CHAPTER 7
SYNTHESIS, CHARACTERIZATION AND EVALUATION ON CATALYTIC ACTIVITY OF BIMETALLIC NANOPARTICLES LOADED SiO₂

7.1. SYNTHESIS, CHARACTERIZATION OF NANO Ag-Pt LOADED SiO₂ AND STUDY OF ITS CATALYTIC APPLICABILITY IN C–C COUPLING REACTION

Condensation of indoles with carbonyl compounds is having importance because this reaction provides a direct and appealing route toward bis(indolyl)methanes synthesis [424]. Various biological and pharmaceutical activities have been reported for this class of compounds [425]. Bis(indolyl)methanes are cruciferous substances useful for promoting beneficial estrogen metabolism in men and women [425a]. They are also effective in the prevention of cancer due to their ability to modulate certain cancer causing estrogen metabolites [425b]. Moreover, these compounds may normalize abnormal cell growth associated with cervical dysplasia [425c]. These compounds are important in pharmaceutical chemistry and their synthesis have receiving increasing attention. So a number of methods have been developed for the synthesis of bis(indolyl)methanes [426]. But most of the methods suffer some disadvantages such as larger reaction time, higher reflux temperature, difficulty in isolation of products and low yield. On the other hand, microwave-assisted organic synthesis is a fast growing area of research, due to the short reaction time scale and
high yield of the resulting products. It may also enhance the regio- and stereoselectivity of the reactions compared to the conventional synthetic methods [427]. Synthesis, characterization and evaluation on catalytic activity of nanobimetallic system such as Au-Ag/SiO₂, Pt-Ni/SiO₂, Au-Cu/SiO₂, Au-Ni/SiO₂, Ag-Ni/SiO₂ has been reported [428-432]. In this context, the present investigation, we report the microwave assisted synthesis of bis(indolyl)methanes compounds catalyzed by the Ag-Pt/SiO₂ nanocatalyst. In this work, characterization of Ag-Pt/SiO₂ and its catalytic activity in the synthesis of bis(indolyl)methanes reactions has been discussed.

7.1.1. Characterization of Ag-Pt/SiO₂ catalyst

7.1.1.1. FT-IR spectra

FT-IR spectrum of bare SiO₂ and bimetal Ag-Pt loaded SiO₂ are shown in Figs. 7.1.1a and 7.1.1b. The absorption band at 3421 cm⁻¹, is corresponding to the O–H stretching frequency and broad band at 1108 cm⁻¹, is due to Si–O–Si stretching vibration, 952 cm⁻¹ is of Si–OH stretching vibration, 807 cm⁻¹ of Si–O bending vibration and 474 cm⁻¹ of Si–O out-of-plane deformation are assigned [433,434]. The bands at 1108, 982, 807 and 474 cm⁻¹ are shifted to lower wavenumbers due to the doping of Ag-Pt BNPs.
Fig. 7.1.1. FT-IR spectra of (a) bare SiO$_2$ and (b) Ag-Pt/SiO$_2$
7.1.1.2. Diffuse reflectance spectra

The diffuse reflectance spectra (DRS) of bare SiO$_2$ and Ag-Pt/SiO$_2$ are shown in Figs. 7.1.2a and 7.1.2b. The absorption intensity is significantly increased in the visible light range for the Ag-Pt BNP loaded SiO$_2$, while bare is not showing any significant absorbance.

In addition to this, $F(R)$ values have been calculated from the UV-vis diffuse reflectance spectra by employing Kubelka-Munk function, $[F(R)E]^{1/2}$. It is plotted against the excitation energy ‘E’ to determine the band gap [435]. The estimated band gap energies are 5.1 eV for the bare SiO$_2$ and 4.36 eV for Ag-Pt/SiO$_2$ nanocomposite catalyst (Figs. 7.1.3a and 7.1.3b).

7.1.1.3. Photoluminescence spectra

Figs. 7.1.4a and 7.1.4b shows the extinction spectra of the bare SiO$_2$ and Ag-Pt/SiO$_2$. It can be seen, the Ag-Pt/SiO$_2$ is showing significant photoluminescence intensity (360 nm) when compared to the bare SiO$_2$ (433 nm). This is because of suppression of recombination of the electron-hole pairs by Ag-Pt BNPs. Ag-Pt BNPs has strong interaction with the radiation field in the UV region. This interaction causes excited conducting electrons to oscillate in a collective manner, called the surface plasmon resonance (SPR). This also leads to the higher catalytic activity of the catalyst. Noble nano metals like Au, Ag can enhance the fluorescence intensity of near-infrared fluorescent (NIRF) molecules, which exist in their electromagnetic field. This phenomenon is called surface plasmon resonance enhancement [436].
Fig. 7.1.2. DRS of (a) bare SiO$_2$ and (b) Ag-Pt/SiO$_2$

Fig. 7.1.3. Direct band gap of (a) bare SiO$_2$ and (b) Ag-Pt/SiO$_2$
Fig. 7.1.4. Photoluminescence spectra of (a) bare SiO$_2$ and (b) Ag-Pt/SiO$_2$
7.1.1.4. XRD analysis

X-Ray diffraction pattern of bare and nano Ag-Pt bimetal loaded catalyst are shown in Figs. 7.1.5a and 7.1.5b. The peaks observed at 38.1, 39.7 and 64.5° are the diffractions of the crystalline planes of Ag (111), (220) and Pt (111), respectively. The prepared catalyst exhibits a diffraction pattern of cubic crystal structure of Ag and Pt, but no diffraction peaks are observed in the bare SiO₂. A broad peak corresponding to characteristic of amorphous SiO₂ is located in the range 20-30°C for both loaded and bare catalyst (Fig. 7.1.5a). It reveals that the SiO₂ is in amorphous state. The particle size of the catalyst is calculated by Debye-Scherrer equation and the size of the particles are found to be 245.8±23.8 nm.

7.1.1.5. HR-SEM analysis

HR-SEM images of the bare SiO₂ and Ag-Pt/SiO₂ are shown in Figs. 7.1.6a and 7.1.6b. Monodispersed particles of size range between diameters of 245-260 nm with spherical morphology is inferred in bare SiO₂. When compared with the bare SiO₂, the size of Ag-Pt/SiO₂ particles are altered to the lower size region. EDX microanalysis and elemental composition assay have been carried out with HR-SEM to identify the components of the bare SiO₂ and Ag-Pt/SiO₂ catalyst (Figs. 7.1.6c and 7.1.6d). The EDX recorded from the selected area of the catalysts are shown in Figs. 7.1.6a and 7.1.6b, it reveals the presence of Si, O in bare SiO₂ and Si, O, Ag and Pt in the Ag-Pt/SiO₂ catalyst.
Fig. 7.1.5. XRD patterns of (a) bare SiO₂ and (b) Ag-Pt/SiO₂

Fig. 7.1.6. HR-SEM images of (a) bare SiO₂ and (b) Ag-Pt/SiO₂; EDX of (c) bare SiO₂ and (d) Ag-Pt/SiO₂
7.1.1.6. TEM analysis

Fig. 7.1.7 shows TEM images of bare SiO$_2$ (Figs. 7.1.7a and 7.1.7b) and Ag-Pt/SiO$_2$ nanocomposites (Figs. 7.1.7d and 7.1.7e) at different magnifications. It can be seen that the particles are in spherical morphology in accordance with TEM. The average size of the Ag-Pt loaded SiO$_2$ particle is close to that of bare SiO$_2$ (≈250 nm). The corresponding SAED pattern (Fig. 7.1.7c) showed a halo ring in bare SiO$_2$. Whereas, the Ag-Pt loaded SiO$_2$ catalyst (Fig. 7.1.7f) shows clear diffraction pattern of polycrystalline material.

7.1.1.7. Thermogravimetric analysis (TGA)

TGA curves of the bare SiO$_2$ and Ag-Pt/SiO$_2$ are shown in Fig. 7.1.8. The TGA pattern of the as-prepared bare SiO$_2$ catalyst is shown in Fig. 7.1.8a. The total weight loss of 10% in the temperature range of 40-600°C is observed. The weight loss demands an understanding of the nature of thermally desorbed species on the surface of silica spheres. The surface of the spherical silica consists of very small portion of free silanol, large amount of hydrogen-bonded silanol and adsorbed water molecules [437,438]. The weight loss occurs in two distinct regions from 40-200°C and from 350-560°C. The weight loss in the first phase is _ca._ 7.5%, whereas in the second phase it is _ca._ 2.5%. The initial weight loss in the temperature range of 40-200°C could be associated with the breakup of the hydrogen-bonded network and expulsion of the adsorbed water from the surface.
Fig. 7.1.7. TEM images of (a, b) bare SiO$_2$ and (d, e) Ag-Pt/SiO$_2$; SAED patterns of (c) bare SiO$_2$ and (f) Ag-Pt/SiO$_2$

Fig. 7.1.8. TGA curves of (a) bare SiO$_2$ and (b) Ag-Pt/SiO$_2$
The second stage weight loss, in the range of 350-560°C, could be associated with desorption of the adsorbed water, as well as water generated by the condensation of part of free silanols on the inner pore wall. These results are in good agreement with the reported results by Pol et al. [439]. The TGA pattern of the synthesized Ag-Pt/SiO$_2$ catalyst shows (Fig. 7.1.8b) a total weight loss of 17% over the temperature ranges of 40-600°C. The weight loss in the first phase was ca. 7.5%, whereas in the second phase it is ca. 9.5%. The total weight loss is higher than the bare SiO$_2$ due to the fact of Ag-Pt BNP are adsorbed on the surface of SiO$_2$.

