Electronic Supplementary Information

Ferromagnetic $\alpha$-Fe$_2$O$_3$ NPs: A potential catalyst in Sonogashira Hagihara cross coupling and Hetero-Diels-Alder reactions

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S4-S5 Table S1: Comparison of catalytic activity of in situ $\alpha$-Fe$_2$O$_3$ nanoparticles for synthesis of C-C cross coupling products by Sonogashira Hagihara reaction over other procedures reported in literature.

S6 Table S2: Comparison of catalytic activity of in situ $\alpha$-Fe$_2$O$_3$ nanoparticles for synthesis of pyran derivatives by hetero Diels Alder reaction over other procedures reported in literature.

S7 Table S3: Comparison table between the present catalytic system and previously reported system (Angew. Chem. Int. Ed. 2008, 47, 4862.).

S8 UV-vis spectroscopic titration of derivative $1$ (5 $\mu$M) in H$_2$O/EtOH (7:3, v/v) upon the addition Fe$^{3+}$ ions (0-25 equiv.) and fluorescence emission spectra of derivative $1$ (5$\mu$M) upon additions of 25 equiv. of 70 wt% tert-butyl hydroperoxide solution in H$_2$O/THF (3/7, v/v).

S9 Fluorescence spectroscopic titration of derivative $1$ (5 $\mu$M) in H$_2$O/EtOH (7:3, v/v) upon the addition Fe$^{3+}$ ions (0-25 equiv.) and UV-vis spectra showing the presence of Fe (0) nanoparticle bands.

S10 UV-vis spectroscopic titration of derivative $1$ (5 $\mu$M) in H$_2$O/EtOH (7:3, v/v) upon additions of 25 equiv. of 70 wt% tert-butyl hydroperoxide solution in H$_2$O/THF (3/7, v/v) and Scheme showing the formation of oxidized species of derivative $1$ on the addition of oxidizing agent.

S11 Overlay of NMR spectra of oxidized species of derivative $1$ and derivative $1$.

S12 Overlay of IR spectra of both oxidized species of derivative $1$ and derivative $1$. 

S1
ESI-MS mass spectra of oxidized species of derivative 1 and TEM, DLS analysis of derivative 1 (5 μM) showing the size of Fe$_2$O$_3$ nanorods at temperature 70°C

TEM, DLS of derivative 1 (5 μM) showing the size of Fe$_2$O$_3$ nanorods at pH (12) and UV-vis spectroscopic titration of derivative 1 (5 μM) in H$_2$O/EtOH (7:3, v/v) by varying Fe$^{3+}$ ions to ligand ratio

TEM images and Raman spectra of α-Fe$_2$O$_3$ nanoparticles prepared by commercial method.

XRD pattern of spherical α-Fe$_2$O$_3$ nanoparticles prepared by commercial method.

UV-vis spectra of reaction mixture show the interaction between substrates & catalyst and UV-vis spectra of reaction mixture showing the completion of reaction.

Kinetic profile showing the formation of product with time when the catalyst loading is 0.005 mol & 0.004 mol.

Kinetic profile showing the formation of product with time when the catalyst loading is 0.0035 mol & 0.0025 mol.

Kinetic profile showing the formation of product with time when the catalyst loading is 0.0015 mol.

Photograph showing the magnetic separation of in situ generated α-Fe$_2$O$_3$ nanoparticles.

XRD & TEM images of recycled α-Fe$_2$O$_3$ nanoparticles.

Atomic Absorption Studies (AAS) of the residual liquid left after the magnetic separation of catalyst.

