Tetramethylguanidine-functionalized silica-coated iron oxide magnetic nanoparticles catalyzed one-pot three-component synthesis of furanone derivatives

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Abstract. Tetramethylguanidine-functionalized silica-coated iron oxide magnetic nanoparticles as a productive and reusable catalyst have been applied for the one-pot three-component synthesis of furanone derivatives (**4a–o**). In addition to the characterization of all products by FT-IR, ¹HNMR and ¹³CNMR spectroscopy, single-crystal X-ray analysis of ethyl 5-oxo-2-phenyl-4-(phenylamino)-2,5-dihydrofuran-3-carboxylate product has been made. Easy recrystallization and good-to-excellent yields (81–92%) of furanone derivatives are notable characteristics of this procedure. The catalyst identification was performed using FT-IR, XRD, SEM, TEM and TGA techniques. It is worth noting that the nanocatalyst can be recycled with an external magnet and reused for several times.

Keywords. Furanone derivatives; three-component reaction; iron oxide; magnetic nanoparticles; tetramethylguanidine.

1. Introduction

During the past few decades, syntheses of important heterocycles have been extensively investigated based on multicomponent reactions (MCRs).^{1–3} Nowadays, three-component reactions taken into consideration in the presence of nanocatalysts, especially magnetic nanoparticles, have garnered much interest because of their unique features such as magnetic property, reusability and eco-friendliness.^{4–7} The tendency of magnetic nanoparticles (e.g., Fe₃O₄) to agglomerate makes it difficult to study their behavior. In the past few years, the surface coating or modification of iron oxide magnetic nanoparticles has emerged as a very important protocol in many applications. The main advantages

of silica-coated iron oxide magnetic nanoparticles are the stability to the iron oxide magnetic nanoparticles in solution, prevention of agglomeration and possibility for linking functional groups to the surface of nanoparticles.^{8–11}

Butenolide skeleton has earned significant interest in organic synthesis.^{12–15} One class of the four-carbon heterocyclic compounds that exhibit medicinal and biological properties are the butenolides corresponding to the family of lactones.¹⁶ 2-Furanone (Figure 1), the simplest butenolide, is a usual portion of important and complex natural compounds.

As shown in Figure 2, L-ascorbic acid (**1**) and penicillic acid (**2**) are two important derivatives of the butenolide.¹⁷ Also, butenolide rings are present in a

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Figure 1. Chemical structure of butenolide.

Figure 2. Chemical structures of some known butenolides.

number of natural compounds.¹⁸ Chemical structures of some known butenolides that are separated from natural compounds like bipinnatin J (**3**),¹⁹ asteriscunolide D (**4**),²⁰ gymnodimine (**5**),²¹ lambertellol C (**6**) and spirofragilide (**7**) are also shown in Figure 2.^{22,23}

Many derivatives of butenolide have shown remarkable medicinal properties such as anti-cancer,²⁴ anti-HIV-1,^{25,26} anti-microbial,²⁷ anti-fungal,²⁸ anti-inflammatory, etc.²⁹

In view of the importance of furanone derivatives, diverse procedures by three-component reaction have been offered for their synthesis. These include the use of β -cyclodextrin,³⁰ tetra-*n*-butyl ammonium bisulfate,³¹ aluminum hydrogen sulfate,³² tin (II) chloride,³³ sucrose,³⁴ vitamin B12,³⁵ silica sulfuric acid (SSA),³⁶ silica gel-supported polyphosphoric acid (PPA/SiO₂),³⁷ trityl chloride (TrCl),³⁸ acetic acid,³⁹ formic acid⁴⁰ and

potassium hydroxide⁴¹ in solvent or solvent-free conditions at room temperature or under heat. Also, acidic ionic liquid ([Bmim]HSO₄)⁴² and ([H-NMP]HSO₄)⁴³ have been reported to catalyze the synthesis of furanone derivatives. Moreover, some furanone derivatives have been synthesized by green and natural catalysts such as watermelon,⁴⁴ barberry⁴⁵ and lemon juice.⁴⁶ In recent reports, nanocatalysts have been employed to synthesize furanone derivatives, using HY Zeolite nano-powder,⁴⁷ ZnO nanoparticles⁴⁸ and sulfamic acid pyridinium chloride-functionalized Fe₃O₄ magnetic nanoparticles⁴⁹ in solvent, graphene oxide nanosheet in solvent-free conditions⁵⁰ and nano-CdZr₄(PO₄)₆ under microwave irradiation.⁵¹ It is worth mentioning, kinetics and mechanism of the reactions between *para*-substituted anilines, benzaldehyde and diethyl ethyne dicarboxylate for the one-pot three-component formation of furanone derivatives in formic acid has been published.⁵²

In quest of clean and efficient synthetic methodologies, we have developed a new methodology for the synthesis of furanone derivatives by tetramethylguanidine-functionalized silica-coated iron oxide magnetic nanoparticles (Fe₃O₄-TMG) as a reusable catalyst in a green solvent at 40 °C (Scheme 1). Most of the above mentioned reports suffer from disadvantages such as low product yield, long reaction time, high cost, toxic organic solvent and high temperature. Furthermore, expense, difficulties in the recyclability of the catalysts and non-eco-friendly catalysts limit the usage of these methods. Easy workup, safety, the cleaner operation of the reactions, excellent yields, magnetically-retrievable and recyclable nanocatalysts are some significant features of the process, we have developed.