7.1.1.8. Differential scanning calorimetry (DSC)

DSC measurement (Figs. 7.1.9a and 7.1.9b) evaluates the thermal behaviour of the bare SiO$_2$ and Ag-Pt/SiO$_2$ catalysts. The endothermic peaks are obtained at 35 to 105°C with the maximum at 75°C for SiO$_2$ and at 50-185°C with the maximum of 123°C for the Ag-Pt/SiO$_2$. It represents the evaporation of the physically adsorbed water molecule from both the catalyst.

7.1.1.9. AFM analysis

AFM images of the surface of bare SiO$_2$ and Ag-Pt/SiO$_2$ are presented in Figs. 7.1.10a and 7.1.10b. Bare SiO$_2$ shows a less structured surface, characteristic of amorphous materials. The existence of nanosized particles in the Ag-Pt/SiO$_2$ catalyst is reflected in its 3D AFM image (Fig. 7.1.10b), which is characterized by a wave type projection in the Z direction (uniform array). The small crystalline size of Ag-Pt/SiO$_2$ is responsible for an enhanced catalytic activity.
Fig. 7.1.9. DSC curves of (a) bare SiO$_2$ and (b) Ag-Pt/SiO$_2$

Fig. 7.1.10. AFM (2D and 3D) images of (a) bare SiO$_2$ and (b) Ag-Pt/SiO$_2$
7.1.1.10. XPS analysis

To detect the oxidation state of various species in the catalyst, XPS analysis is performed. Fig. 7.1.11a shows the XPS survey scan spectrum of the bare SiO$_2$. The binding energies of the selected photoemission lines of Si2s, Si2p and O1s are shown in Fig. 7.1.11a for bare SiO$_2$. In the spectrum, three predominant peaks of Si2s (153.5 eV), Si2p (102.6 eV) and O1s (533.3 eV) are present. The signal Si2p and the signal O1s of bare SiO$_2$ are shown in Figs. 7.1.11b and 7.1.11c.

To understand the surface chemical changes, XPS is recorded for the Ag-Pt/SiO$_2$ catalyst. Fig. 7.2.11d shows the XPS survey scan of Ag-Pt/SiO$_2$ nanocomposites. The detailed XPS scans for Ag3d, Pt4f, O1s and Si2p are shown in Figs. 7.1.11e and 7.1.11f. The binding energies of the selected photoemission lines of Si2s (153.5 eV), Si2p (102.6 eV) and O1s (533.3 eV) are very important and this shows that SiO$_2$ is the main component of the surface. The typical peaks of Ag element at the binding energies Ag3d$_{5/2}$ at 368 eV and Ag3d$_{3/2}$ at 374.29 eV and the splitting of the 3d doublet (6 eV) are revealed in Fig. 7.1.11e denoted that Ag is present in its metallic form. Pt4f regions for Ag-Pt can be fitted into two sets of spin-orbit doublets. Fig. 7.1.11f shows the Pt4f spectrum, and the peaks shown at 71.4 (Pt4f$_{7/2}$) and 74.7 eV (Pt4f$_{5/2}$), respectively provides evidence for the creation of Pt$^0$ nanoparticles. These peaks also demonstrate that the Ag and Pt are in the sample at Ag$^0$ and Pt$^0$ [336,405] oxidation states.
Fig. 7.1.11. XPS of (a) survey scan, (b) high-resolution of Si2p and (c) O1s for bare SiO$_2$; (d) survey scan, (e) high-resolution of Ag3d and (f) Pt4f for Ag-Pt/SiO$_2$
7.1.1.11. BET surface area analysis

The pore structures of the as-synthesized SiO\textsubscript{2} and Ag-Pt/SiO\textsubscript{2} catalyst are characterized by N\textsubscript{2} adsorption-desorption experiment. The corresponding N\textsubscript{2} adsorption-desorption isotherms and Barrett-Joyner-Halenda (BJH) desorption pore distribution of both catalyst are investigated and shown in Fig. 7.1.12. The isotherms shows typical III-type sorption behaviour with H3 type hysteresis loop occur at a relative pressure of 0.8-1.0 (Figs. 7.1.12a and 7.1.12b) structure representing the mesoporous characteristic according to the international union of pure and applied chemistry (IUPAC) classification [440,441]. The apparent increasing step in the adsorption branch combined with the sharp decline in the desorption branch is an obvious indication of mesoporosity [442]. Figs. 7.1.12c and 7.1.12d (inset) shows pore size distribution of bare SiO\textsubscript{2} and Ag-Pt/SiO\textsubscript{2} nanocatalyst, which is obtained from the corresponding desorption branch of the N\textsubscript{2} isotherm. The BET surface area and pore volume for both catalysts are listed in Table 7.1.1. It is found that the specific surface area increase from 56.9 (bare SiO\textsubscript{2}) to 102.6 m\textsuperscript{2} g\textsuperscript{-1} (Ag-Pt/SiO\textsubscript{2}). Also, the average pore diameter coincides with Ag-Pt/SiO\textsubscript{2} crystallite pore size decreased in association with the decrease in the crystallite size of the catalyst compared to the bare SiO\textsubscript{2}.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>( S_{\text{BET}} ) (m\textsuperscript{2} g\textsuperscript{-1})</th>
<th>( V_t ) (cm\textsuperscript{3} g\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO\textsubscript{2}</td>
<td>56.9364</td>
<td>0.3951</td>
</tr>
<tr>
<td>Ag-Pt/SiO\textsubscript{2}</td>
<td>102.6000</td>
<td>0.4374</td>
</tr>
</tbody>
</table>

\( S_{\text{BET}} \) is the specific surface area deduced from the isotherm analysis in the relative pressure range from 0.0-1.0; \( V_t \) is the total pore volume at relative pressure 0.95.
Fig. 7.1.12. $\text{N}_2$ adsorption-desorption isotherms of the as-synthesized (a) bare $\text{SiO}_2$ and (b) $\text{Ag-Pt/SiO}_2$; BJH size distribution of (c) bare $\text{SiO}_2$ and (d) $\text{Ag-Pt/SiO}_2$. 
7.1.1.12. Catalytic activity of Ag-Pt/SiO₂ for coupling reaction

In order to find out the catalytic efficiency, the prepared Ag-Pt/SiO₂ catalyst is used for the coupling reaction between benzaldehyde (1) and indole (2) as shown in Scheme 7.1.1. The product is separated and analyzed by FT-IR, Raman, ¹H, ¹³C NMR and LC-MS measurements. The assignments confirm the formation of the coupled product. There is no significant reaction observed in the absence of catalyst as well as with the presence of bare SiO₂. The experimental and theoretical Raman spectra of 3-((1H-indol-3-yl)(phenyl)methyl)-1H-indole 3a to supports the formation of the C–C coupled product (Figs. 7.1.13a and 7.1.13b). The absence of carbonyl group in the product also confirms the formation of the coupled product. The same method is applied for condensation of indole with bisaldehyde (terephthaldehyde) (Scheme 7.1.2). The reaction of 4 equivalents of indole afforded compound 4 under similar reaction conditions (Scheme 7.1.2).

![Scheme 7.1.1. Condensation of indoles with aldehyde compounds](image1)

![Scheme 7.1.2. Condensation of indole with terephthaldehyde](image2)
Fig. 7.1.13. (a) Theoretical (unscaled) and (b) experimental Raman spectra of 3a
7.1.1.13. Analysis of the product 3-((1H-indol-3-yl)(phenyl)methyl)-1H-indole (3a)

The $^1$H NMR spectrum of 3a shows a low frequency singlet observed at 5.89 ppm and it is assigned to H(10) proton. The high frequency broad singlet exhibit at 7.95 ppm is due to corresponding NH proton. The sharp singlet seen at 6.68 ppm is due to H(13) proton, it is attached with NH moiety. Remaining doublets and triplets are observed in the region of 6.98-7.58 ppm are assigned to aromatic and heterocyclic ring protons. In a similar manner assignments are done for other substituted compounds 3b-3l values are given in section 7.1.1.17.

$^{13}$C NMR spectra have been recorded in CDCl$_3$ for the derivatives 3b-3l. The $^{13}$C NMR spectra of compound 3a gives upfield signal at 40.21 ppm, which is assigned to carbon C(10). The ipso carbons can be easily distinguished from other aromatic and heterocyclic carbons based on small intensities. For the ipso carbons C(11), C(9), C(3) and C(4), signals are at 126.15, 127.12, 136.71 and 144.03 ppm. Among these signals, the low frequency signal at 126.15 ppm is assigned to the quaternary carbon C(11). In the remaining signals at 127.12 and 136.71 ppm, the signal at 127.12 ppm is assigned to the ipso carbon C(9) and 136.71 ppm is assigned to the quaternary carbon C(3). Obviously, the signal at 144.03 ppm is due to C(4) carbon atom. The remaining signals observed in the region 119.25-128.74 ppm are due to the corresponding aromatic and heterocyclic ring carbons. In a similar manner assignments are done for other substituted compounds 3b-3l values are given in section 7.1.1.17.
7.1.1.14. Mechanism

A feasible mechanism for the reaction between indole and carbonyl compound in the presence of Ag-Pt/SiO₂ is given in Scheme 7.1.3. The reaction is likely to proceed via the formation of an azafulvenium salt, which in turn undergoes further addition with the second indole molecule leading to the formation of bis(indolyl)methane derivatives. In order to show the general applicability of this method, various aldehydes were efficiently reacted with two equivalents of indole in similar conditions. As shown in Table 7.1.2, the obtain yields are quantitative in most cases and proceeds in striking lesser time scale.

