-H) = 10.8 Hz, 1H, PCCC*H*), 6.91-6.95 (m, 1H, Ar-*H*), 7.09-7.43 (m, 13H, Ar-*H*), 7.66-7.85 (m, 5H, Ar-*H*).

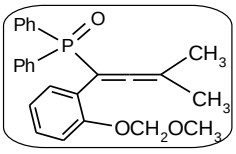
^{13}C NMR: δ 55.9, 94.3, 96.0 (d, *J*(P-C) = 13.5 Hz), 100.5 (d, ^1J(P-C) = 99.7 Hz, P*C*), 114.2, 121.7 (d, *J*(P-C) = 5.4 Hz), 121.9, 127.2 (d, *J*(P-C) = 2.0 Hz), 127.5, 128.0 (d, *J*(P-C) = 1.2 Hz), 128.1 (d, *J*(P-C) = 1.2 Hz), 128.5, 129.4, 130.6 (d, *J*(P-C) = 3.4 Hz), 131.5, 131.6$_1$, 131.6$_4$, 131.7, 132.7 (d, *J*(P-C) = 106.1 Hz), 132.8 (d, *J*(P-C) = 105.2 Hz), 154.7 (d, *J*(P-C) = 4.6 Hz), 213.8 (d, *J*(P-C) = 5.5 Hz).

^{31}P NMR: δ 28.9.

LC-MS: *m/z* 452 $[M]^+$.

Anal. Calcd. for $C_{29}H_{25}O_3P$: C, 76.98; H, 5.57. Found: C, 76.85; H, 5.67.

Compound 13c



This compound was prepared from propargyl alcohol **5c** (0.48 g, 2.2 mmol) and Ph_2PCl (**1e**) (0.48 g, 2.2 mmol). It was isolated by using ethyl acetate-hexane (3:2) mixture as the eluent.

Yield: 0.74 g (84%, gummy material).

IR (Neat): 2907, 1954, 1738, 1593, 1489, 1439, 1366, 1236 cm^{-1}.

^{1}H NMR: δ 1.45 and 1.47 (2 s, 6H, C(C*H*$_3$)$_2$), 3.32 (s, 3H, OC*H*$_3$), 4.95 (s, 2H, OC*H*$_2$), 6.90-6.94 (m, 1H, Ar-*H*), 7.05-7.18 (m, 2H, Ar-*H*), 7.40-7.55 (m, 8H, Ar-*H*), 7.74-7.81 (m, 3H, Ar-*H*).

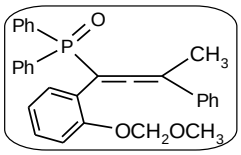
^{13}C NMR: δ 18.8, 18.9, 55.8, 94.5, 94.6 (d, ^{1}J(P-C) = 104.5 Hz, P*C*), 97.4 (d, *J*(P-C) = 13.8 Hz, PCC*C*), 114.4, 121.8, 123.0 (d, *J*(P-C) = 7.0 Hz), 127.9, 128.0, 128.6 (d, *J*(P-C) = 4.1 Hz), 128.7, 128.9, 130.9 (d, *J*(P-C) = 3.7 Hz), 131.2 (d, *J*(P-C) = 2.6 Hz), 131.5, 131.6, 131.8, 133.8 (d, *J*(P-C) = 105.1 Hz), 154.7 (d, *J*(P-C) = 4.3 Hz), 211.4 (d, *J*(P-C) = 6.3 Hz, PC=*C*).

^{31}P NMR: δ 30.6.

LC-MS: *m/z* 405 $[M+1]^{+}$.

Anal. Calcd. for $C_{25}H_{25}O_3P$: C, 74.24; H, 6.23. Found: C, 74.12; H, 6.35.

Compound 13d



This compound was prepared from propargyl alcohol **5d** (0.76 g, 2.7 mmol) and Ph_2PCl (**1e**) (0.59 g, 2.7 mmol). It was isolated by using ethyl acetate-hexane (3:2) mixture as the eluent.

Yield: 1.06 g (85%, gummy material).

IR (Neat): 2955, 1931, 1730, 1595, 1491, 1439 cm^{-1}.

^{1}H NMR: δ 1.86 (s, 3H, C*H*$_3$), 3.27 (s, 3H, OC*H*$_3$), 4.93 (s, 2H, OC*H*$_2$), 6.94-6.97 (m, 1H, Ar-*H*), 7.10-7.46 (m, 13H, Ar-*H*), 7.71-7.80 (m, 5H, Ar-*H*).

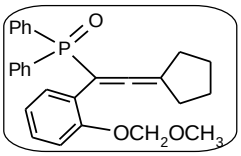
^{13}C NMR: δ 15.7 (d, *J*(P-C) = 5.9 Hz), 55.8, 94.4, 98.4 (d, ^{1}J(P-C) = 100.9 Hz, P*C*), 102.7 (d, *J*(P-C) = 14.1 Hz), 114.3, 121.9, 125.9 (d, *J*(P-C) = 1.5 Hz), 127.2, 127.9, 128.0, 128.1, 128.2, 129.1, 130.8_0, 130.8_2, 131.4, 131.4_9, 131.5_2, 131.5_7, 131.6_0, 132.6, 132.8, 133.0 (d, *J*(P-C) = 105.8 Hz), 133.7, 134.9 (d, *J*(P-C) = 6.6 Hz), 154.8 (d, *J*(P-C) = 4.9 Hz), 213.8 (d, *J*(P-C) = 5.5 Hz).

^{31}P NMR: δ 30.4.

LC-MS: *m/z* 467 $[M+1]^{+}$.

Anal. Calcd. for $C_{30}H_{27}O_3P$: C, 77.24; H, 5.83. Found: C, 77.45; H, 5.76.

Compound 13e



This compound was prepared from propargyl alcohol **5e** (0.62 g, 2.5 mmol) and Ph_2PCl (**1e**) (0.56 g, 2.5 mmol). It was isolated by using ethyl acetate-hexane (3:2) mixture as the eluent.

Yield: 0.89 g (82%, gummy material).

IR (Neat): 2955, 1946, 1593, 1489, 1437, 1236, 1117 cm^{-1}.

^1H NMR: δ 1.32-1.34 (m, 2H, cyclopentyl-*H*), 1.50-1.51 (m, 2H, cyclopentyl-*H*), 1.90-1.95 (m, 2H, cyclopentyl-*H*), 2.33-2.38 (m, 2H, cyclopentyl-*H*), 3.30 (s, 3H, OCH_3), 4.93 (s, 2H, OCH_2), 6.90-6.93 (m, 1H, Ar-*H*), 7.05 (d, ^3J(H-H) = 8.0 Hz, 1H, Ar-*H*), 7.13-7.17 (m, 1H, Ar-*H*), 7.40-7.56 (m, 7H, Ar-*H*), 7.74-7.78 (m, 4H, Ar-*H*).

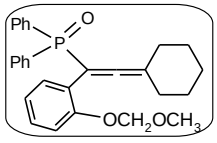
^{13}C NMR: δ 26.9, 30.5_9, 30.6_4, 55.9, 94.6, 96.8 (d, ^1J(P-C) = 105.1 Hz, P*C*), 105.7 (d, *J*(P-C) = 14.5 Hz), 114.4, 121.8, 123.3 (d, *J*(P-C) = 6.9 Hz), 127.9, 128.0, 128.6, 128.8, 130.9, 131.1, 131.5, 131.6, 131.8, 132.5, 134.1 (d, *J*(P-C) = 105.3 Hz), 154.6 (d, *J*(P-C) = 4.1 Hz), 207.1 (d, *J*(P-C) = 5.9 Hz, PC*C*).

^{31}P NMR: δ 31.1.

LC-MS: *m/z* 432 $[M+1]^+$.

Anal. Calcd. for $C_{27}H_{27}O_3P$: C, 75.33; H, 6.32. Found: C, 75.51; H, 6.18.

Compound 13f



This compound was prepared from propargyl alcohol **5f** (0.79 g, 3.0 mmol) and Ph_2PCl (**1e**) (0.67 g, 3.0 mmol). It was isolated by using ethyl acetate-hexane (3:2) mixture as the eluent.

Yield: 1.10 g (82%, gummy material).

IR (Neat): 2930, 1950, 1738, 1591, 1439, 1117 cm^{-1}.

^{1}H NMR: δ 0.98-1.07 (m, 2H, cyclohexyl-*H*), 1.30-1.51 (m, 4H, cyclohexyl-*H*), 1.89-2.06 (m, 4H, cyclohexyl-*H*), 3.34 (s, 3H, OCH_3), 4.96 (s, 2H, OCH_2), 6.92-6.96 (m, 1H, Ar-*H*), 7.08-7.24 (m, 3H, Ar-*H*), 7.41-7.81 (m, 10H, Ar-*H*).

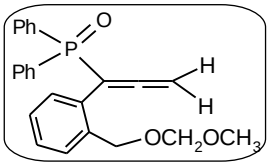
^{13}C NMR: δ 25.4, 26.0, 26.1, 29.6, 29.7, 55.8, 94.5$_2$, 94.5$_4$ (d, ^{1}J(P-C) = 106.3 Hz, P*C*), 103.4 (d, *J*(P-C) = 13.8 Hz), 114.4, 121.8, 123.3 (d, *J*(P-C) = 7.1 Hz), 128.0, 128.1, 128.8, 130.9 (d, *J*(P-C) = 3.6 Hz), 131.1, 131.2 (d, *J*(P-C) = 2.6 Hz), 131.4, 131.6, 131.7, 133.9 (d, *J*(P-C) = 105.3 Hz), 154.7 (d, *J*(P-C) = 4.0 Hz), 208.1 (d, *J*(P-C) = 7.2 Hz).

^{31}P NMR: δ 30.8.

LC-MS: *m/z* 445 $[M+1]^+$.

Anal. Calcd. for $C_{28}H_{29}O_3P$: C, 75.66; H, 6.58. Found: C, 75.48; H, 6.63.

Compound 14a



This compound was prepared from propargyl alcohol **6a** (0.44 g, 2.1 mmol) and Ph_2PCl (**1e**) (0.47 g, 2.1 mmol). It was isolated by using ethyl acetate-hexane (3:2) mixture as the eluent.

Yield: 0.66 g (79%, gummy material).

IR (Neat): 3059, 1933, 1591, 1439, 1262, 1044 cm^{-1}.

^{1}H NMR: δ 3.39 (s, 3H, OCH_3), 4.64 and 4.66 (2 s, 4H, 2 CH_2), 4.85 and 4.87 (2 s, 2H, $=CH_2$), 7.13-7.27 (m, 2H, Ar-*H*), 7.35-7.53 (m, 8H, Ar-*H*), 7.76-7.81 (m, 4H, Ar-*H*).

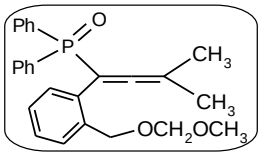
^{13}C NMR: δ 55.4, 66.7, 95.8, 98.3 (d, ^{1}J(P-C) = 97.6 Hz, P*C*), 127.6, 128.1, 128.2, 128.3, 128.7, 129.7 (d, *J*(P-C) = 2.9 Hz), 130.5 (d, *J*(P-C) = 4.9 Hz), 131.6 (d, *J*(P-C) = 105.2 Hz), 131.9, 132.0, 136.9 (d, *J*(P-C) = 4.9 Hz), 212.2 (d, *J*(P-C) = 6.6 Hz).

^{31}P NMR: δ 27.1.

LC-MS: *m/z* 391 $[M+1]^+$.

Anal. Calcd. for $C_{24}H_{23}O_3P$: C, 73.83; H, 5.94. Found: C, 73.91; H, 5.85.

Compound 14b



This compound was prepared from propargyl alcohol **6b** (0.44 g, 1.9 mmol) and Ph_2PCl (**1e**) (0.42 g, 1.9 mmol). It was isolated by using ethyl acetate-hexane (3:2) mixture as the eluent.

Yield: 0.64 g (81%, gummy material).

IR (Neat): 2924, 1948, 1439, 1186, 1117, 1042 cm^{-1}.

^1H NMR: δ 1.48 and 1.49 (2 s, 6H, $C(CH_3)_2$), 3.39 (s, 3H, OCH_3), 4.67 and 4.71 (2 s, 4H, 2 CH_2), 7.12-7.23 (m, 2H, Ar-*H*), 7.40-7.53 (m, 8H, Ar-*H*), 7.73-7.79 (m, 4H, Ar-*H*).

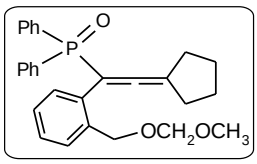
^{13}C NMR: δ 18.8_6, 18.9_0, 55.3, 66.7, 95.7, 96.8 (d, ^1J(P-C) = 100.1 Hz, P*C*), 97.8 (d, *J*(P-C) = 13.6 Hz), 127.3, 127.6, 128.1, 128.1_8, 128.2_0, 129.8 (d, *J*(P-C) = 2.6 Hz), 131.6 (d, *J*(P-C) = 2.3 Hz), 131.6_8, 131.7_2, 132.7 (d, *J*(P-C) = 103.9 Hz), 136.6 (d, *J*(P-C) = 5.5 Hz), 209.8 (d, *J*(P-C) = 6.0 Hz).

^{31}P NMR: δ 30.3.

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

Anal. Calcd. for $C_{26}H_{27}O_3P$: C, 74.62; H, 6.50. Found: C, 74.53; H, 6.58.

Compound 14c



This compound was prepared from propargyl alcohol **6c** (1.23 g, 4.7 mmol) and Ph_2PCl (**1e**) (1.04 g, 4.7 mmol). It was isolated by using ethyl acetate-hexane (3:2) mixture as the eluent.

Yield: 1.51 g (72%, gummy material).

IR (Neat): 2953, 1942, 1437, 1379, 1283, 1188, 1044 cm^{-1}.

^1H NMR: δ 1.30-1.32 (m, 2H, cyclopentyl-*H*), 1.48-1.50 (m, 2H, cyclopentyl-*H*), 1.94-1.99 (m, 2H, cyclopentyl-*H*), 2.32-2.37 (m, 2H, cyclopentyl-

H), 3.39 (s, 3H, OCH_3), 4.68 and 4.70 (2 s, 4H, 2 CH_2), 7.11-7.22 (m, 2H, Ar-*H*), 7.38-7.60 (m, 8H, Ar-*H*), 7.73-7.78 (m, 4H, Ar-*H*).

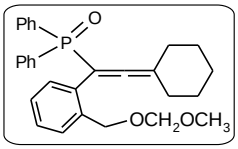
^{13}C NMR: δ 26.9, 30.5$_7$, 30.6$_2$, 55.3, 66.8, 95.8, 98.4 (d, ^1J(P-C) = 100.8 Hz, P*C*), 106.1 (d, *J*(P-C) = 14.1 Hz), 127.3, 127.6, 128.0, 128.1, 128.2, 129.5, 131.5$_6$, 131.6$_3$, 131.7, 132.9 (d, *J*(P-C) = 104.1 Hz), 136.5 (d, *J*(P-C) = 5.5 Hz), 205.9 (d, *J*(P-C) = 5.6 Hz).

^{31}P NMR: δ 31.1.

LC-MS: *m/z* 445 $[M+1]^+$.

Anal. Calcd. for $C_{28}H_{29}O_3P$: C, 75.66; H, 6.58. Found: C, 75.48; H, 6.64.

Compound 14d



This compound was prepared from propargyl alcohol **6d** (2.11 g, 7.7 mmol) and Ph_2PCl (**1e**) (1.70 g, 7.7 mmol). It was isolated by using ethyl acetate-hexane (3:2) mixture as the eluent.

Yield: 2.65 g (75%, gummy material).

IR (Neat): 2932, 1944, 1591, 1437, 1190, 1117, 1044 cm^{-1}.

^{1}H NMR: δ 1.01-1.04 (m, 2H, cyclohexyl-*H*), 1.30-1.48 (m, 4H, cyclohexyl-*H*), 1.92-2.04 (m, 4H, cyclohexyl-*H*), 3.41 (s, 3H, OCH_3), 4.69 and 4.74 (2 s, 4H, 2 CH_2), 7.13-7.25 (m, 2H, Ar-*H*), 7.41-7.57 (m, 8H, Ar-*H*), 7.75-7.80 (m, 4H, Ar-*H*).

^{13}C NMR: δ 25.3, 25.9, 26.0, 29.6, 29.7, 55.3, 66.6, 95.7, 96.6 (d, ^1J(P-C) = 100.3 Hz, P*C*), 103.7 (d, *J*(P-C) = 13.9 Hz), 127.3, 127.5, 127.9, 128.2, 128.3, 129.8 (d, *J*(P-C) = 2.9 Hz), 131.5 (d, *J*(P-C) = 3.0 Hz), 131.7$_7$, 131.8$_4$, 132.0, 132.9 (d, *J*(P-C) = 102.9 Hz), 136.6 (d, *J*(P-C) = 6.4 Hz), 206.5 (d, *J*(P-C) = 6.8 Hz).

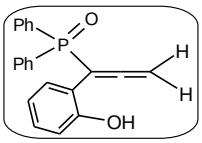
^{31}P NMR: δ 30.2.

LC-MS: *m/z* 457 $[M-1]^+$.

Anal. Calcd. for $C_{29}H_{31}O_3P$: C, 75.96; H, 6.81. Found: C, 75.85; H, 6.72.

3.22 Synthesis of phenol-based allenes 15a-f- General procedure

To a homogeneous solution of allene **13a** (0.20 g, 0.50 mmol) in ethyl acetate (2 mL), hydrochloric acid (35%, 1.0 mL) was added and the contents stirred for 5 min. To this stirred solution, water (10 mL) was added after completion of the reaction (TLC or ^{31}P NMR). The organic layer was separated and the aqueous layer was washed with EtOAc (10 mL). The combined organic layer was washed with brine solution, dried (Na_2SO_4), solvent removed by rotary evaporator, and the product **15a** thus obtained was used as such for the next step. Compounds **15b**-**f** were also prepared similarly.



Yield: 0.16 g (90%).

Mp: 124-126 ^{o}C (white solid).

IR (KBr): 3059, 1925, 1715, 1485, 1437, 1246, 1154, 1121 cm^{-1}.

^{1}H NMR: δ 4.80 and 4.82 (2 s, 2H, =C*H*$_2$), 6.78-6.81 (m, 1H, Ar-*H*), 6.94 (d, ^{3}*J*(H-H) = 8.0 Hz, 1H, Ar-*H*), 7.12-7.17 (m, 2H, Ar-*H*), 7.47-7.57 (m, 6H, Ar-*H*), 7.74-7.79 (m, 4H, Ar-*H*), 10.67 (s, 1H, O*H*).

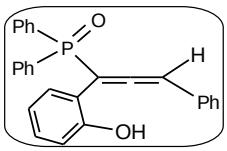
^{13}C NMR: δ 76.4 (d, *J*(P-C) = 12.1 Hz, PCC*C*), 99.5 (d, ^{1}*J*(P-C) = 99.5 Hz, P*C*), 119.4, 120.1, 128.5, 128.6, 129.3, 130.3, 131.9, 132.0, 132.6, 155.7, 214.3 (d, *J*(P-C) = 8.5 Hz, PC*C*).

^{31}P NMR: δ 36.0.

LC-MS: *m/z* 333 [M+1]$^{+}$.

Anal. Calcd. for $C_{21}H_{17}O_2P$: C, 75.90; H, 5.16. Found: C, 75.81; H, 5.23. This compound was crystallized from ethylacetate-hexane (9:1) mixture at 25 ^{o}C. X-ray structure was determined for this sample (Fig. 1 in Chapter 2).

Compound 15b



This product was synthesized from compound **13b** (0.20 g, 0.4 mmol).

Yield: 0.16 g (91%).

Mp: 134-136 ^{o}C (white solid).

IR (KBr): 3061, 1931, 1736, 1439, 1244, 1161, 1119 cm^{-1}.

^{1}H NMR: δ 6.23 (d, ^{4}J(P-H) = 10.8 Hz, 1H, C*H*(Ph)), 6.77-6.81 (m, 1H, Ar-*H*), 6.96-7.52 (m, 14H, Ar-*H*), 7.74-7.81 (m, 4H, Ar-*H*), 10.80 (s, 1H, O*H*).

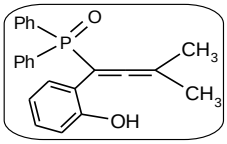
^{13}C NMR: δ 96.5 (d, *J*(P-C) = 12.8 Hz, PCC*C*), 104.3 (d, ^{1}J(P-C) = 97.5 Hz, P*C*), 119.4, 119.7 (d, *J*(P-C) = 4.8 Hz), 120.2, 127.0 (d, *J*(P-C) = 1.6 Hz), 128.1, 128.4, 128.5, 128.6, 128.8, 130.5, 131.6$_{7}$, 131.7$_{2}$, 131.7$_{5}$, 131.9, 132.5 (d, *J*(P-C) = 2.6 Hz), 132.6 (d, *J*(P-C) = 2.6 Hz), 155.7, 213.8 (d, *J*(P-C) = 7.1 Hz).

^{31}P NMR: δ 36.2.

LC-MS: *m/z* 407 [M-1]$^{+}$.

Anal. Calcd. for $C_{27}H_{21}O_2P$: C, 79.40; H, 5.18. Found: C, 79.26; H, 5.22.

Compound 15c



This product was synthesized from compound **13c** (0.20 g, 0.5 mmol).

Yield: 0.17 g (96%).

Mp: 142-144 ^{o}C (white solid).

IR (KBr): 3057, 2924, 1956, 1524, 1437, 1254, 1148 cm^{-1}.

^{1}H NMR: δ 1.47 and 1.48 (2 s, 6H, C(C*H*$_3$)$_2$), 6.76-6.80 (m, 1H, Ar-*H*), 6.92 (d, ^{3}J(H-H) = 7.6 Hz, 1H, Ar-*H*), 7.09-7.15 (m, 2H, Ar-*H*), 7.44-7.55 (m, 6H, Ar-*H*), 7.72-7.76 (m, 4H, Ar-*H*), 10.80 (s, 1H, O*H*).

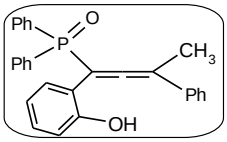
^{13}C NMR: δ 19.0$_{8}$, 19.1$_{3}$, 97.9 (d, ^{1}J(P-C) = 100.9 Hz, P*C*), 98.3 (d, *J*(P-C) = 13.4 Hz, PCC*C*), 119.2, 119.9, 120.9 (d, *J*(P-C) = 6.0 Hz), 128.4, 128.5, 129.9, 130.7 (d, *J*(P-C) = 106.2 Hz), 131.7, 131.8, 132.3, 155.7, 211.8 (d, ^{2}J(P-C) = 7.2 Hz, PC*C*).

^{31}P NMR: δ 37.9.

LC-MS: *m/z* 361 [M+1]$^{+}$.

Anal. Calcd. for $C_{23}H_{21}O_2P$: C, 76.65; H, 5.87. Found: C, 76.75; H, 5.82.

Compound 15d



This product was synthesized from compound **13d** (0.28 g, 0.6 mmol).

Yield: 0.23 g (92%).

Mp: 170-172 ^{o}C (white solid).

IR (KBr): 3059, 1931, 1738, 1439, 1244, 1159, 1121 cm^{-1}.

^{1}H NMR: δ 1.88 (d, *J*(P-H) = 5.6 Hz, 3H, C*H*$_3$), 6.79-6.82 (m, 1H, Ar-*H*), 6.97 (d, ^{3}*J*(H-H) = 8.0 Hz, 1H, Ar-*H*), 7.16-7.53 (m, 13H, Ar-*H*), 7.71-7.77 (m, 4H, Ar-*H*), 10.81 (s, 1H, O*H*).

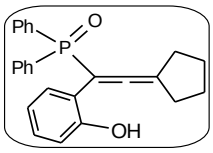
^{13}C NMR: δ 16.2 (d, *J*(P-C) = 5.5 Hz), 102.0 (d, ^{1}*J*(P-C) = 98.6 Hz, P*C*), 103.7 (d, *J*(P-C) = 13.2 Hz, PCC*C*), 116.1, 119.4, 120.1, 125.7, 127.8, 128.3, 128.4, 128.5, 130.2 (d, *J*(P-C) = 106.7 Hz), 130.3, 131.6, 131.7, 131.8, 132.4, 134.2 (d, *J*(P-C) = 6.2 Hz), 155.7, 214.0 (d, *J*(P-C) = 6.3 Hz).

^{31}P NMR: δ 37.1.

LC-MS: *m/z* 423 [M+1]$^{+}$.

Anal. Calcd. for $C_{28}H_{23}O_2P$: C, 79.61; H, 5.49. Found: C, 79.55; H, 5.52.

Compound 15e



This product was synthesized from compound **13e** (0.20 g, 0.5 mmol).

Yield: 0.16 g (90%).

Mp: 148-150 ^{o}C (white solid).

IR (KBr): 3057, 1944, 1595, 1453, 1281, 1152, 1096 cm^{-1}.

^{1}H NMR: δ 1.28 (br, 2H, cyclopentyl-*H*), 1.54 (br, 2H, cyclopentyl-*H*), 1.95 (br, 2H, cyclopentyl-*H*), 2.41-2.42 (m, 2H, cyclopentyl-*H*), 6.77-6.80 (m, 1H, Ar-*H*), 6.91-6.95 (m, 1H, Ar-*H*), 7.13 (br, 2H, Ar-*H*), 7.46-7.53 (m, 6H, Ar-*H*), 7.72-7.76 (m, 4H, Ar-*H*), 10.76 (s, 1H, O*H*).

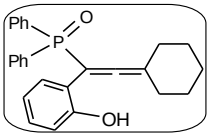
^{13}C NMR: δ 26.9, 31.0 (d, *J*(P-C) = 4.4 Hz, P*C*), 100.1 (d, ^{1}*J*(P-C) = 102.5 Hz, P*C*), 106.3 (d, *J*(P-C) = 13.8 Hz), 119.2, 119.9, 121.2, 128.3, 128.4, 129.9, 131.0 (d, *J*(P-C) = 106.0 Hz), 131.7, 131.8, 132.2, 155.7, 207.3 (d, *J*(P-C) = 8.5 Hz).

^{31}P NMR: δ 38.3.

LC-MS: *m/z* 387 $[M+1]^+$.

Anal. Calcd. for $C_{25}H_{23}O_2P$: C, 77.70; H, 6.00. Found: C, 77.56; H, 6.12.

Compound 15f



This product was synthesized from compound **13f** (0.20 g, 0.4 mmol).

Yield: 0.15 g (94%).

Mp: 162-164 ^{o}C (white solid).

IR (KBr): 3057, 2928, 1941, 1572, 1483, 1439, 1404, 1294, 1244, 1148 cm^{-1}.

^{1}H NMR: δ 0.97-1.48 (m, 6H, cyclohexyl-*H*), 1.81-2.06 (m, 4H, cyclohexyl-*H*), 6.77-6.81 (m, 1H, Ar-*H*), 6.93 (d, ^{3}*J*(H-H) = 8.0 Hz, 1H, Ar-*H*), 7.09-7.16 (m, 2H, Ar-*H*), 7.48-7.55 (m, 6H, Ar-*H*), 7.74-7.89 (m, 4H, Ar-*H*), 10.84 (s, 1H, O*H*).

^{13}C NMR: δ 25.2, 26.1, 29.8$_7$, 29.9$_1$, 97.8 (d, ^{1}*J*(P-C) = 105.9 Hz, P*C*), 104.0 (d, *J*(P-C) = 13.1 Hz), 119.1, 119.9, 121.3 (d, *J*(P-C) = 7.8 Hz), 128.4, 128.6, 129.8, 130.8 (d, *J*(P-C) = 106.7 Hz), 131.8, 131.9, 132.2, 155.7, 208.4 (d, *J*(P-C) = 9.1 Hz).

^{31}P NMR: δ 37.6.

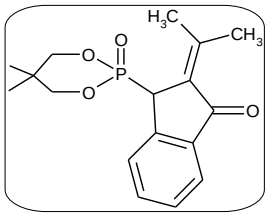
LC-MS: *m/z* 401 $[M+1]^+$.

Anal. Calcd. for $C_{26}H_{25}O_2P$: C, 77.98; H, 6.29. Found: C, 77.81; H, 6.37.

3.23 Phosphono-indanone derivatives 16-19- Representative procedure for 16

To a solution of substituted propargyl alcohol **7a** (0.55 g, 2.90 mmol) in dry THF (30 mL) was added triethylamine (0.29 g, 0.41 mL, 2.90 mmol), the mixture stirred for 5 min., and then ($OCH_2CMe_2CH_2O$)PCl (**1a**) (0.50 g, 2.90 mmol) was added dropwise at 0 ^{o}C. The contents were brought to room temperature, and then

heated under reflux for 6 h. Triethylamine hydrochloride formed was filtered off and the solvent removed under *vacuo* from the filtrate. The product **16** was purified by column chromatography (silica gel; ethyl acetate-hexane 4:1). Compounds **17**-**19** were also prepared similarly.



Yield: 0.71 g (75%).

Mp: 170-172 ^{o}C (white solid).

IR (KBr): 2932, 1696, 1638, 1466, 1252, 1059, 1015 cm^{-1}.

^{1}H NMR: δ 0.75 and 0.85 (2 s, 6H, C(C*H*$_3$)$_2$), 2.17 and 2.45 (2 s, 6H, =C(C*H*$_3$)$_2$), 3.51-3.63 and 4.09-4.18 (2 m, 4H, 2 OC*H*$_2$), 4.56 (d, ^{2}*J*(P-H) = 23.2 Hz, 1H, PC*H*), 7.43-7.47 and 7.58-7.62 (m, 2H, Ar-*H*), 7.75 (d, ^{3}*J*(H-H) = 8.0 Hz, 1H, Ar-*H*), 7.82 (d, ^{3}*J*(H-H) = 6.8 Hz, 1H, Ar-*H*).

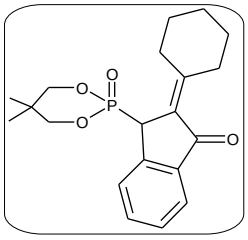
^{13}C NMR: δ 21.0, 21.2, 21.3, 25.8, 32.6 (d, ^{3}*J*(P-C) = 6.2 Hz, *C*(CH$_3$)$_2$), 42.8 (d, ^{1}*J*(P-C) = 136.9 Hz, P*C*H), 75.1, 75.3, 124.0, 127.2, 127.9, 128.5, 133.8, 139.7, 143.4, 153.0, 192.2.

^{31}P NMR: δ 19.8.

LC-MS: *m/z* 319 [M-1]$^{+}$.

Anal. Calcd. for $C_{17}H_{21}O_4P$: C, 63.74; H, 6.61. Found: C, 63.58; H, 6.71.

Compound 17



This compound was prepared by using propargyl alcohol **7b** (0.74 g, 3.3 mmol) and ($OCH_2CMe_2CH_2O$)PCl (**1a**) (0.55 g, 3.3 mmol).

Yield: 0.82 g (70%).

Mp: 162-164 ^{o}C (white solid).

IR (KBr): 2930, 1711, 1599, 1462, 1235, 1053, 1001 cm^{-1}.

^{1}H NMR: δ 0.82 and 0.86 (2 s, 6H, $C(CH_3)_2$), 1.66-1.91 (m, 6H, cyclohexyl-*H*), 2.46-2.58 and 3.07-3.32 (m, 4H, cyclohexyl-*H*), 3.55-3.62 and 4.10-4.21 (2 m, 4H, 2 OCH_2), 4.61 (d, ^{2}J(P-H) = 23.2 Hz, 1H, PC*H*), 7.44-7.48 and 7.59-7.63 (m, 2H, Ar-*H*), 7.75-7.77 (m, 1H, Ar-*H*), 7.83 (d, ^{3}J(H-H) = 7.6 Hz, 1H, Ar-*H*).

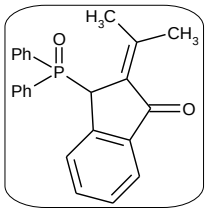
^{13}C NMR: δ 21.3, 21.5, 26.2, 27.9, 28.1, 29.2 (d, *J*(P-C) = 1.8 Hz), 32.6 (d, ^{3}J(P-C) = 6.0 Hz, *C*$(CH_3)_2$), 35.2 (d, *J*(P-C) = 1.3 Hz), 42.3 (d, ^{1}J(P-C) = 136.8 Hz, P*C*H), 75.1 (d, ^{2}J(P-C) = 6.5 Hz, O*C*H_2), 75.2 (d, ^{2}J(P-C) = 6.6 Hz, O*C*H_2), 124.0 (d, *J*(P-C) = 2.4 Hz), 125.2 (d, *J*(P-C) = 7.3 Hz), 127.1 (d, *J*(P-C) = 4.0 Hz), 128.4 (d, *J*(P-C) = 2.9 Hz), 133.8 (d, *J*(P-C) = 3.1 Hz), 140.0 (d, *J*(P-C) = 5.8 Hz), 143.2 (d, *J*(P-C) = 9.5 Hz), 160.2 (d, *J*(P-C) = 5.9 Hz), 192.6.

^{31}P NMR: δ 19.9.

LC-MS: *m/z* 361 $[M+1]^{+}$.

Anal. Calcd. for $C_{20}H_{25}O_4P$: C, 66.66; H, 6.99. Found: C, 66.82; H, 6.91.

Compound 18



This compound was prepared by using propargyl alcohol **7a** (0.55 g, 2.9 mmol) and Ph_2PCl (**1e**) (0.64 g, 2.9 mmol).

Yield: 0.84 g (78%).

Mp: 212-214 ^{o}C (white solid).

IR (KBr): 2934, 1684, 1620, 1435, 1292, 1194, 1111 cm^{-1}.

^{1}H NMR: δ 1.85 (s, 3H, $=C(CH_3)_A$), 2.35 (d, *J*(P-H) = 2.8 Hz, 3H, $=C(CH_3)_B$), 5.01 (d, ^{2}J(P-H) = 17.2 Hz, 1H, PC*H*), 7.01 (d, ^{3}J(H-H) = 7.2 Hz, 1H, Ar-*H*), 7.28-7.51 (m, 10H, Ar-*H*), 7.59 (d, ^{3}J(H-H) = 7.2 Hz, 1H, Ar-*H*), 7.69-7.74 (m, 2H, Ar-*H*).

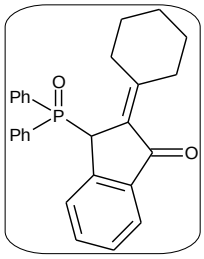
^{13}C NMR: δ 21.0, 25.8, 47.7 (d, ^{1}J(P-C) = 62.7 Hz, P*C*H), 123.9 (d, J(P-C) = 15.5 Hz), 127.8, 128.1, 128.2, 128.6, 130.8, 131.5, 131.7, 132.2, 132.3, 133.4, 140.1, 143.9, 153.6, 192.0.

^{31}P NMR: δ 32.0.

LC-MS: *m/z* 373 $[M+1]^+$.

Anal. Calcd. for $C_{24}H_{21}O_2P$: C, 77.41; H, 5.68. Found: C, 77.35; H, 5.61. This compound was crystallized from tetrahydrofuran (2 mL) at 30 ^{o}C. X-ray structure was determined for this sample (Fig. 2 in Chapter 2).

Compound 19



This compound was prepared by using propargyl alcohol **7b** (0.74 g, 3.3 mmol) and Ph_2PCl (**1e**) (0.73 g, 3.3 mmol).

Yield: 0.97 g (71%).

Mp: 174-176 ^{o}C (white solid).

IR (KBr): 2928, 1705, 1603, 1439, 1186, 1119 cm^{-1}.

^{1}H NMR: δ 1.26-2.35 (m, 8H, cyclohexyl-*H*), 2.82-2.85 and 3.33-3.35 (m, 2H, cyclohexyl-*H*), 5.06 (d, ^{2}J(P-H) = 17.2 Hz, 1H, PC*H*), 6.95-6.97 (m, 1H, Ar-*H*), 7.27-7.60 (m, 11H, Ar-*H*), 7.71-7.75 (m, 2H, Ar-*H*).

^{13}C NMR: δ 26.2, 28.2, 28.3, 29.3, 35.3, 47.1 (d, ^{1}J(P-C) = 62.5 Hz, P*C*H), 123.9 (d, J(P-C) = 2.4 Hz), 125.8 (d, J(P-C) = 4.5 Hz), 126.5 (d, J(P-C) = 3.4 Hz), 128.0, 128.1, 128.4, 128.5, 131.5, 131.6, 132.0 (d, J(P-C) = 3.3 Hz), 132.1 (d, J(P-C) = 2.6 Hz), 132.4, 132.5, 133.2 (d, J(P-C) = 2.6 Hz), 140.5 (d, J(P-C) = 4.6 Hz), 143.8 (d, J(P-C) = 5.1 Hz), 161.2 (d, J(P-C) = 4.9 Hz), 192.4.

^{31}P NMR: δ 32.2.

LC-MS: *m/z* 411 $[M-1]^+$.

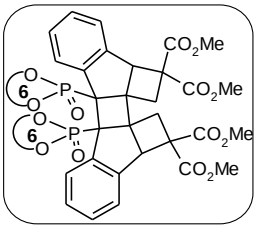
Anal. Calcd. for $C_{27}H_{25}O_2P$: C, 78.62; H, 6.11. Found: C, 78.51; H, 6.02.

3.24 Preparation of fused polycyclics 20-32

(a) Synthesis of compounds 20-23

Compounds **20-23** were prepared by following the procedure mentioned in section 3.23.

Compound 20



This product was synthesized from ($OCH_2CMe_2CH_2O$)PCl (**1a**) (0.34 g, 2.0 mmol) and propargyl alcohol **8a** (0.55 g, 2.0 mmol). It was purified by column chromatography using ethyl acetate as the eluent.

Yield: 0.57 g (70%).

Mp: 220–222 ^oC (white solid).

IR (KBr): 2959, 1730, 1435, 1370, 1265, 1053 cm^{-1}.

^1H NMR: δ 0.79 and 1.04 (2 s, 12H, 2 C(CH_3)$_2$), 2.99 (d, ^2J(H-H) = 14.8 Hz, 2H, CH_AH_B), 3.31-3.38 (m, 2H, OCH_2), 3.53 (s, 6H, 2 CO_2CH_3), 3.58 (d, ^2J(H-H) = 14.8 Hz, 2H, 2 CH_AH_B), 3.64-371 (m, 2H, OCH_2), 3.82 (s, 6H, 2 CO_2CH_3), 3.95-3.98 and 4.05-4.07 (m, 4H, 2 OCH_2), 4.81 (s, 2H, 2 C*H*), 7.19-7.27 (m, 6H, Ar-*H*), 7.70-7.72 (m, 2H, Ar-*H*).

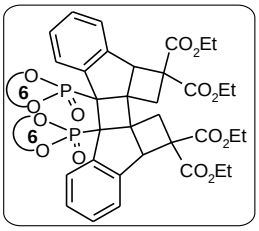
^{13}C NMR: δ 22.2, 23.3, 31.4 (d, ^3J(P-C) = 7.3 Hz, *C*(CH_3)$_2$), 33.0, 51.5, 52.0, 52.8, 53.2_9, 53.3_2, 63.5 (d, ^1J(P-C) = 149.1 Hz, P*C*), 73.6, 74.5, 125.8, 127.1, 128.1, 128.6, 140.2, 145.2 (d, *J*(P-C) = 4.6 Hz), 168.5, 171.9.

^{31}P NMR: δ 20.7.

LC-MS: *m/z* 813 $[M+1]^+$.

Anal. Calcd. for $C_{40}H_{46}O_{14}P_2$: C, 59.11; H, 5.70. Found: C, 59.32; H, 5.63. This compound was crystallized from dichloromethane (2 mL). X-ray structural analysis was determined for this sample (Fig. 3 in Chapter 2).

Compound 21



This compound was obtained by using **1a** (0.34 g, 2.0 mmol) and propargyl alcohol **8b** (0.60 g, 2.0 mmol). It was purified by column chromatography using ethyl acetate as the eluent.

Yield: 1.17 g (67%).

Mp: 134–136 ^{o}C (white solid).

IR (KBr): 2965, 1728, 1472, 1370, 1263, 1071 cm^{-1}.

^{1}H NMR: δ 0.77 (s, 6H, C(C*H*$_3$)$_2$), 1.05-1.09 (m, 12H, 2 CO$_2$CH$_2$C*H*$_3$ + C(C*H*$_3$)$_2$), 1.32 (t, ^{3}J(H-H) = 7.4 Hz, 6H, 2 CO$_2$CH$_2$C*H*$_3$), 2.99 (d, ^{2}J(H-H) = 14.8 Hz, 2H, 2 C*H*$_A$H$_B$), 3.31-3.38 (m, 2H, 2 OC*H*$_A$H$_B$), 3.57 (d, ^{2}J(H-H) = 14.8 Hz, 2H, 2 CH$_A$*H*$_B$), 3.64-3.71 (m, 2H, 2 OCH$_A$*H*$_B$), 3.88-4.08 and 4.25-4.29 (2 m, 12H, 4 CO$_2$C*H*$_2$CH$_3$ + 2 OC*H*$_2$), 4.83 (s, 2H, 2 C*H*), 7.23-7.25 (m, 6H, Ar-*H*), 7.72-7.73 (m, 2H, Ar-*H*).

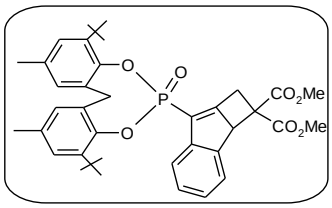
^{13}C NMR: δ 13.9, 14.1, 22.2, 23.4, 31.4 (d, ^{3}J(P-C) = 6.7 Hz, *C*(CH$_3$)$_2$), 33.0, 51.3, 53.3, 53.4, 61.0, 61.5, 63.6 (d, ^{1}J(P-C) = 149.0 Hz, P*C*), 73.4, 74.3, 126.0, 127.0, 128.1, 128.4, 140.2, 145.3, 168.3, 171.5.

^{31}P NMR: δ 21.2.

LC-MS: *m/z* 870 [M+1]$^{+}$.

Anal. Calcd. for C$_{44}$H$_{54}$O$_{14}$P$_2$: C, 60.82; H, 6.26. Found: C, 60.75; H, 6.32.

Compound 22



This compound was obtained by using **1c** (0.60 g, 2.0 mmol) and propargyl alcohol **8a** (0.55 g, 2.0 mmol). It was purified by column chromatography using ethyl acetate-hexane (1:4) mixture as the eluent.

Yield: 0.90 g (70%).

Mp: 212–214 ^{o}C (white solid).

IR (KBr): 2953, 1730, 1435, 1269, 1208, 1107 cm^{-1}.

^{1}H NMR: δ 1.29 and 1.33 (2 s, 18H, 2 C(CH_3)$_3$), 2.31 (s, 6H, 2 Ar-CH_3), 3.42 (s, 3H, CO_2CH_3), 3.63 (d, ^{2}J(H-H) ~ 13.2 Hz, 1H, CH_AH$_B$), 3.85-3.92 (m, 4H, CH$_A$$H_B$ + CO_2CH_3), 4.03 and 4.51 (2 d, ^{2}J(H-H) ~ 16.6 Hz, 2H, CH_2), 5.07 (s, 1H, C*H*C(CO$_2$Me)$_2$), 7.06 and 7.12 (2 br, 4H, Ar-*H*), 7.27-7.39 (m, 2H, Ar-*H*), 7.59-7.61 and 7.96-7.98 (m, 2H, Ar-*H*).

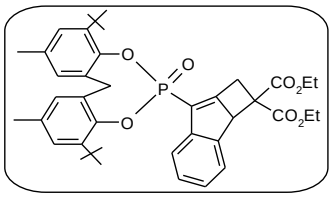
^{13}C NMR: δ 21.0, 31.1, 31.2, 34.9, 42.5 (d, *J*(P-C) = 3.5 Hz), 48.0 (d, *J*(P-C) = 3.6 Hz), 52.5, 53.7, 64.6 (d, *J*(P-C) = 19.0 Hz), 123.8, 125.1 (d, ^{1}J(P-C) = 215.4 Hz, P*C*), 125.3, 125.8, 127.6, 127.7, 127.9, 128.8 (d, *J*(P-C) = 2.0 Hz), 133.1, 134.5 (d, *J*(P-C) = 1.6 Hz), 134.7 (d, *J*(P-C) = 1.4 Hz), 141.5 (d, *J*(P-C) = 4.7 Hz), 141.8 (d, *J*(P-C) = 4.8 Hz), 144.4 (d, *J*(P-C) = 10.3 Hz), 144.7 (d, *J*(P-C) = 6.4 Hz), 144.8 (d, *J*(P-C) = 7.0 Hz), 147.2, 147.4, 156.4 (d, *J*(P-C) = 11.0 Hz), 165.8, 170.6.

^{31}P NMR: δ 4.9.

LC-MS: *m/z* 644 [M+1]$^{+}$.

Anal. Calcd. for $C_{38}H_{43}O_7P$: C, 71.01; H, 6.74. Found: C, 71.12; H, 6.69. This compound was crystallized from dichloromethane (2 mL). X-ray structural analysis was deteremined for this sample (Fig. 4 in Chapter 2).

Compound 23



This compound was obtained by using **1c** (0.60 g, 2.0 mmol) and propargyl alcohol **8b** (0.60 g, 2.0 mmol). It was purified by column chromatography using ethyl acetate-hexane (1:4) as the eluent.

Yield: 0.91 g (68%).

Mp: 222–224 ^{o}C (white solid).

IR (KBr): 2959, 2926, 1732, 1263, 1017 cm^{-1}.

^{1}H NMR: δ 0.92 (t, ^{3}J(H-H) = 7.2 Hz, 3H, $CO_2CH_2CH_3$), 1.31 and 1.34 (2 s, 18H, 2 $C(CH_3)_3$), 1.37 (t, ^{3}J(H-H) = 7.2 Hz, 3H, $CO_2CH_2CH_3$), 2.32 and 2.33 (2 s, 6H, 2 Ar-CH_3), 3.64 (d, ^{2}J(H-H) ~ 13.2 Hz, 1H, CH_AH_B), 3.82-3.93 (m, 3H, CH_AH_B + $CO_2CH_2CH_3$), 4.04-4.08 (m, 1H, CH_AH_B), 4.36-4.41 (m, 2H, $CO_2CH_2CH_3$), 4.52-4.56 (m, 1H, CH_AH_B), 5.11 (s, 1H, $CHC(CO_2Et)_2$), 7.08 (s, 2H, Ar-*H*), 7.12-7.14 (m, 2H, Ar-*H*), 7.28-7.29 (m, 1H, Ar-*H*), 7.38-7.41 (m, 1H, Ar-*H*), 7.61-7.63 and 7.98-8.00 (2 m, 2H, Ar-*H*).

^{13}C NMR: δ 13.8, 14.1, 21.0, 31.1, 31.2, 34.9, 42.4 (d, *J*(P-C) = 3.7 Hz), 47.8 (d, *J*(P-C) = 3.5 Hz), 61.4, 62.7, 64.5 (d, *J*(P-C) = 19.0 Hz), 123.7, 124.9 (d, *J*(P-C) = 215.1 Hz, P*C*), 125.1, 126.1, 127.6, 127.7, 127.8, 128.8 (d, *J*(P-C) = 2.1 Hz), 133.1_7, 133.2_0, 134.5, 134.7 (d, *J*(P-C) = 1.4 Hz), 141.5 (d, *J*(P-C) = 4.6 Hz), 141.8 (d, *J*(P-C) = 4.7 Hz), 144.4 (d, *J*(P-C) = 10.3 Hz), 144.7 (d, *J*(P-C) = 3.5 Hz), 144.8 (d, *J*(P-C) = 3.2 Hz), 147.3, 147.5, 156.7 (d, *J*(P-C) = 11.3 Hz), 165.3, 170.1.

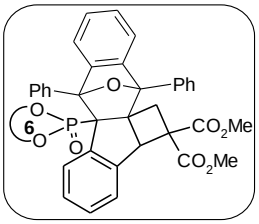
^{31}P NMR: δ 5.0.

LC-MS: *m/z* 669 $[M-1]^+$.

Anal. Calcd. for $C_{40}H_{47}O_7P$: C, 71.62; H, 7.06. Found: C, 71.46; H, 6.97.

(b) Synthesis of diphenylisobenzofuran adduct 24

To a solution of propargyl alcohol **8a** (0.13 g, 0.5 mmol) in THF (20 mL) was added triethylamine (0.05 g, 0.5 mmol) followed by **1a** (0.08 g, 0.5 mmol) at 0 ^{o}C under nitrogen atmosphere and the resulting mixture was stirred at room temperature for 4 h. To this, 1,3-diphenylisobenzofuran (0.20 g, 0.75 mmol) was added and the contents heated under reflux for 6 h. Et_3NHCl was filtered off and the solvent removed by using rotary evaporator. Pure compound **24** was obtained by column chromatography (silica gel 100/200 mesh) by using ethyl acetate-hexane (4:1) mixture as the eluent.



Yield: 0.25 g (78%).

Mp: 220–222 ^{o}C (white solid).

IR (KBr): 2949, 1738, 1725, 1456, 1335, 1235, 1117, 1044 cm^{-1}.

^{1}H NMR: δ 0.85 and 0.97 (2 s, 6H, C(C*H*$_3$)$_2$), 3.15-3.20 (m, 2H, OC*H*$_2$), 3.38 and 3.53 (s, 6H, 2 CO$_2$C*H*$_3$), 3.74-3.82 (m, 2H, C*H* +C*H*$_2$), 3.96-3.99 (m, 1H, C*H*$_2$), 4.26-4.33 (m, 2H, C*H*$_2$), 6.58 (d, ^{3}J(H-H) = 8.0 Hz, 1H, Ar-*H*), 6.82-6.85 (m, 1H, Ar-*H*), 7.11-7.63 (m, 11H, Ar-*H*), 7.87-7.99 (m, 5H, Ar-*H*).

^{13}C NMR: δ 22.5, 23.5, 30.3, 32.8 (d, ^{3}J(P-C) = 6.6 Hz, *C*(CH$_3$)$_2$), 52.0, 53.0, 53.6, 53.8, 61.3, 72.9 (d, ^{1}J(P-C) = 147.7 Hz, P*C*), 73.9 (d, *J*(P-C) = 6.4 Hz), 74.9 (d, *J*(P-C) = 6.3 Hz), 89.3, 92.6 (d, *J*(P-C) = 10.7 Hz), 120.9, 122.4, 125.8, 126.0, 126.3, 127.0, 127.2, 127.4, 127.8, 128.0, 128.5, 135.2, 136.3, 139.8, 143.6, 144.5, 145.7, 168.0, 170.4.

^{31}P NMR: δ 23.5.

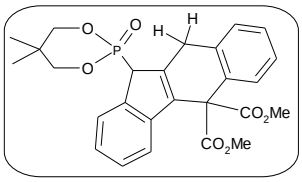
LC-MS: *m/z* 678 [M+1]$^{+}$.

Anal. Calcd. for $C_{40}H_{37}O_8P$: C, 71.00; H, 5.51. Found: C, 59.32; H, 5.63. This compound was crystallized from ethyl acetate (2 mL). X-ray structural analysis was deteremined for this sample (Fig. 5 in Chapter 2).

(c) Synthesis of compounds 25-32

These compounds were prepared by following the procedure mentioned in section 3.23.

Compound 25



This compound was obtained by using **1a** (0.34 g, 2.0 mmol) and propargyl alcohol **8c** (0.70 g, 2.0 mmol). It was purified by column chromatography using ethyl acetate-hexane (4:1) mixture as the eluent.

Yield: 0.71 g (74%).

Mp: 162–164 ^{o}C (white solid).

IR (KBr): 2961, 2926, 1728, 1468, 1287, 1059 cm^{-1}.

^{1}H NMR: δ 0.81 and 0.99 (2 s, 6H, C(C*H*$_3$)$_2$), 3.40-3.46 (m, 1H, OC*H*$_2$), 3.66 (s, 6H, 2 CO$_2$C*H*$_3$), 3.78-3.85 (m, 1H, OC*H*$_2$), 3.95-4.06 (m, 2H,

OCH_2), 4.22-4.38 (m, 3H, PCH + OCH_2), 7.25-7.39 (m, 5H, Ar-H), 7.44-7.46 (m, 1H, Ar-H), 7.55-7.57 (m, 1H, Ar-H), 7.73-7.75 (m, 1H, Ar-H).

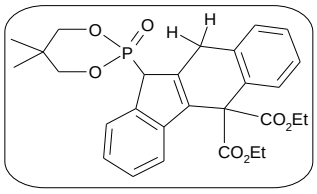
^{13}C NMR: δ 21.5, 21.6, 30.6, 32.6 (d, ^3J(P-C) = 7.4 Hz, C(CH_3)$_2$), 50.5 (d, ^1J(P-C) = 130.7 Hz, PC), 53.0, 53.1, 59.7, 75.5 and 76.5 (2 d, ^2J(P-C) ~ 7.0 Hz, 2 OCH$_2$), 120.7, 124.8, 125.0, 126.7, 127.7, 128.2, 128.4, 129.1, 130.9, 133.4, 134.5 (d, J(P-C) ~ 7.0 Hz), 137.4 (d, J(P-C) = 5.7 Hz), 138.1 (d, J(P-C) = 6.7 Hz), 143.6 (d, J(P-C) = 5.4 Hz), 169.4, 170.0.

^{31}P NMR: δ 18.9.

LC-MS: m/z 483 $[M+1]^+$.

Anal. Calcd. for $C_{26}H_{27}O_7P$: C, 64.73; H, 5.64. Found: C, 64.88; H, 5.71.

Compound 26



This compound was obtained by using **1a** (0.34 g, 2.0 mmol) and propargyl alcohol **8d** (0.76 g, 2.0 mmol). It was purified by column chromatography using ethyl acetate-hexane (4:1) mixture as the eluent.

Yield: 0.74 g (72%).

Mp: 66–68 ^{o}C (white solid).

IR (KBr): 2963, 2926, 1732, 1460, 1381, 1217, 1059 cm^{-1}.

^{1}H NMR: δ 0.77 and 0.94 (2 s, 6H, C(CH_3)$_2$), 1.02-1.10 (m, 6H, 2 CO$_2$CH$_2$CH_3), 3.36-3.42 (m, 1H, OCH_2), 3.76-3.83 (m, 1H, OCH_2), 3.92-4.36 (m, 9H, PCH + CH_2 + OCH_2 + 2 CO$_2$CH_2CH$_3$), 7.21-7.34 (m, 5H, Ar-H), 7.47 (d, ^3J(H-H) = 7.6 Hz, 1H, Ar-H), 7.55 (d, ^3J(H-H) = 7.6 Hz, 1H, Ar-H), 7.71 (d, ^3J(H-H) = 7.6 Hz, 1H, Ar-H).

^{13}C NMR: δ 13.7, 13.8, 21.6 (2 CH$_3$), 30.7, 32.6 (d, ^3J(P-C) = 6.7 Hz, C(CH_3)$_2$), 50.4 (d, ^1J(P-C) = 131.0 Hz, PC), 60.0, 61.9, 62.1, 75.3 and 76.2 (2 d, ^2J(P-C) ~ 6.8 Hz, 2 OCH$_2$), 121.3, 124.7, 124.8 (d, J(P-C) = 2.4 Hz), 126.5, 127.3, 128.0, 128.5, 129.0, 132.1 (d, J(P-C) = 10.0 Hz), 133.4,

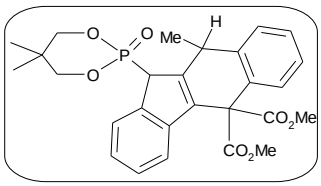
134.8, 137.5, 137.8 (d, *J*(P-C) = 10.1 Hz), 143.7 (d, *J*(P-C) = 4.5 Hz), 168.9, 169.5.

^{31}P NMR: δ 19.4.

LC-MS: *m/z* 509 $[M-1]^+$.

Anal. Calcd. for $C_{28}H_{31}O_7P$: C, 65.87; H, 6.12. Found: C, 65.78; H, 6.18.

Compound 27



This compound was obtained by using **1a** (0.34 g, 2.0 mmol) and propargyl alcohol **8e** (0.73 g, 2.0 mmol). It was purified by column chromatography using ethyl acetate-hexane (4:1) mixture as the eluent.

Yield: 0.72 g (73%).

Mp: 164–166 ^{o}C (white solid).

IR (KBr): 2967, 1736, 1458, 1269, 1229, 1055 cm^{-1}.

^{1}H NMR: δ 0.77 and 0.97 (2 s, 6H, 2 C(C*H*$_3$)$_2$), 1.50 (d, ^{3}*J*(H-H) = 7.2 Hz, 3H, CHC*H*$_3$), 3.36-3.48 (m, 1H, OC*H*$_A$H$_B$), 3.64-3.77 (m, 7H, 2 CO_2CH_3 + OCH$_A$*H*$_B$), 4.00-4.07 and 4.17-4.22 (m, 2H, OC*H*$_2$), 4.42-4.50 (m, 2H, PC*H* + C*H*CH$_3$), 7.26-7.48 (m, 6H, Ar-*H*), 7.54-7.57 (m, 1H, Ar-*H*), 7.77-7.79 (m, 1H, Ar-*H*).

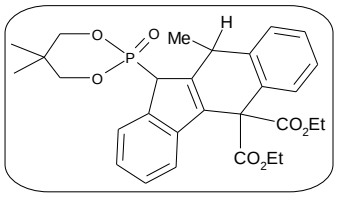
^{13}C NMR: δ 21.5, 21.6, 24.9, 32.6 (d, ^{3}*J*(P-C) = 6.6 Hz), 34.6, 48.6 (d, ^{1}*J*(P-C) = 130.7 Hz, P*C*), 53.0, 53.1, 59.5, 75.5 and 76.3 (2 d, ^{2}*J*(P-C) ~ 6.5 Hz, 2 O*C*H$_2$), 120.9, 124.9 (d, *J*(P-C) = 2.0 Hz), 125.1 (d, *J*(P-C) = 2.5 Hz), 126.6, 127.7 (d, *J*(P-C) = 1.3 Hz), 128.1, 128.4, 128.8, 130.5, 133.8 (d, *J*(P-C) = 10.7 Hz), 137.6 (d, *J*(P-C) = 5.8 Hz), 139.6, 143.4 (d, *J*(P-C) = 6.5 Hz), 143.5 (d, *J*(P-C) = 6.0 Hz), 169.4 (d, *J*(P-C) = 2.6 Hz), 170.1 (d, *J*(P-C) = 3.2 Hz).

^{31}P NMR: δ 18.6.

LC-MS: *m/z* 497 $[M+1]^+$.

Anal. Calcd. for $C_{27}H_{29}O_7P$: C, 65.32; H, 5.89. Found: C, 65.18; H, 5.93.

Compound 28



This compound was obtained by using **1a** (0.34 g, 2.0 mmol) and propargyl alcohol **8f** (0.78 g, 2.0 mmol). It was purified by column chromatography using ethyl acetate-hexane (4:1) mixture as the eluent.

Yield: 0.74 g (70%).

Mp: 128–130 ^{o}C (white solid).

IR (KBr): 2961, 2926, 1740, 1466, 1269, 1221, 1059 cm^{-1}.

^{1}H NMR: δ 0.72 and 0.92 (2 s, 6H, 2 C(C*H*$_3$)$_2$), 1.01 and 1.09 (2 t, ^{3}J(H-H) = 7.2 Hz, 6H, 2 CO$_2$CH$_2$C*H*$_3$), 1.47 (d, ^{3}J(H-H) = 7.2 Hz, 3H, CHC*H*$_3$), 3.38-3.45 and 3.68-3.75 (2 m, 2H, OC*H*$_2$), 3.99-4.20 (m, 6H, 2 CO$_2$C*H*$_2$CH$_3$ + OC*H*$_2$), 4.39-4.47 (m, 2H, PC*H* + C*H*CH$_3$), 7.24-7.39 (m, 5H, Ar-*H*), 7.48-7.50 (m, 1H, Ar-*H*), 7.54-7.56 (m, 1H, Ar-*H*), 7.74-7.76 (m, 1H, Ar-*H*).

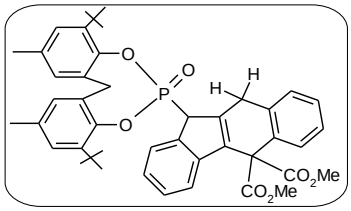
^{13}C NMR: δ 13.8, 21.6, 25.1, 32.6 (d, ^{3}J(P-C) = 8.0 Hz), 34.6, 48.5 (d, ^{1}J(P-C) = 130.0 Hz, P*C*), 59.8, 61.9, 62.0, 75.3 and 76.1 (2 d, ^{2}J(P-C) ~ 6.8 Hz, O*C*H$_2$), 121.4, 124.8, 125.0, 126.4, 127.3, 128.2, 128.7, 130.8, 134.1 (d, *J*(P-C) = 11.1 Hz), 137.7 (d, *J*(P-C) = 6.1 Hz), 139.6, 143.1, 143.6 (d, *J*(P-C) = 6.1 Hz), 168.9, 169.6.

^{31}P NMR: δ 19.1.

LC-MS: *m/z* 525 [M+1]$^{+}$.

Anal. Calcd. for C$_{29}$H$_{33}$O$_7$P: C, 66.40; H, 6.34. Found: C, 66.25; H, 6.41.

Compound 29



This compound was obtained by using **1c** (0.60 g, 2.0 mmol) and propargyl alcohol **8c** (0.70 g, 2.0 mmol). It was purified by column chromatography using ethyl acetate-hexane (3:7) mixture as the eluent.

Yield: 1.00 g (69%).

Mp: 172–174 ^{o}C (white solid).

IR (KBr): 2953, 1734, 1453, 1250, 1202, 920 cm^{-1}.

^{1}H NMR: δ 1.06 and 1.44 (2 s, 18H, 2 C(CH_3)$_3$), 2.29 and 2.34 (2 s, 6H, 2 Ar-CH_3), 3.50 (d, ^{2}J(H-H) = 13.2 Hz, 1H, CH_AH$_B$), 3.67 and 3.69 (2 s, 6H, CO$_2$CH_3), 4.17 (d, ^{2}J(H-H) = 22.4 Hz, 1H, CH_AH$_B$), 4.36 (dd, $^{2,3}J$(H-H) = 13.2 Hz, 2.4 Hz, 1H, CH$_A$$H_B$), 4.58 (dd, $^{2,3}J$(H-H) = 22.4 Hz, 3.2 Hz, 1H, CH$_A$$H_B$), 4.63 (d, ^{2}J(P-H) = 33.6 Hz, 1H, PC*H*), 7.00 (br, 1H, Ar-*H*), 7.08-7.13 (m, 3H, Ar-*H*), 7.29-7.46 (m, 5H, Ar-*H*), 7.57-7.59 (m, 2H, Ar-*H*), 8.07-8.08 (m, 1H, Ar-*H*).

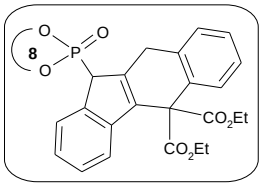
^{13}C NMR: δ 20.9$_7$, 21.0$_3$, 30.7, 31.2, 34.6, 35.0, 51.2 (d, ^{1}J(P-C) = 147.5 Hz, P*C*), 53.0, 53.1, 60.1, 121.0, 125.2, 126.0, 126.8, 127.7, 127.8, 127.9, 128.2, 128.6, 128.9, 129.1, 131.1, 133.1 (d, *J*(P-C) = 1.8 Hz), 133.2, 133.4 (d, *J*(P-C) = 2.7 Hz), 134.8 (d, *J*(P-C) = 11.7 Hz), 134.9 (d, *J*(P-C) = 1.4 Hz), 135.1 (d, *J*(P-C) = 1.2 Hz), 137.1, 138.2 (d, *J*(P-C) = 6.9 Hz), 141.3 (d, *J*(P-C) = 4.5 Hz), 141.5 (d, *J*(P-C) = 4.5 Hz), 143.5 (d, *J*(P-C) = 6.9 Hz), 144.5 (d, *J*(P-C) = 8.0 Hz), 144.6 (d, *J*(P-C) = 8.2 Hz), 169.6 (d, *J*(P-C) = 3.9 Hz), 170.1 (d, *J*(P-C) = 1.6 Hz).

^{31}P NMR: δ 15.9.

LC-MS: *m/z* 719 [M+1]$^{+}$.

Anal. Calcd. for C$_{44}$H$_{47}$O$_7$P: C, 73.52; H, 6.59. Found: C, 73.45; H, 6.63. This compound was crystallized from dichloromethane (2 mL). X-ray structural analysis was deteremined for this sample (Fig. 6 in Chapter 2).

Compound 30



This compound was obtained by using **1c** (0.60 g, 2.0 mmol) and propargyl alcohol **8d** (0.76 g, 2.0 mmol). It was purified by column chromatography using ethyl acetate-hexane (3:7) mixture as the eluent.

Yield: 0.99 g (66%).

Mp: 192–194 ^{o}C (white solid).

IR (KBr): 2924, 1734, 1603, 1451, 1229, 1040 cm^{-1}.

^{1}H NMR: δ 1.08-1.22 (m, 15H, 2 $CO_2CH_2CH_3$ + $C(CH_3)_3$), 1.38 (s, 9H, $C(CH_3)_3$), 2.26 and 2.30 (2 s, 6H, 2 Ar-CH_3), 3.46 (d, ^{2}J(H-H) = 12.8 Hz, 1H, CH_AH_B), 4.10-4.21 (m, 5H, 2 $CO_2CH_2CH_3$ + CH_AH_B), 4.34 (d, ^{2}J(H-H) = 13.6 Hz, 1H, CH_AH_B), 4.51-4.63 (m, 2H, PC*H* + CH_AH_B), 6.98 (br, 1H, Ar-*H*), 7.06-7.09 (m, 3H, Ar-*H*), 7.27-7.39 (m, 5H, Ar-*H*), 7.55-7.59 (m, 2H, Ar-*H*), 8.03-8.04 (m, 1H, Ar-*H*).

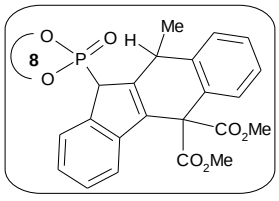
^{13}C NMR: δ 13.9, 21.0, 30.8, 31.2, 34.5, 34.6, 35.0, 51.2 (d, ^{1}J(P-C) = 147.5 Hz, P*C*), 60.4, 62.1 and 62.2 (2 d, *J*(P-C) ~ 3.0 Hz), 121.7, 125.1, 125.6, 126.6, 127.3, 127.8, 127.9, 128.0, 128.6, 128.8, 129.0, 131.4 (d, *J*(P-C) = 4.3 Hz), 133.2 (d, *J*(P-C) = 7.2 Hz), 133.4, 134.9 (d, *J*(P-C) = 10.3 Hz), 135.2, 137.3, 138.1 (d, *J*(P-C) = 6.6 Hz), 141.3, 141.5, 143.5 (d, *J*(P-C) = 6.9 Hz), 144.6, 169.0, 169.6.

^{31}P NMR: δ 15.9.

LC-MS: *m/z* 748 $[M+1]^{+}$.

Anal. Calcd. for $C_{46}H_{51}O_7P$: C, 73.97; H, 6.88. Found: C, 73.85; H, 6.81.

Compound 31



This compound was obtained by using **1c** (0.60 g, 2.0 mmol) and propargyl alcohol **8e** (0.73 g, 2.0 mmol). It was purified by column chromatography using ethyl acetate-hexane (3:7) mixture as the eluent.

Yield: 1.00 g (68%).

Mp: 228–230 ^{o}C (white solid).

IR (KBr): 2955, 2924, 1736, 1435, 1260, 1206, 926 cm^{-1}.

^{1}H NMR: δ 1.19 and 1.48 (2 s, 18H, 2 C(CH_3)$_3$), 2.22-2.35 (m, 9H, 2 Ar-CH_3 + CHCH_3), 3.30 (d, ^{2}J(H-H) = 13.6 Hz, 1H, CH_AH$_B$), 3.44 (s, 3H, CO_2CH_3), 4.06 (br, 4H, CO_2CH_3 + CH$_A$$H_B$), 5.11 (d, ^{2}J(P-H) = 27.6 Hz, 1H, PC*H*), 5.25 (br, 1H, C*H*CH$_3$), 6.92-7.40 (m, 11H, Ar-*H*), 7.85-7.87 (m, 1H, Ar-*H*).