IR spectra of (A) p-nitrobenzaldehyde (B) separated reaction mixture containing p-nitrobenzaldehyde and in situ generated α-Fe$_2$O$_3$ NPs

$^1$H and $^{13}$C NMR of spectrum of 4a

$^1$H and $^{13}$C NMR of spectrum of 4b and 4c

$^1$H and $^{13}$C NMR of spectrum of 4d

$^1$H and $^{13}$C NMR of spectrum of 4e

$^1$H and $^{13}$C NMR of spectrum of 4f
S30 \[^1^H\text{ and }^{13}C\text{ NMR of spectrum of } 4g.\]
S31 \[^1^H\text{ and }^{13}C\text{ NMR of spectrum of } 4h.\]
S32 \[^1^H\text{ and }^{13}C\text{ NMR of spectrum of } 4i.\]
S33 \[^1^H\text{ and }^{13}C\text{ NMR of spectrum of } 4j.\]
S34 \[^1^H\text{ and }^{13}C\text{ NMR of spectrum of } 4k.\]
S35 \[^1^H\text{ and }^{13}C\text{ NMR of spectrum of } 4l.\]
S36 \[^1^H\text{ and }^{13}C\text{ NMR of spectrum of } 4m.\]
S37 \[^1^H\text{ and }^{13}C\text{ NMR of spectrum of } 6.\]
S38 \[^1^H\text{ and }^{13}C\text{ NMR of spectrum of } 8.\]
S39 \[^1^H\text{ and }^{13}C\text{ NMR of spectrum of } 14a.\]
S40 \[^1^H\text{ and }^{13}C\text{ NMR of spectrum of } 14b.\]
S41 \[^1^H\text{ and }^{13}C\text{ NMR of spectrum of } 14c.\]
S42 \[^1^H\text{ and }^{13}C\text{ NMR of spectrum of } 14d.\]
S43 \[^1^H\text{ and }^{13}C\text{ NMR of spectrum of } 14e.\]
S44 \[^1^H\text{ and }^{13}C\text{ NMR of spectrum of } 14f.\]
S45 \[^1^H\text{ and }^{13}C\text{ NMR of spectrum of } 14g\]
S46 \[^1^H\text{ and }^{13}C\text{ NMR of spectrum of } 14h\]
S47 \[^1^H\text{ and }^{13}C\text{ NMR of spectrum of } 14i.\]
S48 \[^1^H\text{ and }^{13}C\text{ NMR of spectrum of } 14j.\]
S49 \[^1^H\text{ and }^{13}C\text{ NMR of spectrum of } 15.\]
S50 \[^1^H\text{ and }^{13}C\text{ NMR of spectrum of } 16.\]
### Table S1: Comparison of catalytic activity of α-Fe₂O₃ NPs for Sonogashira cross coupling reaction over other catalytic system reported in the literature.

