

Cite this: *RSC Adv.*, 2018, 8, 38186

Green synthesis of Au nanoparticles using an aqueous extract of *Stachys lavandulifolia* and their catalytic performance for alkyne/aldehyde/amine A^3 coupling reactions†

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High reaction rate and easy availability make green synthesis of metal nanoparticles noticeable. In the present study, gold nanoparticles with wide applications in different fields were synthesized by an ecofriendly method at room temperature using *Stachys lavandulifolia* extract as the reducing agent. Properties of the synthesized gold nanoparticles (GNP) were identified by different analytical techniques including: UV-Vis absorption spectroscopy verified presence of Au NPs in the solution while functional groups of its extract and synthesized Au NPs were determined by FT-IR. Its crystalline analysis with a fcc plane was verified by X-ray diffraction (XRD) and energy dispersive spectroscopy (EDS) determined elements in the sample. Surface morphology, diverse shapes and sizes of the Au NPs were shown by scanning electron microscopy (SEM), atomic force microscopy (AFM), and transmission electron microscopy (TEM). Beginning and end destruction temperatures of the Au/S. *lavandulifolia* NPs were determined by thermal gravimetric analysis (TGA). The Au nanoparticles were capped with extracts, preventing them from oxidation and agglomeration and were used as an efficient heterogeneous nanocatalyst for a three-component reaction of amines, aldehydes, and alkynes (A^3 coupling). A diverse range of propargylamines were obtained in good yields. Furthermore, the separation and recycling of Au/S. *lavandulifolia* NPs was very simple, effective, and economical.

Received 14th August 2018

Accepted 31st October 2018

DOI: 10.1039/c8ra06819d

rsc.li/rsc-advances

1. Introduction

In general, propargylamines are useful in organic chemistry as precursors and versatile building blocks for preparing different nitrogen-comprising heterocyclic compounds as well as main intermediates for synthesizing biologically active medicines and natural products.¹ Additionally, several propargylamines have been applied to treat neuropsychiatric diseases including Parkinson's and Alzheimer's disorders.² Due to their importance, many synthetic methods have been developed.³ However, the most direct and efficient method for preparation of propargylamines is through transition metal-catalyzed three component coupling of an aldehyde, an amine, and a terminal alkyne, which is known as an A^3 coupling reaction.⁴ In recent years, various homogeneous and heterogeneous catalysts have been employed in the synthesis of propargylamine *via* an A^3 -coupling reaction based on transition metals including Zr,⁵ Mn,⁶ Re,⁷ Fe,⁸ Ru,⁹ Co,¹⁰ Ir,¹¹ Ni,¹² Pd,¹³ Cu,¹⁴ Ag,¹⁵ Au,¹⁶ Zn,¹⁷ Cd,¹⁸ and Hg.¹⁹ Among the different transition metals, copper has been widely studied because of its abundance,

low cost, low toxicity, and high reactivity. Although the majority of the catalytic systems were homogeneous, their loss at the end of a reaction reduces their utility especially for industrial applications. Nowadays, metal NPs are considered as heterogeneous catalysts which possess a high surface-to-volume ratio. Because of their enhanced activity and selectivity, they could be a competitive alternative to classical catalysis.^{20,21} Diverse models of traditional chemical²² and green chemistry^{23,24} approaches were applied to produce metal NPs. Amongst all metallic NPs, Au NPs have been widely used in different fields including medicine and gene delivery,²⁷ imaging,²⁸ heating,²⁹ labeling, sensing,³⁰ and catalysis³¹ because of their unique optical features.^{25,26} Applications of green chemistry comprising diverse parts of herbal extracts such as leaves,³² fruit,³³ roots,³⁴ and seeds³⁵ as a reducing agent for synthesizing gold NPs makes them very useful because they have no hazardous materials and are very cheap. Amongst 34 *Stachys* spices, growing in many regions of Iran, Turkey, and Iraq,^{36,37} *Stachys lavandulifolia* (Fig. 1) is used as an herbal tea in Iran for gastrointestinal disorders and extracts of this plant were introduced to have an anxiolytic effect with a lower sedative activity than diazepam.³⁸ *Stachys lavandulifolia* extracts fractions including flavonoids, phenylpropanoids, polyphenols, and terpenoids from the aerial parts of plants were considered to play an important role in anxiolytic effects.³⁹ Acteoside, as one of the secondary metabolites isolated from *S. lavandulifolia* aerial part's extracts, is

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c8ra06819d



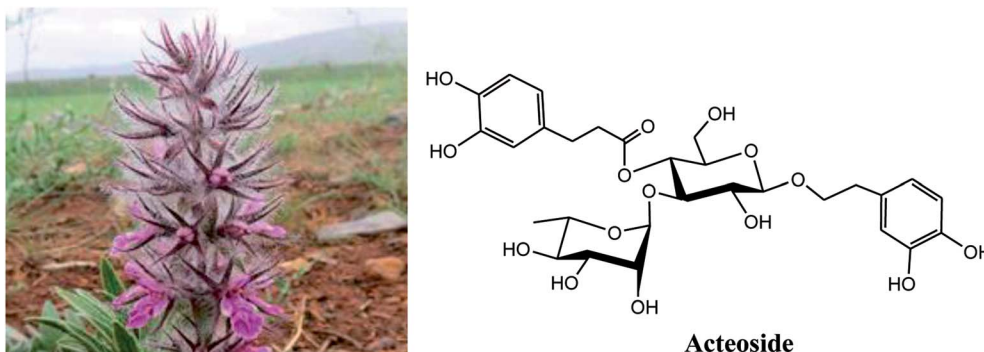


Fig. 1 *Stachys lavandulifolia* image and acteoside structure.

displayed in Fig. 1. Significantly, green preparation of NPs has upsurged as a new nanobiotechnology to produce eco-friendly and inexpensive synthetic procedures for extremely stable NPs and it has emerged as a safer and best alternative to conventional approaches. Due to our ongoing interest on the biosynthesis of metal NPs and heterogeneous catalysts,^{40,41} in the current study Au NPs were prepared for the first time using *Stachys lavandulifolia* through a green method and their morphological, structural, and catalytic applications were studied in detail.

2. Experimental

2.1. Materials and apparatus

All the reagents were purchased from Aldrich and Merck and were used without any purification. Crystalline structures of the samples were evaluated by X-ray diffraction (XRD) analysis on a Bruker D8 Advance Diffractometer with CuK α radiation at 40 kV and 20 mA. Fourier transform infrared (FT-IR) spectra were recorded using KBr pellets with a PerkinElmer 65 spectrophotometer in the range of 400–4000 cm⁻¹. TEM images at an accelerating voltage of 80 KV were taken with a Zeiss-EM10C. Morphology and particle dispersion was investigated by field emission scanning electron microscopy (FESEM) (Cam Scan MV2300). Chemical composition of the prepared nanostructures was measured by EDS (Energy Dispersive X-ray Spectroscopy) performed in SEM. The UV-Vis absorbance spectra were recorded using a double beam UV-visible spectrophotometer (PG Instrument, T80+), equipped with 10 mm quartz cuvettes. The spectra were obtained using a ThermoFisher Scientific K-Alpha XPS spectrometer. Survey spectra were initially obtained at low energy resolution (pass energy –200 eV) followed by the main regions of interest at higher resolution (pass energy –25 eV). A monochromatic Al K α X-ray was used, with a nominal spot size of 400 μ m.

