

Significance of Povarov Reaction in Organic synthesis: An overview

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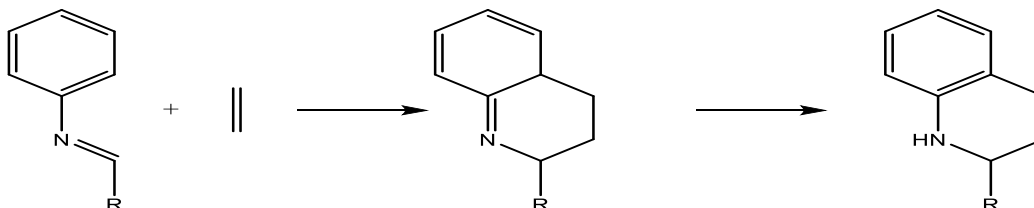
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Abstract: The Povarov reaction has enabled and shaped the art and science of organic synthesis over the last few decades to an extent that has yet to be eclipsed by any other transformation in the current synthetic repertoire. With myriad applications of this magnificent Pericyclic reaction, often as a crucial element in elegant and programmed cascade sequences facilitating complex molecule construction, the Povarov cycloaddition has afforded numerous and unparalleled solutions to a diverse range of synthetic puzzles provided by nature in the form of natural products. Selected examples of the awesome power of the reaction he helped to discover are discussed in this review in the context of organic synthesis to illustrate its overall versatility and underscore its vast potential which has yet to be fully realized.

Key Word: Povarov reaction, multicomponent one-pot synthesis, cycloaddition, molecular diversity, organic synthesis.

I. Introduction

The Povarov reaction is an organic reaction described as a formal cycloaddition between an aromatic imine and an alkene. In this organic reaction imine is a condensation product between aromatic amine and aromatic aldehyde “[1-3]”. The alkene used in such reactions is enol ethers and enamines etc. which are electron-rich and easily able to donate the electrons. The reaction product in the original Povarov reaction is a quinoline (3).

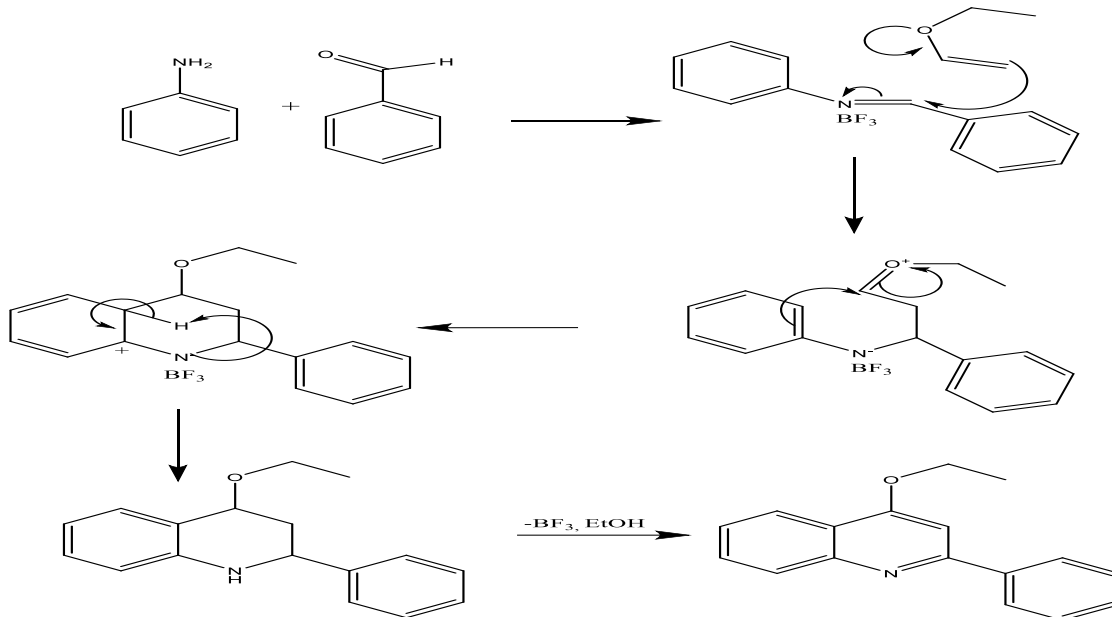


Scheme 1.

The reaction mechanism for the Povarov reaction to the quinoline is outlined (3) in **scheme 1**. In step one reaction between aniline and benzaldehyde, we get the Schiff base in a reaction. The Povarov reaction requires a Lewis acid such as boron trifluoride to activate the imine for an electrophilic addition of the activated alkene. This reaction step

forms an oxonium ion which then reacts with the aromatic ring in a classical electrophilic aromatic substitution. Two additional elimination reactions create the quinoline ring structure.

The Povarov reaction mechanism:



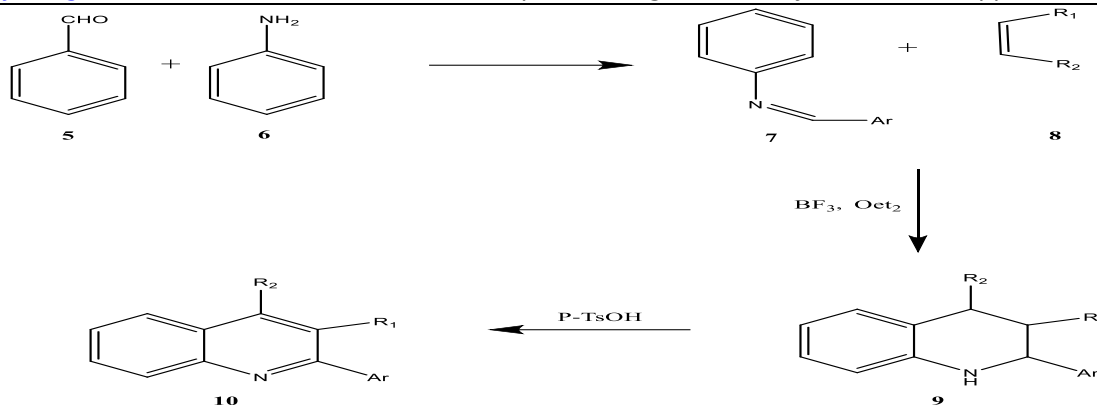
The Povarov reaction, which was developed in the 1960s by the L.S. Povarov (Russian Scientist), can be considered one of the most powerful ideas for the synthesis of heterocyclic compounds. Since the pioneering work of “Povarov and co-workers [1-6]” significant research interest was attracted and a large number of efforts have been implicated in this particular research area, obtaining highly usable synthetic routes to directly access tetrahydroquinoline (THQ) and other interacting heterocyclic scaffolds employing Povarov reaction. There are several publications published coming out each year on these topics and discovering pharmaceutical applications.

The field was previously reviewed by “Kouznetsov [7]” covering the literature up to mid-2008. This review mainly focused on various applications of Povarov reaction; it includes multi-component, eco-friendly, etc. methodologies. In 2011, a general review was published on the chemistry of THQ synthesis, in which some space was also devoted to the Povarov reaction as a tool for synthesizing THQ and covered the literature up to mid-2010.

The Povarov reaction can be catalyzed by various reagents, including Lewis acid, Bronsted acid, Green Reagents, and various metal salts. Recently catalytic multicomponent version inter and intramolecular Povarov reactions have emerged as potential tools in both diversity in the Povarov reaction, a large amount of variation in substrate selectivity concerning the dienes and dienophilic components. Now a day for the synthesis of heterocyclic compounds, the Povarov reaction as the key step has become an attractive and alternative route to create novel heterocycles. In the Povarov original work, the reaction was upgraded into a one-pot, multi-component (MCR) in which the aldehyde was generated in situ [8].

Three-Component Povarov reactions:

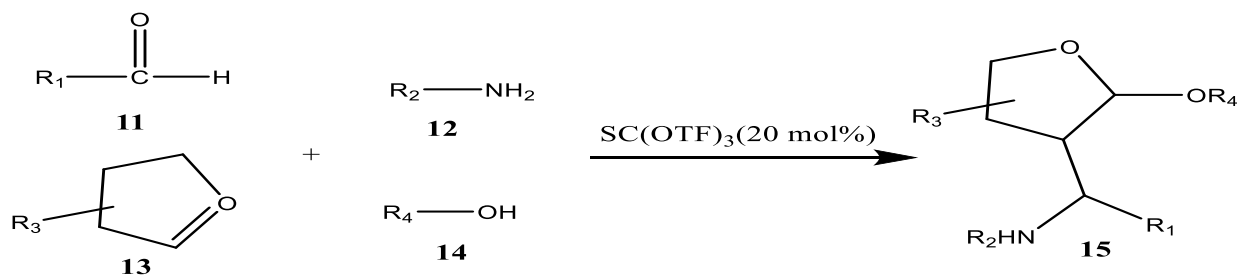
Lewis acid-catalyzed three-component one-pot Povarov reaction was carried out between aromatic aldehydes, aromatic amine, and an alkene to form quinoline outlined in **scheme-2**.



