NEW PHOSPHONO-HETEROCYCLES THROUGH ALLENYLPHOSPHONATES

A THESIS

SUBMITTED FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

BY

PHANI PAVAN MADA

SCHOOL OF CHEMISTRY

UNIVERSITY OF HYDERABAD

HYDERABAD - 500 046

INDIA

JULY 2010

Dedicated

TO

My parents

CONTENTS

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

July 2010

Phani Pavan Mada

CERTIFICATE

This is to certify that the work described in this thesis entitled "New phosphono-heterocycles through allenylphosphonates" has been carried out by Mr. Phani Pavan Mada, under my supervision and the same has not been submitted elsewhere for any degree.

Hyderabad

July 2010

Prof. K. C. Kumara Swamy

(Thesis supervisor)

Dean

School of Chemistry
University of Hyderabad
Hyderabad 500 046
INDIA

ACKNOWLEDGEMENTS

I express my sincere gratitude to Prof. K. C. Kumara Swamy, my research supervisor, for his constant encouragement, cooperation and kind guidance. He has been quite helpful to me in improving my patience and writing skills.

I thank Prof. D. Basavaiah, Dean, School of Chemistry for providing all the necessary facilities to carry out my research work during my stay here. I extend my sincere thanks to former Deans and the entire faculty members for their inspiration and cooperation.

I acknowledge present lab-mates: Rama Suresh, Anjaneyulu, Ramesh, Nagarjuna, Gangadhar and Srinivas for making our lab fun and quiet place to work in. I am also thankful to former lab-mates Dr. Senthil, Dr. Satish, Dr. Pavan, Dr. Manab, Dr. Balaraman, Dr. Bhuvan and Mr. Sridhar for their cooperation in the lab. I express my special thanks to Dr. Balaraman for his help at the initial stage of my work.

I thank my M. Sc. friends, particularly Sekhar, Kurella Srinu, Innus, Ramu, Bhaskar, Satish, Nagaraju, Vikram and Ramkumar for creating a cheerful and competitive atmosphere. I also thank my seniors and friends Chandrasekar, Venu, Basavoju, Mallareddy, Jagadeesh, Raju, Rameshreddy, Aravindu, Siva, Ravi, Ramesh, Kishore, Narayana, Sanjeev, Mallesh, Srinu, Rambabu, Satish, GDP, Chaitanya, DK, Bharat, Santhosh and all my juniors who made my stay here a pleasant one. Thanks are also due to my friends Hareram, Jagadeesh, Dilip, Tatarao, Ramesh and Dharma for their support.

I thank all the non-teaching staff of the School of Chemistry for their help in many ways. In this context, it is my privilege to acknowledge Mr. P. Raghavaiah, Mr. Satyanarayana, Mrs. Asia Parwez, Mr. K. R. B. V. Prasad, Mr. Bhaskar Rao, Mr. Shetty, Mrs. Vijaya Lashmi, Mr. Venkataramana and Mr. Rangaiah.

I express my profound gratitude to my parents **M. Durgarao** and **M. Meenakumari** for their blessings. I am extremely thankful to my sister Sandhya and brother-in-law Suresh for their support.

I thank the Council of Scientific and Industrial Research (CSIR, New Delhi) and Department of Science and Technology (DST, New Delhi) for financial support. I also thank COSIST (UGC), SAP (UGC) and FIST (DST) for various instrumental facilities. Single Crystal X-ray Diffractometer Facility at the University of Hyderabad funded by Department of Science and Technology (New Delhi) is also gratefully acknowledged.

Phani Pavan Mada

LIST OF PUBLICATIONS

1. Unusual products in the reaction of phosphorus(III) compounds with N=N, C≡C or conjugated double bonded systems
   K. C. Kumara Swamy, E. Balaraman, **M. Phani Pavan**, N. N. Bhuvan Kumar and N. Satish Kumar
   J. Chem. Sci. **2006,** *118*, 495.
2. Spiro- and Tricyclic Phosphoranes with Six- and Higher-Membered Rings
   K. C. Kumara Swamy, **M. Phani Pavan**, Venu Srinivas
   Topics in Heterocyclic Chemistry **2009**, 20, 99.
3. Characterization of the first hexacoordinate phosphorus compound with S→P←S bonds
   K. V. P. Pavan Kumar, **M. Phani Pavan** and K. C. Kumara Swamy
   Inorg. Chem. Commun. **2009**, *12*, 544.
4. Pd- Catalyzed reactions of Allenylphosphonates and Related allenes with Functionalized 2-iodophenols, 2-iodobenzoic acid and 2-iodobenzyl alcohol leading to Functionalized Benzofurans, Isocoumarins and benzopyrans
   M. Phani Pavan, Manab Chakravarty and K. C. Kumara Swamy
   Eur. J. Org. Chem. **2009**, 5927.
5. Base catalysed reactions of thiosalicylaldehydes and substituted salicylaldehydes with allenylphosphonates
   M. Phani Pavan, N. N. Bhuvan Kumar and K. C. Kumara Swamy (*to be communicated*).
6. Base catalyzed reactions of 3-chloro 2-formylindole with allenylphosphonates and allenylsulfones in environmentally friendly condition
   M. Phani Pavan and K. C. Kumara Swamy (*to be communicated*).

Additional Publication

7. Spectra, structural and DFT studies of platinum group metal 3,6-bis(2-pyridyl)-4-phenylpyridazine complexes and their ligand bonding modes
   Kota Thirumala Prasad, Gajendra Gupta, A. K. Chandra, **M. Phani Pavan** and Kollipara Mohan Rao.
   J. Organomet. Chem. **2010**, *695*, 707.

Papers presented in symposia

1. Pd-Catalyzed Stereoselective Synthesis of Phosphono- Butadienes, Benzofurans and Benzopyrans: Use of Environmentally Benign Conditions
   M Phani Phavan, Manab Chakravarty, K. C. Kumara Swamy.
   10th National Symposium in Chemistry, IISC Bangalore, INDIA, Feb 1-3, **2008.**
2. Allenylphosphonates as precursors for the synthesis of new phosphono-heterocycles
   M. Phani Pavan and K. C. Kumara Swamy
   Chemfest-2009, School of Chemistry, University of Hyderabad, March-2009
3. Allenylphosphonates as precursors for the synthesis of new phosphono-heterocycles
   M. Phani Pavan and K. C. Kumara Swamy
   Chemfest-2009, School of Chemistry, University of Hyderabad, March-2009 (**Oral Presentation**).

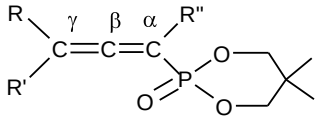
Synopsis

This thesis embodies primarily the results on the investigations related to the [Pd]- or base-catalyzed reactions of allenylphosphonates with functionalized 2-iodophenols, 2-iodobenzyl alcohol and with reactants having -OH/ -SH/ -NH and CHO functional groups that lead to benzofurans, benzopyrans, chromenes, thiochromans, pyrroloindoles etc. Compounds isolated in the present study are, in general, characterized by Mp, IR, NMR, elemental analyses and mass spectra (LC-MS or GC-MS). Wherever feasible, X-ray crystal structures are determined.

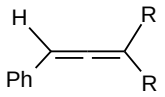
The thesis is divided into three chapters: (1) Introduction, (2) Results and Discussion and (3) Experimental Section. A review of literature on aspects relevant to this work is presented in Chapter 1. In Chapter 2, the results obtained on the above-mentioned aspects are discussed. Chapter 3 deals with the experimental procedures/ conditions. Summary as well as references are compiled at the end of thesis.

The allenes **1a-k, 2a-b, 3** and **4a-b** used in the present study are shown in Chart 1. They have been prepared by standard procedures available in the literature, with minor modifications where necessary. Salient features of the results obtained using these precursors are outlined below.

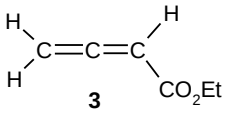
Chart 1



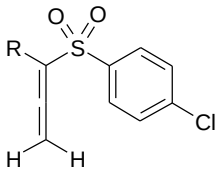
R = R' = R" = H (**1a**; δ(P): 8.7)
R = H, R' = Me, R" = H (**1b**; δ(P): 8.9)
R = R' = Me, R" = H (**1c**; δ(P): 8.8)
R = Me, R' = Et, R" = H (**1d**; δ(P): 9.3)
R = R' = H, R" = Ph (**1e**; δ(P): 6.6)
R = R' = H, R" = 4-Me-C_6H_4 (**1f**; δ(P): 7.8)
R = R' = H, R" = 4-MeO-C_6H_4 (**1g**: δ(P); 7.5)
R = R' = H, R" = 4-Cl- C_6H_4 (**1h**: δ(P); 6.8)
R = R' = H, R" = 4-NO_2-C_6H_4 (**1i**: δ(P); 6.6)
R = R' = H, R" = 1-Naphthyl (**1j**: δ(P); 8.3)
R = R' = H, R" = Me (**1k**: δ(P); 11.2)



R = H (**2a**)
R = Me (**2b**)



3



R = Ph (**4a**)
R = Me (**4b**)

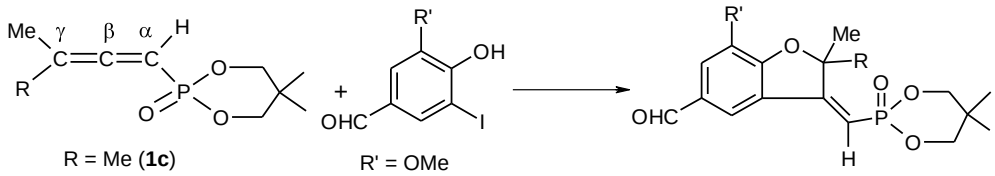
(i) Pd-catalyzed annulation reactions of allenylphosphonates

(a) Reaction with functionalized 2-iodophenols

The Pd-catalyzed [we use this term to mean reactions catalyzed by palladium complexes] reaction of allenylphosphonate **1c** with 5-iodovanillin under previously

reported conditions led to a mixture of products. So we have optimized reaction conditions by changing the Pd-complex, phosphine, base as well as the solvent. It was found that a combination of $Pd(OAc)_2$/ (*o*-tolyl)$_3$P/ K_2CO_3/ PEG-400 leads to phosphono-benzofurans stereo-selectively. Under these conditions, we have treated the allenylphosphonates **1c-d** with functionalized 2-iodophenols for the synthesis of phosphono-benzofurans **5-10** (Scheme 1). The overall isolated yields of all the compounds were moderate to good (57-70%). In all the cases, the (β,γ)-cyclized products with *Z*-configuration were obtained; one of these (**6**) was characterized by single crystal X-ray structure determination.

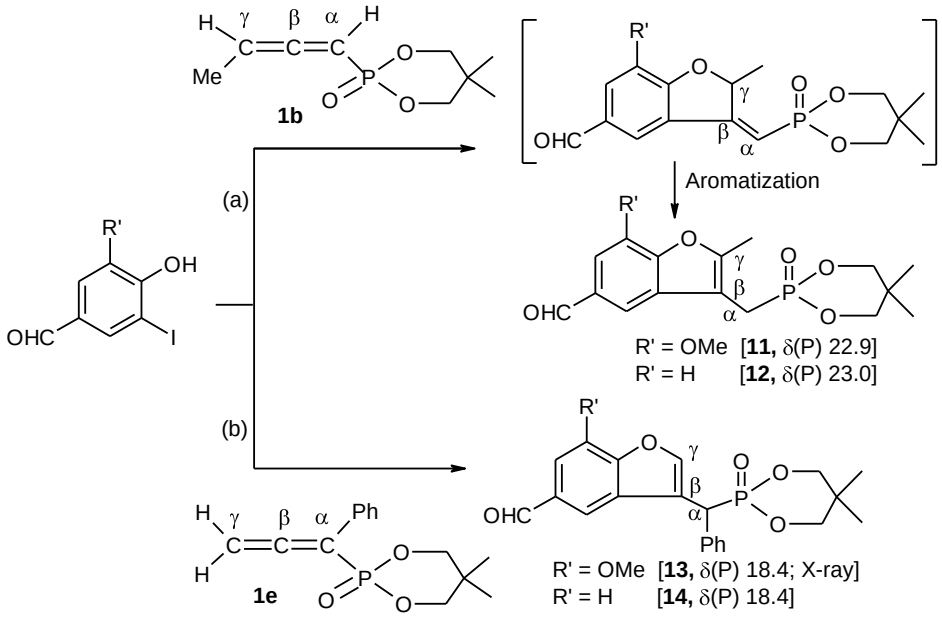
Scheme 1



Conditions: $Pd(OAc)_2$ / (*o*-tolyl)$_3$P/ K_2CO_3 / PEG-400/ 90 ^{0}C/ 12 h
Yields (^{31}PNMR, isolated): 63-81%; 57-70%

To avoid the isomerization of **1a-b** under the conditions used above, we have used CsF instead of K_2CO_3 for the annulation of **1a-b** with functionalized 2-iodopheols. Allene **1b** leads to phosphono-benzofurans **11-12** (Scheme 2a) but allene **1a** gives a mixture of unidentified products. Allene **1e** also led to benzofurans **13-14** (Scheme 2b) that are similar to **11-12**. Here also, the (β,γ)-product is formed but with proton migration to attain aromaticity. The structure of compound **13** is confirmed by X-ray crystallography.

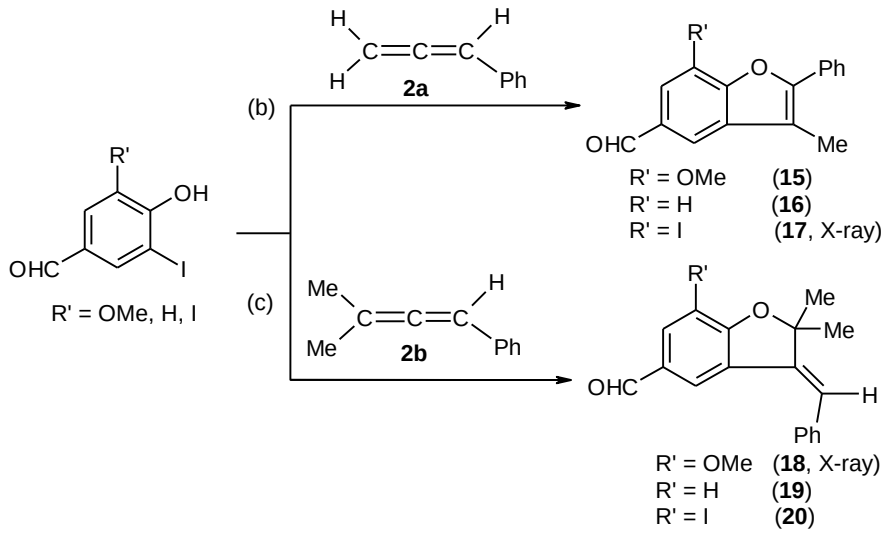
Scheme 2



Conditions: CsF / $Pd(OAc)_2$/ PEG-400/ 90 °C/ 12 h
Yields (^{31}P NMR, isolated): 63-70%; 55-63%

The reaction of phenylallenes **2a-b** with functionalized 2-iodophenols leads to benzofurans **15-20** (Scheme 3) but the structure of the product varies with the type of precursor allene used. Thus the $=CH_2$ terminal allene **2a** gives (β,α) products (followed by aromatization) **15-17** but the $=CMe_2$ terminal allene **2b** affords the (β,γ) products **18-20**. The structures of two of the representative compounds, **17** and **18**, have been confirmed by X-ray crystallography. A plausible pathway for the formation of these benzofurans is discussed.

Scheme 3

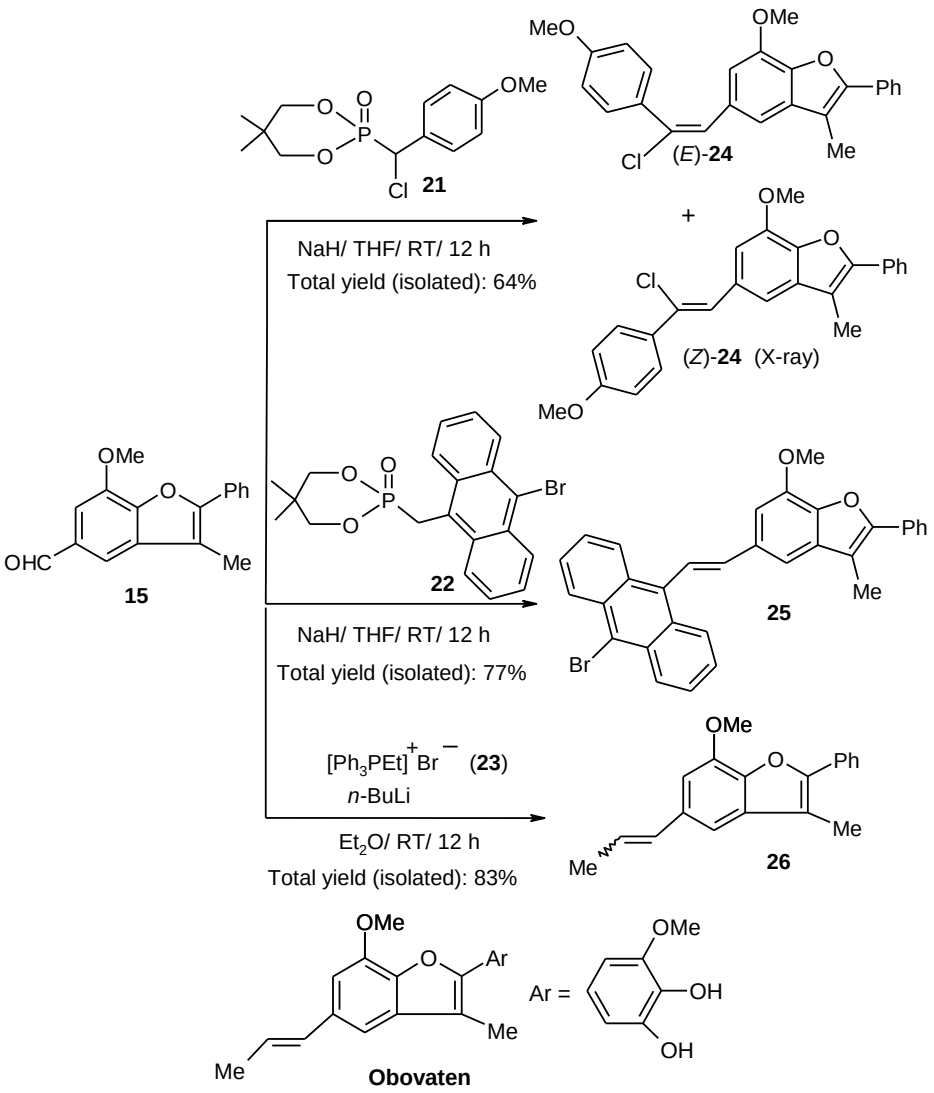


Conditions: $Pd(OAc)_2$ / (*o*-tolyl)$_3$P/ K_2CO_3/ PEG-400/ 90 °C/ 12 h
Yields: 51-69%

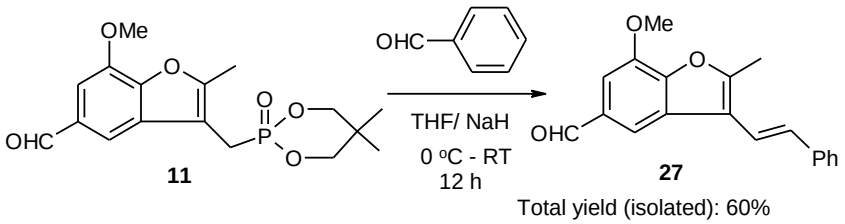
(b) Utility of benzofurans 11 and 15 in Horner-Wadsworth-Emmons (HWE)/ Wittig reaction

With several aldehyde appended benzofurans prepared as above, we thought that it should be possible to use these products in C-C bond forming reactions. This idea is exemplified by using **15** in the Horner-Wadsworth-Emmons (HWE) and Wittig reactions that lead to, say **24-26**, as shown in Scheme 4. In the HWE reaction of **15** with the α-chlorophosphonate **21**, we have been able to isolate both the isomers (*E*)-**24** and (*Z*)-**24**. The stereochemistry of (*Z*)-**24** is confirmed by X-ray crystallography. The Wittig product **26** is similar to Obovaten which is a natural product and a known antitumor agent. Even phosphono-benzofurans of type **11** are of synthetic value as shown by the synthesis of **27** (Scheme 5). Interestingly, in this case, we were able to retain the less reactive aldehyde moiety present in the phosphono-benzofuran **11**.

Scheme 4



Scheme 5

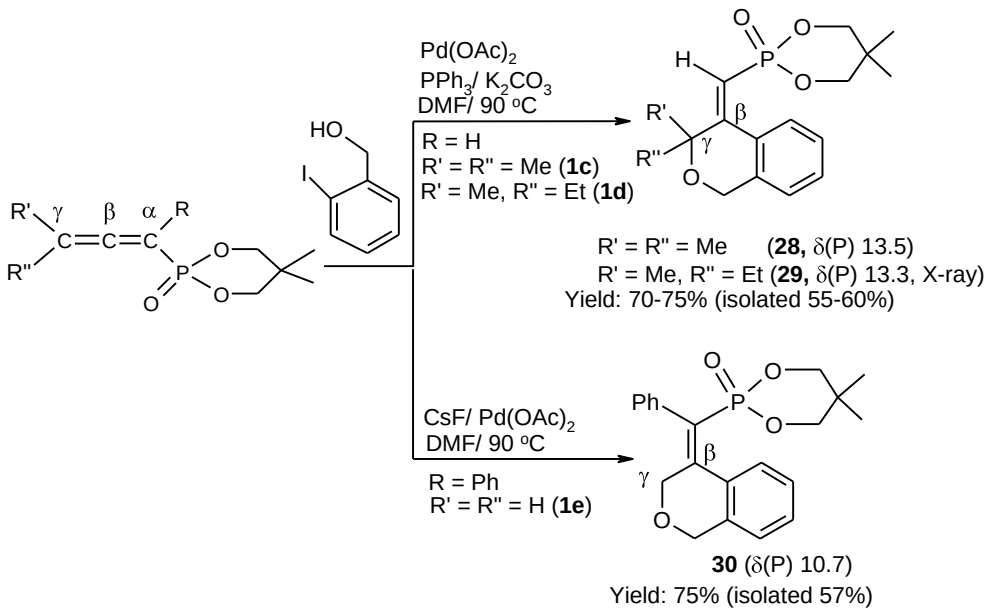


Total yield (isolated): 60%

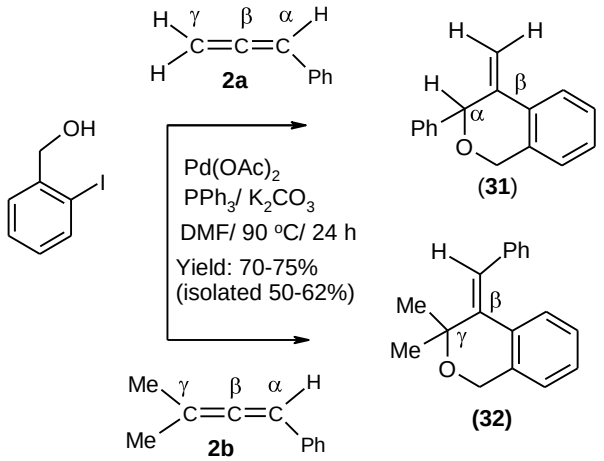
(c) Reaction with 2-iodobenzyl alcohols, 2-iodoanilines, and 2-iodo-t-butylbenzaldimine

The Pd-catalyzed annulation reactions of allenyl phosphonates **1c-d** and **1e** with 2-iodobenzyl alcohol produced phosphono-benzopyrans **28-30** (Scheme 6)**.** A similar reaction with phenylallenes **2a-b** produced benzopyrans **31-32** (Scheme 7)**.** The products formed here are (β,γ)-cyclized products except in case of **2a** where (β,α)-cyclized product (**31**) is favoured.

Scheme 6

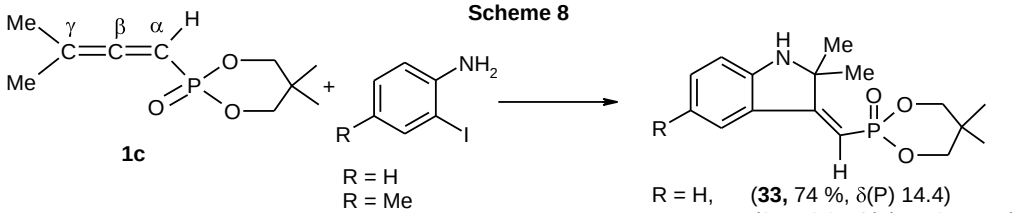


Scheme 7



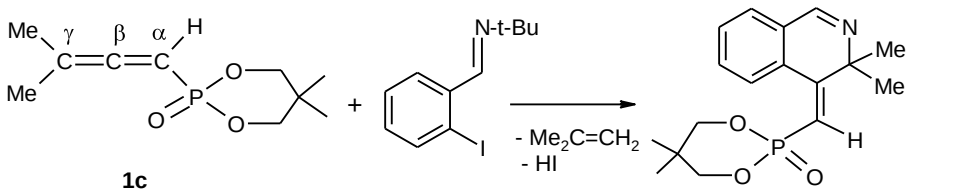
In place of 2-iodophenol, when 2-iodoanilnes are used in the annulation reaction of allenylphosphonate **1c**, phosphono-indoles **33-34** (Scheme 8) are readily obtained. An analogous reaction with 2-iodo-*t*-butylbenzaldimine produces phosphono-isoquinoline **35** (Scheme 9). To our knowledge, this is a new type of reaction using allenes.

Scheme 8



Conditions: $Pd(OAc)_2$ / Ph_3P/ K_2CO_3/ DMF/ 90 °C/ 24 h

Scheme 9



Conditions: $Pd(OAc)_2$ / Ph_3P/ Na_2CO_3 / CH_3CN/ 90 °C/ 24 h

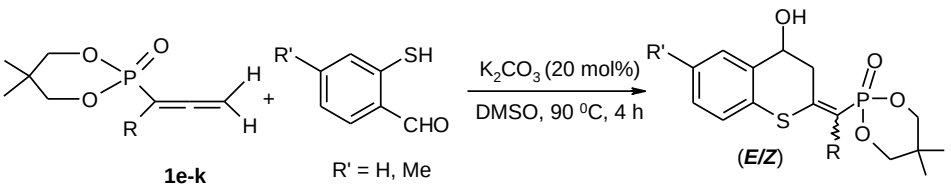
(ii) Base catalyzed cyclization reactions involving allenes

(a) Reactions with 2-mercaptobenzaldehydes

We have conducted the reactions of a variety of allenylphosphonates **1e-k** with 2-mercaptobenzaldehydes for the synthesis of different phosphono-thiochromans **36-**

49, after optimizing the experimental conditions (DMSO/ K_2CO_3) (Scheme 10). The overall (combined) isolated yields of the two isomers are good (63-86%). Only (β,γ)-cyclized products are formed. In most cases, we have separated the individual isomers but in the case of **1k**, only *E* isomer is formed exclusively. The stereochemistry in the case of (*E*)-**38** and (*Z*)-**38** is confirmed by X-ray crystallography (Figure 1).

Scheme 10



1e-k R' = H, Me

R' = H, R = Ph (**36**)
R' = H, R = 4-Me-C_6H_4 (**37**)
R' = H, R = 4-MeO-C_6H_4 (**38,** X-ray)
R' = H, R = 4-Cl-C_6H_4 (**39**)
R' = H, R = 4-NO_2-C_6H_4 (**40**)
R' = H, R = 1-Naphtyl (**41**)
R' = H, R = Me (**42,** X-ray)
R' = Me, R = Ph (**43**)
R' = Me, R = 4-Me-C_6H_4 (**44**)
R' = Me, R = 4-MeO-C_6H_4 (**45**)
R' = Me, R = 4-Cl-C_6H_4 (**46**)
R' = Me, R = 4-NO_2-C_6H_4 (**47**)
R' = Me, R = 1-Naphthyl (**48**)
R' = Me, R = Me (**49**)

Yields (^{31}PNMR, isolted): 74-96%; 63-81%

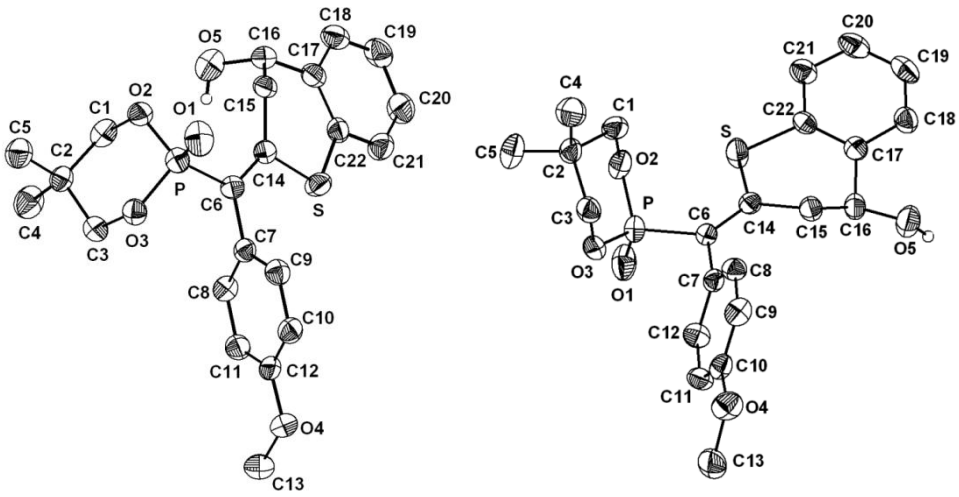
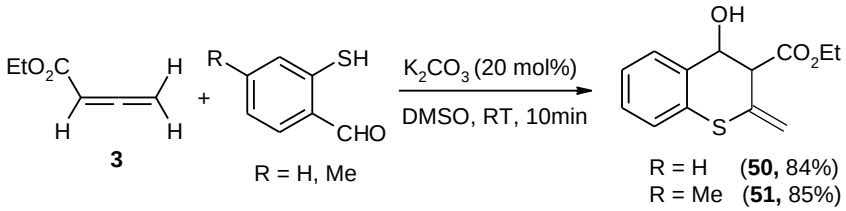


Figure 1. ORTEP diagrams for the compounds (a) (*E*)-**38** and (b) (*Z*)-**38**.

In contrast to the above, the reaction of ester allene **3** with 2-mercaptobenzaldehydes using 20 mol% K_2CO_3 in DMSO at room temperature led to (β,α)-cyclized products **50-51** exclusively (Scheme 11).

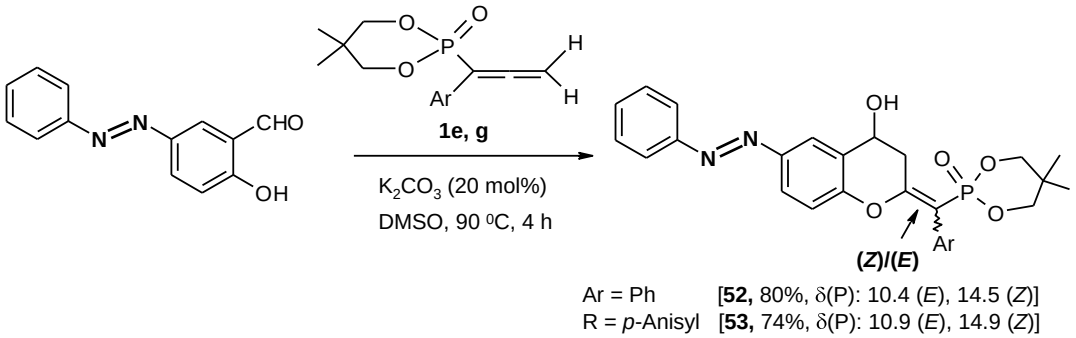
Scheme 11



(b) Reaction of allenylphosphonates with azo-substituted salicylaldehydes

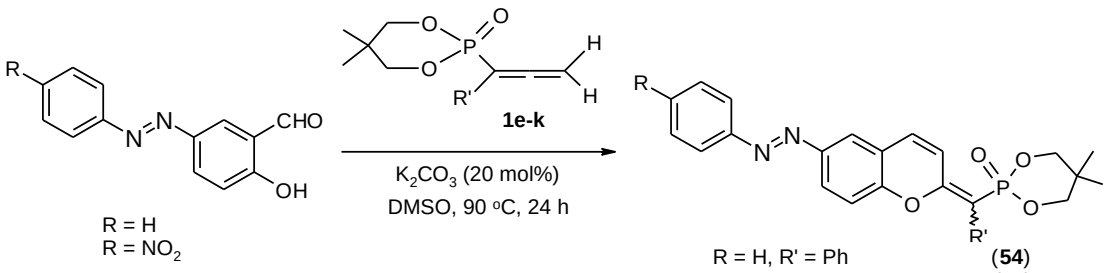
We first treated the *azo*-substituted salicylaldehyde with the allenylphosphonate 1**e** and **1g** in K_2CO_3/ DMSO at 90 ^oC and obtained the phosphono-chromans **52-53** as (*Z*) + (*E*) isomeric mixtures (Scheme 12) in (overall) good yields. The (*Z*) and (*E*) isomers for both **52** and **53** have been separated by using column chromatography.

Scheme 12



Using the above conditions, the reaction of allene **1f** with the *azo*-substituted salicylaldehyde led to a mixture of chromans and chromenes (4 h reaction) because one isomer of chroman underwent faster dehydration. Hence we continued the reaction for 24 h and obtained phosphono-*azo*-chromenes **54-63** exclusively (Scheme 13). We have also separated individual isomers in all cases. The overall (combined) isolated yields of the two isomers are moderate to good (72-80 %). The compound (*E*)-**55** is characterized by X-ray crystallography.

Scheme 13



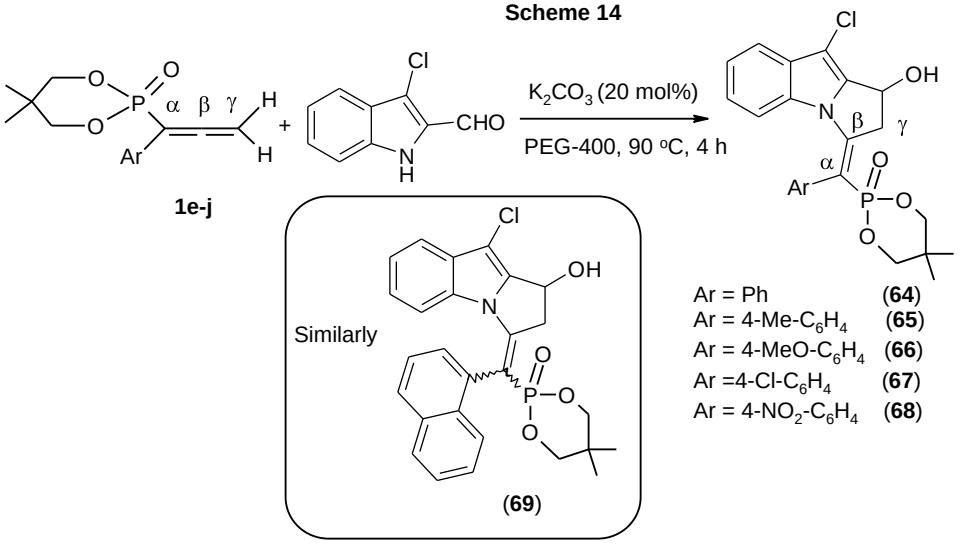
R = H, R' = Ph (**54**)
R = H, R' = 4-Me-C_6H_4 (**55**)
R = H, R' = 4-MeO-C_6H_4 (**56**)
R = H, R' = 4-Cl-C_6H_4 Ph (**57**)
R = H, R' = Me (**58**)
R = NO_2, R' = Ph (**59**)
R = NO_2, R' = 4-Me-C_6H_4 (**60**)
R = NO_2, R' = 4-MeO-C_6H_4 (**61**)
R = NO_2, R' = 4-Cl-C_6H_4 (**62**)
R = NO_2, R' = Me (**63**)

Yields (^{31}PNMR, isolated): 92-95%; 72-80%

(c) Reactions with 3-chloro-2-formylindole

The reaction of allenylphosphonates **1e-j** with 3-chloro-2-formylindole (that contains an NH end and a CHO group favourable for cyclization) using the base-solvent combination K_2CO_3/ PEG-400 led to novel (β,γ)-cyclized phosphono-pyrroloindoles **64-69** (Scheme 14) as exclusive products. A single stereo-isomer (*E*) was formed except in the case of **69** where a mixture of isomers is obtained. The overall isolated yields are good (68-75%). This is also a new type of cyclization.

Scheme 14



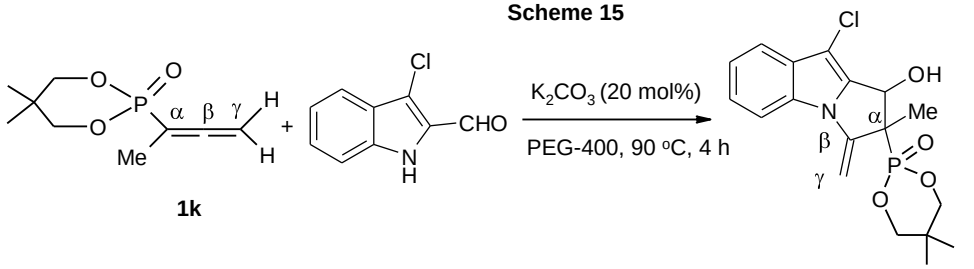
Ar = Ph (**64**)
Ar = 4-Me-C_6H_4 (**65**)
Ar = 4-MeO-C_6H_4 (**66**)
Ar =4-Cl-C_6H_4 (**67**)
Ar = 4-NO_2-C_6H_4 (**68**)

Yields: 68-75 %

A reaction similar to that described above with allenylphosphonate **1k** leads to the (β,α)-cyclized product **70** (Scheme 15) whereas that with ester allene **3** leads to

(β,γ)-cyclized product **71** (Scheme 16). The structures of these compounds are confirmed by X-ray crystallography.

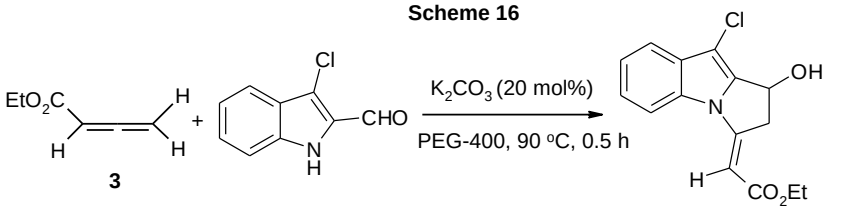
Scheme 15



1k

70 [δ(P);24.6, X-ray]
Isolated yield: 40%

Scheme 16

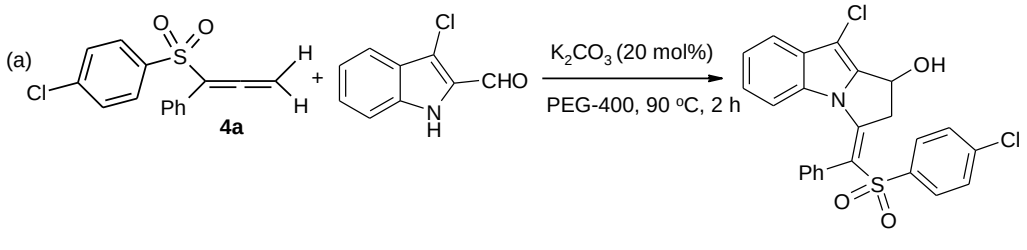


3

71 (75%, X-ray)

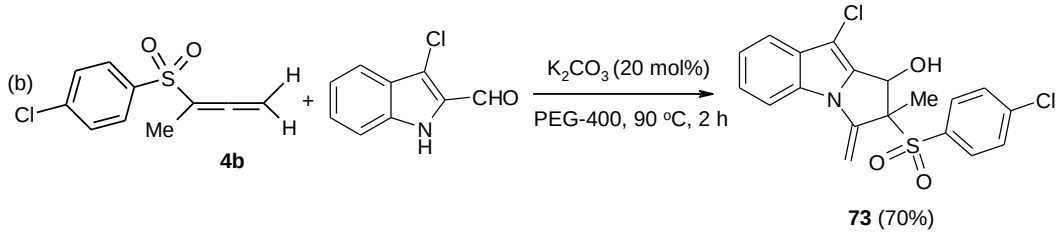
As an electron withdrawing group, the sulfonyl group ($ArSO_2$-) is likely to be comparable to the phosphoryl group [$(RO)_2P(O)$] or the ester group. Thus we desired to compare the reactivity of allenes bearing these groups. In this context, we treated the allenylsulfones **4a-b** with 3-chloro-2-formylindole and obtained sulfonated pyrroloindoles **72** and **73** in good yields (Scheme 17). The α-phenyl allene **4a** gave (β, γ)-cyclized product **72**, while the α-methyl allene **4b** gave the (β, α)-cyclized product **73**.

Scheme 17



4a

72 (74%)



4b

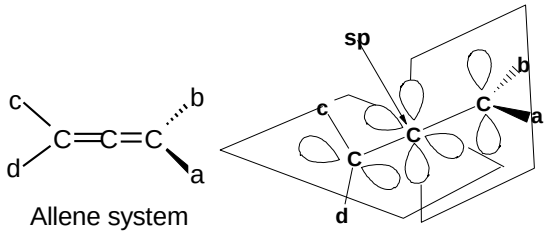
73 (70%)

Thus, under base catalyzed reactions adapted by us, the reactivity order with 3-chloro-2-formylindole is allenylphosphonates (~4h under heating) < allenylsulfones (~2h under heating) < ester allene (~30 min under heating). In the case of α-methyl substituted allenes **1k** and **4b**, (β,α)-attack is favored whereas in the case of α-aryl substituted allenes **1e-j** and **4a,** (β,γ)-product is the major/ exclusive product. Ester allene **3** gave a (β,γ)-product **71**. Mechanistic pathways leading to these pyrroloindoles are also discussed in the thesis.

INTRODUCTION

1.1 General Introduction: Allenes

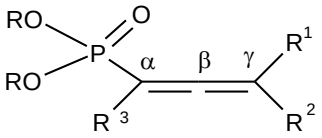
Allenes have two cumulative C=C bonds. The central carbon atom in allenes of type CR_2=*C*=CR'_2 is sp-hybridized with two sets of orthogonal *p*-orbitals and with only two bonding partners; the double bond array is linear as a result.[1] Because of their unique structure, for a long period of time, allenes had been considered to be highly unstable. In fact, the first synthesis of pentadienoic acid was attempted with the purpose of proving the non-existence of allenes.[2] It is now established that many natural products and pharmaceuticals contain the allene moiety.[2] During the last decade, reactivity of allenes has been the subject of numerous synthetic applications.[1-3] Hetero-substituted allenes also serve as extremely useful precursors in the synthesis of pharmaceuticals, dyes and elastomers. Suitably substituted allenes with no element of symmetry are chiral.[3i]



Synthetic potential of allenes arises from their substituent-loading capability, axial chirality and three reactive carbon sites. If one of the substituents on allene is the -$P(O)(OR)_2$ moiety, the resulting compounds are allenylphosphonates (phosphorylated allenes). In the following sections, a brief literature survey on the synthesis and utility of allenes/ allenylphosphonates in organic synthesis will be presented. Wherever possible, comparison will be made between the reactivity of allenylphosphonates and other allenes.

1.2 Allenylphosphonates (phosphorylated allenes)

Due to ready availability, stability and low cost of preparation, allenylphosphonates are valuable precursors in organic synthesis. A variety of phosphorus substituted heterocycles, enynes, tetra-substituted vinylphosphonates and allylphosphonates, *β*-keto- and *β*-amino-phosphonates have been synthesized by starting with allenylphosphonates.[4] Selective activation of a particular centre can be achieved by varying the groups at the phosphorus centre or in the allene part.

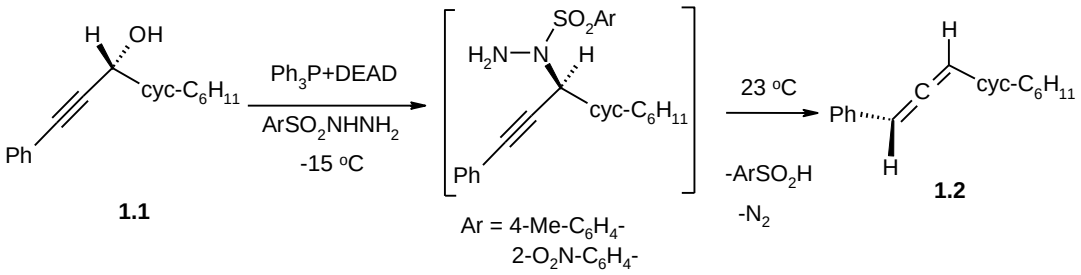


Allenylphosphonate (phosphorylated allene)

1.3 Synthesis of allenes/ allenylphosphonates

Umpteen methods are available for the synthesis of nonphosphorylated allenes in the literature. The best references for these methods are the books published by Bradsma (2004)[2c] and by Krause and Hashmi.[2b] As an example, in one of these methods, Mitsunobu reaction of an activated hydrazine and optically active propargyl alcohol (**1.1**) leads to optically active allene (**1.2**) as shown in Scheme 1.1.[5]

Scheme 1.1



1.1

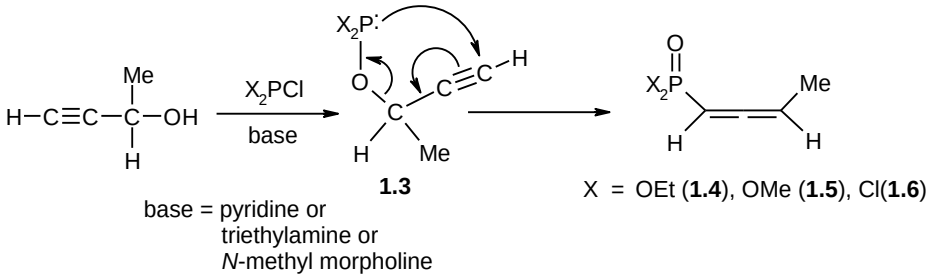
Ar = 4-Me-C_6H_4-
2-O_2N-C_6H_4-

1.2

A convenient and general method for the preparation of allenylphosphonates involves the treatment of trivalent phosphorus chlorides X_2PCl with the propargyl alcohol [e.g. Me(H)C(OH)C≡CH] in the presence of a base such as pyridine, triethylamine or *N*-methyl morpholine in a suitable solvent like ether, THF or toluene.[6]

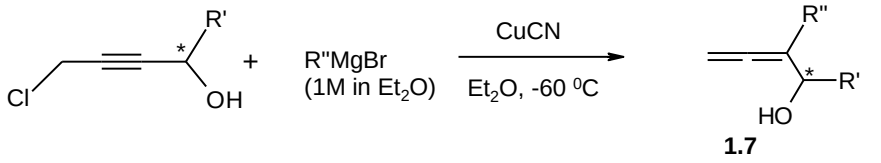
The P(III) intermediate **1.3** undergoes a *pseudo*-Claisen type rearrangement, usually at ambient temperature or below, to afford allenylphosphonates **1.4**–**1.6** (Scheme 1.2).

Scheme 1.2



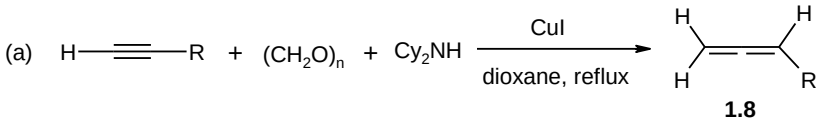
Recently, Ma and co-workers prepared the optically active secondary 2,3-allenols **1.7** in good yields with up-to 99% ee by the reaction of optically active propargyl alcohols with the corresponding Grignard reagents in the presence of CuCN (Scheme 1.3).[7] Since a large number of optically active alcohols are available, we can prepare a diverse range of optically active allenes by this method.

Scheme 1.3

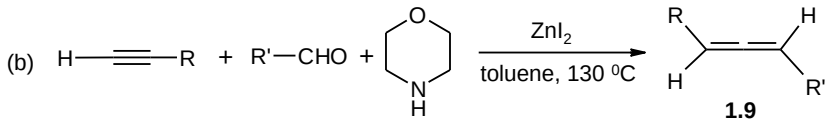


The reaction of terminal alkynes with Cy_2NH and paraformaldehyde mediated by CuI affords the terminal allenes **1.8** in good yields (Scheme 1.4a) and many functional groups such as mesilate, hydroxyl group, amide, etc. are tolerated in this reaction. But this reaction is limited to only paraformaldehyde.[8] As an extension, the same group developed a method for synthesizing 1,3-disubstituted allenes/ allenols **1.9-1.10** from various aldehydes and terminal alkynes by using ZnI_2 and morpholine (Scheme 1.4b, c).[9]

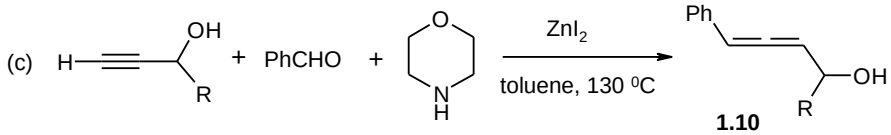
Scheme 1.4



R = $CH_3(CH_2)_7$, $CH_3(CH_2)_9$, *p*-Cl-C_6H_4,
$PhCH_2OCH_2$, *p*-$O_2NC_6H_4CH_2OCH_2$,
p-$EtC_6H_4CH(OH)CH_2$, *p*-$ClC_6H_4CH(OH)CH_2$ etc.



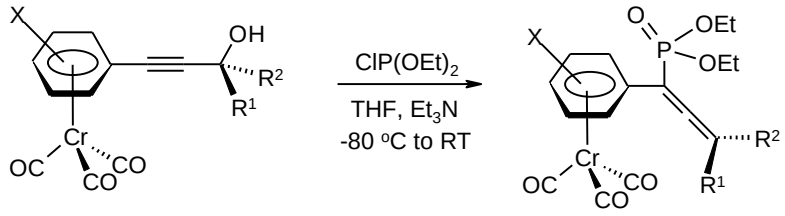
R = $CH_3(CH_2)_7$; R' = Ph, *p*-ClC_6H_4, *p*-BrC_6H_4 etc.
R = *p*-$O_2NC_6H_4CH_2O(CH_2)_2$; R' = Ph, *i*-Pr, *n*-Bu etc.



R = *n*- C_5H_{11}, *n*-C_7H_{15}, *n*- C_9H_{19} etc.

Allenylphosphonates **1.11-1.15** with an *α*-substituted arene-$Cr(CO)_3$ complex structure have been prepared in good yields (68-80%) from the reaction of (chloro)diethylphosphite with the corresponding propargyl alcohol in the presence of triethylamine as shown in Scheme 1.5.[10] Although these compounds are interesting, the method is similar to that described above in Scheme 1.2.

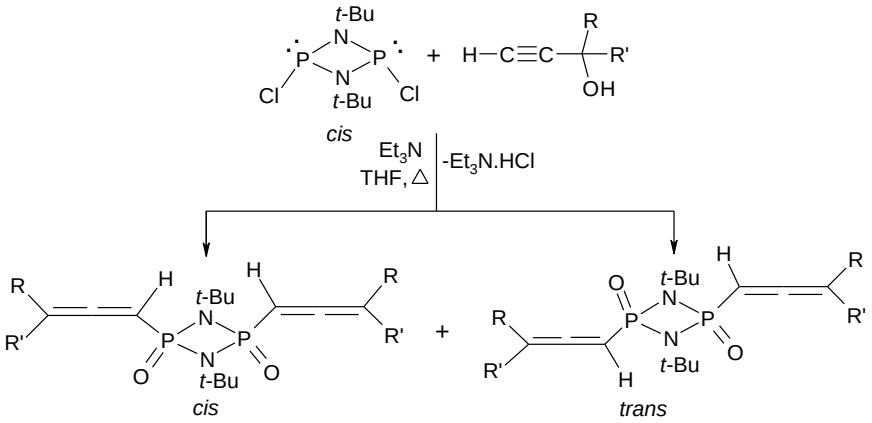
Scheme 1.5



X = H $R^1 = R^2 =$ Me (**1.11**)
X = H R^1 = H, R^2 = Et (**1.12**)
X = o-Me $R^1 = R^2 =$ Me (**1.13**)
X = m-Me $R^1 = R^2 =$ Me (**1.14**)
X =p-Me $R^1 = R^2 =$ Me (**1.15**)

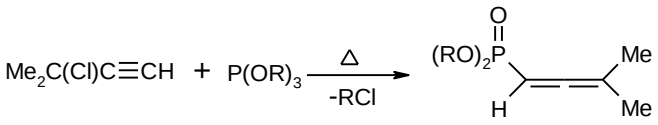
Recently from our research group, the bis-(allenyl)phosphoramidates *cis*-[$(H_2C{=}C{=}CH)(O)P(\mu\text{-N-}t\text{-Bu})]_2$ (**1.16**), *cis*- and *trans*-[$(Me_2C{=}C{=}CH)(O)P(\mu\text{-N-}t\text{-Bu})]_2$ (**1.17a** and **1.17c**) and *cis*- and *trans*-[$(Me)(Et)C{=}C{=}CH)(O)P(\mu\text{-N-}t\text{-Bu})]_2$ (**1.17b** and **1.17d**) based on a cyclodiphosph(V)azane skeleton have been synthesized by treating *cis*-[$ClP(\mu\text{-N-}t\text{-Bu})]_2$ with the respective propargyl alcohols in the presence of triethylamine (Scheme 1.6).[11] If one can use the terminal double bonds at both the ends in these compounds, it should be possible to get new generation of phosphorus containing polymers.

Scheme 1.6



Allenylphosphonates can also be prepared by heating the trialkylphosphites with 3-chloro-3-methyl-1-butyne; thus allenylphosphonates **1.18-1.19** are obtained in moderate to good yields (Scheme 1.7).[12] However, this method is restricted to the use of only terminal alkynes.

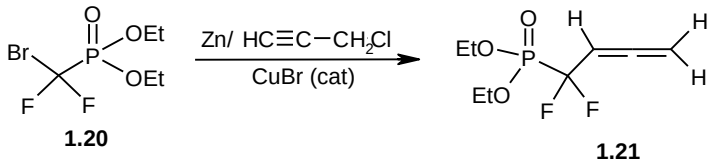
Scheme 1.7



R = Me (**1.18**), Et (**1.19**)

There are other non-conventional routes to specific allenylphosphonates. For example, alkylation of diethyl bromodifluorophosphonate **1.20** with zinc and propynyl chloride affords the allenylphosphonate **1.21** (Scheme 1.8).[13]

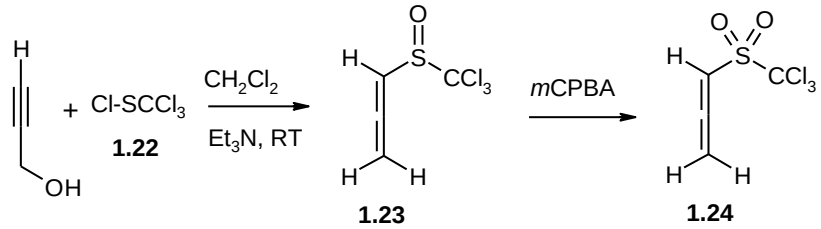
Scheme 1.8



1.20 **1.21**

The reaction of trichlorosulfenyl chloride **1.22** with propargyl alcohol in the presence of triethylamine affords allenylsulfoxide **1.23** which on oxidation by *m*CPBA leads to allenylsulfones **1.24** (Scheme 1.9) in good yields.[14] Due to ready availability of various propargyl alcohols, we can prepare various allenylsulfones. However, this route has not been explored much in the literature.

Scheme 1.9



1.22 **1.23** **1.24**

1.4 Transition metal-catalyzed annulation reactions of allenylphosphonates: Synthesis of heterocycles/ carbocycles

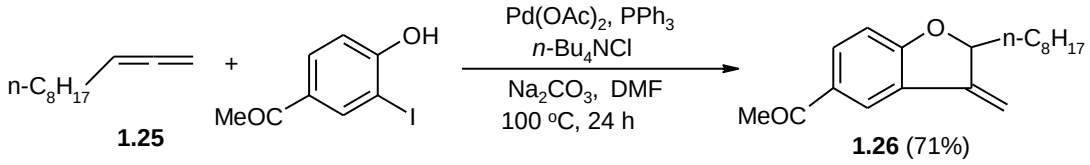
Annulation processes are among the most important reactions in organic synthesis.[15] Transition metal catalyzed annulation of allenes has become an extremely useful method for the construction of heterocycles and carbocycles of significant biological importance.[1] It has been well documented that carbometallation of allenes with an aryl or alkenyl metal halide easily occurs to afford π-allyl complex, which readily undergoes inter- or intra-molecular nucleophilic substitution with various nucleophiles. The feasibility as well as reactivity of these π-allyl species with a wide variety of carbon or heteroatom nucleophiles leads to new bond forming processes. For

such processes, over the last few decades, Pd-catalyzed reactions have attracted great attention because they exhibit a high level of chemo-, regio- and stereo-selectivity in numerous transformations. Here, the term *Pd-catalyst* is implied to describe either *a Pd(II) or a Pd(0) complex* that is used in the catalytic reaction. Studies on coupling reactions of allenylphosphonates with iodoarenes are comparatively few in number.[4d-h] Since phosphorus can impart a different electronic constraint relative to an aryl carbon of aryl-substituted allenes on the intermediates, stereochemistry of the products in palladium-catalyzed coupling using allenylphosphonates and phenyl substituted allenes could be different. Hence coupling reactions of the general allene moiety as relevant to the present work will also be described in this section.

1.41 Synthesis of benzofurans

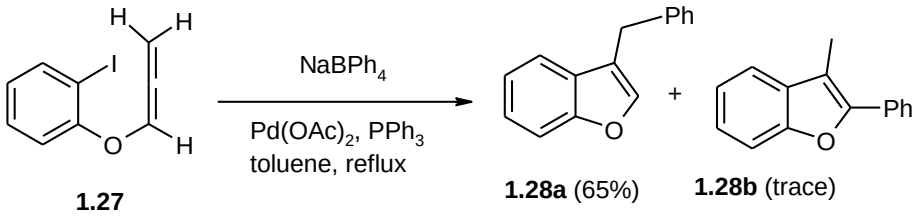
In 1991, Larock and co-workers first reported the Pd-catalyzed heteroannulations of allenes using functionally substituted aryl halides.[16] Thus, the treatment of allene **1.25** with functionalized iodophenol in the presence of $Pd(OAc)_2$/ PPh_3/ *n*-Bu_4NCl/ Na_2CO_3 at 100 ^oC in DMF afforded benzofuran derivative **1.26** in 71 % yield (Scheme 1.10).

Scheme 1.10



An interesting palladium-catalyzed tandem cyclization-anion capture strategy was developed by Grig and co-workers using allenes as the terminating species.[17] Thus the allene **1.27** undergoes cyclization that leads to five-membered heterocycles **1.28a** and **1.28b** (Scheme 1.11).

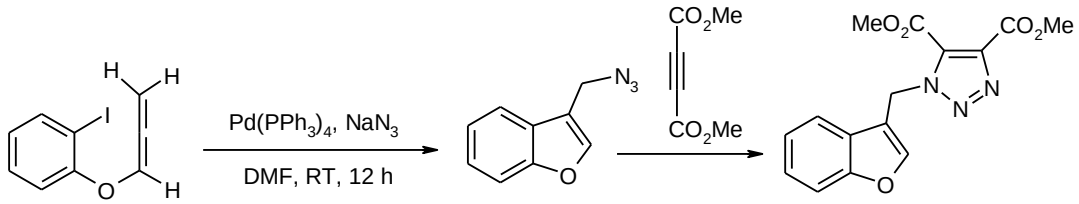
Scheme 1.11



1.27 **1.28a** (65%) **1.28b** (trace)

As an extension of the above reaction, the above research group reported the synthesis of benzofuran attached with an azide group. The reaction of allene **1.27** with sodium azide in the presence of 10 mol% $Pd(PPh_3)_4$ afforded the benzofuran **1.29** regioselectively**.**[18] The latter was then treated with dimethyl acetylenedicarboxylate to give the triazole **1.30** linked with benzofuran (Scheme 1.12).

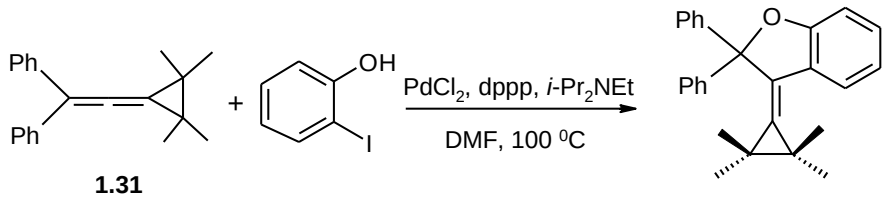
Scheme 1.12



1.27 **1.29** (71%) **1.30** (86%)

The cyclopropane containing benzofuran **1.32** was prepared in good yields by the Pd-catalyzed coupling reaction of diarylvinylidenecyclopropane **1.31** with 2-iodophenols (Scheme 1.13).[19] This is a good method for synthesizing cyclopropane appended benzofurans.

Scheme 1.13

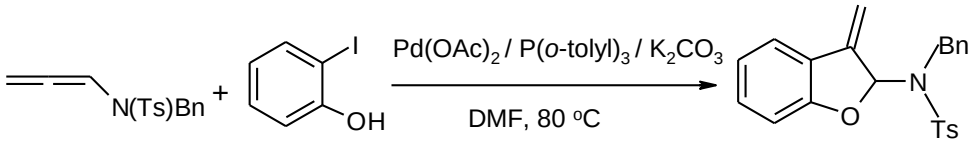


1.31 **1.32** (94%)

dppp = bis(diphenylphosphino)propane

Sakamoto and co-workers reported the highly regioselective synthesis of benzofuran **1.34** in moderate yields by the Pd-catalyzed annulation of heteroatom substituted allene **1.33** with 2-iodophenol (Scheme 1.14).[20] This method, however, is limited to electron donating substituents on allenes.

Scheme 1.14

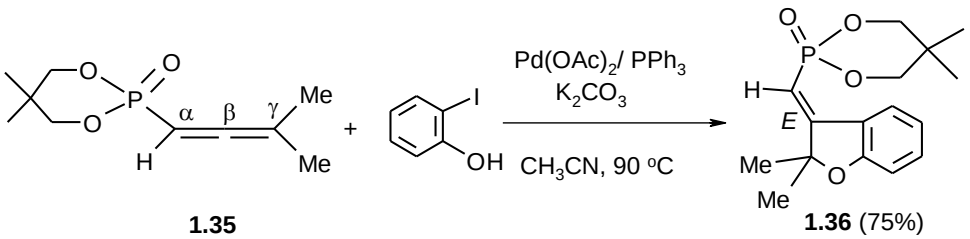


1.33 **1.34** (62%)

Ts = *p*-toluenesulfonyl, Bn = benzyl

From our research group, coupling reactions of various allenylphosphonates with 2-iodophenols in the presence of $Pd(OAc)_2$/ PPh_3 to give diverse phosphono-benzofurans in good yields have been reported (Scheme 1.15).[21a-b] For example, allenylphosphonate **1.35** reacts with 2-iodophenol in the presence of $Pd(OAc)_2$/ PPh_3 and K_2CO_3 to give the corresponding (*E*)-phosphono-benzofurans **1.36** in good yields. Unlike the reactions of non-phosphorylated allenes which led to only two types of furans, allenylphosphonates afforded at least four different types of phosphono-benzofurans.

Scheme 1.15

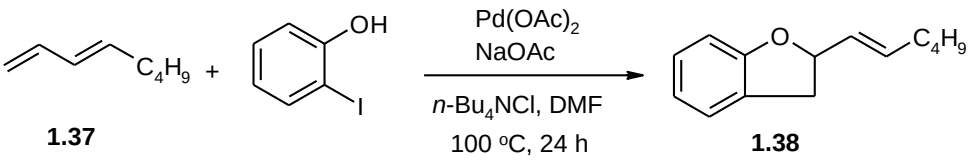


1.35 **1.36** (75%)

Benzofurans can also be prepared by starting with 1,3-butadienes. Thus compound **1.38** was prepared *via* Pd-catalyzed reaction of 1,3-butadiene **1.37** with 2-iodophenol (Scheme 1.16).[22] It is likely that the mechanistic pathway here is analogous to that using allenes (1,2-dienes), and hence this reaction is presented here. However,

we can prepare only 2-substituted benzofurans using 1,3-butadienes whereas in the case of allenes, we can prepare 2,3-disubstituted benzofurans also.

Scheme 1.16

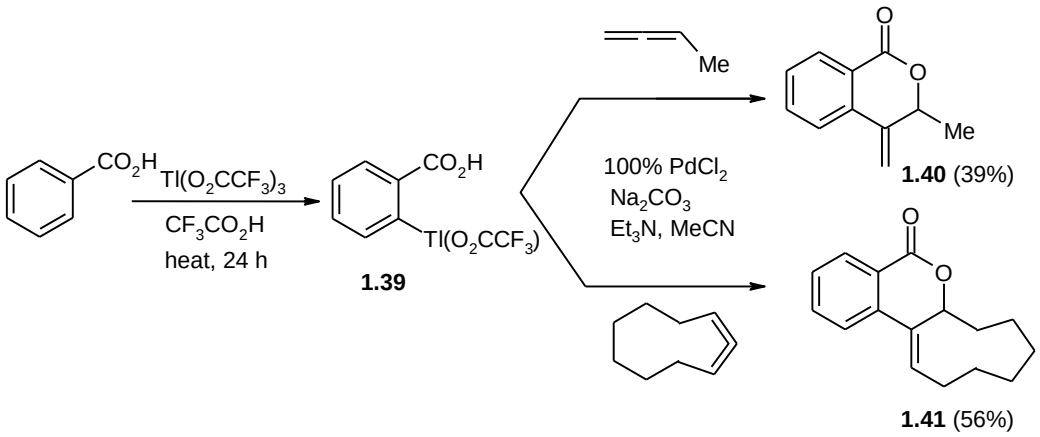


1.37 **1.38**

1.42 Synthesis of isocoumarins and related lactones

Larock and co-workers initially reported a *stoichiometric* Pd(II) promoted cyclization of *ortho*-thallated benzoic acid **1.39** with allenes to afford cyclic benzoannulated *δ*-valerolactones **1.40** and **1.41** in the year 1984 (Scheme 1.17).[23] This reaction was the first example where carbon-palladium bond was formed in a *trans*-metallation reaction from thallium to palladium.

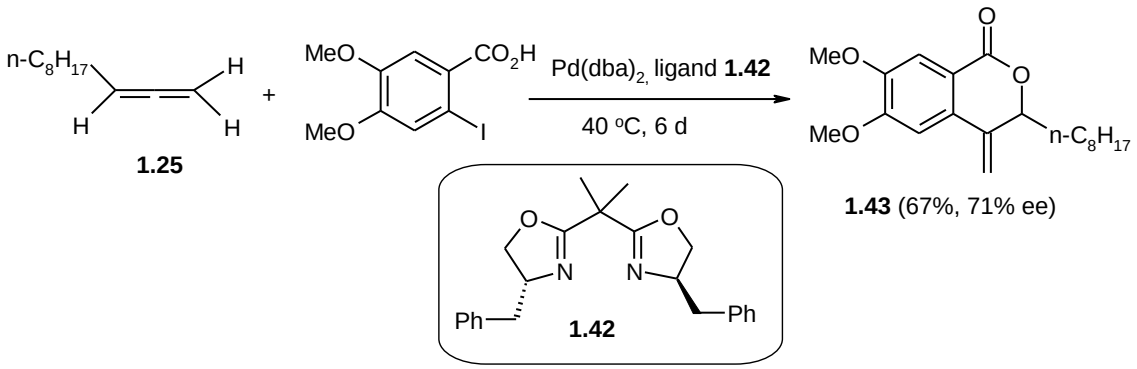
Scheme 1.17



1.39 **1.40** (39%) **1.41** (56%)

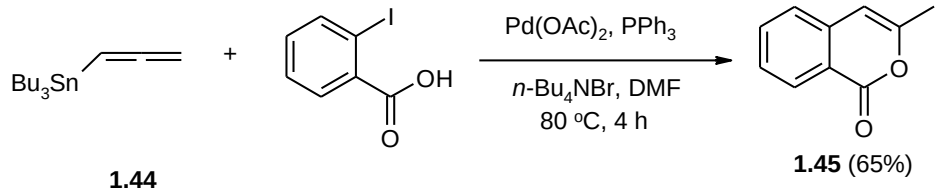
Later, the same group synthesized the chiral isocoumarin derivative **1.43** from the reaction of allene **1.25** with 2-iodobenzoic acid using $Pd(dba)_2$ with chiral bisoxazoline ligand **1.42** (Scheme 1.18).[24] This method is applicable to non-functionalized allenes only.

Scheme 1.18



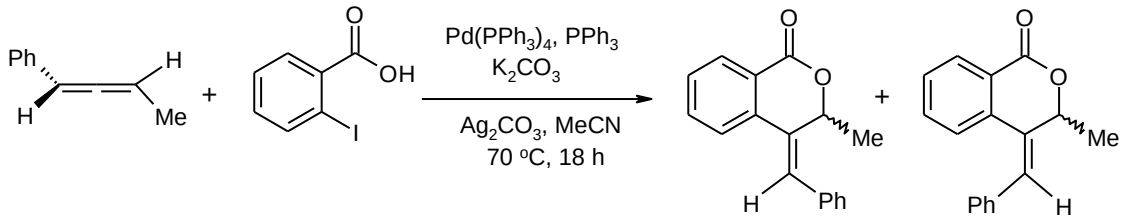
A convenient regio-selective method for the synthesis of 3-substituted coumarin **1.45** in good yields via Pd-catalyzed coupling of 2-iodobenzoic acid and allenyltributyltin **1.44** (Scheme 1.19)**.**[25] This process is limited in scope because only a limited number of Sn-connected allene precursors are available.

Scheme 1.19



Another report on Pd-catalyzed carboxylation of allenes provides isomeric lactones.[26] Thus reaction of the chiral allene (*R*)-**1.46** with 2-iodobenzoic acid in the presence of $Pd(PPh_3)_4$/ PPh_3/ K_2CO_3/ Ag_2CO_3 at 70 ^oC/ 18 h in acetonitrile gives the isocoumarins **1.47a** and **1.47b** (70:30) in good yields (Scheme 1.20). As can be expected, due to the use of excess of base, the enantiomeric purity is only ~5 %.

Scheme 1.20



(*R*)-**1.46**

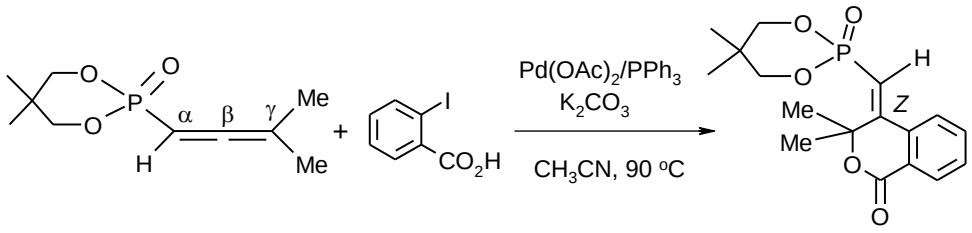
1.47a **1.47b**

total yield~ 79%

1.47a:**1.47b** ~70:30

From our research group, phosphono-isocoumarin **1.48** was prepared stereoselectively by the reaction of allenylphosphonate **1.35** with 2-iodobenzoic acid in the presence of $Pd(OAc)_2$/ PPh_3/ K_2CO_3 in acetonitrile medium(Scheme 1.21).[21a-b] When 4-iodobenzoic acid was used in place of 2-iodobenzoic acid, a normal arylated product with pendant –COOH group was obtained.

Scheme 1.21

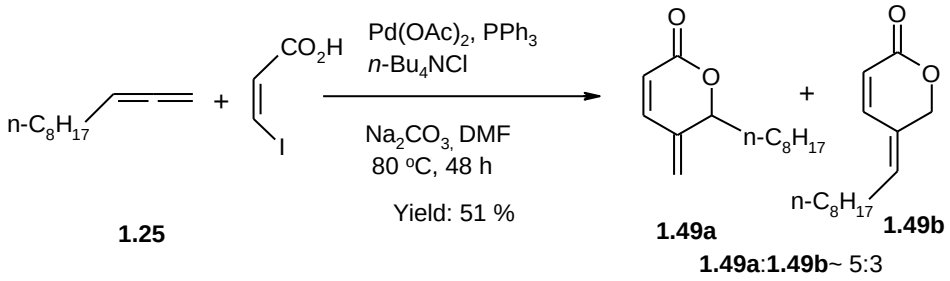


1.35

1.48 (61%)

Vinylic halides with additional functional groups undergo annulation with allenes to produce five- or six–membered ring heterocycles (Scheme 1.22).[27] It can be noted that isomeric products (e.g. **1.49a-b**) may be formed in these cases.

Scheme 1.22



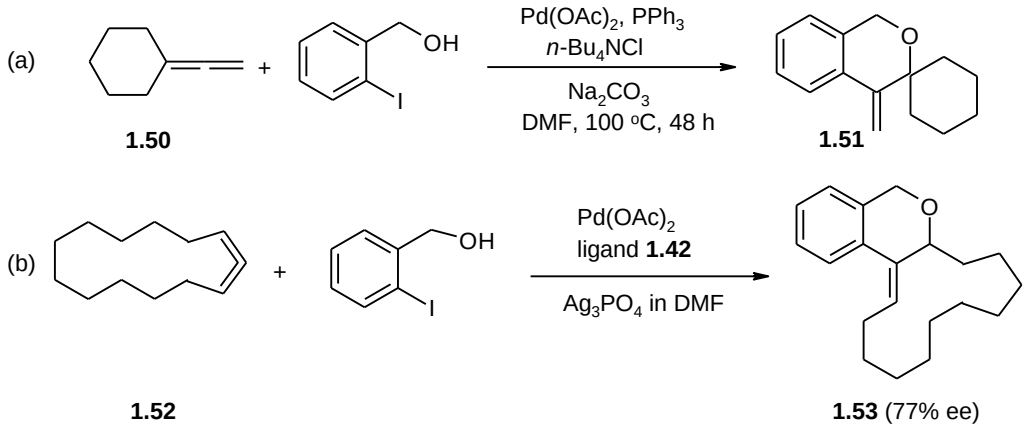
1.25 **1.49a** **1.49b**

1.49a:**1.49b**~ 5:3

1.43 Synthesis of benzopyrans and related compounds

Pd-catalyzed annulations using 2-iodobenzyl alcohol leading to benzopyrans is explored only to a limited extent in the literature.[16,26] The benzopyran **1.51** was synthesized by the Pd-catalyzed annulation of 2-iodobenzyl alcohol with allene **1.50** (Scheme 1.23a). In a similar fashion, optically active benzopyran **1.53** was prepared in up-to 77 % *ee* by starting with the allene **1.52** and by using chiral bisoxazoline **1.42** as a ligand (Scheme 1.23b).[16]

Scheme 1.23

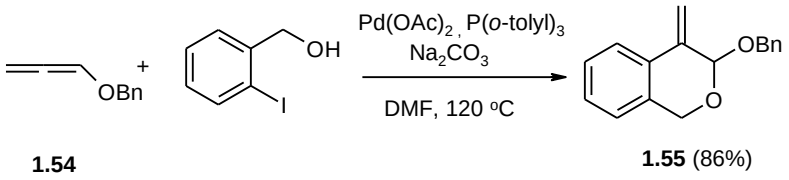


1.50 **1.51**

1.52 **1.53** (77% ee)

The reaction of heteroatom substituted allene **1.54** with 2-iodobenzyl alcohol in the presence of $Pd(OAc)_2$/ $P(o\text{-tol})_3$/ *n*-Bu_4NCl/ Na_2CO_3 at 120 ^oC in DMF afforded the benzopyran **1.55** regioselectively in good yields (Scheme 1.24).[20] This is a good method for the synthesis of heteroatom substituted benzopyrans.

