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Electronic supplementary information (ESI)

Exploration of magnetically separable $Ag@Ag_xNi_y$ core/graded-alloy-shell nanostructures

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Experimental

Chemicals and materials: Nickel chloride hexahydrate ($NiCl_2.6H_2O$, 99.9%) and Silver chloride (AgCl, 99.9%) were from Sigma Aldrich, USA. Hydrazine hydrate ($N_2H_4.H_2O$, 99%) was purchased from Thomas Baker, India. Sodium hydroxide pellets (NaOH), Sodium Sulphate (Na_2SO_4), Sodium Chloride (NaCl) were purchased from Merck, India. Double distilled water was used in all experiments. Indole, 5-Bromoindole, Benzaldehyde, 4-chlorobenzaldehyde, 4-methoxybenzaldehyde, Pyrollidine, N-methylaniline, Sodium sulphate, Sodium chloride have been purchased from Spectrochem. All chemicals were used as received without any further purification.

Hydrothermal synthesis of $Ag@Ag_xNi_y$ core@graded-alloy-shell (CGAS) nanostructures: In a typical synthesis procedure, $NiCl_2.6H_2O$ (0.75 mmol) and AgCl (0.75 mmol) were added to 35 mL of double distilled water followed by addition of CTAB as surfactant. Then pH of the solution was maintained (~10) by addition of 0.5g of NaOH and the whole reaction mixture was stirred for next 30 minutes. Then Hydrazine hydrate (4 mL) was added dropwise while stirring. After vigorous stirring of 30 minutes the resulting reaction mixture was transferred in a stainless steel hydrothermal reaction autoclave vessel (50 mL) with Teflon lining and maintained the vessel at 180 °C for 6 h in a PID controlled oven with controlled heating rate and then cooled to

room temperature naturally. The obtained black product was centrifuged and washed with water/ethanol for three times. The obtained nanoparticles was either redispersed in suitable solvents (such as ethanol or water) or dried in air at 40 °C for 4 h for further use. Similar reaction protocol was used for synthesis of 2h and 4h sample except reaction at 180 °C for 2 h and 4 h respectively.

Synthesis of Ag@Ni core shell NPs: Core shell NPs were separately synthesized following a reported method[1] with minor modifications. In a typical synthesis, 0.4 mmol $Ni(OCOCH_3)_2.4H_2O$ and 0.1 mmol $AgNO_3$ was added to 6 ml of Oleylamine into a three necked round bottom flask equipped with condenser, temperature controller, and magnetic stirring bar. The reaction mixture was stirred and degassed at 80^0 ^oC for 30 minutes. After that mixture of 0.2 mmol triocytlphosphine (TOP) and 0.5 ml Oleylamine was injected into reaction mixture under N_2 environment. The resulting solution was then slowly heated up to a temperature of 200 ^oC and aged for next 40 min under N_2. After the reaction, the mixture was cooled to room temperature naturally and the product was purified by precipitation with ethanol. The as obtained black precipitate was centrifuged and washed with ethanol for three times and finally dispersed in toluene for further characterizations. A fraction of the sample was dried at room temperature for the study of various catalytic activities.

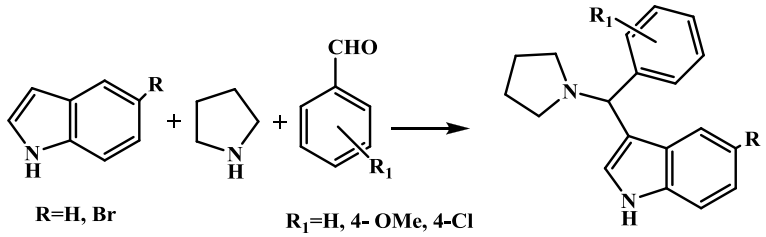
Hydrothermal synthesis of Ni NPs: In a typical synthesis procedure, $NiCl_2.6H_2O$ (1.5 mmol) was added to 35 mL of double distilled water followed by addition of CTAB (4 mmol) as surfactant. Then pH of the solution was maintained (~10) by addition of 0.5g of NaOH and the whole reaction mixture was stirred for next 30 minutes. Then Hydrazine hydrate (4 mL) was added dropwise while stirring. After vigorous stirring of 30 minutes the resulting reaction mixture was transferred in a stainless steel hydrothermal reaction autoclave vessel (50 mL) with Teflon lining and maintained the vessel at 180 °C for 6 h in a PID controlled oven with controlled heating rate and then cooled to room temperature naturally. The obtained black product was centrifuged and washed with water/ethanol for three times. The obtained nanoparticles was either redispersed in suitable solvents (such as ethanol or water) or dried in air at 40 °C for 4 h for further use.

Hydrothermal synthesis of Ag NPs: Ag NPs were synthesized following an earlier reported solvothermal method.[2] In a typical synthesis, 444 mg of PVP was added to 40 mL of PEG and

stirred at 80 °C till the solution become transparent. After that 1 mL of 0.5 M $AgNO_3$ aqueous solution was added. While stirring and heating process, the color of the solution changed from colorless to light yellow. Then, the reaction mixture was transferred to 80 mL Teflon-sealed autoclave and heated at 200 °C for next 24 h. After the reaction was completed, the solution was cooled in air to room temperature and purified by several washings. Finally, the sample was dried in oven at room temperature for further use.

Catalytic synthesis of 3-substituted indole: Catalytic Applications of Ag@Ag_xNi_y, Ag, Ni and simple Ag@Ni Core/shell nanomaterial. The catalytic activity of CGAS was investigated in the synthesis of various 3-substituted indoles. Primarily, the catalytic reaction of CGAS was investigated in a model reaction of indole, benzaldehyde, and pyrrolidine to obtain 3-amino alkylated indole using 10 mg of catalyst in water at 25 ^oC (Scheme S1). The reaction did not proceed in the absence of the catalyst.

In order to study the nanocatalyts, a variety of indole substrates, aromatic aldehydes, and secondary amines were used to obtain various 3-amino alkylated indoles. It is noteworthy that all the reactions proceeded smoothly and generated 3-amino alkylated indoles in good yields (83−93%) within 30 min of reaction time. Furthermore, CGAS is the best catalytic system in terms of activity, selectivity, and greenness of the protocol, with negligible waste generation from the reaction mixture.



Scheme S1: Model reaction of indole, benzaldehyde and pyrrolidine in water (1.5 mL) at 25 ^oC in presence of 10 mg CGAS NPs catalyst.

General Procedure for Synthesis of 3-Amino Alkylated indoles. A mixture of indole (1 mmol), aldehydes (1 mmol), secondary amines (1 mmol), catalyst (10 mg), and water (1.5 mL) were taken in a 10 mL round-bottomed flask and stirred at room temperature (25 ^oC) for 30 min. After completion of the reaction (monitored by TLC), water was decanted from reaction mixture

and EtOH was added to the reaction mixture followed by separation of the solid catalyst magnetically. The organic layer was dried over Na_2SO_4, and the solvent was removed under reduced pressure. The obtained crude product was purified by recrystallization from diethyl ether/n-hexane and yield was measured. All compounds were characterized by melting point, FTIR, NMR and mass.

