Green and Mechanochemical One-Pot Multicomponent Synthesis of Bioactive 2-amino-4H-benzo[b]pyrans via Highly Efficient Amine-Functionalized SiO₂@Fe₃O₄ Nanoparticles

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ABSTRACT: An ecofriendly, magnetically retrievable amine-functionalized SiO₂@Fe₃O₄ catalyst was successfully synthesized and affirmed by several physicochemical characterization tools, such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier-transform infrared spectroscopy (FT-IR), vibrating sample magnetometry (VSM), energy-dispersive X-ray spectroscopy (EDX), and powder X-ray diffraction. Thereafter, the catalytic performance of this environmentally benign NH₂@SiO₂@Fe₃O₄ catalyst was investigated in the one-pot multicomponent synthesis of 2-amino-4H-benzo[b]pyran derivatives. The reaction was simply achieved by grinding of various substituted aromatic aldehydes, dimesone, and malononitrile at room temperature under solvent and waste-free conditions with excellent yields and high purity. Moreover, the developed catalyst not only possesses immense potential to accelerate the synthesis of bioactive pyran derivatives but also exhibits several remarkable attributes such as broad functional group tolerance, durability, improved yield, reusability, and recyclability. Besides, various other fascinating advantages of this protocol are milder reaction conditions, cost effectiveness, short reaction time, and simple work up procedures.

INTRODUCTION

Environmentally benign methods like high efficiency, selectivity, high yield, and simple reaction procedures have become the most important targets to achieve in the field of organic chemistry. To achieve these, multicomponent reactions (MCRs) have recently emerged as the most powerful tools in the synthesis of organic compounds and chemotherapeutic drugs by forming carbon–carbon and carbon–heteroatom bonds using a one-pot procedure.1,2 In MCRs, a number of different starting materials (for example three or more components) are allowed to react to give a desired product using one-pot synthesis.3,4 These reactions have great impact in organic synthesis as they provide various advantages, such as less reaction time, simple separation steps, and cost effectiveness, which eventually provides better yield as compared with multistep synthesis.5 In addition to this, the solvent-free approach is also a widely acceptable greener methodology especially in terms of an economic as well as synthetic point of view, as use of organic solvents has several disadvantages, including toxicity, a tedious work-up procedure in synthesis, and expense.5,6 Further, such reactions are performed under environment-friendly conditions without using strong acids like HCl, H₂SO₄, etc. which can in turn cause corrosion, safety issues, and pollution problems. In this context, one-pot mechaenochemical reactions, i.e., reactions attained by grinding the reactants altogether using a mortar and pestle (also known as “grindstone chemistry”) offers significant advantages such as no column chromatography, no tedious work up, cost effectiveness, and less reaction time over multistep reactions.6