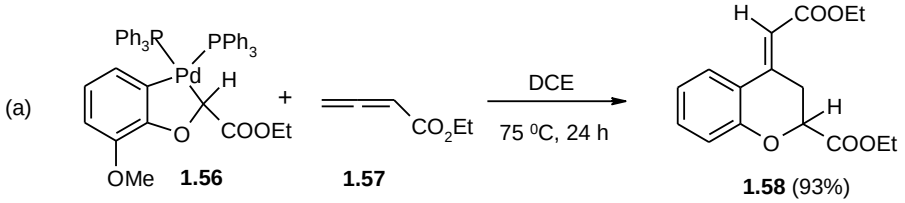
Scheme 1.24

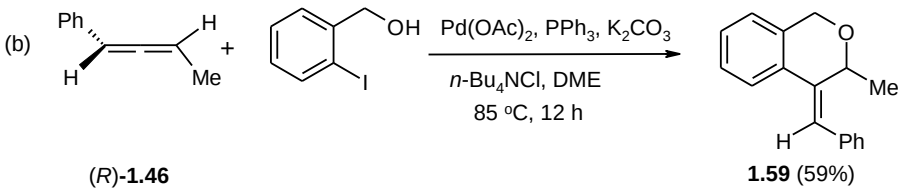


1.54 **1.55** (86%)

The insertion reaction of allene **1.57** into benzannulated oxapalladacycle **1.56** at elevated temperatures provides benzopyran **1.58** in high yields (Scheme 1.25a).[28] This reaction works for allenes with both electron deficient and electron donating substituents. In another system, by means of the reaction of 2-iodobenzyl alcohol with the chiral allene (*R*)-**1.46**, the benzopyran derivative **1.59** was prepared in 59 % yield (Scheme 1.25b).[26] However, chirality of the allene could not be preserved under these palladium-catalyzed reaction conditions.

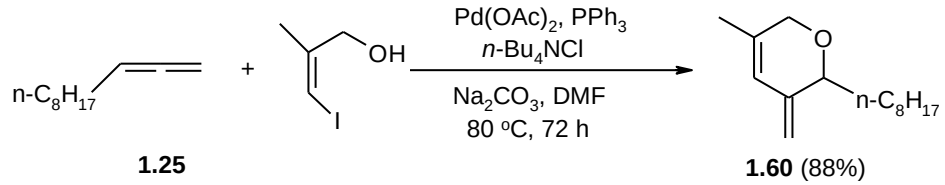
Scheme 1.25





The reaction of (*Z*)-3-iodo-2-methyl-2-propenol with allene **1.25** gives the heterocycle **1.60**, a derivative of pyran, in the presence of $Pd(OAc)_2$/ PPh_3/ *n*-Bu_4NCl and Na_2CO_3 as base using the solvent DMF at 80 ^oC/ 72 h (Scheme 1.26).[27] This is a route that (perhaps) can be readily extended to include many 1-iodo-3-ols with vinylic functionalities.

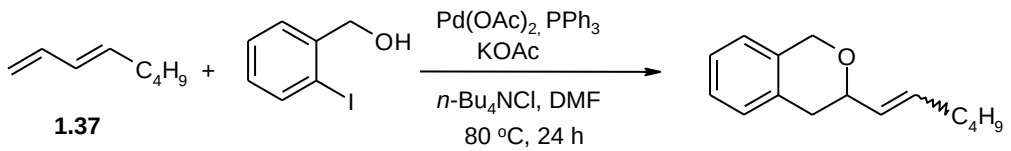
Scheme 1.26



1.25 **1.60** (88%)

Like the benzofurans mentioned above,[22] benzopyran derivatives can also be prepared by using 1,3-butadienes. Thus compound **1.61** was prepared by treating the butadiene **1.37** with 2-iodobenzyl alcohol (Scheme 1.27).[22] This scheme also illustrates that both 1,2-dienes (allenes) and 1,3-dienes are amenable for heterocycle formation by similar routes.

Scheme 1.27



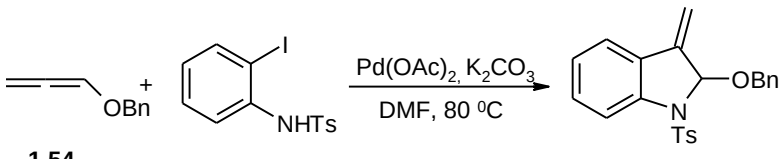
1.37

1.61 (53%)
(*E*/*Z* = 16:1)

1.44 Synthesis of indoles

Sakamoto and co-workers reported the highly regioselective synthesis of indole **1.62** by the Pd-catalyzed annulation reaction of heteroatom substituted allenes **1.54** with N-tosyl-2-iodoaniline (Scheme 1.28).[20] This method is limited for terminal allenes and for those allenes with electron donating substituents.

Scheme 1.28

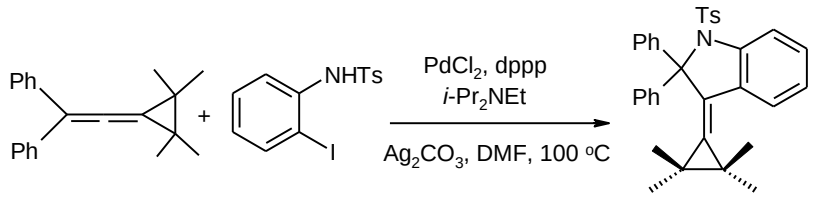


1.54

1.62 (99%)

Li and Shi prepared the cyclopropane appended indole **1.63** in moderate yields by the Pd-catalyzed cross-coupling reaction of diarylvinylidenecyclopropane **1.31** with 2-iodoaniline (Scheme 1.29).[19] This is not a good method for indoles (low yields) although the same route worked well for the synthesis of benzofurans.

Scheme 1.29

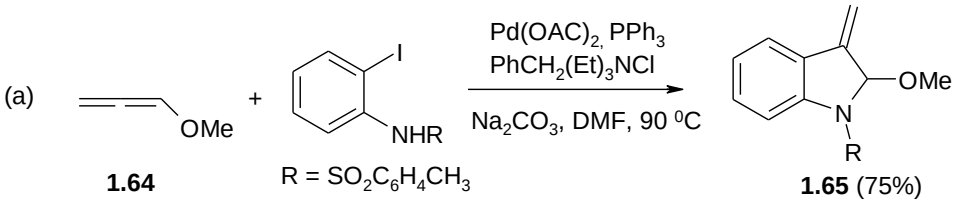


1.31

1.63 (58%)

Desarbre and Merour reported the synthesis of indole **1.65** by the Pd-catalyzed annulation of allene **1.64** with *N*-tosyl-2-iodoaniline (Scheme 1.30a).[29] Larock and co-workers reported the regioselective formation of indole **1.66** through the Pd-catalyzed annulation of allene **1.52** with *N*-tosyl-2-iodoaniline in the presence of $Pd(OAc)_2$/ PPh_3/ *n*-Bu_4NCl/ Na_2CO_3 at 100 ^oC in DMF (Scheme 1.30b).[17] This method, however, is limited to unactivated allenes.

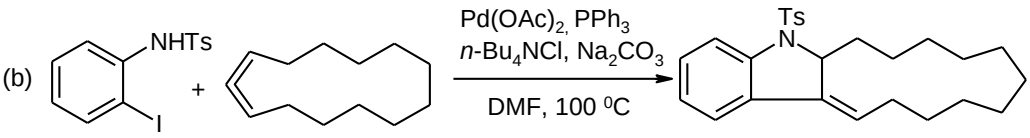
Scheme 1.30



1.64

R = $SO_2C_6H_4CH_3$

1.65 (75%)

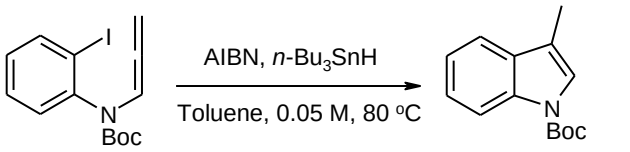


1.52

1.66 (83%)

Shen and Hsung prepared indole **1.68** in good yields by the radical cyclization of allenamine **1.67** at elevated temperatures (Scheme 1.31).[30] This reaction is highly regioselective for the central carbon of allene moiety.

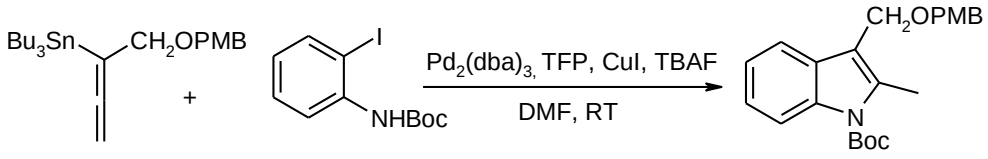
Scheme 1.31



1.67 **1.68** (91%)

The Stille coupling of *N*-Boc-2-iodoanilnes with the 1-(tributylstannyl)-1-substituted allene **1.69** effected the successive formation of the 2-methyl-3-substituted indole **1.70**. Alternatively, the latter compound can also be synthesized in a one-pot operation, which consists of the coupling reaction, followed by TBAF treatment (Scheme 1.32).[31] This procedure was applied to the synthesis of indomethacin, a natural product.

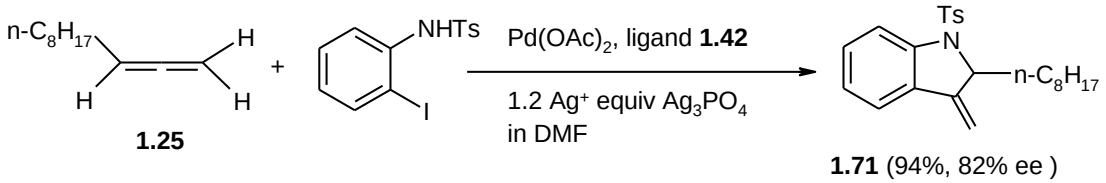
Scheme 1.32



1.69 **1.70** (65%)

Enantioselectivity in the carbopalladation-nucleophilic substitution of allene **1.25** with *N*-tosyl-2-iodoaniline leading to indole **1.71** could be enhanced up to 82% *ee* by using chiral bisoxazoline **1.42** as a ligand (Scheme 1.33).[24] This method is applicable to terminal allenes only.

Scheme 1.33

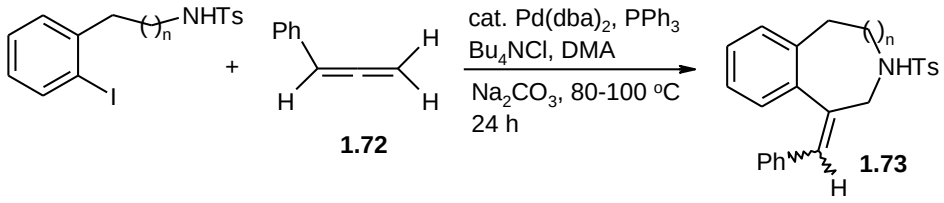


1.25 **1.71** (94%, 82% ee)

1.45 Synthesis of six or higher membered nitrogen heterocycles

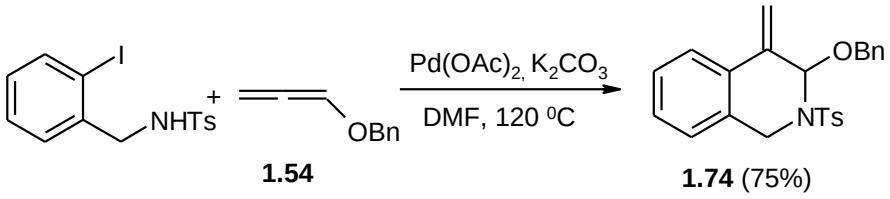
By proper choice of aryl halides, nitrogen containing seven-, eight- and nine-membered ring heterocycles **1.73** can be prepared by the Pd-catalyzed annulation of allene **1.72** (Scheme 1.34).[32] This method can be used for the formation of up-to nine membered rings but success was not achieved for the formation of still higher membered rings.

Scheme 1.34



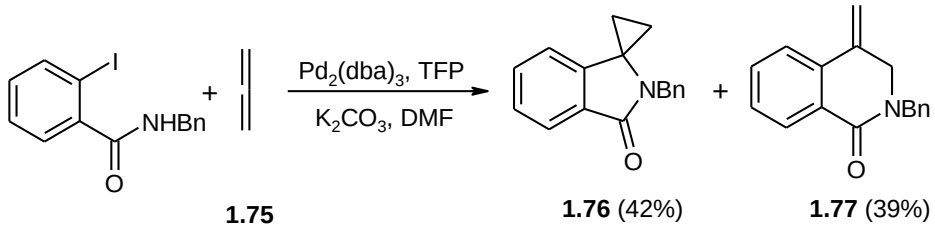
Sakamoto and co-workers synthesized 6-membered nitrogen heterocycle **1.74** in moderate yields by the Pd-catalyzed annulation of heteroatom substituted allene **1.54** with N-tosyl-2-iodobenzyl amine (Scheme 1.35).[20] This method is limited to terminal allenes with electron donating substituents.

Scheme 1.35



2-Iodobenzamides can also be used in annulation reactions with allenes. Thus, Pd-catalyzed cross-coupling reaction of 2-iodobenzamide with allene **1.75** afforded a 1:1 mixture of cyclopropane product **1.76** and the allylation product **1.77** (Scheme 1.36).[33]

Scheme 1.36

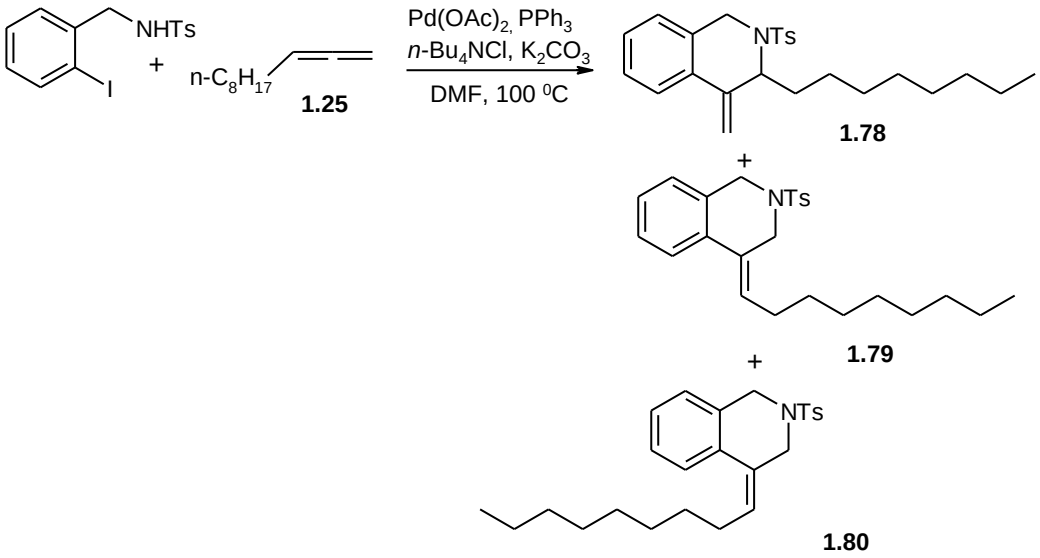


1.75 **1.76** (42%) **1.77** (39%)

TFP = trifurylphosphine

Pd-catalyzed annulation of allene **1.25** with *N*-tosyl-2-iodobenzylamine affords a mixture of dihydroquinolines **1.78-1.80** in good yields but with poor regioselectivity (Scheme 1.37).[16]

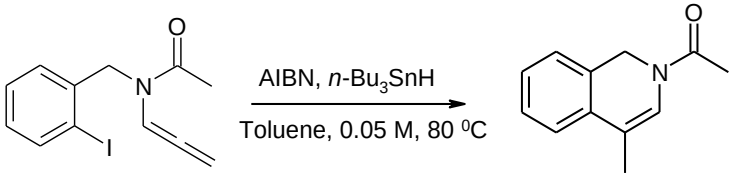
Scheme 1.37



1.25 **1.78** **1.79** **1.80**

Hsung and co-workers reported the synthesis of isoquinoline **1.82** through the radical cyclization of allenamide **1.81**. This reaction was more regioselective towards central carbon atom of allene (Scheme 1.38).[30]

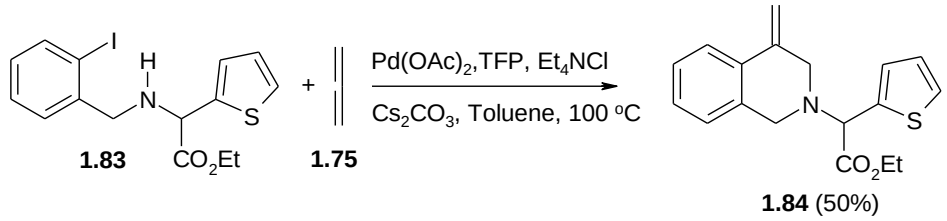
Scheme 1.38



1.81 **1.82**

Grigg and co-workers reported the synthesis of novel isoquinoline derivative **1.84** by the Pd-catalyzed reaction of allene **1.75** with **1.83** (Scheme 1.39).[34] This reaction is similar to that shown in Schemes 1.36 and 1.37.

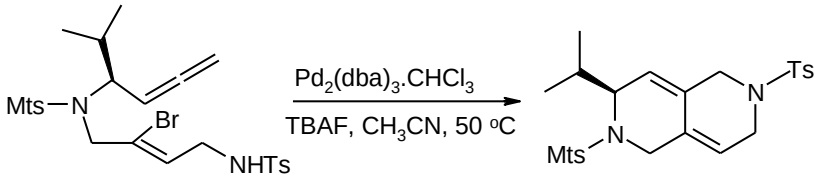
Scheme 1.39



1.83 **1.75** **1.84** (50%)

Fujii, Ohno and co-workers reported that the treatment of allenic bromoalkene **1.85** (bearing a nucleophilic moiety) with a catalytic amount of Pd(0) complex in the presence of TBAF or Cs_2CO_3 in CH_3CN afforded the bicyclic heterocycle **1.86** in high yields through zipper-mode cascade cyclization (Scheme 1.40).[35]

Scheme 1.40



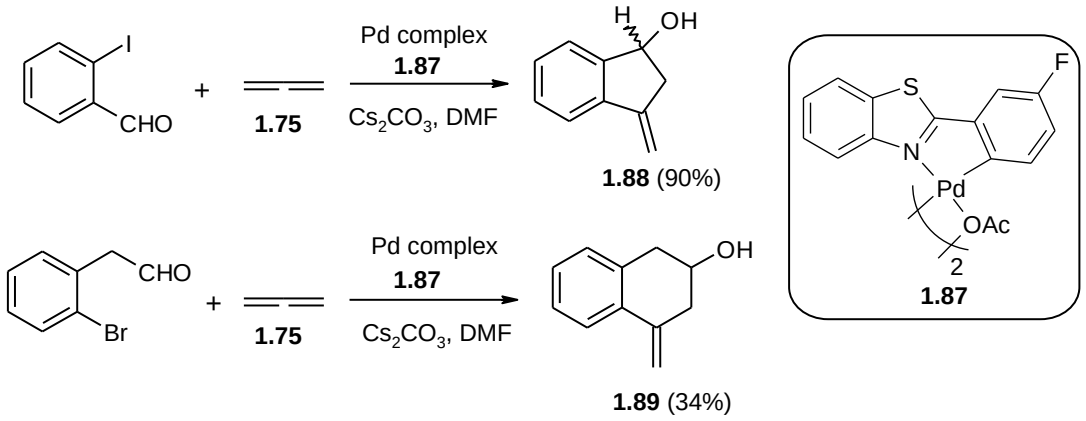
1.85 **1.86** (91%)

Mts = 2,4,6-trimethylphenylsulfonyl

1.46 Synthesis of carbocycles

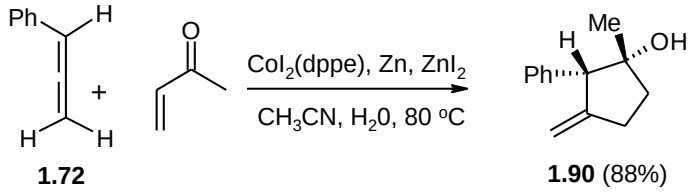
Cross-coupling reaction of 2-halocarbonyl compounds with allene **1.75** in the presence of 2 mol% of a non-phosphine cyclopalladated catalyst **1.87** afforded cyclopentenol **1.88** and cyclohexenol **1.89** via nucleophilic cyclization of π-allyl palladium intermediate species (Scheme 1.41).[36] In general, it may be noted that -CHO groups are unaffected in Pd-catalyzed reactions; however, in the reaction shown here, -CHO group also takes part in the reaction.

Scheme 1.41



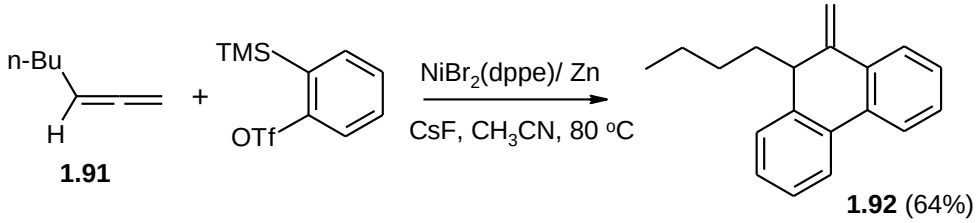
Cheng and co-workers reported a mild and highly diastereoselective cobalt catalyzed intermolecular reductive [3+2] cycloaddition of allene **1.72** with enone leading to the five-membered carbocycle **1.90** in good yield (Scheme 1.42).[37] It may be noted that this as well as the one shown in the previous scheme can afford a cyclopentane ring system with appended –OH and olefin residues.

Scheme 1.42



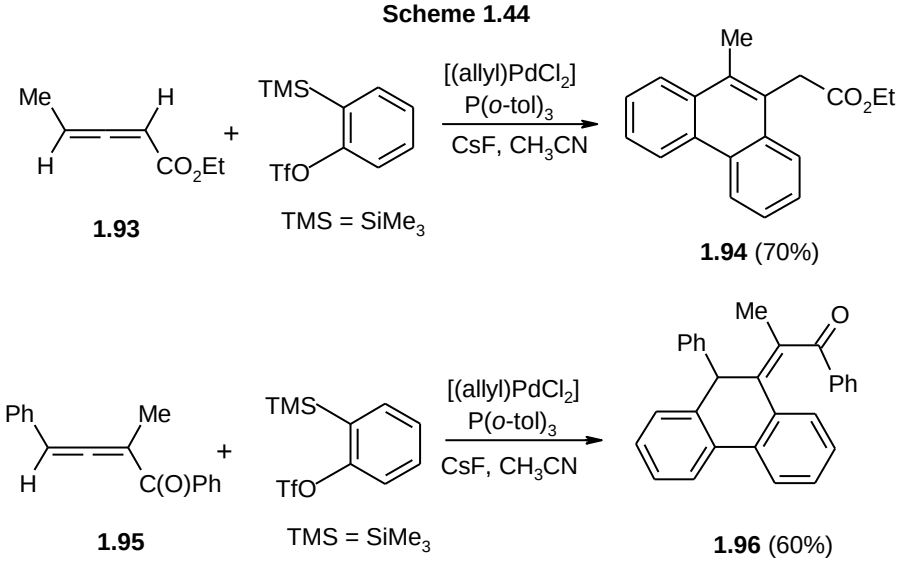
The same group reported the Ni-catalyzed chemoselective cyclotrimerization of benzyne with allene **1.91** leading to 10-methylene-9,10-dihyrophenanthrene **1.92** in moderate yield. This method is limited to terminal allenes only (Scheme 1.43).[38]

Scheme 1.43



Recently, another group reported the synthesis of phenanthrenes **1.94** and **1.96** by the cyclotrimerization of benzyne with allene catalyzed by Pd-complex (Scheme 1.44) [although the original paper terms this as cyclotrimeriztion, the usage of the term is not exact].[39] This method allows for the use of a wide range of a various allenes, including internal and terminal allenes, in the reaction with arynes.

Scheme 1.44

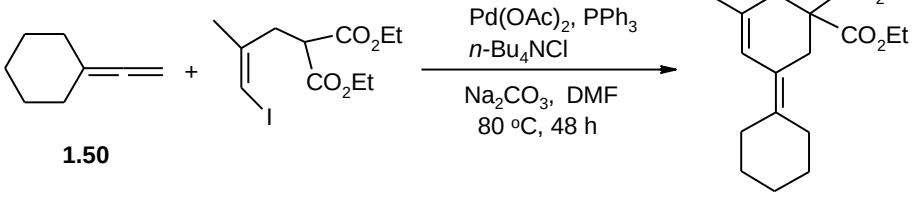


1.93 **1.94** (70%)

1.95 **1.96** (60%)

Another route to carboannulation leading to the formation of six-membered ring carbocycles **1.97** is shown in Scheme 1.45. However, an attempt to make five-membered ring carbocycles was unsuccessful.[27]

Scheme 1.45

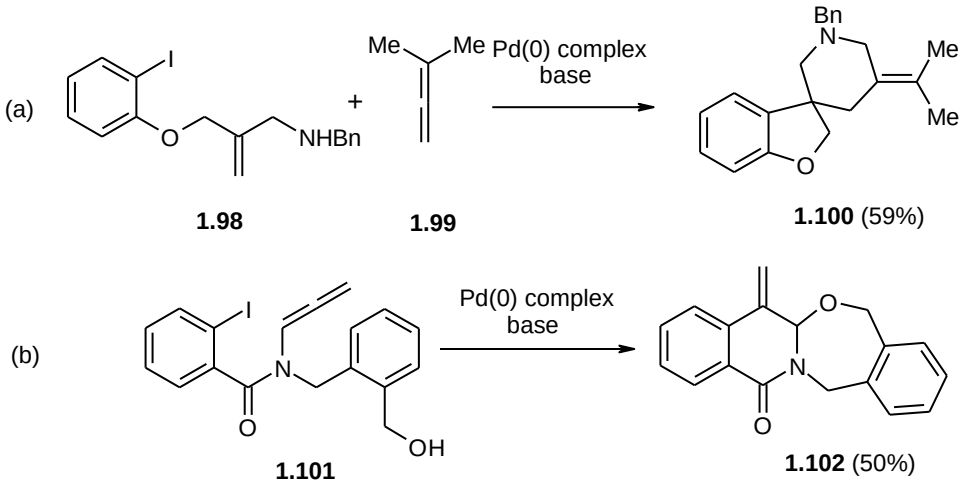


1.50 **1.97** (75%)

1.47 Synthesis of spirocycles

Grigg reported the novel Pd-catalyzed carbo- and hetero-annulation cascade process involving allene **1.99** and **1.101** that affords the unusual spiro- and hetero-cyclic frameworks **1.100** and **1.102** respectively in moderate yields (Scheme 1.46).[40]

Scheme 1.46

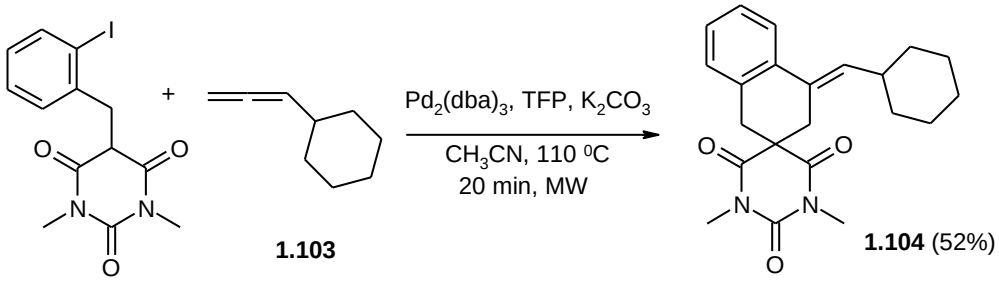


1.98 **1.99** **1.100** (59%)

1.101 **1.102** (50%)

Microwave assisted indirect alkylation of barbituric acid with alcohols followed by spirocyclization by sequential one-pot Ir(III)/ Pd(0)-catalyzed process leads to the formation of six-membered spirocyclic barbiturate **1.104** involving the formation of three C-C bonds (Scheme 1.47).[41]

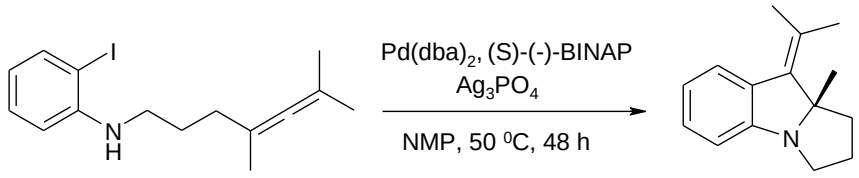
Scheme 1.47



1.103 **1.104** (52%)

Chiral cyclic indole compound **1.106** has been synthesized by asymmetric carbopalladation and subsequent amination of **1.105** using a Pd-catalyst with chiral phosphine ligand (Scheme 1.48).[42]

Scheme 1.48



1.105 **1.106**

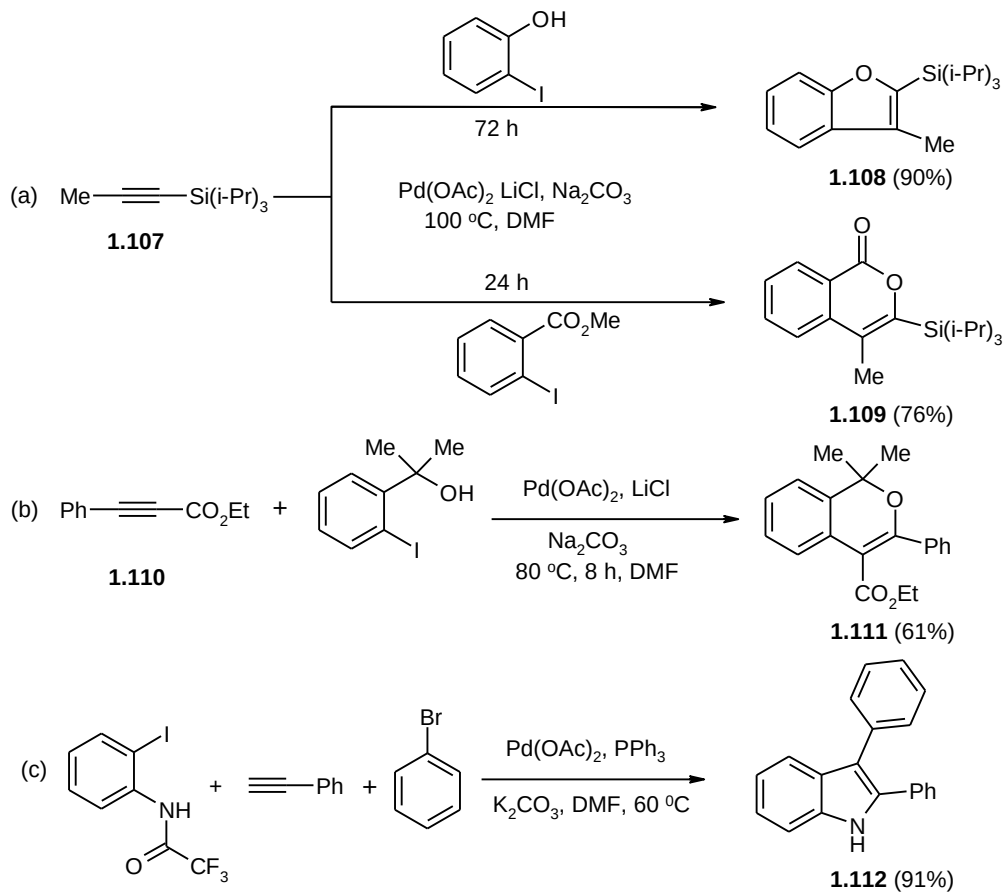
NMP = *N*-methylpyrrolidinone

1.5 Synthesis of benzofuran, isocoumarin and benzopyran derivatives *via* Pd-catalyzed coupling of alkynes

Mechanistically, Pd-catalyzed annulation reactions of alkynes (acetylenes) and allenes are not much different.[43] In this context, it is important to note that some allenylphosphonates undergo isomerization in the presence of base to form alkynylphosphonates and hence the Pd-catalyzed reactions could have common intermediates.[4] Hence a brief discussion on the reaction using alkynes is presented here.

The reaction of acetylene **1.107** with 2-iodophenol or 2-iodo-methylbenzoate in the presence of $Pd(OAc)_2$/ LiCl/ Na_2CO_3 in DMF at 100 ^oC affords benzofuran **1.108** or isocoumarin **1.109**, respectively (Scheme 1.49a). In a similar manner, the benzopyran **1.111** was synthesized by the treatment of alkyne **1.110** with 2-iodobenzyl alcohol (Scheme 1.49b). [43] Indole **1.112** can also be prepared via consecutive Sonogashira and Cachi reaction of phenylacetylene, 2-iodoaniline derivative and aryl bromide (Scheme 1.49c).[43d]

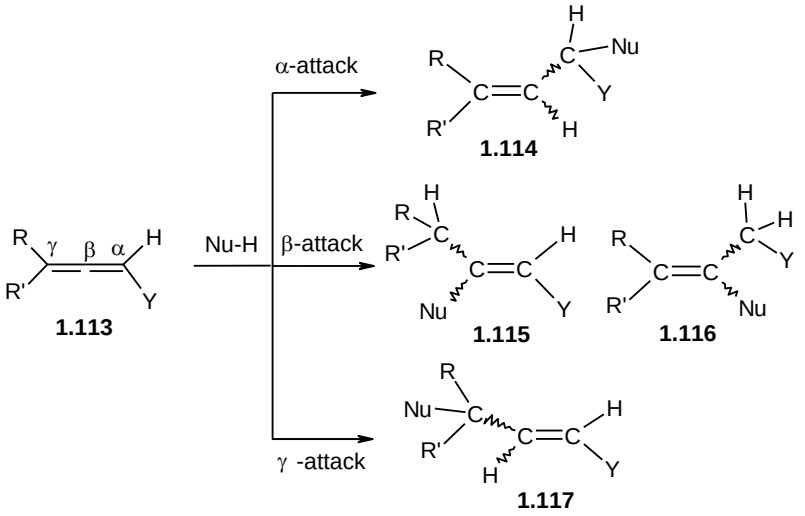
Scheme 1.49



1.6 Nucleophilic addition reactions of allenylphosphonates and other allenes

Unsubstituted allenes do not have tendency towards nucleophilic addition reactions. But, this tendency can be improved by substituting one of the substituents on the allene by electron withdrawing group (e.g. phosphonyl or ester) [44] or by using a transition metal catalyst. Since allene is having two cumulative double bonds, the incoming nucleophile can attack on any one of the three carbon atoms. Simple nucleophilic addition reactions of allenes with the amines, alcohols, phenols, thiols or azides lead to vinyl and allylphosphonates (**1.114**–**1.117**) where the attack generally takes place at the *β*-carbon with only very limited exceptions (Scheme 1.50).

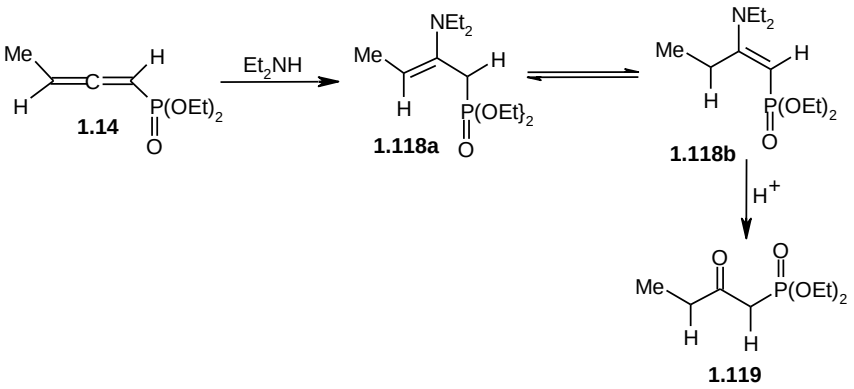
Scheme 1.50



1.61 Addition of amines

The nucleophilic addition reaction of allenylphosphonate **1.14** with diethylamine produces enamines **1.118a** and **1.118b** that are found to be in equilibrium with each other; these enamines are rather unstable to moisture and lead to the *β*-ketophosphonate **1.119** upon subsequent mild acid hydrolysis (Scheme 1.51).[44]

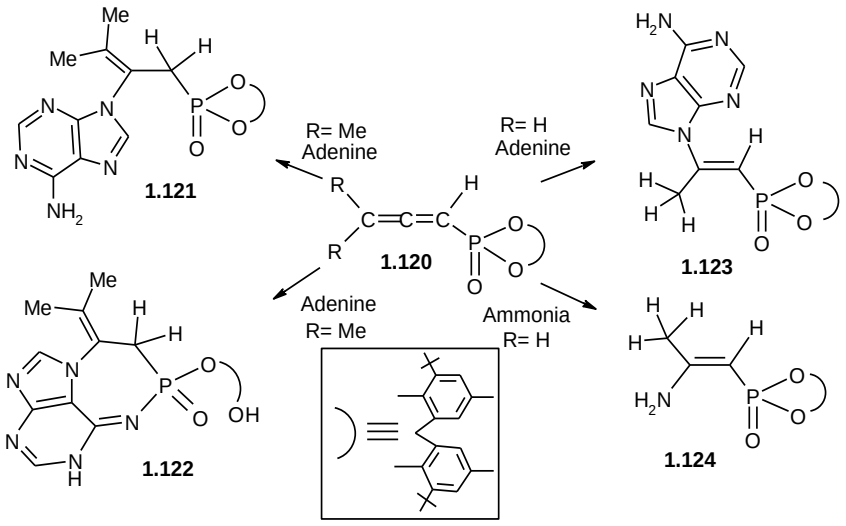
Scheme 1.51



Our research group reported the nucleophilic addition reactions of allene **1.120** with nucleobases and gaseous ammonia.[45] The nucleobases gave both (*E*)-vinyl and allyl products **1.121**-**1.123** whereas in the case of ammonia, the (*Z*)-vinylphosphonate **1.124** is preferentially formed (Scheme 1.52). It is interesting to note that in case of nucleobases both the N(9) (**1.121**) and N(7) (**1.122**) addition products are isolated and

in **1.122** a novel cyclization has occurred after the cleavage of the 1,3,2-dioxaphosphocin ring.

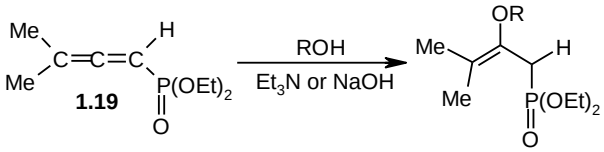
Scheme 1.52



1.62 Addition of alcohols

Nucleophilic addition of alcohols to allenylphosphonate **1.19** in the presence of NaOH or triethylamine leads to enol ethers **1.125a-b** (Scheme 1.53)[46] where the nucleophile attacks at the β-carbon atom.

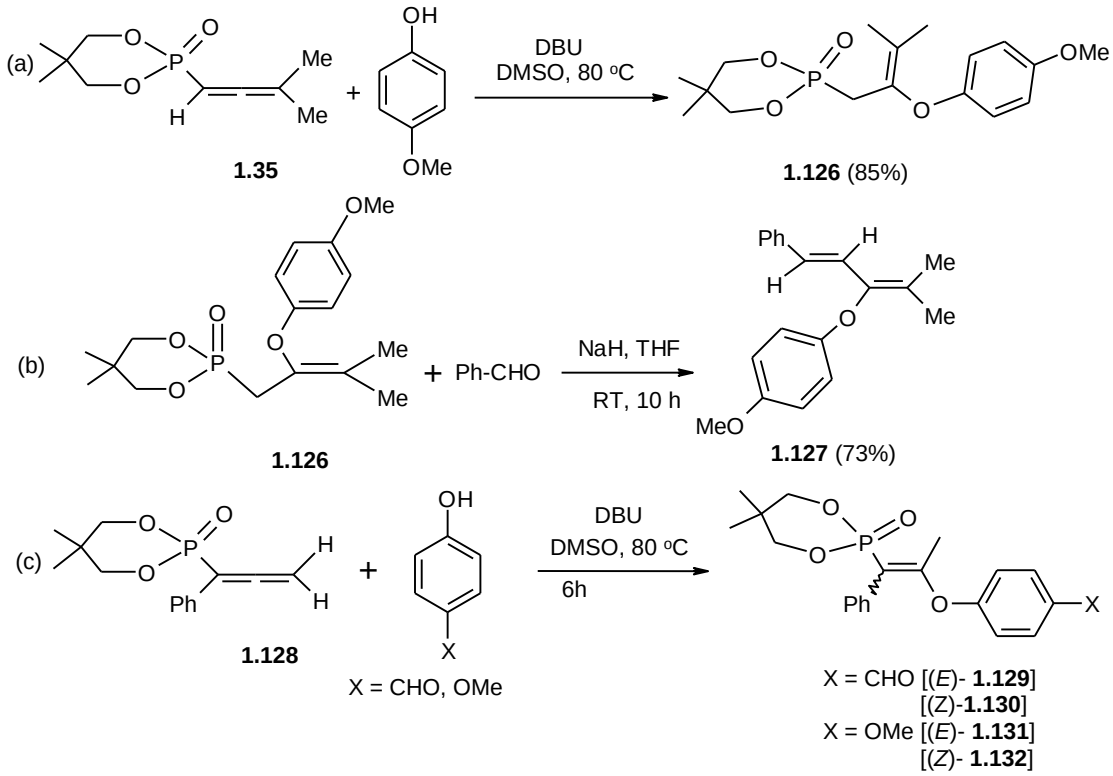
Scheme 1.53



R = CH_3 (**1.125a**), C_2H_5 (**1.125b**)

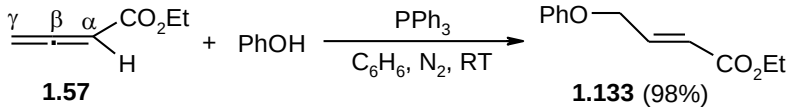
Recently, our research group reported that the activated phenols undergo nucleophilic addition reaction with allenylphosphonate **1.35** to afford the multisubstituted allylphosphonate **1.126** which can be utilized in HWE reaction with aldehydes leading to butadiene **1.127**. However, allenylphosphonate **1.128** led to vinyl phosphonates **1.129-1.132** (Scheme 1.54).[47]

Scheme 1.54



In contrast to above, it may be noted that nucleophilic addition of phenol occurs at the γ-carbon of allenyl ester **1.57** (umpolung addition) under phosphine catalyzed reactions and produces alkene **1.133** in 98 % yield (Scheme 1.55).[48]

Scheme 1.55



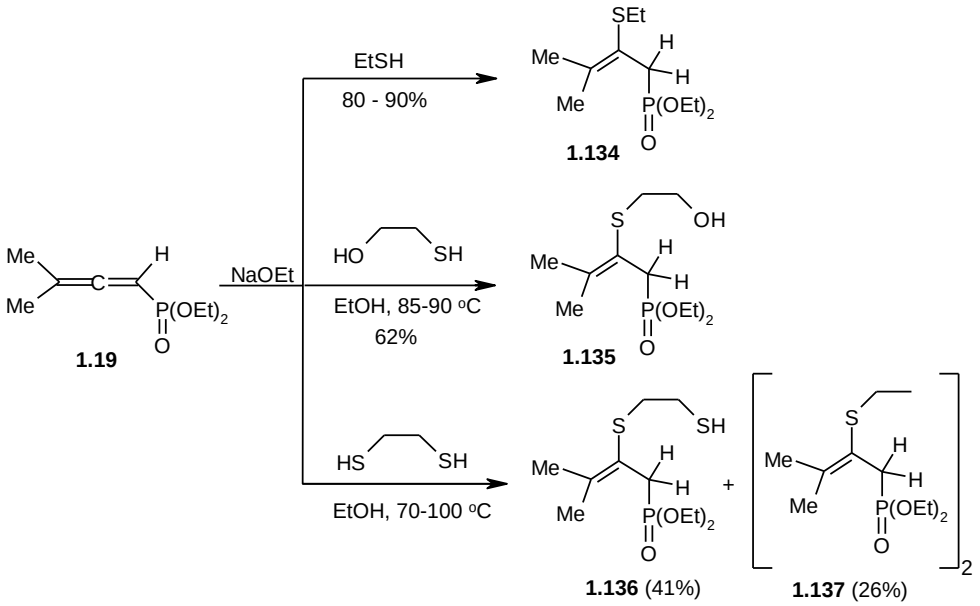
1.57 **1.133** (98%)

1.63 Addition of thiols

Addition of thiols to allenes is a well-known protocol for the preparation of vinylic and allylic sulphides; these reactions were conducted using UV-radiation or palladium catalysis.[49] Reaction of 2-mercaptoethanol with phosphorylated allene **1.19** was performed in the presence of a base (e.g. NaOEt) lead to the addition product **1.134**.[50] The nucleophilic addition of the sulphydryl group to the *β*-carbon atom of the

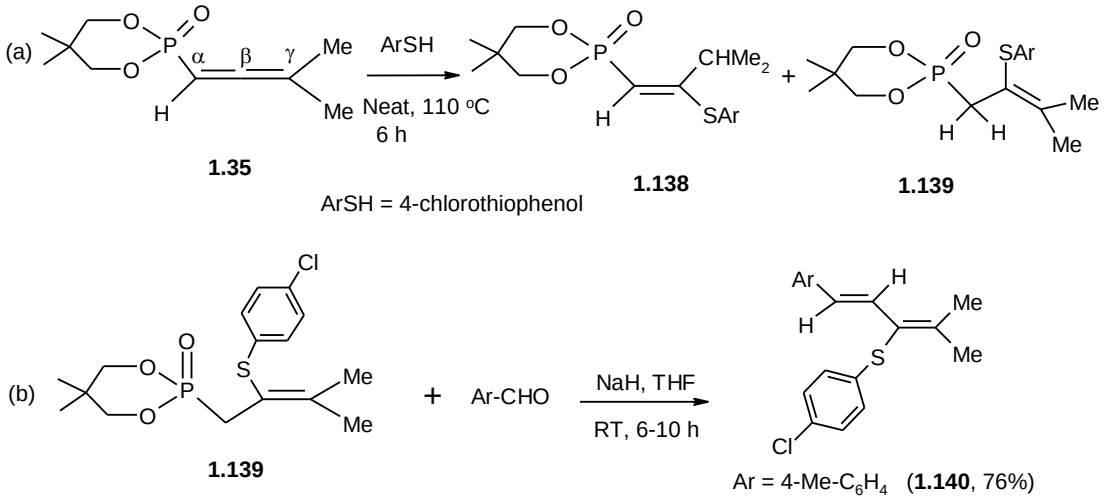
substrate has taken place in the reaction of 2-mercaptoethanol with allene **1.19** to give **1.135** in the presence of EtONa/ EtOH. Phosphonate **1.19** reacts with ethane-1,2-dithiol in presence of NaOEt to give 1:1 and 2:1 adducts (**1.136** and **1.137**) in 41 % and 26 % yields respectively (Scheme 1.56).[50b, 50c] This method requires a base for the addition of thiols.

Scheme 1.56



In a recent paper, our research group has reported the nucleophilic addition reaction of various thiophenols with allenylphosphonate **1.35** under *neat conditions* to give vinyl- or allyl-phosphonates (**1.138-1.139**) in good yields (Scheme 1.57a); interestingly, these reactions did not require the addition of a base.[51] The allylphosphonate **1.139** thus obtained is utilized in HWE reaction to give thionyl diene **1.140** (Scheme 1.57b).

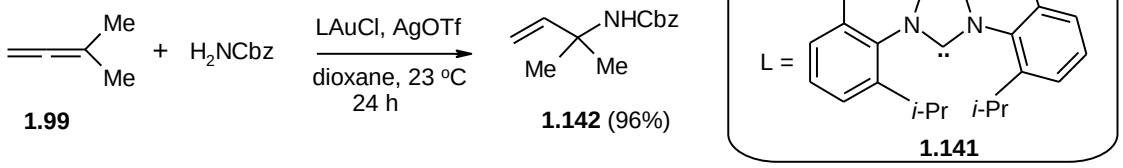
Scheme 1.57



1.64 Hydroamination reactions of unactivated allenes

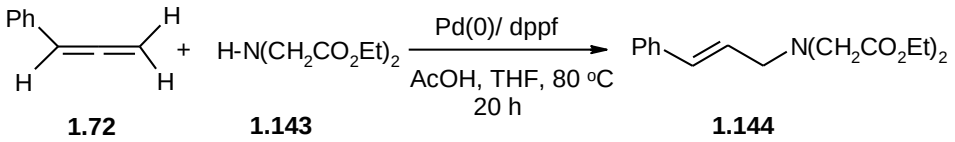
Unlike activated allenes, unactivated allenes do not participate in nucleophilic addition reactions with amines, but this can be achieved by transition metal catalyst which leads to allylic amines. Allylic amines are components of many naturally occurring, biologically active molecules and are versatile building blocks for the synthesis of complex nitrogen-containing molecules. Very recently, Widenhoefer and co-workers developed, gold(I)-catalyzed protocol for the intermolecular hydroamination of allenes.[52] Thus, treatment of allene **1.99** with benzyl carbamate (H_2Ncbz) catalyzed by a 1:1 mixture of LAuCl (L = *N*-heterocyclic carbene **1.141**) and AgOTf gave single regio- and diastereo-isomer of **1.142** in good yield (Scheme 1.58).

Scheme 1.58



The $Pd_2(dba)_3.CHCl_3$/ dppf [1,1'-bis(diphenylphosphino)ferrocene] catalytic system has been used for the hydroamination reaction of allene **1.72** with amine **1.143** in the presence of AcOH/ THF at 80 ^oC/ 20 h to afford **1.144** (Scheme 1.59).[53]

Scheme 1.59

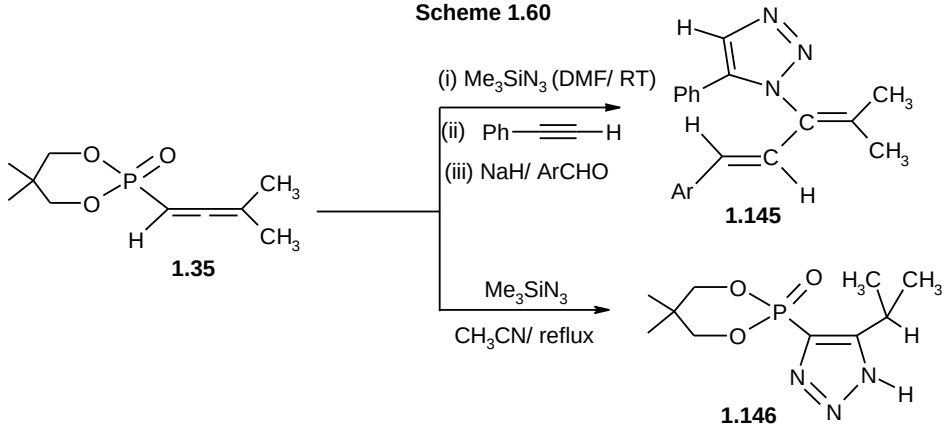


1.72 **1.143** **1.144**

1.65 Addition of azides

Very recently, our research group has reported the reaction of allene **1.35** with trimethylsilyl azide affording the non-cyclized azide product at room temperature, which underwent 1,3-dipolar cycloaddition with activated acetylenes to give 1,2,3-triazoles and subsequent HWE reaction to give diverse *N*-substituted-1,2,3-triazoles **1.145** (Scheme 1.60).[4m] The same allenylphosphonate **1.35** reacted with trimethylsilyl azide in CH_3CN under reflux conditions to give the triazole **1.146** in moderate yields. A similar reaction using ester allenes was also reported before.[54]

Scheme 1.60

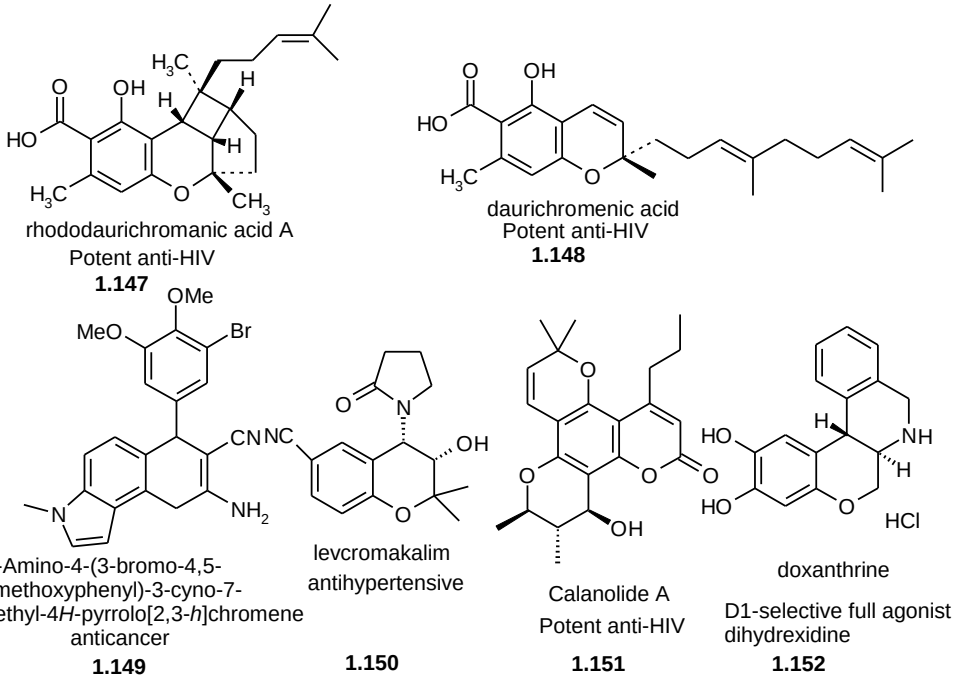


1.35 **1.145** **1.146**

1.7 Reaction of allenes with salicylaldehyde derivatives

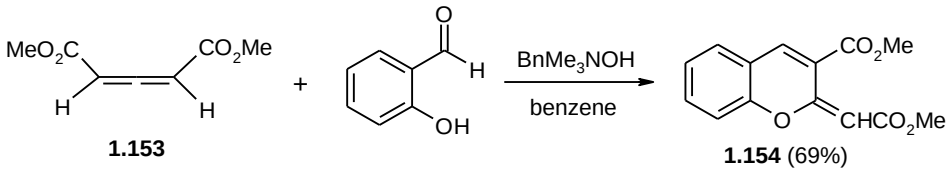
The tandem reaction of salicylaldehydes with α,β-unsaturated compounds leading to a variety of heterocycles such as chromans, chromenes, coumarins and tetrahydroxanthanes has attracted great attention. These heterocycles are widespread in natural products. Chromenes constitute an important class of oxygenated heterocyclic compounds. They are also widespread in natural products and have attracted much attention in diverse areas including physical chemistry (photochromism) and medicinal chemistry (anti HIV, anticancer, antioxidant, and inhibitory effect on histamine release, antihypertensive and antiviral activity) and hence a number of research groups have developed different methodologies to synthesize these compounds. Some representative examples of chromenes (1.147-1.152) are shown in Chart 1.[55] In this section, we discuss synthesis of thiochromans, functionalized chromenes, mainly from allenes and substituted 2-mercaptobenzaldehydes.

Chart 1



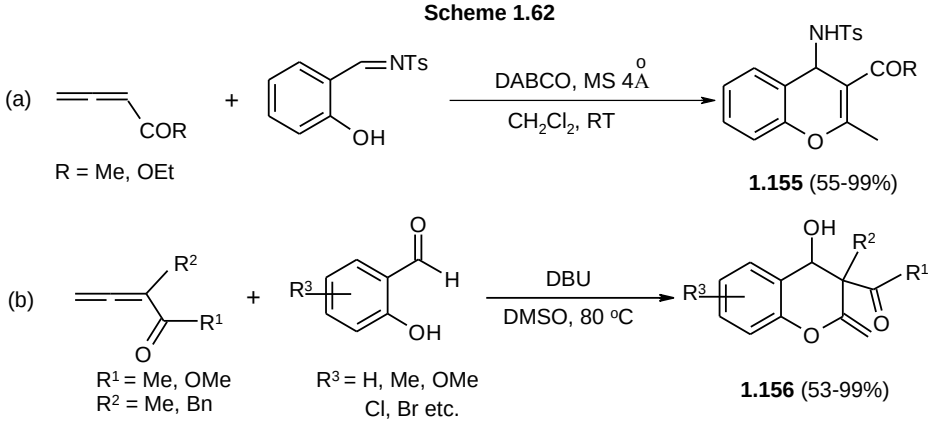
Several decades ago, Scheinmann *et al* reported the reaction of dimethyl penta-2,3-dienedinoate **1.153** with salicylaldehyde in the presence of (benzyl)trimethylammonium hydroxide to give the corresponding chromene **1.154** in good yields (Scheme 1.61).[56]

Scheme 1.61



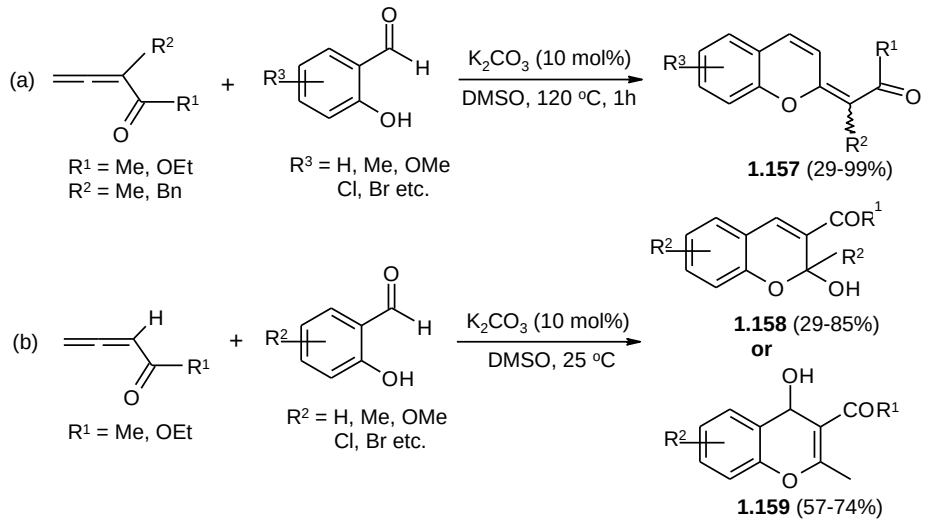
In the year 2005, Shi and co-workers explored the reactions of salicylaldehydes with different allenes in the presence of various catalysts (phosphines, amines and inorganic bases) and obtained different types of chromenes. Among these, tertiary amines [DABCO or DBU (1,8-diazabicyclo[5.4.0]undec-7-ene)] or inorganic bases (K_2CO_3 or Na_2CO_3) gave better results than phosphines. First, they treated salicyl-*N*-tosylimines with ethyl 2,3-butadienoate or penta-3,4-diene-2-one using DABCO as the catalyst to obtain the corresponding chromenes (**1.155**) in good to excellent yields (Scheme 1.62a).[57a] They examined phosphine catalysts like PPh_3 or PPh_2Me also, but in these cases they obtained dihydropyrrole derivatives *via* [3+2] cycloaddition. Later, they performed the reactions of salicylaldehydes with 3-methyl or 3-benzyl substituted penta-3,4-dien-2-one as well as ethyl 2-methylbuta-2,3-dienoate, catalyzed by DBU. Functionalized 2*H*-1-chromans **1.156** were thus obtained diastereoselectively in good yields in some cases (Scheme 1.62b). They screened several bases/ solvents, among which DBU-DMSO combination was shown to be the best.[57b]

Scheme 1.62

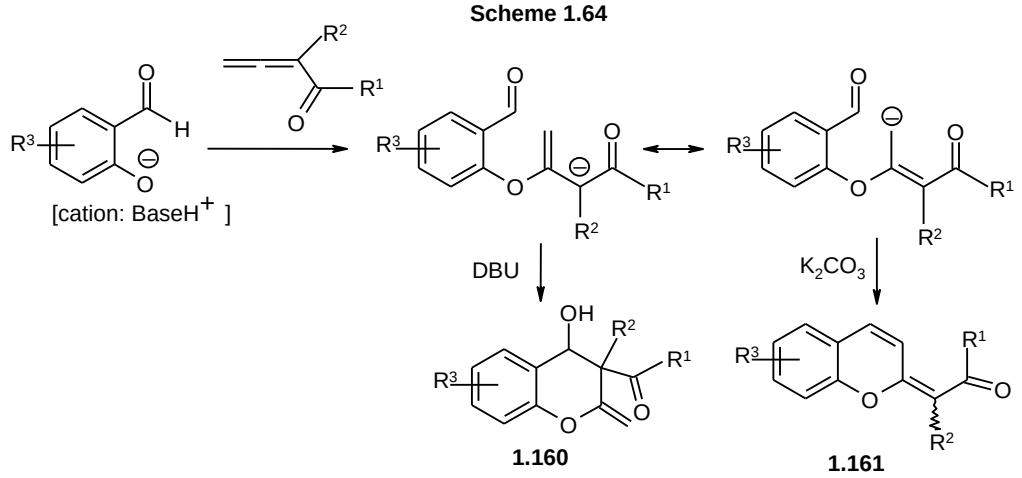


In continuation of this work on the synthesis of functionalized chromenes, Shi and co-workers carried out these reactions in the presence of K_2CO_3 at high temperature (120 ^oC) and obtained different chromenes (**1.157**) (Scheme 1.63a).[57c] In a similar manner, they have carried out the reactions between unsubstituted allenes and salicylaldehydes at 25 ^oC in the presence of K_2CO_3 in DMSO or EtOH. These reactions afforded the corresponding chromenes (**1.158** and **1.159**).[57d] Chroman **1.159** was converted to chromene **1.158** under acidic or neat conditions (Scheme 1.63b). This is also a good example to show that the substituents on the allene and the base/ nucleophile direct the reaction towards different products. A possible mechanism for the formation of these chromenes is depicted in Scheme 1.64.[57e]

Scheme 1.63

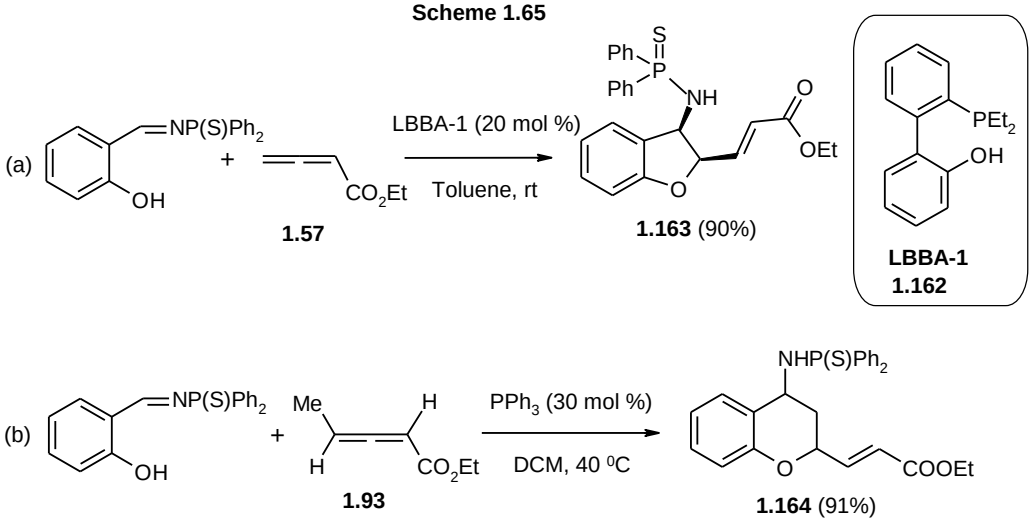


Scheme 1.64



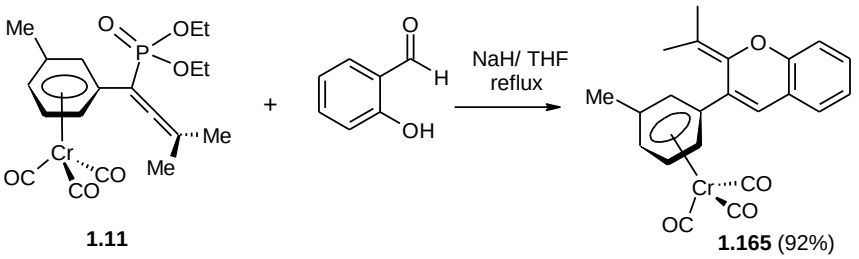
Huang and co-workers reported the novel bifunctional phosphine **1.162** catalyzed aza-MBH/ umpolung addition-domino reaction for the synthesis of *cis*-2,3-dihydrobenzofuran **1.163** with high stereoselectivity from salicyl *N*-thiophosphinyl imines and allenic esters **1.57** (Scheme 1.65a).[58] The same group reported the synthesis of functionalized chroman derivative **1.164** in good yields (Scheme 1.65b) by using simple PPh_3 catalyzed novel domino reaction of allene **1.93** with functionalized salicyl *N*-thiophosphinyl imines in which γ-CH_3 is involved in cyclization. This is the first example in which γ-CH_3 of allene undergoes cyclization [59]

Scheme 1.65



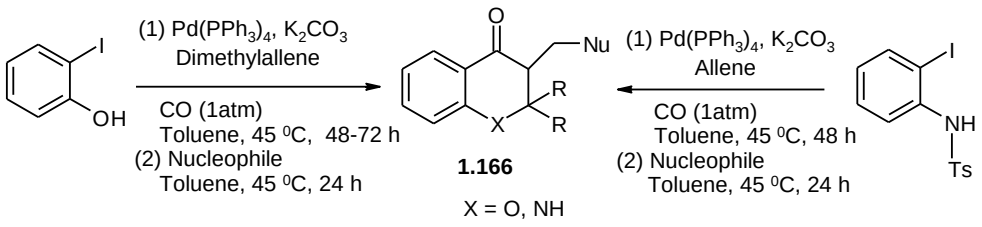
The allenylphosphonate complex **1.11** reacts smoothly with a number of 1,2- and 1,3-difunctional carbonyl compounds like salicylaldehyde in the presence of sodium hydride to give arene-$Cr(CO)_3$ substituted heterocycle **1.165** in good yields as a crystalline solid (Scheme 1.66).[10]

Scheme 1.66



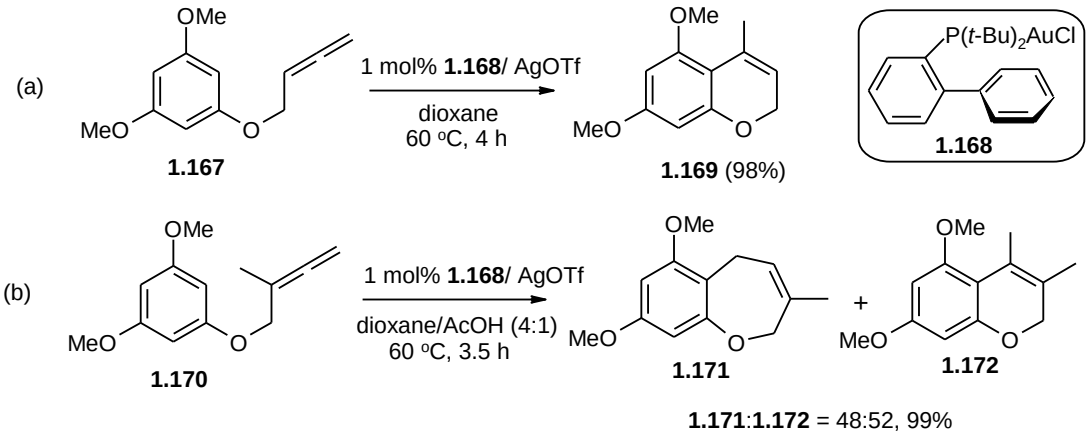
In addition to the base catalyzed synthesis of chromenes from allenes and salicylaldehydes as discussed above, there are other methods available in the literature that uses allenes for the synthesis of chromenes. Two examples are presented here. The first one involves Pd-catalyzed cascade carbonylation-allene insertion reaction of an allene, 2-iodophenol or 2-iodoaniline and CO leading to chromanones **1.166** (Scheme 1.67).[60]

Scheme 1.67



The second route developed by Watanabe et al. is an efficient method for the synthesis of chromenes from allenic compounds by means of gold-catalyzed intramolecular hydroarylation.[65] Thus allenic compound **1.167** is converted to chromene **1.169** in excellent yield using the catalytic system **1.168**/ AgOTf (Scheme 1.68a). When they used substituted allene **1.170** under similar conditions, the seven-membered ring compound **1.171** along with chromene **1.172** was obtained, albeit in low yields (Scheme 1.68b). However, when the solvent system was changed from dioxane to dioxane-acetic acid (4:1) mixture, excellent yields of **1.171** and **1.172** (overall 99%) were obtained.

Scheme 1.68



There are some reports on the base catalyzed synthesis of thiochromans[61-62] or pyrroloindoles[63-64] from thiosalicylaldehydes or 2-formylindoles. But these methods do not use an allene. Base catalyzed synthesis of thiochromans or pyrroloindoles from allenes and thiosalicylaldehydes or thiosalicylaldehydes are not yet investigated.

OBJECTIVES OF THE PRESENT WORK

The objectives of this part of the work were the following:

(i) To investigate Pd-catalyzed annulation reactions of allenylphosphonates with functionalized 2-iodophenols, 2-iodobenzyl alcohol, 2-iodoanilines and 2-iodo-*t*-butylbenzaldimine in an effort to synthesize phosphono-benzofurans/ phosphono-benzopyrans, phosphono-indoles and phosphono-isoquinolines- to explore the use of environmentally friendly protocol for the synthesis of benzofurans,

(ii) To study the utility of aldehyde-functionalized benzofurans obtained as above in Horner-Wadsworth-Emmons (HWE) or Wittig reaction,

(iii) To investigate base-catalyzed reactions of allenylphosphonates with 2-mercaptobenzaldehydes and *azo*-substituted salicylaldehydes, and

(iv) To study base-catalyzed reactions of allenylphosphonates/ allenylsulfones/ ester allene with 3-chloro-2-formylindole that lead to pyrroloindoles under a green protocol (PEG-400 medium).

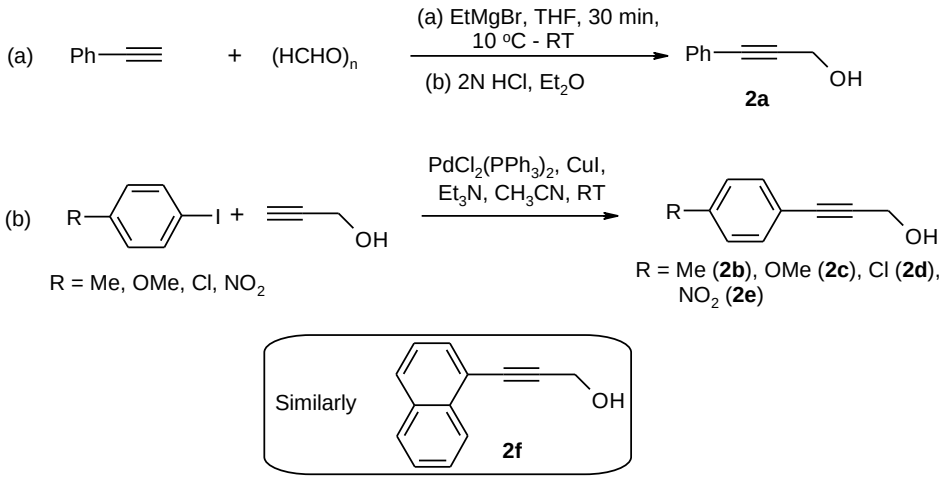
RESULTS AND DISCUSSION

2.1 Synthesis of allenylphosphonates 3a-k

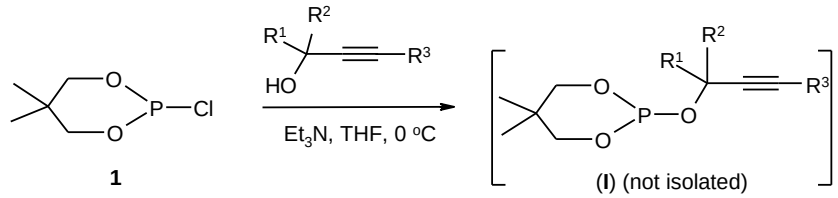
Synthesis of allenylphosphonates is more straightforward when compared to that of allenyl esters and keto-allenes.[66] However, only a few references dealing with allenylphosphonates are available in the literature. In this section, we shall discuss the synthesis and stability of different types of phosphorus-based allenes.

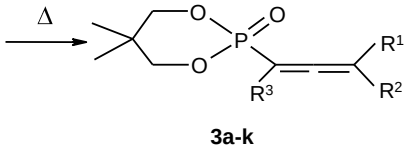
The propargyl alcohol precursors $(HO)C(R^1)(R^2)$-$C{\equiv}CR^3$ [$R^1 = R^2 = R^3 = H$; R^1 = Me, $R^2 = R^3 = H$; $R^1 = R^2$ = Me, $R^3 = H$; R^1 = Me, R^2 = Et, $R^3 = H$; $R^1 = R^2 = H$, R^3 = Me] for the allenes **3a-d** and **3k** are commercially available; the remaining propargyl alcohols (**2a-f**) were prepared by using literature procedures (Scheme 1a-b).[68-69] Subsequent reaction of $(OCH_2CMe_2CH_2O)PCl$ (**1**)[67] with the appropriate propargyl alcohol in the presence of a base (NEt_3) led to the allenylphosphonates (**3a-k**) after rearrangement of the initially formed P^{III} intermediate **(I)** (Scheme 2).[6] Compounds **3a-g** have been prepared earlier in our laboratory[70] but compounds **3h-j** are new.

Scheme 1



Scheme 2





3a-k

$R^1 = R^2 = R^3 = H$	[**3a**, δ(P): 8.7]
$R^1 = R^3 = H$, $R^2 = Me$	[**3b,** δ(P): 8.9]
$R^1 = R^2 = Me$, $R^3 = H$	[**3c**, δ(P): 8.8]
$R^1 = Me$, $R^2 = Et$, $R^3 = H$	[**3d**, δ(P): 9.3]
$R^1 = R^2 = H$, $R^3 = Ph$	[**3e**, δ(P): 6.6]
$R^1 = R^2 = H$, $R^3 = 4\text{-Me-}C_6H_4$	[**3f**, δ(P): 7.8]
$R^1 = R^2 = H$, $R^3 = 4\text{-MeO-}C_6H_4$	[**3g**, δ(P): 7.5]
$R^1 = R^2 = H$, $R^3 = 4\text{-Cl-}C_6H_4$	[**3h**, δ(P): 6.8, 75%]
$R^1 = R^2 = H$, $R^3 = 4\text{-}NO_2\text{-}C_6H_4$	[**3i**, δ(P): 6.7, 75%]
$R^1 = R^2 = H$, $R^3 = 1$-naphthyl	[**3j**, δ(P): 8.3, 80%]
$R^1 = R^2 = H$, $R^3 = Me$	[3**k**, δ(P): 11.2]

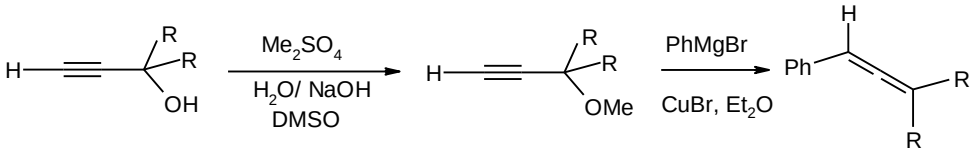
All the allenylphosphonates are crystalline solids and stable under nitrogen. We could preserve them under these conditions for several months. They show a characteristic strong band in the range 1927-1962 cm^{-1} due to υ(C=C=C) stretch in the IR.[71] The ^{31}P NMR spectra show a single peak in the range δ 6.6-7.8 for the new α-aryl allenylphosphonates (**3h-j**). The ^{13}C NMR spectra are also quite useful for the identification of these compounds. The P*C* signal in the ^{13}C NMR spectra appears as a doublet at δ ~94.0 for **3h-j** with ^1J(P-C) ~ 180 Hz. The PC=*C* signal for these compounds also appears as a doublet in the region δ 211-212 [^2J(P-C) = 4.0-6.0 Hz].

2.2 Synthesis of other allenes

2.21 Phenyl-substituted allenes (Ph)CH=C=CR_2 [R = H (4a), R = Me (4b)]

Phenyl-substituted allenes **4a-b** are prepared by treatment of methyl propargylic ether (obtained by the methylation reaction of propargyl alcohol) with PhMgBr in the presence of CuBr as a catalyst (Scheme 3).[72] They had to be distilled prior to use (bp range: 80-85 ^oC/ 20 mm of Hg) and stored under inert atmosphere at low temperature in a dark place as light and oxygen may induce polymerization.[72]

Scheme 3

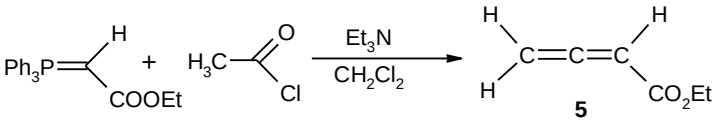


R = H (**4a**)
R = Me (**4b**)

2.22 1,2-Alkadienoate ester (allenyl ester) 5

The main approach to prepare allene **5** is the treatment of α-phosphoranylidene esters (obtained by the reaction of PPh_3 with α-bromoethyl acetate) with acid chlorides in the presence of a base (Scheme 4).[73] This compound has to be distilled prior to use (bp: 70 ^oC/ 15 mm of Hg).