5-Bromo-3-(phenyl(pyrrolidin-1-yl)methyl)-1H-indole (A3-1): Light yellow solid; mp 146–148 ^oC; IR (KBr) 3423, 2959, 2809, 1565, 1450, 1108, 746 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.12 (br s, 1H), 7.94 (s, 1H), 7.52 (d, *J* = 7.6 Hz, 2H), 7.27–7.16 (m, 6H), 4.52 (s, 1H), 2.53–2.34 (m, 4H), 1.78 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 143.87, 134.79, 128.49, 128.25, 127.71, 126.98, 124.85, 123.42, 122.21, 118.99, 112.87, 112.67, 68.07, 53.90, 23.62; LCMS (ES): Calculated 354.0732, found 355.06434;

3-((4-Methoxyphenyl)(pyrrolidin-1-yl)methyl)-1H-indole (A3-2): White solid; mp170–172 ^oC; IR (KBr) 3419, 3045, 2827, 1489, 1341, 1214, 1158, 749 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.06 (br s, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.23 (t, *J* = 8.0 Hz, 2H), 7.06 (t, *J* = 8.0 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 2H), 4.55 (s, 1H), 3.74 (s, 3H), 2.54–2.49 (m, 4H), 1.76 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 158.31, 136.63, 136.21, 128.84, 126.57, 121.94, 121.88, 119.84, 119.42, 113.60, 111.12, 77.44, 77.12, 76.81, 67.39, 55.28, 53.82, 23.62, 1.13; LCMS (ES): Calculated 306.1732, found 306.1678;

3-(phenyl(pyrrolidin-1-yl)methyl)-1H-indole (A3-6). White solid; mp: 145-147 ^oC; IR (KBr): 3415, 2965, 2824, 1601, 1494, 1455, 1097, 742 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 1.80 (s, 4H), 2.63 (d, 4H, *J*=6.5 Hz), 4.66 (s, 1H), 7.06- 7.15(m, 4H), 7.21-7.26 (m, 3H), 7.56 (d, 2H, *J*=7.2Hz), 7.76 (d, 1H,*J*=7.5Hz), 8.22 (br, s, 1H); ^{13}C NMR (100 MHz $CDCl_3$) δ (ppm) 128.33, 127.82, 126.77, 122.16, 121.98, 119.74, 119.49, 111.15, 77.43, 77.11, 76.80, 68.12, 53.84, 23.63; LCMS (ES): Calculated 276.1626; found: 276.1589;

5-Bromo-3-((4-methoxyphenyl)(pyrrolidin-1-yl)methyl)-1H-indole (A3-8): Off white solid; mp 149 ^oC; IR (KBr) 3423, 2964, 2956, 2823, 1609, 1510, 1458, 1096, 758 cm^{-1}; ^1H NMR (400 MHz, CDCl3) δ (ppm) 8.17 (br s, 1H), 7.92 (s, 1H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.25-7.14 (m, 5H), 6.80 (d, *J* = 8.4 Hz, 2H), 4.46 (s, 1H), 3.75 (s, 3H), 2.51-2.46 (m, 4H), 1.77 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 158.41, 136.35, 134.83, 128.74, 128.25, 124.83, 123.02, 122.33,

119.66, 113.72, 112.58, 102.34, 67.34, 55.30, 53.85, 23.60; LCMS (ES): Calculated 384.0837; found: 383.0751;

N-[(4-Chlorophenyl)(1H-indol-3-yl)methyl]-N-methyl benzene amine (A3-9): Brown solid; mp 182 ^{o}C; IR (KBr) 3411, 2923, 2951, 1611, 1517, 1487, 1045, 745 cm^{-1}; ^{1}H NMR (400 MHz, CDCl3): δ (ppm) 7.97 (s, 1H), 7.35 (d, *J* = 4.0 Hz, 2H), 7.17-7.14 (m 5H), 7.00 (d, *J* = 8.0 Hz, 3H), 6.65(s, 1H), 6.55 (d, *J* = 8.0 Hz, 2H), 5.52 (s, 1H), 2.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 143.53, 143.04, 136.75, 130.35, 130.16, 129.71, 129.13, 128.45, 128.33, 125.39, 123.69, 122.16, 119.90, 119.42, 112.49, 111.19, 51.84, 34.77, 29.80; LCMS (ES): Calculated 346.9975; found 347.1327;

Sample characterization: The crystal structure and purity of as synthesized Ag@Ag_xNi_y core shell NPs were characterized by powder X-ray diffraction (XRD) patterns recorded on a Bruker D8 Advance X-ray diffractometer by using Cu Kα as a radiation source at room temperature. Transmission electron microscopy (TEM), high resolution TEM (HRTEM) images and electron dispersive spectroscopy (EDS, both spot and line scan mode) analysis were performed from a Philips Technai G^2 F30 transmission electron microscope operating at an accelerating voltage of 300 kV equipped with an energy dispersive X-ray spectroscopy (EDAX) attachment. The high angle annular dark field imaging and scanning transmission electron microscopy (HAADF-STEM) analyses were also performed with same instrument. TEM samples were made by putting a drop of sample dispersion in ethanol on a carbon coated copper grid and letting the solvent evaporate. Magnetic properties of the nanoparticle samples were studied by a vibrating sample magnetometer (MicroSense EV9) at room temperature (25 °C). ^{1}H and ^{13}C NMR spectra were recorded in DMSO on a Bruker Avance 400 MHz spectrometer. FTIR was recorded in Perkin Elmer (Spectrum-RXI-59333) spectrometer. XPS measurements were made using a custom-built ambient pressure XPS system from Prevac equipped with a VG Scienta monochromator (MX650) using an Al Ka anode (1486.6 eV). The energy of the photoelectrons was determined using a VG Scienta R3000HP differentially pumped analyser. The spectra were recorded at a pass energy of 50 eV. Mass spectra were recorded on an Agilent 6200 series TOF/6500 series instrument by dissolving the samples in methanol.

Table S1. Various control reactions done for synthesis of CGAS nanostructures.

Sample code	Precursors	Solvent	Surfactant	Reductant	Temperature and time
NAH-1	Nickel chloride hexahydrate + Silver chloride (1:1)	Ethanol + water (1:1)	No surfactant	Hydrazine hydrate	125 °C, 6 h
NAH-2	Nickel chloride hexahydrate + Silver chloride (1:1)	water	Polyethylene glycol	Hydrazine hydrate	180 °C, 6 h
NAH-3	Nickel acetate tetrahydrate + Silver nitrate (1:1)	Water	SDS	Sodium borohydride	150 °C, 8 h
NAH-4	Nickel chloride hexahydrate + Silver chloride (1:1)	Water	SDS	Hydrazine hydrate	150 °C, 8 h
NAS-1	Nickel chloride hexahydrate + Silver chloride (1:1)	Ethylene glycol	Polyethylene glycol	Hydrazine hydrate	150 °C, 8 h
NAS-2	Nickel chloride hexahydrate + Silver chloride (1:1)	Ethylene glycol	No surfactant	Hydrazine hydrate	150 °C, 8 h
NAS-3	Nickel acetate tetrahydrate + Silver nitrate (1:1)	Oleylamine	No surfactant	Sodium borohydride	200 °C, 2 h
NAS-4	Nickel nitrate hexahydrate + Silver nitrate (1:1)	Ethylene glycol	No surfactant	Hydrazine hydrate	150 °C, 8 h
NAS-5	Nickel acetate tetrahydrate + Silver nitrate (1:1)	Ethylene glycol	No surfactant	Hydrazine hydrate	150 °C, 8 h

