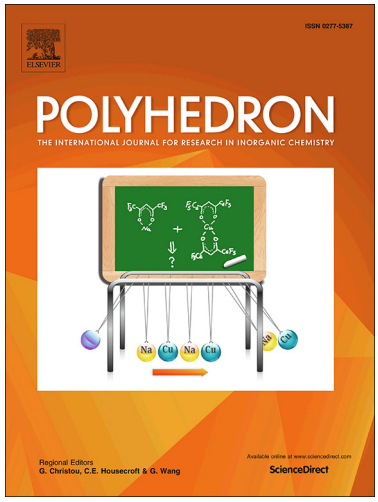


An efficient regioselective three-component synthesis of tetrazoloquinazolines using g-C_3N_4 covalently bonded sulfamic acid

Asadollah Hassankhani, Behnam Gholipour, Sadegh Rostamnia

PII: S0277-5387(19)30662-X
DOI: https://doi.org/10.1016/j.poly.2019.114217
Reference: POLY 114217

To appear in: *Polyhedron*

Received Date: 12 July 2019
Revised Date: 22 October 2019
Accepted Date: 25 October 2019

Please cite this article as: A. Hassankhani, B. Gholipour, S. Rostamnia, An efficient regioselective three-component synthesis of tetrazoloquinazolines using g-C_3N_4 covalently bonded sulfamic acid, *Polyhedron* (2019), doi: https://doi.org/10.1016/j.poly.2019.114217

An efficient regioselective three-component synthesis of tetrazoloquinazolines using g-C_3N_4 covalently bonded sulfamic acid

Asadollah Hassankhani, [a,*] Behnam Gholipour, [b] Sadegh Rostamnia [b,*]

[a] *Department of New Materials, Institute of Science and High Technology and Environmental Sciences, Graduate University of Advanced Technology, Kerman, Iran. Email: hassankhani_a@yahoo.com*
[b] *Organic and Nano Group (ONG), Department of Chemistry, Faculty of Science, University of Maragheh, PO Box 55181-83111, Maragheh, Iran. Tel:+98(421) 2276066; Fax: +98(421) 2276066; Email: rostamnia@maragheh.ac.ir; srostamnia@gmail.com*

Abstract

A green and cost-effective protocol developed using covalently bonded sulfamic acid graphitic carbon nitride (g-C_3N_4/$NHSO_3H$) for the synthesis of quinazoline derivatives using three-component condensation reaction of benzaldehyde, 2- aminotetrazole and dimedone. The XRD, TEM, SEM, EDX and FT-IR techniques were used to identify the physical and chemical properties of g-C_3N_4/$NHSO_3H$. The -$NHSO_3H$ solid catalyst, was reused eight times without significant decrease in activity. This catalyst acts as a benign acid catalyst, a green protocol of a one-pot due to having significant advantages such as active sites containing SO_3H groups, reacting under mild conditions with high efficiency as well as the ability to recover and reuse without decreasing activity.

Keywords: Graphitic carbon nitride, sulfamic acid type g-C_3N_4/$NHSO_3H$, tetrazoloquinazolines, three-component reaction.

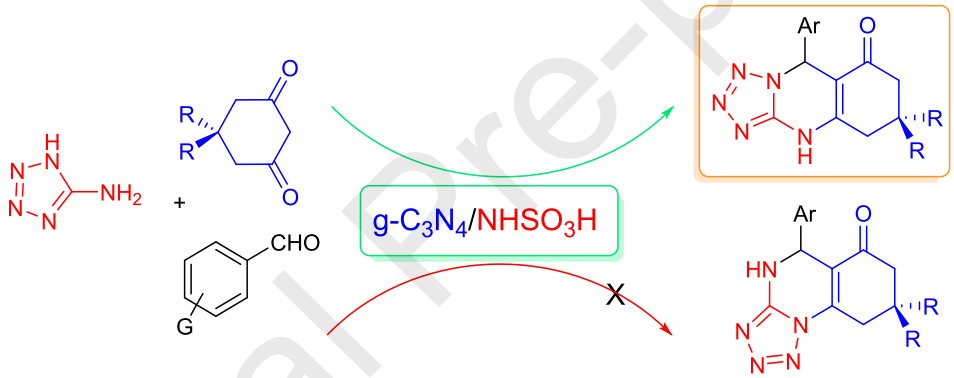
1. Introduction

The use of multi-component (MC) domino strategy has become powerful instrumentation for quickly synthesizing complex structures, which by obviating the need for separation and purification of intermediaries leads to reduced waste and reaction time, improves overall

performance[1]. On the other hand, nitrogen-content heterocycles with a tetrazole ring are one of the common structural units in pharmacological important molecules that span a wide range of targets[2, 3]. The use of these compounds for the treatment of depression, diabetes, thyroid cancer, hypertension, hyperlipidemia, glaucoma, coronary heart disease, atherosclerosis, hypothyroidism, obesity, hypercholesterolemia, cardiac arrhythmias, and congestive heart failure has been reported[4-9].

The synthesis of new heterocyclic compounds because of the extensiveness of its application, a great interest has attracted. Among these compounds, quinazolines and derivatives represents one of the most significant classes of heterocyclic compounds in an extensive range of pharmacological and biological processes[10]. Aminoazoles are known as excellent building units for multicomponent reactions (MCRs) because of the presence of nucleophilic centers of reactivity[11]. Especially the use of 5-aminopyrazoles and 5-aminotriazoles as a substrate for various MCRs has been widely studied. However, the interest in nitrogen-rich compounds such as 5-aminetetrazole has been created in a MCRs only in the past decade, which is expanded due to its unique characteristics. 5-Aminetetrazole is an important part in certain drugs such as curazole, cefazolin and cefoperazone[12]. Cefazolin is an antibiotic to treat a number of bacterial infections[13] and cefoperazone as an effective antibiotic[14]. Given the importance of multicomponent reactions (MCRs) in biological and pharmaceutical compounds, various researchers have attempted to perform MCR reactions using catalysts such as MNPs-SO_3H[15], MNPs-IL-OAc[16], MNPs-guanidine[17], Cu-Adenine@boehmite[18], Fe_3O_4@SiO_2@Propyl–ANDSA[19] and Iodine[20] have been reported. Over the recent years, green, stable and low-cost catalysts, particularly those based on graphic carbon nitride, have attracted a lot of attention. Graphic carbon nitride has advantages such as good chemical stability, low cost, no heavy metal pollution and environmental friendliness

