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Supplementary Information

Yeast supported gold nanoparticles: An efficient catalyst for the synthesis of commercially important aryl amines

Saravanan Krishnan,[a] Paresh N Patel,[a] Kalpattu K Balasubramanian,[a] Anju Chadha[a, b, †]

[a]*Laboratory of Bio-organic Chemistry, Department of Biotechnology, Indian Institute of Technology Madras, Chennai 600 036 India*

[b]*National Center for Catalysis Research, Indian Institute of Technology Madras, Chennai 600 036 India*

†E-mail: anjuc@iitm.ac.in; anjuchadha55@gmail.com & Tel: +91-44-22574106; Fax: +91-44-22574102

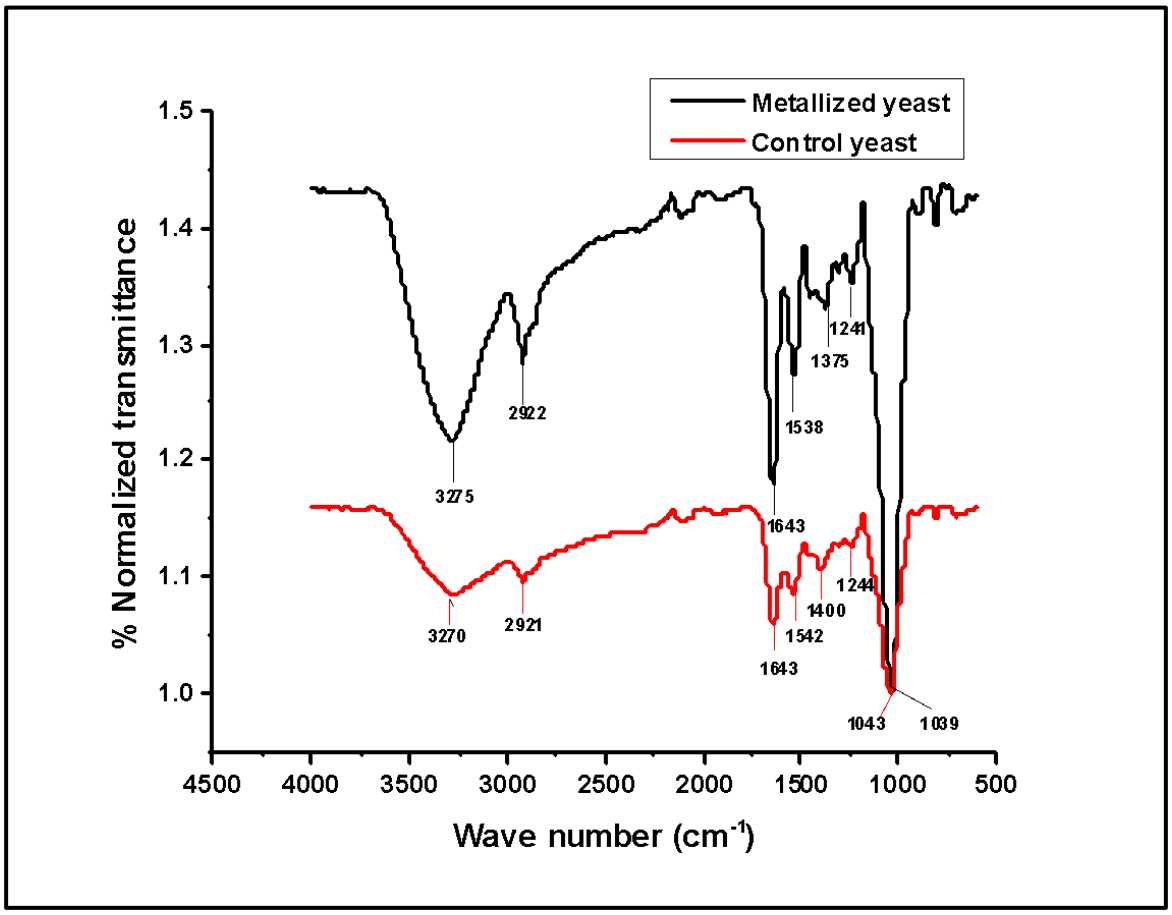


Figure S1. Fourier transform-Infra red spectroscopy analysis of the metalized yeast (CpGNP) and the control biomass

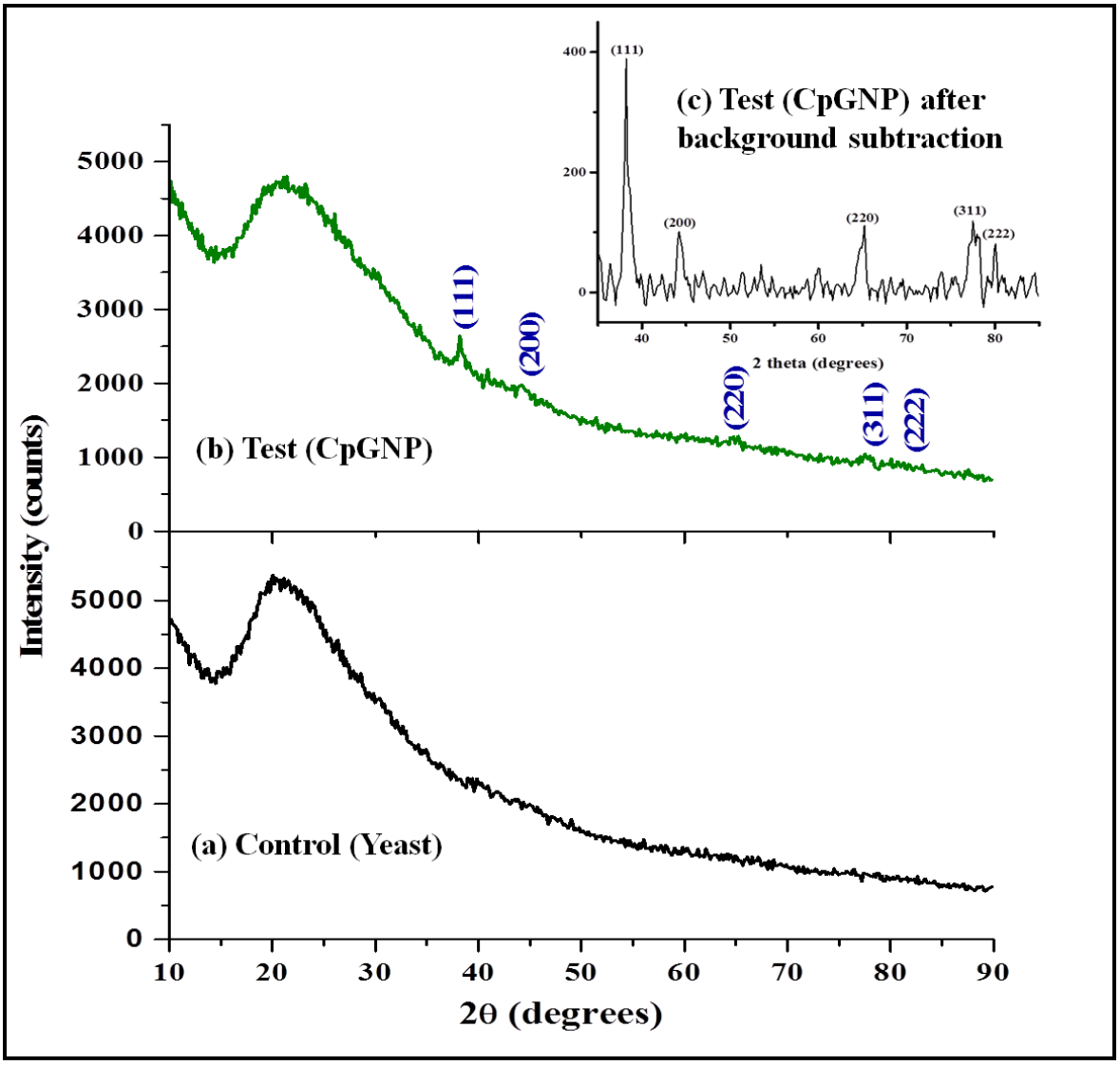


Figure S2. Powder X-ray diffraction analysis (a) control yeast biomass; (b) yeast supported gold nanoparticles (CpGNP) and Inset image (c) CpGNP after background subtraction.

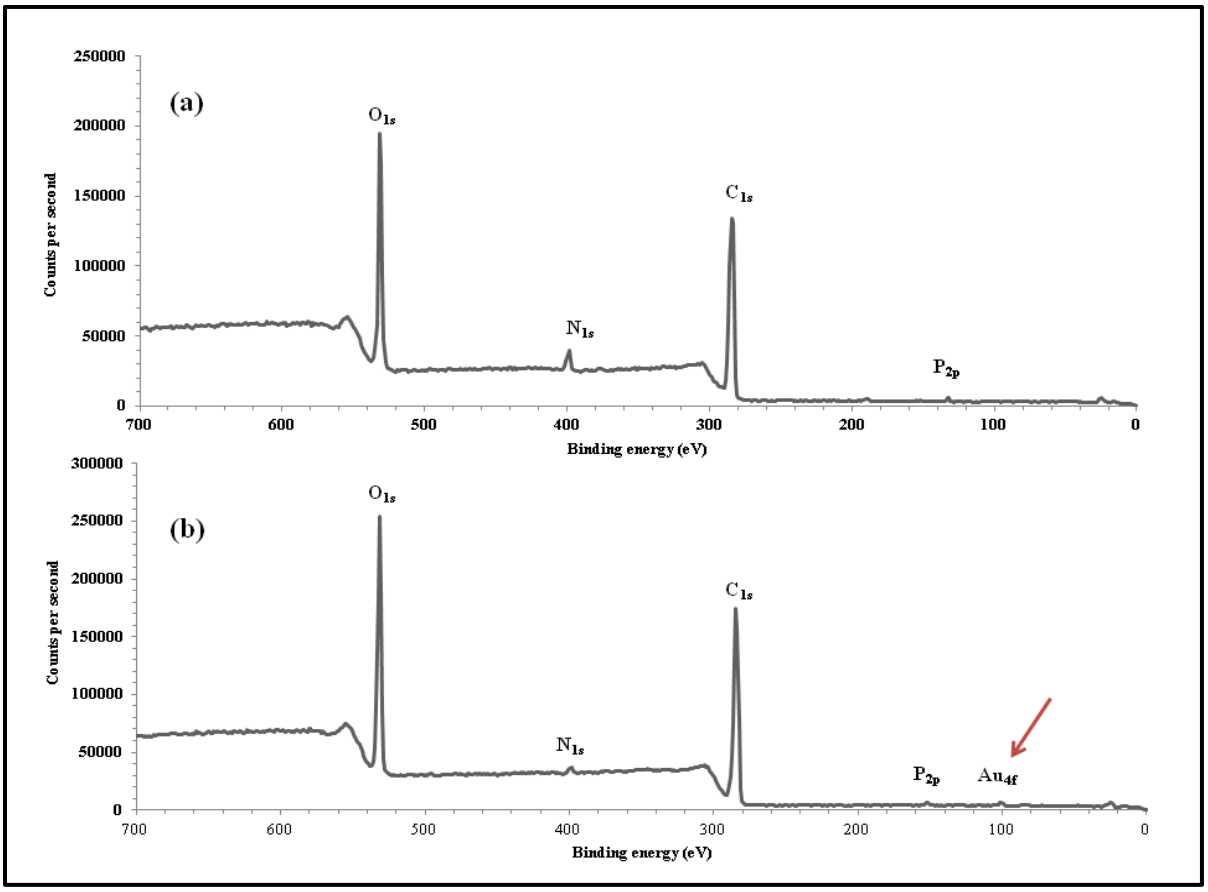


Figure S3. Wide scan spectra of the X-ray photoelectron spectroscopy analysis of the freeze dried samples a) control cells b) cells with biosynthesized Au NPs showing the presence of elemental Au

