

## Supporting Information

### Nano-NiFe<sub>2</sub>O<sub>4</sub> as efficient catalyst for regio- and chemoselective transfer hydrogenation of olefins/alkynes and dehydrogenation of alcohols under Pd-/Ru-free conditions

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## ESI 1. General Information:

All the chemicals were purchased from Aldrich, Sd-Fine, Merck and HIMEDIA (India) and no further purification, except all solvents which were used after distillation. Toluene was distilled from sodium. The reactions were performed with hot air oven-dried glassware under atmospheric condition. Petroleum ether and ethyl acetate were distilled for performing column chromatography. Analytical TLC was performed on Merck 60F254 silica gel plates (0.25 mm thickness).

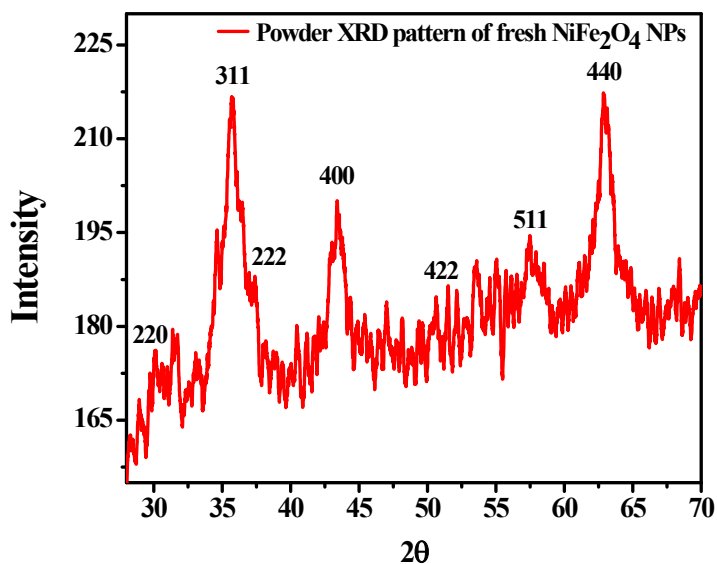
Column chromatography was performed on silica gel (60-120 mesh size, HIMEDIA, India).

$^1\text{H}$  NMR spectra were recorded on Bruker AV 300, AV 400 and AV 500. The  $^1\text{H}$  NMR chemical shifts are reported relative to the center of solvent resonance ( $\text{CDCl}_3$ : 7.26 (1H). Chemical shifts are expressed in parts per million ( $\delta$ ) and the signals were reported as s (singlet), d (doublet), t (triplet), q (quartet) m (multiplet) and coupling constants  $J$  were given in Hz.  $^{13}\text{C}$  NMR spectra were recorded at 75 MHz in  $\text{CDCl}_3$  solution. Chemical shifts are expressed in parts per million ( $\delta$ ) and are referenced to  $\text{CDCl}_3$  ( $\delta = 77.16$ ) as internal standard. The powder XRD patterns of the nano- $\text{NiFe}_2\text{O}_4$  catalysts were performed on a Rigaku Ultima IV Xray diffractometer using Cu  $K\alpha$  radiation of  $\lambda = 1.540806 \text{ \AA}$ . The diffractometer was operated at 40 kV and 40 mA with a step width of  $0.02^\circ$  and the scan rate was used  $0.24^\circ/\text{min}$ . For the TEM analysis the sample was prepared as follows: nano- $\text{NiFe}_2\text{O}_4$  powder was pulverized and dispersed in isopropyl alcohol and one droplet of suspension was put on a formvar coated copper grid and drying the grid, it was inserted in the TEM instrument. The TEM was performed on JEOL 4000 EX/II operating at 400 kV having a point-to-point resolution of 0.165 nm and a JEOL 2010FEG, operating at 200 kV having an information limit of 0.11 nm were used.

## ESI 2. Methods for the preparation of $\text{NiFe}_2\text{O}_4$ Nanoparticles:

$\text{NiFe}_2\text{O}_4$  nanoparticles were synthesized via co-precipitation method from ferric chloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) and nickel chloride ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ), 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 up to 12 and brown colour precipitates were formed. Finally, the precipitates were separated by centrifugation and dried in hot air oven for 4 h at 100 °C and finally, calcinated the powder at 550 °C for 6 h. The formation of NiFe<sub>2</sub>O<sub>4</sub> NPs was confirmed by powder X-ray diffraction and HRTEM studies. The powder XRD pattern (Fig. 1S) reveals that the Bragg reflection peaks were indexed to face centered cubic NiFe<sub>2</sub>O<sub>4</sub>,<sup>1</sup> and *Fd3m* space group (JCPDS file no. 10-0325) and the diffraction peaks at 30.32°, 35.81°, 37.27°, 43.45°, 53.89°, 57.41° and 62.96° are attributed to the reflections of {220}, {311}, {222}, {400}, {422}, {511} and {440} planes of the NiFe<sub>2</sub>O<sub>4</sub>, respectively.



