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Green synthesis of oxazine derivatives using *in situe* production of isoquinoline and Cu@KF/CP NPs

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Abstract: An efficient synthesis of oxazine derivatives *via* one-pot reactions between acetylenic esters, arylisocyanates, phthalaldehyde and ammonium acetate in the presence of Cu@KF/CP NPs as a high performance catalyst in water at room temperature.is described. In addition, for investigation of antioxidant ability radical trapping by DPPH and reducing power of ferric ion experiments was performed. As a result, synthesized compounds show excellent radical trapping by DPPH and good reducing ability of ferric ion. The current procedure has the benefits for instance excellent yield of reaction, green media and easy separation of product and catalyst.

Keywords: Oxazine; Isoquinoline; Arylisocyanate; Dialkyl acetylenedicarboxylate; Cu@KF/CP NPs.

Introduction

The isoquinoline skeleton is found in a large number of naturally occurring and synthetic biologically active heterocyclic compounds [1]. Recently, multicomponent reactions (MCRs) are more interesting type of reaction due to mixing three or more reactants in one-pot and generating one product [2-8] and economically useful and environmentally secure than to multi-step methods. MCRs are very important in the synthesis of new drugs and agrochemicals [9-17]. In addition carrying out synthesis of organic compounds in water media is very interesting because of water is cheap solvent, more available with high amounts. For the reactions that starting compounds aren't solved in water, the rate of reaction improves. Separation of products in these reactions is very easy because of products aren't solved in water and separated by employing filtration [18-20]. Employing suitable catalyst increases the way to green chemistry. In the presence of nanocatalyst, some organic reactions have excellent yields and selectivity of product than to usual sized [21, 22].

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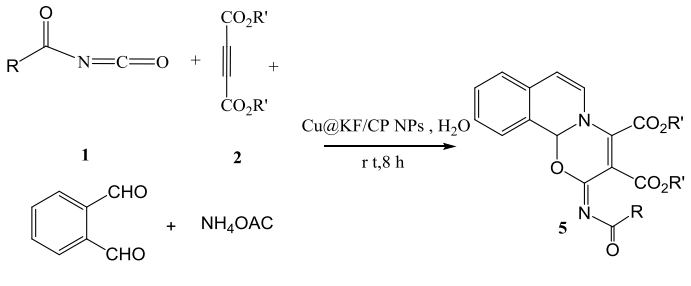
Among heterogeneous catalysts, zeolites have been reported as a new class of promising support and catalysts for the development of environmentally friendly acidic catalysts [23-25]. Due to its higher thermal and hydrothermal stability, zeolite has recently been garnering interest as a novel support [26–33]. Recently, using potassium fluoride supported on zeolites such as clinoptilolite (CP) as new natural and cheap zeolite is very interesting [34-42]. Because of existence of NH_2 group with acidic property in the synthesized compounds these compounds have antioxidant ability. Frequently compounds with antioxidant ability, eliminate the negative property of free radicals and utilize as transitional metals chelators. This result is due to their reducing properties and chemical structure. Also, these compounds could be avoid or decrease many sicknesses such as cardiovascular, inflammatory bowel syndrome, cancer, ageing, and alzheimer [43-45]. In continuation of some research to develop new synthetic process for significant organic compounds with biological ability [46-54], in this study, Cu nanoparticles (NPs) were supported on the surface of natural clinoptilolite zeolite by orange peel aqueous extract as a reducing and

stabilizing agent. In this paper, as part of our ongoing studies on the multicomponent area [55-57], we present herein our results of a novel discovery involving synthesis of thiazine derivatives, using commercially available starting materials in excellent yields. Thus, the reaction of arylisocyanates **1**, activated esters **2** with phthalaldehyde **3** and ammonium acetate **4** in water n the presence of Cu@KF/CP NPs produced oxazine derivatives **5** in good yields (Scheme **1**).



