Preparation and characterization of graphitic carbon nitride-supported L-arginine as a highly efficient and recyclable catalyst for the one-pot synthesis of condensation reactions

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In this work, graphitic carbon nitride-supported L-arginine (g-C$_3$N$_4$@L-arginine) nanocatalyst was synthesized and evaluated using FT-IR, EDX, XRD, TGA, and FESEM analyses. The performance of the prepared nanocatalyst was examined in the synthesis of 1,4-dihydropyridine, 4H-chromene, and 2,3-dihydro quinazoline derivatives. The novel g-C$_3$N$_4$@L-arginine nanocatalyst showed high thermal stability, easy separation from reaction media, the capability to be used in various multicomponent reactions, and acceptable reusability.

These days, most chemical processes are carried out in the presence of catalysts. Among various catalysts, supported catalysts have more application than other catalysts. Synthesis of this class of catalysts requires a support with high surface area for the adequate dispersion of primary catalyst. For this reason, using a suitable support is of high importance in the synthesis of such catalysts. Graphitic carbon nitride (g-C$_3$N$_4$) can be used as a metal-free catalyst or catalyst support due to its excellent properties and exceptional performance. g-C$_3$N$_4$ sheets are an important class of conjugated polymers for the synthesis of new heterogeneous catalysts due to their unique electronic band structure, excellent physical, chemical, and thermal stability, high abrasion resistance, high hardness, low density, versatile performance, low synthesis cost, and recyclability. On the other hand, amino acids are one of the most interesting catalyst substrates due to their unique structure. Arginine is one of the main and semi-essential amino acids in the body of living organisms with advantages such as nontoxicity, ability to easily bind to catalytic support, and low cost for the preparation of acidic catalysts. In addition, acidic catalysts play an important role in the synthesis of organic compounds. Heterocyclic compounds are one of the best candidates in organic synthesis and pharmaceutical chemistry. They are mainly used as medicines, chemicals, veterinary products, disinfectants, expanders, and antioxidants.

The use of inexpensive and non-toxic reagents as well as low waste production is of great importance in green chemistry reactions. Hence, multicomponent reactions (MCRs) are considered as a useful method for the synthesis of heterocyclic organic molecules. Significant advantages of MCRs are the elimination of intermediates, short reaction times, high reaction yield, and easy separation of products. Compounds such as 1,4-dihydropyridine, tetrahydro-4H-chromenes, and dihydroquinazolines, which have high medicinal activity, are synthesized by MCRs.

Dihydropyridines are divided into two classes; symmetrical and asymmetrical. The latter is synthesized by the reaction of an aldehyde, 2 mmol of two different β-keto esters, and a nitrogen donor such as ammonium acetate or ammonia. The product of the initial reaction is dihydropyridine that can later be converted to pyridine. These compounds are an important class of antihypertensive drugs, vasodilators, hypnotic, anti-tumor, anti-inflammatory, anti-diabetic, anti-anxiety, anti-mutation, and are known as calcium channel blockers. Tetrahydro-4H-chromenes are an important class of heterocyclic compounds with simple structure and low side effects. They are synthesized by the single-step condensation of aldehydes with malononitrile and...
dimedone. In addition, their derivatives have important activities such as anticancer, antiviral, anti-inflammatory, antibacterial, antifungal, antioxidant, and anticoagulant. They are also used as cognitive enhancers to treat Alzheimer’s disease.

Dihydroquinazolines are the building blocks of about 150 natural alkaloids which are prepared by the reaction between aldehydes, isotonic anhydride, and ammonium acetate. Moreover, they have a range of pharmaceutical and biological activities such as anti-inflammatory, antimalarial, antibacterial, anticancer, and antiviral activities. Hence, many efforts have been made to synthesize such high-yield compounds. There are various methods for the synthesis of these compounds using different catalysts such as MCM-41@Schiff base-Co (OAC), Yb (NPf2)3, MCM-41@serine@Cu(II), titanium silicon oxide nanopowder, Y(NO3)3.6H2O, etc. despite their numerous advantages, they have some limitations such as long reaction time, expensive reagents, and the possibility of their contamination in final products.

In this paper, new g-C3N4@L-arginine catalyst with the ability to perform various multi-combination reactions with high yield, short reaction time, recyclability, and easy separation from the reaction mixture is synthesized and examined (Fig. 1).

