CHAPTER II

A GREEN SYNTHETIC APPROACH TOWARDS ONE POT MULTI COMPONENT SYNTHESIS OF HEXAHYDROQUINOLINE AND 9-ARYLHEXAHYDROACRIDINE-1,8-

DIONE DERIVATIVES CATALYZED BY SULPHONATED RICE HUSK

II.1 Introduction

Over the past decade, green chemistry has been emerged as an important environmental aspect to reduce the use of toxic and hazardous reagents in synthetic and industrial chemistry. In recent years industrial use of agricultural wastage has received much interest due to economical and environmental reasons. RH is a major agricultural by-product in south Asian countries that can be a promising feedstock of industrial use [1-2]. Rice husk (RH) contains cellulose, hemicelluloses, lignin, ash like other lignocellulosic material. The features like high silica content, high porosity, light weight and high external surface area turn it a good catalyst support for many industrial synthesis [3-4]. The use of eco-friendly catalysts and selected green solvents are demanding in recent years for the synthesis of organic compounds [5]. In terms of

green chemistry, the development of efficient multi-component reactions (MCRs) has attracted much consideration regarding the use of heterogeneous catalyst [2-3]. One-pot MCRs are energy saving processes that eliminates the multiple steps and increases the productivity with high level of structural diversity [5-10]. MCRs are convergent in nature and an important toolbox of green chemistry to synthesize different biologically active heterocyclic compounds. A large variety of MCRs are catalyzed by homogeneous and heterogeneous acid catalyst. However, solid acid catalyst have gained attention due to their heterogeneous nature and are favoured over homogeneous one as they can be easily separated from the reaction system. Quinolines are ubiquitous in nature and they represent a wide variety of pharmaceutical (**Figure II. 3**) and agrochemical products [11]. Substituted quinolines exhibit diverse biological activities and they are found as major building blocks in various natural products [12]. Quinolines possess considerable interest due to their biological activity including antibacterial, antifungal, antioxidant, anticancer, anticonvulsant, and antiviral activity [12-16]. Substituted quinolines and tetrahydroquinolines (THQ) are a class of heterocycles that serve as chemotherapeutic agents also [17-19]. Many heterocyclic [25],

compounds containing the quinoline nucleus display anti-inflammatory activity and they serve as antagonist inhibitors [20]. Quinolines with 1,4-Dihydropyridine (DHP) nucleus have been found efficient in cardiovascular diseases as calcium channel blockers [21-22]. Along with these, this heterocyclic moiety have vast application in agricultural field also [23]. Many recent research works are carried on this unique heterocyclic motif due to its diverse biological activity [24-25]. Several homogeneous and heterogeneous catalysts have been employed for the synthesis of substituted hexahydroquinolines derivatives. Among them, the synthesis using nano-ZnO/ultrasound nano-Fe_3O_4 [26], AcOH [27], K_2CO_3 [28], triethylamine [29], Fe_3-x$TixO_4$@SPDETATSA (N-(3-silyl propyl) diethylene triamine N,N',N''-tri-sulfonic acid immobilized on Fe_3-x$TixO_4$ magnetic nanoparticles [30] are noteworthy to mention.

Acridine derivatives are also important class of heteterocyclic compound and those derivatives containing keto functional groups are found to be good anti-malarial agents and substituted hexahydroacridine-1,8-dione being resemble to dihydropyridine molecule can act as a K-channel openers in urinary-bladder smooth muscle [31-32]. These acridinediones were also found to act as laser dyes due to electron delocalization and exhibit fluorescence and laser

activity [33-34]. The effectiveness of lasing is dependent upon the substituents at C-9 and N-10 of the acridine chromophore. Apart from the above applications, acridinediones also possess other important photo-physical and electrochemical properties [35]. Acridine dyes can bind with photo damaged nucleic acids which have increasing interest as mutagens in micro-organisms[36]. The usefulness of acridines have led to the development of numerous methods of their synthesis by the three component Hantzsch condensation of aldehydes with *β*-diketones and ammonium acetate or appropriate primary amines. Many procedures describe the synthesis of acridinedione derivatives by cyclocondensation between dimedone and aldehyde and primary amine in the presence of heat in organic solvents with a varity of catalysts such as Fe_3O_4@B-MCM-41, [37] $(SO_4)_2/TiO_2$NPs, [38] Scolecite, [39] Pd-nanoparticle, [40] MNPsN-propyl-benzoguanamine-SO_3H, [41] silica bonded N-propyl sulfamic acid,[42] CH_3SO_3H, [43] tetrabutylammonium hexatungstate, [44] Nano-TiO_2, [45] $SiO_2/ZnCl_2$, [46] protic pyridinium ionic liquid,[47] $CsCO_3$,[48] ceric ammonium nitrate(CAN), [49] organocatalysts,[50] Ni-nanoparticles,[51] MgO,[52] thiamine hydrochloride,[53] SnO_2,[54] La_2O_3/TFE (2,2,2-trifluoroethanol),[55] $Cd(NO_3)_2$.$4H_2O$ [56]. However, many protocols

suffer from some limitations such as harsh reaction conditions, costly and non recyclable catalyst and tedious purification, use of toxic reagents and generation of hazardous wastes. By eliminating the drawbacks of previous methods, it is important to find out new greener protocols for the synthesis of substituted quinolines and hexahydroacridine-1,8-dione. Eco-friendly heterogeneous solid acid catalysts have gained much attention over homogeneous catalysts owing to its easy separation process. Amongst them carbon-based sulphonated catalysts are most promising because of the presence of different acidic functional groups and large carbon framework. Owing to the low price and simple preparation, biomass waste (RH) is extensively used in several field as mentioned above. With increasing demand in green chemistry, the use of heterogeneous solid acid catalyst has attracted the researchers regarding environmental issues. An ideal solid acid catalyst should be the one which have excellent stability, high porosity, active acidic sites, low cost and hydrophobic surfaces. Among them carbon-based acidic catalysts are most promising as they can be extensively prepared from biomass material (RH). However, RH based alkaline catalyst and solid acid catalyst under MW irradiation has been reported previously [57-58]. Herein, we report a conventional heating

technique for the preparation of sulphonated RH (SRH) and characterisation as well. We report the use of this novel green catalyst SRH for feasible synthesis of hexahydroquinoline and hexahydroacridine-1,8-diones derivatives in one-pot strategy.

II.2 Quinoline

Quinoline is a weak tertiary organic base and was discovered in 1834 as a colourless hygroscopic liquid by distillation of coal tar by Friedlieb Ferdiland Runge and in 1871, Dewar observed the chemical similarity between pyridine and quinoline having rigid heterocyclic core of benzene ortho-fused with a pyridine ring (**Figure II. 1**). [59] Coal tar is a principal commercial source for quinoline synthesis but numerous reactions have been developed for its laboratory synthesis. Quinoline itself has a few applications but many of its derivatives are useful in various chemical reactions for laboratory synthesis.

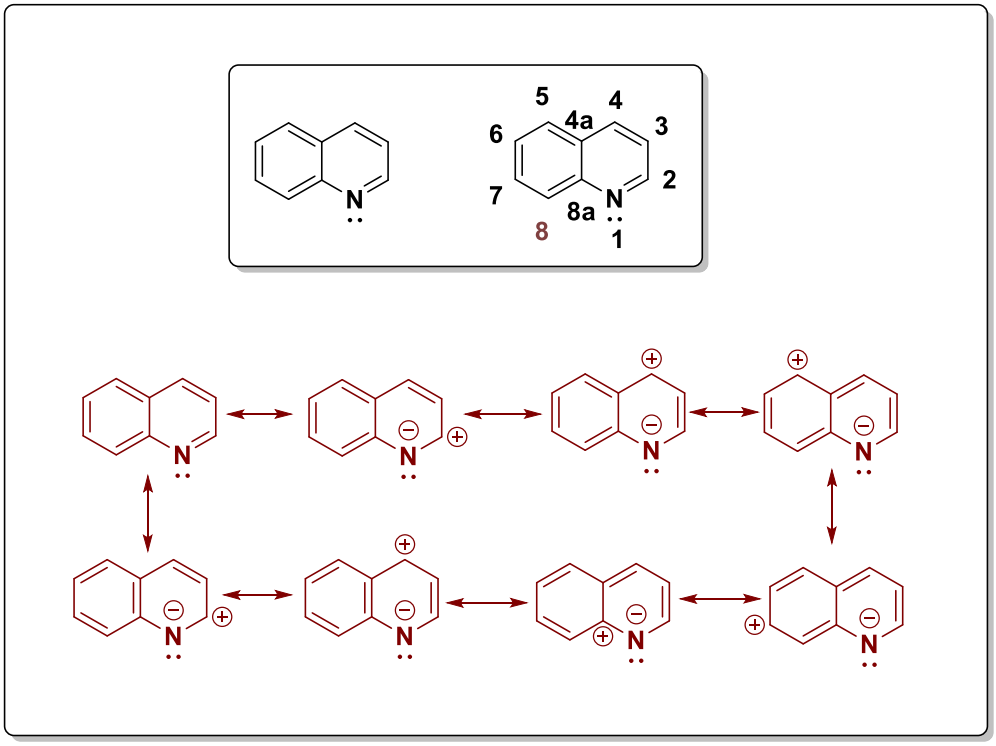


Figure II. 1 Chemical structures and resonating structures of quinoline moiety

There are several reported classical synthetic routes for synthesising the quinoline structural motifs and such classical synthetic routes which are widely used include Skraup reaction, Conrad-Limpach reaction, Doebner reaction, Combes reaction, Povarov reaction, Doebner-Miller reaction, Gould Jacobs reaction and Riehm reaction. Which are majorly utilizes aniline as one of the common reactants (**Figure II. 2**). However, there are several other reactions such as Knorr reaction, Friedländer reaction, Pfitzinger reaction, Niementowski reaction, Meth-Cohn reaction and Camps reaction which requires

special substituted anilines or other substituted reactants to yield quinoline structural motiffs.

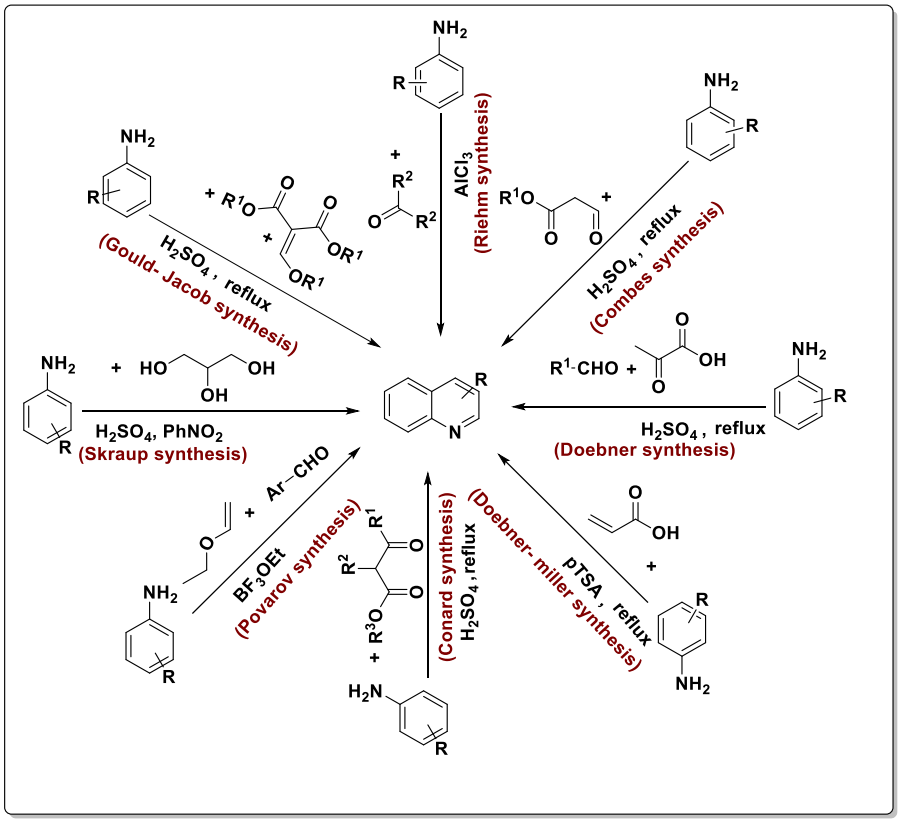


Figure II. 2 Diverse synthetic routes for the synthesis of quinoline structures

II.3 Biological importances of quinolines

Quinoline scaffolds are well-known entity under alkaloid class of natural products and is present in various biologically active plants, pharmaceuticals, agrochemicals, dyes etc.[60-61] They are also used as chelating agent due to multiple N-donor ligands and quinoline pharmacophore is a crucial functionalitydue to variety of pharmacological activities (**Figure II. 3**) such as antimalarial,

antiprotozoal, antitubercular, antibacterial, anticancer, antiproliferative, antitumor, anti-inflammatory, antifungal, antioxidant, DNA binding, antihypertensive, anti-HIV agents. [62-70] High magnitude of pharmacological importance of natural or synthesized quinoline derivatives has urged various chemists world wide to examine the utility and prominence of this scaffold by means of research reviews.

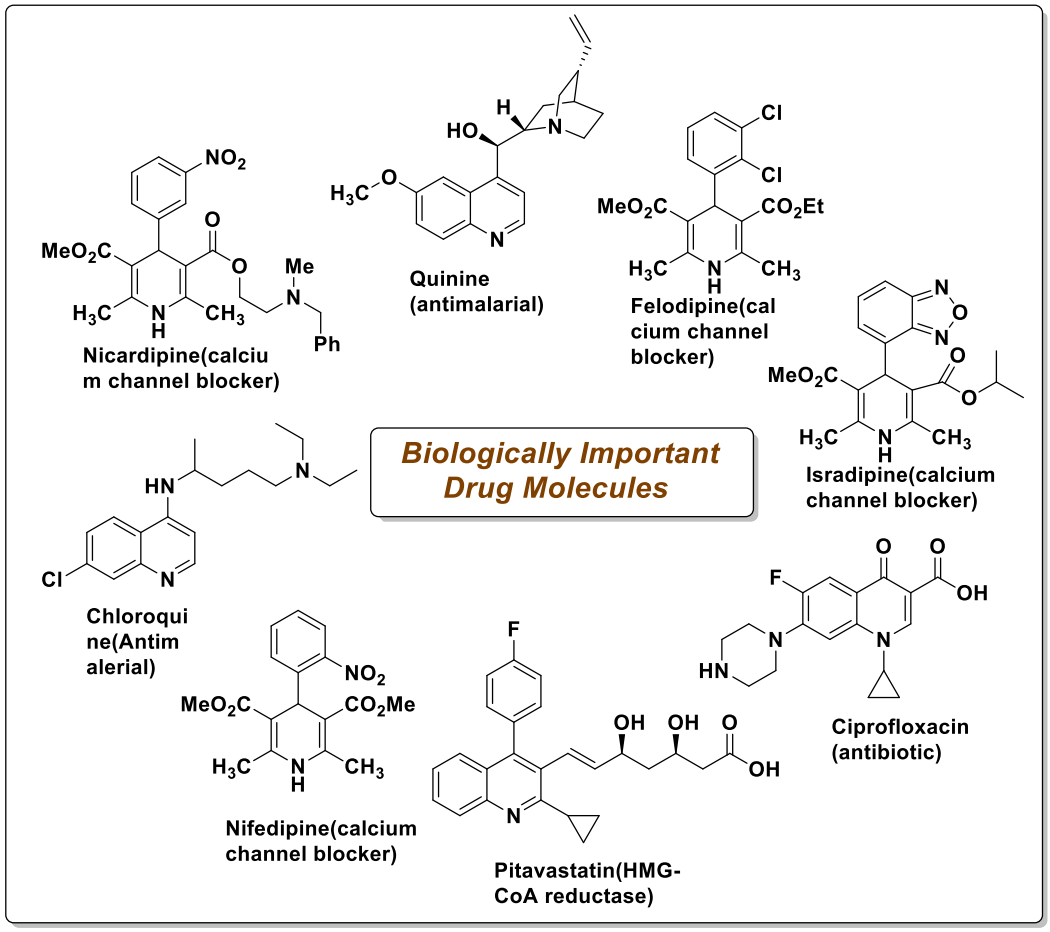
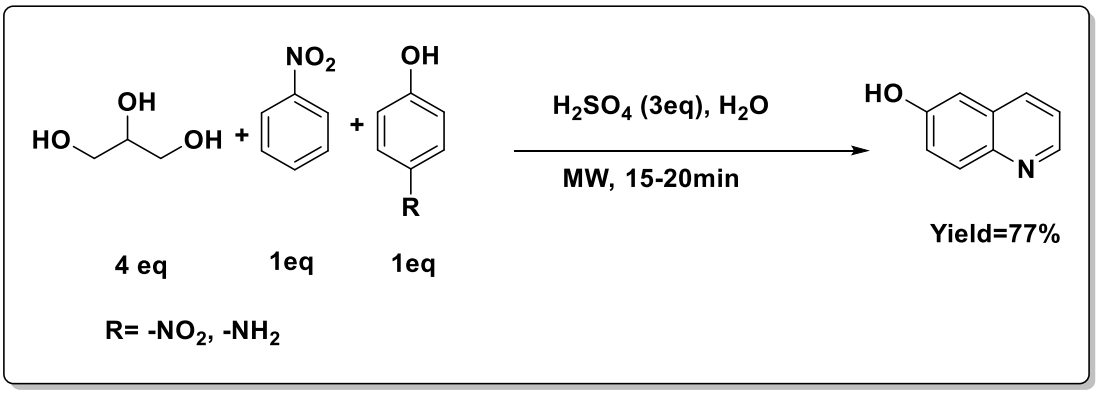


Figure II. 3 Some important pharmaceutically active drug molecule

By doing studies on works in various journals and reviews related to quinolines, substituted quinolines, unsaturated quinolines and their derivatives and taking biological importances of their derivatives in knowledge, in this following part of the chapter II, it has been focused on the synthesis of quinoline derivatives in a new and convenient manner using available laboratory chemicals.

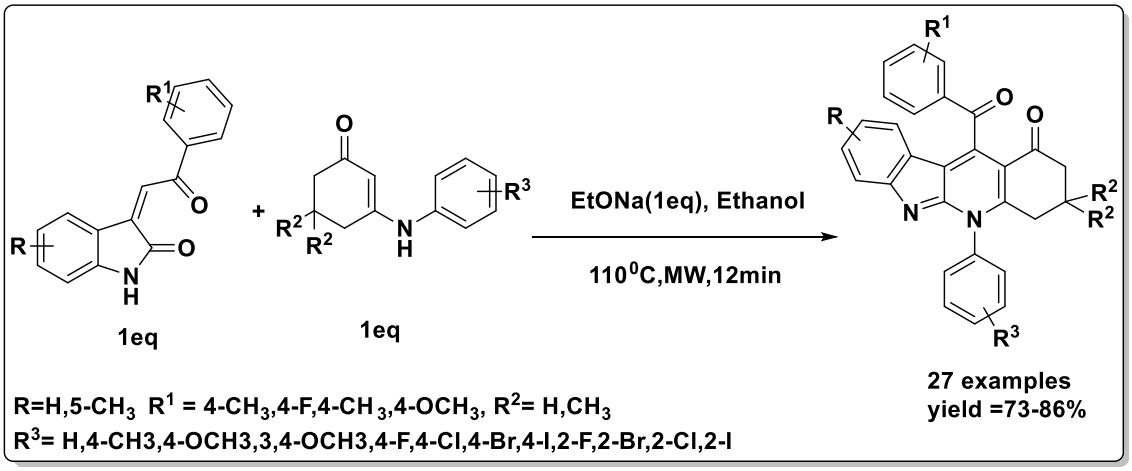
II.4 Previous methods of synthesis of quinoline derivatives

In 2014, Saggadi *et al.* had developed a synthetic method following Skraup reaction and Bamberger rearrangement reaction in water using glycerol, nitrobenzene and *p*-aminophenol or *p*-nitrophenol as reactants under microwave condition (**Scheme II.1).** [71]



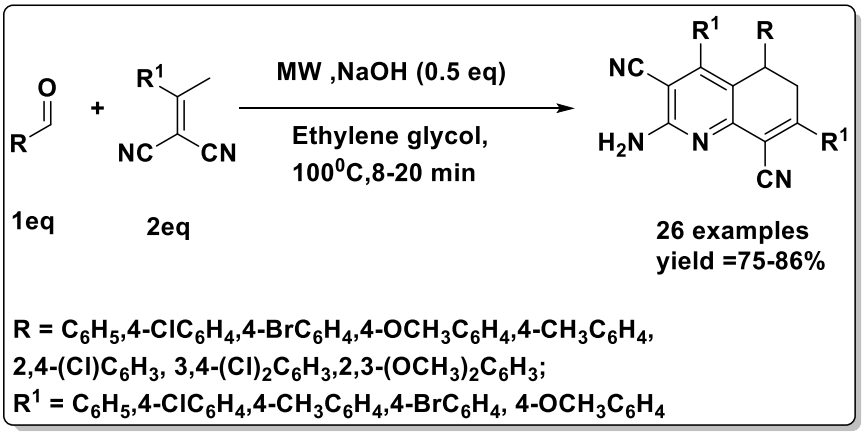
Scheme II.1 Modified Skraup reaction and Bamberger rearrangment reported by Saggadi *et al*.

In 2014, Li *et al*. developed a protocol to synthesize biologically active quinolines using 3-aroylidene-2-oxindoles with enaminones in presence of sodium ethoxide in ethanol at 110°C under microwave condition (**Scheme II.2**). [72]



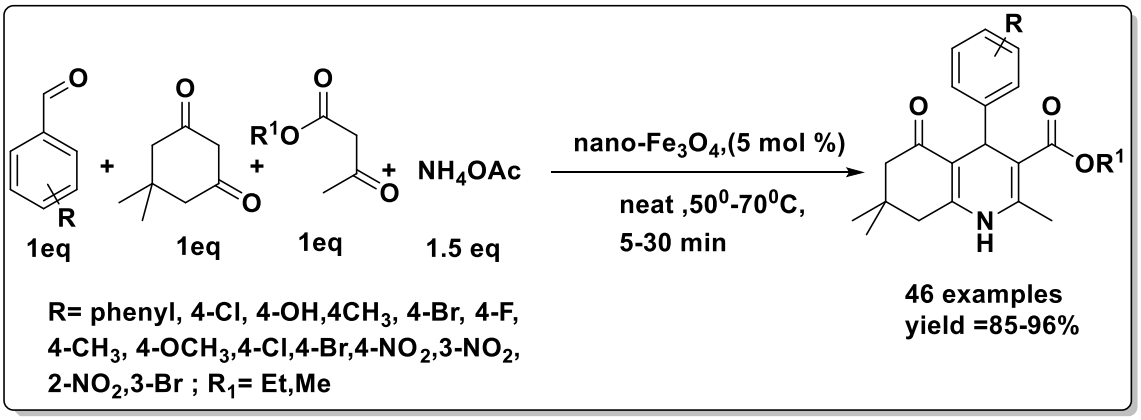
Scheme II.2 Base promoted cycloaddition reaction under microwave condition reported by *Li et al*.

In 2012, *Yu et al*. designed a three component synthesis of polysubstituted dihydroquinoline from aromatic aldehydes and 1-arylethylidenemalononitrile in presence of sodium hydroxide as base in ethylene glycol under microwave irradiation (**Scheme II.3**). [73]



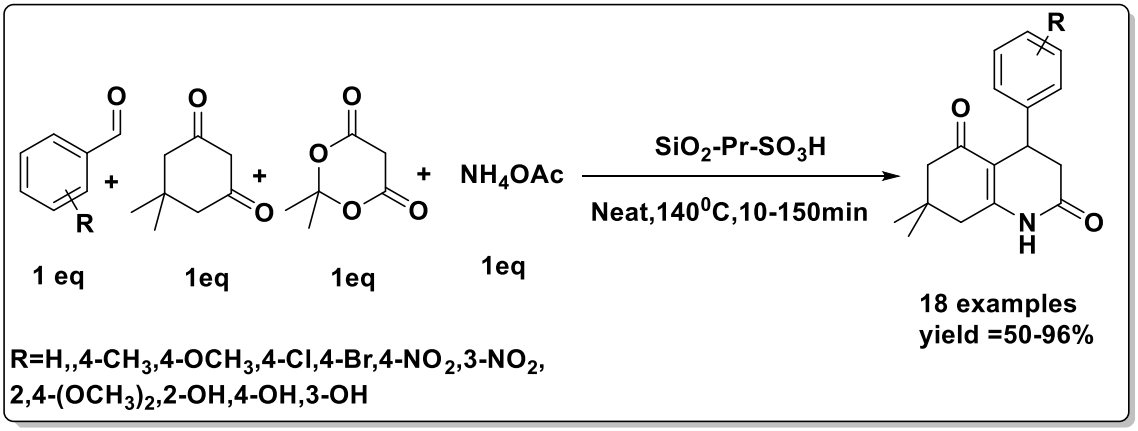
Scheme II.3 Base catalyzed Domino reaction under microwave reported by Yu et al.

In 2014, Esfahani *et al*. and Khazaei *et al*. performed iron (III) oxide nanoparticles catalyzed synthesis of polyhydroquinolines under solvent free conditions using aromatic, cyclic and heterocyclic aldehydes, dimedone, β-ketoesters and ammonium acetate at 50°C under solvent free conditions (**Scheme II.4**). [74-75]



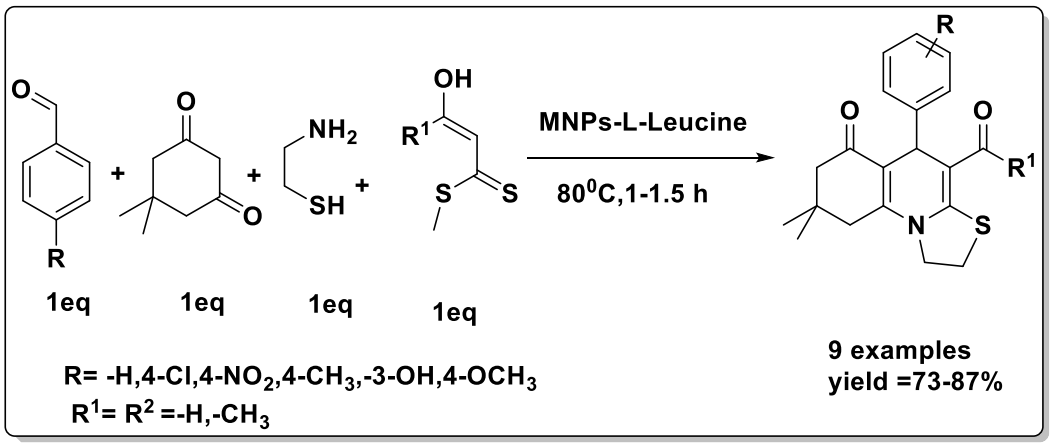
Scheme II.4 Nano-Fe_3O_4 catalysed solvent free reaction reported by Esfahani *et al.*

In 2015, Ziarani *et al.*, synthesized dioxo-octahydroquinolines in one pot method using aromatic aldehydes , dimedone , Meldrum's acid and ammonium acetate and sulfonic acid functionalized SiO_2-Pr-SO_3H as catalyst under solvent-free condition (**Scheme II.5**).[76]



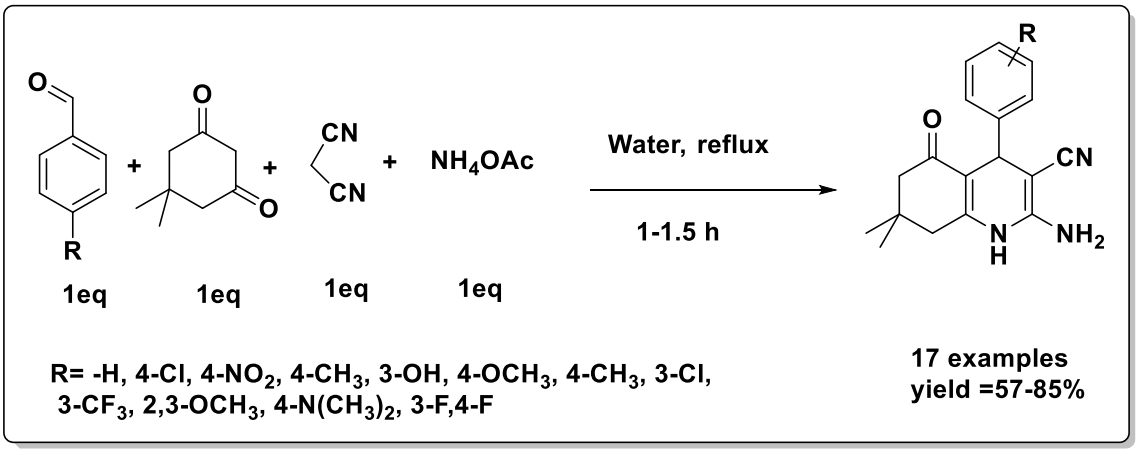
Scheme II.5 Silica based catalyst induced reaction for octahydroquinolines by Ziarani *et al*.

In 2016, Arabpoor *et al*. synthesized synthesis of thiazoloquinolines using superparamagnetic silica-encapsulated ϒ-Fe_2O_3 supported L-Leucine nanoparticles by the four-component reaction of α-enolicdithioesters, cysteamine, aromatic aldehydes and dimedone under thermal solvent-free condition at 80°C in one hour (**Scheme II.6**).[77]



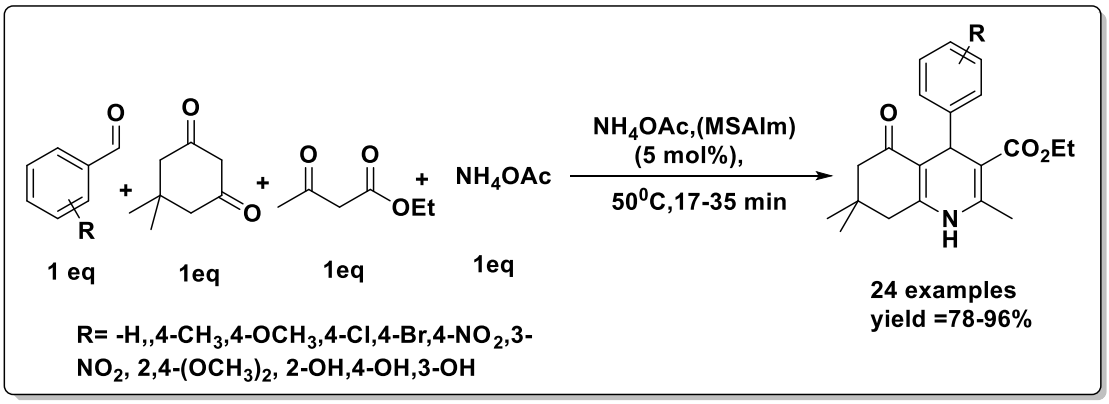
Scheme II.6 MNP-L-Leucine based reaction protocol reported by Arabpoor *et al*.

