# GOLD CATALYZED CYCLIZATIONS OF ALKYNOLS/ PROPARGYLIC ESTERS AND ALLENYLPHOSPHONATES/ ALLENYLPHOSPHINE OXIDES IN CYCLOADDITION/ CYCLIZATION REACTIONS

**A THESIS**

**SUBMITTED FOR THE DEGREE OF**

**DOCTOR OF PHILOSOPHY**

**By**

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**INDIA**

**MARCH 2013**

*Dedicated to*

**AMMA**

# CONTENTS

## PART B

## ALLENYLPHOSPHONATES/ALLENYLPHOSPHINE OXIDES IN CYCLOADDITION/ CYCLIZATION REACTIONS

# 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

March 2013

Ramesh Kotikalapudi

# CERTIFICATE

This is to certify that the work described in this thesis entitled "*Gold Catalyzed Cyclizations of Alkynols/Propargylic Esters and Allenylphosphonates/Allenylphosphine Oxides in Cycloaddition/Cyclization Reactions*" has been carried out by Mr. Ramesh Kotikalapudi, under my supervision and the same has not been submitted elsewhere for any degree.

Hyderabad

March 2013

Prof. K. C. Kumara Swamy

(Thesis supervisor)

Dean

School of Chemistry
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INDIA

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I would like to express my heartfelt thanks to my mother Mrs. Vijaya Lakshmi for her enormous love, kindness, teaching me patience and making me myself. I sincerely acknowledge my brother Phani Kumar and sister-in-law Sravani for their association and affection.

*Ramesh Kotikalapudi ...*

# 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 AgOTf or $Ph_3PAuCl$-$AgSbF_6$ catalyzed cyclization of 1-hydroxy-2-alkynylallylphosphonates/ 2-alkynylallyl alcohols to 2-furylphosphonates/ 2,3,5-trisubstituted furans
**Ramesh Kotikalapudi** and K. C. Kumara Swamy.
*Tetrahedron Lett.* **2012**, *53*, 3831.

3. Nitrenium ion induced tandem S-S coupling, 1,2-prototropic shift and reduction
Manisha Patni, Raakhi Gupta, **Ramesh Kotikalapudi**, K. C. Kumara Swamy and Raj K. Bansal.
*Tetrahedron Lett.* **2013**, *xx*, xxxx. *(In Press, Accepted manuscript)*

4. Gold(I) catalyzed cycloisomerization of β-hydroxy propargylic esters to dihydropyrans/2*H*-pyrans *via* allene intermediates
**Ramesh Kotikalapudi** and K. C. Kumara Swamy *(submitted)*

5. Gold(I) catalyzed synthesis of novel benzofluorenols.
**Ramesh Kotikalapudi** and K. C. Kumara Swamy *(to be communicated)*

6. $FeCl_3$ catalyzed nucleophilic substitution of α-hydroxy allylphosphonates.
**Ramesh Kotikalapudi** and K. C. Kumara Swamy *(to be communicated)*

7. Trifluoroacetic acid mediated synthesis of isocoumarins and phosphono-isocoumarins via nucleophilic cyclization of allenylphosphine oxides.
**Ramesh Kotikalapudi** and K. C. Kumara Swamy (*to be communicated)*

8. $P(n\text{-}Bu)_3$ catalyzed reactions of salicyl *N*-thiophosphinyl imines with allenylphosphonates/phosphine oxide: Synthesis of phosphono-chroman derivatives
R. Rama Suresh, R. N. Prasad Tulichala, **Ramesh Kotikalapudi** and K. C. Kumara Swamy *(to be communicated)*

9. Synthesis of furyl phosphonates from 3-alkynals *via* sequential phosphite addition and 5-*endo*-dig cyclization.
Anasuya Uruvakili, **Ramesh Kotikalapudi** and K. C. Kumara Swamy *(to be communicated)*

10. Conformational Preferences in 2-(2-Pyridinylideneamino)-[1,3,2]-5-oxazaphospholane-2-selenides - X-Ray and DFT level investigations.
Neelima Gupta, Sonia Sharma, Vijaya Kabra, **Ramesh Kotikalapudi** and K. C. Kumara Swamy *(to be communicated)*.

## Posters presented in symposia

1. 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, Feb 6-8, **2009**.

2. $Ph_3PAuCl$/ $AgSbF_6$ or AgOTf as efficient catalyst for the cycloisomerization of 1-hydroxy-2-alkynylallylphosphonates/ 2-alkynyl allyl alcohols to 2-furylphosphonates/ 2,3,5-trisubstituted furans
**Ramesh Kotikalapudi** and K. C. Kumara Swamy.
*Chemfest-2012* (annual inhouse symposium), School of Chemistry, University of Hyderabad, Feb-2012. (**Poster & Oral Presentation**).

3. 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

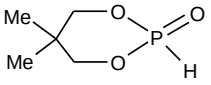
This thesis is divided into two parts: **Part-A** and **Part-B**. In **Part-A**, synthesis of phosphono-furans, phosphono-pyrans and other substituted pyrans *via* cyclization/cycloisomerization of appropriate alkynols is discussed. Formation of a variety of benzofluorenols by the cycloaddition of 1,3-diphenylisobenzofuran and terminal propargylic esters *via* gold catalysis is also described. **Part-B** comprises the cycloaddition of allenylphosphonates with dimethyl acetylenedicarboxylate (DMAD) under thermal activation that lead to phosphono-carbocycles. Nucleophilic cyclization of allenylphosphine oxides tethered with methyl ester group leading to phosphinoyl-isocoumarins in addition to phosphorus-free isocoumarins leading to P-C bond cleavage is also discussed. The reaction of activated arenes with phosphono-allyl alcohols using $FeCl_3$ to obtain vinyl as well as allylphosphonates is also demonstrated.

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

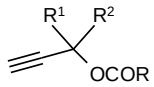
## PART-A

Chapter 1 deals with the review of literature on aspects relevant to this part. In Chapter 2, the results obtained on these aspects are discussed while in Chapter 3, the experimental details are presented. Prominent 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]. They are prepared by methodologies available (with modifications where necessary) in the literature.

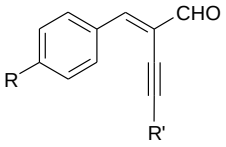
**Chart 1**



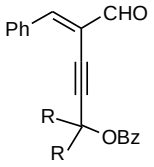
**1** [δ(P): 3.2]



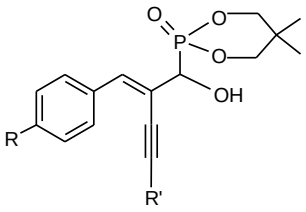
R = Ph, R$^1$ = R$^2$ = H [**2a**]
R = Ph, R$^1$ =R$^2$ = Me [**2b**]
R = Ph, (R$^1$R$^2$) = $(CH_2)_4$ [**2c**]
R = Ph, (R$^1$R$^2$) = $(CH_2)_5$ [**2d**]
R = Ph, R$^1$ =Me, R$^2$ = Et [**2e**]
R = Me, R$^1$ = R$^2$ = Me [**2f**]
R = Et, (R$^1$R$^2$) = Me [**2g**]



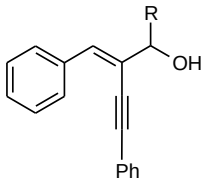
R = H, R' = Ph [**3a**, 91%]
R = H, R' = 4-Me-$C_6H_4$- [**3b**, 90%]
R = H, R' = *n*-butyl [**3c**, 80%]
R = Me, R' = 1-cyclohexenyl [**3d**, 86%]



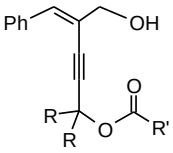
R = H [**4a**, 81%]
(R,R) = $[-CH_2-]_4$ [**4b**, 91%]



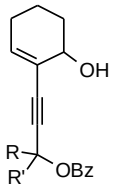
R = H, R' = Ph [**5a**, 94%]
R = H, R' = 4-Me-$C_6H_4$- [**5b**, 92%]
R = H, R' = *n*-butyl [**5c**, 92%]
R = Me, R' = 1-cyclohexenyl [**5d**, 92%]



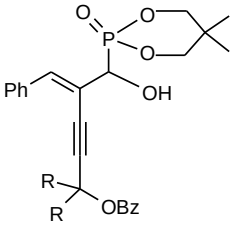
R = *p*-tolyl [**6a**, 62 %]
R = Me [**6b**, 84 %]



R = H, R' = Ph [**7a**, 82%]
R = R' = Me [**7b**, 84%]
(RR) = $(CH_2)_5$, R' = Me [**7c**, 84%]



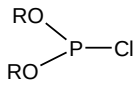
R = R' = Me [**8a**, 86%]
(RR') = $(CH_2)_5$ [**8b**, 81%]
R = Me, R' = *n*-pentyl [**8c**, 72%]



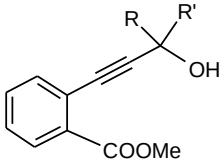
R = H [**9a**, 86%]
(RR) = $(CH_2)_4$ [**9b**, 85%]

Representative precursors are only shown here

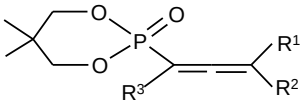
**Chart 2**



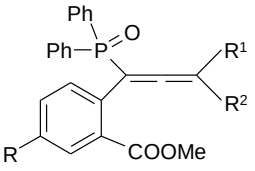
(RR) = $OCH_2(CMe_2)CH_2O$ [**10a**]
R = Ph [**10b**]



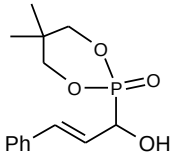
R = H, R' = Me [**11a**]
(RR') = $(CH_2)_5$ [**11b**]



R$^1$ = R$^2$ = H, R$^3$ = Me-$C_6H_4$- [**12a**, δ(P): 7.8]
R$^1$ = R$^2$ = H, R$^3$ = OMe-$C_6H_4$- [**12b**, δ(P): 7.5]
R$^1$ = H, R$^2$ = -CH=CHMe, R$^3$ = Ph [**12c**, δ(P): 6.7]



R = H, (R$^1$R$^2$) = $(CH_2)_5$ [**13a**, δ(P): 29.5]
R = Br, R$^1$ = H, R$^2$ = Me [**13b**, δ(P): 28.7]



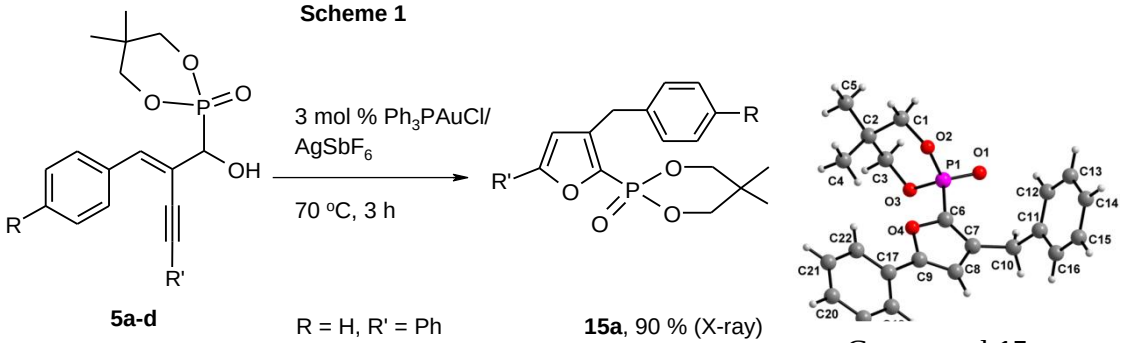
**14** [δ(P): 13.5]

Representative precursors are only shown here

**(i) Synthesis of phosphono-furans and non-phosphorylated furans *via* [Au]-catalysis using phosphono-alkynols**

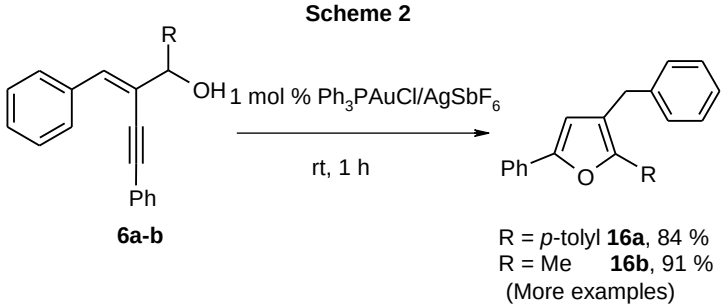
Phosphono-alkynols **5a-d** were treated with $Ph_3PAuCl/AgSbF_6$ in DCE to lead to phosphono-furans **15a-d**, respectively (Scheme 1) in excellent yields. The reaction proceeded through the activation of triple bond by the gold catalyst *via* 5-*endo*-dig cyclization followed by isomerization to form furan derivatives. The structure of compound **15a** was confirmed by X-ray crystallography.

**Scheme 1**




The reactivity of phosphono-alkynols has been compared with non-phosphorylated alkynols. Thus alkynols **6a-b** were successfully cycloisomerized to multi-substituted furans **16a-b** (Scheme 2) in the presence of $Ph_3PAuCl/AgSbF_6$ with lower catalyst loading when compared to the phosphono-alkynols. The reaction was complete at rt in $CH_2Cl_2$. The yields are excellent in these cases.

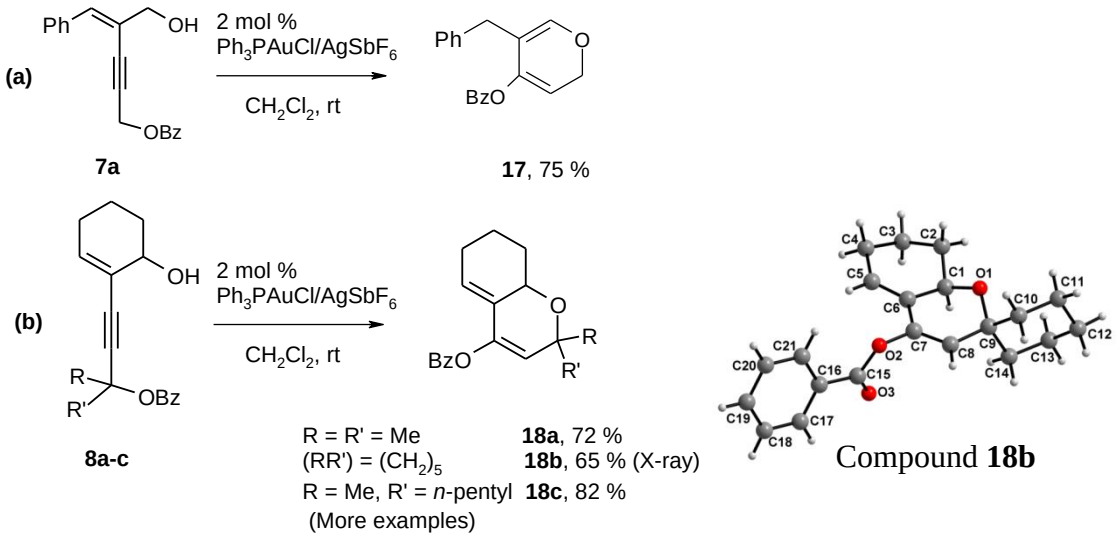
**Scheme 2**



**(ii) Cycloisomerization of propargylic esters *via* [Au]-catalysis leading to pyrans**

In an extension to the above cycloisomerization, we checked for a feasible six membered rings instead of furan. We have been successful in cyclizing β-hydroxy propargylic ester **7a** in the presence of $Ph_3PAuCl/AgSbF_6$ to 2(*H*)-pyran **17** in good yield (Scheme 3a). It proceeds through 1,3-carboxyl migration to form a transient allene intermediate which is attacked by hydroxyl group in 6-*endo*-trig manner with complete regioselectivity to form pyran derivative. In a similar manner, β-hydroxy propargylic esters **8a-c** are cycloisomerized to dihydropyrans **18a-c** (Scheme 3b) in good yields.

**Scheme 3**




**7a**

**17**, 75 %

**8a-c**

R = R' = Me **18a**, 72 %

(RR') = $(CH_2)_5$ **18b**, 65 % (X-ray)

R = Me, R' = *n*-pentyl **18c**, 82 %

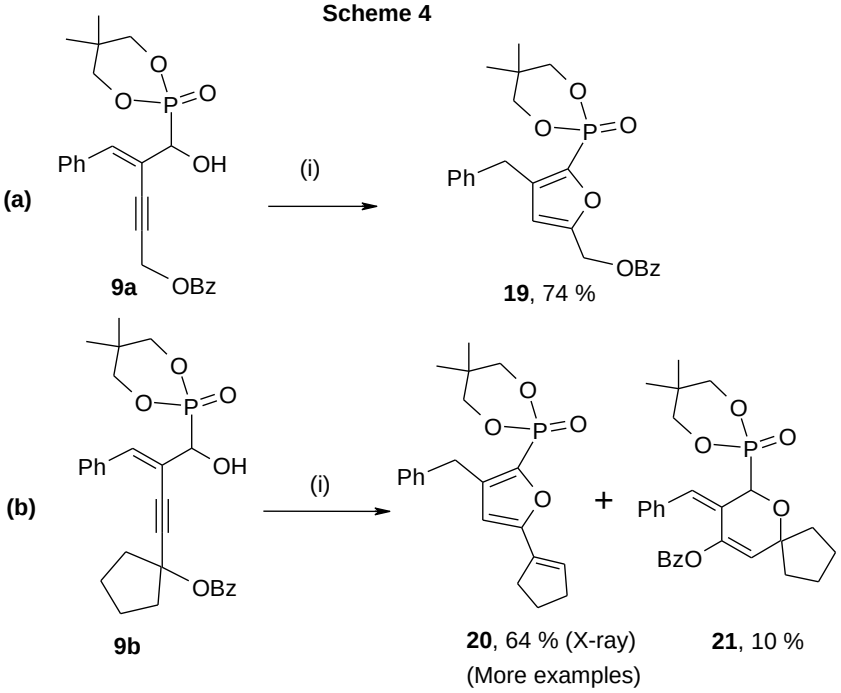
(More examples)




Compound **18b**

To compare the reactivity of β-hydroxy propargylic esters, phosphorus containing precursors are also used in the present study. Thus in the presence of $Ph_3PAuCl/AgSbF_6$, precursor **9a** led to phosphono-furan **19** (Scheme 4a); this reaction is different from the formation of pyrans formed by non-phosphorylated precursors (cf. Scheme 3). Under similar conditions, **9b** led to both phosphono-furan **20** and phosphono-pyran **21** (Scheme 4b). The structure of phosphono-furan **20** has been confirmed by X-ray crystallography (Figure 1). It reveals the formation of new double bond in the cyclopentyl ring by the removal of benzoate as benzoic acid. The overall reaction is quantitative according to $^{31}P$ NMR.

**Scheme 4**




(i) Conditions: 3% $Ph_3PAuCl/AgSbF_6$ in DCE at 70 °C, 3 h

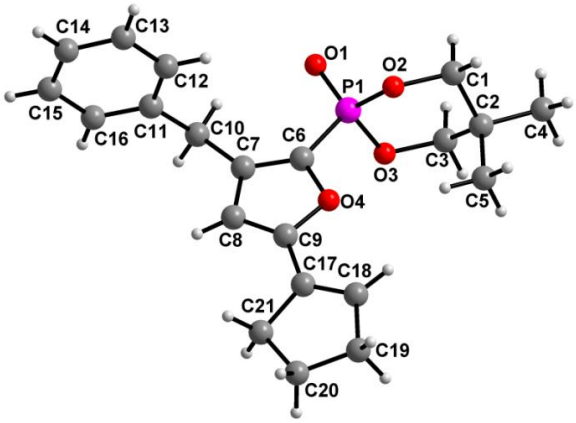
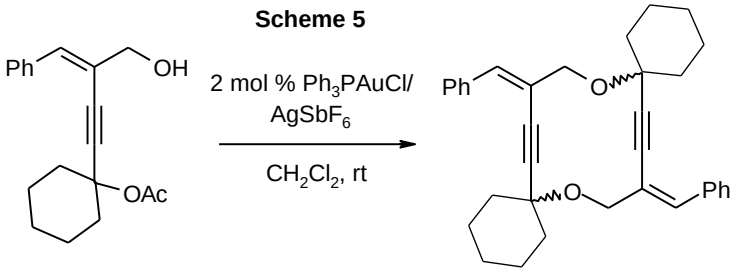



**Figure 1**. Molecular structure of compound **20**.

### (iii) Formation of macrocycles by propargylic esters

When we employed above conditions to precursor **7c**, 12-membered macrocycles **22-23** (Scheme 5) were formed indicating that steric and electronic factors are directing the reactivity of these precursors in a few cases. It is expected that **22** and **23** (X-ray structure available) differ by the presence of two oxygen atoms in the diaxial or diequatorial or axial-equatorial positions of cyclohexyl ring.

**Scheme 5**



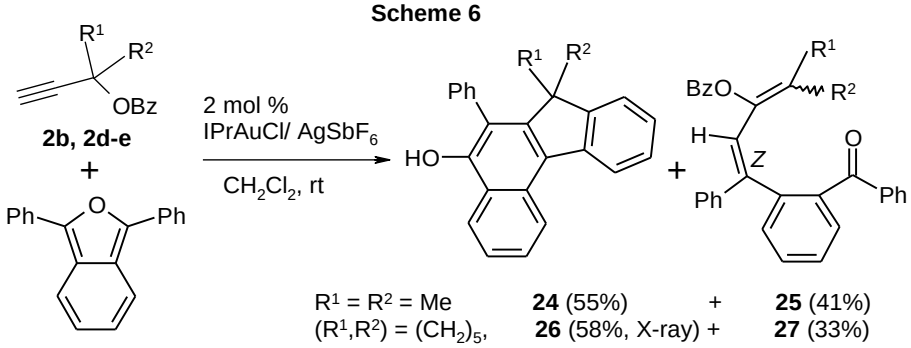

**7c**

**22** (28 %) + **23** (44 %, X-ray)
(More examples)

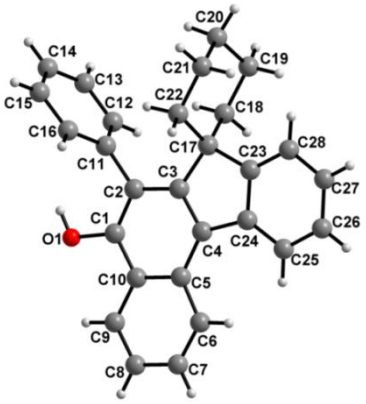
**(iv) [Au]-catalyzed cycloaddition on propargylic esters- Formation of Benzofluorenols and substituted dienes**

Keeping abreast of the recent developments in gold catalysis and also considering the reactivity of propargylic esters in the presence of gold salts, we have probed the cycloaddition reactions on propargylic esters. Thus, in the presence of IPrAuCl/$AgSbF_6$, propargylic ester **2b** upon treatment with IBF (1,3-diphenyl isobenzofuran), the reaction led to the novel benzofluorenol **24** and the substituted diene **25** in an overall yield of 96 % (Scheme 6). Precursors **2d-e** also led to analogous products **26-29** (benzofluorenol and dienes; X-ray structure for compound **26**). The benzofluorenols (e.g., **24**) is most likely formed by sequential gold catalyzed [4+2] cycloaddition of alkyne with IBF, allylation and 1,2-phenyl migration accompanied by the removal of benzoic acid. The substituted diene (e.g., **25**) is formed by [4+3] cycloaddition of propargylic ester with IBF to lead to an intermediate **25'** which could undergo opening up of the ring.

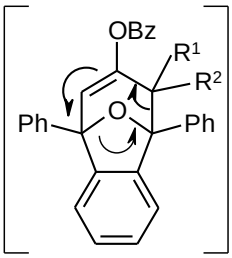
**Scheme 6**




$R^1 = R^2 = Me$ **24** (55%) + **25** (41%)
$(R^1,R^2) = (CH_2)_5$, **26** (58%, X-ray) + **27** (33%)
$R^1 = Me$, $R^2 = Et$ **28** (63%) + **29** (30%)
(More examples)




Compound **26**




**25'**

Likely [4+3] cycloadduct intermediate in the formation of compound **25**

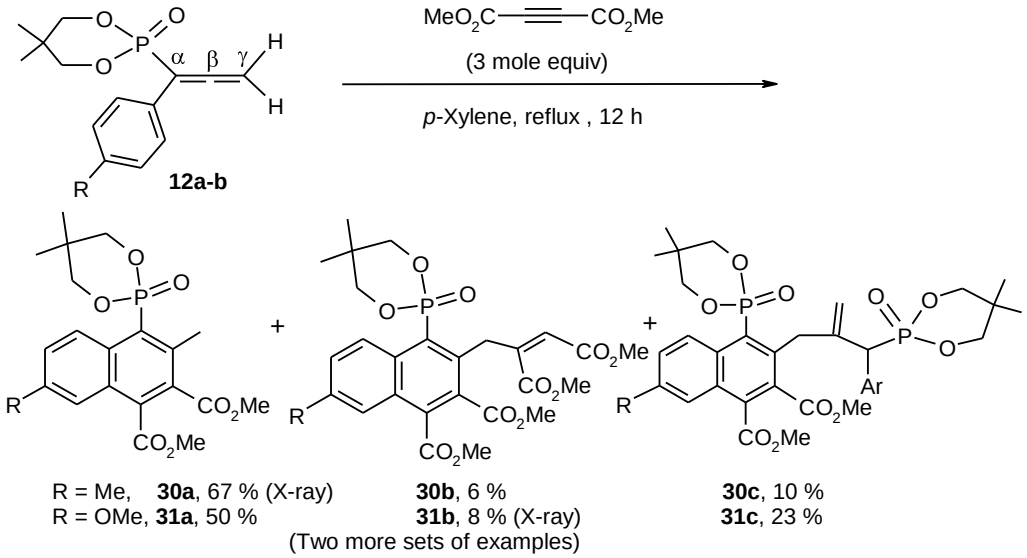
## PART-B

Chapter 4 deals with the review of literature on cycloaddition and nucleophilic cyclization reactions of allenes. 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) Cycloaddition of phosphorylated α-aryl allenes/γ-vinyl allenes with DMAD

As cycloaddition is an important synthetic tool for construction of diverse carbocycles, we surmised that phosphorylated allenes (allenylphosphonates) could be interesting substrates for cycloaddition reactions. Thus α-phenyl phosphorylated allenes **12a-b** were treated with dimethyl acetylenedicarboxylate (Scheme 7). The reaction led to novel phosphono-naphthalenes **30a-31a** which are [4+2] cycloadducts. Interestingly, two other compounds [**30b-31b** and **30c-31c**] are also isolated in each case. These are adducts of allene and alkyne in 1:2 and 2:1 ratio respectively. Thus the overall stoichiometry is maintained. The structures of **30a** and **31b** are shown in Figure 2. Such cycloadditions are hitherto unprecedented in allene chemistry.

**Scheme 7**



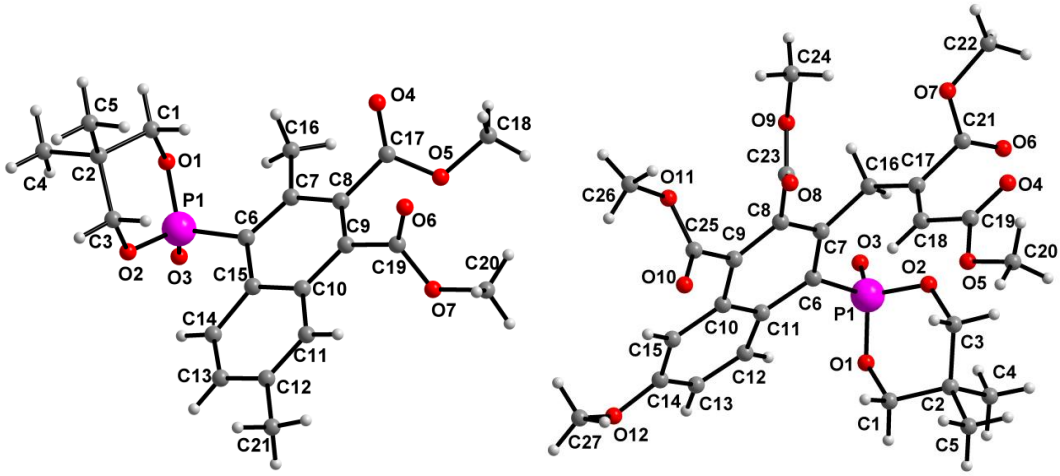
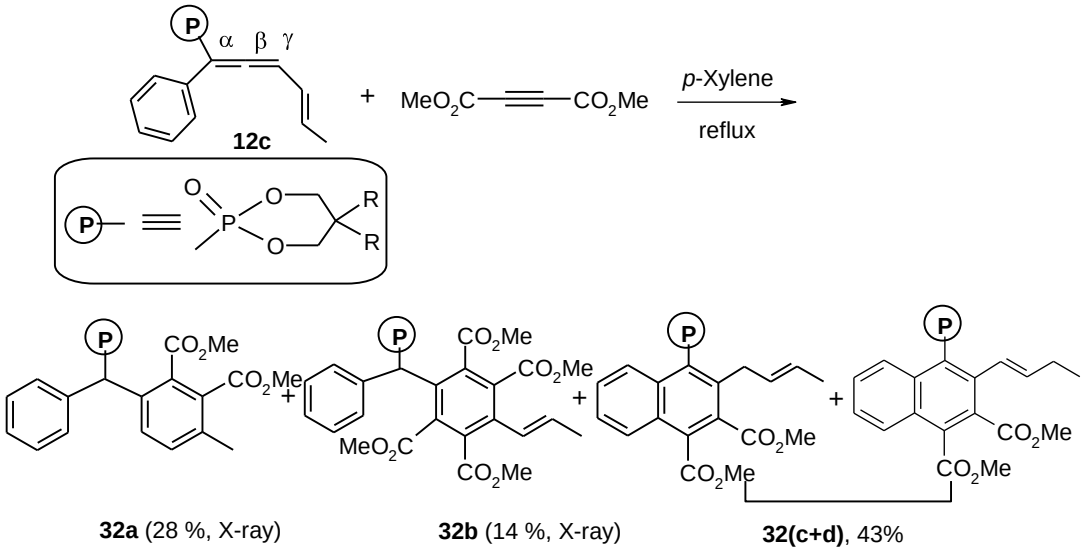



**Figure 2.** Molecular structures of compound **30a** and **31b**

In continuation of the above treatment of α-phenyl, γ-vinyl phosphorylated allene **12c** with DMAD under similar conditions led to ***four different cycloaddition products*** **32a-d**. By utilizing the vinylic end and phenyl end as a diene, [4+2] cycloadducts **32a** and **32(c,d)** are formed (Scheme 8). In contrast, product **32b** is formed *via* [2+2+2] cycloaddition. It is formed by sequential [2+2] cycloaddition at (β,γ)-position of allene, complete opening up of the cyclobutene ring and [4+2] cycloaddition with another molecule of DMAD. Structures of **32a** and **32b** have been confirmed by X-ray crystallography (Figure 3).

**Scheme 8**




(Three more sets of examples)

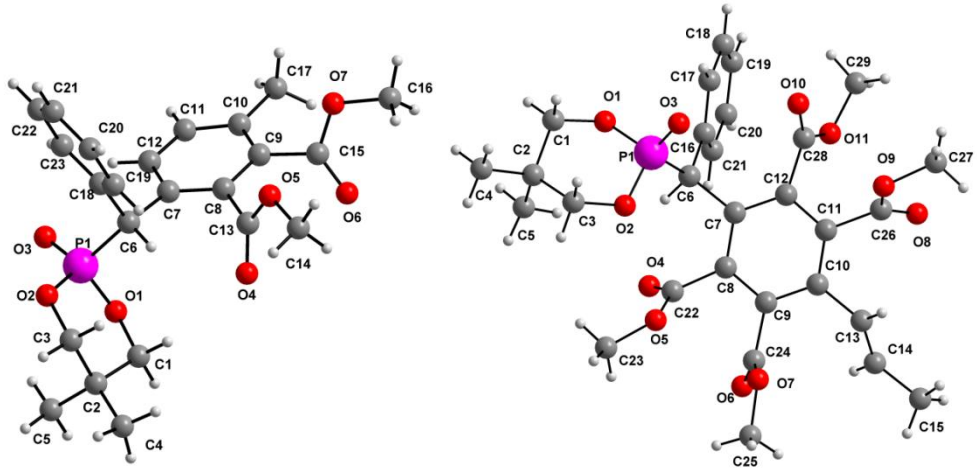
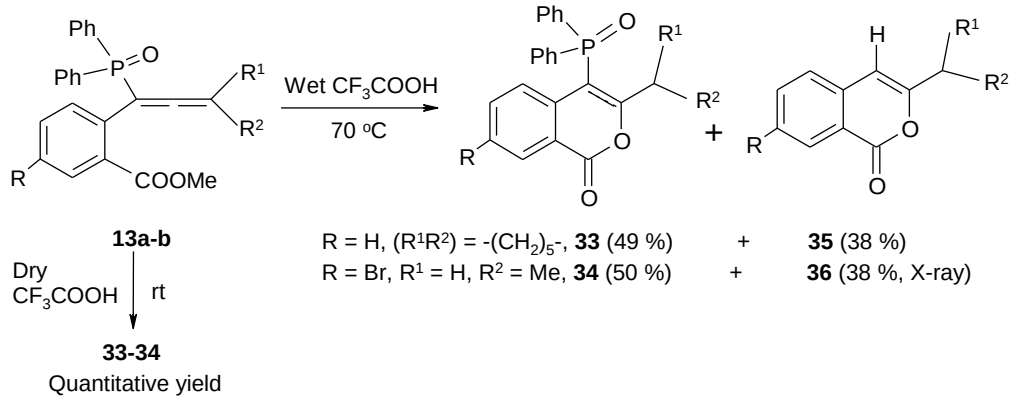


**Figure 3.** Molecular structures of compound **32a** and **32b**

**(ii) Brønsted acid mediated synthesis of phosphono-isocoumarins**

Allenylphosphine oxides tethered with carboxyl methyl ester group **13a-b** upon treatment with trifluoroacetic acid (TFA, Scheme 9) led to phosphinoyl isocoumarins **33** and **34** in quantitative yields. However, when the reaction was performed in wet TFA under reflux conditions, phosphorus-free isocoumarins **35** and **36** were also formed by cleavage of P-C bond. The structure of compound **36** was confirmed by X-ray crystallography. Possible pathways for this reaction are discussed in the thesis.

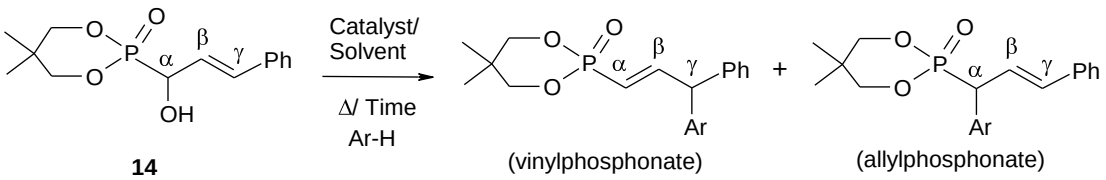
**Scheme 9**

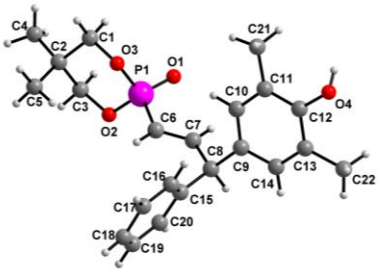



**(iii) Synthesis of vinyl-/allylphosphonates *via* α-hydroxyphosphonates by Friedel-Crafts reaction**

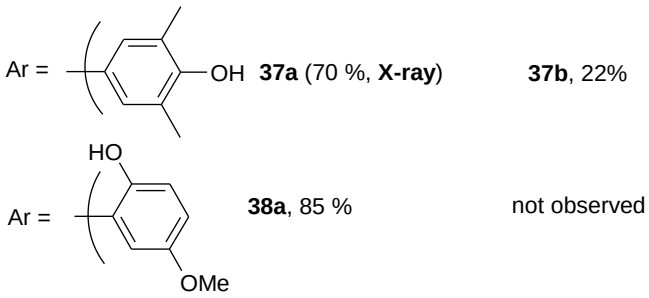
As nucleophilic substitution of allyl alcohols has been proved as important synthetic tool in the construction of new C-C bonds, phosphono-allyl alcohol **14** is utilized to check this protocol. Thus functionalized arenes (e.g., 2,6-dimethyl phenol, 4-methoxy phenol) are reacted with **14** in the presence of $FeCl_3$ in nitromethane (Scheme 10). The reaction resulted in the allylation of arenes to lead to vinylphosphonates **37a-38a** and allylphosphonate **37b** in excellent yields. The structure of compound **37a** was confirmed by X-ray crystallography.

**Scheme 10**




Compound **37a**



# PART-A

## GOLD CATALYZED CYCLIZATIONS OF ALKYNOLS/ PROPARGYLIC ESTERS

Chapter 1

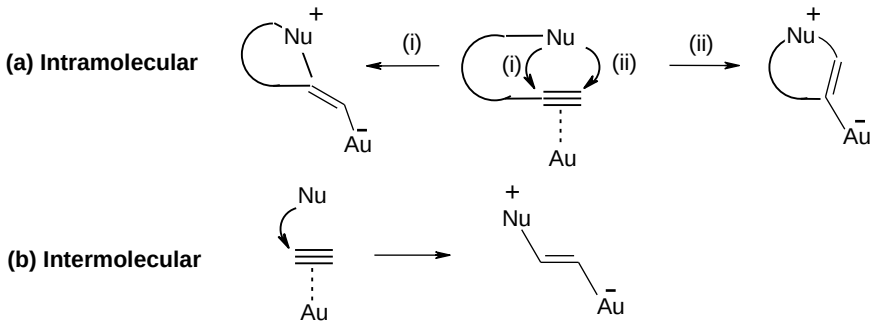
# INTRODUCTION

## 1.1 General Introduction: Gold Catalysis

Gold has been considered as a precious metal and is a symbol of wealth and beauty. By the time new findings in modern synthetic chemistry began to unfold, especially in transition metal catalysis, the development in gold chemistry was subtle since gold was considered as expensive and catalytically inactive. Thomas and coworkers in 1976 reported the addition of nucleophiles to alkynes which proved that gold(I) could perform as a Lewis acid activating the π-system.[1] Being a member of Group 11 in the family of copper and silver, gold attained the unique property of alkynophilicity.[2] These M(I) species are soft acids with the softness increasing from Cu(I) to Au(I) because of increase in atomic size and hence polarizability. According to HSAB theory, soft acids prefer to coordinate to soft bases like alkynes/allenes. Thus cationic gold(I) species show better catalytic activity[3] than the other Group 11 elements. This feature is augmented by the relativistic contraction of *s* and *p* orbitals of gold which corresponds to relatively low lying LUMO according FMO theory.[4]

Gold coordinates to alkyne/allene to form electron deficient metal-alkyne/allene complex which is further attacked by a nucleophile; subsequent protodeauration leads to the addition product. It was found that a wide range of nucleophiles can be added to alkynes/allenes in an intramolecular or intermolecular approach (Scheme 1.1).[5] Subsequent to the year 1990, there is an exponential increase in the number of publications on gold catalysis indicating the enormous interest of researchers in this field.[6]

**Scheme 1.1**




Gold catalysts can process energy efficient transformations[7] and even satisfy greener protocol[8] in many cases. Advantages of gold catalysis are low catalyst loadings, less reaction times, compatibility with greener solvents, ambient reaction temperatures, and environmentally benign byproducts. In many reactions, gold does not need ligands to exhibit its activity.[9] Gold derivatives are catalytically robust but are air/ moisture sensitive. As there is high oxidation potential of Au(I) to Au(III), both the oxidation states are stable and the scope for redox reactions is limited.[4] Hence the Au(I) catalyzed reactions can be carried out in the presence of air. Gold can catalyze the unique transformations for which other catalyst has not been identified.

## 1.2 Gold catalyzed organic transformations

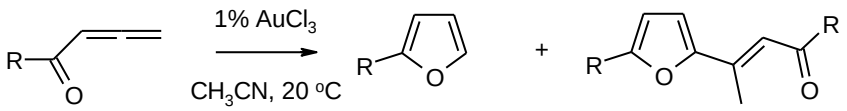
By exploiting the alkynyl/allenyl compounds, gold salts are able to drive many transformations which lead to furans, furanones, coumarins, lactones, phenols, polycycles, pyrans, azepines etc.[2b, 3a, 3c and 10] These reactions involve cyclizations, isomerizations, oxidations, additions and substitutions. In the following sections, gold catalyzed cyclizations and cycloadditions from the literature which are relevant to our work are discussed.

### 1.21 Gold catalyzed cyclizations

The first gold catalyzed cyclization reaction of functionalized allenes was reported by Hashmi.[11] Cycloisomerization/dimerization of terminal allenyl ketone was achieved in which new C-O and C-C bonds were observed. $AuCl_3$ (1 mol %) in $CH_3CN$ was able to accomplish this transformation in a very short reaction time. Allenyl ketone

**1.1** led to a mixture of simple furan derivative **1.2** and the dimeric product **1.3** (Scheme 1.2).

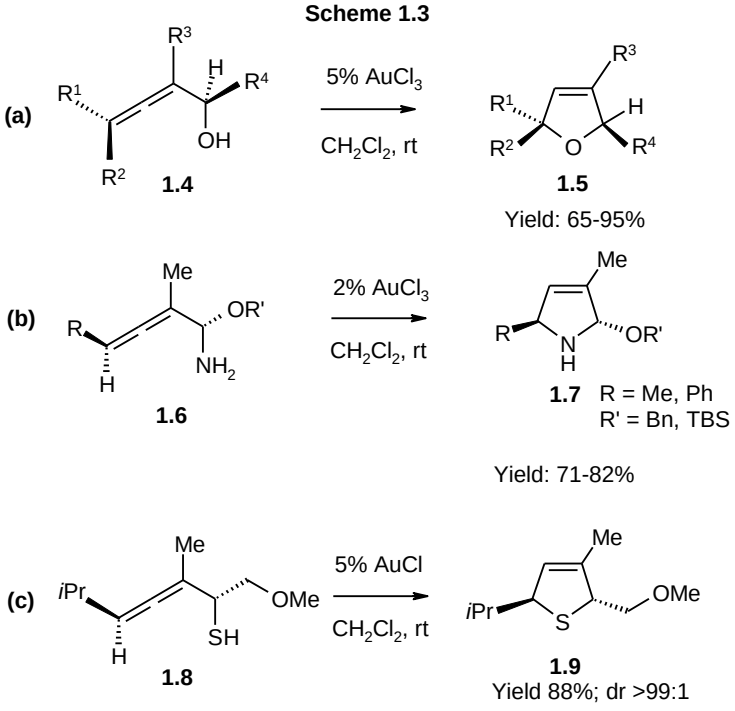
**Scheme 1.2**




**1.1** R = 3-(MeO)$C_6H_4$ **1.2a**, 34% **1.3a**, 38%
R = 4-($O_2$N)$C_6H_4$) **1.2b**, 88% **1.3b**. 4%

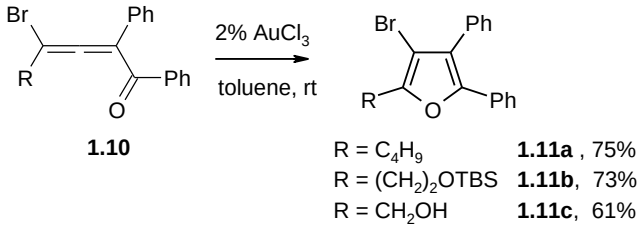
After the above report, Krause and co-workers published a mild and efficient method for the cyclization of α-hydroxyallenes to 2,5-dihydrofurans.[2a] Thus allenol **1.4** undergoes cyclization in the presence of $AuCl_3$ in $CH_2Cl_2$ to provide the dihydrofuran derivative **1.5** in excellent yields (Scheme 1.3a). The same group reported the cycloisomerization of α-aminoallenes **1.6** to 3-pyrrolines **1.7** with complete axis-to-center chirality transfer in excellent diastereoselectivity (Scheme 1.3b).[12b] The first gold catalyzed C-S bond formation was also reported by the same group by stereoselective cycloisomerization of α-thioallenes **1.8** to 2,5-dihydrothiophenes **1.9** (Scheme 1.3c).[12c]

**Scheme 1.3**



An important cycloisomerization of haloallenyl ketones **1.10** to furans with 1,2-halo migration was observed by Gevorgyan and co-workers.[13] Thus gold catalyzed 1,2 migration of iodine, bromine and chlorine proceeds via the formation of halirenium intermediate leading to 3-halo furans **1.11a-c** in moderate to excellent yields (Scheme 1.4). The method is a mild, selective and efficient route to various 3-halofurans.

**Scheme 1.4**

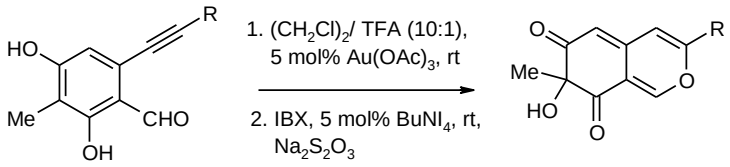



**1.10**

R = $C_4H_9$ **1.11a** , 75%
R = $(CH_2)_2OTBS$ **1.11b**, 73%
R = $CH_2OH$ **1.11c**, 61%

Azophilones, which have structurally diverse natural product core structures, were synthesized by Porco *et al* via gold catalyzed cycloisomerization.[14] The reaction involves [4+2] benzannulation of alkyne and aldehyde. 5 mol% of $Au(OAc)_3$ drives **1.12** into benzopyrilium salt, which on oxidation using IBX leads to azophilones **1.13a-c** (Scheme 1.5).

**Scheme 1.5**



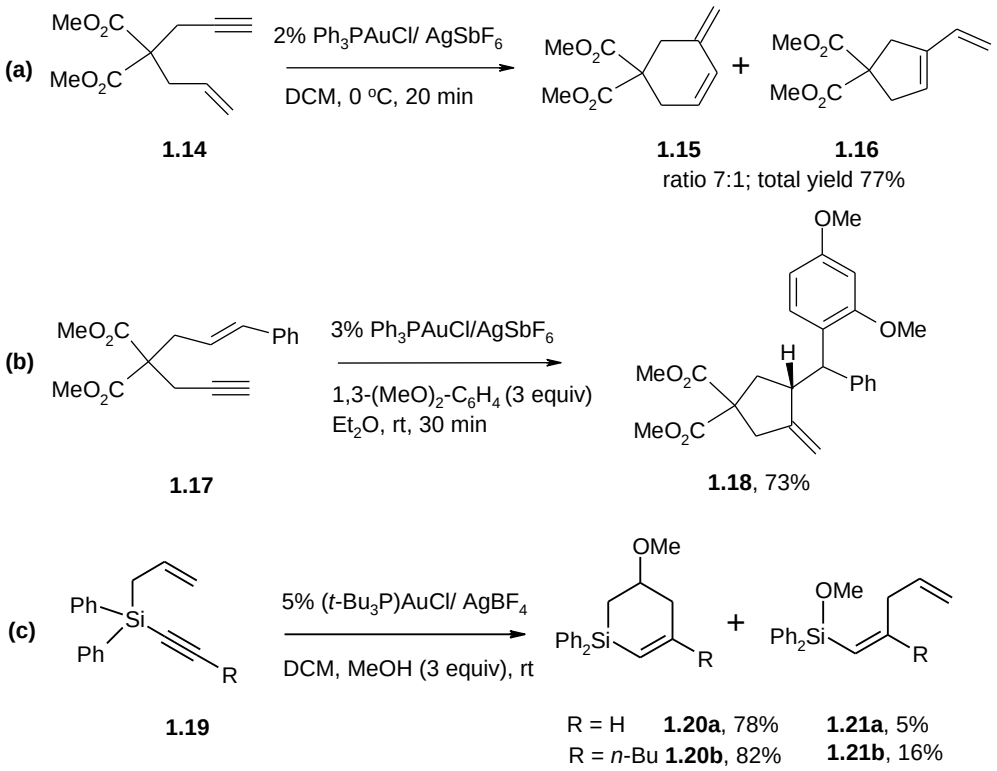

**1.12**

R = 2-cyclohexenyl **1.13a** , 65%
R = Ph **1.13b**, 82%
R = $CH_2OMe$ **1.13c**, 65%

Echavaren reported the cycloisomerization of α,ω-enynes **1.14** by the use of a cationic gold(I) complex to provide cyclized products exo-**1.15** and endo-**1.16** (Scheme 6a).[15] The reaction took a short time for the conversion, with excellent yields of the products. In a similar way, Michelet and co-workers have disclosed nucleophile assisted cyclization of enyne **1.17**.[16] Thus gold(I) catalyzed C-C bond formation through a tandem Friedel-Crafts type addition and carbocyclization was effected to obtain

cyclized products **1.18** in moderate to excellent yields (Scheme 1.6b). In the year 2006, Toste *et al* reported the stereoselective synthesis of vinyl silanes by alcohol triggered gold catalyzed acetylenic sila-Cope rearrangement.[17] The system $(t\text{-Bu})_3$PAuCl/ $AgSbF_6$ (5 mol%) was employed to get vinyl silanes **1.21a-b** along with 6-membered silacycles **1.20a-b** (Scheme 1.6c).

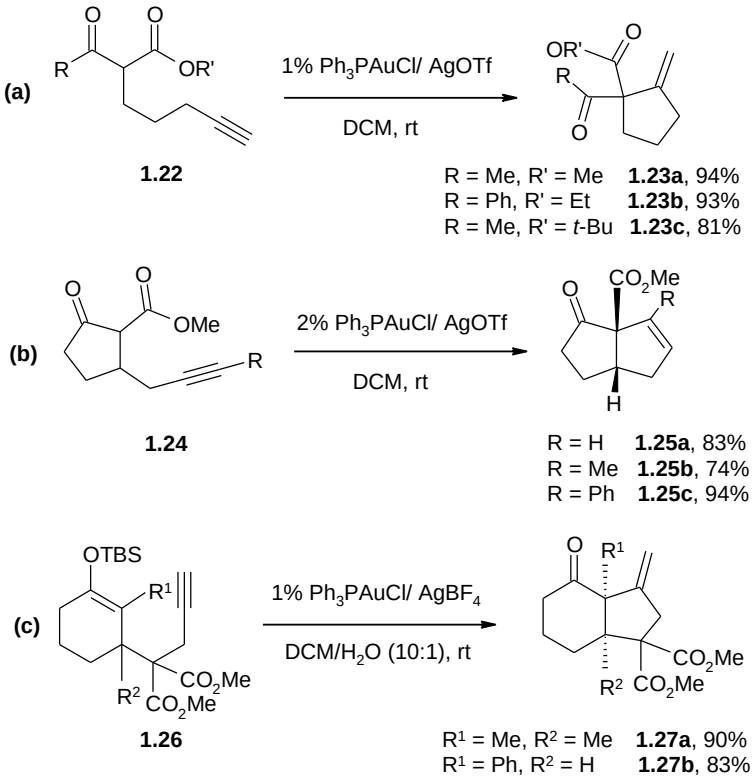
**Scheme 1.6**




Toste and co-workers investigated the cycloisomerization of alkyne tethered *β*–keto esters **1.22**.[18a] The reaction progressed *via* 5-*exo*-*dig* carbocyclization to produce cyclopentanes along with the formation of α-vinyl ketones **1.23a-c** (Scheme 1.7a). High diastereoselectivity under mild reaction conditions was achieved. The same group described a route to cyclopentenones **1.25a-c** *via* gold(I) catalyzed carbocyclization of acetylenic dicarbonyl compounds **1.24** (Scheme 1.7b).[18b] It proceeds through 5-*endo*-*dig* cyclization. The reaction shows excellent tolerance for the variation in ketone, ester and alkyne substituents. Toste's group also reported the gold(I) cyclization of alkyne tethered silyl enol ethers **1.26** to obtain bicyclic frameworks **1.27a-b** (Scheme 1.7c).[19]

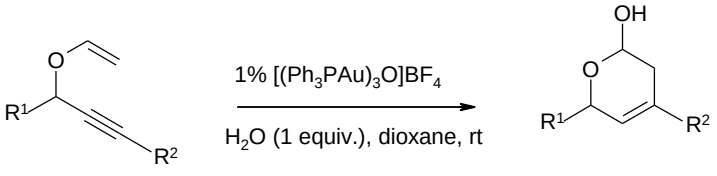
The utility of this carbocyclization was demonstrated by an efficient total synthesis of (+)-lycopladine A.

**Scheme 1.7**



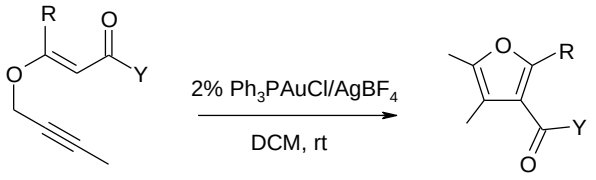

Toste and co-workers have described a method for the synthesis of dihydropyran derivatives *via* gold catalysis.[20] The complex $[(Ph_3PAu)_3O]BF_4$ (1 mol%) could drive the propargyl enol ether **1.28** to oxocarbenium intermediate which was further triggered by a nucleophile to lead to the dihydropyrans **1.29a-d** (Scheme 1.8).

**Scheme 1.8**



Kirsh reported the gold(I) catalyzed synthesis of highly functionalized furans.[21] Cascade reaction of propargyl-Claisen rearrangement and hetero-cyclization of propargyl enol ethers **1.30** to synthesize tri- and tetra-substituted functionalized furans **1.31a-d** was described by this method (Scheme 1.9). The conversion took place with low catalyst loading at room temperature.

**Scheme 1.9**

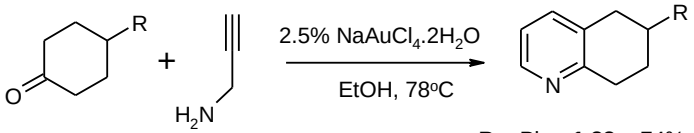



**1.30**

R = Me, Y = OEt **1.31a**, 95%
R = Ph, Y = OEt **1.31b**, 90%
R = H, Y = OEt **1.31c**, 75%
R = Ph, Y = Ph **1.31d**, 72%

Acardi and co-workers described a method for the synthesis of functionalized pyridines through gold catalysis.[22] Sequential amination of carbonyl compound **1.32** followed by regioselective 6-*endo*-*dig* cyclization of *N*-propargyl enamine and aromatization in one pot approach in the presence of $NaAuCl_4.2H_2O$ provided the pyridine derivatives **1.33a-b** (Scheme 1.10).

**Scheme 1.10**



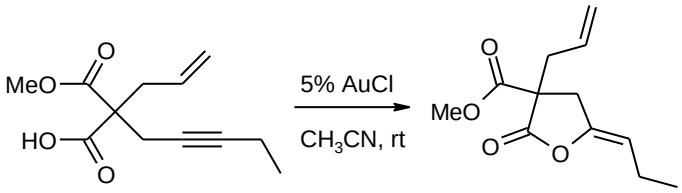

**1.32**

(1.5 equiv)

R = Ph **1.33a**, 74%
R = *t*-Bu **1.33b**, 69%

Mechelet *et al* reported the AuCl catalyzed cyclization of acetylenic acids **1.34** to obtain functionalized γ-lactones **1.35** (scheme 1.11).[23] The cyclization proceeds selectively via 5-*exo*-*dig* mode under extremely mild conditions without the aid of additive salts. The method provides an efficient access to highly valuable building blocks for natural products.

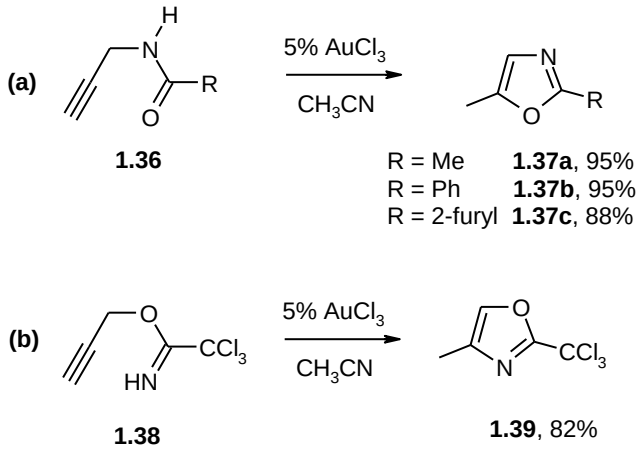
**Scheme 1.11**




**1.34** **1.35**

Hashmi *et al* reported the synthesis of oxazoles under mild $AuCl_3$ catalyzed conditions.[24a] Thus *N*-propargyl carboxamides **1.36** were cycloisomerized to an intermediate which on isomerization led to substituted oxazoles **1.37a-c** (Scheme 1.12a). The same group reported the synthesis of alkylidene oxazolines and oxazoles **1.39** by intramolecular hydroamination of an alkyne by trichloroacetimidate **1.38** (Scheme 1.12b).[24b] The cyclization was much faster than subsequent aromatization.

**Scheme 1.12**




**1.36**

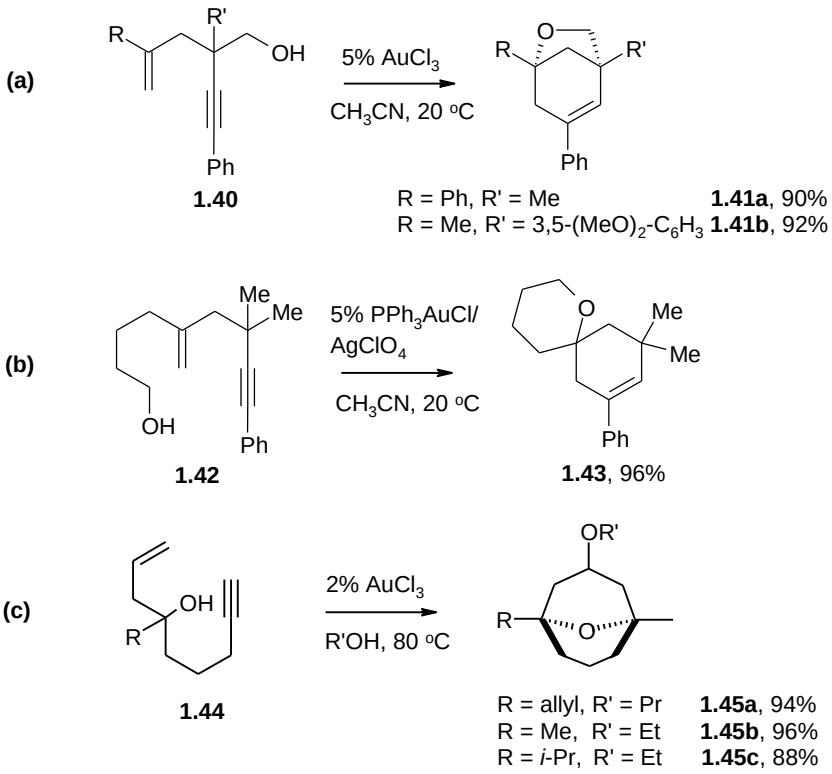
R = Me **1.37a**, 95%
R = Ph **1.37b**, 95%
R = 2-furyl **1.37c**, 88%

**1.38** **1.39**, 82%

Cozmi developed efficient gold catalyzed double cyclization using alcohol **1.40** or **1.42** to access oxa- and aza-bicyclic alkenes **1.41a-b** containing bridged fused spirocycles. It demonstrated the formation of five- (Scheme 1.13a) as well as six-membered heterocycles **1.43** (Scheme 1.13b) in excellent yields.[25] In the year 2006, Barluenga and co-workers reported gold/ platinum catalyzed tandem 6-*exo* cycloisomerization of allyl substituted 5-hexyn-1-ols **1.44**.[26] The reaction was triggered

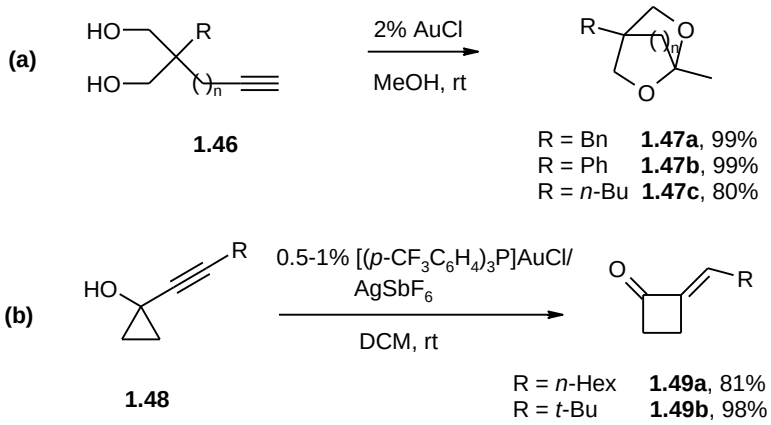
by a nucleophile and involved Prins type of cyclization. Thus eight membered carbocycles **1.45a-c** (Scheme 1.13c) were synthesized diastereoselectively.

**Scheme 1.13**



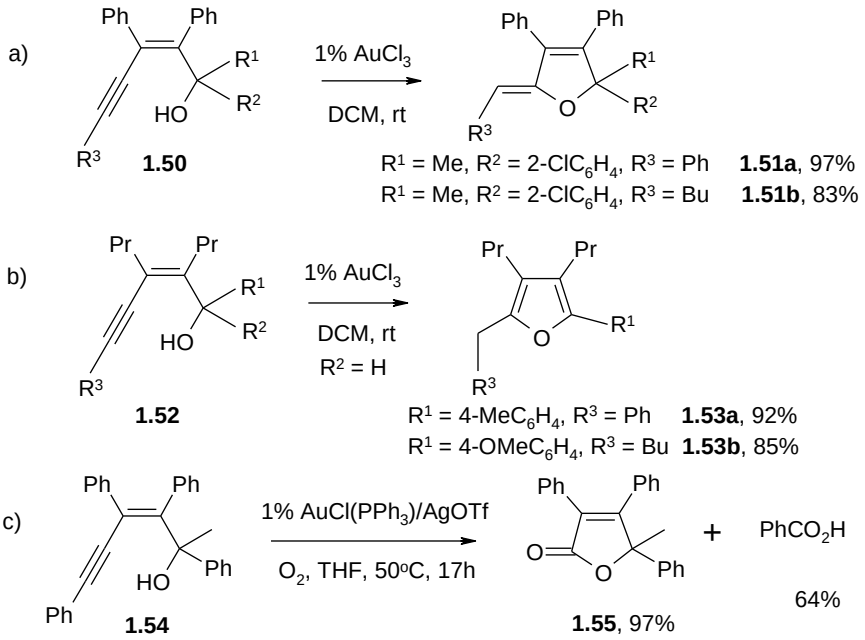

In the year 2005, Michelete reported gold-catalyzed cycloisomerization of bis-homopropargylic diols **1.46**.[27] This route led to highly efficient access to strained bicyclic ketals **1.47a-c** (Scheme 1.14a). The process started from easily accessible starting materials and was found to be general and atom-economical. The yields of the bicyclic ketals are good to excellent (74% to 99%). Similarly, an interesting gold(I) catalyzed ring expansion of cyclopropanols **1.48** and cyclobutanols was discovered by Toste's group.[28] The process provides a single olefin isomer and is stereospecific with regard to substituents on the ring, to obtain cyclobutanones **1.49a-b** (Scheme 1.14b) and cyclopentanones.

**Scheme 1.14**



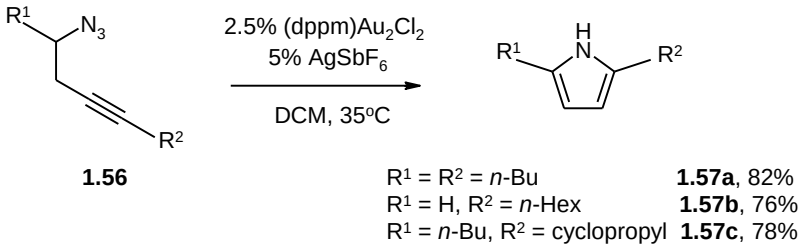

Liu reported the synthesis of completely substituted dihydropyrans **1.51a-b** and furans **1.53a-b** by the cycloisomerization of (*Z*)-2-en-4yn-1-ols **1.50** and **1.52** (Scheme 1.15a-b).[29a] This cycloisomerization offers an extremely mild route to multi-substituted oxacycles. Later, the same group reported the synthesis of butenolide **1.55** starting from (*Z*)-enynols **1.54**.[29b] Highly efficient method for the cyclization of enynol followed by oxidative cleavage with molecular oxygen was disclosed in this process (Scheme 1.15c).

**Scheme 1.15**



Toste *et al* discovered a gold(I) catalyzed C-N bond formation in intramolecular acetylenic Schmidt reaction.[30] Homo-propargyl azides **1.56** were driven under mild conditions to afford multi substituted pyrroles **1.57a-c** (Scheme 1.16). Gold(I) serves both to activate the alkyne toward nucleophilic addition and to donate electron density back into an electron deficient π-system.

**Scheme 1.16**

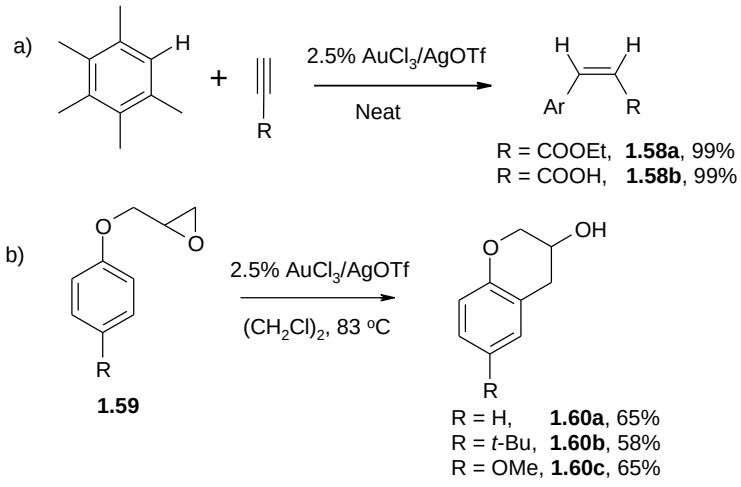



**1.56**

$R^1 = R^2 =$ *n*-Bu **1.57a**, 82%
$R^1$ = H, $R^2$ = *n*-Hex **1.57b**, 76%
$R^1$ = *n*-Bu, $R^2$ = cyclopropyl **1.57c**, 78%

Efficient C-H functionalization[31] of aromatic C-H bonds catalyzed by gold(III) was reported by He and co-workers.[31a] The method involved mild and solvent-free conditions to obtain hydroarylated alkynes **1.58a-b** (Scheme 1.17a). The reaction proved to be efficient in the case of electron deficient alkenes and for intramolecular version as well. The same group reported the cyclo-alkylation of electron rich arenes with epoxides **1.59** to afford 3-chromanols **1.60a-c** in the presence of 2.5 mol% of $AuCl_3$/AgOTf (Scheme 1.17b).[31b] The reaction is stereospecific.

**Scheme 1.17**



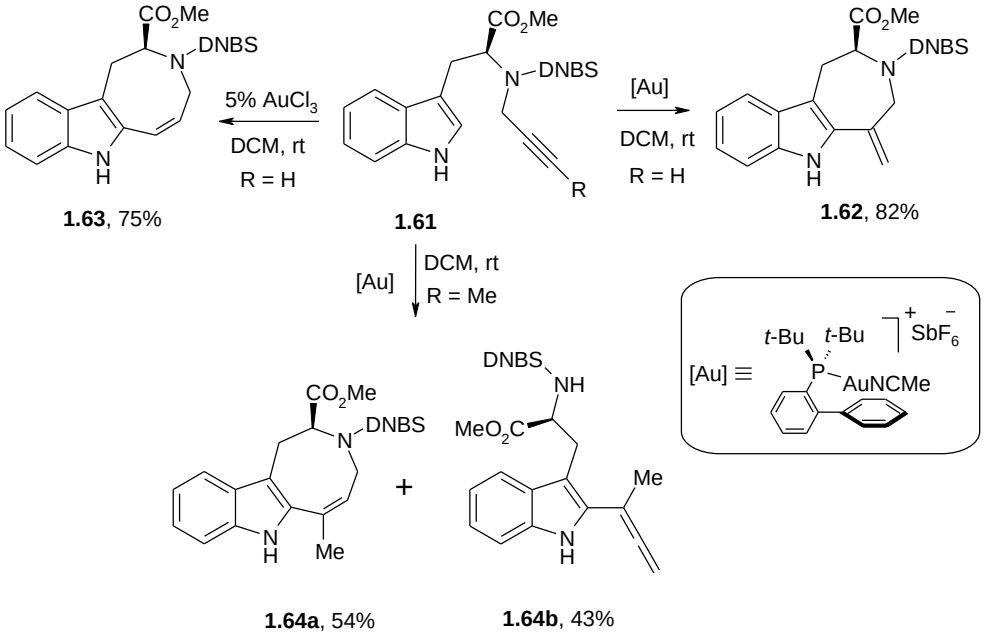

R = COOEt, **1.58a**, 99%
R = COOH, **1.58b**, 99%

**1.59**

R = H, **1.60a**, 65%
R = *t*-Bu, **1.60b**, 58%
R = OMe, **1.60c**, 65%

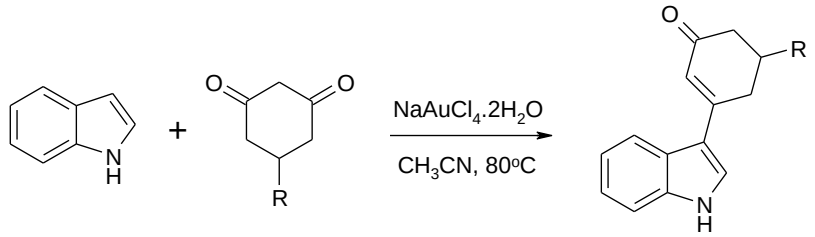
In the year 2006, Echavaren *et al* reported intramolecular hydroarylation of alkynes with indoles.[32] They demonstrated facile formation of six to eight membered rings under gold catalysis. Thus alkyne tethered indoles **1.61** were treated with Au(I) to obtain six and seven membered rings **1.62** via 6-*exo-dig* and 7-*exo-dig* route whereas Au(III) led to eight membered cyclics **1.63** via 8-*endo-dig* cyclization (Scheme 1.18). Interesting and unexpected allenylation was also described in the case of **1.61** to obtain allene derivative **1.64b** along with **1**.**64a**.

**Scheme 1.18**




Acardi *et al* reported new gold catalyzed C-C bond formation by direct coupling of indoles and pyrroles with 1,3-dicarbonyl compounds to provide alkenylated arenes **1.65** (Scheme 1.19).[33] $AuCl_3$ catalyzed direct alkenylation under mild conditions, regioselectivity and high functional group tolerance proved this method efficient for the construction of new C-C bonds.

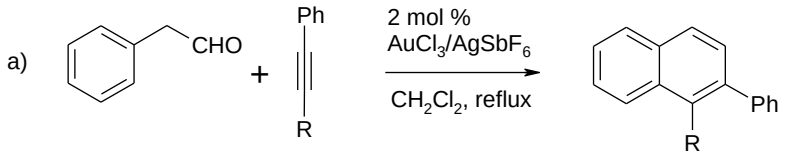
**Scheme 1.19**



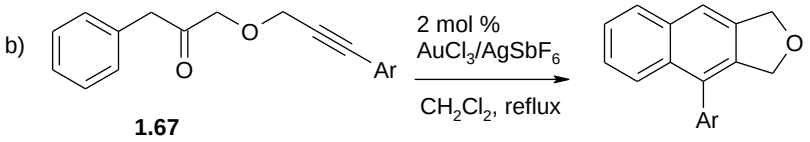

R = H **1.65a**, 54%
R = Me **1.65b**, 80%
R = Ph **1.65c**, 74%

Recently, Balamurugan *et al* reported the electrophilic addition to aryl-alkyne followed by benzannulation to synthesize substituted naphthalenes **1.66a-c** (Scheme 1.20a).[34a] The oxo- and alkyno-philicities of $AuCl_3$/ $AgSbF_6$ led the substrates to products in a facile manner. By using this protocol, the same group reported the intramolecular sequential electrophilic addition and benzannulation of aryl alkynones **1.67** to provide aryl naphthalene derivatives **1.68a-c** (Scheme 1.20b).[34b]

**Scheme 1.20**




R = H **1.66a**, 69%
R = Br **1.66b**, 61%
R = Me **1.66c**, 87 %



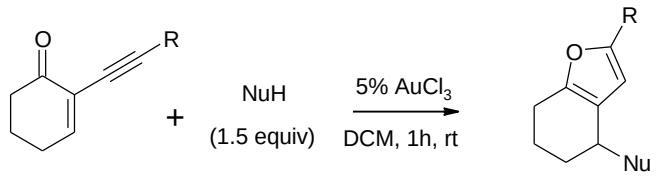

**1.67**

Ar = Ph **1.68a**, 88%
Ar = 4-OMeC$_6$H$_4$- **1.68b**, 91%
Ar = 1-Naphthyl **1.68c**, 91%

An outstanding synthetic methodology was discovered for the formation for multi-substituted furans by Larock *et al* in the year 2004.[35a] 2-(1-Alkynyl)-2-alken-1-ones **1.69** with the aid of nucleophiles were efficiently cyclized to versatile furan derivatives **1.70a-c** in the presence of 1 mol% $AuCl_3$ (Scheme 1.21). The reaction

proceeds likely by a gold containing carbocation intermediate. The concept further witnessed the new synthetic findings in gold catalyzed dipolar cycloadditions which are discussed in the latter part of this chapter. The same group reported electrophile induced synthesis of highly functionalized furans from these precursors also.[35b]

**Scheme 1.21**

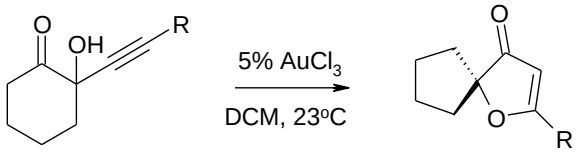



**1.69**

R = Ph, Nu = MeO **1.70a**, 88%
R = Ph, Nu = 3-(N-methylindole) **1.70b**, 90%
R = 1-(2-cyclohexenyl), Nu = MeO **1.70c**, 80%

Kirsch reported a gold catalyzed synthesis of highly substituted 3-(*2H*)-furanones.[36] Alkynyl carbonyl compounds with hydroxyl group at the propargyl position **1.71** were treated with $AuCl_3$ to observe hetero-cyclization and subsequent 1,2-alkyl shift to afford furanone derivatives **1.72a-b** (Scheme 1.22).

**Scheme 1.22**

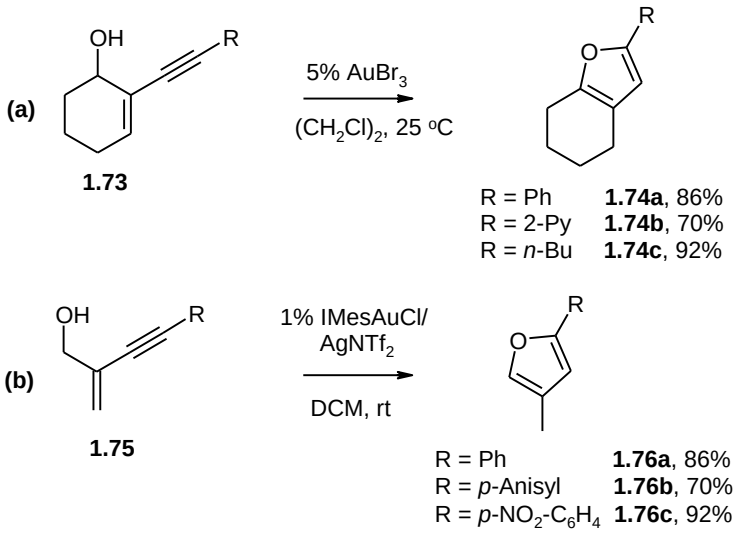



**1.71**

R = 2-MeO-$C_6H_4$- **1.72a**, 81%
R = 4-F-$C_6H_4$- **1.72b**, 70%

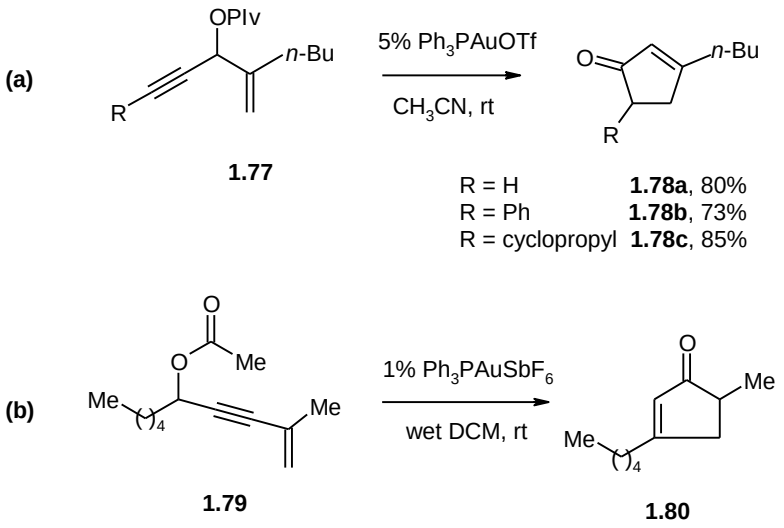
Recently, Perumal *et al* reported $AuBr_3$ catalyzed furannulation of 2-alkynyl cycloalken-2-enols **1.73** to form various fused furans **1.74a-c** (Scheme 1.23a).[37a] Moderate reaction condition was employed for this kind of cycloisomerization. Hashmi *et al* have also reported very mild conditions for the cycloisomerization of 2-alkynyl allyl alcohols **1.75** to obtain highly substituted furans **1.76a-c** (Scheme 1.23b).[37b] A Gold(I) carbene complex was used for this conversion.

**Scheme 1.23**



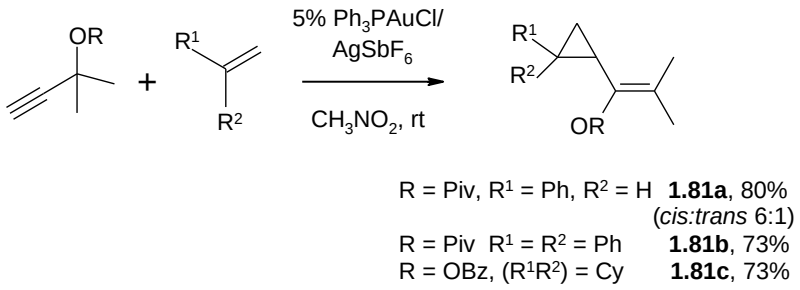

Toste and coworkers investigated gold(I) catalyzed Rautenstrauch rearrangement on propargyl pivolates flanked by an alkene. The method involved the cycloisomerization of propargyl ester **1.77** followed by cyclization and hydrolysis providing cyclopentenones **1.78a-c** (Scheme 1.24a).[38a] Subsequently, Zhang reported the efficient synthesis of cyclopentenones **1.80** from ethynyl acetates **1.79** (Scheme 1.24b).[38b] The reaction proceeds via tandem Au catalyzed [3,3]-rearrangement of propargylic ester and Nazarov cyclization. Wet dichloromethane as solvent led the reaction to cyclopentenones.

**Scheme 1.24**



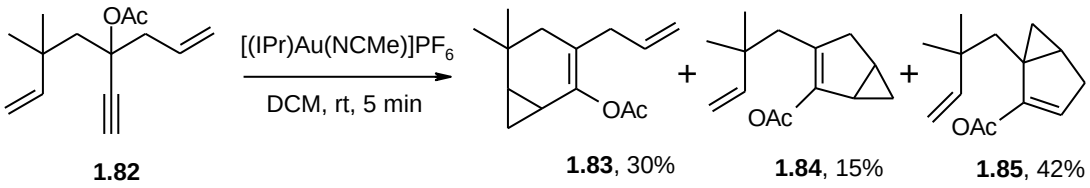

A stereoselective olefin cyclopropanation was reported by Toste *et al.* [39] Propargylic esters on treatment with unactivated olefins in the presence of $Ph_3PAuCl/AgSbF_6$ led to cyclopropane derivatives **1.81a-c** (Scheme 1.25) with high *cis*-selectivity.

**Scheme 1.25**




In the year 2006, Nolan and co-workers reported the unexpected formation of bicyclo[3.1.0]hexanes **1.84** and **1.85** along with bicyclo[4.1.0] derivatives **1.83** in the reaction of 1,5-enynes **1.82** bearing propargylic acetates in the presence of Au(I) (Scheme 1.26).[40]

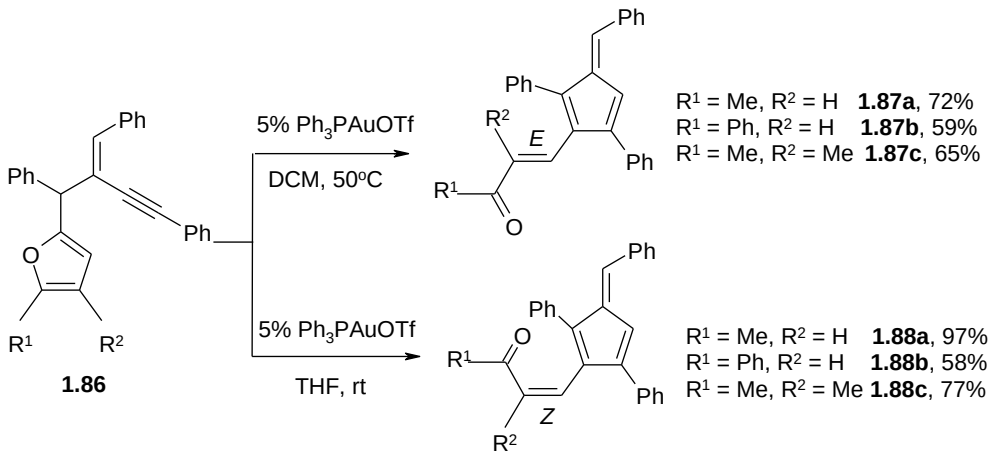
**Scheme 1.26**




**1.82** **1.83**, 30% **1.84**, 15% **1.85**, 42%

Recently, Liu *et al* reported the cycloisomerization of furan-ynes **1.86** to multi-substituted fulvenes (Scheme 1.27).[41] Friedel-Crafts reaction of 2-akynyl allyl alcohols with 2-methyl furan led to furan-yne which on subsequent treatment with Au(I) gave fulvenes via ring opening cyclization. Solvents played a role in directing the stereochemistry of the resultant molecule. In the presence of DCM at 50 $^{o}$C, *E* isomers **1.87a-c** was formed selectively whereas in the presence of THF at room temperature, *Z* isomers **1.88a-c** was formed.

**Scheme 1.27**

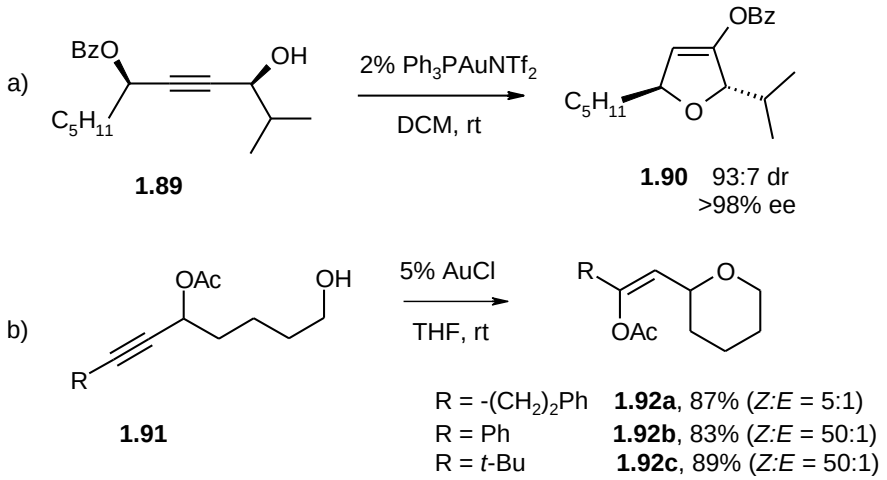



**1.86**

Gagosz *et al* reported the cycloisomerization of hydroxy propargylic ester **1.89** to dihydropyrans **1.90** (Scheme 1.28a).[42] This method involves 1,3-carboxyl migration to allene intermediate which on hydroxyl addition leads to dihydropyran derivatives. The mechanism accounts for the regio- and stereo-selectivities in this transformation. Later, Brabander and co-workers investigated on ω-hydroxy propargylic esters **1.91** in which 1,3-carboxyl migration followed by regioselective hydroxyl addition was

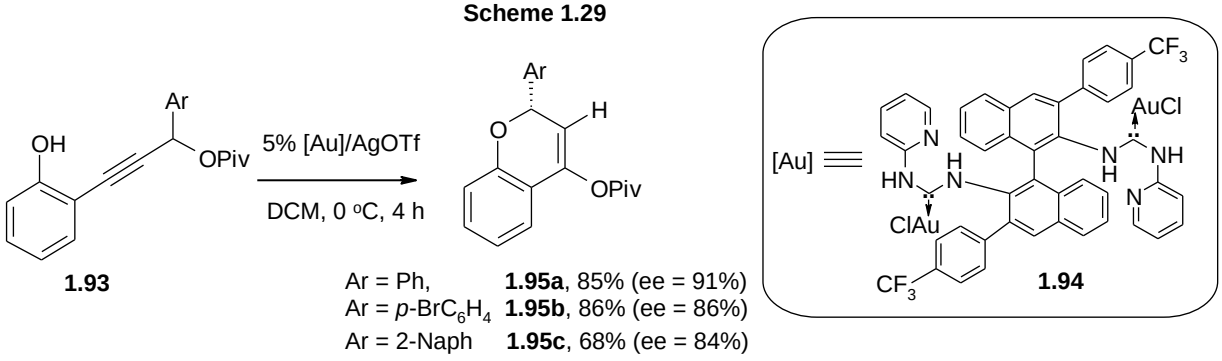
observed.[9d] This cyclo-etherification led to various pyran derivatives **1.92a-c** (Scheme 1.28b) with high *Z*-selectivity.

**Scheme 1.28**




Recently, Toste's group reported the cycloisomerization of propargyl ester **1.93**. The cyclization using chiral (acyclic domino carbene) gold(I) catalyst **1.94** involves dynamic kinetic asymmetric transformation (Scheme 1.29).[43] 3,3'-Substituted BINAM-derived acyclic diaminocarbene ligand was used to achieve the enantio-enriched transformation. Versatile benzopyran derivatives **1.95a-c** were obtained in good yields with high *ee*.

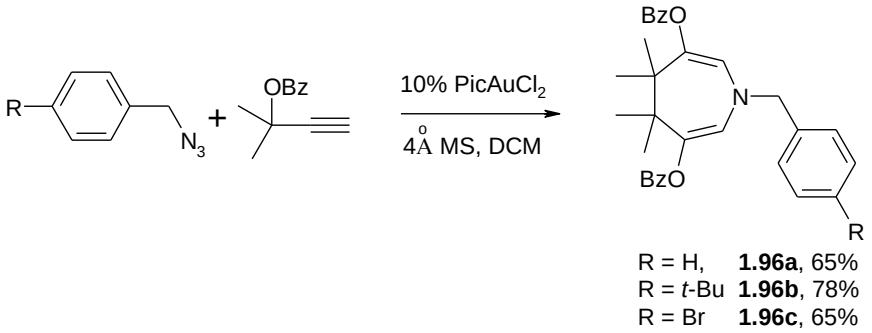
**Scheme 1.29**




Very recently, Hu *et al* developed an efficient new method to construct densely functionalized 4,5-dihydro-1*H*-azepine products **1.96a-c** (Scheme 1.30).[44] The method

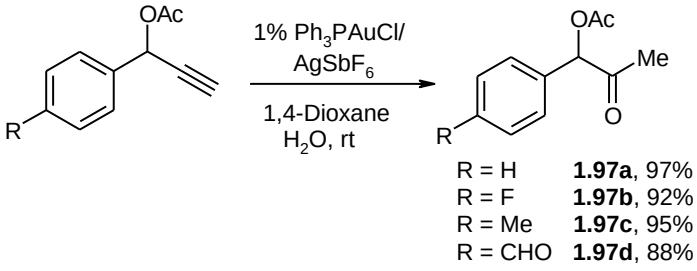
involved the intermolecular cyclization of alkyl azide with propargyl esters from which vinyl gold carbenoid was formed.

**Scheme 1.30**



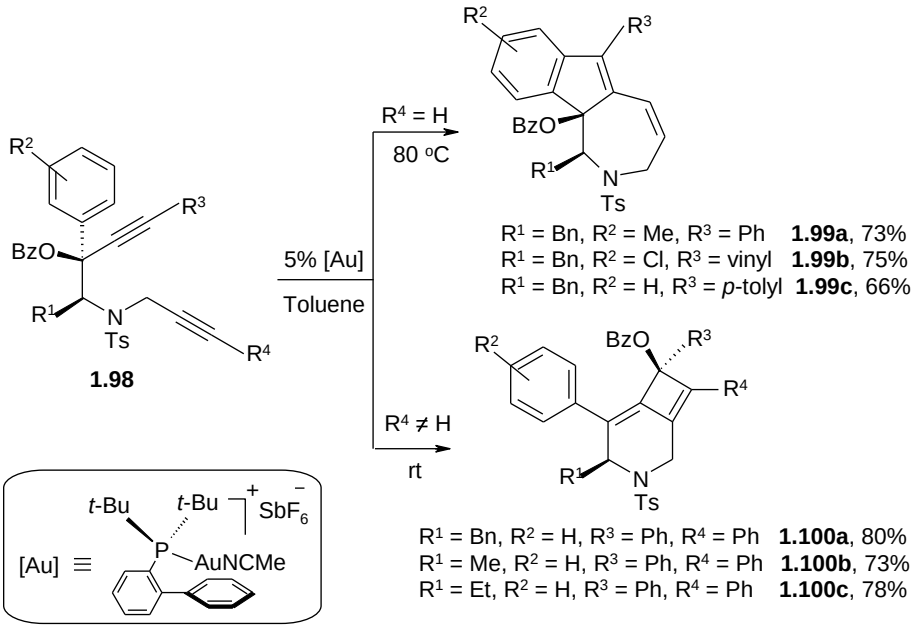

Very recently, Sahoo *et al* reported the efficient hydration of wide range of propargyl acetates to provide α-acyloxy methyl ketones **1.97a-b** (Scheme 1.31).[45] By the use of 1 mol% of $Ph_3PAuCl$/ $AgSbF_6$ in dioxane and water, the hydration takes place regioselectively and proceeds through neighboring carbonyl group interference. By using this protocol, synthesis of biologically active actinopolymorphol B was accomplished.

**Scheme 1.31**




Chan *et al* have reported the cycloisomerization of 1,7-diyne benzoates **1.98** to polycyclic compounds.[46] If the diyne is mono-substituted at the terminal carbon, indeno[1,2-c]azepines **1.99a-c** are formed. If the diyne is disubstituted, azabicyclo[4.2.0]octa-1(8),5-dienes **1.100a-c** are obtained (Scheme 1.32). Complete control of product selectivity is observed by exploiting the steric interactions between the alkyne moieties with the gold catalyst.

**Scheme 1.32**



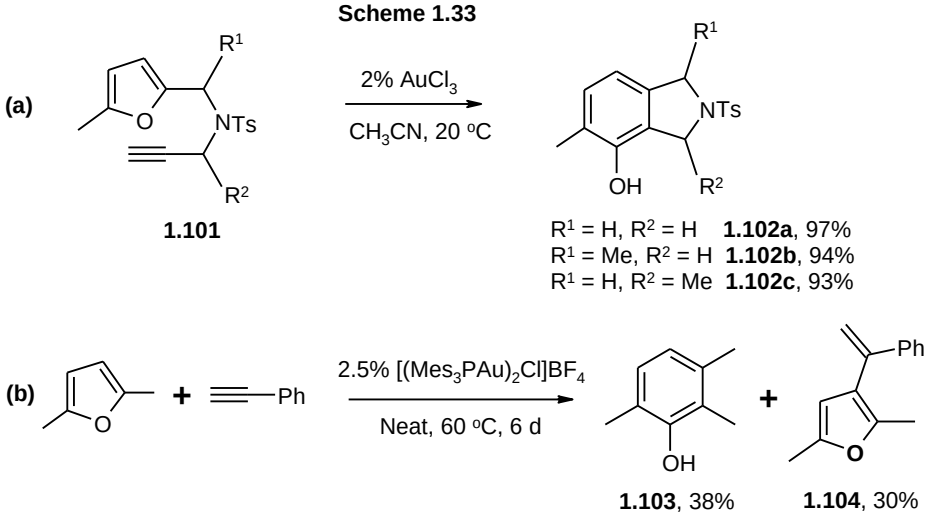

## 1.22 Gold catalyzed cycloadditions

Cycloaddition is a prominent synthetic tool for the construction of new C-C bonds as well as to introduce various functionalities in the resultant product.[47] Transition metal catalysis is one of the deserved platforms to achieve the efficient cycloadditions. Being highly carbophilic and having affinity for π-unsaturated systems, gold complexes play an important role in driving the cycloadditions.[46] Gold salts can induce compounds containing alkyne and carbonyl groups into zwitterionic intermediates which can be further directed to cycloadditions.[48b]

In the year 2000, Hashmi reported highly selective gold catalyzed phenol synthesis from furan-ynes.[9a, 49] The reaction involves the [4+2] cycloaddition of furan **1.101** and alkyne followed by rearrangement to give various substituted phenols **1.102a-c** (Scheme 1.33a). This reaction pattern later led to new synthetic findings in gold catalysis. The same group reported phenol synthesis with cationic binuclear gold(I) complex to get high selectivity for phenolic products. Later, in the year 2006, the same group reported the intermolecular furan and unactivated alkyne cycloaddition to obtain

phenols **1.103** along with hydroarylated alkynes **1.104**. Cationic binuclear gold(I) complex $[(Ph_3PAu)_2Cl]BF_4$ was employed for the synthesis (Scheme 1.33b).[50]

**Scheme 1.33**



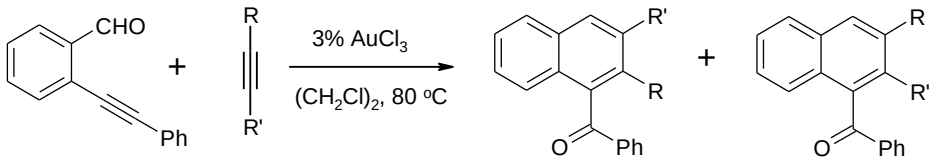

**1.101**

$R^1$ = H, $R^2$ = H **1.102a**, 97%
$R^1$ = Me, $R^2$ = H **1.102b**, 94%
$R^1$ = H, $R^2$ = Me **1.102c**, 93%

**1.103**, 38% **1.104**, 30%

Yamamoto *et al* have reported the [4+2] cycloaddition of *o*-alkynyl benzaldehydes with alkynes. Initially, **1.105** was transformed to zwitterionic intermediate which on reacting with alkyne led to a cycloadduct which further rearranged to naphthyl ketones **1.106a-c** and **1.107a-c** (Scheme 1.34).[9b, 51a] Later, the same group reported the benzannulation with enols by the aid of $AuBr_3$. Naphthyl derivatives were efficiently synthesized from good to excellent yields.[51b]

**Scheme 1.34**



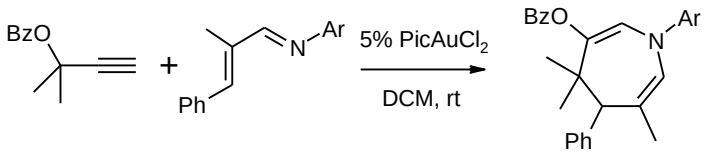

**1.105**

R = $C_3H_7$, R' = H **1.106a**:**1.107a** = 92:8 (91%)
R = Ph, R' = H **1.106b**:**1.107b** = 99:1 (96%)
R = $Me_3Si$, R' = H **1.106c**:**1.107c** = 16:84 (82%)

Toste reported[52] an elegant synthesis of biologically important azipine moieties from the [4+3] annulation of imines with propargyl benzoates. Thus $PicAuCl_2$ catalyzed

isomerization of propargyl benzoates followed by cycloaddition of α,β-unsaturated imines to furnish the azepine products **1.108a-c** (Scheme 1.35). The reaction proceeds by the initial formation of gold carbenoid intermediate and subsequent nucleophilic addition of imine followed by cyclization.

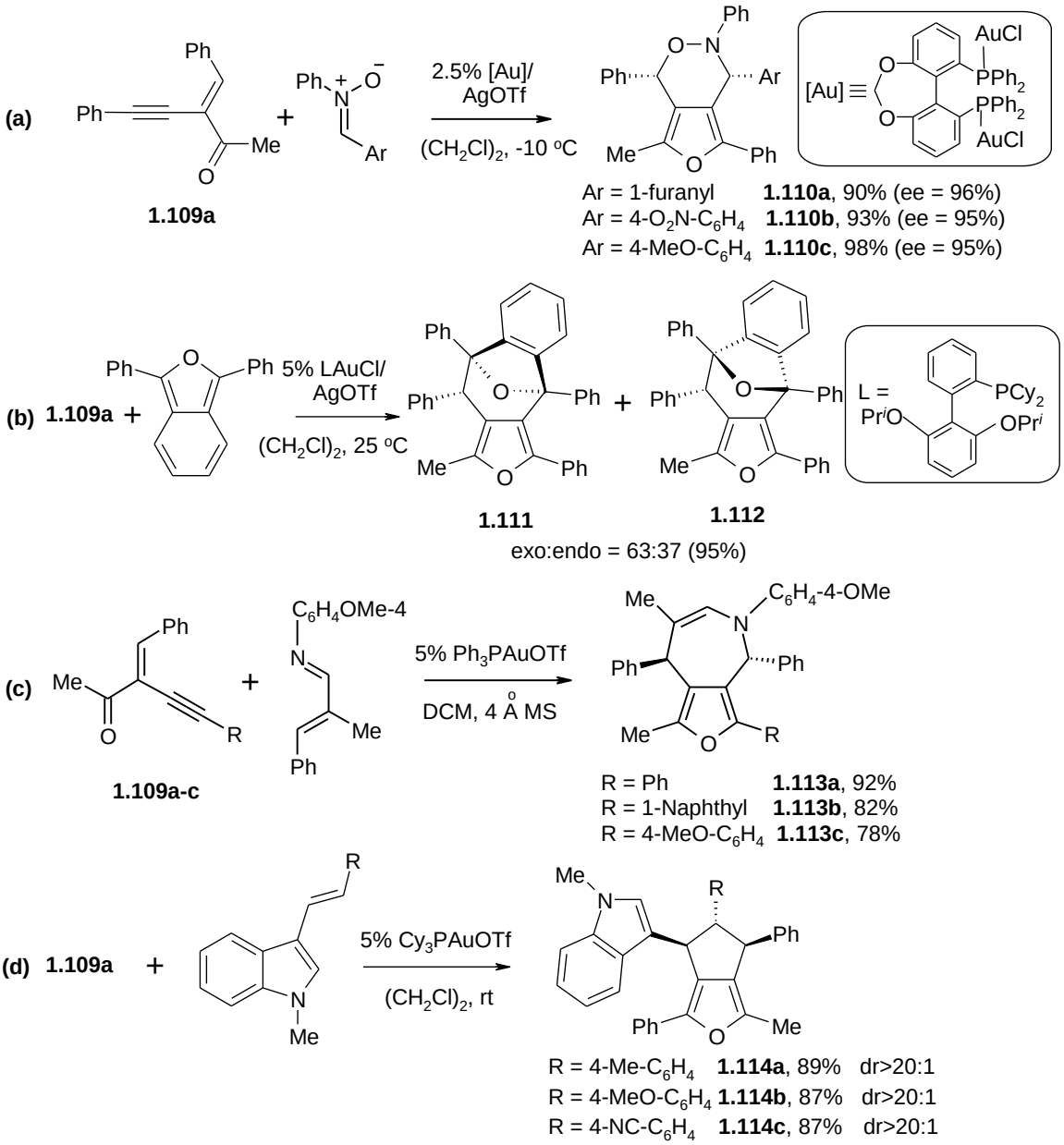
**Scheme 1.35**




Ar = 2,6-$Me_2C_6H_3$ **1.108a** (80%)
Ar = 2,3-$Me_2C_6H_3$ **1.108b** (88%)
Ar = 4-MeO-$C_6H_4$ **1.108c**(65%)

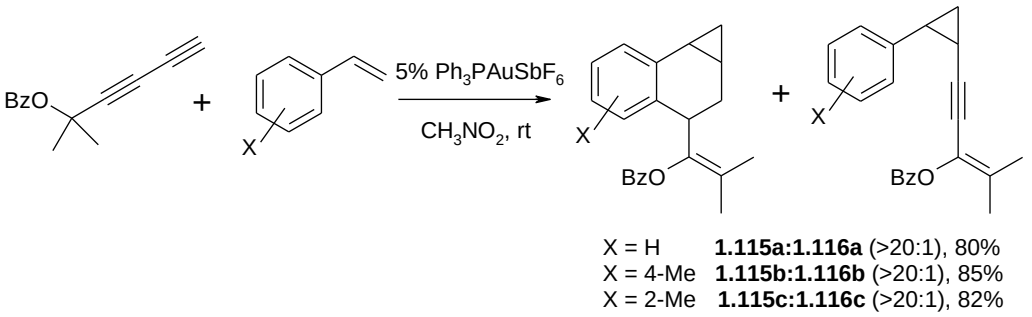
Zhang *et al* investigated extensively on the cycloaddition of zwitterionic form of 2-(1-alkynyl)-2-alken-1-ones with various unsaturated substrates. Nitrones with **1.108** in the presence of Au(I) led to [3+3] cycloaddition to form heterobicyclic furo[3,4-d]-[1,2]oxazines **1.110a-c** with excellent diastereoselectivity (Scheme 1.36a).[53a] The same group further demonstrated the reactivity of **1.109**a with 1,3-diphenylisobenzofuran. Highly fused polycyclic compounds **1.106** and **1.112** with diastereoselectivity were obtained under mild condition (Scheme 1.36b).[53b] The reactivity of α,β-unsaturated imines was also described.[53c] Thus Au(I) catalyzed tandem reaction provided highly substituted furo[3,4-*c*]azepines **1.113a-c** (Scheme 1.36c). Later, it was found that alkenes also successfully participated in this sort of tandem cyclization.[53d] Cyclopent[*c*]furans **1.114a-c** (Scheme 1.36d) were constructed efficiently by this method.

**Scheme 1.36**




In the year 2006, Toste and co-workers reported Au(I) catalyzed tandem cyclopropanation and hydroarylation of diynyl esters and vinyl arenes.[54] The reaction led to [4+3] annulation providing benzanorcaradienes **1.115a-c** along with cyclopropanated products **1.116a-c** with excellent regio- and diastereo-control (Scheme 1.37).

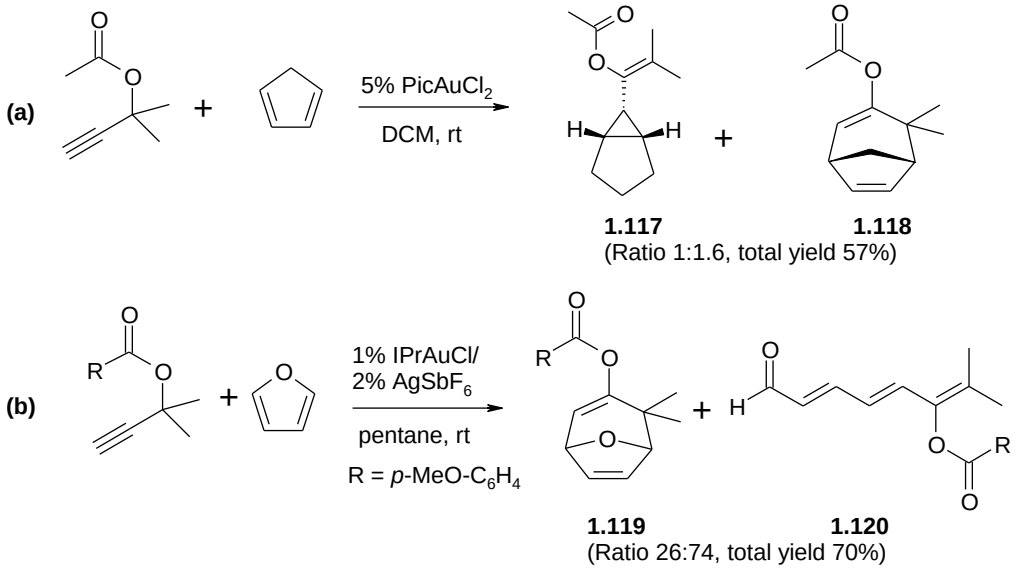
**Scheme 1.37**




X = H **1.115a:1.116a** (>20:1), 80%
X = 4-Me **1.115b:1.116b** (>20:1), 85%
X = 2-Me **1.115c:1.116c** (>20:1), 82%

Gung and co-worker reported the intermolecular cycloaddition of propargyl esters with cyclopentadienes as well as furans to obtain various cycloadducts **1.117-1.119** involving seven membered rings along with ring opened product **1.120** (Scheme 1.38).[57] The yields were moderate to good.

**Scheme 1.38**




**1.117** **1.118**
(Ratio 1:1.6, total yield 57%)

**1.119** **1.120**
(Ratio 26:74, total yield 70%)

Thus it is clear that gold catalysis has emerged as a highly productive area during the last decade, depriving this element of its 'noble metal' status. This feature has acted as an impetus for us to explore new reactions using gold catalysis.

# OBJECTIVES OF THE PRESENT WORK - PART A

The main objective of this part of the present work was to explore the new C-C and C-X bond forming reactions on substrates by starting with 2-iodo-allylic alcohols *via* gold catalysis as given below.

(i) To synthesize of new diverse alkynols (as substrates) including phosphono-alkynols and β–hydroxy propargylic esters starting from 2-iodo-allylic alcohols,

(ii) To investigate the reactivity of phosphono-alkynols and non-phosphorylated alkynols with gold and silver salts to synthesize highly substituted furans,

(iii) To probe on β–hydroxy propargylic esters with the aid of gold salts to synthesize versatile pyran derivatives, macrocycles and phosphono-oxacycles, and

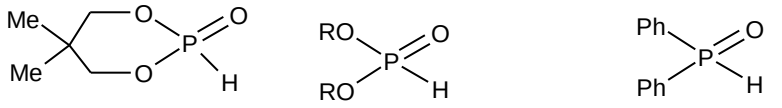
(iv) To study the reactivity of 1,3-diphenylisobenzofuran with propargylic esters in the presence of cationic gold(I) complex to obtain polycyclic naphthols or aromatic diene derivatives.

# RESULTS AND DISCUSSION

In this work, we needed a large number of new precursors containing the alkyne residue; in many cases synthetic procedures involved slight modification of the known synthetic routes. Thus for consistency and continuity, the synthetic methodology is briefly described in the following paragraphs before going into the gold-catalyzed reactions.

The H-phosphonates $(OCH_2CMe_2CH_2O)P(O)H$ (**1a**)[58a], $(RO)_2P(O)H$ [R = Et (**1b**), *i*-Pr (**1c**)][58b] and diphenylphosphine oxide $Ph_2P(O)H$ (**1d**)[58c], used in the present study are shown in Chart 1. All these compounds are prepared from appropriate $P^{III}$-Cl precursors by the addition of water and are distilled prior to use.[59] Added advantages of these compounds are that they are easily accessible and inexpensive.

**Chart 1**



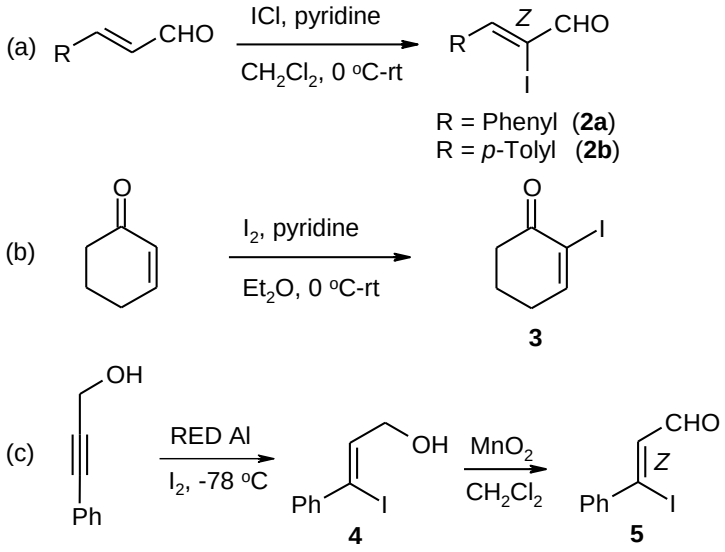

**1a** [δ(P): 3.2] R = Et [**1b**, δ(P): 7.3] = *i*-Pr [**1c**, δ(P): 4.6] **1d** [δ(P): 21.5]

## 2.1 Synthesis of iodo-aldehyde/ketone precursors (2a-b and 3), 3-iodo-allyl alcohol (4), 3-iodocinnamaldehye (5), 2-iodo-allyl alcohols (6-7) and propargylic precursors (8a-i, 9a-h and 10a-h)

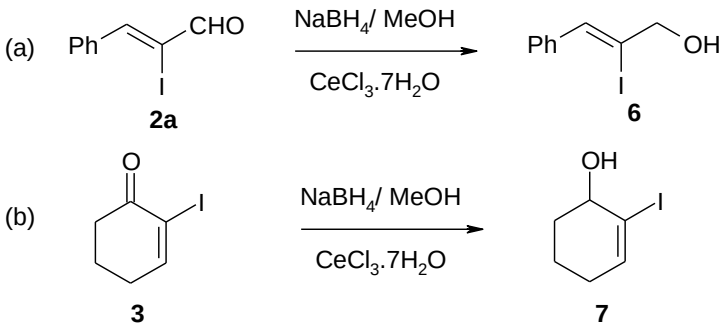
The starting material, *trans*-4-methyl-cinnamaldehyde, was prepared by an established method available in the literature.[60] 2-Iodo-cinnamaldehydes **2a-b** were prepared by using cinnamaldehydes and ICl/ pyridine whereas 2-iodo-cyclohexenone **3** was prepared by using cyclohexenone and $I_2$/pyridine by following reported methods (Scheme 1a-b).[61a-b] 3-Phenylprop-2-yn-1-ol was reduced with the aid of RED Al [sodium bis(2-methoxyethoxy)aluminium hydride] followed by iodination at -78 $^oC$ to obtain 3-iodo-3-phenylprop-2-en-1-ol **4**[62] which on oxidation with $MnO_2$ led to 3-iodo-

cinnamaldehyde **5** (Scheme 1c). 2-Iodo-allyl alcohols **6-7** were prepared by the reduction of corresponding carbonyl precursor with the aid of $NaBH_4$ and $CeCl_3.7H_2O$ (Scheme 2).[63] Various propargylic esters **8a-i** (benzoates/ acetates/ propanoate) were synthesized (Scheme 3) from the appropriate alcohols and acid chlorides by a known method.[64] Additionally, a variety of silyl substituted propargyl benzoates **9a-h** were synthesized (Scheme 4) by sequential Grignard reaction of trimethylsilyl acetylene with appropriate carbonyls and benzoylation.[64a, 65] Propargyl benzoates **10a-h** were obtained by the desilylation of **9a-h** respectively (Scheme 5).[66] Among these precursors, **8h, 9a-g** and **10c-g** are new and the rest are known.[44, 52, 64a]

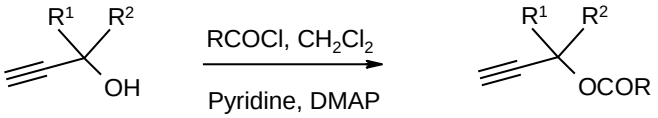
**Scheme 1**




**Scheme 2**

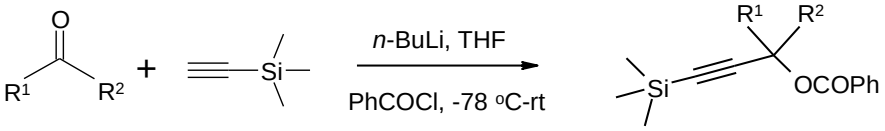


**Scheme 3**



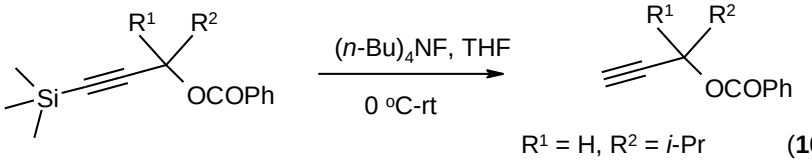

R = Ph, $R^1 = R^2 = H$ (**8a**)
R = Ph, $R^1 = R^2 = Me$ (**8b**)
R = Ph, $(R^1R^2) = (CH_2)_4$ (**8c**)
R = Ph, $(R^1R^2) = (CH_2)_5$ (**8d**)
R = Ph, $R^1 = Me$, $R^2 = Et$ (**8e**)
R = Me, $R^1 = R^2 = Me$ (**8f**)
R = Me, $(R^1R^2) = (CH_2)_5$ (**8g**)
R = Et, $R^1 = R^2 = Me$ (**8h**)
R = Ph, $R^1 = H$, $R^2 = Ph$ (**8i**)

**Scheme 4**




$R^1 = H$, $R^2 =$ *i*-Pr (**9a**)
$R^1 = Me$, $R^2 =$ *i*-Bu (**9b**)
$R^1 = Me$, $R^2 =$ *n*-propyl (**9c**)
$R^1 = Me$, $R^2 =$ *n*-pentyl (**9d**)
$R^1 = Me$, $R^2 =$ *n*-hexyl (**9e**)
$R^1 = R^2 = Et$ (**9f**)
$R^1 = R^2 =$ *n*-propyl (**9g**)
$R^1 = H$, $R^2 =$ *p*-Anisyl (**9h**)

**Scheme 5**




$R^1 = H$, $R^2 =$ *i*-Pr (**10a**)
$R^1 = Me$, $R^2 =$ *i*-Bu (**10b**)
$R^1 = Me$, $R^2 =$ *n*-propyl (**10c**)
$R^1 = Me$, $R^2 =$ *n*-pentyl (**10d**)
$R^1 = Me$, $R^2 =$ *n*-hexyl (**10e**)
$R^1 = R^2 = Et$ (**10f**)
$R^1 = R^2 =$ *n*-propyl (**10g**)
$R^1 = H$, $R^2 =$ *p*-Anisyl (**10h**)

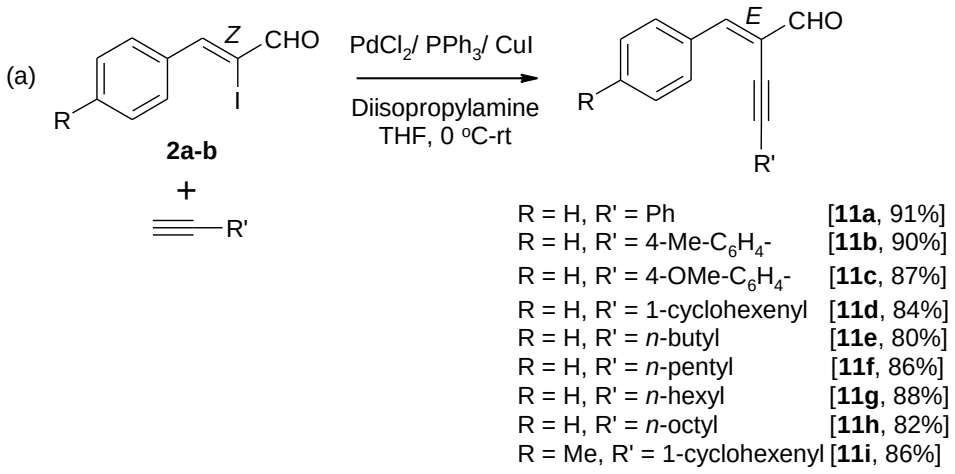
## 2.2 Synthesis of functionalized alkynals and alkynols

### *2.21 Synthesis of 2-alkynyl cinnamaldehydes (11a-i), 2-alkynyl cyclohexenone 12 and alkynal 13*

For the preparation of 2-alkynylcinnamaldehydes,[37, 41] a modified simpler route was employed in the present work. The literature method uses 2-bromo-cinnamaldehyde in the presence of $Pd(PPh_3)_4$ (air- and light-sensitive)/ CuI whereas in the present study, 2-iodo-cinnamaldehyde with catalytic $PdCl_2$/ $PPh_3$/ CuI was used. Precursors **11a-i** and **12** were prepared in good to excellent yields from 2-iodo-cinnmaldehydes **2a-b** and 2-iodo-cyclohexanone **3**, respectively, utilizing Sonogashira coupling conditions (Scheme 6a-b). Among these, **11e-i** are new. Owing to the presence of aldehyde functionality at the vicinity of alkynyl group, these precursors reveal the potential for the synthesis of a variety of derivatives including cyclized products. These are stable, can be stored at room temperature and handled without taking extra precautions. The geometry at the double bond is *E* for **11a-i**, as present in cinnamaldehyde. These compounds show a weak band at ~ 2250 $cm^{-1}$ in IR spectra due the presence of alkyne moiety. A singlet at ~ δ 9.6 in the $^1H$ NMR and a peak at ~ δ 192.0 in the $^{13}C$ NMR are observed due to the –CHO group. These compounds are further characterized by elemental analyses.

