# **Electronic Supplementary Information**

### for

# Nano-NiFe<sub>2</sub>O<sub>4</sub> catalyzed microwave assisted one-pot regioselective synthesis of novel 2-alkoxyimidazo[1,2-*a*] pyridines under aerobic conditions

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#### ESI 1.Detailed method for the preparation of NiFe<sub>2</sub>O<sub>4</sub>:

The NiFe<sub>2</sub>O<sub>4</sub>nanoparticles were prepared by simple co-precipitation method<sup>[1]</sup> from easily available starting materials ferric chloride (FeCl<sub>3</sub>.6H<sub>2</sub>O) and nickel chloride (NiCl<sub>2</sub>.6H<sub>2</sub>O), distilled water and sodium hydroxide. In a typical synthetic protocol, 0.2 M (20 mL water) ferric chloride solution and 0.1 M (20 mL water) solution of nickel chloride were prepared and mixed under vigorous stirring for 2 h at 80 °C.After that, 0.3 M NaOH was added drop by drop into the solutions till the pH is reached upto 12 andbrown colour precipitates were formed. Finally, the precipitates were separated bycentrifugation and dried in hot air oven for 4 h at 100 °C. Then calcinated it at 550°C for 6 h. Formation of NiFe<sub>2</sub>O<sub>4</sub>NPs were confirmed by FT-IR, powder XRD, HR-TEM, FESEM and EDAX studies.

#### ESI 2.Characterization of nano-NiFe<sub>2</sub>O<sub>4</sub>:

#### ESI 2.1.Energy-dispersive X-ray spectroscopy (EDAX) of nano-NiFe<sub>2</sub>O<sub>4</sub>

EDAX of nano-NiFe<sub>2</sub>O<sub>4</sub>proved that the material contains only Ni, Fe, O elements and no other impurities are observed in the material.



Fig. 1S EDAX of nano-NiFe<sub>2</sub>O<sub>4</sub>

# ESI 2.2.FESEM image of nano-NiFe<sub>2</sub>O<sub>4:</sub>

The field emission scanning electron microscope image of  $NiFe_2O_4$  also confirms the formation of spherical particles.



Fig. 2S FESEM image of nano-NiFe<sub>2</sub>O<sub>4</sub>:

## ESI 2.3.FTIR Spectra of nano-NiFe<sub>2</sub>O<sub>4</sub>:

An intrinsic stretching vibrations at 600 and 535 cm-1 were assign for tetrahedral site of ferrite (Fe-O) and 817 cm-1 for Fe-OH group were observed in FT-IR of nano-NiFe2O4 (Fig. 5S).



Fig. 3SFTIR Spectra of nano-NiFe<sub>2</sub>O<sub>4</sub>

#### ESI 3.Methods for the preparation of CuFe<sub>2</sub>O<sub>4</sub>:

The preparation of  $CuFe_2O_4$  nanoparticles were carried out following reported procedure<sup>[3]</sup>. Solution of  $Cu(NO_3)_2(0.001 \text{ mol})$ , and FeCl<sub>3</sub>.6H<sub>2</sub>O (0.002 mol) were prepared and vigorously mixed under stirring for 2 h at 80 °C.Subsequently, 0.3 M NaOH was added drop by drop into the solutions till the pH is reached upto 12 and black precipitate is formed. Then centrifuged and rinsed with distilled water and left in an atmosphere environment to dry. The resulting powder is then calcinated at 850° C in an oven for 2 hours.

#### ESI 4.Preparation of CoFe<sub>2</sub>O<sub>4</sub>

The preparation of  $CoFe_2O_4$  nanoparticles were carried out following reported procedure<sup>[4]</sup>. First, 2.0 g of anhydrous sodium acetate wasdissolved in 30 mL of ethylene glycol, and the mixture was stirred vigorously at room temperature to give a transparent solution. Subsequently, 1.5 mmol of cobalt hydrous chlorides ( $CoCl_2 \cdot 6H_2O$ ) and 3.0 mmol of ferric hydrous chloride (FeCl<sub>3</sub>  $\cdot 6H_2O$ ) was added slowly to the above solution (the stoichiometric molar ratio of  $Co^{2+}/Fe^{3+}$  was 1 : 2). This mixture was then vigorously stirred at 70°C for at least 2 h to form a homogeneous solution. Then centrifuged and rinsed with distilled water and left in an atmosphere environment to dry. The resulting powder is then calcinated at 850° C in an oven for 2 hours.