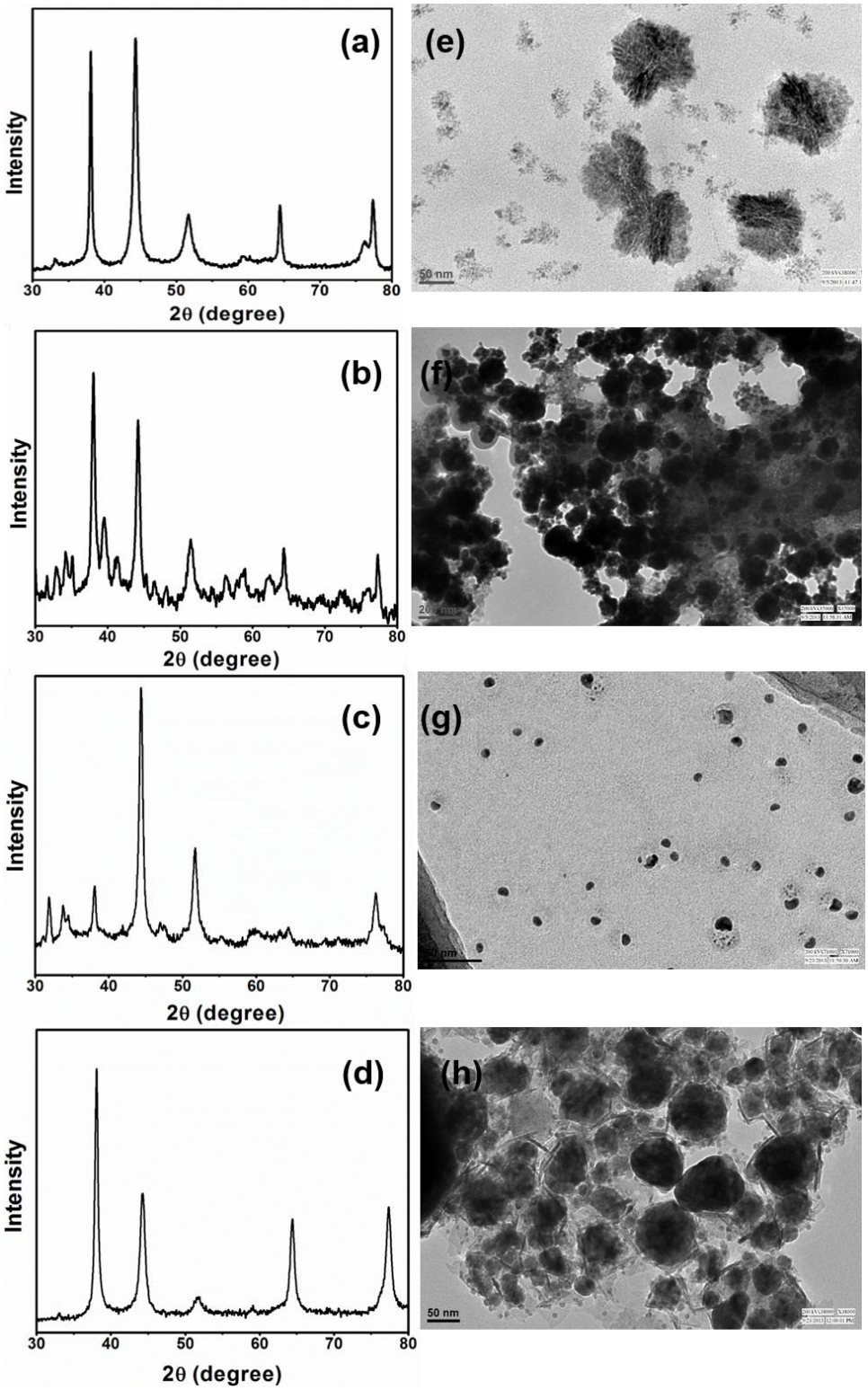


Fig. S1 (a-d) Powder XRD and (e-h) low resolution TEM images of NAH-1, NAH-2, NAH-3 and NAH-4.

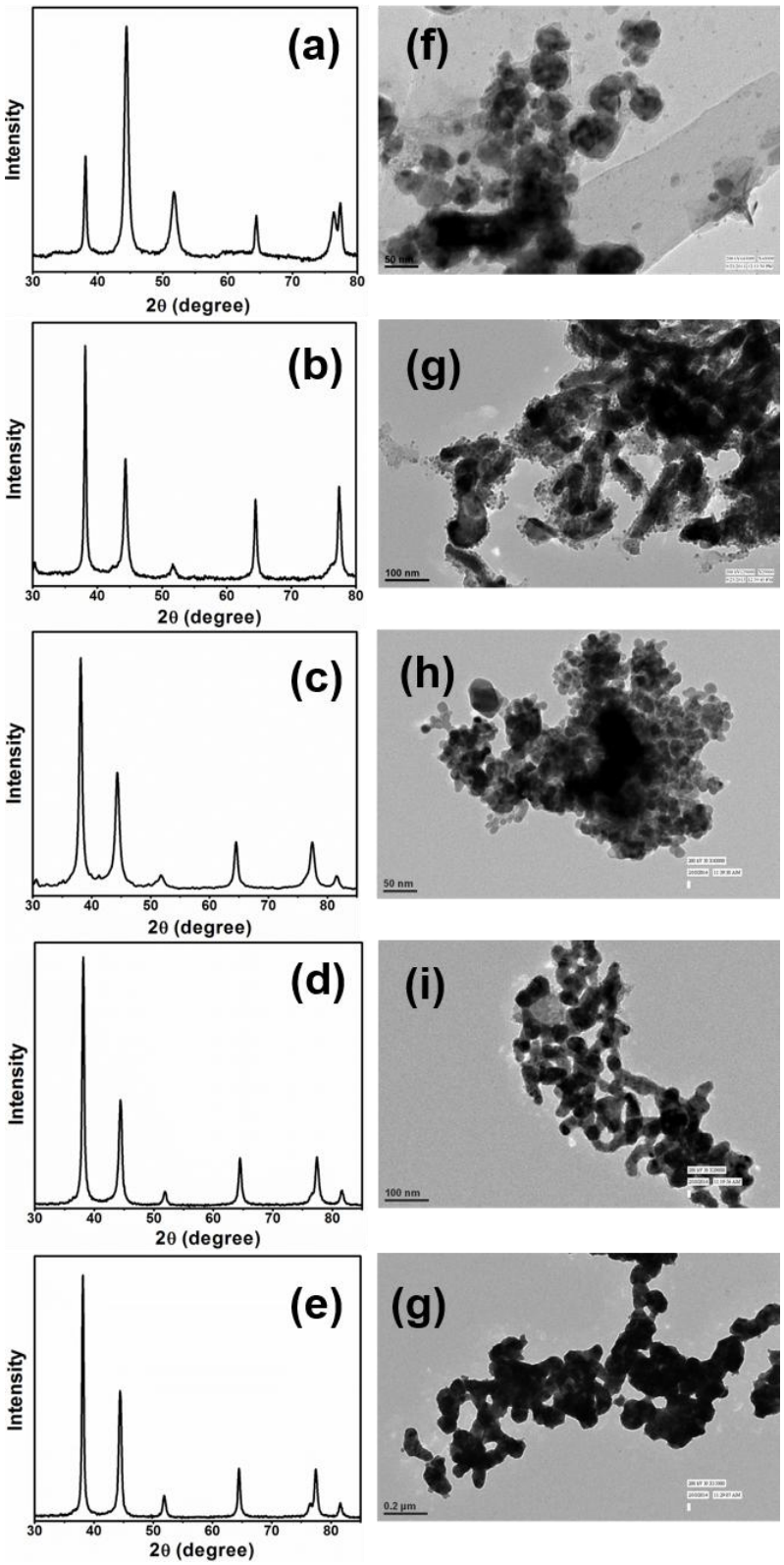


Fig. S2 (a-e) Powder XRD and (f-j) low resolution TEM images of samples NAS-1, NAS-2, NAS-3, NAS-4 and NAS-5.

