

## Electronic Supplementary Information

for

Synergic effect of nano-catalyst and continuous  
flow system: Dakin-West reaction catalyzed by  
Nafion-H@SPIONs in a microreactor

*Zahra Arabloo, Behnaz Shafiee, Ahmad R. Khosropour\**

Department of Chemistry, University of Isfahan, 81746-73441, Isfahan, Iran.

*E-mail: khosropour@chem.ui.ac.ir; Fax: +98 3116689732; Tel: +98 3117932700*

## **METHODS:**

All chemicals and Nafion-H (5% in ethanol) were purchased from Merck and DuPont companies, respectively. Fe<sub>3</sub>O<sub>4</sub> nanocomposite and silica-coated magnetite nanoparticles (SPIONs) was synthesis according to the literature respectively.<sup>29</sup> All known organic products were identified by comparison of their physical and spectral data with those of authentic samples. Thin layer chromatography (TLC) was performed on UV-active aluminum-backed plates of silica gel (TLC Silica gel 60 F254). <sup>1</sup>H, and <sup>13</sup>C NMR spectra were measured on a Bruker DPX 400 MHz spectrometer in CDCl<sub>3</sub> with chemical shift (δ) given in ppm. Coupling constants are given in Hz. The FT-IR spectra were taken on a Nicolet-Impact 400D spectrophotometer in KBr pellets and reported in cm<sup>-1</sup>. Melting points were determined using Stuart Scientific SMP2 apparatus and are uncorrected. The sonication was performed in a UP 400S ultrasonic processor equipped with a 3 mm wide and 140 mm long probe, which was immersed directly into the reaction mixture. The operating frequency was 24 kHz and the output power was 0–400 Watt through manual adjustment. The TEM images were taken with a Philips CM30 unit operated at 150 kV. The magnetic measurements were performed with a vibrating sample magnetometer (VSM) at Meghnatis Daghigh Kavir Co. TGA curve was obtained with a heating rate of 10 °C/min on a TG 50 Mettler thermogravimetric analyzer from 30 °C to 600 °C.

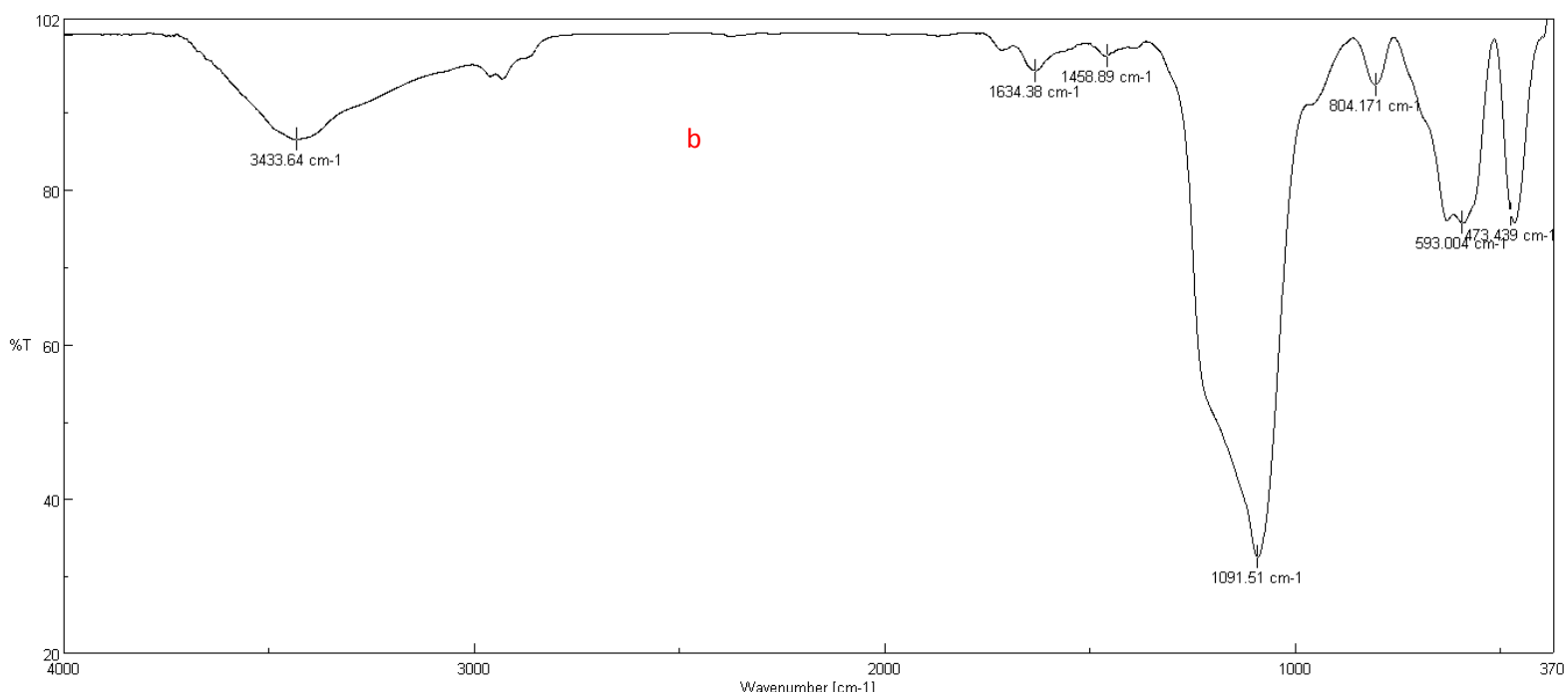
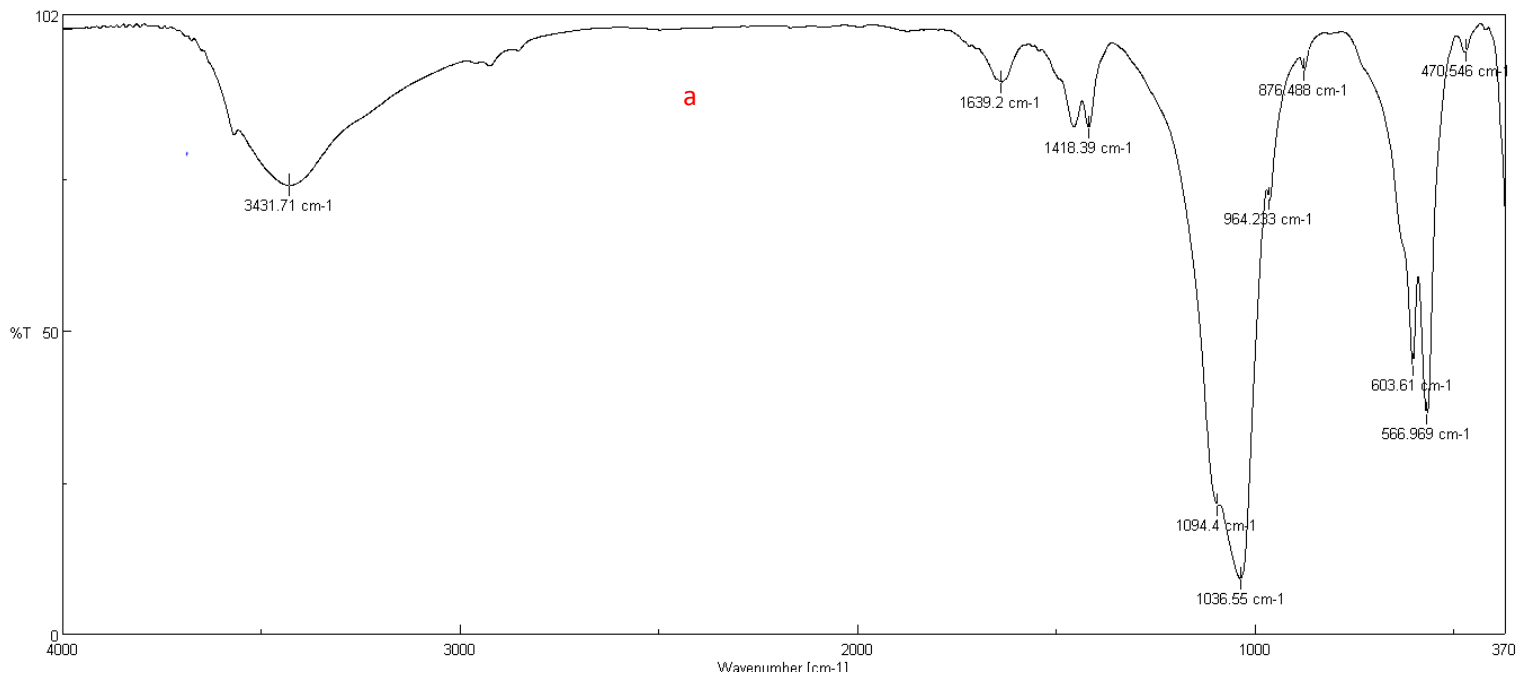
### **Preparation of Nafion-H@SPIONs**

