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Electronic Supplementary Information

Solventless synthesis of Ru(0) composites stabilized with PPH dendrons and their use in catalysis

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Experimental Section

All manipulations were carried out with standard high-vacuum and dry-argon techniques. All solvents and reactants were carefully degassed by freeze and thaw cycles in the case of reactions involving phosphines and colloids. Chemicals were purchased from Sigma-Aldrich, Alfa-Aesar, or Strem and used without further purification; solvents were dried and distilled by routine procedures. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded at 25° C with Bruker AV 300, DPX 300, Avance 400WB (solid state) or AV 400 spectrometers. References for NMR chemical shifts are 85% H_3PO_4 for ^{31}P NMR and $SiMe_4$ for ^{1}H and ^{13}C NMR. The attribution of ^{13}C NMR signals has been done using *J*mod, two-dimensional ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC, and ^{1}H-^{31}P HMQC, Broad Band or CW ^{31}P decoupling experiments when necessary. Typical numbering is depicted on Figure 15. Mass spectrometry was recorded on a Finnigan MAT TSQ 7000, GCT 1er Waters or DSQ Thermo Fisher Scientific. The X-ray photoelectron spectroscopy (XPS) analysis was carried out on a Thermo Fisher-VG Instruments system equipped with a monochromatic Al Kα (1486.7 eV) X-ray source and a hemispherical electron analyzer with seven Channeltron detectors. To optimize resolution, the pass energy employed was 10 eV. The base pressure of the analysis chamber was 10-10 Torr for data acquisition. The powder X-ray spectra were recorded on a theta/theta Panalytical MPDPRO instrument. Electronic microscopy imaging was performed on JEOL instruments (JEM 1011, JEM 1400, JEM 2010, JEM 2100F). The catalytic samples were analyzed by gas chromatography (GC) on a Shimadzu instrument with a Shimadzu GC-2010 Plus AF and a HP5-MS 30 m x 0.25 mm capillary apolar column.

Synthesis of dendrons. The numbering Schemes used for NMR are depicted on Figure 15. Compounds **1a**,[1] **1b**,[2] **2**[3] and **4a-b**[4] were prepared according to published procedures.

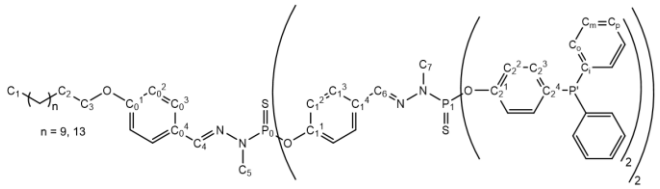


Figure 15. Numbering Scheme for NMR analysis.

3a: To a degassed solution of dimethylacetamide (15 mL) containing compound **1a** (1.0 g, 2.57 mmol), potassium acetate (363.9 mg, 3.09 mmol), and palladium acetate (0.69 mg, 3.57 µmol) diphenylphosphine (0.45 mL, 2.57 mmol) was added dropwise. The reaction was heated to 130°C during 12 h in a pressure flask. After cooling, the mixture was dissolved in water and the product was extracted with dichloromethane. The organic solution was washed with water and dried with magnesium sulfate. After filtration, the solvent was evaporated to dryness under reduced pressure to obtain a dark solid. The crude product was further purified via silica gel column chromatography (hexane/chloroform 8:2 to 7:3, Rf = 0.63) to obtain **3a** as a white solid (0.88 g, 76%). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 161.99 MHz): δ = -6.98 (s, P'); ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 0.92 (t, $^{3}J_{HH}$ = 6.5 Hz, 3H, C_1H), 1.30 (br s, 12H, CH_2), 1.34-1.40 (m, 4H, CH_2), 1.43-1.48 (m, 2H, CH_2), 1.81 (q, $^{3}J_{HH}$ = 6.7 Hz, 2H, C_2H), 3.98 (t, $^{3}J_{HH}$ = 6.5 Hz, 2H, C_3H), 6.91 (d, $^{3}J_{HH}$ = 7.9 Hz, 2H, C_0^2H), 7.20-7.40 (m, 12H, H_{arom}); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75.47 MHz): δ = 14.16 (s, C_1), 22.73 (s, CH_2), 26.09 (s, CH_2), 29.27-29.70 (m, CH_2), 29.26 (s, C_2), 31.95 (s, CH_2), 67.97 (s, C_3), 114.79 (d, $^{3}J_{CP}$ = 8.2 Hz, C_0^2), 127.08 (d, $^{1}J_{CP}$ = 7.0 Hz, C_0^4), 128.43 (d, $^{3}J_{CP}$ = 6.8 Hz, C_m), 128.51 (s, C_p), 133.44 (d, $^{2}J_{CP}$ = 19.0 Hz, C_o), 135.63 (d, $^{2}J_{CP}$ = 21.4 Hz, C_0^3), 137.83 (d, $^{1}J_{CP}$ = 9.9 Hz, C_i), 160.07 (s, C_0^1) ppm. DCI-MS (NH_3) m/z = 447 $[M+H]^+$.

3b: To a degassed solution of dimethylacetamide (15 mL) containing compound **1b** (1.14 g, 2.57 mmol), potassium acetate (363.9 mg, 3.09 mmol), and palladium acetate (0.69 mg, 3.57 µmol), diphenylphosphine (0.45 mL, 2.57 mmol) was added dropwise. The reaction was heated to 130 ºC during 12 h in a pressure flask. After cooling, the mixture was dissolved in water and the product was extracted with dichloromethane. The organic solution was washed with water and dried with magnesium sulfate. After filtration, the solvent was evaporated to dryness under reduced pressure to obtain a dark solid. The crude product was further purified via silica gel column chromatography (hexane/chloroform 7:3 to 6:4, Rf = 0.67) to obtain **3b** as a white solid (0.87 g, 67%). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121.51 MHz): δ = -6.95 (s, P'); ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 0.91 (t, $^{3}J_{HH}$ = 6.5 Hz, 3H, C_1H), 1.29 (br s, 20H, CH_2), 1.33-1.39 (m, 4H, CH_2), 1.42-1.52 (m, 2H, CH_2), 1.80 (q, $^{3}J_{HH}$ = 6.7 Hz, 2H, C_2H), 3.97 (t, $^{3}J_{HH}$ = 6.7 Hz, 2H, C_3H), 6.90 (d, $^{3}J_{HH}$ = 7.9 Hz, 2H, C_5H), 7.20-7.40 (m, 12H, H_{arom}); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75.47 MHz): δ = 14.15 (s, C_1), 22.73 (s, CH_2), 26.08 (s, CH_2), 29.26-29.72 (m, CH_2), 29.26 (s, C_2), 31,96 (s, CH_2), 67.96 (*s*, C_3), 114.77 (d, $^{3}J_{CP}$ = 8.1 Hz, C_0^2), 127.25 (d, $^{1}J_{CP}$ = 7.8 Hz, C_0^4), 128.45 (d, $^{3}J_{CP}$ = 6.4 Hz, C_m), 128.54 (s, C_p), 133.42 (d, $^{2}J_{CP}$ = 19.0 Hz, C_o), 135.62 (d, $^{2}J_{CP}$ = 21.5 Hz, C_0^3), 137.99 (d, $^{1}J_{CP}$ = 10.7 Hz, C_i), 160.02 (s, C_0^1) ppm. DCI-MS (NH_3): m/z = 503 $[M+H]^+$.

