Supporting Information

On-water magnetic NiFe$_2$O$_4$ nanoparticle-catalyzed Michael additions of active methylene compounds, aromatic/aliphatic amines, alcohols and thiols to conjugated alkenes

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ESI 1. General Information:

All the chemicals and solvents were purchased from Sigma Aldrich, Sd-Fine, Merck and HIMEDIA (India). Without any further purification the chemicals were used as received, except all solvents which were used after distillation. Distilled water was used as solvent for the reaction. All the reactions were performed under atmospheric condition with hot air oven-dried glassware. For performing column chromatography distilled petroleum ether and ethyl acetate were used. Analytical thin layer chromatography (TLC) was performed on Merck 60F254 silica gel plates with 0.25 mm thickness.

Silica gel (60-120 mesh size, HIMEDIA, India) was used for performing column chromatography.

The $^1$H NMR spectra were recorded on Bruker AV 300, AV 400 and AV 500. In $^1$H NMR chemical shifts are reported relative to the center of solvent resonance (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), m (multiplet) and coupling constants $J$ were given in Hz. The $^{13}$C NMR spectra were recorded at 75 MHz in CDCl$_3$ solution. Chemical shifts are expressed in parts per million ($\delta$) and are referenced to CDCl$_3$ ($\delta = 77.16$) as internal standard. The powder XRD patterns of the nano-NiFe$_2$O$_4$ catalysts were performed on a Rigaku Ultima IV Xray diffractometer using Cu $K\alpha$ radiation of $\lambda = 1.540806$ Å. The diffractometer was operated at 40 kV and 40 mA with a step width of 0.02° and the scan rate was used 0.24°/min. For the TEM analysis the sample was prepared as follows: nano-NiFe$_2$O$_4$ powder was pulverized and dispersed in isopropyl alcohol and one droplet of suspension was put on a former 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. The experimental procedure for the preparation of NiFe$_2$O$_4$ Nanoparticles:
The NiFe$_2$O$_4$ nanoparticles were synthesized from ferric chloride (FeCl$_3$·6H$_2$O) and nickel chloride (NiCl$_2$·6H$_2$O), distilled water and sodium hydroxide following sol-gel method.$^1$ 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 and stirred for another 2 h. Finally, the precipitates were separated by centrifugation and washed with distilled water to neutralize the precipitate and dried in hot air oven for 4 h at 100 °C. Finally the powder was calcinated at 550 °C for 6 h in a furnace. The formation of NiFe$_2$O$_4$ NPs was confirmed by powder X-ray diffraction, FESEM and HRTEM studies.

ESI 3. The experimental procedure for the preparation of CuFe$_2$O$_4$ nanoparticles:
The nanoparticles of CuFe$_2$O$_4$ were synthesized by following reported procedure.$^2$ A mixture of Cu(NO$_3$)$_2$ (0.001 mol) and FeCl$_3$·6H$_2$O (0.002 mol) (the stoichiometric molar ratio of Cu$^{2+}$/Fe$^{3+}$ 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 was reached up to 12 and black precipitate was formed. Then centrifuged and washed with distilled water and left in a hot air oven to dry at 100 °C for 4 h. Then the resulting powder was calcinated at 550° C in a furnace for 2 hours.

ESI 4. The experimental procedure for the preparation of CoFe$_2$O$_4$ nanoparticles:
CoFe$_2$O$_4$ nanoparticles were synthesized by following reported procedure.$^3$ At first, 2.0 g of anhydrous sodium acetate homogeneous solution was prepared in 30 mL of ethylene glycol by stirring vigorously at room temperature followed by 1.5 mmol of CoCl$_2$·6H$_2$O and 3.0 mmol of FeCl$_3$·6H$_2$O was added slowly to the homogeneous sodium acetate solution (the stoichiometric molar ratio of Co$^{2+}$/Fe$^{3+}$ was 1 : 2). Then the mixture was vigorously stirred at 70 °C for 2 h to form a homogeneous solution. Then the solution was centrifuged and washed with distilled water and dried in an open atmosphere environment. The resulting powder was then calcinated at 550° C in a furnace for 2 hours.
ESI 5. The experimental procedure for the preparation of ZnFe$_2$O$_4$ nanoparticles:
ZnFe$_2$O$_4$ nanoparticles were synthesized by following a reported method.\textsuperscript{4} Mixture of Zn(NO$_3$)$_2$·6H$_2$O (0.1 M) and Fe(NO$_3$)$_3$·9H$_2$O (0.2 M) (stoichiometric molar ratio of Zn$^{2+}$/Fe$^{3+}$ 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 condition at 55 °C until the gel was formed, which was subsequently dried at 100 °C for 1 h in hot air oven. Then the resulting dried gel was calcinated at 550° C in a furnace for 2 hours.