In 2017, Patil *et al*. had done a catalyst-free method for the synthesis of hexahydroquinolinones in single pot four component method taking dimedone, ammonium acetate, aryl aldehydes and malanonitrile as substrate in water (**Scheme II.7**).[78]



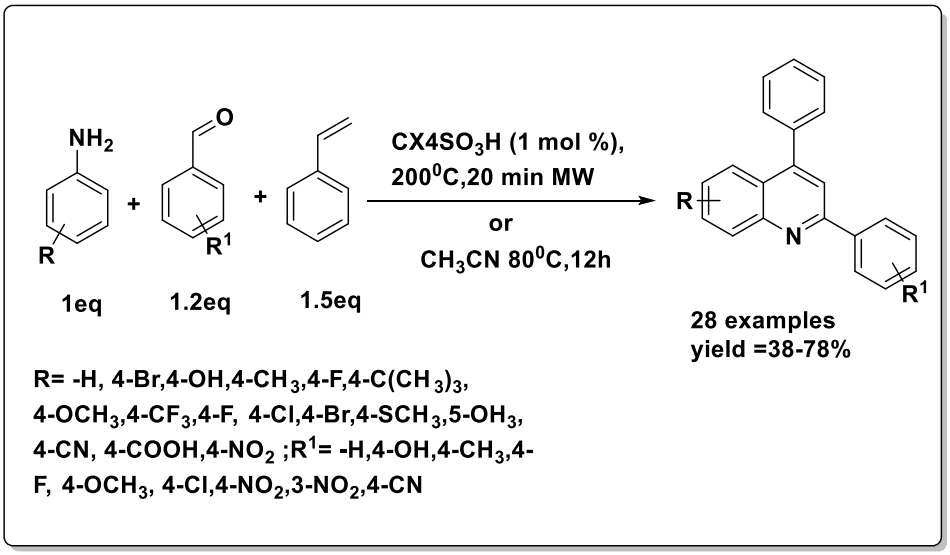
Scheme II.7 Catalyst free synthesis protocol reported by Patil *et al*.

In 2014, Khaligh *et al*. had done a four-component one-pot synthesis of synthesis of unsymmetrical polyhydroquinoline derivatives from aryl/heteroaryl aldehydes, ethylacetoacetate, dimedone and ammonium acetate under solvent-free conditions at 50^0C (**Scheme II.8**). [79]



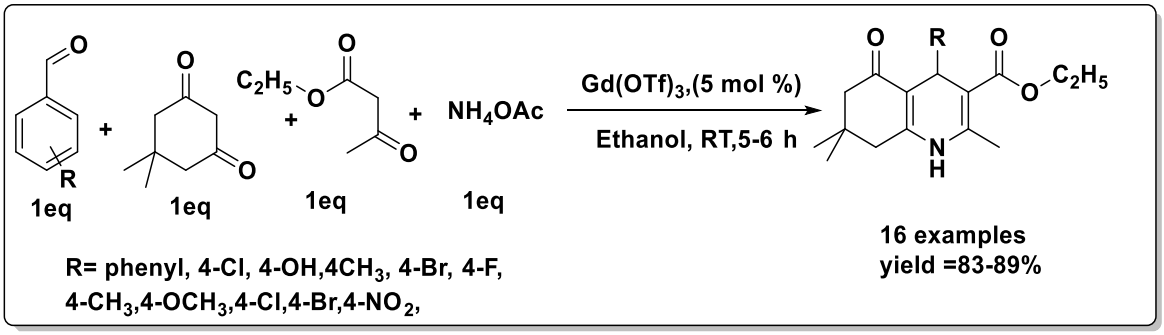
Scheme II.8 MSAIm catalysed Solvent free reaction reported by Khaligh *et al.*

In 2017, Liberto *et al*. has taken a protocol for the synthesis of 2,4-disubstituted quinolines using aromatic aldehydes, aromatic amines, styrene under at 200^0C temperature Microwave condition using CX4SO_3H catalyst or at 80^0C temperature in acetonitrile solvent (**Scheme II.9**). [80]



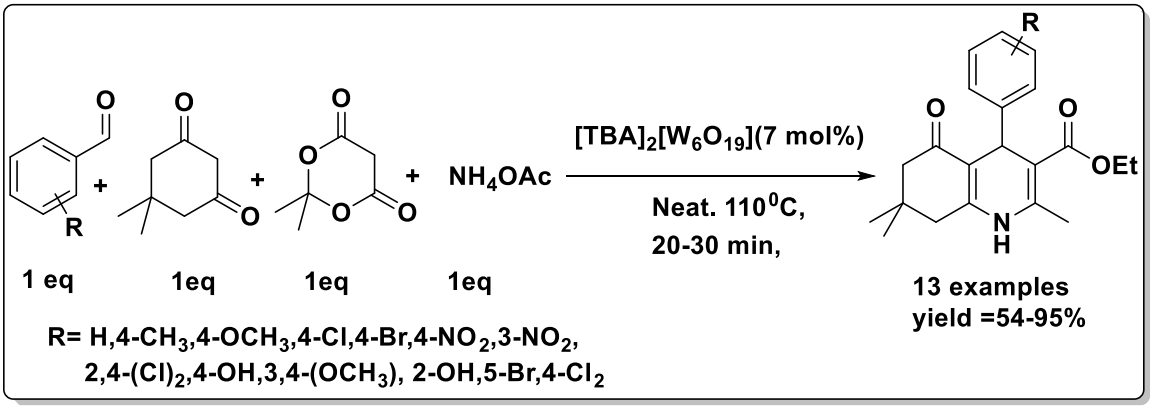
Scheme II.9 Microwave assisted solvent free reaction reported by Liberto *et al*.

In 2017, Mansoor *et al*. reported a muticomponent method by for the synthesis of hexahydeoquinolones by using $Gd(OTf)_3$ as catalyst from aldehydes, 5,5-dimethyl-1,3-cyclohexaedione dimedone, ethyl acetoacetate and ammonium acetate by using $Gd(OTf)_3$ as catalyst at room temperature (**Scheme II.10**). [81]



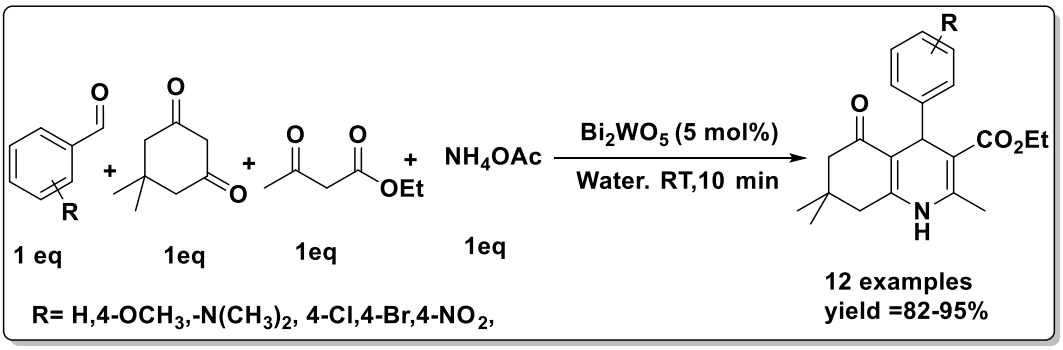
Scheme II.10 $Gd(OTf)_3$ catalysed synthesis of polyhydroquinolines in ethanol reported by Mansoor *et al*.

In 2011, Khojastehnezhad *et al*. reported a synthetic method for the synthesis of hexahydroquinolinones in one-pot, four-component method taking dimedone , aldehydes , ethyl acetoacetate and ammonium acetate under solvent-free conditions using $[TBA]_2[W_6O_{19}]$ catalyst (**Scheme II.11**). [82-83]



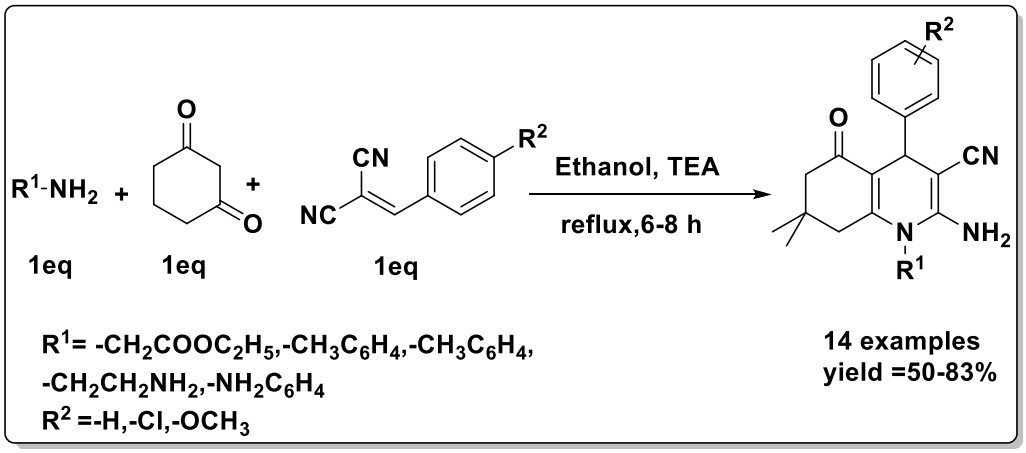
Scheme II.11 Solvent free reaction reported by Davoodnia *et al*. and Khaligh *et al*.

In 2014, Paplal *et al*. synthesized different types of functionalized polyhydroquinolines by reaction of substituted aromatic aldehydes, ethyl acetoacetate, dimedone and ammonium acetate in aqueous medium using Bi_2WO_5 as catalyst (**Scheme II.12**).[84]



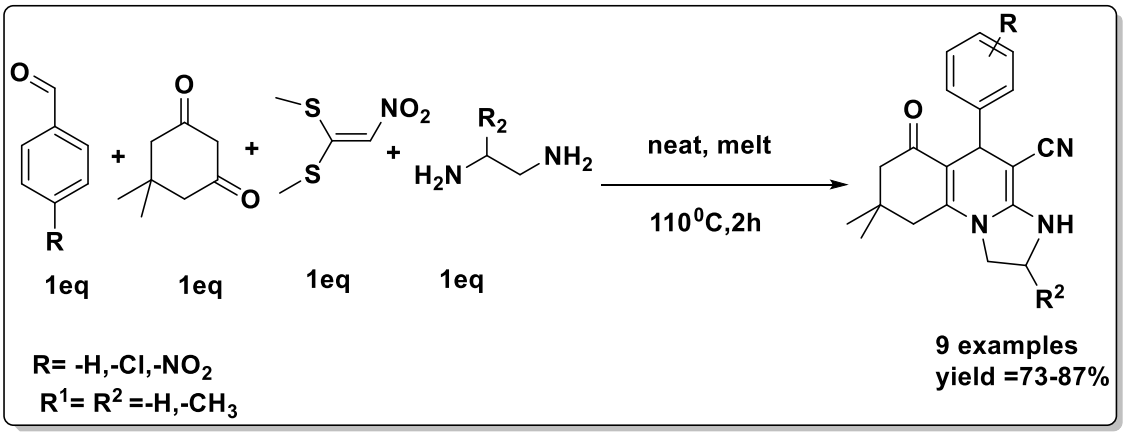
Scheme II.12 Synthesis of functionalized polyhydroquinolines reported by Paplal *et al.*

In 2017, Abdelhamid *et al*. had made a protocol for the three-component cyclocondensation synthetic method of hexahydroquinoline derivatives from 1,3-cyclohexanedione, primary amine in presence of ethanol, TEA under reflux condition (**Scheme II.13**). [85]



Scheme II.13 Three-component cyclocondensation with TEA in ethanol reported by Abdelhamid *et al*.

In 2014, Alizadeh *et al*. sythesised the octahydro-imidazo[1,2-*a*]quinoline derivatives under solvent free conditions from aromatic aldehyde, dimidone as amazor component (**Scheme II.14**). [86].



Scheme II.14 Solvent free reaction reported by Alizadeh *et al*.

II. 5 Acridine

Acridine is a nitrogeneous heterocyclic compound having planner shaped structural motif and it is also structurally closely resembles to anthracene with one of the central C-H group is replaced by 'N' atom. It is a basic organic compound due to the presence of Sp^2-hybridised 'N' atom and the unsubstituted compound is generally colourless crystalline solid.[87] In 1870 Carl Grabe and Heinrich Caro first isolated acidine from coal tar by extracting with dil. H_2SO_4 .[88] Acrinines have broad range of research and industrial applications in various fields such as in medicinal chemistry, fluorescent organic dye, chemosensor, photo catalysis, as hole transport materials in solar cell and photovoltaic applications.[89-97] Acridinium ions are used as efficient organic photo catalyst for many organic transformations due to their long excited state lifetime and tunable redox potential.[98-99] There are various procedures [100-109] for the synthesis of acridine structural motifs but at the very first Bernthsen *et. al* have synthesized it in laboratory by using diphenylamine and carboxylic acid in presence of anhydrous $ZnCl_2$.[110]. There are also other methods (**Figure II. 4**) which have been developed in recent years and which has opened a broad window for the organic synthesis of acridine structural motifs.

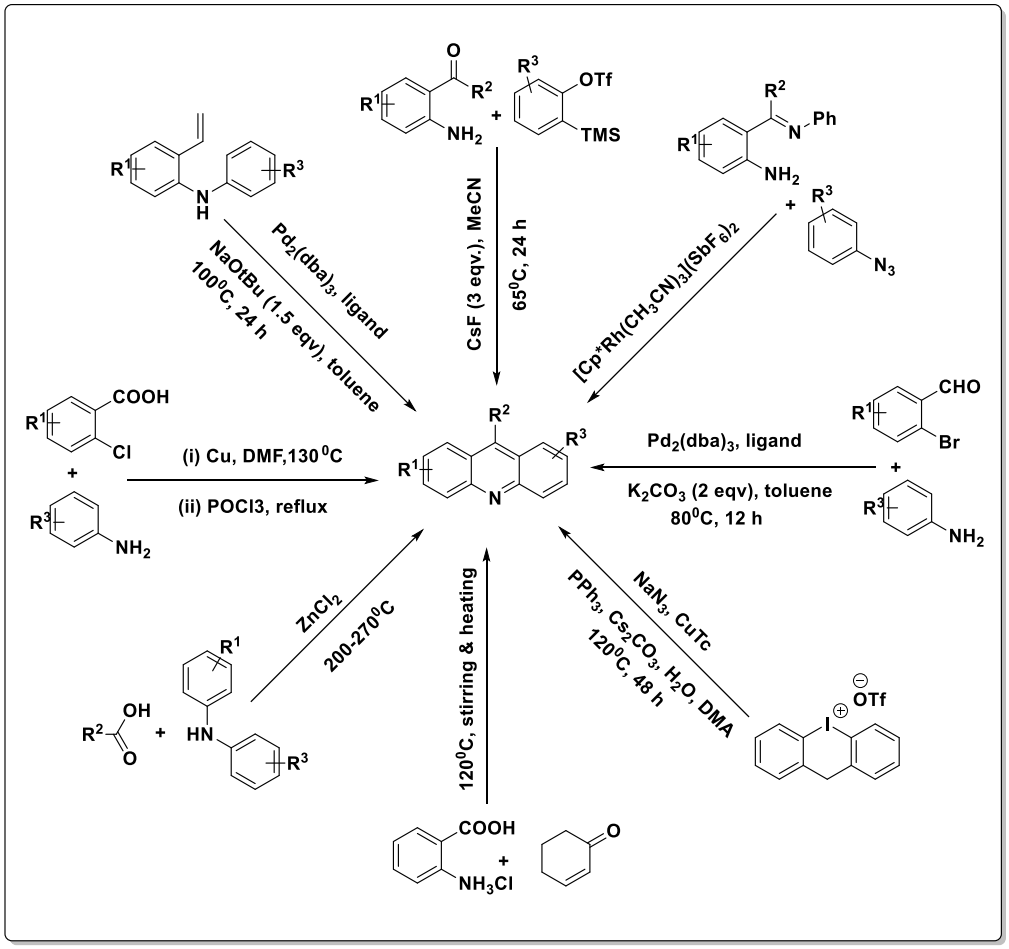


Figure II. 4 Diverse synthetic routes for the synthesis of acridine structures

II. 6 Biological importance of Acridines

Acridine derivatives have been used for the preparation of labeled medicinal conjugates such as nucleic acids, peptides, and proteins that exhibit antitumor and DNA-binding properties [111-113]. Among other acridine derivatives, substituted 1,8-Dioxo-decahydroacridines and their derivatives have been widely used in medicinal chemisty as can behave as alternative 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 1,8-Dioxo-decahydroacridines have been used as calcium channel blockers for the treatment of defibrillation and hypertension disease [114-116]. They also possesses antimalarial, antiviral, antibacterial, antiallergic and anicancer properties and recently, acridines showed some inhibition properties for multidrug resistance in tumour cell lines and some of the acridine drugs are exhibiting promising anticancer activity both in vitro and in vivo against a range of murine and human cancers cells (**Figure II. 5**).[117-120] And additionally due to having fluorescent properties they are being used as molecular probes for monitoring polymerization processes in biological cells.[121]

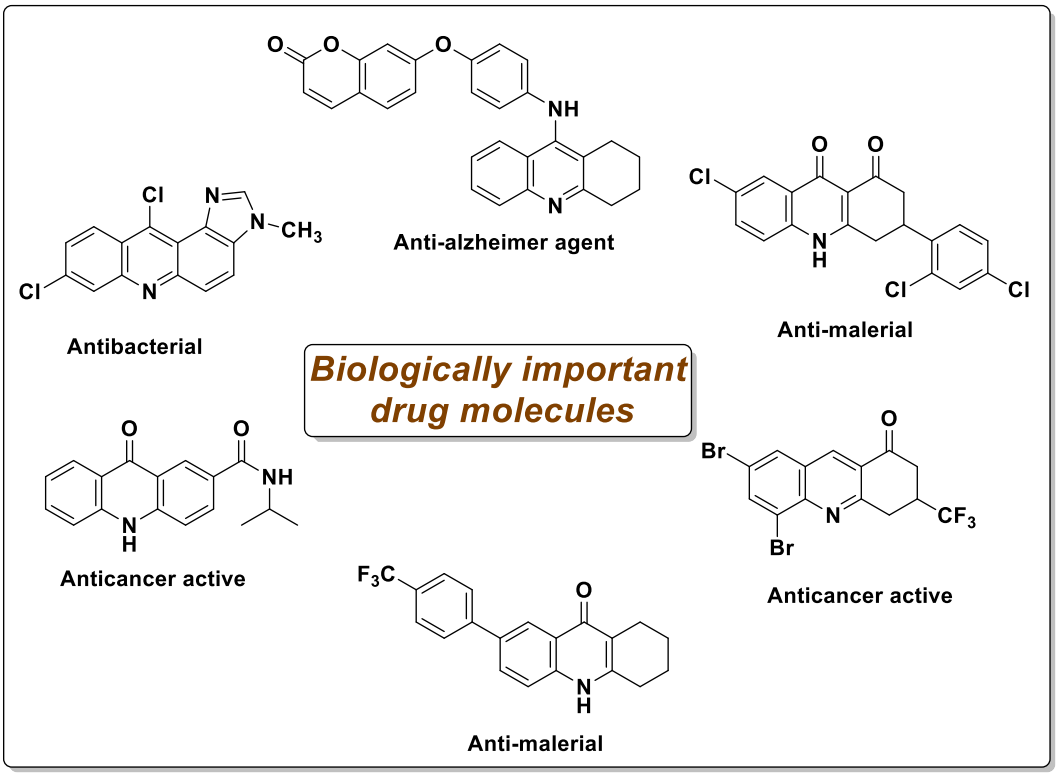


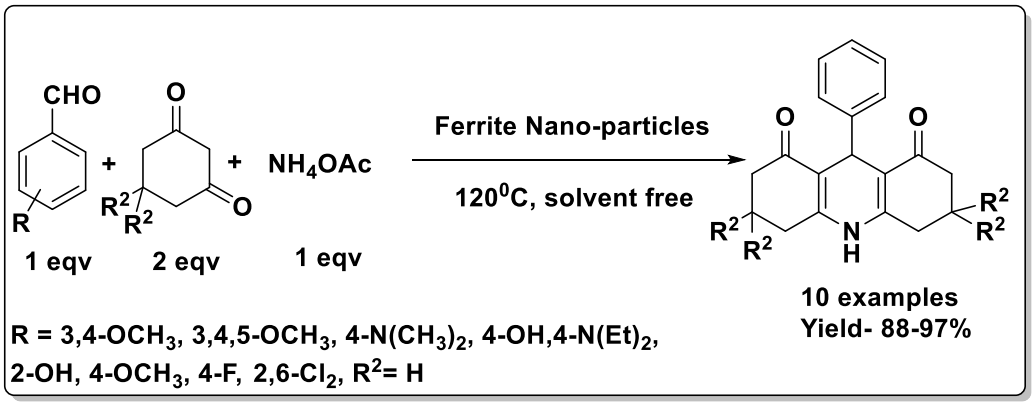
Figure II. 5 Some important pharmaceutically active drug molecule

By doing studies on works in various journals related to acridines, acridinediones and their derivatives and taking biological importances of acridines, acridinediones and their derivatives in knowledge , in this following part of the chapter II, it has been focused on the acridine-dione derivatives in a new and convenient manner using cheap laboratory chemicals.

II. 7 Previous methods synthesis of acridine derivatives

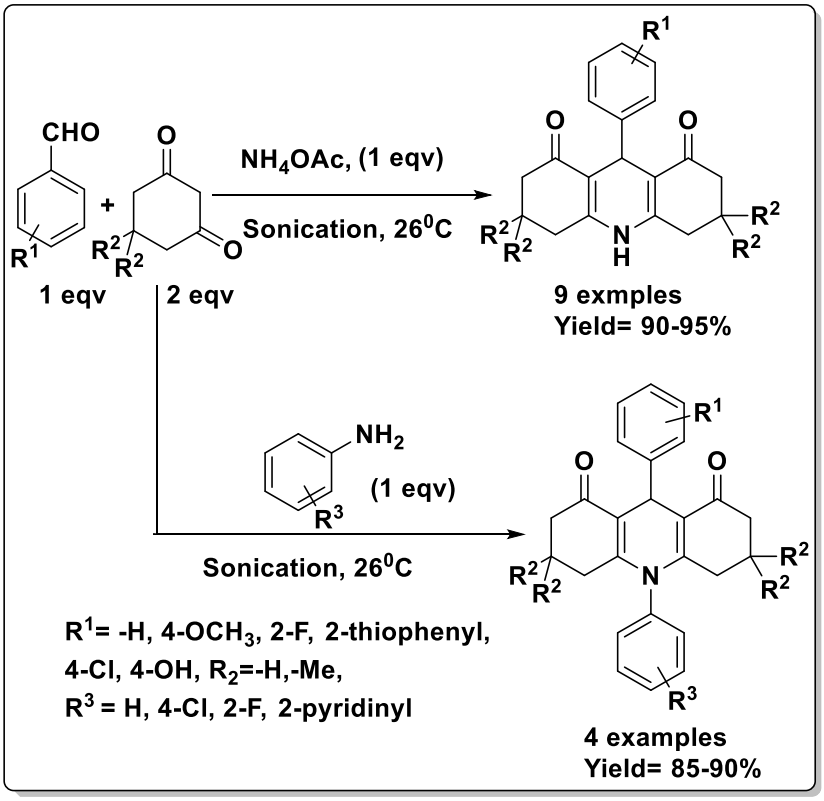
In 2016, Sunkara *et al.* had done the synthesis of 9-aryl substituted acridinedione derivatives under solvent free conditions. A one-pot

reaction methodology was adopted with the use of 1,3-cyclohexanedione, aldehydes and ammonium acetate using nano ferrite at 120^0C for the preparation of acridinediones and their derivatives (**Scheme II.15**).[122]



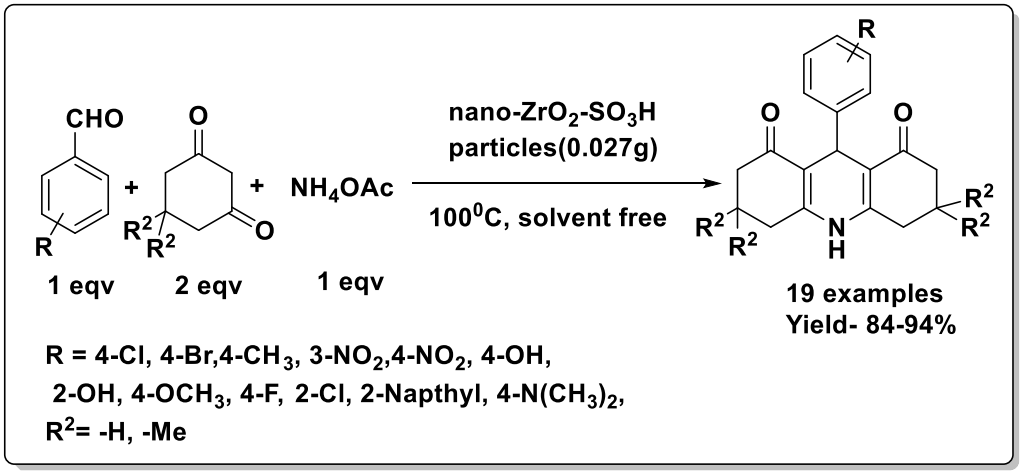
Scheme II.15 Ferrite nano-particles catalysed facile synthesis of acridinediones by Sunkara *et al.*

In 2013, A Facile Synthesis of N-H- and N-Substituted Acridine-1,8-diones under Sonic Condition by Sudha *et. al*. Here ceric ammonium nitrate (CAN) was used along with aromatic aldehydes and aromatic amines or ammonium acetate and dimedone or cyclohexyl-1,3-diones at 26^0C under sonic condition (**Scheme II.16**). [123]



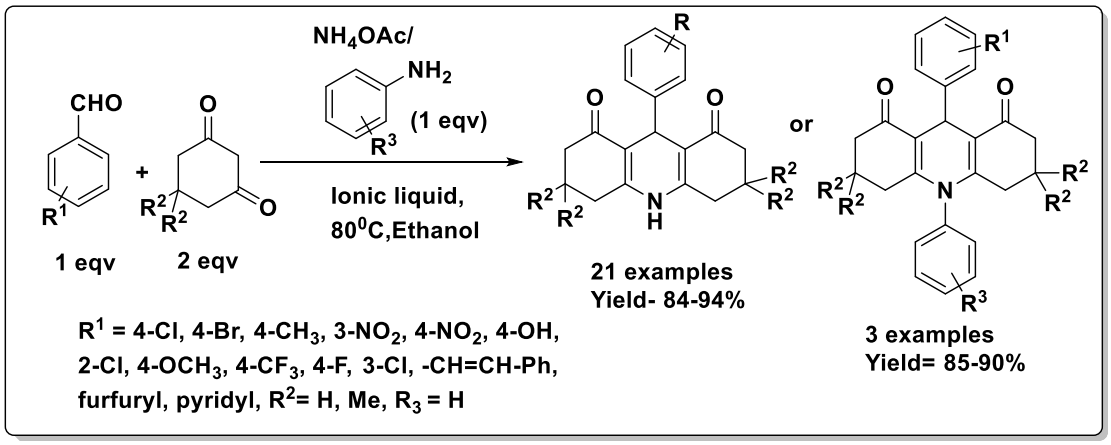
Scheme II.16 Ultasound sonication induced synthesis of acridinedione derivatives by Sudha *et. al*.

In 2016, Amoozadeh *et al*. synthesized 9-arylhexahydroacridines with taking a mixture of various 1,3-cyclic diketone, aromatic aldehydes, and ammonium acetate in presence of n-ZrSA as catalyst at 100 °C (in an oil bath) in solvent free conditions (**Scheme II.17**). [124]



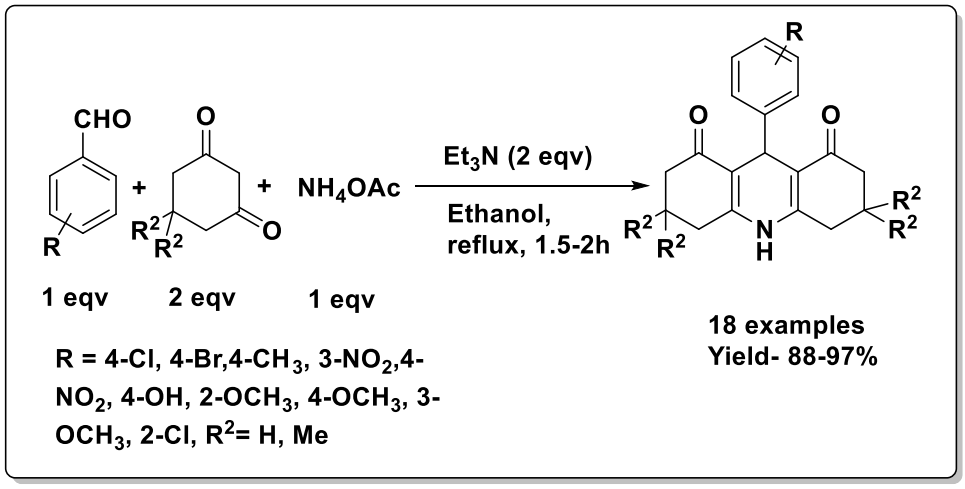
Scheme II.17 Nano-ZrO_2-SO_3H catalysed synthesis of acridinedione derivatives by Amoozadeh *et al*.