Scheme 7.1.3. Feasible mechanism for the condensation reaction

7.1.1.15. Effect of different substituents

All the reactions of indole with substituted aldehydes proceeds very cleanly and no undesirable side-reactions are observed. The yields are highly dependent on the substituents. Structures of bis(indolyl)methane derivatives have been identified by IR, ¹H, ¹³C NMR and LC-MS spectral measurements (Plates 7.1.1-7.1.52). Results in Tables 7.1.2 shows that electron-donating groups in the substituted aldehydes favour the higher yield of the product (Table 7.1.2, entry 4).
Table 7.1.2. Synthesis of bis(indolyl)methanes via the condensation of indole with aldehydes catalyzed by Ag-Pt/SiO₂ in solvent-free condition

<table>
<thead>
<tr>
<th>Entry</th>
<th>Aldehyde</th>
<th>Product</th>
<th>Time (s)</th>
<th>Yield* (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>OHC-苯</td>
<td><img src="image1.png" alt="Image" /></td>
<td>60</td>
<td>92</td>
</tr>
<tr>
<td>2</td>
<td>OHC-苯-Fl</td>
<td><img src="image2.png" alt="Image" /></td>
<td>60</td>
<td>91</td>
</tr>
<tr>
<td>3</td>
<td>OHC-苯-Cl</td>
<td><img src="image3.png" alt="Image" /></td>
<td>60</td>
<td>90</td>
</tr>
<tr>
<td>4</td>
<td>OHC-苯-OCH₃</td>
<td><img src="image4.png" alt="Image" /></td>
<td>120</td>
<td>95</td>
</tr>
<tr>
<td>5</td>
<td>OHC-苯-NO₂</td>
<td><img src="image5.png" alt="Image" /></td>
<td>60</td>
<td>87</td>
</tr>
<tr>
<td>6</td>
<td>OHC-苯-CH₃</td>
<td><img src="image6.png" alt="Image" /></td>
<td>30</td>
<td>94</td>
</tr>
<tr>
<td>Entry</td>
<td>Aldehyde</td>
<td>Product</td>
<td>Time (s)</td>
<td>Yield(^a) (%)</td>
</tr>
<tr>
<td>-------</td>
<td>----------</td>
<td>---------</td>
<td>----------</td>
<td>-----------------</td>
</tr>
<tr>
<td>7</td>
<td>OHC-苯-OH</td>
<td><img src="image" alt="Product" /></td>
<td>90</td>
<td>89</td>
</tr>
<tr>
<td>8</td>
<td>OHC-苯-Cl</td>
<td><img src="image" alt="Product" /></td>
<td>60</td>
<td>86</td>
</tr>
<tr>
<td>9</td>
<td>OHC-苯-Br</td>
<td><img src="image" alt="Product" /></td>
<td>40</td>
<td>78</td>
</tr>
<tr>
<td>10</td>
<td>五氧化-CHO</td>
<td><img src="image" alt="Product" /></td>
<td>60</td>
<td>82</td>
</tr>
<tr>
<td>11</td>
<td>OHC-苯-OCH(_3)</td>
<td><img src="image" alt="Product" /></td>
<td>60</td>
<td>86</td>
</tr>
<tr>
<td>12</td>
<td>OHC-苯-OCH(_3)</td>
<td><img src="image" alt="Product" /></td>
<td>420</td>
<td>93</td>
</tr>
<tr>
<td>13</td>
<td>OHC-苯-CHO</td>
<td><img src="image" alt="Product" /></td>
<td>480</td>
<td>90</td>
</tr>
</tbody>
</table>

\(^a\) Pure, isolated yield after column chromatography.
In contrast, electron-withdrawing groups such as F, Cl, and NO₂ gives lower yields (Table 7.1.2, entries 2, 3 and 5). Bare SiO₂ not favours the formation of the product. The nano Ag loaded SiO₂ (Ag-SiO₂) and nano Pt loaded SiO₂ (Pt-SiO₂) gives product of bis(indolyl)methanes with only moderate yield compared to Ag-Pt/SiO₂. Hence, bimetal nano Ag-Pt loaded catalyst (Ag-Pt/SiO₂) is essential for an effective catalysis.

7.1.1.16. Spectral data for bis(indolyl)methane derivatives (3a-3l and 4)

i) 3-((1H-Indole-3-yl)(phenyl)methyl)-1H-indole (3a)

Pink solid, Yield 92%, m.p. 140-142°C; IR (KBr, cm⁻¹): ν = 3413, 3057, 2964, 2920, 1600, 1506, 1035, 1128 (Plate 7.1.1);
1H NMR (400 MHz, CDCl₃, ppm): δ = 5.89 (s, 1H), 6.68 (s, 2H), 7.02 (t, 2H), 7.19 (d, 2H, J = 8.2 Hz), 7.35 (d, 2H, J = 8.2 Hz), 7.40 (d, 2H, J = 8.0 Hz), 7.58 (d, 2H, J = 8.0 Hz), 7.95 (2H, NH) (Plate 7.1.2);
13C NMR (100 MHz, CDCl₃, ppm): δ = 40.2, 110.0, 119.3, 119.8, 120.0, 121.9, 123.6, 126.2, 127.1, 128.2, 128.7, 136.7, 144.0 (Plate 7.1.3); LC-MS (m/z): 323.20 (Plate 7.1.4). MF: C₂₃H₁₈N₂.

ii) 3-((4-Fluorophenyl)(1H-indol-3-yl)methyl)-1H-indole (3b)

Brown solid, Yield 91%, m.p. 73-75 °C; IR (KBr, cm⁻¹): ν = 3396, 3051, 1599, 1456, 1336, 1095, 744 (Plate 7.1.5); 1H NMR (400 MHz, CDCl₃, ppm): δ = 5.89 (s, 1H), 6.63 (d, 2H, J = 1.6 Hz), 7.06 (t, 2H), 7.20 (t, 2H), 7.22 (t, 2H), 7.28 (2H), 7.37 (d, 2H, J = 6.4 Hz), 7.40 (d, 2H, J = 6.4 Hz), 7.93 (s, 2H, NH) (Plate 7.1.6); 13C NMR (100 MHz, CDCl₃, ppm): δ = 39.5, 111.1, 114.9, 119.3, 119.6, 119.9, 122.0, 123.6, 126.9, 130.1, 136.7, 139.7, 162.4 (Plate 7.1.7); LC-MS (m/z): 341.10 (Plate 7.1.8); MF: C₂₃H₁₇FN₂.
iii) 3-((4-Chlorophenyl)(1H-indol-3-yl)methyl)-1H-indole (3c)

Pink solid, Yield 90%, m.p. 76-78°C; IR (KBr, cm⁻¹): ν = 3419, 3046, 2920, 1616, 1490, 1331, 1084, 750 (Plate 7.1.9); ¹H NMR (400 MHz, CDCl₃, ppm): δ = 5.58 (s, 1H), 6.62 (d, 2H, J = 1.2 Hz), 7.05 (t, 2H), 7.20 (t, 2H), 7.25 (d, 2H, J = 1.6 Hz), 7.28 (d, 2H, J = 2.4 Hz), 7.37 (d, 2H, J = 6.8 Hz), 7.40 (d, 2H, J = 6.8 Hz), 7.97 (s, 2H, NH) (Plate 7.1.10); ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 39.6, 111.2, 119.2, 119.4, 119.8, 122.3, 123.7, 126.9, 128.3, 130.1, 131.8, 136.7, 142.6 (Plate 7.1.11); LC-MS (m/z): 354.95 (Plate 7.1.12); MF: C₂₃H₁₇ClN₂.

iv) 3-((1H-indol-3-yl)(4-methoxyphenyl)methyl)-1H-indole (3d)

Dark brown solid, Yield 95%, m.p. 185-187°C; IR (KBr, cm⁻¹): ν = 3391, 3046, 2832, 1604, 1511, 1095, 1007, 733 (Plate 7.1.13); ¹H NMR (400 MHz, CDCl₃, ppm): δ = 3.81 (s, 3H, OCH₃), 5.86 (s, 1H), 6.66 (d, 2H, J = 6.4 Hz), 6.84 (t, 2H), 7.03 (2H), 7.19 (2H), 7.28 (t, 2H), 7.35 (d, 2H, J = 7.6 Hz), 7.42 (d, 2H, J = 6.8 Hz), 7.91 (s, 2H, NH) (Plate 7.1.14); ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 39.3, 55.2, 111.0, 113.3, 119.2, 120.0, 120.1, 121.9, 123.5, 127.1, 129.6, 136.2, 136.7, 157.9 (Plate 7.1.15); LC-MS (m/z): 353.15 (Plate 7.1.16); MF: C₂₄H₂₀N₂O.

v) 3-((1H-Indol-3-yl)(3-nitrophenyl)methyl)-1H-indole (3e)

Pink solid, Yield 87%, m.p. 219-221°C; IR (KBr, cm⁻¹): ν = 3407, 3057, 1610, 1522, 1451, 1347, 1095, 739 (Plate 7.1.17); ¹H NMR (400 MHz, CDCl₃, ppm): δ = 6.02 (s, 1H), 6.61 (s, 2H), 7.09 (t, 2H), 7.25 (t, 2H), 7.37 (t, 2H), 7.41 (d, 2H, J = 6.2 Hz), 7.70 (d, 1H, J = 7.5 Hz), 8.00 (s, 2H), 8.10 (d, 2H, J = 6.2 Hz), 8.27 (2H, NH) (Plate 7.1.18); ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 40.0, 111.5, 118.1, 119.6, 121.6, 122.3, 123.6, 123.9, 126.7, 129.3, 135.1, 136.8, 146.5, 148.5 (Plate 7.1.19); LC-MS (m/z): 368.10 (Plate 7.1.20); MF: C₂₃H₁₇N₃O₂.
vi) 3-((1H-Indol-3-yl)(p-tolyl)methyl)-1H-indole (3f)

Pink solid, Yield 94%, m.p. 94-96°C; IR (KBr, cm\(^{-1}\)): v = 3408, 3057, 2920, 2860, 1605, 1463, 1419, 1013, 745 (Plate 7.1.21);