We also made an attempt to synthesize 3-alkynyl cinnamaldehyde by treating 3-iodo-cinnamaldehyde **5** with phenyl acetylene,[67] but sequential addition of another molecule of phenyl acetylene occurred to lead to the alkynyl *trans*-butadiene **13** (Scheme 6c). This was confirmed by $^1H$ NMR and HRMS. Since the –CHO functionality in **13** is away from the alkyne,[68] we presumed that cyclization using these two groups will be difficult and hence did not utilize this compound in this work.

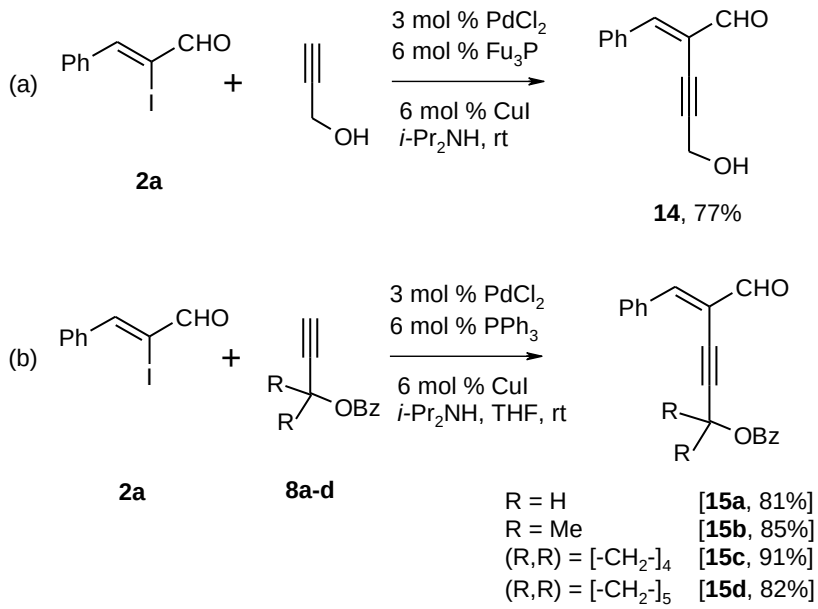
**Scheme 6**




### *2.22 Synthesis of α-formyl propargyl alcohol 14 and benzoates 15a-d*

In our efforts to extend the library of precursors, introducing additional functionality of –OH or –OC(O)R was also accomplished in this study using terminal propargyl alcohol/benzoates. Thus, α-formyl propargyl alcohol **14** and α-formyl propargyl benzoates **15a-d** were synthesized (Scheme 7) by Sonogashira coupling. In the synthesis of **14**, $Fu_3P$ was used in place of $PPh_3$ as phosphine component to obtain better yields.[37b] These precursors possess multiple active reaction centers.

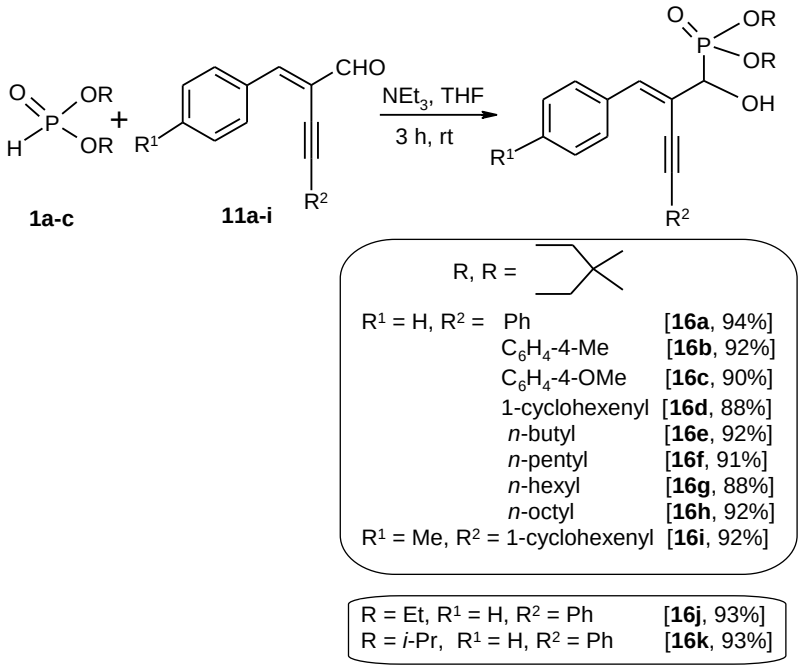
**Scheme 7**




### *2.23 Synthesis of phosphono-alkynols 16a-k*

The aldehyde function of 2-alkynylcinnamadehydes is reactive towards phosphite addition.[58c] This feature was utilized to obtain phosphono-alkynols (hydroxy-phosphonates) **16a-k** in excellent yields from phosphites **1a-c** and aldehydes **11a-i** *via* the Pudovik reaction (Scheme 8). All these compounds are new; they are solids and stable under open atmosphere. They are characterized by IR, NMR [$^{1}$H, $^{13}$C and $^{31}$P], and mass spectra/elemental analyses. The $^{31}$P NMR spectra show a peak at δ ~13.6 for compounds **16a-h** whereas for **16i** and **16k**, peaks at δ 21.0 and δ 19.3, respectively, are observed. A weak band in IR spectrum at ~2200 cm$^{-1}$ due to the alkyne moiety is discernible. For compound **16a**, a doublet at δ 4.93 [$^{2}J$(P-H) = 10.8 Hz, PC*H*) in the $^{1}$H-NMR and a doublet at δ 73.2 [$^{1}J$(P-C) = 157.8 Hz, P*C*] in the $^{13}$C-NMR due to the P*CH* group are observed. Other compounds show similar features.

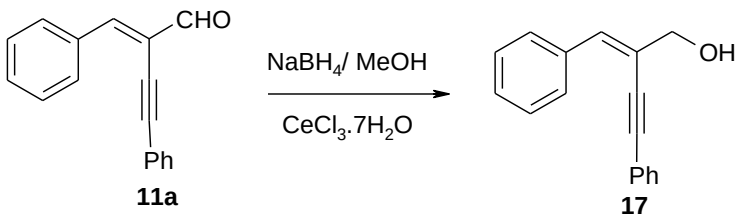
**Scheme 8**



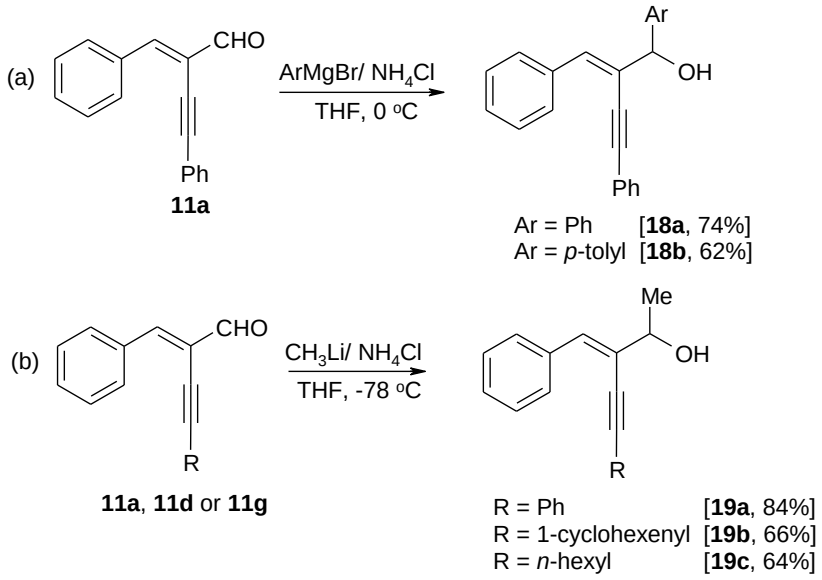

### *2.24 Synthesis of non-phosphorylated alkynols 17, 18a-b and 19a-c*

After the synthesis of a variety of phosphono-alkynols, analogous non-phosphorylated alkynols were thought to be useful for comparative studies. Thus, starting from **11a**, we synthesized alkynol **17** by using $NaBH_4$/ $CeCl_3.7H_2O$ condition (Scheme 9).[63] Alkynols **18a-b** were synthesized in good yields from **11a** by Grignard reaction with phenyl and *p*-tolyl magnesium bromide respectively (Scheme 10a).[69a-b] Alkynols **19a-c** were synthesized by methyllithium addition onto the aldehyde group of **11a, 11d** or **11g** followed by acid work-up (Scheme 10b).[69c] Among these alkynols, **18b** and **19a-c** are new. The disappearance of the –CHO group and formation of –OH was conveniently established by IR and NMR.

**Scheme 9**



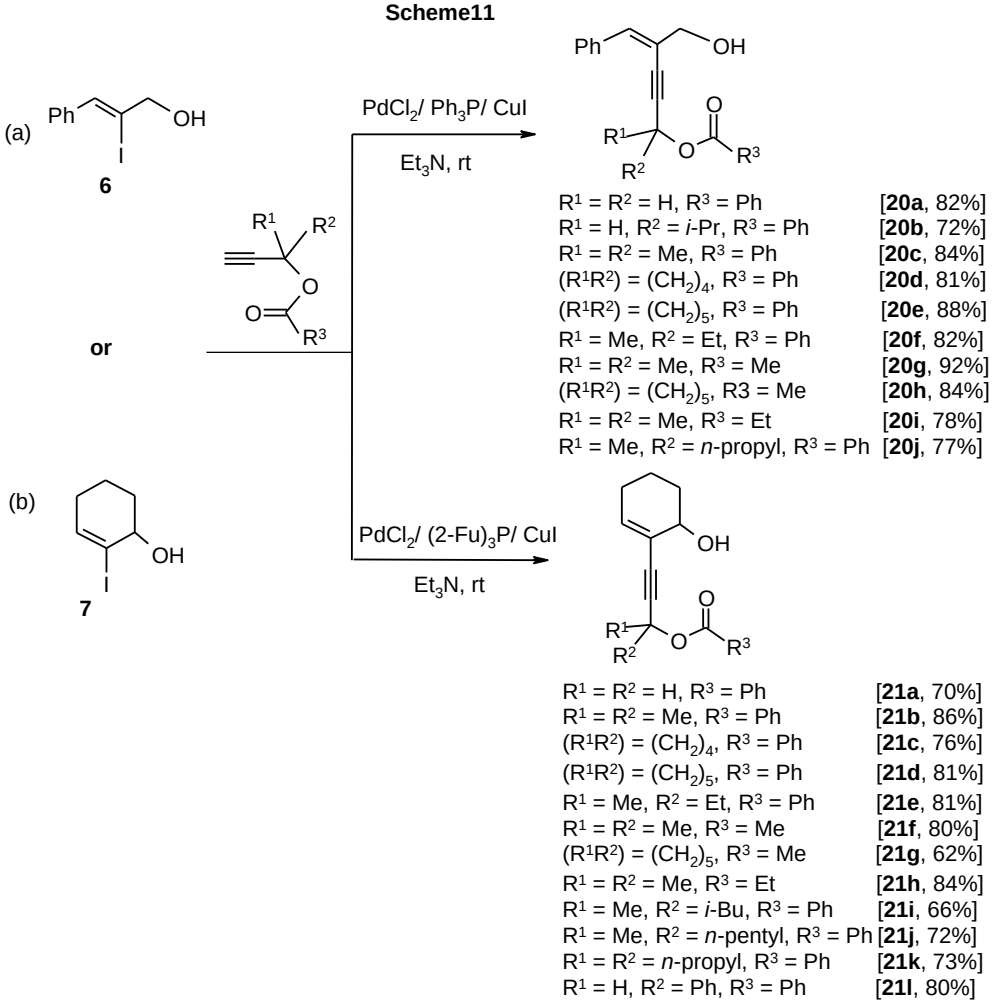
**Scheme 10**




### *2.25 Synthesis of β-hydroxy propargylic esters 20a-j, 21a-l and 22 and γ-hydroxy propargylic ester 23*

In continuation of our efforts to generate a library of alkynols, 2-iodo-cinnamyl alcohol **6** was treated with terminal propargylic esters under Sonogashira coupling condition to synthesize β-hydroxy-propargylic esters **20a-j**. A new route was employed to synthesize **21a-l** from 2-iodocyclohex-2-en-1-ol **7** by using $PdCl_2$/ $(2\text{-furyl})_3P$/ CuI as the catalytic system (Scheme 11). Compound **22** was synthesized from **15d** by methyllithium addition[69c] to the carbonyl group (Scheme 12). γ-Hydroxy propargylic ester **23** was synthesized by a modified route from iodo alcohol **4** and propargylic ester **8f** *via* Sonogashira coupling reaction (Scheme 13). Most of these compounds are gummy liquids and need to be stored in a refrigerator. These compounds show a weak IR band at ~2200 $cm^{-1}$ due to the C≡C bond. A singlet at δ ~4.30 and another singlet at δ ~6.70 due to C$H_2$OH and PhC*H*=C protons, respectively, are observed for compounds **20a-j** in the $^1$H NMR spectra. In the case of **21a-l**, a broad signal at δ~4.20 and another broad signal or a triplet at δ ~6.29 due to C*H*OH and $CH_2$C*H*=C, respectively, are observed in the $^1$H-NMR spectra. A peak at δ ~67.0 in $^{13}$C-NMR due to *C*$H_2$OH/ *C*HOH for the compounds **20a-j** and **21a-l** was also clearly seen. Compounds **22-23** also showed expected spectral features. These data are consistent with the assigned structures. Further confirmation comes from HRMS/CHN analyses.

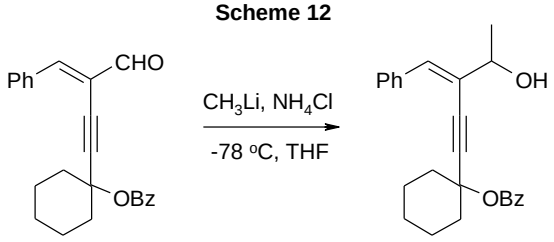
**Scheme11**




$R^1 = R^2 = H$, $R^3 = Ph$ [**20a**, 82%]
$R^1 = H$, $R^2 = i$-Pr, $R^3 = Ph$ [**20b**, 72%]
$R^1 = R^2 = Me$, $R^3 = Ph$ [**20c**, 84%]
$(R^1R^2) = (CH_2)_4$, $R^3 = Ph$ [**20d**, 81%]
$(R^1R^2) = (CH_2)_5$, $R^3 = Ph$ [**20e**, 88%]
$R^1 = Me$, $R^2 = Et$, $R^3 = Ph$ [**20f**, 82%]
$R^1 = R^2 = Me$, $R^3 = Me$ [**20g**, 92%]
$(R^1R^2) = (CH_2)_5$, R3 = Me [**20h**, 84%]
$R^1 = R^2 = Me$, $R^3 = Et$ [**20i**, 78%]
$R^1 = Me$, $R^2 = n$-propyl, $R^3 = Ph$ [**20j**, 77%]

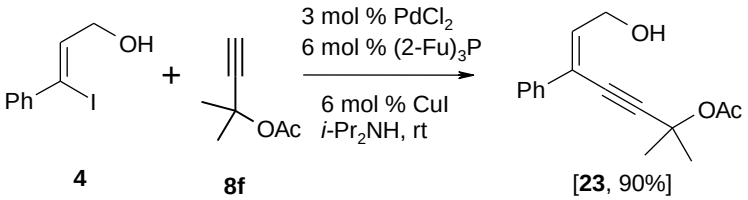
$R^1 = R^2 = H$, $R^3 = Ph$ [**21a**, 70%]
$R^1 = R^2 = Me$, $R^3 = Ph$ [**21b**, 86%]
$(R^1R^2) = (CH_2)_4$, $R^3 = Ph$ [**21c**, 76%]
$(R^1R^2) = (CH_2)_5$, $R^3 = Ph$ [**21d**, 81%]
$R^1 = Me$, $R^2 = Et$, $R^3 = Ph$ [**21e**, 81%]
$R^1 = R^2 = Me$, $R^3 = Me$ [**21f**, 80%]
$(R^1R^2) = (CH_2)_5$, $R^3 = Me$ [**21g**, 62%]
$R^1 = R^2 = Me$, $R^3 = Et$ [**21h**, 84%]
$R^1 = Me$, $R^2 = i$-Bu, $R^3 = Ph$ [**21i**, 66%]
$R^1 = Me$, $R^2 = n$-pentyl, $R^3 = Ph$ [**21j**, 72%]
$R^1 = R^2 = n$-propyl, $R^3 = Ph$ [**21k**, 73%]
$R^1 = H$, $R^2 = Ph$, $R^3 = Ph$ [**21l**, 80%]

**Scheme 12**




**15d** [**22**, 46%]

**Scheme 13**

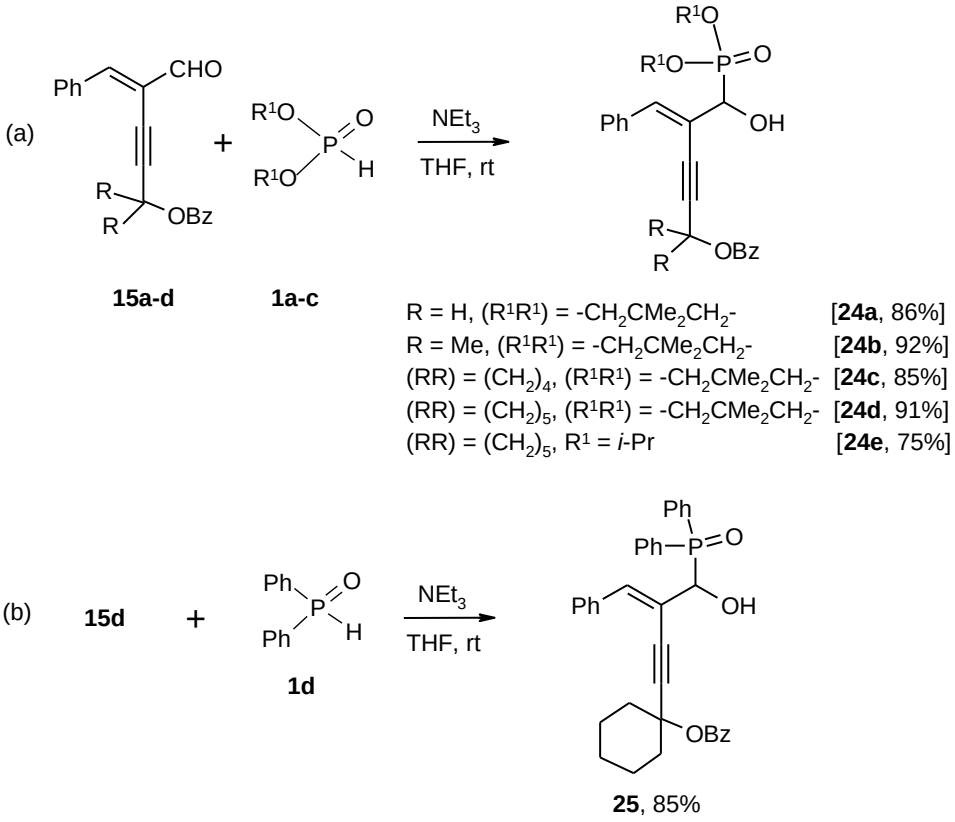



**4** **8f** [**23**, 90%]

### *2.26 Synthesis of phosphorus containing β-hydroxy propargylic esters 24a-e and 25*

In earlier studies from our laboratory, it was found that introducing a phosphorus based moiety in the allenic system had changed the reactivity pattern of the allene.[70] Hence we were interested in phosphorus based propargylic esters also. In this context, H-phosphonates **1a-c** were added[58c] to the aldehyde group of α-formyl propargyl benzoates **15a-d** to synthesize phosphorylated β-hydroxy propargyl benzoates **24a-e** (Scheme 14a). The phosphinoyl precursor **25** was synthesized by a similar addition of diphenylphosphine oxide **1d** to formyl propargyl benzoate **15d** (Scheme 14b). Compounds **24a-e** show NMR characteristic peaks similar to those for **16a-k**. All these compounds exhibit a characteristic doublet due to P-*CH* [$^{2}J$(PH) ~ 11.5 Hz; $^{1}J$(PC) ~ 158 Hz] moiety in the $^{1}$H and $^{13}$C NMR spectra, respectively. Compound **25** shows a singlet at δ 28.9 in the $^{31}$P NMR, a characteristic doublet at δ 5.19 (d, $^{2}J$(P-H) = 6.0 Hz, 1H, PC*H*) in the $^{1}$H NMR and a doublet at δ 74.7 (d, $^{1}J$(P-C) = 79.5 Hz) in the $^{13}$C NMR.

**Scheme 14**



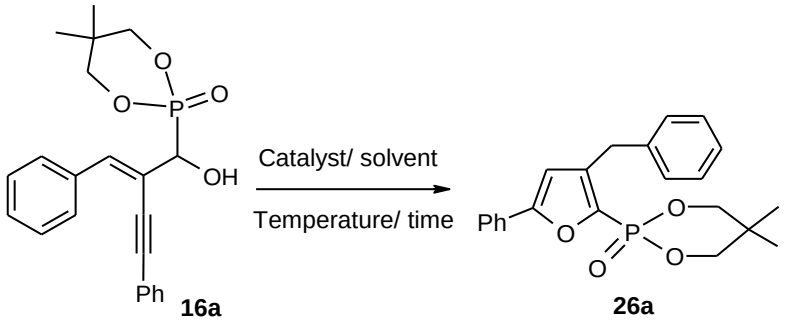
## 2.3 Gold (I) or Silver catalyzed cycloisomerization of alkynols

Many cyclizations of alkynyl compounds have been driven efficiently by silver salts[71] or gold complexes[37] due to their alkynophilicity. These reactions most often result in the formation of 5- or 6- membered rings. In the present work, various conditions have been employed for the cyclization of phosphono-alkynols **16a-k**. The results are discussed below.

### *2.31 Synthesis of phosphono-furans 26a-k*

To accomplish the cyclization, we started with phosphono-alkynol **16a**. Initially, we performed AgOTf catalyzed cyclization of **16a** in 1,2-dichloroethane and obtained 58% of the product **26a** (Scheme 15) when 5 mol % catalyst was used (Table 1, entry 1); increasing the amount of catalyst increased the yield of the *isolated product* to 88% (entry 2). The $^{31}$P NMR monitoring of the reaction mixture showed a single product with the entire phosphorus precursor being consumed. We were able to utilize this condition to isolate cyclized products **26a-k** in yields of 85-94%. Under the conditions employed, $Cu(OTf)_2$, $Zn(OTf)_2$ and $Sc(OTf)_3$ (entry 3) were ineffective. At the same time, we were allured by the prospect of using gold(I) complexes, since it is known that they can effect activation of C≡C bonds at low catalyst loading. Thus by using 3% $Ph_3PAuCl$/ AgOTf, the phosphono-furan **26a** was obtained in 81% isolated yield (Table 1, entry 4). Gratifyingly, use of 3% $Ph_3PAuCl$/ $AgSbF_6$ led to 90 % of the isolated product (Table 1, entry 5). At a lower loading of the catalyst (1%), the yield decreased to 62% (Table 1, entry 6); $AgSbF_6$ alone could not affect the cyclization (Table 1, entry 7). Different solvents like THF, toluene, acetonitrile and $CH_2Cl_2$ were examined in the presence of 3% $Ph_3PAuCl$/ $AgSbF_6$, but these gave a poor yield of the furan (entries 8-11); there was no reaction in nitromethane (entry 12). Thus our studies indicated that either 10% AgOTf or 3% $Ph_3PAuCl$/ $AgSbF_6$ was the most suitable catalytic system for this conversion.

**Scheme 15**




**16a** **26a**

**Table 1.** Effect of catalyst/ solvent in cycloisomerization of **16a** (cf. Scheme 15)

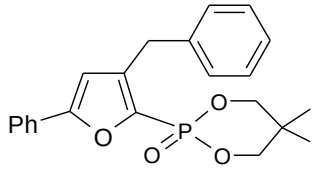
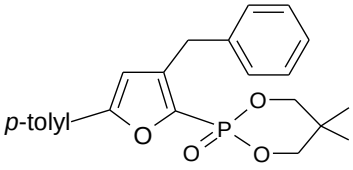
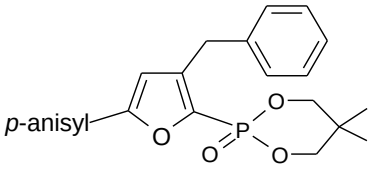
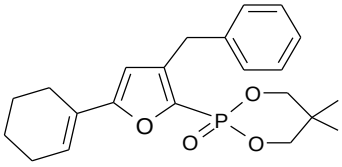
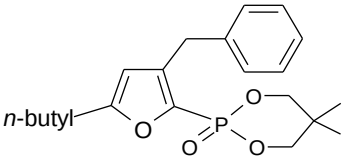
| Entry | Catalyst (mol %) | Temp. ($^{o}$C)[a]/ Time (h) | Solvent | Yield (%)[b] |
|---|---|---|---|---|
| 1 | 5% AgOTf | 70/ 12 | DCE | 58[c] |
| 2 | 10% AgOTf | 70/ 3 | DCE | 88[d] |
| 3 | 5% $Cu(OTf)_2$ or $Zn(OTf)_2$ or $Sc(OTf)_3$ | 70/ 12 | DCE | no reaction |
| 4 | 3% $Ph_3PAuCl$/ AgOTf | 70/ 3 | DCE | 81 |
| 5 | 3% $Ph_3PAuCl$/ $AgSbF_6$ | 70/ 3 | DCE | 90 |
| 6 | 1% $Ph_3PAuCl$/ $AgSbF_6$ | 70/ 12 | DCE | 62[c] |
| 7 | 5% $AgSbF_6$ | 70/ 12 | DCE | trace |
| 8 | 3% $Ph_3PAuCl$/ $AgSbF_6$ | 70/ 12 | THF | 20 |
| 9 | 3% $Ph_3PAuCl$/ $AgSbF_6$ | 70/ 12 | Toluene | 42 |
| 10 | 3% $Ph_3PAuCl$/ $AgSbF_6$ | 70/ 12 | $CH_3CN$ | 32 |
| 11 | 3% $Ph_3PAuCl$/ $AgSbF_6$ | rt/ 12 | DCM | 15 |
| 12 | 3% $Ph_3PAuCl$/ $AgSbF_6$ | 70/ 12 | Nitro-methane | no reaction |

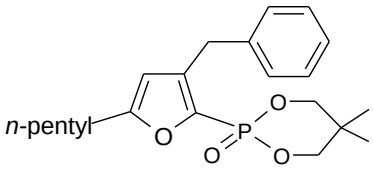
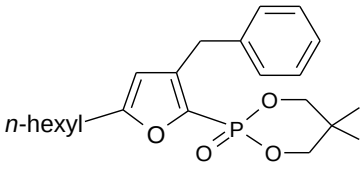
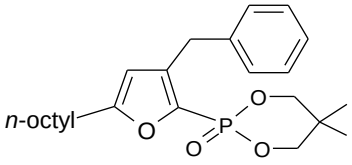
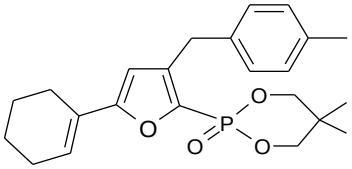
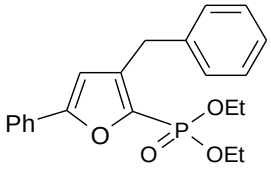
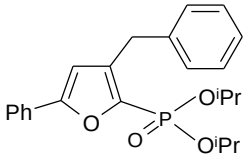
[a] Oil bath temperature. [b] Isolated yield. [c] Starting material remained. [d] This condition could also be used to obtain furans **26a-k** in excellent yields of 85-94%.

The efficacy of the above catalytic conditions, 3 mol % $Ph_3PAuCl/AgSbF_6$ in DCE at 70 $^{o}$C, was verified with various phosphono-alkynols **16a-k** which were

efficiently cycloisomerized to phosphono-furans **26a-k** in excellent yields as summarized in Table 2.

**Table 2.** Synthesis of phosphono-furans (cf. Scheme 15) [a]

| Entry | Phosphono-alkynol | Phosphono-furans | Yield (%)[b] |
|---|---|---|---|
| 1 | **16a** [δ(P): 13.5] |  **26a** [δ(P): -1.6] | 90 |
| 2 | **16b** [δ(P): 13.5] |  **26b** [δ(P): -1.3] | 90 |
| 3 | **16c** [δ(P): 13.5] |  **26c** [δ(P): -1.0] | 93 |
| 4 | **16d** [δ(P): 13.5] |  **26d** [δ(P): -1.2] | 86 |
| 5 | **16e** [δ(P): 13.7] |  **26e** [δ(P): -0.6] | 88 |

| | | | |
|---|---|---|---|
| 6 | **16f** [δ(P): 13.7] |  **26f** [δ(P): -0.6] | 92 |
| 7 | **16g** [δ(P): 13.5] |  **26g** [δ(P): -0.6] | 85 |
| 8 | **16h** [δ(P): 13.7] |  **26h** [δ(P): -0.5] | 91 |
| 9 | **16i** [δ(P): 13.4] |  **26i** [δ(P): -1.1] | 88 |
| 10 | **16j** [δ(P): 21.0] |  **26j** [δ(P): 5.2] | 92 |
| 11 | **16k** [δ(P): 19.3] |  **26k** [δ(P): 2.8] | 93 |

[a] Conditions: Phosphono-alkynol (0.4 mmol), $Ph_3PAuCl/AgSbF_6$ (3 mol %), DCE (2 mL), 70 $^oC$ (oil bath temperature), 3 h.

[b] Yield of the isolated product.

Compounds **26a-i** show a peak at δ ~-1.0 in the $^{31}$P-NMR; compound **26j** showed peak at δ 5.2 while **26k** exhibited a peak at δ 2.8. The marginal differences in the chemical shifts may be attributed to the different substituents present in these products. These values are at least 15 ppm upfield of the precursors and hence are characteristic. Also as an illustration, for compound **26b**, $^{1}$H NMR spectrum shows a doublet at δ 6.46 ($^{4}J$(P-H) = 2.8 Hz) due to the newly formed furyl-*H* (Figure 1). $^{13}$C NMR spectrum shows four doublets at δ 107.3 [$^{3}J$(P-C) = 11.6 Hz, PC=C-*C*], 137.7 [$^{1}J$(P-C) = 237.7 Hz, P*C*], 140.5 [$^{2}J$(P-C) = 26.3 Hz, PC=*C*], 158.5 [$^{3}J$(P-C) = 10.6 Hz, PCO*C*] (Figure 2) which clearly indicate the formation of the furan ring. X-ray structure was determined for **26a** (Figure 3). The C6-C7 and C8-C9 distances of 1.357(3) Å and 1.349(3) Å, respectively, conclusively establish the presence of double bonds between the respective carbon atoms and hence prove our assignment of the structures.

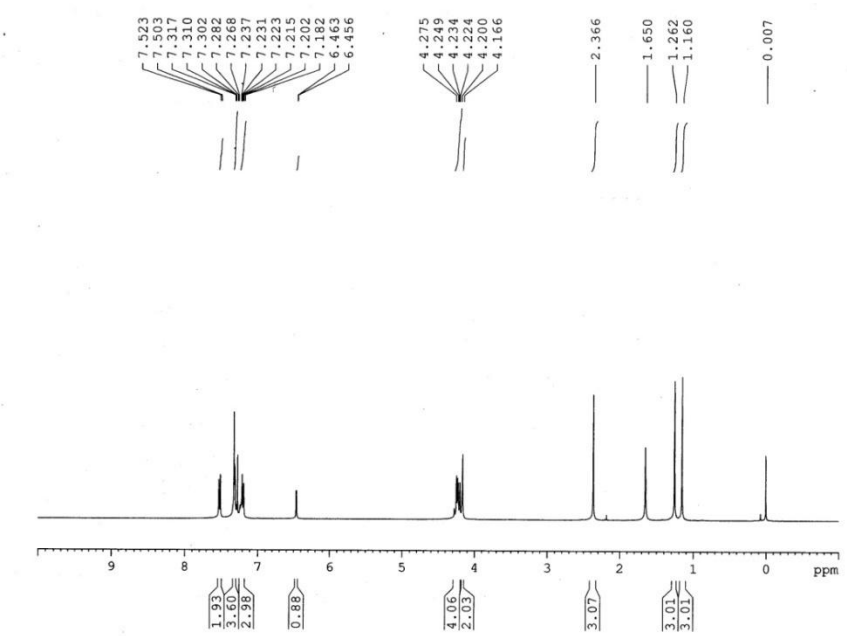



**Figure 1**. $^{1}$H NMR spectrum of phosphono-furan **26b**

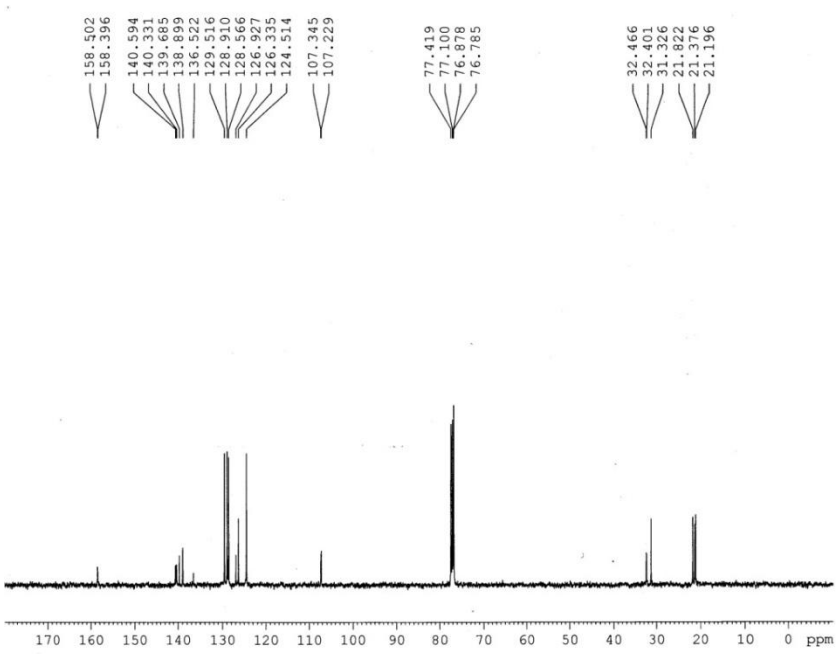



**Figure 2**. $^{13}$C NMR spectrum of phosphono-furan **26b**

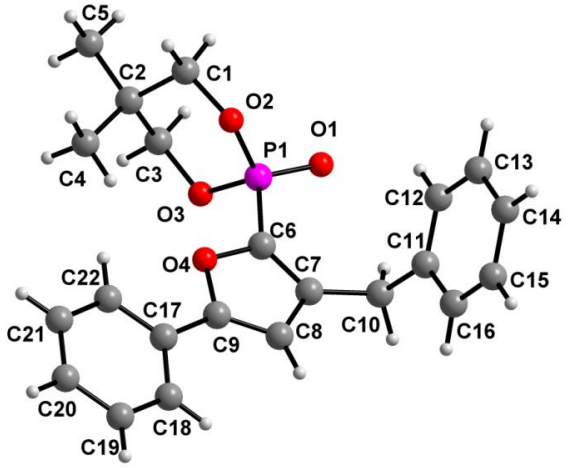
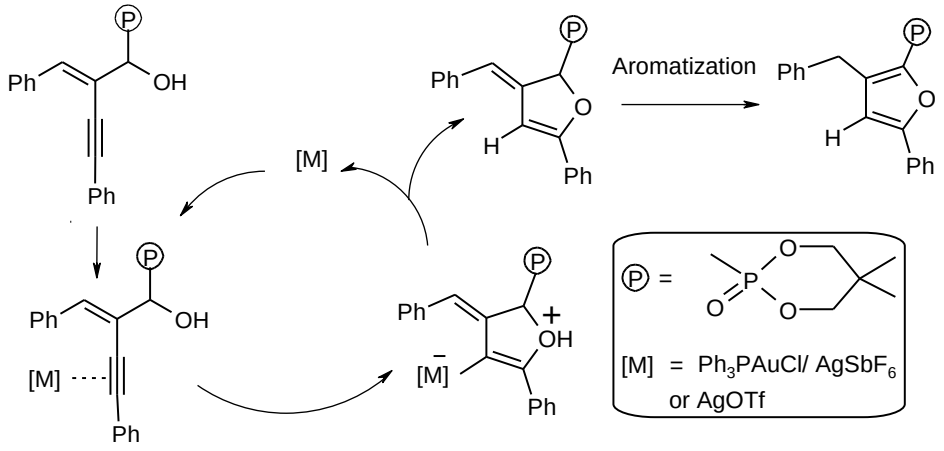



**Figure 3.** Molecular structure of phosphono-furan **26a**. Selected bond lengths [Å] with esd's in parentheses: O4-C9 1.358(3), C6-C7 1.357(3), C7-C10 1.497(3) and C8-C9 1.349(3).

A possible pathway for the formation of the phosphono-furans based on the available literature[37a] is presented in Scheme 16. Initially, the triple bond coordinates to the gold complex and the alcohol is added to form a five membered ring which on

protodeauration followed by aromatization leads to the furan. Since we found that AgOTf also works well, it is likely that silver(I) also coordinates in a manner analogous to gold(I) in these reactions.

**Scheme 16**




### *2.32 Synthesis of multi-substituted furans 27, 28a-b and 29a-c*

The role of gold(I) catalyst in the above cyclization was further explored by applying the catalyst in the cycloisomerization of 2-alkynylallyl alcohols also. Interestingly, alcohol **19a** upon treatment with even 1% $Ph_3PAuCl$/ $AgSbF_6$ in dichloromethane *at room temperature*, led to the multi-substituted furan **29a** (Scheme 17, Table 3) in 91% yield. By changing the catalyst to 1% $Ph_3PAuCl$/ AgOTf, the yield decreased to 72%. The catalyst $AuCl_3$ in DCE at 70 $^oC$ afforded the furan in only 10% yield. Other catalysts $Ph_3PAuCl$, AgOTf or $AgSbF_6$ were not individually effective in the cyclization process. Apart from the metal catalysts, bases also could be useful in alkynol cyclizations.[72] In our case, DBU in DMSO/ 70 $^oC$ did not afford any product, but *t*-BuOK (1 mol equivalent), DMSO/ 70 $^oC$ could effect the cyclization leading to the trisubstituted furan **29a**. However, the base is used in *stoichiometric* and *not catalytic* quantities. The optimization of the conditions leading to **29a** against catalyst as well as base promoted cyclization is shown in Table 3.

**Scheme 17**

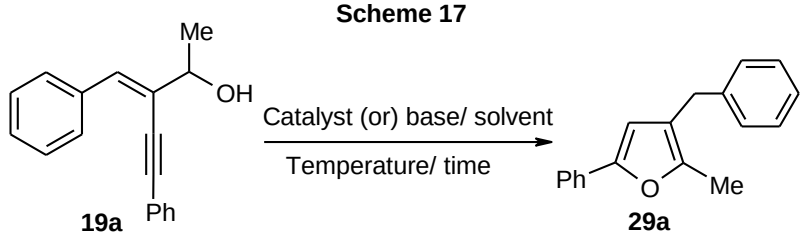


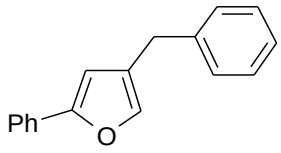
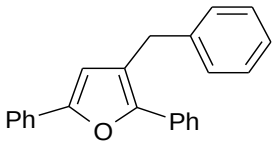
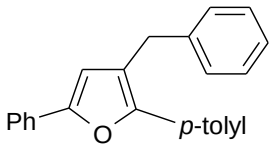
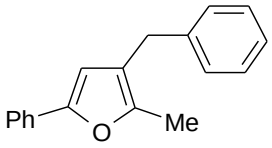
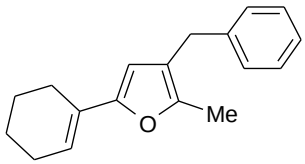
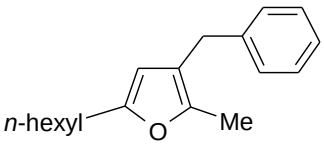

**Table 3.** Effect of catalyst or base/ solvent in cycloisomerization of **19a** (cf. Scheme 17)

| Entry | Catalyst (mol %) | Temp ($^{o}$C)/ Time (h) | Solvent | Yield[a] (%) |
|---|---|---|---|---|
| 1 | 1% $Ph_3PAuCl$/ $AgSbF_6$ | rt/ 1 | DCM | 91 |
| 2 | 1% $Ph_3PAuCl$/ AgOTf | rt/ 1 | DCM | 72 |
| 3 | 1% $AuCl_3$ | 70/ 12 | DCE | 10 |
| 4 | 1% $Ph_3PAuCl$ | 70/ 12 | DCE | Complex mixture |
| 5 | 5% AgOTf | 70/ 12 | DCE | Complex mixture |
| 6 | 5% $AgSbF_6$ | 70/ 12 | DCE | Complex mixture |
| 7 | DBU[b] | 70/ 12 | DMSO | no reaction |
| 8 | *t*-BuOK[b] | 70/ 3 | DMSO | 85 |

[a] Isolated yield. [b] 1 equivalent of base was used

By employing the above catalytic conditions [1% $Ph_3PAuCl$/ $AgSbF_6$ in dichloromethane], alkynols **17**, **18a-b** and **19a-c** were successfully cycloisomerized to furans **27, 28a-b** and **29a-c**. These products along with the corresponding yields are shown in Table 4.

**Table 4.** Gold(I) catalyzed synthesis of various furans (cf. Scheme 17)[a]

| Entry | Alkynol | Furan | Yield (%)[b] |
|---|---|---|---|
| 1 | **17** |  **27** | 90 |
| 2 | **18a** |  **28a** | 88 |
| 3 | **18b** |  **28b** | 84 |
| 4 | **19a** |  **29a** | 91 |
| 5 | **19b** |  **29b** | 52 |
| 6 | **19c** |  **29c** | 92 |

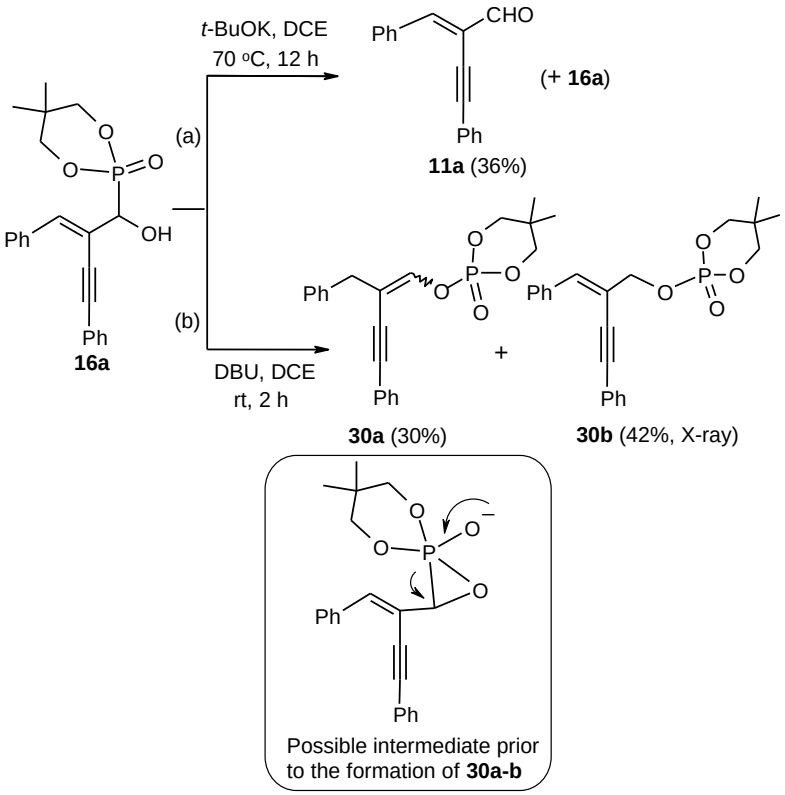
[a] Conditions: Alkynol (0.4 mmol), $Ph_3PAuCl/AgSbF_6$ (1 mol %), DCM (2 mL), rt, 1 h. [b] Yield of the isolated product.

## 2.4 Base induced conversion of phosphono-alkynols to phosphate esters

In continuation of the above work, interestingly, 1 equivalent of *t*-BuOK converted the alcohol **16a** back to aldehyde **11a** (tlc, NMR) while DBU (1 equiv) converted the alcohol to its isomers **30a** and **30b** (Scheme 18). The $^{31}P$ NMR chemical shift value clearly distinguishes the two compounds **16a** [δ(P) 13.5] and **30b** [δ(P) -7.9]. X-ray structure was determined for compound **30b** (Figure 4). The C6-C7 distance is

clearly in the single bond region, as expected. Such a rearrangement from phosphonate to phosphate has been observed earlier in our laboratory (Scheme 19);[73] this reaction could have occurred by deprotonation of **16a** leading to a pentacoordinate phosphorus species (cf. Scheme 18).

**Scheme 18**



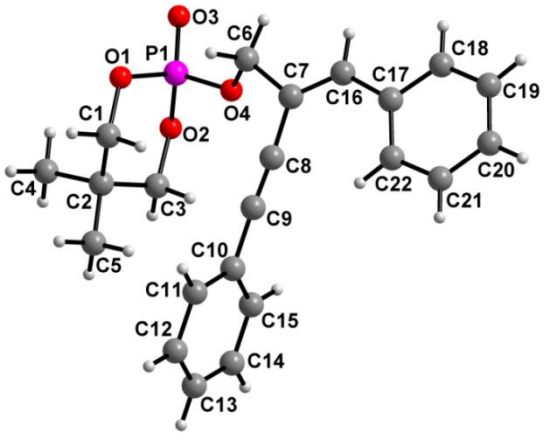
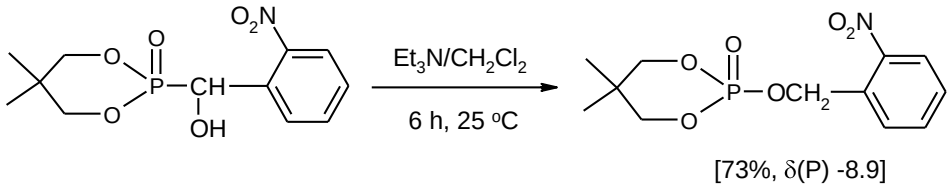




**Figure 4.** Molecular structure of phosphate ester **30b**. Selected bond lengths [Å] with esd's in parentheses: P1-O4 1.561(4), O4-C6 1.456(7) and C6-C7 1.504(8).

**Scheme 19**

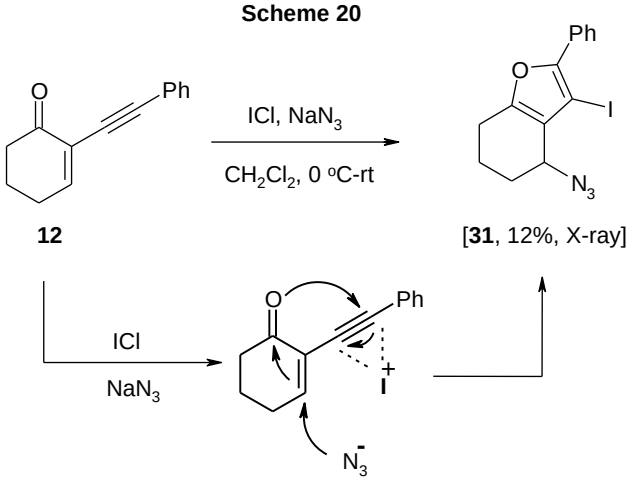



[73%, δ(P) -8.9]

## 2.5 ICl induced cyclization of 2-alkynyl cyclohexenone to furan 31

Similar to gold salts, electrophiles can coordinate to the alkyne moiety and hence analogous cyclizations can be driven by iodine reagents which can be trapped further by a nucleophile to complete cylization.[74] However, although electrophilic iodine induced cyclization of 2-alkynyl cyclohexanone to iodo-furans is reported,[35b] azide ion triggered iodine induced cyclization is not. In our case, we treated 2-alkynyl cyclohexanone **12** with iodine monochloride and sodium azide to lead to iodo-furan **31** in 12 % yield (Scheme 20). The structure of **31** was confirmed by X-ray crystallography (Figure 5). The reaction is expected to proceed through the initial coordination of iodide ion with the alkyne group which is cyclized by vicinal oxygen. The cyclization is complete by the conjugate addition of azide ion to lead to **31**. We tried several conditions which utilized (i) use of phase transfer catalyst [18-crown-6, ($n$-Bu)$_4$NBr], (ii) [py$_2$I][BF$_4$] in place of ICl and (iii) I$_2$ in place of ICl, but were not successful in enhancing the yield of the product **31**. Hence, further work was not carried out.

**Scheme 20**



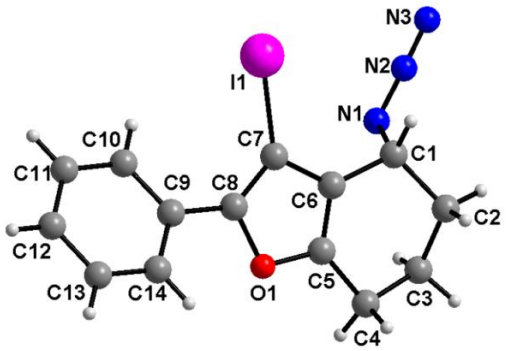



**Figure 5.** Molecular structure of compound **31**. Selected bond lengths [Å] with esd's in parentheses: N1-C1 1.494(6), C1-C6 1.488(6), C5-C6 1.334(5), O1-C5 1.363(5), O1-C8 1.382(4), C7-C8 1.351(5) and I1-C7 2.061(4).

## 2.6 Gold (I) catalyzed cyclization of hydroxy propargylic esters

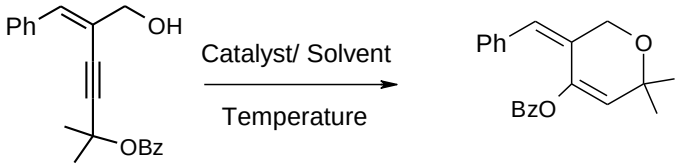
Propargylic esters undergo carboxyl migration in the presence of gold complexes and show diverse reactivity patterns.[25-29, 44-45, 54, 75-76] The rearranged propargylic esters can be attacked by nucleophiles to form new C-C and C-X bonds and many of them involve in 5- or 6-membered heterocycles.[5b, 8c, 12c, 76] Inspired by the above result in getting 5-membered rings from 2-alkynylallyl alcohols, we formulated a feasible 6-membered ring out of this kind of precursors. In this context, we examined the reactivity of β-hydroxy propargylic esters with gold salts and we successfully accomplished the synthesis of pyran derivatives. The results are discussed below.

### *2.61 Synthesis of pyran and dihydropyran derivatives 32a-g, 33a-l and 34*

Towards the cyclization of β-hydroxy propargylic esters, our initial trials were performed on **20c** by treating it with 2 mol % $Ph_3PAuCl/AgOTf$ in dichloromethane (Scheme 21, Table 5). To our delight, the reaction led to pyran **32c** in 82% yield (entry 1). Use of $AgBF_4$ (entry 2) in place of AgOTf reduced the time for completion of reaction from 6 h to 4 h and increased the yield to 84%. By employing $AgSbF_6$ as additive, the reaction time was reduced to 1 h and concomitantly the yield was still higher (90%; entry 3). In the absence of silver additives no product formation was observed even after 12 h; AuCl or $AuCl_3$ as the gold component afforded lower yields after 12 h with some starting material (~25%) remaining (entries 5-6). In the absence of

gold catalyst, $AgSbF_6$ or $AgBF_4$ (5 mol %) gave the product in 78% or 68% yield (entries 7-8), respectively in 6 h whereas AgOTf did not work well (entry 9). Other catalytic systems were also less effective. Solvents like dioxane, THF, toluene and $CH_3CN$ along with 2% $Ph_3PAuCl/AgSbF_6$ led to poor yields (entries 13-16). Thus 2% $Ph_3PAuCl/AgSbF_6$ catalytic system in $CH_2Cl_2$ as the solvent was the best condition (entry 3). Details on optimization of the conditions for the formation of product **32c** under various screening conditions are presented in Table 5.

**Scheme 21**




**20c** **32c**

**Table 5**. **Effect of catalyst/ solvent in the cycloisomerization of 20c to lead to 32c**

| Entry | Catalyst (mol %) | Solvent | Time (h) | Yield (%)[a] |
|---|---|---|---|---|
| 1 | 2% $Ph_3PAuCl$/ AgOTf | $CH_2Cl_2$ | 6 | 82 |
| 2 | 2% $Ph_3PAuCl$/ $AgBF_4$ | $CH_2Cl_2$ | 4 | 84 |
| 3 | 2% $Ph_3PAuCl$/ $AgSbF_6$ | $CH_2Cl_2$ | 1 | 90 |
| 4 | 2% $Ph_3PAuCl$ | $CH_2Cl_2$ | 12 | No reaction[b] |
| 5 | 2% AuCl | $CH_2Cl_2$ | 12 | Trace[b] |
| 6 | 2% $AuCl_3$ | $CH_2Cl_2$ | 12 | 52[b] |
| 7 | 5% $AgSbF_6$ | $CH_2Cl_2$ | 6 | 78 |
| 8 | 5% $AgBF_4$ | $CH_2Cl_2$ | 6 | 68 |
| 9 | 5% AgOTf | $CH_2Cl_2$ | 12 | 18[b] |
| 10 | 2 % $AuCl_3$/ $AgSbF_6$ | $CH_2Cl_2$ | 1 | Complex mixture |
| 11 | 2% AuCl/ $AgSbF_6$ | $CH_2Cl_2$ | 12 | 42[b] |
| 12 | 1% $Ph_3PAuCl$/ $AgSbF_6$ | $CH_2Cl_2$ | 5 | 76 |
| 13 | 2% $Ph_3PAuCl$/ $AgSbF_6$ | Dioxane | 12 | 10[b] |
| 14 | 2% $Ph_3PAuCl$/ $AgSbF_6$ | THF | 12 | Trace[b] |

| | | | | |
|---|---|---|---|---|
| 15 | 2% $Ph_3PAuCl$/ $AgSbF_6$ | Toluene | 12 | 20[b] |
| 16 | 2% $Ph_3PAuCl$/ $AgSbF_6$ | $CH_3CN$ | 12 | Trace[b] |

[a] Isolated yield

[b] Starting material remained.

The generality of the above reaction was checked against different substitutions on β-hydroxy propargylic esters. The precursors **20a-g**, **21a-l** and **22** (Table 6, Scheme 22) were successfully cycloisomerized to six membered oxacycles **32a-g**, **33a-l** and **34** respectively. Among these products, **32a-b** and **33a** are 2(*H*)-pyran derivatives which are formed from unsubstituted/ mono substituted propargylic benzoates **20a-b** and **21a** respectively. The rest of the products are dihydropyran derivatives. The structure of dihydropyran **33d** was confirmed by X-ray crystallography (Figure 6). The newly formed dihydropyran ring comprises the atoms C1, C6, C7, C8, C9 and O1. The double bond in this ring is between C7 and C8.

**Scheme 22**

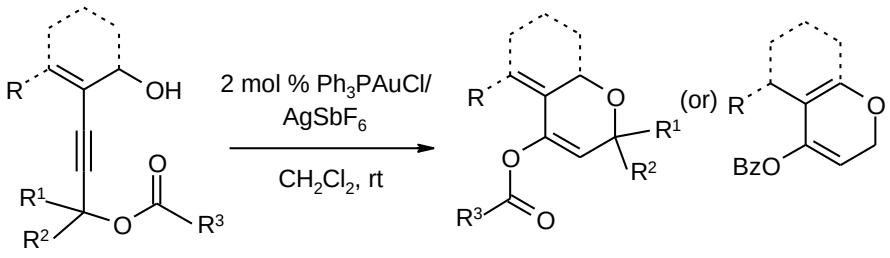
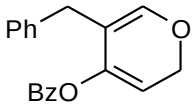
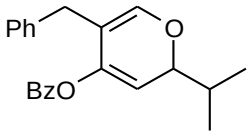
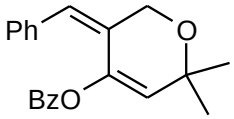
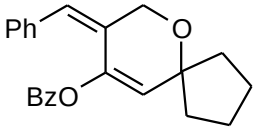
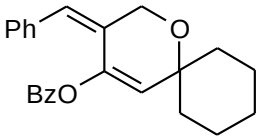
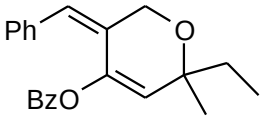
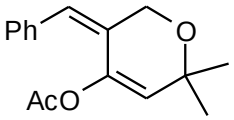
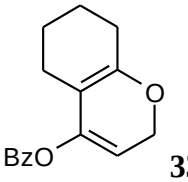
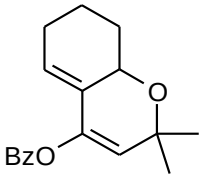
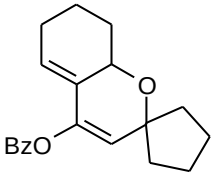
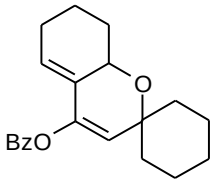
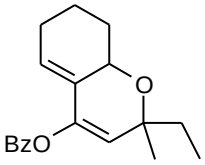
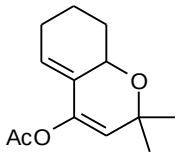
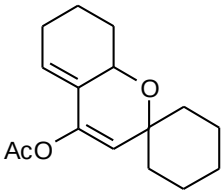
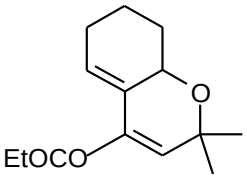
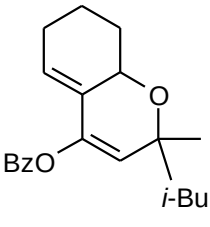
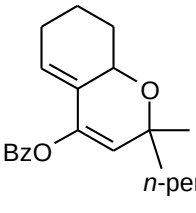
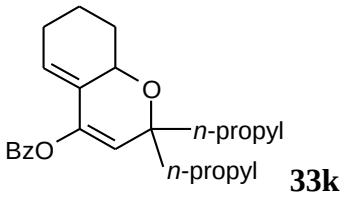
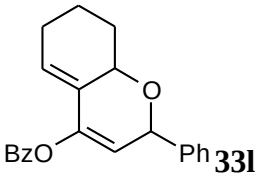
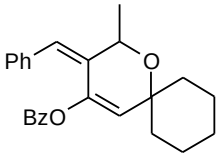



**Table 6**. Details on cycloisomerization of β-hydroxy propargylic esters to pyran derivatives **32a-g**, **33a-l** and **34**

| Entry | β-hydroxy propargylic esters | Pyran/ dihydropyran derivatives | Yield[a] (%) |
|---|---|---|---|
| 1 | **20a** |  **32a** | 64 |

| | | | |
|---|---|---|---|
| 2 | **20b** |  **32b** | 45 |
| 3 | **20c** |  **32c** | 90 |
| 4 | **20d** |  **32d** | 86 |
| 5 | **20e** |  **32e** | 82 |
| 6 | **20f** |  **32f** | 64 |
| 7 | **20g** |  **32g** | 74 |
| 8 | **21a** |  **33a** | 75 |
| 9 | **21b** |  **33b** | 72 |
| 10 | **21c** |  **33c** | 78 |

| | | | |
|---|---|---|---|
| 11 | **21d** |  **33d** (X-ray) | 65 |
| 12[b] | **21e** |  **33e** | 80 |
| 13 | **21f** |  **33f** | 75 |
| 14 | **21g** |  **33g** | 78 |
| 15 | **21h** |  **33h** | 73 |
| 16[b] | **21i** |  **33i** | 78 |
| 17[b] | **21j** |  **33j** | 82 |

| | | | |
|---|---|---|---|
| 18 | **21k** |  **33k** | 81 |
| 19 | **21l** |  **33l** | 40 |
| 20 | **22** |  **34** | 86 |

[a] Isolated yield;[b] Mixture of diastereomers.

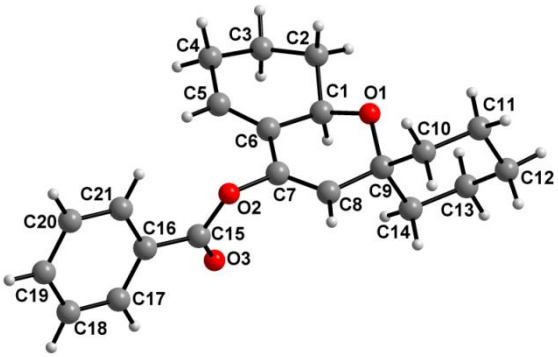


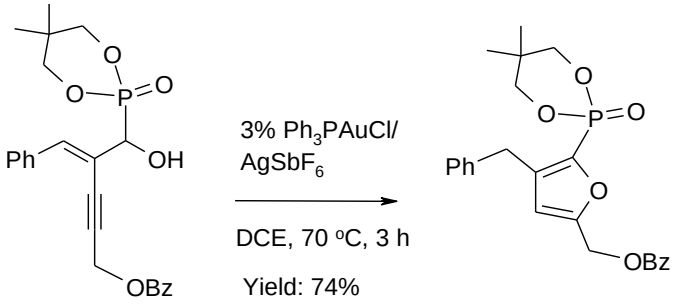

**Figure 6**. Molecular structure for compound **33d**. Selected bond lengths [Å] with esd's in parentheses: O1-C9 1.433(3), C1-C6 1.508(3), C6-C7 1.444(4), C7-C8 1.318(3), O2-C7 1.410(3) and C8-C9 1.504(4).

### *2.62 Synthesis of phosphono-furans and phosphono-pyrans*

Our success in the above cycloisomerization prompted us to check the synthesis of phosphorus containing oxacycles.[70] Hence, phosphorus containing β-hydroxy propargylic esters **24a-e** were utilized in this study. Although these phosphono-alkynols when treated with 3% $Ph_3PAuCl$/ $AgSbF_6$ in dichloroethane did not react at 25 $^oC$, the reaction was complete in 3 h when heated at 70 $^oC$. In most of these cases, two products, *a phosphono-furan and a phosphono-pyran*, with very close $R_f$ values were

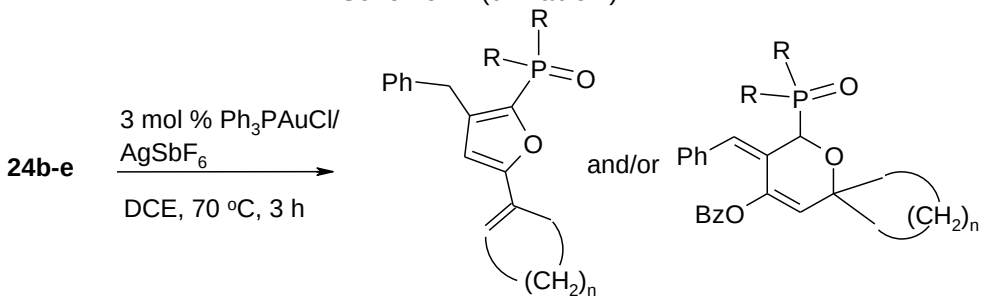
formed [$^{31}$P NMR evidence] in varying proportions, but the reaction was quantitative with all the phosphono-alkynol consumed. When **24a** was used, phosphono-furan **35** (Scheme 23) was obtained 74% yield. The $^{31}$P NMR spectrum of reaction mixture of **24b** showed only two peaks with almost equal intensity. However, the phosphono-furan [$^{31}$P NMR; δ -1.7] was decomposed during the process of isolation by column chromatography. The other product, phosphono-pyran **36** [$^{31}$P NMR; δ 9.1], was separated successfully (Scheme 24, Table 7). Compound **24c** afforded phosphono-furan **37** and phosphono-pyran **38** (Scheme 24, Table 7). Alkynol **24d** led to phosphono-furan **26d** (cf. Tables 2 & 7) as the predominant product. Interestingly, compound **24e** led to phosphono-furan **39** and phosphono-pyran **40** in which **40** was the major product. As the $R_f$ values of phosphono-furans and phosphono-pyrans are very close (Table 7, entries 2 and 4), pure **38** (purity of isolated product ~96%) and **40** (purity of isolated product ~80%) were difficult to obtain.

**Scheme 23**



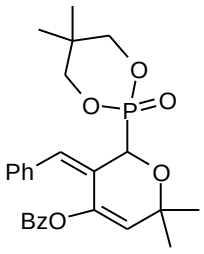
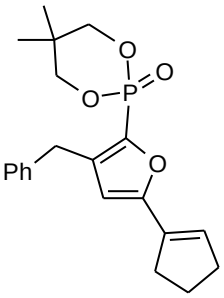
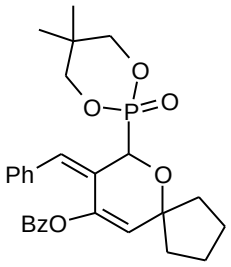
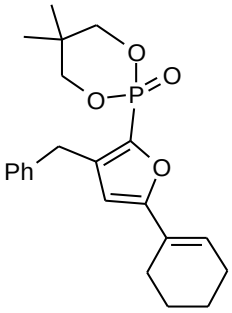
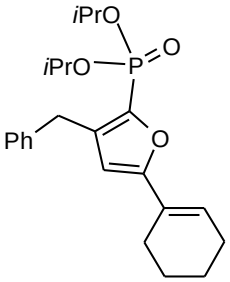
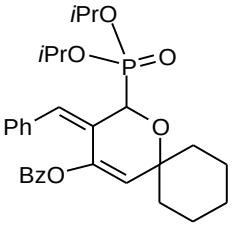
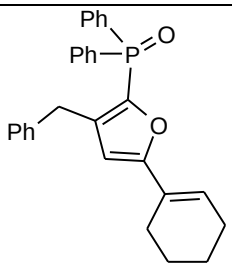

**24a** **35**

**Scheme 24** (cf. Table 7)




Quantitive reaction ($^{31}$P NMR)

**Table 7**. Details on cyclization of phosphorus containing β-hydroxy propargylic esters to phosphono-furans and phosphono-pyrans

| Entry | substrate | Furan derivative (Yield %)[a] | Pyran derivative (Yield %)[a] |
|---|---|---|---|
| 1 | **24b** | not isolated |  **36** (44%) |
| 2 | **24c** |  **37** (64%, X-ray) |  **38** (10%) |
| 3 | **24d** |  **26d** (62%) [see Table 2 also] | not isolated |
| 4 | **24e** |  **39** (33%) |  **40** (55%) |
| 5 | **25** |  **41** (30%) | not isolated |

[a] Isolated yield

All these compounds [**35-41**] are characterized by NMR ($^{31}$P, $^{1}$H and $^{13}$C) and HRMS/elemental analyses. In the $^{31}$P NMR, phosphono-furans **35** and **37** show a peak at δ~-3 and phosphono-pyrans **36** and **38** exhibit a peak at δ~9.0. In the $^{1}$H NMR, the PC*H* proton appears at δ ~5.2 ($^{2}J$(P-H) ~ 13.0 Hz) for phosphono-pyrans which is absent for phosphono-furans. In the $^{13}$C NMR, the P-*C* carbon for phosphono-furans appears at δ ~130 [$^{1}J$(P-C) = 240 Hz] while in phosphono-pyrans this carbon appears in the aliphatic region at δ ~73 [$^{1}J$(P-C) ~ 166 Hz]. The $^{1}$H and $^{13}$C NMR spectra of phosphono-pyrans show similarity in spectra to non-phosphorus pyrans, except for the coupling due to $^{31}$P nucleus. The $^{31}$P NMR spectra for the reaction mixtures resulting from **24e** (leading to phosphono-furan **39** and phosphono-pyran **40**) and **25** (leading to phosphinoyl-furan **41**) are shown Figure 7. The structure of phosphono-furan **37** was confirmed by X-ray crystallography (Figure 8).

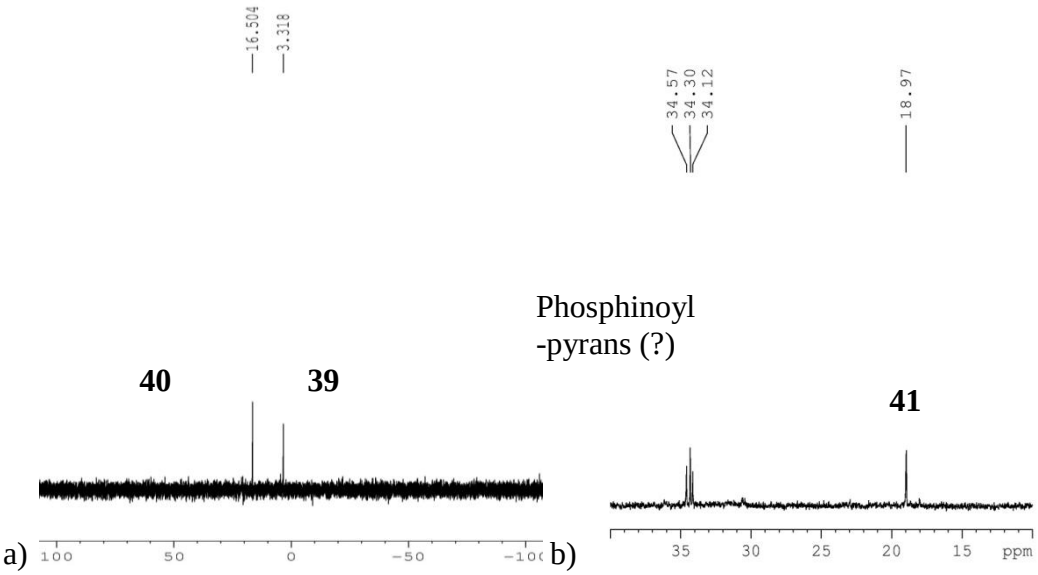



**Figure 7**. $^{31}$P NMR spectra for the reaction mixture resulting from cyclization of a) phosphono-alkynol **24e** and b) phosphinoyl-alkynol **25**.

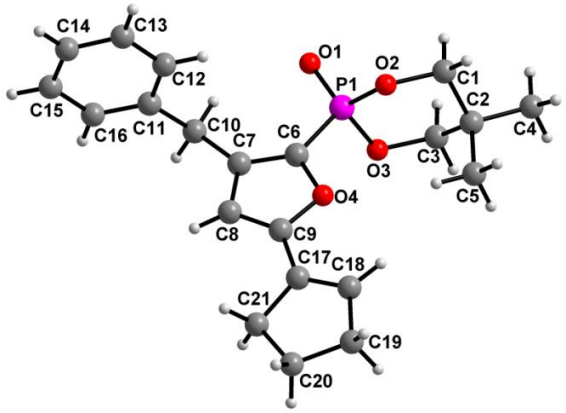


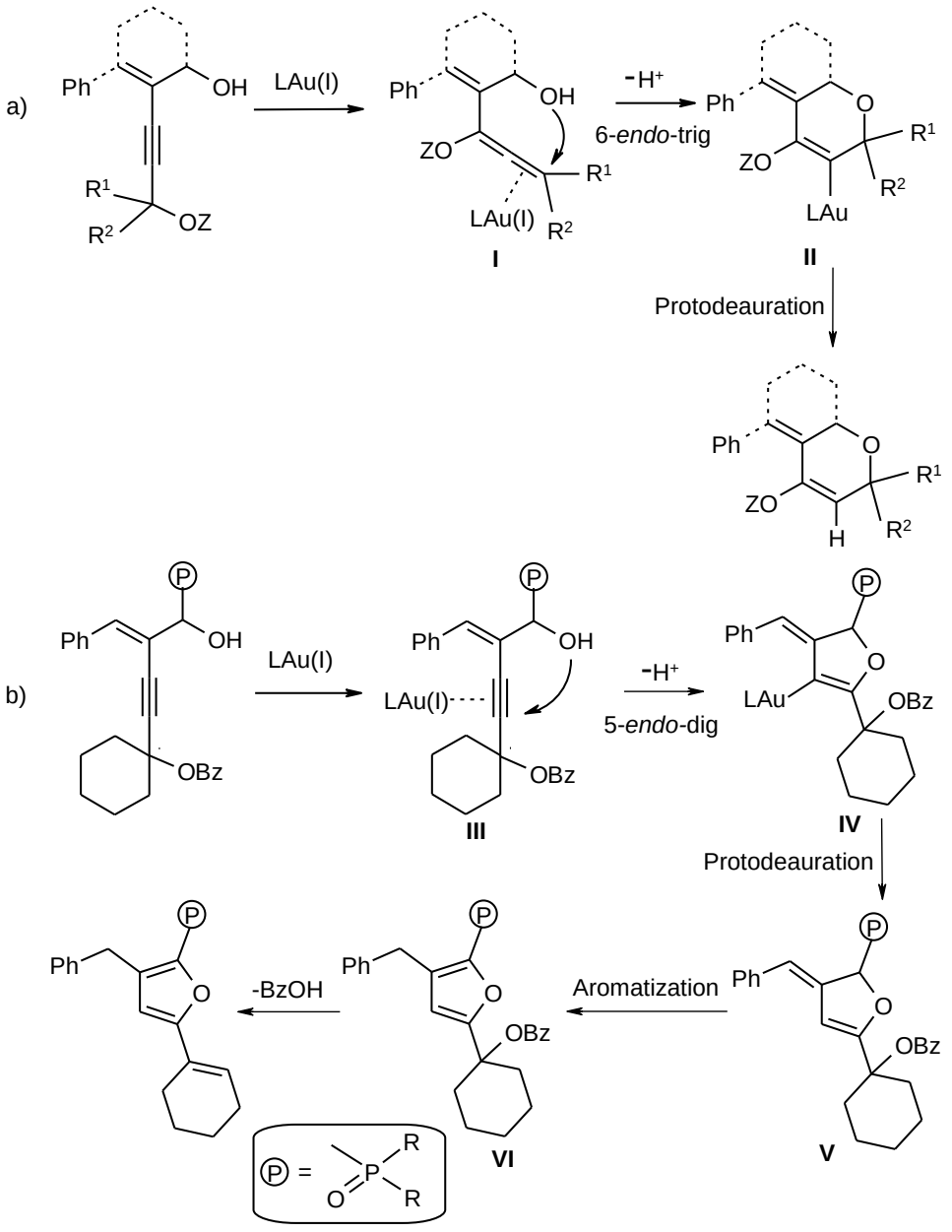

**Figure 8.** Molecular structure of compound **37**. Selected bond lengths [Å] with esd's in parentheses: C6-C7 1.358(3), C10-C7 1.511(3), C9-C8 1.347(3), O4-C9 1.368(3) and C17-C18 1.326(3).

The phosphinoyl-alkynol **25** led to phosphinoyl-furan **41** [$^{31}$P NMR: δ 19.0, Table 7]; however, three more peaks in the phosphono-pyran region were observed in the $^{31}$P NMR [δ 34.1, 34.3, 34.6] spectrum of the reaction mixture (cf. Fig. 7b). The isolated compound **41** shows characteristic peaks at 4.12 (PhC$H_2$), 6.06 (furyl-*H*) and 6.18 (C=C*H*) in the $^{1}$H NMR. The $^{13}$C NMR shows four doublets due to furan ring at 107.1 [$^{3}J$(P-C) = 8.9 Hz, PC=C-*C*], 132.8 [$^{1}J$(P-C) = 100.7 Hz, P-*C*], 140.0 [$^{2}J$(P-C) = 6.3 Hz, P-C-*C*] and 159.9 [$^{3}J$(P-C) = 6.2 Hz, PC-O-*C*], as expected. It is to be noted that in the phosphono-/phosphinoyl-furans **26d**, **37**, **39** and **41**, the *benzoyloxy group* has been eliminated as *benzoic acid* leading to the cycloalkenic double bond at the corresponding site. This elimination cannot occur in the case of phosphono-furan **35** since there is no vicinal C-H moiety available. Overall, the phosphono-alkynol precursors present an interesting variation in the product formation, with both phosphono-furan and phosphono-pyran being present in most cases.

We propose that the reaction leading to ***pyrans*** proceeds *via* Au(I) catalyzed π-activation of propargylic ester which undergoes 1,3-carboxylate migration[11] to form allene intermediate **I** (Scheme 25a) followed by regioselective hydroxyl group addition to allene which is 6-*endo-trig* cyclization, affording the six-membered oxacycle **II**. Subsequently, **II** undergoes proto-deauration to lead to pyran derivative.[9d] Since the reaction occurs with $AgSbF_6$ also, albeit less effectively, an Ag(I) intermediate similar

to **I-II** is feasible. With regard to the cycloisomerization of phosphono-alkynols to *phosphono-pyrans*, the reaction pathway is analogous to the above whereas the formation of *phosphono-furans* has occurred differently.[37] Initially, coordination of Au(I) with alkyne to form **III** (Scheme 25b) which on 5-*endo-dig* cyclization forms the metallo-furan **IV**. Protodeauration of **IV** to dihydrofuran **V** followed by aromatization to furan **VI** and subsequent elimination of benzoic acid leads to the phosphono-furan derivatives.

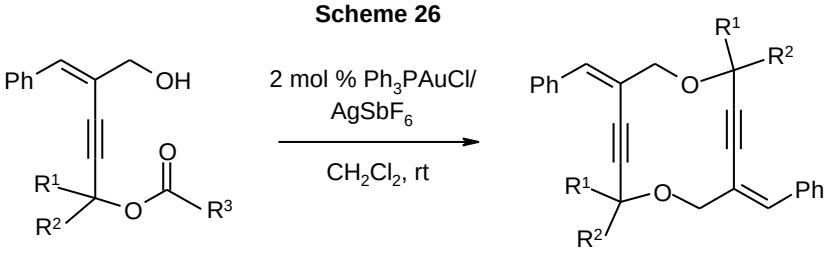
**Scheme 25. Proposed reaction pathways for the cyclizations**



### *2.63 Formation of macrocycles 42-45 in the attempted cyclization of 20h-j*

During the probe on β-hydroxy propargylic esters, some subtle steric/electronic factors were believed to exist. It was found that β-hydroxy propargylic esters **20h-j** underwent self condensation *via* nucleophilic substitution[77] of ester group to afford twelve-membered macrocycles **42-45** (Scheme 26). Among these, **42** and **43** are isomers resulting from **20h**. In the absence of the catalyst, the reaction using **20h** did not give the cyclized products **42-43**. In addition to the steric/electronic factors, perhaps, the oxophilicity of gold(I) complex[77a, 77d-e] might have driven the condensation. The geometry of **43** was confirmed by X-ray crystallography (Figure 9). It is observed that the two oxygens of **43** are present at the equatorial position of the cyclohexyl moiety. It is also noticed that unlike the other propargylic precursors (cf. Scheme 22, Table 6) the C≡C moiety remains unreactive. The first isomer **42** has spectral features similar to **43** and is most likely a conformational isomer.

**Scheme 26**




| | | |
|---|---|---|
| $(R^1R^2)$ = [-$CH_2$-]$_5$, $R^3$ = Me | **20h** | **42** (28%) **+ 43** [**X-ray,** 44%] |
| $R^1$ = $R^2$ = Me, $R^3$ = Et | **20i** | **44** (60%) |
| $R^1$ = Me, $R^2$ = *n*-propyl, $R^3$ = Ph | **20j** | **45** (44%) |

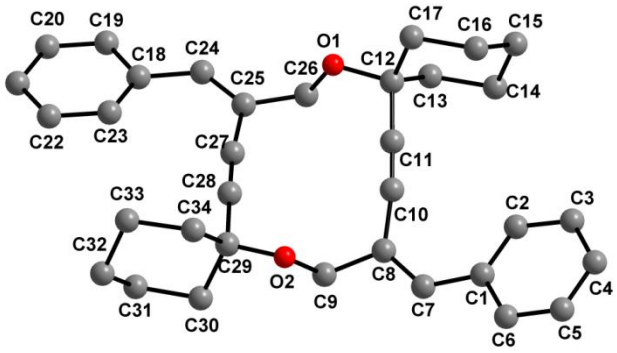
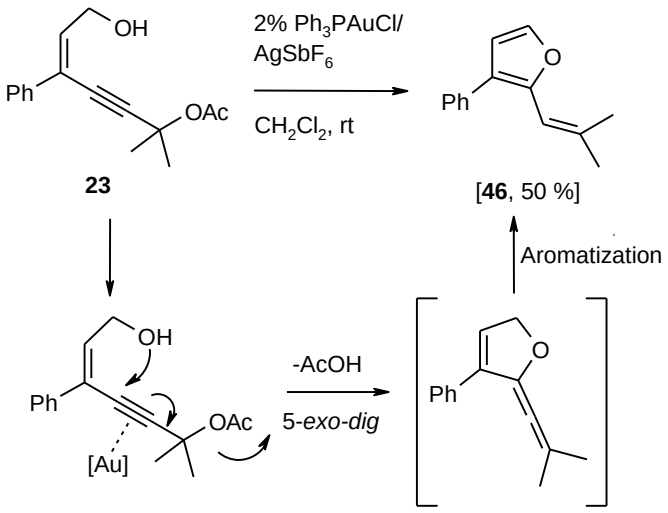


**Figure 9**. Molecular structure for compound **43** (hydrogen atoms are omitted for clarity). Selected bond lengths [Å] with esd's in parentheses: C10-C11 1.192(4) Å and C27-C28 1.172(4) Å.

### *2.64 Gold (I) catalyzed cyclization γ-hydroxy propargylic ester 23 leading to compound 46*

In view of extending the investigation on the cyclization of alkynols, γ-hydroxy propargylic ester **23** was treated with 2 mol % $Ph_3PAuCl/AgSbF_6$ in dichloromethane at rt. The reaction led to the furan derivative **46** (Scheme 27). It proceeded by the addition of hydroxyl group onto alkyne *via* 5-*exo-dig* cyclization to form allene intermediate (different from the one shown in Scheme 22) along with the expulsion of acetic acid. The generated allene further aromatized to lead to alkenyl furan **46**. The methyl proton signals in **46** appear at δ 1.80, while in the precursor **23** they appear at δ 1.20. The furyl protons appear at δ 5.90 and 7.80. Finally, the HRMS shows the peak for $[M+1]^+$ ion.

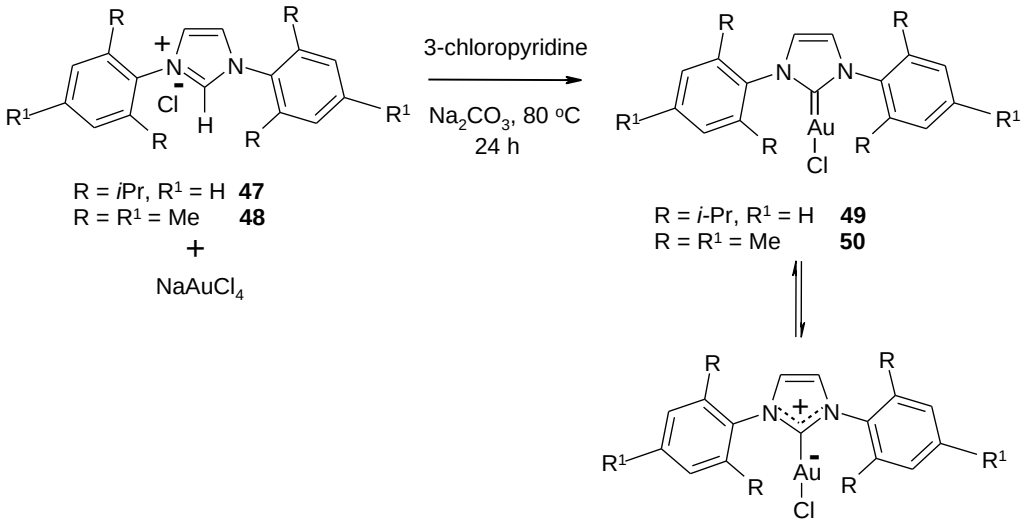
**Scheme 27**



## 2.7 Gold (I) catalyzed cycloaddition of propargylic esters with 1,3-diphenylisobenzofuran

Aforementioned propargylic esters can undergo carboxyl migration in the presence of gold catalysts and keeping abreast of the recent developments[44-46, 52, 54, 57] in gold catalysis, we were impelled to exploit the *in situ* generated metal complexed propargylic ester derivatives by cycloaddition. In such reactions, 1,3-diphenylisobenzofuran is a proven potent cycloaddition partner.[78] Hence it has been used in the present study. The reactivity of propargylic esters with 1,3-diphenylisobenzofuran was checked with different catalysts and hence the investigation needed the synthesis of gold carbene complexes **49**-**50** since the commercially available sample is expensive [**49**: 500 mg: Rs. 11,000/-]. Thus gold-carbene complexes **49**-**50** were synthesized (Scheme 28) according to a literature procedure[79] using 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride **47**[80] or 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride **48**[80] and sodium tetrachloroaurate.

**Scheme 28**

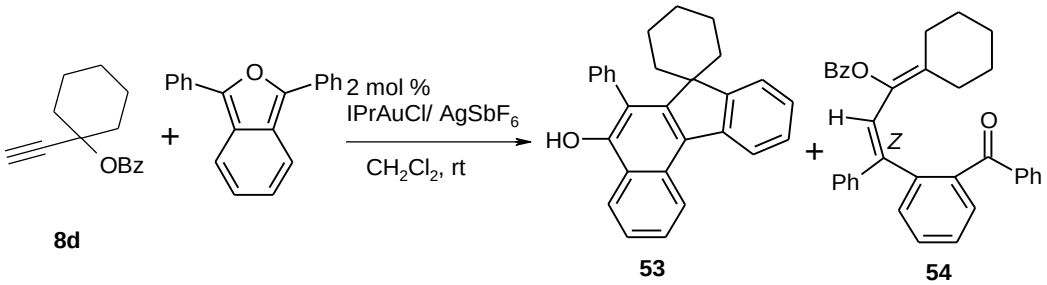



***Synthesis of benzofluorenols and substituted dienes***

To accomplish standardized procedure for the cycloaddition leading to **51**–**66** different conditions were employed using propargyl benzoate **8d** as the precursor (Scheme 29). First we confirmed that **8d** does not react with 1,3-diphenylisobenzofuran

(IBF, 1:1.5 molar ratio) in dichloromethane at rt under catalyst-free conditions (Table 8, entry 1). Then, gold carbene complex was employed as the catalyst. To our delight, we found that 2 mol % each of IPrAuCl and $AgSbF_6$ worked well to lead to benzofluorenols **53** and substituted diene **54** in 36% and 54% yields respectively (Table 8, entry 2) based on **8d**. Despite the fact that combined yield of **53** and **54** is excellent, the formation of benzofluorenol **53** is quite interesting. Hence our trials were directed to improve the yield of benzofluorenol derivatives rather than dienes. Thus when the quantity of 1,3-diphenylisobenzofuran was reduced to 1.2 mol equivalents, the yield of benzofluorenol was increased to 52% whereas yield of diene was 34% [combined yield 86%; Table 8, entry 3]. Equimolar ratio of substrates led to benzofluorenol and diene in 57% and 33% respectively (entry 4) whereas as 1.2:1 ratio of alkyne and IBF afforded improved yield of benzofluorenol (58%) with a combined yield of 91% (entry 5). Interestingly, use of 2 mol % IPrAuCl/AgOTf gave only a diene product in 48% yield (Table 8, entry 6). Changing the silver salt to $AgNTf_2$ and $AgBF_4$ led to benzofluorenol in lower yields (entries 7 and 8). 2 mol % IMesAuCl/$AgSbF_6$ could drive the reaction to obtain benzofluorenol in 50% of yield (entry 9). $PicAuCl_2$, IPrAuCl or$AgSbF_6$ individually were not effective to form benzofluorenol (entries 10, 11 and 12). Use of 2 mol % $Ph_3PAuCl$/ $AgSbF_6$ led to diene product only (entry 13). Solvents like $CH_3CN$ or THF (entries 14 and 15) in the presence of 2 mol% IPrAuCl/ $AgSbF_6$ did not perform well in forming the benzofluorenol. Hence it is proven that 2 mol% IPrAuCl/ $AgSbF_6$ in dichloromethane is the best choice for the formation of the benzofluorenol. Details on the optimization of the products under various screening conditions are presented in Table 8.

**Scheme 29**




**8d** **53** **54**

**Table 8**. Screening for the optimization of the yields of benzofluorenol **53** and diene **54**

| Entry[a] | Alkyne/ IBF | Catalyst | Solvent | Time (h) | Combined yield (%)[b] (Benzofluorenol + Diene) |
|---|---|---|---|---|---|
| 1 | 1/ 1 | No Catalyst | DCM | 12 | 0[c] |
| 2 | 1/ 1.5 | 2% IPrAuCl/ $AgSbF_6$ | DCM | 4 | 90 (36 + 54)[d] |
| 3 | 1/ 1.2 | 2% IPrAuCl/ $AgSbF_6$ | DCM | 4 | 86 (52 + 34) |
| 4 | 1/ 1 | 2% IPrAuCl/ $AgSbF_6$ | DCM | 4 | 90 (57 + 33) |
| 5 | 1.2/ 1 | 2% IPrAuCl/ $AgSbF_6$ | DCM | 4 | 91 (58 + 33) |
| 6 | 1.2/ 1 | 2% IPrAuCl/ AgOTf | DCM | 12 | 48 (0 + 48)[c] |
| 7 | 1.2/ 1 | 2% IPrAuCl/ $AgNTf_2$ | DCM | 12 | 62 (26 + 36)[c] |
| 8 | 1.2/ 1 | 2% IPrAuCl/ $AgBF_4$ | DCM | 4 | 85 (38 + 47) |
| 9 | 1.2/ 1 | 2% IMesAuCl/ $AgSbF_6$ | DCM | 4 | 88 (50 + 38) |
| 10 | 1.2/ 1 | 3% $PicAuCl_2$ | DCM | 12 | 54 (0 + 54)[c] |
| 11 | 1.2/ 1 | 3% IPrAuCl | DCM | 12 | 15 (0 + 15)[c] |
| 12 | 1.2/ 1 | 3% $AgSbF_6$ | DCM | 12 | 68 (0 + 68)[c] |
| 13 | 1.2/ 1 | 2% $Ph_3PAuCl$/ $AgSbF_6$ | DCM | 12 | 65 (0 + 65)[c] |
| 14 | 1.2/ 1 | 2% IPrAuCl/ $AgSbF_6$ | $CH_3CN$ | 12 | ~32 (trace + 32) |
| 15 | 1.2/ 1 | 2% IPrAuCl/ $AgSbF_6$ | THF | 12 | 38 (10 + 28)[c] |

[a] All reactions were performed at room temperature.

[b] Isolated yield.

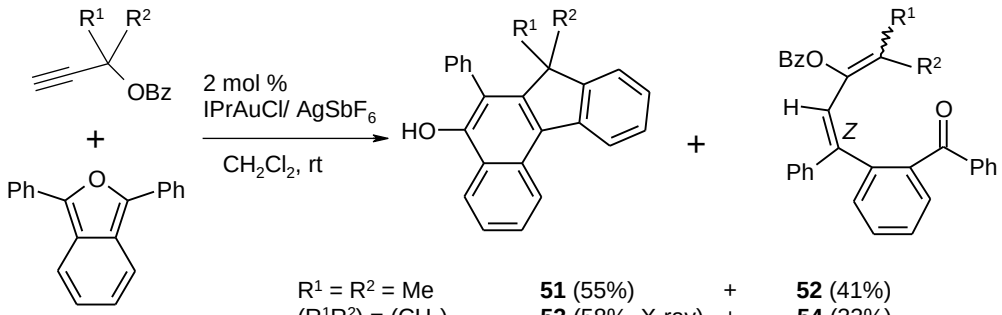
[c] Starting material remained.

[d] Compound **68** was also formed.

To ascertain the efficacy of the above catalytic system, various propargylic benzoates **8b**, **8d-e** and **10c-g** were treated with 1,3-diphenylisobenzofuran (Scheme 30). These reactions afforded products **51-66** (benzofluorenols and dienes) in combined yields of 90-96%. Benzofluorenols were formed in yields of 52-66%. The structure of benzofluorenol **53** was confirmed by X-ray crystallography (Figure 10). The substituents were varied in terms of alkyl groups. If the alkyl groups were unsymmetrically substituted, the diene was formed as *E* + *Z* isomeric mixture, as expected. The $R_f$ values of the two isomers were very close to each other and hence they were not separated. For benzofluorenol, IR spectra show a strong peak at ~3400 $cm^{-1}$ for the phenolic –OH moiety. $^1$H NMR shows a singlet at δ ~5.1 due to phenolic O*H*; the $^{13}$C NMR shows a peak at δ ~53.0 due to the *quaternary carbon* of the cyclopentyl ring.

In the above reactions, the dienes were obtained in 26-42% yields. Although the yields of these compounds can be maximized by using $AgSbF_6$ as the catalyst (entry 12, Table 8) we have not gone for these since our interest was in the benzofluorenols. The geometry at the double bond of these dienes is Z (see below for X-ray structure of an analogous compound). For these dienes, $^1$H NMR spectra show peaks at ~ δ 6.7 due to alkenic-*H* whereas $^{13}$C NMR spectra show peaks at δ ~ 164.0 and ~196.0 due to carbonyl group of ester and ketone respectively.

**Scheme 30**




| | | | |
|---|---|---|---|
| $R^1 = R^2$ = Me | **51** (55%) | + | **52** (41%) |
| $(R^1R^2) = (CH_2)_5$, | **53** (58%, X-ray) | + | **54** (33%) |
| $R^1$ = Me, $R^2$ = Et | **55** (63%) | + | **56** (30%) |
| $R^1$ = Me, $R^2$ = *n*-propyl | **57** (53%) | + | **58** (42%) |
| $R^1$ = Me, $R^2$ = *n*-pentyl | **59** (52%) | + | **60** (38%) |
| $R^1$ = Me, $R^2$ = *n*-hexyl | **61** (54%) | + | **62** (38%) |
| $R^1 = R^2$ = Et | **63** (66%) | + | **64** (26%) |
| $R^1 = R^2$ = *n*-propyl | **65** (56%) | + | **66** (34%) |

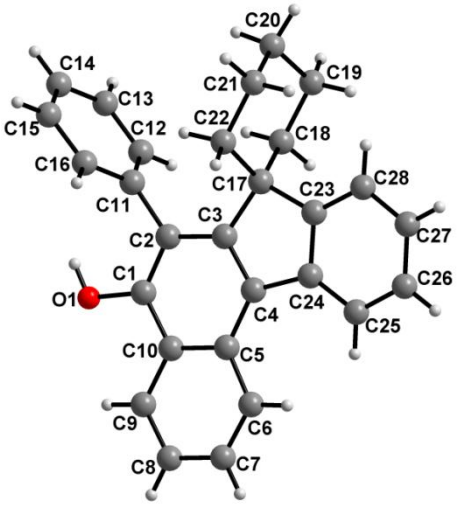
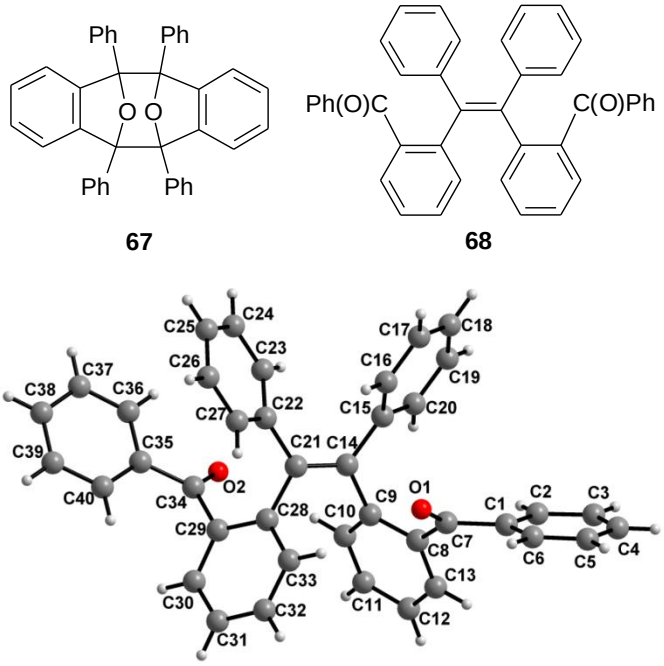



**Figure 10**. Molecular structure for compound **53**. Selected bond lengths [Å] with esd's in parentheses: O1-C1 1.372(3), C2-C1 1.377(4), C3-C2 1.422(4), C4-C3 1.389(3), C11-C2 1.485(3) and C17-C23 1.518(4).

In the above reactions, IBF also can dimerize leading to the compound **67**[81a] that could be isolated. However, in addition to **67**, we have also isolated compound **68**[81b] (also a dimer of IBF) in ca 16% (based on IBF) yield. X-ray crystallography was performed on **68** (Figure 11) to confirm its identity.

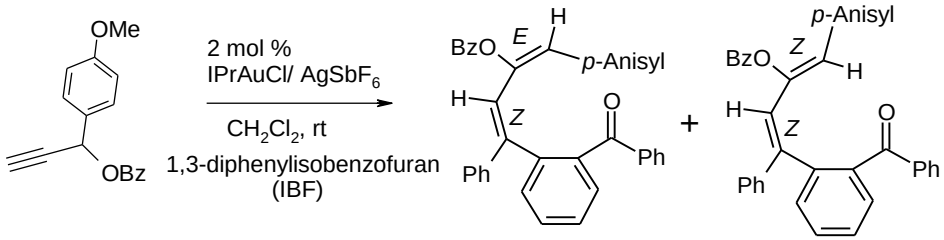



**67** **68**

**Figure 11**. Molecular structure for compound **68**. Selected bond lengths [Å] with esd's in parentheses: O1-C7 1.2130(17), O2-C34 1.2178(18) and C14-C21 1.3514(19).

Apart from disubstituted propargyl benzoates, mono-substituted propargyl benzoate **10h** was also used to study the above protocol. Thus, when **10h** was treated with 1,3-diphenylisobenzofuran under similar conditions, a mixture of dienes was formed (Scheme 31) rather than the benzofluorenol product. In this case, both the isomers **69** and **70** were separated and structure of **69** was confirmed by X-ray crystallography (Figure 12).

**Scheme 31**




**10h** **69**, 44% (X-ray) **70**, 40%

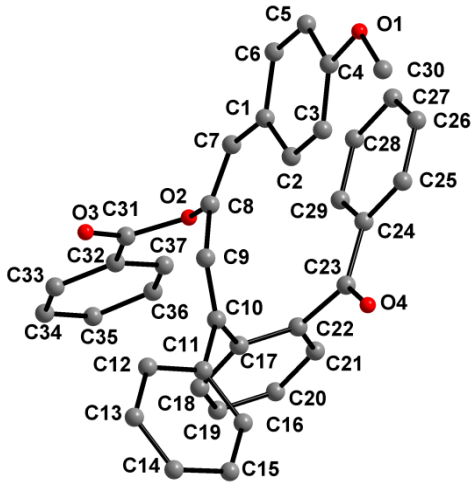
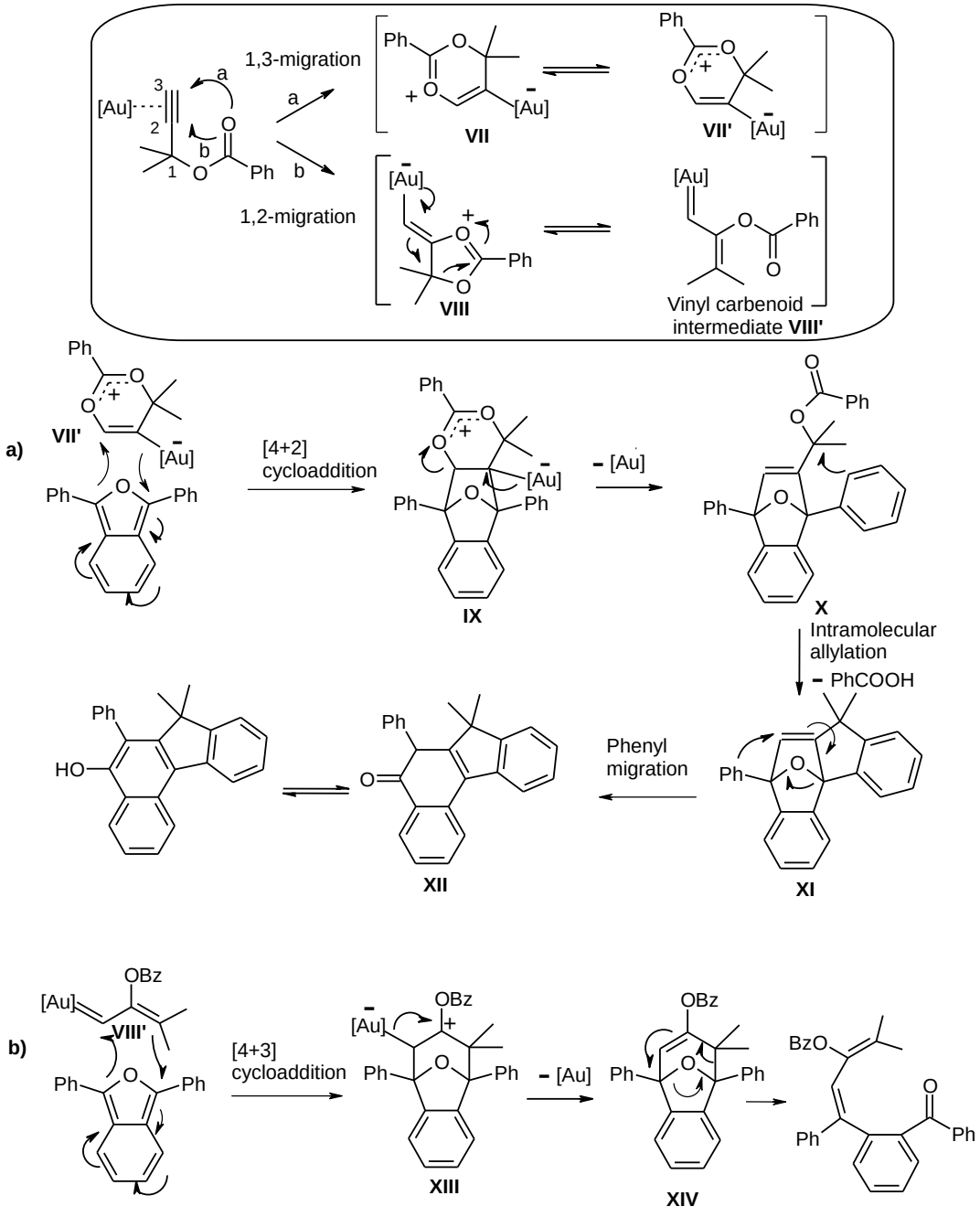



**Figure 12**. Molecular structure for compound **69** (Hydrogen atoms are omitted for clarity). Selected bond lengths [Å] with esd's in parentheses: C7-C8 1.333(7), C8-C9 1.447(7), C9-C10 1.318(7), O2-C8 1.431(6) and O4-C23 1.217(6).

The above reaction is proposed to proceed initially by the coordination of alkyne moiety of propargylic ester with gold to form the intermediates **VII/VII'** and **VIII/VIII'** (Scheme 32) by 1,3- and 1,2-benzoyl group migration[45] to alkyne respectively, which is feasible according to Baldwin's rules.[82] Intermediate **VII'** undergoes [4+2] cycloaddition (Scheme 32a)[52-54] with 1,3-diphenylisobenzofuran to form dipolar cycloadduct **IX** which on demetallation gives **X**. The phenyl substituent at the vicinity of benzoyloxy group undergoes allylation with retention of the allyl group to generate a five membered ring to lead to the polycycle **XI** with bridged oxygen between two phenyl rings. A new C-C bond is formed and benzoic acid is eliminated at this stage. The other phenyl group migrates to the adjacent carbon, which is the γ-position of allylic ether type moiety, to form a second C-C bond leading to **XII**. Species **XII** tautomerizes to the required benzofluorenol derivative. The second product (diene) is formed from the vinyl carbenoid intermediate, **VIII'.** This intermediate **VIII'** undergoes [4+3] cycloaddition (Scheme 32b)[51b-c, 55] to lead to the cycloadduct **XIII** which on demetallation gives **XIV**. The adduct **XIV** rearranges by opening up of the seven membered ring to form the substituted diene.

**Scheme 32 Proposed reaction pathways for the formation of benzofluorenols and substituted dienes**



## SUMMARY – PART A

1) A variety of new propargyl precursors starting from 2-iodo-allylic alcohols, 2-iodo-cinnamadehydes and 2-iodo-cyclohexenone were synthesized. Novel phosphono-alkynols were also prepared from these precursors. The phosphono-alkynols could be cycloisomerized to phosphono-furans in excellent yields using the [Au]-catalytic system $Ph_3PAuCl/AgSbF_6$. It was also discovered that the reaction was very facile with AgOTf. Non-phosphorus alkynols also underwent similar [Au]-catalyzed cycloisomerization to lead to substituted furans in high yields under still milder conditions.
2) New β-hydroxy propargyl esters were synthesized from 2-iodo-allylic alcohols. In the presence of the [Au]-catalytic system $Ph_3PAuCl/AgSbF_6$, the cycloisomerization leads to dihydropyran or 2(*H*)-pyran derivatives *via* a 6-endo-trig cyclization pathway. The yields are good to excellent. This protocol was then extended to phosphorus containing β-hydroxy propargyl esters that led to phosphono-furans and phosphono-pyrans *via* 5-*endo*-dig and 6-*endo*-trig cyclizations, respectively. The overall reaction is quantitative [$^{31}P$ NMR evidence]. In a few cases, β-hydroxy propargyl esters, because of steric/electronic factors, underwent self-condensation to lead to 12-membered macrocycles.
3) Cycloaddition reactions of propargyl benzoates with 1,3-diphenylisobenzofuran (IBF) led to benzofluorenols as well as substituted dienes. Both these products are formed *via* cycloaddition, albeit following different pathways. Thus benzofluorenols are formed *via* a [4+2] cycloaddition followed by sequential allylation, phenyl migration and tautomerization, while the dienes are formed by [4+3] cycloaddition followed by opening up of seven membered ring thus formed. With a mono-substituted propargyl ester, the reaction led to only isomeric dienes rather than benzofluorenols.

# EXPERIMENTAL SECTION

**General**: Chemicals and solvents were procured from Aldrich/ Fluka or local manufacturers. Further purification was done according to standard procedures wherever required.[59] All operations, unless otherwise specified, were carried out under dry nitrogen atmosphere using standard vacuum line techniques.[83]

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

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

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

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

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

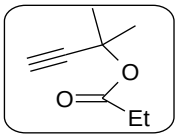
The H-phosphonates $(OCH_2CMe_2CH_2O)P(O)H$ (**1a**)[58a], $(RO)_2P(O)H$ [R = Et (**1b**), *i*-Pr (**1c**)][58b] and diphenylphosphine oxide $Ph_2P(O)H$ (**1d**)[58c] were prepared by well-known methods[58a].

## 3.1 Preparation of iodo-aldehydes/ketones/alcohols [2a-b, 3-7] and propargylic precursors [8a-i, 9a-h and 10a-h]

2-Iodo-cinnamaldehydes **2a-b** were prepared by following a literature procedure using ICl in pyridine.[61a] 2-Iodo-cyclohexenone **3** was prepared using iodine in pyridine

by following a known route.[61b] 3-Iodo-cinnamyl alcohol **4** was prepared by selective iodination of 3-phenyl-prop-2-ynol at -78 $^{o}$C followed by oxidation with $MnO_2$ to lead to 3-iodo-cinnamaldehyde **5** which is reported in the literature.[62] Iodo-allyl alcohols **6** and **7** were prepared by reduction of **2a** and **3** with $NaBH_4/CeCl_3.7H_2O$ respectively by following a literature report.[63] Propargyl esters **8a-i** were obtained from the corresponding propargyl alcohols and acid chlorides by following a known route.[64] Among these, **8h** is new and the rest are known.

***Compound 8h***




2-Methylbut-3-yn-2-ol (0.864 g, 10.3 mmol) was the alcohol component here.

Yield: 1.44 g (85%, colorless oil).

IR (neat): 3293, 3058, 2986, 2937, 2290, 2247, 1734, 1425, 1266, 1195, 1134, 1085, 1041 $cm^{-1}$.

$^{1}$H NMR: δ 1.13 (t, $^{3}J$(H-H) = 7.4 Hz, 3H, C$H_3$CH$_2$), 1.67 (s, 6H, C(C$H_3$)$_2$), 2.30 (qrt, $^{3}J$(H-H) = 7.8 Hz, 2H, CH$_3$C$H_2$), 2.53 (s, 1H, C≡C*H*).

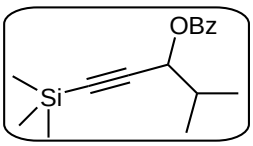
$^{13}$C NMR: δ 8.8 (*C*H$_3$CH$_2$), 28.0 (CH$_3$*C*H$_2$), 28.8 (*C*Me$_2$), 71.2, 72.1, 84.7 (*C*≡*C*H and Me$_2$*C*-O), 172.5 (O*C*OEt).

HRMS (ESI): Calcd. for $C_8H_{12}NaO_2$ [$M^+$+Na]: *m/z* 163.0735. Found: 163.0708.

### *3.11 Synthesis of silyl substituted propargylic esters 9a-h*

These compounds were prepared from trimethylsilyl acetylene, appropriate carbonyl compound and benzoyl chloride.[64a, 65] Among these compounds, **9a-g** are new and **9h** is known.[44]

***Compound 9a***[65]




Trimethylsilyl acetylene (2.07 g, 21.7 mmol) was taken in dry THF (60 mL) and *n*-BuLi (13.6 mL of 1.6M solution) was added slowly at -78 $^{o}$C with continuous stirring.

The temperature of the reaction mixture was allowed to raise to -40 $^{o}$C, maintained at this temperature for 30 min, cooled again to -78 $^{o}$C and then isobutyraldehyde (1.42 g, 21.7 mmol) was added via a syringe. After allowing the temperature to attain rt (25 $^{o}$C), the mixture was stirred for 6 h and cooled to 0 $^{o}$C. Benzoyl chloride (6.50 g, 43.4 mmol) was added at 0 $^{o}$C via a syringe, the mixture brought to rt and stirred for 6 h. Saturated $NaHCO_3$ solution (50 mL) was added and the solubles were extracted with ethyl acetate (2x100 mL). The organic layer was separated and washed with saturated $NaHCO_3$ solution (2x100 mL) followed by brine solution (100 mL). Solvent was removed and the crude product was purified by column chromatography by using ethyl acetate/ hexane mixture (1:50) as the eluent.

Yield: 4.80 g (89%, white solid).

Mp: 44-46 $^{o}$C.

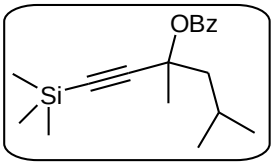
IR (KBr): 2959, 2931, 2893, 2876, 2180, 1715, 1595, 1452, 1326, 1249, 1107, 1205, 1007, 975, 838761, 712 $cm^{-1}$.

$^{1}$H NMR: δ 0.18 (s, 9H, Si(C$H_3$)$_3$), 1.08 and 1.10 (2d, $^{3}J$(H-H) = 6.8 Hz, 6H, (C$H_3$)$_2$CH), 2.11-2.16 (m, 1H, (CH$_3$)$_2$C*H*), 5.49 (d, 1H, $^{3}J$(H-H) = 5.6 Hz, C*H*OBz), 7.44-8.10 (m, 5H, Ar-*H*).

$^{13}$C NMR: δ -0.1 (Si(*C*H$_3$)$_3$), 17.7, 18.3 ((*C*H$_3$)$_2$CH), 32.7 ((CH$_3$)$_2$C*H*), 69.7 (*C*HOBz), 91.0, 101.4 (*C*≡*C*), 128.4, 129.8, 130.1, 133.1 (Ar-C) and 165.5 (O*C*OPh).

HRMS (ESI): Calcd. for $C_{16}H_{22}NaO_2Si$ [$M^{+}$+Na]: *m/z* 297.1287. Found: 297.1288.

***Compound 9b***




This compound was prepared by following a procedure similar to that for **9a** using trimethylsilyl acetylene (2.07 g, 21.7 mmol) and methyl isobutyl-ketone (2.17 g, 21.7 mmol).

Yield: 3.98 g (60%, colorless oil).

IR (neat): 3096, 3063, 2953, 2871, 2175, 1732, 1606, 1474, 1441, 1375, 1277,

1101, 1025, 882, 845, 767, 712 $cm^{-1}$.