2.2. Preparation of *Stachys lavandulifolia* extract

Freshly collected herbal tea (10 g) from the Kermanshah, Zagros region, was washed, dried, and used for preparation of the *Stachys lavandulifolia* extract. The tea (10 g) was added to

100 mL of Milli-Q water and heated at 60 °C for 15 min. Then, the extract was filtered through Whatman no. 1 filter paper and centrifuged at 6000 rpm for 5 min to remove unwanted aggregates. The filtered extract was stored in a refrigerator at 4 °C for further use.

2.3. Green synthesis of Au NPs using *Stachys lavandulifolia* extract

Different amounts of the *Stachys lavandulifolia* extract (5, 10, 15, and 20 mL) were added to an aqueous solution of (1 mM) HAuCl₄ × H₂O (100 mL) at room temperature and stirred for the purpose of studying time effects and extract concentrations on synthesis of gold nanoparticles. The color of the solution turned red during 2 h and the high concentration of extract created a darker red (Fig. 1S†). Then, solutions containing the nanoparticles were centrifuged at 12 000 rpm for 15 min and the upper phase was removed. Obtained nanoparticles were washed for several times with deionized water and finally dried in an oven at 50 °C.

2.4. General procedure for the synthesis of propargylamine derivatives

The Au NPs catalyst (10 mol%) was added to a mixture of aldehyde (1 mmol), phenylacetylene (1 mmol), and amine (1.2 mmol) in toluene (5 mL) and the mixture was stirred at 100 °C. The progress of the reaction was monitored by TLC. After complete conversion of the aldehyde, the mixture was left to cool down to room temperature and then centrifuged. After evaporation of the solvent, the crude product was obtained. Purification was performed by silica gel column chromatography (70 : 30, hexane/EtOAc). All compounds were known and were characterized by spectral analysis or melting points.^{48–61}

3. Results and discussion

A UV-Vis spectroscopy (PerkinElmer, Lambda 25) instrument at wavelengths of 300–700 nm was used to confirm dimensions and effective preparation of gold NPs. Fig. 2 shows the results



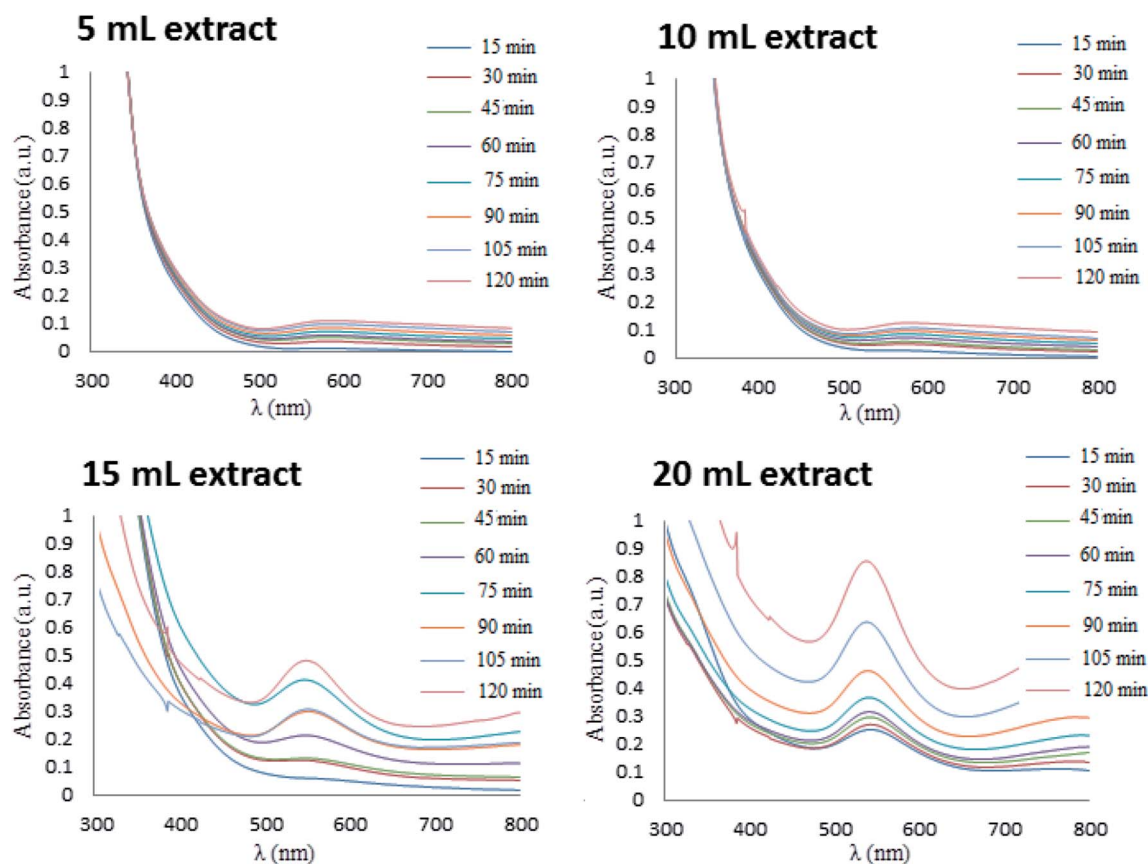


Fig. 2 Extract concentrations and time effect on UV-Vis spectroscopy of synthesized gold nanoparticles.

from comparison of UV-Vis spectra of green synthesized of Au NPs using *Stachys lavandulifolia* extract with diverse levels of extracts at 5, 10, 15, and 20 mL. These results confirm the faster formation of Au NPs in the solution by enhancing contents of the extract. As observed, the amounts of NPs prepared were enhanced over time with all levels of extract.

FT-IR measurements ranging from 400 to 4000 cm^{-1} were applied to identify the responsible phytochemicals during green synthesis of the Au NPs. The FT-IR spectrum of the pure extract, (Fig. 2Sa†) showed several peaks at 3369 cm^{-1} , 2923 cm^{-1} , 1618 cm^{-1} , and 1400 cm^{-1} corresponding to free OH and OH

groups creating hydrogen bonds, saturated hydrocarbons ($\text{Csp}^3\text{-H}$), carbonyl group (C=O), and stretching C=C aromatic ring, respectively. Due to existence of these functional groups in the structure of antioxidant polyphenolics, the spectrum proves the existence of phenolics in the herbal extract and supports the outcomes of relevant research.⁴² Moreover, an FT-IR spectrum corresponding to Au NPs is presented in Fig. 2Sb.† The peaks from Au/*S. lavandulifolia* NPs are nearly identical to Fig. 2Sa† and its representation of the functional groups of biomolecules adsorbed on NPs. The broad band at 3418 cm^{-1} can be attributed to a stretching bond of the hydroxyl functional group and

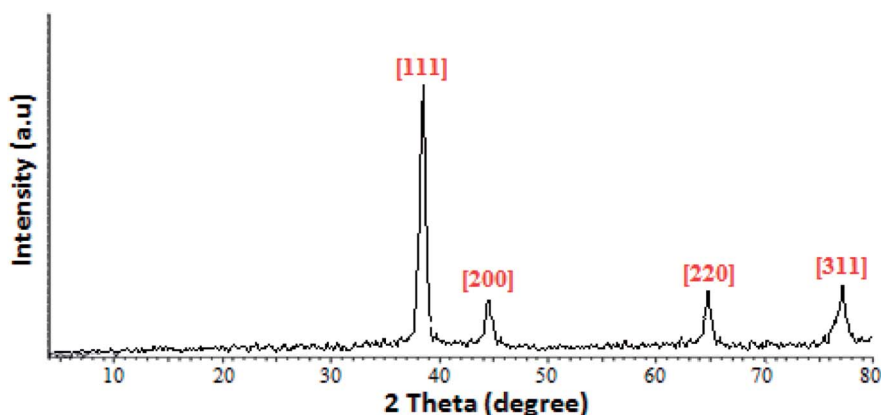


Fig. 3 XRD spectrum of Au/*S. lavandulifolia* NPs.