\(^1\)H NMR (400 MHz, CDCl\(_3\), ppm): \(\delta = 1.30\) (s, 3H, CH\(_3\)), 5.87 (s, 1H, Ar–H), 6.68 (d, 2H, \(J = 8.2\) Hz), 7.02 (t, 2H), 7.19 (t, 2H), 7.21 (t, 2H), 7.23 (d, 2H, \(J = 6.6\) Hz), 7.37 (t, 2H), 7.41 (t, 2H), 7.94 (2H, NH) (Plate 7.1.22);

\(^{13}\)C NMR (100 MHz, CDCl\(_3\), ppm): \(\delta = 29.7, 36.6, 111.0, 118.4, 119.3, 119.8, 119.9, 122.0, 123.8, 126.6, 129.5, 136.8, 141.0, 145.0\) (Plate 7.1.23);

LC-MS (m/z): 337.25 (Plate 7.1.24); MF: C\(_{24}\)H\(_{20}\)N\(_2\).

vii) 4-((1H-indol-3-yl)methyl)phenol (3g)

Pink solid, Yield 89%, m.p. 119-121°C; IR (KBr, cm\(^{-1}\)): v = 3446, 3402, 1594, 1517, 1254, 1084, 745 (Plate 7.1.25);

\(^1\)H NMR (400 MHz, CDCl\(_3\), ppm): \(\delta = 5.84\) (s, 1H), 6.67 (d, 2H, \(J = 1.6\) Hz), 7.15 (t, 2H), 7.23 (d, 2H, \(J = 2.0\) Hz), 7.28 (t, 2H), 7.31 (2H), 7.40 (d, 2H, \(J = 1.6\) Hz), 7.82 (d, 2H, \(J = 1.6\) Hz), 8.00 (2H, NH), 11.50 (s, 1H) (Plate 7.1.26);

\(^{13}\)C NMR (100 MHz, CDCl\(_3\), ppm): \(\delta = 39.4, 111.1, 115.1, 119.2, 120.0, 119.9, 123.5, 123.9, 127.1, 129.6, 132.6, 136.7, 140.2, 153.8\) (Plate 7.1.27); LC-MS (m/z): 339.25 (Plate 7.1.28); MF: C\(_{23}\)H\(_{18}\)N\(_2\)O.

viii) 3-((3-Chlorophenyl)(1H-indol-3-yl)methyl)-1H-indole (3h)

Pink solid, Yield 86%, m.p. 75-77°C; IR (KBr, cm\(^{-1}\)): v = 3402, 3028, 1593, 1489, 1456, 1089, 744 (Plate 7.1.29);

\(^1\)H NMR (400 MHz, CDCl\(_3\), ppm): \(\delta = 6.38\) (s, 1H), 6.64 (s, 2H), 7.04 (t, 1H), 7.06 (t, 2H), 7.14 (t, 2H), 7.22 (t, 2H), 7.37 (d, 2H, \(J = 6.4\) Hz), 7.45 (d, 2H, \(J = 1.5\) Hz), 7.90 (2H, NH) (Plate 7.1.30);

\(^{13}\)C NMR (100 MHz, CDCl\(_3\), ppm): \(\delta = 36.7, 111.1, 118.4, 119.3, 119.9, 122.0, 123.8, 126.7, 127.0, 127.5, 129.5, 130.3, 134.0, 136.7, 141.3\) (Plate 7.1.31); LC-MS (m/z): 355.85 (Plate 7.1.32); MF: C\(_{23}\)H\(_{17}\)ClN\(_2\).
ix) 3-((3-Bromophenyl)(1H-indol-3-yl)methyl)-1H-indole (3i)

Pink solid, Yield 78%, m.p. 92-94°C; IR (KBr, cm⁻¹): ν = 3532, 3410, 2962, 2923, 2852, 1685, 1567, 1435, 1102, 749 (Plate 7.1.33);
¹H NMR (400 MHz, CDCl₃, ppm): δ = 5.86 (s, 1H), 6.67 (s, 2H), 7.03 (t, 1H), 7.18 (t, 2H), 7.35 (d, 2H), 7.36 (t, 2H), 7.51 (d, 2H, J = 4.5 Hz), 7.73 (d, 2H, J = 8.0 Hz), 7.99 (2H, NH) (Plate 7.1.34); ¹³C NMR (100 MHz, CDCl₃, ppm):
δ = 39.9, 111.1, 118.9, 119.4, 119.8, 122.1, 122.4, 122.6, 123.7, 126.9, 127.4, 128.7, 129.4, 129.8, 130.1, 131.7, 133.2, 136.6, 136.7, 146.5 (Plate 7.1.35); LC-MS (m/z): 399.90 (Plate 7.1.36); MF: C₂₃H₁₇BrN₂.

x) 3-((Furan-2-yl)(1H-indol-3-yl)methyl)-1H-indole (3j)

Brown solid, Yield 82%, m.p. 312-314°C; IR (KBr, cm⁻¹):
ν = 3411, 2923, 2855, 1726, 1463, 1375, 1276, 1117, 1073, 745 (Plate 7.1.37);
¹H NMR (400 MHz, CDCl₃, ppm): δ = 5.94 (s, 1H), 6.05 (d, 1H, J = 2.8 Hz), 6.29 (1H, J = 2.5 Hz), 6.84 (d, 2H, J = 1.6 Hz), 7.0 (t, 2H), 7.17 (t, 2H), 7.33 (d, 3H), 7.47 (d, 2H), 7.93 (2H, NH) (Plate 7.1.38); ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 34.1, 106.6, 110.2, 111.2, 117.2, 119.4, 119.7, 122.0, 123.1, 126.8, 128.4, 129.6, 136.6, 141.3, 157.1 (Plate 7.1.39); LC-MS (m/z): 312.60 (Plate 7.1.40); MF: C₂₁H₁₆N₂O.

xi) 4-(Di(1H-indol-3-yl)methyl)-2-methoxyphenol (3k)

Pink solid, Yield 86%, m.p. 145-147°C; IR (KBr, cm⁻¹):
ν = 3260, 2969, 2854, 1665, 1583, 1512, 1287, 1156, 734 (Plate 7.1.41);
¹H NMR (400 MHz, CDCl₃, ppm): δ = 2.04 (1H, OH), 3.71 (3H, OCH₃), 5.79 (s, 1H), 6.57 (d, 2H, J = 1.2 Hz), 6.78 (d, 1H, J = 1.2 Hz), 6.79 (s, 1H),
6.86 (d, 1H, $J = 1.2$ Hz), 6.99 (t, 2H), 7.12 (t, 2H), 7.29 (d, 2H, $J = 6.8$ Hz), 7.38 (d, 2H, $J = 7.6$ Hz), 7.83 (2H, NH) (Plate 7.1.42); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): $\delta = 39.9, 55.91, 111.1, 111.5, 114.1, 119.2, 119.9, 120.0, 121.3, 121.9, 123.7, 127.1, 136.2, 136.7, 143.8, 146.4, 171.4$ (Plate 7.1.43); LC-MS (m/z): 369.45 (Plate 7.1.44); MF: C$_{24}$H$_{20}$N$_2$O$_2$.

d) 3-((1H-indol-3-yl)(3,4-dimethoxyphenyl)methyl)-1H-indole (3l)

Pink solid, Yield 93%, m.p. 194-196°C; IR (KBr, cm$^{-1}$): $\nu = 3380, 2958, 2843, 1671, 1594, 1452, 1265, 1139, 1024, 750$ (Plate 7.1.45); $^1$H NMR (400 MHz, CDCl$_3$, ppm): $\delta = 3.77$ (s, 3H, OCH$_3$), 3.86 (s, 3H, OCH$_3$), 5.85 (s, 1H), 6.68 (s, 2H), 6.77 (d, 1H, $J = 8.0$ Hz), 6.84 (d, 1H), 6.94 (d, 1H, $J = 6.2$ Hz), 7.01 (t, 2H), 7.18 (t, 2H), 7.36 (d, 2H), 7.40 (d, 2H), 7.95 (2H, NH) (Plate 7.1.46); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): $\delta = 29.4, 29.7, 55.8, 57.9, 110.9, 111.0, 112.2, 119.2, 120.0, 120.6, 121.9, 123.5, 127.1, 136.7, 147.3, 148.7$ (Plate 7.1.47); LC-MS (m/z): 383.35 (Plate 7.1.48); MF: C$_{25}$H$_{22}$N$_2$O$_2$.

xiii) 3-((4-(Di(1H-indol-3-yl)methyl)phenyl(1H-indol-3-yl)methyl)-1H-indole (4)

Pink solid, Yield 90%, m.p. 189-191°C; IR (KBr, cm$^{-1}$): $\nu = 3408, 3052, 2920, 2843, 1600, 1457, 1210, 1013, 739$ (Plate 7.1.49); $^1$H NMR (400 MHz, CDCl$_3$, ppm): $\delta = 5.98$ (s, 2H), 6.67 (s, 4H), 7.03 (t, 4H), 7.20 (t, 4H), 7.37 (d, 4H, $J = 0.8$ Hz), 7.52 (d, 4H), 7.80 (d, 4H), 8.0 (4H, NH) (Plate 7.1.50); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): $\delta = 40.5, 111.2, 118.5, 119.4, 119.7, 122.2, 123.7, 126.8, 129.4, 129.9, 136.7, 152.9$ (Plate 7.1.51); LC-MS (m/z): 567.30 (Plate 7.1.52); MF: C$_{40}$H$_{30}$N$_4$. 
7.1.1.17. Reusability of the catalyst

Reusability of the catalyst is one of the most important benefit and makes it useful for the commercial applications. Thus the recovery and reusability of Ag-Pt/SiO$_2$ nanoparticles are investigated. The recycled catalyst has been examined (Table 7.1.3) and found to be active for at least five runs.