Scheme 4

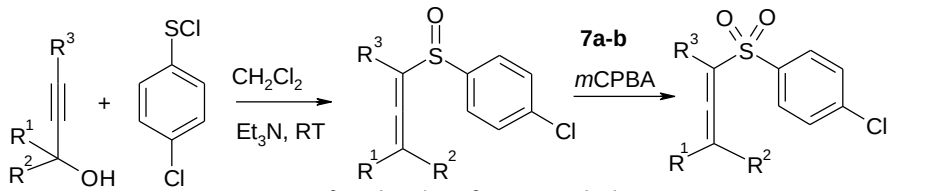


5

2.23 Allenylsulfoxides 7a-f and Allenylsulfones 8a-b

The reaction of 4-chlorophenylsulfenylchloride **6** with the appropriate propargyl alcohol in the presence of a base (Et_3N) led to the allenylsulfoxides (**7a-f**); compounds **7a-b** are oxidized by *m*-chloroperbenzoic acid (*m*CPBA) to give allenylsulfones **8a-b** (Scheme 5).[14] Compounds **7a-b**, **7d-f** and **8a-b** are new.

Scheme 5



6

R^3 = Ph, R^1 = R^2 = H (**7a**)
R^3 = Me, R^1 = R^2 = H (**7b**)
R^3 = R^1 = R^2 = H (**7c**)
R^3 = H, R^1 = R^2 = Me (**7d**)
R^3 = H, R^1 = Me, R^2 = Et (**7e**)
R^3 = H, R^1 = Me, R^2 = Ph (**7f**)

R^3 = Ph, R^1 = R^2 = H (**8a**)
R^3 = Me, R^1 = R^2 = H (**8b**)

All the allenylsulfoxides **7a-f** and allenylsulfones **8a-b** are crystalline solids and are stable under nitrogen for several months at low temperature. They show a characteristic strong band in the range 1900-1970 cm^{-1} due to υ(C=C=C) stretch. In the ^1H NMR spectrum, $=CH_2$ protons appears in the region δ 5.0-6.0 as two singlets.

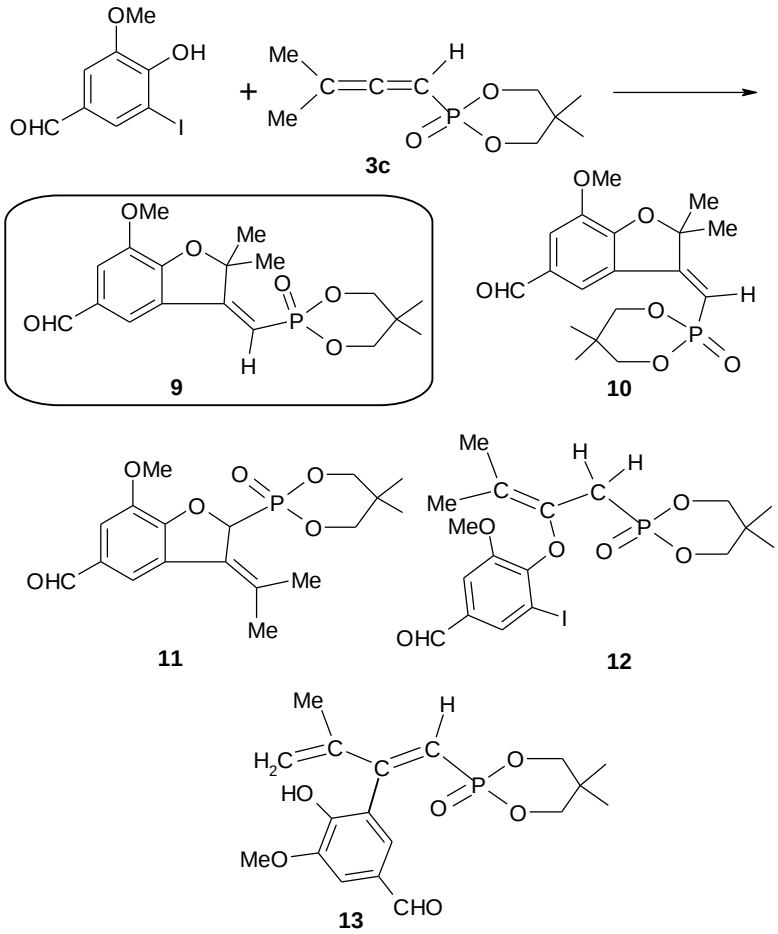
In the ^{13}C NMR spectrum, C=*C*=C signal for these compounds appears at δ 200-210. A notable feature in the ^{13}C NMR spectra is that all the signals in **8b** are downfield to the corresponding signals in **7b** perhaps due to the increased electron withdrawing nature of the sulfone group relative to the sulfoxide.

2.3 Pd-catalyzed annulation reactions of allenes with functionalized 2-iodophenols under environmentally benign condition

2.31 Reaction of allenylphosphonates (OCH$_2$CMe$_2$CH$_2$O)P(O)CH=C=CR(Me) [R= Me (3c), Et (3d)] with functionalized 2-iodophenols 15-17

The reaction of allenylphosphonates with a functionalized 2-iodophenol (5-iodovanillin) leads to a mixture of products under the conditions previously reported from our laboratory [cf. Scheme 6, Table 1 (entry 4) and Figure 1(a)].[21a-b] Hence we wanted to see if the yield of any specific benzofuran may be maximized or not, using allene **3c** and 5-iodovanillin. The ^{31}P NMR spectra of the reaction mixtures for entries 4 and 24 in Table 1 are shown in Figure 1; the former showing more number of products, and identification of all these was difficult. The main product corresponding to the latter (entry 24) shown in Figure 1(b) is phosphono-benzofuran **9**. The assignment of *Z*-stereochemistry for **9** is based on the reaction of **3c** with 3-iodo-4-hydroxybenzaldehyde described below. As regards compound **10**, our research group has characterized a similar compound by X-ray crystallography previously in the reaction of **3c** with iodophenol in methyl cyanide medium.[21a-b] Our group also has recently isolated the phenol addition product **14** [δ(^{31}P): 20.2, structure is given below Table 1] in high yields from the reaction of **3c** with 4-methoxy phenol; the structure of **14** is analogous to **12**.[47] Hence the peaks in the vicinity of δ(^{31}P) 20 in Figure 1(a) may be ascribed to the product **12**. With 2-iodophenols, we have not been able to identify a non-cyclized product of type **13** so far.

Scheme 6



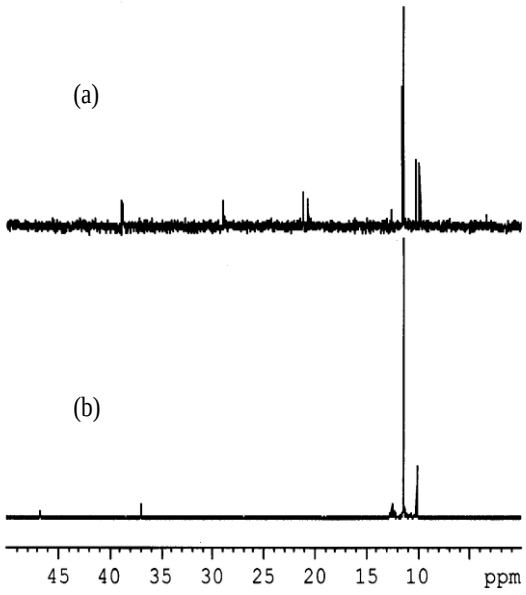


Figure 1. ^{31}P NMR spectra for the reaction mixture of **3c** with 5-iodovanillin in (a) dry DMF at 80 ^{o}C/ 24 h, (b) PEG- 400 at 90 ^{o}C/ 12 h

Table 1. Effect of reaction conditions on the yield of **9** in the reaction of **3c** with 5-iodovanillin[a]

Entry	Palladium catalyst/ phosphine	Base/ solvent	Time(h)/ Temp (^{o}C).	Yield (%)[b]
1	$Pd(OAc)_2$ / PPh_3	K_2CO_3, CH_3CN	24 / 90	No reaction
2	$Pd(OAc)_2$ / PPh_3	K_2CO_3, THF	12 / 80	No reaction
3	$Pd(OAc)_2$ / PPh_3	K_2CO_3, DMSO	24 / 80	7
4	$Pd(OAc)_2$ / PPh_3	K_2CO_3, DMF	24 / 80	59[c,d]
5	$Pd(OAc)_2$ / PPh_3	K_2CO_3, H_2O	48 / RT	No reaction
6	$Pd(OAc)_2$ / PPh_3	K_2CO_3, H_2O	4 / 80	61
7	$Pd(OAc)_2$ / PPh_3	K_2CO_3, DMF+H_2O (9:1)	12 / 80	43[c]
8	$Pd(OAc)_2$ / PPh_3	K_2CO_3, PEG-400+H_2O (9:1)	4 / 80	34
9	$Pd(OAc)_2$ / PPh_3	K_2CO_3, PEG-400+H_2O (9:1)	12 / 80	50
10	$Pd(OAc)_2$ / (*o*-tolyl)$_3$P	K_2CO_3, PEG-400+H_2O (9:1)	12 / 80	52
11	$Pd(OAc)_2$ / (*o*-tolyl)$_3$P	K_2CO_3, PEG-400+H_2O (9:1)	24 / 80	36
12	$Pd(OAc)_2$ / PPh_3	K_2CO_3, PEG-400+H_2O(1:1)	12 / 90	57
13	$Pd(OAc)_2$ / (*o*-tolyl)$_3$P	K_2CO_3, PEG-400+H_2O (1:1)	12 / 90	62
14	$Pd(OAc)_2$ / dppe	K_2CO_3, PEG-400+H_2O (1:1)	12 / 90	No reaction
15	$Pd(OAc)_2$ / TDMPP[e]	K_2CO_3, PEG-400+H_2O (1:1)	12 / 90	40
16	$Pd(OAc)_2$ / (*o*-tolyl)$_3$P	NaOAc, PEG-	12 / 90	54

		400+H_2O (1:1)		
17	$Pd(OAc)_2$ / (*o*-tolyl)$_3$P	K_3PO_4, PEG-400+H_2O (1:1)	12 / 90	55
18	$Pd_2(dba)_3$ / (*o*-tolyl)$_3$P	K_2CO_3, PEG-400+H_2O (1:1)	12 / 90	48
19	$Pd(PPh_3)_2Cl_2$ / (*o*-tolyl)$_3$P	K_2CO_3, PEG-400+H_2O (1:1)	12 / 90	41
20	$PdCl_2$/ (*o*-tolyl)$_3$P	K_2CO_3, PEG-400+H_2O (1:1)	12 / 90	55[c]
21	$Pd(OAc)_2$ / Ph_3P	*n*-Bu_4NBr, K_2CO_3, H_2O	4 / 90	58[c]
22	$Pd(OAc)_2$ / Ph_3P	K_2CO_3, [bmim][BF_4][e]	48 / 90	No reaction
23	$Pd(OAc)_2$	CsF, PEG-400	12 / 90	79
24	$Pd(OAc)_2$/ (*o*-tolyl)$_3$P	K_2CO_3, PEG-400	12 / 90	81

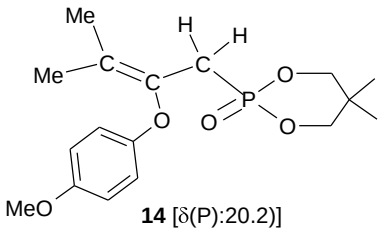
[a]Use of microwave conditions (160 ^oC, 10 min, 160W) with $Pd(OAc)_2$ / PPh_3 /K_2CO_3 / PEG-400 or H_2O led only to <45% of the product.

[b]Yields were calculated by using ^1H/ ^{31}P NMR spectroscopy

[c]Combined yield of (*E*/*Z*) forms

[d]In this case, a mixture of products are obtained, see Figure 1(a).

[e]TDMPP = tris(2,6-dimethoxyphenyl)phosphine, bmim = 1-methyl-3-butyl-imidazole



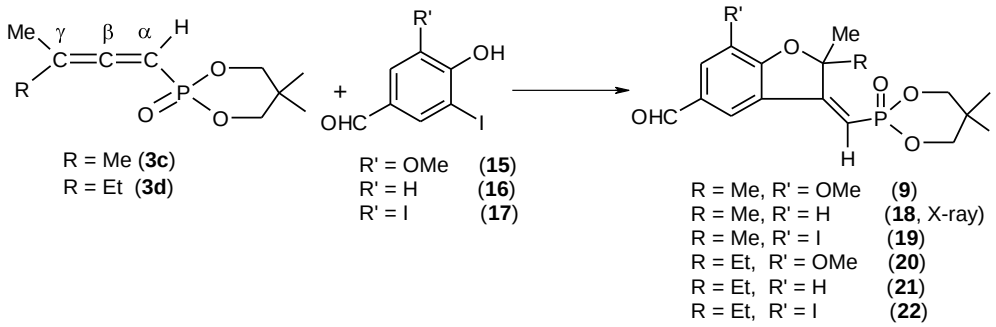
14 [δ(P):20.2)]

As can be seen from Table 1, the conditions previously used in reactions using iodophenol[21a-b] were *ineffective* (entry 1) *or led to a mixture* (entry 4 and Figure 1) wherein the yield of **9** was only moderate. Even under many other conditions, a mixture of isomers [entries 4, 7, 18, 19; δ(P) 11.6 (**9**), 11.4 (**10**), assignment of configu-

ration tentative] was obtained. However, we found that the use of $(o\text{-tol})_3P$ in place of Ph_3P improved the yield (entries 12-13), and the best combination was $Pd(OAc)_2/(o\text{-tolyl})_3P/K_2CO_3$/PEG-400 (entry 24) in which the phosphono-benzofuran formed stereo and regioselectively. In this reaction, we used PEG-400 as a solvent which is known to be an environmentally friendly medium.[21c]

Under the above optimized conditions, we were able to generate the functionalized phosphono-benzofurans **9** and **18**-**22** by the reaction of allenylphosphonates **3c-d** with functionalized 2-iodophenols **15**-**17** (Scheme 7). The highlighting feature of this work is that essentially one product is formed stereoselectively in the environmentally benign (green) solvent PEG-400. The yields and ^{31}P NMR chemical shifts are given in Table 2.

Scheme 7



Conditions: $Pd(OAc)_2$ / $(o\text{-tolyl})_3P$/ K_2CO_3/ PEG-400/ 90 ^oC/ 12 h

Table 2. Details on the yields of benzofurans **9** and **18-22** in PEG-400 medium

Entry	Allene	R' in iodophenol	Compound	Yield % (^{31}P NMR); isolated	^{31}P NMR (δ, ppm)
1	**3c**	OMe	**9**	(81); 70	11.8
2	**3c**	H	**18**	(76); 65	11.4
3	**3c**	I	**19**	(65); 59	10.6
4	**3d**	OMe	**20**	(64); 55	11.8
5	**3d**	H	**21**	(63); 57	11.5
6	**3d**	I	**22**	(63); 57	10.6

All the above phosphono-benzofurans **9** and **18-22** are characterized by IR, NMR [^1H, ^{13}C, ^{31}P] and LC-MS/CHN analyses. As expected, the band corresponding to OH stretching in the IR spectrum and the O*H* peak in the ^1H NMR spectrum

are missing in these compounds. In the ^{1}H NMR spectra, the PC*H* proton appears at δ ~6.04 (^{2}J(PH) = 10.0 Hz) and the C*H*O proton gives a signal around δ ~10.0. The ^{1}H NMR spectrum of compound **18** is shown in Figure 2 as an illustration. In the ^{13}C NMR spectrum, the carbon attached to phosphorus shows a doublet at δ 98.7 (^{1}J(PC) = 198.0 Hz). The large ^{1}J(PC) value is indicative of the presence of P-C=C moiety in these compounds.[22] In the ^{31}P NMR, all these phosphono benzofurans show a single peak in the region δ 10-12. Finally, the *Z*-configuration around the C=C double bond is proven by X-ray crystallography in the case of phosphono-benzofuran **18** (Figure 3). The C(6)-C(7) distance of 1.334(3) Å also clearly shows the vinylic group.

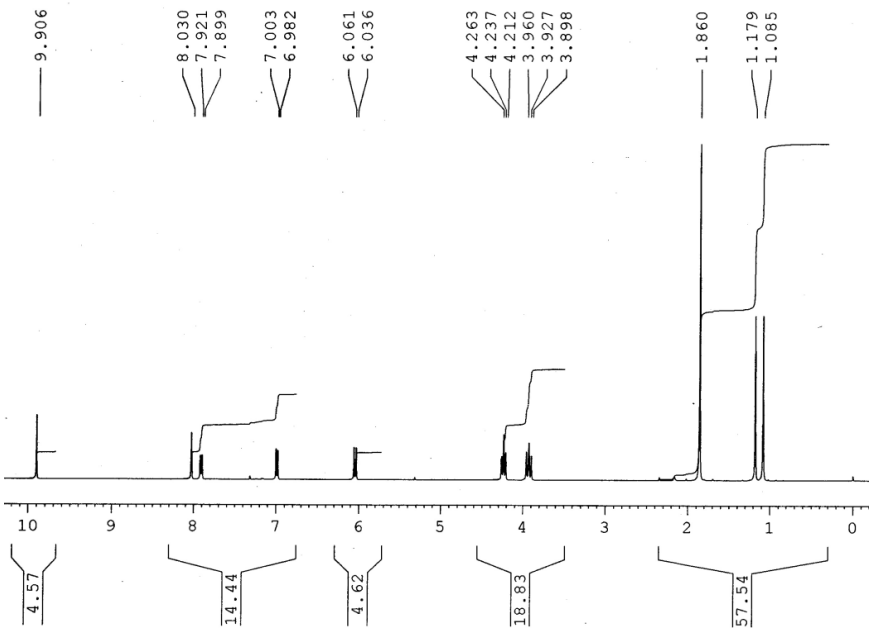


Figure 2. ^{1}H NMR spectrum for compound **18**

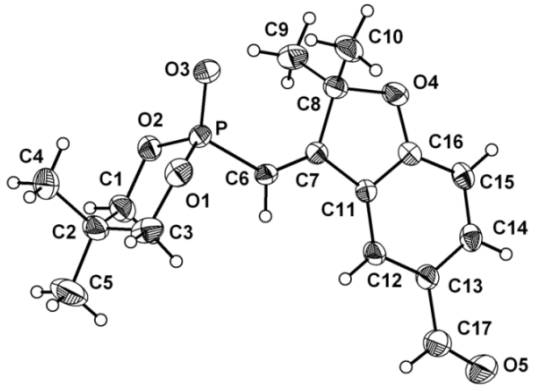
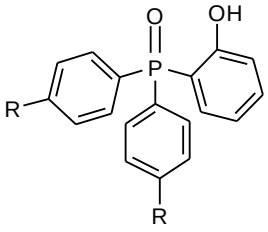
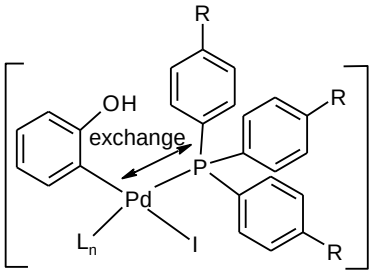


Figure 3. An ORTEP diagram of compound **18**. Selected bond lengths [Å] with esd's in parentheses: P-C(6) 1.768(2), C(6)-C(7) 1.334(3), C(8)-C(9) 1.508(4), C(7)-C(11) 1.457(3), O(4)-C(8) 1.486(3).

It can also be noted that in the ^{31}P NMR spectra shown in Figure 1 above, there is a minor peak at 37± 2 ppm [with slight variability in the chemical shift]. Although we could not isolate the compound corresponding to this, we believe that this is the phosphine oxide with exchange of aryl groups and subsequent oxidation. Such exchange products (cf. (**II-III**) have been characterized before in our laboratory.[21a] Formation of **II-III** could have occurred via the intermediate such as **IV**. These observations, we believe, should act as a caveat while using Pd(II)/ Ar_3P catalytic system.



R = H [**II,** δ(P): 39.6]
OMe [**III,** δ(P): 39.3]

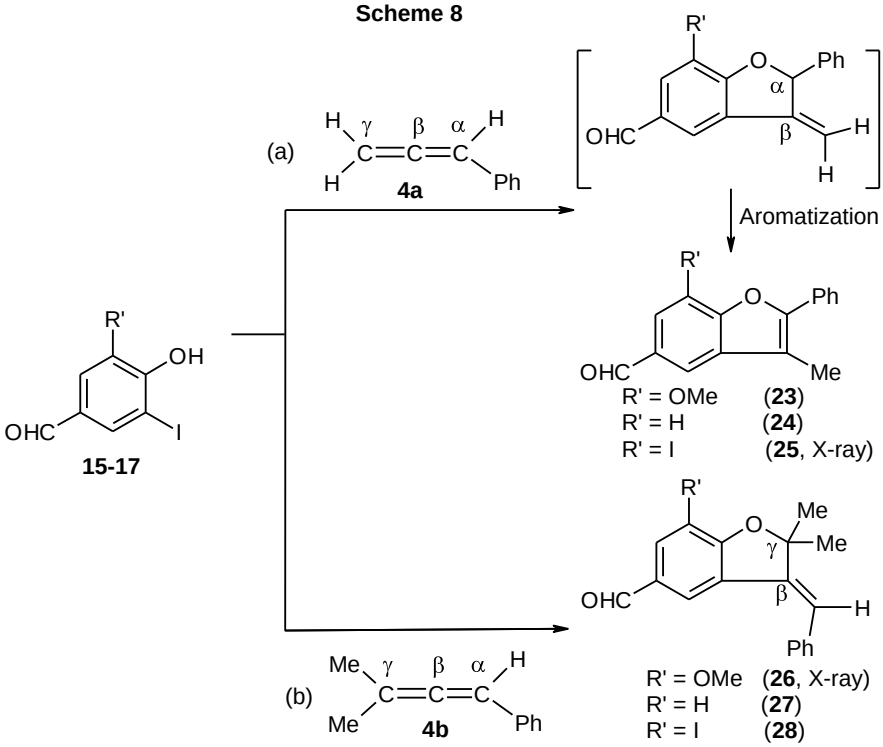


L = OAc
IV

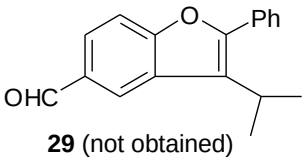
2.32 Reaction of phenylallenes 4a-b with functionalized 2-iodophenols 15-17 in PEG-400 as the medium

Under the optimized reaction conditions, the reaction of phenylallenes **4a-b** with substituted 2-iodophenols **15-17** leads to benzofurans **23-28** (Scheme 8) but the structure of the product varies with the type of precursor allene used. In all these reactions, the initial attack of the aryl iodide (here iodophenol) occurs at the carbon that is β to the phenyl group of the allene. In the next stage, depending on the allene, cyclization utilizing the phenolic -OH takes place at α or γ position. Thus the $=CH_2$ terminal allene **4a** gives (β,α) products (followed by aromatization) **23-25** but the $=CMe_2$ terminal allene **4b** gives the (β,γ) products **26-28**. In the latter case, the (β,α) product **29** was not obtained. The ^1H NMR spectrum/ TLC of the reaction mixture showed that the allene had completely reacted, and only one major product (>90%) was formed; the isolated yields are good (Table 3).

Scheme 8



Conditions: $Pd(OAc)_2$ / (*o*-tolyl)$_3$P/ K_2CO_3/ PEG-400/ 90 ^oC/ 12 h



29 (not obtained)

Table 3. Details on the yields of benzofurans **23-28**

Entry	Allene	R' in iodophenol	Compound	Isolated yield (%)
1	**4a**	OMe	**23**	68
2	**4a**	H	**24**	69
3	**4a**	I	**25**	51
4	**4b**	OMe	**26**	66
5	**4b**	H	**27**	62
6	**4b**	I	**28**	52

All the benzofurans **23-28** are well-characterized by IR, NMR as well as LC-MS/elemental analyses. In ^{1}H NMR spectrum, compound **25** shows a peak at δ 2.54

due to methyl group and the C*H*O proton appears at δ 10.0. While the first feature clearly shows that aromatization by proton shift has taken place, the second feature shows that the aldehyde group is unaffected. For compounds **26**-**28**, the =C*H* proton signal appears at δ ~6.43 and C*H*O proton appears at δ ~9.56 in the ^{1}H NMR spectra. In the alternative structure (i.e., **29** in lieu of **27**) for the product from **4b** and 3-iodo-4-hydroxy-benzaldehyde **16**, the C*H* proton should have appeared in the aliphatic region in the ^{1}H NMR. The structures of two of the representative compounds **25** and **26** have been confirmed by X-ray crystallography [Figures 4-5]. The C(8)-C(9) distance of 1.496(3) Å in compound **25** is in the single bond region, as required by the assigned structure. As can be seen from Figure 5, compound **26** has an *E* configuration around the exocyclic double bond [it must be noted that the assignment of *E*/*Z* stereochemistry is not straightforward by NMR spectroscopy].

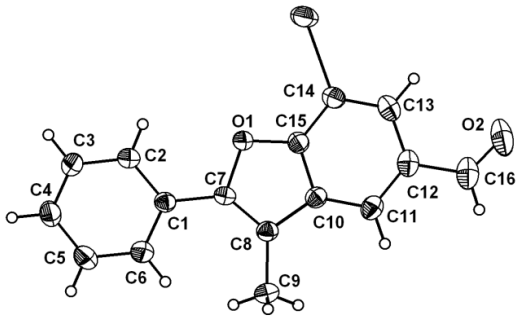


Figure 4. An ORTEP diagram of compound **25.** Selected bond lengths [Å] with esd's in parentheses: C(7)-C(8) 1.356(3), C(8)-C(9) 1.496(3), C(8)-C(10) 1.438(3), O(1)-C(7) 1.401(3).

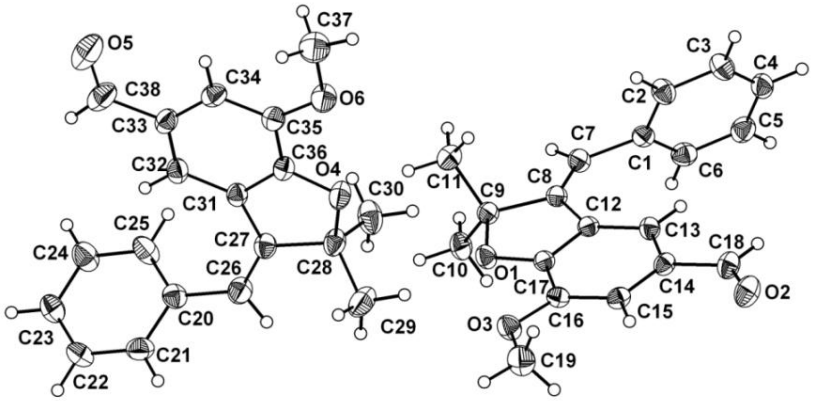
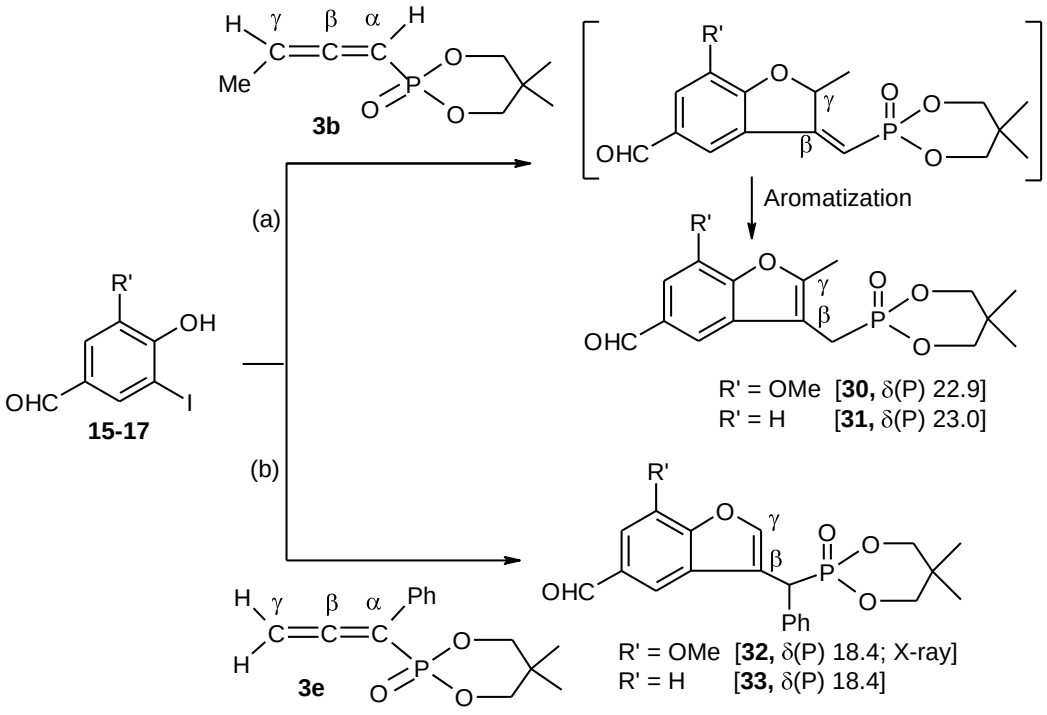


Figure 5. An ORTEP diagram of the compound **26.** Selected bond lengths [Å] with esd's in parentheses: C(7)-C(8) 1.326(2), C(8)-C(9) 1.530(2), C(8)-C(12) 1.466(2), O(1)-C(17) 1.3512(17). C(26)-C(27) 1.330(2), C(27)-C(28) 1.522(2), C(27)-C(31) 1.457(2), O(4)-C(36) 1.3499(19).

2.33 Reaction of allenylphosphonates 3a-b and 3e with functionalized 2-iodophenols 15-17 in PEG-400 as the medium

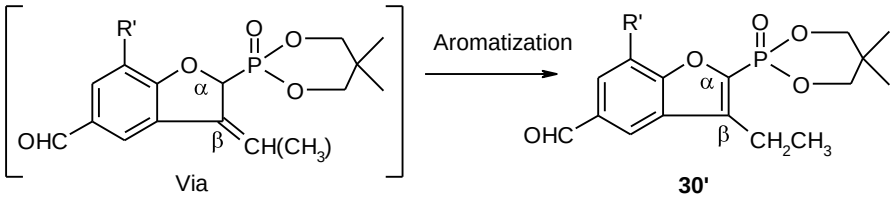
In contrast to the above results, when the allenylphosphonate has a γ-hydrogen as in $(OCH_2CMe_2CH_2O)P(O)CH=C=CH(R)$ [R = H (**3a**), Me (**3b**)], use of triarylphosphine in the Pd-catalyzed reactions with 2-iodophenols does not give clean products. A probable reason for this observation is the isomerization of allenylphosphonate $(OCH_2CMe_2CH_2O)P(O)CH=C=CH(R)$ to the corresponding alkyne $(OCH_2CMe_2CH_2O)P(O)C\equiv CCH_2(R)$ [R= H, Me].[21] Such an isomerization could be minimized by the use of CsF in place of phosphine/ K_2CO_3. However, in the reaction using **3a** or **3c-d** also a mixture of products with close R_f (TLC) values formed, and the separation proved difficult. Using **3b**, though, we were successful. This procedure was then applied to the reaction using $(OCH_2CMe_2CH_2O)P(O)C(Ph)=C=CH_2$ (**3e**). The results, that include the isolation of benzofurans **30**-**33**, are shown in Scheme 9. The isolated yields are moderate to good.

Scheme 9



Conditions: CsF/ $Pd(OAc)_2$/ PEG-400/ 90 °C/ 12 h
Yields (^{31}P NMR, isolated): 63-70%; 55-63%

The ^{1}H NMR spectra of (β,γ)-products **30-31** exhibit the C*H*$_3$ singlet around δ ~2.50, the PC*H*$_2$ doublet at δ ~3.26 (^{2}J(PH) ~20.6 Hz) and the C*H*O signal around δ 10.02. The alternative (β,α)-products (e.g. **30'**) should have exhibited signals corresponding to the C*H*$_2$C*H*$_3$ protons. The ^{1}H NMR spectrum of compound **30** is shown in Figure 6 as an illustration. In the ^{13}C NMR spectra, a doublet around δ 21.0 (^{1}J(PC) ~143.0 Hz) ascribable to P*C*H$_2$ is observed; such a ^{1}J(PC) value is indicative of the presence of P-CH$_2$ moiety.[22] In the ^{31}P NMR spectra, all these phosphono-benzofurans show a single peak in the region δ 18-19. For the phosphono-benzofurans **32-33**, the PC*H* proton appears at δ ~4.74 (^{2}J(PH) ~24.8 Hz) in the ^{1}H NMR spectra; in the ^{13}C NMR, the P*C*H carbon shows up as a doublet around δ 39.6 (^{1}J(PC) ~137.3 Hz). The δ(^{31}P) value of ~23.0 is slightly downfield when compared to that for compounds **30-31**. The structure of phosphono-benzofuran **32** is also confirmed by X-ray crystallography (Figure 7). The C(6)-C(13) distance of 1.504(4) Å is in the range expected for C-C single bond distance; the other molecule in the asymmetric unit also has a similar C-C distance.



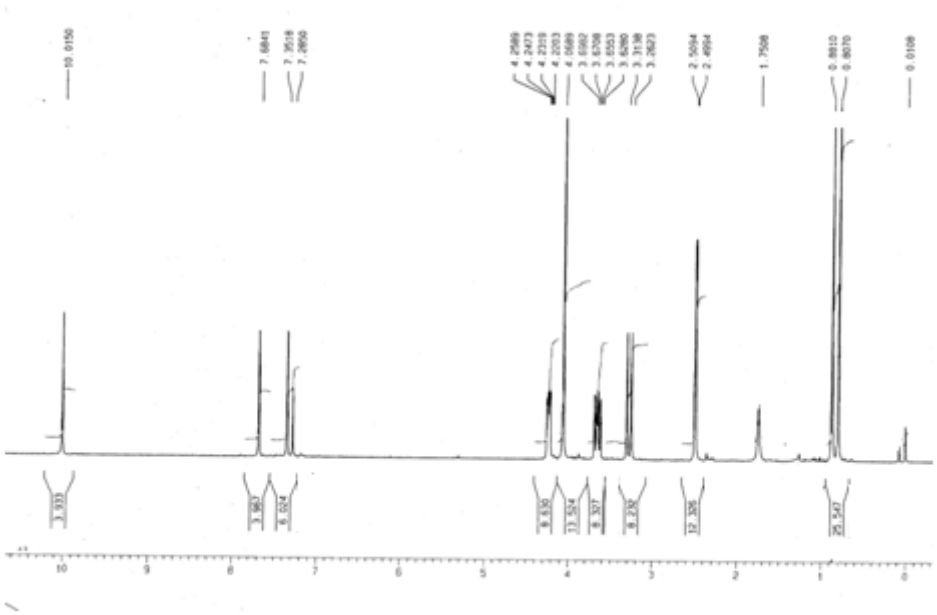


Figure 6. ^{1}H NMR spectrum for phosphono-benzofuran **30**

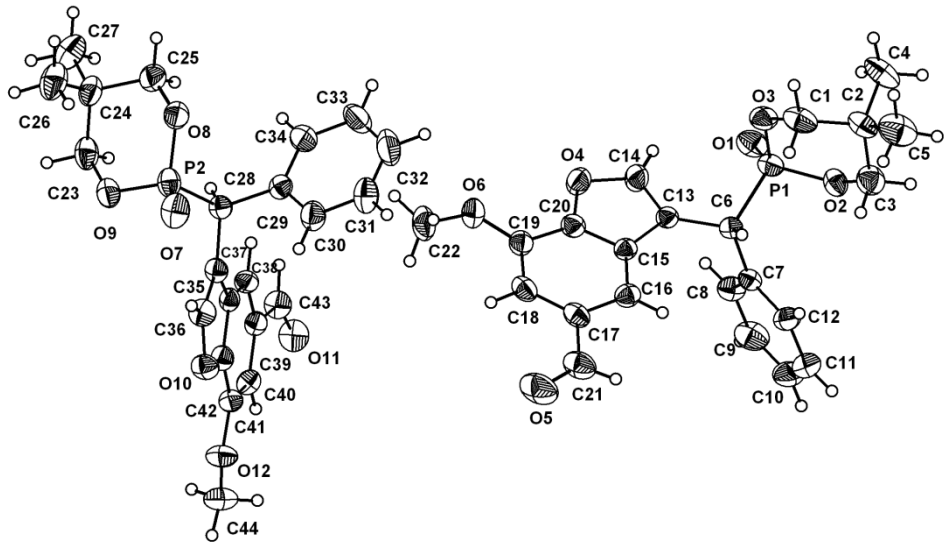
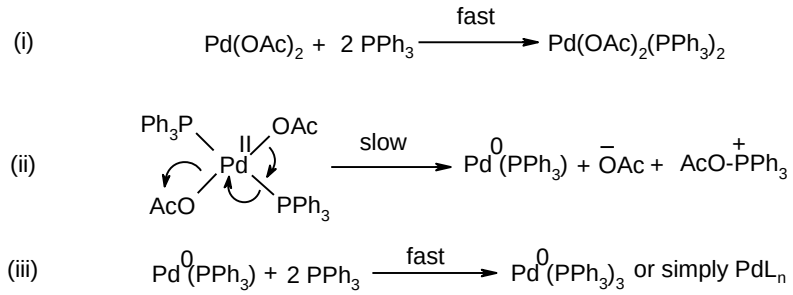


Figure 7. An ORTEP diagram of compound **32.** Selected bond lengths [Å] with esd's in parentheses: P(1)-C(6) 1.810(3), C(6)-C(13) 1.504(4), C(13)-C(14) 1.342(4), C(13)-C(15) 1.439(4), O(4)-C(14) 1.379(4), P(2)-C(28) 1.800(3), C(28)-C(35) 1.496(4), C(35)-C(36) 1.344(4), C(35)-C(37) 1.440(4), O(10)-C(36) 1.382(4).

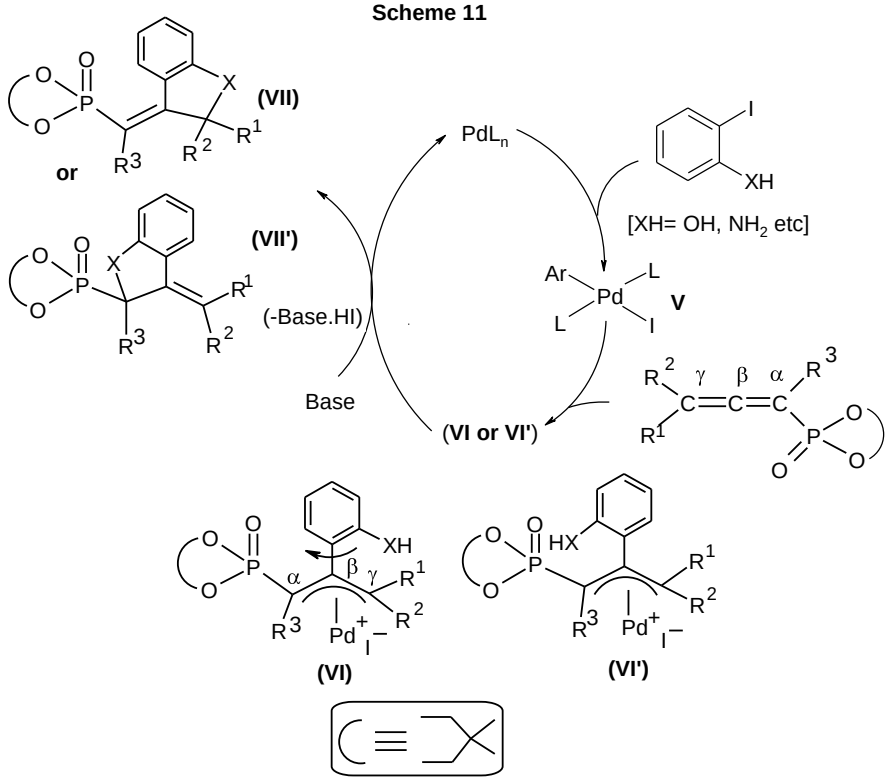
2.34 General mechanism for Pd-catalyzed annulation of allenes with 2-functionalized iodobenzenes

According to the known palladium chemistry, initially the Pd(II) compound [$Pd(OAc)_2$ in our case] should get reduced to Pd(0) in the presence of the phosphine, Ar_3P (Scheme 10).[74] Then aryl iodides undergo oxidative-addition with Pd(0) and form the Pd(II) complex **V**. The π-allyl palladium complex **VI** or **VI'** is formed through the insertion reaction at the β-carbon of allene moiety to **V** as shown in Scheme 11. The difference between **VI** and **VI'** lies in the orientation of the aryl group with respect to phosphorus. Since we did not use Ph_3P in reactions using $(OCH_2CMe_2CH_2O)P(O)C(R^3)=C=CR^1R^2$ [$R^3 = R^2 = H$. $R^1 = Me$ (**3b**); $R^3 = Ph$, $R^1 = R^2 = H$ (**3e**)] the oxidation state of palladium is uncertain and hence the other ligands on palladium are not shown in **VI** and **VI'**. At the end, the cyclization occurs by the elimination of a *proton* from the nucleophilic centre [XH = OH, NH_2 etc] as HI, along with PdL_2 in forming the products **VII**/ **VII'**. In **VII**, if R^1 or R^2 is H, then proton shift leading to aromatization could occur [cf. Scheme 9]. Thus the formation of phosphono-benzofurans [**9**, **18-22**, **30-33**] may be rationalized; this explanation can also be extended to the nonphosphorus benzofurans **23-28**.

Scheme 10



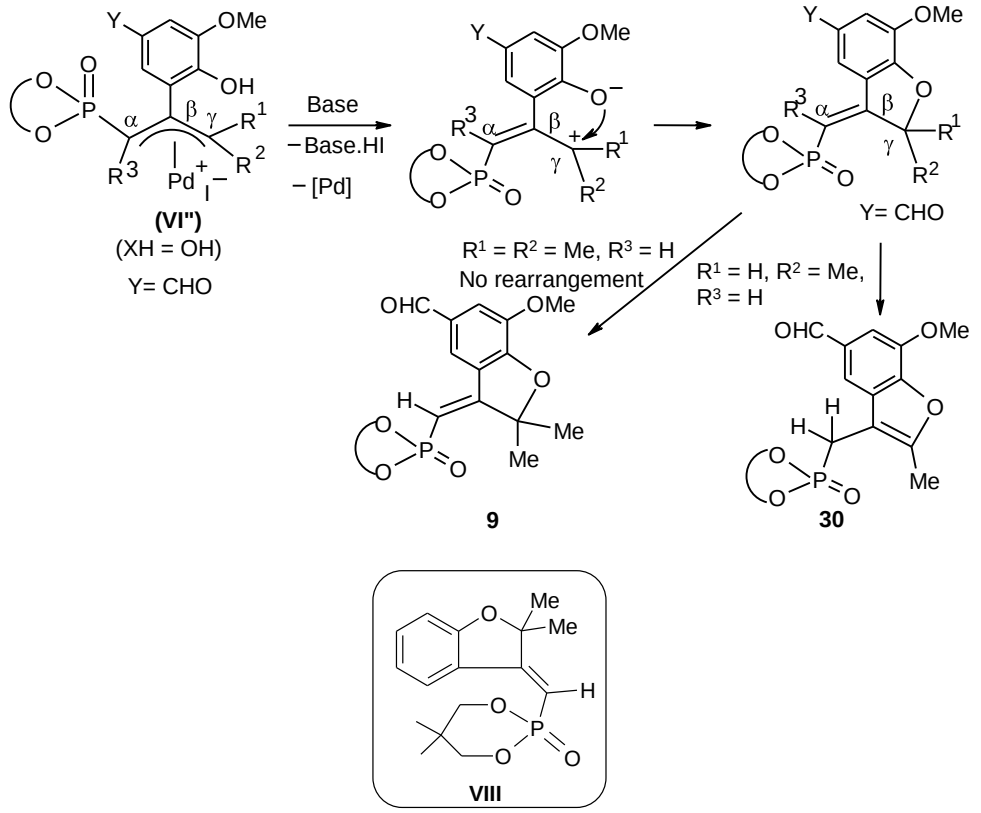
Scheme 11



It can be noted that in all the above cases, aryl group attacks at the *β*-carbon of allene and forms the intermediate **VI** and **VI'**. A proton from the phenolic -OH group is removed from intermediate **VI"** (this is similar to **VI** but with an additional functionality Y = CHO) by the base prior to cyclization (Scheme 12) wherein the phenolic oxygen attacks *γ*-position. Subsequently, a proton moves from the furan skeleton to *α*-carbon in the case of **30**. This movement is not possible for **9** ($R^1 = R^2$ = Me). Formation of the *E*-geometrical isomer **10** (cf. Scheme 6) is possible for **9**, but most likely due to steric effects (-CHO group on the aromatic ring) we are able to see only the *Z* isomer. Evidence for this assertion comes from our earlier studies using unsubstituted 2-iodophenols wherein an *E*-isomer (**VIII**) is crystallographical-

ly characterized.[21] In the case of nonphosphorylated benzofuran **23**, a species similar to **VI'** (Scheme 12) may be responsible for the cyclization by the attack of phenolic oxygen on the α-carbon, resulting in the (β,α)-product; subsequently, proton migration takes place to acquire aromaticity. Formation of **18-22**, **24-25**, and **31-33** can be explained in a manner similar to those for **9**, **23** and **30** respectively. Formation of **26-28** is also similar to that of **9** but only *E* isomer is formed perhaps due to steric hindrance between Ph and the two Me groups. The answer to the question as to why only (β,γ)-product, and not (β,α)-product is formed in the case of allenes **3c-d** and **4b** is due to the fact that after removal of phenolic proton from **VI"**, cyclization occurs at the more electrophilic γ centre (here, positive charge is more stabilized at γ position when compared to α position).

Scheme 12

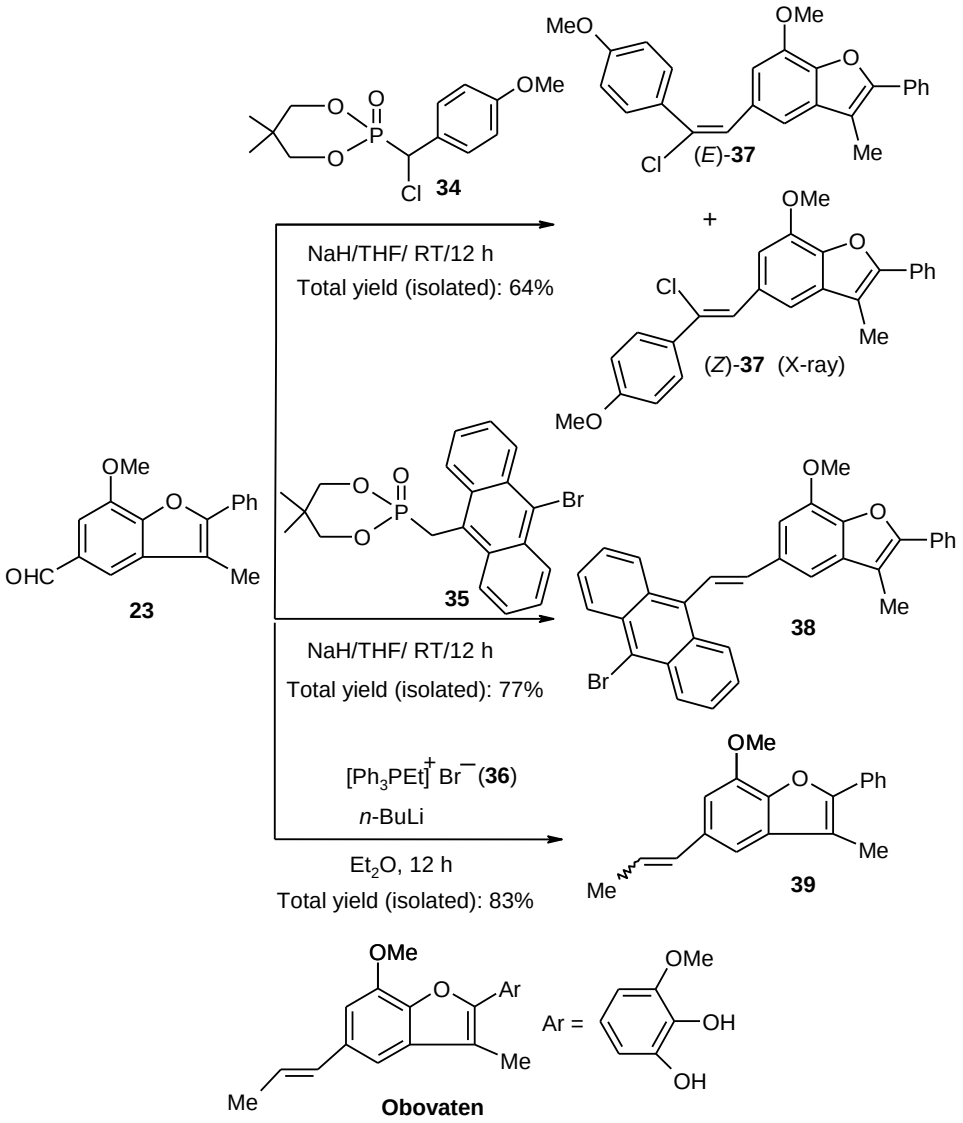


2.35 Utility of benzofurans 23 and 30 in Horner-Wadsworth-Emmons (HWE) / Wittig reaction

With several aldehyde appended benzofurans prepared as above, we thought that it should be possible to synthesize a variety of new 3,5-disubstituted benzofurans. This idea is exemplified by using **23** in the Horner-Wadsworth-Emmons

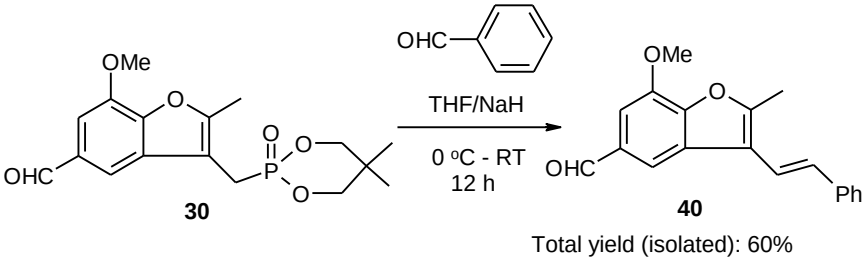
(HWE) or Wittig reaction with compounds **34-36**.[75-76] The products are **37-39** shown in Scheme 13. In the HWE reaction of **23** with the α-chlorophosphonate **34**, we have been able to isolate both the isomers *E*-(**37**) and *Z*-(**37**). It may also be noted that the Wittig product **39** is similar to Obovaten which is a natural product and a known antitumor agent.[77]

Scheme 13



Even phosphono-benzofurans of type **30** are of synthetic value as shown by the synthesis of **40** (Scheme 14). Interestingly, in this case, we were able to retain the less reactive aldehydic moiety present in the precursor phosphono-benzofuran **30** that shows that the reaction takes place intermolecularly.

Scheme 14



Total yield (isolated): 60%

The spectroscopic and analytical data for the HWE/ Wittig products **37-40** are consistent with structures as assigned. In the ^{1}H NMR spectrum of *Z*-(**37**), =C*H* proton signal appears at δ 6.92. The *Z*-stereochemistry of this compound is confirmed by X-ray crystallography (Figure 8). The presence of CHO group in compound **40** is clearly shown by IR and ^{1}H NMR spectra; this feature also proves that this CHO on the benzofuran is not involved in HWE reaction (cf. Scheme 14).

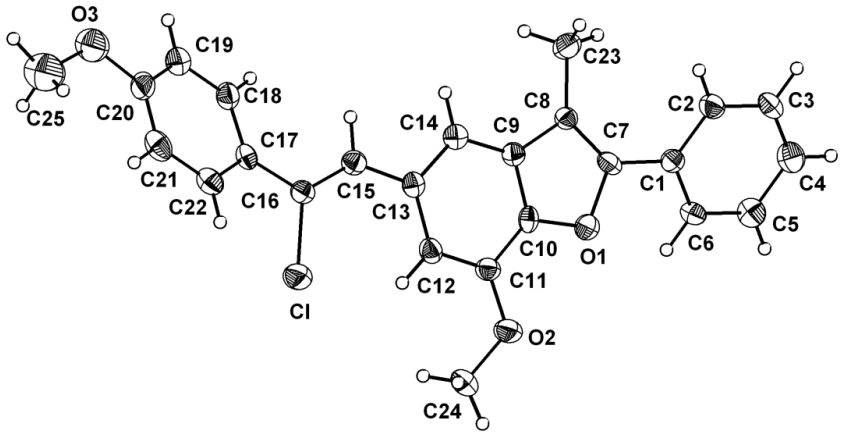


Figure 8. An ORTEP diagram of compound (*Z*)-**37b.** Selected bond lengths [Å] with esd's in parentheses: P(1)-C(6) 1.810(3), C(6)-C(13) 1.504(4), C(13)-C(14) 1.342(4), C(13)-C(15) 1.439(4), O(4)-C(14) 1.379(4).

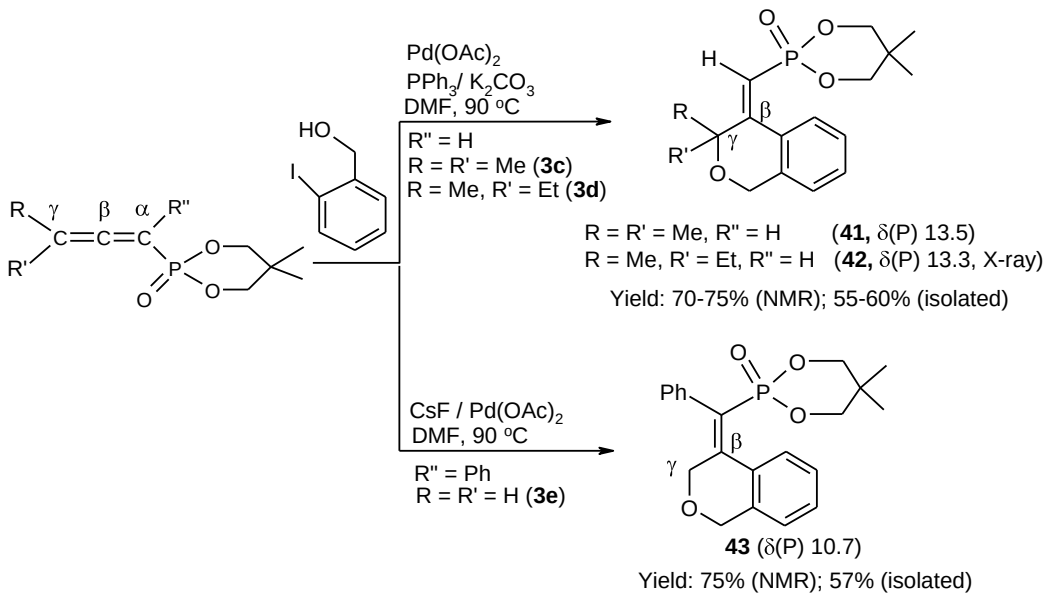
2.4 Pd-catalyzed reactions of allenes with 2-iodobenzyl alcohol, 2-iodoanilnes, aniline and 2-iodo-*t*-benzaldimine

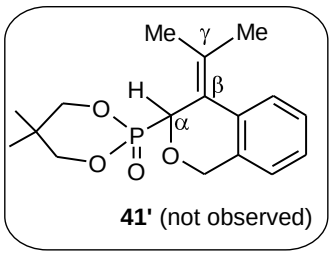
2.41 Reaction of allenyphosphonates ($OCH_2CMe_2CH_2O$)P(O)C(R'')=C=C(RR') [R'' = H, R = R' = Me (3c), R'' = H, R = Me, R' = Et (3d), R'' = Ph, R = R' = H (3e)] with 2-iodobenzyl alcohol

Treatment of allenes **3a-e** with 2-iodobenzylalcohol under the influence of Pd-catalyst is expected to yield benzopyrans, which are six-membered heterocycles. As

observed in the reaction with 2-iodophenols, in the case of **3a** or **3b,** this procedure led only to isomerization and use of CsF in place of Ph_3P/ K_2CO_3 led to a mixture of products. Fortunately, this reaction works smoothly for allenes **3c-d** using $Pd(OAc)_2$/ Ph_3P/ K_2CO_3 in DMF as the solvent; the PEG-400 medium was not efficient here. For **3e**, use of CsF in place of Ph_3P/ K_2CO_3 was necessary. The cyclization process lead to (β,γ)-cyclized products **41-43** (Scheme 15).

Scheme 15





The PC*H* proton for the phosphono-benzopyrans **41-42** appears at δ ~5.59 (^2J(PH) ~12.8 Hz) in the ^{1}H NMR spectra showing that these are (β,γ)-cyclized products. It may be noted that for the (β,α)-cyclized product (**41'**), say in the reaction using **3c**, a $CHMe_2$ signals should have been present. The ^{1}H NMR spectrum of compound **41** is shown in Figure 9. In the ^{13}C NMR spectrum, a doublet around δ 106.4 (^1J(PC) ~179.8 Hz) corresponding to P*C*H=C is seen for **41-42**. The larger ^1J(PC) value (compared to that for **30**-**33**) is consistent with a vinylphosphonate [$(RO)_2P(O)C=CRR'$] structure. In the ^{31}P NMR spectra, phosphono-benzofurans **41-**

42 show a single peak at δ ~13.5 while the signal for **43** appears at δ ~10.7. The *E*-configuration around the double bond in **42** is confirmed by X-ray crystallography (Figure 10).

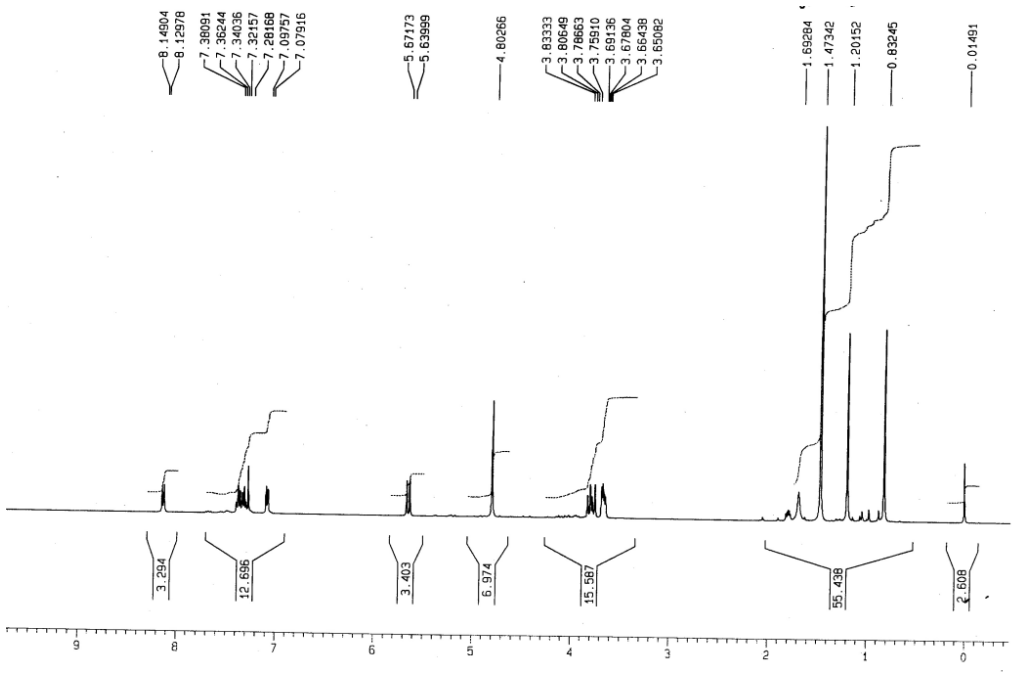


Figure 9. ^{1}H NMR spectrum for phosphono-benzofuran **41**

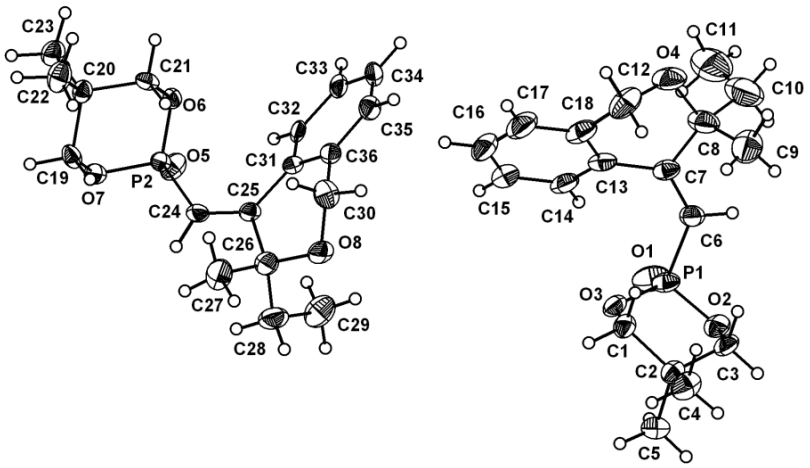
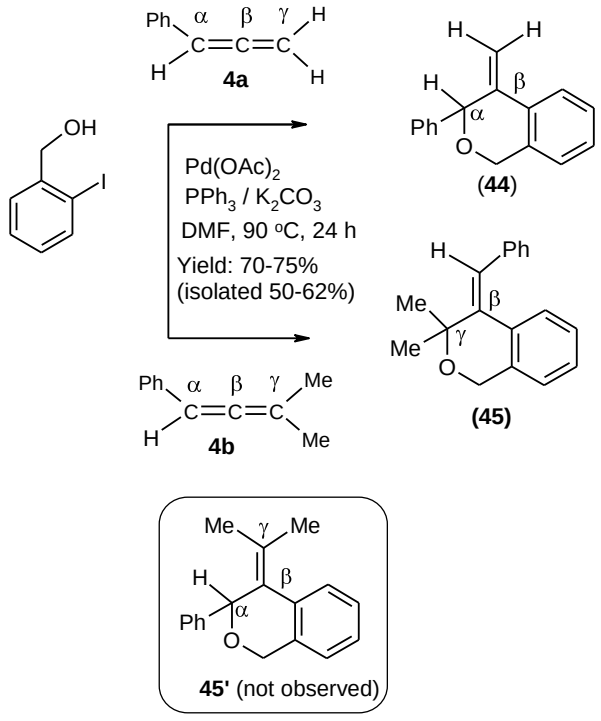


Figure 10. An ORTEP diagram of compound **42.** Both the molecules in the asymmetric unit are shown. Selected bond lengths [Å] with esd's in parentheses: P(1)-C(6) 1.773(5), C(6)-C(7) 1.317(7), C(7)-C(8) 1.552(7), C(7)-C(13) 1.468(7), O(4)-C(8) 1.416(7), P(2)-C(24) 1.775(6), C(24)-C(25) 1.327(8), C(25)-C(26) 1.524(9), C(25)-C(31) 1.476(8), O(8)-C(26) 1.417(8).

2.42 Reaction of phenylallenes PhCH=C=CH_2 (4a) and PhCH=C=CMe_2 (4b) with 2-iodobenzyl alcohol

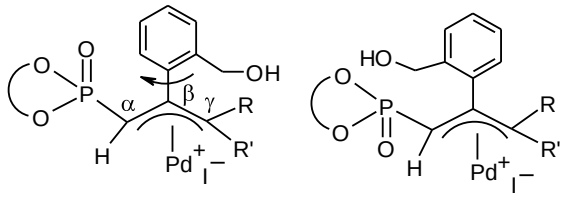
Reaction of phenylallenes **4a-b** with 2-iodobenzyl alcohol leads to benzopyrans **44-45** but the product varies with the type of allene used (Scheme 16). The reaction of phenylallene **4b** leading to **45** was earlier conducted by one of my colleagues in the laboratory using the solvent acetonitrile,[21a] but in the present work it was conducted in DMF to have a tangible comparison. The purpose of performing these reactions lies in the fact that the allenyl phosphonates [$(OCH_2CMe_2CH_2O)P(O)CH=C=CH_2$ (**3a**), and $(OCH_2CMe_2CH_2O)P(O)CH=C=CMe_2$ (**3c**)] that contain terminal $=CH_2$ and $=CMe_2$ groups respectively, differed in their reactivity with 2-iodophenols, as described in sections 2.31 and 2.33. The allene **4a** led to the (β,α) product **44** and allene **4b** led to (β,γ) product **45.** It may be noted that a similar type of reactivity for **4a-b** was observed (with subsequent aromatization, though) in the formation of benzofurans **23-28 (***vide supra*). In the ^{1}H NMR spectra, while compound **44** shows three separate signals for the olefinic and the C(Ph)*H* protons in the region of δ 4.50- 6.00, compound **45** shows a singlet at δ 6.66 due to =C*H*(Ph). For **45**, a single *C*H_3 signal at δ 26.9 is seen in the ^{13}C NMR spectrum suggesting that (β,γ)-cyclization has taken place [for the corresponding (β,α) product (**45'**), we would expect two signals].

Scheme 16



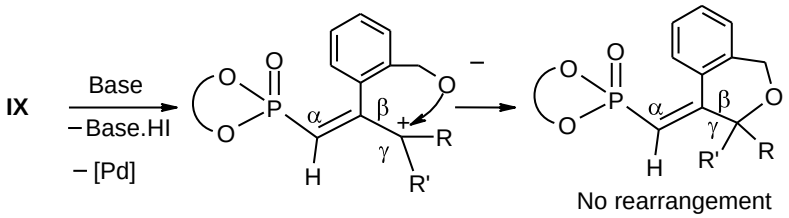
2.43 Mechanistic pathways for the formation of benzopyrans

Formation of benzopyrans can be explained in a manner similar to that for benzofurans described above. Here, the additional group responsible for cyclization is -CH_2OH. The benzopyrans **41-42** are formed via intermediates **IX** and **IX**' (Scheme 17). In the case of **44**, species similar to **IX'** may be responsible for the cyclization by the attack of alcoholic oxygen on the α-carbon. The proton shift from α-carbon to γ-carbon is not possible in case of **44** because the resulting structure does not lead to aromaticity. Compounds **43** and **45** are formed in a fashion similar to **41-42.**



(IX) **(IX')**

Scheme 17



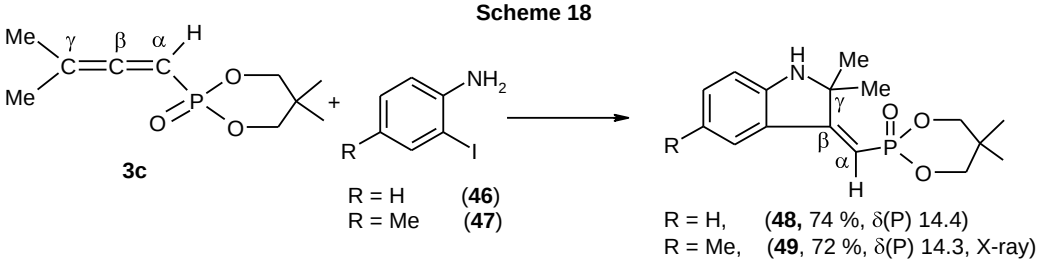
No rearrangement

R = Me, R' = Me (**41**), Et (**42**)

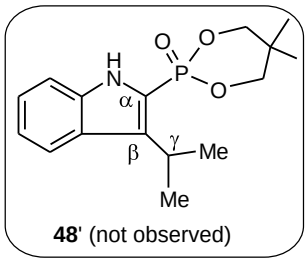
2.44 Reaction of allenylphosphonate ($OCH_2CMe_2CH_2O$)P(O)CH=C=CMe_2 (3c) with 2-iodoanilines 46-47

In the reactions discussed above, use of 2-iodoanilines in place of 2-iodophenols can be expected to yield indole ring systems. Thus Pd-catalyzed annulation of allenylphosphonate **3c** with 2-iodoanilines **46-47** in DMF leads to phosphono-indoles as expected (Scheme 18). The reaction works nicely for allenylphosphonate **3c** with 2-iodoanilines **46-47** using $Pd(OAc)_2$/ Ph_3P/ K_2CO_3 in DMF giving phosphono-indoles **48-49** in moderate yields. In both the cases, the *Z*-isomer is also present to an extent of 5-10% in the reaction mixture, but we could not isolate it.

Scheme 18



Conditions: $Pd(OAc)_2$ / Ph_3P/ K_2CO_3/ DMF/ 90 °C/ 24 h



48' (not observed)

The PC*H* proton for the phosphono-indoles **48-49** appears at δ ~5.20 (^2J(PH) ~13.3 Hz) in the ^{1}H NMR spectrum showing that these are (β,γ)-cyclized products. If it were to be (β,α)-cyclized products (after aromatization, say **48'**), we would expect signals for $CHMe_2$ group. In the ^{13}C NMR, a doublet around δ 95.8 (^1J(PC) ~191.8 Hz) corresponding to P*C*H=C is observed. In the ^{31}P NMR spectra, phosphono-indoles **48-49** show a single peak at δ ~14.3. The *E*-stereochemistry of compound **49** is confirmed by X-ray crystallography (Figure 11) with the olefinic double bond located between C(6) and C(7) [distance =1.347(3)Å]. Interestingly, the structure exhibits C-H...O hydrogen bonding involving an OCH_2-proton and the P=O moiety [C(3)**…**O(3') 3.358(3)Å] in addition to the expected N-H..O(P) [N**…**O(3") 2.743(4)Å] hydrogen bond. The pathway for the formation of these indoles is similar to that for benzofurans and hence is not elaborated here.

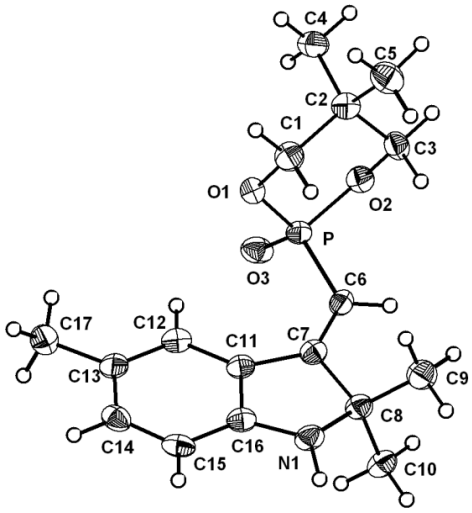


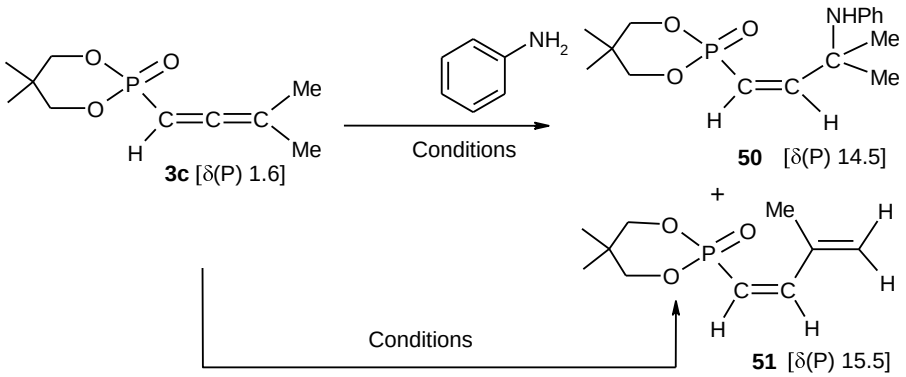
Figure 11. An ORTEP diagram of compound **49**. Selected bond lengths [Å] with esd's in parentheses: P-C(6) 1.769(2), C(6)-C(7) 1.347(3), C(7)-C(8) 1.536(3), C(7)-C(11) 1.457(3), N(1)-C(16) 1.373(3). Hydrogen bond parameters [Å, ^{o}]: C(3)-H(3A)**…**O(3') 0.97, 2.42, 3.358(3), 161.9; N-H**…**O(3") 0.82, 1.93, 2.743(4), 175.1. Symmetry codes are 1+x, 1.5-y, 1/2+z and: x, 1.5-y, -1/2+z, respectively].

2.45 Reaction of allenylphosphonate ($OCH_2CMe_2CH_2O$)P(O)CH=C=CMe_2 (3c) with aniline: Synthesis of a phosphono-butadiene ($OCH_2CMe_2CH_2O$)P(O)CH=CH-C(Me)=CH_2 (51)

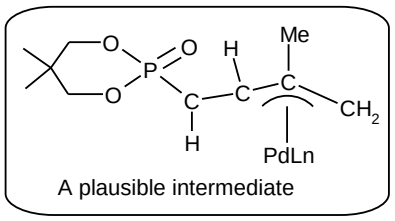
After having experience with Pd-catalyzed annulation reactions of allenes with iodoanilines, we wanted to extend this methodology for CH activation without using iodoarenes. The basis for attempting this reaction is to have an analogy with that in the literature between (MeO_2C)C≡C(CO_2Me) and aniline under similar conditions.[78] Thus, we treated the allenylphosphonate **3c** with aniline in the presence of Pd(II) acetate with O_2 (air)/ pivalic acid as an oxidant (Scheme 19). We did not get the desired annulation product (**48**; Scheme 18) but ended up with the hydroamination product **50** [IR (~3300 cm^{-1}), ^{1}H and ^{31}P NMR**]** and the phosphono-butadiene **51**. Numerous hydroamination products similar to **50** have already been reported from our laboratory before[4i] and hence it is not discussed further. Formation of butadiene **51** is a new result. Interestingly, in the absence of aniline, only butadiene **51** is formed exclusively. Compound **51** shows a peak at δ 1.89 due to =C(C*H*$_3$) and three alkenic protons in the region of δ 5.36-5.77, the remaining alkenic proton appears at δ 7.21-7.31 in the ^{1}H NMR spectrum. A doublet at δ 111.0 in ^{13}C NMR spectrum

with a ^1J(PC) value of 191.0 Hz shows that it is a vinylphosphonate. Although a similar reaction with $Ph_2P(O)(CH=C=CMe_2)$[79] did not give butadiene, formation of **51** from **3c** is quite interesting in the sense that a Pd-allyl complex may have been formed as an intermediate.

Scheme 19



Conditions: $Pd(OAc)_2$, DMA: $(CH_3)_3CCO_2H$ (4:1), air, 120 °C, 2 h

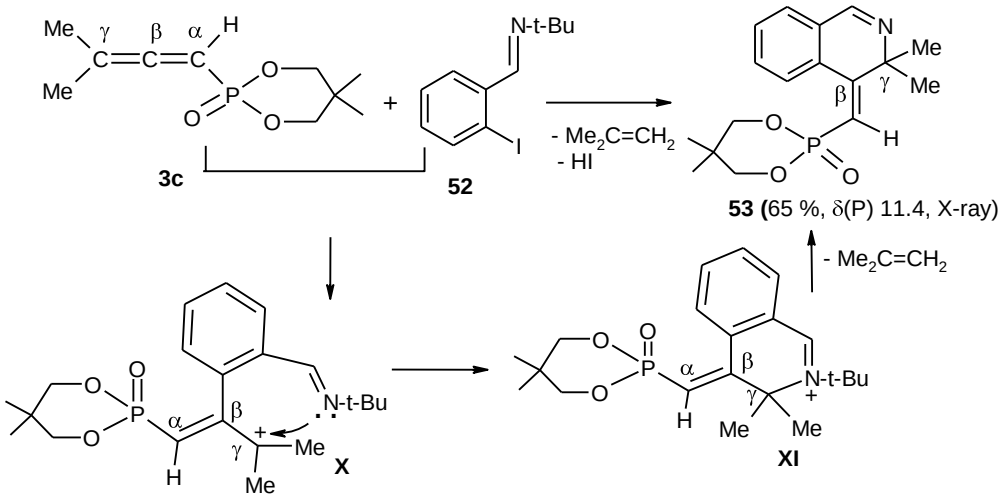


2.46 Reaction of allenylphosphonate ($OCH_2CMe_2CH_2O$)P(O)CH=C=CMe_2 (3c) with 2-iodo-t-butylbenzaldimine 52

It is known from the literature that *t*-butyl benzaldimine eliminates isobutylene in many reactions.[80a-b] Hence we surmised that 2-iodo-*t*-butylbenzaldimine **52**[80c] should be a good reactant in our Pd-catalyzed reactions with allenylphosphonates and would lead to isoquinolines. Thus the treatment of allenylphosphonate **3c** with 2-iodo-*t*-butylbenzaldimine **52** using $Pd(OAc)_2$/ Ph_3P/ Na_2CO_3 in CH_3CN leads to phosphono-isoquinoline **53** in moderate yields with the elimination of isobutylene gas (Scheme 20). Here we have used one equivalent of Na_2CO_3 instead of excess K_2CO_3 (used in the earlier reactions discussed above) to avoid the decomposition of imine. We also performed a similar reaction using the allene ($OCH_2CMe_2CH_2O$)P(O)CH=C=C(Me)(Et) (**3d**), but have not been successful in isolating the pure product so far. The PC*H* proton in **53** appears at δ 5.93 [^2J(PH) ~13.2 Hz] and N=C*H* proton gives a singlet at δ 8.35 in the ^{1}H NMR spectrum. A doublet

at δ 111.0 (^1J(PC) ~177.1 Hz) in the ^{13}C NMR spectrum corresponding to P*C*H=C is also observed. Scheme 20 also depicts a possible pathway for its formation. The *E*-stereochemistry is confirmed by X-ray crystallography (Figure 12). Crystallization was performed in open air and hence in the process of crystallization, half a molecule of water per molecule of **53** is present in the X-ray structure. The water molecule is H-bonded to itself as well as the ring nitrogen atom in the structure [not shown in the Figure].