The catalyst was synthesized via impregnation method. To a mixture of SPIONs (80 mg) in absolute ethanol (10 ml) at 25 °C, 0.4 ml Nafion-H (5% in ethanol) was added and sonicated for 15 minutes. The resulting mixture was stirred for 2h at 100 °C and subsequently calcinated at 120 °C for three hours.

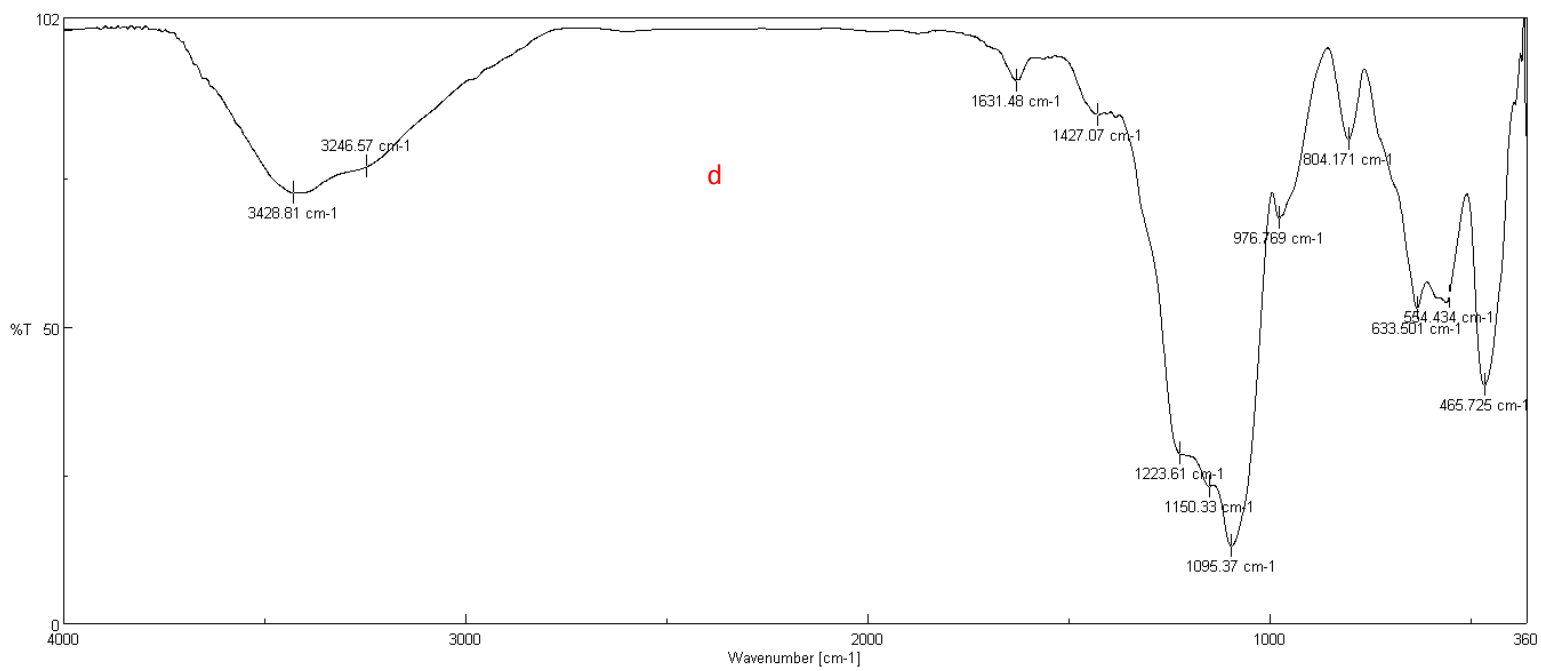
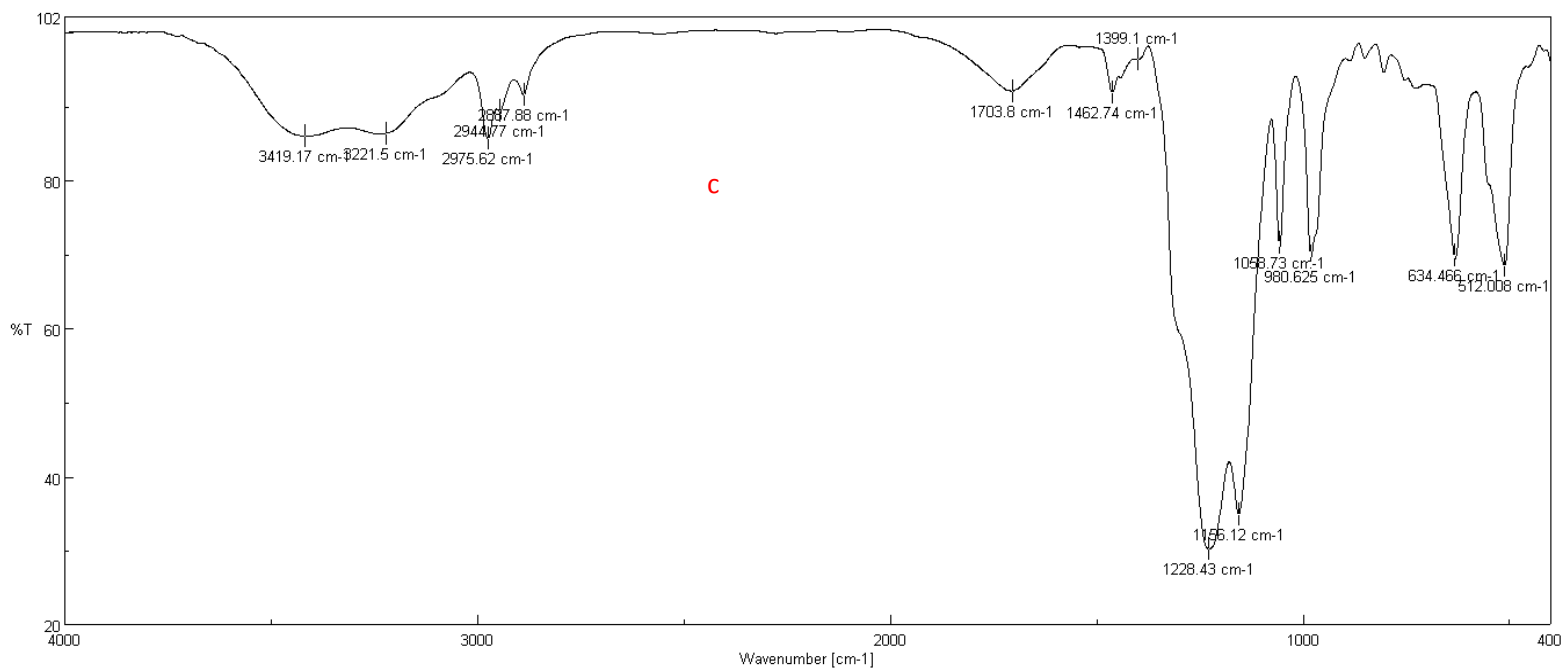
### **General procedure for the Dakin-West reaction catalyzed by Nafion-H@SPIONs in microreactor System**

A microreactor system containing a T-shaped micromixer, microtube reactor immersed in a water bath, and a syringing pump were used. The syringing pump was equipped with two syringes (1 ml). In a syringe, a sonicated solution of aldehyde (1.0 eq.), nitrile (1.0 eq.) and Nafion-H@SPIONs (20 mg containing of 0.35 mol% Nafion-H) using THF as solvent with a concentration of 2 M and in another, a 2 M solution of arylmethyl ketone (1.0 eq.) and acetyl chloride (1.0 eq.) in THF were charged. Next, the mixtures were fed into the system by syringe pump (flow rate: 0.06 ml/min) at 40 °C. After the residence time was reached (10 min), the discharge was collected in a glass vessel equipped with an external permanent magnet. The collected catalyst by the magnet, washed two times with absolute ethanol (2×1 ml), air-dried, and used directly for the next round. After separation of the catalyst from the resulting crude product, the volatile was