ESI 6. The experimental procedure for the preparation of MgFe$_2$O$_4$ nanoparticles:
The MgFe$_2$O$_4$ nanoparticles were prepared by following a reported method.\textsuperscript{5} Mixture of Fe(NO$_3$)$_3$·9H$_2$O (0.5 M), Mg(NO$_3$)$_2$·6H$_2$O (0.25 M) and citric acid (1 M) solution were prepared in 50 mL deionized water. The solution was vigorously stirred for 3 h, at 60 °C and it turned to a puce sol, after that the stabilized nitrate–citrate sol was stirred and heated to 80 °C rapidly. Then sol color changed to transparent stick gel. Then the gel was heated at 200 °C for 2 h and an auto-combustion process took place. At last the brown, fluffy precursor was calcinated at 550 °C for 2 h in a furnace.

ESI 7. General experimental procedure for NiFe$_2$O$_4$ NPs catalyzed classical Michael addition reaction: A mixture of conjugated alkene (1 mmol), active methylene (1.2 mmol) and NiFe$_2$O$_4$ (10 mg) were heated at 100 °C in water-ethanol (1:1) mixture 2 mL under open air for 1 h. The completion of the reactions was checked by monitoring TLC. Then, the reaction mixture was cooled to room temperature and the catalyst was separated by using a strong external magnetic field. The remaining reaction mixture was evaporated in vacuum to reduce the volume and extracted with ethyl acetate (20 mL), washed with water followed by brine solution (3 × 5 mL). Then the extracted solution was dried over anhydrous Na$_2$SO$_4$. The crude product was obtained by evaporation of solvent in vacuum which was purified by short column chromatography over silica gel (60–120 mesh) using mixture of petroleum ether and ethyl acetate (90:10) as an eluting solvent to afford the pure Michael adduct. The formation of the product was confirmed by spectroscopic studies. The NMR spectroscopic data of the compounds has been given below. The $R_f$ values of the pure products were determined using petroleum ether and ethyl acetate mixture (9:1) as an eluting solvent. The $R_f$ values has been supplied in Table 2.
Table 1. The \( Rf \) values of classical Michael addition reaction to conjugated alkenes

<table>
<thead>
<tr>
<th></th>
<th>( Rf )</th>
<th>Yield</th>
<th></th>
<th>( Rf )</th>
<th>Yield</th>
<th></th>
<th>( Rf )</th>
<th>Yield</th>
</tr>
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<tbody>
<tr>
<td>3a</td>
<td>0.37</td>
<td>93%</td>
<td>3b</td>
<td>0.45</td>
<td>98%</td>
<td>3c</td>
<td>0.43</td>
<td>95%</td>
</tr>
<tr>
<td>3d</td>
<td>0.56</td>
<td>93%</td>
<td>3e</td>
<td>0.79</td>
<td>98%</td>
<td>3f</td>
<td>0.67</td>
<td>96%</td>
</tr>
<tr>
<td>3g</td>
<td>0.73</td>
<td>99%</td>
<td>3h</td>
<td>0.74</td>
<td>95%</td>
<td>3i</td>
<td>0.70</td>
<td>93%</td>
</tr>
<tr>
<td>3j</td>
<td>0.13</td>
<td>89%</td>
<td>3k</td>
<td>0.44</td>
<td>91%</td>
<td>3l</td>
<td>0.81</td>
<td>89%</td>
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</table>

ESI 8. General experimental procedure for NiFe\(_2\)O\(_4\) NPs catalyzed aza-Michael addition reaction by aromatic amine: A mixture of conjugated alkene (1.5 mmol), aromatic amine (1.0 mmol) and NiFe\(_2\)O\(_4\) (10 mg) were heated at 100 °C in water medium under open air for 30-45 minutes. The completion of the reactions was checked by monitoring TLC. Then, the reaction mixture was cooled to room temperature and the catalyst was separated by using a strong external magnetic field. Then, the remaining reaction mixture was extracted with ethyl acetate (20 mL), washed with water followed by brine solution (3 × 5 mL). Then the extracted solution was dried over anhydrous Na\(_2\)SO\(_4\). The crude product was obtained by evaporation of solvent in vacuum which was purified by short column chromatography over silica gel (60–120 mesh) using mixture of petroleum ether and ethyl acetate (90:10) as an eluting solvent to afford the pure aza-Michael adduct. The formation of the product was confirmed by spectroscopic studies. The NMR spectroscopic data of the compounds has been given below. The \( Rf \) values of the compounds were checked using petroleum ether and ethyl acetate mixture (9:1) as an eluting agent. The \( Rf \) values has been supplied in Table 2.
Table 2. The Rf values of aza-Michael addition reaction with aromatic amine to conjugated alkenes