Scheme 20



Conditions: $Pd(OAc)_2$ / Ph_3P/ Na_2CO_3/ CH_3CN/ 90 °C/ 24 h

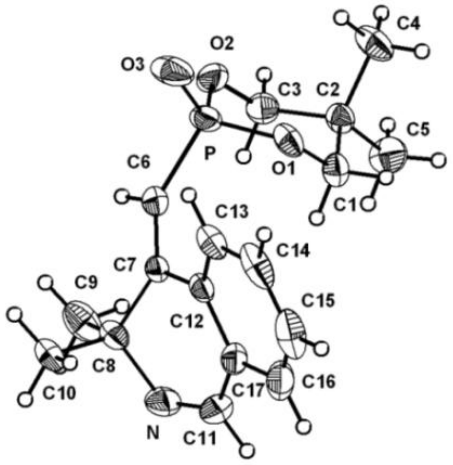


Figure 12. An ORTEP diagram of compound **53.**1/2H_2O. Selected bond lengths [Å] with esd's in parentheses: P-C(6) 1.774(3), C(6)-C(7) 1.332(3), C(7)-C(8) 1.525(3), C(7)-C(12) 1.469(3), N(1)-C(8) 1.477(4), N-C(11) 1.259(4). Hydrogen bond parameters [Å, °]: O(4)-H(4D)...N 0.92(2), 2.55(11), 2.907(6), 104(8); O(4)-H(4D)... O4 0.92(2), 2.13(9), 2.733(14), 122(8). Symmetry codes are x, 1.5-y, 1/2+z and: 1-x, 1-y, 1-z, respectively]

2.5 Base catalyzed reactions of allenylphosphonates with 2-mercaptobenzaldehydes

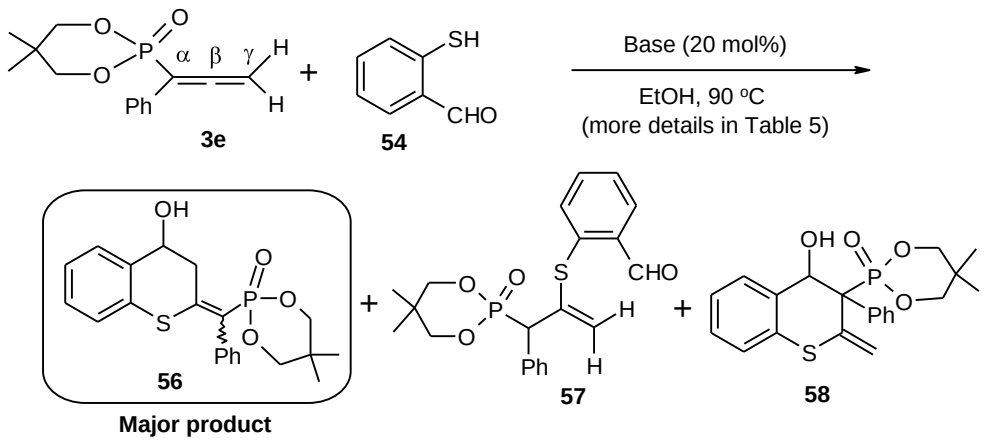
The reaction of 2-mercaptobenzaldehydes[81] with allenylphosphonates in the presence of a base can lead to a variety of phosphono-thiochromans and allylic phosphonates. This section deals with the reaction of several allenylphosphonates with substituted 2-mercaptobenzaldehydes under base catalyzed conditions. The experimental conditions were standardized by using the allenylphosphonate $(OCH_2CMe_2CH_2O)P(O)C(Ph)=C=CH_2$ (**3e**), because the products could be characterized more readily. We have then used the allenes **3f-k** and **5**, which will be discussed later. The choice of these substrates was dictated by the ease of their synthesis.

2.51 Reactions of α-aryl substituted allenylphosphonates $(OCH_2CMe_2CH_2O)P(O)C(Ar)=C=CH_2$ (3e-j) with 2-mercapto benzaldehyde (54) and 5-methyl-2-mercapto benzaldehyde (55)

We treated the allenylphosphonate **3e** with unsubstituted 2-mercaptobenzaldehyde **54** in the presence of K_2CO_3 in ethanol to obtain phosphono-thiochromans **56 (*E/Z*)** and **58** as well as the allylphosphonate **57** (Scheme 21). We wanted to see whether the yield of one of the thiochromans can be maximized or not. The ^{31}P NMR spectra for the reaction mixtures by using ethanol and dimethyl sulfoxide (DMSO) are shown in Figure 13. The former spectrm shows more number of products but each of these has been characterized in this study. The major product in DMSO [Figure 13(b)] is phosphono-thiochroman **56**. The peak in the vicinity of δ(P) 20 in Figure 13(a) may be ascribed to the product **58**; the peak at δ(P) 17 is due to the allylphosphonate **57** as shown by NMR (^1H, ^{13}C and ^{31}P). We have conducted this reaction of **3e** with 2-mercaptobenzaldehyde **54** in the presence of different bases and in different solvents. The results are summarized in Tables 4 and 5. As can be seen from Table 4, the conditions previously used in reactions using salicylaldehyde[47] led to a mixture of products (Table 4, entry 3) wherein the yield of **56** was only moderate. Use of PPh_3 or DMAP as the base afforded only low yields of the desired product (Table 4, entries 10, 11); in some cases, a mixture of isomers (Table 5, entries 3-8) are obtained. It was found that using K_2CO_3 as the base and dimethyl sulfoxide (DMSO) as the solvent, phosphono-thiochroman **56** (*E*-isomer) could be obtained as the major product [^{31}P NMR evidence]. As a solvent, DMSO gave better

results (Table 5, entry 1); PEG-400 also gave good results (Table 5, entry 6), but the yields were lower than that in DMSO and it took more time for the completion of the reaction.

Scheme 21



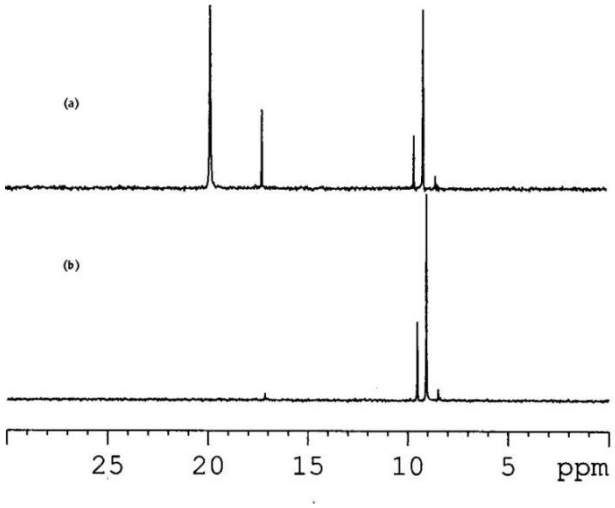


Figure 13. ^{31}P NMR spectra for the reaction mixture of **3e** with 2-mercaptobenzaldehyde in (a) EtOH at 90 °C/ 12 h, (b) DMSO at 90 °C/ 4 h.

Table 4. Effect of base on the yield of product **56** from the reaction of allene **3e** with 2-mercaptobenzaldehyde **54** in DMSO [at 90 °C for 4 h].

Entry	Base	Yield (%)[a], (*E*:*Z*)
1	K_2CO_3	95[b] (0.4:1.0)
2	NaOAc	82 (0.2:1.0)

3	DBU	71 (0.2:1.0)
4	CsF	69 (0.3:1.0))
5	K_3PO_4	68 (0.4:1.0)
6	DABCO	61 (0.5:1.0)
7	Triethanolamine	57 (0.5:1.0)
8	$NaHCO_3$	53 (0.3:1.0)
9	Et_3N	59 (0.2:1.0)
10	PPh_3	37 (0.3:1.0)
11	DMAP	37 (0.5:1.0)

[a]Yields are calculated by using ^{1}H and ^{31}P NMR spectroscopy; [b]isolated yield 80%

Table 5. Effect of solvent on the yield of product **56** from the reaction of allene **3e** with 2-mercaptobenzaldehyde **54**.

Entry	Solvent	Temp. (^{o}C) / Time (h)	Yield[a] (%),(E:Z)
1	DMSO	90 / 4	95[b] (0.4:1.0)
2	DMF	90 / 4	65 (0.5:1.0)
3	Toluene	90 / 6	58 (0.1:1.0)
4	CH_3CN	90 / 6	57 (0.2:1.0))
5	Triethanolamine	90 / 4	57 (0.5:1.0)
6	PEG-400	90 / 4	54 (0.3:1.0)
7	EtOH	100 / 6	46 (0.3:1.0)
8	Dioxane	110 / 6	26 (1.1:1.0)

[a]Yields are calculated by using ^{1}H and ^{31}P NMR spectroscopy; [b]isolated yield 80%

The major isomer of compound **56** shows a band at 3302 cm^{-1} in IR spectrum corresponding to the OH stretch. In the ^{1}H NMR spectrum, *CH*$_2$(CHOH) protons appear as two different multiplets in the region δ 3.45-3.65 showing the presence of ring diastereotopic C*H*$_2$ protons. The *CH*OH proton signal appears at δ 4.9 as a multiplet. The ^{1}H NMR spectrum is shown in Figure 14. In the ^{13}C NMR, a doublet at δ 119.9 with ^{1}*J*(P-C) value of ~ 187.1 Hz corresponding to P*C*=C is seen. The *E*-

stereochemistry around C=C double bond was confirmed by X-ray crystallography (Figure 15); the hydroxyl OH is clearly hydrogen bonded to the phosphoryl oxygen. The ^{31}P NMR chemical shift is 9.0 ppm. Based on these data, we could assign the ^{31}P NMR chemical shifts for the other isomer. The signal for the *E*-isomer [δ(P) = 9.0] appears upfield when compared to that for the *Z*-isomer [δ(P) = 9.8].

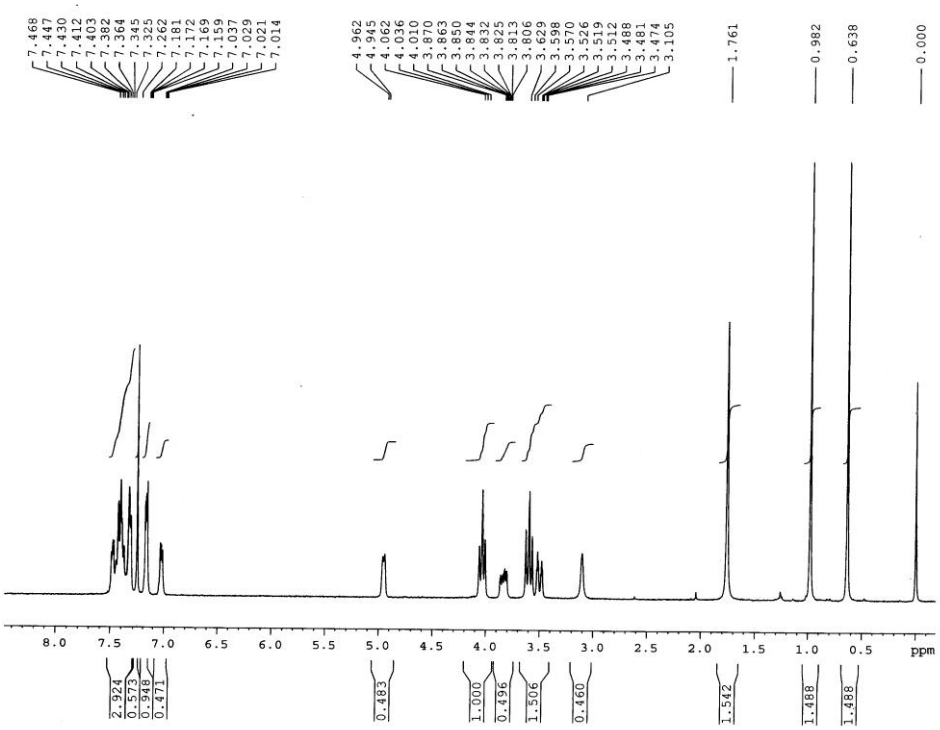


Figure 14. ^{1}H NMR spectrum for phosphono-thiochroman (*E*)-**56**

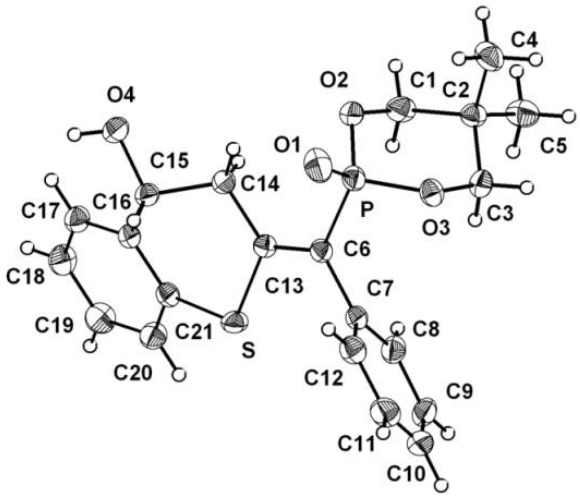


Figure 15. An ORTEP diagram of compound (*E*)-**56**. Selected bond lengths [Å] with esd's in parentheses. P-C(6) 1.798(3), C(6)-C(13) 1.343(4), C(13)-C(14) 1.509(4), S-C(13) 1.758(3), O(4)-C(15) 1.409(4). [Hydrogen bond parameters: O(4)-H(4)**…**O(1) 0.82 1.93 2.743(4) 175.1 ^{o}; symmetry code: 2-x, 2-y, 2-z].

Allylphosphonate **57** shows a doublet at δ 3.94 [^{2}J(P-H) = 24.4 Hz] due to PC*H* proton in the ^{1}H NMR spectrum; olefinic protons appear as a two singlets at δ 5.50 and 6.22. The ^{1}H NMR spectrum of **57** is shown in Figure 16. A doublet at δ 49.4 [^{1}J(PC) = 140.0 Hz] observed in the ^{13}C NMR spectrum corresponds to P*C*H carbon.

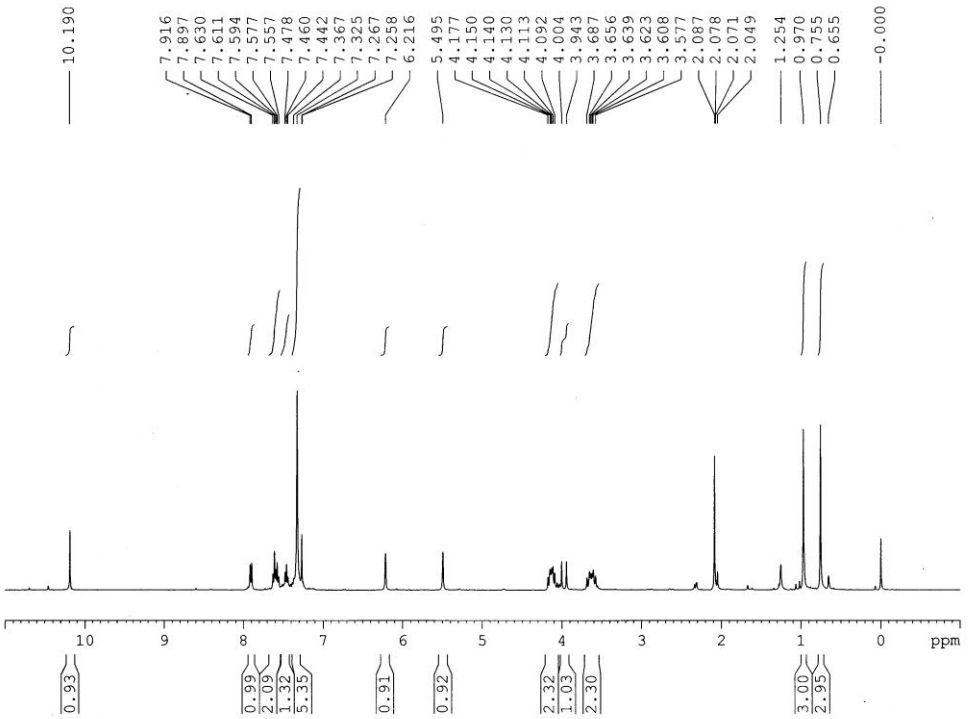
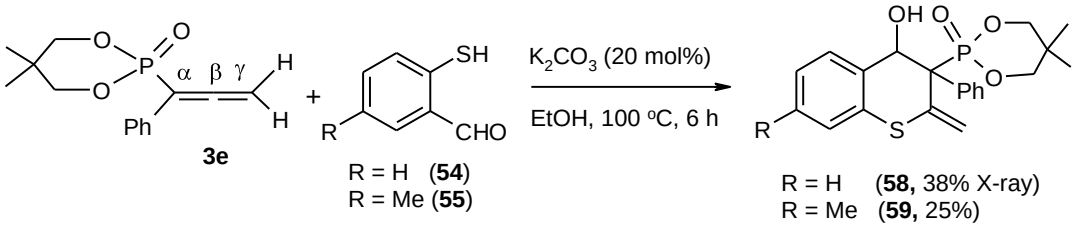


Figure 16. ^{1}H NMR spectrum for compound **57**

Phosphono-thiochroman **58** shows a band at 3302 cm^{-1} in IR spectrum, as expected for the OH stretch. In ^{1}H NMR spectrum, =C*H*$_2$ protons appear at δ 5.70 and 5.80 as doublets (cf. Figure 17). In the ^{13}C NMR spectrum, the carbon attached to phosphorus shows up at δ 58.6 with ^{1}J(P-C) value of 135.6 Hz due to P*C*H group. This derivative has also been characterized by X-ray crystallography (Figure 18). In addition to **58**, we have isolated the analogous product **59** from the reaction of allene **3e** with 5-methyl-2-mercaptobenzaldehyde **55 (**Scheme 22) using ethanol as the medium. This is because the yields of **58**-**59** are better using this solvent.

Scheme 22



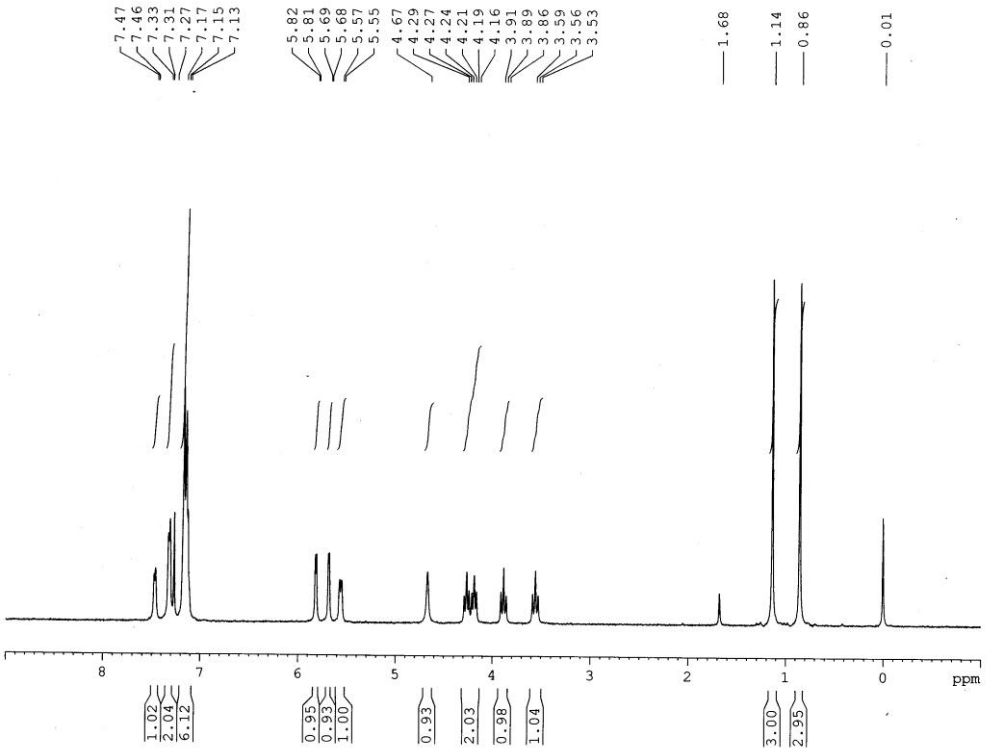


Figure 17. ^{1}H NMR spectrum for compound **58**

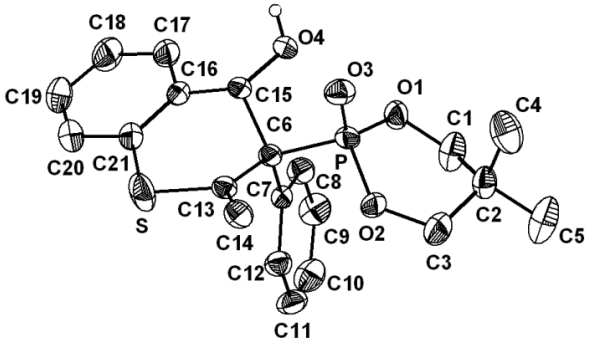


Figure 18. An ORTEP diagram of compound **58**. Hydrogen atoms other than the one attached to oxygen are not shown. Selected bond lengths [Å] with esd's in parentheses. P-C(6) 1.852(2), C(6)-C(7) 1.529(3), C(13)-C(14) 1.319(3), C(6)-C(15) 1.574(3), S-C(13) 1.771(2), O(4)-C(15) 1.406(3). [Hydrogen bond parameters: O(4)-H(4)**…**O(1') 0.84(3) 1.84(3) 2.673(3) 170.1 °; symmetry code: -x, -y, -z].

Under optimized conditions [K_2CO_3/ DMSO], we have conducted the reactions of 2-mercaptobenzaldehydes (thiosalicylaldehydes) **54-55** with allenylphosphonates **3e-j** for the synthesis of phosphono-thiochromans **56** and **60-70** (Scheme 23); this study was done for checking the scope and limitations of the reaction. The yields and *E*/*Z* ratios of the compounds based on the ^{31}P NMR spectra of the reaction mixtures are given in Table 6. We have separated individual isomers in all the cases except in **63, 69** (only *E*-isomer was isolated), **64** and **70** (isolated as mixture of *E* and *Z* isomers); since the R_f values were too close, this separation was tedious. The overall (combined) isolated yields of the two isomers are good (Table 7). Electron withdrawing groups, rather than electron donating groups on allene led to better results. This is possibly because in the presence of electron withdrawing group, the phenolate anion is more readily undergoes addition across allene and thus can lead to higher yields of the products.

Scheme 23

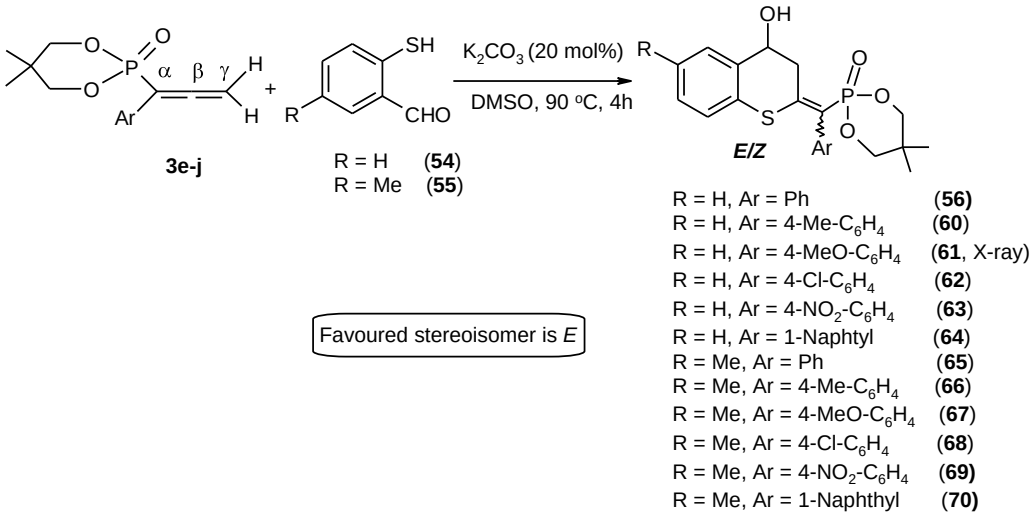


Table 6. Details on the yields of compounds **56** and **60-70** (cf. Scheme 23)

Entry	Compound	X	Ar	Yield (%) (*E*:*Z*)[a]
1	**56**	H	Ph	95 (1.0:0.4)
2	**60**	H	4-Me-C_6H_4	93 (1.0:0.3)
3	**61**	H	4-MeO-C_6H_4	93 (1.0:0.2)
4	**62**	H	4-Cl-C_6H_4	92 (1.0:0.3)
5	**63**	H	4-NO_2-C_6H_4	96 (1.0:0.3)

6	**64**	H	1-Naphthyl	75 (1.0:0.6)
7	**65**	Me	Ph	95 (1.0:0.3)
8	**66**	Me	4-Me-C_6H_4	93 (1.0:0.1)
9	**67**	Me	4-MeO-C_6H_4	91 (1.0:0.2)
10	**68**	Me	4-Cl-C_6H_4	91 (1.0:0.2)
11	**69**	Me	4-NO_2-C_6H_4	96 (1.0:0.3)
12	**70**	Me	1-Naphthyl	74 (1.0:0.4)

[a]Yields are based on ^{31}P NMR spectra of the reaction mixtures. The *E*/*Z* ratios of the compounds are given in the parentheses.

Table 7: ^{31}P NMR data and yields of the compounds **56** and **60-70**

Entry	Compound	δ(P)		Yield (%) (*E*:*Z*)[a]
		(*E*)	(*Z*)	
1	**56**	9.0	9.8	80 (1.0:0.4)
2	**60**	9.2	9.7	78 (1.0:0.3)
3	**61**	9.4	9.9	79 (1.0:0.2)
4	**62**	9.2	9.8	80 (1.0:0.3)
5	**63**	9.2	_	63 (1.0:0.3)
6	**64**	9.0	9.2	68 (1.0:0.6)
7	**65**	9.2	9.7	79 (1.0:0.3)
8	**66**	9.4	9.8	76 (1.0:0.1)
9	**67**	9.4	10.3	78 (1.0 0.2)
10	**68**	9.4	10.0	81(1.0:0.2)
11	**69**	9.4	_	64 (1.0:0.3)
12	**70**	9.2	9.4	67 (1.0:0.4)

[a]Isolated yields of the pure compounds = combined yield of *E* + *Z* isomers.

The structures of both *E* and *Z* isomers of **61** were confirmed by X-ray crystallography (Figure 19). Based on these data, we could assign the ^{31}P NMR chemical shifts for all other compounds. The signal for the *E*-isomer [δ(P) = 9.4] appears slightly upfield compared to that of the *Z*-isomer [δ(P) = 9.9]. For the identification of *E*- and *Z*-isomers, ^{13}C NMR and ^{1}H NMR spectra were also quite useful. In the ^{13}C NMR, the ^{1}J(P-C) value for the *E*-isomer [~ 187.0 Hz] is slightly higher than

that for the *Z*-isomer [~ 181.7 Hz]. In the ^{1}H NMR, the CH_2(CHOH) proton signals appear as two multiplets; for the *E*-isomer, both the multiplets appear in the same region δ 2.68-2.79 and for the Z-isomer, both are downfield to that for the *E*-isomer [δ ~3.45 and 3.78]. The ^{1}H NMR spectra of the *E*- and *Z*- isomers of **61** are shown in Figures 20 and 21 respectively.

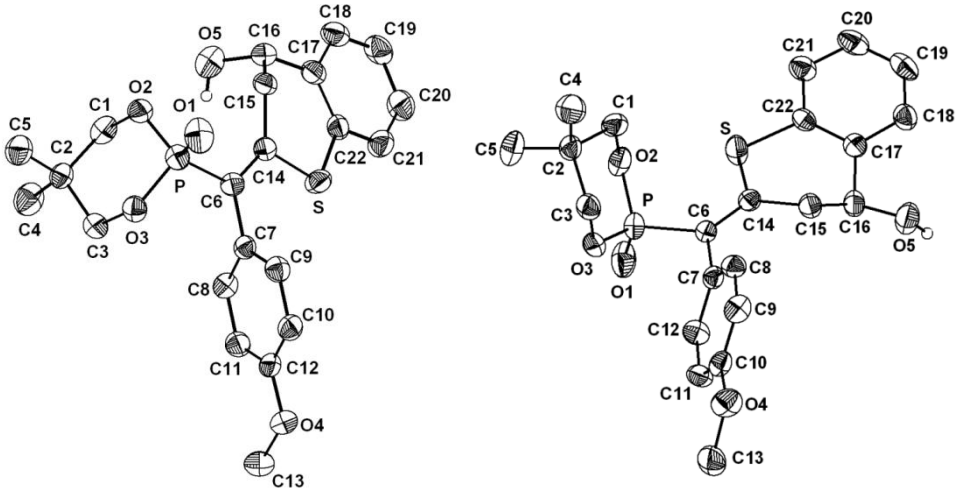


Figure 19. ORTEP diagrams for the compounds (a) (*E*)-**61** and (b) (*Z*)-**61**. Hydrogen atoms except at the OH group are omitted for clarity. Selected bond lengths [Å] with esd's in parentheses: Compound (*E*)-**61:** P-C(6) 1.797(3), C(6)-C(14) 1.346(4), C(14)-C(15) 1.503(4), C(15)-C(16) 1.505(5), S-C(14) 1.754(3), O(5)-C(16) 1.414(3). [Hydrogen bond parameters: O(5)-H(5)**…**O(1) 0.82 1.90 2.715(4) 171.8 ^{o}; symmetry code: 1+x, y, z].Compound (*Z*)-**61:** P-C(6) 1.803(3), C(6)-C(14) 1.344(4), C(14)-C(15) 1.505(4), C(15)-C(16) 1.520(5), S-C(14) 1.765(3), O(5)-C(16) 1.403(4). [Hydrogen bond parameters: O(5)-H(5)**…**O(1) 0.82 2.01 2.809(4) 166.3 ^{o}; symmetry code: 2-x, -y, 1-z].

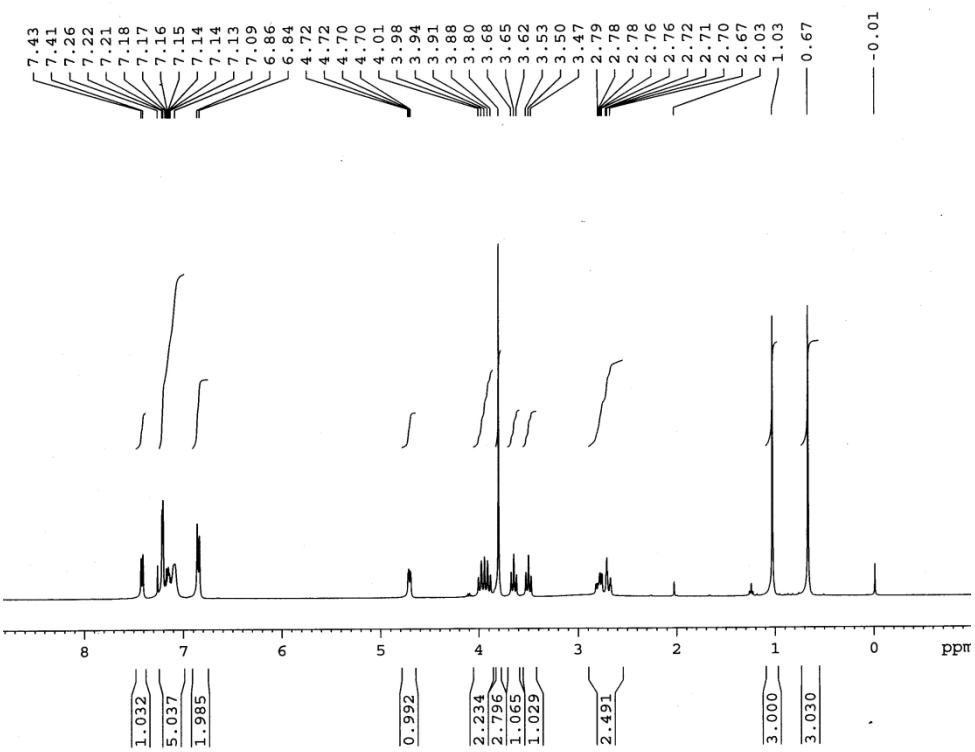


Figure 20. ^{1}H NMR spectrum for compound (*E*)-**61**

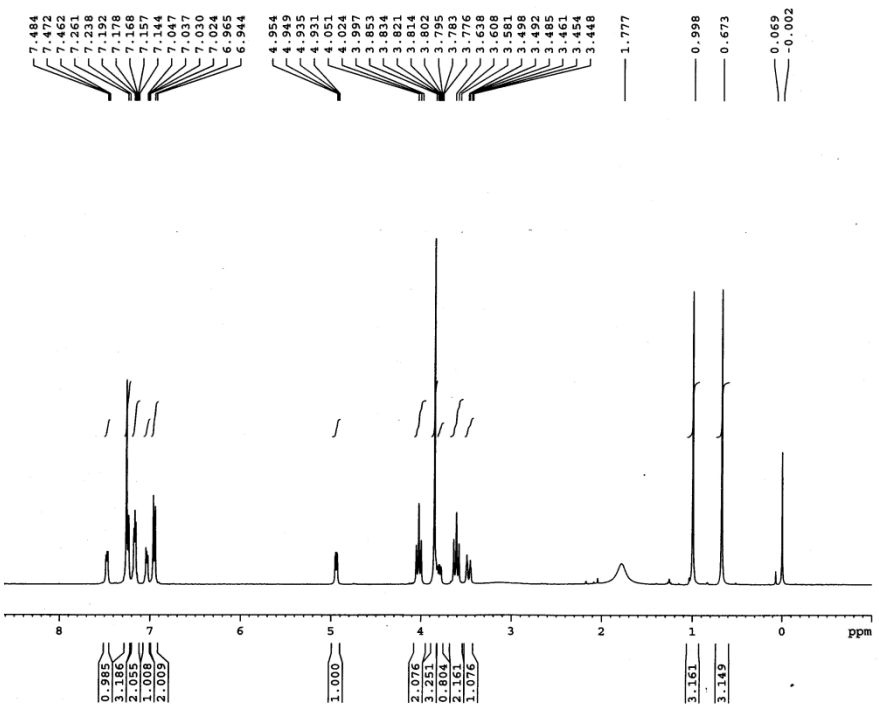
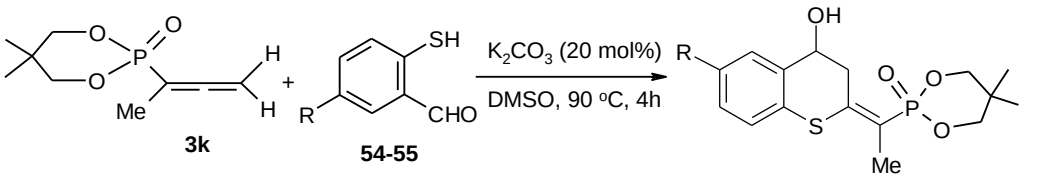


Figure 21. ^{1}H NMR spectrum for compound (*Z*)-**61**

2.52 Reaction of allenylphosphonate ($OCH_2CMe_2CH_2O)P(O)C(Me)=C=CH_2$ (3k) with 2-mercaptobenzaldehydes 54-55

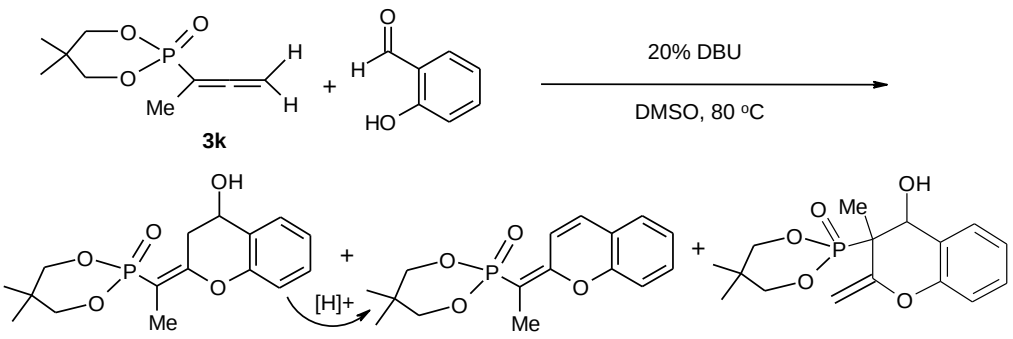
Under the optimized reaction conditions, the reaction of allenylphosphonate **3k** with *2-mercaptobenzaldehydes* **54-55** affords single isomer of phosphono-thiochromans **71-72** exclusively (Scheme 24). This is interesting because the reaction of salicylaldehyde with **3k** led to a mixture of phosphono-chromans and chromenes (Scheme 25) as reported from our laboratory recently.[47] Compound **71** shows a band at 3295 cm^{-1} in the IR spectrum corresponding to the OH stretch. In the ^1H NMR, =C(CH_3) signal appears at δ 2.10 mainly as a doublet [^3J(PH) = 14.0 Hz], but each of these is split further into two lines (J ~ 1.2 Hz) by only one of the ring CH_AH_B protons. This assertion is also consistent with the appearance of two multiplets for the ring CH_AH_B(CHOH) protons at δ 3.26 and 3.67. In the ^{13}C NMR, a doublet at δ 113.8 [^1J(PC) = 185.1] corresponding to the carbon attached to phosphorus is seen. The ^1H NMR spectrum of compound **71** is shown in Figure 22. The assignment of *E*-stereochemistry for the phosphono-thiochroman **71** is based on the X-ray structure which is shown in Figure 23.

Scheme 24



R = H (**71,** δ(P) 14.9, 86 %, X-ray)
R = Me (**72,** δ(P) 15.0, 85 %)

Scheme 25



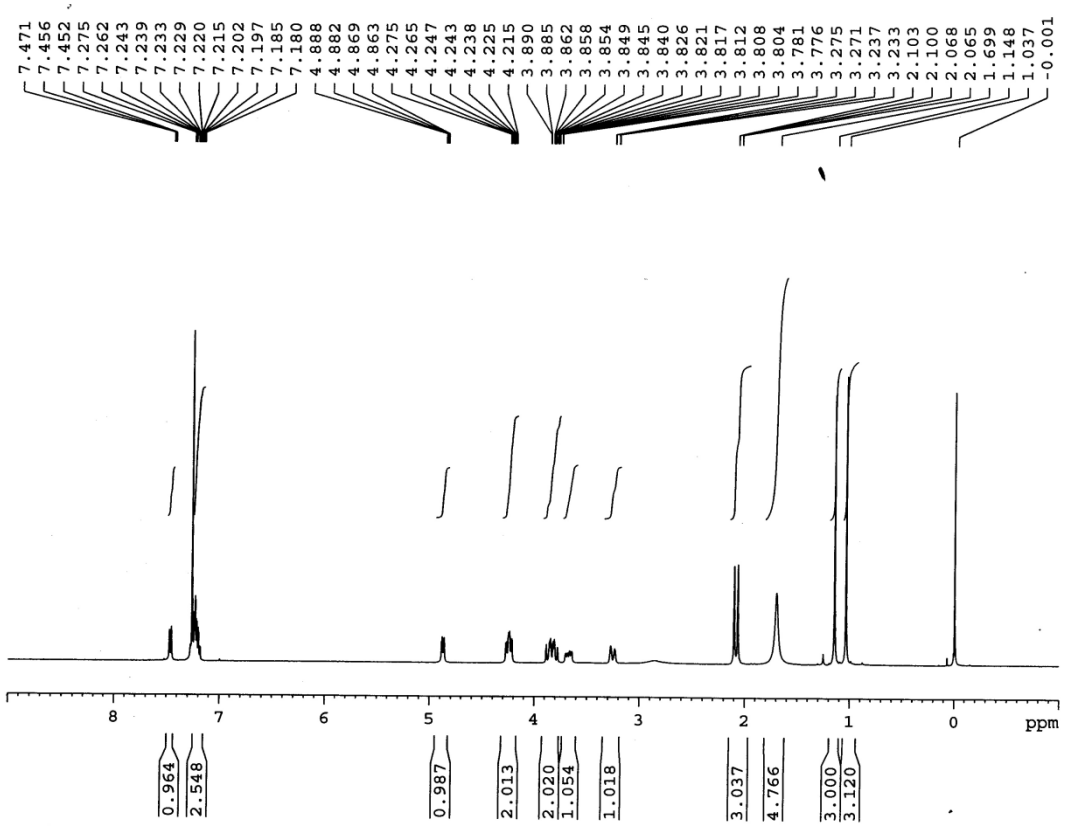


Figure 22. ^{1}H NMR spectrum for compound **71**

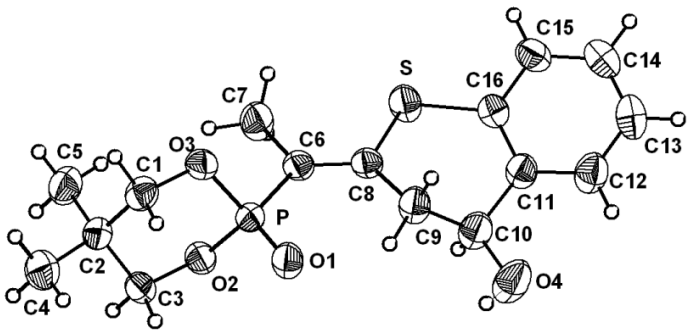


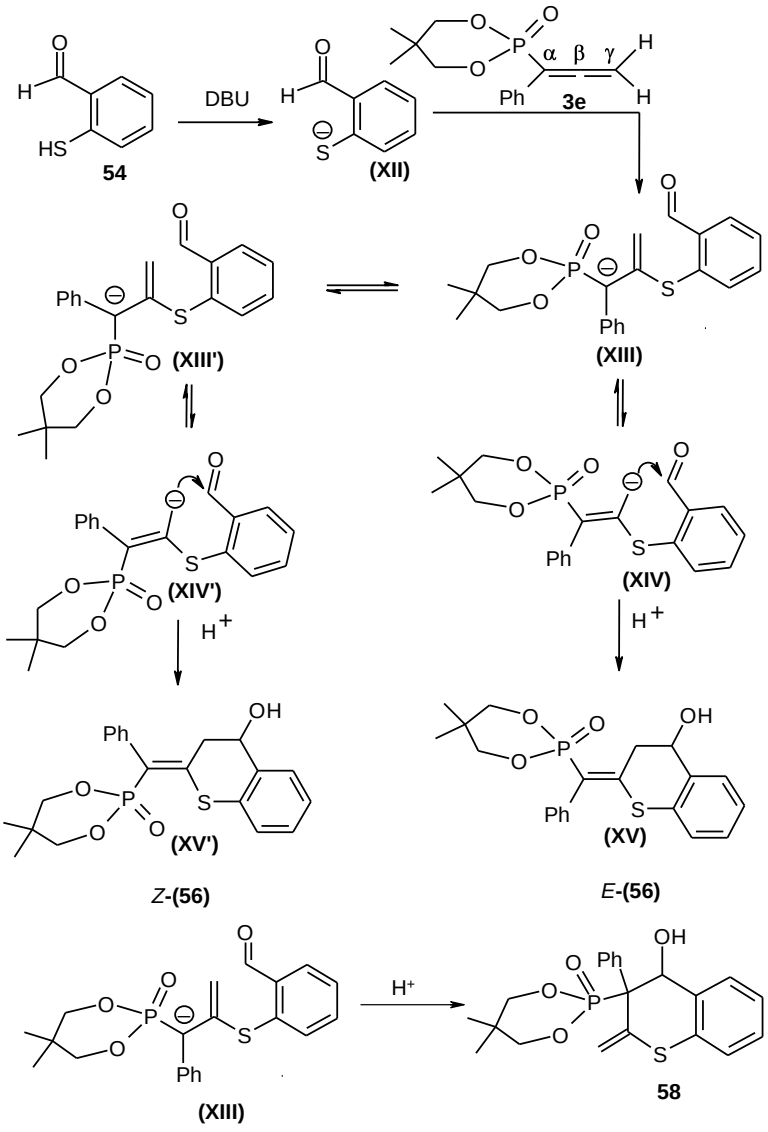
Figure 23. An ORTEP diagram of compound (*E*)-**71**. Selected bond lengths [Å] with esd's in parentheses. P-C(6) 1.772(3), C(6)-C(8) 1.346(4), C(8)-C(9) 1.500(3), C(9)-C(10) 1.532(4), S-C(8) 1.765(2), O(4)-C(10) 1.389(3). [Hydrogen bond parameters: O(4)-H(4)**…**O(1) 0.82 1.90 2.699(3) 164.3 ^{o}; symmetry code: 1-x, 1-y, 1-z].

2.53 Mechanistic aspects of the reaction of allenylphosphonates with 2-mercaptobenzaldehydes

A plausible mechanism for the reaction which proceeds most likely through a

domino oxo-Michael addition followed by aldol condensation[47,57c] is shown in Scheme 26. Here two possibilities exist: (β,α)-attack and (β,γ)-attack. The first one leads to the kinetically controlled product (**58**) and the second one leads to thermodynamically controlled product (**56**). First, the base (K_2CO_3) abstracts proton from 2-mercaptobenzaldehyde and generates thiolate intermediate **XII** which reacts with allenylphosphonate **3e** at β-position to give **XIII.** Species **XIII** is in equilibrium with **XIII'**. These intermediates can give rise to **XIV** or X**IV'**, because γ-addition is preferred at elevated temperatures.[57c] Intermediates **XIV** and **XIV'** undergo intramolecular aldol reaction followed by protonation to afford the final products (*E)*-**56** and (*Z*)-**56**. Formation of **58** occurs *via* **XIII** without the rearrangement of carbanion, as shown by the last equation in Scheme 26.

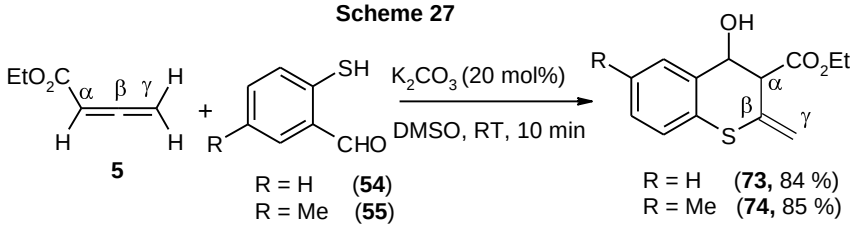
Scheme 26

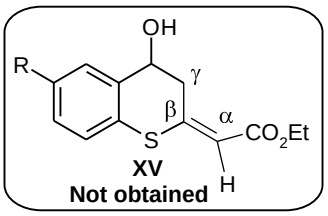


2.54 Reactions of ester allene $(EtO_2C)CH=C=CH_2$ (5) with 2-mercaptobenzaldehydes 54-55

In continuation of the work on thiochromans, we treated ester allene **5** with 2-mercaptobenzaldehydes **54-55** in the presence of 20 mol% K_2CO_3 in DMSO at room temperature. The reaction was completed in 10 min and led to thiochromans **73-74** as exclusive products (Scheme 27). Longer reaction times led to a mixture of products. Compound **73** shows a band centred at 3457 cm^{-1} in the IR spectrum corresponding to OH stretching. In the ^1H NMR, olefinic =CH_2 protons appear as two singlets in the region δ 5.25-5.50 and C*H*(OH) appears as a doublet at δ 5.13 (*J* = 6.0 Hz). Thus this (and **74**) is a (β,α)-product; it may be noted that in the alternative (β,γ)-product **XV**, only one olefinic proton [and an upfield CH_2 multiplet] should have been observed. This reaction is similar to that reported earlier with normal salicylaldehydes.Since the analogous allenylphosphonate $(OCH_2CMe_2CH_2O)P(O)CH=C=CH_2$ (**3a**) underwent isomerization to the alkyne $(OCH_2CMe_2CH_2O)P(O)C{\equiv}CMe$ under these conditions, an exact comparison between the two systems could not be made.

Scheme 27



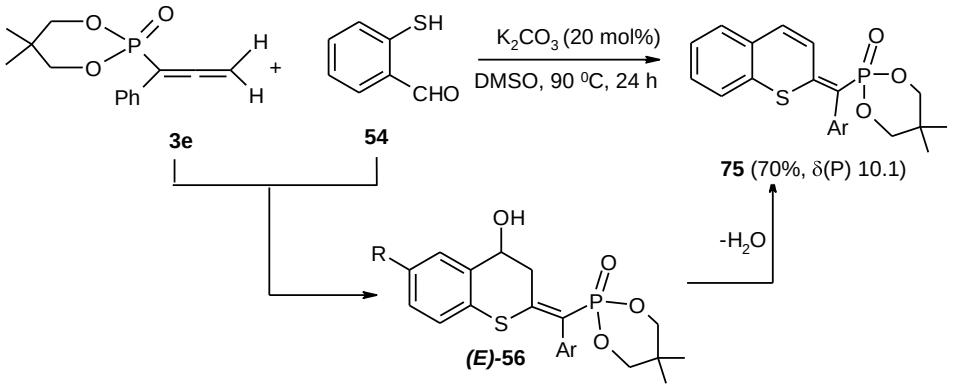


2.55 Synthesis of a phosphono-thiochromene by dehydration of thiochroman 56

After establishing the above reaction, we wanted to synthesize phosphono-thiochromenes, by dehydrating the hydroxyl substituted chromans prepared by us. This could be readily accomplished in the reaction using allenylphosphonate **3e** with 2-mercaptobenzaldehyde **54** by simply prolonging the reaction time from 4 h to 24 h. Thus we could obtain phosphono-thiochromene **75** (Scheme 28) in good yield. In

this compound, appearance of two olefinic protons signals and disappearance of the signals due to thiochroman ring CH_2 protons (present in **56**) in ^{1}H NMR establishes the structure as depicted. Since the isomer of **56** with (*E*)-configuration was the major product prior to dehydration, an analogous (*E*) configuration is assigned to **75**.

Scheme 28



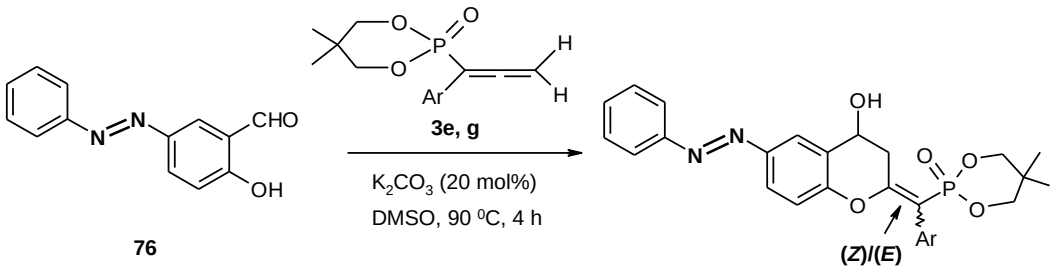
2.56 Comparison of the reactivity of allenylphosphonates with other allenes in their reaction with 2-mercaptobenzaldehydes

Under base catalyzed reactions, the reactivity of allenylphosphonates with 2-mercaptobenzaldehyde is lower (and different) when compared to that with ester-allenes.[57] For example, the reaction of allenylphosphonates with 2-mercaptobenzaldehyde in the presence 20 mol% K_2CO_3 took longer time (4 h under heating) whereas the ester allene $(EtO_2C)CH=C=CH_2$ (**5**) took just 10 min at room temperature (25 ^oC). The allenylphosphonate $(OCH_2CMe_2CH_2O)P(O)CH=C=CH_2$ (**3a**) isomerized to alkyne (i.e. it did not react with 2-mercaptobenzaldehyde) in the presence of a base but ester allene **5** gave chromans. In the case of α-substituted allenylphosphonates (**3e-j** and **3k**), (β,γ)-attack is favored (Scheme 23 and Scheme 24) whereas in the case of ester allene **5** (β,α)-attack is favored (Scheme 27). We suspect that subtle steric factors contribute to these differences, but have not studied this in greater depth.

2.6 Base catalyzed reactions of allenylphosphonates ($OCH_2CMe_2CH_2O$)P(O)C(R)=C=CH_2 3e-k with *azo*-substituted salicylaldehydes 76-77

Although the reaction of simple salicylaldehydes with allenylphosphonates had been studied prior to this work from our laboratory,[47] it was thought useful to extend this part of the work to those salicylaldehydes with pendant chromophores such that the products may be useful as pigments in a later work. With this idea in mind, under the conditions employed for 2-mercaptobenzaldehydes, we first treated the *azo*-substituted salicylaldehyde **76**[82] with the allenylphosphonate **3e** and **3g** and obtained the phosphono-chromans **78-79** as (*Z*) and (*E*) isomeric mixtures (Scheme 29). Both the *azo*-substituted salicylaldehyde **76** and the corresponding phosphono-chromans **78-79** are red in color. The (*Z*) and (*E*) isomers for both **78** and **79** have been isolated by using column chromatography.

Scheme 29



Both the isomers (*E*)-**78** and (*Z*)-**78** show a band at in the region of 3300 cm^{-1} in the IR corresponding to OH stretch. Based on comparison of NMR data with phosphono-thiochromans described in previous sections, we could assign the ^{31}P NMR chemical shifts for these isomers. The signal for the *E*-isomer [δ(P) = 10.4] appears upfield compared to that for the *Z*-isomer [δ(P) = 14.5]. For the identification of *E*- and *Z*-isomers, ^{13}C NMR and ^{1}H NMR spectra were also quite useful. In the ^{13}C NMR, the ^{1}J(P-C) value for the *E*-isomer [~ 169.1 Hz] is lower than that for the *Z*-isomer [~ 188.4 Hz]. In the ^{1}H NMR, the chroman CH_2(CHOH) protons signal appear as two well-separated multiplets for the *Z*-isomer [centered at 3.14 and 3.93] while they show a close multiplet for the *E*-isomer [δ 2.64-2.97] [note: there are also other signals in the same region due to -OCH_2 protons of the 1,3,2-

dioxaphosphorinane ring and the O*H* proton of the chroman]. The ^{1}H NMR spectra of the (*E*)-**78** and (*Z*)-**78** are shown in Figures 24 and 25 respectively.

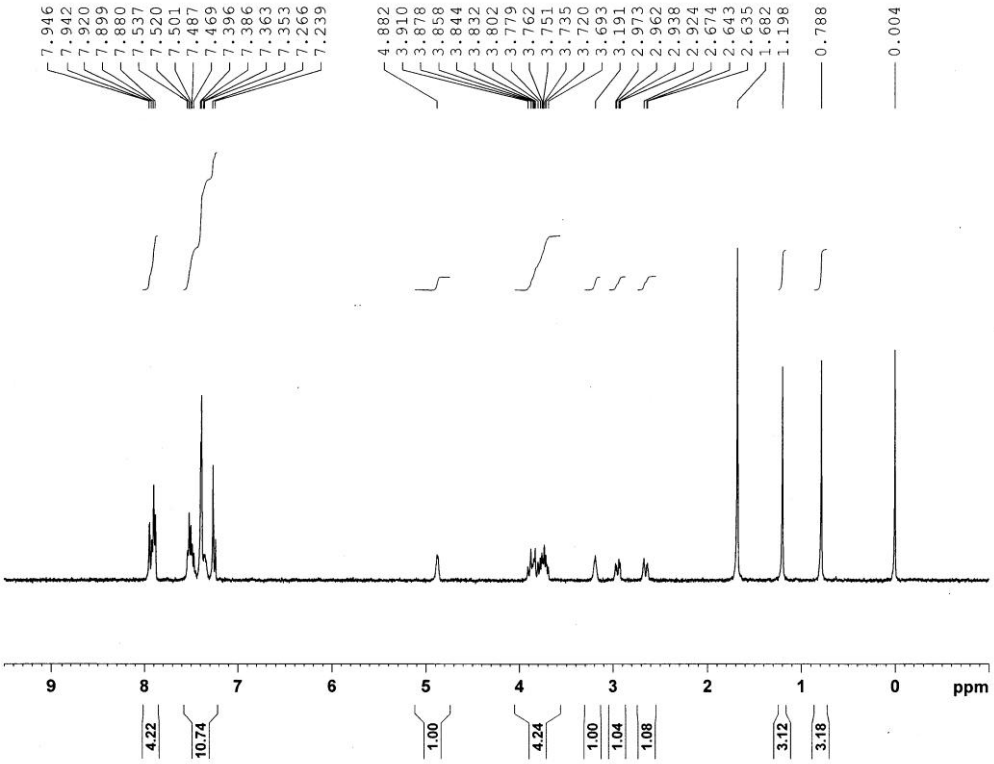


Figure 24. ^{1}H NMR spectrum for compound (*E*)-**78**

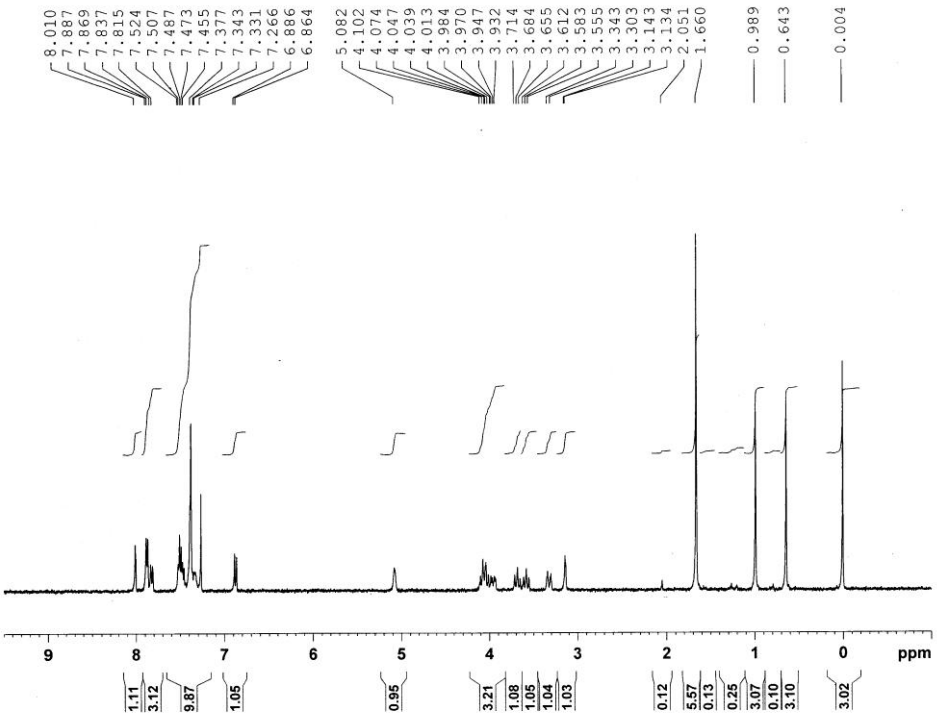


Figure 25. ^{1}H NMR spectrum for compound (*Z*)-**78**

Using the above conditions, the reaction of allene **3f** with the *azo*-substituted salicylaldehyde **76** led to a mixture of chromans and chromenes because one isomer of chroman underwent faster dehydration [cf. section 2.55]. Hence we continued the reaction for 24 h to obtain the chromene exclusively. Under these modified conditions, the reaction of *azo*-substituted salicylaldehydes **76-77** with allenylphosphonates **3e-h** afforded phosphono-*azo*-chromenes **80-87** (Scheme 30). The yields and *E*/*Z* ratio of the compounds based on the ^{31}P NMR spectra of the reaction mixtures are given in Table 8. We have also separated individual isomers in all the cases. The overall (combined) isolated yields of the two isomers are moderate to good (Table 9).

Scheme 30

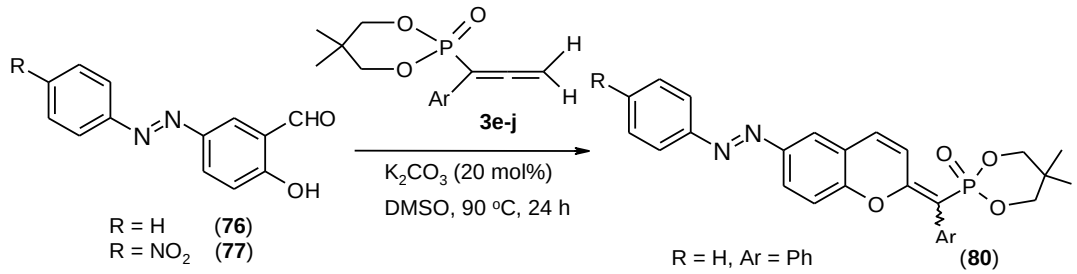


Table 8. Details on the yields of the (*E*) and (*Z*) isomers of **80-87**

Entry	Compound	R	Ar	Yield (%) (*E*:*Z*)[a]
1	**80**	H	Ph	95 (1.0:0.9)
2	**81**	H	4-Me-C_6H_4	94 (0.8:1.0)
3	**82**	H	4-MeO-C_6H_4h	92 (0.7:1.0)
4	**83**	H	4-Cl-C_6H_4	95 (1.0:1.0)
5	**84**	NO_2	Ph	93 (1.0:1.0)
6	**85**	NO_2	4-Me-C_6H_4	94 (1.0:0.6)
7	**86**	NO_2	4-MeO-C_6H_4	92 (1.0:1.0)
8	**87**	NO_2	4-Cl-C_6H_4	95 (1.0:1.0)

[a]Yields are based on ^{31}P NMR spectra of the reaction mixtures. The *E*/*Z* ratios of the compounds are given in parentheses.

Table 9: ^{31}P NMR data and isolated yields of the (*E*) and (*Z*) isomers of **80-87**

Entry	Compound	δ(P)		Yield (%)(*E*:*Z*)[a]
		(*E*)	(*Z*)	
1	**80**	14.9	11.7	76 (1.0:0.9)
2	**81**	15.2	11.9	72 (0.8:1.0)
3	**82**	15.3	12.0	73 (0.7:1.0)
4	**83**	15.0	11.4	74 (1.0:1.0)
5	**84**	14.5	11.2	80 (1.0:1.0)
6	**85**	14.7	11.5	76 (1.0:0.6)
7	**86**	14.9	11.6	76 (1.0:1.0)
8	**87**	14.6	11.0	78 (1.0:1.0)

[a]Isolated yields of the pure compounds = combined yield of *E*+*Z* isomers.

The compound (*E*)-**81** is characterized by X-ray crystallography (Figure 26). Based on this information (and of course, its NMR data), we could assign the ^{31}P NMR chemical shifts for all the other compounds. The signal for the *E*-isomer [δ(P) = 15.2] appears downfield compared to that of the *Z*-isomer [δ(P) = 11.9]. We further confirmed the identity of *E*- and *Z*-isomers by ^{13}C NMR and ^{1}H NMR spectra as explained in earlier sections. Additionally, in the ^{13}C NMR spectra, the signal for PC(Ph)=*C* carbon of *E*-isomer appears as a doublet at δ 158.6 [^{2}J(P-C) = 34.9 Hz] but in the case of *Z*-isomer, it is almost a singlet at δ 158.0 [low ^{2}J(P-C)]. The ^{13}C NMR spectra of the (*E*)-**81** and (*Z*)-**81** are shown in Figures 27 and 28 respectively. In the ^{1}H NMR, the (Ph)C=C-C*H*= proton signal appears as a doublet and is downfield [δ(H) ~ 6.9] in the *E*-isomer when compared to the *Z*-isomer [δ(H) ~ 6.4; in some cases it is a doublet of doublet with low ^{4}J(P-H) of ~ 1.7 Hz].

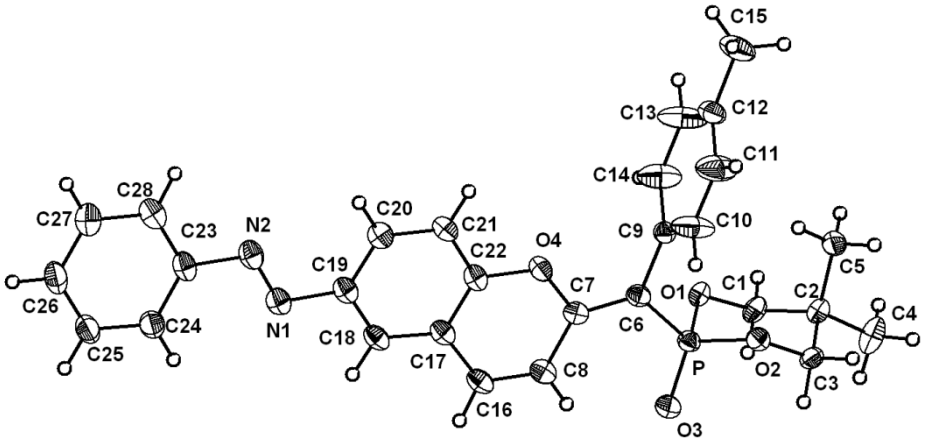


Figure 26. An ORTEP diagram of compound (*E*)-**81**. Selected bond lengths [Å] with esd's in parentheses: P-C(6) 1.766(2), C(6)-C(7) 1.358(3), C(7)-C(8) 1.442(3), C(8)-C(16) 1.337(3), O(4)-C(7) 1.381(2).

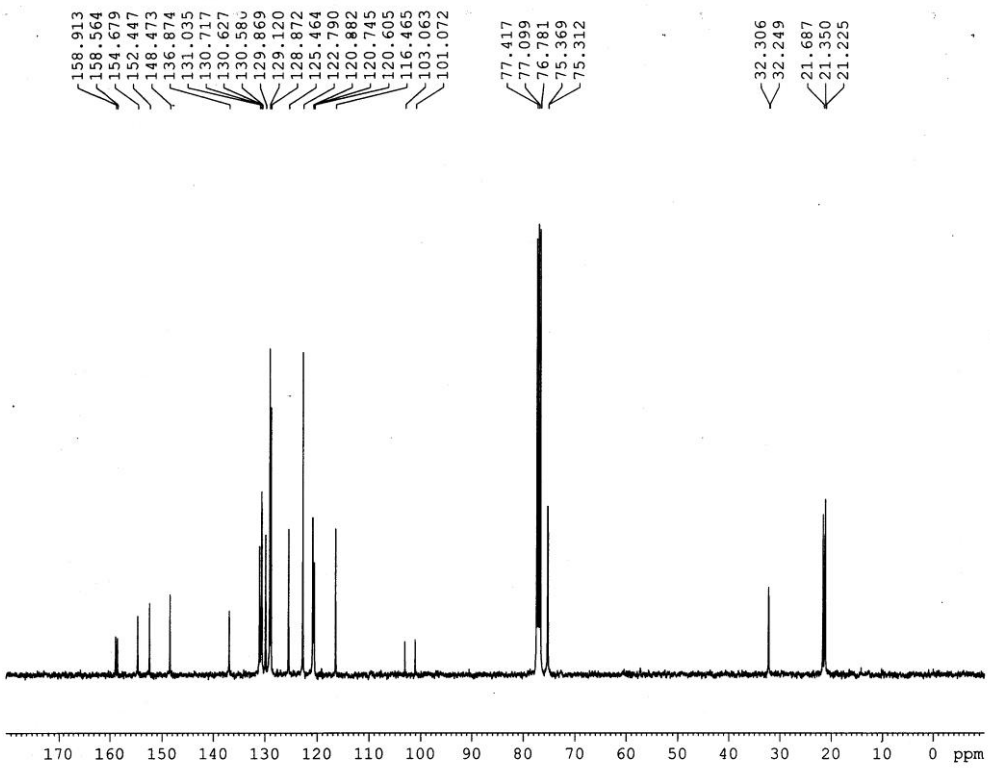


Figure 27. ^{13}C NMR spectrum for the compound (*E*)-**81**

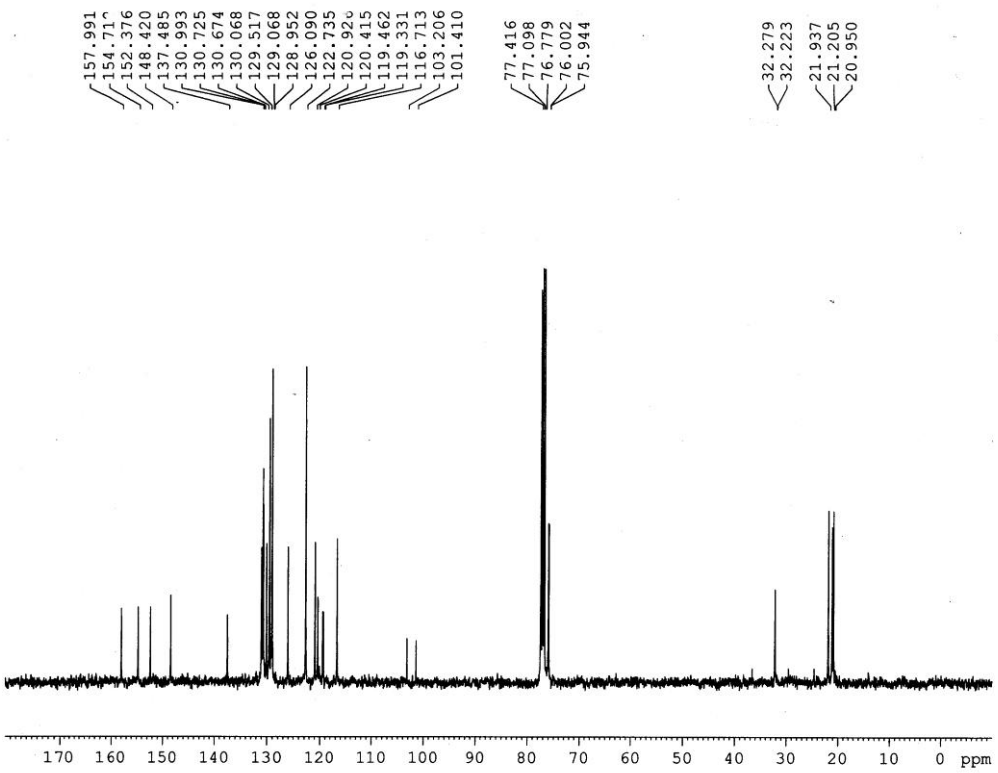
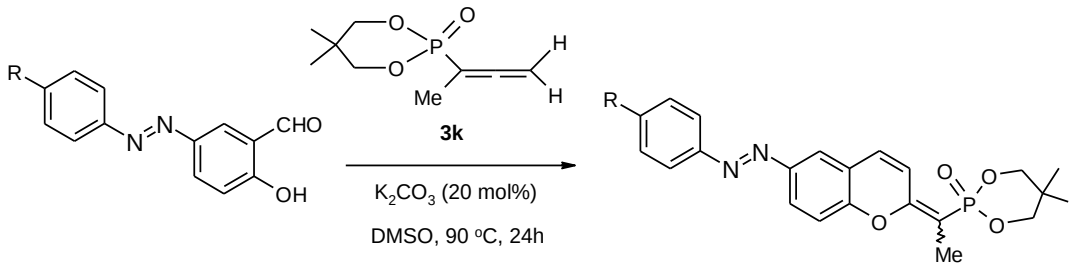


Figure 28. ^{13}C NMR spectrum for the compound (*Z*)-**81**

Under the conditions as described above, the reaction of allene $(OCH_2CMe_2CH_2O)P(O)C(Me)=C=CH_2$ (**3k**) with *azo*-substituted salicylaldehydes gave phosphono-chromenes **88**-**89** (Scheme 31). The ratio of (*E*)/(*Z*) isomers is ~3:2, in favor of the former. In these cases, we were able to obtain the isomers (*E*)-**88**, (*Z*)-**88** and (*E*)-**89** in pure state. Since this result is similar to that discussed above, it is not discussed further.

Scheme 31



Absorption spectroscopy of azo-substituted chromenes 84-87

We have recorded the absorption spectra for the compounds **84-87** (both *E* and *Z*-isomers) in acetonitrile (Figure 29). It can be noted that the longest absorption maximum around 380 ± 3 nm is observed for all the compounds. The nature of the absorption maximum for the *E* and *Z* isomers remained the same except in the region of 250 – 300 nm where an additional band in the higher energy region, 250 – 300 nm is observed for *E*- isomer that may be due to ground state charge transfer which is absent in the Z-isomer (Figure 30). Comparison of the absorption spectra of starting material **77** and the product **85** indicates that a new band arose in the low energy region due to cyclization.

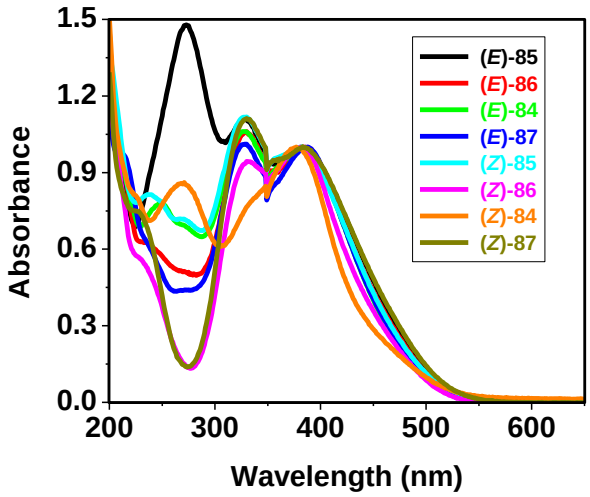


Figure 29: Absorption spectra for the compounds **84-87** in acetonitrile

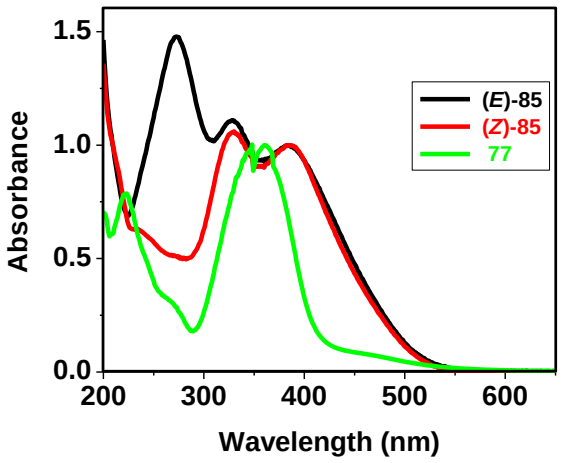


Figure 30: Absorption spectra for the compound (*E*)-**85,** (*Z*)-**85** and *azo*-substituted salicylaldehyde **77** (green) in acetonotrile.

2.7 Base catalyzed reaction of allenes with 3-chloro-2-formylindole - Formation of pyrrolo-indoles

In the formation of chromans/ chromenes discussed above, one of the reactants is a salicylaldehyde that possesses an –OH/ -SH as well as a –CHO group that are required for the cyclization process. Hence we surmised that in cases wherein an =NH and a CHO group are suitably placed in the reactant, cyclization can be effected when such reactants are treated with allenic substrates. 3-Chloro-2-formylindole (**90**) is one such reactant that can be readily prepared.[83] Thus the reaction of allenylphosphonates **3e-k** with **90** in the presence of base can lead to pyrroloindoles; these reactions are discussed here. The experimental conditions were standardized by using the allenylphosphonate **3e**, because the products could be characterized more readily. We have then used an ester allene, allenylphosphonates and allenylsulfones and then compared their reactivity.

2.71 Reaction of $(OCH_2CMe_2CH_2O)P(O)C(Ar)=C=CH_2$ (3e-j) with3-chloro-2-formylindole (90) in PEG-400 (a green medium)

The allenylphosphonate **3e** reacts with 2-formylindole **90** in the presence of K_2CO_3 in DMSO at 90 ^oC/ 4 h leading to the phosphono-pyrroloindole **91** (Scheme 32) in low yield and only 50% of allene is consumed in the reaction. Increase in the reaction time leads to a mixture of products. Hence, we optimized the reaction conditions by checking different bases/ solvents. The results are summarized in the Table 10. As can be seen from Table 10, the conditions previously used in reactions using 2-mercaptobenzaldehydes were ineffective or led to a mixture (Table 10, entries 1 and 2). In some cases, a mixture of isomers (Table 10, entries 4, 5) was obtained. The best combination was K_2CO_3 - PEG-400 (Table10, entry 11). Use of K_2CO_3 as the base and PEG-400 as the medium, the reaction led to phosphono-pyrroloindole **91** (*E*-isomer) exclusively and stereoselectively [^{31}P NMR evidence].