5a: To a solution of **4a** (3 g, 10.3 mmol) in chloroform (40 mL) maintained at 0°C a solution of freshly prepared N-methyldichlorothio-phosphorhydrazide (62.94 mL, 0.18 M) was added dropwise. Once the addition finished, the

reaction was allowed to reach room temperature under stirring and then stirred at room temperature for 12h. The reaction mixture was then evaporated to dryness under reduced pressure. The resulting crude solid was purified via column chromatography (dichloromethane/hexane, 2:1, Rf = 0.73) to give **5a** as a white solid (4.17 g, 89%). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 121.50 MHz): δ = 63.18 (s, P_0); ^{1}H NMR (CD_2Cl_2, 300.13 MHz): δ = 0.92 (t, $^{3}J_{HH}$ = 6.5 Hz, 3H, C_1H), 1.31 (br s, 12H, CH_2), 1.34-1.42 (m, 4H, CH_2), 1.45-1.55 (m, 2H, CH_2), 1.82 (q, $^{3}J_{HH}$ = 6.7 Hz, 2H, C_2H), 3.50 (d, $^{3}J_{HP}$ = 14.5 Hz, 3H, C_5H), 4.03 (t, $^{3}J_{HH}$ = 6.6 Hz, 2H, C_3H), 6.97 (d, $^{3}J_{HH}$ = 8.8 Hz, 2H, C_0^2H), 7.71 (d, $^{3}J_{HH}$ = 8.8 Hz, 2H, C_0^3H), 7.74 (d, $^{4}J_{HP}$ = 2.8 Hz, 1H, C_4H); $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 75.47 MHz): δ =13.88 (s, C_1), 22.70 (s, CH_2), 25.98 (s, CH_2), 29.19-29.66 (m, CH_2), 31.74 (s, C_5), 31.93 (s, CH_2), 68.23 (s, C_3), 114.74 (s, C_0^2), 126.64 (s, C_0^4), 128.84 (s, C_0^3), 142.37 (s, C_4), 161.03 (s, C_0^1) ppm. ESI-MS: m/z = 451 $[M+H]^+$.

5b: To a solution of **4b** (3.57 g, 10.3 mmol) in chloroform (40 mL) maintained at 0°C, a solution of freshly prepared N-methyldichlorothiophosphorhydrazide (62.94 mL, 0.18 M) was added dropwise. Once the addition finished, the reaction was allowed to reach room temperature under stirring and then stirred at room temperature for 12 h. The reaction mixture was then evaporated to dryness under reduced pressure. The resulting crude solid was purified via column chromatography (dichloromethane/hexane, 2:1, Rf = 0.67) to give **5b** as a white solid (4.62 g, 88%). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 121.50 MHz): δ = 63.17 (s, P_0); ^{1}H NMR (CD_2Cl_2, 300.13 MHz): δ = 0.92 (t, $^{3}J_{HH}$ = 6.5 Hz, 3H, C_1H), 1.31 (br s, 20H, CH_2), 1.36-1.42 (m, 4H, CH_2), 1.45-1.55 (m, 2H, CH_2), 1.83 (q, $^{3}J_{HH}$ = 6.6 Hz, 2H, C_2H), 3.50 (d, $^{3}J_{HP}$ = 14.2 Hz, 3H, C_5H), 4.03 (t, $^{3}J_{HH}$ = 6.6 Hz, 2H, C_3H), 6.97 (d, $^{3}J_{HH}$ = 8.8 Hz, 2H, C_0^2H), 7.71 (d, $^{3}J_{HH}$ = 8.8 Hz, 2H, C_0^3H), 7.74 (d, $^{4}J_{HP}$ = 2.9 Hz, 1H, C_4H); $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 75.47 MHz): δ = 13.88 (s, C_1), 22.70 (s, CH_2), 25.98 (s, CH_2), 29.19-29.70 (m, CH_2), 31.74 (s, C_5), 31.93 (s, CH_2), 68.24 (s, C_3), 114.74 (s, C_0^2), 126.63 (s, C_0^4), 128.84 (s, C_0^3), 142.37 (s, C_4), 161.03 (s, C_0^1) ppm. ESI-MS: m/z = 507 $[M+H]^+$.

6a: A mixture of cesium carbonate (736 mg, 2.26 mmol) and compound **2** (407 mg, 1.46 mmol) in THF (15 mL) was maintained under stirring during 12 h at room temperature. Then compound **5a** (300 mg, 0.664 mmol) was added and the reaction mixture was left under stirring for 5 h. The mixture was then centrifuged at 10,000 rpm. The resulting clear solution was filtered through paper, and evaporated to dryness under reduced pressure to obtain **6a** as a white solid (0.51 g, 82%). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 161.99 MHz): δ = 61.68 (s, P_0), -6.39 (s, P'); ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 0.91 (t, $^{3}J_{HH}$ = 6.5 Hz, 3H, C_1H), 1.30 (br s, 12H, CH_2), 1.34-1.40 (m, 4H, CH_2), 1.44-1.53 (m, 2H, CH_2), 1.83 (q, $^{3}J_{HH}$ = 6.7 Hz, 2H, C_2H), 3.37 (d, $^{3}J_{HP}$ = 10.8 Hz, 3H, C_5H), 3,99 (t, $^{3}J_{HH}$ = 6.6 Hz, 2H, C_3H), 6.90 (d, $^{3}J_{HH}$ = 8.8 Hz, 2H, C_0^2H), 7.20-7.38 (m, 28H, H_{arom}), 7.60 (s, C_4H), 7.61 (d, $^{3}J_{HH}$ = 8.8 Hz, 2H, C_0^3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75.47 MHz): δ = 14.16 (s, C_1), 22.72 (s, CH_2), 26.06 (s, CH_2), 29.23-29.69 (m, CH_2), 31.94 (s, CH_2), 32.92 (d, $^{2}J_{CP}$ = 13.3 Hz, C_5), 68.16 (s, C_3), 114.72 (s, C_0^2), 121.55 (d, $^{3}J_{CP}$ = 12.3 Hz, C_1^2), 127.33 (s, C_0^4), 128.43 (s, C_0^3), 128.53 (d, $^{3}J_{CP}$ = 6.9 Hz, C_m), 128.79 (s, C_p), 133.36 (d, $^{1}J_{CP}$ = 19.14 Hz, C_1^4), 133.68 (d, $^{2}J_{CP}$ = 18.6 Hz, C_o), 135.00 (d, $^{2}J_{CP}$ = 19.5 Hz, C_1^3), 137.03 (s, C_i), 139.79 (d, $^{3}J_{CP}$ = 13.7 Hz, C_4), 151.35 (d, $^{2}J_{CP}$ = 7.4 Hz, C_1^1), 160.40 (s, C_0^1) ppm. ESI-MS: m/z = 935 $[M]^+$.

6b: A mixture of cesium carbonate (736 mg, 2.26 mmol) and compound **2** (407 mg, 1.46 mmol) in THF (15 mL) was maintained under stirring during 12 h at room temperature. Then the compound **5b** (336 mg, 0.664 mmol) was added and the reaction mixture was left under stirring for 5 h. The mixture was then centrifuged at 10,000 rpm. The resulting clear solution was filtered through paper, and evaporated to dryness under reduced pressure to obtain **6b** as a white solid (0.56 g, 85%). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121.50 MHz): δ = 61.69 (s, P_0), -6.39 (s, P'); ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 0.92 (t, $^{3}J_{HH}$ = 6.6 Hz, 3H, C_1H), 1.30 (br s, 20H, CH_2), 1.34-1.41 (m, 4H, CH_2), 1.44-1.54 (m, 2H, CH_2), 1.82 (q, $^{3}J_{HH}$ = 6.6 Hz, 2H, C_2H), 3.37 (d, $^{3}J_{HP}$ = 10.8 Hz, 3H, C_5H), 3.99 (t, $^{3}J_{HH}$ = 6.5 Hz, 2H, C_3H), 6.91 (d, $^{3}J_{HH}$ = 8.9 Hz, 2H, C_0^2H), 7.2-7.4 (m, 28H, H_{arom}), 7.61 (s, C_4H), 7.62 (d, $^{3}J_{HH}$ = 8.8 Hz, 2H, C_0^3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75.47 MHz): δ = 14.17 (s, C_1), 22.73 (s, CH_2), 26.07 (s, CH_2), 29.25-29.74 (m, CH_2), 31.97 (s, CH_2), 32.92 (d, $^{2}J_{CP}$ = 13.3 Hz, C_5), 68.17 (s, C_3), 114.74 (s, C_0^2), 121.56 (d, $^{3}J_{CP}$ = 12.3 Hz, C_1^2), 127.34 (s, C_0^4), 128.45 (s, C_0^3), 128.54 (d, $^{3}J_{CP}$ = 7.0 Hz, C_m), 128.81 (s, C_p), 133.37 (d, $^{1}J_{CP}$ = 19.0 Hz, C_1^4), 133.69 (d, $^{2}J_{CP}$ = 20.5 Hz, C_o), 135.00 (d, $^{2}J_{CP}$ = 19.8 Hz, C_1^3), 137.04 (s, C_i), 139.80 (d, $^{3}J_{CP}$ = 13.7 Hz, C_4), 151.36 (d, $^{2}J_{CP}$ = 7.4 Hz, C_1^1), 160.41 (s, C_0^1) ppm. ESI-MS: m/z = 991 $[M]^+$.