In 2017, Zhu *et al*. reported the synthesis of 9-arylhexahydroacridines using aromatic aldehyde, 5,5-dimethyl-1,3-cyclohexanedione, NH_4OAc and corresponding amount of ionic liquid were mixed with 1 ml ethanol, and then heated at 80^0C by using a series of ionic liquids based on betainium cation (Hbet) with different anions (**Scheme II.18**). [125]



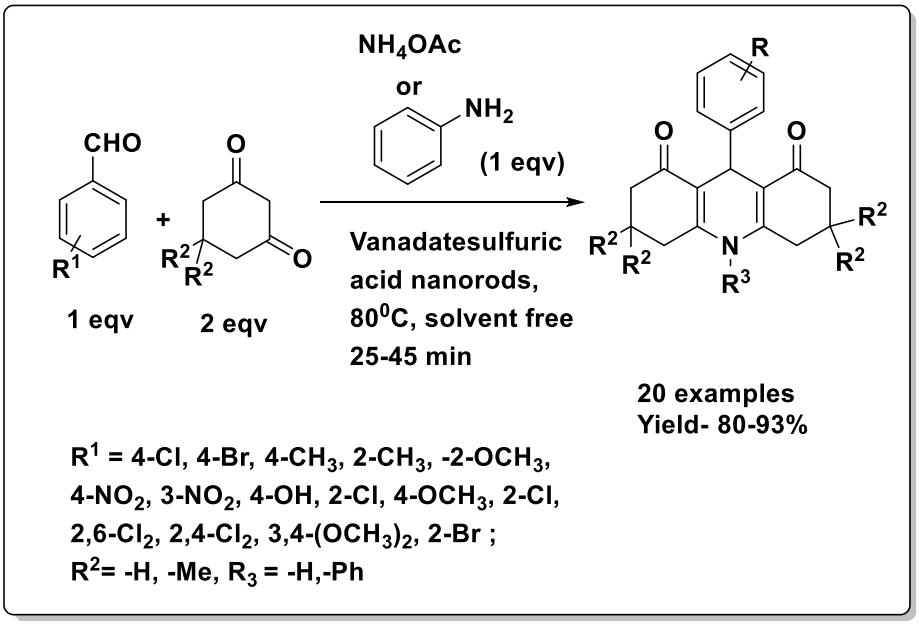
Scheme II.18 Ionic liquids catalysed synthesis of acridinedione derivatives by Zhu *et al*.

In 2018, Djemoui *et al*. reported an efficient approach to the synthesis of 1,8-dioxo-decahydroacridines and hexahydroquinolines via one-pot multi-component condensation of an aromatic aldehyde, cyclic 1,3-diketones and NH_4OAc in ethanol with use of Triethylamine (TEA) at reflux condition (**Scheme II.19**).[126]



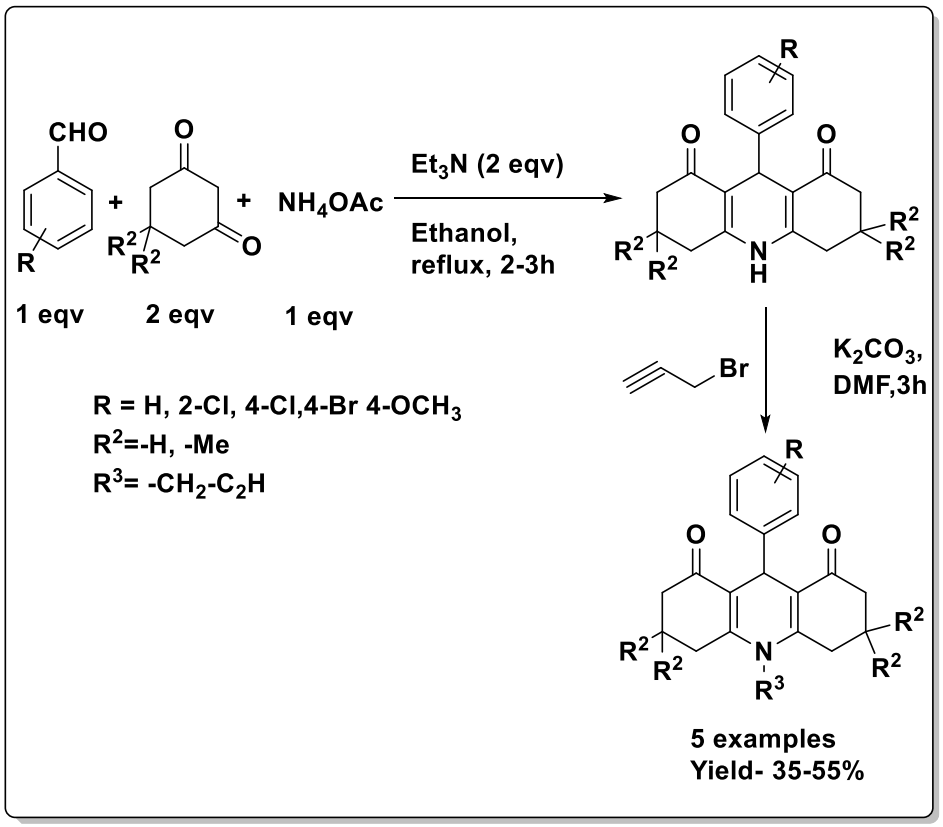
Scheme II.19 Base catalysed synthesis of acridinedione derivatives by Djemoui *et al*.

In 2015, Nasr-Esfahani *et al.* reported a synthesis of hexahydroacridine-1,8-diones using 1,3- cyclohexanedione derivatives, aldehydes and ammonium acetate or aniline under solvent-free conditions. Nanorod vanadatesulfuric acid (VSA-NRs), was used as catalyst as a novel, recyclable and eco-benign catalyst to synthis hexahydroacridine-1,8-diones (**Scheme II.20**). 127]



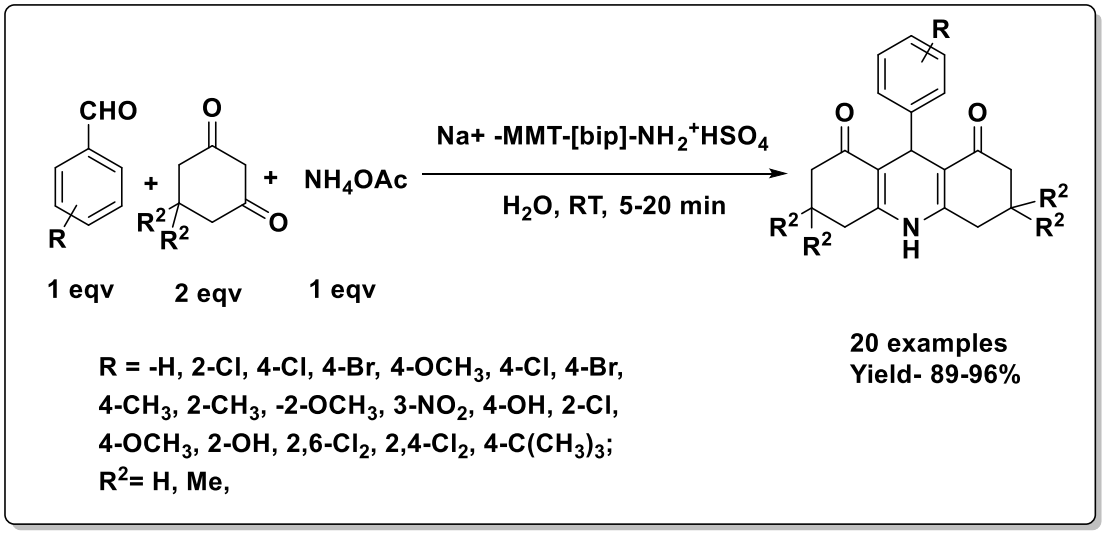
Scheme II.20 Vanadate sulfuric acid catalysed synthesis of acridinedione derivatives by Nasr-Esfahani *et al*.

In 2020, Naouri *et al*. reported a procedure for the preparation of 1,8-dioxodecahydroacridine derivatives via a one-pot three-component condensation of aromatic aldehydes, 1,3-cyclohexanedione and ammonium acetate in ethanolic medium under reflux condition catalyzed by triethylamine (TEA) to give the desired product (**Scheme II.21**).[128]



Scheme II.21 Et_3N catalysed synthesis of acridinedione derivatives by Naouri *et al*.

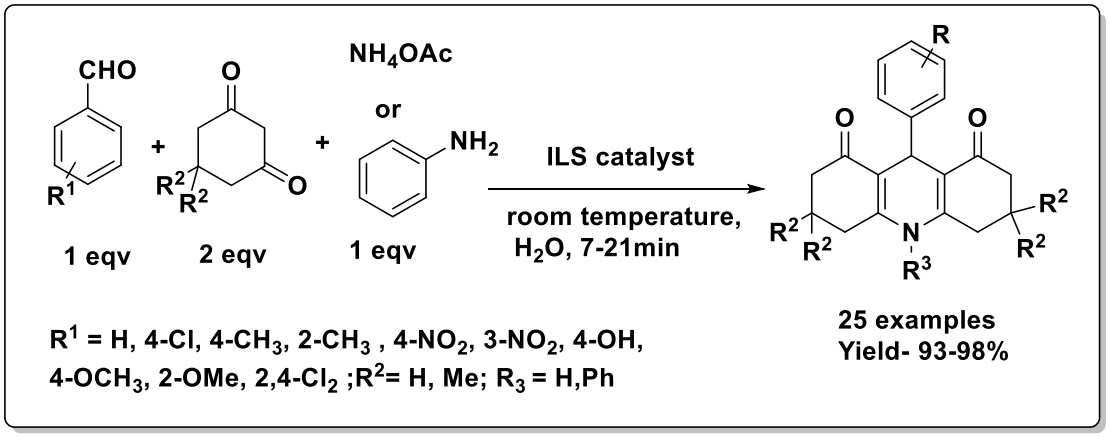
In 2020, Mazloumi *et al*. reported the synthesis of hexahydroquinolines and 1,8-dioxo-decahydroacridines via Hantzsch condensations using a new nanoporous catalyst formulated as Na+ -MMT-[bip]-$NH_2^+HSO_4^-$. All reactions were performed under mild reaction conditions taking mixture of a *β*-ketoester derivative, 1,3-cyclohexanedione derivatives, aldehyde, and ammonium acetate(**Scheme II.22**). [129]



Scheme II.22. Ionic liquid catalysed synthesis of acridinedione derivatives by Mazloumi *et al.*

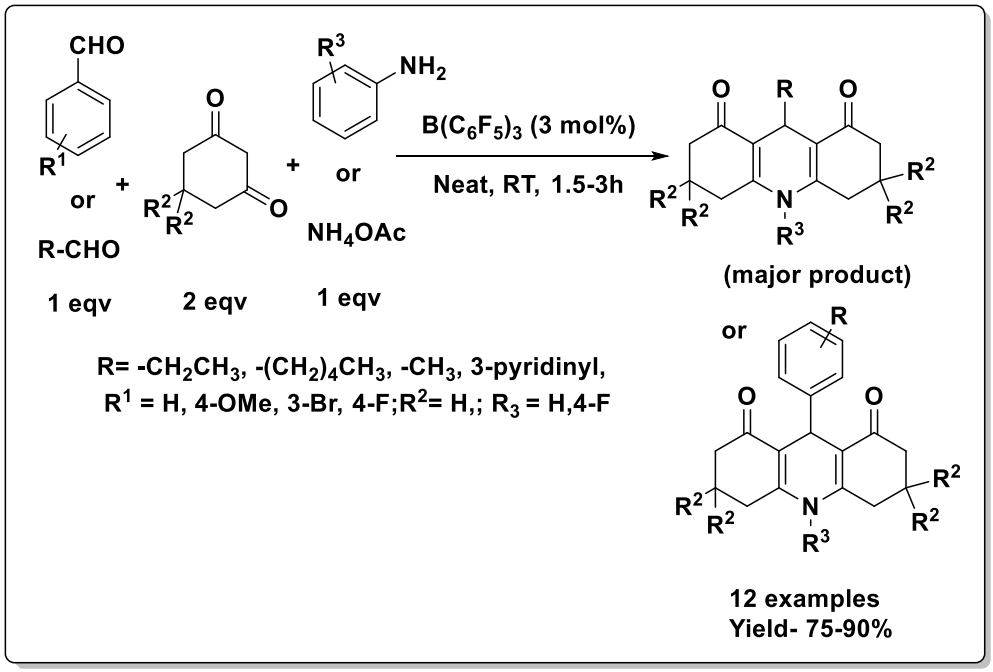
In 2011, Vahdat *et al*. had synthesised 1,8-dioxodecahydroacridines by using ionic liquid with multi-SO_3H groups

attached with it via the one-pot method with excellent yield within at room temperature in water medium (**Scheme II.23**).[130]



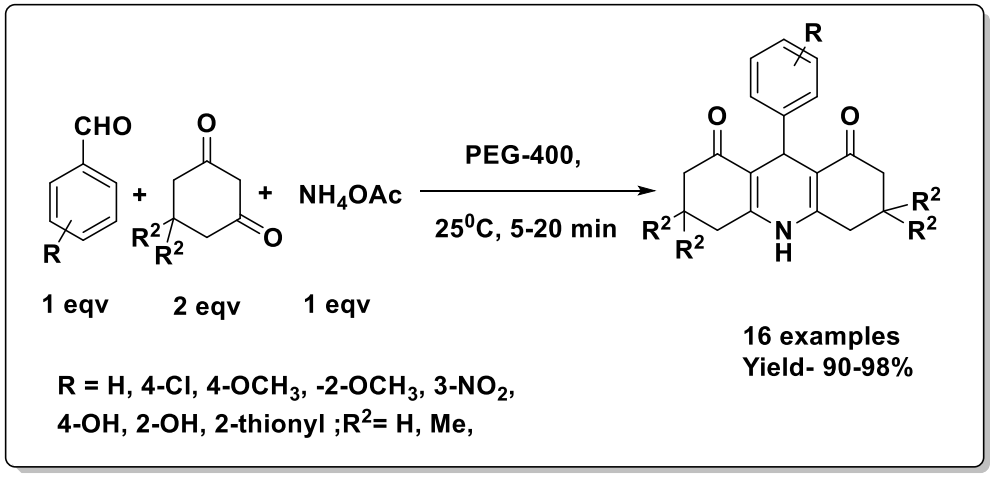
Scheme II.23. Ionic liquid catalysed synthesis of acridinedione derivatives by Vahdat *et al*.

In 2008, A mild and efficient method for the synthesis of 1,8-dioxodecahydroacridines has been developed by Chandrasekhar *et al*. via a three-component reaction of a cyclic 1,3-dione, an aldehyde and an amine, under solvent-free conditions, at room temperature catalyzed by tris(pentafluorophenyl)borane [$B(C_6F_5)_3$] (**Scheme II.24**).[131]



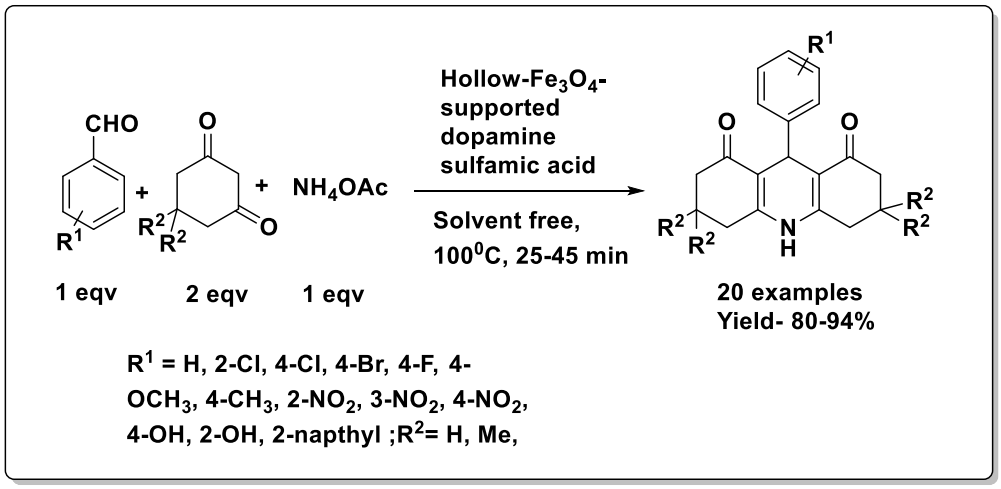
Scheme II.24. $B(C_6F_5)_3$ catalysed synthesis of acridinedione derivatives by Chandrasekhar *et al*.

In 2010, Kidwai *et al*. synthesized decahydroacridine-1,8-diones in the presence of polyethylene glycol (PEG) which was found to be an inexpensive non-toxic and effective medium for one pot synthesis of the product with higher yields (**Scheme II.25**). [132]



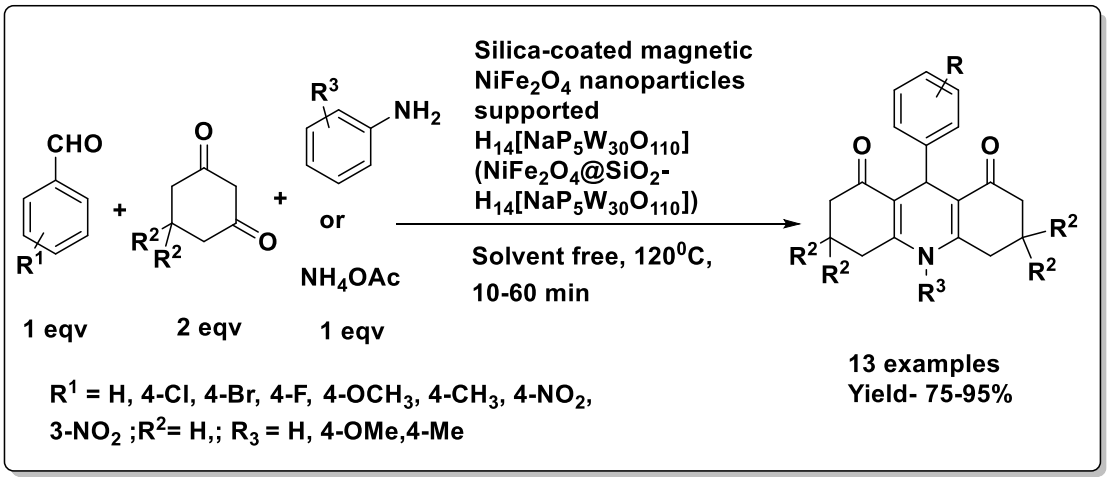
Scheme II.25. PEG-400 catalysed synthesis of acridinedione derivatives by Kidwai *et al*.

In 2017, Mirhosseyni *et al*. reported the synthesis of 1,8-dioxodecahyroacridine derivatives using H-Fe_3O_4@DA-SO_3H as catalyst by using aldehyde , ethyl acetoacetate or 1,3-cyclohexanedione NH_4OAc at 100^0C under solvent-free condition (**Scheme II.26**). [133]



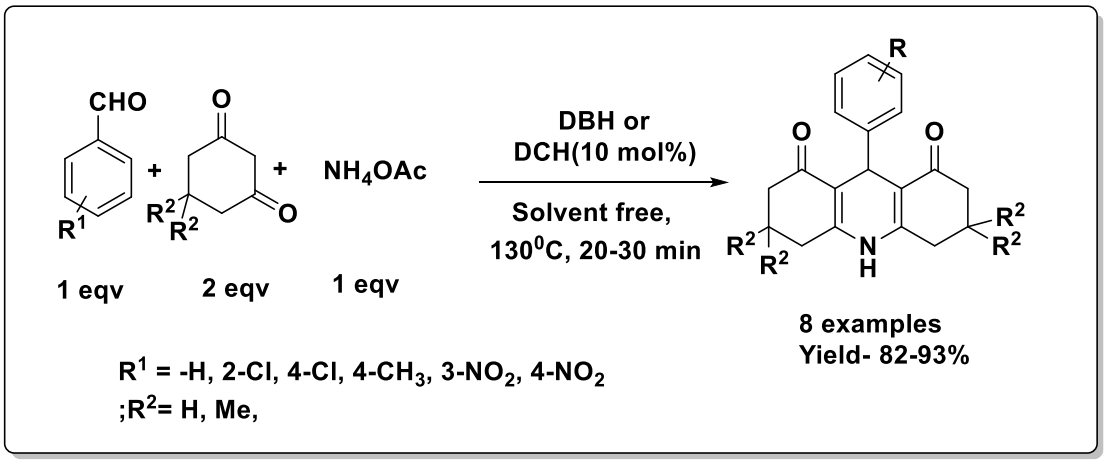
Scheme II.26. Hollow Fe_3O_4 supported dopamine sulfamic acid catalysed solvent free synthesis of acridine dione derivatives by Mirhosseyni *et al*.

In 2017 Malekia *et al*. reported Silica-coated magnetic $NiFe_2O_4$ nanoparticles-supported $NiFe_2O_4@SiO_2$-$H_{14}[NaP_5W_{30}O_{110}]$ was successfully synthesized and shown to be a versatile and highly efficient heterogeneous catalyst for one-pot multicomponent synthesis of 1,4-dihydropyridine derivatives under solvent-free condition. The synthesized catalyst can be magnetically recovered and reused four times without significant loss in catalytic efficiency (**Scheme II.27**).[134]



Scheme II.27. Silica coated magnetic nanoparicles catalysed solvent free synthesis of acridine dione derivatives by Maleki *et al.*

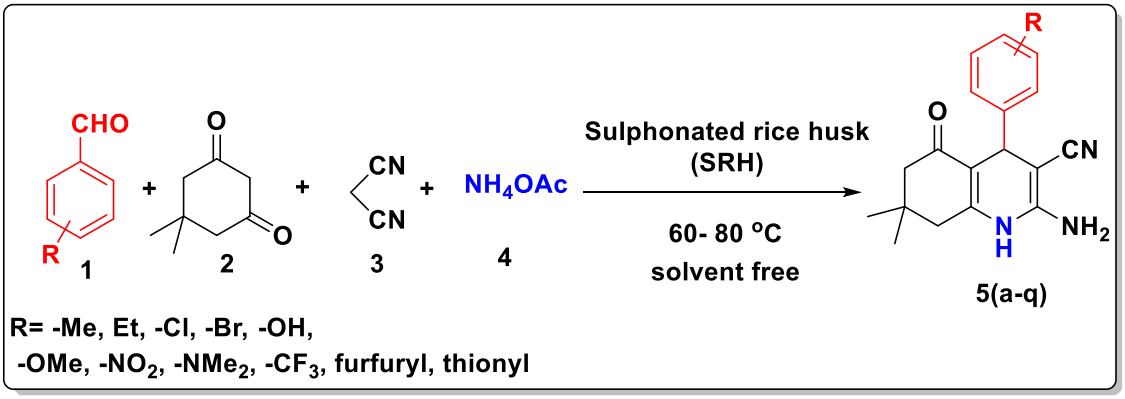
In 2013, Maleki *et al*. reported a solvent free one pot synthesis of 1,8-dioxodecahydro acridine derivatives which have been described via Hantzsch condensation of various aldehydes, ammonium acetate,cyclic 1,3-dicarbonyl compounds in a very simple, efficient and environmentally benign method with excellent yield (**Scheme II.28**). [135]



Scheme II.28. DBH or DCH catalysed solvent free synthrsis of acridine dione derivatives by Maleki *et al*.

II.8 Present work

The present work leads to the synthesis of substituted 5-oxo-1,4,5,6,7,8-hexahydroquinoline derivatives (**Scheme II.29)** by using greener heterogeneous catalyst sulphonated rice husk (SRH) .



Scheme II.29 Synthesis of substituted 5-oxo-1,4,5,6,7,8-hexahydroquinoline derivatives using sulphonated rice husk

II.8.A Result & discussion

II.8.A.1 Catalyst Characterisation

The prepared catalyst was characterised by FTIR spectroscopy, scanning electron microscopy (SEM), powder X-ray diffraction (XRD) and ICP-AES for quantifying weight percentage of sulphur and other elements.The comparison of FTIR, SEM image and XRD pattern of RH and SRH strongly supports the synthesis of the sulphonated catalyst through a completely new method. The comparison of SEM images of RH and SRH shows that a molecular aggregation occurs in SRH resulted from the incorporation of $–SO_3H$ functional group into the skeleton of rice husk material (**Figure II.6**). EDX analysis of sulphonated rice husk

and rice husk showed a measurable difference in the weight percentage of the elements especially carbon, slicon, sulphur and oxygen (Figure II.6, Experimental section of Chapter II. The newly appearing band with a peak 1098cm^{-1} represents the symmetric and asymmetric streatching of S=O bonds of $–SO_3H$ (sulphonic acid).The the new broad band at 3342 cm^{-1} along with the band at 1098 cm^{-1} both confirmly denoting the incorporation of $–SO_3H$ groups in SRH after sulphonation of rice husk (**Figure II.8**) . The powder XRD analysis shows characteristics peaks at $2\theta = 20.82^o, 22.28^o, 26.67^o$ in which a broad peak at around 20^o is due to the carbon composed aromatic sheets which are oriented in a random manner (**Figure II. 7**).[58] ICP-AES analysis showed that weight percentage sulphur is 1% to that of total weight of all the elements present. To make surety in broad aspect all the results and graphs were thoroughly viewd and compared with other sulphonated materials such as sulphonated rice husk ash [59], CBSC (carbon-based sulphonated catalyst) [57] which confirmly showed that SRH was morphologically and compositionally different from those reported sulphonated catalysts. Detailed characterization informations are given into the experimental section (**II.8.A.12.i** and **II.8.A.12.j**) of the Chapter II.

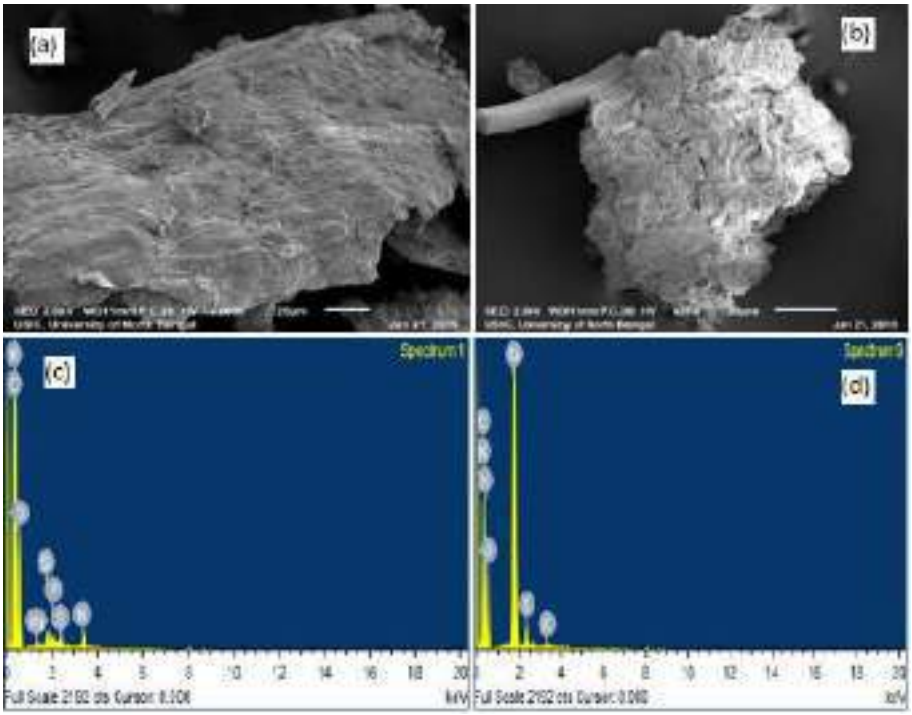


Figure II.6 (a) SEM image of rice husk(RH) (b) SEM image of sulphonatrice husk (SRH) (c)EDX of RH (d) EDX of SRH

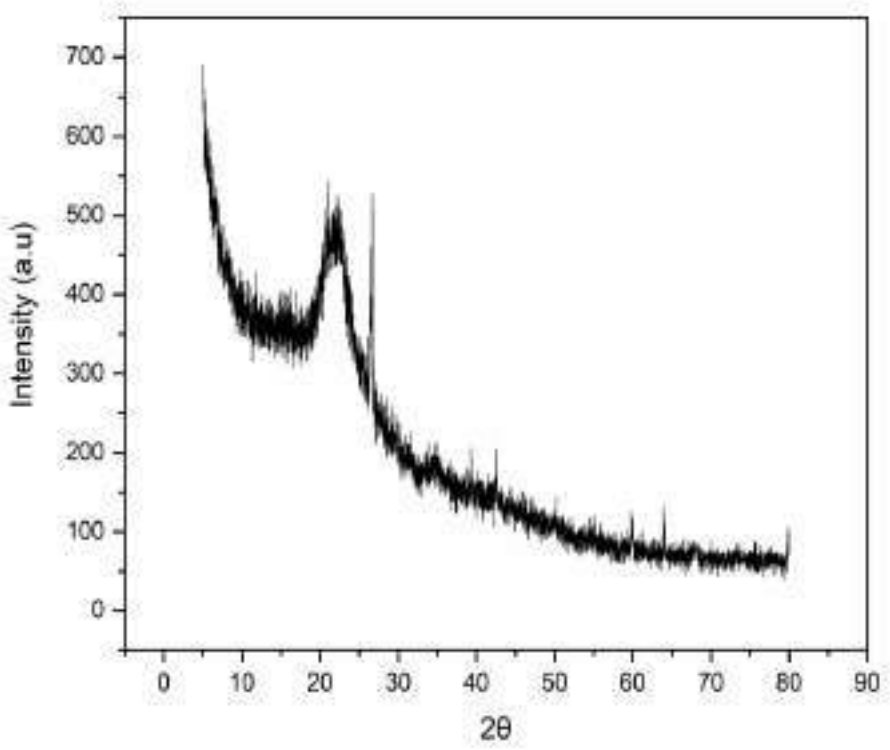


Figure II.7 Powder XRD plot of SRH

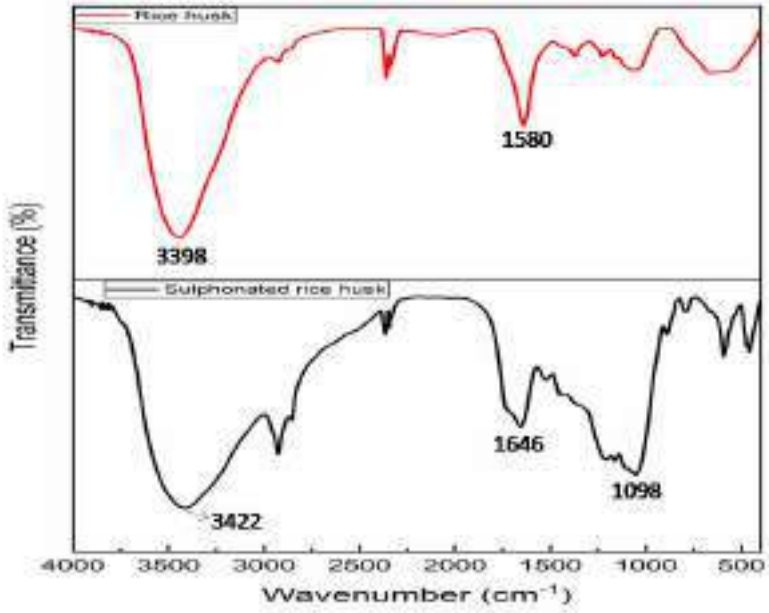


Figure II.8 FTIR of RH and SRH

II.8.A.2 Optimization of the reaction condition for the synthesis of substituted 5-oxo-1,4,5,6,7,8-hexahydroquinolines.[a]

Initially, for screening the reaction *p*-tolualdehyde (1 mmol), malononitrile (1 mmol), ammonium acetate (1.2 mmol) and 5,5-dimethylecyclohex-1,3-dione (1 mmol) were taken in a 25 mL RB. However, in absence of catalyst the formation of the corresponding product was diminished (**Table II.1**, entry 10). Excellent yield was observed in presence of 100 mg of SRH catalyst in ethanol solvent at 80 ^{o}C temperature (**Table II.1**, entry 1). With decreasing the amount of catalyst, the yield of the product decreases slightly in ethanol. From the optimized condition it is clear that SRH catalyst is proved to be suitable for the conversion of hexahydroquinoline with excellent yield in short reaction time. The amount of the catalyst and 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 ^{o}C temperature using 60 mg of catalyst SRH under neat reaction contion (**Table II.1**, entry 13). The progress of the reaction was monitored by thin layer chromatography (TLC) and the pure product was separated by column chromatography with petroleum ether/ethyl acetate (v/v ratio70/30) mixture.

