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# **ARTICLE TYPE**

# Magnetic metal-organic framework as a highly active heterogeneous catalyst for one-pot synthesis of 2-substituted alkyl and aryl(indolyl)kojic acid derivatives

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A novel magnetic metal-organic framework NiFe<sub>2</sub>O<sub>4</sub>@MOF-5 has been prepared and characterized by spectroscopic, microscopic and magnetic techniques (FT-IR, XRD, TEM, SEM, EDX and VSM). This magnetically separable catalyst exhibited high catalytic activity for synthesis of a variety of 2-substituted alkyl and <sup>10</sup> aryl(indolyl)kojic acid derivatives via one-pot, three-component reaction of aldehyde, indole and kojic acid under solvent-free conditions. The catalyst can be easily magnetically separated and exhibits significant recyclability, with no significant loss of activity after six consecutive runs.

#### Introduction

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From the perspective of green and economic chemistry, the <sup>15</sup> design of efficient and recoverable heterogeneous catalysts has become of paramount important topics of research in synthetic organic chemistry, material science and engineering. Metalorganic frameworks (MOFs) as a class of porous materials from metal ions or metallic clusters and multidirectional organic <sup>20</sup> linkers have summoned substantial amount of attention in the past decade with promising performance in gas adsorption and separations, chemical sensors, thin film devices, drug carriers, and biomedical imaging owing to their incredibly large specific surface area, tunable pore distribution, abundant aromatic ligands, <sup>25</sup> outstanding mechanical and solvent stability, high acid-base catalytic activities and ease of functionalization.<sup>1</sup> Some MOFs

- based on Cu, Fe, Co, Zr, Zn and Al have also emerged as effective heterogeneous catalysts for several organic reactions such as oxidation,<sup>2</sup> epoxidation,<sup>3</sup> cyanosilylation,<sup>4</sup> <sup>30</sup> hydroxylation,<sup>5</sup> acetalization,<sup>6</sup> cyclization,<sup>7</sup> cycloaddition,<sup>8</sup> condensation reaction,<sup>9</sup> coupling reactions,<sup>10</sup> ring opening reaction,<sup>11</sup> Friedel–Crafts reaction,<sup>12</sup> Friedländer reaction,<sup>13</sup> as well as multi-component reaction.<sup>14</sup>
- In particular, the magnetic supported catalyst can be <sup>35</sup> separated from the reaction medium by applying an external magnetic field due to the paramagnetic properties of the support. It can make the catalyst removed and recycled more easily than

filtration and centrifugation.<sup>15</sup> Among the various magnetic <sup>45</sup> materials, NiFe<sub>2</sub>O<sub>4</sub> with the general formula (AB<sub>2</sub>O<sub>4</sub>) is one of the most versatile magnetic materials because it has high

- saturation magnetization, strong chemical stability, low toxic and relatively high permeability.<sup>16</sup> If the MOF is bound to the magnetic component, the resulting magnetic MOF will has a <sup>50</sup> magnetic susceptibility and allow the catalyst to facilitate separation and recycle from the reaction medium by applying an external magnet after the reaction. As far as we know, there are few examples on synthesis and application of magnetic MOFs in organic synthesis.<sup>17</sup>
- <sup>55</sup> Moreover, multicomponent reactions (MCRs) have been shown to be able to efficiently obtain a complex target compound with attractive biological properties in a pot mode to ensure atomic economy, high total yield and high selectivity, minimize waste, labor and manpower, reduce time-consuming, and avoid <sup>60</sup> complex purification processes.<sup>18</sup> The combination the merits of multicomponent reactions with the advantage of easily recovered heterogeneous catalyst can meet the requirements of green chemistry.