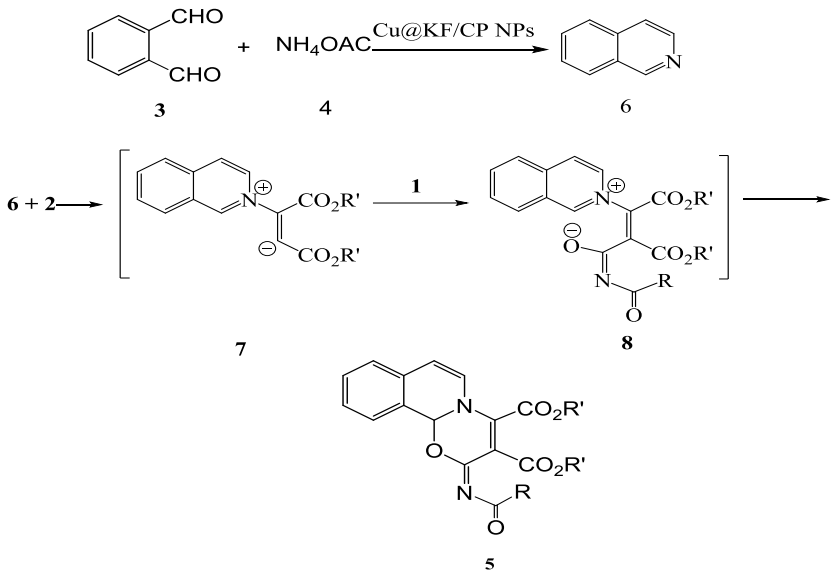
5	R	R'	Yield % of **5**
a	Me	Phenyl	85
b	Me	4-nitrophenyl	94
c	Me	4-bromophenyl	92
d	Me	3-bromophenyl	92

Scheme 1. Synthesis of oxazine derivatives.

As indicated in Scheme **1**, arylisocyanates **1**, activated esters **2,** phthalaldehyde **3** and ammonium acetate **4** undergo a smooth 1:1:1:1 addition reaction in dichloromethane at room temperaure to produced thiazines **4** in 85–92% yields (Scheme **1**).

The data obtained from elemental analysis, IR, ^{1}H NMR, ^{13}C NMR, and mass spectra confirmed all of the proposed products. The mass spectrum of **5b** displayed a molecular ion peak at m/z 451 and more important, an ion peak at m/z 297 indicated that aryl group has been lost and thus the presence of this group on the structure was confirmed. Absorption bands at 1745 and 1732 cm^{-1} are due to the two carbonyl groups. The ^{1}HNMR spectrum of **5b** exhibited two sharp singlet signals recognized as arising from methoxy groups (δ_H = 3.81, 3.92 ppm). Two doublets at 6.98 (2 H, d, ^{3}J = 7.6 Hz, 2 CH), 8.28 (2 H, d, ^{3}J = 7.5 Hz, 2 CH) is attributed to aryl protons. The ^{1}H decoupled ^{13}C NMR spectrum of **5b** showed 23 distinct signals, which were in agreement with the proposed structure. Partial assignment of these resonances for compounds **4** is given in experimental section.

Although we have not established the mechanism of our reaction in an experimental manner, a possible explanation is proposed in Scheme **2**. It is conceivable that, the reaction involves the initial formation of isoquinoline **6** from the reaction of phthalaldehyde **3** and ammonium acetate **4** which reacts with the activated esters **2** to produce either **7**. Intermediate 7 react with arylisocyanates **1** and cyclization of zwitterionic intermediate **8** leads to the **5**.



Scheme 2. Proposed mechanism for the formation of **5**.

For confirmation of structure of nanoparticle, we used SEM, XRD, EDX and TEM image of synthesized Cu@KF/CP NPs. Field emission scanning electron microscopy (FESEM) is a secondary electron detection technique of scanning electron microscope (SEM) combined with field emission source to achieve high-resolution surface imaging in the field of nanomaterials science [38]. In this method, electron release from the surface of a conductor is caused by a strong electric field. The surface morphology of Cu@KF/CP NPs determined by FESEM technique is shown in Figure **1**.