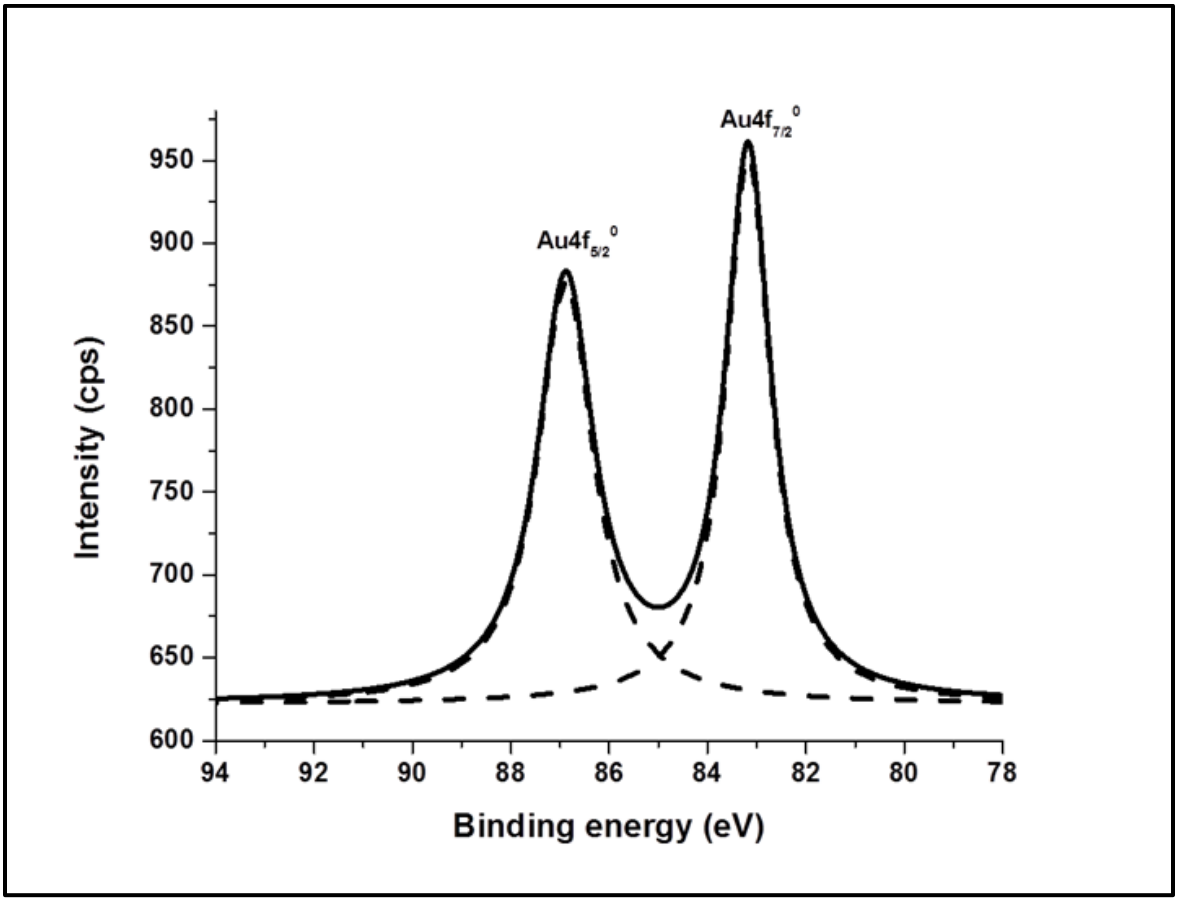
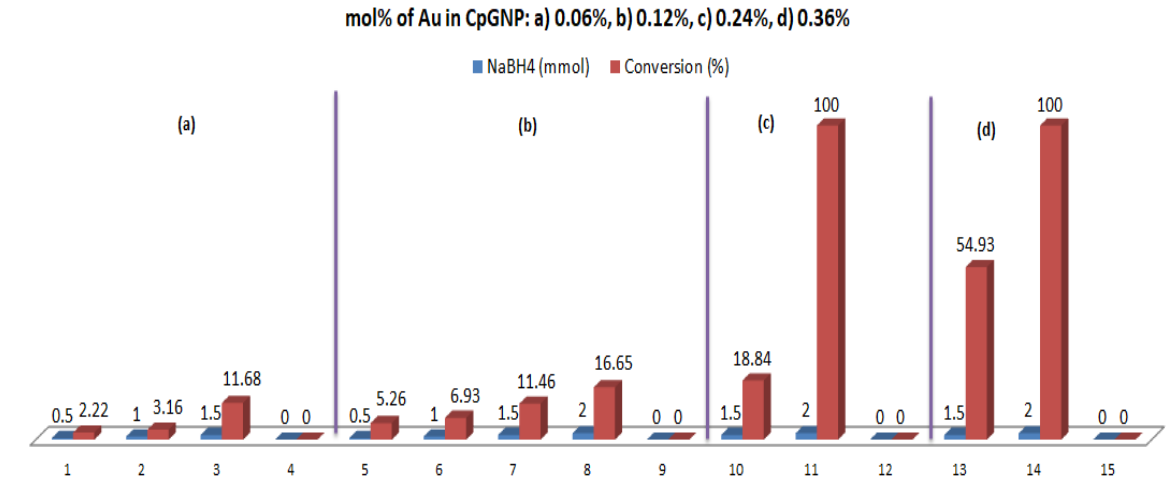


Figure S4. XPS spectra of the Au_{4f} of the freeze dried samples of resting cells after Au NPs synthesis

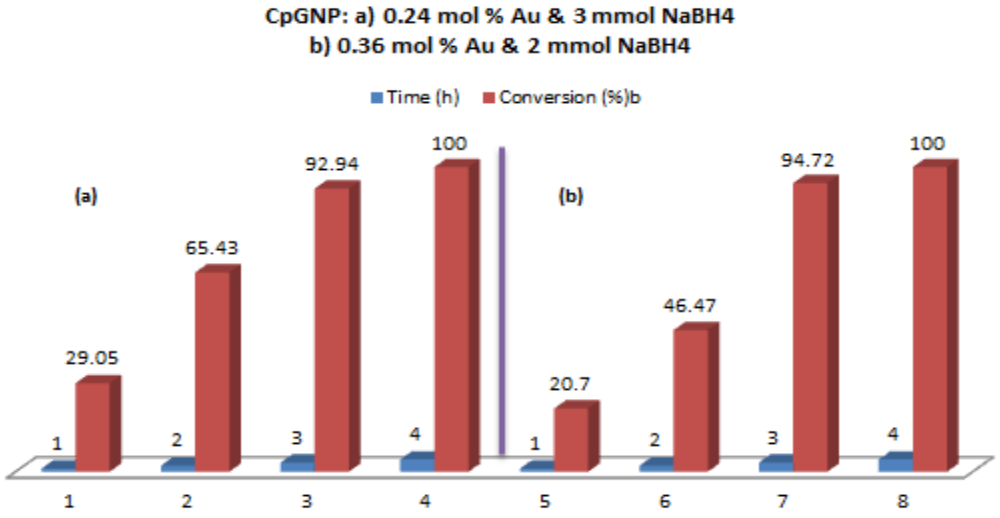


Note: 0.5 mmol of nitrobenzene (0.062 g, 0.052 mL) is used; % conversion is calculated based on HPLC after four hours

Figure S5. Optimization of stoichiometry of CpGNP and $NaBH_4$ for the reduction of nitrobenzene

As a first step, the stoichiometry of the catalyst (CpGNP) to the hydride source ($NaBH_4$) was gradually varied (**Figure S5**) to achieve complete reduction in four hours. For a typical reaction, the amount of CpGNP used was varied in the range of 0.06-0.36 mol % Au with respect to the starting material, nitrobenzene (0.5 mmol, 1 equiv.) in the presence of sodium borohydride (0.5-3.0 mmol). There was no major difference in conversion of nitrobenzene to aniline when the reaction stoichiometry has CpGNP with mol% of Au (0.06 to 0.36) and $NaBH_4$ in the range of 0.5 to 1.5 mmol. Similarly, the amount of $NaBH_4$ (0.5 to 3 mmol) had no major effect on formation of aniline, when the CpGNP is operated at low mol% (0.06 to 0.12 Au). Overall, low stoichiometry of $NaBH_4$ (< 1.5 mmol) and CpGNP (< 0.12 mol% Au) is not sufficient to complete the reaction within four hours. The complete reduction of nitrobenzene (0.5 mmol, 1 equiv.) to aniline by CpGNP (0.24 mol% Au) in the presence of $NaBH_4$ (2.0 mmol, 4 equiv.) was observed at 4 h. Control experiments *i.e.* i) cells alone, ii) the hydride source alone **(Figure S5)**, and iii) the use of

only CpGNP **(Figure S5)** without hydride source indicate that nitrobenzene remains as such in all the cases.



Note: 0.5 mmol of nitrobenzene (0.062 g, 0.052 mL) is used; [b]% conversions are calculated based on HPLC

Figure S6. Percent conversions of nitrobenzene to aniline using higher stoichiometric amounts of CpGNP and $NaBH_4$

To further investigate the importance of the stoichiometry between the CpGNP and $NaBH_4$, experiments were carried out with increasing concentration of either of them (above optimized amounts) while the other parameters were kept constant. Initially, the increase in the CpGNP concentration for a fixed amount of $NaBH_4$ (2 mmol) did not enhance the conversion of nitrobenzene to aniline in lesser time **(Figure S6)**. Similarly, an increase in the amounts of sodium borohydride did not affect the time taken for the complete reduction of nitrobenzene **(Figure S6)**. Taken together, gold nanoparticles (CpGNP) and $NaBH_4$ play a combined role where the formation of Au-H species[1] is involved which drives the reduction of nitrobenzene to aniline. A recent study demonstrate the formation of (Au-H) hydrid species through the primary kinetic isotope effects in the reduction of nitroarenes mediated by Au NPs supported on mesoporous Titania using $NaBH_4$/ 1, 1, 3, 3-tetramethyl disiloxane as electron donor.[2]

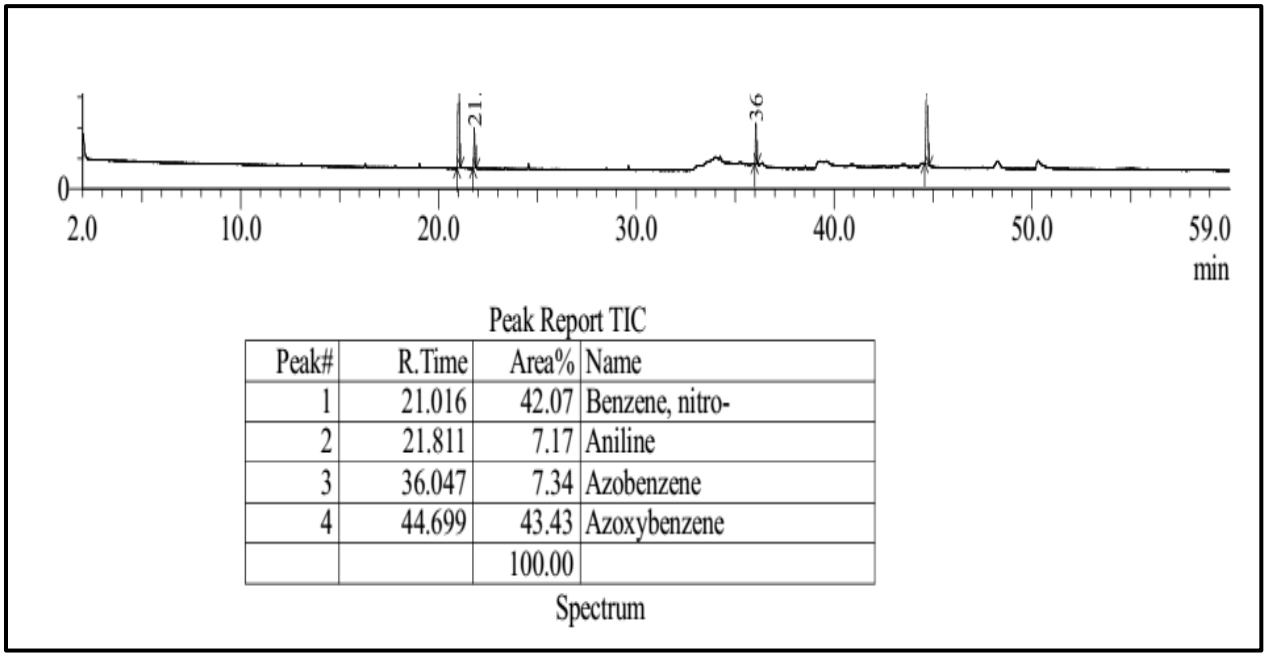
Previous reports have showed the reduction of nitroarenes to aryl amines using bionanocatalysts and hydride source (Table S1). In most of the reports[3], the catalytic

activity of bionanocatalyst is explored for the model reaction, *i.e.*, reduction of 4-nitrophenol to 4-aminophenol where sodium borohydride was used as hydride source (Table S1). At the same time, reaction progress is monitored using UV-Vis spectrophotometer and the isolated yields of products obtained were not reported here and therefore its commercial viability is difficult to predict.