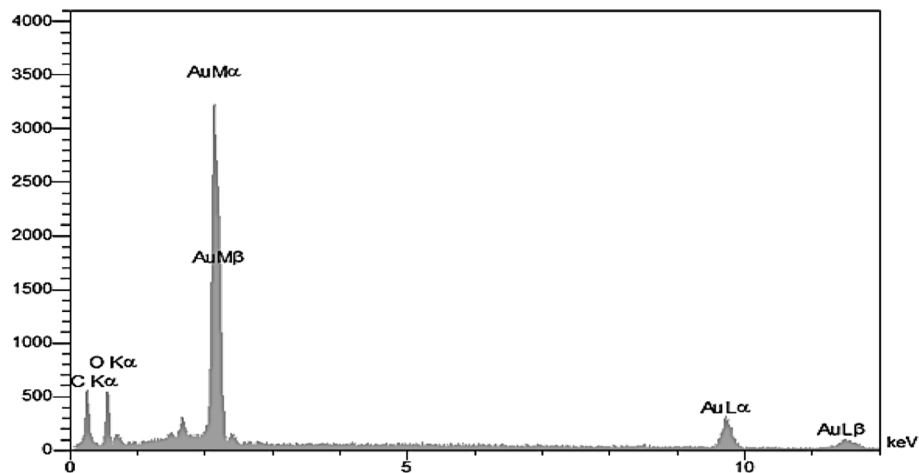


Fig. 4 EDS image of Au/*S. lavandulifolia* NPs.

the band near 1447 cm^{-1} is normally assigned to the bending vibration corresponding to sp^2 -carbon groups of aromatics and 1628 cm^{-1} for a carbonyl functional group.

The structure of prepared Au NPs also was analyzed with XRD by means of a Bruker AXS-D8 Advance instrument working at a voltage of 40 kV and current of 30 mA with CuK radiation. The crystalline feature of Au NPs was confirmed with an X-ray intensity which reflected from crystals which are highest at certain angles. Diffraction peaks appeared at 38.067° , 44.215° , 64.291° , and 77.592° in a 2θ range $100\text{--}80^\circ$ relating to (111), (200), (220), and (311) facets of a face centered cubic crystal structure (JCPDS. no. 004-0784) and showed the crystalline structure of prepared Au NPs with *Stachys lavandulifolia* extract (Fig. 3).

Energy Dispersive X-ray Spectroscopy (TESCAN Vega, USA) verified the existence and purity of particles in the specimens. Fig. 4's EDX spectrum of prepared Au NPs shows a strong signal that reveals presence of pure metallic gold NPs.

A scanning electron microscope (TESCAN Vega Model) was applied for identifying morphology and aggregates of NPs. According to SEM images of Au/*S. lavandulifolia* NPs presented in Fig. 3S,† nanoparticles were formed and their shape was somewhat spherical in nature.

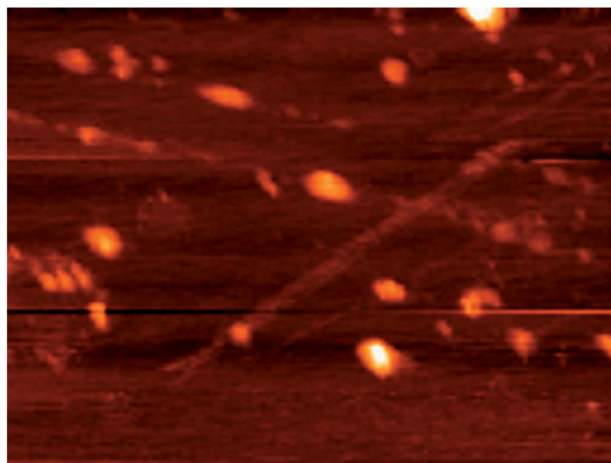


Fig. 5 AFM images of Au/*S. lavandulifolia* NPs.

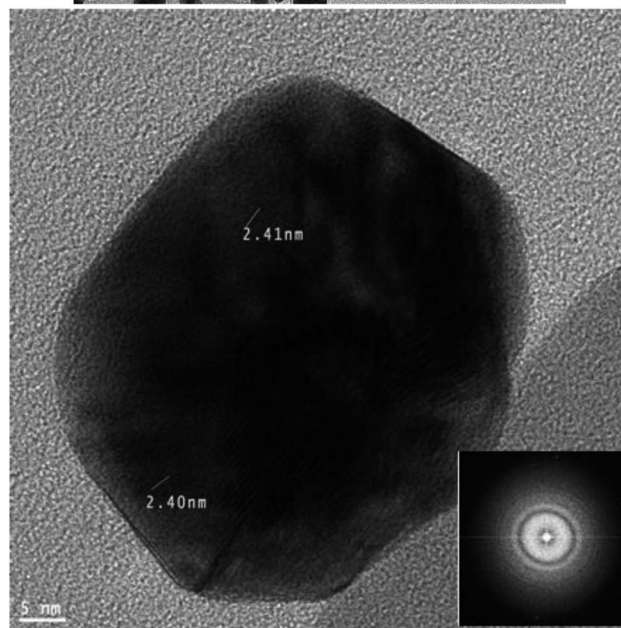
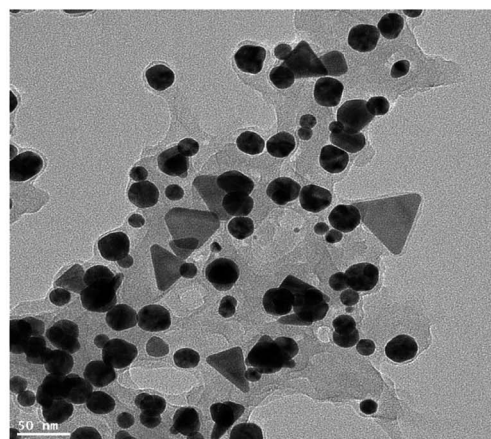


Fig. 6 HR-TEM images of Au/*S. lavandulifolia* NPs and FFT image corresponding to Au NPs (inset).