7a: A mixture of 4-hydroxybenzaldehyde (2.11 g, 17.2 mmol) and cesium carbonate (8.44 g, 62.2 mmol) in THF (100 mL) was maintained under stirring during 12 h at room temperature. Compound **5a** was then added (3.23 g, 7.17 mmol) and the reaction mixture was stirred at room temperature for 4 h. The solvent was then removed under vacuum and the residue was suspended in water. The product was then extracted with dichloromethane. The organic phases were gathered and washed with 10% solution of potassium carbonate, brine, and dried with magnesium sulfate. After filtration, the solvent was evaporated under reduced pressure. Finally, the product was purified via silica gel column chromatography (dichloromethane/ethyl acetate 8:2, Rf = 0.62) to give **7a** as a white solid (3.76 g, 84%) $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 161.99 MHz): δ = 60.65 (*s*, P_0); ^{1}H NMR (CD_2Cl_2, 400.13 MHz): δ = 0.92 (*t*, $^{3}J_{HH}$ = 8.0 Hz, 3H, C_1-H), 1.32 (br s, 12H, CH_2), 1.33-1.44 (m, 4H, CH_2), 1.44 (m, 2H CH_2), 1.82 (*q*, $^{3}J_{HH}$ = 6.7 Hz, 2H, C_2-H), 3.42 (*d*, $^{3}J_{HP}$ = 11.1 Hz, 3H, C_5-H), 4.02 (*t*, $^{3}J_{HH}$ = 6.6 Hz, 2H, C_3-H), 6.95 (*d*, $^{3}J_{HH}$ = 8.8 Hz, 2H, C_0^2-H), 7.45 (*d*, $^{2}J_{HH}$ = 10.0 Hz, 4H, C_1^2-H), 7.63 (*d*, $^{3}J_{HH}$ = 8.8 Hz, 2H, C_0^3-H), 7.70 (*d*, $^{4}J_{HP}$ = 1.7 Hz, 1H, C_4-H), 7.92 (*d*, $^{3}J_{HH}$ = 8.3 Hz, 4H, C_1^3-H), 9.99 (*s*, 2H, CHO); $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 100.62 MHz): δ =13.87 (*s*, C_1), 22.69 (s, CH_2), 25.98 (s, CH_2), 29.19 (s,

CH_2), 29.34-29.66 (*m*, CH_2), 31.92 (s, CH_2), 32.70 (*d*, $^2J_{CP}$ = 13.4 Hz, C_5), 68.21 (*s*, C_3), 114.70 (*s*, C_0^2), 122.01 (*d*, $^3J_{CP}$ = 4.9 Hz, C_1^2), 126.99 (*s*, C_0^4), 128.42 (*s*, C_0^3), 131.26 (*s*, C_1^3), 133.77 (*s*, C_1^4), 140.96 (*d*, $^3J_{CP}$ = 13.8 Hz, C_4), 155.22 (*d*, $^2J_{CP}$ = 7.2 Hz, C_1^1), 160.67 (*s*, C_0^1), 190.64 (*s*, CHO) ppm. DCI-MS: m/z = 623 $[M+H]^+$.

7b: A mixture of 4-hydroxybenzaldehyde (2.11 g, 17.2 mmol) and cesium carbonate (8.44 g, 62.2 mmol) in THF (100 mL) was maintained under stirring during 12 h at room temperature. Compound **5b** was then added (3.63 g, 7.17 mmol) and the reaction mixture was stirred at room temperature for 4 h. The solvent was then evaporated under vacuum and the residue was suspended in water. The product was then extracted with dichloromethane. The organic phases were gathered and washed with 10% solution of potassium carbonate, brine and dried with magnesium sulfate. After filtration, the solvent was evaporated under reduced pressure. Finally, the product was purified via silica gel column chromatography (dichloromethane/ethyl acetate 9:1, Rf = 0.58) to give **7b** as a white solid (4.37 g, 85%). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.50 MHz): δ = 60.65 (s, P_0); ^1H NMR (CD_2Cl_2, 300.13 MHz): δ = 0.92 (t, $^3J_{HH}$ = 6.8 Hz, 3H, C_1H), 1.30 (br s, 20H, CH_2), 1.36-1.42 (m, 4H, CH_2), 1.45-1.54 (m, 2H, CH_2), 1.82 (q, $^3J_{HH}$ = 6.7 Hz, 2H, C_2H), 3.42 (d, $^3J_{HP}$ = 11.1 Hz, 3H, C_5H), 4.02 (t, $^3J_{HH}$ = 6.6 Hz, 2H, C_3H), 6.94 (d, $^3J_{HH}$ = 8.8 Hz, 2H, C_0^2H), 7.63 (d, $^3J_{HH}$ = 8.8 Hz, 2H, C_0^3H), 7.44 (d, $^3J_{HH}$ = 7.0 Hz, 4H, C_1^2H), 7.70 (d, $^4J_{HP}$ = 1.7 Hz, 1H, C_4H), 7.92 (d, $^3J_{HH}$ = 8.3 Hz, 4H, C_1^3H), 9.99 (s, 2H, CHO); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.47 MHz): δ =13.88 (s, C_1), 22.70 (s, CH_2), 26.00 (s, CH_2), 29.20-29.69 (m, CH_2), 31.93 (s, CH_2), 32.71 (d, $^2J_{CP}$ = 13.4 Hz, C_5), 68.22 (s, C_3), 114.69 (s, C_0^2), 121.98 (d, $^3J_{CP}$ = 5.0 Hz, C_1^2), 127.01 (s, C_0^4), 128.43 (s, C_0^3), 131.27 (s, C_1^3), 133.78 (s, C_1^4), 140.96 (d, $^3J_{CP}$ = 13.9 Hz, C_4), 155.22 (d, $^2J_{CP}$ = 7.2 Hz, C_1^1), 160.68 (s, C_0^1), 190.65 (s, CHO) ppm. DCI-MS: m/z = 679 $[M+H]^+$.