Nowadays, nanoparticles are considered as the building blocks for various nanotechnology applications, which frequently display unique size-dependent physical and chemical properties.2 Sometimes, nanoparticles cannot be used directly as they are associated with certain limitations, such as toxicity, hydrophobicity, unnecessary interactions, etc. These problems can often be overcome by introducing an intermediate (layers or shells). Therefore, derivatization for any application of nanoparticles is prerequisite, which can be either by stabilizing the functional cores or by activating the surfaces. In this context, silica-coated magnetic nanoparticles have attracted great attention owing to their various remarkable properties, such as ease of synthesis, functionalization, thermal stability, low toxicity, and effortless separation from the reaction medium using an external magnet. Silica is considered as one of the most flexible and robust surfaces known,8c which is associated with various advantages, such as it is chemically inert and optically transparent (so that chemical reactions can be monitored spectrscopically). Hence, the modified silica shell increases the
mechanical stability as well as enables functionalization and thus has the potential for many new applications. Keeping this background in mind, we proposed an ecofriendly grinding technology for the synthesis of 2-amino-4\(H\)-benzo\([b]\)pyrans using amine-functionalized silica magnetic nanoparticles (NH\(_2@\)SiO\(_2@\)Fe\(_3O_4\)). In the last few years, tetrahydrobenzo-[\(b\)]pyrans and its analogues have attracted great attention as they are part and parcel of various heterocyclic natural products and drugs that exhibit anticoagulant, antitumor, anticancer, antiallergic, diuretic, and antibacterial properties.\(^9\)\(^{−}\)\(^{13}\) Additionally, they exhibit a broad spectrum of applications as cognitive enhancers that are used for treating neurodegenerative diseases, including Alzheimer’s disease, Parkinson’s disease, acquired immune deficiency syndrome (AIDS), and Down’s syndrome.\(^{14}\)\(^{−}\)\(^{15}\) 4\(H\)-benzo[\(b\)]pyran or chromene scaffold is found in several drugs that are pharmacologically active, for example, 2,7,8-triamino-4-(3-bromo-4,5-dimethoxyphenyl)-4\(H\)-chromene-3-carbonitrile (A),\(^{16}\) 2-amino-4-(3-bromo-4,5-dimethoxyphenyl)-4\(H\)-chromene-3-carbonitrile (B),\(^{17}\) ethyl-2-(2-amino-6-bromo-3-cyano-4\(H\)-chromene-4-yl)-2-cyanoacetate (C),\(^{18}\) 2-amino-7-(dimethylamino)-4-(4-(dimethylamino)naphthalene-1-yl)-4\(H\)-chromene-3-carbonitrile (D),\(^{18}\) 2-amino-4-(furan-3-yl)-6,6-dimethyl-5-oxo-5,6,7,8-tetrahydro-4\(H\)-chromene-3-carbonitrile (E),\(^{19}\) and 2-amino-6,6-dimethyl-5-oxo-4-(thiophen-3-yl)-5,6,7,8-tetrahydro-4\(H\)-chromene-3-carbonitrile (F)\(^{19}\) shown in Figure 1. Because of the versatile utilization of substituted pyran analogues in medicinal chemistry, there is an upsurge to develop simple, inexpensive, and high yielding methods for their synthesis.\(^{20}\)\(^{−}\)\(^{24}\) In continuation to this search, we had synthesized new and efficient economically benign catalyst NH\(_2@\)SiO\(_2@\)Fe\(_3O_4\) to optimize its efficacy in the synthesis of tetrahydrobenzo[\(b\)]-pyrans. Adopting the fascinating advantages of MCRs, herein, we wish to report a library of 2-amino-4\(H\)-benzopyran derivatives via condensation of the three-component (aromatic aldehyde, malononitrile, and dimesidine) one-pot reaction.
catalyzed by amine-functionalized silica magnetic nanoparticles (ASMNPs). A large number of derivatives can be rapidly synthesized in high yield using the grinding multicomponent solvent-free technique at room temperature.

## RESULTS AND DISCUSSION

**Catalyst Preparation.** The procedure for synthesis of Fe$_3$O$_4$ and SMNPs is provided in the Experimental Section. To obtain the amine-functionalized SiO$_2$@Fe$_3$O$_4$, 3-aminopropyltriethoxysilane (APTES) (0.5 mL) was slowly added to 100 mL of the ethanolic solution of SMNPs (0.1 g) and then the resulting mixture was allowed to stir at room temperature for 24 h. The resulting NH$_2$@SiO$_2$@Fe$_3$O$_4$ (ASMNPs) was separated magnetically and washed several times with ethanol to remove any unreacted silylating agent and dried under vacuum. The overall synthesis is depicted in Figure 2.

**Catalytic Activity Test.** The catalytic efficiency of NH$_2$@SiO$_2$@Fe$_3$O$_4$ (ASMNPs) was investigated in the synthesis of tetrahydrobenzo[4]pyran analogues, and the reaction conditions were optimized in terms of the amount of catalyst, reaction time, and yields. A model reaction between 4-bromobenzaldehyde, malononitrile, and dimedone was monitored for optimization of various parameters, as demonstrated in Table 1.

