Electronic Supplementary Information

In Situ Synthesis of Ultra-small Platinum Nanoparticles Using Water Soluble Polyphenolic Polymer with High Catalytic Activity

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Catalysis of borohydride reduction of 4-nitrophenol by colloidal Bare-Pt NPs

At first, 2 mL of the as prepared colloidal Bare-Pt NPs ($5.7x10^{-4}$ mmol) taken into a 3 mL quartz cuvette followed by the addition of 0.8 mL water, and an aqueous 4-NP solution (0.1 mL, 3 mM) to that solution. The catalytic reduction of 4-NP was then studied in a spectrophotometer at 25 °C with a stirring speed of 500 rpm by final addition of an aqueous $NaBH_4$ solution (0.1 mL; 300 mM).

Catalysis of borohydride reduction of 4-nitrophenol by colloidal PVPh-Pt_{BH4^-} nanocatalyst

First a stock aqueous colloidal Pt NPs suspension was prepared by dilution of 0.5 mL as-synthesised colloidal Pt NPs to 2.5 mL with Milli-Q water. From this, 2 mL ($5.1x10^{-4}$ mmol) solution was taken into a 3 mL quartz cuvette. To that solution 0.8 mL water, and an aqueous 4-NP solution (0.1 mL, 3 mM) were added and placed the cuvette in a spectrophotometer at 25 °C with stirring at a speed of 500 rpm. To this reaction mixture, an aqueous $NaBH_4$ solution (0.1 mL; 300 mM) was finally added to study the reduction of 4-NP.

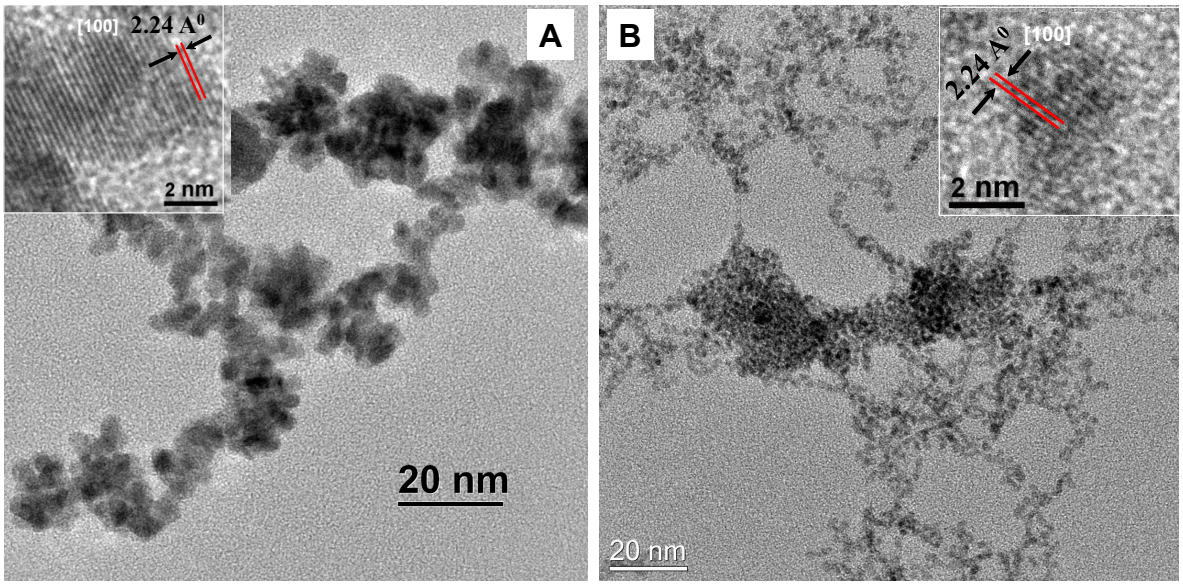

Figure S1. TEM images of (A) colloidal Bare Pt NPs (B) PVPh-Pt_{BH4^-} nanoparticles. Insets in each panel showed the HRTEM of single Pt nanoparticle