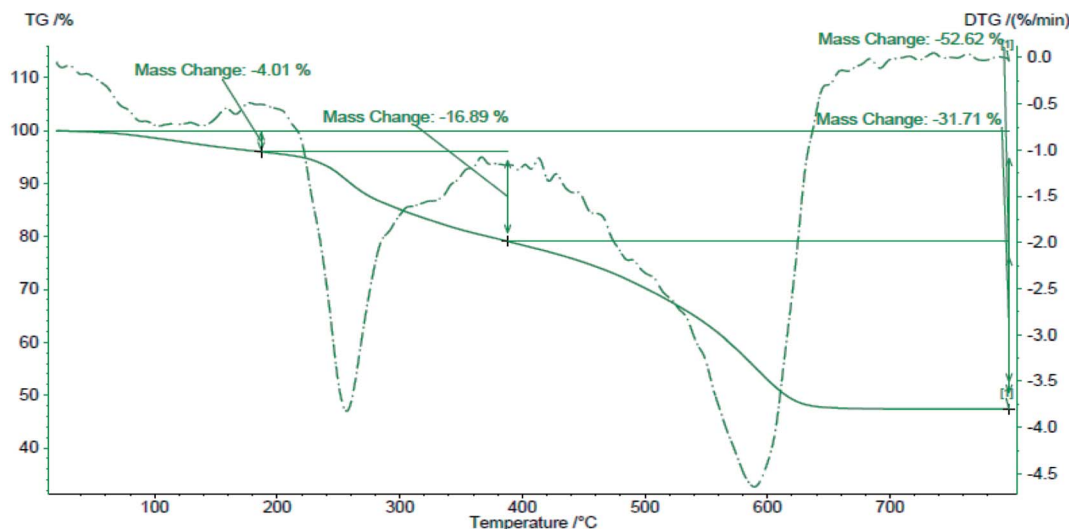


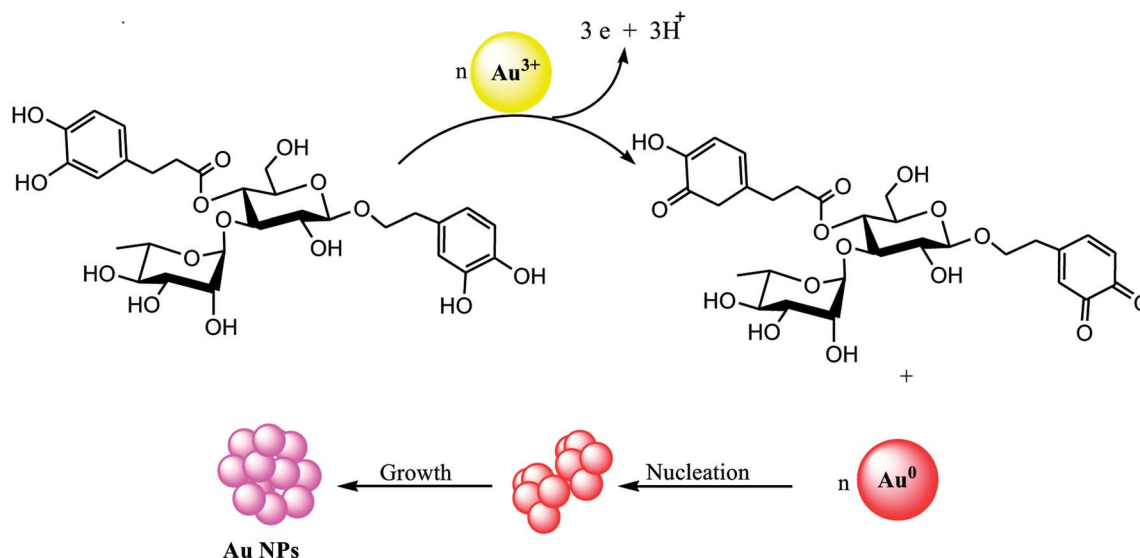
Fig. 7 TGA analysis of Au/S. lavandulifolia NPs.

Atomic force microscopy (AFM) (DME-95-50 E) was used to recognize topological appearance and sizes of NPs. Fig. 5 is an AFM image corresponding to GNP where height measurement indicates sizes ranging from 22 to 30 nm and also represents rough surface of NPs.

High resolution transmission electron microscopy (HR-TEM) was applied to determine the dimension and shape of NPs. Usual TEM images achieved for colloids are presented in Fig. 6. According to the image, it is obvious that gold NPs have a nearly spherical and triangular morphology with an excellent distribution of particles with sizes between 20 and 30 nm. Moreover, Fig. 6 shows a HR-TEM image corresponding to the Au NPs at 5 nm magnification. Based on this image, the Au NPs contained lattice fringes, which confirmed their great crystallinity. Meantime, a Fast Fourier Transform (FFT) image corresponding to the Au NPs (inset) shows bright diffraction spots and ring patterns that prove the crystalline nature of the Au atoms.

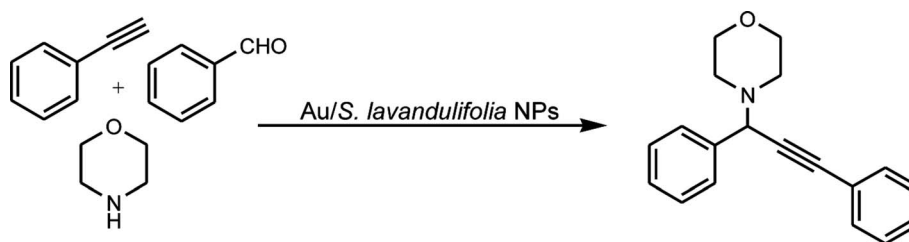
Thermal gravimetric analysis (Netzsch-TGA 209 F1) is an important method to determine beginning and end destruction temperatures of nanoparticles (heat-resistance) and amounts of weight loss during heating at different temperatures. The beginning part of the graph that is straight (Fig. 7) shows that biosynthesized Au NPs are pure (free of impurities and moisture). The earliest weight loss for the synthesized gold nanoparticles occurred at 190 °C and shows a steady weight loss in the temperature range from 180–620 °C with a total weight loss up to 700 °C which is about 52.62% and occurred at 190 °C (4.01%), 390 °C, (16.89%), and 640 °C (31.71%).

Polyphenolic compounds have been revealed as a reducing agent during the biological extract mediated synthesis of nanomaterials.⁴⁴ Moreover, a rich source for polyphenolic compounds and flavonoid groups is the *Stachys lavandulifolia* extract.^{45–47} These polyphenolic compounds (such as acteoside) may play a role as reducing agents to reduce Au³⁺ ions. Scheme



Scheme 1 Probable mechanism for formation of Au NPs using *Stachys lavandulifolia* extract.



Table 1 Optimization of various conditions in the model reaction using Au/*S. lavandulifolia* NPs catalyst^a

Entry	Catalyst (mol%)	Solvent	T (°C)	Yield ^b (%)
1	—	Toluene	60	—
2	10	Toluene	60	75
3	10	Toluene	100	92
4	7	Toluene	100	65
5	5	Toluene	100	50
6	12	Toluene	100	92
7	10	CH ₂ Cl ₂	70	30
8	10	DMF	100	70
9	10	EtOH	80	65
10	10	H ₂ O	100	40
11	10	CH ₃ CN	70	65
12	10	—	100	30

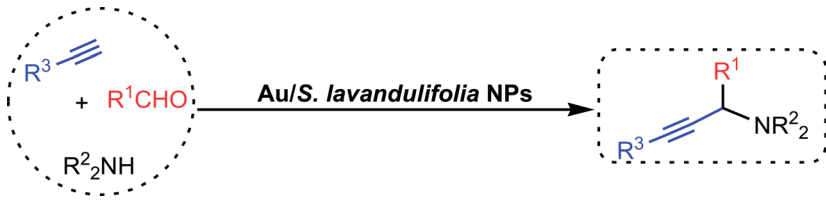
^a Reaction conditions: benzaldehyde (1.0 mmol), morpholine (1 mmol), phenylacetylene (1.2 mmol), Au/*S. lavandulifolia* NPs, solvent (5.0 mL) for 8 h. ^b Yields are based on ¹H NMR.

1 is a schematic representation of possible pathways. In the first phase, as the extract combines with the metal salt solution, hydroxyl groups of the polyphenolic compounds could be reduced into Au atoms. Then, synthesized Au atoms nucleate followed by more growth which causes the NPs formation.