Scheme-2. Lewis Acid Catalyst one pot Povarov reaction

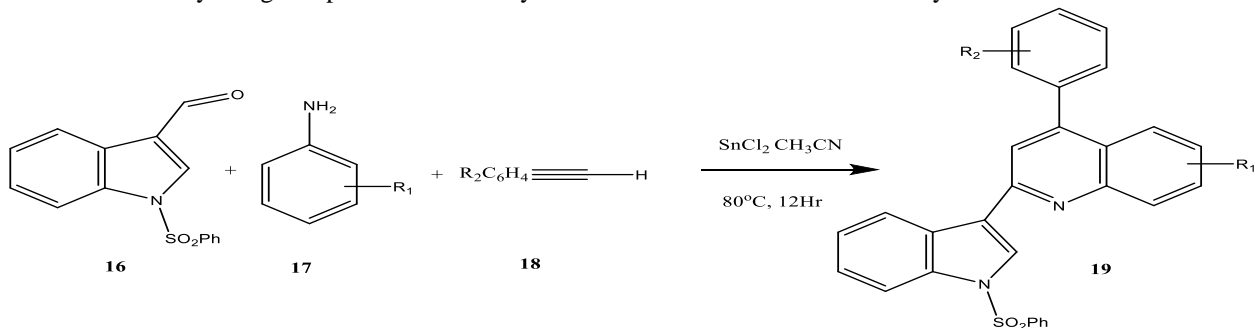
Four Component Povarov reactions:

“Lavilla and co-worker [9]” elegantly exploited a Lewis acid catalyzed four-component Povarov reaction (**scheme-3**) of aldehydes amines, cyclic enol ether and alcohol acts as an external nucleophilic or terminator of the Povarov process, trapping the final oxacarbenium intermediate to the formation of the new compound.



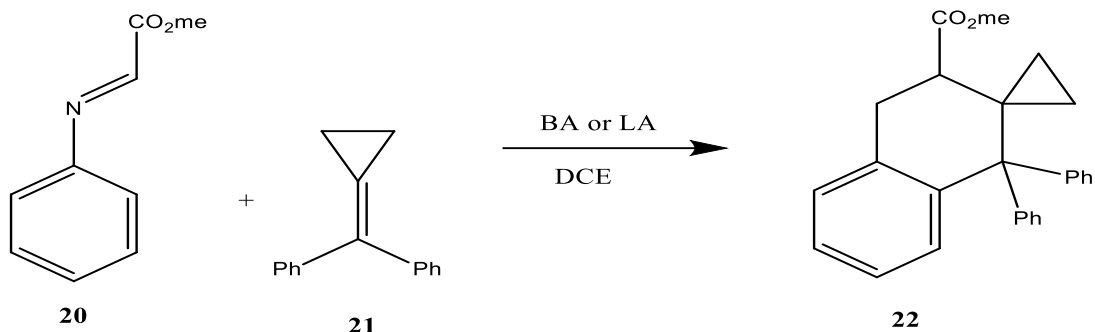
Scheme 3 : Four component Povarov reaction

In 1967, “Hagihara [10]” showed that quinoline derivatives could be synthesized utilizing dicobaltoctacarbonyl as a catalyst instead of $\text{BF}_3/\text{Et}_2\text{O}$. Remarkably, “Kobayashi and co-workers[11]” introduced Lanthanide (III) Triflates as excellent catalysts for three components of Povarov reaction between N- Aryl aldinies and Alkenes. According to “Xia and Lu [12]” they show that molecular iodine can also be used as an inexpensive and readily available catalyst for the one-pot reaction. This might be considered a pivotal advancement from the point of view of toxic metal-free catalyst development. According to “Muthushubramanian and co-workers[13]” reported an efficient, one-pot synthesis of the range of azaidole substituted quinolone derivatives by Povarov reaction in the good yields and diastereoselectivity using inexpensive and readily available SnCl_2 as a Lewis acid catalyst **scheme-4**.



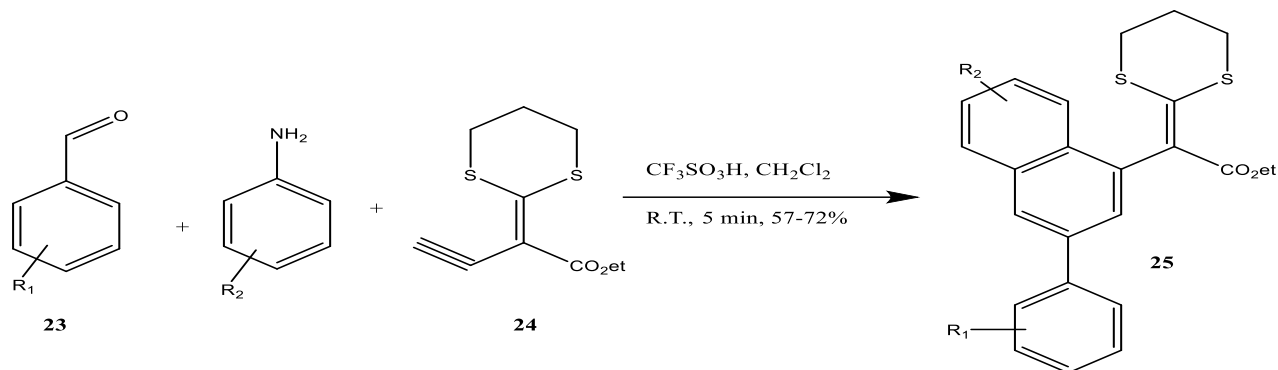
Scheme 4 : Bronsted acid catalyst Povarov reaction

“Zhao and Liu [14]” reported, that several bases are known to catalyze the Povarov reactions. For example, the three component reaction of aromatic aldehydes, anilines, and enynes to synthesis 4- substituted quinoline and the Lewis acid, $\text{BF}_3 \cdot \text{OEt}_2$ and BA, Trifluoromethane sulphonic acid (TfOH) catalyzed reactions of N- phenyl- o-methoxycarbonyl imine with MCP given THQ with good yield **scheme-5**.



Scheme : 5

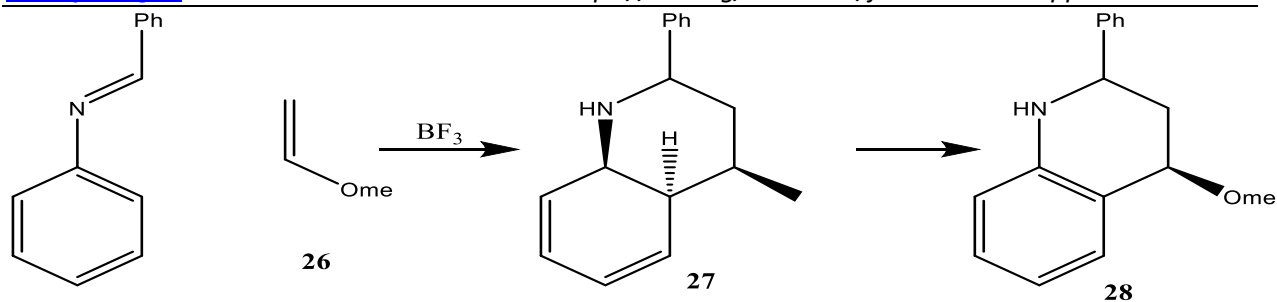
“Legros et.al [15]” reported the use of fluorinated alcohol, for example, trifluoroethanol (TFE) or hexafluoroisopropanol (HFIP) as both solvents as well as a catalyst for three-component Povarov reaction **scheme-6**.