compared to metal based catalysts. g-C_3N_4 is the most stable allotrope of covalent carbon nitride, that has been widely used as a novel metal-free visible light photocatalyst for water reduction and oxidation[21], degradation of organic pollutants[22], CO_2 capture[23] and organic synthesis[24]. Recently, several reports have been reported on the use of graphitic carbon nitride as acid catalyst for organic reactions in the literature, including GN/SO_3H nanocomposite for the synthesis of spirooxindole derivative[25] and sulfonated graphitic carbon nitride for esterification of fatty acids[26].Given the importance of these compounds here, we report the use of -SO_3H bonded graphite carbon nitride (g-C_3N_4/$NHSO_3H$) as a green and cost-effective heterogeneous acid catalyst for the regioselective three-component (3-CRs) synthesis of tetrazoloquinazolines derivatives (Scheme 1).



Scheme 1. The regioselectivity of the 3-CRs synthesis of tetrazoloquinazolines.

2. Experimental

2.1. Materials and apparatus

Melamine was obtained from Merck. The other materials were also purchased from Sigma-Aldrich, Merck (Germany) and Fluka (Switzerland), and were used without further purification. Infrared Raman (IR) spectra were obtained by a Shimadzu IR-460 spectrometer. Scanning Electron Microscopy (SEM) images were recorded by a Zeiss-DSM 960A microscope. Transition Electron Microscopy (TEM) images were recorded on a Zeiss EM 900 TEM. The crystalline structure of

the nanoparticles was examined by X-Ray Diffraction (XRD) instrument (Philips-PW1800 diffractometer).

2.2. Synthesis of g-C_3N_4 nanosheets

g-C_3N_4 nanosheets were synthesized using of melamine based on previously reported[27]. Initially, 10 grams of melamine was placed in the alumina crucible with a cover and heated for 4 h at 550 $^{\circ}$C (heating rate: 3 °C min^{-1}) in an electric tube furnace. After cooling naturally, the yellow product was collected.

2.3. Synthesis of g-C_3N_4/$NHSO_3H$

Synthesis of *g-C_3N_4/$NHSO_3H$* was achieved according to previously reported method by Varma et.al., with using melamine instead urea[26]. Accordingly, 0.5 g of as-synthesized g-C_3N_4 sheets was dispersed in 40 mL dry dichloromethane (DCM) and stirred for 30 min and 30 min again in tip sonicated condition. Next, a solution of 6 mL of chlorosulfonic acid ($ClSO_3H$) in 10 mL dry DCM was added dropwise to the solution and stirred for a 10 h. After that, the g-C_3N_4/$NHSO_3H$ (1.2 $mmol.g^{-1}$ S) were collected and washed with deionized water and ethanol and then dried at 50 ^{o}C for 6h.

2.4. Synthesis of tetrazoloquinazolines

Benzaldehyde (1 mmol), 2- aminotetrazole (1 mmol), dimedone (1 mmol), the catalyst (0.01 g, 1.2 mol%) were added to a 3 mL ethanol and stirred for 4 h at 80 ^{o}C. After completion of the reaction, after separation of the solid catalysis, the reaction temperature was cooled downed to 0

°C to precipitate. Then, the precipitate was washed with water and dried. The crude product was recrystallized by ethanol to afford the final product.

For investigating the reusability of the catalyst after completion the reaction, the mixture was filtered (in 80 ^{o}C) and the g-C_3N_4/$NHSO_3H$ catalyst was rinsed twice with ethyl acetate; the filtrate was dried and the solvent was vaporized under vacuum and was reused for the next run.

2.5. *Spectral data of synthesized compounds*

All compounds are known and are previously reported in the *literatures*[28,29]. For see the NMR data, please see supporting information.

3. Results and discussion

As a part of our continuing effort toward the synthesis of solid catalysis and organic molecules[30], herein, we describe the regioselective 3-CRs synthesis of tetrazoloquinazolines through the condensation reaction of aldehydes, 5- aminotetrazole, and dimedone or 1.3-Cyclohexanedione in the presence of covalently bonded sulfamic acid onto the g-C_3N_4 surfaces (Scheme 1).

Initially, g-C_3N_4 was synthesized through a Varma method[22] and, it was then reacted with chlorosulfonic acid based on Zolfigol's method[31] to obtain g-C_3N_4/$NHSO_3H$ (Fig. 1). Then, the effect of g-C_3N_4/$NHSO_3H$ as Bronsted acid catalyst was investigated in the synthesis of tetrazoloquinazolines.

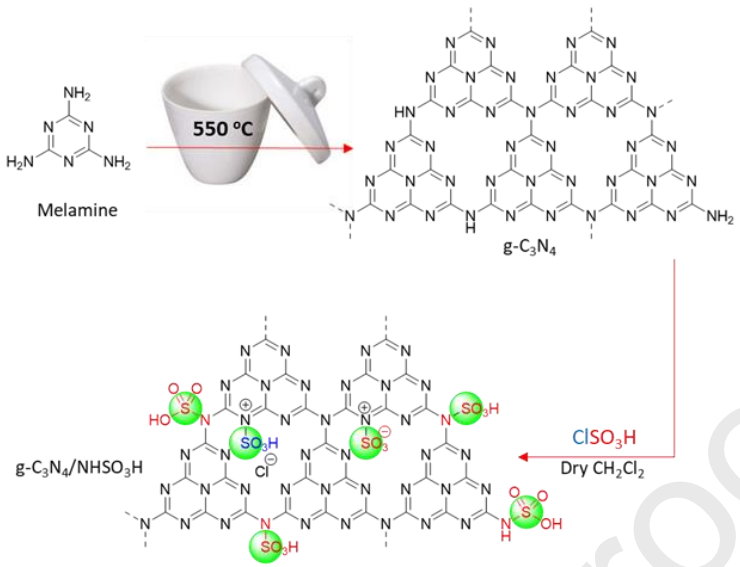


Figure 1. Synthesis of sulfonated graphitic carbon nitride.

