CHAPTER IV

A COLLECTIVE LABORATORY STUDIES ON ONE POT MULTI-COMPONENT SYNTHESIS OF A FEW VARIETIES OF HETEROCYCLIC COMPOUNDS FOLLOWING GREENER APPROACH USING RICE HUSK BASED GREENER CATALYST

IV. 1 Introduction

Aromatic heterocyclic compounds always have a special importance over other class of organic compounds from the very fast age of its discovery. They got the importance when scientists observed their biological activity in various cell related problems and its ability to eradicate viral, fungal and microbial activities. They especially act as drugs for their efficiency in curing various diseases and health problems. They act as inhibitor in various disordered enzyme activities which are generally responsible for the particular diseases in animals and as well as human beings. There are various kinds of aromatic compounds reported previously in literature and among them few types of bicyclic and tricyclic aromatic compounds have got the keen interest from the rearchers due to its significant role in medicinal chemistry. Due to the low natural abundance of some kinds of heterocyclic compounds and for the future interest of new drug discovery, scientists are always in work to invent new types of heterocyclic molecules. Coumarin derivatives, hexahydroqunolines derivatives, and tetrahydroterazoloqunazolines, in this context are observed as an important class of heterocyclic compounds which contain active molecular parts to show biological activities. Coumarins have a basic flavinoid like skeleton which

constitutes a natural privileged scaffold and their analogues have significant application in functional material chemistry for their excellent fluorescent properties and thus used up as molecular probes in cell biology research.[1-2] Dihydro-dichromeno-pyridine-6,8-dione derivatives also contain coumarin scaffolds which are considered as one of the important fused ring heterocyclic bioactive compounds and thus a varity of scientific research have been made towards the targeted synthesis coumarin analogues to find their significant applications in the field of medicinal chemistry. Coumarins can be derived also from natural resources and scaffold can be used extensively for the preparation of derivatives and their derivatives have no doubt a broad range of biological activities such as anti-fungal,[3] anti-inflammatory,[4] anti-tubercular activities,[5] antiviral,[6] anticancer,[7] etc. A number of fused ring coumarin derivatives have been obtained by following conventional techniques using hazardous chemicals [8] and thus a new sustainable development in synthetic procedure is needed for the synthesis of dihydro-dichromeno-pyridine-6,8-dione derivatives as our targeted product.

Another important class of heterocyclic compound is fused ring tetrazole derivatives and tetrazole fused bicyclo aromatic compounds

have prominent biological activity in various biological aspect. Tetrahydrotetrazolo[1,5-*a*] quinazolinones falls in the category of fused ring tetrazole derivatives and they are structurally analogous with tetrazolopyrimidines. Tetrazole fused pyrimidines have broad range of biological properties, including antimicrobial,[9] antituberculosis[10] and antidepressant,[11] activities. There are a few examples of methods reported for the synthesis of tetrazolopyrimidines which involve initial synthesis of base catalysed chalcones followed by cyclocondensation reaction with 5-aminotetrazole. Wang and co-workers had reported also the synthesis of dihydrotetrazolo[1,5-*a*]pyrimidines and tetrahydrotetrazolo[1,5-a] quinazolinones catalysed via heavy metal ion Hg^{2+} [12] moreover a variety of catalysts like Iodine,[13] TBBDA,[14] [bmim+][BF_4^-],[15] acetic acid,[16] di-isopropylammonium trifluoroacetate [17] had been used to mediate the reaction. It remains a challenging task to develop a greener route for the synthesis of a varity of tetrahydrotetrazolo[1,5-a]quinazolinones and isolation and purification of final products and therefore, we intended to develop an sustainable and convenient synthetic route for the synthesis of tetrahydrotetrazolo[1,5-*a*]quinazolinones.

Quinolines and substituted quinolines and quinolinones are also important class of heterocycles which have a wide variety of pharmaceutical and agrochemical activities and they are found as prominent building blocks in various natural products and possess considerable interest due to their broad range of bio-activities such as antibacterial, antifungal, antioxidant, anticancer, anticonvulsant, and antiviral activity [18-22]. Substituted quinolines, quinolinones, tetrahydroquinolines, hexahydroquinolines serve as chemotherapeutic agents also [23-25] and many heterocyclic [26] compounds containing the quinoline nucleus display anti-inflammatory activity and they serve as antagonist inhibitors [27]. Quinolines with 1,4-Dihydropyridine (DHP) nucleus have been found to be efficient in cardiovascular diseases as calcium channel blockers also [28-29]. Due to these collective importances many recent research works are still on progress considering this heterocyclic motif [30-31]. 2,4-diarylhexahydro-quinoline-5-ones in this regard got our interest and it was observed that several homogeneous and heterogeneous catalysts have been employed for their synthesis. A number of methods have been reported such as $HClO_4$-SiO_2, [32] ionic liquid [33], DMF [34], microwave irradiation,[35] but, however, for the synthesis of 2,4-diaryl

hexahydroquinoline-5-ones sustainable and greener procedures have not applied before for the future environmental aspect of large scale industrial synthesis.

One pot multi-component reactions (MCRs) can also give strong support by following the basic principles of "Green Chemistry" for the synthesis of those three types of heterocycles mentioned above. And one-pot MCRs are considered as sustainable technique for making the whole synthetic process smart, energy saving and time consuming. A large number of complex molecules have been synthesized by one-pot MCRs and there exist a considerable importance when heterogeneous catalyst additionally selected excluding the concept of multistep method. Keeping the catalytic activity in one side, heterogeneous catalysts have more importance over homogeneous one in this regard because of easy separation and recovery from the reaction mixture and also for their active surface area where the reaction is conceived to be happened. [36] There are so many reported heterogeneous catalysts developed for the successful synthesis of various multi-component reactions but the use of natural resources as heterogeneous catalyst have attracted us very much and we considered rice husk as prominent greener solid support for catalysis. Rice husk is very common agricultural by-product highly

abundant in south asian countries. It contains cellulose, hemicellulose, lignocellulosic material along with high silica content. [37-38] It is an agricultural waste material and has utility in commercial purpose such as production of cattle food, rice-bran oil etc. A few characteristics like light weight, high external surface area and porosity, economic advantage, non-toxicity, high abundance, and bio-degradability have attracted us to use it as a good bio-derived heterogeneous catalyst for the synthesis of heterocyclic compounds in a suitable convenient manner.[39] Here in this work, we used up the rice husk based heterogeneous catalyst and report the synthesis of dihydro-dichromeno-pyridine-6,8-dione, tetrahydrotetrazolo[5,1-b]quinazolinone and 2,4-diaryl hexahydroquinoline-5-one derivatives using aromatic aldehydes as primary reactant using rice husk based greener catalyst.

IV.2 1,4-dihydropyridine

1,4-dihydropyridines are a class of heterocyclic compound having low molecular weight having both commercial and biolological importance. In 1882, the synthesis of a 1,4-dihydropyridines are three component cyclocondensation reaction of acetoacetic ester, aldehyde and ammonia and after that there several methods of synthesis of 1,4-dihydropyridine

skeleton are innovated by researchers using various novel catalysts (**Figure IV.1**).[40]

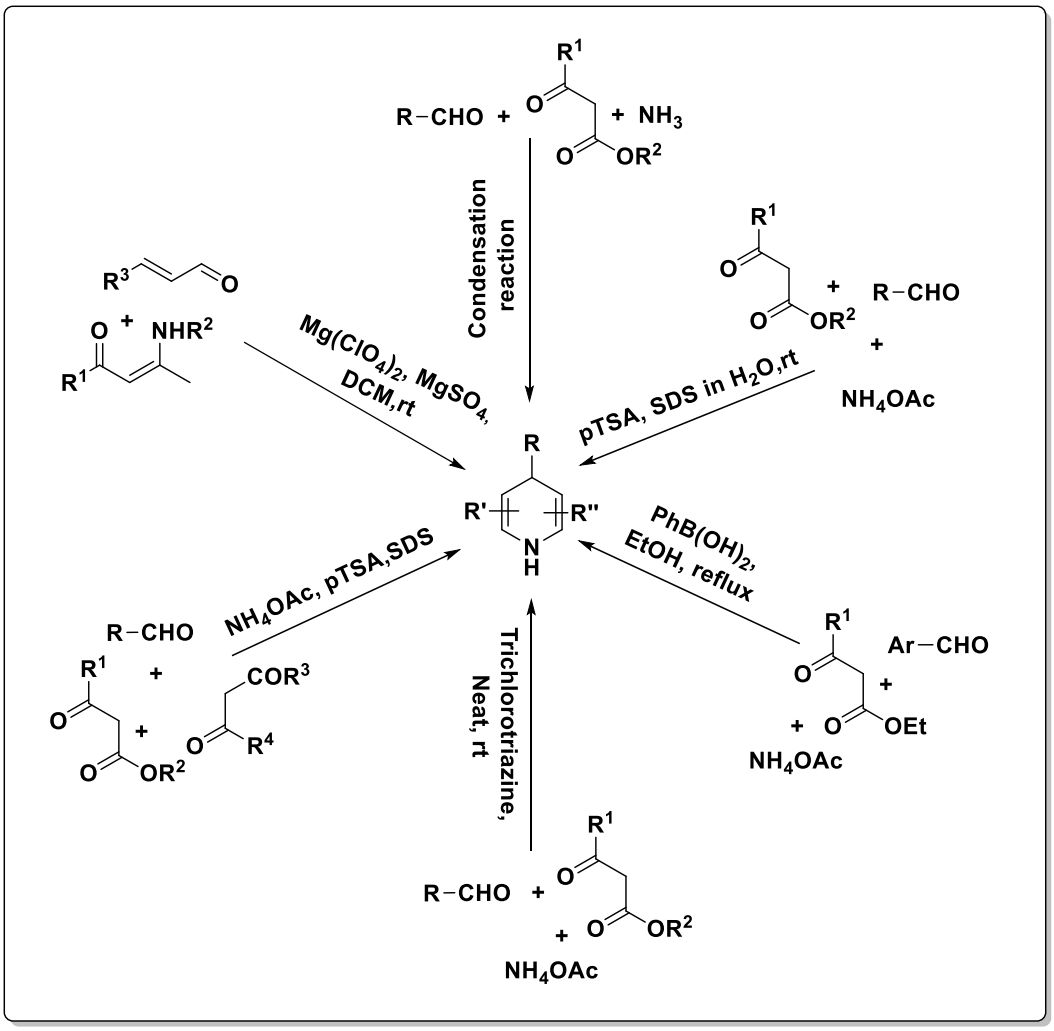


Figure IV. 1 Diverse synthetic routes for the synthesis of 1,4-dihydropyridine structures

Dihydro-chromeno-pyridines are important class of heterocyclic compounds containing a 1,4-dihydropyridine ring fused with chromene moiety. They are treated as polycyclic 1,4-dihydropyridines and as they also belongs to the class of 1,4-dihydropyridine family they have a broad

range of biological importance due to the presence of both dihydropyridine ring and fused chromene ring in it.[41-42] Dihydro-chromeno-pyridines may contain two chromene rings fused with 1,4-dihydropyridine ring or it may contain one chromene ring fused with 1,4-dihydropyridine ring. Inspite of having several synthetic procedures of skeletons of 1,4-dihydropyridines there are few reported synthetic procedure for the synthesis of dihydro-chromeno-pyridines skeleton using various catalysts.

IV.3 Biological importance of 1,4-dihydropyridines and dihyro-chromeno-pyridines

Due to the presence of both chromene moiety and dihydropyridine rings these dihydro-chromeno-pyridine molecules have both biological and pharmaceutical importance.(Figure IV.2) Due to the presence of two bioactive chromene and dihydropyridine moieties these types of bioactive compounds largely exhibit diverse activities such as antimicrobial, anticancer, antitumor, antimalarial, and antidiarrheal effects.[43-54]

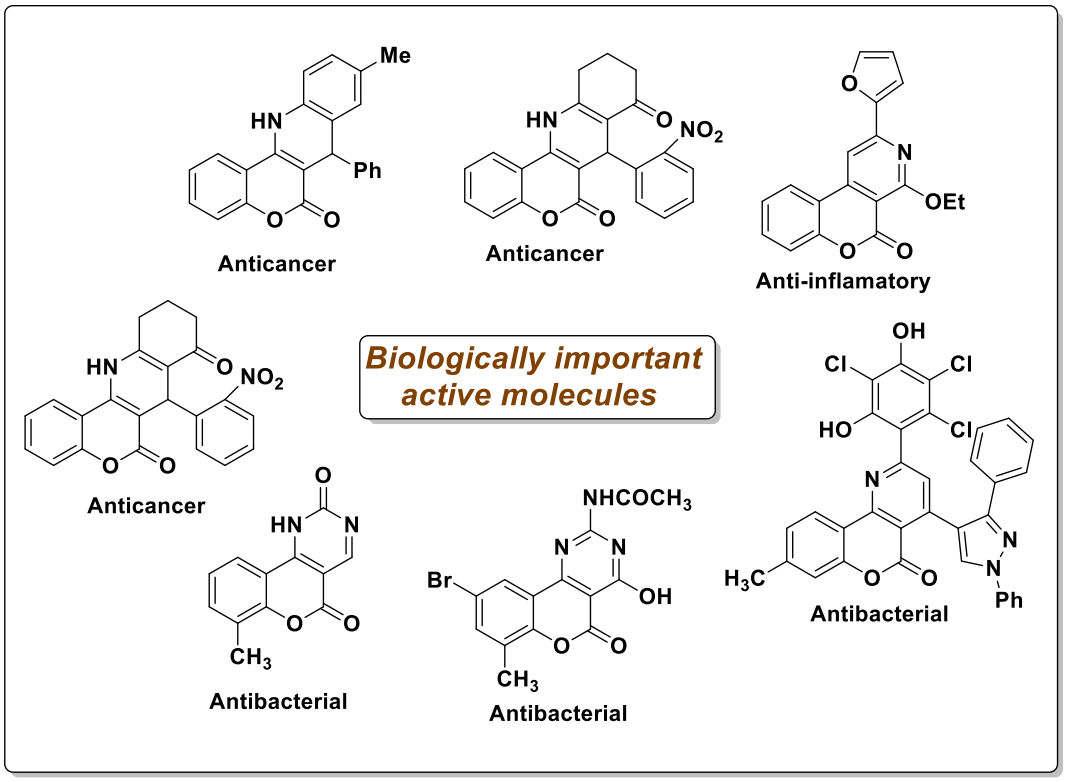
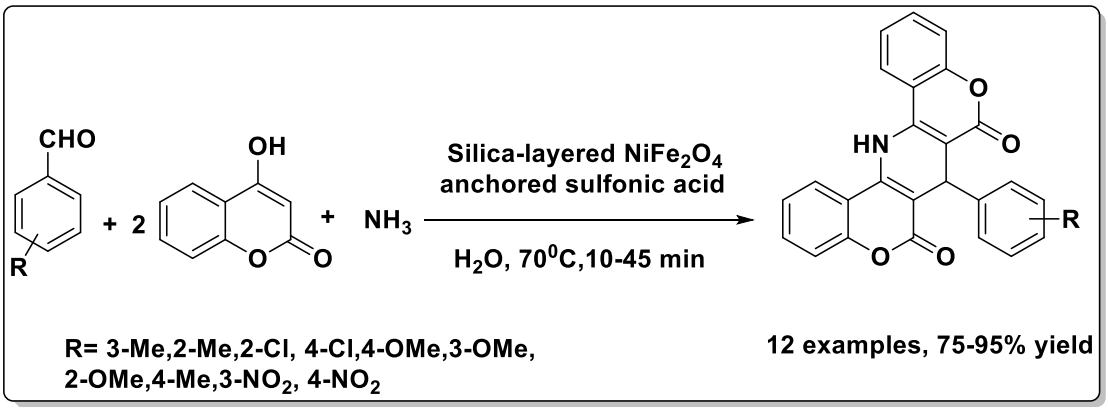


Figure IV.2 Some important pharmaceutically active drug molecule

By doing studies on works in various journals related to dihydropyridines, chromes and chromenopyridines and their derivatives and taking biological importances of dihydropyridines, chromes and chromenopyridines and their derivatives in mind, in this following part of the Chapter IV, it has been focused on the dihydro-dichromeno-pyridine-6,8-diones derivatives in a new and convenient manner using cheap laboratory chemicals.

IV.4 Previous works on Synthesis of dihydro-dichromeno-pyridine-6,8-diones derivatives

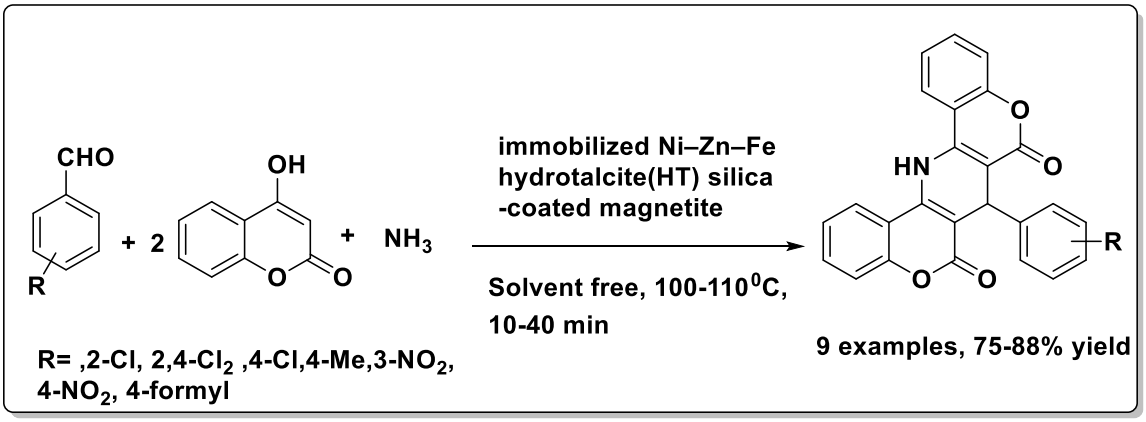
In 2017, Zeynizadeh *et al.* reported the synthesis of dihydro-dichromeno-pyridine-6,8-diones derivatives via one-pot condensation reaction of 1,3-diketones (ethyl acetoacetate or 4-hydroxycoumarin), aromatic aldehydes and aqueous ammonia in H_2O (70^0C) as a green solvent by using silica-layered nickel ferrite, ($NiFe_2O_4$@SiO_2@SO_3H) with excellent yield. (**Scheme IV.1**). [55]



Scheme IV.1 One pot synthesis of dihydro-dichromeno-pyridine-6,8-diones derivatives Zeynizadeh *et al.*

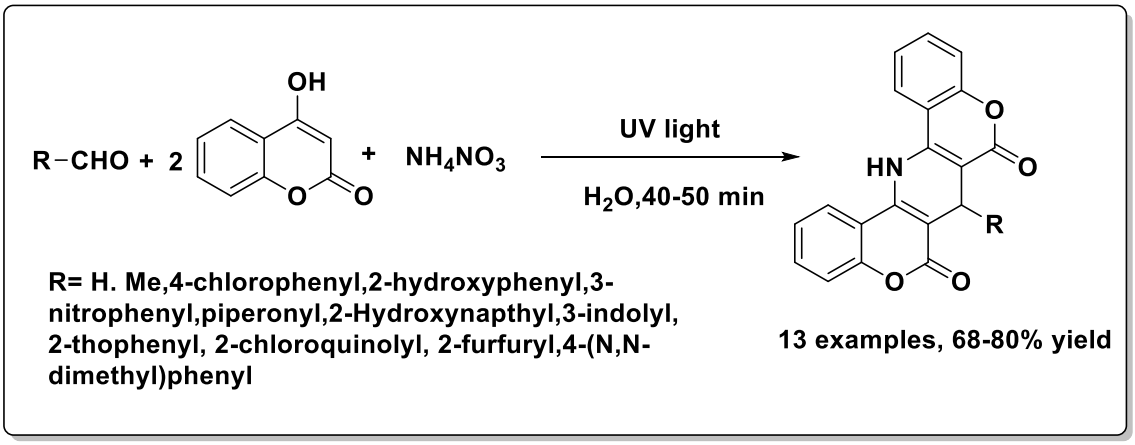
In 2019, Gilanizadeh *et al*. had reported an efcient ecofriendly approach has been developed for one-pot multicomponent synthesis of dihydro-dichromeno-pyridine-6,8-diones derivatives by Tandem condensation of aromatic aldehydes, 4-hydroxycoumarin, and

ammonium acetate by using heterogeneous Fe_3O_4@SiO_2@Ni–Zn–Fe hydrotalcite catalyst under solvent-free conditions (**Scheme IV.2**). [56]



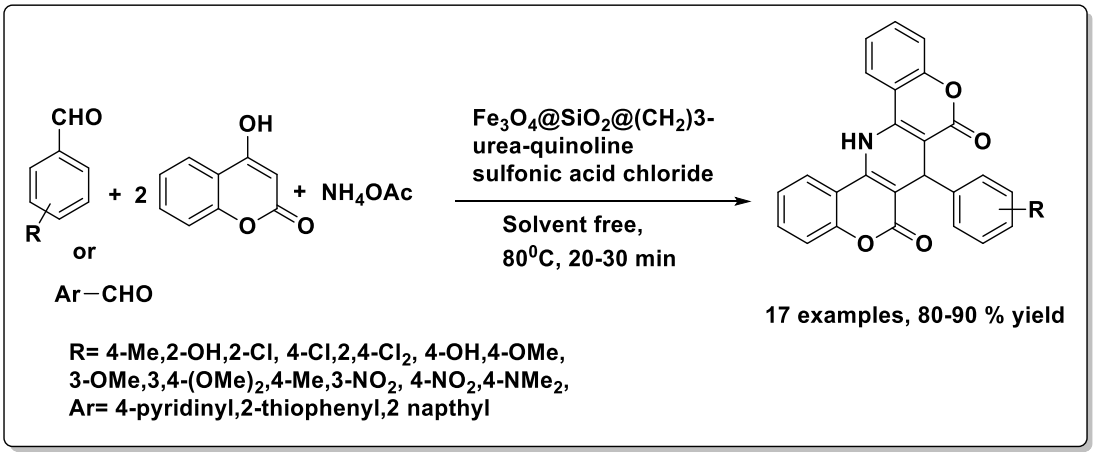
Scheme IV.2 One pot synthesis of dihydro-dichromeno-pyridine-6,8-diones derivatives Gilanizadeh *et al*.

In 2004, Kidwai *et al*. reported an ecofriendly approach for one-pot multicomponent synthesis of fused dihydro-dichromeno-pyridine-6,8-dione derivatives by condensation of aromatic aldehydes, 4-hydroxycoumarin, and ammonium acetate using UV light in presence of water solvent with considerable good product yield (**Scheme IV.3**). [57]



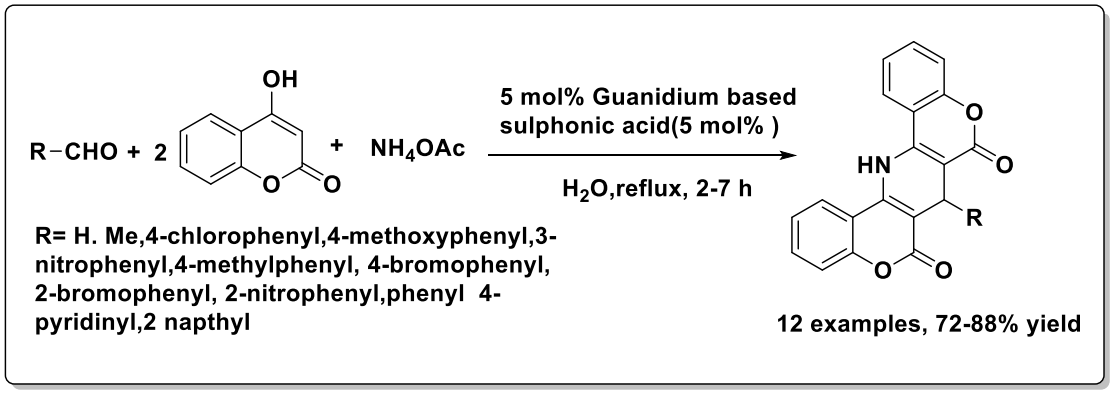
Scheme IV.3 One pot synthesis of dihydro-dichromeno-pyridine-6,8-diones derivatives Kidwai *et al.*

In 2020, Saffarian *et al*. has reported a synthetic method of dihydro-dichromeno-pyridine-6,8-dione derivatives by using Fe_3O_4@SiO_2@$(CH_2)_3$-urea-quinoline sulfonic acid chloride, as nanomagnetic catalyst bearing under solvent free condition at 80^0C temperature with reasonable yield (**Scheme IV.4**). [58]



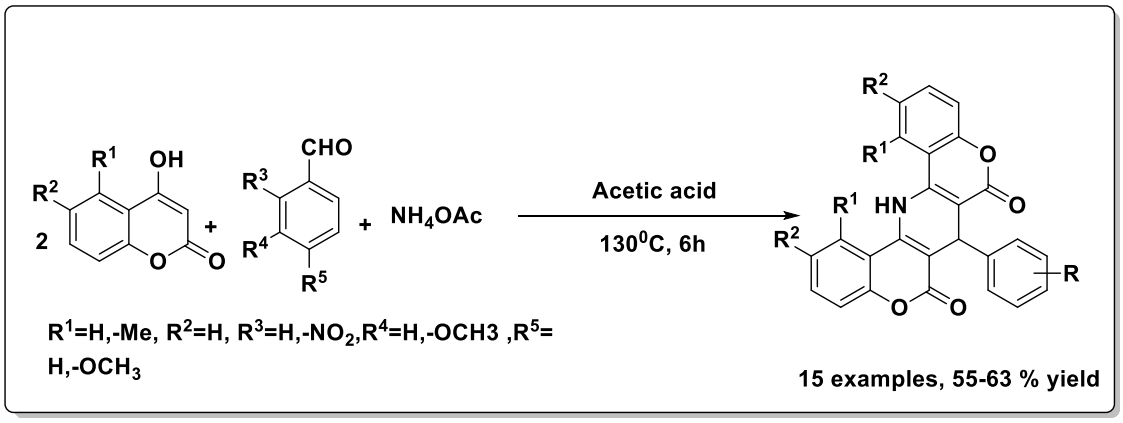
Scheme IV.4 One pot synthesis of dihydro-dichromeno-pyridine-6,8-diones derivatives Saffarian *et al.*

In 2016, Shaabani *et al*. reported a synthetic protocol for the synthesis of dihydro-dichromeno-pyridine-6,8-dione scaffolds with reasonable yield by using guanidinium-based sulfonic acid as a Brønsted acid as well as organocatalyst in water medium under reflux condition (**Scheme IV.5**). [59]



Scheme IV.5 One pot synthesis of dihydro-dichromeno-pyridine-6,8-diones derivatives Shaabani *et al*.

In 2004, Brahmbhatt *et al*. reported a synthetic protocol for the synthesis of dihydro-dichromeno-pyridine-6,8-diones with reasonable yield by using acetic acid as a Brønsted acid as well as organocatalyst as well as solvent at 130^0C temperature (**Scheme IV.6**). [60]



Scheme IV.6 One pot synthesis of dihydro-dichromeno-pyridine-6,8-diones derivatives Brahmbhatt *et al.*

IV.5 Tetrazole

Tetrazoles are a class of synthetic organic heterocyclic compound consisting five membered ring containing four nitrogen atoms and one carbon atoms. The first preparation of tetrazole was carried out from HCN and HN_3. There have different types of tetrazole depending upon

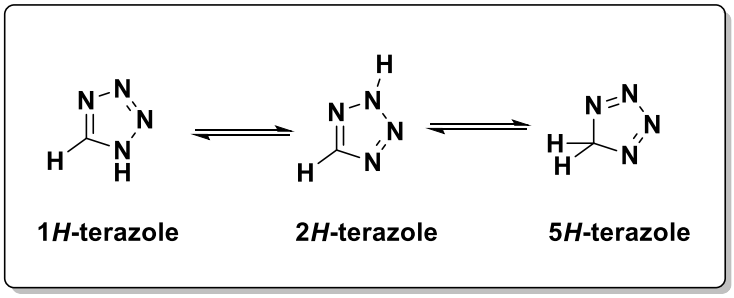


Figure IV. 3 Structures of 3 types of tatumeric tetrazoles

the position of the double bond and the presence of substitution on Carban atom such as 1*H*,2*H*,3*H*-tetrazole, aminotertazoles, thiotetrazole

and several synthetic methods of tetrazole skeletons are reported (**Figure IV. 3, Figure IV. 4**)

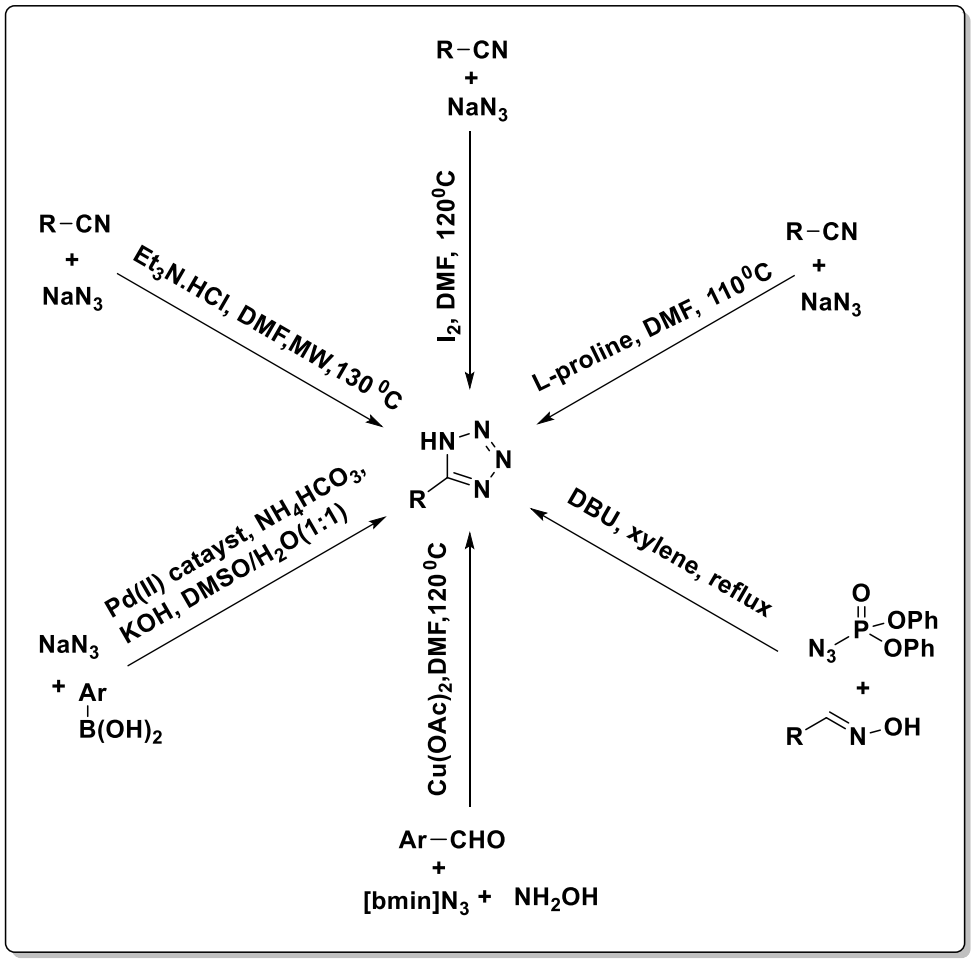


Figure IV. 4 Diverse synthetic routes for the synthesis of 1,4-dihydropyridine structures

IV.6 Quinazolinone

Quinazolinones are generally oxidized derivatives of quinazolines and they are classified into five categories based on the substitution

patterns of the ring system (**Figure IV.5**). According to literature 4(3*H*)-quinazolinones are most abundant as natural products and 2(1*H*)-quinazolinones are predominantly a product of benzamides with nitriles.[62] In the most common approach for the synthesis of quinazolinone compounds 2-aminobenzoic acid is used as a precursor. There are other methods reported for the synthesis of various types of quinazolinones below. (**Figure IV.6**)

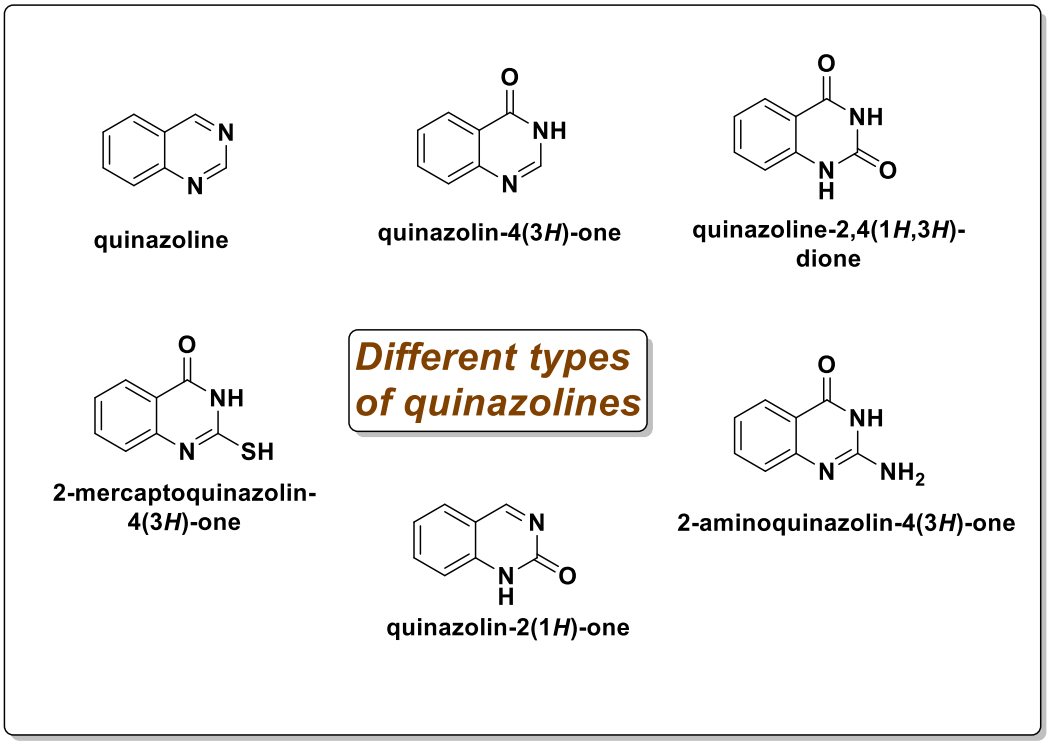


Figure IV.5 Different types of quinazoline scaffolds

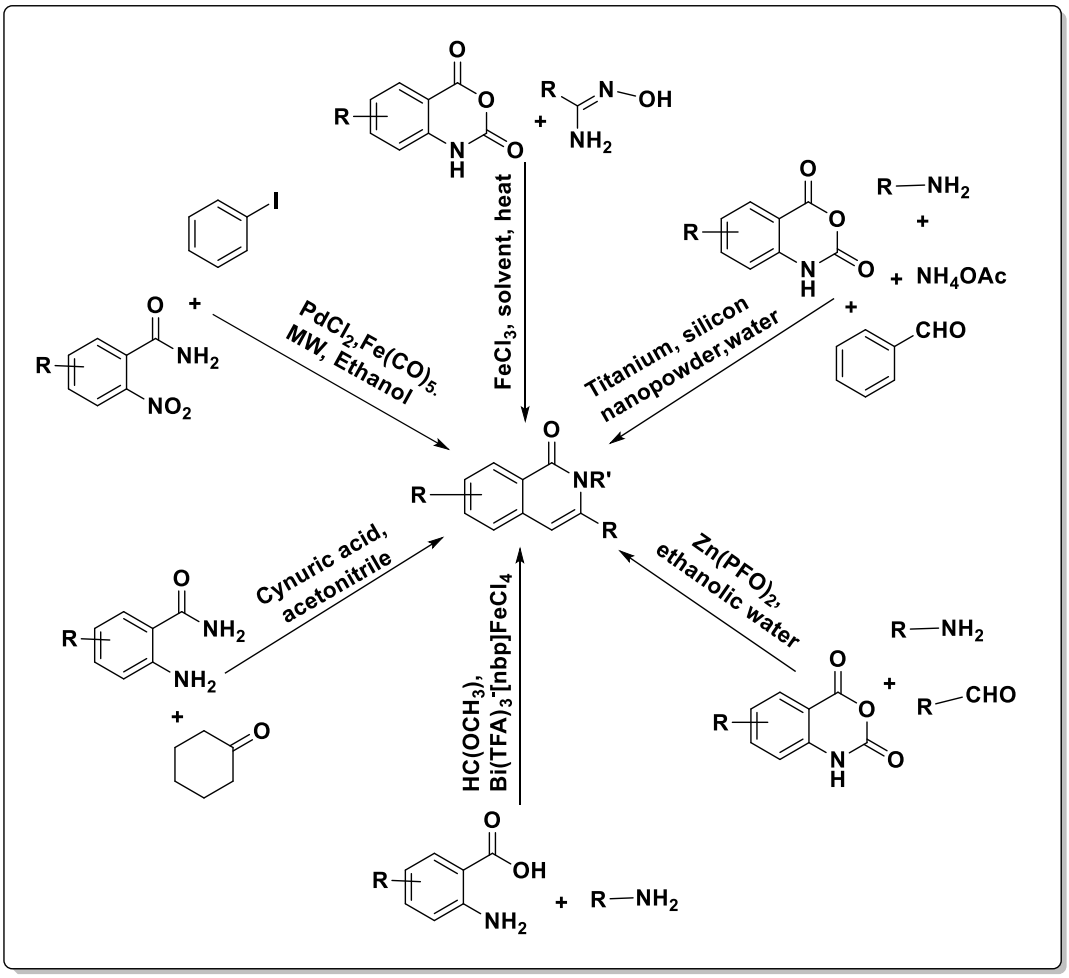


Figure IV.6 Different synthetic routes of quinazolinone skeleton

IV.7 Biological importance of tetrazole and quinazolinone derivatives

Tetrazoles have a broad rang of biological activities such as antibacterial, antifungal, anticancer, analgesic, anti-inflamatory, anti-diabetic, antitubercular activities.[63-69] Quinazolinone moiety is a building block for approximately naturally occurring alkaloids and quinazolinone derivatives have attracted significant attention due to their diverse pharmacological activities such as antimalarial, antimicrobial,

anti-inflammatory, anticonvulsant, antihypertensive, anti-diabetic, cholinesterase inhibition and anticancer activities and kinase inhibitor properties (**Figure IV.7**).[70-79]