<table>
<thead>
<tr>
<th>Serial No.</th>
<th>Publication</th>
<th>Catalyst used</th>
<th>Use of Noble metal</th>
<th>Use of CuI</th>
<th>Use of Amine</th>
<th>Solvent</th>
<th>Nano catalysis</th>
<th>Recycling</th>
<th>Reaction time</th>
<th>Temp. required (in °C)</th>
<th>Isolated Yield (Product, %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Present manuscript</td>
<td>α-Fe₂O₃, K₂CO₃</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Ethylene glycol (green solvent)</td>
<td>Yes</td>
<td>Yes (13 times)</td>
<td>13 h</td>
<td>80</td>
<td>84</td>
</tr>
<tr>
<td>2</td>
<td>Green Chem., 2015, 17, 1893-1898</td>
<td>Pd-CS, Pd-CS-Glu and Pd-CS-SH, K₂CO₃</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>EtOH/Water</td>
<td>Yes</td>
<td>Yes (6 times)</td>
<td>6 h</td>
<td>65</td>
<td>98</td>
</tr>
<tr>
<td>3</td>
<td>Green Chem., 2015, 17, 1071-1076</td>
<td>Pd/C, DABCO</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
<td>γ-Valerolactone</td>
<td>No</td>
<td>No</td>
<td>4 h</td>
<td>60-100</td>
<td>99</td>
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<tr>
<td>4</td>
<td>Green Chem., 2014, 16, 2515-2522</td>
<td>PEG-2000, PdCl₂(PPh₃)₂</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
<td>Water, Et₃N</td>
<td>No</td>
<td>No</td>
<td>24 h</td>
<td>25</td>
<td>95</td>
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<tr>
<td>5</td>
<td>Chem. Commun., 2015, 51, 10871-10874</td>
<td>L₅-Pd</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
<td>DMF</td>
<td>No</td>
<td>Yes (5 times)</td>
<td>1.5 h</td>
<td>90</td>
<td>97</td>
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<tr>
<td>6</td>
<td>Chem. Eur. J., 2014, 20, 1-13</td>
<td>PEGylated g-Fe₂O₃-Pd NPs</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
<td>THF</td>
<td>Yes</td>
<td>Yes</td>
<td>24 h</td>
<td>65</td>
<td>86</td>
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<tr>
<td>7</td>
<td>Org. Lett., 2014, 16, 3724-3727</td>
<td>(N-heterocyclic carbene)-Cu and (N-heterocyclic carbene)-Pd complexes</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>DMSO</td>
<td>No</td>
<td>No</td>
<td>24 h</td>
<td>120</td>
<td>94</td>
</tr>
<tr>
<td>8</td>
<td>J. Mater. Chem. A, 2014, 2, 484-491</td>
<td>Pd-PPh₃-MCM-41@SiO₂@Fe₃O₄ (Very complicated)</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>Water</td>
<td>No</td>
<td>Yes</td>
<td>4 h</td>
<td>70</td>
<td>95</td>
</tr>
<tr>
<td>9</td>
<td>Org. Lett., 2013, 15, 65-67</td>
<td>Pd-Cu dual Reactor</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>DMF</td>
<td>No</td>
<td>No</td>
<td>-</td>
<td>120</td>
<td>95</td>
</tr>
<tr>
<td>10</td>
<td>Angew. Chem. Int. Ed. 2013, 52, 11554-11559</td>
<td>Pd(0) nanoparticle, KOAc</td>
<td>Yes (Pd)</td>
<td>No</td>
<td>Yes</td>
<td>NMP (toxic)</td>
<td>Yes</td>
<td>No</td>
<td>24 h</td>
<td>160</td>
<td>83</td>
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<td>11</td>
<td>Green Chem., 2013, 15, 2349-2355</td>
<td>Pd catalyst, K₂CO₃</td>
<td>Yes (Pd)</td>
<td>No</td>
<td>No</td>
<td>EtOH/Chlorobenzene (flammable)</td>
<td>No</td>
<td>Yes</td>
<td>18 h</td>
<td>60</td>
<td>88</td>
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<td>12</td>
<td>Green Chem., 2013, 15, 2132-2042</td>
<td>Fe₂O₃@SiO₂@PPh₃@Pd(0), NaOH (Very complicated)</td>
<td>Yes (Pd)</td>
<td>No</td>
<td>No</td>
<td>Water</td>
<td>No</td>
<td>Yes</td>
<td>15 min-4 h</td>
<td>80</td>
<td>91</td>
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<td>13</td>
<td>Chem. Eur. J., 2013, 19, 14024-14029</td>
<td>5% Pd-Au/C, K₃PO₄</td>
<td>Yes (Pd, Au)</td>
<td>No</td>
<td>No</td>
<td>tPrOH/H₂O</td>
<td>No</td>
<td>No</td>
<td>20 h</td>
<td>80</td>
<td>73</td>
</tr>
<tr>
<td></td>
<td>Source</td>
<td>Catalyst</td>
<td>Solvent</td>
<td>Ligand(s)</td>
<td>Temp</td>
<td>Yield</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td>15</td>
<td><em>Chem. Commun.</em>, 2010, <strong>46</strong>, 6524-6526</td>
<td>Pd@meso-SiO$_2$ (Very complicated)</td>
<td></td>
<td>EtOH</td>
<td>Yes</td>
<td>35h</td>
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<td>16</td>
<td><em>Angew. Chem. Int. Ed.</em>, 2007, <strong>46</strong>, 1536-1538</td>
<td>Au(I), K$_3$PO$_4$</td>
<td></td>
<td>O-Xylene</td>
<td>No</td>
<td>30 h</td>
<td></td>
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<td>17</td>
<td><em>Langmuir</em>, 2010, <strong>14</strong>, 12225-12229</td>
<td>Au-Ag-Pd trimetallic nanoparticles</td>
<td></td>
<td>DMF-H$_2$O</td>
<td>No</td>
<td>24 h</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>18</td>
<td><em>Org. Lett.</em>, 2000, 2935-2938</td>
<td>Pd(PPh$<em>3$</em>)$_2$, Ag$_2$O</td>
<td></td>
<td>THF</td>
<td>No</td>
<td>2 h</td>
<td></td>
<td></td>
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### Table S2: Comparison of catalytic activity of $\alpha$-Fe$_2$O$_3$ NPs for hetero-Diels–Alder reaction over other catalytic system reported in literature.