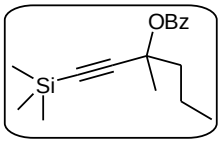
$^1$H NMR: δ 0.17 (s, 9H, Si(C$H_3$)$_3$), 1.04 and 1.06 (2 d, $^3J$(H-H) = 6.4 Hz each, 6H, (C$H_3$)$_2$CH), 1.82 (s, 3H, C$H_3$), 1.84-1.86 (m, 1H, (CH$_3$)$_2$C$H$), 2.05 (d, $^3J$(H-H) = 10.0 Hz, 2H, C$H_2$CH), 7.42-8.03 (m, 5H, Ar-*H*).

$^{13}$C NMR: δ -0.1 (Si(*C*H$_3$)$_3$), 24.1, 24.2, 25.1 and 27.5 ((*C*H$_3$)$_2$*C*H+*C*H$_3$), 49.9 (Me$_2$CH*C*H$_2$), 76.3 (*C*OBz), 90.0 and 105.8 (*C*≡*C*), 128.3, 129.6, 131.4, 132.7 (Ar-*C*) and 164.6 (O*C*OPh).

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

Anal.Calcd. for $C_{18}H_{26}O_2Si$: C, 71.47; H, 8.66. Found: C, 71.52; H, 8.72.

***Compound 9c***




This compound was prepared by following a procedure similar to that for **9a** using trimethylsilyl acetylene (2.07 g, 21.7 mmol) and 2-pentanone (1.87 g, 21.7 mmol,).

Yield: 3.750 g (60%, colorless oil).

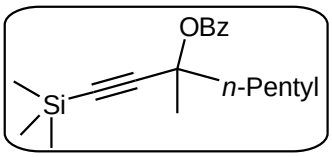
IR (neat): 3441, 2960, 2872, 2168, 1733, 1604, 1449, 1371, 1278, 1252, 1102, 1019, 916, 843, 704 $cm^{-1}$.

$^1$H NMR: δ 0.17 (s, 9H, Si(C$H_3$)$_3$), 1.00 (t, $^3J$(H-H) = 7.6 Hz, 3H, C$H_3$CH$_2$), 1.61 (br s, 2H, CH$_3$C$H_2$), 1.79 (s, 3H, C$H_3$), 1.88-2.11 (m, 2H, CH$_3$CH$_2$C$H_2$), 7.42-8.03 (m, 5H, Ar-*H*)

$^{13}$C NMR: δ 0.0 (Si(*C*H$_3$)$_3$), 14.2, 17.7, 26.7, 44.0 (propyl-*C* + *C*H$_3$), 76.1 (*C*(Me)), 89.7 and 105.6 (*C*≡*C*), 128.3, 129.6, 131.3, 132.7 (Ar-*C*), 164.5 (O*C*OPh).

HRMS (ESI): Calcd. for $C_{17}H_{24}NaO_2Si$ [M$^+$+Na]: *m/z* 311.1444. Found: 311.1453.

***Compound 9d***



This compound was prepared by following a procedure similar to that for **9a** using trimethylsilyl acetylene (2.07 g, 21.7 mmol), 2-heptanone (2.48 g, 21.7 mmol).

Yield: 4.200 g (61%, colorless oil).

IR (neat): 2959, 2937, 2866, 2170, 1732, 1611, 1458, 1370, 1277, 1255, 1112, 926, 844, 762, 707 $cm^{-1}$.

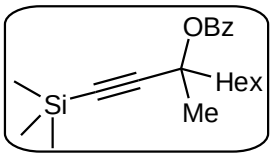
$^1H$ NMR: δ 0.18 (s, 9H, Si(C*H*$_3$)$_3$), 0.92 (t, $^3J$(H-H) = 6.6 Hz, 3H, CH$_2$C*H*$_3$), 1.36-1.59 (m, 6H, pentyl-*H*), 1.79 (s, 3H, C*H*$_3$), 1.90-2.11 (m, 2H, pentyl-*H*), 7.42-8.03 (m, 5H, Ar-*H*).

$^{13}C$ NMR: δ 0.0 (Si(*C*H$_3$)$_3$), 14.1, 22.6, 24.0, 26.7, 31.8 and 41.7 (pentyl-*C* + *C*H$_3$), 76.3 (*C*-OBz), 89.7 and 105.7 (*C*≡*C*), 128.3, 129.6, 131.4, 132.7 (Ar-*C*), 164.6 (O*C*OPh).

LC/MS: *m/z* 317 $[M+1]^+$.

Anal.Calcd. for $C_{19}H_{28}O_2Si$: C, 72.10; H, 8.92. Found: C, 72.31; H, 8.83.

***Compound 9e***




This compound was prepared by following a procedure similar to that for **9a** using trimethylsilyl acetylene (2.07 g, 14.7 mmol) and 2-octanone (1.73 g, 14.7 mmol).

Yield: 2.470 g (54%, gummy liquid).

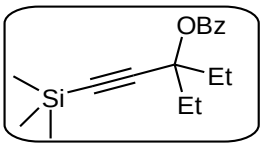
IR (neat): 2954, 2928, 2861, 2172, 1727, 1447, 1276, 1116, 1069, 1027, 847, 712 $cm^{-1}$.

$^1H$ NMR: δ 0.18 (s, 9H, Si(C*H*$_3$)$_3$), 0.92 (t, $^3J$(H-H) = 6.6 Hz, 3H, C*H*$_3$CH$_2$), 1.33-1.61 and 1.80-2.11 (m, 13H, hexyl-*H* + C*H*$_3$), 7.41-8.03 (m, 5H, Ar-*H*).

$^{13}C$ NMR: δ 0.0 (Si(*C*H$_3$)$_3$), 14.2, 22.6, 24.2, 26.7, 29.3, 31.7, 41.7 (Hexyl-*C* + *C*H$_3$), 76.2 (*C*-OBz), 89.7 and 105.7 (*C*≡*C*), 128.3, 129.6, 131.3, 132.7 (Ar-*C*), 164.5 (O*C*OPh).

HRMS (ESI): Calcd. for $C_{20}H_{30}SiO_2$ $[M^+$+Na]: *m/z* 353.1913. Found: 353.1913.

***Compound 9f***




This compound was prepared by following a procedure similar to that for **9a** using trimethylsilyl acetylene (1.38 g, 14.7 mmol), 3-pentanone (1.22 g, 14.7 mmol).

Yield: 2.350 g (56%, gummy liquid).

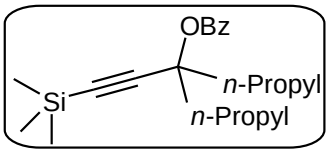
IR (neat): 2970, 2934, 2882, 2158, 1723, 1454, 1273, 1102, 1071, 1024, 843, 766, 704 $cm^{-1}$.

$^{1}H$ NMR: δ 0.01 (s, 9H, $Si(CH_3)_3$), 1.05 (t, $^{3}J$(H-H) = 7.4 Hz, 6H, $CH_3CH_2$), 2.00-2.23 (m, 4H, $CH_3CH_2$), 7.42-8.04 (m, 5H, Ar-*H*).

$^{13}C$ NMR: δ 0.0 ($Si(CH_3)_3$), 8.6 ($CH_3CH_2$), 31.1 ($CH_3CH_2$), 80.8 ($CEt_2$), 90.8, 104.6 (*C*≡*C*), 128.3, 129.6, 131.3, 132.7 (Ar-*C*), 164.5 (O*C*OPh).

HRMS (ESI): Calcd. for $C_{17}H_{24}NaO_2Si$ [$M^+$+Na]: *m/z* 311.1444. Found: 311.1446.

***Compound 9g***




This compound was prepared by following a procedure similar to that for **9a** using trimethylsilyl acetylene (2.07 g, 21.7 mmol) and 3-heptanone (2.47 g, 21.7 mmol).

Yield: 3.570 g (52% colorless oil).

IR (neat): 2970, 2931, 2871, 2175, 1732, 1605, 1452, 1271, 1238, 1178, 1107, 1030, 948, 844, 756, 712 $cm^{-1}$.

$^{1}H$ NMR: δ 0.18 (s, 9H, $Si(CH_3)_3$), 0.97 (t, $^{3}J$(H-H) = 7.4 Hz, 6H, $CH_3CH_2$), 1.51-1.57 (m, 4H, $CH_3CH_2CH_2$), 1.93-2.00 and 2.11-2.17 (m, 4H, $CH_3CH_2CH_2$), 7.41-8.02 (m, 5H, Ar-*H*).

$^{13}C$ NMR: δ 0.0 ($Si(CH_3)_3$), 14.2, 17.6 and 40.8 (propyl-*C*), 79.8 (*C*-OBz), 90.6 and 105.1 (*C*≡*C*), 128.3, 129.6, 131.3, 132.7 (Ar-*C*) and 164.4 (O*C*OPh).

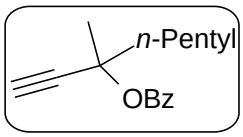
LC/MS: *m/z* 317 $[M+1]^+$.

Anal.Calcd. for $C_{19}H_{28}O_2Si$: C, 72.10; H, 8.92. Found: C, 72.21; H, 8.85.

### *3.12 Synthesis of propargylic esters 10a-h via desilylation*

Desilylation[66] of silyl substituted propargyl esters **9a-h** led to terminal propargyl esters **10a-h** out of which **10a-c** and **10h** are known. Compounds **10d-g** are new.

***Compound 10d***




This compound was obtained by desilylation[2] of **9d** (2.00 g, 6.3 mmol) in dry THF (20 mL) by adding TBAF (1.66 g, 6.3 mmol) at 0 $^{o}$C. The mixture was stirred for 1 h at rt. Solvent was removed under vacuum and the crude product was purified by column chromatography using ethyl acetate/hexane mixture (1:20) as the eluent.

Yield: 1.370 g (89%, colorless oil).

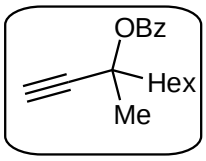
IR (neat): 3304, 3260, 2953, 2932, 2871, 2121, 1726, 1606, 1447, 1375, 1271, 1178, 1156, 1107, 1074, 1030, 882, 718 $cm^{-1}$.

$^{1}$H NMR: δ 0.93 (t, $^{3}J$(H-H) = 6.8 Hz, 3H, C$H_3$CH$_2$), 1.35-1.38, 1.57-1.65 (m, 6H, pentyl-*H*), 1.82 (s, 3H, C$H_3$), 1.95-2.11 (m, 2H, -C(OBz)C$H_2$), 2.61 (s, 1H, C≡C*H*), 7.42-8.03 (m, 5H, Ar-*H*).

$^{13}$C NMR: δ 14.1, 22.6, 23.9, 26.6, 31.8, 41.7 (pentyl-*C* + *C*H$_3$), 73.5 (*C*OBz), 75.6 and 84.0 (*C*≡*C*), 128.4, 129.6, 131.0, 132.9 (Ar-*C*), 164.9 (O*C*OPh).

HRMS (ESI): Calcd. for $C_{16}H_{20}NaO_2$ [$M^+$+Na]: *m/z* 267.1361. Found: 267.1362.

***Compound 10e***




This compound was prepared by following a route similar to that for **10d** using **9e** (0.75 g, 2.4 mmol).

Yield: 0.540 g (87%, colorless oil).

IR (neat): 3304, 2959, 2926, 2867, 2115, 1721, 1600, 1452, 1375, 1271, 1107, 1025, 712 $cm^{-1}$.

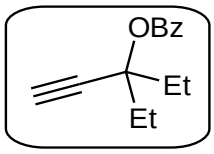
$^{1}$H NMR: δ 0.91 (t, $^{3}J$(H-H) = 6.6 Hz, 3H, C$H_3$CH$_2$), 1.33-1.62 and 1.82-2.11 (m,

13H, hexyl-*H* + C*H*$_3$), 2.61 (s, 1H, ≡C*H*), 7.41-8.03 (m, 5H, Ar-*H*).

$^{13}$C NMR: δ 14.1, 22.7, 24.1, 26.6, 29.3, 31.7 and 41.7 (hexyl-*C* + *C*H$_3$), 73.5 (*C*-OBz), 75.5 and 84.0 (*C*≡*C*), 128.3, 129.6, 130.9, 132.9 (Ar-*C*), 164.8 (O*C*OPh).

HRMS (ESI): Calcd. for $C_{17}H_{22}NaO_2$ [M$^+$+Na]: *m/z* 281.1518. Found: 281.1531.

***Compound 10f***




This compound was prepared by following a route similar to that for **10d** using **9f** (0.85 g, 3.0 mmol).

Yield: 0.550 g (84%, colorless oil).

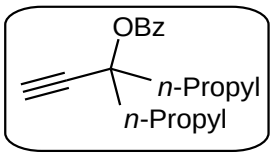
IR (neat): 3301, 3265, 2975, 2934, 2877, 2111, 1723, 1599, 1449, 1268, 1107, 1071, 1030, 916, 714 cm$^{-1}$.

$^1$H NMR: δ 1.07 (t, $^3J$(H-H) = 7.4 Hz, 6H, C*H*$_3$CH$_2$), 2.05-2.24 (m, 4H, CH$_3$C*H*$_2$), 2.62 (s, 1H, ≡C*H*), 7.41-8.04 (m, 5H, Ar-*H*)

$^{13}$C NMR: δ 8.3 (*C*H$_3$CH$_2$), 30.9 (CH$_3$*C*H$_2$), 74.3 (*C*Et$_2$), 79.8, 82.9 (*C*≡*C*), 128.3, 129.5, 130.9, 132.8 (Ar-*C*), 164.7 (O*C*OPh).

HRMS(ESI): Calcd. for $C_{14}H_{16}NaO_2$ [M$^+$+Na]: *m/z* 239.1048. Found: 239.1048.

***Compound 10g***




This compound was prepared by following a route similar to that for **10d** using **9g** (2.00 g, 6.3 mmol).

Yield: 1.330 g (86%, colorless oil).

IR (neat): 3304, 3069, 2959, 2932, 2877, 2121, 1726, 1606, 1447, 1277, 1118, 1096, 1025, 948, 712 cm$^{-1}$.

$^1$H NMR: δ 0.98 (t, $^3J$(H-H) = 7.4 Hz, 6H, C*H*$_3$CH$_2$), 1.53-1.61 (m, 4H, CH$_3$C*H*$_2$CH$_2$), 1.98-2.04 and 2.12-2.17 (m, 4H, CH$_3$CH$_2$C*H*$_2$), 2.62 (s,

1H, ≡C*H*), 7.42-8.03 (m, 5H, Ar-*H*).

$^{13}$C NMR: δ 14.1, 17.4 and 40.6 (*n*-propyl-*C*), 74.2 (*C*-OBz), 79.0 and 83.3 (*C*≡*C*), 128.3, 129.5, 130.9, 132.8 (Ar-*C*) and 164.7 (O*C*OPh).

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

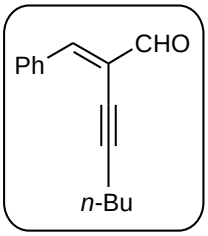
Anal.Calcd. for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.76; H, 8.15.

## 3.2 Synthesis of alkynyl aldehydes/ketones 11a-i, 12-14 and 15a-d

### *3.21 Synthesis of 2-alkynyl cinnamaldehydes 11a-i and 12*

2-Alkynyl cinnamaldehydes **11a-i** were prepared by slightly modifying a known route.[37, 41] Among these, **11a-d** and **12** are known and **11e-i** are new.

***Compound 11e*** *[(E)-2-benzylideneoct-3-ynal]*




To a mixture of 2-iodo-cinnamaldehyde (1.00 g, 3.9 mmol), $PdCl_2$ (36 mg, 0.05 equiv), $PPh_3$ (105 mg, 0.10 equiv) and CuI (77 mg, 0.10 equiv) in dry THF (30 mL) at 0 $^oC$ was added 1-hexyne (637 mg, 2.0 equiv) and diisopropylamine (1.64 mL, 3.0 equiv). The mixture was stirred for 1 h at 0 $^oC$, diluted with $Et_2O$ (100 mL) and washed with 1M HCl (50 mL) followed by saturated brine solution (50 mL). The organic layer was dried over anh. $Na_2SO_4$, filtered and concentrated. The residue was purified by column chromatography using silica gel with EtOAc/ hexane (1:20) as the eluent.

Yield: 0.662 g (80%, gummy liquid)

IR (neat): 3063, 2964, 2926, 2871, 2707, 2225, 2099, 1693, 1600, 1452, 1326, 1184, 1030, 756, 685 $cm^{-1}$.

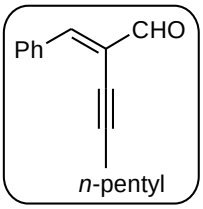
$^1$H NMR: δ 0.97 (d, 3H, $^3J$(H-H) = 7.4 Hz, $CH_2CH_3$), 1.48-1.71 (m, 4H, $CH_2(CH_2)_2CH_3$), 2.58 (t, 2H, $^3J$(H-H) = 7.0 Hz, ≡$CCH_2CH_2$), 7.43-8.12 (m, 6H, C*H*=C + Ar*H*), 9.57 (s, 1H, -C*H*O).

$^{13}$C NMR: δ 13.6, 19.8, 22.1 and 30.5 (*n*-butyl), 74.4 and 103.5 (-*C*≡*C*-), 123.5, 128.7, 130.4, 131.4, 134.3 and 151.1 (ArC + *C*=*C*), 191.8 (-*C*HO).

LC/MS: *m/z* 213 $[M+1]^+$.

Anal.Calcd. for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 84.79; H, 7.65.

***Compound 11f*** *[(E)-2-Benzylidenenon-3-ynal]*




This compound was prepared by following a route similar to that for **11e** using *n*-heptyne and the same molar quantity of the aldehyde.

Yield: 0.760 g (86%, gummy liquid).

IR (neat): 3058, 3025, 2926, 2866, 2225, 1688, 1595, 1452, 1178, 756, 690 $cm^{-1}$.

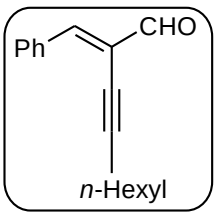
$^1H$ NMR: δ 0.94 (t, 3H, $^3J$(H-H) = 7.2 Hz, $CH_2CH_3$), 1.34-1.52 and 1.65-1.73 (m, 6H, $CH_2(CH_2)_3CH_3$), 2.57 (t, 2H, $^3J$(H-H) = 7.2 Hz, ≡$CCH_2CH_2$), 7.43-8.12 (m, 6H, C*H*=C + Ar*H*), 9.57 (s, 1H, -C*H*O).

$^{13}C$ NMR: δ 14.0, 20.1, 22.3, 28.1, and 31.2 (*n*-pentyl), 74.4 and 103.6 (-*C*≡*C*-), 123.6, 128.7, 130.5, 131.4, 134.3 and 151.0 (ArC + *C*=*C*), 191.9 (-*C*HO).

LC/MS: *m/z* 227 $[M+1]^+$.

Anal.Calcd. for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 84.85; H, 8.12.

***Compound 11g*** *[(E)-2-benzylidenedec-3-ynal]*




This compound was prepared by following a route similar to that for **11e** using *n*-octyne and the same molar quantity of the aldehyde.

Yield: 0.825 g (88%, gummy liquid).

IR (neat): 3068, 3030, 2926, 2855, 2225, 1693, 1595, 1452, 1173, 1030, 751, 685 $cm^{-1}$.

$^1H$ NMR: δ 0.90 (t, 3H, $^3J$(H-H) = 6.8 Hz, $CH_2CH_3$), 1.30-1.70 (m, 8H,

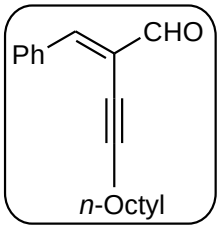
$CH_2(CH_2)_4CH_3$), 2.54 (t, 2H, $^3J$(H-H) = 7.0 Hz, ≡C$CH_2$$CH_2$), 7.40-7.44 and 8.08-8.10 (m, 6H, C*H*=C + Ar*H*), 9.54 (s, 1H, -C*H*O).

$^{13}$C NMR: δ 14.0, 20.0, 22.5, 28.3, 28.6 and 31.3 (*n*-hexyl), 74.3 and 103.5 (-*C*≡*C*-), 123.4, 128.6, 130.3, 131.2, 134.2 and 150.9 (ArC + *C*=*C*), 191.7 (-*C*HO).

LC/MS: *m/z* 241 $[M+1]^+$.

Anal.Calcd. for $C_{17}H_{20}O$: C, 84.96; H, 8.39. Found: C, 85.06; H, 8.31.

***Compound 11h*** *[(E)-2-benzylidenedodec-3-ynal]*




This compound was prepared by following a route similar to that for **11e** using *n*-decyne and the same molar quantity of the aldehyde.

Yield: 0.859 g (82%, gummy liquid).

IR (neat): 3056, 3019, 2915, 2855, 2707, 2225, 1699, 1600, 1447, 1375, 1184, 1030, 756, 685 $cm^{-1}$.

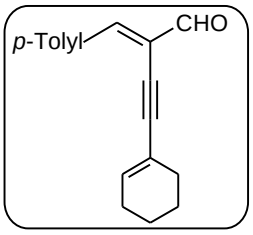
$^1$H NMR: δ 0.89 (t, 3H, $^3J$(H-H) = 6.6 Hz, $CH_2CH_3$), 1.29-1.72 (m, 12H, $CH_2(CH_2)_6CH_3$), 2.57 (t, 2H, $^3J$(H-H) = 7.2 Hz, ≡C$CH_2$$CH_2$), 7.43-7.46 and 8.10-8.12 (m, 6H, C*H*=C + Ar*H*), 9.57 (s, 1H, -C*H*O).

$^{13}$C NMR: δ 14.1, 20.1, 22.7, 28.4, 29.0, $29.1_5$, $29.2_0$, and 31.8 (*n*-octyl), 74.3 and 103.6 (-*C*≡*C*-), 123.5, 128.6, 130.4, 131.3, 134.2 and 151.1 (ArC + *C*=*C*), 191.8 (-*C*HO).

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

Anal.Calcd. for $C_{19}H_{24}O$: C, 85.03; H, 5.96. Found: C, 84.91; H, 9.12.

***Compound 11i*** *[(E)-4-cyclohexenyl-2-(4-methylbenzylidene)but-3-ynal]*




This compound was prepared by following the procedure similar to that for **11e** by using (*Z*)-2-iodo-3-*p*-tolylacrylaldehyde (800 mg, 3.0 mmol).

Yield: 0.646 g (86%, gummy liquid).

IR (neat): 3019, 2931, 2860, 2712, 2192, 1699, 1595, 1430, 1321, 1129, 811, 762, 712 $cm^{-1}$.

$^{1}H$ NMR: δ 1.63-1.73 (m, 4H, $CH_2(CH_2)_2CH_2$), 2.18-2.30 (m, 4H, $CH_2CH{=}CCH_2$), 2.42 (s, $ArCH_3$), 6.34 (dd, $^{3}J$(P-C) = 2.0 and 2.4 respectively, $=CHCH_2$), 7.27-8.01 (m, 5H, C*H*=C + Ar*H*), 9.56 (s, 1H, C*H*O).

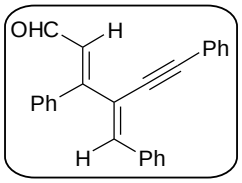
$^{13}C$ NMR: δ 21.4, 21.7, 22.2, 25.9 and 28.8 (cyclohexenyl + $ArCH_3$), 81.0 and 103.0 (-*C*≡*C*-), 120.6, 122.2, 129.5, 130.7, 131.7, 137.1, 142.2, and 150.5 (ArC + *C*=*C*), 191.4 (-*C*HO).

GC/MS: *m/z* 250 $[M]^{+}$.

Anal.Calcd. for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: 86.15; H, 7.21.

### *3.22 Synthesis of (2E,4E)-4-benzylidene-3,6-diphenylhex-2-en-5-ynal 13*[67]

To a mixture of $PdCl_2$ (0.009 g, 0.05 mmol), $PPh_3$ (0.026 g, 0.10 mmol) and triethylamine (1 mL) in $CH_3CN$ (4 mL) was added 3-iodo-cinnamaldehyde **5** (0.258 g, 0.1 mmol), phenyl acetylene (0.204 g, 0.2 mmol) and CuI (0.020 g, 0.01 mmol). The contents were stirred at rt for 4 h. After filtration, the residue was washed with ethyl acetate (10 mL) and the washings added to the filtrate. Volatiles were removed under vacuum and the crude product was purified by column chromatography using ethyl acetate/hexane (1:20) as the eluent.



Yield: 0.260 g (78%, white solid).

M.p.: 76-78 $^{o}$C.

IR (KBr): 3058, 3020, 2844, 2203, 1666, 1573, 1490, 1441, 1200, 1129, 751, 712 $cm^{-1}$.

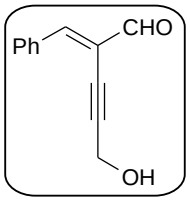
$^{1}$H NMR: δ 6.76 (s, 1H, PhC*H*=C), 6.96 (d, $^{3}J$(H-H) = 8.0 Hz, 1H, =C*H*CHO), 7.36-7.93 (m, 15H, Ar-*H*), 9.44 (d, $^{3}J$(H-H) = 8.0 Hz, -C*H*O).

$^{13}$C NMR: δ 85.6 and 99.1 (*C*≡*C*), 122.6, 122.7, 128.5, 128.6, $129.1_0$, $129.1_2$, 129.2, 129.4, 129.9, 130.1, 130.3, 131.7, 134.9, 135.4, 143.6 and 160.7 (Ar-*C* + alkenyl-*C*), 194.1 (-*C*HO).

HRMS (ESI): Calcd. for $C_{25}H_{19}O$ [$M^{+}$+H]: *m/z* 335.1437. Found: 335.1437.

### *3.23 Synthesis of (E)-2-benzylidene-5-hydroxypent-3-ynal (14)*

To a mixture of $PdCl_2$ (0.011 g, 0.06 mmol) and $Fu_3P$ (0.028 g, 0.12 mmol) in diisopropylamine (6 mL) was added 2-iodo-cinnamaldehyde **2a** (0.516 g, 0.2 mmol), propargyl alcohol (0.170 g, 0.3 mmol) and CuI (0.023 g, 0.12 mmol) subsequently. The contents were stirred at rt for 18 h, filtered and the residue was washed with ethyl acetate (10 mL). The washings were added to the filtrate. Volatiles were removed under vacuum and the crude product was purified by column chromatography using ethyl acetate/hexane (1:5) mixture as the eluent.




Yield: 0.286 g (77%, gummy liquid).

IR (neat): 3414, 3058, 2921, 2849, 2200 (vw), 1682, 1595, 1447, 1184, 1041 761 $cm^{-1}$.

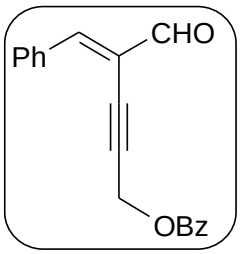
$^{1}$H NMR: δ 2.19 (br s, 1H, -O*H*), 4.61 (s, 2H, C$H_2$OH), 7.48-8.07 (m, 6H, Ar-*H* + PhC*H*=C), 9.54 (d, $^{4}J$(H-H) = 2.0 Hz, 1H, -C*H*O).

$^{13}$C NMR: δ 51.7 (*C*$H_2$OH), 78.8 and 100.1 (*C*≡*C*), 122.2, 128.9, 130.8, 132.0, 133.8 and 153.0 (Ar-*C* + *C*=*C*), 191.8 (-*C*HO).

HRMS (ESI): Calcd. for $C_{12}H_{11}O_2$ [$M^{+}$+H]: *m/z* 187.0760. Found: 187.0755.

### *3.24 Synthesis of α-formyl propargylic esters 15a-d*

***Compound 15a***




This compound was prepared by following a route similar to that for **11e** using (*Z*)-2-iodo-3-phenylacraldehyde **2a** (500 mg, 1.94 mmol) and propargyl ester **8a** (1.5 mol equiv).

Yield: 0.456 g (81%, gummy liquid).

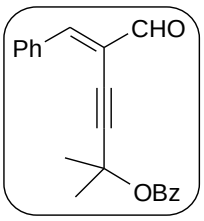
IR (neat): 3063, 3025, 2943, 2844, 2250 (vw), 1726, 1693, 1606, 1452, 1266, 1173, 1090, 1041, 762, 712 $cm^{-1}$.

$^{1}H$ NMR: δ 5.26 (s, 2H, OC$H_2$), 7.37-7.63 and 8.06-8.14 (m, 11H, Ar-*H* + PhC*H*=C), 9.58 (s, 1H, -C*H*O).

$^{13}C$ NMR: δ 53.2 (O*C*$H_2$), 80.1 and 95.1 (*C*≡*C*), 121.6, 128.4, 128.7, 129.7, 130.0, 130.7, 131.9, 133.4, 133.5, 153.5 (Ar*C* + *C*=*C*), 165.7 (O*C*OPh) and 190.9 (-*C*HO).

HRMS (ESI): Calcd. for $C_{19}H_{14}NaO_3$ [$M^+$+Na]: *m/z* 313.0841. Found: 313.0844.

***Compound 15b***




This compound was prepared by following a route similar to that for **11e** using (*Z*)-2-iodo-3-phenylacraldehyde **2a** (500 mg, 1.94 mmol) and propargyl ester **8b** (1.5 mol equiv).

Yield: 0. 525g (85%, white solid).

Mp: 64-66 $^{o}$C.

IR (KBr): 3069, 2981, 2833, 2250 (vw), 1726, 1682, 1589, 1452, 1277, 1145, 1096,

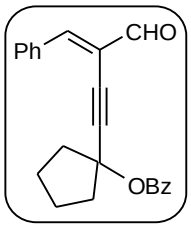
910, 712, 690 $cm^{-1}$.

$^1$H NMR: δ 1.96 (s, 6H, $(CH_3)_2C$), 7.37-8.13 (m, 11H, Ar-*H* + PhC*H*=C), 9.57 (s, 1H, -C*H*O).

$^{13}$C NMR: δ 29.0 ($(CH_3)_2C$), 72.9 ($(CH_3)_2C$-O), 78.2 and 101.8 (*C*≡*C*), 121.9, 128.4, 128.7, 129.7, 130.8, 130.9, 131.7, 133.0, 133.8, 152.2 (Ar*C* + *C*=*C*), 164.9 (O*C*OPh) and 191.0 (-*C*HO).

HRMS (ESI): Calcd. for $C_{21}H_{18}NaO_3$ [$M^+$+Na]: *m/z* 341.1154. Found: 341.1156.

***Compound 15c***




This compound was prepared by following a route similar to that for **11e** using (*Z*)-2-iodo-3-phenylacraldehyde **2a** (500 mg, 1.94 mmol) and propargyl ester **8c** (1.5 mol equiv).

Yield: 0.610 g (91%, white solid).

Mp: 76-78 $^oC$.

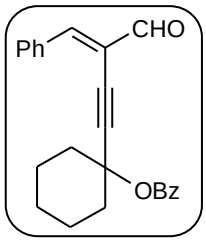
IR (KBr): 3074, 2964, 2849, 1715, 1682, 1589, 1447, 1235, 1282, 1107, 761$cm^{-1}$.

$^1$H NMR: δ 1.86-1.90 and 2.41-2.57 (m, 8H, cyclopentyl-*H*), 7.33-7.59 and 8.08-8.12 (m, 11H, Ar-*H* + PhC*H*=C), 9.55 (s, 1H, -C*H*O).

$^{13}$C NMR: δ 23.5 and 40.5 (cyclopentyl-*C*), 78.8 ($(CH_2)_4C$-O), 81.4 and 101.5 (*C*≡*C*), 122.0, 128.4, 128.6, 129.6, 130.6, 130.8, 131.6, 133.0, 133.8, 151.9 (Ar*C* + *C*=*C*), 165.1 (O*C*OPh) and 190.9 (-*C*HO).

HRMS (ESI): Calcd. for $C_{23}H_{20}NaO_3$ [$M^+$+Na]: *m/z* 367.1310. Found: 367.1310.

***Compound 15d***



This compound was prepared by following a route similar to that for **11e** using (*Z*)-2-iodo-3-phenylacraldehyde **2a** (500 mg, 1.94 mmol) and propargyl ester **8d** (1.5 mol equiv).

Yield: 0.570 g (82%, gummy liquid).

IR (neat): 3057, 2937, 2860, 2350 (w), 1721, 1688, 1600, 1452, 1310, 1277, 1249, 1107, 1019, 712 $cm^{-1}$.

$^{1}H$ NMR: δ 1.43-1.69 and 1.79-2.40 (m, 10H, cyclohexyl-*H*), 7.35-7.60 and 8.09-8.15 (m, 11H, Ar-*H* + PhC*H*=C), 9.58 (s, 1H, -C*H*O).

$^{13}C$ NMR: δ 22.7, 25.3 and 37.2 (cyclohexyl-*C*), 76.4 and 80.3 (*C*≡*C*), 101.4, 122.2, 128.4, 128.7, 129.7, 131.0, 131.7, 133.0, 133.9, 155.6, 155.7 (Ar*C* + *C*=*C*), 164.7 (O*C*OPh) and 191.0 (-*C*HO).

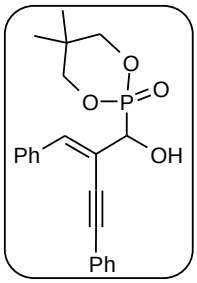
HRMS (ESI): Calcd. for $C_{24}H_{22}NaO_3$ [$M^+$+Na]: *m/z* 381.1467. Found: 381.1465.

## 3.3 Synthesis of phosphono-alkynols 16a-k and non-phosphorylated alkynols 17, 18a-b and 19a-c

### *3.31 Synthesis phosphono-alkynols 16a-k*

By following a known method,[58c] to 2-alkynylcinnamaldehyde **11a-i** (2.0 mmol) and *H*-phosphonate **1a-c** (2.0 mmol) in dry THF (6.0 mL) was added triethylamine (2.0 mmol) and the mixture stirred for 2 h. The solvent was removed under vacuum and the crude product was purified by column chromatography by using silica gel with acetone/ hexane (1:2) mixture as the eluent.

***Compound 16a***




Yield: 0.704 g (92%, white solid).

Mp: 148−150 $^{o}$C.

IR (KBr): 3245, 2959, 2919, 1595, 1487, 1441, 1370, 1244, 1057, 1007, 918, 837,

818, 750, 687 $cm^{-1}$.

$^{1}H$ NMR: δ 0.90 and 1.18 (2 s, 6H, C($CH_3$)$_2$), 1.94 (br s, 1H, -O*H*), 4.04 (dd, 2H, $^{3}J$(P-H) = 2.4 Hz and $^{2}J$(H-H) = 11.0 Hz O$CH_2$), 4.30-4.36 (m, 2H, O$CH_2$), 4.93 (d, $^{2}J$(P-H) = 10.8, PC*H*), 1H, 7.07-7.93 (m, 11H, C*H*=C + Ar*H*).

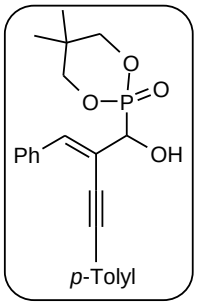
$^{13}C$ NMR: δ 21.0 and 22.0 (2 s, C($CH_3$)$_2$), 32.6 (d, $^{3}J$(P-C) = 7.8 Hz, *C*($CH_3$)$_2$), 73.2 (d, $^{1}J$(P-C) = 157.8 Hz, P*C*), 77.6 and 78.1 (2 d, $^{2}J$(P-C) = 6.9 Hz and 7.2 Hz respectively, O$CH_2$), 86.8 and 98.0 (2 s, *C*≡*C*), 117.3, 123.1, 128.3, 128.5, 128.7, 129.2, 131.6, 135.8, 136.9 (d, $^{2}J$(P-C) = 10.7 Hz, PC-*C*).

$^{31}P$ NMR: δ 13.5.

LC/MS: *m/z* 383 $[M+1]^{+}$.

Anal.Calcd. for $C_{22}H_{23}O_4P$: C, 69.10; H, 6.06. Found: C, 69.03; H, 6.15.

***Compound 16b***




Yield: 0.745 g (94%, white solid).

Mp: 168-170 °C.

IR (KBr): 3212, 2978, 2921, 1597, 1510, 1476, 1244, 1059, 1009, 835, 816, 758, 691 $cm^{-1}$.

$^{1}H$ NMR: δ 0.95 and 1.20 (2 s, 6H, C($CH_3$)$_2$), 2.38 (s, 3H, Ar$CH_3$), 4.06-4.12 (m, 2H, O$CH_2$), 4.27-4.32 (m, 2H, O$CH_2$), 4.88 (d, 1H, $^{2}J$(P-H) = 11.2, PC*H*), 7.04-7.94 (m, 10H, C*H*=C + Ar*H*).

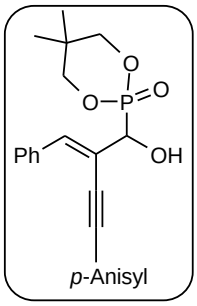
$^{13}C$ NMR: δ 21.2, 21.7 and 22.0 (2 s, C($CH_3$)$_2$ + Ar$CH_3$), 32.6 (d, $^{3}J$(P-C) = 7.4 Hz, *C*($CH_3$)$_2$), 73.2 (d, $^{1}J$(P-C) = 157.1 Hz, P*C*), 77.9 and 78.0 (2 s, O$CH_2$), 86.0 and 98.5 (2 s, *C*≡*C*), 117.2, 119.9, 128.3, 128.8, 129.2, 129.3, 131.5, 135.6, 136.6, 136.7 and 139.1 (Ar-*C* + *C*=*C*).

$^{31}P$ NMR: δ 13.5.

LC/MS: *m/z* 397 $[M+1]^+$.

Anal.Calcd. for $C_{23}H_{25}O_4P$: C, 69.69; H, 6.36. Found: C, 69.75; H, 6.28.

***Compound 16c***




Yield: 0.759 g (92%, white solid).

Mp: 158-160 $^oC$.

IR (KBr): 3247, 2973, 1599, 1510, 1468, 1445, 1372, 1287, 1244, 1175, 1057, 1007, 830, 756, 689, 550 $cm^{-1}$.

$^1H$ NMR: δ 0.95 and 1.20 (2 s, 6H, C($CH_3$)$_2$), 3.84 (s, 3H, O$CH_3$), 4.06-4.12 (m, 2H, O$CH_2$), 4.27-4.33 (m, 2H, O$CH_2$), 4.88 (d, 1H, $^2J$(P-H) = 11.2, PC*H*), 6.88-7.94 (m, 11H, C*H*=C + Ar*H*).

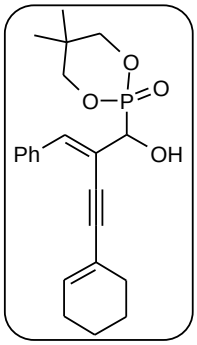
$^{13}C$ NMR: δ 20.8 and 22.0 (2 s, C($CH_3$)$_2$), 32.5 (d, $^3J$(P-C) = 7.7 Hz, *C*($CH_3$)$_2$), 55.3 (s, O$CH_3$), 73.3 (d, $^1J$(P-C) = 158.1 Hz, P*C*), 77.7 and 78.2 (2 d, $^2J$(P-C) = 6.7 Hz and 6.8 Hz respectively, O$CH_2$), 85.7 and 98.1 (2 s, *C*≡*C*), 114.1, 115.2, 117.7, 128.2, 128.4, 129.1, 133.1, 135.8, 135.9, 136.0 and 159.9 (Ar*C* + *C*=*C*).

$^{31}P$ NMR: δ 13.5.

LC/MS: *m/z* 413 $[M+1]^+$.

Anal.Calcd. for $C_{23}H_{25}O_5P$: C, 66.98; H, 6.11. Found: C, 66.91; H, 6.21.

***Compound 16d***




Yield: 0.696 g (90%, white solid).

Mp: 160-162 $^{o}$C.

IR (KBr): 3229, 2921, 2857, 1597, 1474, 1447, 1246, 1057, 1007, 837, 758, 693 $cm^{-1}$.

$^{1}$H NMR: δ 0.90 and 1.18 (2 s, 6H, C(C*H*$_3$)$_2$), 1.59-1.68 (m, 4H, CH$_2$(C*H*$_2$)$_2$CH$_2$), 2.13-2.21 (m, 4H, C*H*$_2$CH=CC*H*$_2$), 4.00 (dd, 2H, $^{3}J$(P-H) = 3.2 Hz and $^{2}J$(H-H) = 10.8 Hz, OC*H*$_2$), 4.29-4.33 (m, 2H, OC*H*$_2$), 4.81 (d, 1H, $^{2}J$(P-H) = 11.6, PC*H*), 6.18-6.20 (m, 1H, =C*H*-CH$_2$), 6.93-7.86 (m, 6H, C*H*=C + Ar*H*).

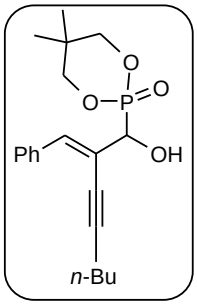
$^{13}$C NMR: δ 20.9, 21.5, 22.0, 22.2, (4 s, C(*C*H$_3$)$_2$ + CH$_2$(*C*H$_2$)$_2$CH$_2$), 25.9 and 28.7 (2 s, CH$_2$*C*H=*C*CH$_2$), 32.5 (d, $^{3}J$(P-C) = 7.7 Hz, *C*(CH$_3$)$_2$), 73.2 (d, $^{1}J$(P-C) = 157.6 Hz, P*C*), 77.6 and 78.1 (2 d, $^{2}J$(P-C) = 6.9 Hz and 7.0 Hz respectively, O*C*H$_2$), 84.1 (d, $^{3}J$(P-C) = 4.3 Hz, =C-*C*≡C), 100.4 (s, C≡*C*), 117.5 (d, $^{3}J$(P-C) = 3.6 Hz, PC*C*=C), 120.8, 128.1, 128.4, 129.0, 135.6, 135.7, 135.9, 136.3 (Ar*C* + *C*=C).

$^{31}$P NMR: δ 13.5.

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

Anal.Calcd. for $C_{22}H_{27}O_4P$: C, 68.38; H, 7.04. Found: C, 68.25; H, 7.12.

***Compound 16e***




Yield: 0.638 g (88%, white solid).

Mp: 84−86 $^{o}$C.

IR (KBr): 3312, 2965, 2211, 1715, 1601, 1474, 1375, 1262, 1055, 1007, 980, 837, 812, 758, 691 $cm^{-1}$.

$^{1}$H NMR: δ 0.89 (s, 3H, -CC*H*$_3$), 0.92 (t, 3H, $^{3}J$(H-H) = 7.4 Hz, $CH_2CH_3$), 1.16 (s, 3H, -CC*H*$_3$), 1.43-1.60 (m, 4H, $CH_2(CH_2)_2CH_3$), 2.46 (t, 2H, $^{3}J$(H-H) = 7.0 Hz, ≡CC*H*$_2$CH$_2$), 4.00 (dd, 2H, $^{3}J$(P-H) = 2.00 Hz and $^{2}J$(H-H) = 11.2 Hz, OC*H*$_2$), 4.26-4.31 (m, 2H, OC*H*$_2$), 4.78 (d, 1H, $^{2}J$(P-H) = 11.6, PC*H*), 6.91-7.86 (m, 6H, C*H*=C + Ar*H*).

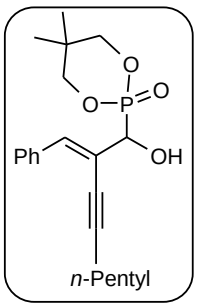
$^{13}$C NMR: δ 13.6 (s, $CH_2CH_3$), 19.6, 20.9, 21.9 and 22.0 (4 s, $C(CH_3)_2$ + $CH_2(CH_2)_2CH_3$), 30.5 (s, ≡C*C*H$_2$), 32.5 (d, $^{3}J$(P-C) = 7.9 Hz, *C*(CH$_3$)$_2$), 73.3 (d, $^{1}J$(P-C) = 157.9 Hz, P*C*), 77.6$_0$ (d, $^{2}J$(P-C) = 6.5 Hz, OCH$_2$), 77.6$_3$ (s, C≡*C*-CH$_2$), 77.9 (d, $^{2}J$(P-C) = 7.1 Hz, O*C*H$_2$), 100.1 (s, *C*≡C-CH$_2$), 117.9 (d, $^{3}J$(P-C) = 3.2 Hz, PC-C=*C*), 128.1, 128.3, 128.8, 135.4 (d, $^{2}J$(P-C) = 11.1 Hz, PC-*C*=C), and 135.8 (d, $^{4}J$(P-C) = 2.5 Hz, Ar-*C*).

$^{31}$P NMR: δ 13.7.

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

Anal.Calcd. for $C_{20}H_{27}O_4P$: C, 66.28; H, 7.51. Found: C, 66.35; H, 7.46.

***Compound 16f***



Yield: 0.685 g (91%, white solid).

Mp: 86-88 $^{o}$C.

IR (KBr): 3308, 2963, 2930, 2863, 2213, 1474, 1375, 1264, 1055, 1007, 837, 812, 758, 693, 467 cm$^{-1}$.

$^{1}$H NMR: δ 0.88-0.92 (m, 6H, -CC*H*$_3$ + CH$_2$C*H*$_3$), 1.17 (s, 3H, -CC*H*$_3$), 1.32-1.62 (m, 6H, CH$_2$(C*H*$_2$)$_3$CH$_3$), 2.45 (t, 2H, $^{3}J$(H-H) = 7.0 Hz, ≡CC*H*$_2$CH$_2$), 4.00 (dd, 2H, $^{3}J$(P-H) = 2.00 Hz and $^{2}J$(H-H) = 11.2 Hz, OC*H*$_2$), 4.26-4.31 (m, 2H, OC*H*$_2$), 4.78 (d, 1H, $^{2}J$(P-H) = 11.6, PC*H*), 6.91-7.86 (m, 6H, C*H*=C + Ar*H*).

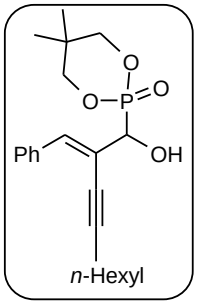
$^{13}$C NMR: δ 14.0 (s, CH$_2$*C*H$_3$), 19.9, 20.9, 21.9, 22.2 and 28.1 (5 s, C(*C*H$_3$)$_2$ + CH$_2$(*C*H$_2$)$_3$CH$_3$), 31.2 (s, ≡C*C*H$_2$), 32.5 (d, $^{3}J$(P-C) = 7.6 Hz, *C*(CH$_3$)$_2$), 73.2 (d, $^{1}J$(P-C) = 157.6 Hz, P*C*), 77.6 (d, $^{2}J$(P-C) = 4.4 Hz, O*C*H$_2$), 77.6 (s, C≡*C*-CH$_2$), 77.9 (d, $^{2}J$(P-C) = 6.9 Hz, O*C*H$_2$), 100.2 (s, *C*≡C-CH$_2$), 117.8 (d, $^{3}J$(P-C) = 3.4 Hz, PC-C=*C*), 128.1, 128.3, 128.8, 135.4 (d, $^{2}J$(P-C) = 10.8 Hz, PC-*C*), 135.8 (d, $^{4}J$(P-C) = 2.9 Hz, Ar-*C*).

$^{31}$P NMR: δ 13.7.

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

Anal.Calcd. for C$_{21}$H$_{29}$O$_4$P: C, 67.01; H, 7.77. Found: C, 67.12; H, 7.71.

***Compound 16g***




Yield: 0.718 g (92%, white solid).

Mp: 116-118 $^{o}$C.

IR (KBr): 3266, 2926, 2849, 2208, 1803, 1600, 1469, 1266, 1058, 1003, 844, 690 cm$^{-1}$.

$^{1}$H NMR: δ 0.90 (t, 3H, $^{3}J$(H-H) = 6.6 Hz, CH$_2$C*H*$_3$), 0.98 and 1.20 (2 s, 6H, C(C*H*$_3$)$_2$), 1.29-1.65 (m, 8H, (C*H*$_2$)$_4$CH$_3$), 2.49 (t, 2H, $^{3}J$(H-H) = 7.0 Hz,

≡CC$H_2$CH$_2$), 4.09 (dd→t, $^3J$(P-H) = $^2J$(H-H) ~ 11.8 Hz, 2H, OC$H_2$), 4.21-4.25 (m, 2H, OC$H_2$), 4.74 (d, 1H, $^2J$(P-H) = 11.2, PC*H*), 6.90-7.87 (m, 6H, C*H*=C + Ar*H*).

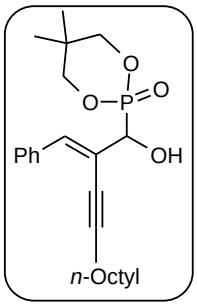
$^{13}$C NMR: δ 14.1 (s, CH$_2$*C*H$_3$), 20.0, 20.9, 21.9, 22.6, 28.4 and 28.7 (6 s, C(*C*H$_3$)$_2$ + CH$_2$(*C*H$_2$)$_4$CH$_3$), 31.4 (s, ≡C*C*H$_2$), 32.4 (d, $^3J$(P-C) = 7.8 Hz, *C*(CH$_3$)$_2$), 73.3 (d, $^1J$(P-C) = 157.6 Hz, P*C*), 77.5 (d, $^2J$(P-C) = 6.5 Hz, O*C*H$_2$), 77.6 (s, C≡*C*-CH$_2$), 78.0 (d, $^2J$(P-C) = 7.2 Hz, O*C*H$_2$), 100.2 (s, *C*≡C-CH$_2$), 117.9 (d, $^3J$(P-C) = 3.6 Hz, PC-C=*C*), 128.0, 128.3, 128.8, 135.4 (d, $^2J$(P-C) = 10.8 Hz, PC-*C*), 135.9 (d, $^4J$(P-C) = 2.3 Hz, Ar-*C*).

$^{31}$P NMR: δ 13.6.

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

Anal.Calcd. for $C_{22}H_{31}O_4P$: C, 67.67; H, 8.00. Found: C, 67.59; H, 8.09.

***Compound 16h***




Yield: 0.737 g (88%, white solid).

Mp: 122-124 $^o$C.

IR (KBr): 3282, 2937, 2855, 2208, 1803, 1600, 1463, 1260, 1047, 1008 cm$^{-1}$.

$^1$H NMR: δ 0.89 (t, 3H, $^3J$(H-H) = 6.8 Hz, CH$_2$C*H*$_3$), 0.97 and 1.20 (2 s, 6H, C(C*H*$_3$)$_2$), 1.29-1.66 (m, 12H, (C*H*$_2$)$_6$CH$_3$), 2.48 (t, 2H, $^3J$(H-H) = 7.0 Hz, ≡CC$H_2$CH$_2$), 4.05-4.27 (m, 4H, OC$H_2$), 4.75 (d, 1H, $^2J$(P-H) = 11.2, PC*H*), 6.90-7.87 (m, 6H, C*H*=C + Ar*H*).

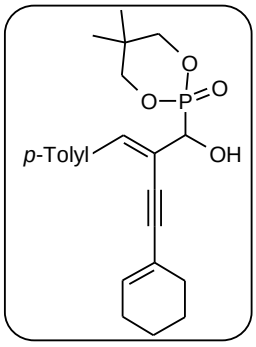
$^{13}$C NMR: δ 14.1 (s, CH$_2$*C*H$_3$), 20.0, 20.9, 22.0, 22.7, 28.5, 29.1, 29.2$_0$ and 29.2$_2$ (8 s, C(*C*H$_3$)$_2$ + CH$_2$(*C*H$_2$)$_6$CH$_3$), 31.9 (s, ≡C*C*H$_2$), 32.5 (d, $^3J$(P-C) = 7.6 Hz, *C*(CH$_3$)$_2$), 73.2 (d, $^1J$(P-C) = 157.3 Hz, P*C*), 77.5 (s, O*C*H$_2$), 77.6 (s, C≡*C*-CH$_2$), 77.9 (d, $^2J$(P-C) = 7.1 Hz, O*C*H$_2$), 100.3 (s, C≡*C*-CH$_2$), 117.9, 128.1, 128.3, 128.8, 135.4 (d, $^2J$(P-C) = 10.8 Hz, PC-*C*), 135.8.

$^{31}$P NMR: δ 13.7.

LC/MS: *m/z* 418 $[M+1]^+$.

Anal.Calcd. for $C_{24}H_{35}O_4P$: C, 68.88; H, 8.43. Found: C, 68.75; H, 8.38.

***Compound 16i***




Yield: 0.737 g (92%, white solid).

Mp: 168-172 $^{o}$C.

IR (KBr): 3229, 2924, 2173, 1599, 1511, 1252, 1061, 1009, 911, 812 $cm^{-1}$.

$^{1}$H NMR: δ 0.94 and 1.20 (2 s, 6H, C(C*H*$_3$)$_2$), 1.61-1.70 (m, 4H, CH$_2$(C*H*$_2$)$_2$CH$_2$), 2.15-2.23 (m, 4H, C=CC*H*$_2$), 2.36 (s, 3H, ArC*H*$_3$), 3.39 (d, 1H, $^3J$(P-H) = 4.0 Hz, O*H*), 4.06 (dd, 2H, $^3J$(P-H) = 2.0 Hz and $^2J$(H-H) = 11.2 Hz, OC*H*$_2$), 4.26-4.30 (m, 2H, OC*H*$_2$), 4.77 (d, 1H, $^2J$(P-H) = 10.0, PC*H*), 6.20-6.22 (m, 1H, =C*H*-CH$_2$), 6.89-7.78 (m, 6H, C*H*=C + Ar*H*).

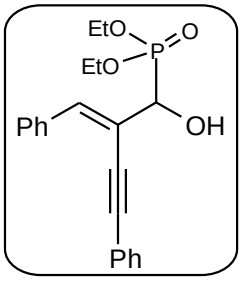
$^{13}$C NMR: δ 21.0, 21.4, 21.5, 22.0 and 22.3 (5 s, C(*C*H$_3$)$_2$ + CH$_2$(*C*H$_2$)$_2$CH$_2$ + Ar*C*H$_3$), 25.9 and 28.8 (2 s, *C*H$_2$C=C*C*H$_2$), 32.5 (d, $^3J$(P-C) = 7.7 Hz, *C*(CH$_3$)$_2$), 73.3 (d, $^1J$(P-C) = 157.5 Hz, P*C*), 77.6 and 78.0 (2 d, $^2J$(P-C) = 7.1 Hz and 6.9 Hz respectively, O*C*H$_2$), 84.2 and 100.3 (2 s, *C*≡*C*), 116.3, 120.9, 128.9, 129.0, 133.1, 135.8 (d, $^2J$(P-C) = 11.0 Hz, PC-*C*), 136.1 and 138.6 (Ar*C* + *C*=C).

$^{31}$P NMR: δ 13.4.

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

Anal.Calcd. for $C_{23}H_{29}O_4P$: C, 68.98; H, 7.30. Found: C, 68.85; H, 7.38.

***Compound 16j***




Yield: 0.689 g (93%, gummy liquid).

IR (neat): 3277, 2975, 2904, 2866, 2356, 2197, 1951, 1589, 1485, 1447, 1386, 1227, 1025, 964, 751, 685 $cm^{-1}$.

$^{1}H$ NMR: δ 1.32 and 1.34 (2 t, 6H, $^{3}J$(H-H) = 7.0 Hz each, $CH_2CH_3$), 3.76 (dd→t, $^{3}J$(P-H) ~ $^{3}J$(H-H) ~ 7.8 Hz, 2H, O*H*), 4.21-4.28 (m, 4H, $OCH_2$), 4.72 (dd, 1H, $^{2}J$(P-H) = 6.8 Hz and $^{3}J$(H-H) = 4.8 Hz, $OCH_2$), 7.02-7.94 (m, 11H, C*H*=C + Ar*H*).

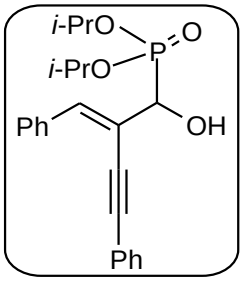
$^{13}C$ NMR: δ 16.5 and 16.6 (2 s, $CH_2CH_3$), 63.2 and 63.7 (2 d, $^{2}J$(P-C) = 6.8 Hz each, $OCH_2$), 72.1 (d, $^{1}J$(P-C) = 159.7 Hz, P*C*), 87.0 and 97.7 (2 s, *C*≡*C*), 117.6, 123.1, 128.3, 128.5, 128.6, 129.1, 129.4, 131.5, 135.9 and 136.5 (d, $^{2}J$(P-C) = 10.2 Hz, PC-*C*).

$^{31}P$ NMR: δ 21.0.

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

Anal.Calcd. for $C_{21}H_{23}O_4P$: C, 68.10; H, 6.26. Found: C, 68.25; H, 6.19.

***Compound 16k***




Yield: 0.741 g (93%, white solid).

Mp: 114-118 $^{o}C$.

IR (KBr): 3162, 2981, 2926, 2696, 1595, 1490, 1441, 1370, 1233, 1189, 1008, 915, 751, 690, 614, 521 $cm^{-1}$.

$^{1}H$ NMR: δ 1.34-1.37 (m, 12H, $CH(CH_3)_2$), 4.70 (d, 1H, $^{2}J$(P-H) = 11.2 Hz, PC*H*),

4.82-4.85 (m, 2H, C*H*$(CH_3)_2$), 7.07-7.94 (m, 11H, C*H*=C + Ar*H*).

$^{13}$C NMR: δ 23.8, 24.0 and 24.1 (3 d, , $^2J$(P-C) = 5.2 Hz, 4.4 Hz and 3.1 Hz respectively, CH(*C*$H_3)_2$), 24.2 (s, CH(*C*$H_3)_2$), 71.6 (d, $^2J$(P-C) = 7.1 Hz, O*C*H), 72.1 (d, $^1J$(P-C) = 162.0 Hz, P*C*), 72.2 (d, $^2J$(P-C) = 6.9 Hz, O*C*H), 87.7 (d, $^3J$(P-C) = 4.0 Hz, -*C*≡CPh), 97.2 (s, C≡*C*Ph), 118.2 (d, $^3J$(P-C) = 3.0 Hz, PCC=*C*), 123.3, 128.1, 128.3, 128.9, 131.4, $136.0_8$, $136.1_0$ and 136.2 (Ar-*C*).

$^{31}$P NMR: δ 19.3.

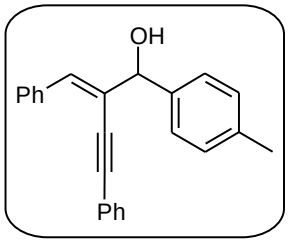
LC/MS: *m/z* 399 $[M+1]^+$.

Anal.Calcd. for $C_{23}H_{27}O_4P$: C, 69.33; H, 6.83. Found: C, 69.23; H, 6.91.

### *3.32 Synthesis non-phosphorylated alkynols 17, 18a-b and 19a-c*

Compound **17** was prepared by reduction of **11a** by following a known method.[37b] Compounds **18a-b** and **19a-c** were also prepared by following a literature procedure.[69] Among these **17** and **18a** are known and the rest are new.

***Compound 18b***




This compound was prepared by addition of *p*-tolyl magnesium bromide (4.7 mmol) to (*E*)-2-benzylidene-4-phenylbut-3-ynal **11a** (4.3 mmol) in dry THF (25 mL) at 0 $^oC$ drop-wise. The temperature was allowed to rise to rt. The mixture stirred for 1 h, quenched with aq. $NH_4Cl$ solution (2x 25 mL) and extracted with ethyl acetate (50 mL). The organic layer was washed with brine solution (50 mL), dried and the solvent removed. The crude product was purified by column chromatography using ethyl acetate/hexane (1:10) mixture as the eluent.

Yield: 0.865 g (62%, gummy liquid).

IR (neat): 3401, 3059, 3027, 2195, 1950, 1892, 2922, 2859, 1669, 1599, 1512, 1491, 1445, 1181, 1030, 920, 820, 756, 693 $cm^{-1}$.

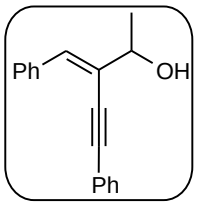
$^{1}$H NMR: δ 2.37 (s, 3H, ArC*H*$_3$), 5.45 (s, 1H, C*H*OH), 7.01-7.94 (m, 11H, C*H*=C + Ar*H*).

$^{13}$C NMR: δ 21.3 (Ar*C*H$_3$), 77.7 (*C*HOH), 87.1 and 98.1 (*C*≡*C*), 123.2, 124.6, 126.6, 128.3, 128.4, 129.0, 129.1, 131.6, 134.0, 136.1, 137.6 and 139.1 (Ar*C* + *C*=*C*).

LC/MS: *m/z* 325 $[M+1]^+$.

Anal.Calcd. for $C_{24}H_{20}O$: C, 88.85; H, 6.21. Found: C, 88.71; H, 6.28.

***Compound 19a***




This compound was prepared by a route similar to that for **18b** using (*E*)-2-benzylidene-4-phenylbut-3-ynal **11a** (1.00 g, 4.3 mmol) and 1.6M $CH_3Li$ (2.8 mL, 1.1 equiv).

Yield: 0.897 g (84%, gummy liquid).

IR (neat): 3401, 3061, 3025, 2195, 1952, 1885, 2976, 2928, 1597, 1489, 1445, 1146, 1071, 918, 754, 691 $cm^{-1}$.

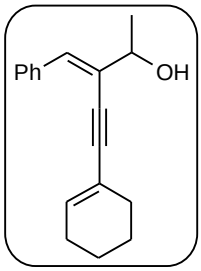
$^{1}$H NMR: δ 1.55 (d, 3H, $^{3}J$(H-H) = 6.4 Hz, CHC*H*$_3$), 1.95 (s, 1H, CHO*H*), 4.56 (q, 1H, $^{3}J$(H-H) = 6.5 Hz, C*H*CH$_3$), 6.86 (s, 1H, C*H*=C), 7.29-7.92 (m, 10H, Ar*H*).

$^{13}$C NMR: δ 23.0 (CH*C*H$_3$), 72.3 (*C*HCH$_3$), 86.7 and 97.8 (*C*≡*C*), 123.2, 126.1, 128.4, 128.5, 128.6, 128.9, 131.6, 133.3 and 136.1 (Ar*C* + *C*=*C*).

LC/MS: *m/z* 249 $[M+1]^+$.

Anal.Calcd. for $C_{18}H_{16}O$: C, 87.06; H, 6.49. Found: C, 86.91; H, 6.57.

***Compound 19b***




This compound was prepared by a route similar to that for **18b** using (*E*)-2-benzylidene-4-cyclohexenylbut-3-ynal **11d** (1.00 g, 4.4 mmol) and 1.6M $CH_3Li$ (3.0 mL, 1.1 equiv).

Yield: 0.733 g (66%, gummy liquid).

IR (neat): 3389, 3061, 3025, 2932, 2863, 2176, 1723, 1667, 1599, 1493, 1447, 1260, 1076, 916, 795, 756, 693 $cm^{-1}$.

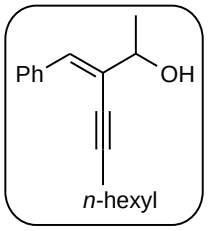
$^1H$ NMR: δ 1.47 (d, 3H, $^3J$(H-H) = 6.4 Hz, CHC*H*$_3$), 1.61-1.73 (m, 4H, $CH_2(CH_2)_2CH_2$), 1.93 (s, 1H, CHO*H*), 2.16-2.25 (m, 4H, =C$H_2$), 4.46 (br s, 1H, C*H*$CH_3$), 6.21-6.23 ($CH_2$C*H*=C), 6.73 (s, 1H, C*H*=C), 7.25-7.86 (m, 5H, Ar*H*).

$^{13}C$ NMR: δ 21.5, 22.3, 22.9, 25.9 and 29.0 (CH*C*$H_3$ + cyclohexenyl), 72.3 (*C*HOH), 84.0 and 100.2 (*C*≡*C*), 120.9, 126.4, 128.1, 128.2, 128.7, 132.0, 136.0 and 136.2 (Ar*C* + *C*=*C*).

LC/MS: *m/z* 253 $[M+1]^+$.

Anal.Calcd. for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.51; H, 7.89.

***Compound 19c***




This compound was prepared by a route similar to that for **18b** using (*E*)-2-benzylidene-4-cyclohexenylbut-3-ynal **11g** (1.00g, 4.2mmol) and 1.6M $CH_3Li$ (2.9 mL, 1.1 equiv).

Yield: 0.689 g (64%, gummy liquid).

IR (neat): 3391, 3061, 3025, 2930, 2859, 2209, 1946, 1885, 1694, 1599, 1493,

1449, 1368, 1325, 1181, 1076, 920, 891, 756, 694 $cm^{-1}$.

$^1$H NMR: δ 0.91 (t, 3H, $^3J$(H-H) = 6.0 Hz, $CH_2CH_3$), 1.31-1.34 (m, 4H, hexyl), 1.45 (d, 3H, $^3J$(H-H) = 6.4 Hz, $CHCH_3$), 1.62-1.67 (m, 2H, hexyl), 1.90 (d, $^3J$(H-H) = 5.6 Hz, CHO*H*), 2.48 (t, 2H, $^3J$(H-H) = 7.0 Hz, $\equiv CCH_2CH_2$), 4.39-4.45 (m, 1H, C*H*OH), 6.70 (s, 1H, C*H*=C), 7.25-7.86 (m, 5H, Ar*H*).

$^{13}$C NMR: δ 14.1, 19.9, 22.6, 22.8, 28.5, 28.7 and 31.4 (*n*-hexyl + $CHCH_3$), 72.4 (*C*HOH), 77.5 and 99.7 (*C*≡*C*), 126.7, 127.9, 128.1, 128.5, 131.6 and 136.2 (ArC + *C*=*C*).

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

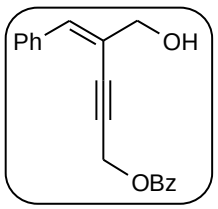
Anal.Calcd. for $C_{18}H_{24}O$: C, 84.32; H, 9.44. Found: C, 84.16; H, 9.38.

## 3.4 Synthesis of β-hydroxy propargylic esters 20a-j, 21a-l and 22, γ-hydroxy propargylic esters 23, phosphorus containing β-hydroxy propargylic esters 24a-e and 25

### *3.41 Synthesis of β-hydroxy propargylic esters 20a-j*

By following a known route,[37b] a mixture of (*Z*)-2-iodo-3-phenylprop-2-en-1-ol **6** (400 mg, 1.54 mmol), $PdCl_2$ (8 mg, 0.03 mol equiv), $PPh_3$ (21 mg, 0.06 mol equiv) and CuI (18 mg, 0.06 mol equiv) in triethylamine (5 mL) was added the appropriate terminal propargylic ester **8a-h**, **10a** and **10c** (1.5 equiv). The contents were stirred for 6 h at rt. The reaction mixture was filtered and the solvent removed from the filtrate in vacuum. The crude product was purified by column chromatography using silica gel with EtOAc/ hexane (1:5) mixture as the eluent.

***Compound 20a***




Yield: 0.369 g (82%, gummy liquid).

IR (neat): 3439, 3063, 3030, 2928, 2859, 2216, 1725, 1601, 1493, 1451, 1269, 1107, 758, 712 $cm^{-1}$.

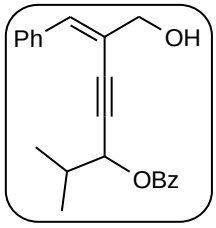
$^{1}$H NMR: δ 4.32 (s, 2H, C*H*$_2$OH), 5.17 (s, 2H, C*H*$_2$OBz), 6.84 (s, 1H, PhC*H*=C), 7.29-8.12 (m, 10H, Ar-*H*).

$^{13}$C NMR: δ 53.5 (*C*H$_2$-OBz), 67.1 (*C*H$_2$OH), 84.6 and 90.9 (*C*≡*C*), 120 3, 128.4, 128.5, 128.6, 128.8, 129.6, 129.9, 133.4, 135.5, 135.6 (Ar*C* + *C*=*C*) and 166.0 (Ph*C*=O).

LC/MS: *m/z* 293 [M+1]$^{+}$.

Anal.Calcd. for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52. Found: C, 77.93; H, 5.61.

***Compound 20b***




Yield: 0.371 g (72%, gummy liquid).

IR (neat): 3446, 3057, 2970, 2926, 2871, 2150 (w), 1721, 1600, 1447, 1266, 1178, 1101, 1074, 1025, 964, 921 cm$^{-1}$.

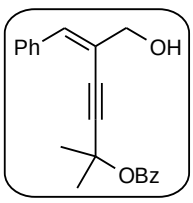
$^{1}$H NMR: δ 1.14 and 1.17 (2 d, 6H, $^{3}J$(H-H) = 6.8 Hz each, (C*H*$_3$)$_2$CH), 2.00 (t, 1H, $^{3}J$(H-H) = 6.6 Hz, CH$_2$O*H*), 2.23-2.28 (m, 1H, (CH$_3$)$_2$C*H*), 4.30 (d, 2H, $^{3}J$(H-H) = 6.0 Hz C*H*$_2$OH), 5.67 (d, $^{3}J$(H-H) = 5.6 Hz, 1H, BzOC*H*-), 6.81-8.12 (m, 11H, Ar-*H* + C*H*=C).

$^{13}$C NMR: δ 18.0, 18.4 ((*C*H$_3$)$_2$CH), 32.7 ((CH$_3$)$_2$*C*H), 67.1 (*C*H-OBz), 70.3 (*C*H$_2$OH), 84.0 and 93.4 (*C*≡*C*), 120 6, 128.2, 128.4, 128.5, 128.7, 129.8, 130.0, 133.3, 134.7, 135.7 (Ar*C* + *C*=*C*) and 165.8 (Ph*C*=O).

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

HRMS (ESI): Calcd. for $C_{22}H_{22}O_3Na$ [M$^{+}$+Na]: *m/z* 357.1467. Found: 357.1469.

***Compound 20c***




Yield: 0.414 g (84%, gummy liquid).

IR (neat): 3434, 3063, 3027, 2986, 2934, 2865, 2207, 1968, 1723, 1451, 1281, 1105, 1026, 756, 714, 693 $cm^{-1}$.

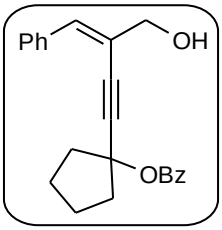
$^1H$ NMR: δ 1.90 (s, 6H, C($CH_3$)$_2$), 2.53 (s, 1H, $CH_2OH$), 4.29 (s, 2H, $CH_2OH$), 6.73 (s, 1H, C*H*=C), 7.28-8.06 (m, 10H, Ar*H*).

$^{13}C$ NMR: δ 29.0 (C($CH_3$)$_2$), 67.3 ($CH_2OH$), 73.1 ($Me_2C$-OBz), 82.5 and 98.4 (*C*≡*C*), 121.1, 128.2, 128.4, 128.7, 129.7, 130.8, 133.1, 134.1, 135.8 (Ar*C* + *C*=*C*) and 165.3 (O*C*OPh).

LC/MS: *m/z* 321 $[M+1]^+$.

Anal.Calcd. for $C_{21}H_{20}O_3$: C, 78.73; H, 6.29. Found: C, 78.65; H, 6.36.

***Compound 20d***




Yield: 0.435 g (81%, gummy liquid).

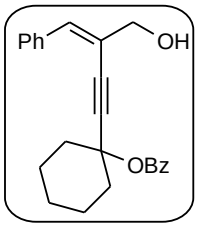
IR (neat): 3436, 3063, 2960, 2867, 2220 (w), 1980 (w), 1718, 1599, 1444, 1278, 1107, 1030 $cm^{-1}$.

$^1H$ NMR: δ 1.02 (t, $^3J$(H-H) = 7.2 Hz, 1H, $CH_2OH$), 1.85-1.89 and 2.31-2.51 (m, 8H, cyclopentyl-*H*), 4.28 (s, 2H, $CH_2OH$), 6.72 (s, 1H, ArC*H*=C), 7.24-8.04 (m, 10H, Ar-*H*).

$^{13}C$ NMR: δ 23.5 and 40.4 (cyclopentyl), 67.2 ($CH_2OH$), 81.7 (*C*OBz), 83.1 and 97.7 (*C*≡*C*), 121.3, 128.2, 128.3, 128.4, 128.6, 129.7, 130.6, 133.1, 133.9, 135.8 (Ar*C* + *C*=*C*) and 165.5 (O*C*OPh).

HRMS (ESI): Calcd. for $C_{23}H_{22}NaO_3$ $[M^+$+Na]: *m/z* 369.1467. Found: 369.1466.

***Compound 20e***




Yield: 0.488 g (88%, gummy liquid).

IR (neat): 3468, 3068, 3025, 2931, 2860, 2197, 1704, 1600, 1452, 1288, 1184, 1118, 1074, 910, 756, 707 $cm^{-1}$.

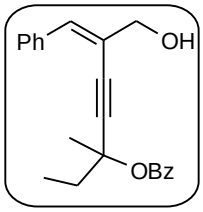
$^1H$ NMR: δ 1.45-1.77 (m, 6H, cyclohexyl-*H*), 2.12-2.35 (m, 4H, cyclohexyl-*H*), 2.72 (s, 1H, $CH_2OH$), 4.29 (s, 2H, $CH_2OH$), 6.72 (s, 1H, C*H*=C), 7.24-8.08 (m, 10H, Ar*H*).

$^{13}C$ NMR: δ 22.6, 25.1 and 37.0 (cyclohexyl-*C*), 67.1 ($CH_2OH$), 76.5 (*C*OBz), 84.3 and 97.5 (*C*≡*C*), 121.3, 128.1, 128.2, 128.3, 128.6, 129.6, 130.8, 133.0, 133.6, 135.8 (Ar*C* + *C*=*C*) and 165.1 (O*C*OPh).

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

Anal.Calcd. for $C_{24}H_{24}O_3$: C, 79.97; H, 6.71. Found: C, 79.85; H, 6.63.

***Compound 20f***




Yield: 0.440 g (82%, gummy liquid).

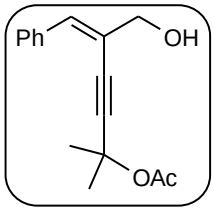
IR (neat): 3446, 3058, 2970, 2934, 2877, 2220 (w), 1723, 1495, 1444, 1268, 1107, 1066, 1024, 714 $cm^{-1}$.

$^1H$ NMR: δ 1.17 (t, $^3J$(H-H) = 7.4 Hz, 1H, $CH_2CH_3$), 1.88 (s, 3H, $CH_3$), 2.03-2.23 (m, 2H, $CH_2CH_3$), 2.62 (s, 1H, $CH_2OH$), 4.30 (s, 2H, $CH_2OH$), 6.72 (s, 1H, ArC*H*=C), 7.26-8.06 (m, 10H, Ar-*H*).

$^{13}C$ NMR: δ 8.8 ($CH_2CH_3$), 26.1 and 34.7 ($CH_3$ + $CH_2CH_3$), 67.3 ($CH_2OH$), 76.8 (*C*OBz), 83.6 and 97.5 (*C*≡*C*), 121.3, 128.2, 128.3, 128.4, 128.6, 129.6, 130.9, 133.0, 133.9, 135.8 (Ar*C* + *C*=*C*) and 165.3 (O*C*OPh).

HRMS (ESI): Calcd. for $C_{22}H_{22}NaO_3$ $[M^+$+Na]: *m/z* 357.1467. Found: 357.1468.

***Compound 20g***



Yield: 0.368 g (92%, gummy liquid).

IR (neat): 3426, 3058, 3025, 2988, 2936, 2865, 2215, 1740, 1600, 1495, 1447, 1368, 1244, 1129, 1019, 756, 694 $cm^{-1}$.

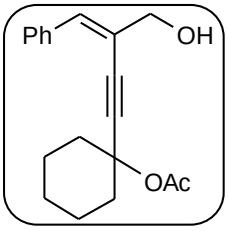
$^1$H NMR: δ 1.74 (s, 6H, $(CH_3)_2C$), 2.06 (s, 3H, $OCOCH_3$), 4.27 (s, 1H, $CH_2OH$), 6.72-7.83 (m, 6H, Ar-*H* + C*H*=C).

$^{13}$C NMR: δ 22.0 ($COCH_3$), 28.8 ($(CH_3)_2C$), 67.0 ($CH_2OH$), 72.4 (*C*-OAc), 82.1 and 98.2 (*C*≡*C*), 121.1, 128.1, 128.3, 128.6, 134.0, 135.8 (Ar*C* + *C*=*C*) and 169.9 ($CH_3C$=O).

LC/MS: *m/z* 259 $[M+1]^+$.

Anal.Calcd. for $C_{16}H_{18}O_3$: C, 74.39; H, 7.02. Found: C, 74.21; H, 7.13.

***Compound 20h***




Yield: 0.268 g (56%, gummy liquid).

IR (neat): 3461, 3060, 3025, 2938, 2861, 2190 (vw), 2310 (w), 1742, 1601, 1495, 1449, 1368, 1267, 1233, 1022, 963, 916, 756, 694 $cm^{-1}$.

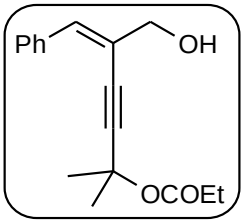
$^1$H NMR: δ 1.57-1.90 (m, 8H, cyclohexyl-*H*), 2.07 (s, 3H, $OCOCH_3$), 2.21-2.24 (m, 2H, cyclohexyl-H), 2.60 (br s, $CH_2OH$), 4.28 (d, $^3J$(H-H) = 4.8 Hz, 2H, $CH_2OH$), 6.71-7.84 (m, 6H, Ar-*H* + C*H*=C).

$^{13}$C NMR: δ 22.1, 22.7, 25.2 and 37.0 (cyclohexyl-*C* + $OCOCH_3$), 67.4 ($CH_2OH$), 76.1 (*C*-OAc), 84.1 and 97.8 (*C*≡*C*), 121.5, 128.2, 128.3, 128.7, 133.7, 135.9 (Ar*C* + *C*=*C*) and 169.9 ($CH_3C$=O).

LC/MS: *m/z* 299 $[M+1]^+$.

Anal.Calcd. for $C_{19}H_{22}O_3$: C, 76.48; H, 7.43. Found: C, 76.58; H, 7.36.

***Compound 20i***




Yield: 0.327 g (78%, gummy liquid).

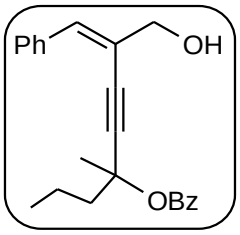
IR (neat): 3459, 3059, 2986, 2940, 2867, 2350 (vw), 2210 (w), 1742, 1599, 1449, 1381, 1362, 1254, 1190, 1125, 1078, 918, 874, 808, 756, 694 $cm^{-1}$.

$^{1}H$ NMR: δ 1.14 (t, 3H, $^{3}J$(H-H) = 7.4 Hz, C*H*$_3$CH$_2$), 1.74 (s, 6H, (C*H*$_3$)$_2$C), 2.33 (qrt, 2H, $^{3}J$(H-H) = 6.8 Hz, CH$_3$C*H*$_2$), 2.52 (br s, 1H, CH$_2$O*H*), 4.27 (s, 2H, C*H*$_2$OH), 6.72-7.83 (m, 6H, Ar-*H* + C*H*=C).

$^{13}C$ NMR: δ 9.0 (CH$_2$*C*H$_3$), 28.3 (*C*H$_2$CH$_3$), 28.8 (C(*C*H$_3$)$_2$), 66.9 (*C*H$_2$OH), 72.2 (*C*-OCOEt), 82.1 and 98.2 (*C*≡*C*), 121.1, 128.1, 128.2, 128.6, 133.8, 135.8 (Ar*C* + *C*=*C*) and 173.3 (CH$_3$*C*=O).

HRMS (ESI): Calcd. for $C_{17}H_{20}NaO_3$ [$M^+$+Na]: *m/z* 295.1310. Found: 295.1310.

***Compound 20j***




Yield: 0.413 g (77%, gummy liquid).

IR (neat): 3452, 3057, 3030, 2959, 2931, 2866, 2150 (w), 1715, 1452, 1282, 1112, 1069, 1025, 712, 690 $cm^{-1}$.

$^{1}H$ NMR: δ 1.03 (t, 3H, $^{3}J$(H-H) = 7.4 Hz, C*H*$_3$CH$_2$), 1.65-1.71 (m, 3H, CH$_3$C*H*$_2$ + CH$_2$O*H*), 1.88 (s. 3H, C*H*$_3$), 2.01-2.15 (m, 2H, CH$_3$CH$_2$C*H*$_2$), 4.29 (s, C*H*$_2$OH), 6.72 (s, 1H, C*H*=C), 7.27-8.05 (m, 10H, Ar-*H*).

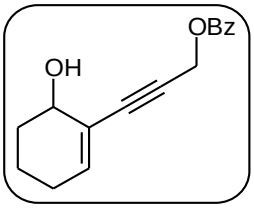
$^{13}C$ NMR (125MHz): δ 14.3, 17.9, 26.3, 43.9 (alkyl-*C*), 67.5 (*C*H$_2$OH), 76.4 (*C*-OCOPh), 83.5 and 98.0 (*C*≡*C*), 121.4, 128.2, 128.4$_0$, 128.4$_2$, 128.7, 129.7, 131.0, 133.1, 133.9, 135.8 (Ar*C* + *C*=*C*) and 165.3 (Ph*C*=O).

HRMS (ESI): Calcd. for $C_{23}H_{24}NaO_3$ [$M^+$+Na]: *m/z* 371.1623. Found: 371.1621.

### *3.42 Synthesis of β-hydroxy propargylic esters 21a-l*

By following a new route[37b], to a mixture of 2-iodocyclohex-2-enol **7** (400 mg, 1.80 mmol), $PdCl_2$ (10 mg, 0.03 mol equiv), $Fu_3P$ (25 mg, 0.06 equiv) and CuI (21 mg, 0.06 equiv) in triethylamine (6 mL) was added the appropriate alkyne **8a-i, 10b, 10d** and **10g** (2.4 mmol, 1.5 equiv) through a micropipette. The contents were stirred for 6 h at rt. The reaction mixture was filtered and the solvent removed in vacuum. The crude product was purified by column chromatography using silica gel with EtOAc/ hexane mixture (1:5) as the eluent.

***Compound 21a***




Yield: 0.325 g (70%, gummy liquid).

IR (neat): 3443, 3061, 2946, 2870, 2300 (w), 2230, 1728, 1603, 1580, 1453, 1271, 1109, 739 $cm^{-1}$.

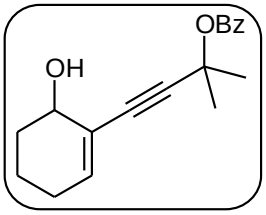
$^1$H NMR: δ 1.57-2.19 (m, 6H, cyclohexenyl-C*H*$_2$), 4.19 (br s, 1H, C*H*OH), 5.06 (s, 2H, C*H*$_2$OBz), 6.29 (t, 1H, $^3J$(H-H) = 4.0 Hz, =C*H*CH$_2$), 7.42-8.08 (m, 5H, Ar-*H*).

$^{13}$C NMR: δ 17.9, 25.9 and 30.6 (cyclohexenyl-*C*H$_2$), 53.4 (O*C*H$_2$), 66.6 (*C*HOH), 82.8 and 85.9 (*C*≡*C*), 123.3, 128.3, 129.5, 129.8, 133.3, 139.1 (Ar-*C* + *C*=*C*) and 166.0 (Ph*C*=O).

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

Anal.Calcd. for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 74.85; H, 6.21.

***Compound 21b***




Yield: 0.437 g (86%, gummy liquid).

IR (neat): 3470, 3063, 2986, 2940, 2868, 2300 (vw), 2220 (w), 1719, 1603, 1584, 1283, 1107, 714 $cm^{-1}$.

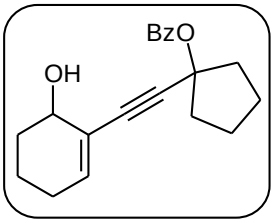
$^{1}H$ NMR: δ 1.55-1.79 (m, 4H, cyclohexenyl-C$H_2$), 1.82 (s, 6H, ($CH_3$)$_2$C), 1.96-2.11 (m, 2H, cyclohexenyl-C$H_2$), 4.20-4.21 (m, 1H, $CH_2$C*H*OH), 6.16 (t, 1H, $^{3}J$(H-H) = 3.8 Hz, =C*H*$CH_2$), 7.40-7.56 and 8.01-8.03 (m, 5H, Ar-*H*).

$^{13}C$ NMR: δ 19.0, 25.8, 29.0, 29.2 and 30.3 (cyclohexenyl-*C*$H_2$ + C(*C*$H_3$)$_2$), 67.2 (*C*HOH), 73.1 (*C*-OBz), 83.6 and 91.1 (*C*≡*C*), 124.4, 128.3, 129.7, 130.9, 132.9, 136.5 (*C*=*C* + Ar-*C*) and 165.4 (Ph*C*=O).

LC/MS: *m/z* 285 $[M+1]^{+}$.

Anal.Calcd. for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09. Found: C, 76.13; H, 7.15.

***Compound 21c***




Yield: 0.426 g (76%, gummy liquid).

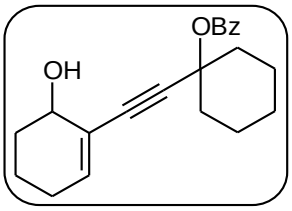
IR (neat): 3467, 2939, 2867, 2215, 1950 (w), 1713, 1599, 1444, 1273, 1164, 1102, 962, 709 $cm^{-1}$.

$^{1}H$ NMR: δ 1.55-1.67, 1.72-1.85, 1.93-1.99, 2.01-2.27 and 2.41-2.44 (m, 14H, cyclohexenyl-C$H_2$ and cyclopentyl-*H*), 4.19 (t, $^{3}J$(H-H) = 6.2 Hz, C*H*OH), 6.15 (t, 1H, $^{3}J$(H-H) = 4.0 Hz, =C*H*$CH_2$), 7.40-8.02 (m, 5H, Ar-*H*).

$^{13}C$ NMR: δ 18.9, 23.5, 25.8, 30.3, 40.6 (cyclopentyl-*C* and cyclohexenyl-*C*$H_2$), 67.1 (*C*HOH), 81.8 (*C*-OBz), 84.2 and 90.3 (*C*≡*C*), 124.5, 128.3, 129.7, 130.0, 133.0, 136.5 (Ar*C* + *C*=*C*) and 165.6 (Ph*C*=O).

HRMS (ESI): Calcd. for $C_{20}H_{22}NaO_3$ $[M^{+}+Na]$: *m/z* 333.1467. Found: 333.1466.

***Compound 21d***




Yield: 0.473 g (81%, gummy liquid).

IR (neat): 3519, 2936, 2861, 2218, 1721, 1601, 1451, 1283, 1250, 1109, 914, 712 $cm^{-1}$.

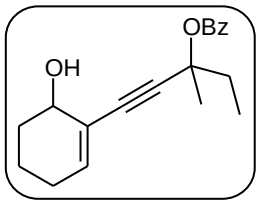
$^{1}H$ NMR: δ 1.45-1.80 and 1.98-2.21 (m, 16H, cyclohexenyl-C$H_2$ + cyclohexyl-C$H_2$), 4.20 (t, 1H, $^{3}J$(H-H) = 5.4 Hz, $CH_2CHOH$), 6.17 (t, 1H, $^{3}J$(H-H) = 4.2 Hz, =C$H$C$H_2$), 7.41-8.05 (m, 5H, Ar-*H*).

$^{13}C$ NMR: δ 19.1, 22.6, 25.2, 25.8, 30.3 and 37.3 (cyclohexenyl-*C*$H_2$ + cyclohexyl-C$H_2$), 67.3 (*C*HOH), 76.5 (*C*-OBz), 85.3 and 90.3 (*C*≡*C*), 124.6, 128.3, 129.7, 131.1, 132.9, 136.4 (Ar*C* + *C*=*C*) and 165.2 (Ph*C*=O).

LC/MS: *m/z* 325 $[M+1]^{+}$.

Anal.Calcd. for $C_{21}H_{24}O_3$: C, 77.75; H, 7.46. Found: C, 77.63; H, 7.36.

***Compound 21e*** (mixture of diastereomers)




Yield: 0.435 g (81%, gummy liquid).

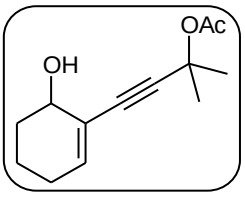
IR (neat): 3482, 2980, 2933, 2876, 2213, 1721, 1447, 1281, 1105, 1022, 717 $cm^{-1}$.

$^{1}H$ NMR: δ 1.10-1.15 (m, 6H, $CH_2CH_3$), 1.54-1.76 and 1.81-2.15 (m, 22H, $CH_3$ + $CH_2CH_3$ + cyclohexenyl-C$H_2$), 3.13 (s, 2H, CHO*H*), 4.19 and 4.23 (2 br s, 2H, C*H*OH), 6.17 (br s, 2H, C=C*H*$CH_2$), 7.41-8.03 (m, 10H, Ar-*H*).

$^{13}C$ NMR: δ 8.8 ($CH_2CH_3$), 19.0, 25.8, 26.3, 30.3, 34.7 and 34.9 (cyclohexenyl-*C*$H_2$ + *C*$H_3$ + *C*$H_2CH_3$), 67.2, 67.3 and 76.8 (*C*HOH + *C*-OBz), 84.7 and 90.0 (*C*≡*C*), 124.5, 128.3, 129.6, 131.0, 132.9, 136.2, 136.5 (*C*=*C* + Ar-*C*), 165.3 and 165.5 (Ph*C*=O).

HRMS (ESI): Calcd. for $C_{19}H_{22}NaO_3$ $[M^{+}+Na]$: *m/z* 321.1467. Found: 321.1465.

***Compound 21f***




Yield: 0.320 g (80%, gummy liquid).

IR (neat): 3470, 2988, 2940, 2870, 2300 (vw), 2224, 1734, 1672, 1368, 1271, 1244, 1129, 1017 $cm^{-1}$.

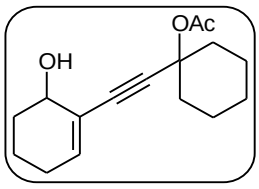
$^{1}H$ NMR: δ 1.52-1.65 (m, 2H, cyclohexenyl-C*H*$_2$), 1.66 (s, 6H, (C*H*$_3$)$_2$C), 1.72-1.79 and 1.93-1.99 (m, 2H, cyclohexenyl-C*H*$_2$), 2.02 (s, 3H, OCOC*H*$_3$), 2.05-2.13 (m, 2H, cyclohexenyl-*H*), 2.86 (br s, 1H, CHO*H*), 4.17 (t, 1H, $^{3}J$(H-H) = 6.2 Hz, CH$_2$C*H*OH), 6.15 (t, 1H, $^{3}J$(H-H) = 3.8 Hz, =C*H*CH$_2$).

$^{13}C$ NMR: δ 18.8, 22.0, 25.7, 28.8, 29.0 and 30.2 (cyclohexenyl-*C*H$_2$+ C(*C*H$_3$)$_2$ + OCO*C*H$_3$), 67.0 (*C*HOH), 72.4 (*C*-OAc), 83.2 and 90.9 (*C*≡*C*), 124.3, 136.5 (*C*=*C*) and 169.9 (CH$_3$*C*=O).

LC/MS: *m/z* 223 $[M+1]^{+}$.

Anal.Calcd. for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.15; H, 8.23.

***Compound 21g***




Yield: 0.294 g (62%, gummy liquid).

IR (neat): 3468, 2938, 2863, 2218, 1740, 1449, 1768, 1269, 1233, 1020 $cm^{-1}$.

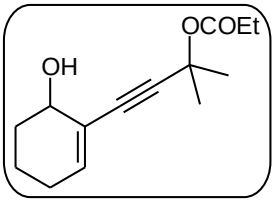
$^{1}H$ NMR: δ 1.28-1.84 (m, 12H, cyclohexenyl-C*H*$_2$ + cyclohexyl-*H*), 2.04 (s, 3H, OCOC*H*$_3$), 2.07-2.13 (m, 4H, cyclohexenyl-C*H*$_2$ + cyclohexyl-H), 2.90 (br s, 1H, CHO*H*), 4.18 (t, 1H, $^{3}J$(H-H) = 6.4 Hz, CH$_2$C*H*OH), 6.16 (t, 1H, $^{3}J$(H-H) = 4.0 Hz, =C*H*CH$_2$).

$^{13}C$ NMR: δ 19.0, 22.1, 22.7, 25.2, 25.8, 30.3, 37.0 and 37.2 (cyclohexenyl-*C*H$_2$ + cyclohexyl-*C* + OCO*C*H$_3$), 67.3 (*C*HOH), 76.0 (*C*-OAc), 85.1 and 90.2 (*C*≡*C*), 124.6, 136.3 (*C*=*C*) and 169.9 (CH$_3$*C*=O).

LC/MS: *m/z* 263 $[M+1]^+$.

Anal.Calcd. for $C_{16}H_{22}O_3$: C, 73.25; H, 8.45. Found: C, 73.16; H, 8.35.

***Compound 21h***




Yield: 0.360 g (84%, gummy liquid).

IR (neat): 3478, 2986, 2942, 2874, 2350 (w), 2220, 1732, 1628, 1462, 1362, 1275, 1190, 1129, 1080, 997 $cm^{-1}$.

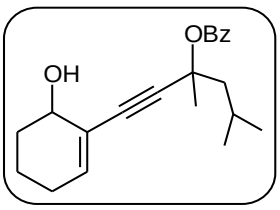
$^1$H NMR: δ 1.11 (t, 3H, $^3J$(H-H) = 7.4 Hz, C*H*$_3$CH$_2$), 1.68-2.11 (m, 12H, (C*H*$_3$)$_2$C + cyclohexenyl-C*H*$_2$), 2.29 (qrt, 2H, $^3J$(H-H) = 7.6 Hz, CH$_3$C*H*$_2$), 2.95 (br s, 1H, CHO*H*), 4.17 (br s, 1H, C*H*OH), 6.14 (t, 1H, $^3J$(H-H) = 4.0 Hz, =C*H*CH$_2$).

$^{13}$C NMR: δ 9.0, 19.0, 25.8, 28.4, 28.9, 29.1 and 30.3 (cyclohexenyl-*C*H$_2$ + C(*C*H$_3$)$_2$ + OCO*C*H$_2$*C*H$_3$), 67.2 (*C*HOH), 72.2 (*C*-OCOEt), 83.1 and 91.3 (*C*≡*C*), 124.5, 136.4 (*C*=*C*) and 173.6 (Et*C*=O).

LC/MS: *m/z* 237 $[M+1]^+$.

Anal.Calcd. for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 71.23; H, 8.45.

***Compound 21i*** (two diastereomers)




Yield: 0.385 g (66%, gummy liquid).

IR (neat): 3485, 3069, 2959, 2850, 2219, 1710, 1606, 1452, 1277, 1107, 1025, 712 $cm^{-1}$.

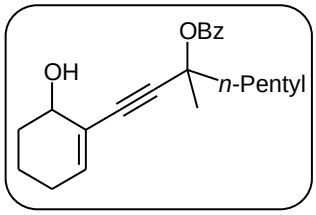
$^1$H NMR: δ 1.03-1.09 (m, 12H, CH(C*H*$_3$)$_2$), 1.61-1.66, 1.74-1.90 and 1.96-2.13 (m, 24H, C*H*$_3$ + C*H*$_2$C*H*Me$_2$ + cyclohexenyl-C*H*$_2$), 3.13 (br s, 2H, CHO*H*), 4.18 and 4.23 (2 t, $^3J$(H-H)=6.2 Hz and 6.0 Hz respectively, 2H,

$CH_2CHOH$), 6.14-6.17 (m, 2H, C=C*H*), 7.40-7.57 and 8.00-8.02 (m, 10H, Ar-*H*).

$^{13}$C NMR: δ 19.0, 24.1, 24.2, 25.1, 25.8, 27.3, 27.5, 30.2, 49.8 and 50.0 ($(CH_3)_2CHCH_2$ + $CH_3$ + cyclohexenyl-$CH_2$), 67.2 and 76.4 (*C*HOH + *C*-OBz), 84.9 and 90.4 (*C*≡*C*), 124.4, 128.4, 128.5, 129.7, 130.2, 131.0, 133.0, 136.2, 136.6 (*C*=*C* + Ar-*C*), 165.4 and 165.6 (Ph*C*=O).

HRMS (ESI): Calcd. for $C_{21}H_{26}NaO_3$ $[M^+ + Na]$: *m/z* 349.1780. Found: 349.1780.

***Compound 21j*** (two diastereomers)




Yield: 0.438 g (72%, gummy liquid).

IR (neat): 3493, 3058, 2939, 2867, 2215, 1713, 1604, 1449, 1273, 1107, 1024, 719 $cm^{-1}$.

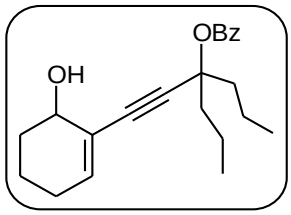
$^1$H NMR: δ 0.92 (br s, 6H, $CH_3CH_2$), 1.36 (br s, 8H, pentyl-*H*), 1.54-1.64, 1.74-1.80 and 1.90-2.10 (m, 26H, $CH_3$ + cyclohexenyl-$CH_2$ + pentyl-*H*), 4.18 and 4.23 (2 br s, 2H, C*H*OH), 6.16 and 6.17 (2 br s, 2H, =C*H*$CH_2$), 7.27-8.01 (m, 10H, Ar-*H*).

$^{13}$C NMR: δ 14.1, 19.0, 22.6, $24.0_0$, $24.0_3$, 25.8, $26.7_5$, $26.8_0$, 30.2, 31.8, 41.6 and 41.8 (cyclohexenyl-$CH_2$ + pentyl-*C* + $CH_3$), 67.2 and 67.3 (*C*HOH), 76.4 and 76.8 (*C*-OBz), $84.6_0$, $84.6_1$ and 90.3 (*C*≡*C*), 124.5, 128.3, 129.7, 131.0, 132.9, 136.2 and 136.6 (*C*=*C* + Ar-*C*), 165.4 and 165.5 (Ph*C*=O).

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

Anal.Calcd. for $C_{22}H_{28}O_3$: C, 77.61; H, 8.29. Found: C, 77.52; H, 8.15.

***Compound 21k***



Yield: 0.445 g (73%, gummy liquid).

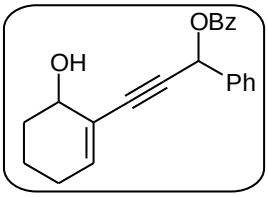
IR (neat): 3485, 2970, 2926, 2866, 2214, 1715, 1606, 1452, 1277, 1112, 1025, 712 $cm^{-1}$.

$^1$H NMR: δ 0.98 (t, $^3J$(H-H) =7.0 Hz, 6H, C*H*$_3$CH$_2$), 1.48-1.78 and 1.95-2.14 (m, 14H, C*H*$_2$C*H*$_2$CH$_3$ + cyclohexenyl-C*H*$_2$), 3.16 (br s, 1H, CHO*H*), 4.21 (br s, 1H, C*H*OH), 6.16 (t, $^3J$(H-H) =3.6 Hz, 1H, CH$_2$C*H*=C), 7.40-8.01 (m, 5H, Ar-*H*).

$^{13}$C NMR: δ 14.3 (*C*H$_3$CH$_2$), 17.6$_5$ and 17.7$_0$ (CH$_3$*C*H$_2$CH$_2$), 19.1, 25.8 and 30.3 (cyclohexenyl-*C*H$_2$), 40.9 and 41.0 (CH$_3$CH$_2$*C*H$_2$), 67.3 (*C*HOH), 79.7 (*C*-OBz), 85.5 and 89.6 (*C*≡*C*), 124.6, 128.4, 129.7, 131.1, 132.9, 136.2 (alkenyl-*C* + Ar-*C*), 165.4 (O*C*OPh).

HRMS (ESI): Calcd. for $C_{22}H_{28}NaO_3$ [$M^+$+Na]: *m/z* 363.1936. Found: 363.1937.

***Compound 21l***




Yield: 0.479 g (80%, gummy liquid).

IR (neat): 3447, 3058, 3030, 2937, 2866, 2219, 1726, 1600, 1496, 1458, 1321, 1260, 1101, 1069 $cm^{-1}$.

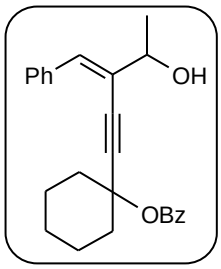
$^1$H NMR: δ 1.36-1.63 and 1.72-2.15 (m, 7H, cyclohexenyl-C*H*$_2$+ O*H*), 4.23 (br s, 1H, CH$_2$C*H*OH), 6.33 and 6.83 (2 s, 2H, PhC*H*OBz + C=C*H*), 7.37-8.09 (m, 10H, Ar-*H*).

$^{13}$C NMR: δ 18.1, 26.0, 30.5 (cyclohexenyl-*C*H$_2$), 66.8 (*C*HOH), 85.7, 85.8 and 86.6 (*C*-OBz + *C*≡*C*), 123.5, 127.8, 128.5, 128.8, 129.0, 130.0, 133.3, 137.2 and 139.1 (Ar-*C* + *C*=*C*), and 165.7 (Ph*C*=O).

HRMS (ESI): Calcd. for $C_{22}H_{20}NaO_3$ [$M^+$+Na]: *m/z* 355.1310. Found: 355.1298.

### *3.43 Synthesis of β-hydroxy propargylic ester 22*

This compound was prepared by following a procedure similar to that for **18b** using (*E*)-1-(3-formyl-4-phenylbut-3-en-1-ynyl)-cyclohexyl benzoate **15d** (400 mg, 1.1 mmol) and 1.6M $CH_3Li$ (0.75 mL, 1.0 mol equiv).




Yield: 0.194 g (46%, gummy liquid).

IR (neat): 3470, 3061, 3027, 2936, 2861, 2350 (w), 2210 (vw), 1723, 1601, 1451, 1316, 1283, 1250, 1107, 1071, 1024, 918, 754, 712 $cm^{-1}$.

$^1H$ NMR: δ 1.28 (d, $^3J$(H-H)=7.2 Hz, 3H, C*H*$_3$CH), 1.40-1.78 (m, 6H, cyclohexyl), 2.05-2.37 (m, 4H, cyclohexyl), 4.42 (qrt, $^3J$(H-H) = 6.2 Hz, 1H, $CH_3$C*H*OH), 6.71 (s, 1H, PhC*H*=C), 7.25-8.07 (m, 10H, Ar*H*).

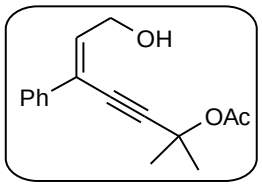
$^{13}C$ NMR: δ 22.7, 23.1, 25.2 and 37.1 (cyclohexyl + *C*$H_3$CH), 72.4 and 76.6 (*C*HOH + *C*-OBz), 83.5 and 98.2 (*C*≡*C*), 126.0, 128.2, 128.3, 128.8, 129.7, 131.0, 132.8, 133.0, 135.9 (Ar*C* + *C*=*C*) and 165.1 (O*C*OPh).

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

Anal.Calcd. for $C_{25}H_{28}O_3$: C, 79.75; H, 7.50. Found: C, 79.86; H, 7.45.

### *3.44 Synthesis of γ-hydroxy propargylic ester 23*

This compound was prepared by following a route[37b] similar to that for **20a-j** by using 3-iodo-cinnamyl alcohol **4** (1.00 g, 3.9 mmol) and the terminal propargyl acetate **8f** (0.732 g, 5.8 mmol).




Yield: 0.906 g (90%, gummy liquid).

IR (neat): 3457, 3063, 2991, 2937, 2250 (vw), 1736, 1621, 1452, 1364, 1249, 1134, 1019 $cm^{-1}$.

$^{1}$H NMR: δ 1.76 (s, 6H, C($CH_3$)$_2$), 2.06 (s, 3H, COC$H_3$), 4.52 (d, $^{3}J$(H-H) = 6.8 Hz, 2H, C$H_2$OH), 6.62 (t, $^{3}J$(H-H) = 6.7 Hz, 1H, =C*H*CH$_2$), 7.30-7.61 (m, 5H, Ar-*H*). The O*H* signal was broad.

$^{13}$C NMR: δ 22.0 (CO*C*H$_3$), 29.0 (C(*C*H$_3$)$_2$), 61.3 (*C*H$_2$OH), 72.3 (O-*C*Me$_2$), 80.6 and 97.5 (*C*≡*C*), 124.4, 126.1, 128.1, 128.4, 136.4 and 137.0 (Ar-*C*), 169.9 (*C*=O).

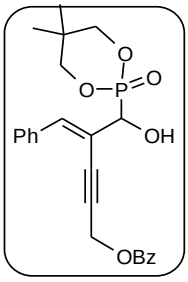
LC/MS: *m/z* 359 [M+1]$^{+}$.

Anal.Calcd. for $C_{25}H_{28}O_3$: C, 74.39; H, 7.02. Found: C, 74.23; H, 7.09.

### *3.45 Synthesis of phosphorus containing β-hydroxy propargylic esters 24a-e and 25*

These compounds were prepared by following a procedure similar to that for **16a-k**.

***Compound 24a***




This compound was synthesized from (*E*)-4-formyl-5-phenylpent-4-en-2-ynyl benzoate **15a** (0.200g, 0.7 mmol) and H-phosphonate (OCH$_2$CMe$_2$CH$_2$O)P(O)H **1a** (0.103 g, 0.7 mmol).

Yield: 0.261 g (86%, white solid).

Mp: 140-142 $^{o}$C.

IR (KBr): 3255, 2970, 2926, 2899, 2877, 2250 (w), 1743, 1452, 1375, 1266, 1112, 1052, 1003, 849, 811, 707 cm$^{-1}$.

$^{1}$H NMR: δ 0.84 and 1.15 (2 s, 6H, (C$H_3$)$_2$C) 3.92-4.00 and 4.28-4.33 (m, 4H, OC$H_2$), 4.44 (br s, 1H, C*H*OH), 4.85 (d, $^{2}J$(P-H) =11.6 Hz, 1H, PC*H*), 5.16 (s, 2H, C$H_2$OBz), 7.03-8.08 (m, 11H, PhC*H*=C + Ar-*H*).

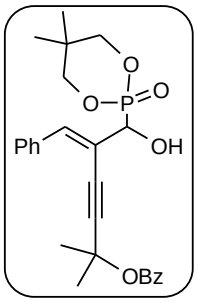
$^{13}$C NMR: δ 20.8, 22.0 (2 s, (*C*H$_3$)C), 32.5 (d, $^{3}J$(P-C)=7.8 Hz, (CH$_3$)*C*), 53.5 (s, *C*H$_2$OBz), 73.1 (d, $^{1}J$(P-C)=158.5 Hz, P*C*), 77.8 and 78.2 (2 d, $^{2}J$(P-C)=

7.0 Hz and 7.1 Hz respectively, O*C*$H_2$), 83.8 and 91.9 (2 s, *C*≡*C*), 116.3 (s, Ph*C*=C), 128.3, 128.6, 128.9, 129.1, 129.5, 129.8, 133.5, 135.3, 138.2, 138.3 (Ar-*C*), 166.0 (O*C*OPh).

$^{31}$P NMR: δ 13.1.

HRMS (ESI): Calcd. for $C_{24}H_{25}NaO_6P$ [$M^+$+Na]: *m/z* 463.1287. Found: 463.1298.

***Compound 24b***




This compound was synthesized from **15b** (0.300 g, 0.9 mmol) and H-phosphonate **1a** $(OCH_2CMe_2CH_2O)P(O)H$ (0.131 g, 0.9 mmol).

Yield: 0.405 g (92%, white solid).

Mp: 148-150 $^oC$.

IR (KBr): 3178, 2986, 2964, 2934, 2250 (vw), 1721, 1474, 1452, 1293, 1260, 1112, 1085, 833, 767, 712 $cm^{-1}$.

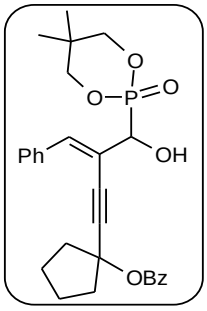
$^1$H NMR: δ 0.88 and 1.18 (2 s, 6H, (C*H*$_3$)$_2$C), 1.89 (s, 6H, (C*H*$_3$)$_2$C-O), 3.90-4.05 (m, 3H, CHO*H* + OC*H*$_2$), 4.33-4.44 (m, 2H, OC*H*$_2$), 4.79 (dd, $^2$*J*(P-H) = 11.2 Hz and $^3$*J*(H-H) = 5.4 Hz, 1H, PC*H*), 6.93 (d, $^4$*J*(P-H) = 4.4 Hz, PhC*H*=C), 7.27-8.04 (m, 10H, Ar*H*).

$^{13}$C NMR: δ 20.8 and 22.0 (2 s, (*C*H$_3$)C), 28.6 and 28.7 (2 s, (*C*H$_3$)C-O), 32.5 (d, $^3$*J*(P-C) =7.6 Hz, (CH$_3$)*C*), 73.1 (s, *C*-OBz), 73.7 (d, $^1$*J*(P-C) = 159.0 Hz, P*C*), 78.1$_0$ and 78.1$_4$ (2 s, O*C*H$_2$), 81.2 (d, $^3$*J*(P-C) = 4.2 Hz, =C-*C*≡C), 99.5 (C≡*C*-C-O), 116.3 (s, Ph*C*=C), 128.2, 128.4, 128.9, 129.1, 129.7, 130.5, 133.3, 135.3 (d, $^4$*J*(P-C) = 2.1 Hz, Ar*C*), 137.8 (d, $^2$*J*(P-C) = 11.1 Hz, PhC=*C*), 165.6 (O*C*OPh).

$^{31}$P NMR: δ 12.9.

HRMS (ESI): Calcd. for $C_{26}H_{29}NaO_6P$ [$M^+$+Na]: *m/z* 491.1600. Found: 491.1612.

***Compound 24c***




This compound was synthesized from **15d** (0.300 g, 0.9 mmol) and H-phosphonate **1a** $(OCH_2CMe_2CH_2O)P(O)H$ (0.131 g, 0.9 mmol).

Yield: 0.366 g (85%, white solid).

Mp: 146-148 $^{o}$C.

IR (KBr): 3244, 3063, 2893, 2250, 1726, 1452, 1266, 1096, 1058, 1008, 833, 712 $cm^{-1}$.

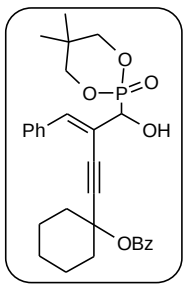
$^{1}$H NMR: δ 0.85 and 1.17 (2 s, 6H, $(CH_3)_2C$), 1.87-2.45 (m, 8H, cyclopentyl-*H*), 3.88-4.03 and 4.33-4.44 (m, 4H, $OCH_2$), 4.79 (d, $^{2}J$(P-H) = 11.2 Hz, 1H, PC*H*), 6.93 (d, $^{4}J$(P-H) = 4.4 Hz, 1H, PhC*H*=C), 7.28-8.03 (m, 10H, Ar-*H*).

$^{13}$C NMR: δ 20.7, 22.0 and 23.5 (3 s, $(CH_3)_2C$ + cyclopentyl-*C*), 32.5 (d, $^{3}J$(P-C) = 8.9 Hz, $(CH_3)C$), 40.2 (s, cyclopentyl-*C*), 73.6 (d, $^{1}J$(P-C) = 156.9 Hz, P*C*), 77.4 and 78.1 (2 s, $OCH_2$), 81.7 and 99.0 (2 s, *C*≡*C*), 116.5 (s, Ph*C*=C), 128.2, 128.5, 128.8, 129.0, 129.7, 130.5, 133.3, 135.4, 137.3 and 137.4 (Ar-*C*), 165.8 (O*C*OPh).

$^{31}$P NMR: δ 12.9.

HRMS (ESI): Calcd. for $C_{28}H_{31}NaO_6P$ [$M^{+}$+Na]: *m/z* 517.1756. Found: 517.1756.

***Compound 24d***




This compound was synthesized from **15c** (0.300 g, 0.8 mmol), and H-phosphonate **1a**

$(OCH_2CMe_2CH_2O)P(O)H$ (0.131 g, 0.9 mmol).

Yield: 0.387 g (91%, white solid).

Mp: 190-192 $^oC$.

IR (KBr): 3150, 2970, 2931, 2855, 2300 (vw), 1720, 1447, 1282, 1255, 1195, 1112, 1085, 1052, 1019, 833, 811, 762, 707 $cm^{-1}$.

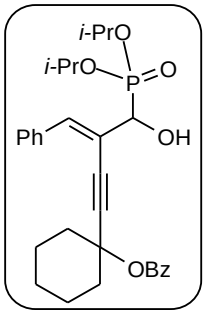
$^1H$ NMR: δ 0.87 and 1.18 (2 s, 6H, $(CH_3)_2C$), 1.75-1.81 and 2.05-2.37 (m, 10H, cyclohexyl-*H*), 3.89-4.05 (m, 2H, $OCH_2$), 4.28-4.33 and 4.41-4.45 (m, 2H, $OCH_2$), 4.78 (d, $^2J$(P-H) = 10.8 Hz, 1H, PC*H*), 6.92 (d, $^4J$(P-H) = 4.0 Hz, 1H, PhC*H*=C), 7.29-8.05 (m, 10H, Ar-*H*).

$^{13}C$ NMR: δ 20.8, 22.0, 22.5, 22.6, 25.1 (4 s, $(CH_3)_2C$ + cyclohexyl-*C*), 32.5 (d, $^3J$(P-C) = 7.2 Hz, $(CH_3)C$), 36.8 and 36.9 (2 s, cyclohexyl-*C*), 73.9 (d, $^1J$(P-C) = 157.9 Hz, P*C*), 78.1 (dd→t, $^2J$(P-C) = 6.8 each, $OCH_2$), 83.9 (d, $^3J$(P-C) = 3.4 Hz, PC-C-*C*≡C), 98.9 (s, -*C*-OBz), 116.5 (s, Ph*C*=C), 128.2, 128.5, 128.8, 129.1, 129.7, 130.7, 133.3, 135.4, 137.6, 137.7 (Ar-*C*), 165.6 (O*C*OPh).

$^{31}P$ NMR: δ 12.9.

HRMS (ESI): Calcd. for $C_{29}H_{33}NaO_6P$ [$M^+$+Na]: *m/z* 531.1913. Found: 531.1913.

***Compound 24e***




This compound was synthesized from **15c** (0.300 g, 0.8 mmol) and H-phosphonate **1c** $(i\text{-PrO})_2P(O)H$ (0.12 g, 0.8 mmol).

Yield: 0.343 g (78%, gummy liquid).

IR (neat): 3255, 2975, 2932, 2860, 2250 (w), 1726, 1452, 1271, 1249, 1107, 997, 718 $cm^{-1}$.

$^1H$ NMR: δ 1.27 and 1.32 (2 d, $^3J$(H-H) = 5.2 Hz and 6.4 respectively, 12H, $CH(CH_3)_2$), 1.33-1.76 and 2.14-2.35 (m, 10H, cyclohexyl-*H*), 3.69 (br s,

1H, CH-O*H*), 4.51 (d, $^{2}J$(P-H) = 12.6 Hz, 1H, PC*H*), 4.72-4.80 (m, 2H, C*H*($CH_3$)$_2$), 6.84 (d, $^{4}J$(P-H) = 3.6 Hz, 1H, PhC*H*=C), 7.29-7.58 and 7.86-8.07 (m, 10H, Ar-*H*).