8a: To a solution of **7a** (1.5 g, 2.41 mmol) in chloroform (10 mL) maintained at 0°C a solution of freshly prepared methyldichlorothiophosphorhydrazide (29 mL, 0.18 M) was added dropwise. Once the addition finished, the reaction was allowed to reach room temperature and then stirred at room temperature for 24 h. The reaction mixture was then evaporated to dryness under reduced pressure. The resulting crude product was purified via column chromatography (dichloromethane/hexane, 1:1, Rf = 0.73) to give **8a** as a white solid (2.02 g, 88.60%). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161.99 MHz): δ = 62.22 (s, P_0), 63.17 (s, P_1); ^1H NMR (CD_2Cl_2, 300.13 MHz): δ = 0.93 (t, $^3J_{HH}$ = 6.47 Hz, 3H, C_1H), 1.32 (br s, 12H, CH_2), 1.36-1.42 (m, 4H, CH_2), 1.45-1.55 (m, 2H, CH_2), 1.83 (q, $^3J_{HH}$ = 6.7 Hz, 2H, C_2H), 3.41 (d, $^3J_{HP}$ = 10.9 Hz, 3H, C_5H), 3.51 (d, $^3J_{HP}$ = 14.1 Hz, 6H, C_7H), 4.03 (t, $^3J_{HH}$ = 6.6 Hz, 2H, C_3H), 6.96 (d, $^3J_{HH}$ = 8.8 Hz, 2H, C_0^2H), 7.35 (d, $^3J_{HH}$ = 7.0 Hz, 4H, C_1^2H), 7.68 (d, $^3J_{HH}$ = 8.8 Hz, 2H, C_0^3H), 7.71 (d, $^4J_{HP}$ = 1.8 Hz, 1H, C_4H), 7.75 (d, 2H, $^4J_{HP}$ = 2.7 Hz, C_6H), 7.78 (d, $^3J_{HH}$ = 8.5 Hz, 4H, C_1^3H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.47 MHz): δ =13.93 (s, C_1), 22.72 (s, CH_2), 26.01 (s, CH_2), 29.23-29.68 (m, CH_2), 31.94 (s, CH_2), 31.82 (d, $^2J_{CP}$ = 13.1 Hz, C_7), 32.84 (d, $^2J_{CP}$ = 13.1 Hz, C_5), 68.22 (s, C_3), 114.71 (s, C_0^2), 121.93 (d, $^3J_{CP}$ = 4.9 Hz, C_1^2), 127.24 (s, C_0^4), 128.41 (s, C_0^3), 128.61 (s, C_1^3), 131.54 (*s*, C_1^4), 140.47 (d, $^3J_{CP}$ = 13.7 Hz, C_4), 141.05 (d, $^3J_{CP}$ = 18.8 Hz, C_6), 152.05 (d, $^2J_{CP}$ = 7.2 Hz, C_1^1), 160.59 (s, C_0^1) ppm. ESI-MS: m/z = 945 $[M]^+$.

8b: To a solution of **7b** (1.63 g, 2.41 mmol) in chloroform (10 mL) maintained at 0°C, a solution of freshly prepared methyldichlorothiophosphorhydrazide (29 mL, 0.18 M) was added dropwise in an ice bath. Once the addition finished, the reaction was allowed to reach room temperature and then stirred at room temperature for 24 h. The reaction mixture was then evaporated to dryness under reduced pressure. The resulting crude product was purified via column chromatography (dichloromethane/hexane, 1:1, Rf = 0.72) to give **8b** as a white solid (2.25 g, 93%). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.51 MHz): δ = 62.23 (s, P_0), 63.01 (s, P_1); ^1H NMR (CD_2Cl_2, 300.13 MHz): δ = 0.93 (t, $^3J_{HH}$ = 6.4 Hz, 3H, C_1H), 1.31 (br s, 20H, CH_2), 1.36-1.42 (m, 4H, CH_2), 1.45-1.54 (m, 2H, CH_2), 1.82 (q, $^3J_{HH}$ = 6.7 Hz, 2H, C_2H), 3.40 (d, $^3J_{HP}$ = 10.9 Hz, 3H, C_5H), 3.51 (d, $^3J_{HP}$ = 14.1 Hz, 6H, C_7H), 4.02 (t, $^3J_{HH}$ = 6.6 Hz, 2H, C_3H), 6.96 (d, $^3J_{HH}$ = 8.8 Hz, 2H, C_0^2H), 7.34 (d, $^3J_{HH}$ = 7.0 Hz, 4H, C_1^2H), 7.67 (d, $^3J_{HH}$ = 8.8 Hz, 2H, C_0^3H), 7.70 (d, $^4J_{HP}$ = 1.8 Hz, 1H, C_4H), 7.75 (d, $^4J_{HP}$ = 2.7 Hz, 2H, C_6H), 7.77 (d, $^3J_{HH}$ = 8.5 Hz, 4H, C_1^3H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.47 MHz): δ =13.91 (s, C_1), 22.71 (s, CH_2), 26.01 (s, CH_2), 29.23-29.71 (m, CH_2), 31.94 (s, CH_2), 31.82 (d, $^2J_{CP}$ = 13.1 Hz, C_7), 32.83 (d, $^2J_{CP}$ = 13.1 Hz, C_5), 68.22 (s, C_3), 114.70 (s, C_0^2), 121.93 (d, $^3J_{CP}$ = 5.0 Hz, C_1^2), 127.24 (s, C_0^4), 128.41 (s, C_1^3), 128.61 (s, C_0^3), 131.54 (s, C_1^4), 140.46 (d, $^3J_{CP}$ = 13.8 Hz, C_4), 141.04 (d, $^3J_{CP}$ = 18.6 Hz, C_6), 152.05 (d, $^2J_{CP}$ = 7.2 Hz, C_1^1), 160.58 (s, C_0^1) ppm. ESI-MS: m/z = 1001 $[M]^+$.

9a: A mixture of cesium carbonate (1.41 g, 4.33 mmol) and compound **2** (770 mg, 2.77 mmol) in THF (20 mL) was maintained under stirring during 12 h at room temperature. Then compound **8a** (600 mg, 0.635 mmol) was added and the reaction mixture was left under stirring for 5 h. The mixture was then centrifuged at 10,000 rpm. The resulting clear solution was filtered, and evaporated to dryness under reduced pressure to give **9a** as a white solid (0.91 g, 75%). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.50 MHz): δ = -6.44 (s, P'), 61.47 (s, P_1), 62.50 (s, P_0); ^1H NMR ($CDCl_3$, 300.13 MHz): δ = 0.91 (t, $^3J_{HH}$ = 6.9 Hz, 3H, C_1H), 1.30 (br *s*, 12H, CH_2), 1.33-1.41 (m, 4H, CH_2), 1.44-1.54 (m, 2H, CH_2), 1.82 (q, $^3J_{HH}$ = 7.0 Hz, 2H, C_2H), 3.35 (d, $^3J_{HP}$ = 7.8 Hz, 3H, C_5H), 3.39 (d, $^3J_{HP}$ = 7.8 Hz, 6H, C_7H), 3.99 (t, $^3J_{HH}$ = 6.6 Hz, 2H, C_3H), 6.93 (d, $^3J_{HH}$ = 8.7 Hz, 2H, C_0^2H), 6.95-7.69 (m, 69H, H_{arom}); ^{13}C NMR ($CDCl_3$, 75.47 MHz): δ =14.15 (s, C_1), 22.73 (s, CH_2), 26.08 (s, CH_2), 29.27-29.70 (m, CH_2), 31.95 (s, CH_2), 31.93 (d, $^2J_{CP}$ = 13.1 Hz, C_7), 32.99 (d, $^2J_{CP}$ = 13.2 Hz, C_5), 68.19 (s, C_3), 114.77 (s, C_0^2), 121.45 (dd, $^3J_{CP}$ = 5.8 Hz, $^3J_{CP}$ = 5.9 Hz, C_2^2), 121.73 (d, $^3J_{CP}$ = 4.8 Hz, C_1^2), 127.28 (s, C_0^4), 128.19 (s, C_1^3), 128.38 (s, C_0^3), 128.50 (s, C_1^3) 128.56 (d, $^3J_{CP}$ = 7.0 Hz, C_m), 128.83 (s, C_p), 132.04 (s, C_1^4), 133.67 (d, $^2J_{CP}$ = 18.9 Hz, C_o), 135.04 (d, $^2J_{CP}$ = 26.4 Hz, C_2^3), 136.98 (d, $^1J_{CP}$ = 10.7 Hz, C_i), 138.84 (d, $^3J_{CP}$ = 13.7 Hz,

C_6), 140.08 (d, $^3J_{CP}$ = 13.8 Hz, C_4), 151.23 (d, $^2J_{CP}$ = 7.2 Hz, C_2^1), 151.49 (d, $^2J_{CP}$ = 7.2 Hz, C_1^1), 160.49 (s, C_0^1) ppm. MALDI-MS: m/z = 1912 $[M]^+$.