Scheme 32

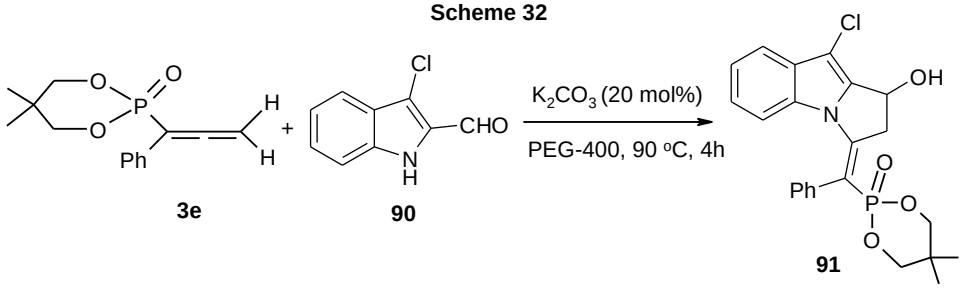


Table 10. Effect of reaction conditions on the yield of **91** in reaction of allene **3e** with **90**

Entry	Base/ Solvent	Time (h)/ temp (^oC).	Yield[a] (%)
1	K_2CO_3/ DMSO	4/ 90	50
2	K_2CO_3/ DMSO	24/ 90	14
3	K_2CO_3/ CH_3CN	12/ 90	46
4	K_2CO_3/ EtOH	12/ 90	37
5	K_2CO_3/ DMF	4/ 90	36
6	PPh_3/ PEG-400	12/ 90	No reaction
7	DABCO/ PEG-400	12/ 90	No reaction
8	NaOAc/ PEG-400	4/ 90	53
9	K_3PO_4/ PEG-400	4/ 90	75
10	DBU/ PEG-400	6/ 90	80
11	K_2CO_3/ PEG-400	4/ 90	82[b]

[a]Yields are calculated by using ^1H and ^{31}P NMR spectroscopy; [b]isolated yield 74%

Under the optimized reaction conditions, we then conducted the reaction of allenylphosphonates **3e-j** with 3-chloro-2-formylindole **90** for the synthesis of different phosphono-pyrroloindoles **91-96** and also for checking the scope of the reaction (Scheme 33). The yields and ^{31}P NMR signal of the compounds are given in Table 11. In most of the cases the yields are good to very good. A single stereoisomer (*E*) is formed except in the case of **96**. As for characterization, we take **93** as the example. In the IR spectrum, a sharp band at 3272 cm^{-1} is observed for the OH stretch. In the ^1H NMR, O*H* signal appears at δ 5.44 and CH_2(CHOH) protons appear as two doublets (AM pattern) in the region of δ 3.52-3.74. In the ^{13}C NMR, a doublet at δ 103.1 (^1J(PC) = 185.0 Hz) corresponding to (Ph)C=*C*P is seen. The ^1H NMR spectrum of compound (*E*)-**93** is illustrated in Figure 31. All these compounds are (β,γ)-cyclized products.

Scheme 33

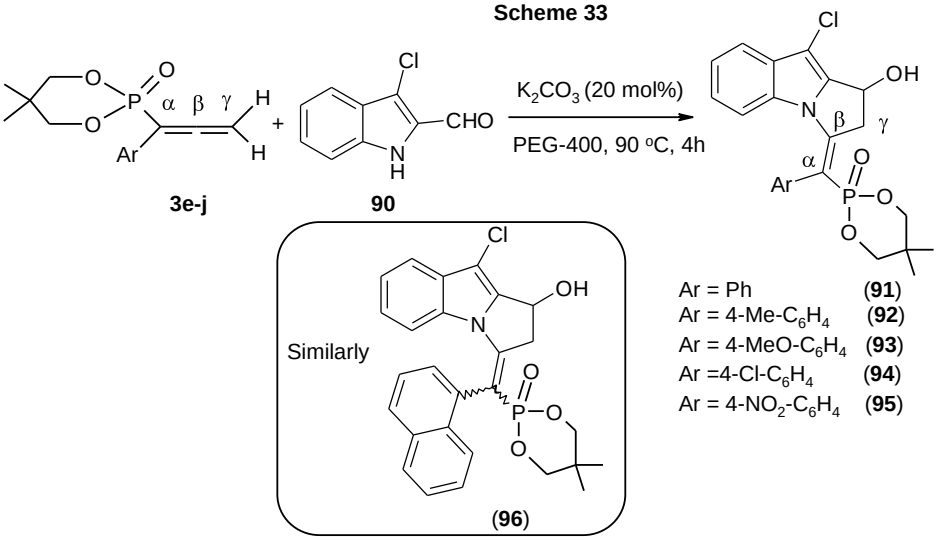


Table 11. Details on the yields and ^{31}P NMR data of compounds **91-96**

Entry	Compound	Ar	δ(P)	Isolated yield (%)
1	**91**	Ph	15.1	74
2	**92**	4-Me-C_6H_4	15.6	70
3	**93**	4-MeO-C_6H_4	15.9	69
4	**94**	4-Cl-C_6H_4	15.2	71
5	**95**	4-NO_2-C_6H_4	14.8	75
6	**96**	1-Naphthyl	13.7, 14.7	68 (combined)

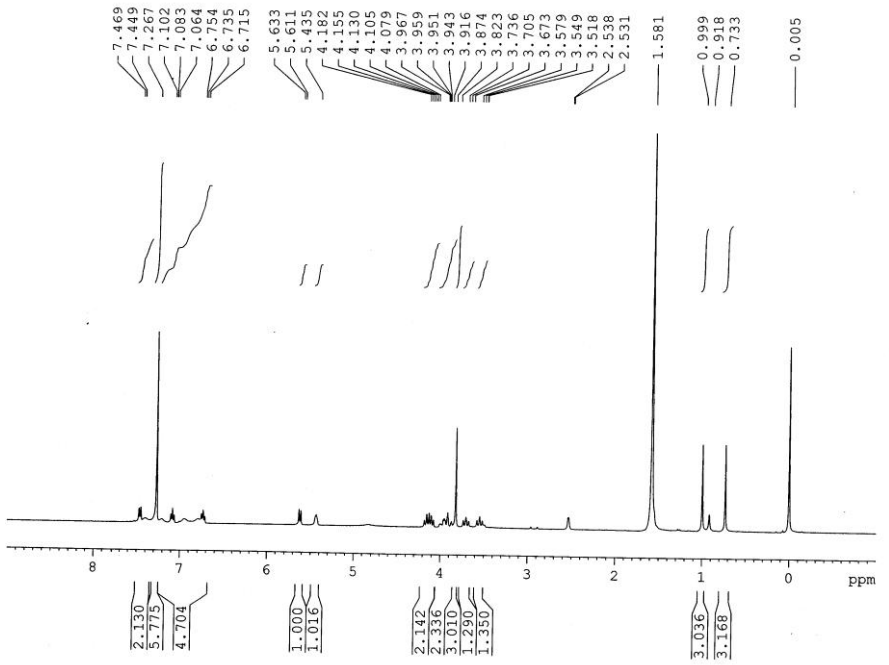
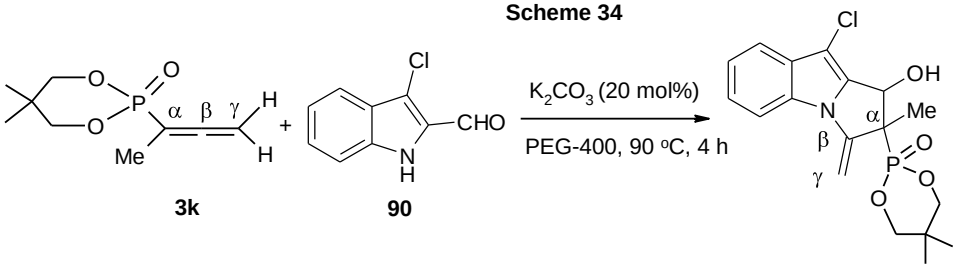


Figure 31. ^{1}H NMR spectrum for the compound (*E*)-**93**

2.72 Reaction of (OCH$_2$CMe$_2$CH$_2$O)P(O)C(Me)=C=CH$_2$ (3k) with 3-chloro-2-formylindole 90

In contrast to the reactions of α-aryl allenylphosphonate **3e-j** discussed above, the α-methyl allenylphosphonate **3k** behaves differently and affords the (β,α)-cyclized product **97** (Scheme 34) as the only product, but ~50% of the allene **3k** is left unreacted. We have not been successful so far in increasing the yield by adding more base or by increasing the reaction time. As regards characterization, IR [OH stretch 3750 cm^{-1}], ^{1}H NMR [δ 1.64 (d, ^{3}J(PH) = 17.2 Hz), =CC(C*H*$_3$); 4.87 (s), 5.34 (s), =C*H*$_2$, 5.62 (d, ^{3}J(PH) = 12.8 Hz, C*H*(OH))] and ^{13}C NMR [δ 53.6 (d,^{1}J(PC) = 137.0 Hz] show distinctive bands/ peaks. Further confirmation of the structure is provided by X-ray crystallography (Figure 32).

Scheme 34



3k **90**

97 [δ(P);24.6, X-ray]
Isolated yield: 40%

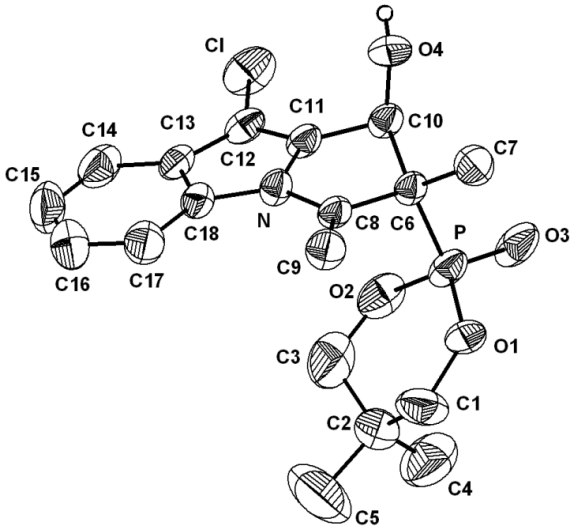


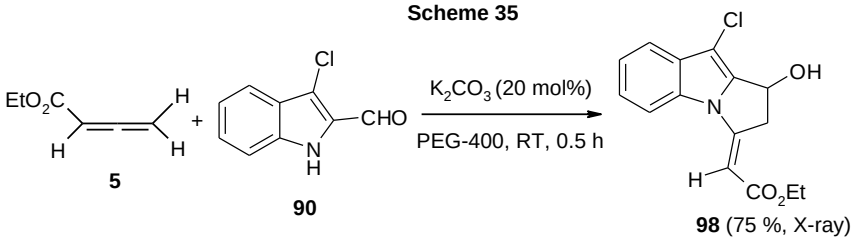
Figure 32. An ORTEP diagram of compound **97**. Hydrogen atoms except at the OH group are omitted for clarity. Selected bond lengths [Å] with esd's in parentheses: P-C(6) 1.816(2), C(6)-C(8) 1.522(3), C(8)-C(9) 1.314(3), C(6)-C(10) 1.580(3), N-C(8) 1.403(3), O(4)-C(10) 1.413(2). [Hydrogen bond parameters: O(4)-H(4)**…**O(1) 0.81 1.94 2.751(3) 172.5 ^{o}; symmetry code: 1-x, 1/2+y, 1/2-z].

2.73 Reaction of ester allene (EtO_2C)CH=C=CH_2 (5) with 3-chloro-2-formyl indole 90

The reaction of allene **5** with **90** leads to the pyrroloindole (*E*)-**98** which is a (β,γ)-cyclized product (Scheme 35). Spectroscopic and analytical data are consistent with the proposed structure; the ^{1}H NMR spectrum is shown in Figure 33. The (*E*)-configuration is established by X-ray crystallography (Figure 34).

This feature may be contrasted with the reaction of the same allene with salicylaldehydes wherein (β,α)-cyclized derivatives are obtained as major products (Scheme 1.62 Chapter 1).[57b] It is to be noted that even with 2-mercaptobenzaldehydes we obtained only (β,α)-cyclized derivatives (Scheme 27 above).

Scheme 35



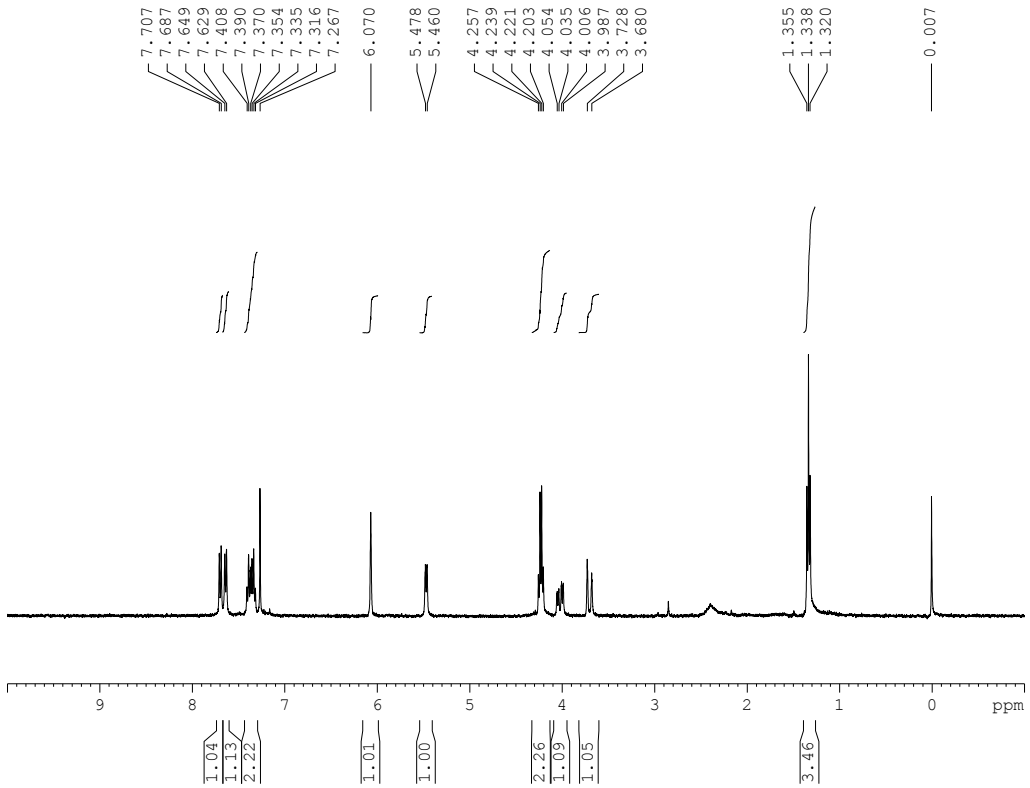


Figure 33. ^{1}H NMR spectrum for the compound **98**

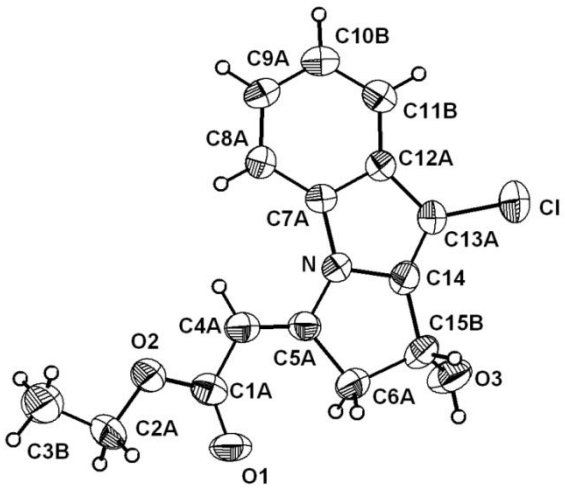
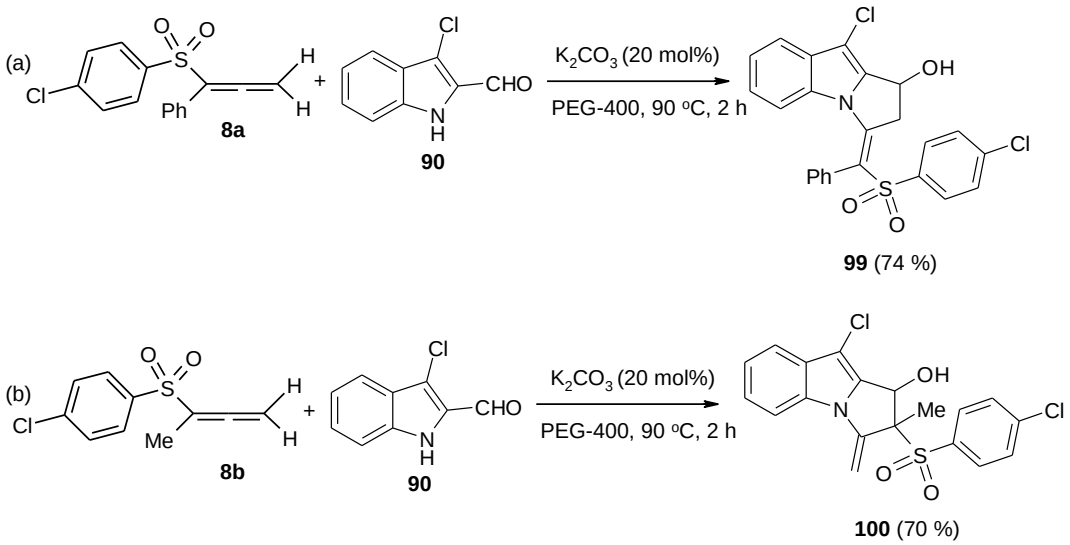


Figure 34. An ORTEP diagram of compound (*E*)-**98**. Selected bond lengths [Å] with esd's in parentheses. C(4A)-C(5A) 1.343(4), C(5A)-C(6A) 1.500(3), C(6A)-C(15B) 1.536(4), N(1)-C(5A) 1.378(3), O(3)-C(15B) 1.415(3). [Hydrogen bond parameters: O(3)-H(3)**…**O(1) 0.82 2.01 2.813(3) 165.6 ^{o}; symmetry code: 1-x, -y, -z].

2.74 Reaction of allenylsulfones 8a-b with 3-chloro-2-formylindole 90

As an electron withdrawing group, the sulfonyl group ($ArSO_2$-) is comparable to the phosphoryl [$(RO)_2P(O)$] or the ester group. Thus we desired to compare the reactivity of allenes bearing these groups. In this context, we treated the allenylsulfones **8a-b** with 3-chloro-2-formylindole (**90**) and obtained sulfonated pyrroloindoles **99** and **100** in good yields (Scheme 36). The α-phenyl allene **8a** gave (β,γ)-cyclized product **99**, while the α-methyl allene **8b** gave the (β, α)-cyclized product **100**. Distinction between the two types of products can be made readily on the basis of ^{1}H NMR by looking at the presence/ absence of the signals due to the olefinic =CH_2 protons.

Scheme 36



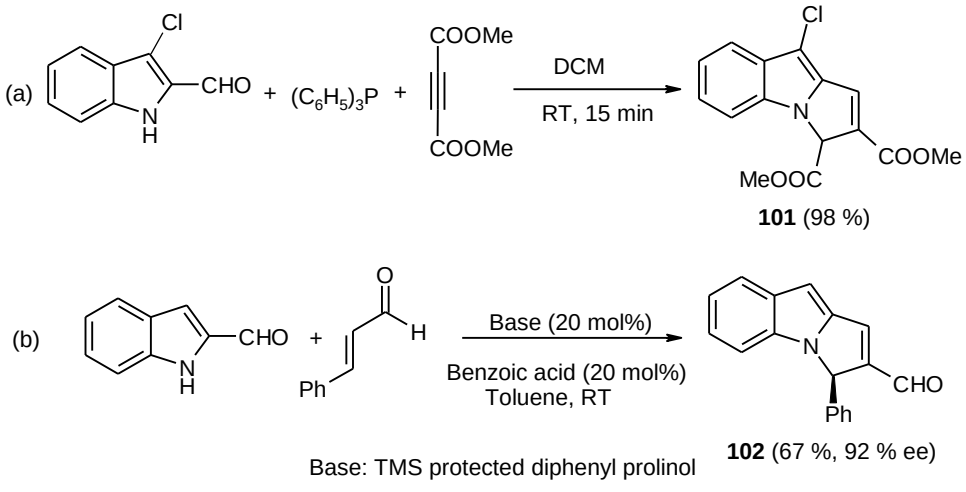
Thus, under base catalyzed reactions adapted by us, the reactivity order with 3-chloro-2-formylindole is allenylphosphonates (~4 h under heating) < allenyl sulfones (~2 h under heating) < ester allene (~30 min under heating). In the case of *α*-methyl substituted allenes **3k** and **8b**, (*β*,*α*)-attack is favoured whereas in the case of *α*-aryl substituted allenes **3e-j** and **8a,** (*β*,*γ*)-product is the major/exclusive product. Ester allene **5** gave (*β*,*γ*)-product, but this allene does not have α-substitution.

2.75 Mechanistic pathways in the formation of pyrrolindoles

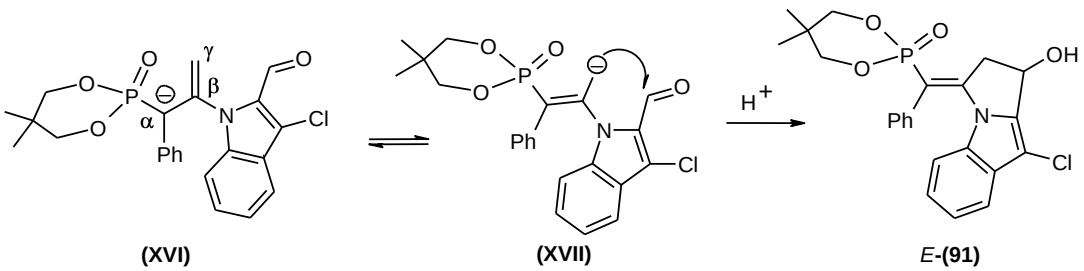
It is likely that the –Cl as well as –CHO groups present in the same ring enhance the acidity [*p*Ka of indole 16.97, *p*Ka of 2-formyl-indole 14.0[64]] of the NH

proton on the 3-chloro-2-formyl-indole. Only two reports of somewhat similar cyclizations (cf. Scheme 37) are available in the literature. The first one involves an alkyne as the substrate while the second one uses an enone.[63-64] However, no allene substrate has been used so far. A brief outline of the mechanistic pathway is shown in Scheme 38. First, the base (K_2CO_3) abstracts proton from 3-chloro-2-formylindole and generates anion which attacks the *α-phenyl* substituted allenylphosphonate ($OCH_2CMe_2CH_2O)P(O)C(Ph)=C=CH_2$ (**3e**) at *β*-position to give **XVI**. This species is in equilibrium with **XVII** which undergoes intramolecular aldol reaction followed by protonation to afford the final product (*E)*-**91**. The *Z*-isomer is not formed perhaps due to steric interaction between the phosphorinane and the indole rings. In the reaction using the *α-methyl* substituted allenylphosphonate ($OCH_2CMe_2CH_2O)P(O)C(Me)=C=CH_2$ (**3k**), cyclization occurs via **XVI** without the rearrangement of carbanion leads to product **98** (not shown in the scheme). Rationalization for the formation of other pyrroloindoles can be made in a similar manner.

Scheme 37



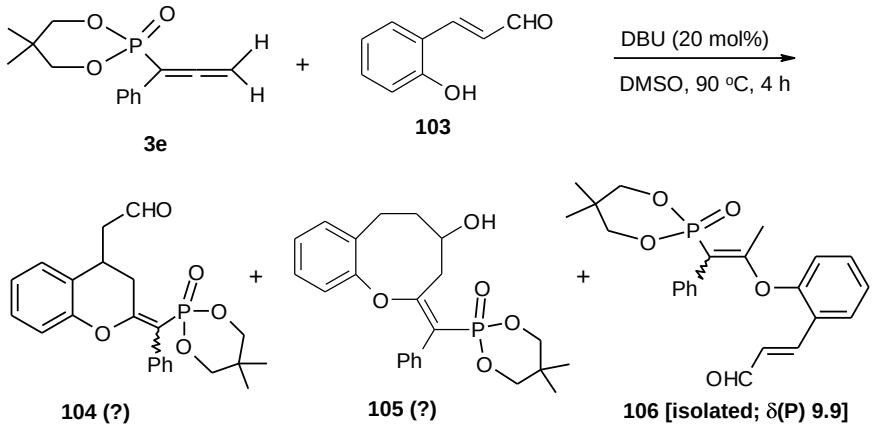
Scheme 38



2.8 Base catalyzed reaction of $(OCH_2CMe_2CH_2O)P(O)C(Ph)=C=CH_2$ (3e) with 2-hydroxy cinnamaldehyde (101)

In continuation of our work using reactants with -OH and CHO functionalities, we also treated the allenylphosphonate **3e** with 2-hydroxy cinnamaldehyde[84] in the presence of K_2CO_3 in DMSO at 90 ^oC/ 4h expecting to obtain 6-membered heterocycle **104** or 8-membered heterocycle **105** (Scheme 39). The reaction led mainly to three products [δ (P) for major (>85%) components: 9.9, 13.1, 13.4]; we were able to isolate only the one with δ (P) 9.9. This product, however, was shown to be the non-cyclized phenol addition product **106**. The residual aldehyde group is observed at δ 9.77 in the ^1H NMR spectrum of this compound. This compound is similar to a phenol addition product recently isolated from our laboratory and hence this part of the study was not pursued further.[47]

Scheme 39



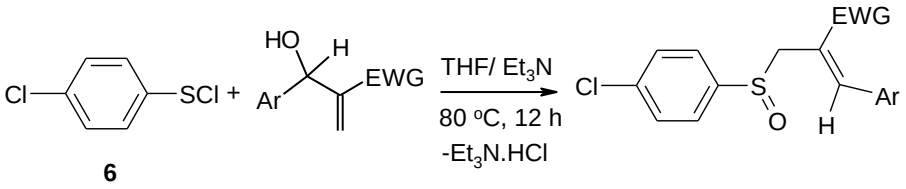
3e **103**

104 (?) **105 (?)** **106 [isolated; δ(P) 9.9]**

2.9 Synthesis of carbomethoxy and cyano substituted allylsulfoxides 107-110 and allylsulfone 111

As an extension to the successful synthesis of the allenylsulfoxides (4-Cl-C_6H_4-S(O)C(R)=C=CR'R" (**7a-f**) [section 2.23], we were curious to synthesize allylsulfoxides in an analogous manner and utilize them further, say, in reactions analogous to Julia olefination reaction.[85] Thus the synthesis of allylsulfoxides **107-110** is accomplished by the reaction of 4-chlorosulfenylchloride **6** with Baylis-Hillman alcohols[86] followed by thermal Arbuzov rearrangement in good yields (Scheme 40). The isolated yields of all the compounds are given in Table 12.

Scheme 40



6

Ar = Ph, EWG = CN (**107**)
Ar = 4-NO_2-C_6H_4, EWG = CN (**108**)
Ar = 4-NO_2-C_6H_4, EWG = CO_2Me (**109**)
Ar = 4-OMe-C_6H_4, EWG = CO_2Me (**110**)

Table 12. Yields of allylsulfoxides **105-108**

Entry	Compound	Ar	EWG	Yield[a] (%)
1	**107**	-C_6H_5	CN	78
2	**108**	4-NO_2-C_6H_4	CN	71
3	**109**	4-NO_2-C_6H_4	CO_2Me	85
4	**110**	4-MeO-C_6H_4	CO_2Me	83

[a]Isolated yields after column chromatography

Each of the allylsulfoxides **107-110** is obtained as a single product. The *Z*-configuration is assigned to these based on the fact that only *Z*-isomer of analogous carbomethoxy phosphonates were formed using ($OCH_2CMe_2CH_2O$)PCl and the Baylis-Hillman alcohols ArCH(OH)C(CO_2Me)=CHAr'.[87] This, however, is in contrast to the cyano allylphosphonates obtained from ($OCH_2CMe_2CH_2O$)PCl and Baylis Hillman alcohols ArCH(OH)C(CN)=CHAr' wherein a mixture of *E/Z* isomers were obtained. Spectroscopic data for these compounds are consistent with the structures as assigned. The *Z*-stereochemistry of these sulfoxides is confirmed by the X-ray structure determination for compound **108** (Figure 35). We tried to utilize **109** in HWE type (Julia olefination) reaction with benzaldehyde/ NaH/ THF for effecting C-C bond formation but were not successful.

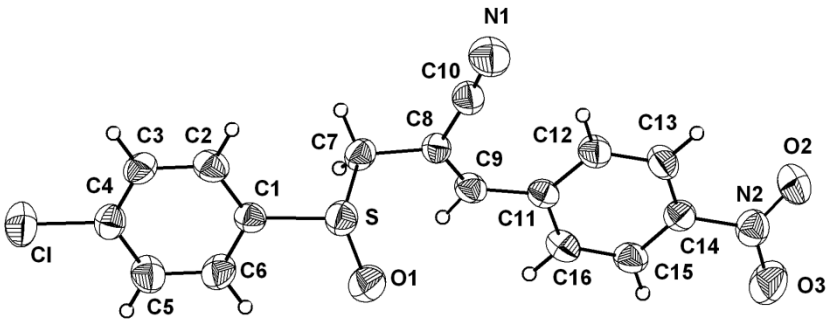
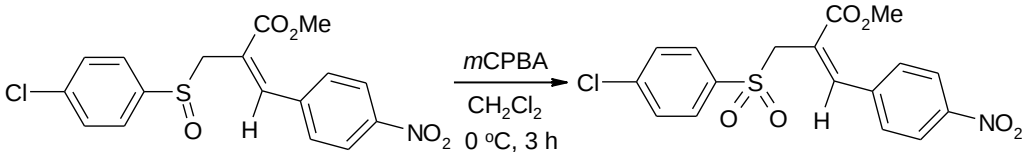


Figure 35. An ORTEP diagram of compound (*Z*)-**108**. Selected bond lengths [Å] with esd's in parentheses. S-O(1) 1.465(2), S-C(7) 1.831(3), C(7)-C(8) 1.504(4), C(8)-C(9) 1.338(4), C(9)-C(11) 1.453(4).

The allylsulfoxide **109** upon subjecting to oxidation with *m*CPBA leads to the allylsulfone **111** in excellent yields (Scheme 41). This compound may be a good substrate for the Julia olefination, but this aspect needs to be investigated in the future.

Scheme 41



109 **111** (92%)

SUMMARY

(1) Several readily accessible and fairly stable new allenylphosphonates $(OCH_2CMe_2CH_2O)P(O)C(Ar)=C=CH_2$ (**3h-j)**, allenylsulfoxides 4-Cl-C_6H_4-S(O)C(R)=C=CR'R'' (**7a-f**), allenylsulfones 4-Cl-C_6H_4-$SO_2C(R)=C=CH_2$ (**8a-b**) that are versatile candidates for exploring allene chemistry have been synthesized. An analogous route has been utilized to synthesize allylsulfoxides [4-Cl-C_6H_4-$S(O)CH_2$ (EWG)C=CHAr, EWG= CN or CO_2Me (**107-110**)].

(2) Pd-catalyzed regioselective coupling reactions of allenylphosphonates $(OCH_2CMe_2CH_2O)P(O)C(R^3)=C=CR^1R^2$ [R^1, R^2, R^3 = H (**3a**), R^1 = Me, R^2, R^3 = H, (**3b**); R^1, R^2 = Me, R^3 = H (**3c**); R^1 = Me, R^2 = Et, R^3 = H (**3d**); R^1, R^2 = H, R^3 = Ph (**3e**)] and phenylallenes $PhCH=C=CR_2$ [R = H (**4a**), Me (**4b**)] with functionalized 2-iodophenols (in PEG-400) and 2-iodobenzyl alcohol lead to benzofurans (with free aldehyde functionalities) and benzopyrans in high yields ($^1H/^{31}P$ NMR) essentially as single isomers under optimized conditions. The synthetic potential of some of these products possessing aldehyde functionality is demonstrated by isolating a compound with Obovaten skeleton and many other 2,3,5,7-tetrasubstituted benzofurans. The structures of key compounds are confirmed by X-ray crystallography. These results establish that in the formation of phosphono-benzofurans or phosphono-benzopyrans, (β,γ)-cyclization product is preferred except in the case of $PhC=C=CH_2$ where (β,α)-cyclized product is observed.

(3) The reaction of 2-mercaptobenzaldehydes with allenylphosphonates in the presence of a base leads to a variety of phosphono-thiochromans and allylic phosphonates. Optimization of reaction conditions reveal that K_2CO_3 (base) in DMSO (solvent) is the best combination. PEG-400 also gives good results, but the yields are lower than that in DMSO. In continuation of this study, allenylphosphonates have been treated with *azo*-substituted salicylaldehydes in the presence of base to afford [bright red colored] *azo*-substituted phosphonochromenes.

(4) The reaction of allenylphosphonates $(OCH_2CMe_2CH_2O)P(O)C(R)=C=CH_2$ (**3e-k**) or allenylsulfones 4-Cl-C_6H_4-$SO_2C(R)=C=CH_2$ [R= Ph (**8a**), R = Me (**8b**)] or ester allene $EtO_2CCH=C=CH_2$ (**5**)with 3-chloro-2-formylindole in the presence of base leads to a new class of pyrroloindoles. Optimization of reaction conditions showed that K_2CO_3 in PEG-400 is the best combination to obtain good yield of a single product.

EXPERIMENTAL SECTION

General: Chemicals and solvents were procured from Aldrich/ Fluka or local manufacturers. Further purification was done according to standard procedures wherever required.[88] All operations, unless otherwise specified, were carried out under dry nitrogen atmosphere using standard vacuum line techniques.[89]

Melting points: 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 200 MHz or 400 MHz NMR spectrometer in $CDCl_3$ solution (unless specified otherwise) with shifts referenced to $SiMe_4$ (^{1}H, ^{13}C: $\delta = 0$) or ext. 85% H_3PO_4 (^{31}P: $\delta = 0$) respectively; *J* values are in Hz.

LC-MS: LC-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 at a flow rate 0.2 mL/ min using MeOH/water (90:10) as eluent.

Absorption spectroscopy: Steady state absorption spectra were recorded on a UV-Vis-NIR scanning spectrophotometer (Shimadzu, model no. UV-3101PC).

Representative ^{13}C NMR spectra are given as appropriate.

3.1 Synthesis of P(III) compound 1, propargyl alcohols 2a-f and other starting materials

Most of these precursors are in use in our laboratory and some of them are previously known. Thus ($OCH_2CMe_2CH_2O$)PCl [**1**; δ(P) 145.8] was prepared by using literature method.[66] The propargyl alcohols **2a**-f,[68-69] 5-iodovanillin (**15**),[90] 3-iodo-4-hydroxybenzaldehyde (**16**),[90] 3,5-diiodo-4-hydroxybenzaldehyde (**17**),[91] the Horner-Wadsworth-Emmons/ Wittig reagents (**32-34**),[76] 2-iodo-*t*-butylbenzaldimine (**52**),[80c] 2-mercaptobenzaldehydes (**54-55**),[81] azo-substituted salicylaldehydes (**76-77**),[82] 3-chloro-2-formyl-indole (**90**),[83] 2-hydroxy cinnamaldehyde (**101**),[84] phenyl allenes (**4a-b**),[72] ester allene (**5**),[73] 4-chloro-phenylsulfenylchloride (**6**),[92] allenylsulfoxides (**7a-f**)[74] and allenylsulfones (**8a-b**)[74] were also prepared by literature procedures.

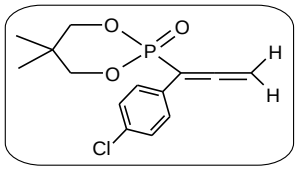
3.2 Synthesis of allenylphosphonates 3a-k

Allenylphosphonates **3a-g** and **3k** were prepared by following a literature procedure.[6] Compounds **3h-j** are new. General procedure for the synthesis of these compounds is given below.

($OCH_2CMe_2CH_2O$)P(O)(CR^3=C=CR^1R^2) (**3h-j**)

To a solution of substituted propargyl alcohol $R^3C{\equiv}CCR^1R^2OH$ (23.5 mmol) in dry THF (50 mL) was added triethylamine (2.37 g, 3.27 mL, 23.5 mmol), the mixture stirred for 5 min, and then ($OCH_2CMe_2CH_2O$)PCl (**1**) (3.95 g, 3.30 mL, 23.5 mmol) in THF (20 mL) was added drop-wise (~ 0.5 h) at 0 ^oC. The contents were brought to room temperature, stirred further for 1 h, and then heated under reflux for 16 h. Triethylamine hydrochloride formed was filtered off and solvent removed *in vacuo* from the filtrate to afford crude allenes **3h-j.** These were purified by column chromatography (silica gel; ethyl acetate-hexane 2:3).

($OCH_2CMe_2CH_2O$)P(O)C(-C_6H_4-4-Cl)=C=CH_2 (**3h**)



Yield: 5.19 g (75%).

Mp: 142-146 ^{o}C.

IR (KBr): 3059, 1964, 1931, 1491, 1263, 1057, 1009 cm^{-1}.

^{1}H NMR: δ 0.91 and 1.30 (2 s, 6H, C(C*H*$_3$)$_2$), 3.98 (m→d, *J* ~ 12.0 Hz, 4H, 2 OC*H*$_2$), 5.38 and 5.41 (2 s, 2H, =C*H*$_2$), 7.31-7.55 (2 d, 4H, Ar *H*).

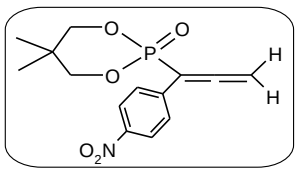
^{13}C NMR: δ 20.7, 21.8, 32.6 (d, *J*(PC) = 6.8 Hz), 77.5, 79.3 (d, *J*(PC) = 14.3 Hz), 94.7 (d, *J*(PC) = 181.6 Hz, P*C*), 128.9, 129.0, 129.1, 129.2, 133.9, 212.7.

^{31}P NMR: δ 6.8.

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

Anal. Calcd. for $C_{14}H_{16}ClO_3P$: C, 56.29; H, 5.40. Found: C, 56.13; H, 5.48.

(OCH$_2$CMe$_2$CH$_2$O)P(O)C(-C$_6$H$_4$-4-NO$_2$)=C=CH$_2$ (3i)



Yield: 5.85 g (75%).

Mp: 128-134 ^{o}C.

IR (KBr): 3069, 1952, 1593, 1517, 1348, 1265, 1055, 1007 cm^{-1}.

^{1}H NMR: δ 0.90 and 1.29 (2 s, 6 H, C(C*H*$_3$)$_2$), 3.98 (m→d, *J*(PH) ~ 12.0 Hz, 4H, 2 OC*H*$_2$), 5.37 and 5.41 (2 s, 2H, =C*H*$_2$), 7.28 and 7.54 (2 d, 4 H, Ar *H*).

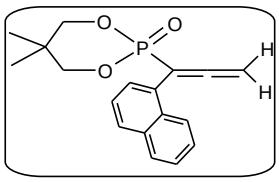
^{13}C NMR: δ 20.7, 21.8, 32.6 (d, *J*(PC) = 6.9 Hz), 77.5, 79.3 (d, *J*(PC) = 14.3 Hz), 94.7 (d, *J*(PC) = 181.2 Hz, P*C*), 128.9, 129.0, 129.1, 129.2, 133.9, 212.8.

^{31}P NMR: δ 6.7.

LC/MS: *m/z* 310 $[M+1]^{+}$.

Anal. Calcd. for $C_{14}H_{16}NO_5P$: C, 54.37; H, 5.21; N, 4.53. Found: C, 54.51; H, 5.27; N, 4.48.

$(OCH_2CMe_2CH_2O)P(O)C(-C_{10}H_7)=C=CH_2$ (3j)



Yield: 5.86 g (80%).

Mp: 176-180 ^oC.

IR (KBr): 3044, 1960, 1931, 1263, 1063, 1017 cm^{-1}.

^1H NMR: δ 0.76 and 1.11 (2 s, 6 H, $C(CH_3)_2$), 3.84–4.06 (m, 4 H, 2 OCH_2), 5.23 and 5.27 (2 s, 2 H, $=CH_2$), 7.46-8.17 (m, 7 H, Ar *H*).

^{13}C NMR: δ 21.0, 21.7, 32.5 (d, *J*(PC) = 6.0 Hz), 76.7, 93.0 (d, *J*(PC) = 187.0 Hz, P*C*), 125.0, 125.4, 126.1, 126.5, 127.4_7, 127.5_1, 128.5_5, 128.6_4, 128.9, 131.5, 134.1, 213.9.

^{31}P NMR: δ 8.3.

LC/MS: *m/z* 315 $[M+1]^+$.

Anal. Calcd. for $C_{18}H_{19}O_3P$: C, 68.78; H, 6.09. Found: C, 68.85; H, 6.13.

3.3 Synthesis of allenylsulfoxides 7a-f and allenylsulfones 8a-b

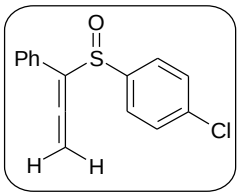
Allenylsulfoxides **7a-f** and allenylsulfones **8a-b** were prepared by following a literature procedure, with slight modifications.[74] General procedure for the synthesis of these compounds is given below.

To a solution of substituted propargyl alcohol (16.0 mmol) in dry CH_2Cl_2 (50 mL) was added triethylamine (1.62 g, 2.23 mL, 16.0 mmol), the mixture stirred for 5 min, and then 4-chlorosulfenyl chloride[93] in CH_2Cl_2 (20 mL) was added drop-wise (~ 0.5 h) at 0^o C. The contents were brought to room temperature, stirred further for 3 h, the mixture washed with water (2 x 20 mL), concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (EtOAc/ Hexane 1:10) to obtain allenylsulfoxides **7a-f**.

The allenylsulfoxide **7a** or **7b** as prepared above was dissolved in CH_2Cl_2, a solution of 70% *m*-chloroperbenzoic acid (*m*CPBA) (16.0 mmol) in CH_2Cl_2 added dropwise at 0 ^oC and then the mixture stirred at 0 ^oC for 4 h. Then it was allowed to warm to room temperature (25-30 ^oC), washed twice with saturated aqueous $NaHCO_3$ solution. The organic layer was separated, dried (Na_2SO_4), filtered, and

concentrated to give crude product which was purified by column chromatography (silica gel; ethyl acetate-hexane 1:10).

Compound 7a



Yield: 3.08 g (70%), gummy solid.

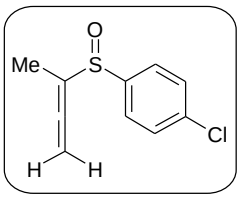
IR (neat): 3059, 1929, 1574, 1474, 1447, 1391, 1090, 1051, 1011 cm^{-1}.

^{1}H NMR: δ 5.45-5.56 (m, 2H, =CH_2), 7.29-7.48 (m, 9 H, Ar *H*).

^{13}C NMR: δ 84.5, 115.9, 126.1, 127.9, 128.7$_5$, 128.7$_8$, 129.2, 129.6, 137.3, 142.0, 205.5.

LC/MS: *m/z* 275 $[M]^+$ and 277 $[M+2]^+$.

Compound 7b



Yield: 2.45 g (72%), gummy solid.

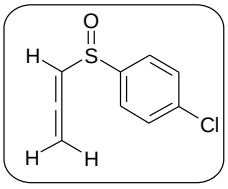
IR(neat): 2982, 2920, 1944, 1574, 1474, 1424, 1391, 1051, 1011 cm^{-1}.

^{1}H NMR: δ 1.68-1.70 (m, 3H, CH_3), 5.16-5.28 (m, 2H, =CH_2), 7.47-7.56 (m, 4 H, Ar *H*).

^{13}C NMR: δ 8.9, 81.0, 108.1, 125.9, 129.4, 137.2, 142.0, 206.1.

LC/MS: *m/z* 213 $[M]^+$and $[M+2]^+$.

Compound 7c



Yield: 2.38 g (75%).

Mp: 44-46 ^{o}C.

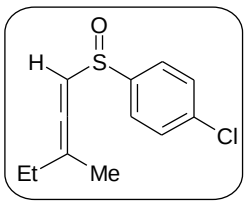
IR (KBr): 1935, 1572, 1474, 1389, 1046, 1009, 814 cm^{-1}.

^{1}H NMR: δ 5.26-5.37(m, 2H, =CH_2), 6.02-6.07 (m, 1H, =C*H*), 7.47-7.60 (m, 4 H, Ar *H*).

^{13}C NMR: δ 82.5, 101.9, 125.6, 129.5, 137.3, 143.1, 207.6.

LC/MS: *m/z* 199 $[M]^{+}$.and 201 $[M+2]^{+}$.

Compound 7e



Yield: 2.95 g (76%).

Mp: 50-54 ^{o}C.

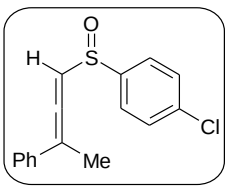
IR (KBr): 2969, 1950, 1470, 1385, 1074, 1044, 1005 cm^{-1}.

^{1}H NMR: δ 0.96-1.06 (m, 3H, CH_2CH_3), 1.77-1.82 (m, 3H, CH_3), 2.03-2.08 (m, 2H, CH_2CH_3), 5.95-5.99 (m, 1H, =C*H*), 7.47-7.58 (m, 4 H, Ar *H*).

^{13}C NMR: δ 11.9_3, 11.9_7, 18.4_8, 18.5_7, 26.8_6, 26.9_3, 102.3, 102.4, 111.4, 111.6, 125.6, 125.7, 129.4, 137.0, 143.7, 143.8, 201.2, 201.6.

LC/MS: *m/z* 243 $[M]^{+}$and 245 $[M+2]^{+}$.

Compound 7f



Yield: 3.61 g (74%).

Mp: 86-90 ^{o}C.

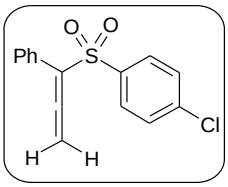
IR (KBr): 2961, 1931, 1574, 1493, 1472, 1074, 1007 cm^{-1}.

^{1}H NMR: δ 2.16 (d, *J* = 1.2 Hz, 3H, CH_3), 6.32 (s, 1H, =C*H*), 7.27-7.60 (m, 9H, Ar *H*).

^{13}C NMR: δ 16.7, 16.8, 104.2, 104.3, 109.9, 125.6$_7$, 125.7$_1$, 126.2, 126.3, 128.4$_9$, 128.5$_4$, 128.8, 129.6, 133.8, 134.1, 137.3, 143.5, 204.0, 204.1.

LC/MS: *m/z* 287 $[M-2]^+$and 289 $[M]^+$.

Compound 8a



Yield: 3.02 g (65%).

Mp: 76-80 ^{o}C.

IR (KBr): 1950, 1906, 1560, 1497, 1476, 1451, 1152, 1084 cm^{-1}.

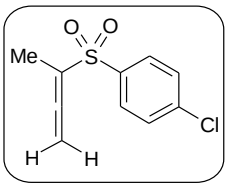
^{1}H NMR: δ 5.59 (s, 2H, =C*H*$_2$), 7.33-7.74 (m, 9 H, Ar *H*).

^{13}C NMR: δ 84.3, 115.0, 128.4, 128.7, 129.0, 129.2, 129.3, 129.7, 138.6, 140.2, 209.1.

LC/MS: *m/z* 289 $[M-2]^+$ and 291 $[M]^+$.

Anal. Calcd. for $C_{15}H_{11}ClO_2S$: C, 61.96; H, 3.81. Found: C, 61.83; H, 3.88.

Compound 8b



Yield: 2.27 g (62%).

Mp: 38-42 ^{o}C.

IR (KBr): 1944, 1580, 1476, 1395, 1314, 1279, 1155, 1074 cm^{-1}.

^{1}H NMR: δ 1.94 (t, *J* = 2.8 Hz, 3H, C*H*$_3$), 5.32 (d, *J* = 2.8 Hz, 2H, =C*H*$_2$), 7.52 and 7.83 (2 d, *J* = 8.4 Hz, 4 H, Ar *H*).

^{13}C NMR: δ 13.5, 83.3, 108.1, 129.4, 129.6, 138.2, 140.2, 208.1.

LC/MS: *m/z* 228 $[M]^+$ and 230 $[M+2]^+$.

Anal. Calcd. for $C_{10}H_9ClO_2S$: C, 52.52; H, 3.97. Found: C, 52.71; H, 3.85.

3.4 Pd-catalyzed Reaction of allenes with functionalized 2-iodophenols

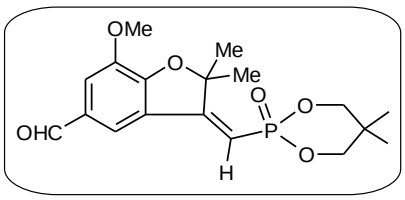
3.41 General procedure leading to benzofuran 9 from allene 3c and 5-iodovanillin-Standardization

To a 25 mL round-bottomed flask containing $(OCH_2CMe_2CH_2O)P(O)(CH=C=CMe_2)$ (**3c**) (0.300 g, 1.39 mmol), $Pd(OAc)_2$ (0.016 g, 0.069 mmol), triphenyl or tri(*o*-tolyl)phosphine (0.21 mmol), 5-iodovanillin (0.466 g, 1.67 mmol) and base [K_2CO_3, K_3PO_4, or NaOAc; 2.78 mmol] the solvent [THF, DMF, DMSO, H_2O, CH_3CN, [bmim][BF_4], PEG-400 or PEG-400+H_2O (1:1); 5 mL] was added under N_2 atmosphere. The contents were evacuated in vacuo for 15 min and then heated at 90-100 ^oC (oil bath; reflux for THF/ CH_3CN) for 4-48 h under N_2 atmosphere. The reaction mixture was quenched with water (5 mL), extracted with ether (3 x 20 mL), dried (Na_2SO_4), filtered, and concentrated under vacuum. The reaction mixture was checked by ^{31}P/ ^1H NMR at this stage. Other details are presented in Table 1 in Results and Discussion.

3.42 Isolation of phosphono-benzofurans 9 and 18-28: Representative procedure for 9

The residue after removing the solvents from the above reaction mixture, using allene $(OCH_2CMe_2CH_2O)P(O)(CH=C=CMe_2)$ (**3c**) (1.39 mmol), $Pd(OAc)_2$ (0.016 g, 0.069 mmol), (*o*-tolyl)$_3$P (0.095 g, 0.21 mmol), 5-iodovanillin (1.67 mmol) and K_2CO_3 (0.384 g, 2.78 mmol) in PEG-400 (5 mL), was subjected to column chromatography (hexane/ EtOAc 3:2) to afford the desired product **9**.

Compound 9



Yield: 0.28 g (70%), gummy solid.

IR(neat): 2973, 1688, 1595, 1495, 1323, 1271, 1121, 1059, 1007 cm^{-1}.

^1H NMR: δ 0.69 (s, 3H, CH_3), 1.21 (s, 3H, CH_3), 1.93 (s, 6H, 2 CH_3), 3.87-3.94 (m, 2H, OCH_2), 4.00 (s, 3H, OCH_3), 4.26-4.31 (m,

2H, OCH_2), 5.97 (d, *J*(PH) = 9.8 Hz, 1H, = C*H*), 7.47 (s, 1H, Ar *H*), 7.62 (s, 1H, Ar *H)*, 9.89 (s, 1H, C*H*O).

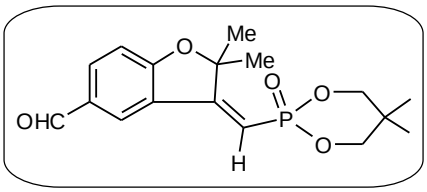
^{13}C NMR: δ 21.4, 21.7, 26.1, 26.1, 32.6 (d, *J*(PC) = 5.0 Hz), 56.3, 75.3 (d, *J*(PC) = 6.0 Hz), 94.9 (d, *J*(PC) = 6.0 Hz), 99.4 (d, *J*(PC) = 199.0 Hz), 113.1, 118.9, 125.9 (d, *J*(PC) = 23.0 Hz), 131.2, 146.3, 156.4, 165.0 (d, *J*(PC)= 9.0 Hz), 190.2.

^{31}P NMR: δ 11.8.

LC/MS: *m/z* 367 $[M+1]^+$.

Anal. Calcd. for $C_{18}H_{23}O_6P$: C, 59.01; H, 6.33. Found: C, 59.15; H, 6.32.

Compound 18



Yield: 0.27 g (65%).

Mp: 142 – 146 ^{o}C.

IR(KBr): 2975, 2812, 1688, 1605, 1487, 1294, 1260 cm^{-1}.

^{1}H NMR: δ 1.09 (s, 3H, CH_3), 1.18 (s, 3H, CH_3), 1.86 (s, 6H, 2 CH_3), 3.90-3.96 (m, 2H, OCH_2), 4.21-4.26 (m, 2H, OCH_2) 6.05 (d, *J* (PH) = 10.0 Hz, 1H, = C*H*) 7.00-8.03 (m, 3H, Ar *H*) 9.91 (s, 1H, C*H*O).

^{13}C NMR: δ 21.4, 21.6, 26.1, 26.1, 32.6 (d, *J*(PC) = 5.0 Hz), 75.4 (d, *J*(PC) = 6.0 Hz), 93.7 (d, *J*(PC)= 5.0 Hz), 99.7 (d, *J*(PC)= 198.0 Hz), 111.9, 124.1, 125.8 (d, *J*(PC)= 23.0 Hz), 130.3, 136.2, 164.3 (d, *J*(PC)= 9.0 Hz), 166.3, 190.1.

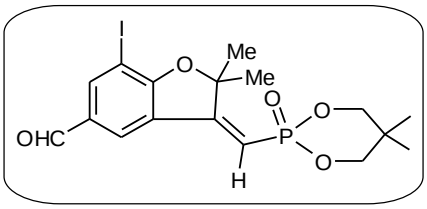
^{31}P NMR: δ 11.4.

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

Anal. Calcd. for $C_{17}H_{21}O_5P$: C, 60.71; H, 6.29. Found: C, 60.75; H, 6.29.

X-ray structure was determined for this sample.

Compound 19



Yield: 0.16 g (59%).

Mp: 162 - 166 ^{o}C.

IR (KBr): 2932, 2884, 1692, 1595, 1273, 1053, 997, 831 cm^{-1}.

^{1}H NMR: δ 1.08 (s, 3H, C*H*$_3$), 1.20 (s, 3H, C*H*$_3$), 1.92 (s, 6H, 2 C*H*$_3$), 3.88 –3.95 (m, 2H, OC*H*$_2$), 4.25-4.30 (m, 2H, OC*H*$_2$), 6.00 (d, *J*(PH) = 9.6 Hz, 1H, = C*H*), 7.97 (s, 1H, Ar *H*), 8.27 (s, 1H, Ar *H*), 9.85 (s, 1H, C*H*O).

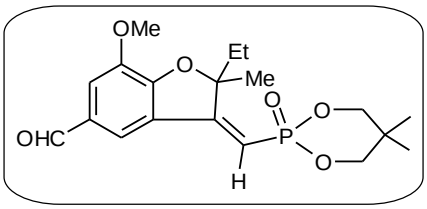
^{13}C NMR: δ 20.4, 20.7, 25.2, 31.6 (d, *J*(PC)= 6.0 Hz), 77.4 (d, *J*(PC) = 6.0 Hz), 93.5, 100.5 (d, *J*(PC) = 198.0 Hz), 122.4, 124.3 (d, *J*(PC) = 23.0 Hz), 130.9, 143.5, 163.3, 163.4, 165.2, 187.8.

^{31}P NMR: δ 10.6.

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

Anal. Calcd. for $C_{17}H_{20}IO_5P$: C, 44.18; H, 4.36. Found: C, 44.12; H, 4.38.

Compound 20



Yield: 0.25 g (55%).

Mp: 118 – 122 ^{0}C.

IR (KBr): 2963, 1682, 1593, 1495, 1462, 1318, 1254, 1146, 1125, 1057, 1011 cm^{1}.

^{1}H NMR: δ 0.83-0.87 (m, 3H, C*H*$_3$), 1.06 (s, 3H, C*H*$_3$), 1.21 (s, 3H, C*H*$_3$), 1.88 (s, 3H, C*H*$_3$), 2.19-2.25 (m, 1H, C*H*$_A$H$_B$), 2.56-2.60 (m, 1H, CH$_A$*H*$_B$), 3.87-3.93 (m, 2H, OC*H*$_2$), 4.00 (s, 3H, OC*H*$_3$), 4.25-4.30 (m, 2H, OC*H*$_2$), 6.02 (d, *J*(PH) = 9.8 Hz,

1H, = (C*H*)P)), 7.46 (s, 1H, Ar *H*), 7.61 (s, 1H, Ar *H*), 9.88 (s, 1H, C*H*O).

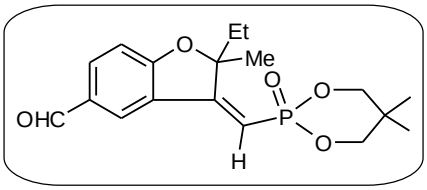
^{13}C NMR: δ 7.9, 21.4, 21.8, 25.2, 32.0, 32.6 (d, *J*(PC) = 5.0 Hz), 56.3, 75.3 (d, *J*(PC) = 2.0 Hz), 75.3$_1$(d, *J*(PC) = 2.0 Hz), 97.9 (d, *J*(PC) = 5.0 Hz), 99.5 (d, *J*(PC)= 199.0 Hz), 113.2, 118.6, 126.7 (d, *J*(PC) = 23.0 Hz), 131.0, 146.0, 157.1, 163.8 (d, *J*(PC) = 9.0 Hz), 190.1.

^{31}P NMR: δ 11.8.

LC/MS: *m/z* 379 $[M-1]^+$.

Anal. Calcd. for $C_{19}H_{25}O_6P$: C, 60.00; H, 6.62. Found: C, 59.97; H, 6.70.

Compound 21



Yield: 0.26 g (57%).

Mp: 126 - 130 ^{o}C.

IR (KBr): 2973, 2880, 1807, 1690, 1605, 1487, 1329, 1256 cm^{-1}.

^{1}H NMR: δ 0.81-0.86 (m, 3H, C*H*$_3$), 1.07 (s, 3H, C*H*$_3$), 1.19 (s, 3H, C*H*$_3$), 1.83 (s, 3H, C*H*$_3$), 2.15-2.20 (m, 1H, C*H*$_A$H$_B$), 2.49-2.54 (m, 1H, CH$_A$*H*$_B$) 3.90-3.94 (m, 2H, OC*H*$_2$), 4.22-4.27 (m, 2H, OC*H*$_2$), 6.08 (d, *J*(PH) = 10.1 Hz, 1H, = C*H*), 7.00-8.02 (m, 3H, Ar *H*), 9.90 (s, 1H, C*H*O).

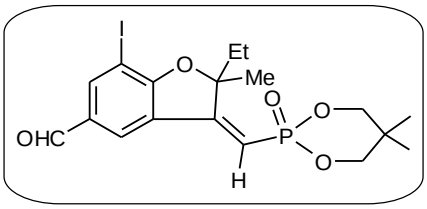
^{13}C NMR: δ 7.9, 21.4, 21.6, 24.9, 32.0, 32.6 (d, *J*(PC) = 6.0 Hz), 75.3 (d, *J*(PC) = 3.0 Hz), 75.4 (d, *J*(PC) = 3.0 Hz), 96.7, 99.8 (d, *J*(PC) = 198.0 Hz), 111.6, 123.8, 126.5 (d, *J*(PC) = 23.0 Hz), 130.2, 136.3, 163.3 (d, *J*(PC) = 9.0 Hz), 167.1, 190.2.

^{31}P NMR: δ 11.5.

LC/MS: *m/z* 351 $[M+1]^+$.

Anal. Calcd. for $C_{18}H_{23}O_5P$: C, 61.71; H, 6.62. Found: C, 61.69; H, 6.58.

Compound 22



Yield: 0.25 g (57%).

Mp: 136 – 140 ^{0}C.

IR (KBr): 2971, 1688, 1591, 1464, 1323, 1275, 1059, 1007, 828 cm^{-1}.

^{1}H NMR: δ 0.84-0.89 (m, 3H, C*H*$_3$), 1.08 (s, 3H, C*H*$_3$), 1.21 (s, 3H, C*H*$_3$), 1.88 (s, 3H, C*H*$_3$), 2.21-2.27 (m, 1H, C*H*$_A$H$_B$), 2.50-2.56 (m, 1H, CH$_A$*H*$_B$), 3.88-3.95 (m, 2H, OC*H*$_2$), 4.24-4.29 (m, 2H, OC*H*$_2$), 6.06 (d, *J*(PH) = 9.6 Hz, 1H, = C*H*), 7.97-8.27 (m, 2H, Ar *H*), 9.8 (s, 1H, C*H*O).

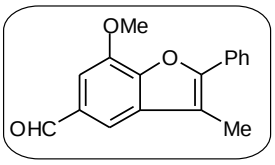
^{13}C NMR: δ 8.4, 21.9, 22.2, 25.5, 32.6, 33.2 (d, *J*(PC) = 5.0 Hz), 75.9 (d, *J*(PC) = 4.0 Hz), 97.9 (d, *J*(PC) = 5.0 Hz), 102.2 (d, *J*(PC) = 198.0 Hz), 123.6, 126.5 (d, *J*(PC) = 23.0 Hz), 132.3, 144.9, 163.8, 163.9, 167.4, 189.4.

^{31}P NMR: δ 10.6.

LC/MS: *m/z* 477 [M+1]$^{+}$.

Anal. Calcd. for $C_{18}H_{22}IO_5P$: C, 45.40; H, 4.66. Found: C, 45.42; H 4.67.

Compound 23



Yield: 0.29 g (68%).

Mp: 102 – 104 ^{o}C.

IR (KBr): 2820, 1682, 1593, 1233, 1140, 1051 cm^{-1}.

^{1}H NMR: δ 2.54, (s, 3H, C*H*$_3$), 4.12 (s, 3H, OC*H*$_3$), 7.41-7.87 (m, 7H, Ar *H*), 10.06 (s, 1H, C*H*O).

^{13}C NMR: δ 9.6, 56.3, 105.1, 112.1, 117.6, 126.9, 128.5, 128.7, 130.5, 132.9, 133.0, 146.0, 146.7, 152.7, 191.8 [Fig. 36].

LC/MS: *m/z* 267 $[M+1]^+$.

Anal. Calcd. for $C_{17}H_{14}O_3$: C, 76.68; H, 5.30. Found: C, 76.60; H, 5.31.

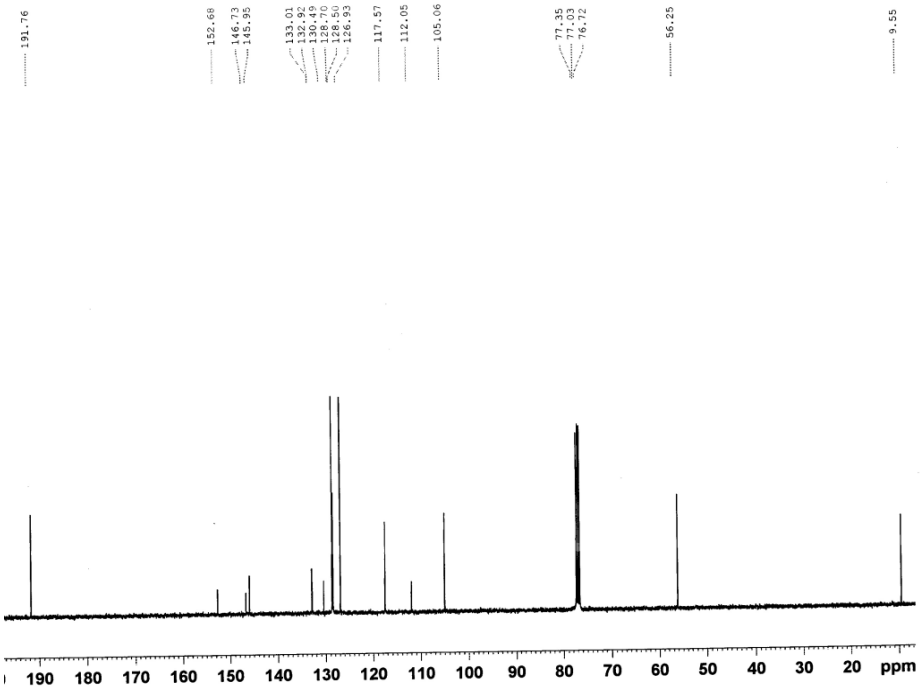
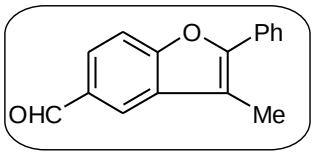


Figure 36. ^{13}C NMR spectrum of compound **23**

Compound 24



Yield: 0.38 g (69%), gummy solid.

IR (neat): 2832, 1688, 1593, 1454, 1263, 1173 cm^{-1}.

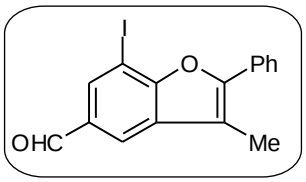
^{1}H NMR: δ 2.53 (s, 3H, C*H*$_3$), 7.41-8.10 (m, 8H, Ar *H*), 10.10 (s, 1H, C*H*O).

^{13}C NMR: δ 9.4, 111.6, 111.7, 122.2, 126.4, 126.8, 128.5, 128.8, 130.6, 131.9, 152.7, 157.3, 191.8.

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

Anal. Calcd. for $C_{16}H_{12}O_2$: C, .81.34; H, 5.12. Found: C, 81.32; H, 5.11.

Compound 25



Yield: 0.15 g (51%).

Mp: 80 – 84 ^{o}C.

IR (KBr): 1690, 1566, 1445, 1422, 1262, 1165, 1071, 801 cm^{-1}.

^{1}H NMR: δ 2.54 (s, 3H, C*H*$_3$), 7.28–8.23 (m, 7H, Ar *H*), 10.03 (s, 1H, C*H*O).

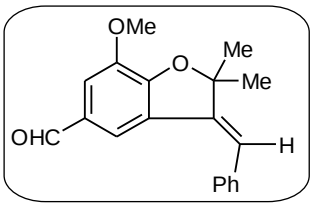
^{13}C NMR: δ 9.7, 75.6, 112.7, 122.0, 127.0, 128.5, 128.9, 128.9, 130.1, 131.5, 133.5, 134.7, 190.4.

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

Anal. Calcd. for $C_{16}H_{11}IO_2$: C, 53.06; H, 3.06. Found: C, 53.08; H, 3.03.

X-ray structure was determined for this sample.

Compound 26



Yield: 0.28 g (66%).

Mp: 128 – 132 ^{o}C.

IR (KBr): 2714, 1688, 1584, 1485, 1356, 1298 cm^{-1}.

^{1}H NMR: δ 1.68 (s, 6H, 2 C*H*$_3$), 3.97 (s, 3H, OC*H*$_3$), 6.43 (s, 1H, =(C*H*)Ph), 7.28–7.44 (m, 7H, Ar *H*), 9.56 (s, 1H, C*H*O).

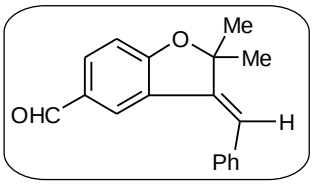
^{13}C NMR: δ 28.8, 56.1, 92.4, 110.3, 120.5, 122.5, 124.9, 127.8, 128.5, 128.7, 130.4, 136.3, 144.1, 146.0, 155.8, 190.7.

LC/MS: *m/z* 295 [M+1]$^{+}$.

Anal. Calcd. for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16. Found: C, 77.52; H, 6.14.

X-ray structure was determined for this sample.

Compound 27



Yield: 0.26 g (62%), gummy solid.

IR (neat): 2978, 2818, 1692, 1599, 1480, 1445, 1285, 1198 cm^{-1}.

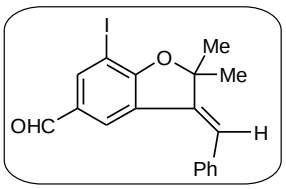
^1H NMR: δ 1.54 (s, 6H, 2 C*H*$_3$), 6.35 (s, 1H, = (C*H*)Ph), 6.83-7.70 (m, 8H, Ar *H*), 9.55 (s, 1H, C*H*O).

^{13}C NMR: δ 28.7, 91.4, 111.3, 121.0, 124.7, 127.0, 128.2, 128.3, 128.8, 129.0, 129.8, 136.3, 143.8, 166.3, 190.5.

LC/MS: *m/z* 265 $[M+1]^+$.

Anal. Calcd. for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.85; H, 6.19.

Compound 28



Yield: 0.09 g (52%).

Mp: 122 – 126 ^oC.

IR (KBr): 2851, 1682, 1586, 1416, 1262, 1094, 801 cm^{-1}.

^1H NMR: δ 1.58 (s, 6H, 2 C*H*$_3$), 6.47 (s, 1H, =(C*H*)Ph), 7.39-7.48 (m, 5H, Ar *H*), 7.66 (s, 1H, Ar *H*), 8.13 (s, 1H, Ar *H*), 9.56 (s, 1H, C*H*O).

^{13}C NMR: δ 28.8, 75.9, 92.0, 122.5, 124.6, 126.2, 128.1, 128.2, 128.9, 131.4, 135.8, 141.1, 143.9, 165.9, 189.1.

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

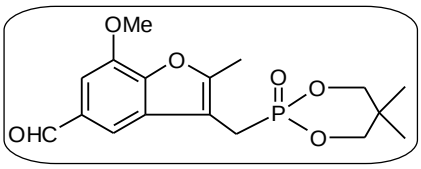
Anal. Calcd. for $C_{18}H_{15}IO_2$: C, 55.40; H, 3.87 Found: C, 55.44; H, 3.88.

3.43 Preparation of phosphono-benzofurans 30-33: General procedure

To a 25 mL round-bottomed flask containing allene **3b** or **3e** (1.39 mmol), $Pd(OAc)_2$ (0.016 g, 0.069 mmol), functionalized 2-iodophenols **15-16** (1.67 mmol) and CsF (0.420 g, 2.78 mmol), PEG-400 (5 mL) was added under N_2 atmosphere.

The contents were heated at 90-100 ^{o}C for 12h, quenched with water (5 mL), extracted with ether (3 x 20 mL), dried (Na_2SO_4), filtered, and concentrated under vacuum. The residue was subjected to column chromatography (hexane/EtOAc; 1:1) to afford the desired products **30-33**.

Compound 30



Yield: by NMR 64%; isolated 0.31 g (60%).

Mp: 150 – 154 ^{o}C.

IR (KBr): 2973, 1694, 1595, 1485, 1368, 1265, 1134 cm^{-1}.

^{1}H NMR: δ 0.81 (s, 3H, C*H*$_3$), 0.88 (s, 3H, C*H*$_3$), 2.50 (d, 3H, C*H*$_3$), 3.29 (d, *J*(PH) = 20.6 Hz, 2H, PC*H*$_2$), 3.63-3.70 (m, 2H, OC*H*$_2$), 4.10 (s, 3H, OC*H*$_3$), 4.22-4.26 (m, 2H, OC*H*$_2$), 7.35 (s, 1H, Ar *H*), 7.68 (s, 1H, Ar *H*), 10.02 (s, 1H, C*H*O).

^{13}C NMR: δ 12.2 (d, *J*(PC) = 3.0 Hz), 21.4 (d, *J*(PC) = 143.0 Hz), 21.1, 21.3, 32.5 (d, *J*(PC) = 6.0 Hz), 56.2, 74.8 (d, *J*(PC) = 7.0 Hz), 103.9, 106.2, (d, *J*(PC) = 11.0 Hz), 118.0, 130.7, 133.2, 145.6, 146.6, 154.9 (d, *J*(PC) = 11.0 Hz), 191.8 [Fig. 37].

^{31}P NMR: δ 22.9.

LC/MS: *m/z* 353 [M+1]$^{+}$.

Anal. Calcd. for $C_{17}H_{21}O_6P$: C, 57.95; H, 6.01. Found: C, 58.07; H, 6.00.

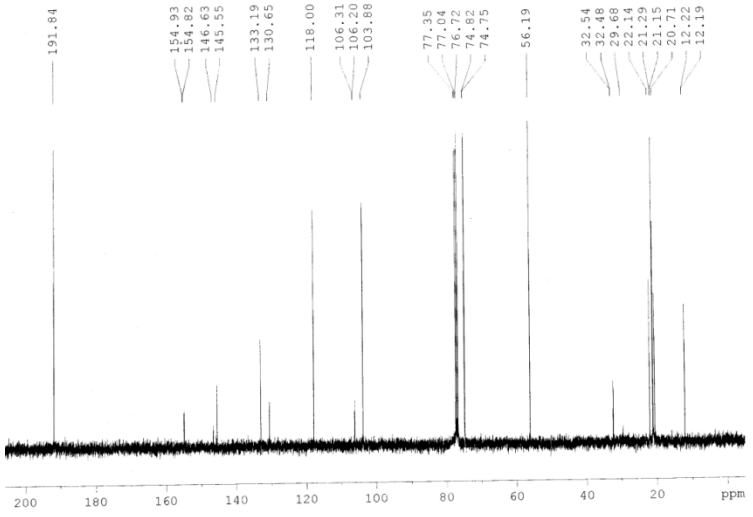
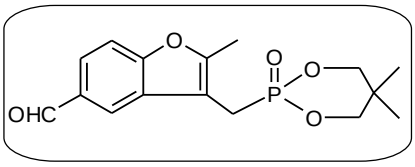


Figure 37. ^{13}C NMR spectrum of compound **30.**

Compound 31



Yield: by NMR 66%; isolated 0.28 g (58%).

Mp: 168 - 172 ^{o}C.

IR (KBr): 2965, 2903, 1684, 1628, 1586, 1476, 1346, 1254, 1055, 1005 cm^{-1}.

^{1}H NMR: δ 0.82 (s, 3H, C*H*$_3$), 0.88 (s, 3H, C*H*$_3$), 2.49-2.50 (d, 3H, C*H*$_3$), 3.29 (d, *J*(PH) = 20.1 Hz, 2H, PC*H*$_2$), 3.64-3.71 (m, 2H, OC*H*$_2$), 4.22-4.26 (m, 2H, OC*H*$_2$), 7.49-8.07 (m, 3H, Ar *H*), 10.06 (s, 1H, C*H*O).

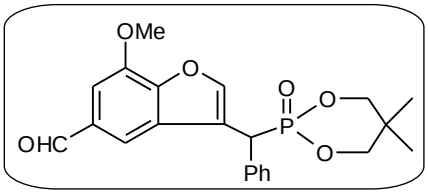
^{13}C NMR: δ 12.2 (d, *J*(PC) = 3.0 Hz), 21.2 (d, *J*(PC) = 142.0 Hz), 21.1, 21.2, 32.5 (d, *J*(PC) = 5.0 Hz), 74.8 (d, *J*(PC) = 7.0 Hz), 105.7 (d, *J*(PC) = 11.0 Hz), 111.4, 122.5, 125.1, 129.6 (d, *J*(PC)= 2.0 Hz), 132.0, 155.1 (d, *J*(PC) = 11.0 Hz), 157.3, 191.9.

^{31}P NMR: δ 23.0.

LC/MS: *m/z* 323 [M+1]$^{+}$.

Anal. Calcd. for $C_{16}H_{19}O_5P$: C, 59.63; H, 5.94. Found: C, 59.61; H, 5.91.

Compound 32



Yield: by NMR 70%; isolated 0.25 g (63%).

Mp: 198 – 200 ^{o}C.

IR (KBr): 2892, 1688, 1618, 1595, 1481, 1404, 1366, 1258, 1142, 1011, 988 cm^{-1}.

^{1}H NMR: δ 0.84 (s, 3H, C*H*$_3$), 1.03 (s, 3H, C*H*$_3$), 3.65-3.82 (m, 2H, OC*H*$_2$), 4.07 (s, 3H, OC*H*$_3$), 4.19-4.25 (m, 2H, OC*H*$_2$), 4.76 (d, *J*(PH) = 24.8 Hz, 1H, P(C*H*)), 7.28-7.48 (m, 7H, Ar *H*), 8.18 (s, 1H, Ar *H*), 9.90 (s, 1H, C*H*O).

^{13}C NMR: δ 21.3, 21.5, 32.6 (d, *J*(PC) = 7.0 Hz), 40.2 (d, *J*(PC) = 137.3 Hz), 56.3, 76.0 (d, *J*(PC) = 6.9 Hz), 104.9, 116.3 (d, *J*(PC) = 4.6 Hz), 118.1, 128.0 (d, *J*(PC) = 2.9 Hz), 128.9 (d, *J*(PC) = 2.3 Hz), 129.0, 129.4 (d, *J*(PC) = 6.1 Hz), 133.2, 134.1 (d, *J*(PC) = 7.6 Hz), 145.6 (d, *J*(PC) = 6.2 Hz), 146.3, 148.1, 191.6.