Scheme : 6

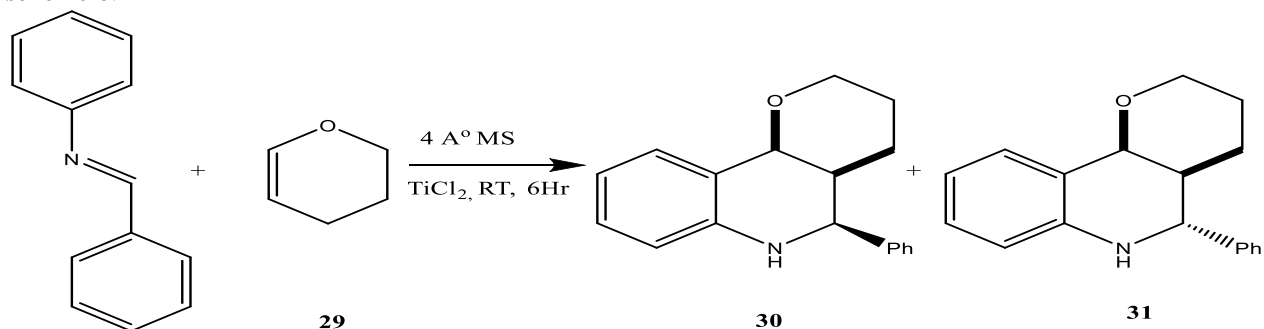
Very few theoretical studies have been devoted to the mechanism of the Povarov reaction “[16-20]”. Recently, with methyl vinyl ether and ethylene, yielding THQ was theoretically studied using DFT methods at the MPWB1K/6-311G (d, p) level of the theory.

“Sundharajan and co-worker [21]” have prepared diene (benzylidene aniline) from benzaldehyde and aniline for further reaction **scheme-7**.



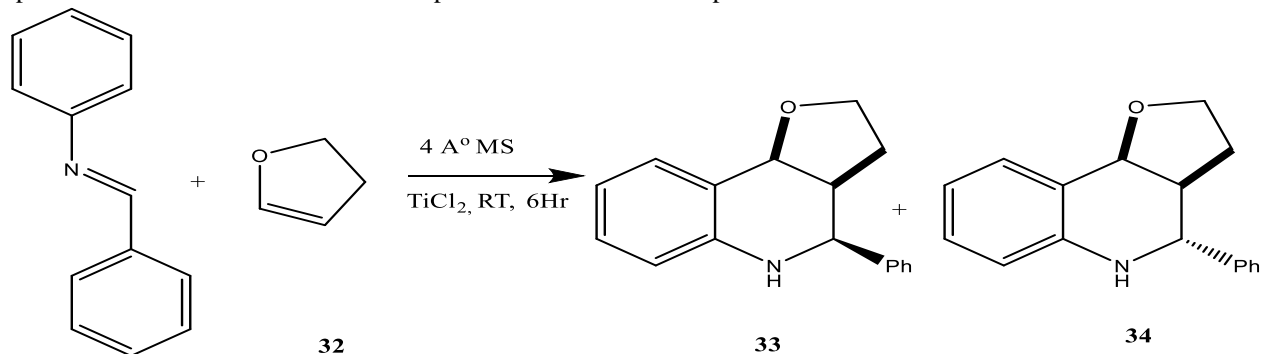
Scheme: 7

The dienophiles used were dihydrofuran, dihydropyran, ethyl vinyl ether, and cyclopentadiene. Firstly, in the reaction carried out in the condition of the presence of dichloromethane medium alone the product was obtained in poor yield. In the presence of pure toluene, there was no reaction, and the catalyst also decomposed over standing for a couple of hours. On switching to dichloromethane and toluene (1:1) mixture, the amount of conversion of the starting material improved by the enantiomeric excess waste was still comparatively low with dichloromethane: toluene (2:1) as a solvent mixture, however, we noted better yields and better enantiomeric excesses outlined in **scheme-8**.



Scheme: 8

“Sundharajan and co-workers[21]” also attempted a three-component coupling reaction in toluene by preparing 2-azadiene in situ (by adding amine and aldehydes) in the presence of dienophile. That addition of molecular sieves to the reaction mixture sometimes increases the enantiomeric excesses of the product formation. This may be due to the absorption of water molecules present in the medium or the formation of certain active species with the molecular sieves in the presence of the TiCl₂ complex outlined in **scheme-9**.

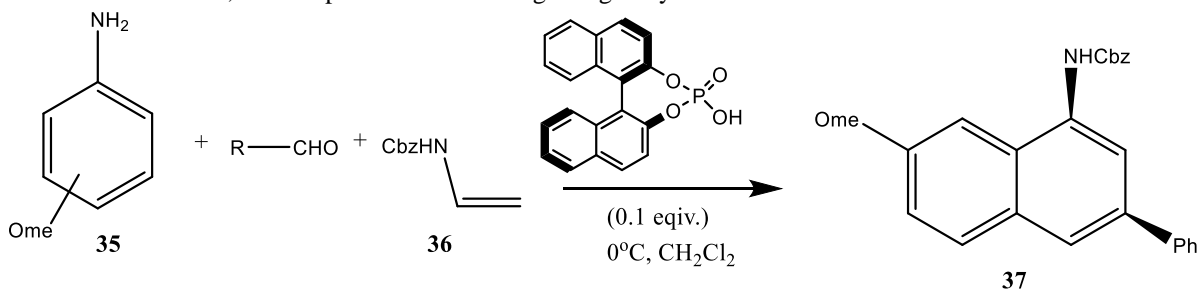


Scheme: 9

“Sundharajan and co-workers[21]” also studied, they tried to increase the % of yield by adding Indium Chloride to

the reaction mixture. The positive role of indium chloride in the Imino Diels-alder reaction has been reported earlier. In this reaction, the $TiCl_2$ complex has been activated by InCl then they were observed to increase the % of yield.

“Hue Liu and co-worker[22]” to develop the enantioselective (2,4-cis)-4-amino-2-alkyl(aryl)- 1,2,3,4-tetrahydroquinoline from Schiff base, Benzyl N-vinyl carbonate in the presence of a catalyst such as phosphoric acid, solvent dichloromethane, and temperature $0^\circ C$ and it given good yield outline in **scheme-10**.

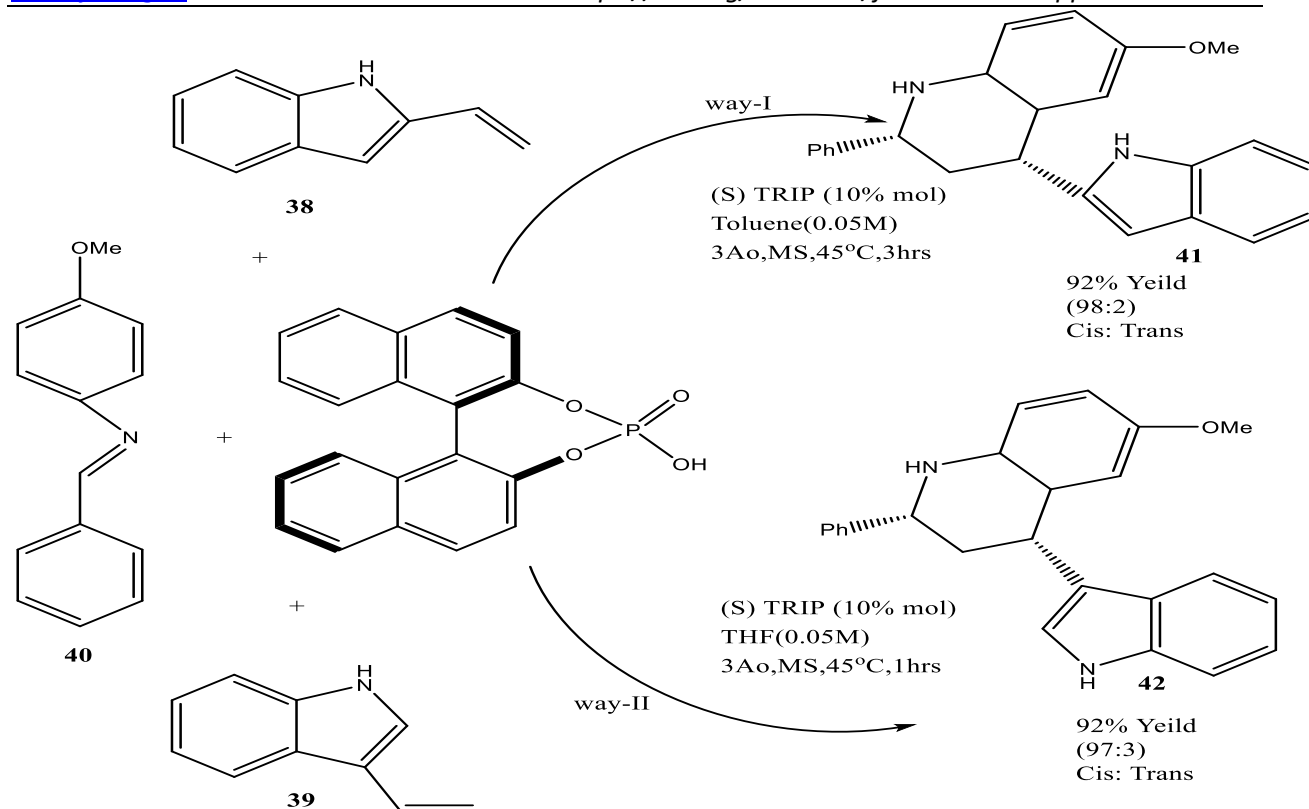


Scheme: 10

The scope of the enantioselective Bronsted acid-catalyzed three-component Povarov reaction was next examined.