### Table 1. Optimized Conditions for Preparation of 2-Amino-4-(4-bromophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile from 4-Bromobenzaldehyde, Malononitrile, and Dimedone

| entry | amount of catalyst (mg) | time (min) | yield (%) |
|-------|------------------------|------------|-----------|
| 1     | nil                    | 30         | nil       |
| 2     | 2                      | 25         | 30        |
| 3     | 5                      | 20         | 70        |
| 4     | 10                     | 2          | 96        |
| 5     | 15                     | 2          | 96        |

“Reaction conditions: aromatic aldehyde (1 mmol), dimerone (1 mmol), malononitrile (1 mmol), catalyst (10 mg), grinding, r.t. Yield refers to isolated products.

**Effect of the Amount of Catalyst and Solvent.** The effect of the amount of catalyst was observed on the selected model reaction and summarized in Figure 3. It is evident from Figure 3 that there was no product formation in the absence of catalyst NH$_2$@SiO$_2$@Fe$_3$O$_4$. Further, there was an increase in percentage yield of the product on increasing the amount of catalyst by 2–10 mg. On further increasing the amount of the catalyst by 15 mg, there was no such augmentation in the yield. Moreover, it was also observed that on varying the solvents such as water, ethanol, and N,N-dimethylformamide (DMF), there was no such hike in the percentage yield of the product, which eventually proves that the catalyst plays a crucial role in ensuring a very efficient reaction time period with excellent yields.

**Quantification of the Active Amine Sites.** Quantification of the number of amine sites on the surface of SiO$_2$ nanoparticles can be easily analyzed by the simple acid–base back titration method, as reported elsewhere. In brief, the amine-modified silica nanoparticles (10 mg) were dispersed in 1.0 mM HCl (20 mL) and the contents were stirred for around 45 min. Later on, nanoparticles were separated with the help of centrifugation at 15,000 rpm for 15 min and 10 mL of the supernatant was collected to be titrated with the standardized 1.0 mM NaOH solution, till neutralization point is reached by taking phenolphthalein as an indicator to evaluate the total active amine sites. The number of amine sites calculated with the help of acid–base back titration was found to be 2.62 e/nm$^2$.

**Green Chemistry Metrics.** Next, we examined the green chemistry parameters for compound 4c. Table 2 outlines several metrics used for evaluation of the green approach in organic synthesis under optimized conditions. It can be seen clearly from Table 2 that the calculated values of green metrics namely E-factor, process mass intensity, reaction mass efficiency, carbon efficiency, and atom economy, are closer to the ideal values. All calculations are provided in the Supporting Information.

Further, on the basis of literature survey, we had investigated the efficacy of ASMNPs in comparison with previously reported catalysts (Table 3). It is evident from Table 3 that the presence of ASMNPs results in high yielding products. Additionally, it was also observed that the presence of ASMNPs provided milder reaction conditions and a shorter reaction time with no use of solvents.

**General Method for Synthesis of 2-Amino-4H-benzo-pyran (4a−4p).** Using the optimized reaction conditions, we investigated the use of various electron-releasing and electron-withdrawing benzaldehydes keeping malononitrile and dimerone constant. Equivalent amounts of benzaldehyde, dimerone, and malononitrile were taken and catalyst ASMNP (10 mg) was added and all ingredients were ground for about 2–10 min at room temperature, which resulted into a wax- or jellylike reaction mixture. Subsequently, 3–4 mL of 95% ethanol was added into
the reaction mixture to dissolve wax or jelly substances. The catalyst was isolated from the reaction mixture with the help of magnet, washed with ethanol thoroughly (3 x 5 mL), dried in air, and reused in subsequent reactions. The crude product was purified by simple recrystallization with ethanol. A wide variety of 2-amino-4H-benzopyrans were synthesized in good to excellent yields by screening an array of benzaldehydes having electron-donating groups (Table 4, entries 12–15) as compared with aromatic aldehydes bearing electron-donating groups (Table 4, entries 2–11). The plausible mechanism for the synthesis of the desired product trihydrobenzo[b]pyran derivatives in the presence of AMNPs catalyst via a three-component coupling strategy is driven by the formation of arylidiene malononitrile via Knoevenagel condensation between malononitrile and aromatic aldehyde in the first step. Michael addition of dimedone to arylidiene malononitrile occurs to form the intermediate in the second step. Finally, intramolecular cyclization occurs followed by protonation to the intermediate, which results in the desired product and regenerate catalyst in the reaction mixture. The establishment of the high accuracy of crystallographic structures is that a "good crystal" of the synthesized compound must be found. To perform the single XRD analyses, it is always a pleasure to look at a crystal that seems to be perfect in the Oxford Diffraction Xcalibur diffractometer. Although all synthesized 2-amino-4H-benzopyrans (4a–4p) compounds were crystalized, the crystalline structure of one of the compounds in the series viz. 4m seemed to have well-formed faces and edges associated with no cracks, striations, and bubbles in the diffractometer. Hence, we have selected compound 4m for single-crystal X-ray analysis to confirm the structure of synthesized 2-amino-4H-benzopyrans. Figure 5 represents the crystal packing structural arrangement of compound 4m, which further proves the stability of tetrahydrobenzo[b]pyran compounds. The crystal structure was solved by using olex2.1.2.28 and winGX software (Shelx86 method).39 All parameters, such as the crystal data and structure refinement table (Table S1), fractional atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) (Table S2), and anisotropic displacement parameters (Å^2 × 10^3) for compound 4m (Table S3), bond lengths (Table S4), and bond angles (Table S5) are provided in the Supporting Information of this article.

**Mechanistic Pathway.** The mechanism of the reaction of tetrahydrobenzo[b]pyran derivatives in the presence of AMNPs catalyst via a three-component coupling strategy is driven by the basic amino sites. It is suggested to occur through the formation of aryldienemalononitrile via Knoevenagel condensation between malononitrile and aromatic aldehyde in the first step. Michael addition of dimedone to aryldienemalononitrile occurs to form the intermediate in the second step. Finally, intramolecular cyclization occurs followed by protonation to the intermediate, which results in the desired product and regenerate catalyst in the reaction mixture. The plausible mechanism for the synthesis of the desired product tetrahydrobenzo[b]pyran is shown in Figure 4.

Further, the molecular structure of compound 4m was established by utilizing single-crystal X-ray diffraction (XRD) analysis. Single X-ray crystallography is one of the most comprehensive techniques that is utilized to determine the chemical structure of compounds. One of the most important requirements for obtaining the high accuracy of crystallographic structures is that a "good crystal" of the synthesized compound must be found. To perform the single XRD analyses, it is always a pleasure to look at a crystal that seems to be perfect in the Oxford Diffraction Xcalibur diffractometer. Although all synthesized 2-amino-4H-benzopyrans (4a–4p) compounds were crystalized, the crystal of one of the compounds in the series viz. 4m seemed to have well-formed faces and edges associated with no cracks, striations, and bubbles in the diffractometer. Hence, we have selected compound 4m for single-crystal X-ray analysis to confirm the structure of synthesized 2-amino-4H-benzopyrans. Figure 5 represents the crystal packing structural arrangement of compound 4m, which further proves the stability of tetrahydrobenzo[b]pyran compounds. The crystal structure was solved by using olex2.1.2/28 and winGX software (Shelx86 method).39 All parameters, such as the crystal data and structure refinement table (Table S1), fractional atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) (Table S2), and anisotropic displacement parameters (Å^2 × 10^3) for compound 4m (Table S3), bond lengths (Table S4), and bond angles (Table S5) are provided in the Supporting Information of this article.

**Recycling Procedure of the Catalyst.** After completion of the first reaction using NH2@SiO2@Fe3O4 (AMNPs), the
reaction mixture was diluted with ethanol and then the catalyst was separated by using an external magnet. The recovered catalyst was washed several times with ethanol to insure no contamination, dried, and reused in the second reaction. Similar steps were carried out after the second reaction. The recovered catalyst can be used up to eight cycles with no significant loss of catalytic activity of the catalyst. To further ensure no loss in activity of the catalyst, it was tested three times for the model reaction. The plot of the conversion percentage and number of runs for eight cycles, which is repeated three times, has been demonstrated in Figure 6. We had observed that there was not much deviation in the conversion percentage in all three runs.