Table S1. Bionanocatalyst for the catalytic reduction of nitroarenes to aryl amines

Entry	Bionanocatalyst	Substrate	Hydride source	Catalytic performance	Reference
Qualitative study					
1.	*Cylindrocladium floridanum* fungal biomass-Au NPs composite	4-nitrophenol	$NaBH_4$	Reaction rate Constant is 0.027 min^{-1}	3a
2.	Bio-supported Au NPs of *Aspergillus japonicus* AJP01	4-nitrophenol	$NaBH_4$	About 58% reduction of 4-nitrophenol occurred within 1 min, and the total reduction up to 90% was achieved within 5 min	3f
3.	*Cupriavidus necator* H16 supported mono- and bi-metallic (Au, Pd) nanoparticles	4-nitrophenol	$NaBH_3$ powder	Reduction rate of p-nitrophenol to p-aminophenol was substantially higher (almost double) for bimetallic Pd(0)-Au(0) and Au(0)-Pd(0) nanoparticles compared to the monometallic Pd(0) nanoparticles	3b
4.	*Rhizopus oryzae* mediated synthesized Pd, Pt, and Ag NPs	4-nitrophenol	$NaBH_4$	Silver, platinum, and palladium biosupported nanoparticles with normalized rate constants of 3.09, 3.75, and 5.87 $mmol^{-1}$ s^{-1}, respectively	3e
5.	Au NPs/ *P. pastoris*	4-nitrophenol	$NaBH_4$	Apparent rate constant is 0.48 min^{-1}	3c
6.	Au NPs/ membrane bound fraction of *E. coli* K12 cells	4-nitrophenol	$NaBH_4$	Rate constant is 1.24 x 10^{-2} min^{-1}	3d
Quantitative study					
7.	*Staphylococcus sciuri* and	4-	H_2	Conversion is 100%	3g

	Cupriavidus necator supported palladium nanoparticles	chloronitrobenzene			
8.	*Candida parapsilosis* ATCC 7330 supported Au NPs	Nitroarenes (35 examples)	$NaBH_4$	Out of 34 nitroarenes, 27 compounds gave 100% conversions	Present study



Peak Report TIC

Peak#	R.Time	Area%	Name
1	21.016	42.07	Benzene, nitro-
2	21.811	7.17	Aniline
3	36.047	7.34	Azobenzene
4	44.699	43.43	Azoxybenzene
		100.00	

Spectrum

Figure S7. Gas chromatography coupled mass spectrometry analysis of the reaction mixture before completion of the reduction of nitrobenzene to aniline

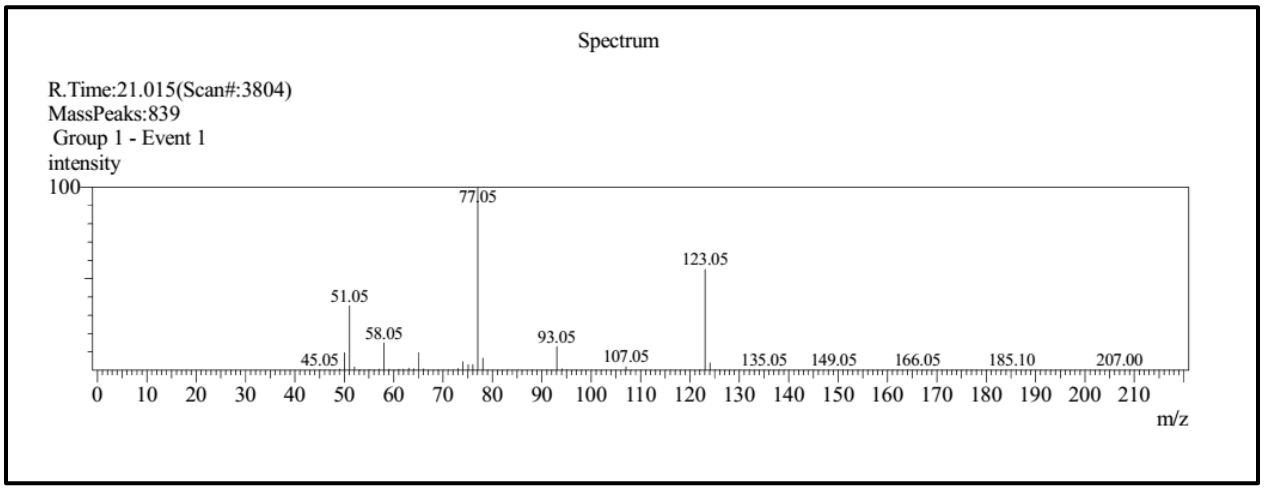


Figure S8. Mass fingerprint spectrum of Nitrobenzene

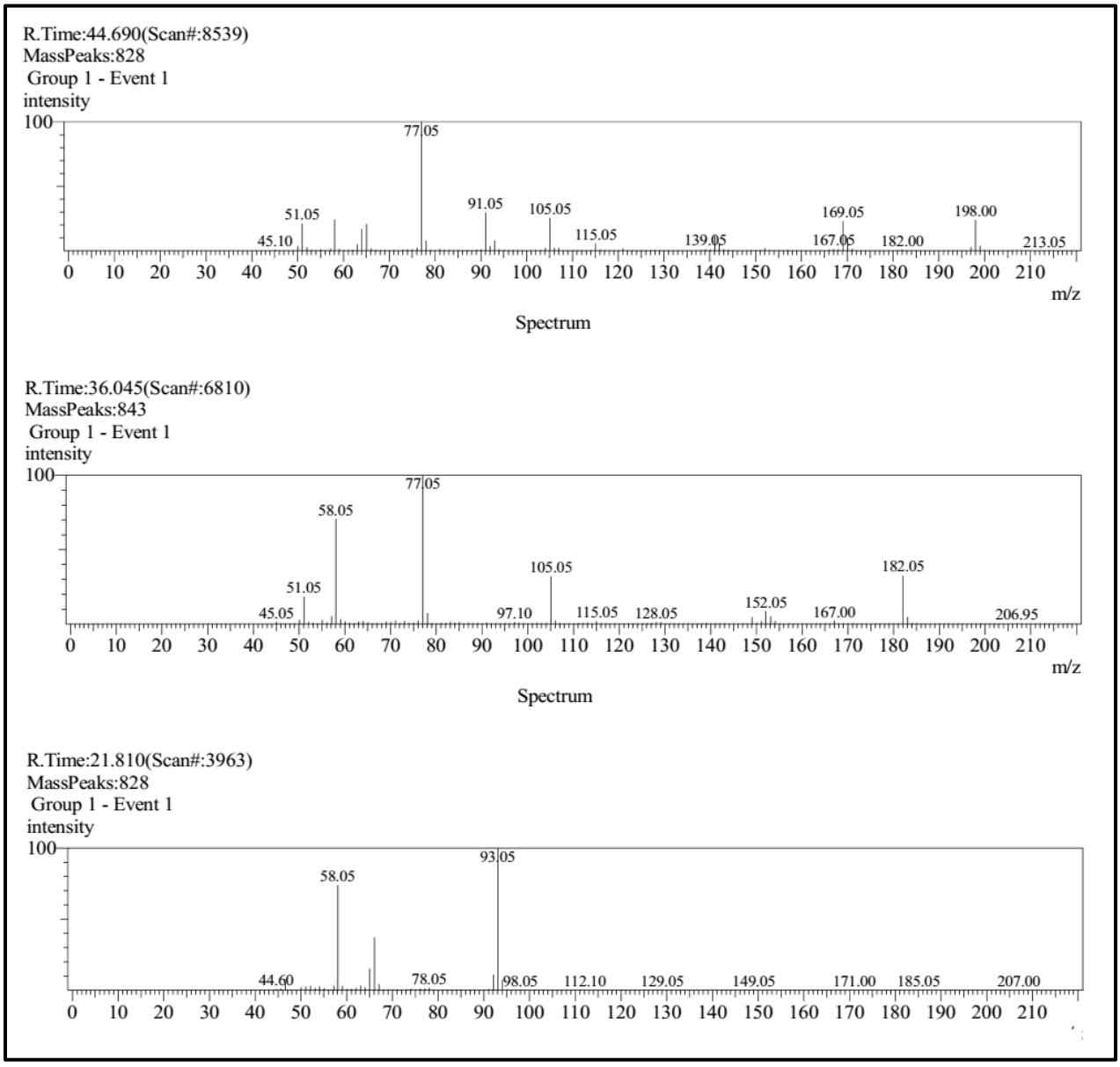
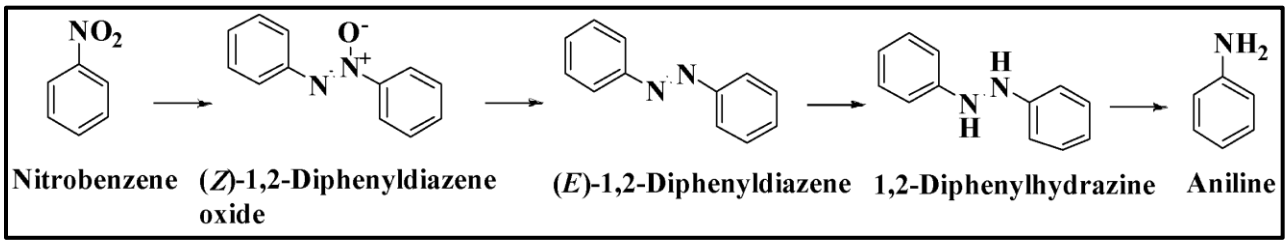


Figure S9. Mass fingerprint spectrum of azoxybenzene, azobenzene and aniline



Scheme S1. Mechanistic route for the reduction of nitrobenzene to aniline using CpGNP/$NaBH_4$

Table S2. Conversion of nitrobenzene to azoxybenzene using CpGNP/$NaBH_4$

Entry	CpGNP (mol% Au)	Substrate: $NaBH_4$ ratio	% Azoxybenzene[a]
1.	0.06	1:1	53.32
2.	0.06	1:2	93.00
3.	0.06	1:3	56.99
4.	0.12	1:1	57.26
5.	0.12	1:2	80.88
6.	0.12	1:3	65.20
7.	0.12	1:4	54.49
8.	0.24	1:3	32.66
9.	0.36	1:3	22.26

Note: 0.5 mmol of nitrobenzene (0.062 g, 0.052 mL) is used; [a]% conversions are calculated based on HPLC

Reduction of Sodium 4-nitrobenzoate using CpGNP/$NaBH_4$

Panel I: 4-nitrobenzoic acid (standard)

Panel II: 4-aminobenzoic acid (standard)

Panel III: Reduction of sodium 4-nitrobenzoate using CpGNP/$NaBH_4$

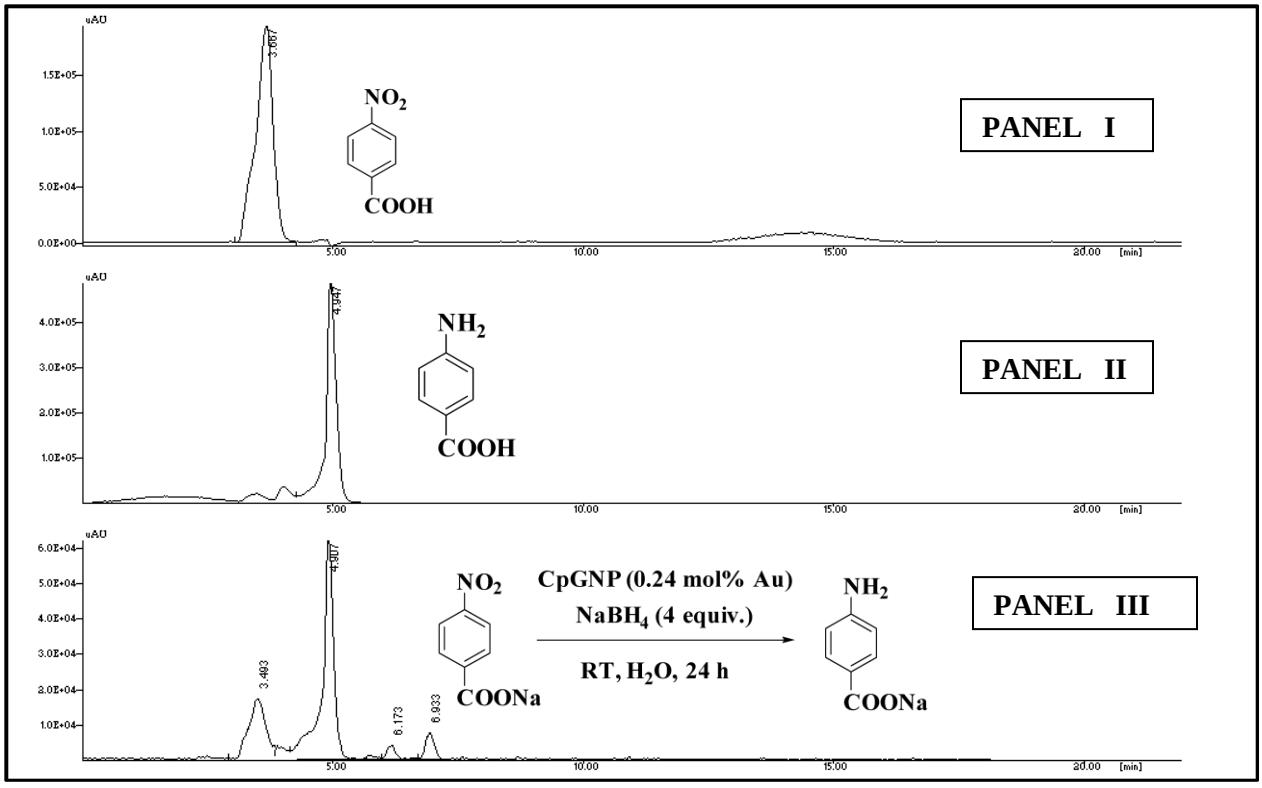


Figure S10. HPLC analysis of the reduction of sodium 4-nitrobenzoate using the /$NaBH_4$