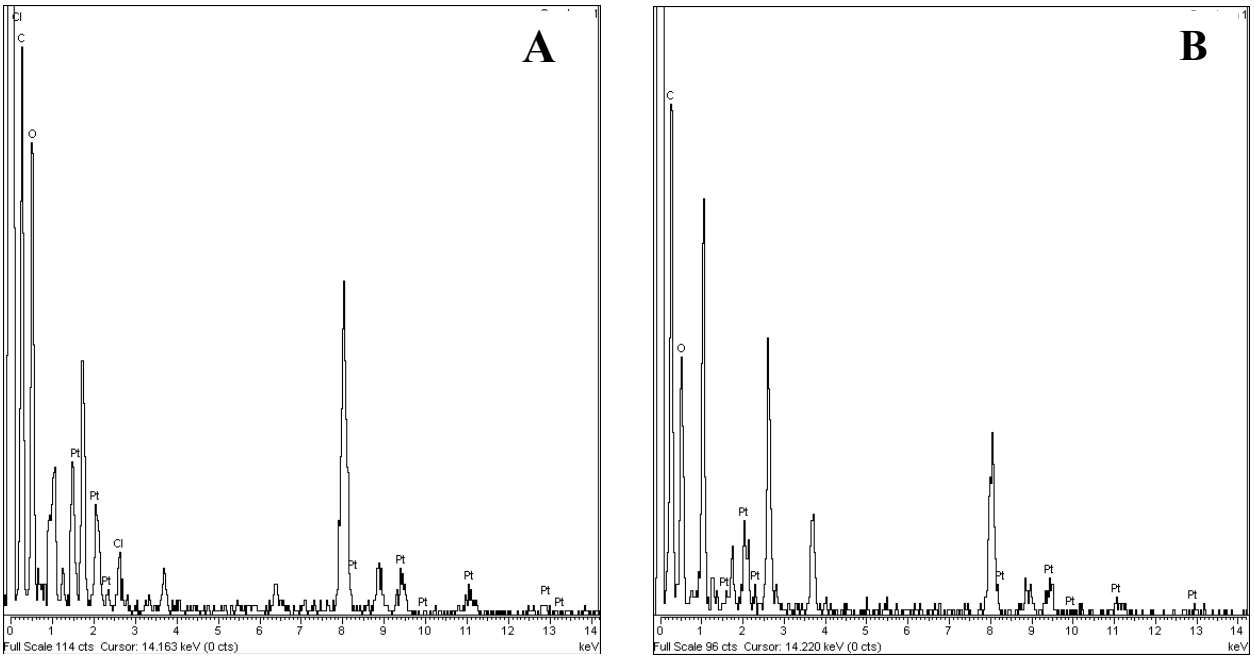

Figure S2 . Energy dispersive X-ray (EDX) analysis of (A) PVPh-$Pt_{1.3}$ (B) PVPh-Pt_5.

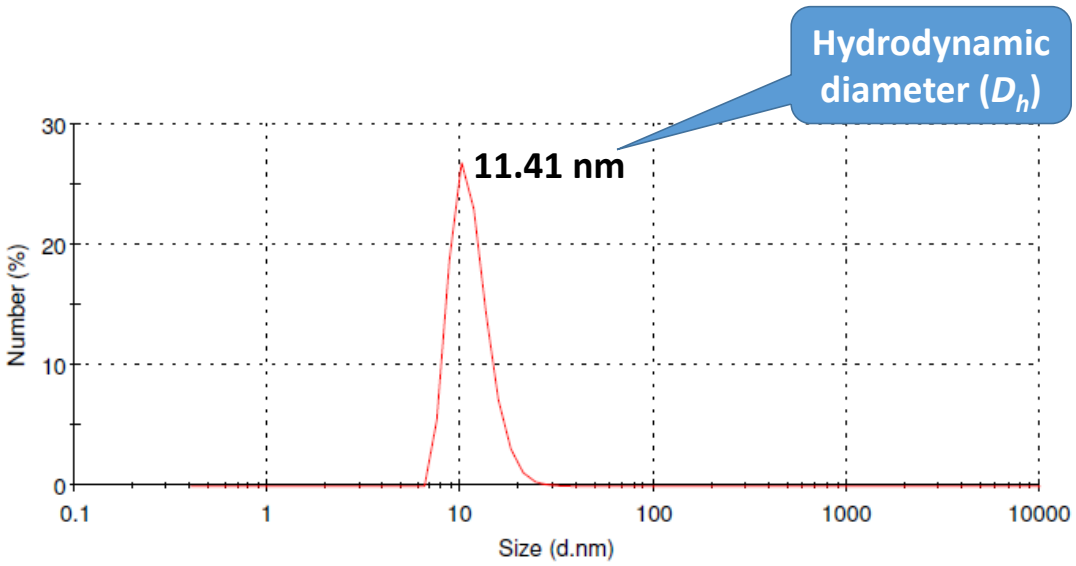

Figure S3. Plot showing log-normal distributions of the sizes of the Pt NPs (PVPh-Pt_5) from DSL measurements.

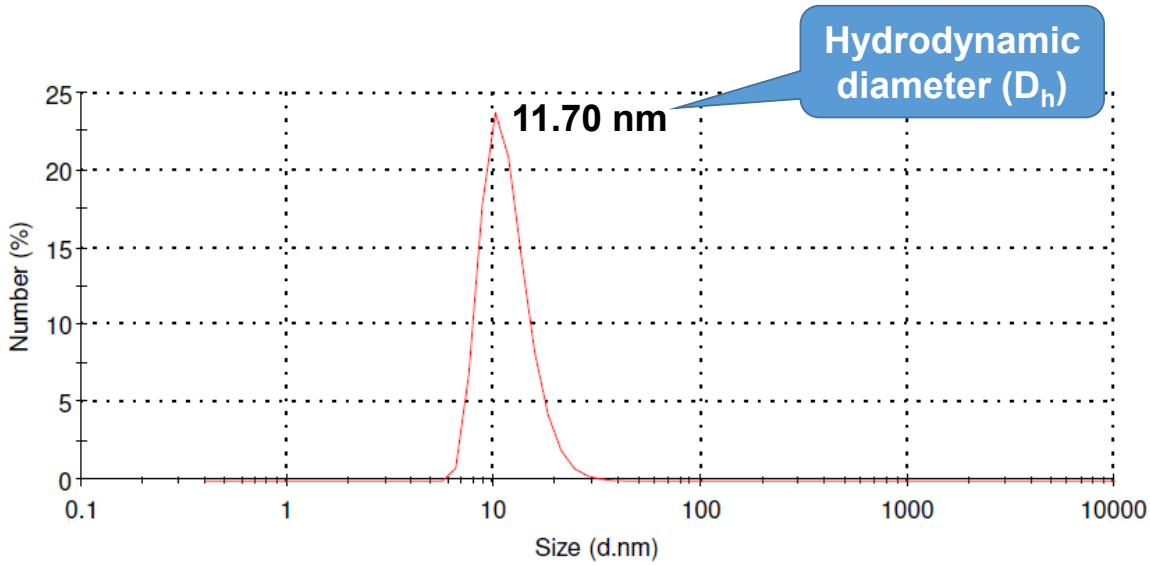

Figure S4. Plot showing log-normal distributions of the sizes of the Pt NPs (PVPh-$Pt_{1.3}$) from DSL measurements