The catalytic behaviour of Au/*S. lavandulifolia* NPs was studied for the A³-coupling reaction of aldehydes, amines, and alkynes to produce propargylamines. Initially, we employed benzaldehyde (1.0 mmol), morpholine (1.0 mmol), and phenylacetylene (1.2 mmol) as model substrates for optimizing different factors including time, temperature, solvents, and catalyst loading. The results are presented in Table 1. First, influence of the catalyst was studied, and as expected, the desired product was not achieved without the catalyst, representing the essential role of Au/*S. lavandulifolia* NPs in the reaction mechanism (Table 1, entry 1). The reaction yield achieved 75% by utilizing a 10 mol% catalyst loading in toluene at 60 °C (Table 1, entry 2). Furthermore, the reaction occurred quantitatively when applying 10 mol% of catalyst at 100 °C (Table 1, entry 3). Lower yields were obtained by decreasing the catalyst level to 7 and 5 mol%, respectively (Table 1, entries 4 and 5). Increasing the catalyst level to 12 mol% did not improve the reaction yield or time (Table 1, entry 6). Applying 10 mol% of catalyst in other solvents including CH₂Cl₂, DMF, EtOH, H₂O, CH₃CN, and neat, resulted in lower reaction yields (Table 1, entries 7–12). Consequently, we chose toluene as the optimum solvent, 10 mol% catalyst loading and 100 °C reaction temperature as the most effective and optimum reaction conditions for studying the scope of this A³ coupling.

Under the optimal reaction conditions, other aldehydes were reacted with different aliphatic amines and phenylacetylene and resulted A³ coupling products with good yields (Table 2). In the primary study of the aldehyde substrate's scope, morpholine, and phenylacetylene were utilized as model substrates and different aldehydes were studied for the A³-coupling reactions (Table 2, entries 1–20). Results showed that aromatic aldehyde's behaviors with functional groups like -Cl, -Br, -OH, -Me, or -OMe could impact the A³-coupling. Moreover, a minor electronic effect was found which is related to reaction of aryl aldehydes with electron-withdrawing groups (Table 2, entries 2–4) and generation of relevant products in excellent yields, while replacement of electron rich groups (Table 2, entries 5–7) on the benzene ring reduced performance and caused lesser yields. Additionally, reactions with challenging heterocyclic compounds such as thiophene-2-carbaldehyde or furan-2-carboxaldehyde with morpholine and phenylacetylene proceeded efficiently and the corresponding propargylamines were obtained in good yields (Table 2, entries 8 and 9). On the other hand, an aliphatic aldehyde (*i.e.*, cyclohexanecarbaldehyde or butyraldehyde) also showed good yields under this optimum condition (Table 2, entries 10 and 11). To expand the scope of amine substrates a mixture of benzaldehyde–phenylacetylene–amine was selected and different amines were studied (Table 2, entries 1 and 12–16). The results indicate that cyclic, heterocyclic (*i.e.*, piperidine, pyrrolidine, or morpholine), and acyclic (*i.e.*, diethyl or dibenzyl) secondary amines also provided high yields of products under the optimal reaction conditions (Table 2, entries 1 and 12–15). However, no product was found when



Table 2 The reactions of aldehydes, amines, and alkynes in the presence of Au/S. *lavandulifolia* NPs catalyst^a


Entry	R ¹	Amine	R ³	Yield ^b (%)	Ref. ^c
1	Ph	Morpholine	Ph	95	48
2	4-ClC ₆ H ₄	Morpholine	Ph	96	59
3	3-ClC ₆ H ₄	Morpholine	Ph	95	61
4	4-BrC ₆ H ₄	Morpholine	Ph	96	51
5	4-OHC ₆ H ₄	Morpholine	Ph	90	59
6	4-MeC ₆ H ₄	Morpholine	Ph	88	48
7	4-OMeC ₆ H ₄	Morpholine	Ph	85	59
8	2-Thiophenyl	Morpholine	Ph	92	43
9	2-Furfuryl	Morpholine	Ph	90	48
10	Cyclohexyl	Morpholine	Ph	90	59
11	C ₃ H ₇	Morpholine	Ph	85	59
12	Ph	Piperidine	Ph	95	59
13	Ph	Pyrrolidine	Ph	95	60
14	Ph	Diethyl	Ph	90	59
15	Ph	Dibenzyl	Ph	90	59
16	Ph	Aniline	Ph	0	59
17	Ph	Morpholine	<i>n</i> -C ₆ H ₁₃	82	49
18	Ph	Piperidine	<i>n</i> -C ₆ H ₁₃	80	59
19	4-ClC ₆ H ₄	Morpholine	<i>n</i> -C ₆ H ₁₃	85	59
20	4-OMeC ₆ H ₄	Morpholine	<i>n</i> -C ₆ H ₁₃	70	59

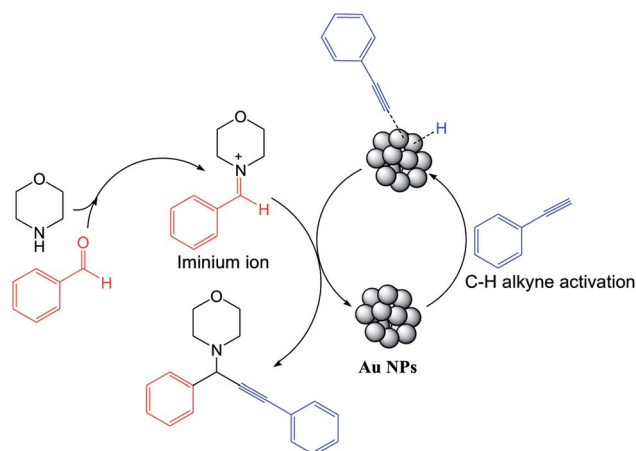
^a Reaction conditions: aldehyde (1.0 mmol), amine (1 mmol), alkyne (1.2 mmol), and Au/S. *lavandulifolia* NPs (10 mol%) were stirred in toluene (5.0 mL) at 100 °C for 8 h. ^b Yields are based on ¹H NMR. ^c Earlier reference of the corresponding product.

using aniline as a substrate (Table 2, entry 16). Remarkably, reaction of the aliphatic alkyne 1-octyne, a substrate which is usually hard to activate, also worked well and resulted in a product with a good yield under optimal conditions (Table 2, entries 17–20).

According to the above outcomes, a suggested reaction pathway for the A³ coupling reaction catalyzed by Au/S.

lavandulifolia NPs under heating conditions is presented in Scheme 2. The first phase involves activating the terminal alkyne using the Au NPs catalyst under heating to result in the related Au–alkylidene complex on the surface of NPs. Next, the reaction between an Au–acetylide intermediate with iminium ion (formed *in situ* from the related aldehyde and amine) occurs to result in the desired propargylamine, with the Au/S. *lavandulifolia* NPs catalyst being reformed for a further cycle of reactions.⁴⁸

Recovering heterogeneous new catalysts is extremely vital in terms of economic and sustainable chemistry views.



Scheme 2 Proposed mechanism for the A³ coupling reaction catalyzed by Au/S. *lavandulifolia* NPs.

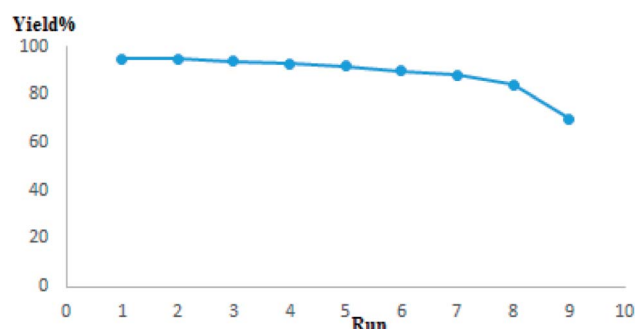


Fig. 8 Recycling of catalyst for the reaction of benzaldehyde, morpholine, and phenylacetylene.



