Supplementary information

ZnO nanoparticle-βcyclodextrin: a recyclable heterogeneous catalyst for synthesis of 3- aryl-4H-benzo[1,4]thiazin-2-amine in water

Hozeyfa Sagir\textsuperscript{a}, Rahila\textsuperscript{a}, Pragati Rai\textsuperscript{a}, Prashant Kumar Singh\textsuperscript{b} and I.R. Siddiqui\textsuperscript{*a}

\textsuperscript{a}Laboratory of Green Synthesis, Department of Chemistry, University of Allahabad, Allahabad-211002, India

\textsuperscript{b}Nanotechnology Application Centre, University of Allahabad, Allahabad-211002, India

*Corresponding author

E-mail address: dr.irsiddiqui@gmail.com ; Tel.: +91-9335153359
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Experimental

Material and methods

All chemical were reagent grade purchased from Aldrich and Alfa Aesar and were used without purification. NMR spectra were recorded on a BRUKER AVANCE II-400FT Spectrometer (400 for 1HNMR, 100MHz for 13C) using DMSO as solvent and TMS as an internal reference. ESI-MS were recorded on a Quattro II (ESI) spectrometer.

Synthesis of ZnO nanoparticles:

25 mL, 1M solution of KOH was added dropwise to 50 mL of 0.05M solution of zinc acetate dihydrated by using dropping funnel for about 1h at 60°C under sonication. The sonication was carried out for another 1h. After centrifugation, mother liquor was removed and collected precipitate was washed with deionized water at least five times. The precipitate was then dried in air and characterized by TEM images, XRD and UV–vis. spectra techniques.

Characterization Techniques Used:

The prepared nanoparticles of ZnO were thoroughly characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM) in order to elaborate structural properties in precise manner. XRD was performed on Rigaku D/max-2200 PC diffractometer operated at 40 kV/40 mA, using CuKα1 radiation with wavelength of 1.54 Å in the wide angle region from 20° to 80° on 2θ scale. The size and morphology of prepared nanoparticles were found using a transmission electron microscope (model Tecnai 30 G2S-Twin electron microscope) operated at 300 KV accelerating voltage by dissolving the as-synthesized powder sample in ethanol and then placing a drop of this dilute ethanolic solution on the surface of a carbon coated 200 mesz copper grid.
To confirm the formation of nano sized ZnO under aqueous condition a UV-Vis study was also performed. The UV visible spectra for ZnO NP shows excitonic absorption peak at 361 nm which is blue shifted compared to bulk ZnO (due to the lower particle size of ZnO) indicate the formation of desired nanoparticles (Fig. S1).

**Typical Procedure for synthesis of N-Cyclohexyl-3-phenyl-4H-benzo[1,4]thiazin-2-amine (4a)**

A mixture of o-aminothiophenol 1 (1 mmol), benzaldehyde 3 (1 mmol), cyclohexylisocyanide 2 (1 mmol), nano ZnO (10 mol%) and β-cyclodextrin (2.5 mol%) in 5 mL of water was stirred at 60°C for 40 min. After completion of the reaction as indicated by TLC, the reaction mixture was cooled to room temperature and the product was precipitated by addition of 10 mL of H₂O. Then the precipitated product was filtered off and washed with H₂O. The residue was crystallized from EtOH to give the pure product.
Spectra of all compounds 4a–4j

(4a) N-Cyclohexyl-3-phenyl-4H-benzo[1,4]thiazin-2-amine: Mp 193°C. IR (KBr, cm⁻¹): v_max = 3169, 3155. ^1H NMR (400 MHz, CDCl₃): δ(ppm) = 1.12–2.14 (m, 10H), 3.58 (m, 1H), 4.34 (s, 1H, NH), 4.67 (s, 1H, NH), 7.44-7.96 (m, 9H, ArH). ^13C NMR (100 MHz, CDCl₃): δ (ppm) = 23.2, 24.7 (2 CH2), 28.8 (2 CH2), 47.7, 121.1 (2 CH), 123.4, 123.9, 124.7, 126.9 (2 CH), 127.7, 130.1, 131.2, 136.1, 137.9, 138.8, 140.3. MS: m/z = 322 [M⁺]; Analysis Calcd for C₂₀H₂₂N₂S: C, 74.49; H, 6.88; N, 8.69(%) Found: C, 73.94; H, 6.39; N, 8.57%.