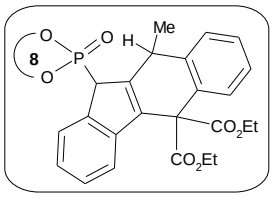
^{13}C NMR: δ 17.6 (d, *J*(P-C) = 3.1 Hz, CH*C*H$_3$), 20.9, 21.0, 30.6, 31.3, 33.9, 34.8, 34.9, 48.2 (d, ^{1}J(P-C) = 148.2 Hz, P*C*), 51.4 (d, *J*(P-C) = 2.4 Hz), 52.6, 53.2, 63.7, 124.1, 124.4 (d, *J*(P-C) = 2.5 Hz), 126.1, 126.5, 127.4, 127.5, 127.6, 128.0 (d, *J*(P-C) = 3.2 Hz), 128.5 (d, *J*(P-C) = 3.9 Hz), 128.7, 130.9 (d, *J*(P-C) = 10.8 Hz), 132.1 (d, *J*(P-C) = 9.4 Hz), 133.1 (d, *J*(P-C) = 2.3 Hz), 133.4 (d, *J*(P-C) = 2.6 Hz), 133.7 (d, *J*(P-C) = 2.7 Hz), 134.6, 134.7 (d, *J*(P-C) = 10.3 Hz), 137.0 (d, *J*(P-C) = 5.0 Hz), 138.3 (d, *J*(P-C) = 8.9 Hz), 141.0$_8$ (d, *J*(P-C) = 2.0 Hz), 141.1$_3$ (d, *J*(P-C) = 2.5 Hz), 142.0 (d, *J*(P-C) = 8.1 Hz), 144.6, 144.7, 144.8, 144.9, 168.9, 172.3.

^{31}P NMR: δ 14.9.

LC-MS: *m/z* 732 [M]$^{+}$.

Anal. Calcd. for $C_{45}H_{49}O_7P$: C, 73.75; H, 6.74. Found: C, 73.62; H, 6.81.

Compound 32



This compound was obtained by using **1c** (0.60 g, 2.0 mmol) and propargyl alcohol **8f** (0.78 g, 2.0 mmol). It was purified by column chromatography using ethyl acetate-hexane (3:7) mixture as the eluent.

Yield: 1.02 g (67%).

Mp: 228–230 ^{o}C (white solid).

IR (KBr): 2961, 1734, 1460, 1263, 1206, 930 cm^{-1}.

^{1}H NMR: δ 0.83 (t, ^{3}J(H-H) ~ 7.2 Hz, 3H, $CO_2CH_2CH_3$), 1.19 (s, 9H, C(CH_3)$_3$), 1.41-1.51 (m, 12H, $CO_2CH_2CH_3$ + C(CH_3)$_3$), 2.22-2.34 (m, 9H, 2 Ar-CH_3 + CHCH_3), 3.30 (d, ^{2}J(H-H) ~ 13.2 Hz, 1H, CH_AH$_B$), 3.81-3.92

(m, 2H, $CO_2CH_2CH_3$), 4.08 (d, ^2J(H-H) ~ 13.2 Hz, 1H, CH_AH_B), 4.53-4.56 (m, 2H, $CO_2CH_2CH_3$), 5.07 (d, ^2J(P-H) = 27.2 Hz, 1H, PC*H*), 5.26 (br, 1H, C*H*CH_3), 6.92-7.39 (m, 11H, Ar-*H*), 7.82-7.84 (m, 1H, Ar-*H*).

^{13}C NMR: δ 13.5, 14.2, 17.6, 20.9, 21.0, 30.7, 31.2, 33.9, 34.8, 34.9, 48.2 (d, ^1J(P-C) = 147.7 Hz, P*C*), 51.2, 61.0, 62.3, 63.7, 124.1, 124.9, 126.0, 126.2, 127.0, 127.4, 127.6, 127.8, 128.4, 128.6 (d, *J*(P-C) = 10.5 Hz), 133.5, 133.7, 134.6, 134.7, 137.1, 141.1, 142.3, 144.6, 144.7, 144.8, 168.5, 171.8.

^{31}P NMR: δ 14.9.

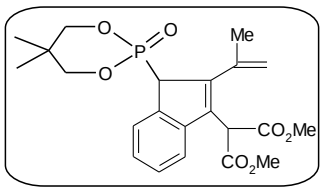
LC-MS: *m/z* 760 $[M]^+$.

Anal. Calcd. for $C_{47}H_{53}O_7P$: C, 74.19; H, 7.02. Found: C, 74.31; H, 7.08.

3.25 Reaction of P(III)-Cl precursors 1a-b with propargylic alcohols 8g-j: Synthesis of fused phosphono-polycyclics 33-40

These polycyclics **33-40** were obtained by following the procedure mentioned in section 3.23.

Compound 33



This compound was obtained by using **1a** (0.34 g, 2.0 mmol) and propargyl alcohol **8g** (0.60 g, 2.0 mmol). It was purified by column chromatography using ethyl acetate-hexane (4:1) mixture as the eluent.

Yield: 0.70 g (81%).

Mp: 98–100 ^oC (white solid).

IR (KBr): 2928, 1732, 1435, 1256, 1057, 1008 cm^{-1}.

^{1}H NMR: δ 0.82 and 1.01 (2 s, 6H, $C(CH_3)_2$), 2.10 (s, 3H, $H_2C=CCH_3$), 3.61-3.77 (m, 8H, 2 OCH_3 + OCH_2), 4.02-4.07 (m, 2H, OCH_2), 4.51 (d, ^2J(P-H) = 32.8 Hz, 1H, PC*H*), 5.14 and 5.17 (2 s, 2H, $=CH_2$), 5.36 (s, 1H, $CH(CO_2CH_3)_2$), 7.27-7.36 (m, 2H, Ar-*H*), 7.48-7.50 and 7.76-7.77 (2 m, 2H, Ar-*H*).

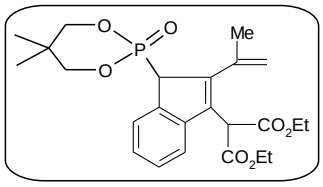
^{13}C NMR: δ 21.6, 21.8, 23.7 (d, *J*(P-C) = 6.0 Hz), 32.6 (d, ^{3}J(P-C) = 7.0 Hz, *C*$(CH_3)_2$), 50.4 (d, ^{1}J(P-C) = 131.0 Hz, P*C*), 50.5, 52.6_5, 52.6_8, 76.0 (d, ^{2}J(P-C) = 7.0 Hz, O*C*H_2), 76.1 (d, ^{2}J(P-C) = 7.0 Hz, O*C*H_2), 117.5, 121.7, 125.2, 125.5, 127.6, 132.9 (d, *J*(P-C) = 11.0 Hz), 137.3 (d, *J*(P-C) = 5.0 Hz), 139.3, 143.5, 144.8, 167.9, 168.0.

^{31}P NMR: δ 17.5.

LC-MS: *m/z* 435 $[M+1]^+$.

Anal. Calcd. for $C_{22}H_{27}O_7P$: C, 60.82; H, 6.26. Found: C, 60.91; H, 6.21. This compound was crystallized from dichloromethane-hexane (3+1 mL) mixture. X-ray structural analysis was done for this sample (Fig. 7 in Chapter 2).

Compound 34



This compound was obtained by using **1a** (0.34 g, 2.0 mmol) and propargyl alcohol **8h** (0.66 g, 2.0 mmol). It was purified by column chromatography using ethyl acetate-hexane (4:1) mixture as the eluent.

Yield: 0.70 g (76%, gummy material).

IR (KBr): 2978, 1732, 1638, 1472, 1372, 1008 cm^{-1}.

^{1}H NMR: δ 0.79 and 0.98 (2 s, 6H, C(C*H*$_3)_2$), 1.17-1.22 (m, 6H, 2 OCH$_2$C*H*$_3$), 2.08 (s, 3H, H$_2$C=CC*H*$_3$), 3.58-3.71 (m, 2H, OC*H*$_2$), 3.99-4.04 (m, 2H, OC*H*$_2$), 4.15-4.23 (m, 4H, 2 OC*H*$_2$CH$_3$), 4.48 (d, ^{2}J(P-H) = 32.8 Hz, 1H, PC*H*), 5.10 and 5.16 (2 s, 2H, =C*H*$_2$), 5.34 (s, 1H, C*H*$(CO_2Et)_2$), 7.20-7.32 (m, 2H, Ar-*H*), 7.49-7.51 and 7.72-7.74 (2 m, 2H, Ar-*H*).

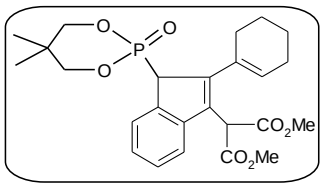
^{13}C NMR: δ 14.0, 21.6, 21.8, 23.8, 32.6 (d, ^{3}J(P-C) = 7.1 Hz, *C*$(CH_3)_2$), 50.3 (d, ^{1}J(P-C) = 127.0 Hz, P*C*), 61.7, 61.8, 76.0 (d, ^{2}J(P-C) = 6.9 Hz, O*C*H_2), 76.1 (d, ^{2}J(P-C) = 6.8 Hz, O*C*H_2), 117.5, 122.0, 125.1, 125.4, 127.5, 133.2 (d, *J*(P-C) = 10.7 Hz), 137.3 (d, *J*(P-C) = 4.9 Hz), 139.3, 143.5 (d, *J*(P-C) = 4.8 Hz), 144.6 (d, *J*(P-C) = 4.8 Hz), 167.5, 167.7 (d, *J*(P-C) = 3.5 Hz).

^{31}P NMR: δ 17.7.

LC-MS: *m/z* 463 $[M+1]^+$.

Anal. Calcd. for $C_{24}H_{31}O_7P$: C, 62.33; H, 6.76. Found: C, 62.21; H, 6.70.

Compound 35



This compound was obtained by using **1a** (0.34 g, 2.0 mmol) and propargyl alcohol **8i** (0.68 g, 2.0 mmol). It was purified by column chromatography using ethyl acetate-hexane (4:1) mixture as the eluent.

Yield: 0.72 g (76%).

Mp: 114–116 ^{o}C (white solid).

IR (KBr): 2936, 1728, 1441, 1256, 1063, 1009 cm^{-1}.

^{1}H NMR: δ 0.86 and 1.00 (2 s, 6H, C(C*H*$_3$)$_2$), 1.62-1.75 (m, 4H, cyclohexenyl-*H*), 1.99-2.03 (m, 1H, cyclohexenyl-*H*), 2.22 (br, 2H, cyclohexenyl-*H*), 2.49-2.53 (m, 1H, cyclohexenyl-*H*), 3.65-3.76 (m, 8H, 2 OC*H*$_3$ + OC*H*$_2$), 3.99-4.10 (m, 2H, OC*H*$_2$), 4.49 (d, ^{2}J(P-H) = 32.8 Hz, 1H, PC*H*), 5.10 (s, 1H, C*H*(CO$_2$CH$_3$)$_2$), 5.90 (br, 1H, =C*H*), 7.21-7.34 (m, 2H, Ar-*H*), 7.42-7.44 and 7.74-7.76 (2 m, 2H, Ar-*H*).

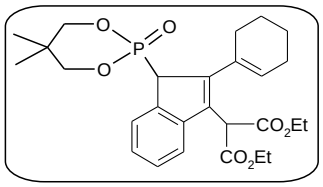
^{13}C NMR: δ 21.6, 21.9, 22.7, 25.5, 29.4, 32.6 (d, ^{3}J(P-C) = 7.1 Hz, *C*(CH$_3$)$_2$), 49.8 (d, ^{1}J(P-C) = 131.2 Hz, P*C*), 50.6, 52.8, 75.8 (d, ^{2}J(P-C) = 6.7 Hz, O*C*H$_2$), 76.0 (d, ^{2}J(P-C) = 6.8 Hz, O*C*H$_2$), 121.2, 125.2 (d, *J*(P-C) = 3.7 Hz), 127.6, 129.6, 131.7 (d, *J*(P-C) = 10.9 Hz), 132.8, 137.1 (d, *J*(P-C) = 4.7 Hz), 143.8 (d, *J*(P-C) = 5.1 Hz), 145.7 (d, *J*(P-C) = 6.6 Hz), 168.2, 168.3.

^{31}P NMR: δ 18.4.

LC-MS: *m/z* 475 $[M+1]^+$.

Anal. Calcd. for $C_{25}H_{31}O_7P$: C, 63.28; H, 6.59. Found: C, 63.15; H, 6.68.

Compound 36



This compound was obtained by using **1a** (0.34 g, 2.0 mmol) and propargyl alcohol **8j** (0.74 g, 2.0 mmol). It was purified by column chromatography using ethyl acetate-hexane (4:1) mixture as the eluent.

Yield: 0.74 g (73%, gummy material).

IR (Neat): 2924, 1728, 1665, 1368, 1223, 1017 cm^{-1}.

^{1}H NMR: δ 0.80 and 1.01 (2 s, 6H, $C(CH_3)_2$), 1.21-1.28 (m, 6H, 2 OCH_2CH_3), 1.62-1.77 (m, 4H, cyclohexenyl-*H*), 2.06-2.08 (m, 1H, cyclohexenyl-*H*), 2.25-2.26 (m, 2H, cyclohexenyl-*H*), 2.49-2.53 (m, 1H, cyclohexenyl-*H*), 3.65-3.73 (m, 2H, OCH_2CH_3), 4.03-4.27 (m, 6H, 2 OCH_2 + OCH_2CH_3), 4.51 (d, ^{2}J(P-H) = 32.0 Hz, 1H, PC*H*), 5.06 (s, 1H, $CH(CO_2Et)_2$), 5.94 (br, 1H, =C*H*), 7.22-7.35 (m, 2H, Ar-*H*), 7.49 and 7.77 (2 d, ^{3}J(H-H) = 8.0 Hz, 2H, Ar-*H*).

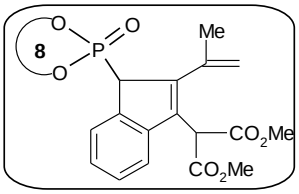
^{13}C NMR: δ 14.0, 21.7, 21.9, 22.8, 25.5, 29.4, 32.6 (d, ^{3}J(P-C) = 7.1 Hz, $C(CH_3)_2$), 49.7 (d, ^{1}J(P-C) = 131.3 Hz, P*C*), 51.0, 51.1, 61.7, 61.8, 75.8 (d, ^{2}J(P-C) = 6.9 Hz, O*C*H_2), 75.9 (d, ^{2}J(P-C) = 7.0 Hz, O*C*H_2), 121.5, 125.1, 127.4, 129.5 (d, *J*(P-C) = 1.3 Hz), 132.1 (d, *J*(P-C) = 7.0 Hz), 132.9, 137.1 (d, *J*(P-C) = 4.8 Hz), 143.9 (d, *J*(P-C) = 5.1 Hz), 145.5 (d, *J*(P-C) = 6.6 Hz), 167.8 (d, *J*(P-C) = 2.1 Hz), 168.0 (d, *J*(P-C) = 4.1 Hz).

^{31}P NMR: δ 18.8.

LC-MS: *m/z* 503 $[M+1]^{+}$.

Anal. Calcd. for $C_{27}H_{35}O_7P$: C, 64.53; H, 7.02. Found: C, 64.38; H, 7.10.

Compound 37



This compound was obtained by using **1c** (0.81 g, 2.0 mmol) and propargyl alcohol **8g** (0.60 g, 2.0 mmol). It was purified by column chromatography using ethyl acetate-hexane (1:4) mixture as the eluent.

Yield: 0.96 g (72%).

Mp: 146–148 ^{o}C (white solid).

IR (KBr): 2955, 1738, 1605, 1439, 1262, 1204, 1028, 922 cm^{-1}.

^{1}H NMR: δ 0.86 and 1.53 (2 s, 18H, 2 C(CH_3)$_3$), 2.18, 2.24 and 2.30 (3 s, 9H, 2 Ar-CH_3 + C(CH_3)=CH_2), 3.36 (d, ^{2}J(H-H) ~ 13.4 Hz, 1H, CH_AH$_B$), 3.72 and 3.73 (2 s, 6H, CO$_2$CH_3), 4.42 (d, ^{2}J(H-H) ~ 13.4 Hz, 1H, CH$_A$$H_B$), 4.74 (d, ^{2}J(P-H) = 32.4 Hz, 1H, PC*H*), 5.18 (s, 1H, C*H*(CO$_2$CH$_3$)$_2$), 5.25 and 5.46 (2 br, 2H, =CH_2), 6.91 and 7.02 (2 br, 2H, Ar-*H*), 7.08-7.10 (m, 2H, Ar-*H*), 7.27-7.31 (m, 1H, Ar-*H*), 7.40 (t, ^{3}J(H-H) ~ 8.0 Hz, 1H, Ar-*H*), 7.64 and 8.00 (2 d, ^{3}J(H-H) ~ 8.0 Hz, 2H, Ar-*H*).

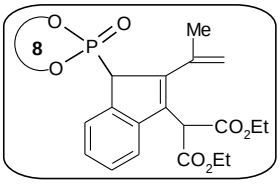
^{13}C NMR: δ 20.9, 21.0, 23.7, 30.4, 31.8, 34.0, 34.3, 35.1, 50.7, 50.8 (d, ^{1}J(P-C) = 146.0 Hz, P*C*), 52.7, 52.8, 119.0, 122.1, 125.7, 126.6, 127.4, 127.8, 128.1, 128.7 (d, *J*(P-C) = 2.3 Hz), 133.0 (d, *J*(P-C) = 11.0 Hz), 133.5 (d, *J*(P-C) = 2.8 Hz), 134.7 (d, *J*(P-C) = 1.3 Hz), 134.9, 136.7, 139.5, 141.2 (d, *J*(P-C) = 4.4 Hz), 141.7 (d, *J*(P-C) = 4.5 Hz), 143.3 (d, *J*(P-C) = 7.1 Hz), 144.3 (d, *J*(P-C) = 12.0 Hz), 144.8 (d, *J*(P-C) = 12.2 Hz), 146.7 (d, *J*(P-C) = 7.6 Hz), 167.8 (d, *J*(P-C) = 4.2 Hz), 168.0 (d, *J*(P-C) = 1.6 Hz).

^{31}P NMR: δ 15.9.

LC-MS: *m/z* 672 [M+1]$^{+}$.

Anal. Calcd. for $C_{40}H_{47}O_7P$: C, 71.62; H, 7.06. Found: C, 71.48; H, 7.15.

Compound 38



This compound was obtained by using **1c** (0.81 g, 2.0 mmol) and propargyl alcohol **8h** (0.66 g, 2.0 mmol). It was purified by column chromatography using ethyl acetate-hexane (1:4) mixture as the eluent.

Yield: 0.95 g (68%).

Mp: 112–114 ^{o}C (white solid).

IR (KBr): 2959, 1736, 1466, 1368, 1273, 1209, 1030 cm^{-1}.

^{1}H NMR: δ 0.86 (s, 9H, C(CH_3)$_3$), 1.21-1.29 (m, 6H, 2 OCH$_2$CH_3), 1.52 (s, 9H, C(CH_3)$_3$), 2.17, 2.23 and 2.29 (3 s, 9H, 2 Ar-CH_3 + C(CH_3)=CH$_2$), 3.35 (d, ^{2}J(H-H) = 13.6 Hz, 1H, CH_AH$_B$), 4.16-4.24 (m, 4H, 2 OCH_2CH$_3$), 4.41 (d, ^{2}J(H-H) = 13.6 Hz, 1H, CH$_A$$H_B$), 4.73 (d, ^{2}J(P-H) = 32.0 Hz, 1H, PC*H*), 5.11 (s, 1H, C*H*(CO$_2$Et)$_2$), 5.25 and 5.45 (2 br, 2H, =CH_2), 6.90 and 7.01 (2 br, 2H, Ar-*H*), 7.07-7.09 (m, 2H, Ar-*H*), 7.26-7.29 (m, 1H, Ar-*H*), 7.38 (t, ^{3}J(H-H) ~ 8.0 Hz, 1H, Ar-*H*), 7.67 and 7.98 (2 d, ^{3}J(H-H) ~ 8.0 Hz, 2H, Ar-*H*).

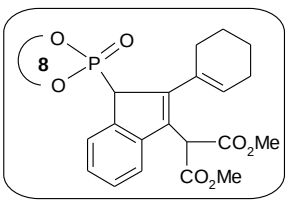
^{13}C NMR: δ 14.0, 20.9, 21.0, 23.8, 30.4, 31.8, 34.0, 34.3, 35.1, 50.8 (d, ^{1}J(P-C) = 146.1 Hz, P*C*), 51.2, 61.7, 61.8, 118.9, 122.5, 125.6, 126.5, 127.4, 127.6, 128.1, 128.7 (d, *J*(P-C) = 6.9 Hz), 133.4 (d, *J*(P-C) = 12.0 Hz), 133.5 (d, *J*(P-C) = 2.7 Hz), 133.8 (d, *J*(P-C) = 2.9 Hz), 134.6, 134.9, 136.7, 139.4, 141.2 (d, *J*(P-C) = 4.3 Hz), 141.7 (d, *J*(P-C) = 4.5 Hz), 143.3 (d, *J*(P-C) = 6.9 Hz), 141.7 (d, *J*(P-C) = 4.5 Hz), 143.4 (d, *J*(P-C) = 6.9 Hz), 144.3 (d, *J*(P-C) = 12.8 Hz), 144.8 (d, *J*(P-C) = 12.4 Hz), 146.6 (d, *J*(P-C) = 7.3 Hz), 167.3 (d, *J*(P-C) = 3.9 Hz), 167.6 (d, *J*(P-C) = 2.1 Hz).

^{31}P NMR: δ 15.9.

LC-MS: *m/z* 700 $[M+1]^{+}$.

Anal. Calcd. for $C_{42}H_{51}O_7P$: C, 72.19; H, 7.36. Found: C, 72.05; H, 7.41.

Compound 39



This compound was obtained by using **1c** (0.81 g, 2.0 mmol) and propargyl alcohol **8i** (0.68 g, 2.0 mmol). It was purified by column chromatography using ethyl acetate-hexane (1:4) mixture as the eluent.

Yield: 0.99 g (70%).

Mp: 184–186 ^{o}C (white solid).

IR (KBr): 2947, 1736, 1439, 1265, 1209, 1030 cm^{-1}.

^{1}H NMR: δ 0.79 and 1.53 (2 s, 18H, 2 C(C*H*$_3$)$_3$), 1.57-1.63 (m, 3H, cyclohexenyl-*H*), 2.06-2.29 (m, 10H, 2 Ar-C*H*$_3$ + cyclohexenyl-*H*), 2.60-2.64 (m, 1H, cyclohexenyl-*H*), 3.38 (d, ^{2}J(H-H) ~ 12.7 Hz, 1H, C*H*$_A$H$_B$), 3.69 and 3.71 (2 s, 6H, 2 OC*H*$_3$), 4.41 (dd, $^{2,3}J$(H-H) ~ 12.7 Hz, 3.0 Hz, 1H, CH$_A$*H*$_B$), 4.71 (d, ^{2}J(P-H) = 33.2 Hz, 1H, PC*H*), 5.09 (s, 1H, C*H*(CO$_2$Me)$_2$), 5.93 (br, 1H, =C*H*), 6.88 and 7.00 (2 br, 2H, Ar-*H*), 7.06-7.09 (m, 2H, Ar-*H*), 7.23-7.27 (m, 1H, Ar-*H*), 7.36 (t, ^{3}J(H-H) ~ 8.0 Hz, 1H, Ar-*H*), 7.58 and 7.98 (2 d, ^{3}J(H-H) ~ 8.0 Hz, 2H, Ar-*H*).

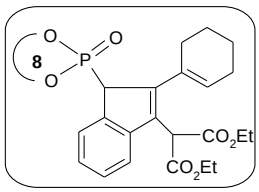
^{13}C NMR: δ 20.9, 21.0, 22.0, 22.7, 25.7, 29.6, 30.4, 31.8, 33.5, 34.3, 35.1, 50.5 (d, ^{1}J(P-C) = 147.1 Hz, P*C*), 50.8, 52.7, 52.8, 121.8, 125.4, 126.8, 127.4, 127.7, 128.1, 128.6, 130.6, 132.2 (d, *J*(P-C) = 10.6 Hz), 133.0, 133.6, 134.8, 136.5, 141.3 (d, *J*(P-C) = 6.5 Hz), 141.7 (d, *J*(P-C) = 3.7 Hz), 143.6, 144.9 (d, *J*(P-C) = 11.0 Hz), 147.7 (d, *J*(P-C) = 6.0 Hz), 168.1 (d, *J*(P-C) = 4.0 Hz), 168.3 (d, *J*(P-C) = 3.9 Hz).

^{31}P NMR: δ 16.4.

LC-MS: *m/z* 710 [M]$^{+}$.

Anal. Calcd. for C$_{43}$H$_{51}$O$_7$P: C, 72.66; H, 7.23. Found: C, 72.85; H, 7.16.

Compound 40



This compound was obtained by using **1c** (0.81 g, 2.0 mmol) and propargyl alcohol **8j** (0.74 g, 2.0 mmol). It was purified by column chromatography using ethyl acetate-hexane (1:4) mixture as the eluent.

Yield: 0.99 g (67%).

Mp: 126–128 ^{o}C (white solid).

IR (KBr): 2924, 1732, 1603, 1454, 1155, 1032 cm^{-1}.

^{1}H NMR: δ 0.82 (s, 9H, C(C*H*$_3$)$_3$), 1.22-1.31 (m, 6H, 2 $CO_2CH_2CH_3$), 1.55 (s, 9H, C(C*H*$_3$)$_3$), 1.61 (br, 2H, cyclohexenyl-*H*), 2.20, 2.24 and 2.31 (3 s, 11H, 2 Ar-C*H*$_3$ + cyclohexenyl-*H*), 2.63-2.67 (m, 1H, cyclohexenyl-*H*), 3.40 (d, ^{2}J(H-H) = 12.8 Hz, 1H, C*H*$_A$H$_B$), 4.16-4.25 (m, 4H, 2 $CO_2CH_2CH_3$), 4.43 (dd, $^{2,3}J$(H-H) = 12.8 Hz, 2.4 Hz, 1H, CH_AH_B), 4.73 (d, ^{2}J(P-H) = 32.8 Hz, 1H, PC*H*), 5.06 (s, 1H, C*H*(CO$_2$Et)$_2$), 5.93 (br, 1H, =C*H*), 6.90 (s, 1H, Ar-*H*), 7.02-7.03 (m, 1H, Ar-*H*), 7.09-7.11 (m, 2H, Ar-*H*), 7.24-7.28 (m, 1H, Ar-*H*), 7.38 (t, ^{3}J(H-H) = 7.6 Hz, 1H, Ar-*H*), 7.64 and 7.98 (2 d, ^{3}J(H-H) = 7.6 Hz, 2H, Ar-*H*).

^{13}C NMR: δ 14.0, 20.9, 21.0, 22.0, 22.7, 25.7, 29.6, 30.4, 30.9, 31.7, 33.5, 34.3, 35.1, 50.4 (d, ^{1}J(P-C) = 146.2 Hz, P*C*), 51.3, 61.6, 61.7, 122.2, 125.3, 126.6, 127.4, 127.5, 128.1, 128.6, 128.7, 130.5, 132.6 (d, *J*(P-C) = 11.1 Hz), 133.0, 133.5 (d, *J*(P-C) = 2.7 Hz), 133.6 (d, *J*(P-C) = 2.9 Hz), 134.6, 134.8, 136.5, 141.3 (d, *J*(P-C) = 4.3 Hz), 141.8 (d, *J*(P-C) = 4.6 Hz), 143.7 (d, *J*(P-C) = 7.0 Hz), 144.3 (d, *J*(P-C) = 12.0 Hz), 144.9 (d, *J*(P-C) = 12.3 Hz), 147.6 (d, *J*(P-C) = 7.1 Hz), 167.5 (d, *J*(P-C) = 3.8 Hz), 167.8 (d, *J*(P-C) = 1.4 Hz).

^{31}P NMR: δ 16.5.

LC-MS: *m/z* 738 $[M-1]^+$.

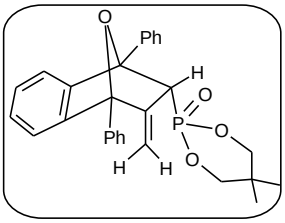
Anal. Calcd. for $C_{45}H_{55}O_7P$: C, 73.15; H, 7.50. Found: C, 73.31; H, 7.42.

3.3 Cycloaddition reactions of allenes with 1,3-diphenylisobenzofuran (IBF), dimethylacetylenedicarboxylate (DMAD) and anthracene

3.31 Reaction of allenes 9a-b, 10a-j, 11a-d and 12c-d with IBF

(a) Synthesis of α,β-adducts 41-49

Compound 41: A mixture of allenylphosphonate **10a** (0.30 g, 1.60 mmol) and 1,3-diphenylisobenzofuran (0.65 g, 2.39 mmol) in *p*-xylene (3 mL) was heated at 80 ^{o}C for 6-12 h. The solvent was removed under reduced pressure and the product **41** was isolated by using silica gel column chromatography [ethyl acetate-hexane (3:2)]. Compounds **42-53** were prepared similarly.



Yield: 0.40 g (55%).

Mp: 144-146 ^{o}C.

IR (KBr): 2965, 1499, 1460, 1350, 1260, 1059, 993 cm^{-1}.

^{1}H NMR: δ 0.87 and 1.04 (2 s, 6H, 2 CH_3), 3.46 and 3.61 (2 dd, ^{3}J(P-H) ~ 16.4 Hz, ^{2}J(H-H) ~ 11.6 Hz, 2H, OCH_2), 4.00 (dd, ^{3}J(P-H) ~ 11.2 Hz, ^{2}J(H-H) ~ 6.0 Hz, 1H, OCH_AH$_B$), 4.08 (d, ^{2}J(P-H) = 18.0 Hz, 1H, PC*H*), 4.15 (dd, ^{3}J(P-H) ~ 11.2 Hz, ^{2}J(H-H) ~ 6.0 Hz, 1H, OCH$_A$$H_B$), 5.34 and 5.41 (br, 2H, C=CH_2), 7.25-7.34 (m, 3H, Ar-*H*), 7.43-7.54 (m, 7H, Ar-*H*), 7.81 (d, ^{3}J(H-H) = 8.2 Hz, 2H, Ar-*H*), 7.97 (d, ^{3}J(H-H) = 8.0 Hz, 2H, Ar-*H*).

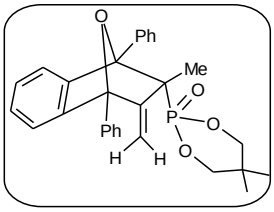
^{13}C NMR: δ 21.6, 22.3, 32.8 (d, ^{3}J(P-C) = 6.7 Hz, *C*(CH$_3$)$_2$), 47.9 (d, ^{1}J(P-C) = 144.3 Hz, P*C*), 74.3 (d, ^{2}J(P-C) = 6.3 Hz, O*C*H$_2$), 74.8 (d, ^{2}J(P-C) = 5.5 Hz, O*C*H$_2$), 89.2 (d, *J*(P-C) = 3.1 Hz, *C*-O), 90.2 (d, *J*(P-C) = 6.7 Hz, *C*-O), 109.1 (d, *J*(P-C) = 4.3 Hz), 119.7, 122.5, 126.7, 127.0, 127.6, 128.1, 128.2, 128.5 (d, *J*(P-C) = 8.3 Hz), 128.8, 135.0, 135.9, 144.7, 145.4, 146.1 (d, *J*(P-C) = 3.1 Hz).

^{31}P NMR: δ 20.8.

LC-MS: *m/z* 459 [M+1]$^{+}$.

Anal. Calcd. for $C_{28}H_{27}O_4P$: C, 73.35; H, 5.94. Found: C, 73.41; H, 5.86.

Compound 42



This compound was prepared by using allenylphosphonate **10e** (0.32 g, 1.60 mmol) and 1,3-diphenylisobenzofuran (0.65 g, 2.39 mmol). It was isolated by using ethyl acetate-hexane (3:2) mixture as the eluent.

Yield: 0.57 g (81%).

Mp: 231-232 ^{o}C.

IR (KBr): 3063, 1659, 1603, 1451, 1300, 1236, 1051, 997 cm^{-1}.

^{1}H NMR: δ 0.81 and 1.03 (2 s, 6H, 2 C*H*$_3$), 1.43 (d, ^{3}J(P-H) = 16.0 Hz, 3H, PCC*H*$_3$), 3.24 and 3.72 (2 dd, ^{3}J(P-H) ~ 17.8 Hz, ^{2}J(H-H) ~ 11.2 Hz, 2H, OC*H*$_2$), 3.91 and 4.26 (2 dd, ^{3}J(P-H) ~ 10.6 Hz, ^{2}J(H-H) ~ 4.0 Hz, 2H, OC*H*$_2$), 5.33 (br s, 2H, C=C*H*$_2$), 7.17-7.19 (m, 2H, Ar-*H*), 7.37-7.58 (m, 8H, Ar-*H*), 7.85 (d, ^{3}J(H-H) = 7.6 Hz, 2H, Ar-*H*), 8.28 (d, ^{3}J(H-H) = 7.6 Hz, 2H, Ar-*H*).

^{13}C NMR: δ 21.6, 22.1, 22.4, 33.0 (d, ^{3}J(P-C) = 6.0 Hz, *C*(CH$_3$)$_2$), 52.6 (d, ^{1}J(P-C) = 142.0 Hz, P*C*), 74.3 (d, ^{2}J(P-C) = 7.0 Hz, OCH$_2$), 74.7 (d, ^{2}J(P-C) = 6.0 Hz, OCH$_2$), 89.8 (d, ^{3}J(P-C) = 6.0 Hz, PCC*C*Ph), 91.3 (d, ^{2}J(P-C) = 7.0 Hz, PC*C*Ph), 108.5 (d, *J*(P-C) = 4.0 Hz), 119.7, 121.8, 126.3, 127.0, 127.3, 127.4, 127.8, 127.9, 128.1, 128.5, 135.6 (d, *J*(P-C) = 6.0 Hz), 144.7, 145.8, 152.4.

^{31}P NMR: δ 26.2.

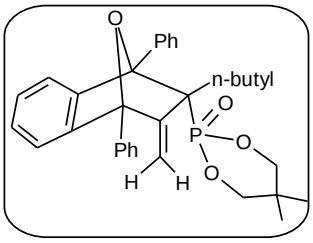
LC-MS: *m/z* 474 [M+1]$^{+}$.

Anal. Calcd. for $C_{29}H_{29}O_4P$: C, 73.71; H, 6.19. Found: C, 73.61; H, 6.28.

Compounds 43/43'

These compounds were prepared by using allenylphosphonate **10f** (0.39 g, 1.60 mmol) and 1,3-diphenylisobenzofuran (0.65 g, 2.39 mmol).

Compound 43



It was eluted by using ethyl acetate-hexane (3:2) mixture as the eluent.

Yield: 0.44 g (70%).

Mp: 240-242 ^{o}C.

IR (KBr): 2963, 1651, 1601, 1497, 1456, 1345, 1258, 1073, 997 cm^{-1}.

^{1}H NMR: δ 0.59 (t, ^{3}J(H-H) = 7.2 Hz, 3H, CH$_2$C*H*$_3$), 0.80 (s, 3H, C*H*$_3$), 0.90-0.98 (m, 5H, C*H*$_2$CH$_3$ + C*H*$_3$), 1.17-1.33 (m, 2H, C*H*$_2$CH$_2$CH$_3$), 1.92-

2.13 (m, 2H, PCCH_2), 3.11 and 3.71 (2 dd, ^3J(P-H) ~17.8 Hz, ^2J(H-H) ~ 11.4 Hz, 2H, OCH_2), 3.81 and 4.23 (2 dd, ^3J(P-H) ~ 11.0 Hz, ^2J(H-H) ~ 4.4 Hz, 2H, OCH_2), 5.26 and 5.37 (2 d, ^2J(H-H) = 4.4 Hz, 2H, C=CH_2), 7.13-7.59 (m, 10H, Ar-*H*), 7.86 (d, ^3J(H-H) = 7.6 Hz, 2H, Ar-*H*), 8.36 (d, ^3J(H-H) = 7.6 Hz, 2H, Ar-*H*).

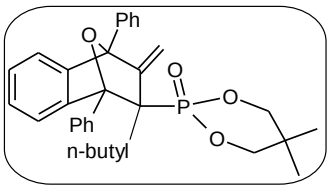
^{13}C NMR: δ 13.5, 21.7, 22.4, 23.0, 25.8, 25.9, 32.7, 32.9 (d, ^3J(P-C) = 5.9 Hz, *C*$(CH_3)_2$), 56.5 (d, ^1J(P-C) = 138.3 Hz, P*C*), 74.5 (d, ^2J(P-C) = 6.6 Hz, O*C*H_2), 74.8 (d, ^2J(P-C) = 6.3 Hz, O*C*H_2), 89.3 (d, ^3J(P-C) = 5.3 Hz, PCC*C*Ph), 91.6 (d, ^2J(P-C) = 7.3 Hz, PC*C*Ph), 108.9 (d, *J*(P-C) = 5.1 Hz), 119.5, 121.8, 126.4, 126.9, 127.1, 127.4, 127.6, 127.9, 128.0, 128.5, 135.8, 145.4, 146.9, 149.2 (d, *J*(P-C) = 3.7 Hz).

^{31}P NMR: δ 25.7.

LC-MS: *m/z* 515 $[M+1]^+$.

Anal. Calcd. for $C_{32}H_{35}O_4P$: C, 74.69; H, 6.86. Found: C, 74.62; H, 6.99.

Compound 43'



It was isolated by using ethyl acetate-hexane (7:3) mixture as the eluent.

Yield: 0.12 g (19%, gummy material).

IR (Neat): 2961, 1649, 1458, 1343, 1256, 1074, 1003, 909 cm^{-1}.

^{1}H NMR: δ 0.63-0.76 (m, 7H, *n*-Bu-*H* + CH_3), 0.98 (s, 3H, CH_3), 1.07-1.63 (m, 4H, *n*-Bu-*H*), 2.28-2.37 (m, 1H, *n*-Bu-*H*), 3.34 and 3.77 (dd→t, ^3J(P-H) ~ ^2J(H-H) ~ 10.7 Hz, 2H, OCH_2), 3.89 and 3.99 (dd→t, ^3J(P-H) ~ ^2J(H-H) ~ 10.0 Hz, 2H, OCH_2), 5.41 and 5.42 (2 s, 2H, C=CH_2), 7.15-7.56 (m, 10H, Ar-*H*), 7.88 (d, ^3J(H-H) = 7.6 Hz, 2H, Ar-*H*), 7.94 (d, ^3J(H-H) = 7.6 Hz, 2H, Ar-*H*).

^{13}C NMR: δ 13.8, 21.9, 22.4, 23.5, 27.3, 27.4, 32.8 (d, ^3J(P-C) = 8.0 Hz, *C*$(CH_3)_2$), 34.9, 57.4 (d, ^1J(P-C) = 135.0 Hz, P*C*), 75.3 (d, ^2J(P-C) = 6.0 Hz, O*C*H_2), 75.9 (d, ^2J(P-C) = 7.0 Hz, O*C*H_2), 89.8, 91.0, 112.0 (d, *J*(P-C) = 6.0 Hz), 119.7, 122.1, 126.6, 127.5, 127.9, 128.3, 128.5,

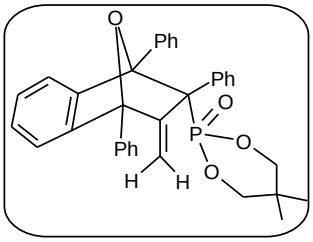
135.5, 136.5, 145.3, 146.9 (d, *J*(P-C) = 12.0 Hz), 149.5 (d, *J*(P-C) = 6.0 Hz).

^{31}P NMR: δ 22.1.

LC-MS: *m/z* 515 $[M+1]^+$.

Anal. Calcd. for $C_{32}H_{35}O_4P$: C, 74.69; H, 6.86. Found: C, 74.62; H, 6.95.

Compound 44



This compound was prepared by using allenylphosphonate **10g** (0.42 g, 1.60 mmol) and 1,3-diphenylisobenzofuran (0.65 g, 2.39 mmol). It was isolated by using ethyl acetate-hexane (3:2) mixture as the eluent.

Yield: 0.51 g (84%).

Mp: 221-223 ^{o}C.

IR (KBr): 2975, 1651, 1601, 1499, 1451, 1256, 1074, 1005 cm^{-1}.

^{1}H NMR: δ 0.85 and 0.94 (2 s, 6H, 2 CH_3), 3.21 and 3.64 (dd, ^{3}J(P-H) ~ 17.0 Hz, ^{2}J(H-H) ~ 11.2 Hz, 2H, OCH_2), 3.85 and 4.21 (dd, ^{3}J(P-H) ~ 10.8 Hz, ^{2}J(H-H) ~ 5.4 Hz, 2H, OCH_2), 5.33 and 5.64 (d, ^{2}J(H-H) ~ 4.6 Hz, 2H, C=CH_2), 7.00-7.01 (m, 3H, Ar-*H*), 7.16-7.27 (m, 5H, Ar-*H*), 7.48-7.56 (m, 4H, Ar-*H*), 7.62-7.65 (m, 2H, Ar-*H*), 7.78 (d, ^{3}J(H-H) = 6.8 Hz, 1H, Ar-*H*), 7.96-8.01 (m, 4H, Ar-*H*).

^{13}C NMR: δ 22.0, 22.7, 33.1 (d, ^{3}J(P-C) = 6.6 Hz, *C*$(CH_3)_2$), 64.3 (d, ^{1}J(P-C) = 145.0 Hz, P*C*), 75.1 (d, ^{2}J(P-C) = 6.1 Hz, O*C*H_2), 75.3 (d, ^{2}J(P-C) = 6.1 Hz, O*C*H_2), 89.5 (s, *C*-O), 93.4 (d, ^{2}J(P-C) = 6.6 Hz, *C*-O), 111.6, 119.4, 122.6, 126.3, 126.8, 126.9, 127.1, 127.3, 127.5, 128.0, 128.4, 128.7, 129.7, 129.8, 130.4 (d, *J*(P-C) = 7.6 Hz), 133.0, 135.6 (d, *J*(P-C) = 10.5 Hz), 137.0, 137.2, 140.0, 145.2, 145.8, 151.1.

^{31}P NMR: δ 22.1.

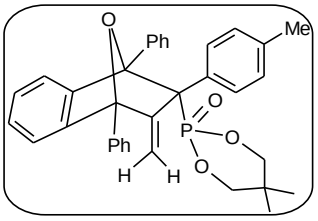
LC-MS: *m/z* 535 $[M+1]^+$.

Anal. Calcd. for $C_{34}H_{31}O_4P$: C, 76.39; H, 5.84. Found: C, 76.32; H, 5.87. This compound was crystallized from dichloromethane-hexane (4:1) mixture at 25 ^oC (Fig. 8 in Chapter 2).

Compounds 45/45'

These compounds were prepared by using allenylphosphonate **10h** (0.44 g, 1.60 mmol) and 1,3-diphenylisobenzofuran (0.65 g, 2.39 mmol).

Compound 45



It was isolated by using ethyl acetate-hexane (3:2) mixture as the eluent.

Yield: 0.39 g (66%).

Mp: 212-214 ^oC.

IR (KBr): 2959, 1653, 1603, 1512, 1458, 1300, 1236, 1078, 1051, 1001 cm^{-1}.

^1H NMR: δ 0.83 and 0.93 (2 s, 6H, 2 CH_3), 2.16 (s, 3H, PCC_6H_4CH_3), 3.16-3.23 and 3.62-3.67 (2 m, 2H, OCH_2), 3.83-3.87 and 4.19-4.22 (2 m, 2H, OCH_2), 5.33 and 5.63 (d, ^2J(H-H) ~ 4.6 Hz, 2H, C=CH_2), 6.81 (d, ^3J(H-H) = 8.4 Hz, 2H, Ar-*H*), 7.17-7.27 (m, 5H, Ar-*H*), 7.41-7.77 (m, 7H, Ar-*H*), 7.95-8.03 (m, 4H, Ar-*H*).

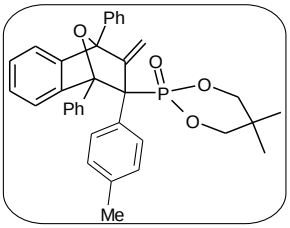
^{13}C NMR: δ 20.9, 21.9, 22.7, 33.0 (d, ^3J(P-C) = 6.6 Hz, *C*$(CH_3)_2$), 63.9 (d, ^1J(P-C) = 144.9 Hz, P*C*), 74.9 (d, ^2J(P-C) = 6.5 Hz, O*C*H_2), 75.2 (d, ^2J(P-C) = 6.3 Hz, O*C*H_2), 89.5 (d, ^3J(P-C) = 5.1 Hz, PCC*C*Ph), 93.4 (d, ^2J(P-C) = 7.3 Hz, PC*C*Ph), 111.6 (d, *J*(P-C) = 4.7 Hz), 119.3, 122.6, 126.3, 127.1, 127.2, 127.3, 127.4, 127.7, 128.0, 128.6, 130.3 (d, *J*(P-C) = 7.2 Hz), 133.8, 135.7 (d, *J*(P-C) = 8.5 Hz), 145.4, 145.8, 151.2 (d, *J*(P-C) = 4.3 Hz).

^{31}P NMR: δ 22.4.

LC-MS: *m/z* 549 $[M+1]^+$.

Anal. Calcd. for $C_{35}H_{33}O_4P$: C, 76.63; H, 6.06. Found: C, 76.81; H, 6.21.

Compound 45'



It was isolated by using ethyl acetate-hexane (7:3) mixture as the eluent.

Yield: 0.16 g (27%).

Mp: 194-196 ^{o}C.

IR (KBr): 2963, 1655, 1460, 1370, 1300, 1246, 1049, 990 cm^{-1}.

^{1}H NMR: δ 0.84 and 1.08 (2 s, 6H, 2 CH_3), 2.29 (s, 3H, PCC$_6$H$_4$CH_3), 2.93-2.99 and 3.90-4.09 (2 m, 4H, 2 OCH_2), 5.40 and 5.48 (2 d, ^{2}J(H-H) ~ 4.8 Hz, 2H, C=CH_2), 6.65 (d, ^{3}J(H-H) = 7.6 Hz, 1H, Ar-*H*), 6.87-7.02 (m, 5H, Ar-*H*), 7.27-7.62 (m, 10H, Ar-*H*), 8.09 (d, ^{3}J(H-H) = 6.8 Hz, 2H, Ar-*H*).

^{13}C NMR: δ 21.0, 22.0, 22.7, 32.9 (d, ^{3}J(P-C) = 8.4 Hz, *C*(CH$_3$)$_2$), 65.3 (d, ^{1}J(P-C) = 137.9 Hz, P*C*), 74.7 (d, ^{2}J(P-C) = 6.3 Hz, O*C*H$_2$), 75.9 (d, ^{2}J(P-C) = 7.7 Hz, O*C*H$_2$), 91.1 (d, ^{3}J(P-C) = 1.3 Hz, PCC*C*Ph), 91.8 (d, ^{2}J(P-C) = 2.1 Hz, PC*C*Ph), 113.3 (d, *J* = 7.1 Hz), 120.0, 123.0, 126.3, 127.7, 127.9 (d, *J* = 7.4 Hz), 128.6, 128.9, 130.2 (d, *J* = 7.5 Hz), 134.4 (d, *J* = 10.1 Hz), 137.1 (d, *J* = 10.3 Hz), 144.2, 146.4 (d, *J* = 11.5 Hz), 152.2 (d, *J* = 8.5 Hz).

31P NMR: δ 20.1.

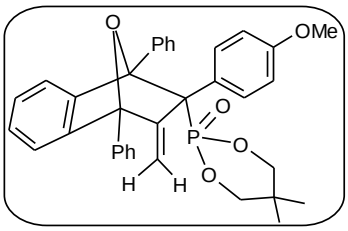
LC-MS: *m/z* 549 [M+1]$^{+}$.

Anal. Calcd. for C$_{35}$H$_{33}$O$_4$P: C, 76.63; H, 6.06. Found: C, 76.58; H, 6.15.

Compounds 46/46'

These compounds were prepared by using allenylphosphonate **10i** (0.47 g, 1.60 mmol) and 1,3-diphenylisobenzofuran (0.65 g, 2.39 mmol).

Compounds 46



It was separated by using ethyl acetate-hexane (3:2) mixture as the eluent.

Yield: 0.40 g (69%).

Mp: 199-201 ^{o}C.

IR (KBr): 2963, 1607, 1512, 1462, 1372, 1296, 1248, 1086, 939 cm^{-1}.

^{1}H NMR: δ 0.83 and 0.94 (2 s, 6H, 2 CH_3), 3.16-3.23 (m, 1H, OCH_AH$_B$), 3.61-3.66 (m, 4H, OCH$_A$$H_B$ + C$_6$H$_4$OCH_3), 3.83-3.87 and 4.20-4.23 (2 m, 2H, OCH_2), 5.34 (s, 1H, C=CH_AH$_B$), 5.63 (d, ^{2}J(H-H) = 4.0 Hz, 1H, C=CH$_A$$H_B$), 6.54 (d, ^{3}J(P-H) = 8.8 Hz, 2H, Ar-*H*), 7.17-7.26 (m, 5H, Ar-*H*), 7.45-7.77 (m, 7H, Ar-*H*), 7.96 (d, *J*(H-H) = 7.2 Hz, 2H, Ar-*H*), 8.01 (d, *J*(H-H) = 7.2 Hz, 2H, Ar-*H*).

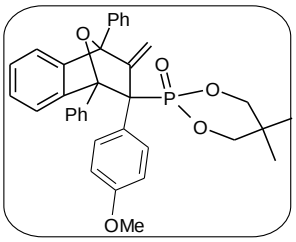
^{13}C NMR: δ 21.9, 22.7, 33.0 (d, ^{3}J(P-C) = 6.5 Hz, *C*(CH$_3$)$_2$), 55.0, 63.5 (d, ^{1}J(P-C) = 145.0 Hz, P*C*), 74.9 (d, ^{2}J(P-C) = 6.4 Hz, OCH$_2$), 75.2 (d, ^{2}J(P-C) = 6.3 Hz, OCH$_2$), 89.5 (d, ^{3}J(P-C) = 5.3 Hz, PCC*C*Ph), 93.5 (d, ^{2}J(P-C) = 7.5 Hz, PC*C*Ph), 111.6 (d, *J*(P-C) = 4.7 Hz), 112.3, 119.3, 122.5, 126.3, 127.1, 127.2 (d, *J*(P-C) = 3.9 Hz), 127.4, 128.0, 128.7, 128.9, 131.6 (d, *J*(P-C) = 7.3 Hz), 135.7 (d, *J*(P-C) = 6.0 Hz), 145.3, 145.7, 151.3 (d, *J*(P-C) = 4.4 Hz), 158.2.

^{31}P NMR: δ 22.4.

LC-MS: *m/z* 563 [M-1]$^{+}$.

Anal. Calcd. for C$_{35}$H$_{33}$O$_5$P: C, 74.45; H, 5.89. Found: C, 74.42; H, 5.85. It was crystallized from dichloromethane-hexane (4:1) mixture at 25 ^{o}C for X-ray structure determination (Fig. 9 in Chapter 2).

Compound 46'



It was separated by using ethyl acetate-hexane (7:3) mixture as the eluent.

Yield: 0.11 g (19%).

Mp: 209-210 ^{o}C.

IR (KBr): 2965, 1607, 1512, 1460, 1341, 1256, 1188, 1074, 1007, 912 cm^{-1}.

^{1}H NMR: δ 0.84 and 1.08 (2 s, 6H, 2 CH_3), 2.94 (dd→t, ^{3}J(P-H) ~ ^{2}J(H-H) ~ 11.4 Hz, 1H, OCH_AH$_B$), 3.77 (s, 3H, C_6H_4OCH_3), 3.89-4.09 (m, 3H, OCH$_A$$H_B$ + OCH_2), 5.40 and 5.48 (2 br s, 2H, C=CH_2), 6.61-6.67 (m, 3H, Ar-*H*), 6.89-7.61 (m, 13H, Ar-*H*), 8.08 (d, ^{3}J(H-H) = 6.8 Hz, 2H, Ar-*H*).

^{13}C NMR: δ 22.0, 22.7, 32.9 (d, ^{3}J(P-C) = 8.1 Hz, *C*(CH$_3$)$_2$), 55.1, 65.0 (d, ^{1}J(P-C) = 138.0 Hz, P*C*), 74.8 (d, ^{2}J(P-C) = 5.8 Hz, O*C*H$_2$), 76.0 (d, ^{2}J(P-C) = 7.4 Hz, O*C*H$_2$), 91.1, 91.8, 112.4, 113.3 (d, *J* = 6.5 Hz), 120.0, 123.0, 126.3, 126.4, 127.8, 128.0, 128.6, 128.9, 129.1, 129.5, 131.6 (d, *J* = 7.2 Hz), 134.4, 137.0, 144.1, 146.4 (d, *J* = 11.4 Hz), 152.4 (d, *J* = 8.3 Hz), 158.7.

^{31}P NMR: δ 20.1.

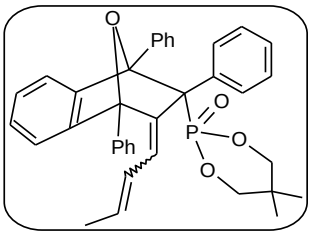
LC-MS: *m/z* 565 $[M+1]^+$.

Anal. Calcd. for $C_{35}H_{33}O_5P$: C, 74.45; H, 5.89. Found: C, 74.39; H, 5.86. This compound was crystallized from dichloromethane-hexane (4:1) mixture at 25 ^{o}C for X-ray structure determination (Fig. 9 in Chapter 2).

Compounds 47/47'

These were prepared by treating allenylphosphonate **10j** (0.36 g, 1.60 mmol) and 1,3-diphenylisobenzofuran (0.65 g, 2.39 mmol) by the procedure mentioned above.

Compound 47



It was isolated by using ethyl acetate-hexane (3:2) mixture as the eluent.

Yield: 0.29 g (32%).

Mp: 178-180 ^{o}C.

IR (KBr): 2965, 1601, 1497, 1447, 1236, 1047, 995 cm^{-1}.

^{1}H NMR: δ 0.85$_5$ and 0.86$_0$ (2 s, 6H, C(CH_3)$_2$), 1.50 (d, ^{3}J(H-H) = 6.4 Hz, 3H, CH_3), 3.19-3.25 and 3.59-3.75 (2 m, 3H, OCH_2), 4.18-4.22 (m, 1H, OCH_2), 5.50-5.55 (m, 1H, =C*H*), 5.85-5.91 (m, 1H, =C*H*), 6.34-6.38 (m, 1H, =C*H*), 6.98 (br, 3H, Ar-*H*), 7.12-7.27 (m, 6H, Ar-*H*), 7.47-

7.53 (m, 3H, Ar-*H*), 7.60-7.64 (m, 2H, Ar-*H*), 7.85-8.05 (m, 5H, Ar-*H*).

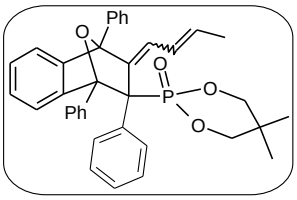
^{13}C NMR: δ 18.0, 22.1, 23.0, 32.8 (d, ^{3}J(P-C) = 8.2 Hz, *C*$(CH_3)_2$), 65.5 (d, ^{1}J(P-C) = 140.4 Hz, P*C*), 74.6 (d, ^{2}J(P-C) = 5.8 Hz), 75.9 (d, ^{2}J(P-C) = 7.7 Hz), 92.2, 92.7, 119.5, 123.5, 125.8, 126.4, 126.8, 127.3, 127.6, 127.8, 128.0, 128.4, 128.6, 129.0, 129.8, 130.0, 132.1, 135.3 (d, *J*(P-C) = 97.8 Hz, P*C*), 137.2, 139.9 (d, *J*(P-C) = 8.7 Hz), 144.9, 145.9, 146.1.

^{31}P NMR: δ 22.2.

LC-MS: *m/z* 574 $[M-1]^+$.

Anal. Calcd. for $C_{37}H_{35}O_4P$: C, 77.33; H, 6.14. Found: C, 77.21; H, 6.19.

Compound 47'



It was isolated by using ethyl acetate-hexane (7:3) mixture as the eluent.

Yield: 0.48 g (53%).

Mp: 182-184 ^{o}C.

IR (KBr): 2969, 1601, 1497, 1447, 1248, 1065, 997 cm^{-1}.

^{1}H NMR: δ 0.82 and 1.10 (2 s, 6H, C(C*H*$_3$)$_2$), 1.46 (d, ^{3}J(H-H) = 6.0 Hz, 3H, C*H*$_3$), 2.93-2.99 and 3.87-4.09 (m, 4H, OC*H*$_2$), 5.42-5.47 (m, 1H, =C*H*), 5.67-5.73 (m, 1H, =C*H*), 6.16-6.20 (m, 1H, =C*H*), 6.61 (d, ^{3}J(H-H) = 7.2 Hz, 1H, Ar-*H*), 6.95-7.37 (m, 8H, Ar-*H*), 7.51-7.57 (m, 8H, Ar-*H*), 8.11-8.13 (m, 2H, Ar-*H*).

^{13}C NMR: δ 18.2, 22.1, 23.0, 32.8 (d, ^{3}J(P-C) = 8.1 Hz, *C*$(CH_3)_2$), 65.5 (d, ^{1}J(P-C) = 140.7 Hz, P*C*), 74.6 (d, ^{2}J(P-C) = 7.3 Hz), 75.9 (d, ^{2}J(P-C) = 7.6 Hz), 92.2, 92.7, 119.5, 123.5, 125.8, 126.4, 126.8, 127.3, 127.6, 127.8, 128.0, 128.6, 129.0, 129.8, 130.1, 131.2, 132.1, 135.2 (d, *J*(P-C) = 99.9 Hz, P*C*), 137.2, 139.9 (d, *J*(P-C) = 9.5 Hz), 144.9, 145.9, 146.0.

^{31}P NMR: δ 19.5.

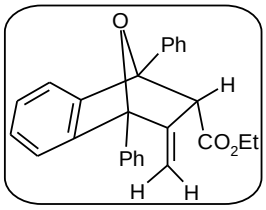
LC-MS: *m/z* 574 $[M-1]^+$.

Anal. Calcd. for $C_{37}H_{35}O_4P$: C, 77.33; H, 6.14. Found: C, 77.45; H, 6.09.

Compounds 48/48'

These compounds were prepared by using allene **9a** (0.18 g, 1.60 mmol) and 1,3-diphenylisobenzofuran (0.65 g, 2.39 mmol).

Compound 48



It was separated by using ethyl acetate-hexane (1:4) mixture as the eluent.

Yield: 0.32 g (31%).

Mp: 90-92 ^{o}C.

IR (KBr): 2975, 2926, 1736, 1661, 1449, 1300, 1179, 997 cm^{-1}.

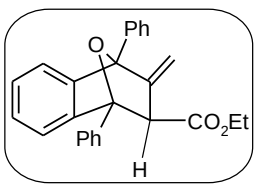
^{1}H NMR: δ 1.15 (t, ^{3}J(H-H) = 7.2 Hz, 3H, $CO_2CH_2CH_3$), 4.04-4.08 (m, 2H, $CO_2CH_2CH_3$), 4.32 (s, 1H, $CHCO_2CH_2CH_3$), 5.22 and 5.25 (2 s, 2H, $C=CH_2$), 7.16-7.25 (m, 4H, Ar-*H*), 7.43-7.55 (m, 6H, Ar-*H*), 7.73 (d, ^{3}J(H-H) = 6.8 Hz, 2H, Ar-*H*), 7.84 (d, ^{3}J(H-H) = 7.2 Hz, 2H, Ar-*H*).

^{13}C NMR: δ 14.1 ($CO_2CH_2CH_3$), 55.1 ($CO_2CH_2CH_3$), 60.9 ($CHCO_2Et$), 89.1 (Ph*C*-O), 90.4 (Ph*C*-O), 107.8, 119.1, 123.0, 126.6, 127.2, 127.4_0, 127.4_2, 128.3, 128.4, 128.5, 128.6, 134.9, 136.8, 145.1, 146.1, 149.1, 170.3 ($CO_2CH_2CH_3$).

LC-MS: *m/z* 383 $[M+1]^{+}$.

Anal. Calcd. for $C_{26}H_{22}O_3$: C, 81.65; H, 5.80. Found: C, 81.62; H; 5.75. It was crystallized from dichloromethane-hexane (4:1) mixture at 25 ^{o}C for X-ray structure determination (Fig. 10 in Chapter 2).

Compound 48'



It was separated by using ethyl acetate-hexane (1:2) as the eluent.

Yield: 0.60 g (59%, gummy material).

IR (Neat): 2978, 1746, 1719, 1499, 1449, 1310, 1254, 1148, 1001 cm^{-1}.

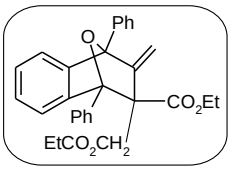
^{1}H NMR: δ 0.92 (t, ^3J(H-H) = 7.2 Hz, 3H, $CO_2CH_2CH_3$), 3.85-4.08 (m, 3H, $CHCO_2Et$ + $CO_2CH_2CH_3$), 5.19 and 5.23 (2 m, 2H, $C=CH_2$), 7.11-7.27 (m, 3H, Ar-*H*), 7.37-7.68 (m, 9H, Ar-*H*), 7.95-7.98 (m, 2H, Ar-*H*).

13C NMR: δ 13.8 ($CO_2CH_2CH_3$), 56.3 ($CO_2CH_2CH_3$), 60.7 ($CHCO_2Et$), 89.2 (Ph*C*-O), 90.2 (Ph*C*-O), 108.5, 119.5, 119.9, 125.2, 127.2, 127.5, 127.6, 127.8, 128.3, 128.4, 128.6, 134.6, 136.2, 145.2, 148.1, 149.6, 170.7 ($CO_2CH_2CH_3$).

LC-MS: *m/z* 381 $[M-1]^+$.

Anal. Calcd. for $C_{26}H_{22}O_3$: C, 81.65; H, 5.80. Found: C, 81.65; H, 5.82.

Compound 49'



This compound was prepared by using allene **9b** (0.32 g, 1.60 mmol) and 1,3-diphenylisobenzofuran (0.65 g, 2.39 mmol). It was isolated by using ethyl acetate-hexane (1:2) mixture as the eluent.

Yield: 0.55 g (78%, gummy material).

IR (Neat): 2982, 1740, 1499, 1449, 1346, 1304, 1182, 1065, 1024, 993 cm^{-1}.

^{1}H NMR: δ 0.89 (t, ^3J(H-H) = 7.2 Hz, 3H, $CH_2CO_2CH_2CH_3$), 1.21 (t, ^3J(H-H) = 7.2 Hz, 3H, $CO_2CH_2CH_3$), 1.83 (d, ^2J(H-H) = 16.8 Hz, 1H, $CH_AH_BCO_2CH_2CH_3$), 3.52 (d, ^2J(H-H) = 16.8 Hz, 1H, $CH_AH_BCO_2CH_2CH_3$), 3.65-3.69 and 3.82-3.86 (2 m, 2H, $CH_2CO_2CH_2CH_3$), 4.07 (q, ^3J(H-H) = 7.2 Hz, 2H, $CO_2CH_2CH_3$), 5.22 and 5.60 (2 s, 2H, $C=CH_2$), 7.25-7.61 (m, 10H, Ar-*H*), 7.79 (d, ^3J(H-H) = 7.6 Hz, 2H, Ar-*H*), 8.03-8.05 (m, 2H, Ar-*H*).

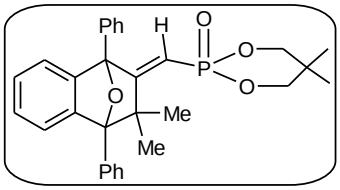
^{13}C NMR: δ 13.6 ($CH_2CO_2CH_2CH_3$), 14.1 ($CO_2CH_2CH_3$), 41.6 ($CH_2CO_2CH_2CH_3$), 60.5 (CCO_2Et), 60.7 ($CH_2CO_2CH_2CH_3$), 60.8 ($CO_2CH_2CH_3$), 90.6 (Ph*C*-O), 91.2 (Ph*C*-O), 110.8, 120.3, 121.5, 125.8, 126.7, 128.1, 128.2, 128.5, 128.6, 128.7, 134.9, 135.6, 144.6, 146.0, 152.8, 170.7 ($CH_2CO_2CH_2CH_3$), 170.8 ($CO_2CH_2CH_3$).

LC-MS: *m/z* 469 $[M+1]^+$.

Anal. Calcd. for $C_{30}H_{28}O_5$: C, 76.90; H, 6.02. Found: C, 76.85; H, 6.10.

(b) Synthesis of β,γ-adducts 50-53

Compound 50



This compound was prepared by using allenylphosphonate **10c** (0.35 g, 1.60 mmol) and 1,3-diphenylisobenzofuran (0.65 g, 2.39 mmol). It was purified by column chromatography using ethyl acetate-hexane (3:2) mixture as the eluent.

Yield: 0.58 g (86%).

Mp: 182-184 ^{o}C.

IR (KBr): 2969, 1636, 1458, 1368, 1248, 1061, 1005, 874 cm^{-1}.

^{1}H NMR: δ 0.99 (br s, 6H, 2 C*H*$_3$), 1.35 and 1.43 (2 s, 6H, C(C*H*$_3$)$_2$), 3.57-3.73 (m, 2H, OC*H*$_2$), 4.03-4.12 (m, 2H, OC*H*$_2$), 5.62 (d, ^{2}J(P-H) = 12.8 Hz, 1H, PC*H*), 7.21-7.59 (m, 10H, Ar-*H*), 7.76 (d, ^{3}J(H-H) = 7.2 Hz, 2H, Ar-*H*), 7.88 (d, ^{3}J(H-H) = 8.4 Hz, 2H, Ar-*H*).

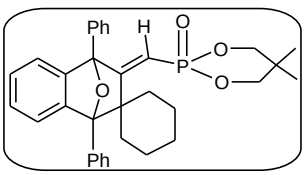
^{13}C NMR: δ 21.5, 21.6, 24.1, 24.3, 32.5 (d, ^{3}J(P-C) = 5.7 Hz, *C*(CH$_3$)$_2$), 50.6 (d, ^{3}J(P-C) = 3.6 Hz), 75.0 (d, ^{2}J(P-C) = 3.2 Hz, O*C*H$_2$), 75.1 (d, ^{2}J(P-C) = 3.5 Hz, O*C*H$_2$), 91.6 (d, ^{3}J(P-C) = 23.4 Hz, PCC*C*Ph), 92.2, 105.6 (d, ^{1}J(P-C) = 190.8 Hz, P*C*), 120.6, 121.6, 125.7, 127.1, 127.5 (d, *J*(P-C) = 7.8 Hz), 128.1, 128.3, 128.7, 128.8, 134.9, 136.4, 142.7 (d, *J*(P-C) = 1.3 Hz), 147.2, 176.2 (d, ^{2}J(P-C) = 6.0 Hz).

31P NMR: δ 12.8.

LC-MS: *m/z* 486 [M]$^{+}$.

Anal. Calcd. for $C_{30}H_{31}O_4P$: C, 74.06; H, 6.42. Found: C, 74.25; H, 6.45.

Compound 51



This compound was prepared by using allenylphosphonate **10d** (0.41 g, 1.60 mmol) and 1,3-diphenylisobenzofuran (0.65 g, 2.39 mmol). It was isolated by using ethyl acetate-hexane (3:2) mixture as the eluent.

Yield: 0.51 g (83%).

Mp: 228-230 ^{o}C.

IR (KBr): 2930, 1634, 1447, 1265, 1063, 1009 cm^{-1}.

^{1}H NMR: δ 0.98 and 1.04 (2 s, 6H, C(C*H*$_3$)$_2$), 1.17-1.77 (m, 7H, cyclohexyl-*H*), 2.23-2.29 and 2.52-2.61 (m, 3H, cyclohexyl-*H*), 3.60-3.74 and 4.11-4.19 (2 m, 4H, 2 OC*H*$_2$), 5.54 (d, ^{2}J(P-H) = 10.5 Hz, 1H, PC*H*), 7.30-7.58 (m, 9H, Ar-*H*), 7.85-7.93 (m, 3H, Ar-*H*), 8.01-8.03 (m, 2H, Ar-*H*).

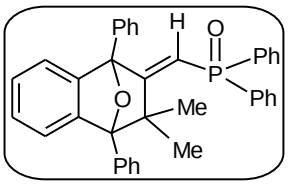
^{13}C NMR: δ 21.4, 21.7, 21.9, 22.7, 23.4, 32.3, 32.5 (d, ^{3}J(P-C) = 5.6 Hz, *C*(CH$_3$)$_2$), 32.8, 54.5 (d, ^{3}J(P-C) = 2.7 Hz), 74.8 (d, ^{2}J(P-C) = 6.1 Hz, O*C*H$_2$), 74.9 (d, ^{2}J(P-C) = 5.9 Hz, O*C*H$_2$), 90.5 (d, ^{3}J(P-C) = 23.9 Hz, PCC*C*Ph), 92.6, 104.4 (d, ^{1}J(P-C) = 192.7 Hz, P*C*), 120.9, 122.4, 127.0, 127.5, 127.6, 127.9, 128.2, 128.6, 128.7, 135.0, 138.0, 143.0, 147.4, 179.1 (d, ^{2}J(P-C) = 6.1 Hz).