9b: A mixture of cesium carbonate (1.41 g, 4.33 mmol) and compound **2** (770 mg, 2.77 mmol) in THF (20 mL) was allowed to stir during 12 h at room temperature. Then compound **8b** (635 mg, 0.635 mmol) was added and the reaction mixture was left under stirring for 5 h. The mixture was then centrifuged at 10,000 rpm. The resulting clear solution was filtered and evaporated to dryness under reduced pressure to give **9b** as a white solid (0.93 g, 74%). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.50 MHz): δ = -6.58 (s, P'), 61.64 (s, P_1), 62.45 (s, P_0); ^1H NMR (CD_2Cl_2, 300.13 MHz): δ = 0.93 (t, $^3J_{HH}$ = 6.2 Hz, 3H, C_1H), 1.32 (br s, 20H, CH_2), 1.36-1.42 (m, 4H, CH_2), 1.45-1.55 (m, 2H, CH_2), 1.82 (q, $^3J_{HH}$ = 7.0 Hz, 2H, C_2H), 3.37 (d, $^3J_{HP}$ = 4.6 Hz, 3H, C_5H), 3.41 (d, $^3J_{HP}$ = 4.4 Hz, 6H, C_7H), 4.01 (t, $^3J_{HH}$ = 6.5 Hz, 2H, C_3H), 6.80 (d, $^3J_{HH}$ = 8.4 Hz, 2H, C_0^2H), 6.95 (d, $^3J_{HH}$ = 8.7 Hz, 4H, C_1^2H), 7.20-7.70 (m, 65H, H_{arom});^{13}C NMR (CD_2Cl_2, 75.47 MHz): δ =13.92 (s, C_1), 22.72 (s, CH_2), 26.03 (s, CH_2), 29.26-29.72 (m, CH_2), 31.95 (s, CH_2), 32.89 (d, $^2J_{CP}$ = 13.1 Hz, C_7), 32.84 (d, $^2J_{CP}$ = 13.2 Hz, C_5), 68.23 (s, C_3), 114.70 (s, C_0^2), 121.41 (d, $^3J_{CP}$ = 6.0 Hz, C_2^2), 121.83 (d, $^3J_{CP}$ = 4.8 Hz, C_1^2), 127.30 (s, C_0^4), 128.14 (s, C_1^3), 128.31 (s, C_0^3), 128.55 (d, $^3J_{CP}$ = 6.9 Hz, C_m), 128.83 (s, C_p), 132.19 (s, C_1^4), 133.26 (d, $^2J_{CP}$ = 19.1 Hz, C_o), 135.02 (d, $^2J_{CP}$ = 20.4 Hz, C_2^3), 137.12 (d, $^1J_{CP}$ = 11.3 Hz, C_i), 139.12 (d, $^3J_{CP}$ = 13.7 Hz, C_6), 140.44 (d, $^3J_{CP}$ = 13.9 Hz, C_4), 151.24 (d, $^2J_{CP}$ = 7.2 Hz, C_2^1), 151.50 (d, $^2J_{CP}$ = 7.1 Hz, C_1^1), 160.56 (s, C_0^1) ppm. MALDI-MS: m/z = 1968 $[M]^+$.

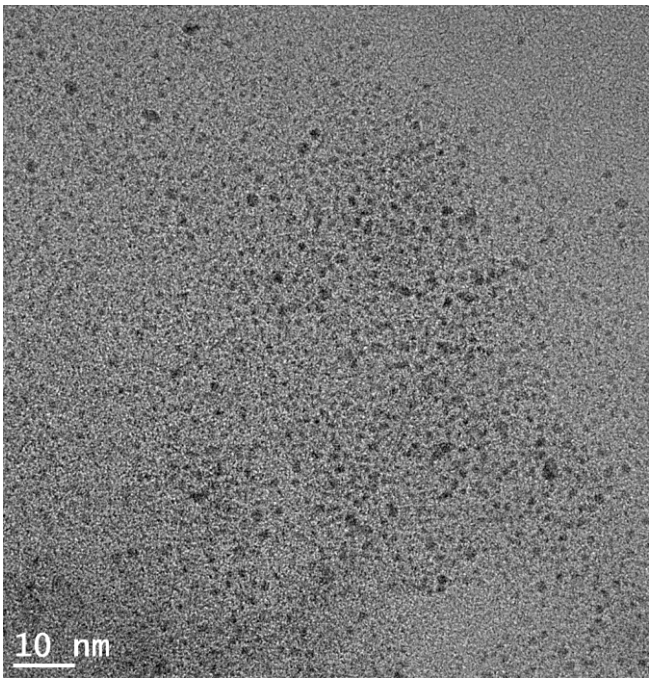
General procedure for the synthesis of colloids: A mixture of commercial ruthenium chloride (100 mg, 0.38 mmol), sodium borohydride (122 mg, 2.94 mmol) and dendron **3a-b** (0.38 mmol)**, 6a-b** (0.19 mmol)**, 7a** (0.38 mmol) or **9a-b** (0.095 mmol) or triphenylphosphine (0.38 mmol) was milled for 20 minutes in an agate mortar. The resulting dark gray mixture was washed with 2 x 10 mL of methanol, followed by washings with 10 mL of water and 10 mL of methanol. Between each washing, a 12,000 rpm centrifugation cycle of 20 minutes was applied. Then, the black powder was dried under vacuum during 2 hours, and finally suspended in THF to an approximated ruthenium concentration of 1.52 mmol.mL^{-1}. The resulting colloids were then analyzed by MAS NMR, TEM, HRTEM and EDX.

General procedure for catalytic reactions: A Fisher-Porter bottle was charged with argon, then 6.3 mL of freshly distilled THF was added, followed by 114 µL (1 mmol) of styrene, and 3.6 mL of ruthenium colloidal solution (1.52 mmol/L Ru, 0.5% Ru). The bottle was then pressurized with 3 bar of molecular hydrogen. The flasks were heated in an oil bath maintained at 40°C under magnetic stirring, during 3.5 hours. At the end of the reaction 168 mg (1 mmol) of standard (1,3,5-trimethoxybenzene) was added, all the mixture was filtered through a small celite column, and diluted for further GC chromatography analysis. GC yields were calculated using 1,3,5-trimethoxybenzene as the standard. GC method: initial temperature: 50°C; initial time: 2 min; Ramp: 40°C/min; final temperature: 230°C; final time: 3 min. Recycling experiments: the supernatant was removed by canula, the solid residue was washed twice with 3 to 5 mL of THF, and engaged in the next run.

References for the ESI

1. L.-B. Xing, B. Yang, X.-J. Wang, J.-J. Wang, B. Chen, Q. Wu, H.-X. Peng, L.-P. Zhang, C.-H. Tung and L.-Z. Wu, *Langmuir*, 2013, **29**, 2843-2848.
2. A. R. Borges, M. Hyacinth, M. Lum, C. M. Dingle, P. L. Hamilton, M. Chruszcz, L. Pu, M. Sabat and K. L. Caran, *Langmuir*, 2008, **24**, 7421-7431.
3. O. Herd, A. Heßler, M. Hingst, M. Tepper and O. Stelzer, *J. Organomet. Chem.*, 1996, **522**, 69-76.
4. A. M. de Almeida, T. Nascimento, B. S. Ferreira, P. P. de Castro, V. L. Silva, C. G. Diniz and M. Le Hyaric, *Bioorg. Med. Chem. Lett.*, 2013, **23**, 2883-2887.