<table>
<thead>
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<th>Sr. No.</th>
<th>Publication</th>
<th>Catalyst Used</th>
<th>Use of noble metal</th>
<th>Cost of catalyst</th>
<th>Use of Nano catalyst</th>
<th>Amount of Catalyst used</th>
<th>Use of activated diene/di enophile</th>
<th>Solvent</th>
<th>Additives</th>
<th>Temp p. (˚C)</th>
<th>Time</th>
<th>Yield %</th>
<th>Recyclability</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>Present manuscript</td>
<td>$\alpha$-Fe$_2$O$_3$ NPs</td>
<td>No</td>
<td>Very cheap</td>
<td>Yes</td>
<td>1 mol %</td>
<td>No</td>
<td>$p$-xylene (90%)/Neat condition (68%)</td>
<td>No</td>
<td>60</td>
<td>10h</td>
<td>Upto 90%</td>
<td>Yes</td>
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<td>2</td>
<td>Org. Lett., 2015, 17, 3506-3509</td>
<td>LiClO$_4$</td>
<td>No</td>
<td>Costly</td>
<td>No</td>
<td>1 equiv.</td>
<td>Yes</td>
<td>DCE/MeCN</td>
<td>Yes</td>
<td>80</td>
<td>2h</td>
<td>94</td>
<td>No</td>
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<td>3</td>
<td>Org. Lett., 2015, 17, 3536-3539</td>
<td>Cull in 4Å MS</td>
<td>No</td>
<td>Costly and Sensitive</td>
<td>No</td>
<td>10 mol%</td>
<td>Yes</td>
<td>THF/t-BuOH (1:1)</td>
<td>Yes (Et$_3$N, Cs$_2$CO$_3$)</td>
<td>25</td>
<td>1-48</td>
<td>90</td>
<td>No</td>
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<td>4</td>
<td>J. Am. Chem. Soc., 2014, 136, 17714-17717</td>
<td>PCN-223 porphyrin ZrMOF</td>
<td>Yes</td>
<td>Costly</td>
<td>No</td>
<td>1 mol%</td>
<td>No</td>
<td>Toluene</td>
<td>AgBF$_4$</td>
<td>80</td>
<td>12 h</td>
<td>99</td>
<td>Yes</td>
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<td>5</td>
<td>Chem. Commun., 2014, 50, 14187-14190</td>
<td>Calcium BINOL-derived phosphates</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
<td>2.5 mol%</td>
<td>Yes</td>
<td>DCM</td>
<td>HCl</td>
<td>Rt</td>
<td>12h</td>
<td>94%</td>
<td>No</td>
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<td>6</td>
<td>Org. Lett., 2014, 16, 3564-3567</td>
<td>Cu(I)OTf$_2$L</td>
<td>No</td>
<td>-</td>
<td>No</td>
<td>10 mol%</td>
<td>Yes</td>
<td>Toluene</td>
<td>Base</td>
<td>0˚C</td>
<td>Upto 24h</td>
<td>90%</td>
<td>No</td>
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<td>Org. Lett., 2013, 15, 9-12</td>
<td>Rh(cod)$_2$BF$_4$</td>
<td>Yes</td>
<td>costly</td>
<td>No</td>
<td>5 mol%</td>
<td>No</td>
<td>DCM</td>
<td>Acid</td>
<td>80˚C</td>
<td>Upto 24h</td>
<td>Upto 90%</td>
<td>No</td>
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<td>8</td>
<td>J. Am. Chem. Soc., 2012, 134, 5512-5515</td>
<td>Iron(III) porphyrin catalyst</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Benzene- upto 90%/ Neat condition- trace yield</td>
<td>No</td>
<td>80˚C</td>
<td>12h</td>
<td>Upto 90%</td>
<td>No</td>
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<td>9</td>
<td>J. Am. Chem. Soc., 2009, 131, 12882-12883</td>
<td>Chiral phosphoric acid</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
<td>2-100 mol%</td>
<td>Yes</td>
<td>Toluene</td>
<td>-</td>
<td>RT</td>
<td>24 h</td>
<td>Upto 95%</td>
<td>No</td>
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<td>10</td>
<td>Org. Lett., 2008, 10, 13-16</td>
<td>1-Np-TADDOL</td>
<td>No</td>
<td>-</td>
<td>No</td>
<td>20 mol%</td>
<td>Yes</td>
<td>Toluene/DCM</td>
<td>Acid chloride</td>
<td>-78˚C</td>
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<td>11</td>
<td>Org. Lett., 2004, 6, 13-16</td>
<td>Ti(OiPr)$_4$</td>
<td>No</td>
<td>costly</td>
<td>No</td>
<td>5 mol%</td>
<td>Yes</td>
<td>Toluene</td>
<td>TFA</td>
<td>0˚C</td>
<td>72 h</td>
<td>Upto 92%</td>
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<td>12</td>
<td>Org. Lett., 2003, 5, 7-10</td>
<td>Diethyl Zinc</td>
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<td>No</td>
<td>10 mol%</td>
<td>Yes</td>
<td>Toluene</td>
<td>Acid</td>
<td>-20˚C</td>
<td>30 h</td>
<td>Upto 99%</td>
<td>No</td>
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Table S3: Comparison table between the present catalytic system and previously reported system for Sonogashira coupling reactions (Angew. Chem. Int. Ed. 2008, 47, 4862-4865).