Table II.1 Optimisation of the reaction condition for the synthesis of substituted 5-oxo-1,4,5,6,7,8-hexahydroquinolines.[a]

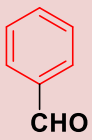
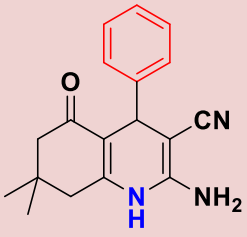
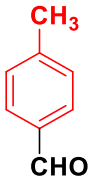
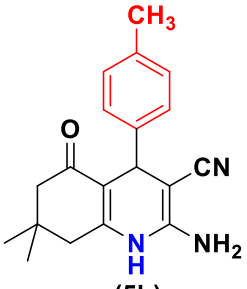
Entry	Catalyst (mg)	Solvent	Temperature (^{o} C)	Time (min)	Yield (%)[b]
1	100	Ethanol	80	40	96
2	80	Ethanol	80	30	96
3	70	Ethanol	80	30	94
4	50	Ethanol	80	30	85
5.	40	Ethanol	80	30	78
6.	40	Ethanol	100	30	80
7.	30	Neat	50	120	80
8.	30	Neat	50	90	70
9.	20	Neat	60	60	64
10.	None	Neat	80	120	30
11	80	Neat	70	40	96
12.	80	Neat	70	30	96
13.	**60**	**Neat**	**70**	**20**	**96**
14	60	Neat	60	20	92
15	80	Methanol	80	30	94

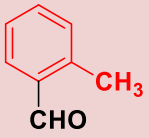
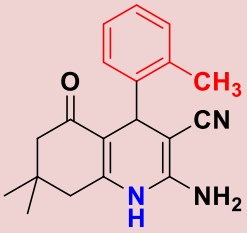
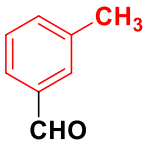
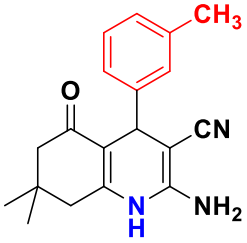
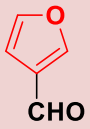
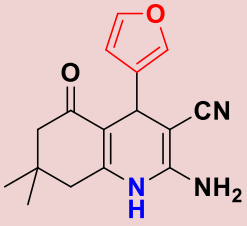
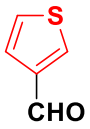
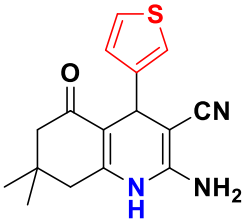
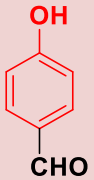
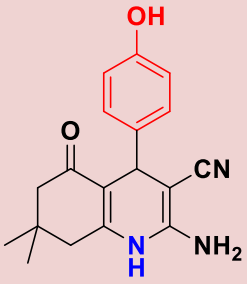
[a] Reaction of p-tolueldehyde (1mmol), malononitrile (1mmol), 5,5-dimethyl-cyclohexane-1,3-dione(1mmol), ammonium acetate (1.2 mmol). [b] Isolated yield after purification through column chromatography.

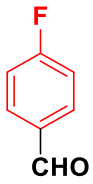
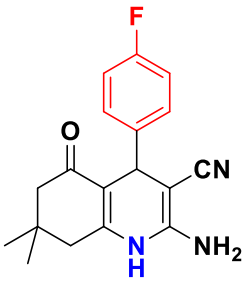
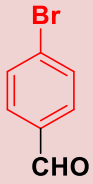
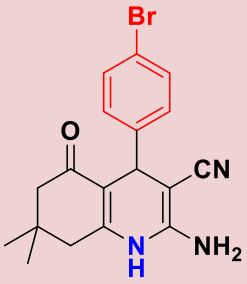
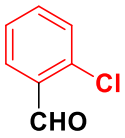
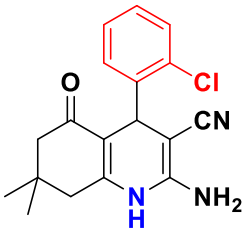
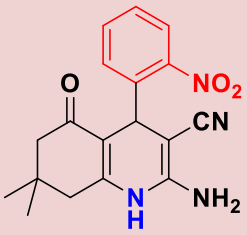
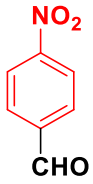
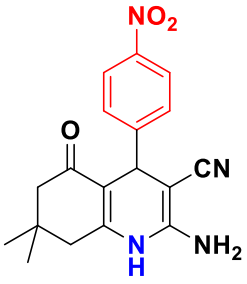
II.8.A.3 Synthesis of substituted 5-oxo-1,4,5,6,7,8-hexahydroquinoline derivatives.[a]

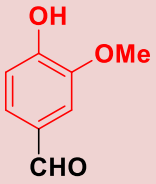
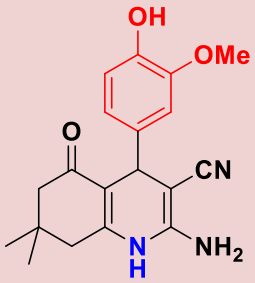
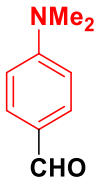
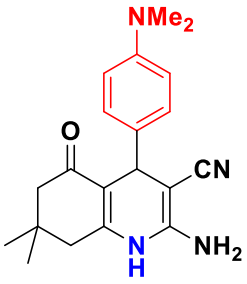
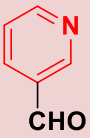
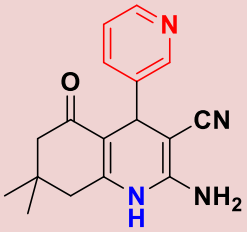
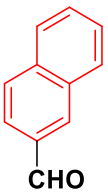
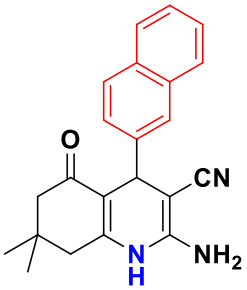
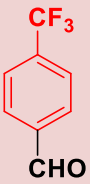
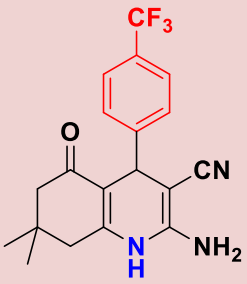
The generality of the reaction was also observed with a variety of aromatic and heterocyclic aldehydes (**Scheme II. 29**). There is no significant difference in the yield of the desired product with electron donating and electron withdrawing substituents at *ortho*, *meta* and *para* position of the aromatic aldehyde. The target compounds (5a-5q) are successively synthesized using SRH as efficient catalyst under neat reaction condition and short reaction time. (**Table II. 2**)

Table II.2 Synthesis of substituted 5-oxo-1,4,5,6,7,8-hexahydroquinolines using sulphonated rice husk.[a]

Entry	Reactant	Product	Time	Yield(%)[b]
1		 (5a)	30 min	96
2		 (5b)	30 min	96

3		 (5c)	30 min	93
4		 (5d)	30 min	96
5		 (5e)	30 min	95
6		 (5f)	30 min	994
7		 (5g)	30 min	95

8		 (5h)	30 min	97
9		 (5i)	30 min	98
10		 (5j)	30 min	96
11		 (5k)	30 min	90
12		 (5l)	30 min	92

13		 (5m)	30 min	95
14		 (5n)	30 min	96
15		 (5o)	30 min	94
16		 (5p)	30 min	92
17		 (5q)	30 min	96

[a] Reaction of aromatic aldehyde (1mmol), malononitrile (1mmol), 5,5-dimethyl-cyclohexane-1,3-dione (1mmol), ammonium acetate (1.2 mmol) and SRH (60 mg). [b]Isolated yield through column chromatography.

II.8.A.4 Comparison of efficiency of the catalyst

Few controlled experiments were carried out to compare our prepared catalyst (SRH) with some conventional solid and liquid acid catalyst (**Table II.3**). It was observed from the results that most of the acid catalyst showed good activity in ethanol solvent. However, some base catalyst was also employed and they exerted the corresponding product with high yield in 30 minutes (**Table II.3**, entry 8-9). The effectiveness of SRH over other acid catalyst was established as it requires very short reaction time under solvent free condition and easily seperable from the reaction mixture (**Table II. 3**, entry 11).

Table II.3 Comparison of efficiency of the catalyst for the synthesis of substituted 5-oxo-1,4,5,6,7,8-hexahydroquinolines.[a]

Entry	Catalyst	Solvent	Temperature (^{o}C)	Time(min)	Yield (%)[b]
1	PTSA(60mg)	Ethanol	80	30	93
2	PEG-400(5mL)	-	80	40	80
3	PEG-	-	80	60	70

	200(5mL)				
4	Glycerol(5mL)	-	80	60	72
5.	H_2SO_4 (5mL)	Ethanol	70	30	85
6.	AcOH (5mL)	-	80	30	80
7.	$HClO_4$ (5mL)	-	70	30	90
8.	K_2CO_3 (60mg)	Neat	80	30	94
9.	Et_3N(5mL)	-	80	30	95
10.	Fe_3O_4 (60 mg)	Neat	80	30	91
11.	SRH (60mg)	**Neat**	**70**	**20**	**96**

[a]Reaction of p-toluealdehyde (1mmol), malononitrile (1mmol), 5,5-dimethyl-cyclohexane-1,3-dione (1mmol), ammonium acetate (1.2 mmol). [b] Isolated yield after purification through column chromatography.

II.8.A.5 Plausible Mechanism

A plausible SRH catalyzed synthesis of hexahydroquinoline is established by considering the acidic behaviour of the catalyst (**Figure II.9**). At very first step of the reaction, protonation occurs at aldehyde oxygen of aromatic aldehyde followed by the Knoevenagel condensation of malononitrile and aromatic aldehyde. After that, Michael addition reaction occurs between 5,5-dimethylecyclohex-1,3-dione and 2-arylidenemalononitrile, resulting a intermediate. However, this

intermediate rapidly undergoes in cyclization and exters the target hexahydroquinoline product.

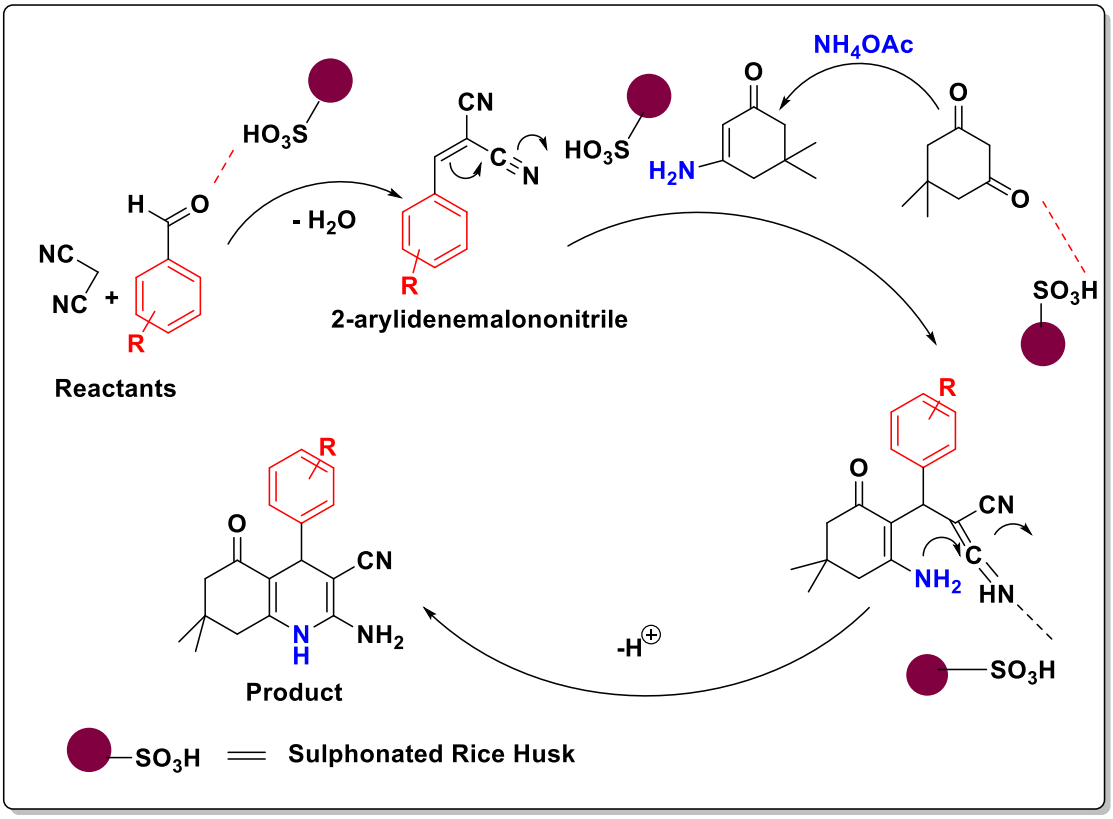
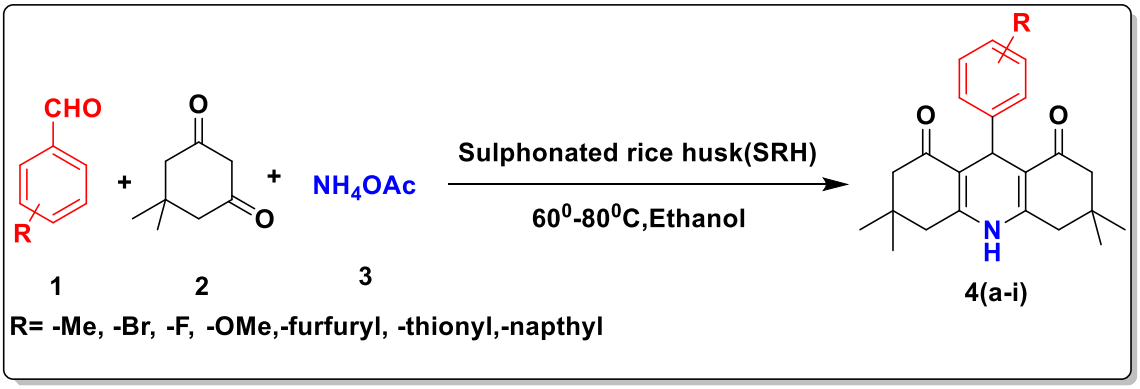


Figure II.9 The plausible mechanism for the synthesis of hexahydroquinoline

The next present work leads to the synthesis of substituted 9-arylhexahydroacridine-1,8-dione derivatives (**Scheme II.30**) by using greener catalyst heterogeneous catalyst sulphonated rice husk (SRH) .



Scheme II.30 Synthesis of substituted 9-arylhexahydroacridine-1,8-dione derivatives using sulphonated rice husk[a]

II.8.A.6 Optimization of the reaction condition for the Synthesis of substituted 9-arylhexahydroacridine-1,8-dione derivatives

Initially, the reaction was started with anisaldehyde (1 mmol), ammonium acetate (1.2 mmol) and 5,5-dimethylecyclohex-1,3-dione (2 mmol) taken in a 25 mL round bottom flask. Excellent yield was observed in presence of 40 mg of SRH catalyst in ethanol solvent at 60 ^{o}C temperature (**Table II.4**, entry 7) with reaction time of 50 minutes. With decreasing the amount of catalyst, the yield of the product decreases slightly in ethanol. However, in absence of catalyst the formation of the product was diminished (**Table II.4**, entry 13). The performance of the reaction is almost similar in methanol solvent but for greener aspect ethanol is considered as more safer solvent than methanol to get the maximum yield. (**Table II.4**, entry 7 & 8). From the optimized

condition it is clear that SRH catalyst is proved to be suitable for the conversion of hexahydroacridine-1,8-dione with excellent yield in short reaction time. The amount of the catalyst and time of the reaction was checked to find out the optimized condition of the reaction. It was observed that the best result was obtained at 60 ^{o}C temperature using minimum amount of catalyst SRH (40 mg) in ethanol (**Table II.4**, entry 7).The progress of the reaction was monitored continuously by thin layer chromatography (TLC) and the pure product was separated only by recrystallisation procedure in ethyl acetate and petroleum ether (1:1)

Table II.4 Optimisation of the reaction condition for the synthesis of hexahydroacridine-1,8-dione. [a]

Entry	Catalyst (mg)	Solvent	Temperature (^{o} C)	Time (min)	Yield (%)[b]
1	90	Ethanol	80	120	97
2	80	Ethanol	80	90	97
3	70	Ethanol	80	70	97
4	60	Ethanol	80	60	97
5.	50	Ethanol	70	60	95
6.	40	Ethanol	70	60	95
7.	**40**	**Ethanol**	**60**	**50**	**95**
8	40	Methanol	60	60	94

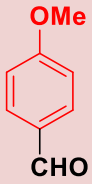
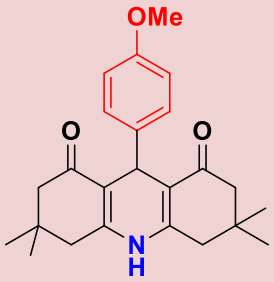
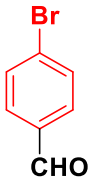
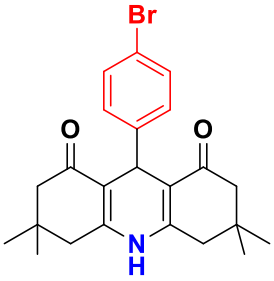
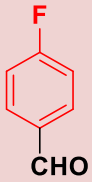
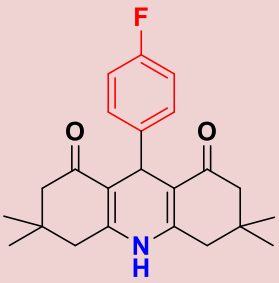
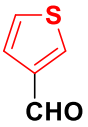
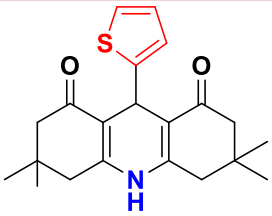
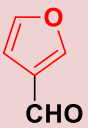
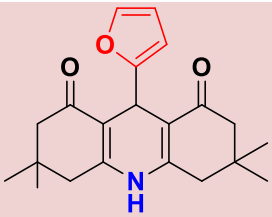
9.	40	Neat	60	50	84
10.	40	Neat	80	90	86
11.	40	Ethanol/H_2O (3:1)	70	60	62
12.	40	Methanol/H_2O(3:1)	70	60	58
13.	None	Ethanol	70	120	20

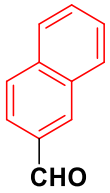
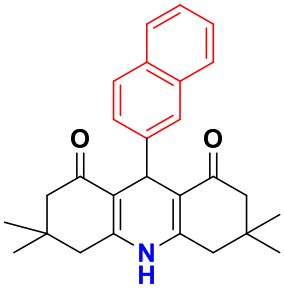
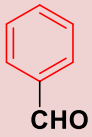
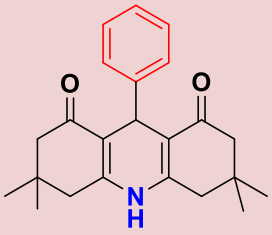
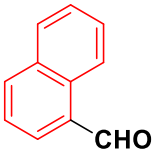
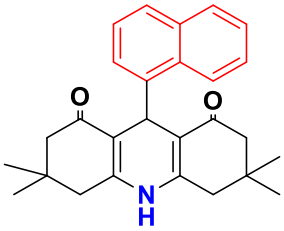
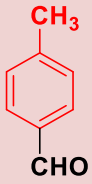
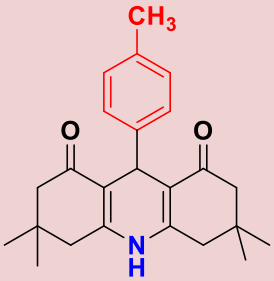
[a] Reaction of anisaldehyde (1mmol), 5,5-dimethyl-cyclohexane-1,3-dione(2mmol), ammonium acetate (1.2 mmol). [b]Isolated yield after purification through recrystalisation procedure.

II.8.A.7 Synthesis of substituted 5-oxo-1,4,5,6,7,8-hexahydroquinoline derivatives.[(a)]

The generality of the reaction was also observed with a variety of aromatic and heterocyclic aldehydes (**Scheme II. 30**). There is no significant difference in the yield of the desired product with electron donating and electron withdrawing substituents at *ortho*, *meta* and *para* position of the aromatic aldehyde. The targeted compounds (5a-5q) are successively synthesized using SRH as efficient catalyst under neat reaction condition and short reaction time. (**Table II. 5**)

Table II.5 Synthesis of substituted 9-arylhexahydroacridine-1,8-dione derivatives using sulphonated rice husk. [a]

Entry	Reactant	Product	Time	Yield(%)[b]
1		 (4a)	50 min	97
2		 (4b)	50 min	94
3		 (4c)	50 min	93
4		 (4d)	50 min	94
5		 (4e)	50 min	92

6		 (4f)	50 min	94
7		 (4g)	50 min	91
8		 (4h)	50 min	94
9		 (4i)	50 min	95

[a] Reaction of aromatic aldehyde (1mmol), 5,5-dimethyl-cyclohexane-1,3-dione (2mmol), ammonium acetate (1.2 mmol) and SRH. [b] The yields are isolated through recrystalisation.

II.8.A.8 Plausible mechanism

A plausible SRH catalyzed synthesis of hexahydroacridine-1,8-dione are established considering the acidic behaviour of the catalyst

(**Figure II.10**). 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 exerts the targeted hexahydroacridine-1,8-dione product.

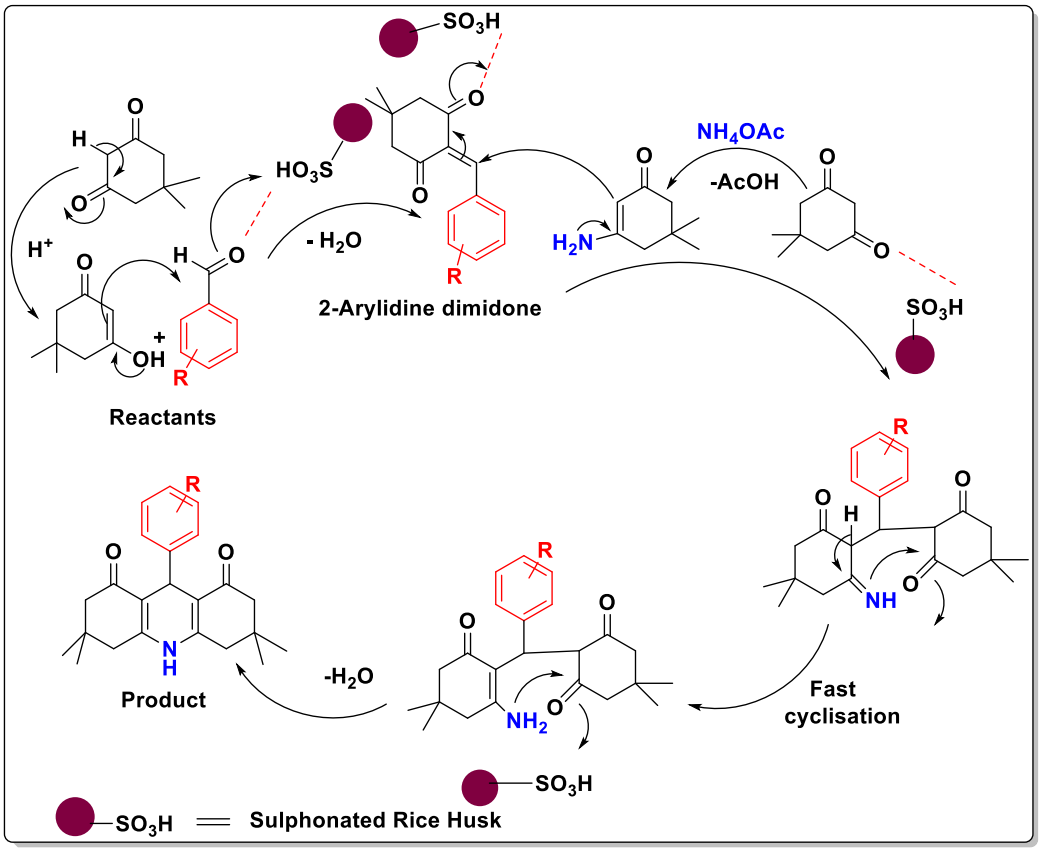


Figure II.10 The plausible mechanism for the synthesis of hexahydroacridine-1,8-dione

II.8.A.9 Catalyst Recyclability Experiment

To check the recyclability of the catalyst, a model reaction between benzaldehyde (1.6mmol), malononitrile(1.6mmol), ammonium acetate(1.92 mmol) and 5,5-dimethylecyclohex-1,3-dione(1 mmol) in presence of 100 mg of sulphonated rice husk was carried out under optimised reaction condition. After successful completion of the each reaction step, ethyl acetate (10 ml) and water was added to the reaction mixture. The supernatant liquid (ethyl acetate extract) was decanted off and this process was repeated thrice. The catalyst was then filtered and washed with water and acetone repeatedly and dried under vaccum. The recovered catalyst weight was measured after every recovery step and the next reaction was repeated in required proportion of the reactants to that of weight of the recovered catalyst. The temperature and time of the reaction were kept constant in this regard. Amount of catalyst, aldehyde, reaction time,temperature and yield percentage of the product have been shown in **Table II.6** (entry 1-7) The catalyst can easily be separated from the reaction mixture by simple filtration and was found to retain its acidic property, even after 7th run (**Figure II.11**). This was further supported by comparing the FTIR spectra of fresh SRH catalyst and recovered catalyst after successive reactions (**Figure II.12**).

Table II.6 Table for the amount of recovred catatyst with isolated product yield in successive runs[a]

Entry	Catalyst (mg)	Aldehyde (x mmol)	Temperature (^{o} C)	Time (min)	Yield (%)[b]
1	100	1.6 mmol	70	20	96
2	80	1.3 mmol	70	20	94
3	60	1.0 mmol	70	20	90
4	50	0.8 mmol	70	20	87
5.	40	0.6 mmol	70	20	82
6.	30	0.5 mmol	70	20	76
7.	20	0.3 mmol	70	20	71

[a] Reaction of benzaldehyde (x mmol), malononitrile (x mmol), 5,5-dimethyl-cyclohexane-1,3-dione (2x mmol), ammonium acetate (1.2x mmol). [b] Isolated yield after purification through recrystalisation.

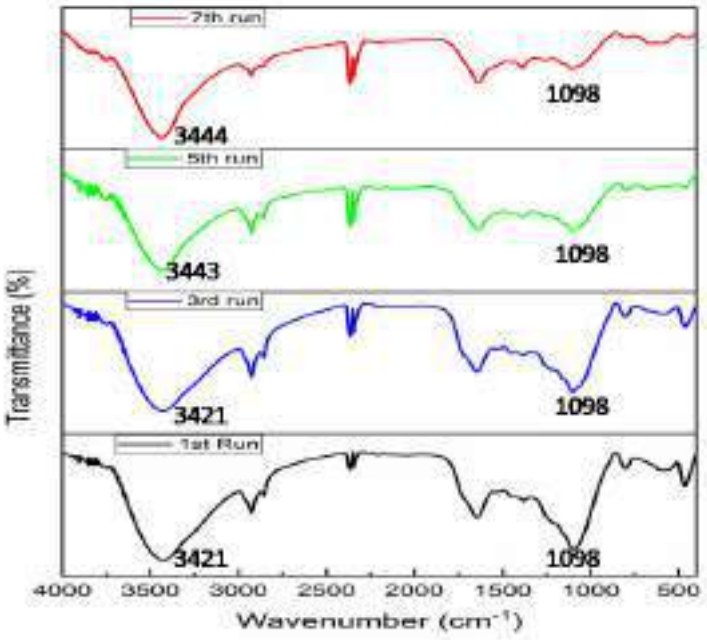


Figure II.11 FTIR spectra of reused catalysts after 1st , 3rd, 5th and 7th run.

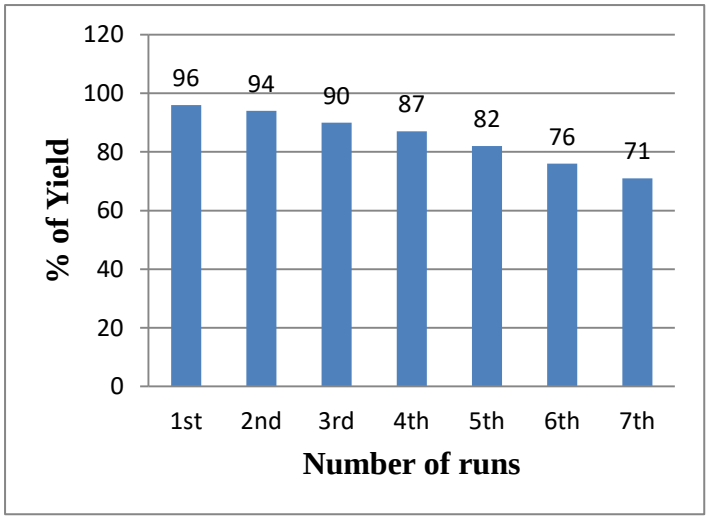


Figure II.12 Recyclability experiment of catalyst

II.8.A.10 Conclusion

In conclusion, a simple and greener methodology for the synthesis of variety of hexahydroquinolines and hexahydroacridine-1,8-dione from commercially available aldehydes has been established. We have introduced a new cheap and green heterogeneous catalyst SRH (Sulphonated rice husk) for the synthesis of substituted 5-oxo-1,4,5,6,7,8-hexahydroquinoline and 9-Arylhexahydroacridine-1,8-dione derivatives with excellent yield. This heterogeneous catalyst is found to be highly efficient for the synthesis of hexahydroquinoline and hexahydroacridine-1,8-dione in short reaction time. The catalyst is highly recyclable upto 7^{th} run and has profound effect to catalyze a wide range of acid-catalysed reactions.