The FT-IR spectrum of g-C_3N_4 and g-C_3N_4/$NHSO_3H$ are illustrated in (Fig. 2). In the IR spectrum of g-C_3N_4 the peaks at 1235,1325, 1434, and 1567 cm^{-1} are related to aromatic C-N stretching vibrations and at the 1541 cm^{-1} and 1644 cm^{-1} are related to C=N stretching vibrations[32]. The peak at 806 cm^{-1} assigned to the vibration of triazine units[33]. The peaks around 2900-3500 cm^{-1} is indicative of the N-H stretching vibrations and O-H groups related to water molecules on the catalyst surface[34]. In the IR spectrum of g-C_3N_4, after sulfonation, in addition to the g-C_3N_4 peaks, the vibration bands at 1068 cm^{-1} (S=O symmetric stretching), 1136 cm^{-1} (S=O asymmetric stretching) and 1413 cm^{-1} (asymmetric SO_2 stretching) were related to the SO_3H groups[35] (Fig. 2).

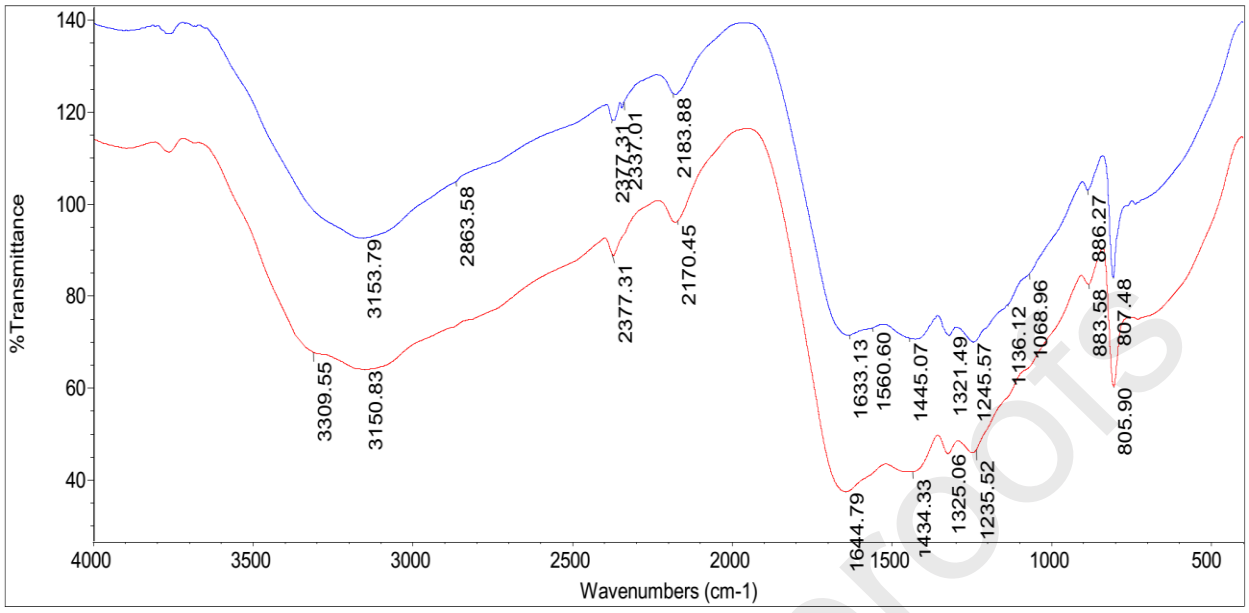


Figure 2. FT-IR spectrum of g-C_3N_4 (red) and g-C_3N_4/$NHSO_3H$ (blue).

Figure 3 shows the SEM (a, b) images of the layered structure of pure g-C_3N_4 and SO_3H functionalized g-C_3N_4. As shown the synthesized graphitic carbon nitrides are as a planar sheet-like form for both g-C_3N_4 and g-C_3N_4/$NHSO_3H$. The SEM image also indicates the 2-D morphology of the synthesized g-C_3N_4 and g-C_3N_4/$NHSO_3H$ structure. It also exhibition that the g-C_3N_4/$NHSO_3H$ morphology has not changed after acid-functionalization. Surface profiles of the planar area from the upside surface of g-C_3N_4/$NHSO_3H$ is shown in Figure 3d, presenting the correspondence topography quantitatively.