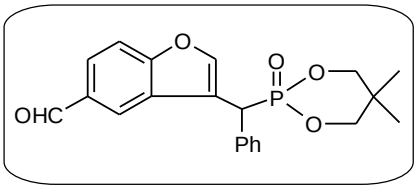
^{31}P NMR: δ 18.4.

LC/MS: *m/z* 415 $[M+1]^+$.

Anal. Calcd. for $C_{22}H_{23}O_6P$: C, 63.77; H, 5.59. Found: C, 63.58; H, 5.62.

X-ray structure was determined for this sample.

Compound 33



Yield: by NMR 63%; isolated 0.25 g (55%).

Mp: 198 – 200 ^{o}C.

IR (KBr): 2803, 1682, 1586, 1476, 1061, 1013 cm^{-1}.

^{1}H NMR: δ 0.85 (s, 3H, C*H*$_3$), 1.03 (s, 3H, C*H*$_3$), 3.66-3.83 (m, 2H, OC*H*$_2$), 4.18-4.24 (m, 2H, OC*H*$_2$), 4.77 (d, *J*(PH) = 24.4 Hz, 1H, P(C*H*)), 7.28-7.86 (m, 8H, Ar *H*), 8.20 (s, 1H, Ar *H*), 9.97 (s, 1H, C*H*O).

^{13}C NMR: δ = 21.3, 21.5, 32.6 (d, *J*(PC) = 6.6 Hz), 40.0 (d, *J*(PC) = 137.0 Hz), 75.9$_8$ (d, *J*(PC) = 5.8 Hz), 76.0 (d, *J*(PC) = 6.4 Hz), 112.4, 115.9 (d, *J*(PC) = 4.5 Hz), 123.0, 126.4, 127.9, 128.1, 128.9 (d, *J*(PC) = 2.5 Hz), 129.4, 132.0, 134.1 (d, *J*(PC) = 7.5 Hz), 145.8 (d, *J*(PC) = 6.7 Hz), 158.5, 191.7.

^{31}P NMR: δ 18.4.

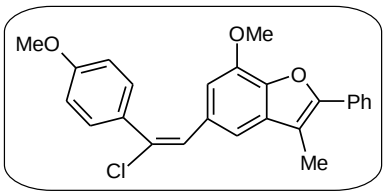
LC/MS: *m/z* 384 $[M]^+$.

Anal. Calcd. for $C_{21}H_{21}O_5P$: C, 65.62; H, 5.51. Found: C, 65.55; H, 5.58.

3.44 Utility of benzofurans in HWE reaction- Synthesis of (E)-37, (Z)-37 and 38: General procedure

To a mixture of NaH (0.026 g, 1.12 mmol) and the appropriate phosphonate [**32** or **33**; 0.75 mmol] in dry THF (10 mL) at 0 ^{o}C was added benzofuran aldehyde **23** (0.200 g, 0.75 mmol). The contents were stirred at room temperature for 12 h. Water (20 mL) was added and the aqueous layer thoroughly extracted with ether (3 x 20 mL). The combined organic layer was dried over anh. Na_2SO_4, filtered and concentrated to give the crude product that was subjected to column chromatography (hexane/ EtOAc) to afford the desired product **37** (in this case both ***E*** and ***Z***-isomers are isolated) or **38**.

Compound (*E*)-37



Yield: (combined yield along with 37(*Z*) >64%) 0.07 g (32%).

Mp: 98 - 102 ^{o}C.

IR (KBr): 2963, 2922, 1603, 1508, 1460, 1250, 1171, 1144 cm^{-1}.

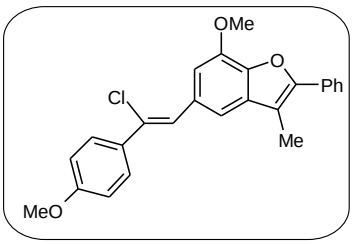
^{1}H NMR: δ 2.35 (s, 3H, CH_3), 3.68 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 6.44 (s, 1H, =(C*H*)Ph), 6.83-7.79 (m, 11H, Ar *H*).

^{13}C NMR: δ 9.7, 55.4, 55.7, 107.6, 108.7, 111.6, 112.6, 113.2, 113.8, 114.0, 125.1, 126.8, 128.0, 128.6, 128.7, 130.3, 130.9, 131.1, 131.8, 132.7, 142.6, 144.5, 151.5, 160.0.

LC/MS: *m/z* 405 $[M]^+$ and 407 $[M+2]^+$.

Anal. Calcd. for $C_{25}H_{21}ClO_3$: C, 74.16; H, 5.23. Found: C, 74.15 ; H, 5.21.

Compound (*Z*)-37



Yield: (combined yield along with 37(*E*)>64%) 0.07 g (32%).

Mp: 146 - 150 ^{o}C.

IR (KBr): 2959, 1613, 1591, 1505, 1458, 1240, 1173, 1146, 1034 cm^{-1}.

^{1}H NMR: δ 2.47 (s, 3H, C*H*$_3$), 3.84 (s, 3H, OC*H*$_3$), 4.07 (s, 3H, OC*H*$_3$), 6.92-7.50 (m, 12H, =(C*H*)Ph and Ar *H*).

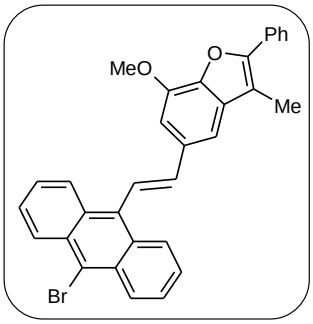
^{13}C NMR: δ 9.7, 55.4, 56.3, 108.6, 111.7, 113.2, 113.8, 125.1, 126.9, 128.0, 128.6, 130.7, 130.9, 131.1, 132.1, 132.8, 142.6, 144.6, 151.5, 160.0.

LC/MS: *m/z* 405 [M]$^{+}$ and 407 [M+2]$^{+}$.

Anal. Calcd. for $C_{25}H_{21}ClO_3$: C, 74.16; H, 5.23. Found: C, 74.15; H, 5.21.

X-ray structure was determined for this sample.

Compound 38



Yield: 0.30 g (77%).

Mp: 204 - 206 ^{o}C.

IR (KBr): 3015, 2930, 1613, 1601, 1318, 1227, 1142 cm^{-1}.

^{1}H NMR: δ 2.55 (s, 3H, C*H*$_3$), 4.18 (s, 3H, OC*H*$_3$), 7.00-8.64 (m, 17H, =(C*H*) Ph and Ar *H*).

^{13}C NMR: δ 9.71, 56.4, 105.4, 110.6, 111.7, 122.5, 123.2, 125.2, 125.4, 125.6, 126.1, 126.7, 126.9, 127.0, 128.1, 128.2, 128.6, 128.7, 130.4, 130.6, 131.1, 132.8, 133.3, 133.9, 138.6, 143.3, 145.4.

LC/MS: *m/z* 519 [M]$^{+}$ and 521 [M+2]$^{+}$.

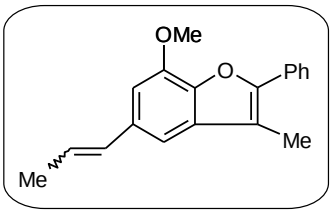
Anal. Calcd. for $C_{32}H_{23}BrO_2$: C, 73.99; H, 4.46. Found: C, 74.06; H, 4.47.

3.45 Synthesis of the Wittig product 39

To *n*-BuLi solution (0.42 mL, from 1.6 M solution in hexane) in dry ether (15 mL), [Ph_3PEt][Br] (obtained from PPh_3 and EtBr in toluene) (0.254 g, 0.68 mmol) was added cautiously and the mixture stirred at room temperature for 4 h.

After this, benzofuran aldehyde **23** (0.200 g, 0.68 mmol) was added and stirring continued. After 12 h, the reaction mixture was filtered and the precipitate washed with ether (2x10 mL). The combined organic layer was dried (Na_2SO_4), filtered, and concentrated. The residue was subjected to column chromatography (hexane/ EtOAc) to afford the desired product **39**.

Compound 39



Yield: 0.13 g (83%; *E*/*Z*= 2:1).

Mp: 72 - 76 ^{o}C.

IR (KBr): 2961, 1597, 1460, 1223, 1144 cm^{-1}.

^{1}H NMR: δ 1.90-1.92 and 1.95-1.97 (m, 3H for two isomers, CH_3), 2.44 and 2.45 (s, 3H for two isomers, CH_3), 4.03_6 and 4.03_9 (s, 3H for two isomers, OCH_3), 5.70-5.85 (m, 2H, 2 = C*H* for minor isomer), 6.19-6.24 (m, 2H, 2 = C*H* for major isomer), 6.47-7.83 (m, 7H, Ar *H*).

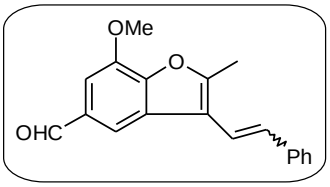
^{13}C NMR: δ 8.6, 13.7, 17.4, 55.1, 55.2 103.9, 107.4, 108.3, 110.6, 110.9, 123.4, 124.8, 125.7_6, $125.7_{9,}$ 126.8, 127.2, 127.5, 129.4, 130.2, 130.5, 131.7, 131.9, 132.0, 132.7, 140.9, 141.4, 143.6, 144.0, 150.2.

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

Anal. Calcd. for $C_{19}H_{18}O_2$: C, 81.99; H, 6.52. Found: C, 82.02; H, 6.52.

3.46 Synthesis of compound 40

Compound **40** was prepared in a manner similar to that for compounds **37-38** using compound **30** (0.75 mmol) and benzaldehyde.



Yield: 0.05 g (60%; *E/Z* = 3:1).

Mp: 108 – 112 ^{o}C.

IR (KBr): 3472, 1682, 1595, 1462, 1400, 1370, 1290, 1142 cm^{-1}.

^{1}H NMR: δ 2.62 (s, 3H, C*H*$_3$), 4.09 (s, 3H, OC*H*$_3$), 7.08-7.98 (m, 9H, =CH & Ar *H*), 10.07 (s, 1H, C*H*O).

^{13}C NMR: δ 12.8, 56.2, 104.6, 114.9, 118.3, 118.5, 126.2, 126.7, 127.8, 128.8, 130.0, 133.4, 137.4, 145.7, 147.1, 155.3, 191.8.

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

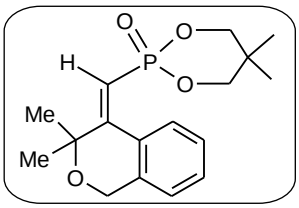
Anal. Calcd. for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52. Found: C, 78.21; H, 5.58.

3.5 Synthesis of benzopyrans, indoles, butadiene and isoquinoline

3.51 Synthesis of benzopyrans 41-45: General procedure

To a mixture of allene **3c-d, 3e** or **4a-b** (1.39 mmol), $Pd(OAc)_2$ (0.016 g, 0.074 mmol), Ph_3P (0.055 g, 0.21 mmol), 2-iodobenzyl alcohol (0.39 g, 1.67 mmol) and K_2CO_3 (0.384 g, 2.78 mmol), DMF (5 mL) was added under N_2 atmosphere. The contents were heated at 90-100 ^{o}C for 24 h. The mixture was then quenched with water (5 mL), extracted with ether (3 x 20 mL). The whole organic layer was washed with water (3 x 20 mL), dried (Na_2SO_4), filtered, and concentrated. The residue was subjected to column chromatography (hexane/ EtOAc; 3:2) to afford the products **41-45.**

Compound 41



Yield: by NMR 73%; isolated 0.40 g (55%).

Mp: 148 - 150 ^{o}C.

IR (KBr): 1597, 1458, 1368, 1258, 1163, 1057, 1001 cm^{-1}.

^{1}H NMR: δ 0.83 and 1.20 (2 s, 6H, 2 C*H*$_3$), 1.47 (s, 6H, 2 C*H*$_3$), 3.65-3.83 (m, 4H, 2 OC*H*$_2$), 4.80 (s, 2H, OC*H*$_2$), 5.65 (d, *J*(PH) = 12.7 Hz, 1H, =C*H*), 7.08 (d, *J* = 8.0 Hz, 1H, Ar *H*), 7.32-7.38 (m, 2H, Ar *H*), 8.14 (d, *J* = 8.0 Hz, 1H, Ar *H*).

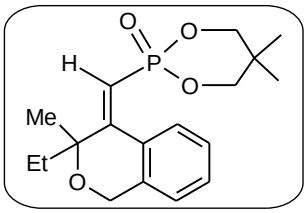
^{13}C NMR: δ 20.8, 21.8, 26.3, 32.4 (d, *J*(PC) = 6.1 Hz), 63.5, 76.0 (d, *J*(PC) = 6.1 Hz), 76.3 (d, *J*(PC) = 6.0 Hz), 106.1 (d, *J*(PC) = 179.6 Hz), 123.5, 126.7, 129.3 (d, *J*(PC) = 7.9 Hz), 130.1, 130.5, 136.5, 160.9.

^{31}P NMR: δ 13.5.

LC-MS: *m/z* 322 $[M]^+$.

Anal. Calcd. for $C_{17}H_{23}O_4P$: C, 63.35; H, 7.19. Found: C, 63.40; H, 7.17.

Compound 42



Yield: by NMR 75%; isolated 0.26 g (60%).

Mp: 178 – 180 ^{o}C.

IR (KBr): 2975, 1597, 1458, 1258, 1053, 999 cm^{-1}.

^{1}H NMR: δ 0.84 (s, 3H, C*H*$_3$), 0.88-0.92 (t, 3H, C*H*$_3$), 1.20 (s, 3H, C*H*$_3$), 1.49 (s, 3H, C*H*$_3$), 1.66-1.80 (m, 2H, C*H*$_2$), 3.51-3.92 (m, 4H, 2 OC*H*$_2$), 4.74-4.79 (m, 2H, OC*H*$_2$), 5.60 (d, *J*(PH) = 12.8 Hz, 1H, =C*H*), 7.09-7.40 (m, 3H, Ar *H*), 8.13 (d, 1H, Ar *H*).

^{13}C NMR: δ 8.4, 20.9, 21.8, 24.1, 31.9, 32.3, 63.4, 76.1 (d, *J*(PC) = 5.9 Hz), 76.4 (d, *J*(PC) = 6.0 Hz), 78.9, 107.3 (d, *J*(PC) = 179.8 Hz), 123.5, 126.9, 130.1, 130.3, 137.0, 160.8.

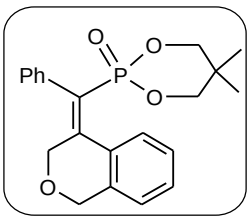
^{31}P NMR: δ 13.3.

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

Anal. Calcd. for $C_{18}H_{25}O_4P$: C, 64.27; H, 7.49. Found: C, 64.37; H, 7.48.

X-ray structure was determined for this sample.

Compound 43



Yield: by NMR 76%; isolated 0.21 g (57%).

Mp: 158 - 162 ^{o}C.

IR (KBr): 2957, 1605, 1476, 1256, 1111, 1057, 1007 cm^{-1}.

^{1}H NMR: δ 0.66 (s, 3H, CH_3), 1.07 (s, 3H, CH_3), 3.53-3.58 (m, 2H, OCH_2), 3.94-4.00 (m, 2H, OCH_2), 4.84 (s, 2H, OCH_2), 5.04 (d, *J* = 2.8 Hz, 2H, OCH_2), 6.60-7.31 (m, 9H, Ar *H*).

^{13}C NMR: δ 21.0, 21.8, 32.3 (d, *J*(PC) = 6.1 Hz), 68.3 (d, *J*(PC) = 7.6 Hz), 68.6, 75.9, 124.4, 125.7 (d, *J*(PC) = 175.5 Hz), 125.6, 127.8, 128.8, 129.9, 130.5, 131.4 (d, *J*(PC) = 21.9 Hz), 137.5 (d, *J*(PC) = 8.2 Hz), 137.8, 147.8 (d, *J*(PC) = 13.7 Hz) [Fig. 38].

^{31}P NMR: δ 10.7.

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

Anal. Calcd. for $C_{21}H_{23}O_4P$: C, 68.10; H, 6.26. Found: C, 68.12; H, 6.25.

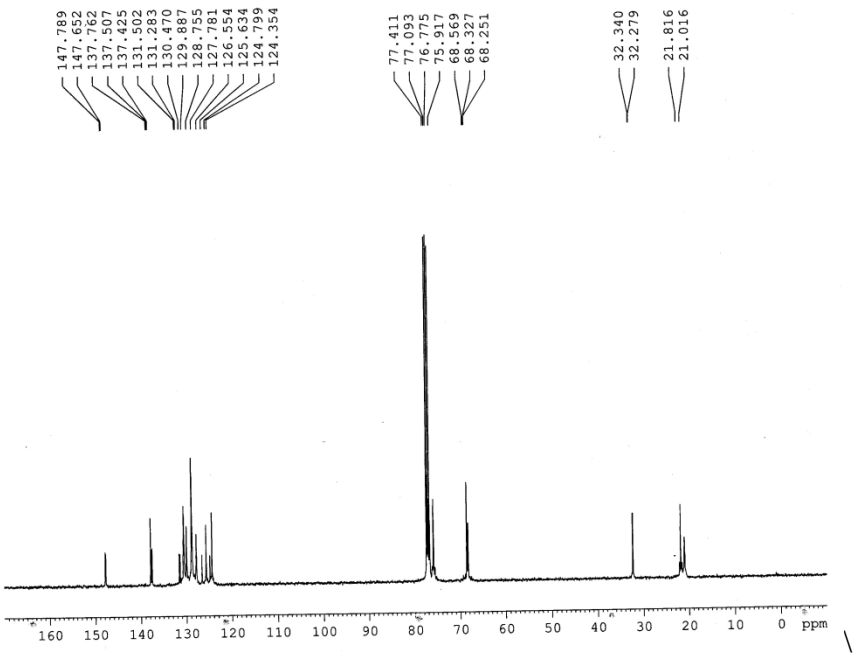
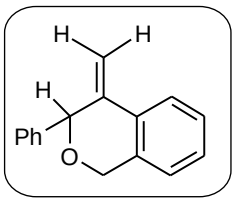


Figure 38. ^{13}C NMR spectrum of compound **43**

Compound 44



Yield: 0.43 g (62%).

Mp: 36 - 38 ^{o}C.

IR (KBr): 3038, 2832, 1817, 1626, 1483, 1451, 1368, 1024 cm^{-1}.

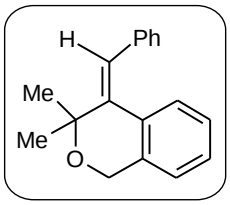
^{1}H NMR: δ 4.76 (d, *J* = 1.2 Hz, 1H, (C*H*)Ph), 4.77 (AB qrt, *J*(PH) = 12.2 Hz, 2H, OCH_2), 5.41 (s, 1H, =CH_AH$_B$), 5.79 (s, 1H, =CH$_A$$H_B$), 7.05-7.42 (m, 9H, Ar *H*).

^{13}C NMR: δ 66.5, 80.3, 110.2, 123.8, 124.5, 127.0, 127.9$_6$, 128.0$_2$, 128.1, 128.4, 131.7, 134.5, 139.4, 141.3.

GC-MS: *m/z* 222 $[M]^{+}$.

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.56; H, 6.28.

Compound 45



Yield: 0.24 g (50%) (viscous liquid).

IR (neat): 1722, 1597, 1485, 1447, 1364, 1144, 1088 cm^{-1}.

^{1}H NMR: δ 1.50 (s, 6H, 2 CH_3), 4.81 (s, 2 H, OCH_2), 6.66 (s, 1H, = (C*H*)Ph), 6.93-7.29 (m, 9H, Ar *H*).

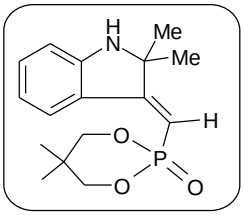
^{13}C NMR: δ 26.9, 63.9, 75.6, 123.3, 124.1, 125.8, 126.8, 127.4, 128.3, 129.2, 129.8, 137.3, 138.1.

Anal. Calcd. for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.32; H, 7.22.

3.52 Synthesis of phosphono-indoles 48-49: General procedure

To a mixture of allene ($OCH_2CMe_2CH_2O$)P(O)(CH=C=CMe_2) (**3c**) (1.39 mmol), $Pd(OAc)_2$ (0.016 g, 0.074 mmol), Ph_3P (0.055 g, 0.21 mmol), 2-iodoaniline (**46** or **47**; 1.67 mmol) and K_2CO_3 (0.384 g, 2.78 mmol) in 25 mL RBF, DMF (5 mL) was added under N_2 atmosphere. The contents were heated at 90-100 ^{o}C for 24 h. The mixture was then quenched with water (5 mL) and extracted with ether (3 x 20 mL). The whole organic layer was washed with water (3 x 20 mL), dried (Na_2SO_4), filtered, and concentrated. The residue was subjected to column chromatography (hexane/ EtOAc; 3:2) to afford the product **48** or **49**.

Compound 48



Yield: 0.31 g (74%).

Mp: 182-186 ^{o}C.

IR(KBr): 3393, 2975, 1591, 1476, 1312, 1263, 1005 cm^{-1}.

^{1}H NMR: δ 0.96 (s, 3H, C*H*$_3$), 1.21 (s, 3H, C*H*$_3$), 1.38 (s, 6H, 2 C*H*$_3$), 3.85-3.90 (m, 2H, OC*H*$_2$), 4.03-4.10 (m, 2H, OC*H*$_2$), 5.24 (d, *J*(PH) = 14.0 Hz, 1H, = C*H*), 6.69 (d, *J* = 8.0 Hz, 1H, Ar *H*), 6.76-6.81 (m, 1H, Ar *H*),7.22-7.27 (m, 1H, Ar H), 8.28 (d, 1H, *J* = 8.0 Hz, Ar *H*).

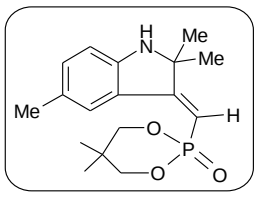
^{13}C NMR: δ 21.2, 21.8, 29.8, 32.7 (d, *J*(PC) = 5.8 Hz), 65.5 (d, *J*(PC) = 22.0 Hz), 76.2 (d, *J*(PC) = 5.8 Hz), 96.0 (d, *J*(PC) = 191.1 Hz), 110.6, 118.9, 128.1, 133.3, 153.6, 169.6 (d, *J*(PC) = 5.4 Hz). Two minor unidentified peaks at δ 121.6 and 132.1 were also found.

^{31}P NMR: δ 14.4.

LC/MS: *m/z* 308 $[M+1]^{+}$.

Anal. Calcd. for $C_{16}H_{22}NO_3P$: C, 62.53; H, 7.22; N, 4.56. Found: C, 62.35; H, 7.28; N, 4.61.

Compound 49



Yield: 0.32 g (72%).

Mp: 162-166 ^{o}C.

IR(KBr): 3345, 2965, 1620, 1586, 1497, 1292, 1250, 1057 cm^{-1}.

^{1}H NMR: δ 0.97 (s, 3H, C*H*$_3$), 1.22 (s, 3H, C*H*$_3$), 1.38 (s, 6H, 2 C*H*$_3$), 2.30 (s, 3H, Ar C*H*$_3$), 3.85-3.90 (m, 2H, OC*H*$_2$), 4.05-4.12 (m, 2H, OC*H*$_2$), 5.21 (d, *J*(PH) = 13.3 Hz, 1H, = C*H*), 6.63 (d, *J* = 8.1 Hz, 1H, Ar *H*), 7.08 (d, *J* = 8.0 Hz, 1H, Ar *H*), 8.13 (s, 1H, Ar *H*).

^{13}C NMR: δ 21.0, 21.2, 21.8, 29.8, 32.6 (d, *J*(PC) = 6.0 Hz), 65.7 (d, *J*(PC) = 22.0 Hz), 76.0 (d, *J*(PC) = 5.8 Hz), 95.8 (d, *J*(PC) = 191.8 Hz), 110.7, 122.0 (d, *J*(PC) = 6.9 Hz), 127.8 (d, *J*(PC) = 3.7 Hz), 128.5 (d, *J*(PC) = 14.7 Hz), 134.5, 151.7, 169.7.

^{31}P NMR: δ 14.3.

LC/MS: *m/z* 322 $[M+1]^+$.

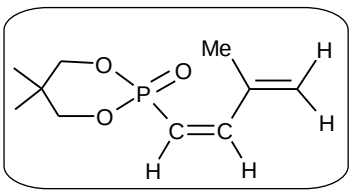
Anal. Calcd. for $C_{17}H_{24}NO_3P$: C, 63.54; H, 7.53; N, 4.36. Found: C, 63.28; H, 7.61; N 4.45.

X-ray structure was determined for this sample.

3.53 Synthesis of a phosphono-butadiene 51

To $Pd(OAc)_2$ (31 mg, 1.4 mmol) and $(OCH_2CMe_2CH_2O)P(O)(CH=C=CMe_2)$ (**3c**) (0.30 g, 1.4 mmol) in a 25 mL RBF, was added dimethylacetamide/ pivalic acid mixture (5 mL; 4:1) and then the reaction mixture was gradually heated from room temperature to 120 ^{o}C in air with the stirring continued for 2 h. The mixture was cooled to 25 ^{o}C, quenched with water (5 mL) and extracted with CH_2Cl_2 (3 x 20 mL). The whole organic layer was washed with water (3 x 20 mL), dried (Na_2SO_4), filtered, and concentrated. The residue was subjected to column chromatography (hexane/ EtOAc; 3:2) to afford the product **51.**

Compound 51



Yield: 0.19 g (65%).

Mp: 94-96 ^{o}C.

IR(KBr): 1626, 1589, 1478, 1260, 1057, 1007, 862 cm^{-1}.

^{1}H NMR: δ 1.05 (s, 3H, C*H*$_3$), 1.14 (s, 3H, C*H*$_3$), 1.89 (s, 3H, C*H*$_3$), 3.82-3.88 (m, 2H, OC*H*$_2$), 4.22-4.27 (m, 2H, OC*H*$_2$), 5.37-5.38 (m, 2H, = C*H*$_2$), 5.67-5.77 (m, 1H, =C*H*), 7.21-7.31 (m, 1H, =C*H*).

^{13}C NMR: δ 17.7, 21.5, 21.7, 32.6 (d, *J*(PC) = 5.7 Hz), 75.5 (d, *J*(PC) = 5.9 Hz), 112.0 (d, *J*(PC) = 191.0 Hz), 124.8, 140.7 (d, *J*(PC) = 23.9 Hz), 152.9 (d, *J*(PC) = 5.9 Hz).

^{31}P NMR: δ 15.6.

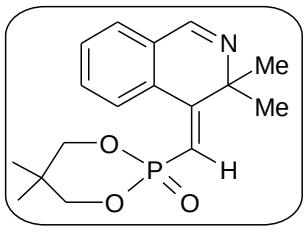
LC/MS: *m/z* 217 $[M+1]^+$.

Anal. Calcd. for $C_{10}H_{17}O_3P$: C, 55.55; H, 7.93. Found: C, 55.68; H, 7.85.

3.54 Synthesis of a phosphono-isoquinoline 53

To $(OCH_2CMe_2CH_2O)P(O)(CH=C=CMe_2)$ (**3c**) (1.39 mmol), $Pd(OAc)_2$ (0.016 g, 0.074 mmol), Ph_3P (0.055 g, 0.21 mmol), 2-iodo-*t*-butylbenzaldimine **52** (1.67 mmol) and Na_2CO_3 (0.147 g, 1.39 mmol) in 25 mL RBF, CH_3CN (5 mL) was added under N_2 atmosphere. The contents were heated under reflux for 24 h. The mixture was then quenched with water (5 mL) and extracted with ether (3 x 20 mL). The whole organic layer was washed with water (3 x 20 mL), dried (Na_2SO_4), filtered, and concentrated. The residue was subjected to column chromatography (hexane/ EtOAc; 2:3) to afford the product **53.**

Compound 53



Yield: 0.30 g (65%).

Mp: 122-126 ^{o}C.

IR(KBr): 2963, 1628, 1588, 1468, 1262, 1063, 1013 cm^{-1}.

^{1}H NMR: δ 0.81 (s, 3H, C*H*$_3$), 1.17 (s, 3H, C*H*$_3$), 1.47 (s, 6H, 2 C*H*$_3$), 2.30 (s, 3H, C*H*$_3$), 3.61-3.65 (m, 2H, OC*H*$_2$), 3.72-3.80 (m,

2H, OCH_2), 5.95 (d, *J*(PH) = 13.2 Hz, 1H, = (C*H*)P), 7.37, 7.54 and 8.17 (br m, together 4H, Ar-H), 8.35 (s, 1H, N=C*H*).

^{13}C NMR: δ 20.8, 21.8, 27.5, 32.4, 61.7 (d, *J*(PC) = 18.9 Hz), 76.4, 111.0 (d, *J*(PC) = 177.1 Hz), 126.9, 129.7, 130.8, 131.3, 131.8, 157.8, 162.7.

^{31}P NMR: δ 11.4.

LC/MS: *m/z* 320 $[M+1]^+$.

Anal. Calcd. for $C_{17}H_{22}NO_3P$: C, 63.94; H, 6.94; N, 4.39. Found: C, 63.85; H, 6.89; N 4.51.

X-ray structure was determined for this sample.

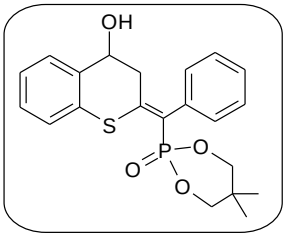
3.6 Base catalyzed reactions of allenylphosphonates with 2-mercaptobenzaldehydes

3.61 Standardization of reaction conditions leading to phosphono-thiochroman 56 from the allene 3e and 2-mercapto benzaldehyde 54

To a 25 mL round-bottomed flask containing $(OCH_2CMe_2CH_2O)P(O)C(Ph)=C=CH_2$ (**3e**) (0.200 g, 0.76 mmol), 2-mercaptobenzaldehyde (0.136 g, 0.98 mmol) and base [K_2CO_3, K_3PO_4, DABCO, DBU or NaOAc; 0.15 mmol], the solvent [THF, DMF, DMSO, CH_3CN, EtOH, PEG-400; 4 mL] was added under N_2 atmosphere. The contents were heated at 90 ^oC for 4-6 h under N_2 atmosphere. The reaction mixture was quenched with water (5 mL) and extracted with CH_2Cl_2 (3 x 25 mL). The whole organic layer was washed with water (3 x 25 mL), dried (Na_2SO_4), filtered, and concentrated under vacuum. The reaction mixture was checked by ^{31}P/ ^{1}H NMR at this stage. Other details are presented in Tables 4 and 5 in the Results and Discussion. In case of the reaction in ethanol, all the products (i.e. phosphono-thiochromans **56, 58** and allylphosphonate **57**; R_f values were in the order: **58**> **57**> **(Z)-56**> **(E)-56**.

Compound 56 (isolated from the reaction in DMSO/ K_2CO_3/ 4 h/ 90 ^oC using ethyl acetate-hexane mixture (1:2) as the eluant)

(*Z*)-56 (purity ~95%)



Yield: 0.09 g (23%).

Mp: 144-148 ^{o}C.

IR (KBr): 3299, 1557, 1472, 1441, 1236, 1053, 1007 cm^{-1}.

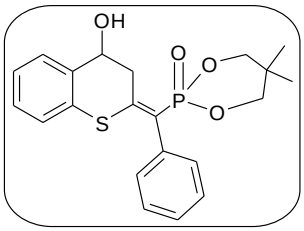
^{1}H NMR: δ 0.62 (s, 3H, CH_3), 1.02 (s, 3H, CH_3), 2.61-2.67 (m, 1H, (OH)CHCH_AH$_B$), 2.84-2.90 (m, 1H, (OH)CHCH$_A$$H_B$) 3.51-3.67 (m, 2H, OC$H_2$), 3.98-4.07 (m, 2H, OC$H_2$), 4.73-4.74 (m, 1H, C*H*(OH)), 7.15-7.40 (m, 9H, Ar *H*). The O*H* peak was broad.

^{13}C NMR: δ 21.1, 21.7, 32.3 (d, *J*(PC) = 6.2 Hz), 38.5 (d, *J*(PC) = 14.7 Hz), 67.8, 75.7, 122.8 (d, *J*(PC) = 182.7 Hz), 126.0, 126.5, 127.0, 127.8, 128.6, 130.1, 130.7, 136.5 (d, *J*(PC) = 8.8 Hz), 151.5 (d, *J*(PC) = 8.5 Hz).

^{31}P NMR: δ 9.8.

LC/MS: *m/z* 385 [M-18+1]$^{+}$.

(*E*)-56



Yield: 0.22 g (57%).

Mp: 244-248 ^{o}C.

IR (KBr): 3302, 1557, 1472, 1235, 1119, 1053, 1007 cm^{-1}.

^{1}H NMR: δ 0.64 (s, 3H, CH_3), 0.98 (s, 3H, CH_3), 3.11 (br s, 1H, O*H*), 3.47-3.53 (m, 1H, (OH)CHCH_AH$_B$), 3.57-3.63 (m, 2H, OCH_2), 3.81-3.87 (m, 1H, (OH)CHCH$_A$$H_B$), 4.01-4.06 (m, 2H, OC$H_2$), 4.95-4.96 (m, 1H, C*H*(OH)), 7.01-7.47 (m, 9H, Ar *H).*

^{13}C NMR: δ 20.3, 21.1, 31.9 (d, *J*(PC) = 6.3 Hz), 37.4 (d, *J*(PC) = 5.4 Hz), 67.0, 75.7 (d, *J*(PC) =5.3 Hz), 120.8 (d, *J*(PC) = 187.1 Hz), 125.6, 125.9, 126.3, 127.8, 128.1, 128.5, 129.7, 130.0 (d, *J*(PC) = 4.5 Hz), 135.5 (d, *J*(PC) = 8.2 Hz), 136.7, 155.7 (d, *J*(PC) = 21.0 Hz).

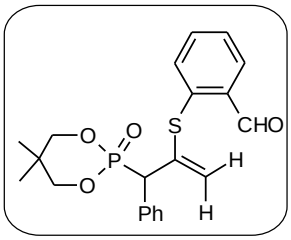
^{31}P NMR: δ 9.0.

LC/MS: *m/z* 402 $[M]^+$.

Anal. Calcd. for $C_{21}H_{23}O_4PS$: C, 62.67; H, 5.76 Found: C, 62.61; H, 5.79.

X-ray structure was determined for this sample.

Compound 57 (isolated from the reaction in EtOH/ K_2CO_3/ 6 h/ 100 ^oC using ethyl acetate-hexane mixture (1:2) as the eluant)



Yield: 0.05 g (16%).

Mp: 136-140 ^oC.

IR (KBr): 1692, 1584, 1478, 1260, 1057, 1009 cm^{-1}.

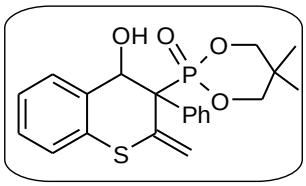
^{1}H NMR: δ 0.66 (s, 3H, C*H*$_3$), 0.97 (s, 3H, C*H*$_3$), 3.58-3.69 (m, 2H, OC*H*$_2$), 3.97 (d, 1H, *J*(PH) = 24.4 Hz, P*CH*), 4.09-4.18 (m, 2H, OC*H*$_2$), 5.50 (s, 1H, =*CH*$_A$H$_B$), 6.22 (s, 1H, =CH$_A$*H*$_B$), 7.26-7.92 (m, 9H, Ar *H*), 10.2 (s, 1H, C*HO*).

^{13}C NMR: δ 21.3, 21.5, 32.6 (d, *J*(PC) = 7.0 Hz), 50.1 (d, *J*(PC) = 133.0 Hz), 75.9, 122.2, 128.1, 128.6, 128.7, 129.5, 129.6, 130.0, 133.5, 134.4, 136.1, 136.8, 139.0, 191.4.

^{31}P NMR: δ 17.3.

LC/MS: *m/z* 403 $[M+1]^+$.

Compound 58 (isolated from the reaction in EtOH/ K_2CO_3/ 6 h/ 100 ^oC using ethyl acetate-hexane mixture (1:2) as the eluant)



Yield: 0.12 g (38%).

Mp: 236-240 ^{o}C.

IR (KBr): 3221, 1588, 1468, 1238, 1067, 1013, 897 cm^{-1}.

^{1}H NMR: δ 0.86 (s, 3H, C*H*$_3$), 1.14 (s, 3H, C*H*$_3$), 3.53-3.91 (dt, 2H, OC*H*$_2$), 4.16-4.29 (m, 2H, OC*H*$_2$), 4.67 (s, 1H, O*H*), 5.56 (d, 1H, *J* = 8.0 Hz, =*CH*(OH)), 5.68 (d, 1H, *J* = 4.0 Hz, =*CH*$_A$H$_B$), 5.81 (d, 1H, *J* = 4.0 Hz, =CH$_A$*H*$_B$), 7.13-7.47 (m, 9H, Ar *H*).

^{13}C NMR (CDCl$_3$ + 5%MeOH): δ 20.6, 21.6, 32.4 (d, *J*(PC) = 8.6 Hz), 59.3 (d, *J*(PC) = 135.6 Hz), 73.3, 77.8 (d, *J*(PC) = 7.7 Hz), 116.4, 124.4, 125.1, 126.2, 127.2, 127.4, 130.5, 130.7, 134.1, 136.4, 136.5, 139.3 [Fig. 39].

^{31}P NMR: δ 20.3.

LC/MS: *m/z* 403 [M+1]$^{+}$.

Anal. Calcd. for $C_{21}H_{23}O_4PS$: C, 62.67; H, 5.76. Found: C, 62.48; H, 5.81.

X-ray structure was determined for this sample.

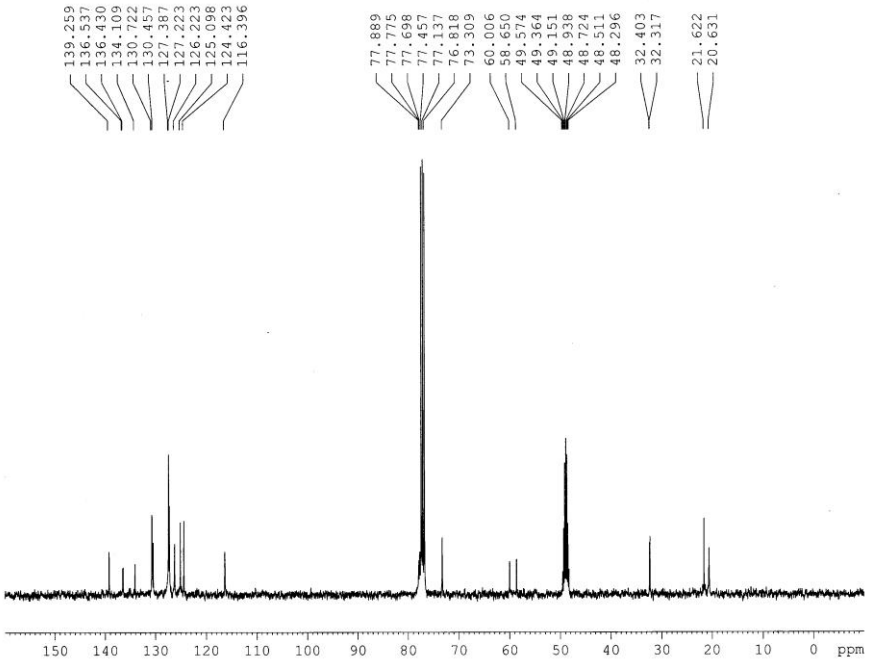
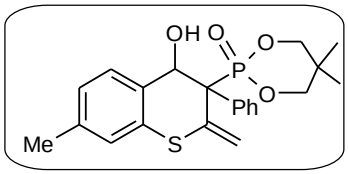


Figure 39. ^{13}C NMR spectrum of compound **58**

Compound 59

This is similar to compound **58**. It was prepared by the reaction allene **3e** with 5-methyl-2-mercapto-benzaldehyde **55** in ethanol using the same molar quantities of the reactants and isolated by column chromatography on silica gel (hexane/ EtOAc; 1:1).



Yield: 0.08 g (25%).

Mp: 202-206 ^{o}C.

IR (KBr): 3264, 1605, 1480, 1240, 1069, 1005 cm^{-1}.

^{1}H NMR: δ 0.85 (s, 3H, C*H*$_3$), 1.15 (s, 3H, C*H*$_3$), 2.26 (s, 3H, Ar C*H*$_3$), 3.56-3.91 (dt, 2H, OC*H*$_2$), 4.16-4.28 (m, 2H, OC*H*$_2$), 4.79 (s, 1H, O*H*), 5.51 (d, 1H, *J* = 8.4 Hz, =*CH*(OH)), 5.64 (d, 1H, *J* = 4.0 Hz, =C*H*$_A$H$_B$), 5.79 (d, 1H, *J* = 5.2 Hz, =CH$_A$*H*$_B$), 6.97-7.30 (m, 8H, Ar *H*).

^{13}C NMR: δ 21.3, 21.5, 22.0, 33.0 (d, *J*(PC) = 8.1 Hz), 60.4 (d, *J*(PC) = 132.8 Hz), 72.8, 77.8 (d, *J*(PC) = 7.7 Hz), 118.8 (d, *J*(PC) = 7.8 Hz), 125.9, 127.2, 127.3, 127.4, 127.5, 128.3, 130.4 (d, *J*(PC) = 6.9 Hz), 135.8, 136.0, 136.4 (d, *J*(PC) = 12.4 Hz), 140.7 (d, *J*(PC) = 7.5 Hz).

^{31}P NMR: δ 20.4.

LC/MS: *m/z* 417 [M+1]$^{+}$.

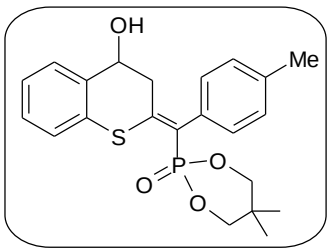
Anal. Calcd. for $C_{22}H_{25}O_4PS$: C, 63.45; H, 6.05. Found: C, 63.34; H, 6.12.

3.62 Reaction of allenes 3e-k and 5 with 2-mercapto benzaldehydes 54-55- Synthesis of thiochromans 56 and 60-74

To a 25 mL round-bottomed flask containing allene **3e-k** (0.76 mmol), 2-mercaptobenzaldehyde **54** or **55** (0.98 mmol) and K_2CO_3 (0.021 g, 0.15 mmol), was added DMSO (4 mL) under N_2 atmosphere. The contents were heated at 90 ^{o}C for 4 h under N_2 atmosphere. The reaction mixture was quenched with water (5 mL) and extracted with CH_2Cl_2 (3 x 25 mL). The whole organic layer was washed with water

(3 x 25 mL), dried (Na_2SO_4), filtered, concentrated and the products were isolated by column chromatography (hexane/ EtOAc; 1:1) on silica gel. Both *Z* and *E* isomers are formed in most cases. Details on the combined yield of *Z* and *E* isomers are given in Chapter 2 (Tables 6 and 7). Isolated yield of individual isomer as applicable in each case is given here. Details on compounds (*Z*)-**56** and (*E*)-**56** are already given above.

Compound (*Z*)-60 (from 3f and 54, higher R_f)



Yield: 0.05 g (18%).

Mp: 186-190 ^{o}C.

IR (KBr): 3391, 1572, 1508, 1472, 1439, 1233 cm^{-1}.

^{1}H NMR: δ 0.68 (s, 3H, CH_3), 1.04 (s, 3H, CH_3), 2.37 (s, 3H, Ar CH_3), 2.61-2.66 (m, 1H, (OH)CHCH_AH$_B$), 2.86-2.93 (m, 1H, (OH)CHCH$_A$$H_B$), 3.52-3.68 (m, 2H, OC$H_2$), 3.96-4.06 (m, 2H, OC$H_2$), 4.72-4.74 (m, 1H, C*H*OH), 7.15-7.39 (m, 8H, Ar *H*).

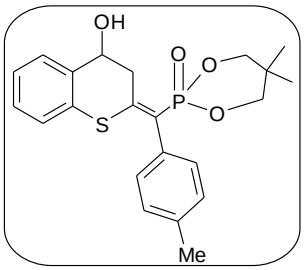
^{13}C NMR: δ 21.0, 21.3, 21.8, 32.3 (d, *J*(PC) = 7.0 Hz), 38.6 (d, *J*(PC) = 15.0 Hz), 67.8, 75.9 (d, *J*(PC) = 6.0 Hz), 122.6 (d, *J*(PC) = 180.0 Hz), 126.0, 126.4, 126.8, 128.4, 129.3, 130.4, 130.6, 133.4 (d, *J*(PC) = 8.0 Hz), 137.0, 137.6, 151.3 (d, *J*(PC) = 8.0 Hz).

^{31}P NMR: δ 9.7.

LC/MS: *m/z* 417 $[M+1]^+$.

Anal. Calcd. for $C_{22}H_{25}O_4PS$: C, 63.45; H, 6.05. Found: C, 63.55; H, 6.10.

Compound (*E*)-60 (from 3f and 54, lower R_f)



Yield: 0.18 g (60%).

Mp: 252-256 ^{o}C.

IR (KBr): 3312, 1557, 1507, 1470, 1233, 1057, 1009 cm^{-1}.

^{1}H NMR: δ 0.68 (s, 3H, CH_3), 1.01 (s, 3H, CH_3), 2.40 (s, 3H, Ar CH_3), 3.42-3.47 (m, 1H, (OH)CHCH_AH$_B$), 3.58-3.65 (m, 2H, OCH_2), 3.81-3-3.88 (m, 1H, (OH)CHCH$_A$$H_B$), 3.98-4.04 (m, 2H, OC$H_2$), 4.94-4.96 (m, 1H, C*H*OH), 7.02-7.48 (m, 8H, Ar *H*).

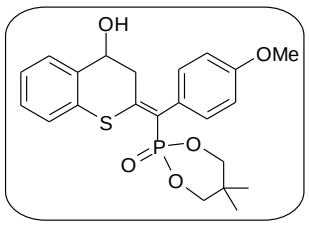
^{13}C NMR: δ 21.0, 21.4, 21.7, 32.3 (d, *J*(PC) = 6.4 Hz), 37.5 (d, *J*(PC) = 5.3 Hz), 67.8, 75.7 (d, *J*(PC) = 6.9 Hz), 122.9 (d, *J*(PC) = 185.6 Hz), 125.9, 127.5, 128.3, 129.3, 129.4, 130.1, 130.4 (d, *J*(PC) = 4.5 Hz), 130.6, 133.0 (d, *J*(PC) = 8.1 Hz), 136.3, 138.2, 154.5 (d, *J*(PC) = 21.8 Hz).

^{31}P NMR: δ 9.2.

LC/MS: *m/z* 417 [M+1]$^{+}$.

Anal. Calcd. for $C_{22}H_{25}O_4PS$: C, 63.45; H, 6.05. Found: C, 63.51; H, 6.03

Compound (*Z*)-61 (from 3g and 54, higher R_f)



Yield: 0.04 g (13%).

Mp: 174-176 ^{o}C.

IR (KBr) : 3308, 1696, 1539, 1250, 1055, 1007 cm^{-1}.

^{1}H NMR: δ 0.67 (s, 3H, CH_3), 1.03 (s, 3H, CH_3), 2.67-2.72 (m, 1H, (OH)CHCH_AH$_B$), 2.76-2.79 (m, 1H, (OH)CHCH$_A$$H_B$), 3.47-

3.68 (m, 2H, OCH_2), 3.80 (s, 3H, OCH_3), 3.88-4.01 (m, 2H, OCH_2), 4.70-4.72 (m, 1H, OC*H*(OH)), 6.84-7.43 (m, 8H, Ar *H*).

^{13}C NMR: δ 21.1, 21.8, 32.6 (d, *J*(PC) = 6.4 Hz), 38.7 (d, *J*(PC) = 14.4 Hz), 55.3, 67.8, 75.8 (d, *J*(PC) = 5.0 Hz), 114.0, 122.1 (d, *J*(PC) = 181.7 Hz), 126.0, 126.4, 126.8, 128.4, 128.6 (d, *J*(PC) = 8.3 Hz), 130.7, 131.6, 137.1, 151.7 (d, *J*(PC) = 9.3 Hz), 159.1.

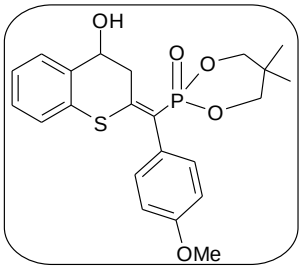
^{31}P NMR: δ 9.9.

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

Anal. Calcd. for $C_{22}H_{25}O_5PS$: C, 61.10; H, 5.83. Found: C, 61.22; H, 5.85.

X-ray structure was determined for this sample.

Compound (*E*)-61 (from 3g and 54, lower R_f)



Yield: 0.19 g (66%).

Mp: 212-214 ^{o}C.

IR (KBr): 3328, 1605, 1562, 1505, 1233, 1057, 1007 cm^{-1}.

^{1}H NMR: δ 0.67 (s, 3H, CH_3), 1.00 (s, 3H, CH_3), 3.45-3.50 (m, 1H, (OH)CHCH_AH$_B$), 3.58-3.64 (m, 2H, OCH_2), 3.78-3.83 (m, 1H, (OH)CHCH$_A$$H_B$), 3.85 (s, 3H, OC$H_3$), 4.00-4.05 (m, 2H, OC$H_2$), 4.93-4.95 (m, 1H, C*H*OH), 6.94-7.48 (m, 8H, Ar *H*).

^{13}C NMR: δ 21.1, 21.7, 32.3 (d, *J*(PC) = 6.0 Hz), 37.5 (d, *J*(PC) = 5.0 Hz), 55.2, 67.7, 75.6 (d, *J*(PC) = 5.0 Hz), 114.1, 122.1 (d, *J*(PC) = 187.0 Hz), 125.9, 126.0, 127.3, 128.2 (d, *J*(PC) = 6.0 Hz), 130.6, 131.6 (d, *J*(PC) = 4.0 Hz), 136.6, 155.3 (d, *J*(PC) = 23.0 Hz), 159.4$_8$, 159.5$_0$.

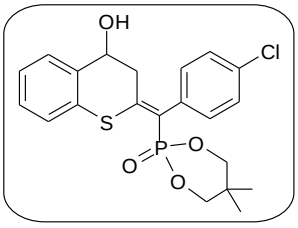
^{31}P NMR: δ 9.4.

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

Anal. Calcd. for $C_{22}H_{25}O_5PS$: C, 61.10; H, 5.83. Found: C, 61.25; H, 5.80.

X-ray structure was determined for this sample.

Compound (*Z*)-62 (from 3h and 54, higher R_f)



Yield: 0.05 g (18%).

Mp: 158-162 ^{o}C.

IR (KBr): 3400, 1701, 1460, 1262, 1092, 1057, 1013 cm^{-1}.

^{1}H NMR: δ 0.69 (s, 3H, CH_3), 1.00 (s, 3H, CH_3), 2.59-2.63 (m, 1H, (OH)CHCH_AH$_B$), 2.84-2.87 (m, 1H, (OH)CHCH$_A$$H_B$), 3.53-3.69 (m, 2H, OC$H_2$), 4.02-4.12 (m, 2H, OC$H_2$), 4.73-4.75 (m, 1H, C*H*(OH)), 7.19-7.40 (m, 8H, Ar *H)*.

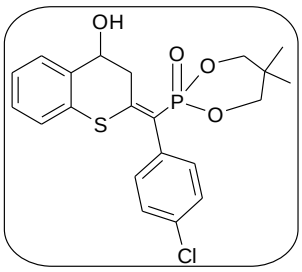
^{13}C NMR: δ 21.1, 21.6, 32.3 (d, *J*(PC) = 6.1 Hz), 38.5 (d, *J*(PC) = 14.5 Hz), 67.7, 75.6 (d, *J*(PC) = 6.3 Hz), 121.2 (d, *J*(PC) = 183.7 Hz), 126.1, 126.5, 127.0, 128.7, 128.7$_8$, 128.7$_9$, 130.5, 131.9, 133.9 (d, *J*(PC) = 2.4 Hz), 135.0 (d, *J*(PC) = 8.4 Hz), 136.4, 152.7 (d, *J*(PC) = 8.6 Hz).

^{31}P NMR: δ 9.8.

LC/MS: *m/z* 419 $[M-18]^+$and 421 $[M-18+2]^+$.

Anal. Calcd. for $C_{21}H_{22}O_4ClPS$: C, 57.73; H, 5.08. Found: C, 57.65; H, 5.12.

Compound (*E*)-62 (from 3h and 54, lower R_f)



Yield: 0.18 g (62%).

Mp: 226-230 ^{o}C.

IR (KBr): 3324, 1555, 1480, 1346, 1236, 1055, 1009 cm^{-1}.

^{1}H NMR: δ 0.69 (s, 3H, CH_3), 0.96 (s, 3H, CH_3), 3.43-3.48 (m, 1H, (OH)CHC$H_A$$H_B$), 3.58-3.65 (m, 2H, OC$H_2$), 3.86-3.93 (m, 1H, (OH)CHC$H_A$$H_B$), 4.08-4.13 (m, 2H, OC$H_2$), 4.94-4.96 (m, 1H, C*H*(OH)), 7.03-7.48 (m, 8H, Ar *H*).

^{13}C NMR: δ 21.0, 21.4, 32.3 (d, *J*(PC) = 6.1 Hz), 37.6, 67.2, 75.5$_6$ (d, *J*(PC) = 5.8 Hz), 75.6 (d, *J*(PC) = 5.9 Hz), 119.8 (d, *J*(PC) = 191.0 Hz), 125.8, 126.3, 126.8, 128.2, 129.0, 129.7, 131.8 (d, *J*(PC) = 4.0 Hz), 134.3 (d, *J*(PC) = 8.0 Hz), 134.4, 136.8, 157.3 (d, *J*(PC) = 21.6 Hz).

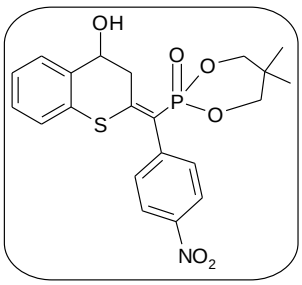
^{31}P NMR: δ 9.2.

LC/MS: *m/z* 419 $[M-18]^+$and 421 [M-18+2].

Anal. Calcd. for $C_{21}H_{22}O_4ClPS$: C, 57.73; H, 5.08 Found: C, 57.85; H, 5.01.

Compound (*E*)-63 (from 3i and 54, lower R_f)

(The *Z*–isomer was only a minor product and hence not isolated)



Yield: 0.18 g (63%).

Mp: 250-254 ^{o}C.

IR (KBr): 3322, 1734, 1653, 1238, 1055 cm^{-1}.

^{1}H NMR: δ 0.69 (s, 3H, CH_3), 0.96 (s, 3H, CH_3), 3.43-3.47 (m, 1H, (OH)CHC$H_A$$H_B$), 3.58-3.65 (m, 2H, OC$H_2$), 3.87-3.92 (m, 1H, (OH)CHC$H_A$$H_B$), 4.08-4.13 (m, 2H, OC$H_2$), 4.94-4.96 (m, 1H, C*H*(OH)), 7.03-7.48 (m, 8H, Ar *H*).

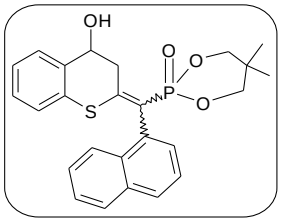
^{13}C NMR: δ 21.0, 21.3, 32.3 (d, *J*(PC) = 6.0 Hz), 37.6 (d, *J*(PC) = 4.6 Hz), 67.2, 75.6 (d, *J*(PC) = 6.0 Hz), 119.7 (d, *J*(PC) = 190.5 Hz), 125.8, 126.3, 126.7, 128.2, 129.0, 129.6, 131.8 (d, *J*(PC) = 3.9 Hz), 134.2 (d, *J*(PC) = 8.1 Hz), 134.4, 136.8, 157.3 (d, *J*(PC) = 21.4 Hz).

^{31}P NMR: δ 9.2.

LC/MS: *m/z* 421 $[M+1-18]^+$.

Anal. Calcd. for $C_{21}H_{22}NO_6PS$: C, 56.37; H, 4.96; N, 3.13. Found: C, 56.38; H, 4.85; N, 3.07.

Compound (*E/Z*)-64 (from 3j and 54)



Yield: 0.20 g (68%).

Mp: 206-210 ^{o}C.

IR (KBr): 3312, 1574, 1447, 1198, 1051, 997 cm^{-1}.

^{1}H NMR: δ 0.48 (s, 3H, C*H*$_3$), 0.92 (s, 3H, C*H*$_3$), 3.32-3.40 (m, 2H, OC*H*$_2$), 3.54-3.60 (m, 1H, (OH)CHC*H*$_A$H$_B$), 3.88-4.00 (m, 2H, OC*H*$_2$), 4.01-4.05 (m, 1H, (OH)CHCH$_A$*H*$_B$), 5.02-5.06 (m, 1H, CHOH), 6.89-8.07 (m, 11H, Ar *H*).

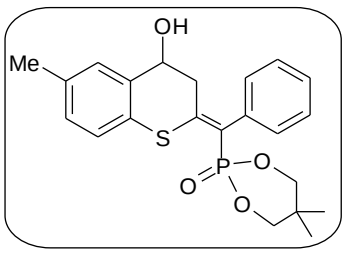
^{13}C NMR: δ 21.0, 21.6, 32.3, 37.7, 67.9, 75.6, 119.8, 125.3, 125.5, 125.7, 125.9, 126.0, 126.2, 126.6, 126.8, 127.2, 128.1, 128.3, 128.5, 128.7, 129.0, 130.4, 131.6, 133.5, 133.8, 136.6.

^{31}P NMR: δ 9.0 and 9.2 (2:5).

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

Anal. Calcd. for $C_{25}H_{25}O_4PS$: C, 66.36; H, 5.57. Found: C, 66.41; H, 5.52.

Compound (*Z*)-65 (from 3e and 55, higher R_f)



Yield: 0.06 g (18%).

Mp: 182-186 ^{o}C.

IR (KBr): 3376, 1684, 1543, 1474, 1262, 1061 cm^{-1}.

^{1}H NMR: δ 0.64 (s, 3H, CH_3), 1.01 (s, 3H, CH_3), 2.32 (s, 3H, Ar CH_3), 2.59-2.64 (m, 1H, (OH)CHCH_AH$_B$), 2.84-2.90 (m, 1H, (OH)CHCH$_A$$H_B$), 3.50-3.67 (m, 2H, OC$H_2$), 3.98-4.06 (m, 2H, OC$H_2$), 4.69-4.70 (m, 1H, C*H*(OH)), 7.06-7.39 (m, 8H, Ar *H*).

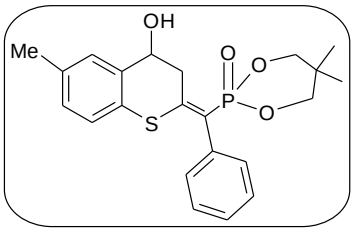
^{13}C NMR: δ 21.0$_6$, 21.0$_8$, 21.8, 32.3 (d, *J*(PC) = 6.0 Hz), 38.8 (d, *J*(PC) = 15.0 Hz), 68.0, 75.7 (d, *J*(PC) = 2.0 Hz), 75.8 (d, *J*(PC) = 3.0 Hz), 122.4 (d, *J*(PC) = 182.0 Hz), 126.5, 127.2, 127.7, 127.8, 128.6, 129.4, 130.7, 136.0, 136.4, 136.7 (d, *J*(PC) = 8.0 Hz), 152.0 (d, *J*(PC) = 8.0 Hz).

^{31}P NMR: δ 9.7.

LC/MS: *m/z* 417 $[M+1]^+$.

Anal. Calcd. for $C_{22}H_{25}O_4PS$: C, 63.45; H, 6.05. Found: C, 63.56; H, 6.11.

Compound (*E*)-65 (from 3e and 55, lower R_f)



Yield: 0.19 g (61%).

Mp: 220-224 ^{o}C.

IR (KBr): 3283, 1561, 1472, 1204, 1121, 1049, 1003 cm^{-1}.

^{1}H NMR: δ 0.64 (s, 3H, CH_3), 0.98 (s, 3H, CH_3), 2.31 (s, 3H, Ar CH_3), 3.43-3.48 (m, 1H, (OH)CHCH_AH$_B$), 3.56-3.63 (m, 2H, OCH_2), 3.83-3.89 (m, 1H, (OH)CHCH$_A$$H_B$), 4.01-4.06 (m, 2H, OC$H_2$), 4.91-4.93 (m, 1H, C*H*OH), 6.91-7.44 (m, 8H, Ar *H*).

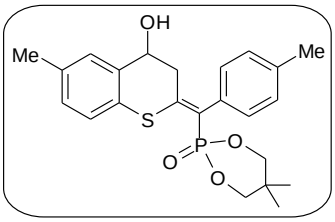
^{13}C NMR: δ 20.9$_8$, 21.0$_3$, 21.6, 32.3 (d, *J*(PC) = 6.3 Hz), 37.6 (d, *J*(PC) = 4.9 Hz), 67.8, 75.5 (d, *J*(PC) = 3.9 Hz), 75.6 (d, *J*(PC) = 3.9 Hz), 122.0 (d, *J*(PC) = 177.2 Hz), 125.8, 126.9, 127.9 (d, *J*(PC) = 4.7 Hz), 128.2, 128.6, 129.0, 130.4 (d, *J*(PC) = 4.4 Hz), 135.9, 136.3 (d, *J*(PC) = 7.9 Hz), 136.5, 155.7 (d, *J*(PC) = 22.0 Hz).

^{31}P NMR: δ 9.2.

LC/MS: *m/z* 416 $[M]^+$.

Anal. Calcd. for $C_{22}H_{25}O_4PS$: C, 63.45; H, 6.05. Found: C, 63.51; H, 6.01.

Compound (*Z*)-66 (~95%) (from 3f and 55, higher R_f)



Yield: 0.02 g (7%).

Mp: 150-154 °C.

IR (KBr): 3351, 1696, 1605, 1507, 1464, 1262, 1057, 1009 cm^{-1}.

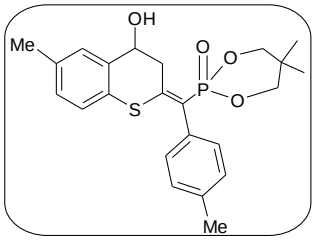
^{1}H NMR: δ 0.68 (s, 3H, C*H*$_3$), 1.04 (s, 3H, C*H*$_3$), 2.32 (s, 3H, Ar C*H*$_3$), 2.37 (s, 3H, Ar C*H*$_3$), 2.60-2.64 (m, 1H, (OH)CHC*H*$_A$H$_B$), 2.85-2.88 (m, 1H, (OH)CHCH$_A$*H*$_B$), 3.52-3.68 (m, 2H, OC*H*$_2$) 3.96-4.05 (m, 2H, OC*H*$_2$), 4.68-4.69 (m, 1H, C*H*(OH)), 7.06-7.26 (m, 7H, Ar *H*)

^{13}C NMR: δ 21.0, 21.2, 21.8, 32.3 (d, *J*(PC) = 6.4 Hz), 38.6 (d, *J*(PC) = 14.7 Hz), 67.9, 75.7 (d, *J*(PC) = 6.1 Hz), 122.4 (d, *J*(PC) = 181.1 Hz), 126.3, 127.1. 127.6, 129.2, 130.1, 133.5 (d, *J*(PC) = 8.3 Hz), 134.2, 135.8, 136.4, 137.5, 151.4 (d, *J*(PC) = 8.8 Hz).

^{31}P NMR: δ 9.8.

LC/MS: *m/z* 413 $[M+1-18]^+$.

Compoud *(E)*-66 (from 3f and 55, lower R_f)



Yield: 0.21 g (69%).

Mp: 230-234 °C.

IR (KBr): 3287, 1564, 1474, 1215, 1196, 1047, 993 cm^{-1}.

^{1}H NMR: δ 0.67 (s, 3H, CH_3), 1.00 (s, 3H, CH_3), 2.31 (s, 3H, Ar CH_3), 2.40 (s, 3H, Ar CH_3), 3.45-3.49 (m, 1H, (OH)CHC$H_A$$H_B$), 3.58-3.64 (m, 2H, OC$H_2$) 3.73-3.79 (m, 1H, (OH)CHC$H_A$$H_B$), 3.97-4.04 (m, 2H, OC$H_2$), 4.90-4.91 (m, 1H, C*H*(OH)), 6.91-7.30 (m, 7H, Ar *H*).

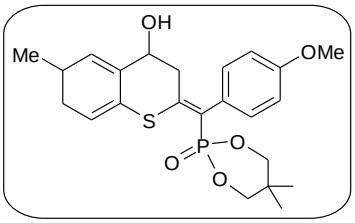
^{13}C NMR: δ 21.1, 21.5, 21.8, 32.4 (d, *J*(PC) = 6.2 Hz), 37.8 (d, *J*(PC) = 5.2 Hz), 67.8, 75.7 (d, *J*(PC) = 5.7 Hz), 122.2 (d, *J*(PC) = 186.1 Hz), 125.9, 127.0, 128.0, 129.0, 129.5, 130.2 (d, *J*(PC) = 4.3 Hz), 133.2 (d, *J*(PC) = 8.0 Hz), 135.9, 136.5, 138.1, 155.2 (d, *J*(PC) = 21.6).

^{31}P NMR: δ 9.4.

LC/MS: *m/z* 430 $[M]^+$.

Anal. Calcd. for $C_{23}H_{27}O_4PS$: C, 64.17; H, 6.32. Found: C, 64.25; H, 6.28.

Compound (*Z*)-67 (from 3g and 55, higher R_f)



Yield: 0.04 g (13%), gummy solid.

IR (neat): 3364, 1605, 1543, 1507, 1474, 1250, 1177 cm^{-1}.

^{1}H NMR: δ 0.68 (s, 3H, CH_3), 1.04 (s, 3H, CH_3), 2.31 (s, 3H, Ar CH_3), 2.63-2.67 (m, 1H, (OH)CHC$H_A$$H_B$),), 2.81-2.87 (m, 1H, (OH)CHC$H_A$$H_B$), 3.51-3.68 (m, 2H, OC$H_2$), 3.82 (s, 3H, OC$H_3$), 3.93-4.02 (m, 2H, OC$H_2$), 4.68-4.69 (m, 1H, C*H*OH), 6.87-7.23 (m, 7H, Ar *H*).

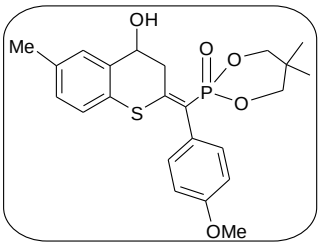
^{13}C NMR: δ 21.1, 21.8, 32.4 (d, *J*(PC) = 6.2 Hz), 38.7 (d, *J*(PC) = 14.4 Hz), 55.3, 68.0, 75.8, 114.0, 122.0 (d, *J*(PC) = 181.7 Hz), 126.4, 127.2, 127.7, 128.7 (d, *J*(PC) = 8.1 Hz), 129.3, 131.3, 131.8, 132.1 (d, *J*(PC) = 10.0 Hz), 135.9, 136.5, 151.8 (d, *J*(PC) = 9.2 Hz), 159.1.

^{31}P NMR: δ 10.3.

LC/MS: *m/z* 447 $[M+1]^+$.

Anal. Calcd. for $C_{23}H_{27}O_5PS$: C, 61.87; H, 6.10. Found: C, 61.75; H, 6.14.

Compound (*E*)-67 (from 3g and 55, lower R_f)



Yield: 0.20 g (65%).

Mp: 232-236 ^oC.

IR (KBr): 3277, 1605, 1562, 1505, 1246, 1202, 999 cm^{-1}.

^1H NMR: δ 0.67 (s, 3H, CH_3), 1.00 (s, 3H, CH_3), 2.31 (s, 3H, Ar CH_3), 3.42-3.47 (m, 1H, (OH)CHC$H_A$$H_B$), 3.58-3.64 (m, 2H, OC$H_2$), 3.79-4.05 (m, 1H, (OH)CHC$H_A$$H_B$), 3.85 (s, 3H, OC$H_3$), 4.00-4.05 (m, 2H, OCH_2), 4.90-4.91 (m, 1H, C*H*OH), 6.92-7.29 (m, 7H, Ar *H*).

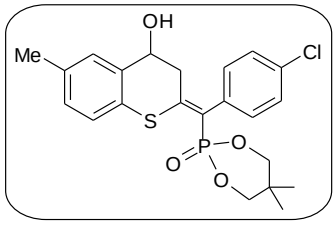
^{13}C NMR: δ 21.0, 21.1, 21.7, 32.4 (d, *J*(PC) = 6.3 Hz), 37.7 (d, *J*(PC) = 5.1 Hz), 55.3, 67.9, 75.6 (d, *J*(PC) = 6.0 Hz) , 114.1, 121.9 (d, *J*(PC) = 187.0 Hz), 125.9, 127.1, 128.1, 128.4 (d, *J*(PC) = 8.3 Hz), 129.1, 131.7 (d, *J*(PC) = 4.4 Hz), 135.9, 136.4, 155.7 (d, *J*(PC) = 22.6 Hz), 159.5.

^{31}P NMR: δ 9.4.

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

Anal. Calcd. for $C_{23}H_{27}O_5PS$: C, 61.87; H, 6.10. Found: C, 61.95; H, 6.14.

Compound (*Z*)-68 (from 3h and 55, higher R_f)



Yield: 0.04 g (14%).

Mp: 168-172 ^oC.

IR (KBr): 3364, 1686, 1545, 1474, 1260, 1055, 1003 cm^{-1}.

^{1}H NMR: δ 0.69 (s, 3H, CH_3), 1.00 (s, 3H, CH_3), 2.33 (s, 3H, Ar CH_3), 2.56-2.60 (m, 1H, (OH)CHC$H_A$$H_B$), 2.83-2.87 (m, 1H, (OH)CHCH$_A$$H_B$), 3.53-3.69 (m, 2H, OC$H_2$), 4.04-4.13 (m, 2H, OC$H_2$), 4.70-4.71 (m, 1H, C*H*(OH)), 7.08-7.40 (m, 7H, Ar *H*).

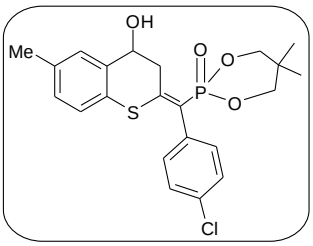
^{13}C NMR: δ 20.8, 21.1, 21.6, 32.4 (d, *J*(PC) = 6.1 Hz), 38.8 (d, *J*(PC) = 14.3 Hz), 67.6, 75.7 (d, *J*(PC) = 5.8 Hz), 120.1 (d, *J*(PC) = 183.6 Hz), 126.3, 126.7, 127.7, 128.8, 129.3, 131.9, 133.8, 135.0 (d, *J*(PC) = 8.3 Hz), 136.1, 136.6, 153.5 (d, *J*(PC) = 8.7 Hz).

^{31}P NMR: δ 10.0.

LC/MS: *m/z* 451$[M]^+$ and 453 $[M+2]^+$

Anal. Calcd. for $C_{22}H_{24}ClO_4PS$: C, 58.60; H, 5.36. Found: C, 58.75; H, 5.26.

Compound (*E*)-68 (from 3h and 55, lower R_f)



Yield: 0.20 g (67%).

Mp: 218-222 ^{o}C.

IR (KBr): 3314, 1576, 1564, 1476, 1208, 1047 cm^{-1}.

^{1}H NMR: δ 0.68 (s, 3H, CH_3), 0.96 (s, 3H, CH_3), 2.32 (s, 3H, ArCH_3), 3.41-3.45 (m, 1H, (OH)CHC$H_A$$H_B$), 3.57-3.65 (m, 2H, OC$H_2$), 3.84-3.90 (m, 1H, (OH)CHCH$_A$$H_B$), 4.07-4.12 (m, 2H, OC$H_2$), 4.90-4.92 (m, 1H, C*H*(OH)), 6.91-7.41 (m, 7H, Ar *H*).

^{13}C NMR: δ 21.1, 21.2, 21.5, 32.3 (d, *J*(PC) = 5.9 Hz), 37.5 (d, *J*(PC) = 4.8 Hz), 67.7, 75.4 (d, *J*(PC) = 3.8 Hz), 120.7 (d, *J*(PC) = 189.6 Hz), 125.8, 126.6, 128.0, 129.0, 129.1, 131.9 (d, *J* = 4.0

Hz), 134.3, 134.7 (d, *J*(PC) = 7.9 Hz), 136.1, 136.3, 156.7 (d, *J*(PC) = 21.3 Hz).

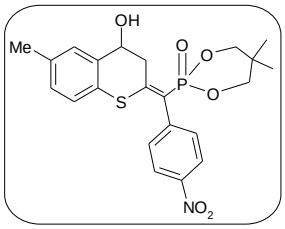
^{31}P NMR: δ 9.4.

LC/MS: *m/z* 433 $[M-18]^+$and 435 [M-18+2].

Anal. Calcd. for $C_{22}H_{24}ClO_4PS$: C, 58.60; H, 5.36. Found: C, 58.56; H, 5.41.

Compound (*E*)-69 (from 3i and 55, lower R_f)

(The *Z*–isomer was only a minor product and hence not isolated)



Yield: 0.19 g (64%).

Mp: 244-248 ^oC.

IR (KBr): 3316, 2971, 1576, 1559, 1476, 1208, 1047 cm^{-1}.

^{1}H NMR: δ 0.68 (s, 3H, CH_3), 0.96 (s, 3H, CH_3), 2.32 (s, 3H, Ar CH_3), 3.45-3.49 (m, 1H, (OH)CHCH_AH$_B$), 3.57-3.65 (m, 2H, OCH_2), 3.80-3.86 (m, 1H, (OH)CHCH$_A$$H_B$), 4.07-4.13 (m, 2H, OC$H_2$), 4.90-4.92 (m, 1H, C*H*(OH)), 6.91-7.41 (m, 7H, Ar *H*).

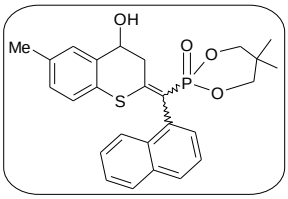
^{13}C NMR: δ 21.1, 21.2, 21.6, 32.4 (d, *J*(PC) = 5.8 Hz), 37.6, 67.8, 75.5, 120.7 (d, *J*(PC) = 189.7 Hz), 125.9, 126.6, 128.1, 129.0, 129.2, 132.0, 134.3, 134.7, 136.3 (d, *J*(PC) = 8.4 Hz), 156.8 (d, *J*(PC) = 21.5 Hz)

^{31}P NMR: δ 9.4.

LC/MS: *m/z* 462 $[M+1]^+$.

Anal. Calcd. for $C_{22}H_{24}NO_6PS$: C, 57.26; H, 5.24; N, 3.04. Found: C, 57.18; H, 5.31; N, 3.13.

Compound (*E/Z*)-70 (from 3j and 55)



Yield: 0.20 g (67%).

Mp: 208-212 ^{o}C.

IR (KBr): 3297, 1572, 1559, 1476, 1198, 1051, 997 cm^{-1}.

^{1}H NMR: δ 0.48 (s, 3H, CH_3), 0.92 (s, 3H, CH_3), 2.29 (s, 3H, Ar CH_3), 3.31-3.39 (m, 2H, OCH_2), 3.54-3.62 (m, 1H, (OH)CHCH_AH$_B$), 3.85-3.93 (m, 2H, OCH_2), 3.96-4.05 (m, 1H, (OH)CHCH$_A$$H_B$), 4.98-5.02 (m, 1H, C*H*(OH)), 6.77-8.07 (m, 10H, Ar *H*). The other isomer was also present, but no distinct signal except for the one at 0.49 ppm could be observed.

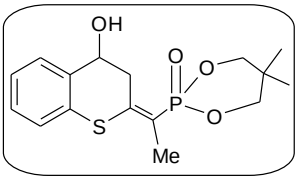
^{13}C NMR: δ 20.9$_1$, 20.9$_5$, 21.6, 32.3 (d, *J*(PC) = 6.3 Hz), 37.5 (d, *J*(PC) = 5.7 Hz), 37.9 (d, *J*(PC) = 4.9 Hz), 53.4, 68.0, 75.6 (d, *J*(PC) = 6.0 Hz), 120.3 (d, *J*(PC) = 188.4 Hz), 125.3, 125.5, 125.7, 125.8, 125.9, 126.2, 126.3, 126.6, 126.7, 126.8, 127.4, 127.8, 128.3, 128.4, 128.5, 128.6, 128.6$_8$, 128.7$_4$, 128.8, 128.9, 129.1, 131.3, 131.6, 131.7, 133.5, 133.6, 133.8, 135.6, 135.8, 136.4, 138.6, 156.5, 156.8.

^{31}P NMR: δ 9.2 and 9.4 (2:3).

