JOC The Journal of Organic Chemistry

Article

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J. Org. Chem., Just Accepted Manuscript • DOI: 10.1021/acs.joc.9b01759 • Publication Date (Web): 16 Sep 2019

Downloaded from pubs.acs.org on September 16, 2019

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On/Off O₂ switchable photocatalytic oxidative and proto decarboxylation of carboxylic acids

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ABSTRACT: Photoredox catalysis in recent years has manifested a powerful branch of science in organic synthesis. Although merging photoredox and metal catalysts have been widely used, switchable heterogeneous photoredox catalysis has rarely considered. Herein we open a new window to use a switchable heterogeneous photoredox catalyst which could be turned On/Off by changing a simple stimulus (O₂) for two opponent reactions namely oxidative and proto decarboxylation. In this strategy we demonstrate that Au@ZnO core-shell nanoparticles could be used as a switchable photocatalyst which has good catalytic activity to absorb visible light due to LSPR effect of gold, decarboxylated a wide range of aromatic and aliphatic carboxylic acids, multiple reusability, and reasonable for synthesis both aldehydes/ketones and alkane/arenes in a large scale set up. Some biologically active molecules are also shown via examples of the direct oxidative and proto decarboxylation which widely provided pharmaceutical agents.

1. INTRODUCTION

Designing new catalysts for new synthetic strategies to produce organic molecules have been continuously interested both in industry and academia. After the first studies by Kellogg in 1978 on the application of photoredox catalysis for organic synthesis, this field until the end of 2000 remained un-important and un-interest.¹ In 2008, simultaneously McMillan and Yoon disclosed a new vision for the use of photocatalysts in organic transformations.^{2,3} After, in the last 10 years, photoredox catalysis using visible light have revolutionized the synthesis of organic molecules and many unparalleled and worth full transformations have been reported.⁴⁻⁶

Rh and Ir polypyridyl complexes moreover organic dyes are the most frequently homogeneous photocatalysts which were used.^{4,7} However, heterogeneous photoredox catalysis such as semiconductor nanoparticles through their advantages, have not been widely used for organic transformations.^{8,9} In addition to the importance of designing and selecting a suitable catalyst, choosing affordable, readily available, easy to handle and store starting materials are one of the most important things to keep in mind. Inexpensive, nontoxicity, stability, readily availability, as well as natural resources of carboxylic acids, make them one of the most suitable and attractive starting materials.^{10,11} Moreover, their decarboxylation which CO₂ as a non-toxic by-product is released is an excellent method for accessing aryl, alkyl, vinyl, and acyl radicals (Scheme 1A).¹²⁻ ¹⁴ Proto decarboxylation is an ideal test and important reaction in syntheses that use for the reduction of carboxylic acids to alkanes, but it requires extremely high temperature and costly ligands.^{11,15} Some methods for proto decarboxylation have been developed using Cu, Pd, Rh, and Ag, but these methods are bounded only to alkynyl and aryl carboxylic acids. 16-19 This transformation is generally achieved by radical methods such as the Barton decarboxylation and Kolbe electrolysis.²⁰ The most generally used method for the reduction of carboxylic acids to alkanes is the Barton decarboxylation through a hydrodecarboxylation mechanism; however, this needs the esterification of carboxylic acids to thiohydroxamic esters as precursors. Barton decarboxylation has been modified by using silanes, thiols, or chloroform as H atom donors, however, these modifications generate significant amounts of unwanted by-products or also need superstoichiometric quantities of H atom donor.^{17,19} Although many photocatalysis has been reported in recent years to accomplishment decarboxylative functionalization,^{13,14,21-23} direct proto decarboxylation of carboxylic acids remains unexplored (Scheme 1B). These methods utilize additive as hydrogen atom donor or limited to a few substrates and were not contain both aromatic and aliphatic carboxylic acids.¹⁷ Synthesis of aldehydes and ketones have attracted significant interest since these compounds exist broad used in the pharmaceutical, functional material industries and in synthetic organic chemistry.^{12,24} The selective oxidation of carboxylic acids to aldehydes is a procedure which is very important in industry, usually, it is carried out at high pressure and temperature and also in environmentally harmful organic solvents. In addition, stoichiometric oxygen donors were used which not only are expensive and toxic but also generate high amounts of dangerous wastes.^{12,25-27} According to our knowledge and literature review photocatalytic oxidative decarboxylation to produce aldehydes and ketones are rare (Scheme 1C-D).^{28,29} and there is not any report on the direct photo oxidative decarboxylation of carboxylic acid.





Scheme 1. The reported oxidative and proto decarboxylation reactions and our work.

Recently, our laboratory started to design and synthesize a new set of semiconductor photocatalysts for specific transformations.³⁰⁻³² The synthesis of two different set of organic compounds (alkanes and aldehydes/ketones) are very important and toward previously reported methods for decarboxylation of carboxylic acids to generated open-shell radicals with various photoredox catalysis, this idea came to our mind that design a switchable photocatalyst.

Also many homo and heterogeneous switchable catalysts have been developed, however a photoredox heterogeneous catalyst which having single active site to adjust two different specific reactions is rare.³³ Among a number of advantages, we recognized that this photoredox catalyst would *1*) be absorb visible light to generate electron/hole pairs and also quenching the electron/hole recombination process, *2*) be selective decarboxylated carboxylic acids to generate aryl and alkyl radicals, *3*) be generate reactive superoxide radical anion (O_2^{\bullet}) through one-electron photoreduction under aerobic condition for oxidation, *4*) be readily adsorb hydrogen for the reduction under inert atmosphere and *5*) be also readily prepared, inexpensive, non-toxic, stable and could operate reactions with wide substrate scope, scalable and simple operationally setup. With regard to all the above key points and according to our previous works on photocatalytic behavior of modified semiconductors such as TiO₂ and ZnO, we design Au@ZnO core-shell nanoparticles photocatalyst for present work (**Scheme 1E**). Low cost and stability properties of Zinc oxide (ZnO) make it the most widely used photocatalyst material. However, pure ZnO nanoparticles exhibit poor photocatalytic activity because of their related to low charge separation efficiency and high recombination of charge carriers.^{34,35} Thus, research group efforts are focused to develop the

photocatalytic performance of ZnO as photocatalysts. One approach for achieving these goals is, to loading noble metals (such as Pd, Pt, Au, Ag...) nanoparticles on the surface of ZnO nanoparticles.^{36,37}

Doping Gold on ZnO increase the photocatalytic properties of ZnO, due to extending light absorption, increasing the efficiency of charge carrier separation and facilitating the formation of electron/hole pairs induced by the localized surface plasmon resonance (LSPR) effect.³⁸⁻⁴³ So, ZnO doped with Au nanoparticles, improved use of UV-visible light due to LSPR absorption as compared pure ZnO. According to the nanochemistry of gold (Au) and due to the size dependent optical properties of gold, small Au nanoparticles with diameter < 5 nm do not show any LSPR absorption, while Au nanoparticles of 5-50 nm shows a sharp absorption band in the 520-530 nm region. As the particles grow bigger, the absorption band broadens and redshifts to longer wavelengths. So, controlling the size and shape of the Au nanoparticle is one of the important points.^{38,39,44-46} One the other hand, to enhance the stability of Au nanoparticles against aggregation, corrosion or dissolution during the operation of reactions as well as enhances the plasmonic absorption of the Au NPs, in particular in the visible spectral region designing a core-shell nanoparticles have significant advantages. However, one problem with the core-shell nanoparticles is that it may reduce the light to reach core (Au nanoparticles).⁴⁷⁻⁵¹ Therefore, assuring that the shell (ZnO) is not density and enough porosity is essential.⁴⁷⁻⁵⁰ By decreasing the thickness of shell (ZnO) the photocatalytic activity increases.^{48,50}

Significant features of this new photocatalyst is I) the capacity for both aliphatic and aromatic carboxylic acids to tolerate CO_2 -extrusion under very mild conditions (room temp, household light bulb), and more important 2) its switchable capacity by the external stimuli for selective aerobic oxidation to aldehydes/ketones and selective reduction to alkanes without use of any oxidants or additive.