<table>
<thead>
<tr>
<th>Number of runs</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield* (%)</td>
<td>92</td>
<td>92</td>
<td>90</td>
<td>90</td>
<td>89</td>
</tr>
</tbody>
</table>

*Yield are isolated.

7.1.2. Conclusion

Nano bimetallic Ag-Pt/SiO$_2$ is an effective catalyst, offers an efficient and green synthetic route for condensation of indole and aldehyde, affording good yield of bis(indolyl)methanes in lesser time scale. This new strategy offers several advantages, including simple experimental condition, high yield, eco-friendly and readily recyclable catalytic use.
7.2. SYNTHESIS AND CHARACTERIZATION OF Ag-Au LOADED SiO\(_2\) AND STUDY OF ITS CATALYTIC APPLICABILITY IN MANNICH REACTION

Mannich reaction is an important carbon-carbon bond forming reaction in organic synthesis [443]. β-Amino carbonyl compounds produced by this reaction are synthetically and biologically important intermediates for the construction of various nitrogen-containing natural products and drugs [444]. This kind of reaction involves two equilibrating components (imine formation and enol tautomerization) and therefore demands drastic reaction conditions. Conventional catalysts for the classical Mannich reaction [445] involve mainly Lewis acids [446]. Several methods have been reported in the literature for the synthesis of β-amino carbonyl compounds [447-449]. However, most of these methods suffer some drawbacks like long reaction time, toxicity and higher reflux temperature. On the other hand, nanoparticles have attracted researchers in the field of synthetic chemistry because of their potency as catalysts [111,450]. Metal-nanoparticles have a characteristic high surface-to-volume ratio that translates into more active sites per unit area compared to the other conventional catalysts. Synthesis, characterization and evaluation of catalytic activity of nano bimetallic systems like Pd-Rh/SiO\(_2\), Cu-Ni/SiO\(_2\), Au-Co/SiO\(_2\), Co–Ru/SiO\(_2\), Au-Ag/SiO\(_2\), Ni–Ag/SiO\(_2\) and Ni-Cu-SiO\(_2\) [432,451-456] and their wide range of industrial and synthetic applications has been reported. Recently nanoparticles have been found to catalyze the Mannich reaction of aromatic ketones, aromatic aldehydes and aromatic amines [457]. Herein, we report the synthesis of Ag-Au/SiO\(_2\) catalyst by Stober method. The present investigation reports the microwave assisted one-pot synthesis of β-amino carbonyl compounds catalyzed by the synthesized Ag-Au/SiO\(_2\) nanocatalyst.
7.2.1. Characterization of the catalyst

7.2.1.1. FT-IR spectra

FT-IR spectrum of bare SiO$_2$ and bimetal Ag-Au loaded SiO$_2$ (Ag-Au/SiO$_2$) are shown in Figs. 7.2.1a and 7.2.1b. The broad absorption band at 3421 cm$^{-1}$ is assigned to O–H stretching frequency and the most intense band at 1108 cm$^{-1}$ is assigned to asymmetric stretching vibration of the Si–O–Si network. 952 cm$^{-1}$ is assigned to Si–OH stretching vibration. The symmetric stretching frequency at 807 cm$^{-1}$ is attributed to Si–O and 474 cm$^{-1}$ is assigned to out-of-plane deformation of Si–O [433,434]. Analysis of the FT-IR spectrum of Ag-Au/SiO$_2$ catalyst shows the prominent bands at 3429, 1107, 961, 802 and 463 cm$^{-1}$, which are assigned to the shifted frequencies due to the doping effect by Ag-Au BNPs. The BNPs exert an influence on the structure of SiO$_2$. Absorption bands below 1000 cm$^{-1}$ are assigned to inter atomic vibrations in the bare and doped silicate [458].

7.2.1.2. Diffuse reflectance spectra

The UV-visible absorption spectra of both bare SiO$_2$ and Ag-Au/SiO$_2$ are shown in Figs. 7.2.2a and 7.2.2b. Two small peaks observed for the bare SiO$_2$ (Fig. 7.2.2a) are assigned to the charge transfer bands of F$^+$ centers (oxygen vacancies with one electron and oxygen vacancies with two electrons) [459,460]. Fig. 7.2.2b depicts the DRS spectrum of Ag-Au BNP (30 nm) loaded on the silicate. It shows Ag-Au BNPs exhibit an intense and broad absorption peak in the visible region (520 nm), which is due to surface plasmon excitation. This phenomenon exists most commonly at the interface between a metal and a dielectric material [461]. The absorption intensity significantly increases in the visible range in the BNP loaded SiO$_2$. 
Fig. 7.2.1. FT-IR spectra of (a) bare SiO₂ and (b) Ag-Au/SiO₂

Fig. 7.2.2. DRS of (a) bare SiO₂ and (b) Ag-Au/SiO₂
F(R) values have been calculated from the UV-vis diffuse reflectance spectra by applying Kubelka-Munk function, $|F(R)E|^{1/2}$. This value is plotted against excitation energy (E), to determine the band gap [435] and the estimated band gap energies are 5.1 eV for the bare SiO$_2$ and 4.4 eV for Ag-Au/SiO$_2$ nanocomposites (Fig. 7.2.3).

**7.2.1.3. Photoluminescence spectra**

Photoluminescence (PL) is useful to understand the fate of the electron-hole pairs in semiconductor particles [462]. Fig. 7.2.4 shows the photoluminescence spectra of the synthesized SiO$_2$ (Fig. 7.2.4a) and Ag-Au/SiO$_2$ (Fig. 7.2.4b) catalysts. The catalysts show a near UV emission band at 430 nm. PL intensity of Ag-Au/SiO$_2$ is at 406 and 430 nm, which is lower than the bare SiO$_2$. This is due to the suppression of recombination of the electron-hole pairs by Ag-Au BNPs in the loaded SiO$_2$. Ag-Au BNPs have strong interaction with the radiation field in the UV region.

**7.2.1.4. XRD analysis**

X-Ray diffraction pattern of bare SiO$_2$ and nanobimetal Ag-Au loaded SiO$_2$ catalyst are shown in Figs. 7.2.5a and 7.2.5b. The broad peak corresponds to the amorphous SiO$_2$ having 20 values in the range of 20-30° (Fig. 7.2.5a). None other diffraction peaks are observed in the bare SiO$_2$ sample. But in the case of Ag-Au/SiO$_2$ catalyst, five peaks are observed (Fig. 7.2.5b) at 38.1, 44.3, 64.5 and 77.5°. It can be indexed to the diffractions of the crystalline planes of (111), (200), (220) and (311) Ag and Au, respectively.
Fig. 7.2.3. Direct band gap of (a) bare SiO$_2$ and (b) Ag-Au/SiO$_2$

Fig. 7.2.4. Photoluminescence spectra of (a) bare SiO$_2$ and (b) Ag-Au/SiO$_2$
Fig. 7.2.5. XRD patterns of (a) bare SiO₂ and (b) Ag-Au/SiO₂
The Ag-Au BNPs exhibited sharper characteristic peaks owing to the small metal particle size. Thus in total, the catalyst exhibited the diffraction pattern of fcc crystal structure of Ag and Au. The particle size of the catalyst is calculated by the Scherrer equation. The size of the particles is found to be 30 and 260 nm.

7.2.1.5. HR-SEM and EDX analysis

HR-SEM images of the bare SiO$_2$ and Ag-Au/SiO$_2$ nanocomposites are shown in Figs. 7.2.6a and 7.2.6c. The monodisperse characteristic and spherical morphology is inferred in bare SiO$_2$ (Fig. 7.2.6a). When compared to the bare SiO$_2$, the size of Ag-Au/SiO$_2$ is altered due to the presence of bimetal nanoparticles as illustrated in Fig. 7.2.6c. From the EDX results (Figs. 7.2.6b and 7.2.6d), the presence of elements like Si, O in bare SiO$_2$ and Si, O, Ag and Au in the Ag-Au/SiO$_2$ catalyst are confirmed.

7.2.1.6. TEM analysis

Fig. 7.2.7 shows TEM image of bare silica nanospheres (Figs. 7.2.7a and 7.2.7b) and Ag-Au/SiO$_2$ nanocomposites (Figs. 7.2.7d and 7.2.7e) at different magnifications. The images of the silicates reveal the samples consist of well-proportioned spherical SiO$_2$ particles. As shown in Figs. 7.2.7a and 7.2.7b the average size of SiO$_2$ nanospheres is $\approx$260 nm. The corresponding SAED pattern (Fig. 7.2.7c) shows a halo ring that reveals the catalyst is in amorphous nature. TEM of the Ag-Au/SiO$_2$ catalyst is shown in Figs. 7.2.7d and 7.2.7e in which small Ag-Au nanoparticles are uniformly adsorbed on the SiO$_2$ nanospheres surface is well evinced.
Fig. 7.2.6. HR-SEM images of (a) bare SiO₂, (c) Ag-Au/SiO₂ and EDX of (b) bare SiO₂, (d) Ag-Au/SiO₂

Fig. 7.2.7. TEM images of (a, b) bare SiO₂, (d, e) Ag-Au/SiO₂ and SAED patterns of (c) bare SiO₂, (f) Ag-Au/SiO₂
The average particle size of the Ag-Au BNPs and bare SiO$_2$ is 30 and 260 nm respectively, fairly in good agreement with the XRD study. The corresponding SAED pattern of the bimetal loaded (Ag-Au) silicate (Fig. 7.2.7f) revealed the face centered cubic crystal structure of the Ag and Au NPs, respectively.

