

RESEARCH PAPER

Synthesis of furans using biosynthesized Ag nanostructures as a highly effective and easily retrievable catalyst

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ABSTRACT

Nano-Ag as a green heterogeneous catalyst was utilized for the synthesis of furans by the three-component reaction of phenylglyoxal, dimethyl acetylenedicarboxylate, and primary amines. The best results were obtained in the presence of 4 mol% of nano-Ag in CH₂Cl₂ at room temperature. The nanocatalyst was characterized by UV-VIS, FT-IR, XRD, SEM and EDS. Ag nanostructures were prepared using extract of Echinium amoenum. Some of the substantial features of this method include experimental simplicity, wide range of products, excellent yields in short reaction times, reusability of the catalyst, and low catalyst loading.

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INTRODUCTION

Furan derivatives indicate anti-oxidation [1], antimicrobial [2], antimalarial [3], anticancer [4], anti-AIDS [5], anti-inflammatory [6], and anti-diabetic [7] activities. Exploring an effective procedure for the synthesis of furans is a serious challenge. The preparation of furans has been studied using catalysts including K[Al(SO₄)₂].12H₂O [8], N-methyl 2-pyrrolidonium hydrogen sulfate [9], formic acid [10], SnCl₂.2H₂O [11] β-cyclodextrin [12], tetra-*n*-butylammonium bisulfate [13], Al(HSO₄)₃ [14], HY Zeolite [15], and Vitamin B12 [16]. Each of these catalysts may have its own benefits but also suffer from such apparent disadvantages as high reaction times, complicated work-up, low efficiency, or unwanted reaction conditions. Despite the use of these procedures, there remains the need for further new ways for the

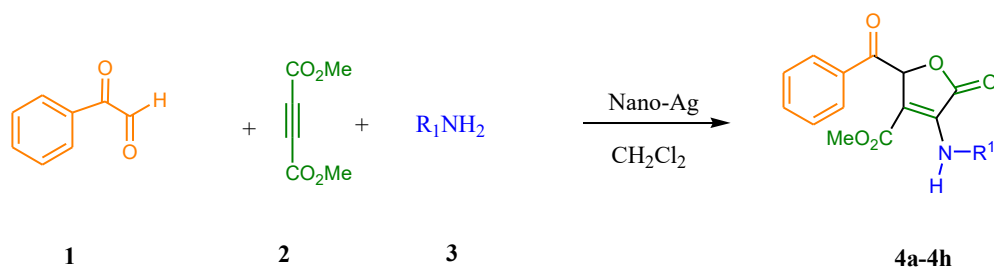
preparation of furans. Nanoparticles have drawn notable attention as effective catalysts in many organic reactions due to their high surface-to-volume ratio and coordination parts which create a larger number of active sites per unit area in comparison with their heterogeneous counter sites [17-18]. Recently, green synthesis of metallic nanoparticles (NPs) has attracted a lot of attention. The biosynthetic ways for the synthesis of metal NPs have several benefits including simplicity, low toxicity, low cost, as well as suitability for biomedical and pharmaceutical applications. Among biosynthetic routes for the synthesis of metal nanoparticles, plant extracts have received substantial attention due to their simple sampling and environmental friendliness. In addition, they have reducing and antioxidant effects [19-26]. Herein, we report the use of Ag nanoparticles as an efficient

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Scheme 1. Synthesis of furans using Ag nanostructures

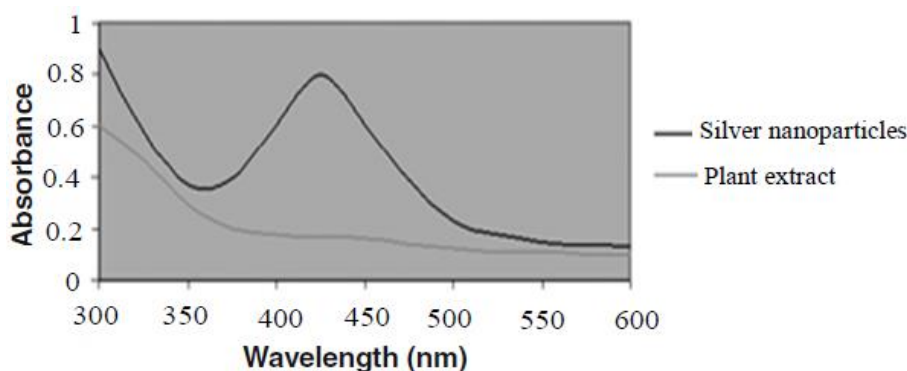


Fig. 1. UV-VIS of Ag nanostructures and plant extract

catalyst for the preparation of furans by the multi-component reactions of phenylglyoxal, dimethyl acetylenedicarboxylate, and primary amines (Scheme 1).