Ru@3a TEM



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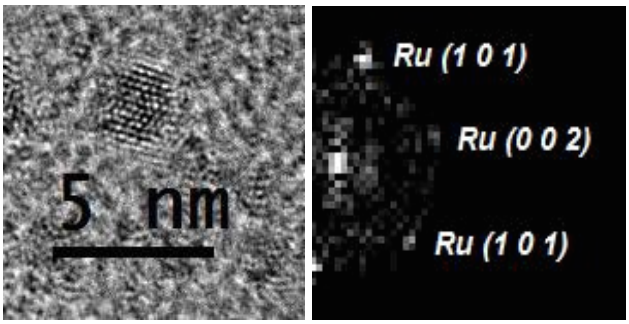

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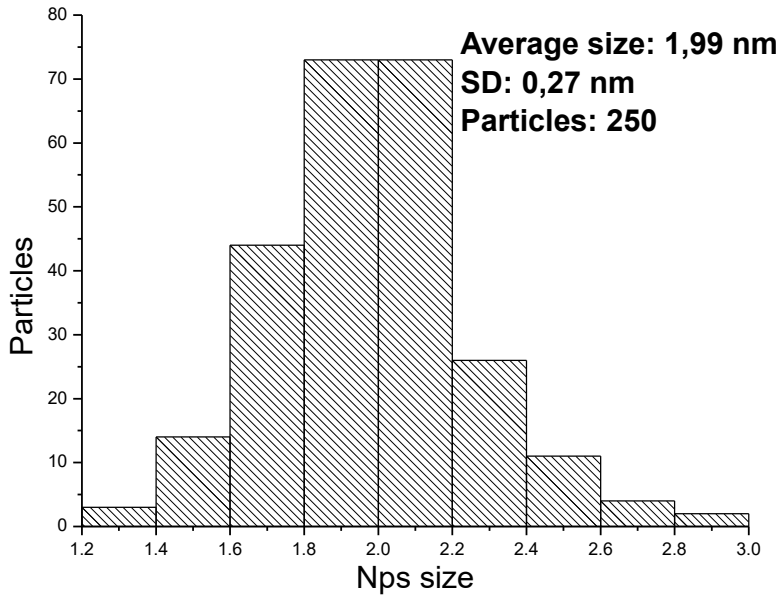

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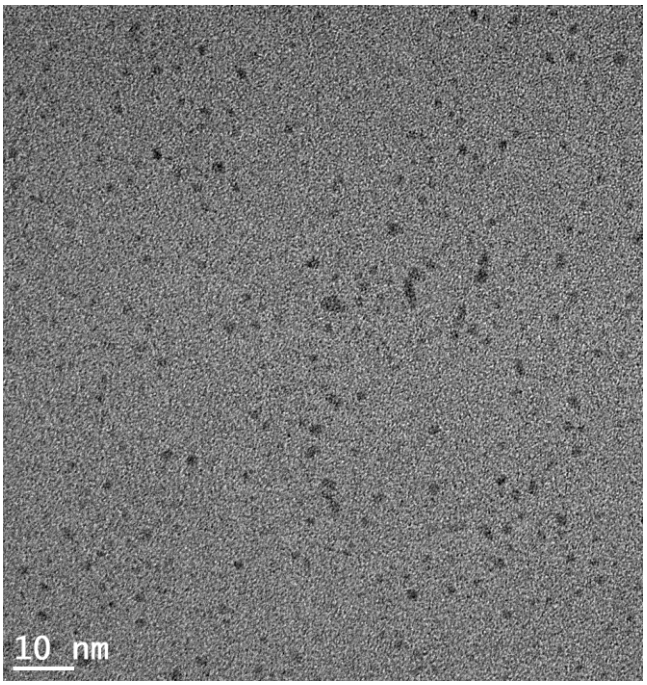

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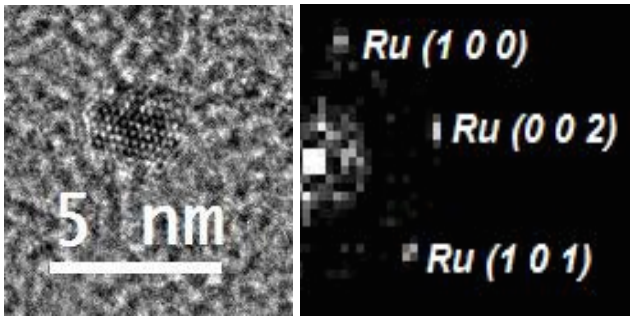

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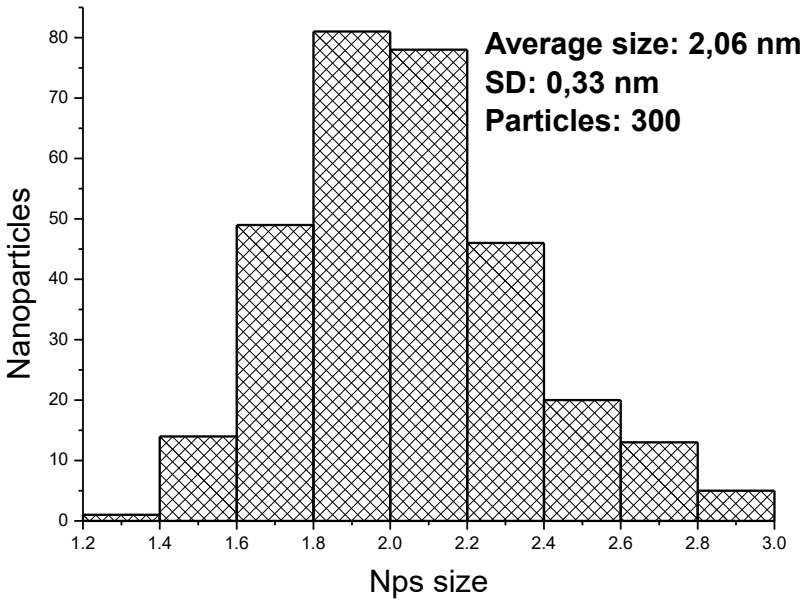

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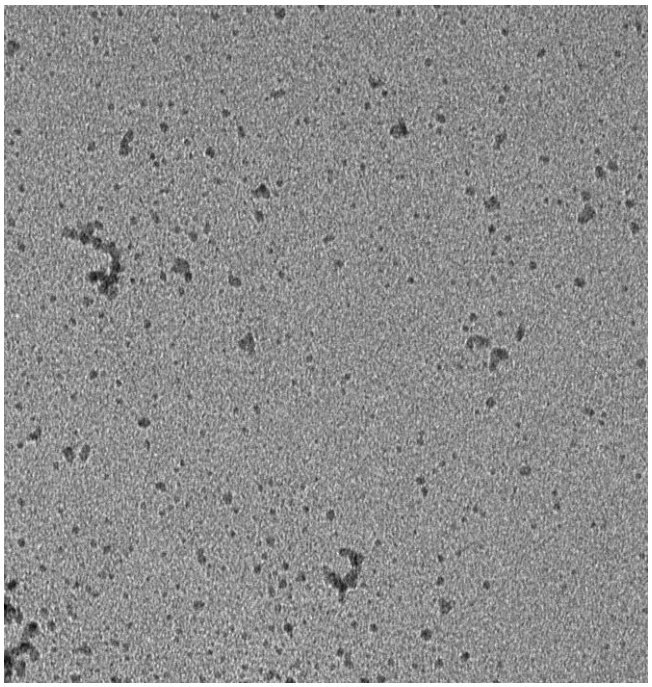