<table>
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<tr>
<th>Sr. No.</th>
<th>Points of Comparison on Reaction Conditions</th>
<th>Present Manuscript</th>
<th>Angew. Chem. Int. Ed. 2008, 47, 4862-4865</th>
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<tbody>
<tr>
<td>1.</td>
<td>Reactivity towards Substrates</td>
<td>Both for aryl iodides and bromides</td>
<td>Only for aryl iodides</td>
</tr>
<tr>
<td>2.</td>
<td>Recyclability of catalyst</td>
<td>Yes (13 times)</td>
<td>No</td>
</tr>
<tr>
<td>3.</td>
<td>Mechanistic Study</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>4.</td>
<td>Base</td>
<td>K$_2$CO$_3$ (mild, Cheap)</td>
<td>Cs$_2$CO$_3$ (Strong, Costly)</td>
</tr>
<tr>
<td>5.</td>
<td>Time</td>
<td>13-24 h</td>
<td>72 h</td>
</tr>
<tr>
<td>6.</td>
<td>Solvent</td>
<td>Ethylene Glycol (green solvent)</td>
<td>Toluene</td>
</tr>
<tr>
<td>7.</td>
<td>Catalyst Loading</td>
<td>Low catalyst loading (0.5 mol %)</td>
<td>High catalyst loading (15 mol %)</td>
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</table>
Upon the addition of equal aliquots (25 equiv.) of \textit{tert}-butyl hydroperoxide (a oxidizing agent) in H$_2$O/EtOH (7:3, v/v) mixture.

**Figure S2:** Fluorescence spectra of derivative 1 (5 µM) after the addition of equal aliquots of \textit{tert}-butyl hydroperoxide (a oxidizing agent) in H$_2$O/EtOH (7:3, v/v) mixture.

**Figure S1:** UV-vis. spectroscopic spectra of derivative 1 (5 µM) in H$_2$O/EtOH (7:3, v/v) upon the addition Fe$^{3+}$ ions (0-25 equiv.).
**Figure S3:** Fluorescence spectra of derivative 1 (5 µM) showing the variation on addition of Fe$^{3+}$ ions (0-25 equiv.) in H$_2$O/EtOH (7:3, v/v) mixture.

**Figure S4:** UV-vis Spectra showing the formation of Fe (0) Nps bands after keeping the solution of derivative 1 and Fe$^{3+}$ ion (0-25 equiv.) in H$_2$O/EtOH (3:7, v/v) mixture under inert atmosphere for 10 min and followed by oxidation resulting in the *in situ* formation of Fe$_2$O$_3$ nanoparticles.
**Figure S5**: UV-vis Spectra of derivative 1 on addition of tert-butyl hydroperoxide (0-25 equiv.) in H$_2$O/EtOH (3:7, v/v) mixture followed by the addition of Fe$^{3+}$ ion (0-25 equiv.).

**Scheme 1**: Oxidation of derivative 1 by using tBuOOH to yield N-oxide derivative.
Figure S6: Overlay of $^1$H NMR spectra of derivative 1 and oxidized species of derivative 1 showing the upfield shifting of all protons.
Figure S7: FT-IR spectrum of oxidized derivative 1 showed stretching band at around 1340 cm\(^{-1}\) corresponding to N\(^{+}\)-O\(^{-}\) stretching frequency.
Figure S8: ESI-MS mass spectrum of residue obtained showed a parent ion peak, m/z = 1043 due to oxidized species of derivative 1.

Figure S9: (A) TEM (Scale bar 20 nm) and (B) DLS analysis of compound 1 (5 μM) showing the size of Fe₂O₃ nanoparticles at temperature 70°C in the range of 60-80 nm.
Figure S10: (A) TEM (Scale bar 50 nm) and (B) DLS analysis of compound 1 (5 μM) showing the size of Fe₂O₃ nanoparticles in the presence of sodium hydroxide (pH=12) in the range of 50-60 nm.

Figure S11: UV-vis. spectra by varying Fe³⁺ ions to ligand ratio a) 2:1, b) 1:1, c) 1:2.
Figure S12: A) TEM images of spherical α-Fe$_2$O$_3$ NPs prepared by literature reported method (*J. Mater. Chem. A*, 2013, 1, 830) B) DLS analysis showing the size of α-Fe$_2$O$_3$ NPs 4-6 nm.

Figure S13: Raman spectrum of spherical α-Fe$_2$O$_3$ NPs prepared by literature reported method (*J. Mater. Chem. A*, 2013, 1, 830); [Reference 1: *CrystEngComm.*, 2014, 16, 10618].
Figure S14: (a-b) XRD diffraction pattern of spherical α-Fe₂O₃ NPs prepared by commercial reported method.
Figure S15: UV-vis. Spectra recorded during the reaction of 1a and 2a in the presence of in situ generated Fe$_2$O$_3$ NPs in ethylene glycol.

Figure S16: UV-vis spectra of reaction between 1a and 2a showing the completion of reaction to give product 4a catalysed by Fe$_2$O$_3$ NPs when the catalyst loading was 0.005 mol.
Figure S17: (a) Kinetic profile showing the formation of product with time when the catalyst loading is 0.005 mol; (b) calibration curve. Reactions were monitored by UV-vis. Spectroscopy.

Multiple R = 0.995
R² = 0.991
Slope = 0.150
Rate = \( \frac{2.303 \times 0.150}{3600} = 0.959 \times 10^{-4} \) sec⁻¹

Figure S18: (a) Kinetic profile showing the formation of product with time when the catalyst loading is 0.004 mol, (b) calibration curve. Reactions were monitored by UV-vis. Spectroscopy.

Multiple R = 0.996
R² = 0.992
Slope = 0.128
Rate = \( \frac{2.303 \times 0.128}{3600} = 0.818 \times 10^{-4} \) sec⁻¹
**Figure S19:** (a) Kinetic profile showing the formation of product with time when the catalyst loading is 0.0035 mol, (b) calibration curve. Reactions were monitored by UV-vis. Spectroscopy.

Multiple R = 0.996
$R^2 = 0.992$
Slope = 0.120
Rate = $(2.303 \times 0.120)/3600 = 0.767 \times 10^{-4}$ sec$^{-1}$

**Figure S20:** (a) Kinetic profile showing the formation of product with time when the catalyst loading is 0.0025 mol, (b) calibration curve. Reactions were monitored by UV-vis. spectroscopy.