II.8.A.11 Acknowledgement

One of the authors (S.D) is thankful to UGC, New Delhi for financial support, USIC (NBU) for SEM, EDX analysis, IIT Bombay for ICP-AES & IACS (Kolakata) for powder XRD analysis for this above work.

II.8.A.12 Experimental

II.8.A.12.a Catalyst preparation

The heterogeneous catalyst (SRH) was prepared by direct sulphonation of rice husk (RH). The rice husk was collected from a nearby rice mill and was blended finely before use. RH was first washed with dilute H_2SO_4 for five times and next thoroughly washed with water followed by methanol. After washing the solvent was fully evaporated through rotary evaporator. 5g of dry material was taken into 250 mL of a round bottom flask and 150 mL dichloromethane (DCM) was added to it. Then, 5 mL of pure Chlorosulphonic acid (98%) was added dropwise with continuous stiring until the whole suspension turned into brown. The suspension was then stirred for 20 h on a magnetic stirrer at room temperature. After stirring the solid catalyst was filtered off and washed with water and acetone repeatedly until the filtrate became light brown colour. Then the sample was dried in reduced pressure and later characterized by different spectroscopic techniques.

II.8.A.12.b General procedure for synthesis of hexahydroquinoline derivatives

A mixture of 5,5-Dimethylcyclohexane-1,3-dione (1 mmol), aromatic aldehyde (1.0 mmol), malononitrile (1 mmol), ammonium acetate (NH_4OAc) (1.2 mmol), and SRH (60 mg) in a 50-mL round bottom flusk was stirred at 60 ^oC temperature for 20 min (Scheme II. 29). The progress of the reaction was monitored by thin-layer

chromatography (TLC) (**Scheme II.29**). 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 further purified by coloumn chromatography using ethyl acetate/petroleum ether (3:7) as eluent to get the pure product. All the synthesized compounds were characterized by ^{1}H and ^{13}C NMR spectroscopy and the spectral data were compared with the reported spectral data of corresponding compound.

II.8.A.12.c General procedure for synthesis of Acridine-1,8-dione derivatives

A mixture of 5,5-Dimethylcyclohexane-1,3-dione (2 mmol), aromatic aldehyde (1 mmol), ammonium acetate (NH_4OAc) (1.2 mmol), and SRH (50 mg) in a 25-mL round bottom flusk was stirred at 60^0C temperature for 60 minutes. The progress of the reaction was monitored by thin-layer chromatography (TLC) (**Scheme II.30**). 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 product was sperated by simple precipitation with petroleum ether and purified by recrystalisation with (1:1) ethylacetate and petroleum ether mixture. After isolation all the synthesized

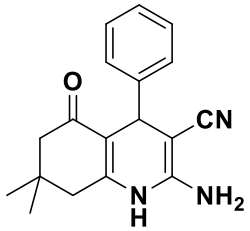
compounds were characterized by ^{1}H and ^{13}C NMR spectroscopy and the spectral data were compared with the reported spectral data of corresponding compound.

II.8.A.12.d 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. ^{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.

II.8.A.12.e Spectral data of the compounds mentioned in Scheme II.29

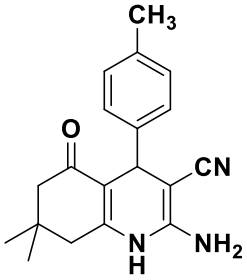
2-Amino-7,7-dimethyl-5-oxo-4-phenyl-1,4,5,6,7,8-hexahydroquinoline-3-carbonitril (5a)



^{1}H-NMR(400MHz,DMSO-d_6)
δ(ppm)0.95(s,3H),1.04(s,3H),2.10(d,1H),2.25(d,1H),2.51(s,2H),4.17(s,1H),7.00 (s,2H),7.13-7.30(m,5H).

^{13}C-NMR(400MHz,DMSO-d_6)
δ(ppm)27.27,28.86,32.27,36.03,50.44,58.76,113.20,120.18,127.02,127.61,128.79, 145.21,158.95,162.95, 196.10.

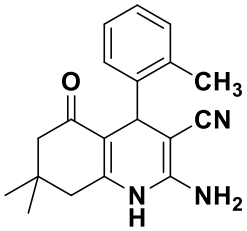
2-Amino-4-(4-methylphenyl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (5b)



^{1}H-NMR(400MHz,DMSO-d_6)
δ(ppm)0.92(s,3H),1.01(s,3H),2.10(m,2H),2.22(s,3H),2.53(s,2H),4.09(s,1H), 6.94(s,2H), 6.98-7.07(m,4H).

^{13}C-NMR(400MHz,DMSO-d_6)
δ(ppm)21.55,27.22,28.88,32.26,35.63,50.45,58.89,113.33,120.22,127.54,129.34,136 .08, 142.29,158.89,162.75, 196.10.

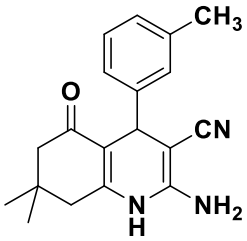
2-Amino-4-(2-methylphenyl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (5c)



^{1}H-NMR(400MHz,DMSO-d_6)
δ(ppm) 0.93(s,3H),1.01(s,3H),2.02-2.23(m,2H),2.43-.55(m,6H),4.44(s,1H),6.92(s,2H), 7.01-7.08(m,4H).

^{13}C-NMR(400MHz,DMSO-d_6)
δ(ppm)19.54,27.26,28.89,31.83,32.34,50.41,58.70,113.92,120.22,126.85,127.74,130 .36, 135.22,144.04,158.74,162.98, 196.25.

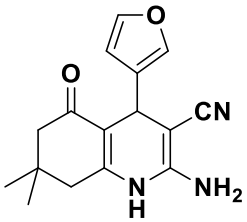
2-Amino-4-(3-methylphenyl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (5d)



^{1}H-NMR(400MHz,DMSO-d_6)
δ(ppm)0.93(s,3H),1.01(s,3H),2.05-2.54(m,7H),4.09(s,1H),6.88-7.16(m,6H).

^{13}C-NMR(400MHz,DMSO-d_6)
δ(ppm)21.55,27.21,28.89,32.29,35.95,50.45,58.86,113.23,120.21,124.76,127.72,128.17, 128.71, 137.76,145.19,158.91,162.90, 196.10.

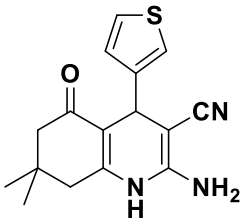
2-Amino-4-(furan-2-yl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (5e)



^{1}H-NMR(400MHz,DMSO-d_6)
δ(ppm)0.96(s,3H),1.00(s,3H),2.14(d,1H),2.26(d,1H),2.40-2.53(m,2H),4.30(s,1H),6.03(d,1H)6.30(dd,1H),7.06(s,2H),7.13-7.45(s,1H).

^{13}C-NMR(400MHz,DMSO-d_6)
δ(ppm)27.01,28.89,29.44,32.28,50.35,55.84,105.52,110.82,120.03,142.21,156.18, 159.77,163.74, 195.92.

2-Amino-4-(thiophene-2-yl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (5f)



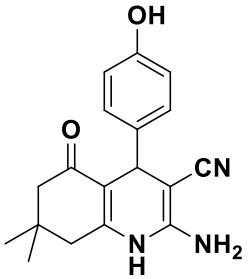
^{1}H-NMR(400MHz,DMSO-d_6)

δ(ppm) 0.94(s,3H),1.00(s,3H),2.03-
.53(m,4H),4.61(s,1H),6.85(d,2H),7.08(s,2H),7.27(d,1H).

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

δ(ppm)26.41,28.63,30.43,31.75,49.89,58.10,112.95,119.59,124.00,124.41,126.81,14
9.28, 158.93,162.49,195.51.

2-Amino-4-(4-hydroxyphenyl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (5g)



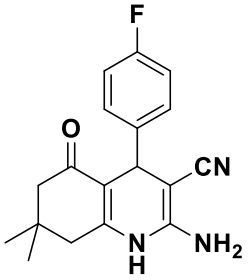
^{1}H-NMR(400MHz,DMSO-d_6)

δ(ppm)0.91(s,3H),1.00(s,3H),2.10(d,1H),2.25(d,1H),2.51(s,2H),4.17(s,1H),7.00(s,2
H),7.13-7.30(m,5H).

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

δ(ppm)27.22,28.89,32.24,35.17,50.50,59.24,113.65,115.45,120.35,128.61,135.63,15
6.44, 158.85, 162.45, 196.12.

2-Amino-4-(4-fluorophenyl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (5h)



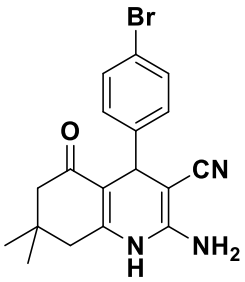
^{1}H-NMR(400MHz,DMSO-d_6)

δ(ppm)0.94(s,3H),1.02(s,3H),1.98(s,1H),2.10(d,1H),2.24(d,1H),2.50(s,2H),
4.20(s,1H), 7.04(s,2H), 7.08-7.19(m,4H).

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

δ(ppm)27.28,28.78,32.25,35.37,50.41,58.53,113.06,120.10,129.47,129.55,141.39,15
8.94, 162.56, 170.79,196.13.

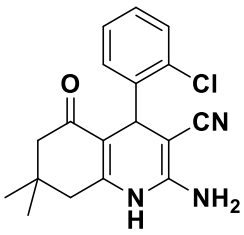
2-Amino-4-(4-bromophenyl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (**5i)**



^{1}H-NMR(400MHz,DMSO-d$_6$)
δ(ppm)0.92(s,3H),1.00(s,3H),1.96(s,1H),2.06(d,1H),2.21(d,1H),2.47(s,2H),4.15(s,1 H), 7.04(s,2H),7.08(d,3H)7.45(d,2H).

^{13}C-NMR(400MHz,DMSO-d$_6$)
δ(ppm)27.35,28.77,32.26,35.67,50.43,58.21,112.75,120.65,129.98,131.66,131.66,14 4.64,158.96,163.08,170.77,196.10.

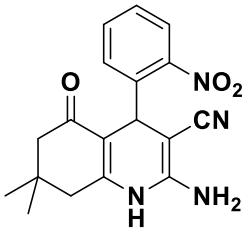
2-Amino-4-(2-chlorophenyl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (5j)



^{1}H-NMR(400MHz,DMSO-d$_6$)
δ(ppm)0.95(s,3H),1.01(s,3H),2.05(d,1H),2.22(d,1H),2.44-2.55(m,3H),4.67(s,1H),7.02(s,2H), 7.14-7.35(m,4H).

^{13}C-NMR(400MHz,DMSO-d$_6$)
δ(ppm)26.88,28.43,31.78,32.86,49.94,56.82,111.79,119.27,127.45,128.21,129.45,129.96,13 2.10, 141.58,158.68,163.16, 195.56.

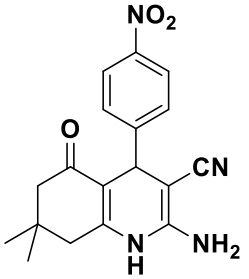
2-Amino-4-(2-nitrophenyl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (5k)



^{1}H-NMR(400MHz,DMSO-d_6)
δ(ppm)0.93(s,3H),1.05(s,3H),2.10(d,1H),2.21(d,1H),2.69(s,2H),5.33(s,1H),7.61-7.72(m,6H),9.51(s,1H).

^{13}C-NMR(400MHz,DMSO-d_6)
δ(ppm)27.40,28.67,32.51,32.75,50.09,58.76,111.83,117.03,126.92,127.02,129.72,128.79, 135.40,149.52,158.34,164.84, 196.42.

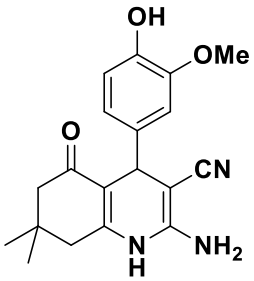
2-Amino-4-(4-nitrophenyl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (5l)



^{1}H-NMR(400MHz,DMSO-d_6)
δ(ppm)0.96(s,3H),1.00(s,3H),1.94(s,1H),2.03(d,1H),2.22(d,1H),2.48(d,2H),4.34(s,1H),7.14 (s,2H),7.41(d,2H),8.13(d,2H).

^{13}C-NMR(400MHz,DMSO-d_6)
δ(ppm)26.93,28.26,31.81,35.68,49.87,57.01,111.75,119.33,123.66,128.63,146.26,152.30, 158.60,163.10,170.32,195.67.

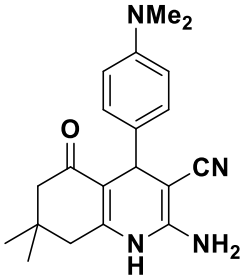
2-Amino-4-(3-methoxy,4-hydroxyphenyl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (5m)



^{1}H-NMR(400MHz,DMSO-d_6)
δ(ppm)0.94(s,3H),1.01(s,3H),2.07(d,1H),2.23(d,1H),2.47(s,2H),3.68(s,3H),4.05(s,1H),6.48-6.65(m,3H),6.89(s,2H),8.80(s,1H).

^{13}C-NMR(400MHz,DMSO-d_6)
δ(ppm)26.62,28.53,31.77,34.97,50.03,55.57,58.71,111.39,113.02,115.33,119.37,135.82, 145.24, 147.23,158.36,162.17, 195.72.

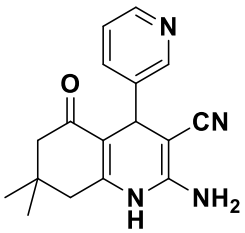
2-Amino-4-(4-N,N dimethylphenyl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (5n)



^{1}H-NMR(400MHz,DMSO-d_6)
δ(ppm)0.92(s,3H),1.00(s,3H),2.06(d,1H),2.22(d,1H),2.47(s,2H),2.81(s,6H),4.01(s,1 H),6.60(d,2H), 6.86-6.92(m,3H).

^{13}C-NMR(400MHz,DMSO-d_6)
δ(ppm)26.75,28.49,30.70,31.78,34.57,50.06,58.94,112.34,113.28,119.95,127.72,132 .54, 149.23,158.35,161.85, 195.67.

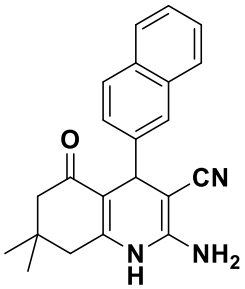
2-Amino-4-(pyridine-3-yl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (5o)



^{1}H-NMR(400MHz,DMSO-d_6)
δ(ppm)0.92(s,3H),1.01(s,3H),2.06(d,1H),2.23(d,1H),2.50(m,3H),4.23(s,1H),7.10(s,2 H), 7.29(dd, 1H),7.51(d,1H),8.38(s,2H).

^{13}C-NMR(400MHz,DMSO-d_6)
δ(ppm)26.93,28.24,31.84,33.40,49.91,57.32,111.79,119.51,123.66,134.75,140.05,147.85,14 8.69, 158.59,162.97, 195.74.

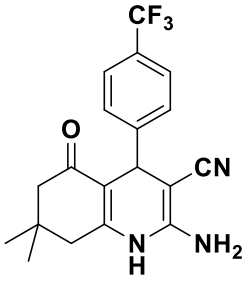
2-Amino-4-(naphthalene-2-yl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (5p)



^{1}H-NMR(400MHz,DMSO-d_6)
δ(ppm)0.93(s,3H),1.02(s,3H),2.07(m,2H),2.23(d,1H),2.53(s,2H),4.36(s,1H),7.05(s,2H), 7.26(d, 1H),7.45(m,2H),7.65(s,1H),7.81-7.87(m,3H).

^{13}C-NMR(400MHz,DMSO-d_6)
δ(ppm)26.75,28.43,30.70,31.83,35.90,50.00,58.10,112.54,119.75,125.56,125.66,126.20, 127.45,127.6 6,128.12,132.01,132.85,142.05, 158.50,162.59, 195.76.

2-Amino-4-(4-trifluoromethylphenyl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydro quinoline-3-carbonitrile (**5q)**



^{1}H-NMR(400MHz,DMSO-d_6)
δ(ppm)0.92(s,3H),1.00 (s,3H),1.95(s,1H),2.07(d,1H),2.22(d,1H),2.46-2.54(m,2H),4.26(s,1H), 7.08(s,2H),7.34(d,2H)7.62(d2H).

^{13}C-NMR(100MHz,DMSO-d_6)
δ(ppm)27.27,28.86,32.27,36.03,50.44,58.76,113.20,120.18,127.02,127.61,128.79,145.21, 158.95,162.95, 196.10.

II.8.A.12.f Sanned copies of compounds mentioned in Scheme II.29

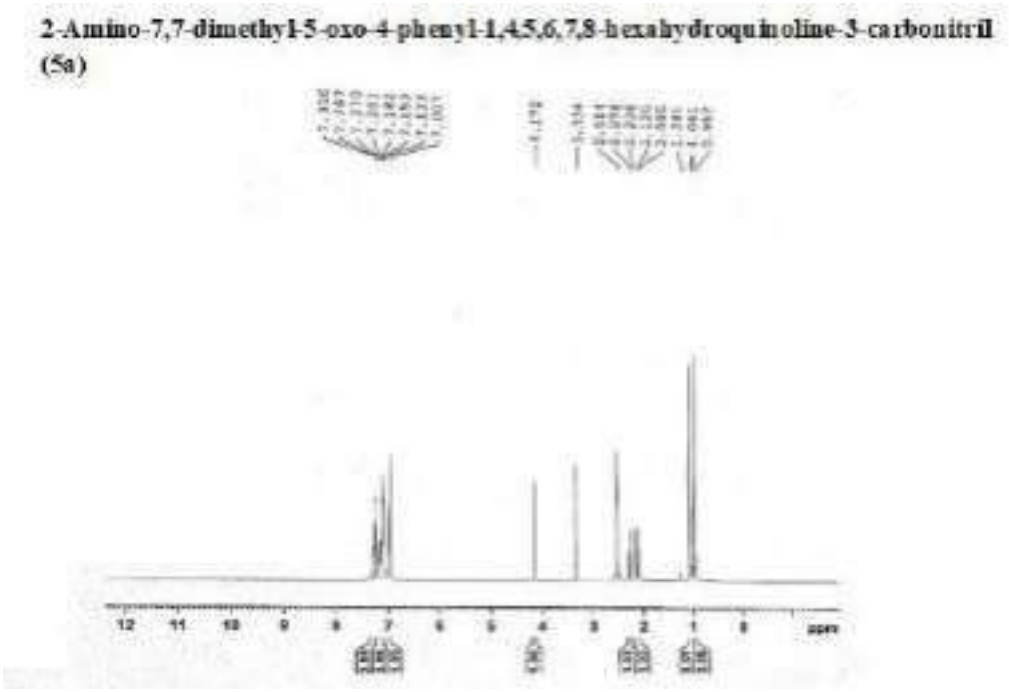


Figure II.13 - ^{1}H-NMR of compound 5a

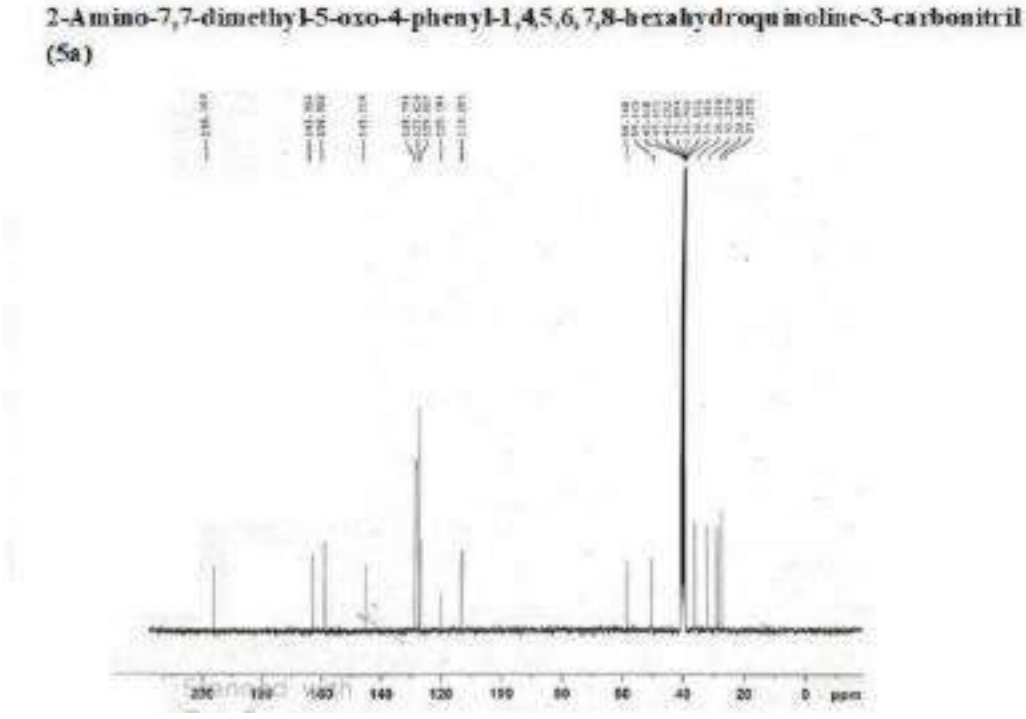


Figure II.14 - ^{13}C-NMR of compound 5a

2-Amino-4-(4-methylphenyl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (5b)

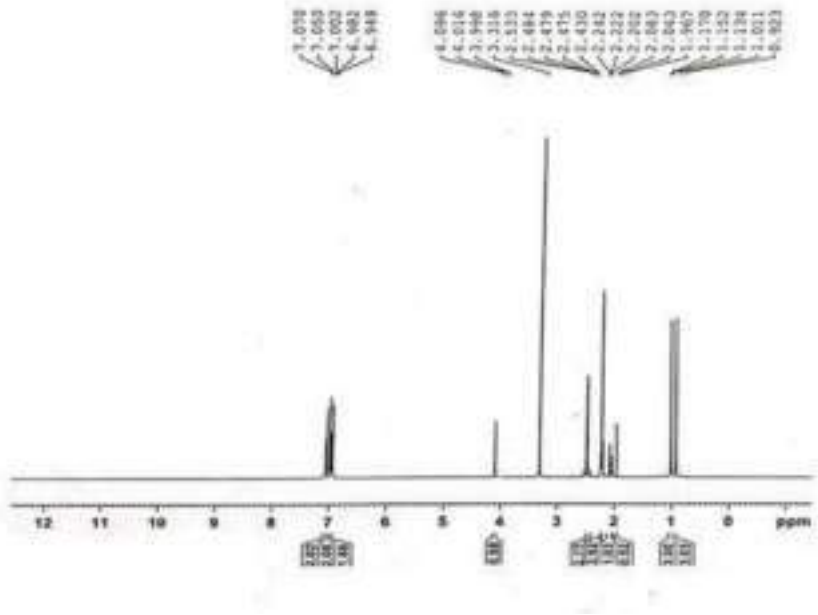


Figure II.15 - ^{1}H-NMR of compound 5b

2-Amino-4-(4-methylphenyl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (5b)

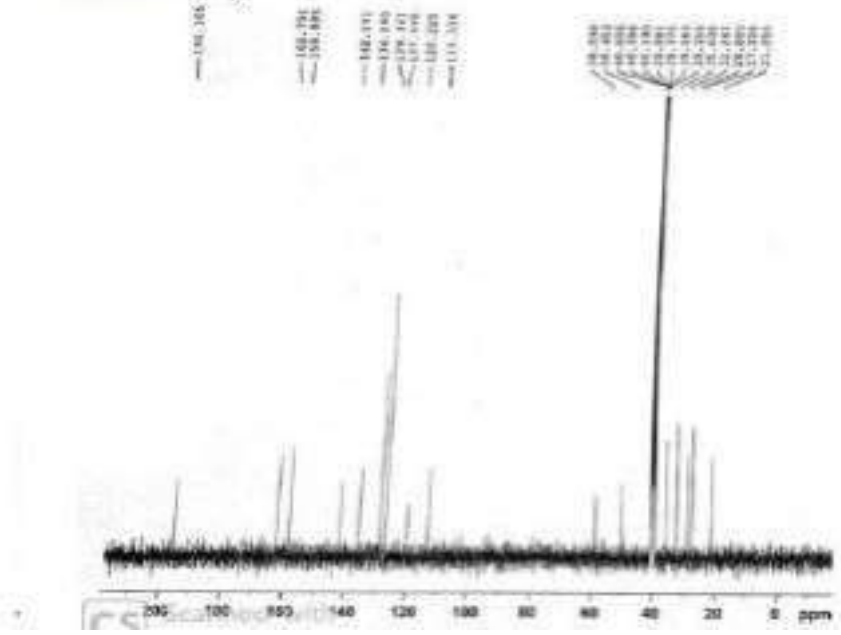


Figure II.16 - ^{13}C-NMR of compound 5b

2-Amino-4-(2-methylphenyl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (5c)

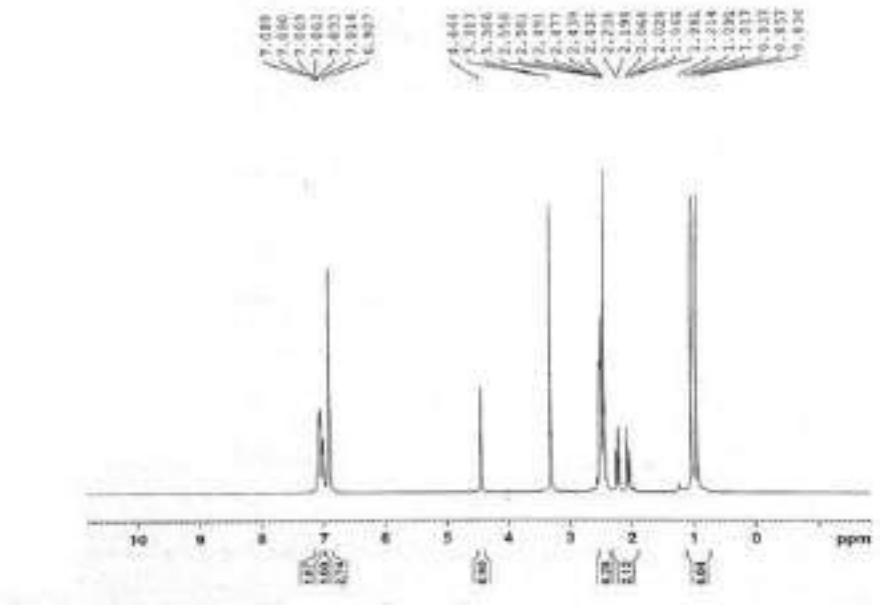


Figure II.17 - ^{1}H-NMR of compound 5c

2-Amino-4-(2-methylphenyl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (5c)

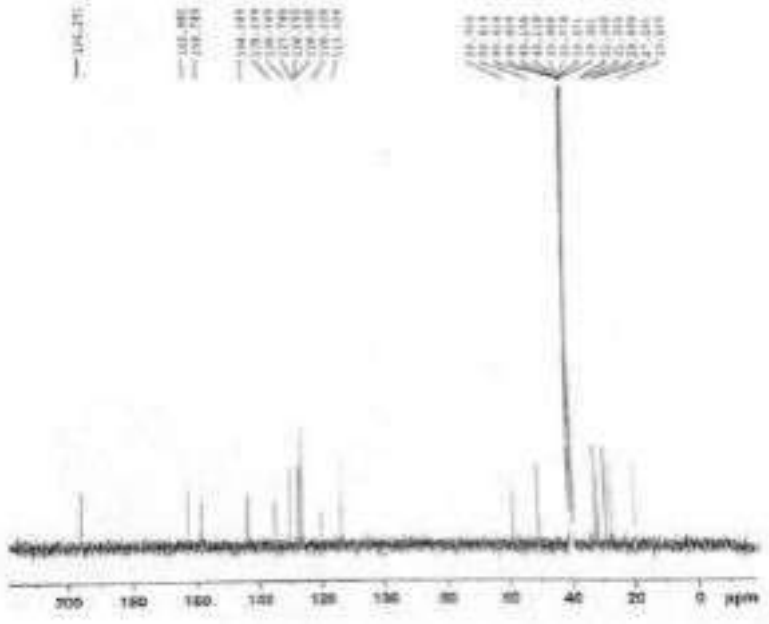


Figure II.18 - ^{13}C-NMR of compound 5c

2-Amino-4-(3-methylphenyl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (5d).