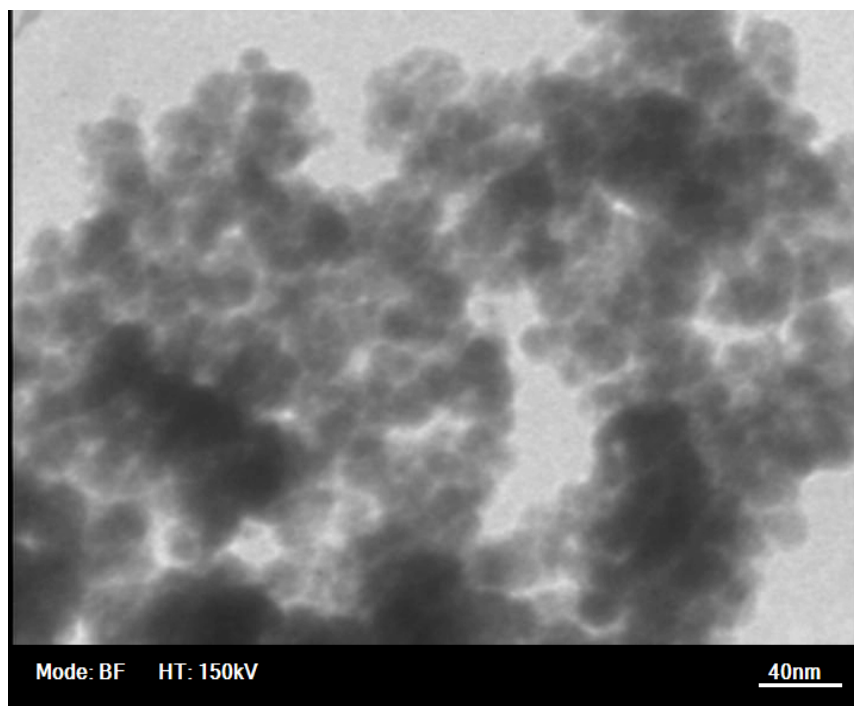
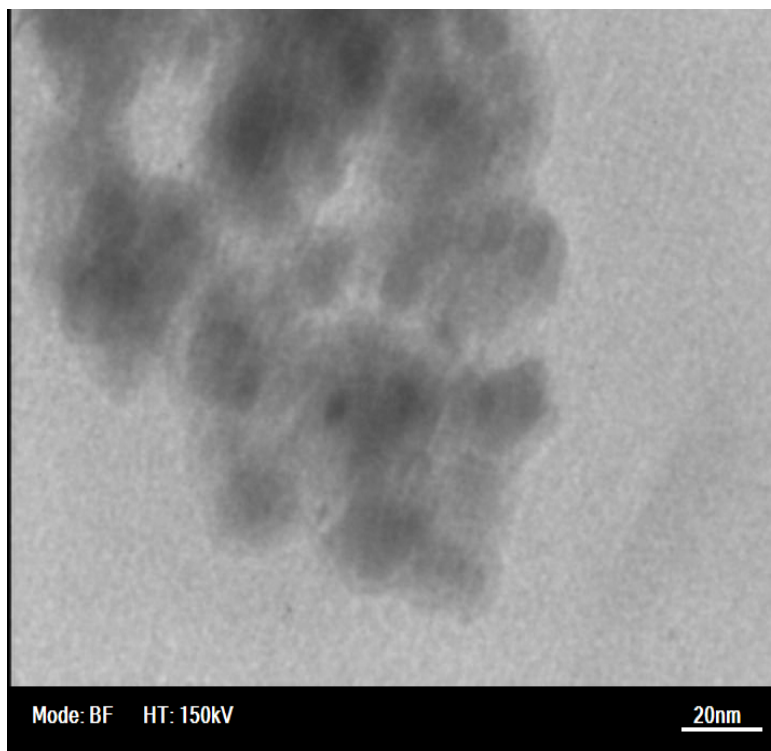
removed in vacuum. The organic residue was washed with water (3×5 ml), decanted and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Purification by flash chromatography (silica gel, ethyl acetate/petroleum ether) afforded the corresponding products in 78-92% yields. Most of the products are known in the literature and were identified by comparison of their FT-IR and NMR with literature data.