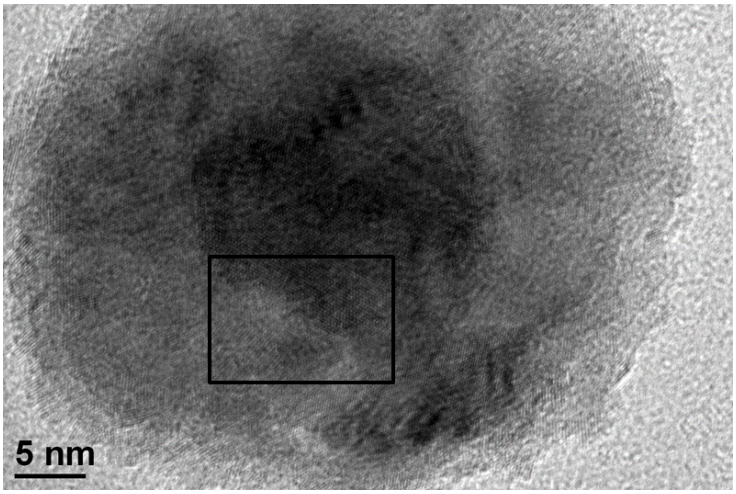


Fig. S3. High resolution TEM image of single Ag@Ag_xNi_y core/graded-alloy-shell nanoparticle.

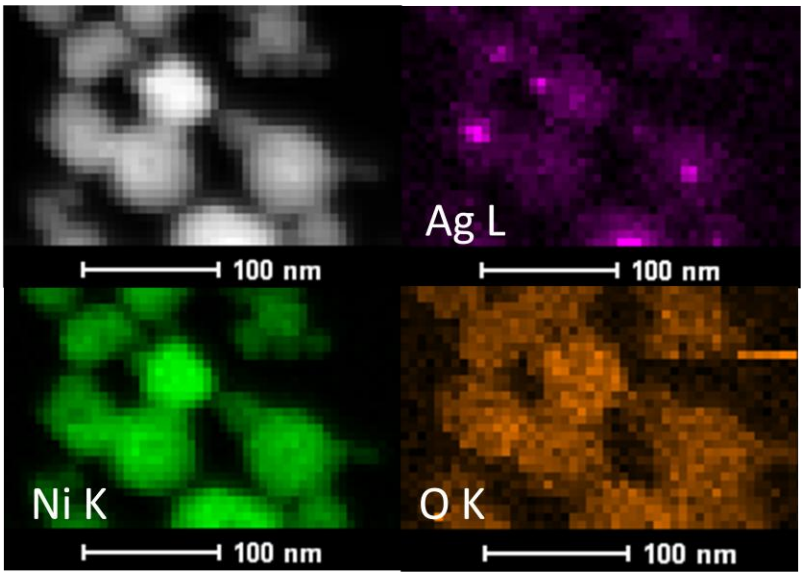


Fig. S4. Ag, Ni and O elemental maps from the same group obtained by filtering the Ag L edge, Ni K edge and O K edge, from the first HAADF image.

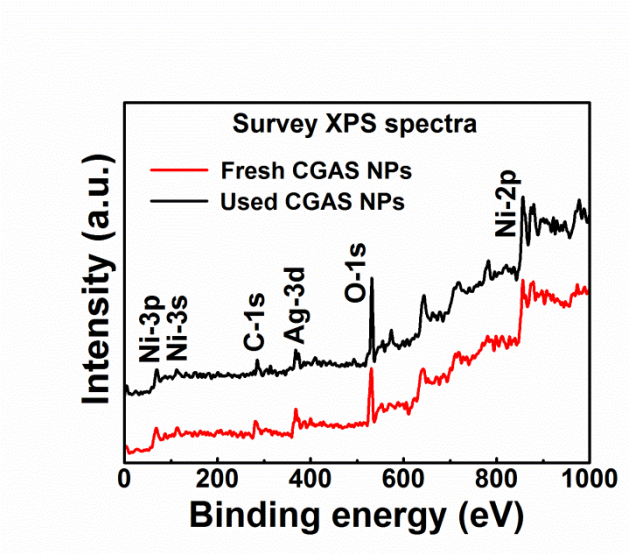


Fig. S5. Wide scan XPS survey spectra of $Ag@Ag_xNi_y$ CGAS.

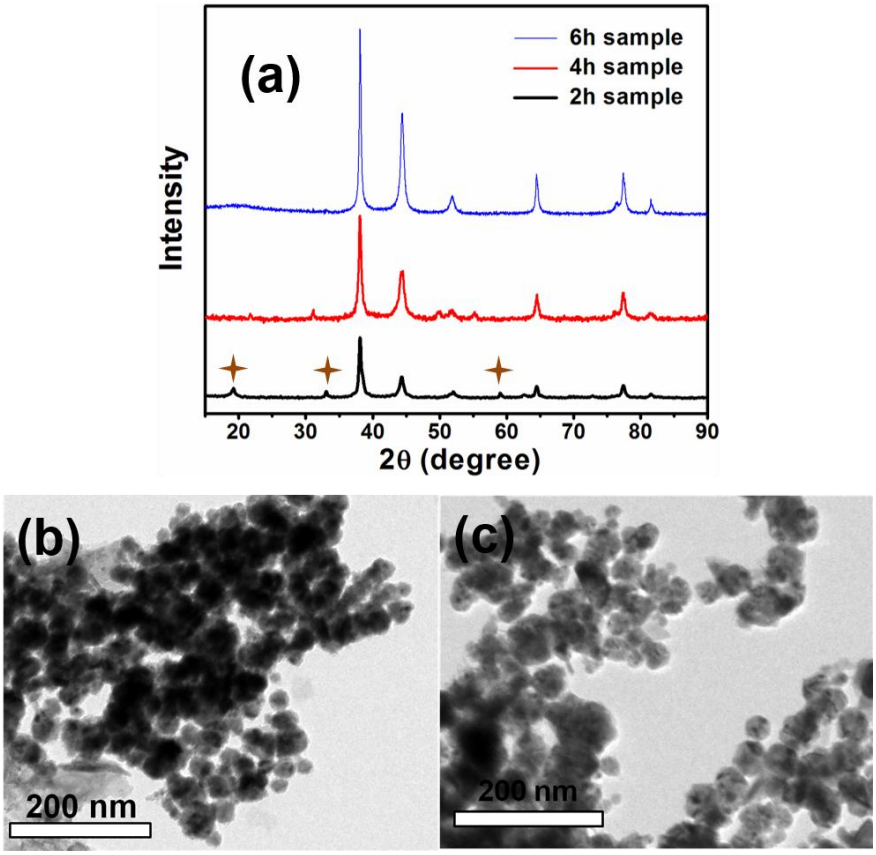


Fig. S6. (i) XRD (peak highlight with star* represent NiO and $Ni(OH)_2$ impurity) and low resolution TEM of (b) 2h, (c) 4h $Ag@Ag_xNi_y$ core shell nanoparticle sample.