^{31}P NMR: δ 13.3.

LC-MS: *m/z* 528 [M+1]$^{+}$.

Anal. Calcd. for $C_{33}H_{35}O_4P$: C, 75.27; H, 6.70. Found: C, 75.12; H, 6.81.

Compound 52



This compound was prepared by using allenylphosphine oxide **12c** (0.43 g, 1.60 mmol) and 1,3-diphenylisobenzofuran (0.65 g, 2.39 mmol). It was isolated by using ethyl acetate-hexane (3:2) mixture as the eluent.

Yield: 0.49 g (80%).

Mp: 200-202 ^{o}C.

IR (KBr): 2969, 1624, 1435, 1348, 1302, 1204, 1115, 995 cm^{-1}.

^{1}H NMR: δ 1.38 (s, 6H, C(C*H*$_3$)$_2$), 5.99 (d, ^{2}J(P-H) = 20.8 Hz, 1H, PC*H*), 7.25-7.57 (m, 20H, Ar-*H*), 7.74 (d, ^{3}J(H-H) = 7.6 Hz, 2H, Ar-*H*), 7.86 (d, *J*(H-H) = 7.2 Hz, 2H, Ar-*H*).

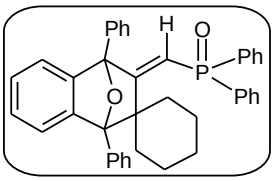
^{13}C NMR: δ 24.7, 24.9, 50.7 (d, ^{3}J(P-C) = 3.0 Hz, *C*(CH$_3$)$_2$), 91.9 (d, ^{3}J(P-C) = 17.0 Hz, PCC*C*Ph), 92.3, 112.1 (d, ^{1}J(P-C) = 102.0 Hz, P*C*H), 120.4, 121.8, 125.7, 127.0, 127.3, 127.5, 128.2, 128.3$_6$, 128.4$_0$ (d, *J*(P-C) = 5.0 Hz), 128.5, 128.7, 128.8, 130.7, 130.7$_5$ (d, *J*(P-C) = 2.0 Hz), 130.8, 131.3 (d, *J*(P-C) = 2.0 Hz), 134.5, 134.8, 135.0, 135.5, 135.8, 136.5, 142.9, 147.5, 174.1.

^{31}P NMR: δ 19.7.

LC-MS: *m/z* 539 [M+1]$^{+}$.

Anal. Calcd. for $C_{37}H_{31}O_2P$: C, 82.51; H, 5.80. Found: C, 82.39; H, 5.87.

Compound 53



This compound was prepared by using allenylphosphine oxide **12d** (0.49 g, 1.60 mmol) and 1,3-diphenylisobenzofuran (0.65 g, 2.39 mmol). It was isolated by using ethyl acetate-hexane (3:2) mixture as the eluent.

Yield: 0.48 g (85%).

Mp: 208-210 ^{o}C.

IR (KBr): 2922, 1618, 1435, 1345, 1198, 1101, 993 cm^{-1}.

^{1}H NMR: δ 1.11-1.73 (m, 7H, cyclohexyl-*H*), 2.20-2.76 (m, 3H, cyclohexyl-*H*), 5.86 (d, ^{2}J(P-H) = 20.0 Hz, 1H, PC*H*), 7.27-7.56 (m, 19H, Ar-*H*), 7.82 (d, ^{3}J(H-H) = 8.0 Hz, 2H, Ar-*H*), 7.93-7.95 (m, 1H, Ar-*H*), 8.01 (d, ^{3}J(H-H) = 7.6 Hz, 2H, Ar-*H*).

^{13}C NMR: δ 22.0, 22.8, 23.5, 33.1, 33.5, 54.4 (d, ^{3}J(P-C) = 2.0 Hz), 90.8 (d, ^{3}J(P-C) = 16.6 Hz, PCC*C*Ph), 92.6 (s, PCCC*C*Ph), 110.8 (d, ^{1}J(P-C) = 102.6 Hz, P*C*H), 120.6, 122.6, 126.9, 127.4, 127.6, 127.9, 128.4 (d, *J* = 3.2 Hz), 128.4$_6$, 128.4$_9$, 128.6, 128.7, 130.8 (d, *J* = 3.0 Hz), 130.9

(d, J = 3.6 Hz), 131.2$_6$, 131.3$_0$, 131.3$_3$, 134.5, 134.8, 135.2, 135.6, 135.9, 138.3, 143.4, 147.7, 176.8.

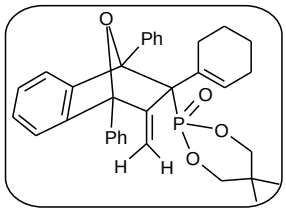
31P NMR: δ 20.6.

LC-MS: *m/z* 580 $[M+1]^+$.

Anal. Calcd. for $C_{40}H_{35}O_2P$: C, 83.02; H; 6.10. Found: C, 83.21; H, 6.03. It was crystallized from dichloromethane-hexane (4:1) mixture at 25 ^oC (Fig. 11 in Chapter 2).

(c) Synthesis of [4+2] adduct 54 and [4+4] cycloadducts 55-58

Compound 54



This compound was prepared by a procedure similar to that for **41** by using allenylphosphonate **11a** (0.30 g, 1.60 mmol) and 1,3-diphenylisobenzofuran (0.65 g, 2.39 mmol). It was isolated by using ethyl acetate-hexane (3:2) mixture as the eluent. In this reaction, in addition to compound **54**, compound **55** (20%, ^{31}P NMR) was also formed.

Yield: 0.41 g (68%).

Mp: 202-204 ^oC.

IR (KBr): 2926, 1827, 1655, 1601, 1451, 1343, 1298, 1256, 1076, 1005 cm^{-1}.

^{1}H NMR: δ 0.81 (s, 3H, CH_3), 0.95 (br s, 4H, cyclohexenyl-*H* + CH_3), 1.15-1.26 (m, 3H, cyclohexenyl-*H*), 1.71-2.05 (m, 4H, cyclohexenyl-*H*), 3.06-3.13 (m, 1H, OCH_AH$_B$), 3.65-3.77 (m, 2H, OCH_2), 4.18-4.22 (m, 1H, OCH$_A$$H_B$), 5.25 and 5.46 (2 d, ^2J(H-H) ~ 4.0 Hz, 2H, C=CH_2), 6.03 (br s, 1H, PCC=C*H*), 7.15-7.67 (m, 10H, Ar-*H*), 7.87 (d, ^3J(H-H) = 8.0 Hz, 2H, Ar-*H*), 8.25 (d, ^3J(H-H) = 7.6 Hz, 2H, Ar-*H*).

^{13}C NMR: δ 21.6, 21.9, 22.7, 22.9, 26.0, 28.3 (d, J(P-C) = 5.9 Hz), 33.0 (d, ^3J(P-C) = 6.4 Hz, *C*(CH$_3$)$_2$), 65.1 (d, ^1J(P-C) = 142.5 Hz, P*C*), 74.7 (d, ^2J(P-C) = 6.5 Hz, O*C*H$_2$), 75.0 (d, ^2J(P-C) = 6.5 Hz, O*C*H$_2$), 89.2 (d, ^3J(P-C) = 5.1 Hz, PCC*C*Ph), 93.1 (d, ^2J(P-C) = 7.3 Hz, PC*C*Ph),

110.8 (d, *J*(P-C) = 5.1 Hz), 119.3, 122.3, 126.3, 127.1 (d, *J*(P-C) = 13.8 Hz), 127.3$_7$, 127.4$_2$, 127.7, 127.9, 128.5, 130.6 (d, *J*(P-C) = 8.9 Hz), 132.8, 135.8, 136.0, 145.7, 146.0, 149.6 (d, *J*(P-C) = 4.3 Hz).

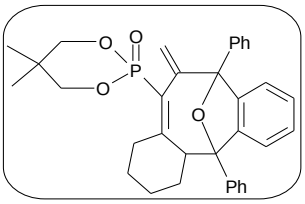
^{31}P NMR: δ 23.4.

LC-MS: *m/z* 537 $[M-1]^+$.

Anal. Calcd. for $C_{34}H_{35}O_4P$: C, 75.82; H, 6.55. Found: C, 75.65; H, 6.71.

Compounds 55-59: Representative procedure for 55

A mixture of allenylphosphonate **11a** (0.30 g, 1.10 mmol) and 1,3-diphenylisobenzofuran (0.41 g, 1.52 mmol) in *p*-xylene (3 mL) was heated at 140 ^oC for 6 h. The solvent was removed *in vacuo* using a rotary evaporator. The product **55** was isolated by using silica gel column chromatography [ethyl acetate-hexane (4:1)]. Compounds **56-59** were also prepared similarly.



Yield: 0.50 g (83%).

Mp: 268-270 ^oC.

IR (KBr): 2936, 1730, 1605, 1447, 1262, 1061, 1013 cm^{-1}.

^{1}H NMR: δ 0.77 and 1.24 (2 s, 6H, 2 C*H*$_3$), 1.51-2.11 (m, 7H, cyclohexyl-*H*), 2.83-2.87 and 3.15-3.18 (m, 2H, cyclohexyl-*H*), 3.37-3.54 (m, 2H, OC*H*$_2$), 3.82-3.91 (m, 2H, OC*H*$_2$), 5.24 (d, ^{2}*J*(H-H) = 2.4 Hz, 1H, C=C*H*$_A$H$_B$), 5.57 (br s, 1H, C=CH$_A$*H*$_B$), 7.11-7.52 (m, 10H, Ar-*H*), 7.80 (d, ^{3}*J*(H-H) = 8.0 Hz, 2H, Ar-*H*), 7.94 (d, ^{3}*J*(H-H) = 7.2 Hz, 2H, Ar-*H*).

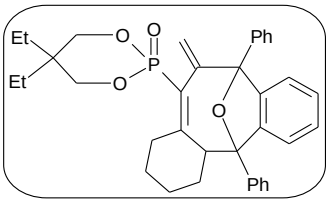
^{13}C NMR: δ 20.5, 22.2, 26.8, 29.7, 31.4, 32.2 (d, ^{3}*J*(P-C) = 5.6 Hz, *C*(CH$_3$)$_2$), 40.0 (d, *J*(P-C) = 9.2 Hz), 61.5 (d, *J*(P-C) = 20.9 Hz), 75.2 (d, ^{2}*J*(P-C) = 6.8 Hz, O*C*H$_2$), 75.5 (d, ^{2}*J*(P-C) = 6.9 Hz, O*C*H$_2$), 88.3, 90.2 (d, ^{3}*J*(P-C) = 10.6 Hz, PCC*C*Ph), 119.2 (d, *J*(P-C) = 4.9 Hz), 120.7 (d, ^{1}*J*(P-C) = 166.6 Hz, P*C*), 121.3, 122.0, 125.4, 126.9, 127.3, 127.4 (d, *J*(P-C) = 6.3 Hz), 128.0, 128.4, 128.6, 141.1, 142.9 (d, *J*(P-C) = 10.5 Hz), 146.0, 147.2 (d, *J*(P-C) = 12.4 Hz), 161.6 (d, *J*(P-C) = 8.2 Hz).

^{31}P NMR: δ 13.4.

LC-MS: *m/z* 539 $[M+1]^+$.

Anal. Calcd. for $C_{34}H_{35}O_4P$: C, 75.82; H, 6.55. Found: C, 75.91; H, 6.71. It was crystallized from dichloromethane-hexane (10:1) mixture at 25 ^oC for X-ray structure determination (Fig. 12 in Chapter 2).

Compound 56



This compound was prepared by using allenylphosphonate **11b** (0.33 g, 1.1 mmol) and 1,3-diphenylisobenzofuran (0.41 g, 1.52 mmol). It was purified by using ethyl acetate-hexane (3:2) mixture as the eluent.

Yield: 0.46 g (80%).

Mp: 140-142 ^oC.

IR (KBr): 2938, 1601, 1448, 1265, 1076, 1032 cm^{-1}.

^{1}H NMR: δ 0.81 and 0.87 (2 t, ^3J(H-H) ~ 7.5 Hz, 6H, 2 CH_2CH_3), 1.06-1.17 (m, 2H, CH_2CH_3), 1.26-1.30 (m, 1H, cyclohexyl-*H*), 1.67-1.81 and 1.88-1.93 (m, 6H, CH_2CH_3 + cyclohexyl-*H*), 2.07-2.10 (m, 2H, cyclohexyl-*H*), 2.85-2.89 and 3.15-3.19 (m, 2H, cyclohexyl-*H*), 3.38-3.41 (m, 1H, OCH_2), 3.67-3.85 (m, 2H, OCH_2), 4.01-4.15 (m, 1H, OCH_2), 5.25 (d, ^2J(H-H) = 2.8 Hz, 1H, $C=CH_AH_B$), 5.59 (d, ^2J(H-H) = 2.4 Hz, 1H, $C=CH_AH_B$), 7.14-7.23 (m, 3H, Ar-*H*), 7.33-7.54 (m, 7H, Ar-*H*), 7.81-7.83 (m, 2H, Ar-*H*), 7.95-7.97 (m, 2H, Ar-*H*).

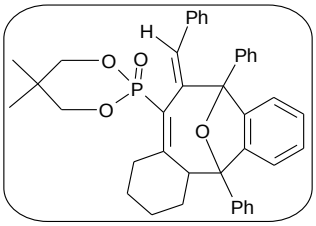
^{13}C NMR: δ 6.9, 7.2, 21.4, 22.4, 26.9, 29.7, 31.4, 32.2, 37.1 (d, ^3J(P-C) = 4.6 Hz, $C(CH_3)_2$), 40.0 (d, *J*(P-C) = 9.3 Hz), 61.4 (d, *J*(P-C) = 21.1 Hz), 72.7 (d, ^2J(P-C) = 7.1 Hz, OCH_2), 73.1 (d, ^2J(P-C) = 6.6 Hz, OCH_2), 88.3, 90.2 (d, ^3J(P-C) = 10.8 Hz, PCC*C*Ph), 119.1 (d, *J*(P-C) = 6.1 Hz), 121.3, 122.0, 125.4, 126.9, 127.3, 127.4, 127.5, 128.0, 128.4, 128.6, 141.1, 142.9 (d, *J*(P-C) = 10.3 Hz), 145.9, 147.2 (d, *J*(P-C) = 12.2 Hz), 161.4 (d, *J*(P-C) = 8.6 Hz), [the doublet due to ^1J(P-C) was not clear].

^{31}P NMR: δ 14.8.

LC-MS: *m/z* 567 $[M+1]^+$.

Anal. Calcd. for $C_{36}H_{39}O_4P$: C, 76.30; H, 6.94. Found: C, 76.41; H, 6.88.

Compound 57



This compound was prepared by using allenylphosphonate **11c** (0.38 g, 1.1 mmol) and 1,3-diphenylisobenzofuran (0.41 g, 1.52 mmol). It was purified by using ethyl acetate-hexane (3:2) mixture as the eluent.

Yield: 0.45 g (82%).

Mp: 108-110 ^oC.

IR (KBr): 2924, 1599, 1460, 1269, 1067, 1001 cm^{-1}.

^{1}H NMR: δ 0.92 and 1.01 (2 s, 6H, C(C*H*$_3$)$_2$), 1.27 (br, 1H, cyclohexyl-*H*), 1.63-1.69 (br, 1H, cyclohexyl-*H*), 1.98 (br, 3H, cyclohexyl-*H*), 2.13-2.16 (br, 2H, cyclohexyl-*H*), 2.93-2.98 and 3.21-3.24 (2 m, 2H, cyclohexyl-*H*), 3.49-3.55 and 3.87-3.95 (m, 4H, OC*H*$_2$), 6.65 (br, 1H, C=C*H*Ph), 7.11-7.26 (m, 7H, Ar-*H*), 7.33-7.42 (m, 5H, Ar-*H*), 7.48-7.56 (m, 4H, Ar-*H*), 7.85-8.03 (m, 3H, Ar-*H*).

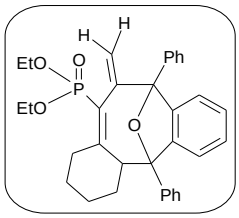
^{13}C NMR: δ 21.3, 22.2, 27.1, 31.0, 31.1, 32.5 (d, ^3J(P-C) = 6.0 Hz, *C*(CH$_3$)$_2$), 40.6 (d, *J*(P-C) = 8.0 Hz), 62.1 (d, *J*(P-C) = 21.0 Hz), 74.1 (d, ^2J(P-C) = 5.0 Hz, O*C*H$_2$), 75.2 (d, ^2J(P-C) = 6.0 Hz, O*C*H$_2$), 88.1, 92.3 (d, *J*(P-C) = 9.0 Hz), 120.2 (d, ^1J(P-C) = 174.0 Hz, PC), 120.9, 122.7, 125.5, 126.9, 127.3, 127.5, 127.6, 127.7, 128.2, 128.4, 128.7, 130.4, 132.3, 136.3, 139.7 (d, *J*(P-C) = 10.0 Hz), 142.2, 142.4, 142.6, 146.3, 164.1 (d, *J*(P-C) = 8.0 Hz).

^{31}P NMR: δ 10.3.

LC-MS: *m/z* 615 $[M+1]^+$.

Anal. Calcd. for $C_{40}H_{39}O_4P$: C, 78.16; H, 6.39. Found: C, 78.23; H, 6.31. It was crystallized from dichloromethane-hexane (10:1) mixture at 25 ^oC for X-ray structure determination (Fig. 13 in Chapter 2).

Compound 58



This compound was prepared by using allenylphosphonate **11d** (0.28 g, 1.11 mmol) and 1,3-diphenylisobenzofuran (0.41 g, 1.52 mmol). It was purified by using ethyl acetate-hexane (3:2) mixture as the eluent.

Yield: 0.49 g (80%, gummy material).

IR (Neat): 2932, 1599, 1447, 1240, 1022, 961 cm^{-1}.

^{1}H NMR: δ 1.28-1.31 (m, 6H, 2 OCH_2CH_3), 1.34-1.38 (m, 2H, cyclohexyl-*H*), 1.59-1.66 (m, 2H, cyclohexyl-*H*), 1.71-1.75 (m, 2H, cyclohexyl-*H*), 2.41-2.49 (m, 1H, cyclohexyl-*H*), 2.68-2.74 (m, 1H, cyclohexyl-*H*), 3.58-3.63 (m, 1H, cyclohexyl-*H*), 3.77-4.04 (m, 4H, 2 OCH_2), 5.29 (d, ^{2}J(H-H) ~ 3.4 Hz, 1H, $C=CH_AH_B$), 5.43 (d, ^{2}J(H-H) ~ 3.4 Hz, 1H, $C=CH_AH_B$), 7.22-7.43 (m, 10H, Ar-*H*), 7.68-7.71 (m, 4H, Ar-*H*).

^{13}C NMR: δ 16.3 (d, ^{3}J(P-C) = 3.0 Hz, OCH_2CH_3), 16.4 (d, ^{3}J(P-C) = 2.9 Hz, OCH_2CH_3), 22.0, 23.2, 27.5, 31.8 (d, *J*(P-C) = 8.1 Hz), 56.4 (d, *J*(P-C) = 21.2 Hz), 61.3 (d, ^{2}J(P-C) = 6.1 Hz, OCH_2), 61.5 (d, ^{2}J(P-C) = 5.9 Hz, OCH_2), 89.6 (d, ^{3}J(P-C) = 7.5 Hz, PCC*C*Ph), 89.8 (d, ^{4}J(P-C) = 1.8 Hz, PCCC*C*Ph), 117.7 (d, *J*(P-C) = 5.3 Hz), 122.5, 123.1, 124.7 (d, ^{1}J(P-C) = 180.7 Hz, PC), 126.0, 127.1, 127.4 (d, *J*(P-C) = 7.4 Hz), 127.5, 127.7_9, 127.8_4, 128.3, 141.5, 143.6, 147.5, 150.1 (d, *J*(P-C) = 10.2 Hz), 160.7 (d, *J*(P-C) = 9.7 Hz).

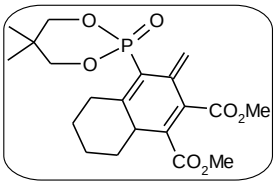
^{31}P NMR: δ 18.9.

LC-MS: *m/z* 527 $[M+1]^+$.

Anal. Calcd. for $C_{33}H_{35}O_4P$: C, 75.27; H, 6.70. Found: C, 75.15; H, 6.81.

3.32 Reaction of allene 11a with DMAD: Synthesis of the [4+2] adduct 59

A mixture of allenylphosphonate **11a** (0.30 g, 1.11 mmol) and DMAD (0.16 g, 1.11 mmol) in *p*-xylene (3 mL) was heated under reflux for 12 h. The solvent was removed under reduced pressure. The product was purified by using silica gel column chromatography [ethyl acetate-hexane (2:3)].



Yield: 0.39 g (85%, gummy solid).

IR (Neat): 2953, 1734, 1640, 1437, 1269, 1059, 1009 cm^{-1}.

^1H NMR: δ 0.84 and 1.32 (2 s, 6H, $C(CH_3)_2$), 1.58-1.66 and 1.84-1.87 (2 m, 3H, cyclohexyl-*H*), 2.07-2.28 (m, 3H, cyclohexyl-*H*), 3.33-3.47 (m, 2H, cyclohexyl-*H*), 3.72-3.78 (m, 2H, cyclohexyl-*H* + OCH_2), 3.81-3.93 (m, 9H, OCH_2 + 2 CO_2CH_3), 5.36 and 5.90 (2 br, 2H, $C=CH_2$).

^{13}C NMR: δ 20.7, 22.2, 26.2, 29.9, 32.2 (d, ^3J(P-C) = 5.7 Hz, $C(CH_3)_2$), 34.2 (d, *J*(P-C) = 6.5 Hz), 36.6, 44.1 (d, *J*(P-C) = 14.7 Hz), 52.5, 52.7, 76.4 (d, ^2J(P-C) = 6.3 Hz, OCH_2), 76.6 (d, ^2J(P-C) = 6.5 Hz, OCH_2), 116.9 (d, ^1J(P-C) = 172.6 Hz, P*C*), 119.2, 128.5, 133.1 (d, *J*(P-C) = 15.9 Hz), 140.5 (d, *J*(P-C) = 10.8 Hz), 160.6 (d, *J* = 8.6 Hz), 165.5, 168.4.

^{31}P NMR: δ 11.0.

LC-MS: *m/z* 411 $[M+1]^+$.

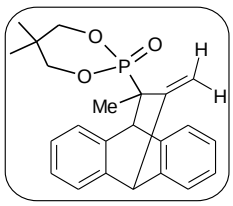
Anal. Calcd. for $C_{20}H_{27}O_7P$: C, 58.53; H, 6.63. Found: C, 58.45; H, 6.69.

3.33 Reaction of allenes 10e-i, 12a, 12e and 12f with anthracene: Synthesis of [4+2] cycloadducts 60-69

Compounds 60 and 61

A mixture of allenylphosphonate **10e** (0.32 g, 1.60 mmol) and anthracene (0.99 g, 5.58 mmol) in *p*-xylene (3 mL) was heated under reflux for 24 h. The solvent was removed under reduced pressure. Products **60** and **61** were purified by using silica gel column chromatography. Compounds **62-69** were also prepared similarly.

Compound 60



The eluent used for compound **60** was ethyl acetate-hexane (3:2) mixture.

Yield: 0.38 g (67%).

Mp: 208-210 ^{o}C.

IR (KBr): 2967, 1470, 1372, 1277, 1059, 1003, 831 cm^{-1}.

^{1}H NMR: δ 0.83 and 1.00 (2 s, 6H, C(C*H*$_3$)$_2$), 1.25 (d, ^{3}J(P-H) = 16.0 Hz, 3H, PCC*H*$_3$), 3.24-3.31 (m, 1H, OC*H*$_2$), 3.68-3.84 (m, 2H, OC*H*$_2$), 4.18-4.22 (m, 1H, OC*H*$_2$), 4.55 (br, 1H, PCCC*H*), 4.75 (s, 1H, PCC*H*), 5.09 and 5.37 (2 d, ^{2}J(H-H) ~ 4.8 Hz, 2H, =C*H*$_2$), 7.10-7.44 (m, 8H, Ar-*H*).

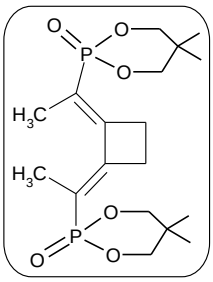
^{13}C NMR: δ 21.7, 22.2, 24.8 (d, ^{2}J(P-C) = 1.8 Hz), 32.8 (d, ^{3}J(P-C) = 6.3 Hz, *C*(CH$_3$)$_2$), 46.0 (d, ^{1}J(P-C) = 139.4 Hz, P*C*), 51.8, 55.8 (d, ^{3}J(P-C) = 3.0 Hz, PC*C*H), 74.6 and 75.4 (2 d, ^{2}J(P-C) ~ 6.8 Hz, O*C*H$_2$), 111.0 (d, ^{2}J(P-C) = 6.8 Hz), 123.0, 123.2, 125.6, 125.9, 126.1, 126.3, 126.6, 140.0, 140.1, 141.0, 141.1 (d, *J*(P-C) = 3.1 Hz), 142.6 (d, *J*(P-C) = 2.9 Hz), 148.6.

^{31}P NMR: δ 26.9.

LC-MS: *m/z* 381 [M+1]$^{+}$.

Anal. Calcd. for $C_{23}H_{25}O_3P$: C, 72.62; H, 6.62. Found: C, 72.65; H, 6.56.

Compound 61



The eluent used for compound **61** was ethyl acetate-hexane (4:1) mixture.

Yield: 0.09 g (15%).

Mp: 258-260 ^{o}C.

IR (KBr): 2969, 2930, 2886, 1632, 1468, 1372, 1262, 1057, 1005, 984 cm^{-1}.

^{1}H NMR: δ 1.07 and 1.08 (2 s, 12H, 4 C*H*$_3$), 1.97 (d, ^{3}J(P-H) = 14.4 Hz, 6H, 2 PCC*H*$_3$), 2.89 (s, 4H, 2 PCCC*H*$_2$), 3.78 (dd→t, ^{3}J(P-H) = ^{2}J(H-H) ~ 11.4 Hz, 4H, 2 OC*H*$_2$), 4.16 (dd→t, ^{3}J(P-H) = ^{2}J(H-H) = 11.0 Hz, 4H, 2 OC*H*$_2$).

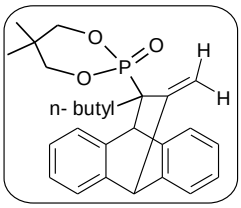
^{13}C NMR: δ 18.0, 18.1, 21.6, 30.5 (d, ^{3}J(P-C) = 5.0 Hz), 32.5 (d, ^{3}J(P-C) = 5.8 Hz, *C*$(CH_3)_2$), 75.3$_0$, 75.3$_3$, 116.8 (d, ^{1}J(P-C) = 174.0 Hz, P*C*), 155.2 (d, ^{2}J(P-C) = 38.5 Hz, PC=*C*).

^{31}P NMR: δ 15.2.

LC-MS: *m/z* 405 $[M+1]^+$.

Anal. Calcd. for $C_{18}H_{30}O_6P_2$: C, 53.46; H, 7.48. Found: C, 53.51; H, 7.40. It was crystallized from dichloromethane-hexane (10:1) mixture at 25 ^{o}C (Fig. 15 in chapter 2).

Compound 62



This compound was prepared by using allenylphosphonate **10f** (0.39 g, 1.60 mmol) and anthracene (0.99 g, 5.58 mmol). It was isolated by using ethyl acetate-hexane (3:2) mixture as the eluent.

Yield: 0.35 g (68%).

Mp: 82-84 ^{o}C.

IR (KBr): 3042, 2957, 1640, 1464, 1370, 1227, 1053 cm^{-1}.

^{1}H NMR: δ 0.81-0.96 (m, 11H, C(C*H*$_3)_2$ + *n*-Bu-*H*), 1.08-1.22 (m, 2H, *n*-Bu-*H*), 1.18-1.93 (m, 2H, *n*-Bu-*H*), 3.27 and 3.60 (2 dd, ^{3}J(P-H) ~ 15.5 Hz, ^{2}J(H-H) ~ 11.0 Hz, 2H, OC*H*$_2$), 3.81 and 4.15 (2 dd, ^{3}J(P-H) ~ 10.8 Hz, ^{2}J(H-H) ~ 6.0 Hz, 2H, OC*H*$_2$), 4.74 (s, 1H, PCCC*H*), 4.84 and 5.06 (2 d, ^{2}J(H-H) ~ 4.0 Hz, 2H, =C*H*$_2$), 5.33 (d, ^{3}J(P-H) = 5.2 Hz, 1H, PCC*H*), 7.07-7.12 (m, 4H, Ar-*H*), 7.24-7.46 (m, 4H, Ar-*H*).

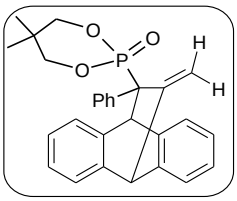
^{13}C NMR: δ 13.8, 22.0, 22.5, 23.2, 26.8, 32.8 (d, ^{3}J(P-C) = 6.6 Hz, *C*$(CH_3)_2$), 39.1, 48.2, 50.1 (d, ^{1}J(P-C) = 136.9 Hz, P*C*), 56.0 (d, ^{3}J(P-C) = 3.2 Hz), 74.5 and 75.2 (2 d, ^{2}J(P-C) ~ 6.5 Hz, O*C*H$_2$), 110.3 (d, *J*(P-C) = 6.7 Hz), 123.0 (d, *J*(P-C) = 6.8 Hz), 125.2, 125.8 (d, ^{3}J(P-C) = 3.5 Hz), 126.0, 126.2, 126.5, 139.8, 140.0, 140.6 (d, *J*(P-C) = 2.8 Hz), 142.3, 142.4, 149.6 (d, *J*(P-C) = 5.3 Hz).

^{31}P NMR: δ 26.1.

LC-MS: *m/z* 424 $[M+1]^+$.

Anal. Calcd. for $C_{26}H_{31}O_3P$: C, 73.91; H, 7.40. Found: C, 74.12; H, 7.48.

Compound 63



This compound was prepared by using allenylphosphonate **10g** (0.42 g, 1.60 mmol) and anthracene (0.99 g, 5.58 mmol). It was isolated by using ethyl acetate-hexane (3:2) mixture as the eluent.

Yield: 0.35 g (70%).

Mp: 176-178 ^oC.

IR (KBr): 3065, 2965, 1638, 1495, 1399, 1370, 1233, 1049 cm^{-1}.

^1H NMR: δ 0.83 and 0.87 (2 s, 6H, 2 CH_3), 3.25-3.31 and 3.57-3.64 (2 m, 2H, OCH_2), 3.82-3.86 and 4.13-4.16 (2 m, 2H, OCH_2), 4.91 (s, 1H, PCCC*H*), 4.98 (d, ^3J(P-C) = 4.0 Hz, 1H, PCC*H*), 5.25 and 5.78 (2 d, ^2J(H-H) ~ 4.2 Hz, 2H, =CH_2), 6.61 (d, ^3J(H-H) = 7.2 Hz, 1H, Ar-*H*), 6.77 (~t, ^3J(H-H) ~ 7.4 Hz, 1H, Ar-*H*), 6.98 (~t, ^3J(H-H) = 7.2 Hz, 1H, Ar-*H*), 7.10-7.55 (m, 10H, Ar-*H*).

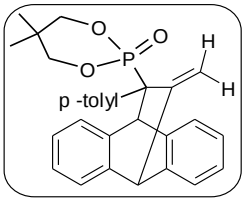
^{13}C NMR: δ 22.1, 22.5, 33.0 (d, ^3J(P-C) = 6.3 Hz, *C*$(CH_3)_2$), 55.6, 56.7, 56.9 (d, ^1J(P-C) = 139.4 Hz, P*C*), 75.1 and 75.8 (2 d, ^2J(P-C) ~ 6.3 Hz, O*C*H_2), 114.9 (d, ^2J(P-C) = 6.0 Hz), 122.9, 123.3, 125.5, 125.8, 126.1, 126.2, 126.3, 126.6, 126.9, 127.8, 128.2 (d, *J*(P-C) = 4.7 Hz), 139.1, 139.8, 140.1, 140.2, 141.3, 142.5, 144.7.

^{31}P NMR: δ 23.5.

LC-MS: *m/z* 443 $[M+1]^+$.

Anal. Calcd. for $C_{28}H_{27}O_3P$: C, 76.00; H, 6.15. Found: C, 76.15; H, 6.14. It was crystallized from dichloromethane at 25 ^oC (Fig. 16 in Chapter 2).

Compound 64



This compound was prepared by using allenylphosphonate **10h** (0.44 g, 1.60 mmol) and anthracene (0.99 g, 5.58 mmol). It was purified by using ethyl acetate-hexane (3:2) mixture as the eluent.

Yield: 0.33 g (67%).

Mp: 144-146 ^{o}C.

IR (KBr): 2967, 1640, 1512, 1460, 1368, 1233, 1051, 1009 cm^{-1}.

1H NMR: δ 0.82 and 0.88 (2 s, 6H, 2 CH_3), 2.22 (s, 3H, CH_3), 3.23-3.30 and 3.57-3.63 (2 m, 2H, OCH_2), 3.82-3.85 and 4.13-4.16 (2 m, 2H, OCH_2), 4.89 (s, 1H, PCCC*H*), 4.96 (s, 1H, PCC*H*), 5.23 (s, 1H, =CH_AH$_B$), 5.75 (s, 1H, =CH$_A$$H_B$), 6.64-7.00 (m, 6H, Ar-*H*), 7.13-7.55 (m, 6H, Ar-*H*).

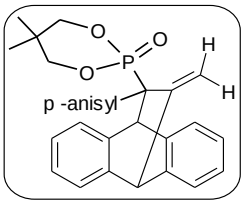
^{13}C NMR: δ 20.9, 22.1, 22.5, 32.9 (d, ^{3}J(P-C) = 3.8 Hz, *C*(CH$_3$)$_2$), 55.6, 56.7 (d, ^{1}J(P-C) = 138.8 Hz, P*C*), 56.8, 75.0, 75.7, 114.7, 122.9, 123.2, 125.6, 125.8, 126.1, 126.3, 126.5, 128.1, 128.6, 136.0, 136.4, 140.0, 140.2 140.3, 141.4, 142.6, 145.0.

^{31}P NMR: δ 23.8.

LC-MS: *m/z* 457 $[M+1]^{+}$.

Anal. Calcd. for $C_{29}H_{29}O_3P$: C, 76.30; H, 6.40. Found: C, 76.55; H, 6.48.

Compound 65



This compound was prepared by using allenylphosphonate **10i** (0.47 g, 1.60 mmol) and anthracene (0 99 g, 5.58 mmol). It was purified by using ethyl acetate-hexane (3:2) mixture as the eluent.

Yield: 0.33 g (69%).

Mp: 152-154 ^{o}C.

IR (KBr): 2957, 1607, 1510, 1464, 1252, 1051, 1009 cm^{-1}.

^{1}H NMR: δ 0.82 and 0.88 (2 s, 6H, 2 C*H*$_3$), 3.27 (dd, ^{3}J(P-H) ~ 16.0 Hz, ^{2}J(H-H) ~ 10.9 Hz, 1H, OC*H*$_2$), 3.61 (dd, ^{3}J(P-H) ~ 16.0 Hz, ^{2}J(H-H) ~ 10.9 Hz, 1H, OC*H*$_2$), 3.71 (s, 3H, C$_6$H$_4$OC*H*$_3$), 3.83 (dd, ^{3}J(P-H) ~ 10.7 Hz, ^{2}J(H-H) ~ 5.7 Hz, 1H, OC*H*$_2$), 4.14 (dd, ^{3}J(P-H) ~ 10.7 Hz, ^{2}J(H-H) ~ 5.7 Hz, 1H, OC*H*$_2$), 4.90 (s, 1H, PCCC*H*), 4.95 (d, ^{3}J(P-H) = 4.4 Hz, 1H, PCC*H*), 5.24 and 5.76 (2 d, ^{2}J(H-H) ~ 4.8 Hz, 2H, =C*H*$_2$), 6.63-6.66 (m, 3H, Ar-*H*), 6.80 (~t, ^{3}J(H-H) ~ 7.4 Hz, 1H, Ar-*H*), 6.99 (~t, ^{3}J(H-H) = 7.2 Hz, 1H, Ar-*H*), 7.11-7.55 (m, 7H, Ar-*H*).

^{13}C NMR: δ 22.0, 22.4, 32.9 (d, ^{3}J(P-C) = 6.7 Hz, *C*(CH$_3$)$_2$), 55.0, 55.5, 56.1 (d, ^{1}J(P-C) = 139.3 Hz, P*C*), 56.6, 75.0 and 75.7 (2 d, ^{2}J(P-C) ~ 6.7 Hz, 2 O*C*H$_2$), 113.0, 114.6 (d, *J*(P-C) = 7.3 Hz), 122.8, 123.1, 125.6, 125.9, 126.0, 126.1, 126.2, 126.5, 129.3 (d, *J*(P-C) = 5.3 Hz), 131.0 (d, *J*(P-C) = 3.4 Hz), 139.8 (d, *J*(P-C) = 2.2 Hz), 140.1, 140.3, 141.2 (d, *J*(P-C) = 3.2 Hz), 142.4, 145.0 (d, *J*(P-C) = 5.4 Hz), 158.1.

^{31}P NMR: δ 24.0.

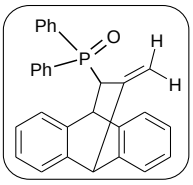
LC-MS: *m/z* 473 [M+1]$^{+}$.

Anal. Calcd. for C$_{29}$H$_{29}$O$_4$P: C, 73.71; H, 6.19. Found: C, 73.85; H, 6.26.

Compounds 66 and 67

These compounds were prepared by using allenylphosphine oxide **12a** (0.38 g, 1.60 mmol) and anthracene (0.99 g, 5.58 mmol). The crude containing products **66-67** were isolated by using ethyl acetate-hexane (3:2) mixture. Pure compounds **66** and **67** were separated by hand–picking after crystallization from dichloromethane-hexane (4:1). Compound **67** appeared as block type of crystals while compound **66** was powdery.

Compound 66



Yield: 0.12 g (23%).

Mp: 180-182 ^{o}C.

IR (KBr): 2930, 1624, 1468, 1435, 1177 cm^{-1}.

^{1}H NMR: δ 3.72 (dd, ^{2}J(P-H) = 16.8 Hz, ^{3}J(H-H) ~ 2.4 Hz, 1H, PC*H*), 4.21-4.23 (m, 1H, PCC*H*), 4.73 (s, 1H, PCCC*H*), 4.98-5.00 and 5.13-5.15 (2 m, 2H, C=CH_2), 6.73 (~t, ^{3}J(H-H) ~ 7.2 Hz, 1H, Ar-*H*), 6.87 (~t, ^{3}J(H-H) ~ 7.4 Hz, 1H, Ar-*H*), 7.00 (d, ^{3}J(H-H) = 8.0 Hz, 1H, Ar-*H*), 7.09-7.19 (m, 5H, Ar-*H*), 7.26-7.61 (m, 10H, Ar-*H*).

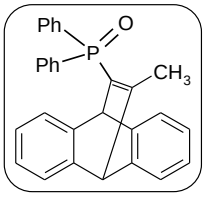
^{13}C NMR: δ 44.7, 46.2 (d, ^{1}J(P-C) = 67.9 Hz, P*C*), 56.4, 111.2 (d, ^{2}J(P-C) = 3.6 Hz), 123.2, 123.3, 123.5, 125.6, 126.0, 126.2, 126.3, 126.5, 127.7, 127.8, 128.5, 128.7, 131.2, 131.4, 131.5, 131.8, 132.0, 132.1, 139.6, 140.5, 142.6, 143.3 [^{1}J(P-C) due to PPh_2 group was difficult to assign].

^{31}P NMR: δ 31.0.

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

Anal. Calcd. for $C_{29}H_{23}OP$: C, 83.24; H, 5.54. Found: C, 83.10; H, 5.48.

Compound 67



Yield: 0.34 g (65%).

Mp: 190-192 ^{o}C.

IR (KBr): 2957, 2201, 1607, 1462, 1437, 1273, 1202, 1051, 999 cm^{-1}.

^{1}H NMR: δ 2.29 (d, ^{4}J(P-H) = 2.8 Hz, 3H, PCCCH_3), 4.80 (d, ^{3}J(P-H) = 8.8 Hz, 1H, PCC*H*), 4.97 (d, ^{4}J(P-H) = 3.2 Hz, 1H, PCCC*H*), 6.89-7.00 (m, 6H, Ar-*H*), 7.30-7.46 (m, 12H, Ar-*H*).

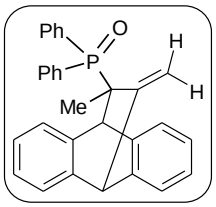
13C NMR: δ 19.6 (d, ^{3}J(P-C) = 4.8 Hz, PCC*C*H_3), 53.6 (d, ^{2}J(P-C) = 12.2 Hz, PC*C*H), 60.5 (d, ^{3}J(P-C) = 10.7 Hz, PCC*C*H), 123.0, 123.3, 124.9, 125.1, 128.6, 128.7, 131.0, 131.8, 131.9, 132.3, 132.7, 132.9 (d, ^{1}J(P-C) = 105.1 Hz, P*C*), 133.7, 144.2 (d, *J*(P-C) = 2.7 Hz), 144.4 (d, *J*(P-C) = 2.7 Hz).

^{31}P NMR: δ 29.6.

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

Anal. Calcd. for $C_{29}H_{23}OP$: C, 83.24; H, 5.54. Found: C, 83.30; H, 5.59. It was crystallized from dichloromethane-hexane (4:1) mixture at 25 ^{o}C for X-ray structure determination (Fig. 17 in Chapter 2).

Compound 68



This compound was prepared by using allenylphosphine oxide **12e** (0.41 g, 1.60 mmol) and anthracene (0.99 g, 5.58 mmol). It was purified by using ethyl acetate-hexane (3:2) mixture as the eluent.

Yield: 0.33 g (65%).

Mp: 210-212 ^{o}C;

IR (KBr): 3056, 2924, 1638, 1437, 1310, 1184, 1119, 1028 cm^{-1}.

^{1}H NMR: δ 1.14 (d, ^{3}J(P-H) = 14.0 Hz, 3H, PCCH_3), 4.77-4.80 (m, 2H, PCC*H* + PCCC*H*), 4.89 and 5.41 (d, ^{2}J(H-H) ~ 4.0 Hz, 2H, C=CH_2), 6.55 (~t, ^{3}J(H-H) ~ 7.2 Hz, 1H, Ar-*H*), 6.64 (~t, ^{3}J(H-H) ~ 7.0 Hz, 1H, Ar-*H*), 7.01 (d, ^{3}J(H-H) = 7.2 Hz, 1H, Ar-*H*), 7.07-7.12 (m, 5H, Ar-*H*), 7.18-7.39 (m, 6H, Ar-*H*), 7.65 (~t, ^{3}J(H-H) ~ 8.8 Hz, 2H, Ar-*H*), 7.74 (~t, ^{3}J(H-H) ~ 8.8 Hz, 2H, Ar-*H*).

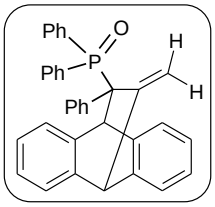
13C NMR: δ 26.8, 48.1 (d, ^{1}J(P-C) = 69.3 Hz, P*C*), 51.5, 56.7, 112.0 (d, ^{2}J(P-C) = 5.4 Hz), 122.8, 123.7, 125.8, 125.9, 126.1, 126.4, 126.6, 126.8, 127.5 (d, *J*(P-C) = 11.3 Hz), 127.9 (d, *J*(P-C) = 11.0 Hz), 130.3, 131.2, 131.6, 131.8 (d, *J*(P-C) = 7.5 Hz), 132.8 (d, *J*(P-C) = 8.2 Hz), 140.5, 141.3 (d, *J*(P-C) = 10.2 Hz), 143.3, 150.2.

^{31}P NMR: δ 31.5.

LC-MS *m/z* 432 $[M]^{+}$.

Anal. Calcd. for $C_{30}H_{25}OP$: C, 83.31; H, 5.83. Found: C, 83.45; H, 5.72.

Compound 69



This compound was prepared by using allenylphosphine oxide **12f** (0.51 g, 1.60 mmol) and anthracene (0.99 g, 5.58 mmol). It was purified by using ethyl acetate-hexane (3:2) mixture as the eluent.

Yield: 0.30 g (64%).

Mp: 212-214 ^{o}C.

IR (KBr): 3052, 2944, 1634, 1433, 1263, 1181, 1092, 945 cm^{-1}.

^{1}H NMR: δ 4.83 (s, 1H, PCC*H*), 4.86 (s, 1H, PCCC*H*), 5.60 and 5.83 (2 s, 2H, =C*H*$_2$), 6.66-7.60 (m, 23H, Ar-*H*).

^{13}C NMR: δ 53.9, 57.7, 59.0 (d, ^{1}J(P-C) = 65.1 Hz, P*C*), 116.9 (d, ^{2}J(P-C) = 5.5 Hz), 122.9, 123.2, 125.6 (d, *J*(P-C) = 7.3 Hz), 126.1, 126.9 (d, *J*(P-C) = 8.0 Hz), 127.2, 127.3, 127.4 (d, *J*(P-C) = 4.1 Hz), 127.5, 130.4, 130.6, 130.9, 131.5, 132.6, 132.7, 132.8, 132.9, 133.9, 139.3, 139.6, 141.4, 141.5, 141.7, 144.4.

^{31}P NMR: δ 32.8.

LC-MS: *m/z* 496 [M+1]$^{+}$.

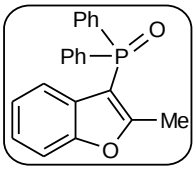
Anal. Calcd. for $C_{35}H_{27}OP$: C, 85.00; H, 5.50. Found: C, 85.12; H, 5.48.

3.4 Nucleophilic addition-cyclization reactions of allenes 14a-d and 15a-f

3.41 Intramolecular cyclization reactions of allenes 15a-f leading to 1,2-disubstituted benzofuran derivatives 70-75

To a solution of allene **15a** (0.10 g, 0.30 mmol) in THF (2 mL), triethylamine (0.04 mL, 0.30 mmol) was added and the mixture stirred at 70^{o}C for 1 h. The solvent was removed by rotary evaporation, and the crude product thus obtained was purified by column chromatography (silica gel; 4:1 ethyl acetate-hexane) to yield the colorless solid product **70**. Compounds **71-75** were also prepared by following the same method.

Compound 70



This compound is known but was prepared by an entirely different (multistep) route.[85]

Yield: 0.10 g (95%).

Mp: 142-144 ^{o}C (white solid).

IR (KBr): 2851, 1925, 1485, 1437, 1246, 1154, 1119 cm^{-1}.

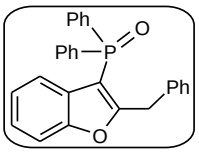
The ^{1}H NMR spectrum was identical to that reported before.[85]

^{13}C NMR: δ 14.5, 105.9 (d, ^{1}J(P-C) = 119.0 Hz, P*C*), 110.9, 120.8, 123.3, 124.1, 128.7, 128.8, 131.7, 131.8, 132.2 (d, *J*(P-C) = 3.0 Hz), 133.1 (d, *J*(P-C) = 109.0 Hz), 154.1 (d, *J*(P-C) = 11.0 Hz), 164.7 (d, *J*(P-C) = 18.0 Hz).

^{31}P NMR: δ 21.3.

LC-MS: *m/z* 333 [M+1]$^{+}$.

Compound 71



This product was synthesized from the allene **15b** (0.10 g, 0.2 mmol). It was isolated by using ethyl acetate-hexane (7:3) mixture as the eluent.

Yield: 0.09 g (89%).

Mp: 140-142 ^{o}C (white solid).

IR (KBr): 3057, 1555, 1453, 1435, 1306, 1254, 1190, 1121 cm^{-1}.

^{1}H NMR: δ 4.49 (s, 2H, PhCH_2), 6.69 (d, ^{3}J(H-H) = 7.2 Hz, 1H, Ar-*H*), 6.99-7.03 (m, 1H, Ar-*H*), 7.18-7.31 (m, 6H, Ar-*H*), 7.44-7.58 (m, 7H, Ar-*H*), 7.73-7.79 (m, 4H, Ar-*H*).

^{13}C NMR: δ 34.2, 106.4 (d, ^{1}J(P-C) = 117.9 Hz, P*C*), 111.3, 121.1, 123.4, 124.4, 126.6, 128.5, 128.7, 128.8, 129.2, 131.7, 131.8, 132.3, 133.2 (d, *J*(P-

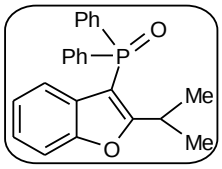
C) = 108.4 Hz), 137.0, 154.5 (d, *J*(P-C) = 11.5 Hz), 166.3 (d, *J*(P-C) = 17.8 Hz).

^{31}P NMR: δ 21.5.

LC-MS: *m/z* 409 $[M+1]^+$.

Anal. Calcd. for $C_{27}H_{21}O_2P$: C, 79.40; H, 5.18. Found: C, 79.55; H, 5.12.

Compound 72



This product was synthesized from the allene **15c** (0.10 g, 0.3 mmol). It was isolated by using ethyl acetate-hexane (7:3) mixture as the eluent.

Yield: 0.09 g (90%).

Mp: 128-130 ^{o}C (white solid).

IR (KBr): 2868, 1559, 1437, 1250, 1194, 1119 cm^{-1}.

^{1}H NMR: δ 1.27 (d, ^{3}J(H-H) = 6.8 Hz, 6H, C(C*H*$_3$)$_2$), 3.65-3.72 (m, 1H, C*H*(CH$_3$)$_2$), 6.61 (d, ^{3}J(H-H) = 7.6 Hz, 1H, Ar-*H*), 6.97-7.01 (m, 1H, Ar-*H*), 7.20-7.23 (m, 1H, Ar-*H*), 7.47-7.59 (m, 7H, Ar-*H*), 7.72-7.76 (m, 4H, Ar-*H*).

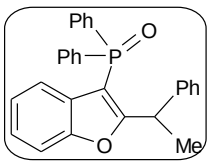
^{13}C NMR: δ 21.1, 27.8, 103.9 (d, ^{1}J(P-C) = 119.6 Hz, P*C*), 111.1, 121.0, 123.2, 124.0, 128.6, 128.7, 131.7, 131.8, 132.1 (d, *J*(P-C) = 2.6 Hz), 133.4 (d, *J*(P-C) = 108.3 Hz), 154.1 (d, *J*(P-C) = 11.7 Hz), 172.7 (d, *J*(P-C) = 18.8 Hz).

^{31}P NMR: δ 21.5.

LC-MS: *m/z* 361 $[M+1]^+$.

Anal. Calcd. for $C_{23}H_{21}O_2P$: C, 76.65; H, 5.87. Found: C, 76.52; H, 5.93.

Compound 73



This product was synthesized from the allene **15d** (0.21 g, 0.5 mmol). It was isolated by using ethyl acetate-hexane (4:1) mixture as the eluent.

Yield: 0.20 g (93%).

Mp: 160-162 ^{o}C (white solid).

IR (KBr): 2975, 1555, 1453, 1437, 1250, 1188, 1121, 1028 cm^{-1}.

^{1}H NMR: δ 1.72 (d, ^{3}J(H-H) = 6.8 Hz, 3H, CH_3), 5.14-5.20 (m, 1H, CHCH$_3$), 6.63 (d, ^{3}J(H-H) = 7.6 Hz, 1H, Ar-*H*), 6.97-7.01 (m, 1H, Ar-*H*), 7.16-7.26 (m, 4H, Ar-*H*), 7.38-7.80 (m, 13H, Ar-*H*).

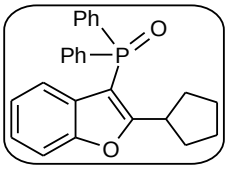
^{13}C NMR: δ 19.5, 37.9, 105.0 (d, ^{1}J(P-C) = 118.4 Hz, P*C*), 111.3, 121.1, 123.4, 124.3, 126.2, 127.9, 128.4, 128.6, 128.7, 128.8, 131.7, 131.8, 131.9, 132.2 (d, *J*(P-C) = 13.5 Hz), 133.2 (d, *J*(P-C) = 108.5 Hz), 133.3 (d, *J*(P-C) = 108.3 Hz), 142.3, 154.4 (d, *J*(P-C) = 11.5 Hz), 169.8 (d, *J*(P-C) = 18.1 Hz).

^{31}P NMR: δ 21.6.

LC-MS: *m/z* 423 [M+1]$^{+}$.

Anal. Calcd. for $C_{28}H_{23}O_2P$: C, 79.61; H, 5.49. Found: C, 79.48; H, 5.57.

Compound 74



This product was synthesized from the allene **15e** (0.10 g, 0.3 mmol). It was isolated by using ethyl acetate-hexane (7:3) mixture.

Yield: 0.09 g (88%).

Mp: 102-104 ^{o}C (white solid).

IR (KBr): 2957, 1555, 1454, 1437, 1312, 1254, 1182, 1121 cm^{-1}.

^{1}H NMR: δ 1.58 (br, 2H, cyclopentyl-*H*), 1.81-1.86 (m, 6H, cyclopentyl-*H*), 3.62-3.67 (m, 1H, cyclopentyl-*H*), 6.62-6.64 (m, 1H, Ar-*H*), 6.97-7.00 (m, 1H, Ar-*H*), 7.18-7.21 (m, 1H, Ar-*H*), 7.45-7.58 (m, 7H, Ar-*H*), 7.72-7.77 (m, 4H, Ar-*H*).

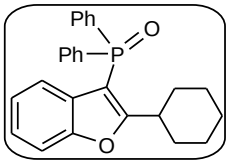
^{13}C NMR: δ 26.2, 32.2, 38.2, 104.9 (d, ^{1}J(P-C) = 120.1 Hz, P*C*), 111.0, 120.9, 123.2, 124.0, 128.6, 128.7, 131.7, 131.8, 132.1, 133.4 (d, *J*(P-C) = 108.2 Hz), 154.1 (d, *J*(P-C) = 11.7 Hz), 171.2 (d, *J*(P-C) = 18.9 Hz).

^{31}P NMR: δ 21.7.

LC-MS: *m/z* 387 $[M+1]^+$.

Anal. Calcd. for $C_{25}H_{23}O_2P$: C, 77.70; H, 6.00. Found: C, 77.85; H, 5.93.

Compound 75



This product was synthesized from the allene **15f** (0.10 g, 0.2 mmol). It was isolated by using ethyl acetate-hexane (7:3) mixture as the eluent.

Yield: 0.09 g (90%).

Mp: 150-152 ^{o}C (white solid).

IR (KBr): 2926, 1551, 1454, 1314, 1256, 1179, 1119, 1042 cm^{-1}.

^{1}H NMR: δ 1.10-1.26 (m, 3H, cyclohexyl-*H*), 1.65-1.74 (m, 7H, cyclohexyl-*H*), 2.92-2.98 (m, 1H, cyclohexyl-*H*), 6.84 (d, ^{3}J(H-H) = 7.6 Hz, 1H, Ar-*H*), 7.00-7.03 (m, 1H, Ar-*H*), 7.20-7.23 (m, 1H, Ar-*H*), 7.46-7.59 (m, 7H, Ar-*H*), 7.73-7.78 (m, 4H, Ar-*H*).

^{13}C NMR: δ 25.7, 25.9, 31.2, 37.2, 104.2 (d, ^{1}J(P-C) = 119.9 Hz, P*C*), 110.9, 121.3, 123.2, 124.0, 128.6, 128.7, 131.7, 131.8, 132.1 (d, *J*(P-C) = 2.6 Hz), 133.4 (d, *J*(P-C) = 108.1 Hz), 154.0 (d, *J*(P-C) = 11.5 Hz), 171.4 (d, *J*(P-C) = 19.5 Hz).

^{31}P NMR: δ 21.2.

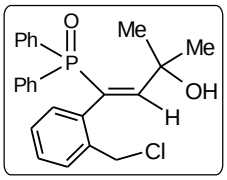
LC-MS: *m/z* 401 $[M+1]^+$.

Anal. Calcd. for $C_{26}H_{25}O_2P$: C, 77.98; H, 6.29. Found: C, 78.12; H, 6.21. This compound was crystallized from dichloromethane-hexane (9:1) at 25 ^{o}C. X-ray structure was determined for this sample (Fig. 18 in Chapter 2).

3.42 Synthesis of γ-hydroxy vinyl phosphonate derivatives 76-77- Representative procedure for compound 76

To a solution of allene **14b** (0.20 g, 0.48 mmol) in EtOAc (2 mL), 35 % hydrochloric acid (1 mL) was added and the contents heated under reflux for 6 h. Water (10 mL) was added after completion of the reaction (TLC). Then EtOAc (10 mL) was added, the phases were separated, and the aqueous layer was extracted with

EtOAc. Organic layers were combined and washed with saturated aq. NaCl. After drying over Na_2SO_4, the solvent was removed by using rotary evaporator. The product **76** was purified by column chromatography (silica gel; ethyl acetate-hexane 2:3). Compound **77** was also prepared similarly.



Yield: 0.17 g (88%).

Mp: 148-150 ^{o}C (white solid).

IR (KBr): 3241, 2976, 1609, 1439, 1225, 1161, 1117 cm^{-1}.

^{1}H NMR: δ 1.56 and 1.70 (2 s, 6H, 2 CH_3), 3.70 and 4.07 (2 d, ^{2}J(H-H) = 11.5 Hz, 2H, CH_2Cl), 6.82-6.91 (m, 2H, =C*H* + O*H*), 7.07-7.26 (m, 7H, Ar-*H*), 7.39-7.43 (m, 1H, Ar-*H*), 7.51-7.62 (m, 3H, Ar-*H*), 7.86-7.90 (m, 3H, Ar-*H*).

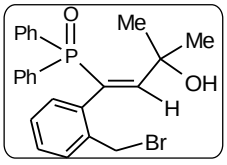
^{13}C NMR: δ 30.5, 31.2, 43.6, 71.0, 127.3 (d, *J*(P-C) = 89.6 Hz), 127.6, 127.7, 128.0, 128.3 (d, *J*(P-C) = 1.5 Hz), 128.5 (d, ^{1}J(P-C) = 106.5 Hz, P*C*), 128.6, 128.7, 130.1 (d, *J*(P-C) = 2.5 Hz), 130.4, 131.9, 132.3, 132.4, 132.5, 132.8, 132.9, 136.7_9, 136.8_2, 138.7 (d, *J*(P-C) = 11.8 Hz), 163.2 (d, *J*(P-C) = 5.4 Hz).

^{31}P NMR: δ 32.0.

LC-MS: *m/z* 411 [M]$^{+}$, 413 [M+2]$^{+}$.

Anal. Calcd. for $C_{24}H_{24}ClO_2P$: C, 70.16; H, 5.89. Found: C, 70.25; H, 5.81. This compound was crystallized from dichloromethane-hexane (9:1) at 25 ^{o}C. X-ray structure was determined for this sample (Fig. 19 in Chapter 2).

Compound 77



This product was synthesized from the allene **14b** (0.20 g, 0.48 mmol) and conc. HBr (1 mL).

Yield: 0.19 g (85%).

Mp: 170-172 ^{o}C (white solid).

IR (KBr): 3262, 2926, 1605, 1437, 1225, 1163, 1117 cm^{-1}.

^{1}H NMR: δ 1.55 and 1.71 (2 s, 6H, 2 C*H*$_3$), 3.63 and 3.91 (2 d, ^{2}J(H-H) ~ 9.8 Hz, 2H, C*H*$_2$Br), 6.79-6.81 (m, 1H, Ar-*H*), 6.88-7.24 (m, 9H, =C*H* + O*H* + Ar-*H*), 7.37-7.60 (m, 4H, Ar-*H*), 7.84-7.89 (m, 2H, Ar-*H*).

^{13}C NMR: δ 30.5, 31.2, 31.3, 71.1 (d, *J*(P-C) = 4.5 Hz), 127.3 (d, *J*(P-C) = 89.7 Hz), 127.5, 127.7, 128.1, 128.4, 128.6, 128.7, 129.1, 130.3, 130.8, 131.7, 131.9, 132.4 (d, *J*(P-C) = 7.8 Hz), 132.5, 132.8 (d, *J*(P-C) = 8.5 Hz), 137.0, 138.6 (d, *J*(P-C) = 11.6 Hz), 163.7 (d, *J*(P-C) = 5.3 Hz).

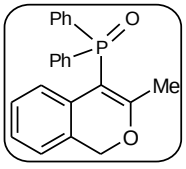
^{31}P NMR: δ 32.3.

LC-MS: *m/z* 455 $[M]^{+}$, 457 $[M+2]^{+}$.

Anal. Calcd. for $C_{24}H_{24}BrO_2P$: C, 63.31; H, 5.31. Found: C, 63.21; H, 5.39.

3.43 Synthesis of 3,4-disubstituted isochromenes 78-81

To a solution of allene **14a** (0.30 g, 0.77 mmol) in MeOH (2 mL), $ZrCl_4$ (0.09 g, 0.38 mmol) was added and the contents heated under reflux for 6 h. Water (10 mL) was added to after completion of the reaction. Then EtOAc (10 mL) was added, the phases were separated, and the aqueous layer was extracted with EtOAc. The combined organic layer was washed with saturated aq. NaCl. After drying over Na_2SO_4, the solvent was removed *in vacuo*. The product **78** was purified by column chromatography (silica gel; ethyl acetate-hexane 4:1). Compounds **79-81** were also prepared similarly.



Yield: 0.24 g (90%, gummy solid).

IR (Neat): 2926, 1588, 1561, 1487, 1437, 1265, 1159, 1049 cm^{-1}.

^{1}H NMR: δ 1.90 (d, ^{4}J(P-H) = 1.2 Hz, 3H, C*H*$_3$), 5.08 (s, 2H, C*H*$_2$), 6.96-6.97 (m, 2H, Ar-*H*), 7.07-7.09 (m, 2H, Ar-*H*), 7.41-7.52 (m, 6H, Ar-*H*), 7.78-7.83 (m, 4H, Ar-*H*).

^{13}C NMR: δ 21.0, 69.3, 104.9 (d, ^{1}J(P-C) = 113.9 Hz, P*C*), 123.9, 124.4 (d, *J*(P-C) = 3.5 Hz), 125.9, 127.0 (d, *J*(P-C) = 7.3 Hz), 127.9, 128.6, 128.8,

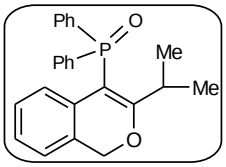
130.7 (d, *J*(P-C) = 7.6 Hz), 131.5, 131.6, 134.6 (d, *J*(P-C) = 105.7 Hz), 168.8 (d, *J*(P-C) = 17.2 Hz).

^{31}P NMR: δ 26.5.

LC-MS: *m/z* 347 $[M+1]^+$.

Anal. Calcd. for $C_{22}H_{19}O_2P$: C, 76.29; H, 5.53. Found: C, 76.41; H, 5.58.

Compound 79



This product was synthesized from the allene **14b** (0.25 g, 0.6 mmol).

Yield: 0.21 g (92%).

Mp: 162-164 ^{o}C (white solid).

IR (KBr): 2971, 1588, 1483, 1437, 1223, 1161, 1117 cm^{-1}.

^{1}H NMR: δ 0.91 (d, ^{3}J(H-H) = 6.4 Hz, 6H, 2 C*H*$_3$), 3.05-3.12 (m, 1H, C*H*(CH$_3$)$_2$), 5.03 (s, 2H, C*H*$_2$), 6.91-6.96 (m, 2H, Ar-*H*), 7.06-7.07 (m, 2H, Ar-*H*), 7.41-7.49 (m, 6H, Ar-*H*), 7.77-7.81 (m, 4H, Ar-*H*).

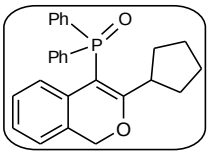
^{13}C NMR: δ 19.8, 32.8 (d, *J*(P-C) = 2.9 Hz), 69.5, 103.6 (d, ^{1}J(P-C) = 114.3 Hz, P*C*), 123.8, 124.9 (d, *J*(P-C) = 3.8 Hz), 125.7, 127.6 (d, *J*(P-C) = 7.3 Hz), 127.7, 128.5, 128.6, 131.2 (d, *J*(P-C) = 8.0 Hz), 131.4 (d, *J*(P-C) = 2.5 Hz), 131.6, 131.7, 135.1 (d, *J*(P-C) = 105.3 Hz), 176.5 (d, *J*(P-C) = 17.8 Hz).

^{31}P NMR: δ 26.7.

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

Anal. Calcd. for $C_{24}H_{23}O_2P$: C, 76.99; H, 6.19. Found: C, 76.85; H, 6.23. This compound was crystallized from dichloromethane-hexane (9:1) at 25 ^{o}C. X-ray structure was determined for this sample (Fig. 20 in Chapter 2).

Compound 80



This product was synthesized from the allene **14c** (0.57 g, 1.3 mmol).

Yield: 0.43 g (84%).

Mp: 152-154 ^{o}C (white solid).

IR (KBr): 2951, 1582, 1553, 1437, 1267, 1175, 1047 cm^{-1}.

^{1}H NMR: δ 1.30-1.31 and 1.53-1.58 (2 m, 8H, cyclopentyl-*H*), 3.02-3.09 (m, 1H, C*H*), 5.03 (s, 2H, OCH_2), 6.95-7.01 (m, 2H, Ar-*H*), 7.07-7.08 (m, 2H, Ar-*H*), 7.40-7.49 (m, 6H, Ar-*H*), 7.77-7.82 (m, 4H, Ar-*H*).

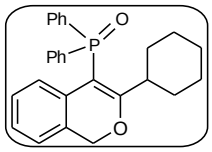
^{13}C NMR: δ 26.5, 31.2, 43.8 (d, *J*(P-C) = 3.3 Hz), 69.6, 104.4 (d, ^{1}J(P-C) = 114.8 Hz, P*C*), 123.8, 124.8 (d, *J*(P-C) = 3.9 Hz), 125.7, 127.5 (d, *J*(P-C) = 7.2 Hz), 127.8, 128.5, 128.6, 131.3 (d, *J*(P-C) = 7.8 Hz), 131.4 (d, *J*(P-C) = 2.6 Hz), 131.6, 131.7, 135.2 (d, *J*(P-C) = 105.3 Hz), 175.0 (d, *J*(P-C) = 17.5 Hz).

^{31}P NMR: δ 26.8.

LC-MS: *m/z* 401 [M+1]$^{+}$.

Anal. Calcd. for $C_{26}H_{25}O_2P$: C, 77.98; H, 6.29. Found: C, 77.85; H, 6.22.

Compound 81



This product was synthesized from the allene **14d** (0.26 g, 0.6 mmol).

Yield: 0.21 g (87%).

Mp: 164-166 ^{o}C (white solid).

IR (KBr): 2928, 1547, 1437, 1273, 1175, 1049 cm^{-1}.

^{1}H NMR: δ 0.71-0.76 and 1.01-1.04 (2 m, 3H, cyclohexyl-*H*), 1.31-1.53 (m, 7H, cyclohexyl-*H*), 2.49-2.55 (m, 1H, cyclohexyl-*H*), 5.00 (s, 2H, OCH_2), 6.97-7.14 (m, 4H, Ar-*H*), 7.41-7.50 (m, 6H, Ar-*H*), 7.79-7.84 (m, 4H, Ar-*H*).

^{13}C NMR: δ 25.6, 25.7, 29.8, 42.7, 69.3, 103.8 (d, ^{1}J(P-C) = 114.7 Hz, P*C*), 123.8, 125.1, 125.7, 127.6 (d, *J*(P-C) = 7.1 Hz), 127.8, 128.5, 128.6, 131.1 (d, *J*(P-C) = 7.4 Hz), 131.4, 131.6, 131.7, 135.3 (d, *J*(P-C) = 105.0 Hz), 174.9 (d, *J*(P-C) = 18.1 Hz).

^{31}P NMR: δ 25.8.

LC-MS: *m/z* 415 [M+1]$^{+}$.

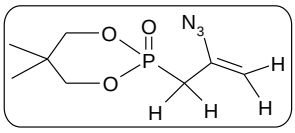
Anal. Calcd. for $C_{27}H_{27}O_2P$: C, 78.24; H, 6.57. Found: C, 78.15; H, 6.63.