2. RESULTS AND DISCUSSION

2.1 Proposed Mechanism

As described more specifically in **Figure 1**, upon exposure to visible light, photocatalyst Au@ZnO core-shell nanoparticles electrons in Au nanoparticle according to LSPR are excited and then transferred to the CB of ZnO. So an electron/hole (e^{-}/h^{+}) generated. Carboxylic acid is oxidatively decarboxylated to the corresponding radical cation by a single-electron transfer to the hole generated in Au nanoparticles under aerobic atmosphere. O₂ will get hold of the electrons from the CB of ZnO, with the result of producing O₂⁺⁻ active species. Then, O₂⁺⁻ will couple with H⁺ to generate HO₂⁺ which then coupling with carbon radical (R₁CH⁺R₂), which was further oxidized into aldehydes (**Figure 1A**). By switching off the oxygen (air), and under inert conditions (N₂ or Ar), reduction of carboxylic acids to alkenes was occurred. This reduction undergoes *via* steps: (*i*) generated e⁻/h⁺ pairs by irradiation of visible-light, (*ii*) electron transfer from carboxylic acid to hole (h⁺), CO₂ and H⁺ extrusion (*iii*) electron transfer from CB of ZnO to H⁺ to generate H⁺ and finally (*iv*) coupling between H⁺ and R₁CH⁺R₂ to generated the desired reductive product (**Figure 1B**).

We began our investigation into the proposed photo oxidative decarboxylation and proto decarboxylation by preparing Au@ZnO core-shell nanoparticles. The photocatalyst is prepared by solution-phase method (with particle size ~30-50 nm). Our method has many potential applications for the synthesis of semiconductor materials in large-scale because it is simple, low-cost, efficient, and requires no heating. Then Au@ZnO core-shell nanoparticles was fully analyzed by XRD, ICP, SEM, TEM, HR-TEM, XPS, BET, elemental mapping and UV-Vis absorption which are indicated in SI (Figures S1-S8 and Tables S1 and S2). Gold exists in one state according to the XPS spectrum (Figure 2A and Figure S1).



Figure 1. Proposed mechanism for the decarboxylation of carboxylic acids with Au@ZnO core-shell nanoparticles photoredoxcatalysis: (A) O₂ on, (B) O₂ off, (C-D) Optimized conditions.

The peaks observed at 91.78 and 89.18 eV, can be ascribed to Au $4f_{5/2}$ and Au $4f_{7/2}$ of the metallic Au, respectively. The transmission electron microscopy (TEM) image (Figure S2), high-resolution TEM image (Figure 2B and Figure S2) and scanning electron microscopy (SEM) images (Figure S3) showed slightly truncated Au@ZnO core-shell nanoparticles with average size of 30-50 nm. From this Figure, we could conclude that Au is covered preferably by ZnO with approximately sphere shape. It is clearly seen from Figure 2B that dark contrasts are the Au and the light contrast parts are the ZnO because Au atom is heavier than Zn and O atoms. Also, Figure 2B presents the lattice fringes of Au@ZnO core-shell nanoparticles, from which the interplanar spacing is found to be 0.283 nm and 0.242 nm, for ZnO (100) and Au (111) planes, respectively. Elemental mapping images demonstrate that the Au@ZnO core-shell nanoparticles are composed of Au, Zn and O and also suggest the successful formation of Au@ZnO core-shell nanoparticles (Figure S4). The Elemental mapping images (Figure S4) also demonstrates the uniform distribution of different nanoparticles (Au and Zn NPs), without any agglomeration and the results are in agreement with HR-TEM and TEM images. Figure 2C and Figure S5 shows the XRD patterns of pure and 1.89 wt% Au supported on ZnO nanoparticles. It can be seen that for the Au@ZnO core-shell nanoparticles, new peaks appear at 20= 38.39° and 44.61° corresponding, to the (111) and (200) planes, respectively, of the cubic phase of Au metal (JCPDS number card 04-0784). The UV-Vis absorption spectra of ZnO nanoparticles and Au@ZnO core-shell nanoparticles are shown in Figure S6. The peak at 549 nm is due to the characteristic LSPR absorption of Au NPs. The shape and size of gold nanoparticles were determined by the maximum wavelength of the surface plasmon resonance absorption band. The induced coupled plasma (ICP) analysis confirmed that the Au@ZnO core-shell nanoparticles photocatalyst contains only 1.89 wt % Au.

Figure 2. (A) XPS spectra of Au4f. (B) HR-TEM image of Au@ZnO core-shell nanoparticles. (C) XRD pattern of 1.89% (wt%) of Au modified ZnO.

After successful preparation and characterization of Au@ZnO core-shell nanoparticles photocatalyst, we were started our investigation with 4-methoxyphenylacetic acid as a model reaction. The optimized results are shown in **Tables S3-S5**. A solution of 4-methoxyphenylacetic acid in CH₃CN was irradiated by 11 W white LED in the attendance of Au@ZnO core-shell nanoparticles as photocatalyst and Cs_2CO_3 for 24 h at room temperature, then the reaction mixture was worked-up and the desired product 4-methoxybenzaldehyde was formed in 76% yield (**Table S3**, entry 1). The photocatalytic decarboxylation using air as oxidant was operated easily over the Au@ZnO core-shell nanoparticles photocatalysts under mild reaction conditions. By comparing the reaction under light on/off conditions, significant difference in conversion confirms that the major driving force for the reactions is light absorption. The reaction of 4-methoxyphenylacetic acid decarboxylation was also tested in the absence of any catalyst, showing a 0% conversion (**Table S5**, entry 6).

So, we changed a lot of factors, including solvent, photocatalyst loading, base, light source and also atmosphere. When the solvent was changed to CHCl₃, 4-methoxybenzaldehyde was obtained in 83% yield (**Table S3**). Afterwards, selection of some bases, the results showed that excess amount of K₂CO₃ (1.5 mmol) was more effective and the yield of 4-methoxybenzaldehyde was increased sharply to 89% (**Table S4**). Also the amounts of Au@ZnO core-shell nanoparticles were optimized, and we were chosen 0.004 g of the catalyst for other investigations because of lower amount of gold loading (**Table S5**). According to the proposed mechanism (**Figure 1**), for good photocatalytic activity, photogeneration of electrons and holes are needed. Only photons with energy larger than the photocatalyst band gap can be absorbed and used for photoelectrons and -holes generation. We were used different wavelengths including red (620-750 nm), green (495-570 nm) and blue (400-495 nm). The yield improved to 94% when the reaction was under irradiation by 11 W blue LED (**Figure S9**). All the light intensities were strictly the same (0.4 W/ cm²) in every wavelength region. Photons with long wavelengths (lower energy, such as red or green) cannot transport enough energy to activate electrons, resulting in decreased selectivity and low conversions; photons with short wavelengths (higher frequency, such as blue) carry more energy than ones with long wavelengths .The dependence of photocatalytic activity on wavelength indicates that energetic electrons excited by light absorption are responsible for the observed photocatalytic activity.

In addition, outdoor ability under sunlight was investigated. This was executed on a summer day, in September, in Shiraz with the sun at 68.5° zenith angles and temperature 28-38 °C ranges. This result shows that the Au@ZnO core-shell nanoparticles catalyst has excellent sunlight applicability (**Figure S10**).

After optimized the reaction conditions, we tried to investigate the scope of the protocols. **Table 1**, is shown the photo oxidative decarboxylation of a wide range of aliphatic and aromatic carboxylic acids to the corresponding aldehydes and

ketones. The results indicated that phenylacetic acids bearing electron-donating groups on the aromatic rings, successfully underwent the decarboxylation reaction, and the desired aldehydes were obtained in excellent yield (1 to 4). Phenylacetic acids possessing electron-withdrawing groups on the aromatic ring shown little activity and lower conversion under standard conditions (5 to 10). Table 1 also shows that our method is lenient to a variety of different functional groups, such as -OH, -NO₂, -OCH₃, -Cl, -CH₃ and -CN. It should be mentioned that the attendance of -OH functionality on the phenyl acetic acid, also gave excellent result (4). It is interesting to show that -OH group with the hole trapping ability due to its electrondonating nature was not inhibited the oxidation reaction. Furthermore, when using the derivatives substituted in the α position on the phenylacetic acids, the yield was little decreased, this can be explained by the steric effect. Also 2-(anthracen-9-yl) acetic acid and 1-naphthylacetic acid reacted excellent and gave the aldehyde in 82% and 84% yields, respectively (16 and 17). Under standard conditions heteroaromatic acetic acids also worked well; for example, 2-pyridinecarboxaldehyde and 2-furancarboxaldehyde were obtained from 2-pyridylacetic acid and 2-furanacetic acid in 85% and 93% yields, respectively (11 and 12). Beside aromatic aldehyde synthesis, our protocol was given good results for synthesis aliphatic aldehydes (18 and 19). We next turned our attention to synthesis of ketones by choosing α -di substituted carboxylic acids (20 to 32). We were pleased to find that arrange of aromatic and aliphatic ketones, could be synthesized in excellent yields. Pending the investigation of the substrate scope, an interesting result was observed. When 2-(benzyloxy)propanoic acid and 2-phenoxy-2-phenylacetic acid were subjected to this photo oxidative decarboxylation strategy, esters as product was obtained (29 and 30). This strategy could be a good electron for synthesis of esters. This is the first report that a photocatalyst could generate aldehydes, ketones and especially esters from carboxylic acids.