2. Experimental

2.1 Materials and methods

All high purity compounds and solvents were purchased from Sigma-Aldrich (Germany), Daejung (Korea), Fluka (Switzerland) and Merck (Germany) and applied without further purification. The structural properties of prepared Fe₃O₄-TMG were analyzed by FT-IR spectrometer and X-ray powder diffraction (XRD) with an X Pert-PRO advanced diffractometer using Cu (K α) radiation (wavelength: 1.5418 Å), operated at 40 kV and 30 mA at room temperature in the range of 2 θ from 20 to 70°. The particle size and morphology of the surfaces of the sample were analyzed by scanning electron microscopy (SEM), (KYKY Co., China, Model: EM 3200). The disc was coated with gold in an ionization chamber. Transmission electron microscopy (TEM) was employed using Zeiss-EM10C TEM instrument with an accelerating voltage of 80 kV. The thermogravimetric analysis (TGA) was

Scheme 1. Synthesis of furanone derivatives in the presence of Fe_3O_4 -TMG.

carried out using a Setaram-SETSYS-16/18 thermogravimetric analyzer, operated under air atmosphere, with a heating rate of $10^\circ\text{C}/\text{min}$ and in the range of 30 – 800°C .

TLC methods were used to follow the reactions. Melting points were measured on an Electrothermal 9100 apparatus (LABEQUIP LTD., Markham, Ontario, Canada) and are uncorrected. ^1H and ^{13}C NMR spectra (CDCl_3) were recorded on a Bruker DRX-250 Avance spectrometer at 250.13 and 62.90 MHz, respectively. FT-IR spectra were measured on a Jasco 6300 FT-IR spectrometer.

2.2 Preparation of the catalyst

2.2a Preparation of Fe_3O_4 MNPs: Fe_3O_4 MNPs were prepared via the co-precipitation method of Fe (III) and Fe (II) ions (molar ratio 2:1) in ammonia solution. FeCl_3 (980 mg), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (900 mg) were dissolved under N_2 atmosphere in deionized water. The dark orange solution was stirred for 15 min at 80°C . The pH value was maintained at 12 by adding ammonia solution (28%) dropwise to the reaction mixture under constant stirring. Stirring was continued for further 30 min before cooling to room temperature. The solvent was removed by an external magnet. The particles were washed several times with water followed by ethanol to make the Fe_3O_4 MNPs free of any residual salts.

2.2b Preparation of Fe_3O_4 MNPs coated by (3-chloropropyl)-trimethoxysilane (Fe_3O_4 -CPTMS): Fe_3O_4 MNPs (1000 mg) was dispersed in 25 mL dry toluene and sonicated for one h by the ultrasonic bath. The dispersion was subsequently refluxed under N_2 atmosphere and stirred with the mechanical stirrer (800 rpm) for 15 min. Then, 3-(chloropropyl) trimethoxysilane (2 mL) was added and the reaction mixture maintained under stirring for 24 h. The reaction mixture was left under stir for an additional 12 h. The solid was collected by magnetic decantation and washed with EtOH (6 times). The final product was dried under vacuum at room temperature for 12 h, affording Fe_3O_4 @CPTMS.

2.2c Preparation of tetramethylguanidine-functionalized silica-coated Fe_3O_4 MNPs (Fe_3O_4 @TMG):

The Fe_3O_4 MNPs-CPTMS (1000 mg) was dispersed in dry toluene (20 mL) by sonication in the ultrasonic bath for 30 min. Subsequently, tetramethylguanidine (4 mmol, 460 mg) and sodium bicarbonate (8 mmol, 672 mg) were added and the mixture was refluxed for 28 h. Then, the final product (Fe_3O_4 @TMG) was separated by magnetic decantation and washed twice by dry CH_2Cl_2 , $\text{C}_2\text{H}_5\text{OH}$ and CH_2Cl_2 respectively to remove the unattached substrates.

2.3 General procedure for the synthesis of furanone derivatives

A solution of aniline **1** (1 mmol), dialkyl ethynedicarboxylate **2** (1 mmol) in ethanol (2 mL) was magnetically stirred at room temperature. Then, aldehyde **3a-o** (1 mmol) and tetramethylguanidine-functionalized silica-coated iron oxide magnetic nanoparticles (80 mg) were added to the mixture and was stirred at 40°C . The reaction was monitored by TLC [petroleum ether: ethyl acetate (9:2)]. After completion of the desired reaction, the resultant mixture was heated in ethanol. The catalyst was separated with an external magnet from the reaction mixture and washed with cold ethanol for reuse. The residue was concentrated under reduced pressure. The pure product was obtained by recrystallization from hot ethanol.

2.4 Spectroscopic data of the products

2.4a Ethyl 5-oxo-2-phenyl-4-(phenylamino)-2,5-dihydrofuran-3-carboxylate (4a**)³⁰:** M.p.: 146 – 149°C ; ^1H NMR (250.13 MHz, CDCl_3): δ (ppm) = 8.21 (br s, 1H, NH), 7.19–7.57 (m, 9H, Ar-H), 6.02 (s, 1H, CH), 4.08 (q, J = 7.00 Hz, 2H, CH_2), 1.10 (t, J = 7.00 Hz, 3H, CH_3); ^{13}C NMR (62.90 MHz, CDCl_3): δ (ppm) = 164.61, 163.90, 138.10, 137.65, 135.92, 129.20, 128.94, 128.53, 127.40, 125.21, 122.83, 114.98, 80.76, 60.67, 13.83; FT-IR (KBr $\nu_{\text{max}}/\text{cm}^{-1}$): 3314, 3048, 2990, 1714, 1686, 1080.