They were observed, an unprecedented (IED) (4+2) cycloaddition “[23]” between N- aryl imine and double bond of 2 and 3 vinyl indoles envisaging the activation of imines by H-bond interaction with a chiral catalytic system. Optimized conditions derived from this screening entailed the use of (S)-TRIP as a catalyst “[24-25]”. Toluene as solvent, in the presence of $3A^\circ$ molecular sieves (MS) at $45^\circ C$, obtained very good yield. Giulia Bargozini and co-worker^{2have} as studied, the asymmetrical Povarov reaction of N- Aryl imine with 2 and 3 Vinyl indole has been developed using a chiral phosphoric acid (s) –TRIP as catalyst **scheme-11**.

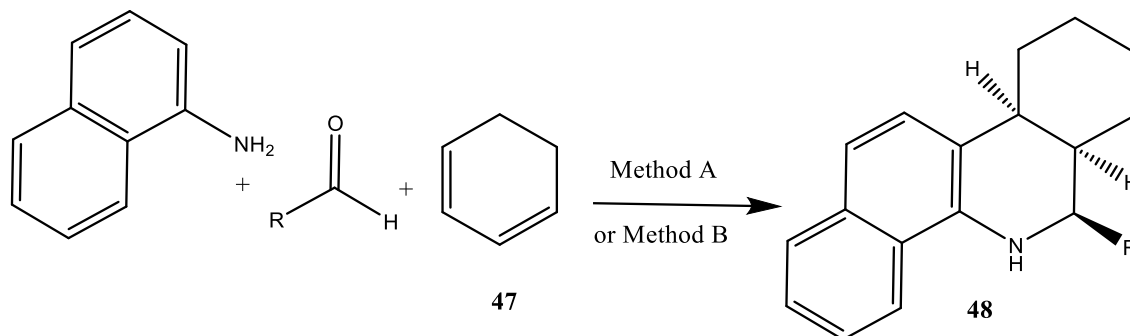
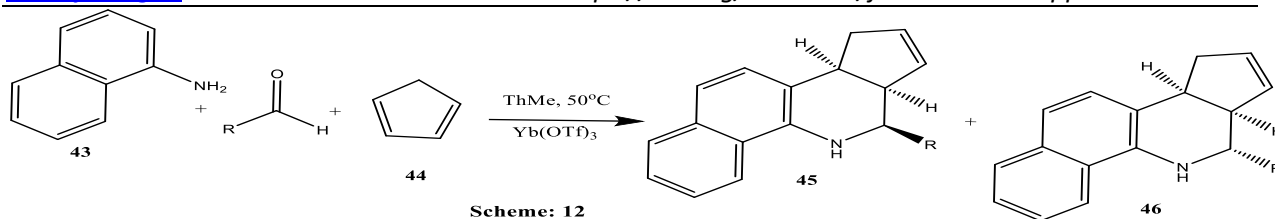
Furnishing the Povarov cyclo-adduct derived from imine is very good yield, as a single cis-diastereoisomer and with almost product enantioselective. Translation of these conditions to the reaction with 3-vinylindole was not possible.



Scheme: 11

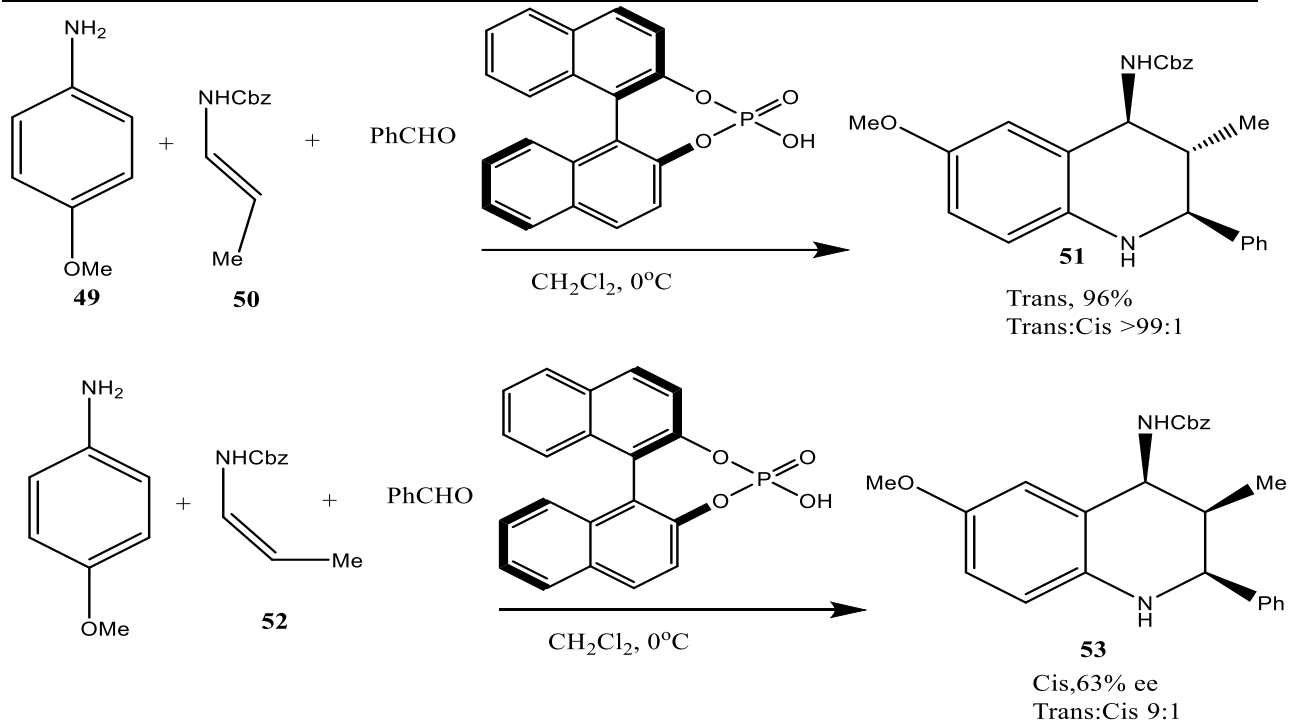
The scope of the catalytic enantioselective Povarov reaction of 4-methoxy aniline derived imines with 2 and 3- vinyl indoles. The Lewis acid “[27]” catalysts - AlCl₃ “[28]” ZnCl₂ “[29]” BF₃.OEt₂ “[30]” TiCl₄ “[31]” InCl₃ “[32]” ZrCl₄ “[33]” trifluoroacetic acid “[34]” p-TsOH “[35]” and HBF₄, lanthanide triflates “[36]”, Ln(OTf) or Sc(OTf) “[37]” CAN “[38]” used in reaction. In a recent study L-proline “[39]” protic acids “[40]” montmorillonite clay “[41]” and polymer-supported benzotriazole “[42]” have been reported to promote this reaction. In this case, quinoline and phenanthridine derivatives generated from one pot Povarov reaction, the addition of α amino naphthalene, aldehydes, cyclopentadiene, and 1,3 cyclohexadiene in the presence of Yb(OTf)₃ catalyst, Toluene or DCM as solvent and temperature.