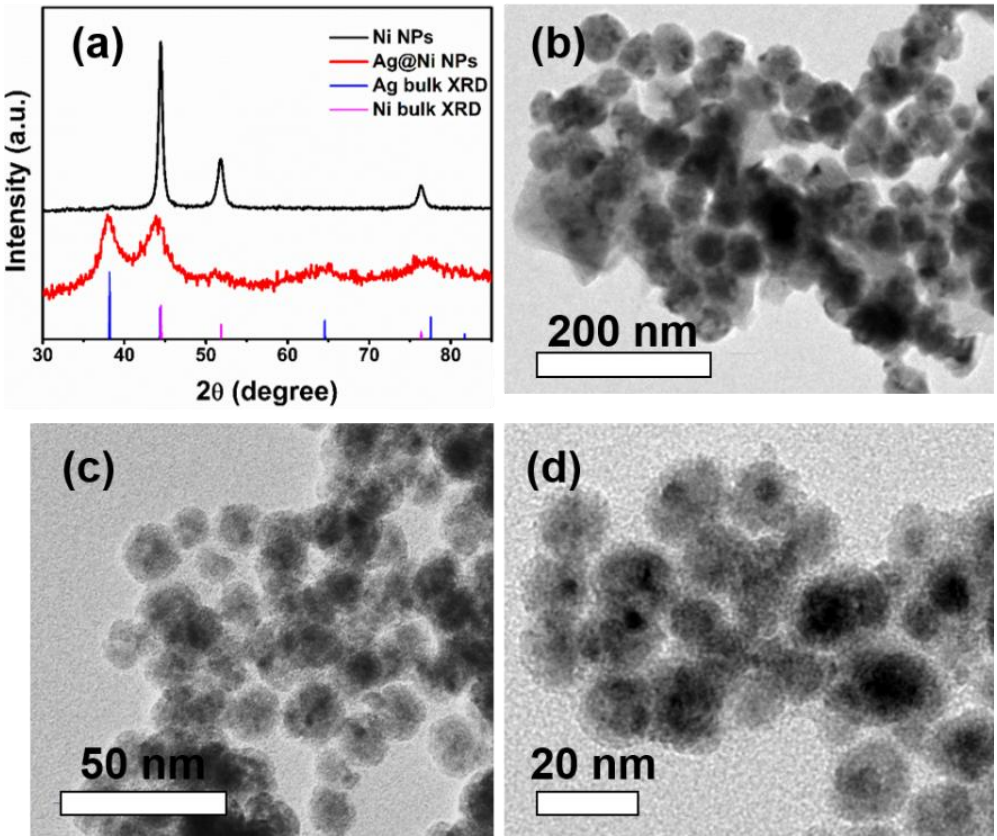
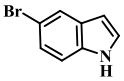
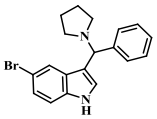
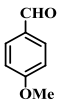
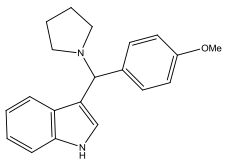
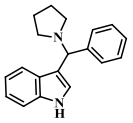
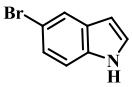
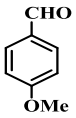
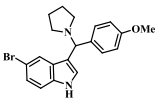
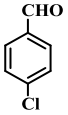
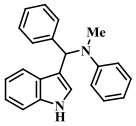


Fig. S7. (a) XRD pattern of Ni and Ag@Ni NPs. Low resolution TEM analysis of (b) Ni NPs and (c-d) simple Ag@Ni core/shell NPs.

Table S2. $Ag@Ag_xNi_y$ CGAS NPs catalysed (10 mg) synthesis of 3-amino alkylated indoles with absolute selectivity (>99.9%) at 25 ^oC in water in one pot reaction condition.

Entry	Indole	Aldehyde	Amine	Product	Yield (%)
1					89
2					90

3					92
4					87
5					85

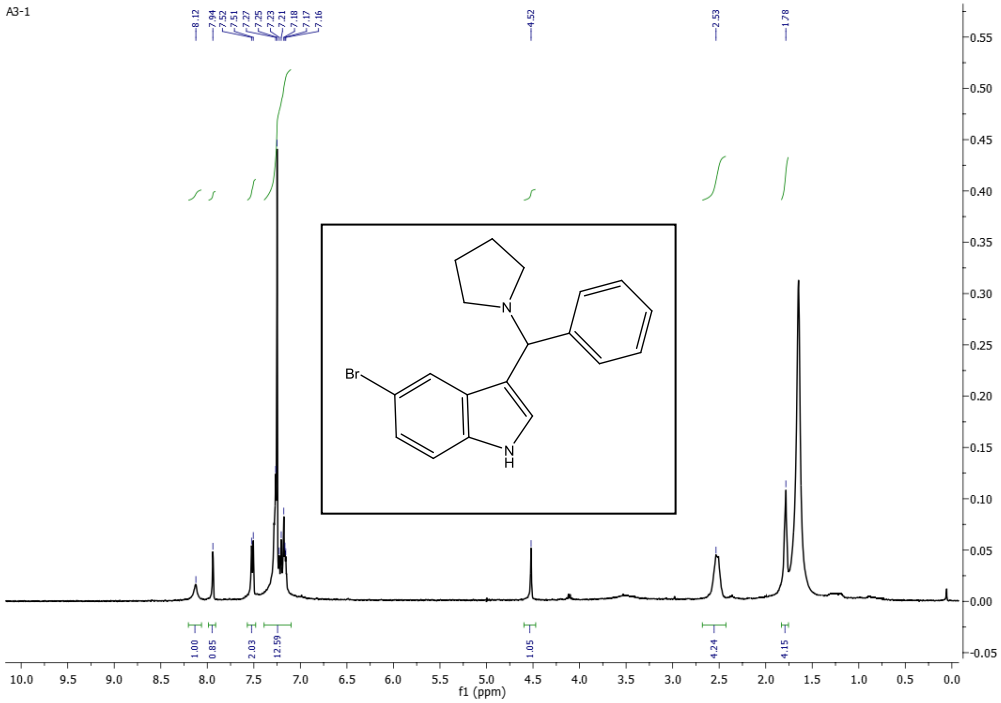


Fig. S8. ^{1}H NMR of 5-Bromo-3-(phenyl(pyrrolidin-1-yl)methyl)-1H-indole.

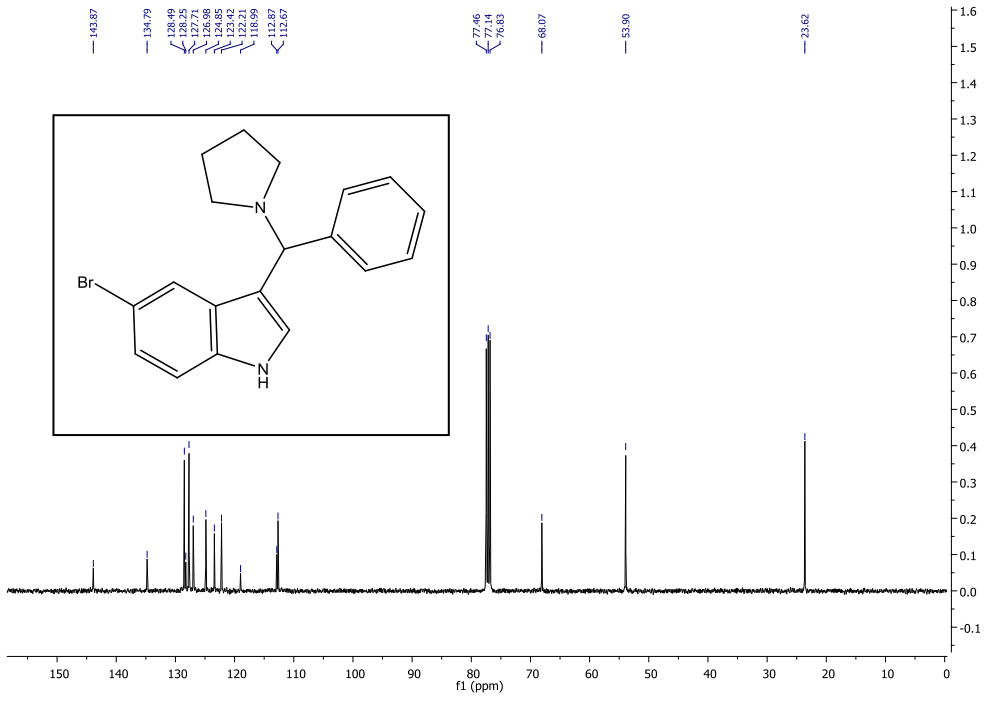


Fig. S9. ^{13}C NMR of 5-Bromo-3-(phenyl(pyrrolidin-1-yl)methyl)-1H-indole.