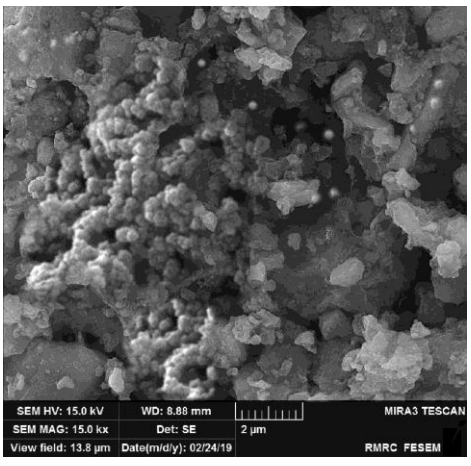


Figure 1. Field emission scanning electron microscopy representation of green Cu@KF/CP NPs.

The X-ray diffraction analysis is a nondestructive method and a key characterization instrument to determine the size, shape, and internal stress of small crystalline areas of unknown nanomaterials. X-ray diffraction spectrum of Cu@KF/CP NPs is shown in Figure **2**. The average crystallite size of Cu@KF/CP NPs was approximately estimated as 30 nm by Debye–Scherrer equation. For the prepared Cu@KF/CP NPs the peaks observed at 2θ values of 43.39°, 50.49° and 74.18° correspond to (111), (200) and (220) planes of metallic Cu. These three peaks were quite consistent with those of the standard JCPDS Card No. 04-0836 for the standard spectrum of the pure fcc (face centered cubic) metallic Cu. The peaks appear at ~ 18.2° (111), 19.9° (110), 21.8°(100), 21.9° (200), 26.7° (101), 29.9° (220), 34.5° (121), 36.8° (222), 41.5° (400), 50.0° (112), 53.0° (422), 62.1° (440) which are indexed to (220), (311), (400), (511) and (440) planes which correspond to the crystal structure of KF/CP nanoparticles and the observed peaks are well matched with the JCPDS card no. 39-1383.

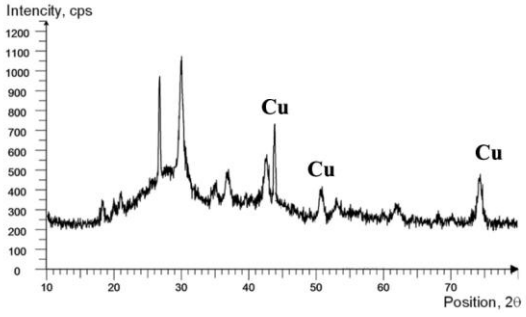


Figure 2. X-ray diffraction spectra of green Cu@KF/CP NPs.

Elemental analysis of the green synthesized Cu@KF/CP NPs was performed by EDX method (Figure **3**). As shown in Figure **3**, successful synthesis of Cu@KF/CP NPs was confirmed by observing the C, Cu, K and F peaks of NPs. In addition, the presence of peak carbon in the EDS spectrum indicates the presence of organic compounds at the nanoscale. There is no impurity peak is observed in the EDX spectra and this confirms that the prepared samples are pure form and also shows the uniform distribution of constituent elements.

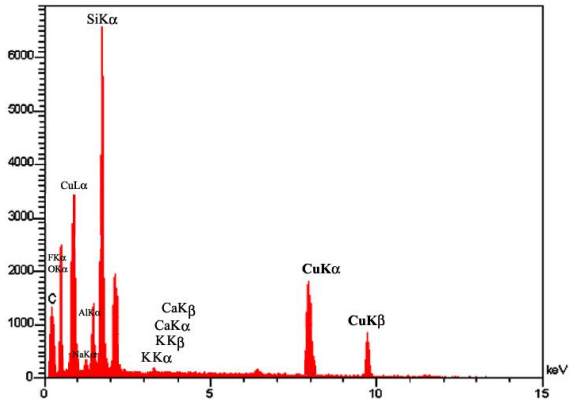


Figure 3. EDX image of green Cu@KF/CP NPs.

The transmission electron microscopy (TEM) analysis is used for achieving the high quality and apparent size, form and structural picture of the Cu@KF/CP NPs (Figure **4**). TEM image exhibited the size of the synthesized Cu@KF/CP NPs to be less than 35 nm.

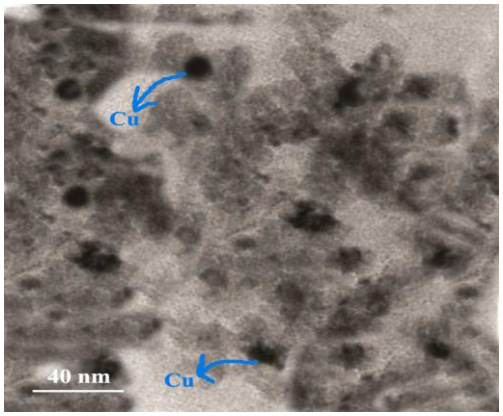


Figure 4. TEM image of the green Cu@KF/CP NPs.

Diphenyl-2-picrylhydrazyl (DPPH) utilizing for evaluation of antioxidant ability:

DPPH radical trapping experiment is generally employed for the approval of antioxidant ability or power of compounds to get free radicals of some synthezied compounds and antioxidant property of them in foods and biological structures [59, 60]. In these experiment, taking one electron or the hydrogen atom of synthezied compounds was performed by DPPH radical and show an valuation of antioxidant capacity basis of free radical trapping. The electron or hydrogen donating power of compounds **5a-5d** to the DPPH radical determined the antioxidant ability of them. The absorption of DPPH radical was decreased from 517 nm when give one electron or hydrogen from antioxidant or a radical typs. In this research, the antioxidant ability or power of compounds **5a-5d** for taking free radicals was compared to synthesized antioxidant such as BHT and TBHQ at different concentrations. Overall, the power of DPPH trapping was obtained TBHQ>BHT>**5b**>**5d**>**5c**>**5a** (Figure **5**).

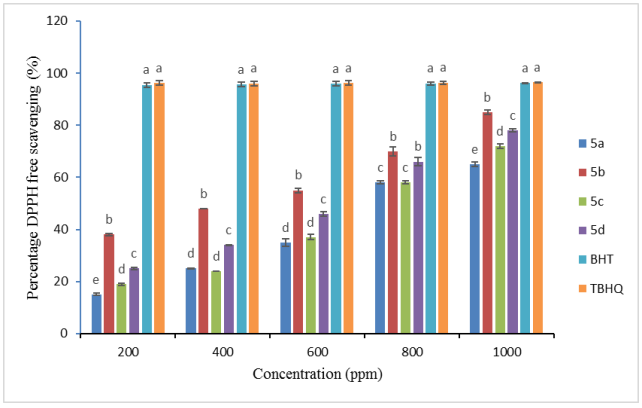


Figure 5. Radical trapping activity (RSA) of compounds **5a-5d.**

As shown in Figure **5**, the new synthesized compounds in all concentrations have moderate distinctions than to BHT and TBHQ. Among selected synthezied compounds, **5b** was shown excellent radical trapping activity relative to standards (BHT and TBHQ).

The potential of synthesized compounds by Ferric ions (Fe^{3+}) reducing:

The ability of reducing ferric ions (Fe^{3+}) by some synthesized compounds such as **5a-5d** are calculated by the quantity of $Fe^{3+/}$ferricyanide reduced to the Fe^{2+}/ferrous at 700 nm [55]. As shown in Figure **6** in this test, compound **5b** was shown good reducing ability than to standard antioxidants such as BHT and TBHQ. The reducing activity trend of the samples was as follows: TBHQ>BHT>**5b**>**5d**>**5c**>**5a**. The outcomes are displayed in Figure **6.**

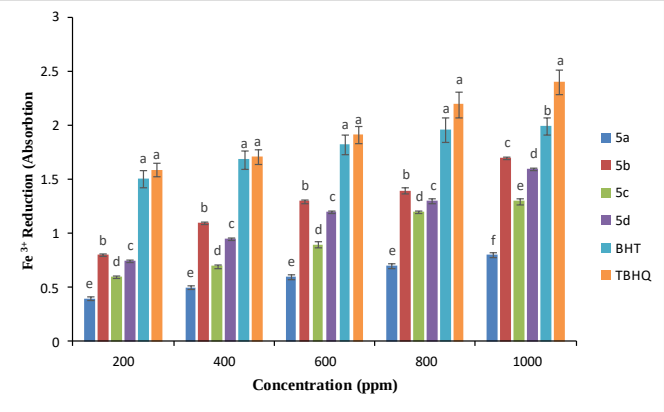


Figure 6. Ferric ions (Fe^{3+}) reducing antioxidant power (FRAP) of compounds **5a-5d**.

Conclusion

In summery, we reported an efficient method for the synthesis of oxazine derivatives. The advantages of our work are as follows: (1) the reaction is performed in in water as a solvent. (2) The simplicity of the present procedure makes it an interesting alternative to the complex multistep approaches.

Experimental

All of starting materials, solvents and other chemicals are bought from Fluka (Buchs, Switzerland) and utilize with any purification. Electrothermal 9100 device are used for measuring the melting points and Shimadzu IR-460 spectrometer are employed for giving IR spectra. BRUKER DRX-500 AVANCE spectrometer at 500 and 125 MHz was employed for giving the ^{1}H, and ^{13}C-NMR spectra. A FINNIGAN-MAT 8430 spectrometer with an ionization potential of 70 eV was utilized for recording mass spectra. The Holland Philips XL30 microscope was used for giving scanning electron microscopy (SEM) image determination of Cu@KF/CP NPs morphology. A Holland Philips Xpert X-ray powder diffractometer, with CuK_{α} radiation (λ=0.15406 nm) and 2θ ranging from 20 to 80°, was employed for X-ray diffraction (XRD) analysis at room temperature and characterization of crystalline structure of Cu@KF/CP NPs. Scherrer's formula; D= 0.9λ/β cosθ was employed for calculating the average crystallite size where D is the diameter of the nanoparticles, λ (CuK_{α}) =1.5406 **Å** and β is the full-width at half-maximum of the diffraction lines. X-ray energy dispersive spectroscopy analysis (EDS) (S3700N) was utilized for chemical analysis of prepared nanostructures. The shape and size of Natrolite zeolite/Cu NPs was identified by transmission electron microscope (TEM) using a Philips EM208 microscope operating at an accelerating voltage of 90 kV.

Green synthesis of Cu@KF/CP NPs:

50 mL of the *orange peel* aqueous extract was added to 20 mL of 0.05 M $CuCl_2$ solution, 1.0 g of KF and 9.0 g nano clinoptilolite and stirred for 12 h at 100 ^{o}C. Then, precipitate was separated by filtration, cleaned by water and dry at 100 °C in a vacuum oven for 12 h.

General procedure:

To a magnetically stirred solution of arylisocyanate **1** and dialkyl acetylenedicarboxylates **2** (2 mmol) in water was added phthalaldehyde **3** (2 mmol) and ammonium acetate **4** slowly and the reaction stirred for 8 h at room temperature. After completion of the reaction, as indicated by TLC (ethyl acetate/n-hexane, 5:1), the reaction mixture was purified by column chromatography to afford pure title compounds.

Dimethyl -2-(benzoylimino)-2H,11bH-[1,3]oxazino [2,3-a]isoquinoline-3,4-dicarboxylate (5a):