Multiple R = 0.9901
$R^2 = 0.981$
Slope = 0.093
Rate = $(2.303 \times 0.093)/3600 = 0.59 \times 10^{-4}$ sec$^{-1}$
Multiple $R = 0.988$
$R^2 = 0.977$
Slope = 0.064
Rate = $(2.303 \times 0.064)/3600 = 0.409 \times 10^{-4}$ sec$^{-1}$
Figure S22: α-Fe$_2$O$_3$ nanoparticles (a) for Sonogashira cross coupling reaction i) dispersed in the reaction mixture, ii) adsorbed on a magnetic stirring bar, iii) an external magnet attracted stirring bar and α-Fe$_2$O$_3$ nanoparticles; (b) for Hetero-Diels-Alder reaction i) dispersed in the reaction mixture, ii) adsorbed on a magnetic stirring bar, iii) an external magnet attracted stirring bar and α-Fe$_2$O$_3$ nanoparticles.
**Figure S23:** XRD of *in situ* generated rod like $\alpha$-Fe$_2$O$_3$ NPs separated after 13 cycles recycling.

**Figure S24:** TEM image of *in situ* generated rod like $\alpha$-Fe$_2$O$_3$ NPs separated after 13 cycles.
Figure S25: Atomic Absorption Studies (AAS) of the residual liquid left after the magnetic separation of catalyst and found that only 0.166 mg/lit = 0.166 ppm of iron leached into the solution.
Figure S26: IR spectra of (a) p-nitrobenzaldehyde; (b) separated reaction mixture containing p-nitrobenzaldehyde and α-Fe$_2$O$_3$ NPs.
Fig. S27A: $^1$H NMR Spectra (CDCl$_3$, 500 MHz, ppm) of compound 4a:

Fig. S27B: $^{13}$C NMR Spectra (CDCl$_3$, 125 MHz, ppm) of compound 4a:
Fig. S28A: $^1$H NMR Spectra (CDCl$_3$, 500 MHz, ppm) of compound 4b & 4c:

![1H NMR Spectrum](image)

Fig. S28B: $^{13}$C NMR Spectra (CDCl$_3$, 125 MHz, ppm) of compound 4b & 4c:

![13C NMR Spectrum](image)
Fig. S29A: $^1$H NMR Spectra (CDCl₃, 500 MHz, ppm) of compound 4d:

Fig. S29B: $^{13}$C NMR Spectra (CDCl₃, 125 MHz, ppm) of compound 4d:
Fig. S30A: $^1$H NMR Spectra (CDCl$_3$, 300 MHz, ppm) of compound 4e:

Fig. S30B: $^{13}$C NMR Spectra (CDCl$_3$, 75 MHz, ppm) of compound 4e:
Fig. S31A: $^1$H NMR Spectra (CDCl$_3$, 300 MHz, ppm) of compound 4f:

![H NMR Spectra](image1)

Fig. S31B: $^{13}$C NMR Spectra (CDCl$_3$, 75 MHz, ppm) of compound 4f:

![C NMR Spectra](image2)
Fig. S32A: $^1$H NMR Spectra (CDCl$_3$, 500 MHz, ppm) of compound 4g:

![H NMR Spectra](image)

Fig. S32B: $^{13}$C NMR Spectra (CDCl$_3$, 125 MHz, ppm) of compound 4g:

![C NMR Spectra](image)
Fig. S33A: $^1$H NMR Spectra (CDCl$_3$, 500 MHz, ppm) of compound 4h:

![1H NMR Spectra](image1)

Fig. S33B: $^{13}$C NMR Spectra (CDCl$_3$, 125 MHz, ppm) of compound 4h:

![$^{13}$C NMR Spectra](image2)
Fig. S34A: $^1$H NMR Spectra (CDCl$_3$, 300 MHz, ppm) of compound 4i:

Fig. S34B: $^{13}$C NMR Spectra (CDCl$_3$, 75 MHz, ppm) of compound 4i:
Fig. S35A: $^1$H NMR Spectra (CDCl$_3$, 300 MHz, ppm) of compound 4j:

Fig. S35B: $^{13}$C NMR Spectra (CDCl$_3$, 75 MHz, ppm) of compound 4j:
Fig. S36A: $^1$H NMR Spectra (CDCl$_3$, 300 MHz, ppm) of compound 4k:

![H NMR Spectra](image1)