2.4b Ethyl 2-(2-nitrophenyl)-5-oxo-4-(phenylamino)-2,5-dihydrofuran-3-carboxylate (4b): M.p.: 140–142 °C; ^1H NMR (250.13 MHz, CDCl_3): δ (ppm) = 8.31 (br s, 1H, NH), 6.76–8.00 (m, 9H, Ar-H), 5.73 (s, 1H, CH), 4.18 (q, J = 6.75 Hz, 2H, CH_2), 0.98 (t, J = 7.00 Hz, 3H, CH_3); ^{13}C NMR (62.90 MHz, CDCl_3): δ (ppm) = 166.14, 163.546, 149.39, 138.74, 13.84, 137.13, 133.25, 130.90, 129.89, 128.78, 128.11, 125.65, 124.90, 123.22, 113.95, 73.98, 61.01; FT-IR (KBr $\nu_{\text{max}}/\text{cm}^{-1}$): 3309, 2991, 2982, 1778, 1688, 1113.

2.4c Ethyl 2-(4-nitrophenyl)-5-oxo-4-(phenylamino)-2,5-dihydrofuran-3-carboxylate (4c)⁵⁰: M.p.: 144–146 °C; ^1H NMR (250.13 MHz, CDCl_3): δ (ppm) = 8.26 (br s, 1H, NH), 7.15–8.23 (m, 9H, Ar-H), 6.12 (s, 1H, CH), 4.00 (q, J = 7.25 Hz, 2H, CH_2), 1.09 (t, J = 7.00 Hz, 3H, CH_3); ^{13}C NMR (62.90 MHz, CDCl_3): δ (ppm) = 166.05, 163.51, 148.34, 143.14, 138.28, 137.10, 128.81, 128.37, 125.76, 123.78, 123.26, 113.43, 79.11, 61.01, 13.94; FT-IR (KBr $\nu_{\text{max}}/\text{cm}^{-1}$): 3423, 3314, 2994, 2853, 1784, 1637, 1199.

2.4d Ethyl 2-(4-fluorophenyl)-5-oxo-4-(phenylamino)-2,5-dihydrofuran-3-carboxylate (4d)³⁶: M.p.: 141–143 °C; ^1H NMR (250.13 MHz, CDCl_3): δ (ppm) = 8.19 (br s, 1H, NH), 7.03–7.34 (m, 9H, Ar-H), 6.04 (s, 1H, CH), 4.19 (q, J = 6.75 Hz, 2H, CH_2), 1.069 (t, J = 7.00 Hz, 3H, CH_3); ^{13}C NMR (62.90 MHz, CDCl_3): δ (ppm) = 166.45, 163.82, 163.14 (d, $^1J_{\text{CF}}$ = 247.95 Hz), 138.18, 137.50, 131.85 (d, $^4J_{\text{CF}}$ = 3.77 Hz), 129.27 (d, $^3J_{\text{CF}}$ = 8.49 Hz), 128.74, 125.36, 122.93, 115.58 (d, $^2J_{\text{CF}}$ = 21.83 Hz), 114.47, 60.75, 79.99, 13.86; FT-IR (KBr $\nu_{\text{max}}/\text{cm}^{-1}$): 3321, 2992, 2984, 1783, 1687, 1030.

2.4e Ethyl 2-(2-chlorophenyl)-5-oxo-4-(phenylamino)-2,5-dihydrofuran-3-carboxylate (4e): M.p.: 204–207 °C; ^1H NMR (250.13 MHz, CDCl_3): δ (ppm) = 9.24 (br s, 1H, NH), 7.16–7.44 (m, 9H, Ar-H), 6.59 (s, 1H, CH), 4.08 (q, J = 7.00 Hz, 2H, CH_2), 1.05 (t, J = 7.00 Hz, 3H, CH_3); ^{13}C NMR (62.90 MHz, CDCl_3): δ (ppm) = 166.48, 163.82, 138.90, 137.50, 133.27, 130.39, 130.08, 128.73, 128.51, 127.05, 125.82, 125.63, 122.96, 113.87, 77.05, 61.34, 13.80; FT-IR (KBr $\nu_{\text{max}}/\text{cm}^{-1}$): 3314, 2921, 1778, 1693, 1499, 1052.

2.4f Ethyl 2-(4-chlorophenyl)-5-oxo-4-(phenylamino)-2,5-dihydrofuran-3-carboxylate (4f)³⁰: M.p.: 158–160 °C; ^1H NMR (250.13 MHz, CDCl_3): δ (ppm) = 8.19 (br s, 1H, NH), 7.14–7.38 (m, 9H, Ar-H), 6.02 (s, 1H, CH), 4.09 (q, J = 7.00 Hz, 2H, CH_2), 1.08 (t, J = 7.00 Hz, 3H, CH_3); ^{13}C NMR (CDCl_3 , 62.90 MHz): δ (ppm) = 166.41, 163.74, 138.15, 137.47, 135.08, 134.58, 128.78, 128.74, 125.39, 122.96, 114.31, 79.89, 60.80, 13.89; FT-IR (KBr $\nu_{\text{max}}/\text{cm}^{-1}$): 3317, 2993, 2982, 1775, 1687, 1014.