Table 3 Comparison efficiency of Au/*S. lavandulifolia* NPs with some reported methods for the A³ coupling reaction between benzaldehyde and piperidine with phenylacetylene

Entry	Reaction conditions	Time (h)	Yield %	Ref.
1	Au/ <i>S. lavandulifolia</i> NPs, toluene, 100 °C	8	95	This work
2	AgI, H ₂ O, 100 °C, N ₂	14	70	49
3	CuSBA-15, toluene, 90 °C	6	80	50
4	Au@PMO-IL, CHCl ₃ , 60 °C	12	87	51
5	FeCl ₃ , 70 °C	14	34	52
6	Ag NPs, PEG, 100 °C	20	77	53
7	Nano Co ₃ O ₄ , 130 °C	15	87	54
8	Fe ₃ O ₄ , toluene, 80 °C	16	75	55
9	Fe ₃ O ₄ @SBA-15, toluene, 110 °C	8	76	56
10	NiCl ₂ , toluene, 111 °C	9	87	57
11	Ag–NaY, neat, 100 °C	15	73	58
12	Ag NPs/plant extract, PEG, 90 °C	18	83	24
13	MNP@Au/NNN-pincer, H ₂ O, 85 °C	7	90	59
14	[CuCl{2,5-bis(2-thienyl)-1-phenylphosphole} ₂], 100 °C	5	92	60
15	InBr ₃ , toluene, 80 °C	6	80	61

Consequently, we investigated recovery of the Au/*S. lavandulifolia* NPs catalyst for the reaction of benzaldehyde, morpholine, and phenylacetylene under optimum reaction conditions. For this goal, at the end of the reaction, the catalyst was isolated from the reaction solution through centrifugation and rinsed with water and ethanol twice, and then was recycled for seven times with no significant change in catalytic performance (Fig. 8). This reusability proves the excellent stability and turnover of the catalyst under working conditions.

Several chosen procedures in the literature and current procedures were compared in Table 3, which indicates that Au/*S. lavandulifolia* NPs are a similar or a more effective catalyst in terms of reaction time and yield than earlier reported ones.

4. Conclusion

In conclusion, a green, effective, simple, and cost-effective technique has been developed for synthesizing Au NPs with *Stachys lavandulifolia* extract as a reducer and stabilizer. Characterization of the prepared Au/*S. lavandulifolia* NPs was carried out using SEM, HR-TEM, FFT, XRD, EDS, TGA, FT-IR, and UV-visible methods. It was found that Au/*S. lavandulifolia* NPs are cost-effective, air stable, and an effective catalyst for synthesis of propargylamines through a one-pot three-component A³-coupling reaction of aldehydes, amines, and alkynes. The products were achieved in good to high yields and the catalyst can be reused up to seven cycles with nearly no change in its performance. The important properties of the presented approach are: (i) high catalytic activity; (ii) excellent yield of the products; (iii) application of the plant extract as a fast and clean synthetic pathway for synthesis of Au NPs; (iv) no surfactant, capping agent, and/or template were utilized in the process; and (v) the Au NPs can be simply retained and reused.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We are thankful to Payame Noor University (PNU) for financial supports.

References

- (a) Y. Liu, *ARKIVOC*, 2014, **1**, 1; (b) E. Vessally, *RSC Adv.*, 2016, **6**, 18619; (c) E. Vessally, L. Edjlali, A. Hosseini, A. Bekhradnia and M. D. Esrafil, *RSC Adv.*, 2016, **6**, 49730; (d) I. Matsuda, J. Sakakibara and H. Nagashima, *Tetrahedron Lett.*, 1991, **32**, 7431; (e) C. P. T. Sar, T. Kalai, J. Jeko and K. Hideg, *ARKIVOC*, 1991, **32**, 47.
- (a) P. H. Yu, B. A. Davis and A. A. Boulton, *J. Med. Chem.*, 1992, **35**, 3705; (b) J. J. Chen, D. M. Swope and K. Dashtipour, *Clin. Ther.*, 2007, **29**, 1825; (c) M. Baranyi, P. F. Porceddu, F. Goloncser, S. Kulcsar, L. Otrokocsi, A. Kittel, A. Pinna, L. Frau, P. B. Huleatt, M. L. Khoo, C. L. L. Chai, P. Dunkel, P. Matyus, M. Morelli and B. Sperlagh, *Mol. Neurodegener.*, 2016, **11**, 2.
- (a) G. Mageur, B. Crousse and D. Bonnet-Delpon, *Tetrahedron Lett.*, 2005, **46**, 2219; (b) P. Kaur, G. Shaky, H. Sun, Y. Pan and G. Li, *Org. Biomol. Chem.*, 2010, **8**, 1091; (c) F. Colombo, M. Benaglia, S. Orlandi, F. Uselli and G. Celentano, *J. Org. Chem.*, 2006, **71**, 2064; (d) C. Wei and C. J. Li, *J. Am. Chem. Soc.*, 2002, **124**, 5638.
- (a) R. P. Herrera and E. Marques-Lopez, *Multicomponent Reactions: Concepts and Applications for Design and Synthesis*, John Wiley & Sons., 2015, p. 94; (b) V. A. Peshkov, O. P. Pereshivko and E. V. Van der Eycken, *Chem. Soc. Rev.*, 2012, **41**, 3790.
- L. C. Akullian, M. L. Snapper and A. H. Hoveyda, *Angew. Chem., Int. Ed.*, 2003, **42**, 4244.
- S. N. Afraj, C. Chen and G. H. Lee, *RSC Adv.*, 2014, **4**, 26301.
- Y. Kuninobu, Y. Inoue and K. Takai, *Chem. Lett.*, 2006, **35**, 1376.