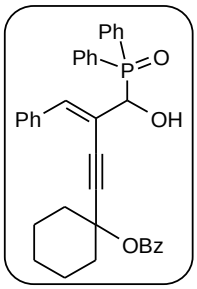
$^{13}$C NMR: δ 22.6 (s, cyclohexyl-*C*), 23.9, 24.0, 24.1 and 24.2 (4 d, $^{3}J$(P-C) = 5.1 Hz, 5.0 Hz, 3.7 Hz and 3.0 Hz respectively, CH(*C*$H_3$)$_2$), 25.2 and 36.9 (2 s, cyclohexyl-*C*), 71.6 and 71.9 (2 d, $^{2}J$(P-C) = 7.4 Hz and 7.1 Hz respectively, O*C*H($CH_3$)$_2$), 72.7 (d, $^{1}J$(P-C)=160.9 Hz, P*C*), 76.4 (s, *C*-OBz), 83.1 and 98.9 (2 s, -*C*≡*C*), 117.7 (s, Ph*C*=C), 128.2, 128.4, 128.6, 129.0, 129.8, 131.0, 133.0, 135.6, 136.7 and 136.8 (Ar-*C*), 165.1 (O*C*OPh).

$^{31}$P NMR: δ 19.2.

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

Anal.Calcd. for $C_{30}H_{37}O_6P$: C, 68.69; H, 7.11. Found: C, 68.56; H, 7.03.

***Compound 25***




This compound was synthesized from **15c** (0.300 g, 0.8 mmol) and H-phosphonate $Ph_2P(O)H$ **1d** (0.162 g, 0.8 mmol).

Yield: 0.400 g (85%, gummy solid).

IR (neat): 3448, 3059, 2935, 2858, 2200 (vw), 1719, 1600, 1437, 1282, 1245, 1107, 713 $cm^{-1}$.

$^{1}$H NMR: δ 1.36-1.95 (m, 10H, cyclohexyl-*H*), 5.19 (d, $^{2}J$(P-H) = 6.0 Hz, 1H, PC*H*), 6.90 (d, $^{4}J$(P-H) = 4.0 Hz, 1H, PhC*H*=C), 7.28-8.02 (m, 20H, Ar-*H*).

$^{13}$C NMR: δ 22.4, 25.0, 36.5 and 36.7 (4 s, cyclohexyl-*C*), 74.7 (d, $^{1}J$(P-C) = 79.5 Hz, P*C*), 75.9 (s, *C*-OBz), 83.0 and 99.1 (2 s, -*C*≡*C*-), 116.4 (s, Ph*C*=C), 128.1, 128.2, $128.3_0$, $128.3_2$, 128.6, 129.0, 129.7, 130.9, 131.5, 131.9,

132.1, 132.2, 132.5, 132.6, 133.1, 135.6, 137.6 and 137.7 (Ar-*C*), 165.0 (O*C*OPh).

$^{31}$P NMR: δ 28.9.

LC/MS: *m/z* 561 $[M+1]^+$.

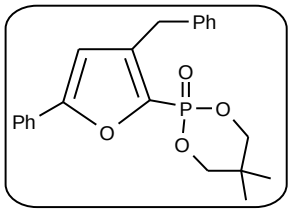
Anal.Calcd. for $C_{36}H_{33}O_4P$: C, 77.13; H, 5.93. Found: C, 77.32; H, 5.85.

## 3.5 Synthesis of phosphono-furans 26a-k, multi-substituted furans 27, 28a-b and 29a-c, phosphates 30a-b and iodo-furan 31

### *3.51 Synthesis of phosphono-furans 26a-k*

To a solution of phosphono-alkynol **16a-k** (0.4 mmol) in dry DCE (2 mL) was added a solution of $Ph_3PAuCl$ (0.03 equiv) and $AgSbF_6$ (0.03 equiv) in DCE (1.5 mL). The contents were stirred for 3 h at 70 $^oC$. The solvent was removed under vacuum and the crude product was purified by column chromatography using silica gel with acetone/ hexane (1:3) mixture as eluent to afford one of the products **26a-k**.

***Compound 26a***




.

Yield: 0.138 g (90%, white solid).

Mp: 158−160 $^oC$.

IR (KBr): 3069, 3025, 2967, 1593, 1476, 1447, 1387, 1260, 1211, 1179, 1061, 1015, 978, 824, 760, 723, 623, 567 $cm^{-1}$.

$^1$H NMR: δ 1.16 and 1.27 (2 s, 6H, C(C*H*$_3$)$_2$), 4.18 (s, 2H, PhC*H*$_2$), 4.21-4.28 (m, 4H, OC*H*$_2$), 6.52 (s, 1H, Ar*H*), 7.23-7.64 (m, 10H, Ar*H*).

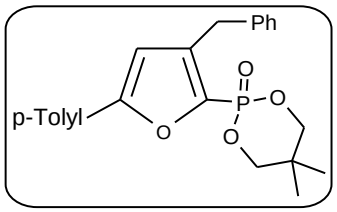
$^{13}$C NMR: δ 21.3 and 21.9 (2 s, C(*C*H$_3$)$_2$), 31.3 (s, Ph*C*H$_2$), 32.5 (d, $^3J$(P-C) = 7.0 Hz, *C*(CH$_3$)$_2$), 76.9$_0$ and 76.9$_1$ (2 s, O*C*H$_2$), 108.0 (d, $^3J$(P-C) = 11.8 Hz, PC=C-*C*), 124.6, 126.4, 128.6, 128.9, 128.9$_3$, 129.6, 138.3 (d, $^1J$(P-C) = 241.5 Hz, P*C*), 139.7, 140.5 (d, $^2J$(P-C) = 26.4 Hz, PC=*C*), 158.2 (d, $^3J$(P-C) = 11.9 Hz, PCO*C*).

$^{31}$P NMR: δ -1.6.

LC/MS: *m/z* 383 $[M+1]^+$.

Anal.Calcd. for $C_{22}H_{23}O_4P$: C, 69.10; H, 6.06. Found: C, 69.25; H, 5.96.

***Compound 26b***




Yield: 0.143 g (90%, white solid).

Mp: 122-126 $^{o}$C.

IR (KBr): 3083, 3027, 2969, 1595, 1489, 1381, 1277, 1254, 1059, 1013, 930, 826, 789, 721, 629, 556 $cm^{-1}$.

$^{1}$H NMR: δ 1.16 and 1.26 (2 s, 6H, C(C*H*$_3$)$_2$), 2.37 (s, 3H, ArC*H*$_3$), 4.17 (s, 2H, PhC*H*$_2$), 4.20-4.28 (m, 4H, OC*H*$_2$), 6.46 (d, $^{4}$*J*(P-H) = 2.8 Hz, 1H, Ar*H*), 7.18-7.52 (m, 9H, Ar*H*).

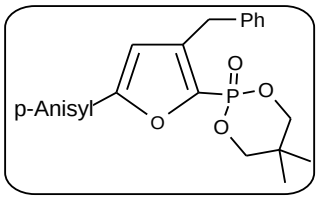
$^{13}$C NMR: δ 21.2 (s, ArCH$_3$), 21.4 and 21.8 (2 s, C(*C*H$_3$)$_2$), 31.3 (s, PhCH$_2$), 32.4 (d, $^{3}$*J*(P-C) = 6.5 Hz, *C*(CH$_3$)$_2$), 76.8 and 76.9 (2 s, OCH$_2$), 107.3 (d, $^{3}$*J*(P-C) = 11.6 Hz, PC=C-*C*), 124.5, 126.3, 126.9, 128.6, 128.9, 129.5, 137.7 (d, $^{1}$*J*(P-C) = 237.7 Hz, P*C*), 139.7, 140.5 (d, $^{2}$*J*(P-C) = 26.3 Hz, PC=*C*), 158.5 (d, $^{3}$*J*(P-C) = 10.6 Hz, PCO*C*).

$^{31}$P NMR: δ -1.3.

LC/MS: *m/z* 397 $[M+1]^+$.

Anal.Calcd. for $C_{23}H_{25}O_4P$: C, 69.69; H, 6.36. Found: C, 69.81; H, 6.45.

***Compound 26c***




Yield: 0.153 g (93%, white solid).

Mp: 126-130 $^{o}$C.

IR (KBr): 2963, 1615, 1536, 1489, 1422, 1372, 1300, 1281, 1250, 1173, 1061, 1026, 1009, 988, 837, 785, 721, 550 $cm^{-1}$.

$^{1}H$ NMR: δ 1.17 and 1.25 (2 s, 6H, C($CH_3$)$_2$), 3.83 (s, 3H, O$CH_3$), 4.16 (s, 2H, PhC$H_2$), 4.21 and 4.23 (2 s, 4H, OC$H_2$), 6.38 (d, $^{4}J$(P-H) = 2.8 Hz, 1H, Ar*H*), 6.90-7.57 (m, 9H, Ar*H*).

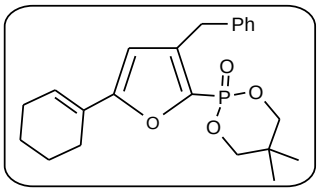
$^{13}C$ NMR: δ 21.2 and 21.7 (2 s, C($CH_3$)$_2$), 31.3 (s, Ph$CH_2$), 32.4 (d, $^{3}J$(P-C) = 7.1 Hz, *C*($CH_3$)$_2$), 55.3 (s, O$CH_3$), 76.7 (s, O$CH_2$), 106.4 (d, $^{3}J$(P-C) = 12.1 Hz, PC=C-*C*), 114.2, 122.5, 126.1, 126.3, 128.5, 128.9, 137.2 (d, $^{1}J$(P-C) = 244.3 Hz, P*C*), 139.7, 140.7 (d, $^{2}J$(P-C) = 26.6 Hz, PC=*C*), 158.4 (d, $^{3}J$(P-C) = 10.8 Hz, PCO*C*), 160.1(s, Ar-*C*).

$^{31}P$ NMR: δ -1.0.

LC/MS: *m/z* 413 $[M+1]^{+}$.

Anal.Calcd. for $C_{23}H_{25}O_5P$: C, 66.98; H, 6.11. Found: C, 66.85; H, 6.07.

***Compound 26d***




Yield: 0.133 g (86%, white solid).

Mp: 116-120 $^{o}$C.

IR (KBr): 3063, 3025, 2930, 1644, 1582, 1512, 1495, 1476, 1455, 1368, 1260, 1175, 1063, 1015, 824, 791, 712 $cm^{-1}$.

$^{1}H$ NMR: δ 1.11 and 1.24 (2 s, 6H, C($CH_3$)$_2$), 1.62-1.70 (m, 4H, $CH_2$($CH_2$)$_2$$CH_2$), 2.21 and 2.22 (2 s, 4H, =CC$H_2$), 4.11 (s, 2H, PhC$H_2$), 4.12-4.24 (m, 4H, OC$H_2$), 6.04 (d, $^{4}J$(P-H) = 2.4 Hz, 1H, Ar*H*), , 6.35 (br s, 1H, C=C*H*), 7.19-7.28 (m, 5H, Ar*H*).

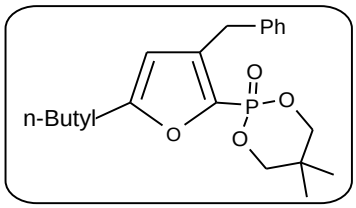
$^{13}C$ NMR: δ 21.2, 21.8, 21.9 and 22.1 (4 s, C($CH_3$)$_2$ + $CH_2$($CH_2$)$_2$$CH_2$), 24.9 and 25.3 (2 s, =CC$H_2$), 31.3 (s, Ph$CH_2$), 32.4 (d, $^{3}J$(P-C) = 6.3 Hz, *C*($CH_3$)$_2$), 76.7 (s, O$CH_2$), 106.5 (d, $^{3}J$(P-C) = 11.8 Hz, PC=C-*C*), 126.1, 126.2, 127.0, 128.5, 128.9, 136.9 (d, $^{1}J$(P-C) = 242.2 Hz, P*C*), 139.8$_4$, 139.8$_7$ (d, $^{2}J$(P-C) = 26.2 Hz, PC=*C*), 159.7 (d, $^{3}J$(P-C) = 10.2 Hz, PCO*C*).

$^{31}$P NMR: δ -1.2.

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

Anal.Calcd. for $C_{22}H_{27}O_4P$: C, 68.38; H, 7.04. Found: C, 68.21; H, 7.12.

***Compound 26e***




Yield: 0.128 g (88%, gummy liquid).

IR (neat): 2924, 1719, 1599, 1524, 1458, 1375, 1248, 1061, 1009, 700 $cm^{-1}$.

$^1$H NMR: δ 0.91 (t, 3H, $^3J$(H-H) = 3.2 Hz, $CH_2CH_3$), 1.11 and 1.22 (2 s, 6H, $C(CH_3)_2$), 1.36 (q, 2H, $^3J$(H-H) = 3.2 Hz, $CH_2CH_3$), 1.60 (quintet, 2H, $CH_2Et$), 2.60 (t, 2H, $^3J$(H-H) = 3.4 Hz, $ArCH_2CH_2$), 4.09 (s, 2H, $PhCH_2$), 4.11-4.20 (m, 4H, $OCH_2$), 5.90 (s, 1H, Ar*H*), 7.20-7.27 (m, 5H, Ar*H*).

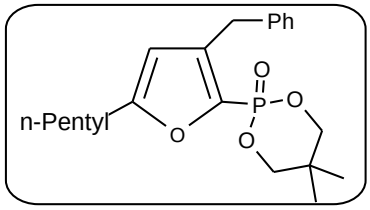
$^{13}$C NMR: δ 13.8 (s, $CH_2CH_3$), 21.2, 21.8, and 22.3 (3 s, $C(CH_3)_2$ + $CH_2CH_3$), 27.9 and 29.6 (2 s, $Ar(CH_2)_2CH_2$), 31.3 (s, $PhCH_2$), 32.4 (d, $^3J$(P-C) = 6.4 Hz, $C(CH_3)_2$), 76.6 and 76.7 (2 s, $OCH_2$), 108.5 (d, $^3J$(P-C) = 11.8 Hz, PC=C-*C*), 126.2, 128.5, 128.9, 136.8 (d, $^1J$(P-C) = 244.0 Hz, P*C*), 139.7, 139.9 162.1 (d, $^3J$(P-C) = 10.0 Hz, PCO*C*).

$^{31}$P NMR: δ -0.6.

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

Anal.Calcd. for $C_{20}H_{27}O_4P$: C, 66.28; H, 7.51. Found: C, 66.35; H, 7.48.

***Compound 26f***




Yield: 0.139 g (92%, gummy liquid).

IR (neat): 3029, 2957, 2932, 2872, 2872, 1601, 1528, 1470, 1211, 1167, 1063, 1011, 916, 826 $cm^{-1}$.

$^{1}$H NMR: δ 0.89 (t, 3H, $^{3}J$(H-H) = 6.8 Hz, $CH_2CH_3$), 1.10 and 1.22 (2 s, 6H, $C(CH_3)_2$), 1.29-1.33 and 1.59-1.63 (m, 6H, $CH_2(CH_2)_3CH_3$), 2.59 (t, 2H, $^{3}J$(H-H) = 7.6 Hz, $ArCH_2CH_2$), 4.09 (s, 2H, $PhCH_2$), 4.11-4.21 (m, 4H, $OCH_2$), 5.90 (d, 1H, $^{4}J$(P-H) = 2.8 Hz Ar*H*), 7.20-7.30 (m, 5H, Ar*H*).

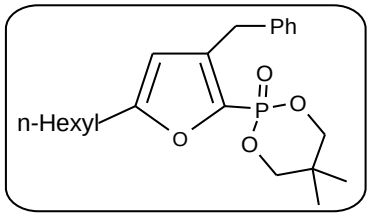
$^{13}$C NMR: δ 13.9 (s, $CH_2CH_3$), 21.1, 21.7 and 22.3 (3 s, $C(CH_3)_2$ + $CH_2CH_3$), 27.2 and 28.1 (2 s, $CH_2(CH_2)_2CH_2$), 31.2 ans 31.3 (2 s, $PhCH_2$ + $ArCH_2$), 32.3 (d, $^{3}J$(P-C) = 6.2 Hz, $C(CH_3)_2$), 76.6$_0$ and 76.6$_2$ (2 s, $OCH_2$), 108.5 (d, $^{3}J$(P-C) = 11.7 Hz, PC=C-*C*), 126.2, 128.4, 128.8, 136.7 (d, $^{1}J$(P-C) = 244.2 Hz, P*C*), 139.6, 139.9 162.1 (d, $^{3}J$(P-C) = 10.2 Hz, PCO*C*).

$^{31}$P NMR: δ -0.6.

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

Anal.Calcd. for $C_{21}H_{29}O_4P$: C, 67.01; H, 7.77. Found: C, 67.12; H, 7.71.

***Compound 26g***




Yield: 0.133 g (85%, gummy liquid).

IR (neat): 2957, 2930, 2859, 1601, 1530, 1470, 1391, 1285, 1165, 1063, 1011, 824 $cm^{-1}$.

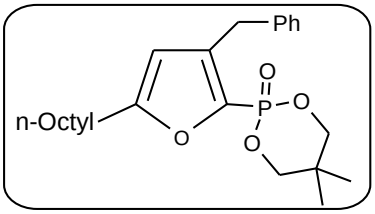
$^{1}$H NMR: δ 0.87 (t, 3H, $^{3}J$(H-H) = 6.6 Hz, $CH_2CH_3$), 1.10 and 1.21 (2 s, 6H, $C(CH_3)_2$), 1.28-1.32 and 1.59-1.64 (m, 8H, $(CH_2)_4CH_3$), 2.59 (t, 2H, $^{3}J$(H-H) = 7.6 Hz, $ArCH_2CH_2$), 4.08 (s, 2H, $PhCH_2$), 4.11-4.20 (m, 4H, $OCH_2$), 5.89 (d, $^{4}J$(P-H) = 2.8 Hz, 1H, Ar*H*), 7.19-7.30 (m, 5H, Ar*H*).

$^{13}$C NMR: δ 14.0 (s, $CH_2CH_3$), 21.1, 21.7, and 22.4 (3 s, $C(CH_3)_2$ + $CH_2CH_3$), 27.4, 28.1, 28.8, 31.2 and 31.3 (5 s, $Ar(CH_2)_4CH_2$ + $PhCH_2$), 31.4 (s, $PhCH_2$), 32.3 (d, $^{3}J$(P-C) = 6.1 Hz, $C(CH_3)_2$), 76.5 and 76.6 (2 s, $OCH_2$), 108.4 (d, $^{3}J$(P-C) = 11.8 Hz, PC=C-*C*), 126.1, 128.4, 128.8, 136.7 (d, $^{1}J$(P-C) = 243.6 Hz, P*C*), 139.5, 139.8 162.1 (d, $^{3}J$(P-C) = 10.3 Hz, PCO*C*).

$^{31}$P NMR: δ -0.6.

HRMS (ESI): Calcd. for $C_{22}H_{31}NaO_4P$ [$M^+$+Na]: *m/z* 413.1858. Found: 413.1858.

***Compound 26h***




Yield: 0.152 g (68%, gummy liquid).

IR (neat): 3059, 3029, 2927, 2857, 1599, 1528, 1495, 1468, 1391, 1285, 1167, 1063, 1011, 947, 916, 826, 774, 635 $cm^{-1}$.

$^1$H NMR: δ 0.88 (t, 3H, $^3J$(H-H) = 6.8 Hz, $CH_2CH_3$), 1.10 and 1.22 (2 s, 6H, $C(CH_3)_2$), 1.26-1.32 and 1.57-1.64 (m, 12H, $(CH_2)_6CH_3$), 2.59 (t, 2H, $^3J$(H-H) = 7.6 Hz, $ArCH_2CH_2$), 4.09 (d, 2H, $^4J$(P-H) = 1.2 Hz, $PhCH_2$), 4.13-4.21 (m, 4H, $OCH_2$), 5.89 (d, $^4J$(P-H) = 2.8 Hz, 1H, Ar*H*), 7.18-7.28 (m, 5H, Ar*H*).

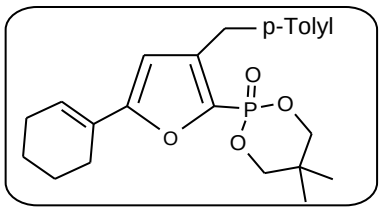
$^{13}$C NMR: δ 14.1 (s, $CH_2CH_3$), 21.2, 21.8, 22.6, 27.5, 28.2, $29.2_0$, $29.2_2$, 31.3, and 31.8 (9 s, $C(CH_3)_2$ + $(CH_2)_7CH_3$), 32.4 (d, $^3J$(P-C) = 6.5 Hz, $C(CH_3)_2$), $76.6_0$ and $76.6_3$ (2 s, $OCH_2$), 108.5 (d, $^3J$(P-C) = 12.2 Hz, PC=C-*C*), 126.2, 128.5, 128.8, 136.7 (d, $^1J$(P-C) = 244.3 Hz, P*C*), 139.7, 139.9 162.1 (d, $^3J$(P-C) = 9.9 Hz, PCO*C*).

$^{31}$P NMR: δ -0.5.

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

Anal.Calcd. for $C_{24}H_{35}O_4P$: C, 68.88; H, 8.43. Found: C, 68.75; H, 8.36.

***Compound 26i***




Yield: 0.141 g (86%).

Mp: 82-84$^o$C.

IR (KBr): 2932, 1580, 1514, 1474, 1370, 1256, 1061, 1013, 826, 791, 629 $cm^{-1}$.

$^{1}$H NMR: δ 1.11 and 1.24 (2 s, 6H, C(C$H_3$)$_2$), 1.62-1.70 (m, 4H, CH$_2$(C$H_2$)$_2$CH$_2$), 2.20 and 2.22 (2 br s, 4H, =CC$H_2$), 2.31 (s, 3H, ArC$H_3$), 4.06 (s, 2H, ArC$H_2$), 4.12-4.23 (m, 4H, OC$H_2$), 6.03 (d, $^{4}J$(P-H) = 2.8 Hz, 1H, Ar*H*), 6.34 (br s, 1H, C=C*H*), 7.08-7.27 (m, 4H, Ar*H*).

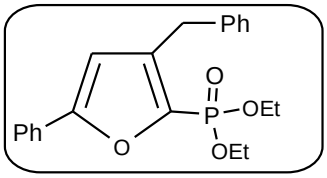
$^{13}$C NMR: δ 21.0, 21.2, 21.8, 21.9 and 22.2 (5 s, C(*C*H$_3$)$_2$ + CH$_2$(*C*H$_2$)$_2$CH$_2$ + Ar*C*H$_3$), 24.9 and 25.3 (2 s, =C*C*H$_2$), 30.8 (s, Ar*C*H$_2$), 32.4 (d, $^{3}J$(P-C) = 6.4 Hz, *C*(CH$_3$)$_2$), 76.7 (s, O*C*H$_2$), 106.5 (d, $^{3}J$(P-C) = 11.7 Hz, PC=C-*C*), 126.0, 127.0, 128.7, 129.2, 136.2 (d, $^{3}J$(P-C) = 12.2 Hz, PC=C*C*), 136.8 (d, $^{1}J$(P-C) = 242.4 Hz, P*C*), 140.2 (d, $^{2}J$(P-C) = 26.4 Hz, PC=*C*), 159.7 (d, $^{3}J$(P-C) = 10.1 Hz, PCO*C*).

$^{31}$P NMR: δ -1.1.

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

Anal.Calcd. for $C_{23}H_{29}O_6P$: C, 68.98; H, 7.30. Found: C, 68.81; H, 7.41.

***Compound 26j***




Yield: 0.136 g (92%, gummy liquid).

IR (neat): 3061, 3027, 2984, 2930, 1593, 1576, 1480, 1449, 1387, 1258, 1163, 1022, 972, 764, 725, 694 cm$^{-1}$.

$^{1}$H NMR: δ 1.36 (t, 6H, $^{3}J$(H-H) = 7.0 Hz, CH$_2$C$H_3$), 4.14-4.25 (m, 6H, OC$H_2$CH$_3$ + PhC$H_2$), 6.52 (d, 1H, $^{4}J$(P-H) = 2.4 Hz, Ar*H*), 7.22-7.68 (m, 10H, Ar*H*).

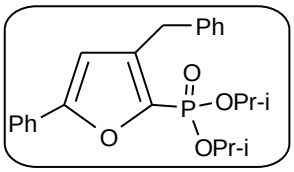
$^{13}$C NMR: δ 16.3 and 16.4 (2 s, CH$_2$*C*H$_3$), 31.4 (s, Ph*C*H$_2$), 62.7 (d, $^{2}J$(P-C) = 4.7 Hz, O*C*H$_2$), 107.9 (d, $^{3}J$(P-C) = 11.4 Hz, PC=C-*C*), 124.6, 126.3, 128.6, 128.7$_0$, 128.7$_4$, 128.8, 129.7, 138.1 (d, $^{1}J$(P-C) = 238.5 Hz, P*C*), 139.9, 140.2, 158.1 (d, $^{3}J$(P-C) = 10.9 Hz, PCO*C*).

$^{31}$P NMR: δ 5.2.

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

Anal.Calcd. for $C_{21}H_{23}O_4P$: C, 68.10; H, 6.26. Found: C, 68.25; H, 6.15.

***Compound 26k***




Yield: 0.148 g (93%, gummy liquid).

IR (neat): 3065, 3027, 2980, 2934, 1593, 1578, 1480, 1451, 1385, 1256, 1179, 1142, 1105, 1059, 988, 766, 725, 694 $cm^{-1}$.

$^{1}H$ NMR: δ 1.28 and 1.40 (2 d, 12H, $^{3}J$(H-H) = 6.4 Hz and 6.0 Hz respectively, $CH(CH_3)_2$), 4.18 (s, 2H, $PhCH_2$), 4.72 (m, 2H, , $CH(CH_3)_2$), 6.51 (d, 1H, $^{4}J$(P-H) = 2.4 Hz, Ar*H*), 7.20-7.68 (m, 10H, Ar*H*).

$^{13}C$ NMR: δ 23.8 and 24.2 (2 d, $^{3}J$(P-C) = 4.5 Hz and 3.6 respectively, $C(CH_3)_2$), 31.4 (s, $PhCH_2$), 71.5 (d, $^{2}J$(P-C) = 4.7 Hz, $C(CH_3)_2$), 108.0 (d, $^{3}J$(P-C) = 11.6 Hz, PC=C-*C*), 124.5, 126.3, 128.5, 128.7, 128.8, 129.8, 139.3 (d, $^{1}J$(P-C) = 238.1 Hz, P*C*), 139.4 (d, $^{2}J$(P-C) = 25.5 Hz, PC=*C*), 140.1 and 157.6 (d, $^{3}J$(P-C) = 10.1 Hz, PCO*C*).

$^{31}P$ NMR: δ 2.8.

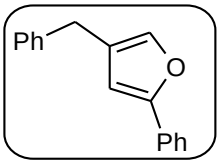
LC/MS: *m/z* 399 $[M+1]^{+}$.

Anal.Calcd. for $C_{23}H_{27}O_4P$: C, 69.33; H, 6.83. Found: C, 69.25; H, 6.77.

### *3.52 Synthesis of multi-substituted furans 27, 28a-b and 29a-c*

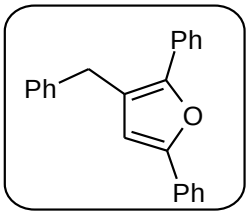
To a solution of alkynol **17, 18** and **19a-c** (0.4 mmol) in dry DCM (2 mL) was added a solution of $Ph_3PAuCl$ (0.01 equiv) and $AgSbF_6$ (0.01 equiv) in DCM (0.4 mL). The mixture was stirred for 1 h at room temperature, solvent was removed in vacuum and the crude product was purified by using silica gel with acetone/ hexane (1:20) as the eluent to procure multi-substituted furans **27, 28a-b and 29a-c**.

***Compound 27***



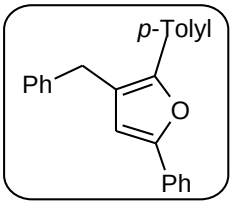
Yield: 0.084 g (90%). The spectroscopic data for this compound are in accordance with the literature.[37b]

***Compound 28a***




Yield: 0.109 g (88%). The spectroscopic data for this compound are in accordance with the reported literature.[69a]

***Compound 28b***




Yield: 0.109 g (84%, gummy liquid).

IR (neat): 3054, 3029, 2921, 2859, 1665, 1601, 1505, 1453, 1183, 1105, 1073, 1028, 934, 820, 760, 725, 693 $cm^{-1}$.

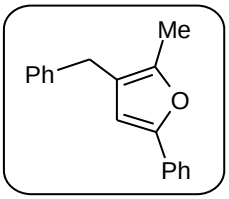
$^{1}H$ NMR: δ 2.39 (s, 3H, ArC$H_3$), 4.08 (s, 2H, PhC$H_2$), 6.53 (s, 1H, Ar*H*), 7.23-7.71 (m, 14H, Ar*H*).

$^{13}C$ NMR: δ 21.3 (Ar*C*$H_3$), 32.2 (Ph*C*$H_2$), 109.8 (OCH=*C*H), 121.2, 123.7, 125.7, 126.3, 127.3, 128.6, 128.7, 129.4, 130.8, 137.1, 140.2, 149.2 and 152.0 (Ar-*C*).

LC/MS: *m/z* 325 $[M+1]^{+}$.

Anal.Calcd. for $C_{24}H_{20}O$: C, 88.85; H, 6.21. Found: C, 88.76; H, 6.29.

***Compound 29a***




Yield: 0.091 g (91%, gummy liquid).

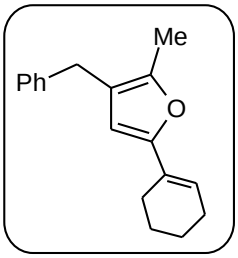
IR (neat): 3061, 3029, 2921, 1669, 1599, 1491, 1451, 1260, 1218, 1073, 1026, 932, 760, 694 $cm^{-1}$.

$^1H$ NMR: δ 2.36 (s, 3H, ArC$H_3$), 3.76 (s, 2H, PhC$H_2$), 6.44 (s, 1H, Ar*H*), 7.22-7.63 (m, 10H, Ar*H*).

$^{13}C$ NMR: δ 11.8 (Ar*C*$H_3$), 31.3 (Ph*C*$H_2$), 107.7 (OCH=*C*H), 120.1, 123.3, 126.1, 126.8, 128.5, 128.6, 131.1, 140.8, 146.1 and 147.8 (Ar-*C*).

HRMS (ESI): Calcd. for $C_{18}H_{16}NaO$ $[M+Na]^+$: *m/z* 271.1099. Found: 271.1099.

***Compound 29b***




Yield: 0.053 g (52%, gummy liquid).

IR (neat): 3059, 3029, 2936, 2865, 1715, 1667, 1520, 1495, 1453, 1377, 1352, 1194, 1076, 1024, 932, 700 $cm^{-1}$.

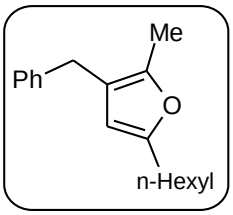
$^1H$ NMR: δ 1.61-1.71 (m, 4 H, -$CH_2$(C$H_2$)$_2$$CH_2$-), 2.19 and 2.20 (2 br s, 4H, C$H_2$C=CC$H_2$), 2.26 (s, 3H, ArC$H_3$), 3.67 (s, 2H, PhC$H_2$), 5.91 (s, 1H, C=C*H*), 6.21 (s, 1H, Ar*H*), 7.17-7.30 (m, 5H, Ar*H*).

$^{13}C$ NMR: δ 11.7 (Ar*C*$H_3$), 22.4 and 22.5 (-$CH_2$(*C*$H_2$)$_2$$CH_2$-), 24.9 and 25.2 (=C*C*$H_2$), 31.3 (Ph*C*$H_2$), 106.3 (OCH=*C*H), 119.0, 121.0, 126.0, 127.3, 128.4, 141.0, 146.6 and 153.1 (Ar-*C* and *C*=*C*).

LC/MS: *m/z* 253 $[M+1]^+$.

Anal.Calcd. for $C_{18}H_{20}O$: C, 85.67; H, 7.99 Found: C, 85.59; H, 7.91.

***Compound 29c***




Yield: 0.094 g (92%, gummy liquid).

IR (neat): 3029, 2928, 2857, 1578, 1495, 1455, 1377, 1235, 1200, 1102, 1030, 941, 793, 731 and 700 $cm^{-1}$.

$^1H$ NMR: δ 0.89 (t, 3H, $^3J$(H-H) = 6.6 Hz, $CH_2CH_3$), 1.25-1.37 and 1.56-1.60 (m, 8H, $CH_2(CH_2)_4CH_3$), 2.23 (s, 3H, $ArCH_3$), 2.52 (t, 2H, $^3J$(H-H) = 7.6 Hz, $ArCH_2CH_2$), 3.65 (s, 2H, $PhCH_2$), 5.72 (s, 1H, Ar*H*), 7.18-7.31 (m, 14H, Ar*H*).

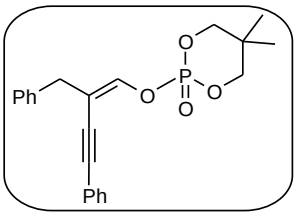
$^{13}C$ NMR: δ 11.6 ($ArCH_3$), 14.2, 22.7, 28.1, 28.2, 29.0, 31.3, 31.7 (*n*-Hexyl + $PhCH_2$), 107.0 (OCH=*C*H), 118.1, 125.9, 128.4, 141.3, 145.6 and 154.0 (Ar-*C*).

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

Anal.Calcd. for $C_{18}H_{24}O$: C, 84.32; H, 9.44. Found: C, 84.15; H, 9.39.

### *3.53 Synthesis of phosphate esters 30a-b*

To a solution of phosphono-alkynol **16a** (153 mg, 0.4 mmol) in dry DCE (2 mL) was added DBU (60 µL, 1.0 equiv) and the mixture stirred for 2 h at room temperature. Solvent was removed under vacuum. Compound **30a** and **30b** were isolated from reaction mixture using silica gel with acetone/ hexane (1:4) as the eluent.




**30a**

Yield: 0.046 g (30%, white solid).

Mp: 124-126 $^oC$.

IR (KBr): 3061, 2969, 1630, 1595, 1491, 1372, 1300, 1150, 1113, 1057, 1007, 887, 858, 783, 752, 729, 694 $cm^{-1}$.

$^1H$ NMR (500 MHz): δ 0.83 and 1.30 (2 s, 6H, $C(CH_3)_2$), 3.68 (s, 2H, $ArCH_2$), 3.89-4.00 (m, 4H, $OCH_2$), 7.11 (d, $^3J$(P-H) = 6.5 Hz, 1H, C=C*H*), 7.23-7.37 (m, 10H, Ar*H*).

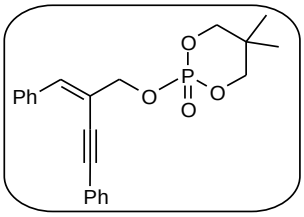
$^{13}C$ NMR (100 MHz): δ 20.0 and 21.6 (2 s, $C(CH_3)_2$), 32.1 (d, $^3J$(P-C) = 6.0 Hz, $C(CH_3)_2$), 34.6 (s, $ArCH_2$), 78.4 and 78.5 (2 s, $OCH_2$), 86.5 and 90.7 (2

s, *C*≡*C*), 110.6 (d, $^{3}J$(P-C) = 12.7 Hz, C=*C*H-O), 123.0, 125.5, 128.2, 128.3, $128.5_0$, $128.5_4$, 131.4, 138.6, 140.3 (d, $^{2}J$(P-C) = 4.5 Hz, $CH_2$*C*=CH).

$^{31}$P NMR (202 MHz) : δ -12.3.

LC/MS: *m/z* 383 $[M+1]^+$.

Anal.Calcd. for $C_{22}H_{23}O_4P$: C, 69.10; H, 6.06. Found: C, 69.25; H, 6.12.




**30b**

Yield: 0.065 g (42%, white solid).

Mp: 84-86 $^{o}$C.

IR (KBr): 2963, 1489, 1458, 1368, 1298, 1262, 1094, 1028, 870, 799, 760 $cm^{-1}$.

$^{1}$H NMR (500 MHz): δ 0.81 and 1.23 (2 s, 6H, C(C$H_3$)$_2$), 3.91 (dd, 2H, $^{3}J$(P-H), $^{2}J$(H-H) = 26.8 Hz, 13.8 Hz, OC$H_2$), 4.24 (d, 2H, $^{2}J$(H-H) = 13.8 Hz, OC$H_2$), 4.85 (d, 2H, $^{3}J$(P-H) = 10.0 Hz, =CC$H_2$OP), 6.92 (s, 1H, ArC*H*=C), 7.34-7.96 (m, 10H, Ar*H*).

$^{13}$C NMR (100 MHz): δ 20.2 and 21.7 (2 s, C(*C*$H_3$)$_2$), 32.1 (d, $^{3}J$(P-C) = 5.1 Hz, *C*(C$H_3$)$_2$), 70.9 (d, $^{2}J$(P-C) = 5.2 Hz, =C*C*$H_2$), 77.9 and 78.0 (2 s, O*C*$H_2$), 87.1 and 96.8 (2 s, *C*≡*C*), 116.4 (d, $^{3}J$(P-C) = 6.9 Hz, CH=*C*C$H_2$), 112.8, 128.4, 128.5, 128.8, 129.0, 131.5, 135.3 and 137.6 (Ar-*C*).

$^{31}$P NMR (202 MHz): δ -7.9.

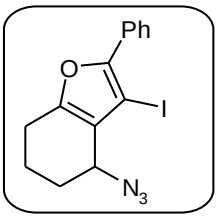
LC/MS: *m/z* 383 $[M+1]^+$.

Anal.Calcd. for $C_{22}H_{23}O_4P$: C, 69.10; H, 6.06. Found: C, 69.18; H, 6.09.

### *3.54 Synthesis of iodo-furan 31*

To a mixture of 2-alkynyl-cyclohexenone (**12**) (0.100 g, 0.5 mmol) and sodium azide (1.5 mmol) in DCE (2 mL) was added ICl (1.5 mmol) at 0 $^{o}$C. The contents were stirred at rt for 2 h, and then filtered. The precipitate was washed with ethyl acetate (5 mL) and the washings added to the filtrate. The volatiles from the filtrate were removed under

vacuum and crude product was purified by column chromatography using ethyl acetate/hexane (1:100) mixture as the eluent.




Yield: 0.022 g (12%).

IR (neat): 3063, 2926, 2849, 2099, 1622, 1483, 1445, 1229, 968, 926 $cm^{-1}$.

$^1$H NMR: δ 1.84-2.29 and 2.59-2.82 (m, 6H, cyclohexenyl-*H*), 4.40 (br s, 1H, C*H*$N_3$), 7.32-7.98 (m, 5H, Ar-*H*).

$^{13}$C NMR: δ 18.8, 23.0 and 29.8 (cyclohexyl-*C*), 54.8 (*C*H$N_3$), 64.1 (*C*-I), 121.3, 126.1, 128.1, 128.4, 130.2, 150.5 and 154.2 (Ar-*C*).

LC/MS: *m/z* 337 $[M+1-N_2]^+$.

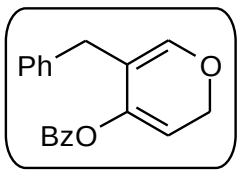
X-ray structure was determined for this compound. Because this compound was obtained in a very small quantity and because the compound decomposed over a period a period of time, analyses were not obtained.

## 3.6 Synthesis of pyran derivatives 32a-g, 33a-l and 34, phosphono-furans/-pyrans 35-40, phosphinoyl-furan 41, macrocycles 42-45 and furan 43

### *3.61 Synthesis of pyran derivatives* 32a-g, 33a-l and 34

To a solution of one of the hydroxyl propargylic esters [**20a-g**, **21a-l** and **22**; 0.5 mmol] in dry DCM (1 mL) was added a solution of $Ph_3PAuCl$ (0.02 equiv) and $AgSbF_6$ (0.02 equiv) in DCM (1 mL). The contents were stirred at room temperature till the starting material was consumed. The solvent was removed under vacuum and crude product was purified by column chromatography using silica gel with ethyl acetate/ hexane (1:100) mixture as eluent to afford the corresponding product among **32a-g, 33a-l** and **34**.

***Compound 32a***



Yield: 0.094 g (64%, gummy liquid).

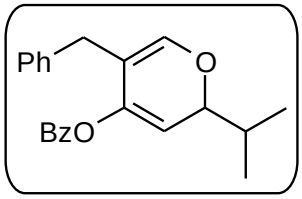
IR (neat): 3063, 3030, 2926, 1769, 1725, 1603, 1584, 1495, 1453, 1269, 1109, 1026, 938, 708 $cm^{-1}$.

$^1H$ NMR: δ 3.76 (s, 2H, PhC*H*$_2$C=C), 5.25 (s, 2H, OC*H*$_2$CH=C), 6.35 (s, 1H, OBzC=C*H*), 7.22-8.07 (m, 11H, Ar-*H* + PhC*H*=C).

$^{13}C$ NMR: δ 31.3 (Ph*C*H$_2$), 58.8 (O*C*H$_2$), 112.4, 125.5, 126.4, 128.4, 129.9, 133.2, 140.3, 150.0 (Ar*C* + alkenyl*C*) and 166.3 (Ph*C*=O).

HRMS (ESI): Calcd. for $C_{19}H_{17}O_3$ [$M^+$+H]: *m/z* 293.1179. Found: 293.1177.

***Compound 32b***




Yield: 0.045 g (45%, gummy liquid).

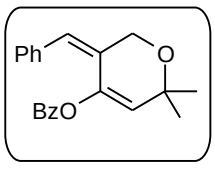
IR (neat): 3053, 2965, 2929, 1723, 1630, 1454, 1262, 1107, 1080, 750, 703 $cm^{-1}$.

$^1H$ NMR: δ 0.94 and 1.07 (2 d, $^3J$(H-H) = 6.4 and 6.8 Hz respectively, 6H, (C*H*$_3$)$_2$CH), 2.41-2.46 (m, 1H, (CH$_3$)$_2$C*H*), 3.74 (s, 2H, PhC*H*$_2$), 5.76 (d, $^3J$(H-H) = 7.6 Hz, 1H, OC*H*CH), 6.25 (s, 1H, BzOC=C*H*), 7.13-8.10 (m, 11H, C=C*H* + Ar*H*).

$^{13}C$ NMR: δ 18.7 and 18.8 (*C*H$_3$)$_2$C), 31.3 and 31.5 ((CH$_3$)$_2$*C* + Ph*C*H$_2$), 74.6 (O*C*H), 110.6 (BzOC=*C*), 124.9, 126.2, 128.4, 128.5, 128.7, 129.8, 130.3, 133.0, 139.4, 140.1, 152.6 (Ar*C* + *C*=*C*) and 165.9 (O*C*OPh).

HRMS (ESI): Calcd. for $C_{22}H_{22}O_3$ [$M^+$]: *m/z* 334.1569. Found: 334.1545.

***Compound 32c***




Yield: 0.144 g (90%, gummy liquid).

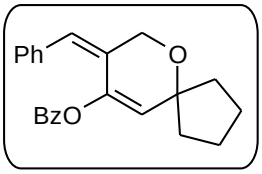
IR (neat): 3059, 2976, 2932, 2851, 1738, 1601, 1493, 1453, 1265, 1206, 1177, 1150, 1109, 1059, 1024, 704 $cm^{-1}$.

$^1$H NMR: δ 1.46 (s, 6H, C(C*H*$_3$)$_2$), 4.48 (d, $^4$*J*(H-H) = 0.8 Hz, 2H, =CC*H*$_2$O), 5.61 (s, 1H, CH=C-C=C*H*), 6.41 (s, 1H, PhC*H*=C), 6.80-7.49 (m, 10H, Ar*H*).

$^{13}$C NMR: δ 27.4 (C(*C*H$_3$)$_2$), 66.7 (s, =C*C*H$_2$O), 74.0 (Me$_2$*C*-O), 125.8, 126.7, 126.8, 127.5, 127.7$_0$, 127.7$_4$, 128.6, 128.8, 129.7, 132.9, 136.5, 142.0 (Ar*C* + *C*=*C*) and 164.2 (O*C*OPh).

HRMS (ESI): Calcd. for $C_{21}H_{20}O_3Na$ [$M^+$+Na]: *m/z* 343.1310. Found: 343.1310.

***Compound 32d***




Yield: 0.149 g (86%, gummy liquid).

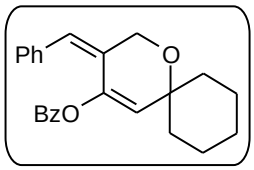
IR (neat): 3062, 3020, 2956, 2913, 2849, 1731, 1656, 1603, 1454, 1262, 1171, 1070, 804, 702 cm$^{-1}$.

$^1$H NMR: δ 1.73 and 1.89 (2 br s, 6H, cyclopentyl-C*H*$_2$), 2.01-2.06 (m, 2H, cyclopentyl), 4.41 (s, 2H, =CC*H*$_2$O), 5.60 (~s, 1H, C*H*=C-OBz), 6.40 (s, 1H, PhC*H*=C), 6.79-7.50 (m, 10H, Ar*H*).

$^{13}$C NMR: δ 24.2 and 38.4 (cyclopentyl-*C*H$_2$), 67.4 (=C*C*H$_2$O), 84.9 (*C*OCH$_2$), 125.6, 125.7, 126.6, 127.6, 127.7, 128.6, 128.9, 129.7, 132.9, 136.6, 142.1 (Ar*C* + *C*=*C*) and 164.2 (O*C*OPh).

HRMS (ESI): Calcd. for $C_{23}H_{24}NaO_3$ [$M^+$+Na]: *m/z* 371.1623. Found: 371.1622.

***Compound 32e***




Yield: 0.148 g (82%, gummy liquid).

IR (neat): 3059, 3027, 2932, 2857, 2245, 1960, 1738, 1601, 1493, 1449, 1262, 1186, 1069, 1024, 704 cm$^{-1}$.

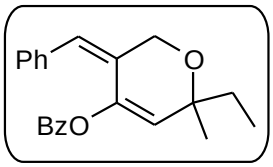
$^1$H NMR: δ 1.33-1.62 and 1.69-1.93 (m, 10H, cyclohexyl), 4.46 (s, 2H, =CC*H*$_2$O), 5.66 (s, 1H, C*H*=C-O), 6.40 (s, 1H, PhC*H*=C), 6.79-7.50 (m, 10H, Ar*H*).

$^{13}$C NMR: δ 21.7, 25.5 and 35.5 (cyclohexyl), 66.1 (s, =C*C*H$_2$O), 74.8 (*C*-O), 125.5, 126.4, 126.6, 127.7$_0$, 127.7$_3$, 127.9, 128.6, 128.9, 129.7, 132.9, 136.6, 142.3 (Ar*C* + *C*=*C*) and 164.2 (O*C*OPh).

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

Anal.Calcd. for $C_{24}H_{24}O_3$: C, 79.97; H, 6.71. Found: C, 79.85; H, 6.76.

***Compound 32f***




Yield: 0.107 g (64%, gummy liquid).

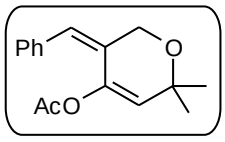
IR (neat): 2970, 2929, 2851, 1733, 1650, 1454, 1257, 1107, 1061, 1024 cm$^{-1}$.

$^1$H NMR: δ 1.03 (t, $^3J$(H-H) = 7.6 Hz, 3H, CH$_2$C*H*$_3$), 1.39 (s, 3H, C*H*$_3$), 1.73-1.78 (m, 2H, C*H*$_2$CH$_3$), 4.38 and 4.54 (2 d, $^2J$(H-H) = 12.4 Hz each, 2H, OC*H*$_A$*H*$_B$), 5.57 (s, 1H, C*H*=C-OBz), 6.41 (s, 1H, PhC*H*=C), 6.83-7.49 (m, 10H, Ar*H*).

$^{13}$C NMR: δ 8.2 (CH$_2$*C*H$_3$), 24.4 and 33.7 (C*H*$_2$CH$_3$ + *C*H$_3$), 66.6 and 76.4 (=C*C*H$_2$O + *C*-OCH$_2$), 125.6, 125.9, 126.7, 127.7, 127.8, 128.6, 128.9, 129.7, 132.9, 136.6, 142.6 (Ar*C* + *C*=*C*) and 164.3 (O*C*OPh).

HRMS (ESI): Calcd. for $C_{22}H_{22}NaO_3$ [M$^+$+Na]: *m/z* 357.1467. Found: 357.1467.

***Compound 32g***




Yield: 0.096 g (74%, gummy liquid).

IR (neat): 3058, 3027, 2979, 2934, 1761, 1620, 1449, 1370, 1198, 1149, 1054, 1019, 900, 739, 700 cm$^{-1}$.

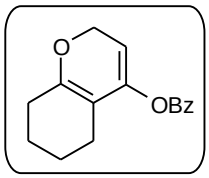
$^1$H NMR: δ 1.27 (s, 3H, C*H*$_3$CO), 1.40 (s, 6H, C(C*H*$_3$)$_2$), 4.41 (s, 2H, =CC*H*$_2$O), 5.45 (s, 1H, C*H*=C-OAc), 6.36 (s, 1H, PhC*H*=C), 7.22-7.30 (m, 5H, Ar-*H*).

$^{13}$C NMR: δ 19.5 (*C*H$_3$CO), 27.3 ((*C*H$_3$)$_2$C), 66.6 and 73.8 (*C*H$_2$O*C*Me$_2$), 125.2,

126.7, 127.0, 127.2, 127.7, 129.2, 136.6, 141.9 and 168.5 ($CH_3$*C*=O).

HRMS (ESI): Calcd. for $C_{16}H_{18}NaO_3$ [$M^+$+Na]: *m/z* 281.1154. Found: 281.1155.

***Compound 33a***




Yield: 0.096 g (75%, gummy liquid).

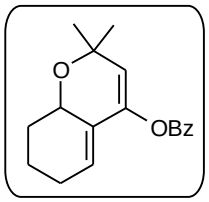
IR (neat): 2930, 2857, 1721, 1603, 1524, 1375, 1177, 1098, 1026, 941, 666 $cm^{-1}$.

$^1$H NMR: δ 1.71-1.87 and 2.40-2.62 (m, 8H, cyclohexenyl-C*H*$_2$), 5.25 (s, 2H, OC*H*$_2$), 6.29 (s, 1H, C*H*=C-OBz), 7.41-8.08 (m, 5H, Ar-*H*).

$^{13}$C NMR: δ 22.1, 23.0, 23.1 and 23.3 (cyclohexenyl-*C*H$_2$), 59.1 (s, O*C*H$_2$), 112.1, 118.0, 128.4, 129.9, 133.1, 147.0, 152.0 (alkenyl-*C* + Ar-*C*), 166.5 (Ph*C*=O).

HRMS (ESI): Calcd. for $C_{16}H_{16}NaO_3$ [$M^+$+Na]: *m/z* 279.0997. Found: 279.0998.

***Compound 33b***




Yield: 0.102 g (72%, gummy liquid).

IR (neat): 3065, 2976, 2938, 2868, 1738, 1601, 1453, 1381, 1316, 1265, 1208, 1177, 1109, 1090, 1069, 1026, 710 $cm^{-1}$.

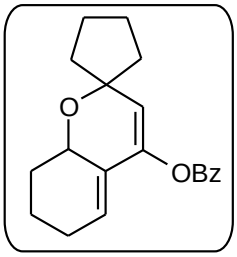
$^1$H NMR: δ 1.40 and 1.44 (2 s, 6H, (C*H*$_3$)$_2$C), 1.60-2.14 (m, 6H, cyclohexenyl-C*H*$_2$), 4.48 (br s, 1H, C*H*OCMe$_2$), 5.54 (s, 1H, C*H*=C-OBz), 5.73 (br s, 1H, C=C*H*CH$_2$), 7.47-8.14 (m, 5H, Ar-*H*).

$^{13}$C NMR: δ 20.7, 25.3, 25.5, 29.3 and 30.1 (cyclohexenyl-*C*H$_2$+ C(*C*H$_3$)$_2$), 67.7 and 72.7 (*C*HO*C*Me$_2$), 121.4, 122.8, 128.6, 130.0, 133.5, 142.0 (alkenyl-*C* + Ar-*C*) and 164.7 (Ph*C*=O).

LC/MS: *m/z* 285 [M+1]$^+$.

Anal.Calcd. for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09. Found: C, 76.12; H, 7.15.

***Compound 33c***




Yield: 0.122 g (78%, gummy liquid).

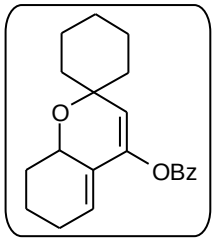
IR (neat): 3047, 2951, 2855, 1732, 1663, 1594, 1444, 1263, 1168, 1066, 1029, 811, 710 $cm^{-1}$.

$^1H$ NMR: δ 1.58-1.94 and 2.04-2.13 (m, 14H, cyclopentyl-*H* + cyclohexenyl-C$H_2$), 4.35 (br s, 1H, $CH_2CH$-O), 5.55 (s, 1H, C*H*=C-OBz), 5.72 (br s, 1H, C=C*H*$CH_2$), 7.47-7.63 and 8.12-8.14 (m, 5H, Ar-*H*).

$^{13}C$ NMR: δ 20.7, 24.1, 24.3, 25.3, 29.3, 36.4 and 40.8 (cyclopentyl-*C*$H_2$ + cyclohexenyl-*C*$H_2$), 68.5 and 83.5 ($CH_2$*C*H-O-*C*), 121.2, 121.9, 128.6, 129.5, 129.9, 130.1, 133.5, 142.1 (Ar-*C* + alkenyl-*C*) and 164.7 (Ph*C*=O).

HRMS (ESI): Calcd. for $C_{20}H_{22}NaO_3$ [$M^+$+Na]: *m/z* 333.1467. Found: 333.1468.

***Compound 33d***




Yield: 0.105 g (65%, white solid).

Mp: 54-56 $^oC$.

IR (KBr): 3063, 2932, 2859, 1738, 1665, 1632, 1601, 1451, 1391, 1264, 1171, 1088, 914, 708 $cm^{-1}$.

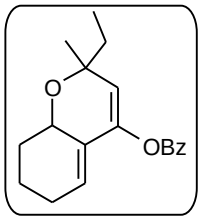
$^1H$ NMR: δ 1.47-2.13 (m, 16H, cyclohexenyl-C$H_2$ + cyclohexyl-C$H_2$), 4.46 (br s, 1H, C*H*OC), 5.62 (s, 1H, C*H*=C-OBz), 5.70 (br s, 1H, C=C*H*$CH_2$), 7.47-7.63 and 8.12-8.15 (m, 5H, Ar-*H*).

$^{13}C$ NMR: δ 20.7, 21.7, 21.9, 25.3, 25.6, 29.3, 33.5 and 38.4 (cyclohexenyl-*C*$H_2$ +

cyclohexyl-*C*$H_2$), 66.9 and 73.5 (*C*H-O-*C*), 121.0, 122.1, 128.3, 128.6, 129.5, 130.0, 130.2, 133.5, 142.4 (alkenyl-*C*) and 164.6 (Ph*C*=O).

HRMS (ESI): Calcd. for $C_{21}H_{25}O_3$ [$M^+$+H]: *m/z* 325.1803. Found: 325.1803.

***Compound 33e*** (two diastereomers)




Yield: 0.119 g (80%, gummy liquid).

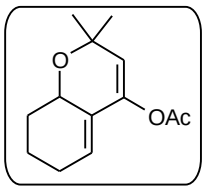
IR (neat): 3063, 2970, 2939, 2867, 1739, 1599, 1449, 1257, 1087, 1020, 709 $cm^{-1}$.

$^1$H NMR: δ 0.96 and 0.97 (2t, $^3J$(H-H) = 7.4 Hz and 7.6 Hz respectively, 6H, $CH_2CH_3$), 1.32 and 1.39 (2 s, 6H, -$CH_3$), 1.58-1.71 and 1.83-2.12 (m, 16H, $CH_2CH_3$ + cyclohexenyl-$CH_2$), 4.43 and 4.48 (2 br s, 2H, CHOC(Me)Et), 5.46 and 5.58 (2 s, 2H, CH=C-OBz), 5.71 and 5.72 (2 br s, 2H, C=C$HCH_2$), 7.46-8.15 (m, 10H, Ar-*H*). Two diastereomers were there and hence the proton numbers are doubled in the assignment given here.

$^{13}$C NMR: δ 8.1 ($CH_2CH_3$), $20.6_1$, $20.6_4$, 24.2, 25.2, 25.9, $29.2_0$, $29.2_4$, 30.5 and 35.5 (cyclohexenyl-$CH_2$+ $CH_2CH_3$ + $CH_3$), 67.3, 67.5, 74.8 and 75.1 (CHOC(Me)Et), 121.0, 121.2, 121.6, 122.7, 128.6, 129.5, 129.6, 129.9, 130.0, 133.5, 141.9, 142.7 (alkenyl-*C* + Ar-*C*) 164.6 and 164.7 (Ph*C*=O).

HRMS (ESI): Calcd. for $C_{19}H_{22}NaO_3$ [$M^+$+Na]: *m/z* 321.1467. Found: 321.1466.

***Compound 33f***




Yield: 0.083 g (75%, gummy liquid).

IR (neat): 2976, 2940, 2870, 1759, 1680, 1634, 1435, 1372, 1198, 1144, 1084, 1040, 941, 901 $cm^{-1}$.

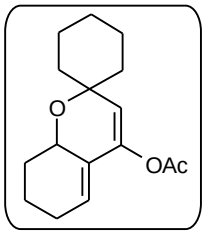
$^1$H NMR: δ 1.34 and 1.38 (2 s, 6H, $(CH_3)_2$C), 1.58-2.16 (m, 6H, cyclohexenyl-*H*),

2.19 (s, 3H, OCOC$H_3$), 4.39 (br s, 1H, C$H$OCMe$_2$), 5.40 (s, 1H, C$H$=C-OAc), 5.65 (t, $^3J$(H-H) = 3.6 Hz, 1H, C=C$H$CH$_2$).

$^{13}$C NMR: δ 20.7, 20.8, 25.3, 25.5, 29.2 and 30.1 (cyclohexenyl-$C$H$_2$+ C($C$H$_3$)$_2$ + OCO$C$H$_3$), 67.6 and 72.5 ($C$HO$C$Me$_2$), 121.1, 122.6, 129.7, 141.9 (alkenyl-$C$) and 168.8 (CH$_3$$C$=O).

HRMS (ESI): Calcd. for $C_{13}H_{19}O_3$ [M$^+$+H]: *m/z* 223.1336. Found: 223.1334.

***Compound 33g***




Yield: 0.102 g (78%, gummy liquid).

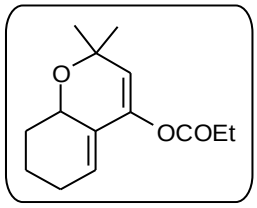
IR (neat): 2936, 2861, 1761, 1676, 1624, 1451, 1370, 1206, 1171, 1082, 737 cm$^{-1}$.

$^1$H NMR: δ 1.45-1.54, 1.58-1.66 and 2.14-2.15 (m, 16H, cyclohexenyl-C$H_2$ + cyclohexyl-$H$), 2.19 (s, 3H, COC$H_3$), 4.38 (br s, 1H, C$H$OC), 5.48 (s, 1H, C$H$=C-OAc), 5.63 (br s, 1H, C=C$H$CH$_2$).

$^{13}$C NMR: δ 20.7, 20.9, 21.7, 21.9, 25.3, 25.6, 29.3, 33.5 and 38.4 (cyclohexenyl-$C$H$_2$ + cyclohexyl-$C$ + OCO$C$H$_3$), 66.8 and 73.4 ($C$HO$C$CH), 120.8, 122.0, 130.2, 142.3 (alkenyl-$C$) and 168.9 (CH$_3$$C$=O).

HRMS (ESI): Calcd. for $C_{16}H_{22}NaO_3$ [M$^+$+Na]: *m/z* 285.1467. Found: 285.1465.

***Compound 33h***




Yield: 0.086 g (73%, gummy liquid).

IR (neat): 2978, 2940, 2868, 1763, 1667, 1632, 1462, 1358, 1177, 1144, 1080 cm$^{-1}$.

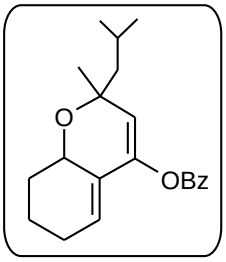
$^1$H NMR: δ 1.22 (t, $^3J$(H-H) = 7.6 Hz, 3H, CH$_2$C$H_3$), 1.34 and 1.39 (2 s, 6H, (C$H_3$)$_2$C), 1.58-1.60 and 1.86-2.16 (m, 6H, cyclohexenyl-C$H_2$), 2.50 (qrt, $^3J$(H-H) = 7.6 Hz, 2H, C$H_2$CH$_3$), 4.40 (br s, 1H, C$H$OCMe$_2$), 5.40 (s,

1H, C*H*=C-OCOEt), 5.64 (br s, =C*H*$CH_2$).

$^{13}$C NMR: δ 9.2 ($CH_3CH_2$), 20.7, 25.3, 25.5, 27.5, 29.2 and 30.1 (cyclohexenyl-$CH_2$ + $C(CH_3)_2$ + $OCOCH_2CH_3$ ), 67.6 and 72.5 ($CHOCMe_2$), 121.0, 122.5, 129.8, 141.7 (alkenyl-*C*) and 172.4 (Et*C*=O).

HRMS (ESI): Calcd. for $C_{14}H_{20}NaO_3$ [$M^+$+Na]: *m/z* 259.1310. Found: 259.1312.

***Compound 33i*** (two diastereomers)




Yield: 0.127 g (78%, gummy liquid).

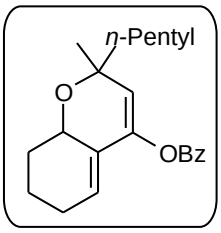
IR (neat): 3063, 3036, 2943, 2860, 1743, 1660, 1633, 1600, 1458, 1386, 1370, 1255, 1178, 1030, 915, 712 $cm^{-1}$.

$^1$H NMR: δ 0.89-1.05 (m, 12H, $CH(CH_3)_2$), 1.37 and 1.39 (2 s, 6H, $CH_3$), 1.45-1.69, 1.80-1.91 and 2.05-2.13 (m, 18H, $CH_2CHMe_2$ + cyclohexenyl-$CH_2$), 4.46 (br s, 2H, C*H*-O-C), 5.49 and 5.52 (2 s, 2H, C*H*=COBz), 5.71 (s, 2H, $CH_2CH$=C), 7.47-7.63 and 8.13-8.15 (m, 10H, Ar-*H*). Two diastereomers were there and hence the proton numbers are doubled in the assignment given here.

$^{13}$C NMR: δ 20.7, 23.8, 24.3, 24.4, 24.5, 24.8, 25.2, 25.3, 25.5, 27.0, 29.1, 29.4, 45.6 and 51.2 (($CH_3)_2CHCH_2$ + $CH_3$ + cyclohexenyl-$CH_2$), 67.3, 67.5, 75.2 and 75.4 ($CH_2$-O-*C*), 121.0, 122.2, 123.4, 128.6, 129.6, $129.8_0$, $129.8_2$, 130.1, 133.5, 141.9 and 142.3 (alkenyl-*C* + Ar-*C*), 164.7 (O*C*OPh).

HRMS (ESI): Calcd. for $C_{21}H_{26}NaO_3$ [$M^+$+Na]: *m/z* 349.1780. Found: 349.1778.

***Compound 33j*** (two diastereomers)




Yield: 0.128 g (82%, gummy liquid).

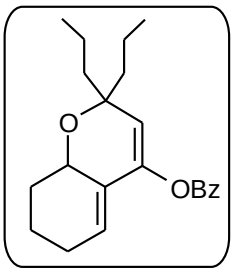
IR (neat): 2959, 2931, 2871, 1737, 1600, 1452, 1375, 1260, 1085, 1063, 1025, 701 $cm^{-1}$.

$^1H$ NMR: δ 0.89 and 0.90 (2 t, $^3J$(H-H)=7.8 Hz and 7.6 Hz respectively, 6H, C*H*$_3$CH$_2$), 1.26-1.87 and 2.07-2.18 (m, 34H, C*H*$_3$ + pentyl-*H* + cyclohexenyl-C*H*$_2$), 4.48 (br s, 2H, C*H*OC), 5.48 and 5.57 (2 s, 2H, C*H*=C-OBz), 5.72 (br s, 2H, C=C*H*CH$_2$), 7.48-8.15 (m, 10H, Ar-*H*). Two diastereomers were there and hence the proton numbers are doubled in the assignment given here.

$^{13}C$ NMR: δ 14.1, 14.3, 20.7, 22.7, 23.4, 23.5, 24.6, 25.3, 26.7, 29.3, 32.3, 37.9, 43.0 (*C*H$_3$ + pentyl-*C* + cyclohexenyl-*C*H$_2$), 67.4, 67.5, 74.8 and 75.0 (*C*HO*C*), 121.1, 121.3, 122.0, 122.9, 128.6, 129.6, 129.7, 129.9, 130.1, 133.6, 141.9, 142.5 (alkenyl-*C* + Ar-*C*) and 164.7 (Ph*C*=O).

HRMS (ESI): Calcd. for $C_{22}H_{28}O_3Na$ [$M^+$+Na]: *m/z* 363.1936. Found: 363.1938.

***Compound 33k***




Yield: 0.138 g (81%, gummy liquid).

IR (neat): 2959, 2940, 2866, 1737, 1458, 1277, 1173, 1085, 1025, 701 $cm^{-1}$.

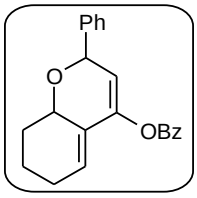
$^1H$ NMR: δ 0.87-0.96 (m, 6H, C*H*$_3$CH$_2$), 1.32-1.87 and 2.04-2.12 (m, 14H, propyl-*H* + cyclohexenyl-*C*H$_2$), 4.46 (br s, 1H, C*H*OC), 5.50 (s, 1H, C*H*=COBz), 5.69 (br s, 1H, CH$_2$C*H*=C), 7.47-8.15 (m, 5H, Ar-H).

$^{13}C$ NMR: δ 14.6 and 14.8 (*C*H$_3$CH$_2$), 16.9 and 17.1 (CH$_3$*C*H$_2$CH$_2$), 20.7, 25.3 and

29.3 (cyclohexenyl-*C*$H_2$), 39.9 and 41.5 ($CH_3CH_2$*C*$H_2$), 67.4 and 77.1 ($CH_2$*C*-O-*C*), 120.9, 121.8, 128.6, 129.5, 129.9, 130.1, 133.5, 142.4 (alkenyl-*C* + Ar-*C*), 164.8 (O*C*OPh).

HRMS (ESI): Calcd. for $C_{22}H_{28}NaO_3$ [$M^+$+Na]: *m/z* 363.1936. Found: 363.1916.

***Compound 33l***




Yield: 0.067 g (40%, gummy liquid, purity ca 90%).

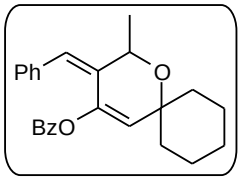
IR (neat): 3069, 2937, 2866, 1748, 1606, 1496, 1452, 1266, 1184, 1069, 1019, 712 $cm^{-1}$.

$^1$H NMR: δ 1.22-1.26 and 1.58-1.97 (m, 6H, cyclohexenyl-C*H*$_2$), 4.23 (br s, 1H, $CH_2$C*H*O), 5.55-5.56 (m, 1H, OC*H*Ph), 5.87 and 5.88 (2 s, 2H, alkenyl-*H*), 7.28-7.67 and 8.14-8.21 (m, 10H, Ar-*H*).

$^{13}$C NMR: δ 20.4, 25.3 and 28.8 (cyclohexenyl-*C*$H_2$), 66.7 and 74.1 (*C*HO*C*HPh), 115.4 (*C*=C-OBz), 122.4, 128.3, 128.5, 128.7, 129.0, 129.3, 129.7, 130.1, 133.7, 139.2, 143.9 (alkenyl-*C* + Ar-*C*), 164.8 (Ph*C*=O).

HRMS (ESI): Calcd. for $C_{22}H_{21}O_3$ [$M^+$+H]: *m/z* 333.1491. Found: 333.1491.

***Compound 34***




Yield: 0.161 g (86%, gummy liquid).

IR (neat): 3061, 2930, 2855, 1736, 1601, 1451, 1262, 1179, 1088, 1024, 739, 704 $cm^{-1}$.

$^1$H NMR: δ 1.33-1.99 (m, 10H, cyclohexyl-*H*), 1.53 (br s, 3H, CHC*H*$_3$), 4.61 (qrt, $^3$*J*(H-H) = 6.0 Hz, 1H, OC*H*$CH_3$), 5.67 (s, 1H, C*H*=C-OBz), 6.46 (s, 1H, PhC*H*=C), 7.00-7.44 (m, 10H, Ar-*H*).

$^{13}$C NMR: δ 18.4, 21.7, 22.1, 25.6, 33.6 and 38.6 (cyclohexyl-*C*$H_2$ + CH*C*$H_3$), 67.7

and 74.2 ($CH_3$*C*HO*C*), 123.4, 125.9, 126.7, 127.7, 128.8, 129.0, 129.7, 130.2, 132.8, 133.1, 137.4, 143.0 (Ar*C* + alkenyl-*C*) and 164.4 (Ph*C*=O).

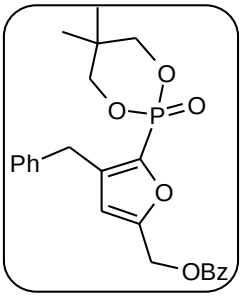
LC/MS: *m/z* 377 $[M+1]^+$.

Anal.Calcd. for $C_{25}H_{26}O_3$: C, 80.18; H, 7.00. Found: C, 80.25; H, 6.91.

### *3.62 Synthesis of phosphono-furans/-pyrans 35-40 and phosphinoyl furan 41*

These compounds were synthesized by following a procedure similar to that for **32a-g**. These are purified by column chromatography using silica gel with ethyl acetate/ hexane (1:1) mixture as the eluent.

***Compound 35***




This compound was synthesized from alkynol **24a**

Yield: 85%, *furan **35*** by $^{31}$P NMR [0.163 g (74%, *furan **35***)], white solid.

Mp: 84-86 $^oC$.

IR (KBr): 3063, 3022, 2965, 2240, 1718, 1599, 1454, 1371, 1273, 1174, 1097, 1066, 1014, 823 $cm^{-1}$.

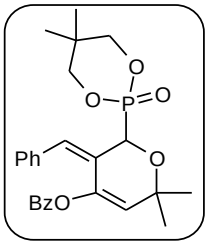
$^1$H NMR: δ 1.03 and 1.25 (2 s, 6H, (C*H*$_3$)$_2$C), 4.08-4.15 (m, 4H, OC*H*$_2$ + PhC*H*$_2$), 4.22 (dd→t, $^3J$(P-H) = $^2J$(H-H)~ 9.2 Hz, 2H, OC*H*$_A$H$_B$), 5.28 (s, 2H, C*H*$_2$OBz), 6.35 (s, 1H, Ar-*H*), 7.22-8.04 (m, 10H, Ar-*H*).

$^{13}$C NMR: δ 20.8, 21.8 (2 s, (*C*H$_3$)C), 31.1 (s, Ph*C*H$_2$), 32.4 (d, $^3J$(P-C) = 6.4 Hz, (CH$_3$)*C*), 58.2 (s, *C*H$_2$OBz), 77.1 (s, O*C*H$_2$), 112.9 (d, $^3J$(P-C) = 11.5 Hz, PC=C-*C*), 126.4, 128.5, 128.6, 128.9, 129.4, 129.7, 133.4, 138.7, 138.8, 139.1, 139.4, 141.1, 154.2 (d, $^3J$(P-C) = 11.0 Hz, PCO*C*), 166.0 (O*C*OPh).

$^{31}$P NMR: δ -2.72.

HRMS (ESI): Calcd. for $C_{24}H_{25}NaO_6P$ $[M^+$+Na]: *m/z* 463.1287. Found: 463.1287.

***Compound 36***




This compound was synthesized from alkynol **24b** to lead to two products, phosphono-furan and phosphono-pyran **36** [$^{31}$P NMR evidence].

Yield: 95%, *furan + pyran **36*** by $^{31}$P NMR [0.103 g (44%, *pyran **36***)], white solid.

Mp: 134-138 $^{o}$C.

IR (KBr): 3058, 2964, 2926, 2855, 1737, 1658, 1452, 1249, 1195, 1096, 1069, 1014, 811, 723 cm$^{-1}$.

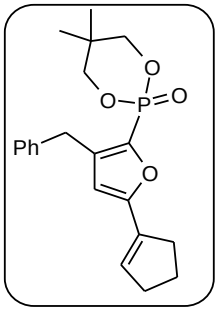
$^{1}$H NMR: δ 0.90 and 1.35 (2 s, 6H, (C*H*$_3$)$_2$C), 1.49 and 1.52 (2 s, 6H, (C*H*$_3$)$_2$C-O), 3.94-4.09 (m, 2H, OC*H*$_2$), 4.60 (dd, $^{3}J$(P-H) = 18.8 Hz and $^{2}J$(H-H) = 10.0 Hz, 2H, OC*H*$_A$H$_B$), 5.19 (dd, $^{2}J$(P-H) = 13.0Hz and $^{4}J$(H-H) = 1.4 Hz,, 1H, PC*H*), 5.75 (d, $^{5}J$(P-H) = 0.8 Hz,, 1H, C(OBz)=C*H*), 6.88-8.12 (m, 11H, PhC=C*H* + Ar-*H*).

$^{13}$C NMR: δ 20.8, 22.4, 25.4 and 29.5 (4 s, (*C*H$_3$)C + (*C*H$_3$)C-O), 32.5 (d, $^{3}J$(P-C) = 8.5 Hz, (CH$_3$)*C*), 73.1 (d, $^{1}J$(P-C)=166.2 Hz, P*C*), 75.2 (d, $^{3}J$(P-C)=14.1 Hz, O-*C*Me$_2$), 79.0 and 79.9 (2 d, $^{2}J$(P-C) =7.0 Hz and 7.3 Hz respectively, O*C*H$_2$), 123.4, 125.6, 126.9, 127.7, 128.4, 128.7, 128.8, 129.6, 130.1, 133.0, 133.4, 136.7, 142.2 (d, $^{2}J$(P-C) = 12.9 Hz, alkenyl-C) and 164.0 (O*C*OPh).

$^{31}$P NMR: δ 9.0.

HRMS (ESI): Calcd. for $C_{26}H_{29}NaO_6P$ [$M^+$+Na]: *m/z* 491.1600. Found: 491.1607.

***Compounds 37 and 38***




**37**

Alkynol **24c** led to two products, phosphono-furan **37** and phosphono-pyran **38** [$^{31}$P NMR evidence].

Yield: 90%, *furan **37** + pyran **38*** by $^{31}$P NMR [0.120 g (64%, isolated **37**)].

Mp: 94-96 $^{o}$C.

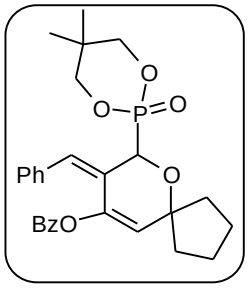
IR (KBr): 3019, 2975, 2893, 2844, 1688, 1578, 1507, 1392, 1255, 1167, 1019, 827 cm$^{-1}$.

$^{1}$H NMR: δ 1.11 and 1.24 (2 s, 6H, (C*H*$_3$)$_2$C), 1.95-1.99 and 2.49-2.57 (m, 6H, cyclopentenyl-C*H*$_2$), 4.11-4.25 (m, 6H, OC*H*$_2$ + PhC*H*$_2$), 6.05 (d, $^{4}J$(P-H) = 2.8 Hz, 1H, furyl-*H*), 6.16 (s, 1H, C*H*=C), 7.20-7.29 (m, 5H, Ar-*H*).

$^{13}$C NMR: δ 21.2, 21.9, 23.3, 31.2 and 32.3 (5 s, (*C*H$_3$)C + cyclopentenyl-*C*H$_2$), 32.4 (d, $^{3}J$(P-C) = 6.6 Hz, (CH$_3$)$_2$*C*), 33.7 (s, Ph*C*H$_2$), 76.8 and 76.9 (2 s, O*C*H$_2$), 108.6 (d, $^{3}J$(P-C)=12.0 Hz, PC=C-*C*), 126.3, 128.5, 128.9, 129.0, 132.4, 137.5 (d, $^{1}J$(P-C) = 241.9 Hz, P-*C*), 139.8, 139.9 (d, $^{2}J$(P-C) = 26.0 Hz, P-C-*C*), 156.5 (d, $^{3}J$(P-C) = 10.8 Hz, PC-O-*C*).

$^{31}$P NMR: δ -1.4.

HRMS (ESI): Calcd. for $C_{21}H_{25}NaO_4P$ [$M^+$+Na]: *m/z* 395.1388. Found: 395.1385.




**38**

Yield: 90%, *furan **37** + pyran **38*** by $^{31}$P NMR [0.025 g (10%, ***38***)], gummy liquid; purity >96%.

IR (neat): 3063, 2964, 2926, 1737, 1600, 1452, 1290, 1074, 1008, 701 cm$^{-1}$.

$^{1}$H NMR: δ 0.91 and 1.34 (2 s, 6H, (C*H*$_3$)$_2$C), 1.66 and 2.00 (m, 8H, cyclopentyl-*H*), 3.94-4.10 and 4.52-4.56 (m, 4H, OC*H*$_2$), 4.06 (d, $^{2}$*J*(P-H)= 13.2 Hz, 1H, PC*H*), 5.69 (s, 1H, C*H*=C-OBz), 6.83-8.12 (m, 11H, PhC=C*H* + Ar-H).

$^{13}$C NMR: δ 20.8, 22.3, 23.9 and 24.2 (4 s, (*C*H$_3$)C + cyclopentyl-*C*H$_2$), 32.5 (d, $^{3}$*J*(P-C)=8.2 Hz, (CH$_3$)*C*), 36.1 and 40.4 (2 s, cyclopentyl-*C*), 73.2 (d, $^{1}$*J*(P-C) = 167.8 Hz, P*C*), 78.7 and 79.5 (2 d, $^{2}$*J*(P-C) = 7.2 Hz and 6.6 Hz respectively, O*C*H$_2$), 86.4 (d, $^{3}$*J*(P-C) = 13.9 Hz, PC-O-*C*), 123.8, 124.1, 126.8, 127.6, 127.8, 128.5, 128.8, 129.7, 130.2, 132.9, 133.6, 134.1, 134.3, 136.9, 142.4 and 142.6 (alkenyl-*C* + Ar-*C*), 164.0 (O*C*OPh).

$^{31}$P NMR: δ 9.2.

HRMS (ESI): Calcd. for $C_{28}H_{31}NaO_6P$ [$M^+$+Na]: *m/z* 517.1756. Found: 517.1756.

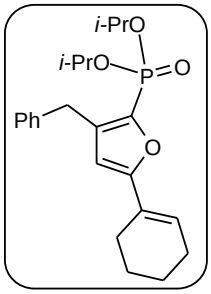
***Compound 26d***

This compound was synthesized from alkynol **24d** to lead to two products, phosphono-furan **26d** and phosphono-pyran. [$^{31}$P NMR evidence].

Yield: Quantitative, *furan **26d** + pyran* by $^{31}$P NMR [0.120 g (62%, **26d**)].

For spectral data see section 3.51.

***Compounds 39 and 40***




**39**

Alkynol **24e** led to two products, phosphono-furan **39** and phosphono-pyran **40** [$^{31}$P NMR evidence].

Yield: Quantitative, *furan **39** + pyran **40*** by $^{31}$P NMR [0.066 g (33%, **39**)]; gummy liquid.

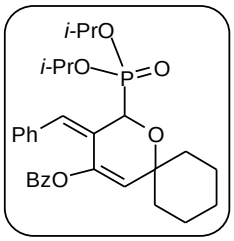
IR (neat): 3063, 2981, 2937, 1606, 1496, 1458, 1392, 1249, 1227, 1173, 997, 718 cm$^{-1}$.

$^{1}$H NMR: δ 1.25 and 1.37 (2 d, $^{3}J$(H-H) = 6.0 Hz each, 12H, CH(C$H_3$)$_2$), 1.36-1.71 and 2.18-2.22 (m, 8H, cyclohexenyl-C$H_2$), 4.11 (s, 2H, PhC$H_2$), 4.64-4.69 (m, 2H, C$H$(CH$_3$)$_2$), 6.02 (d, $^{3}J$(P-H) = 2.8 Hz, 1H, furyl-*H*), 6.41 (s, 1H, cyclohexenyl =C*H*), 7.18-7.28 (m, 5H, Ar-*H*).

$^{13}$C NMR: δ 22.0, 22.2, 23.80, 23.82, 24.1, 24.2, 24.9, 25.3 (8 s, CH(*C*H$_3$)$_2$ + cyclohexenyl-*C*H$_2$), 31.4 (s, Ph*C*H$_2$), 71.4 (d, $^{2}J$(P-C) = 4.9 Hz, *C*H(CH$_3$)$_2$), 106.5 (d, $^{3}J$(P-C) = 12.0 Hz, PC=C-*C*), 125.8, 126.2, 126.9, 128.5, 128.9, 130.1, 133.2, 137.8 (d, $^{1}J$(P-C) = 235.9 Hz, P-*C*), 138.9 (d, $^{2}J$(P-C) = 25.6 Hz, P-C-*C*), 140.3, 159.3 (d, $^{3}J$(P-C) = 12.0 Hz, PC-O-*C*).

$^{31}$P NMR: δ 5.6.

HRMS (ESI): Calcd. for $C_{23}H_{32}O_4P$ [$M^+$+H]: *m/z* 403.2039. Found: 403.2039.




**40**

Yield: Quantitative, *furan **39** + pyran **40*** by $^{31}$P NMR [0.144 g (55%, ***40***)]; gummy liquid, purity 80%, remaining 20% was **39**.

IR (neat): 3063, 2975, 2932, 2860, 1721, 1600, 1452, 1392, 1255, 1173, 997, 707 cm$^{-1}$.

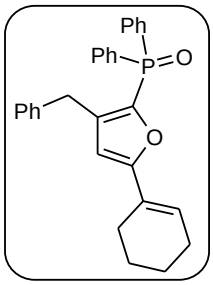
$^{1}$H NMR: δ 1.29-1.53 (m, 12H, CH(C$H_3$)$_2$), 1.54-1.78 (m, 10H, cyclohexyl-*H*), 4.84-4.94 (m, 3H, OC$H$(CH$_3$)$_2$ + PC*H*), 5.78 (s, 1H, C*H*=C-OBz), 6.85-7.19 and 7.37-8.11 (m, 11H, PhC=C*H* + Ar-H).

$^{13}$C NMR: δ 21.7 (s, cyclohexyl-*C*H$_2$), 22.0 (s, CH(*C*H$_3$)$_2$), 24.3 and 24.4 (2 d, $^{3}J$(P-C) = 3.4 and 3.3 Hz respectively, CH(*C*H$_3$)$_2$), 25.4 (s, CH(*C*H$_3$)$_2$), 33.8 and 37.8 (2 s, cyclohexyl-*C*), 70.2 (d, $^{1}J$(P-C) = 172.7 Hz, P*C*), 71.6 and 72.3 (d, $^{2}J$(P-C) = 7.0 Hz and 7.4 Hz respectively, O*C*H(CH$_3$)$_2$), 76.0 (d, $^{3}J$(P-C) = 12.0 Hz, PC-O-*C*), 125.0, 125.6, 126.7, 127.5, 127.7, 128.1, 128.4, 128.5, 129.0, 129.6, 130.1, 133.8, 133.3, 137.2 (alkenyl-*C* + Ar-*C*), 142.2 (d, $^{3}J$(P-C) = 13.4 Hz, alkenyl-*C*), 164.1 (s, O*C*OPh).

$^{31}$P NMR: δ 16.6.

HRMS (ESI): Calcd. for $C_{30}H_{37}NaO_6P$ [$M^+$+Na]: *m/z* 547.2226. Found: 547.2224.

***Compound 41***




This compound was synthesized from alkynol **25** to lead to mixture of products, phosphinoyl furan **41** and others (3 products).

Yield: Quantitative, *furan **41** + others* by $^{31}$P NMR [0.062 g (28%, **41**)].

Mp: 96-98 $^{o}$C.

IR (KBr): 3063, 3030, 2932, 2858, 1666, 1600, 1436, 1266, 1162, 1123, 707 cm$^{-1}$.

$^{1}$H NMR: δ 1.58- 1.67 and 2.13-2.19 (m, 8H, cyclohexenyl-C$H_2$), 4.12 (s, 1H, PhC$H_2$), 6.06 (s, 1H, furyl-*H*), 6.18 (br s, 1H, C=C*H*), 7.16-7.25 and 7.47-8.10 (m, 15H, Ar-*H*).

$^{13}$C NMR: δ 22.0, 22.2, 24.8, 25.3 and 31.2 (5 s, cyclohexenyl-$CH_2$ + Ph$CH_2$), 107.1 (d, $^{3}J$(P-C) = 8.9 Hz, PC=C-*C*), 125.7, 126.1, 126.9, 128.4, 128.6, 129.0, 130.1, 131.7, 131.8, 132.8 (d, $^{1}J$(P-C) = 100.7 Hz, P-*C*), 133.3, 140.0 (d, $^{2}J$(P-C) = 6.3 Hz, P-C-*C*), 140.2, 159.9 (d, $^{3}J$(P-C) = 6.2 Hz, PC-O-*C*).

$^{31}$P NMR: δ 18.5.

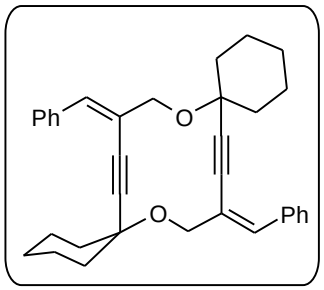
HRMS (ESI): Calcd. for $C_{29}H_{28}O_2P$ [$M^+$+H]: *m/z* 439.1828. Found: 439.1828.

### *3.63 Synthesis of macrocycles 42-45*

These compounds were synthesized by following a method similar to that for **32a-g** using β-hydroxy propargylic esters **20h-j** (0.5 mmol).

***Compounds 42 and 43***

Precursor **20h** led to mixture of products **42** and **43** which were separated successfully.




**42**

Yield: 0.033 g (28%, white solid).

Mp: 120-122 $^{o}$C.

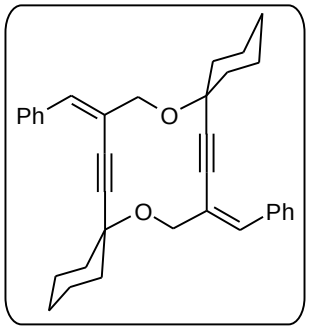
IR (KBr): 3058, 3025, 2934, 2857, 1721, 1599, 1449, 1339, 1289, 1260, 1144, 1084, 752, 693 $cm^{-1}$.

$^{1}$H NMR: δ 1.29-1.35 and 1.55-2.06 (m, 20H, cyclohexyl-*H*), 4.34 (s, 4H, OC*H*$_2$), 6.88 (s, 2H, PhC*H*=C), 7.23-7.85 (m, 10H, Ar-*H*).

$^{13}$C NMR: δ 23.0, 25.6 and 37.3 (cyclohexyl-*C*H$_2$), 66.9 and 75.2 (*C*H$_2$O*C*), 84.6 and 97.3 (*C*≡*C*), 119.6, 127.9, 128.1, 128.7, 132.9 and 136.5 (Ar*C* + alkenyl-*C*).

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

Anal.Calcd. for $C_{34}H_{36}O_2$: C, 85.67; H, 7.61. Found: C, 85.56; H, 7.71.




**43**

Yield: 0.052 g (44%, white solid).

Mp: 178-180 $^{o}$C.

IR (KBr): 2963, 2856, 1948, 1599, 1495, 1447, 1412, 1262, 1103, 866, 801, 693 $cm^{-1}$.

$^{1}$H NMR: δ 1.32 (br s, 2H, cyclohexyl-*H*), 1.63-2.12 (m, 18H, cyclohexyl-*H*), 4.38 (s, 4H, OC*H*$_2$C), 6.71 (s, 2H, PhC*H*=C), 7.27-7.91 (m, 10H, Ar-*H*).

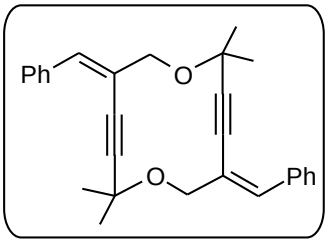
$^{13}$C NMR: δ 23.3, 25.6 and 37.5 (cyclohexyl-*C*H$_2$), 70.3 and 76.8 (*C*H$_2$O*C*), 84.8

and 98.9 (*C*≡*C*), 119.9, 128.1, 128.4, 128.8 and 136.0 (Ar*C* + alkenyl-*C*).

HRMS (ESI): Calcd. for $C_{34}H_{37}O_2$ [$M^+$+H]: *m/z* 477.2795. Found: 477.2793.

X-ray structure has been determined for this compound.

***Compound 44***




Yield: 0.059 g (60%, low melting solid).

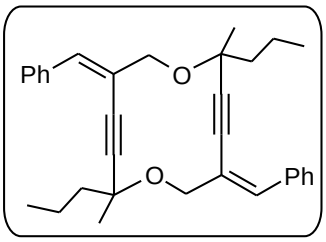
IR (KBr): 2978, 2932, 2859, 2170, 2160, 1659, 1622, 1449, 1360, 1179, 1150, 1073, 739, 696 $cm^{-1}$.

$^1$H NMR: δ 1.61 (s, 12H, $(CH_3)_2C$), 4.37 (s, 4H, $OCH_2$), 6.67 (s, 2H, PhC*H*=C), 7.29-7.84 (m, 10H, Ar-*H*).

$^{13}$C NMR: δ 28.9 ($(CH_3)_2C$), 71.0 and 72.7 ($(CH_3)_2C$-O-$CH_2$), 83.0 and 99.6 (*C*≡*C*), 119.5, 128.2, 128.5, 128.6, 135.8 and 136.0 (*C*=*C* + Ar-*C*).

HRMS (ESI): Calcd. for $C_{28}H_{28}NaO_2$ [$M^+$+Na]: *m/z* 419.1987. Found: 419.1989.

***Compound* 45** (2 diastereomers)




Yield: 0.050 g (44%, gummy liquid).

IR (neat): 2960, 2925, 2872, 2250 (vw), 1650, 1500, 1449, 1371, 1262, 1149, 1128, 1066, 1004, 921, 885, 755, 688 $cm^{-1}$.

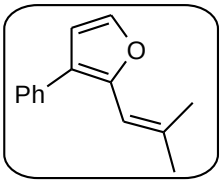
$^1$H NMR: δ 0.95-1.00 (m, 6H, $CH_2CH_3$), 1.54-1.83 (m, 14H, $CH_3$ + $CH_2CH_2CH_3$), 4.27 (d, $^2J$(H-H) = 10.8 Hz, 1H, $OCH_AH_B$), 4.37 (s, 2H, $OCH_2$), 4.47 (d, $^2J$(H-H) = 10.8 Hz, 1H, $OCH_AH_B$), 6.66 (s, 1H, PhC*H*=C), 7.27-7.85 (m, 10H, Ar-*H*). (2 diastereomers in the ratio ~3:2).

$^{13}$C NMR: δ 14.4 ($CH_2CH_3$), 18.1, 18.2, 26.3, 26.7, 43.7 and 44.3 ($CH_3$ +

$CH_2CH_2CH_3$), 70.7 and 76.2 (*C*-O-$CH_2$), 84.3 and 99.1 (*C*≡*C*), 119.8, 128.2, 128.4, 128.7, 135.4 and 136.0 (*C*=*C* + Ar-*C*).

HRMS (ESI): Calcd. for $C_{32}H_{36}NaO_2$ [$M^+$+Na]: *m/z* 475.2613. Found: 475.2610.

### *3.64 Synthesis of furan derivative 46*




This compound was synthesized by using a method similar to that for **32a-g** using γ-hydroxy propargyl ester **23** (0.4 mmol).

Yield: 0.040 g (50%, gummy liquid).

IR (neat): 3058, 2975, 2921, 1611, 1490, 1452, 1381, 1140, 964, 762 $cm^{-1}$.

$^1$H NMR: δ 1.92 and 2.06 (2 s, 6H, =C($CH_3$)$_2$), 6.16 and 6.57 (2 s, 2H, C*H*=C + furyl-*H*), 7.28-7.45 (m, 6H, Ar-*H*).

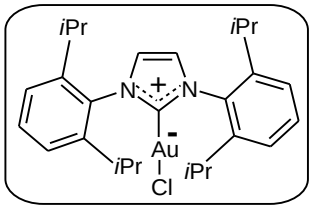
$^{13}$C NMR: δ 20.4 and 27.3 (=C($CH_3$)$_2$), 111.7 and 112.9 (alkenyl-*C*), 122.4, 126.5, 128.2, 128.5, 134.3, 137.0, 140.7 and 149.1 (Ar-*C*).

HRMS (ESI): Calcd. for $C_{14}H_{15}O$ [$M^+$+H]: *m/z* 199.1124. Found: 199.1124.

## 3.7 Synthesis of gold carbene complexes 49-50 (from the corresponding salts 47-48), benzofluorenols/substituted dienes 51-66 and diene derivatives 69-70

### *3.71 Synthesis of gold carbene complexes 49-50*

***Compound 49***



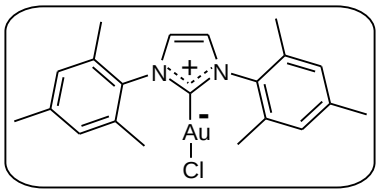

This compound was synthesized from 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride **47**[80] by following a literature procedure.[79] To a solution of IPrHCl (0.160 g, 0.38 mmol), $Na_2CO_3$ (0.190 g, 1.7 mmol) in 3-chloro pyridine (2.0 mL) was added $NaAuCl_4$ (0.140 g, 0.35 mmol) and the contents stirred at

80 $^{o}$C for 24 h. The mixture was cooled to rt and evacuated to remove the volatiles. Dichloromethane (5 mL) was added to the crude product. The solution was loaded into a column containing silica gel and short pad of celite. Compound **49** was eluted with $CH_2Cl_2$. Solvent was evaporated and pentane was added to get the catalyst as precipitate. It was then filtered and dried under vacuum.

Yield: 0.113 g (52 %).

Spectral data are in agreement with the literature report.[79]

***Compound 50***




This compound was synthesized by following a procedure similar to that for **49** using 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride **48** (0.15 mmol, 0.051g).

Yield: 0.030 g (38 %).

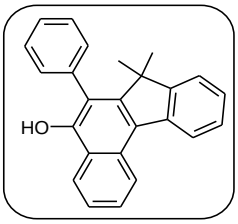
Spectral data are in agreement with the literature report.[79]

### *3.72 Synthesis benzofluorenols/substituted dienes 51-66 and dienes derivatives 69-70*

To a mixture of IPrAuCl [IPr = 1,3-bis(diisopropylphenyl)imidazol-2-ylidene] (0.006 g, 0.01 mmol) and $AgSbF_6$ (0.003 g, 0.01) in DCM (2 mL) was added the corresponding propargyl benzoate **8b**, **8d-e** and **10c-g** (0.6 mmol) and 1,3-diphenylisobenzofuran (0.5 mmol). The contents were stirred at rt (25 $^{o}$C) for 4 h. The solvent was removed in vacuum and the product/s was/were purified by column chromatography. Details on each compound are given below.

***Compounds 51 and 52***

These two products were prepared by the same reaction using 2-methylbut-3yn-2-yl benzoate **8b** (0.113 g, 0.6 mmol) and 1,3-diphenylisobenzofuran (0.135 g, 0.5 mmol). The separation was done using acetone/hexane mixture [1:100 ratio for **51** and 1: 50 for **52**] as the eluent.




7,7-dimethyl-6-phenyl-7*H*-benzo[*c*]fluoren-5-ol (**51**)

Yield: 0.093 g (55%).

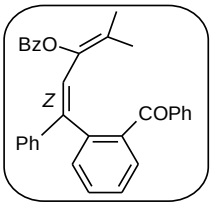
Mp: 150-152 $^{o}$C.

IR (KBr): 3507, 3057, 2981, 2959, 2860, 1578, 1441, 1391, 1216, 1057, 766 cm$^{-1}$.

$^{1}$H NMR: δ 1.30 (s, 6H, C(C*H*$_3$)$_2$), 5.16 (s, 1H, Ar-O*H*), 7.28-7.60, 8.30-8.35 and 8.80-8.82 (m, 13H, Ar-*H*).

$^{13}$C NMR: δ 26.6 (C(*C*H$_3$)$_2$), 48.6 (*C*(CH$_3$)$_2$), 120.4, 121.9, 122.2, 123.5, 123.8, 124.8, 125.4, 126.5, 127.0, 127.2, 127.3, 127.9, 129.0, 129.9, 132.4, 134.0, 140.0, 149.1, 149.8 and 154.9 (Ar-*C*).

HRMS (ESI): Calcd. for $C_{25}H_{20}O$ [$M^+$+H]: *m/z* 337.1593. Found: 337.1592.




**52**

Yield: 0.094 g (41%, gummy liquid).

IR (neat): 3063, 2915, 2854, 1726, 1665, 1599, 1457, 1309, 1287, 1117, 701 cm$^{-1}$.

$^{1}$H NMR: δ 1.41 and 1.62 (2 s, 6H, =C(C*H*$_3$)$_2$), 6.69 (s, 1H, PhC=C*H*), 7.10-7.74 (m, 19H, Ar-*H*).

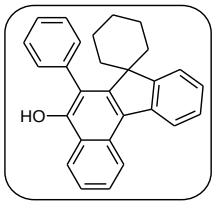
$^{13}$C NMR: δ 18.5 and 19.2 (=C(*C*H$_3$)$_2$), 121.6, 126.4, 127.0, 127.5, 127.9, 128.5, 129.2, 129.3, 129.8, 130.0, 130.2, 130.6, 131.3, 132.6, 132.9, 137.1, 139.1, 139.3, 140.2, 140.7, 142.4 (Alkenyl-*C* + Ar-*C*), 164.1 (O*C*OPh), 196.4 (Ar*C*OPh).

HRMS (ESI): Calcd. for $C_{32}H_{26}O_3$ [$M^+$+H]: *m/z* 459.1961. Found: 459.1964.

***Compounds 53 and 54***

These compounds were prepared by using 1-ethynylcyclohexyl benzoate **8d** (0.137 g, 0.6 mmol) and 1,3-diphenylisobenzofuran (0.135 g, 0.5 mmol). The separation

was done using acetone/hexane mixture [1:100 ratio for **53** and 1: 50 for **54**] as the eluent.




**53**

Yield: 0.109 g (58%).

Mp: 230-232 $^{o}$C.

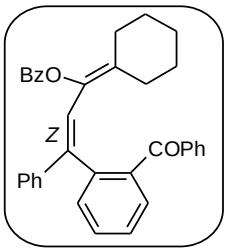
IR (KBr): 3534, 3052, 2953, 2932, 2843, 1622, 1563, 1439, 1391, 1343, 1219, 1065, 1024, 752, 710, 666 $cm^{-1}$ .

$^{1}$H NMR: δ 0.75-0.79, 1.32-1.54, 1.76-2.00 and 2.21-2.28 (m, 10H, cyclohexyl-*H*), 5.10 (s, 1H, Ar-O*H*), 7.23-7.96, 8.36-8.42 and 8.86-8.88 (m, 13H, Ar-*H*).

$^{13}$C NMR: δ 22.3, 25.1, 32.6 and 52.4 (cyclohexyl-*C*$H_2$), 120.3, 122.2, 123.6, 123.7, 124.3, 124.8, 125.2, 126.7, 126.8, 127.4, 129.0, 129.2, 129.6, 130.5, 132.8, 134.2, 140.8, 149.4, 149.8 and 153.6 (Ar-*C*).

HRMS (ESI): Calcd. for $C_{28}H_{25}O$ [$M^{+}$+H]: *m/z* 377.1906. Found: 377.1904.

X-ray structure has been determined for this compound.




**54**

Yield: 0.82 g (33%, gummy liquid).

IR (neat): 3063, 2926, 2854, 1726, 1671, 1599, 1452, 1276, 1068, 701 $cm^{-1}$.

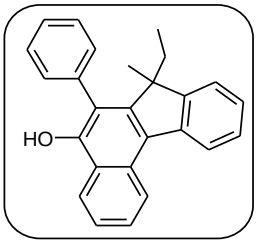
$^{1}$H NMR: δ 1.31-1.53 and 1.87-2.10 (m, 10H, cyclohexyl-*H*), 6.73 (s, 1H, PhC=C*H*), 7.10-7.76 (m, 19H, Ar-*H*).

$^{13}$C NMR: δ 26.2, 26.6, 27.0, 28.1, 29.4 (cyclohexyl-*C*), 121.1, 126.3, 127.5, 128.$0_0$, 128.$0_2$, 129.1, 129.3, 129.4, 129.7, 130.1, 130.2, 131.3, 132.6, 132.9, 134.1, 136.4, 137.2, 139.2, 140.4, 141.0, 142.6 (Alkenyl-C + Ar-*C*), 164.3 (O*C*OPh), 196.3 (Ar*C*OPh).

HRMS (ESI): Calcd. for $C_{35}H_{30}O_3$ [$M^+$+H]: *m/z* 499.2274. Found: 499.2274.

***Compounds 55 and 56***

These compounds were prepared by using 3-methylpenty-1-yn-3-yl benzoate **8e** (0.121 g, 0.6 mmol) and 1,3-diphenylisobenzofuran (0.135 g, 0.5 mmol). The separation was done using acetone/hexane mixture [1:100 ratio for **55** and 1: 50 for **56**] as the eluent. Compound **56** has two geometrical isomers (*EZ* and *ZZ*).




**55**

Yield: 0.110 g (63%).

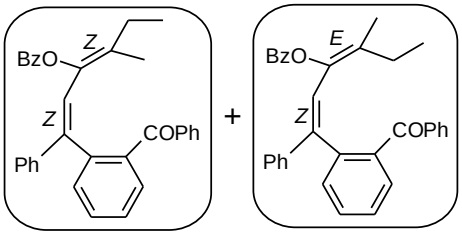
Mp: 118-120 $^oC$.

IR (KBr): 3436, 3063, 2970, 2920, 2860, 1660, 1594, 1452, 1277, 1069, 932 $cm^{-1}$.

$^1H$ NMR: δ 0.24 (t, $^3J$(H-H) = 7.2 Hz, 3H, C$H_3$CH$_2$), 1.31 (s, 3H, C$H_3$CAr), 1.69-1.72 and 1.78-1.82 (m, 2H, C$H_2$CH$_3$), 5.14 (s, 1H, Ar-O*H*), 7.28-7.71 and 8.29-8.80 (m, 13H, Ar-*H*).

$^{13}C$ NMR: δ 8.7 (*C*H$_3$CH$_2$), 26.6 and 31.8 (CH$_3$*C*H$_2$ + *C*H$_3$CAr), 53.1 (Ar*C*(Me)Et), 120.2, 121.7, 121.9, 123.5, 123.7, 124.8, 125.3, 126.9, 127.2, 128.0, 129.1, 129.8, 131.1, 132.3, 134.0, 141.3, 147.4, 149.0 and 152.8 (Ar-*C*).

HRMS (ESI): Calcd. for $C_{26}H_{23}O$ [$M^+$+H]: *m/z* 351.1750. Found: 351.1749.




**56**

Yield: 0.071 g (30%, gummy liquid).

IR (neat): 3057, 2964, 2931, 1732, 1660, 1595, 1452, 1310, 1277, 1063, 773, 707 $cm^{-1}$.

$^1H$ NMR: δ 0.75 and 0.85 (2 t, $^3J$(H-H) = 6.4 Hz each, 6H, C$H_3$CH$_2$), 1.41 and 1.60 (2 s, 6H, C$H_3$C=C), 1.65 and 2.04 (2 br s, 4H, C$H_2$CH$_3$), 6.67 and 6.73

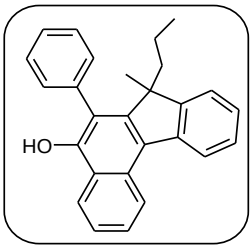
(2 s, 2H, PhC=C*H*), 7.07-7.77 (m, 38H, Ar-*H*). In the assignment, the proton numbers are doubled to show the presence of both the isomers.

$^{13}$C NMR: δ 11.7 and 12.0 (2 *C*$H_3$C$H_2$), 15.8, 16.5, 25.2 and 26.2 (2 C$H_3$C*H*$_2$ and 2 *C*$H_3$C=C), 120.6, 121.8, 126.3, 126.5, 127.5, 127.9, 128.1, 129.1, 129.4, 129.7, 129.8, 129.9, 130.1, 130.2, 131.1, 131.3, 132.5, 132.6, 132.9, 137.2, 137.3, 138.7, 139.0, 139.4, 140.0, 140.6, 140.9, 142.4, 142.5 (Ar-*C*), 163.9, 164.3 (O*C*OPh), 196.5 (Ar*C*OPh).

HRMS (ESI): Calcd. for $C_{33}H_{28}NaO_3$ [$M^+$+Na]: *m/z* 495.1936. Found: 495.1938.

***Compounds 57 and 58***

These compounds were prepared by using 3-methylhexy-1-yn-3-yl benzoate **10c** (0.130 g, 0.6 mmol) and 1,3-diphenylisobenzofuran (0.135 g, 0.5 mmol). The separation was done using acetone/hexane mixture [1:100 ratio for **57** and 1: 50 for **58**] as the eluent. Compound **58** has two geometrical isomers (*EZ* and *ZZ*).




**57**

Yield: 0.097 g (53%).

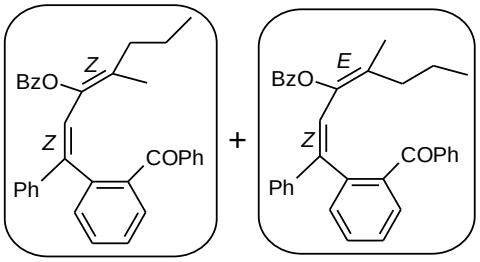
Mp: 120-122 $^{o}$C.

IR (KBr): 3518, 2959, 2926, 2860, 1578, 1441, 1397, 1238, 1222, 1069, 795, 751, 707, 669 cm$^{-1}$.

$^1$H NMR: δ 0.60 (t, $^3J$(H-H) = 6.4 Hz, 3H, C*H*$_3$CH$_2$), 1.31 (s, 3H, C*H*$_3$CAr), 1.62-1.75 (m, 4H, C*H*$_2$C*H*$_2$CH$_3$), 5.13 (s, 1H, Ar-O*H*), 7.27-7.70 and 8.28-8.81 (m, 13H, Ar-*H*).

$^{13}$C NMR: δ 14.1, 17.5, 27.0, 41.2 (*C*H$_3$ + propyl-*C*), 52.7 (Ar*C*(Me)propyl), 120.2, 121.6, 121.9, 123.6, 124.8, 125.3, 126.9, 127.2, 127.7, 128.4, 129.1, 129.6, 129.8, 131.1, 132.3, 134.0, 141.0, 147.9, 149.0 and 153.3 (Ar-*C*).

HRMS (ESI): Calcd. for $C_{26}H_{23}O$ [$M^+$+H]: *m/z* 351.1750. Found: 351.1749.




**58**

Yield: 0.102 g (42%, gummy liquid).

IR (neat): 3058, 2955, 2929, 2872, 1728, 1666, 1599, 1444, 1314, 1278, 1071, 931, 698 $cm^{-1}$.

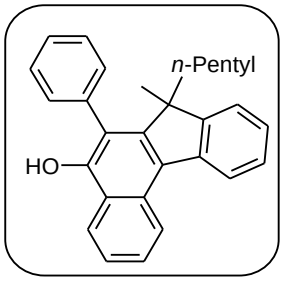
$^{1}H$ NMR: δ 0.77 and 0.83 (2 t, $^{3}J$(H-H) = 7.4 Hz and 7.2 Hz respectively, 6H, C*H*$_3$CH$_2$), 0.86-0.97, 1.22-1.65 (m, 14H, C*H*$_3$ + C*H*$_2$C*H*$_2$CH$_3$), 6.68 and 6.73 (2 s, 2H, PhC=C*H*), 6.81-7.74 (m, 38H, Ar-*H*).

$^{13}C$ NMR: δ 14.0, 14.2, 16.4, 17.1, 20.5, 21.0, 34.3 and 35.1 (propyl-*C* + *C*H$_3$), 121.1, 121.9, 126.3, 126.5, 127.5, 127.9, 128.1, 129.1, 129.5, 129.8, 129.9, 130.2, 130.3, 130.6, 131.2, 131.3, 132.4, 132.6, 132.8, 137.3$_0$, 137.3$_4$, 139.3, 139.7, 139.9, 140.1, 140.6, 140.9, 142.4 and 142.6 (Ar-*C*), 163.9, 164.3 (O*C*OPh), 196.4 (Ar*C*OPh).

HRMS (ESI): Calcd. for $C_{34}H_{31}O_3$ [$M^+$+H]: *m/z* 487.2274. Found: 487.2273.

***Compounds 59-60***

These compounds were prepared by using 3-methylocty-1-yn-3-yl benzoate (0.147 g, 0.6 mmol) **10d** and 1,3-diphenylisobenzofuran (0.135 g, 0.5 mmol). The separation was done using acetone/hexane mixture [1:100 ratio for **59** and 1: 50 for **60**] as the eluent. Compound **60** has two geometrical isomers (*EZ* and *ZZ*).




**59**

Yield: 0.102 g (52%).

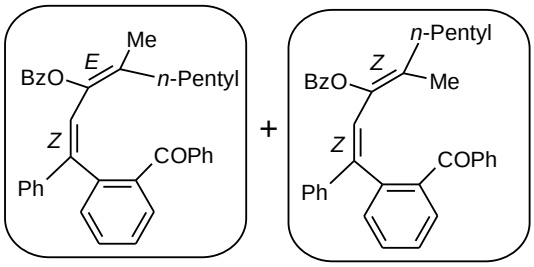
Mp: 116-118 $^{o}$C.

IR (KBr): 3496, 2948, 2931, 2855, 1584, 1386, 1222, 1069, 751, 712 $cm^{-1}$.

$^{1}$H NMR: δ 0.44 (br s, 1H, pentyl-*H*), 0.71 (t, $^{3}J$(H-H) = 6.0 Hz, 3H, C*H*$_3$CH$_2$), 0.95-1.04 (m, 5H, pentyl-*H*), 1.05 (s, 3H, C*H*$_3$), 1.59-1.75 (m, 2H, pentyl-*H*), 5.13 (s, 1H, Ar-O*H*), 7.29-7.71 and 8.28-8.82 (m, 13H, Ar-*H*).

$^{13}$C NMR: δ 14.2, 22.4, 23.8, 27.0, 32.1, 38.9 (*C*H$_3$ + pentyl-*C*), 52.5 (Ar-*C*(Me)*n*-pentyl), 120.3, 122.0, 123.5, 124.7, 125.3, 126.7, 127.1, 128.3, 129.1, 129.6, 131.1, 132.3, 133.9, 141.0, 147.9 and 153.2 (Ar*C*).

HRMS (ESI): Calcd. for $C_{29}H_{29}O$ [$M^+$+H]: *m/z* 393.2219. Found: 393.2217.




**60**

Yield: 0.098 g (38%, gummy liquid).

IR (neat): 3047, 2959, 2931, 2855, 1732, 1666, 1595, 1452, 1315, 1266, 1244, 1156, 767, 740, 712 cm$^{-1}$.

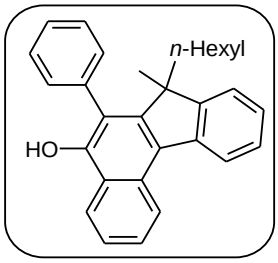
$^{1}$H NMR: δ 0.81 and 0.86 (2 t, $^{3}J$(H-H) = 7.0 Hz and 6.8 Hz respectively, 6H, C*H*$_3$CH$_2$), 1.13-1.31 (m, 12H, pentyl-*H*), 1.43 and 1.66 (2 br s, 10H, pentyl-*H* + C*H*$_3$), 6.69 and 6.72 (2 s, 2H, PhC=C*H*), 6.74-7.79 (m, 38H, Ar-*H*).

$^{13}$C NMR: δ 14.0, 16.4, 17.1, 22.4, 22.6, 26.8, 27.0, 27.4, 31.8, 32.1 and 33.2 (n-pentyl-*H* + C*H*$_3$), 121.0, 121.9, 126.3, 126.5, 126.7, 127.5, 127.9, 128.1, 128.4, 129.1, 129.4, 129.8, 130.2, 130.8, 131.2, 131.4, 132.4, 132.6, 132.8, 137.4, 139.2, 139.3, 139.5, 139.8, 140.1, 140.7, 142.5 and 142.6 (Alkenyl-*C* + Ar-*C*), 164.3 (O*C*OPh), 196.4 (Ar*C*OPh).

HRMS (ESI): Calcd. for $C_{36}H_{35}O_3$ [$M^+$+H]: *m/z* 515.2587. Found: 515.2589.

***Compounds 61 and 62***

These compounds were prepared by using 3-methylnon-1-yn-3-yl benzoate (0.155 g, 0.6 mmol) **10e** and 1,3-diphenylisobenzofuran (0.135 g, 0.5 mmol). The separation was done using acetone/hexane mixture [1:100 ratio for **61** and 1: 50 for **62**] as the eluent. Compound **62** has two geometrical isomers (*EZ* and *ZZ*).




**61**

Yield: 0.110 g (54%).

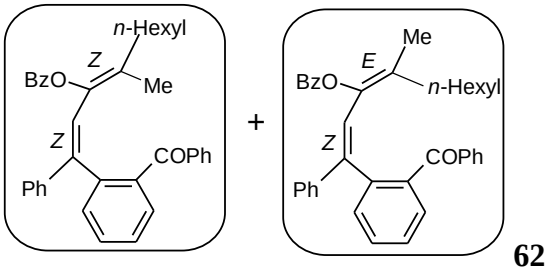
Mp: 114-116 $^{o}$C.

IR (KBr): 3534, 3063, 2955, 2924, 2851, 1625, 1583, 1459, 1438, 1392, 1350, 1273, 1221, 1061, 760, 703, 667 cm$^{-1}$.

$^{1}$H NMR: δ 0.49 and 0.72 (2 br s, 2H, hexyl-*H*), 0.80 (t, $^{3}J$(H-H) = 7.4 Hz, 3H, C*H*$_3$CH$_2$), 1.03-1.78 (m, 11H, C*H*$_3$ + hexyl-*H*), 5.18 (s, 1H, Ar-O*H*), 7.31-7.73 and 8.32-8.86 (m, 13H, Ar-*H*).