2.4g Ethyl 2-(4-bromophenyl)-5-oxo-4-(phenylamino)-2,5-dihydrofuran-3-carboxylate (4g)⁴⁶: M.p.: 170–

173 °C; ^1H NMR (250.13 MHz, CDCl_3): δ (ppm) = 8.19 (br s, 1H, NH), 7.13–7.25 (m, 9H, Ar-H), 6.01 (s, 1H, CH), 4.08 (q, J = 7.15 Hz, 2H, CH_2), 1.07 (t, J = 7.15 Hz, 3H, CH_3); ^{13}C NMR (62.90 MHz, CDCl_3): δ (ppm) = 166.42, 163.73, 138.12, 137.42, 135.07, 131.74, 129.07, 128.74, 125.41, 123.27, 122.96, 114.25, 79.94, 60.83, 13.91; FT-IR (KBr $\nu_{\text{max}}/\text{cm}^{-1}$): 3316, 2994, 1775, 1687, 1030.

2.4h Ethyl 2-(naphthalen-2-yl)-5-oxo-4-(phenylamino)-2,5-dihydrofuran-3-carboxylate (4h)³⁰: M.p.: 178–181 °C; ^1H NMR (250.13 MHz, CDCl_3): δ (ppm) = 8.24 (br s, 1H, NH), 7.18–7.87 (m, 12H, Ar-H), 6.24 (s, 1H, CH), 4.05 (q, J = 7.00 Hz, 2H, CH_2), 1.02 (t, J = 7.00 Hz, 3H, CH_3); ^{13}C NMR (62.90 MHz, CDCl_3): δ (ppm) = 166.73, 163.95, 137.63, 138.17, 133.66, 133.18, 133.08, 128.76, 128.50, 128.09, 127.77, 127.59, 126.67, 126.46, 125.27, 123.98, 122.89, 114.97, 80.93, 60.72, 13.86; FT-IR (KBr $\nu_{\text{max}}/\text{cm}^{-1}$): 3309, 3046, 2992, 2970, 1775, 1687, 1080.

2.4i Ethyl 5-oxo-4-(phenylamino)-2-(p-tolyl)-2,5-dihydrofuran-3-carboxylate (4i)³⁰: M.p.: 157–162 °C; ^1H NMR (250.13 MHz, CDCl_3): δ (ppm) = 8.17 (br s, 1H, NH), 7.15–7.37 (m, 9H, Ar-H), 6.04 (s, 1H, CH), 4.08 (q, J = 7.13 Hz, 2H, CH_2), 1.07 (t, J = 7.13 Hz, 3H, CH_3), 2.37 (s, 3H); ^{13}C NMR (62.90 MHz, CDCl_3): δ (ppm) = 166.82, 163.93, 139.14, 137.94, 137.77, 132.90, 129.25, 128.70, 127.34, 125.12, 122.75, 115.14, 80.76, 60.69, 21.28, 13.88; FT-IR (KBr $\nu_{\text{max}}/\text{cm}^{-1}$): 3316, 2993, 1775, 1688, 1029.

2.4j Ethyl 2-(4-(methylthio) phenyl)-5-oxo-4-(phenylamino)-2,5-dihydrofuran-3-carboxylate (4j): M.p.: 158–160 °C; ^1H NMR (250.13 MHz, CDCl_3): δ (ppm) = 8.19 (br s, 1H, NH), 7.06–7.51 (m, 9H, Ar-H), 6.04 (s, 1H, CH), 4.09 (q, J = 7.00 Hz, 2H, CH_2), 2.49 (s, 3H), 1.07 (t, J = 6.75 Hz, 3H, CH_3); ^{13}C NMR (62.90 MHz, CDCl_3): δ (ppm) = 166.62, 163.84, 140.02, 138.05, 137.64, 132.53, 128.71, 127.84, 126.23, 125.23, 122.82, 114.70, 80.41, 60.72, 15.53, 13.89; FT-IR (KBr $\nu_{\text{max}}/\text{cm}^{-1}$): 3309, 2992, 2922, 1773, 1686, 1033.

2.4k Methyl 5-oxo-2-phenyl-4-(phenylamino)-2,5-dihydrofuran-3-carboxylate (4k)³³: M.p.: 160–163 °C; ^1H NMR (250.13 MHz, CDCl_3): δ (ppm) = 8.20 (br s, 1H, NH), 7.16–7.38 (m, 10H, Ar-H), 6.06 (s, 1H, CH), 3.62 (s, 3H, CH_3); ^{13}C NMR (62.90 MHz, CDCl_3): δ (ppm) = 166.49, 164.28, 138.39, 137.55, 135.90, 129.28, 128.72, 128.65, 127.37, 125.35, 123.03, 114.36, 80.70, 51.61; FT-IR (KBr $\nu_{\text{max}}/\text{cm}^{-1}$): 3313, 3028, 2952, 1774, 1676, 1077.