“Emel and co-workers[42]” has been studied, the preparation of quinoline and phenanthridine derivatives from different methods, such as MS Technique, heating, distillations, etc. furthermore lanthanide triflate is stable in water and only a catalytic amount of the triflate is enough to complete these reactions. In this study, they have reported one-pot three component ytterbium (III) triflate catalytic Aza-Diels-alder (ADA) reaction under ultrasonic conditions. In the three component, ADA reaction, 2,3-dihydrofuran, and 3,4- dihydro-2H-pyran compounds have been extensively used, there are very limited examples of tetrahydroquinoline and hexahydrophenanthridine derivatives synthesized by ADA reactions of cyclopentadiene and 1,3- cyclohexadiene. The reaction was first explored by stirring a mixture of 1-naphthylamine, benzaldehyde, and cyclopentadiene with 10 mol % of ytterbium (III) triflate at room temperature in CH₃CN for 24 hours at that situation suitable product was not formed. After screening, solvents, and temperature conditions they are getting good yield product in toluene at reflux condition at 110°C under ultrasonic conditions outlined in the **scheme - 12 and scheme -13**.



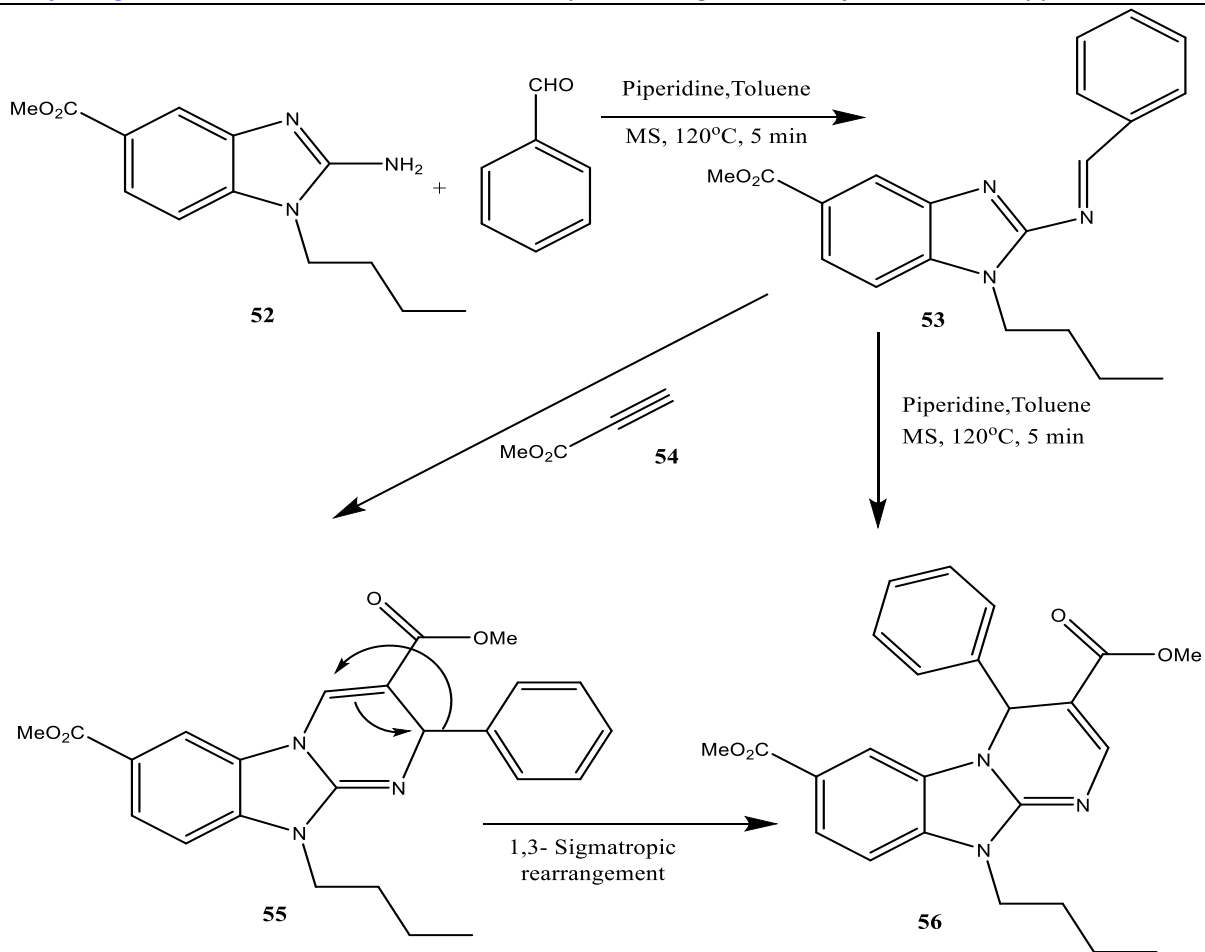
Conditions (Both scheme have same conditions): Method A: 1-naphthalene (1mmol), aromatic aldehydes (1 mmol), cyclopentadiene (3 mmol), 10 mol%, Yb(OTf)₃, reflux in Toluene at 110°C for 6 h. Method B: 1-naphthalene (1mmol), aromatic aldehydes (1 mmol), cyclopentadiene (3 mmol), 2 mol%, Yb(OTf)₃, Ultrasound in Toluene at 50°C for 40 min. “Guillaume and co-workers[43]” has been studied, A chiral phosphoric acid-catalyzed three-component Povarov reaction of aldehydes, anilines, and enecarbamates afforded cis-4-amino-2-aryl(alkyl)-1,2,3,4-tetrahydroquinolines in high yields with excellent diastereoselectivities (more than 95%) and almost complete enantioselectivities (up to more than 98%). For the first time, aliphatic aldehydes were used in the enantioselective Povarov reaction with β-substituted acyclic enecarbamates, 2,3,4-trisubstituted 1,2,3,4-tetrahydroquinolines with For three For contiguous For stereogenic For centers were For produced in For excellent din stereo - and enantioselectivities (87 to > 99%). A detailed study of the active catalytic species allowed us to reduce the catalyst loading from 10% to 0.5% with no deterioration of enantiomeric excess. In 2009, they reported the first example of a three-component phosphoric acid-catalyzed enantioselective Povarov reaction for the synthesis of 4-amino-1,2,3,4-tetrahydroquinolines

scheme-14



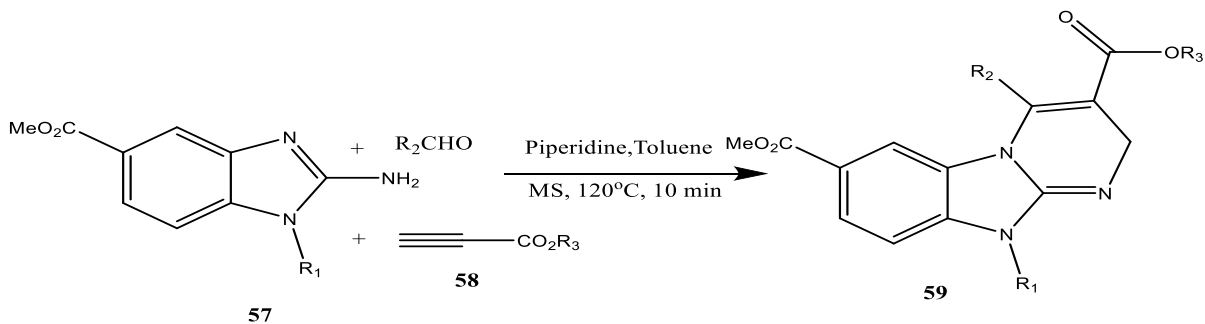
Scheme: 14

“Chih-Hau and co-workers [44]” has been discovered 4, 10-dihydropyridine [1,2a] benzimidazoles from base-catalyzed Povarov reaction of arylamines, aldehydes, electron-deficient dienophiles through [1, 3] sigmatropic rearrangement under microwave irradiation **scheme-15**.



Scheme 15

The scope of Povarov reaction:



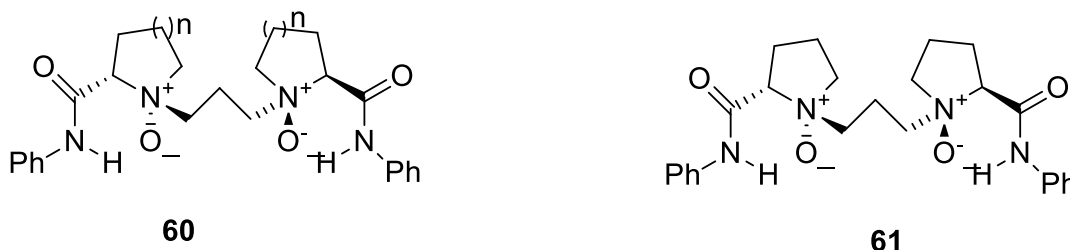
Scheme 16

“Feng and co-workers[45]” has been reported as the asymmetric synthesis of optically active tetrahydroquinoline derivatives with a quaternary stereocenter catalyzed by an N, N-dioxide-Sc(OTf)₃ complex in excellent yields and with good diastereoselectivities and enantioselectivities.