Yellow powder, mp 135-137°C, yield 85%. IR (KBr) (ν_{max}/cm^{-1}): 1725, 1720, 1685, 1587, 1432 and 1129 cm^{-1}. ^{1}H-NMR: δ 3.65 (3 H, s, MeO), 3.82 (3 H, s, MeO), 7.25 (1 H, s, CH), 7.54 (1 H, d, ^{3}J = 7.6 Hz, CH), 7.53 (2 H, t, ^{3}J = 7.2, 2 CH), 7.61 (1 H, t, ^{3}J = 7.2, CH), 7.69 (1 H, t, ^{3}J = 7.2 Hz, CH), 7.73 (1 H, t, ^{3}J = 7.2 Hz, CH), 7.93 (1 H, d, ^{3}J = 7.5 Hz, CH), 8.02 (2 H, d, ^{3}J = 7.3, 2 CH), 8.69 (1 H, d, ^{3}J = 7.5 Hz, CH), 9.31 (1 H, d, ^{3}J = 7.6 Hz, CH) ppm. ^{13}C-NMR: δ 52.5 (MeO), 53.0 (MeO), 65.2 (CH), 103.4 (CH), 112.4 (C), 120.3 (2 CH), 122.3 (CH), 123.6 (CH), 125.4 (CH), 125.7 (CH), 128.7 (2 CH), 129.0 (CH), 138.2 (C), 133.5 (C), 139.7 (C), 140.1 (C), 148.7 (C-N), 157.4 (C=N), 160.7 (C=O), 161.5 (C=O) ppm. Anal. Calcd for $C_{23}H_{19}NO_4S$ (406.45): C, 65.01; H, 4.46; N, 6.89 found: C, 64.95; H, 4.38; N, 6.75.

Dimethyl -2-(4-nitrobenzoylimino)-2H,11bH-[1,3] oxazino [2,3-a]isoquinoline-3,4-dicarboxylate (5b):

Pale yellow crystals, mp 153-155°C, yield 94%. IR (KBr) (ν_{max}/cm^{-1}): 1745, 1732,, 1658, 1587, 1489, 1365, 1258 and 1157 cm^{-1}. ^{1}H-NMR: δ 3.81 (3 H, s, MeO), 3.92 (3 H, s, MeO), 6.98 (2 H, d, ^{3}J = 7.6, 2 CH), 7.28 (1 H, s, CH), 7.49 (1 H, d, ^{3}J = 7.6 Hz, CH), 7.65 (1 H, t, ^{3}J = 7.3 Hz, CH), 7.68 (1 H, t, ^{3}J = 7.3 Hz, CH), 7.88 (1 H, d, ^{3}J =7.5 Hz, CH), 8.28 (2 H, d, ^{3}J = 7.5, 2 CH), 8.65 (1 H, d, ^{3}J = 7.5 Hz, CH), 9.27 (1 H, d, ^{3}J = 7.6 Hz, CH) ppm. ^{13}C-NMR: δ 53.2 (MeO), 53.8 (MeO), 65.4 (CH), 103.8 (CH), 111.4 (C), 120.0

(2 CH), 123.5 (CH), 126.1 (2 CH), 127.2 (CH), 127.8 (CH), 128.5 (CH), 130.8 (CH), 139.6 (C), 141.6 (C), 146.8 (C), 154.2 (C), 154.9 (C-N), 156.2 (C=N), 160.7 (C=O), 166.5 (C=O). Anal. Calcd for $C_{22}H_{17}N_3O_6S$ (451.45): C, 58.53; H, 3.80; N, 9.31 found: C, 58.48; H, 3.75; N, 9.28.

Dimethyl -2-(4-bromobenzoylimino)-2H,11bH-[1,3] oxazino [2,3-a]isoquinoline-3,4-dicarboxylate (5c):

Orange crystals, mp 165-167°C, yield 92%. IR (KBr) (ν_{max}/cm^{-1}): 1725, 1715, 1658, 1424. 1310, 1258 and 1100 cm^{-1}. ^{1}H-NMR: δ 3.81 (3 H, s, MeO), 3.91 (3 H, s, MeO), 6.76 (2 H, d, ^3J = 7.8, 2 CH), 7.19 (1 H, d, ^3J = 7.7 Hz, CH), 7.32 (1 H, s, CH), 7.51 (2 H, d, ^3J = 8.0, 2 CH), 7.54 (1 H, t, ^3J = 7.4 Hz, CH), 7.59 (1 H, t, ^3J = 7.4 Hz, CH), 7.70 (1 H, d, ^3J = 7.5 Hz, CH), 8.44 (1 H, d, ^3J = 7.5 Hz, CH), 9.23 (1 H, d, ^3J = 7.7 Hz, CH) ppm. ^{13}C-NMR: δ 52.6 (MeO), 53.2 (MeO), 64.3 (CH), 103.5 (CH), 112.0 (C), 121.2 (2 CH), 124.3 (CH), 126.7 (2 CH), 127.8 (CH), 128.2 (CH), 128.9 (CH), 131.2 (CH), 139.5 (C), 142.6 (C), 145.8 (C), 153.8 (C), 155.4 (C-N), 158.9 (C=N), 161.7 (C=O), 164.5 (C=O).