3.5 Synthesis of vinyl azides, substituted pyrroles, triazoles and pyrazines *via* allenes

3.51 Synthesis of vinyl azides 82-89

They are prepared by a procedure developed in our laboratory.[45] To a solution of Me_3SiN_3 (0.15 g, 1.3 mmol) in DMF (5 mL) was added the allene **10a** (0.21 g, 1.1 mmol) and mixture stirred at room temperature for 2-4 h. The solvent was removed under reduced pressure to give the crude product **82**, which was purified by column chromatography on silica gel using EtOAc-hexane (3:2) as the eluent. Compounds **83-88** were also prepared similarly. Among these, **82**, **84** and **86-88** are new. The vinyl azide **89** is synthesized from ester allene **9a** by using a reported method.[44]

Compound 82



Yield: 0.22 g (88%).

Mp: 64-66 ^oC (white solid).

IR (KBr): 2976, 2101, 1630, 1478, 1265, 1059, 1009, 982 cm^{-1}.

^1H NMR: δ 1.05 and 1.15 (2 s, 6H, $C(CH_3)_2$), 2.74 (d, ^2J(P-H) = 21.2 Hz, 2H, PCH_2), 3.87–3.93 and 4.23–4.28 (2 m, 4H, 2 OCH_2), 4.91–4.93 and 5.01-5.02 (2 dd, J ~ 2.0, 5.0 Hz, 2H, $=CH_2$).

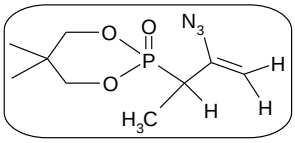
^{13}C NMR: δ 21.4, 21.5, 30.5 (d, ^1J(P-C) = 136.7 Hz, PCH_2), 32.6 (d, ^3J(P-C) = 6.1 Hz, $C(CH_3)_2$), 75.5, 75.6, 102.7 (d, J(P-C) = 10.6 Hz), 137.1 (d, J(P-C) = 11.6 Hz).

^{31}P NMR: δ 19.8.

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

Anal. Calcd. for $C_8H_{14}N_3O_3P$: C, 41.56; H, 6.10; N, 18.18. Found: C, 41.63; H, 6.14; N, 18.25.

Compound 84



This azide was synthesized from the allene **10e** (0.20 g, 1.0 mmol). It was isolated by using ethyl acetate-hexane (3:2) mixture as the eluent.

Yield: 0.21 g (87%).

Mp: 76-78 ^{o}C (white solid).

IR (KBr): 2967, 2128, 1744, 1476, 1229, 1057, 1013, 853 cm^{-1}.

^{1}H NMR: δ 0.99 and 1.12 (2 s, 6H, C(C*H*$_3$)$_2$), 1.43 (dd, ^{3}J(P-H) ~ 18.2 Hz, ^{3}J(H-H) ~ 7.0 Hz, 3H, CHC*H*$_3$), 2.66-2.77 (m, 1H, C*H*CH$_3$), 3.78–3.89 and 4.21–4.26 (2 m, 4H, 2 OC*H*$_2$), 4.89 and 5.04 (2 br, 2H, =C*H*$_2$).

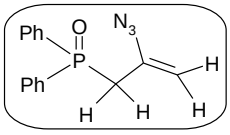
^{13}C NMR: δ 13.5 (d, *J*(P-C) = 5.5 Hz), 21.4, 21.7, 32.8 (d, ^{3}J(P-C) = 5.8 Hz, *C*(CH$_3$)$_2$), 35.8 (d, ^{1}J(P-C) = 135.7 Hz, P*C*H), 75.1 (d, ^{2}J(P-C) = 2.2 Hz, O*C*H$_2$), 75.2 (d, ^{2}J(P-C) = 2.5 Hz, O*C*H$_2$), 101.0 (d, *J*(P-C) = 10.0 Hz), 143.3 (d, *J*(P-C) = 9.3 Hz).

^{31}P NMR: δ 23.9.

LC-MS: *m/z* 246 [M+1]$^{+}$.

Anal. Calcd. for $C_9H_{16}N_3O_3P$: C, 44.08; H, 6.58; N, 17.14. Found: C, 44.16; H, 6.51; N, 17.12.

Compound 86



This azide was synthesized from the allene **12a** (0.50 g, 2.1 mmol). It was isolated by using ethyl acetate-hexane (3:2) mixture as the eluent.

Yield: 0.52 g (89%).

Mp: 102-104 ^{o}C (white solid).

IR (KBr): 3056, 2124, 1616, 1437, 1186, 1121, 853 cm^{-1}.

^{1}H NMR: δ 3.08 (d, ^{2}J(P-H) = 13.2 Hz, 2H, PC*H*$_2$), 4.79 and 4.90 (2 br, 2H, =C*H*$_2$), 7.48-7.54 and 7.74-7.79 (2 m, 10H, Ar-*H*).

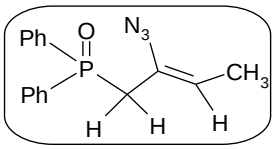
^{13}C NMR: δ 36.1 (d, ^{1}J(P-C) = 66.4 Hz, P*C*H$_2$), 102.9 (d, *J*(P-C) = 7.8 Hz), 128.6, 128.7, 131.0, 131.1, 131.9 (d, *J*(P-C) = 100.2 Hz, P*C*), 132.1, 137.5 (d, *J*(P-C) = 9.4 Hz).

^{31}P NMR: δ 28.1.

LC-MS: *m/z* 284 $[M+1]^+$.

Anal. Calcd. for $C_{15}H_{14}N_3OP$: C, 63.60; H, 4.98; N, 14.83. Found: C, 63.51; H, 4.91; N, 14.75.

Compound 87 [isomeric purity ca 90%)



This azide was synthesized from the allene **12b** (0.41 g, 1.6 mmol). It was isolated by using ethyl acetate-hexane (3:2) mixture as the eluent.

Yield: 0.39 g (83%).

Mp: 98-100 ^{o}C (white solid).

IR (KBr): 3057, 2116, 1437, 1271, 1177, 1119, 843 cm^{-1}.

^{1}H NMR: δ 1.55-1.57 (m, 3H, =CHC*H*$_3$), 3.13 (d, ^{2}J(P-H) = 14.0 Hz, 2H, PC*H*$_2$), 5.30-5.35 (m, 1H, =C*H*CH$_3$), 7.46-7.56 and 7.76-7.81 (2 m, 10H, Ar-*H*).

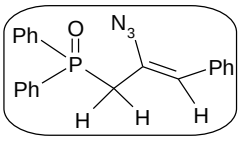
^{13}C NMR: δ 13.2, 32.3 (d, ^{1}J(P-C) = 66.7 Hz, P*C*H$_2$), 114.0 (d, *J*(P-C) = 8.8 Hz), 128.5, 128.6, 129.2 (d, *J*(P-C) = 10.9 Hz), 131.1, 131.2, 132.0, 132.3 (d, *J*(P-C) = 99.1 Hz).

^{31}P NMR: δ 28.3.

LC-MS: *m/z* 298 $[M+1]^+$.

Anal. Calcd. for $C_{16}H_{16}N_3OP$: C, 64.64; H, 5.42; N, 14.13. Found: C, 64.51; H, 5.38; N, 14.25.

Compound 88



This azide was synthesized from the allene **12h** (0.28 g, 0.9 mmol). It was isolated by using ethyl acetate-hexane (7:3) mixture as the eluent.

Yield: 0.20 g (63%, gummy material).

IR (KBr): 3057, 2105, 1437, 1275, 1196, 1121, 999 cm^{-1}.

^{1}H NMR: δ 3.36 (d, ^2J(P-H) = 13.6 Hz, 2H, PCH_2), 6.39 (d, ^4J(P-H) = 2.8 Hz, 1H, =C*H*Ph), 7.24-7.31 (m, 5H, Ar-*H*), 7.44-7.52 (m, 6H, Ar-*H*), 7.67-7.72 (m, 4H, Ar-*H*).

^{13}C NMR: δ 32.8 (d, ^1J(P-C) = 65.9 Hz, P*C*H_2), 119.2 (d, *J*(P-C) = 9.0 Hz), 125.7, 127.2, 128.1, 128.5, 128.6, 128.8 (d, *J*(P-C) = 3.0 Hz), 131.0, 131.1, 131.9 (d, *J*(P-C) = 2.5 Hz), 132.1, 132.6, 132.8, 135.0 (d, *J*(P-C) = 2.6 Hz).

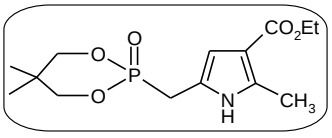
^{31}P NMR: δ 28.3.

LC-MS: *m/z* 360 $[M+1]^+$.

Anal. Calcd. for $C_{21}H_{18}N_3OP$: C, 70.19; H, 5.05; N, 11.69. Found: C, 70.25; H, 5.12; N, 11.55.

3.52 Synthesis of substituted pyrrole derivatives 90-107

To a solution of Me_3SiN_3 (0.77 g, 6.7 mmol) in DMF (10 mL) was added the allene **10a** (1.05 g, 5.6 mmol) and the reaction mixture stirred for 2-4 h. To this, a solution of ethyl acetoacetate (1.10 g, 8.4 mmol), $Mn(OAc)_3.2H_2O$ (0.15 g, 0.56 mmol) and acetic acid (0.67 g, 11.2 mmol) in MeOH (5 mL) was added and the mixture irradiated in a photoreactor [λ = 254 nm] for further 4 h. Solvent was removed under reduced pressure and the crude product treated with ethyl acetate (20 mL). The resulting slurry was filtered through a plug of silica pad. Ethyl acetate was removed from the filtrate and the product **90** was purified by column chromatography (EtOAc-hexane: 7:3). Compounds **91-107** were also prepared similarly.



Yield: 1.42 g (80%).

Mp: 110-112 ^oC (white solid).

IR (KBr): 3248, 2969, 1699, 1599, 1263, 1063, 1007 cm^{-1}.

^{1}H NMR: δ 0.96 and 1.06 (2 s, 6H, C(CH_3)$_2$), 1.30 (t, ^{3}J(H-H) ~ 7.0 Hz, 3H, $CO_2CH_2CH_3$), 2.37 (s, 3H, CH_3), 3.23 (d, ^{2}J(P-H) = 19.6 Hz, 2H, PCH_2), 3.80–3.86 and 4.07–4.12 (m, 4H, 2 OCH_2), 4.21–4.22 (m, 2H, $CO_2CH_2CH_3$), 6.35 (s, 1H, C*H*), 9.67 (br, 1H, N*H*).

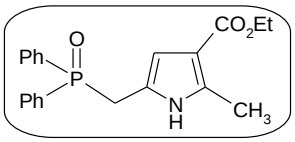
^{13}C NMR: δ 13.1, 14.5, 21.3, 21.4, 23.8 (d, ^{1}J(P-C) = 136.8 Hz, P*C*H$_2$), 32.6 (d, ^{3}J(P-C) = 6.4 Hz, *C*(CH$_3$)$_2$), 59.3, 75.9, 76.0, 110.1 (d, *J*(P-C) = 10.0 Hz), 111.9, 117.7 (d, *J*(P-C) = 11.1 Hz), 136.0, 165.5.

^{31}P NMR: δ 20.0.

LC-MS: *m/z* 316 [M+1]$^{+}$.

Anal. Calcd. for $C_{14}H_{22}NO_5P$: C, 53.33; H, 7.03; N, 4.44. Found: C, 53.41; H, 6.92; N, 4.62. This compound was crystallized from dichloromethane-hexane (9:1) at 25 ^{o}C. X-ray structure was determined for this sample (Fig. 21 in Chapter 2).

Compound 91



This pyrrole was prepared from allene **12a** (0.41 g, 1.7 mmol) and ethyl acetoacetate (0.34 g, 2.6 mmol). It was isolated by using ethyl acetate-hexane (7:3) mixture as the eluent.

Yield: 0.52 g (83%).

Mp: 178-180 ^{o}C (white solid).

IR (KBr): 3208, 2924, 1688, 1437, 1331, 1177, 1073 cm^{-1}.

^{1}H NMR: δ 1.28 (t, ^{3}J(H-H) ~ 7.0 Hz, 3H, $CO_2CH_2CH_3$), 2.25 (s, 3H, CH_3), 3.66 (d, ^{2}J(P-H) = 11.6 Hz, 2H, PCH_2), 4.17–4.21 (m, 2H, $CO_2CH_2CH_3$), 6.10 (s, 1H, C*H*), 7.45-7.71 (m, 10H, Ar-*H*), 10.43 (br, 1H, N*H*).

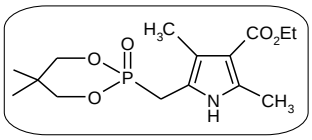
^{13}C NMR: δ 13.1, 14.5, 29.6 (d, ^{1}J(P-C) = 68.0 Hz, P*C*H), 59.2, 109.9, 111.5, 119.0, 128.7, 128.9, 130.9, 131.3, 132.2, 136.1, 165.7.

^{31}P NMR: δ 30.9.

LC-MS: *m/z* 368 [M+1]$^{+}$.

Anal. Calcd. for $C_{21}H_{22}NO_3P$: C, 68.66; H, 6.04; N, 3.81. Found: C, 68.56; H, 6.12; N, 3.76.

Compound 92



This pyrrole was prepared from allene **10b** (0.38 g, 1.9 mmol) and ethyl acetoacetate (0.38 g, 2.9 mmol). It was isolated by using ethyl acetate-hexane (7:3) mixture as the eluent.

Yield: 0.51 g (81%).

Mp: 162-164 ^{o}C (white solid).

IR (KBr): 3250, 1686, 1262, 1165, 1049, 1001 cm^{-1}.

^{1}H NMR: δ 0.98 and 1.04 (2 s, 6H, C(C*H*$_3$)$_2$), 1.33 (t, ^{3}J(H-H) = 7.2 Hz, 3H, $CO_2CH_2CH_3$), 2.18 (d, *J*(P-H) = 2.8 Hz, 3H, C*H*$_3$), 2.42 (d, *J*(P-H) = 1.2 Hz, 3H, C*H*$_3$), 3.17 (d, ^{2}J(P-H) = 19.6 Hz, 2H, PC*H*$_2$), 3.76–3.82 (m, 2H, OC*H*$_2$), 4.12–4.27 (m, 4H, OC*H*$_2$ + $CO_2CH_2CH_3$), 9.01 (br, 1H, N*H*).

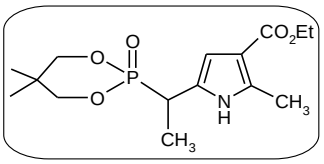
^{13}C NMR: δ 11.1, 13.8, 14.5, 21.2, 21.4, 22.1 (d, ^{1}J(P-C) = 135.5 Hz, P*C*H$_2$), 32.6 (d, ^{3}J(P-C) = 6.1 Hz, *C*(CH$_3$)$_2$), 59.0, 75.8, 75.9, 110.7, 114.6 (d, *J*(P-C) = 11.5 Hz), 118.7 (d, *J*(P-C) = 9.7 Hz), 135.7, 166.2.

^{31}P NMR: δ 21.3.

LC-MS: *m/z* 330 [M+1]$^{+}$.

Anal. Calcd. for $C_{15}H_{24}NO_5P$: C, 54.71; H, 7.35; N, 4.25. Found: C, 54.91; H, 7.36; N, 4.32.

Compound 93



This pyrrole was prepared from allene **10e** (0.10 g, 0.5 mmol) and ethyl acetoacetate (0.09 g, 0.7 mmol). It was isolated by using ethyl acetate-hexane (7:3) mixture as the eluent.

Yield: 0.13 g (79%).

Mp: 124-126 ^{o}C (white solid).

IR (KBr): 3233, 2922, 1694, 1260, 1061 cm^{-1}.

^{1}H NMR: δ 0.97 and 1.04 (2 s, 6H, C(CH_3)$_2$), 1.30 (t, ^{3}J(H-H) ~ 7.0 Hz, 3H, $CO_2CH_2CH_3$), 1.56 (dd, ^{3}J(P-H) ~ 18.2 Hz, ^{3}J(H-H) = 7.2 Hz, 3H, CHCH_3), 2.39 (s, 3H, CCH_3), 3.28-3.39 (m, 1H, CHCH$_3$), 3.69–3.84 and 4.14–4.24 (2 m, 6H, 2 OCH_2 + $CO_2CH_2CH_3$), 6.37 (s, 1H, CH), 9.60 (br, 1H, NH).

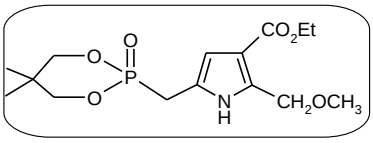
^{13}C NMR: δ 13.1, 14.0, 14.6, 21.4, 21.6, 30.0 (d, ^{1}J(P-C) = 137.2 Hz, PCH), 32.7 (d, ^{3}J(P-C) = 5.9 Hz, C(CH$_3$)$_2$), 59.2, 75.2 (d, ^{2}J(P-C) = 6.6 Hz, OCH$_2$), 75.4 (d, ^{2}J(P-C) = 6.5 Hz, OCH$_2$), 108.6 (d, J(P-C) = 9.2 Hz), 111.6 (d, J(P-C) = 1.4 Hz), 124.3 (d, J(P-C) = 9.5 Hz), 136.1, 165.6.

^{31}P NMR: δ 24.7.

LC-MS: *m/z* 330 [M+1]$^{+}$.

Anal. Calcd. for $C_{15}H_{24}NO_5P$: C, 54.71; H, 7.35; N, 4.25. Found: C, 54.81; H, 7.28; N, 4.33.

Compound 94



This pyrrole was prepared from allene **10a** (0.24 g, 1.3 mmol) and ethyl-4-chloro acetoacetate (0.31 g, 1.9 mmol). It was isolated by using ethyl acetate-hexane (7:3) mixture as the eluent.

Yield: 0.34 g (78%).

Mp: 126-128 ^{o}C.

IR (KBr): 3246, 1699, 1597, 1269, 1055, 1001 cm^{-1}.

^{1}H NMR: δ 0.99 and 1.01 (2 s, 6H, C(CH_3)$_2$), 1.32 (t, ^{3}J(H-H) ~ 7.0 Hz, 3H, $CO_2CH_2CH_3$), 3.24 (d, ^{2}J(P-H) = 20.0 Hz, 2H, PCH_2), 3.43 (s, 3H, OCH_3), 3.77–3.84 and 4.16–4.27 (2 m, 6H, 2 OCH_2 + $CO_2CH_2CH_3$), 4.75 (s, 2H, CH_2O), 6.41 (s, 1H, CH), 9.20 (br, 1H, NH).

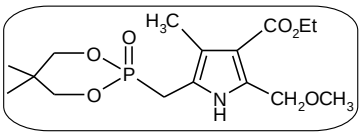
^{13}C NMR: δ 14.5, 21.3$_7$, 21.4$_0$, 24.2 (d, ^{1}J(P-C) = 138.1 Hz, PCH$_2$), 32.6 (d, ^{3}J(P-C) = 6.3 Hz, C(CH$_3$)$_2$), 58.6, 59.5, 66.8, 75.6, 75.7, 110.2 (d, J(P-C) = 9.1 Hz), 112.0, 119.4 (d, J(P-C) = 10.9 Hz), 135.9, 164.9.

^{31}P NMR: δ 20.5.

LC-MS: *m/z* 346 [M+1]$^{+}$.

Anal. Calcd. for $C_{15}H_{24}NO_6P$: C, 52.17; H, 7.01; N, 4.06. Found: C, 52.05; H, 7.11; N, 4.12.

Compound 95



This pyrrole was prepared from allene **10b** (0.36 g, 1.8 mmol) and ethyl-4-chloro acetoacetate (0.44 g, 2.7 mmol). It was isolated by using ethyl acetate-hexane (7:3) mixture as the eluent.

Yield: 0.44 g (69%).

Mp: 170-172 ^{o}C (white solid).

IR (KBr): 3353, 1688, 1472, 1372, 1269, 1169, 1059, 1009 cm^{-1}.

^{1}H NMR: δ 0.94 and 0.99 (2 s, 6H, C(C*H*$_3$)$_2$), 1.34 (t, ^{3}J(H-H) ~ 7.2 Hz, 3H, $CO_2CH_2CH_3$), 2.19 (s, 3H, C*H*$_3$), 3.20 (d, ^{2}J(P-H) = 19.6 Hz, 2H, PC*H*$_2$), 3.43 (s, 3H, OC*H*$_3$), 3.72–3.81 (m, 2H, OC*H*$_2$), 4.16–4.28 (m, 4H, OC*H*$_2$ + $CO_2CH_2CH_3$), 4.72 (s, 2H, C*H*$_2$O), 9.12 (br, 1H, N*H*).

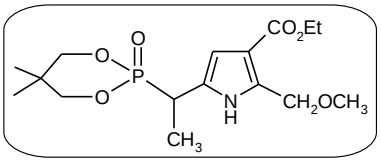
^{13}C NMR: δ 14.5, 20.8, 21.4, 21.5, 24.3 (d, ^{1}J(P-C) = 138.8 Hz, P*C*H$_2$), 32.7 (d, ^{3}J(P-C) = 6.3 Hz, *C*(CH$_3$)$_2$), 58.6, 59.6, 66.9, 75.6$_7$, 75.7$_2$, 110.3 (d, *J*(P-C) = 8.8 Hz), 112.0, 119.5 (d, *J*(P-C) = 11.3 Hz), 135.9, 165.0.

^{31}P NMR: δ 21.3.

LC-MS: *m/z* 360 $[M+1]^{+}$.

Anal. Calcd. for $C_{16}H_{26}NO_6P$: C, 53.48; H, 7.29; N, 3.90. Found: C, 53.36; H, 7.36; N, 3.82.

Compound 96



This pyrrole was prepared from allene **10e** (0.24 g, 1.2 mmol) and ethyl-4-chloro acetoacetate (0.30 g, 1.8 mmol). It was isolated by using ethyl acetate-hexane (7:3) mixture as the eluent.

Yield: 0.33 g (77%).

Mp: 134-136 ^{o}C (white solid).

IR (KBr): 3351, 1692, 1468, 1375, 1227, 1059, 1009 cm^{-1}.

^{1}H NMR: δ 0.94 and 1.02 (2 s, 6H, C(C*H*$_3$)$_2$), 1.32 (t, ^{3}J(H-H) = 7.2 Hz, 3H, CO$_2$CH$_2$C*H*$_3$), 1.59 (dd, ^{3}J(P-H) = 18.2 Hz, ^{3}J(H-H) ~ 7.4 Hz, 3H, CHC*H*$_3$), 3.30-3.39 (m, 1H, C*H*CH$_3$), 3.42 (s, 3H, OC*H*$_3$), 3.69–3.80 and 4.20–4.27 (2 m, 6H, 2 OC*H*$_2$ + CO$_2$C*H*$_2$CH$_3$), 4.75 (s, 2H, C*H*$_2$O), 6.42 (s, 1H, C*H*), 9.43 (br, 1H, N*H*).

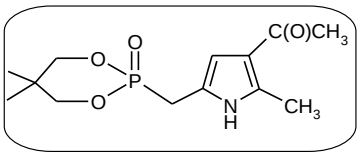
^{13}C NMR: δ 13.8, 14.5, 21.3, 21.6, 30.1 (d, ^{1}J(P-C) = 137.7 Hz, P*C*H), 32.7 (d, ^{3}J(P-C) = 5.6 Hz, *C*(CH$_3$)$_2$), 58.6, 59.6, 66.8, 75.1, 75.2, 108.7 (d, *J*(P-C) = 8.8 Hz), 111.7, 125.9 (d, *J*(P-C) = 9.2 Hz), 135.8, 165.0.

^{31}P NMR: δ 24.8.

LC-MS: *m/z* 360 [M+1]$^{+}$.

Anal. Calcd. for C$_{16}$H$_{26}$NO$_6$P: C, 53.48; H, 7.29; N, 3.90. Found: C, 53.62; H, 7.23; N, 3.81.

Compound 97



This pyrrole was prepared from allene **10a** (0.17 g, 0.9 mmol) and acetyl acetone (0.14 g, 1.4 mmol). It was isolated by using ethyl acetate-hexane (7:3) mixture as the eluent.

Yield: 0.19 g (72%).

Mp: 86-88 ^{o}C (white solid).

IR (KBr): 3221, 2975, 1655, 1258, 1061, 1007 cm^{-1}.

^{1}H NMR: δ 0.99 and 1.05 (2 s, 6H, C(C*H*$_3$)$_2$), 2.34 (s, 3H, CC*H*$_3$), 2.41 (s, 3H, C(O)C*H*$_3$), 3.24 (d, ^{2}J(P-H) = 20.0 Hz, 2H, PC*H*$_2$), 3.81–3.87 and 4.11–4.16 (2 m, 4H, 2 OC*H*$_2$), 6.31 (s, 1H, C*H*), 9.79 (br, 1H, N*H*).

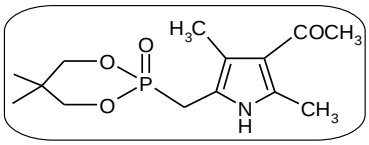
^{13}C NMR: δ 13.8, 21.3, 21.4, 24.0 (d, ^{1}J(P-C) = 137.3 Hz, P*C*H$_2$), 28.5, 32.6 (d, ^{3}J(P-C) = 6.1 Hz, *C*(CH$_3$)$_2$), 75.9, 76.0, 110.2 (d, *J*(P-C) = 9.4 Hz), 117.7 (d, *J*(P-C) = 10.9 Hz), 121.2, 135.7, 194.7 (*C*=O).

^{31}P NMR: δ 20.4.

LC-MS: *m/z* 284 [M-1]$^{+}$.

Anal. Calcd. for $C_{13}H_{20}NO_4P$: C, 54.73; H, 7.07; N, 4.91. Found: C, 54.65; H, 7.15; N, 4.85. This compound was crystallized from dichloromethane-hexane (9:1) at 25 ^oC. X-ray structure was determined for this sample (Fig. 23 in Chapter 2).

Compound 98



This pyrrole was prepared from allene **10b** (0.42 g, 2.1 mmol) and acetyl acetone (0.32 g, 3.2 mmol). It was isolated by using ethyl acetate-hexane (7:3) mixture as the eluent.

Yield: 0.45 g (72%).

Mp: 178-180 ^oC (white solid).

IR (KBr): 3223, 1644, 1478, 1250, 1053, 999 cm^{-1}.

^1H NMR: δ 1.03 and 1.07 (2 s, 6H, $C(CH_3)_2$), 2.23 (d, *J*(P-H) = 2.8 Hz, 3H, CH_3), 2.41 (s, 3H, CH_3), 2.45 (s, 3H, $C(O)CH_3$), 3.20 (d, ^2J(P-H) = 19.6 Hz, 2H, PCH_2), 3.80–3.86 and 4.15–4.21 (2 m, 4H, 2 OCH_2), 9.22 (br, 1H, N*H*).

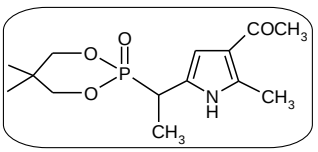
^{13}C NMR: δ 11.8, 15.1, 21.4, 21.6 (d, ^1J(P-C) = 138.0 Hz, PCH_2), 30.9 (d, *J*(P-C) = 3.2 Hz), 32.6 (d, ^3J(P-C) = 6.1 Hz, $C(CH_3)_2$), 75.6, 75.7, 115.0 (d, *J*(P-C) = 11.1 Hz), 118.2 (d, *J*(P-C) = 9.8 Hz), 121.4, 134.9 (d, *J*(P-C) = 7.3 Hz), 195.1 (d, *J*(P-C) = 4.8 Hz, *C*=O).

^{31}P NMR: δ 21.3.

LC-MS: *m/z* 300 $[M+1]^+$.

Anal. Calcd. for $C_{14}H_{22}NO_4P$: C, 56.18; H, 7.41; N, 4.68. Found: C, 56.35; H, 7.32; N, 4.81.

Compound 99



This pyrrole was prepared from allene **10e** (0.20 g, 1.0 mmol) and acetyl acetone (0.15 g, 1.5 mmol). It was isolated by using ethyl acetate-hexane (7:3) mixture as the eluent.

Yield: 0.21 g (71%).

Mp: 104-106 ^{o}C.

IR (KBr): 3212, 2978, 1649, 1474, 1256, 1065, 1011 cm^{-1}.

^{1}H NMR: δ 0.97 and 1.10 (2 s, 6H, C(C*H*$_3$)$_2$), 1.59 (dd, ^{3}J(P-H) = 18.0 Hz, ^{3}J(H-H) = 7.2 Hz, 3H, CHC*H*$_3$), 2.37 (s, 3H, C*H*$_3$), 2.48 (s, 3H, C(O)C*H*$_3$), 3.27-3.38 (m, 1H, C*H*CH$_3$), 3.74–3.85 and 4.22–4.25 (m, 4H, 2 OC*H*$_2$), 6.34 (s, 1H, C*H*), 9.30 (br, 1H, N*H*).

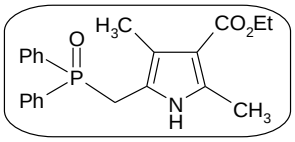
^{13}C NMR: δ 14.0, 14.1 (d, *J*(P-C) = 5.1 Hz), 21.3, 21.7, 28.5, 29.9 (d, ^{1}J(P-C) = 137.4 Hz, P*C*H), 32.7 (d, ^{3}J(P-C) = 5.8 Hz, *C*(CH$_3$)$_2$), 75.1, 75.2, 108.9 (d, *J*(P-C) = 9.5 Hz), 120.9, 124.2 (d, *J*(P-C) = 9.2 Hz), 135.6, 194.7 (*C*=O).

^{31}P NMR: δ 25.1.

LC-MS: *m/z* 300 [M+1]$^{+}$.

Anal. Calcd. for $C_{14}H_{22}NO_4P$: C, 56.18; H, 7.41; N, 4.68. Found: C, 56.32; H, 7.48; N, 4.61.

Compound 100



This pyrrole was prepared from allene **12b** (0.53 g, 2.1 mmol) and ethyl acetoacetate (0.40 g, 3.1 mmol). It was isolated by using ethyl acetate-hexane (7:3) mixture as the eluent.

Yield: 0.64 g (81%).

Mp: 116-118 ^{o}C (white solid).

IR (KBr): 3229, 1699, 1439, 1267, 1175, 953 cm^{-1}.

^{1}H NMR: δ 1.30 (t, ^{3}J(H-H) ~ 7.0 Hz, 3H, CO$_2$CH$_2$C*H*$_3$), 1.85 (d, *J*(P-H) = 2.0 Hz, 3H, C*H*$_3$), 2.31 (s, 3H, C*H*$_3$), 3.57 (d, ^{2}J(P-H) = 12.0 Hz, 2H, PC*H*$_2$), 4.20 (qrt, ^{3}J(H-H) ~ 7.0 Hz, 2H, CO$_2$C*H*$_2$CH$_3$), 7.41-7.54 and 7.64-7.69 (2 m, 10H, Ar-*H*), 10.19 (br, 1H, N*H*).

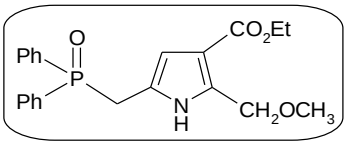
^{13}C NMR: δ 10.8, 14.0, 14.5, 27.6 (d, ^{1}J(P-C) = 69.1 Hz, P*C*H$_2$), 58.9, 110.4, 115.9 (d, *J*(P-C) = 9.6 Hz), 118.6 (d, *J*(P-C) = 7.3 Hz), 128.7, 128.8, 130.8, 131.0, 132.0 (d, *J*(P-C) = 98.3 Hz), 132.2, 136.0, 166.4.

^{31}P NMR: δ 30.8.

LC-MS: *m/z* 382 $[M+1]^+$.

Anal. Calcd. for $C_{22}H_{24}NO_3P$: C, 69.28; H, 6.34; N, 3.67. Found: C, 69.12; H, 6.29; N, 3.75.

Compound 101



This pyrrole was prepared from allene **12a** (0.29 g, 1.2 mmol) and ethyl-4-chloro acetoacetate (0.31 g, 1.9 mmol). It was isolated by using ethyl acetate-hexane (7:3) mixture as the eluent.

Yield: 0.38 g (80%).

Mp: 182-184 ^{o}C (white solid).

IR (KBr): 3351, 2122, 1703, 1618, 1437, 1285, 1186, 1024 cm^{-1}.

^{1}H NMR: δ 1.30 (t, ^{3}J(H-H) ~ 7.0 Hz, 3H, CO$_2$CH$_2$C*H*$_3$), 3.37 (s, 3H, OC*H*$_3$), 3.62 (d, ^{2}J(P-H) = 12.8 Hz, 2H, PC*H*$_2$), 4.21 (qrt, ^{3}J(H-H) ~ 7.0 Hz, 2H, CO$_2$C*H*$_2$CH$_3$), 4.69 (s, 2H, C*H*$_2$O), 6.24 (s, 1H, C*H*), 7.44-7.55 and 7.66-7.70 (2 m, 10H, Ar-*H*), 9.92 (br, 1H, N*H*).

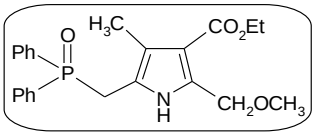
^{13}C NMR: δ 14.5, 29.5 (d, ^{1}J(P-C) = 68.2 Hz, P*C*H$_2$), 58.5, 59.5, 66.8, 110.2 (d, *J*(P-C) = 7.4 Hz), 111.6, 120.9 (d, *J*(P-C) = 9.2 Hz), 128.7, 128.8, 130.8, 130.9, 131.8 (d, *J*(P-C) = 99.3 Hz), 132.2, 135.9, 165.0.

^{31}P NMR: δ 30.5.

LC-MS: *m/z* 398 $[M+1]^+$.

Anal. Calcd. for $C_{22}H_{24}NO_4P$: C, 66.49; H, 6.09; N, 3.52. Found: C, 66.59; H, 6.14; N, 3.45.

Compound 102



This pyrrole was prepared from allene **12b** (0.43 g, 1.7 mmol) and ethyl-4-chloro acetoacetate (0.41 g, 2.5 mmol). It was isolated by using ethyl acetate-hexane (7:3) mixture as the eluent.

Yield: 0.54 g (77%).

Mp: 120-122 ^{o}C (white solid).

IR (KBr): 3250, 2926, 1698, 1437, 1181, 1100 cm^{-1}.

^{1}H NMR: δ 1.32 (t, ^{3}J(H-H) ~ 7.0 Hz, 3H, $CO_2CH_2CH_3$), 2.01 (s, 3H, CH_3), 3.40 (s, 3H, OCH_3), 3.53 (d, ^{2}J(P-H) = 12.4 Hz, 2H, PCH_2), 4.22 (qrt, ^{3}J(H-H) ~ 7.0 Hz, 2H, $CO_2CH_2CH_3$), 4.70 (s, 2H, CH_2O), 7.46-7.56 and 7.65-7.69 (2 m, 10H, Ar-*H*), 9.65 (br, 1H, N*H*).

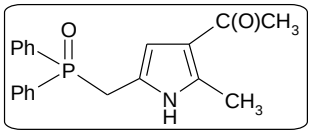
^{13}C NMR: δ 10.5, 14.5, 27.3 (d, ^{1}J(P-C) = 68.9 Hz, PCH_2), 58.6, 59.2, 67.6, 110.1, 117.7 (d, J(P-C) = 9.0 Hz), 118.9 (d, J(P-C) = 7.4 Hz), 128.7, 128.8, 130.7_6, 130.8_3, 132.0_6 (d, J(P-C) = 98.6 Hz), 132.1_1, 132.1_3, 135.9, 165.7.

^{31}P NMR: δ 30.8.

LC-MS: *m/z* 412 $[M+1]^{+}$.

Anal. Calcd. for $C_{23}H_{26}NO_4P$: C, 67.14; H, 6.37; N, 3.40. Found: C, 67.25; H, 6.41; N, 3.34.

Compound 103



This pyrrole was prepared from allene **12a** (0.29 g, 1.2 mmol) and acetyl acetone (0.19 g, 1.9 mmol). It was isolated by using ethyl acetate-hexane (7:3) mixture as the eluent.

Yield: 0.28 g (70%).

Mp: 92-94 ^{o}C (white solid).

IR (KBr): 3289, 1645, 1437, 1175, 1115, 945 cm^{-1}.

^{1}H NMR: δ 2.21 (s, 3H, C*H*$_3$), 2.41 (s, 3H, C*H*$_3$), 4.16 (d, ^{2}J(P-H) = 12.4 Hz, 2H, PC*H*$_2$), 6.61 (s, 1H, C*H*), 7.37-7.49 and 7.71-7.76 (2 m, 10H, Ar-*H*), 10.90 (br, 1H, N*H*).

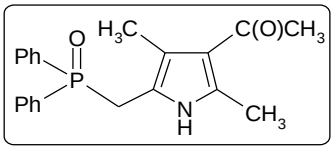
^{13}C NMR: δ 13.9, 28.4, 29.5 (d, ^{1}J(P-C) = 68.4 Hz, P*C*H$_2$), 110.2 (d, *J*(P-C) = 7.8 Hz), 119.2 (d, *J*(P-C) = 9.6 Hz), 121.0, 128.7, 128.8, 130.8, 130.9, 131.3, 131.7 (d, *J*(P-C) = 99.5 Hz), 131.8 (d, *J*(P-C) = 10.9 Hz), 132.3, 135.6, 194.5 (*C*=O).

^{31}P NMR: δ 33.0.

LC-MS: *m/z* 338 [M+1]$^{+}$.

Anal. Calcd. for $C_{20}H_{20}NO_2P$: C, 71.21; H, 5.98; N, 4.15. Found: C, 71.36; H, 5.88; N, 4.21.

Compound 104



This pyrrole was prepared from allene **12b** (0.33 g, 1.3 mmol) and acetyl acetone (0.19 g, 1.9 mmol). It was isolated by using ethyl acetate-hexane (7:3) mixture as the eluent.

Yield: 0.33 g (73%).

Mp: 180-182 ^{o}C (white solid).

IR (KBr): 3148, 1630, 1437, 1169, 1116, 965 cm^{-1}.

^{1}H NMR: δ 2.01 (s, 3H, C*H*$_3$), 2.05 (s, 3H, C*H*$_3$), 2.34 (s, 3H, C*H*$_3$), 4.10 (d, ^{2}J(P-H) = 12.8 Hz, 2H, PC*H*$_2$), 7.41-7.50 and 7.45-7.79 (2 m, 10H, Ar-*H*), 9.51 (br, 1H, N*H*).

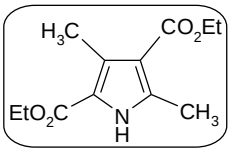
^{13}C NMR: δ 11.0, 15.3, 27.7 (d, ^{1}J(P-C) = 69.1 Hz, P*C*H$_2$), 30.4, 109.2 (d, *J*(P-C) = 9.5 Hz), 120.6, 126.7 (d, *J*(P-C) = 6.7 Hz), 128.0, 128.1, 131.4, 131.5, 132.8, 133.0 (d, *J*(P-C) = 96.2 Hz), 195.0 (*C*=O).

^{31}P NMR: δ 32.0.

LC-MS: *m/z* 352 [M+1]$^{+}$.

Anal. Calcd. for $C_{21}H_{22}NO_2P$: C, 71.78; H, 6.31; N, 3.99. Found: C, 71.65; H, 6.39; N, 3.89.

Compound 105



This pyrrole was prepared from allene **9a** (0.11 g, 1.0 mmol) and ethyl acetoacetate (0.20 g, 1.6 mmol). It was isolated by using ethyl acetate-hexane (1:4) mixture as the eluent.

Yield: 0.18 g (75%).

Mp: 90-92 ^{o}C (white solid).

IR (KBr): 3289, 1669, 1445, 1215, 1157, 1028 cm^{-1}.

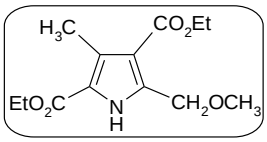
^{1}H NMR: δ 1.36-1.41 (m, 6H, 2 $CO_2CH_2CH_3$), 2.54 and 2.58 (2 s, 6H, 2 CH_3), 4.29–4.38 (m, 4H, 2 $CO_2CH_2CH_3$), 9.00 (br, 1H, NH).

^{13}C NMR: δ 11.9, 14.3, 14.4, 14.5, 59.5, 60.3, 113.7, 117.9, 130.9, 138.7, 161.6, 165.4.

LC-MS: *m/z* 240 $[M+1]^{+}$.

Anal. Calcd. for $C_{12}H_{17}NO_4$: C, 60.24; H, 7.16; N, 5.85. Found: C, 60.32; H, 7.08; N, 5.81.

Compound 106



This pyrrole was prepared from allene **9a** (0.35 g, 3.1 mmol) and ethyl-4-chloro acetoacetate (0.76 g, 4.6 mmol). It was isolated by using ethyl acetate-hexane (1:4) mixture as the eluent.

Yield: 0.60 g (72%).

Mp: 110-112 ^{o}C (white solid).

IR (KBr): 3366, 1651, 1429, 1155, 1030 cm^{-1}.

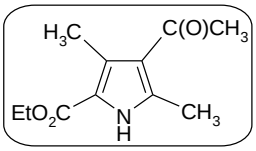
^{1}H NMR: δ 1.32-1.36 (m, 6H, 2 $CO_2CH_2CH_3$), 2.42 (s, 3H, CH_3), 3.43 (s, 3H, OCH_3), 4.26–4.33 (m, 4H, 2 $CO_2CH_2CH_3$), 4.65 (s, 2H, CH_2O), 8.73 (br, 1H, NH).

^{13}C NMR: δ 12.5, 14.3, 58.5, 60.1$_6$, 60.2$_1$, 66.4, 112.4, 112.7, 132.8, 133.1, 164.7, 165.3.

LC-MS: *m/z* 270 $[M+1]^+$.

Anal. Calcd. for $C_{13}H_{19}NO_5$: C, 57.98; H, 7.11; N, 5.20. Found: C, 57.85; H, 7.16; N, 5.31.

Compound 107



This pyrrole was prepared from allene **9a** (0.45 g, 4.0 mmol) and acetyl acetone (0.58 g, 5.8 mmol). It was isolated by using ethyl acetate-hexane (1:4) mixture as the eluent.

Yield: 0.59 g (71%).

Mp: 122-124 ^oC (white solid).

IR (KBr): 3281, 1649, 1556, 1281, 1202, 1022 cm^{-1}.

^1H NMR: δ 1.38 (t, ^3J(H-H) = 7.2 Hz, 3H, $CO_2CH_2CH_3$), 2.45 (s, 3H, CH_3), 2.53 (s, 3H, CH_3), 2.59 (s, 3H, CH_3), 4.31–4.37 (m, 2H, $CO_2CH_2CH_3$), 9.21 (br, 1H, NH).

^{13}C NMR: δ 12.7, 14.5, 15.2, 31.4, 60.4, 118.0, 123.6, 129.4, 138.2, 161.7, 195.6.

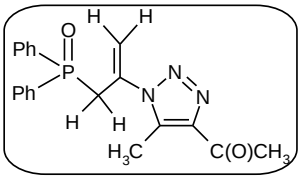
LC-MS: *m/z* 210 $[M+1]^+$.

Anal. Calcd. for $C_{11}H_{15}NO_3$: C, 63.14; H, 7.23; N, 6.69. Found: C, 63.06; H, 7.31; N, 6.75. This compound was crystallized from ethyl acetate-hexane (9:1) at 25 ^oC. X-ray structure was determined for this sample (Fig. 25 in chapter 2).

3.53 Reaction of vinyl azides with dicarbonyls or alkynes: Synthesis of 1,2,3-triazoles

(a) Synthesis of triazoles 108-112

To the solution of acetyl acetone (0.14 g, 1.4 mmol) and triethylamine (0.14 g, 1.4 mmol) in DMF (2 mL), added azide **86** (0.20 g, 0.7 mmol) and the mixture was stirred at room temperature for 24 h. Solvent was removed under reduced pressure and the crude product thus obtained was purified by column chromatography (silica gel; ethyl acetate-hexane) to obtain products **108** and **109**. Compounds **110-112** were also prepared by following the same method.



108

This compound was isolated by using ethyl acetate-hexane (4:1) mixture as the eluent.

Yield: 0.18 g (68%, gummy solid).

IR (Neat): 3057, 1682, 1557, 1437, 1194, 1119, 1065 cm^{-1}.

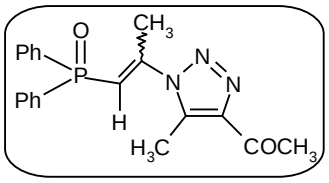
^{1}H NMR: δ 2.25 (s, 3H, C*H*$_3$), 2.58 (s, 3H, C(O)C*H*$_3$), 3.89 (d, ^{2}J(P-H) = 12.8 Hz, 2H, PC*H*$_2$), 5.23 and 5.73 (2 dd, ^{4}J(P-H) ~ 1.4 Hz, ^{2}J(H-H) ~ 4.3 Hz, 2H, =C*H*$_2$), 7.35-7.46 and 7.60-7.65 (2 m, 10H, Ar-*H*).

^{13}C NMR: δ 10.2, 27.7, 37.4 (d, ^{1}J(P-C) = 64.0 Hz, P*C*H$_2$), 117.2, 117.3 (d, *J*(P-C) = 8.0 Hz), 128.6, 128.7, 130.5, 130.6, 130.7, 131.7 (d, *J*(P-C) = 6.7 Hz), 132.1 (d, *J*(P-C) = 2.4 Hz), 133.1 (d, *J*(P-C) = 10.1 Hz), 137.7, 143.1, 193.6 (*C*=O).

^{31}P NMR: δ 26.0.

LC-MS: *m/z* 366 $[M+1]^{+}$.

Anal. Calcd. for $C_{20}H_{20}N_3O_2P$: C, 65.75; H, 5.52; N, 11.50. Found: C, 65.84; H, 5.62; N, 11.41.



109

This compound was isolated by using ethyl acetate-hexane (7:3) mixture as the eluent.

Yield: 0.05 g (18%, gummy solid).

IR (Neat): 3057, 1684, 1638, 1555, 1437, 1198, 1121, 970 cm^{-1}.

^{1}H NMR: δ 2.62 (s, 3H, C*H*$_3$), 2.70-2.72 (m, 6H, 2 C*H*$_3$), 6.27 (d, ^{2}J(P-H) = 17.6 Hz, 1H, PC*H*), 7.49-7.59 and 7.74-7.79 (2 m, 10H, Ar-*H*).

^{13}C NMR: δ 10.5, 19.8 (d, *J*(P-C) = 4.3 Hz), 27.9, 120.3 (d, ^{1}J(P-C) = 97.3 Hz, P*C*H), 128.5, 128.6 (d, *J*(P-C) = 12.5 Hz), 129.0, 129.1, 130.8$_7$, 130.9$_5$, 130.0, 131.1, 132.1 (d, *J*(P-C) = 2.4 Hz), 132.3, 132.4 (d, *J*(P-

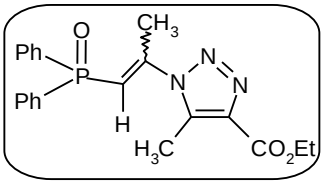
C) = 2.9 Hz), 133.1, 136.4, 143.8, 149.3 (d, *J*(P-C) = 9.9 Hz), 194.2 (*C*=O).

^{31}P NMR: δ 20.3.

LC-MS: *m/z* 366 $[M+1]^+$.

Anal. Calcd. for $C_{20}H_{20}N_3O_2P$: C, 65.75; H, 5.52; N, 11.50. Found: C, 65.71; H, 5.58; N, 11.64.

Compound 110



This product was synthesized from azide **86** (0.20 g, 0.7 mmol) and ethyl acetoacetate (0.18 g, 1.4 mmol). It was isolated by using ethyl acetate-hexane (7:3) mixture as the eluent.

Yield: 0.18 g (65%, gummy material).

IR (Neat): 2926, 1717, 1638, 1437, 1242, 1202, 1119, 972 cm^{-1}.

^{1}H NMR: δ 1.41 (t, ^3J(H-H) ~ 6.0 Hz, 3H, $CO_2CH_2CH_3$), 2.61 (s, 3H, CH_3), 2.70 (s, 3H, CH_3), 4.40-4.45 (m, 2H, $CO_2CH_2CH_3$), 6.27 (d, ^2J(P-H) = 17.2 Hz, 1H, PC*H*), 7.51-7.58 and 7.74-7.79 (2 m, 10H, Ar-*H*).

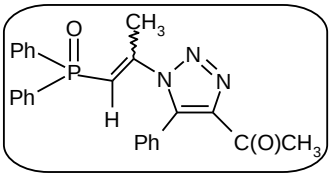
^{13}C NMR: δ 10.4, 14.3, 19.8 (d, *J*(P-C) = 3.8 Hz), 61.2, 120.3 (d, ^1J(P-C) = 97.4 Hz, P*C*H), 128.9, 129.0, 130.9, 131.0, 132.4 (d, *J*(P-C) = 2.5 Hz), 132.7 (d, ^1J(P-C) = 107.6 Hz), 137.1, 137.8, 149.5 (d, *J*(P-C) = 9.5 Hz), 161.4.

^{31}P NMR: δ 20.3.

LC-MS: *m/z* 396 $[M+1]^+$.

Anal. Calcd. for $C_{21}H_{22}N_3O_2P$: C, 63.79; H, 5.61; N, 10.63. Found: C, 63.85; H, 5.71; N, 10.48.

Compound 111



This product was synthesized from azide **86** (0.20 g, 0.7 mmol) and benzoyl acetone (0.23 g, 1.4 mmol). It was isolated by using ethyl acetate-hexane (7:3) mixture as the eluent.

Yield: 0.20 g (68%).

Mp: 180-182 ^{o}C (white solid).

IR (KBr): 3057, 1696, 1638, 1551, 1485, 1402, 1184, 1071 cm^{-1}.

^{1}H NMR: δ 2.64 (s, 3H, CH_3), 2.71 (s, 3H, C(O)CH_3), 5.99 (d, ^{2}J(P-H) = 17.2 Hz, 1H, PC*H*), 7.27-7.54 (m, 15H, Ar-*H*).

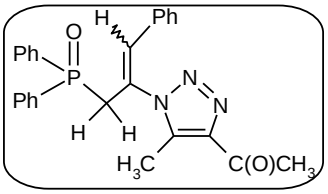
^{13}C NMR: δ 19.4, 28.3, 120.3 (d, ^{1}J(P-C) = 98.1 Hz, P*C*H), 126.1, 128.7, 128.8, 128.9, 129.7, 130.2, 130.8 (d, *J*(P-C) = 10.0 Hz), 132.0, 132.1, 133.1, 138.5, 143.6, 149.0 (d, *J*(P-C) = 10.0 Hz), 193.6 (*C*=O).

^{31}P NMR: δ 20.0.

LC-MS: *m/z* 426 [M-1]$^{+}$.

Anal. Calcd. for $C_{25}H_{22}N_3O_2P$: C, 70.25; H, 5.19; N, 9.83. Found: C, 70.18; H, 5.12; N, 9.75.

Compound 112



This product was synthesized from azide **88** (0.03 g, 0.08 mmol) and acetyl acetone (0.02 g, 0.16 mmol). It was isolated by using ethyl acetate-hexane (7:3) mixture as the eluent.

Yield: 0.026 g (70%).

Mp: gummy solid.

IR (KBr): 3057, 1682, 1557, 1437, 1283, 1198, 1119, 953 cm^{-1}.

^{1}H NMR: δ 2.41 (s, 3H, CH_3), 2.55 (s, 3H, C(O)CH_3), 4.10 (d, ^{2}J(P-H) = 12.5 Hz, 2H, PCH_2), 6.76 (d, ^{4}J(P-H) = 4.0 Hz, 1H, =C*H*), 7.36-7.49 (m, 9H, Ar-*H*), 7.61-7.65 (m, 4H, Ar-*H*), 7.83-7.84 (m, 2H, Ar-*H*).

^{13}C NMR: δ 10.5, 27.5, 34.5 (d, ^{1}J(P-C) = 65.3 Hz, P*C*H$_2$), 125.7, 127.0 (d, *J*(P-C) = 11.5 Hz), 128.6, 128.7, 128.9, 129.0 (d, *J*(P-C) = 1.1 Hz), 129.1, 130.3$_6$, 130.4$_3$, 131.0, 131.1, 131.2, 131.9 (d, *J*(P-C) = 2.6 Hz), 132.0,

132.9 (d, *J*(P-C) = 2.3 Hz), 134.1 (d, *J*(P-C) = 8.6 Hz), 143.0, 193.3 (*C*=O).

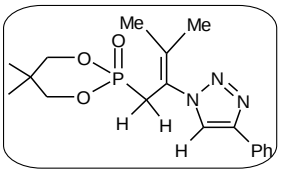
^{31}P NMR: δ 25.5.

LC-MS: *m/z* 442 $[M+1]^+$.

Anal. Calcd. for $C_{26}H_{24}N_3O_2P$: C, 70.74; H, 5.48; N, 9.52. Found: C, 70.61; H, 5.42; N, 9.65.

(b) Synthesis of phosphono-1,2,3-triazole 113

To a mixture of **85** (0.100 g, 0 40 mmol), phenyl acetylene (0.040 g, 0.40 mmol) in anhydrous acetonitrile (3 mL) was added copper(I) iodide (0.007 g,.0.03 mmol). The resulting mixture was stirred for 2 d at room temperature. Solvent was removed by reduced pressure. Compound **113** was purified by column chromatography [silica gel, ethyl acetate-hexane (4:1)].



Yield: 0.112 g (80%).

Mp: 125-127 ^{o}C (white solid).

IR (KBr): 1628, 1480, 1426, 1373, 1281, 1011, 986 cm^{-1}.

^{1}H NMR: δ 0.95, 1.03 (2s, 6H), 1.64-1.65 (m, 3H), 2.08-2.09 (m, 3H), 3.28 (d, *J* = 20.0 Hz, 2H), 3.67 (dd → t, *J* ~12.0 Hz each, 2H), 3.97 (dd → t, *J* ~ 12.0 Hz each, 2H), 7.32-7.87 (m, 5H), 7.98 (s, 1H).

^{13}C NMR: δ 20.5, 20.7, 21.3, 21.5, 29.1 (d, *J* = 133.4 Hz), 32.5 (d, *J* = 6.0 Hz), 75.8 (d, *J* = 7.3 Hz), 121.2 (d, *J* = 12.0 Hz), 122.3, 125.8, 125.8, 128.2, 128.9, 130.5, 137.1 (d, *J* = 10.9 Hz), 146.9.

^{31}P NMR: δ 19.3.

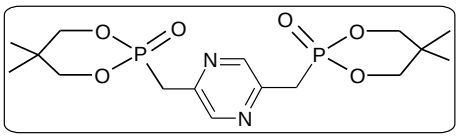
LC-MS: *m/z* 362 $[M+1]^+$.

Anal. Calcd. for $C_{18}H_{24}N_3O_3P$: C, 59.81; H, 6.67; N, 11.63. Found: C, 59.88; H, 6.69; N, 11.73.

3.54 Synthesis of phosphorus-based pyrazines 114-118

Azide **82** (0.20g, 0.80 mmol) was taken in a round bottommed flask, stoppered and heated at 120 ^{o}C for 15 min. The reaction mixture was cooled to r.t

and the product **114** was precipitated by adding ethyl acetate (5 mL). Compounds **115-118** were also synthesized by following the same method.



Yield: 0.27 g (78%).

Mp: 224-226 ^{o}C (white solid).

IR (KBr): 2982, 1487, 1408, 1265, 1065, 1003 cm^{-1}.

^{1}H NMR: δ 0.89 and 1.01 (2 s, 12H, 2 C(C*H*$_3$)$_2$), 3.51 (d, ^{2}J(P-H) = 20.8 Hz, 4H, 2 PC*H*$_2$), 3.85–3.91 and 4.14-4.19 (2 m, 8H, 4 OC*H*$_2$), 8.60 (s, 2H, Ar-*H*).

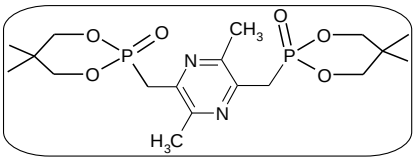
^{13}C NMR: δ 21.3, 21.4, 32.2 (d, ^{1}J(P-C) = 131.8 Hz, P*C*H$_2$), 32.5 (d, ^{3}J(P-C) = 5.9 Hz, *C*(CH$_3$)$_2$), 75.6, 75.7, 144.8, 146.5 (d, *J*(P-C) = 2.5 Hz).

^{31}P NMR: δ 19.1.

LC-MS: *m/z* 405 [M+1]$^{+}$.

Anal. Calcd. for $C_{16}H_{26}N_2O_6P_2$: C, 47.53; H, 6.48; N, 6.93. Found: C, 47.62; H, 6.52; N, 6.85.

Compound 115



This product was synthesized from the azide **83** (0.15 g, 0.6 mmol).

Yield: 0.20 g (75%).

Mp: 222-224 ^{o}C (white solid).

IR (KBr): 2965, 1474, 1377, 1244, 1055, 1015 cm^{-1}.

^{1}H NMR: δ 0.90 and 1.06 (2 s, 12H, 2 C(C*H*$_3$)$_2$), 2.64 (s, 6H, 2 CC*H*$_3$), 3.53 (d, ^{2}J(P-H) = 20.4 Hz, 4H, 2 PC*H*$_2$), 3.89–3.95 and 4.11-4.16 (2 m, 8H, 4 OC*H*$_2$).

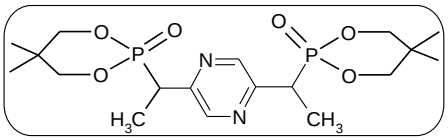
^{13}C NMR: δ 21.1, 21.5, 21.6, 32.1 (d, ^{1}J(P-C) = 131.1 Hz, P*C*H$_2$), 32.5 (d, ^{3}J(P-C) = 6.5 Hz, *C*(CH$_3$)$_2$), 75.7, 75.8, 144.2, 149.9.

^{31}P NMR: δ 19.3.

LC-MS: *m/z* 431 [M-1]$^{+}$.

Anal. Calcd. for $C_{18}H_{30}N_2O_6P_2$: C, 50.00; H, 6.99; N, 6.48. Found: C, 50.12; H, 6.92; N, 6.41. This compound was crystallized from methanol (2 mL) at 25 ^oC. X-ray structure was determined for this sample (Fig. 26 in Chapter 2).

Compound 116



This product was synthesized from the azide **84** (0.15 g, 0.6 mmol).

Yield: 0.20 g (74%).

Mp: 222-224 ^oC (white solid).

IR (KBr): 2922, 2114, 1647, 1534, 1269, 1047, 1017 cm^{-1}.

^1H NMR: δ 0.91 and 0.96 (2 s, 12H, 2 C(CH_3)$_2$), 1.73 (dd, ^3J(P-H) = 18.0 Hz, ^3J(H-H) ~ 7.2 Hz, 6H, 2 CHCH_3), 3.59–3.87 (m, 6H, 2 C*H*CH_3 + 2 OCH_2), 4.16-4.25 (m, 4H, 2 OCH_2), 8.64 (s, 2H, Ar-*H*).

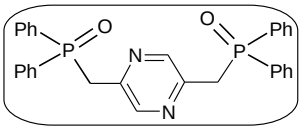
^{13}C NMR: δ 13.6, 21.3$_9$, 21.4$_5$, 32.6 (br), 37.3 (d, ^1J(P-C) = 133.1 Hz, P*C*H), 75.1, 75.2, 144.1, 151.3.

^{31}P NMR: δ 23.5.

LC-MS: *m/z* 431 $[M-1]^+$.

Anal. Calcd. for $C_{18}H_{30}N_2O_6P_2$: C, 50.00; H, 6.99; N, 6.48. Found: C, 49.95; H, 7.06; N, 6.55.

Compound 117



This product was synthesized from the azide **86** (0.20 g, 0.7 mmol).

Yield: 0.26 g (72%).

Mp: 258-260 ^oC (white solid).

IR (KBr): 3052, 1483, 1437, 1402, 1177, 1121, 1032 cm^{-1}.

^1H NMR: δ 3.87 (d, ^2J(P-H) = 13.6 Hz, 4H, 2 PCH_2), 7.43-7.55 and 7.69-7.74 (2 m, 20H, Ar-*H*), 8.42 (s, 2H, Ar-*H*).

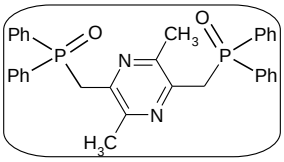
^{13}C NMR: δ 38.3 (d, ^{1}J(P-C) = 63.7 Hz, P*C*H$_2$), 128.6, 128.6$_6$, 128.7$_2$, 131.0$_2$, 131.0$_7$, 131.1$_2$, 131.8 (d, *J*(P-C) = 100.7 Hz), 132.1, 144.9, 146.5.

^{31}P NMR: δ 29.3.

LC-MS: *m/z* 507 $[M-1]^+$.

Anal. Calcd. for $C_{30}H_{26}N_2O_2P_2$: C, 70.86; H, 5.15; N, 5.51. Found: C, 70.73; H, 5.08; N, 5.60.

Compound 118



This product was synthesized from the azide **87** (0.20 g, 0.7 mmol).

Yield: 0.26 g (73%).

Mp: 232-234 ^{o}C (white solid).

IR (KBr): 2951, 1435, 1227, 1186, 1121, 1074 cm^{-1}.

^{1}H NMR: δ 2.29 (s, 6H, 2 C*H*$_3$), 3.83 (d, ^{2}J(P-H) = 14.0 Hz, 4H, 2 PC*H*$_2$), 7.42-7.51 and 7.71-7.75 (2 m, 20H, Ar-*H*).

^{13}C NMR: δ 21.2, 37.8 (d, ^{1}J(P-C) = 64.0 Hz, P*C*H$_2$), 128.3$_1$, 128.3$_7$, 128.4$_3$, 131.2$_5$, 131.3$_1$, 131.9, 132.9, 144.1, 150.1.

^{31}P NMR: δ 30.6.

LC-MS: *m/z* 537 $[M+1]^+$.

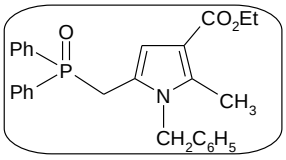
Anal. Calcd. for $C_{32}H_{30}N_2O_2P_2$: C, 71.63; H, 5.64; N, 5.22. Found: C, 71.52; H, 5.68; N, 5.16.

3.55 Application of phosphorus-based heterocycles in Horner-Wadsworth-Emmons (HWE) reaction: Synthesis of alkenyl-pyrroles 120-121, 123-124 and alkenyl-triazoles 125-128

(a) Synthesis of *N*-benzylation of pyrrole 119

Pyrrole **91** (0.20 g, 0.54 mmol) was added to toluene (5 mL) and aq. NaOH (2 mL 50% solution). To this suspension, tetrabutylammonium iodide (2.00 mg, 0.01 mmol) and benzyl bromide (0.09 g, 0.54 mmol) were added. The mixture was heated under reflux for 24 h. The solvent was removed under reduced pressure, water (10 mL) was added. The mixture was extracted with ethyl acetate (3 x 10 mL),

dried (Na_2SO_4), filtered and the solvent removed from the filtrate to give the crude product. Pure compound **119** was obtained by column chromatography (silica gel, ethyl acetate-hexane-1:1) as a white solid.



Yield: 0.17 g (68%).

Mp: 162-164 ^{o}C (white solid).

IR (KBr): 2926, 1696, 1437, 1184, 1069 cm^{-1}.

^{1}H NMR: δ 1.31 (t, ^{3}J(H-H) = 7.2 Hz, 3H, $CO_2CH_2CH_3$), 2.45 (s, 3H, CH_3), 3.50 (d, ^{2}J(P-H) = 12.0 Hz, 2H, PCH_2), 4.22 (qrt, ^{3}J(H-H) = 7.2 Hz, 2H, $CO_2CH_2CH_3$), 5.29 (s, 2H, NCH_2Ph), 6.17 (s, 1H, CH), 6.85 (d, ^{3}J(H-H) = 6.8 Hz, 2H, Ar-*H*), 7.25-7.32 (m, 3H, Ar-*H*), 7.45-7.57 (m, 6H, Ar-*H*), 7.65-7.70 (m, 4H, Ar-*H*).

^{13}C NMR: δ 11.5, 14.5, 29.6 (d, ^{1}J(P-C) = 68.6 Hz, PCH_2), 47.0, 59.3, 111.4 (d, *J*(P-C) = 4.5 Hz), 111.9, 121.2 (d, *J*(P-C) = 6.7 Hz), 125.6, 127.3, 128.5, 128.7, 128.9, 131.0, 131.1, 131.4, 131.5, 131.9 (d, *J*(P-C) = 98.4 Hz), 132.0_0 (d, *J*(P-C) = 98.6 Hz), 132.0_1, 132.0_3, 136.8, 137.1, 165.4.

^{31}P NMR: δ 28.8.

LC-MS: *m/z* 457 $[M-1]^{+}$.

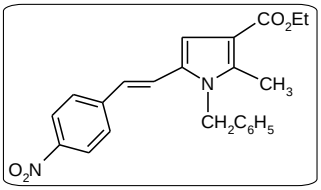
Anal. Calcd. for $C_{28}H_{28}NO_3P$: C, 73.51; H, 6.17; N, 3.06. Found: C, 73.45; H, 6.22; N, 3.12.

(b) Synthesis of alkenyl-pyrroles 120-121, 123-124

The phosphonate **119** (0.14 g, 0.30 mmol) was dissolved in dry THF (5 mL) and added drop-wise (10 min) to a suspension of NaH (0.014 g, 0.60 mmol) in THF (5 mL) at 0 °C with stirring. The mixture was stirred further at this temperature for 0.5 h. Then 4-nitrobenzaldehyde (0.05 g, 0.30 mmol) in THF (2 mL) was added and the mixture stirred for 12 h at room temperature. Water (10 mL) was added and the aqueous layer thoroughly extracted with diethyl ether (3 x 20 mL). The organic layer was collected, dried (Na_2SO_4), filtered and the solvent removed from the filtrate to give a residue that was purified by column chromatography [silica gel, ethyl acetate-

hexane (1:4)] to furnish **120**. Compounds **121**, **123-124** were also synthesized in a manner similar to compound **120**.

Compound 120



Yield: 0.09 g (73%).

Mp: 124-126 ^{o}C (yellow solid).

IR (KBr): 2963, 1703, 1588, 1343, 1262, 1020 cm^{-1}.

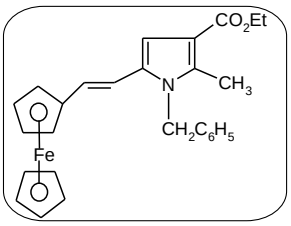
^{1}H NMR: δ 1.39 (t, ^{3}J(H-H) = 7.2 Hz, 3H, $CO_2CH_2CH_3$), 2.54 (s, 3H, CCH_3), 4.32 (qrt, ^{3}J(H-H) = 7.2 Hz, 2H, $CO_2CH_2CH_3$), 5.24 (s, 2H, NCH_2), 6.95-7.01 (m, 3H, Ar-*H*), 7.08 (s, 1H, Ar-*H*), 7.30-7.46 (m, 6H, Ar-*H*), 8.12-8.15 (m, 2H, Ar-*H*).

^{13}C NMR: δ 11.5, 14.5, 47.0, 59.7, 109.6, 113.6, 120.6, 124.2, 124.6, 125.6, 126.2, 127.9, 128.1, 128.6, 129.2, 130.4, 136.5, 138.4, 144.0, 165.1.

LC-MS: *m/z* 391 $[M+1]^{+}$.

Anal. Calcd. for $C_{23}H_{22}N_2O_4$: C, 70.75; H, 5.68; N, 7.17. Found: C, 70.68; H, 5.75; N, 7.22.

Compound 121



This compound was prepared from **119** (0.34 g, 0.75 mmol) and ferrocene carboxaldehyde (0.16 g, 0.75 mmol). It was isolated by using hexane as the eluent.

Yield: 0.24 g (74%).

Mp: 118-120 ^{o}C (violet solid).

IR (KBr): 3372, 2926, 1696, 1427, 1240, 1211, 1161, 1028 cm^{-1}.