In 1996, “Ishitani and Kobayashi[46]” group have been developed the first catalytic asymmetric Povarov reaction with cyclopentadiene and vinyl ethers as dienophiles by using chiral binaphthol ytterbium complexes.

In 2006, “Akiyama and coworkers [47]” reported the reaction with vinyl ethers as dienophiles promoted by a chiral phosphoric acid. Later, enecarbamates and vinyl indoles were used as dienophiles in reactions with chiral phosphoric acids as catalysts by “Zhu and Masson’s group [47b] and Bernardi and Ricci’s [47c]” respectively.

In 2010, “Jacobsen and co-workers[47d]” has been developed an intramolecular Povarov reaction of vinyl ethers, enecarbamates, and enamides (dienophiles) by using strong Bronsted acids (Prolinol silyl ether). It has been reported, that benzaldehyde, O-hydroxyl aniline, styrene, and a catalytic amount of N, N-dioxide- Sc(OTf)₃ in the dichloromethane as solvent at 30°C. Following four chiral ligands (L) were selected for the preparation of a good catalyst.



L1- Ar= Ph, N=2

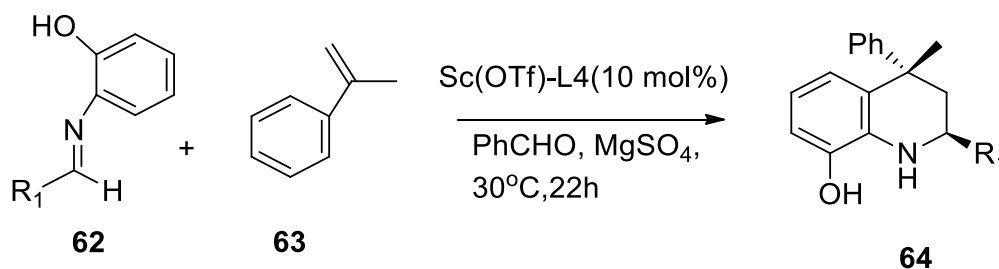
L4 – Ar =2,6-iPr₂C₆H₃

L2- Ar = 2,6-iPr₂C₆H₃,n=2

L3 – Ar =2,6-iPr₂C₆H₃,n=2

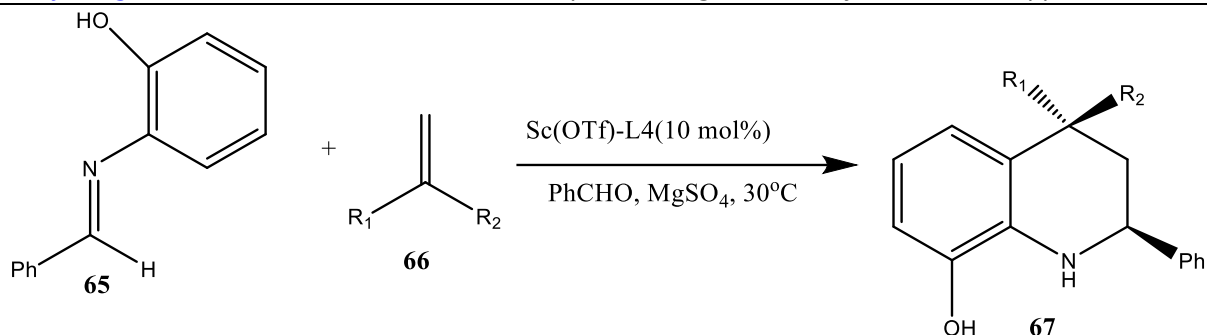
After Screening of the central metal ions for the formation of suitable catalyst [Mg(OTf)₂, Cu(OTf)₂, Yb(OTf)₃, Y(OTf)₃, La(OTf)₃, Sc(OTf)₃, Sc(OiPr)₃, Ce(OTf)₃, Pr(OTf)₃, and Nd(OTf)₃] they get the excellent yield by using Sc(OTf)₃-L1 experiments reaction. Then in the screening of ligands and solvent effect in the asymmetric Povarov reaction of N- aryl imine and α-methyl styrene, they were observed the L4 with CH₂Cl₂ give a good yield compared to other L1, L2, and L3 ligands and THF, CHCl₃, etc. solvents.

“Mingsheng and co-workers[48]” was observed that the possible cause of decomposition of imines in the presence of a Lewis acid. To decrease the decomposition of imine by adding benzaldehyde and MgSO₄, greatly improved the yield **scheme-17**.



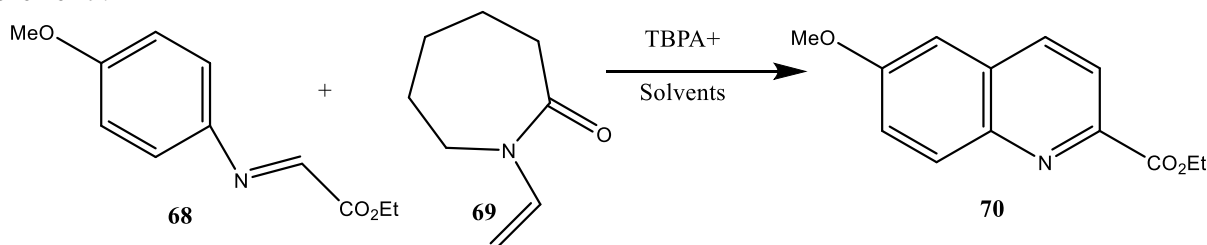
Scheme-17.

Both electron-rich and poor dienophiles were applied and resulted in excellent diastereoselectivities and enantioselectivities **scheme-18**.



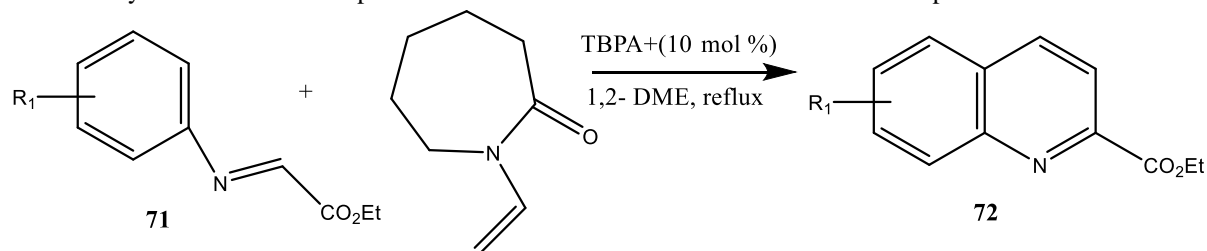
Scheme 18: The scope of dienophiles tolerated in the asymmetrical Povarov reaction

“Xiaodong and co-workers[49]” have been reported as preparation of quinolone-2- carboxylates from iminoethyl glycolate, N-vinyl amides in presence of TBPA⁺ catalyst (catalytic radical cation) in 1,2-dichloroethane as solvent **scheme-19**.