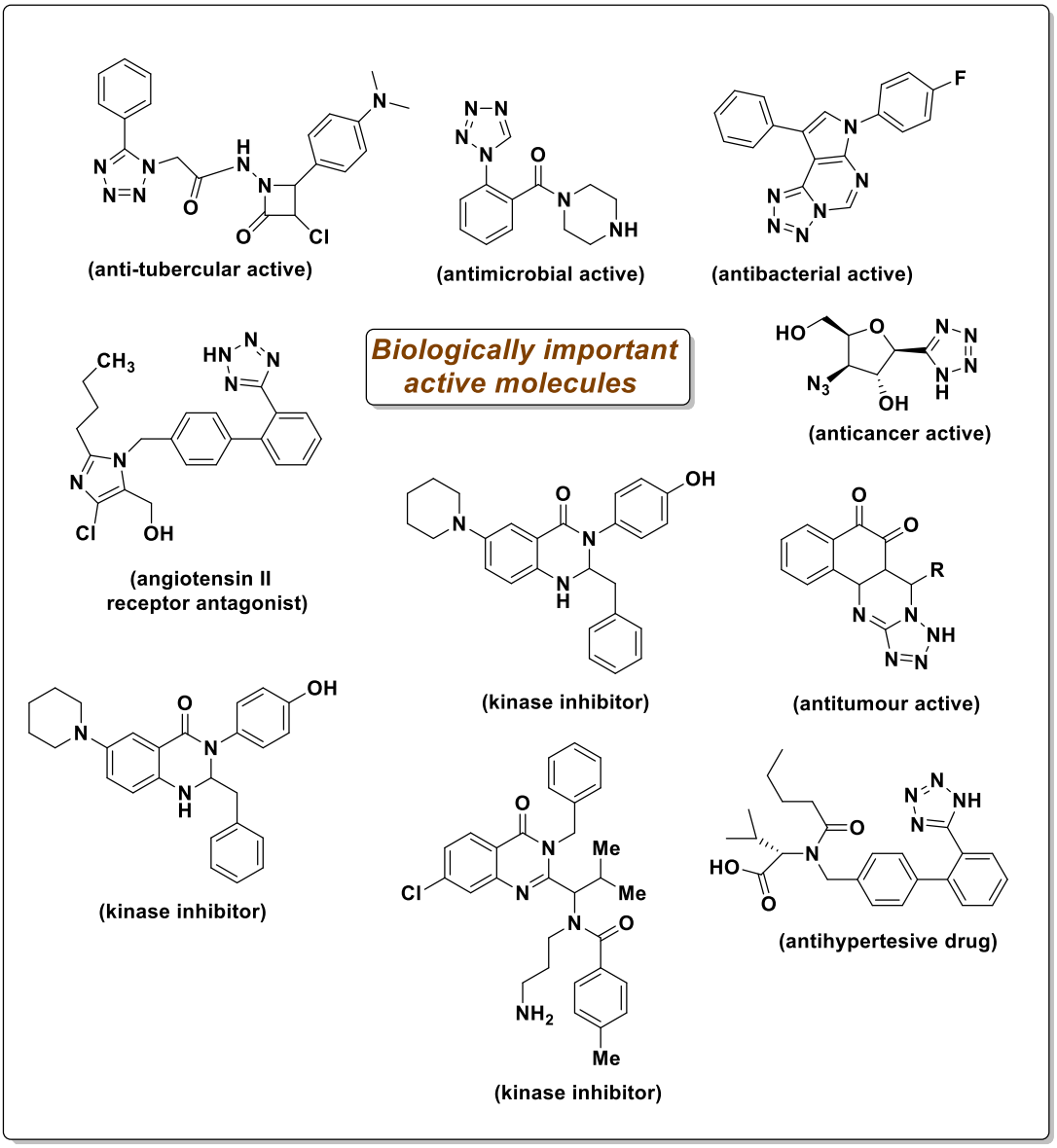


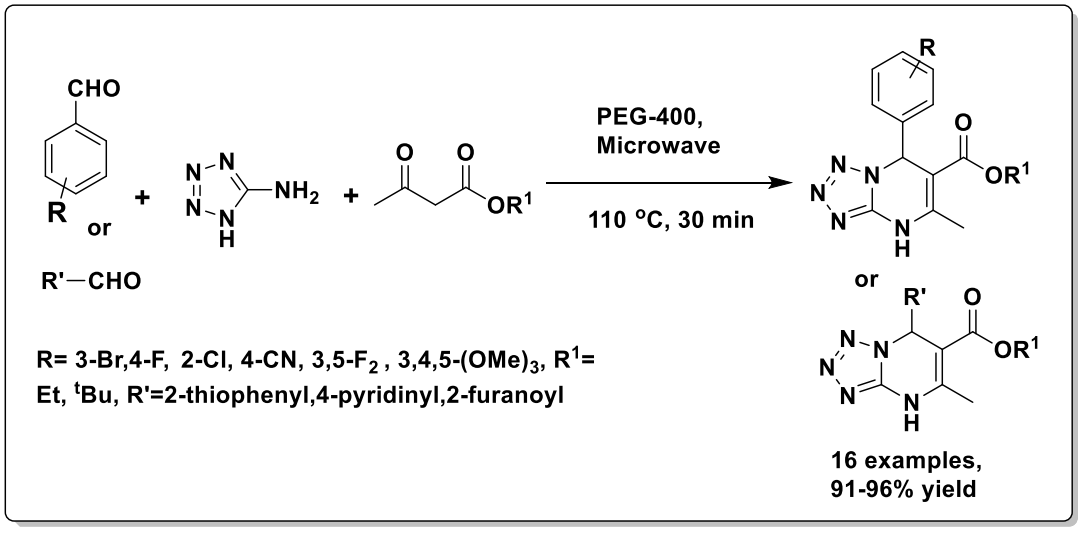
Figure IV.7 Some important pharmaceutically active drug molecule

By doing studies on works in various journals related to tetrazoles, quinazoline, quinazolinones and their derivatives and taking biological

importances of tetrazoles, quinazoline, quinazolinones and their derivatives in mind, in this following part of the Chapter IV, it has been focused on the synthesis of tetrahydrotetrazolo[5,1-*b*]quinazolinone derivatives in a new and convenient manner using cheap laboratory chemicals.

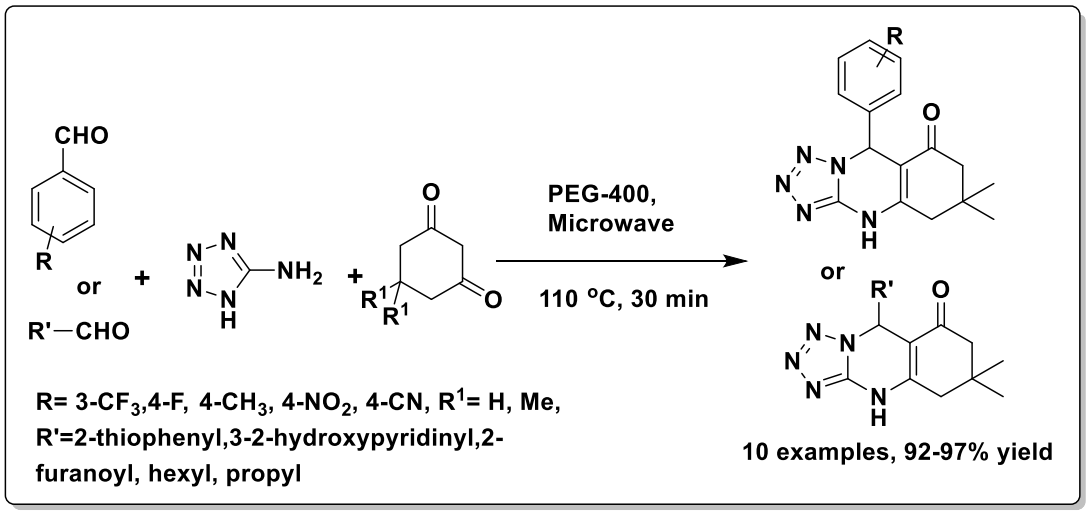
IV.8 Previous works on synthesis of tetrahydrotetrazolo[5,1-*b*]quinazolinone derivatives

In 2019, Basha *et al.* reported a facile one-pot synthesis of tetrazolo[1,5-*a*]pyrimidine derivatives via a one pot three-component reaction between aldehydes, 5-aminotetrazole and 1,3-diketones in PEG-400 under microwave irradiation at 110^0C. (**Scheme IV.7**). [80]



Scheme IV.7 One-pot synthesis of tetrazolo[1,5-*a*]pyrimidine derivatives by Basha *et al.*

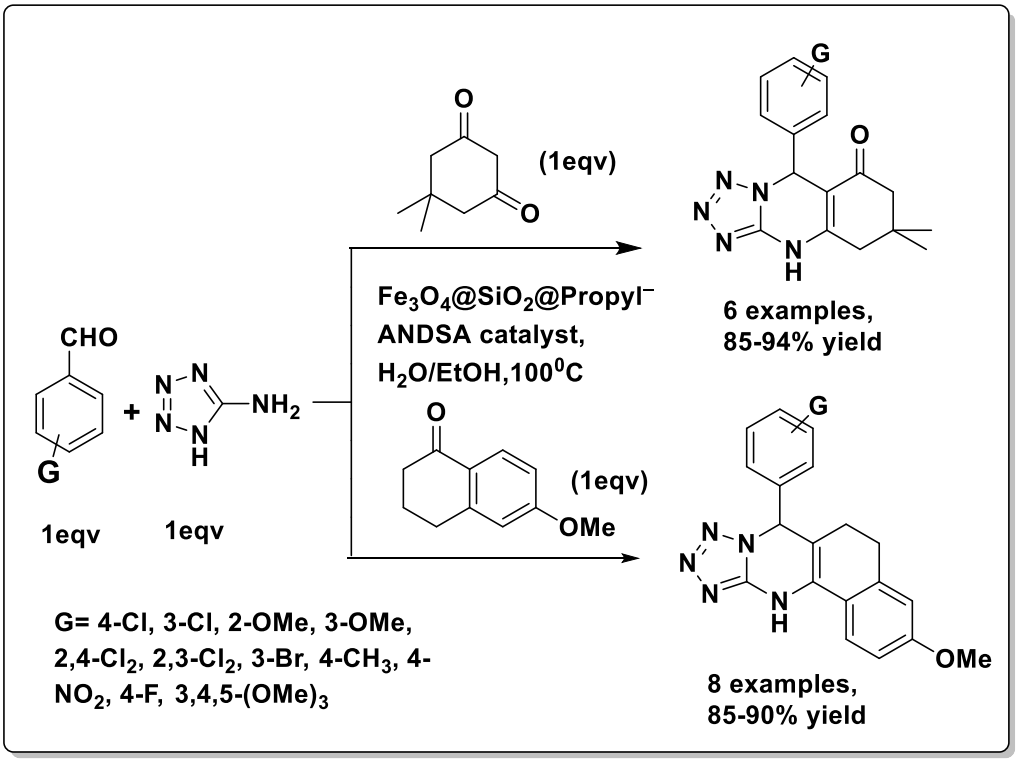
In 2019, Basha *et al.* also reported a facile synthesis of tetrahydrotetrazolo [5,1-*b*]quinazolinones via one one pot method by the reactions of aldehydes , 5-aminotetrazole and dimidone in presence of PEG-400 solvent under microwave irradiation at 110^0C temperature. (**Scheme IV.8**). [81]



Scheme IV.8 One-pot synthesis of tetrahydrotetrazolo [5,1-*b*]quinazolinones derivatives by Basha *et al*.

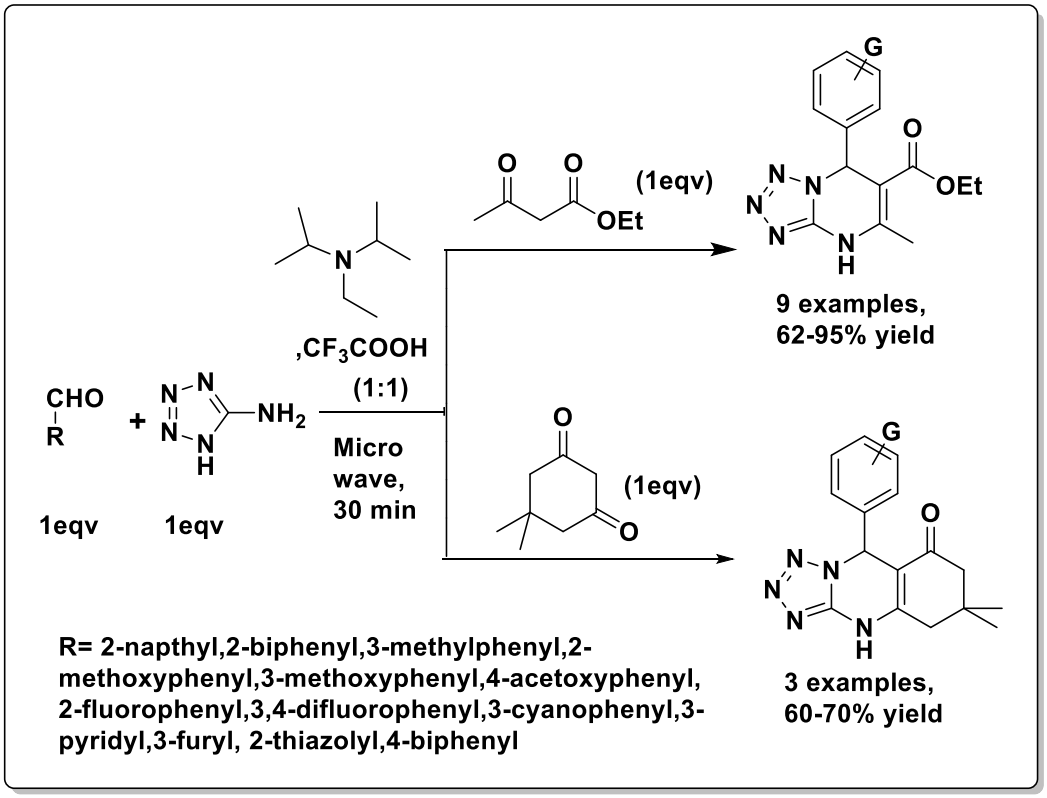
In 2019, Ghorbani-Vaghei *et al*. has reported a facile synthesis of tetrahydrotetrazolo[1,5-*b*]quinazolines and tetrahydrobenzo[h] tetrazolo[5,1-b]quinazolines from the reaction of aldehydes, 5-aminotetrazole, and dimedone as cyclic 1,3 diketone in presence of

Fe_3O_4@SiO_2@Propyl–ANDSA catalyst at 100^0C in H_2O/EtOH as the solvent. (**Scheme IV.9**). [82]



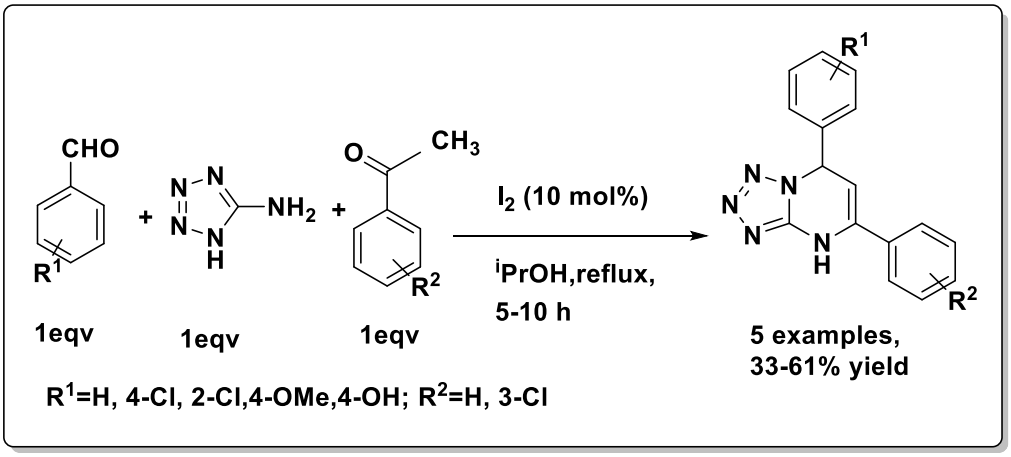
Scheme IV.9 A facile synthesis of tetrahydrotetrazolo[1,5-*b*]quinazolines and tetrahydrobenzo[*h*]tetrazolo[5,1-*b*] quinazolines by Ghorbani-Vaghei *et al*.

In 2012, Raju *et al*. has reported a facile synthesis of tetrazolo[1,5-a]pyrimidine derivatives from the reaction of aldehydes, 5-aminotetrazole, and ethylacetoacetate as acyclic 1,3 diketone in presence of a 1:1 mixture of N,N,N-triisopropylamine and CF_3COOH under microwave condition having reasonable yield (**Scheme IV.10**). [83]



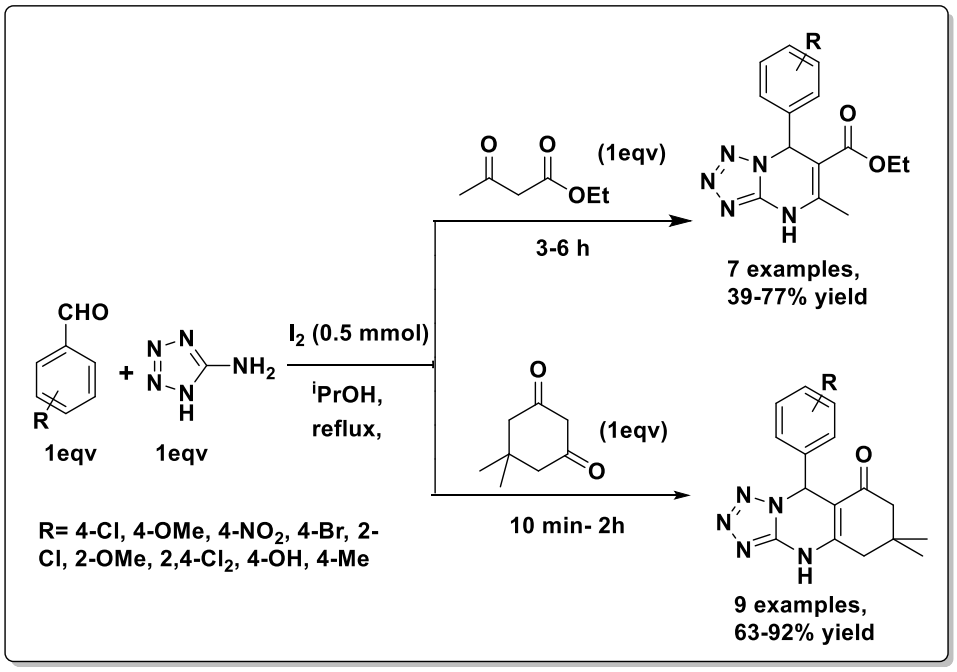
Scheme IV.10 A facile synthesis of tetrazolo[1,5-*a*]pyrimidine derivatives by Raju *et al*.

In 2010, Zeng *et al*. reported a novel reaction for the synthesis of dihydrotetrazolo[1,5-*a*]pyrimidines by the reaction of 5-aminotetrazole with aryl aldehydes and acetophenone catalyzed by iodine in presence of isopropyl alcohol under refluxing condition in one pot method (**Scheme IV.11**). [84]



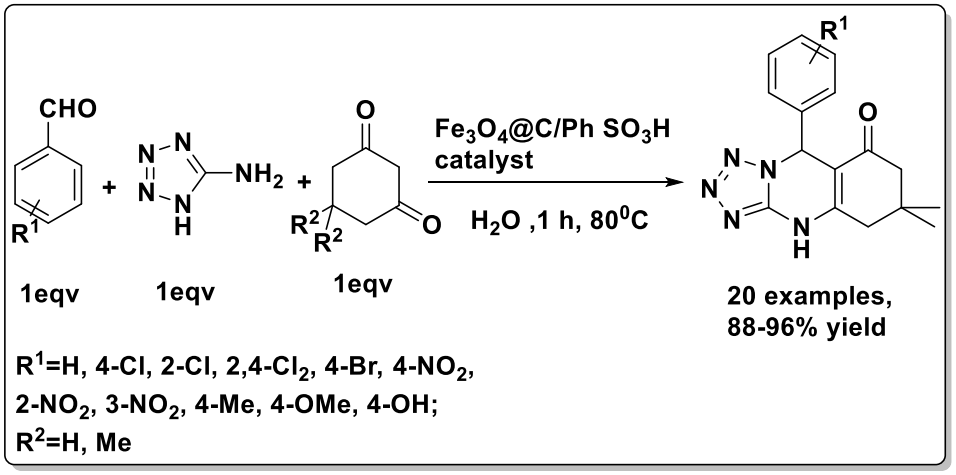
Scheme IV.11 A facile synthesis of dihydrotetrazolo[1,5-*a*]pyrimidines by Zeng *et al*.

In 2010, Zeng *et al*. also reported methods for the synthesis of dihydrotetrazolo[1,5-*a*]pyrimidine and tetrahydrotetrazolo[5,1-*b*]quinazolinone derivatives in one pot method in presence of iodine in isopropyl alcohol under reflux condition (**Scheme IV.12**). [85]



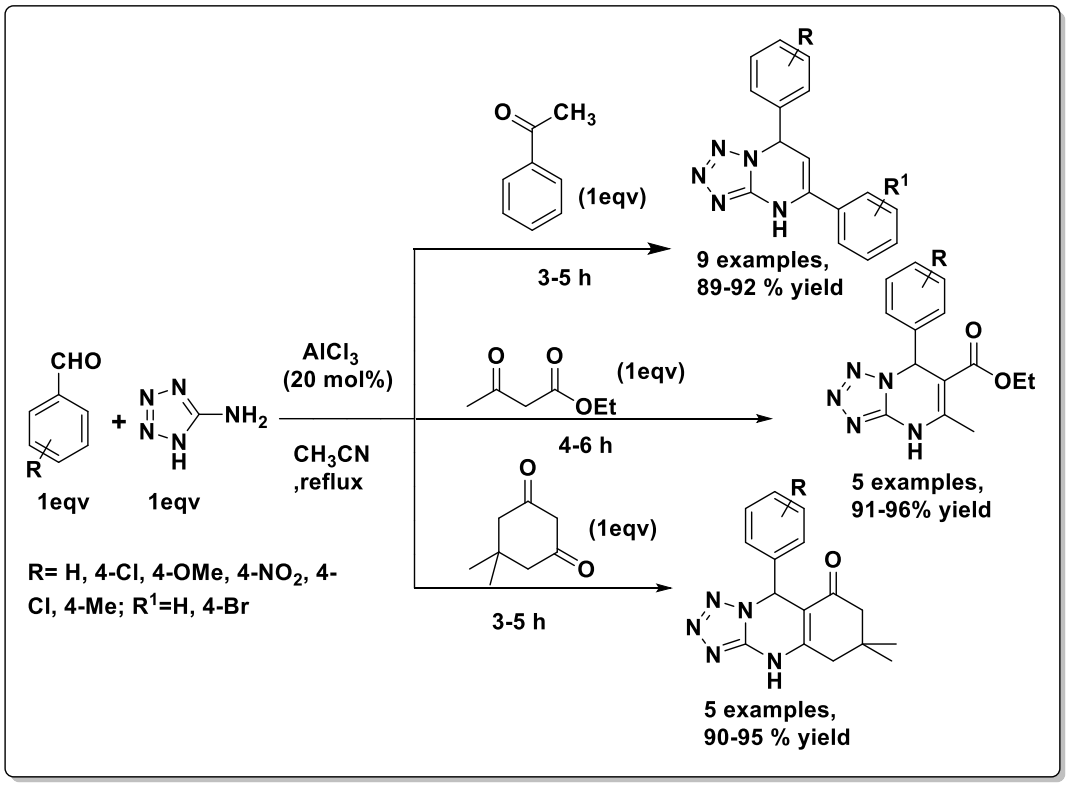
Scheme IV.12 Synthesis of dihydrotetrazolo[1,5-*a*]pyrimidine and tetrahydrotetrazolo[5,1-*b*]quinazolinone derivatives by Zeng *et al*.

In 2021, Hassankhani *et al*. reported a synthetic method for the synthesis of tetrahydrotetrazolo[5,1-b]quinazolinone derivatives by using synthesized Fe_3O_4@meso-C immobilized with activated 4-aminobenzenesulfonic acid as catalyst in presence of water at 80^0C with good yields (**Scheme IV.13**). [86]



Scheme IV.13 Synthetis of tetrahydrotetrazolo[5,1-*b*]quinazolinone derivatives by Hassankhani *et al.*

In 2017, Kour *et al*. reported facile synthetic methods for the synthesis of dihydrotetrazolo[1,5-*a*]pyrimidines and tetrahydrotetrazolo[1,5-*a*]quinazolinones via one pot multi-component method by the reaction of 5-aminotetrazole, aldehyde and active methylene compounds (e.g. acetophenone, alkylacetoacetates, dimedone) in presence of $AlCl_3$ catalyst under reflux condition in acetonitrile solvent with reasonable yields (**Scheme IV.14**). [87]



Scheme IV.14 One pot synthesis of dihydrotetrazolo[1,5-*a*]pyrimidines and tetrahydrotetrazolo[1,5-*a*]quinazolinones by Kour *et al*.

IV.9 2,4-diaryl hexahydroquinoline-5-one

2,4-diarylhexahydroquinolines are a class of quinoline family having 2 double bonds at 3 and 5 position of the biclyclic system having aryl groups attached with 2 and 4 position. This 2,4-diarylhexahydroquinlones are generally synyhesised from Chalcones followed by addition of basic ammonium salt and cyclic-1,3-diketo compounds. Sometimes aldehydes with acetophenones are used in absence of chalcone. There are several synthetic methods for the

synthesis of the synthesis of hexahydroquinoline (**Figure IV.8**) skeleton but there is still a shortage of reported methods related to green synthesis of hexahydroquinolines.

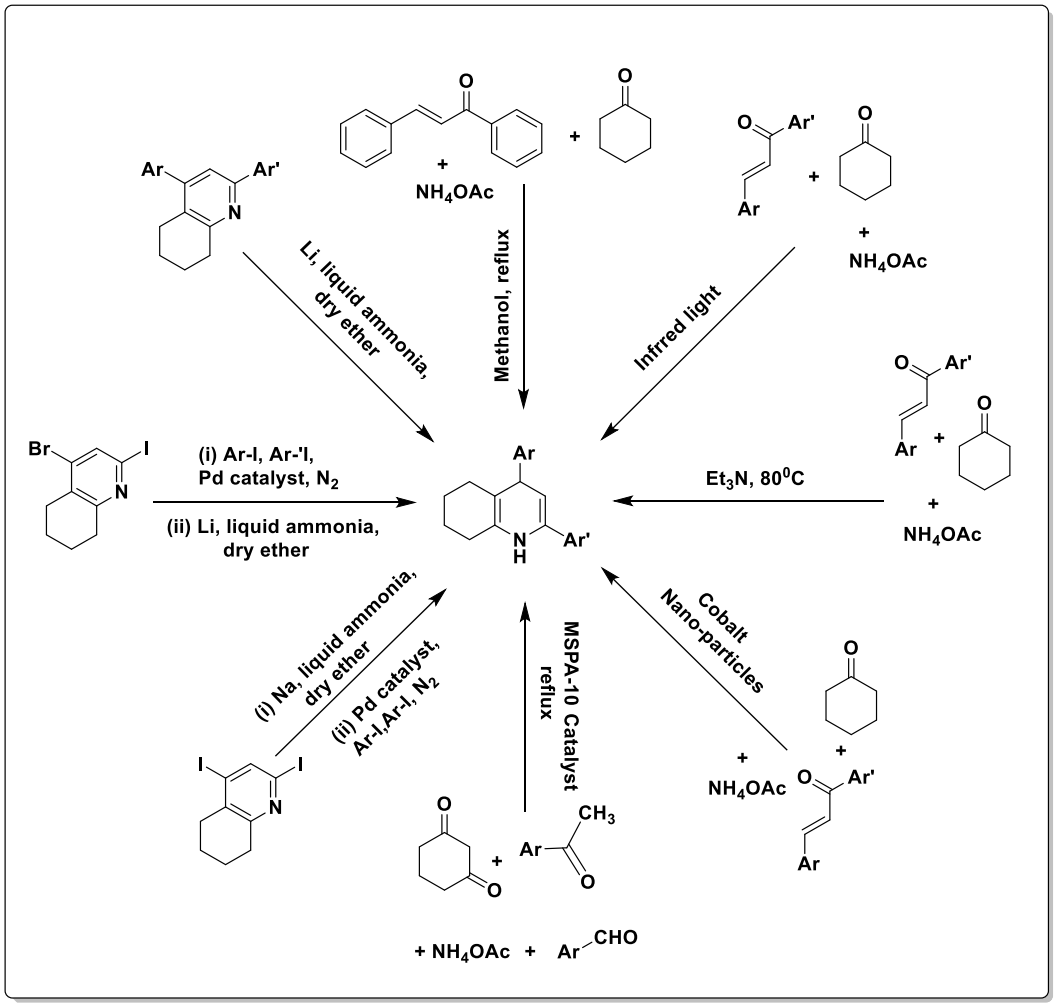


Figure IV.8 Diverse synthetic route for the synthesis of 2,4-diarylhexahydroquinoline ring synthesis

IV.10 Biological importance of 2,4-diaryl hexahydroquinoline-5-one derivatives

2,4-diarylhexahydroquinoline derivatives have structural resemlence with 1,4-dihydropyridines have thus they can behave as alternatives of 1,4-dihydropyridines from a variety of viewpoints such as biological activities and due to close resemblance with 1,4-dihydropyridines in respect of the biological properties (**Figure IV.9**) their derivatives can be used as calcium channel blockers for the treatment of defibrillation and hypertension disease [88]. They also possesses antimalarial, antiviral, antibacterial, antiallergic and anicancer properties and recently, acridines showed some inhibition properties [89-93]

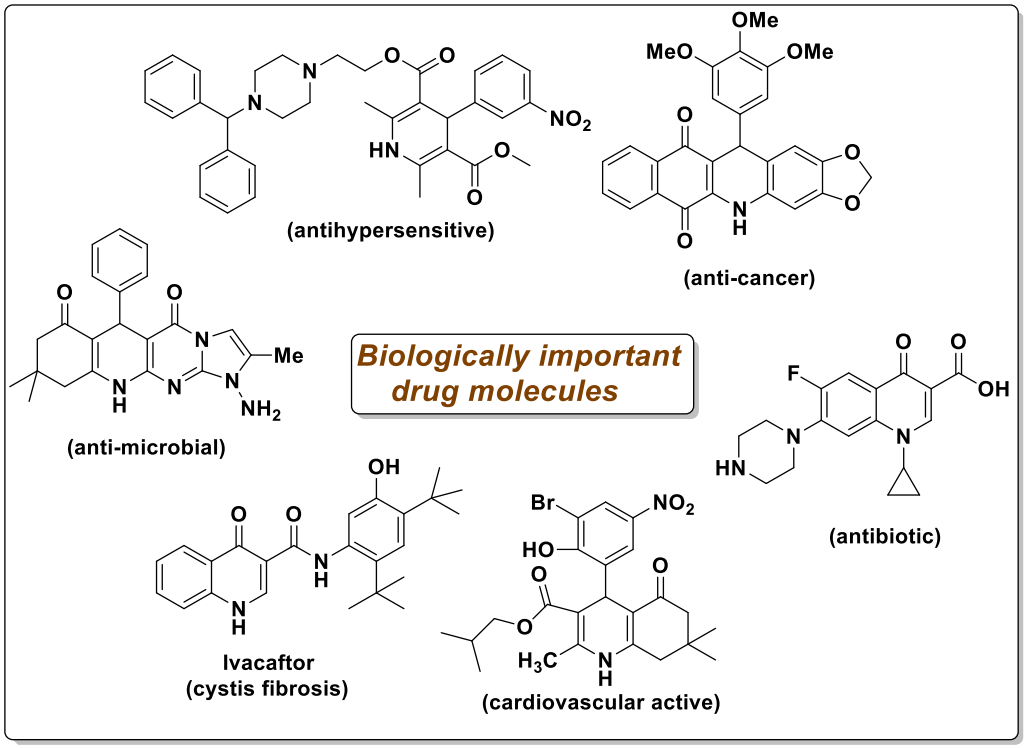
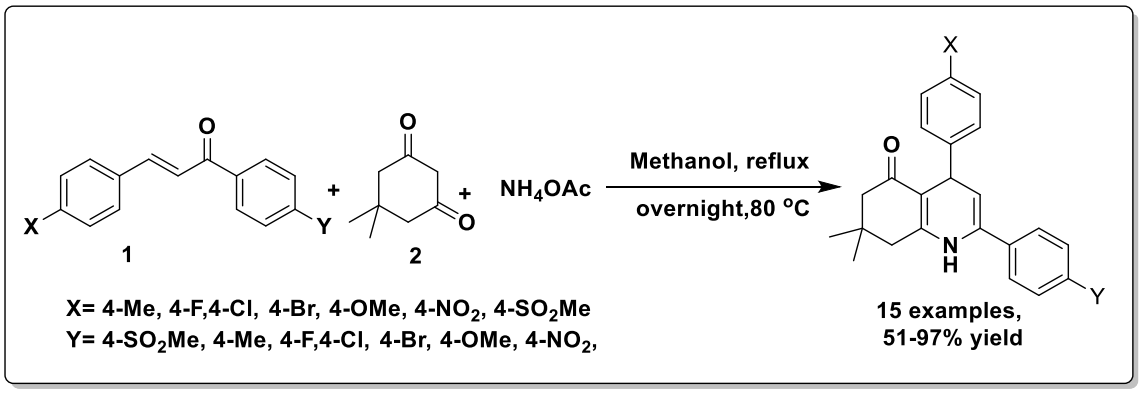


Figure IV.9 Some important pharmaceutically active drug molecule

By observing various journals among quinolines, quionolones and their derivatives and taking biological importances of quinolines and quinolones and their derivatives in mind, in this following part of the chapter IV, it has been focused on the synthesis of 2,4-diaryl hexahydroquinoline-5-one derivatives in a new and convenient manner using cheap laboratory chemicals.

