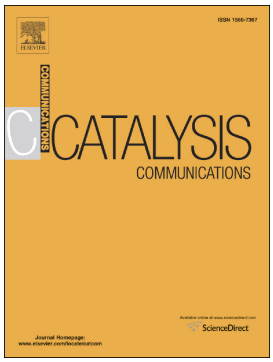

A heterogeneous catalytic and solvent-free approach to 1,2-dihydroquinoline derivatives from aromatic amines and alkynes by tandem hydroarylation-hydroamination

Vasu Amrutham, Agliullin Marat Radikovich, Naresh Mameda, Krishna Sai Gajula, Nellya Gennadievna Grigor'eva, Kutepov Boris Ivanovich, Venugopal Akula, Narender Nama

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A heterogeneous catalytic and solvent-free approach to 1,2-dihydroquinoline derivatives from aromatic amines and alkynes by tandem hydroarylation-hydroamination

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ABSTRACT

This study describes a mesoporous aluminosilicate (ASM) catalyst-induced one-step synthesis of substituted dihydroquinolines *through* a hydroarylation/hydroamination cascade reaction under solvent-free conditions. A sol-gel method was utilized to prepare the ASM catalyst using tetraethyl orthosilicate (TEOS) and aluminum nitrate ($Al(NO_3)_3.9H_2O$). The catalytic protocol, utilizing simple starting materials and a heterogeneous catalyst in a clean reaction environment, is considered an alternative and economically viable route to synthesize a wide range of 1,2-dihydroquinoline derivatives.

Keywords: Dihydroquinolines, Mesoporous aluminosilicates, Sol-gel method, Solvent-free conditions, Zeolites.

1. Introduction

The growth of novel approaches that offer high synthetic efficiency and atom economy has been a vital assignment for synthetic chemists. Tandem reactions are considered a suitable applicant for this objective and are a promptly developing area [1,2]. They complete numerous chemical transformations in one pot and offer a robust method for the construction of complex molecules by employing simple starting materials. The key advantages of tandem reactions are a drop in overall stages by avoiding the separation of often very reactive intermediates; minimizing waste generated by the stepwise reactions; and decreasing the number of reagents, adsorbents, solvents, and energy. Thus, from the synthetic and industrial point of view, eco-friendly tandem processes have gained increasing interest.

The 1,2-dihydroquinoline (1,2-DHQ) moiety is a valuable building block of numerous natural products that hold a wide range of biological activities and potential pharmaceutical applications [3-5]. 1,2-DHQs have also been employed as essential intermediates in the synthesis of organic and natural products [6-8], and they have the surplus benefit of reducing to 1,2,3,4-tetrahydroquinolines, which also have vital significance as pharmaceuticals and agrochemicals [9,10]. Conventionally, Skraup and Bischler-Napieralski reactions, which involve the use of aniline and a ketone or the intramolecular condensation of an aromatic amide, were used to obtain 1,2-DHQ compounds [11-13]. Different synthetic routes using transition metal catalysts have been developed for the synthesis of dihydroquinoline derivatives [14-23]. However, the generation of undesirable by-products, use of expensive catalysts and *in situ*-generated starting materials, and need for organic solvents are some of the limitations of the existing approaches. Thus, a modest, effective, inexpensive heterogeneous catalytic approach under solvent-free conditions would be prominently desirable to produce this class of composites.

Solvent-free synthesis is an integral part of green chemistry because of the necessity to eradicate the use of toxic organic solvents, which are the source for the mainstream of

waste and pollution created by chemical methods. Additionally, there are separate benefits to these solvent-free procedures, such as low cost, fewer energy supplies, quicker reaction rates, and, consequently, decrease in reactor size and capital investment [24,25]. In the past few years, use of zeolite catalysts has become an attractive research area in heterogeneous catalysis because of their unique physical and chemical properties [26-28]. However, their microporosity causes accessibility and diffusion problems, which considerably restricts their broad catalytic applications. Thus, a mesoporous structure (mesoporous aluminosilicates [ASMs]) with surface acid sites is highly desirable to provide effective diffusion of components in the liquid phase acid–base transformations with ever-increasing frequency [29-31]. The ASMs have a system of mesopores (pore size distributions from 2 to 50 nm), which are similar to zeolite pores, and can accommodate large reactant and product molecules that mitigate the diffusion and accessibility issues. In the extension of our investigation to develop novel and eco-friendly synthetic routes for valuable compounds using micro- and mesoporous materials, we aim to describe a proficient, straightforward, and environmentally benign cascade methodology for the synthesis of substituted 1,2-DHQs directly from alkynes and anilines in the presence of the ASM catalyst under solvent-free conditions. The ASM catalyst (Si/Al ratio of 80) was prepared according to our previous work [32]. To the best of our knowledge, ASMs have not been utilized as a heterogeneous catalyst for the synthesis of 2,2,4-substituted 1,2-DHQs from alkynes and anilines.

2. Results and Discussion

The surface analysis (pore structure) of the ASM catalyst was carried out, and the results are presented in Fig. 1. The nitrogen adsorption–desorption isotherm results indicated a type IV isotherm according to the IUPAC classification, which is characteristic of mesoporous materials (Fig. 1a). The ASM catalyst exhibits a narrow pore size distribution in the range of 2-5 nm (Fig. 1b); seemingly, the ASM has a microporous volume of 0.05 cm^3/g,

a mesoporous volume of 0.5 cm^3/g, and Brunauer Emmett Teller (BET) specific surface area of 670 m^2/g. Fig. 1c shows a transmission electron microscopic image of the ASM sample. The porous structure of the ASM is formed by spherical particles of size 10-15 nm, which are not densely packed together, and the voids formed between the particles are mesoporous. According to the temperature programmed desorption of ammonia, the ASM has a total acidity of 427 μmol/g. The IR spectra of adsorbed CO show the presence of both strong Bronsted acid centers (28 μmol/g) and Lewis acid centers (119 μmol/g). More detailed information on the characterization of ASM has been presented elsewhere [32,33].

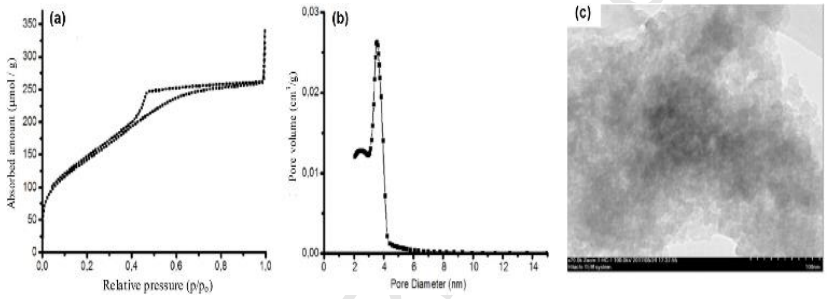


Fig. 1. Porous structure of mesoporous aluminosilicate: (a) nitrogen sorption isotherms, (b) pore size distribution by BJH, (c) TEM image.

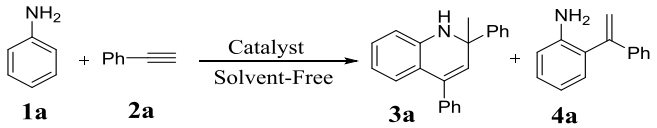
First, we explored the proper reaction conditions for the cascade approach to the synthesis of substituted 1,2-DHQs by the reaction of phenylacetylene (**1a**) with aniline (**2a**) as a model reaction. The reaction was evaluated with various catalysts, their amounts (100-200 mg), and reaction temperatures (120 to 140 °C) in a sealed vial for 24 h under clean conditions (Table 1). The main product of the reaction of aniline with phenylacetylene in the presence of zeolite catalysts is *ortho*-hydroarylation product (**4a**) which is formed as a result of the linear condensation of the starting compounds (Table 1, entries 1-3). The absence of the desired compound (**3a**) in the reaction mass can be explained by the fact that the dihydroquinoline molecule is bulkier than the molecule of product **4a** and is difficult for it to form inside the micropores of zeolite catalysts, in which the strongest acidic bridging OH-groups are located. Among the studied microporous catalysts, the ones with the largest pores are zeolite H-Y catalysts, for which the diameter of the large cavity (1.2 nm) is more than the

diameter of the entrance windows (0.75 nm). Such a structure of zeolite HY can lead to rapid blocking of acid sites in large cavities by the formed 1,2-DHQ bulky molecules (**3a**), which will, consequently, cause the deactivation of the zeolite H-Y catalyst. This deactivation apparently explains the lowest yield of the product **4a** (23%) observed among zeolite catalysts.

Why 1,2-DHQ (**3a**) is not formed on the external surface acid sites of zeolites, where there is no steric hindrance for its synthesis? Perhaps this is because the surface acid groups of zeolites are mainly formed by silanol groups, the strength of which is much lower than the strength of the bridging OH-groups.

Notably, the ASM catalyst demonstrated better catalytic activity and selectivity toward the desired product (**3a**, 24%) than the zeolites, which is attributed to the presence of mesopores with strong acid sites (Table 1, entry 4) [32,33]. The presence of mesopores in the aluminosilicate described above contributes to the reduction of steric hindrance for the transport of reagents and development of conditions for the formation of compound **3a**. In addition, the concentration of the reacting molecules may be higher in mesopores, which leads to an increase in the number of chemical interactions of reagents and an increase in the degree of their conversion. In an attempt to improve the yield of **3a**, various amounts of the ASM catalyst and reaction temperatures were considered (Table 1, entries 6-10). The results revealed that the amount of catalyst increases the yield of **3a** (24-83%), but further increase in reaction temperature (140 °C) did not boost the yield (Table 1, entry 10), which implied that increasing the catalyst amount increases the number of active sites on the surface of the ASM. The findings of the optimization study showed that 200 mg of the ASM catalyst at 135 °C achieves the highest yield of **3a** from 1:2 mole ratio of **1a** and **2a** under solvent-free conditions (Table 1, entry 7).

Table 1. Optimization of conditions for the cascade reaction (**1a** +**2a** → **3a**)[a]



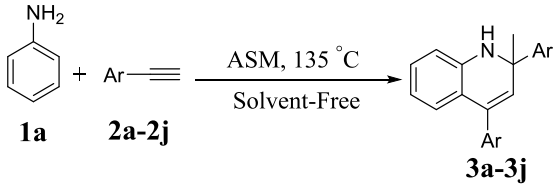
1a **2a** **3a** **4a**

Entry	Catalyst	Amount (mg)	T (˚C)	Isolated yield of **3a** (%)	Isolated yield of **4a** (%)
1	H-Mordenite	100	135	-	44
2	H-Y	100	135	-	23
3	H-Beta	100	135	-	60
4	ASM	100	135	24	20
5	Absence catalyst	-	135	-	-
6	ASM	150	135	43	17
7	ASM	200	135	83	4
8	ASM	200	120	62	8
9	ASM	200	130	70	5
10	ASM	200	140	82	4

[a] Conditions: **1a** (1 mmol), **2a** (2 mmol), 24 h, sealed vial.

Having the optimized conditions, the generality of this catalytic method was investigated for a variety of aromatic alkynes with aniline, and the results are presented in Table 2. Most of the cases, particular *ortho*-hydroarylated products, were obtained as a minor product that may be converted to the desired 1,2-DHQs upon prolonged reaction times. The methyl-substituted phenyl acetylenes **2b-2c** reacted smoothly and provided the **3b-3c** in good yields. Noticeably, *meta*-substituted aromatic alkyne (**2c**) displayed lower reactivity than *para*-substituted alkyne (**2b**) under identical conditions because of steric hindrance, which may affect the interaction with the catalyst surface (Table 2, entries 2 and 3). The higher alkane chain bearing aromatic alkynes (**2d** and **2e**) produced the desired dihydroquinolines (**3d** and **3e**) selectively in 89% and 90% yields (Table 2, entries 4 and 5), respectively. The halo-substituted aromatic alkynes (**2f-2i**) showed diverse reactivity with aniline to their respective products under similar conditions (Table 2 entries 6-9). The F-substituted alkynes **2f** and **2g** furnished the respective dihydroquinoline products **3f** and **3g** in 73% and 87% yields (Table 2, entry 6), respectively, whereas Br- and Cl-substituted phenylacetylenes (**2h** and **2i**) yielded

Table 2: Substituted dihydroquinolines from aniline and aryl acetylenes in the presence of the ASM catalyst[a]



1a **2a-2j** **3a-3j**

Entry	Ar (aromatic alkyne, **2a-2j**)	Isolated yield of **3a-3j** (%)
1	Ph	83 (4)[b]
2	CH_3-4-C_6H_4	84
3	CH_3-3-C_6H_4	68 (16)[b]
4	CH_3-CH_2-CH_2-CH_2-4-C_6H_4	89
5	CH_3-CH_2-CH_2-CH_2-CH_2-4-C_6H_4	90
6	F-4-C_6H_4	73 (21)[b]
7	F-4-CH_3-3-C_6H_3	87 (12)[b]
8	Br-4-C_6H_4	- (47)[b]
9	Cl-3-C_6H_4	- (20)[b]
10	C_4H_4S	75

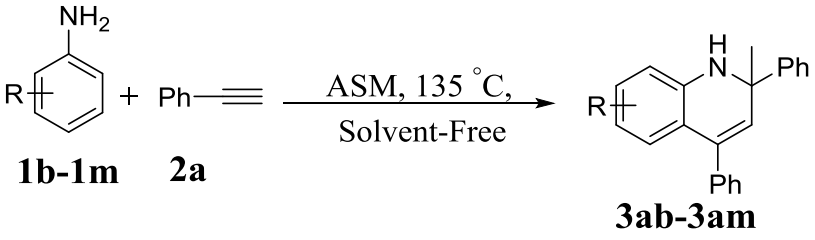
[a] Conditions: **1a** (1 mmol), **2a-2j** (2 mmol), ASM (200 mg), 135 °C, 24 h, sealed vial. [b] *ortho*-alkenylated product was obtained.

the corresponding *ortho*-hydroarylated products instead of the preferred products (Table 2 entries 8 and 9). Interestingly, the electron-rich heterocyclic alkyne (**2j**) also generated the selectively desired product **3j** in 75% yield (Table 2, entry 10). Unfortunately, aromatic alkynes having strong electron-withdrawing groups (-NO_2, -COOMe, and -CF_3) were not active to react with aniline and recovered without any change, which is not included in Table 2.

We explored this cascade reaction by reacting a variety of anilines with phenylacetylene **(2a)** to extend more possibilities of this catalytic process and observed the longer reaction time (72 h) required to provide dihydroquinoline compounds with good yields (Table 3). The *ortho*- and *meta*-methoxy-substituted anilines **1b** and **1c** produced the respective dihydroquinolines **3ab** and **3ac** in 63% and 58% yields, respectively, along with 36% and 42% of *ortho*-hydroarylated products (Table 3, entries 1 and 2). On the other hand, the *para*-methoxy-substituted aniline **1d** furnished the *ortho*-hydroarylated and di-*ortho*-

hydroarylated products in 23% and 69% yields, respectively, instead of the desired dihydroquinoline product **3ad** (Table 3, entry 3). Alkyl-substituted anilines **1e** and **1f** transformed into the corresponding dihydroquinolines **3ae** and **3af** in 60% and 62% yields along with their *ortho*-hydroarylated products (Table 3, entries 4 and 5). Particularly, longer alkyl chain-bearing anilines (**1g** and **1h**) did not provide selectivity toward the desired products, and substantial amounts of *ortho*-hydroarylated products were also obtained (Table 3, entries 6 and 7). Halo-substituted anilines **1i-1l** contributed well to this catalytic reaction to give the respective dihydroquinoline derivatives in good yields (54-76%) irrespective of the position of halogen (Cl) groups on the phenyl ring (Table 3, entries 8-11). 2-Benzylaniline also showed good reactivity with phenylacetylene to give **3am** (Table 3, entry 12). Regrettably, the synthetic potential of this reaction is limited to substrates containing electron-withdrawing groups (-NO_2, -CN, and -COOH) and substrates were recovered without change even longer reaction time.

Table 3: Dihydroquinoline derivatives from substituted anilines with phenylacetylene in the presence of the ASM catalyst[a]



Entry	R (Aniline, **1b-1m)**	Isolated yield of

		3ab-3am (%)
1	2-MeO	63 (36)[b]
2	3-MeO	58 (42)[b]
3	4-MeO	-(23)[b] (69)[c]
4	4-Me	60 (37)[b]
5	4-*tert*-Butyl	62 (31)[b]
6	4-*n*-Butyl	22 (53)[b] (25)[c]
7	4-*n*-Pentyl	16 (56)[b] (27)[c]
8	2-F	54
9	3-Cl	76 (18)[b]
10	2-Cl	67
11	3,4-Cl	75 (16)[b]
12	Benzyl (Ph-CH_2)	75(25)[b]

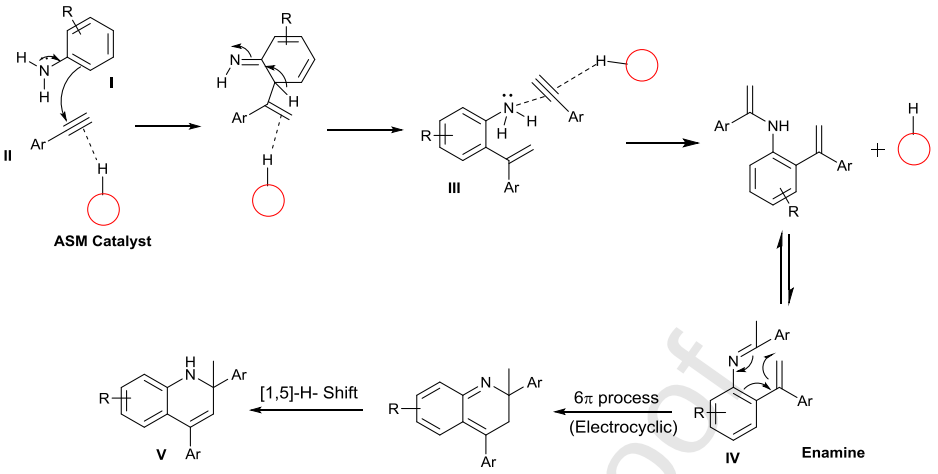
[a] Conditions: **1b-1j** (1 mmol), **2a** (2 mmol), ASM catalyst (200 mg), 135 °C, 72 h, sealed vial. [b] *ortho*-alkenylated product was obtained. [c]di-*ortho* alkenylated product was obtained.

The reaction of phenylacetylene (**1a**) with aniline (**2a**) was carried out at different reaction intervals (6-24 h) using the ASM catalyst at 135 °C to determine the intermediates of this cascade reaction, and the outcomes are included in Fig. S1. The *ortho*-hydroarylation product (**4a**) was afforded as a significant (primary) product in 6 h; however, the yield of **4a** gradually decreased and the yield of the desired product (**3a**) increased with time. The results suggest that the *ortho*-hydroarylation product (**4a**) underwent hydroamination reaction with another mole of phenylacetylene (**2a**) transformed to the desired product (**3a**). On the basis of the above results and literature reports [34,35], a reasonable mechanism for the synthesis of substituted 1,2-DHQs from anilines with alkynes in the presence of the ASM catalyst is anticipated as outlined in

Scheme 1.

It is predicted that aromatic terminal alkyne (**II**) adsorbs onto the acid sites of ASMs that successively reacts with aniline (**I**) to offer the *ortho*-hydroarylation product (**III**). The *ortho*-hydroarylation product (**III)** underwent hydroamination with another terminal alkyne (**II)** to generate an enamine (**IV**), followed by a 6π-electrocyclic rearrangement and [1,5]-H

shift [35] to yield the respective 1,2-DHQ product (**V**) in the presence of acidic sites of the ASM catalyst.



Scheme 1. A plausible reaction mechanism to generate dihydroquinoline derivatives from anilines and aromatic alkynes using the ASM catalyst.

3. Conclusions

In summary, the ASM catalyst was successfully prepared by the sol-gel method and utilized for the synthesis of substituted 1,2-DHQs by tandem *ortho*-hydroarylation-hydroamination under solvent-free conditions. Comparison of the catalytic properties of microporous zeolites and ASM shows that the porosity of the catalyst, along with acidity, plays an important role in the implementation of the studied reaction. The main product of the reaction of aniline with phenylacetylene in the presence of zeolite catalysts is *ortho*-hydroarylation product (**4a**), which is due to the manifestation of the molecular sieve effect of the microporous zeolite lattice. The presence of mesopores in the aluminosilicate contributes to the reduction in steric hindrance for the transport of reagents and development of conditions for the formation of 1,2-DHQs. The probability and limitations of the catalytic route are presented with a variety of aromatic amines and alkynes. Conversely, deactivated substrates (having strong electron-withdrawing groups) failed to give the desired products. Noticeable benefits of this protocol are the user of a nonhazardous heterogeneous catalyst,

absence of solvent, single-step approach, ready availability of starting materials, and easy setup and work-up procedure.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

A heterogeneous catalytic and solvent-free approach to 1,2-dihydroquinoline derivatives from aromatic amines and alkynes by tandem hydroarylation-hydroamination

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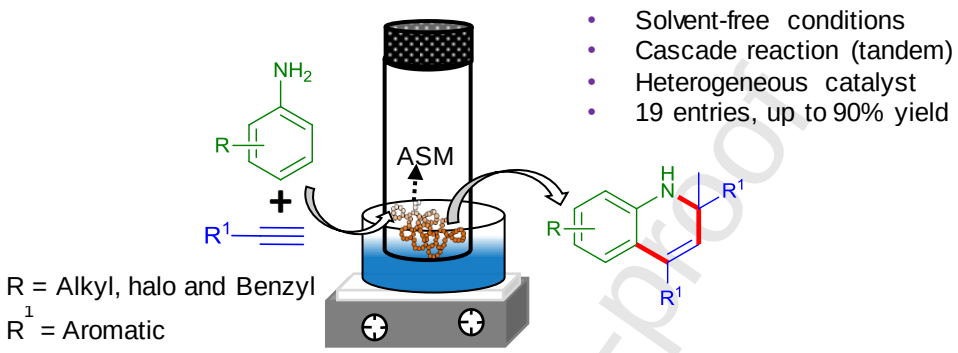

- Mesoporous aluminosilicate (ASM) was well prepared by the sol-gel method.
- ASM showed good activity to create 1,2-dihydroquinolines in solvent-free conditions.
- Possibility of the catalytic way are presented with a range of amines and alkynes.
- The desired products were obtained in decent yields.
- A probable mechanism is anticipated for the production of 1,2-dihydroquinolines.