**Fourier Transform Infrared Spectroscopy (FT-IR).** FT-IR spectroscopy was employed for qualitative detection and confirmation of different functional groups present in all three nanocomposites. The comparative study for FT-IR spectra of all three powdered samples was carried out using KBr pellets in the range of $\bar{\nu} = 400 - 4000 \text{ cm}^{-1}$. It is obvious from Figure 7a that the intense vibration band peak at $583 \text{ cm}^{-1}$ is the characteristic peak of stretching vibration of Fe–O bond of Fe$_3$O$_4$ NPs. The broad band at $3418 \text{ cm}^{-1}$ corresponds to the O–H stretching vibrations arising from surface –OH groups. Further, the coating of silica over the surface of MNPs can be confirmed by the appearance of characteristic peaks at 804, 958, and 1098 cm$^{-1}$, which were assigned to the Si–O–Si symmetric, Si–O symmetric, and Si–O–Si asymmetric stretching modes, respectively, as shown in Figure 7b. Also, the reduction in the intensity of the Fe–O adsorption vibration suggested the formation of desired SiO$_2$@Fe$_3$O$_4$ NPs. Further, the function-
alization of amino propyl group over the surface of SMNPs was confirmed by two distinct bands (Figure 7c) at 1637 and 2912 cm⁻¹ corresponding to the primary amine (−NH₂) and methylene (−CH₂) groups, respectively.⁴¹

**Powder X-ray Diffraction (PXRD) Analysis.** To acquire information about purity and crystallographic structure of prepared nanocomposites, PXRD analysis was done and represented in Figure 8. PXRD of bare Fe₃O₄ nanoparticles is depicted in Figure 8a, which displayed diffraction patterns consistent with standard PXRD data of the Joint Committee on Powder Diffraction Standards card no. (19-0629) for pure cubic inverse spinel structure of Fe₃O₄ crystals. Figure 8a displayed Bragg peaks at 2Θ = 30.3, 35.6, 43.3, 57.4, 62.9°, which are attributed to (2 2 0), (3 1 1), (4 0 0), (5 1 1), and (4 4 0) crystallographic faces of magnetite, respectively. Similar peaks were obtained for SiO₂@Fe₃O₄ nanoparticles (Figure 8b), which indicated the retention of the crystalline magnetic core. The PXRD pattern of SMNPs (Figure 8b) showed a weak broad hump centered at 2Θ = 20–25°, which confirmed the presence of amorphous silica coating around the magnetic core.⁴² Apart from these, no extra peaks were obtained, demonstrating highly pure magnetic nanoparticles. Figure 8c,d represented the powder X-ray diffraction analysis of ASMNPs and recovered ASMNPs, respectively.

**Transmission Electron Microscopy (TEM) Analysis.** To know about surface morphologies and size of synthesized nanoparticles, TEM analysis of MNP, SMNP, ASMNP, and recovered ASMNP was conducted. As the coating of silica was done on iron oxide nanoparticles, the size of nanoparticles increased, and after the incorporation of amine sites, we found that the size of nanoparticles was approximately 28 nm. Further, the size of the recycled nanoparticles became less (approximately 20 nm after eight runs) due to the grinding process. The high-resolution TEM micrograph (Figure 9a) of Fe₃O₄ NPs showed that it is composed of tiny particles possessing a spherical shape with an average diameter of 20 nm. Furthermore, the HRTEM of ASMNP also confirmed the spherical morphology of these nanoparticles (Figure 9c). The HRTEM of the recovered catalyst after eight consecutive runs was also done (Figure 9d), which showed no significant changes in the morphology.

**Scanning Electron Microscopy (SEM) Analysis.** For particle morphology and texture elucidation, SEM images of the synthesized MNP, SMNP, ASMNP, and recovered ASMNP were also obtained and shown in Figure 10. The rougher structures of SMNP and ASMNP could be attributed to successful surface coating. Also, it can be concluded that the size of nanoparticles after coating with silica and anchoring of amine group is not significantly changed, revealing that MNP were coated by a thin layer of silica. The thickness of silica onto surface of MNP could be increased by varying the molar ratio of H₂O/tetra-ethyl orthosilicate (TEOS).³³ On increasing the molar ratio, the size of silica coating also increases. The SEM images supported the formation of spherically shaped Fe₃O₄ NPs, which was in accordance with TEM analysis.