EXPERIMENTAL SECTION

General

All materials were commercially purchased from Merck and Sigma-Aldrich. Samples of *Echium amoenum* were collected from Jennat Rudbar area (Mazandaran, Iran). Powder X-ray diffraction (XRD) was carried out on a Philips diffractometer of X'pert Company with monochromatized Ag K α radiation ($\lambda = 1.5406 \text{ \AA}$). Electronic spectrum of the samples was taken on a JASCO UV-vis scanning spectrometer (Model V-670). The Scanning Electron Microscopy and Energy Dispersive X-ray analysis (MIRA3-TESCAN FESEM) was used to provide information about morphology and elemental composition. Furthermore, Fourier transform infrared measurements were carried out on Magna 550 instrument by using potassium bromide (KBr) plates. NMR spectra were recorded on a Bruker 400 MHz spectrometer with DMSO- d_6 as solvent and TMS as internal standard.

Biosynthesized silver nanoparticles

Samples of *Echium amoenum* were completely powdered. 20 g of *Echium amoenum* powder was mixed with 200 ml of deionized water in a 500-ml flask. Then it was placed under a magnetic stirrer for 24 hours at 70 °C and extraction was performed by centrifugation. In the next step, 10 ml of the extract with 90 ml solution of AgNO $_3$ 1 mM was placed on a magnetic stirrer for 3 hours and centrifuged again and the resulting precipitate was dried in an oven for 20 hours. XRD, FT-IR, FE-SEM, Mapping, and EDAX analyses were employed to confirm the final product. Further, the supernatant of the centrifuged sample was used for UV-VIS testing

Synthesis of furans using biosynthesized Ag nanostructures

A mixture of amine (1 mmol) dimethyl acetylenedicarboxylate (1 mmol), phenylglyoxal (1 mmol), and Ag nanocatalyst (4 mol%) was stirred in dichloromethane (10 mL) at room temperature. After completion, as indicated by TLC (EtOAc-petroleum ether, 2:8), the nanocatalyst was separated from the mixture using filtration. The solvent was evaporated under vacuum and the products were obtained. The characterization data of the compounds are given below.