Table 1. A broad range of aliphatic and aromatic aldehydes/ketones/esters synthesis^a

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^{*a*} Reaction conditions: Carboxylic acids (1 mmol), Au@ZnO core-shell nanoparticles (0.004 g, 1.89 wt % Au), K₂CO₃ (1.5 mmol), CHCl₃ (3 mL), at room temperature, 11 W blue LED (wavelength in the range 400-495 nm), air atmosphere, 24 h, yields refer to isolated yield (conversion). Yield of product **18**, **19**, **31** and **32** was determined by HPLC analysis.

During the optimization of the atmosphere for oxidative decarboxylation reaction of 4-methoxyphenylacetic acid, when the reactions were carried out in the argon or N_2 instead of air, surprising results were observed. Instead of 4-methoxybenzaldehyde, 1-methoxy-4-methylbenzene was obtained in 85%. It showed the first step is the decarboxylation to generate a radical, and then this radical without any O_2 which need for further oxidation to yield a carbonyl group trapped at this stage (Figure 1B).

This interesting result cause that we switch to test our system in photo proto decarboxylation with O_2 switch off (**Table 2**). The reaction yields range from good to excellent.

To advance illustrate the usefulness of this photocatalytic protocol, we accomplish a series of medicinal and agrochemical agent. As can be seen from **Table 2**, some biologically and medicinally relevant systems could be synthesized from their carboxylic acid by our simple method.⁵²⁻⁵⁴ Remarkably, 3,4-dimethoxybenzaldehyde could be produced in high excellent yield (95%), which is a notable intermediate for the synthesis of some pharmaceutical drugs such as amiquinsin, hoquizil, piquizil, prazosin, quinazocin, tiapamil, toborinone, verazide, and vetrabutine.

Benefits of heterogeneous catalysts are simple photocatalyst removal and they can be recycled after separation. Also in some cases, recycling capability catalyst has a great impact on the economical possibility of a given protocol or the scale up of the reaction, due to the in expensive and abundance of Au its reusability is critical. Therefore, the recycling capability of the catalyst was studied by running the oxidative and proto decarboxylation reaction for 4-methoxyphenylacetic acid under optimized conditions for five runs. After each run, the catalyst was regained by centrifugation and washed with water followed by ethanol and dried at 80°C, and then the catalyst was directly applied in another cycle without further treatment or regeneration. Au@ZnO core-shell nanoparticles exhibits excellent reusability (**Figure S11**) and the catalyst capability were not remarkably decreased even after 5 runs. The amount of leached gold was also determined by ICP analysis (**Tables S6-S7**). The negligible metal loss is the reason for the good reusability of the photocatalyst.

Table 2. Substrate scope^a Au@ZnO (0.004 g), K_2CO_3 (1.5 mmol) CHCl₃ (3 mL). Argon, r.t $R_1, R_2 = H$ or alkyl or aryl Aromatics and Aliphatic -CH₃ CH₂ O_2N CH-35, 79% (86 %) 38, 59% (66 %) 33, 81% (84 %) 37, 72% (76%) 34, 75% (81%) 36,87% (92%) CH(OCH₃)₂ NO_2 H₃CH₂C OMe . OMe MeC 39, 61% (68 %) 40, 79% (86 %) 41,68% (77%) 42, 63% (66%) 43, 61% (65%) 44, 53% (57%) Н 47, 51 % 46, 56% (59%) 45, 55% (59%) **Biologically Active Molecules** CH₃ ĊΗ₃ H 48,68% (74%) 49,65% (69%) Antipyrine Coumarin (nonsteroidal anti-inflammatory drug NSAID)) Uricosuric effect Treatment of lymphedema H₃CO. .CHO СНО CHO H₂CO HO H₃CO OCH₂ 4,86% (92%) 2,96% (100%) 3,95% (100%) Antiepileptic and Antifungal activity anticonvulsive activity

^{*a*} Reaction conditions: Carboxylic acids (1 mmol), Au@ZnO core-shell nanoparticles (0.004 g, 1.89 wt % Au), K₂CO₃ (1.5 mmol), CHCl₃ (3 mL), at room temperature, 11 W blue LED (wavelength in the range 400-495 nm), argon atmosphere, 24 h, yields refer to the isolated (conversion). Yield of product 47 was determined by HPLC analysis.

The low-cost and availability of 4-methoxyphenylacetic acid and also the simplicity of the reaction operation allow us to investigate on a process scale. A comparable yield was provided when a reaction run using 10 g of 4-methoxyphenylacetic acid to that obtained on a small scale (7.78 g, 94%). This primary result shows that the method is potentially applicable to large-scale. In addition, using continuous processing is another attractive option for scale up. So we decided to investigate the behavior of this reaction in a continuous flow. By using a column, glass beads, silicagel, and the Au@ZnO core-shell

nanoparticles catalyst, a simple and recyclable continuous-flow photo reactor were prepared (**Figure S13**, for details, see the SI). The use of a continuous flow reactor resulted in shortening of the reaction time which show the potential application and highlighting the practicality of our method.

In order to understand the reaction mechanism, a set of control experiments were managed (**Figure 3**). 2,2,6,6-Tetramethylpiperidinyl-1-oxy (TEMPO[•]) and 5,5-dimethy-1-pyroline-*N*-oxide (DMPO[•]) are stable nitroxide radicals and standard electron-trapping agents that they could capture electrons from Au nanoparticles or CB of ZnO.^{55,56} When 2 mmol of TEMPO or DMPO (2:1, TEMPO[•] or DMPO[•]/ 4-methoxyphenylacetic acid) were added to the reactions system, the conversion of 4-methoxyphenylacetic acid decreased (**Figure 3**). Triethanolamine (TEA), ammonium oxalate, methanol and ethylenediaminetetraacetic acid (EDTA) were employed as a scavenger to trap the photogenerated holes on the surface of Au nanoparticles.^{55, 57-58} The conversion of 4-methoxyphenylacetic acid also decreased when (TEA), ammonium oxalate, methanol or (EDTA) was added to the reactions system (**Figure 3**). These phenomena indicate that the oxidative and proto decarboxylation of carboxylic acids reactions cannot proceed without the reduction of electrons or oxidation of holes.

The deficiency of any reaction in the dark declared that the products formation activated and deactivated by visible light. To find this "On-Off" visible light irradiation experiment was operated. These preparative results only show that radical-chain propagation in this transformation is not a key step (**Figure S12**).

In summary, we have demonstrated that Au@ZnO core-shell nanoparticles can be utilized as an efficient heterogeneous photoredox catalyst in the direct oxidative/proto decarboxylation of carboxylic acids under mild and operationally simple conditions. Au@ZnO core-shell nanoparticles shows a benefit switchable photoredox catalyst which could absorb visible light due to LSPR effect of gold nanoparticles and by On/Off a simple stimulus (O_2), the reaction could be turned for synthesis both aldehyde/ketone/esters and alkane/arenes. This method shows the excellent result for the synthesis of medically important compounds. In addition, this strategy will expand the productivity of decarboxylation both in organic synthesis and industrial.

EXPERIMENTAL SECTION

General information

Chemical materials used in this study were obtained from Sigma-Aldrich, Fluka and Merck. The progresses of the reactions were checked by thin-layer chromatography (TLC) using silicagel SILG/UV 254 plates or by GC. Column chromatography was accomplished on small columns of silicagel. Infrared spectra of the samples were recorded on a Shimadzu FTIR-8300 spectrophotometer using KBr pellets. The amount of gold nanoparticles catalyst (Au@ZnO) was measured by inductively coupled plasma (ICP). Power X-ray diffraction patterns were meter with Cu K α (λ = 1.54178 Å) radiation. The morphology of the Au@ZnO core-shell nanoparticles was determined by scanning electron microscopy (SEM). The specific surface areas (SSA_{BET}; [m²g⁻¹]) of the catalyst were analyzed with the nitrogen adsorption measurement, using the BET method at 77 K. The porous structural parameter was taken by Barret-Joyner-Halenda (BJH) data. The size of the synthesized nanoparticles was also confirmed by high-resolution transmission electron microscopy (HR-TEM). Elemental analysis was performed using Thermofinigan Flash EA-1112 CHNS rapid elemental analyzer. UV–vis diffuse reflectance spectrum was performed with a Shimadzu UV-2450 spectrophotometer. Melting points were determined by Buchi Melting Point B-545 electrical melting point apparatus. ¹H and ¹³C NMR spectra were recorded on Bruker, Avance 400 (400 MHz and 100 MHz respectively). UV-Vis spectra recorded on a Lambda 25 UV-Vis spectrometer using a 1 cm quartz cuvette.