7.2.1.7. Thermogravimetric analysis

TGA curves of the bare silicate and Ag-Au/SiO$_2$ are shown in Fig. 7.2.8. The TGA pattern of the as-prepared bare SiO$_2$ catalyst is shown in Fig. 7.2.8a. The total weight loss of 10% at the temperature range of 40-600°C is observed. The weight loss demands an understanding of the nature of thermally desorbed species on the surface of silica spheres. The surface of the spherical silica consists of very small portion of free silanol, a large portion of hydrogen bonded silanol and some adsorbed water molecules [437,438]. The weight loss occurred in two distinct regions, one at 40 to 200°C and another at 350 to 560°C. The weight loss in the first step is ca. 7.5%, whereas in the second step the weight loss is ca. 2.5%. The initial stage (I) weight loss in the temperature range of 40-200°C could be associated with the breakup of the hydrogen-bonded network and the expulsion of the adsorbed water from the surface. The subsequent stage (II) weight loss, in the range of 350-560°C, could be associated with desorption of adsorbed water and water generated by the condensation of free silanols on the inner pore wall. These results are in good agreement with the reported results by Pol et al. [439].
Fig. 7.2.8. TGA curves of (a) bare SiO$_2$ and (b) Ag-Au/SiO$_2$
The TGA pattern of the synthesized Ag-Au/SiO$_2$ catalyst shows (Fig. 7.2.8b) a total weight loss of 22% over the temperature ranges of 40-600°C. The weight loss in the first step is ca. 7.5%, whereas in the second step the weight loss is ca. 14.5%. The total weight loss is higher than the loss in bare SiO$_2$ due to fact that the Ag-Au BNPs are adsorbed on the surface of SiO$_2$.

**7.2.1.8. Differential scanning calorimetry (DSC)**

DSC measurement in Figs. 7.2.9a and 7.2.9b provides the thermal behaviour of the bare SiO$_2$ and Ag-Au/SiO$_2$ catalysts. An endothermic peak is obtained at 35 to 105°C with the maximum at 75°C for SiO$_2$ and 45 to 175°C with the maximum of 105°C for the Ag-Au/SiO$_2$. It represents the evaporation of the physically adsorbed water molecule from both catalysts.

**7.2.1.9. AFM analysis**

Surface morphological measurements are evaluated by AFM analysis. Figs. 7.2.10a, 7.2.10b, 7.2.10d, 7.2.10e and 7.2.10c, 7.2.10f shows the bare SiO$_2$ and Ag-Au/SiO$_2$ in two and three dimensional surface feature with their corresponding height profile. Bare SiO$_2$ shows a less structured surface, characteristic to the amorphous materials (Fig. 7.2.10a) and also shows large agglomeration. The height profile of the SiO$_2$ is given in Fig. 7.2.10c. But Ag-Au/SiO$_2$ shows a considerable occurrence of spherical Ag-Au nanoparticles uniformly adsorbed on the silica surface with an average size of about 260 nm. Individual particles are fused together to form an agglomeration as shown in Fig. 7.2.10d. The average grain size of each particle is estimated as ≈260 nm (Fig. 7.2.10f) by examining the height profile.
Fig. 7.2.9. DSC curves of (a) bare SiO$_2$ and (b) Ag-Au/SiO$_2$.

Fig. 7.2.10. AFM (2D and 3D) images of (a, b) bare SiO$_2$, (d, e) Ag-Au/SiO$_2$ and (c, f) corresponding height profile.
7.2.1.10. XPS analysis

To detect the oxidation states of various species in the catalyst, XPS analysis is performed. Fig. 7.2.11a shows XPS survey scan spectrum of the bare SiO$_2$. The binding energies of the selected photoemission lines of Si2s, Si2p and O1s are shown in Fig. 7.2.11a for bare SiO$_2$. In the spectrum three predominant peaks of Si2s (153.5 eV), Si2p (102.6 eV) and O1s (533.3 eV) are present. The signal Si2p and O1s of bare SiO$_2$ are shown in Figs. 7.2.11b and 7.2.11c. Fig. 7.2.11d shows the XPS survey scan of Ag-Au/SiO$_2$ nanocomposite. The detailed XPS scans for Ag3d, Au4f, O1s and Si2p are shown in Figs. 7.2.11e and 7.2.11f. The binding energies of the selected photoemission line of Si2s (153.5 eV), Si2p (102.6 eV) and O1s (533.3 eV) are very important and this shows that SiO$_2$ is the main component of the surface. The peaks for Ag are at the binding energies such as, Ag3d$_{5/2}$ at 368 eV and Ag3d$_{3/2}$ at 374.29 eV with the splitting of the 3d doublet (6 eV) (Fig. 7.2.11e). Au4f regions for Ag-Au can be fitted into two sets of spin-orbit doublets. In Fig. 7.2.11f, Au4f$_{7/2}$ and Au4f$_{5/2}$ lines appears at 83.93 and 87.79 eV, respectively and these peaks demonstrate the Ag as well as Au are present as Ag$^0$ and Au$^0$ [405,463].
Fig. 7.2.11. XPS of (a) survey scan, (b) high-resolution of Si2p and (c) O1s for bare SiO₂; (d) survey scan, (e) high-resolution of Ag3d and (f) Au4f for Ag-Au/SiO₂
7.2.1.11. BET surface area analysis

The texture of the as-synthesized silicates are characterized by N\textsubscript{2} adsorption-desorption experiment. The N\textsubscript{2} adsorption-desorption isotherms and Barrett-Joyner-Halenda (BJH) desorption pore distribution are shown in Fig. 7.2.12. The isotherms show typical III-type sorption behavior with H3 type hysteresis loop occur at a relative pressure of 0.8-1.0 (Figs. 7.2.12a and 7.2.12b), a structure representing the mesoporous characteristic according to the international union of pure and applied chemistry (IUPAC) classification [440,441]. The apparent increasing step in the adsorption branch combined with the sharp decline in the desorption branch is an indication of mesoporosity [442]. Figs. 7.2.12a-7.2.12d (inset) show a pore size distribution of bare SiO\textsubscript{2} and Ag-Au/SiO\textsubscript{2} nanocatalyst. The BET surface area and pore volume for both bare SiO\textsubscript{2} and Ag-Au/SiO\textsubscript{2} are listed in Table 7.2.1. It is found that the specific surface area increases from 56.9 (bare SiO\textsubscript{2}) to 114.0 m\textsuperscript{2} g\textsuperscript{-1} in Ag-Au/SiO\textsubscript{2} nanocatalyst. The average pore diameter coincides with Ag-Au/SiO\textsubscript{2} crystallite size. The average pore size decreases in association with the decrease in the crystallite size of the catalyst compared to the bare SiO\textsubscript{2}.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>(S_{\text{BET}}) (m\textsuperscript{2} g\textsuperscript{-1})</th>
<th>(V_{T}) (cm\textsuperscript{3} g\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO\textsubscript{2}</td>
<td>56.9364</td>
<td>0.3951</td>
</tr>
<tr>
<td>Ag-Au/SiO\textsubscript{2}</td>
<td>114.0634</td>
<td>0.6936</td>
</tr>
</tbody>
</table>

\(S_{\text{BET}}\) is the specific surface area deducted from the isotherm analysis in the relative pressure range from 0.0-1.0; \(V_{T}\) is the total pore volume at relative pressure 0.95.
Fig. 7.2.12. N\textsubscript{2} adsorption-desorption isotherms of the as-synthesized (a) bare SiO\textsubscript{2} and (b) Ag-Au/SiO\textsubscript{2}; BJH size distribution of (c) bare SiO\textsubscript{2} and (d) Ag-Au/SiO\textsubscript{2}
7.2.1.12. Catalytic activity of Ag-Au/SiO₂ for coupling reaction

In order to find out the catalytic efficiency, the prepared Ag-Au BNP loaded SiO₂ catalyst is tested as a catalyst for the Mannich reaction. The condensation of various substituted aromatic aldehydes (1), aromatic amine (2) and aromatic ketone (3) in the presence of 1 mol% of Ag-Au/SiO₂ nanocatalyst under microwave irradiation are carried out. The corresponding β-amino carbonyl products 4a-4j are shown in Scheme 7.2.1. The products are confirmed by FT-IR, ¹H, ¹³C NMR and LC-MS spectroscopic results, which confirms the formation of the coupled product (β-amino carbonyl compounds). There is no significant reaction observed in the absence of catalyst as well as the presence of bare SiO₂.

In order to show the general applicability of this method, various aldehydes were efficiently reacted with amine and acetophenone in similar conditions. As shown in Table 7.2.2, the obtained yields are almost impressive in most cases and proceeds in striking lesser time scales.

Scheme 7.2.1. One-pot three-component direct Mannich reaction
7.2.1.13. Analysis of the product 1,3-diphenyl-3-(phenylamino)propan-1-one (4a)

The $^1$H NMR spectrum of β-amino carbonyl (4a) reveals two doublet of doublet centered at 3.54 and 3.44 ppm ($J = 5.2$ and 16.0 Hz) and they are assigned to methylene protons $H_a$(8) and $H_b$(8) respectively, and this methylene moiety is attached with carbonyl carbon. Another doublet of doublet centered at 5.04 ppm ($J = 5.2$ and 7.6 Hz) is due to methine proton $H$(9). The broad signal at 4.75 ppm (internal corresponds to one proton) is assigned to NH proton of H(10). The remaining aromatic proton signals are shown in the region 6.50-7.94 ppm. In a similar manner assignments are done for other substituted β-amino carbonyl products (4b-4j). The chemical shift values are given in section 7.2.1.16.

$^{13}$C NMR spectra is recorded in CDCl$_3$ for 4a-4j (the assignments of signals in compound are made follows). The high frequency signal at 198.3 ppm is due to the carbonyl carbon C(1) and it is attached to methylene moiety at C(8). The low frequency signals at 46.1 and 54.8 ppm are representing to the methylene carbon C(8) and methine carbon C(9), respectively. The $^{13}$C NMR spectrum further reveals three signals for quaternary carbons [C(2), C(11) and C(17)] at 136.7, 142.9 and 147.0 ppm, which can be easily distinguished from other carbons. The high frequency signal at 147.0 ppm is assigned to ipso carbon C(11) and this assignment is based on the high deshielding nature of the nitrogen atom. The signal at 142.9 ppm is assigned to the ipso carbon C(2) since it is linked to the carbonyl
carbon C(1). Another *ipso* carbon at 136.7 ppm is due to C(17). The remaining signals in the range 113.0-134.0 ppm are assigned to aromatic carbon attached to phenyl moieties in a similar assignments are done for the other substituted β-amino carbonyl products (4b-4j). The chemical shift values are given in section 7.2.1.16.

### 7.2.1.14. Mechanism

A probable mechanism of the Mannich type reaction in the presence of Ag-Au/SiO$_2$ catalyst is proposed (Scheme 7.2.2). The first step shows the formation of imine (Schiff base I) due to the nucleophilic addition of amine with aldehyde and subsequent loss of water molecule. Consequently the enol (II) forms from the keto group. In second step the enol (II) carbonyl carbon is attacked with imine (I) (nucleophilic nitrogen) to form the product of β-amino carbonyl compound (III).

*Scheme 7.2.2. Feasible mechanism for the Mannich reaction*
7.2.1.15. Effect of different substituents

The condensation of various substituted aromatic aldehydes, aromatic amines and aromatic ketones in the presence of nanocatalyst under microwave irradiation proceeds very cleanly without any undesirable side-reactions. The product yield is highly dependent on the substituents present. Structures of the product (β-amino carbonyl derivatives) have been identified by IR, $^1$H $^{13}$C NMR and LC-MS spectral measurements (Plates 7.2.1-7.2.40). Results in Table 7.2.2 shows that electron-donating groups at the substituted aldehydes favours the formation of product (Table 7.2.2, entries 2, 6, 7 and 10). In contrast, electron-withdrawing groups Cl, Br and F gives slightly lower yields (Table 7.2.2, entries 3-5) with longer reaction times. Electron-withdrawing group NO$_2$ in meta position results is very low yield (Table 7.2.2, entry 9 – 84.0%). Nano Ag loaded SiO$_2$ (Ag-SiO$_2$) and Au loaded SiO$_2$ (Au-SiO$_2$) catalyst also gives the product β-amino carbonyl compound from benzaldehydes, aniline and acetophenone, but with low yields. Hence, bimetal nano Ag-Au loaded catalyst (Ag-Au/SiO$_2$) shows good catalytic behaviour for Mannich reaction.
Table 7.2.2. Synthesis of β-amino carbonyl compounds (4a–4j) via the condensation of acetophenone, aromatic aldehydes and aromatic amines catalyzed by Ag-Au/SiO₂ in solvent-free condition

<table>
<thead>
<tr>
<th>Entry</th>
<th>Aldehyde</th>
<th>Product</th>
<th>Time (min)</th>
<th>Yield* (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td><img src="image1" alt="Diagram" /></td>
<td>2</td>
<td>92</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td><img src="image2" alt="Diagram" /></td>
<td>4</td>
<td>93</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td><img src="image3" alt="Diagram" /></td>
<td>8</td>
<td>88</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td><img src="image4" alt="Diagram" /></td>
<td>6</td>
<td>87</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td><img src="image5" alt="Diagram" /></td>
<td>8</td>
<td>88</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td><img src="image6" alt="Diagram" /></td>
<td>5</td>
<td>91</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td><img src="image7" alt="Diagram" /></td>
<td>4</td>
<td>94</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td><img src="image8" alt="Diagram" /></td>
<td>7</td>
<td>87</td>
</tr>
<tr>
<td>9</td>
<td></td>
<td><img src="image9" alt="Diagram" /></td>
<td>12</td>
<td>84</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td><img src="image10" alt="Diagram" /></td>
<td>5</td>
<td>92</td>
</tr>
</tbody>
</table>

* The yield refer to isolated products.
7.2.1.16. Spectral data for Mannich products (compounds 4a-4j)

i) 1,3-Diphenyl-3-(phenylamino)propan-1-one (4a)

Brown solid, Yield 92%, m.p. 175-176°C; IR (KBr, cm⁻¹): ν = 3386, 3057, 2920, 1670, 1500, 1336, 1221, 1023, 755 (Plate 7.2.1);
¹H NMR (400 MHz, CDCl₃, ppm): δ = 3.44 (dd, 1H, J = 7.6, 16.0 Hz), 3.54 (dd, 1H, J = 5.6, 7.6 Hz), 4.58 (s, NH), 5.03 (dd, 1H, J = 5.6, 7.6 Hz), 6.59 (d, 2H, Ar–H), 6.69 (t, 1H, Ar–H), 7.11 (t, 2H, Ar–H), 7.26 (t, 1H, Ar–H), 7.34 (t, 2H, Ar–H), 7.46 (t, 2H, Ar–H), 7.48 (t, 2H, Ar–H), 7.59 (t, 1H, Ar–H), 7.93 (d, 2H, Ar–H) (Plate 7.2.2); ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 46.3, 54.8, 113.8, 117.8, 126.4, 127.4, 128.2, 128.7, 128.8, 129.1, 133.4, 136.7, 143.0, 147.0 (Plate 7.2.3); LC-MS (m/z): 302.15 (Plate 7.2.4); MF: C₂₁H₁₉NO.

ii) 1-Phenyl-3-(phenylamino)-3-p-tolylpropan-1-one (4b)

Brown solid, Yield 93%, m.p. 128-129°C; IR (KBr, cm⁻¹): ν = 3380, 3063, 2920, 1665, 1605, 1446, 1210, 1019, 690 (Plate 7.2.5);
¹H NMR (400 MHz, CDCl₃, ppm): δ = 1.27 (s, 3H), 3.45 (dd, 1H, J = 7.5, 15.8 Hz), 3.52 (dd, 1H, J = 5.4, 7.5 Hz), 4.50 (s, NH), 5.01 (dd, 1H, J = 5.4, 7.4 Hz), 6.56 (d, 2H, Ar–H), 6.66 (t, 1H, Ar–H), 7.09 (m, 2H, Ar–H), 7.15 (t, 2H, Ar–H), 7.43 (m, 2H, Ar–H), 7.47 (t, 2H, Ar–H), 7.56 (t, 1H, Ar–H), 7.94 (d, 2H, Ar–H) (Plate 7.2.6); ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 21.1, 46.4, 54.5, 113.8, 117.7, 126.3, 128.2, 128.5, 128.7, 129.1, 132.2, 137.0, 140.0, 145.0, 147.1, 198.4 (Plate 7.2.7); LC-MS (m/z): 316.10 (Plate 7.2.8); MF: C₂₂H₂₁NO.

iii) 3-(4-Chlorophenyl)-1-phenyl-3-(phenylamino)propan-1-one (4c)

White solid, Yield 88%, m.p. 117-118°C; IR (KBr, cm⁻¹): ν = 3390, 3052, 2920, 1665, 1594, 1495, 1260, 1046 and 695 (Plate 7.2.9);
¹H NMR (400 MHz, CDCl₃, ppm): δ = 3.77 (s, 2H), 4.60 (s, NH), 5.02 (t, 1H),
6.85 (d, 2H, Ar–H), 6.94 (d, 1H, Ar–H), 7.16 (d, 2H, Ar–H), 7.40 (d, 2H, Ar–H), 7.57 (t, 2H, Ar–H), 7.75 (s, 1H, Ar–H), 7.84 (d, 2H, Ar–H), 8.02 (d, 2H, Ar–H) (Plate 7.2.10); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): $\delta$ = 45.6, 55.3, 115.0, 119.4, 126.2, 128.2, 128.8, 129.0, 129.2, 133.3, 133.6, 136.5, 140.5, 150.4, 160.0, 197.6 (Plate 7.2.11); LC-MS (m/z): 336.35 (Plate 7.2.12); MF: C$_{21}$H$_{18}$ClNO.

iv) 3-(4-Bromophenyl)-1-phenyl-3-(phenylamino)propan-1-one (4d)

Brown solid, Yield 87%, m.p. 140-142$^\circ$C; IR (KBr, cm$^{-1}$): $\nu$ = 3396, 2958, 1660, 1605, 1495, 1265, 1024, 800 (Plate 7.2.13); $^{1}$H NMR (400 MHz, CDCl$_3$, ppm): $\delta$ = 3.44 (dd, 1H, $J$ = 4.4, 7.2 Hz), 3.47 (dd, 1H, $J$ = 2.8, 7.6 Hz), 4.58 (s, NH), 4.97 (dd, 1H, $J$ = 3.0, 6.5 Hz), 6.55 (dd, 2H, Ar–H), 6.70 (t, 1H, Ar–H), 7.10 (m, 2H, Ar–H), 7.43–7.48 (m, 4H, Ar–H), 7.56–7.58 (m, 2H, Ar–H), 7.89 (t, 2H, Ar–H), 7.92 (d, 2H, Ar–H) (Plate 7.2.14); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): $\delta$ = 46.0, 54.2, 113.9, 118.1, 126.2, 128.2, 128.7, 128.8, 129.2, 131.9, 133.6, 136.5, 142.1, 146.7, 161.5, 197.9 (Plate 7.2.15); LC-MS (m/z): 380.15 (Plate 7.2.16); MF: C$_{21}$H$_{18}$BrNO.

v) 3-(4-Fluorophenyl)-1-phenyl-3-(phenylamino)propan-1-one (4e)