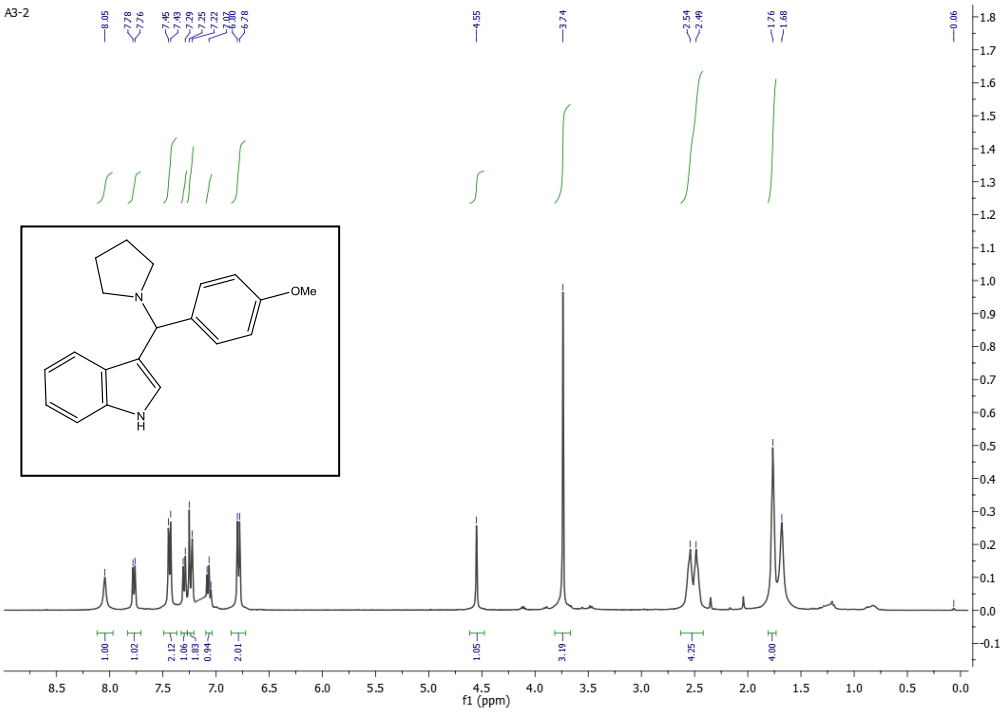


Fig. S10. ^{1}H NMR of 3-((4-Methoxyphenyl)(pyrrolidin-1-yl)methyl)-1H-indole.

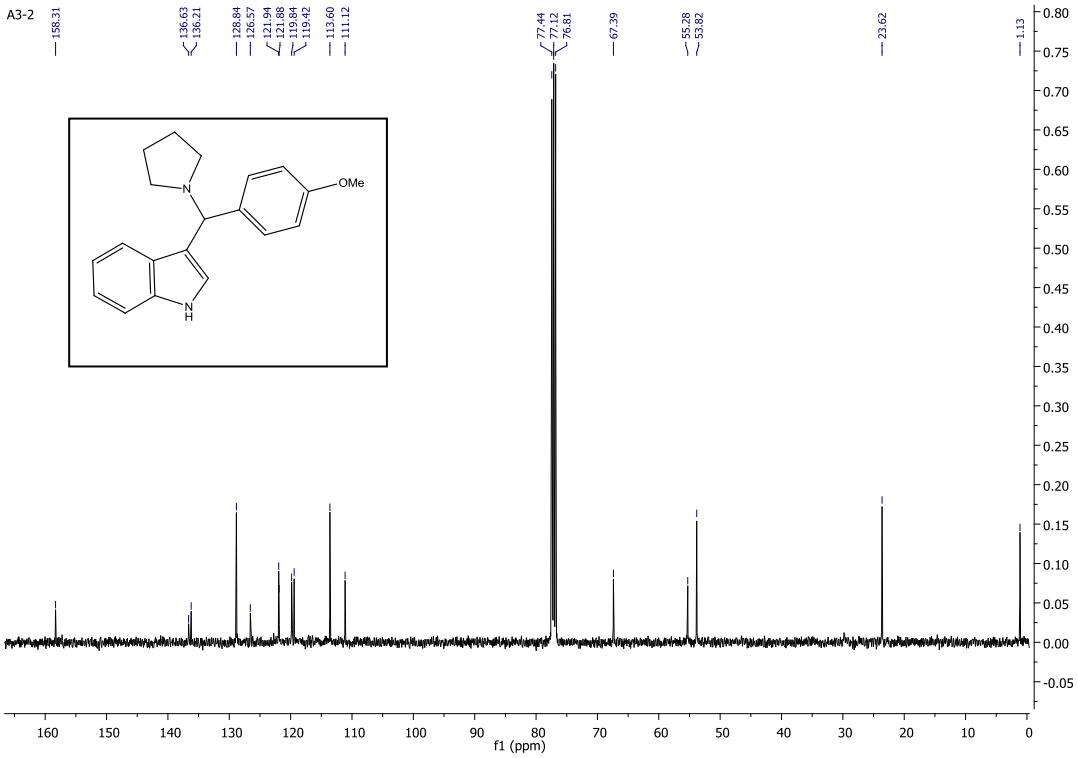


Fig. S11. ^{13}C NMR of 3-((4-Methoxyphenyl)(pyrrolidin-1-yl)methyl)-1H-indole.

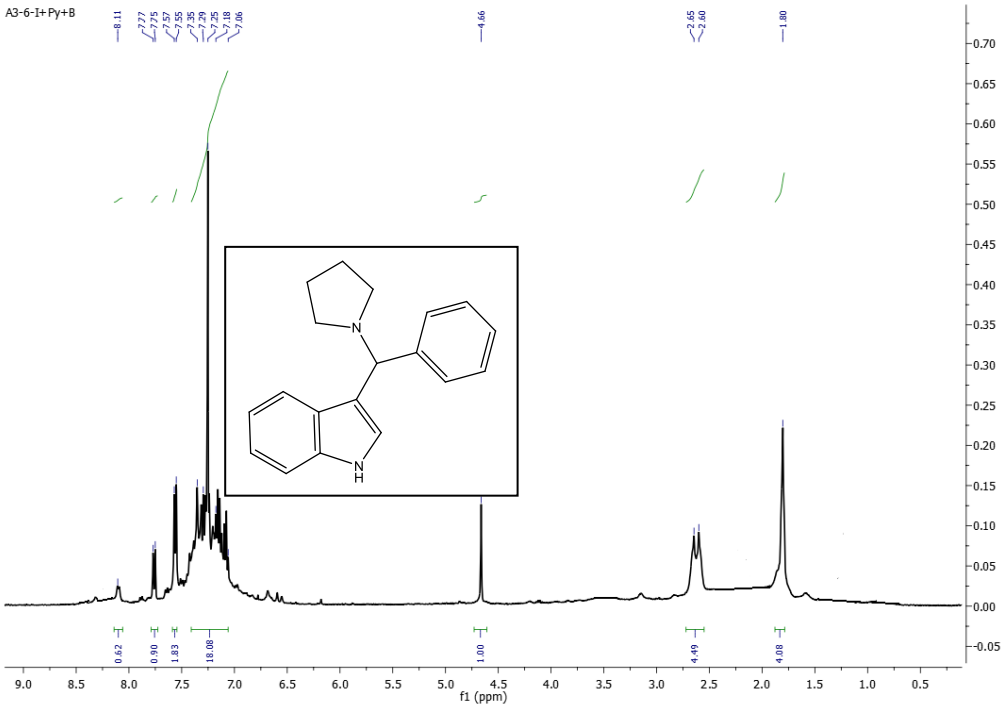


Fig. S12. ^{1}H NMR of 3-(Phenyl(pyrrolidin-1-yl)methyl)-1H-indole.