The light source used for photochemical experiments were 11 W white LED (wavelength in the range 400-750 nm), 11 W blue LED (wavelength in the range 400-495 nm), 11 W green LED (wavelength in the range 495-570 nm), 11 W red LED (620-750 nm). Light intensities were strictly the same (0.4 W/cm²) in each wavelength area. Manufacturer: Iran; model: ED A60; distance from the light source to the irradiation vessel: 3 cm; material of the irradiation vessel: borosilicate reaction tube and not use any filters.

Preparation of Au@ZnO Core-Shell Nanoparticles

Au@ZnO core-shell nanoparticles were prepared with the modified procedure reported by Sun et.al.⁵⁹ In a round bottom flask, 20 mL aqueous solution of 2.6×10^{-4} M tri-sodium citrate and 2.6×10^{-4} M HAuCl₄.3H₂O were prepared. Afterwards, 1 mL 0.1 M fresh aqueous sodium borohydride (NaBH₄) was added and stirring for 5 h at room temperature. The solution turned red after adding of NaBH₄. Next 20 mL 60 mM cetyltrimethylammonium bromide (CTAB) and 0.2 M Zn(NO₃)₂ in ethanol was mixed with previous solution. Afterward, 20 mL 0.5 M NaOH ethanolic solution was added and stirring was for 30 min. Finally, white pink suspension was obtained, centrifuged, washed with ethanol and distilled water to get the Au@ZnO core-shell nanoparticles.

General Procedure for the Oxidative Decarboxylation of Carboxylic Acids

A mixture of carboxylic acids (1 mmol), K_2CO_3 (207.3 mg, 1.5 mmol), Au@ZnO core-shell nanoparticles (4 mg) and CHCl₃ (3 mL) was put into a Pyrex glass tube with a magnetic stirrer and placed 3 cm from 11 W blue LED, and the reactant mixture was carried out under air atmosphere at room temperature for 24 h. After the reaction was complete, it was centrifuged to remove the catalyst and the mixture was purified by column chromatography on silicagel (Petroleumether:Ethyl acetate) to give the desired product.

General Procedure for the Protodecarboxylation of Carboxylic Acids

A mixture of carboxylic acids (166.0 mg, 1 mmol), K₂CO₃ (207.3 mg, 1.5 mmol), Au@ZnO core-shell nanoparticles (4 mg) and CHCl₃ (3 mL) was put into a Pyrex glass tube with a magnetic stirrer and placed 3 cm from 11 W blue LED, and the reactant mixture was carried out under argon atmosphere at room temperature for 24 h. After the reaction was complete, it was centrifuged to remove the catalyst and the mixture was purified by column chromatography on silicagel (Petroleumether:Ethyl acetate) to give the desired product.

Protodecarboxylation of 4-(2, 3-dimethyl-5-oxo-2, 5-dihydro-1H-pyrazol-1-yl) benzoic acid (10 gram scale)

A mixture of 4-(2,3-dimethyl-5-oxo-2,5-dihydro-1*H*-pyrazol-1-yl)benzoic acid (10009.5 mg, 43.1 mmol), K₂CO₃ (8935 mg, 64.65 mmol), Au@ZnO core-shell nanoparticles (172.4 mg) and CHCl₃ (130 mL) was put into a Pyrex glass with a magnetic stirrer and placed 3 cm from 11 W blue LED, and the reactant mixture was carried out under argone atmosphere at room temperature for 24 h. After the reaction was complete, it was centrifuged to remove the catalyst and the mixture was purified by column chromatography on silicagel (Petroleumether:Ethyl acetate) to give the desired product.

Catalyst Recyclability for the Oxidative Decarboxylation of Carboxylic Acids

A mixture of 4-methoxyphenylacetic acid (1 mmol), K_2CO_3 (207.3 mg, 1.5 mmol), Au@ZnO core-shell nanoparticles (4 mg) and CHCl₃ (3 mL) was put into a pyrex glass tube with a magnetic stirrer and placed 3 cm from 11 W blue LED, and the reactant mixture was carried out under air atmosphere at room temperature for 24 h. After the reaction was completed, it was diluted with EtOAc and centrifuged to remove the catalyst. Then the catalyst was washed with water followed by ethanol (twice) and dried at 80°C in an oven. After each run, the catalyst was weighted and then it was directly applied in next cycle without further treatment or regeneration (details are presented in Table S6).

Catalyst Recyclability for the Protodecarboxylation of Carboxylic Acids

A mixture of 4-methoxyphenylacetic acid (1 mmol), K₂CO₃ (207.3 mg, 1.5 mmol), Au@ZnO core-shell nanoparticles (4 mg) and CHCl₃ (3 mL) was put into a pyrex glass tube with a magnetic stirrer and placed 3 cm from 11 W blue LED, and the reactant mixture was carried out under argon atmosphere at room temperature for 24 h. After the reaction was completed, it was diluted with EtOAc and centrifuged to remove the catalyst. Then the catalyst was washed with water followed by ethanol (twice) and dried at 80°C in an oven. After each run, the catalyst was weighted and then it was directly applied in next cycle without further treatment or regeneration (details are presented in Table S7).

Characterization data:

4-Methoxybenzaldehyde (1)¹²

94% yield (128.0 mg); clear liquid; TLC (Petroleumether:Ethyl acetate, 85:15 v/v): R_f = 0.31. IR (thin film) 3076, 2964, 2936, 2841, 2736, 1702, 1688, 1511, 1460, 1442, 1390, 1261, 1182, 1108, 1036, 855cm⁻¹; ¹H NMR (400 MHz, CDCl₃, ppm) δ 9.82 (s, 1H), 7.79-7.76 (d, 2H, *J* = 8 Hz,), 6.96-6.93 (d, 2H, *J* = 8 Hz), 3.83 (s, 3H); ¹³C {¹H} NMR (100 MHz, CDCl₃, ppm) δ 190.6, 164.5, 131.8, 129.8, 114.2, 55.4; UV/Vis (CH₃CN): λ_{max} 272 nm.

3, **5**-Dimethoxybenzaldehyde (2)⁶⁰

96% yield (159.5 mg); colorless solid, m.p: 45-48 °C (lit. 45-48 °C); TLC (Petroleumether:Ethyl acetate, 80:20 v/v): R_f = 0.26; IR (thin film) 3086, 2966, 2935, 2843, 2808, 1706, 1607, 1595, 1470, 1432, 1388, 1302, 1250, 1207, 1160, 1066 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, ppm) δ 9.91 (s, 1H), 7.02 (s, 2H), 6.71 (s, 1H), 3.85 (s, 6H); ¹³C {¹H} NMR (100 MHz, CDCl₃, ppm) δ 191.9, 161.2, 138.4, 107.1, 107.1, 55.6; UV/Vis (CH₃CN): λ_{max} 267 nm; Anal. Calcd for C₉H₁₀O₃: C, 65.05; H, 6.07. Found: C, 65.22; H, 6.21.

3, 4-Dimethoxybenzaldehyde (3)⁶¹

95% yield (157.9 mg); peach colored crystals, m.p: 43-45 °C (lit. 44.5-45 °C); TLC (Petroleumether:Ethyl acetate, 80:20 v/v): $R_f = 0.27$; IR (thin film) 3009, 2970, 2942, 2842, 2762, 1683, 1597, 1587, 1514, 1466, 1424, 1398, 1269, 1190, 1178, 1137, 1034, 1022 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, ppm) δ 9.85 (s, 1H), 7.48-7.45 (d, 1H, J = 12 Hz), 7.41 (s, 1H), 6.99-6.96 (d, 1H, J = 12 Hz), 3.97 (s, 3H), 3.94 (s, 3H); ¹³C {¹H} NMR (100 MHz, CDCl₃, ppm) δ 190.9, 154.5, 149.6, 130.1, 126.9, 110.4, 108.9, 56.2, 56.0; UV/Vis (CH₃CN): λ_{max} 274 nm; Anal. Calcd for C₉H₁₀O₃: C, 65.05; H, 6.07. Found: C, 65.20; H, 6.16.