Results and discussion

The g-C3N4@L-arginine synthesis process consists of three main steps, as shown in Fig. 1. The first step is the synthesis of nanosheet g-C3N4 from melamine, which melamine was polymerized to bulk g-C3N4, then nanosheet g-C3N4 is synthesized by liquid exfoliation and sonication. In the second step, g-C3N4 nanosheets were modified by 1,3-dibromopropane at 100 °C for 24 h under nitrogen atmosphere. Finally, the g-C3N4@L-arginine was obtained via the reaction between L-arginine and modified g-C3N4 nanosheets. In this work, various techniques such as FTIR, EDX, XRD, FESEM, and TGA have been used to identify and characterize the novel nanocatalyst.
FTIR spectra of g-C$_3$N$_4$ nanosheets (Fig. 2a) and g-C$_3$N$_4$@l-arginine nanocatalyst (Fig. 2b) are shown in Fig. 2. The strong and broad peak in the range of 3000–3300 cm$^{-1}$ is related to stretching vibration of N–H bonds, breadth peak can be assigned to N–H groups involved in H-bonding or the presence of O–H groups due to water adsorption by nanosheets g-C$_3$N$_4$ $^{28,29}$. The stretching vibration peak of C=N can be observed at 1602 cm$^{-1}$. The peaks at 1303 and 1082 cm$^{-1}$ are attributed to the stretching vibration of C–N bonds formed between triazine and N–H groups, while the stretching vibration of C–N bonds in the ring is easily visible at 1448 and 1379 cm$^{-1}$ $^{29,30}$. In addition, the peak at 786 cm$^{-1}$ is associated with the vibration of tri-s-triazine units $^{1}$ (Fig. 3a). Figure 3b shows that the g-C$_3$N$_4$ nanosheets has been modified with 1,3-dibromopropane; the peak at 3000–2800 cm$^{-1}$ is related to C–H stretching vibration.

The spectrum of g-C$_3$N$_4$@l-arginine is presented in Fig. 3c in which the existence of l-arginine on the surface of g-C$_3$N$_4$ nanosheets can be confirmed based on the 1705 cm$^{-1}$ and 1307 cm$^{-1}$ peaks relating to the stretching
vibration of C=O and C-O bonds, respectively. O–H and C-H bonds already existed in the structure of modified nanosheets g-C$_3$N$_4$.

The presence of carbon and nitrogen elements in the structure of g-C$_3$N$_4$ nanosheets is visible in Fig. 4a. The presence of Br element in the structure proves that g-C$_3$N$_4$ nanosheets have been modified by 1,3-dibromopropane (Fig. 4b). Finally, the presence of carbon, nitrogen, and oxygen in the final structure (g-C$_3$N$_4$@l-arginine) confirmed the synthesis of g-C$_3$N$_4$@l-arginine nanocatalyst (Fig. 4c).

The morphology of g-C$_3$N$_4$ nanosheets and g-C$_3$N$_4$@l-arginine was investigated by FE-SEM. Figure 5a-d shows FE-SEM images of g-C$_3$N$_4$ nanosheets. As shown in Figs. 5a-c, the g-C$_3$N$_4$ nanosheets have a smooth and flat surface, while in Fig. 5d, g-C$_3$N$_4$ nanosheets are irregular and connected together. FE-SEM images of g-C$_3$N$_4$@l-arginine are shown in Fig. 5e-h. It can be seen from Fig. 5e-g that g-C$_3$N$_4$ nanosheets have a flake-like morphology with a relatively rough surface, mainly due to the presence of l-arginine on the surface of g-C$_3$N$_4$ nanosheets. In Fig. 5h, more irregular-shape g-C$_3$N$_4$ nanosheets with tiny particles on the surface are observed, which again confirms the deposition of l-arginine on the g-C$_3$N$_4$ nanosheets.

XRD patterns of g-C$_3$N$_4$ nanosheets and g-C$_3$N$_4$@l-arginine are shown in Figs. 6a and 6b, respectively. The diffraction peaks at 2θ = 27.69 and 15.96 (Fig. 6a) prove the successful synthesis of g-C$_3$N$_4$ nanosheets, while the diffraction peaks at 2θ = 6.07, 10.85, 12.21, 23.60, and 30.97 (Fig. 6b) correspond to l-arginine (JCPDS card no. 00–004-0180), confirming the presence of l-arginine on the surface of g-C$_3$N$_4$ nanosheets.