Dimethyl -2-(3-bromobenzoylimino)-2H,11bH-[1,3] oxazino [2,3-a]isoquinoline-3,4-dicarboxylate (54):

White powder, yield: (92%); m.p. 169-171°C. IR(KBr)(ν_{max}/cm^{-1}): 1723, 1714, 1699, 1523, 1489, 1358 and 1124 cm^{-1}. ^{1}H-NMR: δ 3.81 (3 H, s, MeO), 3.91 (3 H, s, MeO), 6.81 (1 H, t, ^3J = 7.8, CH), 7.09 (1 H, d, ^3J = 7.8 Hz, CH), 7.25 (1 H, d, ^3J = 7.8 Hz, CH), 7.34 (1 H, s, CH), 7.50 (1 H, d, 3J = 7.7 Hz, CH), 7.71 (1 H, d, ^3J = 7.2 Hz, CH), 7.73 (1 H, t, ^3J = 7.2 Hz, CH), 7.93 (1 H, t, ^3J = 7.5 Hz, CH), 8.55 (1 H, d, ^3J = 7.5 Hz, CH), 9.21 (1 H, d, ^3J = 7.7 Hz, CH) ppm. ^{13}C-NMR: δ 53.2 (MeO), 53.7 (MeO), 62.7 (CH), 105.2 (CH), 112.5 (C), 121.8 (2 CH), 125.0 (CH), 126.8 (2 CH), 128.2 (CH), 128.7 (CH), 129.2 (CH), 131.8 (CH), 138.6 (C), 142.5 (C), 145.8 (C), 154.0 (C), 155.6 (C-N), 157.5 (C=N), 161.5 (C=O), 163.4 (C=O).

Determination of antioxidant activity using radical trapping test by (DPPH):

The radical trapping experiment by DPPH was employed for valuation of antioxidant ability for some generated compounds such as **5a-5d** as indicated by Shimada et al [60] procedure. For achieving to this purpose, different concentrations (200–1000 ppm) of compounds **5a-5d** were added to DPPH methanolic solution (1 mmol/L) with an equal volume. The mixtures were mixed for 30 min at ambient temperature and after this time puted in a dark room. Then, the mixture absorbance was calculated and recorded at 517 nm. The compounds **5a-5d** was exchanged with methanol (3 mL) in the standard type. The standard antioxidant such as Butylated hydroxytoluene (BHT) and 2-tertbutylhydroquinone (TBHQ) were employed as standard control sample. The percentage inhibition of the DPPH radical was measured using Yen and Duh [62] formula.

Evaluation of reducing ability for synthesized compounds:

The ability of reducing iron (III) was evaluated for the compounds **5a-5d** using Yildirim et al. method [61]. For this purpose, the samples (1 mL), phosphate buffer (2.5 mL, 0.2 mol/L, pH 6.6) and potassium ferricyanide ($K_3Fe(CN)_6$; 2.5 mL, 10g/L) were combined together and sustained for 30 min at 50 ^{o}C. Then, trichloroacetic acid (2.5 mL, 10% w/v) was added to the previous solution and centrifuged for 10 min. In the end, the supernatant (2.5 mL) was mixed with distilled water (2.5 mL) and FeCl3 (0.5 mL, 1 g/L) and the samples absorbance was computed at 700 nm. The higher reducing power was attributed to higher absorbance. For accuracy of calculating, each calculation was performed in three times. The SPSS software version 18.0 was used for data analyzation of compounds by running one way analysis of variance (ANOVA) that confirmed variation in the mean value of samples and control. All removing were done by Duncan multiple range tests employing the importance level of 95% ($P < 0.05$).

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