4-Hydroxybenzaldehyde (4)54

86% yield (105.0 mg); yellow powder, m.p: 113-116 °C (lit. 112-116 °C); TLC (Petroleumether:Ethyl acetate, 75:25 v/v): R_{f} = 0.2; IR (thin film) 3194, 3009, 2855, 2765, 1695, 1561, 1511, 1466, 1431, 1397, 1217, 1129, 1098 cm⁻¹; ¹H NMR (400 MHz, DMSO-*d*₆, ppm) δ 10.62 (s, 1H), 9.79 (s, 1H), 7.78-7.75 (d, 2H, *J* = 12 Hz), 6.95-6.92 (d, 2H, *J* = 12 Hz); UV/Vis (CH₃CN): λ_{max} 270 nm; Anal. Calcd for C₇H₆O₂: C, 68.85; H, 4.95. Found: C, 69.10; H, 5.16.

4-Chlorobenzaldehyde (5)⁶²

89% yield (125.1 mg); white solid, m.p: 46-48 °C (lit. 47.5 °C); TLC (Petroleumether:Ethyl acetate, 90:10 v/v): $R_f = 0.29$; IR (thin film) 3061, 2814, 2729, 1713, 1673, 1591, 1483, 1414, 1317, 1296, 1261, 1164, 1055, 1015 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, ppm) δ 9.99 (s, 1H), 7.84-7.82 (d, 2H, *J*= 8 Hz), 7.53-7.51 (d, 2H, *J*= 8 Hz); ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm) δ 191.0, 141.0, 134.7, 130.9, 129.5; UV/Vis (CH₃CN): λ_{max} 240 nm; Anal. Calcd for C₇H₅ClO: C, 59.81; H, 3.59. Found: C, 60.02; H, 3.81.

4-Nitrobenzaldehyde (6)¹²

87% yield (131.5 mg); slightly yellow powder, m.p: 103-105.5 °C (lit. 13-106 °C); TLC (Petroleum ether:Ethyl acetate, 80:20 v/v): $R_f = 0.3$; IR (thin film) 3066, 2854, 2732, 1706, 1681, 1608, 1599, 1554, 1454, 1464, 1379, 1346, 1302, 1287, 1164 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, ppm) δ 10.18 (s, 1H), 8.43-8.40 (d, 2H, *J*= 12 Hz), 8.11-8.08 (d, 2H, *J*= 12 Hz); ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm) δ 190.3, 151.2, 140.0, 130.5, 124.3; UV/Vis (CH₃CN): λ_{max} 264 nm; Anal. Calcd for C₇H₅NO₃: C, 55.64; H, 3.34; N, 9.27. Found: C, 55.72; H, 3.39; N, 9.38.

3-Nitrobenzaldehyde (7)⁶³

87% yield (131.5 mg); slightly yellow powder, m.p: 57-59 °C (lit. 58 °C); TLC (Petroleum ether:Ethyl acetate, 90:10 v/v): R_f = 0.28; IR (thin film) 3068, 2858, 2736, 1716, 1603, 1569, 1559, 1455, 1464, 1372, 1346, 1267, 1134 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, ppm) δ 10.14 (s, 1H), 8.73 (s, 1H), 8.52-8.49 (d, 1H, *J* = 12 Hz), 8.27-8.24 (d, 1H, *J* = 12 Hz), 7.81-7.77 (t,

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1H, J = 8 Hz); ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm) δ 189.8, 148.8, 137.4, 134.7, 130.4, 128.6, 124.4; UV/Vis (CH₃CN): λ_{max} 262 nm; Anal. Calcd for C₇H₅NO₃: C, 55.64; H, 3.34. Found: C, 55.86; H, 3.69.

2-Nitrobenzaldehyde (8)¹²

84% yield (126.9 mg); slightly yellow powder, m.p: 41-43 °C (lit. 43 °C); TLC (Petroleum ether: Ethyl acetate, 90:10 v/v): $R_f = 0.24$; IR (thin film) 3051, 2854, 2738, 1701, 1623, 1601, 1554, 1519, 1464, 1443, 1358, 1326, 1261, 1165 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, ppm) δ 10.42 (s, 1H), 8.13-8.11 (d, 1H, *J* = 8 Hz), 7.96-7.94 (d, 1H, *J* = 8 Hz), 7.82-7.78 (m, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm) δ 188.2, 134.1, 133.7, 131.3, 129.6, 124.5; UV/Vis (CH₃CN): λ_{max} 250 nm; Anal. Calcd for C₇H₅NO₃: C, 55.64; H, 3.34; N, 9.27. Found: C, 55.71; H, 3.41; N, 9.15.

4-Formylbenzonitrile (9)64

86% yield (112.8 mg); white solid, m.p: 101-102.5 °C (lit. 100-102.5 °C); TLC (Petroleum ether:Ethyl acetate, 92:8 v/v): $R_f = 0.26$; IR (thin film) 3057, 2830, 2751, 2235, 1739, 1608, 1539, 1507, 1380, 1312, 1297, 1174, 832 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, ppm) δ 10.11 (s, 1H), 8.02-8.00 (d, 2H, *J*= 8 Hz), 7.87-7.85 (d, 2H, *J*= 8 Hz); ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm) δ 190.7, 138.7, 132.9, 129.9, 117.7, 117.6; Anal. Calcd for C₈H₅NO: C, 73.27; H, 3.84; N, 10.68. Found: C, 73.53; H, 3.79; 10.62.

2-Chloro-3-nitrobenzaldehyde (10)65

81% yield (150.3 mg); white solid, m.p: 92-95 °C (lit 93-95 °C); TLC (Petroleumether:Ethyl acetate, 88:12 v/v): $R_f = 0.21$; IR (thin film) 3083, 3072, 2859, 2739, 1702, 1688, 1599, 1542, 1478, 1465, 1359, 1271, 1146, 1052, 976cm⁻¹; ¹H NMR (400 MHz, CDCl₃, ppm) δ 10.43 (s, 1H), 8.69-8.68 (d, 1H, *J*= 4 Hz), 8.33-8.30 (t, 1H, *J*= 6 Hz), 7.63-7.61 (d, 1H, *J*= 8 Hz); ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm) δ 187.4, 147.0, 143.6, 133.1,132.0, 128.8, 124.5; UV/Vis (CH₃CN): λ_{max} 235 nm; Anal. Calcd for C₇H₄ClNO₃: C, 45.31; H, 2.17; N, 7.55. Found: C, 45.47; H, 2.04; N, 7.47.

Isonicotinaldehyde (11)⁶⁶

87% yield (93.2 mg); slight brown liquid; TLC (Petroleumether:Ethyl acetate, 85:15 v/v): $R_f = 0.18$; IR (thin film) 3042, 2858, 2728, 1712, 1605, 1573, 1536, 1489, 1354, 1228, 1182, 1023 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, ppm) δ 10.02 (s, 1H), 8.83-8.81 (d, 2H, *J* = 8 Hz), 7.65-7.63 (d, 2H, *J* = 8 Hz); ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm) δ 191.5, 151.2, 141.3, 122.0; UV/Vis (CH₃CN): λ_{max} 268 nm.

Picolinaldehyde (12)67

85% yield (91.0 mg); clear brown liquid; TLC (Petroleumether:Ethyl acetate, 85:15 v/v): R_f = 0.23; IR (thin film) 3064, 2879, 2736, 1701, 1622, 1558, 1512, 1429, 1328, 1212, 1161, 1059 cm⁻¹; ¹H NMR (400 MHz CDCl₃, ppm) δ 10.07 (s, 1H), 8.79-8.77 (d, 1H, *J*= 8 Hz), 7.96-7.94 (d, 1H, *J*= 8 Hz), 7.89-7.87 (t, 1H, *J*= 4 Hz), 7.54-7.50 (m, 1H); ¹³C {¹H} NMR (100 MHz, CDCl₃, ppm) δ 193.5, 152.8, 150.2, 137.0, 127.9, 121.7; UV/Vis (CH₃CN): λ_{max} 259 nm.

Furan-2-carbaldehyde (13)68

93% yield (89.4 mg); colorless liquid; TLC (Petroleumether:Ethyl acetate, 88:12 v/v): R_f = 0.23; IR (thin film) 3063, 2841, 2763, 1710, 1683, 1571, 1478, 1395, 1278, 1237, 1160, 1084, 1018, 931, 888 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, ppm) δ 9.64 (s, 1H), 7.68-7.66 (d, 1H, *J*= 8 Hz), 7.25-7.21 (t, 1H, *J*= 8 Hz), 6.60-6.58 (d, 1H, *J*= 8 Hz); ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm) δ 177.8, 152.9, 148.1, 121.1, 112.6.

Thiophene-2-carbaldehyde (14)¹²

95% yield (106.5 mg); colorless brown oil; TLC (Petroleumether:Ethyl acetate, 88:12 v/v): $R_f = 0.22$; IR (thin film) 3082, 2863, 2729, 1706, 1597, 1587, 1503, 1489, 1362, 1269, 1138, 1074 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, ppm) δ 9.87 (s, 1H), 7.74 (m, 2H), 7.16 (m, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm) δ 183.0, 143.9, 136.6, 135.2, 128.4; UV/Vis (CH₃CN): λ_{max} 274 nm.

1H-Indole-2-carbaldehyde (15)69

89% yield (129.2 mg); clear yellow solid, m.p: 196-198 °C (lit. 197-198 °C); TLC (Petroleum ether:Ethyl acetate, 70:30 v/v): $R_f = 0.18$; IR (thin film) 3056, 2856, 2741, 1708, 1529, 1441, 1380, 1258, 1153 cm⁻¹; ¹H NMR (400 MHz, DMSO-*d*₆, ppm) δ 11.33 (s, 1H), 9.58 (s, 1H), 8.11-8.09 (d, 1H, *J* = 8 Hz), 7.71 (s, 1H), 7.33 (m, 1H), 7.14 (m, 2H); ¹³C{¹H} NMR (100 MHz, DMSO-*d*₆, ppm) δ 183.0, 143.9, 136.6, 135.2, 128.4; UV/Vis (CH₃CN): λ_{max} 311 nm; Anal. Calcd for C₉H₇NO: C, 74.47; H, 4.86; N, 9.95. Found: C, 74.89; H, 5.01; N, 10.17.

1-Naphthaldehyde (16)¹²

84% yield (131.2 mg); clear yellow liquid, TLC (Petroleumether:Ethyl acetate, 80:20 v/v): $R_f = 0.28$; IR (thin film) 3073, 2858, 2739, 1691, 1532, 1469, 1372, 1269, 1161, 1058 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, ppm) δ 10.40 (s, 1H), 9.29-9.27 (d, 1H, *J*= 8 Hz), 8.09-8.07 (d, 1H, *J*= 8 Hz), 7.97-7.96 (d, 1H, *J*= 4 Hz), 7.93-7.91 (d, 1H, *J*= 8 Hz), 7.71-7.68 (t. 1H, *J*= 6 Hz), 7.63 (m, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm) δ 193.6, 136.7, 135.3, 133.7, 131.4, 130.5, 129.0, 128.5, 127.0, 124.9; UV/Vis (CH₃CN): λ_{max} 312 nm.

Anthracene-9-carbaldehyde (17)⁷⁰

82% yield (169.1 mg); yellow crystals; m.p: 103-105 °C (lit. 102-106 °C); TLC (Petroleum ether:Ethyl acetate, 80:20 v/v): $R_{f}= 0.31$; IR (thin film) 3061, 2855, 2742, 1668, 1626, 1523, 1464, 1368, 1282, 1175, 1049 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, ppm) δ 11.38 (s, 1H), 8.87-8.84 (d, 2H, *J*= 12 Hz), 8.53 (s, 1H), 7.93-7.91 (d, 2H, *J*= 8 Hz), 7.56-7.54 (t, 2H, *J*= 4 Hz), 7.45-7.43 (t, 2H, *J*= 4 Hz); ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm) δ 190.9, 163.3, 132.1, 128.4, 115.8; UV/Vis (CH₃CN): λ_{max} 261 nm; Anal. Calcd for C₁₅H₁₀O: C, 87.36; H, 4.89. Found: C, 87.48; H, 4.73.

1-(4-Nitrophenyl) ethan-1-one (20)⁷¹

88% yield (145.3 mg); light yellow solid; m.p: 79-81 °C (lit. 80-81 °C); TLC (Petroleumether:Ethyl acetate, 90:10 v/v): $R_f = 0.34$; IR (thin film): v = 3062, 2980, 2965, 1685, 1563, 1427, 1373, 1256, 1032, 956, 854, 768, 654; ¹H NMR (250 MHz, DMSO-*d*₆, ppm) δ 8.28 (d, 2H); 8.15 (d, 2H), 2.65 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm) δ 196.4, 150.3, 141.4, 129.3, 123.8, 27.0; Anal. Calcd for $C_8H_7NO_3$: C, 58.18; H, 4.27; N, 8.48. Found: C, 58.36; H, 4.10; N, 8.40. **1-(4-Methoxyphenyl) ethan-1-one (21)**⁶¹ 88% yield (132.1 mg); white solid, m.p: 36-38 °C (lit. 38 °C); TLC (Petroleumether:Ethyl acetate, 90:10 v/v): $R_f = 0.36$; IR (thin film): v = 3045, 2961, 2973, 1669, 1534, 1516, 1465, 1364, 1110, 1032, 946, 849, 778, 654; ¹H NMR (250 MHz, DMSO-*d*₆, ppm) δ 7.50 (d, 2H); 6.99 (d, 2H), 3.76 (s, 3H); 2.48 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm) δ 196.6, 163.5, 130.5, 113.7, 55.4, 26.2; Anal. Calcd for $C_9H_{10}O_2$: C, 71.98; H, 6.71. Found: C, 71.83; H, 6.86.

1-(4-Bromophenyl) ethan-1-one (22)⁷²

88% yield (175.2 mg); white solid, m.p: 48-50 °C (lit. 50 °C); TLC (Petroleumether:Ethyl acetate, 90:10 v/v): $R_f = 0.39$; IR (thin film): v = 3045, 2995, 2957, 1674, 1589, 1478, 1357, 1265, 11722, 956, 817, 709, 586; ¹H NMR (250 MHz, DMSOd₆, ppm) δ 7.85-7.88 (d, 2H); 7.70-7.73 (d, 2H), 2.55 (s, 3H); ¹³C {¹H} NMR (100 MHz, CDCl₃, ppm) δ 197.0, 135.8, 131.8, 129.8, 128.3, 26.5; Anal. Calcd for C₈H₇BrO: C, 48.27; H, 3.54. Found: C, 48.59; H, 3.22.

9H-fluoren-9-one (23)73

79% yield (142.4 mg); yellow solid; m.p: 83-85 °C (lit. 84 °C); TLC (Petroleum ether:Ethyl acetate, 85:15 v/v): $R_f = 0.27$; ¹H NMR (400 MHz, CDCl₃, ppm) δ 7.66-7.64 (d, 2H, *J*= 8 Hz); 7.51-7.47 (m, 4H), 7.31-7.29 (d, 2H, *J*= 8 Hz); ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm) δ 193.9, 144.4, 134.7, 134.1, 129.1, 124.3, 120.3; Anal. Calcd for $C_{13}H_8O$: C, 86.65; H, 4.47. Found: C, 86.86; H, 4.67.

Anthracen-9(10*H*)-one (24)⁷³

75% yield (145.7 mg); light yellow solid; m.p: 155-158 °C (lit. 155-158 °C); TLC (Petroleum ether:Ethyl acetate, 85:15 v/v): $R_f = 0.32$; IR (thin film): v = 3058, 2968, 1683, 1543, 1476, 1313, 1256, 1166, 1067; ¹H NMR (400 MHz, CDCl₃, ppm) δ 8.36-8.34 (d, 2H, *J*= 8 Hz); 7.59-7.57 (d, 2H, *J*= 8 Hz), 7.46-7.42 (m, 4H), 4.29 (s, 2H); ¹³C {¹H} NMR (100 MHz, CDCl₃, ppm) δ 184.2, 140.5, 132.7, 132.0, 128.5, 127.5, 127.0, 32.4; Anal. Calcd for C₁₄H₁₀O: C, 86.57; H, 5.19. Found: C, 86.91; H, 5.28.

Phenyl (pyridin-2-yl) methadone (25)73

70% yield (128.2 mg); light yellow crystalline; m.p.: 41-46 °C (lit. 41-46 °C); TLC (Petroleum ether:Ethyl acetate, 80:20 v/v): $R_f = 0.28$; IR (thin film): v = 3088, 1668, 1601, 1580, 1559, 1520, 1457, 1447, 1319, 1283, 1220, 1182, 1074, 966; ¹H NMR (400 MHz, CDCl₃, ppm) δ 8.82-8.81 (d, 2H, J = 4 Hz); 7.83-7.81 (d, 2H, J = 8 Hz), 7.67-7.63 (t, 1H, J = 8 Hz), 7.59-7.58 (d, 2H, J = 4 Hz), 7.54-7.50 (t, 2H, J = 8 Hz); ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm) δ 195.2, 166.0, 152.8, 150.4, 144.3, 135.9, 133.5, 130.1, 128.7, 122.9; Anal. Calcd for C₁₂H₉NO: C, 78.67; H, 4.95; N, 7.65. Found: C, 78.86; H, 5.11; N, 7.52.