Heterocyclic compounds containing indole or kojic acid <sup>65</sup> nucleus have been found numerous applications in medical, agrochemicals and functional materials. The indole nucleus is another important structural motif and occurs in many biologically active natural products, alkaloids, pharmaceuticals and other functional molecules.<sup>19</sup> Kojic acid is a naturally <sup>70</sup> occurring fungal metabolite produced from carbohydrate sources in an aerobic process by various fungi and bacteria and has shown antimicrobial, antibacterial, and antifungal activities. In addition, kojic acid and its derivatives have been used in the food industry as an additive to prevent the browning of food materials

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<sup>†</sup>Electronic Supplementary Information (ESI) available: <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of all compounds. See DOI: 10.1039/b000000x/

and utilized as a skin-lightener and antibrowning agent in cosmetic products owing to their potent tyrosinase inhibition activity.<sup>20</sup> In this regard, we sought to explore the establishment of a single structural framework by combining indole and kojic s acid motifs which could enhance biological and pharmacological activity.

Bearing these facts in mind and continuing our efforts toward the design of magnetic nanocatalysts<sup>21</sup> and sustainable synthesis development,<sup>22</sup> herein, we report on the preparation of a new type <sup>10</sup> of magnetic metal-organic framework NiFe<sub>2</sub>O<sub>4</sub>@MOF-5 and its application for the synthesis of 2-substituted alkyl and aryl(indolyl) kojic acid derivatives via one-pot, three-component reaction of aldehyde, indole and kojic acid under solvent-free conditions (Scheme 1).



Scheme 1 NiFe<sub>2</sub>O<sub>4</sub>@MOF-5 catalyzed one pot, three-component reaction of aldehyde, indole and kojic acid

#### **Results and discussion**

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As shown in Scheme 2, magnetic MOF-5 (NiFe<sub>2</sub>O<sub>4</sub>@MOF-5) <sup>20</sup> was prepared in a three-step process by using NiFe<sub>2</sub>O<sub>4</sub> as a magnetic core, the zinc ion as a connector and terephthalic acid (H<sub>2</sub>BDC) as a linker. Firstly, the NiFe<sub>2</sub>O<sub>4</sub> particles were synthesized by a chemical co-precipitation method using FeCl<sub>3</sub> and NiCl<sub>2</sub>. Next, citrate-functionalized NiFe<sub>2</sub>O<sub>4</sub> was obtained by <sup>25</sup> stirring of NiFe<sub>2</sub>O<sub>4</sub> suspension in water solution of trisodium citrate. Finally, MOF-5 was deposited on citrate-functionalized NiFe<sub>2</sub>O<sub>4</sub> by dispersing NiFe<sub>2</sub>O<sub>4</sub> in *N*,*N*-dimethylformamide (DMF) of zinc nitrate hexahydrate and H<sub>2</sub>BDC and heating at 130 °C in a teflon-lined steel autoclave. The morphology, <sup>30</sup> structure, and composition of as-prepared NiFe<sub>2</sub>O<sub>4</sub>@MOF-5 nanospheress are investigated by different characterizing techniques.





The crystalline nature of NiFe<sub>2</sub>O<sub>4</sub>@MOF-5 was determined by using X-ray diffraction analysis (Fig. 1). The diffraction peaks <sup>40</sup> at 8.70°, 17.33°, 27.91° provide evidences to support the existence of MOF-5. The diffraction peaks of NiFe<sub>2</sub>O<sub>4</sub>@MOF-5  $2\theta$  = 30.29°, 35.70°, 37.31°, 43.36°, 53.80°, 57.36° and 62.92° are associated to the corresponding indices of the (220), (311), (222), (400), (422), (511) and (440), which can be well indexed to the

<sup>45</sup> cubic spinel phase of NiFe<sub>2</sub>O<sub>4</sub> (JCPDS 10-0325).<sup>23</sup> The results demonstrated that the two crystalline phases of NiFe<sub>2</sub>O<sub>4</sub> and MOF-5 were presented in NiFe<sub>2</sub>O<sub>4</sub>@MOF-5.