$^{13}$C NMR: δ 14.1, 22.7, 24.1, 27.1, 29.5, 31.6, 39.0 (*C*H$_3$ + hexyl-*C*), 52.6 (Ar*C*(Me)hexyl), 120.2, 121.6, 121.9, 123.5, 123.8, 124.7, 125.3, 126.9, 127.2, 127.7, 128.3, 129.1, 129.6, 129.8, 131.2, 132.3, 141.0, 147.9, 148.9 and 153.3 (Ar-*C*).

HRMS (ESI): Calcd. for $C_{30}H_{31}O$ [$M^{+}$+H]: *m/z* 407.2376. Found: 407.2373.




**62**

Yield: 0.100 g (38%).

IR (neat): 3053, 3022, 2924, 2856, 1733, 1661, 1599, 1449, 1268, 926 cm$^{-1}$.

$^{1}$H NMR: δ 0.80 and 0.86 (2 t, $^{3}J$(H-H) = 7.0 Hz and 7.4 each, 6H, C*H*$_3$CH$_2$), 1.15-1.27 (m, 16H, hexyl-*H*), 1.43-1.66 (2 s, 6H, C*H*$_3$), 1.71-1.74 and 2.00-2.04 (m, 2H, hexyl-*H*), 6.69 and 6.74 (2 s, 2H, PhC=C*H*), 7.05-7.20, 7.27-7.37, 7.44-7.49, 7.54-7.76 (m, 38H, Ar-*H*).

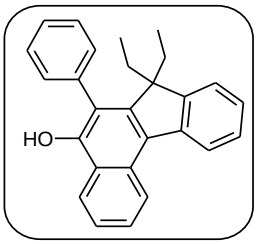
$^{13}$C NMR: δ 14.1, 14.2, 16.4, 17.1, 22.6, 24.7, 27.1, 27.7, 29.2, 31.6, 31.8, 32.1, 33.2, 36.7 (*n*-*C*$_6$H$_{13}$ + *C*H$_3$), 121.0, 121.8, 126.3, 126.5, 127.1, 127.5,

127.9, 128.$0_0$, 128.$0_4$, 129.0, 129.4, 129.7, 129.9, 130.2, 130.9, 131.1, 131.3, 131.5, 132.5, 132.6, 132.8, 132.9, 137.2, 137.3, 139.1, 139.2, 139.4, 139.8, 140.0, 140.6, 140.9, 142.4, 142.6 (Alkenyl-*C* + Ar-*C*), 163.9 and 164.2 (O*C*OPh), 196.5 (Ar*C*OPh).

HRMS (ESI): Calcd. for $C_{37}H_{37}O_3$ [$M^+$+H]: *m/z* 529.2743. Found: 529.2742.

***Compounds 63 and 64***

These compounds were prepared by using 3-ethylpenty-1-yn-3-yl benzoate **10f** (0.130 g, 0.6 mmol) and 1,3-diphenylisobenzofuran (0.135 g, 0.5 mmol). Separation was done using acetone/hexane mixture [1:100 ratio for **63** and 1: 50 for **64**] as the eluent.




**63**

Yield: 0.120 g (66%).

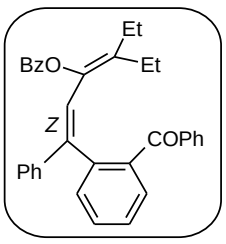
Mp: 126-128 $^oC$.

IR (KBr): 3490, 2953, 2857, 1584, 1562, 1392, 1211, 1058, 756, 701 $cm^{-1}$.

$^1H$ NMR: δ 0.23 (t, $^3J$(H-H) = 7.2 Hz, 6H, C$H_3$C$H_2$), 1.67-1.82 (m, 4H, C$H_3$C$H_2$), 5.12 (s, 1H, Ar-O*H*), 7.27-7.69 and 8.27-8.82 (m, 13H, Ar-*H*).

$^{13}C$ NMR: δ 8.3 (*C*$H_3$C$H_2$), 31.8 (C$H_3$*C*$H_2$), 58.3 (Ar*C*(Et)$_2$), 120.1, 121.7, 123.7, 124.7, 125.3, 126.9, 127.1, 128.4, 129.3, 129.6, 131.0, 134.0, 142.7, 145.1, 148.8 and 150.9 (Ar-*C*).

HRMS (ESI): Calcd. for $C_{27}H_{24}O$ [$M^+$+H]: *m/z* 365.1906. Found: 365.1903.




**64**

Yield: 0.063 g (26%, gummy liquid).

IR (neat): 3063, 2970, 2871, 1726, 1665, 1599, 1452, 1271, 1090, 706 $cm^{-1}$.

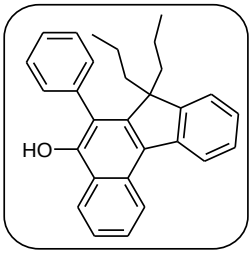
$^{1}$H NMR: δ 0.75 and 0.83 (2 t, $^{3}J$(H-H) = 7.4 Hz each, 6H, C*H*$_3$CH$_2$), 1.98 and 2.13 (2 br s, 4H, CH$_3$C*H*$_2$), 6.72 (s, 1H, PhC=C*H*), 7.00-7.72 (m, 19H, Ar-*H*).

$^{13}$C NMR: δ 12.1 and 12.6 (CH$_2$*C*H$_3$), 22.8 and 23.6 (*C*H$_2$CH$_3$), 121.2, 126.4, 127.5, 127.9, 128.1, 128.4, 129.1, 129.4, 129.7, 129.9, 130.1, 130.2, 131.1, 132.6, 132.9, 137.3, 137.8, 139.0, 139.5, 139.8, 140.8, 142.6 (Alkenyl-*C* + Ar-*C*), 164.1 (O*C*OPh), 196.4 (Ar*C*OPh).

HRMS (ESI): Calcd. for $C_{34}H_{30}O_3$ [M$^+$+H]: *m/z* 487.2274. Found: 487.2272.

***Compounds 65 and 66***

These compounds were prepared by using 4-ethynylheptan-4-yl benzoate **10g** (0.147 g, 0.6 mmol) and 1,3-diphenylisobenzofuran (0.135 g, 0.5 mmol). The separation was done using acetone/hexane mixture [1:100 ratio for **65** and 1: 50 for **66**] as the eluent.




**65**

Yield: 0.110 g (54%).

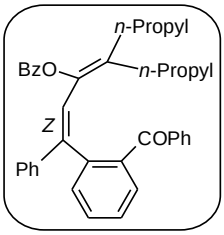
Mp: 112-114 $^{o}$C.

IR (KBr): 3529, 3036, 2953, 2926, 2871, 1578, 1463, 1436, 1392, 1222, 1145, 767, 707 cm$^{-1}$.

$^{1}$H NMR: δ 0.23 (t, $^{3}J$(H-H) = 7.2 Hz, 6H, C*H*$_3$CH$_2$), 1.60-1.74 (m, 8H, CH$_3$CH$_2$C*H*$_2$), 5.14 (s, 1H, Ar-O*H*), 7.29-7.71 and 8.27-8.82 (m, 13H, Ar-*H*).

$^{13}$C NMR: δ 14.2, 16.9, 41.6 (*C*$_3$H$_7$), 57.3 (Ar-*C*(*n*-propyl)$_2$), 120.0, 121.4, 121.7, 123.5, 123.7, 124.7, 125.2, 126.8, 127.2, 128.8, 129.3, 131.1, 134.0, 142.1, 146.1, 148.8 and 151.8 (Ar*C*).

HRMS (ESI): Calcd. for $C_{29}H_{29}O$ [M$^+$+H]: *m/z* 393.2219. Found: 393.2217.




**66**

Yield: 0.088 g (34%, gummy liquid).

IR (neat): 3063, 2959, 2931, 2866, 1732, 1666, 1600, 1452, 1315, 1266, 1063, 762, 712 $cm^{-1}$.

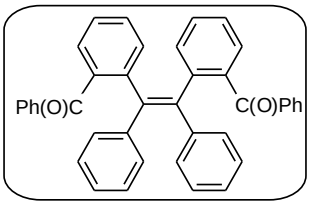
$^{1}H$ NMR: δ 0.79 and 0.86 (2 t, $^{3}J$(H-H) = 7.4 Hz and 7.2 Hz respectively, 6H, C*H*$_3$CH$_2$), 1.22-1.45 and 1.74-2.14 (m, 8H, CH$_3$C*H*$_2$C*H*$_2$), 6.76 (s, 1H, PhC=C*H*), 6.81-6.83, 6.98-7.54 and 7.60-7.71 (m, 19H, Ar-*H*).

$^{13}C$ NMR: δ 14.2, 14.4, 20.9, 21.5, 32.4 and 33.0 (propyl-*C*), 126.3, 127.1, 127.4, 127.6, 127.8, 127.9, 128.0, 129.2, 129.5, 129.6, 130.0, 130.1, 131.1, 131.6, 131.8, 132.5, 132.7, 135.2, 137.3, 139.0, 139.3, 139.5, 140.0, 140.7, 142.6 and 144.7 (Alkenyl-*C* + Ar-*C*), 164.1 (O*C*OPh), 196.5 (Ar*C*OPh).

HRMS (ESI): Calcd. for $C_{36}H_{35}O_3$ [$M^+$+H]: *m/z* 515.2587. Found: 515.2585.

***Compound 68***

This compound[81b] was formed as an additional product in the reaction of 1-ethynylcyclohexyl benzoate **8c** (0.114 g, 0.50 mmol) with 1,3-diphenylisobenzofuran (0.203 g, 0.75 mmol) along with benzofluorenol **53** and diene **54** (cf Table 8, Chapter 2). The separation was done using acetone/hexane (1:50) mixture as the eluent.



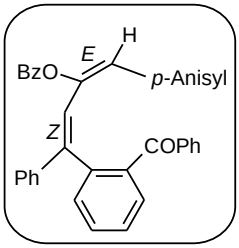

Yield: 0.067 g (16% base on IBF).

X-ray structure was determined for this sample.

***Compounds 69 and 70***

Isomers **69** and **70** were prepared by using 1-(4-methoxyphenyl)-prop-2-ynyl benzoate **10h** (0.160 g, 0.6 mmol) and 1,3-diphenylisobenzofuran (0.135 g, 0.5 mmol).

The separation was done using acetone/hexane mixture (1:50) as the eluent.




**69**

Yield: 0.118 g (44%).

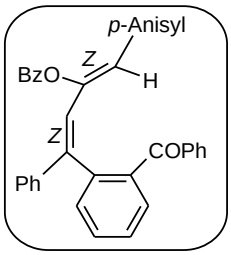
Mp: 94-96 $^{o}$C.

IR (KBr): 3057, 3030, 2838, 1726, 1660, 1594, 1501, 1265, 1249, 1139, 1024, 706 $cm^{-1}$.

$^{1}$H NMR: δ 3.79 (s, 3H, OC*H*$_3$), 6.22 (s, 1H, BzO-C=C*H*), 6.76-6.83 and 7.12-7.73 (m, 23H, PhC=C*H* + Ar-*H*).

$^{13}$C NMR: δ 55.3 (O*C*H$_3$), 113.8, 121.6, 124.1, 126.8, 127.3, 127.9, 128.1$_0$, 128.1$_4$, 129.3, 129.5, 129.8, 130.1, 130.3, 130.5, 131.2, 132.7, 133.0, 136.9, 139.3, 140.5, 142.0, 142.9, 143.9, 159.2 (Alkenyl-C + Ar-*C*), 164.5 (O*C*OPh), 196.6 (Ar*C*OPh).

HRMS (ESI): Calcd. for $C_{37}H_{28}NaO_4$ [$M^+$+Na]: *m/z* . 559.1886 Found: 559.1886.




**70**

Yield: 0.107 g (40%).

Mp: 116-118 $^{o}$C.

IR (KBr): 3057, 3014, 2937, 2838, 1732, 1666, 1595, 1507, 1255, 1238, 1184, 1063, 773 $cm^{-1}$

$^{1}$H NMR: δ 3.74 (s, 3H, OC*H*$_3$), 6.22 (s, 1H, BzO-C=C*H*), 6.59-6.73 and 7.06-7.73 (m, 23H, PhC=C*H* + Ar-*H*).

$^{13}$C NMR: δ 55.2 (O*C*H$_3$), 114.0, 123.1, 124.8, 126.7, 127.1, 127.6, 127.7, 127.8, 128.0, 129.1, 129.3, 129.7, 130.1, 130.2, 131.4, 132.5, 133.2, 137.5, 139.4, 139.6, 140.0, 141.8, 143.9, 159.1 (Alkenyl-C + Ar-*C*), 163.5

(O*C*OPh), 197.2 (Ar*C*OPh).

HRMS (ESI): Calcd. for $C_{37}H_{28}NaO_4$ [$M^+$+Na]: *m/z* . 559.1886 Found: 559.1886.

### 3.8 X-ray crystallography

A suitable crystal was mounted on a glass fiber (for **26a, 30b, 31, 33d, 37, 43, 53, 68** and **69**) and X-ray data were collected at 293 K on a Bruker AXS-SMART or on an OXFORD diffractometer using Mo-$K_\alpha$ radiation ($\lambda$ = 0.71073 Å). Structures were solved and refined using standard methods.[84] 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 Table 9a-c.

**Table 9a**. Crystal data for compounds **26a, 30b, 31** and **33d**[a]

| Compound | **26a** | **30b** | **31** | **33d**[b] |
|---|---|---|---|---|
| Emp. formula | $C_{22}H_{23}O_4P$ | $C_{22}H_{23}O_4P$ | $C_{14}H_{12}IN_3O$ | $C_{21}H_{24}O_3$ |
| Formula weight | 382.37 | 382.37 | 365.17 | 324.40 |
| Crystal system | Monoclinic | Triclinic | Monoclinic | Orthorhombic |
| Space group | $P2_1/c$ | $P\bar{1}$ | $P2_1/c$ | *Pn2(1)a* |
| *a* /Å | 10.3422(10) | 9.6007(17) | 11.792(2) | 10.0016(6) |
| *b* /Å | 11.1844(11) | 9.9546(17) | 13.512(3) | 9.3235(8) |
| *c* /Å | 19.7253(16) | 12.827(3) | 8.8639(18) | 18.6290(17) |
| $\alpha$/deg | 90 | 108.662(18) | 90 | 90 |
| $\beta$/deg | 121.159(4) | 96.950(17) | 97.03(3) | 90 |
| $\gamma$/deg | 90 | 114.322(17) | 90 | 90 |
| *V* /Å$^3$ | 1952.5(3) | 1012.0(3) | 1401.7(5) | 1737.2(2) |
| *Z* | 4 | 2 | 4 | 4 |
| *D*calc /g cm$^{-3}$] | 1.301 | 1.255 | 1.730 | 1.240 |
| $\mu$ /mm$^{-1}$ | 0.165 | 0.160 | 2.280 | 0.082 |
| *F*(000) | 808 | 404 | 712 | 735 |
| Data/ restraints/ parameters | 3431/0/246 | 3413/0/247 | 2464/0/172 | 2763/1/217 |
| S | 1.146 | 0.956 | 1.205 | 1.026 |
| R1 [I>2σ(I)] | 0.0596 | 0.0961 | 0.0391 | 0.0442 |
| wR2 [all data] | 0.1330 | 0.2145 | 0.0757 | 0.0976 |
| Max./min. residual electron dens. [eÅ$^{-3}$] | 0.267/-0.314 | 0.511/-0.329 | 0.896/-0.226 | 0.347/-0.165 |

[a]$R1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$ and $wR2 = [\Sigma w(Fo^2-Fc^2)^2/\Sigma wFo^4]^{0.5}$
[b]Flack parameter -1.4(15)

**Table 9b**. Crystal data for compounds **37, 43, 53** and **68** [a]

| Compound | **37**[b] | **43** | **53** | **68** |
|---|---|---|---|---|
| Emp. formula | $C_{21}H_{25}O_4P$ | $C_{34}H_{36}O_2$ | $C_{28}H_{24}O$ | $C_{40}H_{28}O_2$ |
| Formula weight | 372.38 | 476.63 | 376.47 | 540.62 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Monoclinic |
| Space group | *P2(1)* | *C2/c* | $P2_1/c$ | $P2_1/n$ |
| *a* /Å | 6.533(4) | 28.650(4) | 8.8110(8) | 11.8178(5) |
| *b* /Å | 9.469(5) | 9.8296(11) | 20.9480(13) | 11.1901(4) |
| *c* /Å | 16.085(10) | 22.383(2) | 10.5926(7) | 23.1887(9) |
| $\alpha$/deg | 90 | 90.00 | 90 | 90 |
| $\beta$/deg | 96.069(8) | 121.736(17) | 90.386(7) | 103.940(4) |
| $\gamma$/deg | 90 | 90.00 | 90 | 90 |
| *V* /Å$^3$ | 989.5(10) | 5360.9(11) | 1955.1(3) | 2976.2(2) |
| *Z* | 2 | 8 | 4 | 4 |
| *D*calc /g cm$^{-3}$] | 1.250 | 1.181 | 1.279 | 1.207 |
| $\mu$ /mm$^{-1}$ | 0.161 | 0.071 | 0.076 | 0.073 |
| *F*(000) | 396 | 2235 | 825 | 15 |
| Data/ restraints/ parameters | 3461/1/237 | 4715/0/325 | 3176/0/263 | 4271/0/379 |
| S | 1.067 | 0.928 | 0.980 | 1.002 |
| R1 [I>2σ(I)] | 0.0361 | 0.0653 | 0.0616 | 0.0368 |
| wR2 [all data] | 0.0917 | 0.0878 | 0.1025 | 0.0841 |
| Max./min. residual electron dens. [eÅ$^{-3}$] | 0.176/-0.205 | 0.175/-0.222 | 0.194/-0.225 | 0.165/-0.141 |

[a] $R1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$ and $wR2 = [\Sigma w(Fo^2-Fc^2)^2/\Sigma wFo^4]^{0.5}$

[b] Flack parameter 0.02(9)

**Table 9c**. Crystal data for compounds **69**

| Compound | **69** |
|---|---|
| Emp. formula | $C_{37}H_{28}O_4$ |
| Formula weight | 536.59 |
| Crystal system | Monoclinic |
| Space group | $P2_1/c$ |
| *a* /Å | 10.6039(14) |
| *b* /Å | 16.2297(16) |
| *c* /Å | 16.165(2) |
| $\alpha$/deg | 90 |
| $\beta$/deg | 91.124(12) |
| $\gamma$/deg | 90 |
| *V* /Å$^3$ | 2781.5(6) |
| *Z* | 4 |
| *D*calc /g cm$^{-3}$] | 1.281 |
| $\mu$ /mm$^{-1}$ | 0.082 |
| *F*(000) | 1170 |
| Data/ restraints/ parameters | 4888/0/371 |
| S | 0.826 |
| R1 [I>2σ(I)] | 0.0771 |
| wR2 [all data] | 0.0907 |
| Max./min. residual electron dens. [eÅ$^{-3}$] | 0.212/-0.203 |

[a]R1 = Σ||Fo| - |Fc||/Σ|Fo| and wR2 = [Σw(Fo$^2$-Fc$^2$)$^2$/ΣwFo$^4$]$^{0.5}$

## References


1. Norman, R. O. C.; Parr, W. J. E.; Thomas, C. B. *J. Chem. Soc., Perkin Trans. 1* **1976**, 1983.
2. (a) Lipshutz, B. H.; Yamamoto, Y. *Chem. Rev.* **2008,** *108*, 2793. (b) Patil, N. T.; Yamamoto, Y. *Chem. Rev.* **2008,** *108*, 3395. (c) Limaa, J. C.; Rodriguez, L. *Chem. Soc. Rev*. **2011**, *40*, 5442.
3. (a) Marion, N.; Nolan, S. P. *Chem. Soc. Rev*. **2008**, *37*, 1776. (b) Galan, P. P.; Delpont, N.; Gomez, E. H.; Maseras, F.; Echavarren, A. M. *Chem.-Eur. J*. **2010**, *16*, 5324. (c) Gorin, D. J.; Sherry, B. D.; Toste, F. D. *Chem. Rev.* **2008,** *108*, 3351.
4. Gorin, D. J. *Stabilized cationic reaction intermediates in homogeneous gold catalysis*: University of California: Berkeley, 2008: pp 516-520.
5. (a) Sohel, S. M. B.; Liu, R. S. *Chem. Soc. Rev*. **2009**, *38*, 2269. (b) Krause, N.; Winter, C. *Chem. Rev*. **2011**, *111*, 1994. (c) Corma, A.; Perez, A. L.; Sabater, M. J. *Chem. Rev*. **2011**, *111*, 1657.
6. (a) Hutchings, G. J. *Gold Bulletin* **2004**, 37, 1. (b) Hashmi, A. S. K. *Gold Bulletin* **2004**, *37*, 51. (c) Zhang, Y.; Cui, X.; Shi, F.; Deng, Y. *Chem. Rev.* **2012**, *112*, 2467.
7. Arcadi, A. *Chem. Rev.* **2008**, *108*, 3266.
8. (a) Arcadi, A.; Bianchi, G.; Giuseppe, S. D.; Marinelli, F. *Green Chem.* **2003**, *5*, 64. (b) Arcadi, A.; Bianchi, G.; Marinelli, F. *Synthesis* **2004**, 610. (c) Winter, C.; Krause, N. *Green Chem.* **2009**, *11*, 1309. (d) Ye, D.; Wang, J.; Zhang, X.; Zhou, Y.; Ding, X.; Feng, E.; Sun, H.; Liu, G.; Jiang, H.; Liu, H. *Green Chem.* **2009**, *11*, 1201. (e) Feng, E.; Zhou, Y.; Zhao, F.; Chen, X.; Zhang, L.; Jiang, H.; Liu, H. *Green Chem*. **2012**, *14*, 1888.
9. (a) Hashmi, A. S. K.; Frost, T. M.; Bats, J. W. *Org. Lett.* **2001**, *3*, 3769. (b) Asao, N.; Takahashi, K.; Lee, S.; Kasahara, T.; Yamamoto, Y. *J. Am. Chem. Soc*. **2002**, *124*, 12650. (c) Hashmi, A. S. K.; Ding, L.; Bats, J. W.; Fischer, P.; Frey, W. *Chem.-Eur. J*. **2003**, *9*, 4339.(d) De Brabander, J. K.; Liu, B.; Qian, M. *Org. Lett.* **2008**, *10*, 2533.
10. (a) Hashmi, A. S. K. *Chem. Rev*. **2007,** *107*, 3180.(b) Patil, N. T.; Yamamoto, Y. *Arkivoc* **2007**, 6. (c) Li, Z.; Brouwer, C.; He, C. *Chem. Rev.* **2008,** *108*, 3239.(d) Nunez, E. J.; Echavarren, A. M. *Chem. Rev.* **2008,** *108*, 3326. (e) Hashmi, A. S. K.; Rudolph, M. *Chem. Soc. Rev*. **2008**, *37*, 1766. (f) Rudolph, M.; Hashmi, A. S. K. *Chem. Soc. Rev*. **2012**, *41*, 2448.
11. Hashmi, A. S. K.; Schwarz, L.; Choi, J. H, Frost, T. M. *Angew. Chem. Int. Ed*. **2000**, *39*, 2285.
12. (a) Röder, A. H.; Krause, N. *Org. Lett*. **2001**, *3*, 2537. (b) Morita, N.; Krause, N. *Org. Lett*. **2004**, *6*, 4121. (c) Morita, N.; Krause, N. *Angew. Chem. Int. Ed.* **2006**, *45*, 1897.
13. Sromek, A. W.; Rubina, M, Gevorgyan, V. *J. Am. Chem. Soc*. **2005**, *127*, 10500.
14. Zhu, Z.; Germain, A. R.; Porco Jr, J. A. *Angew. Chem. Int. Ed*. **2004**, *43*, 1239.
15 Oberhuber, C. N.; Muoz, M. P.; Buñuel, E.; Nevado, C.; Cárdenas, D. J.; Echavarren, A. M. *Angew. Chem. Int. Ed*. **2004**, *43*, 2402.

16. Toullec, P. Y.; Genin, E.; Leseurre, L.; Genet, J. P.; Michelet, V. *Angew. Chem. Int. Ed*. **2006**, *45*, 7427.
17. Horino, Y.; Luzung, M. R.; Toste, F. D. *J. Am. Chem. Soc.* **2006**, *128*, 11364.
18. (a) Smith, J. J. K.; Staben, S. T.; Toste, F. D. *J. Am. Chem. Soc*. **2004**, *126*, 4526. (b) Staben, S. T.; Smith, J. J. K.; Toste, F. D. *Angew. Chem. Int. Ed*. **2004**, *43*, 5350.
19. Staben, S. T.; Smith, J. J. K.; Huang, D.; Corkey, B. K.; LaLonde, R. L.; Toste, F. D. *Angew. Chem. Int. Ed*. **2006**, *45*, 5991.
20. Sherry, B. D.; Maus, L.; Laforteza, B. N.; Toste, F. D. *J. Am. Chem. Soc.* **2006**, *128*, 8132.
21. Suhre, M. H.; Reif, M.; Kirsch, S. F. *Org. Lett.* **2005**, *7*, 3925.
22. Abbiati, G.; Arcadi, A.; Bianchi, G.; Di Giuseppe, S.; Marinelli, F.; Rossi, E. *J. Org. Chem*. **2003**, *68*, 6959.
23. Genin, E.; Toullec, P. Y.; Antoniotti, S.; Brancour, C.; Genet, J. P.; Michelet, V. *J. Am. Chem. Soc*. **2006**, *128*, 3112.
24. (a) Hashmi, A. S. K.; Weyrauch, J. P.; Frey, W.; Bats, J. W. *Org. Lett*. **2004**, *6*, 4391. (b) Hashmi, A. S. K.; Rudolph, M.; Schymura, S.; Visus, J.; Frey, W. *Eur. J. Org. Chem.* **2006**, 4905.
25. Zhang, L.; Kozmin, S. A. *J. Am. Chem. Soc*. **2005**, *127*, 6962.
26. Barluenga, J.; Diguez, A.; Fernndez, A.; Rodrguez, F.; Faans, F. J. *Angew. Chem. Int. Ed*. **2006**, *45*, 2091.
27. Antoniotti, S.; Genin, E.; Michelet, V.; Genet, J. P. *J. Am. Chem. Soc.* **2005**, *127*, 9976.
28. Markham, J. P.; Staben, S. T.; Toste, F. D. *J. Am. Chem. Soc*. **2005**, *127*, 9708.
29. (a) Liu, Y.; Song, F.; Song, Z.; Liu, M.; Yan, B. *Org. Lett*. **2005**, *7*, 5409. (b) Liu, Y.; Song, F.; Guo, S. *J. Am. Chem. Soc.* **2006**, *128*, 11332.
30. Gorin, D. J.; Davis, N. R.; Toste, F. D. *J. Am. Chem. Soc*. **2005**, *127*, 11260.
31. (a) Shi, Z.; He, C. *J. Org. Chem*. **2004**, *69*, 3669. (b) Shi, Z.; He, C. *J. Am. Chem. Soc.* **2004**, *126*, 5964. (c) Boorman, T. C.; Larrosa, I. *Chem. Soc. Rev.* **2011**, *40*, 1910.
32. Ferrer, C.; Echavarren, A. M. *Angew. Chem. Int. Ed*. **2006**, *45*, 1105.
33. Arcadi, A.; Alfonsi, M.; Bianchi, G.; D'Anniballe, G.; Marinelli, F. *Adv. Synth. Catal*. **2006**, *348*, 331.
34. (a) Balamurugan, R.; Gudla, V. *Org. Lett.* **2009**, *11*, 3116. (b) Gudla, V.; Balamurugan, R. *J. Org. Chem.* **2011**, *76*, 9919.
35. (a) Yao, T.; Zhang, X.; Larock, R. C. *J. Am. Chem. Soc.* **2004**, *126*, 11164. (b) Yao, T.; Zhang, X.; Larock, R. C. *J. Org. Chem.* **2005**, *70*, 7679.
36. Kirsch, S. F.; Binder, J. T.; Libert, C.; Menz, H. *Angew. Chem. Int. Ed*. **2006**, *45*, 5878.
37. (a) Praveen, C.; Kiruthiga, P.; Perumal, P. T. *Synlett* **2009**, *12*, 1990. (b) Hashmi, A. S. K.; Häffner, T.; Rudolph, M.; Rominger, F. *Eur. J. Org. Chem.* **2011**, 667.
38. (a) Shi, X.; Gorin, D.J.; Toste, F. D. *J. Am. Chem. Soc*. **2005**, *127*, 5802. (b) Zhang, L.; Wang, S. *J. Am. Chem. Soc.* **2006**, *128*, 1442.
39. Johansson, M. J.; Gorin, D. J.; Staben, S. T.; Toste, F. D. *J. Am. Chem. Soc.* **2005**, *127*, 18002.

40. Marion, N.; Fremont, P.; Lemiere, G.; Stevens, E. D.; Fensterbank, L.; Malacria, M.; Nolan, S. P. *Chem. Commun*. **2006**, 2048.
41. Chen, Y.; Liu, Y. *J. Org. Chem*. **2011**, *76*, 5274.
42. Buzas, A.; Istrate, F.; Gagosz, F. *Org. Lett*. **2006**, *8*, 1957.
43. Wang, Y. M.; Kuzniewski, C. N.; Rauniyar, V.; Hoong, C.; Toste, F. D. *J. Am. Chem. Soc*. **2011**, *133*, 12972.
44. Liu, H.; Li, X.; Chen, Z,; Hu, W. X. *J. Org. Chem*. **2012**, *77*, 5184.
45. Ghosh, N.; Nayak, S.; Sahoo, A. K. *J. Org. Chem*. **2011**, *76*, 500.
46. Rao, W.; Koh, M. J.; Kothandaraman, P.; Chan, P. W. H. *J. Am. Chem. Soc*. **2012**, *134*, 10811.
47. (a) Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996,** *96*, 49. (b) Winkler, J. D. *Chem. Rev.* **1996**, *96*, 167. (c) Kobayashi, S.; Jørgensen, K. A. *Cycloaddition Reactions in Organic Synthesis*, Ed.; Wiley VCH: Weinheim, 2001. (d) Tran, Y. S.; Kwon, O. *Org. Lett.* **2005**, *7*, 4289. (e) Tang, X.; Zhang, B.; He, Z.; Gao, R.; He, Z. *Adv. Synth. Catal.* **2007**, *349*, 2007. (f) Wallace, D. J.; Sidda , R. L.; Reamer, R. A. *J. Org. Chem.* **2007**, *72*, 1051. (g) Alcaide, B.; Almendros, P.; Aragoncillo, C. *Chem. Soc. Rev*. **2010**, *39*, 783.
48. (a) Benitez, D.; Tkatchouk, E.; Gonzalez, A. Z.; Goddard, W. A.; Toste, F. D. *Org. Lett.* **2009**, *11*, 4798 (b) López, F.; Mascareñas, J. L. *Beilstein J. Org. Chem.* **2011,** *7*, 1075.
49. Hashmi, A. S. K.; Frost, T. M.; Bats, J. W. *J. Am. Chem. Soc.* **2000,** *122*, 11553.
50. Hashmi, A. S. K.; Blanco, M. C.; Kurpejovic, E.; Frey, W.; Bats, J. W. *Adv. Synth. Catal*. **2006**, *348*, 709.
51. (a) Asao, N.; Nogami, T.; Lee, S.; Yamamoto, Y. *J. Am. Chem. Soc*. **2003**, *125*, 10921. (b) Asao, N.; Aikawa, H.; Yamamoto, Y. *J. Am. Chem. Soc*. **2004**, *126*, 7458.
52. Shapiro, N. D.; Toste, F. D.; *J. Am. Chem. Soc.* **2008**, *130*, 9244.
53. (a) Liu, F.; Qian, D.; Li, L.; Zhao, X.; Zhang, J. *Angew. Chem. Int. Ed*. **2010**, *49*, 6669. (b) Gao, H.; Wua, X.; Zhang, J. *Chem. Commun.* **2010**, *46*, 8764. (c) Gao, H.; Zhao, X.; Yu, Y.; Zhang, J. *Chem.-Eur. J*. **2010**, *16*, 456. (e) Gao, H.; Wu, X.; Zhang, J. *Chem.-Eur. J*. **2011**, *17*, 2838.
54. Gorin, D. J.; Dube, P.; Toste, F. D. *J. Am. Chem. Soc*. **2006**, *128*, 14480.
55. Barluenga, J.; Calleja, J.; Mendoza, A.; Rodriguez, F.; Fananas, F. J. *Chem.-Eur. J*. **2010**, *16*, 7110.
56. Rao, W.; Susanti, D.; Chan, P. W. *J. Am. Chem. Soc.* **2011**, *133*, 15248.
57. (a) Gung, B. W.; Craft, D. T.; Bailey, L. N.; Kirschbaum, K. *Chem.-Eur. J*. **2010**, *16*, 639. (b) Gung, B. W.; Bailey, L. N.; Wonser, J. *Tetrahedron Lett.* **2010**, *51*, 2251.
58. (a) Kumara Swamy, K. C.; Kumaraswamy, S.; Senthil Kumar, K.; Muthiah, C. *Tetrahedron Lett.* **2005**, *46*, 3347. (b) Chen, S.-B.; Li, Y.-M.; Luo, S.-Z.; Zhao, G.; Tan, B.; Zhao, Y.-F. *Phosphorus, Sulfur, Silicon Relat. Elem*. **2000**, *164*, 277. (c) Muthiah, C.; Praveen Kumar, K.; Aruna Mani, C.; Kumara Swamy, K. C. *J. Org. Chem.* **2000**, *65*, 3733.
59. Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, Pergamon, Oxford, 1986.
60. Thangavela, V.; Chadhab, A. *Tetrahedron* **2007**, *63*, 4126.

61. (a) Bowman, W. R.; Bridge, C. F.; Brookes, P.; Cloonan, M. O.; Leach, D. C. *J. Chem. Soc*., *Perkin Trans. 1* **2002**, 58. (b) Shufeng, C.; Jianbo, W. *J. Org. Chem.* **2007**, *72*, 4993.
62. Mantilli, L.; Gérard, D.; Torche, S.; Besnard, C.; Mazet, C. *Chem.-Eur. J*. **2010**, *16*, 12736.
63. (a) Lautens, M.; Maddess, M. L.; Sauer, E. L. O.; Quellet, S. G. *Org. Lett*. **2002**, *4*, 83. (b) Sha, C. K.; Huang, S. J.; Zhan, J. P. *J. Org. Chem.* **2002**, *67*, 831.
64. (a) Kulakarni, A. A.; Diver, S. T. *Organic Syntheses;* Wiley & Sons: New York, 2006; Vol 83, pp 200-208. (b) Cordonnier, M. C.; Blanc, A.; Pale, P. *Org. Lett*. **2008**, *10*, 1569.
65. Pagar, V. V.; Jadhav, A. M.; Liu, R. S. *J. Am. Chem.Soc*. **2011**, *133*, 20728.
66. Lin, M. Y.; Das, A.; Liu, R. S. *J. Am. Chem. Soc*. **2006**, *128*, 9340.
67. Isogai, Y.; Menggenbateer; Khan, F. N.; Asao, N. *Tetrahedron* **2009**, *65*, 9575.
68. One of our colleagues (Dr. Anasuya) has determined the X-ray structure for an analogous compound.
69. (a) Drewes, S. E.; Hogan, C. J. *Synth. Comm.* **1989**, *19*, 2101. (b) Grant, T. N.; West, F. G. *J. Am. Chem. Soc.* **2006**, *128*, 9348.
70. (a) Chakravarty, M.; Kumara Swamy, K. C. *J. Org. Chem.* **2006**, *71*, 9128. (b) Bhuvan Kumar, N. N.; Nagarjuna Reddy, M.; Kumara Swamy, K. C. *J. Org. Chem.* **2009**, *74*, 5395. (c) Srinivas, V.; Sajna, K. V.; Kumara Swamy, K. C. *Tetrahedron Lett.* **2011**, *52*, 5323. (d) Sajna, K. V.; Kotikalapudi, R.; Chakravarty, M.; Bhuvan Kumar, N. N.; Kumara Swamy, K. C. *J. Org. Chem.* **2011**, *76*, 920.
71. Zhang, D.; Yuan, C. *Eur. J. Org. Chem.* **2007**, 3916.
72. (a) Marshall, J. A.; DuBay, W. J. *J. Org. Chem.* **1993**, *58*, 3435. (b) Wang, F.; Wang, Y.; Cai, L.; Miao, Z.; Chen, R. *Adv. Synth. Catal*. **2008**, *350*, 2733.
73. Kumaraswamy, S.; Selvi, R. S.; Kumara Swamy, K. C. *Synthesis* **1997**, 207.
74. Liu, Y.; Zhou, S. *Org. Lett.* **2005**, *7*, 4609.
75. (a) Egi, M.; Azechi, K.; Akai, S. *Org. Lett.* **2009**, *11*, 5002. (b) Praveen, C.; Kalyanasundaram, A.; Perumal, P. T. *Synlett* **2010**, 0777.
76. (a) Zhang, L. *J. Am. Chem. Soc.* **2005**, *127*, 16804. (b) Suhre, M. H.; Reif, M.; Kirsch, S. F. *Org. Lett*. **2005**, *7*, 2005. (c) Schwier, T.; Sromek, A. W.; Yap, D. M. L.; Chernyak, D.; Gevorgyan, V. *J. Am. Chem. Soc*. **2007**, *129*, 9868. (d) Zhang, Z.; Bender, C. F.; Widenhoefer, R. A. *J. Am. Chem. Soc*. **2007**, *129*, 14148. (e) Egi, M.; Azechi, K.; Saneto, M.; Shimizu, K.; Akai, S. *J. Org. Chem.* **2010**, *75*, 2123. (f) Alcaide, B.; Almendros, P.;Alonso, J. M. *Org. Biomol. Chem*. **2011**, *9*, 4405.
77. (a) Georgy, M.; Boucard, V.; Campagne, J. M. *J. Am. Chem. Soc*. **2005**, *127*, 14180. (b) Blanc, A.; Alix, A.; Weibel, J. M.; Pale, P. *Eur. J. Org. Chem*. **2010**, 1644. (c) Debleds, O.; Gayon, E.; Vrancken, E.; Campagne, J. M. *Beilstein J. Org. Chem*. **2011**, ***7***, 866. (d) Balamurugan, R.; Kothapalli, R. B.; Thota, G. K. *Eur. J. Org. Chem.* **2011**, 1557. (e) Pennell, M. N.; Turner, P. G.; Sheppard, T. D.; *Chem.-Eur. J*. **2012**, *18*, 4748.
78. (a) Back, T. G.; Parvez, M.; Zhai, H. *J. Org. Chem.* **2006**, *71*, 5254. (b) Dyke, A. M.; Gill, D. M.; Harvey, J. N.; Hester, A. J.; Lloyd-Jones, G. C.; Muñoz, M. P.; Shepperson, I. R. *Angew. Chem. Int. Ed.* **2008**, *47*, 5067. (c) Shastin, A. V.;

Nenajdenko,V. G.; Muzalevskiy, V. M.; Balenkova, E. S.; Fröhlich, R.; Haufe, G. *Tetrahedron* **2008**, *64*, 9725. (d) Quintana, I.; Peña, D.; Pérez, D.; Guitián, E. *Eur. J. Org. Chem.* **2009**, 5519. (e) Patrick, T. B.; Li, H. *J. Flourine Chem.* **2009**, *130*, 544.

79. Zhu, S.; Liang, R.; Chen, L.; Wang, C.; Ren, Y.; Jiang, H. *Tetrahedron Lett.* **2012**, *53*, 815.
80. Arduengo III, A. J.; Krafczyk, R.; Schmutzler, R. *Tetrahedron* **1999**, *55*, 14523.
81. (a) Schonberg, A.; Mustafa, A.; Barakat, M. Z.; Latif, N.; Moubasher, R.; Mustafa, A. *J. Chem. Soc.* **1948**, 2126. (b) Berre, L.; Georges, L. *Bull. Soc. Chim. Fr.* **1967**, *11*, 4328.
82. Smith, M. B.; March, J. *Advanced Organic Chemistry:Reaction, Mechanism and Structure*, 6th ed.; Wiley: Hoboken, NJ, 2007.
83. Shriver, D. F.; Dresdzon, M. A. *The Manipulation of Air Sensitive Compounds*, 2nd Ed, Wiley Interscience, New York, 1986.
84. (a) Sheldrick, G. M. *SADABS, Siemens Area Detector Absorption Correction*, University of Göttingen, Germany, **1996**. (b) Sheldrick, G. M., SHELX-97- *A program for crystal structure solution and refinement*, University of Göttingen, **1997**. (c) Sheldrick, G. M. *SHELXTL NT Crystal Structure Analysis Package*, Bruker AXS, Analytical X-ray System, WI, USA, **1999**, version 5.10.

# PART-B

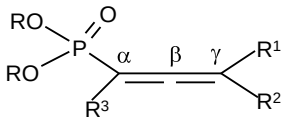
## ALLENYLPHOSPHONATES/ ALLENYLPHOSPHINE OXIDES IN CYCLOADDITION/ CYCLIZATION REACTIONS

# INTRODUCTION

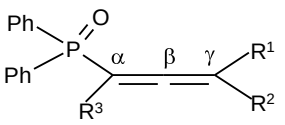
## 4.1 General Introduction: Allenes

As a consequence of the presence of cumulative double bonds, substituent loading capability and intrinsic axial chirality, allenes are always of regio- as well as stereo-chemical interest.[1,2] As the reaction centre spreads over three cumulative carbons, allenes opened the access for complex target molecules[3] and hence have found their utility in industrial and biological applications.[4] Although they were considered to be unstable for a long period of time, many natural products[5] including carotenoids and terpenoids (e.g.: mimulaxanthins,[5b] fucoxanthin[5c-d] and grasshopper ketone[5e]) consist of allenic structure. Allenes are versatile precursors for the synthesis of heterocycles, carbocycles, multisubstituted alkenes, dienes, alkynes, cycloadducts and also for the synthesis of pharmaceuticals, dyes and corrosive resistant materials.[6] The saga of new discoveries in allene chemistry has been extending day by day.

Allenes constituting $-P(O)(OR)_2$ or $P(O)(Ph)_2$ group as substituent are called as allenylphosphonates (**I**) or allenylphosphine oxides (**II**). These allenes are inexpensive and easy to handle. The presence of these groups is quite useful in interpreting the reaction pathways by means of monitoring the progress by $^{31}P$ NMR.[7] In many cases, the withdrawing nature of the phosphorus moiety leads the products towards better regioselectivity. In the following sections, a brief literature survey on the preparation and utility of allenylphosphonates/ allenylphosphine oxides will be presented.




**I**
Allenylphosphonate



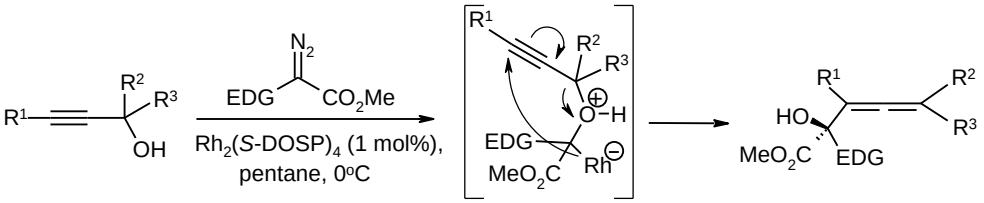

**II**
Allenylphosphine oxide

## 4.2 Synthesis of allenes/allenylphosphonates/allenylphosphine oxides

Methods for the synthesis of allenes are numerous in the literature.[8] Many of them are described clearly in the book 'Modern Allene Chemistry' by Krause and Hashmi.[9] Recent trends in allene synthesis is outlined briefly here.

Davies and co-workers reported rhodium catalyzed enantioselective allenes by the reaction of tertiary propargyl alcohols with methyl/ aryl/ styryl diazoacetates.[10] This reaction is catalyzed by dirhodium tetraprolinate complex $Rh_2$(*S*-DOSP)$_4$ and proceeds by [2,3]-sigmatropic rearrangement of oxonium ylide **4.1** to allene **4.2** (Scheme 4.1).

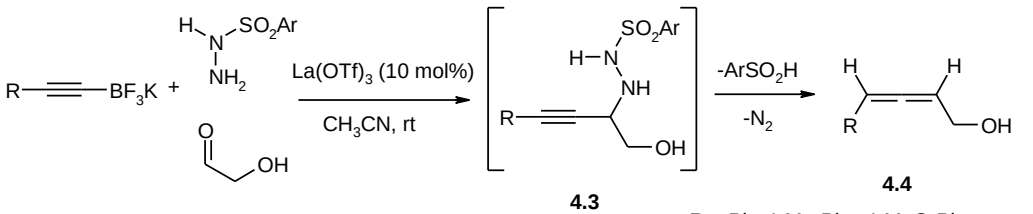
**Scheme 4.1**




$R^1$ = Me, Et, *n*-Bu, Ph etc.
$R^2$ = *c*-hex, *i*-Pr, *t*-Bu etc.
$R^3$ = Me
EDG = H, Ph, Styryl etc.

Thomson and co-workers reported one pot synthesis of allenes by 2-nitrobenzenesulfonylhydrazide mediated coupling of hydroxy aldehydes/ ketones with alkynyl trifluoroborate salts.[11] The reaction involves the formation of sulfonylhydrazone which reacts with alkynyl borate to form transient propargyl hydrazide **4.3**. This upon decomposition produces allene **4.4** (Scheme 4.2).

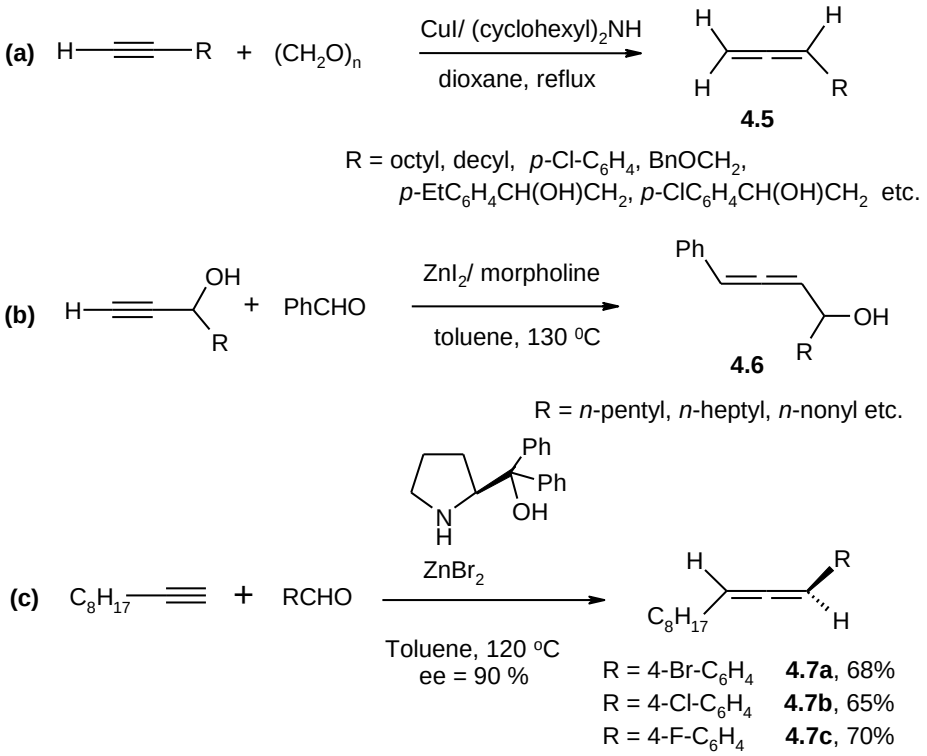
**Scheme 4.2**




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

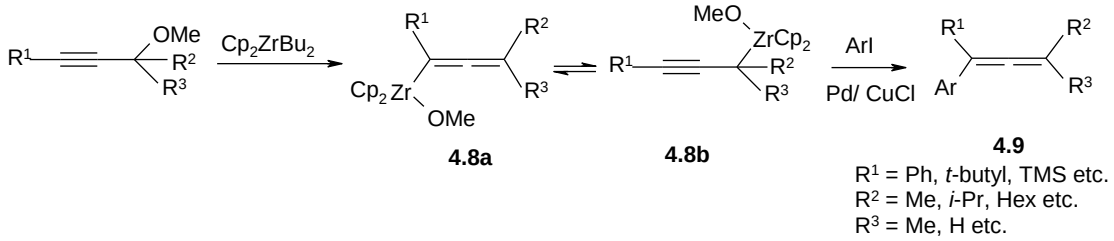
In an earlier work, Crabbe had reported the synthesis of allene **4.5** from terminal alkyne, formaldehyde, diisopropylamine and CuBr in dioxane.[12] This reaction suffers from a drawback that it works for the synthesis of mono substituted allenes only. Kuang and Ma have modified Crabb homologation by replacing CuBr/ diisopropylamine with CuI/ dicyclohexylamine to obtain terminal allenes **4.5** (Scheme 4.3).[13a] But this method again has limitation and is applicable only to paraformaldehyde; as a consequence, only monosubstituted allenes can be synthesized. In a later paper, Ma and coworkers reported the synthesis of 1,3-disubstituted allenes/ allenols [e.g., **4.5**] from various aldehydes and terminal alkynes using $ZnI_2$ and morpholine.[13b] Disubstituted as well as hydroxy substituted allenes **4.6** (Scheme 4.3b) can also be synthesized by this method. Very recently, Periasamy's group reported the synthesis of chiral allenes **4.7a-c** with excellent enantioselectivities.[13c] The reaction was promoted by zinc halide and involved sequential chirality transfer from the *in situ* generated propargyl amine intermediate to resultant allene in a single pot operation.

**Scheme 4.3**



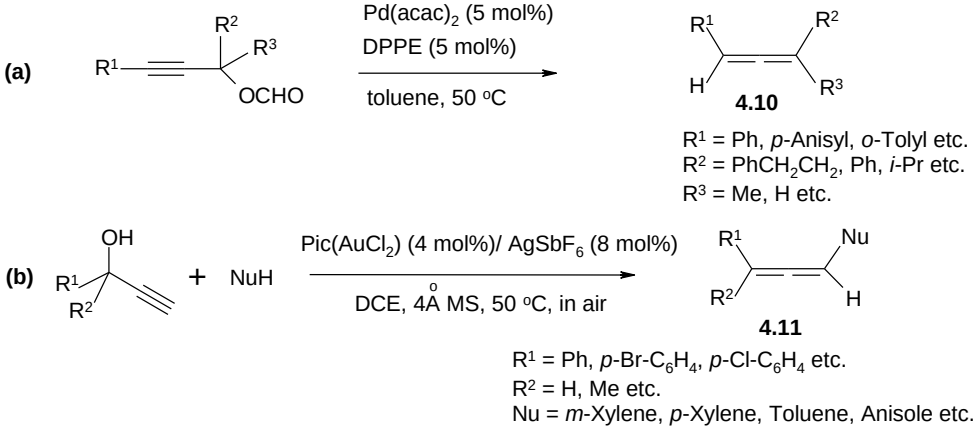
Palladium catalyzed synthesis of multi-substituted allenes was reported by Li and co-workers.[14] The *in situ* formation of allenic/ propargylic zirconium species **4.8** from methyl propargyl ether and dibutylzirconocene complex (Negishi reagent) followed by coupling with aryl iodide led to multi-substituted allenes **4.9** (Scheme 4.4).

**Scheme 4.4**



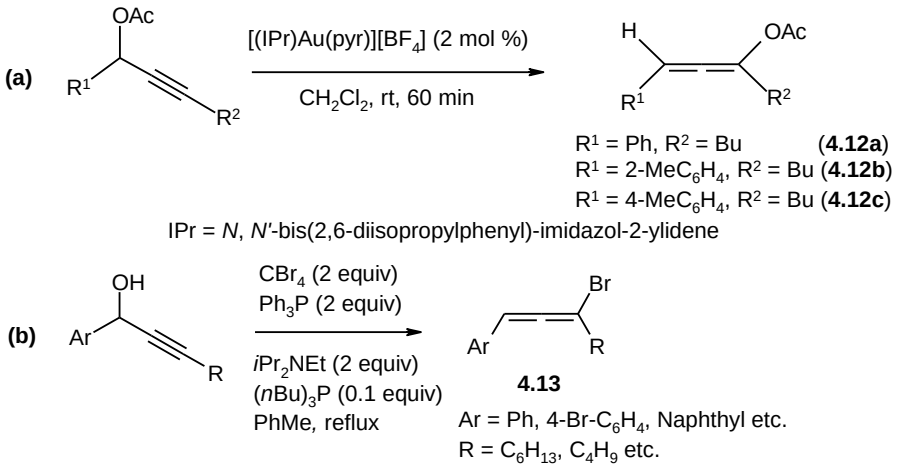

Recently, Sawamura *et al* developed palladium catalyzed ligand controlled regioselective decarboxylative hydrogenolysis of propargylic formates which led to selective synthesis of allenes **4.10** (Scheme 4.5a).[15] Internal allenes can be synthesized with excellent selectivity when DPPE was used as the ligand. More recently, Li and co-workers reported the synthesis of functionalized allenes **4.11** by the intermolecular nucleophilic substitution of propargylic alcohols with aromatic compounds *via* gold catalysis (Scheme 4.5b).[16] The reaction was performed under mild condition with easily accessible starting materials.

**Scheme 4.5**



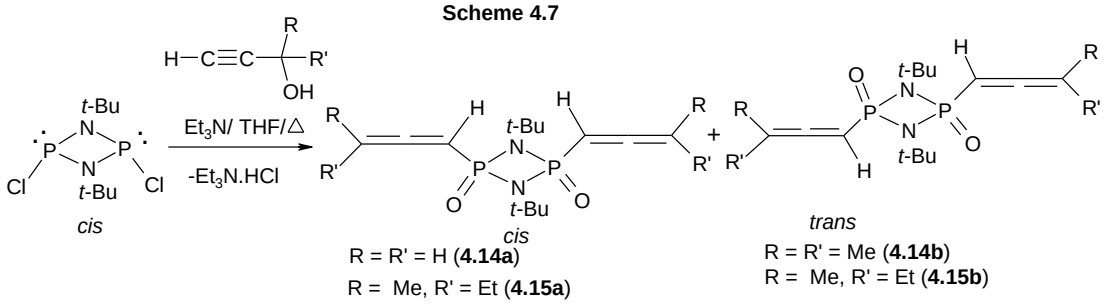
Nolan *et al* discovered a synthetic route to substituted allenes **4.12a-c** from propargylic acetates catalyzed by cationic gold(I) complex [(IPrAu(pyr)][$BF_4$] generated *in situ* from the air and moisture stable precatalyst [(IPr)AuOH] and ammonium or pyridinium salt (Scheme 4.6a).[17] Various aryl and alkyl substituted allenes were synthesized by this method. Phosphine [(*n*-Bu)$_3$P] catalyzed synthesis of halo-allenes **4.13** (Scheme 4.6b) with Appel type reaction conditions containing $Ph_3P$, $CBr_4$, and *i*-$Pr_2$NEt was achieved by Sakai *et al*.[18]

**Scheme 4.6**



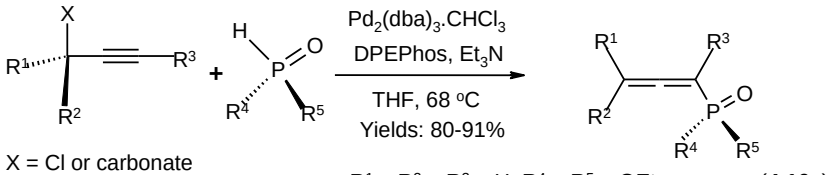

Synthesis of allenylphosphonates/ allenylphosphine oxides is accomplished by the treatment of phosphorus(III) chlorides [$X_2PCl$, X = OMe, OEt, Ph] with propargyl alcohols [e.g. Me(H)C(OH)C≡CH] in the presence of a base [pyridine, triethylamine etc.] in a suitable solvent like THF, ether or toluene.[7a-c, 7e and 19] The P(III) intermediate undergoes a *pseudo*-Claisen type rearrangement to afford allenylphosphonates/ allenylphosphine oxides (see Chapter 5). A variety of pentaerythritol[19c] and cyclodiphosphazane[19d] containing allenes **4.14-4.15** (Scheme 4.7) were also synthesized by using this methodology in our laboratory.

**Scheme 4.7**




Recently, Stawinski and co-workers reported a novel method for the construction of allenylphosphonates **4.16** and related compounds. The reaction involves a Pd(0)/DPEPhos-[bis(2-phenylphosphinophenyl)ether-] catalyzed coupling of propargyl chlorides or carbonates with *H*-phosphonate diesters or their analogues (Scheme 4.8).[20] The reaction permits stereoselective and stereospecific construction of an allenic moiety with complete transfer of chiral center to axial chirality and retention of configuration at the phosphorus center.

**Scheme 4.8**




## 4.3 Allenes/allenylphosphonates/allenylphosphine oxides in organic synthesis

Several systems in allene chemistry that involve transition metal catalyzed, base catalyzed, Brønsted acid catalyzed and non-catalytic reactions to lead to a variety of molecules having biological and pharmaceutical significance have been discovered. In the following sections selected cycloaddition and cyclization reactions of allenes that are relevant to our work are presented.

### 4.31 Cycloaddition reactions of allenylphosphonates or related allenes

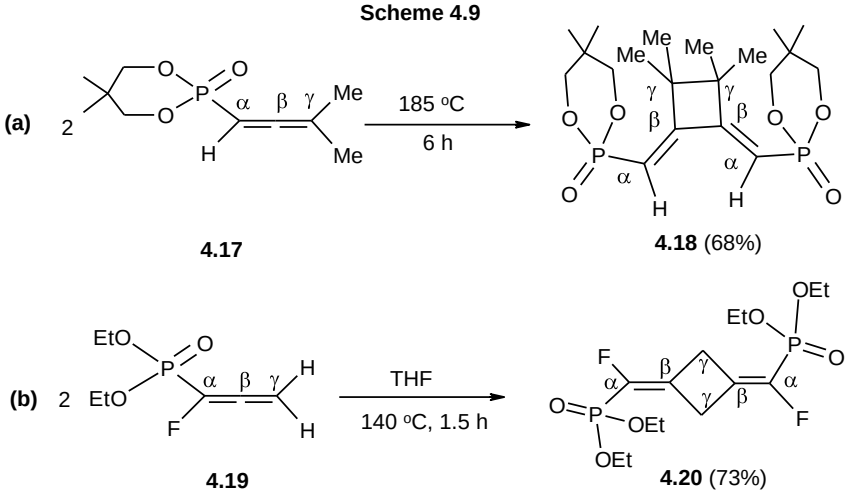
As a consequence of the presence cumulative π electron system, allenes can undergo cycloaddition reactions hence are excellent precursors for [2+2] and [4+2]

cycloadducts.[1 and 21] In these reactions, allenes can act as dienes (if an additional double bond is accessible) as well as dienophiles. Cycloadditions are atom economical and hence grab the attention of synthetic chemists.

### 4.311 [2+2] Cycloaddition reactions

[2+2] Cycloaddition reaction between allenes or allene and an alkene shows an important approach for the synthesis of variety of cyclobutanes which are useful building blocks for construction of more complex structures.[22] An allene can undergo [2+2] cycloaddition with itself to form a dimer either head-to-head or tail-to-tail adduct. The selectivity depends on the substituent's nature in steric and electronic platforms. From our laboratory, a head-to-head [2+2] dimerization of allene **4.17** involving the β,γ-position under thermal conditions has been reported.[7e] The cycloadduct **4.18** was formed *via* a concerted diradical mechanism exclusively with the defined stereochemistry as shown in Scheme 4.9a. In contrast, heating of α-fluoroallenylphosphonate **4.19** in a sealed tube provided the tail-to-tail dimer **4.20** exclusively at the β,γ-position (Scheme 4.9b).[23] The bulky phosphorus substituent on the allene moiety allowed rotation in the bisallyl diradical intermediate yielding the corresponding dimer.

**Scheme 4.9**

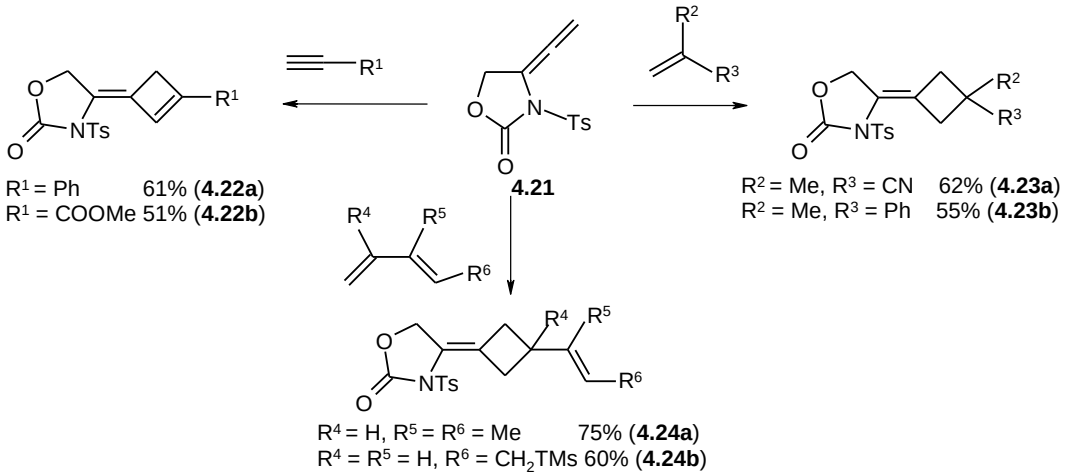



**4.17** **4.18** (68%) **4.19** **4.20** (73%)

Tamaru reported thermal intermolecular [2+2] cycloaddition of vinylideneoxazolidin-2-ones **4.21** with terminal alkyne or alkene which led to (*Z*)-methylene-cyclobutenes **4.22** or **4.23** (Scheme 4.10) in good to excellent yields.[24]

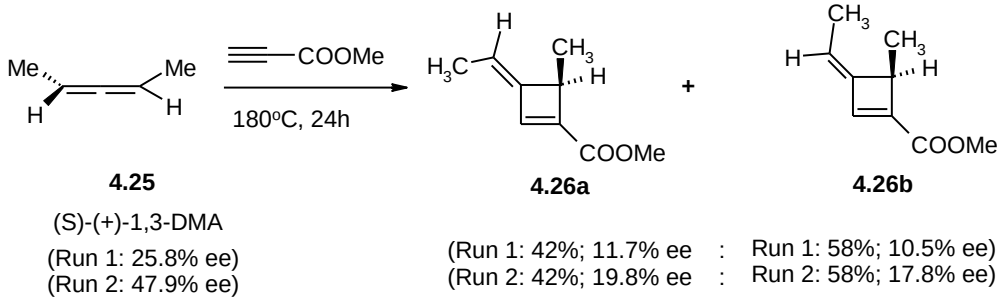
Reaction of the same allene with 1,3-diene also afforded [2+2] cycloaddition product **4.24,** rather than [4+2] cycloaddition product.

**Scheme 4.10**




Stereochemical features of [2+2] cycloaddition reactions of chiral 1,3-dimethylallene were reported by Pasto[25]. [2+2] Cycloaddition of methyl propiolate with enantioenriched 1,3-dimethylallene **4.25** afforded two cycloadducts **4.26a-b** in the ratio of 42:58 along with some unreactive allene (Scheme 4.11). The chirality of 1,3-dimethylallene was partially transferred to the products.

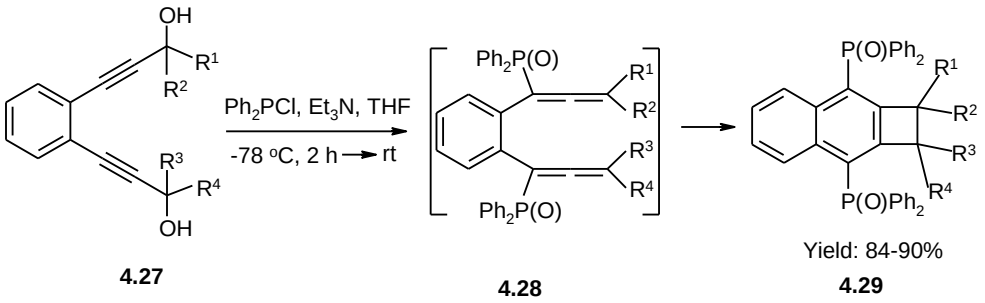
**Scheme 4.11**




Kitagaki and Mukai reported that the reaction of benzene-bridged bis(propargyl alcohols) **4.27** with $Ph_2PCl$ afforded 3,8-bis(dialkylphosphinyl)-naphtho[*b*]cyclobutenes **4.29**.[26] Initially, a dual [2,3]-sigmatropic rearrangement of the bisalkynols furnished

intermediate 1,2-bis-(a-phosphinylallenyl)benzenes **4.28**, which spontaneously undergoes intramolecular [2+2] cycloaddition (Scheme 4.12) to lead to **4.29**.

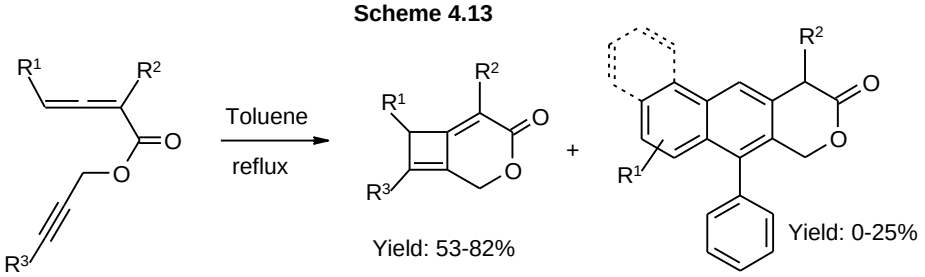
**Scheme 4.12**




**4.27** **4.28** **4.29**

Recently Jiang and Ma reported the intra-molecular [2+2] cycloaddition of propargylic 2,3-allenoates **4.30** which on conventional heating afforded 3-oxabicyclo[4.2.0]octa-1(8),5-dien-4-ones **4.31** (Scheme 4.13). When γ-substituent on the allene was aryl group and terminal substituent on alkyne was phenyl group, Diels-Alder adducts **4.32** were formed as side products in lower yields.[27]

**Scheme 4.13**

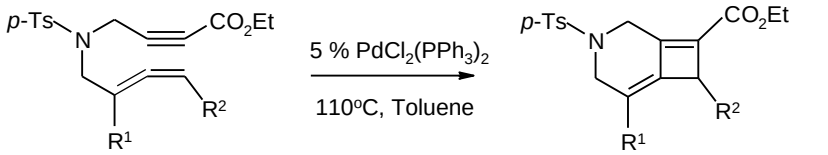



**4.30** **4.31** **4.32**

$R^1$ = Ph, naphthyl,
$R^2$ = Me, Et, *n*-Pr, *n*-Bu, TMS
$R^3$ = Ph, TMS

A photocycloaddition of optically active *t*-butyl substituted allenes with enones was reported by Carreira.[28] Many metal catalyzed (Pd, Ru, Au, Pt etc.) cycloaddition reactions are also reported in the literature. Oh *et al* reported palladium catalyzed [2+2] cycloaddition of 1,6 and 1,7 allenyne **4.33**.[29] The reaction led to bicyclic compounds **4.34** with fused cyclobutene (Scheme 4.14) in the presence of 5 mol % $PdCl_2(PPh_3)_2$ in toluene under reflux condition with excellent yields.

**Scheme 4.14**

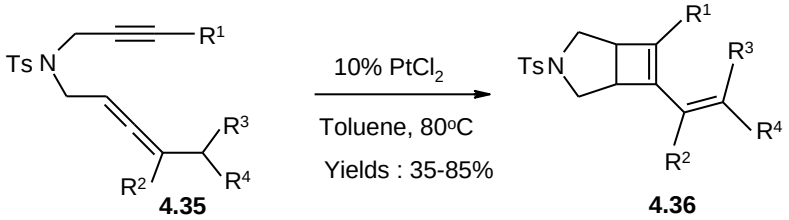



**4.33**

$R^1$ = Me, $R^2$ = H 75% **4.34a**
$R^1$ = H, $R^2$ = Me 82% **4.34b**

Platinum complexes were also used in the cycloisomerization reactions of enynes. Murakami and co-workers reported that the treatment of allene tethered with alkyne **4.35** with catalytic amount of platinum(II) chloride in toluene at 80 $^oC$ afforded bicyclic cyclobutene **4.36** (Scheme 4.15).[30]

**Scheme 4.15**

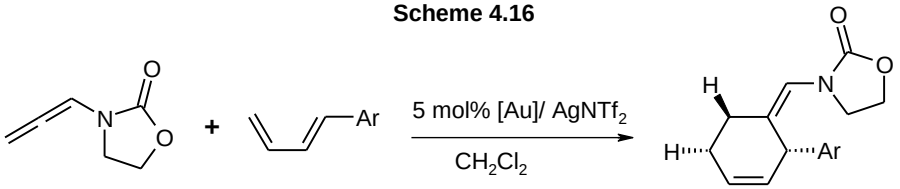



**4.35** **4.36**

## 4.312 [4+2] Cycloaddition reactions

Allenes can act as dienophiles in [4+2] cycloadditions whereas vinyl/aryl substituted allenes can act as dienes.[31] Fernandez *et al* reported asymmetric gold(I) catalyzed intermolecular [4+2] cycloaddition of allenamide **4.37** and diene. Axially chiral triazoloisoquinolin-3-ylidene was used as ligand to accomplish the enantiomeric excess of the cycloadduct **4.38** (Scheme 4.16).[32] The reaction provided moderate to good yields (50-88%) of optically active cyclohexanes with three chiral centers.

**Scheme 4.16**

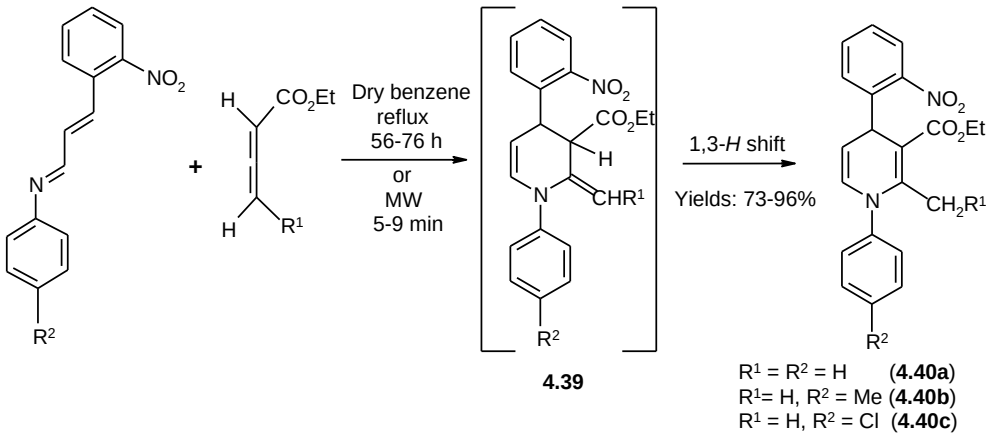



**4.37**

Ar = Ph 82% (ee 94 %) **4.38a**
Ar = 4-Br-$C_6H_4$ 55% (ee 96%) **4.38b**

Thermal [4+2] cycloaddition of 1,4-diaryl-1-aza-1,3-butadienes with allenic esters was investigated by Ishar and coworkers.[31b] The reaction led to cycloadducts **4.39**, which after a 1,3-*H* shift furnished substituted unsymmetrical 2-alkyl-1,4-diaryl-3-ethoxycarbonyl-1,4-dihydropyridines **4.40** in high yields (Scheme 4.17). They also succeeded in getting the same products under microwave (MW) irradiation with much shortened reaction time (5-9 min).

**Scheme 4.17**

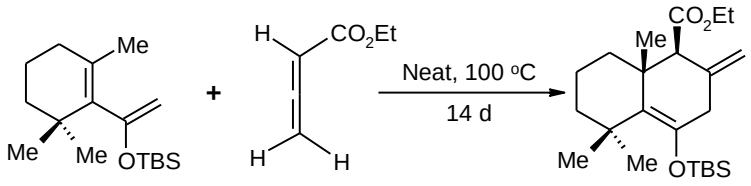



**4.39**

$R^1 = R^2 = H$ (**4.40a**)
$R^1$= H, $R^2$ = Me (**4.40b**)
$R^1$ = H, $R^2$ = Cl (**4.40c**)

Jung and co-workers described the [4+2] cycloaddition reaction of sterically hindered diene and ester allene (Scheme 4.18).[33] This synthetic methodology was used as a key step for the total synthesis of (±)-hedychenone **4.41**,[33a] (±)-hedychilactone B,[33b] and (±)-kellermanoldione.[33c]

**Scheme 4.18**

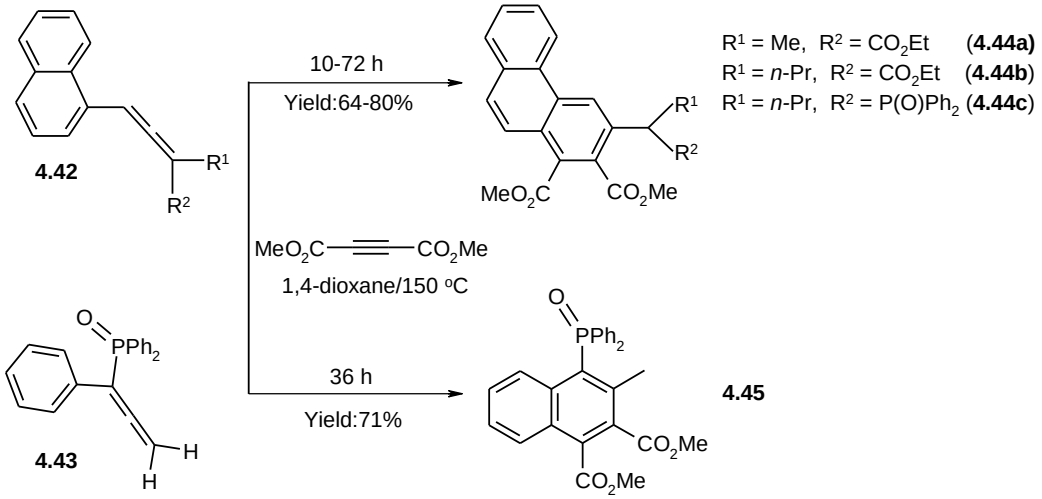



**4.41** (43%)

Only a very few reports in which arylallenes act as dienes in [4+2] cycloaddition reaction are available.[34] Ma and co-workers observed an intermolecular [4+2]

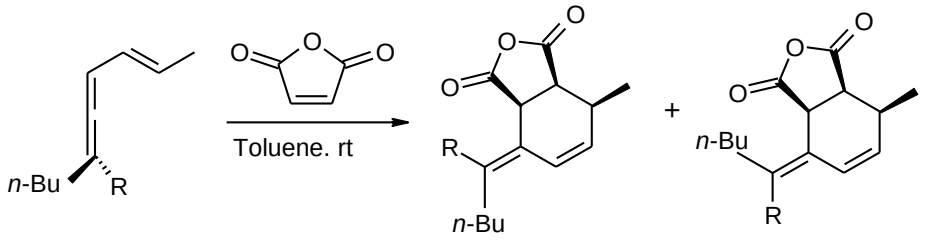
cycloaddition reaction of 1-aryl-1,2-allenes **4.42** or **4.43** with dimethyl acetylenedicarboxylate ($Me_2OC{\equiv}CCO_2Me$, DMAD) providing phenanthrenes **4.44** or naphthalene **4.45** respectively (Scheme 4.19).[34b]

**Scheme 4.19**




Investigation on vinyl allenes which act as dienes in [4+2] cycloaddition was reported by Spino *et al*.[35] Thus allenes **4.46** were treated with activated alkenes at room temperature to provide cycloadducts **4.47** in moderate to excellent yields (Scheme 4.20). The products contained stereoselective exocyclic tetrasubstituted double bond.

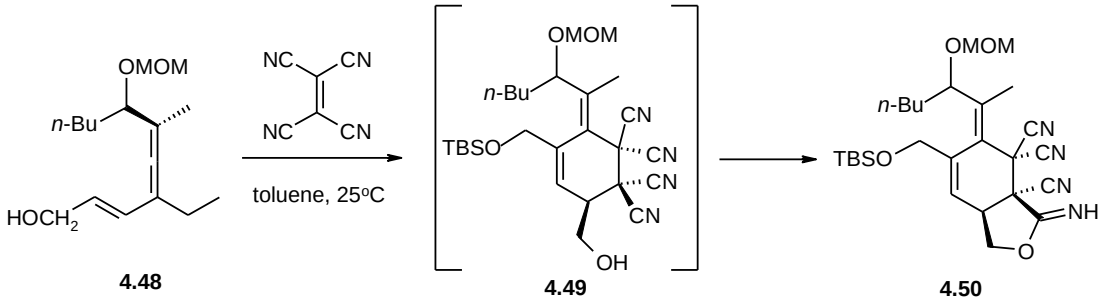
**Scheme 4.20**




**4.47a** R = H, 96%, *E*:*Z* ; 8:1
**4.47b** R = Me, 82%, *E*:*Z* ; 3:1

Sipino *et al* reported that vinyl allene **4.48**, which could act as a diene, when treated with tetracyanoethylene yielded the [4+2]-cycloadduct forming cyclohexene derivative **4.49**, which was followed by the intramolecular attack of the hydroxyl group on the neighboring nitrile group to form bicyclic iminolactone **4.50** (Scheme 4.21).[36]

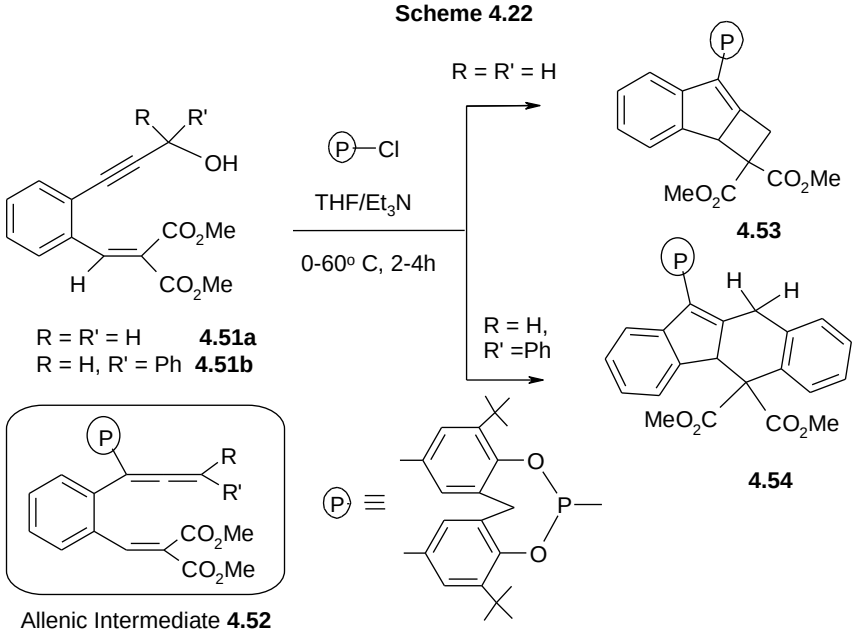
**Scheme 4.21**




**4.48** **4.49** **4.50**

Very recently, our group reported the synthesis of phosphono-polycyclics in which intramolecular [4+2]/ [2+2] cycloaddition was involved.[37] Activated alkene tethered propargylic alcohols **4.51** were treated with P(III)Cl compounds which underwent *in situ* allene **4.52** formation followed by [2+2]/ [4+2] cycloadditions depending on the substitutions on the propargylic alcohols to lead to polycyclics **4.53** and **4.54** (Scheme 4.22).

**Scheme 4.22**




R = R' = H **4.51a**
R = H, R' = Ph **4.51b**

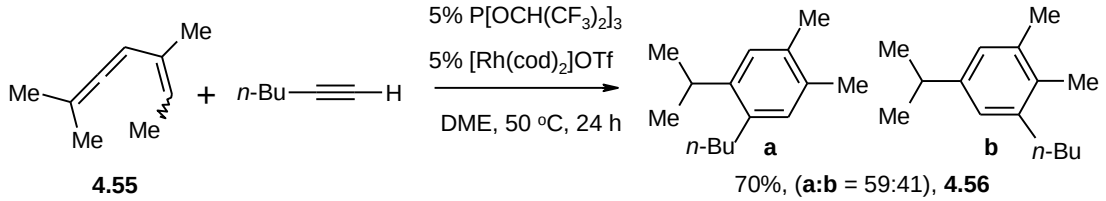
Allenic Intermediate **4.52**

**4.53** **4.54**

Murakami and Ito reported Rhodium intermolecular [4+2] cycloaddition of unactivated allene **4.55** and alkyne.[38] In this reaction, vinylallene and terminal acetylene were used as diene and dienophile respectively in the presence of $[Rh(cod)_2]OTf$/

$P[OCH(CF_3)_2]_3$ in DME. Tetrasubstituted benzenes **4.56** were formed as a mixture of regioisomers (Scheme 4.23).

**Scheme 4.23**

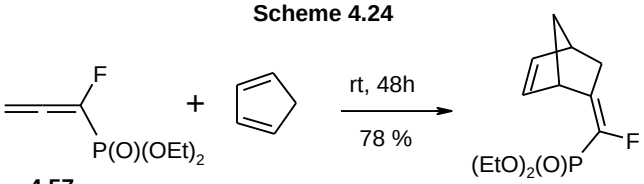



**4.55**

70%, (**a:b** = 59:41), **4.56**

Hammond and co-workers reported that 1-fluoropropadienyl phosphonate **4.57** could undergo intermolecular [4+2]-cycloaddition with cyclopentadiene at room temperature to provide the *endo*-product **4.58** with high selectivity (Scheme 4.24).[39] However, a report on detailed studies has not appeared so far.

**Scheme 4.24**

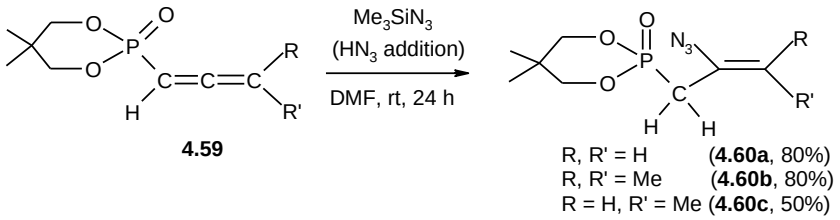



**4.57** **4.58**

## 4.32 Nucleophilic addition and cyclization reactions of allenes

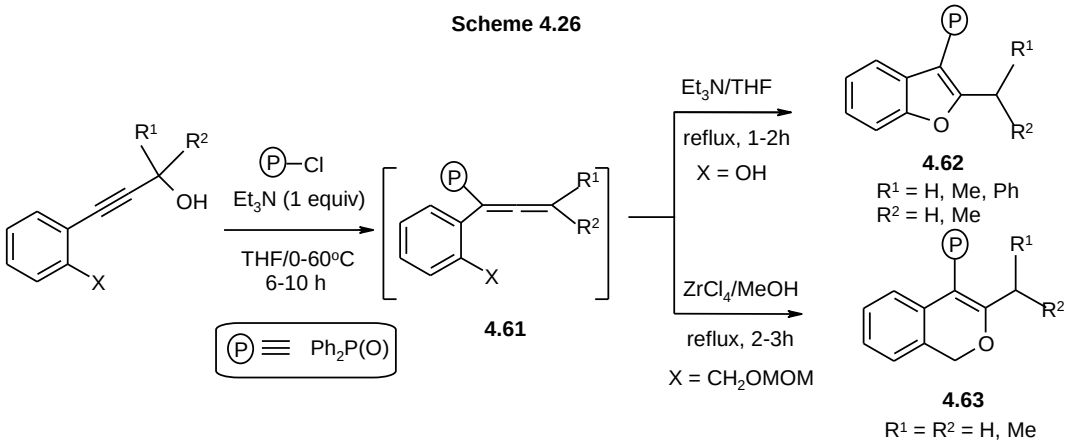
Allenes are susceptible for nucleophilic addition reactions which are prominent synthetic tools for heterocyclic rings[40] and many functionalized molecules.[41] If one of the substituents on allene is an electron withdrawing group (e.g. ester or phosphonate), nucleophile attacks at β–carbon of allene with very limited exceptions.[42] Our research group reported the addition of nucleobases to allenylphosphonates to discover a route to β–amino phosphonates.[43] More recently, the regioselective synthesis of phosphorus based vinyl azides **4.60a-c** by the reaction of allenylphosphonates **4.59** and trimethylsilyl azide at ambient temperature was reported (Scheme 4.25).[44] These azides underwent 1,3-dipolar cycloaddition with activated acetylenes to give the 1,2,3-triazoles in good yields.

**Scheme 4.25**



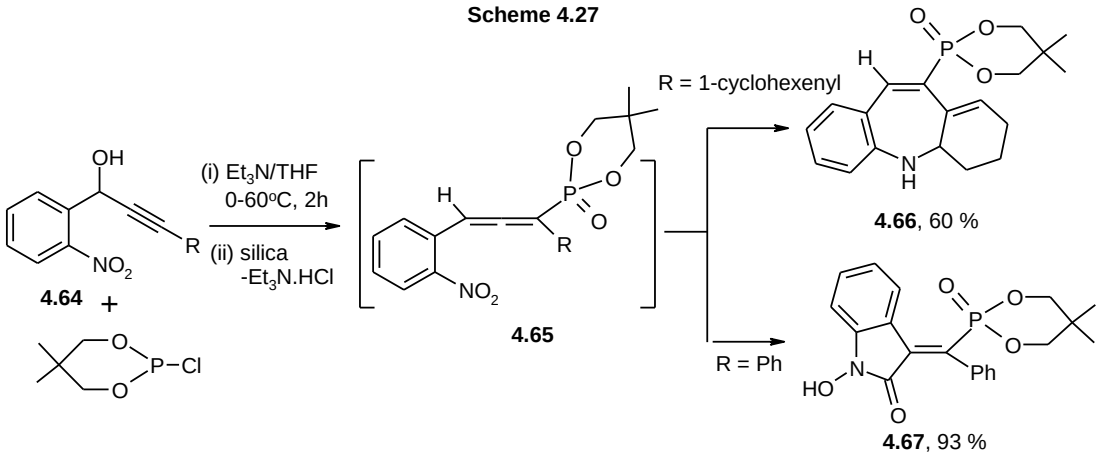

Very recently, nucleophilic intramolecular cyclizations of allenylphosphine oxides **4.61**, which are assumed to be intermediates, leading to phosphorus based benzofurans **4.62** and isochromenes **4.63,** have been reported from our laboratory.[45] The final products were formed by simple nucleophilic addition at β–carbon in the presence of $Et_3N$ and $ZrCl_4$ respectively (Scheme 4.26). Synthesis of phosphorus based indenes and indenones was also reported by using alkylidene and aldehyde groups as nucleophiles.

**Scheme 4.26**



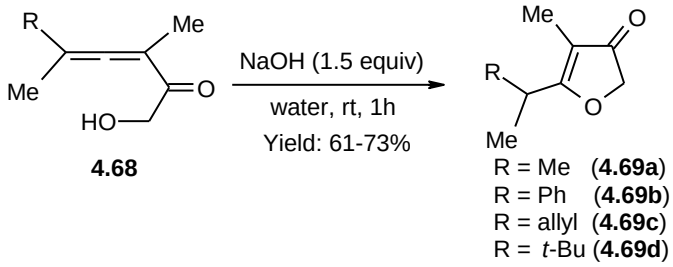

In addition to the above, synthesis of phosphono azepine/ indoline derivatives was also reported from our group.[37] The *in situ* formed allene intermediates **4.65** in the reaction of nitro-based propargyl alcohols **4.64** and P(III)-Cl precursors underwent a dramatic cycloaddition followed by $CO_2$ elimination to yield novel phosphono benzapine/ indoline derivatives. If the terminal substituent on the propargyl alcohol was cyclohexenyl group, the product was (tetrahydro)dibenzazepine **4.66** whereas with the phenyl substituent the product was phosphono-*N*-hydroxyindolinone **4.67** (Scheme 4.27).

**Scheme 4.27**



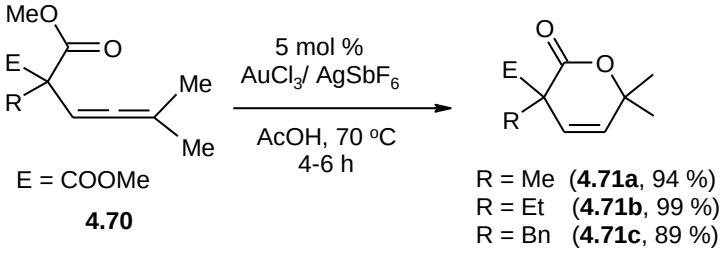

Very recently, Krause and Poonoth disclosed a novel route to the synthesis of 3(2*H*)-furanones **4.69a-d** by cycloisomerization of allenic hydroxy ketones **4.68** with aqueous NaOH (Scheme 4.28).[46] This transformation is achieved in water and in the absence of a metal catalyst.

**Scheme 4.28**



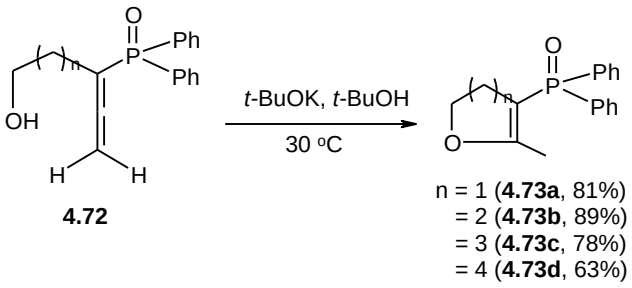

Piera and Backvall reported gold catalyzed cyclization of allene-substituted malonic esters **4.70** with the aid of acetic acid. The reaction furnished β,γ-unsaturated δ-lactones **4.71a-c**. The reaction proceeded in the presence of 5 mol % $AuCl_3/AgSbF_6$ at 70 $^oC$ in which the nucleophile attacked the γ–carbon of allene (Scheme 4.29).[47]

**Scheme 4.29**



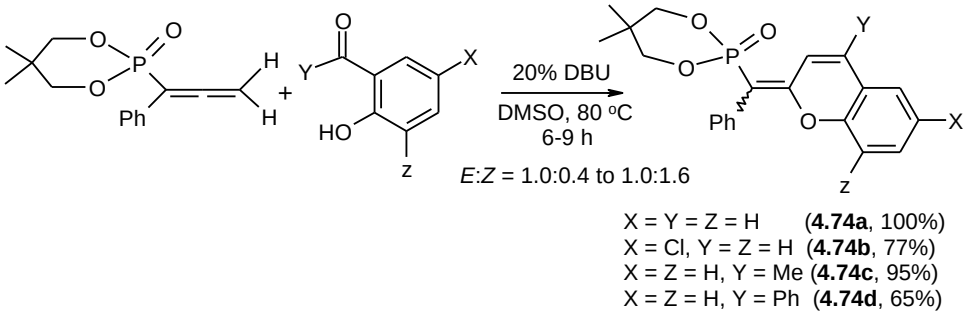

Mukai and co-workers developed a method for the construction five- to eight-membered oxacycles. Thus, allenes **4.72** substituted with phosphine oxide group and tethered with hydroxyl function underwent an *endo* type ring closing reaction to provide oxacycles **4.73** in good yields (Scheme 4.30).[48] This method also worked well for allenes having $–PO(OEt)_2$, -SOPh and $-SO_2Ph$ groups.

**Scheme 4.30**



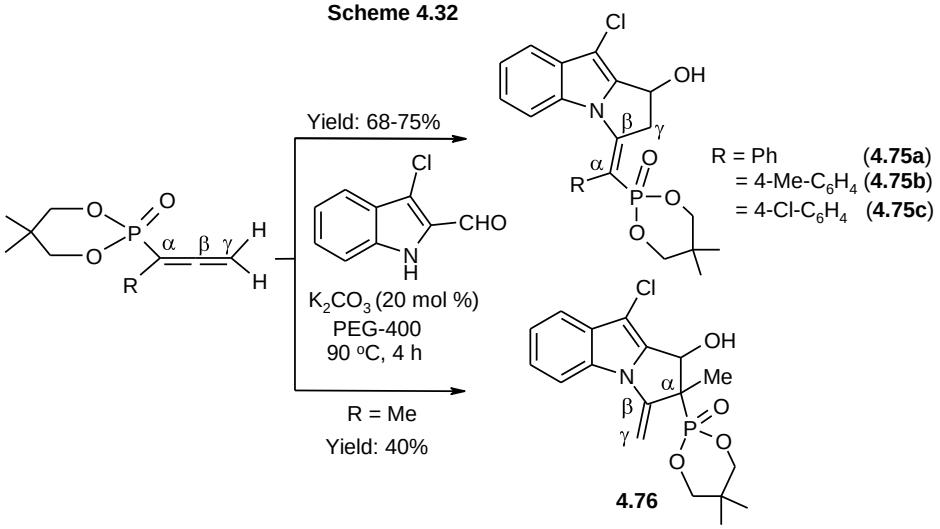

Base catalyzed nucleophilic addition reactions were investigated by our group.[49] Thus, DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) catalyzed cyclization reaction of allenylphosphonates with salicylaldehydes or hydroxyaceto-/benzophenones led to phosphono-chromenes. Phosphorylated allene reacted with salicylaldehydes or hydroxyaceto-/benzophenones in the presence of DBU (20 mol%) in DMSO as the solvent afforded phosphono-chromenes **4.74a-d** in good yields with an *E*/*Z* ratio up to 1.0:0.4 (Scheme 4.31). This reaction involves a nucleophilic attack of phenoxide ion at the β-position of allene followed by the cyclization. Very recently, on the same notion, thiochromenes and aza-linked chromenes in the presence of $K_2CO_3$/DMSO were synthesized in our laboratory.[50a]

**Scheme 4.31**




In continuation of the above work, pyrrolo[1,2-a]indoles were synthesized *via* base catalyzed domino cyclization of activated allenes with 3-chloro-2-formylindole in PEG-400 medium.[50b] α-Aryl substituted allenylphosphonates were treated with 3-chloro-2-formylindoles gave the (β,γ)-cyclized product **4.75a-c**, while the α-methyl substituted allenylphosphonate resulted in the (β,α)-cyclized product **4.76** (Scheme 4.32). Thus the structure of the product depends on the type of substituent present on the allene. The allene containing a sulfonyl group ($ArSO_2$-) in place of phosphoryl group provided a result similar to that of allenylphosphonates.

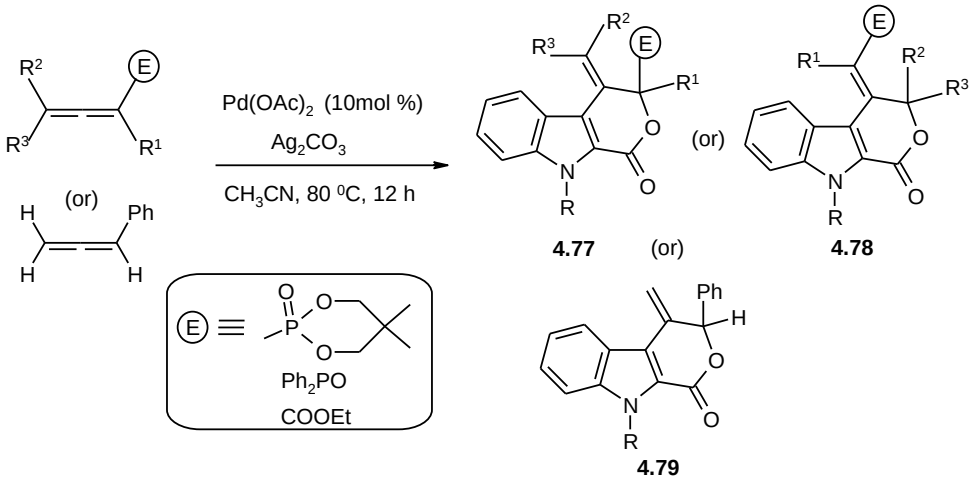
**Scheme 4.32**




From our research group, Pd-catalyzed coupling reactions of allenylphosphonates with aryl iodides, iodophenols, and iodobenzoic acid were investigated to synthesize various phosphono heterocycles.[7a] Very recently, our group

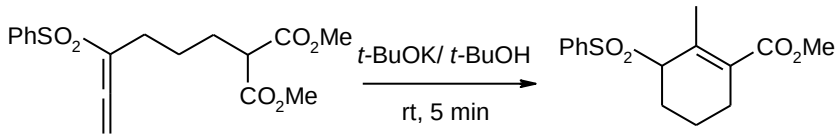
also reported the Pd-catalyzed annulation of allenes with indole-2-carboxylic acid derivatives.*via* C-H functionalization to accomplish indolo[2,3-*c*]pyrane1-one **4.77-4.79** (Scheme 4.33).[50c]

**Scheme 4.33**




Mukai and coworkers reported the synthesis of six membered carbocycles from 1-phenylsulfonylallene **4.80** having active methine substitution (Scheme 4.34).[50d] The reaction was carried out by stoichiometric quantity of *t*-BuOK and it proceeded by *endo* mode ring closing reaction followed by demethoxy carbonylation to lead to carbocycle **4.81**. This methodology also worked well in forming five and seven membered carbocycles.

**Scheme 4.34**




**4.80** **4.81**, 92 %

Apart from the above, various reactions involving the nucleophilic additions onto allenes leading to a variety of cyclic/acyclic functionalized molecules, are available in the literature.[51] The presentation given here is restricted (by choice) to mainly, phosphorus based systems.

## OBJECTIVES OF THE PRESENT WORK - PART B

The main objective of this part of the present work is to investigate on the synthesis of various organophosphorus compounds as given below.

(i) To synthesize functionalized allenylphosphonates using propargyl alcohols and a suitable $P^{III}$-Cl precursor,

(ii) To investigate the reactivity of phosphorus-based allenes in the cycloaddition reactions with dialkyl acetylenedicarboxylates,

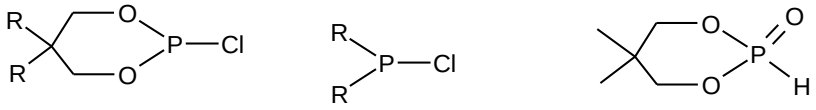
(iii) To study the Brønsted acid medium cyclization of functionalized allenylphosphine oxides leading to phosphinoyl-isocoumarins and

(iv) To explore the reactivity of α-hydroxy allylphosphonates in the preparation of vinyl/allylphosphonates via nucleophilic substitution.

# RESULTS AND DISCUSSION

The $P^{III}$-Cl precursors $(OCH_2CR_2CH_2O)PCl$ [R = Me (**1a**)[52a], Et (**1b**)[52b]], $Ph_2PCl$ (**1c**), $[(i\text{-}Pr)_2N]_2PCl$ (**1d**)[52c] and $(OCH_2CMe_2CH_2O)POH$ (**2**)[53] used in the present study are shown in Chart 1. These $P^{III}$-Cl compounds are sensitive to moisture but can be handled under inert atmosphere conditions.

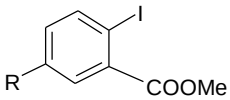
**Chart 1**



R = Me [**1a**, δ(P): 145.8] R = Ph [**1c,** δ(P): 82.1] **2** [δ(P): 3.2]
= Et [**1b**, δ(P): 148.2] = $(i\text{-}Pr)_2N$ [**1d**, δ(P): 138.8]

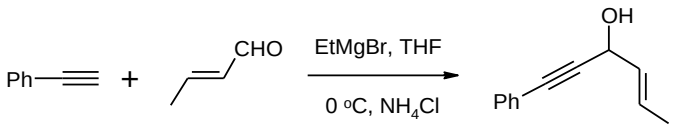
## 5.1 Synthesis of substituted haloarenes 3-4 and propargylic precursors 5-7

The iodoarenes **3**[54a] and **4**[54b] were synthesized by esterification of the corresponding benzoic acids in methanol in the presence of catalytic amount of sulfuric acid. Propargylic alcohol **5**[55] was synthesized by Grignard reaction of phenyl acetylene and crotonaldehyde (Scheme 1). Functionalized propargyl alcohols **6**[56a] and **7a-h**[56b] were obtained by following a standard method *via* Sonogashira coupling (Scheme 2). Among these propargyl alcohols, compounds **7c** and **7e-h** are new. They have been characterized by IR [υ(C≡C) ~2200 and υ(OH) ~ 3400 (br) $cm^{-1}$] and NMR [$^1H$, $^{13}C$] spectroscopic techniques. They are stable viscous liquids.



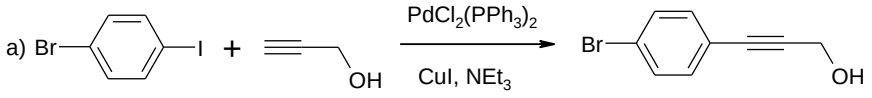
R = H, **3**
R = Br, **4**

**Scheme 1**

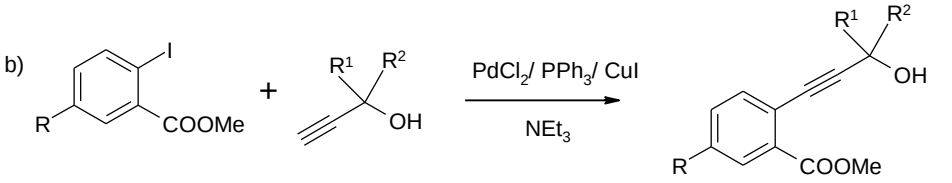



**5**, 84%

**Scheme 2**




**6**, 89%



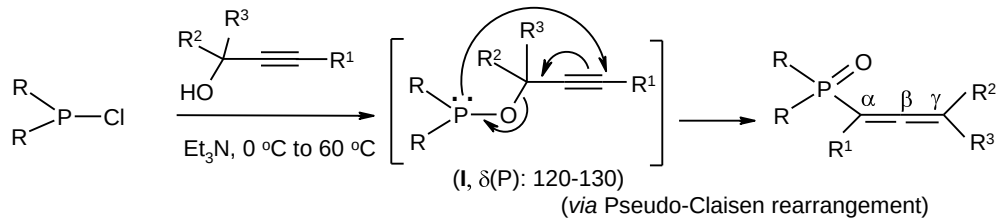

R = R¹ = R² = H (**7a**)
R = R¹ = H, R² = Me (**7b**)
R = H, (R¹R²) = -$(CH_2)_5$- (**7c**)
R = H, R¹ = R² = Me (**7d**)
R = Br, R¹ = R²= H (**7e**)
R = Br, R¹ = H, R² = Me (**7f**)
R = Br, (R¹R²) = -$(CH_2)_5$- (**7g**)
R = Br, R¹ = R² = Me (**7h**)

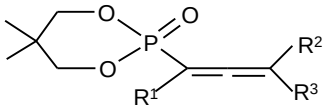
## 5.2 Synthesis of allenylphosphonates 8a-e/ 10a-b and allenylphosphine oxides 9a-b/ 11a-h

Allenylphosphonates **8a-e/ 10a-b** and allenylphosphine oxides **9a-b/ 11a-h** are synthesized by following a method previously reported from our laboratory (Scheme 3).[19d-e, 57] Allenes **8d**, **10b** and **11a-h** are new. These allenes are quite stable in the solid state in air for a day, and can be preserved for a few months at low temperature (4 $^{o}$C) under an inert atmosphere. In the IR spectra, they show a characteristic strong band at 1920-1975 $cm^{-1}$ due to $\nu_{asym}$(C=C=C).[58] The $^{31}$P NMR spectra of allenylphosphonates **8a-e** and **10a-b** show a peak in the range from δ 6-12, whereas allenylphosphine oxides **9a-b** and **11a-h** show a peak in the range δ 19-31. In the $^{13}$C NMR spectra, the *α*-carbon (to phosphorus) appears as a doublet at δ ~ 92.0 [$^{1}J$(P-C) ~ 183.0 Hz] for **8a-e** and **10a-b** whereas it is at δ 95-100 [$^{1}J$(P-C) ~ 180 Hz] for **9a-b** and **11a-h**. The PC=*C* signal for

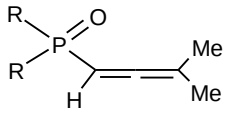
all these compounds appears as a doublet in the region δ 206-214 [$^2J$(P-C) ~ 6.0-7.0 Hz]. Since this protocol is fairly well-known, it is not elaborated here.

**Scheme 3**

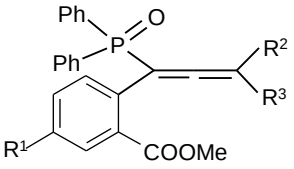


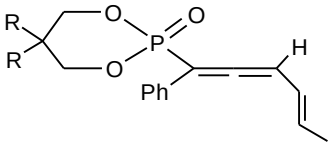

$R^1$ = H, $R^2$ = $R^3$ = Me [**8a**, δ(P): 9.8; 69%]
$R^1$ = Ph, $R^2$ = $R^3$ = H [**8b**, δ(P): 6.6; 70%]
$R^1$ = Me-$C_6H_4$-, $R^2$ = $R^3$ = H [**8c**, δ(P): 7.8; 81%]
$R^1$ = Br-$C_6H_4$-, $R^2$ = $R^3$ = H [**8d**, δ(P): 6.5; 95%]
$R^1$ = OMe-$C_6H_4$-, $R^2$ = $R^3$ = H [**8e**, δ(P): 7.5; 79%]




R = Ph [**9a**, δ(P): 27.1; 74%]
R = ($i$-Pr)$_2$N [**9b**, δ(P): 19.6; 79%]




$R^1$ = $R^2$ = $R^3$ = H [**11a**, δ(P): 27.7; 85%]
$R^1$ = H, $R^2$ = H, $R^3$ = Me [**11b**, δ(P): 28.8; 79%]
$R^1$ = H, $R^2$ = $R^3$ = -$(CH_2)_5$- [**11c**, δ(P): 29.5; 90%]
$R^1$ = H, $R^2$ = $R^3$ = Me [**11d**, δ(P): 29.8; 88%]
$R^1$ = Br, $R^2$ = $R^3$ = H [**11e**, δ(P): 27.6; 86%]
$R^1$ = Br, $R^2$ = Me, $R^3$ = H [**11f**, δ(P): 28.7; 84%]
$R^1$ = Br, $R^2$ = $R^3$ = -$(CH_2)_5$- [**11g**, δ(P): 29.5; 74%]
$R^1$ = Br, $R^2$ = $R^3$ = Me [**11h**, δ(P): 29.8; 91%]




R = Me [**10a**, δ(P): 6.7; 72%]
R = Et [**10b**, δ(P): 7.5; 80%]

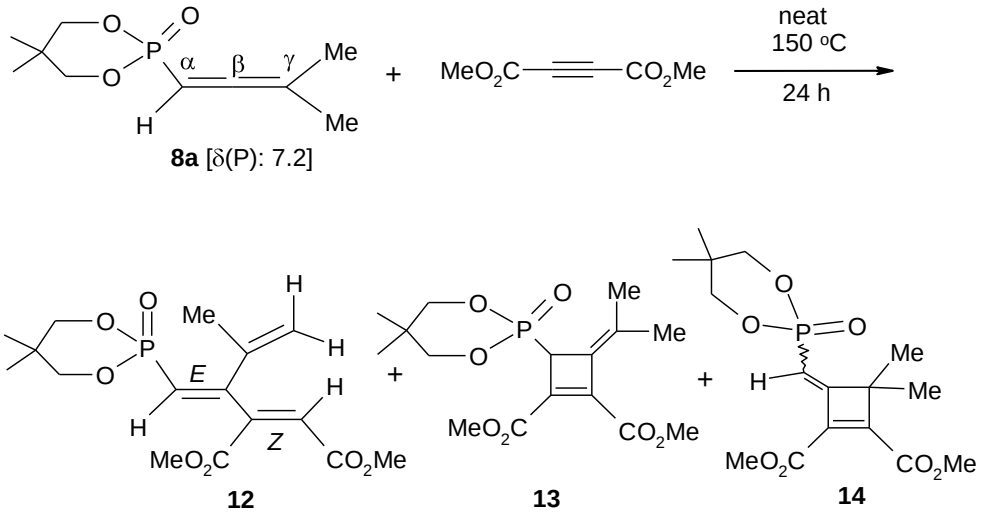
## 5.3 Cycloaddition and ene type reactions of allenes

Allenes which are activated by containing electron withdrawing groups can undergo cycloaddition easily to lead to cycloadducts. This reactivity pattern of allenes prompted us to perform cycloaddition reactions. In the following subsections, we discuss the reactivity of the allenes **8a-e** and **10a-b** towards the cycloaddition reaction with the activated alkynes. In addition, ene type reaction of allenes **9a-b** with dimethyl acetylenedicarboxylate (DMAD) is also discussed.

### *5.31 Reaction of phosphorus containing allenes with activated alkynes*

We started our investigation by treating the allenylphosphonate $(OCH_2CMe_2CH_2O)P(O)(H)C=C=CMe_2$ (**8a**) with DMAD under neat conditions at 150 $^oC$ for 24 h. The $^{31}P$ NMR spectrum of the reaction mixture showed several peaks [Figure 1], but compounds **12-14** were the major components [total ~85%] that could be readily isolated (Scheme 4). Among these, compound **12** is an ene type addition product which is isolated in 20 % yield. Compounds **13** and **14** are [2+2] cycloadducts formed at (α,β)- and (β,γ)- positions of allenes. Products **13** and **14** are isolated in yields of 10 % and 15 % respectively.

**Scheme 4**




**8a** [δ(P): 7.2]

| | **12** | **13** | **14** |
|---|---|---|---|
| δ(P): | 9.3 | 18.7 | 10.4 |
| Yield [$^{31}P$ NMR]: | 25% | 30% | 30% |
| Yield [isolated]: | 20% | 10% | 15% |

In the $^1H$ NMR spectrum, compound **12** shows peaks at δ 5.11 and 5.37 (=C$H_AH_X$), 5.83 ($^2J$(P-H) = 15.6 Hz, PC*H*) and 6.16 (=C*H*). This feature clearly shows that a proton from one of the terminal methyls present in the precursor **8a** has moved to the DMAD residue. Such a rearrangement in other reactions of **8a** has been observed earlier.[19e] In the $^{13}C$ NMR spectrum, a doublet at 119.1 ($^1J$(P-C) = 185.3 Hz, P-*C*) is observed. This coupling constant suggests that the phosphorus is connected to an *olefinic carbon*. Compound **13** exhibits peaks at δ 1.90 and 1.92 (=C(C$H_3$)$_2$) in the $^1H$ NMR showing that the two methyl groups are still intact here. The $^{31}P$ NMR chemical

shift [δ 18.7] is distinct and different from that of the precursor **8a** or the products **12** and **14**, as expected from the difference in structures. The two methyls in compound **14** are connected to a saturated carbon and hence the corresponding protons appear up-field at δ 1.60 in the $^{1}$H NMR; the PC*H* proton expectedly appears in the olefinic region [δ 6.01, $^{2}J$(P-H) = 16.0 Hz]. It is also noted that in the $^{13}$C NMR, the P-*C* carbon in compound **14** appears in the olefinic region [δ 103.5, $^{1}J$(P-C) = 191.0 Hz] while in compound **13** the P-*C* carbon appears at δ 43.3 [$^{1}J$(P-C) = 145.1 Hz]. In general, as noted elsewhere,[19e] increase in the *s*-character of the carbon increases the $^{1}J$(*P-C*) values and the present data are consistent with this. The X-ray structures of compounds **12** and **13** have been reported by one of my colleagues in the laboratory earlier.[59]

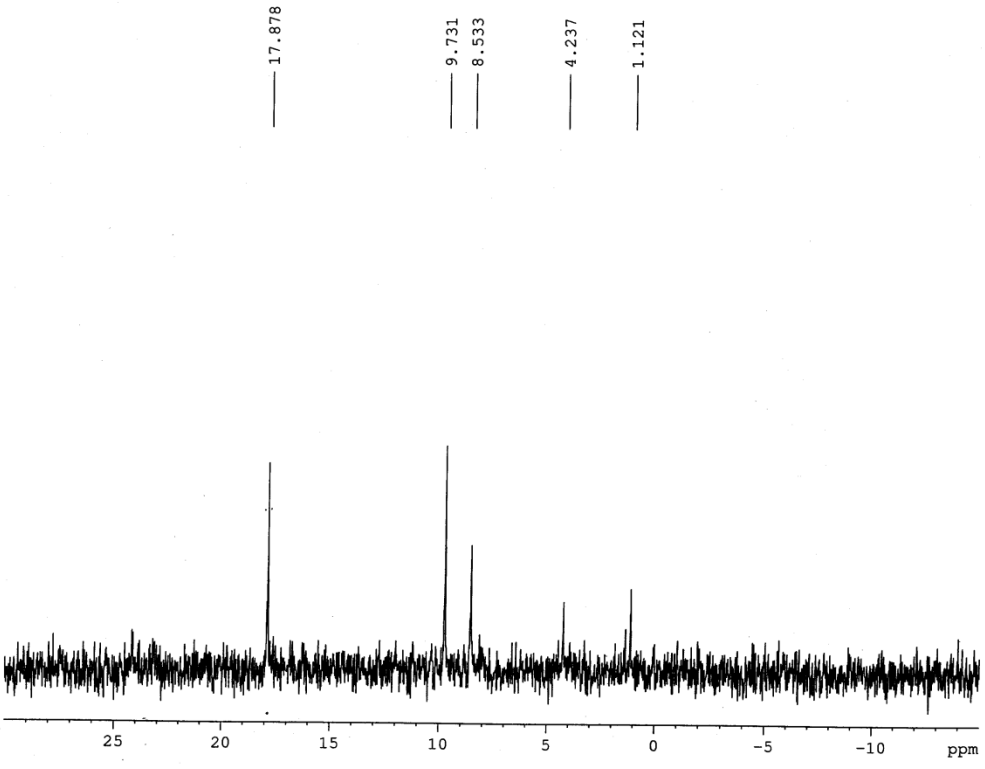
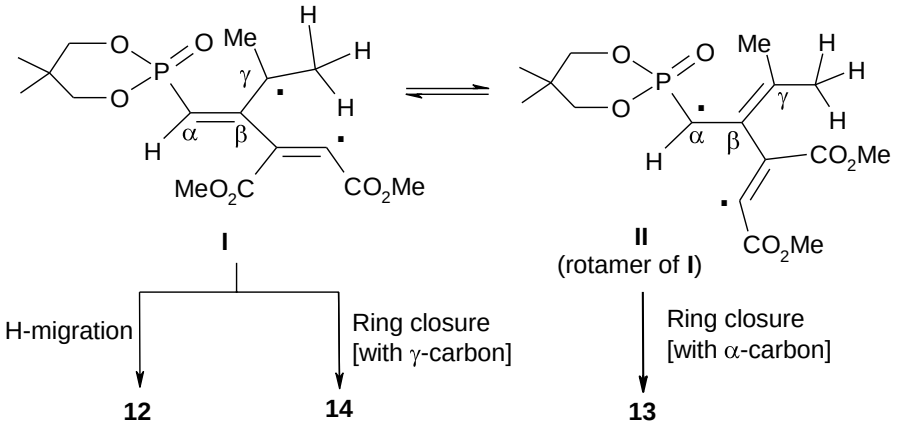



**Figure 1**. $^{31}$P NMR spectrum of reaction mixture resulting from **8a**

The normal rationalization for the formation of alkylidenecyclobutenes **13-14** is a stepwise diradical or a concerted [2+2] cycloaddition.[1d, 9a, 19e, 60] However, all the three products **12-14** can also be formed *via* the common intermediate **I** (Scheme 5). Compound **12** can be formed[60] by H-migration from **I,** and the ring closure involving γ-

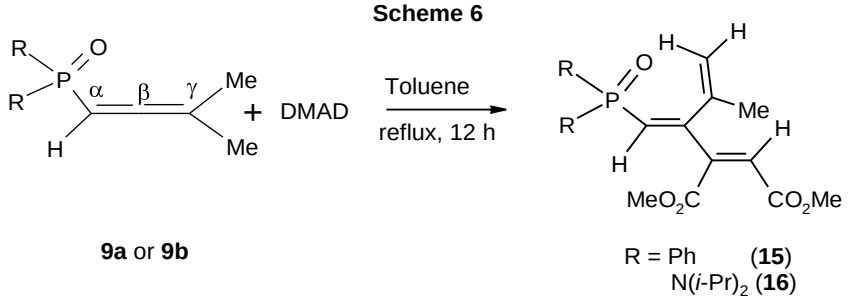
carbon leads to cyclobutene **14**. Similarly, the rotamer **II** affords product **13** by ring closure involving α-carbon.