Reduction of 2-nitrocinnamaldehyde using CpGNP/$NaBH_4$

Panel I: 2- Nitrocinnamaldehyde (standard)

Panel II: Reduction of 2- nitrocinnamaldehyde using CpGNP/$NaBH_4$

Panel III: Quinoline (standard)

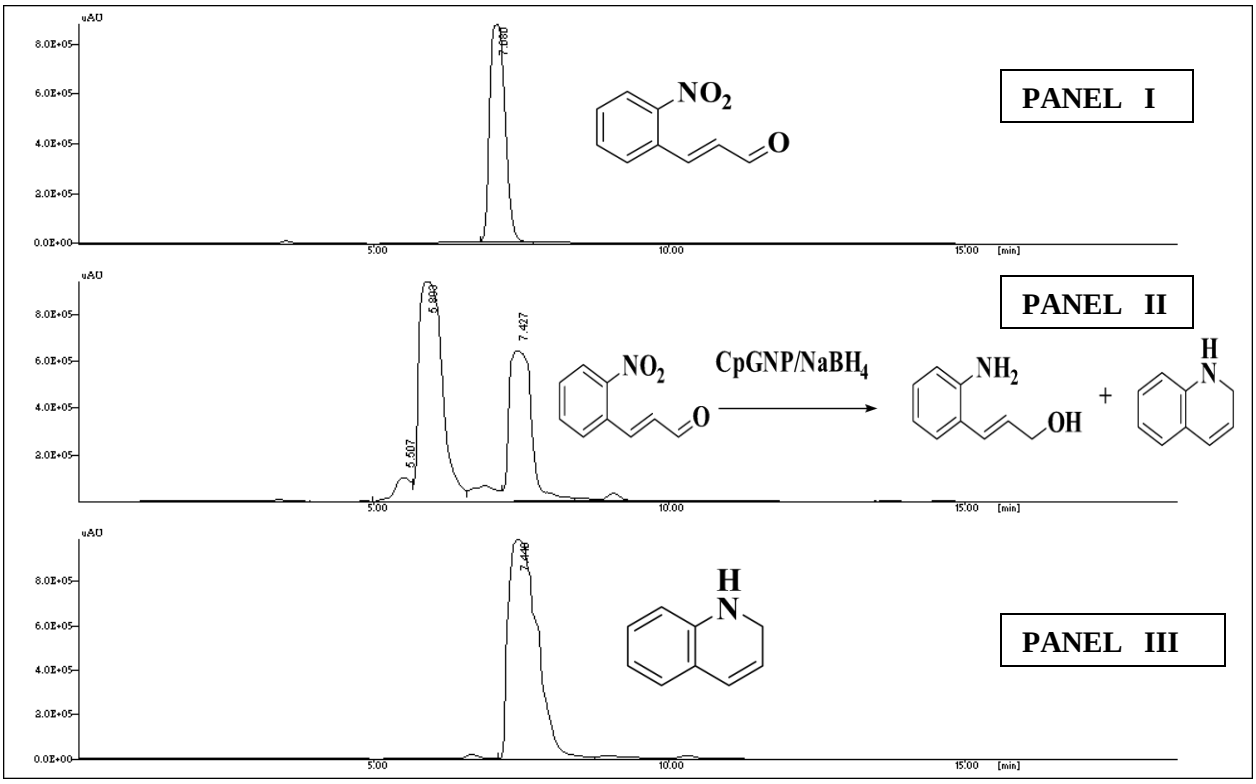


Figure S11. HPLC analysis of the reduction of 2-nitrocinnamaldehyde using CpGNP/$NaBH_4$

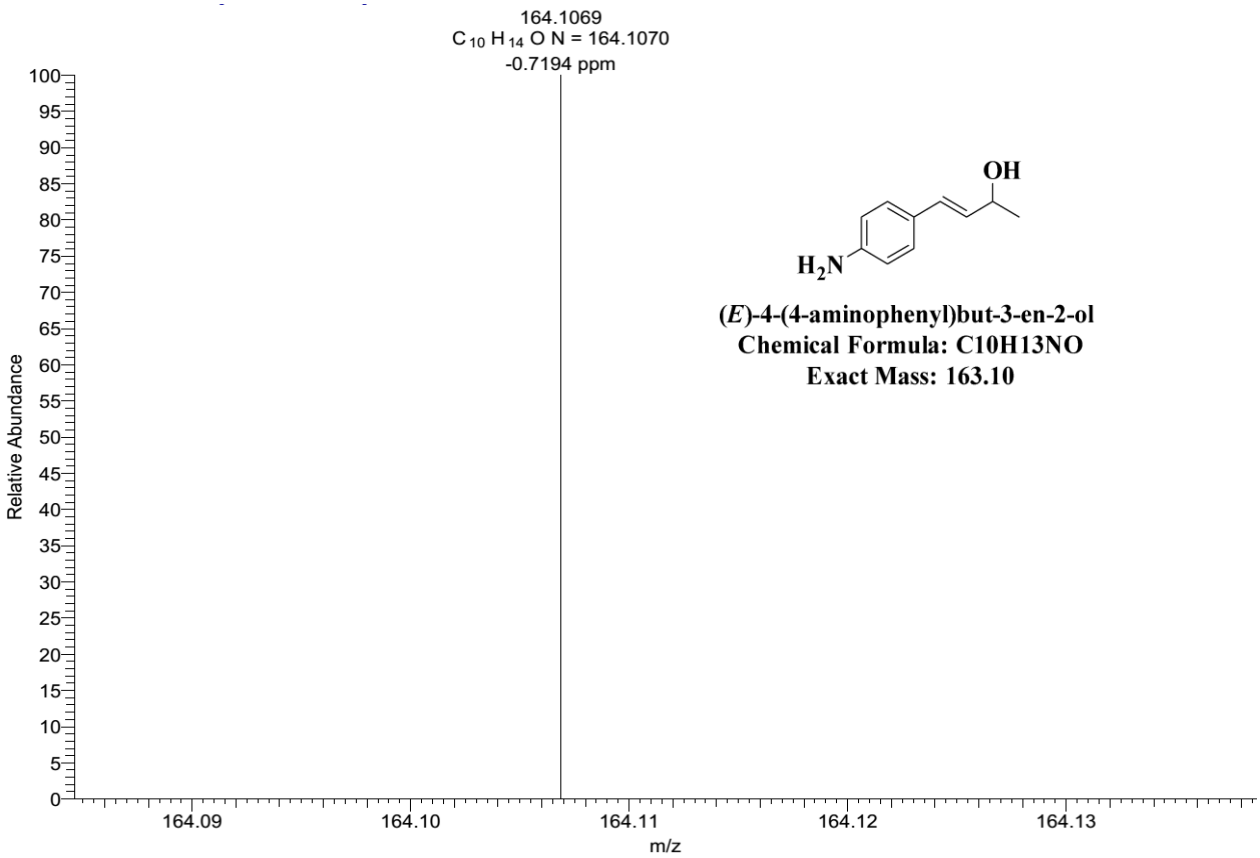


Figure S12. High resolution mass spectra of the 4-(4-aminophenyl) but-3-en-2-ol

This compound was characterized by HR-MS. HRMS: m/z, Calcd. Mass: 164.1070 [(M + H)$^+$], Found: 164.1069 [(M + H)$^+$].