#### **ESI 5. General Information:**

All reagents were obtained from commercial sources and used as received, except all solvents which were distilled prior to use. All reactions were carried out with oven-dried glassware under air and all the M.W. reactions were carried out in a sealed M.W. tube under closed air system. A monomode microwave reactor (CEM Discover 908005 Microwave Digestion System with Max. Microwave Power 300W, Volts 90/140 VAC, Freq. 50/60 Hz from CEM Corporation, USA) has been used for all the reactions. Technical grade petroleum ether and ethyl acetate were used for column chromatography. Analytical TLC was performed on Merck 60 F254 silica gel plates (0.25 mm thickness). Column chromatography was performed on silica gel (60-120 mesh size, HIMEDIA, India). <sup>1</sup>H NMR spectra were

determined on a Bruker 500, 400 and 300 MHz spectrometer as solutions in CDCl<sub>3</sub>. Chemical shifts are expressed in parts per million ( $\delta$ ) and the signals were reported as s (singlet), d (doublet), t (triplet), m (multiplet) and coupling constants *J* were given in Hz. <sup>13</sup>C NMR spectra were recorded at 125, 100 and 75 MHz in CDCl<sub>3</sub> solution. Chemical shifts are expressed in parts per million ( $\delta$ ) and are referenced to CDCl<sub>3</sub> ( $\delta$  = 77.16) as internal standard. All FT-IR was recorded on a BRUKER ALPHA spectrophotometer.

# ESI 6. General method for the synthesis of 2-alkoxy-3-arylimidazo[1,2-*a*]pyridines: Representative experimental procedure for the 2-ethoxy-3-phenylimidazo[1,2-*a*]pyridine:

#### (a) Conventional heating Condition:

A mixture of  $\beta$ -nitrostyrene (1 mmol), 2-aminopyridine (1.3 mmol), ethanol (2 ml) and NiFe<sub>2</sub>O<sub>4</sub> (10 mol %) refluxed for 4 hours under open atmosphere. After completion of the reaction (monitored by TLC) the reaction mixture was cooled to room temperature and extracted with ethyl acetate, washed with water with Brine solution. The organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The crude product was obtained by evaporation of solvent in vacuum which was purified by column chromatography over silica gel (60–120 mesh) using mixture of petroleum ether and ethyl acetate (9:1) as an eluting solvent to afford the pure product.

#### (b) MW irradiation Conditions:

A mixture of  $\beta$ -nitrostyrene (1 mmol), 2-aminopyridine (1.3 mmol) and ethanol (2 ml) was taken in a sealed MW tube with a magnetic bar in presence of NiFe<sub>2</sub>O<sub>4</sub> (10 mol %) and was irradiated at under MW condition (70 W) for 5 minutes. After that, the mixture was cooled to room temperature and the catalyst separated by a strong external magnet and finally, product was extracted with ethyl acetate, washed with water with Brine solution. The organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The crude product was obtained by evaporation of solvent in vacuum which was purified by column chromatography over silica gel (60–120 mesh) using mixture of petroleum ether and ethyl acetate (9:1) as an eluting solvent to afford pure 2-ethoxy-3-phenylimidazo[1,2-*a*]pyridine. This protocol was followed for all the products listed in Table 2. The products were confirmed by FT-IR, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopy and elemental analysis. The spectroscopic data and elemental analysis of all the compounds has been given in S7.

# ESI 7. Detailed spectral data of the 2-alkoxy-imidazopyridine derivatives listed in Table 2.

The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded 300 MHz, 400 MHz or 500 MHzBruker NMR spectrometer and CDCl<sub>3</sub> was used as solvent.



Gummy mass (entry 1, Table 2, Isolated yield 85%); <sup>1</sup>H NMR (300MHz, CDCl<sub>3</sub>):  $\delta$  8.31 (d, J = 3.0 Hz, 1H), 7.32-7.27 (m, 4H), 7.23 (t, J = 3.0 Hz,1H), 6.88 (t,J = 3.0 Hz, 1H), 6.56 (d, J = 3.0 Hz), 4.50-4.43(m, 2H), 1.45 (t,J = 7.2 Hz, 3H); <sup>13</sup>C NMR (75MHz, CDCl<sub>3</sub>):  $\delta$  161.38, 161.02, 148.87, 137.69, 131.69, 131.64, 130.27, 129.21, 128.10, 118.22, 116.48, 63.08, 14.37; Anal calc for C<sub>17</sub>H<sub>17</sub>ClN<sub>2</sub>O: C, 66.06; H, 4.80; N, 10.27 %; Found: C, 66.01; H, 4.85; N, 10.30 %.



Gummy mass (entry 2, Table 2, Isolated yield 80%); <sup>1</sup>H NMR (300MHz, CDCl<sub>3</sub>):  $\delta$  8.15 (d, J = 5.1 Hz, 1H), 7.18 (d, J = 6.3 Hz, 2H), 7.27 (d, J = 6.3 Hz, 2H), 6.73 (d, J = 5.1 Hz, 1H), 6.44 (s, 1H), 4.43 (q, J = 6.9Hz, 2H), 2.22 (s, 3H), 1.43 (t, J = 6.9 Hz, 3H); <sup>13</sup>C NMR (75MHz, CDCl<sub>3</sub>):  $\delta$  161.02, 149.16, 148.59, 139.65, 138.01, 136.40, 130.66, 130.17, 128.41, 119.77, 116.78, 63.16, 21.09, 14.37; Analcalc for C<sub>16</sub>H<sub>15</sub>ClN<sub>2</sub>O: C, 67.02; H, 5.27; N, 9.75 %; Found: C, 66.91; H, 5.30; N, 9.79 %.



Gummy mass (entry 3, Table 2, Isolated yield 85%); <sup>1</sup>H NMR (300MHz, CDCl<sub>3</sub>):  $\delta$  7.32-7.25 (m, 4H), 7.21-7.16 (m, 2H), 6.73 (d, J = 6.0 Hz 1H), 6.25 (d, J = 8.1 Hz 1H), 4.48-4.41 (m, 2H), 2.45 (s, 3H), 1.41 (t,J = 6.9 Hz, 3H); <sup>13</sup>C NMR (75MHz, CDCl<sub>3</sub>):  $\delta$ 160.86, 160.81, 157.72, 137.90, 131.66, 130.21, 129.23, 128.01, 117.50, 113.09, 62.98, 24.48, 14.36. Anal calc for C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>O: C, 76.16; H, 6.39; N, 11.10 %; Found: C, 76.12; H, 6.43; N, 11.16 %.



Gummy mass (Table 2, entry 4, yield 84%); <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>):  $\delta$  8.31 (d, J = 4.8Hz, 1H), 7.53-7.49 (m, 1H), 7.26-7.18 (m, 4H), 6.92 (t,J = 5.2 Hz, 1H), 4.41-4.10 (t, J = 6.4 Hz, 2H), 1.82-1.76 (m, 2H), 1.53-1.47 (m, 2H), 1.00-0.97 (t,J = 7.2 Hz, 3H); <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>):  $\delta$  161.31, 157.75, 148.82, 138.60, 137.67, 134.40, 132.31, 129.17, 128.10, 118.20, 116.47, 67.44, 30.85, 21.17, 14.45. Anal calc for C<sub>17</sub>H<sub>17</sub>ClN<sub>2</sub>O: C, 67.88; H, 5.70; N, 9.31 %; Found: C, 67.3; H, 5.75; N, 9.27 %.



Gummy mass (Table 2, entry 5, Isolated yield- 85%); <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>):  $\delta$  8.16 (d, J = 5.0 Hz, 1H), 7.33-7.26 (m, 3 H), 7.23-7.20 (m, 2H), 6.71-6.70 (d, J = 5.0 Hz 1H), 6.412 (s, 1H), 4.47-4.43 (m, 2H), 2.20(s, 1H), 1.45-1.43 (t, J = 7.0 Hz,3H);<sup>13</sup>C NMR (125MHz, CDCl<sub>3</sub>):  $\delta$  161.25, 160.70, 149.04, 148.30, 131.78, 130.25, 129.22, 128.94, 127.36, 119.53, 116.92, 63.03, 21.04, 14.39. Anal calc for C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>O:



C, 76.16; H, 6.39; N, 11.10 %; Found: C, 76.12; H, 6.44; N, 11.16 %.