**Fig. 1S:** Powder XRD pattern of fresh nano-NiFe<sub>2</sub>O<sub>4</sub>

**ESI 3. The preparation procedure of CuFe<sub>2</sub>O<sub>4</sub> nanoparticles:**

The CuFe<sub>2</sub>O<sub>4</sub> nanoparticles were prepared by following reported procedure.<sup>2</sup> Mixture of Cu(NO<sub>3</sub>)<sub>2</sub> (0.001 mol) and FeCl<sub>3</sub>·6H<sub>2</sub>O (0.002 mol) (the stoichiometric molar ratio of Cu<sup>2+</sup>/Fe<sup>3+</sup> was 1 : 2) solution were prepared and vigorously mixed under stirring for 2 h at 80 °C. Subsequently, 0.3 M NaOH solution was added drop by drop into the solutions till the pH is reached up to 12 and black precipitate is formed. Then centrifuged and washed with distilled water and left in an atmosphere environment to dry. The resulting powder was then calcinated at 550° C in a furnace for 2 hours.

**ESI 4. The preparation procedure of CoFe<sub>2</sub>O<sub>4</sub> nanoparticles:**

The CoFe<sub>2</sub>O<sub>4</sub> nanoparticles were prepared by following reported procedure.<sup>3</sup> At first, 2.0 g of anhydrous sodium acetate solution was prepared in 30 mL of ethylene glycol and the solution was stirred vigorously at room temperature to give a homogeneous solution. Then, 1.5 mmol of CoCl<sub>2</sub>·6H<sub>2</sub>O and 3.0 mmol of FeCl<sub>3</sub>·6H<sub>2</sub>O was added slowly to the above solution (the stoichiometric molar ratio of Co<sup>2+</sup>/Fe<sup>3+</sup> was 1 : 2). This mixture was then vigorously stirred at 70 °C for 2 h to form a homogeneous solution. Then centrifuged and washed with distilled water and left in an atmosphere environment to dry. The resulting powder was then calcinated at 550° C in a furnace for 2 hours.

**ESI 5. The preparation procedure of ZnFe<sub>2</sub>O<sub>4</sub> nanoparticles:**

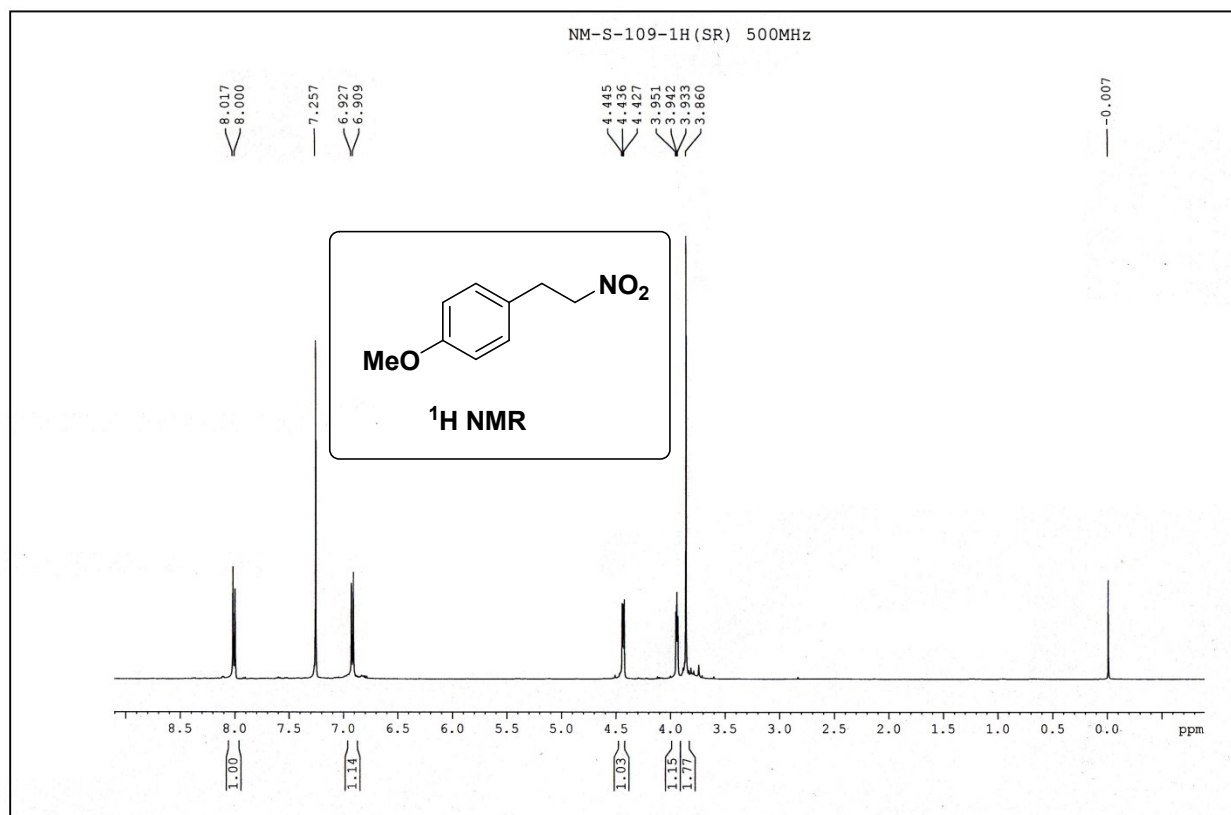
The ZnFe<sub>2</sub>O<sub>4</sub> nanoparticles were prepared by following reported procedure.<sup>4</sup> Mixture of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.1 M) and Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (0.2 M) (the stoichiometric molar ratio of Zn<sup>2+</sup>/Fe<sup>3+</sup> was 1 : 2) solution were prepared in 50 ml distilled water and was gelated by using 0.1 M (300 ml) of urea solution. The resulting solution was mixed vigorously under stirring at 55 °C until the gel was formed, which was subsequently dried at 100 °C for some time in oven. Then the resulting dried gel was calcinated at 550° C in a furnace for 2 hours.