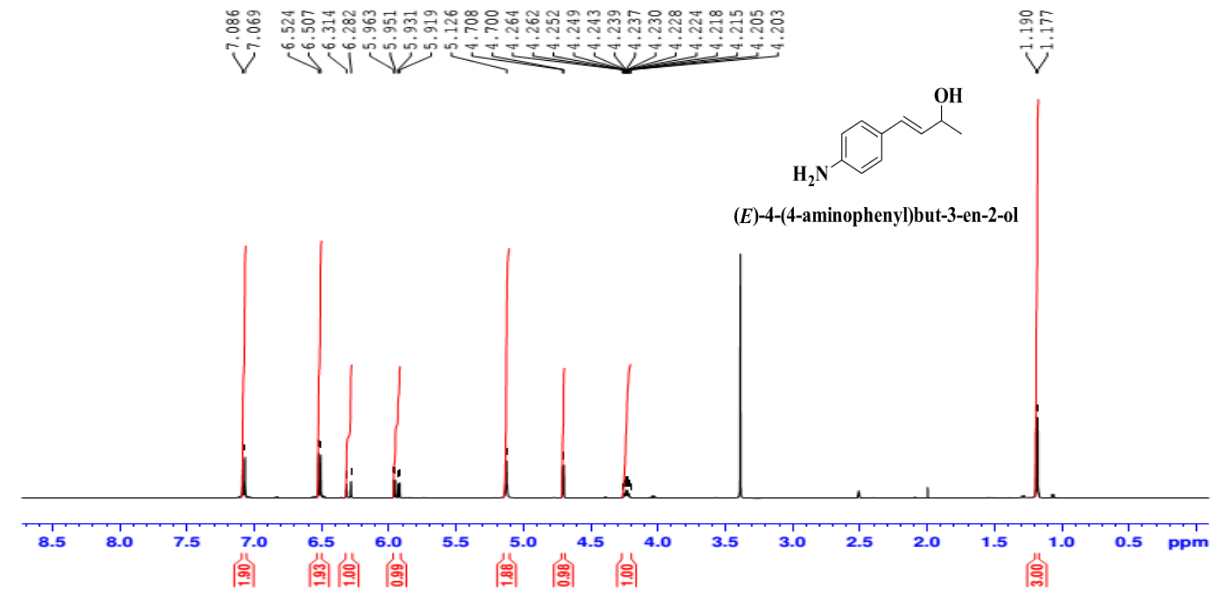


Figure S13. ^{1}H NMR of 4-(4-aminophenyl) but-3-en-2-ol

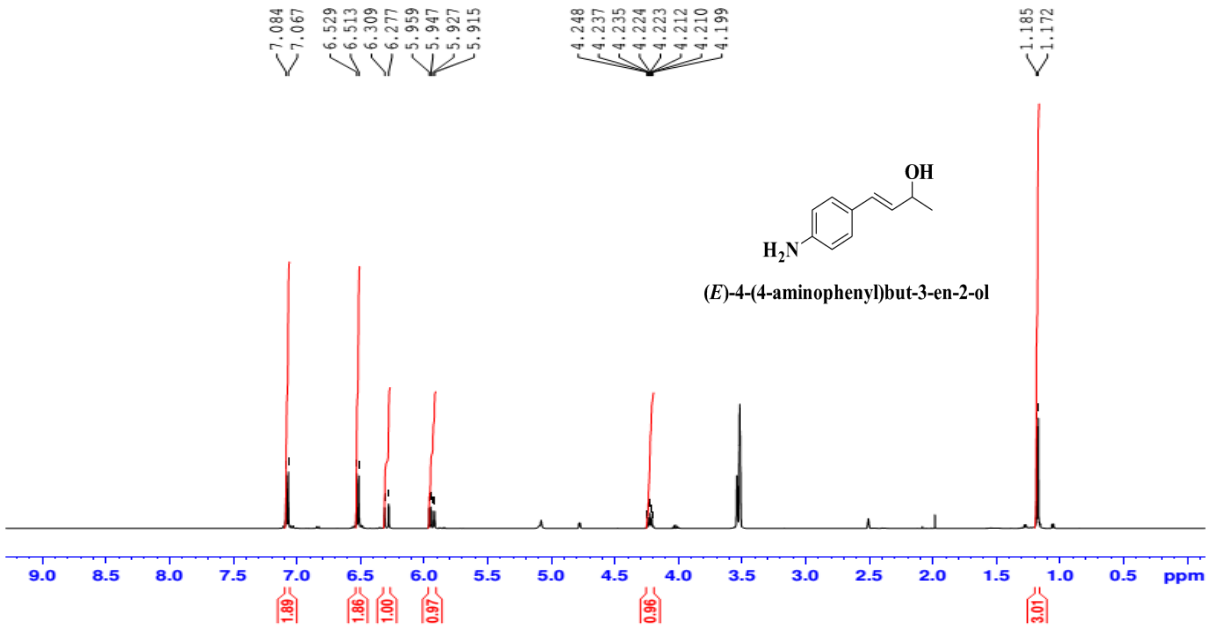
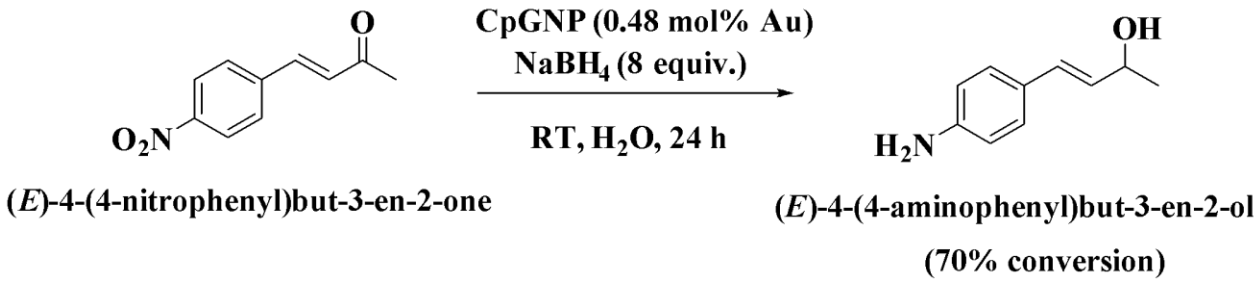


Figure S14. ^{1}H NMR analysis of 4-(4-aminophenyl) but-3-en-2-ol after D_2O exchange

Reduction of 4-(4-nitrophenyl) but-3-en-2-one using CpGNP/$NaBH_4$

Panel I: 4-(4 nitrophenyl) but 3-en 2-one (substrate standard)

Panel II & III: Reduction of 4-(4 nitrophenyl) but 3-en 2-one using CpGNP/$NaBH_4$ (duplicate reactions)



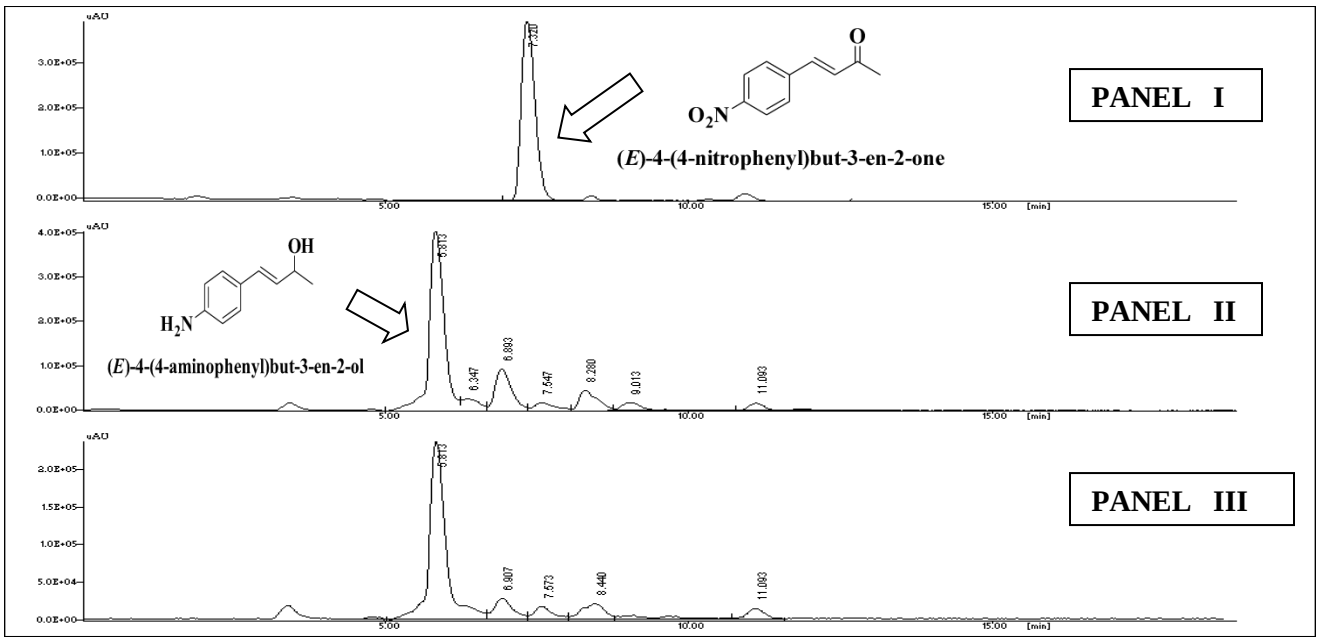


Figure S15. HPLC analysis of the reaction with the substrate 4-(4-nitrophenyl) but-3-en-2-one

Control experiments in the reduction of 4-(4 nitrophenyl) but 3-en 2-one

Panel I: 4-(4 nitrophenyl) but 3-en 2-one (substrate standard)

Panel II: Substrate in the presence of control cells after 24 h

Panel III: Substrate in the presence of metalized cells (Au NPs) after 24 h

Panel IV: Substrate in the presence of $NaBH_4$ after 24 h (4-(4-nitrophenyl) but-3-en-2-ol is observed)

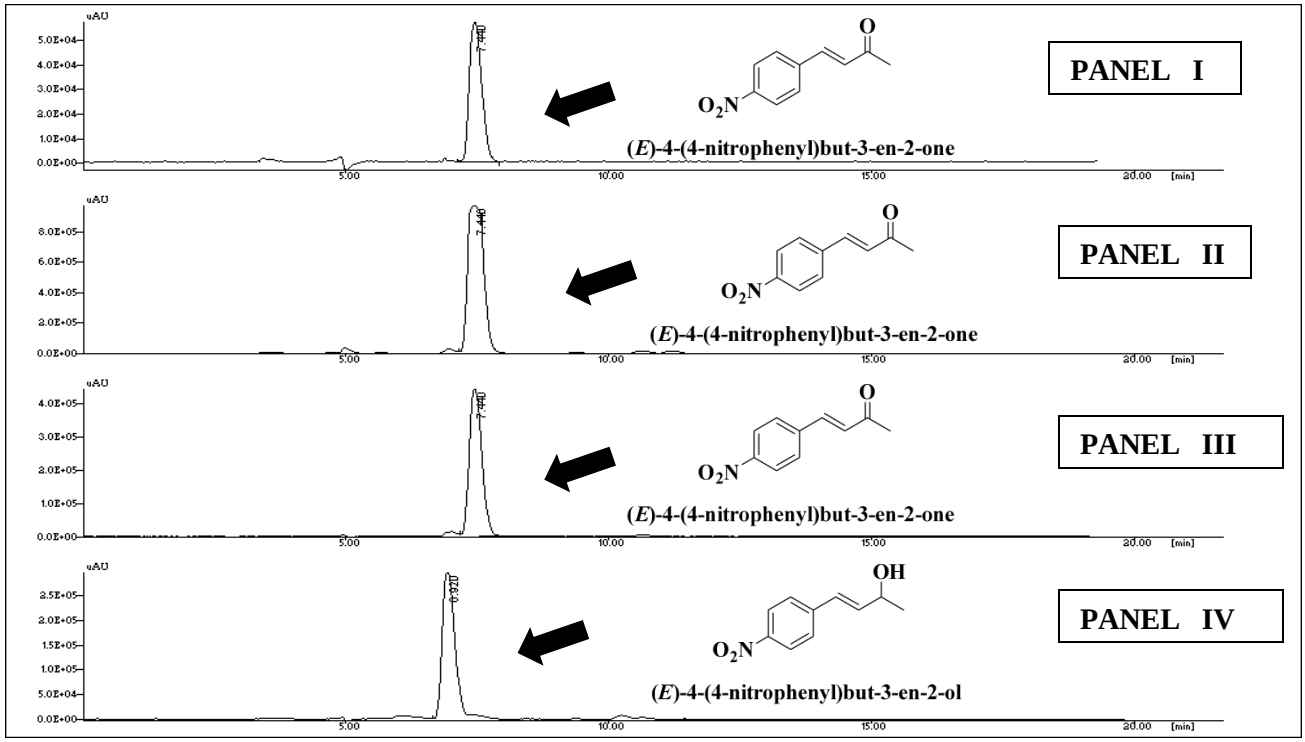
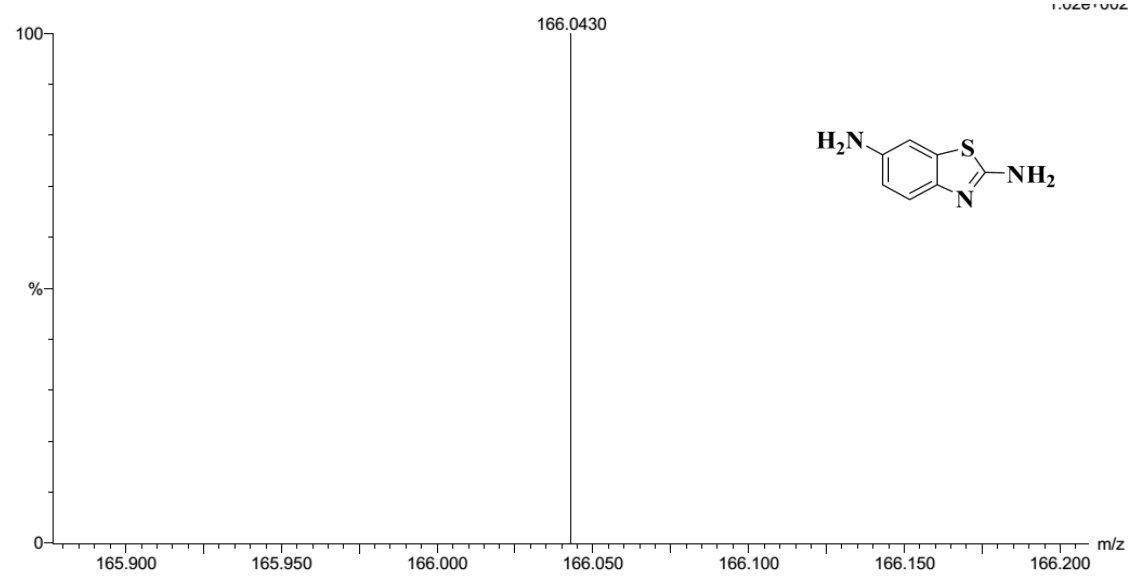


Figure S16. HPLC analysis of the control reactions with the 4-(4-nitrophenyl) but-3-en-2-one



Minimum:				-1.5		
Maximum:		5.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
166.0430	166.0439	-0.9	-5.4	5.5	n/a	C7 H8 N3 S

Figure S17. HRMS spectrum of 6-aminobenzo[*d*]thiazol-2-amine

Reduction of nitrobenzene using catalyst filtrate

Panel I: Nitrobenzene (standard)

Panel II: Aniline (standard)

Panel III: Reduction of nitrobenzene using catalyst filtrate in the presence of $NaBH_4$