^{1}H NMR: δ 1.39 (t, ^{3}J(H-H) = 7.2 Hz, 3H, $CO_2CH_2CH_3$), 2.52 (s, 3H, CH_3), 4.02 (s, 5H, ferrocenyl-*H*), 4.21-4.30 (m, 6H, ferrocenyl-*H* + $CO_2CH_2CH_3$), 5.16 (s, 2H, NCH_2), 6.39 (d, ^{3}J(H-H) ~ 15.8 Hz, 1H,

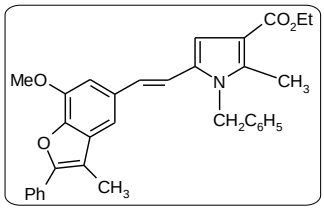
CH_A=CH$_B$), 6.66 (d, ^3J(H-H) ~ 15.8 Hz, 1H, CH$_A$=CH_B), 6.84 (s, 1H, Ar-*H*), 6.99-7.01 (m, 2H, Ar-*H*), 7.29-7.36 (m, 3H, Ar-*H*).

^{13}C NMR: δ 11.3, 14.6, 46.9, 59.4, 66.5, 68.9, 69.2, 83.4, 106.3, 112.6, 114.0, 125.8, 126.6, 127.6, 128.9, 131.9, 136.4, 137.1, 165.5.

LC-MS: *m/z* 452 $[M-1]^+$.

Anal. Calcd. for $C_{27}H_{27}NO_2Fe$: C, 71.53; H, 6.00; N, 3.09. Found: C, 71.42; H, 6.08; N, 3.15.

Compound 123



This compound was prepared from **119** (0.14 g, 0.3 mmol) and compound **122**[58] (0.08 g, 0.3 mmol). It was isolated by using ethyl acetate-hexane (1:4) mixture as the eluent.

Yield: 0.11 g (76%).

Mp: 120-122 ^{o}C (white solid).

IR (KBr): 2976, 2930, 1694, 1597, 1453, 1215, 1100, 1055 cm^{-1}.

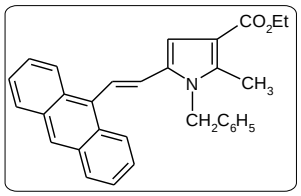
^{1}H NMR: δ 1.39 (t, ^3J(H-H) ~ 7.0 Hz, 3H, $CO_2CH_2CH_3$), 2.45 (s, 3H, CH_3), 2.53 (s, 3H, CH_3), 4.03 (s, 3H, OCH_3), 4.32 (qrt, ^3J(H-H) ~ 7.0 Hz, 2H, $CO_2CH_2CH_3$), 5.23 (s, 2H, NCH_2), 6.76-6.79 (m, 2H, Ar-*H*), 6.96 (s, 1H, Ar-*H*), 7.02-7.09 (m, 4H, Ar-*H*), 7.27-7.38 (m, 4H, Ar-*H*), 7.45-7.49 (m, 2H, Ar-*H*), 7.80-7.82 (m, 2H, Ar-*H*).

^{13}C NMR: δ 9.7, 11.4, 14.6, 47.1, 56.3, 59.5, 105.1, 107.2, 109.9, 111.6, 112.8, 115.4, 125.9, 126.8, 127.6, 128.0, 128.6, 128.8, 129.0, 131.1, 131.6, 133.1, 136.9$_6$, 137.0$_3$, 142.8, 145.1, 151.5, 165.5.

LC-MS: *m/z* 506 $[M+1]^+$.

Anal. Calcd. for $C_{33}H_{31}NO_4$: C, 78.39; H, 6.18; N, 2.77. Found: C, 78.26; H, 6.21; N, 2.71.

Compound 124



This compound was prepared from **119** (0.30 g, 0.7 mmol) and 9-anthraldehyde (0.14 g, 0.7 mmol). It was isolated by using ethyl acetate-hexane (1:4) mixture as the eluent.

Yield: 0.23 g (78%).

Mp: 128-130 ^{o}C (yellow solid).

IR (KBr): 2986, 2928, 1698, 1443, 1242, 1211, 1169, 1069 cm^{-1}.

^{1}H NMR: δ 1.43 (t, ^{3}J(H-H) ~ 7.0 Hz, 3H, $CO_2CH_2CH_3$), 2.61 (s, 3H, CH_3), 4.37 (qrt, ^{3}J(H-H) ~ 7.0 Hz, 2H, $CO_2CH_2CH_3$), 5.21 (s, 2H, NCH_2), 6.68 (d, ^{3}J(H-H) ~ 16.2 Hz, 1H, CH_A=CH_B), 6.98-6.99 (m, 2H, Ar-*H*), 7.21 (s, 1H, Ar-*H*), 7.28-7.45 (m, 7H, Ar-*H*), 7.72 (d, ^{3}J(H-H) ~ 16.2 Hz, 1H, CH_A=CH_B), 7.95-7.97 (m, 2H, Ar-*H*), 8.08-8.10 (m, 2H, Ar-*H*), 8.34 (s, 1H, Ar-*H*).

^{13}C NMR: δ 11.4, 14.6, 47.0, 59.6, 107.8, 112.9, 123.6, 125.1, 125.4, 125.7, 125.8, 126.0, 126.3, 127.6, 128.6, 129.0, 129.6, 131.2, 131.4, 132.6, 136.8, 137.3, 165.5.

LC-MS: *m/z* 446 $[M+1]^{+}$.

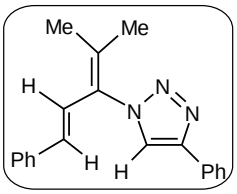
Anal. Calcd. for $C_{31}H_{27}NO_2$: C, 83.57; H, 6.11; N, 3.14. Found: C, 83.45; H, 6.17; N, 3.19. This compound was crystallized from ethyl acetate-hexane (9:1) at 25 ^{o}C. X-ray structure was determined for this sample (Fig. 28 in Chapter 2).

(c) Synthesis of alkenyl-triazoles 125-128

The phosphonate **113** (0.100 g, 0.30 mmol) was dissolved in dry THF (5 mL) and slowly added to a suspension of NaH (0.013 g, 0.60 mmol) in THF (5 mL) at 0°C and the mixture stirred at this temperature for 0.5 h. Then, benzaldehyde (0.032 g, 0.30 mmol) in THF (2 mL) was added and the mixture stirred for 2 h. Water (10 mL) was added and the aqueous layer was thoroughly extracted with ether (3x20 mL). The organic layer was collected, dried (Na_2SO_4), filtered and solvent removed from the filtrate to give a residue that was purified by column chromatography to

obtain compound **125** as colorless solid. Compounds **126-128** were synthesized similarly by using same molar quantities.

Compound 125



Yield: 0.063 g (75%).

Mp: 118-120 ^{o}C (white solid).

IR (KBr): 1636, 1483, 1426, 1219, 1019, 949 cm^{-1}.

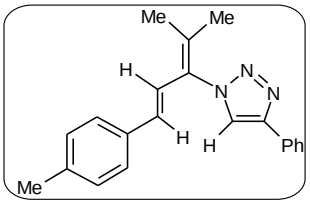
^{1}H NMR: δ 1.62 (s, 3H), 2.15 (s, 3H), 5.80 (d, *J* = 16.0 Hz, 1H), 7.20-7.95 (m, 12H).

^{13}C NMR: δ 20.0, 21.0, 121.7, 122.2, 125.9, 126.8, 128.1, 128.4, 128.8, 129.0, 129.6, 130.7, 131.1, 136.6, 137.1, 147.4.

LC-MS: *m/z* 302 [M+1]$^{+}$.

Anal. Calcd. for $C_{20}H_{19}N_3$: C, 79.70; H, 6.35; N, 13.94. Found: C, 79.77; H, 6.40; N, 14.10.

Compound 126



Yield: 0.069 g (78%).

Mp: 121-122 ^{o}C (white solid).

IR (KBr): 1611, 1510, 1424, 1227, 1020 cm^{-1}.

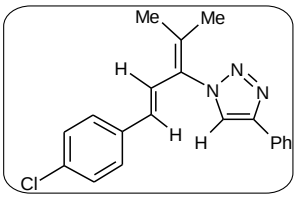
^{1}H NMR: δ 1.62 (s, 3H), 2.15 (s, 3H), 2.32 (s, 3H), 5.77 (d, *J* = 16.0 Hz, 1H), 7.11-7.95 (m, 11H).

^{13}C NMR: δ 20.0, 20.9, 21.3, 121.3, 121.8, 125.9, 126.7, 128.3, 129.0, 129.5, 131.1, 133.8, 136.4, 138.1, 147.4.

LC-MS: *m/z* 316 [M+1]$^{+}$.

Anal. Calcd. for $C_{21}H_{21}N_3$: C, 79.97; H, 6.71; N, 13.32. Found: C, 79.90; H, 6.51; N, 13.48.

Compound 127



Yield: 0.070 g (75%).

Mp: 60-62 ^{o}C (white solid).

IR (KBr): 1640, 1489, 1424, 1227, 1090, 1020 cm^{-1}.

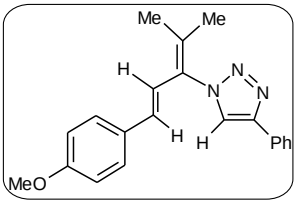
^{1}H NMR: δ 1.63 (s, 3H), 2.16 (s, 3H), 5.73 (d, *J* = 16.0 Hz, 1H), 7.17-7.94 (m, 11H).

^{13}C NMR: δ 20.0, 21.0, 121.7, 122.7, 125.8, 127.9, 128.2, 128.4, 128.9, 129.0, 130.5, 130.8, 133.7, 135.1, 137.8, 147.5.

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

Anal. Calcd. for $C_{20}H_{18}N_3$: C, 71.53; H, 5.40; N, 12.51. Found: C, 71.52; H, 5.39; N, 12.47.

Compound 128



Yield: 0.071 g (76%).

Mp: 123-125 ^{o}C (white solid).

IR (KBr): 1605, 1510, 1424, 1242, 1179, 1032 cm^{-1}.

^{1}H NMR: δ 1.61 (s, 3H), 2.14 (s, 3H), 3.79 (s, 3H), 5.74 (d, *J* = 15.6 Hz, 1H), 6.80-7.96 (m, 11H).

^{13}C NMR: δ 20.0, 21.0, 55.4, 114.2, 120.2, 121.8, 125.8, 128.0, 128.3, 129.0, 129.1, 129.3, 130.7, 131.1, 135.7, 147.3, 159.7.

LC-MS: *m/z* 332 $[M+1]^{+}$.

Anal. Calcd. for $C_{21}H_{21}N_3O$: C, 76.11; H, 6.39; N, 12.68. Found: C, 76.08; H, 6.41; N, 12.78.

3.6 X-ray crystallography

A suitable crystal was mounted on a glass fiber (for **15a**, **18**, **20**.CH_2Cl_2, **22**, **24**, **29**.2CH_3CN, **33**, **44**, **46**.CH_2Cl_2, **46'**, **48**, **53**, **55**, **57**, **61**, **63**, **67**, **75**, **76**, **79**, **90**, **97**.H_2O, **107**, **115** and **124**) 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.[101] 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. Crystal data are summarized in Tables 9-15.

Table 9. Crystal data for compounds **15a**, **18**, **20**.CH_2Cl_2 and **22**[a]

Compound	**15a**	**18**	**20.CH_2Cl_2**	**22**
Emp. formula	$C_{21}H_{17}O_2P$	$C_{24}H_{21}O_2P$	$C_{41}H_{48}Cl_2O_{14}P_2$	$C_{38}H_{43}O_7P$
Formula weight	332.32	372.38	897.63	642.69
Crystal system	Monoclinic	Monoclinic	Orthorombic	Monoclinic
Space group	*P2(1)/c*	*P2(1)/c*	*P2(1)2(1)2(1)*	*P2(1)/n*
a /Å	12.678(2)	6.6332(6)	11.3587(9)	13.1399(11)
b /Å	17.397(3)	19.8814(18)	18.5030(13)	11.3816(10)
c /Å	17.716(5)	15.5910(14)	20.2698(12)	24.2961(17)
α/deg	90	90	90	90
β/deg	114.278(18)	105.794(8)	90	114.555(4)
γ/deg	90	90	90	90
V /Å^3	3561.9(13)	1978.5(3)	4260.1(5)	3304.9(5)
Z	8	4	4	4
D_{calc} /g cm^{-3}]	1.239	1.250	1.400	1.292
μ /mm^{-1}	0.163	0.154	0.294	0.133
F(000)	1392	784	1880	1368
Data/ restraints/ parameters	5114/0/439	3465/0/246	7420/0/540	5831/0/425
S	0.866	1.026	1.010	1.127
R1 [I>2σ(I)]	0.0426	0.0518	0.0467	0.0827

wR2 [all data]	0.0916	0.1307	0.1239	0.2002
Max./min. residual electron dens. [eÅ^{-3}]	0.163/-0.264	0.463/-0.231	0.312/-0.507	0.772/-0.342

[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 10. Crystal data for compounds **24**, **29**.2CH_3CN, **33**, and **44**[a]

Compound	**24**	**29.2CH_3CN**	**33**	**44**
Emp. formula	$C_{82}H_{78}Cl_3O_{16}P_2$	$C_{48}H_{53}N_2O_7P$	$C_{22}H_{27}O_7P$	$C_{34}H_{31}O_4P$
Formula weight	1487.73	800.89	434.41	534.56
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	*P21/n*	*P-1*	*P2(1)/c*	*P2(1)/c*
a /Å	10.1875(3)	9.7058(15)	13.0951(10)	11.7888(17)
b /Å	16.8758(5)	14.241(2)	9.4194(7)	14.997(2)
c /Å	21.7741(6)	16.630(2)	20.0552(12)	16.960(4)
α/deg	90	69.432(14)	90	90
β/deg	103.217(3)	84.421(13)	117.713(4)	112.545(16)
γ/deg	90	76.489(14)	90	90
V /Å^3	3644.29(18)	2092.2(5)	2190.0(3)	2769.3(8)
Z	2	2	4	4
D_{calc} /g cm^{-3}]	1.356	1.271	1.317	1.282
μ /mm^{-1}	0.240	0.121	0.166	0.137
F(000)	1558	852	920	1128
Data/ restraints/ parameters	5408/0/470	7245/0/535	3836/0/ 276	4861/0/354
S	1.050	0.854	1.035	1.031
R1 [I>2σ(I)]	0.0522	0.0419	0.0498	0.0350
wR2 [all data]	0.1526	0.0816	0.1268	0.0913
Max./min. residual electron dens. [eÅ^{-3}]	0.354/-0.414	0.305/-0.284	0.405/-0.324	0.253/-0.306

[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 11. Crystal data for compounds **46**.CH_2Cl_2, **46'**, **48** and **53**[a]

Compound	**46.CH_2Cl_2**	**46'**	**48**	**53**
Emp. formula	$C_{36}H_{35}Cl_2O_5P$	$C_{35}H_{33}O_5P$	$C_{26}H_{22}O_3$	$C_{40}H_{35}O_2P$
Formula weight	649.51	564.58	382.44	578.65
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	*P2(1)/c*	*P2(1)/c*	*P-1*	*P-1*
a /Å	9.9415(2)	10.3316(7)	9.315(5)	9.8726(6)
b /Å	27.0182(6)	16.5344(11)	10.467(6)	11.7485(7)
c /Å	14.0924(4)	17.8866(16)	11.211(6)	14.2263(9)
α/deg	90	90	76.848(9)	94.0200(10)
β/deg	124.847(2)	108.912(7)	76.187(10)	91.4210(10)
γ/deg	90	90	75.850(10)	111.2630(10)
V /Å^3	3106.47(13)	2890.6(4)	1012.5(10)	1531.73(16)
Z	4	4	2	2
D_{calc} /g cm^{-3}]	1.389	1.297	1.254	1.255
μ /mm^{-1}	0.304	0.138	0.081	0.125
F(000)	1360	1192	404	612
Data/ restraints/ parameters	5461/0/400	5083/0/373	3561/0/263	5395/0/388
S	1.073	0.958	1.043	1.042
R1 [I>2σ(I)]	0.0684	0.0383	0.0785	0.0457
wR2 [all data]	0.1876	0.0956	0.1891	0.1136
Max./min. residual electron dens. [eÅ^{-3}]	1.715/-1.245	0.241/-0.302	0.252/-0.242	0.324/-0.242

[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 12. Crystal data for compounds **55**, **57**, **61**, and **63**[a]

Compound	**55**	**57**	**61**	**63**
Emp. formula	$C_{34}H_{35}O_4P$	$C_{40}H_{39}O_4P$	$C_{18}H_{30}O_6P_2$	$C_{28}H_{27}O_3P$
Formula weight	538.59	614.68	404.36	442.47
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	*P2(1)/c*	*P2(1)/c*	*Pbcn*	*P2(1)/c*
a /Å	13.2152(16)	15.8406(19)	16.291(6)	9.9536(8)
b /Å	14.2689(15)	14.0154(11)	12.324(4)	16.2868(13)
c /Å	17.500(3)	19.0996(19)	10.331(4)	14.8946(12)
α/deg	90	90	90	90
β/deg	121.267(10)	108.257(12)	90	105.6560(10)
γ/deg	90	90	90	90
V /Å^3	2820.6(7)	4026.9(7)	2074.1(13)	2325.0(3)
Z	4	4	4	4
D_{calc} /g cm^{-3}]	1.268	1.014	1.295	1.264
μ /mm^{-1}	0.135	0.102	0.239	0.146
F(000)	1144	1304	864	936
Data/ restraints/ parameters	4948/0/ 354	6919/0/408	2536/0/121	4587/0/291
S	0.938	0.918	1.102	1.134
R1 [I>2σ(I)]	0.0446	0.0807	0.0463	0.0608
wR2 [all data]	0.1148	0.2890	0.1292	0.1410
Max./min. residual electron dens. [eÅ^{-3}]	0.336/-0.364	0.722/-0.315	0.357/-0.235	0.365/-0.278

[a]$R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma wF_o^4]^{0.5}$

Table 13. Crystal data for compounds **67**, **75**, **76**, and **79**[a]

Compound	**67**	**75**	**76**	**79**
Emp. formula	$C_{29}H_{23}OP$	$C_{26}H_{25}O_2P$	$C_{24}H_{24}ClO_2P$	$C_{24}H_{23}O_2P$
Formula weight	418.44	400.43	410.85	374.39
Crystal system	Monoclinic	Triclinic	Orthorhombic	Monoclinic
Space group	*Cc*	*P-1*	*Pna2(1)*	*P2(1)/c*
a /Å	15.8800(15)	9.892(3)	17.5578(8)	11.4961(7)
b /Å	9.9538(9)	11.884(4)	8.6412(4)	14.8975(11)
c /Å	15.1330(14)	18.630(6)	28.8289(17)	16.1208(12)
α/deg	90	97.442(5)	90	90
β/deg	107.2870(10)	98.266(6)	90	132.778(4)
γ/deg	90	90.151(5)	90	90
V /Å^3	2284.0(4)	2148.6(12)	4373.9(4)	2026.5(2)
Z	4	4	8	4
D_{calc} /g cm^{-3}]	1.217	1.238	1.248	1.227
μ /mm^{-1}	0.138	0.147	0.264	0.151
F(000)	880	848	1728	792
Data/ restraints/ parameters	4351/2/281	7550/0/523	4599/0/509	3525/0/246
S	1.076	1.114	0.950	0.983
R1 [I>2σ(I)]	0.0381	0.0674	0.0397	0.0584
wR2 [all data]	0.0938	0.1789	0.0893	0.1145
Max./min. residual electron dens. [eÅ^{-3}]	0.193/-0.247	0.406/-0.260	0.178/-0.165	0.222/-0.275

[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 14. Crystal data for compounds **90**, **97**.H_2O, **107** and **115**[a]

Compound	**90**	**97.H_2O**	**107**	**115**
Emp. formula	$C_{14}H_{22}NO_5P$	$C_{13}H_{22}NO_5P$	$C_{11}H_{15}NO_3$	$C_{18}H_{30}N_2O_6P_2$
Formula weight	315.30	303.29	209.24	432.38
Crystal system	Orthorhombic	Triclinic	Monoclinic	Monoclinic
Space group	*Pna2(1)*	*P-1*	*P2(1)/c*	*P2(1)/c*
a /Å	22.0358(19)	5.5991(8)	8.0841(11)	15.587(2)
b /Å	6.0237(5)	10.8370(15)	6.8413(9)	6.0979(8)
c /Å	24.783(2)	13.4812(18)	20.348(3)	11.5256(15)
α/deg	90	104.942(12)	90	90
β/deg	90	99.962(11)	103.655(5)	103.146(2)
γ/deg	90	96.168(11)	90	90
V /Å^3	3289.6(5)	768.43(18)	1093.6(3)	1066.8(2)
Z	8	2	4	2
D_{calc} /g cm^{-3}]	1.273	1.311	1.271	1.346
μ /mm^{-1}	0.186	0.197	0.093	0.240
F(000)	1344	324	448	460
Data/ restraints/ parameters	5788/4/391	2604/0/189	1921/0/140	1886/0/130
S	1.173	1.081	1.058	1.077
R1 [I>2σ(I)]	0.0790	0.0483	0.0548	0.0385
wR2 [all data]	0.1962	0.1337	0.1447	0.1021
Max./min. residual electron dens. [eÅ^{-3}]	0.478/-0.267	0.367/-0.258	0.227/-0.154	0.194/-0.321

[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 15. Crystal data for compound **124**[a]

Compound	**124**
Emp. formula	$C_{31}H_{27}NO_2$
Formula weight	445.54
Crystal system	Monoclinic
Space group	*P2(1)/c*
a /Å	11.605(3)
b /Å	20.308(5)
c /Å	10.711(3)
α/deg	90
β/deg	106.598(5)
γ/deg	90
V /Å^3	2419.1(11)
Z	4
D_{calc} /g cm^{-3}]	1.223
μ /mm^{-1}	0.076
F(000)	944
Data/ restraints/ parameters	4220/0/309
S	1.003
R1 [I>2σ(I)]	0.1027
wR2 [all data]	0.1973
Max./min. residual electron dens. [eÅ^{-3}]	0.162/-0.155

[a]$R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma wF_o^4]^{0.5}$

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PART-B

PALLADIUM-CATALYZED DIARYLATION OF ALKYNES

INTRODUCTION

4.1 General Introduction: Phosphono-alkynes and diarylalkynes

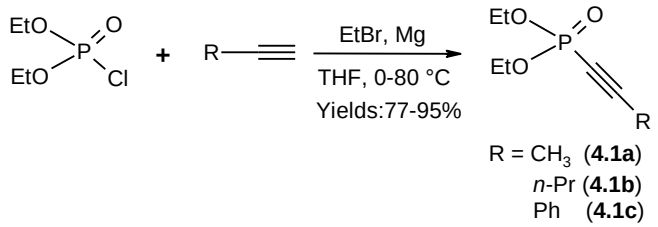
Alkynylphosphonates are valuable synthetic intermediates as Michael acceptors and as components of cycloaddition reactions.[1] The reactivity and versatility of alkynylphosphonates have made them synthetically more valuable precursors compared to other phosphonates. Two important reactions wherein alkynylphosphonates are employed include (i) the synthesis of highly substituted vinylphosphonates *via* metallation reactions[2] and (ii) the preparation of biaryl or biaryl-like framework *via* cycloaddition reactions.[3] As far as reactions of alkynes are concerned, numerous variations of the well established reactions like Suzuki-Miyaura and Sonogashira couplings are available in the literature.[4] A brief survey of the literature on phosphono-alkynes as pertinent to this work is outlined below.

4.2 Synthesis of phosphono-alkynes

The first 1-alkynylphosphonate (diethyl 1-propynylphosphonate) was prepared by Jacobson *et al*. in 1957.[5] Subsequently, four main synthetic routes for alkynylphosphonates have been developed. These include the Michaelis-Arbuzov and Michaelis-Becker reactions, the phosphite-allenylphosphonate rearrangement, carbanionic displacements at pentavalent phosphorus centers [$S_NP(V)$], and conversion of vinyl to alkynylphosphonates by addition-elimination reactions.[6] Some of the other significant routes to phosphonoalkynes are discussed below.

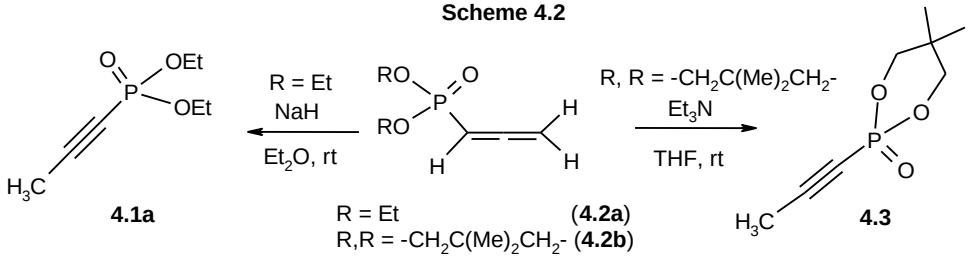
Synthesis of phosphonoalkynes (e. g. **4.1a-c**) by the treatment of alkynylmagnesium bromides with phosphorochloridates is a well established procedure[7] (Scheme 4.1). This method provides a very useful synthetic strategy for the formation of alkyl or aryl substituted phosphonoalkynes.

Scheme 4.1



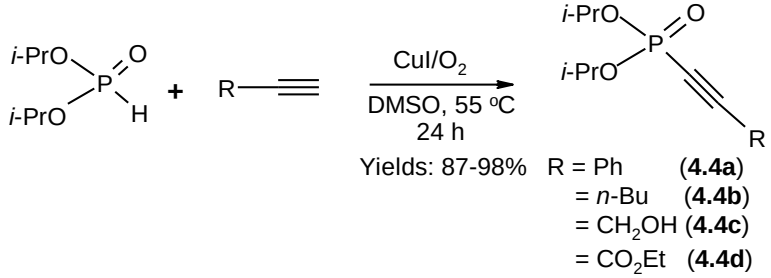
A simple approach to methyl substituted alkynylphosphonates of the type **4.1a** is the rearrangement of corresponding allene **4.2a** in the presence of a base (NaH).[8a] The new phosphono-alkyne **4.3** was prepared in our laboratory by the same route using Et_3N as a base (Scheme 4.2). [8b]

Scheme 4.2



Han and co-workers disclosed a new methodology for the construction of P-C bonds via an aerobic oxidative coupling of terminal alkynes with *H*-phosphonates[9] (Scheme 4.3). This reaction is efficiently catalyzed by CuI to generate alkynylphosphonates **4.4a-d** in high yields. It provides an easy access to various substituted alkynylphosphonates.

Scheme 4.3



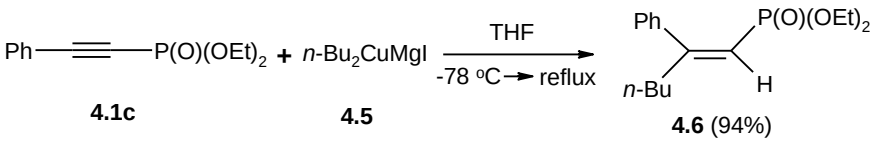
4.3 Reactions of alkynes

4.31 Reactions of phosphonoalkynes (alkynylphosphonates)

As discussed above, metallation and cycloaddition are the two major classes of reactions of alkynylphosphonates. Recently, some transition-metal or base-catalyzed cyclization reactions are also reported. In this section, selected substitution, cycloaddition and cyclization reactions of phosphonoalkynes are discussed.

Oh and Gil reported a synthetic route for vinylic phosphonates **4.6** via the addition of organocopper(I) reagent **4.5** to 1-alkynylphosphonates **4.1c** (Scheme 4.4).[10] Subsequent capture of the vinylcopper intermediate by several electrophiles resulted in 1,2,2-trisubstituted vinylic phosphonates in high regio- and stereo-selectivity and good yields.

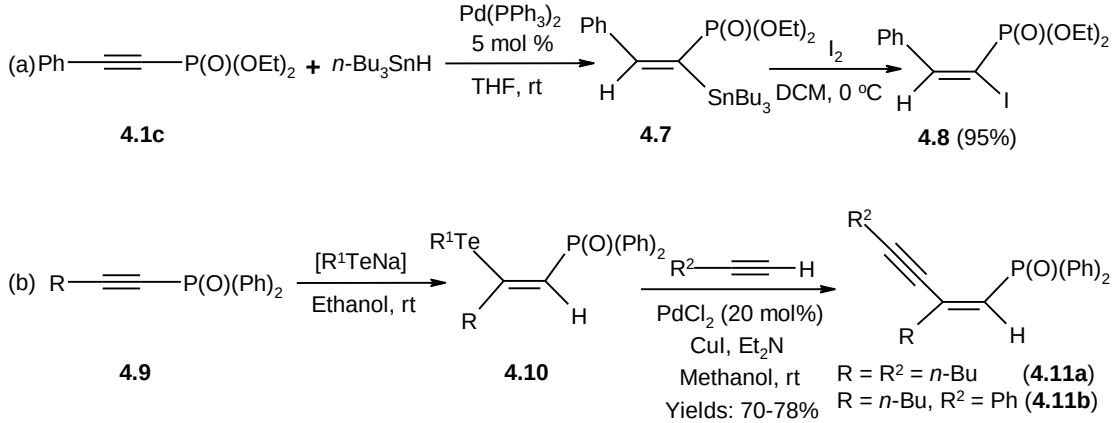
Scheme 4.4



4.1c **4.5** **4.6** (94%)

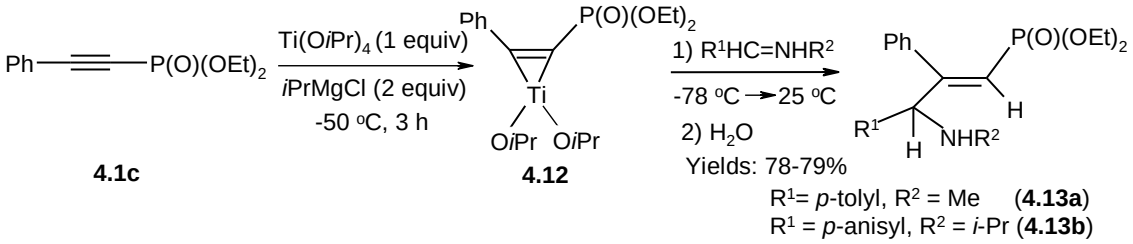
Huang and Xiong developed a facile route to the 1,2-disubstituted vinylphosphonate **4.8** from (*E*)-*α*-stannyl 1-alkenylphosphonates **4.7** which in turn was obtained *via* palladium catalyzed hydrostannation of 1-alkynylphosphonates **4.1c** (Scheme 4.5a).[11a] This method has the advantages of mild reaction conditions and simple procedure, in addition to high regio- and stereo-selectivity. In a similar manner, Braga *et al*. synthesized *β*-organotelluro vinylphosphine oxide (**4.10**) by the treatment of 1-alkenylphosphine oxides (**4.9**) with tellurolate anions (Scheme 4.5b). These products were utilized in coupling reaction with terminal alkynes in the presence of $PdCl_2$/CuI, triethylamine and methanol to give *β*-alkynyl vinylphosphine oxides **4.11a-b**.[11b]

Scheme 4.5



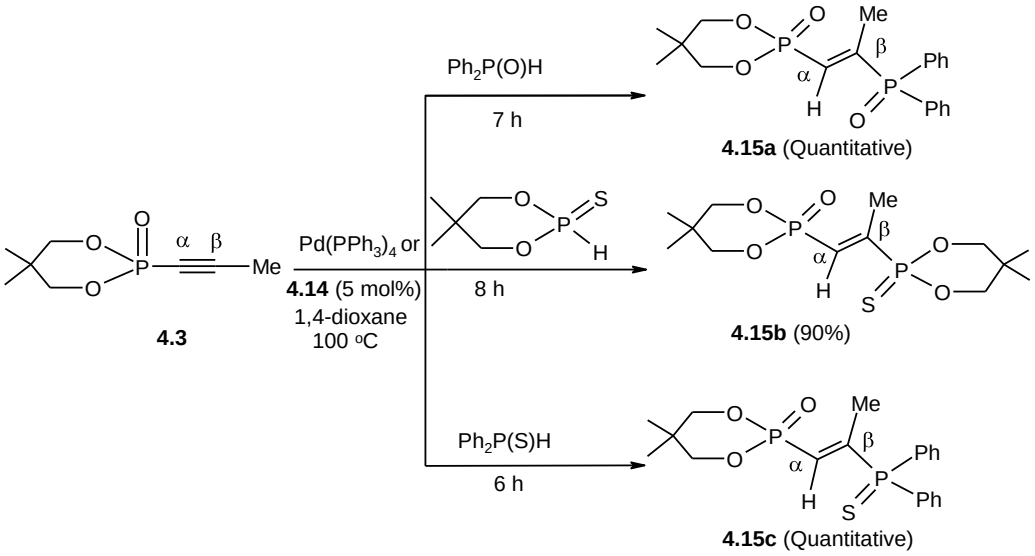
Srebnik *et al*. developed a new methodology for the synthesis of 3-amino-1-alkenylphosphonates **4.13a-b** by the reaction of imines and alkynylphosphonate **4.1c** in the presence of Ti(O*i*Pr)$_4$ (Scheme 4.6).[12] This synthetic route proceeds *via* alkynylphosphonate titanium(II) complex **4.12** formed from 1-alkynylphosphonate, Ti(O*i*Pr)$_4$ and *i*PrMgCl leading to **4.13a-b** regio- and stereo-selectively in high yields.

Scheme 4.6



From our laboratory, an effective, recoverable, dinuclear palladium(I)-catalyst [(OCH$_2$CMe$_2$CH$_2$O)P-S-Pd(PPh$_3$)]$_2$ (**4.14**) is developed and employed in P(X)H [X = O or S] addition reactions of phosphonoalkyne **4.3**.[13] As shown in Scheme 4.7, in all the cases the incoming phosphorus moiety attacked at the *β*-position of alkyne **4.3** to afford **4.15a-c** in excellent yields.

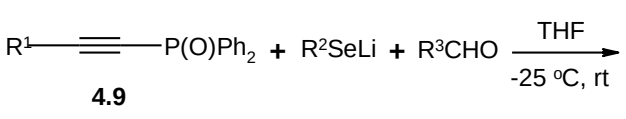
Scheme 4.7



4.14 = $[(OCH_2CMe_2CH_2O)P\text{-}S\text{-}Pd(PPh_3)]_2$

Xiong and Huang developed an efficient one-pot three-component Michael/aldol/Horner–Wadsworth–Emmons (HWE) tandem reaction for the synthesis of selenium-substituted allenes **4.16** from lithium alkylselenolates, 1-alkynylphosphine oxides **4.9** and aldehydes (Scheme 4.8).[14] This method has the advantages of readily available starting materials, mild reaction conditions and good yields of products.

Scheme 4.8



4.9

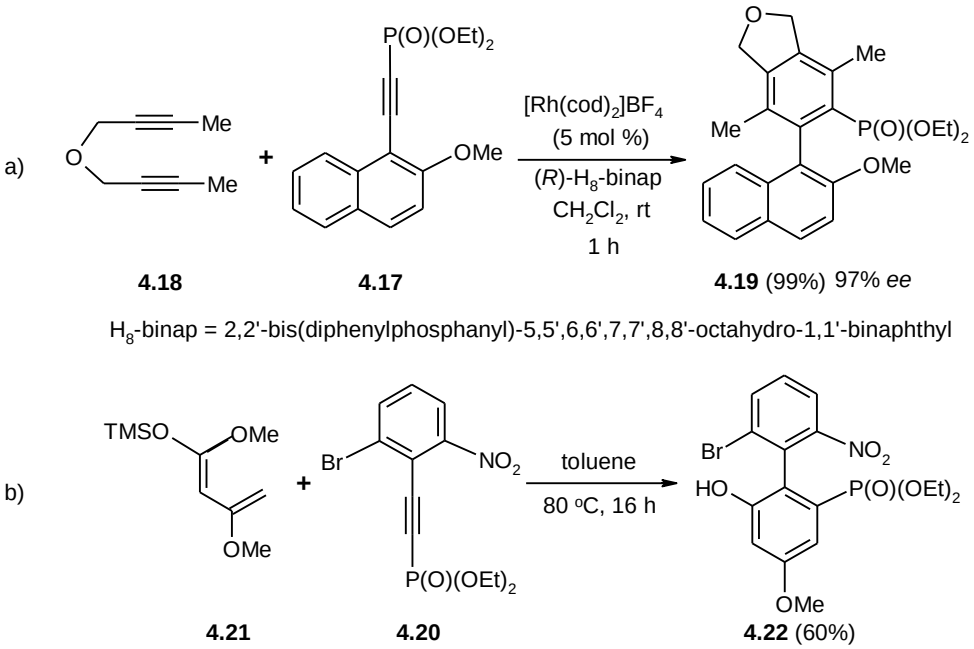
Yields: 71-89%

R^1 = Ph, R^2 = *n*-Bu, R^3 = 4-ClC_6H_4 (**4.16a**)
R^1 = Ph, R^2 = *n*-Bu, R^3 = Ph (**4.16b**)
R^1 = Ph, R^2 = *i*-Pr, R^3 = 4-$MeOC_6H_4$ (**4.16c**)
R^1 = CH_2OCH_3, R^2 = *n*-Bu, R^3 = Ph (**4.16d**)

Alkynyl phosphonates/ phosphine oxides are employed for the preparation of a range of axially chiral biaryl phosphorus compounds in which the aromatic ring bonded to the phosphorus atom is highly substituted. For example, Tanaka and co-workers investigated a Rh-catalyzed asymmetric [2+2+2] cycloaddition of alkynylphosphonate **4.17** and 1,3-diyne compound **4.18** to form tetra-ortho-substituted axially chiral biaryl

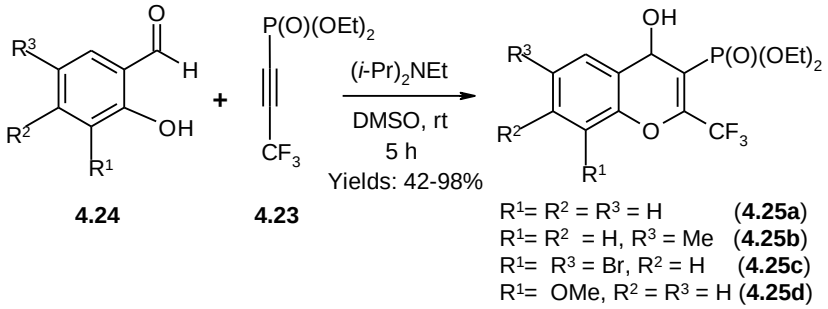
phosphonate **4.19** (Scheme 4.9a).[15a] Carter and co-workers also employed the Diels-Alder approach for the construction of highly substituted, orthogonally functionalized biaryl compound **4.22** by the thermally assisted [4+2] cycloaddition of phosphonoalkyne **4.20** and 1,3-butadiene derivative **4.21** (Scheme 4.9b).[15b,c]

Scheme 4.9



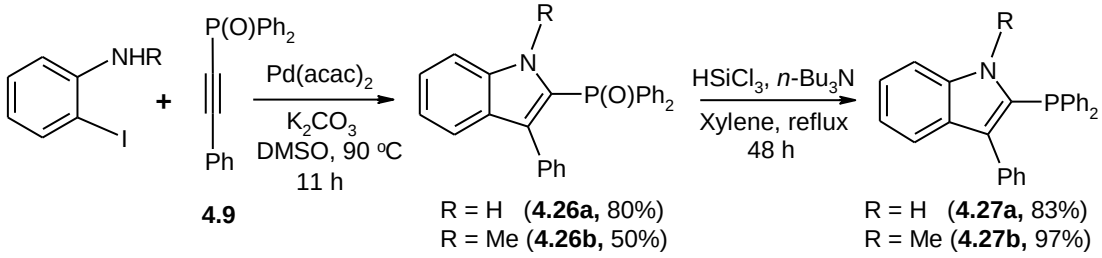
Tverdomed *et al.* established a regioselective synthetic route to 2-perfluoralkyl 4*H*-chromen-3-ylphosphonates **4.25** *via* the cycloaddition of 2-hydroxybenzaldehyde derivatives **4.24** to perfluoroalkynephosphonates **4.23** using trialkyl amines or phosphines as mediators (Scheme 4.10).[16] The substituent loading on the aromatic ring of salicylaldehyde resulted in various 2-perfluoralkyl 4*H*-chromen-3-ylphosphonates (**4.25a-d**).

Scheme 4.10



Oshima and co-workers reported a new method for the synthesis of bulky indole-based heteroarylphosphine oxides **4.26a-b** by Pd-catalyzed annulation of 1-alkynylphosphine oxide **4.9** with 2-iodoanilines (Scheme 4.11).[17] Reduction of **4.26** led to trivalent heteroarylphosphines **4.27**. Thus, this sequential annulation/reduction protocol offers an efficient alternative to the conventional approach to heteroarylphosphines.

Scheme 4.11



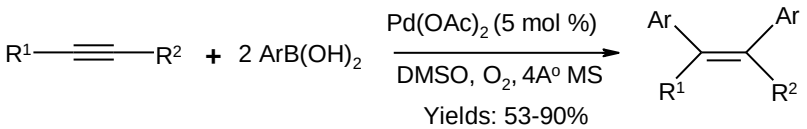
4.32 Palladium-catalyzed coupling reactions of alkynes

As mentioned above, reactions of diarylalkynes are rather unlimited. For the Pd-catalyzed synthesis of tetrasubstituted olefins (including those with internal cyclization) *via* alkynes several modifications have become available; in favorable cases using appropriate stoichiometry, cyclization or multiple-coupling may also be accomplished.[5] Some of the Pd-catalyzed coupling reactions relevant to this part of work are discussed here.

Larock *et al*. reported a novel Pd-catalyzed reaction between an arylboronic acid and an internal alkyne to obtain a wide variety of tetrasubstituted olefins **4.28a-d** in

good to excellent yields (Scheme 4.12).[18] This reaction is conducted by using molecular oxygen as an oxidant in the absence of any base. Other added advantages of this method are very mild reaction conditions and tolerance of a wide variety of functional groups, including alcohol, aldehyde, ester, TMS and acetal.

Scheme 4.12



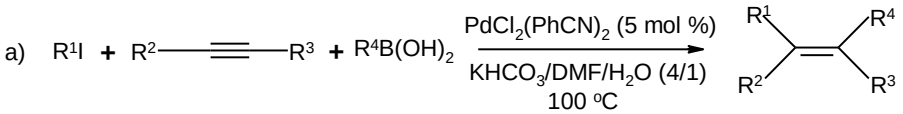
Yields: 53-90%

R^1 = Et, R^2 = Ph, Ar = Ph (**4.28a**)
R^1 = Et, R^2 = Ph, Ar = MeC_6H_4 (**4.28b**)
R^1 = CHO, R^2 = Ph, Ar = MeC_6H_4 (**4.28c**)
R^1 = CH_2OH, R^2 = Ph, Ar = MeC_6H_4 (**4.28d**)

The same group investigated a one-step Pd-catalyzed route, which entails three-component coupling of aryl iodides, internal alkynes and arylboronic acids, leading to tetrasubstituted olefins **4.29a-d** in good yields (Scheme 4.13a).[19] This simple protocol involves *cis*-addition of the aryl groups from both aryl iodide and arylboronic acid. Ishihara and co-workers reported new fluoroalkylated tetrasubstituted alkenes **4.30a-d** *via* a similar one-pot method starting from a variety of fluoroalkylated alkynes, aryl halides and arylboronic acids (Scheme 4.13b).[20]

Scheme 4.13

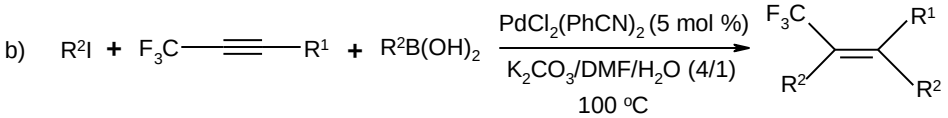
a)



Yields: 77-92%

R^1 = R^2 = R^3 = R^4 = Ph (**4.29a**)
R^1 = Ph, R^2 = Me, R^3 = R^4 = Ph (**4.29b**)
R^1 = Ph, R^2 = Me, R^3 = CO_2Et, R^4 = Ph (**4.29c**)
R^1 = 4-HOC_6H_4, R^2 = R^3 = R^4 = Ph (**4.29d**)

b)

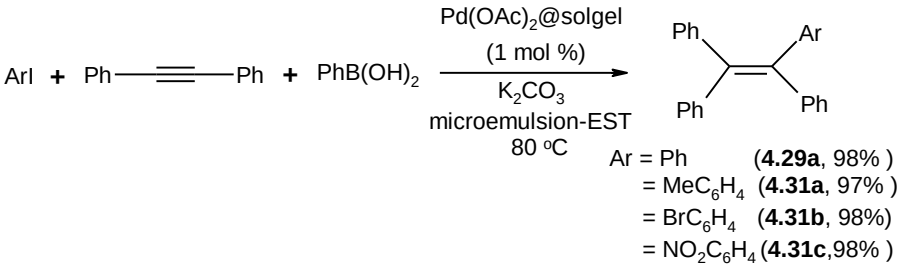


Yields: 81-93%

R^1 = 4-ClC_6H_4, R^2 = Ph (**4.30a**)
R^1 = 4-ClC_6H_4, R^2 = 4-$MeOC_6H_4$ (**4.30b**)
R^1 = 4-ClC_6H_4, R^2 = 4-MeC_6H_4 (**4.30c**)
R^1 = 4-$MeOC_6H_4$, R^2 = Ph (**4.30d**)

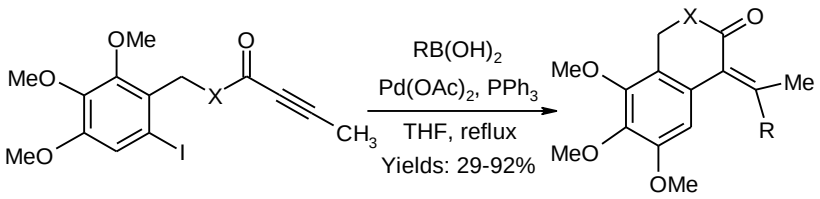
Blum and Tsvelikhovsky performed the above mentioned three component coupling to form tetrasubstituted olefins **4.29a**, **4.31a-c** under greener conditions (Scheme 4.14).[21a] This type of reaction can be carried out even with water-insoluble hydrophobic substrates by using a three-phase microemulsion/sol–gel transport system. In a related study, Wang *et al.* accomplished stereoselective synthesis of tetrasubstituted olefins *via* palladium-catalyzed three-component coupling of aryl iodides, internal alkynes, and arylboronic acids in supercritical carbon dioxide ($scCO_2$).[21b] The presence of $scCO_2$ improved the yields of the desired tetrasubstituted olefins.

Scheme 4.14



If the alkyne moiety and the iodoaryl entity are in the same molecule, cyclization in conjunction with arylation can be accomplished. Thus, Florent and co-workers reported a synthetic route for highly substituted arylethylidene-isoquinolinones **4.33a-d** *via* a tandem carbopalladation/ Suzuki-Miyaura coupling sequence[22] (Scheme 4.15).

Scheme 4.15



4.32

X = NH, R = 4-$MeOC_6H_4$ (**4.33a**)
X = NMe, R = 4-$Me_2NC_6H_4$ (**4.33b**)
X = O, R = 4-$MeOC_6H_4$ (**4.33c**)
X = O, R = 4-$Me_2NC_6H_4$ (**4.33d**)

Even though the utility of these alkynes in various metal catalyzed-coupling reactions or cyclization reactions is well documented, to our knowledge, the Pd-catalyzed coupling reactions of phosphono-alkynes leading to multiply substituted vinyl phosphonates are not reported.

OBJECTIVES OF THE PRESENT WORK - PART B

The main objective of this part of the present work is to investigate Pd-catalyzed arylation reactions of alkynes. Specifically, it is intended to explore

(i) The reactivity of phosphorus-based alkynes in three-component coupling reaction under greener conditions and to compare this with that of diarylalkynes,

(ii) The Pd-catalyzed coupling reaction of phosphonoalkynes with arylboronic acid in an effort to synthesize trisubstituted vinylphosphonates and

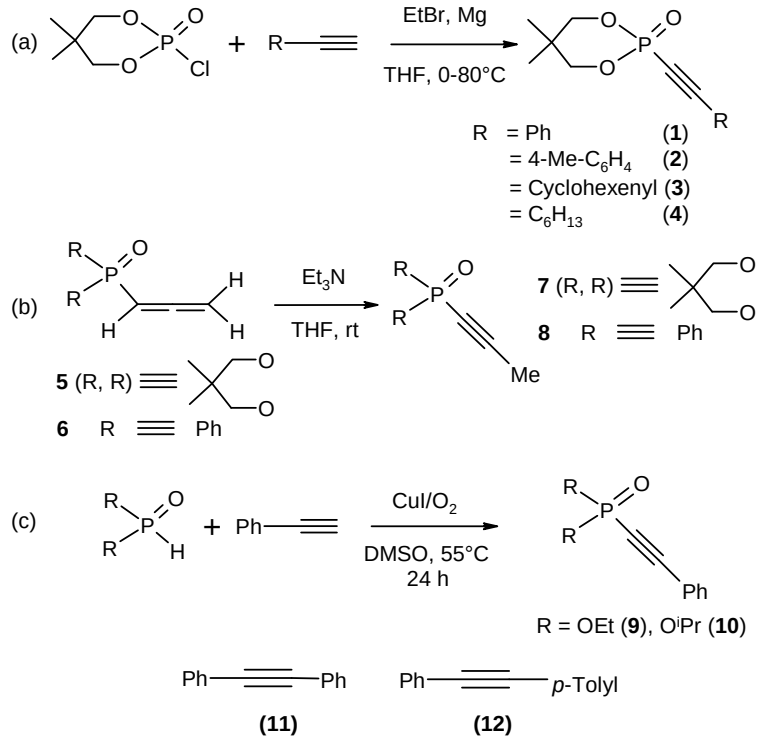
(iii) Comparing the efficiency of the new dinuclear Pd(I)-catalyst $[(OCH_2CMe_2CH_2O)P\text{-}S\text{-}Pd(PPh_3)]_2$[13] in various well known name reactions (e.g. Suzuki, Sonogashira).

RESULTS AND DISCUSSION

5.1 Synthesis of phosphorus-based alkynes 1-4/ 7-10, diarylalkynes 11-12 and the dinuclear Pd(I) catalyst 13

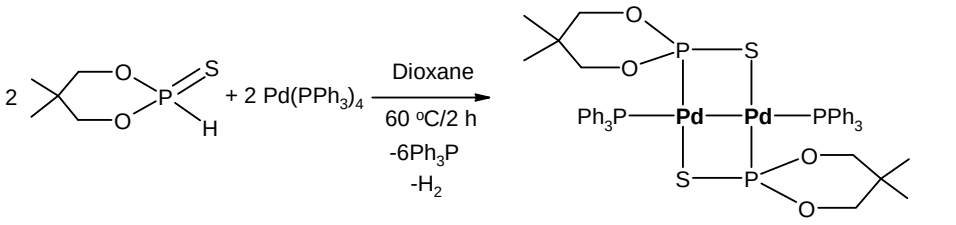
The phosphonate/ phosphine oxide precursors used for the present study are prepared by the routes shown in Scheme 1.[7-9] The alkynes **1-4** were synthesized by the reaction of $(OCH_2CMe_2CH_2O)P(O)Cl$ with various alkynylmagnesium bromides (Scheme 1a).[7] The alkynes **7-8** were obtained *via* isomerization of corresponding allenes **5-6** in the presence of base (Scheme 1b).[8b] The phosphonate precursors **9-10** were prepared by following a known literature procedure (Scheme 1c).[9] Among these, the alkynes **1-4** are new. The diarylalkynes **11-12** were synthesized by well established Sonogashira coupling procedure.[5]

Scheme 1



The dinuclear Pd(I) catalyst $[(OCH_2CMe_2CH_2O)P\text{-}S\text{-}Pd(PPh_3)]_2$ **13** (Scheme 2) was prepared by following a method reported recently from our laboratory.[13]

Scheme 2



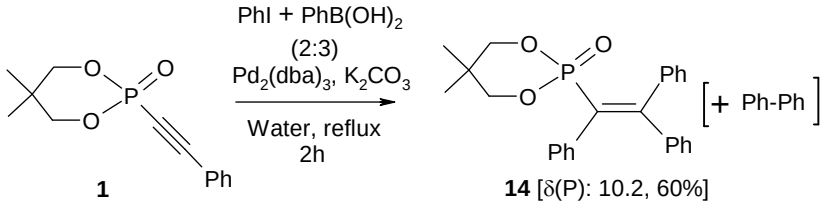
13

[δ(P): 15.3, 148.0 (d each, ^2J(P-P) = 12.2 Hz)]

5.2 Synthesis of symmetrically diarylated vinylphosphonates 14-29 and vinylphosphine oxides 30-32

Initially, in an attempt to obtain tetrasubstituted vinylphosphonates, we treated phosphonoalkyne **1** with iodobenzene and phenylboronic acid in the presence of Pd_2 (dba)$_3$ as the catalyst and K_2CO_3 as a base in water under reflux for 2 h. The expected vinylphosphonate **14** was formed in 60% yield (Scheme 3). This compound showed a band at 1591 cm^{-1} in the IR spectrum corresponding to C=C stretch. In the ^{1}H NMR spectrum, a multiplet at δ 6.98-7.46 was observed. The integrated intensity ratio of the 1,3,2-dioxaphosphorinane ring protons to the aromatic protons were in agreement with the presence of 15 aromatic protons. In the ^{13}C NMR spectrum, it exhibited a doublet at 129.4 with ^1J(P-C) of 173.0 Hz due to P*C* alkenic carbon.

Scheme 3

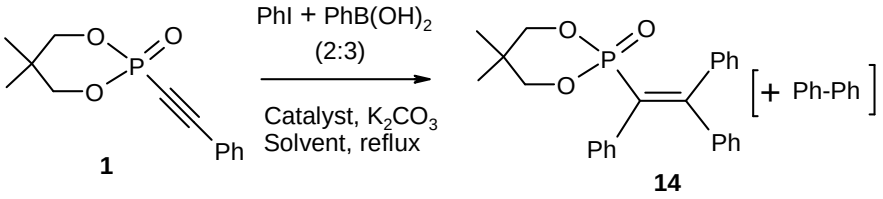


1 **14** [δ(P): 10.2, 60%]

In order to maximize the yield with a shorter reaction time, we optimized the conditions for the reaction of alkyne **1** with iodobenzene and phenylboronic acid (Scheme 4, Table 1) that leads to the vinylphosphonate **14**. As can be seen from Table 1, in both PEG-400 and water, using the new dinuclear palladium(I) complex **13** (at 1 mol % of Pd), the reaction was quantitative with all the alkyne **1** consumed within ½ h (entries 5-6). In DMF/H_2O (4:1) mixture, there was no improvement in the rate of reaction compared to water alone as a solvent (75% after 6 h). Although Pd_2(dba)$_3$ also worked well, it needed a longer reaction time (entry 7, cf. Figure 1)

and at the end of 4 h, there were some other unidentified minor peaks in the ^{31}P NMR spectrum of the reaction mixture. Other Pd-catalysts $PdCl_2(PPh_3)_2$, $PdCl_2(PhCN)_2$, $Pd(OAc)_2$, or $PdCl_2$ were less effective (entries 8-11). In the case of $PdCl_2$ the reaction was incomplete even after 12 h reflux. Either K_2CO_3 or $KHCO_3$ as a base was better than Na_2CO_3 or $NaHCO_3$. Hence, we have used the system **13**+K_2CO_3/water as the medium for the double arylation reactions.

Scheme 4



1 **14**

Table 1. Details on optimization studies for double arylation as per Scheme 4[a]

Entry	Catalyst	Solvent/duration	Yield (%)[b]
1	**13**	CH_3CN/ ½ h	n.r.
		CH_3CN/ 2 h	20
2	**13**	THF/ ½ h	n.r
		THF/ 2 h	60
3	**13**	Dioxane/ ½ h	n.r
		Dioxane/ 2 h	30
4	**13**	DMF/ ½ h	40
5	**13**	PEG-400/ ½ h	Quantitative
6	**13**	**Water/ ½ h**	**Quantitative**
7	$Pd_2(dba)_3$	Water/ ½ h	n.r.
	$Pd_2(dba)_3$	Water/ 2 h	~60
	$Pd_2(dba)_3$	Water/ 4 h	~90[c]
8	$PdCl_2(PPh_3)_2$	Water/ ½ h	10
9	$PdCl_2(PhCN)_2$	Water/ ½ h	40
10	$Pd(OAc)_2$	Water/ ½ h	20
11	$PdCl_2$	Water/ ½ h	30
12	**9** + Na_2CO_3[d]	Water/ ½ h	80
13	**9** + $NaHCO_3$[d]	Water/ ½ h	80
14	**9** + $KHCO_3$[d]	Water/ ½ h	Quantitative

[a]The ratio of alkyne:iodobenzene:arylboronic acid is 1:2:3. Alkyne **1** (0.5 mmol), PhI (1.0 mmol), $PhB(OH)_2$ (1.5 mmol), K_2CO_3 (1.5 mmol), catalyst (0.005 mmol) in solvent (5 mL) under reflux. The isolated yields are in general ca 5% lower than the ^{31}P NMR yields.

[b]There was no reaction in the absence of catalyst; in DMSO and $C_2H_4Cl_2$ in the presence of catalyst **13** also, there was no reaction. Yields were based on ^{31}P NMR spectra.

[c]Although the starting material was absent; there were several minor peaks in the ^{31}P NMR.

[d]Here, Na_2CO_3, $NaHCO_3$ or $KHCO_3$ was used in lieu of K_2CO_3.

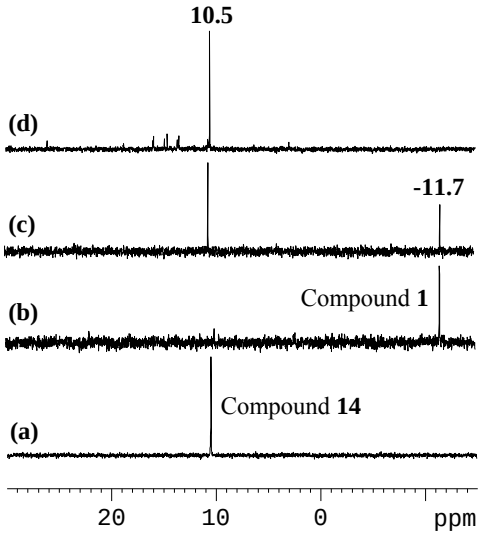
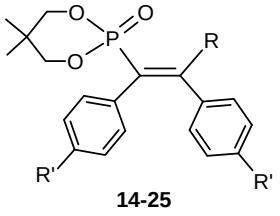


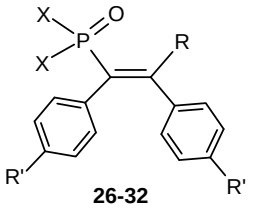
Figure 1. A diagram showing ^{31}P NMR spectra of the reaction shown in Scheme 3 by (a) using Pd(I) complex **13** after ½ h, (b) using $Pd_2(dba)_3$ after ½ h, (c) using $Pd_2(dba)_3$ after 2 h and (d) using $Pd_2(dba)_3$ after 4 h.

Under optimized conditions, we have conducted the reactions of a variety of substituted phosphorus-based alkynes [**1-4**, **7-10**] with different iodoarenes and arylboronic acids to form symmetrically substituted vinylphosphonates **14-32** (Table 2). Despite the heterogeneous nature of the components used, the reaction works well in aqueous medium affording the phosphonate products in yields that are essentially quantitative with the only minor limitation being the formation of the biaryls.[19, 24] All of these compounds were characterized by IR, NMR (^1H, ^{13}C and ^{31}P), LC-MS and CHN analyses.

Table 2. Details on the products obtained in double arylation[a]



14-25



26-32

X = OEt (**26-27**), O^{i}Pr (**28-29**)
Ph (**30-32**)

Yields (based on ^{31}P NMR/ TLC): Quantitative

Product	R	R'	$\delta(^{31}P)$[b]	Isolated Yield (%)
14	Ph	H	10.2	92
15	Ph	Me	10.8	87
16	Ph	OMe	11.3	85
17	4-Me-C_6H_4	H	10.5	86
18	4-Me-C_6H_4	Me	11.1	81
19	4-Me-C_6H_4	OMe	11.5	81
20	Me	H	12.2	79
21	Me	Me	12.8	85
22	Me	OMe	13.1	84
23	*cycl*-C_6H_9[c]	H	11.7	80
24	*cycl*-C_6H_9[c]	Me	12.4	82
25	*cycl*-C_6H_9[c]	OMe	12.8	79
26	Ph	H	15.7	86
27	Ph	OMe	16.5	84
28	Ph	H	13.7	88
29	Ph	OMe	14.4	82
30	Me	H	28.7	79
31	Me	Me	28.9	85
32	Me	OMe	29.1	80

[a]The ratio of alkyne:iodobenzene:arylboronic acid was 1:2:3. Alkyne (0.4 mmol), ArI (0.8 mmol), $ArB(OH)_2$ (1.2 mmol), K_2CO_3 (1.2 mmol), **13** (1.0 mol% based on Pd) in H_2O (5 mL) at 100 ^{o}C for 0.5 h.

[b]The variation in chemical shifts was within ±0.3 ppm for the reaction mixture and pure compounds.

[c]cyclohexenyl group

X-ray structures of two of these symmetrically double arylated products **22** and **26** (Fig. 2) have been determined. From the ORTEP diagrams of compounds **22** and **26**, it is clear that the incoming aryl groups from both aryl iodide and arylboronic acid add *cis* to alkynes. The distances of C6-C7 1.346(3) and C5-C6 1.353(5) Å in compounds **22** and **26** confirm the presence of double bond between the respective carbon atoms.

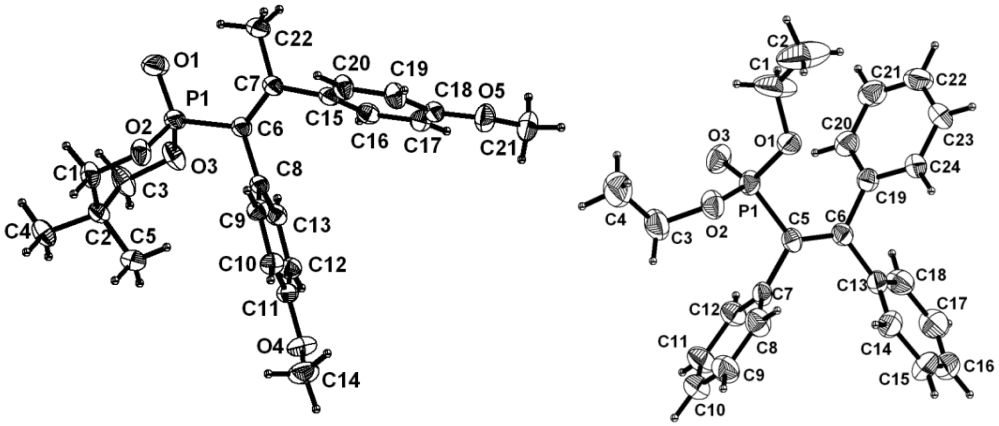
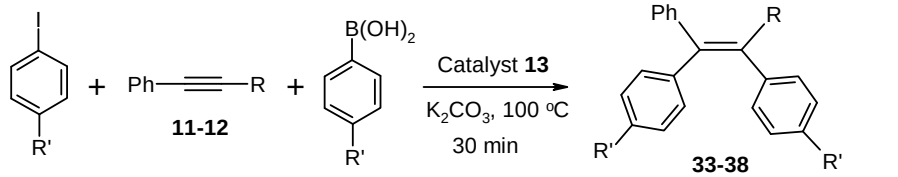


Figure 2. ORTEP diagrams of products **22** [left] and **26** [right]. Selected distances with estimated standard deviations are given in parentheses. **22**: P1-O1 1.449(2), P1-O2 1.573(2), P1-O3 1.567(2), P1-C6 1.786(2), C6-C7 1.346(3) Å. **26**: Two molecules are present in the asymmetric unit. Second molecule is not shown for clarity. P1-O3 1.458(3), P1-C5 1.803(4), C5-C6 1.353(5), C5-C7 1.501(5), C6-C13 1.502(5), C6-C19 1.493(5) Å.

5.3 Synthesis of symmetrically diarylated alkynes 33-38

As a demonstration of the efficacy of this novel route, we have extended the methodology to include the disubstituted alkynes **11-12** and obtained the tetrasubstituted alkenes **33-38** by double arylation (Table 3). In these cases also, compounds **33-38** were the sole arylated products. The slightly lower isolated yields of the pure products are only because of the nearly same R_f values of the biaryls and **33-38**; otherwise, the arylation process was quantitative. In the literature also a similar problem was encountered; it is reported that the purity of a sample was only ~95%.[19] However, in our case, the compounds were obtained in a pure state.

Table 3. Details on the products obtained in double arylation of alkynes[a]



Yields (based on TLC): Quantitative

Product	R	R'	Isolated yield (%)
33	Ph	H	60
34	Ph	Me	58
35	Ph	OMe	55
36	4-Me-C_6H_4	H	66
37	4-Me-C_6H_4	Me	62
38	4-Me-C_6H_4	OMe	62

[a]The ratio of alkyne:iodobenzene:arylboronic acid was 1:2:3. Alkyne (0.4 mmol), ArI (0.8 mmol), $ArB(OH)_2$ (1.2 mmol), K_2CO_3 (1.2 mmol), **13** (1.0 mol% based on Pd) in H_2O (5 mL) at 100 ^oC for 0.5 h.

5.4 Synthesis of unsymmetrically diarylated vinylphosphonates 39-48

After synthesizing the symmetrically doubly arylated vinylphosphonates and alkenes, we ventured into preparing unsymmetrically double arylated products **39-48** by using the above methodology (Scheme 5). The yields (^{31}P NMR) were again quantitative with the incoming aryl groups *cis* to each other. In most cases, the isomer with the aryl moiety from the boronic acid entering the position *geminal* to the phosphorus was dominant and the other isomer was the minor product. This assertion is based on (a) a report on double arylation of nonphosphorylated alkynes,[19, 24] and (b) X-ray structure of the major products **43b** and **44b** (Fig. 3). Distinction between the two isomers, we should admit, has not always been easy in the ^{31}P NMR because of the closeness of chemical shifts; however, the O*C*H_2 carbons showed distinct ^{13}C NMR signals in all the cases. For the numbering of compounds obtained as per Scheme 5/Table 4, see Figure 4. These compounds (**39-48**) were not separated into individual isomers.

Scheme 5

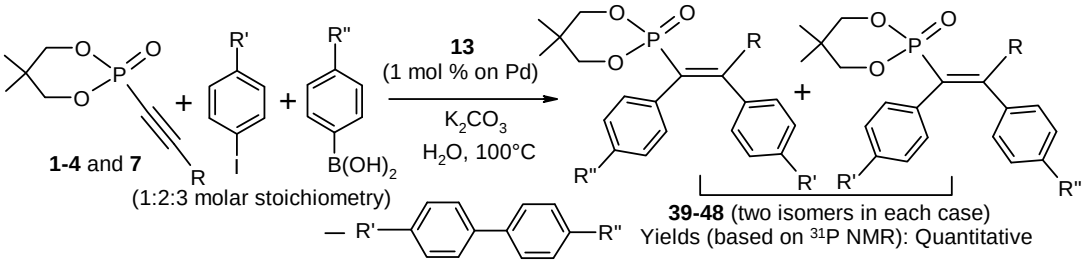


Table 4. Details on the unsymmetrical double arylation products (cf. Scheme 5)[a]

Entry	Products	R	R'	R''	$\delta(^{31}P)$[b]	Combined Isolated yield (%)[c]
1	**39**	Ph	H	Me	10.5_7, 10.6_4	87
2	**39**	Ph	Me	H	same as above	80
3	**40**	Ph	H	OMe	10.7, 10.8	83
4	**40**	Ph	OMe	H	same as above	83
5	**41**	4-Me-C_6H_4	H	Me	10.5, 10.6	93
6	**41**	4-Me-C_6H_4	Me	H	same as above	81
7	**42**	4-Me-C_6H_4	H	OMe	10.8, 10.9	71
8	**42**	4-Me-C_6H_4	OMe	H	same as above	71
9	**43**	Me	H	Me	12.7	75
10	**43**	Me	Me	H	same as above	86
11	**44**	Me	H	OMe	12.8_1, 12.8_5	84
12	**44**	Me	OMe	H	same as above	75
13	**45**	*cycl*-C_6H_9	H	Me	11.9	87
14	**45**	*cycl*-C_6H_9	Me	H	same as above	87
15	**46**	*cycl*-C_6H_9	H	OMe	12.1	90
16	**46**	*cycl*-C_6H_9	OMe	H	same as above	92
17	**47**	C_6H_{13}	H	Me	12.4	81
18	**47**	C_6H_{13}	Me	H	same as above	87
19	**48**	C_6H_{13}	H	OMe	12.8	86
20	**48**	C_6H_{13}	OMe	H	same as above	84

[a]The molar ratio of alkyne:iodobenzene: arylboronic acid was 1:2:3. Alkyne (0.4 mmol), ArI (0.8 mmol), $ArB(OH)_2$ (1.2 mmol), K_2CO_3 (1.2 mmol), **13** (1.0 mol% based on Pd) in H_2O (5 mL) at 100 ^oC for 0.5 h. Two entries are there for each compound because of the interchange of the aryl group between the boronic acid

and the iodoarene.