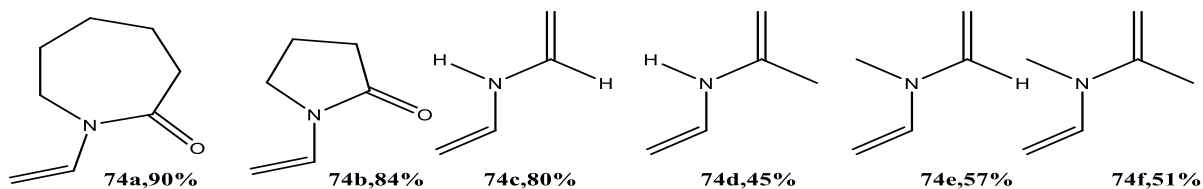
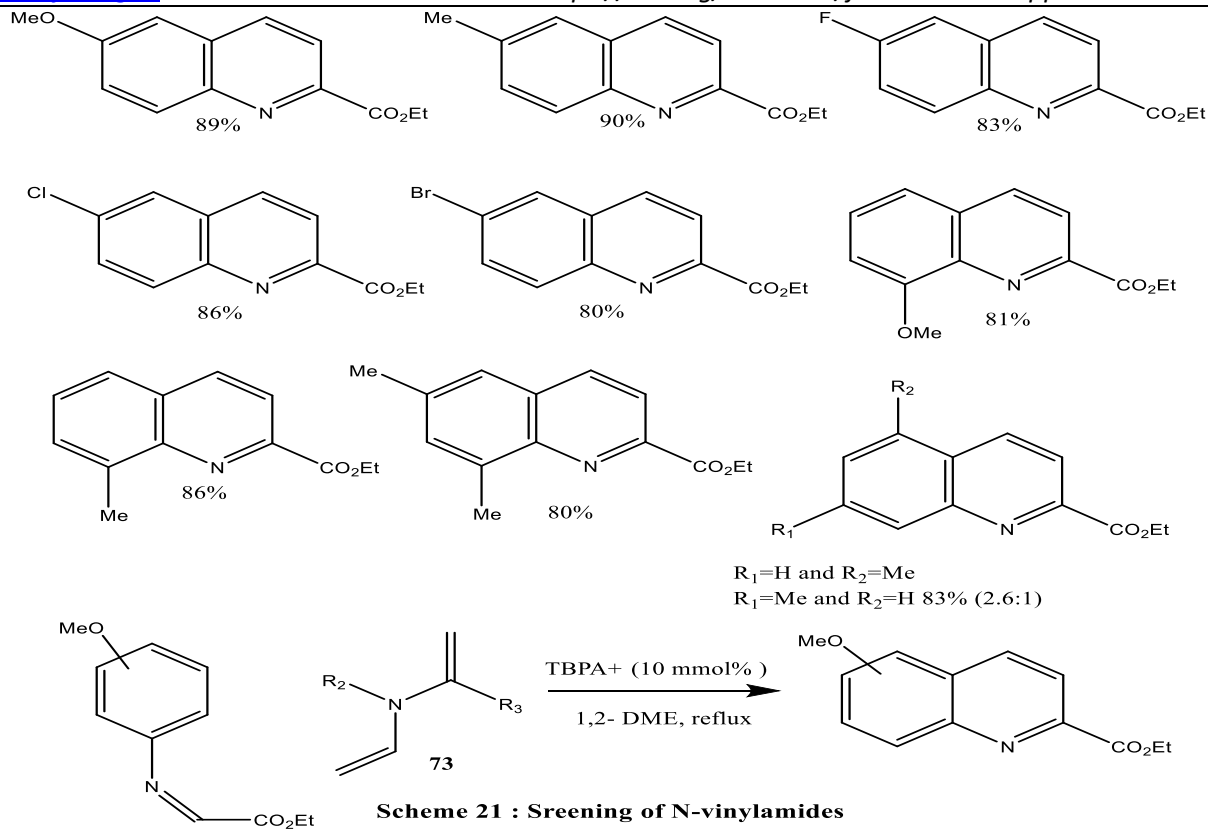
Scheme 19

After the screening of various solvents and reaction conditions gave a higher yield of the product in dichloromethane under refluxing conditions; the desired product could be obtained compared under argon conditions. They used several N-vinyl amides under the optimized reaction conditions to test the effect of dienophiles **scheme-20**.

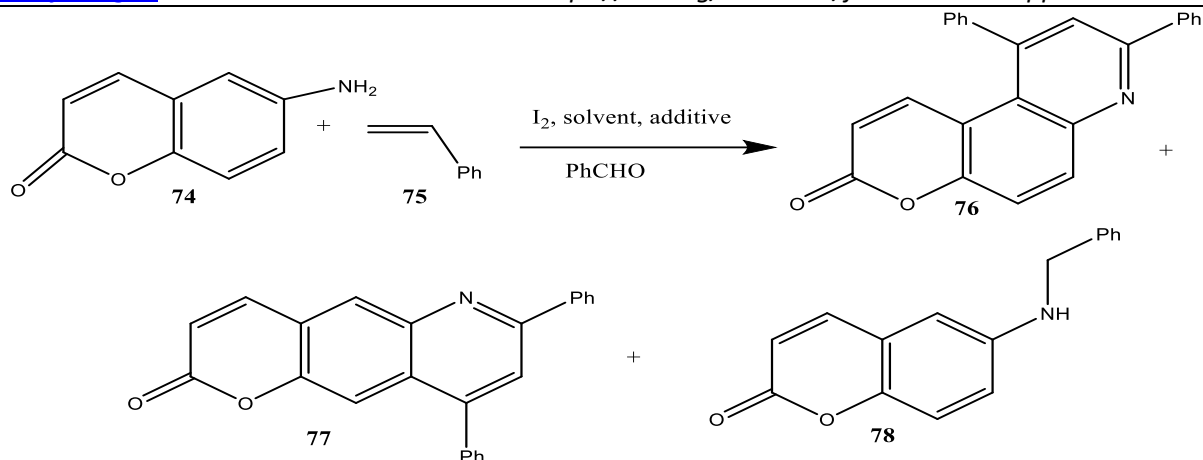


Scheme 20

Scope of reaction:

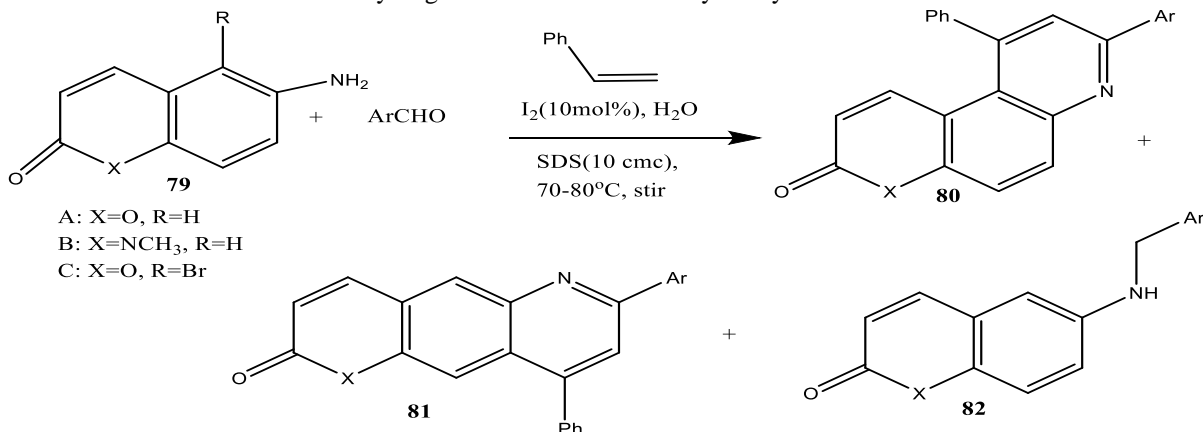


“Nemai and Sumanta [50]” reported a one-pot three components reaction between 6-aminocoumarin, benzaldehyde, and styrene under auto-tandem catalysis of iodine in aqueous medium **scheme-22**.



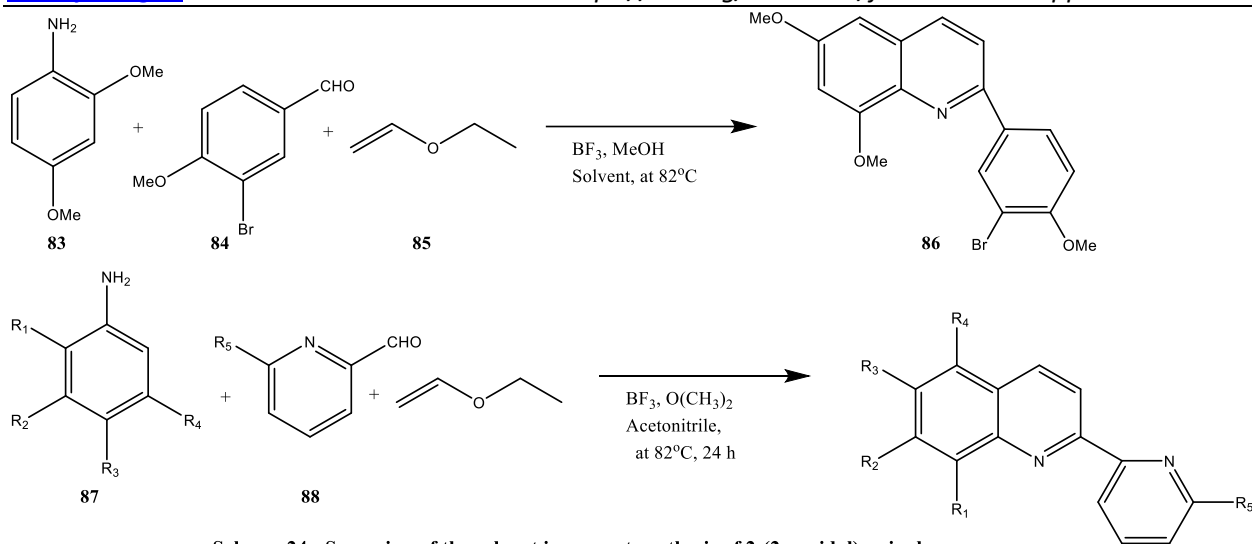
Scheme 22: Screening of the solvent, catalyst and additives

Cascade Povarov – hydrogen transfer reaction catalyzed by I_2 outlined in **scheme-23**.