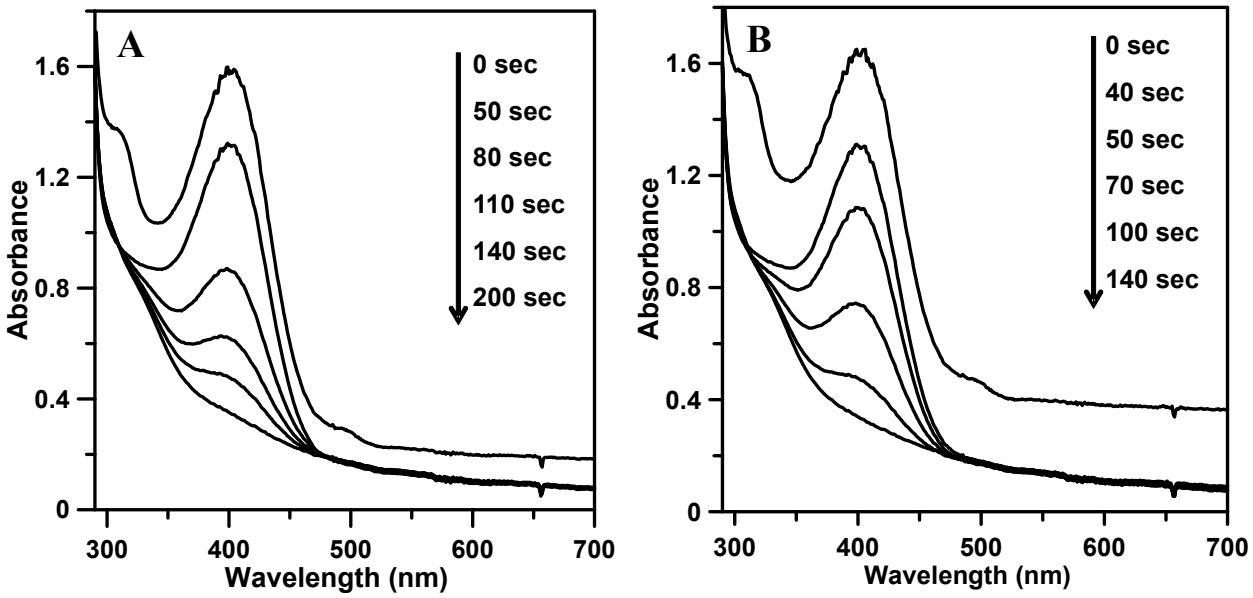

Figure S5. Time-dependent absorption spectra of the 4-NP reduction in the presence of PVPh-$Pt_{1.3}$ at (A) 30 ºC (B) 40 ºC

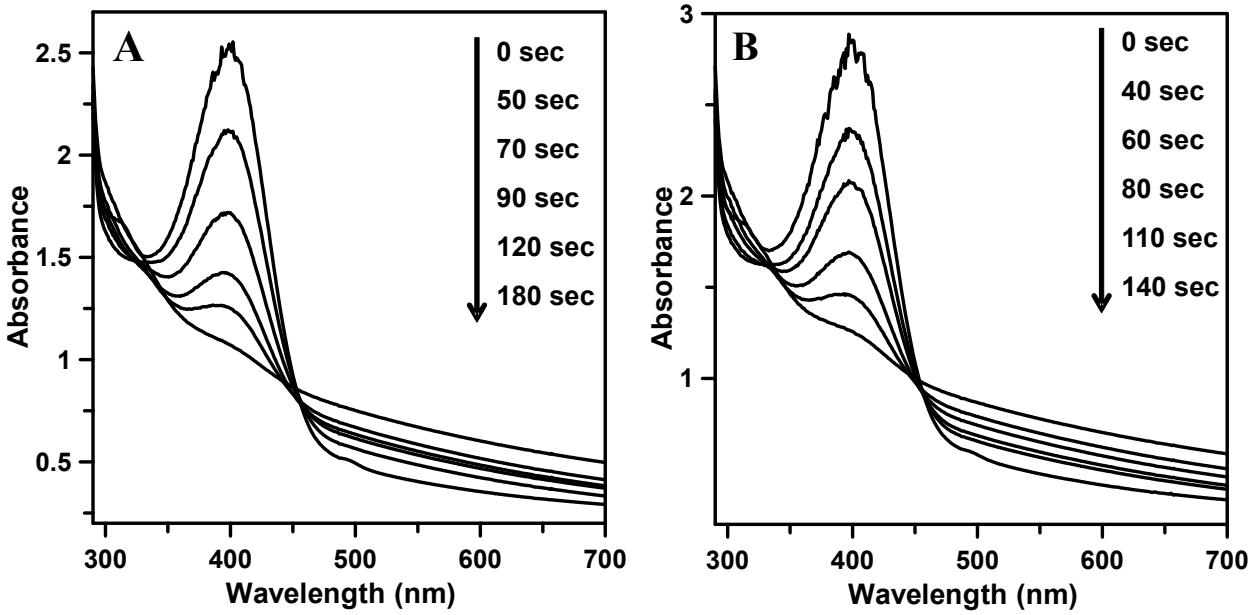

Figure S6. Time-dependent absorption spectra of the 4-NP reduction in the presence of PVPh-Pt_5 at (A) 30 °C (B) 40 °C

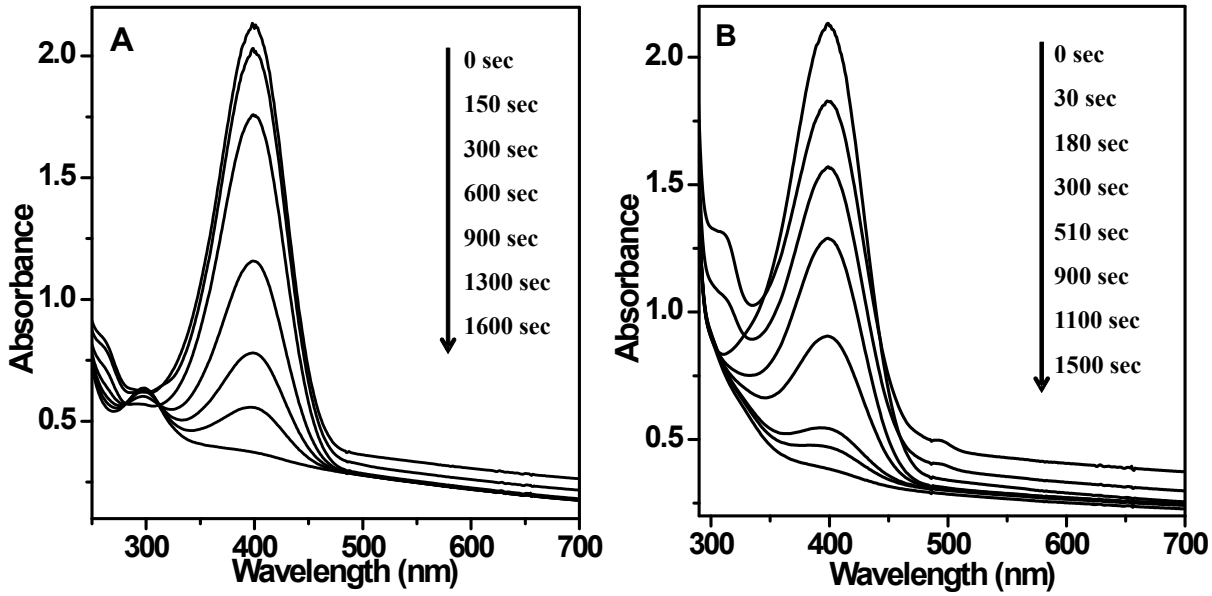

Figure S7. Time-dependent absorption spectra of the 4-NP reduction at 25 °C in the presence of (A) colloidal bare Pt NPs (B) PVPh-Pt_{BH4^-}

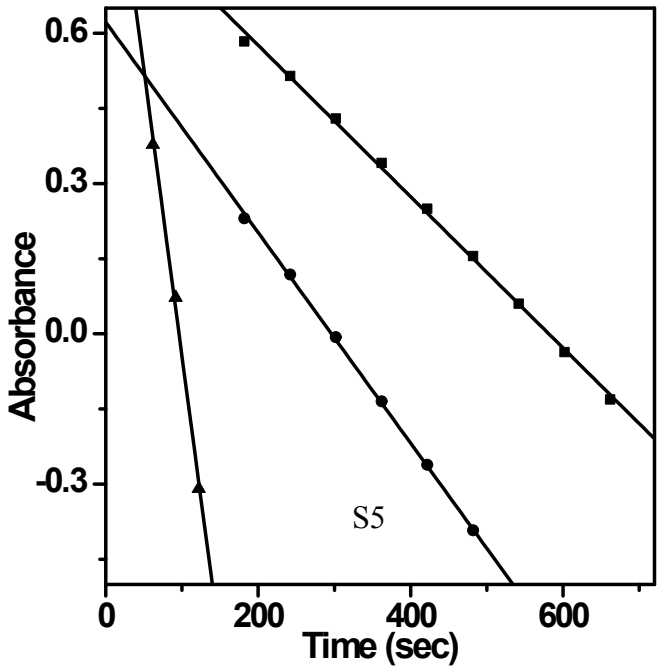

Figure S8. Plots of ln A (A = absorbance at 400 nm of p-nitrophenolate ion) versus time for the reduction of p-nitrophenol at 25 °C using catalyst (A)▲ PVPh-$Pt_{1.3}$ (B)● PVPh-Pt_{BH4^-} (C)■ Colloidal bare Pt NPs

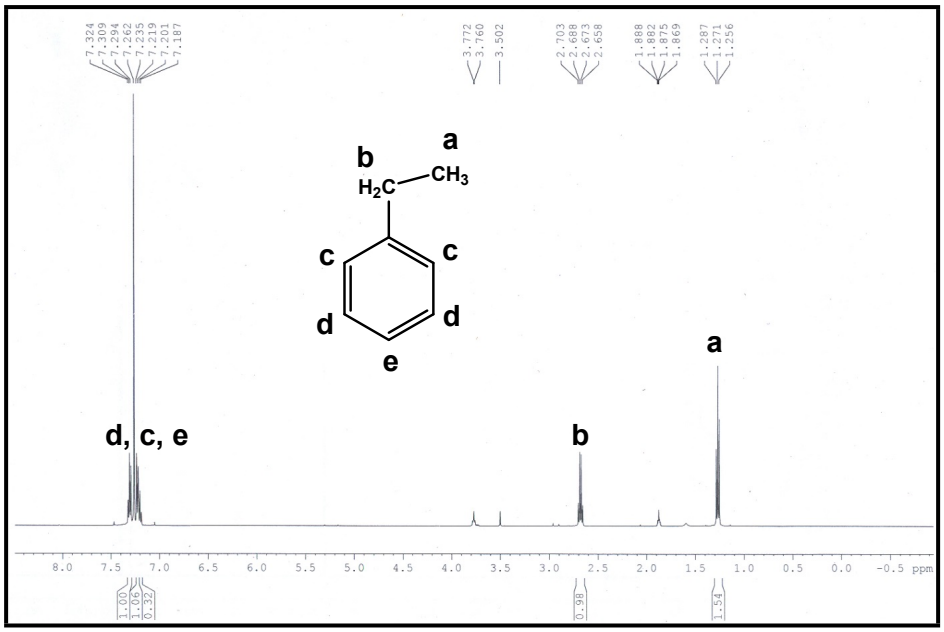

Figure S9. ^{1}H NMR spectrum of ethyl benzene. ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 1.27 (t, 3H, CH_3), 1.88 (q, 2H, CH_2), 7.20 (dd, 1H),7.23 (m, 2H), 7.30 (m, 1H, CH), (The ^{1}H NMR peak at δ 7.26 ppm corresponds to $CHCl_3$ present in $CDCl_3$).

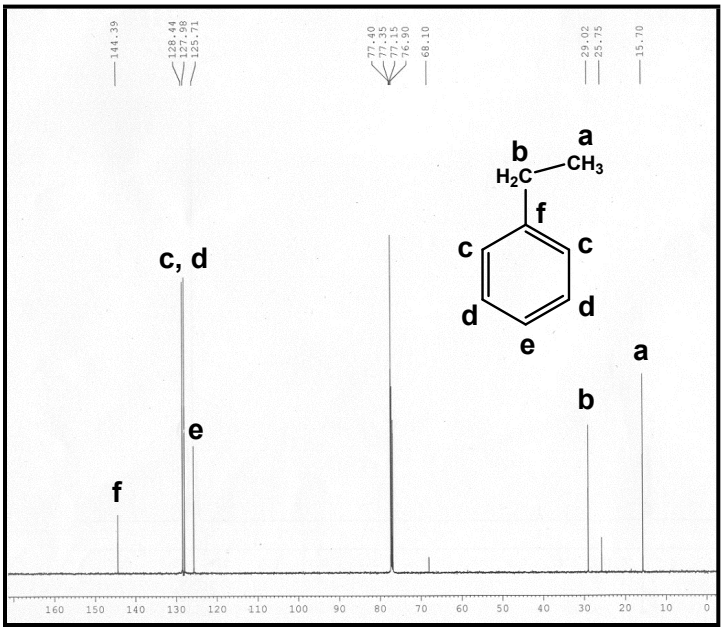

Figure S10. **^{13}C** NMR spectrum of ethyl benzene. ^{13}C NMR (500 MHz, $CDCl_3$, δ ppm): 15.70 (a-CH_3), 29.02 (b-CH_2), 125.71 (e-CH), 127.9 (d-CH), 128.4 (c-CH), 144.4 (f-CH) (The ^{13}C NMR peak at δ 77.26 ppm corresponds to $CHCl_3$ present in $CDCl_3$).

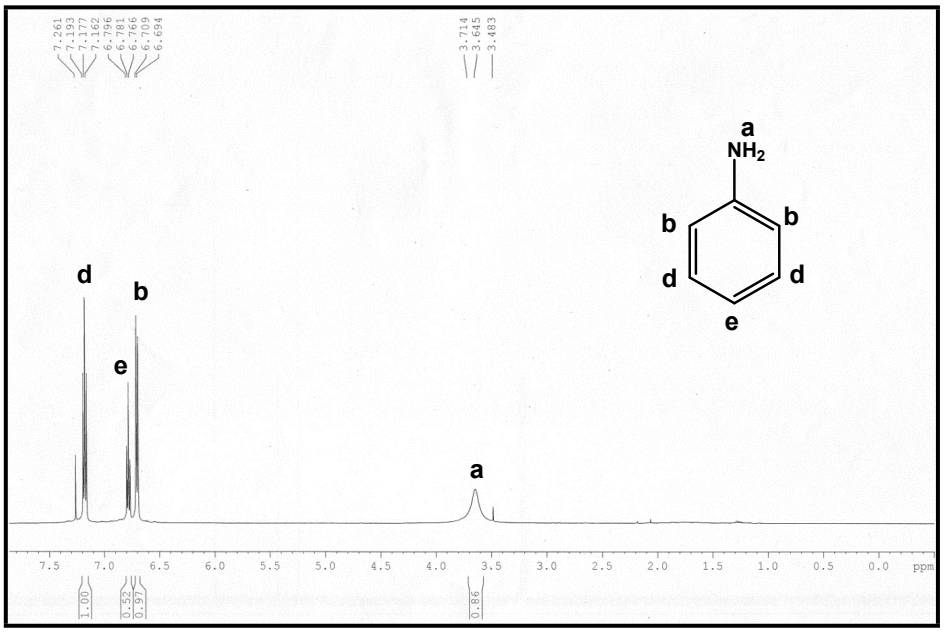

Figure S11. ^{1}H NMR spectrum of aniline. 1H NMR (500 MHz, $CDCl_3$, δ ppm): 3.36 (2H, Nh_2), 6.70 (d, 2H), 6.78 (t, 1H), 7.17 (t, 2H) (The ^{1}H NMR peak at δ 7.26 ppm corresponds to $CHCl_3$ present in $CDCl_3$).

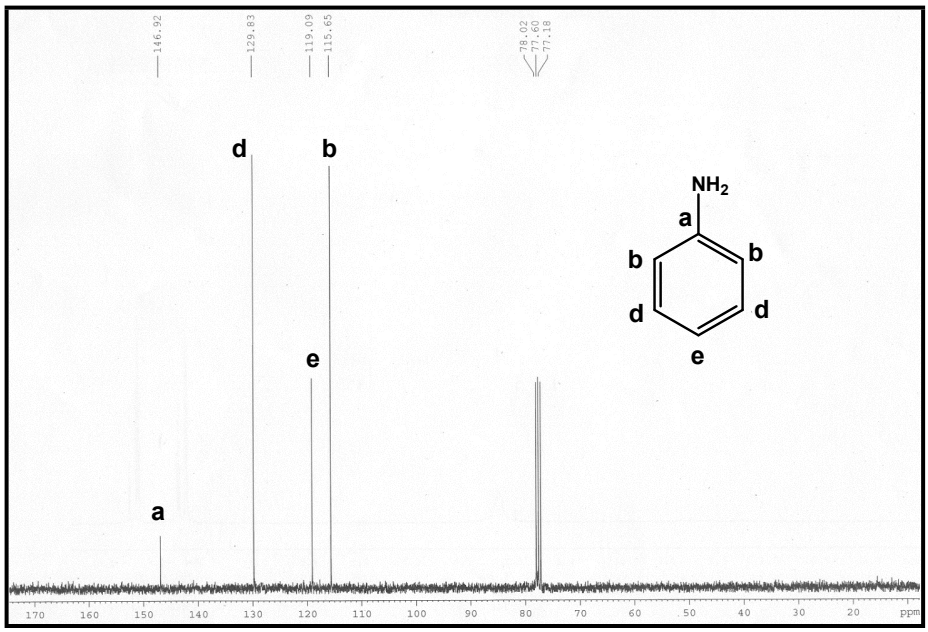

Figure S12. **^{13}C** NMR spectrum of aniline. ^{13}C NMR (500 MHz, $CDCl_3$, δ ppm): 115.65 (b-CH), 119.09 (e-CH), 129.83 (d-CH), 146.92 (a-CH) (The ^{13}C NMR peak at δ 77.26 ppm corresponds to $CHCl_3$ present in $CDCl_3$).

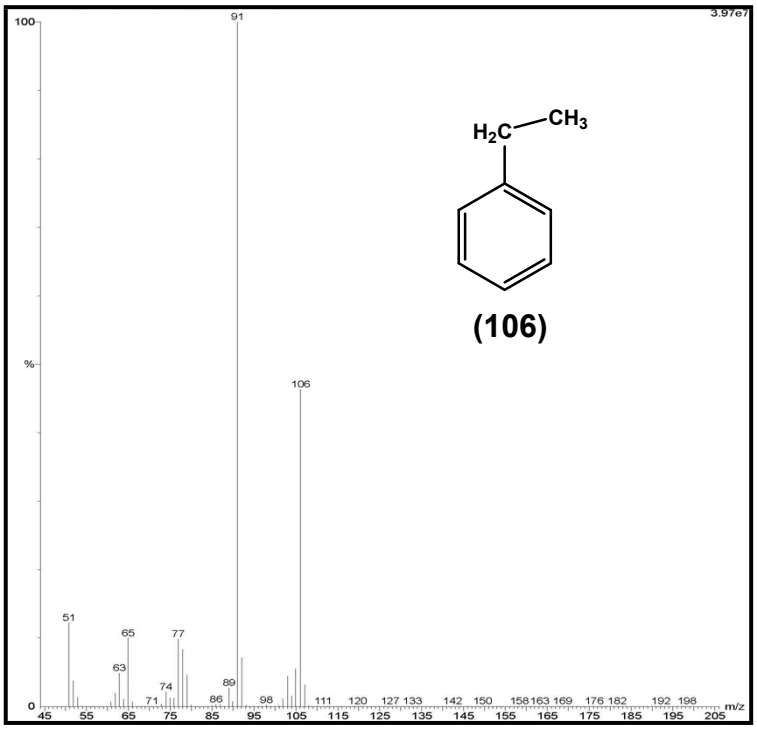

Figure S13. Mass spectra of GC-MS of ethyl benzene obtained after removal of catalyst.

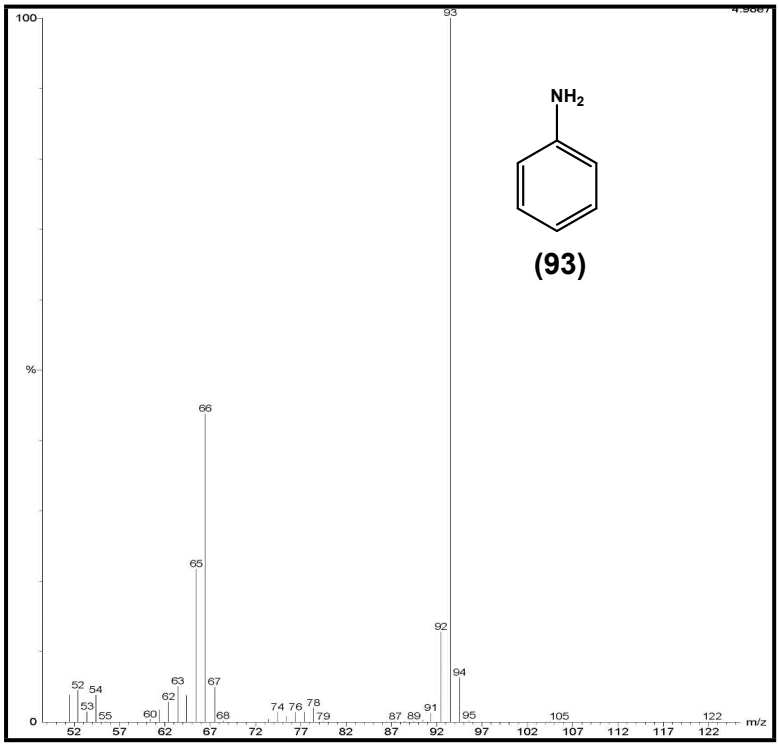

Figure S14. Mass spectra of GC-MS of aniline obtained after removal of catalyst.

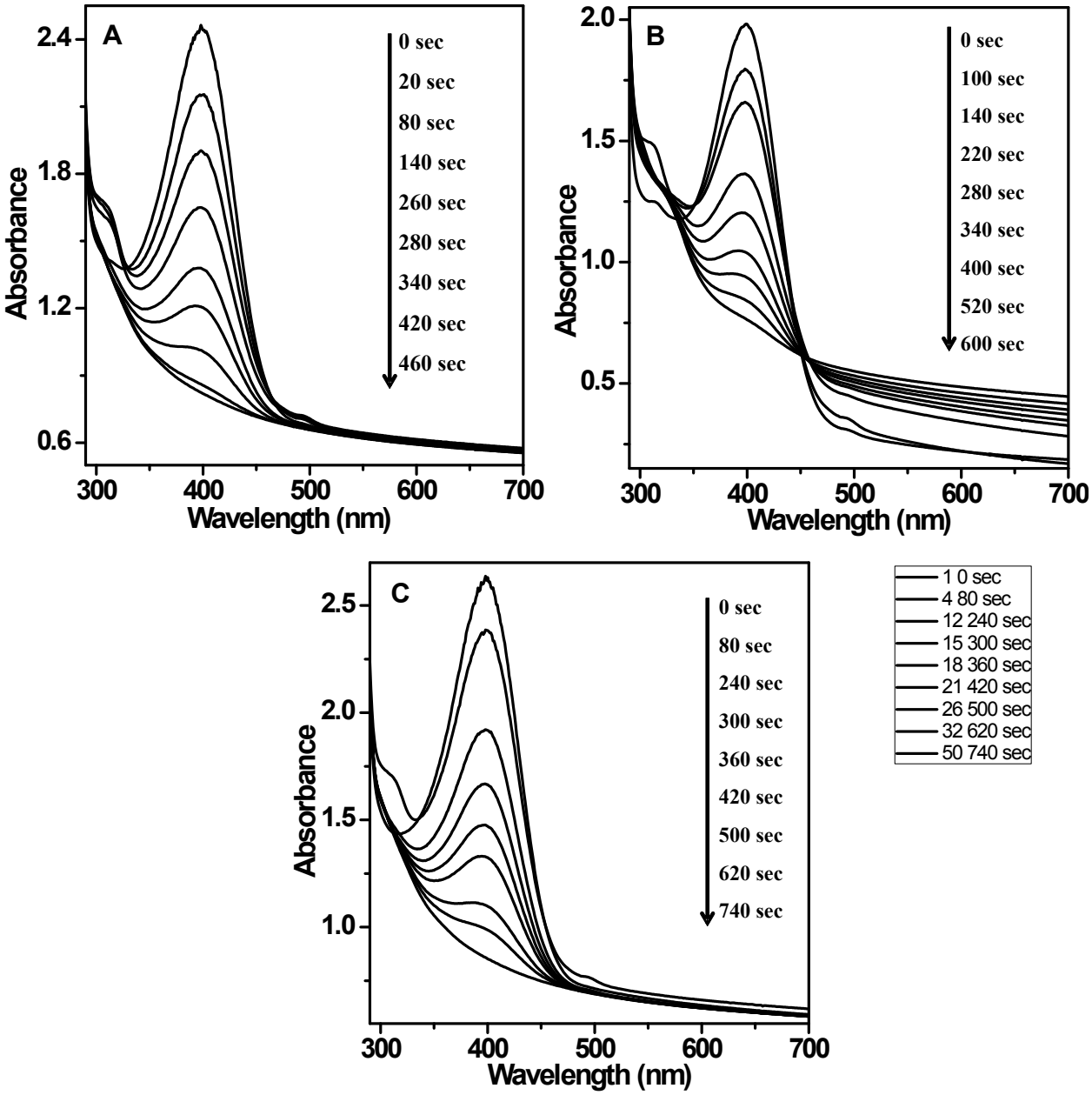
A
0 sec
20 sec
80 sec
140 sec
260 sec
280 sec
340 sec
420 sec
460 sec
Absorbance
Wavelength (nm)
B
0 sec
100 sec
140 sec
220 sec
280 sec
340 sec
400 sec
520 sec
600 sec
Absorbance
Wavelength (nm)
C
0 sec
80 sec
240 sec
300 sec
360 sec
420 sec
500 sec
620 sec
740 sec
Absorbance
Wavelength (nm)
1 0 sec
4 80 sec
12 240 sec
15 300 sec
18 360 sec
21 420 sec
26 500 sec
32 620 sec
50 740 sec

Figure S15. Time-dependent absorption spectra of the 4-NP reduction in the presence of PVPh-$Pt_{1.3}$ at (A) 2nd cycle, (B) 3rd cycle and (C) 4th cycle of catalysis.

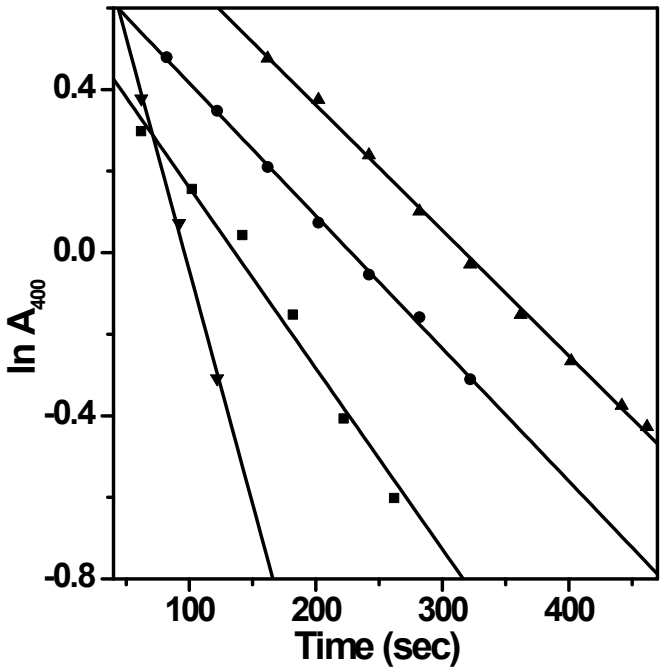

Figure S16. Plots of ln A (A = absorbance at 400 nm of p-nitrophenolate ion) versus time for the reduction of p-nitrophenol sample at 25 ºC using PVPh-$Pt_{1.3}$ for (A)▼1st cycle (B) ■ 2nd cycle (C)● 3rd cycle (D)▲ 4th cycle of catalysis

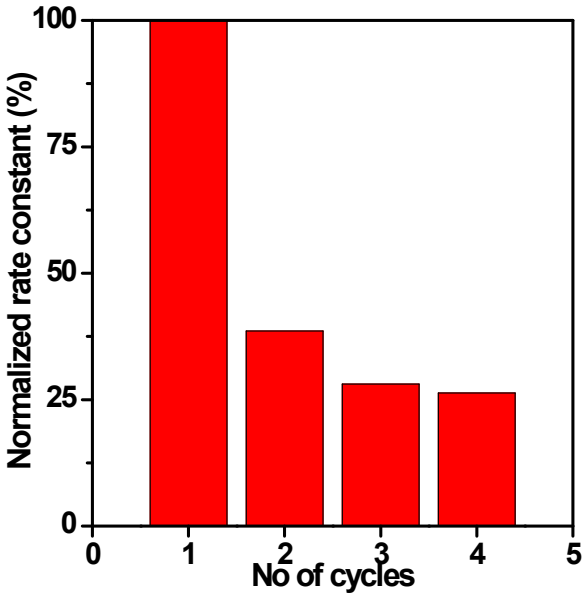

Figure S17. Plot showing the variation in normalized rate constant in different cycles of the borohydride reduction of p-nitrophenol using PVPh-$Pt_{1.3}$ sample.

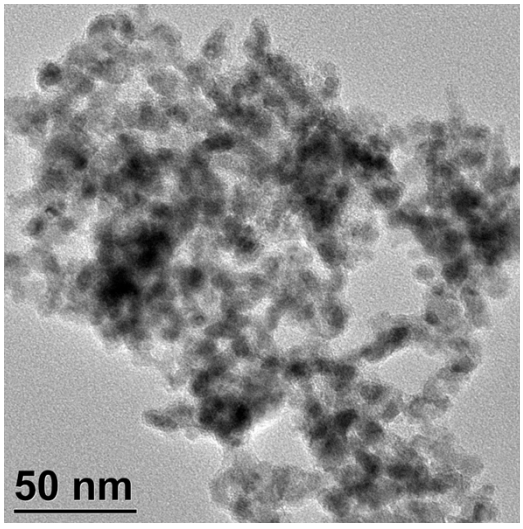

Figure S18. TEM image of the sample PVPh-$Pt_{1.3}$ after 3rd cycle of the catalysis