(4b) N-Cyclohexyl-3-(4-chlorophenyl)-4H-benzo[1,4]thiazin-2-amine: Mp 204°C. IR (KBr, cm⁻¹): v_max = 3189, 3163. ^1H NMR (400 MHz, CDCl₃): δ(ppm) = 1.24–2.27 (m, 10 H), 3.44 (m, 1 H), 4.37 (s, 1 H, NH), 4.68 (s, 1 H, NH), 7.40–8.28 (m, 8 H, ArH). ^13C NMR (100 MHz, CDCl₃): δ (ppm) = 22.3, 26.4 (2 CH2), 33.6 (2 CH2), 49.1, 121.8 (2 CH), 123.5, 124.1 (2 CH), 127.1, 129.6, 130.3, 131.5, 138.4, 140.2, 142.3, 147.8, 149.9 (CCl). MS: m/z = 356 [M⁺]. Analysis Calcd (%) for C₂₀H₂₁N₂SCl: C, 67.30; H, 5.93; N, 7.85. Found: C, 67.13; H, 5.65; N, 7.93.

(4c) N-Cyclohexyl-3-(4-methoxyphenyl)-4H-benzo[1,4]thiazin-2-amine: Mp 188°C. IR (KBr, cm⁻¹): v_max = 3162, 3149. ^1H NMR (400 MHz, CDCl₃): δ(ppm) = 1.16–2.24 (m, 10 H), 2.98 (s, 3H) 3.34 (m, 1 H), 4.23 (s, 1 H, NH), 4.54 (s, 1 H, NH), 7.28–8.11 (m, 8 H, ArH). ^13C NMR (100 MHz, CDCl₃): δ (ppm) = 23.1, 24.1 (2CH2), 26.5 (2CH2), 49.9, 121.1 (2CH), 122.5, 123.8 (2CH), 125.1, 127.2, 130.9, 132.3, 136.7, 139.1, 142.9, 147.8, 149.2 ppm. MS: m/z = 352 [M⁺]. Analysis Calcd (%) for C₂₁H₂₄N₂SO: C, 71.55; H, 6.86; N, 7.95. Found: C, 70.81; H, 6.24; N, 7.25.

(4d) N-Cyclohexyl-3-(4-nitrophenyl)-4H-benzo[1,4]thiazin-2-amine: Mp 209°C. IR (KBr, cm⁻¹): v_max = 3176, 3152. ^1H NMR (400 MHz, CDCl₃): δ(ppm) = 1.14–2.36 (m, 10 H), 3.53 (m, 1 H), 4.37 (s, 1 H, NH), 4.73 (s, 1 H, NH), 7.44–8.37 (m, 8 H, arom). ^13C NMR (125 MHz, CDCl₃):
\( \delta \text{ (ppm)} = 23.4, 24.3 \) (2 CH2), 26.2 (2 CH2), 48.6, 121.9 (2 CH), 123.7, 125.3 (2 CH), 126.2, 128.0, 131.3, 137.4, 139.5, 141.6, 142.1, 146.9, 150.2 (CNO2). MS: m/z = 367 [M+]. Analysis Calcd (%) for C20H21N2SO2: C, 65.37; H, 5.76; N, 11.43. Found: C, 65.20; H, 5.79; N, 11.35.

**N-Cyclohexyl-3-(4-methylphenyl)-4H-benzo[1,4]thiazin-2-amine:** Mp 207°C. IR (KBr, cm-1): \( \nu_{\text{max}} = 3167, 3153 \). \(^1\)H NMR (400 MHz, CDCl3): \( \delta \text{ (ppm)} = 1.14–2.26 \) (m, 10 H), 2.42 (s, 3 H), 3.67 (m, 1 H), 4.45 (s, 1 H, NH), 4.76 (s, 1 H, NH), 7.27–8.04 (m, 8 H, arom). \(^{13}\)C NMR (100 MHz, CDCl3): \( \delta \text{ (ppm)} = 23.1, 24.1 \) (2 CH2), 27.1 (2 CH2), 40.8, 53.5, 124.6 (2 CH), 122.5, 125.4 (2 CH), 127.1, 128.7, 129.2, 137.1, 138.5, 140.6, 141.0, 143.9, 149.9. MS: m/z = 336 [M+]. Analysis Calcd (%) for C21H24N2S: C, 74.96; H, 7.19; N, 8.32. Found: C, 79.80; H, 7.24; N, 8.25.