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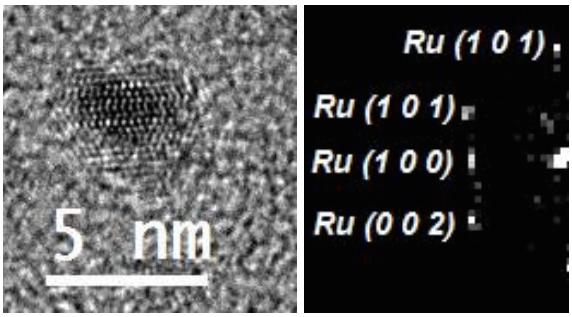

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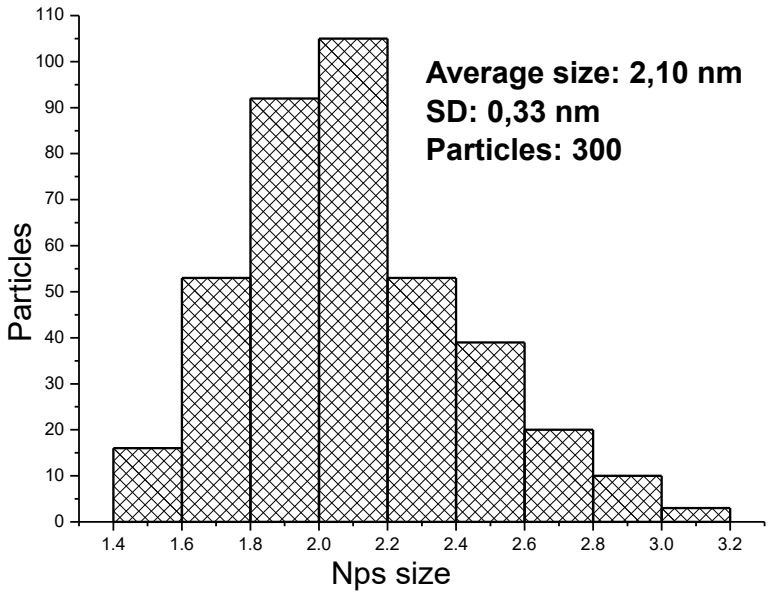

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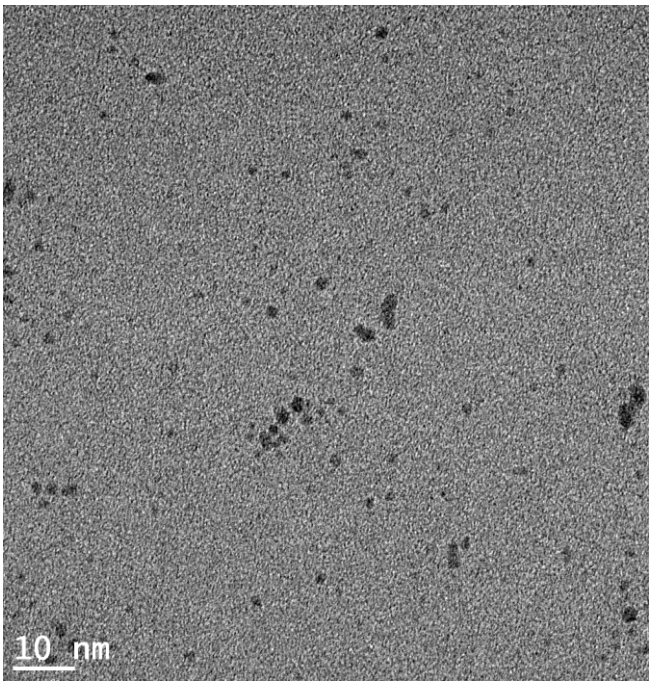

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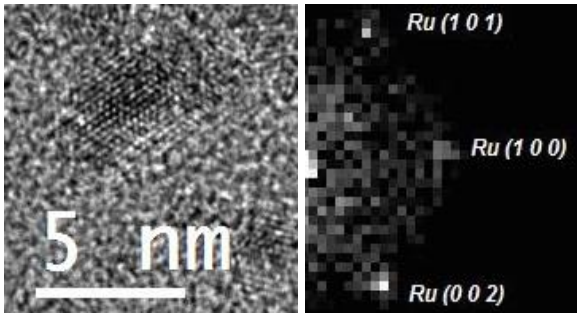

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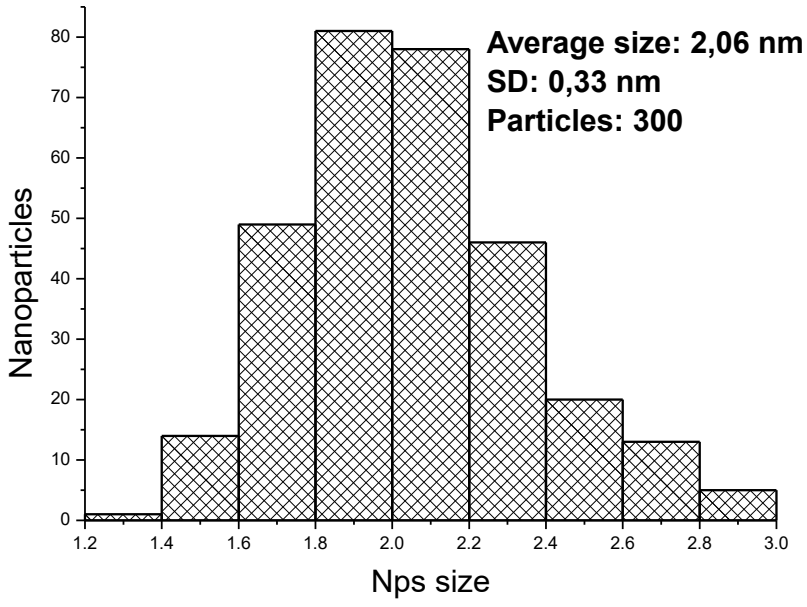

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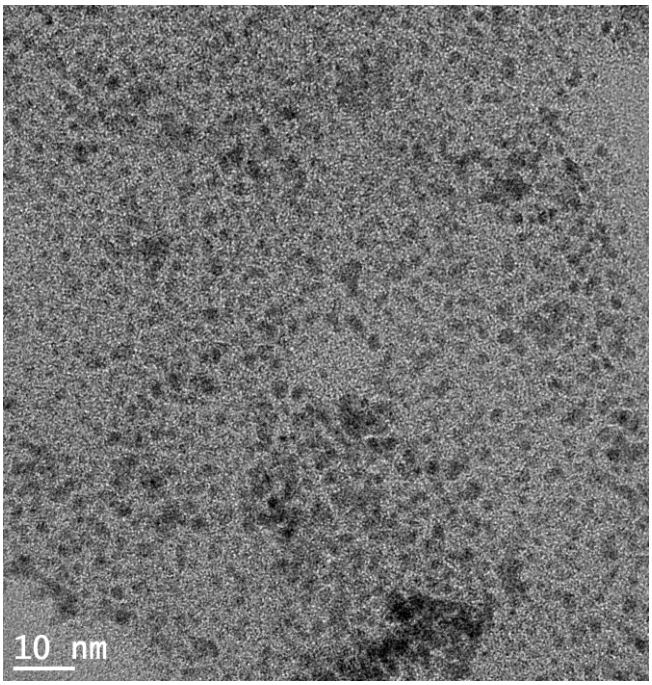

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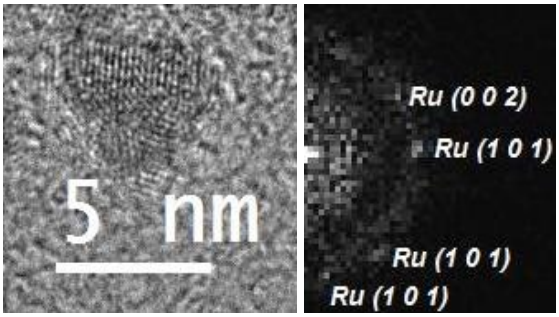