Figure 7 shows the thermal stability of the synthesized g-C$_3$N$_4$@l-arginine in the range of 50–800 °C. As can be seen, the weight ratio has gradually decreased by increasing the temperature from 100 to 200 °C, which is most likely related to the removal of water absorbed on the surface of g-C$_3$N$_4$@l-arginine. Then, another weight loss is observed in the range of 200 to 400 °C, which is attributed to the separation of l-arginine from the structure. Finally, there is another weight loss in the range of 400 to 700 °C due to the decomposition of g-C$_3$N$_4$ nanosheets.

Model reactions. The performance of the prepared g-C$_3$N$_4$@l-arginine nanocatalyst was evaluated for the synthesis of 1,4-dihydropyridine, 4H-chromene, and 2,3-dihydro quinazoline derivatives. For this purpose, various parameters such as reaction time, catalyst concentration, and the solvent were examined (Table 1). The reaction of 4-chlorobenzaldehyde (1 mmol), ethyl acetoacetate (1 mmol), dimedone (1 mmol), and ammonium acetate (1 mmol) for the synthesis of 1,4-dihydropyridine derivatives, the reaction of 4-chlorobenzaldehyde (1 mmol), dimedone (1 mmol), and malononitrile (1 mmol) for the synthesis of 4H-chromene derivatives, and the reaction of 4-chlorobenzoic acid (1 mmol), isonic anhydride (1 mmol), and ammonium acetate (1 mmol) for the synthesis of 2,3-dihydro quinazoline derivatives were considered as model reactions with and without g-C$_3$N$_4$@l-arginine nanocatalyst under different conditions. The reaction progress was monitored by Thin-layer
**Figure 5.** FE-SEM image of nanosheets g-C$_3$N$_4$ (a, b, c, and d), and g-C$_3$N$_4$@l-arginine (e, f, g, h).

**Figure 6.** XRD pattern of (a) nanosheets g-C$_3$N$_4$, (b) g-C$_3$N$_4$@l-arginine.

**Figure 7.** TGA analysis of g-C$_3$N$_4$@l-arginine.
chromatography (TLC). As can be seen in Table 1 (entries 1 and 2), no progress was observed for the model reactions without nanocatalyst. By introducing 1.00 mg of g-C₃N₄@l-arginine (Table 1, entry 3), however, the model reactions occurred easily. Then, the influence of other parameters including catalyst concentration, reaction time, and solvent were examined. As can be seen, time had not significant effect on the reaction progress, thus 15 min was considered as the optimum reaction time for all the model reactions (Table 1, entries 7, 8, and 9). Furthermore, the highest product yield was obtained using ethanol as solvent at 80 °C in the presence of 20.00 mg of g-C₃N₄@l-arginine (Table 1, entry 5).

In the following, various aldehydes were applied for the synthesis of 1,4-dihydropyridine, 4H-chromene, and 2,3-dihydro quinazoline derivatives under optimal reaction conditions. Based on model reactions that are provided in Tables 2, 3 and 4, a wide range of different derivatives of the desired multicomponent reactions were prepared with high yield.

**Table 1.** Optimization of different parameters for model reactions 1 to 3. a Reaction of 4-chlorobenzaldehyde (1 mmol), ethyl acetoacetate (1 mmol), dimedone (1 mmol), and ammonium acetate (1 mmol) for the synthesis of 1,4-dihydropyridine. b Reaction of 4-chlorobenzaldehyde (1 mmol), dinedone (1 mmol), and malononitrile (1 mmol) for the synthesis of 4H-chromene. c Reaction of 4-chlorobenzaldehyde (1 mmol), isotonic anhydride (1 mmol), and ammonium acetate (1 mmol) for the synthesis of 2,3-dihydroquinazoline.