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

Anal. Calcd. for $C_{26}H_{27}O_4PS$: C, 66.94; H, 5.83. Found: C, 66.85; H, 5.87.

Compound (*E*)-71 (from 3k and 54) (The *Z*–isomer was not observed)



Yield: 0.29 g (86%).

Mp: 168-172 ^{o}C.

IR (KBr): 3295, 1572, 1472, 1447, 1217, 1196, 1047, 992 cm^{-1}.

^{1}H NMR: δ 1.04 (s, 3H, CH_3), 1.15 (s, 3H, CH_3), 2.07-2.10 (dd, *J* = 13.4 and 1.2 Hz, 3H, =C(CH_3)), 3.23-3.28 (m, 1H, (OH)CHC$H_A$$H_B$), 3.64-3.70 (m, 1H, (OH)CHC$H_A$$H_B$), 3.78-3.89 (m, 2H, OC$H_2$), 4.22-4.28 (m, 2H, OC$H_2$), 4.86-4.89 (m, 1H, C*H*(OH)), 7.18-7.47 (m, 4H, Ar *H*).

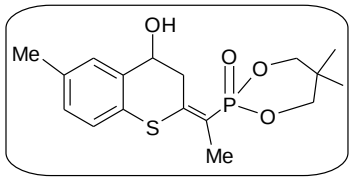
^{13}C NMR: δ 16.5 (d, *J*(PC) = 9.2 Hz), 21.6, 21.8, 32.5 (d, *J*(PC) = 5.6 Hz), 37.7 (d, *J*(PC) = 6.1 Hz), 67.7, 75.0 (d, *J*(PC) = 4.8 Hz), 114.7 (d, *J*(PC) = 185.1 Hz), 126.0_7, 126.1_2, 127.4, 128.3, 129.8, 136.9, 150.5 (d, *J*(PC) = 20.4 Hz).

^{31}P NMR: δ 14.9.

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

X-ray structure was determined for this sample.

Compound (*E*)-72 (from 3k and 55) (The *Z*–isomer was not observed)



Yield: 0.30 g (85%).

Mp: 204-208 ^{o}C.

IR (KBr): 3378, 1730, 1698, 1549, 1472, 1262, 1061 cm^{-1}.

^{1}H NMR: δ 1.03 (s, 3H, CH_3), 1.15 (s, 3H, CH_3), 2.05-2.09 (dd, *J* = 14.0 and 1.2 Hz, 3H, = C(CH_3)), 2.33 (s, 3H, Ar CH_3), 3.23-3.26 (m, 1H, (OH)CHC$H_A$$H_B$), 3.77-3.80 (m, 1H, (OH)CHC$H_A$$H_B$), 3.80-3.88 (m, 2H, OC$H_2$), 4.21-4.27 (m, 2H, OC$H_2$), 4.82-4.85 (m, 1H, C*H*(OH)), 7.06-7.29 (m, 3H, Ar *H*).

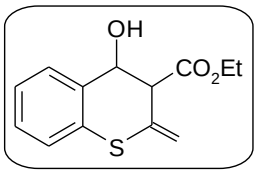
^{13}C NMR: δ 16.5 (d, *J*(PC) = 9.3 Hz), 21.1, 21.6, 21.8, 32.5 (d, *J*(PC) = 5.5 Hz), 37.9 (d, *J*(PC) = 6.2 Hz), 67.8, 75.1 (d, *J*(PC) = 5.9 Hz), 114.0 (d, *J*(PC) = 185.4 Hz), 126.0, 126.2, 128.0, 129.0, 136.1, 136.9, 151.2 (d, *J*(PC) = 20.4).

^{31}P NMR: δ 15.0.

LC/MS: *m/z* 354 $[M]^+$.

Anal. Calcd. for $C_{17}H_{23}O_4PS$: C, 57.61; H, 6.54. Found: C, 57.68; H, 6.51.

Compound 73 (same as 3.62 using 5 and 54 at room temperature)



Yield: 0.30 g (84%).

Mp: 54-56 ^oC.

IR (KBr): 3457, 1732, 1713, 1589, 1445, 1260 cm^{-1}.

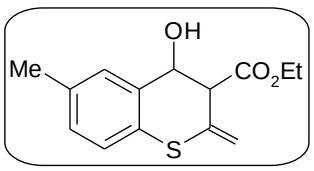
^1H NMR: δ 1.14 (t, *J* = 7.2 Hz, 3H, OCH_2CH_3), 3.77 (d, *J* = 6.4 Hz, 1H, $CH(CO_2Et)$), 4.11-4.18 (m, 2H, OCH_2CH_3), 5.13 (d, *J* = 6.0 Hz, 1H, *CH*(OH)), 5.31 (s, 1H, $=CH_AH_B$), 5.48 (s, 1H, $=CH_AH_B$), 7.13-7.46 (m, 4H, Ar *H*).

^{13}C NMR: δ 14.0, 54.5, 61.4, 69.8, 114.3, 125.3, 125.7, 128.7, 129.0, 131.0, 133.7, 134.0, 169.6.

LC/MS: *m/z* 250 $[M]^+$.

Anal. Calcd. for $C_{13}H_{14}O_3S$: C, 62.38; H, 5.64. Found: C, 62.25; H, 5.68.

Compound 74 (same as 3.62 using 5 and 55 at room temperature)



Yield: 0.28 g (85%).

Mp: 42-46 ^oC.

IR (KBr): 3401, 1732, 1605, 1474, 1370, 1331, 1179 cm^{-1}.

^1H NMR: δ 1.14 (t, *J* = 8.0 Hz, 3H, OCH_2CH_3), 2.31 (s, 3H, Ar CH_3), 3.74 (d, *J* = 8.0 Hz, 1H, $CH(CO_2Et)$), 4.11-4.16 (m, 2H, OCH_2CH_3), 5.06-5.09 (m, 1H, *CH*(OH)), 5.29 (s, 1H, $=CH_AH_B$), 5.46 (s, 1H, $=CH_AH_B$), 7.00-7.27 (m, 3H, Ar *H*).

^{13}C NMR: δ 14.1, 21.0, 54.7, 61.4, 70.0, 114.2, 125.6, 127.4, 129.6_7, 129.7_4, 133.6, 134.3, 135.2, 169.7.

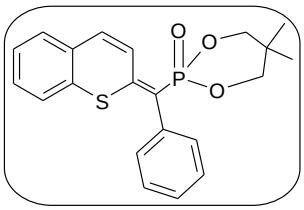
LC/MS: *m/z* 264 $[M]^+$.

Anal. Calcd. for $C_{14}H_{16}O_3S$: C, 63.61; H, 6.10. Found: C, 63.75; H, 6.16.

3.63 Synthesis of phosphono-chromene 75

The quantities, procedure and the work up were the same as in section 3.62 above except that the reaction time was 24 h (instead of 4 h).

Compound (*E*)-75 (isomeric purity ~95%)



Yield: 0.22 g (70%).

Mp: 150-154 ^oC.

IR (KBr): 1611, 1514, 1485, 1385, 1260, 1219, 1057 cm^{-1}.

^1H NMR: δ 0.60 (s, 3H, C*H*$_3$), 0.92 (s, 3H, C*H*$_3$), 3.54-3.61 (m, 2H, OC*H*$_2$), 4.09-4.14 (m, 2H, OC*H*$_2$), 6.85-8.12 (m, 11H, 2 = C*H* & Ar *H*).

^{13}C NMR: δ 21.1, 21.6, 32.2 (d, *J*(PC) = 5.8 Hz), 75.2 (d, *J*(PC) = 6.0 Hz), 113.7 (d, *J*(PC) = 193.5 Hz), 122.1 (d, *J*(PC) = 6.6 Hz), 124.8, 126.1, 127.6, 128.2, 128.7, 129.4, 129.7, 130.4, 132.7, 133.4, 136.8 (d, *J*(PC) = 6.4 Hz), 152.1 (d, *J*(PC) = 22.1 Hz).

^{31}P NMR: δ 10.1 (other isomer 12.4 (5%)).

LC/MS: *m/z* 385 $[M+1]^+$.

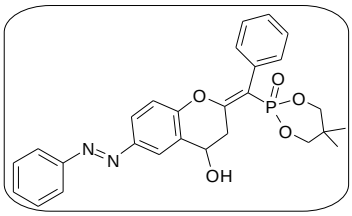
3.7 Reactions of allenylphosphonates with *azo*-substituted salicylaldehydes

3.71 Reaction of allenylphosphonate 3e and 3g with azo-substituted salicylaldehydes 76-77: Synthesis of phosphono-chromans 78-79

To the allenylphosphonate **3e** or **3g** (0.76 mmol), *azo*-substituted salicylaldehyde **76** (0.221 g, 0.98 mmol) and K_2CO_3 (0.021 g, 0.15 mmol) in a 25 mL RBF, was added DMSO (4 mL) and the contents heated at 90 ^oC for 4 h. The reaction mixture was quenched with water (5 mL) and extracted with CH_2Cl_2 (3 x 25 mL). The whole organic layer was washed with water (3 x 25 mL), dried (Na_2SO_4), filtered, concentrated and the products were isolated by column chromatography

(hexane/ EtOAc; 2:3) on silica gel. Here, the *E*-isomer eluted before the *Z*-isomer in each case. [i.e. (R_f(*E*-isomer)> R_f(*Z*-isomer)].

Compound (*E*)-78



Yield: 0.10 g (27%).

Mp: 206-208 ^{o}C.

IR (KBr): 3358, 1644, 1609, 1480, 1235, 1059, 1005 cm^{-1}.

^{1}H NMR: δ 0.79 (s, 3H, CH_3), 1.20 (s, 3H, CH_3), 2.64-2.67 (m, 1H, (OH)CHCH_AH$_B$), 2.93-2.97 (m, 1H, (OH)CHCH_AH$_B$), 3.19 (br, 1H, O*H*), 3.69-3.91 (m, 4H, 2 OCH_2), 4.88 (m, 1H, C*H*(OH)), 7.24-7.95 (m, 13H, Ar *H*).

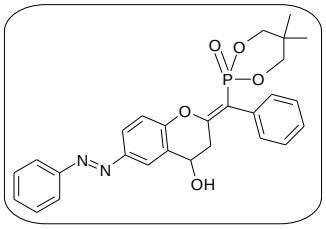
^{13}C NMR (DMSO-d_6): δ 20.2, 21.5, 32.2 (d, *J*(PC) = 6.3 Hz), 33.0 (d, *J*(PC) = 9.6 Hz), 31.7, 75.9, 108.3 (d, *J*(PC) = 169.1 Hz), 117.3, 122.1, 122.6, 124.9, 127.5, 127.8, 128.7, 129.7, 129.6 (d, *J*(PC) = 4.8 Hz), 131.5, 134.2 (d, *J*(PC) = 6.2 Hz), 147.5, 152.1, 153.3, 159.3.

^{31}P NMR: δ 10.4.

LC/MS: *m/z* 473 $[M-18+1]^{+}$.

Anal. Calcd. for $C_{27}H_{27}N_2O_5P$: C, 66.12; H, 5.55; N, 5.71. Found: C, 66.35; H, 5.48; N, 5.65.

Compound (*Z*)-78



Yield: 0.20 g (53%).

Mp: 206-208 ^{o}C.

IR (KBr): 3310, 1636, 1607, 1483, 1236, 1165, 1057 cm^{-1}.

^{1}H NMR: δ 0.64 (s, 3H, CH_3), 0.99 (s, 3H, CH_3), 3.13-3.14 (m, 1H, (OH)CHC$H_A$$H_B$), 3.30-3.34 (m, 1H, (OH)CHC$H_A$$H_B$), 3.56-3.71 (m, 2H, OC$H_2$), 3.93-4.10 (m, 2H, OC$H_2$), 5.08 (m, 1H, C*H*(OH)), 6.86-8.01 (m, 13H, Ar *H*)

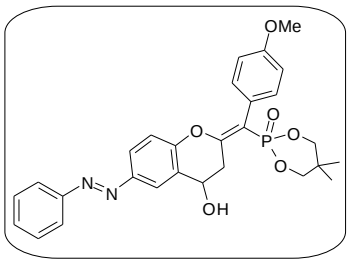
^{13}C NMR (DMSO-d_6): δ 20.4, 21.5, 32.2, 33.5, 62.0, 75.9 (d, *J*(PC) = 15.4 Hz), 108.9 (d, *J*(PC) = 188.4 Hz), 117.5, 122.3, 122.9, 124.9, 127.8, 128.1, 128.6, 130.0, 130.7, 131.9, 134.0, 147.8, 152.3, 153.3, 160.0 (d, *J*(PC) = 32.2 Hz).

^{31}P NMR: δ 14.5.

LC/MS: *m/z* 473 $[M-18+1]^+$.

Anal. Calcd. for $C_{27}H_{27}N_2O_5P$: C, 66.12; H, 5.55; N, 5.71. Found: C, 66.35; H, 5.46; N, 5.88.

Compound (*E*)-79



Yield: 0.10 g (28%).

Mp: 206-208 °C.

IR (KBr): 3368, 1638, 1605, 1510, 1480, 1244, 1061 cm^{-1}.

^{1}H NMR: δ 0.77 (s, 3H, CH_3), 1.20 (s, 3H, CH_3), 2.63-2.67 (m, 1H, (OH)CHC$H_A$$H_B$), 2.93-2.94 (m, 1H, (OH)CHC$H_A$$H_B$), 3.70-3.78 (m, 2H, OC$H_2$), 3.82 (s, 3H, OC$H_3$), 3.85-3.90 (m, 2H, OC$H_2$), 4.87 (br m, 1H, C*H*(OH)), 6.90-7.90 (m, 12H, Ar *H*).

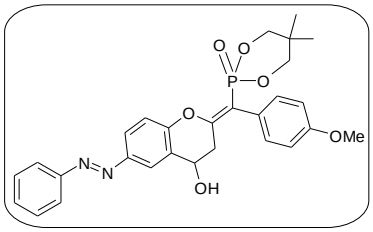
^{13}C NMR (DMSO-d_6): δ 20.2, 21.8, 32.1 (d, *J*(PC) = 5.8 Hz), 33.2, 55.6, 62.0, 76.2, 107.9 (d, *J*(PC) = 169.1 Hz), 114.3, 117.5, 122.4, 122.8, 125.2, 126.3 (d, *J*(PC) = 5.8 Hz), 127.7, 130.0, 131.8, 132.1, 147.7, 152.3, 153.6, 159.1, 159.5.

^{31}P NMR: δ 10.9.

LC/MS: *m/z* 503 $[M-18+1]^+$.

Anal. Calcd. for $C_{28}H_{29}N_2O_6P$: C, 64.61; H, 5.62; N, 5.38. Found: C, 64.48; H, 5.55; N, 5.45.

Compound (*Z*)-79



Yield: 0.16 g (46%).

Mp: 206-208 ^{o}C.

IR (KBr): 3306, 1636, 1605, 1510, 1481, 1242, 1177, 1059, 1007 cm^{-1}.

^{1}H NMR: δ 0.68 (s, 3H, CH_3), 1.00 (s, 3H, CH_3), 3.32-3.36 (m, 1H, (OH)CHCH_AH$_B$), 3.56-3.62 (m, 1H, (OH)CHCH$_A$$H_B$), 3.67-3.90 (m, 2H, OC$H_2$), 3.85 (s, 3H, OC$H_3$), 3.99-4.09 (m, 2H, OC$H_2$), 5.07 (m, 1H, C*H*(OH)), 6.88-8.02 (m, 12H, Ar *H*).

^{13}C NMR (DMSO-d_6): δ 20.4, 21.6, 32.1 (d, *J*(PC) = 5.8 Hz), 33.5, 55.5, 62.1, 75.9 (d, *J*(PC) = 14.6 Hz), 108.4 (d, *J*(PC) = 188.1 Hz), 113.9, 117.5, 122.2, 122.8, 124.8, 125.9, 128.2, 130.0, 131.8, 147.7, 152.3, 153.4, 158.7, 159.8 (d, *J*(PC) = 32.7 Hz).

^{31}P NMR: δ = 14.9.

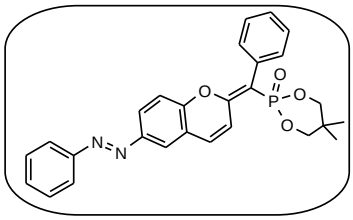
LC/MS: *m/z* 503 $[M-18+1]^+$.

Anal. Calcd. for $C_{28}H_{29}N_2O_6P$: C, 64.61; H, 5.62; N, 5.38. Found: C, 64.75; H, 5.56; N, 5.45.

3.72 Reaction of allenylphosphonates 3e-h and 3k with azo-substituted salicylaldehydes76-77- Synthesis of phosphono-chromenes 80-89

The quantities, procedure and the work up were the same as in section 3.71 above except that the reaction time was 24 h (instead of 4 h).

Compound (*E*)-80



Yield: 0.14 g (40%).

Mp: 202-206 ^{o}C.

IR (KBr): 1630, 1562, 1470, 1260, 1235, 1055, 1003 cm^{-1}.

^{1}H NMR: δ 0.65 (s, 3H, C*H*$_3$), 0.94 (s, 3H, C*H*$_3$), 3.58-3.64 (m, 2H, OC*H*$_2$), 4.10-4.15 (m, 2H, OC*H*$_2$), 6.87 (d, *J* = 10.0 Hz, =C*H*), 7.05 (d, *J* = 10.0 Hz, =C*H*), 7.27-7.89 (m, 13H, Ar *H*).

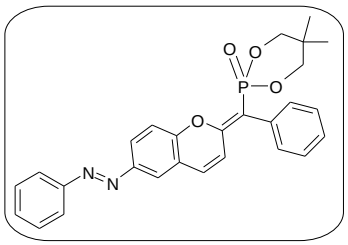
^{13}C NMR: δ 21.2, 21.6, 32.3 (d, *J*(PC) = 6.0 Hz), 75.2 (d, *J*(PC) = 6.0 Hz), 102.1 (d, *J*(PC) = 201.0 Hz), 116.5, 120.5, 120.7, 120.9, 122.8, 125.5, 127.3, 128.1, 129.1, 130.1, 130.9 (d, *J*(PC) = 5.0 Hz), 131.1, 133.9, 148.5, 152.5, 154.6, 159.0 (d, *J*(PC) = 35.0 Hz).

^{31}P NMR: δ 14.9.

LC/MS: *m/z* 473 [M+1]$^{+}$.

Anal. Calcd. for $C_{27}H_{25}N_2O_4P$: C, 68.64; H, 5.33; N, 5.93. Found: C, 68.43; H, 5.41; N, 5.85.

Compound (*Z*)-80



Yield: 0.13 g (36%).

Mp: 164-168 ^{o}C.

IR (KBr): 1628, 1574, 1555, 1472, 1433, 1258, 1059, 1009 cm^{-1}.

^{1}H NMR: δ 0.81 (s, 3H, C*H*$_3$), 1.21 (s, 3H, C*H*$_3$), 3.72-3.76 (m, 2H, OC*H*$_2$), 3.88-3.95 (m, 2H, OC*H*$_2$), 6.37 (d, *J* = 10.0 Hz, =C*H*), 6.86 (dd, *J* = 10.0 and ~2.0 Hz, =C*H*), 7.27-7.95 (m, 13H, Ar *H)*.

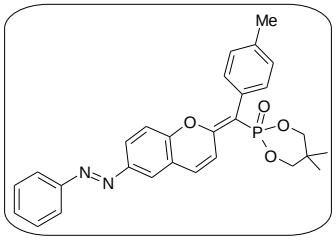
^{13}C NMR: δ 21.1, 21.9, 32.4 (d, *J*(PC) = 5.7 Hz), 75.9, 102.2 (d, *J*(PC) = 181.9 Hz), 116.9, 119.3 (d, *J*(PC) = 12.8 Hz), 120.2, 120.4, 121.0, 122.8, 126.3, 127.8, 128.9, 129.2, 130.5, 131.1, 133.9 (d, *J*(PC) = 5.2 Hz), 148.5, 152.5, 154.7, 158.5.

^{31}P NMR: δ 11.7.

LC/MS: *m/z* 473 $[M+1]^+$.

Anal. Calcd. for $C_{27}H_{25}N_2O_4P$: C, 68.64; H, 5.33; N, 5.93. Found: C, 68.71; H, 5.25; N, 6.07.

Compound (*E*)-81



Yield: 0.11 g (32%).

Mp: 176-178 ^{o}C.

IR (KBr): 1628, 1559, 1468, 1445, 1262, 1235 cm^{-1}.

^{1}H NMR: δ 0.69 (s, 3H, C*H*$_3$), 0.98 (s, 3H, C*H*$_3$), 2.41 (s, 3H, Ar C*H*$_3$), 3.59-3.65 (m, 2H, OC*H*$_2$), 4.07-4.12 (m, 2H, OC*H*$_2$), 6.90 (d, *J* = 8.0 Hz, =C*H*), 7.02 (d, *J* = 8.0 Hz, =C*H*), 7.20-7.89 (m, 12H, Ar *H*).

^{13}C NMR: δ 21.2, 21.4, 21.7, 32.3 (d, *J*(PC) = 5.7 Hz), 75.3 (d, *J*(PC) = 5.3 Hz), 102.1 (d, *J*(PC) = 191.0 Hz), 116.5, 120.6, 120.7, 120.9, 122.8, 125.5, 128.9, 129.1, 129.9, 130.6 (d, *J*(PC) = 4.7 Hz), 130.7, 131.0, 136.9, 148.5, 152.4, 154.7, 158.7 (d, *J*(PC) = 34.9 Hz).

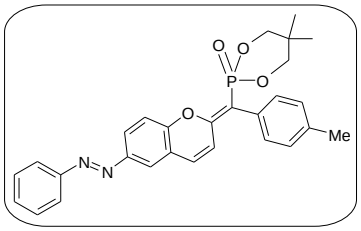
^{31}P NMR: δ 15.2.

LC/MS: *m/z* 487 $[M+1]^+$.

Anal. Calcd. for $C_{28}H_{27}N_2O_4$ P: C, 69.13; H, 5.59; N, 5.76. Found: C, 69.32; H, 5.51; N, 5.66.

X-ray structure was determined for this sample.

Compound (*Z*)-81



Yield: 0.14 g (40%).

Mp: 190-194 ^{o}C.

IR (KBr): 1630, 1615, 1574, 1476, 1435, 1258, 1236 cm^{-1}.

^{1}H NMR: δ 0.81 (s, 3H, C*H*$_3$), 1.21 (s, 3H, C*H*$_3$), 2.38 (s, 3H, Ar C*H*$_3$), 3.73-3.77 (m, 2H, OC*H*$_2$), 3.85-3.92 (m, 2H, OC*H*$_2$), 6.38 (d, *J* = 10.0 Hz, =C*H*), 6.81 (dd, *J* = 10.0 and ~2.0 Hz, 1H, =C*H*), 7.20-7.96 (m, 12H, Ar *H*).

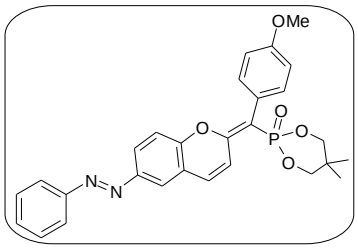
^{13}C NMR: δ 21.0, 21.2, 21.9, 32.3 (d, *J*(PC) = 5.6 Hz), 76.0 (d, *J*(PC) = 5.8 Hz), 102.3 (d, *J*(PC) = 179.6 Hz), 116.7, 119.4 (d, *J*(PC) = 13.1 Hz), 120.4, 120.9, 122.7, 126.1, 129.0, 129.1, 129.5, 130.1, 130.7 (d, *J*(PC) = 5.1 Hz), 131.0, 137.5, 148.4, 152.4, 154.7, 158.0.

^{31}P NMR: δ 11.9.

LC/MS: *m/z* 487 [M+1]$^{+}$.

Anal. Calcd. for $C_{28}H_{27}N_2O_4P$: C, 69.13; H, 5.59; N, 5.76. Found: C, 69.05; H, 5.63; N, 5.82.

Compound (*E*)-82



Yield: 0.10 g (30%).

Mp: 162-166 ^{o}C.

IR (KBr): 1628, 1607, 1561, 1468, 1262, 1231 cm^{-1}.

^{1}H NMR: δ 0.69 (s, 3H, C*H*$_3$), 0.96 (s, 3H, C*H*$_3$), 3.59-3.65 (m, 2H, OC*H*$_2$), 3.87 (s, 3H, OC*H*$_3$), 4.09-4.14 (m, 2H, OC*H*$_2$), 6.90

(d, *J* = 8.0 Hz, =C*H*), 7.02 (d, *J* = 8.0 Hz, =C*H*), 6.94-7.96 (m, 12H, Ar *H*).

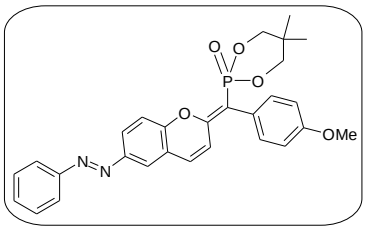
^{13}C NMR: δ 21.3, 21.7, 32.3 (d, *J*(PC) = 5.7 Hz), 55.3, 75.3 (d, *J*(PC) = 5.7 Hz), 101.7 (d, *J*(PC) = 200.2 Hz), 116.5, 120.1, 120.6, 120.8, 120.9, 122.8, 125.5, 126.0, 129.2, 129.9, 131.1, 132.0 (d, *J*(PC) = 4.7 Hz), 148.5, 152.5, 154.7, 159.0 (d, *J*(PC) = 36.7 Hz).

^{31}P NMR: δ 15.3.

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

Anal. Calcd. for $C_{28}H_{27}N_2O_5P$: C, 66.93; H, 5.42; N, 5.57. Found: C, 66.85; H, 5.39; N, 5.62.

Compound (*Z*)-82



Yield: 0.15 g (43%).

Mp: 172-175 ^{o}C.

IR (KBr): 1630, 1613, 1574, 1435, 1236 cm^{-1}.

^{1}H NMR: δ 0.82 (s, 3H, CH_3), 1.21 (s, 3H, CH_3), 3.73-3.77 (m, 2H, OCH_2), 3.85 (s, 3H, OCH_3), 3.88-3.95 (m, 2H, OCH_2), 6.38 (d, *J* = 10.0 Hz, 1H, =C*H*), 6.85 (dd, *J* = 10.0 and 3.0 Hz, 1H, =C*H*), 6.93-7.94 (m, 12H, Ar *H*).

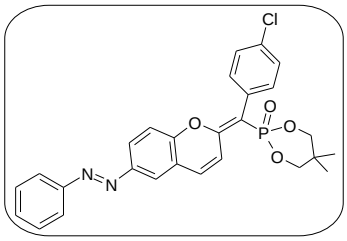
^{13}C NMR: δ 21.1, 22.0, 32.4, 55.3, 76.0, 102.0 (d, *J*(PC) = 180.8 Hz), 114.3, 116.8, 119.5 (d, *J*(PC) = 12.0 Hz), 120.5, 121.0, 122.8, 125.9, 126.2, 129.2, 130.1, 131.1, 132.1, 148.5, 152.5, 154.8, 158.1, 159.1.

^{31}P NMR: δ 12.0.

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

Anal. Calcd. for $C_{28}H_{27}N_2O_5P$: C, 66.93; H, 5.42; N, 5.57. Found: C, 66.78; H, 5.35; N, 5.66.

Compound (*E*)-83



Yield: 0.16 g (37%).

Mp: 200-202 ^{o}C.

IR (KBr): 1628, 1578, 1468, 1445, 1262, 1235 cm^{-1}.

^{1}H NMR: δ 0.70 (s, 3H, CH_3), 0.93 (s, 3H, CH_3), 3.59-3.66 (m, 2H, OCH_2), 4.16-4.21 (m, 2H, OCH_2), 6.90 (d, *J* = 10.0 Hz, =C*H*), 7.07 (d, *J* = 10.0 Hz, =C*H*), 7.33-7.90 (m, 12H, Ar *H*).

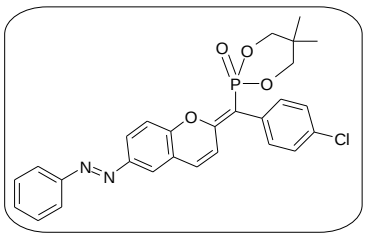
^{13}C NMR: δ 21.4, 21.6, 32.3 (d, *J*(PC) = 5.6 Hz), 75.1 (d, *J*(PC) = 5.5 Hz), 100.5 (d, *J*(PC) = 202.9 Hz), 116.5, 120.3, 120.7, 121.1, 122.9, 125.6, 128.4, 129.2, 130.6, 131.2, 132.4 (d, *J*(PC) = 4.6 Hz), 132.6, 133.2, 148.7, 152.5, 154.5, 159.6 (d, *J*(PC) = 34.6 Hz).

^{31}P NMR: δ 15.0.

LC/MS: *m/z* 507 $[M]^+$ and 509 $[M+2]^+$

Anal. Calcd. for $C_{27}H_{24}N_2O_4ClP$: C, 63.97; H, 4.77; N, 5.53. Found: C, 63.85; H, 4.71; N, 5.65.

Compound (*Z*)-83



Yield: 0.16 g (37%).

Mp: 188-192 ^{o}C.

IR (KBr): 1630, 1574, 1480, 1435, 1258, 1236 cm^{-1}.

^{1}H NMR: δ 0.85 (s, 3H, CH_3), 1.20 (s, 3H, CH_3), 3.72-3.77 (m, 2H, OCH_2), 3.93-4.00 (m, 2H, OCH_2), 6.34 (d, *J* = 10.4 Hz, =C*H*),

6.91 (dd, *J* = 10.4 and ~2.0 Hz, 1H, =C*H*), 7.32-7.89 (m, 12H, Ar *H*).

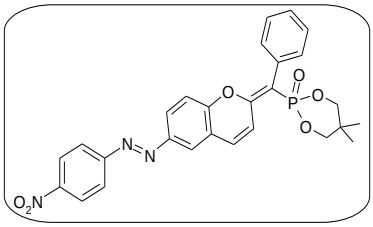
^{13}C NMR: δ 21.2, 22.0, 32.5, 76.0, 101.2 (d, *J*(PC) = 182.0 Hz), 116.9, 118.9 (d, *J*(PC) = 12.6 Hz), 120.3, 121.2, 122.9, 126.4, 129.2, 131.0, 131.2, 132.4, 132.7, 133.8, 148.6, 152.5, 154.6, 158.5.

^{31}P NMR: δ 11.4.

LC/MS: *m/z* 507 $[M]^+$ and 509 $[M+2]^+$

Anal. Calcd. for $C_{27}H_{24}N_2O_4ClP$: C, 63.97; H, 4.77; N, 5.53. Found: C, 63.85; H, 4.69; N, 5.61.

Compound (*E*)-84



Yield: 0.16 g (40%).

Mp: 234-236 ^{o}C.

IR (KBr): 1630, 1559, 1522, 1460, 1339, 1235 cm^{-1}.

^{1}H NMR: δ 0.64 (s, 3H, CH_3), 0.94 (s, 3H, CH_3), 3.58-3.64 (m, 2H, OCH_2), 4.12-4.16 (m, 2H, OCH_2), 6.89 (d, *J* = 10.0 Hz, =C*H*), 7.04 (d, *J* = 10.0 Hz, =C*H*), 7.35-8.37 (m, 12H, Ar *H*).

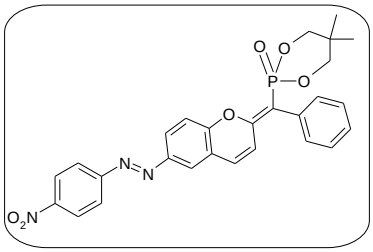
^{13}C NMR: δ 21.2, 21.6, 32.3 (d, *J*(PC) = 5.8 Hz), 75.3 (d, *J*(PC) = 5.8 Hz), 102.9 (d, *J*(PC) = 200.5 Hz), 116.8, 121.0, 121.6, 123.4, 124.8, 126.2, 127.4, 128.2, 129.7, 130.8 (d, *J*(PC) = 4.6 Hz), 133.8, 148.5 (d, *J*(PC) = 30.8 Hz), 155.6 (d, *J*(PC) = 5.9 Hz) 158.5, 158.9.

^{31}P NMR: δ 14.5.

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

Anal. Calcd. for $C_{27}H_{24}N_3O_6P$: C, 62.67; H, 4.67; N, 8.12. Found: C, 62.55; H, 4.72; N, 8.28.

Compound (*Z*)-84



Yield: 0.16 g (40%).

Mp: 218-222 ^{o}C.

IR (KBr): 1612, 1572, 1518, 1343, 1273, 1240 cm^{-1}.

^{1}H NMR: δ 0.80 (s, 3H, C*H*$_3$), 1.20 (s, 3H, C*H*$_3$), 3.71-3.75 (m, 2H, OC*H*$_2$), 3.88-3.94 (m, 2H, OC*H*$_2$), 6.39 (d, *J* = 9.6 Hz, =C*H*), 6.86 (dd, *J* = 10.4 and ~3.0 Hz, 1H, =C*H*), 7.27-8.39 (m, 12H, Ar *H*).

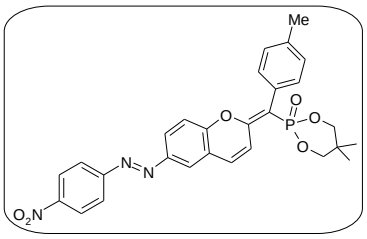
^{13}C NMR: δ 21.0, 22.0, 32.4 (d, *J*(PC) = 5.6 Hz), 76.1, 103.4 (d, *J*(PC) = 180.0 Hz), 117.2, 119.8 (d, *J*(PC) = 13.1 Hz), 120.7, 121.8, 123.3, 123.4, 123.8, 124.8, 126.9, 128.0, 129.0, 130.0, 130.9, 133.8, 148.5 (d, *J*(PC) = 29.1 Hz), 155.7 (d, *J*(PC) = 17.4 Hz), 158.0.

^{31}P NMR: δ 11.2.

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

Anal. Calcd. for $C_{27}H_{24}N_3O_6P$: C, 62.67; H, 4.67; N, 8.12. Found: C, 62.54; H, 4.58; N, 8.22.

Compound (*E*)-85



Yield: 0.18 g (48%).

Mp: 238-240 ^{o}C.

IR (KBr): 1630, 1609, 1557, 1520, 1460, 1339, 1262, 1235 cm^{-1}.

^{1}H NMR: δ 0.69 (s, 3H, C*H*$_3$), 0.97 (s, 3H, C*H*$_3$), 2.41 (s, 3H, Ar C*H*$_3$), 3.59-3.65 (m, 2H, OC*H*$_2$), 4.08-4.13 (m, 2H, OC*H*$_2$), 6.92 (d, *J* = 10.0 Hz, =C*H*), 7.01 (d, *J* = 10.0 Hz, =C*H*), 7.21-8.36 (m, 11H, Ar *H*).

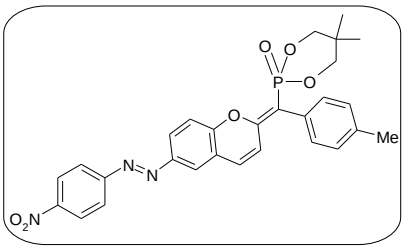
^{13}C NMR: δ 21.3, 21.4, 21.7, 32.3 (d, *J*(PC) = 5.8 Hz), 75.4 (d, *J*(PC) = 5.8 Hz), 103.1 (d, *J*(PC) = 198.7 Hz), 116.8, 121.1, 121.6, 123.4, 124.8, 126.1, 128.9, 129.4, 130.5, 130.6, 137.1, 148.5 (d, *J*(PC) = 32.0 Hz), 155.7 (d, *J*(PC) = 11.8 Hz), 158.3, 158.6.

^{31}P NMR: δ 14.7.

LC/MS: *m/z* 532 $[M+1]^+$.

Anal. Calcd. for $C_{28}H_{26}N_3O_6P$: C, 63.27; H, 4.93; N, 7.91. Found: C, 63.12; H, 4.88; N, 7.85.

Compound (*Z*)-85



Yield: 0.11 g (28%).

Mp: 244-246 ^{o}C.

IR (KBr): 1611, 1559, 1524, 1456, 1435, 1260 cm^{-1}.

^{1}H NMR: δ 0.81 (s, 3H, C*H*$_3$), 1.21 (s, 3H, C*H*$_3$), 2.39 (s, 3H, Ar C*H*$_3$), 3.72-3.76 (m, 2H, OC*H*$_2$), 3.87-3.94 (m, 2H, OC*H*$_2$), 6.41 (d, *J* = 9.6 Hz, =C*H*), 6.83 (dd, *J* = 13.2 and ~3.2 Hz, 1H, =C*H*), 7.21-8.40 (m, 11H, Ar *H*).

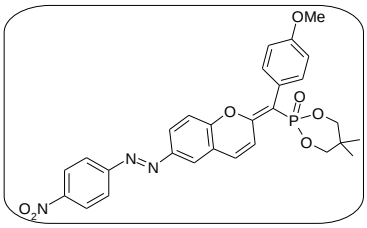
^{13}C NMR: δ 21.0, 21.3, 22.0, 32.3 (d, *J*(PC) = 6.0 Hz), 76.1 (d, *J*(PC) = 6.0 Hz), 103.4 (d, *J*(PC) = 179.0 Hz), 117.1, 119.8 (d, *J*(PC) = 13.0 Hz), 120.7, 121.7, 123.4, 124.8, 126.8, 129.6, 129.7, 130.7 (d, *J*(PC) = 4.0 Hz), 137.7, 148.3 (d, *J*(PC) = 29.0 Hz), 155.6, 155.8, 157.7.

^{31}P NMR: δ 11.5.

LC/MS: *m/z* 532 $[M+1]^+$.

Anal. Calcd. for $C_{28}H_{26}N_3O_6P$: C, 63.27; H, 4.93; N, 7.91. Found: C, 63.41; H, 4.88; N, 7.81.

Compound (*E*)-86



Yield: 0.14 g (38%).

Mp: 238-242 ^oC.

IR (KBr): 1630, 1609, 1553, 1522, 1341, 1227 cm^{-1}.

^1H NMR: δ 0.69 (s, 3H, C*H*$_3$), 0.96 (s, 3H, C*H*$_3$), 3.59-3.65 (m, 2H, OC*H*$_2$), 3.87 (s, 3H, OC*H*$_3$), 4.10-4.15 (m, 2H, OC*H*$_2$), 6.91-8.36 (m, 13H, 2 =C*H* & Ar *H*).

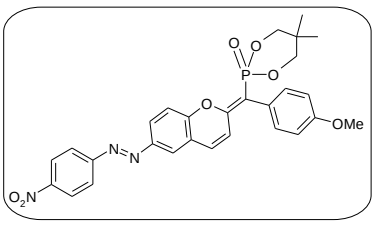
^{13}C NMR: δ 21.3, 21.7, 32.3 (d, *J*(PC) = 5.9 Hz), 55.3, 75.4 (d, *J*(PC) = 5.8 Hz), 102.6 (d, *J*(PC) = 199.8 Hz), 113.7, 116.8, 121.1, 121.6, 123.4, 124.8, 125.8, 126.2, 129.5, 132.0 (d, *J*(PC) = 5.8 Hz), 148.5 (d, *J*(PC) = 30.9 Hz), 155.6, 155.7, 158.5, 158.9.

^{31}P NMR: δ 14.9.

LC/MS: *m/z* 548 $[M+1]^+$.

Anal. Calcd. for $C_{28}H_{26}N_3O_7P$: C, 61.43; H, 4.79; N, 7.67. Found: C, 61.32; H, 4.68; N, 7.56.

Compound (*Z*)-86



Yield: 0.14 g (38%).

Mp: 206-208 ^oC.

IR (KBr): 1628, 1611, 1578, 1528, 1343, 1238 cm^{-1}.

^{1}H NMR: δ 0.82 (s, 3H, CH_3), 1.21 (s, 3H, CH_3), 3.71-3.76 (m, 2H, OCH_2), 3.85 (s, 3H, OCH_3), 3.88-3.95 (m, 2H, OCH_2), 6.40 (d, *J* = 10.0 Hz, =C*H*), 6.83 (dd, *J* = 13.6 and ~3.6 Hz, 1H, =C*H*), 6.93-8.01 (m, 11H, Ar *H*).

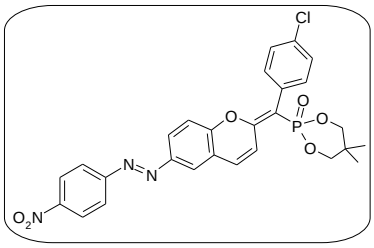
^{13}C NMR: δ 21.1, 22.0, 32.4 (d, *J*(PC) = 6.0 Hz), 55.4, 76.0 (d, *J*(PC) = 6.0 Hz), 102.9 (d, *J*(PC) = 180.4 Hz), 114.4, 117.1, 119.9 (d, *J*(PC) = 12.8 Hz), 120.8, 121.7, 123.4, 124.8, 125.7 (d, *J*(PC) = 5.6 Hz), 126.8, 129.8, 132.1 (d, *J*(PC) = 4.9 Hz), 148.5 (d, *J*(PC) = 29.6 Hz), 155.6, 155.8, 157.9, 159.3.

^{31}P NMR: δ 11.6.

LC/MS: *m/z* 548 $[M+1]^+$.

Anal. Calcd. for $C_{28}H_{26}N_3O_7P$: C, 61.43; H, 4.79; N, 7.67. Found: C, 61.55; H, 4.65; N, 7.58.

Compound (*E*)-87



Yield: 0.14 g (39%).

Mp: 226-228 ^{o}C.

IR (KBr): 1628, 1611, 1572, 1557, 1524, 1385, 1339, 1238 cm^{-1}.

^{1}H NMR: δ 0.69 (s, 3H, CH_3), 0.92 (s, 3H, CH_3), 3.59-3.66 (m, 2H, OCH_2), 4.17-4.22 (m, 2H, OCH_2), 6.92 (d, *J* = 10.0 Hz, =C*H*), 7.07 (d, *J* = 10.0 Hz, =C*H*), 7.33-8.39 (m, 11H, Ar *H*).

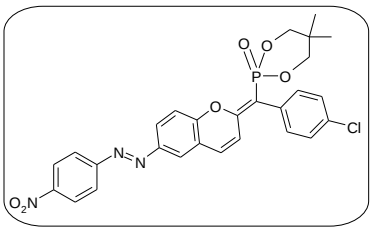
^{13}C NMR: δ 21.3, 21.5, 32.3 (d, *J*(PC) = 5.5 Hz), 75.2 (d, *J*(PC) = 5.6 Hz), 101.4 (d, *J*(PC) = 202.3 Hz), 116.8, 120.7, 120.9, 121.8, 123.4, 124.8, 126.2, 128.5, 130.1, 132.3 (d, *J*(PC) = 4.7 Hz), 133.3, 148.5 (d, *J*(PC) = 26.7 Hz), 155.5 (d, *J*(PC) = 7.5 Hz), 159.0, 159.4.

^{31}P NMR: δ 14.6.

LC/MS: *m/z* 552 $[M]^+$ and 554 $[M+2]^+$.

Anal. Calcd. for $C_{27}H_{23}ClN_3O_6P$: C, 58.76; H, 4.20; N, 7.61. Found: C, 58.62; H, 4.28; N, 7.88.

Compound (*Z*)-87



Yield: 0.14 g (39%).

Mp: 202-204 ^{o}C.

IR (KBr): 1626, 1559, 1522, 1458, 1343, 1458, 1244, 1049 cm^{-1}.

^{1}H NMR: δ 0.85 (s, 3H, C*H*$_3$), 1.19 (s, 3H, C*H*$_3$), 3.71-3.76 (m, 2H, OC*H*$_2$), 3.95-4.01 (m, 2H, OC*H*$_2$), 6.37 (d, *J* = 9.6 Hz, =C*H*), 6.90 (dd, *J* = 10.0 and ~2.0 Hz, 1H, =C*H*), 7.33-8.38 (m, 11H, Ar *H)*.

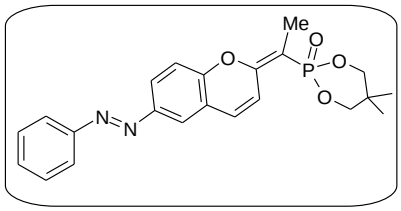
^{13}C NMR: δ 21.2, 21.9, 32.4 (d, *J*(PC) = 6.0 Hz), 76.0 (d, *J*(PC) = 6.0 Hz), 102.1 (d, *J*(PC) = 182.2 Hz), 117.2, 119.4 (d, *J*(PC) = 12.7 Hz), 120.6, 121.9, 123.5, 124.8, 126.9, 129.2, 130.6, 132.3, 132.4, 134.0, 148.5 (d, *J*(PC) = 26.3 Hz), 155.6 (d, *J*(PC) = 7.4 Hz), 158.2.

^{31}P NMR: δ 11.0.

LC/MS: *m/z* 552 $[M]^+$ and 554 $[M+2]^+$.

Anal. Calcd. for $C_{27}H_{23}ClN_3O_6P$: C, 58.76; H, 4.20; N, 7.61. Found: C, 58.85; H, 4.31; N, 7.55.

Compound (*E*)-88



Yield: 0.20 g (50%).

Mp: 238-242 ^{o}C.

IR (KBr): 1634, 1609, 1578, 1472, 1433, 1231 cm^{-1}.

^{1}H NMR: δ 0.97 (s, 3H, CH_3), 1.27 (s, 3H, CH_3), 2.02 (d, *J* = 14.0 Hz, 3H, CH_3), 3.76-3.83 (m, 2H, OCH_2), 4.34-4.38 (m, 2H, OCH_2), 6.86 (d, *J* = 10.0 Hz, =C*H*), 7.19 (d, *J* = 10.0 Hz, =C*H*), 7.47-7.91 (m, 8H, Ar *H*).

^{13}C NMR: δ 12.1 (d, *J*(PC) = 4.0 Hz), 21.5, 22.3, 32.5 (d, *J*(PC) = 5.0 Hz), 74.5 (d, *J*(PC) = 5.3 Hz), 94.6 (d, *J*(PC) = 202.6 Hz), 116.1, 120.7, 120.9, 122.8, 125.4, 128.0, 129.1, 131.0, 148.5, 152.5, 154.9, 159.0 (d, *J*(PC) = 36.1 Hz) [Fig. 40].

^{31}P NMR: δ 20.9.

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

Anal. Calcd. for $C_{22}H_{23}N_2O_4P$: C, 64.39; H, 5.65; N, 6.83. Found: C, 64.55; H, 5.58; N, 6.75.

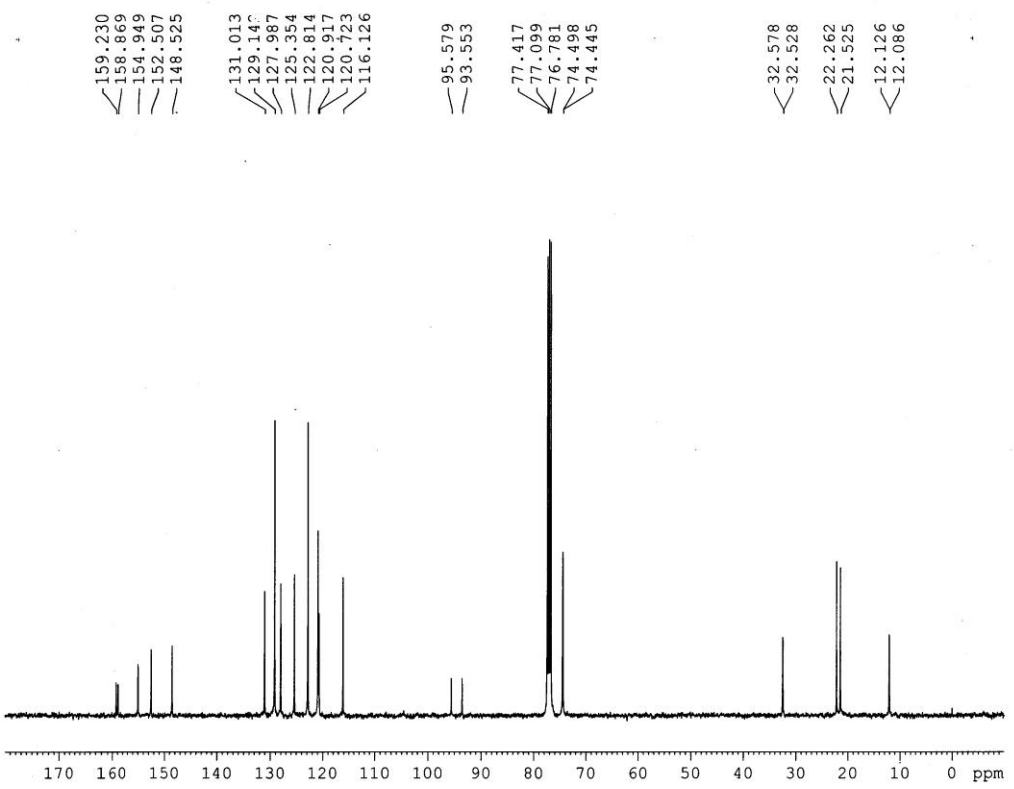
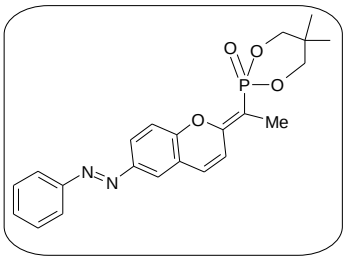


Figure 40. ^{13}C NMR spectrum of compound (*E*)-**88**

Compound (*Z*)-88



Yield: 0.12 g (30%).

Mp: 196-200 ^{o}C.

IR (KBr): 1628, 1580, 1472, 1262, 1231 cm^{-1}.

^{1}H NMR: δ 1.05 (s, 3H, C*H*$_3$), 1.22 (s, 3H, C*H*$_3$), 1.94 (d, *J* = 14.8 Hz, 3H, C*H*$_3$), 3.87-3.92 (m, 2H, OC*H*$_2$), 4.12-4.18 (m, 2H, OC*H*$_2$), 6.61 (d, *J* = 10.0 Hz, =C*H*), 6.93 (dd, *J* = 13.2 and ~3.6 Hz, 1H, =C*H*), 7.18-7.90 (m, 8H, Ar *H*).

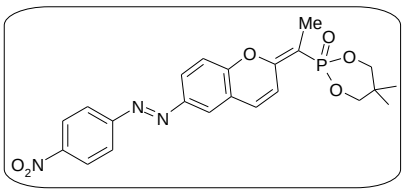
^{13}C NMR: δ 12.3 (d, *J*(PC) = 6.9 Hz), 21.6, 21.9, 32.5 (d, *J*(PC) = 5.6 Hz), 75.6 (d, *J*(PC) = 5.9 Hz), 93.0 (d, *J*(PC) = 182.5 Hz), 116.3, 118.0 (d, *J*(PC) = 14.2 Hz), 120.3, 121.0, 122.8, 126.2, 129.1, 129.8, 131.0, 148.3, 152.5, 155.0, 156.2.

^{31}P NMR: δ 17.0.

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

Anal. Calcd. for $C_{22}H_{23}N_2O_4P$: C, 64.39; H, 5.65; N, 6.83. Found: C, 64.51; H, 5.71; N, 6.75.

Compound (*E*)-89



Yield: 0.22 g (49%).

Mp: 244-248 ^{o}C.

IR (KBr): 1632, 1562, 1510, 1339, 1231, 1051 cm^{-1}.

^{1}H NMR: δ 0.97 (s, 3H, C*H*$_3$), 1.28 (s, 3H, C*H*$_3$), 2.03 (d, *J* = 12.0 Hz, 3H, C*H*$_3$), 3.76-3.83 (m, 2H, OC*H*$_2$), 4.35-4.39 (m, 2H,

OCH_2), 6.86 (d, *J* = 8.0 Hz, =C*H*), 7.22 (d, *J* = 8.0 Hz, =C*H*), 7.81-8.03 (m, 7H, Ar *H*).

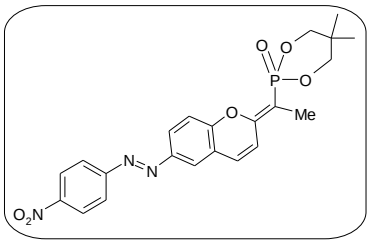
^{13}C NMR: δ 12.1 (d, *J*(PC) = 4.3 Hz), 21.5, 22.3, 32.5 (d, *J*(PC) = 5.3 Hz), 74.5 (d, *J*(PC) = 5.4 Hz), 94.6 (d, *J*(PC) = 202.0 Hz), 116.4, 121.1, 121.2, 121.5, 123.3, 124.8, 126.0, 127.5, 148.4, 148.6, 155.6, 155.9 (d, *J*(PC) = 3.1 Hz), 158.7 (d, *J*(PC) = 36.2 Hz).

^{31}P NMR: δ 20.5.

LC/MS: *m/z* 456 $[M+1]^+$.

Anal. Calcd. for $C_{22}H_{22}N_3O_6P$: C, 58.02; H, 4.87; N, 9.23: Found: C, 58.21; H, 4.78; N, 9.45.

Compound (*Z*)-89 (~90%; the remaining was the *E*-isomer.)



Yield: 0.11 g (25%).

Mp: 146-150 ^{o}C.

IR (KBr): 1638, 1605, 1526, 1462, 1343, 1262, 1053 cm^{-1}.

^{1}H NMR (major): δ 1.07 (s, 3H, CH_3), 1.21 (s, 3H, CH_3), 1.95 (d, *J* = 14.8 Hz, 3H, CH_3), 3.87-3.92 (m, 2H, OCH_2), 4.14-4.20 (m, 2H, OCH_2), 6.63 (d, *J* = 9.6 Hz, =C*H*), 6.94 (dd, *J* = 10.0 and ~2.0 Hz, 1H, =C*H*), 7.21-8.40 (m, 7H, Ar *H*).

^{13}C NMR: δ 12.2, 21.5, 22.3, 32.5 (d, *J*(PC) = 5.0 Hz), 74.5 (d, *J*(PC) = 5.7 Hz), 92.1, 116.4, 121.2, 121.5, 123.4, 124.7_7, 124.7_8, 126.0, 127.5, 148.4, 148.7, 155.6 (d, *J*(PC) = 31.1 Hz). The doublet due to P-*C* carbon could not be clearly identified due to low intensity.

^{31}P NMR: δ 16.6.

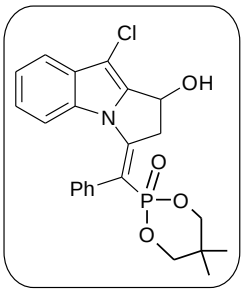
LC/MS: *m/z* 456 $[M+1]^+$.

Anal. Calcd. for $C_{22}H_{22}N_3O_6P$: C, 58.02; H, 4.87; N, 9.23: Found: C, 58.12; H, 4.91; N, 9.12.

3.8 Reaction of allenylphosphonates 3e-k, ester allene 5, allenylsulfones 8a-b with 3-chloro-2-formylindole 90- Synthesis of pyrroloindoles 91-100

To the allene (0.76 mmol), 3-chloro-2-formylindole **90** (0.176 g, 98 mmol) and K_2CO_3 (0.021 g, 0.15 mmol) in 25 mL RBF, was added PEG-400 (2 mL) and the contents heated at 90 ^oC for 4 h. The reaction mixture was quenched with water (5 mL) and extracted with CH_2Cl_2 (3 x 25 mL). The whole organic layer was washed with water (3 x 25 mL), dried (Na_2SO_4), filtered, concentrated and the products were isolated by column chromatography (hexane/ EtOAc; 1:4) on silica gel.

Compound 91



Yield: 0.25 g (74%).

Mp: 210-214 ^oC.

IR (KBr): 3316, 1634, 1601, 1443, 1327, 1308, 1061 cm^{-1}.

^1H NMR: δ 0.68 (s, 3H, C*H*$_3$), 0.97 (s, 3H, C*H*$_3$), 3.53-3.56 (m, 1H, (OH)CHC*H*$_A$H$_B$), 3.67-3.70 (m, 1H, (OH)CHCH$_A$*H*$_B$) 3.95-4.00 (m, 2H, OC*H*$_2$), 4.07-4.16 (m, 2H, OC*H*$_2$), 5.43-5.47 (2H, C*H*(OH) and O*H*), 6.64-7.45 (m, 9H, Ar *H*).

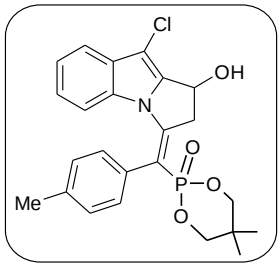
^{13}C NMR($CDCl_3$ + 5%MeOH): δ 20.7, 21.3, 32.1, 62.4, 75.7, 76.1, 105.3 (d, *J*(PC) = 190.4 Hz), 114.5, 118.0, 122.3, 123.5, 128.2, 128.7, 131.0, 131.3, 131.7, 135.6, 142.0, 150.9 (d, *J*(PC) = 27.3 Hz).

^{31}P NMR: δ 15.1.

LC/MS: *m/z* 442 $[M-2]^+$ and 444 $[M]^+$.

Anal. Calcd. for $C_{23}H_{23}ClNO_4P$: C, 62.24; H, 5.22; N, 3.16: Found: C, 62.35; H, 5.28; N, 3.22.

Compound 92



Yield: 0.23 g (70%).

Mp: 216-220 ^{o}C.

IR (KBr): 3302, 1634, 1599, 1445, 1308, 1235, 1061 cm^{-1}.

^{1}H NMR: δ 0.72 (s, 3H, CH_3), 1.00 (s, 3H, CH_3), 2.38 (s, 3H, Ar CH_3), 3.51-3.57 (m, 1H, (OH)CHCH_AH$_B$), 3.67-3.73 (m, 1H, (OH)CHCH$_A$$H_B$), 3.92-3.97 (m, 2H, OC$H_2$), 4.05-4.16 (m, 2H, OC$H_2$), 5.42-5.44 (m, 1H, O*H*), 5.51 (d, *J* = 2.2 Hz, 1H, C*H*(OH)), 6.66-7.46 (m, 8H, Ar *H*).

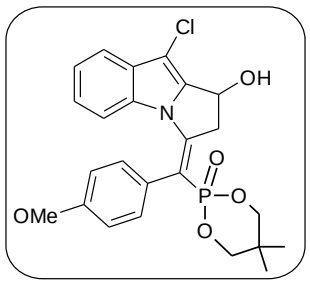
^{13}C NMR ($CDCl_3$ + 8%MeOH): δ 20.6, 20.8, 21.3, 32.1 (d, *J*(PC) = 6.3 Hz), 62.4, 75.7, 75.8, 104.2, 105.3 (d, *J*(PC) = 189.5 Hz), 114.7, 117.9, 122.2, 123.3, 129.3, 130.9, 131.2, 131.4, 132.4, 138.1, 141.9, 150.6 (d, *J*(PC) = 27.5 Hz).

^{31}P NMR: δ 15.1.

LC/MS: *m/z* 456 [M-2]$^{+}$ and 458 [M]$^{+}$.

Anal. Calcd. for $C_{24}H_{25}ClNO_4P$: C, 62.95; H, 5.50; N, 3.06: C, 62.88; H, 5.56; N, 3.12.

Compound 93



Yield: 0.22 g (69%).

Mp: 248-252 ^{o}C.

IR (KBr): 3272, 1634, 1595, 1445, 1308, 1235, 1055 cm^{-1}.

^{1}H NMR: δ 0.73 (s, 3H, CH_3), 1.00 (s, 3H, CH_3), 3.52-3.58 (m, 1H, (OH)CHCH_AH$_B$), 3.67-3.74 (m, 1H, (OH)CHCH$_A$$H_B$), 3.82 (s, 3H, OC$H_3$), 3.87-3.97 (m, 2H, OC$H_2$), 4.08-4.18 (m, 2H, OC$H_2$), 5.44 (m, 1H, O*H*), 5.62 (d, *J* = 8.8 Hz, 1H, C*H*(OH)), 6.72-7.47 (m, 8H, Ar *H*).

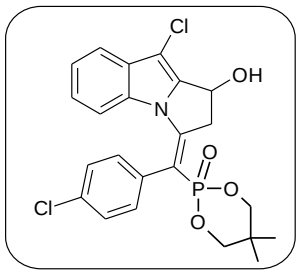
^{13}C NMR (DMSO-d_6): δ 20.9, 21.6, 32.3 (d, *J*(PC) = 6.0 Hz), 47.1 (d, *J*(PC) = 3.0 Hz), 55.8, 62.7, 75.5, 102.2, 107.0 (d, *J*(PC) = 185.0 Hz), 114.7, 114.8, 118.0, 122.7, 123.6, 128.5 (d, *J*(PC) = 5.0 Hz), 130.9, 133.0, 144.0, 150.0 (d, *J*(PC) = 28.0 Hz), 159.5 (d, *J*(PC) = 2.0 Hz)

^{31}P NMR: δ 15.3.

LC/MS: *m/z* 474 $[M]^+$ and 476 $[M+2]^+$.

Anal. Calcd. for $C_{24}H_{25}ClNO_5P$: C, 60.83; H, 5.32; N, 2.96: Found: C, 60.75; H, 5.22; N, 3.07.

Compound 94



Yield: 0.23 g (71%).

Mp: 212-216 ^{o}C.

IR (KBr): 3279, 1638, 1601, 1443, 1310, 1209, 1057, 1001 cm^{-1}.

^{1}H NMR: δ 0.75 (s, 3H, CH_3), 0.96 (s, 3H, CH_3), 3.55-3.61 (m, 1H, (OH)CHCH_AH$_B$), 3.66-3.72 (m, 1H, (OH)CHCH$_A$$H_B$) 3.94-3.97 (m, 2H, OC$H_2$), 4.15-4.22 (m, 2H, OC$H_2$), 5.42 (m, 1H, O*H*), 5.58 (d, *J* = 8.8 Hz, 1H, C*H*(OH)), 6.76-7.48 (m, 8H, Ar *H*).

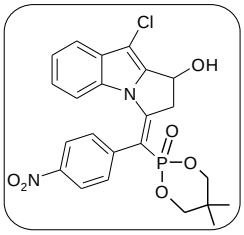
^{13}C NMR ($CDCl_3$ + 20%MeOH): δ 20.7, 21.1, 32.1, 46.8, 62.3, 75.5, 75.9, 103.9 (d, *J*(PC) = 193.0 Hz), 104.6, 114.2, 118.2, 122.4, 123.5, 128.8, 130.7, 131.4, 132.9, 134.1, 141.9, 151.6 (d, *J*(PC) = 28.0 Hz).

^{31}P NMR: δ 15.2.

LC/MS: *m/z* 476 $[M-2]^+$ and 478 $[M]^+$.

Anal. Calcd. for $C_{23}H_{22}Cl_2NO_4P$: C, 57.76; H, 4.64; N, 2.93: Found: C, 57.45; H, 4.71; N, 2.86.

Compound 95



Yield: 0.24 g (75%).

Mp: 216-220 ^oC.

IR (KBr): 3289, 1640, 1597, 1514, 1443, 1348, 1306, 1209, 1055, 1001 cm^{-1}.

^1H NMR: δ 0.77 (s, 3H, C*H*$_3$), 0.97 (s, 3H, C*H*$_3$), 3.50-3.74 (m, 2H, (OH)CHC*H*$_2$), 3.99-4.01 (m, 2H, OC*H*$_2$), 4.24-4.31 (m, 2H, OC*H*$_2$), 5.48 (m, 1H, O*H*), 5.54 (d, *J* = 8.4 Hz, 1H, C*H*(OH)), 6.70-8.28 (m, 8H, Ar *H*).

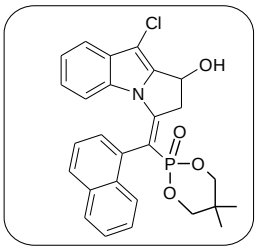
^{13}C NMR (DMSO-d_6): δ 20.9, 21.4, 32.4 (d, *J*(PC) = 5.8 Hz), 47.6, 62.8, 75.7 (d, *J*(PC) = 6.0 Hz), 75.9 (d, *J*(PC) = 6.4 Hz), 103.0, 105.4 (d, *J*(PC) = 186.4 Hz), 114.0, 118.4, 123.2, 123.9, 124.3, 130.4, 131.3, 133.0, 144.0 (d, *J*(PC) = 4.5 Hz), 147.0$_1$, 147.0$_3$, 151.8 (d, *J*(PC) = 24.5 Hz).

^{31}P NMR: δ 14.8.

LC/MS: *m/z* 487 $[M-2]^+$ and 489 $[M]^+$.

Anal. Calcd. for $C_{23}H_{22}ClN_2O_6P$: C, 56.51; H, 4.54; N, 5.73. Found: C, 56.45; H, 4.61; N, 5.65.

Compound 96 (two isomers in ~1:1 ratio)



Yield: 0.21 g (68%) gummy solid.

IR: 3285, 1630, 1588, 1445, 1236, 1057, 1009 cm^{-1}.

^1H NMR: δ 0.44 (s, 3H, CH_3), 0.95 (s, 3H, CH_3), 3.36-3.49 (m, 1H, (OH)CHC$H_A$$H_B$), 3.71-3.77 (m, 1H, (OH)CHC$H_A$$H_B$) 3.94-4.27 (m, 4H, 2 OC$H_2$), 5.06-5.08 (d, *J* = 8.8 Hz, 1H, C*H*(OH)), 5.49-5.52 (m, 1H, O*H*), 6.37-8.08 (m, 11H, Ar *H*).

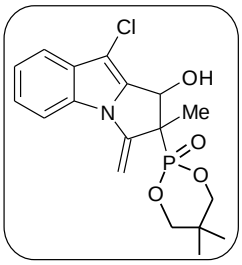
^{13}C NMR: δ 20.9, 21.0, 21.6, 21.7, 32.3, 46.6, 46.8, 62.5, 62.7, 75.4, 75.8, 102.0103.9, 104.4, 105.0, 114.2, 114.5, 118.0, 118.1, 122.3, 123.5, 125.1, 125.4, 126.3, 126.5, 126.8, 127.0, 128.3, 128.4, 129.2, 130.2, 130.8, 131.0, 131.2, 131.5, 132.1, 132.9, 133.0, 133.5, 133.7, 142.3, 142.4, 151.5, 151.8, 152.1, 152.4.

^{31}P NMR: δ 13.7 and 14.7.

LC/MS: *m/z* 492 $[M-2]^+$ and 494 $[M]^+$.

Anal. Calcd. for $C_{27}H_{25}ClNO_4P$: C, 65.66; H, 5.10; N, 2.84: Found: C, 65.82; H, 5.16; N, 2.75.

Compound 97



Yield: 0.14 g (38%).

Mp: 180-184 ^oC.

IR (KBr): 3274, 1665, 1454, 1383, 1233, 1063, 1011 cm^{-1}.

^1H NMR: δ 0.88 (s, 3H, CH_3), 1.02 (s, 3H, CH_3), 1.66 (d, *J* = 17.2 Hz, 3H, CH_3), 3.47-3.53 (m, 2H, OCH_2), 4.00-4.23 (m, 2H, OCH_2), 4.87 (s, 1H, =C$H_A$$H_B$), 5.34 (s, 1H, =C$H_A$$H_B$), 5.63 (d, *J*(PH) = 12.8 Hz, 1H, C*H*(OH)), 7.23-7.63 (m, 4H, Ar *H*).

^{13}C NMR($CDCl_3$ + 1%MeOH): δ 15.2, 21.4, 21.8, 33.0 (d, *J*(PC) = 6.0 Hz), 54.3 (d, *J*(PC) = 137.0 Hz), 75.5 (d, *J*(PC) = 6.0 Hz), 76.3 (d, *J*(PC) = 7.0 Hz), 92.1 (d, *J*(PC) = 7.0 Hz), 101.7, 111.8, 119.2, 121.9, 123.9, 130.1, 131.4, 138.3, 144.3.

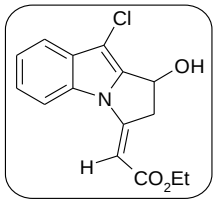
^{31}P NMR: δ 24.6.

LC/MS: *m/z* 482 $[M]^+$ and 484 $[M+2]^+$.

Anal. Calcd. for $C_{18}H_{21}ClNO_4P$: C, 56.63; H, 5.54; N, 3.67: Found: C, 56.75; H, 5.58; N, 3.57.

X-ray structure was determined for this sample.

Compound 98



Yield: 0.18 g (75%).

Mp: 108-112 ^{o}C.

IR (KBr): 3468, 1698, 1644, 1603, 1453, 1385, 1148, 1092 cm^{-1}.

^{1}H NMR: δ 1.34 (t, *J* = 7.2 Hz, 3H, OCH_2CH_3), 3.68-3.73 (m, 1H, $(HOCH)CH_AH_B$), 3.99-4.05 (m, 1H, $(HOCH)CH_AH_B$), 4.20-4.26 (m, 2H, OCH_2CH_3), 5.47 (d, *J* = 7.2 Hz, 1H, C*H*(OH)), 6.07 (s, 1H, O*H*), 7.27-7.71 (m, 4H, Ar *H*).

^{13}C NMR: δ 14.4, 29.7, 44.7, 60.1, 63.6, 95.7, 104.2, 113.0, 119.4, 123.3, 124.9, 130.2, 132.2, 140.9, 152.3, 167.5 [Fig. 41].

LC/MS: *m/z* 290 $[M-2]^+$ and 292 $[M]^+$.

Anal. Calcd. for $C_{15}H_{14}ClNO_3$: C, 61.76; H, 4.84; N, 4.80: Found: C, 61.59; H, 4.92; N, 4.68.

X-ray structure was determined for this sample.

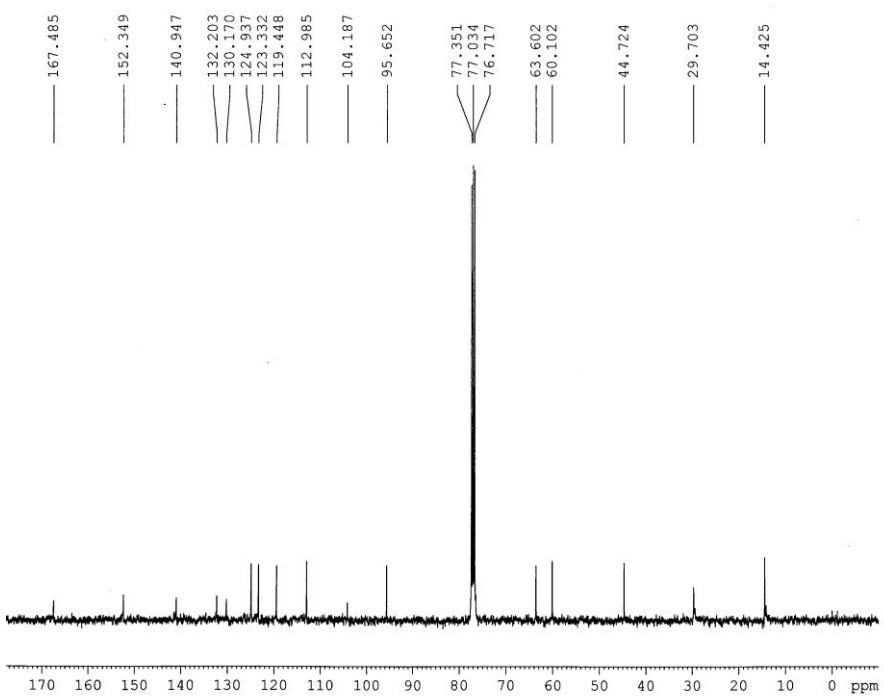
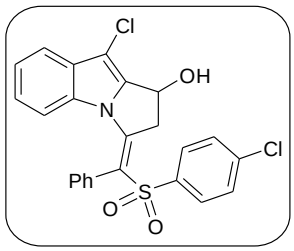


Figure 41. ^{13}C NMR spectrum of compound **98**

Compound 99



Yield: 0.24 g (74%).

Mp: 156-160 ^{o}C.

IR (KBr): 3347, 1640, 1603, 1443, 1308, 1150, 1080 cm^{-1}.

^{1}H NMR: δ 4.08 (d, *J* = 4.4 Hz, 2H, C*H*$_2$), 5.44 (m, 1H, O*H*), 5.65 (d, *J* = 8.8 Hz, 1H, C*H*(OH)), 6.67-7.72 (m, 13H, Ar *H*).

^{13}C NMR ($CDCl_3$ + 8% MeOH): δ 46.8, 62.1, 105.2, 114.3, 118.2, 120.2, 122.6, 123.9, 128.7, 129.0, 129.3, 130.9, 131.5, 132.6, 132.9, 133.1, 139.4, 139.5, 141.6, 148.1 [Fig 42].

LC/MS: *m/z* 468 $[M-2]^+$ and 470 $[M]^+$.

Anal. Calcd. for $C_{24}H_{17}Cl_2NO_3S$: C, 61.28; H, 3.64; N, 2.98. Found: C, 61.48; H, 3.76.

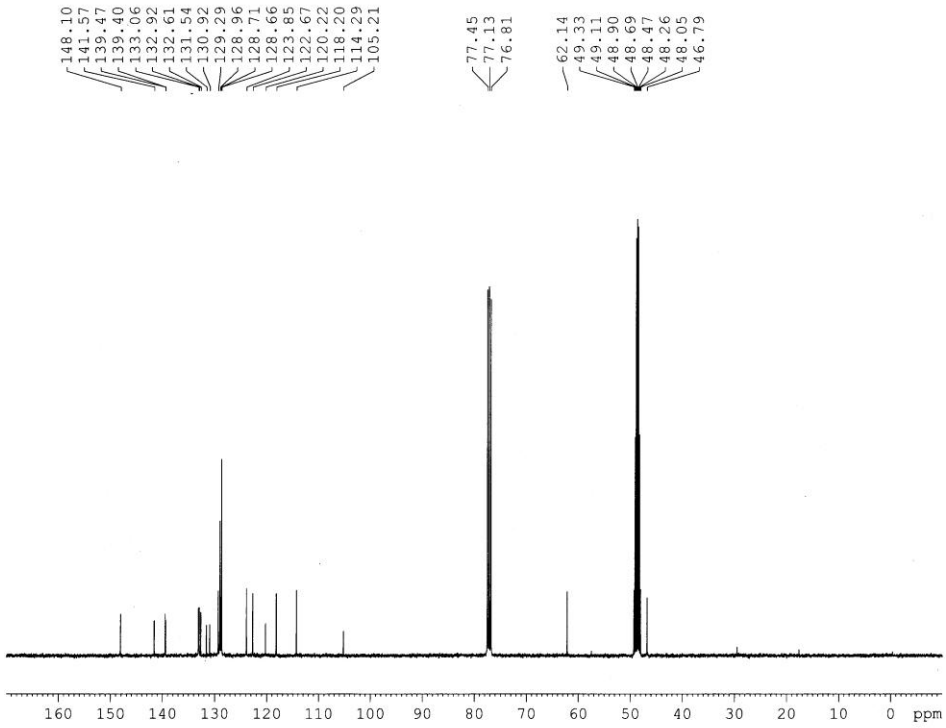
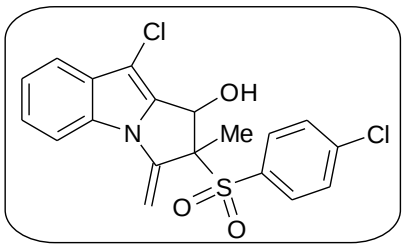


Figure 42. ^{13}C NMR spectrum of compound **99**

Compound 100



Yield: 0.25 g (70%).

Mp: 150-154 ^{o}C.

IR (KBr): 3472, 1659, 1453, 1308, 1148, 1086, 1042 cm^{-1}.

^{1}H NMR: δ 1.90 (s, 3H, CH_3), 5.06 (d, J = 7.0 Hz, 1H, =CH_AH$_B$), 5.40 (d, J = 7.0 Hz, 1H, =CH_AH$_B$), 5.56 (s, 1H, CH(OH)), 6.98-7.49 (m, 8H, Ar H).

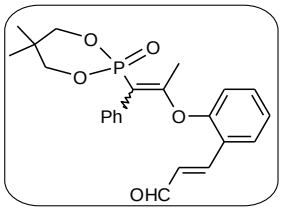
^{13}C NMR ($CDCl_3$ + 5%MeOH): δ 12.6, 66.9, 81.1, 95.8, 102.6, 111.2, 119.1, 122.4, 124.5, 128.2, 129.0, 130.3, 130.4, 132.6, 136.7, 140.7, 141.3.

LC/MS: *m/z* 408 [M]$^{+}$ and 410 [M+2]$^{+}$.

Anal. Calcd. for $C_{19}H_{15}Cl_2NO_3S$: C, 55.89; H, 3.70; N, 3.43. Found: C, 55.72; H, 3.76.