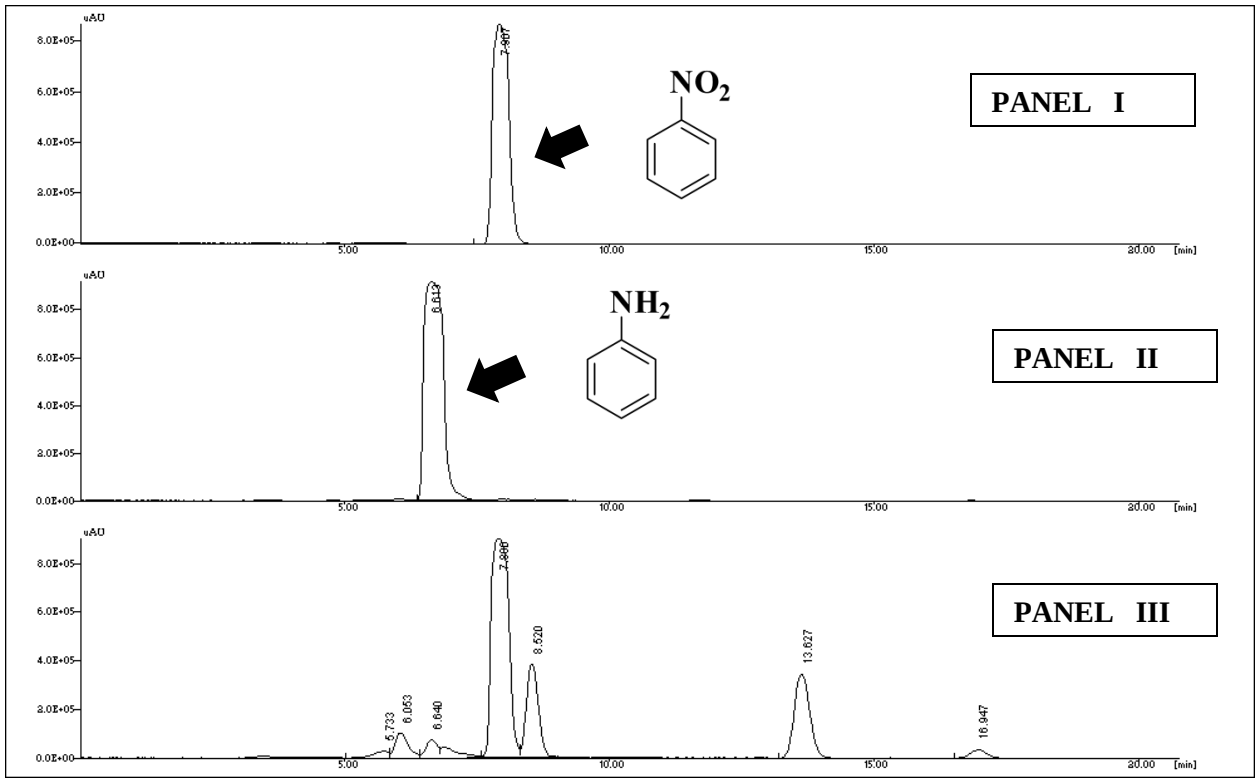


Figure S18. HPLC analysis of the reduction of nitrobenzene using catalyst filtrates

Table S3. Experiments to separate/extract gold nanoparticles from the yeast

Entry	Method	Procedure	Centrifugation	Filtration	Observation
1.	Addition of cell lysis buffer and sonication	To cell suspension containing nanoparticles, equal volume of cell lysis buffer was added, and sonicated for 45 min.	550 x g, 15 mins, 4 °C	Pellet resuspended in water was passed through 0.2 μm syringe filter, filtrate colourless; color retained in the filter	Supernatant was colourless
2.	Ultrasonication	Ultrasonication for 20 min (1 sec On/Off) at 35% Amplitude	-	Identical samples filtered through Whatman filter or 0.2 μm syringe filter	Filtrate was colourless
3.	Ultrasonication followed by solvent based extraction	As a follow up after entry 3, different organic solvents (Ethyl acetate, ethanol, acetonitrile, dichloromethane and hexane) were used to extract nanoparticles.	-		Nanoparticles rich fraction was not miscible with the non polar fraction whereas turbidity was seen with polar solvents
4.	French press	35 Kpsi, 4 °C, five passes	550 x g, 15 min, 4 °C		Supernatant was colourless; colour is retained with the pellet

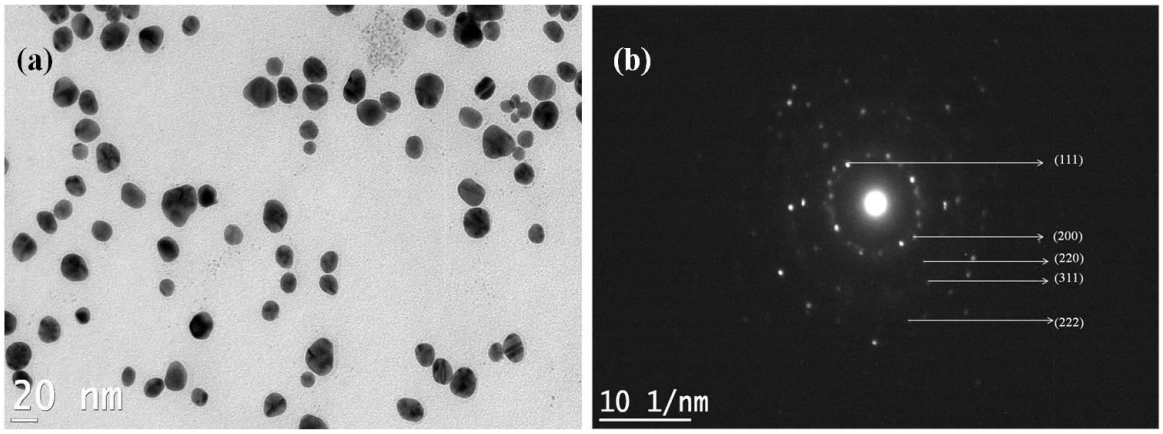


Figure S19. Gold nanoparticles extracted from CpGNP using ultrasonication. (a) Transmission electron micrograph (b) Selected area electron diffraction pattern of gold nanoparticles.

SAED pattern indicated the presence of face crystalline cubic gold nanoparticles with d-spacing distance for the lattice planes (111), (200), (220), (311) and (222) was found to be 0.233 nm, 0.214 nm, 0.141 nm, 0.123 nm and 0.115 nm respectively. These values are in agreement with the d-spacing according to characteristic XRD peaks (FCC) of gold nanoparticles (ICDD card no. 00-04-0784).

Figure S20. Visual inspection of the metalized yeast (CpGNP)

Reduction of nitrobenzene using freeze dried CpGNP

Panel I: Nitrobenzene (standard)

Panel II: Aniline (standard)

Panel III: Reduction of nitrobenzene to aniline using lyophilized CpGNP/$NaBH_4$

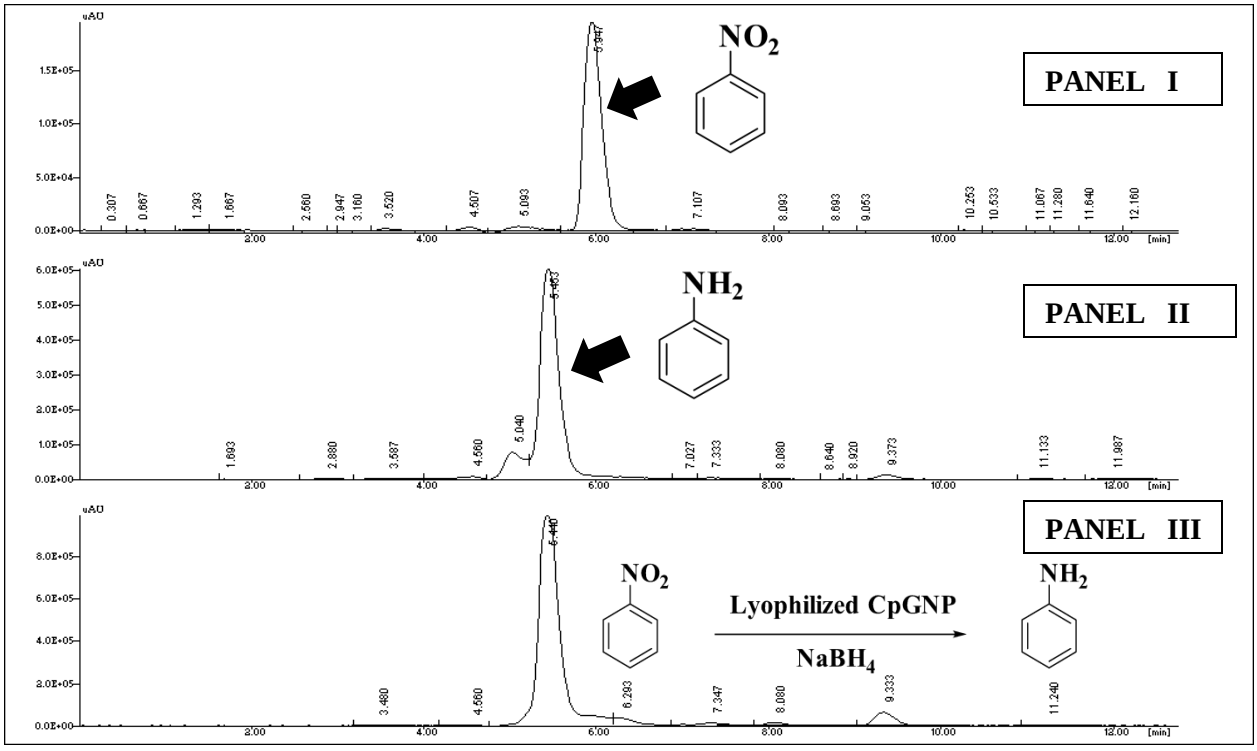


Figure S21. HPLC analysis of the reduction of nitrobenzene using the lyophilized CpGNP/$NaBH_4$

Reduction of nitrobenzene using freeze dried CpGNP stored for 8 months

Panel I: Aniline (standard)

Panel II: Reduction of nitrobenzene using catalyst stored for 8 months at 4 °C in the presence of $NaBH_4$

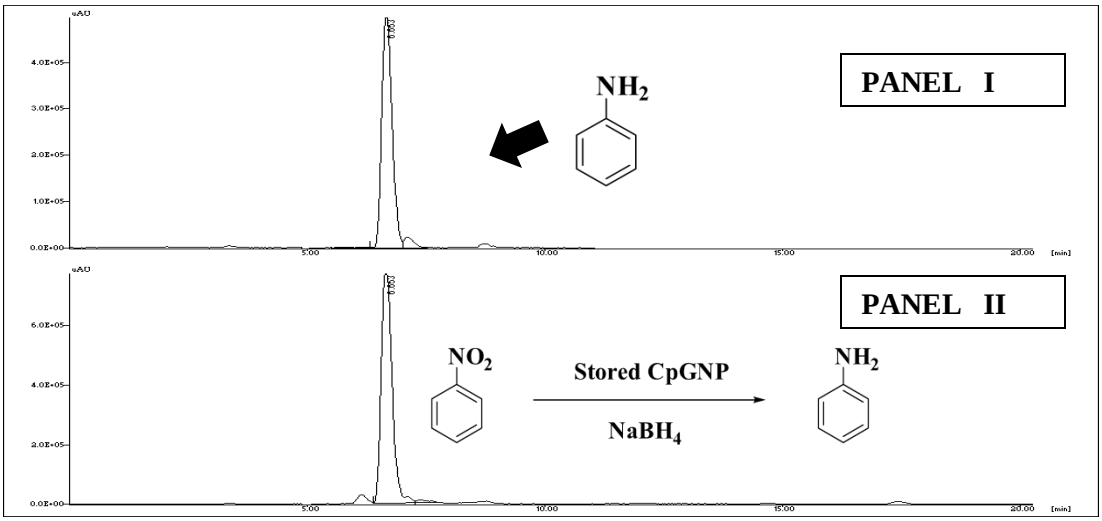
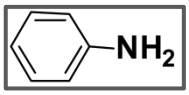


Figure S22. HPLC analysis of the reduction of nitrobenzene using CpGNP (stored for 8 months at 4 °C) in the presence of $NaBH_4$

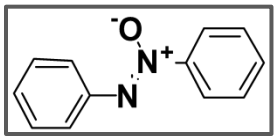
Spectroscopic characterisation

Aniline[4]



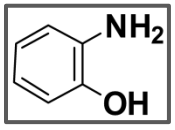
^{1}H NMR (CDCl$_3$; 500 MHz; δ in ppm): 7.19 (td, 2H, *J* = 1.5, 7.5 Hz), 6.79 (tt, 1H, *J* =1.5, 7.5 Hz), 6.73 (m, 2H), 3.66 (br s, 2H, D_2O exchanged); **^{13}C NMR (CDCl$_3$; 125 MHz; δ in ppm):** 146.32, 129.30, 118.58, 115.12

(*Z*)-1,2-diphenyldiazene 1-oxide[5]



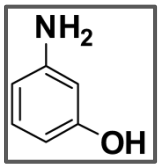
^{1}H NMR (CDCl$_3$; 500 MHz; δ in ppm): 7.43 (tt, 1H, *J* = 1.5, 7.5 Hz), 7.56-7.52 (m, 4H), 7.59 (tt, 1H. *J*=1.5, 7.5 Hz), 8.20-8.18 (m, 2H), 8.36-8.33 (m, 2H); **^{13}C NMR (CDCl$_3$; 125 MHz; δ in ppm):** 148.38, 144.04, 131.62, 129.63, 128.83, 128.73, 125.55, 122.38; **HRMS**: m/z; Calcd. Mass: 199.0865 [$(M + H)^+$], Found: 199.0866 [$(M + H)^+$].