| Entry | Catalyst | Catalyst loading (mg) | Solvent | Time (min) | Temperature (°C) | Yield (%) | Reaction 1 | Reaction 2 | Reaction 3 |
|-------|----------|-----------------------|---------|------------|------------------|-----------|------------|------------|------------|
| 1     | -        | -                     | EtOH    | 60         | r.t              | -         | -          | -          | -          |
| 2     | -        | -                     | EtOH    | 60         | Reflux           | -         | -          | -          | -          |
| 3     | g-C₃N₄@l-arginine | 1.00     | EtOH    | 15         | Reflux           | 53        | 60         | 57         |            |
| 4     | g-C₃N₄@l-arginine | 10.00    | EtOH    | 15         | Reflux           | 85        | 90         | 87         |            |
| 5     | g-C₃N₄@l-arginine | 20.00    | EtOH    | 15         | Reflux           | 94        | 97         | 96         |            |
| 6     | g-C₃N₄@l-arginine | 30.00    | EtOH    | 15         | Reflux           | 95        | 98         | 96         |            |
| 7     | g-C₃N₄@l-arginine | 20.00    | EtOH    | 10         | Reflux           | 89        | 97         | 93         |            |
| 8     | g-C₃N₄@l-arginine | 20.00    | EtOH    | 20         | Reflux           | 95        | 98         | 93         |            |
| 9     | g-C₃N₄@l-arginine | 20.00    | EtOH    | 30         | Reflux           | 96        | 98         | 94         |            |
| 10    | g-C₃N₄@l-arginine | 20.00    | CH₂Cl₂  | 15         | Reflux           | 54        | 67         | 60         |            |
| 11    | g-C₃N₄@l-arginine | 20.00    | DMF     | 15         | Reflux           | 52        | 56         | 55         |            |
| 12    | g-C₃N₄@l-arginine | 20.00    | H₂O     | 15         | Reflux           | 75        | 78         | 77         |            |
| 13    | g-C₃N₄@l-arginine | 20.00    | EtOH    | 15         | r.t              | 57        | 66         | 68         |            |

**Mechanistic study of the prepared nanocatalyst in the synthesis of 1,4-dihydropyridine, 4H-chromene, and 2,3-dihydro quinazoline derivatives.** In Fig. 10, the suitable mechanism for the formation of 1,4-dihydropyridine, 2,3-dihydro quinazoline, and 4H-chromene derivatives are provided. In each reaction, the presence of g-C₃N₄@l-arginine can activate reactants and different intermediates. As can be seen in Fig. 10a, 1,4-dihydropyridine derivatives can be synthesized in two methods. In the first method, aldehyde and dinedone produce intermediate I in the presence of g-C₃N₄@l-arginine, and the intermediate II is formed from the reaction between ethyl acetoacetate and ammonium acetate. But in the second method, dinedone and ammonium acetate produce intermediate III in the presence of g-C₃N₄@l-arginine, and the reaction between ethyl acetoacetate and aldehyde forms intermediate IV. Both methods ultimately lead to the formation of product V.
A suggested mechanism for the formation of 2,3-dihydro quinazoline derivatives is shown in Fig. 10b. At first, isoticonic anhydride reacts with ammonium acetate in the presence of g-C₃N₄@l-arginine and produces intermediate I, then aldehyde activates by g-C₃N₄@l-arginine and adds to intermediate II. Finally, after removing H, the desired product IV is synthesized.

Table 2. Synthesis of 1,4-dihydropyridine derivatives using g-C₃N₄@l-arginine nanocatalyst. Reaction conditions: benzaldehyde (1 mmol), ethyl acetooacetate (1 mmol), dimedone (1 mmol), and ammonium acetate (1 mmol), g-C₃N₄@l-arginine (20 mg) and ethanol (7 mL) under reflux conditions.

| Entry | R  | Product | Time (min) | Mp (°C) | Mp (°C, ref.) | Yield (%) |
|-------|----|---------|------------|---------|---------------|-----------|
| 1     | H  | 5a      | 10         | 217–219 | 218–220 ¹⁷    | 95        |
| 2     | 4-Cl | 5b   | 15         | 240–242 | 241–243 ¹⁷    | 94        |
| 3     | 4-OH | 5c   | 20         | 230–232 | 231–232 ¹⁴    | 89        |
| 4     | 4-NO₂ | 5d   | 15         | 239–241 | 240–242 ¹⁴    | 90        |
| 5     | 4-Me | 5e    | 25         | 254–256 | 250 ¹⁵        | 87        |

Table 3. Synthesis of 4H-chromene derivatives using g-C₃N₄@l-arginine nanocatalyst. Reaction conditions: Reaction of benzaldehyde (1 mmol), dimedone (1 mmol), and malononitrile (1 mmol) g-C₃N₄@l-arginine (20 mg) and ethanol (7 mL) under reflux conditions.