**N-tert-Butyl-3-(4-methoxyphenyl)-4H-benzo[1,4]thiazin-2-amine:** Mp 228°C. IR (KBr, cm-1): \( \nu_{\text{max}} = 3159, 3147 \). \(^1\)H NMR (400 MHz, CDCl3): \( \delta \text{ (ppm)} = 1.28 \) (s, 9H), 3.36 (s, 3H, OCH3), 4.21 (s, 1H, NH), 4.56 (s, 1 H, NH), 7.17–8.04 (m, 8 H, arom). \(^{13}\)C NMR (125 MHz, CDCl3): \( \delta \text{ (ppm)} = 23.2 \) (3 CH3), 41.1, 121.1 (2 CH), 122.2, 123.6 (2 CH), 124.9, 125.1, 131.0, 131.9, 133.2, 138.9, 142.5, 148.4, 149.0. MS: m/z = 326 [M+]. Analysis Calcd (%) for C19H22N2SO: C, 69.90; H, 6.79; N, 8.58. Found: C, 69.88; H, 6.09; N, 8.45.

**N-Cyclohexyl-3-(4-hydroxyphenyl)-4H-benzo[1,4]thiazin 2-amine:** Mp 186°C. IR (KBr, cm-1): \( \nu_{\text{max}} = 3161, 3145 \). \(^1\)H NMR (400 MHz, CDCl3): \( \delta \text{ (ppm)} = 1.14–2.25 \) (m, 10 H), 3.38 (m, 1 H), 4.24 (s, 1 H, NH), 4.66 (s, 1 H, NH), 4.91 (s, 1 H, OH), 7.32–8.07 (m, 8 H, arom). \(^{13}\)C NMR (100 MHz, CDCl3): \( \delta \text{ (ppm)} = 23.4, 24.8 \) (2 CH2), 26.7 (2 CH2), 52.1, 121.1 (2 CH), 123.3, 124.3 (2 CH), 125.2, 130.9, 131.4, 133.5, 137.1, 139.1, 143.0, 148.8, 149.2. MS: m/z = 338 [M+]. Analysis Calcd (%) for C20H22N2SO: C, 70.97; H, 6.56; N, 8.28. Found: C, 70.83; H, 6.31; N, 8.13.
(4h)N-tert-Butyl-3-phenyl-4H-benzo[1,4]thiazin-2-amine Mp 233°C. IR (KBr, cm–1): $v_{\text{max}}$ = 3154, 3141 cm–1. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) = 1.34 (s, 9 H), 4.16 (s, 1 H, NH), 4.66 (s, 1 H, NH), 7.24–7.95 (m, 9 H, arom). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) = 26.3 (3 CH$_3$), 40.4, 122.5 (2 CH), 124.6, 124.8, 125.4, 126.8 (2 CH), 128.7, 131.7, 132.8, 136.8, 137.6, 138.9, 141.5. MS: m/z = 296 [M+]. Analysis Calcd (%) for C$_{18}$H$_{20}$N$_2$S: C, 72.93; H, 6.80; N, 9.45. Found: C, 72.86; H, 6.60; N, 9.36.

(4i)N-tert-Butyl-3-(4-nitrophenyl)-4H-benzo[1,4]thiazin-2-amine: Mp 210°C. IR (KBr, cm–1): $v_{\text{max}}$ = 3172, 3158 cm–1. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 1.34 (s, 9 H), 4.28 (s, 1 H, NH), 4.78 (s, 1 H, NH), 7.32–8.42 (m, 8 H, arom). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) = 28.6 (3 CH$_3$), 48.9, 121.5 (2 CH), 123.7, 124.98 (2 CH), 126.7, 128.1, 131.3, 134.4, 138.5, 141.7, 142.2, 147.0, 149.9. MS: m/z = 341 [M+]. Analysis Calcd (%) for C$_{18}$H$_{19}$N$_3$O$_2$S: C, 63.32; H, 5.61; N, 12.31. Found: C, 63.46; H, 5.72; N, 12.39.

(4j)N-Cyclohexyl-6-methyl-3-phenyl-4H-benzo[1,4]thiazin-2-amine: Mp 242°C. IR (KBr, cm–1): $v_{\text{max}}$ = 3166, 3158 cm–1. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) = 1.12–2.24 (m, 10 H), 3.05 (s, 3 H), 3.66 (m, 1 H), 4.62 (s, 1 H, NH), 4.96 (s, 1 H, NH), 7.25–7.91 (m, 8 H, arom). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) = 24.1, 24.4 (2 CH$_2$), 28.8 (2 CH$_2$), 30.9, 47.9, 121.9 (2 CH), 124.4, 124.7, 125.3, 126.8 (2 CH), 127.1, 130.8, 131.4, 136.5, 137.9, 138.4, 140.9 ppm. MS: m/z = 336 [M+]. Analysis Calcd (%) for C$_{21}$H$_{24}$N$_2$S: C, 74.96; H, 7.19; N, 8.32. Found: C, 74.87; H, 7.05; N, 8.23.