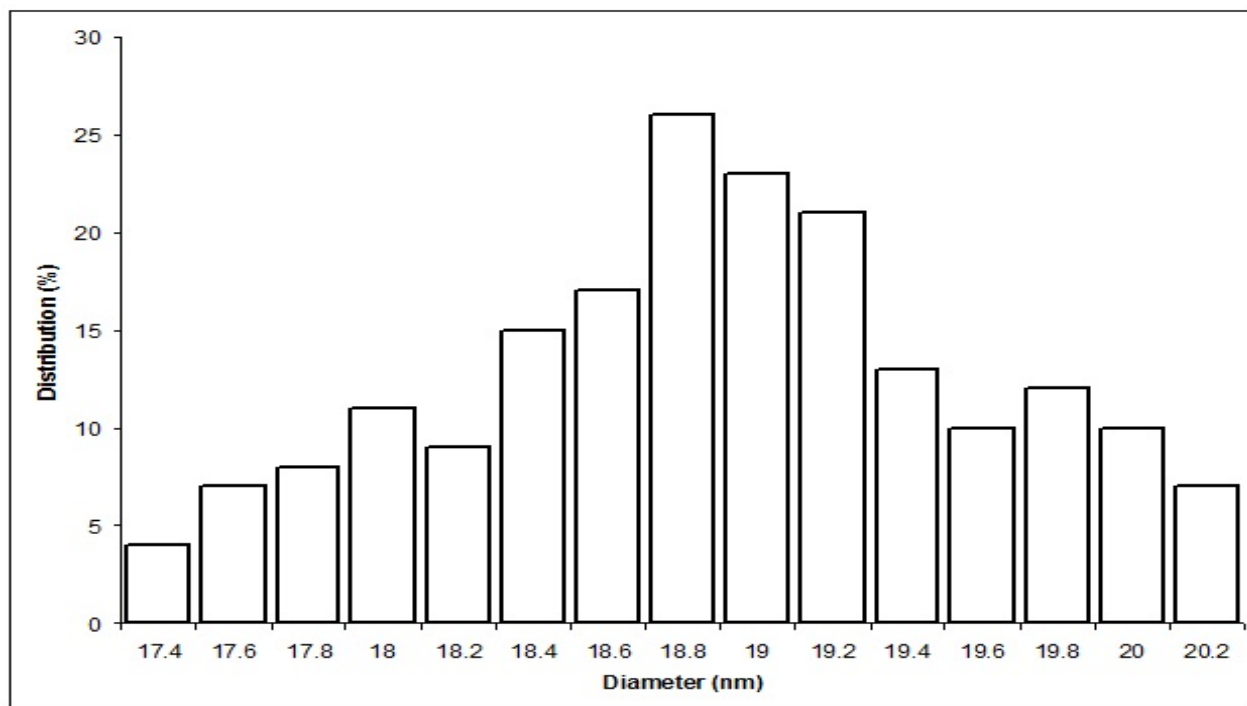
**Figure S1:** FT-IR spectrums of (a) nano-Fe<sub>3</sub>O<sub>4</sub> and (b) SPIONs