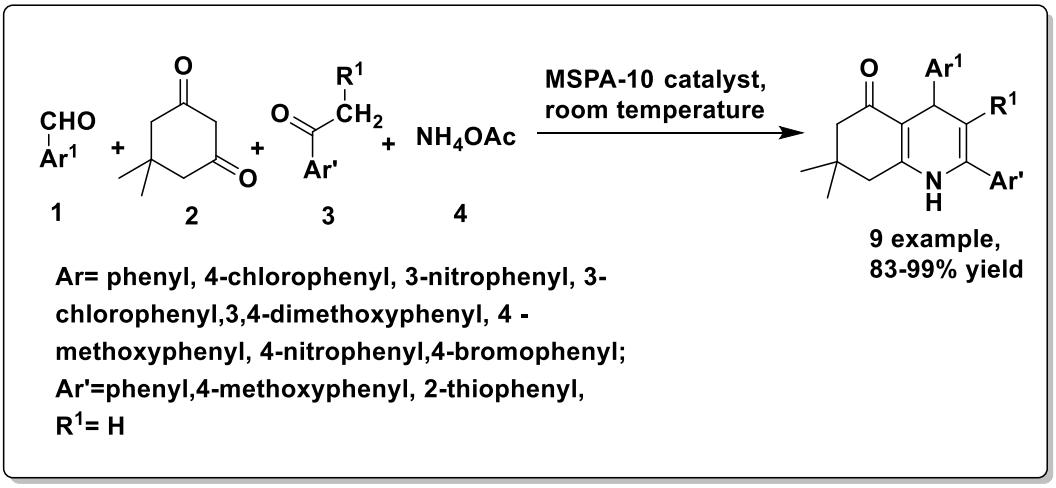
IV.11 Previous works on synthesis of 2,4-diaryl hexahydroquinoline-5-one derivatives

In 2014, Zarghia *et al*. has reported a synthesis of 2,4-diarylhexahydroquinolines by the one pot reaction between mixture of 5, 5-dimethyl-1,3-cyclohexandion, 1,3-diaryl-2-propen1-one, ammonium acetate in methanol under refluxed condition at 80^0C for overnight (**Scheme IV.15**). [94]



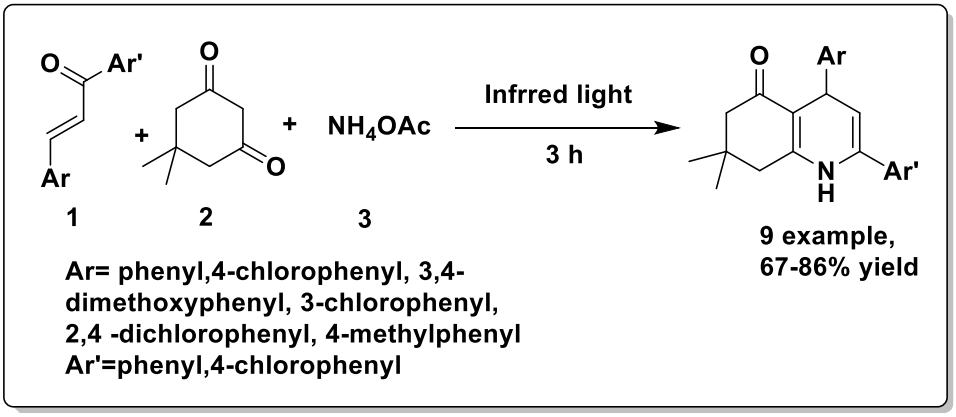
Scheme IV.15 One pot synthesis of 2,4-diarylhexahydroquinolines by Zarghia *et al.*

In 2013, Ray *et al*. has reported a synthesis of 2,4-diarylhexahydroquinolines by carring out a one pot 4-component reactions between aromatic aldehydes, dimedone and acetophenone and ammonium acetate by using a new heterogeneous MCM-41 silica supported HPF_6 catalyst (**Scheme IV.16**). [95]



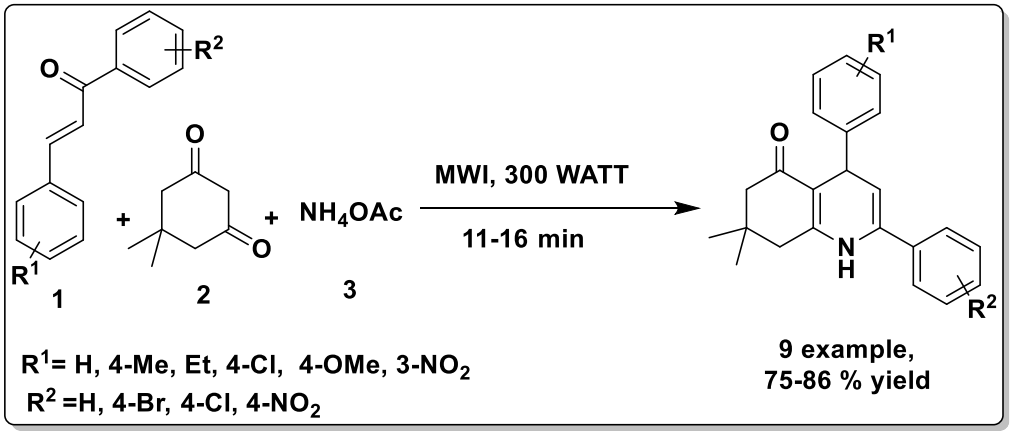
Scheme IV.16 One pot synthesis of 2,4-diarylhexahydroquinolines by Ray *et al.*

In 2006, Wang *et al*. reported a synthetic procedure for the synthesis of 2,4-diarylhexahydroquinolines by doing a one pot 3-component reactions between Chalcones, dimedone and ammonium acetate by infrared irradiation (IR) irradiation promoted the synthesis with 67-86% yield (**Scheme IV.17**). [96]



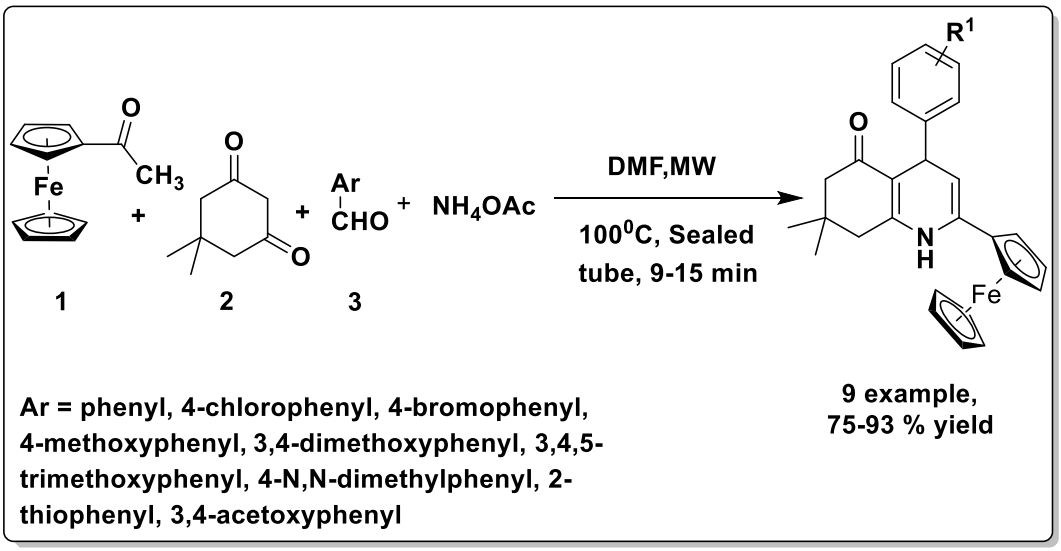
Scheme IV.17 One pot synthesis of 2,4-diarylhexahydroquinolines by Wang *et al.*

In 2005, Hua *et al*. reported a synthetic procedure for the synthesis of 2,4-diarylhexahydroquinolines by doing a one pot 3-component reactions between Chalcones, dimedone and ammonium acetate by microwave irradiation (mwi 300 watt) the synthesis with 75-86% yield (**Scheme IV.18**). [97]



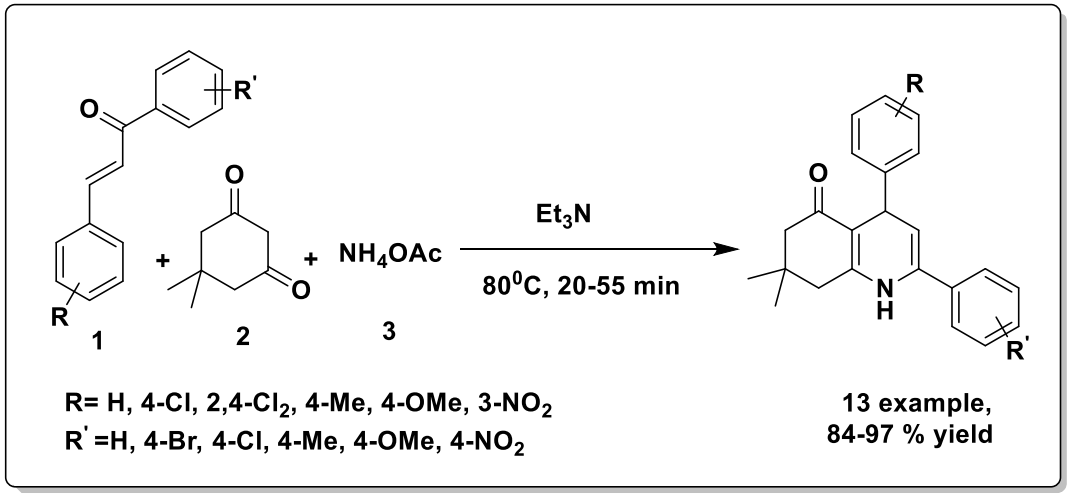
Scheme IV.18 One pot synthesis of 2,4-diarylhexahydroquinolines by Hua *et al*.

In 2009, Tu *et al*. reported a synthetic procedure for the synthesis of 2,4-diarylhexahydroquinolines by doing a one pot 4-component reactions between aromatic aldehydes, dimedone, ammonium acetate and ferrocenyl active metheline compound by microwave irradiation (MW) in presence of DMF solvent with 75-93% yield (**Scheme IV.19**). [98]



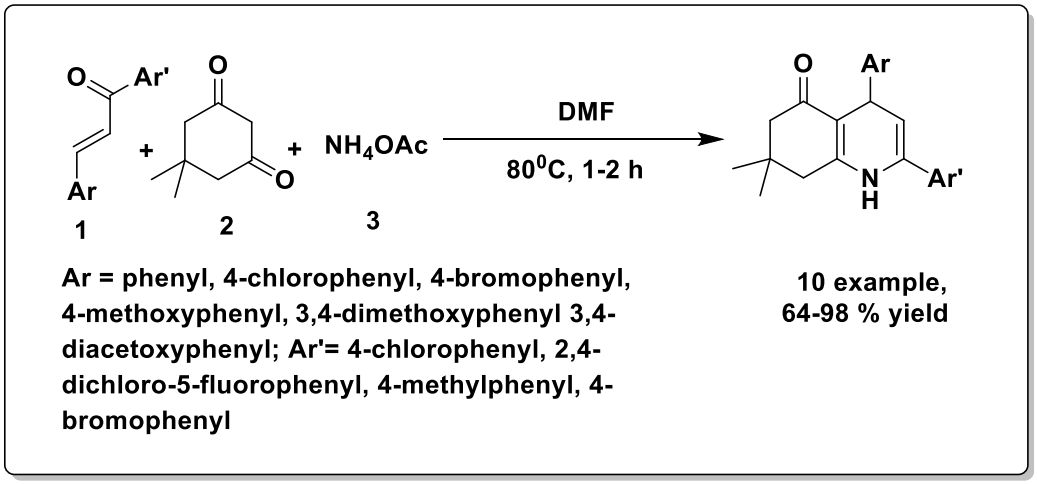
Scheme IV.19 One pot synthesis of 2,4-diarylhexahydroquinolines by Tu *et al*.

In 2015, Karimi-Jaberi *et al.* reported a convenient and efficient protocol for the synthesis of 2,4-diaryl hexahydroquinoline derivatives by a three-component reaction between Chalcones, dimedone and ammonium acetate catalyzed by triethylamine under solvent-free conditions with yield 84-97% (**Scheme IV.20**). [99]



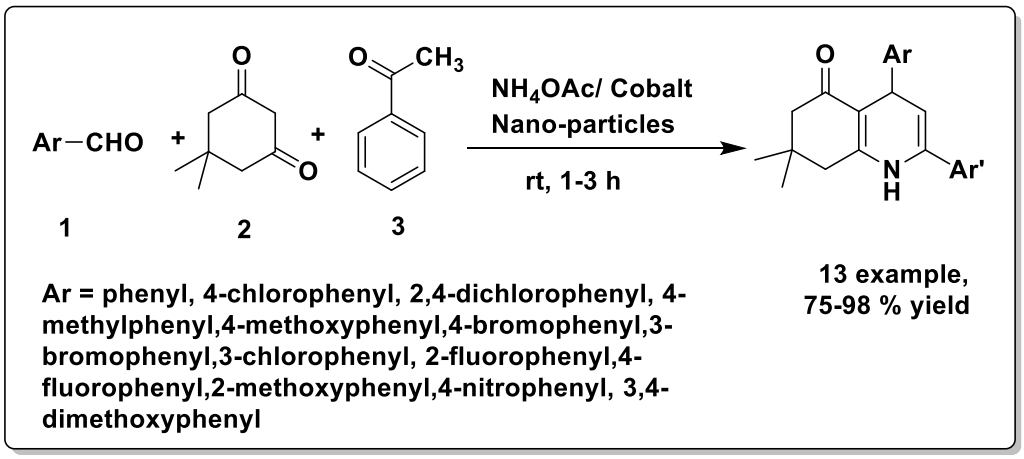
Scheme IV.20 One pot synthesis of 2,4-diarylhexahydroquinolines by Karimi-Zaberi *et al.*

In 2002, Wang *et al*. reported a series of substituted 2,4-diarylhexahydroquinoline derivatives by a 3-component reaction of dimedone ammonium acetate and 1,3-diaryl-2-propen-1-one (Chalcones) in DMF at 80^0C temperature with yields 64–98% (**Scheme IV.21**). [100]



Scheme IV.21 One pot synthesis of 2,4-diarylhexahydroquinolines by Wang *et al*.

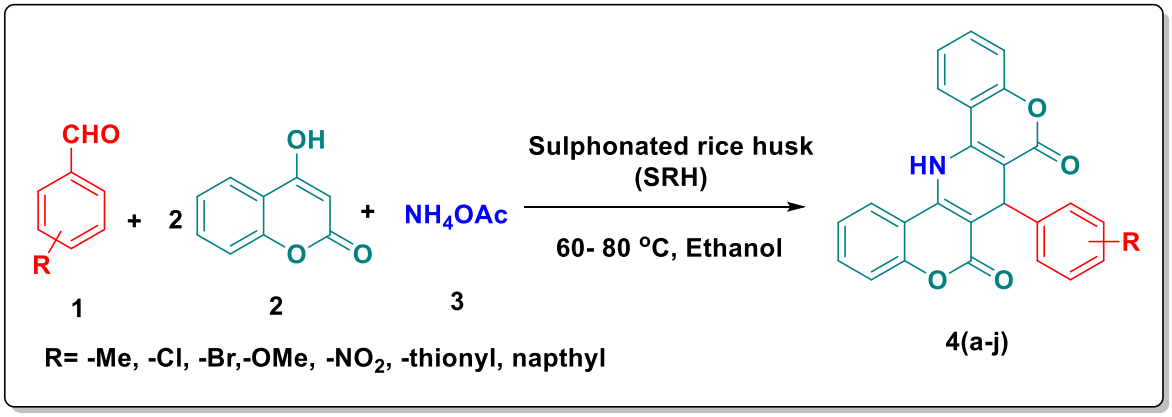
In 2011, Safari *et al*. reported a straightforward method for the synthesis of 2,4-diarylhexahydroquinoline derivatives by the reaction between dimedone, acetophenone, aromatic aldehydes, and ammonium acetate in the presence of a catalytic amount of Cobalt nanoparticles at room temperature with 75-98% yield (**Scheme IV.22**). [101]



Scheme IV.22 One pot synthesis of 2,4-diarylhexahydroquinolines by Safari *et al.*

IV. 12 Present Work

The present work leads to the synthesis of dihydro-dichromeno-pyridine-6,8-dione derivatives (**Scheme IV.23**) by using greener catalyst heterogeneous catalyst sulphonated rice husk (SRH) .



Scheme IV.23 Synthesis of substituted dihydro-dichromeno-pyridine-6,8-dione derivatives using sulphonated rice husk[a]

IV.12.A Results and discussion

IV.12.A.1 Catalyst characterization

The prepared catalyst was characterized by powder XRD, FTIR spectroscopy and SEM-EDX analysis. Detailed literature studies along with comparison of the physical characterization data of the material including of FTIR spectra (**Figure IV.10a**) and SEM-EDX analysis (**Figure IV.11**) and power XRD data (Figure IV.10) curves of both the catalyst (SRH) to that of rice husk (RH) clearly indicated the formation of the rice husk based heterogeneous catalyst. The the new broad band arround 3400 cm^{-1} along with the band arround 1100cm^{-1} indicating the incorporation of $–SO_3H$ groups into RH surface after sulphonation and the band arround 1100cm^{-1} represents the symmetric and asymmetric

streatching of S=O bonds of $–SO_3H$ groups groups.[61] SEM-DEX (**Figure IV. 11**)analysis and powder XRD have made a clear pathway for comparison of RH and SRH and confirmation of the prepared catalyst from the rice husk. The powder XRD analysis of both RH and SRH shows characteristic changes in 2θ values and different nature of both RH and SRH clearly indicates the SRH has been formed from RH due to sulphonation. (**Figure IV. 10b**). Detailed characterization informations EDX analysisof SRH and RH are given into the experimental section (**IV.12.A.14.l.**) of the Chapter IV.

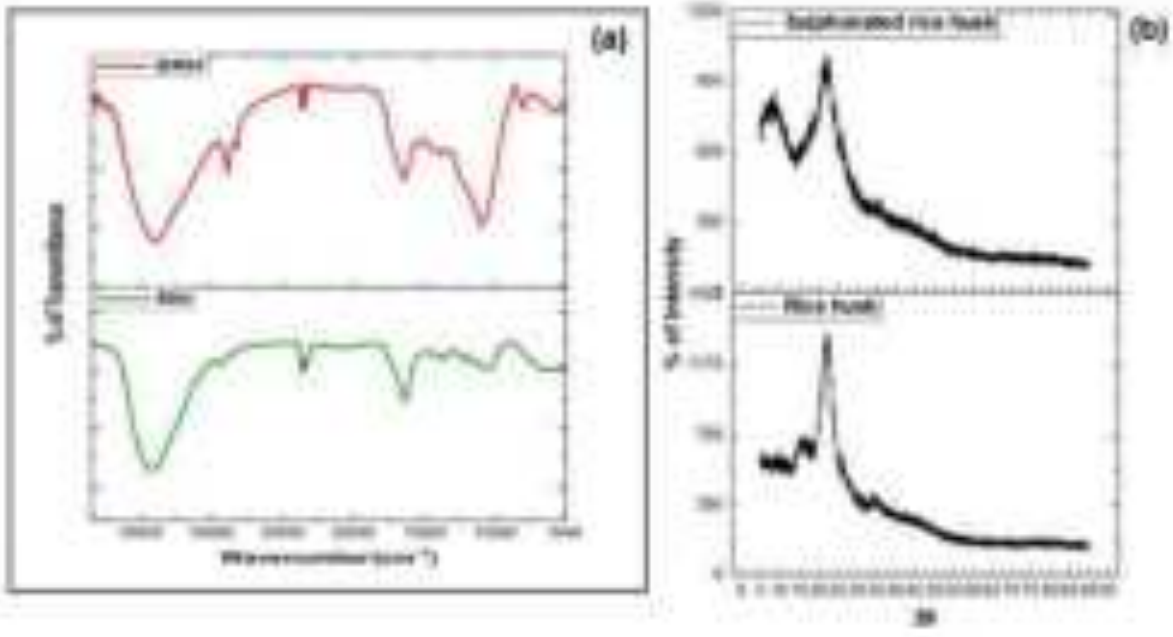


Figure IV.10 (a) FTIR spectra of RH and SRH. (b) Powder XRD spectra of RH and SRH

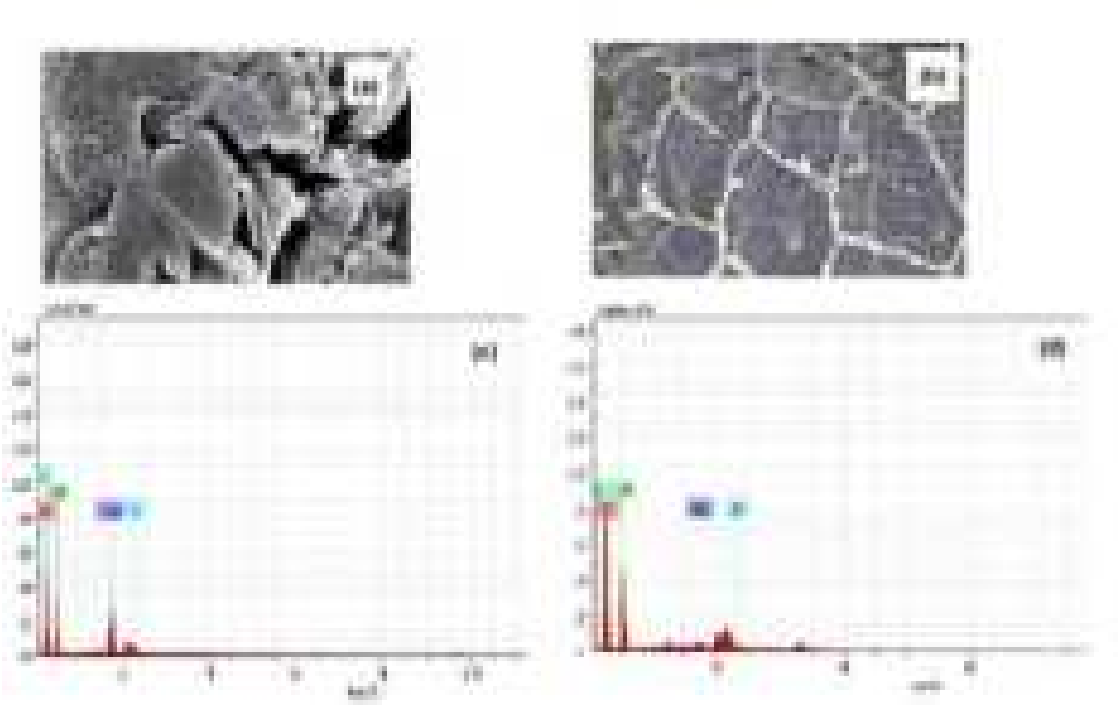


Figure IV.11 (a) SEM image of SRH. (b) SEM image of RH. (c) EDX-image of SRH. (d) EDX-image of RH

IV.12.A.2 Optimisation of the reaction condition for the synthesis of dihydro-dichromeno-pyridine-6,8-dione

Initially the reaction was started with taking anisaldehyde (1 mmol), 4-hydroxycoumarine (2 mmol), ammonium acetate (1.2 mmol) at a time in a 25 mL glass made sealed reaction tube vessel. In absence of catalyst, it was observed that the formation of the corresponding product had a poor yield produced may be due to by solvent induced catalysis (**Table IV.1,** entry 11) but excellent yield was observed in presence of arbitrary amount of 100 mg of SRH catalyst in ethanol solvent at 80^0 C temperature (**Table IV.1,** entry 2). The role of catalytic efficiency was

observed by decreasing the amount of catalyst through sequence wise experiment and the yield of the product was observed with amount of catalyst. From the optimized condition, it is clear that SRH catalyst is suitable as a greener catalyst for the conversion of dihydro-dichromeno-pyridine-6,8-dione with excellent yield in short reaction time. The amount of the catalyst and the time of the reaction was further checked to find out the optimized condition of the reaction. It was observed that the best result was obtained at 70^0 C temperature using 60 mg of catalyst SRH in ethanol (**Table IV.1, entry 7**). A comparison experiment was done with our prepared catalyst (SRH) with other conventional acid catalysts (**Table IV.7**) following the above reaction scheme (**Scheme IV.23**) and it was observed that the yield of product for few acid catalyst is almost similar which had suggested a comparison of effectiveness of SRH with other acid catalyst taking a short reaction time. The generality of the reaction was observed with a variety of aromatic and heterocyclic aldehydes (**Scheme IV.23**) having electron donating and electron withdrawing substituents of the aromatic aldehydes. The targeted compounds (4a-4j) are successively synthesized using SRH as an efficient catalyst under greener reaction condition and the progress of the reaction was monitored by thin layer chromatography (TLC) and the

pure product was separated by recrystallisation of the crude product in petroleum ether/ethyl acetate (v/v ratio70/30) mixture.

Table IV.1 Optimisation of the reaction condition for the synthesis of dihydro-dichromeno-pyridine-6,8-dione.[a]

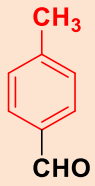
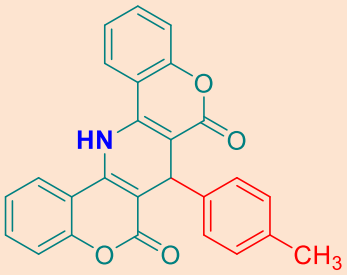
Entry	Catalyst (mg)	Solvent	Temperature (^{o} C)	Time (min)	Yield (%)[b]
1	110	Ethanol	90	360	98
2	100	Ethanol	80	318	98
3	90	Ethanol	80	300	98
4	80	Ethanol	80	258	98
5.	70	Ethanol	70	240	98
6.	70	Ethanol	70	198	98
7.	**60**	**Ethanol**	**70**	**180**	**96**
8.	50	Ethanol	70	180	94
9.	50	Ethanol	60	180	90
10.	50	Ethanol	60	150	90
11.	None	Ethanol	70	190	60
12.	None	Methanol	70	190	50
13.	60	Methanol	70	200	95
14.	80	Ethanol/H_2O (4:1)	70	200	90
15.	80	Ethanol/H_2O (1:1)	70	200	84

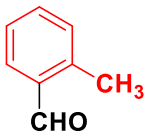
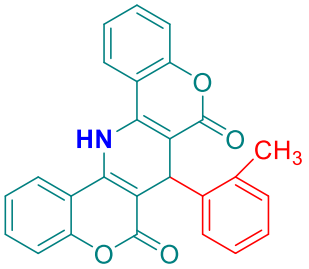
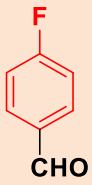
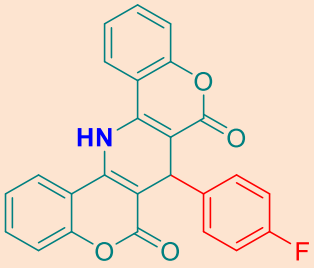
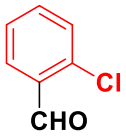
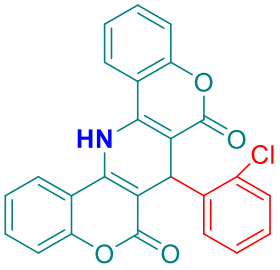
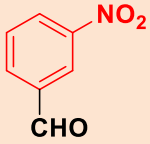
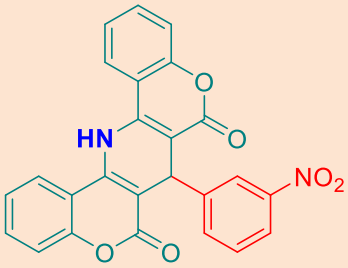
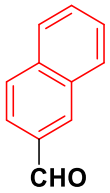
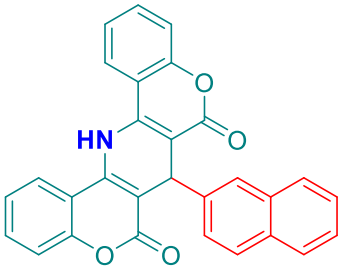
[a] Reaction of anisaldehyde (1 mmol), 4-hydroxycoumarine (2 mmol), and ammonium acetate(1.2 mmol) [b] Isolated yield after purification through recrystalisation.

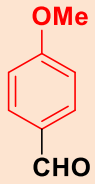
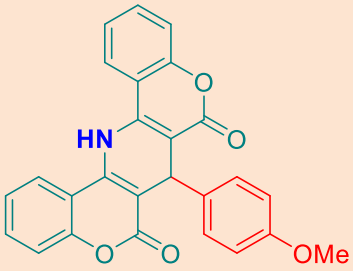
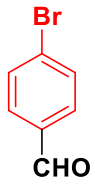
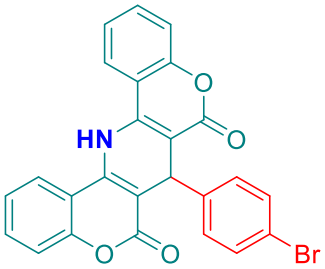
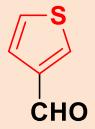
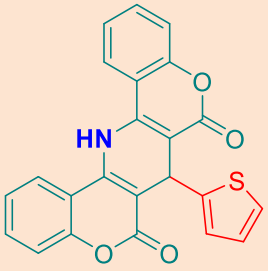
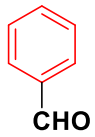
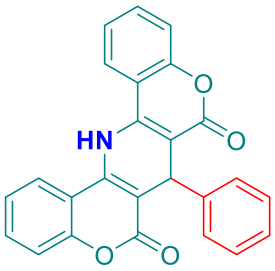
IV. 12.A.3 Synthesis of dihydro-dichromeno-pyridine derivatives

The generality of the reaction was observed with a variety of aromatic and heterocyclic aldehydes (**Scheme IV.23**) having electron donating and electron withdrawing substituents at *ortho*, *meta* and *para* position of the aromatic aldehyde. The targeted compounds (4a-4j) are successively synthesized using SRH as an efficient catalyst under greener reaction condition. (**Table IV.2**) The progress of the reaction was monitored by thin layer chromatography (TLC) and the pure product was separated by recrystallisation of the crude product in petroleum ether/ethyl acetate mixture given in experimental section.

Table IV.2 Synthesis of dihydro-dichromeno-pyridine-6,8-dione derivatives using sulphonated rice husk[a]

Entry	Reactant	Product	Time	Yield(%)[b]
1		 (4a)	240 min	96

2		 (4b)	240 min	93
3		 (4c)	240 min	95
4		 (4d)	240 min	94
5		 (4e)	240 min	97
6		 (4f)	240 min	92

7		 (4g)	240 min	98
8		 (4h)	240 min	97
9		 (4i)	240 min	92
10		 (4j)	240 min	96

[a] Reaction of p-toluealdehyde (1 mmol), 4-hydroxycoumarine (2 mmol), and ammonium acetate(1.2 mmol) [b] Isolated yield after purification through recrystalisation.

IV.12.A.4 Plausible Mechanism

A plausible mechanism for the synthesis of dihydro-dichromeno-pyridine-6,8-dione is established by considering the acidic behaviour of the catalyst (**Figure IV.12**). At the very first step of the reaction, protonation occurs at aldehyde oxygen of aromatic aldehyde and then a successive condensation reaction occurs between 2 molecules of 4-hydroxy coumarine with 1 molecule of aldehyde to give a bis-coumarol intermediate.[62] Now, the bis-coumarol intermediate undergo totomerisation followed by a cyclocondensation reaction with NH_4OAc to give the final product dihydro-dichromeno-pyridine-6,8-dione

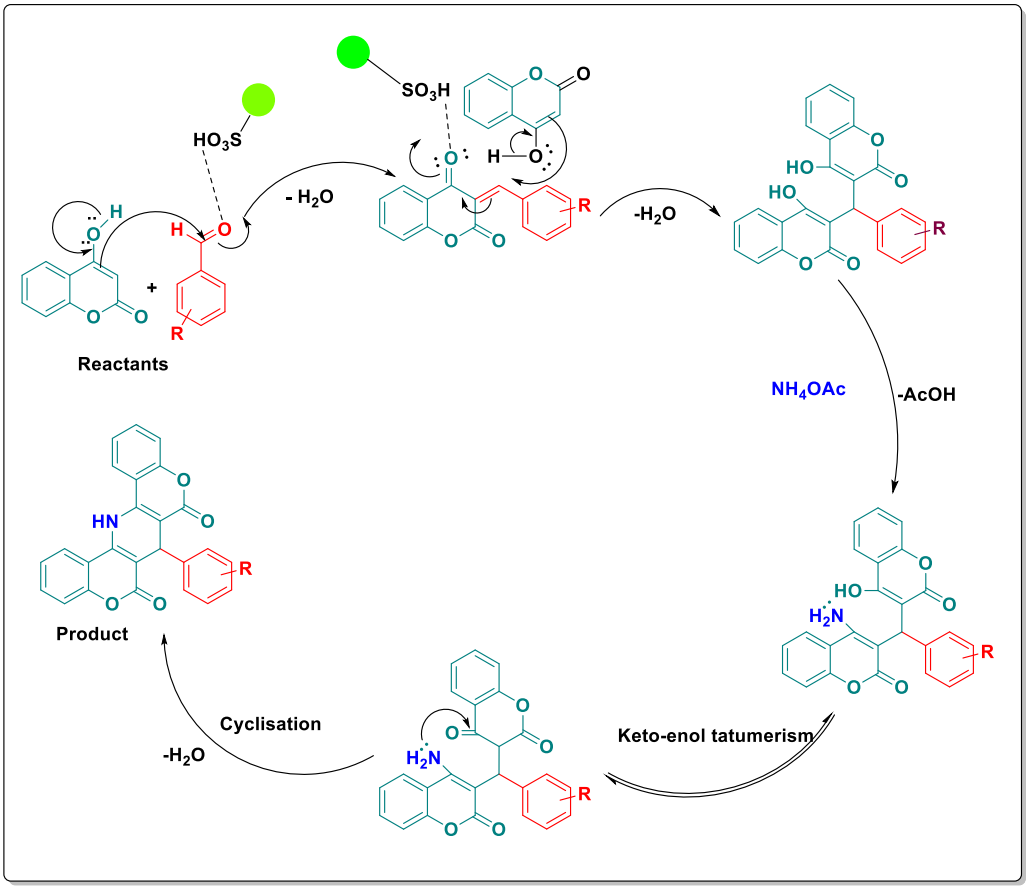
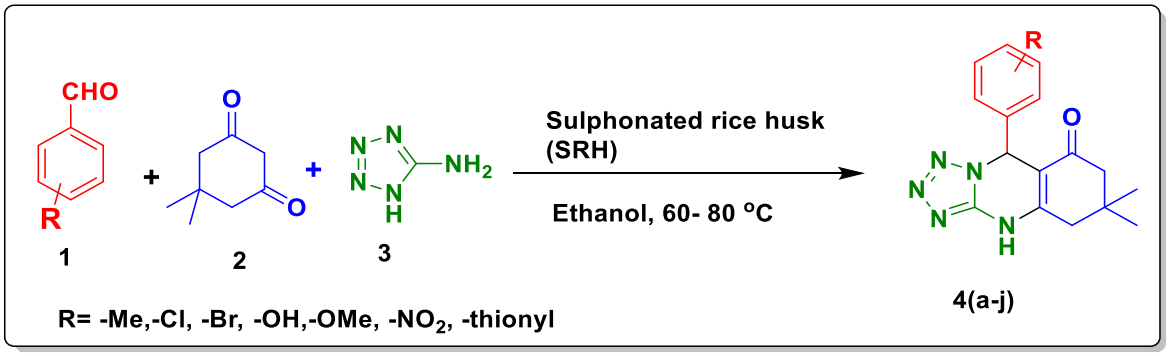


Figure IV.12The plausible mechanism for the synthesis of dihydro-dichromeno pyridine-6,8-dione

The next present work leads to the synthesis of tetrahydrotetrazolo[5,1-*b*]quinazolinone derivatives (**Scheme IV.24**) by using greener catalyst heterogeneous catalyst sulphonated rice husk (SRH) .