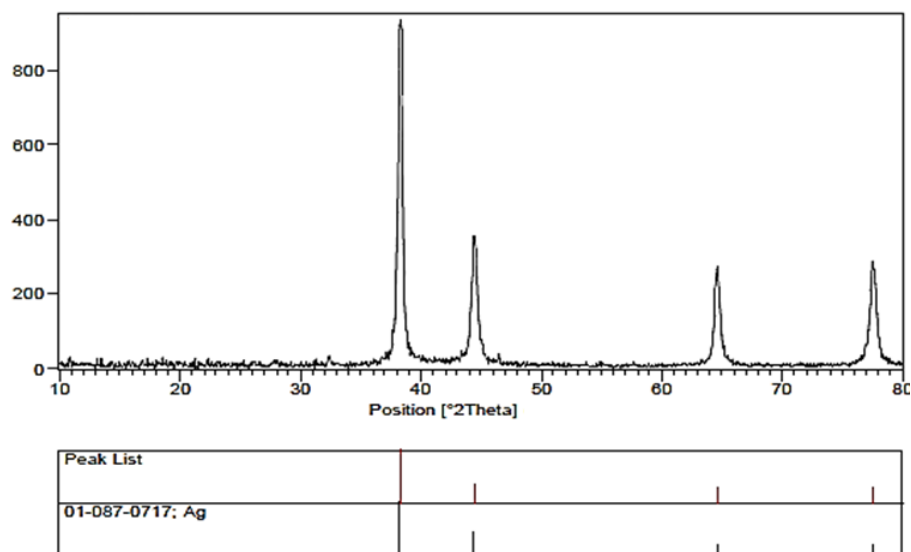


Fig. 2. XRD of Ag nanostructures

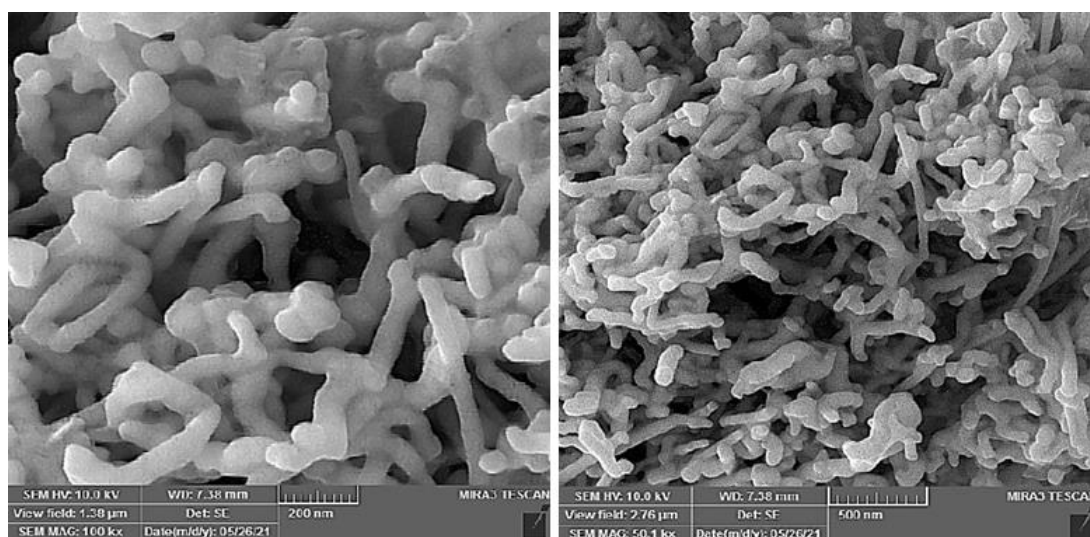


Fig. 3. SEM of Ag nanostructures

Methyl 2-benzoyl-4-[(2-methoxybenzyl)amino]-5-oxo-2,5-dihydro-3-furancarboxylate (4a):

Yellow oil, FT-IR (KBr): 3402, 3052, 3004, 1771, 1705, 1675, 1604, 1476, 1122 cm^{-1} ; $^1\text{H NMR } \delta$ 8.04-6.92 (m, 9H, ArH), 6.25 (s, 1H, CH), 5.02-4.95 (m, 2H, CH_2), 3.87, 3.56 (2s, 6H, 2MeO), 2.20 (s, 1H, NH). $^{13}\text{C NMR } \delta$ 192.4, 164.5, 164.4, 157.3, 136.4, 135.2, 129.5, 129.4, 128.4, 128.1, 127.4, 126.7, 124.3, 110.6, 105.3, 76.1, 56.9, 52.5, 42.8. Anal. Calcd. for $\text{C}_{21}\text{H}_{19}\text{NO}_6$: C 66.13, H 5.02, N 3.67. Found: C 66.16, H 4.94, N 3.721.

Methyl 2-benzoyl-4-[(4-methoxybenzyl)amino]-5-oxo-2,5-dihydro-3-furancarboxylate (4b):

Yellow oil, FT-IR (KBr): 3302, 3105, 3006, 1752, 1702, 1675, 1602, 1478, 1468, 1379, 1102 cm^{-1} ; $^1\text{H NMR } \delta$ 8.09-6.92 (m, 9H, ArH), 6.42 (s, 1H, CH), 4.92-4.80 (m, 2H, CH_2), 3.84, 3.52 (2s, 6H, 2MeO), 2.69 (s, 1H, NH), $^{13}\text{C NMR } \delta$ 192.6, 169.1, 162.4, 159.2, 156.4, 155.2, 154.1, 153.2, 135.2, 135.1, 107.2, 105.4, 76.1, 60.2, 57.4, 44.6. Anal. Calcd. for $\text{C}_{21}\text{H}_{19}\text{NO}_6$: C, 66.13; H, 5.02; N, 3.67;. Found: C, 66.15; H, 5.07; N, 3.72.