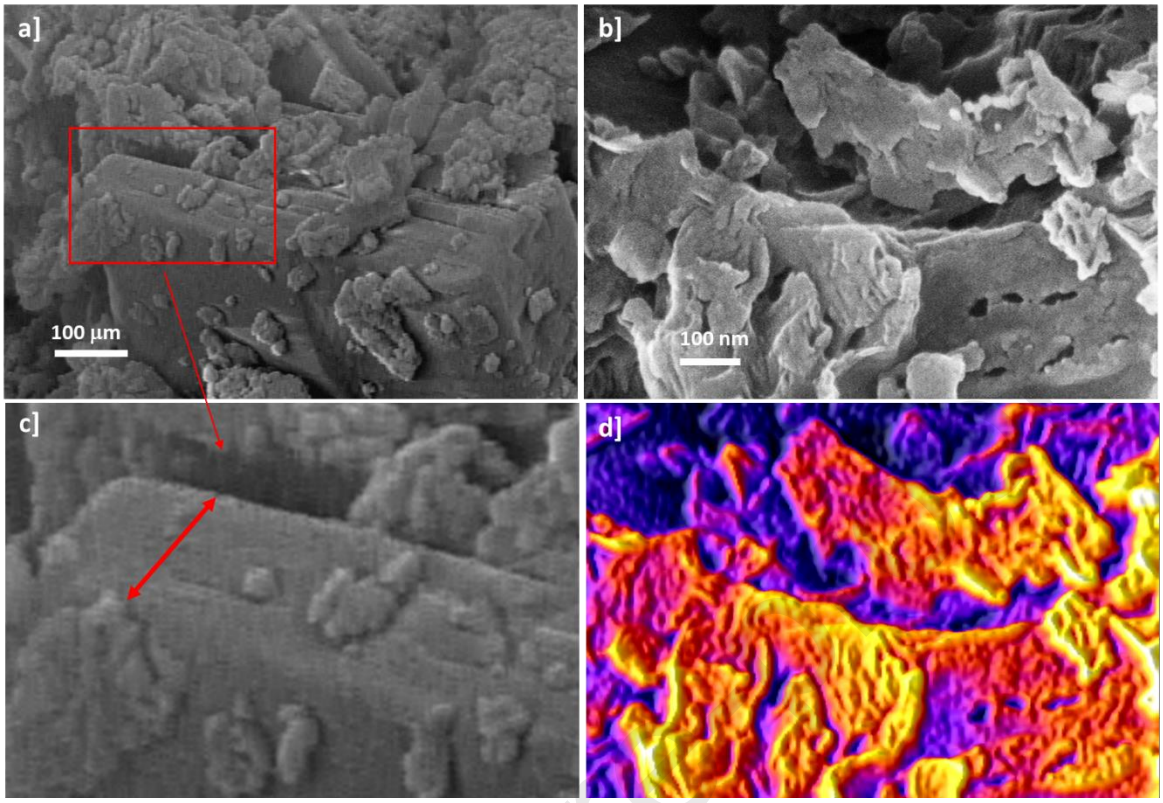


Figure 3. (**a**) SEM image of g-C_3N_4 and its zoomed image (**c**); (**b**) SEM image of g-C_3N_4/$NHSO_3H$ and its surface profile (**d**).

A nanosheet-like morphology of g-C_3N_4 and g-C_3N_4/$NHSO_3H$ were depicted in the TEM image. Characterization showed that the morphologies of the g-C_3N_4 and g-C_3N_4/$NHSO_3H$ are distinctly similar and both of them have 2D nanosheet morphology (Figure 4a, b). The energy dispersive X-ray spectroscopy (EDX) of the g-C_3N_4/$NHSO_3H$ nanosheet is shown in (Fig. 4c). In the EDX spectrum of g-C_3N_4/$NHSO_3H$ certain peaks for the O, C, N and S elements. The presence of sulfur can clearly be seen, which confirmed the presence of SO_3H components in the synthesized g-C_3N_4/$NHSO_3H$. The crystallinity and phase structure of the 2D g-C_3N_4/$NHSO_3H$ nanosheet was determined by X-ray diffraction. The XRD patterns of g-C_3N_4 and g-C_3N_4/$NHSO_3H$ illustrate in Fig. 4d. The characteristic peaks located at 2θ values of 27.5° and 13.1°, matching with the (002) and (100) peaks of g-C_3N_4 surface which accordance with the results reported in the *literatures*[36,37].

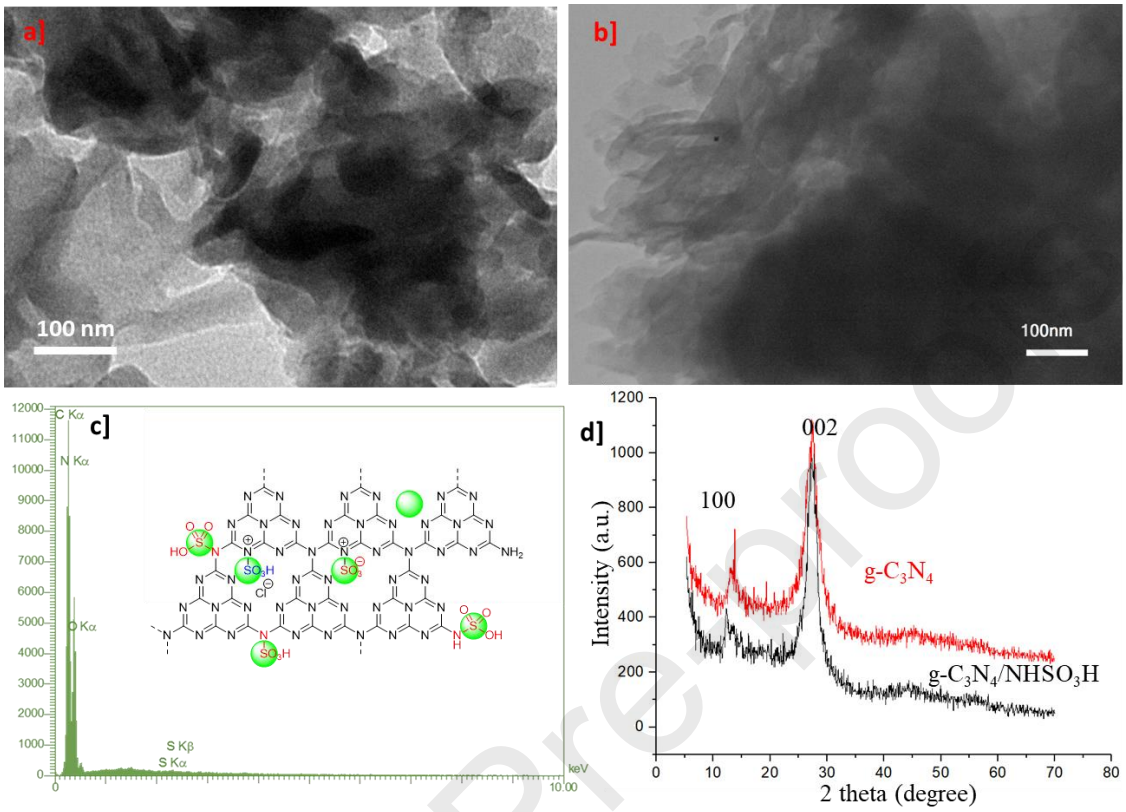
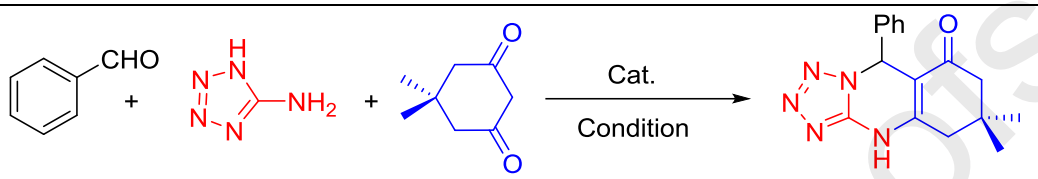


Figure 4. (**a** and **b**) TEM image of g-C_3N_4 and g-C_3N_4/$NHSO_3H$. (**c**) EDX spectra of g-C_3N_4/$NHSO_3H$. (**d**) XRD pattern of g-C_3N_4 and g-C_3N_4/$NHSO_3H$.