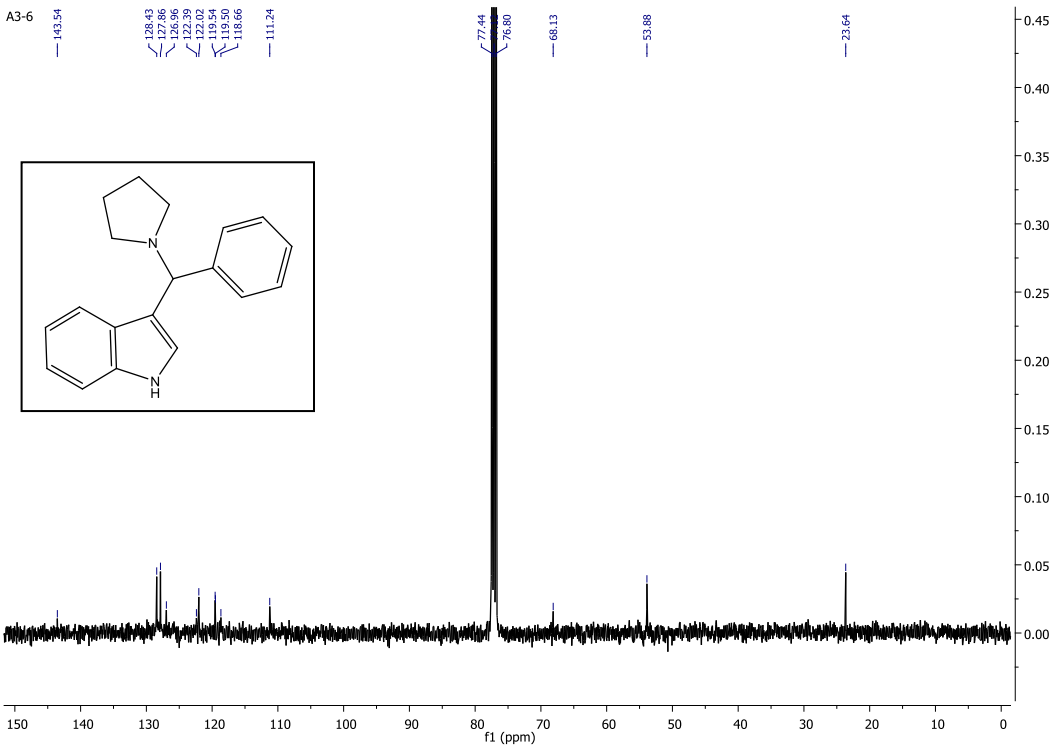


Fig. S13. ^{13}C NMR of 3-(Phenyl(pyrrolidin-1-yl)methyl)-1H-indole.

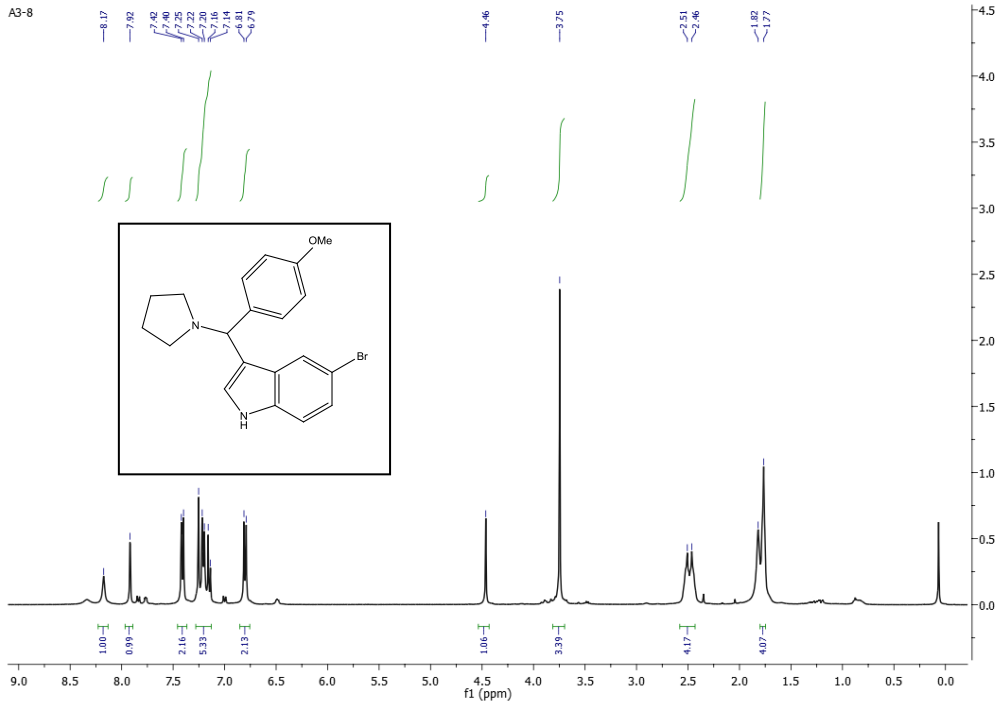


Fig. S14. ^{1}H NMR of 5-Bromo-3-((4-methoxyphenyl)(pyrrolidin-1-yl)methyl)-1H-indole.

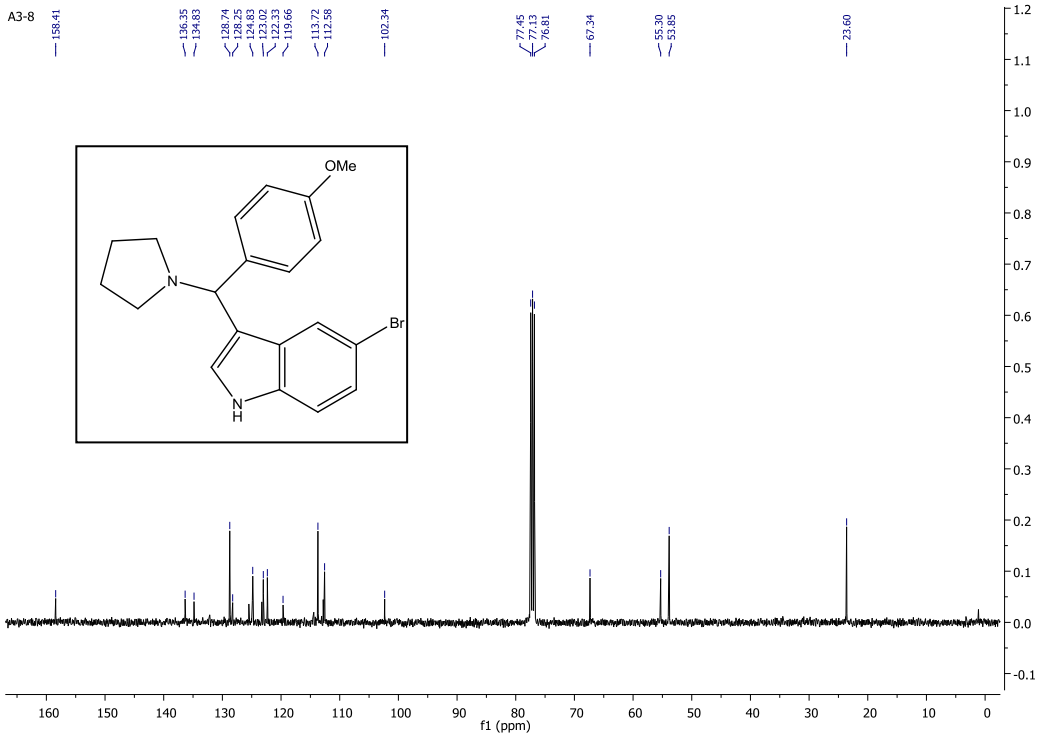


Fig. S15. ^{13}C NMR of 5-Bromo-3-((4-methoxyphenyl)(pyrrolidin-1-yl)methyl)-1H-indole.