[b]In some cases, the $\delta(^{31}P)$ values of the two isomers were the same.

[c]Two isomers are obtained generally in the ratio 7:3 to 9:1 in favor of boronic acid residue geminal to phosphorus moiety. In the case of compound **42** only, both the isomers are formed in nearly equal quantities.

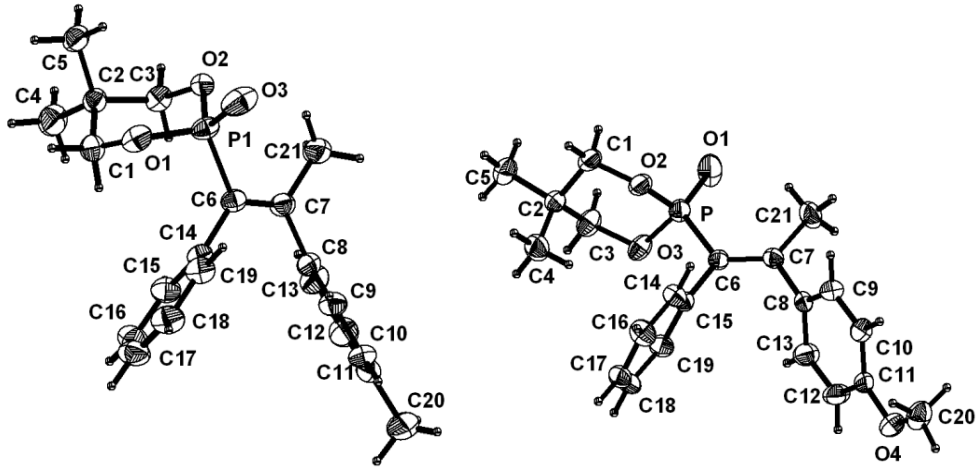
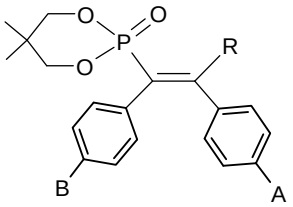


Figure 3. ORTEP diagrams of the major isomers **43b** (entry 10 in Table 4, left) and **44b** (entry 12 in Table 4, right). Selected bond lengths [Å] with esd's in parentheses. **43b**: P1-O3 1.455(2), P1-O2 1.5722(17), P1-O1 1.574(2), P1-C6 1.805(2), C6-C7 1.342(3). **44b**: P-O1 1.456(2), P-O2 1.578(2), P-O3 1.576(2), P-C6 1.789(2), C6-C7 1.344(3).



R = Ph	A = H, B = Me (**39a**)	R = *cycl*-C_5H_9	A = H, B = Me (**45a**)
	A = Me, B = H (**39b**)		A = Me, B = H (**45b**)
	A = H, B = OMe (**40a**)		A = H, B = OMe (**46a**)
	A = OMe, B = H (**40b**)		A = OMe, B = H (**46b**)
R = 4-Me-C_6H_4	A = H, B = Me (**41a**)	R = C_6H_{13}	A = H, B = Me (**47a**)
	A = Me, B = H (**41b**)		A = Me, B = H (**47b**)
	A = H, B = OMe (**42a**)		A = H, B = OMe (**48a**)
	A = OMe, B = H (**42b**)		A = OMe, B = H (**48b**)
R = Me	A = H, B = Me (**43a**)		
	A = Me, B = H (**43b**)		
	A = H, B = OMe (**44a**)		
	A = OMe, B = H (**44b**)		

Figure 4. Structures of the unsymmetrical diarylated vinyl phosphonates **39-48**.

In addition to the above, we also note the following points:

(i) Under the conditions employed, there was no reaction (^{31}P NMR evidence) with the use of only one of the arylating agents, ArI or $PhB(OH)_2$ even after 10 h of reflux. This is to say that it was mandatory to use both ArI and

$ArB(OH)_2$ for the disubstitution to occur. It must be noted that in these reactions the mono-arylated addition product was not observed in the ^{31}P NMR.

(ii) Despite being conducted in a heterogeneous system the reaction works extremely well affording the phosphonate products in high yields (quantitative on the basis of alkyne used, by ^{31}P NMR).

(iii) Using our phosphonate precursors and $Pd(OAc)_2/O_2$/DMSO in the presence of 4Å molecular sieves,[18] mono- and disubstituted products were formed along with unreacted starting material. Hence this procedure was not adapted in the present work.

(iv) There was no reaction of alkyne **1** with (a) $PhB(OH)_2$ using $Pd(OAc)_2/Ag_2CO_3$/1-propanol+H_2O (9:1)/ 120 ^oC[25] or (b) PhI using $Pd(OAc)_2$/NaOAc/PPh_3/(*n*-Bu)$_4$NCl/DMF/ 100 ^oC.[26]

5.5 Mechanistic aspects involved in the diarylation of alkynes

Based on the available literature,[19, 24] for the double arylation, we propose that the Pd-complex first reacts with iodoarene and then with arylboronic acid. The aryl group from the iodoarene preferentially goes to the carbon β to phosphonyl group. As regards the role of the catalyst (or procatalyst) **13**, at least four possible intermediates (**I-IV**, Figure 5) are possible in the initial stages, either by retaining the Pd-Pd bond or by its cleavage[27] leading to the formation of a mononuclear species. In either case, one of the active species should be of the type **(V**, Figure 5).

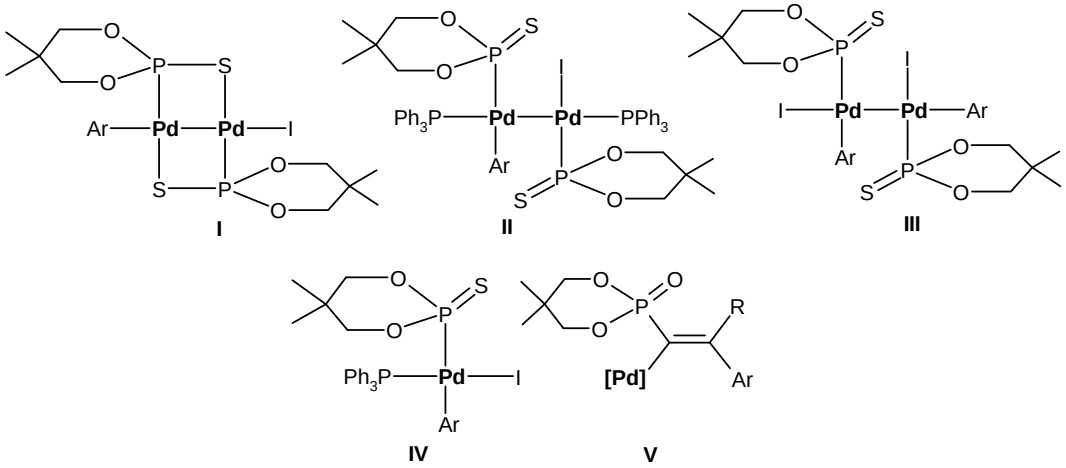


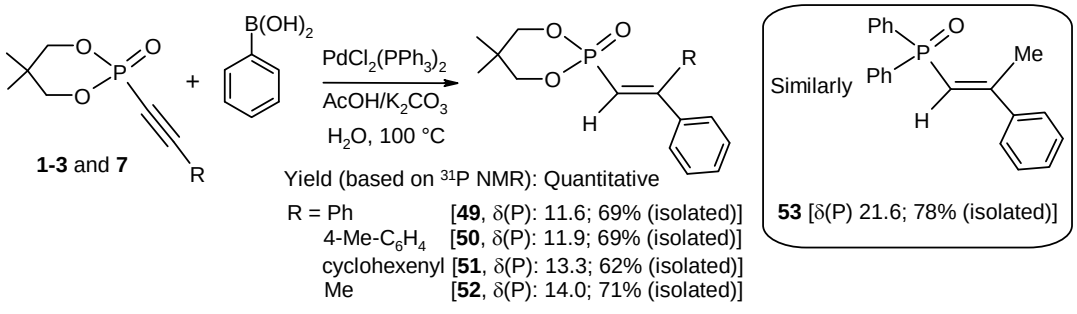
Figure 5. Possible intermediates in the formation of diarylated products.

In a preliminary experiment, when a solution of the catalyst **13** (1 equiv) and PhI (2 equiv) was heated at 100 ^{o}C in 1,4-dioxane for 30 min, the color changed from yellow to dark brown and the peaks corresponding to the catalyst (δ 15.3 and 148.0) disappeared in the ^{31}P NMR spectrum. New peaks were seen at δ 30.2 and δ 86.0 may be due to the -PPh_3 and/or thiophosphorus (P=S) bound ArPdI moiety (**II** or **IV**). Addition of alkyne **1** [1.0 equiv; δ(P) -12.0] at this stage did not give any change in the ^{31}P NMR. Upon addition of $PhB(OH)_2$ (3 equiv) and K_2CO_3 (3 equiv), the intensity of alkyne **1** peak gradually decreased (after 1 h) with the increase in intensity of a peak at δ 10.2 (^{31}P NMR) due to diarylated product (**14**). In lieu of the peak at δ(P) 86.0 a new peak appeared at δ(P) 23.0. After 3 h the alkyne fully disappeared and the product **14** was formed quantitatively. There was no change in the ^{31}P NMR when Pd-catalyst **13** was heated with only $PhB(OH)_2$ under the above mentioned conditions. Attempts towards the isolation of the intermediate/s have not been successful as yet.

5.6 Synthesis of monoarylated vinylphosphonates 49-52/ vinylphosphine oxide 53

After obtaining various diarylated vinylphosphonates, we attempted for the synthesis of monoarylated vinylphosphonates. We were successful in getting mono-arene (Ar-H) addition products **49-53** by the reaction of phosphorus-base alkynes **1-3** and **7-8** with phenylboronic acid in the presence of $PdCl_2(PPh_3)_2$/AcOH/K_2CO_3 system in H_2O at 100 ^{o}C (Scheme 6). In the ^{1}H NMR spectra of these compounds, the doublet for PC*H* proton appeared at δ ~ 6.02 with ^{2}J(P-H) of around 19.0 Hz. The characteristic peak for P*C* carbon observed at δ ~ 111.4 [^{1}J(P-C) = 183.9 Hz] for compounds **49-52** in the ^{13}C NMR spectra. In the case of product **53**, ^{1}J(P-C) is lower [103.9 Hz].

Scheme 6



Yield (based on ^{31}P NMR): Quantitative

R = Ph [**49**, δ(P): 11.6; 69% (isolated)]
4-Me-C_6H_4 [**50**, δ(P): 11.9; 69% (isolated)]
cyclohexenyl [**51**, δ(P): 13.3; 62% (isolated)]
Me [**52**, δ(P): 14.0; 71% (isolated)]

53 [δ(P) 21.6; 78% (isolated)]

A similar method was reported for the preparation of mono-arylated addition product for nonphosphorylated alkynes but by using $NaBPh_4$ in place of phenylboronic acid.[28] Due to the ready availability of various substituted arylboronic acids, our method is preferred over the literature method.

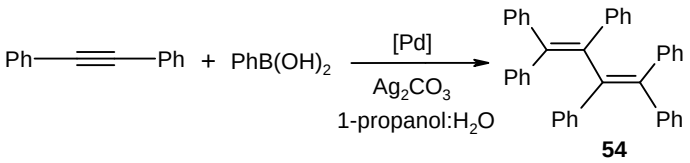
5.7 Use of dinuclear palladium(I) catalyst 13 in various coupling reactions-A comparative study

To explore the efficacy of our dinuclear palladium(I)-catalyst **13**, we have performed a few well known coupling reactions and compared these with the traditional palladium catalyzed [$Pd(OAc)_2$ and $Pd(PPh_3)_4$] reactions.[25, 29-30] The results are discussed in the following sections [**5.71-5.73**].

5.71 Synthesis of butadiene derivative 54

Miura *et al.* reported the coupling reaction of phenylboronic acid with diphenylacetylene in the presence of $Pd(OAc)_2$ (2.5 mol %) and Ag_2CO_3 (1 equiv) in 1-propanol/H_2O (9:1) at 120 ^oC to give multiarylated butadiene **54** in 67% yield (Scheme 7).[25] We made an attempt to improve the yield of this product by employing our dinuclear palladium(I) catalyst **13** under similar conditions. Gratifyingly, we were successful in obtaining the product **54** in 80% yield with our catalyst (Scheme 7). Thus, catalyst **13** is superior to $Pd(OAc)_2$ in this reactions.

Scheme 7



54

Entry	[Pd] (mol %)	Product	Time (h)	Yield (%)[a]
1	**13** (0.5)	**54**	0.5	80
2	$Pd(OAc)_2$ (2.5)	**54**	0.5	67

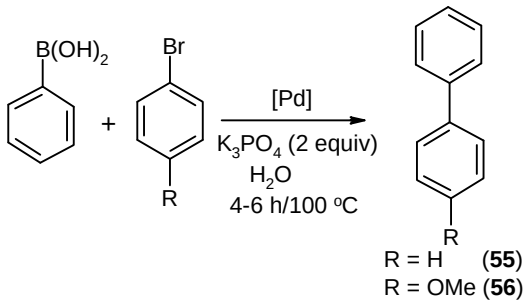
[a] Isolated yield

5.72 Synthesis of biaryls 55-56

Modifications to Suzuki coupling reaction by varying catalyst or ligand are numerous in the literature.[30] We used the coupling reaction of phenylboronic acid with aryl bromide in the presence of $Pd(PPh_3)_4/K_3PO_4$/water system as the standard method for comparison. When catalyst **13** was used instead of $Pd(PPh_3)_4$ in this

reaction, the products were obtained in good yields (Scheme 8). The results suggest that our catalyst is at least as active as $Pd(PPh_3)_4$ for Suzuki reaction.

Scheme 8



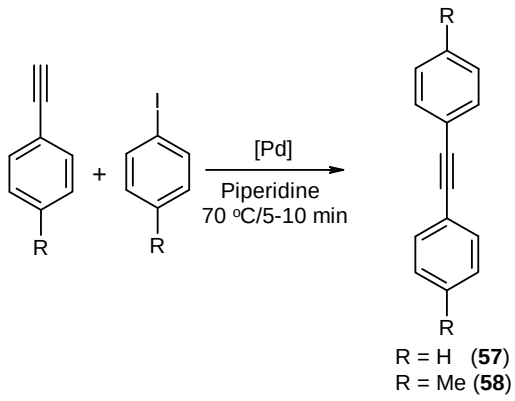
Entry	[Pd] (mol %)	Product	Time (h)	Yield (%)[a]
1	**13** (0.5)	**55**	4	82
2	$Pd(PPh_3)_4$ (1.0)	**55**	4	74
3	**13** (0.5)	**56**	6	78
4	$Pd(PPh_3)_4$ (1.0)	**56**	6	76

[a] Isolated yield

5.73 Synthesis of diarylalkynes 57-58

Inspired by above results, we compared the efficiency of catalyst **13** in the Sonogashira coupling reaction also. For this reason, we performed the coupling reaction of phenylacetylene with iodobenzene [and also *p*-tolylacetylene with *p*-iodotoluene] under a standard procedure which involve $Pd(PPh_3)_4$ as a catalyst and piperidine as a base[29a] and compared with that of our catalyst **13** (Scheme 9). The result suggests that our catalyst is at least as active as or better than the other catalysts [e.g. $Pd(PPh_3)_4$] under the similar reaction conditions (Scheme 9).

Scheme 9



Entry	[Pd] (mol %)	Product	Yield (%)[a]
1	**13** (0.5)	**57**	89
2	$Pd(PPh_3)_4$ (1.0)	**57**	87
3	**13** (0.5)	**58**	85
4	$Pd(PPh_3)_4$ (1.0)	**58**	80

[a]Isolated yield

In conclusion, we have shown that the dinuclear palladium(I) catalyst $[(OCH_2CMe_2CH_2O)P\text{-}S\text{-}Pd(PPh_3)]_2$ **13** is as effective as or better than traditional palladium catalysts [$Pd(OAc)_2$ and $Pd(PPh_3)_4$]. The added advantage in the case of catalyst **13** is its stability to air. Further work in utilizing the catalyst **13** is underway in our laboratory.[13, 23]

SUMMARY – PART B

1) Synthesis of diarylated vinylphosphonates *via* three-component coupling reaction of phosphonoalkynes with iodoarene and arylboronic acid is accomplished by using a novel dinuclear palladium(I) catalyst $[(OCH_2CMe_2CH_2O)P\text{-}S\text{-}Pd(PPh_3)]_2$ **13** under environmental friendly conditions in a stereo-selective manner. This methodology worked well for the preparation of tetrasubstituted alkenes also. In the case of unsymmetrical double arylation, the isomer with the aryl moiety from the boronic acid entering the position *geminal* to the phosphorus is dominant and the other isomer is the minor product.

2) Monoarylated vinylphosphonates were readily prepared by the reaction of phosphorus-based alkynes with phenylboronic acid in the presence of $PdCl_2(PPh_3)_2/AcOH/K_2CO_3$ system in water medium. These Ar-H addition reactions took place in a *cis* mode with the incoming aryl group at β-position to phosphonoalkyne.

3) The efficacy of dinuclear Pd-catalyst $[(OCH_2CMe_2CH_2O)P\text{-}S\text{-}Pd(PPh_3)]_2$ is compared with that of traditional palladium catalysts [$Pd(OAc)_2$ and $Pd(PPh_3)_4$] in various coupling reactions [Suzuki and Sonogashira]. The results suggest that our catalyst is at least effective as or better than the other catalysts.

EXPERIMENTAL SECTION

Details of instruments, standards etc. are already given in Chapter 3.

6.1 Preparation of phosphorus-based alkynes 1-4/ 7-10, diarylalkynes 11-12 and dinuclear Pd(I) catalyst 13

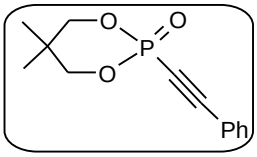
Precursors $(OCH_2CMe_2CH_2O)P(O)C{\equiv}CR$ [R= Ph (**1**), 4-Me-C_6H_4 (**2**), cyclohexenyl (**3**), C_6H_{13} (**4**)] were prepared by using a slightly modified version of literature procedure as given below.[7] Alkynes $(OCH_2CMe_2CH_2O)P(O)C{\equiv}CCH_3$ (**7**) and $Ph_2P(O)C{\equiv}CCH_3$ (**8**) were synthesized by treatment of corresponding allenes [$(OCH_2CMe_2CH_2O)P(O)CH{=}C{=}CH_2$ (**5**) and $Ph_2P(O)CH{=}C{=}CH_2$ (**6**) respectively] with triethylamine (80% yield).[8b] The phosphonate precursors $(RO)_2P(O)C{\equiv}CPh$ [R = Et (**9**), *i*-Pr (**10**)][9] and alkynes $PhC{\equiv}CAr$ [Ar = Ph (**11**), *p*-tol (**12**)][5] were prepared according to reported procedures. The dinuclear palladium(I) catalyst $[(OCH_2CMe_2CH_2O)P\text{-}S\text{-}Pd(PPh_3)]_2$ (**13**) [mp: 220 ^oC(d); ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.3 and 148.0 (d each, J = 12.2 Hz)] was prepared by reacting $Pd(PPh_3)_4$ with $(OCH_2CMe_2CH_2O)P(S)H$ in 1:1 molar stoichiometry in 1,4-dioxane at 60 ^oC.[13, 23, 31]

Representative procedure for synthesis of alkynes 1-4

A solution of phenyl acetylene (3.72 g, 36.5 mmol) in THF (5 mL) was added drop-wise to a stirred solution of EtMgBr (36.5 mmol) in THF (30 mL) at -10 ^oC under nitrogen atmosphere. The contents were stirred further at room temperature for 30 min. To this mixture was added a solution of $(OCH_2CMe_2CH_2O)P(=O)Cl$ (36.5 mmol) in THF (45 mL) drop-wise keeping the temperature at -10 ^oC. After attaining room temperature (25 ^oC), stirring continued for further 3 h, the mixture quenched with saturated NH_4Cl solution (10 mL) and extracted with dichloromethane (20 mL). Aqueous layer was washed with dichloromethane (2 x 30 mL), the combined organic layer washed thrice (3 x 20 mL) with water and brine solution (20 mL), and finally dried over anhyd. Na_2SO_4. Removal of the solvent

afforded yellow colored gummy material, which was chromatographed (EtOAc-hexane = 3:7) to afford the pure product **1**. Compounds **2-4** were also synthesized in a manner similar to compound **1** using same molar quantities. Spectroscopic and analytical data for these compounds are given below.

Compound 1



Yield: 6.10 g (67%).

Mp: 161-162^{o}C (white solid).

IR (KBr): 2975, 2186, 1823, 1489, 1373, 1283, 1055, 1001, 918 cm^{-1}.

^{1}H NMR: δ 0.93 and 1.34 (2 s, 6H, 2 C*H*$_3$), 3.95–4.04 and 4.23–4.26 (2 m, 4H, 2 OC*H*$_2$), 7.41–7.61 (m, 5H, Ar-*H*).

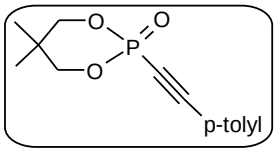
^{13}C NMR: δ 20.4, 22.0, 32.4 (d, *J* = 6.0 Hz, *C*(CH$_3$)$_2$), 76.5 (d, *J* = 287.2 Hz, P*C*), 77.4, 77.5, 100.7 (d, *J* = 50.4 Hz, PC*C*), 119.2 (d. *J* = 5.4 Hz, PCC*C*), 128.7, 131.0, 132.7 (d, *J* = 2.2 Hz).

^{31}P NMR: δ -11.7.

LC-MS: *m/*z 251 [M+1]$^{+}$.

Anal. Calcd. for $C_{15}H_{19}O_3P$: C, 64.74; H, 6.88. Found: C, 64.82; H, 6.87.

Compound 2



Yield: 6.70 g (70%).

Mp: 172-174^{o}C (white solid).

IR (KBr): 2976, 2184, 1605, 1510, 1476, 1372, 1053, 999, 916 cm^{-1}.

^{1}H NMR: δ 0.91 and 1.33 (2 s,6H, 2 C*H*$_3$), 2.40 (s, 3H, C$_6$H$_4$C*H*$_3$), 3.93–4.01 and 4.21–4.24 (2 m, 4H, 2 OC*H*$_2$), 7.20 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.48 (d, *J* = 8.0, 2H, Ar-*H*).

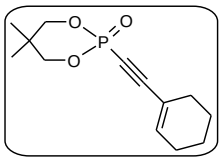
^{13}C NMR: δ 20.5, 21.8, 22.0, 32.4 (d, *J* = 6.0 Hz, *C*(CH$_3$)$_2$), 75.9 (d, *J* ~ 295.6 Hz, P*C*), 77.3, 77.4, 101.3 (d, *J* = 51.0 Hz, PC*C*), 116.1 (d, *J* = 5.4 Hz, PCC*C*), 129.5, 132.7 (d, *J* = 2.5 Hz), 141.7.

^{31}P NMR: δ -14.0.

LC-MS: *m/z* 265 $[M+1]^+$.

Anal. Calcd. for $C_{14}H_{17}O_3P$: C, 63.63; H, 6.48. Found: C, 63.49; H, 6.53.

Compound 3



Yield: 6.00 g (65%).

Mp : 125−126 ^oC (white solid).

IR (KBr): 2948, 2353, 2168, 1624, 1478, 1373, 1285, 1181, 916, 843 cm^{-1}.

^{1}H NMR: δ 0.90 and 1.30 (2 s, 6H, 2 CH_3), 1.62–1.66 (m, 4H, (CH_2)$_2$), 2.17–2.18 (m, 4H, (CH_2)$_2$), 3.88–3.96 (m, 2H, OCH_2), 4.13–4.15 (m, 2H, OCH_2), 6.48 (s, 1H, PCC(C=C*H*)).

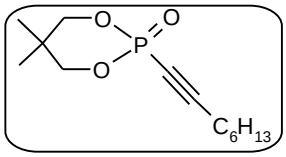
^{13}C NMR: δ 20.5, 21.0, 21.8, 22.0, 25.9, 28.0, 32.4 (d, *J* = 5.9 Hz, *C*(CH$_3$)$_2$), 73.8 (d, *J* = 290.0 Hz, P*C*), 77.2, 77.3, 103.1 (d, *J* = 50.4 Hz, PC*C*), 118.2 (d, *J* = 5.7 Hz, PCC*C*), 142.6 (d, *J* = 3.1 Hz).

^{31}P NMR: δ -11.1.

LC-MS: *m/z* 255 $[M+1]^+$.

Anal. Calcd. for $C_{13}H_{19}O_3P$: C, 61.41; H, 7.53. Found: C, 61.55; H, 7.57.

Compound 4



Yield: 6.80 g (72%, brown liquid).

IR (KBr): 3482, 2932, 2201, 1824, 1634, 1374, 1294, 1188, 1059, 1068 cm^{-1}.

^{1}H NMR: δ 0.89–0.91 (many lines, 6H), 1.29–1.31 (many lines, 7H), 1.41–1.44 (m, 2H), 1.59–1.63 (m, 2H), 2.36–2.39 (m, 2H, PCCCH_2), 3.87–3.96 and 4.11–4.14 (2 m, 4H, 2 OCH_2).

^{13}C NMR: δ 14.0, 19.2, 19.3, 20.5, 22.0, 22.4, 27.4$_2$, 27.4$_4$, 28.5, 31.1, 32.3 (d, *J* = 6.0 Hz, *C*(CH$_3$)$_2$), 68.7 (d, *J* = 290.5 Hz, P*C*), 77.1, 77.2, 104.9 (d, *J* = 50.7 Hz, PC*C*).

^{31}P NMR: δ -12.0.

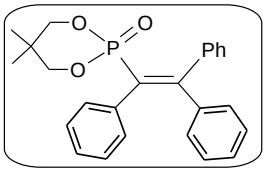
LC-MS: *m/z* 259 [M+1]$^+$.

Anal. Calcd. for $C_{13}H_{23}O_3P$: C, 60.45; H, 8.98. Found: C, 60.56; H, 9.05.

6.2 Preparation of symmetrically diarylated vinylphosphonates 14-29/ vinylphosphine oxides 30-32- General procedure for the synthesis of tetrasubstituted olefins 14-32

A mixture of the acetylene **1** (0.10 g, 0.40 mmol), phenylboronic acid (0.15 g, 1.20 mmol), K_2CO_3 (0.17 g, 1.20 mmol), catalyst **13** (4.0 mg, 1.0 mol % based on Pd) and iodobenzene (0.16 g, 0.80 mmol) in water (5 mL) was heated under reflux for 0.5 h. The reaction mixture was extracted with EtOAc (20 mL), dried over anhyd. Na_2SO_4, the solvent removed and pure compound **14** was isolated by silica gel column chromatography (EtOAc-hexane = 1:1). Compounds **15-32** were also synthesized similarly by using same molar quantities.

Compound 14



Yield: 0.15 g (92%).

Mp: 244−246 ^{o}C (white solid).

IR (KBr): 2965, 1591, 1491, 1445, 1372, 1253, 1061, 1013, 980 cm^{-1}.

^{1}H NMR: δ 0.70 and 0.99 (2 s, 6H, 2 C*H*$_3$), 3.61 (dd→t, *J* ~ 10.4 Hz, 2H, OC*H*$_2$), 3.77–3.84 (m, 2H, OC*H*$_2$), 6.98–7.46 (m, 15H, Ar-*H*).

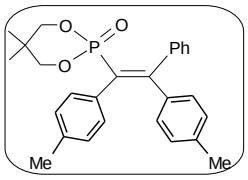
^{13}C NMR: δ 21.1, 21.7, 32.1 (d, *J* = 6.0 Hz, *C*(CH$_3$)$_2$), 75.6, 75.7, 127.1 (d, *J* = 2.0 Hz), 127.4, 127.6, 127.8, 128.3, 128.9$_3$, 128.9$_4$, 129.4 (d, ^{1}*J*(P-C) = 173.0 Hz), 129.5, 131.0, 131.1, 137.3, 137.4, 141.0$_6$, 141.1$_3$, 141.3, 141.5, 159.4, 159.5.

^{31}P NMR: δ 10.2.

LC-MS: *m/z* 405 [M+1]$^+$.

Anal. Calcd. for $C_{25}H_{25}O_3P$: C, 74.24; H, 6.23. Found: C, 74.21; H, 6.32.

Compound 15



Yield: 0.15 g (87%).

Mp: 260−262 ^{o}C (white solid).

IR (KBr): 2971, 1589, 1510, 1447, 1252, 1157, 1013, 986 cm^{-1}.

^{1}H NMR: δ 0.71 and 1.00 (2 s, 6H, 2 C*H*$_3$), 2.19 (s, 3H, C$_6$H$_4$C*H*$_3$), 2.27 (s, 3H, C$_6$H$_4$C*H*$_3$), 3.61 (dd→t, *J* ~ 9.8 Hz, 2H, OC*H*$_2$), 3.72-3.79 (m, 2H, OC*H*$_2$), 6.87 (s, 4H, Ar-*H*), 7.00 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 7.18 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 7.34-7.35 (m, 3H, Ar-*H*), 7.43-7.45 (m, 2H, Ar-*H*).

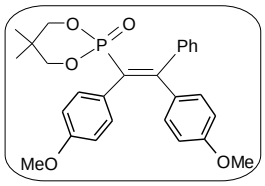
^{13}C NMR: δ 21.1, 21.1$_5$, 21.2$_1$, 21.8, 32.1 (d, *J* = 5.9 Hz, *C*(CH$_3$)$_2$), 75.6, 75.7, 127.8, 128.2, 128.3, 129.0, 129.5, 129.6, 130.8, 130.9, 134.4, 134.5, 136.7, 137.2, 138.4, 138.7, 141.5, 141.6, 158.9, 159.0, [the doublet due to ^{1}J(P-C) was not clear].

^{31}P NMR: δ 10.8.

LC-MS: *m/z* 433 [M+1]$^{+}$.

Anal. Calcd. for C$_{27}$H$_{29}$O$_3$P: C, 74.98; H, 6.76. Found: C, 74.81; H, 6.91.

Compound 16



Yield: 0.16 g (85%).

Mp: 216−218 ^{o}C (white solid).

IR (KBr): 2961, 2835, 1611, 1510, 1445, 1252, 1182, 1059, 1009 cm^{-1}.

^{1}H NMR: δ 0.71 and 0.98 (2 s, 6H, 2 C*H*$_3$), 3.60 (dd→t, *J* = 10.4 Hz, 2H, OC*H*$_2$), 3.69 (s, 3H, C$_6$H$_4$OC*H*$_3$), 3.76-3.83 (m, 5H, OC*H*$_2$ + C$_6$H$_4$OC*H*$_3$), 6.58 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 6.74 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 6.88 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 7.21 (d, *J* = 7.2 Hz, 2H, Ar-*H*), 7.35-7.41 (m, 5H, Ar-*H*).

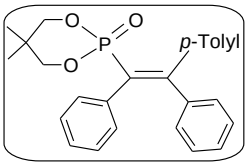
^{13}C NMR: δ 21.2, 21.7, 32.1 (d, *J* = 6.0 Hz, *C*$(CH_3)_2$), 55.1, 55.2, 75.4, 75.5, 113.0, 113.5, 127.4 (d, *J* = 174.0 Hz, P*C*), 127.8, 128.2, 129.2, 130.0, 130.1, 131.5, 132.3$_6$, 132.4$_2$, 133.8, 134.0, 158.5, 158.7.

^{31}P NMR: δ 11.3.

LC-MS: *m/z* 465 $[M+1]^+$.

Anal. Calcd. for $C_{27}H_{29}O_5P$: C, 69.82; H, 6.29. Found: C, 69.75; H, 6.38.

Compound 17



Yield: 0.14 g (86%).

Mp: 244–246 ^{o}C (white solid).

IR (KBr): 2967, 1586, 1481, 1440, 1250, 1059, 1013, 984 cm^{-1}.

^{1}H NMR: δ 0.69 and 1.00 (2 s, 6H, 2 C*H*$_3$), 2.36 (s, 3H, $C_6H_4CH_3$), 3.62 (dd→t, *J* = 10.4 Hz, 2H, OC*H*$_2$), 3.82 (dd→t, *J* ~ 12.6 Hz, 2H, OC*H*$_2$), 6.97-6.99 (m, 2H, Ar-*H*), 7.04-7.05 (m, 3H, Ar-*H*), 7.13-7.18 (m, 5H, Ar-*H*), 7.28 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.36 (d, *J* = 7.6 Hz, 2H, Ar-*H*).

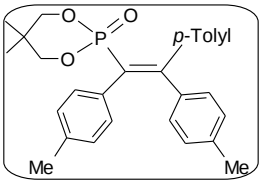
^{13}C NMR: δ 21.0, 21.4, 21.8, 32.1 (d, *J* = 5.9 Hz, *C*$(CH_3)_2$), 75.5, 75.6, 127.0, 127.3, 127.6, 127.8, 128.0, 128.6, 128.9, 129.5, 129.7, 131.0, 131.1, 137.5, 137.6, 138.2, 141.5, 141.7, 159.8, 159.9, [the doublet due to ^{1}J(P-C) was not clear].

^{31}P NMR: δ 10.7.

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

Anal. Calcd. for $C_{26}H_{27}O_3P$: C, 74.62; H, 6.50. Found: C, 74.45; H, 6.61.

Compound 18



Yield: 0.14 g (81%).

Mp: 245–247 ^{o}C (white solid).

IR (KBr): 2961, 1613, 1512, 1404, 1254, 1115, 1063, 1013, 988 cm^{-1}.

^1H NMR: δ 0.71 and 1.01 (2 s, 6H, 2 CH_3), 2.19 (s, 3H, $C_6H_4CH_3$), 2.26 (s, 3H, $C_6H_4CH_3$), 2.35 (s, 3H, $C_6H_4CH_3$), 3.62 (dd→t, *J* = 10.0 Hz, 2H, OCH_2), 3.78 (dd→t, *J* ~ 12.8 Hz, 2H, OCH_2), 6.86 (br s, 4H, Ar-*H*), 6.99 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 7.15-7.18 (m, 4H, Ar-*H*), 7.33 (d, *J* = 7.6 Hz, 2H, Ar-*H*).

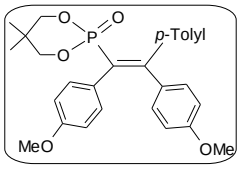
^{13}C NMR: δ 21.1, 21.2, 21.3, 21.4, 21.9, 32.2 (d, *J* = 5.9 Hz, *C*$(CH_3)_2$), 75.6, 75.7, 127.3, 128.3, 128.5, 128.6, 129.0, 129.7, 130.9, 131.0, 134.6, 134.7, 136.6, 137.2, 138.1, 138.7, 138.8, 139.0, 159.4, 159.5, [the doublet due to ^1J(P-C) was not clear].

^{31}P NMR: δ 11.1.

LC-MS: *m/z* 447 $[M+1]^+$.

Anal. Calcd. for $C_{28}H_{31}O_3P$: C, 75.32; H, 7.00. Found: C, 75.36; H, 7.12.

Compound 19



Yield: 0.15 g (81%).

Mp: 208–210 ^oC (white solid).

IR (KBr): 2959, 1609, 1512, 1462, 1250, 1181, 1059, 1011, 984 cm^{-1}.

^1H NMR: δ 0.70 and 0.98 (2 s, 6H, 2 CH_3), 2.36 (s, 3H, $C_6H_4CH_3$), 3.61 (dd→t, *J* ~ 10.6 Hz, 2H, OCH_2), 3.67 (s, 3H, $C_6H_4OCH_3$), 3.74-3.84 (m, 5H, $C_6H_4OCH_3$ + OCH_2), 6.57 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 6.73 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 6.87 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 7.15-7.21 (m, 4H, Ar-*H*), 7.30 (d, *J* = 7.6 Hz, 2H, Ar-*H*).

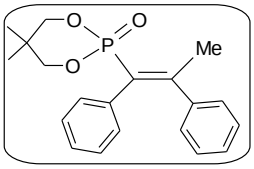
^{13}C NMR: δ 21.1, 21.4, 21.8, 32.1 (d, *J* = 5.9 Hz, *C*$(CH_3)_2$), 55.0, 55.1, 75.4, 75.5, 113.0, 113.4, 127.0 (d, *J* = 174.5 Hz), 128.5, 129.2, 130.1, 130.2, 131.5, 132.3_9, 132.4_4, 134.1, 134.3, 138.0, 138.7_7, 138.8_4, 158.5_0, 158.5_2, 158.7, 159.1, 159.2.

^{31}P NMR: δ 11.5.

LC-MS: *m/z* 479 $[M+1]^+$.

Anal. Calcd. for $C_{28}H_{31}O_5P$: C, 70.28; H, 6.53. Found: C, 70.41; H, 6.52.

Compound 20



Yield: 0.15 g (79%).

Mp: 192−194 ^{o}C (white solid).

IR (KBr): 2969, 1607, 1441, 1369, 1260, 1213, 1094, 1059, 1005, 982 cm^{-1}.

^{1}H NMR: δ 0.70 and 1.08 (2 s, 6H, 2 CH_3), 2.64 (d, J = 3.2 Hz, 3H, C=CCH_3), 3.56 (dd→t, J ~ 10.2 Hz, 2H, OCH_2), 3.96 (dd→t, J ~ 12.2 Hz, 2H, OCH_2), 6.95 (d, J = 6.8 Hz, 2H, Ar-H), 7.07-7.08 (br m, 8H, Ar-H).

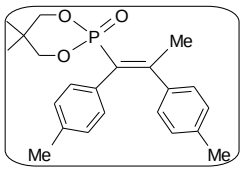
^{13}C NMR: δ 21.1, 21.8, 24.1 (d, J = 7.0 Hz, C=CCH$_3$), 32.3 (d, J = 6.0 Hz, C(CH$_3$)$_2$), 75.5, 75.6, 126.7$_1$, 126.7$_3$, 127.6$_6$, 127.7$_2$, 128.5, 130.7, 130.8, 137.5, 137.6, 142.6, 142.8, 157.4, 157.5, [the doublet due to ^{1}J(P-C) was not clear].

^{31}P NMR: δ 12.2.

LC-MS: m/z 343 [M+1]$^{+}$.

Anal. Calcd. for $C_{20}H_{23}O_3P$: C, 70.16; H, 6.77. Found: C, 70.32; H, 6.82.

Compound 21



Yield: 0.17 g (85%).

Mp: 179−181 ^{o}C (white solid).

IR (KBr): 2961, 1611, 1510, 1406, 1370, 1258, 1057, 1003, 916 cm^{-1}.

^{1}H NMR: δ 0.71 and 1.10 (2 s, 6H, 2 CH_3), 2.21 (s, 3H, C$_6$H$_4$CH_3), 2.23 (s, 3H, C$_6$H$_4$CH_3), 2.59 (d, J = 3.6 Hz, 3H, C=CCH_3), 3.56 (dd→t, J ~ 9.8 Hz, 2H, OCH_2), 3.87-3.94 (m, 2H, OCH_2), 6.83–6.96 (m, 8H, Ar-H).

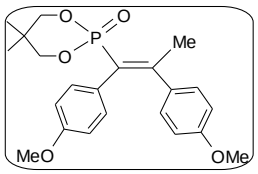
^{13}C NMR: δ 21.0, 21.1, 21.2, 24.2 (d, J = 6.9 Hz, C=CCH$_3$), 32.3 (d, J = 6.1 Hz, C(CH$_3$)$_2$), 75.6, 75.7, 126.2, 127.8, 128.4, 128.5, 130.4$_7$, 130.5$_2$, 134.5, 134.6, 136.2, 136.7, 139.6, 139.9, 156.6, 156.8, [the doublet due to ^{1}J(P-C) was not clear].

^{31}P NMR: δ 12.8.

LC-MS: *m/z* 372 $[M+1]^+$.

Anal. Calcd. for $C_{22}H_{27}O_3P$: C, 71.33; H, 7.35. Found: C, 71.45; H, 7.43.

Compound 22



Yield: 0.18 g (84%).

Mp: 161−163 ^{o}C (white solid).

IR (KBr): 2838, 1605, 1508, 1464, 1291, 1240, 1181, 1059, 1005, 916 cm^{-1}.

^{1}H NMR: δ 0.71 and 1.09 (2 s, 6H, 2 C*H*$_3$), 2.58 (d, *J* = 3.6 Hz, 3H, C=CC*H*$_3$), 3.55 (dd→t, *J* ~ 10.0 Hz, 2H, OC*H*$_2$), 3.70 (s, 3H, C_6H_4OC*H*$_3$), 3.72 (s, 3H, C_6H_4OC*H*$_3$), 3.88-3.94 (m, 2H, OC*H*$_2$), 6.62–6.67 (m, 4H, Ar-*H*), 6.88 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 6.95-6.98 (m, 2H, Ar-*H*).

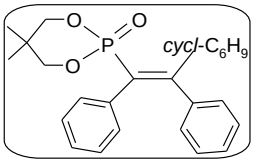
^{13}C NMR: δ 21.1, 21.9, 24.0 (d, *J* = 7.0 Hz, C=C*C*H$_3$), 32.3 (d, *J* = 7.0 Hz, *C*(CH$_3$)$_2$), 55.1, 75.5, 75.6, 113.1, 113.2$_4$, 113.2$_5$, 126.3 (d, ^{1}J(P-C) = 173.0 Hz), 129.4, 130.0, 131.0, 131.8$_5$, 131.9$_0$, 134.9, 135.1, 156.3, 156.4, 158.1$_8$, 158.2$_0$, 158.4.

^{31}P NMR: δ 13.1.

LC-MS: *m/z* 403 $[M+1]^+$.

Anal. Calcd. for $C_{22}H_{27}O_5P$: C, 65.66; H, 6.76. Found: C, 65.56; H, 6.88. This compound was crystallized from dichloromethane-hexane mixture (2+1 mL). X-ray structure was determined for this sample (Fig. 2 in Chapter 5).

Compound 23



Yield: 0.13 g (80%).

Mp: 200–202 ^{o}C (white solid).

IR (KBr): 2928, 1584, 1489, 1439, 1372, 1252, 1061, 1013, 984 cm^{-1}.

^{1}H NMR: δ 0.70 and 1.01 (2 s, 6H, 2 C*H*$_3$), 1.63 (br s, 4H), 2.02 (br s, 2H), 2.23 (br s, 2H), 3.60 (dd→t, *J* = 11.4 Hz, 2H, OC*H*$_2$), 4.00 (dd→t, *J* ~ 11.4 Hz, 2H, OC*H*$_2$), 6.09 (br s, 1H, PC=C(C=C*H*)(Ph)), 7.03-7.16 (m, 10H, Ar-*H*).

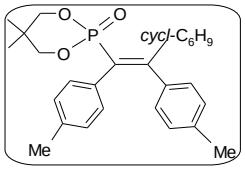
^{13}C NMR: δ 21.1, 21.6, 21.7, 22.4, 25.5, 27.5, 32.2 (d, *J* = 5.3 Hz, *C*(CH$_3$)$_2$), 75.3, 75.4, 126.3, 126.9, 127.3, 127.5, 128.1, 129.1, 131.2, 137.2, 137.4, 138.4, 138.6, 138.9, 139.1, 163.0, 163.1, [the doublet due to ^{1}*J*(P-C) was not clear].

^{31}P NMR: δ 11.7.

LC-MS: *m/z* 409 [M+1]$^{+}$.

Anal. Calcd. for $C_{25}H_{29}O_3P$: C, 73.51; H, 7.16. Found: C, 73.45; H, 7.23.

Compound 24



Yield: 0.14 g (82%).

Mp: 245–247 ^{o}C (white solid).

IR (KBr): 2919, 1588, 1510, 1250, 1179, 1061, 1013, 920 cm^{-1}.

^{1}H NMR: δ 0.71 and 1.02 (2 s, 6H, 2 C*H*$_3$), 1.62 (br s, 4H), 1.78 (br s, 2H), 2.21-2.23 (m, 8H, cyclohexenyl C*H*$_2$+ 2 C$_6$H$_4$C*H*$_3$), 3.60 (dd→t, *J* = 10.8 Hz, 2H, OC*H*$_2$), 3.97 (dd→t, *J* = 11.6 Hz, 2H, OC*H*$_2$), 6.04 (br s, 1H, PC=C(C=C*H*)(*p*-tolyl)), 6.87–6.94 (m, 6H, Ar-*H*), 7.04 (d, *J* = 7.6 Hz, 2H, Ar-*H*).

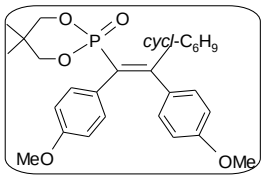
^{13}C NMR: δ 21.3, 21.8, 21.9, 22.5, 25.6, 27.7, 32.3 (d, *J* = 5.7 Hz, *C*(CH$_3$)$_2$), 75.3, 75.4, 126.5 (d, *J* = 179.3 Hz), 128.0, 128.3, 128.4, 129.3, 131.1, 131.2, 134.4, 134.5, 135.9, 136.1, 136.4, 137.2, 138.7, 138.8, 162.6, 162.8.

^{31}P NMR: δ 12.4.

LC-MS: *m/z* 437 [M+1]$^{+}$.

Anal. Calcd. for $C_{27}H_{33}O_3P$: C, 74.29; H, 7.62. Found: C, 74.45; H, 7.59.

Compound 25



Yield: 0.15 g (79%).

Mp: 186–188 ^{o}C (white solid).

IR (KBr): 2932, 1607, 1510, 1373, 1248, 1109, 1061, 1011 cm^{-1}.

^{1}H NMR: δ 0.71 and 1.00 (2 s, 6H, 2 C*H*$_3$), 1.63 (br s, 4H), 1.98 (br s, 2H), 2.22 (br s, 2H), 3.59 (dd→t, *J* = 12.0 Hz, 2H, OC*H*$_2$), 3.71 (s, 3H, C$_6$H$_4$OC*H*$_3$), 3.73 (s, 3H, C$_6$H$_4$OC*H*$_3$), 4.01 (dd→t, *J* ~ 10.0 Hz, 2H, OC*H*$_2$), 6.01 (br s, 1H, PC=C(C=C*H*)(*p*-anisyl)), 6.61 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 6.68 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 6.97 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.08 (d, *J* = 8.0 Hz, 2H, Ar-*H*).

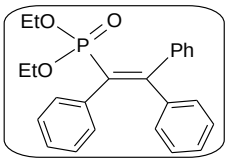
^{13}C NMR: δ 21.3, 21.8, 22.5, 25.5, 27.7, 32.2 (d, *J* = 6.0 Hz, *C*(CH$_3$)$_2$), 55.0, 55.1, 75.1, 75.2, 113.0, 113.2, 125.5 (d, *J* = 181.0 Hz), 128.1$_5$, 128.1$_7$, 129.8, 129.9, 130.9, 131.2, 132.5$_8$, 132.6$_3$, 138.8, 138.9, 158.3, 158.8, 162.4, 162.5.

^{31}P NMR: δ 12.8.

LC-MS: *m/z* 469 [M+1]$^{+}$.

Anal. Calcd. for C$_{27}$H$_{33}$O$_5$P: C, 69.22; H, 7.10. Found: C, 69.31; H, 7.12.

Compound 26



Yield: 0.14 g (86%).

Mp: 92−94 ^{o}C (white solid).

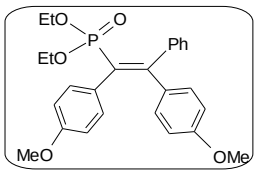
^{1}H NMR: data are consistent with that reported in the literature.[32]

^{13}C NMR: δ 15.9$_7$, 16.0$_3$, 61.8$_6$, 61.9$_2$, 126.9, 127.1, 127.5, 127.6, 127.7, 127.9, 129.4, 129.7, 131.1 (d, *J* = 180.1 Hz), 131.4 (d, *J* = 4.4 Hz), 134.3, 137.8, 137.9, 141.8 (d, *J* = 6.7 Hz), 141.9 (d, *J* = 5.8 Hz), 156.9 (d, *J* = 8.5 Hz).

LC-MS: *m/z* 393 $[M+1]^+$.

This compound was crystallized from ethyl acetate (2 mL). X-ray structure was obtained on this sample (Fig. 2 in Chapter 5).

Compound 27



Yield: 0.15 g (84%, gummy material).

IR (Neat): 2982, 2838, 1605, 1508, 1248, 1179, 1028 cm^{-1}.

^1H NMR: δ 0.98-1.01 (m, 6H, 2 OCH_2CH_3), 3.55-3.63 (m, 2H, OCH_2CH_3), 3.67 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3), 3.79-3.86 (m, 2H, OCH_2CH_3), 6.54-6.56 (m, 2H, Ar-*H*), 6.72-6.74 (m, 2H, Ar-*H*), 6.80-6.82 (m, 2H, Ar-*H*), 7.19-7.21 (m, 2H, Ar-*H*), 7.32-7.36 (m, 3H, Ar-*H*), 7.40-7.42 (m, 2H, Ar-*H*).

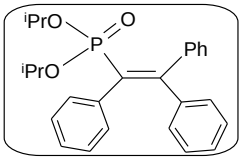
^{13}C NMR: δ 16.0, 16.1, 55.0, 55.1, 61.7, 61.8, 112.9, 113.2, 127.6, 127.8, 129.2 (d, ^1J(P-C) = 181.6 Hz, P-*C*), 129.7, 130.4 (d, *J* = 10.0 Hz), 131.6, 132.7, 132.8, 134.4 (d, *J* = 20.4 Hz), 142.4 (d, *J* = 7.3 Hz), 156.1 (d, *J* = 10.9 Hz), 158.4, 158.5.

^{31}P NMR: δ 16.5.

LC-MS: *m/z* 453 $[M+1]^+$.

Anal. Calcd. for $C_{26}H_{29}O_5P$: C, 69.02; H, 6.46. Found: C, 69.15; H, 6.38.

Compound 28



Yield: 0.15 g (88%, gummy material).

IR (Neat): 2978, 2187, 1597, 1491, 1445, 1385, 1238, 1107, 1015 cm^{-1}.

^1H NMR: δ 0.85 (d, *J* = 6.4 Hz, 6H, $OCH(CH_3)_2$), 1.13 (d, *J* = 6.4 Hz, 6H, $OCH(CH_3)_2$), 4.37-4.45 (m, 2H, 2 $OCH(CH_3)_2$), 6.91-6.93 (m, 2H,

Ar-*H*), 7.00-7.03 (m, 3H, Ar-*H*), 7.10-7.16 (m, 3H, Ar-*H*), 7.24-7.27 (m, 2H, Ar-*H*), 7.29-7.36 (m, 3H, Ar-*H*), 7.45-7.47 (m, 2H, Ar-*H*).

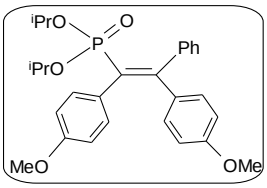
^{13}C NMR: δ 23.2 (d, *J* = 4.5 Hz), 24.0 (d, *J* = 2.8 Hz), 70.8 (d, *J* = 5.4 Hz), 126.7 (d, *J* = 2.0 Hz), 126.9, 127.2 (d, *J* = 10.6 Hz), 127.4, 127.4_7, 127.5_4, 127.6, 128.8, 129.6, 129.7, 131.4_9, 131.5_3, 138.4 (d, *J* = 9.9 Hz), 142.1 (d, *J* = 7.1 Hz), 142.3, 142.5, 156.3 (d, *J* = 10.0 Hz), [the doublet due to ^{1}J(P-C) was not clear].

^{31}P NMR: δ 13.7.

LC-MS: *m/z* 421 $[M+1]^+$.

Anal. Calcd. for $C_{26}H_{29}O_3P$: C, 74.27; H, 6.95. Found: C, 74.15; H, 6.88.

Compound 29



Yield: 0.16 g (82%, gummy material).

IR (Neat): 2978, 2836, 1605, 1508, 1248, 1179, 1019, 988 cm^{-1}.

^{1}H NMR: δ 0.89 (d, *J* = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.11 (d, *J* = 5.6 Hz, 6H, CH(CH_3)$_2$), 3.66 and 3.74 (2 s, 6H, 2 OCH_3), 4.37-4.46 (m, 2H, 2 OC*H*(CH$_3$)$_2$), 6.53-6.55 (m, 1H, Ar-*H*), 6.65-6.72 (m, 2H, Ar-*H*), 6.79-6.90 (m, 3H, Ar-*H*), 7.00-7.02 (m, 1H, Ar-*H*), 7.14-7.20 (m, 2H, Ar-*H*), 7.27-7.40 (m, 4H, Ar-*H*).

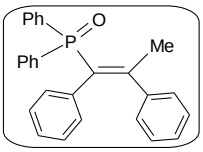
^{13}C NMR: δ 23.4 (d, *J* = 5.0 Hz), 24.0 (d, *J* = 4.0 Hz), 55.0, 55.1, 70.8 (d, *J* = 6.7 Hz), 112.8, 113.1, 113.5, 127.5 (d, *J* = 8.7 Hz), 129.1, 129.9, 130.8, 131.5, 132.9, 134.8, 135.0, 135.9, 137.5, 142.6, 156.2, 158.4, [the doublet due to ^{1}J(P-C) was not clear].

^{31}P NMR: δ 14.4.

LC-MS: *m/z* 481 $[M+1]^+$.

Anal. Calcd. for $C_{28}H_{33}O_5P$: C, 69.99; H, 6.92. Found: C, 69.78; H, 6.86.

Compound 30



Yield: 0.13 g (79%).

Mp: 129−131 ^{o}C (white solid).

IR (KBr): 2919, 1589, 1487, 1437, 1192, 1105, 1024, 914 cm^{-1}.

^{1}H NMR: δ 2.53 (d, *J* = 2.8 Hz, 3H, C=CC*H*$_3$), 6.71–6.72 (m, 2H, Ar-*H*), 6.79-6.80 (m, 3H, Ar-*H*), 7.01-7.11 (m, 5H, Ar-*H*), 7.31-7.42 (m, 6H, Ar-*H*), 7.62-7.67 (m, 4H, Ar-*H*).

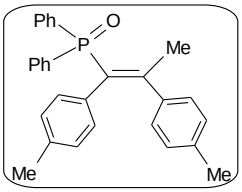
^{13}C NMR: δ 24.6 (d, *J* = 7.0 Hz, C=C*C*H$_3$), 125.9$_1$, 125.9$_3$, 126.9, 127.3$_1$, 127.3$_3$, 127.7$_0$, 127.7$_3$, 128.0, 128.2, 130.8, 130.9, 131.1$_5$, 131.1$_8$, 131.5, 131.6, 132.5, 133.3, 133.4, 134.4, 138.6, 138.7, 143.3, 143.4, 157.0, 157.1, [the doublet due to ^{1}J(P-C) was not clear].

^{31}P NMR: δ 28.7.

LC-MS: *m/z* 395 [M+1]$^{+}$.

Anal. Calcd. for $C_{27}H_{23}OP$: C, 82.21; H, 5.88. Found: C, 82.31; H, 5.87.

Compound 31



Yield: 0.15 g (85%).

Mp: 173−175 ^{o}C (white solid).

IR (KBr): 2917, 1894, 1597, 1510, 1435, 1290, 1181, 1113, 1020, 912 cm^{-1}.

^{1}H NMR: δ 1.86 (s, 3H, C$_6$H$_4$C*H*$_3$), 2.06 (s, 3H, C$_6$H$_4$C*H*$_3$), 2.50 (s, 3H, C=CC*H*$_3$), 6.57-6.62 (m, 4H, Ar-*H*), 6.89-6.91 (m, 4H, Ar-*H*), 7.30-7.41 (m, 6H, Ar-*H*), 7.61-7.63 (m, 4H, Ar-*H*).

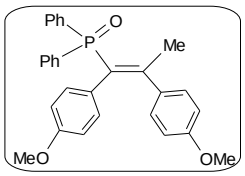
^{13}C NMR: δ 20.9, 21.1, 24.6 (d, *J* = 7.0 Hz, C=C*C*H$_3$), 127.8, 128.0, 128.1, 128.4, 130.7, 130.8, 131.0$_1$, 131.0$_3$, 131.6, 131.7, 131.9, 132.8, 133.6, 134.6, 135.3$_7$, 135.3$_9$, 135.6, 135.7, 136.5, 140.5, 140.6, 156.7, 156.8, [the doublet due to ^{1}J(P-C) was not clear].

^{31}P NMR: δ 28.9.

LC-MS: *m/z* 424 $[M+1]^+$.

Anal. Calcd. for $C_{29}H_{27}OP$: C, 82.44; H, 6.44. Found: C, 82.51; H, 6.41.

Compound 32



Yield: 0.15 g (80%).

Mp: 120−122 ^{o}C (white solid).

IR (KBr): 3056, 2838, 1750, 1607, 1439, 1377, 1177, 1113, 1032, 910 cm^{-1}.

^{1}H NMR: δ 2.50 (s, 3H, C=CC*H*$_3$), 3.60 (s, 3H, $C_6H_4OCH_3$), 3.71 (s, 3H, $C_6H_4OCH_3$), 6.36 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 6.59-6.65 (m, 4H, Ar-*H*), 6.96 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.32-7.42 (m, 6H, Ar-*H*), 7.60-7.65 (m, 4H, Ar-*H*).

^{13}C NMR: δ 24.5 (d, *J* = 8.0 Hz, C=C*C*H$_3$), 55.0, 55.1, 112.9, 113.1, 128.1, 128.2, 129.3, 131.1, 131.3, 131.5, 131.6, 132.1, 133.6, 134.7, 135.7, 135.8, 156.5, 157.6, 158.3, [the doublet due to ^{1}J(P-C) was not clear].

^{31}P NMR: δ 29.1.

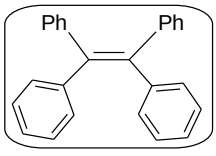
LC-MS: *m/z* 455 $[M+1]^+$.

Anal. Calcd. for $C_{29}H_{27}O_3P$: C, 76.64; H, 5.99. Found: C, 76.35; H, 5.85.

6.3 Synthesis of symmetrically diarylated alkynes 33-38

Compounds **33-38** were synthesized by following the method described in section **6.2** by using same molar quantities.

Compound 33



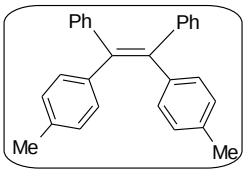
Acetylene **11**, phenylboronic acid and iodobenzene were used in this reaction.

Yield: 0.12 g (60%).

Mp: 218−220 °C (white solid) (lit.[18b] Mp. 222-224 °C); spectral data are consistent with that reported in literature.[18b]

LC-MS: *m/z* 333 $[M+1]^+$.

Compound 34



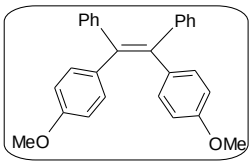
Acetylene **11**, *p*-tolylboronic acid and 4-iodotoluene were used in this reaction.

Yield: 0.12 g (58%).

Mp: 140−142 °C (white solid) (lit. [18a, 33a] Mp. 143-145 °C) spectral data are consistent with that reported in literature.[18a, 33a]

LC-MS: *m/z* 361 $[M+1]^+$.

Compound 35



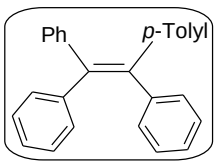
Acetylene **11**, *p*-anisylboronic acid and 4-iodoanisole were used in this reaction.

Yield: 0.11 g (55%).

Mp: 182–184 °C (white solid) (lit.[33b] Mp. 186-187 °C); spectral data are consistent with that reported in literature.[33b]

LC-MS: *m/z* 393 $[M+1]^+$.

Compound 36



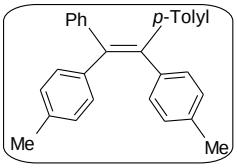
Acetylene **12**, phenylboronic acid and iodobenzene were used in this reaction.

Yield: 0.12 g (66%).

Mp: 150–152 °C (white solid) (lit.[24b, 33c] Mp. 146-148 °C); spectral data are consistent with that reported in literature.[24b, 33c]

LC-MS: *m/z* 347 $[M+1]^+$.

Compound 37



Acetylene **12**, *p*-tolylboronic acid and 4-iodotoluene were used in this reaction.

Yield: 0.11 g (62%).

Mp: 140–142 ^oC (white solid).

IR (KBr): 2920, 1904, 1597, 1510, 1443, 1265, 1182, 1111, 1022 cm^{-1}.

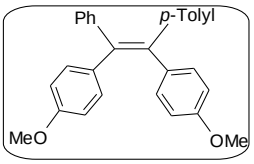
^1H NMR: δ 2.25 (s, 3H, $C_6H_4CH_3$), 2.27 (s, 6H, 2 $C_6H_4CH_3$), 6.90-6.91 (m, 12H, Ar-*H*), 7.02-7.09 (m, 5H, Ar-*H*).

^{13}C NMR: δ 21.1_7, 21.2_0, 126.1, 127.6, 128.2_8, 128.3_4, 131.2, 131.3, 131.4, 135.7_6, 135.7_9, 135.8_1, 139.9, 140.3, 141.1_2, 141.1_4, 144.4.

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

Anal. Calcd. for $C_{29}H_{26}$: C, 93.00; H, 7.00. Found: C, 92.85; H, 7.06.

Compound 38



Acetylene **12**, *p*-anisylboronic acid and 4-iodoanisole were used in this reaction.

Yield: 0.13 g (62%).

Mp: 139–141 ^oC (white solid).

IR (KBr): 2836, 1605, 1508, 1246, 1173, 1107, 1028, 824 cm^{-1}.

^1H NMR: δ 2.27 (s, 3H, $C_6H_4CH_3$), 3.77 (s, 6H, 2 $C_6H_4OCH_3$), 6.67 (d, J = 8.0 Hz, 4H, Ar-*H*), 6.92-6.99 (m, 8H, Ar-*H*), 7.04-7.26 (m, 5H, Ar-*H*).

^{13}C NMR: δ 21.2, 55.1, 113.1, 126.1, 127.6, 128.3, 131.3, 131.4, 132.5, 135.8, 136.7, 139.2, 139.6, 141.2, 144.5, 157.8_8, 157.9_3.

LC-MS: *m/z* 407 $[M+1]^+$.

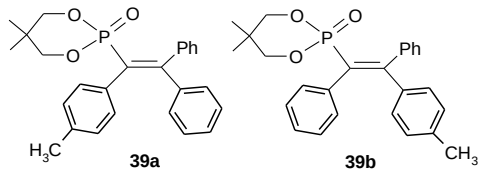
Anal. Calcd. for $C_{29}H_{26}O_2$: C, 85.68; H, 6.45. Found: C, 85.48; H, 6.55.

6.4 Unsymmetrically diarylated vinylphosphonates 39-48

Compounds **39-48** were synthesized by using the procedure given in Section **6.2**.

Compound 39 (isomer ratio 2:1)

Acetylene **1**, *p*-tolylboronic acid and iodobenzene were used in this reaction.



Yield: 0.15 g (87%).

Mp: 223−225 ^{o}C (white solid).

IR (KBr): 2963, 1589, 1510, 1442, 1371, 1256, 1061, 1011, 982 cm^{-1}.

^{1}H NMR: (for major isomer): δ 0.71 and 1.00 (2 s, 6H, 2 CH_3), 2.20 (s, 3H, $C_6H_4CH_3$), 3.59–3.66 and 3.75–3.85 (2 m, 4H, 2 OCH_2), 6.87–7.49 (m, 14H, Ar-*H*).

^{1}H NMR: (for minor isomer): δ 0.74 and 1.03 (2 s, 6H, 2 CH_3), 2.27 (s, 3H, $C_6H_4CH_3$), remaining peaks were merged with major isomer peaks.

^{13}C NMR: δ 21.0, 21.1, 21.3, 21.6, 21.7, 32.0 (d, J = 6.0 Hz, $C(CH_3)_2$), 75.5_1 and 75.5_7 (minor), 75.6_3 and 75.6_9 (major), 127.0, 127.2, 127.5, 127.6, 127.7, 127.8, 128.2, 128.3, 128.5, 128.8, 129.4, 129.5, 130.7 (d, J = 4.9 Hz), 131.0 (d, J = 4.7 Hz), 136.7 (d, J = 2.1 Hz), 137.3, 141.1 (d, J = 7.3 Hz), 141.4, 141.5, 158.8 (d, J = 11.4 Hz), 159.3, 159.4 [the spectrum was complicated due the peaks for both the isomers].

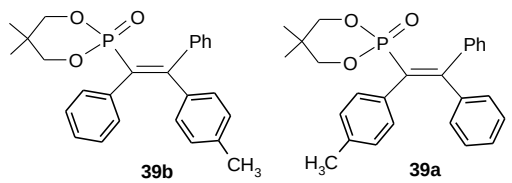
^{31}P NMR: δ 10.5_7 (minor) and 10.6_4 (major).

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

Anal. Calcd. for $C_{26}H_{27}O_3P$: C, 74.62; H, 6.50. Found: C, 74.64; H, 6.61.

Compound 39 (isomer ratio 3:2)

Acetylene **1**, phenylboronic acid and 4-iodotoluene were used in this reaction.



Yield: 0.13 g (80%).

Mp: 220–224 ^{o}C (white solid).

IR (KBr): 2963, 1589, 1491, 1373, 1254, 1157, 1063, 1011, 990 cm^{-1}.

^{1}H NMR: (for major isomer): δ 0.71 and 1.00 (2 s, 6H, 2 CH_3), 2.25 (s, 3H, $C_6H_4CH_3$), 3.58–3.63 and 3.73–3.80 (2 m, 4H, 2 OCH_2), 6.85–7.47 (m, 14H, Ar-*H*).

^{1}H NMR: (for minor isomer): δ 0.69 and 0.98 (s, 6H, 2 CH_3), 2.18 (s, 3H, $C_6H_4CH_3$), remaining peaks were merged with major isomer peaks.

^{13}C NMR: δ 21.0$_7$, 21.1$_1$, 21.7, 21.8, 32.1 (d, *J* = 6.0 Hz, *C*$(CH_3)_2$), 75.5 and 75.6 (minor), 75.6$_6$ and 75.7$_2$ (major), 127.1, 127.3, 127.6, 127.7$_8$, 127.8$_2$, 127.8$_4$, 127.9. 128.2, 128.3, 128.6, 128.9$_2$, 128.9$_3$, 129.0 (d, *J* = 1.3 Hz), 129.4 (d, *J* = 172.0 Hz), 129.5, 129.6, 130.8 (d, *J* = 4.8 Hz), 131.1 (d, *J* = 4.8 Hz), 134.2 (d, *J* = 9.2 Hz), 136.7$_5$, 136.8, 137.3, 137.6, 137.7, 138.3, 138.6, 141.2, 141.3, 141.4, 141.6, 158.8 (d, *J* = 12.0 Hz) [the spectrum was complicated due the peaks for both the isomers].

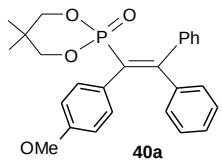
^{31}P NMR: δ 10.5$_5$ (minor) and 10.6$_1$ (major).

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

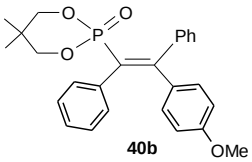
Anal. Calcd. for $C_{26}H_{27}O_3P$: C, 74.62; H, 6.50. Found: C, 74.73; H, 6.64.

Compound 40 (isomer ratio 2:1)

Acetylene **1**, *p*-anisylboronic acid and iodobenzene were used in this reaction.



40a



40b

Yield: 0.15 g (83%).

Mp: 202–204 ^{o}C (white solid).

IR (KBr): 2961, 1607, 1508, 1443, 1250, 1181, 1061, 1011, 986 cm^{-1}.

^{1}H NMR: (for major isomer): δ 0.68 and 0.97 (2 s, 6H, 2 CH_3), 3.57–3.64 (m, 2H, 2 OCH_2), 3.68 (s, 3H, $C_6H_4OCH_3$), 3.79–3.85 (2 m, 2H, 2 OCH_2), 6.56–7.44 (m, 14H, Ar-*H*).

^{1}H NMR: (for minor isomer): δ 0.73 and 1.01 (s, 3H, 2 CH_3), 3.74 (s, 3H, $C_6H_4OCH_3$), remaining peaks were merged with major isomer peaks.