**Scheme 5**



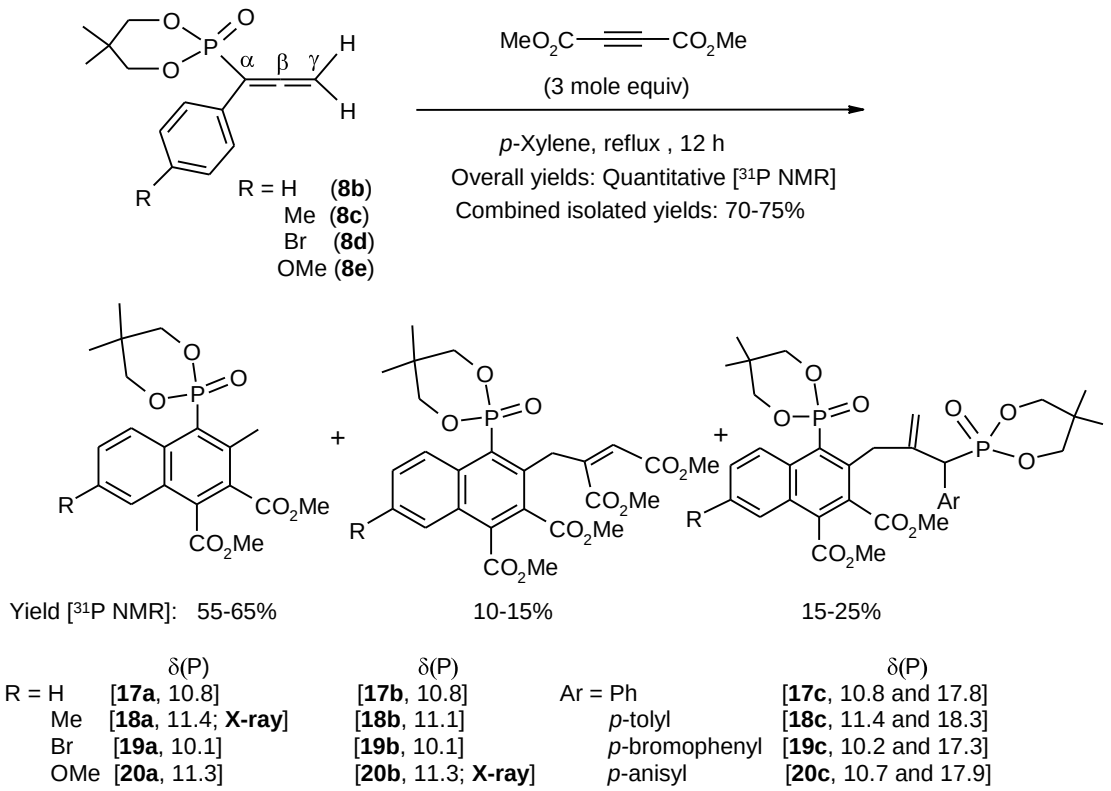

When allenylphosphine oxide **9a** or allenylphosphoramide **9b** is heated along with DMAD in toluene under reflux conditions, the ene type[61] of reaction products **15-16**, respectively, are obtained. These compounds have structures similar to compound **12** (Scheme 6).

**Scheme 6**




Allenes $(OCH_2CMe_2CH_2O)P(O)(R^1)C=C=CH_2$ [$R^1$ = Ph (**8b**), *p*-tolyl (**8c**), *p*-bromophenyl (**8d**), *p*-anisyl (**8e**)] with a terminal $=CH_2$ group behaved in a manner entirely different from that of **8a** (Scheme 8). Heating one of these allenes with DMAD in *p*-xylene under reflux conditions led to [4+2] cycloaddition products **17(a-c)-20(a-c)** (Scheme 7). Thus in each case, three distinct products are isolated.

**Scheme 7**




| | δ(P) | | δ(P) | | δ(P) |
|---|---|---|---|---|---|
| R = H | [**17a**, 10.8] | | [**17b**, 10.8] | Ar = Ph | [**17c**, 10.8 and 17.8] |
| Me | [**18a**, 11.4; **X-ray**] | | [**18b**, 11.1] | *p*-tolyl | [**18c**, 11.4 and 18.3] |
| Br | [**19a**, 10.1] | | [**19b**, 10.1] | *p*-bromophenyl | [**19c**, 10.2 and 17.3] |
| OMe | [**20a**, 11.3] | | [**20b**, 11.3; **X-ray**] | *p*-anisyl | [**20c**, 10.7 and 17.9] |

While formation of [4+2] cycloaddition compounds analogous to **17a**-**20a** has been reported recently by Ma and coworkers,[34b] the other two types of [4+2] cycloaddition products **17(b-c)-20(b-c)** are new and are formed from allene and DMAD in 1:2 and 2:1 ratios respectively. Thus the overall stoichiometry of the reaction is maintained. It is clear that if an additional C=C bond is present next to the α-carbon of the allene, [4+2] cycloaddition is the preferred reaction.

In the $^{31}$P NMR spectra, the three products show peaks at similar δ [around 11] due to the presence of aryl group attached to phosphorus; however, for compounds **17c-20c**, an additional resonance at δ ~18.0, corresponding to the second phosphonyl moiety is observed, as expected. The $^{31}$P NMR spectra of **18a-c** are shown in Figure 2. The integrated intensity of the peaks in the $^{1}$H NMR is clearly indicative of the 1:1, 1:2 and 2:1 addition for the series **17a-20a, 17b-20b** and **17c-20c**, respectively. In the $^{1}$H NMR, compounds **17a-20a** show peaks due to newly formed *methyl* group which is absent in others. For compounds **17b-20b** four methyl groups due to *carboxyl ester* [δ~3.6-4.0]

and a *methylene* group [δ~4.5] are clearly discernible in the $^{1}$H NMR; this feature proves the presence of second DMAD moiety in these molecules. For compounds **17c-20c**, four methyl signals in the range δ~0.8-1.3 due to the presence of two phosphorus containing rings are clearly visible. Also, a doublet at δ 46.4 ($^{1}J$(P-C) = 129.0 Hz) in the $^{13}$C NMR spectra clearly establishes the presence of saturated carbon attached to phosphorus (which is not present in the other compounds). These compounds also exhibit the expected resonances for P-C*H*(Ar), =C$H_2$ and C$H_2$C=CH$_2$ moieties in the $^{1}$H NMR spectra which are consistent with the assigned structures.

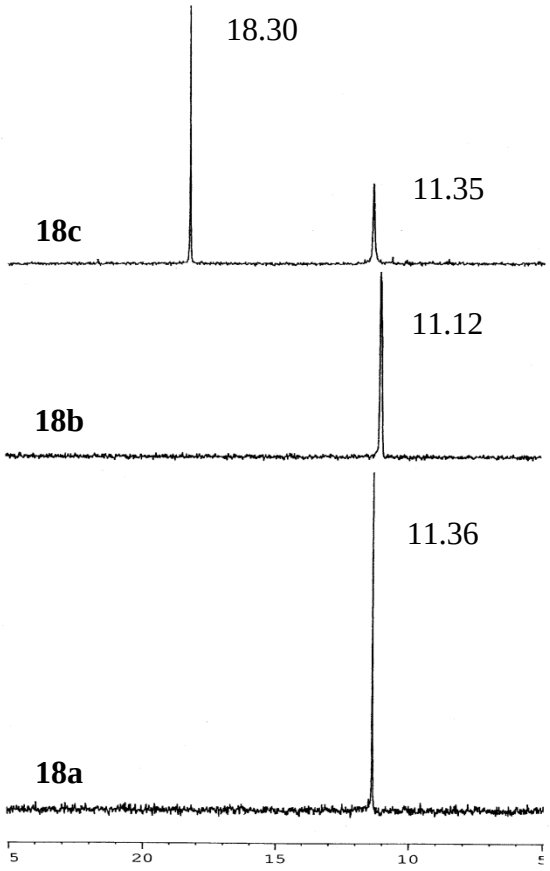



**Figure 2.** $^{31}$P NMR spectra of compounds **18a-c**

Further confirmation of the structures in the case of **18a** and **20b** has been accomplished by single crystal X-ray structures (Figure 3). Compound **20b** has *Z*-stereochemistry at the terminal [-(MeO$_2$C)C=CH(CO$_2$Me)] moiety. The atom C16 in **18a** corresponds to the additional methyl group that was alluded to in the above

discussion on NMR. The newly formed aromatic ring has the expected aromatic C-C bond distances; this is the case with the structure of **20b** also. With regard to products **17b**-**20b** and **17c**-**20c**, despite relatively low yields, given the consistency with which they are formed in all the four reactions, a possible rationale is provided in Scheme 8. Although the [4+2] cycloaddition is expected to be concerted, the aromatization step is not and hence the DMAD or the allene could react further to lead to **17b**-**20b** and **17c**-**20c**. A common intermediate in all these cases is **III**.

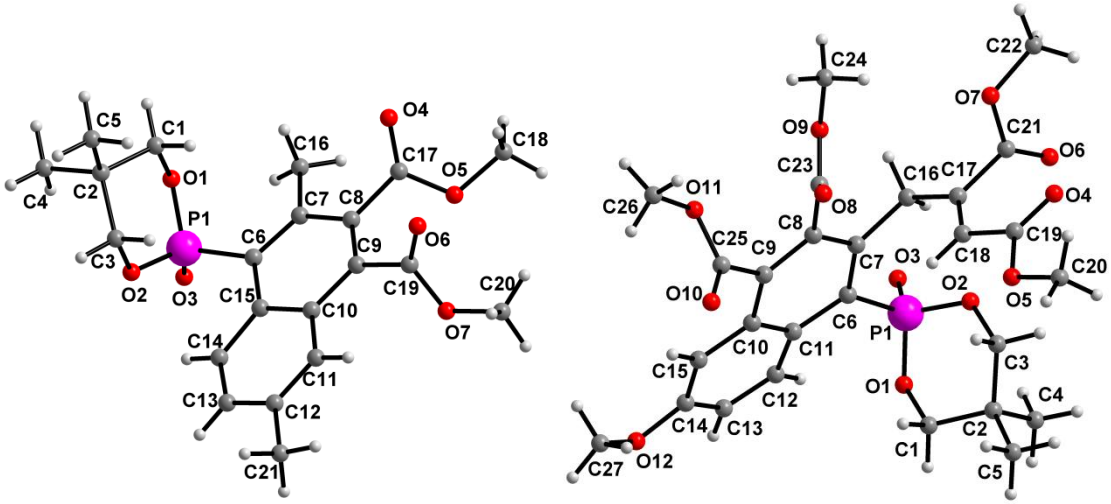
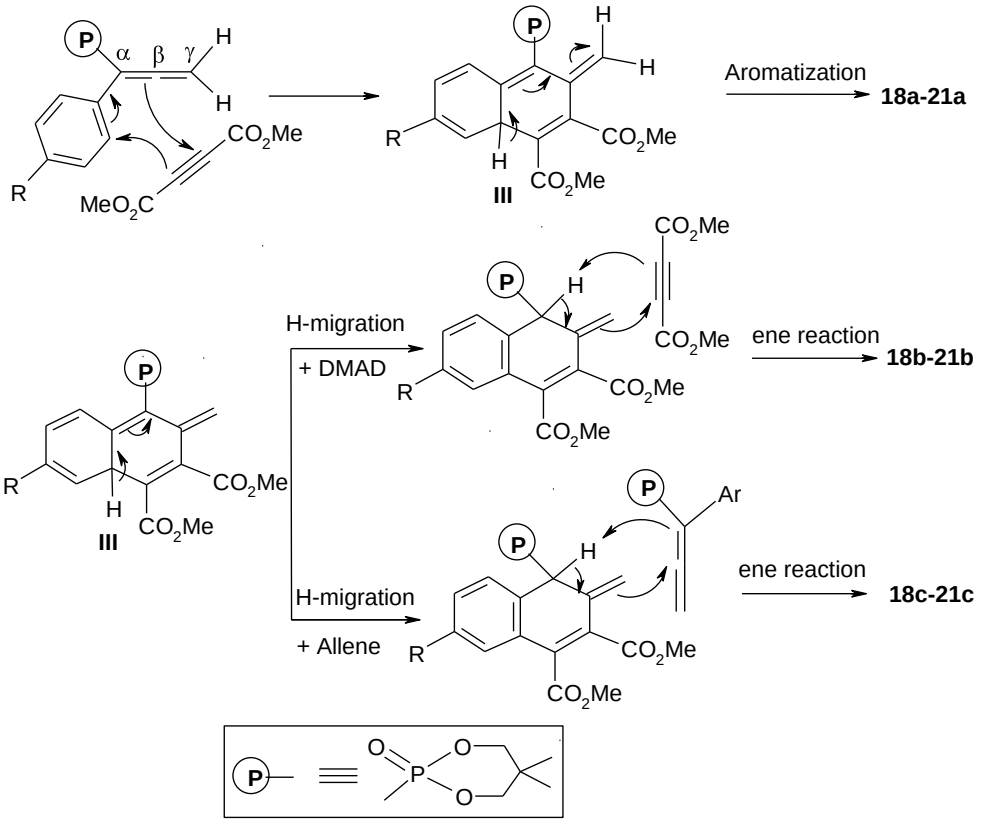


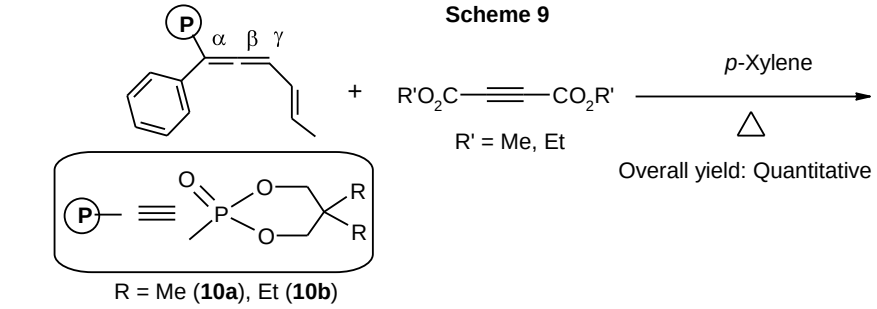

**Figure 3.** Molecular structures of compounds **18a** and **20b**.$CHCl_3$. Selected bond lengths [Å] with esd's in parentheses. **18a**: P1-C6 1.813(3), C6-C7 1.386(3), C7-C8 1.423(4), C8-C9 1.372(3), C9-C10 1.416(4), C10-C15 1.418(4), C6-C15 1.448(4), C7-C16 1.514(4). **20b**.$CHCl_3$: P1-C6 1.833(5), C6-C7 1.389(6), C7-C8 1.422(6), C8-C9 1.392(6), C9-C10 1.412(6), C10-C11 1.424(6), C6-C11 1.442(6), C7-C16 1.530(6), C16-C17 1.504(6), C17-C18 1.323(6).

**Scheme 8**

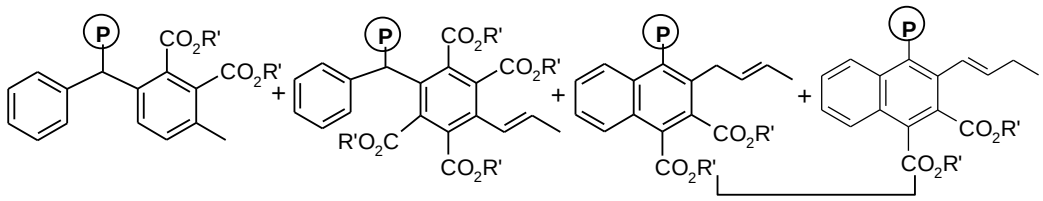



Perhaps more interesting is the reaction of the vinyl allenes **10a-b** with DMAD/DEAD using a higher molar stoichiometry of the latter reagents (Scheme 9). In 1:1 stoichiometric reaction, some unreacted allene remained. Four products are formed in each case. The $^{31}$P NMR spectrum of the reaction mixture resulting from **10a** and DMAD is shown in Figure 4. It clearly shows four new products [**21a-d**] with starting material being completely consumed. Compounds **21a** and **21b** were successfully isolated whereas **21c** and **21d** were eluted as a mixture since these compounds had close $R_f$ values to each other. Isolation of compounds in the other reaction mixtures **22(a-d)-24(a-d)** was performed in a manner similar to that for **21(a-d)**.

**Scheme 9**




R = Me (**10a**), Et (**10b**)




| | δ(P) | δ(P) | δ(P) |
|---|---|---|---|
| R = R' = Me | [**21a,** 19.0; **X-ray**] | [**21b**, 17.6; **X-ray**] | [**21(c+d)**, 9.7 and 11.1] |
| R = Me, R' = Et | [**22a**, 19.1] | [**22b**, 17.2] | [**22(c+d)**, 9.9 and 11.3] |
| R = Et, R' = Me | [**23a**, 19.9] | [**23b**, 18.3] | [**23(c+d)**, 11.0 and 12.5] |
| R = Et, R' = Et | [**24a**, 20.0] | [**24b**, 17.8] | [**24(c+d)**, 11.1 and 12.6] |

Product ratio **a:b:(c+d)** = **3: 2: 5**

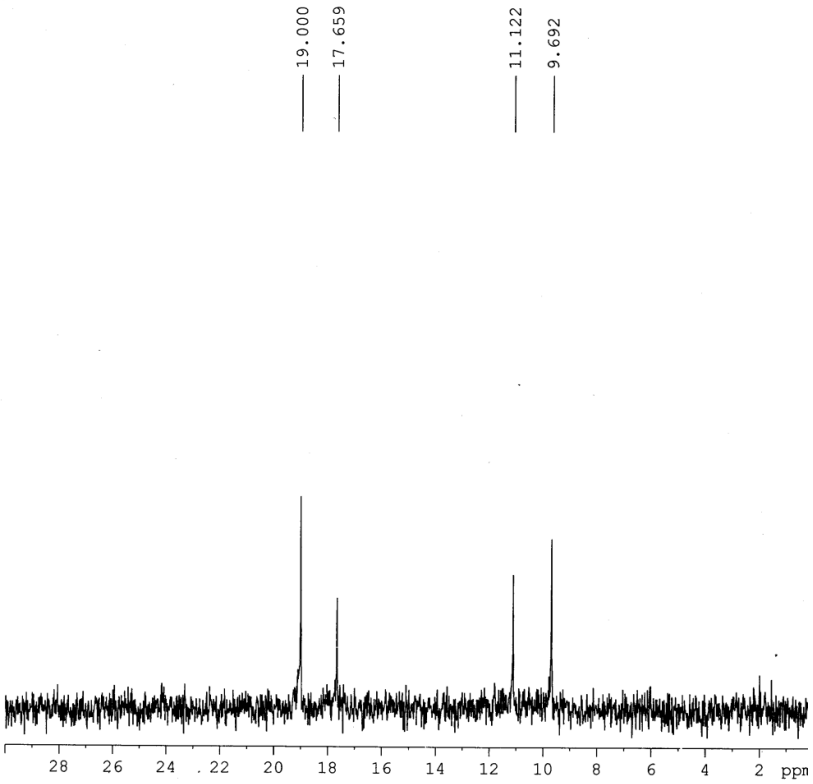
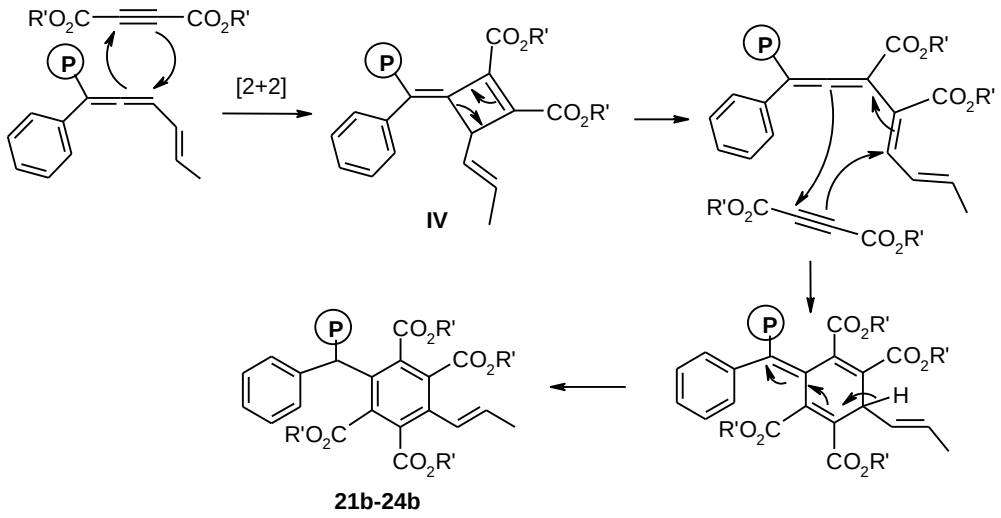



**Figure 4**. $^{31}$P NMR spectrum of the reaction mixture resulting from **10a** and DMAD

The $^{31}$P NMR spectra of compounds **21a-b** to **24a-b** show peaks in the range δ 17.0-19.0 while **21(c,d)-24(c,d)** show peaks in the range δ 9.0-12.0. Hence, by $^{31}$P NMR, **21a-b** to **24a-b** can easily be distinguished from **23(c,d)-26(c,d)**. In the $^{1}$H NMR, compounds **21a-24a** and **21b-24b** show a doublet δ~5.4 [$^{2}J$(P-H) ~ 24 Hz] due to PC*H* proton. However, the integrated intensity in the $^{1}$H NMR spectra readily facilitates the distinction between the these two sets of compounds. Compounds **21a-24a/21b-24b** [δ(C) ~43.0] are also distinguishable from **21c-24c/21d-24d** [δ(C) in aromatic region]. The isomeric pairs **21(c,d)-24(c,d)** are distinguisahble in aliphatic region in the $^{1}$H NMR.

X-ray structures for **21a-b** were determined (Figure 5). Clearly, there was competition between the vinylic end[62] and aryl group with regards to [4+2] cycloaddition. The ***unique*** disubstituted products **21b-24b** resulted from ***complete opening up*** of the C(β)=C(γ) double bond. To our knowledge, there is no precedence for such a reaction in allene chemistry. Formation of **21a-24a, 21c-24c** and **21d-24d** may be rationalized by using the pathways similar to that shown in Scheme 9. In the case of **21b-24b**, we believe that [2+2] cycloaddition happens first [cf. structure **IV** in Scheme 10] followed by cyclobutene ring cleavage and subsequent addition of a second molecule of DMAD/DEAD. It may be noted that unlike compounds **13-14**, wherein the cyclization site on the allene is either the C(α)=C(β) or C(β)=C(γ) double bond, the formation of **21b-24b** involves only the C(β)=C(γ) double bond. Use of $^{31}$P NMR spectroscopy in conjunction with chromatography during the course of this reaction was essential to identify and separate the products.

**Scheme 10**



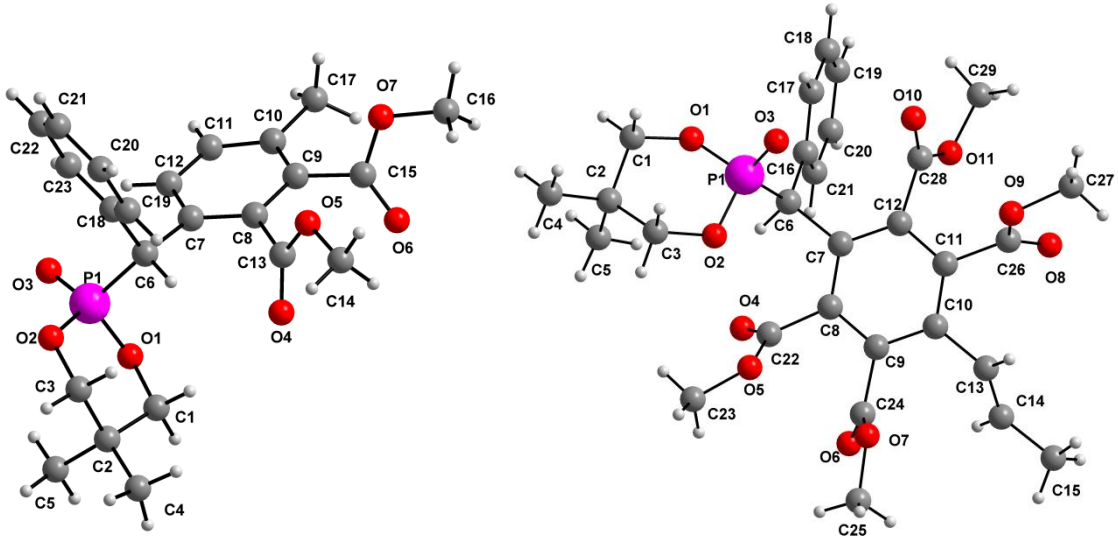
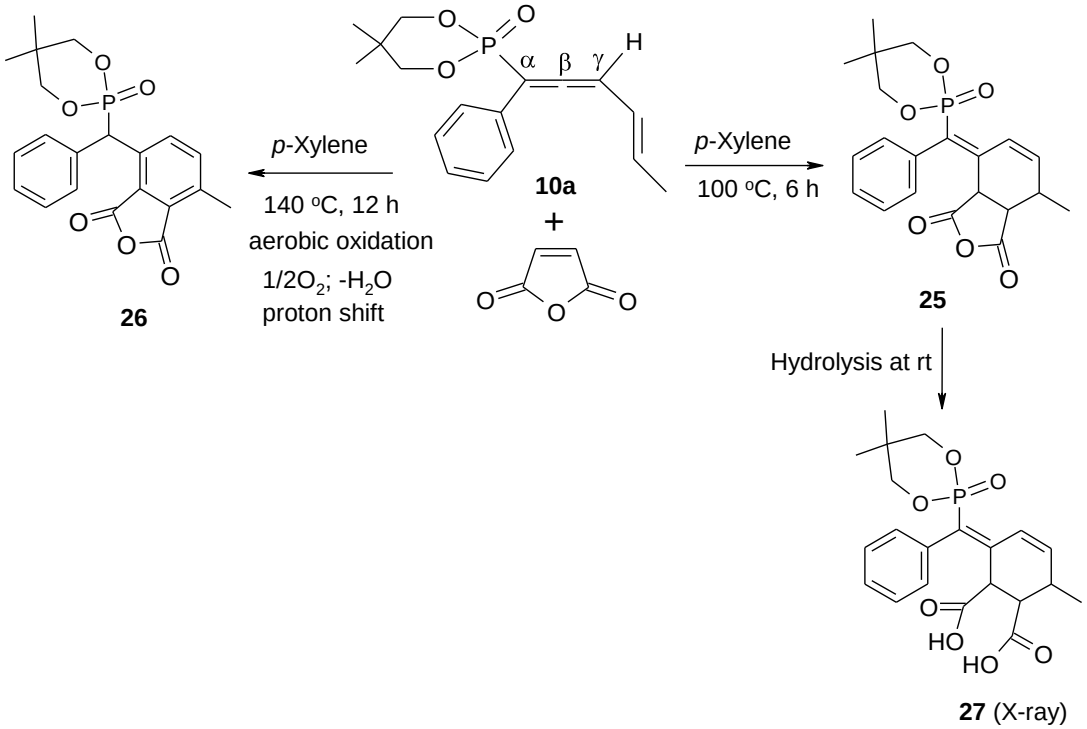




**Figure 5.** Molecular structures of **21a** and **21b**.$H_2O$ (solvent molecule is omitted). Selected bond lengths [Å] with estimated standard deviations are given in parentheses. **21a**: P1-C6 1.818(3), C6-C7 1.530(4). **21b.**$H_2O$: P1-C6 1.813(2), C6-C13 1.532(3).

Delighted by the above results, we have extended our investigation to the cycloaddition of vinyl allene **10a** with maleic anhydride at 100 $^oC$. A [4+2] cycloadduct **25** (Scheme 11) was observed due to the reaction at the vinylic end. Compound **25** was characterized by NMR, mass and elemental analysis. In addition to the additional CH moieties contributed by maleic anhydride, the up-field shift in the δ value for the CH(Me) group in the $^1H$ NMR spectrum is consistent with the assigned structure. When

the reaction was performed at elevated temperature (140 $^{o}$C), cycloadduct **26** was formed presumably by initial formation of **25** followed by the aerobic oxidation[63] to attain aromatization. In our attempt to effect crystallization from dichloromethane-hexane (1:1) solution, the maleic anhydride part of compound **25** was hydrolyzed to **27**.

**Scheme 11**




In the $^{31}$P NMR, compounds **25** [δ 8.9] and **26 [**δ 16.7] are clearly distinguishable. They also show recognizable P-*C* signals in the $^{13}$C NMR [**25:** δ 129.9, $^{1}J$(P-C) = 172.4 Hz; **26:** δ 41.2 ($^{1}J$(P-C) = 133.4 Hz] due to P-*C*. For compound **26**, $^{1}$H NMR shows a doublet at δ 6.01 ($^{2}J$(P-H) = 22.0 Hz) establishing the presence of PC*H* moiety. Finally, single crystal X-ray data on **27** (the hydrolysis product of **25**) (Figure 6) clearly establishes the identity of **25**. Since this product **27** is not very soluble, and only a few crystals are obtained, we have not recorded spectroscopic data for it.

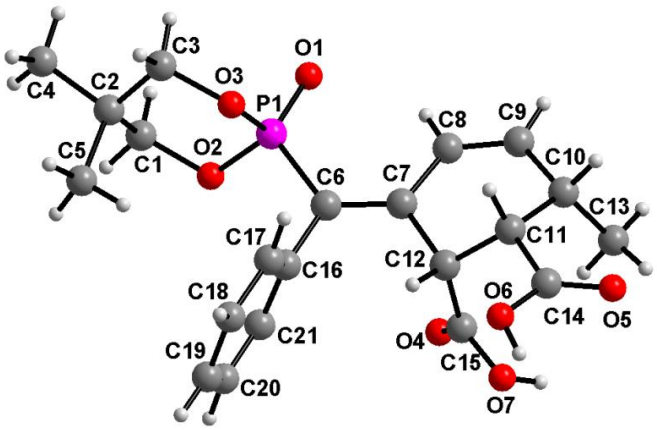
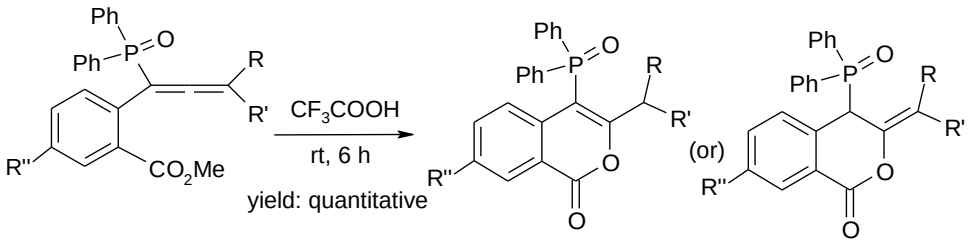



**Figure 6.** Molecular structure of **27**.$CH_2Cl_2$ (solvent molecule is omitted for clarity). Selected bond lengths [Å] with estimated standard deviations are given in parentheses: C7-C8 1.457(18), C9-C8 1.32(2), C9-C10 1.528(17), C11-C10 1.523(19), C11-C12 1.543(17) and C7-C12 1.543(15).

## 5.4 Cyclization reactions of functionalized allenylphosphine oxides

In continuation of our studies on the synthesis of cyclization products by intermolecular addition in the earlier part of this chapter, we became interested in the systems involving heteroatoms that could lead to phosphono/ phosphinoyl heterocycles.[7, 37, 50-51] Thus we treated the functionalized allene precursors **11a-h**, that are tethered with methyl ester group, with an excess of trifluoroacetic acid at rt (25 $^{o}$C). Gratifyingly, they readily led to the phosphinoyl isocoumarins **28-35** (Scheme 12) in quantitative yields.

**Scheme 12**




**11a-h**

(**28**) R = R' = H, R'' = H (X-ray)
(**29**) R = H, R' = Me, R'' = H
(**30**) (RR') = -$(CH_2)_5$-, R'' = H
(**31**) R = R' = H, R'' = Br
(**32**) R = H, R' = Me, R'' = Br
(**33**) R = R' = Me, R'' = H
(**34**) (RR') = -$(CH_2)_5$-, R'' = Br
(**35**) R = R' = Me, R'' = Br

Compounds **33-35** show a doublet in the $^{1}$H NMR spectra at δ~4.78 ($^{2}J$(P-H) = 18.0 Hz) due to the presence of PC*H* which is absent in compounds **28-32**. Also, in the $^{13}$C NMR, compounds **28-32** show doublet at δ~105.0 ($^{1}J$(P-C) = 105.2 Hz) due to presence of P-*C* while compounds **33-35** show doublet at δ~45.5 ($^{1}J$(P-C) = 57.5 Hz) proving the presence of P*C*H. The difference in the value of $^{1}J$(P-C) is consistent with the hybridization at the corresponding α-carbon in the corresponding compounds as explained earlier. Finally, X-ray structure was determined for **28** (Figure 7).

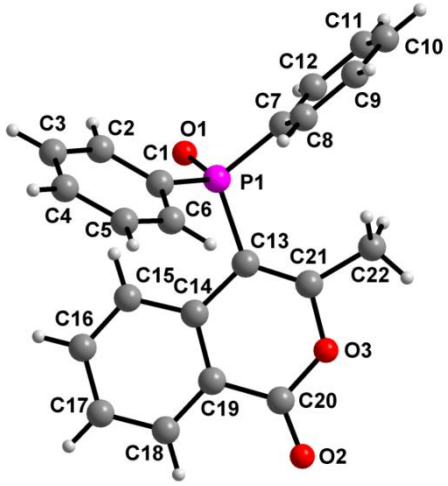
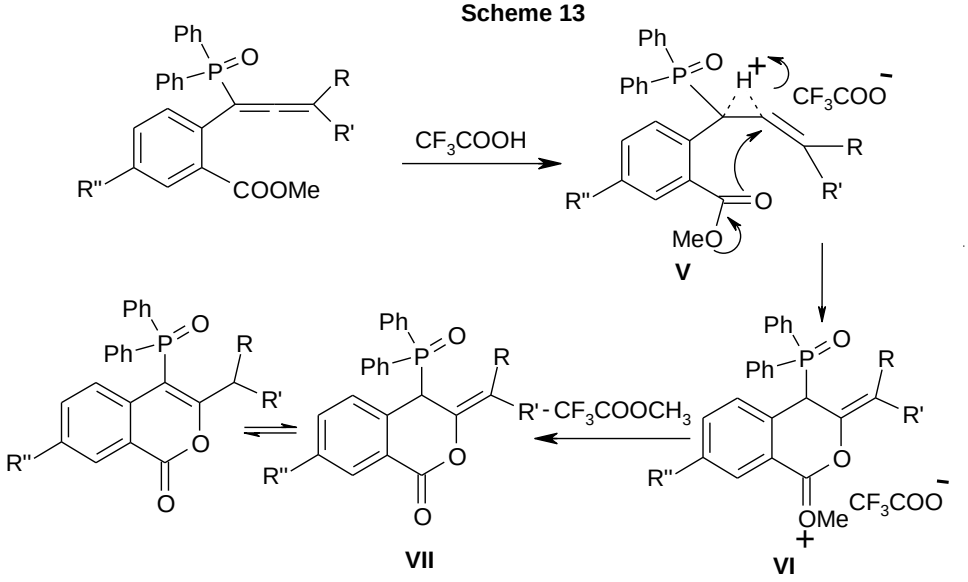



**Figure 7.** Molecular structure of **28**. Selected bond lengths [Å] with estimated standard deviations are given in parentheses: O3-C21 1.386(2), C21-C22 1.486(3).

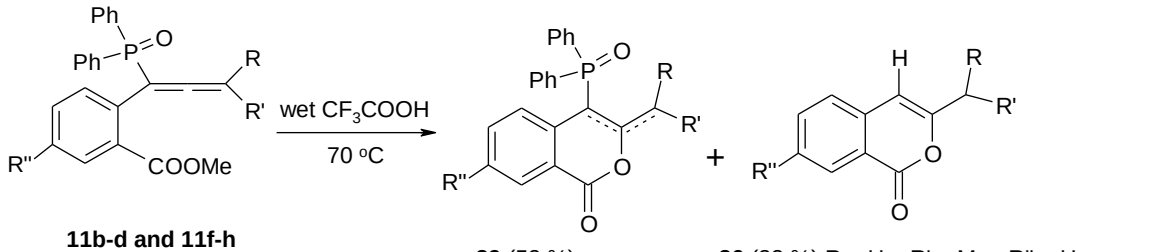
The above reaction is believed to proceed by the initial interaction of $H^{+}$ with α,β-allenic double bond to lead to **V** (Scheme 13) which on subsequent attack of oxygen of ester group onto the β-position of allene forms **VI**. Intermediate **VI** on demethylation leads to phosphinoyl isocoumarin **VII**. This product **VII** further involves the double bond isomerization to lead to phosphinoyl isocoumarins **28-32**. The isomerization is not observed in the case of **33-35**. Alternatively, perhaps the cyclization proceeds by the hydrolysis of ester group due to the presence of moisture in trifluoroacetic acid.

**Scheme 13**




When the above reaction was performed in wet trifluoroacetic acid (TFA:$H_2O$=20:1) under reflux conditions (70 $^oC$), phosphinoyl-isocoumarins were formed in all the cases, but additionally, simple isocoumarins **36-41** (Scheme 14)[64] are also formed in the case of terminal substituted allenes.

**Scheme 14**



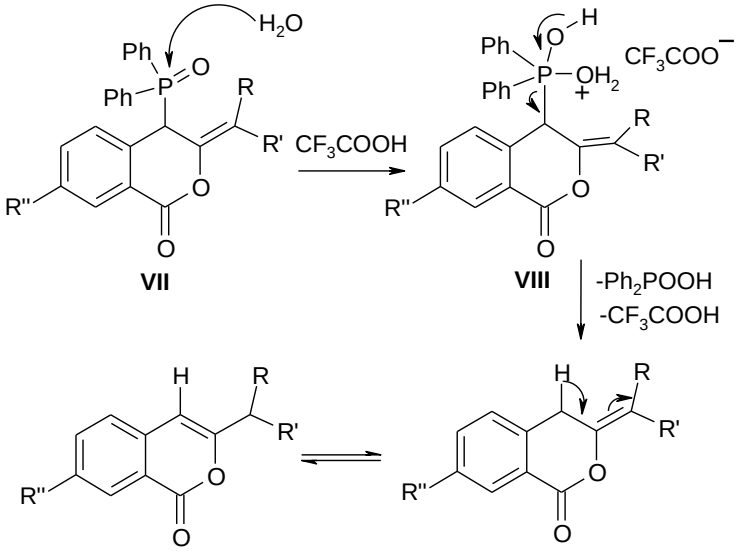

**11b-d and 11f-h**

| | | |
|---|---|---|
| **29** (52 %) | + | **36** (32 %) R = H, R' = Me, R'' = H |
| **30** (49 %) | + | **37** (38 %) (RR') = -$(CH_2)_5$-, R'' = H |
| **32** (50 %) | + | **38** (38 %, X-ray) R = H, R' = Me, R'' = Br |
| **33** (46 %) | + | **39** (41 %) R = Me, R' = Me, R'' = H |
| **34** (45 %) | + | **40** (42 %) (RR') = -$(CH_2)_5$-, R'' = Br |
| **35** (55 %) | + | **41** (35 %) R = Me, R' = Me, R'' = Br |

In the $^1H$ NMR spectra, compounds **36-41** show a singlet at δ~6.20 due to newly formed alkenyl C*H*. In the $^{13}C$ NMR, peak at δ~101.0 is clearly seen due to alkenyl C*H* which is not observed in phosphinoyl-isocoumarins **28-35**. We have also determined the X-ray structure of compound **38** (Figure 8) for final confirmation.

Formation of the phosphorus-free isocoumarins **36-41** can be explained by the pathway depicted in Scheme 15. At first, the allenylphosphine oxide having methyl ester group, with the aid of TFA, gives phosphinoyl isocoumarin **VII**. The phosphinoyl-isocoumarin gets protonated on P=O bond followed by attack of $H_2O$ molecule to form the intermediate **VIII**. The phosphorus moiety of **VIII** is then cleaved as $Ph_2POOH$ to form the phosphorus-free isocoumarins.

**Scheme 15**



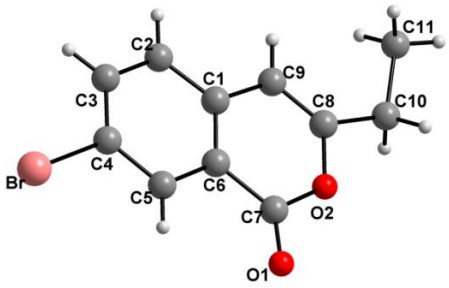
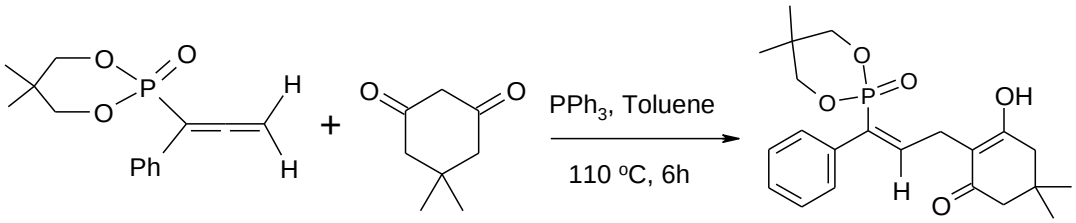




**Figure 8.** Molecular structure of **38**. Selected bond lengths [Å] with estimated standard deviations are given in parentheses: O2-C8 1.377(6), C8-C10 1.492(6).

In contrast to what has been discussed above, phosphine catalyzed nucleophilic addition on allenes would also be an interesting protocol to synthesize diverse functionalized molecules.[65] In many cases, 'umpolung' addition is expected to take

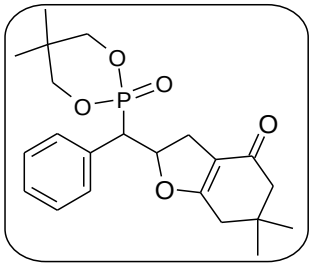
place.[66] As a preliminary study, the phosphorylated allene **8b** was treated with dimedone in the presence of triphenylphosphine in toluene at 110 $^{o}$C. The reaction was expected to lead to a dihydrofuran derivative **42'** but only the product **42** was obtained (Scheme 16). This product was formed by umpolung addition of dimedone to allene at γ-position of allene to form a new C-C bond and the further intramolecular conjugate addition did not occur. It must be noted here that normal nucleophilic addition on allenes take place at the β-carbon of the allene[7a, 44, 49] and hence the present result adds a new facet to the diverse chemistry of allenes.

**Scheme 16**




**8b**

**42** (64 %, X-ray)




**42'** (Not formed)

In the $^{31}$P NMR, compound **42** shows a peak at δ 14.8; in the $^{1}$H NMR a doublet of triplet is observed at δ 6.55 ($^{3}J$(P-H) = 50.0 Hz, $^{3}J$(H-H) = 9.0 Hz) due to the presence of PC=C*H*. The large $^{3}J$(P-H) value is consistent with the *trans* disposition of the proton with respect to the phosphorus.[37] In addition to these, the structure of **42** was confirmed by X-ray crystallography (Figure 9).

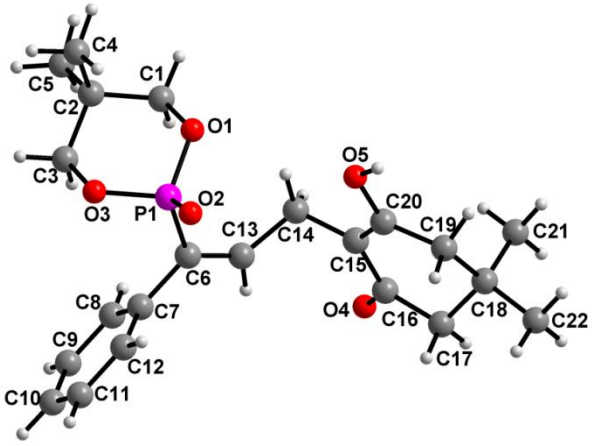
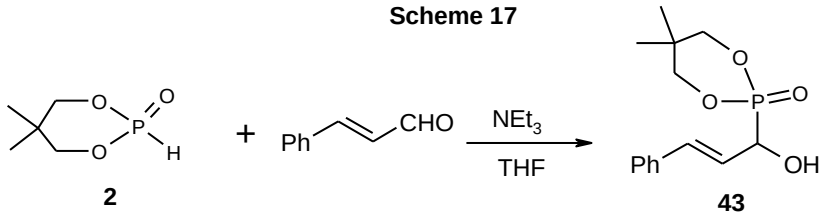



**Figure 9.** Molecular structure of **42**. Selected bond lengths [Å] with estimated standard deviations are given in parentheses: C14-C13 1.499(3), C14-C15 1.508(3).

## 5.5 Nucleophilic substitution of phosphono-allylic alcohols with functionalized arenes:

Nucleophilic substitution of allyl alcohols has been proved as an efficient route to construct new C-C and C-X bonds and hence it is of enormous significance in organic synthesis.[67] Phosphono-allylic alcohols resemble simple allylic alcohols and can undergo nucleophilic substitution. For this purpose, we synthesized phosphono-allylic alcohol, by the addition of H-phosphonate **2** to cinnamaldehyde to get **43** (Scheme 17).[54]

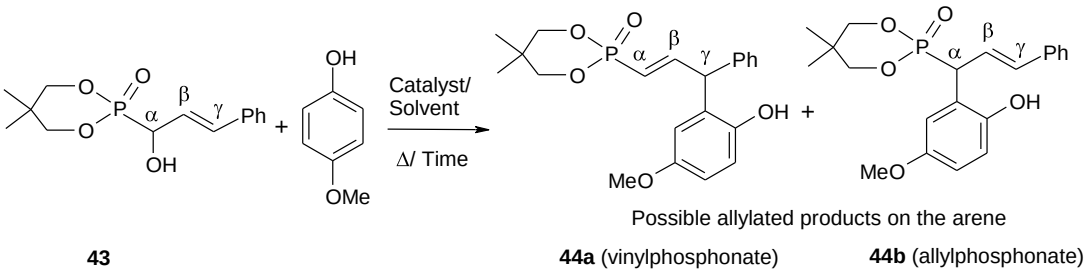
**Scheme 17**




We envisioned that electron rich functionalized arenes could undergo the nucleophilic substitution fairly well in Freidel-Crafts allylic alkylation of arenes[68] and hence started probing with 4-methoxyphenol in the presence of $FeCl_3$. Two products are possible: one with γ-carbon of the phosphonate attached to the arene leading to vinylphosphonate **44a** and the other with α-carbon of the phosphonate attached to the arene leading to allylphosphonate **44b** (Scheme 18). Phosphono-allyl alcohol **43** was

stirred in nitromethane with 10 mol % $FeCl_3$ at 70 $^oC$; after 6 h, the starting material was completely consumed. The crude product showed a major peak in the $^{31}P$ NMR at δ 15.7 corresponding to the allylated product (vinylphosphonate) **44a** which was isolated in good yield (84%). This product is formed by an 'umpolung' type of substitution with complete regioselectivity. Delighted by this result, we then checked with different catalysts and solvents for the optimization of the product **44a**. The performance of other catalysts was poor in this reaction and the details are shown in Table 1.

**Scheme 18**




**43** **44a** (vinylphosphonate) **44b** (allylphosphonate)

**Table 1**. Effect of catalyst/ solvent in the optimization of **44a** in the allylation of the arene.

| Entry | Catalyst (10 mol %) | Solvent | Temp ($^oC$)[a]/ Time (h) | Yield[b] (%) |
|---|---|---|---|---|
| 1 | $FeCl_3$ | $CH_3NO_2$ | 80/ 6 | 84 |
| 2 | $Sc(OTf)_3$ | $CH_3NO_2$ | 80/ 12 | 0[c] |
| 3 | $TiCl_4$ | $CH_3NO_2$ | 80/ 12 | 0[c] |
| 4 | $InCl_3$ | $CH_3NO_2$ | 80/ 12 | 0[c] |
| 5 | $BF_3.Et_2O$ | $CH_3NO_2$ | 80/ 12 | 0[c] |
| 6 | $AuCl_3$ | $CH_3NO_2$ | 80/ 12 | Trace[c] |
| 7 | $FeCl_3$ | DCE | 80/ 12 | 65[c] |
| 8 | $FeCl_3$ | THF | 80/ 12 | 0[c] |
| 9 | $FeCl_3$ | Dioxane | 80/ 12 | 80[c] |

[a] Oil bath temperature

[b] Yield of the isolated products

[c] Starting material remained

To ascertain the effectiveness of the catalytic system ($FeCl_3$/ nitromethane) in allylation on arenes, various substrates were used. In all the cases, the starting material **43** had completely reacted ($^{31}P$ NMR evidence). In most cases, vinylphosphonates **44a-51a** with regioselectivity on arene, were formed (Table 2). In the case of reactions using 2,6-dimethylphenol and 2'-hydroxy benzophenone that lead to vinylphosphonates **50a-51a**, allylphosphonates **50b** and **51b** (entries 7 and 8) were also formed and isolated successfully. The $^{31}P$ NMR spectrum of the reaction mixture resulting from 2,6-dimethylphenol is shown in Figure 10. Allylphosphonates **52b** and **53b** were only isolated due to the close $R_f$ values in the case of salicylaldehyde and 2'-hydroxy-acetophenone albeit other isomers (vinyl phosphonates **52a** and **53a**) were also formed [$^{31}P$ NMR evidence].

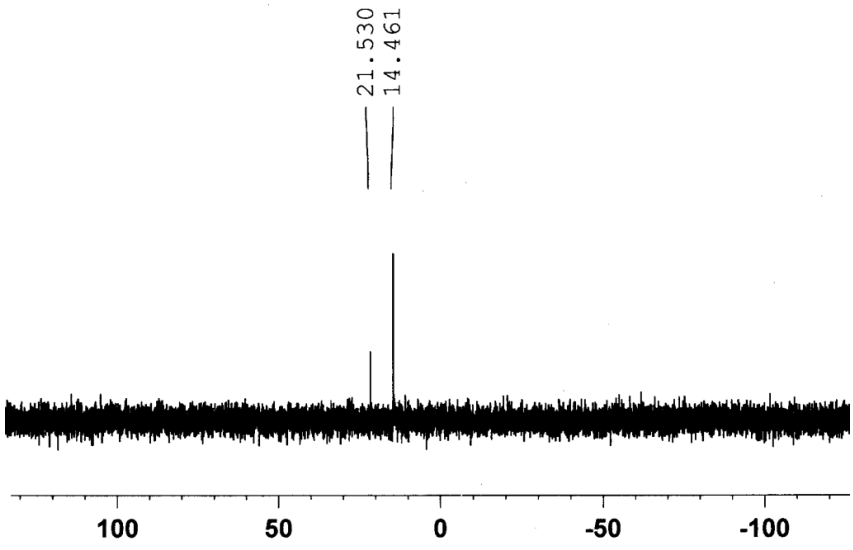
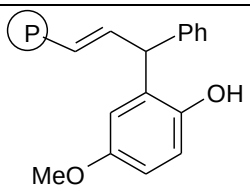
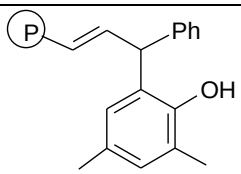
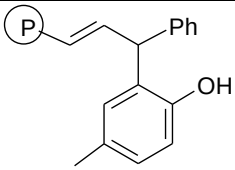
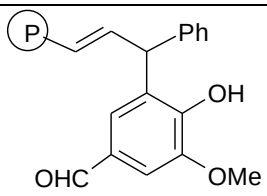
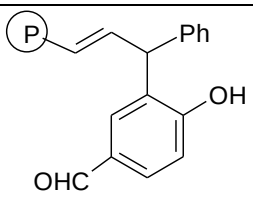
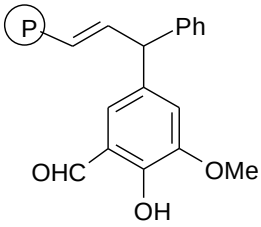
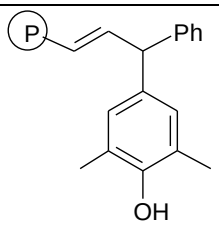
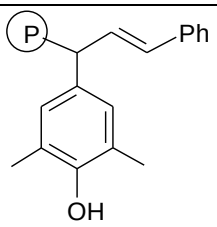
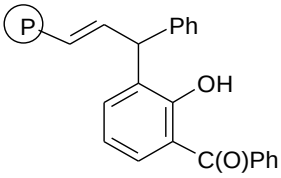
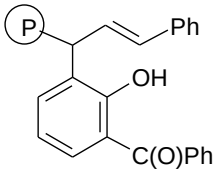
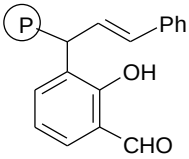
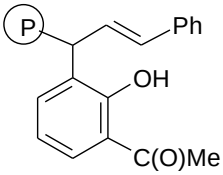
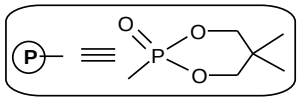



**Figure 10**: $^{31}P$ NMR spectrum of the reaction mixture resulting from 2,6-dimethylphenol and **43**

**Table 2**: Details on allylation of arenes using $FeCl_3$

| Entry | Arene | Vinylphosphonate[a]/ Yield[b] | Allylphosphonate[a]/ Yield[b] |
|---|---|---|---|
| 1 | 4-Methoxyphenol |  **44a**/ 85% | Not observed |
| 2 | 2,4-Dimethylphenol |  **45a**/ 92% | Not observed |
| 3 | *p*-Cresol |  **46a**/ 90% | Not observed |
| 4 | Vanillin |  **47a**/ 90% | Not observed |
| 5 | 4-Hydroxy benzaldehyde |  **48a**/ 84% | Not observed |
| 6 | *o*-Vanillin |  | Formed but not isolated |

| | | | |
|---|---|---|---|
| | | **49a** (X-ray)/ 30% | |
| 7 | 2,6-Dimethylphenol |  **50a**(X-ray)/ 70% |  **50b**/ 22% |
| 8 | 2'-Hydroxy benzophenone |  **51a**/ 15% |  **51b**/ 75% |
| 9 | Salicylaldehyde | Formed but not isolated[c] |  **52b**/ 30% |
| 10 | 2'-Hydroxy acetophenone | Formed but not isolated[c] |  **53b**/ 66% |

a 

[b] Yields of isolated products.

[c] In these cases both the products were formed but we could isolate only one of them in pure form.

In the $^{1}$H NMR, the vinylphosphonates **44a-51a** show dd→triplet for the PC*H*=CH proton [e.g., **50a**: δ 5.58, $^{2}J$(P-H) ~ $^{3}J$(H-H) ~ 19.0 Hz]. For the allylphosphonates a clear doublet of doublets (dd) is seen for the PC*H* proton [e.g., **50b**: δ 3.99 $^{2}J$(P-H) = 24.4 Hz, $^{3}J$(H-H) = 8.0 Hz]. Also the P-*C* carbons are clearly distinguishable in the two types of compounds [e.g., **50a**: δ 116.2, $^{1}J$(P-C) = 186.0 Hz;

**50b**: δ 47.2, $^{1}J$(P-C) = 134.5 Hz]. All these compounds were further characterized by mass spectra and/or elemental analyses. Structures of **49a** and **50a** were confirmed by single crystal X-ray crystallography (Figure 11). The C6-C7 distance in both the compounds is of olefinic type, as expected.

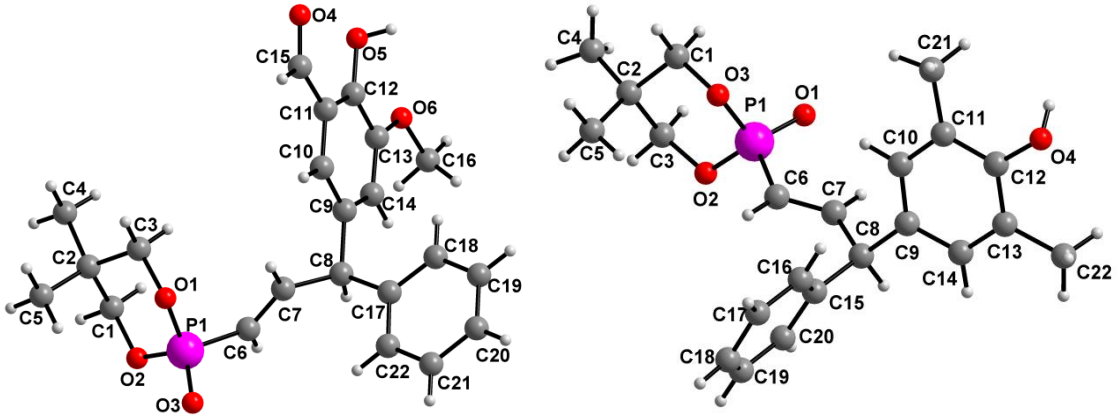



**Figure 11**. Molecular structures of **49a** and **50a.1/2$C_6H_6$** (Solvent molecule is omitted). Selected bond lengths [Å] with estimated standard deviations are given in parentheses. **49a**: C6-C7 1.305(4), C7-C8 1.504(4), C8-C9 1.524(4). **50a.1/2$C_6H_6$**: C7-C6 1.318(9), C8-C7 1.493(9), C9-C8 1.501(8).

Thus the results of this section demonstrate that Friedel-Crafts reaction of arenes by α-hydroxy phosphonates affords vinylphosphonates, but in a few cases allylphosphonates are also obtained.

# SUMMARY – PART B

1) Allenylphosphonate $(OCH_2CMe_2CH_2O)P(O)CH=C=CMe_2$ upon reacting with dimethylacetylene dicarboxylate (DMAD) leads to primarily three products: a phosphono-triene and two distinct phosphono-cyclobutenes *via* [2+2] cycloaddition. Such a reactivity has not been reported before. α-Aryl substituted allenes $(OCH_2CMe_2CH_2O)P(O)C(Ar)=C=CH_2$ also afford three distinct products but the reactivity is entirely *different*; these are 1:1, 1:2 and 2:1 products derived from the [4+2] cycloaddition. Phosphono-vinylallenes $(OCH_2CMe_2CH_2O)P(O)C(Ph)=C=CH(CH=CHMe)$ also form [4+2] cycloadducts but the reaction occurs either at vinylic or at phenyl end. More interestingly, a novel [2+2+2] cycloaddition is also observed.
2) Allenylphosphine oxides tethered with methyl ester group undergo cyclization in the presence of trifluoroacetic acid to lead to phosphinoyl isocoumarins. The same reaction in wet TFA under reflux leads to phosphinoyl isocoumarins along with phosphorus-free isocoumarins which is formed by the hydrolysis of P-C bond.
3) Nucleophilic substitution of phosphono-allyl alcohols with electron rich functionalized arenes is successfully achieved. Catalytic $FeCl_3$ in nitromethane is effective for this reacttion. In all the cases vinylphosphonates are formed and in a few cases allylphosphonates are also obtained. Regioselectivity is also observed with respect to arene substrates in all the examples studied in this work.

# EXPERIMENTAL SECTION

Details of instruments, standards etc. are already given in Chapter 3.

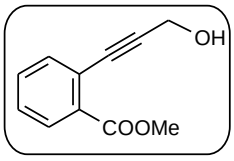
The $P^{III}$-Cl precursors ($OCH_2CR_2CH_2O$)PCl [R = Me (**1a**),[52a] Et (**1b**)[52b]], [(*i*-Pr)$_2$N]$_2$PCl (**1d**)[52c] and H-phosphonate ($OCH_2CMe_2CH_2O$)P(O)H (**2**)[53] were prepared by well-known methods. Chlorodiphenylphosphine ($Ph_2PCl$, **1c**), procured from Aldrich, was distilled prior to use. 2-Iodo-methylbenzoate (**3**)[54a] and 5-bromo-2-iodo-methylbenzoate (**4**)[54b] were prepared by esterification of the corresponding carboxylic acid with methanol.

## 6.1 Preparation of propargylic precursors 5, 6 and 7a-h

Propargyl alcohol **5** was prepared *via* Grignard reaction of phenyl acetylene and crotonaldehyde.[55] Propargylic precursors **6** and **7a-h** were synthesized by Sonogashira reaction of aryl halides with appropriate terminal propargyl alcohols by following a literature procedure.[56] Among these propargyl alcohols, **7c** and **7e-h** are new. General procedure for the synthesis of these compounds is given below.

### *6.11 Synthesis of propargylic alcohols 7a-h via Sonogashira reaction*

***Compound 7a***

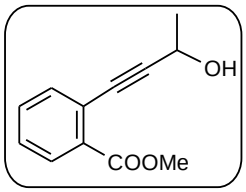



This compound was prepared by following a literature procedure.[56] To a stirred solution of aryl iodide (2.62 g, 10 mmol), $PdCl_2$ (0.018 g, 0.1 mmol), $PPh_3$ (0.053 g, 0.2 mmol) and CuI (0.039 g, 0.2 mmol) in triethylamine (15 mL) was added propargyl alcohol (1.07 g, 20 mmol) at rt (25 $^oC$). The contents were stirred at reflux for 10 h. After all the starting material was consumed (tlc), the reaction mixture was filtered and the solvent removed by vacuum. The product was purified by column chromatography using silica gel with ethyl acetate/ hexane mixture (1:4) as the eluent.

Yield: 1.67 g (88 %).

The spectral data are in accordance with the literature report.[69]

***Compound 7b***

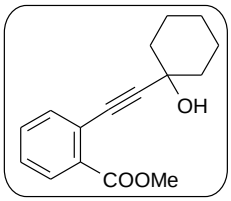



This compound was synthesized by using a procedure similar to that for **7a** by using same molar quantities.

Yield: 1.65 g (81 %).

The spectral data are in accordance with the literature report.[70]

***Compound 7c***




This compound was synthesized by using a procedure similar to that for **7a** by using same molar quantities.

Yield: 2.17 g (84%, gummy liquid).

IR (neat): 2932, 2857, 1730, 1717, 1447, 1254, 1134, 1082, 965, 758 $cm^{-1}$.

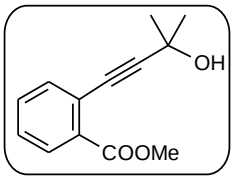
$^1H$ NMR: δ 1.55-2.06 (m, 10H, cyclohexyl-*H*), 3.42 (br s, 1H, C-O*H*), 3.87 (s, 3H, COOC$H_3$), 7.31-7.89 (m, 4H, Ar*H*).

$^{13}C$ NMR: δ 23.4, 25.3 and 39.9 (cyclohexyl-*C*), 52.2 (COO*C*$H_3$), 69.1 (*C*-OH), 82.8 and 98.4 (*C*≡*C*), 123.5, 127.8, 130.3, 131.6, 131.8 and 134.2 (Ar-*C*), 166.8 (*C*=O).

LC/MS: *m/z* 259 $[M+1]^+$.

Anal.Calcd. for $C_{16}H_{18}O_3$: C, 74.39; H, 7.02. Found: C, 74.61; H, 6.93.

***Compound 7d***

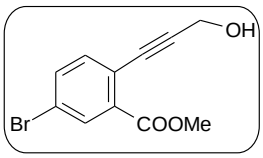


This compound was synthesized by using a procedure similar to that for **7a** by using same molar quantities.

Yield: 2.00 g (92%).

The spectral data are in accordance with the literature report.[70]

***Compound 7e***




This compound was synthesized by using a procedure similar to that for **7a** by using 5-bromo-2-iodo-methylbenzoate (1.70 g, 5 mmol) and propargyl alcohol (1.10 mol equiv).

Yield: 1.05 g (78%, low melting solid).

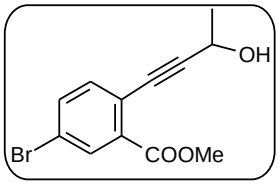
IR (neat): 3472, 3013, 1721, 1582, 1472, 1431, 1358, 1296, 1248, 1092, 1033, 965, 841, 785, 754, 542 $cm^{-1}$.

$^{1}H$ NMR: δ 3.91 (s, 3H, COOC$H_3$), 4.53 (s, 2H, C$H_2$OH), 7.37-8.06 (m, 3H, Ar*H*).

$^{13}C$ NMR: δ 51.7 (*C*$H_2$OH), 52.6 (COO*C*$H_3$), 83.3 and 94.1 (*C*≡*C*), 122.1, 122.3, 133.1, 133.4, 135.0 and 135.4 (Ar-*C*), 165.2 (*C*=O).

HRMS (ESI): Calcd. for $C_{11}H_9NaBrO_3$ [$M^+$+Na]: *m/z* 290.9629. Found: 290.9629 and 292.9602.

***Compound 7f***




This compound was synthesized by using a procedure similar to that for **7e** by using 5-bromo-2-iodo-methylbenzoate (1.70 g, 5 mmol) and but-3-yn-2-ol (1.10 mol equiv).

Yield: 1.20 g (85%, gummy liquid).

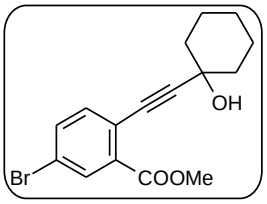
IR (neat): 3445, 2982, 2951, 1728, 1717, 1584, 1551, 1478, 1435, 1395, 1291, 1242, 1096, 1034, 968, 864, 830, 787, 745 $cm^{-1}$.

$^{1}H$ NMR: δ 1.58 (d, 3H, $^{3}J$(H-H) = 4.0 Hz, $CH_2CH_3$), 2.05 (s, 1H, CHO*H*), 3.93 (s, 3H, COOC$H_3$), 4.79 (qrt, 1H, $CH_3CH$OH), 7.38-8.08 (m, 3H, Ar*H*).

$^{13}$C NMR: δ 24.0 (s, *C*H$_3$CH), 52.5 (s, COO*C*H$_3$), 58.8 (s, CH$_3$*C*HOH), 81.7 and 97.6 (2 s, Ar*CC*CH), 122.0, 122.3, 133.2, 133.4, 134.8, 135.3 (Ar-*C*), 165.3 (s, *C*=O).

HRMS (ESI): Calcd. for $C_{12}H_{11}NaBrO_3$ [$M^+$+Na]: *m/z* 304.9790. Found: 304.9793 and 306.9790.

***Compound 7g***




This compound was synthesized by a procedure similar to that for **7e** by using 5-bromo-2-iodo-methylbenzoate (1.70 g, 5 mmol) and 1-ethynyl-cyclohexanol (1.10 mol equiv).

Yield: 1.35 g (80%, gummy liquid).

IR (neat): 3446, 3063, 2931, 2855, 2214, 1726, 1485, 1436, 1288, 1238, 1074, 970, 784 cm$^{-1}$.

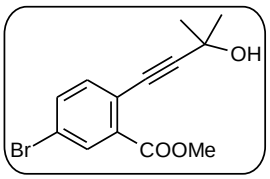
$^1$H NMR: δ 1.28-2.03 (m, 10H, cyclohexyl-*H*), 3.05 (br s, 1H, C-O*H*), 3.90 (s, 3H, COOC*H*$_3$), 7.34-8.05 (m, 3H, Ar-*H*).

$^{13}$C NMR: δ 23.3, 25.5 and 39.8 (cyclohexyl-*C*), 52.5 (COO*C*H$_3$), 69.2 (*C*-OH), 82.0 and 99.6 (*C*≡*C*), 121.7, 122.4, 133.3, 134.7, 135.4 (Ar-*C*), 165.4 (*C*=O).

LC/MS: *m/z* 338 [M+1]$^+$.

Anal.Calcd. for $C_{16}H_{17}BrO_3$: C, 56.99; H, 5.08. Found: C, 56.85; H, 5.19.

***Compound 7h***




This compound was synthesized by using a procedure similar to that for **7e** by using 5-bromo-2-iodo-methylbenzoate (1.70 g, 5 mmol) and 2-methyl-but-3-yn-2-ol (1.10 mol equiv).

Yield: 1.16 g (78%).

Mp: 116−118 $^{o}$C.

IR (KBr): 3436, 3074, 2975, 2953, 2931, 2225, 1726, 1649, 1474, 1430, 1282, 1244, 1173, 1090, 970, 745 cm$^{-1}$.

$^{1}$H NMR: δ 1.63 (s, 6H, C(C*H*$_3$)$_2$), 2.65 (s, 1H, CO*H*), 3.93 (s, 3H, COOC*H*$_3$), 7.36-8.07 (m, 3H, Ar*H*).

$^{13}$C NMR: δ 31.0 and 31.1 (2 s, C(*C*H$_3$)$_2$), 52.5 (s, COO*C*H$_3$), 65.5 (s, *C*HOH), 79.9 and 100.4 (2 s, Ar*CC*C), 121.8, 122.4, 133.3, 134.8, 135.3, 138.1 (Ar-*C*), 165.4 (s, *C*=O).

HRMS (ESI): Calcd. for $C_{13}H_{13}NaBrO_3$ [M$^{+}$+Na]: *m/z* 318.9946. Found: 318.9948 and 320.9921.

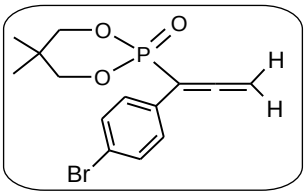
## 6.2 Reactions of P$^{III}$-Cl compounds with propargyl alcohols

### *6.21 General procedures for the synthesis of allenylphosphonates [8a-f, 10a-b], allenylphosphine oxides [9a, 11a-h] and allenylphosphoramide 9b*

Phosphorus-based allenes **8a-f, 9a-b, 10a-b** and **11a-h** were synthesized according to literature procedures.[19, 57] Among these, allenes **8d**, **10b** and **11a-h** are new. Spectroscopic and analytical data for these compounds are given below.

***Compound 8d***

This compound was prepared by using 3-(4-bromophenyl)-prop-2-yn-1-ol (1.00 g, 4.7 mmol) and (OCH$_2$CMe$_2$CH$_2$O)PCl (1.04 g, 4.7 mmol) and purified by eluting from ethyl acetate/hexane (1:1) mixture as the eluent.




Yield: 1.54 g (95%).

Mp: 78−80 $^{o}$C.

IR (KBr): 2984, 2961, 1964, 1931, 1485, 1264, 1154, 1053, 1003, 843, 787 cm$^{-1}$.

$^{1}$H NMR: δ 0.85 and 1.26 (2 s, 6H, C(C*H*$_3$)$_2$), 3.88-3.95 (m, 4H, OC*H*$_2$), 5.34 and 5.37 (2 s, 2H, =C*H*$_2$), 7.43 (br s, 4H, Ar-*H*).

$^{13}$C NMR: δ 20.6 and 21.8 (2 s, C(*C*H$_3$)$_2$), 32.6 (d, $^{3}$*J*(P-C) = 6.8 Hz, *C*(CH$_3$)$_2$), 77.4

and 77.5 (2 s, O*C*$H_2$), 79.4 (d, $^3J$(P-C) = 14.2 Hz, PC=C=*C*$H_2$), 94.6 (d, $^1J$(P-C) = 181.3 Hz, P*C*), 122.0, 129.2 (d, $^3J$(P-C) = 6.0 Hz), 129.6 (d, $^2J$(P-C) = 7.3 Hz), 131.8, 212.6 (d, $^2J$(P-C) = 3.9 Hz, PC=*C*=C).

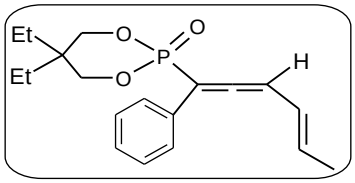
$^{31}$P NMR: δ 6.5.

LC/MS: *m/z* 342 $[M]^+$ and 344 $[M+2]^+$.

Anal. Calcd. for $C_{14}H_{16}BrO_3P$: C, 49.00; H, 4.70. Found: C, 49.12; H, 4.65.

***Compound 10b***

This compound was prepared by using 1-phenyl-4-hexen-1-yn-3-ol (0.70 g, 4.0 mmol) and ($OCH_2CEt_2CH_2O$)PCl (1.00 g, 4.0 mmol) and purified by eluting from ethyl acetate/hexane (1:2) mixture as the eluent.




Yield: 1.06 g (80%, gummy solid).

IR (neat): 2971, 1923, 1717, 1462, 1385, 1252, 1075, 1030, 845 $cm^{-1}$.

$^1$H NMR: δ 0.82 and 0.91 (2 t, $^3J$(H-H) = 7.6 Hz and 7.4 Hz respectively, 6H, C($CH_2CH_3$)), 1.12-1.28 (m, 2H, C($CH_2CH_3$)), 1.76-1.84 (m, 5H, C($CH_2CH_3$) + =CH$CH_3$), 3.97-4.13 (m, 4H, O$CH_2$), 5.88 and 6.00 (m, 2H, C*H*=C*H*), 6.42 (dd, $^4J$(P-H) = 2.4 Hz , $^3J$(H-H) ~ 9.9 Hz each, 1H, PCCC*H*), 7.29-7.61 (m, 5H, Ar-*H*).

$^{13}$C NMR: δ 6.7 and 6.9 (2 s, C($CH_2CH_3$)$_2$, 18.1 (s, =CH-$CH_3$), 22.0 and 22.8 (2 s, C($CH_2Me$)$_2$), 37.1 (d, $^3J$(P-C) = 6.0 Hz, *C*$Et_2$), 74.4 and 74.7 (2 d, $^3J$(P-C) = 7.0 Hz each, O$CH_2$), 96.8 (d, $^1J$(P-C) = 181.0 Hz, P*C*), 97.4 (d, $^3J$(P-C) = 14.0 Hz, PC=C=*C*$H_2$), 122.4 (d, $^2J$(P-C) = 10.0 Hz), 127.4 (d, $^3J$(P-C) = 6.0 Hz), 127.7, 128.4, 130.9 (d, $^3J$(P-C) = 8.0 Hz), 131.9 (d, $^3J$(P-C) = 5.0 Hz).

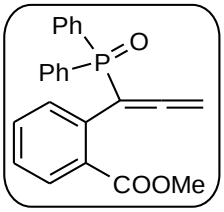
$^{31}$P NMR: δ 7.5.

LC/MS: *m/z* 334 $[M+2]^+$.

Anal. Calcd. for $C_{19}H_{25}O_3P$: C, 68.66; H, 7.58. Found: C, 68.51; H, 7.62.

***Compound 11a***

This compound was prepared by following a literature procedure[19] using propargyl alcohols **7a** (0.95 g, 5.0 mmol) and chlorodiphenylphosphine (0.90 mL, 5.0 mmol) and purified by ethyl acetate/ hexane (1:1) mixture as eluent.




Yield: 1.66 g (85%).

Mp: 64-66 $^{o}$C.

IR (KBr): 3040, 2955, 1931, 1713, 1593, 1485, 1437, 1269, 1186, 1088, 864, 797, 758, 702, 546 cm$^{-1}$.

$^{1}$H NMR: δ 3.88 (s, 3H, COOC*H*$_3$), 4.80 (d, 2H, $^{4}J$(P-H) = 10.4 Hz, PC*H*), 7.30-7.91 (m, 14H, Ar*H*).

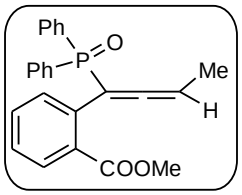
$^{13}$C NMR: δ 52.3 (s, COO*C*H$_3$), 99.0 (d, $^{1}J$(P-C) = 100.8 Hz, P*C*CCH$_2$), 127.6, 128.1, 128.2, 128.5, 128.6, 130.2, 130.6, 130.9, 131.2, 131.5, 131.7$_5$, 131.8, 131.9, 132.3, 132.6, 132.7 (Ar-*C* + PCC*C*), 168.0 (s, *C*OOMe) and 212.9 (d, $^{2}J$(P-C) = 6.3 Hz, PC*C*CH$_2$).

$^{31}$P NMR: δ 27.7.

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

Anal.Calcd. for $C_{23}H_{19}O_3P$: C, 73.79; H, 5.12. Found: C, 73.65; H, 5.18.

***Compound 11b***




This compound was prepared by a procedure similar to that for **11a** using propargyl alcohol **7b** (1.02 g, 5.0 mmol).

Yield: 1.47 g (79%).

Mp: 78-80 $^{o}$C.

IR (KBr): 3059, 2949, 1946, 1717, 1593, 1487, 1437, 1373, 1262, 1188, 1119, 754, 706 cm$^{-1}$.

$^{1}$H NMR: δ 1.47 (t, $^{3}J$(H-H) = 6.8 Hz, =CHC$H_3$), 3.87 (s, 3H, COOC$H_3$), 5.14-5.28 (m, 1H, =C*H*Me), 7.24-7.87 (m, 14 H, Ar*H*).

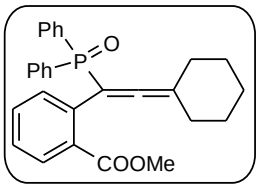
$^{13}$C NMR: δ 11.6 (d, $^{4}J$(P-C) = 5.0 Hz, PCC*C*$H_2$), 52.1 (s, COO*C*$H_3$), 88.5 (d, $^{3}J$(P-C) = 13.0 Hz, PCC*C*Me), 99.1 (d, $^{1}J$(P-C) = 103.0 Hz, P*C*CCMe), 127.0, 127.3, 127.9, 128.0, 129.9, 130.4, $131.0_0$, $131.0_3$, 131.2, 131.5, 131.6, 131.7, 131.8, 132.5, 132.9, 133.4, 133.5 (Ar-*C*), 168.1 (s, *C*OOMe) and 211.3 (d, $^{2}J$(P-C) = 6.0 Hz, PC*C*CH$_2$).

$^{31}$P NMR: δ 28.8.

LC/MS: *m/z* 389 $[M+1]^+$.

Anal.Calcd. for $C_{24}H_{21}O_3P$: C, 74.22; H, 5.45. Found: C, 74.12; H, 5.58.

***Compound 11c***




This compound was prepared by a procedure similar to that for **11a** using propargyl alcohol **7c** (1.29 g, 5.0 mmol).

Yield: 2.00 g (90%).

Mp: 100-102 $^{o}$C.

IR (KBr): 2932, 2855, 1941, 1719, 1485, 1435, 1262, 1161, 1123, 1084, 795, 779, 756, 723, 702 cm$^{-1}$.

$^{1}$H NMR: δ 0.97-1.98 (m, 10H, cyclohexyl-*H*), 3.88 (s, 3H, COOC$H_3$), 7.23-7.94 (m, 14H, Ar*H*).

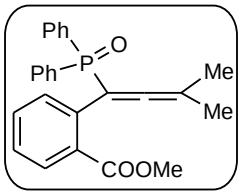
$^{13}$C NMR: δ 25.4 and 26.2 (2 s, cyclohexyl-*C*), 29.1 (d, $^{4}J$(P-C) = 4.6 Hz, cyclohexyl-*C*), 52.1 (s, COO*C*$H_3$), 97.8 (d, $^{1}J$(P-C) = 104.4 Hz, P*C*CC), 105.0 (d, $^{3}J$(P-C) = 13.0 Hz, PCC*C*), 127.1, 128.1, 128.2, 130.0, 130.7, 131.2, 131.5, 131.9, 132.0, 132.3, 133.4, 134.6 (d, $^{2}J$(P-C) = 8.3 Hz, Ar-*C*), 168.5 (s, *C*OOMe), 206.7 (d, $^{2}J$(P-C) = 6.3 Hz, PC*C*C).

$^{31}$P NMR: δ 29.5.

LC/MS: *m/z* 442 $[M]^+$.

Anal.Calcd. for $C_{28}H_{27}O_3P$: C, 76.00; H, 6.15. Found: C, 76.12; H, 6.21.

***Compound 11d***




This compound was prepared by a procedure similar to that for **11a** using propargyl alcohol **7d** (1.09 g, 5.0 mmol).

Yield: 1.70 g (88%).

Mp: 122-124 $^{o}$C.

IR (KBr): 3052, 2986, 2951, 2915, 1946, 1725, 1591, 1487, 1439, 1372, 1291, 1264, 1184, 1086, 924, 760, 721, 698, 554 $cm^{-1}$.

$^{1}$H NMR: δ 1.46 and 1.48 (2 s, 6H, =C(C$H_3$)$_2$), 3.86 (s, 3H, COOC$H_3$), 7.24-7.91 (m, 14H, Ar*H*).

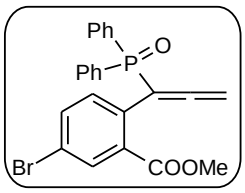
$^{13}$C NMR: δ 18.3 (s, =C(*C*H$_3$)$_2$), 51.9 (s, COO*C*H$_3$), 97.6 (d, $^{1}J$(P-C) = 103.8 Hz, P*C*CCMe$_2$), 98.9 (d, $^{3}J$(P-C) = 12.6 Hz, PCC*C*Me$_2$), 127.0, 127.9, 128.0, 129.8, 130.5, 131.0, 131.3, 131.6, 131.7, 132.0, 133.1, 134.0 (d, $^{2}J$(P-C) = 8.5 Hz, Ar-*C*), 168.2 (s, *C*OOMe) and 209.7 (s, PC*C*CMe$_2$).

$^{31}$P NMR: δ 29.8.

LC/MS: *m/z* 403 $[M+1]^{+}$.

Anal.Calcd. for $C_{25}H_{23}O_3P$: C, 74.62; H, 5.76. Found: C, 74.53; H, 5.68.

***Compound 11e***




This compound was prepared by a procedure similar to that for **11a** using propargyl alcohol **7e** (0.67 g, 2.5 mmol).

Yield: 0.94 g (86%).

Mp: 74-76 $^{o}$C.

IR (KBr): 3052, 2969, 2946, 1946, 1912, 1723, 1480, 1435, 1289, 1242, 1192, 1092, 963, 723, 694, 552 $cm^{-1}$.

$^{1}$H NMR: δ 3.89 (s, 3H, COOC$H_3$), 4.80 (d, 2H, $^{4}J$(P-H) = 10.4 Hz, PCCC$H_2$), 7.43-7.89 (m, 13H, Ar*H*).

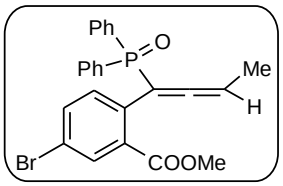
$^{13}$C NMR: δ 52.6 (s, COO*C*H$_3$), 77.5 (d, $^{3}J$(P-C) = 10.0 Hz, PCC*C*H$_2$), 98.4 (d, $^{1}J$(P-C) = 100.5 Hz, P*C*CCH$_2$), 121.7, 128.2, 128.3, 131.1, 131.8, 131.9, 132.1, 132.6$_0$, 132.6$_4$, 133.2, 134.5, 166.7 (s, *C*OOMe) and 212.9 (d, $^{2}J$(P-C) = 7.1 Hz, PC*C*CH$_2$).

$^{31}$P NMR: δ 27.6.

LC/MS: *m/z* 452 $[M]^+$ and 454 $[M+2]^+$.

Anal.Calcd. for $C_{23}H_{18}BrO_3P$: C, 60.95; H, 4.00. Found: C, 60.85; H, 4.08.

***Compound 11f***




This compound was prepared by a procedure similar to that for **11a** using propargyl alcohol **7f** (0.71 g, 2.5 mmol).

Yield: 0.98 g (84%).

Mp: 90-92 $^{o}$C.

IR (KBr): 3052, 2953, 1951, 1726, 1583, 1485, 1436, 1288, 1244, 1184, 1096, 970 cm$^{-1}$.

$^{1}$H NMR: δ 1.47 (dd→t, 3H, $^{4}J$(P-H) ~ $^{3}J$(H-H)~6.6 Hz, =CHC$H_3$), 3.88 (s, 3H, COOC$H_3$), 5.14-5.22 (m, 1H, =C*H*Me), 7.41-7.92 (m, 13H, Ar*H*).

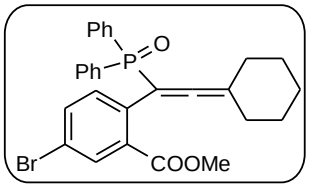
$^{13}$C NMR: δ 11.6 (d, $^{4}J$(P-C) = 5.0 Hz, =CH*C*H$_3$), 52.4 (s, COO*C*H$_3$), 89.0 (d, $^{3}J$(P-C) = 12.0 Hz, PCC*C*H$_2$), 98.5 (d, $^{1}J$(P-C) = 103.0 Hz, P*C*CCH$_2$), 121.4, 128.1, 128.2, 130.3, 131.7, 131.8, 131.9, 132.1, 132.4, 132.6, 132.7, 132.8, 133.0, 134.3, 166.8 (s, *C*OOMe) and 211.4 (d, $^{2}J$(P-C) = 5.0 Hz, PC*C*C).

$^{31}$P NMR: δ 28.7.

LC/MS: *m/z* 467 $[M]^+$ and 469 $[M+2]^+$.

Anal.Calcd. for $C_{24}H_{20}BrO_3P$: C, 61.69; H, 4.31. Found: C, 61.52; H, 4.38.

***Compound 11g***




This compound was prepared by a procedure similar to that for **11a** using propargyl alcohol **7g** (0.84 g, 2.5 mmol).

Yield: 0.97 g (74%).

Mp: 102-104 $^{o}$C.

IR (KBr): 3057, 2931, 2849, 1951, 1732, 1479, 1436, 1293, 1249, 1189, 1096, 723 $cm^{-1}$.

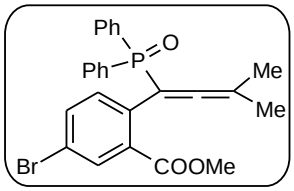
$^{1}$H NMR: δ 0.94 (br s, 2H, cyclohexyl-*H*), 1.22-1.28 (m, 2H, cyclohexyl-*H*), 1.38-1.41 (m, 2H, cyclohexyl-*H*), 1.93 and 1.94 (2 br s, 4H, cyclohexyl-*H*), 3.87 (s, 3H, COOC$H_3$), 7.40-7.91 (m, 13H, Ar*H*).

$^{13}$C NMR: δ 25.3 and 26.1 (2 s, cyclohexyl-*C*), 28.9 (d, $^{4}J$(P-C) = 4.4 Hz, cyclohexyl-*C*), 52.4 (s, COO*C*$H_3$), 97.0 (d, $^{1}J$(P-C) = 104.4 Hz, P*C*CC), 105.4 (d, $^{3}J$(P-C) = 12.8 Hz, PCC*C*), 121.1, 128.2, 128.3, 131.6, 131.9, 132.0, 132.1, 132.2, 133.0, 133.1, 133.8, 134.1, 167.1 (s, *C*OOMe) and 206.8 (d, $^{2}J$(P-C) = 6.1 Hz, PC*C*C).

$^{31}$P NMR: δ 29.5.

HRMS (ESI): Calcd. for $C_{28}H_{27}BrO_3P$ [$M^{+}$+H]: *m/z* 521.0882 and 523.0882. Found: 521.0882 and 523.0866.

***Compound 11h***




This compound was prepared by a procedure similar to that for **11a** using propargyl alcohol **7h** (0.74 g, 2.5 mmol).

Yield: 1.10 g (91%).

Mp: 132-134 $^{o}$C.

IR (KBr): 3052, 2953, 2915, 2849, 1956, 1732, 1649, 1479, 1430, 1288, 1249,

1184, 1101, 838, 740 $cm^{-1}$.

$^{1}H$ NMR: δ 1.45 and 1.47 (2 s, 6H, =C($CH_3$)$_2$), 3.87 (s, 3H, COO$CH_3$), 7.43-7.91 (m, 13H, Ar*H*).

$^{13}C$ NMR: δ 18.3 (d, $^{4}J$(P-C) = 5.3 Hz, =C($CH_3$)$_2$), 52.3 (s, COO$CH_3$), 96.9 (d, $^{1}J$(P-C) = 103.3 Hz, P*C*CC), 99.4 (d, $^{3}J$(P-C) = 12.9 Hz, PCC*C*), 121.1, 128.0, 128.2, 131.6, $131.7_0$, $131.7_4$, 132.1, 132.7, 132.8, $133.0_0$, $133.0_3$, 133.1, 133.2, 134.0 (Ar-*C*), 166.9 (s, *C*OOMe) and 209.9 (d, $^{2}J$(P-C) = 5.4 Hz, PC*C*$CH_2$).

$^{31}P$ NMR: δ 29.8.

HRMS (ESI): Calcd. for $C_{25}H_{23}BrO_3P$ [$M^+$+H]: *m/z* 481.0569 and 483.0569. Found: 481.0568 and 483.0545.

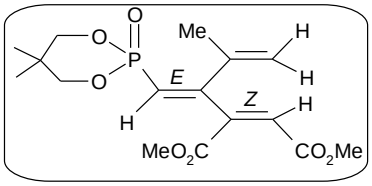
## 6.3 Cycloaddition reactions of terminally substituted allenes, α-aryl allenes and vinyl allenes with dimethyl acetylenedicarboxylate (DMAD)/ DEAD and maleic anhydride

### *6.31 Reaction of allenes 8a and 9a-b with DMAD*

***General procedure for the synthesis of compounds 12-14 and 16-17***

A mixture of allenylphosphonate **8a** (0.40 g, 1.80 mmol) and DMAD (0.27 g, 1.80 mmol) was heated under neat condition at 150 $^{o}$C for 12 h. Compounds **12-14** were separated by using EtOAc/hexane mixture.

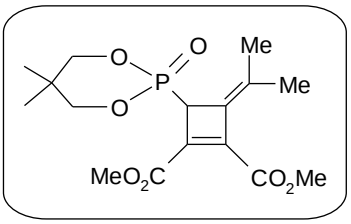
***Compound 12***




This compound[59] was eluted by using ethyl acetate/hexane (2:3) mixture.

Yield: 85% [combined, **12**+**13**+**14**, ratio 5:6:6, by $^{31}P$ NMR] 0.14 g (isolated, 20%, **12**).

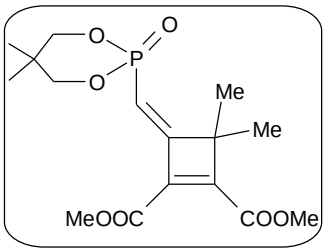
***Compound 13***




This compound[59] was eluted by using ethyl acetate/hexane (3:2) mixture.

Yield: 85% [combined, **12**+**13**+**14**, by $^{31}$P NMR] 0.07 g (isolated, 10 %, **13**).

***Compound 14***




This compound was eluted by using ethyl acetate/hexane (1:2) mixture.

Yield 85% [combined, **12**+**13**+**14**, by $^{31}$P NMR] 0.11 g (isolated, 15 %, **14**).

Mp: 166-168 $^{o}$C.

IR (KBr): 2961, 2930, 1742, 1723, 1669, 1437, 1260, 1059, 1009, 824 cm$^{-1}$.

$^{1}$H NMR: δ 1.07 and 1.12 (2 s, 6H, C(C$H_3$)$_2$), 1.60 (s, 6H, =C-C(C$H_3$)$_2$), 3.85 and 3.87 (2 s, 6H, 2 COOC$H_3$), 3.91 (t, buried in the signals due to COOC$H_3$ protons, 2H, OC$H_A$H$_B$), 4.19 (dd→t, $^{3}J$(H-H) ~ $^{2}J$(P-H) ~ 12.0 Hz each, 2H, CH$_A$$H_B$), 6.01 (d, $^{2}J$(P-H) = 16.0 Hz, 1H, PC$H$).

$^{13}$C NMR: δ 21.4 and 21.5 (2 s, C(*C*H$_3$)$_2$), 21.9 (s, =C-C(*C*H$_3$)$_2$), 32.5 (d, $^{3}J$(P-C) = 6.0 Hz, *C*(CH$_3$)$_2$), 52.1 and 52.3 (2 s, COO*C*H$_3$), 53.4 (d, $^{3}J$(P-C) = 10.0 Hz, =C-*C*Me$_2$), 75.4$_0$ and 75.4$_4$ (2 s, O*C*H$_2$), 103.5 (d, $^{1}J$(P-C) = 191.0 Hz, P-*C*), 136.0 (d, $^{2}J$(P-C) = 27.0 Hz, P-C=*C*), 159.0 (s, =*C*COOMe), 159.9 and 161.5 (2 s, *C*OOMe), 164.3 (d, $^{3}J$(P-C) = 9.0 Hz, =C-*C*COOMe).

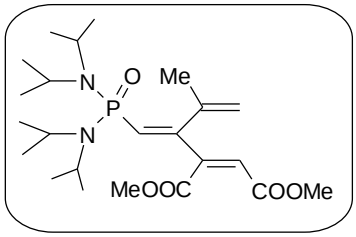
$^{31}$P NMR: δ 10.4.

LC/MS: m/z 359 [M+1]$^{+}$.

Anal. Calcd. for $C_{16}H_{23}O_7P$: C, 53.63; H, 6.47. Found: C, 53.21; H, 6.12.

***Compound 15***

This compound was prepared from allenylphosphonate **9a** (0.50 g, 1.60 mmol) and DMAD (0.23 g, 1.60 mmol); it was isolated by column chromatography using ethyl acetate/hexane (2:3) mixture as the eluent. Although the starting material was completely consumed, there were at least three other products [δ(P) 19.0, 21.6 26.1; total ~45%] in the reaction mixture.




Yield: 53 % by $^{31}$P NMR; 0.33 g (isolated, 45%).

Mp: 128-130 $^{o}$C.

IR (KBr): 2970, 1744, 1719, 1613, 1370, 1335, 1264, 1020, 986, 882, 789 cm$^{-1}$.

$^{1}$H NMR: δ 1.19 and 1.26 (2 d, $^{4}J$(P-H) ~ 6.7 Hz for each, (12+12 = 24)H, N(CH(C$H_3$)$_2$)$_2$), 2.05 (s, 3H, =C(C$H_3$)), 3.51-3.59 (m, 4H, N(C$H$(CH$_3$)$_2$)$_2$), 3.74 and 3.89 (2s, 6H, COOC$H_3$), 4.82 (s, 1H, =C$H_A$H$_B$), 5.30 (m, 1H, =CH$_A$$H_B$), 5.88 (d, $^{2}J$(P-H) = 12.4 Hz, 1H, PC$H$), 6.19 (s, 1H, =C$H$(COOMe).

$^{13}$C NMR: δ 23.1 and 23.4 (2 s, C($C$H$_3$)$_2$), 45.7 (d, $^{2}J$(P-C) = 4.8 Hz, $C$Me$_2$), 52.1 and 52.6 (2 s, CO$_2$$C$H$_3$), 117.2 (s, =$C$H$_2$), 120.6 (s, =$C$HCOOMe), 128.6 (d, $^{1}J$(P-C) = 144.3 Hz , P$C$H), 140.0 (d, $^{3}J$(P-C) = 5.2 Hz, =$C$(CH$_3$)), 148.0 (d, $^{3}J$(P-C) = 7.3 Hz, =$C$(CO$_2$Me)), 149.8 (d, $^{2}J$(P-C) = 21.6 Hz, P-C=$C$), 165.7 and 168.3 (2 s, $C$O$_2$Me).

$^{31}$P NMR: δ 17.9.

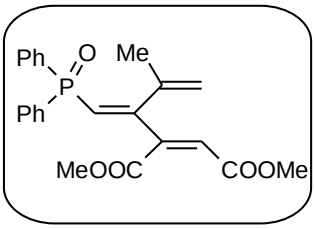
LC/MS: m/z 456 [M]$^{+}$.

Anal.Calcd. For $C_{23}H_{41}N_2O_5P$: C, 60.51; H, 9.05; N, 6.14. Found: C, 60.25; H, 8.89; N 6.12.

***Compound 16***

This compound was prepared from allenylphosphonate **(9b)** (0.50 g, 1.87 mmol) and DMAD (0.26 g, 1.87 mmol). The $^{31}$P NMR spectrum of the reaction mixture at this

stage showed compound **16** (ca 60%) along with other minor products [δ(P) 7.8, 26.2, 28.1, 45.2]. The reaction mixture was chromatographed by using ethyl acetate/hexane (2:3) mixture as the eluent to obtain compound **16** in a pure state.




Yield: >60% by $^{31}$P NMR, 0.34 g (isolated, 44%).

Mp: 110-112 $^{o}$C.

IR (KBr): 3058, 2961, 1730, 1617, 1435, 1262, 1102, 1017, 797, 696 cm$^{-1}$.

$^{1}$H NMR: δ 1.72 (s, 3H, =C(C*H*$_3$)), 3.76 and 3.88 (2 s, 6H, COOC*H*$_3$), 4.86 and 5.11 (2 s , 2H, =CH$_2$), 6.10 (s, 1H, =C*H*(COOMe)), 6.43 (d, $^{2}J$(P-H) = 19.2 Hz, 1H, PC*H*), 7.44-7.73 (m, 10H, Ar-*H*).

$^{13}$C NMR: δ 22.3 (s, =C(*C*H$_3$)), 52.3 and 52.9 (2 s, CO$_2$*C*H$_3$), 120.5 (s, =*C*H$_2$), 122.4 (s, =*C*HCOOMe), 126.6 (d, $^{1}J$(P-C) = 100.0 Hz, P-*C*=C), 128.4 (d, $^{2}J$(P-C) = 16.0 Hz), 131.1 (d, $^{3}J$(P-C) = 10.0 Hz), 131.8, 133.8 (d, $^{1}J$(P-C) = 106.0 Hz), 139.0 (d, $^{3}J$(P-C) = 6.3 Hz, =*C*(CH$_3$)), 147.3 (d, $^{2}J$(P-C) = 18.1 Hz, P-C=*C*), 156.3 (s, =*C*-CO$_2$Me), 165.1 and 167.5 (2 s, *C*O$_2$Me).

$^{31}$P NMR: δ 17.9.

LC/MS: m/z 411 [M+1]$^{+}$.

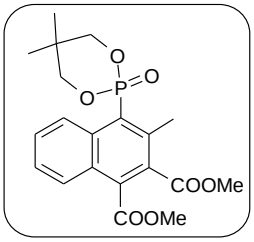
Anal. Calcd. For $C_{23}H_{23}O_5P$: C, 67.31; H, 5.65. Found: C, 66.85; H, 5.63.

### *6.32 Reaction of allenes 8b-e and 10a-b with DMAD/DEAD/maleic anhydride:*

#### *General procedure for the synthesis of compounds 17-20 and 21-24*

A mixture of allenylphosphonate **(8b)** (0.80 g, 3.03 mmol) and DMAD (1.29 g, 9.08 mmol) in xylene (6 mL) was heated under reflux for 12 h. The solvent was removed under reduced pressure. The products **17a-c** were eluted by using EtOAc/hexane mixture. Similarly, other compounds in this series [**18a-c** to **21a-c** and **22a-d to 24a-d**] were prepared.

***Compound 17a***




This compound was isolated by using ethyl acetate/hexane (2:3) mixture.

Yield: 80% [combined, **17a**+**17b**+**17c**, ratio 4:1:3, by $^{31}$P NMR], 0.43 g (isolated, 35%, **17a**), white solid.

Mp: 120-122 $^{o}$C.

IR (KBr): 2955, 2886, 1736, 1439, 1343, 1252, 1202, 1156, 1059, 1009, 830, 816, 785 cm$^{-1}$.

1H NMR: δ 0.72 and 1.37 (2 s, 6H, C(C*H*$_3$)$_2$), 2.78 (d, $^4J$(P-H) = 2.0 Hz, 3H, Ar-C*H*$_3$), 3.61-3.58 (m, 2H, OC*H*$_2$), 3.91–4.01 (m, 2H, OC*H*$_2$), 3.96 and 4.03 (2 s, 6H, 2 COOC*H*$_3$), 7.59–8.70 (m, 4H, Ar-*H*).

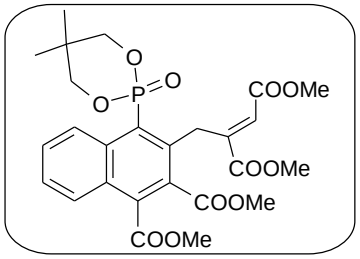
$^{13}$C NMR: δ 20.3 (s, C(*C*H$_3$)$_2$), 20.6 (d, $^3J$(P-C) = 5.1 Hz, Ar-*C*H$_3$), 22.1 (s, C(*C*H$_3$)$_2$), 32.1 (d, $^3J$(P-C) = 5.7 Hz, *C*(CH$_3$)$_2$), 52.9 and 53.1 (2 s, COO*C*H$_3$), 76.6$_0$ and 76.6$_3$ (2 s, O*C*H$_2$), 125.3, 126.2, 126.3 (d, $^3J$(P-C) = 4.3 Hz), 127.5, 127.8 (d, $^2J$(P-C) = 12.7 Hz), 128.9, 132.5 (d, $^2J$(P-C) = 17.2 Hz), 133.9 (d, $^3J$(P-C) = 5.4 Hz), 134.0 (d, $^4J$(P-C) = 2.8 Hz), 138.9 (d, $^3J$(P-C) = 11.0 Hz, Ar-*C*), [The doublet due to $^1J$(P-C) was not clear], 167.7 and 168.2 (2 s, *C*OOCH$_3$).

$^{31}$P NMR: δ 10.8.

LC/MS: m/z 407 [M+1]$^+$.

Anal. Calcd. For $C_{20}H_{23}O_7P$: C, 59.11; H, 5.70. Found: C, 58.91; H, 5.75.

***Compound 17b***




Compound **17b** was isolated by using ethyl acetate/hexane (3:2) mixture.

Yield: [**17a**+**17b**+**17c**] 80% by $^{31}$P NMR, 0.12 g (isolated, 7%, **17b**), white solid.

Mp: 124-126 $^{o}$C.

IR (KBr): 2955, 1744, 1732, 1651, 1435, 1373, 1150, 1059, 918, 828, 783 cm$^{-1}$.

1H NMR: δ 0.84 and 1.20 (2 s, 6H, C(C$H_3$)$_2$), 3.67 (s, 3H, COOC$H_3$), 3.75 (t, 2H, OC$H_2$), 3.85, 3.90 and 4.02 (3 s, 9H, COOC$H_3$), 4.20 (t, 2H, OC$H_2$), 4.48 (s, 2H, Ar-C$H_2$), 5.41 (s, H, C*H*COOMe), 7.66–8.81 (m, 4H, Ar-*H*).

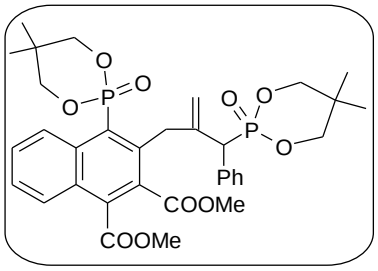
$^{13}$C NMR: δ 21.1 and 21.7 (2 s, C(*C*H$_3$)$_2$), 32.4 (d, $^{3}J$(P-C) = 5.0 Hz, *C*(CH$_3$)$_2$), 36.4 (s, Ar*C*H$_2$), 51.9, 52.7 and 53.2 (3 s, all COO*C*H$_3$), 76.8 (s, O*C*H$_2$), 122.4, 126.4, 127.1, 128.3, 128.7 (d, $^{2}J$(P-C) = 13.0 Hz), 129.3, 130.0, 131.4 (d, $^{2}J$(P-C) = 17.0 Hz), 134.0 (d, $^{3}J$(P-C) = 18.5 Hz), 135.4, 135.6, 135.7, 146.8 [The doublet due to $^{1}J$(P-C) was not clear], 165.6, 167.6, 167.7 and 167.8 (4 s, *C*OOCH$_3$).

$^{31}$P NMR: δ 10.8.

LC/MS: m/z 549 [M+1]$^{+}$.

Anal. Calcd. For $C_{26}H_{29}O_{11}P$: C, 56.94; H, 5.33. Found: C, 57.21; H, 5.35.

***Compound 17c***




Compound **17c** was eluted by using ethyl acetate/hexane (4:1) mixture.

Yield: [**17a**+**17b**+**17c**] 80% by $^{31}$P NMR, 0.47 g (isolated, 23%, **17c**), white solid.

Mp: 160-162 $^{o}$C.

IR (KBr): 2955, 1734, 1644, 1543, 1456, 1260, 1059, 1009, 828, 781, 519 cm$^{-1}$.

$^{1}$H NMR: δ 0.67, 0.82, 1.10 and 1.28 (4 s, 12H, C(C$H_3$)$_2$), 3.50–4.07 (m, 15H, COOC$H_3$ + OC$H_2$ + P-C*H*-Ar), 4.27 (s, 2H, Ar-C$H_2$), 4.89 and 5.92 (2 s, 2H, C=C$H_2$), 5.92 (s, H, C=C*H*), 7.12–8.74 (m, 9H, Ar-*H*).

$^{13}$C NMR: δ 20.5, 20.8, 21.9 and 22.0 (4 s, C(*C*H$_3$)$_2$), 32.2 and 32.5 (2 d, $^{3}J$(PC) = 5.0 Hz and 7.0 Hz respectively, C(*C*H$_3$)$_2$), 40.9 (d, $^{3}J$(P-C) = 11.0 Hz, Ar-*C*H$_2$), 47.2 (d, $^{1}J$(P-C) = 125.0 Hz, P-*C*H), 52.7 and 53.0 (2 s, COO*C*H$_3$), 76.3 and 76.4 (2 d, $^{3}J$(P-C) = 7.0 Hz each, O*C*H$_2$), 117.2 (s, = *C*H$_2$), 126.3, 126.6,

126.9, 127.4, 127.8, 128.2, 128.4, 128.6, 129.0, 129.5 (d, $^{3}J$(P-C) = 7.0 Hz, Ar-*C*), 131.6 (d, $^{2}J$(P-C) = 17.0 Hz, Ar-*C*), 133.9, 134.0, 135.1, 139.6 (d, $^{2}J$(P-C) = 11.0 Hz, Ar-*C*), 142.0 (m, Ar-*C*) [The doublet due to the second $^{1}J$(P-C) was not clear], 167.6 and 167.7 (2 s, *C*OOMe).

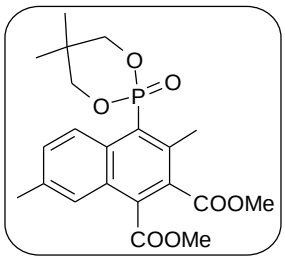
$^{31}$P NMR: δ 10.8 and 17.8.

LC/MS: m/z 670 $[M]^{+}$.

Anal. Calcd. For $C_{34}H_{40}O_{10}P_2$: C, 60.89; H, 6.01. Found: C, 60.75; H 6.11.

***Compound 18a***

Compounds **18a-c** were prepared by using allenylphosphonate (**8c**) (1.00 g, 3.6 mmol) and DMAD (1.60 g, 10.8 mmol).




Compound **18a** was isolated by using ethyl acetate/hexane (2:3) mixture.

Yield: 97% [combined, **18a**+**18b**+**18c**, ratio 15:2:3, by $^{31}$P NMR], 1.02 g (isolated, 67%, **18a**), white solid.

Mp: 122-124 $^{o}$C.

IR (KBr): 2957, 2919, 1732, 1568, 1505, 1441, 1061, 1009, 945, 916, 835, 785 $cm^{-1}$.

$^{1}$H NMR: δ 0.71 and 1.37 (2 s, 6H, C(C*H*$_3$)$_2$), 2.52 (s, 3H, Ar-C*H*$_3$), 2.75 (d, $^{4}J$(P-H) = 2.0 Hz, 3H, P-C=C-C*H*$_3$), 3.58-3.60 (m, 2H, OC*H*$_2$), 3.89–3.98 (m, 2H, OC*H*$_2$), 3.96 and 4.03 (2 s, 6H, COOC*H*$_3$), 7.46–8.58 (m, 3H, Ar-*H*).

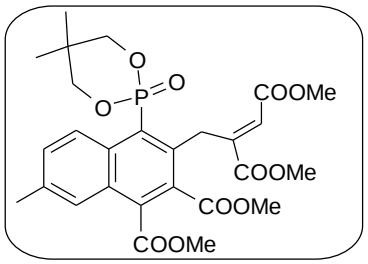
$^{13}$C NMR: δ 20.2 (s, Ar-*C*H$_3$), 20.3 (d, $^{3}J$(P-C) = 4.8 Hz, PCC-*C*H$_3$), 21.5 and 22.0 (2 s, C(*C*H$_3$)$_2$), 31.9 (d, $^{3}J$(P-C) = 5.5 Hz, *C*(CH$_3$)$_2$), 52.7 and 52.9 (2 s, COO*C*H$_3$), 76.5$_0$ and 76.5$_3$ (2 s, O*C*H$_2$), 124.9, 125.7 (d, $^{1}J$(P-C) = 171.0 Hz), 125.9 (d, $^{3}J$(P-C) = 4.0 Hz), 128.0 (d, $^{2}J$(P-C) = 12.7 Hz), 131.1, 132.2, 132.3 (d, $^{2}J$(P-C) = 28.7 Hz), 133.3, 137.5, 137.7 (d, $^{2}J$(P-C) = 11.0 Hz), 167.7and 168.2 (2 s, *C*OOCH$_3$).

$^{31}$P NMR: δ 11.4.

LC/MS: m/z 421 $[M+1]^+$.

Anal. Calcd. For $C_{21}H_{25}O_7P$: C, 60.00; H, 5.99. Found: C, 60.21; H, 5.88.

***Compound 18b***




Compound **18b** was isolated by using ethyl acetate/hexane (3:2) mixture.

Yield: [**18a**+**18b**+**18c**] 97% by $^{31}$P NMR 0.12 g (isolated, 6%, **18b**), white solid.

Mp: 132-134 $^{o}$C.

IR (KBr): 2953, 1741, 1437, 1362, 1267, 1055, 1007, 831, 785, 529 $cm^{-1}$.

$^1$H NMR: δ 0.82 and 1.20 (2 s, 6H, C(C$H_3$)$_2$), 2.54 (s, 3H, Ar-C$H_3$), 3.66 (s, 3H, COOC$H_3$), 3.73 (dd→t, $^3J$(P-H) = $^2J$(H-H) ~ 11.0 Hz each, 2H, OC$H_A$H$_B$), 3.84, 3.89 and 4.00 (3 s, 9H, COOC$H_3$), 4.18 (dd→t, $^3J$(P-H) = $^2J$(H-H) ~ 11.0 Hz each, 2H, OCH$_A$$H_B$), 4.46 (s, 2H, Ar-C$H_2$), 5.41 (s, H, C*H*COOMe), 7.52–8.70 (m, 3H, Ar-*H*).

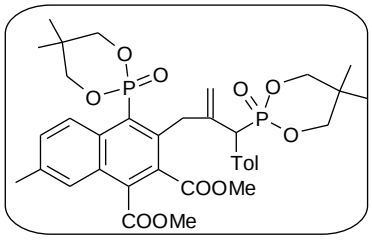
$^{13}$C NMR: δ 21.1 and 21.8 (2 s, C(*C*H$_3$)$_2$), 32.4 (br, *C*(CH$_3$)$_2$), 36.4 (s, Ar*C*H$_2$), 51.9, 52.7 and 53.2 (s each, COO*C*H$_3$), 76.8 (s, OCH$_2$), 122.3, 125.2, 126.9, 128.8 (d, $^1J$(P-C) = 174.8 Hz), 129.0 (d, $^2J$(P-C) = 13.8 Hz), 131.3, 131.6, 132.4 (d, $^2J$(P-C) = 10.3 Hz), 134.6 (d, $^3J$(P-C) = 8.5 Hz), 134.9, 138.6, 147.0, 165.7 and 167.8 (s each, *C*OOCH$_3$).

$^{31}$P NMR: δ 11.1.

LC/MS: m/z 563 $[M+1]^+$.

Anal. Calcd. For $C_{27}H_{31}O_{11}P$: C, 57.65; H, 5.55. Found: C, 57.48; H, 5.65.

***Compound 18c***



Compound **18c** was isolated by using ethyl acetate/hexane (4:1) mixture.

Yield: [**18a**+**18b**+**18c**] 97% by $^{31}$P NMR, 0.25 g (isolated, 10%, **18c**), white solid.

Mp: 164-166 $^{o}$C.

IR (KBr): 2957, 2892, 1732, 1724, 1644, 1437, 1256, 1059, 1009, 828, 783, 530 cm$^{-1}$.

$^{1}$H NMR: δ 0.65, 0.84, 1.10 and 1.28 (4 s, 12H, C(C$H_3$)$_2$), 2.23 and 2.25 (2 s, 6H, Ar-C$H_3$), 3.49–4.03 (m, 15H, COOC$H_3$ + OC$H_2$ + P-C*H*-Ar), 4.24 (s, 2H, Ar-C$H_2$), 4.87 and 5.89 (2 s, 2H, C=C$H_2$), 6.89–8.62 (m, 7H, Ar-*H*).

$^{13}$C NMR: δ 20.4, 20.7, 20.9, 21.5, 21.8 and 21.9 (6 s, C(*C*H$_3$)$_2$ + Ar-*C*H$_3$), 32.0 and 32.4 (2 d, $^{3}J$(P-C) = 6.0 Hz each, *C*(CH$_3$)$_2$), 40.7 (d, $^{3}J$(P-C) = 9.0 Hz, Ar-*C*H$_2$), 46.4 (d, $^{1}J$(P-C) =129.0 Hz, P-*C*), 52.5 and 52.8 (2 s, COO*C*H$_3$), 76.2 and 76.3 (2 d, $^{3}J$(P-C) = 7.0 Hz and 6.0 Hz respectively, O*C*H$_2$), 116.9 (s, =*C*H$_2$), 124.9, 126.2, 126.3, 128.0, 128.4, 128.5, 128.7, 129.1 (d, $^{3}J$(P-C) = 6.0 Hz, Ar-*C*), 130.6 (d, $^{3}J$(P-C) = 7.0 Hz, Ar-*C*), 131.2, 131.4 (d, $^{2}J$(P-C) = 18.0 Hz, Ar-*C*), 132.2 (d, $^{2}J$(P-C) = 12.0 Hz, Ar-*C*), 134.4, 136.8, 137.8, 138.5 (d, $^{2}J$(P-C) = 11.0 Hz, Ar-*C*), 142.1 [The doublet due to $^{1}J$(P-C) was not clear], 167.6 and 167.7 (s each, *C*OOCH$_3$).

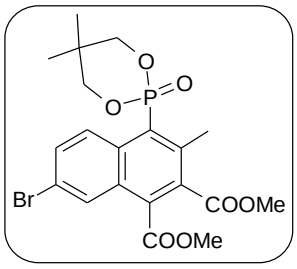
$^{31}$P NMR: δ 10.8 and 17.8.

LC/MS: m/z 700 [M+2]$^{+}$.

Anal. Calcd. For $C_{36}H_{44}O_{10}P_2$: C, 61.89; H, 6.35 Found: C, 61.75; H, 6.41.

***Compound 19a***

Compounds **19a-c** were prepared by using allenylphosphonate (**8d**) (0.50 g, 1.46 mmol) and DMAD (0.62 g, 4.38 mmol).




This compound was isolated by using ethyl acetate/hexane (2:3) mixture.

Yield: 95% [combined,**20a**+**20b**+**20c**, ratio 12:2:5, by $^{31}$P NMR], 0.39 g (isolated, 55%, **20a**), white solid.

Mp: 136-138 $^{o}$C.

IR (KBr): 2959, 2878, 1732, 1435, 1273, 1055, 1011, 821, 523 cm$^{-1}$.

$^{1}$H NMR: δ 0.74 and 1.36 (2 s, 6H, C(C*H*$_3$)$_2$), 2.75 (s, 3H, Ar-C*H*$_3$), 3.59-3.90 (m, 4H, OC*H*$_2$), 3.96 and 4.03 (2 s, 6H, 2 COOC*H*$_3$), 7.69–8.58 (m, 3H, Ar-*H*).

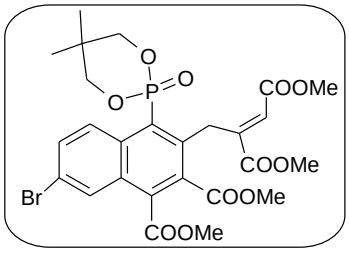
$^{13}$C NMR: δ 20.4 (s, C(*C*H$_3$)$_2$), 20.6 (d, $^{3}J$(P-C) = 4.6 Hz, Ar-*C*H$_3$), 22.0 (s, C(*C*H$_3$)$_2$), 32.1 (d, $^{3}J$(P-C) = 5.5 Hz, *C*(CH$_3$)$_2$), 53.0 and 53.3 (2 s, COO*C*H$_3$), 76.7 (s, O*C*H$_2$), 122.2, 126.8 (d, $^{1}J$(P-C) = 172.1 Hz), 128.0 (d, $^{3}J$(P-C) = 3.8 Hz), 128.3, 129.2 (d, $^{2}J$(P-C) = 12.6 Hz), 132.2, 132.3, 132.5, 133.9 (d, $^{2}J$(P-C) = 16.8 Hz), 139.2 (d, $^{3}J$(P-C) = 10.8 Hz, Ar-*C*), 167.0 and 168.0 (2 s, *C*OOCH$_3$).

$^{31}$P NMR: δ 10.1.

LC/MS: m/z 485 [M+1]$^{+}$ and 487 [M+3]$^{+}$.

Anal. Calcd. for $C_{20}H_{22}BrO_7P$: C, 49.50; H 4.57. Found: C, 49.61; H 4.48.

***Compound 19b***




Compound **19b** was isolated by using ethyl acetate/hexane (1:1) mixture.

Yield: [**19a**+**19b**+**19c**] 95% by $^{31}$P NMR 0.06 g (isolated, 6%, **19b**), white solid.

Mp: 144-146 $^{o}$C.

IR (KBr): 2955, 1732, 1651, 1437, 1256, 1057, 1013, 830 cm$^{-1}$.

$^{1}$H NMR: δ 0.84 and 1.17 (2 s, 6H, C(C*H*$_3$)$_2$), 3.65 (s, 3H, COOC*H*$_3$), 3.72-3.78 (m, 2H, OC*H*$_2$), 3.83, 3.88 and 4.00 (3 s, 9H, COOC*H*$_3$), 4.18 (dd→t, 2H, $^{3}J$(P-H) = $^{2}J$(H-H) = 12.0 Hz, OC*H*$_2$), 4.43 (s, 2H, Ar-C*H*$_2$), 5.37 (s, 1H, C*H*COOMe), 7.73–8.68 (m, 4H, Ar-*H*).

$^{13}$C NMR: δ 21.2 and 21.6 (2 s, C(*C*H$_3$)$_2$), 32.5 (d, $^{3}J$(P-C) = 6.0 Hz, *C*(CH$_3$)$_2$), 36.4 (d, $^{3}J$(P-C) = 3.7 Hz, Ar*C*H$_2$), 52.0, 52.7, 53.3 and 53.4 (4 s, COO*C*H$_3$), 76.8 and 76.9 (2s, O*C*H$_2$), 122.6, 123.2, 128.4, 128.9 (d, $^{3}J$(P-C) = 3.5 Hz), 129.9 (d, $^{2}J$(P-C) = 12.5 Hz), 132.4, 132.5, 132.8 (d, $^{2}J$(P-C) = 16.9 Hz), 134.0,

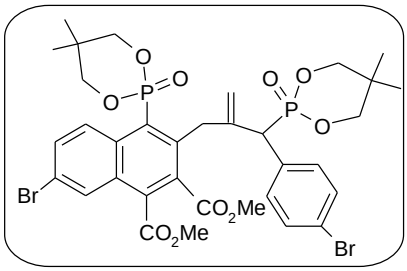
135.9 (d, $^{3}J$(P-C) = 10.9 Hz), 146.4 [The doublet due to $^{1}J$(P-C) was not clear], 165.5, 166.9, 167.3 and 167.7 (4 s, *C*OOCH$_3$).

$^{31}$P NMR: δ 10.1.

LC/MS : m/z 627 $[M+1]^+$ and 629 $[M+3]^+$.

Anal. Calcd. for $C_{26}H_{28}BrO_{11}P$: C, 49.78; H 4.50. Found: C, 49.62; H, 4.58.

***Compound 19c***




Yield: [**19a**+**19b**+**19c**] 95 % by $^{31}$P NMR 0.22 g (isolated, 18%, **19c**), pale yellow solid.

Mp: 168-170 $^{o}$C.

IR (KBr): 2957, 2888, 1736, 1721, 1641, 1576, 1476, 1256, 1067, 828, 785, 741, 687 cm$^{-1}$.

$^{1}$H NMR: δ 0.70, 0.88, 1.12 and 1.33 (4 s, 12H, C(C*H*$_3$)$_2$), 3.46–4.15 (m, 15H, COOC*H*$_3$ + OC*H*$_2$ + P-C*H*-Ar), 4.31 (s, 2H, Ar-C*H*$_2$), 5.06 and 5.91 (2 s, 2H, C=C*H*$_2$), 6.97–8.59 (m, 7H, Ar-*H*).

$^{13}$C NMR: δ 20.4, 20.7, 21.9 and 22.0 (4 s, C(*C*H$_3$)$_2$), 32.1 and 32.5 (2 d, $^{3}J$(P-C) = 5.4 Hz and 6.3 Hz respectively, C(*C*H$_3$)$_2$), 41.4 (d, $^{3}J$(P-C) = 8.3 Hz, Ar-*C*H$_2$), 45.2 (d, $^{1}J$(P-C) = 113.0 Hz, P-*C*H), 52.8 and 53.2 (2 s, COO*C*H$_3$), 76.3 and 76.5 (2 d, $^{3}J$(P-C) = 6.5 Hz and 5.8 Hz, O*C*H$_2$), 118.6 (s, = *C*H$_2$), 121.2, 122.7, 126.8, 127.9 (d, $^{3}J$(P-C) = 2.7 Hz, Ar-*C*), 128.4, 129.4 (d, $^{2}J$(P-C) = 13.0 Hz, Ar-*C*), 130.7, 132.3, 132.4, 132.6, 132.8, 134.1, 140.1 (d, $^{2}J$(P-C) = 11.5 Hz, Ar-*C*), 141.0 [The doublet due to the second $^{1}J$(P-C) was not clear], 167.0 and 167.1 (2 s, *C*OOMe).

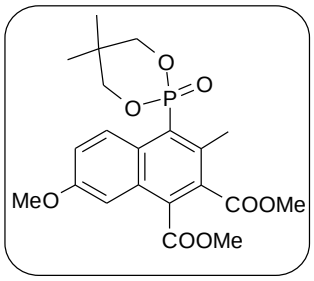
$^{31}$P NMR: δ 10.2 and 17.3.

LC/MS: m/z 827 $[M+1]^+$, 829 $[M+3]^+$ and 831 $[M+5]^+$.

Anal. Calcd. For $C_{34}H_{38}Br_2O_{10}P_2$: C, 49.29; H, 4.62. Found: C, 49.38; H 4.56.

***Compound 20a***

Compounds **20a-c** were prepared by using allenylphosphonate (**8e**) (0.40 g, 1.36 mmol) and DMAD (0.58 g, 4.08 mmol).




This compound was isolated by using ethyl acetate/hexane (1:1) mixture.

Yield: 98% [combined, **20a**+**20b**+**20c**, ratio 12:3:5 , by $^{31}$P NMR], 0.30 g (isolated, 50%, **20a**), white solid.

Mp: 148-150 $^{o}$C.

IR (KBr): 2955, 2882, 1732, 1624, 1507, 1435, 1227, 1150, 1059, 1005, 912, 830, 783, 527 cm$^{-1}$.

$^{1}$H NMR: δ 0.71 and 1.36 (2 s, 6H, C(C*H*$_3$)$_2$), 2.72 (d, $^{4}J$(P-H) = 2.0 Hz, 3H, Ar-C*H*$_3$), 3.58-3.61 (m, 2H, OC*H*$_2$), 3.90-4.01 (m, 11H, 2 COOC*H*$_3$ + OC*H*$_3$ + OC*H*$_2$), 7.27–8.60 (m, 3H, Ar-*H*).

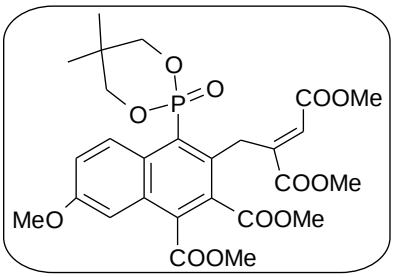
$^{13}$C NMR: δ 20.2 (d, $^{3}J$(P-C) = 5.0 Hz, Ar-*C*H$_3$), 20.3 and 22.1 (2 s, C(*C*H$_3$)$_2$), 32.0 (d, $^{3}J$(P-C) = 5.0 Hz, *C*(CH$_3$)$_2$), 52.8 and 53.0 (2 s, COO*C*H$_3$), 55.3 (s, O*C*H$_3$), 76.6$_0$ and 76.6$_1$ (2 s, O*C*H$_2$), 104.4, 121.3, 126.2 (d, $^{1}J$(P-C) = 170.6 Hz), 127.8 (d, $^{3}J$(P-C) = 4.1 Hz), 129.4, 129.6, 129.7, 129.8, 131.9, 133.5 (d, $^{2}J$(P-C) = 17.1 Hz), 135.8 (d, $^{2}J$(P-C) = 10.8 Hz), 158.4, 167.7 and 168.5 (2 s, *C*OOCH$_3$).

$^{31}$P NMR: δ 11.3.

LC/MS: m/z 437 [M+1]$^{+}$.

Anal. Calcd. For $C_{21}H_{25}O_8P$: C, 57.80; H, 5.77. Found: C, 57.68; H, 5.86.

***Compound 20b***




Compound **20b** was isolated by using ethyl acetate/hexane (1:1) mixture.

Yield: [**20a**+**20b**+**20c**] 98% by $^{31}$P NMR 0.06 g (isolated, 8%, **20b**), white solid.

Mp: 158-160 $^{o}$C.

IR (KBr): 2957, 1740, 1622, 1507, 1437, 1377, 1264, 1169, 1057, 1009, 830, 511 cm$^{-1}$.

$^{1}$H NMR: δ 0.83 and 1.20 (2 s, 6H, C(C*H*$_3$)$_2$), 3.67 (s, 3H, COOC*H*$_3$), 3.74 (dd→t, 2H, $^{3}J$(P-H) = $^{2}J$(H-H) = 12.0 Hz, OC*H*$_2$), 3.85, 3.89, 3.94 and 4.00 (4 s, 12H, COOC*H*$_3$ + OC*H*$_3$), 4.16 (dd→t, 2H, $^{3}J$(P-H) = $^{2}J$(H-H) = 12.0 Hz, OC*H*$_2$), 4.42 (s, 2H, Ar-C*H*$_2$), 5.40 (s, 1H, C*H*COOMe), 7.32–8.72 (m, 4H, Ar-*H*).

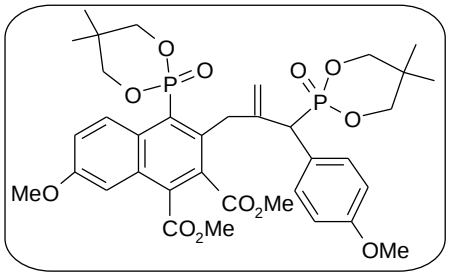
$^{13}$C NMR: δ 21.1 and 21.7 (2 s, C(*C*H$_3$)$_2$), 32.4 (d, $^{3}J$(P-C) = 5.6 Hz, *C*(CH$_3$)$_2$), 36.2 (s, Ar*C*H$_2$), 51.9, 52.6, and 53.1 (3 s, all COO*C*H$_3$), 55.5 (s, OC*H*$_3$), 76.8 (s, O*C*H$_2$), 104.4, 121.7, 122.2, 128.7, 129.6 (d, $^{2}J$(P-C) = 11.9 Hz), 129.9, 130.7 (d, $^{2}J$(P-C) = 14.7 Hz), 132.4, 132.5, 132.6, 133.5, 147.1, 159.0 [The doublet due to $^{1}J$(P-C) was not clear], 165.6, 167.7, and 167.9 (3 s, all *C*OOCH$_3$).

$^{31}$P NMR: δ 11.3.

LC/MS: m/z 578 [M]$^{+}$.

Anal. Calcd. For $C_{27}H_{31}O_{12}P$: C, 56.06; H, 5.40. Found: C, 56.18; H, 5.35.

***Compound 20c***




Compound **20c** was eluted by using ethyl acetate/hexane (4:1) mixture.

Yield: [**20a**+**20b**+**20c**] 98% by $^{31}$P NMR 0.23 g (isolated, 23%, **20c**), white solid.

Mp: 170-172 $^{o}$C.

IR (KBr): 2968, 1740, 1620, 1510, 1264, 1009, 828 cm$^{-1}$.

$^{1}$H NMR: δ 0.67, 0.85, 1.11 and 1.31 (4 s, 12H, C(C*H*$_3$)$_2$), 3.49–4.05 (m, 21H, 2 COOC*H*$_3$ + 4 OC*H*$_2$ + 2 OC*H*$_3$ + P-C*H*-Ar), 4.23 (s, 2H, Ar-C*H*$_2$), 4.91 and 5.87 (2 s, 2H, C=C*H*$_2$), 6.59–8.65 (m, 7H, Ar-*H*).

$^{13}$C NMR: δ 20.3, 20.7, 21.8 and 22.0 (4 s, C(*C*H$_3$)$_2$), 32.0 and 32.4 (2 d $^{3}J$(P-C) = 5.0 Hz and 6.4 Hz respectively, C(*C*H$_3$)$_2$), 40.7 (s, Ar-*C*H$_2$), 45.5 (d, $^{1}J$(P-C) = 123.2 Hz, P-*C*H), 52.6 and 53.8 (2 s, COO*C*H$_3$), 55.0 and 55.3 (2 s, O*C*H$_3$), 76.2 and 76.3 (2 d, $^{3}J$(P-C) = 6.9 and 6.4 Hz respectively, O*C*H$_2$), 104.2, 113.3, 117.0 (d, $^{3}J$(P-C) = 4.0 Hz), 121.3, 125.2, 125.5 (d, $^{3}J$(P-C) = 5.2 Hz), 127.9, 128.1, 129.0, 129.4 (d, $^{2}J$(P-C) = 11.6 Hz), 130.0, 130.1, 130.2 (d, $^{3}J$(P-C) = 4.6 Hz), 132.4 (d, $^{2}J$(P-C) = 16.7 Hz), 133.2, 136.7 (d, $^{2}J$(P-C) = 10.4 Hz), 142.1, 158.5, 158.7 [The doublet due to the second $^{1}J$(P-C) was not clear], 167.7 (s, 2 *C*OOMe).

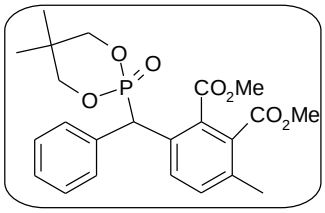
$^{31}$P NMR: δ 10.7 and 17.9.

LC/MS: m/z 731 [M+1]$^{+}$.

Anal. Calcd. For $C_{36}H_{44}O_{12}P_2$: C, 59.18; H, 6.07. Found: C, 59.32; H, 5.95.

***Compound 21a***

Compounds **21a-d** were prepared by using allenylphosphonate (**10a**) (0.7 g, 2.3 mmol) and DMAD (0.81 g, 6.9 mmol).




Compound **21a** was isolated by using ethyl acetate/hexane (1:1) mixture.

Yield: quantitative **[21a+21b+21(c,d)**, ratio 3:2:5 by $^{31}$P NMR], 0.24 g (isolated, 28%, **21a**).

Mp: 134–136 $^{o}$C.

IR (KBr): 2953, 2882, 1732, 1715, 1601, 1435, 1406, 1373, 1161, 1109, 1057, 833, 787, 700 cm$^{-1}$.

$^{1}$H NMR: δ 0.89 and 1.06 (2 s, 6H, C(C*H*$_3$)$_2$), 2.38 (s, 3H, Ar-C*H*$_3$), 3.79 and 3.85 (2 s, 6H, COOC*H*$_3$), 3.88–4.13 (m, 4H, OC*H*$_2$), 5.44 (d, $^{2}J$(P-H) = 24.0 Hz, 1H, PC*H*), 7.22–8.00 (m, 7H, Ar-*H*).

$^{13}$C NMR: δ 19.9 (s, Ar-*C*H$_3$), 21.1 and 21.6 (2 s, C(*C*H$_3$)$_2$), 32.5 (d, $^{3}J$(P-C) = 6.0 Hz, *C*(CH$_3$)$_2$), 43.1 (d,$^{1}$ *J*(P-C) = 134.0 Hz, P*C*H), 52.4 and 52.6 (2 s, COO*C*H$_3$), 76.0 (d, $^{2}J$(P-C) = 7.0 Hz, O*C*H$_2$), 76.2 (d, $^{2}J$(P-C) = 6.0 Hz, O*C*H$_2$), 127.5, 128.7, 129.6 (d, $^{2}J$(P-C) = 8.0 Hz), 131.9 (d, $^{2}J$(P-C) = 11.0 Hz), 132.3 (d, $^{3}J$(P-C) = 5.0 Hz), 132.5, 133.0 (d, $^{3}J$(P-C) = 3.0 Hz), 133.1, 135.7 (d, $^{3}J$(P-C) = 6.0 Hz), 136.1, 168.5 and 168.6 (2 s, *C*OOCH$_3$).

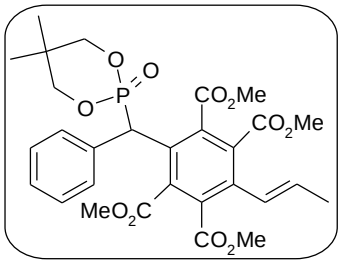
$^{31}$P NMR: δ 19.0.

LC/MS: m/z 447 [M+1]$^{+}$.

Anal. Calcd. For $C_{23}H_{27}O_7P$: C, 61.88; H, 6.10. Found: C, 61.68; H, 6.02.

This compound was crystallized from ethyl acetate/hexane (4:1) mixture at 25 $^{o}$C. X-ray structure was determined for this compound.

***Compound 21b***




Compound **21b** was isolated by using ethyl acetate/hexane (3:2) mixture.

Yield: quantitative [**21a+21b+21(c,d)**] by $^{31}$P NMR, 0.19 g (isolated, 14%, **21b**).

Mp: 126-128 $^{o}$C.

IR (KBr): 2953, 1732, 1439, 1314, 1254, 1204, 1059, 1007, 824, 696, 534 cm$^{-1}$.

$^{1}$H NMR: δ 0.87 and 0.99 (2 s, 6H, C(C*H*$_3$)$_2$), 1.83 (d, $^{3}J$(H-H) = 6.4 Hz, 3H, CH=CH-C*H*$_3$), 3.64 (s, 6H, COOC*H*$_3$), 3.67-3.88 (m, 2H, OC*H*$_2$) 3.80 (s, 3H, COOC*H*$_3$), 4.13-4.21 (m, 2H, OC*H*$_2$), 5.78-5.85 (m, 2H, Ar-C*H*=C*H*-CH$_3$), 6.43 (d, $^{2}J$(P-H) = 16.0 Hz, 1H, PC*H*), 7.22–7.47 (m, 5H, Ar-*H*).

$^{13}$C NMR: δ 19.0 (CH=CH-*C*H$_3$), 21.4 and 21.6 (2 s, C(*C*H$_3$)$_2$), 32.6 (d, $^3J$(P-C) = 7.0 Hz, *C*(CH$_3$)$_2$), 44.6 (d, $^1J$(P-C) = 139.0 Hz, P*C*H), 52.7 and 52.8 (2 s, COO*C*H$_3$), 75.7 (d, $^2J$(P-C) = 4.0 Hz, O*C*H$_2$), 125.3, 127.0, 128.1, 129.9 (d, $^2J$(P-C) = 10.0 Hz), 131.6 (d, $^2J$(P-C) = 7.0 Hz), 134.0, 134.8, 135.2, 135.4, 135.5$_1$, 135.5$_7$, 166.7 and 167.5 (2 s, *C*OOCH$_3$).

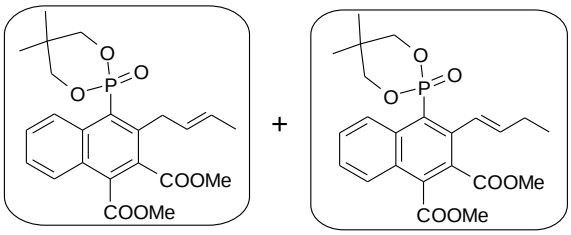
$^{31}$P NMR: δ 17.6.

LC/MS: m/z 589 $[M+1]^+$.

Anal. Calcd. For $C_{29}H_{33}O_{11}P$: C, 59.18; H, 5.65. Found: C, 59.15; H 5.58.

This compound was crystallized from ethyl acetate at 25 $^o$C. X-ray structure was determined for this compound.

***Compounds 21(c,d)***




Isomeric compounds **21(c,d)** were eluted by using ethyl acetate/hexane (2:3) mixture.

Yield: quantitative **[21a+21b+21(c,d)**] by $^{31}$P NMR, 0.44 g (isolated, 43%, **21(c,d)** ~ 1:1), gummy.

IR (neat): 2963, 2928, 1734, 1447, 1416, 1261, 1094, 1019, 801 cm$^{-1}$.

$^1$H NMR: δ 0.66 and 0.67 (2 s, 6H, C-C*H*$_3$), 0.81 (t, $^3J$(H-H) = 7.0 Hz, 3H, CH$_2$-C*H*$_3$, isomer **21d**), 1.27 and 1.29 (2 s, 6H, C-C*H*$_3$), 1.57 (d, $^3J$(H-H) = 4.4 Hz, 2H, CH-C*H*$_3$, isomer **21c**), 3.54-3.77 (m, 4H, OC*H*$_2$), 3.82-3.83 (2 s, 6H, COOC*H*$_3$), 3.86-3.94 (m, 4H, OC*H*$_2$), 3.96–3.97 (2 s, 6H, COOC*H*$_3$), 4.06 (s, 2H, Ar-C*H*$_2$, isomer **21c**), 5.38-5.46 (m, 2H, CH=C*H*), 5.75-5.81 (m, 1H, C*H*=CH), 6.67 (d, $^3J$(H-H) = 11.2 Hz, 1H, C*H*=CH, isomer **21d**), 7.52–8.70 (m, 8H, Ar-*H*).

$^{13}$C NMR: δ 20.5, 20.5$_2$, 22.0 and 22.1 (4 s, C(*C*H$_3$)$_2$ + CH$_2$*C*H$_3$), 32.1$_0$, 32.1$_1$, and 32.2 (3 s, *C*(CH$_3$)$_2$ + CH-*C*H$_2$-CH$_3$), 35.7 (d, $^3J$(P-C) = 5 Hz, Ar-*C*H$_2$), 52.7, 53.1$_0$, and 53.1$_3$ (3 s, all COO*C*H$_3$), 76.9 and 77.0 (2 s, O*C*H$_2$), 125.2, 125.3, 125.4, 125.9, 126.1, 126.2, 126.6 (d, $^3J$(P-C) = 4.0 Hz, Ar-*C*), 126.9, 127.1

(d, $^{3}J$(P-C) = 4.0 Hz, Ar-*C*), 127.6, 127.9, 128.0, 128.5 (d, $^{2}J$(P-C) = 12.0 Hz, Ar-*C*), 128.9, 129.0, 131.5, 131.7, 133.6, 133.7, 133.9 (d, $^{2}J$(P-C) = 12.0 Hz, Ar-*C*), 135.0 (d, $^{3}J$(P-C) = 4.0 Hz, Ar-*C*), 138.5, 138.8 (d, $^{2}J$(P-C) = 11.0 Hz, Ar-*C*), 142.2 (d, $^{2}J$(P-C) = 12.0 Hz, Ar-*C*), [The doublet due to $^{1}J$(P-C) was not clear], 167.5 167.9 and 168.1 (3 s, all *C*OOCH$_3$).

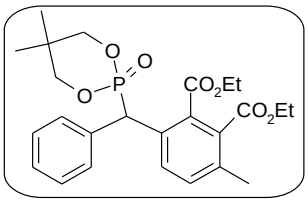
$^{31}$P NMR: δ 9.7 and 11.1.

LC/MS: m/z 447 $[M+1]^{+}$.

Anal. Calcd. For $C_{23}H_{27}O_7P$: C, 61.88; H, 6.10. Found: C, 61.75; H 6.22.

***Compound 22a***

Compounds **22a-d** were prepared by using allenylphosphonate (**10a**) (0.80 g, 2.63 mmol) and DEAD (1.34 g, 7.89 mmol).




Compound **22a** was isolated by using ethyl acetate/hexane (1:1) mixture.

Yield: quantitative [**22a**+**22b**+**22(c,d)**, ratio 3:2:5 by $^{31}$P NMR], 0.25 g (isolated, 25%, **22a**).

Mp: 128–130 $^{o}$C.

IR (KBr): 2973, 2926, 1728, 1472, 1370, 1285, 1059, 826, 700 cm$^{-1}$.

$^{1}$H NMR: δ 0.89 and 1.07 (2 s, 6H, C(C*H*$_3$)$_2$), 1.26 and 1.36 (2 t, $^{3}J$(H-H) = 6.0 Hz each, 6H, CH$_2$-C*H*$_3$), 2.39 (s, 3H, Ar-C*H*$_3$), 3.86-4.13 (m, 4H, OC*H*$_2$), 4.25 and 4.32 (2 qrt, 4H, COOC*H*$_2$CH$_3$), 5.46 (d, $^{2}J$(P-H) = 24.0 Hz, 1H, PC*H*), 7.22–8.02 (m, 7H, Ar-*H*).

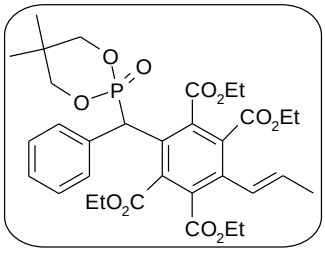
$^{13}$C NMR: δ 13.8 and 14.0 (2 s, CH$_2$-*C*H$_3$), 19.8 (s, Ar-*C*H$_3$), 21.0 and 21.5 (2 s, C(*C*H$_3$)$_2$), 32.4 (d, $^{3}J$(P-C) = 6.0 Hz, *C*(CH$_3$)$_2$), 43.0 (d,$^{1}J$(P-C) = 134.0 Hz, P*C*H), 61.4 and 61.7 (2 s, COO*C*H$_2$CH$_3$), 75.9 and 76.1 (2 d, $^{2}J$(P-C) = 6.0 Hz each, O*C*H$_2$), 127.3, 128.6, 129.5 (d, $^{2}J$(P-C) = 8.0 Hz), 132.0 (d, $^{3}J$(P-C) = 5.0 Hz), 132.1 (d, $^{2}J$(P-C) = 11.0 Hz), 132.7, 132.8, 135.6 (d, $^{3}J$(P-C) = 6.0 Hz), 135.7, 168.0$_0$ and 168.0$_2$ (2 s, *C*OOCH$_3$).

$^{31}$P NMR: δ 19.1.

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

Anal. Calcd. For $C_{25}H_{31}O_7P$: C, 63.28, H, 6.59. Found: C, 63.41; H, 6.52.

***Compound 22b***




Compound **22b** was isolated by using ethyl acetate/hexane (3:2) mixture.

Yield: quantitative [**22a**+**22b**+**22(c,d)**] by $^{31}$P NMR, 0.25 g (isolated, 15%, **22b**).

Mp: 124-126 $^{o}$C.

IR (KBr): 2975, 2926, 1728, 1727, 1470, 1414, 1370, 1198, 1061, 1013, 824, 700 $cm^{-1}$.

$^1$H NMR: δ 0.82 and 1.00 (2 s, 6H, C($CH_3$)$_2$), 1.10 and 1.29 (2 t, 12H, $^3J$(H-H) = 6.6 Hz and 6.8 Hz respectively, $CH_2$-$CH_3$), 1.81 (d, $^3J$(H-H) = 6.0 Hz, 3H, =CH-$CH_3$), 3.67 (dd→t, $^3J$(P-H) = $^2J$(H-H) ~ 12.0 Hz each, 2H, O$CH_AH_B$), 3.84 (dd→t, $^3J$(P-H) = $^2J$(H-H) ~ 12.0 Hz each, 2H, O$CH_AH_B$), 4.12 and 4.26 (2 qrt, 8H, COO$CH_2$$CH_3$), 5.74-5.86 (m, 2H, Ar-C*H*=C*H*-$CH_3$), 6.43 (d, $^2J$(P-H) = 15.6 Hz, 1H, PC*H*), 7.19–7.46 (m, 5H, Ar-*H*).

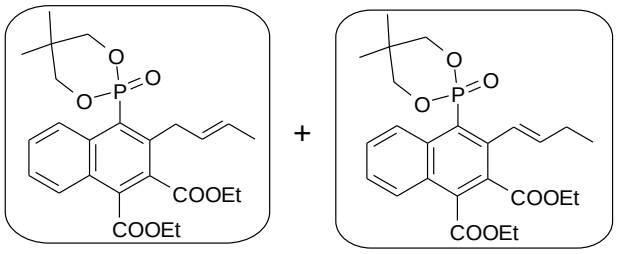
$^{13}$C NMR: δ 13.5 and 14.0 (2 s, $CH_2$$CH_3$), 18.7 (CH=CH-$CH_3$), 21.3 and 21.7 (2 s, C($CH_3$)$_2$), 32.5 (d, $^3J$(P-C) = 6.9 Hz, $C$($CH_3$)$_2$), 44.9 (d, $^1J$(P-C) = 138.5 Hz, P*C*H), 61.8 and 62.1 (2 s, COO$CH_2$$CH_3$), 75.9 and 76.0 (2 s, O$CH_2$), 125.6, 126.9, 128.0, 130.1 (d, $^2J$(P-C) = 8.9 Hz), 131.1 (d, $^2J$(P-C) = 7.4 Hz), 133.5, 134.8, 135.2 (d, $^3J$(P-C) = 5.4 Hz), 135.7 (d, $^3J$(P-C) = 6.4 Hz), 166.2 and 167.1 (2 s, *C*OO$CH_3$).

$^{31}$P NMR: δ 17.2.

LC/MS: m/z 645 $[M+1]^+$.

Anal. Calcd. For $C_{33}H_{41}O_{11}P$: C, 61.48; H, 6.41. Found: C, 61.32; H, 6.45.

***Compounds 22(c,d)***




Isomeric compounds **22(c,d)** were eluted by using ethyl acetate/hexane (2:3) mixture.

Yield: quantitative **[22a**+**22b**+**22(c,d)**] by $^{31}$P NMR, 0.41 g (isolated, 42%, **22(c,d)** ~ 1:1), gummy.

IR (neat): 2978, 2942, 1730, 1470, 1372, 1258, 1059, 828, 785 cm$^{-1}$.

$^{1}$H NMR: δ 0.71 and 0.73 (2 s, 6H, C-C*H*$_3$), 0.87 (t, $^{3}J$(H-H) = 8.0 Hz, 3H, CH$_2$C*H*$_3$, isomer **22d**), 1.29-1.47 (m, 18H, 2 C-C*H*$_3$ + 4 CH$_2$C*H*$_3$), 1.62 and 1.64 (2 br s, 5H, =CHC*H*$_2$Me of isomer **22d** + =CHC*H*$_3$ of isomer **22c**), 3.58-3.97 (m, 8H, OC*H*$_2$), 4.12 (s, 2H, Ar-C*H*$_2$, isomer **22c**), 4.29-4.50 (m, 8H, COOC*H*$_2$Me), 5.45-5.85 (m, 3H, C*H*=C*H* + CH=C*H*), 6.71 (d, $^{3}J$(H-H) = 12.0 Hz, 1H, C*H*=CH, isomer **22d**), 7.59-8.74 (m, 8H, Ar-*H*).

$^{13}$C NMR: δ 13.3, 13.8, 14.0$_0$, 14.0$_3$ and 14.1 (5 s, CH$_2$*C*H$_3$ + COOCH$_2$*C*H$_3$), 17.9 (s, =C*C*H$_2$Me), 20.4 , 20.5, 21.9$_5$, 22.0$_3$ and 22.1 (5 s, C(*C*H$_3$)$_2$), 32.0 and 32.1 (2 d, $^{3}J$(P-C) = 5.0 Hz and 7.0 Hz respectively, *C*(CH$_3$)$_2$), 35.5 (d, $^{3}J$(P-C) = 5.0 Hz, Ar-*C*H$_2$, isomer **22c**), 61.8, 61.9, 62.3 and 63.3 (4 s, COO*C*H$_2$Me), 76.3 and 76.5 (2 d, $^{3}J$(P-C) = 7.0 and 5.0 Hz respectively, 2 O*C*H$_2$), 76.9$_0$ and 76.9$_2$ (2 s, 2 O*C*H$_2$), 125.4, , 125.6, 126.0, 126.1, 126.5 (d, $^{3}J$(P-C) = 4.0 Hz), 127.0 (d, $^{3}J$(P-C) = 4.0 Hz), 127.3, 127.5, 127.7, 127.9, 128.1, 128.5, 128.6, 128.7, 128.8, 131.6 (d, $^{2}J$(P-C) = 18.0 Hz), 132.1 (d, $^{2}J$(P-C) = 17.0 Hz), 133.5, 133.6, 133.7, 133.8, 133.9, 135.1 (d, $^{3}J$(P-C) = 4.0 Hz), 138.4, 138.8 (d, $^{2}J$(P-C) = 11.0 Hz), 142.3 (d, $^{2}J$(P-C) = 9.0 Hz), 167.0, 167.5 and 167.6 (3 s, all *C*OOEt).

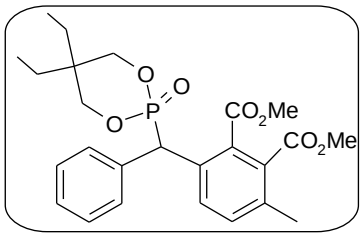
$^{31}$P NMR: δ 9.9 and 11.3.

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, 6.62.

***Compound 23a***

Compounds **23a-d** were prepared by using allenylphosphonate (**10b**) (0.35 g, 1.1 mmol) and DMAD (0.45 g, 3.2 mmol).




Compound **23a** was isolated by using ethyl acetate/hexane (2:3) mixture.

Yield: quantitative [**23a**+**23b**+**23(c,d)**, ratio 3:2:5 by $^{31}$P NMR], 0.13 g (isolated, 24%, **23a**).

Mp: 132–134 $^{o}$C.

IR (KBr): 2963, 1742, 1721, 1601, 1433, 1281, 1196, 1076, 1032, 835, 787, 696, 517 cm$^{-1}$.

$^{1}$H NMR: δ 0.77 and 0.82 (2 t, $^{3}J$(H-H) = 6.0 Hz and 8.0 Hz respectively, 6H, C(CH$_2$C*H*$_3$)$_2$), 1.19 and 1.49 (2 qrt, 4H, C(C*H*$_2$Me)$_2$), 2.38 (s, 3H, Ar-C*H*$_3$), 3.80 and 3.85 (2 s, 6H, COOC*H*$_3$), 3.87–4.16 (m, 4H, OC*H*$_2$), 5.45 (d, $^{2}J$(P-H) = 24.0 Hz, 1H, PC*H*), 7.23–7.99 (m, 7H, Ar-*H*).

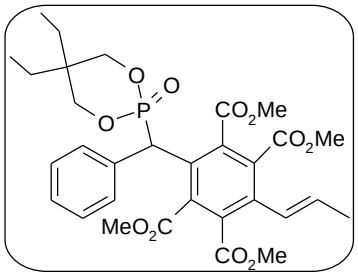
$^{13}$C NMR: δ 7.0 and 7.1 (2 s, C(CH$_2$*C*H$_3$)$_2$), 19.9 (s, Ar-*C*H$_3$), 22.5 and 22.8 (2 s, C(*C*H$_2$CH$_3$)$_2$), 37.4 (d, $^{3}J$(P-C) = 5.7 Hz, *C*(Et)$_2$), 43.1 (d, $^{1}J$(P-C) = 133.4 Hz, P*C*H), 52.4 and 52.6 (2 s, COO*C*H$_2$Me), 73.4 and 73.6 (2 d, $^{3}J$(P-C) = 6.5 Hz and 6.3 Hz respectively, O*C*H$_2$), 127.5, 128.7, 129.6, 129.7, 131.9, 132.3 (d, $^{3}J$(P-C) = 5.1 Hz), 132.6, 133.1, 135.8 (d, $^{3}J$(P-C) = 5.0 Hz), 136.1, 168.5$_1$ and 168.5$_4$ (s, 2 *C*OOEt).

$^{31}$P NMR: δ 19.9.

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 6.62.

***Compound 23b***




Compound **23b** was isolated by using ethyl acetate/hexane (2:3) mixture.

Yield: quantitative [**23a**+**23b**+**23(c,d)**] by $^{31}$P NMR, 0.10 g (isolated, 14%, **23b**).

Mp: 124-126 $^{o}$C.

IR (KBr): 2965, 1732, 1636, 1439, 1395, 1256, 1075, 941, 831, 733, 704 cm$^{-1}$.

$^{1}$H NMR: δ 0.69 and 0.79 (2 t, $^{3}J$(H-H) = 8.0 Hz each, 6H, C(CH$_2$C*H*$_3$)$_2$), 1.13 and 1.37 (2 qrt, 4H, C(C*H*$_2$CH$_3$)$_2$), 1.83 (d, $^{3}J$(H-H) = 4.0 Hz, 3H, =CHC*H*$_3$), 3.62 and 3.79 (2 s, 12H, COOC*H*$_3$), 3.93 (dd→t, $^{3}J$(P-H) = $^{2}J$(H-H) ~ 12.0 Hz, 2H, OC*H*$_2$), 4.18 (dd→t, $^{3}J$(P-H) = $^{2}J$(H-H) ~ 10.0 Hz, 2H, OC*H*$_2$), 5.74-5.86 (m, 2H, C*H*=C*H*Me), 6.42 (d, $^{2}J$(P-H) = 16.0 Hz, 1H, PC*H*), 7.21-7.47 (m, 5H, Ar-*H*).

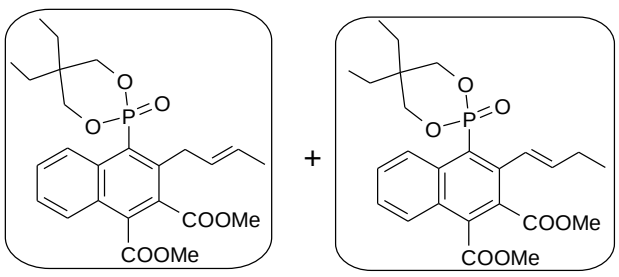
$^{13}$C NMR: δ 7.0 (s, C(CH$_2$*C*H$_3$)$_2$), 19.0 (s, CH=CH*C*H$_3$)$_2$), 22.3 and 23.3 (2 s, C(*C*H$_2$CH$_3$)$_2$), 37.4 (d, $^{3}J$(P-C) = 5.0 Hz, *C*(Et)$_2$), 44.8 (d, $^{1}J$(P-C) = 138.0 Hz, P*C*H), 52.7 and 52.9 (2 s, COO*C*H$_3$), 73.0 and 73.4 (2 d, $^{3}J$(P-C) = 6.0 Hz each, O*C*H$_2$), 125.3, 127.1, 128.2, 130.1, 130.2, 131.8 (d, $^{3}J$(P-C) = 7.0 Hz), 134.0, 134.8, 135.4 (d, $^{2}J$(P-C) = 22.0 Hz), 135.6 (d, $^{3}J$(P-C) = 6.0 Hz), 166.7 and 167.6 (2 s, *C*OOCH$_3$).

$^{31}$P NMR: δ 18.3.

LC/MS: m/z 618 [M+1]$^{+}$.

Anal. Calcd. For $C_{31}H_{37}O_{11}P$: C, 60.39; H, 6.05. Found: C, 60.29; H, 6.12.

***Compounds 23(c,d)***



Isomeric compounds **23(c,d)** were eluted by using ethyl acetate/hexane (1:2) mixture.

Yield: quantitative [**23a**+**23b**+**23(c,d)**] by $^{31}$P NMR, 0.22 g (isolated, 42%, **23 (c,d)**, ratio ~1:1), gummy.

IR (neat): 2967, 2888, 1734, 1647, 1445, 1254, 1075, 833, 783 cm$^{-1}$.

$^{1}$H NMR: δ 0.67-1.10 (m, 23H, 4 C(C*H*$_2$C*H*$_3$) + CH$_2$C*H*$_3$ of isomer **23d**), 1.63 (d, $^{3}J$(H-H) = 4.0 Hz, 3H, CH-C*H*$_3$, isomer **23c**), 1.77-1.86 (m, 2H, isomer **23d**) =CC*H*$_2$Me), 3.57-3.61 (m, 4H, OC*H*$_2$), 3.87, 3.88, 4.02 and 4.03 (4 s, 12H, COOC*H*$_3$), 4.05-4.13 (m, 6H, OC*H*$_2$ + ArC*H*$_2$ of isomer **23c**), 5.44-5.86 (m, 3H, C*H*=C*H* + CH=C*H*), 6.72 (dd, $^{3}J$(H-H) = 11.8 Hz, $^{4}J$(P-H) ~ 1.8 Hz, 1H, Ar-C*H*=CH of isomer **23d**), 7.57-8.75 (m, 8H, Ar-*H*).

$^{13}$C NMR: δ 6.8 and 7.3 (2 s, C(CH$_2$*C*H$_3$)$_2$), 13.4 (s, CH$_2$*C*H$_3$), 18.0, 22.0, 22.1$_0$, 22.1$_4$ and 22.9 (5 s, C(*C*H$_2$CH$_3$)$_2$ + =C*C*H$_2$Me), 35.6 (d, $^{3}J$(P-C) = 4.7 Hz, Ar-*C*H$_2$), 37.1 and 37.2 (2 d, $^{3}J$(P-C) = 5.7 Hz and 5.0 Hz respectively), 52.7, 53.1$_0$ and 53.1$_3$ (3 s, 4 COO*C*H$_3$), 73.8 and 74.0 (2 s, O*C*H$_2$), 74.4 (d, $^{3}J$(P-C) = 6.3 Hz, O*C*H$_2$), 125.4, 125.5 (d, $^{3}J$(P-C) = 4.0 Hz), 126.1, 126.2, 126.8 (d, $^{3}J$(P-C) = 3.7 Hz), 127.1, 127.2, 127.6, 128.0$_0$, 128.0$_2$, 128.1, 128.2, 128.5, 128.8, 129.0, 131.6 (d, $^{2}J$(P-C) = 16.8 Hz), 132.1 (d, $^{2}J$(P-C) = 16.8 Hz), 133.6, 133.7, 133.8, 133.9, 134.0, 134.1, 134.9, 138.4, 138.8 (d, $^{2}J$(P-C) = 11.0 Hz), 142.1 (d, $^{2}J$(P-C) = 12.6 Hz) [The doublet due to $^{1}J$(P-C) was not clear], 167.6, 168.0$_0$, 168.0$_2$ and 168.1.

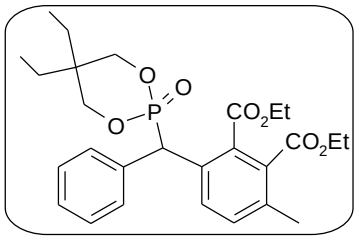
$^{31}$P NMR: δ11.0 and 12.5.

LC/MS: m/z 474 [M]$^{+}$.

Anal. Calcd. For $C_{25}H_{31}O_7P$: C, 63.28; H, 6.59. Found: C, 63.45; H, 6.51.

***Compound 24a***

Compounds **24a-d** were prepared by using allenylphosphonate (**10b**) (0.40 g, 1.20 mmol) and DEAD (0.62 g, 3.60 mmol).



Compound **24a** was isolated by using ethyl acetate/hexane (1:1) mixture.

Yield: quantitative [**24a**+**24b**+**24(c,d)**, ratio 3:2:5 by $^{31}$P NMR], 0.13 g (isolated, 22%, **24a**), gummy.

IR (neat): 2980, 2938, 1728, 1468, 1075, 1024, 835, 698 cm$^{-1}$.

$^{1}$H NMR: δ 0.76 and 0.82 (2 t, $^{3}J$(H-H) = 7.6 Hz each, 6H, C(CH$_2$C*H*$_3$)$_2$), 1.14 (m, 8H, C(C*H*$_2$CH$_3$ + COOCH$_2$C*H*$_3$), 1.49 (qrt, 2H, C(C*H*$_2$CH$_3$), 2.39 (s, 3H, Ar-C*H*$_3$), 3.91 and 4.19 (m, 4H, OC*H*$_2$), 4.24 and 4.32 (2 qrt, 4H, COOC*H*$_2$Me), 5.47 (d, $^{2}J$(P-H) = 23.6 Hz, 1H, PC*H*), 7.22–8.00 (m, 7H, Ar-*H*).

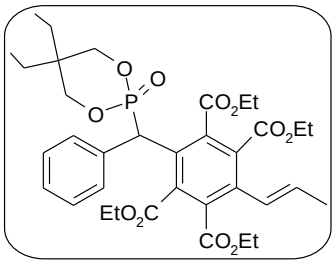
$^{13}$C NMR: δ 7.0 and 7.1 (2 s, C(CH$_2$*C*H$_3$)$_2$), 13.9 and 14.1 (2 s, COOCH$_2$-*C*H$_3$), 19.9 (s, Ar-*C*H$_3$), 22.5 and 22.8 (2 s, C(CH$_2$*C*H$_3$)$_2$), 37.3 (d, $^{3}J$(P-C) = 5.0 Hz, *C*(Et)$_2$), 43.0 (d,$^{1}J$(P-C) = 134.0 Hz, P*C*H), 61.4 and 61.7 (2 s, COO*C*H$_2$CH$_3$), 73.4 and 73.5 (2 d, $^{3}J$(P-C) = 8.0 Hz and 7.0 Hz respectively, O*C*H$_2$), 127.4, 128.6, 129.6 (d, $^{2}J$(P-C) = 8.0 Hz), 132.1 (d, $^{3}J$(P-C) = 5.0 Hz), 132.3, 132.8, 135.8, 168.0 and 168.1 (2 s, *C*OOEt).

$^{31}$P NMR: δ 20.0.

LC/MS: m/z 502 [M]$^{+}$.

Anal. Calcd. For $C_{27}H_{35}O_7P$: C, 64.53; H, 7.02. Found: C, 64.59; H, 6.93.

***Compound 24b***



Compound **24b** was isolated by using ethyl acetate/hexane (3:2) mixture.

Yield: quantitative [**24a**+**24b**+**24(c,d)**] by $^{31}$P NMR, 0.11 g (isolated, 13%, **24b**), gummy.

IR (neat): 2975, 2938, 1732, 1603, 1470, 1416, 1287, 1192, 1076, 1032, 938, 843, 787, 700, 623 $cm^{-1}$.

$^{1}H$ NMR: δ 0.67 and 0.79 (2 t, $^{3}J$(H-H) = 7.4 Hz and 7.6 respectively, 6H, $C(CH_2CH_3)_2$), 1.05-1.44 (m, 16H, $C(CH_2CH_3)$ + $COOCH_2CH_3$), 1.82 (d, $^{3}J$(H-H) = 6.4 Hz, 3H, $C{=}CCH_3$), 3.92-4.32 (m, 12H, 4 $COOCH_2CH_3$ + 2 $OCH_2$), 5.79-5.87 (m, 2H, CH=CH), 6.43 (d, $^{2}J$(P-H) = 16.0 Hz, 1H, P-CH), 7.20–7.47 (m, 5H, Ar-*H*).

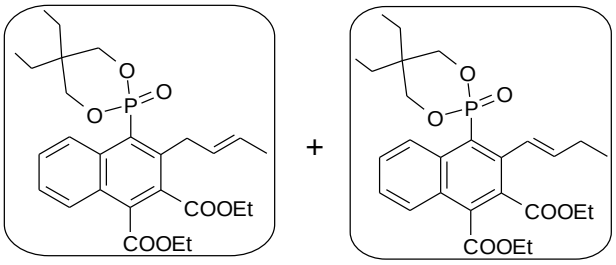
$^{13}C$ NMR: δ $7.0_0$ and $7.0_3$ (2 s, $C(CH_2CH_3)_2$), 13.5 and 14.0 (2 s, $COOCH_2$-$CH_3$), 18.8 (s, C=C-$CH_3$), 22.3 and 23.4 (2 s, $C(CH_2CH_3)_2$), 37.3 (d, $^{3}J$(P-C) = 5.7 Hz, $C(Et)_2$), 45.0 (d, $^{1}J$(P-C) = 137.7 Hz, PCH), 61.8 and 62.1 (2 s, $COOCH_2CH_3$), 73.1 and 73.4 (2 d, $^{3}J$(P-C) = 6.4 Hz and 6.8 Hz, $OCH_2$), 125.5, 126.9, 128.0, 130.4 (d, $^{2}J$(P-C) = 9.9 Hz), 131.5 (d, $^{3}J$(P-C) = 6.3 Hz), 133.5, 134.7, 135.0, 135.2, 135.6 (d, $^{3}J$(P-C) = 7.7 Hz), 166.2 and 167.1 (2 s, COOEt).

$^{31}P$ NMR: δ 17.8.

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

Anal. Calcd. For $C_{35}H_{45}O_{11}P$: C, 64.53; H, 7.02. Found: C, 62.31; H, 6.82.

***Compounds 24(c,d)***




Isomeric compounds **24(c,d)** were eluted by using ethyl acetate/hexane (2:3) mixture.

Yield: quantitative [**24a**+**24b**+**24(c,d)]** by $^{31}P$ NMR, 0.24 g (isolated, 40%, **24 (c,d)**, ratio ~ 1:1), gummy.

IR (neat): 2976, 2936, 1732, 1719, 1555, 1464, 1372, 1262, 1154, 1075, 1034, 938, 835, 737, 700, 625 $cm^{-1}$.

$^{1}H$ NMR: δ 0.70-1.07 (m, 23H, 4 $C(CH_2CH_3)$ + $CH_2CH_3$ of isomer **24d**), 1.35-1.46 (m, 12H, 4 $COOCH_2CH_3$), 1.62 (d, $^{3}J$(H-H) = 4.4 Hz, 3H, =CH-$CH_3$, isomer **24c**), 1.77-1.86 (m, 2H, $=CCH_2Me$, isomer **24d**), 3.57 and 3.60 (m each, 4H,

2 OC$H_2$), 4.04-4.12 (m, 6H, 2 OC$H_2$ + Ar-C$H_2$ of isomer **24c**), 4.32 and 4.49 (2 qrt, 8H, 4 COOC$H_2$CH$_3$), 5.45-5.85 (m, 3H, C*H*=C*H* + CH=C*H*), 6.72 (d, $^3J$(H-H) = 11.2 Hz, 1H, C*H*=CH, isomer **24d**), 7.57-8.74 (m, 8H, Ar-*H*).

$^{13}$C NMR: δ 6.8 and 7.3 (2 s, C(CH$_2$*C*H$_3$)$_2$), 13.4, 13.9, 14.0, 14.1$_0$ and14.1$_3$ (5 s, 4 COOCH$_2$*C*H$_3$ + CH$_2$*C*H$_3$), 18.0 (s, =C*C*H$_2$Me), 21.9, 22.1 and 22.8 (3 s, 4 C(*C*H$_2$CH$_3$)$_2$), 35.5 (d, $^3J$(P-C) = 3.6 Hz, Ar-*C*H$_2$), 37.0 and 37.1 (2 d, $^3J$(P-C) = 4.9 Hz and 5.4 Hz respectively), 61.8, 61.9, 62.3$_0$ and 62.3$_4$ (4 s, 4 COO*C*H$_2$Me), 74.3 and 74.4 (2 s, O*C*H$_2$), 125.1, 125.5 (d, $^3J$(P-C) = 4.0 Hz), 125.7 (d, $^2J$(P-C) = 9.4 Hz), 125.9, 126.0, 126.1, 126.6, 126.7 (d, $^3J$(P-C) = 4.1 Hz), 126.9, 127.1 (d, $^3J$(P-C) = 4.5 Hz), 127.5, 127.7, 127.9, 128.0$_0$, 128.0$_4$, 128.1, 128.3, 128.7, 128.8, 129.7, 129.8 (d, $^3J$(P-C) = 5.3 Hz), 131.3, 131.5, 131.7, 132.1, (d, $^3J$(P-C) = 5.6 Hz), 133.5, 133.7, 133.8, 133.9, 135.1, 135.2, 138.4, 138.8, 142.0 (d, $^2J$(P-C) = 11.8 Hz), 146.2, 147.5 [The doublet due to $^1J$(P-C) was not clear], 167.5 and 167.6 (2 s, 4 *C*OOEt).

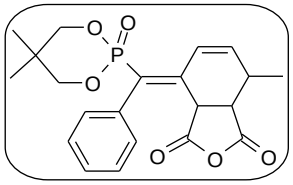
$^{31}$P NMR: δ 11.1 and 12.6.

LC/MS: m/z 503 $[M+1]^+$.

Anal. Calcd. For $C_{27}H_{35}O_7P$: C, 64.53; H, 7.02. Found: C, 64.42; H, 7.11.

***Compound 25 (and its hydrolysis product 27)***

A mixture of allenylphosphonate **10a** (0.30 g, 1.00 mmol) and maleic anhydride (0.29 g, 3.00 mmol) in xylene (3 mL) was heated under reflux for 12 h. The solvent was removed under reduced pressure to obtain a solid. From this, the product **25** was separated by column chromatography using 1:1 EtOAc/hexane mixture as the eluent. In our attempts to crystallize **25**, a few crystals of **27** was obtained for which X-ray structure was determined; no further data were collected for **27**.



Yield: 0.25 g (62 %).

Mp: 166-168 $^o$C.

IR (KBr): 2915, 1704, 1638, 1595, 1567, 1463, 1436, 1260, 866, 784 $cm^{-1}$.

$^1$H NMR: δ 0.66 and 1.04 (2 s, 6H, C(C$H_3$)$_2$), 1.26 (d, $^3J$(H-H) = 8.0 Hz, 3H, CH-C$H_3$), 2.75 (br s, 1H, C*H*-$CH_3$), 3.33–3.35 (m, 2H, COC*H*-C*H*CO), 3.73-4.11 (m, 4H, OC$H_2$), 6.10 (d, $^4J$(P-H) = 12.0 Hz, 1H, PC=C-C*H*, ), 7.24–7.43 (m, 5H, Ar-*H*), 7.64 (br s, 1H, =C-CH=C*H*).

$^{13}$C-NMR: δ 17.4 (s, CH-*C*$H_3$), 21.0 and 21.8 (2 s, C(*C*$H_3$)$_2$), 28.5 (s, *C*H-$CH_3$), 32.4 (d, $^3J$(P-C) = 6.5 Hz *C*(CH$_3$)$_2$), 43.9 (s, CH-*C*H-COO), 45.0 (d, $^2J$(P-C) = 18.5 Hz, =C-*C*H-CO), 76.0 (d, $^2J$(P-C) = 6.2 Hz, O*C*H$_2$), 76.1 (d, $^2J$(P-C) = 6.4 Hz, O*C*H$_2$), 126.4$_0$, 126.4$_3$, 128.6, 129.9 (d, $^1J$(P-C) = 172.4 Hz, P-*C*), 132.5, 135.1, 135.2, 138.3, 140.3 (d, $^3J$(P-C = 14.6 Hz, alkenyl-*C*), 169.8 and 170.3 (2 s, CH-*C*OO*C*O-CH).

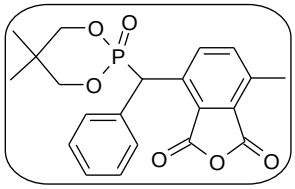
$^{31}$P NMR: δ 8.9.

LC/MS: m/z 403 $[M+1]^+$.

Anal. Calcd. For $C_{21}H_{23}O_6P$: C, 62.68; H, 5.76. Found: C, 62.78; H, 5.71.

***Compound 26***

A mixture of allenylphosphonate **10a** (0.30 g, 1.00 mmol) and maleic anhydride (0.29 g, 3.00 mmol) in xylene (3 mL) was heated at 100 $^oC$ for 6 h. The solvent was removed under reduced pressure to obtain a solid from this the product **26** was separated by column chromatography using 1:1 EtOAc/hexane mixture as the eluent.



Yield: 0.344 g (86 %).

Mp: 172-174 $^oC$.

IR (KBr): 2969, 2926, 1734, 1727, 1622, 1472, 1215, 1057, 1005, 837, 704 $cm^{-1}$.

$^1$H NMR: δ 0.97 and 1.13 (2 s, 6H, C(C$H_3$)$_2$), 2.68 (s, 3H, Ar-C$H_3$), 3.94-4.11 (m, 4H, OC$H_2$), 6.01 (d, $^2J$(P-H) = 22.0 Hz, 1H, PC*H*), 7.29-8.31 (m, 7H, Ar-*H*).

$^{13}$C-NMR: δ 17.5 (s, Ar*C*H$_3$), 21.1 and 21.6 (2 s, C(*C*H$_3$)$_2$), 32.6 (d, $^3J$(P-C) = 6.7 Hz *C*(CH$_3$)$_2$), 41.2 (d, $^1J$(P-C) = 133.4 Hz, P-*C*), 76.7$_0$ and 76.7$_2$ (2 s, O*C*H$_2$),

127.9, 128.0, 128.1, 128.4, 128.8, 129.1, 129.5, 129.6, 134.7, 134.9, 137.7, 137.8, 138.7, 139.7 (Ar-*C*), 162.3 and 164.0 (2 s, CH-*C*OO*C*O-CH).

$^{31}$P NMR: δ 16.7.

HRMS (ESI): Calcd. for $C_{21}H_{22}O_6P$ [$M^+$+H]: *m/z* 401.1155. Found: 401.1266.

Anal. Calcd. For $C_{21}H_{21}O_6P$: C, 63.00; H, 5.29. Found: C, 63.12; H, 5.38.

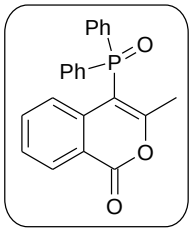
## 6.4 Intramolecular nucleophilic cyclization of functionalized allenylphosphine oxides

### *6.41 General procedure for the synthesis of compounds 28-35*

One of the allenes among **11a-h** (0.5 mmol) was treated with trifluoroacetic acid (2 mL) at rt for 6 h. Solvent was removed by vacuum and the crude product was purified by column chromatography using ethyl acetate/hexane (2:3 v/v) mixture as the eluent to obtain one of the phosphinoyl isocoumarins **28-35**.

***Compound 28***

This compound was prepared from allenylphosphine oxide **11a** (0.18 g, 0.5 mmol).




Yield: 0.159 g (88%).

Mp: 134-136 $^{o}$C.

IR (KBr): 3059, 2961, 1738, 1605, 1480, 1437, 1264, 1184, 1080, 1036, 801, 762, 687, 542, 523 cm$^{-1}$.

$^{1}$H NMR: δ 2.15 (s, 3H, C=CC*H*$_3$), 7.40-8.28 (m, 14H, Ar*H*).

$^{13}$C NMR: δ 21.2 (s, C=C*C*H$_3$), 105.8 (d, $^{1}J$(P-C) = 105.0 Hz, P-*C*), 120.1 (d, $^{2}J$(P-C) = 8.0 Hz, Ar-*C*), 126.8, 128.0, 129.0, 129.1, 129.5, 131.4, 131.5, 132.4, 132.7, 133.8, 134.3, 136.4 (d, $^{2}J$(P-C) = 8.0 Hz, Ar-*C*), 161.1 (s, *C*OO), 163.2 (d, $^{2}J$(P-C) = 18.0 Hz, P-C=*C*).

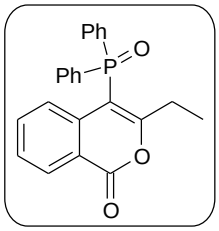
$^{31}$P NMR: δ 27.5.

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

Anal.Calcd. for $C_{22}H_{17}O_3P$: C, 73.33; H, 4.76. Found: C, 73.48; H, 4.65.

***Compound 29***

This compound was prepared from allenylphosphine oxide **11b** (0.194 g, 0.5 mmol).




Yield: 0.153 g (82%).

Mp: 132-134 $^{o}$C.

IR (KBr): 3054, 2976, 2915, 1719, 1599, 1483, 1439, 1291, 1194, 1123, 1088, 1065, 777, 698, 540, 517 $cm^{-1}$.

$^{1}$H NMR: δ 1.03 (t, 3H, $^{3}J$(H-H) = 7.4 Hz, $CH_2CH_3$), 2.60 (qrt, 2H, $^{3}J$(H-H) = 7.3 Hz, $CH_2CH_3$), 7.39-7.83 (m, 14H, Ar*H*).

$^{13}$C NMR: δ 12.4 (s, $CH_2CH_3$), 27.2 (s, $CH_2CH_3$), 105.1 (d, $^{1}J$(P-C) = 105.2 Hz, P-*C*), 120.3 (d, $^{2}J$(P-C) = 7.6 Hz, Ar-*C*), 127.1, 128.0, 129.0, 129.1, 129.6, 131.6, 131.7, 132.5, 132.9, 134.0, 134.3, 136.6 (d, $^{2}J$(P-C) = 7.8 Hz, Ar-*C*), 161.4 (s, *C*OO), 168.0 (d, $^{2}J$(P-C) = 18.6 Hz, P-C=*C*).

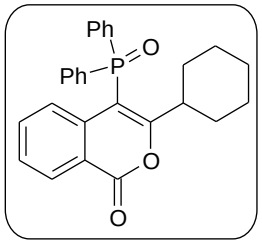
$^{31}$P NMR: δ 28.4.

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

Anal.Calcd. for $C_{23}H_{19}O_3P$: C, 73.79; H, 5.12. Found: C, 73.65; H, 5.18.

***Compound 30***

This compound was prepared from allenylphosphine oxide **11c** (0.221 g, 0.5 mmol).




Yield: 0.178 g (83%).

Mp: 148-150 $^{o}$C.

IR (KBr): 2931, 2849, 1742, 1605, 1578, 1479, 1177, 1112, 1062, 777 cm$^{-1}$.

$^{1}$H NMR: δ 0.57-0.67, 1.04-1.11 and 1.45-1.69 (m, 10H, cyclohexyl), 2.54 (m, 1H, cyclohexyl-C*H*), 7.39-8.30 (m, 14H, Ar*H*).

$^{13}$C NMR: δ 25.2, 25.6, 29.9 (3 s, -(*C*H$_2$)$_5$-), 41.2 (s, CH$_2$*C*HCH$_2$), 104.8 (d, $^{1}J$(P-C) = 106.6 Hz, P-*C*), 120.4 (d, $^{2}J$(P-C) = 7.9 Hz, Ar-*C*), 127.5, 128.0, 128.3, 128.5, 129.1, 129.2, 129.5, 130.1, 131.5, 131.6, 132.4, 133.3, 133.7, 134.4, 136.7, 136.8, 161.3 (s, *C*OO), 169.0 (d, $^{2}J$(P-C) = 18.9 Hz, P-C=*C*).

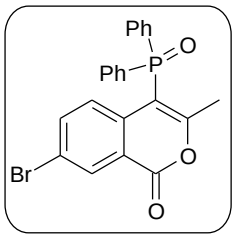
$^{31}$P NMR: δ 28.1.

LC/MS: *m/z* 429 [M+1]$^{+}$.

Anal.Calcd. for C$_{27}$H$_{25}$O$_3$P: C, 75.69; H, 5.88. Found: C, 75.48; H, 5.96.

***Compound 31***

This compound was prepared from allenylphosphine oxide **11e** (0.227 g, 0.5 mmol).




Yield: 0.196 g (89%).

Mp: 186-188 $^{o}$C.

IR (KBr): 3058, 2924, 2855, 1746, 1599, 1474, 1437, 1316, 1265, 1231, 1186, 1119, 1078, 814, 725, 698 cm$^{-1}$.

$^{1}$H NMR: δ 2.08 (s, 3H, C=CC*H*$_3$), 7.50-8.40 (m, 13H, Ar*H*).

$^{13}$C NMR: δ 21.4 (s, C=C*C*H$_3$), 105.7 (d, $^{1}J$(P-C) = 102.8 Hz, P-*C*=C), 121.8, 122.0, 128.6, 129.2, 129.3, 131.5, 131.6, 132.0, 132.4, 132.7, 133.4, 135.4 (d, $^{2}J$(P-C) = 6.5 Hz, Ar-*C*), 159.9 (s, Ar*C*OO), 163.3 (d, $^{2}J$(P-C) = 17.8 Hz, P-C=*C*).

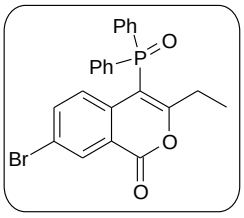
$^{31}$P NMR: δ 27.6.

LC/MS: *m/z* 439 [M+1]$^{+}$ and 441 [M+3]$^{+}$.

Anal.Calcd. for $C_{22}H_{16}BrO_3P$: C, 60.16; H, 3.67. Found: C, 60.26; H, 3.61.

***Compound 32***

This compound was prepared from allenylphosphine oxide **11f** (0.237 g, 0.5 mmol).




Yield: 0.195 g (86%).

Mp: 192-194 $^{o}$C.

IR (KBr): 3052, 2920, 2849, 1742, 1599, 1473, 1430, 1183, 1090, 728 cm$^{-1}$.

$^{1}$H NMR: δ 0.99 (t, 3H, $^{3}J$(H-H) = 7.4 Hz, $CH_2CH_3$), 2.53 (qrt, 2H, $^{3}J$(H-H) = 7.1 Hz, $CH_2CH_3$), 7.51-8.42 (m, 13H, Ar*H*).

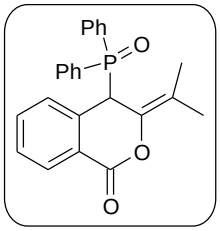
$^{13}$C NMR: δ 12.2 (s, $CH_2CH_3$), 27.3 (s, $CH_2CH_3$), 104.9 (d, $^{1}J$(P-C) = 104.7 Hz, P-*C*=C), 122.0, 128.8, 129.1, 129.3, 131.5, 131.6, 132.0, 132.7, 137.4, 160.1 (s, *C*OO), 167.9 (d, $^{2}J$(P-C) = 18.9 Hz, P-C=*C*).

$^{31}$P NMR: δ 27.9.

HRMS (ESI): Calcd. for $C_{23}H_{18}BrNaO_3P$ [$M^{+}$+Na]: *m/z* 475.0075 and 477.0075. Found: 475.0087 and 477.0070.

***Compound 33***

This compound was prepared from allenylphosphine oxide **11d** (0.201 g, 0.5 mmol).




Yield: 0.169 g (87%).

Mp: 200-202 $^{o}$C.

IR (KBr): 3058, 2928, 2855, 1730, 1678, 1595, 1439, 1231, 1183, 1161, 1117, 700, 534 cm$^{-1}$.

$^{1}$H NMR: δ 1.26 and 1.75 (2 d, 6H, $^{5}J$(P-H) = 3.6 Hz and 5.2 Hz respectively, =CH(C$H_3$)$_2$), 4.78 (d, 1H, $^{2}J$(P-H) = 18.0 Hz, PC*H*), 7.29-7.94 (m, 14H, Ar*H*).

$^{13}$C NMR: δ 17.0 and 18.3 (2 s, C(*C*H$_3$)$_2$), 45.5 (d, $^{1}J$(P-C) = 57.5 Hz, P*C*H), 118.6 (d, $^{2}J$(P-C) = 9.8 Hz, C-C=*C*), 125.2, 127.7, 128.2, 128.4, 128.5, 128.9, 129.9, 130.0, 131.5, 131.6, 132.4, 132.6, 133.7, 134.3, 135.9 (d, $^{2}J$(P-C) = 9.4 Hz, Ar-*C*), 162.1 (s, *C*OO).

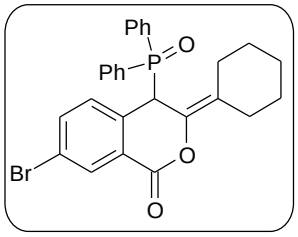
$^{31}$P NMR: δ 28.7.

LC/MS: *m/z* 389 [M+1]$^{+}$.

Anal.Calcd. for $C_{24}H_{21}O_3P$: C, 74.22; H, 5.45. Found: C, 74.11; H, 5.61.

***Compound 34***

This compound was prepared from allenylphosphine oxide **11g** (0.261 g, 0.5 mmol).




Yield: 0.216 g (85%).

Mp: 210-212 $^{o}$C.

IR (KBr): 3057, 2931, 2860, 1742, 1583, 1446, 1177, 701 cm$^{-1}$.

$^{1}$H NMR: δ 0.85-2.32 (m, 10H, cyclohexyl-*H*), 4.76 (d, 1H, $^{2}J$(P-H) = 12.0 Hz, PC*H*), 7.06-8.09 (m, 13H, Ar*H*).

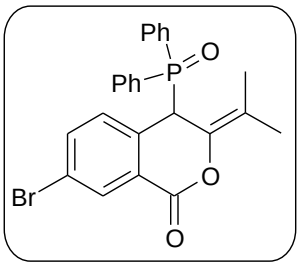
$^{13}$C NMR: δ 26.0, 26.2, 26.5 and 28.8 (4 s, cyclohexyl-*C*), 44.5 (d, $^{1}J$(P-C) = 57.0 Hz, P-*C*), 122.2, 126.4, 127.1, 127.8, 128.5, 128.6, 128.8, 129.5, 131.6, 131.7, 132.3, 132.5, 132.7, 132.8, 133.1, 133.5 and 136.5 (Ar-*C*), 161.3 (s, *C*=O).

$^{31}$P NMR: δ 28.8.

HRMS (ESI): Calcd. for $C_{27}H_{25}BrO_3P$ [M$^{+}$+H]: *m/z* 507.0725 and 509.0725. Found: 507.0723 and 509.0670.

***Compound 35***

This compound was prepared from allenylphosphine oxide **11h** (0.241 g, 0.5 mmol).




Yield: 0.215 g (92%).

Mp: 240-242 $^{o}$C.

IR (KBr): 3057, 2920, 2854, 1726, 1682, 1435, 1232, 1172, 706 cm$^{-1}$.

$^{1}$H NMR: δ 1.23 and 1.73 (2 s, 6H, C(C*H*$_3$)$_2$), 4.72 (d, 1H, $^{2}J$(P-H) = 16.4 Hz, PC*H*), 7.09-8.08 (m, 13H, Ar*H*).

$^{13}$C NMR: δ 17.1 and 18.4 (2 s, C(*C*H$_3$)$_2$), 45.2 (d, $^{1}J$(P-C) = 57.1 Hz, P*C*H), 119.2 (d, $^{2}J$(P-C) = 9.3 Hz, *C*(CH$_3$)$_2$), 122.3, 126.9, 127.7, 128.4, 128.6, 128.7, 129.7, 131.6, 131.7, 132.3, 132.4, 132.6, 132.8, 133.3, 135.5 (d, $^{2}J$(P-C) = 9.9 Hz, Ar-*C*), 136.6 and 160.9 (s, *C*=O).

$^{31}$P NMR: δ 28.3.

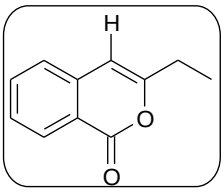
HRMS (ESI): Calcd. for $C_{24}H_{20}BrNaO_3P$ [M$^{+}$+Na]: *m/z* 489.0231 and 491.0231. Found: 489.0270 and 491.0247.

### *6.42 General procedure for the synthesis of compounds 36-41*

One of the allenes **11b-d** or **11f-h** (0.5 mmol) was treated with trifluoroacetic acid (2 mL) at 70 $^{o}$C for 12 h. Solvent was removed by vacuum and the crude product was purified by column chromatography using ethyl acetate/hexane (2:3 v/v) mixture as the eluent to obtain one of phosphinoyl-isocoumarins **29-30**, **32-35** in addition to one of the non-phosphorus isocoumarins **36-41**.

***Compound 36***

Allenylphosphine oxide **11b** (0.194 g, 0.5 mmol) was used to obtain compounds **29** and **36**. Compound **29** is already described above. Compound **36** was isolated by column chromatography using ethyl acetate/hexane (1:20) mixture as the eluent.

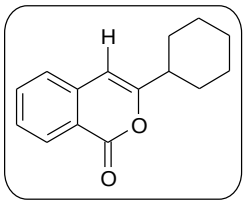


Yield: 84% (**29** + **36**, isolated); 0.028 g (32%, **36**).

The spectral data are in accordance with the literature reports.[64]

***Compound 37***

Allenylphosphine oxide **11c** (0.221 g, 0.5 mmol) was used to obtain compound **37** in a manner similar to compound **36**.

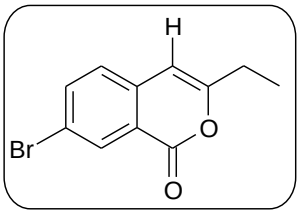


Yield: 87% (**30** + **37**, isolated); 0.055 g (38%, **37**).

The spectral data are in accordance with the literature reports.[70]

***Compound 38***

Allenylphosphine oxide **11f** (0.237 g, 0.5 mmol) was used to obtain compound **38** in a manner similar to **36**.



Yield: 88% (**32** + **38**, isolated); 0.048 g (38%, **38**).

Mp: 74-76 $^{o}$C.

IR (KBr): 3068, 2920, 2849, 1737, 1660, 1474, 1156, 1041, 849 cm$^{-1}$.

$^{1}$H NMR: δ 1.28 (t, 3H, $^{3}J$(H-H) = 7.4 Hz, $CH_2CH_3$), 2.56 (qrt, 2H, $^{3}J$(H-H) = 7.3 Hz, $CH_2CH_3$), 6.23 (s, 1H, C*H*=CEt), 7.24-8.38 (m, 3H, Ar*H*).

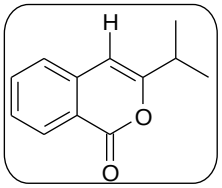
$^{13}$C NMR: δ 11.2 ($CH_2CH_3$), 26.8 ($CH_2CH_3$), 101.4, 120.9, 121.6, 126.8, 132.1, 136.4, 137.9 and 160.2 (Ar-C), 161.8 (*C*OO).

HRMS (ESI): Calcd. for $C_{11}H_9BrNaO_2$ [M$^{+}$+Na]: *m/z* 274.9684 and 276.9684. Found:

274.9684 and 276.9670.

***Compound 39***

Allenylphosphine oxide **11d** (0.201 g, 0.5 mmol) was used to obtain compounds **39** in a manner similar to that for **36**.

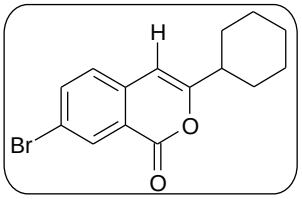



Yield: 87% (**33** + **39**, isolated); 0.039 g (41%, **39**).

The spectral data are in accordance with the literature reports.[71]

***Compound 40***

Allenylphosphine oxide **11g** (0.261 g, 0.5 mmol) was used to obtain **40** in a manner similar to **36**.




Yield: 87 % (**34** + **40**, isolated); 0.065 g (42%, **40**).

Mp: 138-140 $^{o}$C.

IR (KBr): 2926, 2849, 1721, 1649, 1452, 1260, 855, 805 cm$^{-1}$.

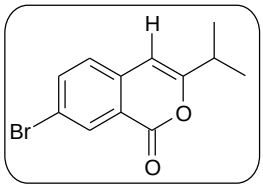
$^{1}$H NMR: δ 1.25-2.46 (m, 11H, cyclohexyl-*H*), 6.20 (s, 1H, C*H*=C), 7.24-8.37 (m, 3H, Ar*H*).

$^{13}$C NMR: δ 25.8, 26.0, 30.6 and 42.0 (cyclohexyl-*C*), 100.4, 120.8, 121.8, 127.0, 132.0, 136.5, 137.8 and 161.9 (Ar-*C*), 163.0 (*C*OO).

HRMS (ESI): Calcd. for $C_{15}H_{15}BrNaO_2$ [$M^+$+Na]: *m/z* 329.0153 and 331.0153. Found: 329.0170 and 331.0151.

***Compound 41***

Allenylphosphine oxide **11h** (0.241 g, 0.5 mmol) was used to obtain **41** in a manner similar to **36**.



Yield: 90 % (**35** + **41**, isolated); 0.047 g (35%, **41**).

Mp: 78-80 $^{o}$C.

IR (KBr): 2959, 2921, 2855, 1726, 1655, 1480, 1074, 844 cm$^{-1}$.

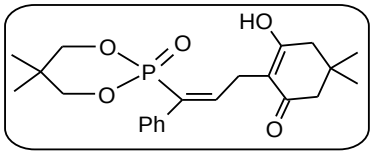
$^{1}$H NMR: δ 1.25-1.30 (m, 6H, CH(C*H*$_3$)$_2$), 2.76-2.80 (m, 1H, C*H*Me$_2$), 6.23 (s, 1H, C*H*=C), 7.25-8.39 (m, 3H, Ar-*H*).

$^{13}$C NMR: δ 20.2 (CH(*C*H$_3$)$_2$), 32.5 (*C*HMe$_2$), 100.1, 120.9, 121.8, 127.0, 132.1, 136.5, 137.8 and 161.8 (Ar-*C*), 163.7 (*C*OO).

HRMS (ESI): Calcd. for $C_{12}H_{11}BrNaO_2$ [M$^{+}$+Na]: *m/z* 288.9840 and 290.9840. Found: 288.9868 and 290.9847.

### *6.43 Synthesis of compound 42*

To a mixture of allenylphosphonate **8b** (0.5 mmol, 0.132 g) and triphenylphosphine (0.1 mmol) in toluene (3 mL) was added 5,5-dimethylcyclohexan-1,3-dione (0.5 mmol). The contents were stirred under reflux for 12 h. Solvent was removed by vacuum and the crude product was purified by column chromatography using silica gel with ethyl acetate/hexane (1:1) mixture as the eluent.



**42**

Yield: 0.129 g (64%).

IR (KBr): 3408, 2959, 2926, 1627, 1469, 1397, 1255, 1058, 1008, 795 cm$^{-1}$.

$^{1}$H NMR: δ 0.75 and 1.03 (2 s, 6H, (C*H*$_3$)$_2$C), 1.04 (s, 6H, (C*H*$_3$)$_2$C), 2.22-2.35 (2 s, 4H, cyclohexenyl-C*H*$_2$), 3.59-3.70 (m, 4H, OC*H*$_2$ + =CC*H*$_2$), 4.10 (dd→t, $^{3}J$(P-H) = $^{2}J$(H-H) = 10.8 Hz, 2H, OC*H*$_2$), 6.55 (dt, $^{3}J$(P-H) = 50.0 Hz, $^{3}J$(H-H) = 9.0 Hz, 1H, PC=C*H*), 7.28-7.32 (m, 5H, Ar-*H*), 10.71 (s, 1H, C=C-O*H*).

$^{13}$C NMR: δ 21.2, 21.6, 24.6, 28.3 and 31.7 (5 s, (*C*H$_3$)$_2$C + (*C*H$_3$)$_2$*C*CH$_2$), 32.5 (d,

$^{3}J$(P-C) = 6.1 Hz, $Me_2C$), 43.5 and 50.4 (2 s, $COCH_2$ + $=CCH_2$), 75.8 and 75.9 (2 s, $OCH_2$), 109.1 (s, *C*=C-OH), 127.3, 127.9, 128.2, 128.9, 138.1 (d, $^{2}J$(P-C) = 11.8 Hz), 152.1 (d, $^{2}J$(P-C) = 12.0 Hz, Ar-*C*), 173.4 (s, C=*C*-OH), 198.0 (s, *C*=O). The signal for P-*C* carbon was buried in the aromatic region.

$^{31}$P NMR: δ 14.8.

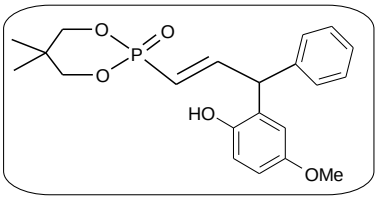
HRMS (ESI): Calcd. for $C_{22}H_{30}O_5P$ [$M^{+}$+Na]: *m/z* 405.1832. Found: 405.1828.

## 6.5 $FeCl_3$ catalyzed Friedel-Crafts allylation of α-hydroxy allylphosphonates with functionalized arenes: General procedure for the synthesis of compounds 44a-51a and 50b-53b

To phosphono-allylic alcohol **43** (0.282 g, 1 mmol) and $FeCl_3$ (0.016 g, 0.1 mmol) in nitromethane (3 mL) was added 4-methoxyphenol (0.620 g, 5 mmol) and the mixture stirred at 80 $^{o}$C. After the starting material was consumed completely, solvent was removed under vacuum. The crude product was purified by column chromatography using silica gel with ethyl acetate/ hexane (1:1) mixture as the eluent.

***Compound 44a***

This compound was prepared from 4-methoxy phenol (0.62 g, 5 mmol).




Yield: 0.330 g (85%).

Mp: 184-186 $^{o}$C.

IR (KBr): 3260, 2969, 1638, 1597, 1510, 1431, 1372, 1244, 1213, 1053, 997, 822, 806, 698, 498 $cm^{-1}$.

$^{1}$H NMR: δ 1.04 and 1.06 (2 s, 6H, $C(CH_3)_2$), 3.70 (s, 3H, $OCH_3$), 3.82 (dd, $^{3}J$(P-H) ~ 11.8 Hz, $^{2}J$(H-H) ~ 10.6 Hz, 2H, $OCH_2$), 4.17 (dd→t, $^{3}J$(P-H) ~ $^{2}J$(H-H) ~ 10.6 Hz, 2H, $OCH_2$), 5.21 (br s, 1H, =CHC*H*Ar), 5.59 (dd, $^{2}J$(P-H) = 20.4 Hz and $^{3}J$(H-H) = 18.4 Hz, 1H, PC*H*=CH), 6.57-7.34 (m, 9H, Ar*H* + PCH=C*H*). The O*H* peak was broad.

$^{13}$C NMR: δ 21.5 and 21.6 (2 s, C($C$H$_3$)$_2$), 32.5 (d, $^3J$(P-C) = 5.8 Hz, $C$(CH$_3$)$_2$), 49.0 (d, $^3J$(P-C) = 22.0 Hz, =CH$C$HAr), 75.6 and 75.7 (2 s, O$C$H$_2$), 112.8, 115.7, 116.0 (d, $^1J$(P-C) = 185.9 Hz, P$C$=C), 116.8, 127.0, 128.5, 128.7, 128.9, 140.1, 148.0, 153.4, 156.2.

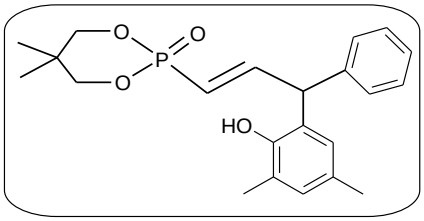
$^{31}$P NMR: δ 14.5.

LC/MS: *m/z* 389 [M+1]$^+$.

Anal.Calcd. for $C_{21}H_{25}O_5P$: C, 64.94; H, 6.49. Found: C, 65.10; H, 6.41.

***Compound 45a***

This compound was prepared by following a procedure similar to that for **44a**, using 2,4-dimethylphenol (0.611 g, 5 mmol).




Yield: 0.302 g (92%).

Mp: 192-194 $^o$C.

IR (KBr): 3245, 2965, 2917, 1626, 1597, 1485, 1260, 1190, 1061, 1009, 830, 706, 515 cm$^{-1}$.

$^1$H NMR: δ 1.03 and 1.06 (2 s, 6H, C(C$H_3$)$_2$), 2.19 and 2.21 (2 s, 6H, ArC$H_3$), 3.81 (dd→t, $^3J$(P-H) = $^2J$(H-H) ~ 12.2 Hz, 2H, OC$H_2$), 4.17 (dd→t, $^3J$(P-H) = $^2J$(H-H) ~ 10.6 Hz, 2H, OC$H_2$), 5.21 (d, 1H, $^3J$(H-H) = 2.8 Hz, CHC$H$Ar), 5.52-5.62 (m, 1H, PC$H$=CH), 6.70-7.37 (m, 8H, Ar$H$ + PCH=C$H$). The O$H$ peak was broad.

$^{13}$C NMR: δ 16.1 and 20.7 (2 s, Ar$C$H$_3$), 21.5 and 21.7 (2 s, C($C$H$_3$)$_2$), 32.5 (d, $^3J$(P-C) = 5.6 Hz, $C$(CH$_3$)$_2$), 49.1 (d, $^3J$(P-C) = 22.0 Hz, =CH$C$HAr), 75.4 and 75.5 (2 s, O$C$H$_2$), 116.4 (d, $^1J$(P-C) = 185.9, P$C$), 124.1, 127.1, 127.2, 127.7, 128.8, 128.8$_3$, 129.7, 130.5, 140.3, 149.5, 156.2 and 156.3.

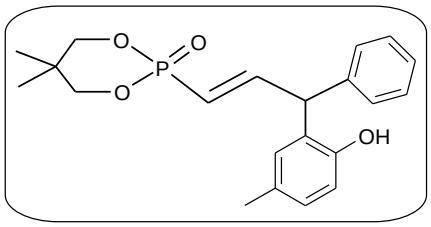
$^{31}$P NMR: δ 14.5.

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

Anal.Calcd. for $C_{22}H_{27}O_4P$: C, 68.38; H, 7.04. Found: C, 68.25; H, 7.12.

***Compound 46a***

This compound was prepared by following a procedure similar to that for **44a**, using 4-cresol (0.541 g, 5 mmol).




Yield: 0.335 g (90%).

Mp: 190-192 $^{o}$C.

IR (KBr): 3482, 2915, 1624, 1512, 1456, 1372, 1240, 1057, 1005, 872, 505, 469, 421 cm$^{-1}$.

$^{1}$H NMR: δ 1.02 and 1.06 (2 s, 6H, C(C*H*$_3$)$_2$), 2.22 (2 s, 3H, ArC*H*$_3$), 3.78-3.84 (m, 2H, OC*H*$_2$), 4.16 (dd→t, $^{3}J$(P-H) = $^{2}J$(H-H) ~ 12.0 Hz, 2H, OC*H*$_2$), 5.20-5.21 (m, 1H, CHC*H*Ar), 5.52-5.63 (m, 1H, PC*H*=CH), 6.71-7.32 (m, 9H, Ar*H* + PCH=C*H*). The O*H* peak was broad.

$^{13}$C NMR: δ 20.7 (2 s, Ar*C*H$_3$), 21.5 and 21.7 (2 s, C(*C*H$_3$)$_2$), 32.6 (d, $^{3}J$(P-C) = 6.1 Hz, *C*(CH$_3$)$_2$), 49.0 (d, $^{3}J$(P-C) = 22.1 Hz, =CH*C*HAr), 75.5 and 75.6 (2 s, O*C*H$_2$), 116.0, 116.2 (d, $^{1}J$(P-C) = 187.7, P*C*=C), 127.0, 127.2, 128.7, 128.8, 128.9, 130.1, 140.3, 151.4, 156.3 and156.4.

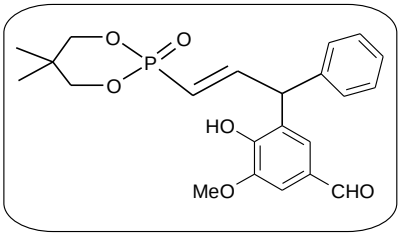
$^{31}$P NMR: δ 14.8.

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

Anal.Calcd. for $C_{21}H_{25}O_4P$: C, 67.73; H, 6.77. Found: C, 67.85; H, 6.71.

***Compound 47a***

This compound was prepared by following a procedure similar to that for **44a**, using vanillin (0.761 g, 5 mmol).




Yield: 0.375 g (90%).

Mp: 142-144 $^{o}$C.

IR (KBr): 3291, 2961, 2928, 1682, 1593, 1455, 1053, 830, 700 cm$^{-1}$.

$^{1}$H NMR: δ 1.02 and 1.08 (2 s, 6H, C(C*H*$_3$)$_2$), 3.82 (dd→t, $^{3}J$(P-H) = $^{2}J$(H-H) ~ 11.6 Hz, 2H, OC*H*$_2$), 3.93 (s, 3H, OC*H*$_3$), 4.20 (dd→t, $^{3}J$(P-H) = $^{2}J$(H-H) ~ 10.0 Hz, 2H, OC*H*$_2$), 5.34 (br s, 1H, =CHC*H*Ar), 5.63 (dd→t, $^{2}J$(P-H) = $^{3}J$(H-H) ~ 19.2 Hz, PC*H*=CH), 7.13-7.34 (m, 8H, Ar*H* + PCH=C*H*), 9.75 (s, 1H, ArC*H*O). The O*H* peak was broad.

$^{13}$C NMR: δ 21.4 and 21.7 (2s, C(*C*H$_3$)$_2$), 32.6 (d, $^{3}J$(P-C) = 5.5 Hz, *C*(CH$_3$)$_2$), 48.0 (d, $^{3}J$(P-C) = 21.1 Hz, P*C*CH), 75.5 (dd→t, $^{2}J$(P-C) ~ 6.2 Hz, OCH$_2$), 107.7, 117.1 (d, $^{1}J$(P-C) = 186.3 Hz, P*C*=C), 127.1, 127.3, 128.7, 128.8, 129.2, 139.6, 147.3, 149.2, 154.8, 190.9 (s, Ar*C*HO).

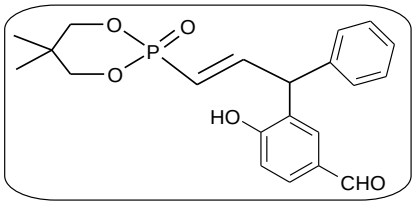
$^{31}$P NMR: δ 14.0.

LC/MS: *m/z* 415 [M-1]$^{+}$.

Anal.Calcd. for $C_{22}H_{25}O_6P$: C, 63.46; H, 6.05. Found: C, 63.36; H, 6.12.

***Compound 48a***

This compound was prepared by following a procedure similar to that for **44a**, using 4-hydroxy benzaldehyde (0.611 g, 5 mmol).




Yield: 0.324 g (84%).

Mp: 188-190 $^{o}$C.

IR (KBr): 3360, 3059, 3030, 2969, 1690, 1601, 1474, 1373, 1246, 1161, 1059, 1009, 830, 702, 615 cm$^{-1}$.

$^{1}$H NMR: δ 1.08 (s, 6H, C(C*H*$_3$)$_2$), 3.88 (dd→t, $^{3}J$(P-H) = $^{2}J$(H-H) ~ 10.0 Hz, 2H, OC*H*$_2$), 4.16 (dd→t, $^{3}J$(P-H) = $^{2}J$(H-H) ~ 10.0 Hz, 2H, OC*H*$_2$), 5.25 (br s, 1H, =CHC*H*Ar), 5.61 (dd→t, $^{2}J$(P-H) = $^{3}J$(H-H) ~ 20.0 Hz, 1H, PC*H*=CH), 7.03-7.61 (m, 8H, Ar*H* + PCH=C*H*), 9.40 (br s, 1H, O*H*), 9.73 (s, 1H, ArC*H*O).

$^{13}$C NMR: δ 21.5$_0$ and 21.5$_1$ (2 s, C(*C*H$_3$)$_2$), 32.6 (d, $^{3}J$(P-C) = 4.0 Hz, *C*(CH$_3$)$_2$),

48.9 (d, $^{3}J$(P-C) = 23.0 Hz, =CH*C*HAr), 76.1 and 76.2 (2 s, O*C*$H_2$), 115.7 (d, $^{1}J$(P-C) = 186.0 Hz, P*C*=C), 116.4, 127.2, 128.3, 128.8, 131.6, 139.6, 156.2, 161.1, 191.1 (s, Ar*C*HO).

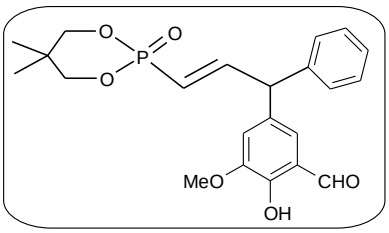
$^{31}$P NMR: δ 15.0.

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

Anal.Calcd. for $C_{21}H_{23}O_5P$: C, 65.28; H, 6.00. Found: C, 65.41; H, 5.93.

***Compound 49a***

This compound was prepared by following a procedure similar to that for **44a**, using *o*-vanillin (0.761 g, 5 mmol). Mixture of products was formed of which only **49a** was separated.




Yield: 0.125 g (30%).

Mp: 130-132 $^{o}$C.

IR (KBr): 3250, 2964, 2904, 1655, 1474, 1397, 1255, 1058, 1008, 800 $cm^{-1}$.

$^{1}$H NMR: δ 1.01 and 1.12 (2 s, 6H, C(C*H*$_3$)$_2$), 3.77-3.83 (m, 2H, OC*H*$_2$), 3.85 (s, 3H, OC*H*$_3$), 4.25 (d, $^{3}J$(P-H) = 9.4 Hz, 2H, OC*H*$_2$), 4.90 (s, 1H, =CHC*H*Ar), 5.64 (dd→t, $^{2}J$(P-H) = $^{3}J$(H-H) ~ 19.2 Hz, 1H, PC*H*=CH), 6.87-7.37 (m, 8H, Ar*H* + PCH=C*H*), 9.86 (s, 1H, ArC*H*O), 11.08 (s, 1H, ArO*H*).

$^{13}$C NMR: δ 21.4 and 21.8 (2s, C(*C*H$_3$)$_2$), 32.6 (d, $^{3}J$(P-C) = 5.5 Hz, *C*(CH$_3$)$_2$), 54.4 (d, $^{3}J$(P-C) = 22.0 Hz, =CH*C*HAr), 56.4 (s, OCH$_3$), 75.3 (d, $^{2}J$(P-C) = 5.6 Hz, O*C*H$_2$), 117.7 (d, $^{1}J$(P-C) = 187.1 Hz, P*C*=C), 118.6, 120.4, 123.8, 127.5, 128.6, 129.0, 132.4, 140.1, 148.7, 150.9, 155.6 (d, $^{3}J$(P-C) = 5.8 Hz, P*C*), 196.6 (s, Ar*C*HO).

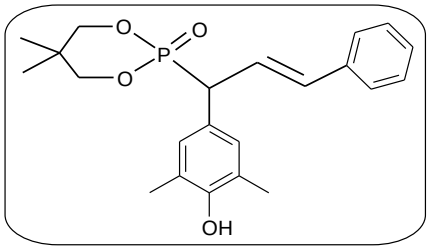
$^{31}$P NMR: δ 13.8.

LC/MS: *m/z* 417 $[M+1]^{+}$.

Anal.Calcd. for $C_{22}H_{25}O_6P$: C, 63.46; H, 6.05. Found: C, 63.32; H, 6.15.

***Compounds 50a and 50b***

These were prepared by following a procedure similar to that for **44a**, using 2,6-dimethylphenol (0.611 g, 5 mmol). The two isomers were separated successfully by column chromatography using silica gel with ethyl acetate/ hexane (1:1) mixture as the eluent.




**50a** (higher $R_f$)

Yield: 0.085 g (22%).

Mp: 196−198 $^{o}$C.

IR (KBr): 3339, 2961, 2917, 1487, 1256, 1184, 1057, 1003, 982, 833, 812, 694, 473 $cm^{-1}$.

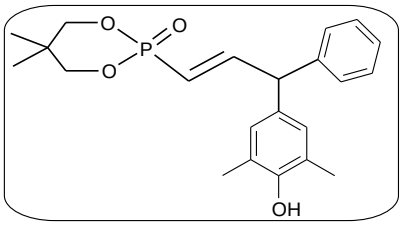
$^{1}$H NMR: δ 0.96 and 1.06 (2 s, 6H, C(C*H*$_3$)$_2$), 2.20 (s, 6H, ArC*H*$_3$), 3.75-3.82 (m, 2H, OC*H*$_2$), 3.99 (dd, 1H, $^{2}J$(P-H) = 24.4 Hz and $^{3}J$(P-H) = 8.0 Hz, PC*H*), 4.20-4.27 (m, 2H, OC*H*$_2$), 6.48-6.60 (m, 2H, C*H*=C*H*Ar), 7.03-7.39 (m, 8H, Ar*H*). The O*H* peak was broad.

$^{13}$C NMR: δ 16.1 (s, Ar*C*H$_3$), 21.5 and 21.8 (2s, C(*C*H$_3$)$_2$), 32.8 (s, *C*(CH$_3$)$_2$), 47.2 (d, $^{1}J$(P-C) = 134.5 Hz, P*C*CH), 75.2 and 75.3 (2 s, O*C*H$_2$), 123.9, 124.4 (d, $^{2}J$(P-C) = 9.0 Hz, Ar-*C*), 125.9, 126.6, 127.7, 128.6, 129.1 (d, $^{3}J$(P-C) = 7.1 Hz, Ar-*C*), 133.6, 133.8, 136.8, 152.0.

$^{31}$P NMR: δ 21.9.

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

Anal.Calcd. for $C_{22}H_{27}O_4P$: C, 68.38; H, 7.04. Found: C, 68.25; H, 7.12.




**50b** (lower $R_f$)

Yield: 0.270 g (70%).

Mp: 190-192 $^{o}$C.

IR (KBr): 3308, 2971, 1734, 1622, 1489, 1372, 1237, 1200, 1148, 1059, 1007, 824, 702, 615 cm$^{-1}$.

$^{1}$H NMR: δ 1.02 and 1.08 (2s, 6 H, C(C*H*$_3$)$_2$), 2.20 (s, 6H, ArC*H*$_3$), 3.80 (dd→t, $^{3}J$(P-H) = $^{2}J$(H-H) ~ 12.0 Hz, 2H, OC*H*$_2$), 4.20 (dd→t, $^{3}J$(P-H) = $^{2}J$(H-H) ~ 9.6 Hz, 2H, OC*H*$_2$), 4.76 (br s, 1H, =CHC*H*Ar), 5.58 (dd→t, $^{2}J$(P-H) = $^{3}J$(H-H) ~ 19.0 Hz, 1H, PC*H*=CH), 6.57-7.62 (m, 8H, Ar*H* + PCH=C*H*). The O*H* peak was broad.

$^{13}$C NMR: δ 16.1 (s, Ar*C*H$_3$), 21.4 and 21.7 (2 s, C(*C*H$_3$)$_2$), 32.5 (d, $^{3}J$(P-C) = 6.0 Hz, *C*(CH$_3$)$_2$), 54.5 (d, $^{3}J$(P-C) = 22.0 Hz, =CH*C*HAr), 75.3 (s, O*C*H$_2$), 116.2 (d, $^{1}J$(P-C) = 186.0 Hz, P*C*=C), 123.5, 126.9, 128.6, 128.7, 128.7$_2$, 132.1, 141.3, 151.4, 157.0.

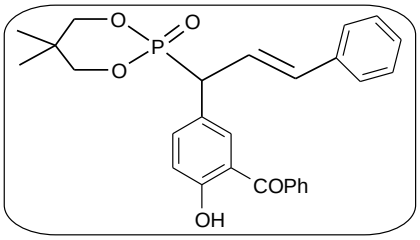
$^{31}$P NMR: δ 14.5.

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

Anal.Calcd. for $C_{22}H_{27}O_4P$: C, 68.38; H, 7.04. Found: C, 68.25; H, 7.12.

***Compounds 51a and 51b***

These compounds were prepared by following a procedure similar to that for **44a**, using salicylaldehyde (0.611 g, 5 mmol).




**51a** (higher $R_f$)

Yield: 0.347 g (75%).

Mp: 140-142 $^{o}$C.

IR (KBr): 2963, 2926, 1707, 1630, 1601, 1480, 1449, 1335, 1258, 1059, 1007, 828, 758, 700 cm$^{-1}$.

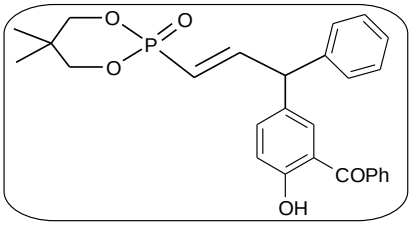
$^{1}$H NMR: δ 0.95 and 1.02 (2 s, 6H, C(C*H*$_3$)$_2$), 3.74-3.80 (m, 2H, OC*H*$_2$), 4.05 (dd, 1H, $^{2}J$(P-H) = 24.8 Hz and $^{3}J$(P-H) ~ 8.0 Hz, PC*H*), 4.26 (br s, 2H, OC*H*$_2$), 6.44-6.60 (m, 2H, C*H*=C*H*Ar), 7.09-7.74 (m, 13H, Ar*H*), 11.98 (s, 1H, ArO*H*).

$^{13}$C NMR: δ 21.4 and 21.8 (2 s, C($CH_3$)$_2$), 32.7 (d, $^3J$(P-C) = 6.0 Hz, $C$(CH$_3$)$_2$), 46.7 (d, $^1J$(P-C) = 135.7 Hz, P$C$CH), 75.1 and 75.2 (2 d, , $^2J$(P-C) = 6.0 Hz and 7.0 Hz respectively, O$C$H$_2$), 118.9, 119.1, 123.0, 123.1, 125.4, 126.5, 128.0, 128.4, 128.6, 129.6, 132.3, 134.2 (d, $^3J$(P-C) = 7.0 Hz, Ar-*C*), 134.6 (d, $^2J$(P-C) = 14.0 Hz, Ar-*C*), 136.4, 137.0, 137.6, 162.5, 201.1 (s, Ar$C$OPh).

$^{31}$P NMR: δ 21.1.

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

Anal.Calcd. for $C_{27}H_{27}O_5P$: C, 70.12; H, 5.88. Found: C, 70.25; H, 5.76.




**51b** (lower $R_f$)

Yield: 0.069 g (15%).

Mp: 136-138 $^o$C.

IR (KBr): 3300 (br), 2967, 2930, 1630, 1601, 1480, 1244, 1061, 1009, 826, 737, 700 cm$^{-1}$.

$^1$H NMR: δ 1.01 and 1.07 (2 s, 6H, C(C$H_3$)$_2$), 3.76 (dd, $^3J$(P-H) ~ 12.8 Hz, $^2J$(H-H) ~ 9.4, 2H, OC$H_2$), 4.21 (dd→t, $^3J$(P-H) = $^2J$(H-H) ~ 9.4 Hz, 2H, OC$H_2$), 4.83 (br s, 1H, =CHC$H$Ar), 5.59 (dd→t, $^2J$(P-H) = $^3J$(H-H) ~ 18.6 Hz, PC$H$=CH), 7.04-7.59 (m, 14H, Ar$H$ + PCH=C$H$), 11.96 (s, 1H, ArO$H$).

$^{13}$C NMR: δ 21.4 and 21.8 (2 s, C($CH_3$)$_2$), 32.5 (d, $^3J$(P-C) = 5.0 Hz, $C$(CH$_3$)$_2$), 54.1 (d, $^3J$(P-C) = 22.0 Hz, =CH$C$HAr), 75.3 (2 s, O$C$H$_2$), 117.4 (d, $^1J$(P-C) = 243.0 Hz, P$C$=C), 118.9, 119.0, 127.3, 128.5, 128.6, 128.9, 129.4, 131.1, 132.2, 133.6, 136.6, 137.5, 140.4, 155.9, 162.3, 201.2 (s, Ar$C$OPh).

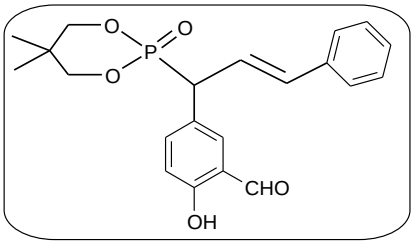
$^{31}$P NMR: δ 13.8.

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

Anal.Calcd. for $C_{27}H_{27}O_5P$: C, 70.12; H, 5.88. Found: C, 70.06; H, 5.93.

***Compound 52b***

This compound was prepared by following a procedure similar to that for **44a**, using salicylaldehyde (0.611 g, 5 mmol). Mixture of products was formed from which only **52b** was separated.




Yield: 0.116 g (30%).

Mp: 188-190 $^{o}$C.

IR (KBr): 3401, 2967, 2915, 1665, 1586, 1482, 1258, 1057, 1009, 831, 787, 756, 694, 480 cm$^{-1}$.

$^{1}$H NMR: δ 0.96 and 1.05 (2 s, 6H, C(C*H*$_3$)$_2$), 3.78-3.82 (m, 2H, OC*H*$_2$), 4.08-4.16 (m, 1H, PC*H*), 4.24-4.31 (m, 2H, OC*H*$_2$), 6.52-6.60 (m, 2H, C*H*=C*H*Ar), 7.02-7.70 (m, 8H, Ar*H*), 9.92 (s, 1H, ArC*H*O), 11.00 (s, 1H, ArO*H*).

$^{13}$C NMR: δ 21.4 and 21.8 (2 s, C(*C*H$_3$)$_2$), 32.8 (d, $^{3}J$(P-C) = 5.6 Hz, *C*(CH$_3$)$_2$), 46.7 (d, $^{1}J$(P-C) = 135.7 Hz, P*C*CH), 75.3 (dd→t, $^{2}J$(P-C) ~ 6.8 Hz, O*C*H$_2$), 118.3, 120.8, 123.0 (d, $^{3}J$(P-C) = 9.3 Hz, Ar-*C*), 126.6, 128.2, 128.7, 134.1 (d, $^{3}J$(P-C) = 7.1 Hz, Ar-*C*), 134.8 (d, $^{2}J$(P-C) = 13.6 Hz, Ar-*C*), 136.3, 137.9 (d, $^{3}J$(P-C) = 3.9 Hz, Ar-*C*), 161.1, 196.6 (s, Ar*C*HO).

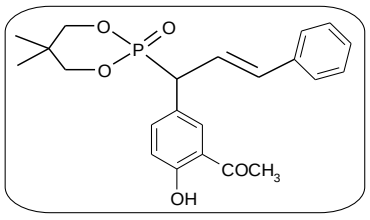
$^{31}$P NMR: δ 20.8.

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

Anal.Calcd. for $C_{21}H_{23}O_5P$: C, 65.28; H, 6.00. Found: C, 65.14; H, 6.08.

***Compound 53b***

This compound was prepared by following a procedure similar to that for **44a**, using 2'-hydroxy-acetophenone (0.681 g, 5 mmol). Mixture of isomers was formed from which only **55a** was separated.



Yield: 0.264 g (66%).

Mp: 170-172 $^{o}$C.

IR (KBr): 3400 (br), 2968, 1723, 1647, 1485, 1370, 1265, 1059, 1009, 914, 826, 480 $cm^{-1}$.

$^{1}$H NMR: δ 0.96 and 1.05 (2 s, 6H, C(C*H*$_3$)$_2$), 2.67 (s, 3H, ArCOC*H*$_3$), 3.75-3.84 (m, 2H, OC*H*$_2$), 4.09 (dd→t, $^{2}J$(P-H) = $^{3}J$(H-H) ~ 7.8 Hz, 1H, PC*H*), 4.24-4.31 (m, 2H, OC*H*$_2$), 6.49-6.62 (m, 2H, C*H*=C*H*Ar), 6.99-7.86 (m, 8H, Ar*H*), 12.26 (s, 1H, ArO*H*).

$^{13}$C NMR: δ 21.4 and 21.8 (2 s, C(*C*H$_3$)$_2$), 26.9 (s, CO*C*H$_3$), 32.8 (s, *C*(CH$_3$)$_2$), 46.9 (d, $^{1}J$(P-C) = 135.5 Hz, P*C*CH), 75.2 and 75.3 (2 s, O*C*H$_2$), 119.0, 119.9, 123.2 (d, $^{3}J$(P-C) = 9.2 Hz, Ar-*C*), 126.6, 128.1, 128.7, 131.4, 134.6 (d, $^{2}J$(P-C) = 13.4 Hz, Ar-*C*), 136.3, 137.3, 161.8, 204.6 (s, Ar*C*OMe).

$^{31}$P NMR: δ 21.1.

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

Anal.Calcd. for $C_{22}H_{25}O_5P$: C, 65.99; H, 6.29. Found: C, 65.85.15; H, 6.35.

## 6.6 X-ray crystallography

A suitable crystal was mounted on a glass fiber (for **18a, 20b.CHCl$_3$, 21a, 21b.H$_2$O, 27.CH$_2$Cl$_2$, 28, 38, 42, 49a and 50a.1/2C$_6$H$_6$**) and X-ray data were collected at 293 K on a Bruker AXS-SMART or on an OXFORD diffractometer using Mo-$K_\alpha$ radiation (λ = 0.71073 Å). Structures were solved and refined using standard methods.[72] 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 Table 3a-c.