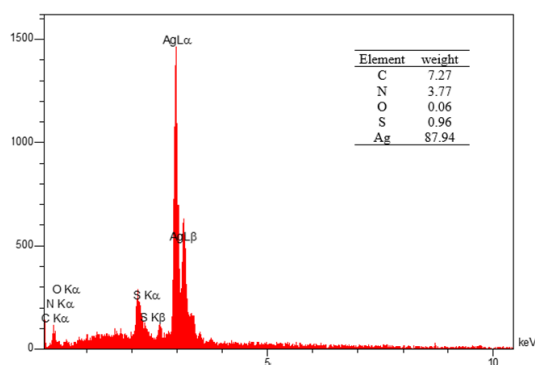


Fig. 4. EDS of nanocatalyst

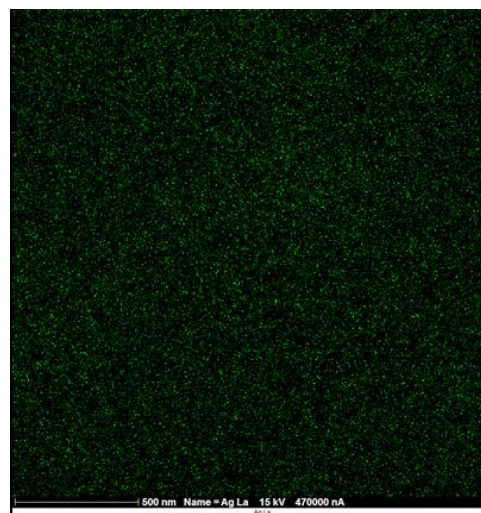


Fig. 5. The elemental mapping of nanostructure in the extract

Table 1: Optimization of reaction conditions ^a

Entry	Solvent	Catalyst (mol%)	Time (min)	Yield ^b %
1	CH ₂ Cl ₂	—	400	12
2	CH ₂ Cl ₂	Et ₃ N (5)	250	38
3	CH ₂ Cl ₂	ZrOCl ₂ .8H ₂ O (6)	300	24
4	CH ₂ Cl ₂	<i>p</i> -TSA (10)	350	16
5	CH ₂ Cl ₂	SnCl ₂ (5)	350	40
6	CH ₂ Cl ₂	nano-CuI (5)	250	53
7	CH ₂ Cl ₂	nano-AgO (8)	200	43
8	CH ₂ Cl ₂	nano-Ag (2)	80	85
9	CH ₂ Cl ₂	nano-Ag (4)	80	94
10	CH ₂ Cl ₂	nano-Ag (5)	80	94
11	CH ₃ CN	nano-Ag (5)	120	52
12	CHCl ₃	nano-Ag (5)	100	84
13	DMF	nano-Ag (5)	120	62
14	EtOH	nano-Ag (5)	160	40

^a Reaction conditions: 2-methoxybenzylamine (1 mmol) dimethyl acetylenedicarboxylate (1 mmol), phenylglyoxal (1 mmol)

^b Isolated yield

Methyl 2-benzoyl-4-[(4-methylbenzyl)amino]-5-oxo-2,5-dihydro-3-furancarboxylate (4c):

Yellow oil, FT-IR (KBr): 3455, 3054, 3005, 1738, 1704, 1605, 1473, 1468, 1105 cm⁻¹; ¹H NMR δ 8.06-7.10 (m, 9H, ArH), 6.25 (s, 1H, CH), 4.82-4.92 (m, 2H, CH₂), 3.65 (s, 3H, OCH₃), 2.95 (s, 1H, NH), 2.28 (s, 3H, CH₃). ¹³C NMR δ 192.8, 168.2, 164.7, 138.2, 137.5, 136.7, 130.2, 129.8, 128.4, 127.8, 127.5, 127.4, 105.6, 76.1, 50.2, 48.6, 22.4. Anal. Calcd. for C₂₁H₁₉NO₅: C 69.03, H 5.24, N 3.83. Found: C 69.09, H 5.21, N 3.87.

RESULTS AND DISCUSSION

Ag nanostructures were synthesized using

Echium amoenum extract. In this study we focused on the preparation of nanoparticles in aqueous media using reducing activities of antioxidant phytochemicals inside the plant especially polyphenolics and polyhydroxyl as the main reducing and highly polar agents, respectively, in *Echium amoenum* extract. The UV-VIS absorption spectrum of plant extract and prepared Ag nanoparticles is given in Fig. 1 which shows a characteristic peak centered at 400 nm in the visible light area.