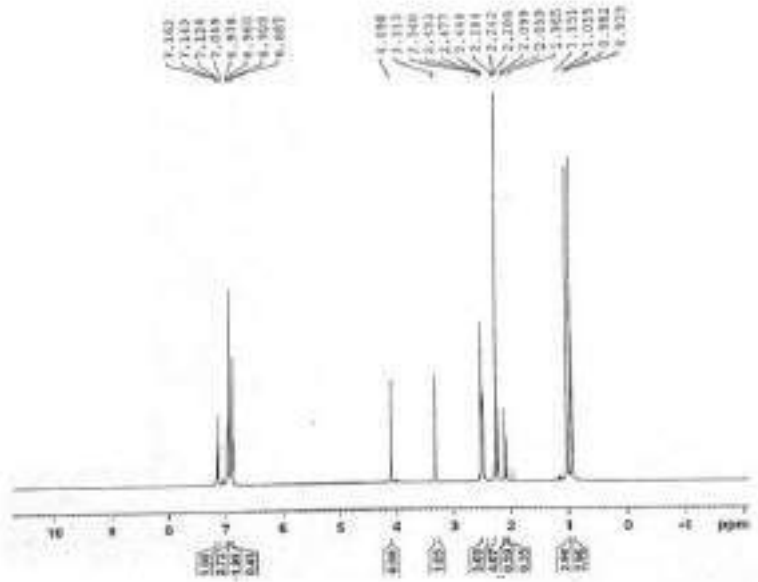


Figure II.19 - ^{1}H-NMR of compound 5d

2-Amino-4-(3-methylphenyl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (5d)

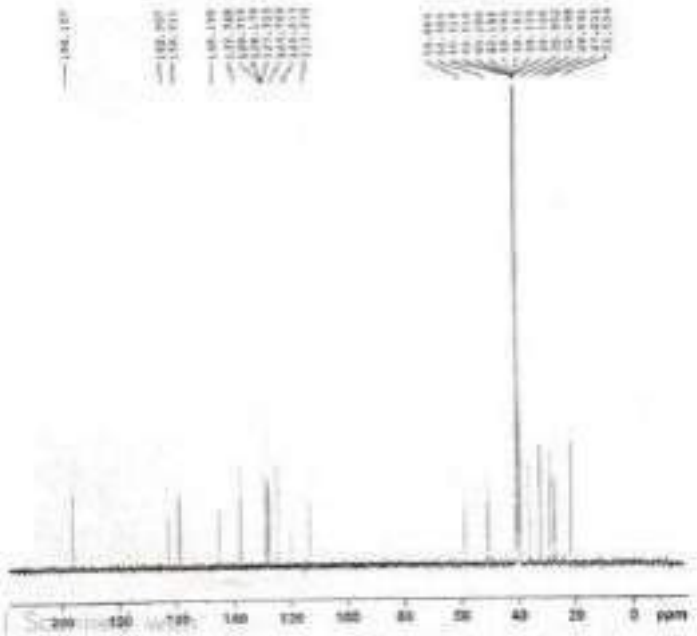


Figure II.20 - ^{13}C-NMR of compound 5d

2-Amino-4-(furan-2-yl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (5e)

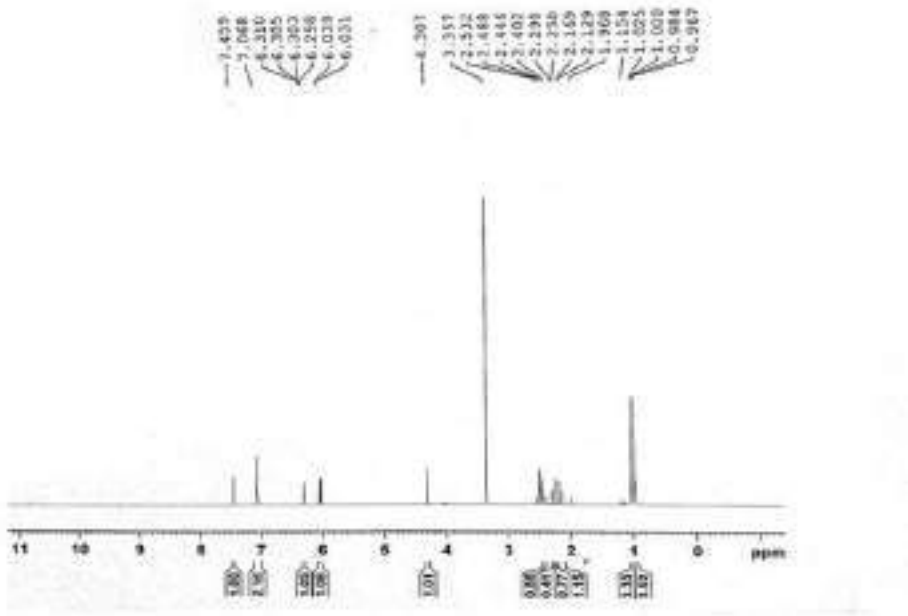


Figure II.21 - ^{13}C-NMR of compound 5e

2-Amino-4-(furan-2-yl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (5e)

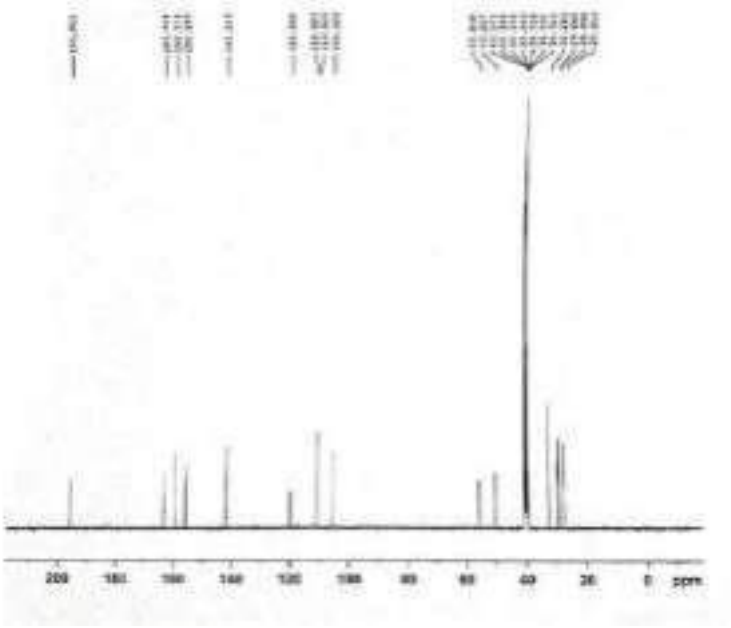


Figure II.22- ^{13}C-NMR of compound 5e

2-Amino-4-(thiophene-2-yl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (5f)

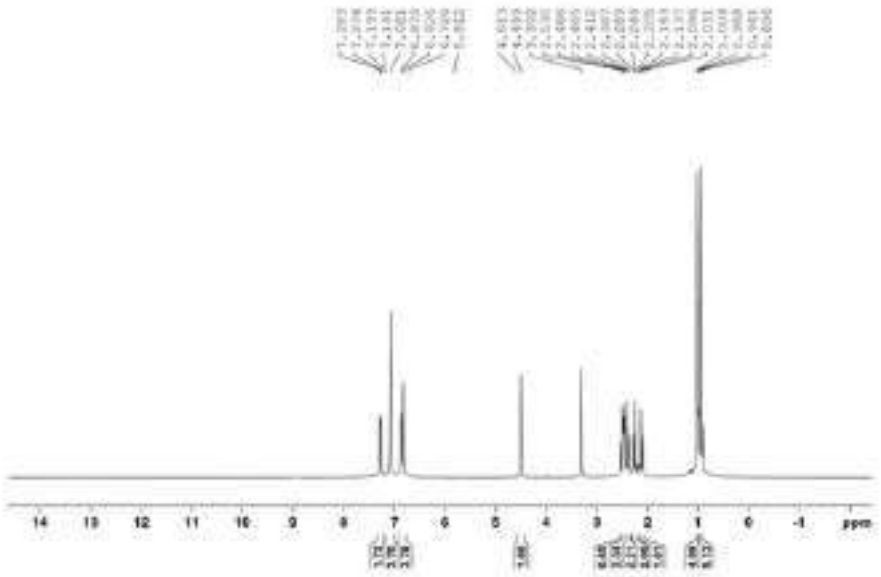


Figure II.23 - ^{1}H-NMR of compound 5f

2-Amino-4-(thiophene-2-yl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (5f)

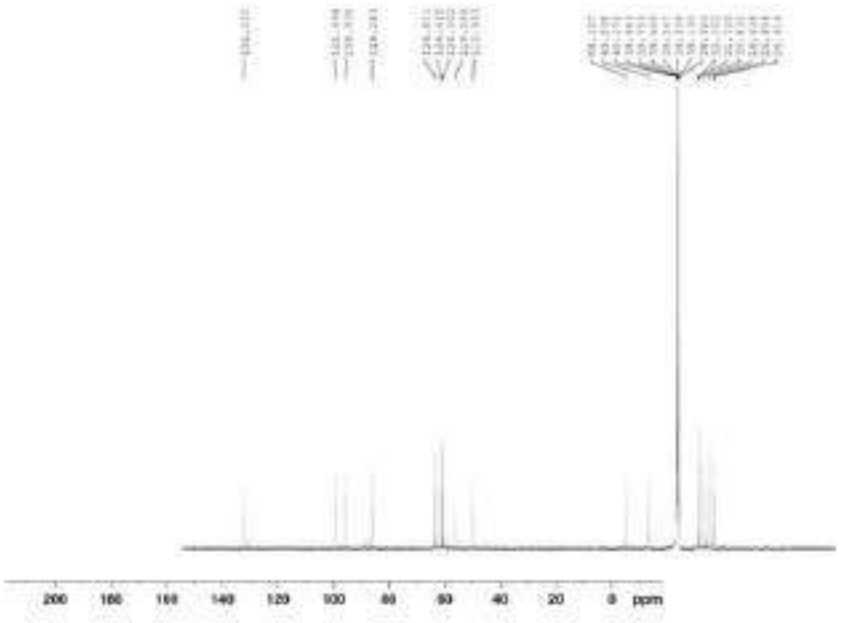


Figure II.24 - ^{13}C-NMR of compound 5f

2-Amino-4-(4-hydroxyphenyl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (5g)

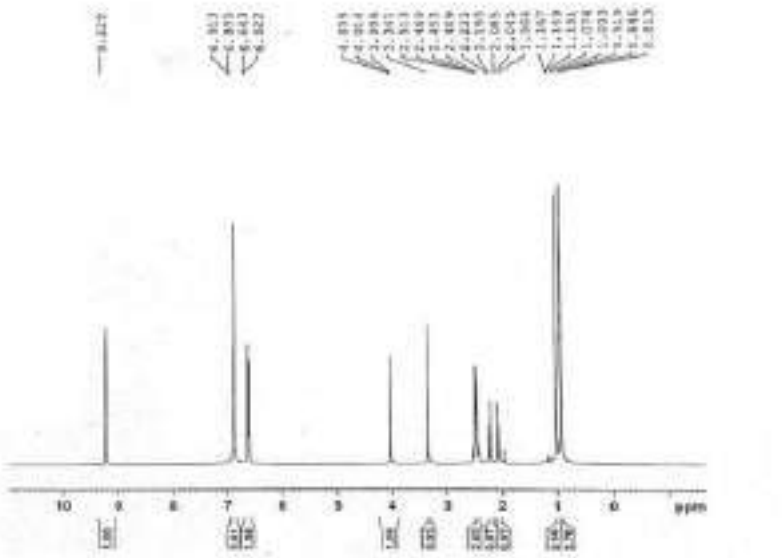


Figure II.25 - ^{1}H-NMR of compound 5g

2-Amino-4-(4-hydroxyphenyl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (5g)

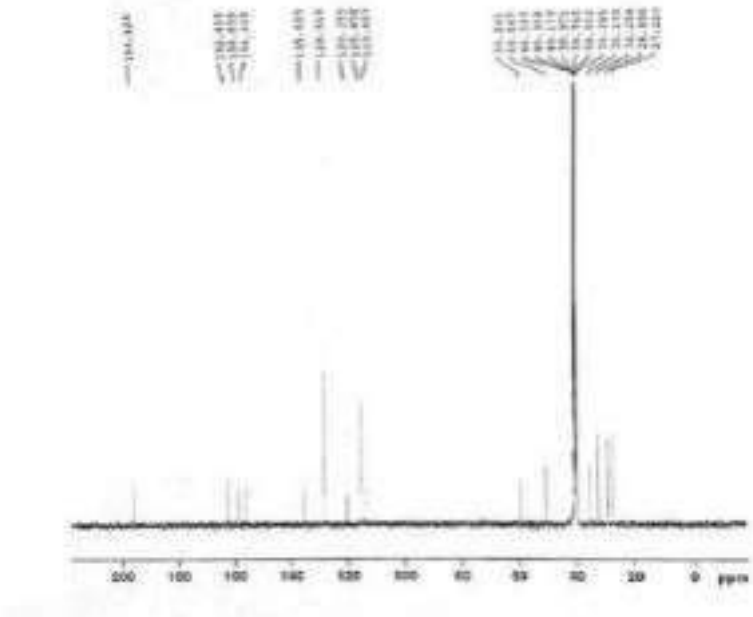


Figure II.26 - ^{13}C-NMR of compound 5g

2-Amino-4-(4-fluorophenyl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (5h)

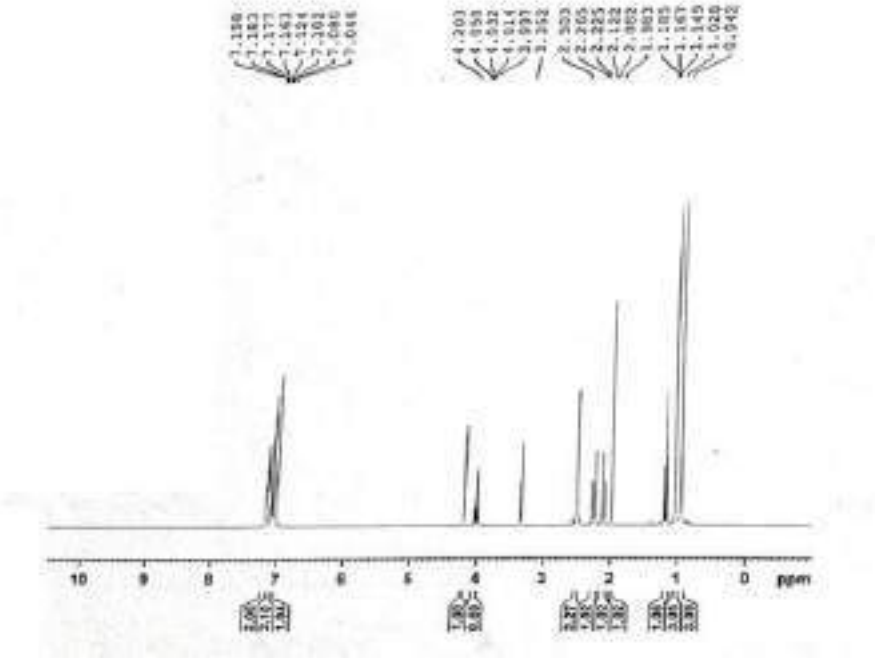


Figure II.27 - ^{1}H-NMR of compound 5h

2-Amino-4-(4-fluorophenyl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (5h)

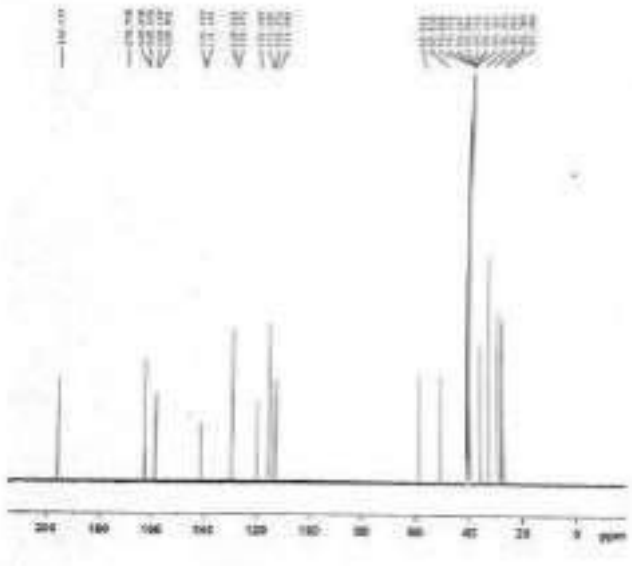


Figure II.28 - ^{13}C-NMR of compound 5h

2-Amino-4-(4-bromophenyl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (5i)

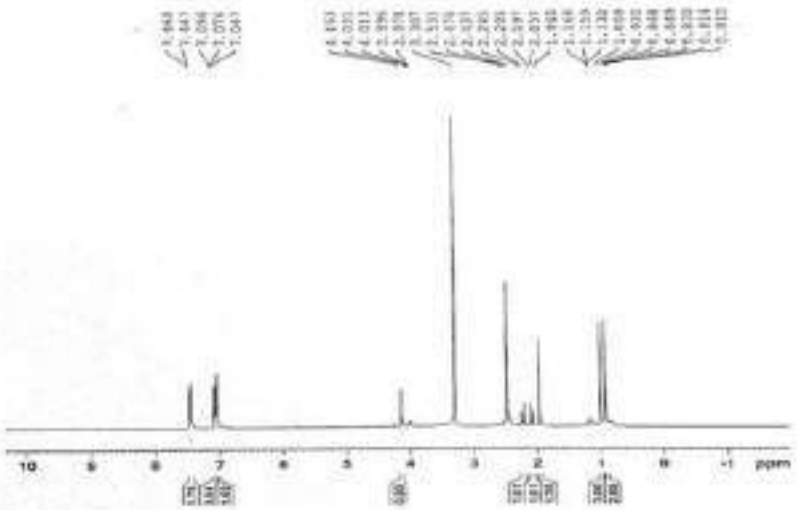


Figure II.29 - ^{1}H-NMR of compound 5i

2-Amino-4-(4-bromophenyl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (5i)

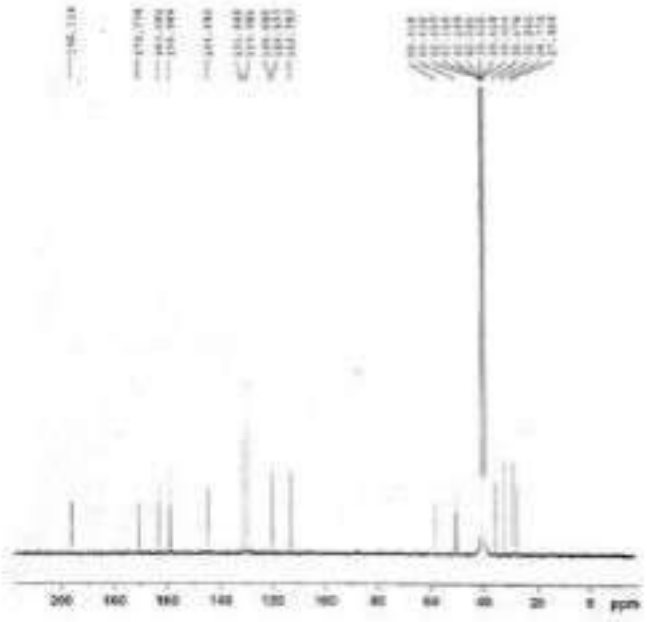


Figure II.30- ^{13}C-NMR of compound 5i

2-Amino-4-(2-chlorophenyl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (5j)

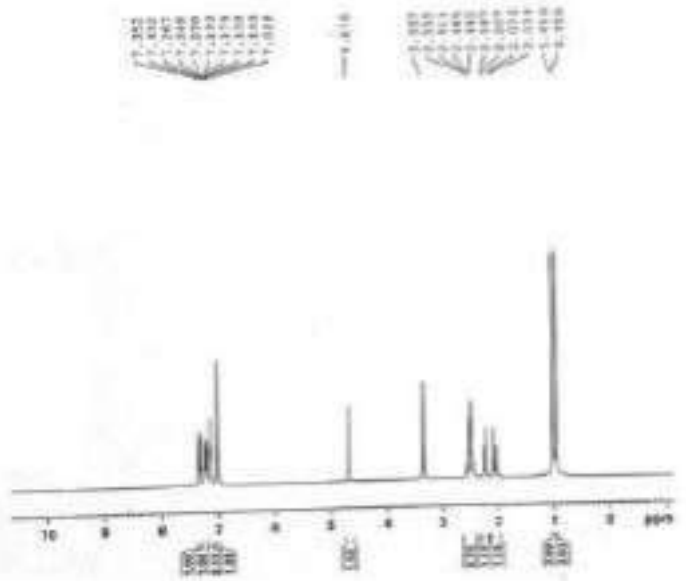


Figure II.31 - ^{1}H-NMR of compound 5j

2-Amino-4-(2-chlorophenyl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (5j)

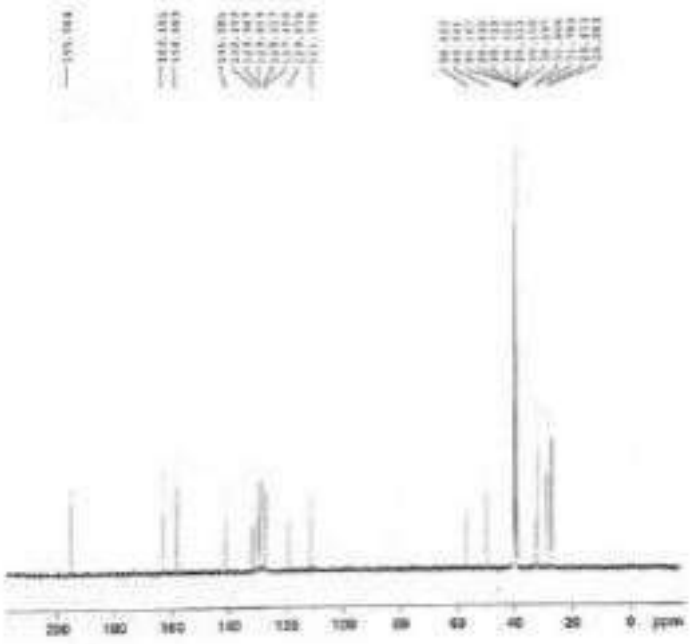


Figure II.32- ^{13}C-NMR of compound 5j

2-Amino-4-(2-nitrophenyl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (5k)

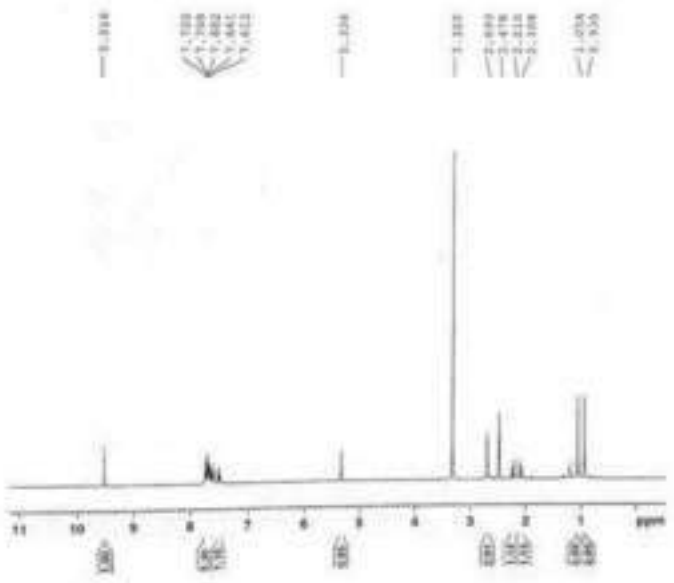


Figure II.33-^{1}H-NMR of compound 5k

2-Amino-4-(4-nitrophenyl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (5l)

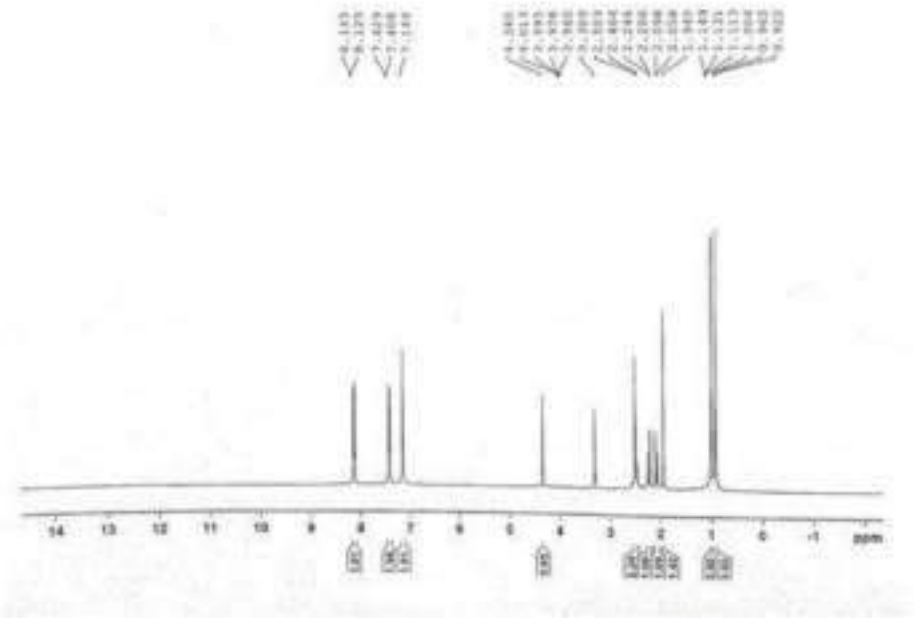


Figure II.34 - ^{1}H-NMR of compound 5l

2-Amino-4-(4-nitrophenyl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (5l)

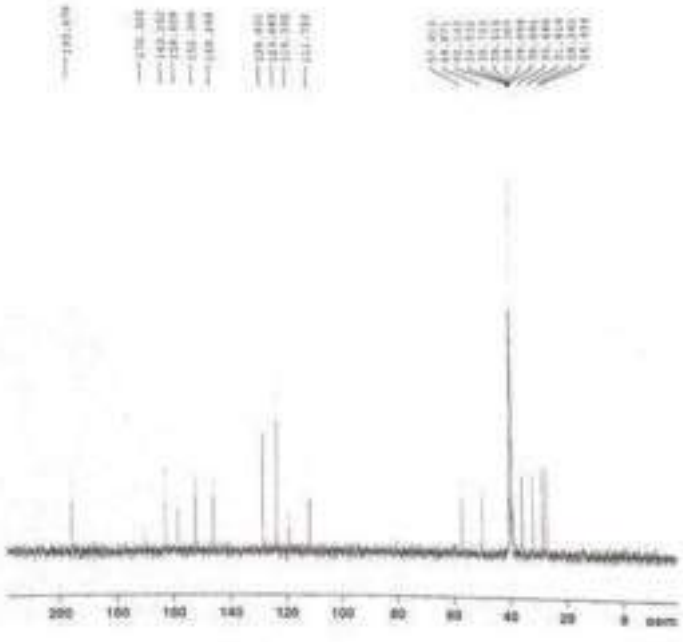


Figure II.35- ^{13}C-NMR of compound 5l

2-Amino-4-(3-methoxy,4-hydroxyphenyl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydro quinoline-3-carbonitrile (5m)

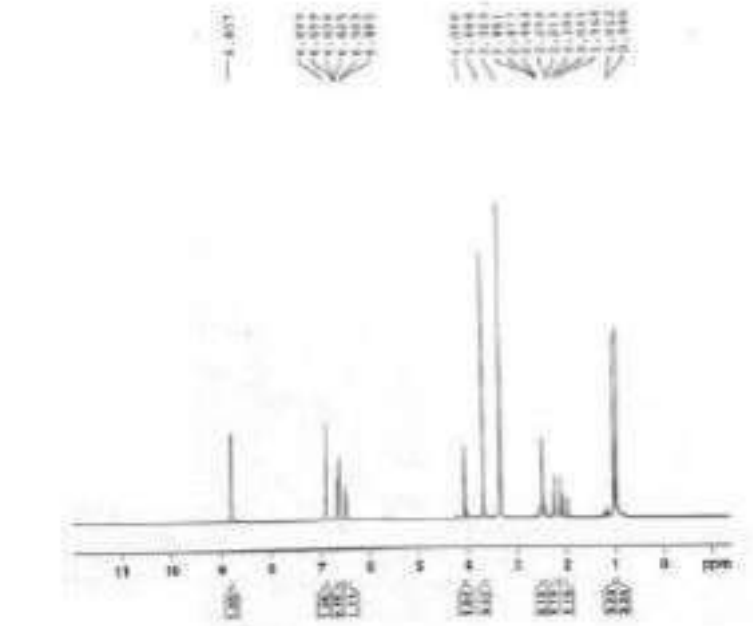


Figure II.36-^{1}H-NMR of compound 5m

2-Amino-4-(3-methoxy,4-hydroxyphenyl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydro quinoline-3-carbonitrile (5m)

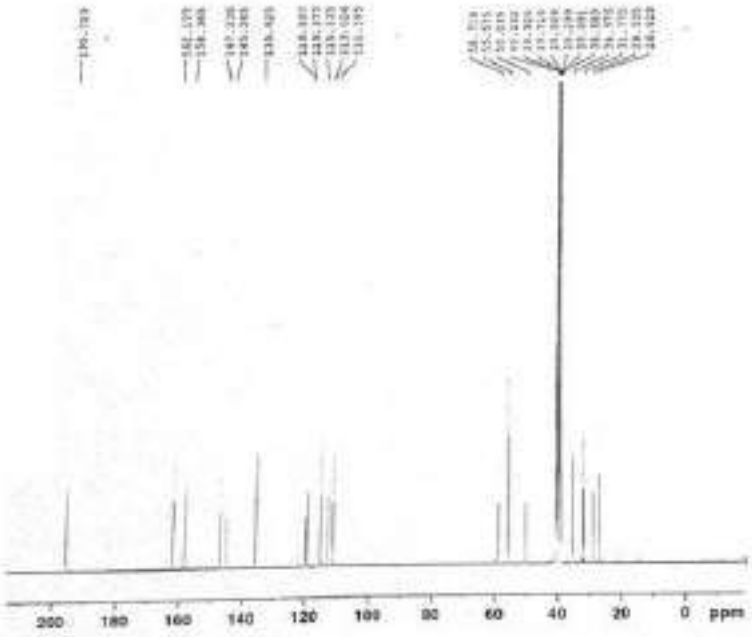


Figure II.37-^{13}C-NMR of compound 5m

2-Amino-4-(4-N,N dimethylphenyl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydro quinoline-3-carbonitrile (5n)

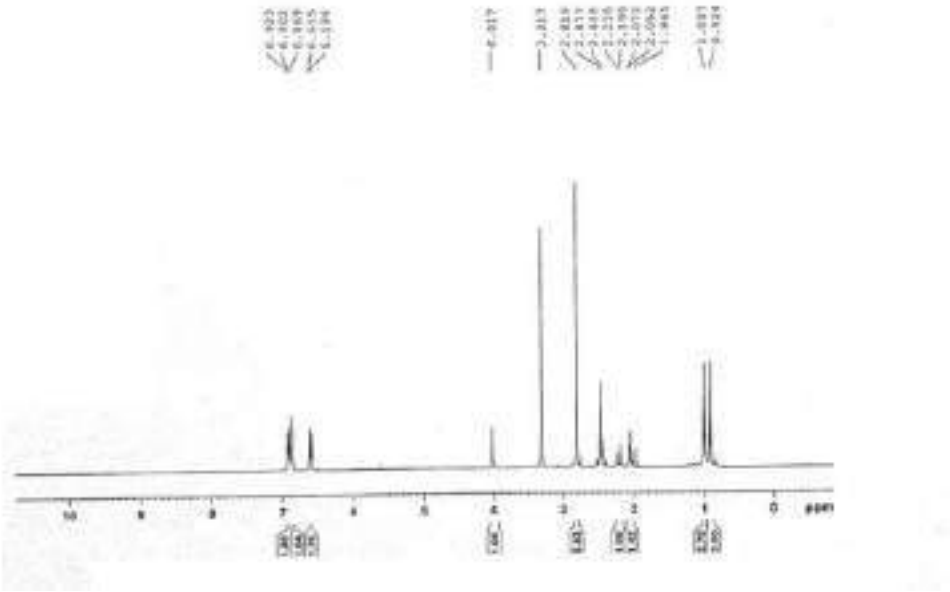


Figure II.38 - ^{1}H-NMR of compound 5n

2-Amino-4-(4-N,N dimethylphenyl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydro quinoline-3-carbonitrile (5n)