**ESI 6. General experimental procedure for NiFe<sub>2</sub>O<sub>4</sub> NPs catalyzed transfer hydrogenation of alkenes:** Alkene (1.0 mmol) and NiFe<sub>2</sub>O<sub>4</sub> nanoparticles (10 mg) were heated at 80 °C in isopropyl alcohol (2 mL) for 3 hours in open air. The completion of the reactions was checked by monitoring TLC. Then, the reaction mixture was cooled to room temperature and magnetic NPs were separated by using strong external magnet. The remaining mixture was extracted with ethyl acetate (25 mL), washed with water followed by brine solution (3 × 5 mL) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After evaporation of solvent in vacuum left the crude product which was purified by column chromatography on silica gel (ethyl acetate: petroleum ether = 5:95 to provide pure hydrogenated alkane product. The formation of the product was confirmed by spectroscopic studies. The NMR spectroscopic data of the compounds has been given below.

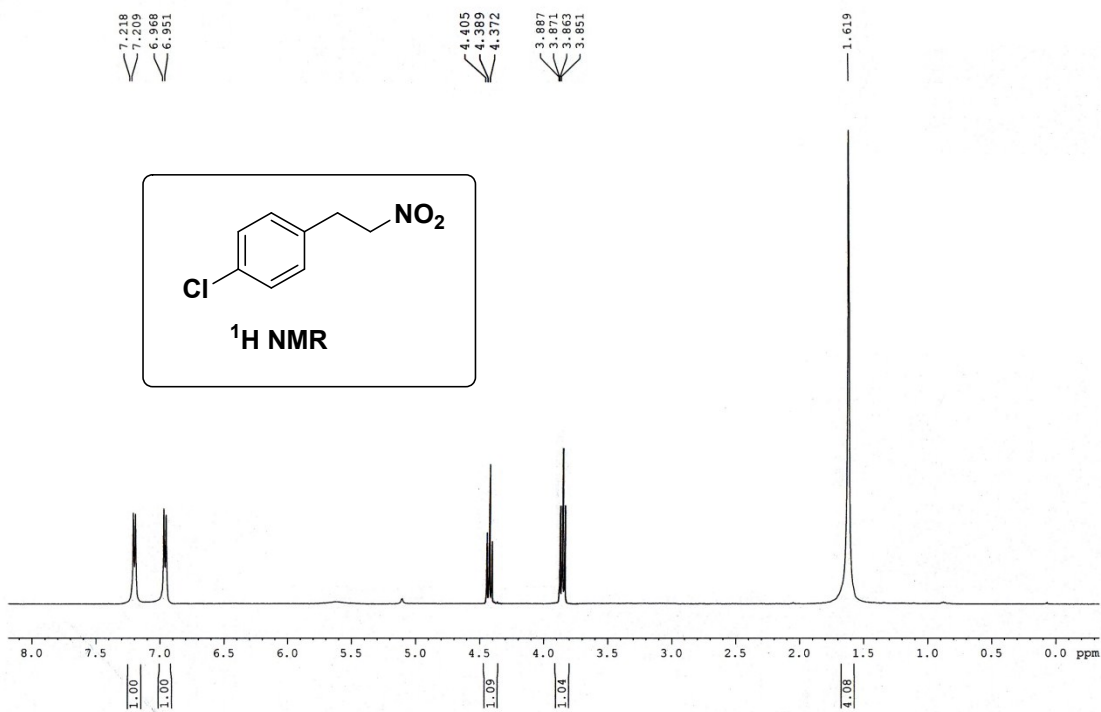
**ESI 7. General experimental procedure for NiFe<sub>2</sub>O<sub>4</sub> NPs catalyzed transfer hydrogenation of alkyne:** Alkyne (1.0 mmol) and NiFe<sub>2</sub>O<sub>4</sub> nanoparticles (10 mg) were heated at 80 °C in isopropyl alcohol (2 mL) for 3-4 hours in open air. The completion of the reactions was checked by monitoring TLC. Then, the reaction mixture was cooled to room temperature and magnetic NPs were separated by using strong external magnet. The remaining mixture was extracted with ethyl acetate (25 mL), washed with water followed by brine solution (3 × 5 mL) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After evaporation of solvent in vacuum left the crude product which was purified by column chromatography on silica gel (ethyl acetate: petroleum ether = 5:95 to provide pure hydrogenated alkene product. The formation of the product was confirmed by spectroscopic studies. The NMR spectroscopic data of the compounds has been given in below.

