Nickel (II) complex covalently anchored on core shell structured SiO$_2$@Fe$_3$O$_4$ nanoparticles: A robust and magnetically retrievable catalyst for direct one-pot reductive amination of ketones

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**Fig. S1** FTIR spectrum of recovered catalyst (obtained after 8 runs).
Fig. S2 TEM images of (a) SiO$_2$@Fe$_3$O$_4$, (c) recovered Ni-2AF@Am-SiO$_2$@Fe$_3$O$_4$ nanocatalyst (obtained after 8 runs) and SEM images of (b) SiO$_2$@Fe$_3$O$_4$, (d) recovered Ni-2AF@Am-SiO$_2$@Fe$_3$O$_4$ nanocatalyst (obtained after 8 runs).

Table S1 Screening of various catalysts for the synthesis of secondary amines via direct one-pot reductive amination of ketones$^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conversion (%)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>No catalyst</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>NiSO$_4$.6H$_2$O</td>
<td>58</td>
</tr>
<tr>
<td>3.</td>
<td>NiCl$_2$</td>
<td>87</td>
</tr>
<tr>
<td>4.</td>
<td>NiBr$_2$</td>
<td>82</td>
</tr>
<tr>
<td>5.</td>
<td>Ni(NO$_3$)$_2$.6H$_2$O</td>
<td>65</td>
</tr>
<tr>
<td>6.</td>
<td>Ni(OAc)$_2$.4H$_2$O</td>
<td>99</td>
</tr>
<tr>
<td>7.</td>
<td>Ni-ACF@Am-SiO$_2$@Fe$_3$O$_4$</td>
<td>100</td>
</tr>
</tbody>
</table>

$^a$Reaction Conditions: [Aniline (1mmol), acetone (1 mmol), NaBH$_4$ (1 mmol), catalyst (25 mg), r.t.].

$^b$Conversion % was determined by GC-MS.
Table S2 Effect of reductant on the synthesis of secondary amines via direct one-pot reductive amination of ketones

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Reductant</th>
<th>Conversion (%)(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>DIBAL</td>
<td>Trace</td>
</tr>
<tr>
<td>2.</td>
<td>Glucose</td>
<td>NR(^c)</td>
</tr>
<tr>
<td>3.</td>
<td>Zinc</td>
<td>40</td>
</tr>
<tr>
<td>4.</td>
<td>NaBH(OAc)(_3)</td>
<td>95</td>
</tr>
<tr>
<td>5.</td>
<td>NaBH(_4)</td>
<td>100</td>
</tr>
</tbody>
</table>

\(^a\)Reaction Conditions: [Aniline (1 mmol), acetone (1 mmol), reductant (1 mmol), Ni-ACF@Am-SiO\(_2\)@Fe\(_3\)O\(_4\) (25 mg), r.t.].

\(^b\)Conversion % was determined using GC-MS.

\(^c\)No reaction.

\(^{13}\)C CPMAS SOLID-STATE NMR of non-magnetic silica analog

\(^{13}\)C cross-polarization-magic angle spinning (CP-MAS) solid-state NMR spectroscopy provides information regarding the coordination environment of carbon atoms present in the silica based organic-inorganic hybrid materials. The above figure depicts the \(^{13}\)C CPMAS NMR spectrum of non magnetic silica analog containing organonickel complex. The
spectrum exhibits signals at $\delta = 10.4$, 23.7 and 57.9 ppm which are assigned to the three methylene groups (Si–CH$_2$–, –CH$_2$– and –N–CH$_2$–) of the propyl chain of APTES. The peak at 42.8 ppm refers to the uncomplexed –N–CH$_2$– group. In addition to these peaks, the peaks appearing in the range of 120-160 ppm are attributed to the various aromatic carbons. Furthermore, the appearance of a new predominant peak at 165.4 ppm can be assigned to the carbon of C=N which clearly confirms the covalent grafting of organo nickel complex on the surface of the amine functionalized support material.

**Mass spectra of synthesized amine products**

**Table 1 in the manuscript**

Entry 1

![Mass spectrum of synthesized amine products](image)

Entry 2
Entry 5
Entry 6

Entry 7
Entry 10

Entry 11