2-aminophenol[6]



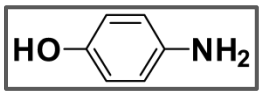
^{1}H NMR (DMSO-*d6*; 500 MHz; δ in ppm): 7.71 (dd, 1H, *J* = 1.5, 8.0 Hz), 7.50 (dd, 1H, *J* = 1.5 , 8.0 Hz), 7.46 (dt, 1H, *J* = 1.5, 8.0 Hz), 7.39 (dt, 1H, *J* = 1.5, 6.5 Hz), 6.82 (br s, 2H, D_2O exchanged), 6.36 (s, 1H, D_2O exchanged); **^{13}C NMR (DMSO-*d6*; 125 MHz; δ in ppm):** 155.2, 137.6, 133.6, 125.0, 120.2, 1198

3-aminophenol[7]



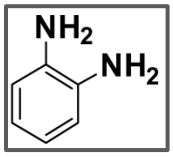
^{1}H NMR (DMSO-*d6*; 500 MHz; δ in ppm): 8.77 (s, 1H), 6.71 (t, 1H, *J* = 8 Hz), 6.08 (s, 1H), 5.95 (d, 1H, *J* = 7.5 Hz), 5.87 (d, 1H, *J* = 7 Hz), 4.82 (br s, 2H, D_2O exchanged); **^{13}C NMR (DMSO-*d6*; 125 MHz; δ in ppm):** 163.27, 155.04, 134.61, 110.60, 108.48, 106.15

4-aminophenol[8]



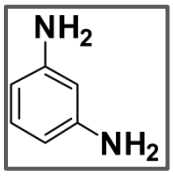
^{1}H NMR (DMSO-*d6*; 500 MHz; δ in ppm): 8.33 (s, 1H), 6.47 (dd, 2H, *J* = 3, 9 Hz), 6.41 (dd, 2H, *J* = 3, 8.5 Hz), 4.40 (br s, 2H, D_2O exchanged); **^{13}C NMR (DMSO-*d6*; 125 MHz; δ in ppm):** 148.69, 141.08, 115.99, 115.71

Benzene-1,2-diamine[9]



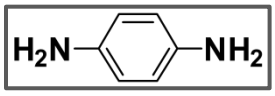
^{1}H NMR ($CDCl_3$; 500 MHz; δ in ppm): 6.74 (m, 4H, *J* = 1 Hz), 3.40 (br s, 4H, D_2O exchanged); **^{13}C NMR ($CDCl_3$; 125 MHz; δ in ppm):** 134.74, 120.29, 116.76

Benzene-1,3-diamine[10]



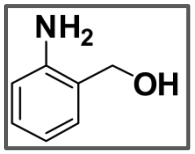
^{1}H NMR ($CDCl_3$; 500 MHz; δ in ppm): 6.66 (s, 1H), 5.78 (m, 3H), 4.64 (br s, 4H); **^{13}C NMR ($CDCl_3$; 125 MHz; δ in ppm):** 149.81, 128.10, 104.15, 100.96

Benzene-1,4-diamine[11]



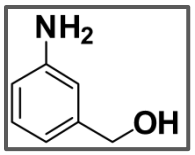
^{1}H NMR ($CDCl_3$; 500 MHz; δ in ppm): 6.59 (s, 4H), 3.35 (br s, 4H, D_2O exchanged); **^{13}C NMR ($CDCl_3$; 125 MHz; δ in ppm):** 138.60, 116.73

(2-aminophenyl) methanol[12]



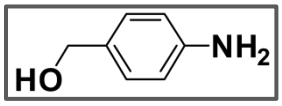
^{1}H NMR ($CDCl_3$; 500 MHz; δ in ppm): 7.15 (dt, 1H, *J* = 1.5, 7.5 Hz), 7.07 (d, 1H, *J* = 7.5 Hz), 6.74 (dt, 1H, *J* = 1, 7.5 Hz), 6.71 (d, 1H, *J* = 7.5 Hz), 4.63 (s, 2H); **^{13}C NMR ($CDCl_3$; 125 MHz; δ in ppm):** 145.96, 129.34, 129.21, 124.94, 118.24, 116.10, 64.21

(3-aminophenyl) methanol[13]



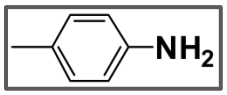
^{1}H NMR (500 MHz, $CDCl_3$, δ in ppm): 7.15 (t, *J* = 8 Hz, 1H), 6.75 (d, *J* = 8 Hz, 1H), 6.70 (s, 1H), 6.63 (dd, *J* = 1.5, 8 Hz, 1H), 4.60 (s, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ in ppm: 146.62, 142.27, 129.52, 117.14, 114.42, 113.62, 65.32

(4-aminophenyl) methanol[8]



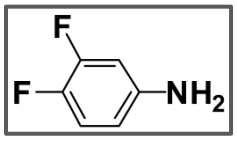
^{1}H NMR ($CDCl_3$; 500 MHz; δ in ppm): 7.16 (d, 2H, *J* = 8.5 Hz), 6.68 (d, 2H, *J* = 8 Hz), 4.54 (s, 2H)**; ^{13}C NMR ($CDCl_3$; 125 MHz; δ in ppm):** 146.01, 131.08, 128.79, 115.19, 65.24

***p*-toluidene**[13]



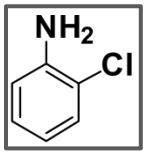
^{1}H NMR (DMSO-*d6*, 500 MHz; δ in ppm): 6.81 (d, 2H, *J* = 8 Hz), 6.46 (d, 2H, *J* = 6.5 Hz), 4.72 (br s, 2H, D_2O exchanged), 2.12 (s, 3H); **^{13}C NMR (DMSO-*d6*; 125 MHz; δ in ppm):** 146.52, 129.68, 124.38, 114.50, 20.58

3, 4-difluoroaniline[14]



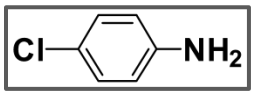
^{1}H NMR (DMSO-*d6*; 500 MHz; δ in ppm): 7.01(dd, 1H, *J* = 9, 18 Hz), 6.48 (ddd, 1H, *J* = 2.5, 7, 13.5Hz), 6.31(dd, 1H, *J* = 4, 5 Hz), 5.22 (br s, 2H, D_2O exchanged); **^{13}C NMR (DMSO-*d6*; 125 MHz; δ in ppm):** 151.19, 149.28, 140.48, 117.66, 109.68, 102.17

2-chloroaniline[15]



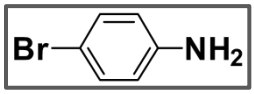
^{1}H NMR (DMSO-*d6*; 500 MHz; δ in ppm): 7.17 (d, 1H, *J* = 10 Hz), 7.01 (t, 1H, J = 10 Hz), 6.78 (d, 1H, *J* = 8 Hz), 6.53 (t, 1H, *J* = 10 Hz), 5.30 (br s, 2H, D_2O exchanged); **^{13}C NMR (DMSO-*d6*; 125 MHz; δ in ppm):** 145.12, 129.41, 128.10, 117.51, 117.24, 115.00

4-chloroaniline[16]



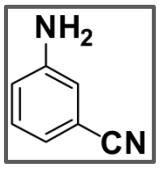
^{1}H NMR (DMSO-*d6*; 500 MHz; δ in ppm): 7.01 (dd, 2H, *J* = 2.5, 8.5 Hz), 6.56 (dd, 2H, *J* = 2.5, 8.5 Hz), 5.21 (br s, 2H, D_2O exchanged); **^{13}C NMR (DMSO-*d6*; 125 MHz; δ in ppm):** 148.09, 128.95, 119.22, 115.66

4-bromoaniline[11]



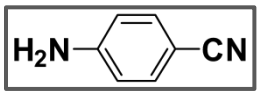
^{1}H NMR (DMSO-*d6*; 500 MHz; δ in ppm): 7.11 (d, 2H, *J* = 8.5 Hz), 6.51 (d, 2H, *J* = 8.5 Hz), 5.22 (br s, 2H, D_2O exchanged); **^{13}C NMR (DMSO-*d6*; 125 MHz; δ in ppm):** 148.48, 131.73, 116.25, 106.52

3-aminobenzonitrile[17]



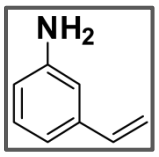
^{1}H NMR (DMSO-*d6*; 500 MHz; δ in ppm): 7.18 (s, 1H), 6.86 (m, 3H), 5.60 (br s, 2H, D_2O exchanged); **^{13}C NMR (DMSO-*d6*; 125 MHz; δ in ppm):** 149.95, 130.54, 119.96, 119.19, 118.85, 116.19, 111.94

4-aminobenzonitrile[7]



^{1}H NMR (DMSO-*d6*; 500 MHz; δ in ppm): 7.38 (d, 2H, *J* = 8.5 Hz), 6.61 (d, 2H, *J* = 8.5 Hz), 5.94 (br s, 2H, D_2O exchanged); **^{13}C NMR (DMSO-*d6*; 125 MHz; δ in ppm):** 153.45, 133.88, 121.11, 113.91, 96.01

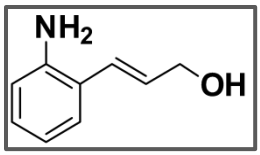
3-vinylaniline[12]



^{1}H NMR (DMSO-*d6*; 500 MHz; δ in ppm): 6.98 (s, 1H), 6.65-6.55 (m, 3H), 6.48 (dd, 1H, *J* = 2, 8 Hz), 5.64 (dd, 1H, *J* = 1, 17.5 Hz), 5.15 (dd, 1H, *J* = 1, 11 Hz) 5.05 (br s, 2H, D_2O exchanged); **^{13}C NMR (DMSO-*d6*; 125 MHz; δ in ppm):** 149.26, 138.04, 137.94, 129.47, 114.55, 114.31, 113.40, 111.81

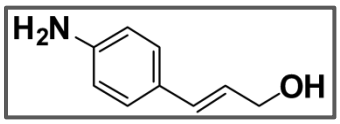
(*E*)-3-(2-aminophenyl)prop-2-en-1-ol[18]

^{1}H NMR ($CDCl_3$; 500 MHz; δ in ppm): 7.24 (dd, 1H, *J* = 1, 7.5 Hz), 7.07 (dt, 1H, *J* = 1.5, 8 Hz), 6.75 (dt, 1H, *J* = 1.5, 7.5 Hz), 6.67 (s, 1H), 6.66-6.64 (m, 1H), 6.23-6.17 (m,



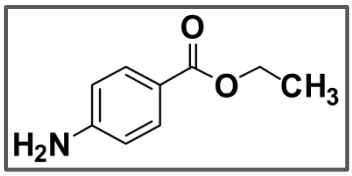
1H), 4.29 (dd, 2H, *J* = 1, 5.5 Hz), 2.06 (s, 1H); **^{13}C NMR ($CDCl_3$; 125 MHz; δ in ppm):** 143.67, 130.40, 128.56, 127.39, 126.21, 123.28, 119.07, 116.28, 63.51

(*E*)-3-(4-aminophenyl)prop-2-en-1-ol[19]



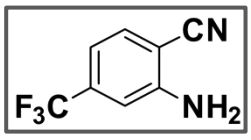
^{1}H NMR (DMSO-*d6*; 500 MHz; δ in ppm): 7.09 (d, 2H; *J* = 8.5 Hz), 6.52 (d, 2H, *J* = 8 Hz), 6.35 (d, 1H, *J* = 16 Hz), 5.13 (br s, 2H, D_2O exchanged), 4.68 (t, 1H, *J* = 5.5 Hz), 4.05 (t, 2H, *J* = 5.5 Hz), 3.38 (s, 1H); **^{13}C NMR (DMSO-*d6*; 125 MHz; δ in ppm):** 148.64, 130.05, 127.56, 125.29, 125.15, 114.35, 62.45

Ethyl 4-aminobenzoate[20]