2.4l Methyl 2-(3-chlorophenyl)-5-oxo-4-(phenylamino)-2,5-dihydrofuran-3-carboxylate (4l): M.p.: 132–134 °C; ^1H NMR (250.13 MHz, CDCl_3): δ (ppm) = 8.23 (br s, 1H, NH), 7.16–7.39 (m, 9H, Ar-H), 6.01 (s, 1H, CH), 3.65 (s, 3H, CH_3); ^{13}C NMR (62.90 MHz, CDCl_3):

Scheme 2. The preparation of Fe_3O_4 -TMG.

δ (ppm) = 166.11, 164.09, 138.53, 138.02, 137.29, 134.53, 129.93, 129.46, 128.74, 127.47, 125.63, 125.59, 123.24, 113.51, 79.76, 51.70; FT-IR (KBr $\nu_{\text{max}}/\text{cm}^{-1}$): 3316, 3051, 2960, 1788, 1692, 1027.

2.4m Methyl-2-(4-chlorophenyl)-5-oxo-4-(phenylamino)-2,5-dihydrofuran-3-carboxylate (4m)³³: M.p.: 151–153 °C; ^1H NMR (250.13 MHz, CDCl_3): δ (ppm) = 8.23 (br s, 1H, NH), 7.14–7.38 (m, 9H, Ar-H), 6.02 (s, 1H, CH), 3.63 (s, 3H, CH_3); ^{13}C NMR (62.90 MHz, CDCl_3): δ (ppm) = 166.27, 164.12, 138.42, 137.35, 135.15, 128.90, 128.79, 124.51, 125.54, 123.16, 123.08, 113.75, 79.81, 51.71; FT-IR (KBr $\nu_{\text{max}}/\text{cm}^{-1}$): 3316, 3051, 2960, 1788, 1692, 1027.

2.4n Methyl-2-(4-bromophenyl)-5-oxo-4-(phenylamino)-2,5-dihydrofuran-3-carboxylate (4n)⁵¹: M.p.: 164–166 °C; ^1H NMR (250.13 MHz, CDCl_3): δ (ppm) = 8.20 (br s, 1H, NH), 7.14–7.53 (m, 9H, Ar-H), 6.01 (s, 1H, CH), 3.62 (s, 3H, CH_3); ^{13}C NMR (62.90 MHz, CDCl_3): δ (ppm) = 166.25, 164.11, 138.41, 137.32, 135.02, 131.85, 129.05, 125.55, 123.36, 123.36, 122.06, 113.68, 51.72, 79.88; FT-IR (KBr $\nu_{\text{max}}/\text{cm}^{-1}$): 3321, 3051, 2956, 1778, 1693, 1028.

2.4o Methyl-2-(naphthalen-2-yl)-5-oxo-4-(phenylamino)-2,5-dihydrofuran-3-carboxylate (4o): M.p.: 176–178 °C; ^1H NMR (250.13 MHz, CDCl_3): δ (ppm) = 8.30 (br s, 1H, NH), 7.23–7.88 (m, 12H, Ar-H), 6.24 (s, 1H, CH), 3.59 (s, 3H, CH_3); ^{13}C NMR (62.90 MHz, CDCl_3): δ (ppm) = 166.22, 164.39, 138.54, 137.51, 133.72, 133.31, 128.77, 128.66, 128.21, 127.81, 127.65, 126.77, 126.52, 125.43, 124.01, 123.10, 114.33, 80.93, 51.75; FT-IR (KBr $\nu_{\text{max}}/\text{cm}^{-1}$): 3314, 3048, 2956, 1781, 1640, 1027.

2.5 X-ray crystallography

Synthesized pure powder of ethyl 5-oxo-2-phenyl-4-(phenylamino)-2,5-dihydrofuran-3-carboxylate (**4a**) was solved in hot ethanol. X-ray quality crystals of **4a** were obtained in excellent yield after gradual evaporation of the mother liquor at room temperature.

The crystallographic measurement of **4a** was carried out on a Kuma KM4-CCD κ -geometry automated four-circle diffractometer equipped with a CCD Sapphire2 camera, respectively, and graphite-monochromatized $\text{MoK}\alpha$ radiation ($\lambda =$

Figure 3. FT-IR spectra of (a) Fe_3O_4 MNPs, (b) Fe_3O_4 -CPTMS and (c) Fe_3O_4 -TMG.

Figure 4. XRD patterns of (a) Fe_3O_4 MNPs and (b) Fe_3O_4 -TMG.

0.71073 Å). The data were gathered at 100(2) by using the Oxford-Cryosystems cooler. Data were corrected for Lorentz and polarization effects. Data collection, cell refinement, data reduction and analysis were done with *CrysAlisCCD* and *CrysAlisRED*, respectively.⁵³ The structure was solved by direct methods with the *SHELXS97* program,⁵⁴ and refined by a full-matrix least-squares technique with *SHELXL2014*⁵⁵ and anisotropic thermal parameters for all non-H atoms. H atoms were found in difference Fourier maps. In the final refinement cycles, the C-bonded H atoms were repositioned in their calculated positions and refined using a riding model, with C–H = 0.95–1.00 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for CH, CH_2 and $1.5U_{\text{eq}}(\text{C})$ for CH_3 . N-bonded H atom was refined freely. Figures were made with the Diamond

Figure 5. (a) SEM and (b) TEM images of Fe_3O_4 -TMG.

program.⁵⁶ Details of the conditions for the data collection and the structure refinement are given in the crystallographic information file (CIF) deposited with The Cambridge Crystallographic Data Centre (www.ccdc.cam.ac.uk/; deposition number CCDC-1468805) and provided as Supplementary Information.