<p>| | | |</p>
<table>
<thead>
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<tbody>
<tr>
<td>Rf:0.18</td>
<td>98%</td>
<td>Rf:0.24</td>
</tr>
<tr>
<td>5a</td>
<td>5b</td>
<td>5c</td>
</tr>
<tr>
<td>Rf:0.15</td>
<td>89%</td>
<td>Rf:0.14</td>
</tr>
<tr>
<td>5d</td>
<td>5e</td>
<td>5f</td>
</tr>
<tr>
<td>Rf:0.21</td>
<td>97%</td>
<td>Rf:0.17</td>
</tr>
<tr>
<td>5g</td>
<td>5h</td>
<td>5i</td>
</tr>
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ESI 9. General experimental procedure for NiFe₂O₄ NPs catalyzed aza-Michael addition reaction by aliphatic amine: A mixture of conjugated alkene (1.5 mmol), aliphatic amine (1.0 mmol) and NiFe₂O₄ (10 mg) were stirred at room temperature in water medium under open atmosphere for 20-30 minutes. The completion of the reactions was checked by monitoring TLC. Then the catalyst was separated by using a strong external magnetic field. Then, the remaining reaction mixture was extracted with ethyl acetate (20 mL), washed with water followed by brine solution (3 × 5 mL). Then the extracted solution was dried over anhydrous Na₂SO₄. The crude product was obtained by evaporation of solvent in vacuum which was purified by short column chromatography over silica gel (60–120 mesh) using mixture of petroleum ether and ethyl acetate (90:10) as an eluting solvent to afford the pure aza-Michael adduct. The formation of the product was confirmed by spectroscopic studies. The NMR spectroscopic data of the compounds has been given below. The Rf values of the pure products were determined using petroleum ether and ethyl acetate mixture (9:1) as an eluting agent. The Rf values has been supplied in Table 3.

Table 3. The Rf values of aza-Michael addition reactions of aliphatic amines to conjugated alkenes

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<tbody>
<tr>
<td>Rf:0.19</td>
<td>99%</td>
<td>Rf:0.15</td>
</tr>
<tr>
<td>7a</td>
<td>7b</td>
<td>7c</td>
</tr>
<tr>
<td>Rf:0.28</td>
<td>93%</td>
<td>Rf:0.21</td>
</tr>
<tr>
<td>7d</td>
<td>7e</td>
<td>7f</td>
</tr>
<tr>
<td>Rf:0.39</td>
<td>92%</td>
<td>Rf:0.15</td>
</tr>
<tr>
<td>7g</td>
<td>7h</td>
<td>7i</td>
</tr>
</tbody>
</table>
ESI 10. General experimental procedure for NiFe$_2$O$_4$ NPs catalyzed oxa-Michael addition reaction to β-nitrostyrene by aliphatic alcohol:

A mixture of β-nitrostyrene (1.0 mmol), aliphatic alcohol (2 mL) and NiFe$_2$O$_4$ (10 mg) were stirred and heated at 80 °C under open atmosphere for 1.5-2.0 hours. The completion of the reactions was checked by monitoring TLC. Then, the reaction mixture was cooled to room temperature and the catalyst was separated by using a strong external magnetic field. The remaining reaction mixture was evaporated in vacuum to reduce the volume and extracted with ethyl acetate (20 mL), washed with water followed by brine solution (3 × 5 mL). Then the extracted solution was dried over anhydrous Na$_2$SO$_4$. The crude product was obtained by evaporation of solvent in vacuum which was purified by short column chromatography over silica gel (60–120 mesh) using mixture of petroleum ether and ethyl acetate (90:10) as an eluting solvent to afford the pure oxa-Michael adduct. The formation of the product was confirmed by spectroscopic studies. The NMR spectroscopic data of the compounds has been given below. The $R_f$ values of the compounds were determined using petroleum ether and ethyl acetate mixture (9:1) as an eluting agent. The $R_f$ values has been supplied in Table 4.