Gummy mass (Table 2, entry 6, Isolated yield- 85%); <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>):  $\delta$  8.33 (d, J = 4.0 Hz, 1H), 7.47 (t, J = 6.0 Hz, 1 H), 7.33-7.21 (m, 5H), 6.89 (d, J = 5.0 Hz, 1H), 6.56 (d, J = 8.0 Hz, 1H), 4.50-4.46 (m, 2H), 1.27 (t, J = 7.5 Hz,3H);<sup>13</sup>C NMR (75MHz, CDCl<sub>3</sub>):  $\delta$  161.37, 160.98, 148.86, 147.92, 131.67, 130.26, 129.19, 128.90, 127.37, 120.00, 116.46, 63.06, 14.35. Anal calc for C<sub>15</sub>H<sub>14</sub>N<sub>2</sub>O: C, 75.65; H, 6.92; N, 11.76 %; Found: C, 75.60; H, 5.95; N, 11.82 %.



Gummy mass (Table 2, entry 7, Isolated yield-84%); <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>):  $\delta$  8.34 (d, J = 4.0Hz, 1H), 7.49 (t,J = 8.0 Hz, 1H), 7.26 (t,J = 4.5 Hz, 1H), 6.89 (d, J = 5.5 Hz 1H), 6.72 (d, J = 8.5 Hz, 1H), 6.57 (d, J = 8.0 Hz 1H), 4.38 (t,J = 6.5 Hz, 2H), 1.84-1.78(m, 2H), 1.55-1.49 (m, 2H), 1.007-0.978 (t, 3H);<sup>13</sup>C NMR (125MHz, CDCl<sub>3</sub>):  $\delta$  165.95, 161.31, 148.56, 144.79, 137.73, 133.67, 130.61, 128.55, 128.49, 118.48, 118.43, 116.57, 67.48, 30.80, 21.16, 19.61. Anal calc for C<sub>18</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>: C, 72.95; H, 6.80; N, 9.45 %; Found: C, 72.91; H, 6.77; N, 9.40 %.



Gummy mass (Table 2, entry 8, Isolated yield-86%); <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>):  $\delta$  8.17 (d, J = 5.0 Hz, 1H), 7.28 (t, J = 8.0 Hz,2H), 7.2 (d,J = 8.0 Hz, 1H), 7.00 (d, J = 8.0 Hz, 1H), 6.88 (d, J = 5.0 Hz, 1H), 6.71 (d, J = 5.0 Hz 1H), 4.447-4.404 (m, 2H), 2.25(s, 3H), 1.42 (t, J = 7.0 Hz,3H); <sup>13</sup>C NMR (125MHz, CDCl<sub>3</sub>):  $\delta$  161.28, 149.16, 148.57, 138.46, 138.01, 135.19, 131.61, 130.28, 128.56, 119.33, 116.68, 63.66, 21.13, 14.21. Anal calc. for C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>O: C, 76.16; H, 6.39; N, 11.10 %; Found: C, 76.12; H, 6.44; N, 11.06 %.







Gummy mass (Table 2, entry 9, Isolated yield- 81%); <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>):  $\delta$  7.99 (d, J = 6.5 Hz, 1H), 7.91 (d, J = 8,5 Hz, 2H), 7.40 (d, J = 8.5 Hz, 2H), 6.96 (d, J = 6.5 Hz, 1H), 6.70 (t,J = 6.5 Hz, 1H), 4.15-4.11 (m, 2H), 2.67 (s, 3H), 1.27 (t,J = 9.0Hz, 3H); <sup>13</sup>C NMR (125MHz, CDCl<sub>3</sub>):  $\delta$  161.17, 149.29, 148.55, 139.21, 137.82, 135.90, 130.68, 130.07, 128.63, 119.17, 116.66, 63.93, 21.01, 14.67; Anal calc. for C<sub>16</sub>H<sub>15</sub>ClN<sub>2</sub>O: C, 67.02; H, 5.27; N, 9.77 %; Found: C, 66.93; H, 5.23; N, 9.80 %.

Gummy mass (Table 2, entry 10, Isolated yield-80%); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.30 (d, J = 6.5Hz, 1H), 7.48 (t, J = 6.5 Hz, 1H), 7.25 (d, J = 8.5 Hz, 1H), 6.92 (d, J = 6.5 Hz, 2H), 6.74 (d,J = 6.5 Hz, 2H), 6.55 (d,J = 6.5 Hz, 1H), 4.41-4.35 (m, 2H), 3.76 (s, 3H), 1.85-1.67 (m, 2H), 1.00 (t,J = 9.0 Hz, 3H); <sup>13</sup>C NMR (125MHz, CDCl<sub>3</sub>):  $\delta$  171.28, 148.77, 142.06, 137.89, 136.91, 131.12, 129.11, 128.41, 118.06, 116.53, 113.48, 67.04, 60.51, 21.15, 14.30. Anal calc. for C<sub>16</sub>H<sub>15</sub>ClN<sub>2</sub>O: C, 72.32; H, 6.43; N, 9.92 %; Found: C, 72.29; H, 6.46; N, 9.96%.

Gummy mass (Table 2, entry 11, Isolated yield-86%); <sup>1</sup>H NMR (300MHz, CDCl<sub>3</sub>):  $\delta$  8.38 (d, J = 5.1 Hz, 1H), 7.65 (d, J= 6.3 Hz, 2H), 7.58 (d, J = 6.3 Hz, 2H), 6.68 (d, J = 5.1 Hz, 1H), 6.46 (s, 1H), 4.46 (q, J= 6.9 Hz, 2H), 3.85 (s, 3H), 2.31 (s, 3H), 1.76 (m, 2H), 1.5 (m, 1H), 0.91 (t, 3H); <sup>13</sup>C NMR (75MHz, CDCl<sub>3</sub>):  $\delta$  161.15, 148.07, 147.17, 131.14, 129.13, 125.14, 119.43, 118.13, 113.50, 62.95, 55.39, 55.38, 29.84, 21.17, 14.43; Analcalc for C<sub>19</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>: C, 73.52; H, 7.14; N, 9.03 %; Found: C, 73.44; H, 7.19; N, 9.09 %.



Gummy mass (Table 2, entry 12, Isolated yield-83%); <sup>1</sup>H NMR (300MHz, CDCl<sub>3</sub>):  $\delta$  8.18 (d, J = 4.2Hz, 1H), 7.30 (d, J = 4.8 Hz, 2H), 7.25 (d, J = 4.8 Hz, 2H), 6.69 (d, J = 5.1 Hz, 1H), 6.46 (s, 1H), 4.43 (q, J= 7.2 Hz, 2H), 3.75 (s, 3H), 2.23 (s, 3H), 1.71 (m, 2H), 0.89 (t,J = 6.6 Hz. 3H); <sup>13</sup>C NMR (75MHz, CDCl<sub>3</sub>):  $\delta$  160.98, 148.86, 147.92, 131.64, 130.23, 129.19, 128.92, 128.08, 120.01, 116.43, 60.54, 30.85, 21.18, 19.11, 14.34; Analcalc for C<sub>18</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>: C, 72.95; H, 6.80; N, 9.45 %; Found: C, 72.91; H, 6.76; N, 9.49.

ESI 8. Copy of <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of all compounds:











































# ESI9.Recyclability of Catalyst:

We have examined reusability of the catalyst for the synthesis 2-ethoxy-3phenylimidazopyridine. After each cycle nano-NiFe<sub>2</sub>O<sub>4</sub> was recovered simply by using an external magnet, washed with ethanol and reused for subsequent reactions. The magnetic nano-catalyst was reused for eight times with minimum loss of catalytic activity (Figure 5S).



Fig. 4S Recyclability of nano-NiFe<sub>2</sub>O<sub>4</sub>catalyst



Fig. 5S Separation of magnetic f nano-NiFe<sub>2</sub>O<sub>4</sub>catalyst by using an external magnet.

## ESI 10.References:

[1]. For preparation of NiFe<sub>2</sub>O<sub>4</sub>: P. Sivakumar, R. Ramesh, A. Ramanand, S.Ponnusamy, C. Muthamizhchelvan, *J. Alloys and Compounds*, **2013**, *563*, 6–11.

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[4] For preparation of CoFe<sub>2</sub>O<sub>4</sub>: B. Y. Yu, S. Y.Kwak, Dalton Trans., 2011, 40, 9989