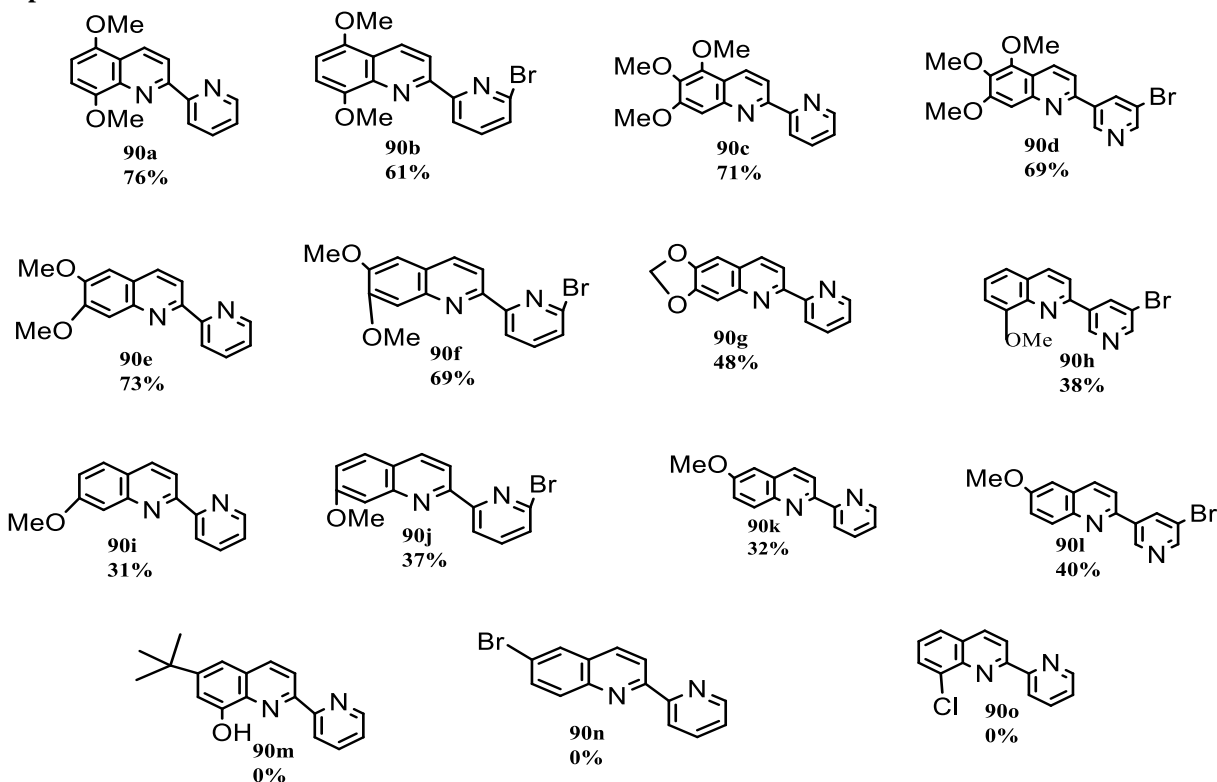
Scheme 23

“Carmino and co-workers [51]” reported a synthesis of 2-(2-pyridyl) quinolones from three-component Povarov reaction, aromatic aldehyde, anilines, and ethyl vinyl ether under the boron trifluoride methyl etherate ($BF_3 \cdot O(CH_3)_2$) acid catalysis. Best yields were obtained with di- and tri-substituted aniline-bearing electron-donating groups. In general, all the reactions proceeded well affording a wide range of pyridyl quinoline in moderate to good yields.

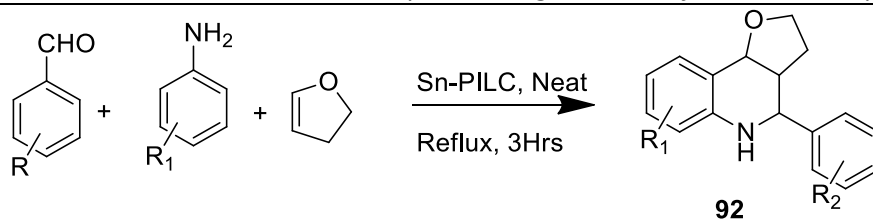


Scheme 24 : Screening of the solvent in one pot synthesis of 2-(2-pyridyl) quinolones

Scope of reaction:

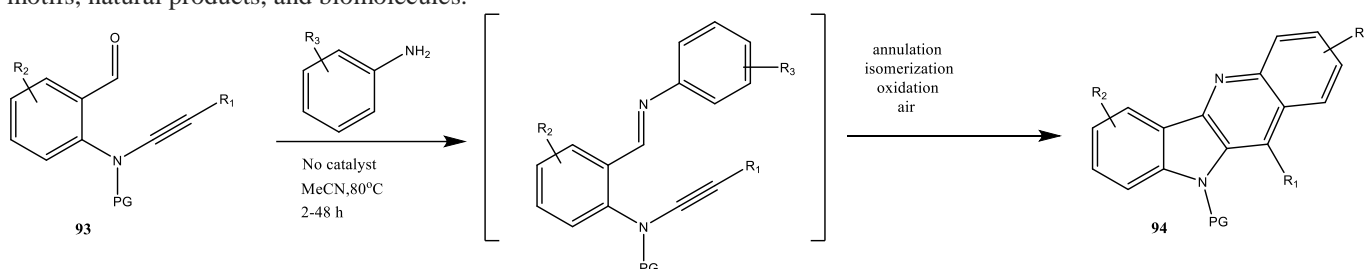


“Megha, Shivaji, and Mazahar [52]” were carried out the Povarov’s inverse-electron-demand hetero Diels–Alder one-pot three components reaction of aromatic aldehyde, aromatic amine with DHF by using Sn-PILC as a catalyst under a neat condition **Scheme-25** which may helpful to society to get pharmacologically more active compounds.



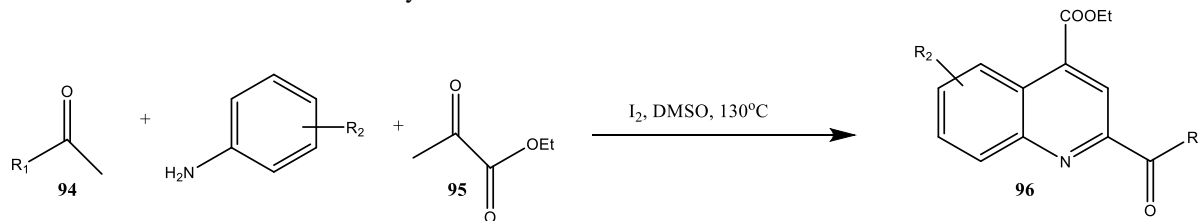
Scheme-25

Zhang et al. [53] reported a catalyst-free and regioselectivity Povarov reaction of formyl-ynamides with anilines for the rapid and practical synthesis of a wide range of quindolines. **Scheme-26** applies to synthesize fused polycyclic motifs, natural products, and biomolecules.



Scheme 26

Gao et al. [54] developed an Iodine-catalyzed Povarov-type reaction of methyl ketones, arylamines, and α -ketoesters. This reaction utilizes a catalytic amount of HI coproduct as a promoter for the synthesis of broad-range quinolones. **Scheme-27** is a new form of reactivity for the Povarov reaction.



Scheme 27

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Conflict of interest: Authors state no conflict of interest.

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