Scheme IV.24 Synthesis of substituted tetrahydrotetrazolo[5,1-*b*]quinazolinone derivatives using sulphonated rice husk[a]

IV.12.A.5 Optimization of synthesis of substituted tetrahydrotetrazolo[5,1-*b*]quinazolinone derivatives

One pot synthesis of tetrahydrotetrazolo[5,1-*b*]quinazolinones, initially carried out with taking anisaldehyde (1 mmol), 5-amino-1*H*-tetrazole (1 mmol) and 5,5-dimethylecyclohex-1,3-dione (1 mmol) taken in a 25 mL RB. It was observed that in presence of 100 mg of the catalyst in ethanol solvent at 70^0 C temperature (**Table IV.3,** entry 7) with reaction

time of 13 hours maximum yield was observed. The optimized reaction condition was observed with the amount of catalyst and for screening the optimized reaction condition, anisaldehyde (1 mmol) along with 5-amino-1*H*-tetrazole (1 mmol) and 5,5-dimethylecyclohex-1,3-dione (1 mmol) were taken in ethanol. In absence of catalyst the formation of the expected product was not formed (**Table IV.3,** entry 13) and with addition of 100 mg of catalyst, the performance of the reaction was observed with satisfactory yield (84%) in ethanol solvent. (**Table IV.3,** entry 7). The amount of the catalyst and time of the reaction was checked thoroughly to find out the optimized reaction condition and it was observed that the best result was obtained at 70^0C temperature using minimum amount of catalyst SRH (90 mg) in presence of ethanol solvent (**Table IV.3**, entry 9). The generality of the reaction was observed with a variety of aromatic and heterocyclic aldehydes (**Scheme IV.24**) containing electron donating and electron withdrawing substituents and the targeted compounds (4a-4i) are successively synthesized using SRH as an efficient greener catalyst under greener reaction condition. The progress of the reaction was monitored continuously by thin layer chromatography (TLC) and the crude product was separated from ethylacetate extract by addition of petroleum ether

followed by purification through washing with ethylacetate and petroleum ether mixture {petroleum ether/ethyl acetate (v/v ratio70/20) mixture}.

Table IV.3 Optimisation of the reaction condition for the synthesis of tetrahydrotetrazolo[5,1-*b*]quinazolinone derivatives [a]

Entry	Catalyst (mg)	Solvent	Temperature (^{o} C)	Time	Yield (%)[b]
1	100	Ethanol	90	15 h	84
2	120	Ethanol	100	16 h	70
3	120	Ethanol	80	16 h	84
4	110	Ethanol	80	16 h	84
5.	110	Ethanol	70	15 h	84
6.	100	Ethanol	70	14 h	84
7.	100	Ethanol	70	13 h	84
8.	90	Ethanol	70	12 h	84
9.	90	Ethanol	70	11 h	84
10.	90	Ethanol	70	10 h	83
11.	90	Ethanol	60	11 h	72
12.	90	Ethanol	60	15 h	73
13.	None	Ethanol	70	15 h	Trace
14.	90	H_2O	70	15 h	-
15.	80	Ethanol/H_2O(4:1)	70	10 h	Trace
16.	80	Ethanol/H_2O(1:1)	70	10 h	Trace

17.	90	Methanol	70	10 h	83

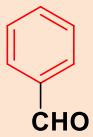
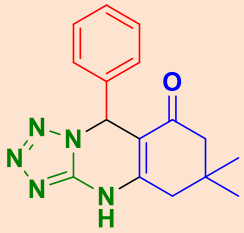
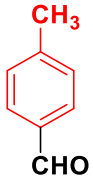
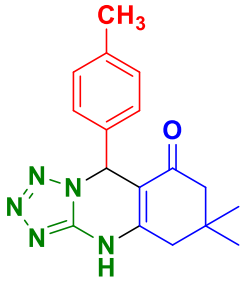
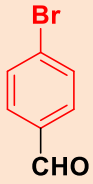
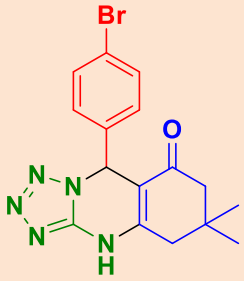
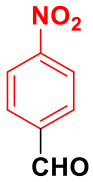
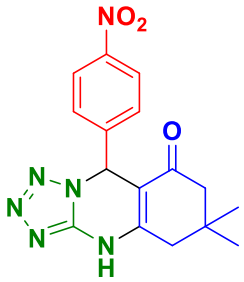
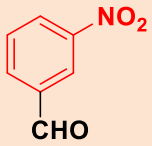
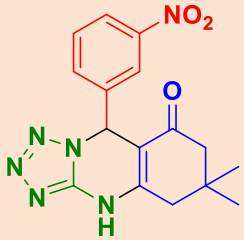
[a]Reaction of anisaldehyde (1 mmol), 5-amino-1*H*-tetrazole (1 mmol) and 5,5-dimethylecyclohex-1,3-dione (1 mmol) . [b]The yields are isolated through recrystalisation.

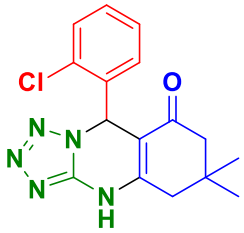
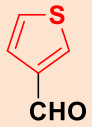
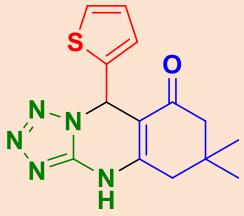
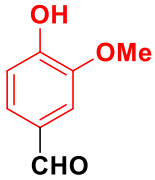
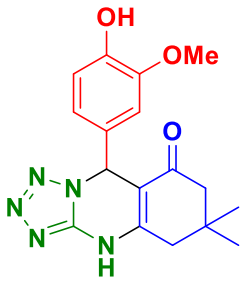
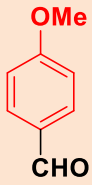
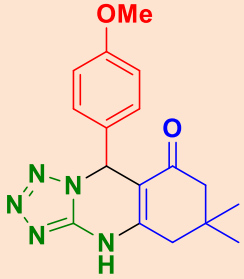
IV.12.A.6 Synthesis of substituted tetrahydrotetrazolo[5,1-*b*]quinazolinone derivatives

The generality of the reaction was observed with a variety of aromatic and heterocyclic aldehydes (**Scheme IV. 24**) having electron donating and electron withdrawing substituents at *ortho*, *meta* and *para* position of the aromatic aldehyde. (**Table IV.4**) The targeted compounds (4a-4j) are successively synthesized using SRH as an efficient catalyst under greener reaction condition. The progress of the reaction was monitored continuously by thin layer chromatography (TLC) and the crude product was separated from ethylacetate extract by addition of petroleum ether followed by purification through washing with ethylacetate and petroleum ether mixture given in experimental section.

Table IV. 4 Synthesis of tetrahydrotetrazolo[5,1-*b*]quinazolinone derivatives[a]

Entry	Reactant	Product	Time	Yield(%)[b]

1		 (4a)	14 h	80
2		 (4b)	12 h	84
3		 (4c)	11 h	83
4		 (4d)	10 h	82
5		 (4e)	10 h	80

6		 **(4f)**	14 h	82
7		 **(4g)**	15 h	83
8		 **(4h)**	15 h	84
9		 **(4i)**	13 h	86

[a]Reaction of aromatic aldehydes (1 mmol), 5-amino-1*H*-tetrazole (1 mmol) and 5,5-dimethylecyclohex-1,3-dione (1 mmol) . [b]The yields are isolated through recrystalisation.

IV.12.A.7 Plausible Mechanism

A plausible SRH catalyzed synthesis of tetrahydrotetrazolo[5,1-*b*]quinazolinone derivatives are established considering the acidic

behaviour of the catalyst (**Figure III.13**). At very first step of the reaction, protonation occurs at aldehyde oxygen of aromatic aldehyde followed by Hantzsch condensation of aldehydes with β-diketones and ammonium acetate. Intermediates are produced in situ rapidly undergo cyclization and exters the targeted tetrahydrotetrazolo[5,1-*b*]quinazolinone derivatives product.

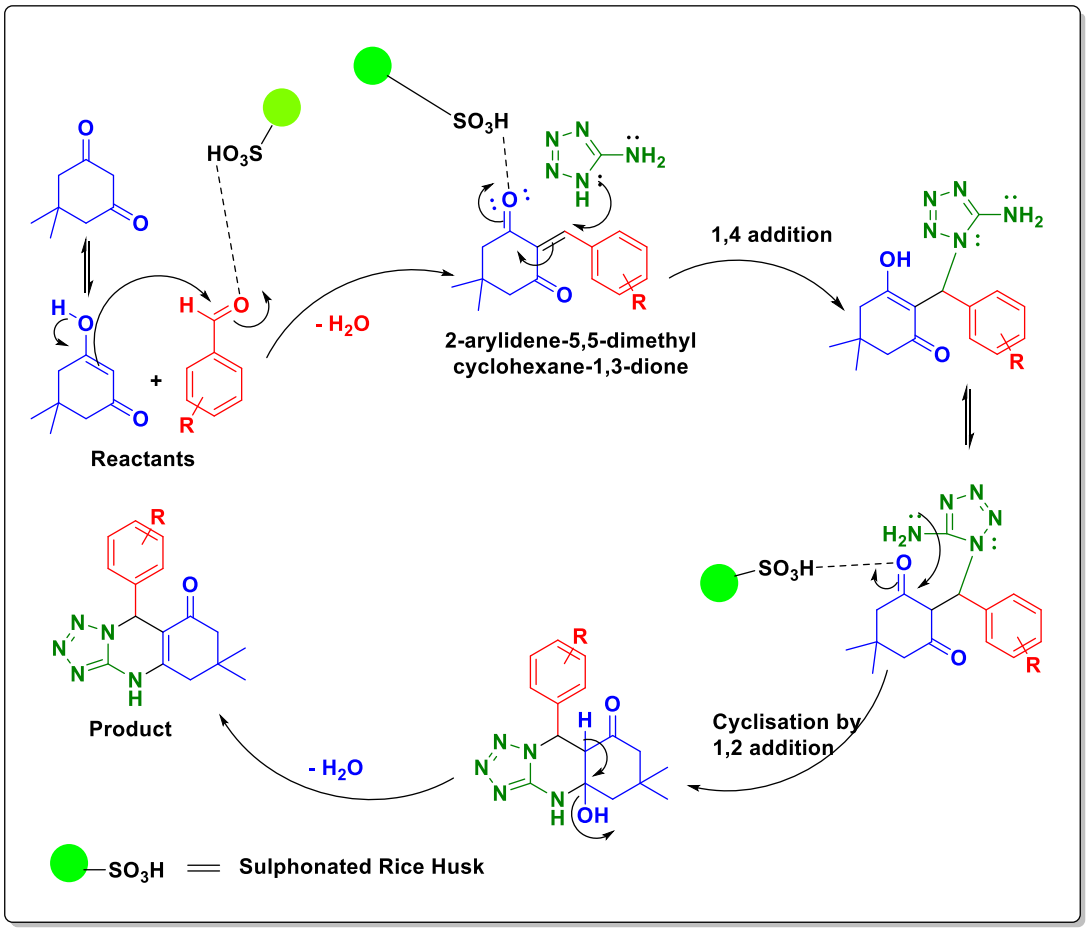
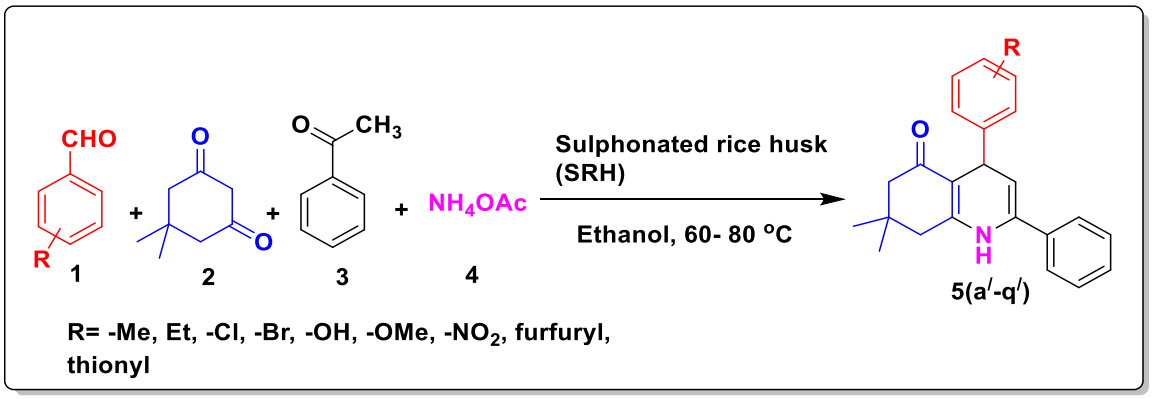


Figure IV.13 The plausible mechanism for the synthesis of tetrahydrotetrazolo[5,1-*b*]quinazolin-8(4*H*)-one

The next present work leads to the synthesis of 2,4-diaryl hexahydroquinoline-5-one derivatives (**Scheme IV.25**) by using greener catalyst heterogeneous catalyst sulphonated rice husk (SRH) .



Scheme IV.25 Synthesis of substituted 2,4-diaryl hexahydroquinoline-5-one derivatives using sulphonated rice husk[a]

IV.12.A.8 Optimization of synthesis of substituted 2,4-diarylhexahydroquinoline-5-one derivatives

One pot synthesis of 2,4-diarylhexahydroquinoline-5-one derivatives was initially carried out with taking aromatic aldehyde (1 mmol) along with acetophenone (1 mmol) and 5,5-dimethylecyclohex-1,3-dione (1 mmol) and ammonium acetate (1 mmol) taken in a 15 mL glassed sealed reaction tube. It was observed that when the reactants are taken at a time in a vessel to react randomly in presence of 120 mg arbitrary amount of catalyst, it produced 9-arylhexahydroacridine as a

major product. Literature studies along with a few controlled experiment suggested that formation of in situ chalcone derivative is important for the synthesis of 2,4-diaryl hexahydroquinoline-5-one as major product. After observing the science behind it, the reaction was started first with condensation reaction between the participated aromatic aldehyde (1 mmol) and acetophenone (1 mmol) in presence of SRH catalyst only for 1 hour followed by addition of 5,5-dimethylecyclohex-1,3-dione (1 mmol) and ammonium acetate (1 mmol) at a time into the reaction mixture. After addition of 5,5-dimethylecyclohex-1,3-dione (1 mmol) and ammonium acetate (1 mmol) the progress of the reaction was monitored continuously by thin layer chromatography (TLC) until the reaction was adequately completed. For determining the optimized reaction condition, vaniline (1 mmol) was taken as the participating aromatic aldehyde along with other substituents. The variation of the amount of catalyst along with temperature were made to determine the precise optimized condition for the reaction (**Table IV.5**). The optimized reaction condition was followed for the synthesis of other compounds under **Scheme IV.25** (5a-5k). The generality of the reaction was observed for the aromatic aldehydes having electron withdrawing, electron donating substituents along with fluorinated, heterocyclic and

polyaromatic aromatic aldehydes. All the products were isolated from ethyl acetate extract of the reaction mixture by column chromatograpy using petroleum ether/ethyl acetate (v/v 70:30).

Table IV.5 Optimization of the reaction condition for the synthesis of 2,4-diaryl hexahydroquinoline-5-one derivatives[a]

Entry	Catalyst (mg)	Solvent	Temperature (^{o} C)	Time	Yield (%)[b]
1	100	Ethanol	100	15 h	85
2	120	Ethanol	100	15 h	85
3	120	Ethanol	120	15 h	85
4	110	Ethanol	90	15 h	85
5.	100	Ethanol	90	14 h	85
6.	90	Ethanol	80	13 h	85
7.	90	Ethanol	70	12 h	85
8.	80	Ethanol	70	12 h	85
9.	70	Ethanol	70	12 h	84
10.	**70**	**Ethanol**	**70**	**11 h**	**82**
11	60	Ethanol	70	11 h	74
12.	70	Neat	70	12 h	30
13.	70	H_2O	70	12 h	-
14	70	Ethanol/H_2O	70	12 h	-
15	70	Methanol	80	12 h	70

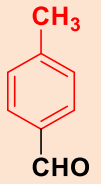
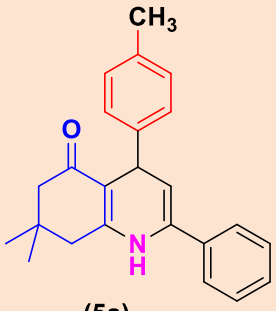
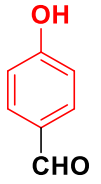
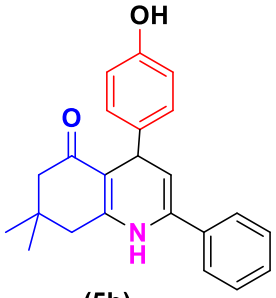
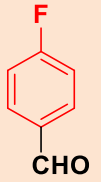
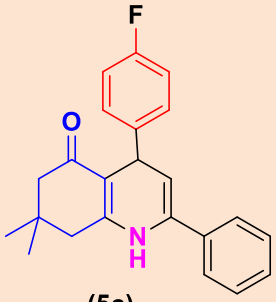
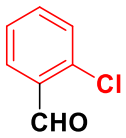
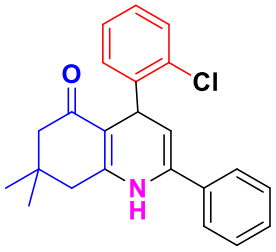
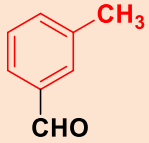
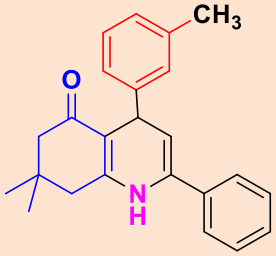
[a] Reaction of Vaniline (1mmol), acetophenone (1mmol), 5,5-dimethyl-cyclohexane-1,3-dione (1mmol), ammonium acetate (1.2 mmol) and SRH (60 mg). [b] The yields are isolated through column chromatography.

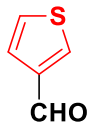
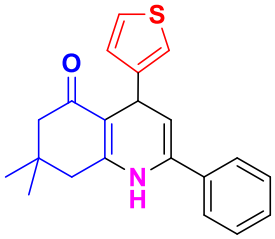
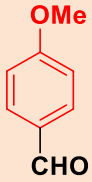
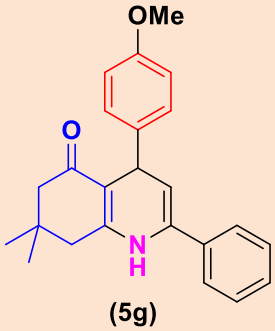
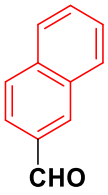
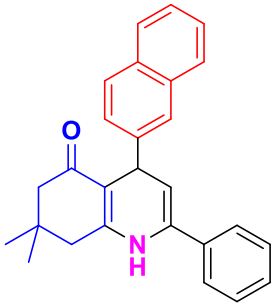
IV.12.A.9 Synthesis of 2,4-diaryl hexahydroquinoline-5-one derivatives

The generality of the reaction was observed with a variety of aromatic and heterocyclic aldehydes (**Scheme IV.25**) having electron donating and electron withdrawing substituents at *ortho*, *meta* and *para* position of the aromatic aldehyde. The targeted compounds (4a-4j) are successively synthesized using SRH as an efficient catalyst under greener reaction condition.(**Table IV.6**) The progress of the reaction was monitored continuously by thin layer chromatography (TLC) and the crude product was separated from ethylacetate extract by addition of petroleum ether followed by purification through washing with petroleum ether/ethyl acetate mixture given in experimental section.

Table IV.6 Synthesis of 2,4-diaryl hexahydroquinoline-5-one derivatives[a]

Entry	Reactant	Product	Time	Yield(%)[b]

1		 **(5a)**	12 h	86
2		 **(5b)**	12 h	86
3		 **(5c)**	12 h	83
4		 **(5d)**	12 h	86
5		 **(5e)**	12 h	85

6		 (5f)	12 h	84
7		 (5g)	12 h	85
8		 (5h)	12 h	87

[a] Reaction of aromatic aldehyde (1mmol), 5,5-dimethyl-cyclohexane-1,3-dione (1 mmol), acetophenone (1 mmol) cyclohexylamine (1 mmol) and SRH (50 mg). The yields are isolated through column chromatography.

IV.12.A.10 Plausible Mechanism

The mechanism of the reaction starts with the protonation of the aldehyde and the condensation of aldehyde and acetophenone to give chalcone derivative. (**Figure IV.14**) And then successive cyclocondensation of chalcone, present dimedone and ammonium

acetate (NH_4OAc) catalysed by SRH catalyst gives rise to the formation of 2,4-diarylhexahydroquinoline.

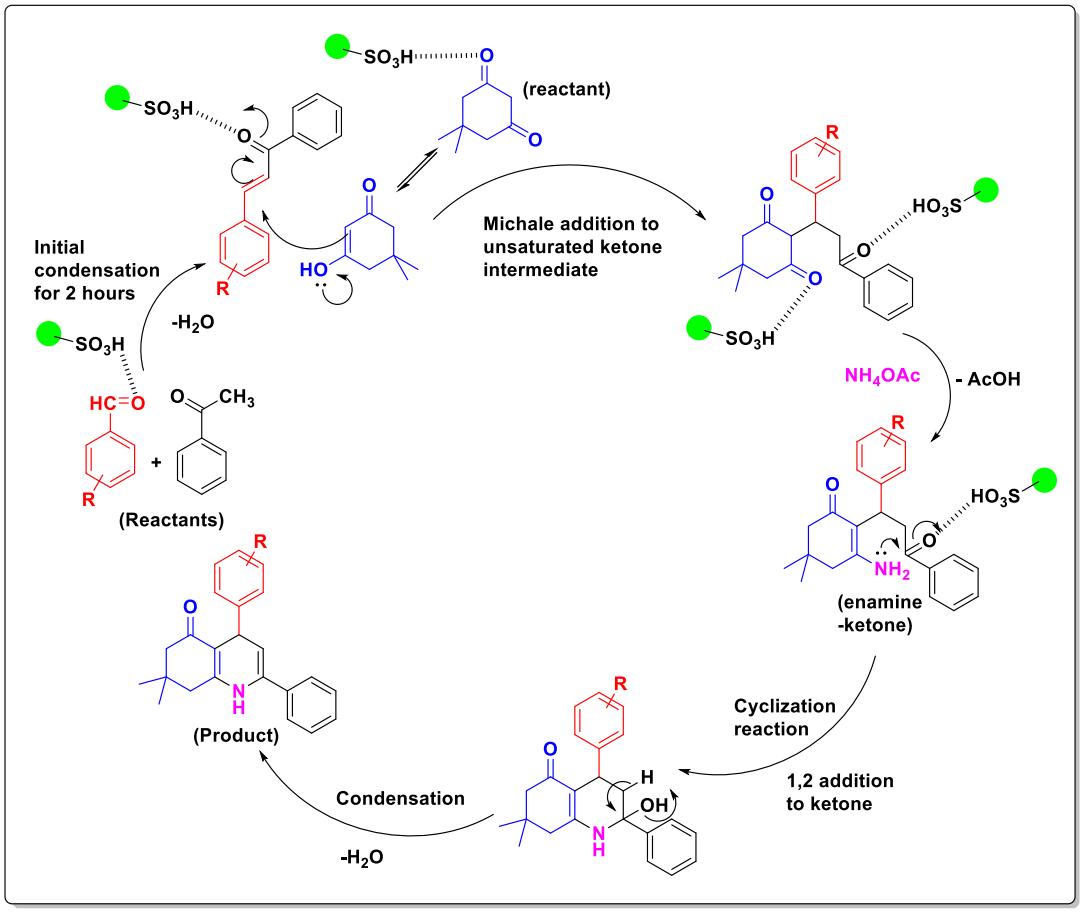


Figure IV.14 The plausible mechanism for the synthesis of 2,4-diaryl hexahydroquinoline-5-one derivatives

IV.12.A.11 Catalyst Recyclability Experiment

To check the recyclability of the catalyst, a model reaction between benzaldehyde (2 mmol), 4-hydroxycoumarine (4 mmol), ammonium acetate (2 mmol) in presence of 120 mg of sulphonated rice husk was

carried out under optimised reaction condition. (**Scheme IV.25, Table IV.7**) After successful completion of the each reaction step, ethyl acetate (10 ml) was added to the reaction mixture. The supernatant liquid (ethyl acetate extract) was decanted off and this process was repeated until the catalyst was free from reaction mixture. Then the recovered catalyst was washed with acetone repeatedly and dried under vaccum. The recovered catalyst weight was measured after every recovery step and the next reaction was repeated with that amount of recovered catalyst by following proportionality with the aldehyde amount (mmol). The temperature and time of the reaction were kept constant following optimized reaction condition. Amount of catalyst, reactant (aldehyde), reaction time, temperature and yield percentage of the product have been shown in **Table IV.7** (**entry 1-6**). The FTIR spectra of recovered SRH catalyst after successive reactions was added here for further support of the catalyst efficiency. (**Figure IV. 15 and Figure IV. 16**).

Table IV.7 Table for the amount of recovered catatyst with isolated [a]

Entry	Catalyst (mg)	Aldehyde (x mmol)	Temperature (^{o} C)	Time (min)	Yield (%)[b]
1	120	2.00 mmol	70	180	98
2	110	1.83 mmol	70	180	94

3	100	1.66 mmol	70	180	87
4	90	1.50 mmol	70	180	80
5.	80	1.33 mmol	70	180	75
6.	70	1.16 mmol	70	180	70

[a] Reaction of anisaldehyde (x mmol), 4-hydroxycoumarine (2x mmol), ammonium acetate (x mmol), [b] Isolated yield

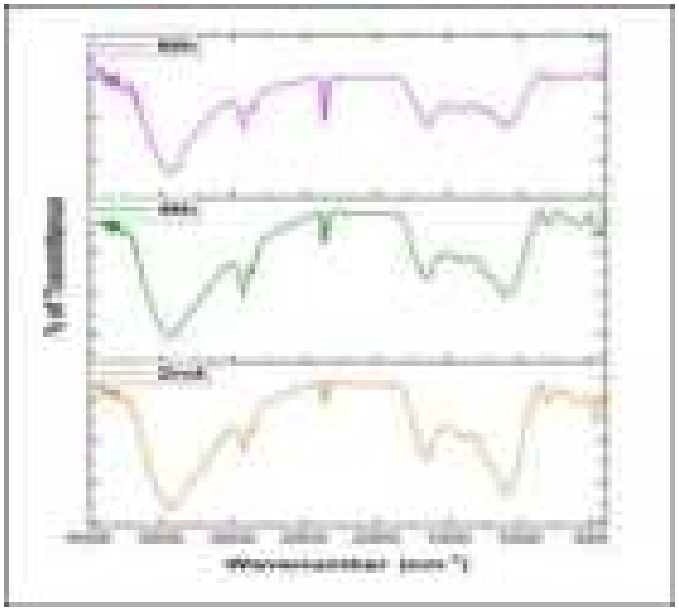


Figure IV.15 FTIR spectra of reused catalysts after 2nd, 4th and 6th run.

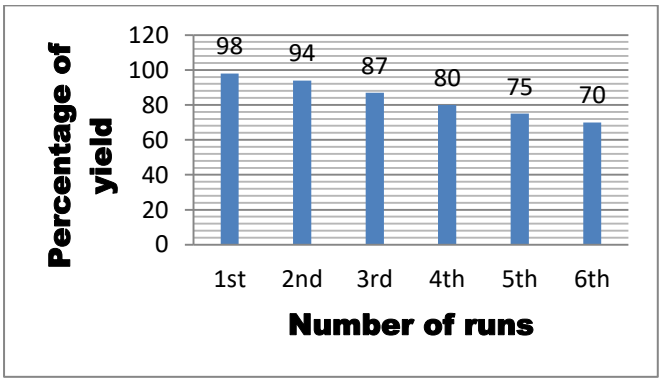


Figure IV.16 Recyclability experiment of catalyst

IV.12.A.12 Conclusion

In conclusion, a simple and greener methodology for the synthesis of a variety of substituted dihydro-dichromeno-pyridine-6,8-diones, tetrahydrotetrazolo[5,1-*b*]quinazolin-8(4*H*)-ones and 2,4-diarylhexahydroquinolinone derivatives with a good yield. This heterogeneous catalyst is found to be sufficiently efficient for the synthesis of dihydro-dichromeno-pyridine-6,8-diones, tetrahydrotetrazolo[5,1-*b*]quinazolin-8(4*H*)-ones and 2,4-diarylhexahydroquinolinone derivatives in a greener way. The greener catalyst is highly recyclable upto 6^{th} run and has the ability to catalyse wide range of acid-catalysed reactions or cyclocondensation reactions.

IV.12.A.13 Acknowledgement

. One of the authors (S.D) is thankful to UGC, New Delhi for financial support, PU Saif for SEM, EDX, powder XRD and NMR analysis for this above work.

IV.12.A.14 Experimental

IV.12.A.14.a Catalyst preparation

The heterogeneous catalyst (SRH) was prepared by direct sulphonation of rice husk (RH) already described in Chapter II .[102]

IV.12.A.14.b General procedure for synthesis of dihydro-dichromeno-pyridine-6,8-dione derivatives

A mixture of 4-hydroxycoumarine (2 mmol), aromatic aldehyde (1 mmol), ammonium acetate (NH_4OAc) (1.2 mmol), and SRH (60 mg) in a 20-mL glass sealed tube was stirred at 60^0C temperature for 240 min. The progress of the reaction was monitored by thin-layer chromatography (TLC) (**Scheme IV.23**). After completion of the reaction, the product was first extracted with ethyle acetate solvent and the catalyst was separated by simple filtration with filter paper. Then ethyl acetate extract was concentrated and the product was isolated in petroleum ether and the crude product was purified by washing the crude with petroleum ether, ethylacetate-petroleum ether mixed solvent (1:6 and 1:4).

IV.12.A.14.c General procedure for synthesis of tetrahydrotetrazolo[5,1-b]quinazolin-8(4H)-one derivatives

A mixture of 5,5-Dimethylcyclohexane-1,3-dione (1 mmol), aromatic aldehyde (1 mmol), 5-aminoterazole (1.2 mmol), and SRH (100 mg) in a 25-mL round bottom flusk was stirred at 70 ^{o}C temperature for 15h in

ethanol. The progress of the reaction was monitored by thin-layer chromatography (TLC) (**Scheme IV.24**). After completion of the reaction, the product was extracted with ethyle acetate and the catalyst was separated by simple filtration. Then ethyl acetate extract was concentrated and crude product was sperated by simple preceipitation in petroleum ether then was purified by washing the crude with ethyacetate/petroleum ether mixture (1:4)

IV.12.A.14.d General procedure for synthesis of 2,4-diarylhexahyroquinolines

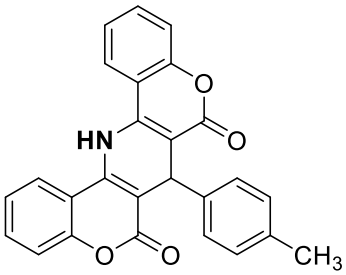
A mixture aromatic aldehyde (1 mmol) and acetophenone (1 mmol) was strirred at 70^0C temperature for 1 hour in a sealed tube in ethanol in presence of SRH catalyst then of 5,5-Dimethylcyclohexane-1,3-dione (2 mmol) and ammonium acetate (NH_4OAc) (1.2 mmol) was added to it and stirred at 70 ^{o}C temperature for 60 minutes. The progress of the reaction was monitored by thin-layer chromatography (TLC) (Scheme IV.25). After completion of the reaction, the product was extracted with ethyle acetate and the pure product was separated by column chromatography.

IV.12.A.14.e General Procedure for ^{1}H & ^{13}C NMR

NMR spectra of all the products were taken in DMSO-d_6 (TMS as an internal standard) using a Bruker 400MHz spectrometer(operating for ^{1}H at 400 MHz and for ^{13}C at 100 MHz) and Bruker Advance NEO 500MHz spectrometer(operating for ^{1}H at 500 MHz and for ^{13}C at 125 MHz). ^{1}H-NMR spectroscopic data are represented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet, br = broad), integration, coupling constants in Hertz (Hz). ^{13}C NMR spectroscopic data are reported in ppm.

IV.12.A.14.f Spectral data of the compounds mentioned in Scheme IV.23

7-(p-tolyl)-7,14-dihydro-6*H*,8*H*-dichromeno[4,3-*b*:3',4'-*e*]pyridine-6,8-dione(4a)



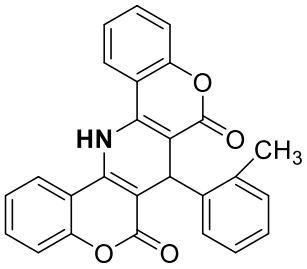
^{1}H-NMR(500MHz,DMSO-d_6)

δ(ppm)2.23(s,3H),6.25(s,1H),6.97-7.01(m,5H),7.23-7.26(q,2H),7.27-7.28(d,2H),7.49-7.53(m,2H),7.83-7.85(m,2H).

^{13}C-NMR(500MHz,DMSO-d_6)

δ(ppm)20.42,35.67,103.57,115.43,119.59,122.91,123.99,126.51,128.26,130.92,133.54,138.71,152.36,164.64,167.29.