| Entry | R  | Product | Time (min) | Mp (°C) | Mp (°C, ref.) | Yield (%) |
|-------|----|---------|------------|---------|---------------|-----------|
| 1     | H  | 9a      | 7          | 228–229 | 225–228 ¹¹    | 95        |
| 2     | 4-Cl | 9b   | 10         | 210–212 | 209–213 ¹¹    | 97        |
| 3     | 4-NO₂ | 9c   | 15         | 178–179 | 177–179 ¹⁴    | 88        |
| 4     | 2,4-Cl | 9d   | 10         | 118–120 | 115–117 ¹⁴    | 95        |
| 5     | 4-OH | 9e    | 20         | 206–208 | 208–210 ¹⁴    | 93        |
| 6     | 4-Me | 9f    | 30         | 217–220 | 220–221 ¹        | 91        |
| 7     | 3-NO₂ | 9g   | 20         | 206–207 | 206–209 ¹        | 93        |
| 8     | 2-Cl | 9h    | 15         | 213–214 | 211–213 ¹        | 96        |
| 9     | 4-CN | 9i    | 25         | 184–187 | 184–186 ¹        | 89        |
| 10    | 4-OMe | 9j   | 30         | 203–204 | 196–198 ¹⁵      | 87        |

A suggested mechanism for the formation of 4H-chromene derivatives is shown in Fig. 10c. In this mechanism, intermediate I is produced from the reaction between aldehyde and dimedone. Then, addition of malononitrile leads to the formation of intermediate II. At last, product IV is obtained.
Catalytic activity of the synthesized nanocatalyst. Tables 5, 6 and 7 show the performance of g-C3N4@l-arginine in comparison with the catalysts reported in the literature for the synthesis of 1,4-dihydropyridine, 4H-chromene, and 2,3-dihydro quinazoline derivatives. For this purpose, various parameters such as catalyst concentration, reaction time, reaction temperature, and reaction yield were investigated. According to the data presented in each table, g-C3N4@l-arginine can be considered as a unique heterogonous nanocatalyst that can be used in a wide range of condensation reactions in addition to simple separation conditions of the reaction mixture. On the other hand, this nanocatalyst exceptionally showed higher synthesis yield at shorter reaction times.

Experimental
Reagents and apparatus. All chemicals were purchased from Merck and Sigma-Aldrich Co. Fourier Transform Infrared (FTIR) spectra were recorded on Tensor27. Nuclear Magnetic Resonance (NMR) data were acquired on a Varian-Inova 500 MHz. X-Ray Diffraction (XRD) patterns were obtained using Dron-8 diffractometer. Energy-dispersive X-ray (EDX) spectrum was recorded on Numerix DXP-X10P. Thermal gravimetric
Field Emission Scanning Electron Microscopy (FESEM) images were recorded with TESCAN-MIRA III.

**Preparation of bulk g-C₃N₄ and g-C₃N₄ nanosheets.** For the synthesis of bulk g-C₃N₄, the melamine was heated at 550 °C in a furnace at the heating rate of 2.5 °C min⁻¹ in static air for 4 h. A yellow powder was obtained which was then grounded in a ball mill. For the synthesis of g-C₃N₄ nanosheets, bulk g-C₃N₄ (1.0 g) was first stirred in H₂SO₄ (20 mL) at 90 °C for 5 h. The solution was then diluted with ethanol (200 mL) and stirred again at room temperature for 2 h. The resulting product was dispersed in 100.0 mL water/isopropanol (1:1) solution and sonicated for 6 h. Finally, the formed suspension was centrifuged at 5000 rpm to separate g-C₃N₄ nanosheets.

**Preparation of g-C₃N₄@l-arginine.** g-C₃N₄ (1.0 g) nanosheets were dispersed in dry toluene (20.0 mL). Then, the reaction mixture was refluxed under N₂ atmosphere for 24 h after addition of 1,3-dibromopropane (2.0 mL). Finally, the product was filtered and washed with ethyl acetate, and dried at room temperature. The resulting product was dissolved in a mixture of water and methanol (1:1) followed by the addition of l-arginine (1 mmol), K₂CO₃ (1.0 mmol), and NaI (1.0 mmol). The solution was stirred at room temperature for 24 h. The reaction mixture was then washed with water and methanol and dried at room temperature.