Crystal data for 4a: $\text{C}_{19}\text{H}_{17}\text{NO}_4$, $M_w = 323.33$, yellowish block, crystal size $0.55 \times 0.42 \times 0.33$ mm, orthorhombic, space group $Pbca$, $a = 16.317(5)$, $b = 7.390(2)$, $c = 25.973(8)$ Å, $V = 3131.9(16)$ Å³, $T = 100(2)$ K, $Z = 8$, $\mu = 0.10$ mm⁻¹ (for MoK α , $\lambda = 0.71073$ Å), multi-scan absorption correction, $T_{\min} = 0.765$, $T_{\max} = 1.000$, 25010 reflections measured, 5116 unique ($R_{\text{int}} = 0.054$), 3732 observed ($I > 2\sigma(I)$), $(\sin\theta/\lambda)_{\max} 0.840$ Å⁻¹, 222 parameters, 0 restraints, $R = 0.055$, $wR = 0.142$ (observed refl.), $GOOF = S = 1.00$, $(\Delta\rho_{\max}) = 0.50$ and $(\Delta\rho_{\min}) = -0.27$ e · Å⁻³.

3. Results and Discussion

3.1 Characterization of catalyst

Tetramethylguanidine-functionalized silica-coated iron oxide magnetic nanoparticles (Fe_3O_4 -TMG) as a catalyst was prepared by the indicated summary path in Scheme 2. The detailed description of the catalyst preparation is given in preparation section of catalyst.

The catalyst was characterized using a variety of different techniques. The FT-IR spectrum of the Fe_3O_4 MNPs is demonstrated in Figure 3a. The principle absorption band at 630 cm⁻¹ corresponded to the characteristic vibration absorption peak of Fe–O bond.

Table 1. The effect of the solvents on the synthesis of furanone derivatives.

Entry	Solvent	Time (h)	Yield (%) ^a
1	Water	12	32
2	Water–Ethanol	12	82
3	Ethanol	12	91
4	Methanol	12	74
5	Water–acetonitrile	12	69
6	Acetonitrile	12	75

Reaction conditions: aniline **1** (1 mmol), diethyl ethynedicarboxylate **2** (1 mmol), 4-chlorobenzaldehyde **3f** (1 mmol), tetramethylguanidine-functionalized silica-coated iron oxide magnetic nanoparticles (80 mg) in different solvents (2 mL) at 40°C .

^a Isolated yield.

Moreover, a broad absorption band is present at 3423 cm⁻¹ for stretching mode of the large number of OH groups.

Fe_3O_4 MNPs coated by (3-chloropropyl)-trimethoxysilane (Fe_3O_4 @CPTMS) is confirmed by the bands at 2922 , 2852 and 1099 cm⁻¹ assigned C–H stretching vibrations and Fe–O–Si, respectively in Figure 3b. In addition, tetramethylguanidine-functionalized silica-coated iron oxide magnetic nanoparticle (Fe_3O_4 @TMG) is affirmed with 1443 and 1635 cm⁻¹ bands corresponding to the C–N and C=N stretch respectively are shown in Figure 3c.

The X-ray powder diffraction (XRD) measurements uncoated Fe_3O_4 MNPs and coated Fe_3O_4 -TMG were

Scheme 3. Synthesis of **4f** in the presence of Fe_3O_4 -TMG.

determined by XRD analysis (Figure 4). The results indicate that the cubic spinel structure of Fe_3O_4 MNPs (JSPDS Card no. 01-075-0449). Observed Miller indices in (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), and (4 4 0) planes is related to a series of diffraction peaks at $2\theta = 30.66^\circ, 35.78^\circ, 43.53^\circ, 53.47^\circ, 57.83^\circ$ and 63.25° , respectively. The average diameter of the Fe_3O_4 -TMG nanoparticles was characterized to be 20 nm by the well-known Debye-Scherrer equation via XRD data ($D = 0.94\lambda/B \cos \theta$) according to the broadening of the (3 1 1) characteristic peak of the XRD pattern. The results show prosperous grafting of tetramethylguanidinone to magnetic nanoparticles (Figure 4). Although peak height has decreased because of coating, the cubic spinel structure of Fe_3O_4 MNPs has been preserved during grafting.

The scanning electron microscopy (SEM) image demonstrated external morphology and particle size and of the Fe_3O_4 -TMG powder as a catalyst (Figure 5a). It can be seen from the SEM image, the size of the grains of nanoparticles with spherical morphology is 18–25 nm that is according with the XRD pattern. The morphology and particles size of the Fe_3O_4 -TMG was investigated by transmission electron microscopy (TEM) image (Figure 5b). This image has revealed more accurate information on the grains measure and morphology of nanocatalyst. The mean size of the spherical particles was 20 nm which is fully consistent with the sizes of the XRD pattern and SEM image.

The thermogravimetric analysis (TGA) curves illustrate the decomposition of the Fe_3O_4 -CPTMS and Fe_3O_4 -TMG. In both curves, the first step at 25–150 °C is ascribed to the elimination of physical and chemical absorption of water. In the next step, the weight loss of organic groups (3-chloropropyl)-trimethoxysilane

Table 2. The effect of temperature on the synthesis of furanone derivatives.