- 8 (a) D. A. Kotadia and S. S. Soni, *Appl. Catal., A*, 2014, **488**, 231; (b) T. Zeng, W. W. Chen, C. M. Cirtiu, A. Moores, G. Song and C. J. Li, *Green Chem.*, 2010, **12**, 570; (c) B. Sreedhar, A. S. Kumar and P. S. Reddy, *Tetrahedron Lett.*, 2010, **51**, 1891; (d) W. W. Chen, R. V. Nguyen and C. J. Li, *Tetrahedron Lett.*, 2009, 2895; (e) P. Li, Y. Zhang and L. Wang, *Chem.-Eur. J.*, 2009, **15**, 2045; (f) R. Sharma, S. Sharma and G. Gaba, *RSC Adv.*, 2014, **4**, 49198.
- 9 (a) C. J. Li and C. Wei, *Chem. Commun.*, 2002, **3**, 268; (b) E. R. Bonfield, *Org. Biomol. Chem.*, 2007, **5**, 435.
- 10 W. W. Chen, H. P. Bi and C. J. Li, *Synlett*, 2010, 475.
- 11 (a) S. Sakaguchi, T. Kubo and Y. Ishii, *Angew. Chem., Int. Ed.*, 2001, **40**, 2534; (b) S. Sakaguchi, T. Mizuta, M. Furuwan, T. Kubo and Y. Ishii, *Chem. Commun.*, 2004, 1638; (c) C. Fischer and E. M. Carreira, *Org. Lett.*, 2001, **3**, 4319.
- 12 (a) S. Samai, G. C. Nandi and M. Singh, *Tetrahedron Lett.*, 2010, **51**, 5555; (b) K. Namitharan and K. Pitchumani, *Eur. J. Org. Chem.*, 2010, 411.
- 13 R. Manikandana, P. Anithaa, P. Viswanathamurthia and J. G. Malecki, *Polyhedron*, 2016, **119**, 300.
- 14 For some examples see: (a) S. Cheng, N. Shang, C. Feng, S. Gao, C. Wang and Z. Wang, *Catal. Commun.*, 2017, **89**, 91; (b) M. Varyani, P. K. Khatri and S. L. Jain, *Catal. Commun.*, 2016, **77**, 113; (c) M. M. Islam, A. S. Roy and S. M. Islam, *Catal. Lett.*, 2016, **146**, 1128; (d) S. Kumari, A. Shekhar and D. D. Pathak, *RSC Adv.*, 2016, **6**, 15340; (e) M. Gholinejad, F. Saadati, S. Shaybanizadeh and B. Pullithadathil, *RSC Adv.*, 2016, **6**, 4983; (f) M. Abdolia, H. Saeidian and A. Kakanejadifard, *Synlett*, 2016, **27**, 2473; (g) P. Li, S. Regati, H. C. Huang, H. D. Arman, B.-L. Chen and J. C.-G. Zhao, *Chin. Chem. Lett.*, 2015, **26**, 6; (h) B. Kodicherla, P. C. Perumgani and M. R. Mandapati, *Appl. Organomet. Chem.*, 2014, **28**, 756; (i) M. Abdollahi-Alibeik and A. Moaddeli, *RSC Adv.*, 2014, **4**, 39759; (j) S. Nakamura, M. Ohara, Y. Nakamura, N. Shibata and T. Toru, *Chem.-Eur. J.*, 2010, **16**, 2360; (k) M. K. Patil, M. Keller, B. M. Reddy, P. Pale and J. Sommer, *Eur. J. Org. Chem.*, 2008, 4440; (l) J. B. Bariwal, D. S. Ermolat'ev and E. V. Van der Eycken, *Chem.-Eur. J.*, 2010, **16**, 3281; (m) A. Fodor, A. Kiss, N. Debreczeni, Z. Hell and I. Gresits, *Org. Biomol. Chem.*, 2010, **8**, 4575; (n) H. B. Chen, Y. Zhao and Y. Liao, *RSC Adv.*, 2015, **5**, 37737; (o) B. M. Choudary, C. Sridhar, M. L. Kantam and B. Sreedhar, *Tetrahedron Lett.*, 2004, **45**, 7319; (p) L. Shi, Y.-Q. Tu, F.-M. Zhang and C. A. Fan, *Org. Lett.*, 2004, **6**, 1001; (q) S. B. Park and H. Alper, *Chem. Commun.*, 2005, 1315; (r) H. Naeimi and M. Moradian, *Appl. Catal., A*, 2013, **467**, 400; (s) M. Wang, P. Li and L. Wang, *Eur. J. Org. Chem.*, 2008, 2255; (t) M. J. Aliaga, D. J. Ramón and M. Yus, *Org. Biomol. Chem.*, 2010, **8**, 43.
- 15 For some examples see: (a) C. Wei, Z. Li and C. J. Li, *Org. Lett.*, 2003, **5**, 4473; (b) P. Li, L. Wang, Y. Zhang and M. Wang, *Tetrahedron Lett.*, 2008, **49**, 6650; (c) Z. Li, C. Wei, L. Chen, R. S. Varma and C. J. Li, *Tetrahedron Lett.*, 2004, **45**, 2443; (d) K. M. Reddy, N. S. Babu, I. Suryanarayana, P. S. Sai Prasad and N. Lingaiah, *Tetrahedron Lett.*, 2006, **47**, 7563; (e) M. Trose, M. Dell'Acqua, T. Pedrazzini, V. Pirovano, E. Gallo, E. Rossi, A. Caselli and G. Abbiati, *J. Org. Chem.*, 2014, **79**, 7311; (f) Y. He, M. F. Lv and C. Cai, *Dalton Trans.*, 2012, 1248; (g) Y. Zhao, X. Zhou, T. A. Okamura, M. Chen, Y. Lu, W. Y. Sun and J. Q. Yu, *Dalton Trans.*, 2012, 5889; (h) X. Zhou, Y. Lu, L. L. Zhai, Y. Zhao, Q. Liu and W. Y. Sun, *RSC Adv.*, 2013, **3**, 1732; (i) Y. Li, X. Chan, Y. Song, L. Fang and G. Zou, *Dalton Trans.*, 2011, **40**, 2046.
- 16 For some example see: (a) M. Gholinejad, F. Hamed and C. Nájera, *Synlett*, 2016, **27**, 1193; (b) C. Wetzel, P. C. Kunz, I. Thiel and B. Spingler, *Inorg. Chem.*, 2011, **50**, 7863; (c) C. Wei and C.-J. Li, *J. Am. Chem. Soc.*, 2003, **125**, 9584; (d) G. Villaverde, A. Corma, M. Iglesias and F. Sánchez, *ACS Catal.*, 2012, **2**, 399; (e) G. A. Price, A. K. Brisdon, K. R. Flower, R. G. Pritchard and P. Quayle, *Tetrahedron Lett.*, 2014, **55**, 151; (f) P. Oña-Burgos, I. Fernández, L. Rocas, L. Torre Ferenández, S. García-Granda and F. López Ortiz, *Organometallics*, 2009, **28**, 1739; (g) L. Lili, Z. Xin, R. Shumin, Y. Ying, D. Xiaoping, G. Jinsen, X. Chunming and H. Jingb, *RSC Adv.*, 2014, **4**, 13093; (h) F. M. Moghaddam, S. E. Ayati, S. H. Hosseinib and A. Pourjavadi, *RSC Adv.*, 2015, **5**, 34502; (i) J.-L. Huang, D. G. Gray and C.-J. Li, *Beilstein J. Org. Chem.*, 2013, **9**, 1388; (j) V. Kar-Yan Lo, K. Ka-Yan Kung, M.-K. Wong and C.-M. Che, *J. Organomet. Chem.*, 2009, **694**, 583; (k) M. Kidwai, V. Bansal, A. Kumarb and S. Mozumdarb, *Green Chem.*, 2007, **9**, 742.
- 17 (a) Y. Qiu, Y. Qin, Z. Ma and W. Xia, *Chem. Lett.*, 2014, **43**, 1284; (b) N. P. Eagalapatia, A. Rajacka and Y. L. N. Murthy, *J. Mol. Catal. A: Chem.*, 2014, **381**, 126; (c) K. V. V. Satyanarayana, P. A. Ramaiah, Y. L. N. Murty, M. R. Chandra and S. V. N. Pammi, *Catal. Commun.*, 2012, **25**, 50; (d) C. Mukhopadhyay and S. Rana, *Catal. Commun.*, 2009, **11**, 28; (e) E. Ramu, R. Varala, N. Sreelatha and S. R. Adapa, *Tetrahedron Lett.*, 2007, **48**, 7184; (f) M. Periasamy, P. O. Reddy, A. Edukondalu, M. Dalai, L. M. Alakonda and B. Udaykumar, *Eur. J. Org. Chem.*, 2014, 6067.
- 18 D. S. Raghuvanshi and K. N. Singh, *Synlett*, 2011, 373.
- 19 P. H. Li and L. Wang, *Chin. J. Chem.*, 2005, **23**, 1076.
- 20 D. Astruc, *Nanoparticles and Catalysis*, Wiley-VCH, Weinheim, 2008.
- 21 V. Polshettiwar and R. S. Varma, *Green Chem.*, 2010, **12**, 743.
- 22 Y. Sun and Y. Xia, *Science*, 2002, **298**, 2176.
- 23 S. Iravani, *Green Chem.*, 2011, **13**, 2638.
- 24 S. A. Aromal and D. Philip, *Spectrochim. Acta, Part A*, 2012, **97**, 1.
- 25 W. Rechberger, A. Hohenau, A. Leitner, J. R. Krenn, B. Lamprecht and F. R. Aussenegg, *Opt. Commun.*, 2003, **220**, 137.
- 26 C. L. Nehl, H. Liao and J. H. Hafner, *Nano Lett.*, 2006, **6**, 683.
- 27 (a) D. Pissuwan, T. Niidome and M. B. Cortie, *J. Controlled Release*, 2011, **149**, 65; (b) G. Han, P. Ghosh, M. De and V. M. Rotello, *NanoBiotechnology*, 2007, **3**, 40.
- 28 E. Boisselier and D. Astruc, *Chem. Soc. Rev.*, 2009, **38**, 1759.
- 29 D. Pissuwan, S. M. Valenzuela and M. B. Cortie, *Trends Biotechnol.*, 2006, **24**, 62.