**ESI 8. General experimental procedure for NiFe<sub>2</sub>O<sub>4</sub> NPs catalyzed dehydrogenation alcohol:** Alcohol (1.0 mmol) and NiFe<sub>2</sub>O<sub>4</sub> nanoparticles (10 mg) were refluxed at 120 °C in toluene (2 mL) for 6 hours in open air. The completion of the reactions was checked by monitoring TLC. Then, the reaction mixture was cooled to room temperature and magnetic NPs were separated by using strong external magnet. The remaining mixture was extracted with ethyl acetate (25 mL), washed with water followed by brine solution (3 × 5 mL) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After evaporation of solvent in vacuum left the crude product which was purified by column chromatography on silica gel (ethyl acetate: petroleum ether = 5:95 to provide pure hydrogenated alkene product. The formation of the product was confirmed by spectroscopic studies. The NMR spectroscopic data of the compounds has been given in below.

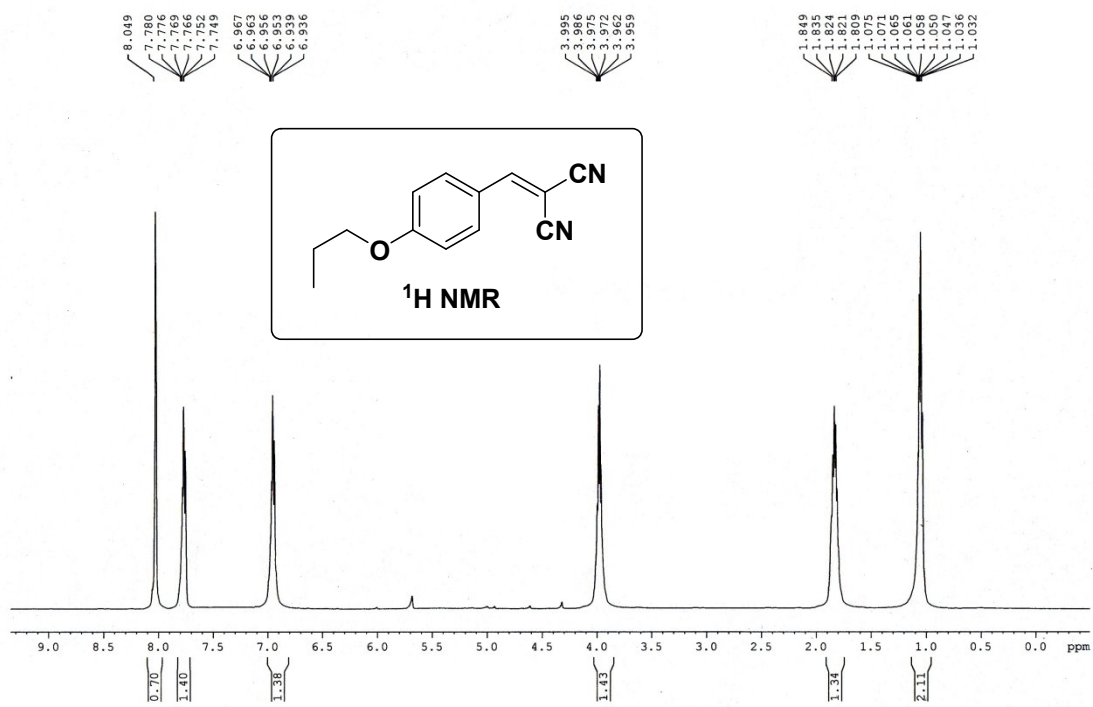
ESI-9: Copy of  $^1\text{H}$  NMR spectra of few hydrogenated alkenes and alkynes listed in Table 2 and 3.



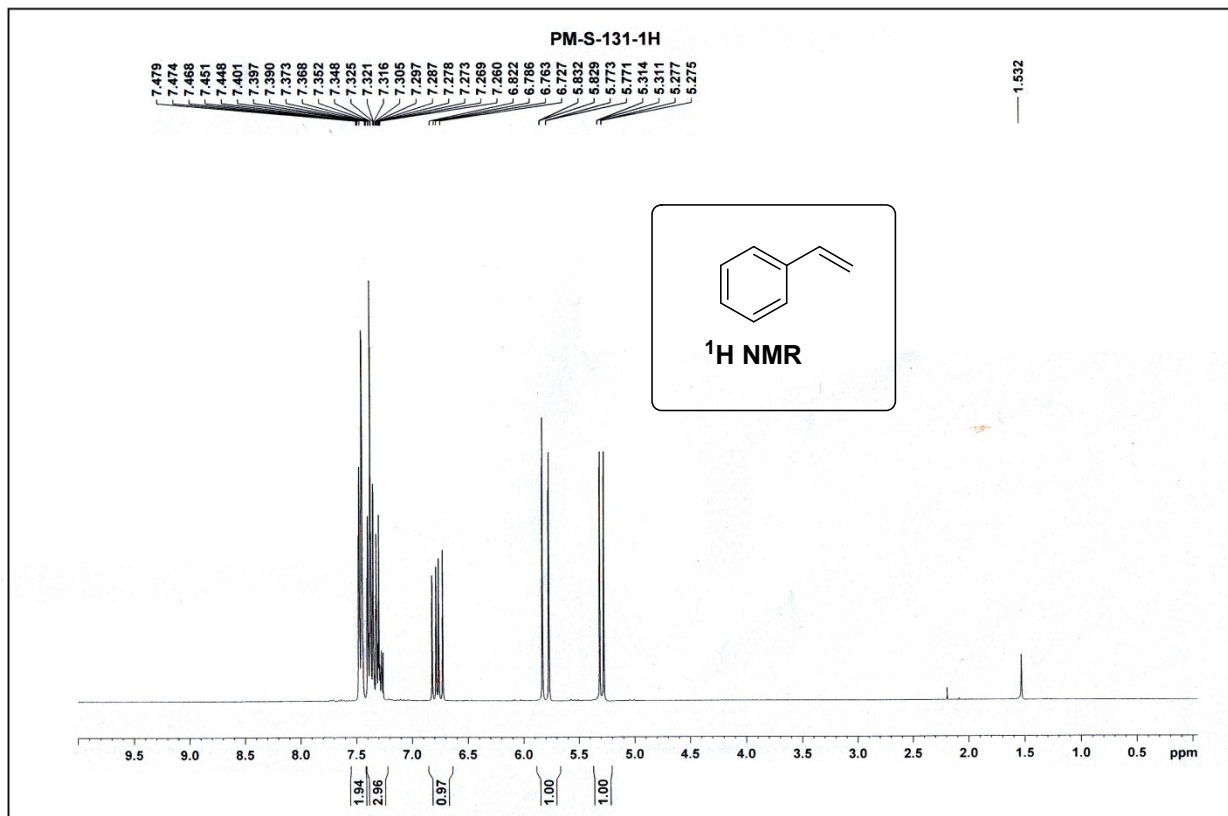
PMS.121-1H (SKD) 11aug15.10

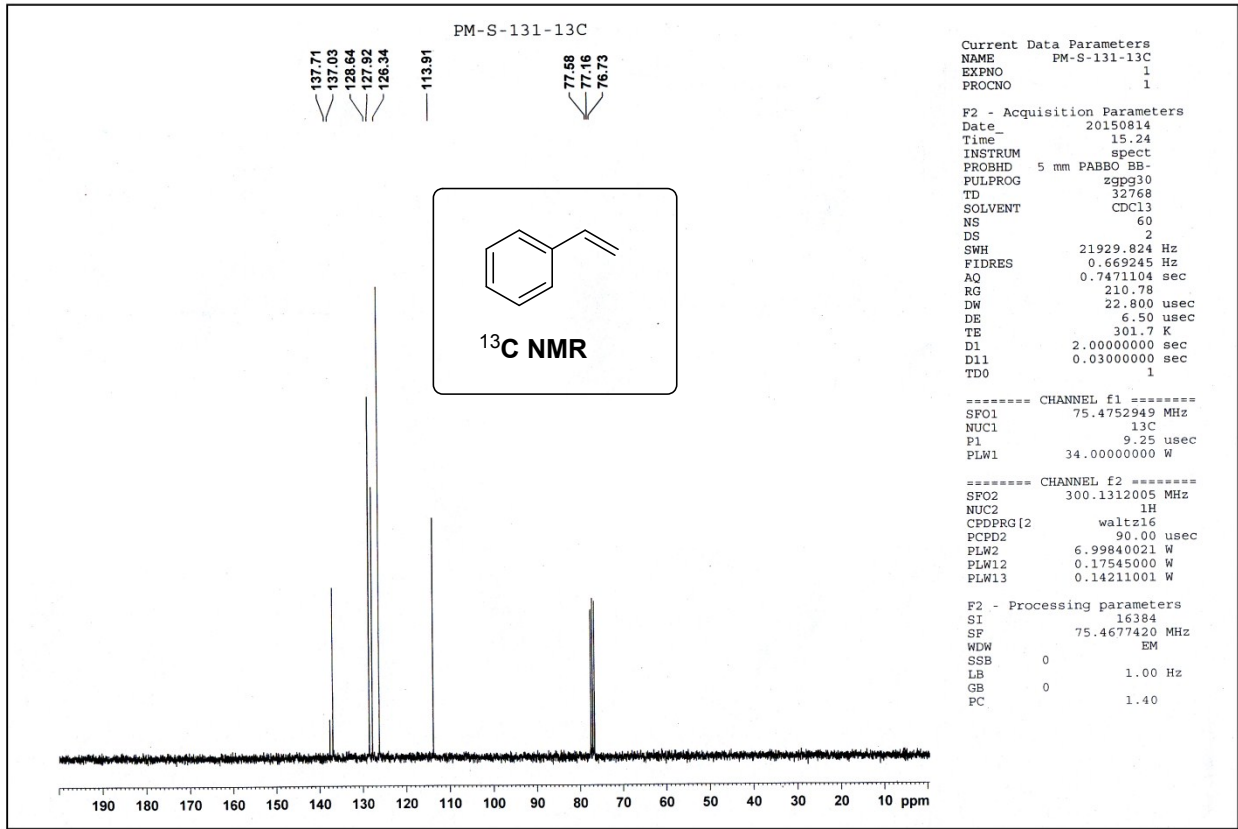


PM,S.122-1H(SKD) 11aug15.12

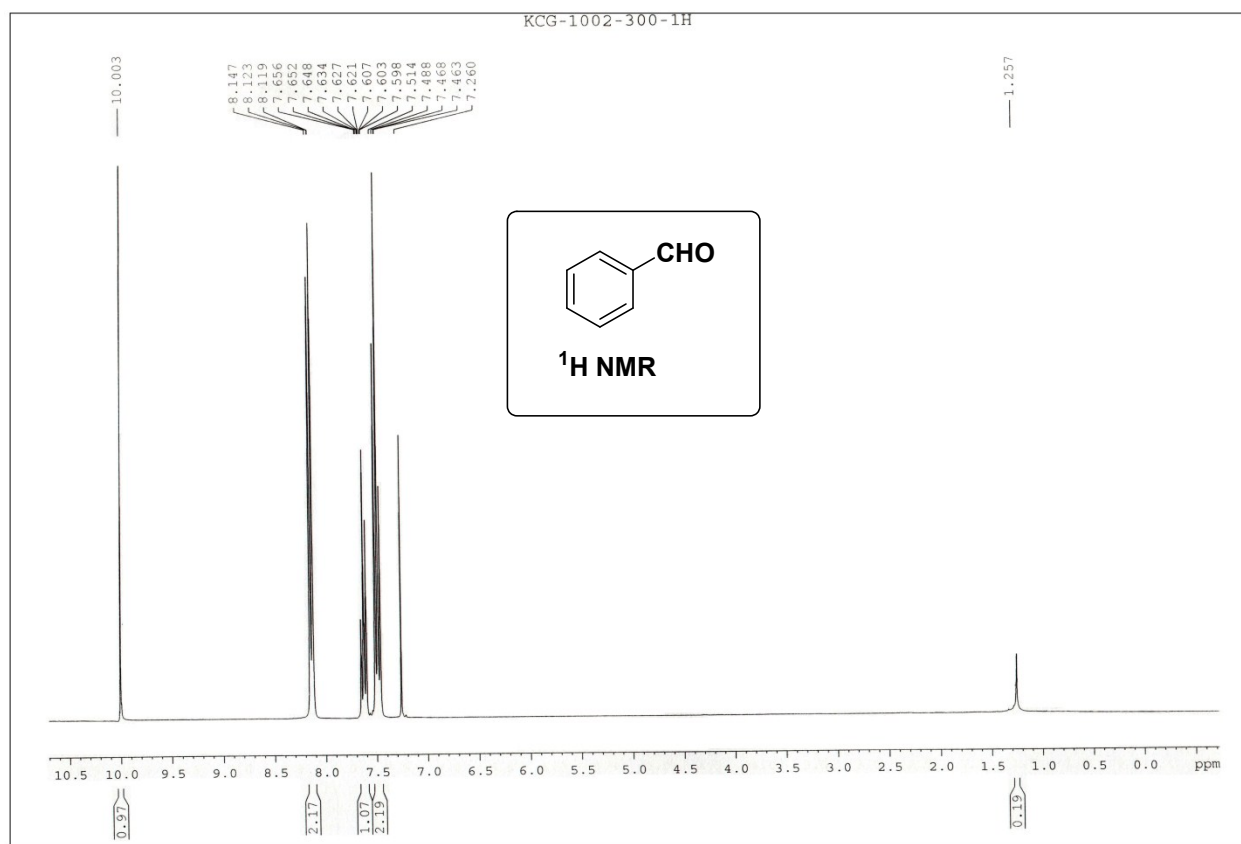




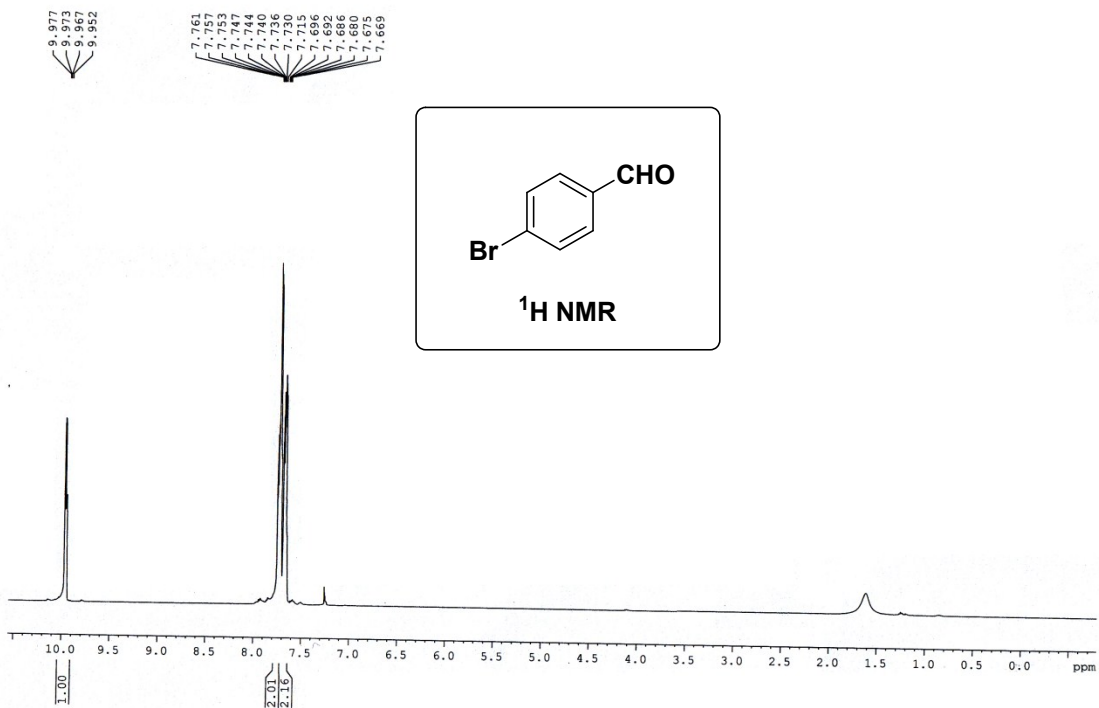


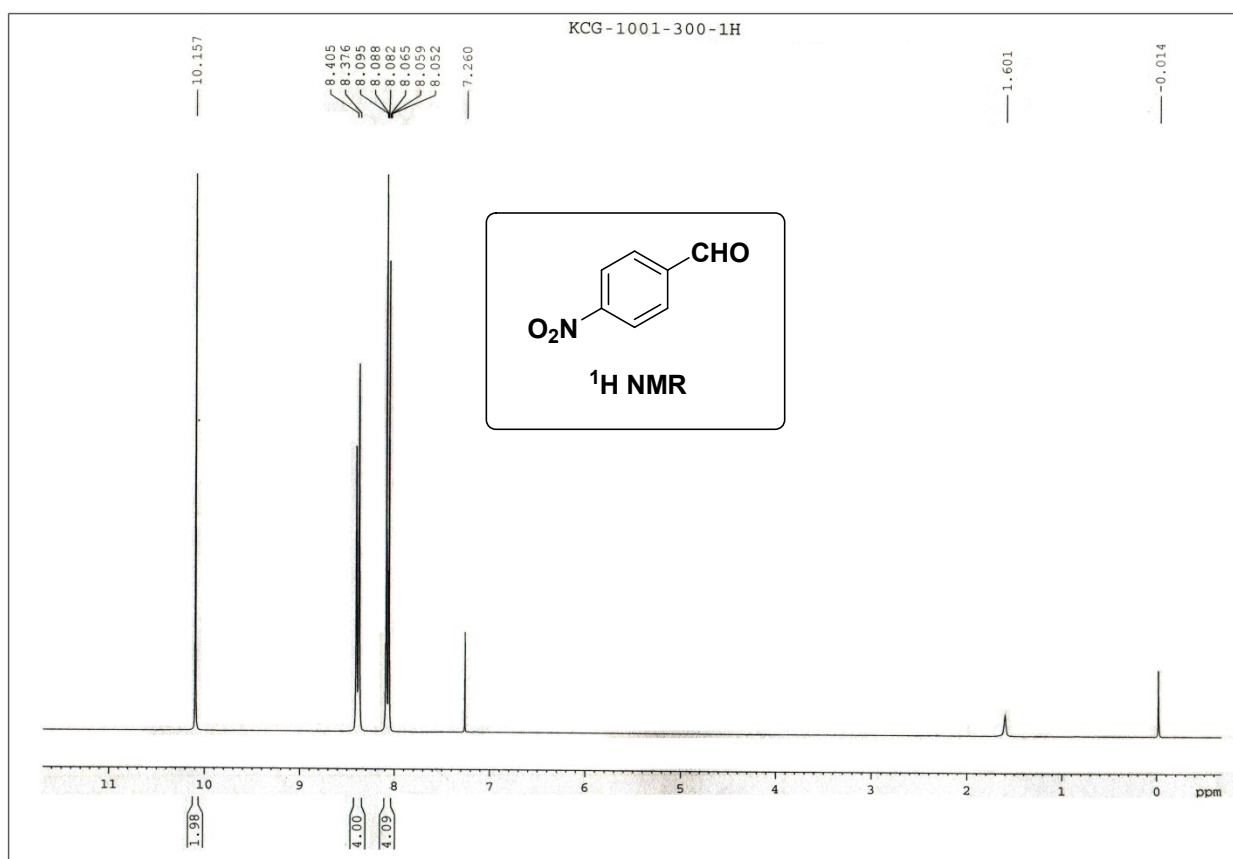