Fig. 1 XRD pattern of MOF-5, NiFe<sub>2</sub>O<sub>4</sub> and NiFe<sub>2</sub>O<sub>4</sub>@MOF-5

The composition of NiFe<sub>2</sub>O<sub>4</sub>@MOF-5 was further investiged by fourier transform infrared (FT-IR) (Fig. 2). Compared to that of NiFe<sub>2</sub>O<sub>4</sub>, the spectrum of NiFe<sub>2</sub>O<sub>4</sub>@MOF-5 displayed additional adsorption bands which are associated with the MOF-5 structure. For example, characteristics peaks at 1685, 1482, 1420 55 cm<sup>-1</sup>, and 1284, 732cm<sup>-1</sup> are assigned to the C=O and C-H in the BDC ring, which clearly indicates the presence of MOF-5. The presence of Ni-O and Fe-O bonds in the magnetic particles was confirmed by the characteristic peak appeared at 590 cm<sup>-1</sup>. Elemental mapping by energy-dispersive X-ray spectroscopy 60 (EDX) confirmed the presence of C, O, Fe, Ni and Zn elements in the structure of the material (Figure 3). Further examination by atomic absorption spectroscopy (AAS) for NiFe<sub>2</sub>O<sub>4</sub>@MOF-5 was also showed that the contents of Fe, Ni and Zn were 16.18%, 8.22 and 9.06%, respectively. The result indicated that Ni/Fe molar 65 ratio is about 1:2 and the amount of MOF-5 supported on NiFe<sub>2</sub>O<sub>4</sub> nanoparticles is approximately 27.19% based on  $Zn_4O(BDC)_3$ .<sup>24</sup>



Fig. 2 IR spectra of NiFe<sub>2</sub>O<sub>4</sub>, MOF-5, NiFe<sub>2</sub>O<sub>4</sub>@MOF-5 (fresh) and <sup>70</sup> NiFe<sub>2</sub>O<sub>4</sub>@MOF-5 (recovered)

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Fig. 3 EDS spectra of MOF-5, NiFe<sub>2</sub>O<sub>4</sub> and NiFe<sub>2</sub>O<sub>4</sub>@MOF-5

The scanning electron microscopy (SEM) observation showed that NiFe<sub>2</sub>O<sub>4</sub>@MOF-5 was composed of relatively uniform quasi-<sup>5</sup> spherical particles (Fig. 4). The estimated mean diameter of these particles is around 40-60 nm, which shows a quite agreement with the values calculated by XRD data. The transmission electron microscopy (TEM) showed formation of MOF shells on the surfaces of the magnetic nanoparticles (Fig. 5).



Fig. 4 SEM profile of MOF-5 (a) NiFe<sub>2</sub>O<sub>4</sub> (b) and NiFe<sub>2</sub>O<sub>4</sub>@MOF-5 (c)



Fig. 5 TEM profile of MOF-5 (a) NiFe<sub>2</sub>O<sub>4</sub> (b) and NiFe<sub>2</sub>O<sub>4</sub>@MOF-5 (c)

The BET surface area of the MOF-5 and NiFe<sub>2</sub>O<sub>4</sub>@MOF-5 <sup>15</sup> was confirmed by N<sub>2</sub> adsorption experiments at 77 K (Figure 6). The surface areas of MOF-5 and NiFe<sub>2</sub>O<sub>4</sub>@MOF-5 were calculated by the Brunauer-Emmett-Teller method to be 240 and 123 m<sup>2</sup>g<sup>-1</sup>, respectively. The appreciable decreases in surface area indicated that the cavities of MOF-5 were partially occupied by <sup>20</sup> dispersed NPs or/and blocked by the NPs located on the surface.



Fig. 6  $N_2$  adsorption/desorption curves of MOF-5,  $NiFe_2O_4$  and  $NiFe_2O_4@MOF-5$ 

The thermal stability of NiFe<sub>2</sub>O<sub>4</sub>@MOF-5 was examined by <sup>25</sup> carrying out TGA experiments. As shown in Fig. 7, two main steps of weight loss were observed. The first step displayed a weight loss of 2.11% that attributable to the loss of adsorbed solvent or water molecules before 140 °C. The second step showed a weight loss about 12.47 wt% from 140 °C to 450 °C, <sup>30</sup> resulting from thermal decomposition of MOF-5.



Fig. 7 TGA profile of MOF-5, NiFe<sub>2</sub>O<sub>4</sub> and NiFe<sub>2</sub>O<sub>4</sub>@MOF-5

The magnetic properties of the NiFe<sub>2</sub>O<sub>4</sub> and NiFe<sub>2</sub>O<sub>4</sub>@MOF-5 were evaluated by vibrating sample magnetometery (VSM) at <sup>35</sup> room temperature. As illustrated in Fig. 8, the magnetic saturation (MS) values of the NiFe<sub>2</sub>O<sub>4</sub> MNPs is 51.2 emug<sup>-1</sup>, and the NiFe<sub>2</sub>O<sub>4</sub>@MOF-5 composite is 19.6 emug<sup>-1</sup>. The slightly lower MS value of NiFe<sub>2</sub>O<sub>4</sub>@MOF-5 mainly results from the introduction of MOF-5. The presence of suitable magnetic <sup>40</sup> properties allows NiFe<sub>2</sub>O<sub>4</sub>@MOF-5 to be completely, efficiently and rapidly separated from the reaction mixture by an external magnet.



Fig. 8 Magnetization curve of NiFe2O4 and NiFe2O4@MOF-5

The activity of the prepared catalyst was tested for one-pot three-component reaction of benzaldehyde, indole and kojic acid 5 under solvent-free conditions. As shown in Table 1, almost no reaction occurred in the absence of catalyst and the starting materials were recovered when the reaction mixture was heated at 110 °C under solvent-free conditions (Table 1, entry 1). We next investigated this reaction by using some magnetic nano catalysts 10 such as Fe<sub>3</sub>O<sub>4</sub>, CuFe<sub>2</sub>O<sub>4</sub>, CoFe<sub>2</sub>O<sub>4</sub> and NiFe<sub>2</sub>O<sub>4</sub>, the desired product 4a can be isolated in very low yields (Table 1, entries 2-5). This result encouraged us to optimize the reaction paramters to enhance the yield of 4a on this model reaction. Pleasingly, we found that this reaction proceeded smoothly to afford the target 15 product 4a in 92% yield in the presence of our prepared NiFe<sub>2</sub>O<sub>4</sub>@MOF-5 (Table 1, entry 8). In comparison, low catalytic activity was observed with other magnetic MOF such as NiFe2O4@Cu-BTC or NiFe2O4@Fe-MIL as catalyst (entries 6 and 7). Some solvents such as water, tetrahydrofuran, ethanol, n-20 hexane, toluene, N.N-dimethylformamide were examined, but the results were disappointing. The yield was greatly affected by the reaction temperature. A higher reaction temperature (120 °C) does not make an obvious difference in the yield of product (entry 20), but a lower temperature resulted in no product or gave

- <sup>25</sup> poor yield (Table 1, entries 15-19). The catalytic amount of NiFe<sub>2</sub>O<sub>4</sub>@MOF-5 was found to be crucial. Decreasing the amount of catalyst from 20 to 15 and 10 mg led to a reduction in yield to 86 and 77%, respectively (entries 21 and 22). Increasing the amount of catalyst to 25 mg did not affect the reaction.
- <sup>30</sup> Consequently, performing the reaction in the presence of 20 mg NiFe<sub>2</sub>O<sub>4</sub>@MOF-5 at 110 °C under solvent-free was chosen as the optimal conditions.

To demonstrate the practical usefulness of this method, we also enlarged the reaction scale to 50-mmol for the model <sup>35</sup> reaction. An isolated yield of 93% of brown solid of **4a** was obtained after workup and recrystallization.