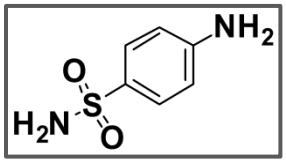
^{1}H NMR (DMSO-*d6*; 500 MHz; δ in ppm): 7.64 (d, 2H, *J* = 8 Hz), 6.57 (d, 2H, *J* = 8.5 Hz), 5.94 (br s, 2H, D_2O exchanged), 4.19 (q, 2H, *J* = 7.5 Hz), 1.26 (t, 3H, *J* = 7.5 Hz); **^{13}C NMR (DMSO-*d6*; 125 MHz; δ in ppm):** 166.35, 153.88, 131.48, 116.54, 113.10, 59.92, 14.81

2-amino-4-(trifluoromethyl) benzonitrile[17]



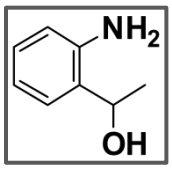
^{1}H NMR (DMSO-*d6*; 500 MHz; δ in ppm): 7.70 (d, 1H, *J* = 8 Hz), 7.04 (s, 1H), 6.87 (br s, 2H, D_2O exchanged), 6.75 (d, 1H, *J* = 8 Hz); **^{13}C NMR (DMSO-*d6*; 125 MHz; δ in ppm):** 170.67, 150.64, 132.20, 130.34, 125.53, 117.22, 112.99, 110.39

4-aminobenzene sulfonamide[4]



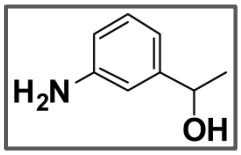
^{1}H NMR (DMSO-*d6*; 500 MHz; δ in ppm): 7.46 (d, 2H, *J* = 8.5 Hz), 6.90 (br s, 2H, D_2O exchanged), 6.60 (d, 2H, *J* = 8.5 Hz), 5.79 (br s, 2H, D_2O exchanged); **^{13}C NMR (DMSO-*d6*; 125 MHz; δ in ppm):** 152.37, 130.49, 127.89, 112.93

1-(2-amino phenyl) ethan-1-ol[21]



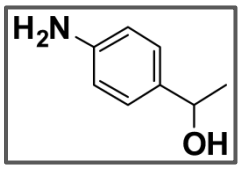
^{1}H NMR (DMSO-*d6*; 500 MHz; δ in ppm): 7.10 (dt, 1H, *J* = 1.5, 8 Hz), 6.74 (dt, 1H, *J* = 1, 7.5 Hz), 6.66 (d, 1H, *J* = 8 Hz), 6.52 (d, 1H, *J* = 8 Hz), 4.90 (q, 1H, *J* = 7 Hz), 1.57 (d, 3H, *J* = 7.5 Hz); **^{13}C NMR (DMSO-*d6*; 125 MHz; δ in ppm):** 152.68, 145.07, 128.50, 126.55, 118.14, 116.67, 69.47, 21.54

1-(3-amino phenyl) ethan-1-ol[22]



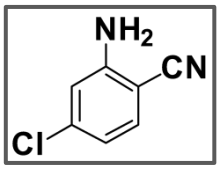
^{1}H NMR (DMSO-*d6*; 500 MHz; δ in ppm): 6.93 (t, 1H, *J* = 7.5 Hz), 6.58 (s, 1H), 6.47 (d, 1H, *J* = 7.5 Hz), 6.41 (td, 1H, *J* = 1.5, 7.5 Hz), 4.95 (s, 1H, D_2O exchanged), 4.94 (br s, 2H, D_2O exchanged), 4.55 (m, 1H), 1.26 (d, 3H, *J* = 7.5 Hz); **^{13}C NMR (DMSO-*d6*; 125 MHz; δ in ppm):** 148.76, 148.54, 128.83, 113.49, 112.69, 111.47, 68.80, 26.39.

1-(4-amino phenyl) ethan-1-ol[15]



^{1}H NMR (DMSO-*d6*; 500 MHz; δ in ppm): 6.98 (d, 2H, *J* = 8 Hz), 6.51 (d, 2H, *J* = 8 Hz), 4.86 (br s, 2H, D_2O exchanged), 4.54 (m, 1H), 1.26 (d, 3H, *J* = 7 Hz); **^{13}C NMR (DMSO-*d6*; 125 MHz; δ in ppm):** 147.66, 135.09, 126.53, 113.96, 68.45, 26.29

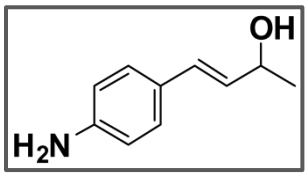
2-amino-4-chlorobenzonitrile[23]



^{1}H NMR ($CDCl_3$; 400 MHz; δ in ppm): 3.85 (br s, 2H), 6.98 (d, 1H, *J* = 8.2 Hz), 7.25 (d, 1H, *J* = 2.4 Hz), 7.88 (dd, 1H, *J* = 8.2, 2.4 Hz); **^{13}C NMR ($CDCl_3$, 101 MHz; δ in ppm):** 159.69, 152.41, 130.52, 129.32, 125.51, 120.67, 114.33 ; **HRMS**: m/z, Calcd. Mass: 175.0039 [(M + $Na)^+$], Found: 175.0015 [(M + $Na)^+$].

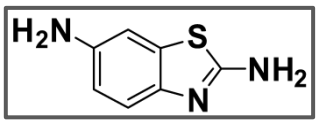
(*E*)-4-(4-aminophenyl) but-3-en-2-ol

Yellow liquid; **^{1}H NMR (DMSO-*d6*; 500 MHz; δ in ppm):** 7.07 (dd, 2H, *J* = 2, 7 Hz), 6.51 (dd, 2H, *J* = 2, 7 Hz), 6.30 (d, 1H, *J* = 15.5 Hz), 5.94 (dd, 1H, *J* = 6, 15 Hz), 5.12 (br



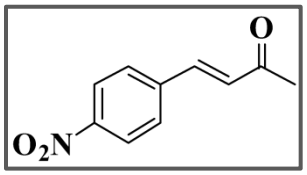
s, 2H, D_2O exchanged), 4.70 (s, 1H, D_2O exchanged), 4.23 (m, 1H), 1.18 (d, 3H, *J* = 7 Hz); **^{13}C NMR (DMSO-*d6*; 125 MHz; δ in ppm):** 148.57, 130.30, 128.31, 127.52, 125.11, 114.35, 67.50, 24.57; **IR (cm^{-1}):** 3354, 2967, 1607, 1514, 1372, 1245, 1045.

Benzo[*d*]thiazole-2, 6-diamine[24]



^{1}H-NMR (CDCl$_3$; 500 MHz; δ in ppm): 2.3 (br s, 2H), 4.2 (br s, 2H), 7.8-8.8 (m, 3H); **^{13}C NMR (CDCl$_3$; 125 MHz; δ in ppm):** 103.5, 113.3, 117.5, 130.6, 143.7, 144.5 and 159.2; **HRMS**: m/z, Calcd. Mass: 166.0439 [(M + H)$^+$], Found: 166.0430 [(M + H)$^+$].

(*E*)-4-(4-nitrophenyl) but-3-en-2-one[25]



^{1}H NMR (DMSO-*d6*; 500 MHz; δ in ppm): 8.26 (d, 2H, *J* = 8.5 Hz), 7.71 (d, 2H, *J* = 8.5 Hz), 7.54 (d, 1H, *J* = 16.5 Hz), 6.82 (d, 1H, *J* = 16 Hz), 2.43 (s, 3H); **^{13}C NMR (DMSO-*d6*; 125 MHz; δ in ppm):** 197.57, 148.58, 140.68, 140.08, 130.39, 128.82, 124.20, 28.04; **HRMS**: m/z, Calcd. Mass: 192.0661 [(M + H)$^+$], Found: 192.0663 [(M + H)$^+$].

References

1 (a) I. Langmuir, *T Faraday Soc*, 1922, **17**, 621-654; (b) C. N. Hinshelwood, *Annu Rep Progr Chem*, 1930, **27**, 11-51.

2 S Fountoulaki, V. Daikopoulou, P. L. Gkizis, I. Tamiolakis, G. S. Armatas, and I. N. Lykakis. *ACS Catal*, 2014, **4**, 3504-11.

3 (a) K. B. Narayanan and N. Sakthivel, *J Hazard Mater*, 2011, **189**, 519-525; (b) B. Hosseinkhani, L. S. Søbjerg, A. E. Rotaru, G. Emtiazi, T. Skrydstrup and R. L. Meyer, *Biotechnol. Bioeng*, 2011, **109**, 45-52; (c) L. Lin, W. Wu, J. Huang, D. Sun, N. U. M. Waithera, Y. Zhou, H. Wang and Q. Li, *Chem Eng J*, 2013, **225**, 857-864; (d) S. K. Srivastava, R. Yamada, C. Ogino and A. Kondo, *Nanoscale Res Lett*, 2013, **8**, 70; (e) S. K. Das, T. Parandhaman, N. Pentela, A. Maidul Islam, A. B. Mandal and M. Mukherjee, *J Phys Chem C*, 2014, **118**, 24623-24632; (f) A. Bhargava, N. Jain, S. Gangopadhyay and J. Panwar, *Process Biochem*, 2015, **50**, 1293-1300; (g) L. S.

Søbjerg, A. T. Lindhardt, T. Skrydstrup, K. Finster and R. L. Meyer, *Colloids Surf B Biointerfaces*, 2011, **85**, 373-378.

4 W. Guo, R. Pleixats, and A. Shafir, *Asian J Chem*, 2015, **10**, 2437-2443.

5 J. R. Hwu, A. R. Das, C. W. Yang, J. J. Huang, and M. H. Hsu, *Org Lett*, 2005, **7**, 3211-3214.

6 M. Karthik and P. Suresh, *Chemistry Select*, 2017, **2**, 6916-6928.

7 K. Layek, M. L. Kantam, M. Shirai, D. Nishio-Hamane, T. Sasaki, and H. Maheswaran, *Green chem*, 2012, **14**, 3164-3174.

8 Q. Ge, J. Ran, L. Wu and T. Xu, *J Appl Polym Sci*, 2015, **132**.

9 M. R. Nabid, Y. Bide, M. Shojaipour and F. Dastar, *Catal Lett*, 2016, **146**, 229-237.

10 H. Rao, H. Fu, Y. Jiang and Y. Zhao, *Angew Chem Int Ed*, 2009, **48**, 1114-1116.

11 W. G. Jia, H. Zhang, T. Zhang, D. Xie, S. Ling, and E. H. Sheng, *Organometallics*, 2016, **35**, 503-512.

12 E. Vasilikogiannaki, C. Gryparis, V. Kotzabasaki, I. N. Lykakis and M. Stratakis, *Adv Synth Catal*, 2013, **355**, 907-911.

13 M. Dabiri, N. F. Lehi, and S. K. Movahed, *Catal Lett*, 2016,**146**, 1674-1686.

14 V. Venepally, R. Prasad, Y. Poornachandra, C. G. Kumar, and R. C. R. Jala, *Bioorg Med Chem Lett*, 2016, **26**, 613-617.

15 Y. Motoyama, K. Kamo, and H. Nagashima, *Org Lett*, 2009, **11**, 1345-1348.

16 Y. Guo, J. Li, F. Zhao, G. Lan, L. Li, Y. Liu, Y. Si, Y. Jiang, B. Yang and R. Yang, *RSC Adv*, 2016, **6**, 7950-7954.

17 R. J. Rahaim Jr and R. E. Maleczka Jr, *Synthesis*, 2006, **2006**, 3316-3340.

18 J. M. Cuerva, D. J. Cárdenas and A. M. Echavarren, *Perkin Trans*, 2002, **1**, 1360-1365.

19 A. S. Kumar, S. Tateyama, K. Yasaki, M. A. Ali, N. Takaya, R. Singh and T. Kaneko, *Polym J*, 2016, **83**, 182-189.

20 A. J. MacNair, M. M. Tran, J. E. Nelson, G. U. Sloan, A. Ironmonger and S. P. Thomas, *Org Biomol Chem*, 2014, **12**, 5082-5088.

21 T. Stopka and M. Niggemann, *Chem Commun*, 2016, **52**, 5761-5764.

22 B. Zeynizadeh, I. Mohammadzadeh, Z. Shokri and S. A. Hosseini, *J Colloid Interface Sci*, 2017, **500**, 285-293.

23 G. Dou and D. Shi, *ACS Comb Sci*, 2009, **11**, 1073-1077.

24 S. N. Sawhney, and D. W. Boykin, *J Org Chem*, 1979, **44**, 1136-1142.

25 N. Solin, L. Han, S. Che and O. Terasaki , *Catal Commun*, 2009, **10**, 1386-1389.