**Figure S2:** FT-IR spectrums of (c) Nafion-H and (d) Nafion-H@SPIONs

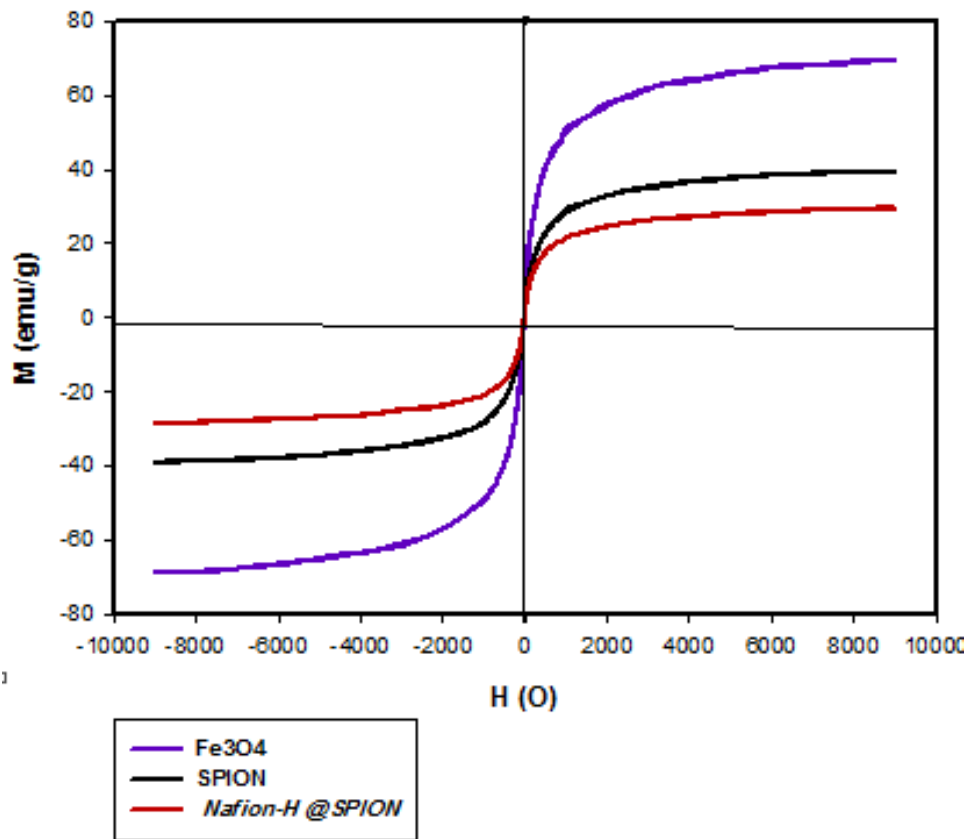


**Figure S3:** HR-TEM image of Nafion-H@SPIONs (scale bar correspond to 20 and 40 nm respectively)

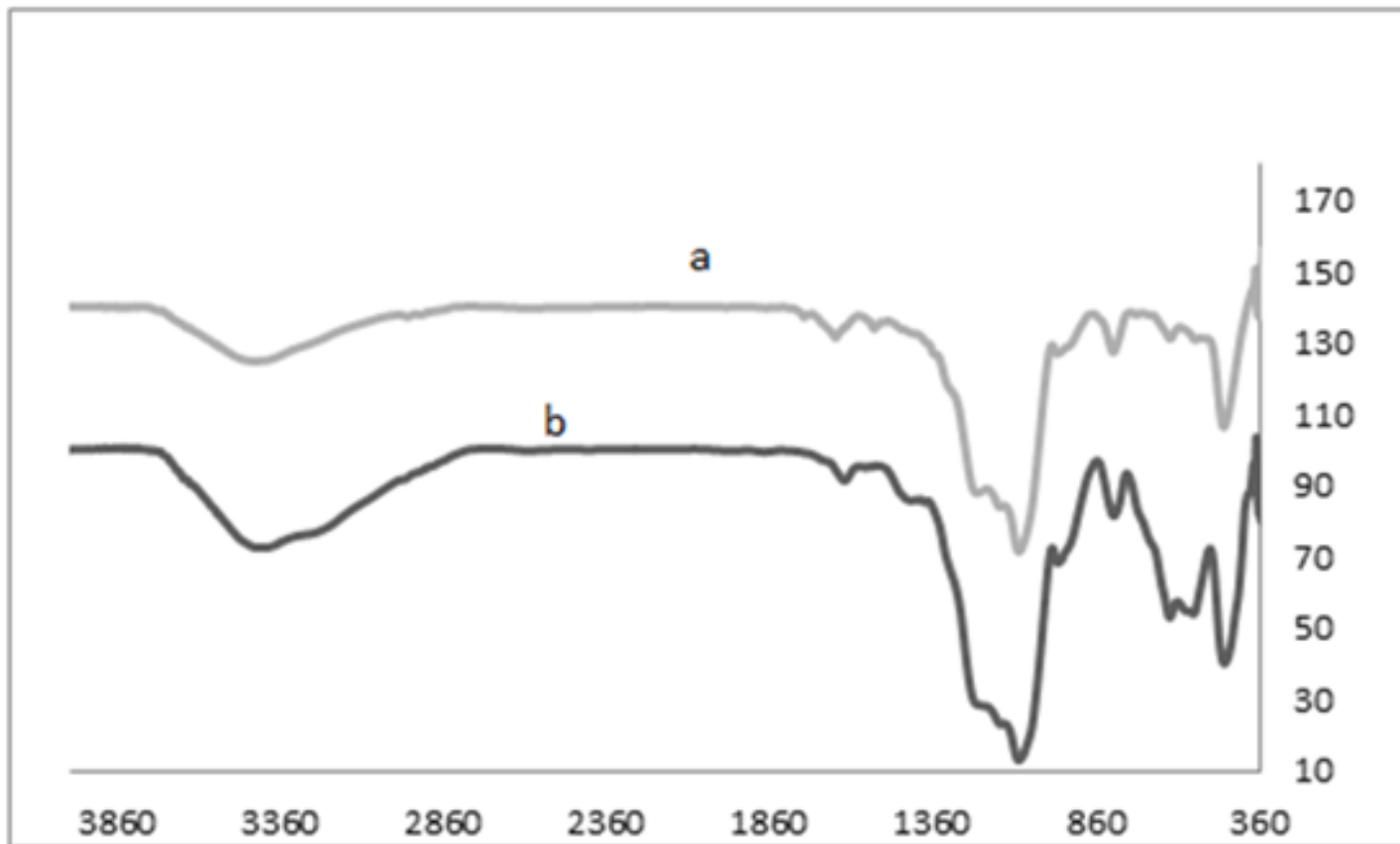


**Figure S4:** Nafion-H@SPIONs particle size distribution histogram



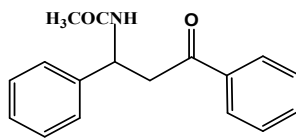


**Figure S4:** The dc magnetic characterization of the nanoparticles



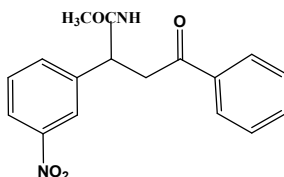
**Figure S5:** FT-IR spectrums of (a) Nafion-H@SPIONs after 7 runs and (b) fresh Nafion-H@SPIONs

1.  $\beta$  – Acetamido- $\beta$ -(phenyl) propiophenone



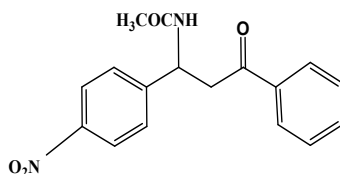
M.p: 100-102 °C. IR (KBr)  $\nu_{\max}/\text{cm}^{-1}$ : 3252, 1667, 1654.  $^1\text{H}$ - NMR (400MHz;  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 2.03 (s, 3H,  $\text{CH}_3$ ), 3.34 (dd,  $J= 6.0$  and  $9.7\text{Hz}$ , 1H,  $\text{CH}_2$ ), 3.70 (dd,  $J= 6.5$  and  $9.7\text{ Hz}$ , 1H,  $\text{CH}_2$ ), 5.60 (m, 1H, methyne H), 7.32 (d,  $J= 8.0\text{ Hz}$ , 1H, NH), 7.60 (d,  $J= 9.1\text{ Hz}$ , 2H, Ar-H), 7.70-7.90 (m, 8H, Ar-H);  $^{13}\text{C}$ - NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 198.50, 169.40, 140.30, 136.50, 131.50, 132.60, 132.60, 131.80, 128.90, 128.40, 128.20, 127.48, 126.51, 121.30, 49.40, 43.20, 23.20.