7-(o-tolyl)-7,14-dihydro-6*H*,8*H*-dichromeno[4,3-*b*:3',4'-*e*]pyridine-6,8-dione(4b)



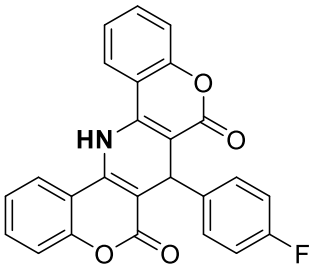
^{1}H-NMR(500MHz,DMSO-d$_6$)

δ(ppm)2.08(s,3H),6.09(s,1H),6.69-7.02(m,3H),7.20-7.29(m,6H),7.47-7.50(m,2H),7.80-7.82(m,2H).

^{13}C-NMR(500MHz,DMSO-d$_6$)

δ(ppm)19.47,35.44,103.05,115.80,119.82,122.77,123.94,124.62,124.98,128.16,129.92,130.64,135.47,152.24,163.98,167.81.

7-(4-fluorophenyl)-7,14-dihydro-6*H*,8*H*-dichromeno[4,3-*b*:3',4'-*e*]pyridine-6,8-dione(4c)



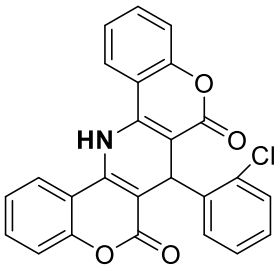
^{1}H-NMR(500MHz,DMSO-d$_6$)

δ(ppm)6.26(s,1H),6.97-7.14(m,2H),7.22(m,2H),7.24-7.28(m,2H),7.33-7.37(m,2H),7.49-7.53(m,2H),7.82-7.84(m,2H),17.59(broad s,1H).

^{13}C-NMR(500MHz,DMSO-d$_6$)

δ(ppm)36.52,103.33,114.12,114.28,115.42,119.89,122.89,124.07,128.23,128.29,130.95138.07,138.09,152.14,159.23,161.04,164.58,167.79.

7-(2-chlorophenyl)-7,14-dihydro-6*H*,8*H*-dichromeno[4,3-*b*:3',4'-*e*]pyridine-6,8-dione(4d)



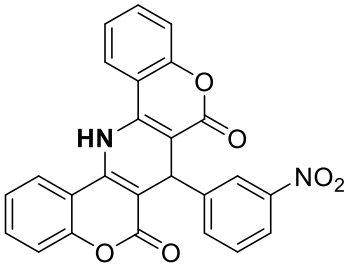
^{1}H-NMR(500MHz,DMSO-d_6)

δ(ppm)6.18(s,1H),7.20-7.26(m,9H),7.42-7.51(m,3H),7.82-7.84(m,2H),17.15(broad s,1H).

^{13}C-NMR(500MHz,DMSO-d_6)

δ(ppm)36.02,90.71,103.29,115.33,116.24,119.84,122.73,123.74,124.66,126.54,126.56,127.56,130.76,132.51,142.29,152.40,153.45,161.85,164.44,165.84,167.57.

7-(3-nitrophenyl)-7,14-dihydro-6*H*,8*H*-dichromeno[4,3-*b*:3',4'-*e*]pyridine-6,8-dione(4e)



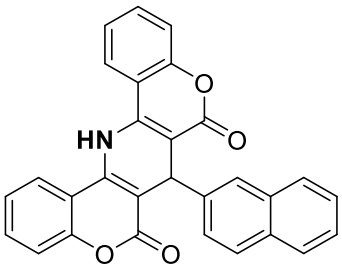
^{1}H-NMR(500MHz,DMSO-d_6)

δ(ppm)6.39(s,1H),7.24-7.31(m,4H),7.49-7.55(m,3H),7.59-7.61(m,1H),7.83-7.85(m,2H),7.92(d,1H), 8.00-8.02(m,2H),17.48(broad s,1H).

^{13}C-NMR(500MHz,DMSO-d_6)

δ(ppm)36.19,102.59,115.55,119.59,120.28,121.01,123.06,124.13,129.31,131.76,145.00,147.70,152.49,164.44,167.99.

7-(naphthalen-2-yl)-7,14-dihydro-6*H*,8*H*-dichromeno[4,3-*b*:3',4'-*e*]pyridine-6,8-dione(4f)



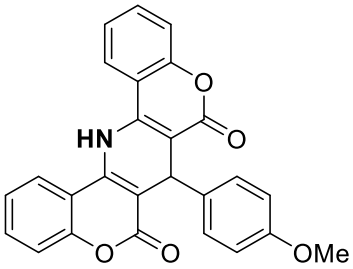
^{1}H-NMR(400MHz,DMSO-d_6)

δ(ppm)6.44(s,1H),7.23-7.31(m,5H),7.36-7.40(m,3H),7.51-7.59(m,3H),7.70-7.72(m,2H),7.78-7.80(m,2H),7.82-7.84(m,2H),17.55(broad s,1H).

^{13}C-NMR(500MHz,DMSO-d_6)

δ(ppm)36.43,103.30,114.32,115.43,115.72,116.26,116.70,119.88,122.85,123.11,123.15,123.82,124.06,124.08,124.67,125.45,126.21,127.03,127.05,127.36,130.88,131.30,132.04,132.60,132.94,140.02,152.47,153.43,153.59,155.50,161.54,161.82,164.59,165.58,167.88.

7-(4-methoxyphenyl)-7,14-dihydro-6*H*,8*H*-dichromeno[4,3-*b*:3',4'-*e*]pyridine-6,8-dione(4g)



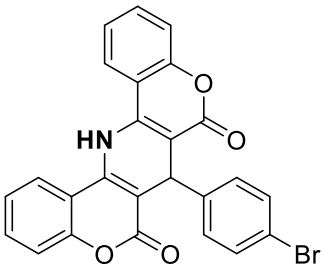
^{1}H-NMR(500MHz,DMSO-d_6)

δ(ppm)3.68(s,3H),6.20(s,1H),6.72-6.74(dd,2H),7.00(d,2H),7.21-7.26(m,4H),7.48-7.51(m,2H),7.80-7.82(dd,2H),17.59(broad s,1H).

^{13}C-NMR(500MHz,DMSO-d_6)

δ(ppm)35.25,54.77,103.56,113.01,115.32,119.86,122.74,123.98,127.50,130.73,133.94,152.37,156.69,164.50,167.54.

7-(4-bromophenyl)-7,14-dihydro-6*H*,8*H*-dichromeno[4,3-*b*:3',4'-*e*]pyridine-6,8-dione(4h)



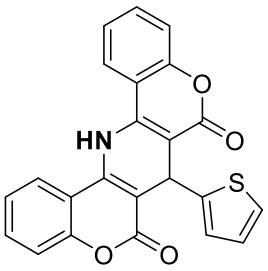
^{1}H-NMR(500MHz,DMSO-d_6)

δ(ppm)6.23(s,1H),7.06-7.08(m,2H),7.22-7.28(m,4H),7.34-7.37(m,2H),7.49-7.53(m,2H),7.82-7.84(m,2H),17.53(broad s,1H).

^{13}C-NMR(500MHz,DMSO-d_6)

δ(ppm)35.77,103.00,115.43,117.74,119.73,122.89,124.06,128.94,130.46,130.98,141.79,152.43,164.50,167.78.

7-(thiophen-2-yl)-7,14-dihydro-6*H*,8*H*-dichromeno[4,3-*b*:3',4'-*e*]pyridine-6,8-dione(4i)



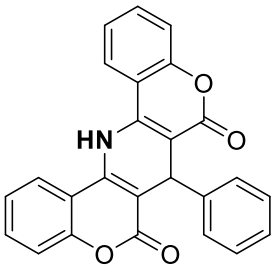
^{1}H-NMR(500MHz,DMSO-d_6)

δ(ppm)6.42(s,1H),6.60-6.61(m,1H),6.80-6.81(dd,1H),7.14-7.15(dd,1H),7.23-7.27(m,5H),7.50-7.53(m,2H),7.85-7.87(dd,3H),17.91(broad s,1H).

^{13}C-NMR(500MHz,DMSO-d_6)

δ(ppm)32.85,103.64,115.42,119.79,122.55,122.89,122.94,124.14,126.02,131.02,147.96,152.39,164.08,167.88.

7-phenyl-7,14-dihydro-6*H*,8*H*-dichromeno[4,3-*b*:3',4'-*e*]pyridine-6,8-dione(4j)



^{1}H-NMR(500MHz,DMSO-d_6)

δ(ppm)6.27(s,1H),7.05-7.10(m,3H),7.14-7.17(m,2H),7.21-7.26(m,4H),7.33-7.37(m,1H),7.485-7.519(m,2H),7.62-7.66(m,1H),7.80-7.84(m,3H).

^{13}C-NMR(500MHz,DMSO-d_6)

δ(ppm)36.02,103.29,116.24,119.84,122.73,123.74,124.66,126.54,127.56,130.76,132.51,142.29, 153.45,164.44,167.57.