^{13}C NMR: δ 21.1, 21.7, 32.1 (d, *J* = 5.9 Hz, *C*(CH$_3$)$_2$), 55.0$_6$ (major), 55.1$_2$ (minor), 75.4$_9$ and 75.5$_5$ (major isomer), 75.6 and 75.7 (minor isomer), 113.0, 113.3, 127.1, 127.3, 127.7, 127.7$_7$, 127.8$_2$, 128.0, 128.3, 128.8, 129.2, 129.6, 131.3 (d, *J* = 4.4 Hz), 131.5, 132.2 (d, *J* = 4.6 Hz), 133.5, 133.7, 137.8 (d, *J* = 8.1 Hz), 141.2, 141.3, 141.5 (d, *J* = 7.4 Hz), 159.0 (d, *J* = 11.5 Hz), [the doublet due to ^{1}*J*(P-C) was not clear].

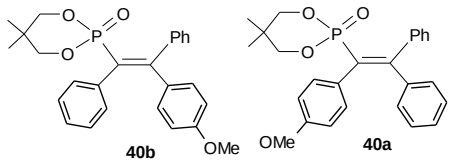
^{31}P NMR: δ 10.7 (minor) and 10.8 (major).

LC-MS: *m/z* 435 [M+1]$^+$.

Anal. Calcd. for $C_{26}H_{27}O_4P$: C, 71.88; H, 6.26. Found: C, 71.67; H, 6.19.

Compound 40 (isomer ratio 3:2)

Acetylene **1**, phenylboronic acid and 4-iodoanisole were used in this reaction.



Yield: 0.15 g (83%).

Mp: 223–226 ^{o}C (white solid).

IR (KBr): 2963, 1510, 1443, 1252, 1180, 1061, 1011, 986 cm^{-1}.

^{1}H NMR: (for major isomer): δ 0.70 and 0.99 (2 s, 6H, 2 C*H*$_3$), 3.70 (s, 3H, C$_6$H$_4$OC*H*$_3$), 3.58–3.66 and 3.78–3.87 (2 m, 4H, 2 OC*H*$_2$), 6.58–7.46 (m, 14H, Ar-*H*).

^{1}H NMR: (for minor isomer): δ 0.75 and 1.02 (s, 3H, 2 C*H*$_3$), 3.76 (s, 3H, C$_6$H$_4$OC*H*$_3$), remaining peaks were merged with major isomer peaks.

^{13}C NMR: δ 21.0$_9$, 21.1$_4$, 21.6, 21.7, 32.1 (d, *J* = 6.0 Hz, *C*(CH$_3$)$_2$), 55.0$_5$ and 55.1$_1$ (minor), 75.4 and 75.5 (major isomer), 75.5$_6$ and 75.6$_3$ (minor isomer), 113.0, 113.3, 127.1, 127.2, 127.3, 127.7, 127.8 (d, *J* = 5.2 Hz), 128.3, 128.8, 129.0, 129.2, 129.5, 131.2, 131.3 (d, *J* = 4.8 Hz), 131.4, 132.2 (d, *J* = 4.8 Hz), 133.6, 137.8, 137.9, 141.5 (d, *J* = 8.0 Hz), 158.9 [the spectrum was complicated due the peaks for both the isomers].

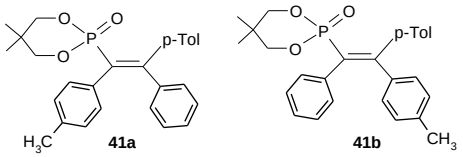
^{31}P NMR: δ 10.7$_8$ (major) and 10.8$_8$ (minor).

LC-MS: *m/z* 435 [M+1]$^+$.

Anal. Calcd. for $C_{26}H_{27}O_4P$: C, 71.88; H, 6.26. Found: C, 71.65; H, 6.38.

Compound 41 (isomer ratio 3:1)

Acetylene **2**, *p*-tolylboronic acid and iodobenzene were used in this reaction.



Yield: 0.15 g (93%).

Mp: 232–234 ^{o}C (white solid).

IR (KBr): 2963, 1611, 1508, 1474, 1250, 1115, 1061, 1013, 988 cm^{-1}.

^{1}H NMR: (for major isomer): δ 0.68 and 0.98 (2 s, 6H, 2 CH_3), 2.17 (s, 3H, $C_6H_4CH_3$), 2.35 (s, 3H, $C_6H_4CH_3$), 3.57–3.62 and 3.78–3.84 (2 m, 4H, 2 OCH_2), 6.84–7.33 (m, 13H, Ar-*H*).

^{1}H NMR: (for minor isomer): δ 0.71 and 1.01 (2 s, 6H, 2 CH_3), 2.24 (s, 3H, $C_6H_4CH_3$), remaining peaks were merged with major isomer peaks.

^{13}C NMR: δ 21.1, 21.4, 21.8, 22.7, 32.1 (d, J = 5.9 Hz, $C(CH_3)_2$), 75.5, 75.6, 127.0, 127.2, 127.6, 127.8, 128.3, 128.5, 129.0, 129.5, 129.7, 130.9, 131.2, 137.3, 138.1, 138.6 [the doublet due to ^{1}J(P-C) was not clear and the spectrum was complicated due the peaks for both the isomers].

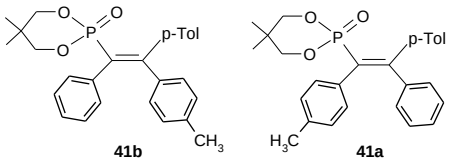
^{31}P NMR: δ 10.5 (minor) and 10.6 (major).

LC-MS: *m/z* 433 [M+1]$^{+}$.

Anal. Calcd. for $C_{27}H_{29}O_3P$: C, 74.98; H, 6.76. Found: C, 74.81; H, 6.90.

Compound 41 (isomer ratio 3:1)

Acetylene **2**, phenylboronic acid and 4-iodotoluene were used in this reaction.



Yield: 0.13 g (81%).

Mp: 237–238 ^{o}C (white solid).

IR (KBr): 2963, 1904, 1609, 1373, 1250, 1061, 1013, 988 cm^{-1}.

^{1}H NMR: (for major isomer): δ 0.68 and 0.98 (2 s, 6H, 2 CH_3), 2.17 (s, 3H, $C_6H_4CH_3$), 2.35 (s, 3H, $C_6H_4CH_3$), 3.58–3.64 and 3.74–3.84 (2 m, 4H, 2 OCH_2), 6.84–7.36 (m, 13H, Ar-*H*).

^{1}H NMR: (for minor isomer): δ 0.71 and 1.01 (2 s, 6H, 2 CH_3), 2.24 (s, 3H, $C_6H_4CH_3$), remaining peaks were merged with major isomer peaks.

^{13}C NMR: δ 21.0_5, 21.1_1, 21.4, 21.7_5, 21.8_0, 32.1 (d, *J* = 6.0 Hz, *C*$(CH_3)_2$), 75.5 and 75.6 (major), 75.6_2 and 75.6_8 (minor), 127.0, 127.2-129.6 (many lines), 130.8 (d, *J* = 5.0 Hz), 131.2 (d, *J* = 5.0 Hz), 134.3, 136.7, 137.2, 137.7_5, 137.8_4, 138.4, 138.6, 138.8, 159.8 (d, *J* = 12.0 Hz) [the spectrum was complicated due the peaks for both the isomers].

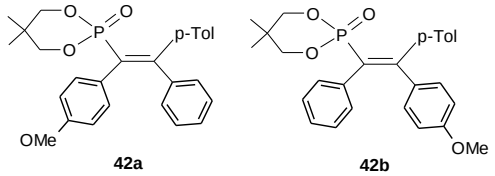
^{31}P NMR: δ 10.5 (minor) and 10.6 (major).

LC-MS: *m/z* 433 $[M+1]^+$.

Anal. Calcd. for $C_{27}H_{29}O_3P$: C, 74.98; H, 6.76. Found: C, 75.10; H, 6.72.

Compound 42 (isomer ratio 4:3)

Acetylene **2**, *p*-anisylboronic acid and iodobenzene were used in this reaction.



42a **42b**

Yield: 0.12 g (71%).

Mp: 208–210 ^{o}C (white solid).

IR (KBr): 2965, 1609, 1510, 1373, 1250, 1179, 1059, 1010 cm^{-1}.

^{1}H NMR: (for major isomer): δ 0.67 and 0.97 (2 s, 6H, 2 CH_3), 2.36 (s, 3H, $C_6H_4CH_3$), 3.57–3.64 (m, 2H, OCH_2), 3.67 (s, 3H, $C_6H_4OCH_3$), 3.77–3.86 (m, 2H, OCH_2), 6.55–7.34 (m, 13H, Ar-*H*).

^{1}H NMR: (for minor isomer): δ 0.72 and 1.00 (2 s, 6H, 2 CH_3), 3.73 (s, 3H, $C_6H_4OCH_3$), remaining peaks were merged with major isomer peaks.

^{13}C NMR: δ 21.0_7, 21.1_2, 21.3_8, 21.3_9, 21.7, 21.8, 32.1 (d, *J* = 5.9 Hz), 55.0, 55.1, 75.4_0, 75.4_7, 75.5_4, 75.6_0, 112.9, 113.3, 127.0-129.5 (many lines), 131.3 (d, *J* = 4.8 Hz), 131.4, 132.2 (d, *J* = 4.5 Hz), 134.0, 138.1, 138.7, 158.8 [the doublet due to ^{1}J(P-C) was not clear; the spectrum was complicated due the peaks for both the isomers].

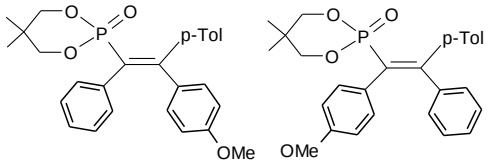
^{31}P NMR: δ 10.7_6 (minor) and 10.8_6 (major).

LC-MS: *m/z* 449 $[M+1]^+$.

Anal. Calcd. for $C_{27}H_{29}O_4P$: C, 72.31; H, 6.52. Found: C, 72.22; H, 6.51.

Compound 42 (isomer ratio 3:1)

Acetylene **2**, phenylboronic acid and 4-iodoanisole were used in this reaction.



42b **42a**

Yield: 0.12 g (71%).

Mp: 223–225 ^oC (white solid).

IR (KBr): 2967, 1607, 1508, 1252, 1061, 1013 cm^{-1}.

^1H NMR: (for major isomer): δ 0.67 and 0.96 (s, 6H, 2 C*H*$_3$), 2.36 (s, 3H, $C_6H_4CH_3$), 3.56–3.64 (m, 2H, OC*H*$_2$), 3.67 (s, 3H, $C_6H_4OCH_3$), 3.76–3.86 (m, 2H, OC*H*$_2$), 6.54–7.34 (m, 13H, Ar-*H*).

^1H NMR: (for minor isomer): δ 0.71 and 1.00 (s, 3H, 2 C*H*$_3$), 2.35 (s, 3H, $C_6H_4CH_3$), 3.73 (s, 3H, $C_6H_4OCH_3$), remaining peaks were merged with major isomer peaks.

^{13}C NMR: δ 21.0_7, 21.1_1, 21.4, 21.7, 32.1 (d, *J* = 5.9 Hz, *C*$(CH_3)_2$), 55.0, 75.4 and 75.5 (major), 75.6 and 75.7 (minor), 112.9, 127.0, 127.6, 127.8, 127.9 (d, *J* = 162.4 Hz, P*C*=C), 128.3, 128.5, 129.0, 129.2, 129.5, 129.6, 131.2 (d, *J* = 9.1 Hz), 131.3 (d, *J* ~ 9.1 Hz), 131.5, 137.3, 138.1, 158.8 [the spectrum was complicated due the peaks for both the isomers].

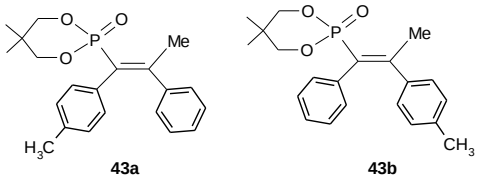
^{31}P NMR: δ 10.7 (minor) and 10.8 (major).

LC-MS: *m/z* 449 $[M+1]^+$.

Anal. Calcd. for $C_{27}H_{29}O_4P$: C, 72.31; H, 6.52. Found: C,72.41; H, 6.62.

Compound 43 (isomer ratio 7:3)

Acetylene **7**, *p*-tolylboronic acid and iodobenzene were used in this reaction.



43a **43b**

Yield: 0.14 g (75%).

Mp: 156−158 ^{o}C (white solid).

IR (KBr): 2965, 1607, 1595, 1375, 1262, 1092, 1059, 1005, 918 cm^{-1}.

^{1}H NMR: (for major isomer): δ 0.74 and 1.12 (2 s, 6H, 2 CH_3), 2.24 (s, 3H, $C_6H_4CH_3$), 2.64 (s, 3H, C=CCH_3), 3.57–3.62 (m, 2H, OCH_2), 3.92–3.99 (m, 2H, OCH_2), 6.85–6.99 (m, 5H, Ar-*H*), 7.10-7.14 (m, 4H, Ar-*H*).

^{1}H NMR: (for minor isomer): δ 0.72 and 1.10 (2 s, 6H, 2 CH_3), 2.23 (s, 3H, $C_6H_4CH_3$), 2.63 (s, 3H, C=CCH_3), remaining peaks were merged with major isomer peaks.

^{13}C NMR: δ 21.1, 21.8, 21.9, 24.1 (d, J = 6.8 Hz, C=C*C*H$_3$), 32.3 (d, J = 6.1 Hz, *C*(CH$_3$)$_2$), 75.4$_7$ and 75.5$_4$ (minor isomer), 75.5$_8$ and 75.6$_4$ (major isomer), 126.6, 126.9, 127.7, 127.8, 128.4, 130.4$_7$, 130.5$_2$, 130.7$_6$, 130.8$_1$, 136.3.

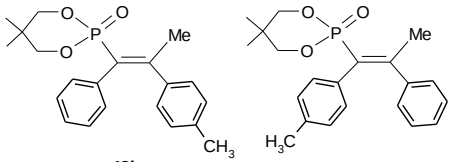
^{31}P NMR: δ 11.7.

LC-MS: *m/z* 357 [M+1]$^{+}$.

Anal. Calcd. for $C_{21}H_{25}O_3P$: C, 70.77; H, 7.07. Found: C, 70.79; H, 7.13.

Compound 43 (isomer ratio 9:1)

Acetylene **7**, phenylboronic acid and 4-iodotoluene were used in this reaction.



Yield: 0.16 g (86%).

Mp: 190−192 ^{o}C (white solid).

IR (KBr): 2967, 1609, 1510, 1441, 1262, 1094, 1059, 1007 cm^{-1}.

^{1}H NMR: (for major isomer): δ 0.72 and 1.10 (2 s, 6H, 2 CH_3), 2.23 (s, 3H, $C_6H_4CH_3$), 2.64 (s, 3H, C=CCH_3), 3.58 (dd→t, J ~ 10.3 Hz, 2H, OCH_2), 3.97 (dd→t, J ~ 12.4 Hz, 2H, OCH_2), 6.86–6.93 (m, 4H, Ar-*H*), 7.10–7.14 (m, 5H, Ar-*H*).

^{1}H NMR: (for minor isomer): δ 0.74 and 1.12 (s, 6H, 2 CH_3), 2.19 (s, 3H, $C_6H_4CH_3$), 2.65 (s, 3H, C=CCH_3), remaining peaks are merged with major isomer peaks.

^{13}C NMR: δ 21.0, 21.1, 21.8, 24.2 (d, *J* = 6.8 Hz, C=C*C*H$_3$), 32.3 (d, *J* = 6.1 Hz, *C*(CH$_3$)$_2$), 75.5, 75.6, 126.6$_3$, 126.6$_5$, 127.2 (d, *J* = 173.0 Hz), 127.7, 127.8, 128.4, 130.7$_3$, 130.7$_8$, 136.8, 137.7, 137.8, 139.5, 139.7, 157.2, 157.5.

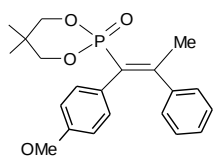
^{31}P NMR: δ 12.7.

LC-MS: *m/z* 357 $[M+1]^+$.

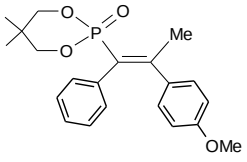
Anal. Calcd. for $C_{21}H_{25}O_3P$: C, 70.77; H, 7.07. Found: C, 70.74; H, 7.13. This compound was crystallized from dichloromethane-hexane mixture (4:1). X-ray structure was determined for this sample (Fig. 3 in Chapter 5).

Compound 44 (isomer ratio 2:1)

Acetylene **7**, *p*-anisylboronic acid and iodobenzene were used in this reaction.



44a



44b

Yield: 0.17 g (84%).

Mp: 166−168 ^{o}C (white solid).

IR (KBr): 2961, 1611, 1510, 1258, 1186, 1057, 1005 cm^{-1}.

^{1}H NMR: (for major isomer): δ 0.75 and 1.12 (2 s, 6H, 2 C*H*$_3$), 2.64 (s, 3H, C=CC*H*$_3$), 3.54–3.62 (m, 2H, OC*H*$_2$), 3.74 (s, 3H, C$_6$H$_4$OC*H*$_3$), 3.93–4.01 (m, 2H, OC*H*$_2$), 6.63–6.90 (m, 2H, Ar-*H*), 6.97-6.99 (m, 3H, Ar–*H*), 7.10–7.15 (m, 4H, Ar-*H*).

^{1}H NMR: (for minor isomer): δ 0.72 and 1.10 (2 s, 6H, 2 C*H*$_3$), 2.63 (s, 3H, C=CC*H*$_3$), 3.72 (s, 3H, C$_6$H$_4$OC*H*$_3$), 6.99–6.92 (d, *J* = 8.0 Hz, 2H, Ar-*H*), remaining peaks were merged with major isomer peaks.

^{13}C NMR: δ 20.9, 21.0, 21.8, 24.0 (d, *J* = 6.8 Hz, C=C*C*H$_3$), 32.1 (minor d, *J* ~ 6.2 Hz, *C*(CH$_3$)$_2$), 32.2 (major d, *J* = 6.2 Hz, *C*(CH$_3$)$_2$), 54.9$_6$, 54.9$_8$, 75.4$_8$ (minor), 75.5$_5$, 75.6$_1$, 126.6, 126.9, 127.0 (d, *J* = 172.3 Hz), 127.7, 129.3, 129.5, 129.6, 130.6$_8$, 130.7$_3$, 134.6, 134.8, 137.7, 137.8, 142.6, 142.8, 156.6, 156.9, 158.2, 158.4.

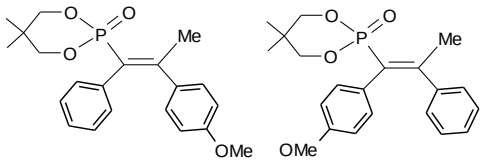
^{31}P NMR: δ 12.8$_1$ (minor) and 12.8$_5$ (major).

LC-MS: *m/z* 373 $[M+1]^+$.

Anal. Calcd. for $C_{21}H_{25}O_4P$: C, 67.75; H, 6.77. Found: C, 67.86; H, 6.75.

Compound 44 (isomer ratio 7:3)

Acetylene **7**, phenylboronic acid and 4-iodoanisole were used in this reaction.



44b **44a**

Yield: 0.15 g (75%).

Mp: 167−170 ^{o}C (white solid).

IR (KBr): 2961, 1611, 1510, 1441, 1372, 1260, 1175, 1059, 1003, 980 cm^{-1}.

^{1}H NMR: (for major isomer): δ 0.71 and 1.10 (2 s, 6H, 2 CH_3), 2.63 (s, 3H, C=CCH_3), 3.54–3.61 (m, 2H, OCH_2), 3.72 (s, 3H, C_6H_4OCH_3), 3.93–3.99 (m, 2H, OCH_2), 6.63–6.67 (m, 2H, Ar–*H*), 6.90–6.98 (m, 3H, Ar–*H*), 7.08–7.15 (m, 4H, Ar–*H*).

^{1}H NMR: (for minor isomer): δ 0.74 and 1.11 (2 s, 6H, 2 CH_3), 2.64 (s, 3H, C=CCH_3), 3.73 (s, 3H, C_6H_4OCH_3), remaining peaks were merged with major isomer peaks.

^{13}C NMR: δ 21.0, 21.8, 24.1 (d, *J* = 6.8 Hz, C=C*C*H$_3$), 32.3 (d, *J* = 6.1 Hz, *C*(CH$_3$)$_2$), 55.1, 75.5, 75.6, 113.1, 126.0, 126.7, 127.8, 129.3, 130.7$_7$, 130.8$_2$, 131.8, 134.7, 134.9, 137.8, 137.9, 156.6, 156.8, 158.5, [the doublet due to ^{1}J(P-C) was not clear].

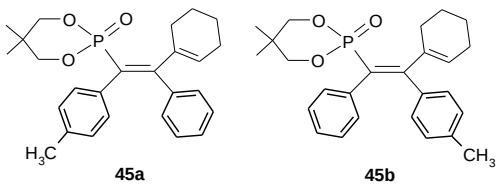
^{31}P NMR: δ 12.7$_9$ (major) and 12.8$_3$ (minor).

LC-MS: *m/z* 373 [M+1]$^{+}$.

Anal. Calcd. for $C_{21}H_{25}O_4P$: C, 67.73; H, 6.77. Found: C, 67.55; H, 6.85. This compound was crystallized from dichloromethane-hexane mixture (4:1). X-ray structure was determined for this sample (Fig. 3 in Chapter 5).

Compound 45 (isomer ratio 2:1)

Acetylene **3**, *p*-tolylboronic acid and iodobenzene were used in this reaction.



45a **45b**

Yield: 0.15 g (87%).

Mp: 205–206 ^{o}C (white solid).

IR (KBr): 2922, 1651, 1477, 1373, 1250, 1140, 1063, 1015, 986 cm^{-1}.

^1H NMR: (for major isomer): δ 0.71 and 1.03 (2 s, 6H, 2 C*H*$_3$), 1.62 (br s, 4H), 2.00 (br s, 2H), 2.21 (br s, 5H, C*H*$_2$ + C_6H_4C*H*$_3$), 3.55–3.63 (m, 2H, OC*H*$_2$), 3.94–4.02 (m, 2H, OC*H*$_2$), 6.06 (br s, 1H, PC=C(C=C*H*)(*p*-tolyl)), 6.85–6.91 (m, 2H, Ar-*H*), 7.02–7.15 (m, 7H, Ar-*H*).

^1H NMR: (for minor isomer): δ 0.68 and 0.99 (2 s, 6H, 2 C*H*$_3$), 2.19 (s, 3H, C_6H_4C*H*$_3$), remaining peaks were merged with major isomer peaks.

^{13}C NMR: δ 21.1_0, 21.1_8, 21.2_3, 21.7_2, 21.7_3, 21.8, 22.5, 25.5, 27.5, 27.6, 32.1 (minor, d, *J* = 5.9 Hz, *C*$(CH_3)_2$), 32.2 (major, d, *J* = 5.9 Hz, *C*$(CH_3)_2$), 75.2 and 75.3 (minor), 75.4 and 75.5 (major), 125.7, 126.2, 127.0 (d, *J* = 2.0 Hz), 127.3, 127.5, 127.6, 128.1 (d, *J* = 2.2 Hz), 128.3_4, 128.3_5, 129.1, 129.3, 131.0 (d, *J* = 4.9 Hz), 131.4 (d, *J* = 4.8 Hz), 134.1 (d, *J* = 10.4 Hz), 135.7, 135.9, 136.4 (d, *J* = 2.2 Hz), 137.3, 137.5, 138.5 (d, *J* = 7.7 Hz), 138.7 (d, *J* = 7.0 Hz), 138.6, 139.0, 139.2, 162.7 (d, *J* = 12.4 Hz), [the doublet due to ^1J(P-C) was not clear and the spectrum was complicated due the peaks for both the isomers].

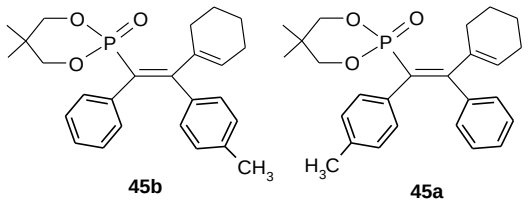
^{31}P NMR: δ 11.9.

LC-MS: *m/z* 423 $[M+1]^+$.

Anal. Calcd. for $C_{26}H_{31}O_3P$: C, 73.91; H, 7.40. Found: C, 74.02; H, 7.38.

Compound 45 (isomer ratio 4:3)

Acetylene **3**, phenylboronic acid and 4-iodotoluene were used in this reaction.



Yield: 0.15 g (87%).

Mp: 200–202 ^oC (white solid).

IR (KBr): 2926, 1585, 1510, 1373, 1252, 1140, 1063, 1013, 990 cm^{-1}.

^1H NMR: (for major isomer): δ 0.68 and 0.99 (2 s, 6H, 2 C*H*$_3$), 1.63 (br s, 4H), 2.00 (br s, 2H), 2.19 (br s, 5H, C*H*$_2$ + C_6H_4C*H*$_3$), 3.56–3.64

(m, 2H, OCH_2), 3.94–4.02 (m, 2H, OCH_2), 6.07 (s, 1H, PC=C(C=C*H*)(*p*-tolyl)), 6.86–6.92 (m, 2H, Ar-*H*), 7.02–7.16 (m, 7H, Ar-*H*).

^{1}H NMR: (for minor isomer): δ 0.72 and 1.03 (2 s, 6H, 2 CH_3), 2.22 (s, 3H, $C_6H_4CH_3$), 6.06 (br s, 1H, PC=C(C=C*H*)(*p*-Tolyl)), remaining peaks were merged with major isomer peaks.

^{13}C NMR: δ 21.1$_9$, 21.2$_4$, 21.3, 21.8, 21.9, 22.5, 25.6, 26.7, 27.6, 32.3 (d, *J* = 5.7 Hz, *C*$(CH_3)_2$), 75.2$_8$, and 75.3$_4$ (major), 75.4$_2$ and 75.4$_8$ (minor), 125.8, 126.3, 126.8, 127.3, 127.5, 127.6, 128.1 (d, *J* = 2.2 Hz), 128.3, 128.4, 129.2, 129.3, 131.1 (d, *J* = 4.4 Hz), 131.4 (d, *J* = 4.4 Hz), 134.2 (d, *J* = 10.0 Hz), 135.8, 136.0, 136.4, 137.3, 137.6, 137.7, 138.6, 138.7 (d, *J* = 7.6 Hz), 138.8, 139.1, 139.3, 163.2 (d, *J* = 12.0 Hz), [the doublet due to ^1J(P-C) was not clear; the spectrum was complicated due the peaks for both the isomers].

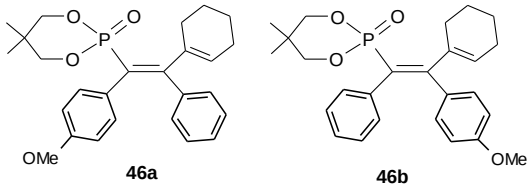
^{31}P NMR: δ 11.8$_9$ (major) and 11.8$_6$ (minor).

LC-MS: *m/z* 423 $[M+1]^+$.

Anal. Calcd. for $C_{26}H_{31}O_3P$: C, 73.91; H, 7.40. Found: C, 73.89; H, 7.49.

Compound 46 (isomer ratio 4:1)

Acetylene **3**, *p*-anisylboronic acid and iodobenzene were used in this reaction.



46a **46b**

Yield: 0.15 g (90%).

Mp: 212–214 ^{o}C(white solid).

IR (KBr): 2919, 1609, 1508, 1373, 1250, 1177, 1063, 1013, 984 cm^{-1}.

^{1}H NMR: (for major isomer): δ 0.73 and 1.02 (2 s, 6H, 2 CH_3), 1.63 (br s, 4H), 2.00 (br s, 2H), 2.22 (br s, 2H), 3.54–3.64 (m, 2H, OCH_2), 3.71 (s, 3H, $C_6H_4OCH_3$), 3.98–4.03 (m, 2H, OCH_2), 6.06 (br s, 1H, PC=C(C=C*H*)(*p*-anisyl)), 6.64 (d, *J* ~ 8.3 Hz, 2H, Ar-*H*), 7.01–7.16 (m, 7H, Ar-*H*).

^{1}H NMR: (for minor isomer): δ 0.67 and 0.98 (2 s, 6H, 2 C*H*$_3$), 1.59 (br s, 4H), 3.69 (s, 3H, $C_6H_4OCH_3$), 6.04 (br s, 1H, PC=C(C=C*H*)(*p*-anisyl)), 6.59 (d, *J* ~ 8.7 Hz, 2H, Ar-*H*), 6.96 (d, *J* ~ 8.6 Hz, 2H, Ar-*H*), remaining peaks were merged with major isomer peaks.

^{13}C NMR: δ 21.2$_5$ (minor), 21.3$_5$ (major), 21.7$_7$ (minor), 21.8$_3$ (major), 22.5, 25.6, 27.6, 27.8, 32.3 (d, *J* = 5.6 Hz, *C*$(CH_3)_2$), 55.1, 75.3, 75.4, 113.0, 113.1, 126.8, 127.4, 127.6, 127.7, 128.3, 129.3, 131.0, 131.6, 132.5, 159.8, [the doublet due to ^{1}J(P-C) was not clear].

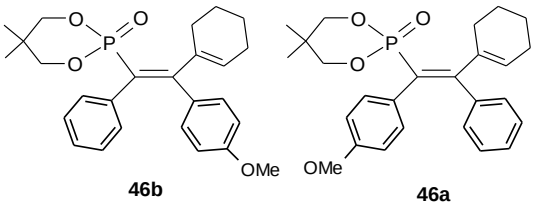
^{31}P NMR: δ 12.1.

LC-MS: *m/z* 439 $[M+1]^+$.

Anal. Calcd. for $C_{26}H_{31}O_4P$: C, 71.22; H, 7.13. Found: C, 71.35; H, 7.16.

Compound 46 (isomer ratio 4:1)

Acetylene **3**, phenylboronic acid and 4-iodoanisole were used in this reaction.



46b **46a**

Yield: 0.16 g (92%).

Mp: 201–202 ^{o}C (white solid).

IR (KBr): 2922, 1607, 1510, 1373, 1250, 1179, 1063, 1013 cm^{-1}.

^{1}H NMR: (for major isomer): δ 0.67 and 0.99 (2 s, 6H, 2 C*H*$_3$), 1.64 (br s, 4H), 2.00 (br s, 2H), 2.23 (br s, 2H), 3.57 (dd→t, *J* ~ 11.4 Hz, 2H, OC*H*$_2$), 3.70 (s, 3H, $C_6H_4OCH_3$), 4.01 (dd→t, *J* ~ 11.0 Hz, 2H, OC*H*$_2$), 6.03 (br s, 1H, PC=C(C=C*H*)(*p*-anisyl)), 6.59 (d, *J* ~ 8.7 Hz, 2H, Ar-*H*), 6.96 (d, *J* ~ 8.6 Hz, 2H, Ar-*H*), 7.12–7.16 (m, 5H, Ar-*H*).

^{1}H NMR: (for minor isomer): δ 0.73 and 1.01 (2 s, 6H, 2 C*H*$_3$), 3.71 (s, 3H, $C_6H_4OCH_3$), the other peaks were merged with those due to the major isomer.

^{13}C NMR: δ 21.1, 21.7, 22.5, 25.5, 27.7, 32.1 (d, *J* = 5.7 Hz, *C*$(CH_3)_2$), 55.0, 75.1$_7$ and 75.2$_4$ (major), 75.3 and 75.4 (minor), 112.9, 125.0-131.5 (many lines), 132.3 (d, *J* = 5.1 Hz), 137.7 (d, *J* = 10.3 Hz), 138.7 (d, *J*

= 7.7 Hz), 159.9, 162.7 (d, *J* = 12.4 Hz), [the doublet due to ^{1}J(P-C) was not clear].

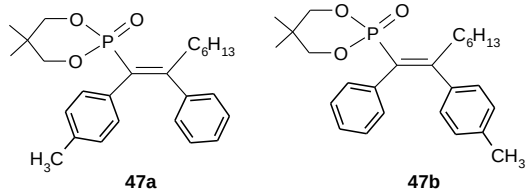
^{31}P NMR: δ 12.1.

LC-MS: *m/z* 439 $[M+1]^{+}$.

Anal. Calcd. for $C_{26}H_{31}O_4P$: C, 71.22; H, 7.13. Found: C, 71.36; H, 7.21.

Compound 47 (isomer ratio >9:1)

Acetylene **4**, *p*-tolylboronic acid and iodobenzene were used in this reaction.



47a **47b**

Yield: 0.13 g (81%).

Mp: 105–107 ^{o}C (white solid).

IR (KBr): 2857, 1611, 1510, 1250, 1181, 1057, 1009 cm^{-1}.

^{1}H NMR: (for major isomer): δ 0.71 (s, 3H, C*H*$_3$), 0.82 (t, *J* = 7.2 Hz, 3H, C*H*$_3$), 1.05 (s, 3H, C*H*$_3$), 1.20–1.22 (m, 4H, (C*H*$_2$)$_2$), 1.35 (br s, 4H, (C*H*$_2$)$_2$), 2.18 (s, 3H, C$_6$H$_4$C*H*$_3$), 3.02–3.03 (m, 2H, C*H*$_2$), 3.55 (dd→t, *J* ~ 10.5 Hz, 2H, OC*H*$_2$), 3.95 (dd→t, *J* ~ 11.8 Hz, 2H, OC*H*$_2$), 6.79–6.92 (m, 5H, Ar-*H*), 7.04–7.10 (m, 4H, Ar-*H*).

^{1}H NMR: (for minor isomer): δ 0.80 and 1.02 (2 s, 6H, C*H*$_3$), 2.15 (s, 3H, C$_6$H$_4$C*H*$_3$), remaining peaks are merged with major isomer peaks.

^{13}C NMR: δ 14.1, 21.1, 21.2, 21.9, 22.6, 28.4, 29.3, 31.6, 32.4 (d, *J* = 6.3 Hz, *C*(CH$_3$)$_2$), 37.0 (d, *J* = 6.7 Hz, PC=C*C*H$_2$), 75.4, 75.5, 126.7, 127.2 (d, *J* = 173.3 Hz, P*C*=C), 127.6, 128.3 (d, *J* = 4.1 Hz), 130.6 (d, *J* = 4.8 Hz), 131.0 (d, *J* ~ 4.0 Hz), 134.5 (d, *J* = 10.4 Hz), 136.1, 141.3 (d, *J* = 11.7 Hz), 162.4 (d, *J* = 14.2 Hz).

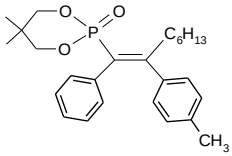
^{31}P NMR: δ 12.4.

LC-MS: *m/z* 427 $[M+1]^{+}$.

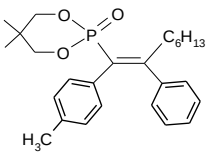
Anal. Calcd. for $C_{26}H_{35}O_3P$: C, 73.22; H, 8.27. Found: C, 73.32; H, 8.24.

Compound 47 (isomer ratio 9:1)

Acetylene **4**, phenylboronic acid and 4-iodotoluene were used in this reaction.



47b



47a

Yield: 0.14 g (87%).

Mp: 143–145 ^{o}C (white solid).

IR (KBr): 2928, 1591, 1510, 1372, 1260, 1057, 1005, 980 cm^{-1}.

^{1}H NMR: (for major isomer): δ 0.68 (s, 3H, C*H*$_3$), 0.82 (t, *J* = 6.6 Hz, 3H, C*H*$_3$), 1.03 (s, 3H, C*H*$_3$), 1.22–1.26 (m, 4H, (C*H*$_2$)$_2$), 1.35–1.38 (m, 4H, (C*H*$_2$)$_2$), 2.20 (s, 3H, C$_6$H$_4$C*H*$_3$), 3.03–3.06 (m, 2H, C*H*$_2$), 3.54 (dd→t, *J* ~ 12.2 Hz, 2H, OC*H*$_2$), 3.99 (dd→t, *J* ~ 11.5 Hz, 2H, OC*H*$_2$), 6.81 (d, *J* = 7.8 Hz, 2H, Ar-*H*), 6.88 (d, *J* = 7.8 Hz, 2H, Ar-*H*), 7.03–7.08 (m, 5H, Ar-*H*).

^{1}H NMR: (for minor isomer): δ 0.71 and 1.05 (s, 3H, 2 C*H*$_3$), remaining peaks were merged with major isomer peaks.

^{13}C NMR: δ 14.1, 21.1, 21.2, 21.8, 22.6, 28.5, 29.4, 31.6, 32.4 (d, *J* = 6.1 Hz, *C*(CH$_3$)$_2$), 37.0 (d, *J* = 6.6 Hz, PC=C*C*H$_2$), 75.3, 75.4, 126.5, 126.7 (d, *J* = 174.4 Hz), 127.5, 128.2, 128.3, 130.9 (d, *J* = 4.6 Hz), 136.5, 137.8, 137.9, 138.1, 163.1 (d, *J* = 13.5 Hz).

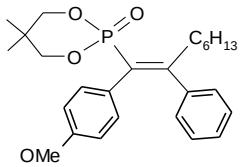
^{31}P NMR: δ 12.1 (minor) and 12.4 (major).

LC-MS: *m/z* 427 [M+1]$^{+}$.

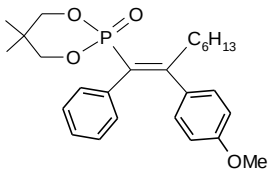
Anal. Calcd. for C$_{26}$H$_{35}$O$_3$P: C, 73.22; H, 8.27. Found: C, 73.38; H, 8.14.

Compound 48 (isomer ratio >9:1)

Acetylene **4**, *p*-anisylboronic acid and iodobenzene were used in this reaction.



48a



48b

Yield: 0.15 g (86%).

Mp: 81–83 ^{o}C (white solid).

IR (KBr): 2928, 1611, 1250, 1181, 1057, 1009, 820 cm^{-1}.

^{1}H NMR: (for major isomer): δ 0.72 (s, 3H, C*H*$_3$), 0.81–0.84 (m, 3H, C*H*$_3$), 1.05 (s, 3H, C*H*$_3$), 1.22 and 1.35 (2 br s, 8H, (C*H*$_2$)$_4$), 3.05 (br s, 2H,

CH_2), 3.54–3.59 (m, 2H, OCH_2), 3.70 (s, 3H, C_6H_4OCH_3), 3.96–4.02 (m, 2H, OCH_2), 6.62 (d, J = 8.6, 2H, Ar-H), 6.91–7.11 (m, 7H, Ar-H).

^{1}H NMR: (for minor isomer): δ 0.68 and 1.03 (2 s, 6H, 2 CH_3), remaining peaks were merged with major isomer peaks.

^{13}C NMR: δ 14.0, 21.2, 21.8, 22.5, 28.3, 29.3, 31.6, 32.3 (d, J = 6.3 Hz, C(CH_3)$_2$), 36.9 (d, J = 6.4 Hz, PC=CCH_2), 55.0, 75.3, 75.4, 113.0, 126.7, 127.6, 128.2, 131.9 (d, J = 5.0 Hz), 141.3, 158.2, 162.9 (d, J = 13.3 Hz), [the doublet due to ^1J(P-C) was not clear].

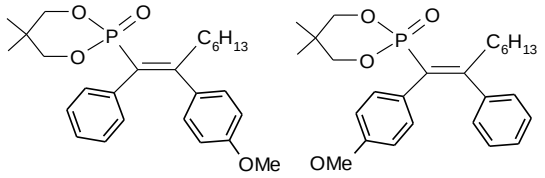
^{31}P NMR: δ 12.8.

LC-MS: m/z 443 $[M+1]^+$.

Anal. Calcd. for $C_{26}H_{35}O_4P$: C, 70.57; H, 7.97. Found: C, 70.55; H, 7.96.

Compound 48 (isomer ratio 1:0)

Acetylene **4**, phenylboronic acid and 4-iodoanisole were used in this reaction.



48b **48a**

Yield: 0.15 g (84%).

Mp: 108–110 ^{o}C (white solid).

IR (KBr): 2929, 1611, 1510, 1368, 1250, 1181, 1057, 1009 cm^{-1}.

^{1}H NMR: δ 0.68 (s, 3H, CH_3), 0.81–0.83 (m, 3H, CH_3), 1.03 (s, 3H, CH_3), 1.22 and 1.36 (2 br s, 8H, C_4H_8), 3.05 (br s, 2H, CH_2), 3.51–3.57 (m, 2H, OCH_2), 3.70 (s, 3H, C_6H_4OCH_3), 3.96–4.02 (m, 2H, OCH_2), 6.62 (d, J = 8.6 Hz, 2H, Ar-H), 6.85 (d, J = 8.4 Hz, 2H, Ar-H), 7.05–7.10 (m, 5H, Ar-H).

^{13}C NMR: δ 14.1, 21.2, 21.8, 22.6, 28.6, 29.3, 31.6, 32.4 (d, J = 6.1 Hz, C(CH_3)$_2$), 37.0 (d, J = 6.4 Hz, PC=CCH_2), 55.1, 75.3, 75.4, 113.0, 125.9, 126.5, 127.6, 129.6, 131.9 (d, J = 4.7 Hz), 133.3, 133.5, 137.9, 138.0, 158.4, 162.7 (d, J = 13.3 Hz), [the doublet due to ^1J(P-C) was not clear].

^{31}P NMR: δ 12.5.

LC-MS: *m/z* 443 $[M+1]^+$.

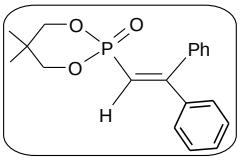
Anal. Calcd. for $C_{26}H_{35}O_4P$: C,70.57; H, 7.97. Found: C, 70.81; H, 8.00.

6.5 Preparation of monoarylated vinylphosphonates 49-52 and vinylphosphine oxide 53

General procedure for the synthesis of trisubstituted olefins 49-53

Alkyne **1** (0.10 g, 0.40 mmol), phenylboronic acid (0.05 g, 0.40 mmol), K_2CO_3 (0.06 g, 0.40 mmol), $PdCl_2(PPh_3)_2$ (8.42 mg, 3 mol%) and HOAc (46 µL, 0.80 mmol) in water (2 mL) were refluxed for 2 h. The reaction mixture was extracted with EtOAc (20 mL), dried over anhyd. Na_2SO_4, the solvent removed and pure compound **49** was isolated by silica gel column chromatography (EtOAc-hexane= 1:1). Compounds **50-53** were synthesized in a manner similar to compound **49** using the same molar quantities.

Compound 49



Yield: 0.09 g (69%).

Mp: 184–186 ^oC (white solid).

IR (KBr): 2974, 1595, 1572, 1471, 1447, 1373, 1263, 1059, 1007, 914 cm^{-1}.

^1H NMR: δ 0.85 and 1.13 (2 s, 6H, 2 C*H*$_3$), 3.72-3.82 (m, 4H, OC*H*$_2$), 6.14 (d, *J* = 16.0 Hz, 1H, PC*H*=CPh), 7.30-7.42 (m, 10H, Ar-*H*).

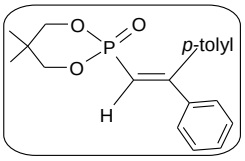
^{13}C NMR: δ 21.0, 21.8, 32.3 (d, *J* = 6.2 Hz, *C*$(CH_3)_2$), 76.0, 76.1, 112.3 (d, *J* = 182.0 Hz), 128.0, 128.3, 128.4, 129.2, 129.7, 129.8, 138.2$_6$, 138.3$_3$, 141.1, 141.3, 162.1, 162.2.

^{31}P NMR: δ 11.6.

LC-MS: *m/z* 329 $[M+1]^+$.

Anal. Calcd. for $C_{19}H_{21}O_3P$: C, 69.50; H, 6.45. Found: C, 69.71; H, 6.31.

Compound 50



Yield: 0.09 g (69%).

Mp: 180–182 ^{o}C (white solid).

IR (KBr): 2967, 1586, 1508, 1346, 1267, 1059, 1005, 918 cm^{-1}.

^{1}H NMR: δ 0.85 and 1.14 (2 s, 6H, 2 C*H*$_3$), 2.38 (s, 3H, C=CC$_6$H$_4$C*H*$_3$), 3.75-3.79 (m, 4H, OC*H*$_2$), 6.07 (d, *J* = 16.0 Hz, 1H, PC*H*), 7.20 (br s, 1H, Ar-*H*), 7.27-7.33 (m, 8H, Ar-*H*).

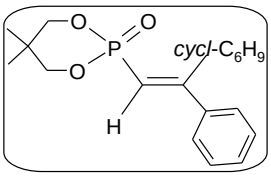
^{13}C NMR: δ 21.0, 21.4, 21.8, 32.3 (d, *J* = 8.0 Hz, *C*(CH$_3$)$_2$), 76.0, 76.1, 111.6 (d, *J* = 181.0 Hz, P*C*H), 128.3, 128.4, 128.7, 129.7, 135.3$_6$, 135.4$_2$, 139.3, 141.4, 141.6, 162.4$_8$, 162.5$_4$.

^{31}P NMR: δ 11.9.

LC-MS: *m/z* 343 [M+1]$^{+}$.

Anal. Calcd. for $C_{20}H_{23}O_3P$: C, 70.16; H, 6.77. Found: C, 70.35; H, 6.69.

Compound 51



Yield: 0.08 g (62%).

Mp: 140–142 ^{o}C (white solid).

IR (KBr) 2934, 1738, 1595, 1263, 1059, 1007, 818 cm^{-1}.

^{1}H NMR: δ 0.99 and 1.18 (2 s, 6H, 2 C*H*$_3$), 1.68 (br s, 4H), 2.00 (br s, 2H), 2.24 (br s, 2H), 3.88 (dd→t, *J* ~ 10.2 Hz, 2H, OC*H*$_2$), 4.02-4.09 (m, 2H, OC*H*$_2$), 5.79 (d, *J* = 19.6 Hz, 1H, PC*H*), 6.09 (br s, 1H, PC=C(C=C*H*)(Ph)), 7.37-7.38 (m, 3H, Ar-*H*), 7.43-7.45 (m, 2H, Ar-*H*).

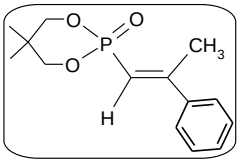
^{13}C NMR: δ 21.3, 21.8, 22.5, 25.5, 28.0, 32.5 (d, *J* = 5.8 Hz, *C*(CH$_3$)$_2$), 75.7$_6$, 75.8$_2$, 110.2 (d, *J* = 186.6 Hz, P*C*H), 127.4, 128.5, 129.5, 130.8$_7$, 130.8$_9$, 135.5, 135.6, 138.8, 139.0, 165.8, 165.9.

^{31}P NMR: δ 13.3.

LC-MS: *m/z* 333 [M+1]$^{+}$.

Anal. Calcd. for $C_{19}H_{25}O_3P$: C, 68.66; H, 7.58. Found: C, 68.55; H, 7.76.

Compound 52



Yield: 0.10 g (71%).

Mp: 88–90 ^{o}C (white solid).

IR (KBr): 2969, 1605, 1572, 1472, 1256, 1055, 999, 947 cm^{-1}.

^{1}H NMR: δ 1.06 and 1.15 (2 s, 6H, 2 C*H*$_3$), 2.55 (s, 3H, C=CC*H*$_3$), 3.89 (dd→t, *J* ~ 10.0 Hz, 2H, OC*H*$_2$), 4.17 (dd→t, *J* =12.0 Hz, 2H, OC*H*$_2$), 5.95 (d, *J* = 20.0 Hz, 1H, PC*H*), 7.39-7.49 (m, 5H, Ar-*H*).

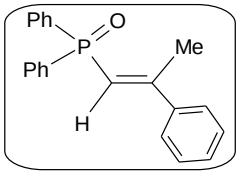
^{13}C NMR: δ 19.7 (d, *J* = 7.0 Hz), 21.4, 21.6, 32.6 (d, *J* = 6.0 Hz, *C*(CH$_3$)$_2$), 75.4$_5$, 75.5$_1$, 111.3 (d, *J* = 186.0 Hz, P*C*H), 126.0, 127.1, 128.6 (d, *J* = 18.0 Hz), 129.0, 141.5 (d, *J* = 23.0 Hz), 160.2.

^{31}P NMR: δ 14.0.

LC-MS: *m/z* 267 [M+1]$^{+}$.

Anal. Calcd. for $C_{14}H_{19}O_3P$: C, 63.15; H, 7.19. Found: C, 63.31; H, 7.15.

Compound 53



Yield: 0.10 g (78%).

Mp: 68–70 ^{o}C (white solid).

IR (KBr): 3057, 1595, 1435, 1316, 1231, 1169, 1119, 1101, 995 cm^{-1}.

^{1}H NMR: δ 2.51 (d, *J* = 1.2 Hz, 3H, C=CC*H*$_3$), 6.14 (d, *J* = 23.6 Hz, 1H, PC*H*=CCH$_3$), 7.36-7.51 (m, 11H, Ar-*H*), 7.77-7.82 (m, 4H, Ar-*H*).

^{13}C NMR: δ 19.7 (d, *J* = 7.4 Hz, *C*H$_3$), 118.4 (d, *J* = 103.9 Hz, P*C*H), 126.0, 128.5, 128.6, 128.9, 129.2, 130.9, 131.0, 131.2, 131.5, 131.6, 134.2, 135.3, 142.1, 142.2, 159.3$_2$, 159.3$_4$.

^{31}P NMR: δ 21.6.

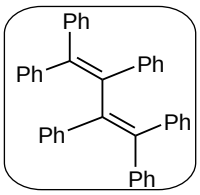
LC-MS: *m/z* 317 [M-1]$^{+}$.

Anal. Calcd. for $C_{21}H_{19}OP$: C, 79.23; H, 6.02. Found: C, 79.35; H, 5.88.

6.6 Use of dinuclear palladium(I) catalyst 13 in various coupling reactions

6.61 Synthesis of compound 54

A mixture of diphenylacetylene (0.20 g, 1.1 mmol), phenylboronic acid (0.14 g, 1.1 mmol), Ag_2CO_3 (0.31 g, 2.2 mmol), catalyst **13** (6.0 mg, 0.005 mmol) or $Pd(OAc)_2$ (6.5 mg, 0.025 mmol) in 1-propanol/water mixture (2 mL, 9:1) was heated at 120 ^oC for 0.5 h. The solvent (isopropanol) was removed *in vacuo*, the mixture extracted with EtOAc (20 mL), dried (Na_2SO_4) and the solvent removed. Pure compound **54** was isolated by silica gel column chromatography (hexane).

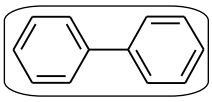


Yield: 0.46 g (80%, by using catalyst **13**), 0.38 g (67%, by using $Pd(OAc)_2$). Spectral data are consistent with that reported in literature.[25]

6.62 Synthesis of compounds 55-56

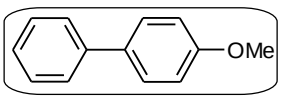
A mixture of aryl bromide (1.0 mmol), phenylboronic acid (0.15 g, 1.2 mmol), K_3PO_4 (0.44 g, 2.0 mmol), catalyst **13** (5.0 mg, 0.005 mmol) or $Pd(PPh_3)_4$ (12 mg, 0.01 mmol) in water (3 mL) was heated at 100 ^oC for 4-6 h. The mixture was extracted with diethyl ether (20 mL), dried (Na_2SO_4), the solvent removed and pure compound **55** was isolated by silica gel column chromatography (hexane).

Compound 55



Yield: 0.13 (82%, by using catalyst **13**); 0.11 g (74%, by using $Pd(PPh_3)_4$). Spectral data are consistent with that reported in literature.[29a]

Compound 56

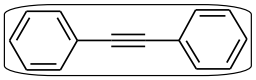


Yield: 0.14 g (78%, by using catalyst **13**); 0.13 g (76%, by using $Pd(PPh_3)_4$). Spectral data are consistent with that reported in literature.[29a]

6.63 Preparation of compounds 57-58

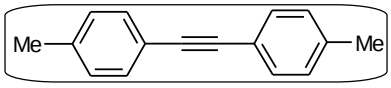
A mixture of aryl alkyne (0.5 mmol), aryl iodide (0.6 mmol), catalyst **13** (1.3 mg, 0.0025 mmol) or $Pd(PPh_3)_4$ (2.9 mg, 0.05 mmol) in piperidine (3 mL) was heated at 70 ^oC for 5-10 min. The reaction mixture was quenched with dil. HCl (10% v/v) and extracted with diethyl ether (2 x 20 mL), The combined organic layer was washed with brine solution (10 mL) followed by water (2 x 10 mL) and dried (Na_2SO_4). The solvent was removed and pure compound **57** was isolated by silica gel column chromatography (hexane).

Compound 57



Yield: 0.08 g (89%, by using catalyst **13**), 0.078 g (87%, by using $Pd(PPh_3)_4$). Spectral data are consistent with that reported in literature.[29b]

Compound 58



Yield: 0.09 g (85%, by using catalyst 1**3**), 0.08 g (80%, by using $Pd(PPh_3)_4$). Spectral data are consistent with that reported in literature.[29c]

6.7 X-ray crystallography

The methodology was similar to that given in Chapter 3.[34] Crystal data are summarized in Table 5.

Table 5. Crystal data for compounds **22**, **26**, **43b** and **44b**[a]

Compound	**22**	**26**	**43b**	**44b**
Emp. formula	$C_{22}H_{27}O_5P$	$C_{24}H_{25}O_3P$	$C_{21}H_{25}O_3P$	$C_{21}H_{25}O_4P$
Formula weight	402.41	392.41	356.38	372.38
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	*P-1*	*P-1*	*P2(1)/c*	*P2(1)/c*
a /Å	8.7513(17)	11.2268(12)	16.838(5)	9.3094(9)
b /Å	9.4022(18)	13.6175(15)	6.2071(18)	20.331(2)
c /Å	14.290(3)	15.0322(17)	19.499(6)	10.6254(10)
α/deg	103.871(3)	83.132(9)	90	90
β/deg	105.484(3)	73.282(10)	104.944(5)	99.477(2)
γ/deg	101.307(3)	79.617(9)	90	90
V /Å^3	1056.7(4)	2159.4(4)	1969.06(10)	1983.6(3)
Z	2	4	4	4
D_{calc} /g cm^{-3}]	1.265	1.207	1.202	1.247
μ /mm^{-1}	0.159	0.148	0.155	0.161
F(000)	428	832	760	792
Data/ restraints/ parameters	3698/0/258	6211/0/509	3487/0/230	3492/0/239
S	1.060	0.947	1.086	1.042
R1 [I>2σ(I)]	0.0510	0.0688	0.0560	0.0475
wR2 [all data]	0.1316	0.2017	0.1377	0.1271
Max./min. residual electron dens. [eÅ^{-3}]	0.222/-0.436	0.573/-0.344	0.321/-0.201	0.269/-0.176

[a]$R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma wF_o^4]^{0.5}$

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A) Copies of $^{1}H/^{13}C$ NMR spectra for representative compounds