2.  $\beta$  – Acetamido- $\beta$ -(3-nitrophenyl) propiophenone



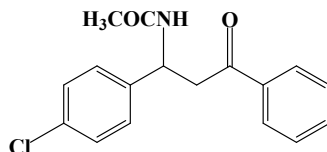
M.p: 110-112 °C. IR (KBr)  $\nu_{\max}/\text{cm}^{-1}$ : 3289.96, 1687.41, 1651.73.  $^1\text{H}$ - NMR (400MHz;  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 2.07 (s, 3H,  $\text{CH}_3$ ), 3.50 (dd,  $J= 6.0$  and  $16.0\text{ Hz}$ , 1H,  $\text{CH}_2$ ), 3.80 (dd,  $J= 5.2$  and  $16.0\text{ Hz}$ , 1H,  $\text{CH}_2$ ), 5.70- 5.72 (m, 1H, methyne H), 7.10 (d,  $J= 8.0\text{ Hz}$ , 1H, NH), 7.45-7.61 (m, 5H, Ar-H), 7.73 (d,  $J=8.0\text{ Hz}$ , 1H, Ar-H), 7.91 (d,  $J=7.2\text{ Hz}$ , 1H, Ar-H), 8.10 (d,  $J=8.0\text{ Hz}$ , 1H, Ar-H) 8.242 (s, 1H, Ar-H);  $^{13}\text{C}$ - NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 198.08, 169.82, 148.40, 143.44, 136.16, 134.01, 132.96, 129.57, 128.88, 128.10, 126.37, 124.87, 122.41, 121.34, 49.06, 42.74, 23.42.

3.  $\beta$  – Acetamido- $\beta$ -(4-nitrophenyl) propiophenone



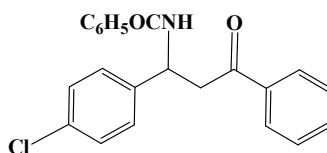
M.p: 148-150 °C. IR (KBr)  $\nu_{\max}/\text{cm}^{-1}$ : 3288.04, 1687.41, 1650.71.  $^1\text{H}$ - NMR (400MHz;  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 2.01 (s, 3H,  $\text{CH}_3$ ), 3.42 (dd,  $J= 5.2$  and  $20.0\text{ Hz}$ , 1H,  $\text{CH}_2$ ), 3.73 (dd,  $J= 5.2$  and  $20.0\text{ Hz}$ , 1H,  $\text{CH}_2$ ), 5.60- 5.61 (m, 1H, methyne H), 6.90 (d,  $J= 8.4\text{ Hz}$ , 1H, NH), 6.80 (d,  $J=8.0$ , 1H, NH), 7.31-7.54 (9H, Ar-H);  $^{13}\text{C}$ - NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 199.09, 170.50, 139.94, 137.42, 136.66, 134.02, 133.28, 133.00, 132.05, 132.43, 128.98, 128.66, 128.45, 128.01, 49.89, 42.94, 23.74.

4.  $\beta$  – Acetamido- $\beta$ -(4-chlorophenyl) propiophenone



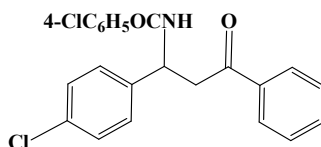
M.p: 147-148 °C. IR (KBr)  $\nu_{\max}/\text{cm}^{-1}$ : 3289, 1678.41, 1650.77.  $^1\text{H}$ - NMR (400MHz;  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 2.05 (s, 3H,  $\text{CH}_3$ ), 3.30 (dd,  $J= 5.6$  and  $20.0$  Hz, 1H,  $\text{CH}_2$ ), 3.80 (dd,  $J= 5.2$  and  $24.0$  Hz, 1H,  $\text{CH}_2$ ), 5.54- 5.60 (m, 1H, methyne H), 6.80 (d,  $J= 8.0$  Hz, 1H, NH), 7.20 (d, 2H, Ar-H), 7.22 (d, 2H, Ar-H), 7.50 (t,  $J=8.0$  Hz, 2H, Ar-H), 7.60 (t,  $J=8.8$  Hz, 1H, Ar-H), 7.50 (d,  $J=7.2$  Hz, 2H, Ar-H), 7.50 (t,  $J=8.0$  Hz, 2H, Ar-H), 7.60 (t,  $J=8.8$  Hz, 1H, Ar-H), 7.50 (d,  $J=7.2$  Hz, 2H, Ar-H);  $^{13}\text{C}$ - NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 198.49, 169.50, 139.54, 136.48, 133.72, 133.18, 132.78, 131.56, 129.10, 128.78, 128.76,

5.  **$\beta$  – Benzamido- $\beta$ -(4-chlorophenyl) propiophenone**



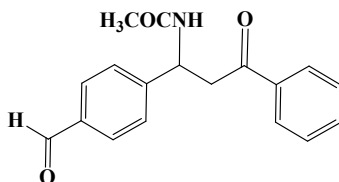
M.p: 141-143 °C. IR (KBr)  $\nu_{\max}/\text{cm}^{-1}$ : 3275.5, 1683.55, 1643.05.  $^1\text{H}$ - NMR (400MHz;  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 3.42 (dd,  $J=4.8$  and  $20.0$  Hz, 1H,  $\text{CH}_2$ ), 3.80 (dd,  $J= 4.8$  and  $12.0$  Hz, 1H,  $\text{CH}_2$ ), 5.65- 5.70 (m, 1H, methyne H), 7.60 (d,  $J= 1.6$  Hz, 1H, NH), 7.20-7.85(14H, Ar-H);  $^{13}\text{C}$ - NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 199.06, 166.68, 139.58, 136.52, 134.06, 133.82, 133.43, 133.37, 133.24, 131.75, 128.82, 128.73, 128.65, 128.60, 128.16, 128.02, 128.00, 127.94, 127.90, 127.06, 49.74, 42.66.

6.  **$\beta$  –4-chloro-benzamido- $\beta$ -(4-chlorophenyl) propiophenone**



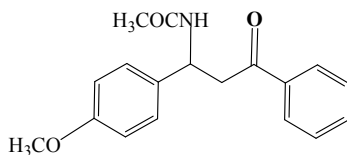
M.p: 154-155 °C. IR (KBr)  $\nu_{\max}/\text{cm}^{-1}$ : 3277.4, 1685.06, 1645.16.  $^1\text{H}$ - NMR (400MHz;  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 3.28 (dd,  $J=5.6$  and  $20.0$  Hz, 1H,  $\text{CH}_2$ ), 3.59 (dd,  $J= 3.59$  and  $16.0$  Hz, 1H,  $\text{CH}_2$ ), 5.41- 5.43 (m, 1H, methyne H), 6.64 (d,  $J= 8.4$  , 1H, NH), 7.12-7.84(13H, Ar-H).