IV.12.A.14.g Sanned copies of compounds mentioned in Scheme IV.23

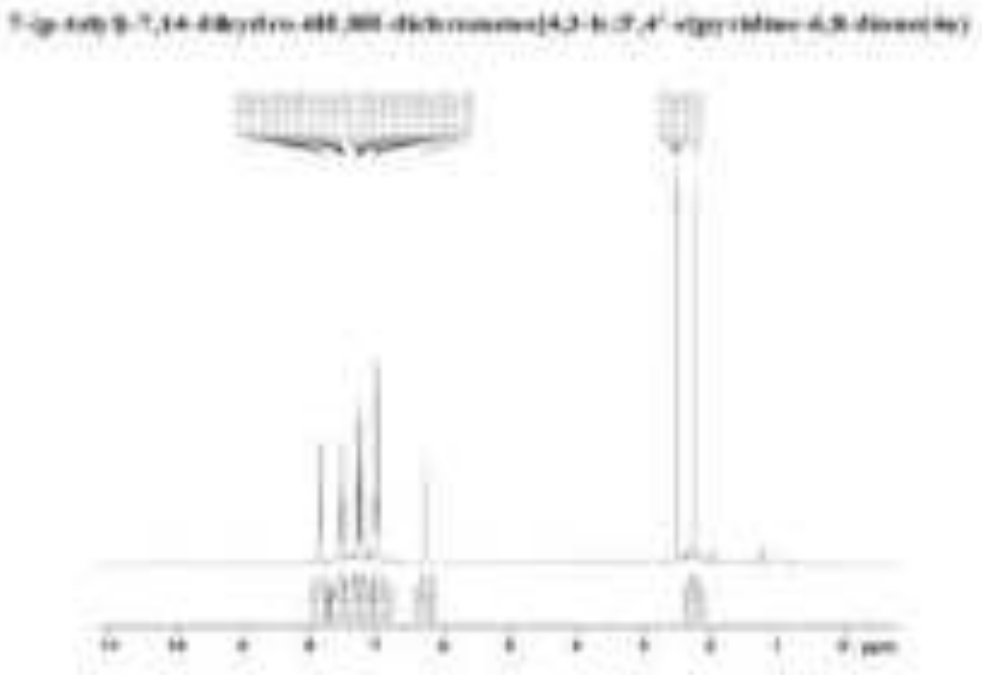


Figure IV.17-^{1}H-NMR of compound 4a

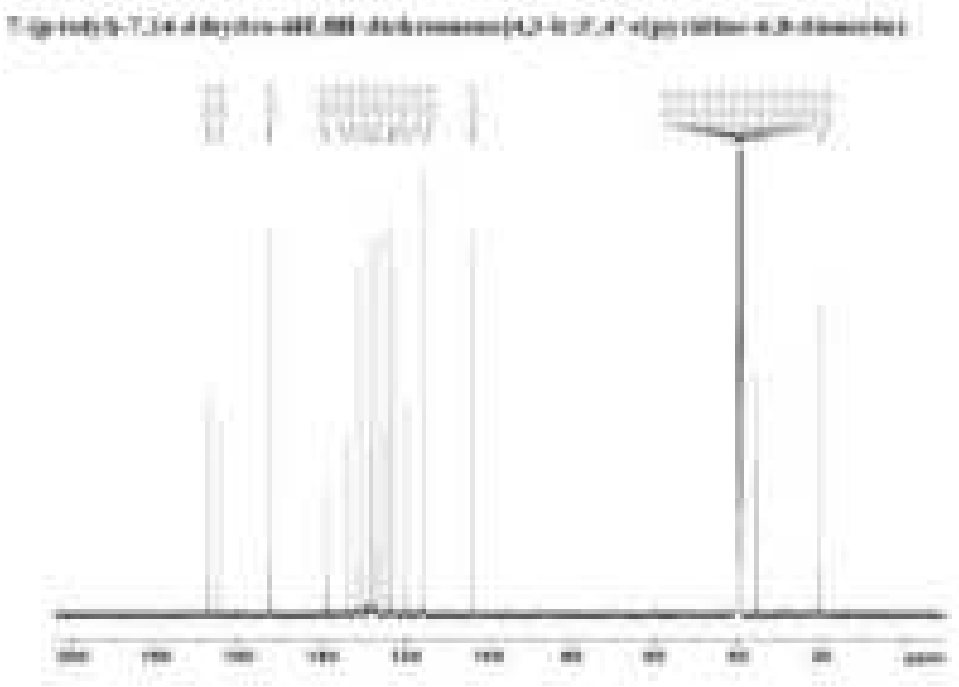


Figure IV.18-^{13}C-NMR of compound 4a

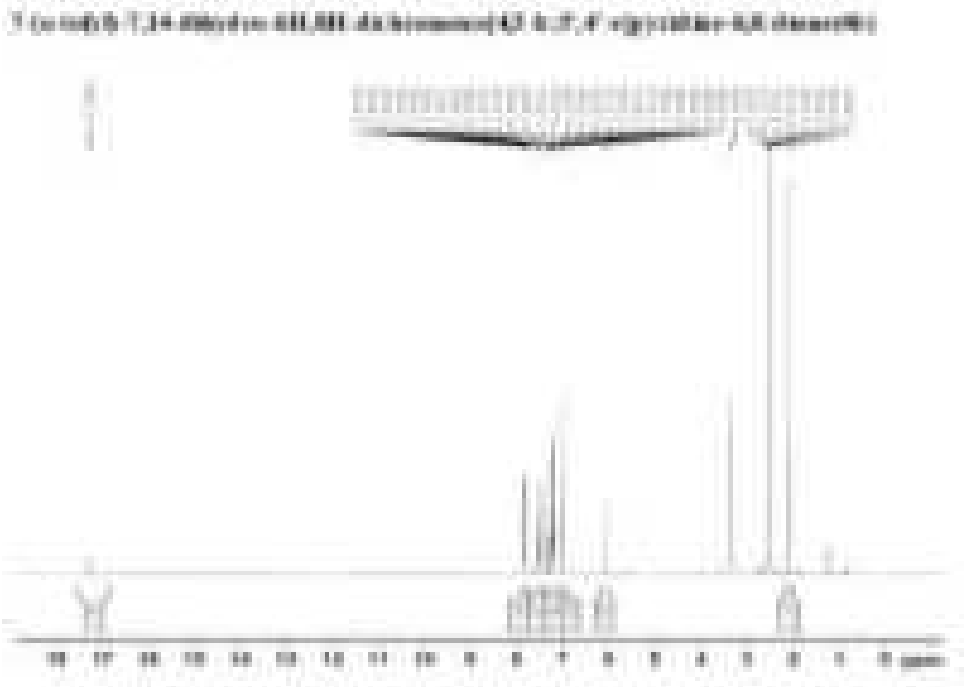


Figure IV.19-^{1}H-NMR of compound 4b

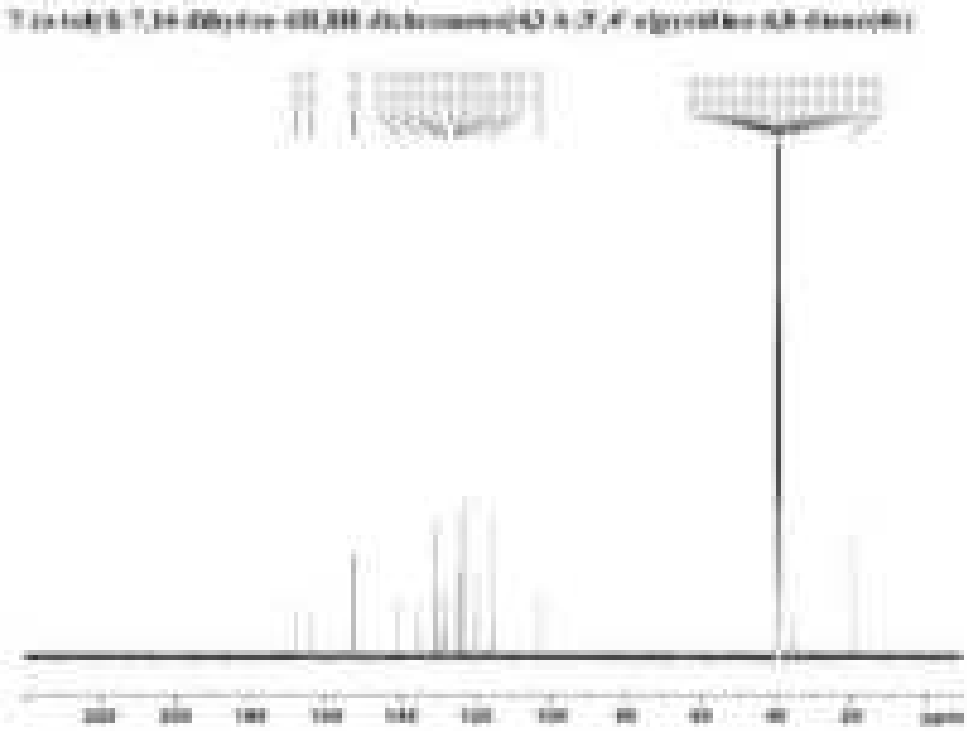


Figure IV.20-^{13}C-NMR of compound 4b

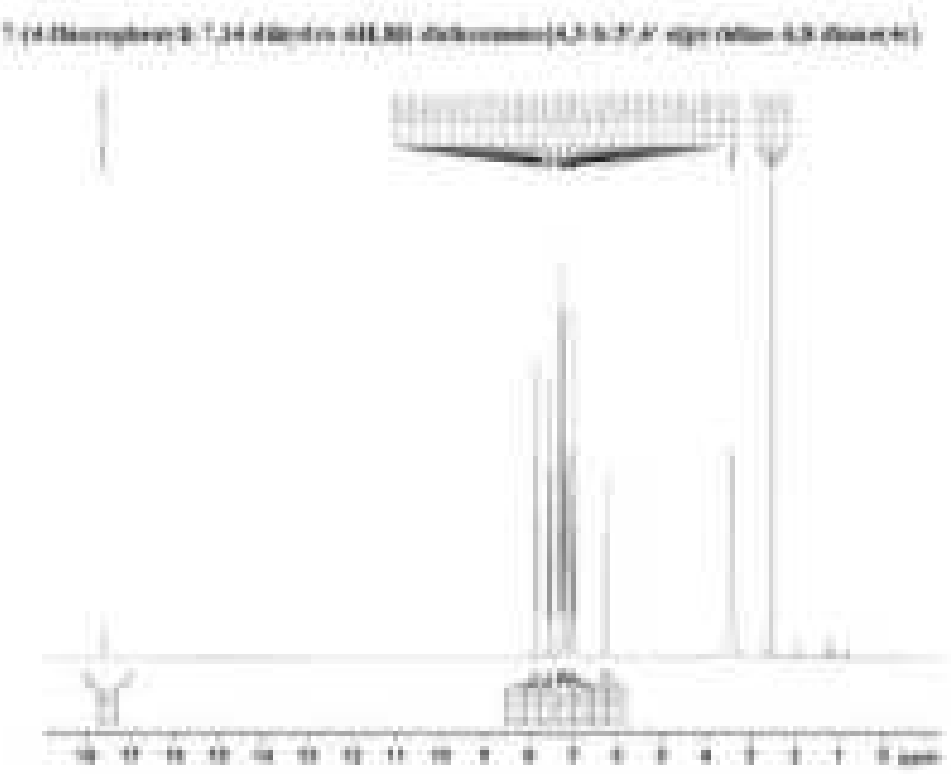


Figure IV.21-^{1}H-NMR of compound 4c

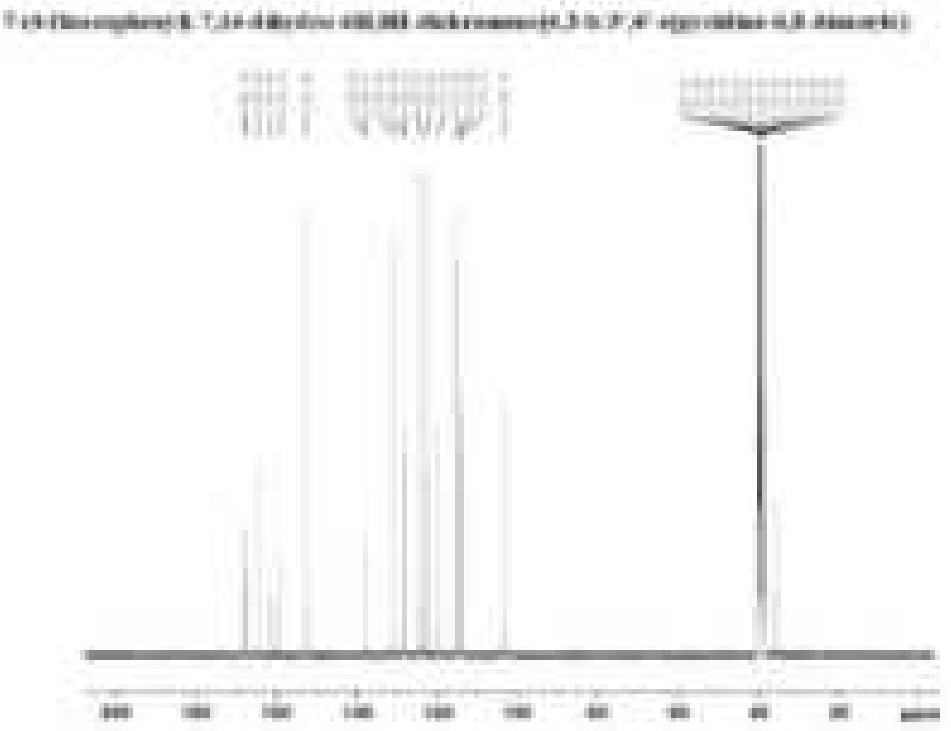


Figure IV.22-^{13}C-NMR of compound 4c

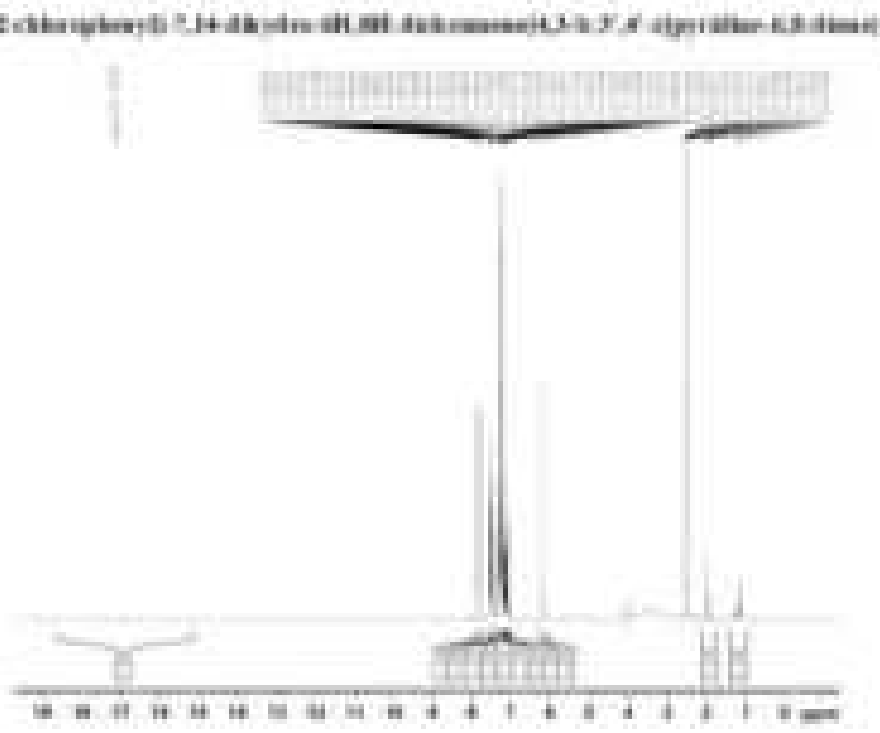


Figure IV.23-^{1}H-NMR of compound 4d

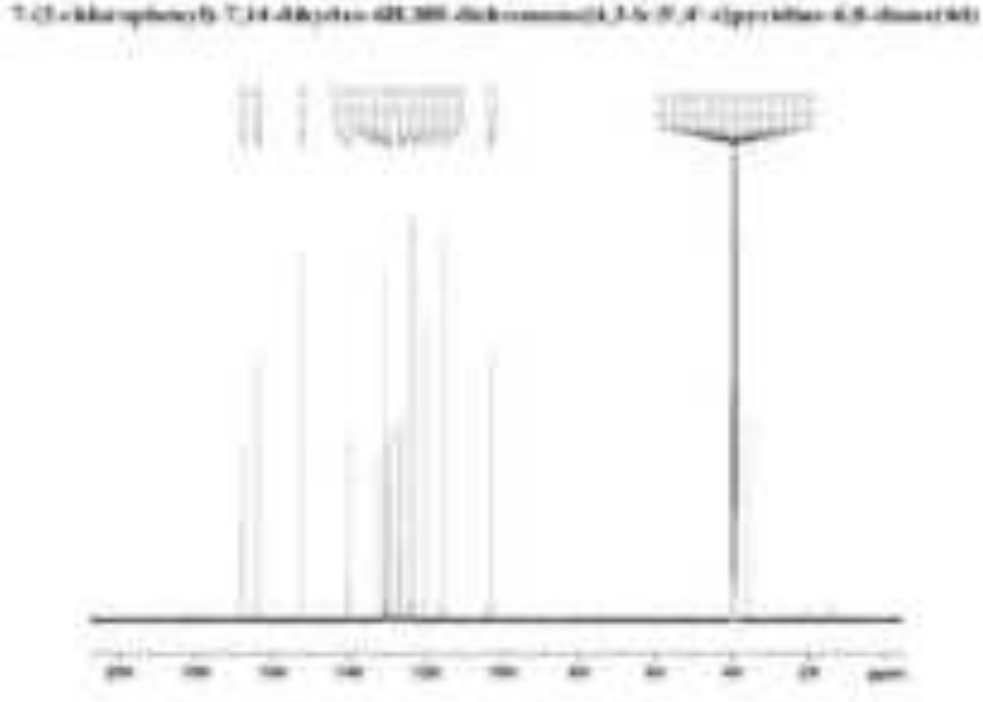


Figure IV.24-^{13}C-NMR of compound 4d

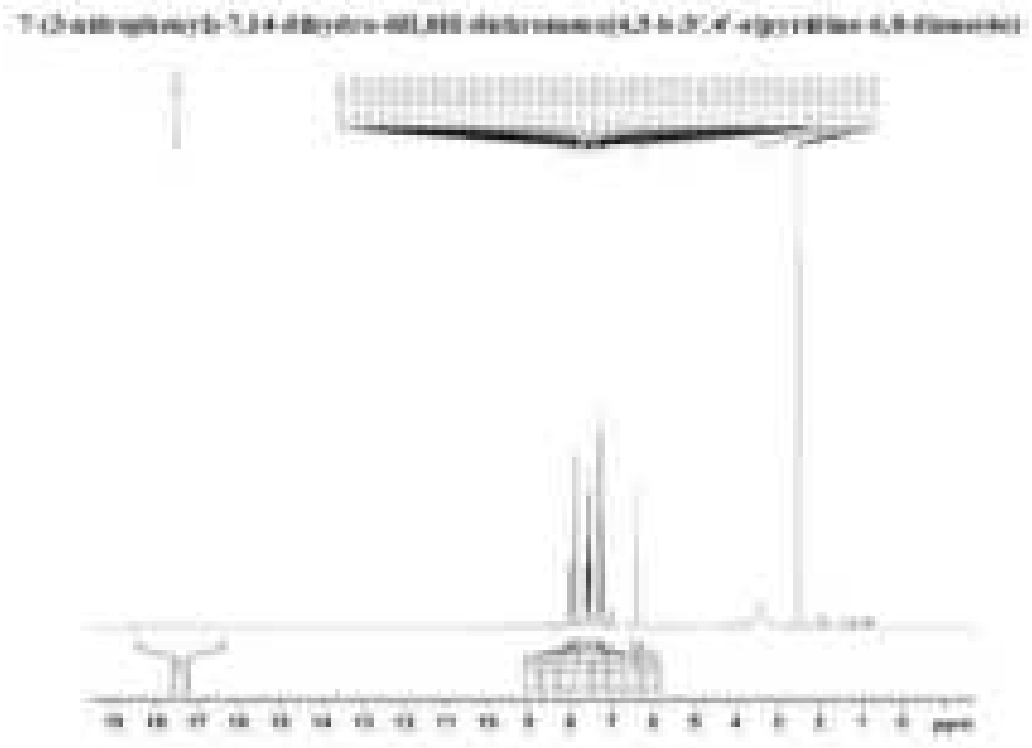


Figure IV.25-^{1}H-NMR of compound 4e

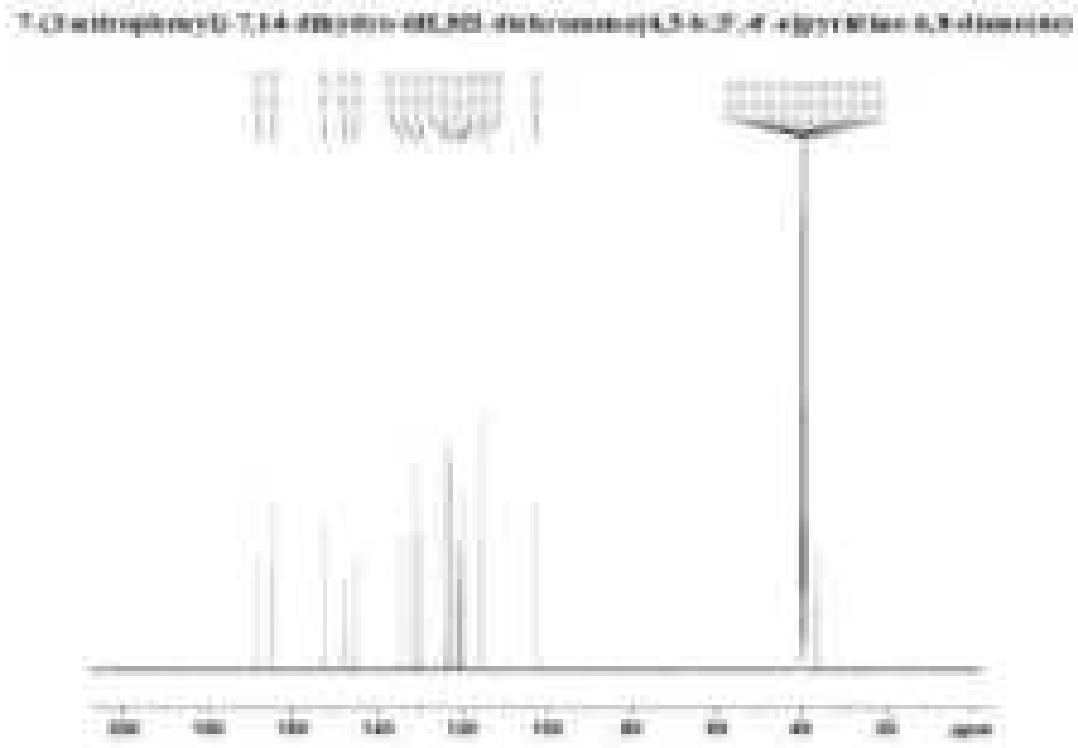


Figure IV.26-^{13}C-NMR of compound 4e

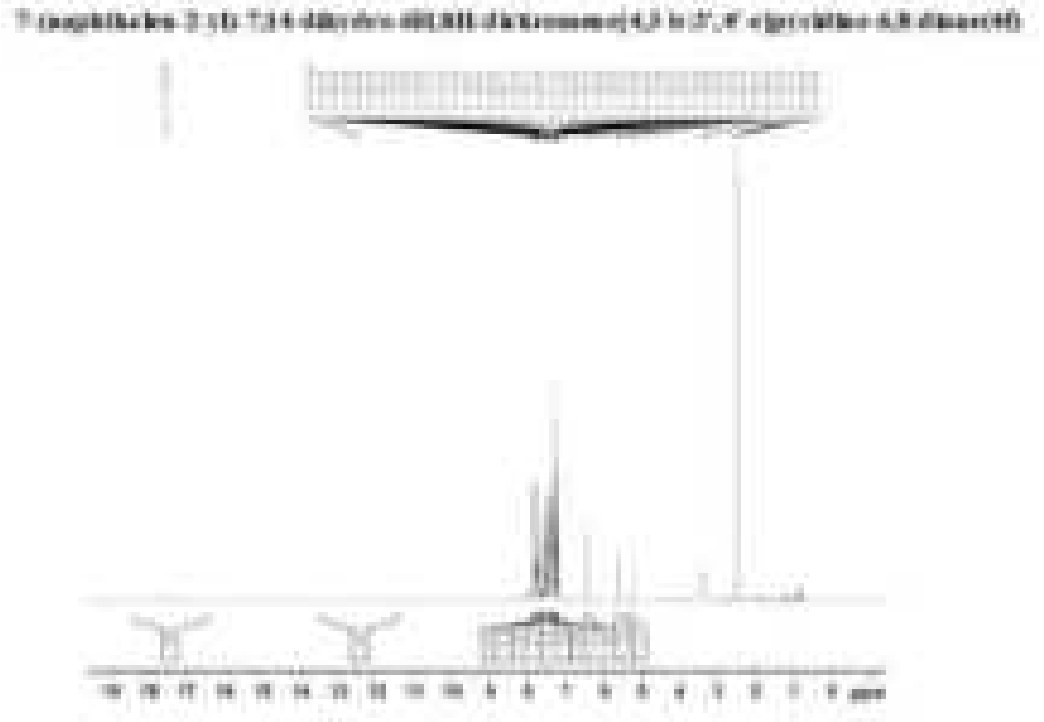


Figure IV.27-^{1}H-NMR of compound 4f

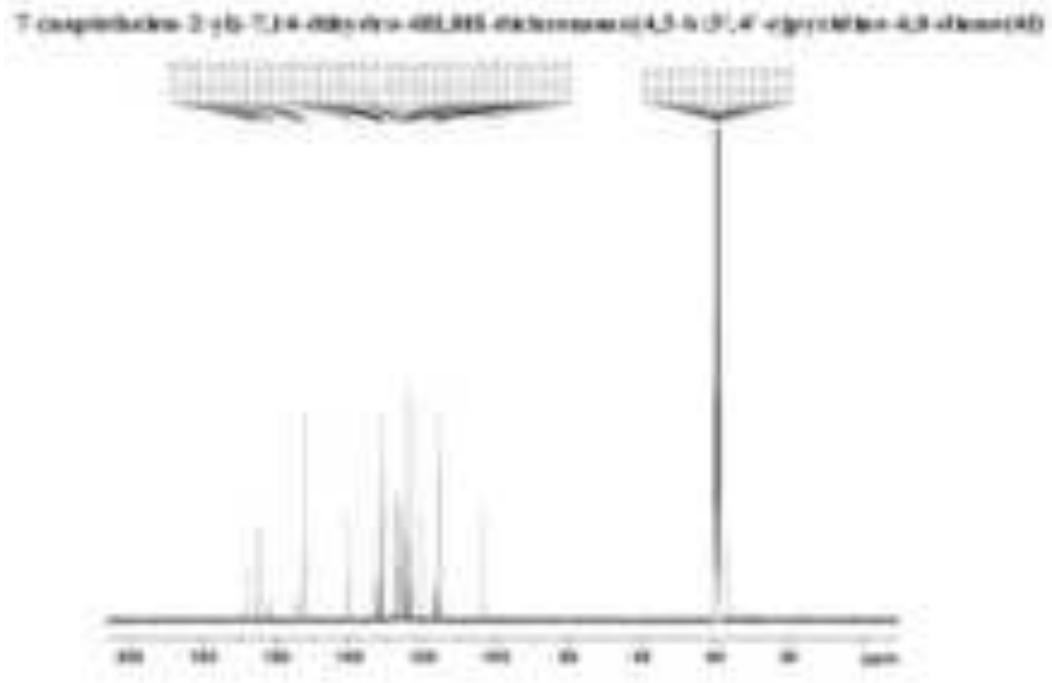


Figure IV.28-^{13}C-NMR of compound 4f

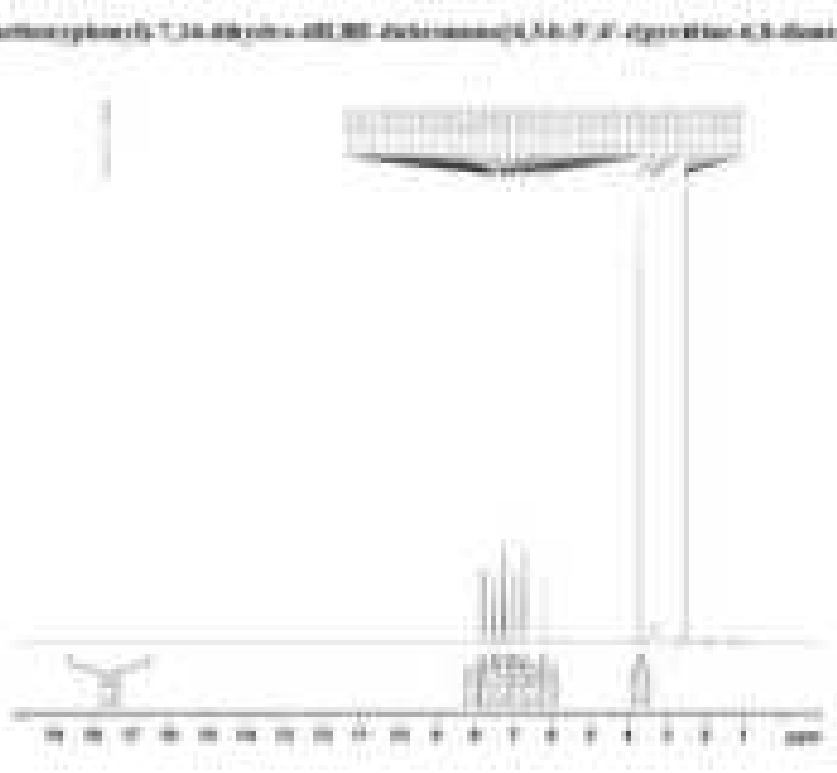


Figure IV.29-^{1}H-NMR of compound 4g

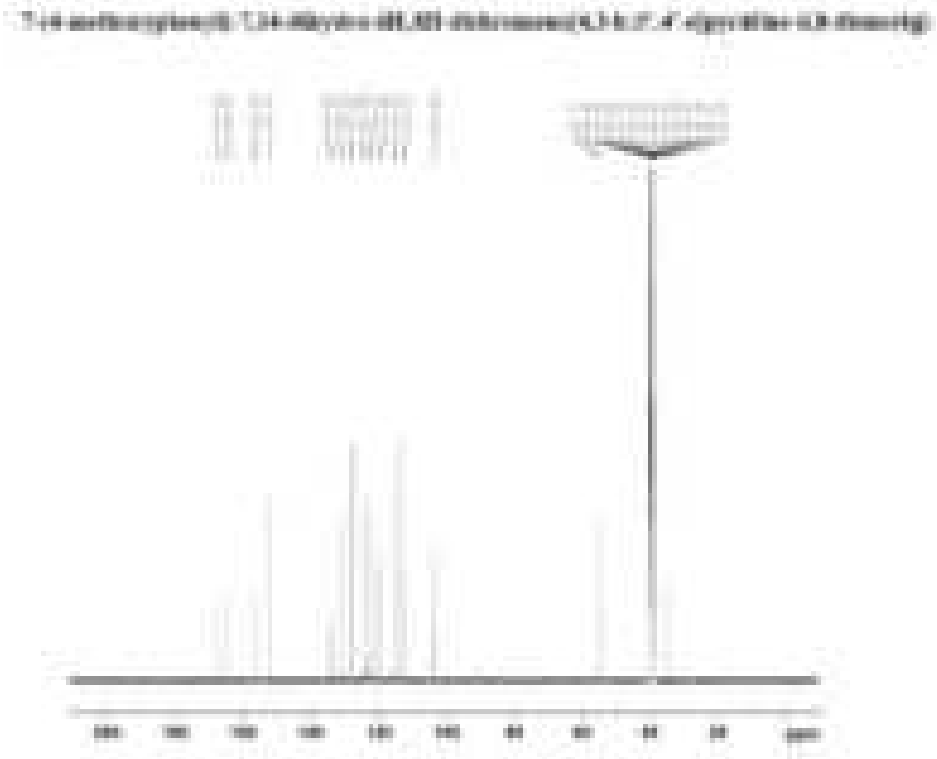


Figure IV.30-^{13}C-NMR of compound 4g

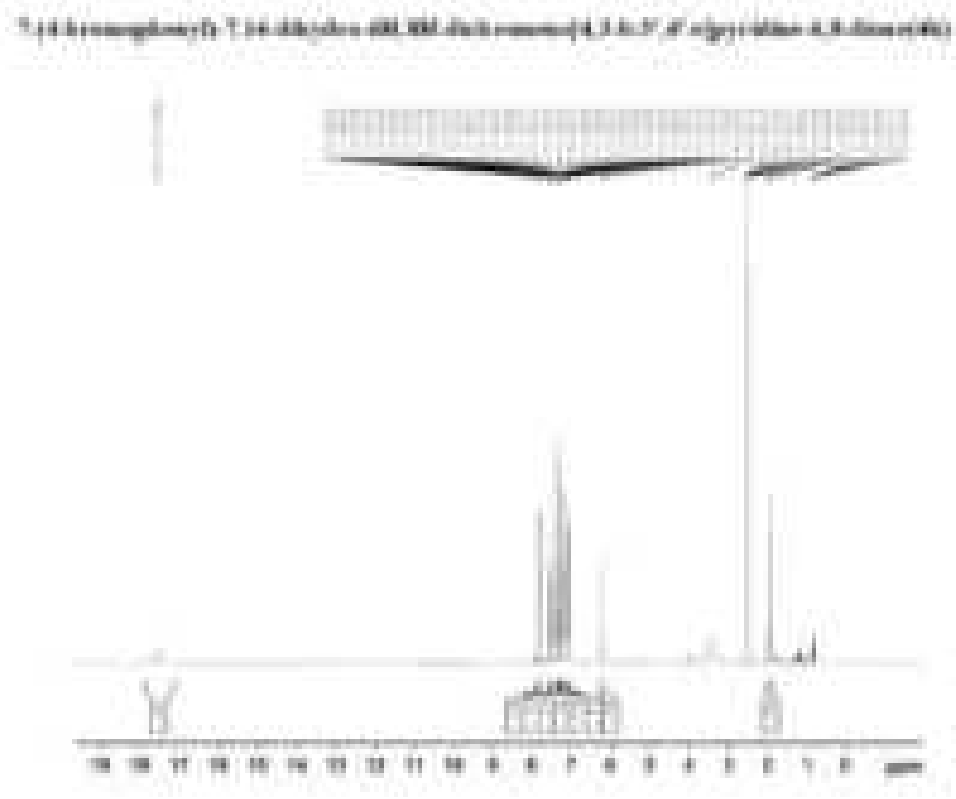


Figure IV.31-^{1}H-NMR of compound 4h

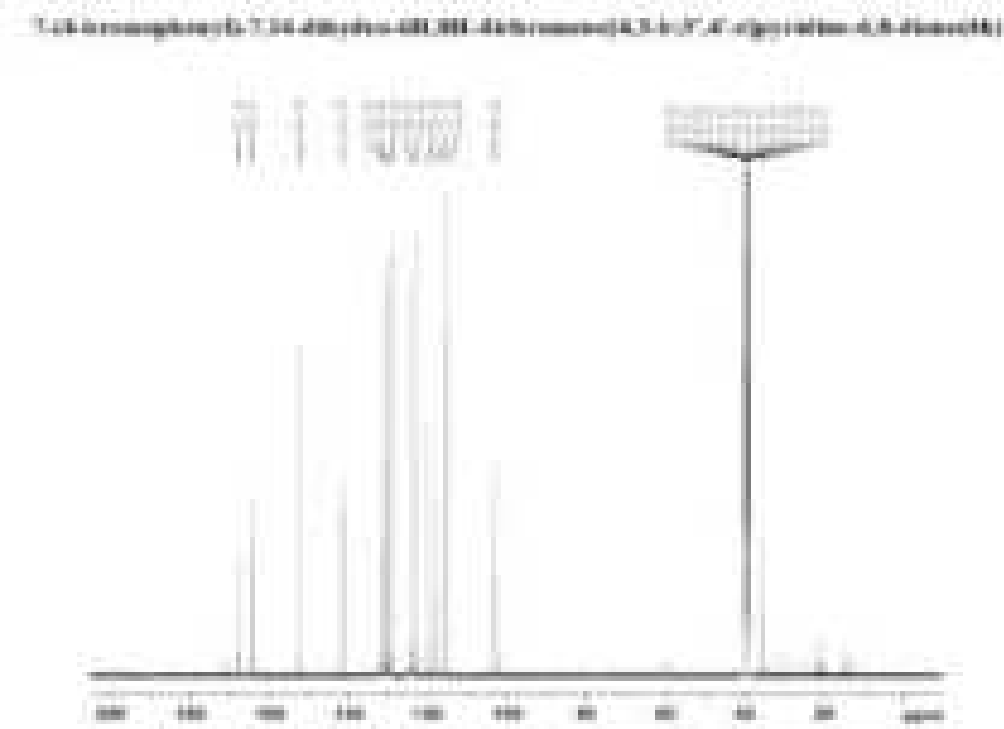


Figure IV.32-^{13}C-NMR of compound 4h

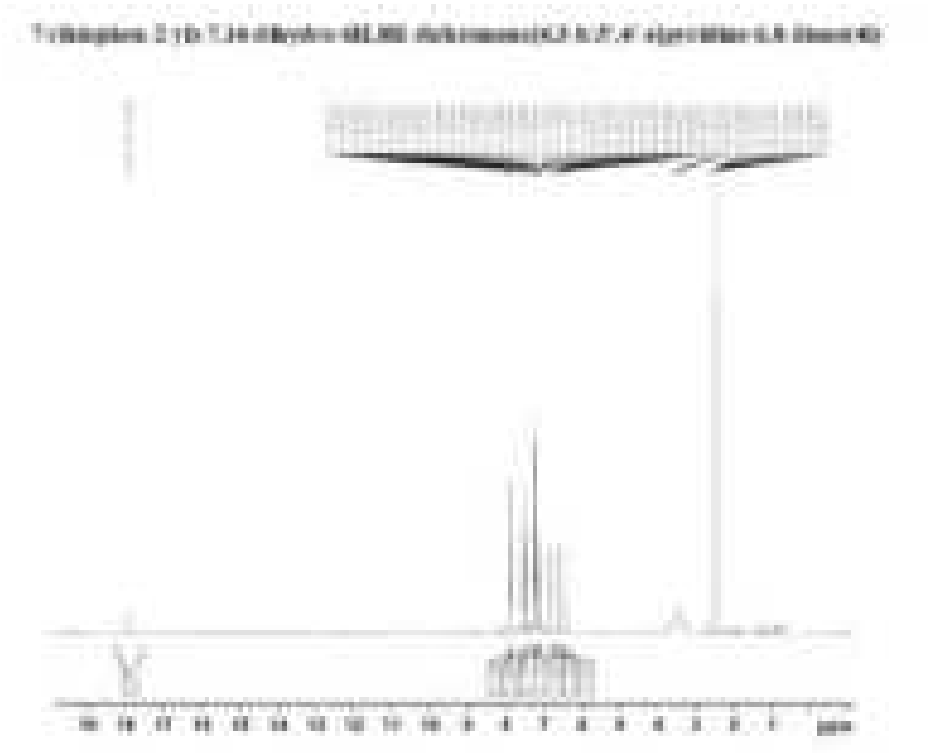


Figure IV.33-^{1}H-NMR of compound 4i

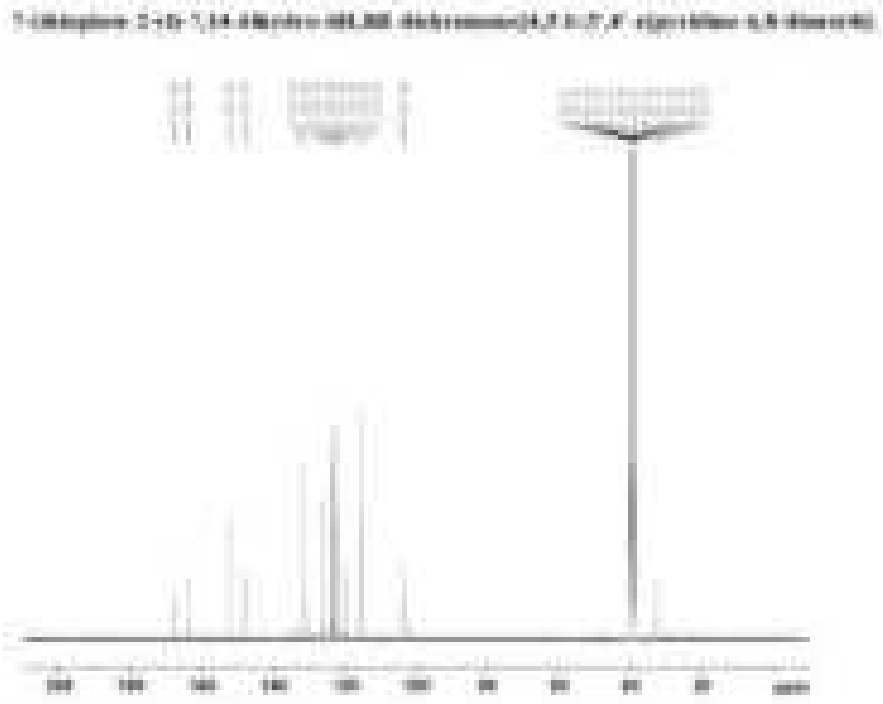


Figure IV.34-^{13}C-NMR of compound 4i

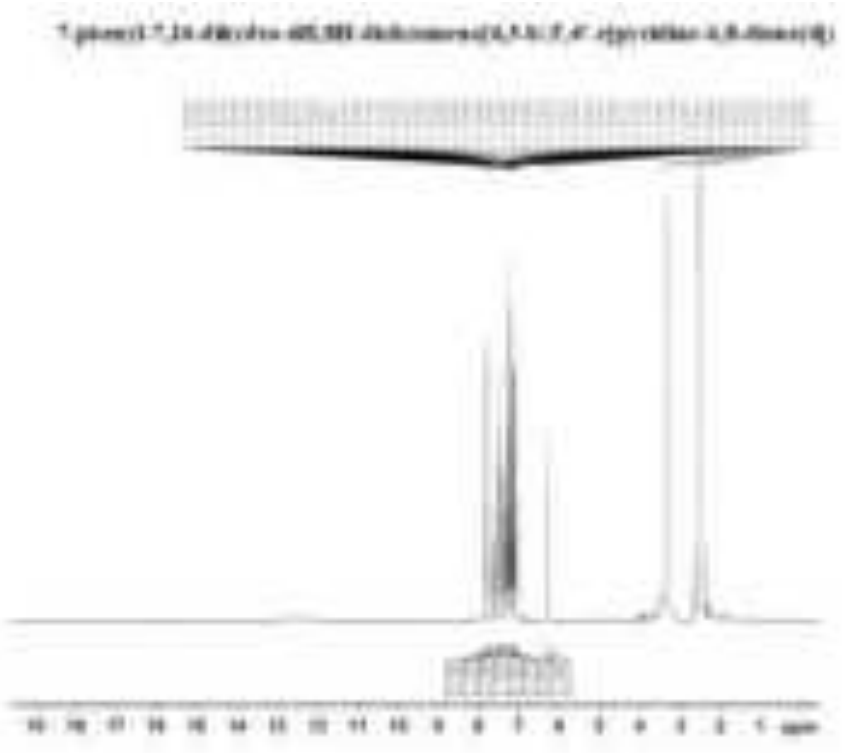


Figure IV.35-^{1}H-NMR of compound 4j

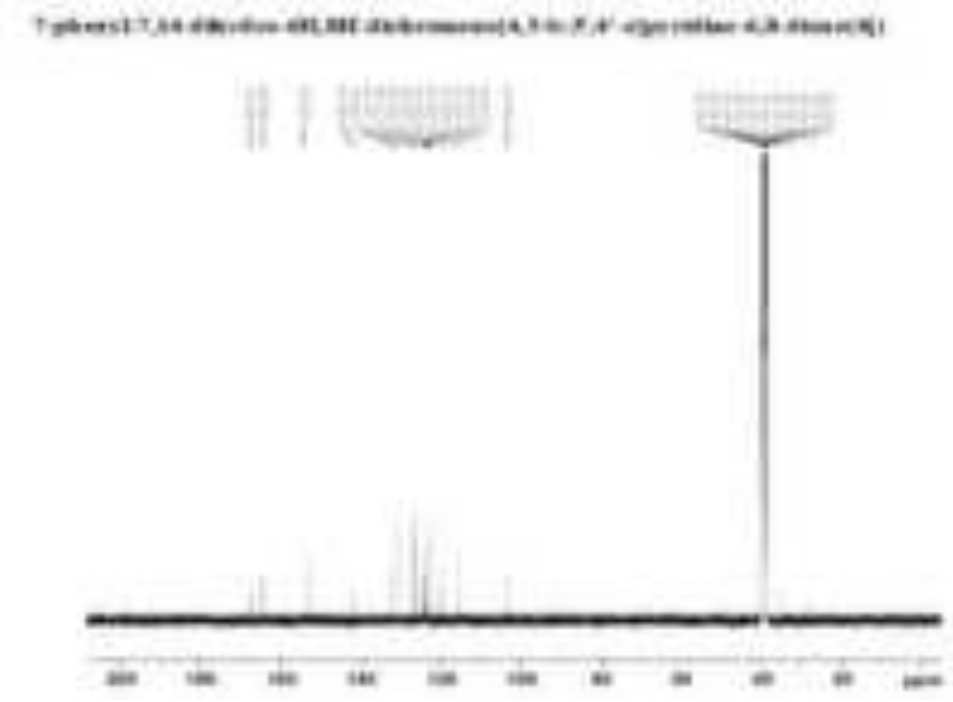
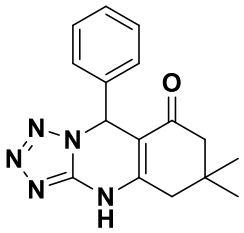


Figure IV.36-^{13}C-NMR of compound 4j

IV.12.A.14.h Spectral data of the compounds mentioned in Scheme IV. 24

6,6-dimethyl-9-phenyl-5,6,7,9-tetrahydrotetrazolo[5,1-*b*]quinazolin-8(4*H*)-one (4a)



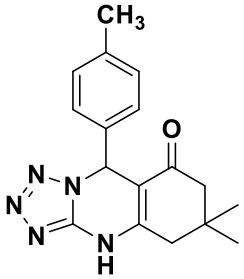
^{1}H-NMR(500MHz,DMSO-d$_6$)

δ(ppm)1.00(s,3H),1.06(s,3H),2.13(d,1H),2.23(d,1H),2.60-2.64(dd,2H),6.63(s,1H),7.13-7,17(m,3H),7.34-7.36(m,2H),11.62(broad s,1H).

^{13}C-NMR(500MHz,DMSO-d$_6$)

δ(ppm)26.97,28.06,32.18,38.91,49.69,56.66,105.36,115.19,115.37129.21,129.28136.64,136.66,148.27,150.45,160.71,162.66,192.91.

6,6-dimethyl-9-(p-tolyl)-5,6,7,9-tetrahydrotetrazolo[5,1-*b*]quinazolin-8(4*H*)-one (4b)



^{1}H-NMR(500MHz,DMSO-d$_6$)

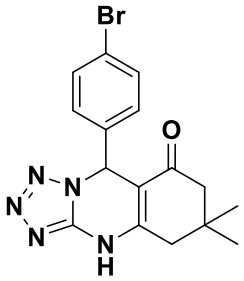
δ(ppm)1.00(s,3H),1.05(s,3H),2.12(d1H),2.22(d,1H),2.24(s,3H),2.59(s,2H),6.55

(s,1H),7.11-7.17(dd,4H),11.56(broad s,1H).

^{13}C-NMR(500MHz,DMSO-d$_6$)

δ(ppm)20.51,26.83,28.19,23.16,49.71,57.07,105.67,126.91,128.99,137.55,137.59,148.32,150.19,192.85.

9-(4-bromophenyl)-6,6-dimethyl-5,6,7,9-tetrahydrotetrazolo[5,1-*b*]quinazolin-8(4*H*)-one (4c)



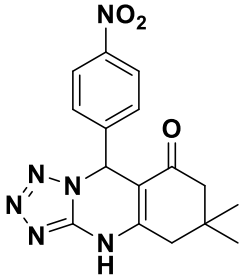
^{1}H-NMR(500MHz,DMSO-d$_6$)

δ(ppm)0.99(s,3H),1.05(s,3H),2.12-2.24(dd,2H),2.56-2.63(m,2H),6.61(s,1H),7.25-7.28(m,2H),7.51-7.54(m,2H),11.65(s,1H).

^{13}C-NMR(500MHz,DMSO-d$_6$)

δ(ppm)20.51,26.83,28.19,23.16,49.71,57.07,105.67,126.91,128.99,137.55,137.59,148.32,150.19,192.85.

6,6-dimethyl-9-(4-nitrophenyl)-5,6,7,9-tetrahydrotetrazolo[5,1-*b*]quinazolin-8(4*H*)-one (4d)



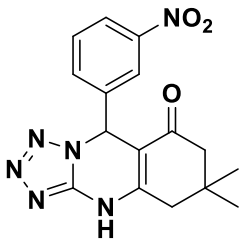
^{1}H-NMR(500MHz,DMSO-d$_6$)

δ(ppm)0.99(s,3H),1.01(s,3H),2.14(dd,1H),2.23(dd,1H),2.51-2.62(m,2H),6.78(s,1H),7.60-7.63(m,2H),8.17-8.20(m,2H),11.76(s,1H).

^{13}C-NMR(500MHz,DMSO-d$_6$)

δ(ppm)27.04,27.97,32.25,49.62,56.83,104.83,123.69,128.73,146.94,147.22,148.33,151.00,192.99.

6,6-dimethyl-9-(3-nitrophenyl)-5,6,7,9-tetrahydrotetrazolo[5,1-*b*]quinazolin-8(4*H*)-one (4e)



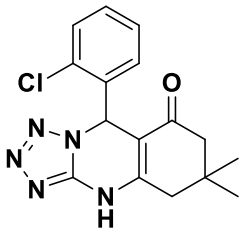
^{1}H-NMR(500MHz,DMSO-d_6)

δ(ppm)1.02(s,3H),1.04(s,3H),1.99-2.26(m,2H),2.63(d,2H),6.84(s,1H),7.66(t,1H),7.77(m,1H),8.15-8.21(m,2H), 11.65(s,1H).

^{13}C-NMR(500MHz,DMSO-d_6)

δ(ppm)26.94,28.05,32.26,49.62,56.74,104.66,122.04,123.27,130.26,133.84,142.14,147.66,148.28,151.18,193.05.

9-(2-chlorophenyl)-6,6-dimethyl-5,6,7,9-tetrahydrotetrazolo[5,1-*b*]quinazolin-8(4*H*)-one (4f)



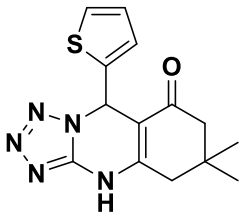
^{1}H-NMR(500MHz,DMSO-d_6)

δ(ppm)1.03(s,3H),1.06(s,3H),2.10(d,1H),2.22(d,1H),2.52-2.59(m,2H),6.44(s,1H),6.9.(s,1H),7.30-7.33(m,2H),7.42-7.44(m,2H),11.68(s,1H).

^{13}C-NMR(500MHz,DMSO-d_6)

δ(ppm)26.89,27.74,28.13,32.11,49.69,104.50,127.34,129.76,130.00,132.06,148.45,151.04,156.36,192.84.

6,6-dimethyl-9-(thiophen-2-yl)-5,6,7,9-tetrahydrotetrazolo[5,1-*b*]quinazolin-8(4*H*)-one (4g)



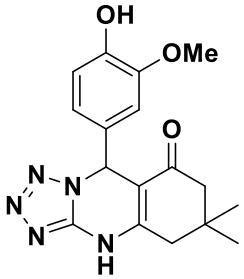
^{1}H-NMR(500MHz,DMSO-d_6)

δ(ppm)1.04(s,3H),1.08(s,3H),2.19(d,1H),2.29(d,1H),2.54-2.65(m,2H),6.96-6.97(m,2H),7.12-7.13(m,1H),7.44-7.45(m,1H),11.69(s,1H).

^{13}C-NMR(500MHz,DMSO-d_6)

δ(ppm)26.64,28.49,32.10,49.65,52.01,105.41,126.52,126.98,143.39,148.08,150.65,192.86.

9-(4-hydroxy-3-methoxyphenyl)-6,6-dimethyl-5,6,7,9-tetrahydrotetrazolo[5,1-*b*]quinazolin-8(4*H*)-one (4h)



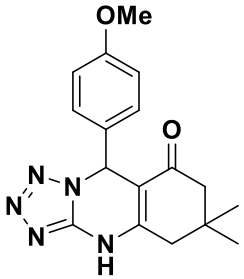
^{1}H-NMR(500MHz,DMSO-d_6)

δ(ppm)1.03-1.17(m,6H),2.10-2.16(m,1H),2.23-2.27(m,1H),2.60(d,2H),3.73(s,3H),6.50(s,1H),6.60-6.71(m,2H),6.87(d,1H),9.09(s,1H),11.51(s,1H).

^{13}C-NMR(500MHz,DMSO-d_6)

δ(ppm)26.71,28.39,32.12,40.00,49.77,55.55,57.08,105.71,111.42,112.42,114.63,114.89,115.32,119.53,120.20,131.42,135.34,144.83,146.63,146.80,147.31,148.22,150.19,162.51,192.95,196.03.

9-(4-methoxyphenyl)-6,6-dimethyl-5,6,7,9-tetrahydrotetrazolo[5,1-*b*]quinazolin-8(4*H*)-one (4i)



^{1}H-NMR(500MHz,DMSO-d_6)

δ(ppm)1.00(s,3H),1.02(s,3H),2.13(d,1H),2.23(d,1H),2.60(s,2H),3.71(s,1H),6.56(s,1H),6.87(dd,2H),7.21(dd,2H),11.57(s,1H).

^{13}C-NMR(500MHz,DMSO-d_6)

δ(ppm)26.09,28.03,31.96,38.73,49.56,54.79,56.62,105.53,113.60,128.09,132.42,148.11,149.95,158.83,192.69.