PART A: Compounds 18, 20, 31, 37, 41, 50, 55, 71, 90, and 118

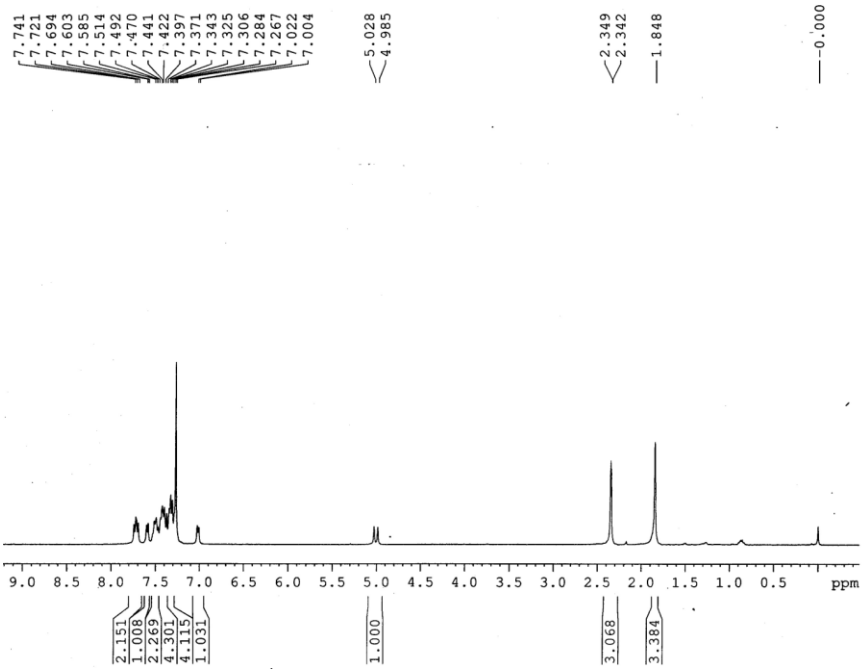

Fig. A1. ^{1}H NMR spectrum of compound **18**

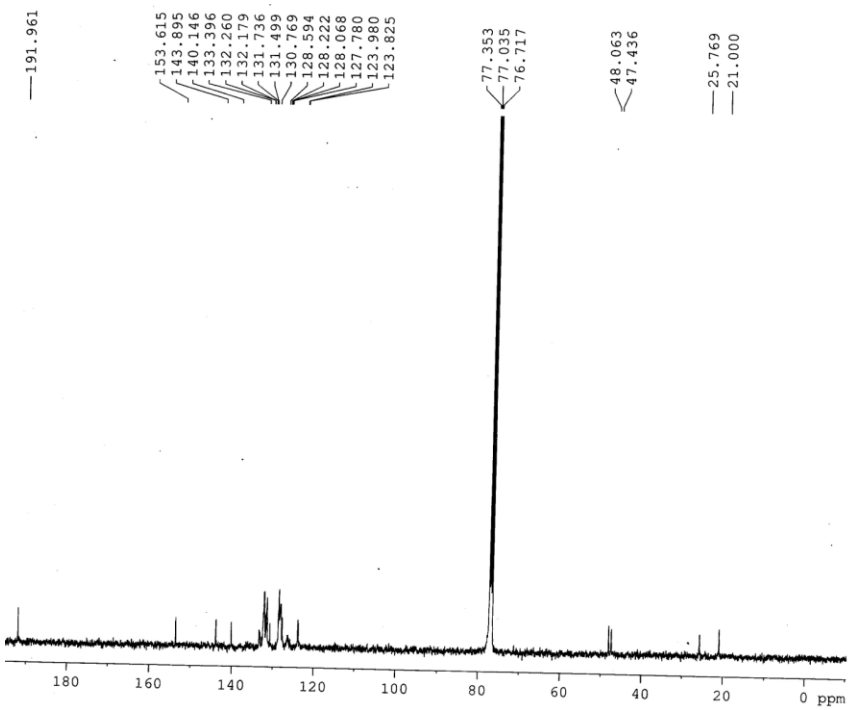

Fig. A2. ^{13}C NMR spectrum of compound **18**

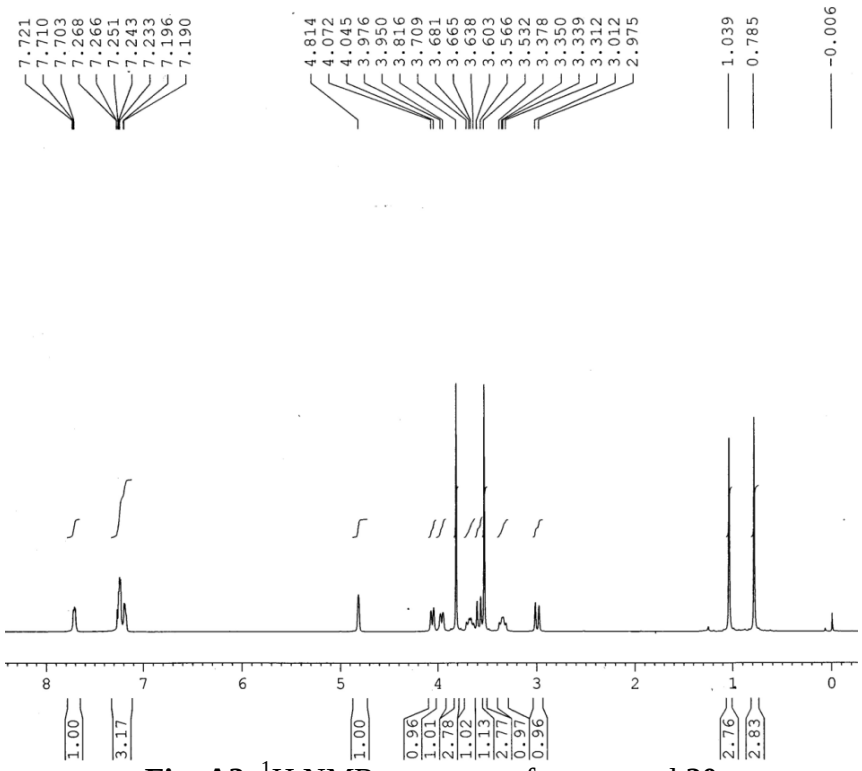

Fig. A3. ^{1}H NMR spectrum of compound **20**

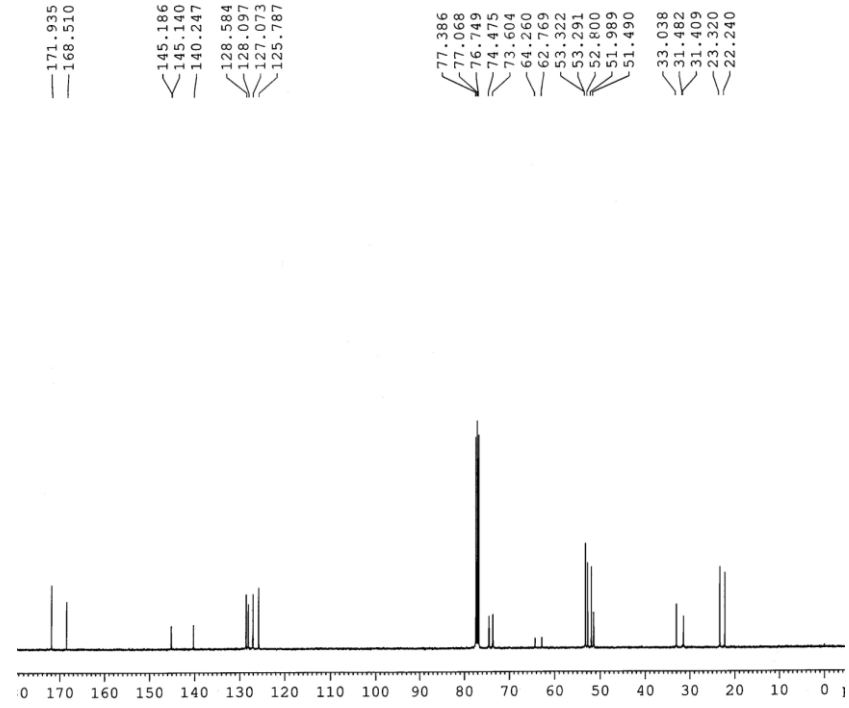

Fig. A4. ^{13}C NMR spectrum of compound **20**

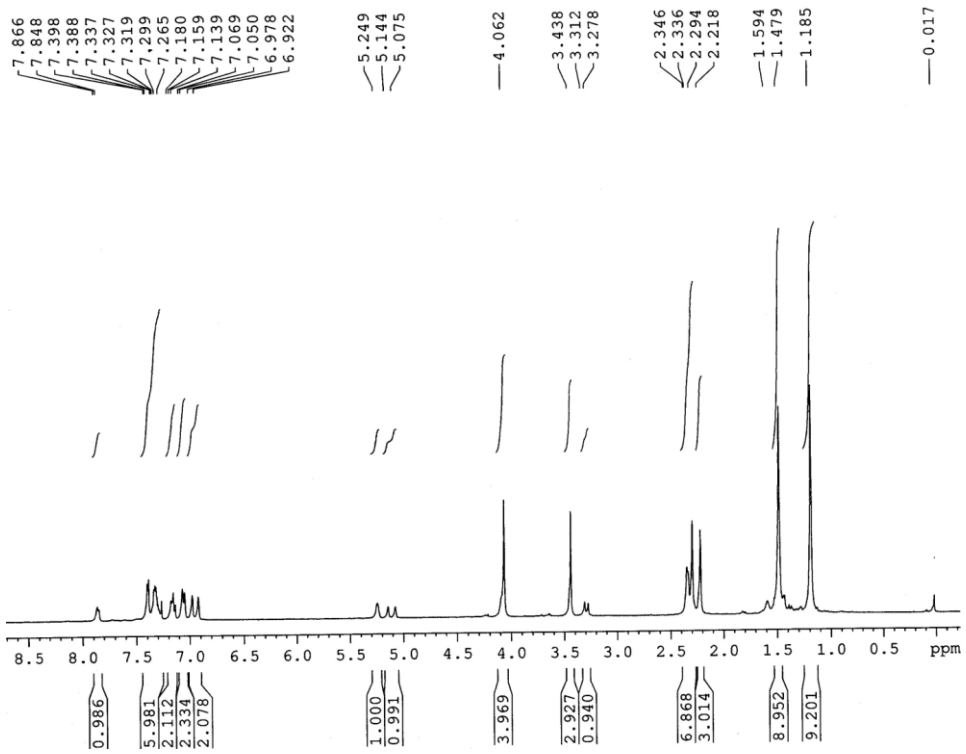

Fig. A5. ^{1}H NMR spectrum of compound **31**

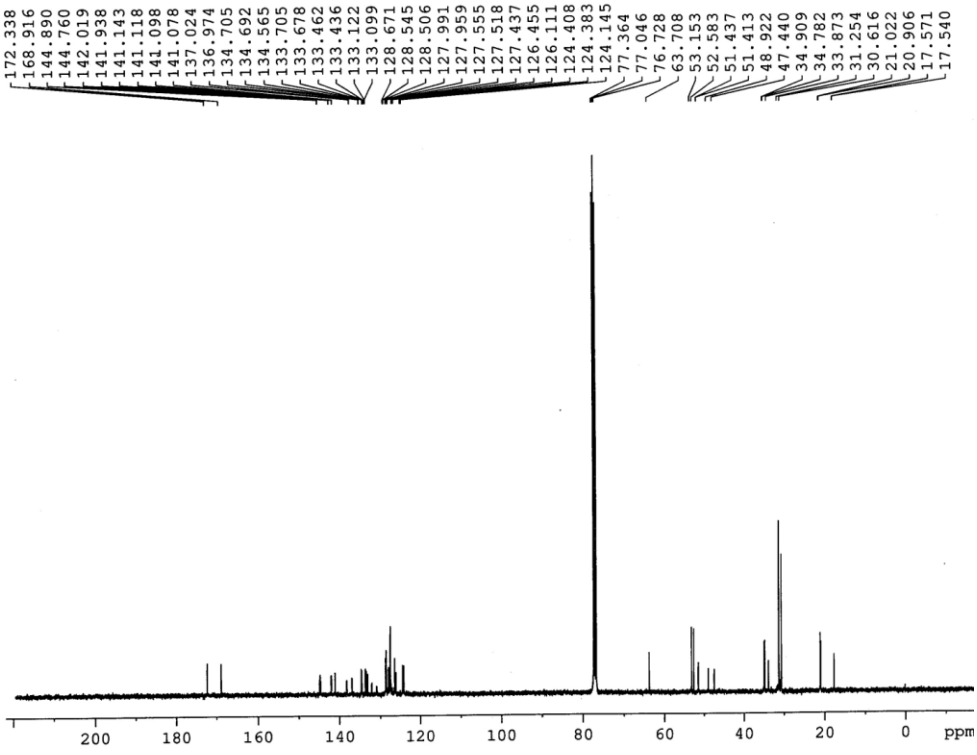

Fig. A6. ^{13}C NMR spectrum of compound **31**

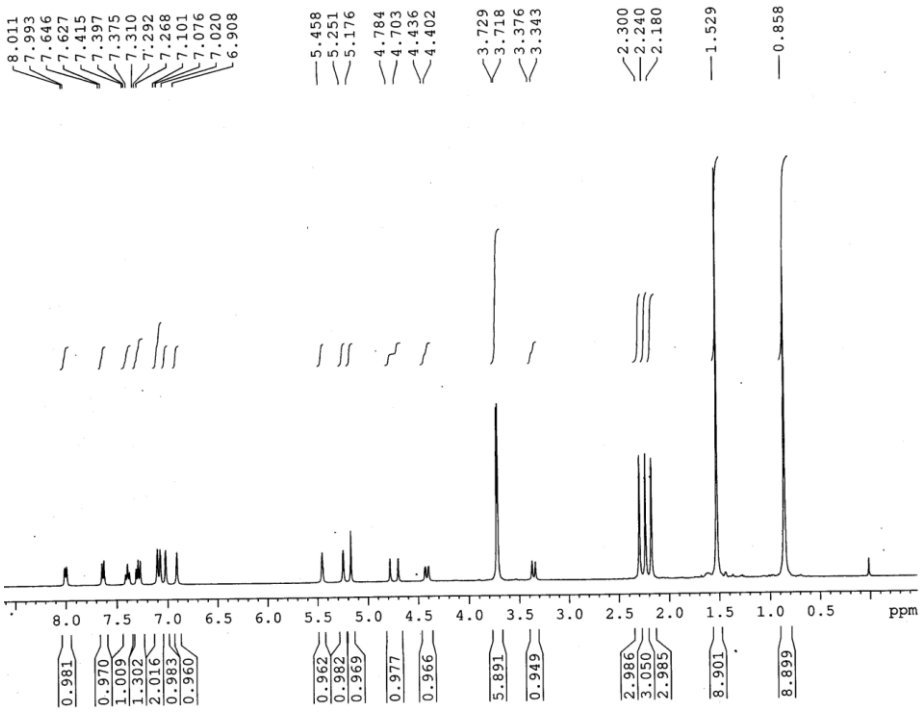

Fig. A7. ^{1}H NMR spectrum of compound **37**

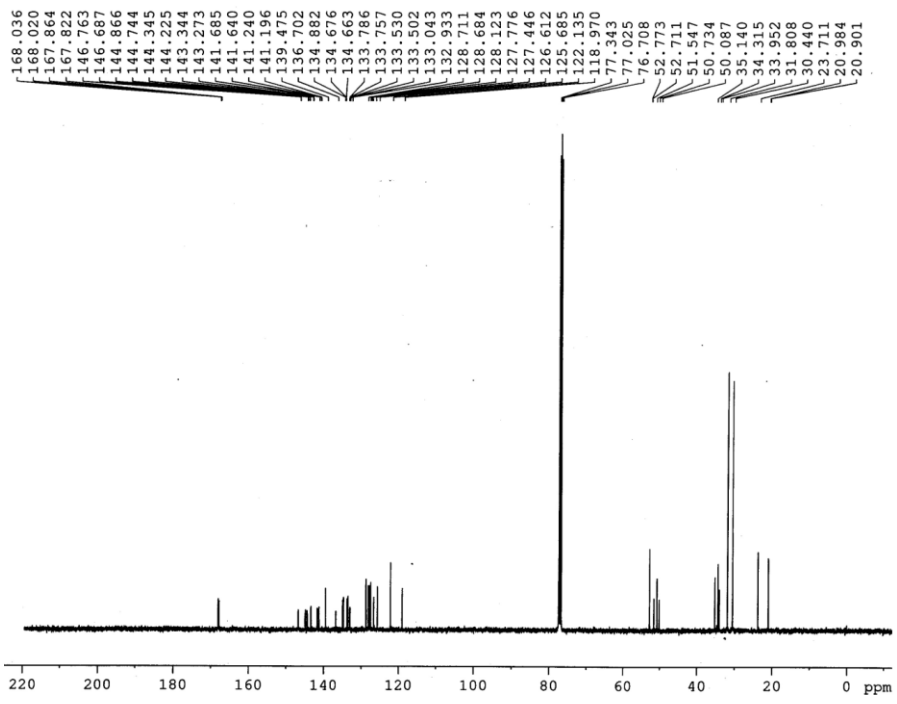

Fig. A8. ^{13}C NMR spectrum of compound **37**

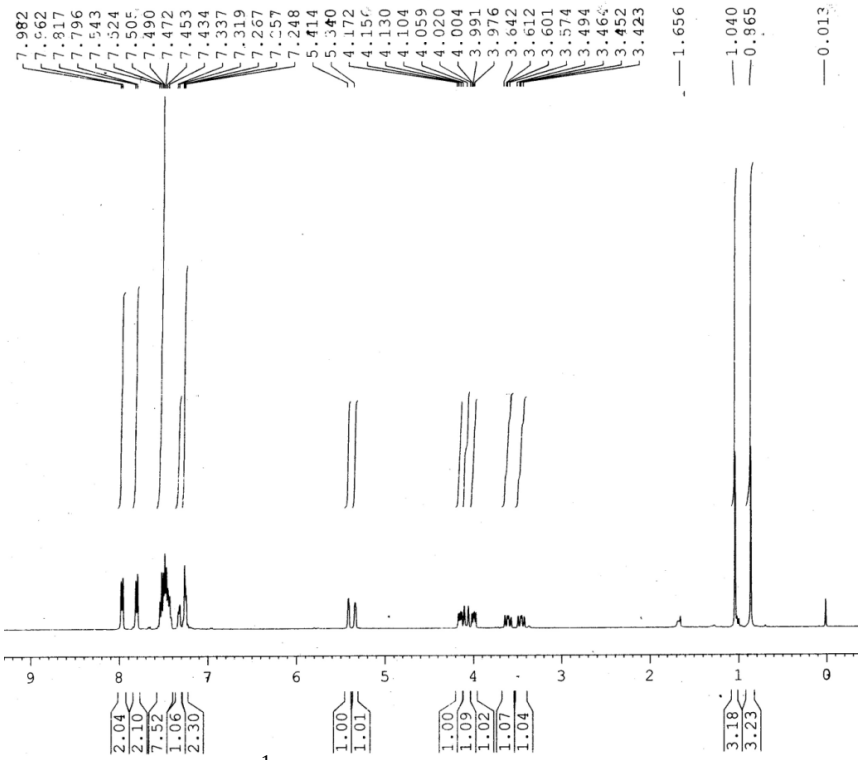

Fig. A9. ^{1}H NMR spectrum of compound **41**

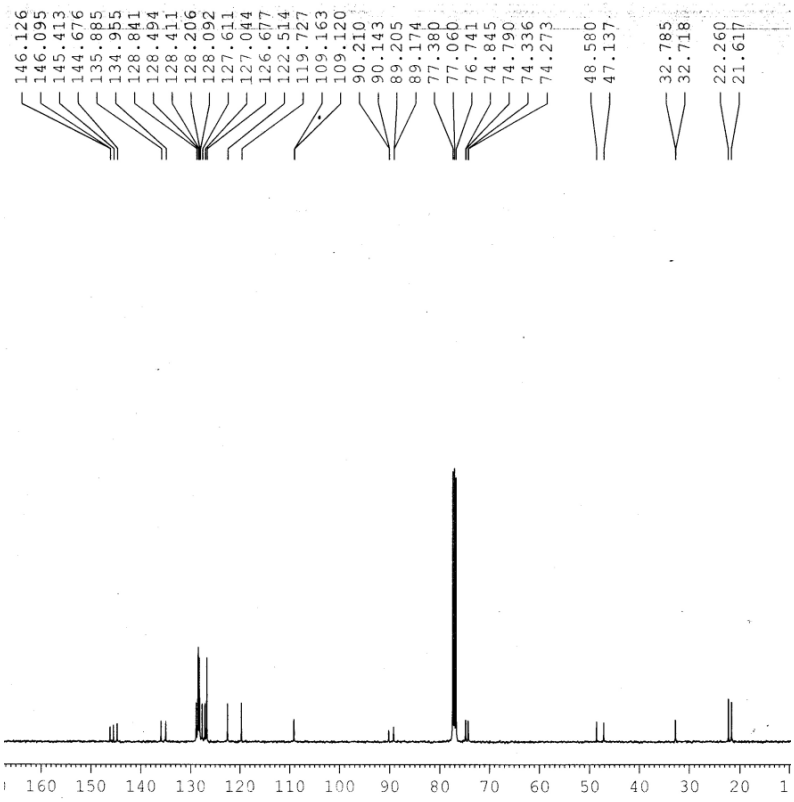

Fig. A10. ^{13}C NMR spectrum of compound **41**

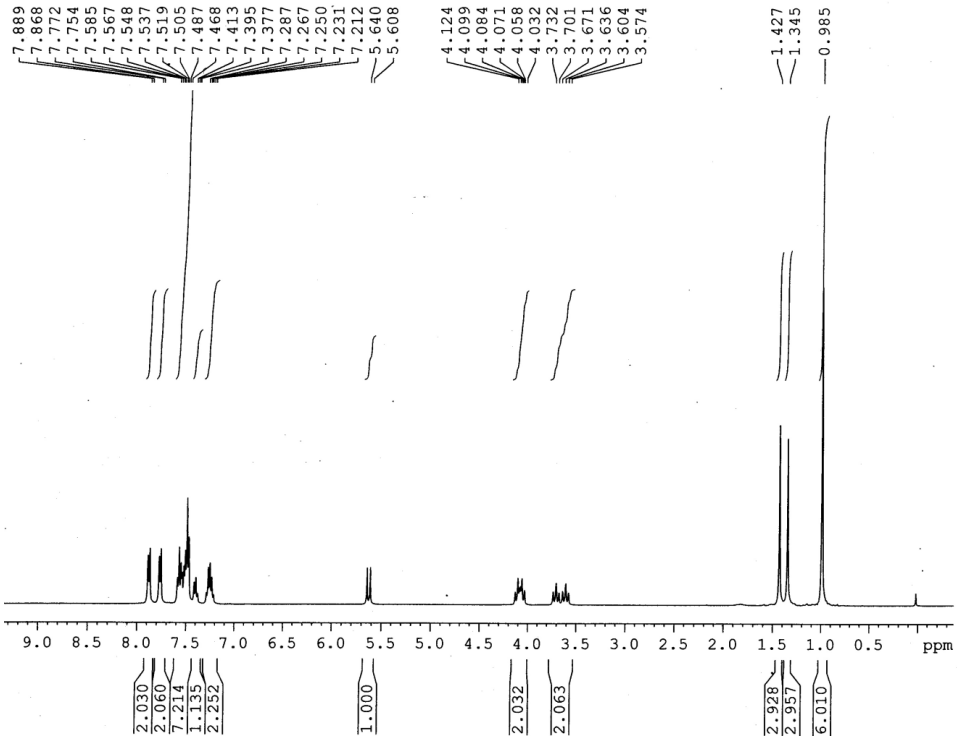

Fig. A11. ^{1}H NMR spectrum of compound **50**

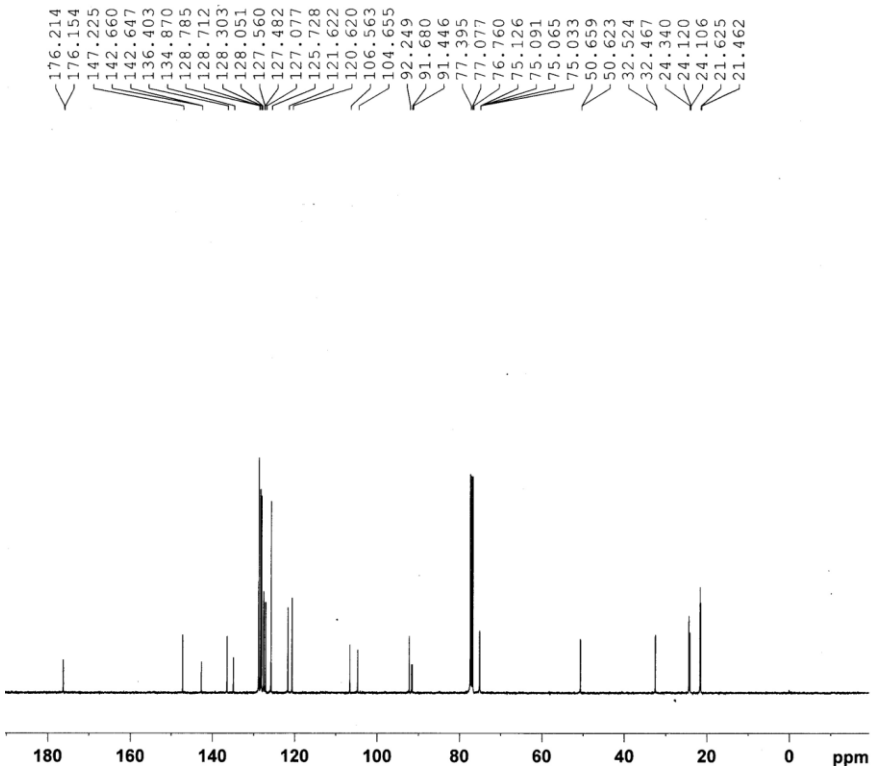

Fig. A12. ^{13}C NMR spectrum of compound **50**

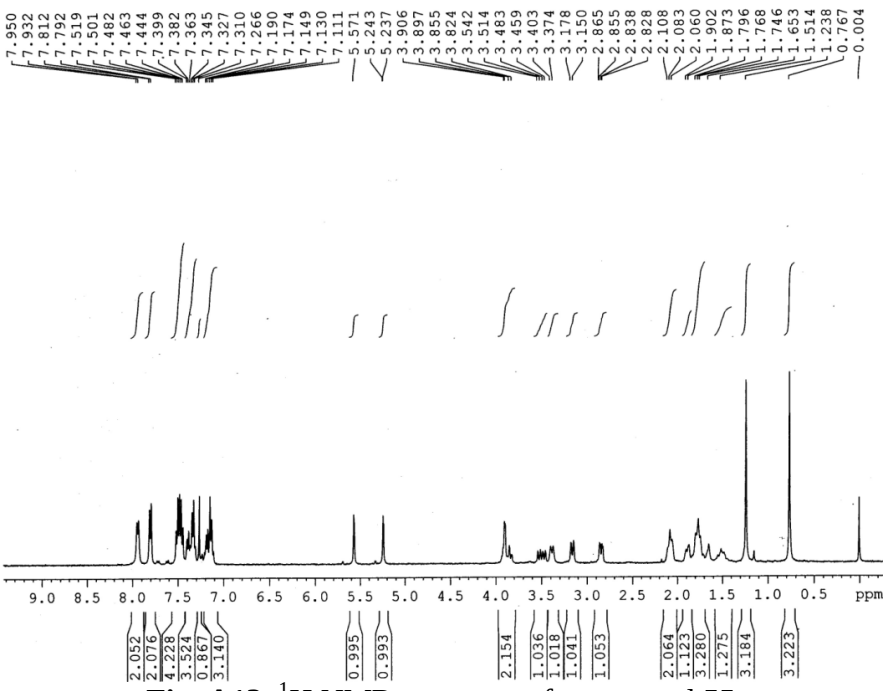

Fig. A13. ^{1}H NMR spectrum of compound **55**

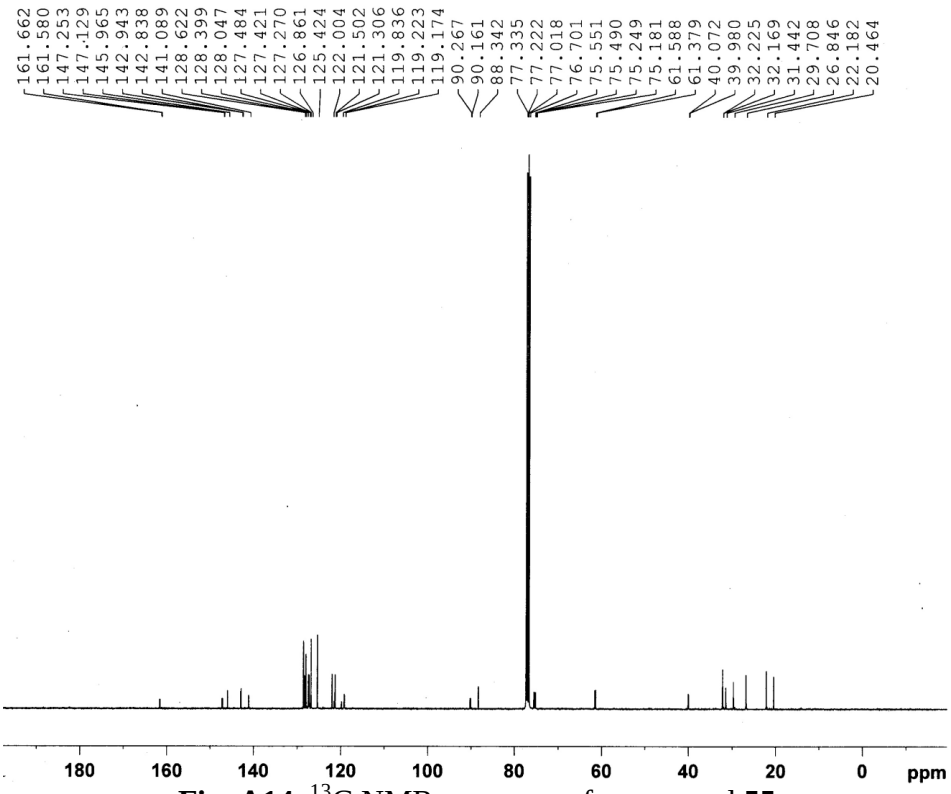

Fig. A14. ^{13}C NMR spectrum of compound **55**

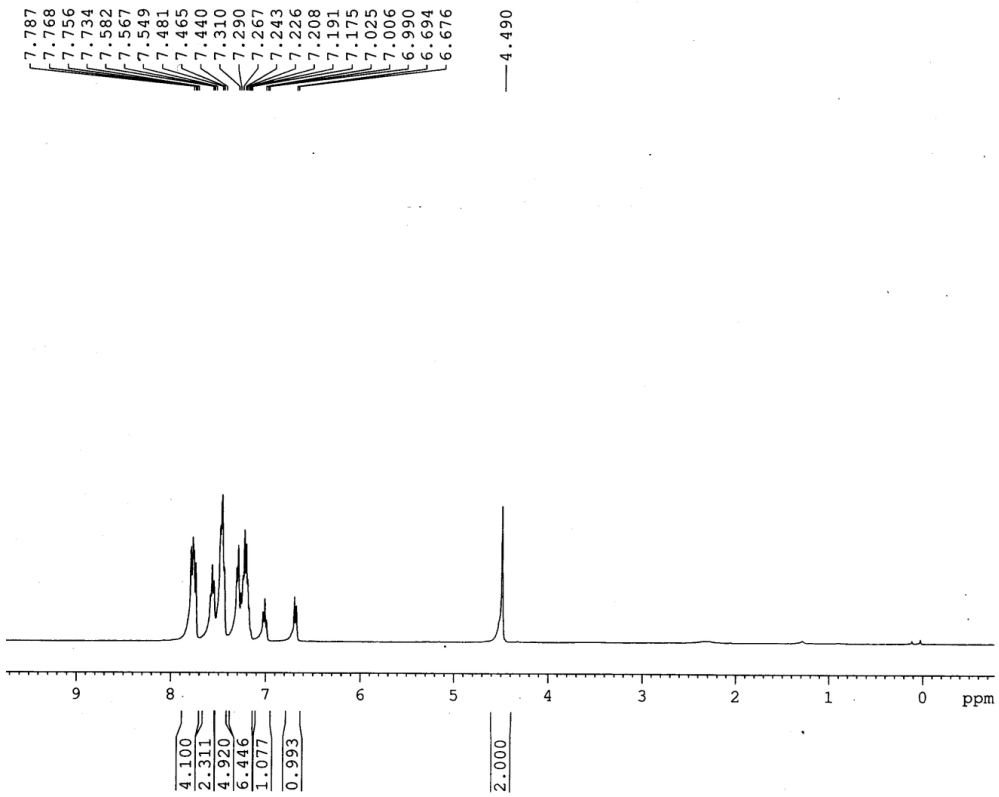

Fig. A15. ^{1}H NMR spectrum of compound **71**

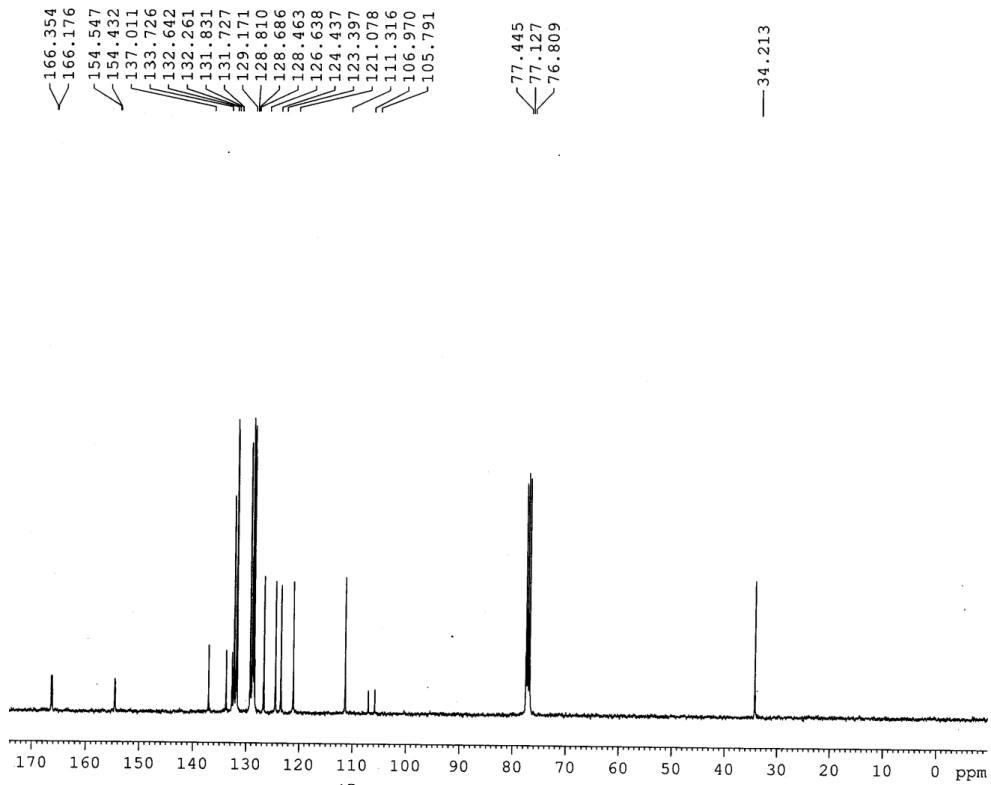

Fig. A16. ^{13}C NMR spectrum of compound **71**

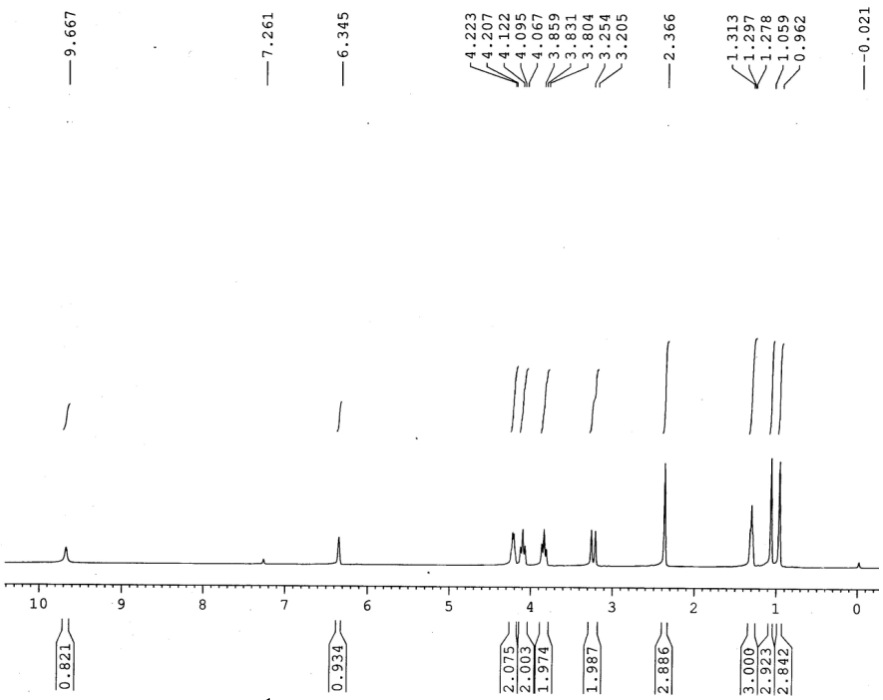

Fig. A17. ^{1}H NMR spectrum of compound **90**

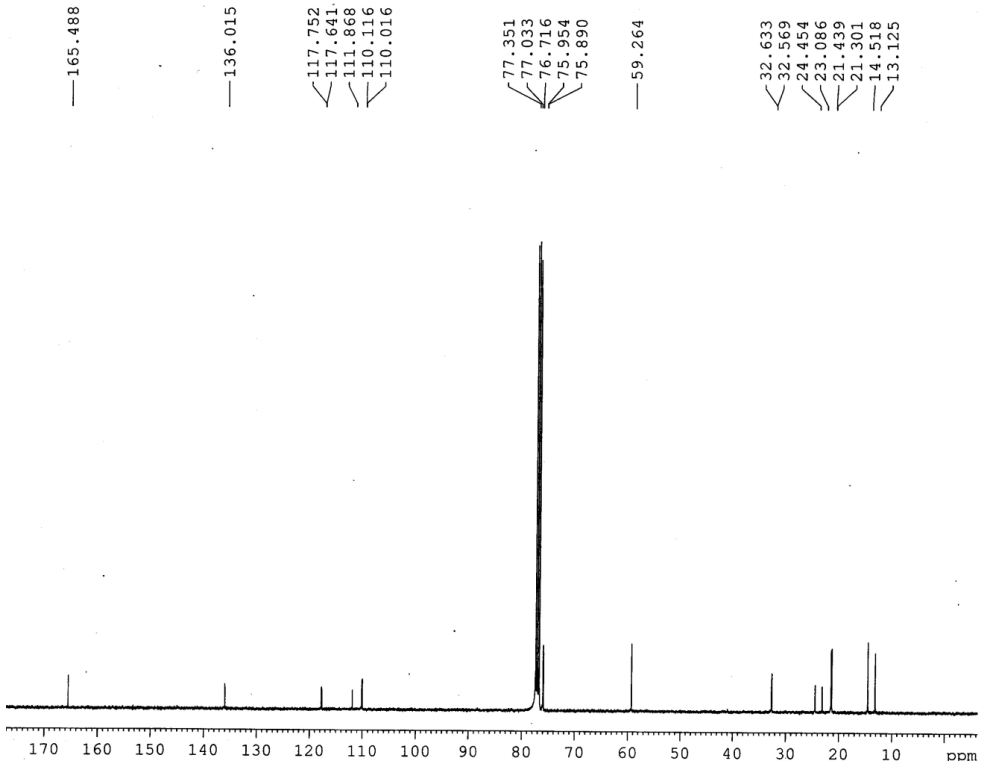

Fig. A18. ^{13}C NMR spectrum of compound **90**

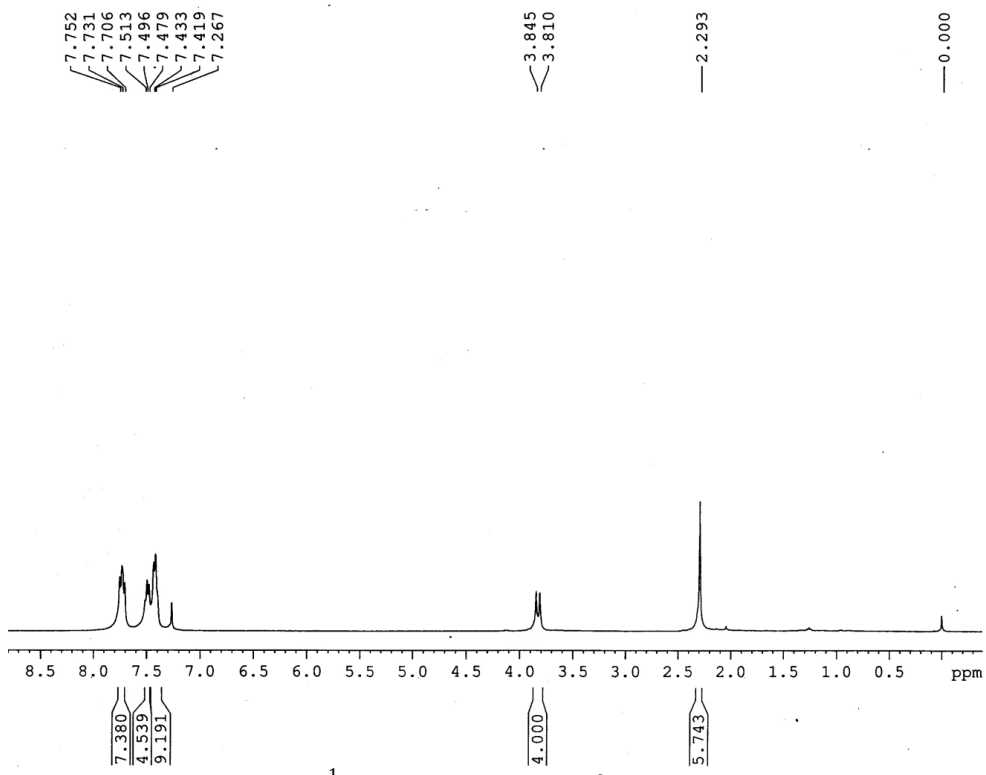

Fig. A19. ^{1}H NMR spectrum of compound **118**

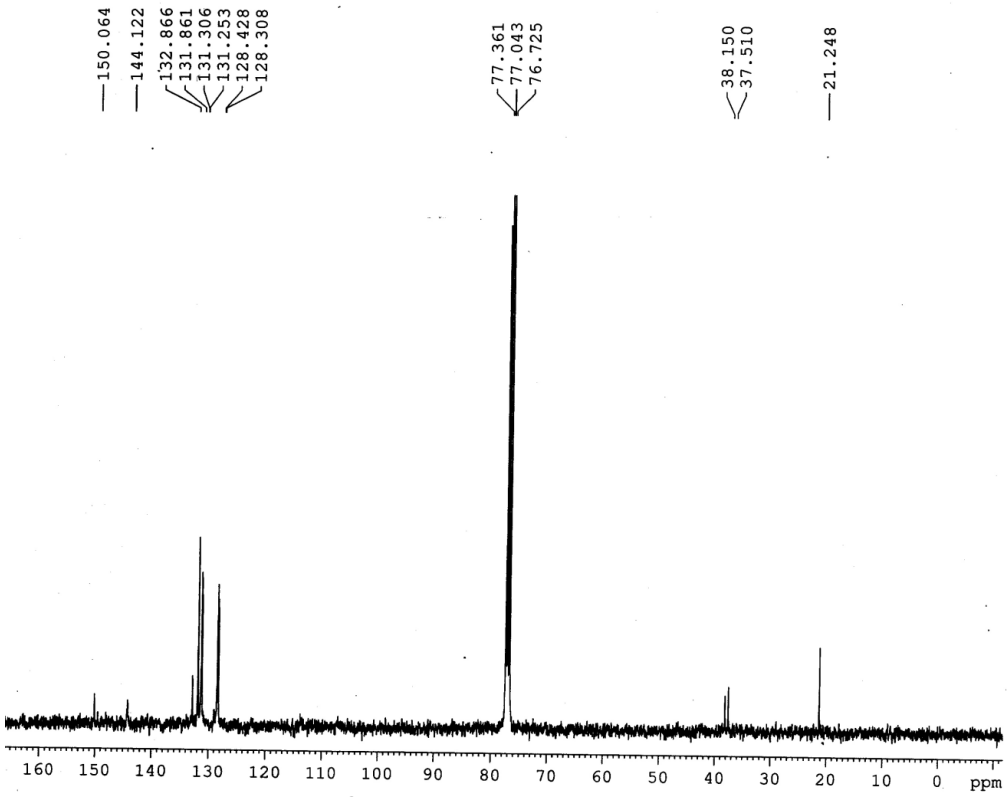

Fig. A20. ^{13}C NMR spectrum of compound **118**

PART B: Compounds 18 and 52

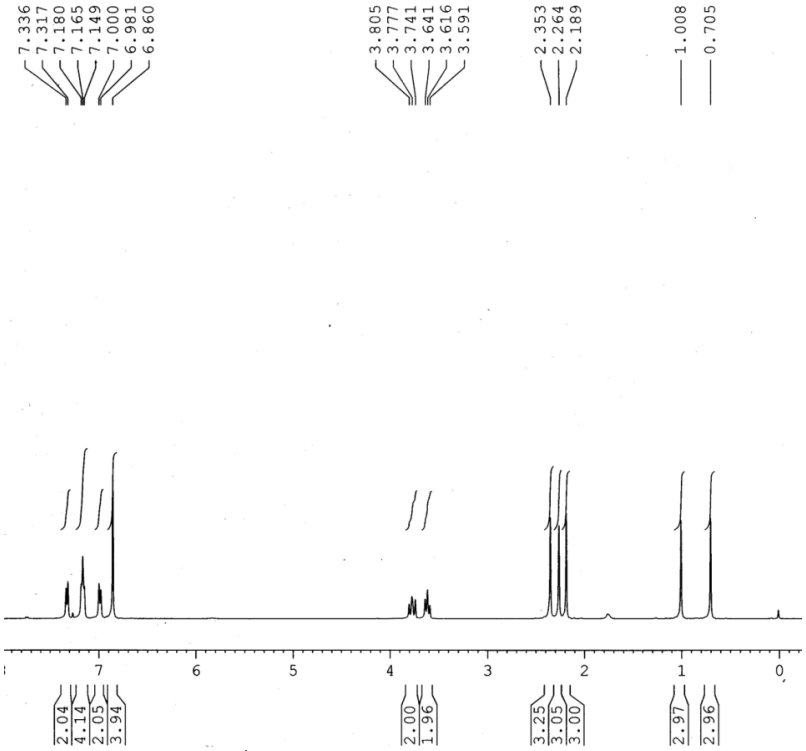

Fig. A21. ^{1}H NMR spectrum of compound **18**

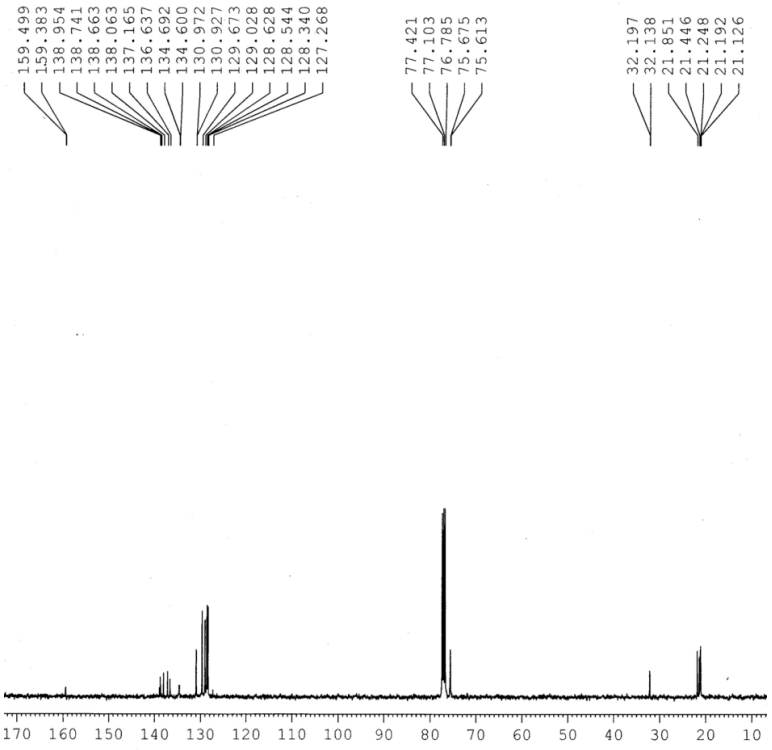

Fig. A22. ^{13}C NMR spectrum of compound **18**

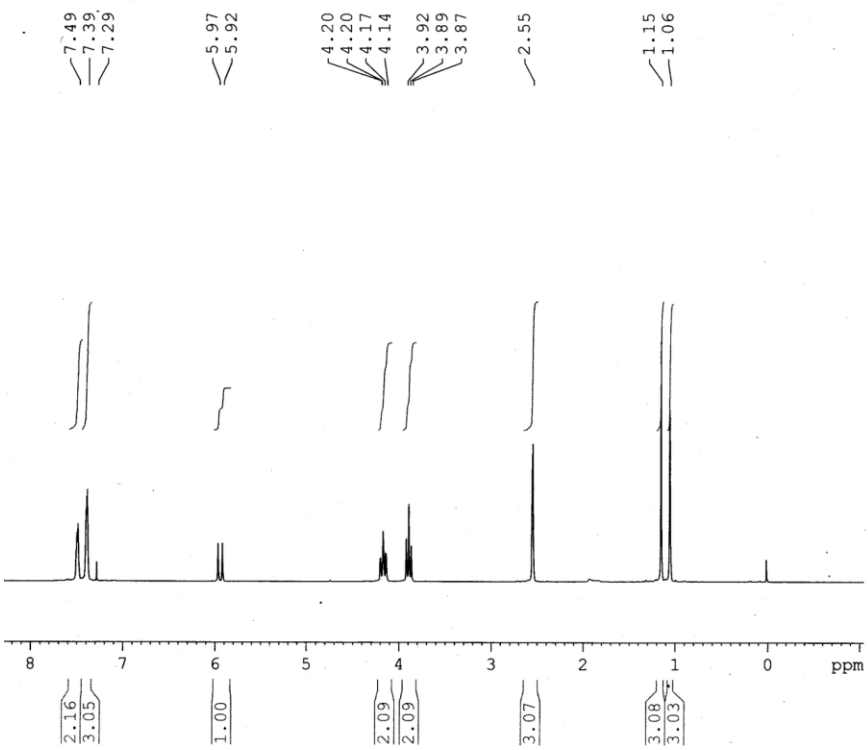

Fig. A23. ^{1}H NMR spectrum of compound **52**

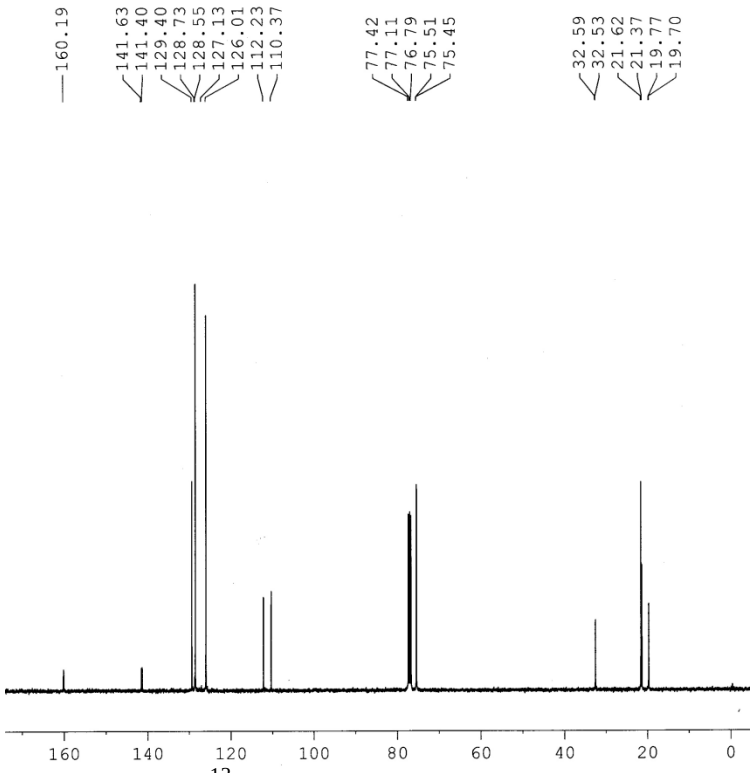

Fig. A24. ^{13}C NMR spectrum of compound **52**

B) Publication numbers and atomic coordinates for X-ray structures reported in this thesis

I. Publication numbers for the published compounds

PART A: Compounds 20.CH_2Cl_2**, 22, 29**.2CH_3CN**, 44, 46**.CH_2Cl_2**, 46', 48, 53, 55, 57, 61, 63, and 67:**

Publication no. 1 and 3 (Contents, p. xi)

PART B: Compounds 22, 26, 43b and 44b:

Publication no. 2 (Contents, p. xi)

II. Selected atomic coordinates for compounds 15a, 18, 24, 33, 75, 76, 79, 90, 97.H_2O**, 107, 115, 124 from PART A.**

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 15a

Atom	x	y	z	U(eq)
P(1)	5969(1)	4740(1)	2203(1)	52(1)
P(2)	8739(1)	-240(1)	2166(1)	45(1)
O(1)	4718(2)	4812(1)	2030(1)	72(1)
O(2)	4281(2)	6288(1)	1863(2)	84(1)
O(3)	9833(1)	-145(1)	2050(1)	58(1)
O(4)	9995(2)	1340(1)	1862(1)	73(1)
C(1)	6826(3)	4428(1)	3235(2)	52(1)
C(2)	6281(3)	4069(2)	3676(2)	72(1)
C(3)	6930(5)	3809(2)	4468(3)	99(2)
C(4)	8088(5)	3896(2)	4828(3)	105(2)
C(5)	8642(3)	4249(2)	4400(3)	85(1)
C(6)	8012(3)	4519(2)	3608(2)	65(1)
C(7)	6199(2)	4105(2)	1493(2)	48(1)
C(8)	5438(3)	4149(2)	675(2)	70(1)
C(9)	5593(3)	3707(2)	83(2)	86(1)
C(10)	6494(3)	3206(2)	308(2)	76(1)
C(11)	7241(3)	3137(2)	1118(2)	72(1)
C(12)	7094(3)	3586(2)	1710(2)	64(1)
C(13)	6551(2)	5653(1)	2094(2)	44(1)
C(14)	7156(2)	5694(1)	1658(2)	47(1)
C(15)	7762(4)	5731(2)	1222(3)	74(1)
C(16)	6379(3)	6353(1)	2528(2)	45(1)
C(17)	5282(3)	6635(2)	2387(2)	58(1)
C(18)	5188(3)	7322(2)	2741(2)	74(1)
C(19)	6140(4)	7728(2)	3224(2)	77(1)
C(20)	7226(3)	7452(2)	3381(2)	68(1)
C(21)	7331(3)	6769(2)	3034(2)	53(1)
C(22)	8992(2)	-530(1)	3194(2)	44(1)
C(23)	10016(3)	-899(2)	3676(2)	64(1)
C(24)	10223(3)	-1127(2)	4473(2)	82(1)
C(25)	9432(4)	-987(2)	4788(2)	80(1)
C(26)	8418(3)	-629(2)	4314(2)	71(1)
C(27)	8191(2)	-400(1)	3522(2)	56(1)
C(28)	7781(2)	-913(1)	1449(2)	45(1)

C(29)	7118(3)	-1431(2)	1647(2)	61(1)
C(30)	6417(3)	-1946(2)	1068(2)	76(1)
C(31)	6372(3)	-1945(2)	287(2)	75(1)
C(32)	7015(3)	-1428(2)	74(2)	74(1)
C(33)	7717(3)	-919(2)	651(2)	61(1)
C(34)	7977(2)	661(1)	2016(2)	41(1)
C(35)	6877(3)	667(1)	1568(2)	46(1)
C(36)	5773(3)	641(2)	1124(3)	75(1)
C(37)	8625(2)	1348(1)	2490(2)	43(1)
C(38)	9584(2)	1647(2)	2401(2)	54(1)
C(39)	10111(3)	2300(2)	2822(2)	72(1)
C(40)	9717(3)	2658(2)	3336(2)	82(1)
C(41)	8779(3)	2365(2)	3450(2)	70(1)
C(42)	8249(2)	1716(2)	3027(2)	53(1)

Compound 18

Atom	x	y	z	U(eq)
P(1)	7205(1)	6723(1)	2023(1)	36(1)
O(1)	5298(3)	6799(1)	2340(1)	54(1)
O(2)	926(3)	6275(1)	178(2)	66(1)
C(1)	8296(4)	7529(1)	1848(2)	39(1)
C(2)	7155(5)	8094(2)	1951(2)	62(1)
C(3)	7839(7)	8729(2)	1806(3)	85(1)
C(4)	9647(6)	8809(2)	1560(2)	75(1)
C(5)	10817(5)	8256(2)	1463(2)	66(1)
C(6)	10144(4)	7616(1)	1607(2)	53(1)
C(7)	9254(4)	6263(1)	2810(2)	38(1)
C(8)	8911(5)	6101(1)	3625(2)	56(1)
C(9)	10429(8)	5757(2)	4257(2)	83(1)
C(10)	12285(7)	5573(2)	4077(3)	88(1)
C(11)	12641(5)	5727(2)	3284(3)	72(1)
C(12)	11138(4)	6068(1)	2644(2)	52(1)
C(13)	6595(3)	6263(1)	955(2)	32(1)
C(14)	4613(4)	6581(1)	342(2)	40(1)
C(15)	2816(4)	6146(1)	430(2)	41(1)
C(16)	3713(4)	5516(1)	840(2)	42(1)
C(17)	2669(5)	4917(2)	933(2)	53(1)
C(18)	3824(5)	4377(2)	1293(2)	59(1)
C(19)	6011(6)	4411(2)	1567(2)	65(1)
C(20)	7068(5)	4994(1)	1497(2)	51(1)
C(21)	5865(4)	5563(1)	1111(2)	37(1)
C(22)	4484(4)	7089(1)	-233(2)	50(1)
C(23)	2409(5)	7345(2)	-822(2)	76(1)
C(24)	6352(5)	7426(2)	-380(2)	64(1)

Compound 24

Atom	x	y	z	U(eq)
Cl(1)	5000	10000	5000	430(7)
Cl(2)	3469(9)	9700(7)	4174(7)	779(12)
P(1)	3743(1)	1031(1)	1144(1)	30(1)
O(1)	3586(2)	233(1)	1500(1)	37(1)
O(2)	2467(2)	1520(1)	1225(1)	38(1)
O(3)	3802(2)	940(1)	484(1)	46(1)
O(4)	7557(2)	1398(1)	2011(1)	31(1)
O(5)	4969(3)	1481(1)	4116(1)	67(1)
O(6)	6179(2)	2534(1)	3974(1)	60(1)
O(7)	3295(3)	2995(2)	3339(2)	115(1)
O(8)	2628(2)	2390(2)	2441(1)	72(1)
C(1)	2317(3)	-180(2)	1249(2)	44(1)

C(2)	1091(3)	322(2)	1291(2)	43(1)
C(3)	1180(3)	1112(2)	973(2)	48(1)
C(4)	-170(3)	-120(2)	931(2)	65(1)
C(5)	976(4)	439(2)	1970(2)	67(1)
C(6)	5221(2)	1535(1)	1617(1)	27(1)
C(7)	5049(2)	2429(2)	1550(1)	29(1)
C(8)	4693(3)	2868(2)	995(1)	38(1)
C(9)	4620(3)	3683(2)	1035(2)	47(1)
C(10)	4898(3)	4064(2)	1611(2)	49(1)
C(11)	5254(3)	3634(2)	2163(1)	39(1)
C(12)	5332(3)	2815(2)	2130(1)	32(1)
C(13)	5739(3)	2246(1)	2661(1)	31(1)
C(14)	4711(3)	1998(2)	3068(1)	33(1)
C(15)	4558(3)	1179(2)	2737(1)	33(1)
C(16)	5607(2)	1406(1)	2359(1)	26(1)
C(17)	5292(3)	1959(2)	3780(1)	40(1)
C(18)	6732(5)	2565(3)	4648(2)	83(1)
C(19)	3469(3)	2512(2)	2976(1)	42(1)
C(20)	1481(4)	2914(3)	2261(3)	105(2)
C(21)	6977(3)	952(2)	2451(1)	31(1)
C(22)	6722(2)	157(2)	2117(1)	32(1)
C(23)	6621(3)	-603(2)	2335(2)	42(1)
C(24)	6368(3)	-1214(2)	1893(2)	52(1)
C(25)	6217(3)	-1062(2)	1261(2)	51(1)
C(26)	6284(3)	-295(2)	1038(1)	42(1)
C(27)	6534(3)	316(2)	1475(1)	32(1)
C(28)	6587(2)	1218(2)	1432(1)	30(1)
C(29)	7022(3)	1643(2)	903(1)	36(1)
C(30)	6606(3)	1416(2)	273(1)	45(1)
C(31)	7015(4)	1834(2)	-193(2)	57(1)
C(32)	7831(4)	2487(2)	-49(2)	62(1)
C(33)	8233(4)	2729(2)	568(2)	63(1)
C(34)	7834(3)	2308(2)	1040(2)	48(1)
C(35)	7920(3)	982(2)	3096(1)	37(1)
C(36)	9118(3)	1407(2)	3181(2)	47(1)
C(37)	10004(4)	1437(2)	3767(2)	66(1)
C(38)	9730(4)	1047(3)	4271(2)	74(1)
C(39)	8559(4)	620(2)	4200(2)	66(1)
C(40)	7652(3)	585(2)	3610(1)	48(1)
C(41)	5548(15)	9646(6)	4327(9)	345(11)

Compound 33

Atom	x	y	z	U(eq)
P(1)	10373(1)	5950(1)	7031(1)	25(1)
O(1)	10140(2)	4665(2)	6579(1)	34(1)
O(2)	10388(1)	5652(2)	7809(1)	28(1)
O(3)	11592(1)	6611(2)	7239(1)	28(1)
O(4)	6866(2)	4897(2)	4348(1)	38(1)
O(5)	6838(2)	5970(2)	3344(1)	41(1)
O(6)	5479(2)	8129(2)	3726(1)	43(1)
O(7)	6881(2)	9742(2)	4293(1)	38(1)
C(1)	10989(2)	6602(3)	8454(1)	32(1)
C(2)	12195(2)	6958(2)	8588(1)	29(1)
C(3)	12130(2)	7591(2)	7873(1)	30(1)
C(4)	12970(2)	5635(2)	8826(1)	32(1)
C(5)	12679(2)	8087(3)	9203(2)	39(1)
C(6)	9337(2)	7365(2)	6567(1)	24(1)
C(7)	8153(2)	7028(2)	6479(1)	26(1)
C(8)	7790(2)	6839(2)	7019(1)	31(1)
C(9)	6627(2)	6553(3)	6778(2)	35(1)
C(10)	5852(2)	6463(3)	6014(2)	33(1)
C(11)	6217(2)	6679(2)	5475(1)	30(1)
C(12)	7374(2)	6967(2)	5709(1)	26(1)
C(13)	8008(2)	7276(2)	5284(1)	27(1)
C(14)	9129(2)	7526(2)	5761(1)	26(1)

C(15)	7465(2)	7352(3)	4436(1)	31(1)
C(16)	6477(2)	8421(3)	4104(1)	32(1)
C(17)	6031(3)	10864(3)	3987(2)	45(1)
C(18)	7021(2)	5924(3)	4054(1)	31(1)
C(19)	6350(3)	4685(3)	2920(2)	49(1)
C(20)	10073(2)	7877(3)	5575(1)	31(1)
C(21)	10767(2)	9160(3)	5928(2)	37(1)
C(22)	10279(2)	7044(3)	5105(2)	41(1)

Compound 75

Atom	x	y	z	U(eq)
P(1)	9(1)	251(1)	1839(1)	40(1)
O(1)	457(2)	1370(2)	1687(1)	52(1)
O(2)	881(2)	497(2)	3998(1)	55(1)
C(1)	734(3)	-902(2)	1307(1)	39(1)
C(2)	177(3)	-1175(2)	581(2)	46(1)
C(3)	751(3)	-1989(3)	127(2)	57(1)
C(4)	1877(4)	-2539(3)	399(2)	63(1)
C(5)	2457(3)	-2290(3)	1117(2)	66(1)
C(6)	1895(3)	-1453(3)	1574(2)	54(1)
C(7)	-1815(3)	56(2)	1602(1)	40(1)
C(8)	-2521(3)	811(3)	1196(2)	57(1)
C(9)	-3902(4)	694(3)	989(2)	77(1)
C(10)	-4610(4)	-178(3)	1190(2)	69(1)
C(11)	-3928(3)	-933(3)	1592(2)	60(1)
C(12)	-2546(3)	-823(2)	1798(2)	52(1)
C(13)	401(3)	40(2)	2775(1)	43(1)
C(14)	374(3)	-988(2)	3114(2)	46(1)
C(15)	159(3)	-2146(3)	2874(2)	56(1)
C(16)	248(4)	-2887(3)	3386(2)	67(1)
C(17)	551(4)	-2503(3)	4126(2)	71(1)
C(18)	763(4)	-1377(3)	4376(2)	65(1)
C(19)	672(3)	-651(3)	3860(2)	51(1)
C(20)	704(3)	902(2)	3330(2)	46(1)
C(21)	900(3)	2142(2)	3367(2)	48(1)
C(22)	153(4)	2799(3)	3934(2)	82(1)
C(23)	337(5)	4072(3)	3952(2)	83(1)
C(24)	1810(5)	4406(3)	4086(2)	94(2)
C(25)	2538(5)	3774(4)	3513(4)	118(2)
C(26)	2367(4)	2494(3)	3484(3)	96(2)
P(2)	5936(1)	5169(1)	1882(1)	43(1)
O(3)	5395(2)	6304(2)	1780(1)	55(1)
O(4)	6126(2)	5187(2)	4024(1)	59(1)
C(27)	7640(3)	5031(2)	1654(1)	41(1)
C(28)	8472(3)	4128(3)	1791(2)	52(1)
C(29)	9743(3)	4060(3)	1584(2)	57(1)
C(30)	10217(3)	4893(3)	1244(2)	66(1)
C(31)	9402(4)	5794(3)	1101(2)	77(1)
C(32)	8123(3)	5873(3)	1310(2)	58(1)
C(33)	4942(3)	4054(2)	1300(2)	43(1)
C(34)	5155(3)	3840(2)	573(2)	46(1)
C(35)	4342(3)	3075(3)	84(2)	57(1)
C(36)	3319(3)	2498(3)	307(2)	64(1)
C(37)	3082(3)	2692(3)	1019(2)	64(1)
C(38)	3889(3)	3476(3)	1517(2)	56(1)
C(39)	6027(3)	4852(2)	2799(2)	47(1)
C(40)	6193(3)	3774(3)	3095(2)	47(1)
C(41)	6260(4)	2640(3)	2809(2)	61(1)
C(42)	6386(4)	1845(3)	3292(2)	69(1)
C(43)	6439(4)	2144(4)	4032(2)	76(1)
C(44)	6373(4)	3253(3)	4327(2)	69(1)
C(45)	6248(3)	4041(3)	3843(2)	53(1)
C(46)	5998(3)	5657(3)	3381(2)	50(1)
C(47)	5824(3)	6910(3)	3456(2)	51(1)
C(48)	4340(4)	7219(3)	3411(2)	72(1)

C(49)	4172(4)	8488(3)	3445(2)	83(1)
C(50)	4973(5)	9105(4)	4129(2)	89(1)
C(51)	6444(5)	8810(3)	4188(3)	98(2)
C(52)	6632(4)	7532(3)	4152(2)	82(1)

Compound 76

Atom	x	y	z	U(eq)
Cl(1)	5866(1)	4726(2)	9045(1)	77(1)
P(1)	4147(1)	1540(1)	10119(1)	46(1)
O(1)	4680(2)	576(3)	10398(1)	56(1)
O(2)	5256(2)	-1241(3)	9734(1)	64(1)
C(1)	3207(3)	670(6)	10079(2)	52(1)
C(2)	3113(3)	-520(6)	9761(2)	69(2)
C(3)	2435(4)	-1345(6)	9742(3)	82(2)
C(4)	1871(4)	-982(8)	10063(3)	81(2)
C(5)	1957(4)	175(8)	10370(2)	80(2)
C(6)	2625(4)	1033(7)	10382(2)	69(2)
C(7)	4062(3)	3438(5)	10374(2)	45(1)
C(8)	3494(3)	4491(6)	10280(2)	62(2)
C(9)	3548(5)	5985(7)	10460(2)	93(2)
C(10)	4135(5)	6437(8)	10728(3)	96(2)
C(11)	4694(4)	5382(7)	10831(2)	84(2)
C(12)	4656(3)	3916(6)	10669(2)	62(2)
C(13)	4448(3)	1893(4)	9529(2)	42(1)
C(14)	4037(3)	3157(5)	9277(2)	42(1)
C(15)	3331(3)	2859(5)	9067(2)	56(1)
C(16)	2957(4)	4039(8)	8842(2)	74(2)
C(17)	3246(4)	5533(8)	8827(2)	82(2)
C(18)	3937(4)	5782(6)	9024(2)	71(2)
C(19)	4345(3)	4624(5)	9256(2)	50(1)
C(20)	5109(3)	5020(6)	9464(2)	60(2)
C(21)	5036(3)	1182(4)	9313(2)	45(1)
C(22)	5607(3)	-30(5)	9464(2)	52(1)
C(23)	5899(3)	-870(5)	9028(2)	72(2)
C(24)	6246(3)	732(5)	9724(2)	73(2)
Cl(2)	4798(1)	9561(2)	7973(1)	90(1)
P(2)	3103(1)	6437(1)	6794(1)	42(1)
O(3)	3633(2)	5434(3)	6521(1)	53(1)
O(4)	4196(2)	3603(3)	7179(1)	62(1)
C(25)	3051(3)	8341(5)	6546(2)	46(1)
C(26)	3646(3)	8797(6)	6265(2)	55(1)
C(27)	3697(4)	10294(7)	6092(2)	77(2)
C(28)	3152(5)	11322(7)	6207(3)	94(2)
C(29)	2553(4)	10940(7)	6493(2)	86(2)
C(30)	2493(3)	9437(6)	6659(2)	65(2)
C(31)	2155(3)	5615(5)	6835(2)	46(1)
C(32)	1569(3)	6032(7)	6557(2)	73(2)
C(33)	869(4)	5227(8)	6567(2)	88(2)
C(34)	767(4)	4056(7)	6881(3)	78(2)
C(35)	1362(4)	3629(6)	7150(3)	87(2)
C(36)	2056(3)	4382(6)	7138(2)	71(2)
C(37)	3406(2)	6746(4)	7392(2)	37(1)
C(38)	2978(3)	8009(5)	7649(2)	40(1)
C(39)	2260(3)	7729(5)	7826(2)	54(1)
C(40)	1859(3)	8837(6)	8069(2)	69(2)
C(41)	2176(4)	10271(7)	8116(2)	79(2)
C(42)	2889(4)	10616(6)	7940(2)	72(2)
C(43)	3303(3)	9461(5)	7707(2)	49(1)
C(44)	4079(3)	9847(5)	7532(2)	59(2)
C(45)	3981(3)	6038(4)	7607(2)	43(1)
C(46)	4540(3)	4771(5)	7459(2)	46(1)
C(47)	5204(3)	5547(5)	7197(2)	67(2)
C(48)	4834(3)	3947(5)	7891(2)	68(2)

Compound 79

Atom	x	y	z	U(eq)
P(1)	7705(1)	7982(1)	2586(1)	33(1)
O(1)	8264(2)	7109(1)	2512(2)	43(1)
O(2)	3051(2)	7590(2)	-45(2)	55(1)
C(1)	8388(3)	8926(2)	2314(2)	32(1)
C(2)	7364(4)	9534(2)	1459(3)	43(1)
C(3)	7905(4)	10209(2)	1204(3)	56(1)
C(4)	9494(4)	10286(2)	1816(3)	54(1)
C(5)	10534(4)	9690(3)	2665(3)	57(1)
C(6)	9993(3)	9003(2)	2914(3)	46(1)
C(7)	8423(3)	8089(2)	3985(3)	32(1)
C(8)	8062(4)	7381(2)	4336(3)	47(1)
C(9)	8661(4)	7355(3)	5422(3)	58(1)
C(10)	9620(4)	8025(3)	6171(3)	59(1)
C(11)	10002(4)	8729(2)	5840(3)	58(1)
C(12)	9402(4)	8760(2)	4750(3)	46(1)
C(13)	5585(3)	8089(2)	1624(3)	33(1)
C(14)	4789(3)	8714(2)	1827(3)	35(1)
C(15)	5477(4)	9491(2)	2471(3)	46(1)
C(16)	4595(4)	10086(2)	2517(3)	60(1)
C(17)	3025(5)	9929(3)	1920(4)	65(1)
C(18)	2323(4)	9167(3)	1270(3)	60(1)
C(19)	3193(4)	8561(2)	1224(3)	43(1)
C(20)	2509(4)	7724(2)	535(3)	61(1)
C(21)	4662(4)	7637(2)	636(3)	39(1)
C(22)	5139(4)	7193(2)	66(3)	49(1)
C(23)	4995(5)	6174(2)	38(4)	89(1)
C(24)	4188(5)	7582(3)	-1121(3)	90(1)

Compound 90

Atom	x	y	z	U(eq)
P(1)	4930(1)	912(2)	10314(1)	45(1)
O(1)	5491(1)	2357(5)	10173(1)	49(1)
O(2)	4964(2)	536(6)	10946(2)	65(1)
O(3)	4926(2)	-1188(6)	10027(2)	89(2)
O(4)	3650(3)	4984(10)	7893(2)	121(2)
O(5)	3210(4)	1961(12)	8242(2)	155(3)
N(1)	4434(2)	5187(7)	9445(2)	49(1)
C(1)	5689(2)	4138(9)	10532(2)	57(1)
C(2)	5752(2)	3298(8)	11108(2)	53(1)
C(3)	5157(3)	2376(10)	11293(2)	64(1)
C(4)	6254(3)	1594(11)	11147(3)	76(2)
C(5)	5903(4)	5335(13)	11459(3)	102(3)
C(6)	4264(2)	2576(8)	10208(2)	49(1)
C(7)	4170(2)	3342(7)	9637(2)	45(1)
C(8)	3810(2)	2501(8)	9239(2)	51(1)
C(9)	3869(3)	3893(9)	8789(2)	62(1)
C(10)	4266(2)	5620(8)	8929(2)	56(1)
C(11)	3585(4)	3744(14)	8257(3)	93(2)
C(12)	2744(5)	1940(20)	7791(5)	161(5)
C(13)	3155(7)	811(18)	7433(6)	177(6)
C(14)	4495(3)	7546(10)	8625(3)	77(2)
P(2)	2500(1)	3517(2)	5057(1)	52(1)
O(6)	2472(2)	4128(7)	4441(2)	72(1)
O(7)	3067(1)	1978(6)	5126(2)	59(1)
O(8)	2550(2)	5495(7)	5388(2)	94(2)
O(9)	1194(4)	-953(13)	7467(3)	142(3)
O(10)	753(3)	1993(14)	7140(3)	137(3)
N(2)	2015(2)	-868(8)	5931(2)	62(1)

C(15)	2627(3)	2487(12)	4033(3)	78(2)
C(16)	3239(3)	1438(11)	4162(3)	74(2)
C(17)	3214(3)	411(10)	4705(3)	72(2)
C(18)	3763(3)	3152(15)	4113(4)	102(3)
C(19)	3304(6)	-455(16)	3736(4)	143(4)
C(20)	1839(2)	1852(9)	5191(2)	63(1)
C(21)	1740(2)	1061(9)	5735(2)	57(1)
C(22)	1381(2)	1747(10)	6145(3)	66(2)
C(23)	1437(3)	257(11)	6582(3)	68(2)
C(24)	1829(3)	-1387(9)	6427(3)	64(2)
C(25)	1133(4)	274(17)	7109(3)	95(2)
C(26)	471(7)	1940(30)	7692(5)	207(8)
C(27)	14(7)	3610(30)	7673(6)	220(8)
C(28)	2070(4)	-3383(11)	6714(3)	91(2)

Compound 97.H_2O

Atom	x	y	z	U(eq)
P(1)	10524(1)	4469(1)	2973(1)	40(1)
O(1)	12490(3)	3768(2)	3274(2)	61(1)
O(2)	9037(3)	4832(1)	3851(1)	42(1)
O(3)	11581(3)	5784(1)	2796(2)	50(1)
O(4)	4314(4)	-1983(2)	1428(2)	67(1)
N(1)	5543(3)	2107(2)	2380(2)	39(1)
C(1)	7741(4)	5944(2)	3987(2)	45(1)
C(2)	9326(4)	7151(2)	3931(2)	41(1)
C(3)	10143(5)	6837(2)	2892(2)	50(1)
C(4)	7729(5)	8216(2)	3944(3)	65(1)
C(5)	11520(5)	7601(2)	4862(2)	59(1)
C(6)	8379(5)	3589(2)	1787(2)	51(1)
C(7)	7253(4)	2274(2)	1789(2)	41(1)
C(8)	7617(4)	1072(2)	1274(2)	43(1)
C(9)	6071(4)	140(2)	1560(2)	41(1)
C(10)	4803(4)	827(2)	2253(2)	37(1)
C(11)	3016(5)	421(2)	2852(2)	51(1)
C(12)	5805(5)	-1265(2)	1173(2)	45(1)
C(13)	7415(5)	-1820(2)	453(2)	59(1)
O(5)	2873(11)	5295(3)	490(3)	170(2)

Compound 107

Atom	x	y	z	U(eq)
O(1)	7992(4)	-1842(4)	11753(1)	136(1)
O(2)	8967(2)	4164(2)	9257(1)	74(1)
O(3)	7332(2)	1839(2)	8682(1)	61(1)
N(1)	9095(2)	2325(3)	10456(1)	54(1)
C(1)	8216(3)	1535(3)	9856(1)	49(1)
C(2)	7503(2)	-200(3)	9998(1)	51(1)
C(3)	7971(3)	-415(3)	10714(1)	56(1)
C(4)	8970(3)	1195(4)	10975(1)	56(1)
C(5)	8228(3)	2624(3)	9247(1)	52(1)
C(6)	7288(3)	2948(4)	8069(1)	73(1)
C(7)	6074(4)	1939(5)	7507(1)	91(1)
C(8)	6452(3)	-1538(4)	9477(1)	67(1)
C(9)	7526(3)	-1944(4)	11141(1)	74(1)
C(10)	6477(4)	-3649(4)	10839(2)	88(1)
C(11)	9850(3)	1784(4)	11674(1)	79(1)

Compound 115

Atom	x	y	z	U(eq)
P(1)	7524(1)	1962(1)	9165(1)	37(1)
O(1)	6557(1)	1088(2)	9080(1)	41(1)
O(2)	7722(1)	1464(2)	7914(1)	42(1)
O(3)	7601(1)	4288(2)	9461(1)	54(1)
N(1)	9366(1)	-1468(3)	9449(1)	42(1)
C(1)	6299(1)	-994(3)	8486(2)	41(1)
C(2)	6476(1)	-1072(3)	7248(2)	38(1)
C(3)	7452(1)	-649(3)	7351(2)	42(1)
C(4)	5908(1)	586(4)	6425(2)	53(1)
C(5)	6266(2)	-3386(3)	6768(2)	56(1)
C(6)	8226(1)	203(3)	10234(2)	43(1)
C(7)	9171(1)	146(3)	10125(2)	38(1)
C(8)	9809(1)	1651(3)	10686(2)	41(1)
C(9)	9622(2)	3506(4)	11440(2)	62(1)

Compound 124

Atom	x	y	z	U(eq)
O(1)	3919(3)	3418(2)	1188(3)	79(1)
O(2)	1919(3)	3504(2)	538(4)	86(1)
N(1)	3171(3)	3156(2)	4845(4)	49(1)
C(1)	3695(4)	3208(2)	3852(5)	51(1)
C(2)	2795(5)	3294(2)	2711(5)	50(1)
C(3)	1693(4)	3284(2)	3034(5)	55(1)
C(4)	1925(4)	3205(2)	4335(5)	49(1)
C(5)	3814(4)	3156(2)	6231(4)	57(1)
C(6)	4134(4)	3834(2)	6786(5)	51(1)
C(7)	4740(4)	3896(3)	8083(5)	67(2)
C(8)	5065(5)	4511(4)	8602(6)	96(2)
C(9)	4787(6)	5058(3)	7866(8)	106(3)
C(10)	4195(6)	4997(3)	6594(7)	112(2)
C(11)	3859(5)	4387(2)	6052(5)	80(2)
C(12)	5026(4)	3176(2)	4123(5)	79(2)
C(13)	2981(6)	3410(2)	1452(5)	59(2)
C(14)	1914(6)	3628(3)	-809(6)	108(2)
C(15)	1828(7)	4317(4)	-1055(7)	158(3)
C(16)	1111(5)	3173(2)	5142(5)	69(2)
C(17)	-18(5)	3108(3)	4767(5)	90(2)
C(18)	-873(5)	3102(4)	5568(5)	73(2)
C(19)	-1343(5)	2497(4)	5814(6)	75(2)
C(20)	-1038(5)	1889(4)	5356(6)	94(2)
C(21)	-1484(7)	1314(4)	5653(7)	113(2)
C(22)	-2283(8)	1303(5)	6425(8)	125(3)
C(23)	-2615(6)	1864(5)	6870(7)	111(3)
C(24)	-2154(6)	2482(4)	6588(6)	81(2)
C(25)	-2472(5)	3064(5)	7071(6)	90(2)
C(26)	-2017(6)	3661(4)	6826(6)	81(2)
C(27)	-2342(6)	4261(5)	7322(6)	111(2)
C(28)	-1889(8)	4838(4)	7079(8)	136(3)
C(29)	-1117(8)	4870(4)	6285(8)	150(3)
C(30)	-774(6)	4313(4)	5805(7)	117(3)
C(31)	-1207(6)	3687(4)	6045(6)	81(2)