3.9 Reaction of 3e with 2-hydroxycinnamaldehyde- Synthesis of compound 106

To the allene $(OCH_2CMe_2CH_2O)P(O)C(Ph)=C=CH_2$ (**3e**) (0.76 mmol), 2-hydroxycinnamaldehyde (0.11 g, 0.98 mmol) and DBU (0.15 mmol) in 25 mL RBF, was added DMSO (2 mL) and the contents heated at 90 ^oC for 6 h. The reaction mixture was quenched with water (5 mL) and extracted with CH_2Cl_2 (3 x 25 mL). The whole organic layer was washed with water (3 x 25 mL), dried (Na_2SO_4), filtered, and concentrated to get the crude product which was isolated by column chromatography (hexane/ EtOAc; 3:2) on silica gel.



Yield: 0.09 g (30%).

Mp: 150-154 ^oC.

IR (KBr): 2857, 1678, 1622, 1481, 1260, 1229, 1059, 1007 cm^{-1}.

^1H NMR: δ 0.85 (s, 3H, C*H*$_3$), 1.06 (s, 3H, C*H*$_3$), 1.86 (s, 3H, C*H*$_3$), 3.67-3.72 (m, 2H, OC*H*$_2$), 3.92-3.98 (m, 2H, OC*H*$_2$), 6.78-8.02 (m, 11H, =CH & Ar *H*), 9.77 (d, *J* = 7.6 Hz, 1H, C*H*O).

^{13}C NMR: δ 17.6 (d, *J*(PC) = 10.7 Hz), 21.2, 21.7, 32.4 (d, *J*(PC) = 5.9 Hz), 75.7 (d, *J*(PC) = 6.1 Hz), 116.4 (d, *J*(PC) = 176.8 Hz), 119.0, 124.5, 125.9, 127.9, 128.5, 128.7, 130.0$_7$, 130.1, 132.4, 134.6 (d, *J*(PC) = 6.4 Hz), 146.9, 153.6, 163.2, 194.4.

^{31}P NMR: δ 9.8

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, 6.13.

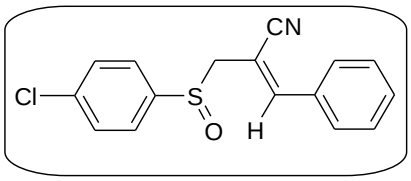
3.10 Synthesis of allylsulfoxides 107-110 and allylsulfones 111

To a solution of a substituted Baylis-Hillman alcohol $ArCH(OH)C(CO_2Me)=CH_2$ (16.0 mmol) in dry THF (40 mL) was added triethylamine (1.62 g, 2.23 mL, 16.0 mmol), the mixture stirred for 5 min, and then 4-chlorosulfenyl chloride[93] in THF (20 mL) was added drop-wise (~ 0.5 h) at 0^o C.

The contents were heated under reflux for 12h, brought to room temperature, filtered and the solution concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/ hexane; 1:10) to give allylsulfoxides **107-110**.

The allylsulfoxide **109** (0.40 g, 1.1 mmol) was dissolved in CH_2Cl_2 (15 mL), a solution of 70% *m*-chloro perbenzoic acid (*m*CPBA, 0.27 g, 1.1 mmol) in CH_2Cl_2 was added dropwise (10 min) at 0 ^oC and the contents stirred at 0 ^oC for 2 h. Then the mixture was allowed to warm to room temperature (25-30 ^oC) and washed twice with saturated aqueous $NaHCO_3$ solution.The organic layer was separated, dried over anh. Na_2SO_4, filtered, and concentrated to give crude product which was purified by column chromatography on silica gel (EtOAc/ hexane; 1:10) to afford pure allylsulfone **111**.

Compound (*Z*)-107



Yield: 1.48 g (78%).

Mp: 120-124 ^oC.

IR (KBr): 2212, 1613, 1574, 1472, 1453, 1389, 1292 cm^{-1}.

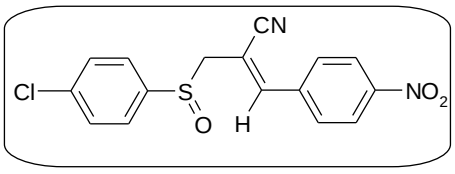
^1H NMR: δ 3.71 (d, *J* = 12.0 Hz, 1H, S(O)CH_AH_B), 3.81 (d, *J* = 12.0 Hz , 1H, S(O)CH_AH_B), 7.01 (s, 1H, =C*H*), 7.44-7.71 (m, 9H, Ar *H*).

^{13}C NMR: δ 61.6, 97.6, 117.5, 125.7, 128.9, 129.1, 129.6, 131.2, 132.6, 138.0, 139.7, 150.5.

LC/MS: *m/z* 302 $[M]^+$ and 304 $[M+2]^+$.

Anal. Calcd. for $C_{16}H_{12}ClNOS$: C, 63.68; H, 4.01; N 4.64. Found: C, 63.85; H, 4.10; N 4.55.

Compound (*Z*)-108



Yield: 0.60 g (71%).

Mp: 140-144 ^{o}C.

IR (KBr): 2209, 1595, 1520, 1474, 1348, 1059 cm$^{-1.}$

^{1}H NMR: δ 3.70 (d, *J* = 13.4 Hz, 1H, S(O)CH$_A$*H$_B$*), 3.87 (d, *J* = 13.4 Hz , 1H, S(O)C*H$_A$*H$_B$), 7.11 (s, 1H, =C*H*), 7.57-8.31 (2 d & s, 8H, Ar *H*).

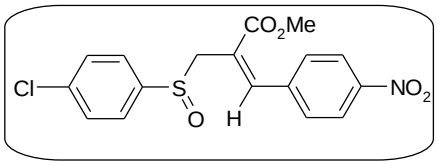
^{13}C NMR: δ 61.1, 102.2, 116.6, 124.2, 125.7, 130.0, 138.4, 138.6, 139.1, 147.7, 148.7.

LC/MS: *m/z* 347 $[M]^+$ and 349 $[M+2]^+$.

Anal. Calcd. for $C_{16}H_{11}ClN_2O_3S$: C, 55.41; H, 3.20; N 8.08. Found: C, 55.32; H,3.14; N 8.16.

X-ray structure was determined for this sample.

Compound (*Z*)-109



Yield: 1.09 g (85%).

Mp: 142-146 ^{o}C.

IR (KBr): 1707, 1516, 1343, 1265, 1045 cm$^{-1.}$

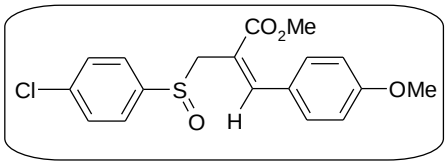
^{1}H NMR: δ 3.84 (s, 3H, OC*H$_3$*), 3.91-3.99 (AB m, 2H, S(O)C*H$_2$*), 7.46-8.25 (m, 9H, =C*H* & Ar *H*).

^{13}C NMR: δ 52.9, 56.7, 123.7, 125.2, 125.5, 129.6, 130.1, 137.7, 140.2, 142.1, 143.8, 148.1, 166.4;

LC/MS: *m/z* 380 $[M]^+$ and 382 $[M+2]^+$.

Anal. Calcd. for $C_{17}H_{14}ClNO_5S$: C, 53.76; H, 3.72; N 3.69. Found: C, 53.85; H, 3.78; N 3.56.

Compound (*Z*)-110



Yield: 1.02 g (83%).

Mp: 60-62 ^{o}C.

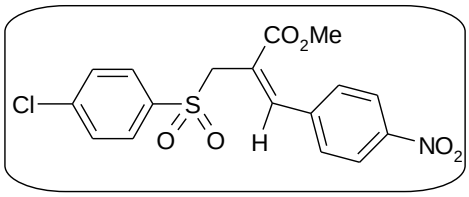
IR (KBr): 2951, 1709, 1603, 1512, 1437, 1308 cm^{-1}

^{1}H NMR: δ 3.75 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 4.06 (d, J = 12.6 Hz, 1H, S(O)CH$_A$$H_B$), 4.21 (d, J = 8.8 Hz , 1H, S(O)CH_AH$_B$), 6.91 (d, J = 12.6 Hz , 1H, =CH), 7.42-7.97 (m, 8H, Ar H).

^{13}C NMR: δ 52.4, 55.3, 56.9, 114.1, 119.2, 125.7, 126.3, 129.2, 131.4, 137.4, 142.3, 146.0, 160.9, 167.4.

LC/MS: m/z 365 [M]$^{+}$ and 367 [M+2]$^{+}$.

Compound (*Z*)-111



Yield: 0.39 g (93 %).

Mp: 154-158 ^{o}C.

IR (KBr): 1713, 1518, 1435, 1346, 1325, 1269, 1140, 1084 cm$^{-1.}$

^{1}H NMR: δ 3.67 (s, 3H, OCH_3), 4.42 (s, 2H, SO_2CH_2), 7.48-8.27 (4d, 8H, =CH & Ar H).

^{13}C NMR: δ 52.9, 55.0, 123.9, 124.0, 129.5, 129.9, 130.0, 137.4, 139.9, 141.0, 143.8, 148.1, 166.0.

LC/MS: m/z 396 [M]$^{+}$ and 398 [M+2]$^{+}$.

Anal. Calcd. for $C_{17}H_{14}ClNO_6S$: C, 51.59; H, 3.57; N 3.54. Found: C, 51.42; H, 3.51; N 3.66.

3.11 X-ray crystallography

A suitable crystal was mounted on a glass fiber (for **18, 25, 26, 32, 37b, 42, 49, 53, (*E*)-56, 58, (*E*)-61, (*Z*)-61, (*E*)-71, (*E*)-81, 97, (*E*)-98** and (*Z*)-**108**) and X-ray data were collected at 293 K on an OXFORD diffractometer or on a Bruker AXS-SMART diffractometer using Mo-K_α radiation (λ = 0.71073 Å). Structures were solved and refined using standard methods.[93] Absorption corrections were done using SADABS program, where applicable. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were fixed by geometry or located by a Difference Fourier and refined isotropically. Crystal data are summarized in Tables 12-16.

Table 12. Crystal data for compounds **18, 25, 26 and 32**[a]

Compound	**18**	**25**	**26**	**32**
Emp. formula	$C_{17}H_{21}O_5P$	$C_{16}H_{11}IO_2$	$C_{19}H_{18}O_3$	$C_{22}H_{23}O_6P$
Formula weight	336.31	362.15	294.33	414.37
Crystal system	Orthorhombic	Monoclinic	Triclinic	Triclinic
Space group	*Pbca*	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a /Å	15.453(3)	7.5106(17)	9.1407(6)	12.457(3)
b /Å	11.092(2)	10.308(2)	9.4304(6)	13.536(3)
c /Å	20.668(4)	17.818(4)	18.9283(13)	13.599(3)
α/deg	90	90	83.9640(10)	94.92(3)
β/deg	90	93.047(4)	80.3730(10)	107.88(3)
γ/deg	90	90	80.3500(10)	100.94(3)
V /Å^3	3542.9(12)	1377.5(5)	1599.63(18)	2117.07(7)
Z	8	4	4	4
D_{calc} /g cm^{-3}]	1.261	1.746	1.222	1.300
μ /mm^{-1}	0.176	2.319	0.082	0.165
F(000)	1424	704	624	872
Data/ restraints/ parameters	3122/ 0/ 212	2430/ 0/ 174	5619/ 0/ 403	7435/ 0 /529
S	1.063	1.051	1.055	0.926
R1 [I>2σ(I)]	0.0547	0.0239	0.0453	0.0599
wR2 [all data]	0.1269	0.0611	0.1247	0.1036
Max./ min. residual electron dens. [eÅ^{-3}]	0.309/ -0.276	0.528/ -0.457	0.391/ -0.176	0.188/ -0.153

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma wF_o^4]^{0.5}$

Table 13. Crystal data for compounds (*Z*)-**37b, 42, 49** and **53**[a]

Compound	(*Z*)-**37b**	**42**	**49**	**53.** .1/2H_2O
Emp. formula	$C_{25}H_{21}ClO_3$	$C_{18}H_{25}O_4P$	$C_{17}H_{24}NO_3P$	$C_{17}H_{22}NO_3P$ .1/2H_2O
Formula weight	404.87	336.35	321.34	319.34
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*P2(1)/n*	*P2(1)*	*P2(1)/c*	*P2(1)/c*
a /Å	9.5190(19)	13.557(3)	9.2496(7)	13.775(5)
b /Å	16.437(3)	6.4360(13)	16.2134(12)	11.496(4)
c /Å	13.307(3)	19.936(4)	12.1845(7)	11.446(4)
α/deg	90	90	90	90
β/deg	74.57(3)	90.00(3)	116.382(4)	97.752(6)
γ/deg	90	90	90	90
V /Å^3	1962.9(7)	1739.5(6)	1637.0(2)	1796.3(10)
Z	4	4	4	4
D_{calc} /g cm^{-3}]	1.370	1.284	1.304	1.573
μ /mm^{-1}	0.219	0.715	0.180	0.607
F(000)	848	720	688	851
Data/ restraints/ parameters	3461 /0 /265	6208 / 1/ 423	2879 /0 / 204	3171/ 0/ 212
S	0.972	1.238	1.128	1.030
R1 [I>2σ(I)]	0.0750	0.0879	0.0452	0.0580
wR2 [all data]	0.1267	0.1789	0.0957	0.1435
Max./ min. residual electron dens. [eÅ^{-3}]	0.524/-0.256	0.399/ -0.258	0.334/ -0.348	0.222/ -0.172

[a] R1 = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$ and wR2 = $[\Sigma w(F_o^2-F_c^2)^2/\Sigma wF_o^4]^{0.5}$

Table 14. Crystal data for compounds (*E*)-**56, 58,** (*E*)-**61** and (*Z*)-**61**[a]

Compound	(*E*)-**56**	**58**	(*E*)-**61**	(*Z*)-**61**
Emp. formula	$C_{21}H_{23}O_4PS$	$C_{21}H_{23}O_4PS$	$C_{22}H_{25}O_5PS$	$C_{22}H_{25}O_5PS$
Formula weight	402.43	402.43	432.35	432.46
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*P2(1)/c*	*P2(1)/c*	*P2(1)/c*	*P2(1)/c*
a /Å	10.667(2)	9.127(2)	5.952(2)	12.3185(7)
b /Å	9.913(2)	17.133(3)	9.834(4)	12.0813(7)
c /Å	20.138(4)	12.580(3)	36.141(14)	18.8019(8)
α/deg	90	90	90	90
β/deg	111.543(9)	93.34(2)	94.321(7)	130.587(2)
γ/deg	90	90	90	90
V /Å^3	1980.7(7)	1963.9(7)	2109.4(14)	2124.98(19)
Z	4	4	4	4
D_{calc} /g cm^{-3}]	1.350	1.361	1.362	1.352
μ /mm^{-1}	0.268	0.270	0.260	0.258
F(000)	848	848	912	912
Data/ restraints/ parameters	3484/ 0/ 246	3436/ 0/ 251	3712/ 0/ 266	3752/ 0/ 265
S	1.301	0.869	1.077	1.168
R1 [I>2σ(I)]	0.0697	0.0415	0.0593	0.0687
wR2 [all data]	0.1355	0.0871	0.1458	0.1544
Max./ min. residual electron dens. [eÅ^{-3}]	0.481/ -0.266	0.324/ -0.230	0.718/ -0.265	0.752/ -0.237

[a] R1 = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$ and wR2 = $[\Sigma w(F_o^2-F_c^2)^2/\Sigma wF_o^4]^{0.5}$

Table 15. Crystal data for compounds **(*E*)-71, (*E*)-81, 97** and **(*E*)-98**[a]

Compound	**(*E*)-71**	(*E*)-**81**	**97**	**(*E*)-98**
Emp. formula	$C_{16}H_{21}O_4PS$	$C_{28}H_{27}N_2O_4P$	$C_{18}H_{21}ClNO_4P$	$C_{15}H_{14}ClNO_3$
Formula weight	340.37	486.49	381.78	291.72
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*P2(1)/c*	*P2(1)/c*	*P2(1)/c*	*P2(1)/c*
a /Å	6.8884(5)	21.0466(15)	8.144(3)	12.965(5)
b /Å	22.6134(16)	11.4539(8)	11.694(5)	16.482(4)
c /Å	11.3005(7)	9.9034(7)	21.145(10)	19.375(5)
α/deg	90	90	90	90
β/deg	111.284(3)	91.0190(10)	110.98(4)	4120(2)
γ/deg	90	90	90	90
V /Å^3	1640.22(19)	2387.0(3)	1880.3(14)	3251.0(11)
Z	4	4	4	12
D_{calc} /g cm^{-3}]	1.378	1.354	1.349	1.411
μ /mm^{-1}	0.309	0.154	0.310	0.284
F(000)	720	1024	800	1824
Data/ restraints/ parameters	2884/ 0/ 202	4198/ 0/ 319	7794/ 0/ 229	7243/ 0/ 547
S	1.132	1.082	1.048	0.610
R1 [I>2σ(I)]	0.0497	0.0474	0.0592	0.0503
wR2 [all data]	0.1166	0.1156	0.0806	0.1013
Max./ min. residual electron dens. [eÅ^{-3}]	0.463/ -0.233	0.432/ -0.399	0.306/ -0.316	0.193/ -0.229

[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 16. Crystal data for compounds **(*Z*)-108**[a]

Compound	**(*Z*)-108**
Emp. formula	$C_{16}H_{11}ClN_2O_3S$
Formula weight	346.79
Crystal system	Monoclinic
Space group	*P2(1)/c*
a /Å	6.4609(3)
b /Å	21.0584(13)
c /Å	12.2104(9)
α/deg	90
β/deg	107.714(5)
γ/deg	90
V /Å^3	1582.53(17)
Z	4
D_{calc} /g cm^{-3}]	1.456
μ /mm^{-1}	0.389
F(000)	712
Data/ restraints/ parameters	2268/ 0/ 208
S	0.904
R1 [I>2σ(I)]	0.0460
wR2 [all data]	0.1017
Max./ min. residual electron dens. [eÅ^{-3}]	0.510/ -0.225

[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) Yamamoto, Y.; Radhakrishnan, U. *Chem. Soc. Rev.* **1999**, *28*, 199. (b) Lu, X.; Zhang, C.; Xu, Z. *Acc. Chem. Res.* **2001**, *34*, 535. (c) Bates, R. W.; Satcharoen, V. *Chem. Soc. Rev.* **2002**, *31*, 12. (d) Wei, L-L.; Xiong, H.; Hsung, R. P. *Acc. Chem. Res.* **2003**, *36*, 773. (e) Ma, S. *Acc. Chem. Res.* **2003**, *36*, 701.

2) Selected recent reviews: (a) Hoffmann-Röder, A.; Krause, N. *Angew. Chem. Int. Ed.* **2004**, *43*, 1196. (b) Krause, N.; Hashmi, A. S. K. (Eds.) *Modern Allene Chemistry*; Wiley-VCH: Weinheim, 2004; (c) Brandsma, L. *Synthesis of Acetylenes, Allenes and Cumulenes: Methods and Techniques*; Elsevier: Kidlington, Oxford, UK, 2004**.** (d) Ma, S. *Chem. Rev.* **2005**, *105*, 2829. (e) Nair, V.; Menon, R. S.; Sreekanth, A. R.; Abhilash, N.; Biju, A. T. *Acc. Chem. Res.* **2006**, *39*, 520. (f) Ma, S. *Aldrichimica Acta* **2007**, *40*, 91. (g) Pacheco, M. C.; Purser, S.; Gouverneur, V. *Chem. Rev.* **2008**, *108*, 1943. (h) Brasholz, M.; Reissig, H.-U.; Zimmer, R. *Acc. Chem. Res.* **2009**, *42*, 45. (i) Ma, S. *Acc. Chem. Res.* **2009**, *42*, 1679. (j) Deagostino, A.; Prandi, C.; Tabasso, S.; Venturello, P. *Molecules* **2010**, *15*, 2667.

3) (a) Zimmer, R.; Dinesh, C.; Nandanan, E.; Khan, F. A. *Chem. Rev.* **2000**, *100*, 3067. (b) Marshall, J. *Chem. Rev.* **2000**, *100*, 3163. (c) Hashmi, A. S. K. *Angew. Chem. Int. Ed.* **2000**, *39*, 3590.

4) (a) Schuster, H. F.; Coppola, G. M. *Allenes in Organic Synthesis*, John Wiley & Sons, New York, 1984, pp 247-252. (b) Alabugin, I. V.; Brei, V. K. *Russ. Chem. Rev.* **1997**, *66*, 205. (c) Zapata, A. J.; Gu, Y.; Hammond, G. B. *J. Org. Chem.* **2000**, *65*, 227. (d) Zhao, C. Q.; Han, L. B.; Tanaka, M. *Organometallics* **2000**, *19*, 4196. (e) Rubin, M.; Markov, J.; Chuprakov, S.; Wink, D. J.; Gevorgyan, V. *J. Org. Chem*. **2003**, *68*, 6251. (f) Nishimura, T.; Hirabayashi, S.; Hayashi, T. *J. Am. Chem. Soc.* **2006**, *126*, 2556. (g) Nishimura, T.; Hirabayashi, S.; Yasuhara, Y.; Hayashi, T. *J. Am. Chem. Soc.* **2006**, *128*, 2556. (h) Ma, S.; Guo, H.; Yu, F. *J. Org. Chem.* **2006**, *71*, 6634. (i) Kumara Swamy, K. C.; Balaraman, E.; Satish Kumar, N. *Tetrahedron* **2006**, *62*, 10152. (j) Chakravarty, M.; Kumara Swamy, K. C. *Synthesis* **2007**, 3171. (k) Yu, F.; Lian, X.; Ma, S. *Org. Lett.* **2007**, *9*, 1703. (l) Bravo-Altamirano, K.; Abrunhosa-Thomas, I.; Montchamp, J.-L. *J. Org. Chem.* **2008**, *73* - , N.; Marinetti, A. *Eur. J. Org. Chem.* **2008**, 3826. (n) Chakravarty, M.; Bhuvan Kumar, N. N.; Sajna, K. V.; Kumara Swamy, K. C. *Eur. J. Org. Chem.* **2008**, 4500. (o) He, G.; Guo, H.; Qian, R.; Guo, Y.; Fu, C.; Ma, S. *Tetrahedron* **2009**, *65*, 4877 (allenylphosphine oxides).

5) (a) Myers, A. G.; Zheng, B. *J. Am. Chem. Soc.* **1996**, *118*, 4492. (b) Myers, A. G.; Zheng, B. *Tetrahedron Lett.* **1996**, *37*, 4841. (c) Myers, A. G.;

Movassaghi, M.; Zheng, B. *Tetrahedron Lett.* **1997**, *38*, 6569. (d) Myers, A. G.; Zheng, B. *Organic Syntheses, Coll. Vol. 10*, **2004**, 165.

6) (a) Guillemin, J. C.; Savignac, P.; Denis, J. M. *Inorg. Chem.* **1991**, *30*, 2170. (b) Iorga, B.; Eymery, F.; Carmichael, D.; Savignac, P. *Eur. J. Org. Chem.* **2000**, 3103.
7) Li, J.; Kong, W.; Fu, C.; Ma, S. *J. Org. Chem.* **2009**, *74*, 5104.
8) Kuang, J.; Ma, S. *J. Org. Chem.* **2009**, *74*, 1763.
9) Kuang, J.; Ma, S. *J. Am. Chem. Soc.* **2010**, *132*, 1786.
10) Müller, T. J. J.; Ansorge, M. *Tetrahedron* **1998**, *54*, 1457.
11) Bhuvan Kumar, N. N.; Kumara Swamy, K. C. *Polyhedron* **2006**, *26*, 883.
12) Pudovik, A. N. *J. Gen. Chem*. **1950**, *29*, 97.
13) Burton, D. H.; Sprague, L. G. *J. Org. Chem.* **1989**, *54*, 613.
14) (a) Scheufler, F.; Maier, M. E. *Eur. J. Org. Chem.* **2000**, 3945. (b) Braverman, S.; Lior, Z. *Tetrahedron Lett.* **1994**, *35*, 6725.
15) (a) Nakamura, I.; Yamamoto, Y. *Chem. Rev.* **2004**, *104*, 2127. (b) Zeni, G.; Larock, R. C. *Chem. Rev.* **2004**, *104*, 2285. (c) Larock, R. C. *Pure. Appl. Chem.* **1999**, *71*, 1435.
16) Larock, R. C.; Berrios-Peña, N. G.; Fried, C. A. *J. Org. Chem*. **1991**, *56*, 2615.
17) Grigg, R. *J. Heterocycl. Chem.* **1994**, *31*, 631.
18) Gardiner, M.; Grigg, R; Sridharan, V.; Vicker, N. *Tetrahedron Lett*. **1998**, *39*, 435.
19) Li, W.; Shi, M. *Eur. J. Org. Chem.* **2009**, 270.
20) Inamoto, K.; Yamamoto, A.; Ohsawa, K.; Hiroya, K.; Sakamoto, T. *Chem. Pharm. Bull.* **2005**, *53*, 1502.
21) (a) Chakravarty, M.; Kumara Swamy, K. C. *J. Org. Chem.* **2006**, *71*, 9128. (b) Manab chakravarthy. "*Investigations on Catalytic and Noncatalytic Reactions of Allenylphosphonates, α-Methoxy Phosphonates and Phosphazanes possessing N-P=X [X= O, S, Se] Skeleton*", Ph.D. thesis, 2007, University of Hyderabad, India. (c) Phani Pavan, M.; Chakravarty, M.; Kumara Swamy, K. C. *Eur. J. Org. Chem.* **2009**, 5927.
22) Larock, R.C.; Berrios-Peña, N. G.; Narayanan, K. *J. Org. Chem.* **1990**, *55*, 3477.
23) Larock, R. C.; Varapath, S.; Lau, H. H.; Fellows, C. A. *J. Am. Chem. Soc.* **1984**, *106*, 5274.
24) Larock, R. C.; Zenner, J. M. *J. Org. Chem*. **1995**, *60*, 482.
25) Cherry, K.; Parrain, J.-L.; Thibonnet, J.; Duchene, A.; Abarbri, M. *J. Org. Chem.* **2005**, *70*, 6669.
26) Kato, F.; Hiroi, K. *Chem. Pharm. Bull.* **2004**, *52*, 95.
27) Larock, R. C.; He, Y.; Leong, W. W.; Han, X.; Refvik, M. D.; Zenner, J. M. *J. Org. Chem*. **1998**, *63*, 2154.

28) Lu, G.; Malinakova, H. C. *J. Org. Chem.* **2004**, *69*, 8266.
29) Desarbre, E; Merour, J.-Y. *Tetrahedron. Lett.* **1996**, *37*, 43.
30) Shen, L.; Hsung, R. P. *Org. Lett*. **2005**, *7*, 775.
31) Mukai, C.; Takahashi, Y. *Org. Lett*. **2005**, *7*, 5793.
32) Larock, R.C.; Tu, C.; Pace, P. *J. Org. Chem.* **1998**, *63*, 6859.
33) Grigg, R.; Kordes, M. *Eur. J. Org. Chem*. **2001**, 707.
34) Grigg, R.; Sridharan, V.; Thayaparan, A. *Tetrahedron Lett.* **2003**, *44*, 9017.
35) Okano, A.; Mizutani, T.; Oishi, S.; Tanaka, T.; Ohno, H.; Fujii, N. *Chem. Commun.* **2008**, 3534.
36) Gai, X.; Grigg, R.; Collard, S.; Muir, J. E. *Chem. Commun.* **2000**, 1765.
37) Chang, H.-T.; Jayanth, T. T.; Cheng, C.-H. *J. Am. Chem. Soc.* **2007**, *129*, 4166.
38) Hsieh, J.-C.; Rayabarapu, D. K.; Cheng, C.-H. *Chem. Commun.* **2004**, 532.
39) Liu, Y.-L.; Liang, Y.; Pi, S.-F.; Huang, X.-C.; Li, J.-H. *J. Org. Chem.* **2009**, *74*, 3199.
40) Grigg, R.; Koppen, I.; Rasparini, M.; Sridharan, V. *Chem.Commun.* **2001**, 964.
41) Lofberg, C.; Grigg, R.; Keep, A.; Derrick, A.; Sridharan, V.; Kilnera, C. *Chem. Commun.* **2006**, 5000.
42) Hiroi, K.; Hiratsuka, Y.; Watanabe, K.; Abe, I.; Kato, F.; Hiroi, M. *Tetrahedron: Asymmetry* **2002**, *13*, 1351.
43) (a) Zeni, G.; Larock, R. C. *Chem. Rev.* **2006**, *106*, 4644. (b) Larock, R. C.; Yum, E. K.; Doty, M. J.; Sham, K. K. C. *J. Org. Chem.* **1995**, *60*, 3270. (c) Kundu, N. G.; Pal, M.; Mahanty, J. S.; De, M. *J. Chem. Soc., Perkin Trans. I* **1997**, 2815. (d) Lu, B. Z.; Zhao, W.; Wei, H.-X.; Dufour, M.; Farina, V.; Senanayake, C. H. *Org. Lett.* **2006**, *8*, 3271.
44) Altenbach, H.; Korff, R. *Tetrahedron Lett*. **1981**, *22*, 5175.
45) Kumara Swamy, K. C.; Balaraman, E.; Satish Kumar, N. *Tetrahedron* **2006**, *62*, 10152.
46) (a) Pudovik, A. N.; Khusainova, N. V. *J. Gen. Chem*. **1966**, *36*, 1251. (b) Altenbach, H.; Korff, R. *Angew Chem. Int. Ed.* **1982**, *21*, 371.
47) Bhuvan Kumar, N. N.; Nagarjuna Reddy, M.; Kumara Swamy, K. C. *J. Org. Chem.* **2009**, *74*, 5395.
48) Zhang, C.; Lu, X. *Synlett* **1995**, 645
49) (a) Jacobs, T. L.; Jr. Illingworth, G. E. *J. Org. Chem*. **1963**, *28*, 2692. (b) Pasto, D. J.; Warren, S. E.; Morrison, M. A. *J. Org. Chem*. **1981**, *46*, 2837. (c) Ogawa, A.; Kawakami, J.; Sonoda, N.; Hirao, T. *J. Org. Chem*. **1996**, *61*, 4161.
50) (a) Pudovik, A. N.; Khusainova, N. G.; Abdulina, T. A. *J. Gen. Chem*. **1967**, *37*, 809. (b) Khusainova, N. G.; Mostovaya, O. A.; Berdnikov, E. A.; Cherkasov, R. A. *Russ. Chem. Bull.* **2004**, *53*, 2253. (c) Khusainova, N. G.;

Mostovaya, O. A.; Berdnikov, E. A.; Efremov, Y. Y.; Sharafutdinova, D. R.; Cherkasov, R. A. *Russ. Chem. Bull.* **2004**, *53*, 2253.

51) Chakravarty, M.; Kumara Swamy, K. C. *Syntheis* **2007**, 3171.

52) Kinder, R. E.; Zhang, Z.; Widenhoefer, R. A. *Org. Lett.* **2008**, *10*, 3157.

53) Al-Masum, M.; Meguro, M.; Yamamoto, Y. *Tetrahedron Lett*. **1997**, *38*, 6071.

54) Huang, X.; Shen, R.; Zhang, T. *J. Org. Chem.* **2007**, *72*, 1534.

55) (a) Frigoli, M.; Mehl, G. H. *Chem. Commun.* **2004**, 2040. (b) Liu, K.; Chougnet, A.; Woggon, W.-D. *Angew. Chem. Int. Ed.* **2008**, *47*, 1. (c) Lee, Y. R.; Choi, J. H.; Yoon, S. H. *Tetrahedron Lett.* **2005**, *46*, 7539. (d) Lee, Y. R.; Wang, X. *Org. Biomol. Chem.* **2005**, *3*, 3955. (e) Flavin, M. T.; Rizzo, J. D.; Khilevich, A.; Kucherenko, A.; Sheinkman, A. K.; Vilaychack, V.; Lin, L.; Chen, W.; Greenwood, E. M.; Pengsuparp, T.; Pezzuto, J. M.; Hughes, S. H.; Flavin, T. M.; Cibulski, M.; Boulanger, W. A.; Shone, R. L.; Xu, Z.-Q. *J. Med. Chem.* **1996**, *39*, 1303. (f) Cueva, J. P.; Giorgioni, G.; Grubbs, R. A.; Chemel, B. R.; Watts, V. J.; Nichols, D. E. *J. Med. Chem.* **2006**, *49*, 6848. (g) Kemnitzer, W.; Drewe, J.; Jiang, S.; Zhang, H.; Crogan-Grundy, C.; Labreque, D.; Bubenick, M.; Attardo, G.; Denis, R.; Lamothe, S.; Gourdeau, H.; Tseng, B.; Kasibhatla, S.; Cai, S. X. *J. Med. Chem.* **2008,** *51*, 417. (h) Bulman Page, P. C.; Buckley, B. R.; Heaney, H.; Blacker, A. J. *Org. Lett.* **2005**, *7*, 375. (i) Shi, Y.-L.; Shi, M. *Org. Biomol. Chem.*, **2007**, *5*, 1499. (j) Liu, F.; Evans, T.; Das, B. C. *Tetrahedron Lett.* **2008**, *49*, 1578.

56) Nixon, N. S.; Scheinmann, F. *Tetrahedron Lett.* **1983**, *24*, 597.

57) (a) Shi, Y.-L.; Shi, M. *Org. Lett.* **2005**, *7*, 3057. (b) Zhao, G.-L.; Shi, Y.-L.; Shi, M. *Org. Lett.* **2005**, *7*, 4527. (c) Shi, M.; Dai, L.-Z.; Shi, Y.-L.; Zhao, G.-L. *Adv. Synth. Catal.* **2006**, *348*, 967. (d) Dai, L.-Z.; Shi, Y.-L.; Zhao, G.-L.; Shi, M. *Chem.-Eur. J.* **2007**, *13*, 3701. (e) Shi, Y.-L.; Shi, M. *Org. Biomol. Chem.* **2007**, *5*, 1499.

58) Meng, X.; Huang, X.; Chen, R. *Org. Lett.* **2009**, *11*, 137.

59) Meng, X.; Huang, Y.; Zhao, H.; Xie, P.; Ma, J.; Chen, R. *Org. Lett.* **2009,** *11*, 991.

60) Grigg, R.; Liu, A.; Shaw, D.; Suganthan, S.; Woodalla, D. E.; Yoganathana, G. *Tetrahedron Lett.* **2000**, *41*, 7125.

61) (a) Wang, W.; Wang, H. L. J.; Zu, L. *J. Am. Chem. Soc* **2006**, *128*, 10354. (b) Zu, L.; Wang, J.; Li, H.; Xie, H.; Jiang, W.; Wang, W. *J. Am. Chem. Soc.* **2007**, *129*, 1036.

62) Zu, L.; Zhang, S.; Xie, H.; Wang, W. *Org. Lett.* **2009**, *11*, 1627.

63) Yavari, I.; Adib, M.; Sayahi, M. H. *J. Chem. Soc., Perkin Trans. I* **2002**, 1517.

64) Hong, L.; Sun, W.; Liu, C.; Wang, L.; Wang, R. *Chem.-Eur. J.* **2010**, *16*, 440.

65) Watanabe, T.; Oishi, S.; Fujii, N.; Ohno, H. *Org. Lett*. **2007**, *9*, 4821.
66) Enchev, D. D.; Kirilov, M. *Phosphorus, Sulfur, and Silicon* **2005**, *180*, 2269.
67) Zwierzak, A. *Can. J. Chem*. **1967**, *45*, 2501.
68) Fuji, K.; Morimoto, T.; Tsutsumi, K.; Kakiuchi, K. *Chem. Commun*. **2005**, 3295.
69) Tang, Y.; Deng, L.; Zhang, Y.; Dong, G.; Chen, J.; Yang, Z. *Org. Lett.* **2005**, *7*, 1657.
70) Bhuvan Kumar, N. N.; Chakravarty, M.; Satish Kumar, N.; Sajna, K. V.; Kumara Swamy, K. C. *J. Chem. Sci*. **2009**, *121*, 23.
71) Boutagy, J.; Thomas, R. *Chem. Rev*. **1974**, *74*, 87.
72) Brandsma, L. *Synthesis of Acetylenes, Allenes and Cumulenes: Methods and Techniques*; Elsevier: Kidlington, Oxford, UK, 2004**,** p. 243.
73) (a) Lang, R. W.; Hansen, H.-J. *Organic Synthesis Coll. Vol. 7*, p. 232. (b) Ma, S.; Jiao, N.; Zhao, S.; Hou, H. *J. Org. Chem.* **2002**, *67*, 2837.
74) (a) Amatore, C.; Jutand, A.; M'Barki, M. A. *Organometallics* **1992**, *11*, 3009. (b) Amatore, C.; Carré, E.; Jutand, A.; M'Barki, M. A. *Organometallics* **1995**, *14*, 1818. (c) Amatore, C.; Carré, E.; Jutand, A.; M'Barki, M. A.; Meyer, G. *Organometallics* **1995**, *14*, 5605.
75) (a) Kumaraswamy, S.; Selvi, R. S.; Kumara Swamy, K. C. *Synthesis* **1997**, 207. **(**b) Praveen Kumar, K.; Muthiah, C.; Kumaraswamy, S.; Kumara Swamy, K. C. *Tetrahedron Lett*. **2001**, *42*, 3219. (c) Kumara Swamy, K. C.; Srinivas, V.; Pavan Kumar, K. V. P.; Praveen Kumar, K. *Synthesis* **2007**, 893.
76) Wittig, G.; Schoellkopf, U. *Org. Synth.* **1960**, *40*, 66.
77) (a) Kao, C.-L.; Chern, J.-W. *J. Org. Chem.* **2002**, *67*, 6772. (b) Yue, D.; Yao, T.; Larock, R. C. *J. Org. Chem.* **2005**, *70*, 10292.
78) Shi, Z.; Zhang, C.; Li, S.; Pan, D.; Ding, S.; Cui, Y.; Jiao, N. *Angew. Chem. Int. Ed.* **2009,** 48, 1.
79) (a) Schmittel, M.; Kiau, S.; Siebert, T.; Strittmatter, M. *Tetrahedron Lett*. **1996**, *37*, 7691. (b) Boisselle, A. P.; Meinhardt, N. A. *J. Org. Chem*. **1962**, *27*, 1828. (c) Santelli-Rouvier, C.; Toupet, L.; Santelli, M. *J. Org. Chem.* **1997**, *62*, 9039.
80) (a) Dai, G.; Larock, R. C. *J. Org. Chem*. **2003**, *68*, 920. (b) Koviri, R. P.; Cheng, C.-H. *Org. Lett.* **2005**, *7*, 5179. (c) Simion, A.; Simion, C.; Kanda, T.; Nagashima, S.; Yoshiharu, M.; Yamada, T.; Mimura, K.; Tashiro, M. *J. Chem. Soc., Perkin Trans. I* **2001**, 2071.
81) (a) Toste, F. D.; Lough, A. J.; Still, I. W. J. *Tetrahedron Lett*. **1995**, *36*, 6619. (b) Figuly, G. D.; Loop, C. K.; Martin, J. C. *J. Am. Chem. Soc*. **1989**, *111*, 654. (c) Block, E.; Eswarakrishnan, V.; Gernon, M.; Oforo-Okai, G.; Saha, C.; Tang, K.; Zubieta, J. *J. Am. Chem. Soc*. **1989**, *111*, 658. (c) Smith, K.; lindsav, C. M.; Pritchard, G. J. *J. Am. Chem. Soc.* **1989**, *111*, 665.

82) Basu Baul, T. S.; Dhar, S.; Pyke, S. M.; Tieknik, E. R. T.; Rivarola, E.; Butcher, R.; Smith, F. E. *J. Organomet. Chem*. **2001**, *633*, 7.

83) Majo, V. J.; Perumal, P. T. *J. Org. Chem*. **1996**, *61*, 6523.

84) Kim. J. H.; Lee, S.; kwon, M.-G.; Park, Y. S.; Choi, S.-K.; Kwon, B.-M. *Synth. Commun*. **2004**, *7*, 1223.

85) (a) Julia, M.; Paris, J.-M. *Tetrahedron Lett.* **1973**, *14*, 4833. (b) Kocienski, P. J.; Lythgoe, B.; Ruston, S. J. *J. Chem. Soc., Perkin Trans. I* **1978**, 829. (c) Keck, G. E.; Savin, K. A.; Weglarz, M. A. *J. Org. Chem*. **1995**, *60*, 3194.

86) (a) Basavaiah, D.; Rao, K. V.; Reddy, J. *Chem. Soc. Rev.* **2007**, ***36***, 1581. (b) Basavaiah, D.; Rao, P. D.; Hyma, R. S. *Tetrahedron* **1996**, *52*, 8001 and references cited there in.

87) Muthiah, C.; Senthil Kumar, K.; Vittal, J. J.; Kumara Swamy, K. C. *Synlett*, **2002**, 1787.

88) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, Pergamon, Oxford, 1986.

89) Shriver, D. F.; Dresdzon, M. A. *The Manipulation of Air Sensitive Compounds*, 2nd Edn, Wiley Insterscience, New York, 1986.

90) (a) Harapanhalli, R. S.; McLaughlin, L. W.; Howell, R. W.; Rao, D. V.; Adelstein, S. J.; Kassis, A. I. *J. Med. Chem.* **1996,** *39*, 4804. (b) Smith, P. *J. Chem. Soc*. **1958**, 3740.

91) (a) Woollett, G. H.; Johnson, W. W. *Org. Synth.* **1934**, *14*, 52. (b) Emmanuvel, L.; Shukla, R. K.; Sudalai, A.; Gurunath, S.; Sivaram, S. *Tetrahedron Lett*. **2006**, *47*, 4793.

92) Barrett, A. G. M.; Dhanak, D.; Graboski, G. G.; Taylor, S. J. *Org. Synth.* **1990**, *68*, 8.

93) (a) Sheldrick, G. M. *SADABS, Siemens Area Detector Absorption Correction*, University of Göttingen, Germany, **1996**. (b) Sheldrick, G. M. *SHELXTL NT Crystal Structure Analysis Package*, Bruker AXS, Analytical X-ray System, WI, USA, **1999**, version 5.10.

Publication numbers and atomic coordinates for X-ray structures reported in this thesis

I. Publication numbers for the published compounds

Compounds 18, 25, 26, 32, (*Z*)-37b and 42: Publication no. 4 (Contents, p. ix)

II. Selected atomic coordinates for compounds 49, 53, (*E*)-56, 58, (*Z*)-61, (*E*)-61, (*E*)-71, (*E*)-81, 97 (*E*)-98 and (*Z*)-108.

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.

Compound 18

Atom	x	y	z	U(eq)
P(1)	2159(1)	3541(1)	4755(1)	45(1)
O(1)	1739(1)	3894(2)	4089(1)	52(1)
O(2)	3162(1)	3686(2)	4653(1)	59(1)
O(3)	1943(2)	2316(2)	4946(1)	66(1)
O(4)	114(1)	4331(2)	6507(1)	61(1)
O(5)	1174(2)	9778(2)	6958(2)	125(1)
C(1)	3506(2)	4631(3)	4243(2)	67(1)
C(2)	3054(2)	4693(3)	3597(2)	63(1)
C(3)	2102(2)	4890(3)	3722(1)	62(1)
C(4)	3410(3)	5778(3)	3226(2)	108(2)
C(5)	3205(3)	3539(3)	3213(2)	92(1)
C(6)	1859(2)	4694(2)	5301(1)	42(1)
C(7)	1257(2)	4719(2)	5765(1)	39(1)
C(8)	643(2)	3730(2)	6001(1)	49(1)
C(9)	1092(2)	2701(3)	6339(2)	69(1)
C(10)	17(2)	3326(3)	5482(2)	68(1)
C(11)	1042(2)	5779(2)	6149(1)	39(1)
C(12)	374(2)	5482(2)	6567(1)	45(1)
C(13)	21(2)	6299(3)	7000(1)	51(1)
C(14)	355(2)	7438(2)	7000(1)	51(1)
C(15)	1026(2)	7772(2)	6580(1)	52(1)
C(16)	1366(2)	6934(2)	6151(1)	49(1)
C(17)	1382(3)	8993(3)	6596(2)	87(1)

Compound 25

atom	x	y	z	U(eq)
I	2349(1)	4063(1)	716(1)	71(1)
O(1)	2781(2)	852(1)	680(1)	46(1)
O(2)	274(3)	3587(3)	-2375(1)	97(1)
C(1)	3414(3)	-1239(2)	1224(1)	43(1)
C(2)	3184(4)	-734(2)	1940(1)	53(1)
C(3)	3639(4)	-1452(3)	2573(1)	62(1)
C(4)	4335(4)	-2675(3)	2513(2)	63(1)
C(5)	4561(4)	-3188(3)	1812(2)	62(1)
C(6)	4117(3)	-2481(2)	1175(1)	53(1)
C(7)	2919(3)	-485(2)	553(1)	42(1)
C(8)	2498(3)	-782(2)	-176(1)	44(1)
C(9)	2412(4)	-2080(3)	-552(1)	58(1)
C(10)	2059(3)	427(2)	-544(1)	45(1)
C(11)	1509(3)	784(2)	-1272(1)	52(1)
C(12)	1180(3)	2086(3)	-1420(1)	55(1)
C(13)	1396(3)	3031(3)	-853(2)	56(1)
C(14)	1951(3)	2682(2)	-133(1)	50(1)
C(15)	2257(3)	1385(2)	8(1)	45(1)
C(16)	606(4)	2489(3)	-2188(2)	74(1)

Compound 26

Atom	x	y	z	U(eq)
O(1)	689(1)	2689(1)	3255(1)	61(1)
O(2)	-3070(2)	4231(2)	6211(1)	87(1)
O(3)	-2013(1)	4029(1)	3428(1)	69(1)
O(4)	6525(1)	1386(1)	1512(1)	74(1)
O(5)	6459(2)	-3128(2)	-729(1)	139(1)
O(6)	5020(2)	-1116(1)	1771(1)	82(1)
C(1)	3341(2)	1091(2)	5224(1)	54(1)
C(2)	2480(2)	54(2)	5655(1)	69(1)
C(3)	2542(2)	-210(2)	6377(1)	75(1)
C(4)	3476(2)	550(2)	6687(1)	69(1)
C(5)	4336(2)	1573(2)	6270(1)	75(1)
C(6)	4287(2)	1837(2)	5544(1)	68(1)
C(7)	3285(2)	1316(2)	4444(1)	60(1)
C(8)	2152(2)	1858(2)	4145(1)	51(1)
C(9)	2075(2)	1893(2)	3342(1)	56(1)
C(10)	3331(2)	2694(2)	2853(1)	72(1)
C(11)	1887(2)	413(2)	3130(1)	77(1)
C(12)	760(2)	2512(2)	4471(1)	49(1)
C(13)	155(2)	2773(2)	5169(1)	54(1)
C(14)	-1210(2)	3462(2)	5291(1)	55(1)
C(15)	-1969(2)	3904(2)	4720(1)	55(1)
C(16)	-1386(2)	3667(2)	4026(1)	53(1)
C(17)	-4(2)	2969(2)	3915(1)	50(1)
C(18)	-1862(2)	3714(2)	6023(1)	70(1)
C(19)	-3467(2)	4631(3)	3534(1)	93(1)
C(20)	9288(2)	3264(2)	-817(1)	66(1)
C(21)	10313(2)	2224(2)	-1033(1)	84(1)
C(22)	10879(2)	2146(3)	-1747(1)	90(1)
C(23)	10452(2)	3106(2)	-2262(1)	82(1)
C(24)	9456(3)	4150(2)	-2064(1)	86(1)
C(25)	8876(2)	4236(2)	-1353(1)	78(1)
C(26)	8693(2)	3374(2)	-49(1)	76(1)
C(27)	7985(2)	2382(2)	427(1)	63(1)
C(28)	7539(2)	2582(2)	1223(1)	72(1)
C(29)	8859(3)	2368(3)	1615(1)	99(1)

C(30)	6673(3)	3947(2)	1366(1)	102(1)
C(31)	7425(2)	992(2)	338(1)	56(1)
C(32)	7515(2)	167(2)	-235(1)	64(1)
C(33)	6785(2)	-1117(2)	-133(1)	66(1)
C(34)	5948(2)	-1593(2)	528(1)	67(1)
C(35)	5813(2)	-786(2)	1103(1)	62(1)
C(36)	6573(2)	504(2)	991(1)	58(1)
C(37)	6936(3)	-1971(3)	-755(1)	96(1)
C(38)	4245(3)	-2423(3)	1899(1)	113(1)

Compound 32

atom	x	y	z	U(eq)
P(1)	3383(1)	8722(1)	2521(1)	54(1)
P(2)	1412(1)	2361(1)	9809(1)	61(1)
O(1)	2160(2)	8308(2)	2345(2)	75(1)
O(2)	3593(2)	9092(2)	1524(2)	61(1)
O(3)	3901(2)	9668(2)	3414(2)	67(1)
O(4)	3399(2)	6838(2)	5086(2)	68(1)
O(5)	8156(3)	5498(2)	6001(3)	115(1)
O(6)	4421(2)	5935(2)	6800(2)	77(1)
O(7)	2669(2)	2581(2)	10106(2)	80(1)
O(8)	958(2)	3285(2)	10188(2)	66(1)
O(9)	911(2)	1435(2)	10286(2)	68(1)
O(10)	1995(2)	-22(2)	7614(2)	63(1)
O(11)	-2884(2)	-1168(2)	4017(2)	75(1)
O(12)	1248(2)	-1684(2)	5999(2)	70(1)
C(1)	4892(3)	10440(3)	3417(3)	76(1)
C(2)	4722(3)	10809(3)	2385(3)	66(1)
C(3)	4557(3)	9902(3)	1578(3)	79(1)
C(4)	3691(3)	11301(3)	2109(3)	98(2)
C(5)	5838(3)	11571(3)	2443(4)	109(2)
C(6)	4267(3)	7808(2)	2889(2)	45(1)
C(7)	4068(3)	7028(2)	1944(3)	47(1)
C(8)	3090(3)	6246(3)	1573(3)	65(1)
C(9)	2912(4)	5571(3)	675(4)	86(1)
C(10)	3717(5)	5665(4)	179(4)	92(2)
C(11)	4682(4)	6430(4)	545(4)	86(1)
C(12)	4857(3)	7103(3)	1425(3)	64(1)
C(13)	4111(3)	7361(2)	3824(2)	46(1)
C(14)	3230(3)	7301(3)	4204(3)	66(1)
C(15)	4921(3)	6887(2)	4512(3)	47(1)
C(16)	5992(3)	6686(2)	4566(3)	56(1)
C(17)	6522(3)	6201(3)	5369(3)	58(1)
C(18)	6037(3)	5941(2)	6130(3)	61(1)
C(19)	4979(4)	6132(3)	6098(3)	59(1)
C(20)	4447(3)	6593(3)	5255(3)	55(1)
C(21)	7638(4)	5968(3)	5395(3)	82(1)
C(22)	5074(4)	5667(3)	7752(3)	93(1)
C(23)	-230(3)	1322(3)	10399(3)	73(1)
C(24)	-365(4)	2294(3)	10947(3)	69(1)
C(25)	-179(3)	3128(3)	10306(3)	73(1)
C(26)	513(4)	2569(3)	12056(3)	99(2)
C(27)	-1610(3)	2138(3)	10971(3)	99(2)
C(28)	694(3)	2048(2)	8418(2)	49(1)
C(29)	902(3)	2987(3)	7897(2)	51(1)
C(30)	1908(3)	3293(3)	7674(3)	72(1)
C(31)	2102(4)	4165(4)	7248(3)	91(1)
C(32)	1294(6)	4730(4)	7006(4)	102(2)
C(33)	285(5)	4434(3)	7210(3)	91(1)
C(34)	89(3)	3562(3)	7653(3)	70(1)
C(35)	1011(3)	1146(3)	7961(3)	49(1)
C(36)	2012(3)	838(3)	8251(3)	63(1)
C(37)	278(3)	422(3)	7054(3)	46(1)
C(38)	-854(3)	298(3)	6388(3)	51(1)

C(39)	-1274(3)	-501(3)	5570(3)	49(1)
C(40)	-607(3)	-1181(3)	5401(3)	54(1)
C(41)	506(3)	-1081(3)	6062(3)	54(1)
C(42)	914(3)	-263(3)	6872(3)	51(1)
C(43)	-2435(3)	-586(3)	4826(3)	64(1)
C(44)	779(3)	-2613(3)	5293(3)	85(1)

Compound (*Z*)-37b

Atom	x	y	z	U(eq)
Cl	6379(1)	1975(1)	6665(1)	65(1)
O(1)	1405(3)	64(2)	2574(2)	47(1)
O(2)	3570(3)	1260(2)	2876(2)	60(1)
O(3)	7706(4)	1112(2)	11794(3)	91(1)
C(1)	-502(4)	-920(2)	1804(3)	40(1)
C(2)	-189(4)	-870(2)	842(4)	43(1)
C(3)	-1111(5)	-1189(3)	-71(4)	54(1)
C(4)	-2395(5)	-1577(3)	-25(4)	59(1)
C(5)	-2702(5)	-1627(2)	922(4)	49(1)
C(6)	-1776(5)	-1304(2)	1839(4)	50(1)
C(7)	507(4)	-566(2)	2771(4)	43(1)
C(8)	809(4)	-701(2)	3832(3)	37(1)
C(9)	234(5)	-1353(3)	4386(3)	57(1)
C(10)	1940(4)	-135(2)	4347(3)	38(1)
C(11)	2258(4)	307(2)	3553(3)	39(1)
C(12)	3339(4)	896(3)	3742(4)	43(1)
C(13)	4079(4)	1045(2)	4792(3)	43(1)
C(14)	3781(4)	620(2)	5638(3)	39(1)
C(15)	2704(4)	27(2)	5398(3)	41(1)
C(16)	4748(5)	1832(3)	3062(4)	66(2)
C(17)	4531(4)	758(2)	6757(3)	44(1)
C(18)	5590(4)	1255(2)	7301(3)	40(1)
C(19)	6184(4)	1253(3)	8468(3)	39(1)
C(20)	6193(4)	549(3)	9058(4)	48(1)
C(21)	6676(4)	534(3)	10130(4)	57(1)
C(22)	7220(5)	1217(4)	10687(4)	58(1)
C(23)	7261(5)	1923(3)	10153(4)	57(1)
C(24)	6747(4)	1946(3)	9046(4)	52(1)
C(25)	8612(7)	1677(4)	12378(5)	111(2)

Compound 42

Atom	x	y	z	U(eq)
P(1)	1963(1)	7680(2)	9943(1)	35(1)
P(2)	7187(1)	10722(2)	5124(1)	51(1)
O(1)	2188(3)	9858(6)	9876(2)	58(1)
O(2)	937(2)	7327(6)	10276(2)	44(1)
O(3)	2711(2)	6533(5)	10409(2)	37(1)
O(4)	2958(3)	3123(6)	7865(2)	56(1)
O(5)	7136(4)	12861(8)	5323(2)	85(2)
O(6)	6198(3)	9583(6)	5230(2)	50(1)
O(7)	7416(3)	10468(7)	4362(2)	57(1)
O(8)	9082(4)	5826(9)	6822(2)	83(2)
C(1)	700(3)	5303(9)	10537(3)	45(1)
C(2)	1474(4)	4586(8)	11037(3)	41(1)
C(3)	2448(4)	4504(8)	10679(3)	39(1)
C(4)	1545(4)	6068(9)	11635(3)	55(2)
C(5)	1203(5)	2431(10)	11267(3)	65(2)
C(6)	1864(4)	6315(9)	9174(3)	44(1)
C(7)	2537(4)	5414(8)	8796(2)	39(1)
C(8)	2169(4)	4207(11)	8171(3)	59(2)

C(9)	1336(5)	2620(12)	8353(3)	73(2)
C(10)	1769(5)	5620(14)	7662(3)	77(2)
C(11)	2542(6)	7191(10)	7453(4)	81(2)
C(12)	3587(5)	2132(9)	8331(3)	59(2)
C(13)	3602(4)	5433(9)	8929(2)	39(1)
C(14)	4093(4)	7039(8)	9251(2)	40(1)
C(15)	5098(4)	6901(10)	9379(3)	47(1)
C(16)	5613(4)	5190(10)	9194(3)	54(2)
C(17)	5131(4)	3611(10)	8865(3)	51(2)
C(18)	4141(4)	3723(9)	8723(3)	43(1)
C(19)	7242(5)	8418(10)	4063(3)	58(2)
C(20)	6210(4)	7677(9)	4165(3)	47(1)
C(21)	6024(4)	7579(10)	4916(3)	52(1)
C(22)	5472(4)	9116(10)	3815(3)	59(2)
C(23)	6135(6)	5499(11)	3883(3)	72(2)
C(24)	8152(4)	9292(10)	5510(3)	56(2)
C(25)	8226(4)	8238(8)	6080(3)	48(1)
C(26)	9163(5)	7007(12)	6225(4)	73(2)
C(27)	9421(6)	5533(15)	5652(4)	95(3)
C(28)	10084(8)	8430(20)	6257(6)	132(4)
C(29)	9985(9)	9660(20)	6769(7)	164(6)
C(30)	8186(7)	4803(11)	6874(4)	83(2)
C(31)	7441(4)	8157(9)	6592(3)	50(2)
C(32)	6792(5)	9769(11)	6709(3)	60(2)
C(33)	6055(5)	9525(14)	7179(3)	79(2)
C(34)	5984(6)	7688(19)	7532(3)	92(3)
C(35)	6631(7)	6142(16)	7427(4)	88(3)
C(36)	7378(6)	6355(11)	6961(3)	66(2)

Compound 49

Atom	x	y	z	U(eq)
P	1687(1)	7956(1)	951(1)	15(1)
O(1)	1481(2)	8929(1)	954(1)	18(1)
O(2)	1394(2)	7758(1)	-403(1)	17(1)
O(3)	505(2)	7543(1)	1251(1)	22(1)
N(1)	7164(2)	8298(1)	4722(2)	19(1)
C(1)	2325(3)	9427(1)	428(2)	20(1)
C(2)	1893(3)	9170(1)	-885(2)	19(1)
C(3)	2256(2)	8260(1)	-914(2)	18(1)
C(4)	113(3)	9339(1)	-1728(2)	23(1)
C(5)	2951(3)	9657(2)	-1328(2)	25(1)
C(6)	3749(2)	7723(1)	1860(2)	16(1)
C(7)	4728(2)	7971(1)	3009(2)	15(1)
C(8)	6531(2)	7751(1)	3639(2)	17(1)
C(9)	7388(3)	7922(2)	2847(2)	23(1)
C(10)	6722(3)	6846(1)	4058(2)	20(1)
C(11)	4411(2)	8457(1)	3884(2)	15(1)
C(16)	5901(2)	8607(1)	4904(2)	16(1)
C(15)	5954(3)	9044(1)	5906(2)	18(1)
C(14)	4519(3)	9313(1)	5870(2)	19(1)
C(13)	3014(3)	9161(1)	4872(2)	17(1)
C(12)	2982(2)	8734(1)	3885(2)	16(1)
C(17)	1485(3)	9445(1)	4902(2)	22(1)

Compound 53.1/2H_2O

Atom	x	y	z	U(eq)

P	2278(1)	4740(1)	2343(1)	87(1)
O(1)	1417(1)	5078(2)	1358(2)	78(1)
O(2)	2743(2)	3606(2)	1861(2)	100(1)
C(7)	3190(2)	6932(2)	2216(2)	57(1)
C(12)	2280(2)	7614(2)	2079(2)	60(1)
C(2)	1931(2)	3805(2)	-152(2)	68(1)
O(3)	1929(2)	4544(2)	3462(2)	145(1)
C(17)	2236(2)	8542(3)	1292(2)	74(1)
C(1)	1584(2)	5004(2)	151(2)	73(1)
C(6)	3229(2)	5782(2)	2361(2)	71(1)
C(3)	2870(2)	3552(3)	633(3)	85(1)
N	3949(2)	8463(2)	1122(2)	95(1)
C(8)	4104(2)	7660(2)	2138(2)	71(1)
C(11)	3097(3)	8823(3)	771(3)	96(1)
C(13)	1496(2)	7414(3)	2678(3)	81(1)
C(10)	4303(2)	8410(3)	3263(3)	88(1)
C(5)	2138(3)	3818(3)	-1422(3)	105(1)
C(4)	1158(2)	2893(3)	-2(3)	105(1)
C(15)	615(3)	8980(4)	1645(5)	127(2)
C(9)	5013(2)	6954(3)	2000(4)	112(1)
C(16)	1388(3)	9204(3)	1061(3)	107(1)
C(14)	660(3)	8109(4)	2450(4)	111(1)
C(100)	4425(4)	900(6)	10093(6)	209(3)

Compound (*E*)-56

Atom	x	y	z	U(eq)
S	11615(1)	8531(1)	8478(1)	46(1)
P	7511(1)	7759(1)	8369(1)	41(1)
O(1)	6967(3)	8985(3)	8557(2)	65(1)
O(2)	7804(2)	6654(3)	8970(1)	51(1)
O(3)	6463(2)	7095(2)	7680(1)	43(1)
O(4)	11517(3)	8929(3)	10654(1)	54(1)
C(1)	7948(4)	5262(4)	8789(2)	53(1)
C(2)	6723(3)	4787(4)	8166(2)	41(1)
C(3)	6571(4)	5677(4)	7529(2)	44(1)
C(4)	5466(4)	4857(4)	8359(2)	60(1)
C(5)	6962(4)	3340(4)	7980(2)	59(1)
C(6)	9026(3)	8025(3)	8191(2)	36(1)
C(7)	8845(3)	8245(4)	7422(2)	37(1)
C(8)	9322(4)	7310(4)	7059(2)	48(1)
C(9)	9191(4)	7530(5)	6360(2)	58(1)
C(10)	8562(5)	8668(5)	6010(2)	67(1)
C(11)	8061(4)	9593(5)	6352(2)	65(1)
C(12)	8214(4)	9386(4)	7061(2)	50(1)
C(13)	10235(3)	8136(3)	8721(2)	36(1)
C(14)	10513(3)	8002(4)	9509(2)	42(1)
C(15)	11571(3)	8986(4)	9967(2)	41(1)
C(16)	12936(3)	8626(3)	9948(2)	38(1)
C(21)	13033(3)	8384(3)	9286(2)	38(1)
C(20)	14250(3)	8084(4)	9230(2)	48(1)
C(19)	15393(4)	8006(4)	9839(2)	57(1)
C(18)	15318(4)	8214(4)	10499(2)	55(1)
C(17)	14094(3)	8522(4)	10552(2)	47(1)

Compound 58

Atom	x	y	z	U(eq)
P	1717(1)	1073(1)	1354(1)	35(1)
S	1008(1)	-825(1)	3675(1)	66(1)

O(3)	188(2)	1140(1)	964(2)	47(1)
O(4)	1850(2)	-386(1)	255(2)	42(1)
O(1)	2827(2)	1146(1)	459(1)	45(1)
C(6)	2060(3)	137(1)	2064(2)	31(1)
O(2)	2208(2)	1720(1)	2188(1)	44(1)
C(7)	3704(3)	55(1)	2345(2)	31(1)
C(15)	1403(3)	-514(1)	1292(2)	34(1)
C(8)	4661(3)	-211(1)	1608(2)	42(1)
C(12)	4304(3)	298(1)	3331(2)	41(1)
C(16)	1752(3)	-1334(1)	1697(2)	35(1)
C(17)	2206(3)	-1919(1)	1033(2)	48(1)
C(11)	5785(3)	265(2)	3576(2)	50(1)
C(2)	3465(3)	2510(1)	873(2)	47(1)
C(9)	6145(3)	-237(2)	1852(3)	51(1)
C(21)	1502(3)	-1524(1)	2745(2)	41(1)
C(10)	6717(3)	-8(2)	2846(3)	54(1)
C(18)	2351(3)	-2680(2)	1393(3)	63(1)
C(19)	2044(3)	-2876(2)	2418(3)	63(1)
C(1)	3968(3)	1730(2)	477(3)	61(1)
C(20)	1617(3)	-2298(2)	3091(3)	55(1)
C(4)	2189(4)	2825(2)	170(3)	81(1)
C(3)	3058(4)	2404(2)	2001(3)	72(1)
C(5)	4733(4)	3094(2)	861(3)	89(1)
C(13)	1174(3)	94(1)	3049(2)	35(1)
C(14)	514(3)	672(2)	3522(2)	47(1)

Compound (*E*)-61

Atom	x	y	z	U(eq)
P	4574(1)	4185(1)	870(1)	40(1)
S	9557(2)	6107(1)	1652(1)	51(1)
O(1)	2318(4)	4706(3)	916(1)	65(1)
O(2)	5474(4)	4642(2)	492(1)	46(1)
O(3)	4535(4)	2588(2)	848(1)	45(1)
O(4)	7734(5)	816(3)	2416(1)	58(1)
O(5)	10253(6)	6972(3)	627(1)	75(1)
C(1)	7408(6)	3939(4)	361(1)	48(1)
C(2)	6962(5)	2431(4)	322(1)	42(1)
C(3)	6370(6)	1876(4)	697(1)	48(1)
C(4)	9116(7)	1715(5)	227(1)	68(1)
C(5)	5094(7)	2171(4)	18(1)	59(1)
C(6)	6633(5)	4607(3)	1242(1)	37(1)
C(7)	6996(5)	3586(3)	1547(1)	37(1)
C(8)	8872(6)	2745(3)	1579(1)	42(1)
C(9)	5438(6)	3478(4)	1812(1)	44(1)
C(10)	5758(6)	2560(4)	2100(1)	46(1)
C(11)	9176(6)	1811(4)	1865(1)	46(1)
C(12)	7617(6)	1718(3)	2125(1)	42(1)
C(13)	9496(8)	-169(4)	2433(1)	73(1)
C(14)	7641(5)	5832(3)	1267(1)	39(1)
C(15)	7146(6)	7043(3)	1021(1)	42(1)
C(16)	9163(6)	7765(4)	887(1)	47(1)
C(17)	10779(6)	8254(3)	1199(1)	44(1)
C(22)	11087(6)	7563(3)	1533(1)	41(1)
C(21)	12716(6)	7982(4)	1806(1)	54(1)
C(20)	13990(7)	9110(4)	1752(1)	60(1)
C(19)	13675(7)	9841(4)	1426(1)	58(1)
C(18)	12105(6)	9406(4)	1155(1)	52(1)

Compound (*Z*)-61

Atom	x	y	z	U(eq)
S	7387(1)	-105(1)	3041(1)	55(1)
P	7204(1)	2533(1)	3088(1)	42(1)
O(1)	7181(3)	2611(2)	3850(2)	68(1)
O(2)	5824(2)	1955(2)	2208(2)	49(1)
O(3)	7196(3)	3715(2)	2724(2)	48(1)
O(4)	13188(3)	4812(2)	4575(2)	60(1)
O(5)	11859(3)	-1290(2)	4608(2)	62(1)
C(1)	5516(4)	2052(3)	1320(3)	52(1)
C(2)	5429(4)	3255(3)	1054(2)	43(1)
C(3)	6845(4)	3792(3)	1824(3)	47(1)
C(4)	5200(5)	3273(4)	155(3)	65(1)
C(5)	4203(4)	3836(3)	912(3)	64(1)
C(6)	8748(3)	1829(3)	3394(2)	35(1)
C(7)	9959(3)	2596(2)	3730(2)	36(1)
C(8)	10545(3)	2651(3)	3303(2)	42(1)
C(9)	11614(4)	3393(3)	3604(2)	47(1)
C(10)	12114(3)	4115(3)	4327(2)	41(1)
C(11)	11544(4)	4081(3)	4760(2)	46(1)
C(12)	10472(4)	3324(3)	4454(2)	44(1)
C(13)	13784(4)	5546(3)	5342(3)	71(1)
C(14)	8841(3)	722(3)	3385(2)	36(1)
C(15)	10143(3)	117(3)	3675(3)	44(1)
C(16)	10514(4)	-914(3)	4259(3)	47(1)
C(17)	9368(4)	-1788(3)	3690(2)	39(1)
C(22)	7951(3)	-1484(2)	3148(2)	36(1)
C(21)	6864(4)	-2270(3)	2673(3)	49(1)
C(20)	7211(5)	-3371(3)	2740(3)	59(1)
C(19)	8612(5)	-3678(3)	3248(3)	57(1)
C(18)	9674(4)	-2898(3)	3712(2)	47(1)

Compound (*E*)-71

Atom	x	y	z	U(eq)
S	2518(1)	6972(1)	2347(1)	51(1)
P	2130(1)	5969(1)	5538(1)	35(1)
O(1)	3683(3)	5497(1)	5772(2)	49(1)
O(2)	-134(3)	5739(1)	5315(2)	42(1)
O(3)	2594(3)	6405(1)	6700(2)	43(1)
O(4)	5398(5)	5234(1)	2209(2)	85(1)
C(1)	2306(4)	6157(1)	7818(2)	45(1)
C(2)	93(4)	5931(1)	7511(3)	42(1)
C(3)	-440(4)	5488(1)	6428(2)	43(1)
C(4)	33(6)	5605(2)	8687(3)	62(1)
C(5)	-1447(5)	6444(1)	7168(3)	57(1)
C(6)	1800(4)	6453(1)	4246(2)	39(1)
C(7)	196(5)	6937(1)	4070(3)	55(1)
C(8)	2947(4)	6413(1)	3507(2)	38(1)
C(9)	4526(5)	5950(1)	3542(3)	49(1)
C(10)	4282(5)	5746(1)	2203(3)	54(1)
C(11)	5010(4)	6236(1)	1555(2)	45(1)
C(16)	4316(4)	6806(1)	1606(2)	40(1)
C(15)	4919(4)	7269(1)	1020(3)	50(1)
C(14)	6221(5)	7167(2)	369(3)	58(1)
C(13)	6957(5)	6610(2)	324(3)	60(1)
C(12)	6366(5)	6146(2)	916(3)	58(1)

Compound (*E*)-81

Atom	x	y	z	U(eq)
P	3593(1)	3325(1)	11076(1)	22(1)
N(1)	498(1)	2240(2)	4710(2)	28(1)
N(2)	204(1)	2964(2)	3982(2)	29(1)
O(1)	4229(1)	3785(1)	10393(1)	22(1)
O(2)	3601(1)	4000(1)	12477(1)	24(1)
O(3)	3573(1)	2051(1)	11210(1)	30(1)
O(4)	2185(1)	4103(1)	8511(1)	25(1)
C(1)	4806(1)	3648(2)	11208(2)	26(1)
C(2)	4755(1)	4261(2)	12572(2)	25(1)
C(3)	4174(1)	3800(2)	13290(2)	25(1)
C(4)	5343(1)	3954(2)	13430(2)	41(1)
C(5)	4701(1)	5578(2)	12369(2)	31(1)
C(6)	2990(1)	4029(2)	10118(2)	23(1)
C(7)	2585(1)	3421(2)	9299(2)	23(1)
C(8)	2524(1)	2172(2)	9165(2)	25(1)
C(9)	2978(1)	5337(2)	10135(2)	23(1)
C(10)	2586(2)	5952(2)	10972(3)	54(1)
C(11)	2576(2)	7163(2)	10976(3)	55(1)
C(12)	2952(1)	7799(2)	10121(2)	32(1)
C(13)	3326(1)	7181(2)	9268(3)	56(1)
C(14)	3341(1)	5975(2)	9268(3)	48(1)
C(15)	2938(1)	9116(2)	10117(3)	46(1)
C(16)	2121(1)	1693(2)	8266(2)	26(1)
C(17)	1731(1)	2417(2)	7390(2)	25(1)
C(18)	1303(1)	2004(2)	6405(2)	26(1)
C(19)	930(1)	2767(2)	5655(2)	26(1)
C(20)	981(1)	3973(2)	5872(2)	28(1)
C(21)	1413(1)	4396(2)	6814(2)	26(1)
C(22)	1780(1)	3621(2)	7564(2)	24(1)
C(23)	-246(1)	2452(2)	3062(2)	28(1)
C(24)	-387(1)	1266(2)	2993(2)	33(1)
C(25)	-834(1)	882(2)	2054(2)	38(1)
C(26)	-1149(1)	1666(2)	1210(2)	38(1)
C(27)	-1012(1)	2845(2)	1282(2)	35(1)
C(28)	-552(1)	3234(2)	2201(2)	32(1)

Compound 97

Atom	x	y	z	U(eq)
Cl	8276(1)	9480(1)	4019(1)	70(1)
P	6687(1)	5218(1)	2924(1)	46(1)
O(1)	7222(2)	4009(1)	2747(1)	50(1)
O(2)	7823(2)	5439(1)	3681(1)	60(1)
O(3)	4797(2)	5286(1)	2795(1)	71(1)
O(4)	6713(2)	8232(1)	2084(1)	53(1)
N(1)	9972(2)	7101(1)	3121(1)	38(1)
C(1)	8649(3)	3309(2)	3156(2)	70(1)
C(2)	9199(4)	3532(2)	3894(2)	65(1)
C(3)	9452(4)	4804(3)	4011(1)	91(1)
C(4)	7878(4)	3065(2)	4175(2)	100(1)
C(5)	10987(4)	2933(3)	4252(2)	138(2)
C(6)	7334(3)	6265(2)	2424(1)	36(1)
C(7)	6321(3)	5989(2)	1681(1)	55(1)
C(8)	9325(3)	6252(2)	2624(1)	37(1)
C(9)	10259(3)	5574(2)	2388(1)	51(1)
C(10)	6954(3)	7501(2)	2642(1)	39(1)
C(11)	8634(3)	7767(2)	3197(1)	38(1)
C(12)	9361(3)	8487(2)	3727(1)	43(1)
C(13)	11216(3)	8298(2)	3991(1)	41(1)
C(14)	12624(4)	8781(2)	4516(1)	60(1)
C(15)	14300(4)	8381(3)	4632(2)	74(1)
C(16)	14603(4)	7519(2)	4241(2)	72(1)
C(17)	13275(3)	7018(2)	3726(1)	57(1)

C(18)	11573(3)	7422(2)	3601(1)	43(1)

Compound (*E*)-98

Atom	x	y	z	U(eq)
O(3)	10661(5)	-982(1)	971(1)	67(1)
Cl	13763(2)	-1172(1)	2785(1)	71(1)
O(1)	3281(5)	1488(1)	193(1)	66(1)
O(2)	3310(4)	2689(1)	732(1)	58(1)
N	9777(5)	735(1)	1897(1)	42(1)
C(1A)	4246(6)	1914(2)	676(1)	48(1)
C(2A)	1142(7)	3005(2)	187(1)	60(1)
C(3B)	627(9)	3877(2)	350(2)	94(1)
C(4A)	6455(6)	1699(2)	1254(1)	49(1)
C(5A)	7689(6)	954(2)	1344(1)	41(1)
C(6A)	7127(6)	208(2)	905(1)	50(1)
C(15B)	8602(6)	-507(2)	1327(1)	48(1)
C(14)	10385(6)	-96(2)	1930(1)	44(1)
C(13A)	12335(6)	-247(2)	2498(1)	45(1)
C(12A)	13117(6)	504(2)	2843(1)	42(1)
C(11B)	15077(7)	711(2)	3426(1)	56(1)
C(10B)	15359(7)	1513(2)	3611(1)	61(1)
C(9A)	13710(7)	2109(2)	3231(1)	59(1)
C(8A)	11752(6)	1931(2)	2648(1)	50(1)
C(7A)	11448(6)	1119(2)	2456(1)	40(1)

Compound (Z)-108

atom	x	y	z	U(eq)
N(1)	11903(6)	5504(2)	1373(3)	83(1)
C(10)	10340(6)	5715(2)	1450(3)	56(1)
Cl	-2446(2)	5435(1)	-4235(1)	83(1)
S	6093(1)	6416(1)	-649(1)	58(1)
O(3)	12920(5)	7819(2)	6854(2)	93(1)
O(2)	15411(5)	7147(1)	6860(2)	79(1)
O(1)	5522(4)	6992(1)	-134(2)	74(1)
N(2)	13591(6)	7363(2)	6448(3)	62(1)
C(5)	-181(6)	6200(2)	-2537(3)	67(1)
C(6)	1701(6)	6406(2)	-1736(3)	64(1)
C(1)	3645(5)	6111(2)	-1634(3)	48(1)
C(2)	3719(6)	5609(2)	-2341(3)	58(1)
C(3)	1833(7)	5402(2)	-3142(3)	59(1)
C(4)	-85(6)	5698(2)	-3226(3)	54(1)
C(7)	6401(5)	5792(2)	433(3)	52(1)
C(8)	8276(5)	5952(2)	1475(3)	46(1)
C(9)	7990(5)	6302(2)	2333(3)	50(1)
C(11)	9500(5)	6537(2)	3395(3)	46(1)
C(16)	8691(6)	6950(2)	4054(3)	56(1)
C(15)	9987(6)	7220(2)	5055(3)	56(1)
C(14)	12156(6)	7069(2)	5405(3)	49(1)
C(13)	13021(6)	6651(2)	4806(3)	58(1)
C(12)	11695(6)	6388(2)	3798(3)	57(1)