After demonstrated main structure for g-C_3N_4/$NHSO_3H$ as a Bronsted sulfonic acid functionalized 2D nanosheet *N*-rich solid acid, the application of that was explored for the synthesis of tetrazoloquinazolines using benzaldehyde (2 mmol), 2- aminotetrazole (2 mmol), and dimedone (2 mmol). To obtain optimum conditions, different parameters such as solvent, reaction time and temperature were investigated. At first, the reaction progress was investigated in the absence of the catalyst, and after 24 hours no product was observed (Table 1, entries 1). Subsequently, various amounts of catalysts were selected for the reaction and 0.01 g was selected as the desired amount. In this reaction, various temperatures were investigated and it was found that 80 ° C is the optimum

temperature for the reaction (Table 1, entries 5-10). In the next step, the effect of variant solvents was investigated and the isopropyl alcohol solvent was selected as the appropriate solvent.

Table 1. Reaction optimization for the synthesis of tetrazoloquinazolines. [a]

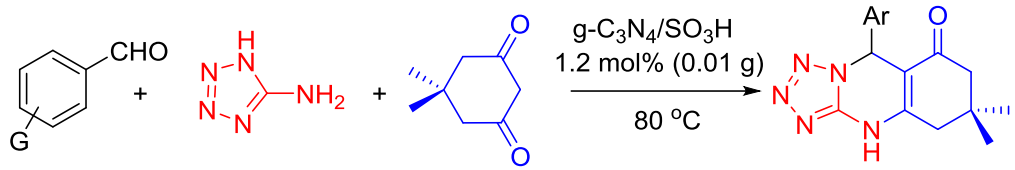


Entry	Catalyst (amount of Cat.)	solvent	T (°C)	Time (h)	Yield (%)
1	-	i-PrOH	100	24	-
2	$AlCl_3$ (10 mol %)	i-PrOH	80	4	trace
3	$FeCl_3$ (10 mol %)	i-PrOH	80	4	30
4	CuO (10 mol %)	i-PrOH	80	4	35
5	g-C_3N_4/$NHSO_3H$ (0.005gr)	i-PrOH	80	4	65
6	g-C_3N_4/$NHSO_3H$(0.01gr)	i-PrOH	80	2	75
7	g-C_3N_4/$NHSO_3H$(0.01gr)	i-PrOH	80	4	95
8	g-C_3N_4/$NHSO_3H$(0.01gr)	i-PrOH	100	4	95
9	g-C_3N_4/$NHSO_3H$(0.02gr)	i-PrOH	80	4	95
10	g-C_3N_4/$NHSO_3H$(0.01gr)	i-PrOH	60	4	70
11	g-C_3N_4/$NHSO_3H$(0.01gr)	EtOH	80	4	75
12	g-C_3N_4/$NHSO_3H$(0.01gr)	CH_3CN	80	4	60
13	g-C_3N_4/$NHSO_3H$(0.01gr)	DMF	80	4	70
14	g-C_3N_4/$NHSO_3H$(0.01gr)	DMSO	80	4	55
15	g-C_3N_4/$NHSO_3H$(0.01gr)	Toluene	80	4	20

[a] Reaction conditions: benzaldehyde (1 mmol), 2- aminotetrazole (1 mmol), and dimedone (1 mmol) in 3 mL of solvent.

Subsequently, optimal conditions for a wide range of aromatic aldehyde and dimedone were applied to investigate the scope of the current protocol. As shown in Table 2, the use aromatic aldehydes including electron- deficient groups such as 4-NO_2, 4-Cl, 4-Br and 2,6-Cl_2 and an electron- rich such as 4-Me and 2,5-(OMe) in the same period of 4-6 hours leads to tetrazoloquinazolines in high yields. These results clearly show how the g-C_3N_4/$NHSO_3H$ catalyst plays an important role in synthesis tetrazoloquinazolines.

Table 2. Three-component coupling synthesis of tetrazoloquinazolines. [a]

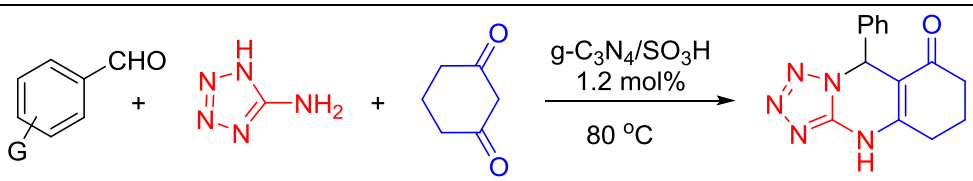


Entry	Ar	β-diketone	Time (h)	Yield (%)	Melting point (^{o}C)	Reported melting point^{ref} (^{o}C)
1	Ph	dimedone	4	95	> 270	> 270 [38]
2	2,4-Cl_2-C_6H_4	dimedone	4	94	> 270	> 270 [38]
3	4-Cl-C_6H_4	dimedone	4	94	255-257	254-256 [38]
4	2-Cl-C_6H_4	dimedone	5	89	> 270	> 270 [38]
5	4-Br-C_6H_3	dimedone	6	87	250-253	246-249 [38]
6	3-O_2N-C_6H_4	dimedone	4	93	279-282	281-283 [39]
7	2-O_2N-C_6H_4	dimedone	5	90	262-264	261-263 [38]
8	4-O_2N-C_6H_4	dimedone	4	95	248-250	248-249 [38]
9	4-OCH_3-C_6H_4	dimedone	4.5	91	268-270	270-272 [39]
10	4-CH_3-C_6H_4	dimedone	4.5	92	302-306	304-305 [39]

[a] Reaction condition: aldehyde (1 mmol), 2- aminotetrazole (1 mmol), and dimedone (1 mmol) in 3 mL i-PrOH at 80 ^{o}C in presence of 1.2 mol% of catalyst.