IV.12.A.14.i Scanned copies of compounds mentioned in Scheme IV.24

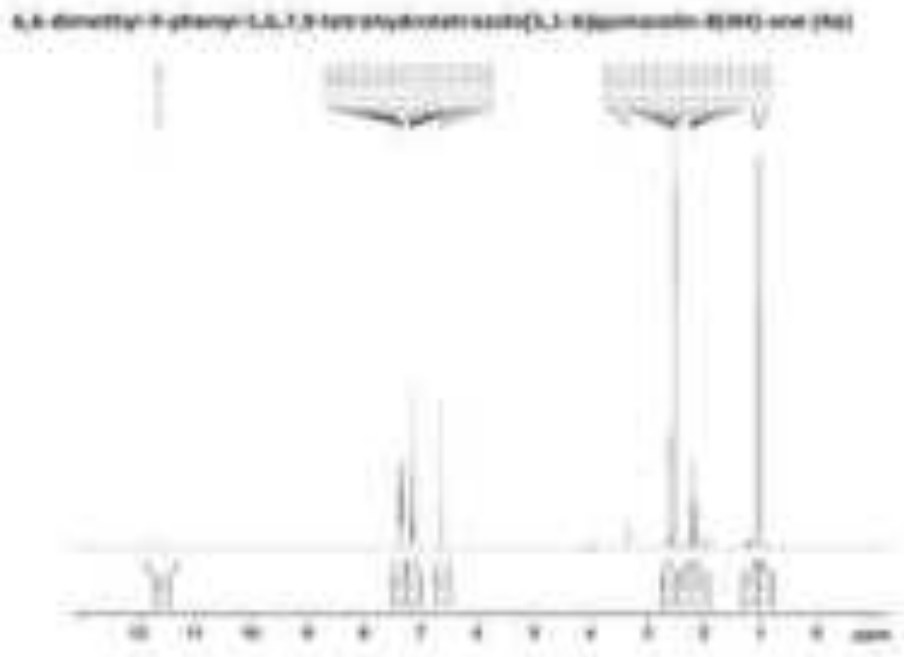


Figure IV.37-^{1}H-NMR of compound 4a

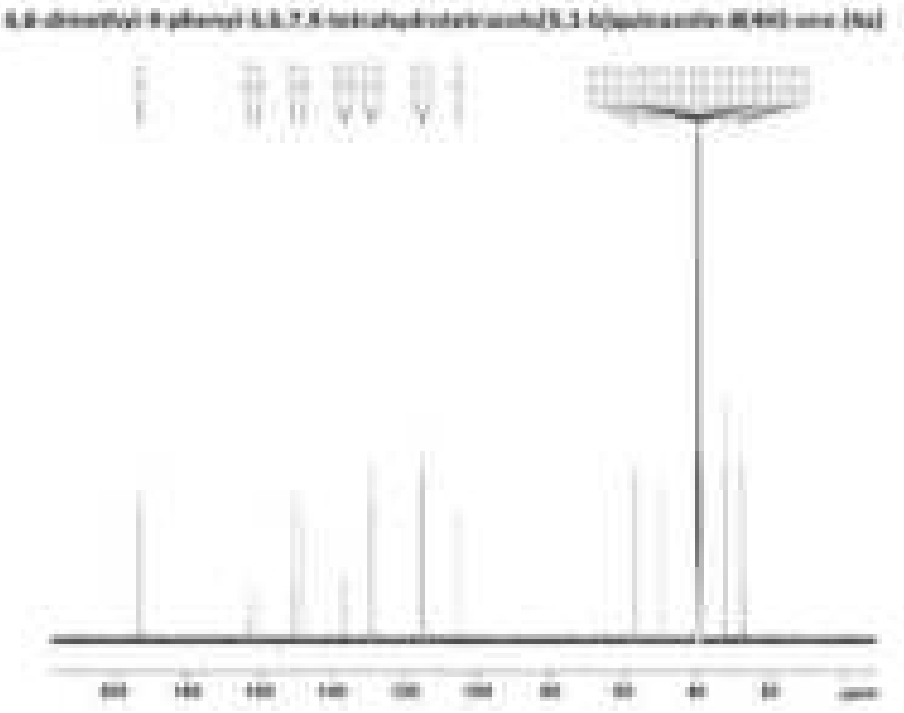


Figure IV.38-^{13}C-NMR of compound 4a

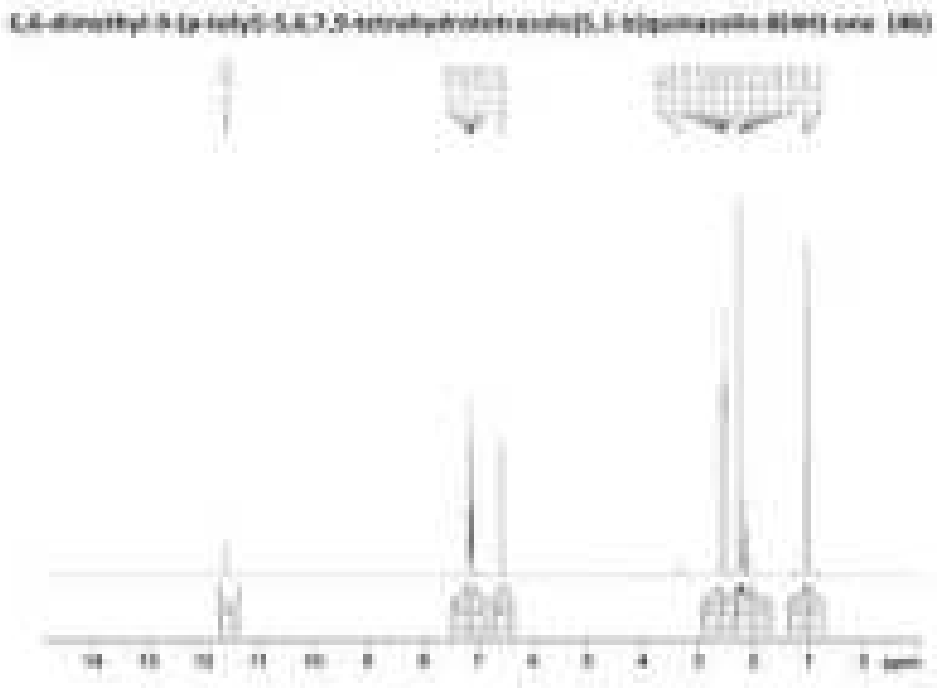


Figure IV.39-^{1}H-NMR of compound 4b

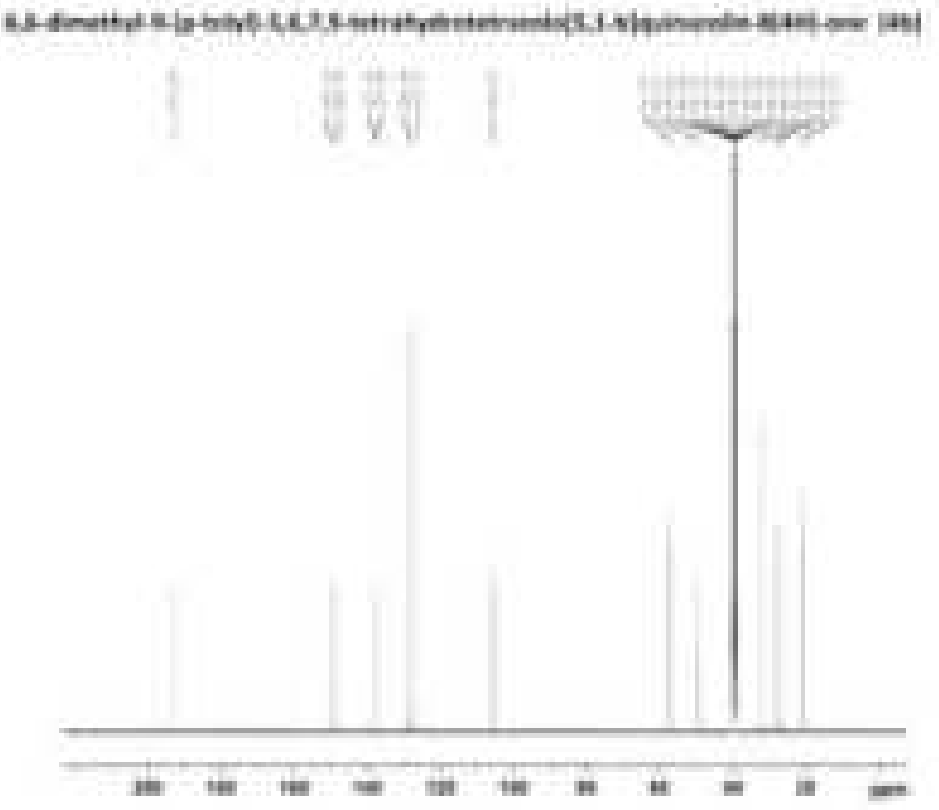


Figure IV.40-^{13}C-NMR of compound 4b

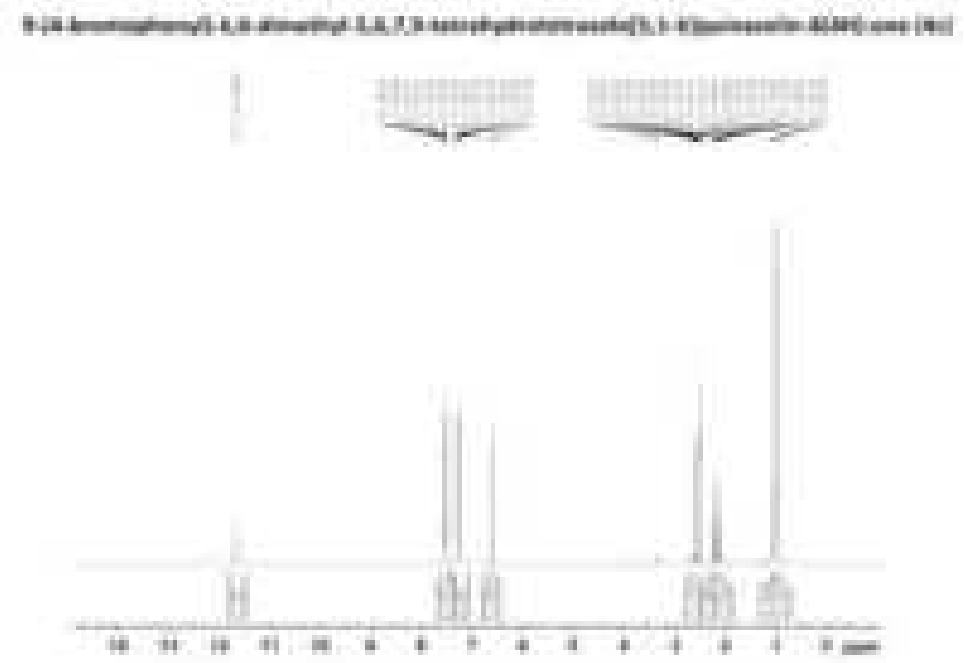


Figure IV.41-^{1}H-NMR of compound 4c

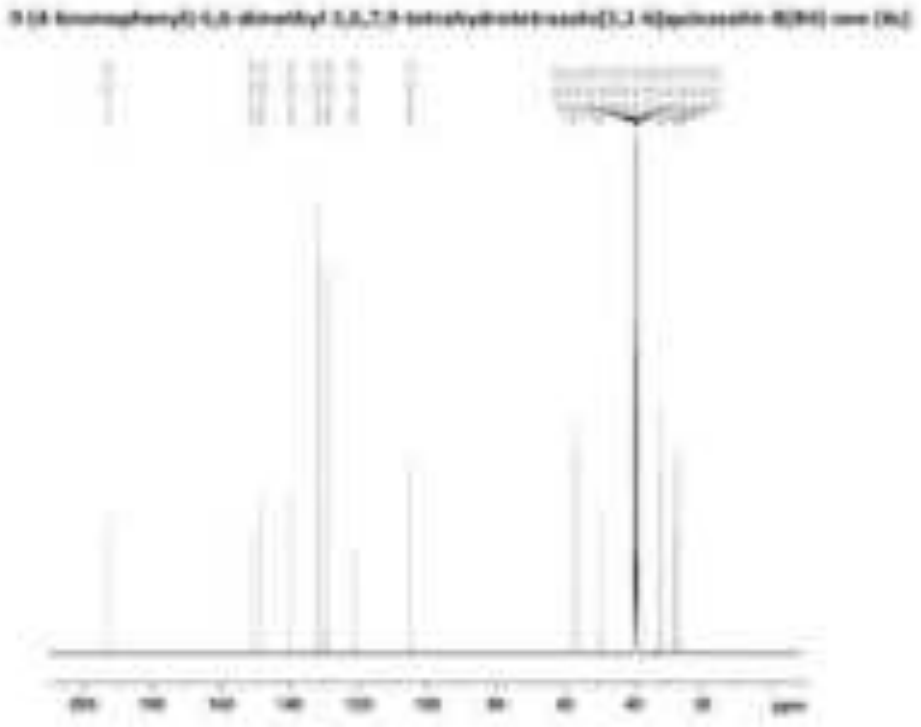


Figure IV.42-^{13}C-NMR of compound 4c

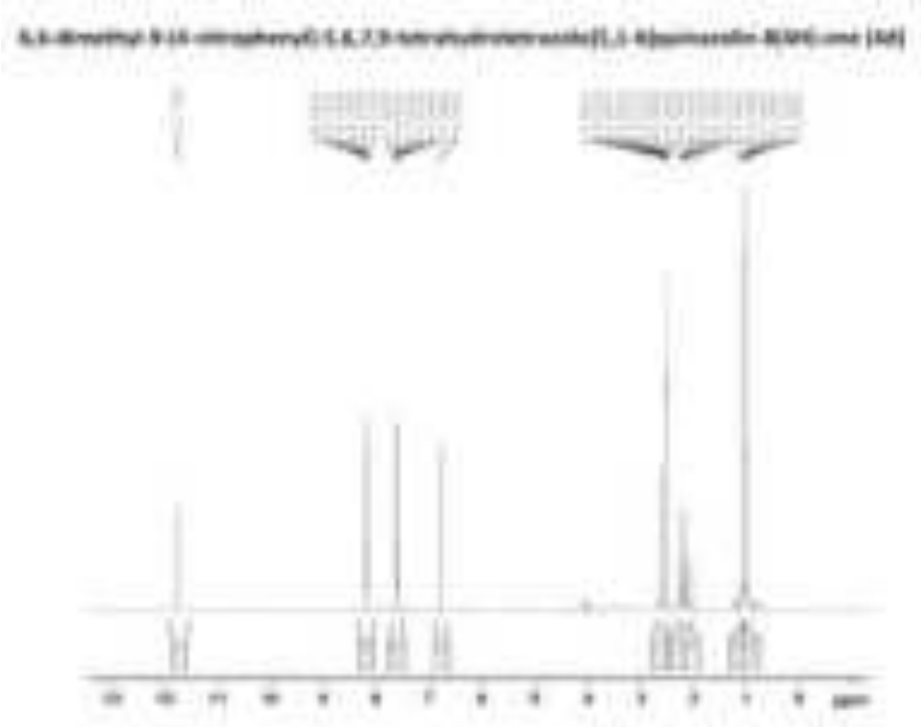


Figure IV.43-^{1}H-NMR of compound 4d

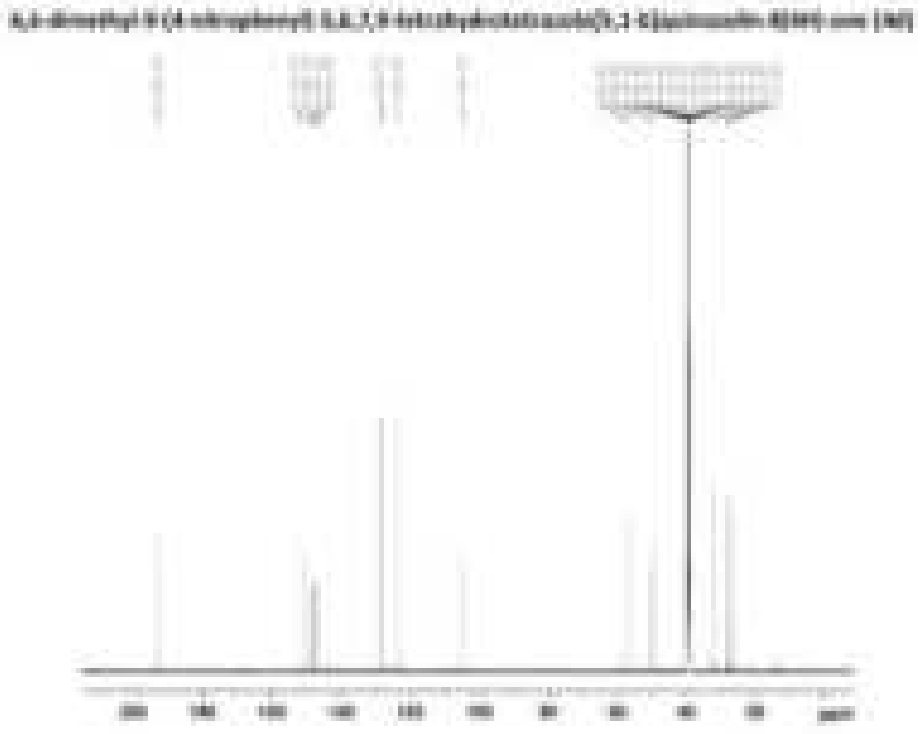


Figure IV.44-^{13}C-NMR of compound 4d

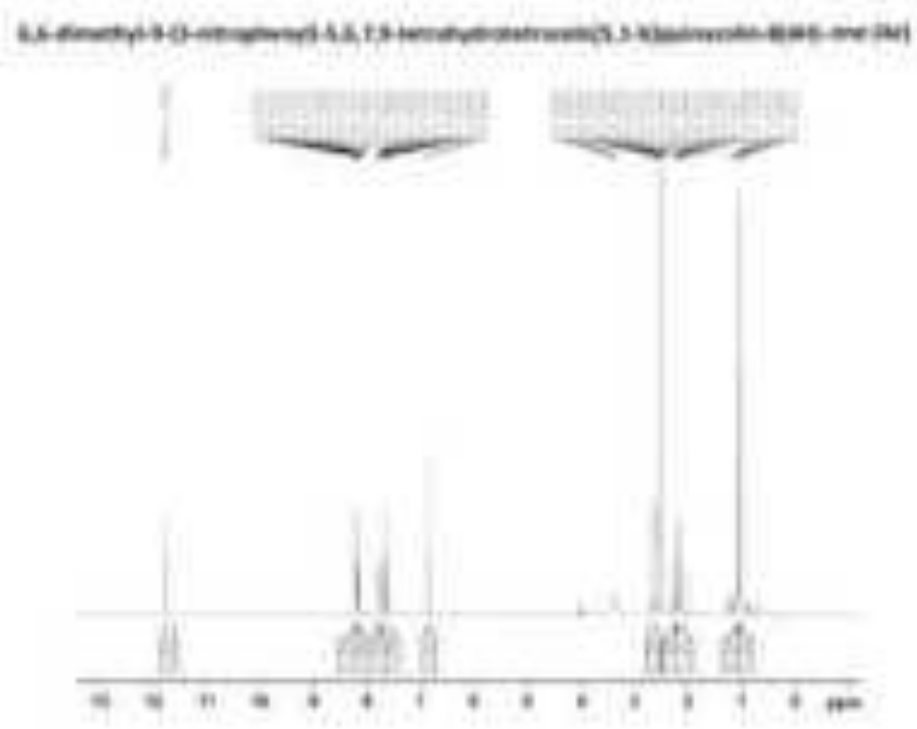


Figure IV.45-^{1}H-NMR of compound 4e

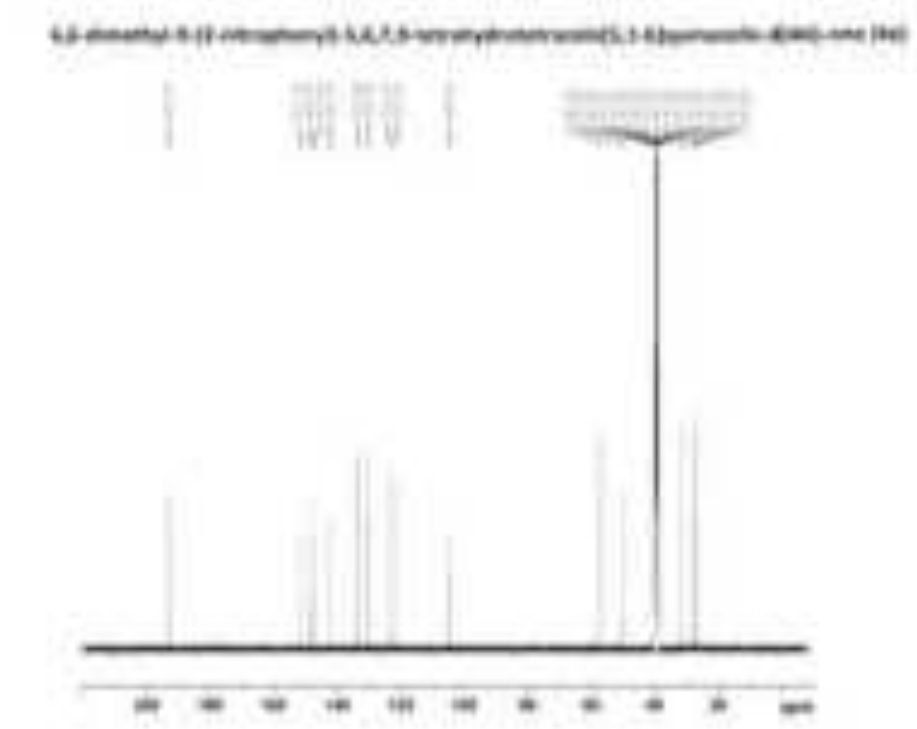


Figure IV.46-^{13}C-NMR of compound 4e

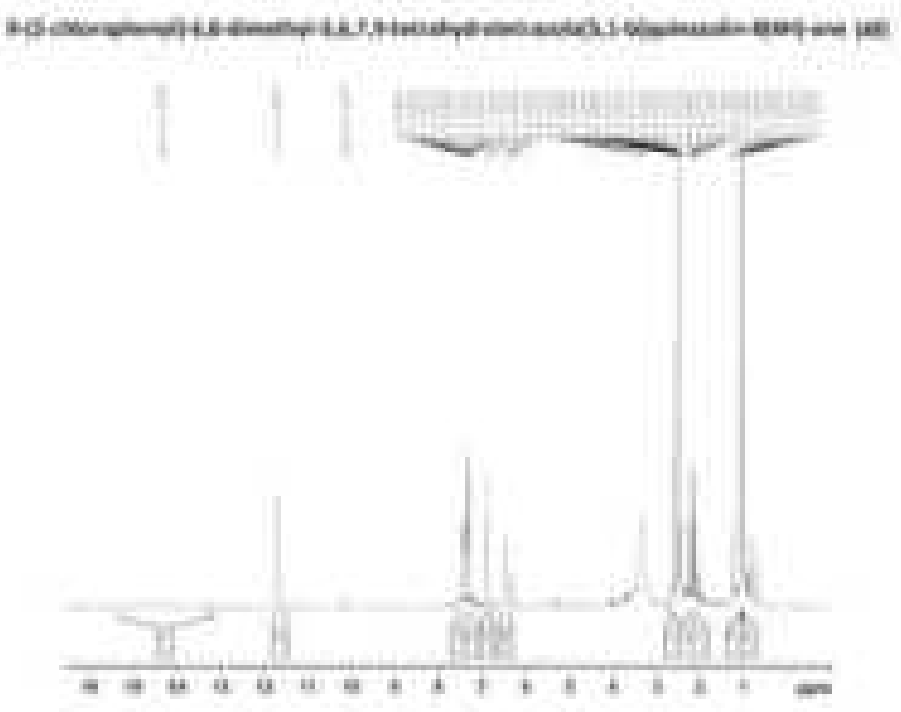


Figure IV.47-^{1}H-NMR of compound 4f

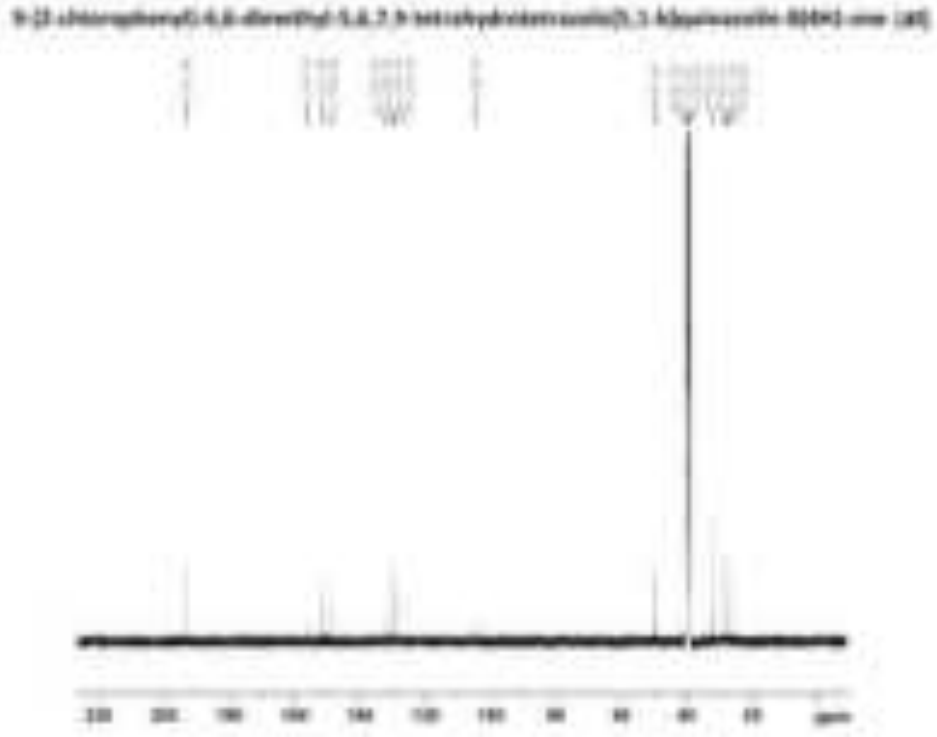


Figure IV.48-^{13}C-NMR of compound 4f

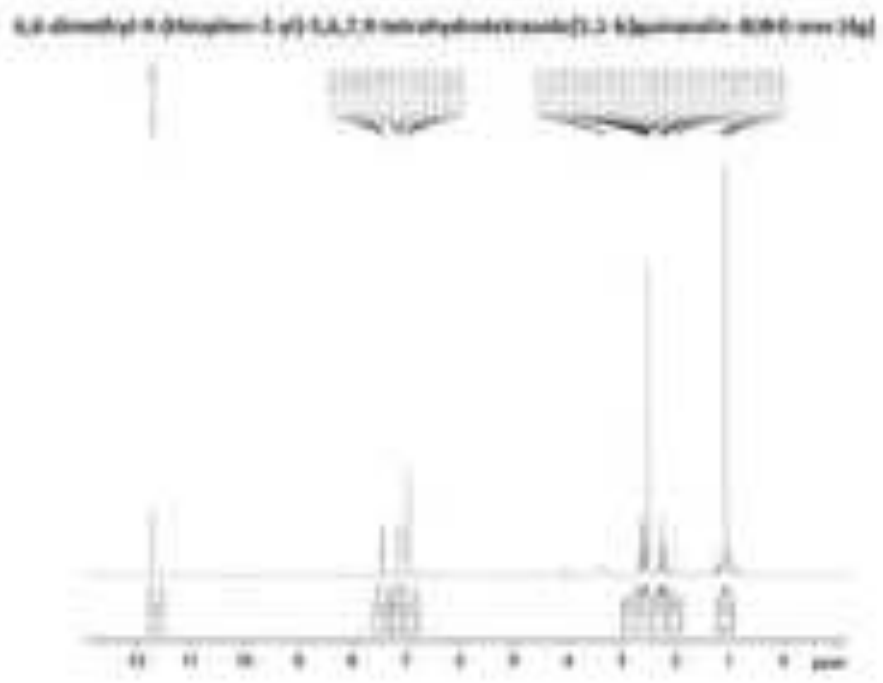


Figure IV.49-^{1}H-NMR of compound 4g

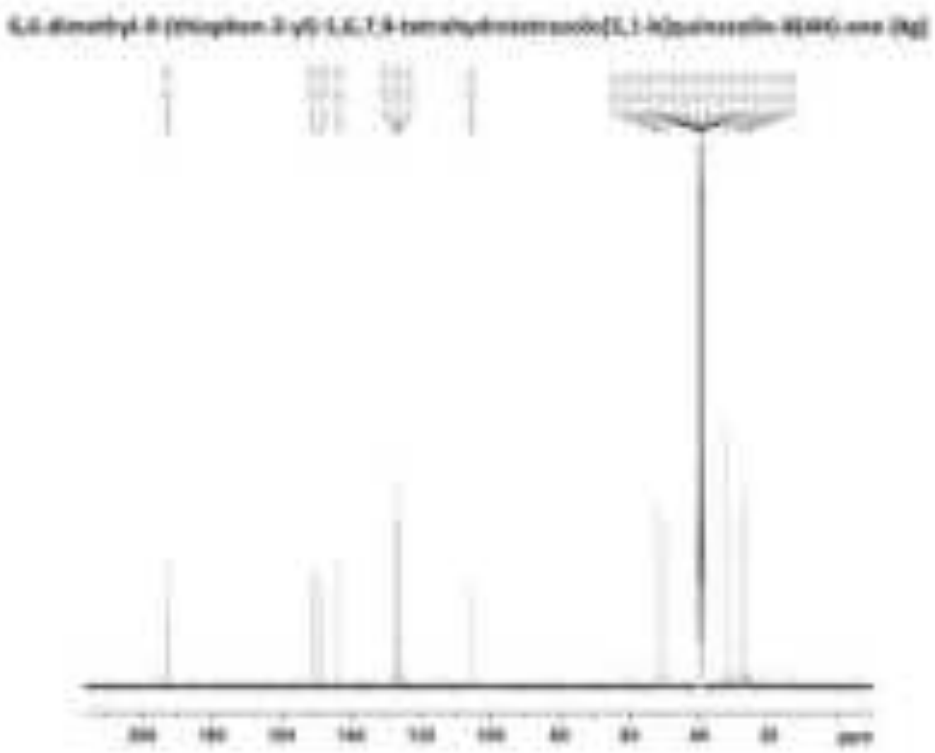


Figure IV.50-^{13}C-NMR of compound 4g

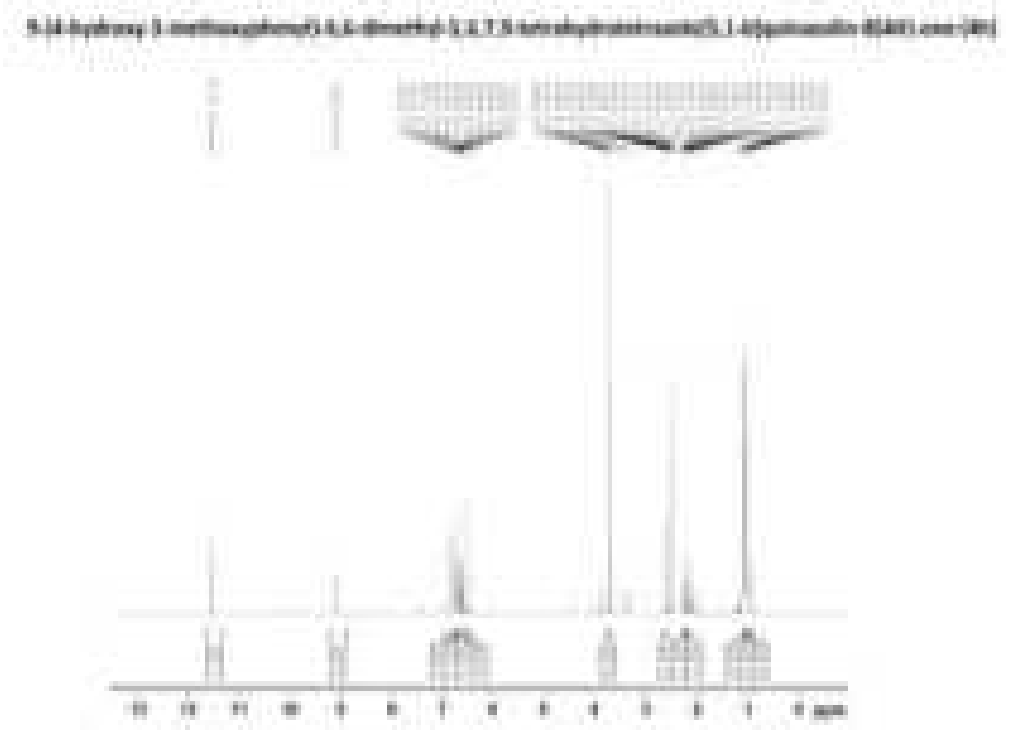


Figure IV.51-^{1}H-NMR of compound 4h

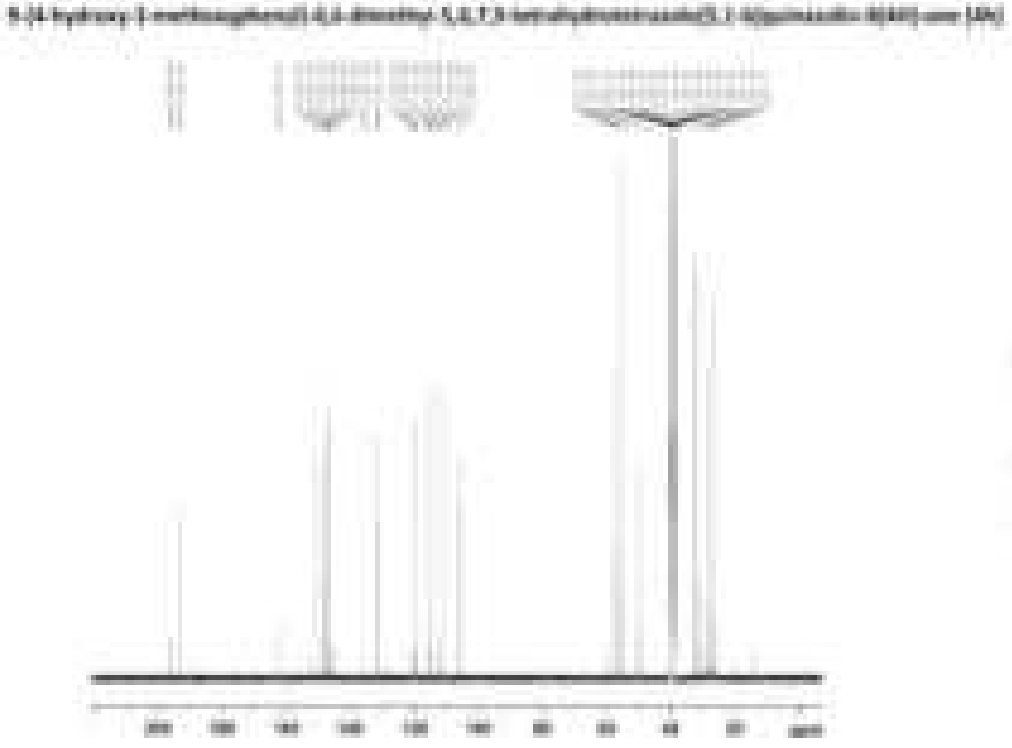


Figure IV.52-^{13}C-NMR of compound 4h

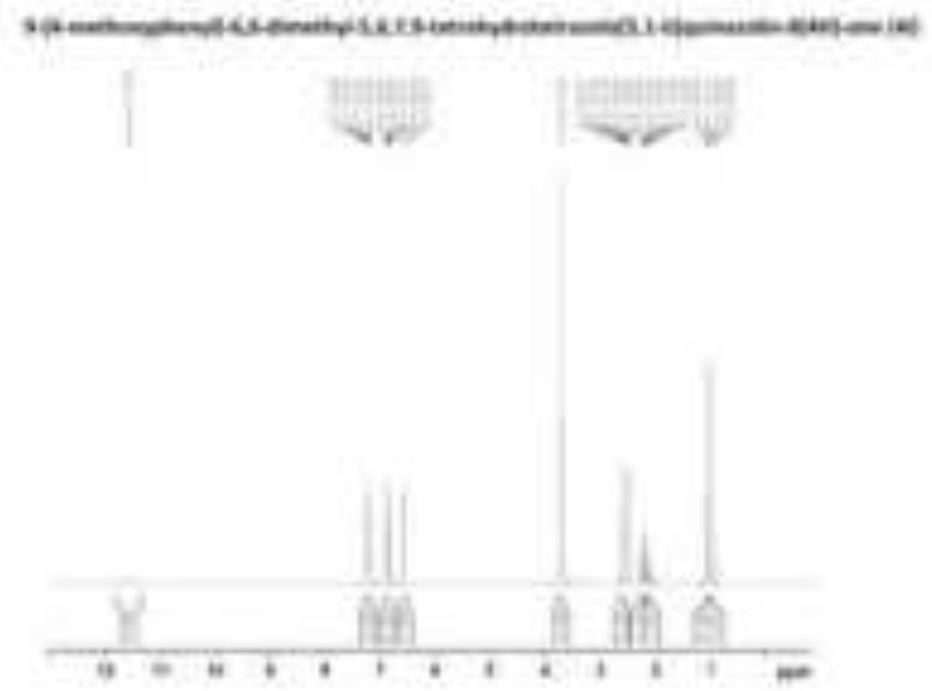


Figure IV.53-^{1}H-NMR of compound 4i

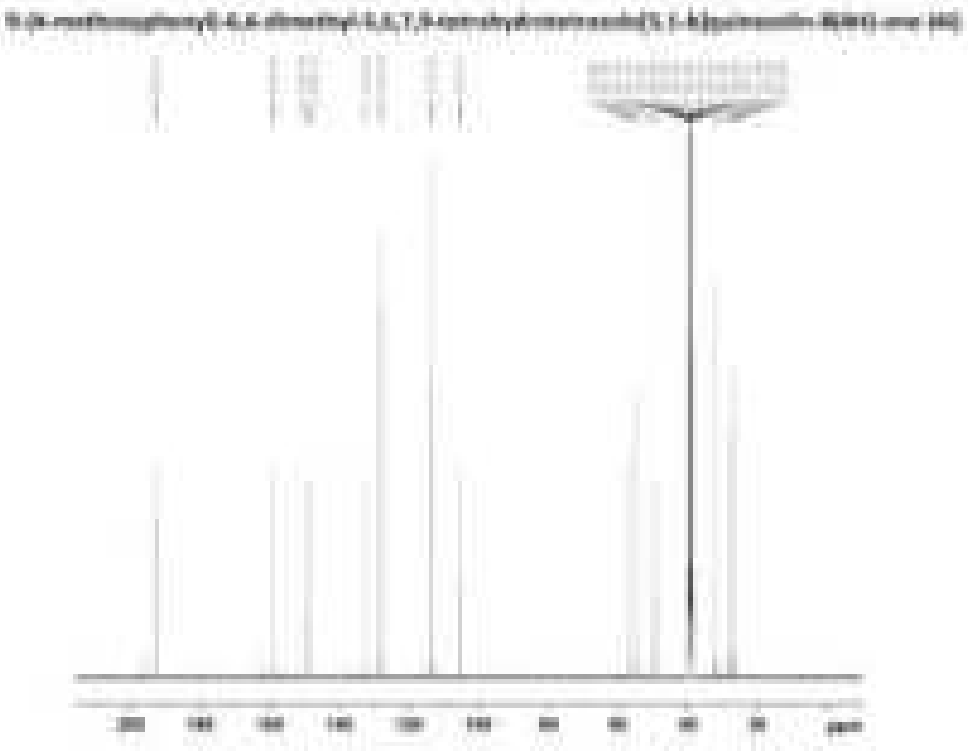
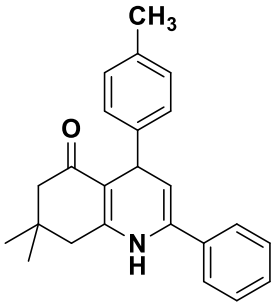


Figure IV.54-^{13}C-NMR of compound 4i

IV.12.A.14.j Spectral data of the compounds mentioned in Scheme IV. 25

7,7-dimethyl-2-phenyl-4-(p-tolyl)-4,6,7,8-tetrahydroquinolin-5(1*H*)-one (5a)



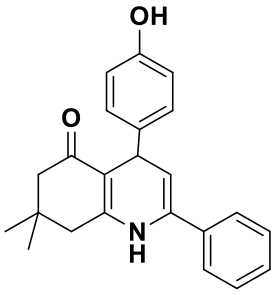
^{1}H-NMR(400MHz,DMSO-d$_6$)

δ(ppm)0.92(s,3H),1.05(s,3H),1.94-1.98(m,1H),2.12-2.18(m,1H),2.34(s,3H),2.39-2.47(m,2H),3.65(s,3H),4.49(d,1H),5.16(dd,1H),7.01(d,2H),7.09(d,2H),7.29-7.38(m,3H), 7.43-7.46(m,2H),8.57(s,1H).

^{13}C-NMR(400MHz,DMSO-d$_6$)

δ(ppm)21.15,27.40,29.80,29.80,32.44,37.35,50.97,106.68,106.72,126.09,127.83,128.81,128.99,129.16,134.88,135.01,135.79,146.15,152.84,194.43.

4-(4-hydroxyphenyl)-7,7-dimethyl-2-phenyl-4,6,7,8-tetrahydroquinolin-5(1*H*)-one (5b)



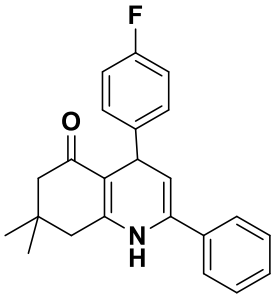
^{1}H-NMR(400MHz,DMSO-d$_6$)

δ(ppm)1.07(s,6H),2.49-2.57(m,2H),3.12(s,2H),6.78(d,2H),7.19(d,2H),7.50(m,4H), 7.65(d,2H),9.61(s,1H).

^{13}C-NMR(400MHz,DMSO-d$_6$)

δ(ppm)28.43,32.95,47.65,53.84,115.27,121.54,124.51,127.79,129.36,130.45,130.57, 130.79,138.06,151.99,158.01,158.20,163.63,198.16

4-(4-fluorophenyl)-7,7-dimethyl-2-phenyl-4,6,7,8-tetrahydroquinolin-5(1*H*)-one (5c)



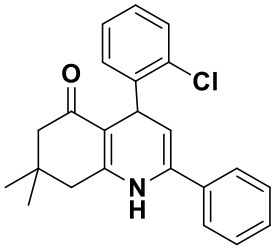
^{1}H-NMR(400MHz,DMSO-d_6)

δ(ppm)0.94(s,3H),1.32(s,3H),2.00(d,1H),2.17(d,1H),2.46-2.51(m,2H),4.58(d,1H),5.21(t,1H),7.03-7.08(m,2H),7.23-7.26(m,2H),7.33-7.41(m,3H), 7.48-7.50(m,2H),8.66(s,1H).