Table 1.	Reaction of	benzaldehyde,	indole	and	kojic	acid	under	different
reaction	conditions <sup>a</sup>							

react Entry	y catalyst	Solvent	Temperature (°C)	Time/h	Yield/%
1	no	no	110	5.0	trace
2	Nano Fe <sub>3</sub> O <sub>4</sub>	no	110	2.0	10
3	Nano CuFe <sub>2</sub> O <sub>4</sub>	no	110	2.0	21
4	Nano CoFe <sub>2</sub> O <sub>4</sub>	no	110	2.0	23
5	Nano NiFe <sub>2</sub> O <sub>4</sub>	no	110	2.0	30
6	NiFe2O4@Cu-BTC	no	110	2.5	75
7	NiFe2O4@Fe-MIL	no	110	3.0	48
8	NiFe2O4@MOF-5	no	110	1.0	92
9	NiFe2O4@MOF-5	$H_2O$	reflux	1.0	trace
10	NiFe2O4@MOF-5	THF	reflux	1.0	10
11	NiFe2O4@MOF-5	EtOH	reflux	1.0	trace
12	NiFe2O4@MOF-5	n-Hexan	ereflux	1.0	trace
13	NiFe2O4@MOF-5	Toluene	reflux	1.0	trace
14	NiFe2O4@MOF-5	DMF	110	1.0	trace
15	NiFe2O4@MOF-5	no	25	1.0	trace
16	NiFe2O4@MOF-5	no	40	1.0	trace
17	NiFe2O4@MOF-5	no	60	1.0	trace
18	NiFe2O4@MOF-5	no	80	1.0	40
19	NiFe2O4@MOF-5	no	100	1.0	84
20	NiFe2O4@MOF-5	no	120	1.0	92
21 <sup>c</sup>	NiFe2O4@MOF-5	no	110	1.0	77
22 <sup><i>d</i></sup>	NiFe <sub>2</sub> O <sub>4</sub> @MOF-5	no	110	1.0	86
23 <sup>e</sup>	NiFe2O4@MOF-5	no	110	1.0	92
2 Af	NIE2 O @MOE 5	20	110	1.0	02

<sup>a</sup>Reaction condition: benzaldehyde (1 mmol), indole (1 mmol), kojic acid (1 mmol), catalyst ( 20 mg) in solvent (2 ml) otherwise specified in the table. <sup>b</sup> Isolated yields. <sup>c</sup> 10 mg catalyst was used. <sup>d</sup> 15 mg catalyst was used. <sup>e</sup> 25 mg catalyst was used. <sup>f</sup> The reaction was carried out in 50 mmol scale.

Under the optimal reaction conditions, the scope of substrates 45 for the synthesis of 2-substituted alkyl and aryl(indolyl) kojic acid derivatives 4 was investigated and the selected results are outlined in Table 2. It was generally observed that high to excellent yields of the products were obtained for aromatic aldehydes. Electron-donating and electron-withdrawing 50 substituents on the aromatic ring of benzaldehyde were welltolerated and show no significant influence on the reaction times and the yields of the products. In addition, 1-naphthaldehyde was also a suitable substrate and gave the desired product 4n in 92% yield (Table 2, entry 14). This reaction was also successful for 55 heteroaromatic carbaldehydes such as 5-methyl-2-furaldehyde, 2thiophene-carbaldehyde and 1H-indole-3-carbaldehyde (Table 2, entries 15-17). To our satisfaction, aliphatic aldehydes such as cyclohexanecarbaldehyde and lilestralis are also approprite staring materials under these reaction conditions, but give

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60 relatively low yields (Table 2, entries 18 and 19).

Table 2 NiFe<sub>2</sub>O<sub>4</sub>@MOF-5 catalyzed one-pot synthesis of 2-substituted alkyl and aryl(indolyl)kojjc acid derivatives<sup>a</sup>

	R + R	<sup>1</sup> СНО + 0 НО 0	OH NiFe <sub>2</sub> O <sub>4</sub> / solvent-fi	@MOF-5	R <sup>1</sup> N HO	ОН
Entry	1 Aldehvde	2 3 R	Product	Time/min	Yield/% <sup>b</sup>	∎ mp/°C
	N GHO					P
1	PhCHO	Н	4a	60	92	81-82(79-81)-2
2	$2-OCH_3C_6H_4CHO$	Н	4b	70	92	115-117
3	$3-OCH_3C_6H_4CHO$	Н	4c	75	92	93-95
4	$4-OCH_3C_6H_4CHO$	Н	4d	65	90	98-99 (97-99)
5	$4-CH_3C_6H_4CHO$	Н	4e	85	90	142-144
6	$3-OH-C_6H_4CHO$	Н	41	80	86	100-102
7	2-FC <sub>6</sub> H <sub>4</sub> CHO	Н	4g	60	90	140-142
8	$4-CIC_6H_4CHO$	Н	4h	60	92	93-95
9	4-Br-C <sub>6</sub> H <sub>4</sub> CHO	Н	41	60	95	90-91 (87-89)-
10	$2-NO_2C_6H_4CHO$	Н	4j	65	90	168-170 (169-171) <sup>20</sup>
11	$3-NO_2C_6H_4CHO$	Н	4k	70	90	170-171 (172-174)20
12	$4-NO_2-C_6H_4CHO$	Н	41	65	92	169-170 (167-169) <sup>20</sup>
13	4-CN-C <sub>6</sub> H <sub>4</sub> CHO	Н	4m	60	90	98-100
14	1-Naphthaldehyde	Н	4n	90	92	193-195
15	5-Methyl-2-furaldehyde	Н	40	75	80	94-96
16	2-Thiophene-carbaldehyde	Н	4p	65	85	190-192
17	1 <i>H</i> -indole-3-carbaldehyde	Н	4q	80	90	116-118
18	Cyclohexanecarbaldehyde	Н	4r	90	73	99-101
19	3-(4-(tert-Butyl)phenyl)-2-	Н	<b>4s</b>	180	70	98-100
	methylpropanal					
20	PhCHO	4-OCH <sub>3</sub>	4t	75	90	128-130
21	PhCHO	4-CH <sub>3</sub>	4u	85	90	112-114
22	PhCHO	6-F	4v	65	92	84-86
23	PhCHO	5-Cl	4w	70	90	94-96
24	PhCHO	6-Cl	4x	70	91	93-95
25	PhCHO	5-Br	4y	75	91	86-88
26	PhCHO	6-Br	4z	75	92	92-94
27	4-OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CHO	5-Br	<b>4</b> aa	80	89	107-109
28	PhCHO	1-CH <sub>3</sub>	4ab	85	82	116-118

<sup>a</sup> Reaction conditions: aldehyde (1 mmol), indole (1 mmol), kojjc acid (1 mmol) and NiFe<sub>2</sub>O<sub>4</sub>@MOF-5 (20 mg) under solvent-free condition at 110 °C.

<sup>b</sup> Isolated yield.



Scheme 3 Terephthalaldehyde was involved in the reactions

Subsequently, a variety of indoles were evaluated in this three-component reaction. The results indicated that the position and nature of the substituents on the phenyl ring of indoles had little influence on the efficiency of the reaction. Notably, 5 halogen-substituted indoles were well-tolerated under this reaction to afford the corresponding 4w-4aa, possessing chloro or bromo groups amenable to further functionalization. In addition, the scope of the reaction was further extended to N-protected indole such as 1-methyindole and delivered product 4ab in 82% 10 yield (Table 2, entry 28).

Stimulated by these results, we then extended the scope of this reaction to a substrate containing two aldehyde groups such as terephthalaldehyde. As shown in Scheme 3, treatment of terephthalaldehyde (1 mmol) with indole (1 mmol) and kojic 15 acid (1 mmol) under above optimal conditions led to formation of the corresponding product 4ac in 89% yield. However, the reaction of terephthalaldehyde (1 mmol) with indole (2 mmol) and kojic acid (2 mmol) furnished 5 as a major product.

Finally, the catalyst recyclability has been evaluated in the 20 model reaction of benzaldehyde, indole and kojic acid. After the completion of reaction, ethyl acetate was added and the catalyst was separated magnetically from the reaction mixtures and washed with ethyl acetate. The recovered catalyst was dried, and then reused directly for the next round under same reaction 25 conditions. As can be seen from Fig. 9, the reaction was repeated for up to six consecutive runs without significant loss of catalytic activity.



Fig. 9 Recyling of the catalyst

- The leaching of metal from NiFe2O4@MOF-5 was also determined by inductively coupled plasma (ICP). It was found that the contents of the Ni, Fe and Zn after sixth cycles were 0.60, 0.32 and 0.36 ppm in ethyl acetate (5 ml), respectively. The result confirmed that only a slight loss of the catalyst
- 35 occurred during the course of work-up process. In addition, the recovered catalyst was subjected to FTIR analysis. A result of FTIR spectrum indicates that the catalyst was intact even after sixth cycles of reactions (Fig. 2).
- Based on the experimental results described above and <sup>40</sup> previous literature report,<sup>25</sup> a plausible reaction mechanism for this three-component reaction is proposed (Scheme 4). It is assumed that catalyst plays an important role in promoting reaction between benzaldehyde and kojic acid by activation of carbonyl carbon of benzaldehyde through interaction between the 45 catalyst and the oxygen of the aldehyde carbonyl group to give
- intermediate I, followed by dehydration generated an enone



Scheme 4 The plausible mechanism for the synthesis of 2-substituted alkyl and aryl(indolyl)kojic acid derivatives

#### Conclusions

In conclusion, a novel type of magnetically recoverable metal-organic framework NiFe2O4@MOF-5 was preparated and characterized by XRD, FT-IR, TEM, SEM, TGA, EDX, and VSM techniques. It was proved to be an efficient heterogenerous catalyst for one-pot thre-component reaction of aldehyde, indole 60 and kojic acid under solvent-free conditions. A wide of aldehydes and indoles can be tolerated, giving the structural diversity of 2substituted alkyl and aryl(indolyl)kojic acid derivatives in good to excellent yields. Morever, this novel heterogenerous catalyst could be easily recovered by a magnet and showed no significant 65 loss of its activity even after six consective runs.

#### **Experimental Section**

General Methods: All reagents and solvents are commercially available and were used as received without further purification. Melting points were determined on an X-5 digital melting point 70 apparatus and are uncorrected. The FT-IR spectra were recorded on a Bruker Tensor 27 fourier transform infrared spectroscope using KBr pellets. Power X-ray diffraction data were obtained from a PANalytical X'Pert Pro X-ray diffractometer using Cu-Ka  $(\lambda = 1.5406 \text{ Å})$  radiation as the X-ray source in the range of 20 75 value between 20 and 80° at room temperature. Transmission electron microscope (TEM) and energy dispersive X-ray spectroscopy (EDX) analyses were carried out on a Hitachi H-7650 instrument operating at 80 KV. Scanning electron microscope (SEM) images of samples were obtained from a 80 Hitachi S-4800 instrument. Nitrogen adsorption-desorption measurements of the materials were detected on a Quantachrome NOVA 4000e surface area analyzer and surface area was calculated by the BET equation. Thermogravimetric analysis (TGA) was performed under nitrogen using a NETZSCH STA

<sup>5</sup> 449 F3 thermogravimetric analyzer. The magnetic measurements were carried out using a Physical Property Measurement System (PPMS-6700). All <sup>1</sup>H and <sup>13</sup>C NMR spectra of the products were obtained from DMSO solution with TMS as an internal standard using a Bruker DRX-500 spectrometer at 500 and 125 MHz, <sup>10</sup> respectively. Mass spectra were performed on a 3200 Qtrap instrument with an ESI source.