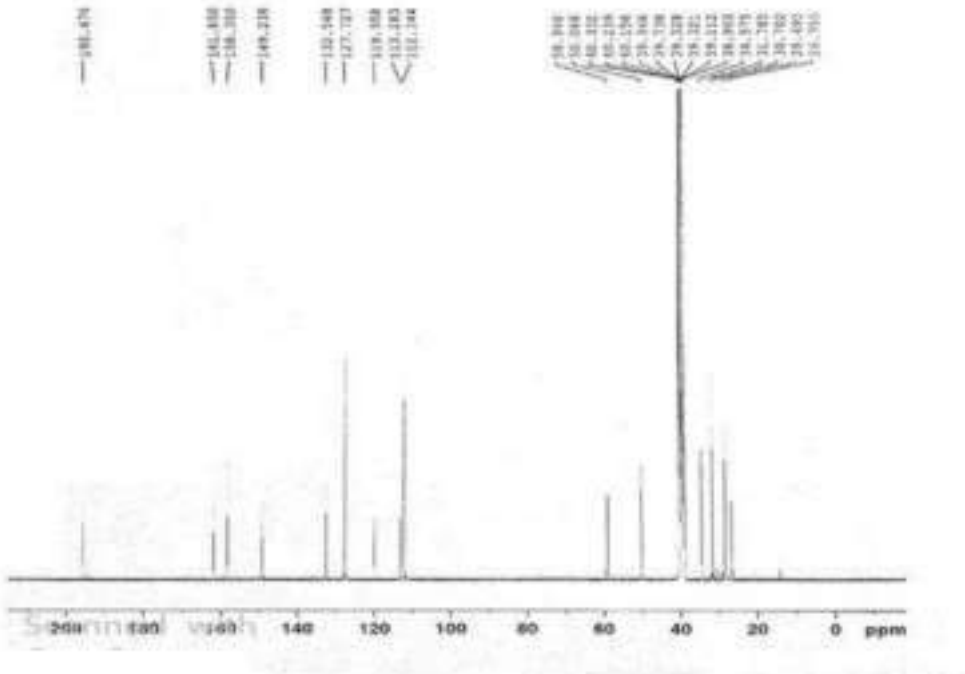


Figure II.39- ^{13}C-NMR of compound 5n

2-Amino-4-(pyridine-3-yl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquino line-3-carbonitrile (5o)

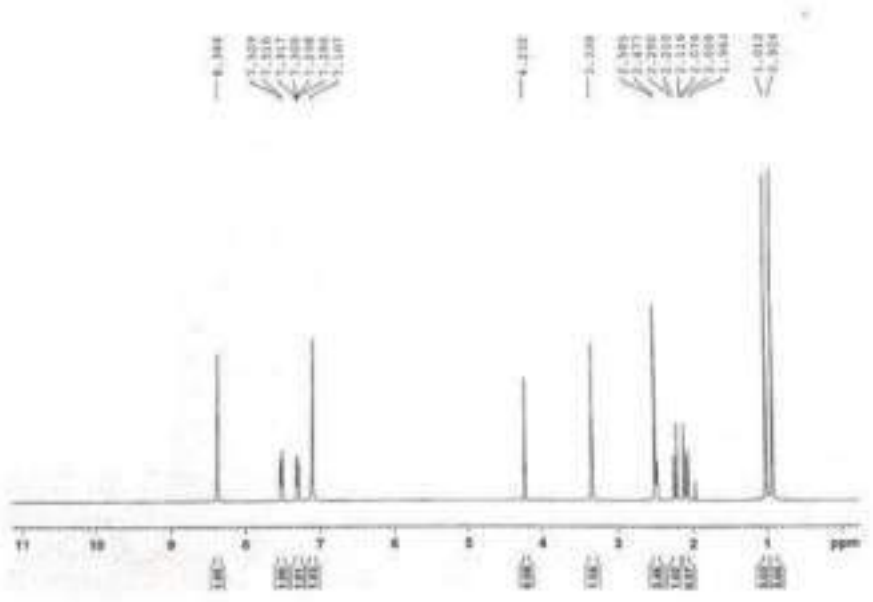


Figure II.40 -[1]H-NMR of compound 5o

2-Amino-4-(pyridine-3-yl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquino line-3-carbonitrile (5o)

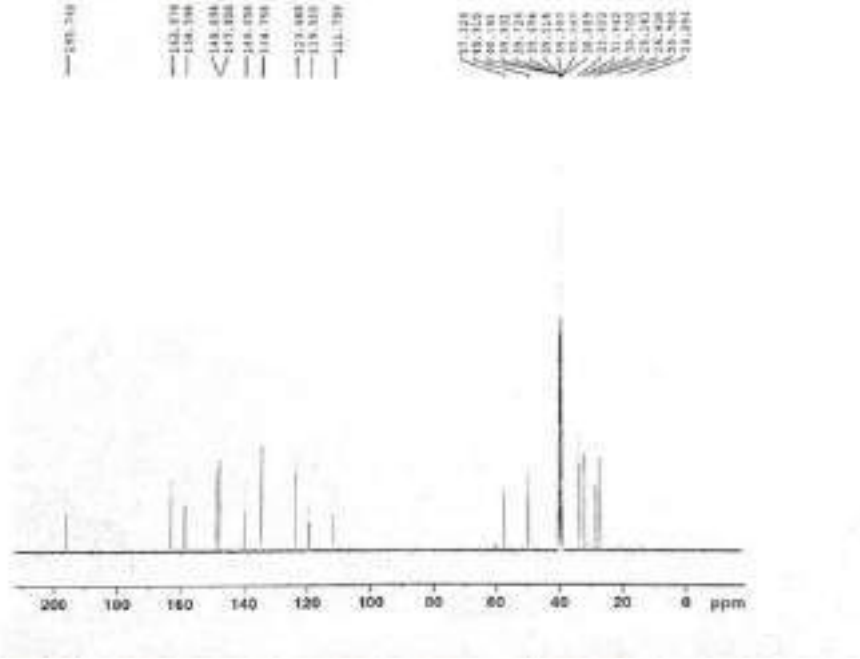


Figure II.41-[13]C-NMR of compound 5o

2-Amino-4-(naphthalene-2-yl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydro quinoline-3-carbonitrile (5p)

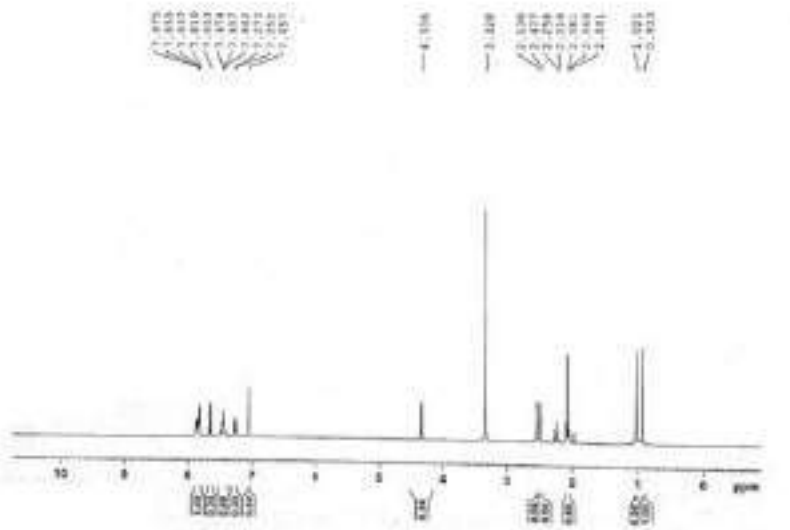


Figure II.42 - ^{1}H-NMR of compound 5p

2-Amino-4-(4-trifluoromethylphenyl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydro quinoline-3-carbonitrile (5q)

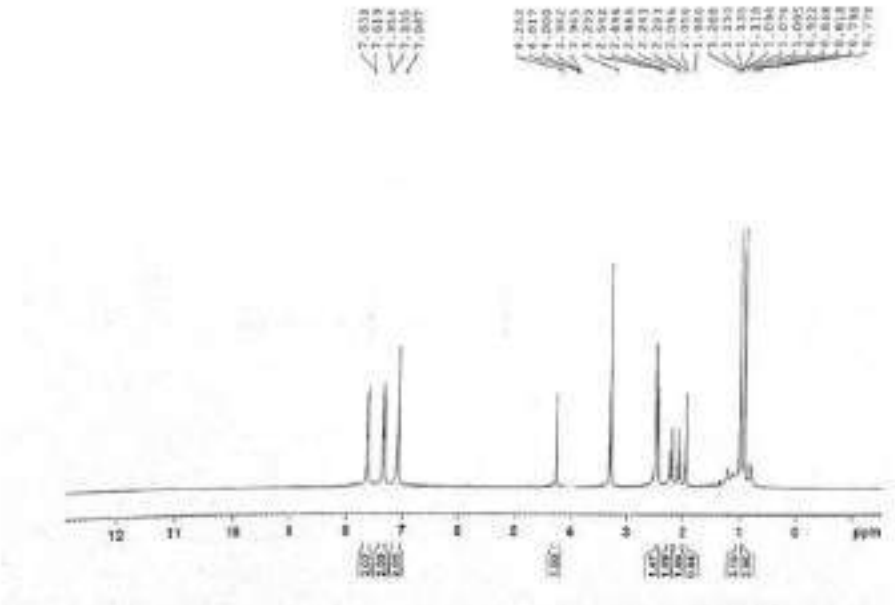


Figure II.43- ^{13}C-NMR of compound 5q

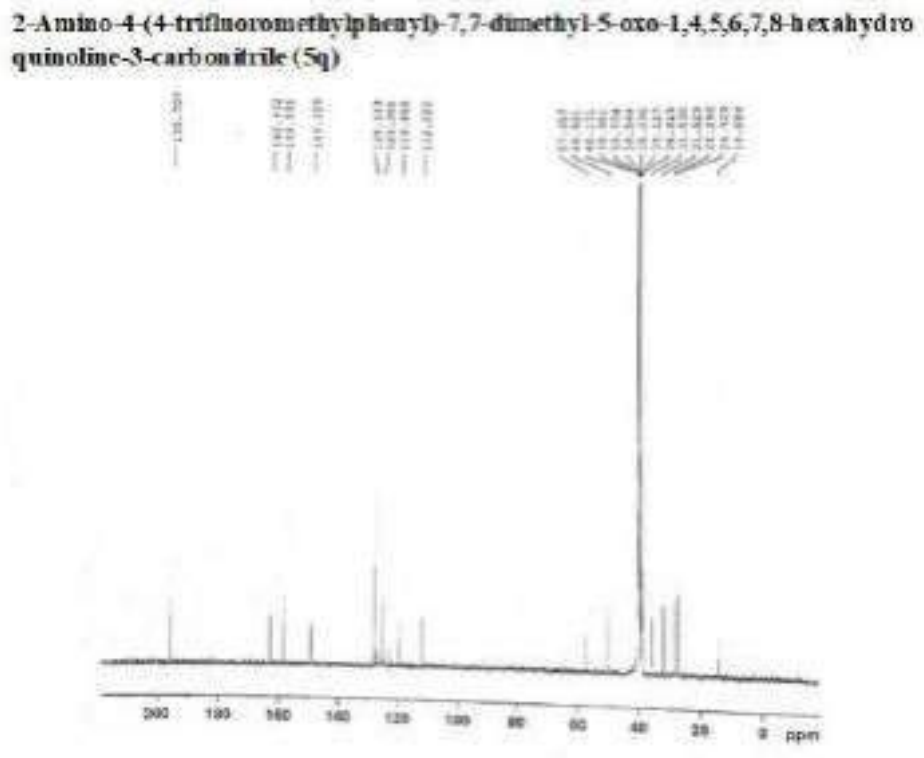
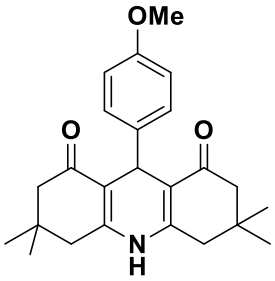


Figure II.44-^{13}C-NMR of compound 5q

II.8.A.12.g. Spectral data of the compounds mentioned in Scheme II.30

9-(4-methoxyphenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione(4a)

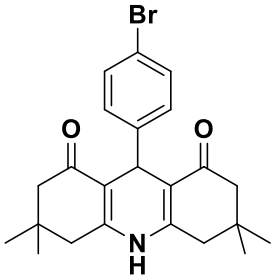


^{1}H-NMR(400MHz,DMSO-d_6)

δ(ppm)0.84(s,6H),0.98(s,6H),1.95(d,2H),2.14(d,2H),2.13(d,2H),2.39-2.481(m,2H),3.66(s,3H), 4.72(s,1H),6.68(d,2H),7.02(d,2H),9.21(s,1H).

^{13}C-NMR(400MHz,DMSO-d_6)
δ(ppm)27.05,29.66,32.43,32.67,50.82,55.37,112.25,113.47,129.63,140.69,149.59,157.62, 194.94.

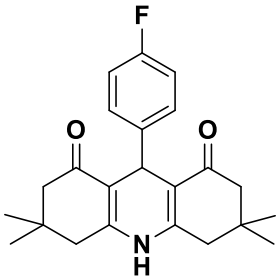
9-(4-bromophenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione(4b)



^{1}H-NMR(400MHz,DMSO-d_6)
δ(ppm)0.83(s,6H),1.03(s,6H),1.96(d,2H),2.12(d,2H),2.30(d,2H),2.40-2.481(m,2H), 4.77(s,1H), 6.95(m,2H),7.11-7.15(m,2H),9.21(s,1H).

^{13}C-NMR(400MHz,DMSO-d_6)
δ(ppm)27.03,28.48,32.69,32.84,50.74,111.86,114.63,114.84,143.90,149.93, 194.94.

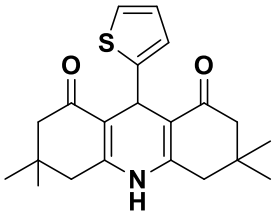
9-(4-fluorophenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (4c)



^{1}H-NMR(400MHz,DMSO-d_6)
δ(ppm)0.84(s,6H),0.98(s,6H),1.88-2.32(m,8H) 4.63(s,1H), 6.95(m,2H), 7.03(d,2H), 9.21(s,1H).

^{13}C-NMR(400MHz,DMSO-d_6)
δ(ppm)27.05,29.66,32.43,32.67,50.82,55.37,112.25,113.47,129.063,140.069,149.59, 157.62, 194.94.

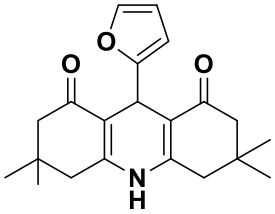
3,3,6,6-tetramethyl-9-(thiophen-2-yl)-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione(4d)



^{1}H-NMR(400MHz,DMSO-d_6)
δ(ppm)0.91(s,6H),0.96(s,6H),1.96-1.48(m,8H), 5.12(s,1H),6.63(s,1H),6.75-6.77(m,1H), 7.10-7.12(m,1H),9.41(s,1H).

^{13}C-NMR(400MHz,DMSO-d_6)
δ(ppm)27.07,27.84,29.74,32.64,50.75,111.43,123.40,123.62,126.78,149.59,150.21,151.54, 194.91.

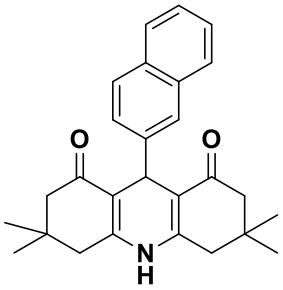
9-(furan-2-yl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione(4e)



^{1}H-NMR(400MHz,DMSO-d_6)
δ(ppm)0.86(s,6H),0.96(s,6H),1.96-2.48(m,8H),5.12(s,1H),6.62(d,1H), 6.77(t,1H), 7.12(t,1H), 9.21(s,1H).

^{13}C-NMR(400MHz,DMSO-d_6)
δ(ppm)27.07,27.84,29.73,32.64,50.74,111.43,123.40,123.64,126.77,150.21,151.53, 194.91.

3,3,6,6-tetramethyl-9-(naphthalen-2-yl)-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (4f)

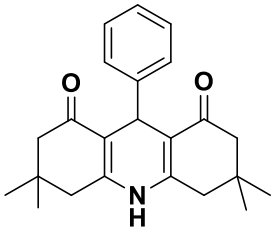


^{1}H-NMR(400MHz,DMSO-d_6)

δ(ppm)0.83(s,6H),0.96(s,6H),1.88-1.96(m,2H),2.16(d,2H),2.32-2.48(m,4H),4.96(s,1H),7.34-7.41(m,4H),7.68-7.76(m,3H),9.36(s,1H).

^{13}C-NMR(400MHz,DMSO-d$_6$)
δ(ppm)26.95,29.68,32.70,33.82,50.82,111.83,125.61,126.12,126.26,127.38,127.64, 127.78, 128.09,132.09,133.28,145.13,150.02, 194.98.

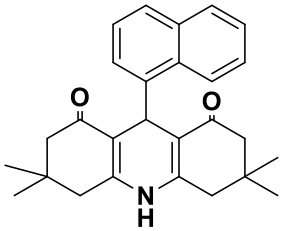
3,3,6,6-tetramethyl-9-phenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione(4g)



^{1}H-NMR(400MHz,DMSO-d$_6$)
δ(ppm)0.84(s,6H),0.98(s,6H),1.95(d,2H),2.14(d,2H),2.30(d,2H),2.32-2.53(m,2H), 4.78(s,1H), 6.68(d,2H),7.12-7.18(m,5H),9.26(s,1H).

^{13}C-NMR(400MHz,DMSO-d$_6$)
δ(ppm)27.01,29.64,32.69,33.37,50.80,112.00,126.00,128.11,128.15,149.87,194.91.

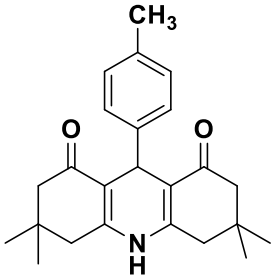
3,3,6,6-tetramethyl-9-(naphthalen-1-yl)-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione(4h)



^{1}H-NMR(400MHz,DMSO-d$_6$)
δ(ppm)0.79(s,6H),0.98(s,6H),1.84(d,2H),2.12(d,2H),2.33(d,2H),2.48-2.50 (m,2H,DMSO-6H), 5.56(s,1H),7.27-7.61(m,7H),9.37(s,1H).

^{13}C-NMR(400MHz,DMSO-d$_6$)
δ(ppm)26.83,28.90,29.71,32.67,50.75,113.72,125.38,125.60,125.90,126.52,126.68,126.81, 128.02,131.23,133.32.149.43,195.03.

3,3,6,6-tetramethyl-9-(p-tolyl)-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione(4i)



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

δ(ppm)0.83(s,6H),0.96(s,6H),1.88-1.96(d,2H),2.1-2.15(m,2H),2.(d,2H),2.26-2.39(m,2H,DMSO-6H), 2.48(s,3H),4.73(s,1H),6.92(d,2H),7.00(d,2H),9.23(s,1H).

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

δ(ppm)21.11,27.11,29.67,31.24,32.96,50.82,112.16,128.09,128.67,134.80,144.86, 149.68, 194.89.

II.8.A.12.h. Sanned copies of compounds mentioned in Scheme II.30

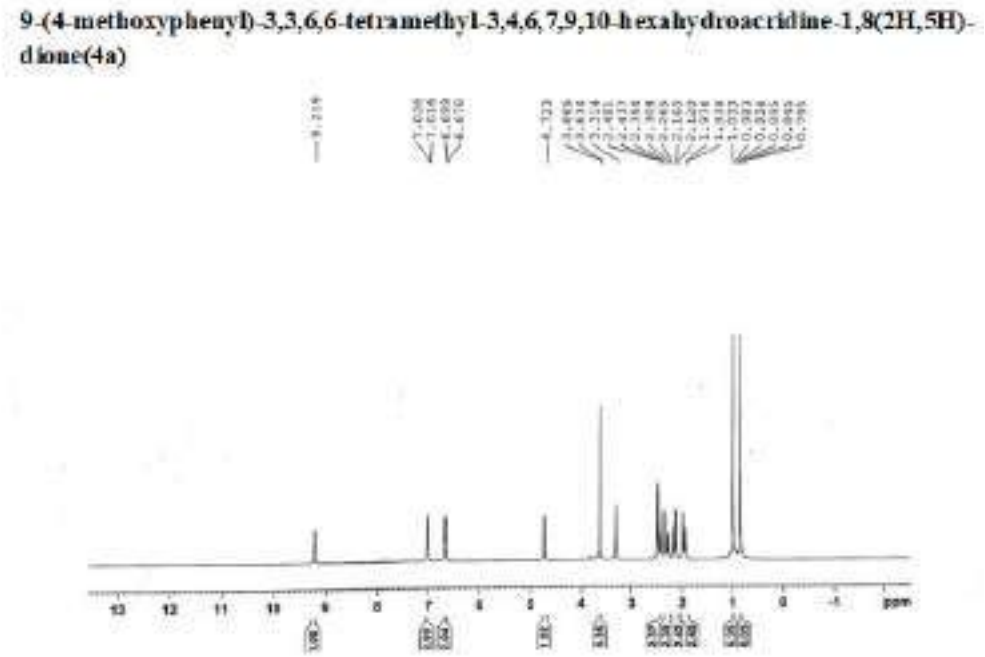


Figure II.45-^{1}H-NMR of compound 4a

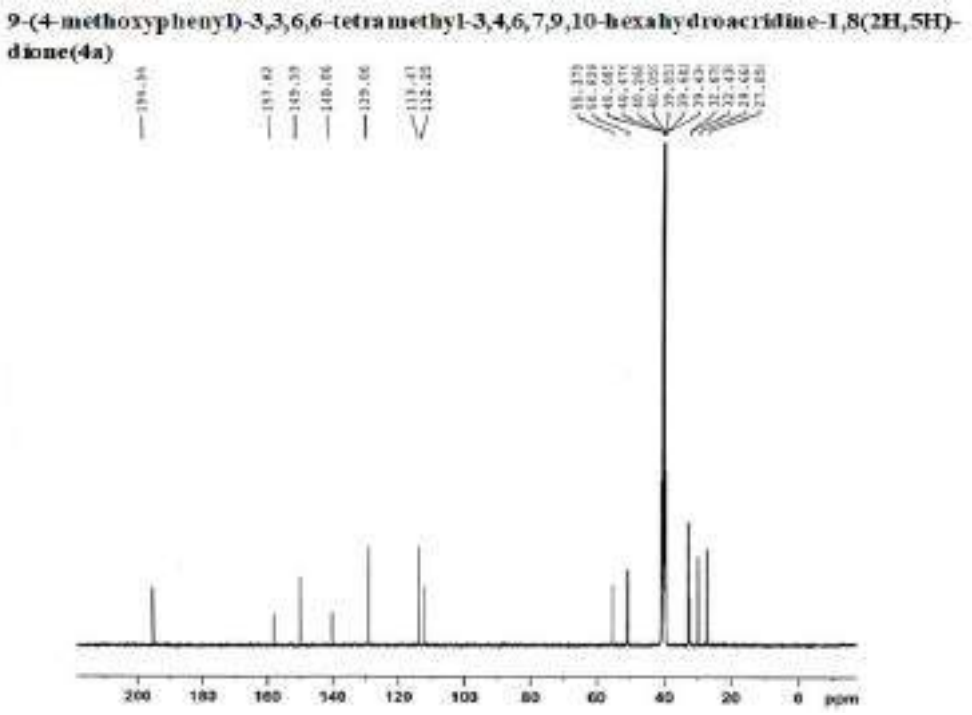


Figure II.46-^{13}C-NMR of compound 4a

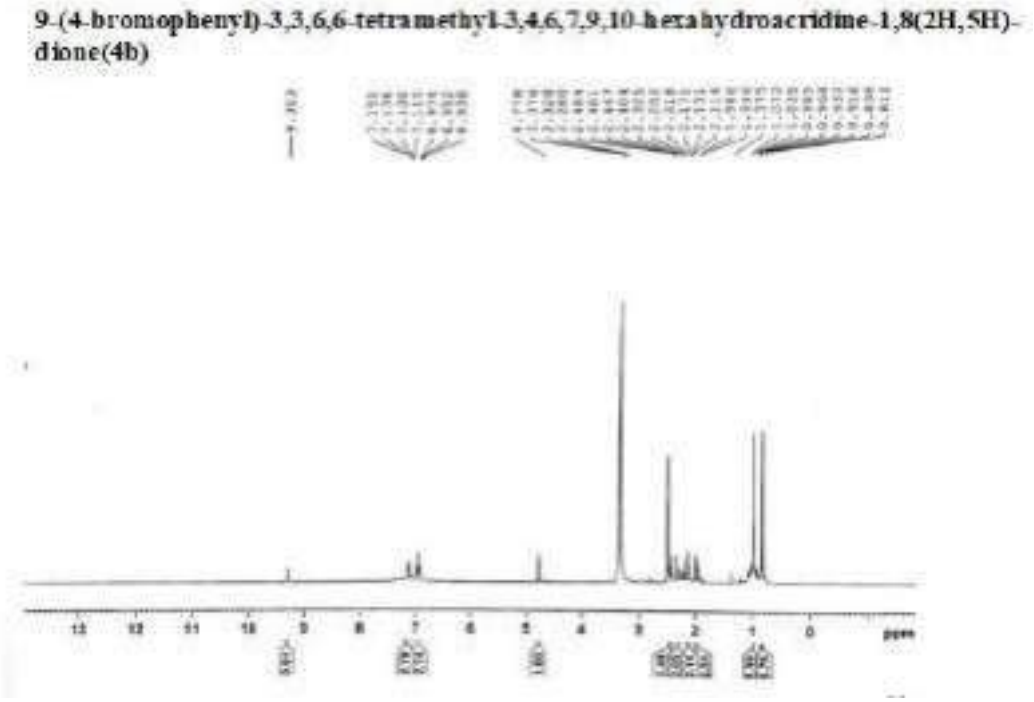


Figure II.47-^{1}H-NMR of compound 4b

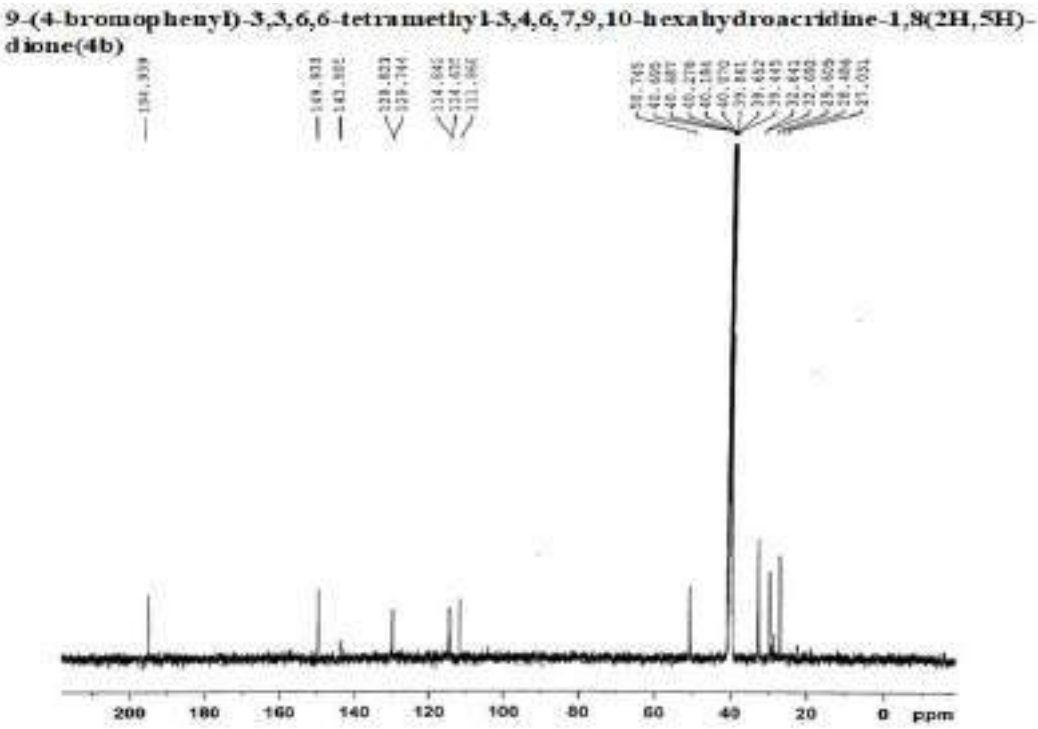


Figure II.48-^{13}C-NMR of compound 4b

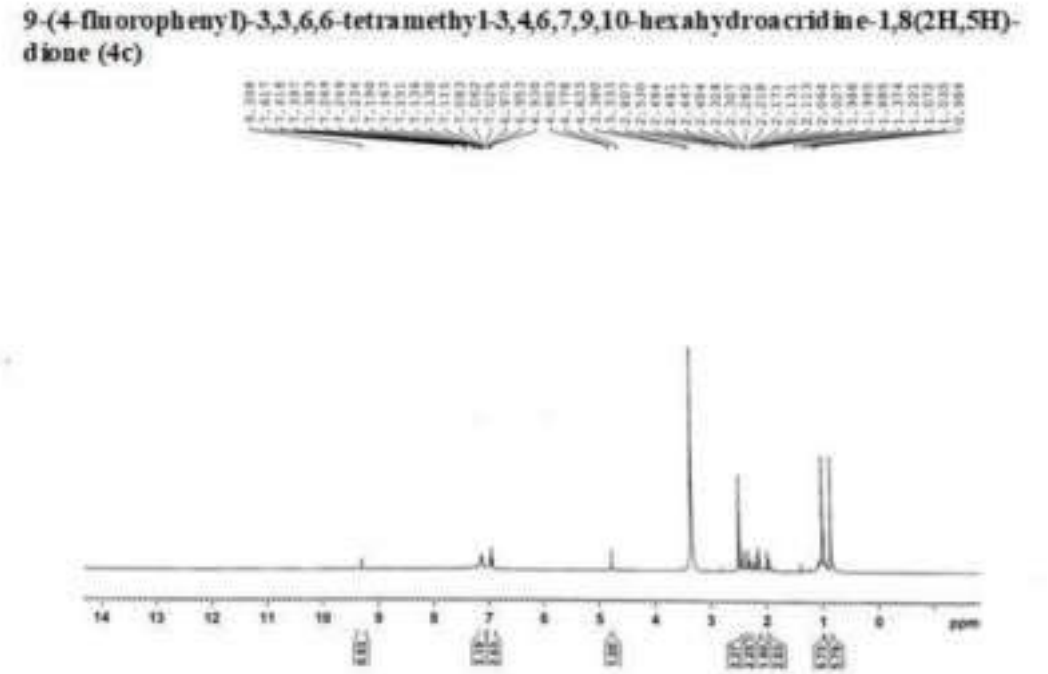


Figure II.49-^{1}H-NMR of compound 4c

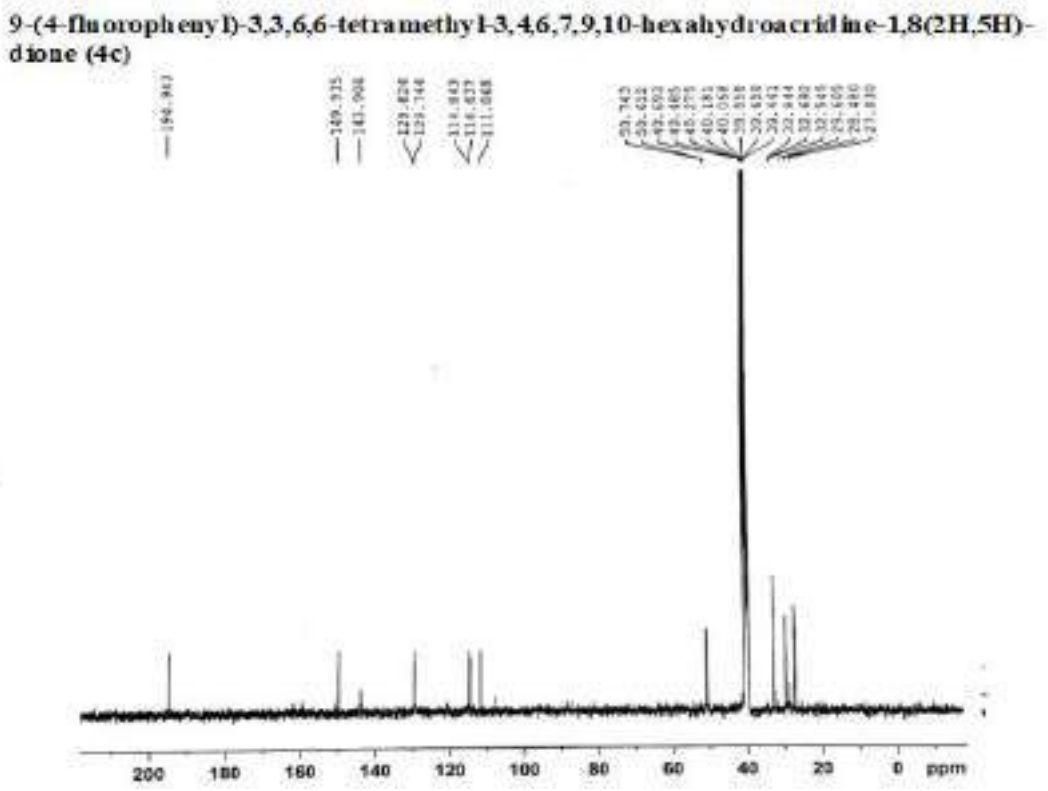


Figure II.50-^{13}C-NMR of compound 4c

3,3,6,6-tetramethyl-9-(thiophen-2-yl)-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione(4d)