**Elemental and Compositional Analysis.** Energy-dispersive X-ray (EDX) spectroscopy represents a powerful tool in the
elemental analysis of samples with great accuracy. Here, Figure 11a,b represents the EDX spectra of Fe₃O₄ and SiO₂@Fe₃O₄, respectively. The EDX spectrum of Fe₃O₄ (MNPs) shows the presence of Fe and O, while the EDX spectrum of NH₂@SiO₂@Fe₃O₄ (ASMNPs) shows the presence of Fe, O, Si, C, and N, which confirmed the presence of silane shell and amine group around the magnetic core material.

Vibrating Sample Magnetometric Analysis (VSM). Magnetization measurements were investigated at room temperature using a vibration sample magnetometer (VSM) at room temperature in the external magnetic range of −10 000 to +10 000 Oe. The magnetic hysteresis curves of MNPs, SMNPs, and ASMNPs indicated the super magnetic behavior of these nanoparticles. It is obvious from Figure 12a that the synthesized Fe₃O₄ nanoparticles (MNPs) showed a saturation magnetization value of 56 emu/g, which decreased to 43 and 37 emu/g for SMNPs and ASMNPs, respectively (Figure 12b,c) NPs. This decrease in saturation magnetization was attributed to the presence of nonmagnetic amorphous coatings of SiO₂ and functional groups over the surface of Fe₃O₄ NPs. Regardless of the sequential decrease in Mₛ values, all obtained nanoparticles can be separated effortlessly from solution via an external magnet.

**CONCLUSIONS**

In conclusion, we have successfully synthesized a variety of tetrahydrobenzo[b]pyrans in good to excellent yields using efficient and economic amine-functionalized magnetic nanoparticles under solvent and waste-free reaction conditions. High tolerance of this procedure toward different functional groups, easy work up of the desired products, high reusability of the catalyst, and shorter reaction time are the additional advantages for its application to academic and industrial purposes. From a

![Figure 10. SEM image of (a) MNPs, (b) SMNPs, (c) ASMNPs, and (d) recovered ASMNPs at various magnifications.](image1)

![Figure 11. SEM coupled EDX pattern of (a) MNPs and (b) ASMNPs.](image2)

![Figure 12. Magnetization curves obtained using VSM for the (a) MNPs, (b) SMNPs, and (c) ASMNPs at room temperature.](image3)
sustainability point of view, green chemistry parameters like E-factor (0.08), atom economy (95.4%), and carbon efficiency (96%) are in good agreement with the ideal values. The structure of synthesized tetrahydrobenzo[4]pyran (4m) was confirmed by single X-ray diffraction analysis (CCDC 1919512).

### EXPERIMENTAL SECTION

**General Remarks.** Ferric sulfate and ferrous sulfate were purchased from Sisco Research Laboratory (SRL). Tetra-ethyl orthosilicate (TEOS) and APTES were obtained from Sigma-Aldrich. All other reagents used were of analytical grade and obtained from Spectrochem and Merck. Double-distilled water was used throughout the experiment. Thin-layer chromatography was performed on Merck precoated silica gel aluminum plates with 60 F254 indicator. The structural assignments of synthesized compounds were based on 1H NMR, 13C NMR, mass spectroscopy, and single X-ray diffraction analysis. Nuclear magnetic resonance (NMR) was acquired at 400 and 100 MHz for 1H NMR and 13C NMR, respectively, on a JEOL JNM-ECS 400 spectrometer instrument using CDCl3 and dimethyl sulfoxide (DMSO)-d6 as solvents. Tetramethylsilane (TMS) was taken as reference in NMR, and data were processed with its delta software. The coupling constant (J) is reported in Hertz, and chemical shift values are reported in ppm for 1H NMR and multiplicities: s (singlet), d (doublet), and m (multiplet). High-resolution mass spectroscopy was generated by an Agilent ESI-TOF mass spectrometer. X-ray analysis was carried out on an Oxford Diffraction Xcalibur Four-circle Diffractometer with an Eos CCD detector using graphite monochromatized Mo-Ka radiation (λ = 0.71073 Å).