Brown solid, Yield 88%, m.p. 110-111$^\circ$C; IR (KBr, cm$^{-1}$): $\nu$ = 3360, 2920, 1665, 1604, 1511, 1215, 1155, 1013, 837 (Plate 7.2.17); $^{1}$H NMR (400 MHz, CDCl$_3$, ppm): $\delta$ = 3.64 (d, 2H, $J$ = 5.2 Hz), 4.61 (s, NH), 5.03 (t, 1H), 6.73 (d, 2H, Ar–H), 6.83 (t, 1H, Ar–H), 7.01 (m, 2H, Ar–H), 7.43-7.47 (m, 4H, Ar–H), 7.56–7.59 (m, 2H, Ar–H), 7.89 (d, 2H, Ar–H) (Plate 7.2.18); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): $\delta$ = 45.3, 54.5, 115.6, 115.8, 122.8, 128.2, 128.6, 128.7, 129.2, 133.6, 136.5, 142.3, 148.6, 163.2, 197.6 (Plate 7.2.19); LC-MS (m/z): 320.60 (Plate 7.2.20); MF: C$_{21}$H$_{18}$FNO.
vi) 3-(4-Hydroxyphenyl)-1-phenyl-3-(phenylamino)propan-1-one (4f)

Yellow solid, Yield 91%, m.p. 170-171°C; IR (KBr, cm⁻¹): 
ν = 3265, 2931, 1649, 1605, 1578, 1512, 1221, 838 (Plate 7.2.21); 
¹H NMR (400 MHz, CDCl₃, ppm): δ = 3.31 (dd, 1H, J = 6.0, 13.2 Hz), 
3.51 (dd, 1H, J = 5.2, 13.2 Hz), 4.66 (s, NH), 5.40 (d, 1H, J = 4.0 Hz), 
6.92 (d, 2H, Ar–H), 7.01 (d, 1H, Ar–H), 7.54 (m, 2H, Ar–H), 7.58–7.61 
(m, 3H, Ar–H), 7.81 (d, 1H, Ar–H), 8.03 (d, 2H, Ar–H), 10.88 (s, 1H) 
(Plate 7.2.22); ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 45.1, 54.7, 115.9, 
116.1, 120.9, 127.7, 128.2, 128.5, 128.6, 130.5, 132.7, 137.5, 138.4, 
144.9, 158.1, 196.9 (Plate 7.2.23); LC-MS (m/z): 318.15 (Plate 7.2.24); 
MF: C₂₁H₁₉NO₂.

vii) 3-(4-Methoxyphenyl)-1-phenyl-3-(phenylamino)propan-1-one (4g)

White solid, Yield 94%, m.p. 149-150°C; IR (KBr, cm⁻¹): 
ν = 3370, 2931, 1660, 1600, 1501, 1260, 1178, 1035, 832 (Plate 7.2.25); 
¹H NMR (400 MHz, CDCl₃, ppm): δ = 3.85 (d, 1H, J = 0.8 Hz), 3.87 (d, 1H, 
J = 0.4 Hz), 3.88 (s, 3H, OCH₃), 4.53 (s, NH), 5.48 (d, 1H, J = 3.0 Hz), 
6.93 (d, 1H, Ar–H), 6.99 (t, 2H, Ar–H), 7.22 (t, 2H, Ar–H), 7.26 (d, 2H, 
Ar–H), 7.44 (d, 2H, Ar–H), 7.48 (t, 2H, Ar–H), 7.60 (t, 1H, Ar–H), 
7.93 (d, 2H, Ar–H) (Plate 7.2.26); ¹³C NMR (100 MHz, CDCl₃, ppm): 
δ = 46.8, 55.5, 55.6, 114.4, 120.9, 126.0, 128.4, 128.6, 129.1, 130.0, 
132.3, 138.5, 144.7, 147.5, 164.6, 198.6 (Plate 7.2.27); LC-MS (m/z): 
332.30 (Plate 7.2.28); MF: C₂₂H₂₁NO₂.

viii) 3-(2-Chlorophenyl)-1-phenyl-3-(phenylamino)propan-1-one (4h)

White solid, Yield 87%, m.p. 163-164°C; IR (KBr, cm⁻¹): 
ν = 3380, 3057, 2925, 1659, 1599, 1445, 1215, 1013, 749 (Plate 7.2.29); 
¹H NMR (400 MHz, CDCl₃, ppm): δ = 3.50 (dd, 1H, J = 6.5, 12.4 Hz), 
3.73 (dd, 1H, J = 3.2, 12.8 Hz), 4.60 (s, NH), 5.41 (m, 1H), 6.76 (t, 1H, Ar–H),
7.35 (t, 2H, Ar–H), 7.47 (d, 2H, Ar–H), 7.52 (t, 1H, Ar–H), 7.64 (t, 2H, Ar–H), 7.79 (d, 1H, Ar–H), 7.91 (t, 1H, Ar–H), 7.97 (d, 2H, Ar–H), 8.04 (d, 1H, Ar–H) (Plate 7.2.30); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): δ = 43.4, 53.2, 119.6, 127.8, 128.9, 129.7, 129.8, 132.9, 133.3, 135.5, 137.9, 140.7, 143.0, 149.2, 161.2, 198.1 (Plate 7.2.31); LC-MS (m/z): 335.20, 337 [M+2] (Plate 7.2.32); MF: C$_{21}$H$_{18}$ClNO.

ix) 3-(2-Nitrophenyl)-1-phenyl-3-(phenylamino)propan-1-one (4i)

Yellow solid, Yield 84%, m.p. 120–122°C; IR (KBr, cm$^{-1}$): ν = 3360, 2926, 1671, 1600, 1528, 1435, 1347, 1194, 1079, 767 (Plate 7.2.33); $^1$H NMR (400 MHz, CDCl$_3$, ppm): δ = 3.46 (d, 1H, J = 7.2 Hz), 3.50 (d, 1H, J = 7.0 Hz), 4.60 (s, NH), 5.43 (s, 1H), 7.26 (t, 1H, Ar–H), 7.38–7.77 (d and t, 7H, Ar–H) 7.96 (t, 1H, Ar–H), 8.10 (t, 1H, Ar–H), 8.32 (d, 1H, Ar–H) (Plate 7.2.34); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): δ = 43.6, 54.2, 119.9, 127.9, 129.8, 129.9, 130.8, 131.7, 133.0, 133.5, 137.8, 138.3, 138.7, 144.0, 149.1, 160.4, 198.9 (Plate 7.2.35); LC-MS (m/z): 347.05 (Plate 7.2.36); MF: C$_{21}$H$_{18}$N$_2$O$_2$.

x) 3-(3-Methoxyphenyl)-1-phenyl-3-(phenylamino)propan-1-one (4j)

Brown solid, Yield 92%, m.p. 157–159°C; IR (KBr, cm$^{-1}$): ν = 3326, 3052, 2920, 1665, 1594, 1495, 1260, 1046, 778 (Plate 7.2.37); $^1$H NMR (400 MHz, CDCl$_3$, ppm): δ = 3.89 (s, 3H, OCH$_3$), 3.92 (d, 2H), 5.00 (s, NH), 5.43 (s, 1H), 7.27–7.83 (d and t, 10H, Ar–H), 8.05 (d, 1H, Ar–H), 8.45 (s, 1H, Ar–H) (Plate 7.2.38); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): δ = 44.5, 55.4, 55.5, 120.8, 126.1, 128.5, 128.6, 129.1, 129.3, 129.7, 129.9, 130.0, 132.7, 137.8, 144.7, 152.3, 160.3, 198.6 (Plate 7.2.39); LC-MS (m/z): 332.30 (Plate 7.2.40); MF: C$_{22}$H$_{21}$NO$_2$. 
All the synthesized compounds are unambiguously established on the basis of their spectral analysis by IR, $^1$H, $^{13}$C NMR and LC-MS and melting points.

### 7.2.1.17. Reusability of the catalyst

The reusability of the catalyst is one of the most important criteria and makes it useful for the commercial applications. Thus the recovery and reusability of Ag-Au/SiO$_2$ nanoparticles are investigated. The recycled catalyst has been examined (Table 7.2.3) and there is no appreciable loss in its catalytic activity even after 4 runs.

<table>
<thead>
<tr>
<th>Number of runs</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield* (%)</td>
<td>90</td>
<td>90</td>
<td>89</td>
<td>89</td>
</tr>
</tbody>
</table>

*Yield are isolated.

### 7.2.2. Conclusion

In conclusion, a novel Ag-Au/SiO$_2$ catalyzed microwave assisted Mannich reaction of various substituted aldehydes, amines and ketones were examined. It offers several advantages such as easy, economic and faster method for the synthesis of $\beta$-amino carbonyl compounds. The Ag-Au/SiO$_2$ catalyst can be recovered and reused making this procedure more environment friendly.
Selective BNPs and selective bimetal loaded SiO$_2$ catalysts *viz.*, a) Ag-Pt, b) Ag-Au, c) Ag-Pd, d) Ag-Pt/SiO$_2$ and e) Ag-Au/SiO$_2$ were synthesized and characterized by UV-visible spectra, X-ray diffraction (XRD), high-resolution scanning electron microscopy (HR-SEM), field-emission scanning electron microscopy (FE-SEM), energy dispersive X-ray spectrometry (EDX), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HR-TEM), atomic force microscopy (AFM), diffuse reflectance spectra (DRS), dynamic light scattering (DLS), zeta potential (ZP) analysis, photoluminescence (PL) spectra, Brunauer-Emmett-Teller (BET) surface area measurements, X-ray photoelectron spectroscopy (XPS) and density functional theory (DFT) methods. The important applications were evaluated for the prepared BNP based materials.

The key findings are summarized as follows.

### 8.1. SYNTHESIS, CHARACTERIZATION OF Ag-Pt CORE-SHELL BIMETALLIC NANOPARTICLES AND ITS APPLICATION IN SENSING OF ADENINE AND URIC ACID

#### 8.1.1. Synthesis and characterization of Ag-Pt BNPs

Ag-Pt BNPs were synthesized *via* chemical reduction method. TEM studies of Ag-Pt BNPs suggested core shell structured spherical nanoparticles. The average diameter of the Ag-Pt BNPs were