7.  **$\beta$  –Acetamido- $\beta$ -(4-formylphenyl) propiophenone**



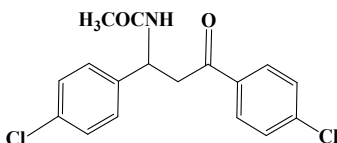
M.p: 141-143 °C. IR (KBr)  $\nu_{\max}/\text{cm}^{-1}$ : 3275.5, 1683.55, 1543.05.  $^1\text{H}$ - NMR (400MHz;  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 2.03 (s, 3H,  $\text{CH}_3$ ), 3.42 (dd,  $J= 6.0$  and  $16.0$  Hz, 1H,  $\text{CH}_2$ ), 3.72 (dd,  $J=5.2$  and  $16\text{Hz}$ , 1H,  $\text{CH}_2$ ), 5.50- 5.55 (m, 1H, methyne H), 6.89 (d,  $J= 5.0$  Hz , 1H, NH), 7.31- 7.75 (3H, Ar-H), 8.02 (d,  $J=7.8$  Hz, 2H, Ar-H), 8.10 (d,  $J=7.8$  Hz, 2H, Ar-H), 9.98 (s, 1H, CHO).

8.  **$\beta$  – Acetamido- $\beta$ -(4-methoxyphenyl) propiophenone**



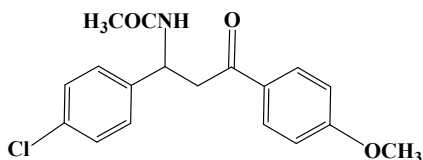
M.p: 110-112 °C. IR (KBr)  $\nu_{\max}/\text{cm}^{-1}$ : 3297.68, 1686.44, 1657.52.  $^1\text{H}$ - NMR (400MHz;  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 1.93 (s, 3H,  $\text{CH}_3$ ), 3.33 (dd,  $J= 6.3$  and  $16.4$  Hz, 1H,  $\text{CH}_2$ ), 3.63 (dd,  $J= 5.5$  and  $16.4$  Hz, 1H,  $\text{CH}_2$ ), 3.70(s, 3H,  $\text{CH}_3$ ), 5.41- 5.50 (m, 1H, methyne H), 6.62 (d,  $J= 7.7$  Hz, 1H, NH), 6.75 (d, 2H, Ar-H), 6.80 (d, 2H, Ar-H), 7.20 (t,  $J=6.3$  Hz, 2H, Ar-H), 7.24 (t,  $J=7.8$  Hz, 1H, Ar-H), 7.28 (d,  $J=7.2$  Hz, 2H, Ar-H), 7.50 (t,  $J=8.0$  Hz, 2H, Ar-H), 7.60 (t,  $J=8.8$  Hz, 1H, Ar-H), 7.50 (d,  $J=7.2$  Hz, 2H, Ar-H);  $^{13}\text{C}$ - NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 198.80, 169.80, 158.90, 148.90, 147.65, 138.45, 137.36, 136.70, 133.60, 133.10, 128.80, 128.20, 127.90, 114.10, 55.30, 49.70, 43.40, 23.40.

9.  **$\beta$  – Acetamido- $\beta$ -(4-chlorophenyl)-4-chloropropiophenone**



M.p: 120-122 °C. IR (KBr)  $\nu_{\max}/\text{cm}^{-1}$ : 3289.11, 1678.04, 1650.55.  $^1\text{H}$ - NMR (400MHz;  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 2.01 (s, 3H,  $\text{CH}_3$ ), 3.52 (dd,  $J= 5.6$  and  $16.0$  Hz, 1H,  $\text{CH}_2$ ), 3.82 (dd,  $J= 4.8$  and  $20.0$  Hz, 1H,  $\text{CH}_2$ ), 5.66- 5.68 (m, 1H, methyne H), 6.90 (d,  $J= 8.4$  Hz, 1H, NH), 7.40 (d,  $J=7.2$  Hz, 2H, Ar-H), 7.81 (d,  $J=7.2$ , 2H, Ar-H), 8.12 (d,  $J=2.1$  Hz, 2H, Ar-H).

10.  **$\beta$  – Acetamido- $\beta$ -(4-chlorophenyl)-4-methoxypropiophenone**



M.p: 110-112 °C. IR (KBr)  $\nu_{\max}/\text{cm}^{-1}$ : 3290.01, 1675.34, 1650.41.  $^1\text{H}$ - NMR (400MHz;  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 1.99 (s, 3H,  $\text{CH}_3$ ), 3.34 (dd,  $J= 5.2$  and  $16.0$  Hz, 1H,  $\text{CH}_2$ ), 3.66 (dd,  $J= 5.2$  and  $16.0$  Hz, 1H,  $\text{CH}_2$ ), 3.73 (s, 3H,  $\text{CH}_3$ ), 5.53- 5.58 (m, 1H, methyne H), 6.85 (d,  $J= 1.6$  Hz, 2H, Ar-H), 7.10 (d,  $J=8.4$  Hz, 1H, NH), 7.63 (d,  $J=8.0$  Hz, 2H, Ar-H), 7.80 (d,  $J=2.0$  Hz, 2H, Ar-H), 7.80 (d,  $J=1.6$  Hz, 2h, Ar-H).