**Table 3a**. Crystal data for compounds **18a, 20b.**$CHCl_3$**, 21a** and **21b.**$H_2O$ [a]

| Compound | **18a** | **20b.**$CHCl_3$ | **21a** | **21b**.$H_2O$ |
|---|---|---|---|---|
| Emp. formula | $C_{21}H_{25}O_7P$ | $C_{109}H_{125}Cl_3O_{48}P_4$ | $C_{23}H_{27}O_7P$ | $C_{29}H_{35}O_{12}P$ |
| Formula weight | 420.38 | 2433.32 | 446.42 | 606.54 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Monoclinic |
| Space group | *P2/c* | *C2/c* | $P2_1/c$ | $P2_1/c$ |
| *a* /Å | 16.4839(11) | 17.863(3) | 9.7156(4) | 14.9743(8) |
| *b* /Å | 6.6740(4) | 24.4265(19) | 12.7031(6) | 10.9942(6) |
| *c* /Å | 22.516(2) | 16.784(2) | 20.6130(10) | 18.6852(10) |
| $\alpha$/deg | 90 | 90 | 90 | 90 |
| $\beta$/deg | 120.625(6) | 118.377(18) | 112.620(4) | 91.7590(10) |
| $\gamma$/deg | 90 | 90 | 90 | 90 |
| *V* /Å$^3$ | 2131.6(3) | 6443.4(14) | 2348.32(19) | 3074.7(3) |
| *Z* | 4 | 4 | 4 | 4 |
| $D_{calc}$ /g cm$^{-3}$] | 1.310 | 1.254 | 1.263 | 1.310 |
| $\mu$ /mm$^{-1}$ | 0.168 | 0.204 | 0.157 | 0.150 |
| *F*(000) | 888 | 2548 | 944 | 1280 |
| Data/ restraints/ parameters | 3068/0/268 | 5613/0/376 | 4117/0/284 | 5398/3/392 |
| S | 0.880 | 0.983 | 1.060 | 1.044 |
| R1 [I>2σ(I)] | 0.0447 | 0.0807 | 0.0595 | 0.0470 |
| wR2 [all data] | 0.0990 | 0.2176 | 0.1789 | 0.1235 |
| Max./min. residual electron dens. [eÅ$^{-3}$] | 0.329/-0.261 | 0.448/-0.540 | 1.066/-0.394 | 0.360/-0.240 |

[a] $R1 = \Sigma||F_O| - |F_C||/\Sigma|F_O|$ and $wR2 = [\Sigma w(F_O^2-F_C^2)^2/\Sigma wF_O^4]^{0.5}$

**Table 3b**. Crystal data for compounds **27.**$CH_2Cl_2$**, 28, 38** and **42**[a]

| Compound | **27.**$CH_2Cl_2$ | **28** | **38** | **42** |
|---|---|---|---|---|
| Emp. formula | $C_{22}H_{27}Cl_2O_7P$ | $C_{17}H_{34}O_6$ | $C_{11}H_9BrO_2$ | $C_{22}H_{29}O_5P$ |
| Formula weight | 505.31 | 360.35 | 253.08 | 404.42 |
| Crystal system | Monoclinic | Triclinic | Triclinic | Triclinic |
| Space group | $P2_1/c$ | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ |
| *a* /Å | 13.383(2) | 9.7440(19) | 7.9413(19) | 8.8518(7) |
| *b* /Å | 10.210(2) | 9.9918(17) | 7.9674(19) | 11.8107(8) |
| *c* /Å | 19.565(3) | 10.2864(18) | 9.746(2) | 11.9986(9) |
| $\alpha$/deg | 90 | 84.229(14) | 66.05(2) | 108.491(7) |
| $\beta$/deg | 104.688(14) | 76.556(16) | 79.379(19) | 92.471(7)) |
| $\gamma$/deg | 90 | 66.323(18) | 62.93(2) | 109.291(7) |
| $V$ /Å$^3$ | 2586.1(8) | 892.0(3) | 501.8(2) | 1107.42(15) |
| $Z$ | 4 | 2 | 2 | 2 |
| $D_{calc}$ /g cm$^{-3}$] | 1.298 | 1.342 | 1.675 | 1.213 |
| $\mu$ /mm$^{-1}$ | 0.350 | 0.184 | 4.064 | 0.147 |
| $F$(000) | 130 | 468 | 399 | 394 |
| Data/ restraints/ parameters | 3716/0/294 | 4039/0/236 | 1643/0/128 | 3807/0/258 |
| S | 1.178 | 0.989 | 1.065 | 1.027 |
| R1 [I>2σ(I)] | 0.1312 | 0.0471 | 0.0452 | 0.0506 |
| wR2 [all data] | 0.3425 | 0.1130 | 0.1051 | 0.1134 |
| Max./min. residual electron dens. [eÅ$^{-3}$] | 0.984/-0.725 | 0.214/-0.283 | 0.822/-0.584 | 0.231/-0.374 |

[a]$R1 = \Sigma||F_O| - |F_C||/\Sigma|F_O|$ and $wR2 = [\Sigma w(F_O^2-F_C^2)^2/\Sigma wF_O^4]^{0.5}$

**Table 3c**. Crystal data for compounds **49a** and **50a.**$1/2C_6H_6$[a]

| Compound | **49a** | **50a.**$1/2C_6H_6$ |
|---|---|---|
| Emp. formula | $C_{22}H_{25}O_6P$ | $C_{25}H_{30}O_4P$ |
| Formula weight | 416.39 | 425.46 |
| Crystal system | Monoclinic | Triclinic |
| Space group | *C2/c* | $P\bar{1}$ |
| *a* /Å | 21.054(3) | 9.0851(11) |
| *b* /Å | 10.8878(14) | 10.4186(17) |
| *c* /Å | 20.100(3) | 14.7018(18) |
| $\alpha$/deg | 90 | 85.515(3) |
| $\beta$/deg | 113.955(2) | 79.025(2) |
| $\gamma$/deg | 90 | 64.209(2) |
| *V* /Å$^3$ | 4210.7(9) | 1230.0(3) |
| *Z* | 8 | 2 |
| $D_{calc}$ /g cm$^{-3}$] | 1.314 | 1.149 |
| $\mu$ /mm$^{-1}$ | 0.166 | 0.138 |
| *F*(000) | 1760 | 454 |
| Data/ restraints/ parameters | 3693/0/266 | 4752/9/276 |
| S | 1.011 | 0.932 |
| R1 [I>2σ(I)] | 0.0583 | 0.0675 |
| wR2 [all data] | 0.1343 | 0.1537 |
| Max./min. residual electron dens. [eÅ$^{-3}$] | 0.255/-0.251 | 0.382/-0.206 |

[a]$R1 = \Sigma||F_O| - |F_C||/\Sigma|F_O|$ and $wR2 = [\Sigma w(F_O^2-F_C^2)^2/\Sigma wF_O^4]^{0.5}$

## References


1. (a) Zimmer, R.; Dinesh, C. U.; Nandanan, E.; Khan, F. A. *Chem. Rev*. **2000**, *100*, 3067. (b) Lu, X.; Zhang, C.; Xu, Z. *Acc. Chem. Res*. **2001**, *34*, 535. (c) Ma, S. *Acc. Chem. Res*. **2009**, 42, 1679. (d) Alcaide, B.; Almendros, P.; Aragoncillo, C. *Chem. Soc. Rev*. **2010**, *39*, 783. (e) Krause, N.; Winter, C. *Chem. Rev*. **2011**, *111*, 1994. (f) Fuentes, P. R.; Diederich, F. *Angew. Chem. Int. Ed*. **2012**, *51*, 2818.
2. Ma, S. *Acc. Chem. Res*. **2003**, *36*, 701.
3. Sydnes, L. K. *Chem. Rev*. **2003**, *103*, 1133.
4. Yu, S.; Ma, S. *Angew. Chem. Int. Ed*. **2012**, *51*, 3074.
5. (a) Roder, A. H.; Krause, N. *Angew. Chem. Int. Ed*. **2004**, *43*, 1196. (b) Goodwin, T. W.; Thomas, D. M. *Phytochemistry* **1964**, *3*, 47. (c) Willstatter, R.; Page, H. J. *Justus Liebigs Ann. Chem*. **1914**, *404*, 237. (d) Bonnett, R.; Spark, A. A.; Tee, J. L.; Weedon, B. C. L. *Proc. Chem. Soc. London* **1964**, 419. (e) Ito, M.; Yamano, Y.; Sumiya, S.; Wada, A. *Pure Appl. Chem.* **1994**, *66*, 939.
6. Taylor, D. R. *Chem. Rev.* **1967**, *67*, 317.
7. (a) Chakravarty, M.; Kumara Swamy, K. C. *J. Org. Chem*. **2006**, *71*, 9128. (b) Chakravarty, M.; Kumara Swamy, K. C. *Synthesis* **2007**, 3171. (c) Sajna, K. V.; Kotikalapudi, R.; Chakravarty, M.; Bhuvan Kumar, N. N.; Kumara Swamy, K. C. *J. Org. Chem.* **2011**, *76*, 920.
8. a) Wittig, G.; Schollkopf, U.; *Chem. Ber*. **1954**, *87*, 1318. (b) Marshall, J. A.; Wolf, M. A.; Wallace, E. M. *J. Org. Chem*. **1997**, *62*, 367. (c) Ibrahim-Quali, M.; Sinibaladi, M.-E.; Troin, Y.; Gardette, D.; Gramain, J.-C. *Synth. Commun*. **1997**, *27*, 1827 (d) Ma, S.; Shi, Z.; Li, L. *J. Org. Chem.* **1998**, *63*, 4522. (e) Kumar, K.; Kaur, S.; Ishar, M. P. S. *Synlett* **1999**, 1237. (f) Ma, S.; Shi, Z.; Yu, Z. *Tetrahedron Lett*. **1999**, *40*, 2393. (g) Yamazaki, J.; Watanabe, T.; Tanaka, K. *Tetrahedron: Asymmetry* **2001**, *12*, 669. (h) Ma, S.; Jiao, N.; Zhao, S.; Hou, H. *J. Org. Chem*. **2002**, *67*, 2837. (i) Han, H. Y.; Kim, M. S.; Son, J. B.; Jeong, I. H. *Tetrahedron Lett*. **2005**, *47*, 209. (j) Kilbas, B.; Azizoglu, A.; Balci, M. *Helv. Chim. Acta* **2006**, *89*, 1449. (k) Ogata, A.; Nemoto, M.; Kobayashi, K.; Tsubouchi, A.; Takeda, T. *Chem.-Eur. J*. **2007**, *13*, 1320. (l) Li, C.-Y.; Wang, X.-B.; Sun, X.-L.; Tang, Y.; Zheng, J.-C.; Xu, Z.-H.; Zhou, Y.-G.; Dai, L.-X. *J. Am. Chem. Soc*. **2007**, *129*, 1494. (m) Li, C.-Y.; Zhu, B.-H.; Ye, L.-W.; Jing, Q.; Sun, X.-L.; Tang, Y.; Shen, Q. *Tetrahedron* **2007**, *63*, 8046. (n) Yua, S.; Ma, S. *Chem. Commun.* **2011**, *47*, 3528.
9. (a) Krause, N.; Hashmi, A. S. K. *Modern Allene Chemistry*; Eds.; Wiley-VCH: Weinheim, 2004. (b) Ma, S. *Aldrichimica Acta* **2007**, *40*, 91.
10. Li, Z.; Boyarskikh, V.; Hansen, J. H.; Autschbach, J.; Musaev, D. G.; Davies, H. M. L. *J. Am. Chem. Soc*. **2012**, *134*, 15497.
11. Mundal, D. A.; Lutz, K. E.; Thomson, R. J. *J. Am. Chem. Soc*. **2012**, *134*, 5782.
12. Crabbe, P.; Fillion, H.; Andre´, D.; Luche, J.-L. *J. Chem. Soc., Chem. Commun.* **1979**, 859.
13. (a) Kuang, J.; Ma, S. *J. Org. Chem.* **2009**, *74*, 1763. (b) Kuang, J.; Ma, S. *J. Am. Chem. Soc.* **2010**, *132*, 1786.
14. Zhang, H.; Fu, X.; Chen, J.; Wang, E.; Liu, Y.; Li, Y. *J. Org. Chem*. **2009**, *74*, 9351.

15. Ohmiya, H; Yang, M.; Yamauchi, Y.; Ohtsuka, Y.; Sawamura, M. *Org. Lett*. **2010**, *12*, 1796.
16. Xu, C. F.; Xu, M.; Yang, L. Q.; Li, C. Y. *J. Org. Chem*. **2012**, *77*, 3010.
17. Nun, P.; Gaillard, S.; Slawin, A. M. Z.; Nolan, S. P. *Chem. Commun*. **2010**, *46*, 9113.
18. Sakai, N.; Maruyama, T.; Konakahara, T. *Synlett* **2009**, *13*, 2105.
19. (a) Patois, C.; Richard, L.; Savignac, P. *J. Chem. Soc., Perkin Trans. I* **1990**, 1577. (b) Guillemin, J. C.; Savignac, P.; Denis, J. M. *Inorg. Chem.* **1991**, *30*, 2170. (c) Bhuvan Kumar, N. N.; Kumara Swamy, K. C. *Polyhedron* **2007**, *26*, 883. (d) Bhuvan Kumar, N. N.; Chakravarty, M.; Satish Kumar, N.; Sajna, K. V.; Kumara Swamy, K. C. *J. Chem. Sci*. **2009**, *121*, 23.
20. Kalek, M.; Johansson, T.; Jezowska, M.; Stawinski, J. *Org. Lett.* **2010**, *12*, 4702.
21. Ma, S. *Chem. Rev*. **2005**, *105*, 2829.
22. (a) Baldwin, J. E.: Trost, B. M.; Fleming, I. *Comprehensive Organic Synthesis*, ed.; Pergamon Press: Oxford, 1991; vol. 5, pp. 63–84. (b) Crimmins, M. T.; Trost, B. M.; Fleming, I.; *Comprehensive Organic Synthesis*, ed.; Pergamon Press: Oxford, 1991; vol 5, pp. 123–150. (c) Rappoport, Z.; Liebman, J. F. *The Chemistry of Cyclobutanes*, ed.; Wiley, 2005. (d) Helmchen, G.; Hoffmann, R. W.; Mulzer, J.; Schaumann, E. *Stereoselective Synthesis, Methods of Organic Chemistry* (Houben-Weyl), ed.; Thieme: Stuttgart, Germany, 1996; vol. 5, pp. 3061–3125. (e) Ruff, E. L.; Mladenova, G. *Chem. Rev*. **2003**, *103*, 1449.
23. Gu, Y.; Hama, T.; Hammond, G. B. *Chem. Commun*. **2000**, 395.
24. Horino, Y.; Kimura, M.; Tanaka, S.; Okajima, T.; Tamaru, Y. *Chem.-Eur. J.* **2003**, *9*, 2419.
25. Pasto, D. J.; Sugi, K. D. *J. Org. Chem*. **1992**, *57*, 1146.
26. Kitagaki, S.; Okumara. Y.; Mukai, C. *Tetrahedron* **2006**, *62*, 10311.
27. Jiang, X.; Ma, S. *Tetrahedron* **2007**, *63*, 7589.
28. Carreria, E. M.; Hastings, C. A.; Shepard, M. S.; Yerkey, L. A.; Millward, D. B. *J. Am. Chem. Soc*. **1994**, *116*, 6622.
29. Oh, C. H.; Gupta, A. K.; In Park, D.; Kim, N. *Chem. Commun*. **2005**, 5670.
30. Matsuda, T.; Kadowaki, S.; Goya, T.; Murakami, M. *Synlett* **2006**, 575.
31. (a) Wender, P. A.; Jenkins, T. E.; Suzuki, S. *J. Am. Chem. Soc.* **1995**, *117*, 1843. (b) Ishar, M. P. S.; Kumar, K.; Kaur, S.; Kumar, S.; Girdhar, N. K.; Sachar, S.; Marwaha, A.; Kapoor, A. *Org. Lett.* **2001**, *3*, 2133. (c). Alcaide, B.; Almendros, P.; Aragoncillo, C. *Org. Lett.* **2003**, *5*, 3795. (d) Ma, S.; Gu, Z.; Deng, Y. *Chem. Commun.* **2006**, 94. (e) Yoshino, T.; Ng, F.; Danishefsky, S. J. *J. Am. Chem. Soc.* **2006**, *128*, 14185. (f) Lohse, A. G.; Hsung, R. P. *Org. Lett.* **2009**, *11*, 3430.
32. Francos, J.; Carmona, F. G.; Faustino, H.; Siguenza, J. I.; Díez, E.; Alonso, I.;Fernández, R.; Lassaletta, J.; López, F.; Mascareñas, J. *J. Am. Chem. Soc*. **2012**, *134*, 14322.
33. (a) Jung, M. E.; Murakami, M. *Org. Lett.* **2006**, *8*, 5857. (b) Jung, M. E.; Murakami, M. *Org. Lett.* **2007**, *9*, 461. (c) Jung, M. E.; Cordova, J.; Murakami, M. *Org. Lett.* **2009**, *11*, 3882.
34. (a) Pasto, D. J.; Yang, S. H. *J. Org. Chem.* **1986**, *51*, 1676. (b) Jiang, X.; Kong, W.; Chen, J.; Ma, S. *Org. Biomol. Chem.* **2008**, *6*, 3606.
35. Spino, C.; Thibault, C.; Gingras, S.; *J. Org. Chem*. **1998**, *63*, 5283.

36. Spino, C.; Frechette, S. *Tetrahedron Lett*. **2000**, *41*, 8033.
37. Srinivas, V.; Sajna, K. V.; Kumara Swamy, K. C. *Chem. Commun*. **2011**, *47*, 5629.
38. Murakami, M.; Ubukata, M.; Itami, K.; Ito, Y. *Angew. Chem. Int. Ed*. **1998**, *37*, 16.
39. Zhang, X.-C.; Cao, S.-H.; Wei, Y.; Shi, M. *Org. Lett.* **2011**, *13*, 1142.
40. Winkler, J. D. *Chem. Rev.* **1996**, *96*, 167.
41. Kobayashi, S.; Jørgensen, K. A. *Cycloaddition Reactions in Organic Synthesis*; Ed.; Wiley VCH: Weinheim, 2001.
42. Bates, R. W.; Satcharoen, V. *Chem. Soc. Rev.* **2002**, *31*, 12.
43. Kumara Swamy, K. C.; Balaraman, E.; Satish Kumar N. *Tetrahedron* **2006**, *62*, 10152
44. Chakravarty, M.; Bhuvan Kumar, N. N.; Sajna, K. V.; Kumara Swamy, K. C. *Eur. J. Org. Chem.* **2008**, 4500.
45. Sajna, K. V.; Kumara Swamy, K. C. *J. Org. Chem.* **2012**, *77*, 5345.
46. Poonoth, M.; Krause, N. *J. Org. Chem.* **2011**, *76*, 1934.
47. Piera, J.; Krumlinde, P.; Strubing, D.; Backvall, J. E. *Org. Lett*. **2007**, *9*, 2235.
48. Mukai, C.; Ohta, M.; Yamashita, H.; Kitagaki, S. *J. Org. Chem.* **2004**, *69*, 6867.
49. Bhuvan Kumar, N. N.; Nagarjuna Reddy, M.; Kumara Swamy, K. C. *J. Org. Chem.* **2009**, *74*, 5395.
50. (a) Phani Pavan, M.; Nagarjuna Reddy, M.; Bhuvan Kumar, N. N.; Kumara Swamy, K. C. *Org. Biomol. Chem*. **2012**, *10*, 8113. (b) Phani Pavan, M.; Kumara Swamy, K. C. *Synlett* **2011**, 1288. (c) Rama Suresh, R.; Kumara Swamy, K. C. *J. Org. Chem*. **2012**, *77*, 6959. (d) Mukai, C.; Kuroda, N.; Ukon, R.; Itoh, R. *J. Org. Chem*. **2005**, *70*, 6282.
51. (a) Van Henegouwen, W. G. B.; Hiemstra, H. *J. Org. Chem*. **1997**, *62*, 8862. (b) Van Henegouwen, W. G. B.; Fieseler, R. M.; Rutjes, F. P. J. T.; Hiemstra, H. *J. Org. Chem.* **2000**, *65*, 8317. (c) Mukai, C.; Yamashita, H.; Hanaoka, M. *Org. Lett*. **2001**, *3*, 3385. (d) Mukai, C.; Ukon, R.; Kuroda, N. *Tetrahedron Lett*. **2003**, *44*, 1583. (e) Mukai, C.; Kobayashi, M.; Kubota, S.; Takahashi, Y.; Kitagaki, S. *J. Org. Chem*. **2004**, *69*, 2128. (f) Gockel, B.; Krause, N. *Org. Lett*. **2006**, *8*, 4485. (g) Hashmi, A. S. K.; Blanco, M. C.; Fischer, D.; Bats, J. W. *Eur. J. Org. Chem*. **2006**, 1387. (h) Lemiere, G.; Gandon, V.; Agenet, N.; Goddard, J.-P.; De Kozak, A.; Aubert, C.; Fensterbank, L.; Malacria, M. *Angew. Chem., Int. Ed*. **2006**, *45*, 7596. (i) Bianchi, L.; Maccagno, M.; Petrillo, G.; Rizzato, E.; Sancassan, F.; Severi, E.; Spinelli, D.; Stenta, M.; Galatini, A.; Tavani, C. *Tetrahedron* **2009**, *65*, 336.
52. (a) Kumara Swamy, K. C.; Kumaraswamy, S.; Senthil Kumar, K.; Muthiah, C. *Tetrahedron Lett.* **2005**, *46*, 3347. (b) Morita, I.; Kunimoto, K.; Tsuda, M.; Tada, S.; Kise, M.; Kimura, K. *Chem. Pharmaceut. Bull.* **1987**, *35*, 4144. (c) King, R. B.; Sundaram, P. M. *J. Org. Chem.* **1984**, *49*, 1784.
53. Muthiah, C.; Praveen Kumar, K.; Aruna Mani, C.; Kumara Swamy, K. C. *J. Org. Chem.* **2000**, *65*, 3733.
54. (a) Larock, R. C.; Harrison, L. W. *J. Am. Chem. Soc*. **1984**, *106*, 4218. (b) Zhou, N.; Wang, Li.; Thompson, D. W. Zhao, Y. *Org. Lett*, **2008**, *10*, 3001.
55. Shu, X. Z.; Liu, X. Y.; Xiao, H. Q.; Ji, K. G.; Guo, L. N.; Qi, C. Z.; Liang, Y. M. *Adv. Synth. Catal.* **2007**, *349*, 2493.
56. Kleinbeck, F.; Toste. F. D. *J. Am. Chem. Soc*. **2009**, *131*, 9178.

57. Iorga, B.; Eymery, F.; Carmichael, D.; Savignac, P. *Eur. J. Org. Chem.* **2000**, 3103.
58. Boutagy, J.; Thomas, R. *Chem. Rev*. **1974**, 74, 87.
59. Manab Chakravarty "*Investigations on catalytic and noncatalytic reactions of allenylphosphonates, α-methoxyphosphonates and phosphazanes possessing N-P=X [X = O, S, Se] skeleton*" Ph.D-Thesis 2007, University of Hyderabad, India.
60. Pasto, D. J.; Kong, W. *J. Org. Chem.* **1988**, *53*, 4807.
61. (a) Chia, H.-A.; Kirk, B. E.; Taylor, D. R. *J. Chem. Soc., Perkin Trans. I* **1974**, 1209. (b) Shibata, T.; Takesue, Y.; Kadowaki, S.; Takagi, K. *Synlett* **2003**, 268.
62. (a) Angelov, C. M.; Mondeshka, D. M.; Tancheva, T. N. *J. Chem. Soc., Chem. Commun*. **1985**, 647 (b) Mondeshka, D.; Tancheva, C.; Angelov, C. *Chem. Ber.* **1990**, *123*, 1381. (c) Murakami, M.; Itami, K.; Ito, Y. *J. Am. Chem. Soc.* **1997**, *119*, 7163. (d) Hakuba, H.; Kitagaki, S.; Mukai, C. *Tetrahedron* **2007**, *63*, 12639. (e) Zhou, H.; Zhu, D.; Xie, Y.; Huang, H.; Wang, K. *J. Org. Chem*. **2010**, *75*, 2706.
63. Bruckner, R.; Huisgen, R.; Schmid, J. *Tetrahedron Lett*. **1990**, *31*, 7129.
64. Cherry, K.; Parrain, J. L.; Thibonnet, J.; Duchene, A.; Abarbri, M. *J. Org. Chem.* **2005**, *70*, 6669.
65. Lu, C.; Lu, X. *Org. Lett.* **2002**, *4*, 4677.
66. (a) Trost, B. M.; Li, C. J. *J. Am. Chem. Soc*. **1994**, *116*, 3167. (b) Martin, T. J.; Vakhshori, V. G.; Tran, Y. S.; Kwon, O. *Org. Lett* **2011**, *13*, 2586.
67. (a) Larock, R. C. *Comprehensive Organic Transformations*, VCH, New York, 1999; (b) Olah, G. A.; Krishnamurti, R. and Prakash, G. K. S., In *Comprehensive Organic Synthesis*, ed. Trost, B. M. and Fleming, I., Pergamon, Oxford, 1991, vol. 3, pp. 293–339; (c) Roberts, R. M. and Khalaf, A. A. *Friedel–Crafts Alkylation Chemistry. A Century of Discovery*, Dekker, New York, 1984; (d) Olah, A., *Friedel–Crafts and Related Reactions*, Wiley-Interscience, New York, 1964, vol. II, Part 1
68. Rao, W.; Chan, P. W. H. *Org. Biomol. Chem*. **2008**, *6*, 2426.
69. Sato, Y.; Ohashi, K.; Mori, M. *Tetrahedron Lett.* **1999**, *40*, 5231.
70. Mikhailovskaya, T. F.; Vasilevsky, S. F. *Russ. Chem. Bull. Int. Ed.* **2010**, *59*, 632.
71. Hauser, F. M.; Baghdanov, V. M. *J. Org. Chem.* **1988**, *53*, 4676.
72. (a) Sheldrick, G. M. *SADABS, Siemens Area Detector Absorption Correction*, University of Göttingen, Germany, **1996**. (b) Sheldrick, G. M., SHELX-97- *A program for crystal structure solution and refinement*, University of Göttingen, **1997**. (c) Sheldrick, G. M. *SHELXTL NT Crystal Structure Analysis Package*, Bruker AXS, Analytical X-ray System, WI, USA, **1999**, version 5.10.

## A) Copies of $^{1}H/^{13}C$ NMR spectra for representative compounds

## PART A: Compounds 26i, 32a, 32f, 33f, 36, 41, 44, 52 and 53

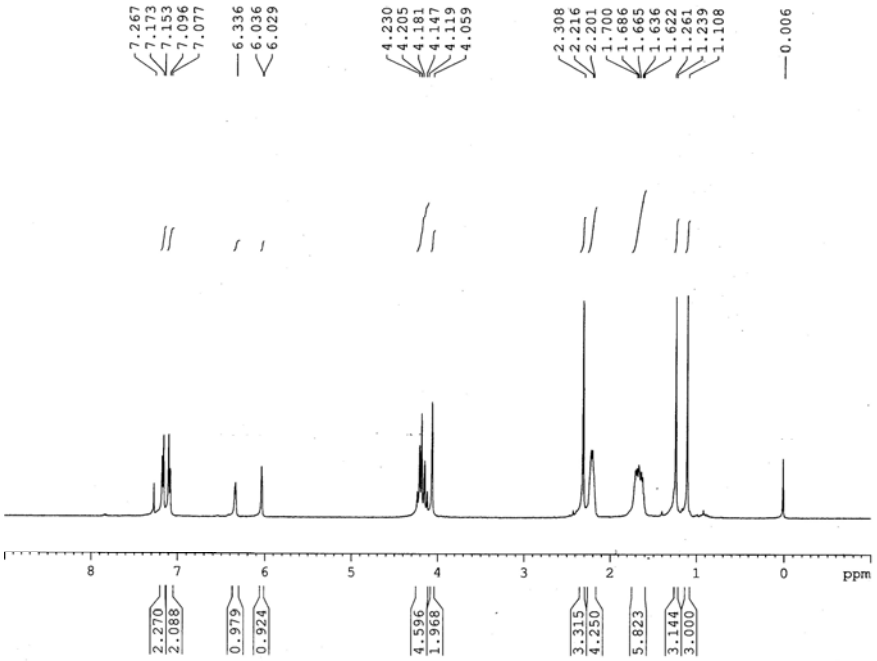



**Figure A1.** $^{1}H$ NMR spectrum of compound **26i**

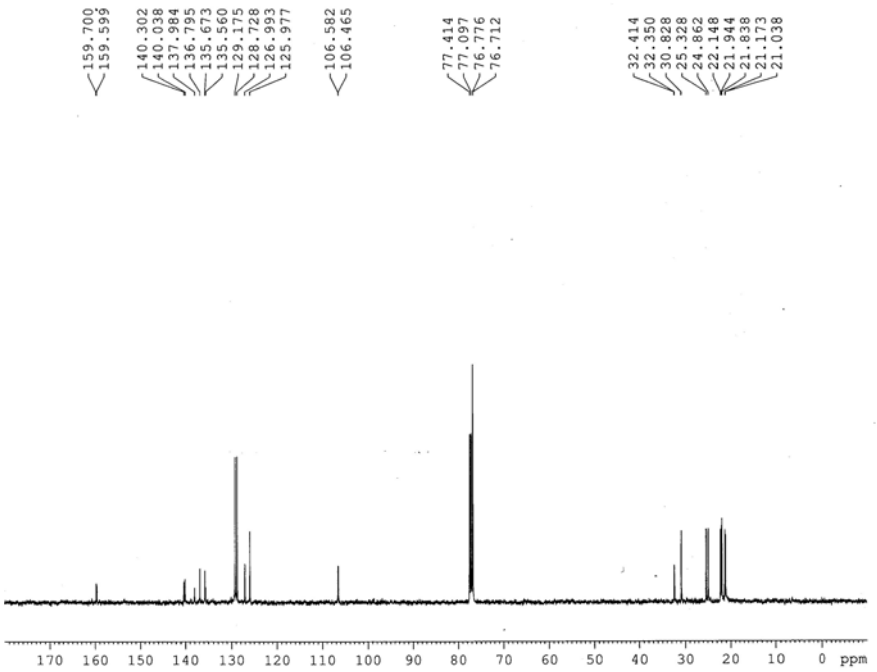



**Figure A2.** $^{13}C$ NMR spectrum of compound **26i**

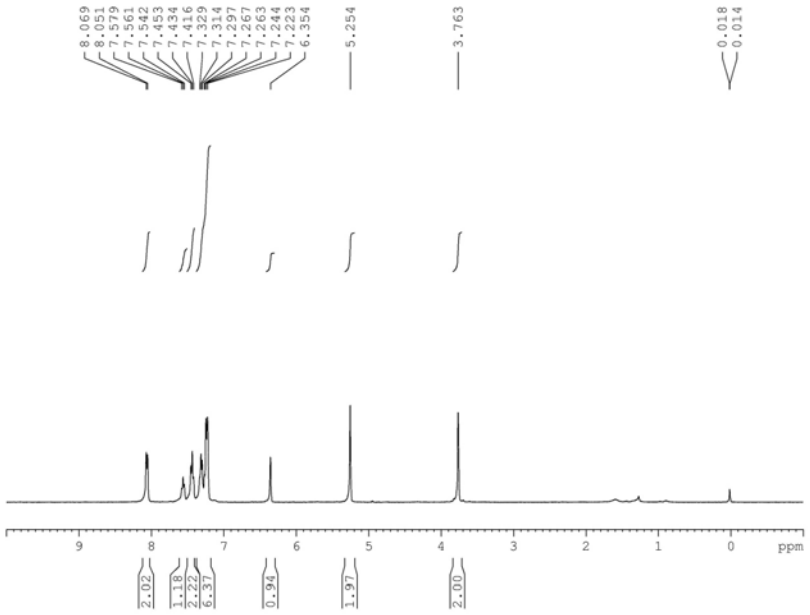



**Figure A3.** $^{1}$H NMR spectrum of compound **32a**

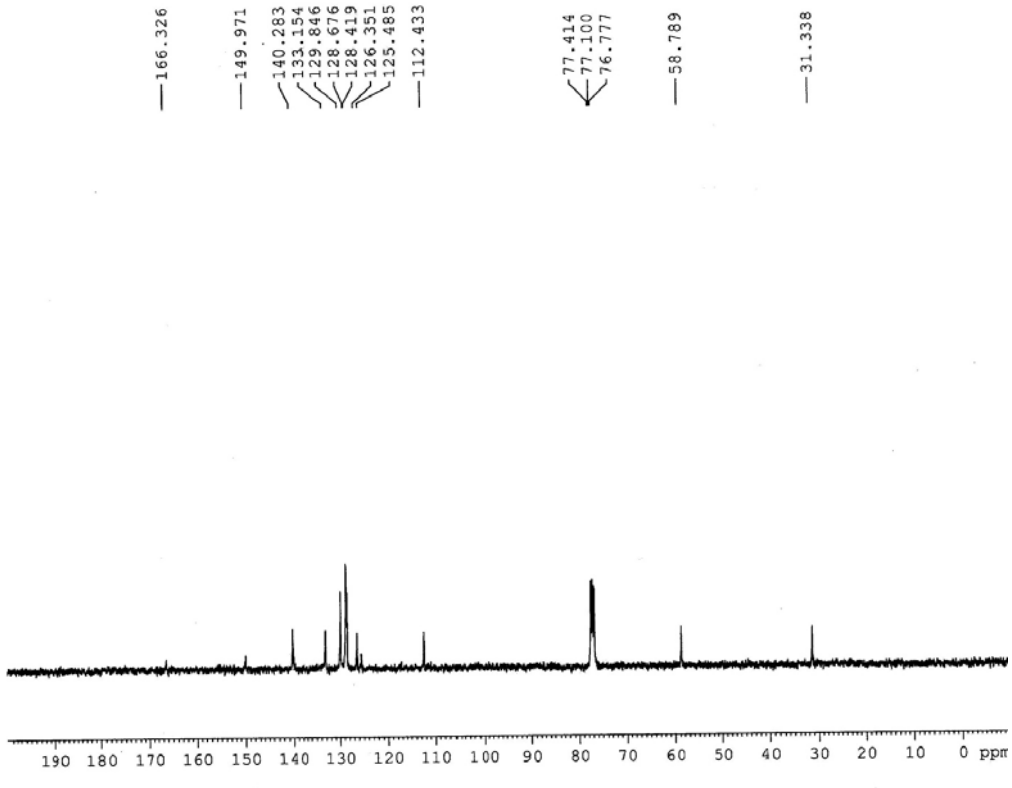



**Figure A4.** $^{13}$C NMR spectrum of compound **32a**

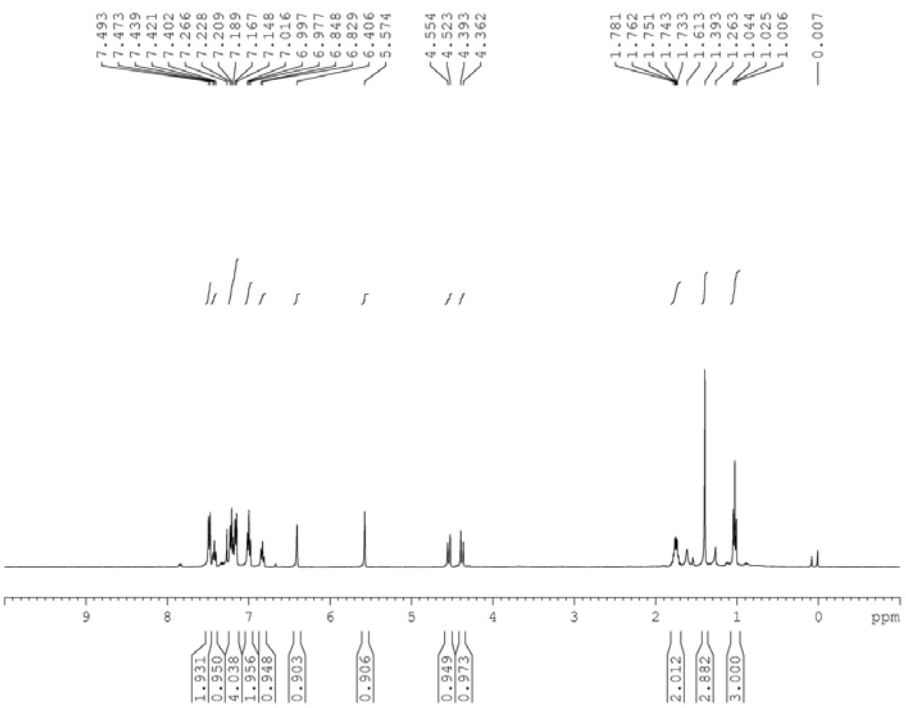



**Figure A5.** $^{1}$H NMR spectrum of compound **32f**

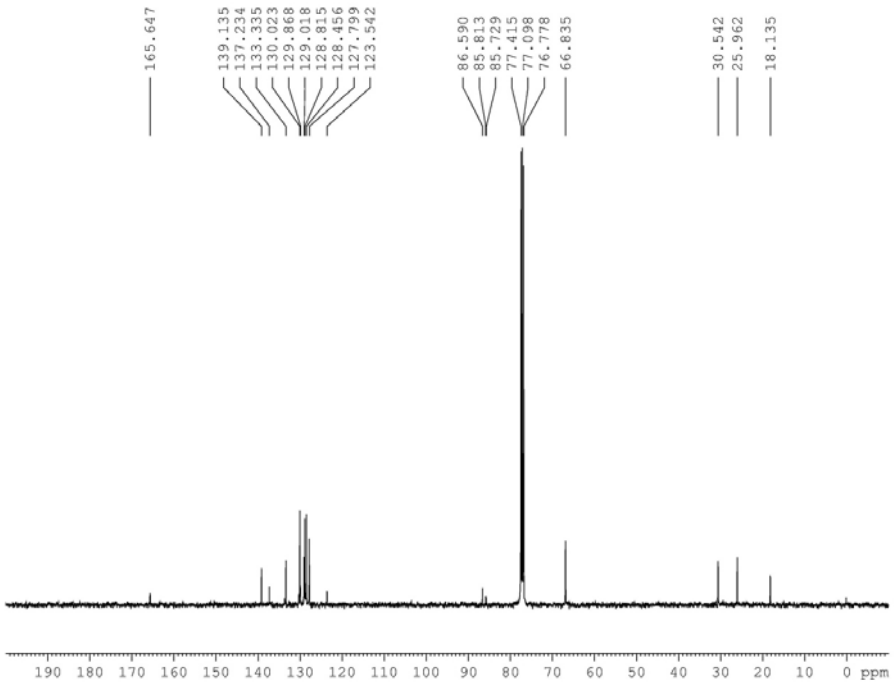



**Figure A6.** $^{13}$C NMR spectrum of compound **32f**

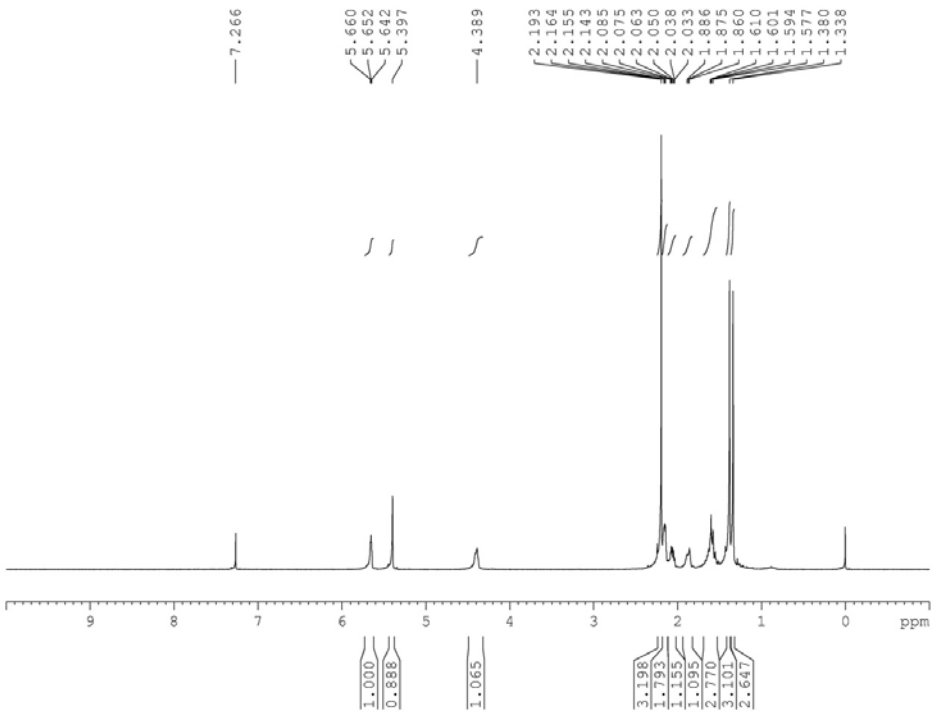



**Figure A7.** $^{1}$H NMR spectrum of compound **33f**

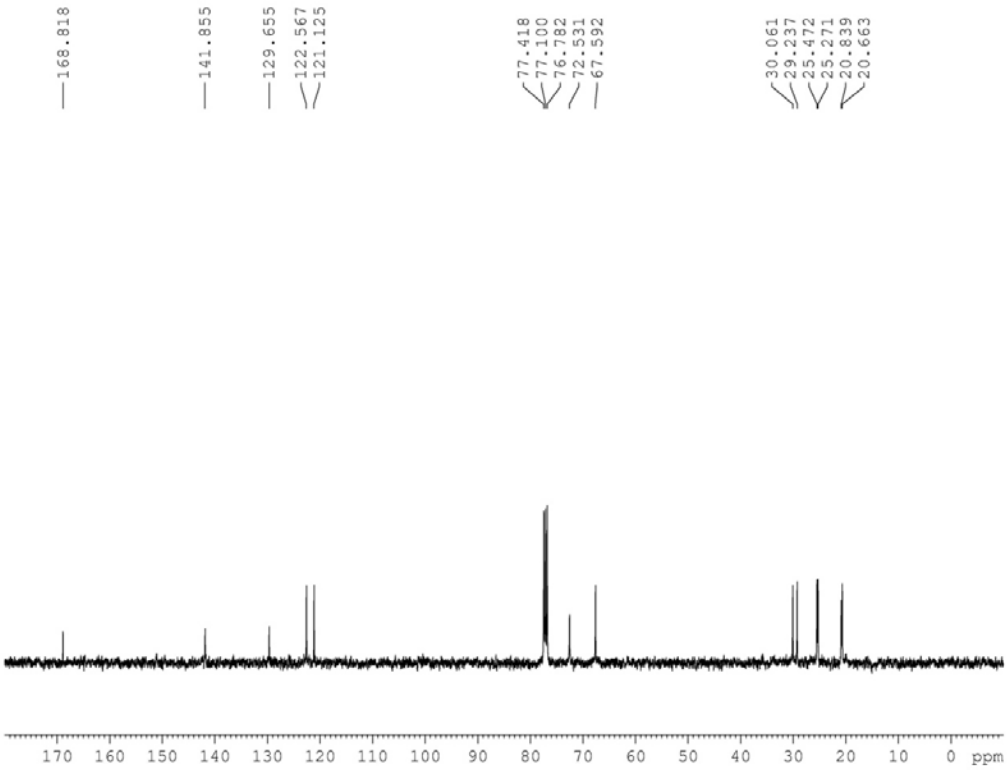



**Figure A8.** $^{13}$C NMR spectrum of compound **33f**

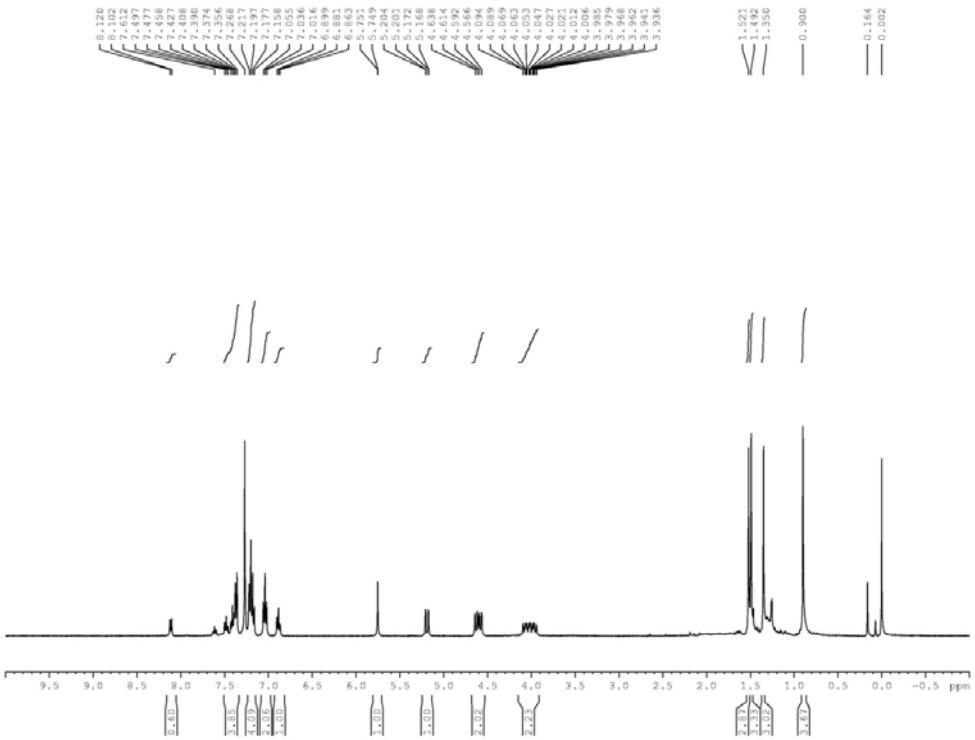


**Figure A9.** $^{1}$H NMR spectrum of compound **36**

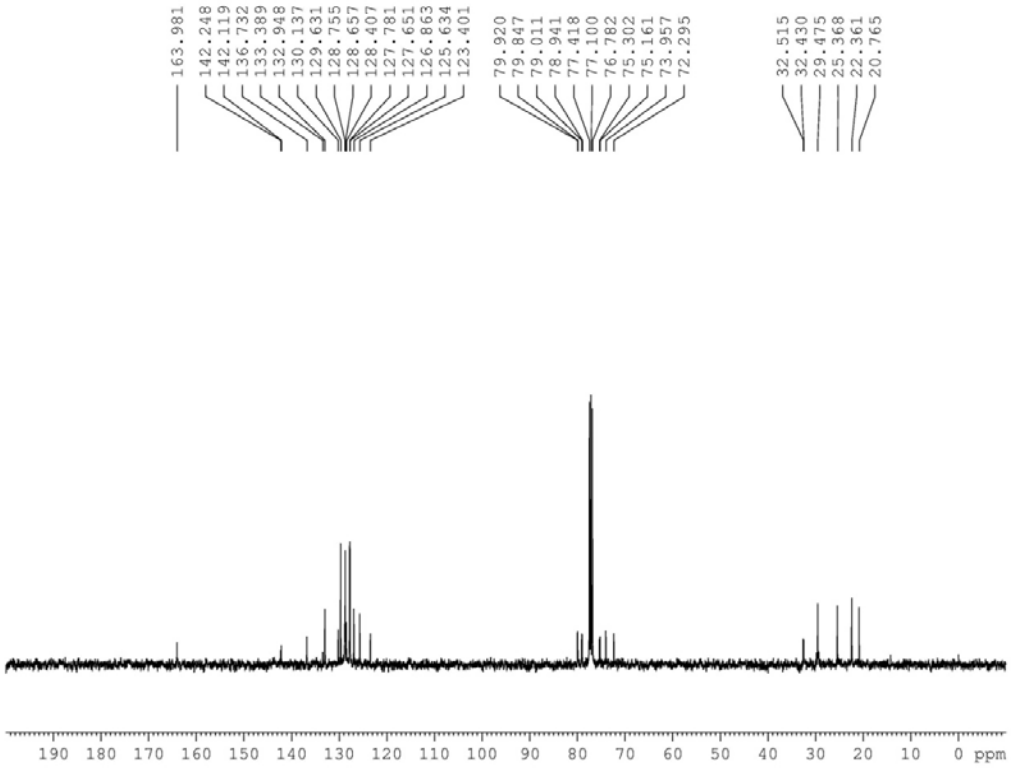


**Figure A10.** $^{13}$C NMR spectrum of compound **36**

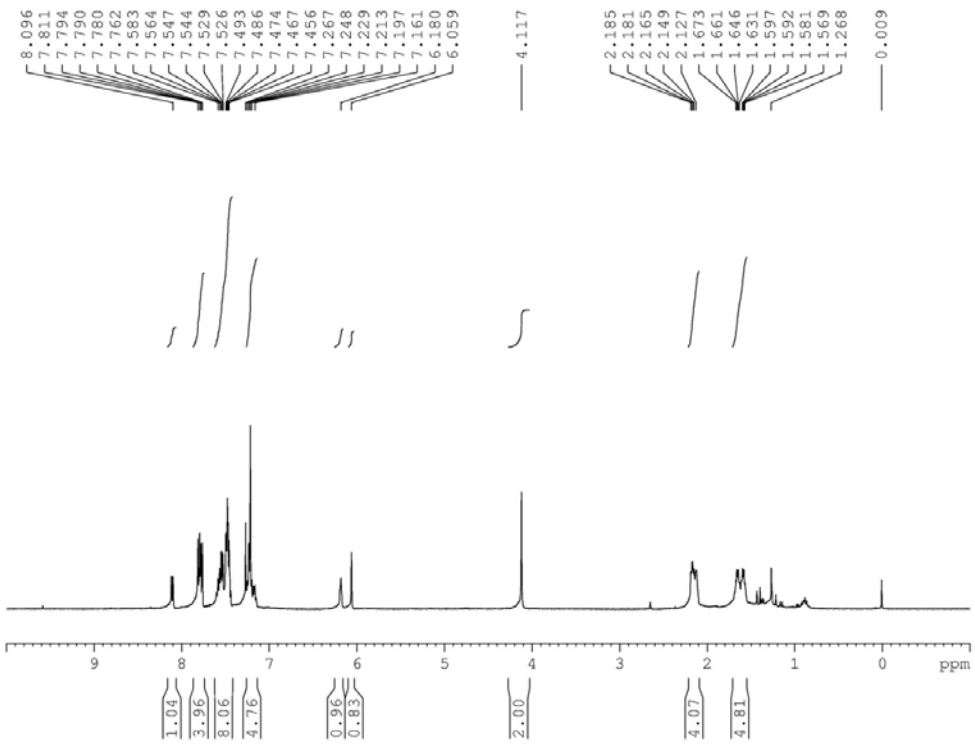



**Figure A11.** $^{1}$H NMR spectrum of compound **41**

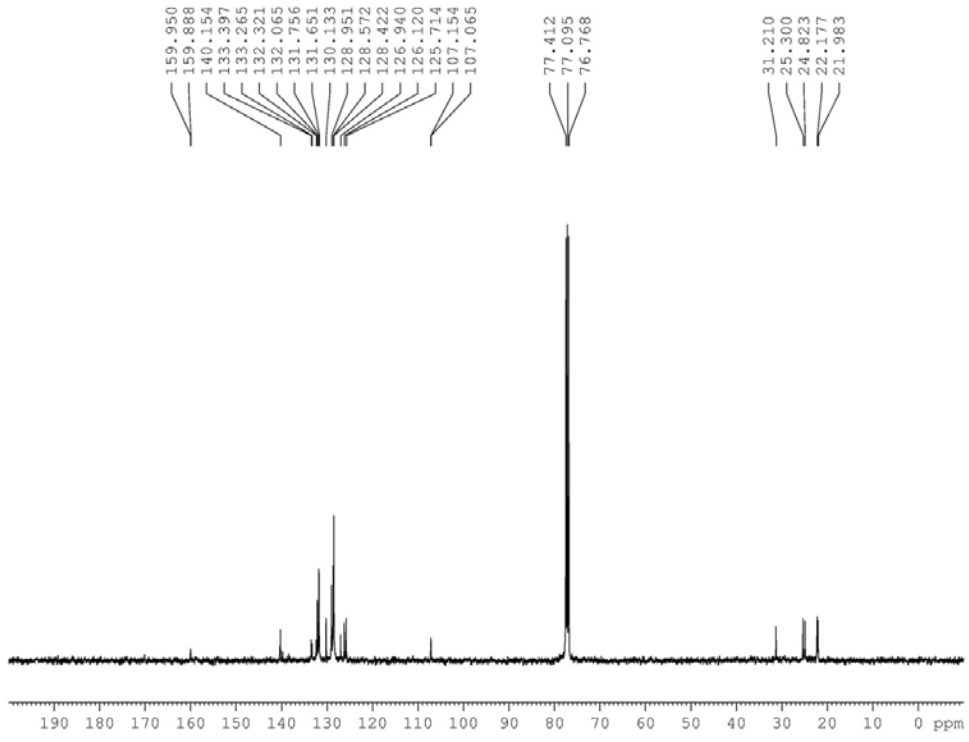



**Figure A12.** $^{13}$C NMR spectrum of compound **41**

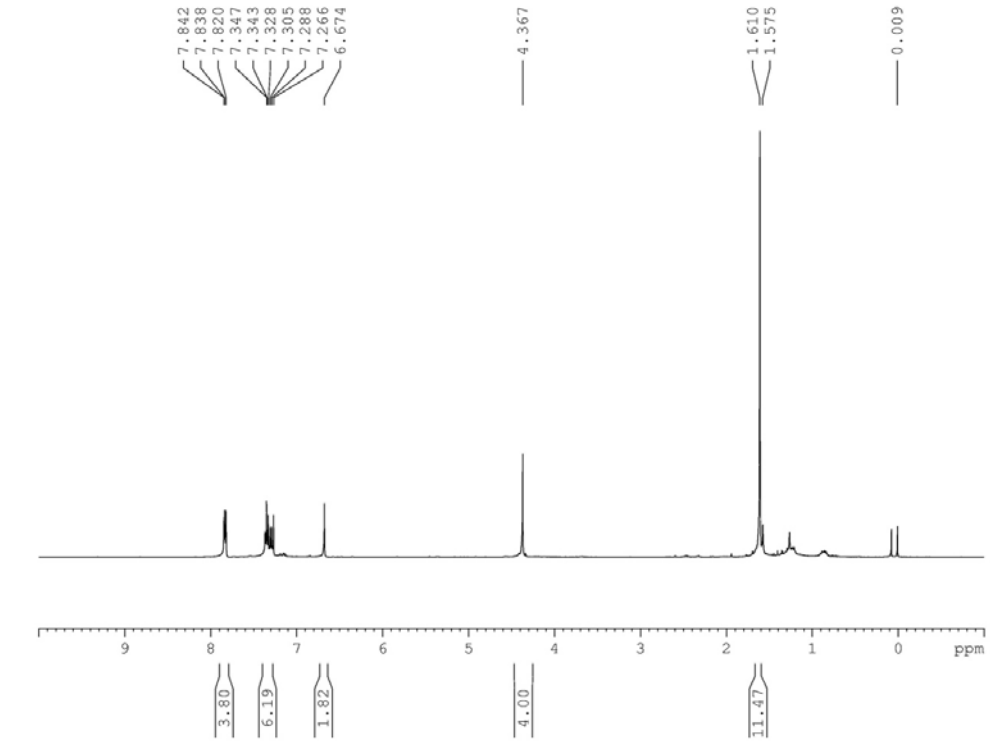



**Figure A13.** $^{1}$H NMR spectrum of compound **44**

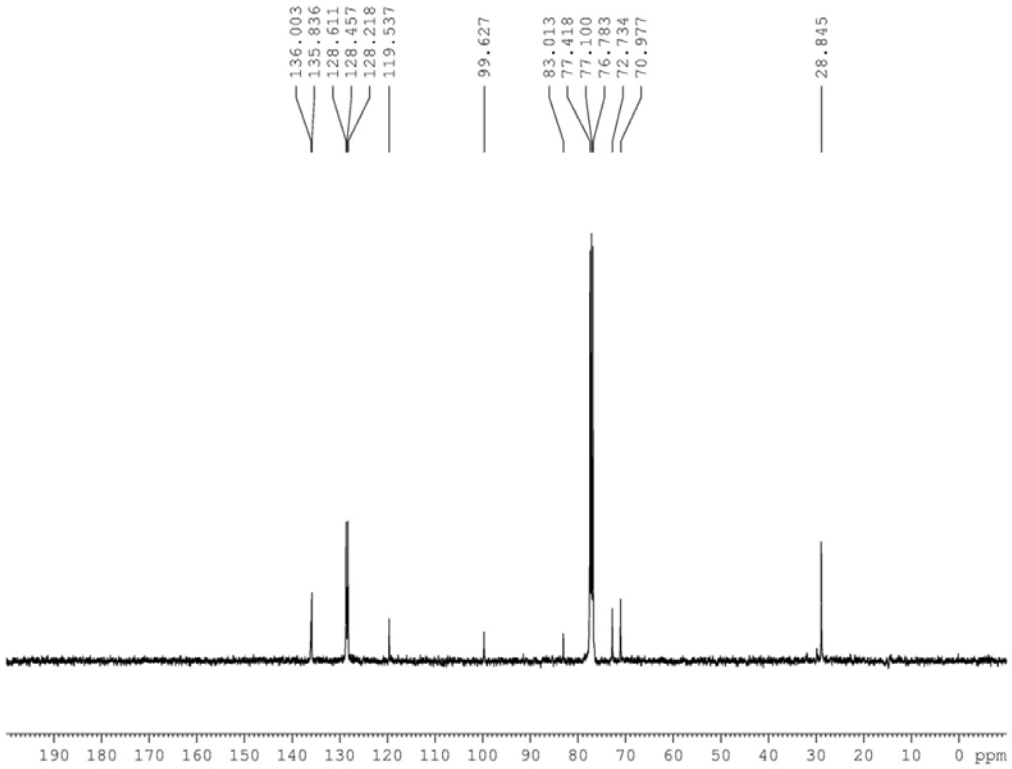



**Figure A14.** $^{13}$C NMR spectrum of compound **44**

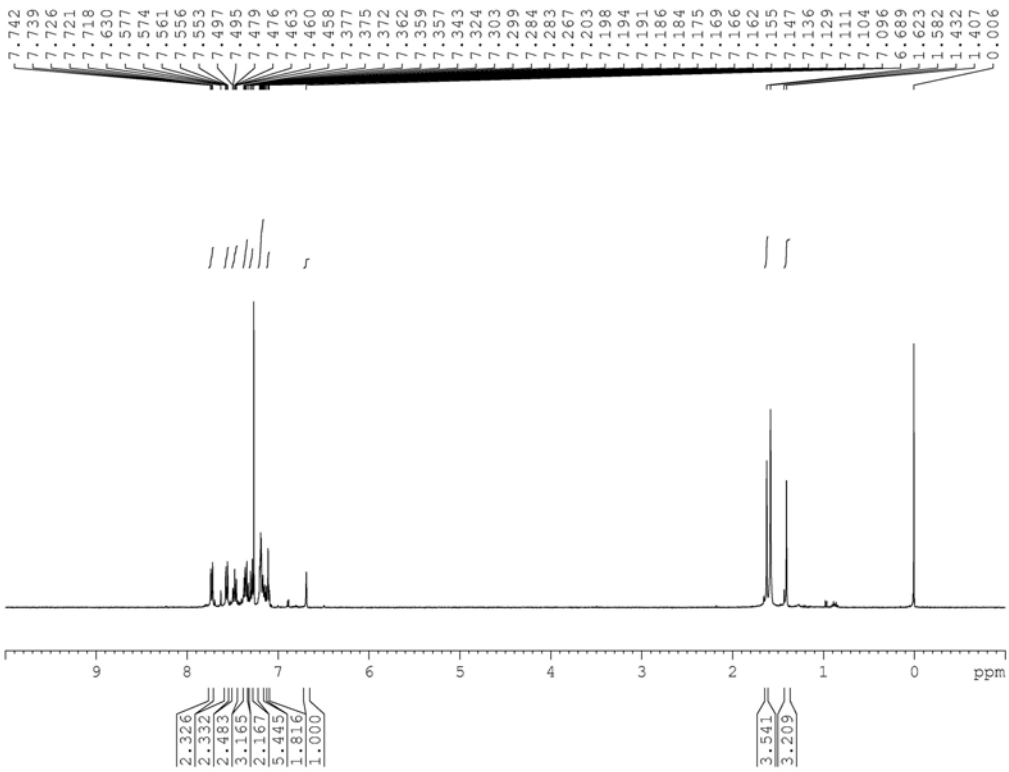



**Figure A15.** $^{1}$H NMR spectrum of compound **52**

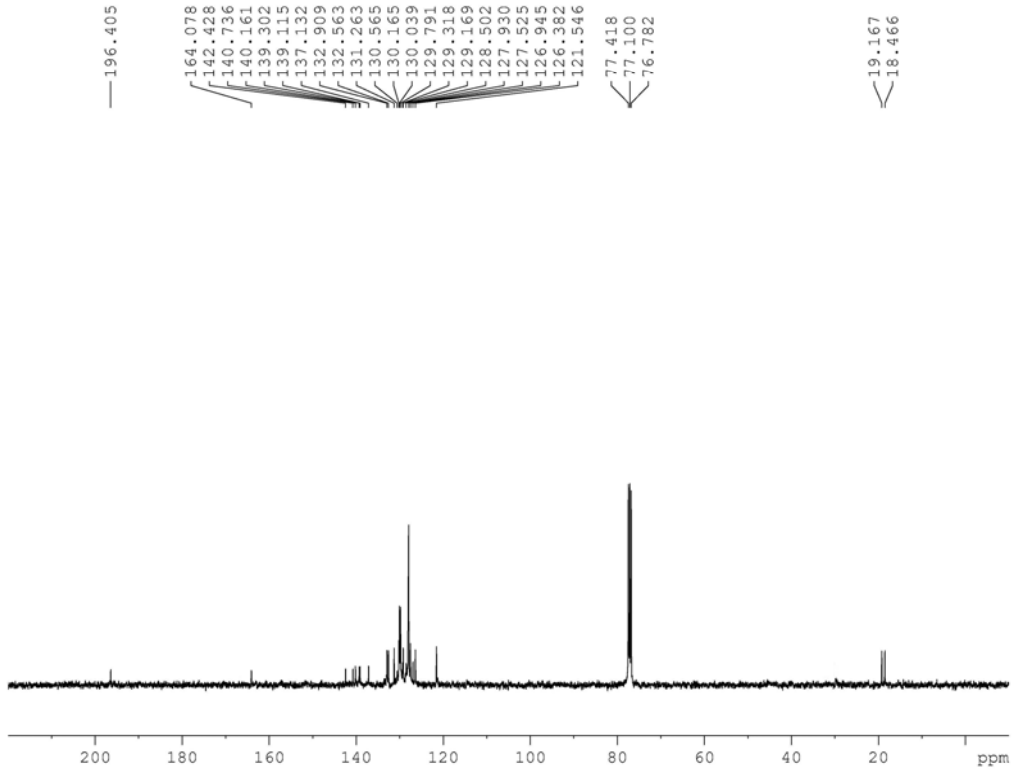



**Figure A16.** $^{13}$C NMR spectrum of compound **52**

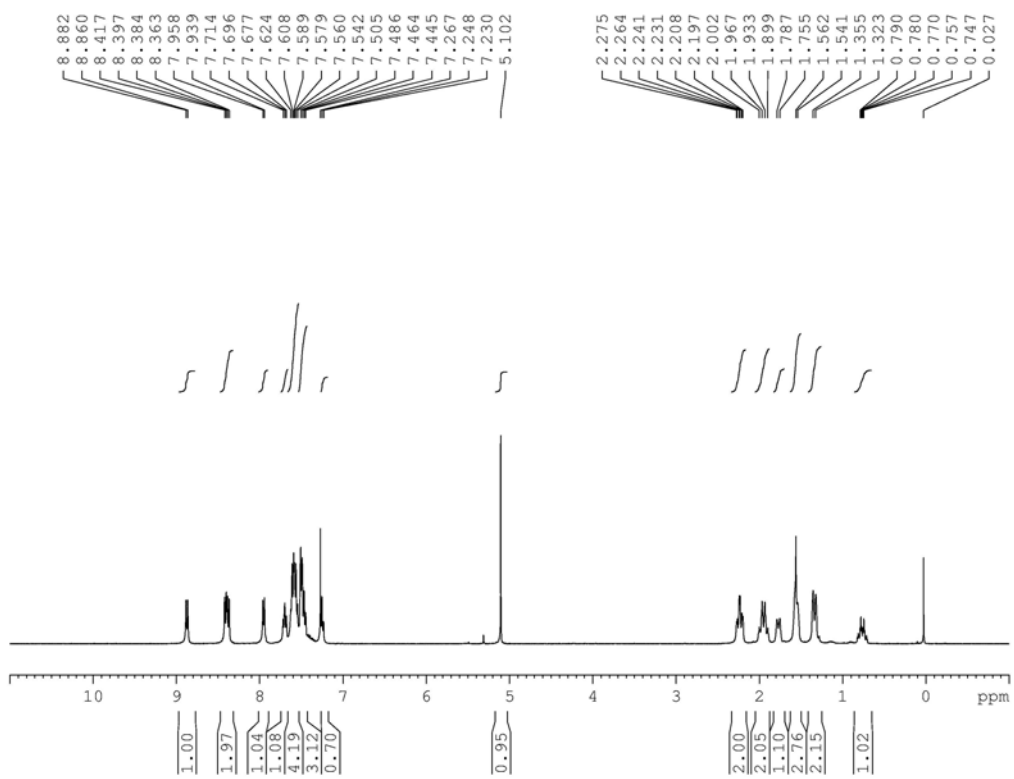



**Figure A17.** $^{1}$H NMR spectrum of compound **53**

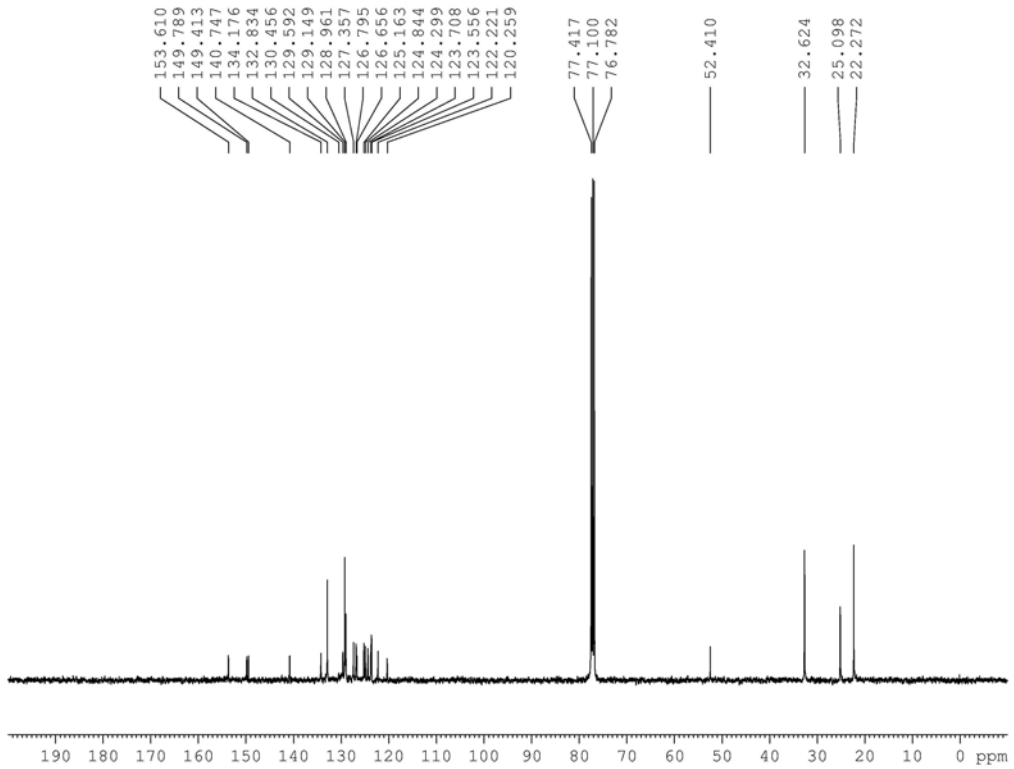



**Figure A18.** $^{13}$C NMR spectrum of compound **53**

## PART B: Compounds 14, 19c, 21b and 51a

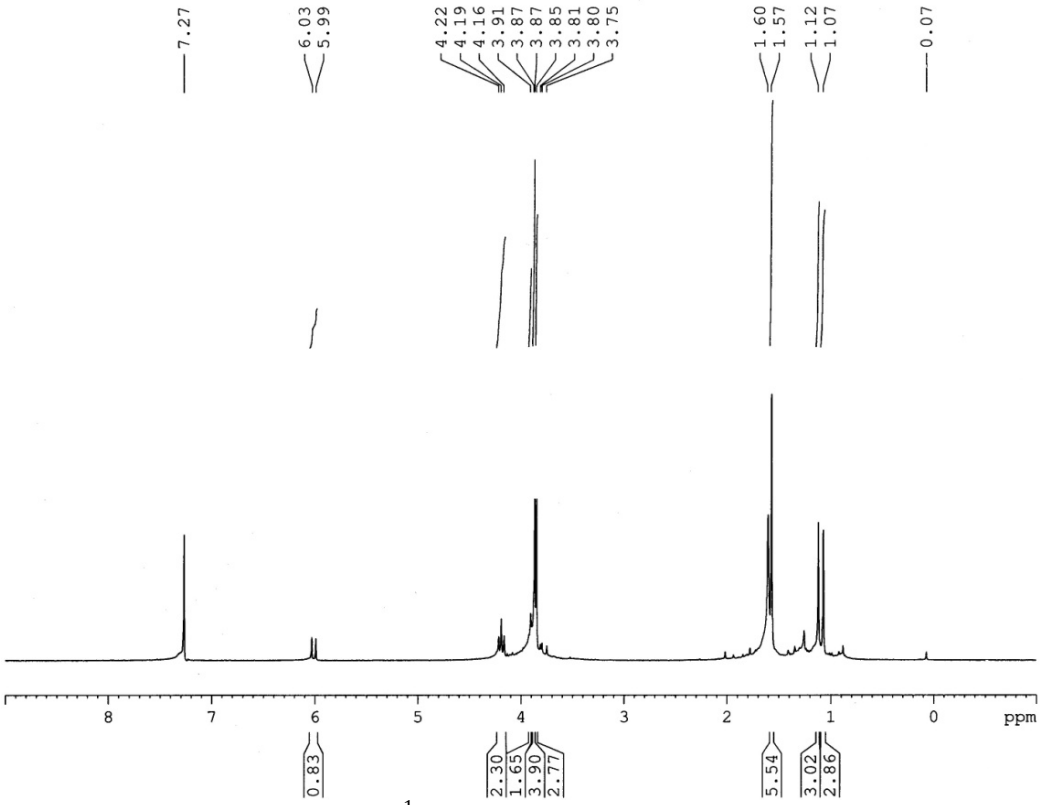



**Figure A19.** $^{1}$H NMR spectrum of compound **14**

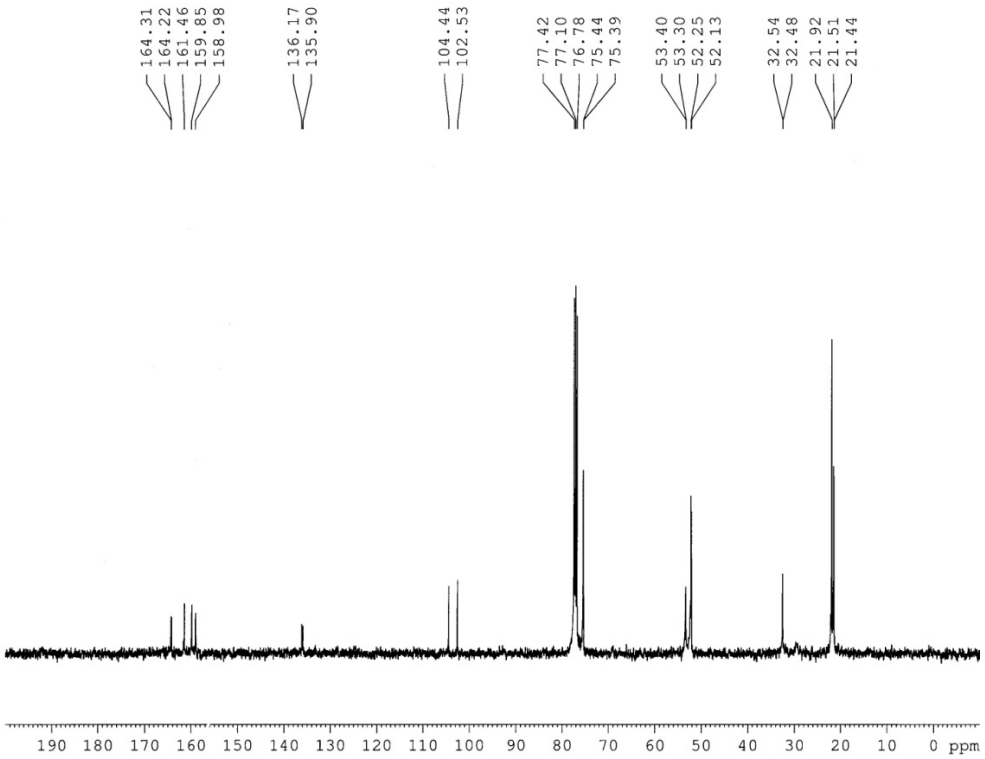



**Figure A20.** $^{13}$C NMR spectrum of compound **14**

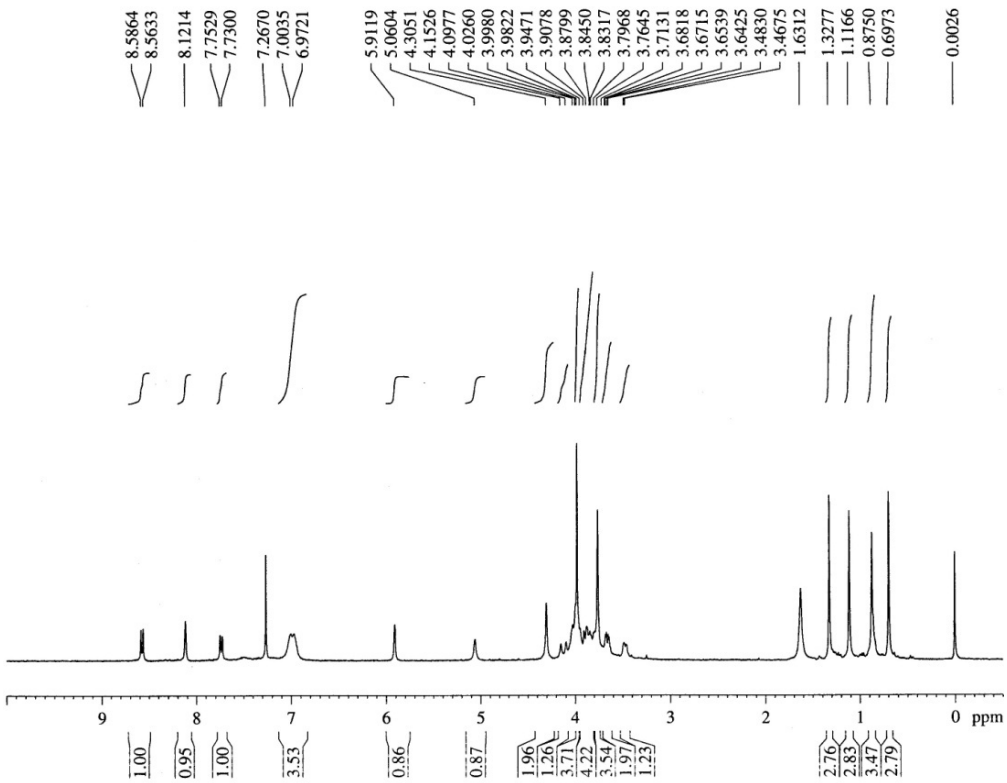



**Figure A21.** $^{1}$H NMR spectrum of compound **19c**

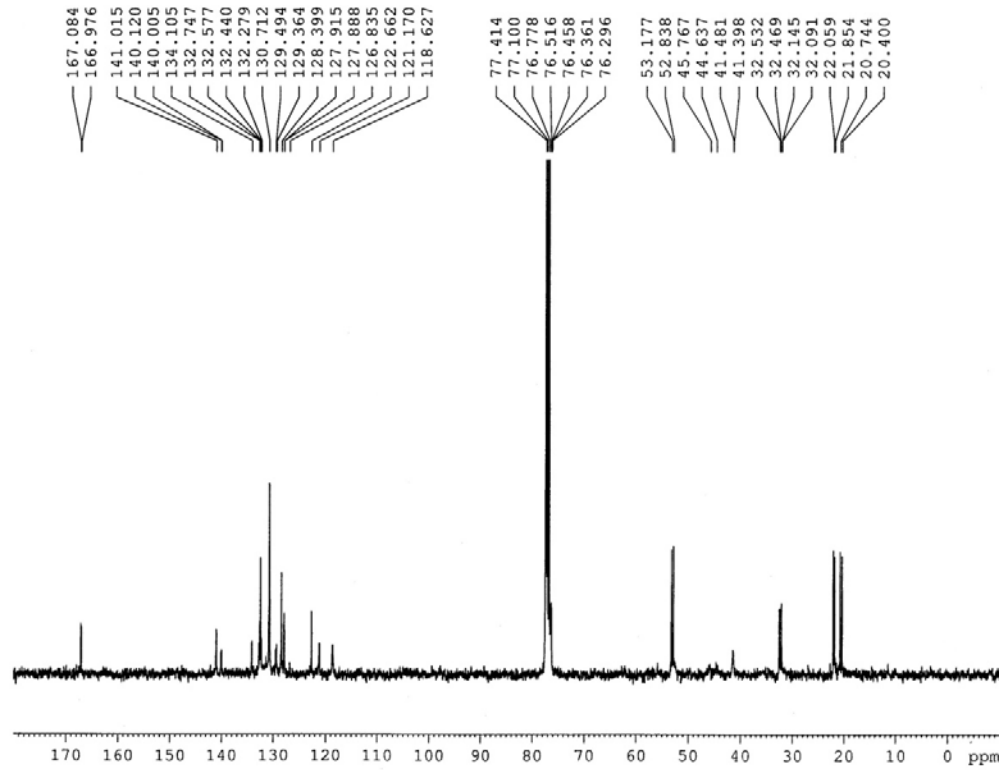



**Figure A22.** $^{13}$C NMR spectrum of compound **19c**

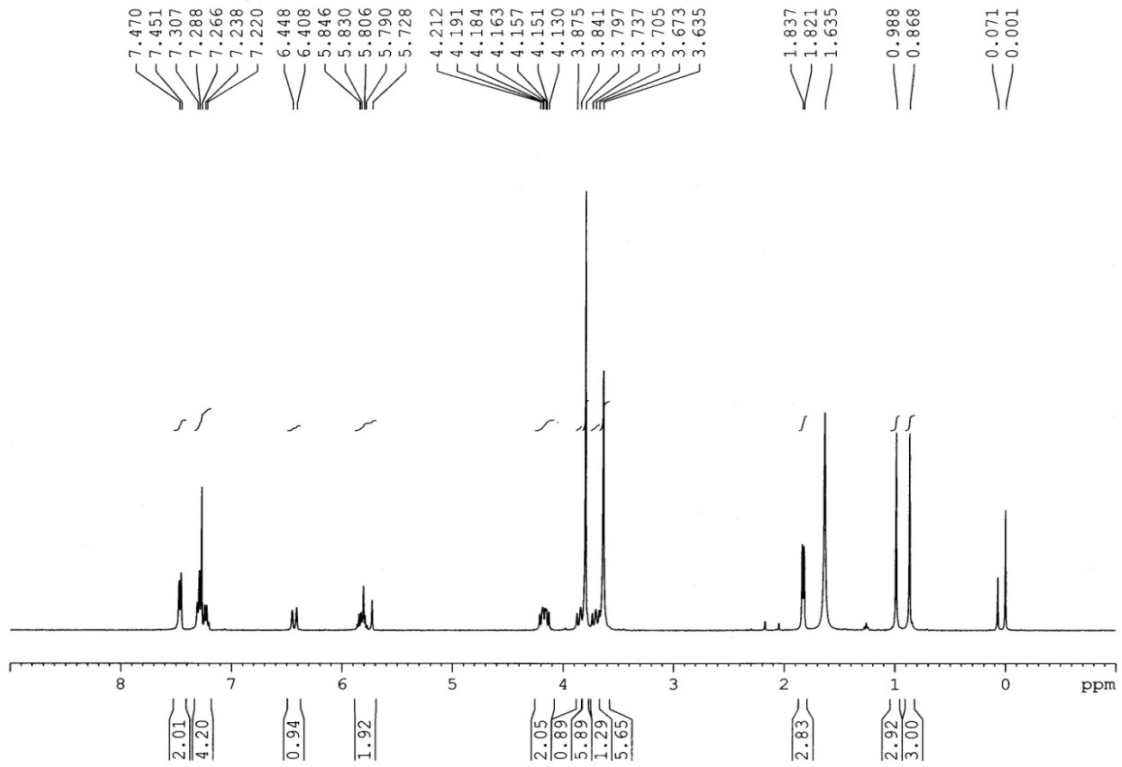



**Figure A23.** $^{1}$H NMR spectrum of compound **21b**

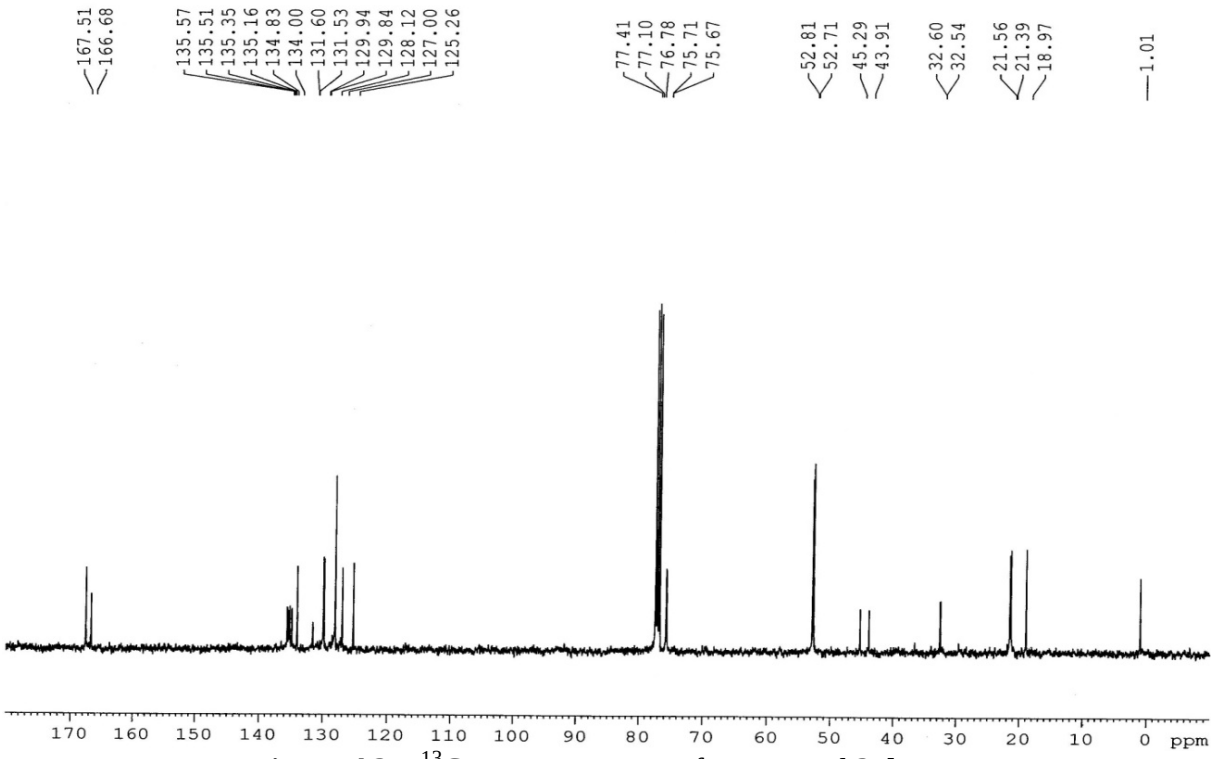



**Figure A24.** $^{13}$C NMR spectrum of compound **21b**

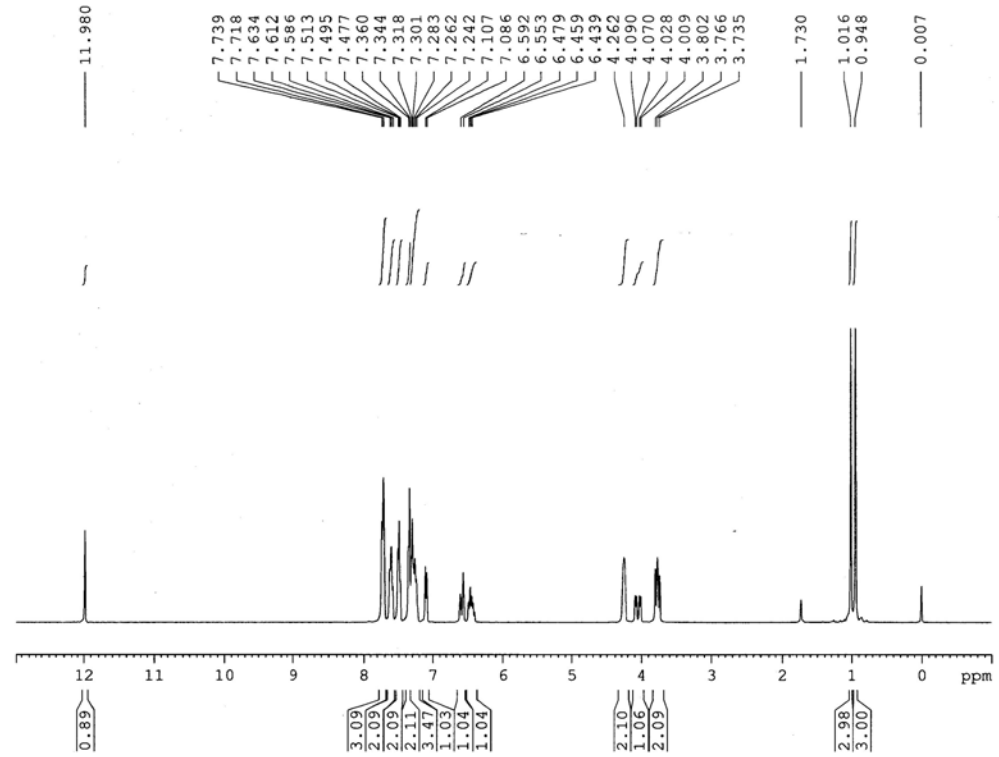



**Figure A25.** $^{1}$H NMR spectrum of compound **51a**

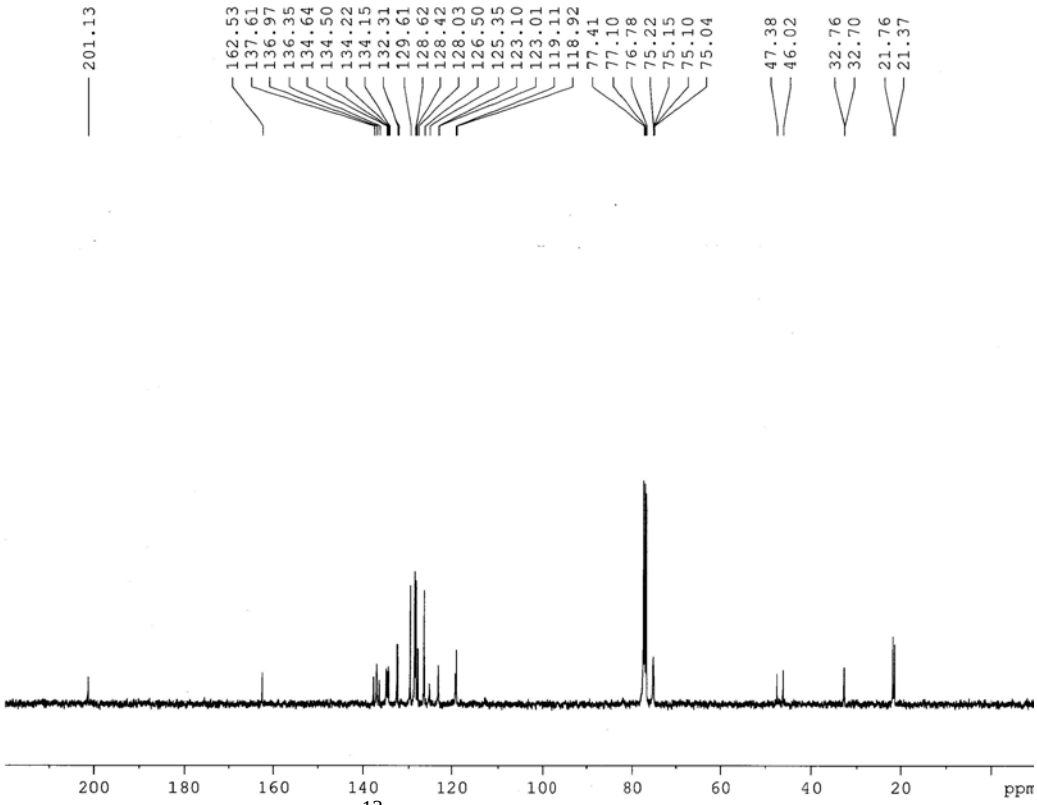



**Figure A26.** $^{13}$C NMR spectrum of compound **51a**

**B) Publication numbers and atomic coordinates for X-ray structures reported in this thesis**

**I. Publication numbers for the published compounds**

**PART A: Compounds 26a**
**Publication no. 2 (Contents, p. xi)**

**PART B: Compounds 18a, 20b.$CHCl_3$, 21a, 21b.$H_2O$**
**Publication no. 1 (Contents, p. xi)**

**II. Selected atomic coordinates for compounds 30b, 31, 33d, 37, 43, 53 and 69 from PART A and for compounds, 27, 28, 38, 42, 49a and 50a from PART B.**

Atomic coordinates (x $10^4$) and equivalent isotropic displacement parameters ($Å^2$ x $10^3$) for 4. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

## PART A

**Compound 30b**

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| C(8) | 2076(8) | 5048(7) | 4703(5) | 51(2) |
| P(1) | 2251(2) | 3017(2) | 7088(2) | 55(1) |
| O(4) | 2093(5) | 3110(4) | 5890(3) | 53(1) |
| O(1) | 1608(5) | 4115(5) | 7792(4) | 59(1) |
| O(3) | 1493(7) | 1415(5) | 7066(4) | 96(2) |
| O(2) | 4093(5) | 3954(5) | 7641(3) | 61(1) |
| C(2) | 4226(9) | 6568(7) | 8615(5) | 58(2) |
| C(1) | 2446(9) | 5814(7) | 8013(6) | 60(2) |
| C(16) | 221(7) | 2369(6) | 3132(5) | 45(2) |
| C(7) | 925(7) | 3355(6) | 4243(5) | 45(2) |
| C(10) | 4417(8) | 8047(7) | 5736(5) | 48(2) |
| C(3) | 4914(8) | 5670(7) | 7884(6) | 63(2) |
| C(17) | 334(7) | 2725(6) | 2133(5) | 45(2) |
| C(6) | 580(8) | 2708(7) | 5146(5) | 54(2) |
| C(9) | 3100(8) | 6429(8) | 5177(5) | 57(2) |
| C(19) | -531(10) | 1667(9) | 41(6) | 82(2) |
| C(21) | 1278(9) | 4445(9) | 1127(7) | 69(2) |
| C(22) | 1259(8) | 4238(7) | 2138(6) | 59(2) |
| C(12) | 5546(10) | 10913(7) | 6758(6) | 65(2) |
| C(18) | -528(9) | 1452(8) | 1045(6) | 68(2) |
| C(4) | 4502(10) | 6575(8) | 9829(5) | 82(2) |
| C(13) | 7045(10) | 11090(7) | 6845(6) | 67(2) |
| C(11) | 4216(9) | 9392(7) | 6189(5) | 61(2) |
| C(20) | 409(10) | 3161(10) | 69(7) | 75(2) |
| C(15) | 5946(9) | 8260(7) | 5838(6) | 61(2) |
| C(14) | 7245(9) | 9779(8) | 6386(6) | 73(2) |
| C(5) | 5016(12) | 8298(7) | 8716(6) | 102(3) |

## Compound 31

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| I(1) | 4389(1) | 5762(1) | 2402(1) | 66(1) |
| O(1) | 4789(2) | 2838(2) | 4127(3) | 54(1) |
| N(1) | 1567(4) | 4411(3) | 2545(5) | 78(1) |
| N(2) | 972(4) | 5137(4) | 2297(5) | 82(1) |
| N(3) | 378(5) | 5765(4) | 1950(9) | 138(3) |
| C(1) | 2248(4) | 4373(3) | 4080(5) | 62(1) |
| C(2) | 1657(5) | 3727(5) | 5156(6) | 84(2) |
| C(3) | 1762(5) | 2641(4) | 4849(6) | 84(2) |
| C(4) | 2999(4) | 2293(4) | 5073(6) | 75(1) |
| C(5) | 3691(4) | 3035(3) | 4365(5) | 53(1) |
| C(6) | 3386(3) | 3945(3) | 3896(4) | 49(1) |
| C(7) | 4351(4) | 4353(3) | 3281(4) | 47(1) |
| C(8) | 5191(3) | 3667(3) | 3450(4) | 48(1) |
| C(9) | 6377(3) | 3615(3) | 3155(5) | 53(1) |
| C(10) | 6752(4) | 4142(4) | 1972(6) | 70(1) |
| C(11) | 7886(5) | 4090(5) | 1720(7) | 90(2) |
| C(12) | 8637(5) | 3513(5) | 2625(8) | 90(2) |
| C(13) | 8272(4) | 2989(4) | 3780(8) | 84(2) |
| C(14) | 7156(4) | 3037(3) | 4059(6) | 67(1) |

## Compound 33d

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| O(1) | 462(2) | 9999(2) | 1388(1) | 54(1) |
| O(2) | 3470(1) | 7002(2) | 1488(1) | 55(1) |
| C(6) | 2825(2) | 9506(3) | 1380(1) | 45(1) |
| C(7) | 2458(2) | 8011(3) | 1336(1) | 46(1) |
| C(9) | 89(2) | 8613(3) | 1123(1) | 45(1) |
| C(15) | 4286(2) | 6606(3) | 940(1) | 43(1) |
| O(3) | 4095(2) | 6958(3) | 334(1) | 64(1) |
| C(8) | 1229(2) | 7573(3) | 1205(1) | 50(1) |
| C(11) | -2270(2) | 9154(4) | 1518(1) | 62(1) |
| C(1) | 1718(2) | 10518(3) | 1166(2) | 50(1) |
| C(16) | 5404(2) | 5701(3) | 1187(1) | 42(1) |
| C(10) | -1077(2) | 8168(3) | 1605(1) | 54(1) |
| C(3) | 3320(3) | 12508(4) | 1323(2) | 76(1) |
| C(5) | 4010(2) | 9990(4) | 1592(2) | 60(1) |
| C(19) | 7539(3) | 4038(3) | 1604(2) | 69(1) |
| C(14) | -397(2) | 8683(3) | 345(1) | 55(1) |
| C(21) | 5807(2) | 5682(3) | 1897(1) | 54(1) |
| C(20) | 6882(3) | 4863(4) | 2101(2) | 67(1) |
| C(17) | 6074(2) | 4872(3) | 695(2) | 54(1) |
| C(13) | -1602(2) | 9648(4) | 257(1) | 59(1) |
| C(2) | 1923(2) | 11982(3) | 1458(2) | 61(1) |
| C(4) | 4359(3) | 11531(4) | 1656(2) | 75(1) |
| C(18) | 7123(3) | 4024(3) | 904(2) | 64(1) |
| C(12) | -2729(2) | 9214(4) | 749(2) | 63(1) |

## Compound 37

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| P(1) | 9379(1) | 5964(1) | 6280(1) | 48(1) |
| O(4) | 10500(2) | 3519(2) | 7055(1) | 49(1) |
| O(3) | 9083(2) | 5131(2) | 5424(1) | 60(1) |

| | | | | |
|---|---|---|---|---|
| O(2) | 11725(2) | 6369(1) | 6401(1) | 48(1) |
| C(1) | 12752(3) | 6818(2) | 5683(1) | 46(1) |
| O(1) | 7948(3) | 7132(2) | 6349(1) | 74(1) |
| C(2) | 12477(3) | 5722(2) | 4991(1) | 43(1) |
| C(6) | 9109(3) | 4618(2) | 7027(1) | 48(1) |
| C(3) | 10187(3) | 5561(3) | 4725(1) | 52(1) |
| C(10) | 5784(4) | 5240(3) | 7681(2) | 69(1) |
| C(9) | 9897(3) | 2556(2) | 7614(1) | 52(1) |
| C(17) | 11093(4) | 1267(2) | 7734(1) | 56(1) |
| C(5) | 13437(4) | 4314(2) | 5300(2) | 57(1) |
| C(4) | 13481(4) | 6246(3) | 4235(2) | 65(1) |
| C(11) | 5717(4) | 5719(3) | 8565(1) | 61(1) |
| C(7) | 7645(3) | 4356(3) | 7546(1) | 52(1) |
| C(21) | 10353(5) | 32(3) | 8208(2) | 88(1) |
| C(8) | 8184(3) | 3028(3) | 7923(1) | 58(1) |
| C(18) | 12884(4) | 989(3) | 7452(2) | 65(1) |
| C(16) | 4041(5) | 5441(4) | 8979(2) | 89(1) |
| C(20) | 12062(6) | -1056(3) | 8196(3) | 97(1) |
| C(15) | 3939(9) | 5942(6) | 9794(3) | 130(2) |
| C(19) | 13652(5) | -467(3) | 7686(2) | 88(1) |
| C(13) | 7192(9) | 7019(6) | 9759(3) | 141(2) |
| C(12) | 7285(6) | 6508(4) | 8952(2) | 103(1) |
| C(14) | 5546(12) | 6704(7) | 10162(3) | 141(2) |

## Compound 43

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| O(1) | 1818(1) | 10331(2) | 3897(1) | 43(1) |
| O(2) | 3280(1) | 8286(2) | 3554(1) | 45(1) |
| C(18) | 3612(1) | 8370(3) | 4310(1) | 40(1) |
| C(1) | 1464(1) | 10049(3) | 3160(1) | 38(1) |
| C(9) | 2371(1) | 7750(3) | 2619(1) | 38(1) |
| C(12) | 1850(1) | 7686(3) | 1281(1) | 42(1) |
| C(8) | 2028(1) | 8618(3) | 2733(1) | 40(1) |
| C(6) | 1299(1) | 11443(3) | 2816(1) | 48(1) |
| C(11) | 2286(1) | 7340(3) | 1998(1) | 46(1) |
| C(28) | 2665(1) | 9665(3) | 5591(1) | 46(1) |
| C(25) | 2958(1) | 9029(3) | 4771(1) | 41(1) |
| C(10) | 2873(1) | 7245(3) | 3285(1) | 45(1) |
| C(24) | 3251(1) | 8745(3) | 4574(1) | 41(1) |
| C(19) | 4030(1) | 9480(3) | 4460(1) | 47(1) |
| C(7) | 1774(1) | 9271(3) | 2916(1) | 38(1) |
| C(26) | 2557(1) | 9335(3) | 4952(1) | 39(1) |
| C(23) | 3909(1) | 7029(3) | 4630(1) | 47(1) |
| C(22) | 4325(1) | 7175(3) | 5411(1) | 57(1) |
| C(20) | 4453(1) | 9627(3) | 5241(1) | 54(1) |
| C(29) | 3187(2) | 9791(3) | 6257(1) | 46(1) |
| C(13) | 1350(1) | 8231(3) | 1097(2) | 55(1) |
| C(5) | 899(1) | 11335(3) | 2028(1) | 60(1) |
| C(2) | 948(1) | 9282(3) | 2997(1) | 51(1) |
| C(17) | 1951(1) | 7414(3) | 750(2) | 56(1) |
| C(16) | 1563(2) | 7704(4) | 60(2) | 70(1) |
| C(27) | 1972(1) | 9182(3) | 4353(1) | 50(1) |
| C(14) | 960(2) | 8513(3) | 404(2) | 66(1) |
| C(3) | 537(1) | 9165(4) | 2211(1) | 61(1) |
| C(21) | 4737(1) | 8286(4) | 5555(2) | 66(1) |
| C(30) | 3688(2) | 9755(4) | 6323(2) | 78(1) |
| C(33) | 3658(2) | 9996(4) | 7512(2) | 83(2) |
| C(15) | 1068(2) | 8249(4) | -115(2) | 73(1) |
| C(34) | 3181(2) | 9935(3) | 6865(2) | 59(1) |
| C(4) | 388(1) | 10552(4) | 1860(2) | 71(1) |
| C(32) | 4153(2) | 9947(4) | 7566(2) | 88(2) |
| C(31) | 4169(2) | 9819(4) | 6969(2) | 97(2) |

## Compound 53

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| C(17) | -1350(3) | 2298(1) | 5750(2) | 32(1) |
| C(23) | -2412(4) | 2845(1) | 5425(2) | 37(1) |
| C(11) | 1789(3) | 1718(1) | 6854(2) | 36(1) |
| C(10) | 2314(4) | 3505(1) | 7070(2) | 38(1) |
| C(18) | -958(4) | 1892(1) | 4571(2) | 41(1) |
| C(5) | 922(4) | 3752(1) | 6609(2) | 36(1) |
| C(22) | -2000(3) | 1853(1) | 6785(2) | 41(1) |
| C(24) | -1715(4) | 3436(1) | 5637(2) | 37(1) |
| C(28) | -3894(4) | 2829(2) | 4972(2) | 48(1) |
| C(15) | 1997(4) | 795(2) | 8199(3) | 55(1) |
| C(21) | -3255(4) | 1417(1) | 6330(2) | 46(1) |
| C(20) | -2798(4) | 1032(1) | 5181(2) | 55(1) |
| C(6) | 735(4) | 4426(1) | 6663(2) | 51(1) |
| C(12) | 2438(4) | 1363(1) | 5892(2) | 46(1) |
| C(14) | 2605(4) | 446(2) | 7227(3) | 59(1) |
| C(19) | -2240(4) | 1460(1) | 4125(2) | 49(1) |
| C(9) | 3468(4) | 3924(1) | 7506(2) | 50(1) |
| C(7) | 1846(4) | 4814(2) | 7107(3) | 61(1) |
| C(16) | 1601(4) | 1421(1) | 8018(2) | 44(1) |
| C(13) | 2819(4) | 732(2) | 6075(3) | 57(1) |
| C(25) | -2484(4) | 3996(1) | 5343(2) | 52(1) |
| C(8) | 3233(4) | 4570(2) | 7514(3) | 60(1) |
| C(27) | -4665(4) | 3393(2) | 4726(2) | 56(1) |
| C(26) | -3959(4) | 3971(2) | 4894(2) | 58(1) |
| O(1) | 3880(2) | 2639(1) | 7599(2) | 57(1) |
| C(4) | -196(4) | 3316(1) | 6163(2) | 35(1) |
| C(3) | 45(3) | 2661(1) | 6223(2) | 32(1) |
| C(2) | 1430(3) | 2407(1) | 6702(2) | 34(1) |
| C(1) | 2515(4) | 2836(1) | 7104(2) | 39(1) |

## Compound 69

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| C(7) | 8171(5) | 1006(3) | 743(4) | 46(2) |
| C(3) | 4612(6) | 1021(3) | 574(4) | 57(2) |
| C(32) | 11887(5) | 380(3) | 2130(4) | 50(2) |
| C(16) | 6887(5) | -136(4) | 4144(5) | 52(2) |
| C(37) | 12181(5) | 1181(4) | 2340(4) | 63(2) |
| C(6) | 6672(6) | 1330(4) | -391(4) | 68(2) |
| C(24) | 7939(6) | 2588(4) | 2105(4) | 51(2) |
| C(11) | 7375(5) | -372(3) | 3401(4) | 43(2) |
| C(2) | 5822(6) | 945(3) | 900(4) | 55(2) |
| C(12) | 7251(5) | -1204(4) | 3172(4) | 60(2) |
| C(28) | 9333(6) | 3220(4) | 1155(5) | 65(2) |
| C(4) | 4457(6) | 1253(4) | -235(5) | 54(2) |
| C(13) | 6687(7) | -1755(4) | 3709(6) | 82(3) |
| C(33) | 12743(6) | -237(4) | 2304(4) | 71(2) |
| C(29) | 9143(6) | 2763(3) | 1855(5) | 58(2) |
| C(15) | 6314(5) | -688(5) | 4663(4) | 65(2) |
| C(5) | 5468(6) | 1423(4) | -725(4) | 78(2) |
| C(36) | 13311(6) | 1367(4) | 2716(4) | 75(2) |
| C(14) | 6228(6) | -1514(5) | 4454(6) | 79(3) |
| C(27) | 8309(7) | 3507(4) | 690(4) | 78(2) |
| C(25) | 6912(6) | 2878(4) | 1649(5) | 65(2) |
| C(35) | 14177(6) | 756(5) | 2905(4) | 75(2) |
| C(34) | 13875(6) | -40(4) | 2687(5) | 87(3) |
| C(26) | 7121(7) | 3336(4) | 951(5) | 83(3) |
| O(2) | 9889(3) | 820(2) | 1646(3) | 50(1) |
| O(3) | 10353(4) | -532(2) | 1534(3) | 75(2) |

| | | | | |
|---|---|---|---|---|
| C(8) | 8587(5) | 673(3) | 1451(4) | 42(2) |
| O(1) | 3303(4) | 1352(3) | -636(3) | 79(2) |
| C(30) | 2205(6) | 1161(3) | -170(5) | 79(3) |
| C(9) | 7902(5) | 196(3) | 2051(4) | 43(2) |
| C(31) | 10657(6) | 149(4) | 1738(4) | 52(2) |
| C(1) | 6878(6) | 1080(3) | 421(4) | 46(2) |
| C(10) | 8035(5) | 219(3) | 2863(4) | 36(2) |
| O(4) | 6629(4) | 1904(2) | 3056(3) | 74(2) |
| C(23) | 7689(6) | 2050(4) | 2821(5) | 55(2) |
| C(21) | 9659(6) | 2151(4) | 3695(4) | 60(2) |
| C(20) | 10614(6) | 1815(4) | 4149(4) | 72(2) |
| C(19) | 10732(6) | 975(4) | 4203(4) | 73(2) |
| C(22) | 8793(5) | 1648(4) | 3272(4) | 51(2) |
| C(17) | 8901(5) | 789(3) | 3323(4) | 45(2) |
| C(18A) | 9881(5) | 468(4) | 3799(4) | 58(2) |

# PART B

## Compound 27

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| P(1) | 1782(3) | 8985(5) | 10266(2) | 60(1) |
| O(2) | 2868(6) | 9477(10) | 10705(4) | 70(3) |
| O(1) | 1248(7) | 8138(10) | 10680(4) | 73(3) |
| O(5) | 538(9) | 4884(14) | 6954(5) | 98(4) |
| O(6) | 1189(8) | 6873(11) | 7016(4) | 76(3) |
| C(11) | 827(10) | 6069(15) | 8055(6) | 57(4) |
| O(3) | 1183(7) | 10257(11) | 9976(4) | 68(3) |
| O(7) | 2935(9) | 5401(13) | 8028(5) | 92(4) |
| C(7) | 1643(9) | 7131(16) | 9210(6) | 58(4) |
| C(14) | 867(9) | 5866(18) | 7283(7) | 56(4) |
| C(16) | 2664(10) | 9142(14) | 9148(6) | 53(4) |
| O(4) | 3383(8) | 5687(13) | 9176(5) | 109(4) |
| C(12) | 1838(10) | 6675(15) | 8503(5) | 58(4) |
| C(6) | 2034(9) | 8329(15) | 9483(6) | 51(4) |
| C(3) | 1180(11) | 11343(16) | 10475(7) | 74(5) |
| C(9) | 513(12) | 5220(20) | 9160(7) | 87(5) |
| C(13) | 1116(14) | 3579(16) | 8416(7) | 88(5) |
| C(8) | 1028(12) | 6219(17) | 9508(7) | 79(5) |
| C(15) | 2795(12) | 5867(18) | 8613(7) | 76(5) |
| C(17) | 2190(13) | 10027(18) | 8649(7) | 85(5) |
| C(5) | 2840(15) | 12400(20) | 10340(8) | 121(7) |
| C(10) | 503(11) | 4859(17) | 8401(6) | 68(4) |
| C(1) | 2857(11) | 10534(17) | 11224(7) | 73(5) |
| C(21) | 3719(13) | 9118(18) | 9327(8) | 81(5) |
| C(2) | 2238(12) | 11699(18) | 10864(8) | 76(5) |
| C(18) | 2780(20) | 10830(20) | 8314(10) | 117(7) |
| C(19) | 3861(19) | 10710(30) | 8525(13) | 128(9) |
| C(4) | 2162(14) | 12690(20) | 11446(8) | 120(7) |
| C(20) | 4301(17) | 9830(30) | 9037(13) | 120(8) |

## Compound 28

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| P(1) | 2744(1) | 3399(1) | 3603(1) | 41(1) |
| O(3) | -785(1) | 5604(1) | 1658(1) | 51(1) |
| O(1) | 2380(2) | 2811(1) | 4964(1) | 56(1) |
| C(13) | 1156(2) | 3940(2) | 2757(2) | 39(1) |
| O(2) | -2117(2) | 4959(2) | 578(2) | 66(1) |
| C(19) | -432(2) | 3081(2) | 1752(2) | 44(1) |
| C(1) | 4313(2) | 2037(2) | 2514(2) | 39(1) |
| C(14) | 675(2) | 2779(2) | 2524(2) | 42(1) |

| | | | | |
|---|---|---|---|---|
| C(7) | 3332(2) | 4880(2) | 3658(2) | 41(1) |
| C(6) | 4641(2) | 2156(2) | 1137(2) | 49(1) |
| C(2) | 5207(2) | 780(2) | 3127(2) | 52(1) |
| C(8) | 4333(2) | 5251(2) | 2625(2) | 49(1) |
| C(20) | -1173(2) | 4554(2) | 1271(2) | 48(1) |
| C(15) | 1258(2) | 1349(2) | 3049(2) | 54(1) |
| C(21) | 382(2) | 5308(2) | 2335(2) | 45(1) |
| C(9) | 4718(2) | 6410(2) | 2769(2) | 57(1) |
| C(3) | 6390(2) | -340(2) | 2358(3) | 64(1) |
| C(10) | 4135(3) | 7189(2) | 3939(2) | 60(1) |
| C(4) | 6714(2) | -203(2) | 1003(3) | 65(1) |
| C(22) | 512(2) | 6719(2) | 2460(2) | 62(1) |
| C(11) | 3184(3) | 6809(2) | 4965(2) | 67(1) |
| C(18) | -902(2) | 2019(2) | 1479(2) | 61(1) |
| C(5) | 5856(3) | 1053(2) | 383(2) | 62(1) |
| C(12) | 2793(3) | 5663(2) | 4830(2) | 57(1) |
| C(16) | 774(3) | 309(2) | 2768(3) | 70(1) |
| C(17) | -278(3) | 622(2) | 1975(3) | 72(1) |

## Compound 38

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| Br | 12940(1) | 1718(1) | -4188(1) | 60(1) |
| C(4) | 11886(6) | 1811(8) | -2287(6) | 40(1) |
| O(2) | 6844(4) | 5152(6) | 585(4) | 50(1) |
| O(1) | 6669(5) | 6591(6) | -1899(5) | 61(1) |
| C(7) | 7557(7) | 5207(9) | -840(7) | 45(1) |
| C(5) | 10140(6) | 3431(8) | -2272(6) | 44(1) |
| C(8) | 7774(6) | 3674(8) | 1895(6) | 43(1) |
| C(10) | 6615(7) | 4097(9) | 3205(6) | 53(1) |
| C(3) | 12826(7) | 343(8) | -999(7) | 48(1) |
| C(11) | 7624(8) | 2731(10) | 4724(7) | 69(2) |
| C(9) | 9434(6) | 2161(8) | 1872(6) | 45(1) |
| C(2) | 12068(6) | 423(8) | 371(6) | 47(1) |
| C(6) | 9392(6) | 3481(7) | -855(5) | 34(1) |
| C(1) | 10317(6) | 2029(7) | 454(6) | 42(1) |

## Compound 42

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| P(1) | 7332(1) | 4351(1) | 2028(1) | 35(1) |
| O(1) | 6200(2) | 4294(1) | 952(1) | 39(1) |
| O(2) | 9015(2) | 5153(2) | 2099(2) | 54(1) |
| O(4) | 7215(2) | -658(2) | -842(2) | 53(1) |
| C(6) | 7083(2) | 2766(2) | 1972(2) | 32(1) |
| O(5) | 9028(2) | 3437(2) | -1051(2) | 60(1) |
| C(7) | 7190(3) | 2588(2) | 3149(2) | 35(1) |
| C(14) | 6682(3) | 1687(2) | -308(2) | 39(1) |
| O(3) | 6641(2) | 4950(2) | 3163(1) | 51(1) |
| C(16) | 8226(3) | 194(2) | -1085(2) | 38(1) |
| C(13) | 6853(2) | 1778(2) | 969(2) | 37(1) |
| C(15) | 8061(3) | 1417(2) | -894(2) | 34(1) |
| C(19) | 10495(3) | 2046(2) | -1890(2) | 46(1) |
| C(20) | 9146(3) | 2283(2) | -1259(2) | 38(1) |
| C(8) | 5893(3) | 1747(2) | 3419(2) | 48(1) |
| C(1) | 4456(3) | 3858(2) | 936(3) | 53(1) |
| C(18) | 10262(3) | 641(2) | -2467(2) | 42(1) |
| C(17) | 9700(3) | -6(2) | -1560(2) | 49(1) |
| C(2) | 4024(3) | 4618(3) | 2062(3) | 56(1) |
| C(3) | 4883(4) | 4496(3) | 3106(3) | 69(1) |

| | | | | |
|---|---|---|---|---|
| C(4) | 4522(4) | 6028(3) | 2182(3) | 66(1) |
| C(21) | 8982(3) | 17(3) | -3588(2) | 66(1) |
| C(11) | 8677(4) | 3082(3) | 5075(3) | 69(1) |
| C(12) | 8594(3) | 3270(2) | 3999(2) | 54(1) |
| C(22) | 11861(3) | 515(3) | -2793(3) | 67(1) |
| C(9) | 5989(4) | 1576(3) | 4507(3) | 65(1) |
| C(10) | 7369(4) | 2244(3) | 5326(3) | 66(1) |
| C(5) | 2186(4) | 4035(4) | 2007(4) | 109(2) |

## Compound 49a

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| P(1) | 2615(1) | 8941(1) | 1293(1) | 68(1) |
| O(3) | 3345(1) | 9228(2) | 1704(1) | 95(1) |
| O(1) | 2434(1) | 8754(2) | 460(1) | 68(1) |
| O(2) | 2135(1) | 10021(2) | 1335(1) | 74(1) |
| O(4) | 109(2) | 3641(3) | -1433(2) | 110(1) |
| O(5) | -284(1) | 2959(2) | -422(1) | 86(1) |
| O(6) | -49(1) | 2992(2) | 972(2) | 102(1) |
| C(6) | 2340(2) | 7616(3) | 1599(2) | 70(1) |
| C(7) | 2271(2) | 6539(3) | 1293(2) | 62(1) |
| C(8) | 2134(2) | 5343(3) | 1585(2) | 59(1) |
| C(9) | 1489(2) | 4715(3) | 1032(2) | 58(1) |
| C(10) | 1345(2) | 4678(3) | 300(2) | 61(1) |
| C(11) | 751(2) | 4092(3) | -197(2) | 62(1) |
| C(12) | 298(2) | 3522(3) | 46(2) | 65(1) |
| C(13) | 442(2) | 3547(3) | 791(2) | 68(1) |
| C(14) | 1028(2) | 4140(3) | 1269(2) | 66(1) |
| C(17) | 2786(2) | 4516(3) | 1832(2) | 58(1) |
| C(22) | 3423(2) | 5002(3) | 2253(2) | 91(1) |
| C(21) | 4013(2) | 4280(5) | 2501(2) | 112(2) |
| C(20) | 3967(2) | 3056(4) | 2323(2) | 99(1) |
| C(19) | 3338(2) | 2558(3) | 1912(2) | 81(1) |
| C(18) | 2752(2) | 3284(3) | 1663(2) | 67(1) |
| C(3) | 1713(2) | 8850(3) | -54(2) | 73(1) |
| C(2) | 1386(2) | 10047(3) | 34(2) | 70(1) |
| C(1) | 1424(2) | 10078(3) | 806(2) | 79(1) |
| C(5) | 1768(2) | 11141(3) | -106(2) | 97(1) |
| C(4) | 622(2) | 10046(4) | -503(2) | 104(1) |
| C(15) | 621(2) | 4108(3) | -957(2) | 81(1) |
| C(16) | 83(2) | 2959(4) | 1727(2) | 120(2) |

## Compound 50a

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| P(1) | -505(2) | 3151(2) | 1766(1) | 47(1) |
| O(2) | -2188(5) | 4370(5) | 2222(3) | 56(1) |
| O(4) | 6556(5) | -1358(6) | -2686(3) | 64(1) |
| O(1) | 947(5) | 3391(5) | 1848(3) | 61(1) |
| C(9) | 1996(7) | 1767(6) | -1496(4) | 41(1) |
| C(8) | 373(7) | 2957(6) | -1094(5) | 45(2) |
| C(12) | 5080(7) | -375(6) | -2265(4) | 43(2) |
| C(14) | 2796(7) | 1887(7) | -2390(5) | 51(2) |
| O(3) | -514(6) | 1759(5) | 2239(4) | 70(2) |
| C(15) | -1147(7) | 2838(6) | -1290(4) | 44(2) |
| C(10) | 2802(7) | 547(7) | -1019(4) | 48(2) |
| C(11) | 4324(7) | -538(7) | -1384(5) | 49(2) |
| C(7) | 323(7) | 3128(6) | -88(5) | 47(2) |
| C(13) | 4307(8) | 817(8) | -2790(4) | 51(2) |
| C(6) | -732(7) | 3005(7) | 625(5) | 53(2) |

| | | | | |
|---|---|---|---|---|
| C(16) | -1144(8) | 1591(7) | -1512(5) | 57(2) |
| C(19) | -4019(9) | 3995(9) | -1396(7) | 80(2) |
| C(17) | -2555(9) | 1544(9) | -1675(6) | 72(2) |
| C(3) | -2648(10) | 4354(9) | 3214(6) | 73(2) |
| C(2) | -2638(11) | 2954(10) | 3583(6) | 80(3) |
| C(20) | -2649(9) | 4058(8) | -1224(6) | 70(2) |
| C(1) | -925(13) | 1782(10) | 3235(6) | 91(3) |
| C(18) | -4018(9) | 2769(9) | -1636(6) | 69(2) |
| C(21) | 5109(9) | -1855(8) | -817(6) | 80(3) |
| C(4) | -2900(20) | 3007(16) | 4615(8) | 161(6) |
| C(22) | 5184(11) | 995(10) | -3748(6) | 89(3) |
| C(5) | -3947(14) | 2694(15) | 3202(9) | 147(6) |