The morphology of the synthesized MNPs and its derivatives obtained after modifications was examined through a TECNAI 200 kV transmission electron microscope (Fei, Electron Optics) equipped with digital imaging and a 35 mm photography system and scanning electron microscopy (SEM) (Jeol Japan Mode: JSM 6610LV). The X-ray diffraction patterns of Fe3O4 NPs and SiO2@Fe3O4 NPs were recorded using Cu Kα radiation (11/4 1.5406 Å) on a powder X-ray diffractometer (Bruker, D8 Advanced, Germany) at room temperature in a 2θ interval of 10–80. The FT-IR spectra were recorded using a PERKIN ELMER 2000 FT-IR spectrophotometer in the range of 400–4000 cm⁻¹ at room temperature using KBr pellets. The magnetic properties of bare and immobilized nanoparticles were determined with a vibrating sample magnetometer (EV-9, Microsense, ADE) in the magnetic field sweeping between −10 000 and +10 000 Oe at room temperature.

**Experimental Procedure for the Synthesis of Fe3O4 (MNPs).** Fe3O4 NPs were prepared by the coprecipitation method, as reported elsewhere.25 Briefly, Fe2(SO4)3 (6.0 g) and FeSO4 (4.2 g) were dissolved in 250 mL of deionized water and the reaction mixture stirred at 60 °C till the appearance of a yellowish-orange solution. Then, ammonium hydroxide (25%) was added slowly to adjust the pH of the solution to 10 and the reaction mixture was allowed to stir continuously for 1 h at 60 °C. NPs were precipitated as a black substance, which were separated by an external magnet and washed with deionized water and ethanol several times until the filtrate showed pH 7 and then finally dried under vacuum.

**Experimental Procedure for the Synthesis of SMNPs.** The coating of silica over prepared MNPs was achieved using the sol–gel approach.25 Briefly, a suspension of 0.5 g of MNPs and 0.1 mL HCl (2.2 mL) was prepared in the mixture of ethanol (200 mL) and water (50 mL) under sonication for 1 h at room temperature. After this period, 25% NH4OH (5 mL) was added to this solution, followed by the addition of TEOS (1 mL) dropwise and the resulting solution was stirred at 60 °C for 6 h. The resulting SMNPs were then separated magnetically and washed several times with ethanol and then dried under vacuum.

**Procedure for Catalytic Activity Test for Compound 4c.** A mixture of 4-bromobenzaldehyde (1 mmol), dimedone (1 mmol), malononitrile (1 mmol), and ASMNPs (10 mg) was taken in a mortar and ground, till it converts into a thick pastelike reaction mixture, at room temperature. After completion of the reaction, 3–4 mL of 95% ethanol was added into the reaction mixture to dissolve the thick paste substance. Subsequently, ASMNPs were recovered with the help of a magnet, washed with ethanol thoroughly, dried overnight, and reused. The crude product was obtained by the simple recrystallization technique with ethanol. Recrystallized 2-amino-4H-benz[4]pyrans were characterized by 1H NMR and 13C NMR spectroscopy.

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b04117.

The CCDC No. 1919512 for compound (4m) contains the supplementary crystallographic data that can be obtained free of charge at https://www.ccdc.cam.ac.uk/News/List/2018-07-new-joint-services/ or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: 44(0)1223-336033 or Email: deposit@ccdc.cam.ac.uk.

Calculation of green chemistry parameters; single X-ray crystallographic parameters; 1H NMR and 13C NMR chemical shift values; 1H NMR, 13C NMR, and ESI–MS spectra of all compounds (PDF)

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**Author Contributions**

P.S. and P.Y. contributed equally and shared the first authorship. The manuscript was written through contribution of all authors. All authors have given approval to the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.
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