The powder X-ray diffraction (XRD) pattern of the synthesized Ag nanoparticles is depicted in Fig. 2. The pattern agrees well with the reported pattern

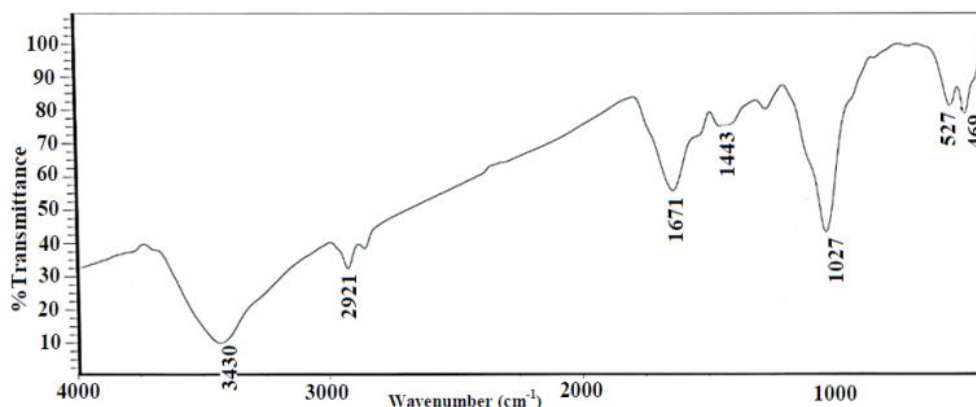
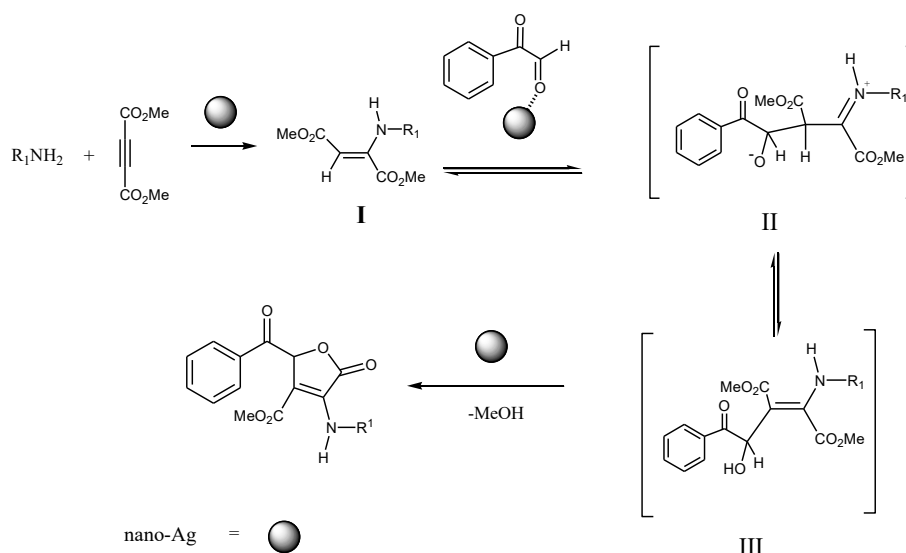


Fig. 6. FT-IR of Ag nanostructures -Echinium amoenum extract



Scheme 2. Schematic mechanism for the catalytic activity of Ag nanocatalyst for the synthesis of furans

for Ag nanoparticles (JCPDS No. 01-087-0717). Using XRD data, the crystal size was estimated to be roughly 60 nm.