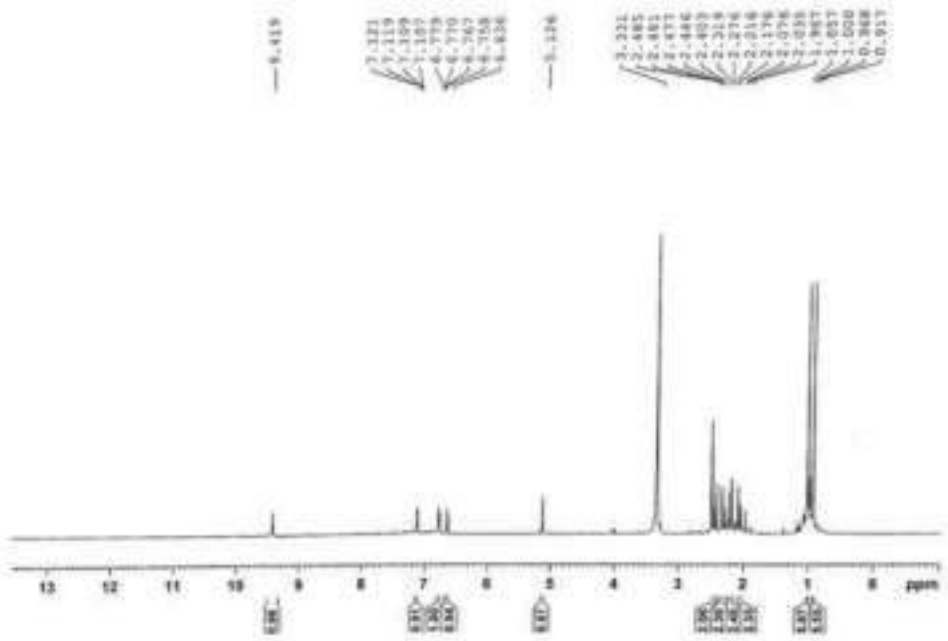


Figure II.51-^{1}H-NMR of compound 4d

3,3,6,6-tetramethyl-9-(thiophen-2-yl)-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione(4d)

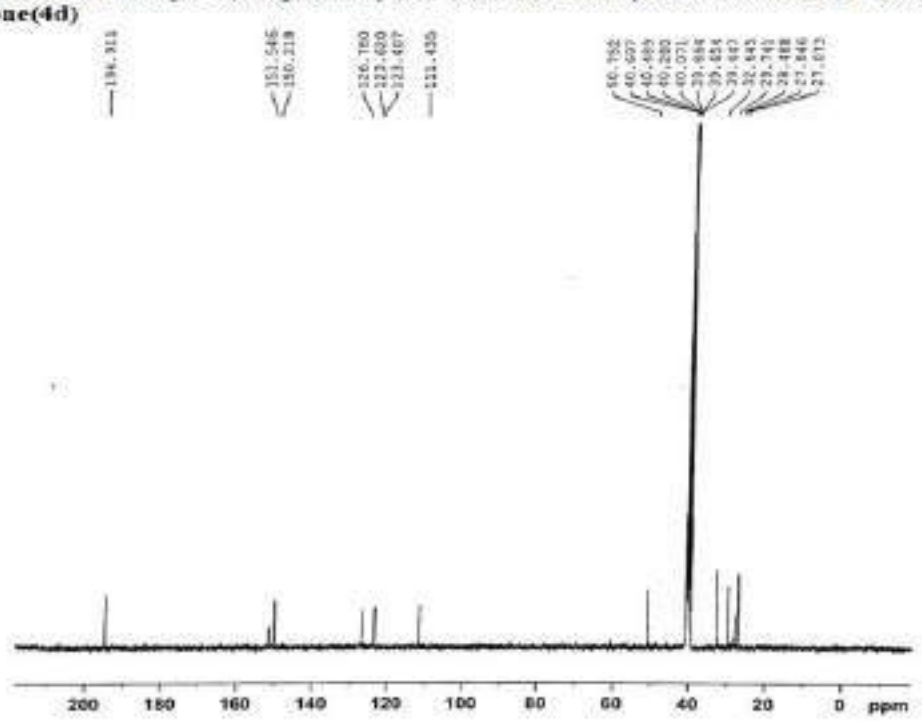


Figure II.52-^{13}C-NMR of compound 4d

9-(furan-2-yl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione(4e)

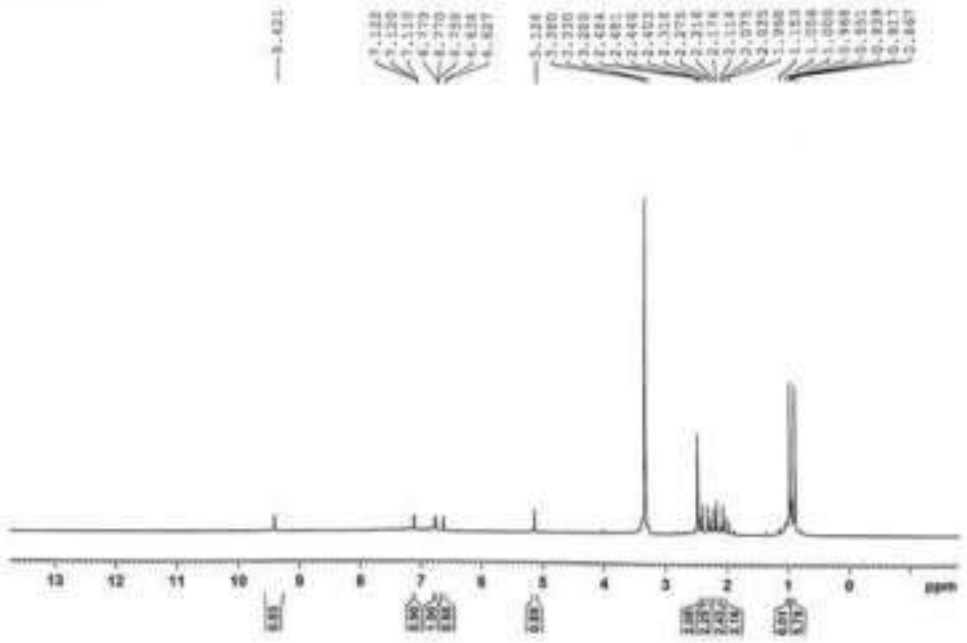


Figure II.53-^{1}H-NMR of compound 4e

9-(furan-2-yl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione(4e)

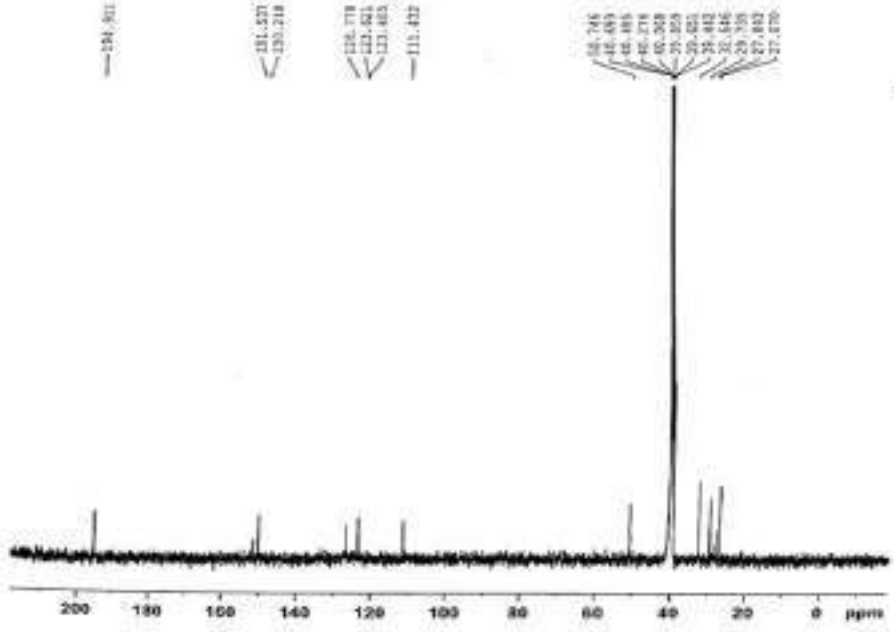


Figure II.54-^{13}C-NMR of compound 4e

3,3,6,6-tetramethyl-9-(naphthalen-2-yl)-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione (4f)

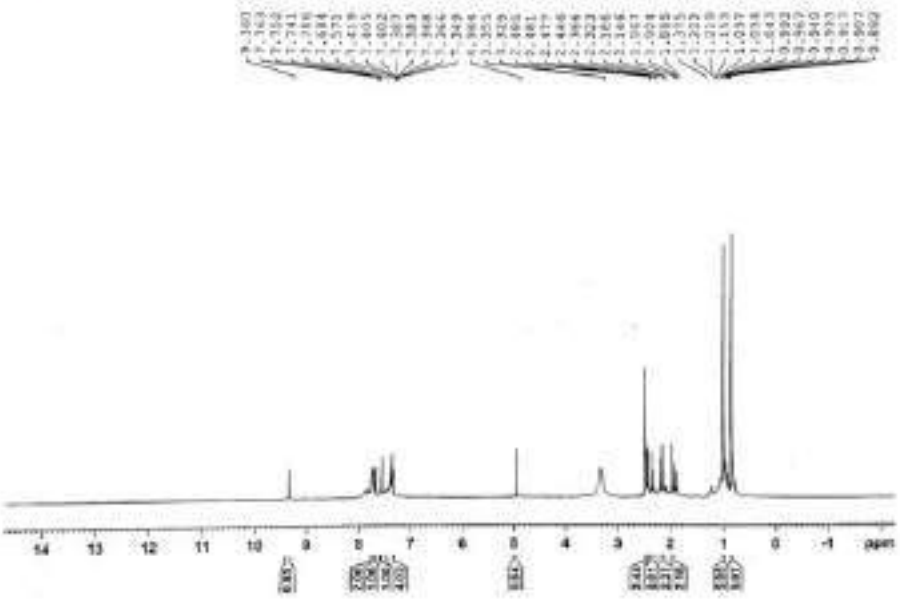


Figure II.55-^{1}H-NMR of compound 4f

3,3,6,6-tetramethyl-9-(naphthalen-2-yl)-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione (4f)

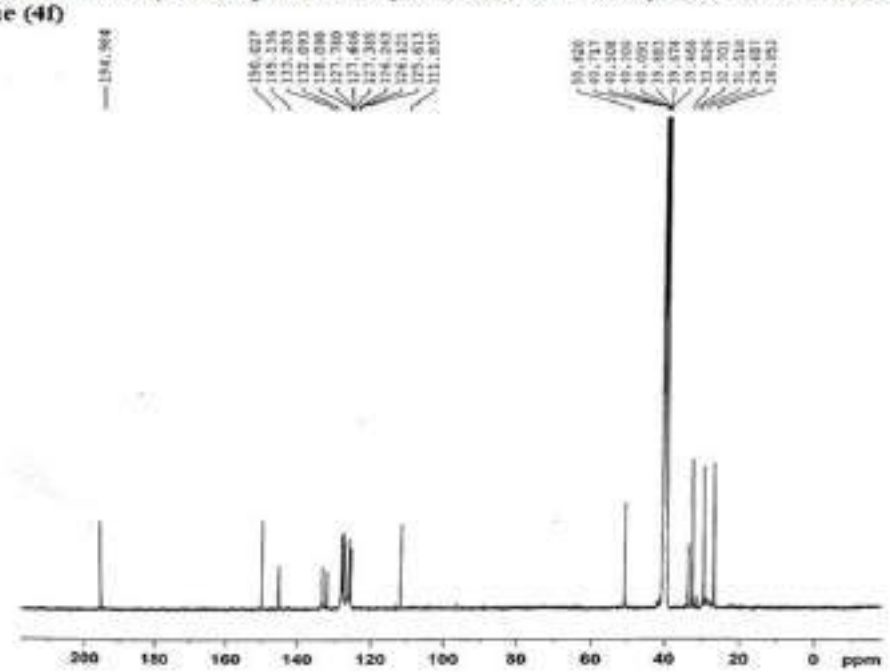


Figure II.56-^{13}C-NMR of compound 4f

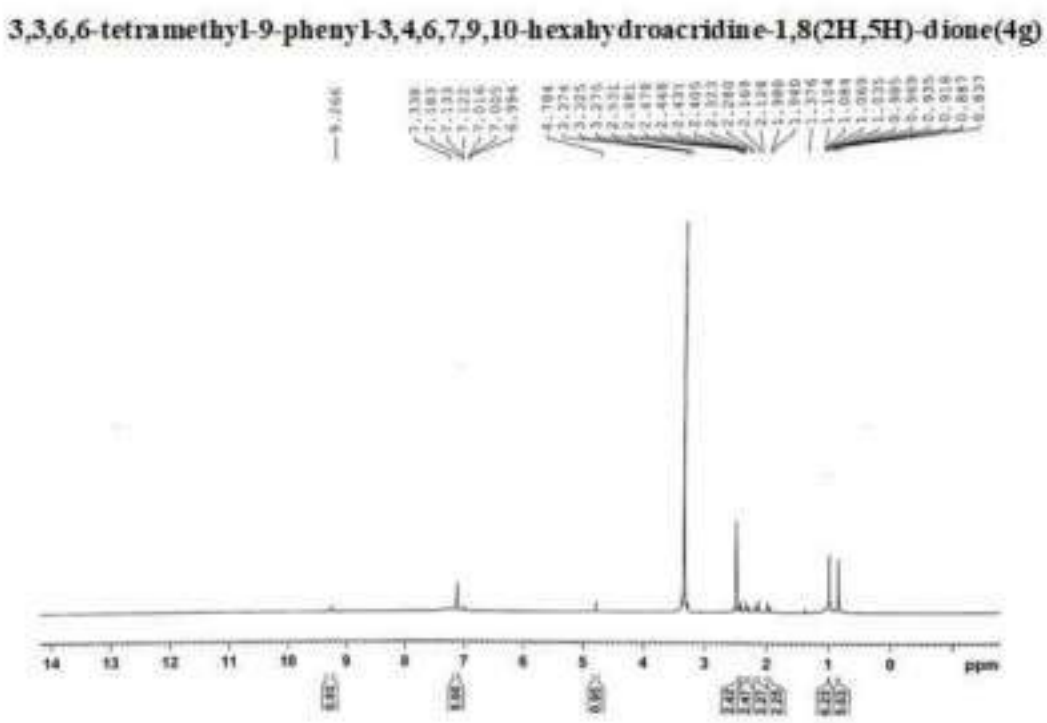


Figure II.57-^{1}H-NMR of compound 4g

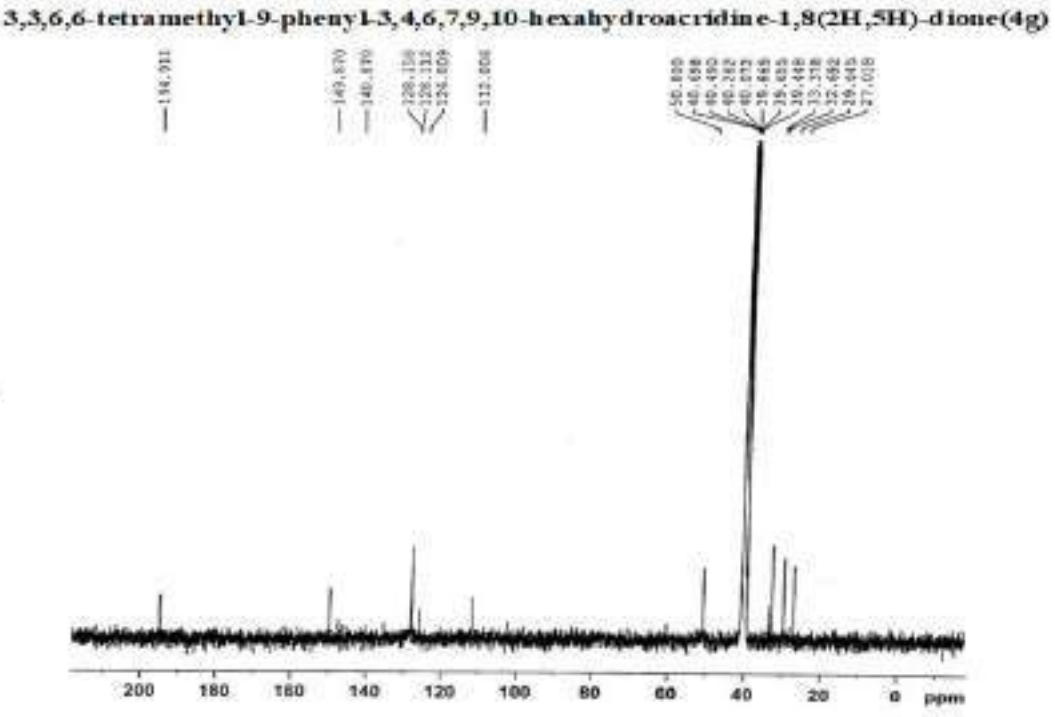


Figure II.58-^{13}C-NMR of compound 4g

3,3,6,6-tetramethyl-9-(naphthalen-1-yl)-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione(4h)

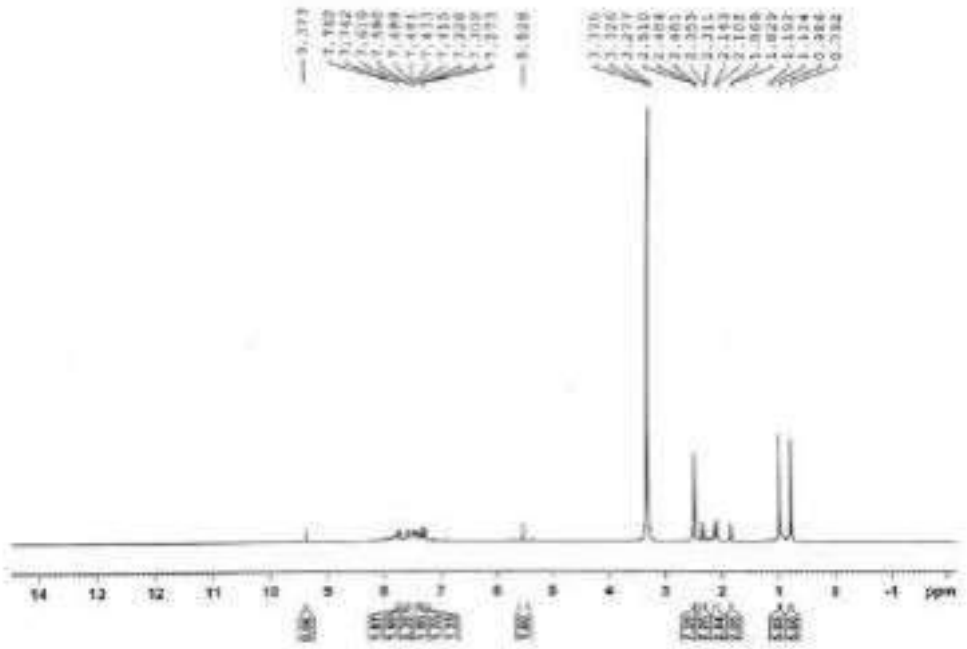


Figure II.59-^{1}H-NMR of compound 4h

3,3,6,6-tetramethyl-9-(naphthalen-1-yl)-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione(4h)

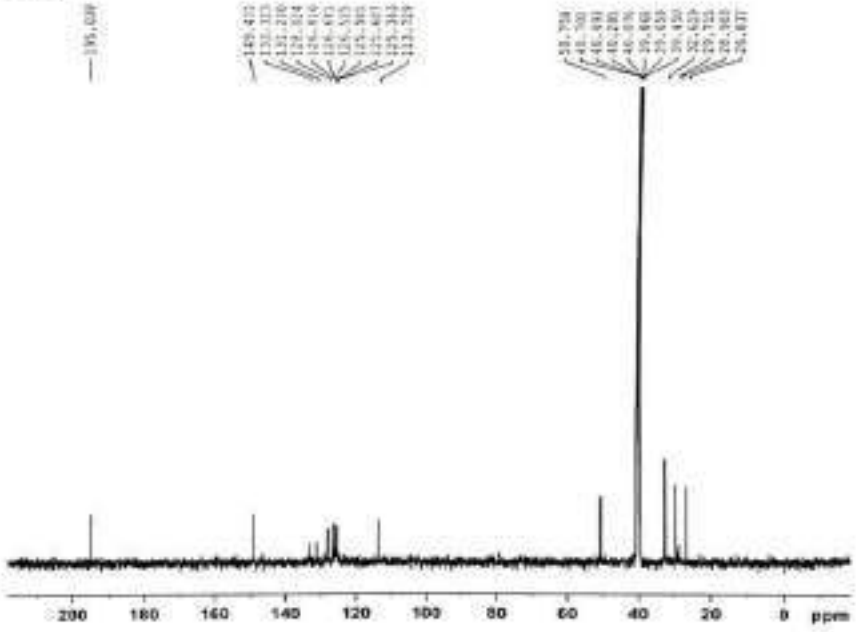


Figure II.60-^{13}C-NMR of compound 4h

3,3,6,6-tetramethyl-9-(p-tolyl)-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione(4i)

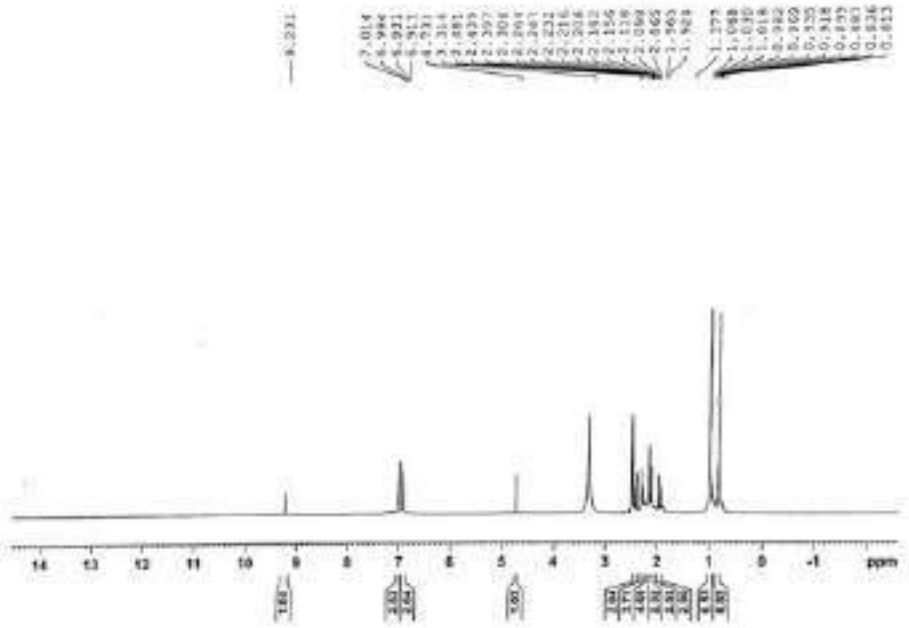


Figure II.61-^{1}H-NMR of compound 4i

3,3,6,6-tetramethyl-9-(p-tolyl)-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione(4i)

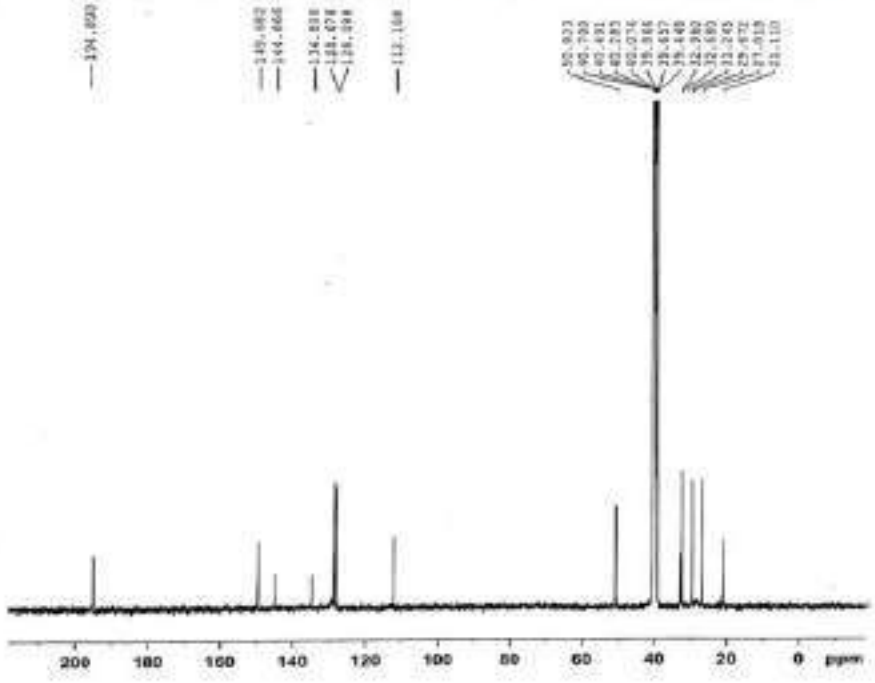


Figure II.62-^{13}C-NMR of compound 4i

II.8.A.12.i EDX data of sulphonated rice husk and rice husk

EDX data of sulphonated rice husk and rice husk are given below respectively

EDX data of sulphonated rice husk

Spectrum processing :

Peaks possibly omitted : 8.022, 8.603 keV

Processing option : All elements analyzed (Normalised)

Number of iterations = 7

Standard :

C CaCO3 1-Jun-1999 12:00 AM

N Not defined 1-Jun-1999 12:00 AM

O SiO2 1-Jun-1999 12:00 AM

Si SiO2 1-Jun-1999 12:00 AM

S FeS2 1-Jun-1999 12:00 AM

K MAD-10 Feldspar 1-Jun-1999 12:00 AM

Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
C K	59.21	0.5571	50.22	1.32	59.25
N K	1.16	0.0766	7.14	1.57	7.22
O K	22.42	0.3340	31.71	1.03	28.09
Si K	18.60	0.8924	9.85	0.29	4.97
S K	1.61	0.8551	0.89	0.06	0.39
K K	0.43	1.0184	0.20	0.03	0.07
Totals			100.00		

EDX data of rice husk

Spectrum processing :

Peaks possibly omitted : 8.039, 8.622 keV

Processing option : All elements analyzed (Normalised)

Number of iterations = 5

Standard :

C CaCO3 1-Jun-1999 12:00 AM

O SiO2 1-Jun-1999 12:00 AM

Mg MgO 1-Jun-1999 12:00 AM

Si SiO2 1-Jun-1999 12:00 AM

P GaP 1-Jun-1999 12:00 AM

S FeS2 1-Jun-1999 12:00 AM

K MAD-10 Feldspar 1-Jun-1999 12:00 AM

Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
C K	141.00	1.0152	51.20	0.71	58.76
O K	55.00	0.4323	46.90	0.71	40.41
Mg K	0.56	0.5959	0.35	0.05	0.20
Si K	0.76	0.8312	0.34	0.04	0.17
P K	1.40	1.2425	0.42	0.04	0.19
S K	0.27	0.9292	0.11	0.03	0.05
K K	1.98	1.0586	0.69	0.04	0.24
Totals			100.00		

II.8.A.12.j ICP-AES data of sulphonated rice husk

ICP-AES data of sulphonated rice husk is given below

ICP-AES (weight percentage of Sulphur) data for sulphonated rice husk

Ref: -ICP-AES-106
Date: 30/09/2019

Analytical report of the samples submitted by **Mr. Sourav Dey, University of North Bengal, Darjeeling-734013,** using Inductively Coupled Plasma Atomic Emission Spectroscopy.

Sample	**S**
	%
SAMPLE	**1.04**

II.9 References

References are given in BIBLIOGRAPHY under Chapter II.