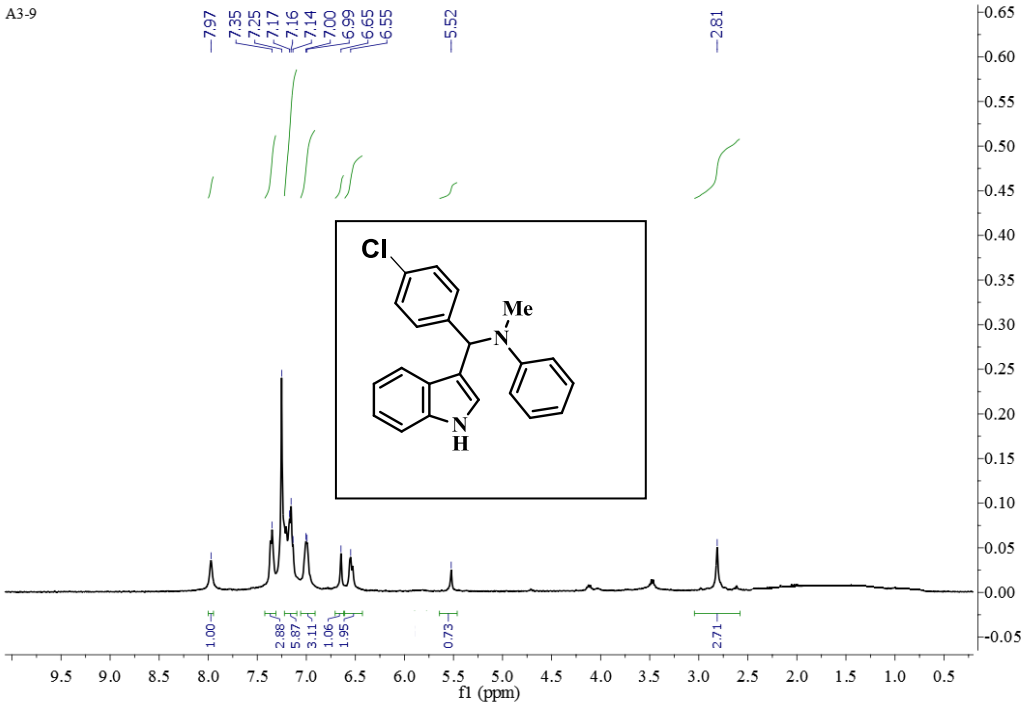


Fig. S16. ^{1}H NMR of N-[(4-Chlorophenyl)(1H-indol-3-yl)methyl]-N-methyl benzene amine.

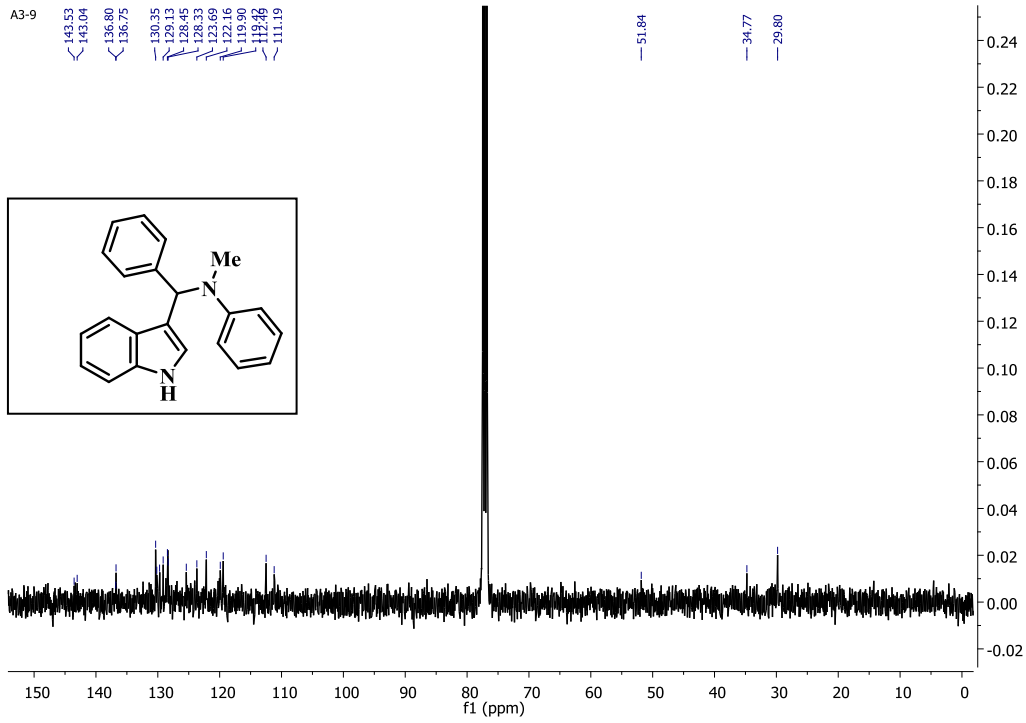


Fig. S17. ^{13}C NMR of N-[(4-Chlorophenyl)(1H-indol-3-yl)methyl]-N-methyl benzene amine.

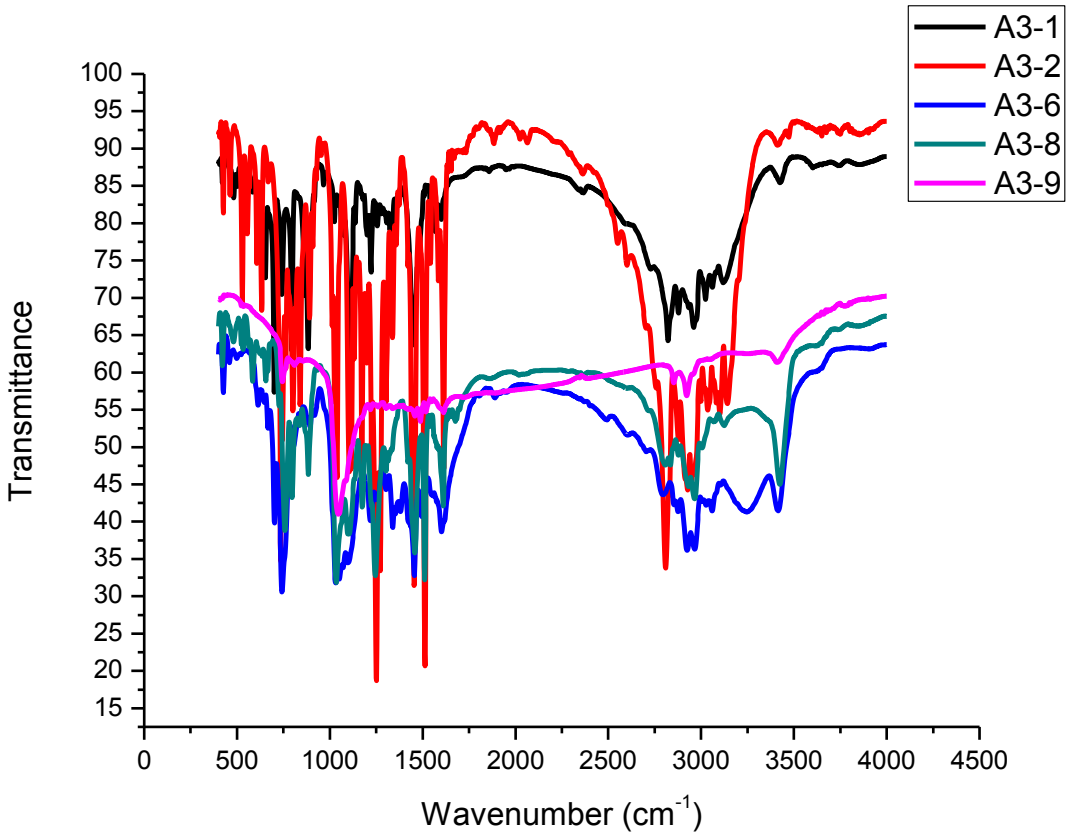


Fig. S18. FTIR spectra of as synthesized 3-substituted indoles.

References.

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