**Figure 9.** EDX (b) and FT-IR spectra (a) of g-C₃N₄@l-arginine after the five-times recycling.
Figure 10. Proposed mechanism for synthesis of 4H-chromene derivatives (a), 2,3-dihydro quinazoline (b), and 1,4-dihydropyridine (c) by using g-C$_3$N$_4$@l-arginine.
Table 5. Comparison of catalytic activity of g-C₃N₄@l-arginine with other reported catalysts for the synthesis of 4H-chromene derivatives. Reaction conditions: benzaldehyde (1 mmol), dimedone (1 mmol), malononitrile (1.5 mmol), g-C₃N₄@l-arginine catalyst (20.00 mg), and ethanol (7 mL) under reflux.

| Entry | Catalyst | Solvent/temperature | Time (min) | Chromene yield (%) | Ref |
|-------|----------|---------------------|------------|-------------------|-----|
| 1     | Fe₃O₄@MCM-41@Zr-piperazine-MNPs | EtOH/H₂O/75 °C | 40 | 74 | 37 |
| 2     | AIL@MNP | Solvent-free/90 °C | 25 | 89 | 38 |
| 3     | MCM-41@Schiff base-Co(OAC)₂ | H₂O/50 °C | 180 | 94 | 23 |
| 4     | Yb(NPf₂)₃ | EtOH/80 °C | 240 | 91 | 24 |
| 5     | g-C₃N₄@l-arginine | EtOH/reflux | 7 | 95 | This work |

Table 6. Comparison of catalytic activity of g-C₃N₄@l-arginine with other reported catalysts for the synthesis of 1,4-dihydropyridine derivatives. Reaction conditions: Reaction of benzaldehyde (1 mmol), dimedone (1 mmol), and malononitrile (1 mmol) g-C₃N₄@l-arginine catalyst (20.00 mg) and ethanol (7 mL) under reflux.

| Entry | Catalyst | Solvent/temperature | Time (min) | Hantzsch yield (%) | Ref |
|-------|----------|---------------------|------------|-------------------|-----|
| 1     | BNPs @ S(Ch2)3@NH SOH | EtOH/reflux | 25 | 95 | 39 |
| 2     | Aluminized polyborate | Solvent-free/100 °C | 15 | 94 | 14 |
| 3     | Cell-Pr-NHSO₃H | EtOH/reflux | 45 | 91 | 40 |
| 4     | MCM-41@serine@Cu(II) | EtOH/80 °C | 170 | 96 | 25 |
| 5     | g-C₃N₄@l-arginine | EtOH/reflux | 10 | 95 | This work |
General procedure for the synthesis of 1,4-dihydropyridine derivatives. A mixture of aldehyde (1.0 mmol), ethyl acetoacetate (1.0 mmol), dimedone (1.0 mmol), ammonium acetate (1.0 mmol), g-C₃N₄@l-arginine (20.0 mg), and ethanol (2.0 mL) was added in a round bottom flask and refluxed at 70 °C. When the reaction was completed (monitored by TLC), the catalyst was separated by filtration and washed with ethanol, and then to purifying the product was used recrystallization.

General procedure for the synthesis of 2,3-dihydro quinazoline derivatives. In a round bottom flask, aldehyde (1.0 mmol), isotonic anhydride (1.0 mmol), ammonium acetate (2.0 mmol), and g-C₃N₄@l-arginine (20.0 mg) were added and refluxed in ethanol (2.0 mL) at 70 °C. After reaction completion (monitored by TLC), the catalyst was removed by filtration and washed with ethanol, and then to purifying the product was used recrystallization.

General procedure for the synthesis of 4H-chromene derivatives. In a round bottom flask was added aldehyde (1.0 mmol), dimedone (1.0 mmol), malononitrile (1.0 mmol), g-C₃N₄@l-arginine (20.0 mg), and ethanol (2.0 mL). The mixture was then refluxed at 70 °C until the reaction was completed (monitored by TLC). At last, catalyst separation by filtration and washed with ethanol, and then to purifying the product was used recrystallization.

Conclusions
In summary, heterogeneous g-C₃N₄@-arginine nanocatalyst was prepared and used for the synthesis of 1,4-dihydropyridine, 4H-chromene, and 2,3-dihydro quinazoline derivatives as important products in pharmacologically active compounds. The main advantages of this nanocatalyst is its reusability, simple separation from the reaction mixture, applicability for a broad range of high efficiency condensation reactions, and short reaction time. In addition, the use of an easy and convenient method for the preparation of the nanocatalyst is another advantage of this catalyst over other reported catalysts.