In continuing on the basis of results obtained the use of 1.3-cyclohexanedione to extend the synthesis of tetrazoloquinazolines was studied. Similar results according to Table 2 for both groups of electron- deficient and electron- rich on the aromatic ring were observed (Table 3). These results clearly show how the g-C_3N_4/$NHSO_3H$ catalyst plays an important role in synthesis tetrazoloquinazolines.

Table 3. g-C_3N_4/$NHSO_3H$ catalyzed the MC-synthesis of tricyclic tetrazoloquinazolines.

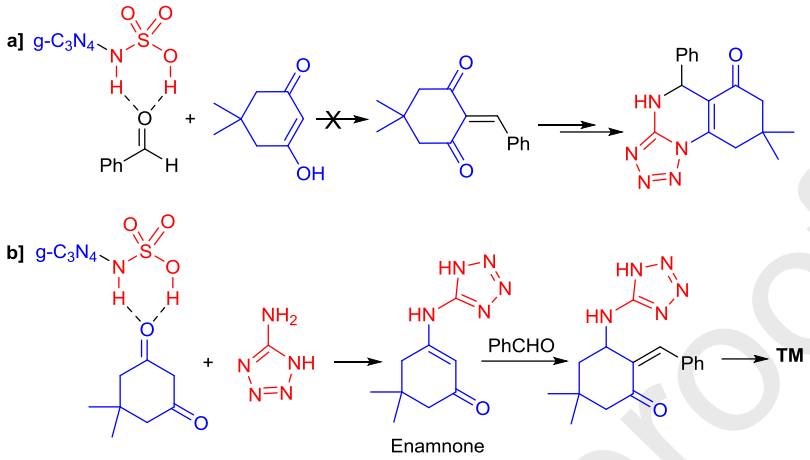


Entry	Ar	Ketone	Time (h)	Yield (%)
1	Ph	1,3-Cyclohexanedione	4	94
2	4-Br-C_6H_4	1,3-Cyclohexanedione	4	92
3	4-Cl-C_6H_4	1,3-Cyclohexanedione	4	91
4	2-Cl-C_6H_4	1,3-Cyclohexanedione	6	88
5	2,4-Cl_2-C_6H_3	1,3-Cyclohexanedione	6	90
6	3-O_2N-C_6H_4	1,3-Cyclohexanedione	4	95
7	2-O_2N-C_6H_4	1,3-Cyclohexanedione	4	91
8	4-O_2N-C_6H_4	1,3-Cyclohexanedione	4	95
9	4-OCH_3-C_6H_4	1,3-Cyclohexanedione	4	88
10	4-CH_3-C_6H_4	1,3-Cyclohexanedione	5	90

Reaction condition: aldehyde (1 mmol), 2- aminotetrazole (1 mmol), and 1, 3-cyclohexanedione (1 mmol) in 3 mL i-PrOH at 80 °C.

The proposed mechanism for g-C_3N_4/$NHSO_3H$ is illustrate in Scheme 2. This catalyst with having ionic liquid type (IL-type) acid groups (H^+) which can act as electrophoretic species. In pathway **a**, the aldehyde have to protonated in the presence of g-C_3N_4/$NHSO_3H$, and in the next step, Knoevenagel condensation with dimedone resulted in the formation of a conjugated *α,β*-unsaturated diketone compound which the results of NMR studies don't show progress of this pathway. study it goes to After the reaction of Michael addition with 5-aminotetrazole as nucleophile, cyclization leads to the formation of the desired product. A possible mechanism is shown in Scheme 2. In pathway **b**, it is conceivable that the initially, tetrazole-enaminone as an intermediate formed from reaction between 2- aminotetrazole and dimedone. The latter then with formation of *β*- aminotetrazole conjugated *α,β*-unsaturated compound, 6,6-dimethyl-9-phenyl-

5,6,7,9-tetrahydrotetrazolo[5,1-b]quinazolin-8(4H)-one as target molecule (TM) of tetrazoloquinazoline produces by ring annulation (Scheme 2).



Scheme 2. The possible mechanism for the synthesis of tetrazoloquinazolines over catalysis of g-C_3N_4/$NHSO_3H$.

The recovery and reuse of the catalyst using the model reaction (benzaldehyde (1 mmol), 2-aminotetrazole (1 mmol), and dimedone (1 mmol) in 3 mL i-PrOH at 80 ^oC in presence of 1.2 mol% of g-C_3N_4/$NHSO_3H$ catalyst.) were also investigated. During successive cycles, the model reacts under optimized conditions there was no significant decrease in activity. After completion of the reaction, the catalyst was separated by a centrifuge and washed using ethyl acetate and water. The g-C_3N_4/SO_3H catalyst was able to work up to 8 times without loss of catalytic power, indicating that the catalyst g-C_3N_4/$NHSO_3H$ is stable under the reaction conditions. The TEM image after 8 times reuse shows that the g-C_3N_4/SO_3H morphology is preserved.

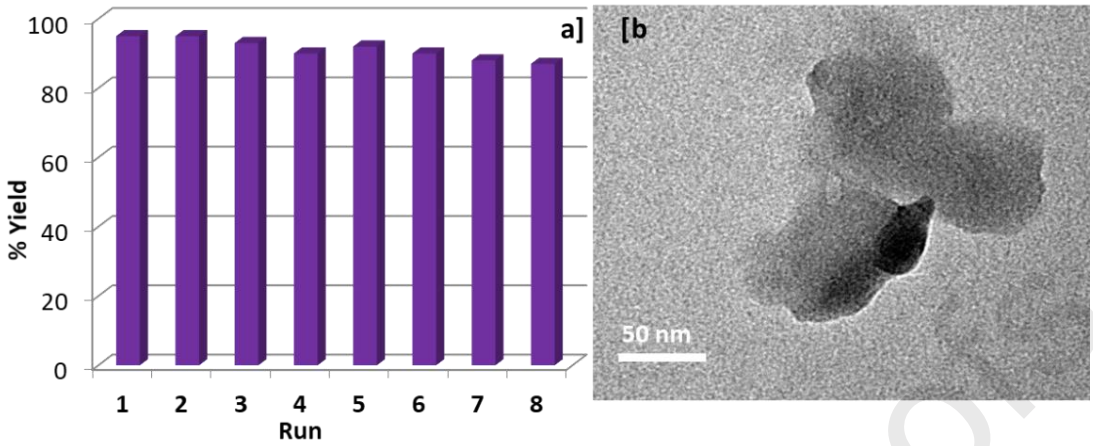


Fig. 6 (a) Reusability of g-C_3N_4/$NHSO_3H$ in the synthesis of tetrazoloquinazoline and its (b) TEM image.

The results of our work are summarized in Table 4 in comparison with the catalysts previously reported in the literature. As can be seen, this metal-free catalyst exhibited good catalytic activity with excellent yields (95%) in shorter time than most of the reported works.

Table 4. Comparison of different methods in the synthesis of tetrazoloquinazolines using different reagents and reaction conditions.

Entry	Catalyst	Conditions	Time (h)	Yield (%)[Ref]
1	NaN_3 (2 mmol), Hg(OAc)2	HOAc, 100°C	6	67 [40]
2	TsOH (10 mol%)	solvent-free, 30°C	8	84 [41]
3	$AlCl_3$ (20 mol%)	CH_3CN, Reflux	4	92 [42]
4	Iodine (10 mol%)	i-PrOH, refluxing	20 min	83 [38]
5	g-C_3N_4/$NHSO_3H$ (0.01gr)	i-PrOH, 80°C	4	This work

Conclusion

In conclusion, g-C_3N_4/$NHSO_3H$ was studied as a green and stable catalyst with the ability to recovery and reuse for the synthesis of tetrazoloquinazolines under mild conditions. Physical and chemical properties of g-C_3N_4/$NHSO_3H$ have been proven using various analytical techniques. All derivatives of tetrazoloquinazolines using various aromatic aldehydes and dimedone and 1, 3-

cyclohexanedione ketones in the presence of 2-aminotetrazole with high yield were synthesized. The results showed that g-C_3N_4 is an excellent substrate for the support of organic groups as catalyst. The g-C_3N_4/$NHSO_3H$ catalyst can be recovered after the reaction so that it can be reused at least 8 times without a slight decrease in the reaction efficiency.

Competing interests

The author(s) declare no competing interests.

Acknowledgement

The authors are thankful for financial supports from Iran National foundation of Science (INSF).

References

1. (a) Lu P, Wang YG. *Synlett*. **2010**;165; (b) Ganem B. *Acc Chem Res*. **2009**; 42:463; (c) Domling A. *Chem Rev*. **2006**; 106:17; (d) Ramón DJ, Yus M. *Angew Chem Int Ed*. **2005**;44:1602; (e) Orru RVA, de Greef M. *Synthesis*. **2003**;1471; (f) Ugi I, Heck *S.* Comb Chem *High Throughput Screening*. **2001**; 4:1; (g) Weber L, Illgen K, Almstetter M. *Synlett*. **1999**;366; (h) Weber L. *Drug Discovery Today*. **2002**; 7:143; (i) Domling A. Curr Opin Chem Biol. 2002; 6:306; (j) Veluri R, Oka I, Wagner-Dobler I, Laatsch H. *J Nat Prod*. **2003**;66:1520; (k) Yao T, He D. *Org Lett*. **2017**; 19:842.
2. Hussein, A.M. and Ahmed, O.M. Regioselective onepot synthesis and anti-proliferative and apoptotic effects of some novel tetrazolo[1,5-a] pyrimidine derivatives", Bioorg. Med. Chem., 18, pp. 2639-2644 **(2010)**.
3. Hussein, A.M. Synthesis of some new purinerelated compounds: Regioselective one-pot synthesis of new tetrazolo[1,5-a] pyrimidine, pyrazolo [1,5- a] pyrimidine and pyrimido[1,6-a]pyrimidine derivatives", J. Saudi Chem. Soc., 14, pp. 61-68 **(2010)**.
4. Takayama, Y., Yoshida, Y. and Uehata, M. \Visual function disorder improving agents", US Patent 7109208 **(2006)**.

5. Fujii, A., Tanaka, H., Otsuki, M., Kawaguchi, T. and Oshita, K.\Antitumor e ect potentiators", US Patent 6930115 **(2005)**.
6. Takaya, T., Murata, M. and Ito, K. Pyrimidine compounds having activity as a cardiotonic antihypertensive cerebrovascular vasodilator and antiplatelet aggregation agent", US Patent 4725600 **(1988)**.
7. Utsunomiya, T., Niki, T., Kikuchi, T., Watanabe, J., Yamagishi, K., Nishioka, M., Suzuki, H., Furusato, T. and Miyake, T. WO\Tetrazole compounds and pest control agent", 006380 PCT JP 1998, 003397 **(1999)**.
8. Aspnes, G.E. and Chiang, Y.P. Tetrazole compounds as thyroid receptor ligands", US Patent 6441015 **(2002)**.
9. Uehata, M., Ono, T., Satoh, H., Yamagami, K. and Kawahara, T. \ Medicines comprising Rho kinase inhibitor", US Patent 6218410 **(2001)**.
10. (a) G. Ouyang, P. Zhang, G. Xu, B. Song, S. Yang, L. Jin, W. Xue, D. Hu, P. Lu, Z. Chen, *Molecules* **2006**, 11, 383. (b) R. Rohini, K. Shanker, P. M. Reddy, Y. P. Ho, V. Ravinder, *Eur. J. Med. Chem*. **2009**, 44, 3330. (c) S. Yang, Z. Li, L. Jin, B. Song, G. Liu, J. Chen, Z. Chen, D. Hu, W. Xue, R. Xu, Bioorg. *Med. Chem. Lett*. **2007**, 17, 2193. (d) G. F. Xu, B. A. Song, P. S. Bhadury, S. Yang, P. Q. Zhang, L. H. Jin, W. Xue, D. Y. Hu, P. Lu, Bioorg. Med. Chem. 2007, 15, 3768. (e) L. Y. Zeng, C. Cai, *J. Comb. Chem*. **2010**, 12, 35.
11. V. A. Chebanov, K. A. Gura, and S. M. Desenko, *Top. Heterocycl. Chem.*, 2010, **23**, 41.
12. M. D. Mashkovskii, Lekarstvennye sredstva (Drugs), Novaya Volna, Moscow **2010**.
13. G. Michel, J. Bergeron, L. John, *Anti microb. Agent Chemother*. **1973**, 396.
14. Y. W. Lam, M. H. Duroux, J. G. Gambertoglio, S. L. Barriere, B. J. Guglielmo, *Anti microb. Agents Chemother* **1988**, 32, 298.
15. J. Safari, Z. Zarnegar, *Journal of Molecular Catalysis A*, **2013, 379,** 269-276.
16. J. Safari, Z. Zarnegar, *Ultrasonics Sonochemistry*, **2014**, 21, 1132-1139.
17. B. Atashkar, A. Rostami, H. Gholami, B. Tahmasbi, *Res Chem Intermed,* **2015**, *41*, 3675–3681.
18. A. Ghorbani-Choghamarani, P. Moradi, B. Tahmasbi, *Polyhedron*, **2019**, 163, 98-107.
19. R. G. Vaghei, S. Alavinia, N. Sarmast, *Appl Organometal Chem*, **2017**, 32, e4038.
20. L.Zeng, F. Ji and C. Cai, J. Heterocyclic Chem., **2012**, 49, 237-241.