**Synthesis of NiFe<sub>2</sub>O<sub>4</sub> Nanoparticles.** Magnetic NiFe<sub>2</sub>O<sub>4</sub> NPs were prepared by the reported coprecipitation method. Briefly, FeCl<sub>3</sub>·6H<sub>2</sub>O (1.35g, 5 mmol), NiCl<sub>2</sub>·6H<sub>2</sub>O (0.595g, 2.5 mmol)<sup>15</sup> were dissolved in distilled water (10 ml) to form a clear solution. Subsequently, 20 ml of 5 mol/l NaOH solution was added into the mixture and stirred for 15 min. The resulting mixture was transferred into 50 ml Teflon-lined autoclave and heated at 180 °C for 12 h. After cooling slowly to room temperature, the black <sup>20</sup> product was washed with distilled water for several times until

the solution pH value became neutral. The black precipitate was separated by a permanent magnet, followed by washing three times with ethanol and drying at 100 °C in vacuum for 24 h.

# Synthesis of Citrate-functionalized NiFe<sub>2</sub>O<sub>4</sub> Nanoparticles.

- <sup>25</sup> Citrate-functionalized NiFe<sub>2</sub>O<sub>4</sub> was synthesized according to a previous report method with a modification.<sup>27</sup> NiFe<sub>2</sub>O<sub>4</sub> nanoparticles (0.1 g) and trisodium citrate (0.1 g) were dissolve in H<sub>2</sub>O (80 ml) under ultrasonication. The mixture was stirring for 5 h. The obtained citrate-functionalized NiFe<sub>2</sub>O<sub>4</sub> was
  <sup>30</sup> separated by a permanent magnet and washed several times with water, then dried in an oven at 100 °C for 12 h.
- Synthesis of NiFe<sub>2</sub>O<sub>4</sub>@MOF-5. The citrate-functionalized NiFe<sub>2</sub>O<sub>4</sub> (0.1g) was dispersed into 5 ml DMF solution of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.193 g) under ultrasonication for 15 min at 130 <sup>35</sup> °C, then magnetic separated and washed with DMF for three times. The obtained material was added to DMF solution of H<sub>2</sub>BDC (0.041 g) for 30 min at 130 °C, then magnetic separated and washed with DMF for three times, NiFe<sub>2</sub>O<sub>4</sub>@MOF-5 precursors were obtained. The NiFe<sub>2</sub>O<sub>4</sub>@MOF-5 precursors were
- <sup>40</sup> dispersed into the mixture solution of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (1.93 g), H<sub>2</sub>BDC (0.41 g) in DMF under stirring. The resulting turbid mixture was sealed in a Teflon-lined autoclave and heated at 130 °C for 24 h. Finally, the obtained black NiFe<sub>2</sub>O<sub>4</sub>@MOF-5 was separated by a permanent magnet and washed several times with <sup>45</sup> DMF, then dried under vacuum at 60 °C for 12 h.
- General procedure for synthesis of 2-substituted alkyl and aryl(indolyl)kojic acid derivatives: The mixture of aldehyde (1 mmol), indole (1 mmol), and kojic acid (1 mmol), NiFe<sub>2</sub>O<sub>4</sub>@MOF-5 (20 mg) was heated at 110 °C (monitored by
- <sup>50</sup> TLC). After completion of the reaction, the reaction mixture was cooled to room temperature and ethyl acetate (5 ml) was added. The catalyst was separated magnetically, washed with ethyl acetate, and reused for subsequent cycles after drying under vacuum. The solvent was concentrated under vacuum and gave

ss crude product. The crude product was further purified by column chromatography on silica gel using ethyl acetate/hexane as the eluent.

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### **Graphical Abstract:**

Magnetic metal-organic framework as a highly active heterogeneous

catalyst for one-pot synthesis of 2-substituted alkyl and aryl(indolyl)kojic

acid derivatives

Hong-Yan Zhang , Xiao-Peng Hao, Li-Ping Mo, Sha-Sha Liu, Wen-Bo Zhang and

Zhan-Hui Zhang\*

A novel magnetic metal-organic framework NiFe<sub>2</sub>O<sub>4</sub>@MOF-5 was prepared and demonstrated to be a high efficient and magnetic separable catalyst for one-pot three-component reaction of aldehyde, indole and kojic acid.