Selected spectral data

| Compound | FTIR (KBr, cm⁻¹) | 1H NMR (500 MHz, DMSO) |
|----------|------------------|------------------------|
| Ethyl 2,7,7-trimethyl-5-oxo-4-(4-hydroxylphenyl)-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (5c). | 3270, 3194, 3071, 2957, 1678, 1645, 1481, 1377, 1214 cm⁻¹. | δ H (ppm) = 0.85(s, 3H, CH₃), 1.0(s, 3H, CH₃), 1.13(t, 3H, CH₃), 1.9–2.41(m, 4H, 2CH₂), 2.25(s, 3H, CH₃), 3.95–3.99(q, 2H, OCH₂), 4.73(s, 1H, Ar–CH), 6.54(d, 2H, Ar–H), 6.93(d, 2H, Ar–H), 8.95(s, 1H, NH), 9.01(s,1H, OH). |
| Ethyl 1,4,7,8-tetrahydro-2,7,7-trimethyl-4-(4-nitrophenyl)-5(6H)-oxoquinoline-3-carboxylate (5d). | 3276, 3210, 3076, 2969, 2902, 1703, 1641, 1530, 1379 cm⁻¹. | δ H (ppm) = 0.83(s, 3H, CH₃), 1.01(s, 3H, CH₃), 1.11(t, 3H, CH₃), 1.96–2.46(m,4H, 2CH₂), 2.31(s, 3H, CH₃), 3.93–4.0(m, 2H, OCH₂), 4.97(s, 1H, Ar–CH), 7.5–7.61 (m, 4H, Ar–H), 7.97(s, 1H, NH), 9.23(s,1H, OH). |
| 2-amino-4-(4-nitrophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (9c). | 3303, 3172, 2969, 2881, 2181, 1668, 1626, 1517, 1345, 856 cm⁻¹. | δ H (ppm) = 0.95(s, 3H, CH₃), 1.04(s, 3H, CH₃), 2.09–2.53(m, 4H, 2CH₂), 4.36(s, 1H, CH), 7.1(s, 2H, NH), 7.43–8.17(m, 4H, Ar–H). |
| 2-phenyl-2,3-dihydro-4(1H)-quinazolinone (13a). | 3305, 3184, 3062, 1654, 1606, 1431, 1090, 749 cm⁻¹. | δ H (ppm) = 5.73(s, 1H, CH), 6.67(t, 1H, Ar–H), 6.74(d, 1H, Ar–H), 7.1(s, 1H, NH), 7.23(t, 1H, Ar–H), 7.34(t, 1H, Ar–H), 7.38(t, 1H, Ar–H), 7.49(d, 1H, Ar–H), 7.60(d, 1H, Ar–H), 8.27(s, 1H, CONH). |
| 2-(4-chlorophenyl)-2,3-dihydro-1H-quinazoline-4-one (13b). | 3305, 3184, 3062, 1654, 1606, 1431, 1090, 749 cm⁻¹. | δ H (ppm) = 5.77(s, 1H, CH), 6.68(t, 1H, Ar–H), 6.74(d, 1H, Ar–H), 7.1(s, 1H, NH), 7.24(t, 1H, Ar–H), 7.45(d, 1H, Ar–H), 7.50(d, 1H, Ar–H), 7.81(d, 1H, Ar–H), 8.27(s, 1H, CONH). |

**Table 7.** Comparison of catalytic activity of g-C₃N₄@-arginine with other reported catalysts for the synthesis of 2,3-dihydro quinazoline derivatives. Reaction condition: 4-chlorobenzaldehyde (1mmol), isotonic anhydride (1mmol), and ammonium acetate (1mmol), g-C₃N₄@-arginine catalyst (20.00 mg), and ethanol (7 mL) under reflux.

| Entry | Catalyst | Solvent/temperature | Time (min) | Quinazoline yield (%) | Ref |
|-------|----------|---------------------|------------|-----------------------|-----|
| 1     | Titanium silicon oxide nanopowder | H₂O/100 °C | 120 | 94 | 26 |
| 2     | Wang-OSO₃H | H₂O/100 °C | 24 | 84 | 22 |
| 3     | Y(NO₃)₃·6H₂O | CH₃CN | 300 | 97 | 41 |
| 4     | Montmorillonite-KSF | Solvent-free/100 °C | 150 | 93 | 43 |
| 5     | g-C₃N₄@l-arginine | EtOH/reflux | 15 | 96 | This work |
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Author contributions
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Competing interests
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