- 30 K. Saha, S. S. Agasti, C. Kim, X. Li and V. M. Rotello, *Chem. Rev.*, 2012, **112**, 2739.
- 31 (a) G. Li and R. Jin, *Nanotechnol. Rev.*, 2013, **5**, 529; (b) Y. Chen, C. Liu, H. Abroshan, Z. Li, J. Wang, G. Li and M. Haruta, *J. Catal.*, 2016, **340**, 287.
- 32 S. P. Dubey, M. Lahtinen and M. Sillanpää, *Colloids Surf., A*, 2010, **364**, 34.
- 33 M. V. Sujitha and S. Kannan, *Spectrochim. Acta, Part A*, 2013, **102**, 15.
- 34 T. Y. Suman, S. R. Rajasree, R. Ramkumar, C. Rajthilak and P. Perumal, *Spectrochim. Acta, Part A*, 2014, **118**, 11.
- 35 C. Jayaseelan, R. Ramkumar, A. Rahuman and P. Perumal, *Ind. Crops Prod.*, 2013, **45**, 423.
- 36 V. Mozaffarian, *Latin, English, Persian*, Farhang Mo'aser, 1996.
- 37 A. A. Basaran, I. Calis, C. Anklin, S. Nishibe and O. Sticher, *Chim. Acta*, 1988, **71**, 1483.
- 38 G. H. Amin, *Popular medicinal plants of Iran*, Ministry of Health., 1991, p. 40.
- 39 M. Rabbani, S. E. Sajjadi and H. R. Zarei, *J. Ethnopharmacol.*, 2003, **89**, 271.
- 40 (a) H. Veisi, S. Taheri and S. Hemmati, *Green Chem.*, 2016, **18**, 6337; (b) F. Bonyasi, M. Hekmati and H. Veisi, *J. Colloid Interface Sci.*, 2017, **496**, 177; (c) E. Farzad and H. Veisi, *J. Ind. Eng. Chem.*, 2018, **60**, 114–124; (d) H. Veisi, S. Najafi and S. Hemmati, *Int. J. Biol. Macromol.*, 2018, **113**, 186–194; (e) H. Veisi, A. Sedrpoushan and S. Hemmati, *Appl. Organomet. Chem.*, 2015, **29**, 825; (f) M. Pirhayati, H. Veisi and A. Kakanejadifard, *RSC Adv.*, 2016, **6**, 27252; (g) H. Veisi, S. Azizi and P. Mohamadi, *J. Cleaner Prod.*, 2018, **170**, 1536–1543; (h) F. Heidari, M. Hekmati and H. Veisi, *J. Colloid Interface Sci.*, 2017, **501**, 175–184; (i) H. Veisi, S. A. Mirshokraie and H. Ahmadian, *Int. J. Biol. Macromol.*, 2018, **108**, 419–425; (j) S. Lebaschi, M. Hekmati and H. Veisi, *J. Colloid Interface Sci.*, 2017, **485**, 223; (k) H. Veisi, M. Pirhayati, A. Kakanejadifard, P. Mohammadi, M. R. Abdi, J. Gholami and S. Hemmati, *ChemistrySelect*, 2018, **3**, 1820–1826; (l) H. Veisi, M. Ghadermazi and A. Naderi, *Appl. Organomet. Chem.*, 2016, **30**, 341.
- 41 (a) H. Veisi, A. Rashtiani and V. Barjasteh, *Appl. Organomet. Chem.*, 2016, **30**, 231; (b) H. Veisi, S. Hemmati, H. Shirvani and H. Veisi, *Appl. Organomet. Chem.*, 2016, **30**, 387.
- 42 M. Nasrollahzadeh and S. M. Sajadi, *RSC Adv.*, 2015, **5**, 46240.
- 43 M. Nasrollahzadeh, S. M. Sajadi and M. Maham, *RSC Adv.*, 2015, **5**, 40628.
- 44 V. Kumar, S. Mohan, D. K. Singh, D. K. Verma, V. K. Singh and S. H. Hasan, *Mater. Sci. Eng., C*, 2017, **71**, 1004.
- 45 H. J. D. Dorman and S. G. Deans, *J. Appl. Microbiol.*, 2000, **88**, 308.
- 46 A. Shtayeh, Z. Yaniv and J. Mahajna, *J. Ethnopharmacol.*, 2000, **73**, 221.
- 47 G. Tumen, N. Ermin, T. Ozek, M. Kurkcuglu and K. H. C. Baser, *J. Essent. Oil Res.*, 1994, **6**, 463.
- 48 X. Xiong, H. Chen and R. Zhu, *J. Catal.*, 2014, **35**, 2006.
- 49 C. Wei, Z. Li and C. J. Li, *Org. Lett.*, 2003, **5**, 4473.
- 50 M. Srinivasa, P. Srinivasua, S. K. Bhargava and M. Lakshmi Kantam, *Catal. Today*, 2013, **208**, 66.
- 51 B. Karimi, M. Gholinejad and M. Khorasani, *Chem. Commun.*, 2012, **48**, 8961.
- 52 W. Chen, R. V. Nguyen and C. J. Li, *Tetrahedron Lett.*, 2009, **50**, 2895.
- 53 W. Yan, R. Wang, Z. Xua, X. u Jiangke, L. Lin, Z. Shen, Y. Zhou and J. Mol, *J. Mol. Catal. A: Chem.*, 2006, **255**, 81.
- 54 K. D. Bhatte, D. N. Sawant, K. M. Deshmukh and B. M. Bhanage, *Catal. Commun.*, 2011, **16**, 114.
- 55 B. Sreedhar, A. S. Kumar and P. S. Reddy, *Tetrahedron Lett.*, 2010, **51**, 1891.
- 56 M. Lakshmi Kantam, S. Laha, J. Yadav and S. Bhargava, *Tetrahedron Lett.*, 2008, **49**, 3083.
- 57 S. Samai, G. C. Nandi and M. S. Singh, *Tetrahedron Lett.*, 2010, **51**, 5555.
- 58 R. Maggi, A. Bello, C. Oro, G. Sartori and L. Soldi, *Tetrahedron Lett.*, 2008, **64**, 1435.
- 59 N. Zohreh, S. H. Hosseini, M. Jahani, M. S. Xaba and R. Meijboom, *J. Catal.*, 2017, **356**, 255.
- 60 J. R. Cammarata, R. Rivera, F. Fuentes, Y. Otero, E. Ocampo-Mavárez, A. Arce and J. M. Garcia, *Tetrahedron Lett.*, 2017, **58**, 4078.
- 61 J. S. Yadav, B. V. Subba Reddy, A. V. Hara Gopal and K. S. Patil, *Tetrahedron Lett.*, 2009, **50**, 3493.