**ESI-10: Copy of  $^1\text{H}$  NMR spectra of few de-hydrogenated product of alcohol listed in Table 4.**

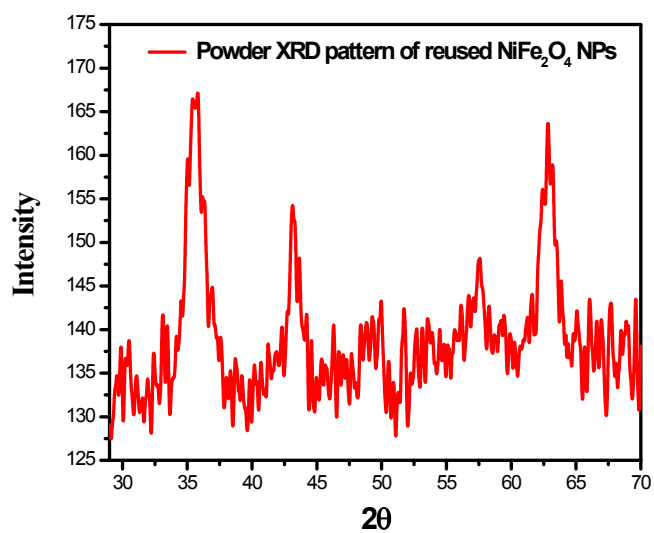


PM.S.126-1H(SKD) 13aug15.10

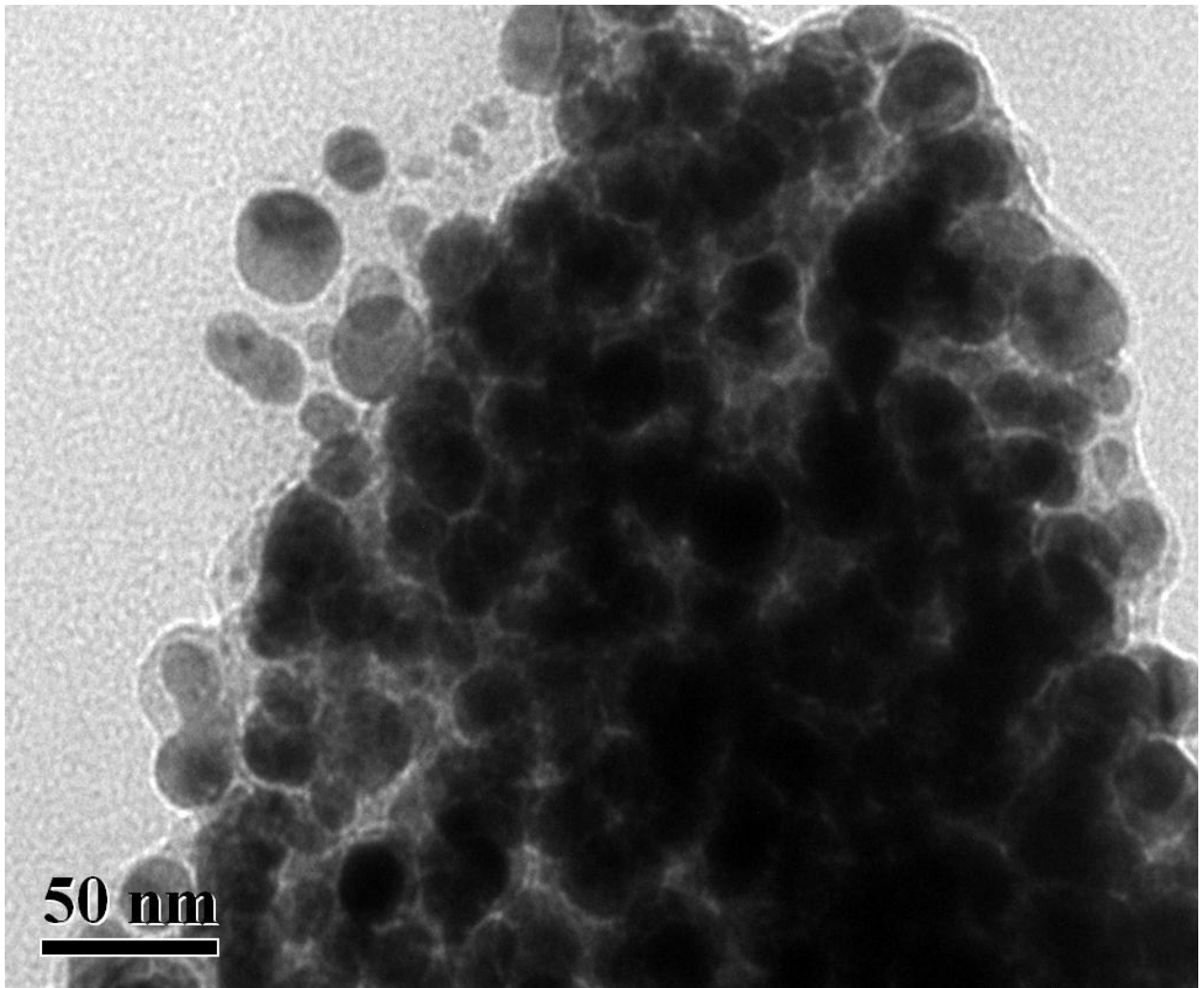




ESI-11. Powder XRD pattern of reused nano-NiFe<sub>2</sub>O<sub>4</sub> after 5<sup>th</sup> cycle:



ESI-12. HRTEM image of reused nano-NiFe<sub>2</sub>O<sub>4</sub> after 5<sup>th</sup> cycle:



### ESI-13. References:

- [1] R. Ramesh, A. Ramanand, S. Ponnusamy and C. Muthamizhchelvan, *Mater. Lett.*, 2011, **65**, 1438.
- [2] For preparation of  $\text{CuFe}_2\text{O}_4$ : K. Pradhan, S. Paul and A. R. Das, *Catal. Sci. Technol.*, 2014, **4**, 822.
- [3] For preparation of  $\text{CoFe}_2\text{O}_4$ : B. Y. Yu, S. Y. Kwak, *Dalton Trans.*, 2011, **40**, 9989.
- [4] For preparation of  $\text{ZnFe}_2\text{O}_4$ : M. Atif , S. K. Hasanain, M. Nadeem, *Solid State Commun.*, 2006, **138**, 416.