^{13}C-NMR(400MHz,DMSO-d_6)

δ(ppm)27.42,29.71,32.46,37.03,50.91,106.18,106.56,115.09,115.30,126.18,128.92,129.01,129.54,129.62,135.30,135.68,145.15,152.93,159.80,162.20,194.44

4-(2-chlorophenyl)-7,7-dimethyl-2-phenyl-4,6,7,8-tetrahydroquinolin-5(1*H*)-one (5d)



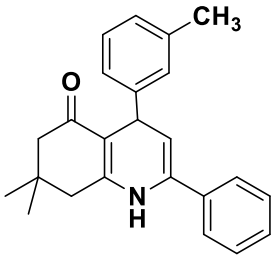
^{1}H-NMR(400MHz,DMSO-d_6)

δ(ppm)1.06(s,3H),1.08(s,3H),2.06(d,1H),2.19(d,1H),2.54(d,2H),4.97(d,1H),5.16(dd,1H),7.12-7.21(m,3H),7.33-7.39(m,4H),7.42-7.44(m,2H),8.69(s,1H).

^{13}C-NMR(400MHz,DMSO-d_6)

δ(ppm)28.12,29.53,32.48,35.37,50.85,104.28,104.96,126.12,127.80,128.01,129.02,129.63,129.97,131.36,135.56,145.48,154.39,194.20

7,7-dimethyl-2-phenyl-4-(m-tolyl)-4,6,7,8-tetrahydroquinolin-5(1*H*)-onev (5e)



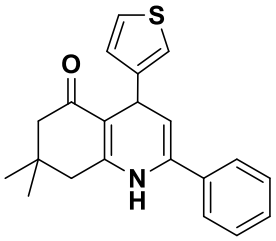
^{1}H-NMR(400MHz,DMSO-d_6)

δ(ppm)0.98(s,3H),1.04(s,3H),1.99(d,1H),2.17(d,1H),2.24(s,3H),2.47-2.50(m,2H+2H,H_2O),4.51(d,1H),5.19(dd,1H),6.91(d,1H),7.01(d,2H),7.13(d,1H),7.34-7.40(m,3H),7.46-7.49(m,2H),8.59(s,1H).

^{13}C-NMR(400MHz,DMSO-d_6)

δ(ppm)21.73,27.43,29.80,32.47,37.76,50.97,106.49,106.69,125.07,126.08,126.79,128.50,128.57,128.83129.00,134.83,135.74,137.37,149.01,153.00,194.39

7,7-dimethyl-2-phenyl-4-(thiophen-3-yl)-4,6,7,8-tetrahydroquinolin-5(1*H*)-one (5f)



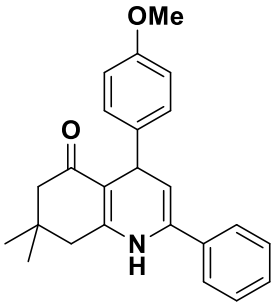
^{1}H-NMR(400MHz,DMSO-d_6)

δ(ppm)0.91(s,3H),1.01(s,3H),2.04(d,1H),2.21(d,1H),2.37-2.46(m,2H),4.88(d,1H),5.30(dd,1H),6.80(d,1H),6.87(q,1H)7.22(dd,1H),7.35-7.44(m,3H), 7.50-7.52(m,2H),8.79(s,1H).

^{13}C-NMR(400MHz,DMSO-d_6)

δ(ppm)27.15,29.95,32.12,32.41,50.88,105.13,106.66,122.92,124.14,126.37,127.05,129.06,135.62,135.85,152.61,153.82,194.40.

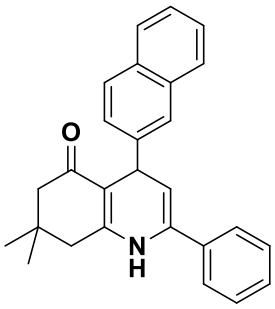
4-(4-methoxyphenyl)-7,7-dimethyl-2-phenyl-4,6,7,8-tetrahydroquinolin-5(1*H*)-one (5g)



^{1}H-NMR(400MHz,DMSO-d_6)

δ(ppm)0.92(s,3H),0.94(s,3H),1.94(d,1H),2.14(d,1H),2.43(m,2H),3.65(s,3H),4.47(d,1H),5.16(dd,1H),6.77(d,2H),7.11(d,2H),7.32(m,3H), 7.45-7.47(m,2H),8.55(s,1H).

7,7-dimethyl-4-(naphthalen-2-yl)-2-phenyl-4,6,7,8-tetrahydroquinolin-5(1*H*)-one (5h)



^{1}H-NMR(400MHz,DMSO-d_6)

δ(ppm)0.95(s,3H),1.02(s,3H),1.97(d,1H),2.17(d,1H),2.48(s,2H+3H,H_2O),4.73(s,1H),5.25(s,1H),7.34-7.47(m,9H),7.63(s,1H),7.78-7.80(d,3H),8.66(s,1H).

IV.12.A.14.k Sanned copies of compounds mentioned in Scheme IV.25

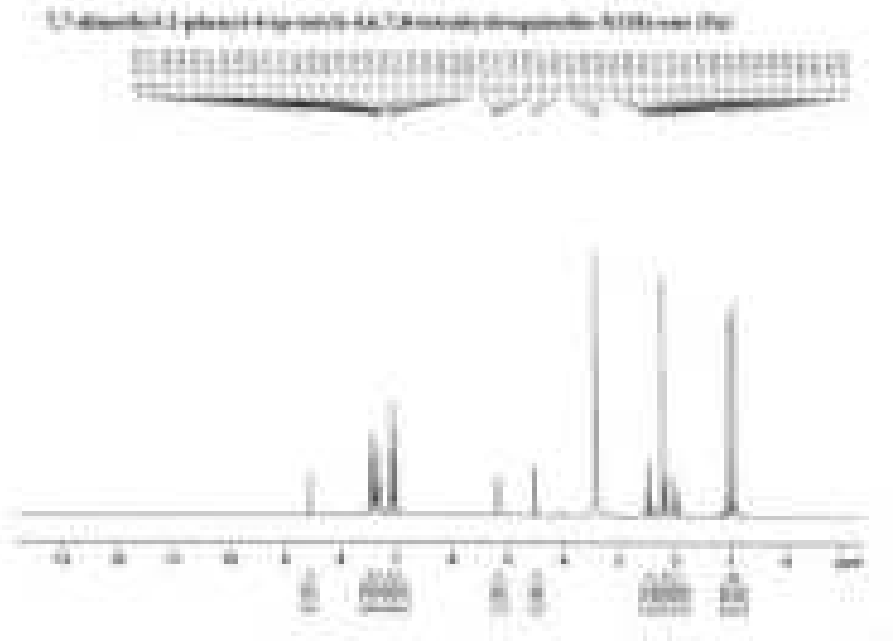


Figure IV.55-^{1}H-NMR of compound 5a

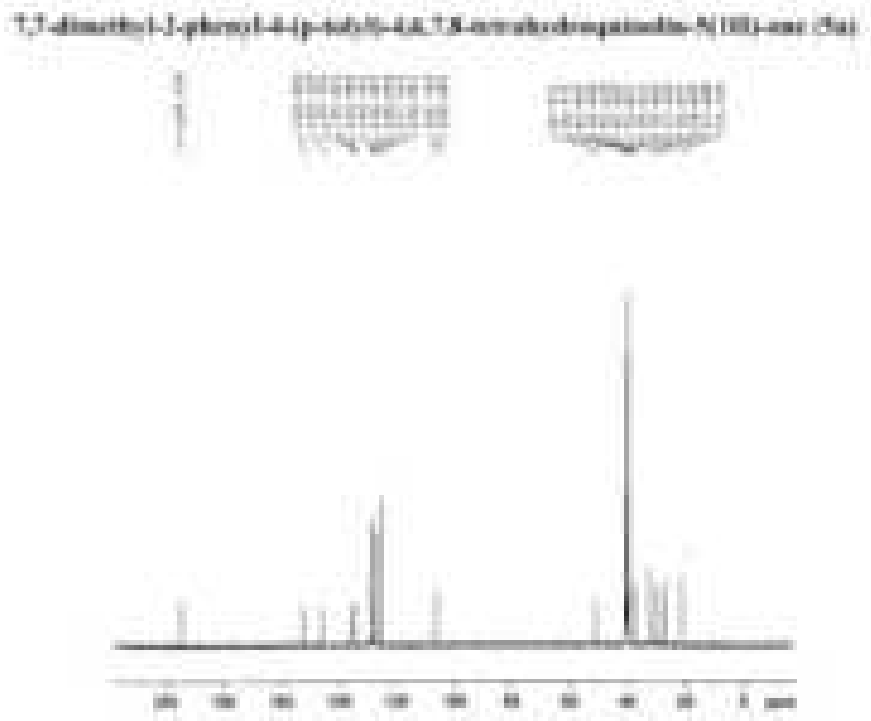


Figure IV.56-^{13}C-NMR of compound 5a

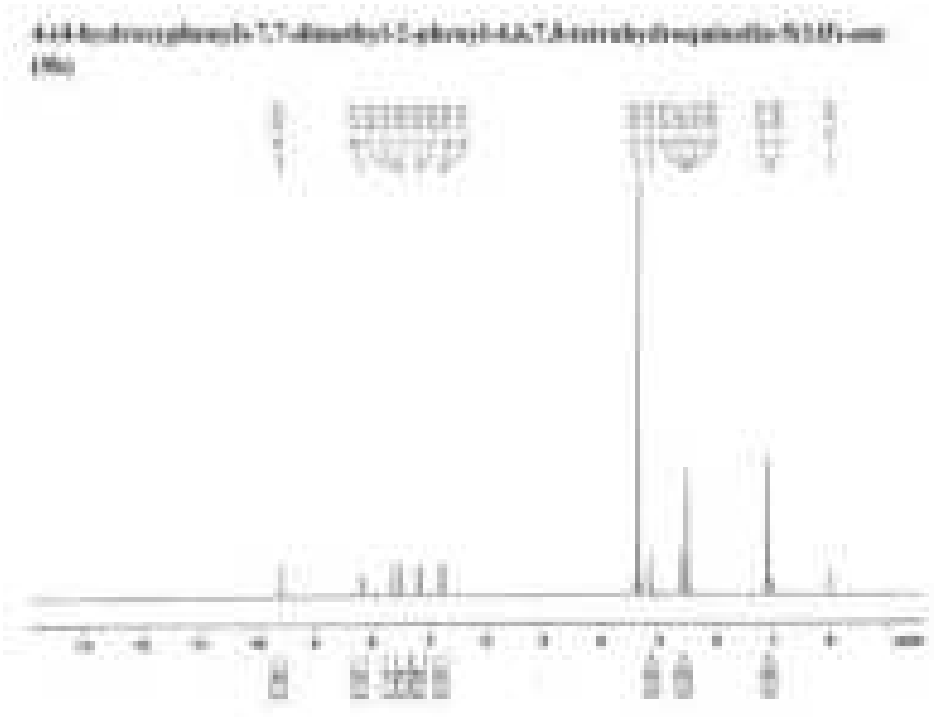


Figure IV.57-^{1}H-NMR of compound 5b

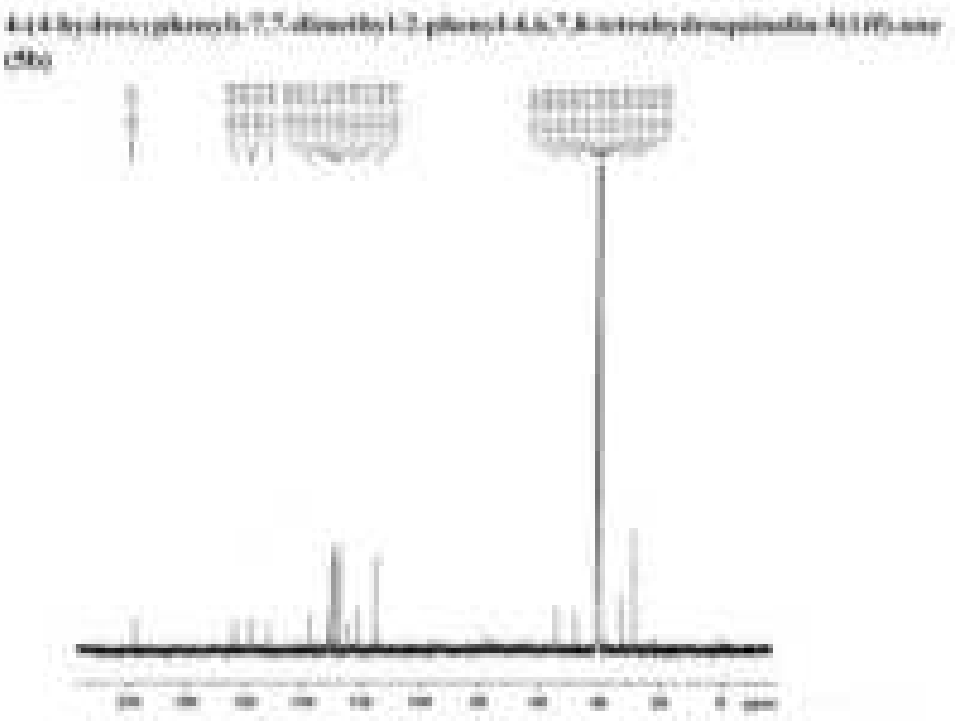


Figure IV.58-^{13}C-NMR of compound 5b

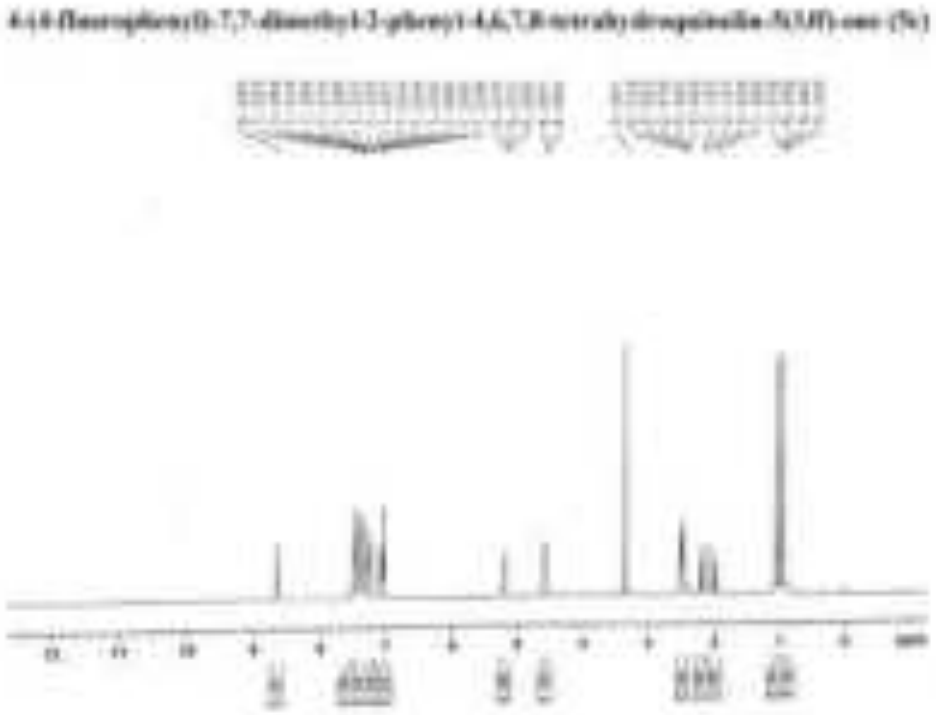


Figure IV.59-^{1}H-NMR of compound 5c

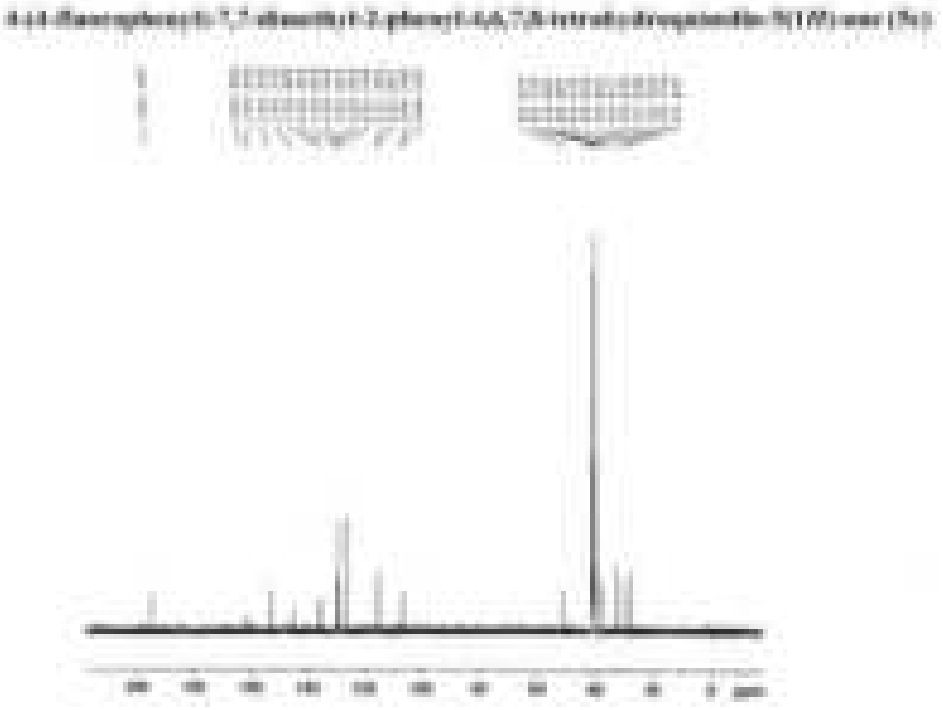


Figure IV.60-^{13}C-NMR of compound 5c

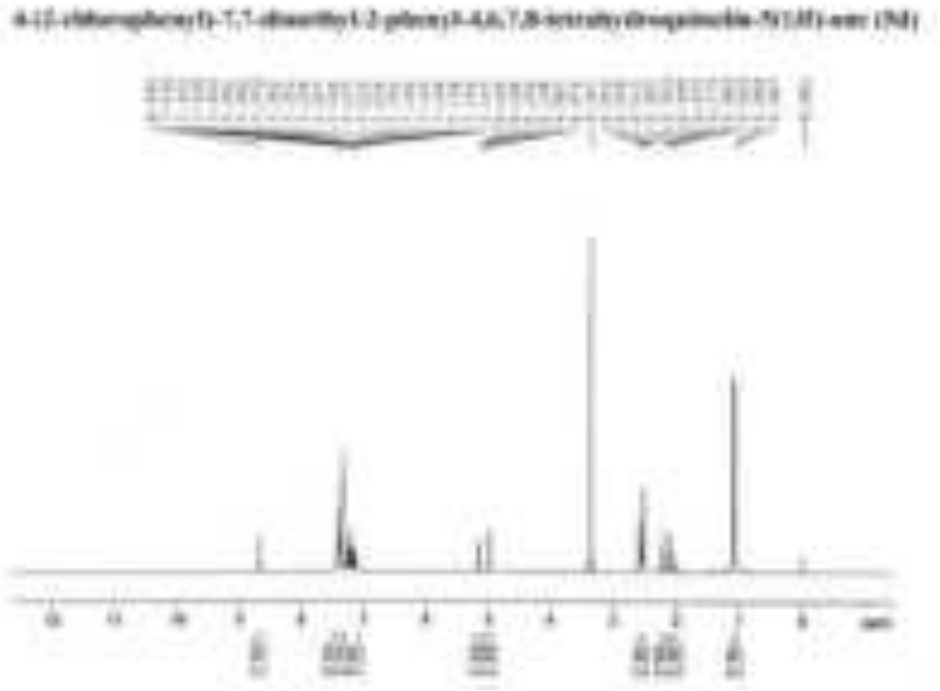


Figure IV.61-^{1}H-NMR of compound 5d

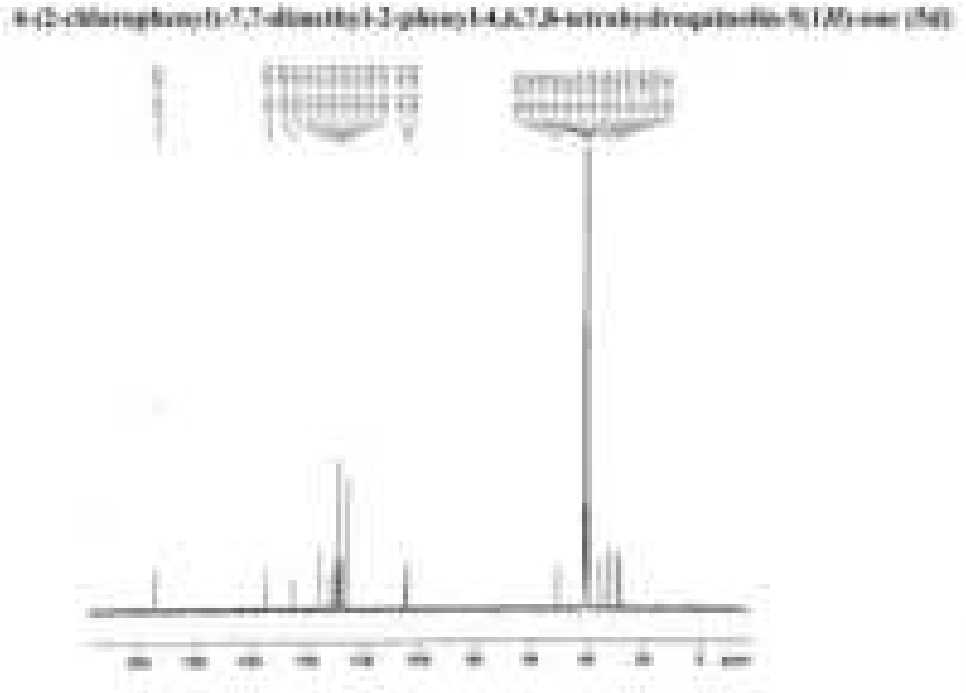


Figure IV.62-^{13}C-NMR of compound 5d

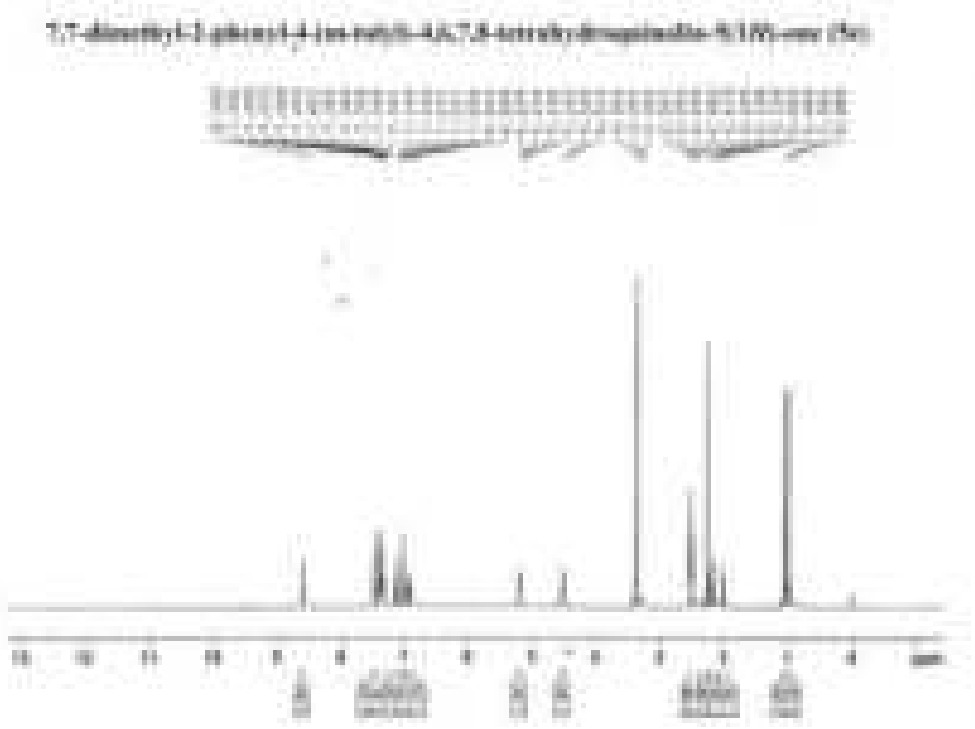


Figure IV.63-^{1}H-NMR of compound 5e

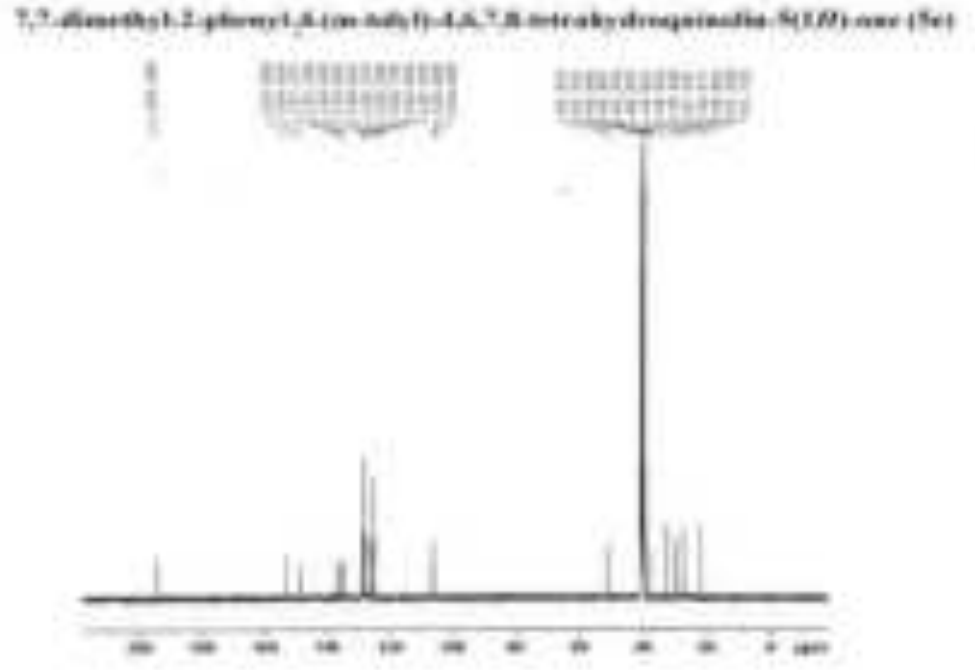


Figure IV.64-^{13}C-NMR of compound 5e

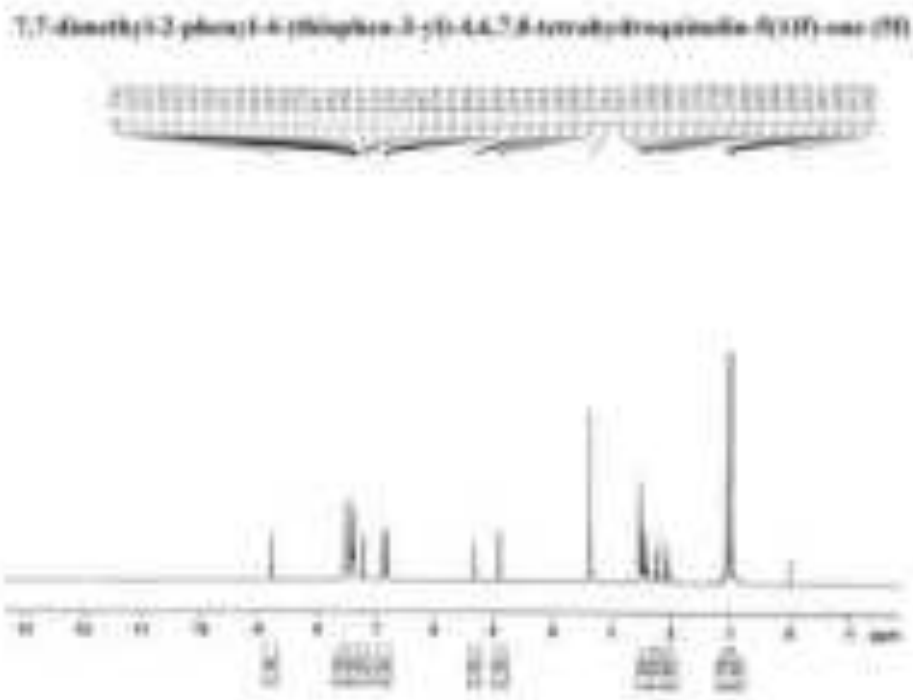


Figure IV.65-^{1}H-NMR of compound 5f

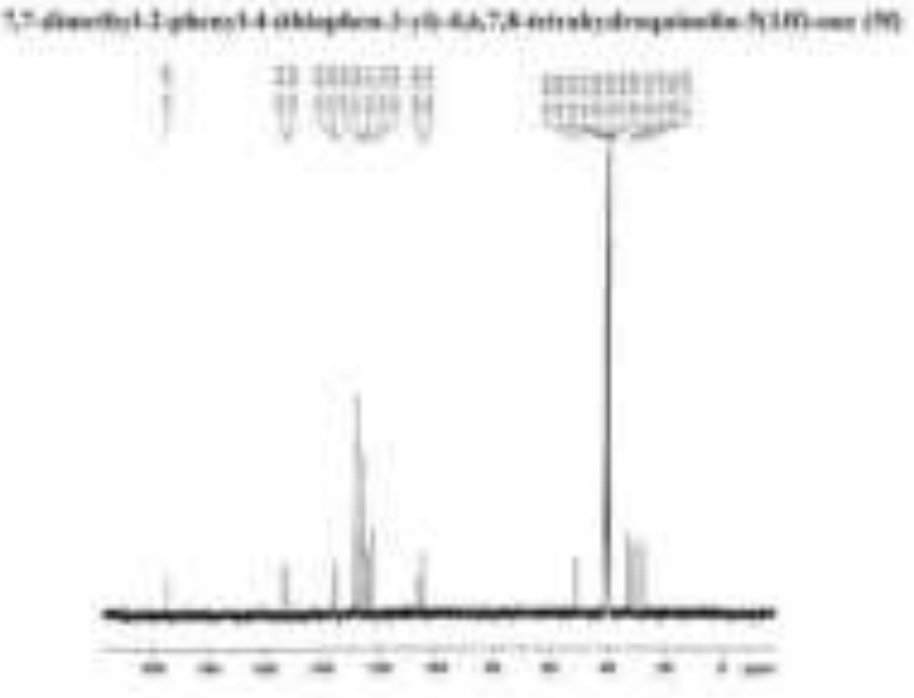


Figure IV.66-^{13}C-NMR of compound 5f

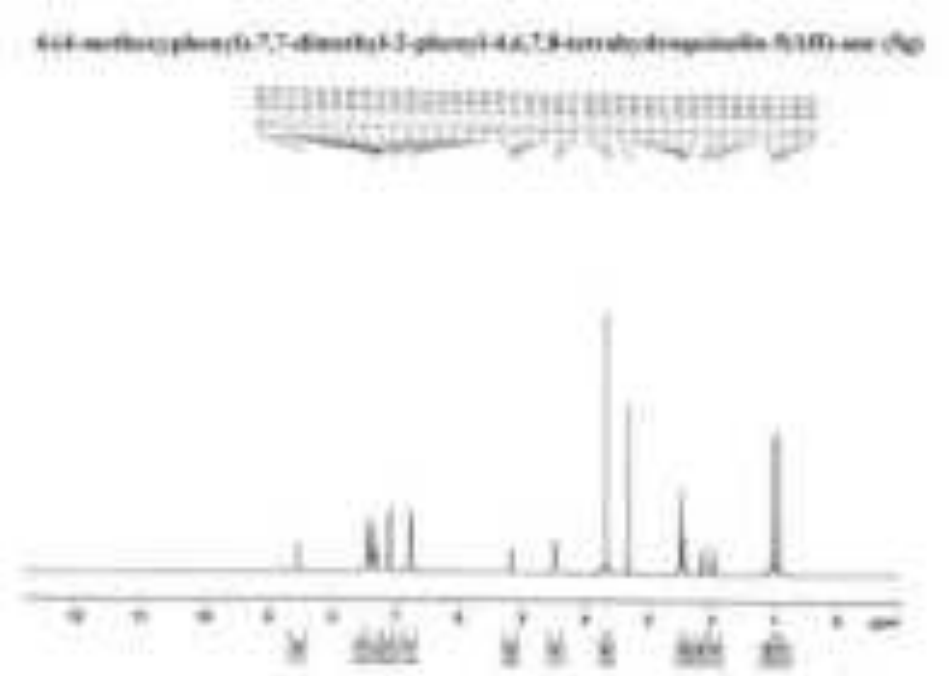


Figure IV.67-^{1}H-NMR of compound 5g

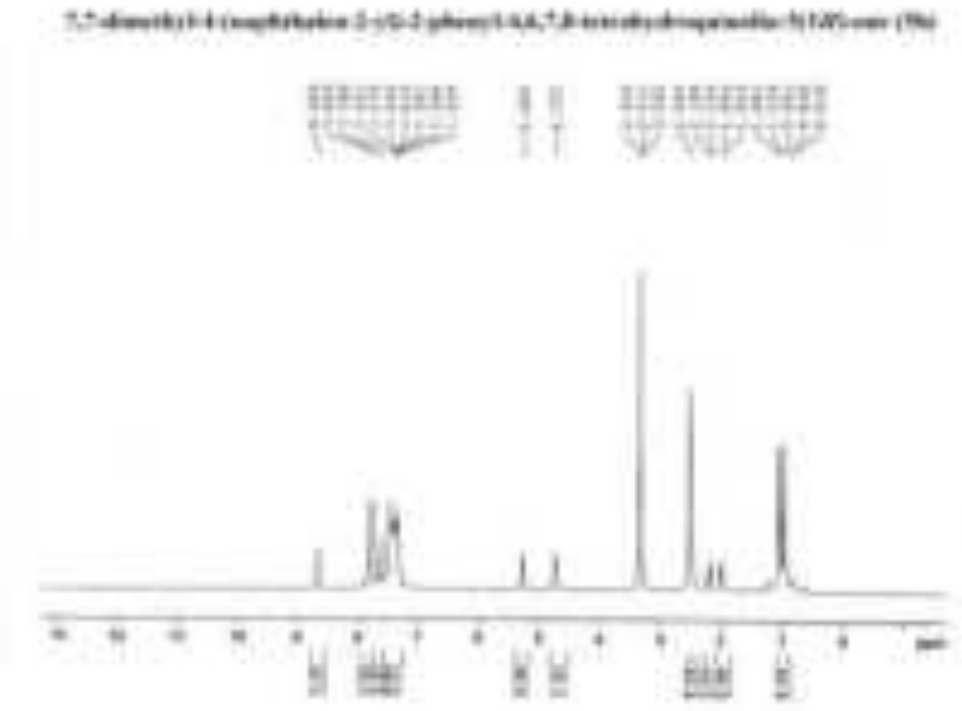


Figure IV.68-^{1}H-NMR of compound 5h

IV.12.A.14.l EDX data of SRH and RH

Spectrum: test 12881

Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (3 Sigma) [wt.%]
Carbon	K-series	52.78	52.78	62.02	24.63
Oxygen	K-series	37.84	37.84	33.20	19.57
Silicon	K-series	7.10	7.10	5.07	1.16
Sulfur	K-series	1.48	1.48	0.74	0.36
Total:		100.00	100.00	100.00	

EDX data of SRH

Spectrum: test 12888

Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (3 Sigma) [wt.%]
Carbon	K-series	53.01	55.01	62.95	21.11
Oxygen	K-series	85.78	85.00	34.62	18.18
Silicon	K-series	0.81	0.81	0.40	0.22
Sulfur	K-series	0.54	0.54	0.23	0.18
Total:		100.00	100.00	100.00	

EDX data of RH

IV.13 References

References are given in BIBLIOGRAPHY under Chapter IV.