Fig. S36B: $^{13}$C NMR Spectra (CDCl$_3$, 75 MHz, ppm) of compound 4k:

![C NMR Spectra](image2)
Fig. S37A: $^1$H NMR Spectra (CDCl$_3$, 500 MHz, ppm) of compound 4l:

Fig. S37B: $^{13}$C NMR Spectra (CDCl$_3$, 125 MHz, ppm) of compound 4l:
Fig. S38A: $^1$H NMR Spectra (CDCl$_3$, 500 MHz, ppm) of compound 4m:

Fig. S38B: $^{13}$C NMR Spectra (CDCl$_3$, 125 MHz, ppm) of compound 4m:
Fig. S39A: $^1$H NMR Spectra (CDCl$_3$, 500 MHz, ppm) of compound 6:

Fig. S39B: $^{13}$C NMR Spectra (CDCl$_3$, 125 MHz, ppm) of compound 6:
Fig. S40A: $^1$H NMR Spectra (CDCl$_3$, 500 MHz, ppm) of compound 8:

Fig. S40B: $^{13}$C NMR Spectra (CDCl$_3$, 125 MHz, ppm) of compound 8:
Fig. S41A: $^1$H NMR Spectra (CDCl$_3$, 500 MHz, ppm) of compound 14a:

Fig. S41B: $^{13}$C NMR Spectra (CDCl$_3$, 125 MHz, ppm) of compound 14a:
Fig. S42A: $^1$H NMR Spectra (CDCl$_3$, 500 MHz, ppm) of compound 14b:

Fig. S42B: $^{13}$C NMR Spectra (CDCl$_3$, 125 MHz, ppm) of compound 14b:
Fig. S43A: $^1$H NMR Spectra (CDCl$_3$, 500 MHz, ppm) of compound 14c:

Fig. S43B: $^{13}$C NMR Spectra (CDCl$_3$, 125 MHz, ppm) of compound 14c:
Fig. S44 A: $^1$H NMR Spectra (CDCl$_3$, 300 MHz, ppm) of compound 14d:

Fig. S44B: $^{13}$C NMR Spectra (CDCl$_3$, 125 MHz, ppm) of compound 14d:
Fig. S45A: $^1$H NMR Spectra (CDCl$_3$, 500 MHz, ppm) of compound 14e:

![NMR Spectra](image)

Fig. S45B: $^{13}$C NMR Spectra (CDCl$_3$, 125 MHz, ppm) of compound 14e:

![NMR Spectra](image)
Fig. S46A: $^1$H NMR Spectra (CDCl$_3$, 500 MHz, ppm) of compound 14f:

Fig. S46B: $^{13}$C NMR Spectra (CDCl$_3$, 125 MHz, ppm) of compound 14f:
Fig. S47A: $^1$H NMR Spectra (CDCl$_3$, 500 MHz, ppm) of compound 14g:

Fig. S47B: $^{13}$C NMR Spectra (CDCl$_3$, 125 MHz, ppm) of compound 14g:
Fig. S48A: $^1$H NMR Spectra (CDCl$_3$, 500 MHz, ppm) of compound 14h:

Fig. S48B: $^{13}$C NMR Spectra (CDCl$_3$, 125 MHz, ppm) of compound 14h:
Fig. S49A: $^1$H NMR Spectra (CDCl$_3$, 300 MHz, ppm) of compound 14i:

Fig. S49B: $^{13}$C NMR Spectra (CDCl$_3$, 125 MHz, ppm) of compound 14i:
Fig. S50A: $^1$H NMR Spectra (CDCl$_3$, 300 MHz, ppm) of compound 14j:

![H NMR Spectra](image)

Fig. S50B: $^{13}$C NMR Spectra (CDCl$_3$, 125 MHz, ppm) of compound 14j:

![C NMR Spectra](image)
Fig. S51: $^1$H NMR Spectra (CDCl$_3$, 300 MHz, ppm) of compound 15:

Fig. S52A: $^1$H NMR Spectra (CDCl$_3$, 300 MHz, ppm) of compound 16:
Fig. S52B: $^{13}$C NMR Spectra (CDCl$_3$, 125 MHz, ppm) of compound 16: