ABSTRACT OF THE THESIS

The thesis entitled "**Total synthesis of Pectinolide H, Stagonolide G and development of new synthetic methodologies**" has been divided into five chapters.

Chapter-I: This chapter deals with the introduction of natural products total synthesis and describes about the biologically active five membered lactones and ten membered macrolides.

Chapter-II: This chapter deals with the brief introduction to 5-membered lactones and first stereoselective total synthesis of Pectinolide H.

Chapter-III: This chapter deals with the brief introduction to 10 membered macrolides and asymmetric total synthesis of Stagonolide G.

Chapter-IV: This chapter deals with the development of new synthetic methodologies involving oxidative coupling, which is further divided into two sections.

Section 4.1. Metal-free oxidative C-C bond formation of active methylenic sp^3 C-H bonds with benzylic sp^3 C-H and allylic sp^3 C-H bonds mediated by DDQ.

Section 4.2. DDQ-mediated direct oxidative coupling of amides with benzylic and allylic sp^3 C-H bonds under metal-free conditions.

Chapter-V: This chapter deals with the development of new synthetic methodologies using $[HMim]^+[BF_4]^-$ acidic ionic liquid as a catalyst and solvent, which is further divided into two sections.

Section 5.1. Efficient and rapid stereoselective synthesis of *trans*-4,5-diaminocyclopent-2-enones by acidic ionic liquid under solvent-free conditions.

Section 5.2. Solvent-free alkylation of 1,3-dicarbonyl compounds with benzylic, propargylic and allylic alcohols using acidic ionic liquid $[(HMim)BF_4]$.

Chapter-I

Introduction to five and ten membered lactone natural products

Chapter-I describes about the natural products total synthesis, biologically active five membered lactones and ten membered macrolides.

Most of the valuable pharmaceutical agents are produced from natural sources such as macrolide antibiotics, steroidal harmones, and β-lactam antibiotics. These are very useful class of natural products and give significant medicinal agents. These secondary metabolites play important role in regulation of various biological processes continue to offer the motivation for synthesis of natural products. In most of the time, natural products isolated from the natural resources are small in quantities, such cases total synthesis of natural product is necessary to facilitate biological evaluation and it is an important step to decide if the natural product deserves further examination as a lead structure for development of drug. It includes the unique capability of chemists to develop new methods and to design molecules with a preferred set of properties.

Intrigued by the significant biological properties and interesting structural features of lactone containing molecules, along with in continuation of our studies towards total synthesis of lactone containing compounds, we became involved in the synthesis of five membered and ten membered lactones as a part of our research work.

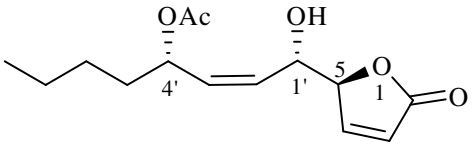
Five membered lactone (γ-lactone) containing natural products are known to exhibit various biological activities such as antitumor, cytotoxic, cyclooxygenase or phospholipase A2 inhibition. These are of fungal, bacterial or marine source. Biological activities, structural complexities of γ-lactone molecules, and challenges to synthesize in optically pure form, which are made them an attractive target for various total syntheses.

Naturally occurring macrolides, particularly 10-membered ring-containing lactones have continued to attract synthetic chemists as well as biologists during recent years, due to their interesting structural properties and strong biological activities. While the scarce availability of these macrolides, only few of them evaluated for biological activity. Several examples, mainly 10-membered macrolides exhibited significant biological properties, for instance pinolidoxin and putaminoxin. The key metabolite, stagonolide displays phytotoxic property and stagonolide F shows antifungal and antibacterial activity. Stagonolide G-I, nonenolides formed by *Stagonopora crisis* Davis, a fungal pathogen isolated from *Cirsium arvense* and anticipated as a strong mycoherbicide of this perennial noxious weed, generates phytotoxic metabolites in liquid and solid cultures.

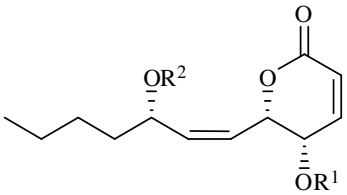
Chapter-II

First stereoselective total synthesis of pectinolide H

Five membered ring lactone containing a substitution at the γ-position is a significant structural subunit in various bio-active compounds. Natural products, which containing a γ-lactone moiety known to display a variety of biological properties, including anti-fungal, anti-bacterial, anti tumor, cytotoxic, cyclooxygenase or phospholipase A_2 inihibition. Pectinolide H (**1**) is a γ-lactone that has been isolated from the chloroform extract of the aerial parts of a Mexican terrestrial plant *Hyptis pectinata*. Pectinolides A-C (**2**-**4**) are also isolated from the same plant and exhibit antimicrobial and cytotoxic properties. Especially, pectinolide H (**1**) displayed strong antimicrobial activity against a panel of multidrug-resistant strains of *Staphylococcus aureus*. The structure and stereo chemistry of **1** was determined on the basis of spectral, chiroptical data and chemical evidence.



Pectinolide H (1)

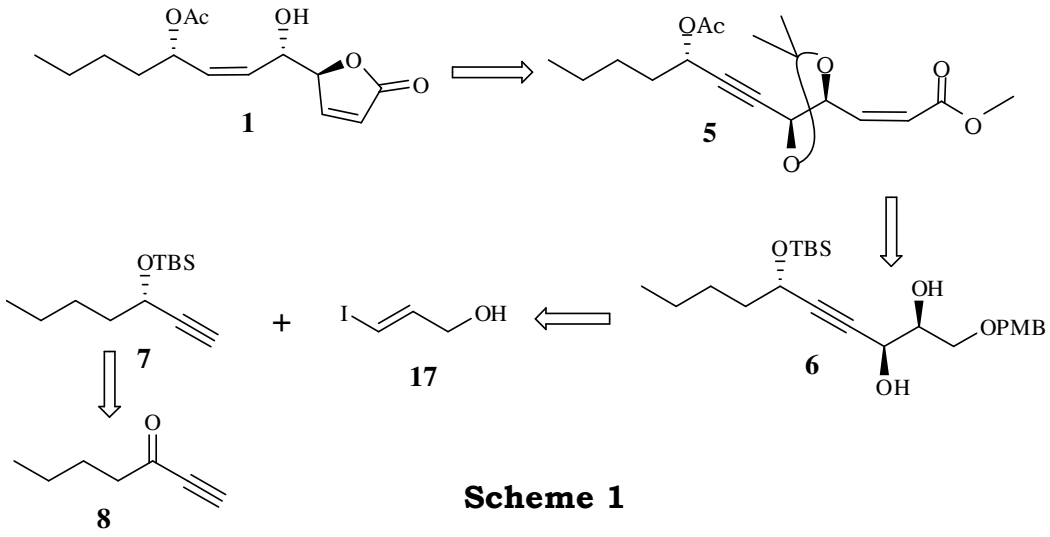


Pectinolide A; R^1=R^2=Ac (**2**)

Pectinolide B; R^1=Ac, R^2=H (**3**)

Pectinolide C; R^1=H, R^2=Ac (**4**)

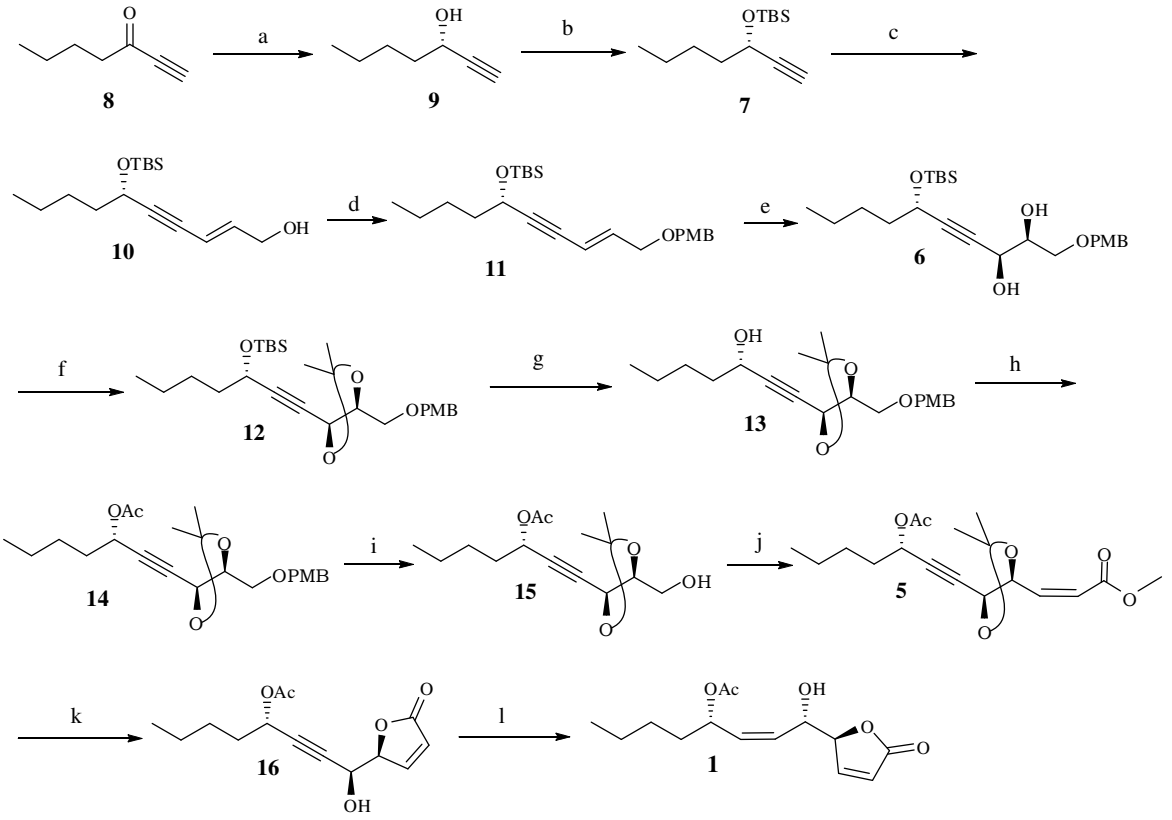
In continuation of our interest in the total synthesis of biologically active natural products, accompanied by important biological activities and significant structural features of **1** encouraged us to explore the synthesis of this molecule. To the best of our knowledge, there is no report on the synthesis of **1**.



Scheme 1

The retro synthetic analysis of **1** is described in Scheme 1. The target molecule **1** can be easily envisaged from the *cis* olefinic ester (**5**) by one pot acetonide deprotection and lactonization followed by Lindlar's reaction. The intermediate **5** in turn can be achieved from the Still-Gennari olefination and other sequential reactions of diol (**6**). The intermediate **6** was prepared from the Sonogashira cross coupling of alkyne (**7**) and (*E*)-3-iodoprop-2-en-1-ol (**17**). In addition, compound **7** was prepared from the acetylenic ketone (**8**) by stereoselective asymmetric reduction (Scheme 1).

The synthesis of pectinolide H **1** was commenced from the acetylenic ketone (**8**) and the first stereogenic centre was generated by the enantioselective reduction of **8** with (*S*)-alpine borane (**18**) in THF at r.t. for 8 h provided the chiral propargyl alcohol (**9**) in 75% yield (*ee* 75%). The alcohol (**9**) was protected with TBSCl, imidazole in CH_2Cl_2 at r.t. for 3 h to give TBS ether (**7**) in 94% yield. The terminal alkyne in **7** was subjected to sonogashira cross coupling with (*E*)-3-iodoprop-2-en-1-ol (**17)** in the presence of $[Pd(PPh_3)_4]$, CuI, $^{i}Pr_2NH$, dry benzene at r.t. for 2 h to afford allylic alcohol **10** in 88% yield.



Scheme 2

Scheme 2: *Reagents and Conditions*: (a) (*S*)-Alpine borane (**18**), THF, 8 h, r.t., 75%; (b) imidazole, TBDMSCl, DCM, r.t., 3 h; (c) (*E*)-3-iodoprop-2-en-1-ol (**17**), *i*Pr_2NH, $Pd(PPh_3)_4$, CuI, dry benzene, r.t., 2 h, 88%; (d) NaH, PMBCl, dry THF, 0 °C to r.t., 4 h, 93%; (e) AD-mix-α, $MeSO_2NH_2$, *t*-BuOH/H_2O (1:1), 0 °C, 24 h, 82%; (f) 2,2-dimethoxypropane, PTSA, dry DCM, r.t., 12 h, 90%; (g) TBAF, THF, r.t., 2 h, 97%; (h) Ac_2O, pyridine, r.t., 4 h, 96%; (i) DDQ, DCM/H_2O (10:1), r.t., 2 h, 95%; (j) 1) Dess-Martin periodinane, DCM, 0 °C to r.t., 2 h, 94%; 2) $(F_3CCH_2O)_2POCH_2COOMe$, 18-crown ether, KHMDS, dry THF, -78 °C, 4 h, 86%; (k) 80% AcOH, 0 °C to r.t., 20 h, 96% ; (l) Lindlar's catalyst, quinoline, ethyl acetate, r.t., 2 h, 88%.

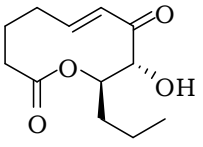
The primary alcohol in **10** was protected with *p*-methoxybenzyl chloride using NaH in dry THF at r.t for 4 h to afford compound **11** in 93% yield. Sharpless dihydroxylation of **11** with AD-mix-α in t-Butanol/H_2O (1:1) at 0 °C furnished diol **6** in 82% yield (*de* 96%). The diol (**6**) was protected with 2,2-dimethoxy propane in the presence of a catalytic amount of PTSA in CH_2Cl_2 to obtain **12** with 90% yield. The TBS group in **12** was removed using TBAF in THF to give secondary alcohol **13** in 97% yield. The secondary alcohol **13** was acetylated using acetic anhydride in pyridine to afford compound **14** in 96% yield. The *p*-methoxybenzyl group in **14** was removed employing DDQ in CH_2Cl_2/H_2O (10:1) at r.t. for 2 h to give primary alcohol **15** in 95% yield. The alcohol

15 was oxidized with dess-martin periodinane (DMP) in CH_2Cl_2 to afford aldehyde, which was further subjected to *Z*-selective still-gennari olefination by employing bis((2,2,2-trifluoroethyl)(methoxycarbonyl- ethyl phosphonate)), 18-crown ether, KHMDS in THF to afford *cis*-olefinic ester (**5**) in 86% yield. Deprotection of acetonide group in **15** and lactonization were achieved in one pot using 80% AcOH to give acetylenic lactone **16** with 96% yield. Finally, partial hydrogenation of triple bond in **16** over Lindlar's catalyst, quinoline in ethylacetate furnished the target natural product, pectinolide H (**1**) in 88% yield.

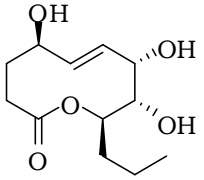
Chapter-III

Asymmetric total synthesis of stagonolide G

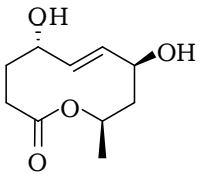
Macrolides containing 10-membered ring lactone have known to show various interesting structural properties and strong biological activities. Several examples, mainly 10-membered macrolides exhibited significant biological properties, for instance pinolidoxin and putaminoxin. The key metabolite, stagonolide displays phytotoxic property and stagonolide F shows antifungal and antibacterial activity.



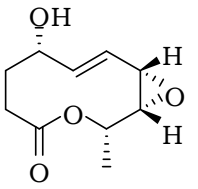
Stagonolide A (19)



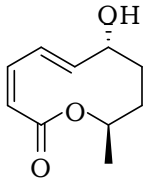
Stagonolide B (20)



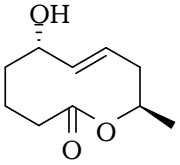
Stagonolide C (21)



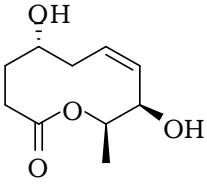
Stagonolide D (22)



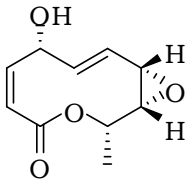
Stagonolide E (23)



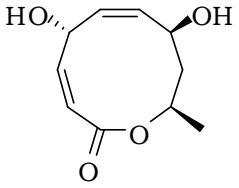
Stagonolide F (24)



Stagonolide G (25)



Stagonolide H (26)



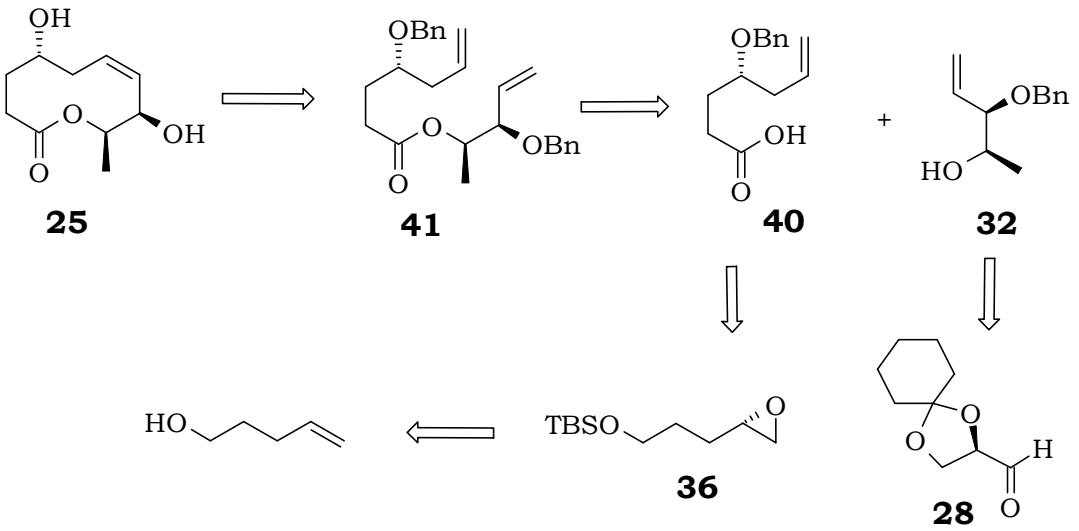
Stagonolide I (27)

A. Evidente *et. al* isolated new phytotoxic metabolites from *Stagonospora cirsii*, which is a fungal pathogen isolated from *Cirsium arvense* and anticipated as a potential mycoherbicide of this perennial toxic weed, generates phytotoxic metabolites in solid and liquid cultures. Stagonolides A-D (**19-22**), with phytotoxic activities, were isolated from a liquid culture. The same fungus, grown in solid culture, showed an improved ability to produce five new nonenolides, called stagonolides E-I (**23-27**).

In continuation of our interest towards total synthesis of lactone containing molecules, we have synthesized 10-membered macrolides, such as stagonolide A, stagonolide B, herbarumin-I and now we are interested in the synthesis of stagonolide G (**25)**.

In this chapter a simple asymmetric total synthesis of stagonolide G (**25**) is described. Asymmetric dihydroxylation, regio selective epoxide ring opening and vinyl Grignard reactions are involved in generating the

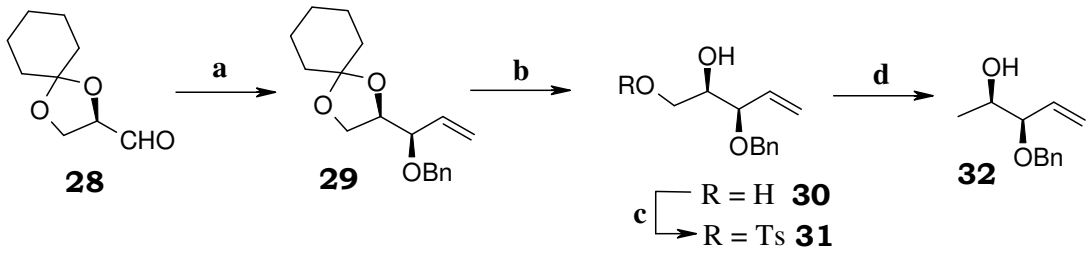
stereogenic centers at C-4 and C-8, followed by Grubbs catalyzed ring-closing metathesis (RCM).



Scheme 3: Retrosynthetic analysis

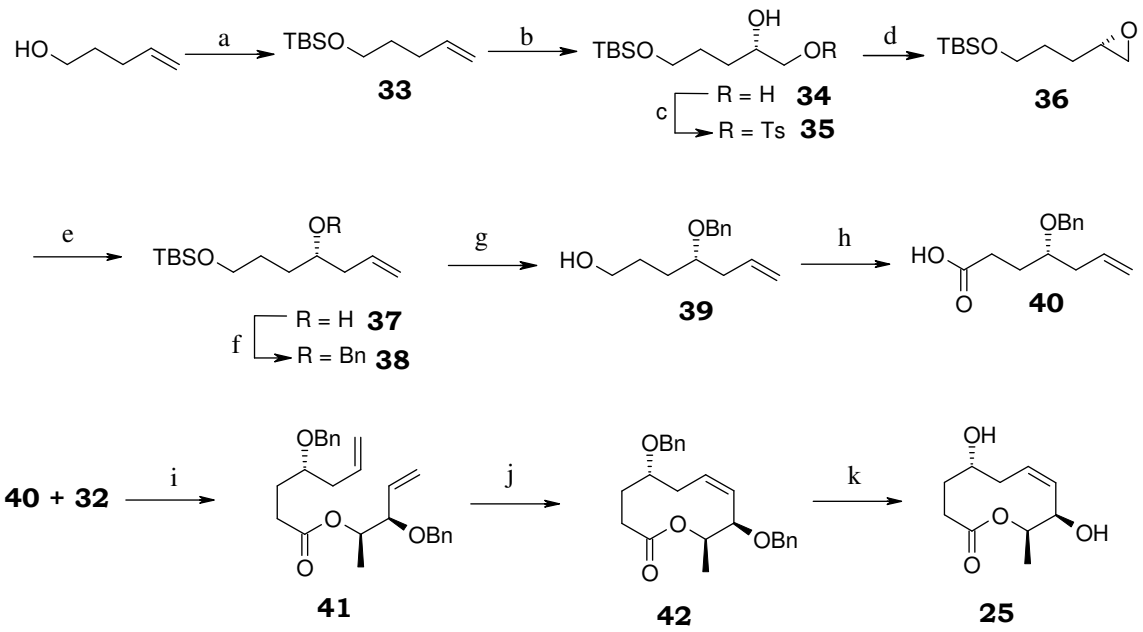
The retrosynthetic analysis of stagonolide G (**25**) is summarized in Scheme 1. Stagonolide G can be achieved from bis-olefin **41** by ring closing metathesis (RCM) protocol, a key reaction method that has been commonly used for the synthesis of macrolides. Additionally, this bis-olefin ester **41** in turn can be attained by steglich-esterification of acid **40** and alcohol **32**. The fragment **32** is envisaged from (*R*)-(+)-glyceraldehyde and fragment **40** can be easily synthesized from commercially available 4-penten-1-ol. Therefore, in the present strategy the two stereo centers C-4 and C-8 are constructed: one by asymmetric dihydroxylation on **33** for (4*S*)-hydroxyl group and the second asymmetric (8R) hydroxyl group is generated by vinyl *Grignard* reaction with **28**.

The synthesis of stagonolide G was commenced from 2,3-di-*O*-cyclo-hexylidine-(*R*)-(+)-glyceraldehyde **28**, which was reacted with vinylmagnesium bromide in THF to give an inseparable mixture of alcohols in a ratio of 1:1. Benzylation of the secondary alcohol with NaH and benzyl bromide in THF afforded compound **29**, and the required isomer was separated by column chromatography. The hexylidine protection in **29** was removed by using Dowex H^+ resin in MeOH to give the diol **30** 91% yield.



Scheme 4. *Reagents and conditions*: (a) i) Vinylmagnesium bromide, THF, 3h, 89%; ii) NaH, BnBr, THF, 4h, 41% (separation of isomers); (b) Dowex H^+ resin, MeOH, 20h, 91%; (c) TEA, TsCl, $^nBu_2SnO$, DCM, 4h, 92%; (d) LAH, THF, 1h, 86%.

The primary hydroxyl group in **30** was selectively protected with *p*-toluenesulfonyl chloride using triethylamine in the presence of dibutyltin oxide in dry CH_2Cl_2 to obtain mono tosylate **31** in 92% yield. The tosyl group in **31** was reduced with $LiAlH_4$ in THF to afford the key intermediate **32** in 86% yield.



Scheme 5. *Reagents and conditions*: (a) imidazole, TBSCl, dry DCM, 3h, 93%; (b) AD-mix-α, ^{t}BuOH : H_2O, 24h, 94%; (c) TEA, TsCl, $^{n}Bu_2SnO$, DCM, 4h, 91%; (d) K_2CO_3, MeOH 2h, 89%; (e) vinylmagnesium bromide, CuI, THF, 3h, 86%; (f) NaH, BnBr, THF, 4h, 93%; (g) TBAF, THF, 3h, 92%; (h) BAIB, TEMPO, ACN : H_2O, 3h, 84%; (i) DCC, DMAP, DCM, 12h, 83%; (j) Grubbs II catalyst, DCM, 3h, 88%; (k) TiCl4, DCM, 3h, 73%.

The commercially available 4-penten-1-ol was protected with *tert*-butyldimethylsilyl chloride to give TBS ether **33**. The asymmetric dihydroxylation of the terminal olefine in **33** with AD-mix-α [$K_2OsO_2(OH)_4$, $K_3Fe(CN)_6$, K_2CO_3, $(DHQ)_2PHAL$] at 0 ^{o}C furnished diol **34** in 94% yield. The primary hydroxyl group in diol **34** was selectively protected with *p*-toluenesulfonyl chloride using triethylamine in the presence of catalytic amount of dibutyltin oxide in dry CH_2Cl_2 afforded

mono tosylate **35** in 91% yield. The tosylate compound **35** was treated with K_2CO_3 in methanol to give epoxide **36** in 89% yield. The regioselective ring opening of epoxide **36** with vinylmagnesium bromide in the presence of CuI afforded homo allylic alcohol **37** in 86% yield. The secondary alcohol in **37** was protected as benzyl ether using NaH and benzyl bromide to furnish compound **38** in 93% yield. Deprotection of *tert*-butyldimethylsilyl group in **38** with TBAF in THF afforded **39** in 92% yield. The primary alcohol **39** was oxidized with BAIB, catalytic amount of TEMPO in CH_3CN:H_2O (2:1) at r.t to give corresponding acid in 84% yield. The acid **40** was esterified with the alcohol **32** in the presence of DCC and DMAP in CH_2Cl_2 at 0 ^oC to provide the bis olefine ester **41** in 83% yield. The bis olefine ester **41** was subjected to ring closure metathesis (RCM) using Grubbs-II catalyst in CH_2Cl_2 at 40 ^oC to afford the dibenzyl protected macrolide **42** in 63% yield. Deprotection of the benzyl groups in **42** was achieved using $TiCl_4$ in CH_2Cl_2 at 0 ^oC to provide the natural product stagonolide G (**25**) in 73% yield.

Chapter-IV

Development of new synthetic methodologies involving oxidative coupling

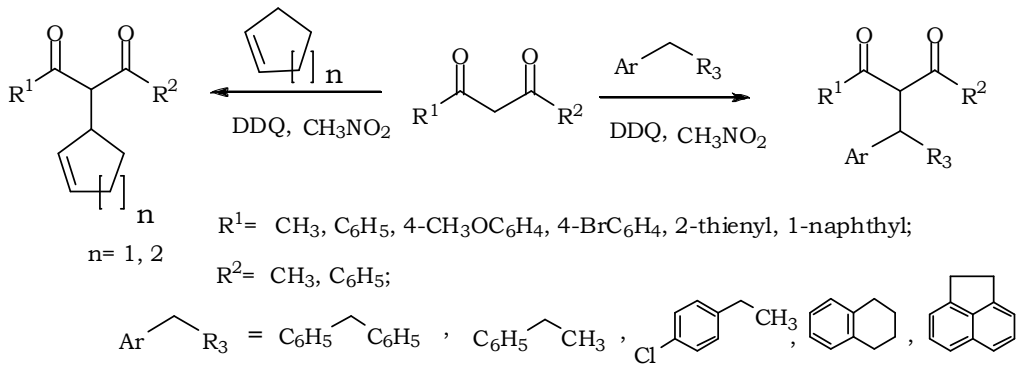
This chapter describes the development of new synthetic methodologies involving oxidative coupling, which is further divided into two sections based on the C-C (section 4.1) and C-N (section 4.2) bond formation.

Section 4.1. Metal-free oxidative C-C bond formation of active methylenic sp^3 C-H bonds with benzylic sp^3 C-H and allylic sp^3 C-H bonds mediated by DDQ.

The formation of carbon-carbon bond is an essential step in organic chemistry and is the basis for synthesis of complex molecules from simple precursors. Metal catalyzed coupling reactions of several reactive functional groups are among the most valuable methods for the formation of C-C bond. The reaction can be further developed from the perspective of atom efficiencyand green chemistry, the development of direct C-C bond formation from the unfunctionalized C-H substrates is a significant task and attracted more concern in recent years. These methods will avoid the pre-functionalization of C-H bonds and make the synthetic route shorter and atom-economical. In this perspective, significant development has been made toward direct employment of benzylic and allylic sp^3 C-H bond rather than pre-functionalization. The majority of the methods based on cross-coupling reactions of sp^3 C-H bonds restricted to α-hetero aromatic compounds or require carbene

precursors, directing groups and stoichiometric metal reagents. Recently, some approaches have been reported for the direct coupling of active methylenic sp^3 C-H bonds with allylic sp^3 C-H bonds in presence of $CuBr/CoCl_2/^{ter}BuOOH$ catalyst system, in the same way with simple benzylic sp^3 C-H bonds using $FeCl_2/^{ter}BuOO^{ter}Bu$ catalyst system and $Cu(ClO_4)_2/^{ter}BuOOBz$/bathophenanthroline ligand system.

Despite of great benefits of these reactions, there are still certain restrictions such as one or two transition metals are required for the formation of C-C bond. Additionally, peroxide is utilized as an oxidizing reagent under heating conditions and also there are some general difficulties with the metal catalyzed reactions for instance, difficulty in preparation of ligand or catalyst, cost of metal catalyst, heavy metal residues in drug development and some metals are toxic in nature. Furthermore, in view of the improved awareness to environmental problems, metal-free methodologies are useful for the coupling reactions.



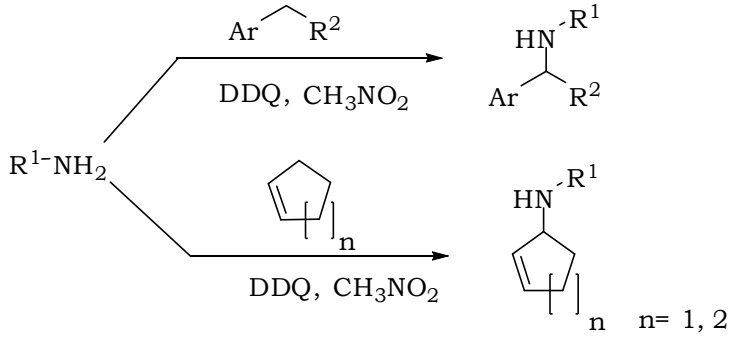
Scheme 6

In conclusion, we have developed a simple and metal-free method for the direct oxidative coupling of active methylenic sp^3 C-H bonds with allylic and benzylic sp^3 C-H bonds by employing DDQ as an oxidant. This method has various advantages: (1) No metal is needed for the reaction. (2) It proceeds devoid of additional reagent. (3) Simple allylic and benzylic substrates can be used directly without pre-functionalization. (4) It gives the required products in good to excellent yields.

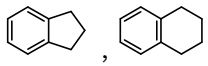
Section 4.2. DDQ-mediated direct oxidative coupling of amides with benzylic and allylic sp^3 C-H bonds under metal-free conditions.

Selective and proficient activation of C-H bonds to generate functional compounds with minimal toxicity, energy, cost and environmental tribulations is one of the challenging areas in synthetic chemistry. Direct conversion of unmodified C-H bonds into C-N bonds is the significant method for the synthesis of important nitrogen containing compounds, which are common in pharmaceuticals, fine chemicals and natural relevance. In most of the methods C-N bond can be formed rely on various functional group interconversions. The reaction may be further improved from the view point of atom efficiency and green chemistry. The development of amidation reactions of prior un-functionalized substrates is an excellent alternative, which makes the synthetic path shorter, simpler and atom economical. In this viewpoint, considerable achievements have been made toward direct utilization of benzylic and allylic sp^3 C-H bonds.

In the reported methods, most of the amidation reactions based on nitrene derivatives as the primary nitrogen source or hypervalent iodine reagents. Additionally, metal catalysts such as Cu, Ru, Rh, Fe, Ag, Pd and Co were necessary to the activation of C-H bond for the C-N formation. In view of the increased awareness toward environmental problems transition metal-free methods are preferable for the amidation reactions.



R^1= C_6H_5CO, $PhCH_2OCO$, 4-$CH_3C_6H_4SO_2$, 4-$BrC_6H_4SO_2$, 4-$CH_3OC_6H_4SO_2$

Ar–R^2 = C_6H_5–C_6H_5 , C_6H_5–CH_3 ,  ,

Scheme 7

In conclusion, we have developed a metal-free and simple method for the direct amidation of benzylic and allylic sp^3 C-H bonds using DDQ as an oxidizing reagent. This method provides numerous merits specifically (i) reaction proceeds without metal or metal catalyst, (ii) a range of amides including benzamide, benzyl carbamate and substituted sulfonamides can be utilized, (iii) un-functionalized benzylic and allylic sp^3 C-H substrates can be used directly, (iv) no additional reagents are required for the reaction (v) DDQ is an inexpensive and readily available oxidizing reagent.

Chapter-V

Development of new synthetic methodologies using $[HMim]^+[BF_4]^-$ ionic liquid as a catalyst and solvent

This chapter describes the development of new synthetic methodologies using $[HMim]^+[BF_4]^-$ acidic ionic liquid, which is further divided into two sections.

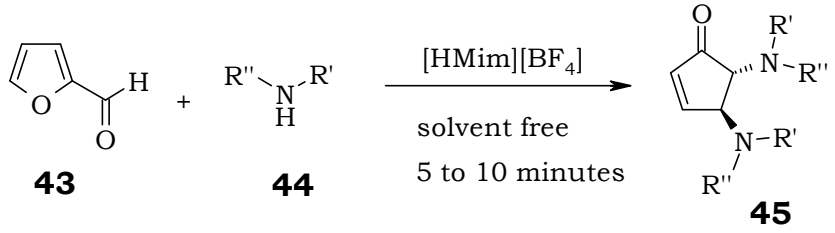
Section 5.1. Efficient and rapid stereoselective synthesis of *trans*-4,5-diaminocyclopent-2-enones by acidic ionic liquid under solvent free conditions

The synthesis and selective functionalisation of cyclopentenones have been the focus in the recent years. Recently, (-)-agelastatin A, an architecturally remarkable antineoplastic alkaloid has been isolated from the axinellid sponge *Agelas dendromorpha* by Pietra and co-workers. The retrosynthesis analysis of (-)-agelastatin A guides to have embedded a trans diaminocyclopentane moiety (**45**).

In addition pioneering studies of Lewis and Mulquiney, afforded low yield of **45** from the reaction of furfural (**43**) and amines (**44**) in harsh conditions specifically refluxing in methanol in presence of hydrochloric acid. Recently, Sze-Wan Li and Robert A. Batey reported a method for exclusive formation of trans 4,5-diaminocyclopente-2-enone (**45**) using $Sc(OTf)_3$ and $Dy(OTf)_3$.

However, most of these reported methods suffer from one or other limitations, such as expensive reagents, strictly anhydrous conditions,

long reaction time and harsh reaction conditions. Further, all of the known methods use highly polar organic solvents leading to complex isolation and recovery methods. Hence, we sought to develop a more convenient and efficient method for synthesis of trans-4,5-diaminocyclopent-2-enones, which avoids these drawbacks.



43 **44** **45**

Scheme 8

In conclusion, we have expalined the fast and efficient synthesis of *trans* 4,5-diaminocyclopent-2-enones in IL [HMim][BF_4] as catalyst and reusable reaction medium. In addition to simplicity, solvent free conditions this method offers excellent yields of 4,5-diaminocyclopent-2-enones exclusively trans selectivity, in short reaction times (3-10 min), which makes it, a useful and important addition to the existing methods.

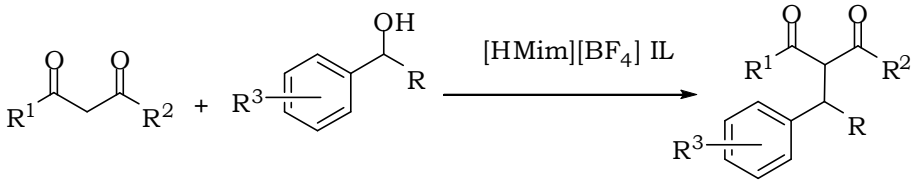
Section 5.2. Solvent-free alkylation of 1,3-dicarbonyl compounds with benzylic, propargylic and allylic alcohols using acidic ionic liquid [(HMim)BF_4]

The formation of carbon-carbon bonds is an important concern in modern organic chemistry. The standard method for the alkylation of

1,3-dicarbonyl compounds is use of a stoichiometric amount of base and organic halide as alkylating agent, which would produce unnecessary by-products and decrease the yield. Synthetic strategy aiming at environmentally benign chemistry reduces the formation of by-products, to afford high atom-efficient chemical process. Even though, the use of alcohols as alternatives for halides and acetate compounds as electrophiles, it is an ideal method because it avoids waste salt formations. While the hydroxyl group in alcohols is having poor leaving ability needs equimolar or greater amounts of reagents or promoter to develop the leaving ability of the hydroxy group. Alkylation of 1,3 dicarbonyl with alcohols has been reported using transition metal based reagents such as tetrakis (triphenylphosphine)-palladium in the presence of a carboxylic acids and cobalt (III) dimethylglyoxime complex in acetic acid. Recently, various Lewis acid catalysts such as $BF_3.OEt_2$, $InCl_3$, $Bi(OTf)_3$, $Yb(OTf)_3$, PTSA and H-montmorillonite have also been reported to catalyze these reactions.

However, the majority of these reported methods suffer from one or more limits such as use of highly volatile, hazardous, and polar solvents. Most of them explained only the reactions of 2^o alcohols with 1,3-dicarbonyl compounds, with expensive reagents, strong acidic conditions, long reaction time, selectivity, complexity in preparation of catalysts, and requires inert conditions. Therefore we sought to develop a more proficient and convenient method for three types of alkylation

reactions such as benzylation, propargylation, and allylation including 1° allylic alcohols on 1,3-dicarbonyl compounds using mild and inexpensive catalyst and avoiding usage of toxic or volatile organic solvent in an environmentally benign process which avoids these drawbacks.



Scheme 9

In conclusion, we have described an efficient and a convenient protocol for the direct alkylation of 1,3-dicarbonyl compounds with benzylic, propargylic and allylic alcohols using [HMim][BF_4] IL as a catalyst and solvent. The reactions proceeded in excellent yields with high selectivity. Moreover, short reaction time and avoided the usage of hazardous or volatile organic solvent that makes the current protocol is attractive and important addition to the existing methods.