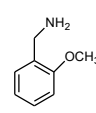
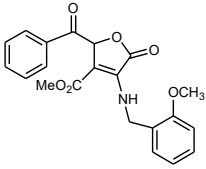
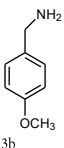
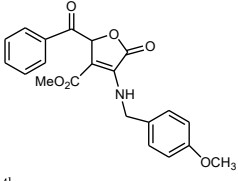
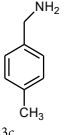
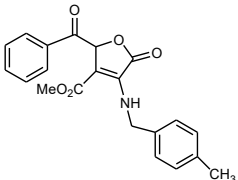
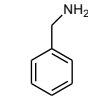
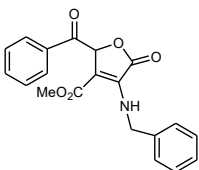
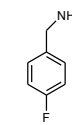
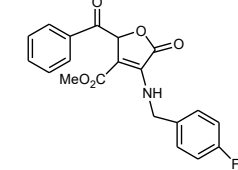
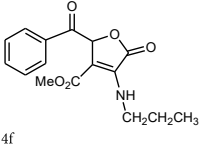
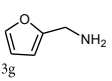
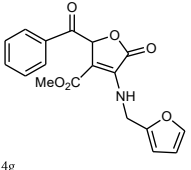
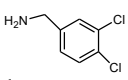
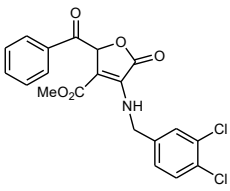
Fig. 3 displays the SEM (scanning electron microscope) images of Ag nanostructures which shows that the nanostructure is a rod with a size of about nanometers.

The elemental compositions of the nanocatalyst were studied by Energy Dispersive Spectroscopy (EDS) (Fig. 4). The elements in the extract include carbon, nitrogen, oxygen, sulfur, and the element in the nanostructure includes silver. In addition, the elemental mapping demonstrates the proper and uniform distribution of the nanostructure in the extract (Fig. 5).

Fig. 6 shows the FT-IR spectra of Ag nanostructures synthesized using *Echinium amoenum* extract. The absorption peak at 3430 cm^{-1} is related to the stretching vibrational absorptions of -OH groups. The peaks at 1670 and 1410 cm^{-1} correspond to the C=O and C=C, respectively, in extract.

At first, to find the optimum conditions, the one-pot reaction of 2-methoxybenzylamine, dimethyl acetylenedicarboxylate, and phenylglyoxal in the presence of the diverse catalysts and solvents was selected as the model reaction for the preparation of 5-oxo-2,5-dihydro-3-furancarboxylates. The best results were gained in dichloromethane, and we found that the reaction gave convincing results in the presence of nano-Ag (4 mol%) at room

Table 2: Synthesis of 5-oxo-2,5-dihydro-3-furancarboxylates using nano-Ag^a

Entry	primary amine	product	Time (min)	Yield ^b %
1			80	94
2			80	92
3			90	89
4			100	87
5			120	84
6	CH ₃ CH ₂ CH ₂ NH ₂ 3f		110	81
7			100	86
8			110	84

a Reaction conditions: primary amines (1 mmol) dimethyl acetylenedicarboxylate (1 mmol), henylglyoxal (1 mmol)

b Isolated yields

temperature (Table 1).

After that, the obtained optimal conditions were applied to perform the reaction of different primary amines in the presence of nano-Ag as the catalyst, in order to afford the corresponding products in high to excellent yields (Table 2).

The reusability of nanocatalyst was studied for the model reaction, and it was found that the product yields lessened only to a very small extent on each reuse (run 1, 94%; run 2, 94%; run 3, 93%; run 4, 93%; run 5, 92%, run 6, 92%). After the completion of the reaction (as determined by TLC), CH_2Cl_2 was added. The nano-Ag was insoluble in CH_2Cl_2 and it could therefore be obtained by simple filtration. The catalyst was washed four times with ethanol and dried at room temperature for 15 h prior to re-use.

Scheme 2 shows a plausible mechanism for this reaction in the presence of nano-Ag. At first, the nucleophilic attack by the amine on dimethyl acetylenedicarboxylate generates the aminobutendioate **I** as an electron-rich enaminone. The subsequent nucleophilic attack of aminobutendioate **I** to the aldehyde carbonyl group of the phenylglyoxal would yield iminium-oxoanion intermediate **II**, which can be tautomerized to intermediate **III**. γ -Lactonization of intermediate **III** would produce the 5-oxo-2,5-dihydro-3-furancarboxylates.

CONCLUSIONS

In this study, we developed a simple way for the synthesis of furans using Ag nanocatalyst as an efficient catalyst in dichloromethane at room temperature. The Ag nanoparticles were prepared using extract of *Echium amoenum* as a green way. The catalyst was characterized by UV-VIS, FT-IR, XRD, SEM and EDS. The structures of the products were deduced from their ^1H NMR, ^{13}C NMR, FT-IR, and elemental analyses. The advantages of this method include its simplicity, the reusability of the catalyst, low catalyst loading, and easy separation of products.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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