Benzophenone (26)⁶¹

77 yield (140.3 mg); white solid; m.p: 47- 49°C (lit. 48.5 °C); TLC (Petroleumether:Ethyl acetate, 90:10 v/v): $R_f = 0.35$; IR (thin film): v = 3061, 1680, 1622, 1536, 1288, 1167, 1003, 803; ¹H NMR (400 MHz, CDCl₃, ppm) δ 7.83-7.81 (d, 4H, J = 8 Hz); 7.62-7.58 (t, 2H, J = 8 Hz), 7.51-7.47 (t, 4H, J = 8 Hz); ¹³C {¹H} NMR (100 MHz, CDCl₃, ppm) δ 196.7, 137.6, 132.4, 130.1, 128.3; Anal. Calcd for $C_{13}H_{10}O$: C, 85.69; H, 5.53. Found: C, 85.86; H, 5.71.

4-Chlorobenzophenone (27)⁶¹

72% yield (156.0 mg); white solid; m.p: 73-75 °C (lit. 75 °C); TLC (Petroleum ether:Ethyl acetate, 90:10 v/v): $R_f = 0.32$; IR (thin film): v = 3073, 1678, 1614, 1529, 1417, 1276, 1158, 759; ¹H NMR (400 MHz, CDCl₃, ppm) δ 7.81-7.77 (m, 4H); 7.64-7.61 (t, 1H, J = 4 Hz), 7.53-7.51 (d, 2H, J = 8 Hz), 7.50-7.47 (d, 2H, J = 4 Hz); ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm) δ 195.5, 138.9, 137.2, 135.9, 132.7, 131.5, 129.9, 128.6, 128.4; Anal. Calcd for C₁₃H₉ClO: C, 72.07; H, 4.19. Found: C, 72.16; H, 4.28.

1-([1, 1'-biphenyl]-4-yl) ethan-1-one (28)⁷⁴

82% yield (160.9 mg); white solid; m.p: 119-120 °C (lit. 119-120 °C); TLC (Petroleum ether: Ethyl acetate, 90:10 v/v): $R_f = 0.26$; ¹H NMR (400 MHz, CDCl₃, ppm) δ 7.07-7.05 (d, 2H, *J*= 8 Hz); 7.73-7.71 (d, 2H, *J*= 8 Hz), 7.67-7.65 (d, 2H, *J*= 8 Hz), 7.52-7.48 (t, 2H, *J*= 8 Hz), 7.45-7.41 (t, 1H, *J*= 8 Hz), 2.67 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm) δ 197.8, 145.8, 139.9, 135.9, 129.0, 128.9, 128.2, 127.3, 127.2, 26.7; Anal. Calcd for C₁₄H₁₂O: C, 85.68; H, 6.16. Found: C, 85.78; H, 6.01.

Phenyl benzoate (29)75

46% yield (91.2 mg); white solid; m.p: 68-70 °C (lit. 69 °C); TLC (Petroleumether:Ethyl acetate, 85:15 v/v): $R_f = 0.22$; IR (thin film): v = 3061, 1707, 1597, 1573, 1491, 1367, 1245, 1193, 1175, 1096, 1022; ¹H NMR (400 MHz, CDCl₃, ppm) δ 8.27-8.25 (d, 2H, J= 8 Hz); 7.68-7.64 (t, 1H, J= 8 Hz), 7.58-7.54 (t, 2H, J= 8 Hz), 7.50-7.46 (t, 2H, J= 8 Hz), 7.33-7.31 (t. 1H), 7.28-7.26 (d, 2H, J= 8 Hz); ¹³C {¹H} NMR (100 MHz, CDCl₃, ppm) δ 165.3, 151.0, 133.6, 130.2, 129.5, 128.6, 126.0, 121.8; Anal. Calcd for C₁₃H₁₀O₂: C, 78.77; H, 5.09. Found: C, 78.86; H, 4.98.

Benzyl acetate (30)⁷⁶

52% yield (78.0 mg); colorless liquids; TLC (Petroleum ether:Ethyl acetate, 90:10 v/v): $R_f = 0.28$; IR (thin film): v = 3058, 2984, 2966, 2954, 1738, 1603, 1450, 1392, 1234, 1212, 1153, 1081, 1026; ¹H NMR (400 MHz, CDCl₃, ppm) δ 7.41-7.35 (m, 5H); 5.15 (s, 2H), 2.14 (s, 4H); ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm) δ 170.9, 136.0, 128.6, 128.3, 128.3, 66.3, 21.0.

1-Methyl-4-nitrobenzene (33)77

81% yield (111.1 mg); yellow solid, m.p: 50-52 °C (lit. 52 °C); TLC (Petroleum ether: Ethyl acetate, 93:7 v/v): $R_f = 0.40$; IR (thin film) 3037, 2972, 2937, 1677, 1608, 1525, 1497, 1380, 1341, 1259, 1178, 1111 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, ppm) δ 8.14-8.11 (d, 2H, *J*= 12 Hz), 7.35-7.32 (d, 2H, *J*= 12 Hz), 2.48 (s, 3H); ¹³C {¹H} NMR (100 MHz, CDCl₃, ppm) δ 146.0, 129.8, 123.5, 21.6; Anal. Calcd for C₇H₇NO₂: C, 61.31; H, 5.15; N, 10.21. Found: C, 61.62; H, 5.23; N, 10.38.

1-Methyl-2-nitrobenzene (34)¹²

75% yield (102.8 mg); yellow liquid; TLC (Petroleumether:Ethyl acetate, 92:8 v/v): $R_f = 0.42$; IR (thin film) 3094, 3032, 2960, 2947, 1662, 1553, 1527, 1482, 1382, 1316, 1290, 1267, 1162, 1097, 1044 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, ppm) δ 7.28-7.26 (m, 4H), 2.43 (s, 1H), ¹³C {¹H} NMR (100 MHz, CDCl₃, ppm) δ 139.9, 134.1, 129.5, 129.3, 127.3, 125.7, 21.2; UV/Vis: λ_{max} 277 nm.

2-Methylpyridine (35)78

79% yield (73.6 mg); colorless liquid; TLC (Petroleumether:Ethyl acetate, 80:20 v/v): $R_f = 0.2$; IR (thin film) 3029, 2992, 2931, 1608, 1563, 1511, 1497, 1445, 1380, 1224, 1211, 1070, 1042 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, ppm) δ 8.47-8.46 (d, 1H, *J*= 4 Hz), 7.54-7.50 (t, 1H, *J*= 8 Hz), 7.12-7.10 (d, 1H, *J*= 8 Hz), 7.05 (m, 1H), 2.52 (s, 3H); ¹³C {¹H} NMR (100 MHz, CDCl₃, ppm) δ 158.3, 149.1, 136.2, 123.2, 120.6, 24.4.

2-Methylthiophene (36)79

87% yield (85.4 mg); colorless oil, TLC (Petroleumether:Ethyl acetate, 90:10 v/v): R_f = 0.29; IR (thin film) 3039, 2975, 2937, 1593, 1557, 1503, 1486, 1369, 1277, 1204, 1128, 1038 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, ppm) δ 7.16-7.14 (d, 1H, *J*= 8 Hz), 6.99–6.97 (t, 1H, *J*= 4 Hz), 6.58-6.56 (d, 1H, *J*= 8 Hz), 2.58 (s, 3H); ¹³C {¹H} NMR (100 MHz, CDCl₃, ppm) δ 139.6, 127.0, 125.2, 123.1, 20.7.

3-Methyl-1*H*-indole (37)⁸⁰

72% yield (94.4 mg); crystalline powder, m.p: 93-97 °C (lit. 93-97 °C); TLC (Petroleum ether:Ethyl acetate, 80:20 v/v): $R_f = 0.21$; IR (thin film) 3338, 3056, 2953, 1529, 1441, 1380, 1363, 1258, 1218, 1143, cm⁻¹; ¹H NMR (400 MHz, CDCl₃, ppm) δ 7.66-7.64 (d, 2H, *J*= 8 Hz), 7.29-7.27 (d, 1H, *J*= 8 Hz), 7.24-7.20 (m, 2H), 6.33 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm) δ 136.1, 135.3, 129.1, 121.0, 119.7, 110.4, 100.4, 13.7; Anal. Calcd for C₉H₉N: C, 82.41; H, 6.92; N, 10.68. Found: C, 82.22; H, 6.83; N, 10.95.