Table 4. The $R_f$ values of oxa-Michael addition of alcohols to conjugated alkenes

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<thead>
<tr>
<th></th>
<th>$R_f$</th>
<th>Yield (%)</th>
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<tr>
<td>9a</td>
<td>0.88</td>
<td>88%</td>
</tr>
<tr>
<td>9b</td>
<td>0.91</td>
<td>85%</td>
</tr>
<tr>
<td>9c</td>
<td>0.84</td>
<td>87%</td>
</tr>
<tr>
<td>9d</td>
<td>0.81</td>
<td>89%</td>
</tr>
<tr>
<td>9e</td>
<td>0.84</td>
<td>73%</td>
</tr>
<tr>
<td>9f</td>
<td>0.81</td>
<td>77%</td>
</tr>
<tr>
<td>9g</td>
<td>0.92</td>
<td>85%</td>
</tr>
<tr>
<td>9h</td>
<td>0.94</td>
<td>87%</td>
</tr>
<tr>
<td>9i</td>
<td>0.86</td>
<td>90%</td>
</tr>
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</table>
ESI 11. General experimental procedure for NiFe₂O₄ NPs catalyzed thia-Michael addition reaction by thiophenol derivatives:

A mixture of Michael acceptor (1.5 mmol), aromatic thiol (1.0 mmol) and NiFe₂O₄ (10 mg) were stirred at room temperature in water (2 mL) under open atmosphere for 10-15 minutes. The completion of the reactions was checked by monitoring TLC. Then, the catalyst was separated by using a strong external magnetic field. The remaining reaction mixture was extracted with ethyl acetate (20 mL), washed with water followed by brine solution (3 × 5 mL). Then the extracted solution was dried over anhydrous Na₂SO₄. The crude product was obtained by evaporation of solvent in vacuum which was purified by short column chromatography over silica gel (60–120 mesh) using mixture of petroleum ether and ethyl acetate (90:10) as an eluting solvent to afford the pure thia-Michael adduct. The formation of the product was confirmed by spectroscopic studies. The NMR spectroscopic data of the compounds has been given below. The \( R_f \) values of the pure products were determined using petroleum ether and ethyl acetate mixture (9:1) as an eluting solvent. The \( R_f \) values has been supplied in Table 5.

Table 5. The \( R_f \) values of thia-Michael addition reactions to conjugated alkenes

<table>
<thead>
<tr>
<th>Product</th>
<th>( R_f ) Value</th>
<th>Yield</th>
</tr>
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<tbody>
<tr>
<td>11a</td>
<td>0.74</td>
<td>98%</td>
</tr>
<tr>
<td>11b</td>
<td>0.77</td>
<td>99%</td>
</tr>
<tr>
<td>11c</td>
<td>0.26</td>
<td>98%</td>
</tr>
<tr>
<td>11d</td>
<td>0.61</td>
<td>93%</td>
</tr>
<tr>
<td>11e</td>
<td>0.56</td>
<td>91%</td>
</tr>
<tr>
<td>11f</td>
<td>0.59</td>
<td>95%</td>
</tr>
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</table>
ESI-12. Copy of $^1$H NMR spectra of classical Michael addition reaction listed in Table 2
PM.S.173-1H(SKD) 500MHz

$\text{EtO}_2\text{C}\text{--}\text{CO}_2\text{Et}$

$\text{O}$

$\text{Bu}$

$^1\text{H NMR}$
ESI 13. Copy of $^1$H NMR and $^{13}$C NMR spectra of aza-Michael addition reaction by aromatic amine listed in Table 3
ESI 14. Copy of $^1$H NMR and $^{13}$C NMR spectra of aza-Michael addition reaction by aliphatic amine listed in Table 4
ESI 15. Copy of $^1$H NMR and $^{13}$C NMR spectra of oxa-Michael addition reaction by aliphatic alcohol listed in Table 5
$^{13}$C NMR

![Carbon-13 NMR Spectrum](image-url)
ESI 16. Copy of $^1$H NMR spectra of thia-Michael addition reaction by thiophenol derivatives listed in Table 6
PM-S-193-1H

1H NMR
ESI 17. Powder XRD pattern of reused NiFe$_2$O$_4$ NPs after 10$^{\text{th}}$ catalytic cycle cycle:

![Powder XRD pattern of recycled NiFe$_2$O$_4$ NPs](image)

*Fig. 1S: Powder XRD pattern of reused nano-NiFe$_2$O$_4$ after 10$^{\text{th}}$ catalytic cycle.*
ESI 18. References: