

Electronic Supporting Information:

Urea-stabilized air-stable Pt nanoparticles for thin film deposition

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Experimental:

Synthesis: All operations were carried out using standard Fischer-Porter bottle or in a glove-box under argon. Solvents were purified just before use. Synthesis of Platinum colloids was performed as follow. Dimethyl(1,5-cyclooctadiene)platinum(II) (Pt(Me)₂(COD), 8.3 mg, 2,5.10⁻⁵ mol, STREM) was introduced in a Fischer-Porter bottle with 1-hexadecylamine (HDA, 6 mg, 2,5.10⁻⁵ mol, Aldrich) and cis-9-Octadecenoic acid (oleic acid, OA, 8 μL, 2,5.10⁻⁵ mol, Aldrich). 5 mL of purified toluene was then added. The resulting colorless solution was stirred 1 hour at room temperature under 1 bar of carbon monoxide (CO) then the solution was allowed to react for 1 night at 110°C. A gray solution with a black-brown precipitate was obtained and after elimination of CO in excess, the bottle was pressurized at room temperature under 3 bar of synthetic air. After a few minutes under stirring, a homogeneous brown solution was obtained.

After evaporation of toluene, the solid oil obtained was washed with methanol (3 mL) and centrifugated (5000 rpm, 10 min). The supernatant is removed and the platinum nanoparticles are dried under vacuum.

Transmission Electron Microscopy (TEM): TEM specimens were prepared by slow evaporation in a glove-box of a drop of colloidal solution deposited onto a holey carbon

covered copper grid. The TEM experiments were performed on a JEOL JEM 1011 transmission electron microscope operating at 100 kV with a resolution of 4,5 Å.

HR-TEM analysis was carried out a JEOL JEM 2100F field emission gun transmission electron microscope (FED-TEM) operating at 200 kV with a resolution of 2.3 Å (point-point) and 1 Å (line).

Scanning Electron Microscopy (SEM): SEM analysis was carried out using a JEOL JSM 6700F scanning electron microscope operated with a 0.5-30 kV scale acceleration voltage.

Nuclear Magnetic Resonance (NMR): 1D and 2D ^1H and ^{13}C NMR experiments in liquid state were recorded on a Bruker Avance 500 spectrometer equipped with a 5 mm triple resonance inverse Z-gradient probe (TBI ^1H , ^{31}P , BB). Solid-state NMR experiments were performed on a Bruker Avance 400WB instrument equipped with 4 mm probe with the sample rotation frequency being set at 12 kHz unless otherwise indicated. We used toluene- d_8 for solvent and ^{13}CO for reducing agent for platinum nanoparticles synthesis. All chemical shifts for ^1H and ^{13}C are referenced to tetramethylsilane (TMS) at 0 ppm. In the present study, ^1H and ^{13}C NMR spectroscopy were used for the characterization of platinum complexes. All the ^1H and ^{13}C signals were assigned on the basis of chemical shifts, spin-spin coupling constants, splitting patterns and signal intensities, and by using ^1H - ^1H COSY45, ^1H - ^{13}C HMQC and ^1H - ^{13}C HMBC experiments. HRMAS: high resolution magic angle spinning. CPMAS: cross polarization magic angle spinning

NMR data for :

HDA: ^1H NMR (500 MHz, Tol- d_8 , δ): 2.57 (t, 2H, $J = 6$ Hz, CH_2 - α), 1.35 (m, 2H, CH_2 - β), 1.35-1.30 (m, 14H, 7CH_2), 0.96 (t, 3H, $J = 7$ Hz, CH_3); ^{13}C NMR (125 MHz, Tol- d_8 , δ): 42.4 (C_α), 34.3 (C_β), 32.1-22.8 (7CH_2), 14.0 (CH_3)

OIAc: ^1H NMR (500 MHz, Tol- d_8 , δ): 12.60 (s, 1H, COOH), 5.48 (m, 2H, CH=CH), 2.13 (t, 2H, $J = 6$ Hz, $\text{CH}_2\text{-}\alpha$), 2.12 (m, 4H, $\text{CH}_2\text{-C=C}$), 1.49 (m, 2H, $\text{CH}_2\text{-}\beta$), 1.49-1.15 (m, 20H, CH_2), 0.94 (t, 3H, $J = 7$ Hz, CH_3); ^{13}C NMR (125 MHz, Tol- d_8 , δ): 180.5 (COOH), 129.8 (C=C), 33.8 (C_α), 27.3 ($\text{CH}_2\text{-C=C}$), 24.6 (C_β), 32.0-22.8 (10 CH_2), 14.0 (CH_3)

Pt(COD)(CH₃)₂: ^1H NMR (500 MHz, Tol- d_8 , δ): 4.58 (m, 4H, $J_{\text{H-Pt}} = 40$ Hz, CH=CH), 1.86-1.77 (m, 8H; CH_2), 1.17 (t, 3H, $J_{\text{H-Pt}} = 83$ Hz, CH_3); ^{13}C NMR (125 MHz, Tol- d_8 , δ): 97.8 (C=C, $J_{\text{C-Pt}} = 55$ Hz), 29.6 (CH_2), 5.7 (CH_3 , $J_{\text{C-Pt}} = 783$ Hz)

cis-Pt(CH₃)₂(CO)(HDA): ^1H NMR (500 MHz, Tol- d_8 , δ): 2.27 (m, 2H, $\text{CH}_2\text{-}\alpha$), 1.14 (m, 2H, $\text{CH}_2\text{-}\beta$), 1.39 (t, 3H, $J_{\text{H-Pt}} = 92$ Hz, Pt- CH_3), 1.35-1.30 (m, 14H, 7 CH_2), 0.96 (t, 3H, $J = 7$ Hz, CH_3), 0.62 (t, 3H, $J_{\text{H-Pt}} = 65$ Hz, Pt- CH_3); ^{13}C NMR (125 MHz, Tol- d_8 , δ): 181.4 (CO, $J_{\text{C-Pt}} = 1082$ Hz), 48.0 (C_α), 26.5 (C_β), 32.1-22.8 (7 CH_2), 14.0 (CH_3), 10.8 (Pt- CH_3 , $J_{\text{C-Pt}} = 60$ Hz), -23.3 (Pt- CH_3 , $J_{\text{C-Pt}} = 648$ Hz); IR (KBr): $\nu = 2038$ cm^{-1} (CO)

cis-Pt(CH₃)₂(CO)₂: ^1H NMR (500 MHz, Tol- d_8 , δ): 1.04 (t, 6H, $J_{\text{H-Pt}} = 78$ Hz, Pt- CH_3); ^{13}C NMR (125 MHz, Tol- d_8 , δ): 177.6 (CO, $J_{\text{C-Pt}} = 909$ Hz), -2.1 (Pt- CH_3 , $J_{\text{C-Pt}} = 78$ Hz); IR (KBr): $\nu = 2114$ and 2064 cm^{-1} (CO)

COD: ^1H NMR (500 MHz, Tol- d_8 , δ): 5.57 (m, 4H, CH=CH), 2.24 (m, 8H; CH_2); ^{13}C NMR (125 MHz, Tol- d_8 , δ): 128.4 (C=C), 28.0 (CH_2)

CH₃CONHR: ^1H NMR (500 MHz, Tol- d_8 , δ): 4.36 (br s, 1H, NH), 3.04 (m, 2H, $\text{CH}_2\text{-}\alpha$), 1.57 (d, 3H, $J_{\text{H-C}} = 6$ Hz, *CO- CH_3), 1.27 (m, 2H, $\text{CH}_2\text{-}\beta$), 1.35-1.30 (m, 14H, 7 CH_2), 0.96 (t, 3H, $J = 7$ Hz, CH_3); ^{13}C NMR (125 MHz, Tol- d_8 , δ): 168.0 (CO), 39.2 (C_α), 27.0 (C_β), 32.1-22.8 (7 CH_2), 22.4 (*CO- CH_3 , $J_{\text{C-C}} = 52$ Hz), 14.0 (CH_3); IR (KBr): $\nu_{\text{CO}} = 1651$ cm^{-1} .

CH₃CO CH₃: ^1H NMR (500 MHz, Tol- d_8 , δ): 1.61 (d, 6H, $J_{\text{H-C}} = 6$ Hz, CH_3); ^{13}C NMR (125 MHz, Tol- d_8 , δ): 202.8 (CO), 29.6 (CH_3 , $J_{\text{C-C}} = 38$ Hz)

CH₄: ^1H NMR (500 MHz, Tol- d_8 , δ): 0.41 (s, 4H, CH_4); ^{13}C NMR (125 MHz, Tol- d_8 , δ): -4.8 (CH_4)

CO: ^{13}C NMR (125 MHz, ToI-d_8 , δ): 184.8 (CO)

CO₂: ^{13}C NMR (125 MHz, ToI-d_8 , δ): 124.5 (CO₂)

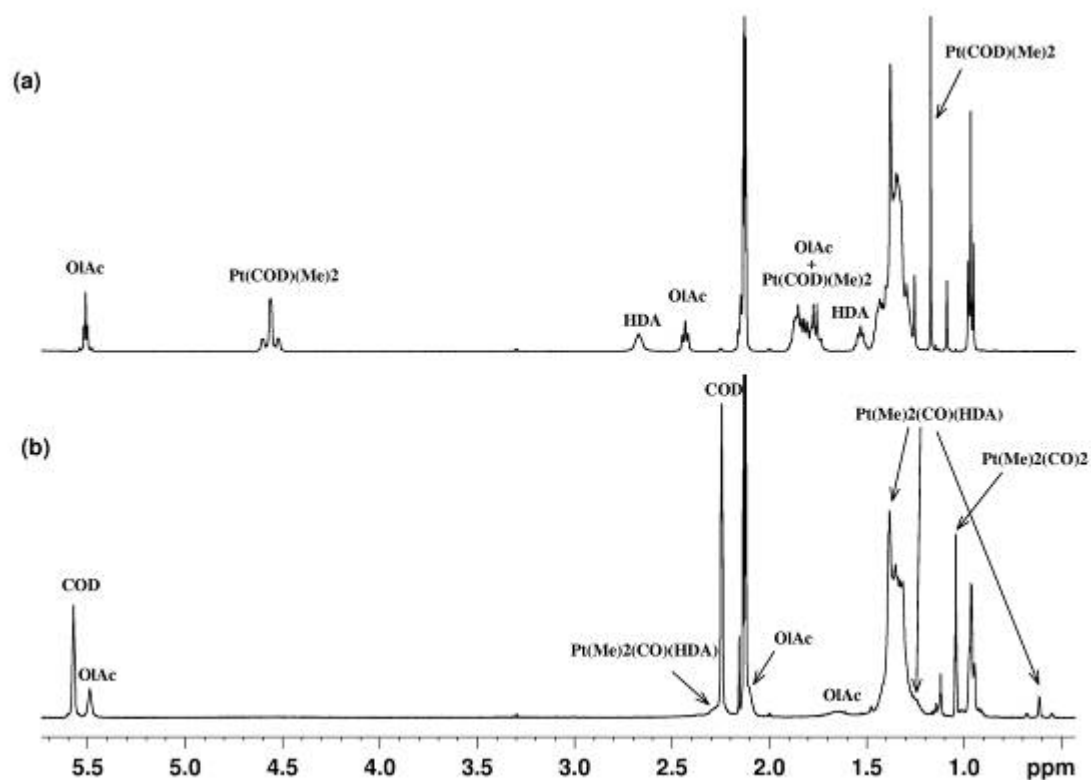


Figure S1. ^1H NMR spectra of the mixture that contains one eq. of $\text{Pt}(\text{COD})(\text{CH}_3)_2$, one eq. of hexadecylamine (HDA) and one eq. of oleic acid (OIAc) before (a) and after (b) the addition of ^{13}C -labeled carbon monoxide.

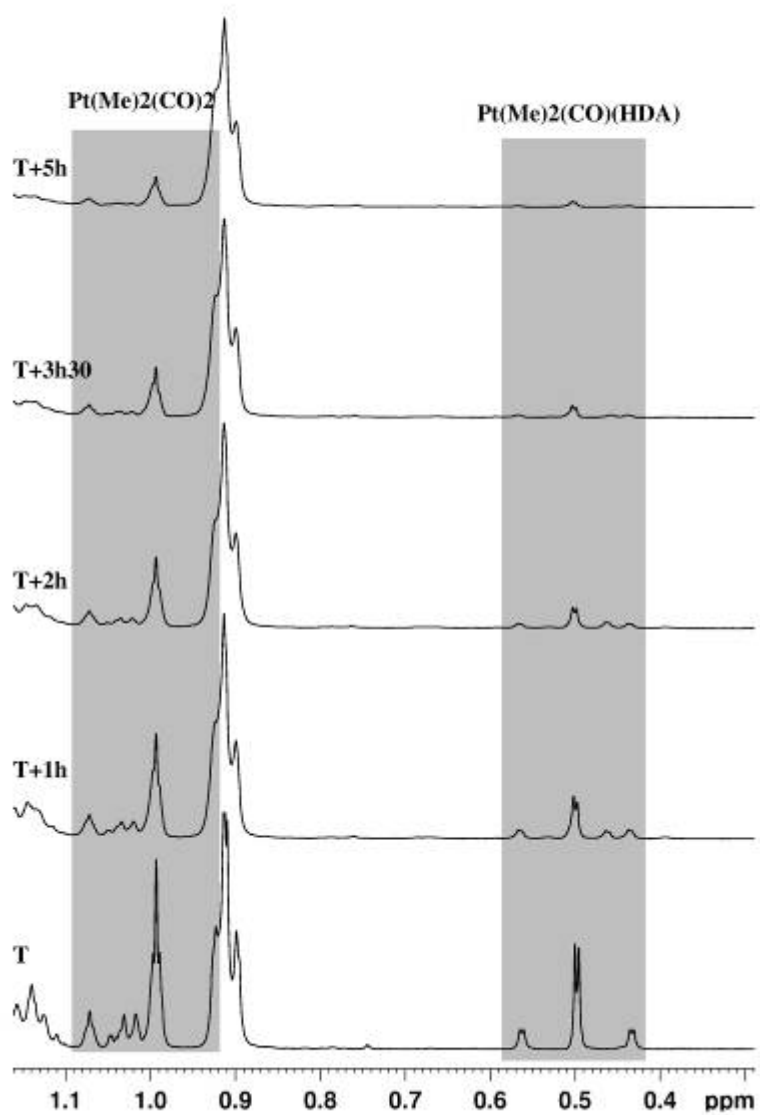


Figure S2. Disappearance of CH_3 peaks of $\text{cis-Pt}(\text{CH}_3)_2(\text{CO})_2$ and $\text{cis-Pt}(\text{CH}_3)_2(\text{CO})(\text{HDA})$ during thermolysis by ^1H NMR spectra in toluene- d_8 at 110°C .

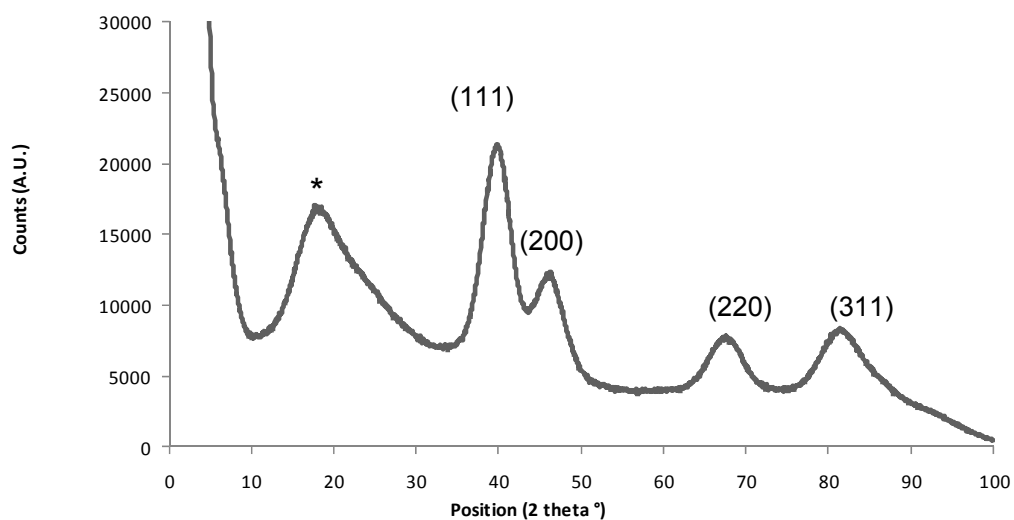


Figure S3. XRD diagram of black precipitated Pt nanoparticles obtained under CO atmosphere and heating at 110°C (*: carbon compounds).

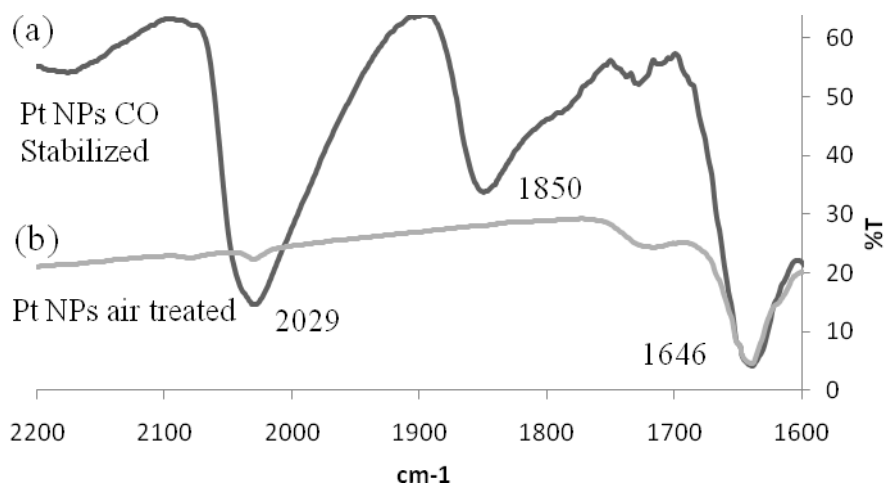


Figure S4. IR spectra of KBr pellet with Pt nanoparticles (a) before and (b) after air exposure.

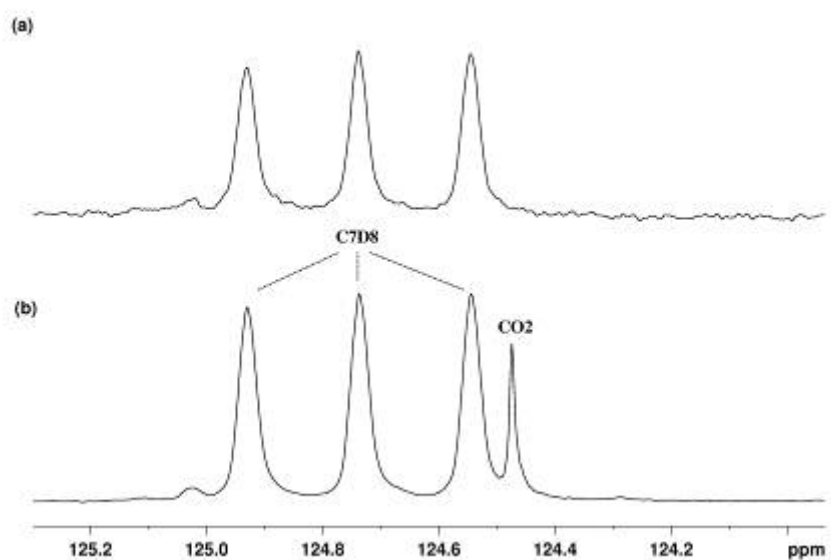


Figure S5. Comparison of selected region of $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of Pt colloidal solution (a) before and (b) after air exposure.

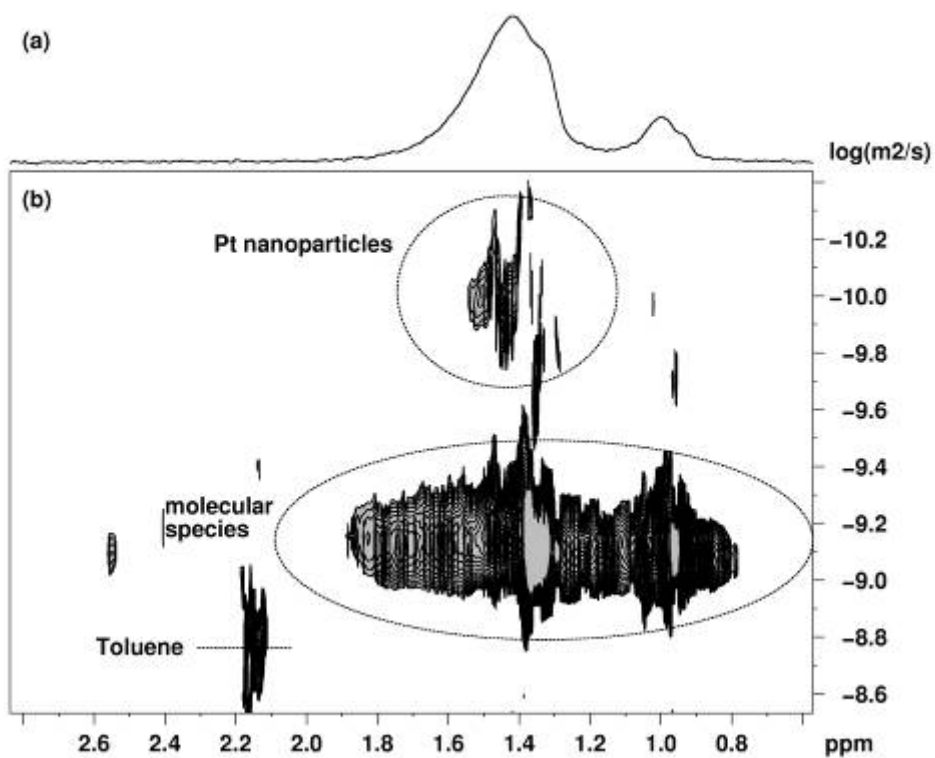


Figure S6. Diffusion NMR experiments on Pt colloidal solution after air exposure: (a) 1D diffusion-filtered spectra where only the slow diffusing species persist, (b) 2D DOSY NMR spectrum.

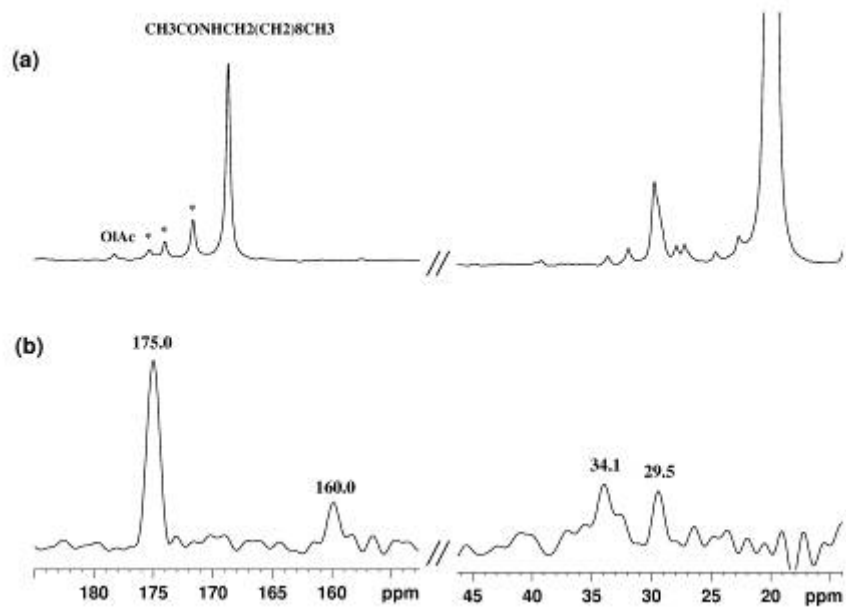


Figure S7. Comparison of carbonyl region of $^{13}\text{C} \{^1\text{H}\}$ NMR spectra of Pt colloidal solution obtain by (a) HRMAS and (b) CPMAS * Secondary products generated during thermolysis.

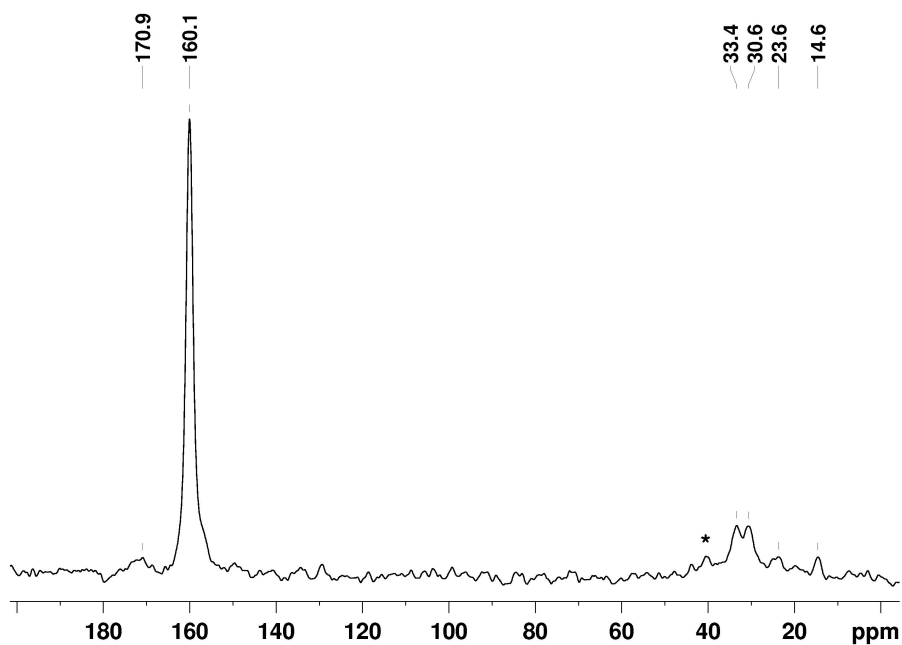


Figure S8. CPMAS analysis of platinum nanoparticles obtained after washing and precipitation with methanol.