Entry	Temperature	Time (h)	Yield (%) ^a
1	Room temperature	12	75
2	40	12	91
3	60	12	91
4	80	12	88

Reaction conditions: aniline **1** (1 mmol), diethyl ethynedicarboxylate **2** (1 mmol), 4-chlorobenzaldehyde **3f** (1 mmol), tetramethylguanidine-functionalized silica-coated iron oxide magnetic nanoparticles (80 mg) in ethanol solvent (2 mL) at different temperature.

^a Isolated yield.

Table 3. The effect of the catalyst amount on the synthesis of furanone derivatives.

Entry	Catalyst (mg)	Time (h)	Yield (%) ^a
1	–	12	38
2	25	12	66
3	50	12	75
4	80	12	91

Reaction conditions: aniline **1** (1 mmol), diethyl ethynedicarboxylate **2** (1 mmol), 4-chlorobenzaldehyde **3f** (1 mmol), various amounts of tetramethylguanidine-functionalized silica-coated iron oxide magnetic nanoparticles in ethanol solvent (2 mL) at 40 °C.

^a Isolated yield.

(CPTMS) and tetramethylguanidine (TMG) was calculated 3.3% and 14.36% at 200–800 °C, respectively (Figures S46 and S47 in Supplementary Information).

Table 4. Tetramethylguanidine-functionalized silica-coated iron oxide magnetic nanoparticles catalyzed synthesis of furanone derivatives.

Entry	Ar	R	Product	Time (h)	Yield (%) ^a
1	Ph	Et	4a	12	85
2	2-NO ₂ -C ₆ H ₄	Et	4b	12	82
3	4-NO ₂ -C ₆ H ₄	Et	4c	10	89
4	4-F-C ₆ H ₄	Et	4d	10	91
5	2-Cl-C ₆ H ₄	Et	4e	12	90
6	4-Cl-C ₆ H ₄	Et	4f	12	91
7	4-Br-C ₆ H ₄	Et	4g	12	85

Table 4. (contd.)

Entry	Ar	R	Product	Time (h)	Yield (%) ^a
8	2-Naphthal	Et	4h	12	90
9	4-Me-C ₆ H ₄	Et	4i	13	92
10	4-MeS-C ₆ H ₄	Et	4j	11	89
11	Ph	Me	4k	12	91
12	3-Cl-C ₆ H ₄	Me	4l	13	87
13	4-Cl-C ₆ H ₄	Me	4m	12	89
14	4-Br-C ₆ H ₄	Me	4n	12	87
15	2-Naphthal	Me	4o	12	89

Reaction conditions: aniline **1** (1 mmol), dialkylethylenedicarboxylate **2** (1 mmol), aldehyde **3a–o** (1 mmol), tetramethylguanidine-functionalized silica-coated iron oxide magnetic nanoparticles (80 mg) in ethanol solvent (2 mL) at 40 °C.

^b Isolated yield.

Figure 6. X-ray structure of (*R*)-**4a**, showing the atom-numbering scheme and the symmetry-independent hydrogen bond (dashed line). Displacement ellipsoids are drawn at the 50% probability level.

3.2 Application of Fe_3O_4 -TMG in the synthesis of furanone derivatives

To survey the appropriate conditions for the synthesis of furanone derivatives (**4a–o**), various reaction conditions have been checked. We optimized the reaction conditions such as effects of solvent, temperature and catalyst amount.

To begin, different solvents listed in Table 1 were investigated in the synthesis of **4f** as a sample compound (Scheme 3). The foremost option was selected by the reaction of aniline **1**, diethyl acetylenedicarboxylate **2**, 4-chlorobenzaldehyde **3f** and tetramethylguanidine-functionalized silica-coated iron oxide magnetic nanoparticles as a catalyst in ethanol solvent at 40 °C to produce **4f** in 12 h with 91% yield (Table 1, entry 3). Other solvents are in (Table 1, entries 1, 2 and 4–6) afforded low to moderate yields of the desired products.

It may be mentioned that we tested some reactions (Scheme 3) at room temperature 40, 60 and 80 °C in 12 h (Table 2). At room temperature, the mixture of starting materials was seen during the reaction. After increasing the temperature to 40 °C, after 12 h the reaction was completed with 91% yield (Table 2, entry 2). Raising the temperature to 60 °C did not have any great impact on the yield of the reaction. Of course, increasing the temperature to 80 °C has caused reducing the main product. Therefore, the temperature, 40 °C was chosen as the appropriate temperature for the reactions.

To find out the optimized amount of the magnetic nanoparticles supported tetramethylguanidine catalyst for the synthesis of compound **4f** (Table 4, entry 6) was carried out by varying the quantity of catalyst, as shown below (Table 3, entries 2–4). The maximum yield of the compound **4f** was seen when 80 mg of catalyst was applied.