9H-Fluorene (38)⁷³

59% yield (98.0 mg); white solid, m.p: 115-117 °C (lit. 116 °C); TLC (Petroleum ether:Ethyl acetate, 100:0 v/v): $R_f = 0.29$; IR (thin film) 3068, 2982, 1601, 1537, 1494, 1473, 1283, 1269 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, ppm) δ 7.87-7.85 (d, 2H, *J*= 8 Hz), 7.62-7.60 (d, 2H, *J*= 8 Hz, 7.46-7.43 (t, 3H, *J*= 6 Hz), 7.38-7.36 (t, 2H, *J*= 4 Hz); ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm) δ 143.3, 141.8, 126.8, 126.7, 125.1, 119.9, 36.9; Anal. Calcd for $C_{13}H_{10}$: C, 93.94; H, 6.06. Found: C, 93.82; H, 6.18.

Diphenylmethane (39)⁸¹

61% yield (102.6 mg); colorless oil, TLC (Petroleumether:Ethyl acetate, 100:0 v/v): R_f = 0.21; IR (thin film) 3056, 2969, 1577, 1508, 1493, 1435, 1346, 1219, 1128, cm⁻¹; ¹H NMR (400 MHz, CDCl₃, ppm) δ 7.37-7.33 (m, 4H), 7.28-7.25 (m, 6H), 4.05 (s, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm) δ 141.2, 129.0, 128.5, 126.1, 42.0.

Ethylbenzene (40)⁸²

79% yield (83.9 mg); colorless liquid; TLC (Petroleumether:Ethyl acetate, 95:5 v/v): $R_f = 0.48$; IR (thin film) 3066, 2967, 2948, 1608, 1547, 1496, 1453, 1376, 1329, 1178, 1061, 1030 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, ppm) δ 77.48-7.37 (m, 5H), 2.84-2.80 (q, 2H, *J*= 8 Hz), 1.46-1.42 (t, 3H, *J*= 8 Hz); ¹³C {¹H} NMR (100 MHz, CDCl₃, ppm) δ 144.4, 128.5, 128.0, 125.8, 29.1, 15.8.

1, 4-Dimethoxybenzene (41)⁸³

68% yield (93.9 mg); white crystals; m.p: 54-55 °C (lit. 54-56 °C); TLC (Petroleumether: Ethyl acetate, 95:5 v/v): $R_f = 0.24$; IR (thin film) 3077, 2982, 2941, 1582, 1513, 1474, 1463, 1372, 1043 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, ppm) δ 6.88 (s, 4H), 3.80 (s, 6H); ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm) δ 153.8, 114.7, 55.7; Anal. Calcd for $C_8H_{10}O_2$: C, 69.55; H, 7.30. Found: C, 69.72; H, 7.41.

2-Methoxynaphthalene (42)⁸⁴

63% yield (99.7 mg); white solid; m.p: 70-73 °C (lit. 70-73 °C); TLC (Petroleum ether:Ethyl acetate, 90:10 v/v): $R_f = 0.29$; IR (thin film) 3042, 2989, 2956, 1613, 1557, 1503, 1487, 1452, 1357, 1248, 1181, 1056, 1011 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, ppm) δ 7.86-7.80 (m, 3H), 7.54-7.50 (t, 1H, *J*= 8 Hz), 7.44-7.40 (t, 1H, *J*= 8 Hz), 7.25-7.21 (d, 1H, *J*= 8 Hz), 7.21 (s, 1H), 3.98 (s, 3H); ¹³C {¹H} NMR (100 MHz, CDCl₃, ppm) δ 157.7, 134.6, 129.5, 129.0, 127.7, 126.8, 126.4, 123.7, 118.8, 105.8, 55.3; Anal. Calcd for C₁₁H₁₀O: C, 83.52; H, 6.37. Found: C, 83.64; H, 6.51.

(Dimethoxy methyl) benzene (43)85

61% yield (92.8 mg); colorless liquid; TLC (Petroleum ether:Ethyl acetate, 95:5 v/v): $R_f = 0.25$; IR (thin film) 3039, 2995, 2953, 1614, 1587, 1513, 1486, 1443, 1363, 1250, 1190, 1101, 1076, 1037, 1019 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, ppm) δ 77.51-7.49 (d, 2H, *J*= 8 Hz), 7.44-7.41 (t, 2H, *J*= 6 Hz), 7.39-7.36 (t, 1H, *J*= 6 Hz), 5.4 (s, 1H), 3.40 (s, 6H); ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm) δ 138.1, 128.5, 128.2, 126.7, 103.2, 52.7; Anal. Calcd for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found: C, 71.23; H, 8.11.

1-Nitronaphthalene (44)⁸⁶

53% yield (91.8 mg); yellow crystals; m.p: 60-62 °C (lit. 61.5 °C); TLC (Petroleum ether:Ethyl acetate, 90:10 v/v): $R_f = 0.32$; IR (thin film) 3069, 1520, 1480, 1376, 1340, 1261, 1198, 1149, 1080, 1050 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, ppm) δ 8.60-8.58 (d, 1H, *J*= 8 Hz), 8.27-8.25 (d, 1H, *J*= 8 Hz), 8.15-8.13 (d, 1H, *J*= 8 Hz), 7.99-7.97 (d, 1H, *J*= 8 Hz), 7.76-7.74 (t, 1H, *J*= 4 Hz), 7.73-7.67 (t, 1H, *J*= 12 Hz), 7.63-7.57 (t, 1H, *J*= 12 Hz); ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm) δ 146.6, 134.7, 134.3, 129.5, 128.6, 127.4, 125.1, 124.1, 124.0, 123.1; Anal. Calcd for C₁₀H₇NO₂: C, 69.36; H, 4.07. Found: C, 69.51; H, 4.25.

Chlorobenzene (45)87

55% yield (61.9 mg); colorless liquid; TLC (Petroleumether:Ethyl acetate, 100:0 v/v): $R_f = 0.29$; IR (thin film) 3072, 1585, 1479, 1447, 1035, 1024, 742 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, ppm) δ 7.42-7.40 (d, 2H, *J*= 8 Hz), 7.37-7.35 (d, 2H, *J*= 8 Hz), 7.33-7.30 (t, 1H, *J*= 6 Hz); ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm) δ 134.3, 129.8, 128.7, 126.5.

Benzonitrile (46)88

56% yield (57.7 mg); colorless liquid; TLC (Petroleumether:Ethyl acetate, 95:5 v/v): $R_f = 0.34$; IR (thin film) 3062, 2229, 1553, 1451, 1453, 1336, 1289, 1193, 1093cm⁻¹; ¹H NMR (400 MHz, CDCl₃, ppm) δ 7.68-7.65 (d, 2H), 7.62-7.60 (d, 1H), 7.51-7.47 (t, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm) δ 132.8, 132.1, 129.1, 118.9, 112.24.

1,5-Dimethyl-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one (48)⁸⁹

68% yield (128.0 mg); white solid, m.p: 111-113 °C (lit. 111-113 °C); TLC (Petroleumether:Ethyl acetate, 70:30 v/v): $R_f = 0.26$; IR (thin film) 3093, 2962, 2908, 1681, 1573, 1450, 1326, 1226, 1172, 1341, 1049 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, ppm) δ 7.48-7.46 (m, 2H), 7.34-7-32 (m, 3H), 5.31 (s, 1H), 3.03 (s, 3H), 2.23 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm) δ 165.5, 158.0, 135.4, 128.9, 125.9, 123.4, 96.7, 35.2, 12.5. UV/Vis: λ_{max} 277 nm; Anal. Calcd for $C_{11}H_{12}N_2O$: C, 70.19; H, 6.43; O, 8.50; N, 14.88. Found: C, 70.42; H, 6.61; N, 14.60.

2H-Chromen-2-one (49)⁶¹

65% yield (95.0 mg); colorless crystalline, m.p: 70-72°C (lit. 70.6 °C); TLC (Petroleumether:Ethyl acetate, 75:25 v/v): $R_f = 0.28$; IR (thin film) 3062, 1735, 1612, 1519, 1461, 1360, 1280, 1119, 1026, 987 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, ppm) δ 7.71 (d, 1H), 7.49 (m, 2H), 7.28 (m, 2H), 6.40 (d, 1H); ¹³C {¹H} NMR (100 MHz, CDCl₃, ppm) δ 160.8, 154.0, 143.6, 131.8, 127.9, 124.5, 118.8, 116.8, 116.56. UV/Vis (CH₃CN): λ_{max} 272 nm; Anal. Calcd for C₉H₆O₂: C, 73.97; H, 4.14. Found: C, 73.87; H, 4.23.

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ACKNOWLEDGEMENTS

This work was supported by the Shiraz University and financially supported by the Iran National Science Foundation (Grant No. 96003604).

SUPPORTING INFORMATION

The catalyst characterization (XRD, ICP, SEM, TEM, HR-TEM, XPS, BET, elemental mapping and UV-Vis absorption), optimization of the reactions, spectra for all compounds. Additional investigations on reaction conditions, and mechanistic studies.

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