21. X. C. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen and M. Antonietti, *Nat. Mater*., **2009**,8, 76.
22. S. Z. Hu, F. Y. Li, Z. P. Fan, F. Wang, Y. F. Zhao and Z. B. Lv, *Dalton Trans*., **2015**,44, 1084.
23. Q. F. Deng, L. Liu, X. Z. Lin, G. H. Du, Y. P. Liu and Z. Y. Yuan, *Chem. Eng. J*., **2012**, 203, 63.
24. M. B. Ansari, H. L. Jin, M. N. Parvin and S. E. Park,Catal. Today, **2012**,185, 211.
25. A. Allahresani, B.Taheri, M. A. Nasseri, *Research on Chemical Intermediates*, **2018**, 44, 6979–6993.
26. R. B. N. Baig, S. Verma, M. N. Nadagouda and R.S. Varma, room temperature synthesis of biodiesel using sulfonated graphitic carbon nitride, **2016**, *Nature*, *6*, 39387.
27. X.J. Bai, R.L. Zong, C.X. Li, D. Liu, Y.F. Liu, Y.F. Zhu, *Appl. Catal. B: Environ*. **2014**, 147, 82–91.
28. L-Y. Zeng and C. Cai, Iodine catalyzed one-pot multicomponent synthesis of a library of compounds containing tetrazolo [1,5-a] pyrimidine core, **2010,** J. *Comb. Chem*, 12, pp. 35-40.
29. X.C. Wang, Y. Wei, Y.X. Da, Z. Zhang and Z. JQuan, One-step synthesis of tetrazolo [1,5-a] pyrimidines by cyclization reaction of dihydropyrimidine-2-thiones with sodium azide, **2011**, *Heterocycles*, 83, pp. 2811-2822.
30. S. Rostamnia, A. Hassankhani, H.G. Hossieni, B. Gholipour, H. Xin, Brønsted acidic hydrogensulfate ionic liquid immobilized SBA-15: [MPIm][HSO_4]@SBA-15 as an environmentally friendly, metal- and halogen-free recyclable catalyst for Knoevenagel–Michael-cyclization processes, **2014**, *Journal of Molecular Catalysis A: Chemical*, 395, 463-469.
31. M.A. Zolfigol, M. Yarie, Fe_3O_4@TiO_2@$O_2PO_2(CH_2)$ $NHSO_3H$ as a novel nanomagneticcatalyst: Application to the preparation of 2- amino- 4,6 diphenylnicotinonitriles via anomeric based oxidation, **2016**, *Appl. Organometal. Chem*, 31, 5, 3598.
32. Xu M, Han L and Dong S J. Facile fabrication of highly efficient g-C_3N_4/Ag_2O heterostructured photocatalysts with enhanced visible-light photocatalytic activity, **2013,** *ACS Appl. Mater. Interfaces* 5 12533-40.

33. Yang S B, Gong Y J, Zhang J S, Zhan L, Ma L L, Fang Z Y, Vajtai R, Wang X C and Ajayan P. Exfoliated Graphitic Carbon Nitride Nanosheets as Efficient Catalysts for Hydrogen Evolution Under Visible Light, **2013**, *Adv. Mater* 25**,** 2452-6.
34. Yuan X Y, Zhou C, Jin Y R, Jing Q Y, Yang Y L, Shen X, Tang Q, Mu Y H and Du A. Facile synthesis of 3D porous thermally exfoliated g-C_3N_4 nanosheet with enhanced photocatalytic degradation of organic dye, **2016**, *J. All. Compd*. 468**,** 211-9.
35. A. Ghorbani-Choghamarani, M. Hajjami, B. Tahmasbi, N. Noori, *J IRAN CHEM SOC*, **2016**, 13, 2193–2202.
36. X. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J.M. Carlsson, K. Domen, M. Antonietti, *Nat. Mater*. **2008**, 8,76-80.
37. Y. Wang, X. Wang, M. Antonietti, *Angew. Chem. Int*. Ed. **2012**, 51, 68-89.
38. L.Y. Zeng and C. Cai, *J. Comb. Chem*, **2010**, 12, 35–40.
39. X.C. Wang, Y. Wei, Y.X Da, Z. Zhang and, Z. JQuan, *Heterocycles*, **2011**, 83, 2811-2822.
40. S. Shen, H. Zhang, C. Yu, C. Yao, T. Li, B. Qin, J. Lu, and D. Wang, *Res. Chem. Intermed*, **2013**, 39, 1799.
41. P. Kour, V. P. Singh, B. Khajuria, T. Singh, A. Kumar, *Tetrahedron Letters*, **2017**, 58, 4179-4185.
42. L.Y. Zeng and C. Cai, *J. Comb. Chem*, **2010**, 12, 35–40.