After detecting more efficient and green solvent, the desired temperature and amount of catalyst, all reactions were examined with optimized values conforming to Scheme 1. Thereafter, aromatic aldehydes (**3a–o**) containing different groups on the aromatic ring at *ortho*, *meta*, and *para* positions were appraised. As shown in (Table 4), the reaction times lasted from 10 to 13 h and yields of the isolated products were good-to-excellent (81–92%). Some aldehydes such as trans-cinnamaldehyde, salicylaldehyde, 5-bromosalicylaldehyde, 4-(dimethylamino) benzaldehyde, acetaldehyde, 2-hydroxy-1-naphthaldehyde, pyrrole-2-carboxaldehyde, thiophene-2-carboxaldehyde, furfural, 3-phenylpropionaldehyde, isobutyraldehyde, formaldehyde and glyoxal under the reaction conditions were tested, but desired product could not be produced and the mixture of starting materials and another product was seen (based on TLC investigation). 3-pyridinecarboxaldehyde, 4-pyridinecarboxaldehyde and 4-hydroxybenzaldehyde had low yield under the same conditions.

Eventually, the reusability and catalytic activity of Fe_3O_4 -TMG under the model reaction for the synthesis of compound **4f** (Table 4, entry 6) were considered. Every time, the catalyst was separated with an external magnet from the reaction mixture, rinsed with ethanol, dried at room temperature to remove any remaining ethanol and reused in the subsequent reactions. The yields for five consecutive runs were 91, 90, 91, 89 and 92%, respectively. The results showed that the catalyst could be reused for five times without any excessive reduction in its function.

As far as we know, this procedure is the most efficient, clean and convenient procedure, and is applicable

Table 5. Hydrogen-bond and C–H $\cdots$ π contacts geometry (Å, °) for **4a**.

<i>D</i> –H $\cdots$ <i>A</i>	<i>D</i> –H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> –H $\cdots$ <i>A</i>
N1–H1N $\cdots$ O3	0.89(2)	2.19(2)	2.842(2)	130(2)
C6–H6 $\cdots$ O3 ⁱ	0.95	2.50	3.272(2)	139
C15–H15 $\cdots$ O2 ⁱⁱ	0.95	2.46	3.286(2)	146
C19–H19 $\cdots$ Cg1 ⁱ	0.95	2.60	3.407(2)	143

Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x + 1/2, y - 1/2, z$; Cg1 is the centroid of the C5 ~ C10 ring.

Figure 7. The arrangement of the molecules of **4a** in the crystal lattice: centrosymmetric molecular dimers built up from two molecules (*e.g.*, indigo-grey) joined by two C–H...O and two C–H... π interactions (dashed and dotted lines, respectively), and the inter-dimeric C15–H15...O2ⁱⁱ contacts. Symmetry codes are given in Table 5; (iii) $x + 0.5, -y + 1.5, -z + 1$.

for the synthesis of different furan-2(5*H*)-ones. The structures of all products were concluded by FT-IR, ¹H NMR and ¹³C NMR spectral data. The structure of compound **4a** was additionally confirmed by single-crystal X-ray diffraction. The compound crystallizes in the centrosymmetric space group *Pbca*. Thus, the crystal contains racemic compound **4a**. The molecular structure of (*R*)-enantiomer is presented in Figure 6.

The C(O)OEt group is coplanar with the plane of the furan-2(5*H*)-one ring, which is reflected by the values of the following torsion angles that are close to 0° or 180°: [C11–O4–C12–C13 179.44(10)°; C12–O4–C11–O3 3.20(16)°; C2–C3–C11–O3 3.78(18)°; N1–C2–C3–C11–3.46(19)°]. The C=O_{ester}, C–NH *syn*-periplanar arrangement is stabilized by the intramolecular N1–H1N...O3 hydrogen bond (H...O 2.19(2) Å, N...O 2.842(2) Å, N–H...O angle 130(2)°). The N-bonded phenyl ring is slightly displaced out of the furan 2(5*H*)-one plane [C14–N1–C2–C1–29.06(17)°], and is additionally twisted relative to the N1–C2 bond [C2–N1–C14–C15–24.35(17)°]. Thus, the angle between the Ph ring and furan 2(5*H*)-one moiety is about 45°. The geometrical parameters for **4a** are given in the crystallographic information file (CIF) provided as Supplementary Information.

In the crystal lattice of **4a**, two molecules of the opposite chirality are joined to each other by two C–H...O and two C–H... π interactions (Table 5). The adjacent dimers are joined to each other by the C15–H15...O2ⁱⁱ contacts to form tapes displayed in Figure 7.

4. Conclusions

One-pot three-component synthesis of a variety of furanone derivatives has been developed using tetramethylguanidine-functionalized silica-coated iron oxide magnetic nanoparticles (Fe₃O₄-TMG) as a green, efficient and recyclable catalyst. The mild reaction conditions, simple work-up, the good-to-high yield of products and use of magnetic nanocatalyst are some of the superior features of this method.

Supplementary Information (SI)

Copies of the original spectra, FT-IR (Figures S1, S4, S7, S10, S13, S16, S19, S22, S25, S28, S31, S34, S37, S40, S43), ¹H NMR (Figures S2, S5, S8, S11, S14, S17, S20, S23, S26, S29, S32, S35, S38, S41, S44), ¹³C NMR (S3, S6, S9, S12, S15, S18, S21, S24, S27, S30, S33, S36, S39, S42, S45) of all the compound reported in the experimental section, TGA (Figures S46 and S47) and FT-IR spectrum of tetramethylguanidine (Figure S48) and crystallographic information of compound **4a** (CIF file) provided are included in Supplementary Information. Supplementary Information is available at www.ias.ac.in/chemsci.

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