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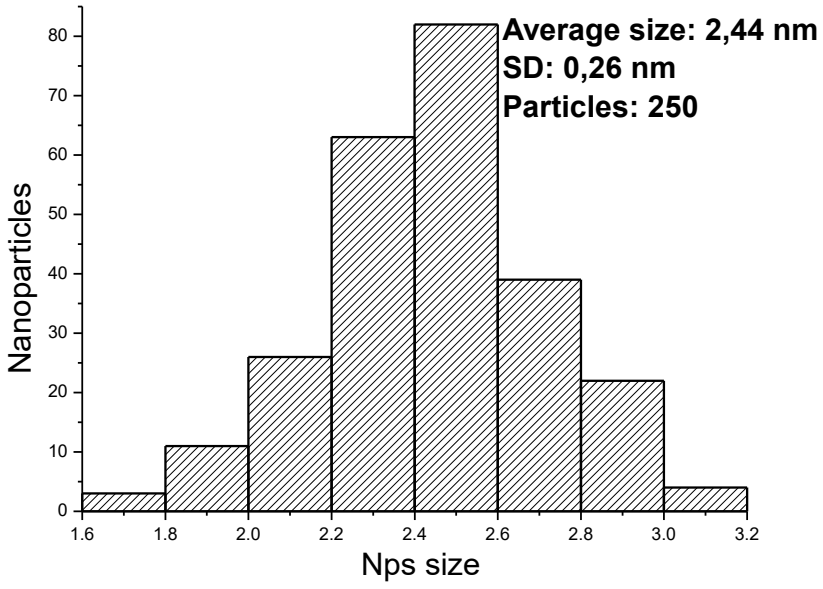

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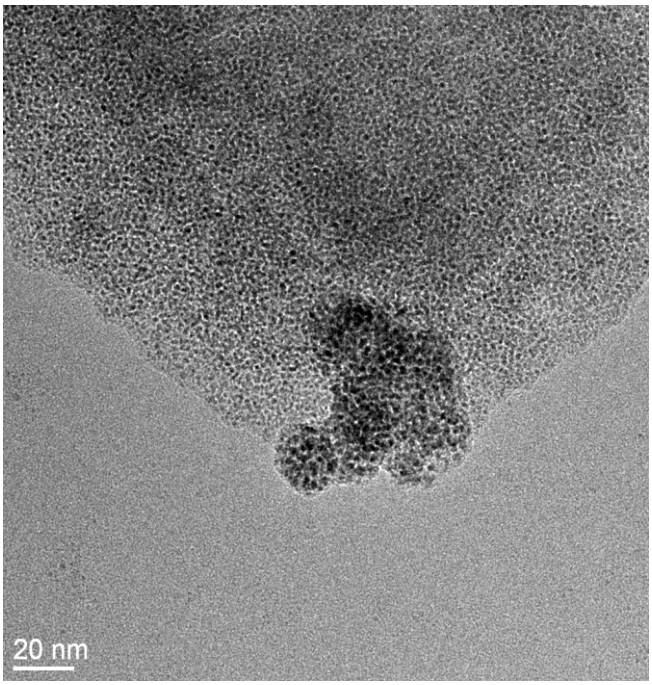

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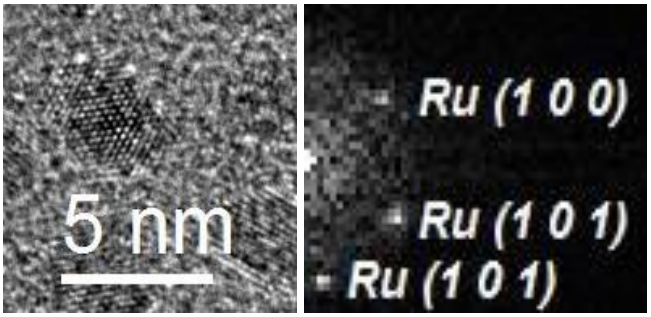

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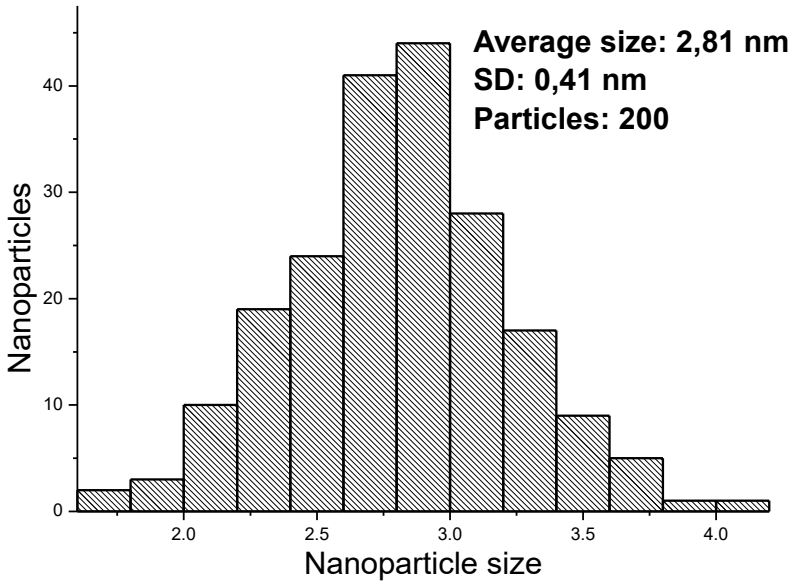
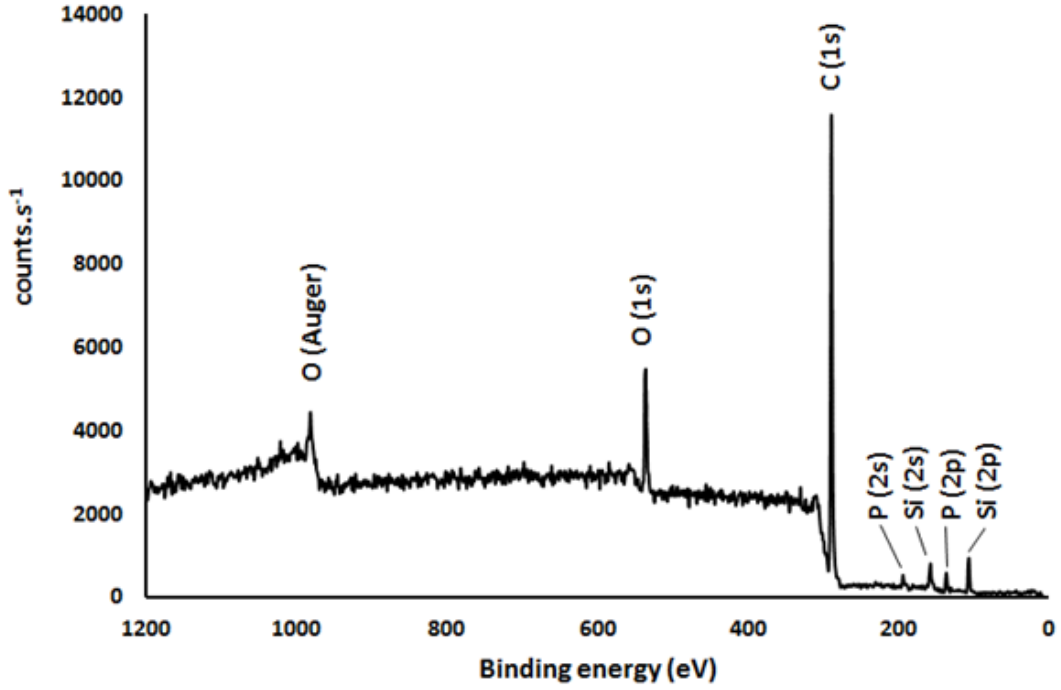
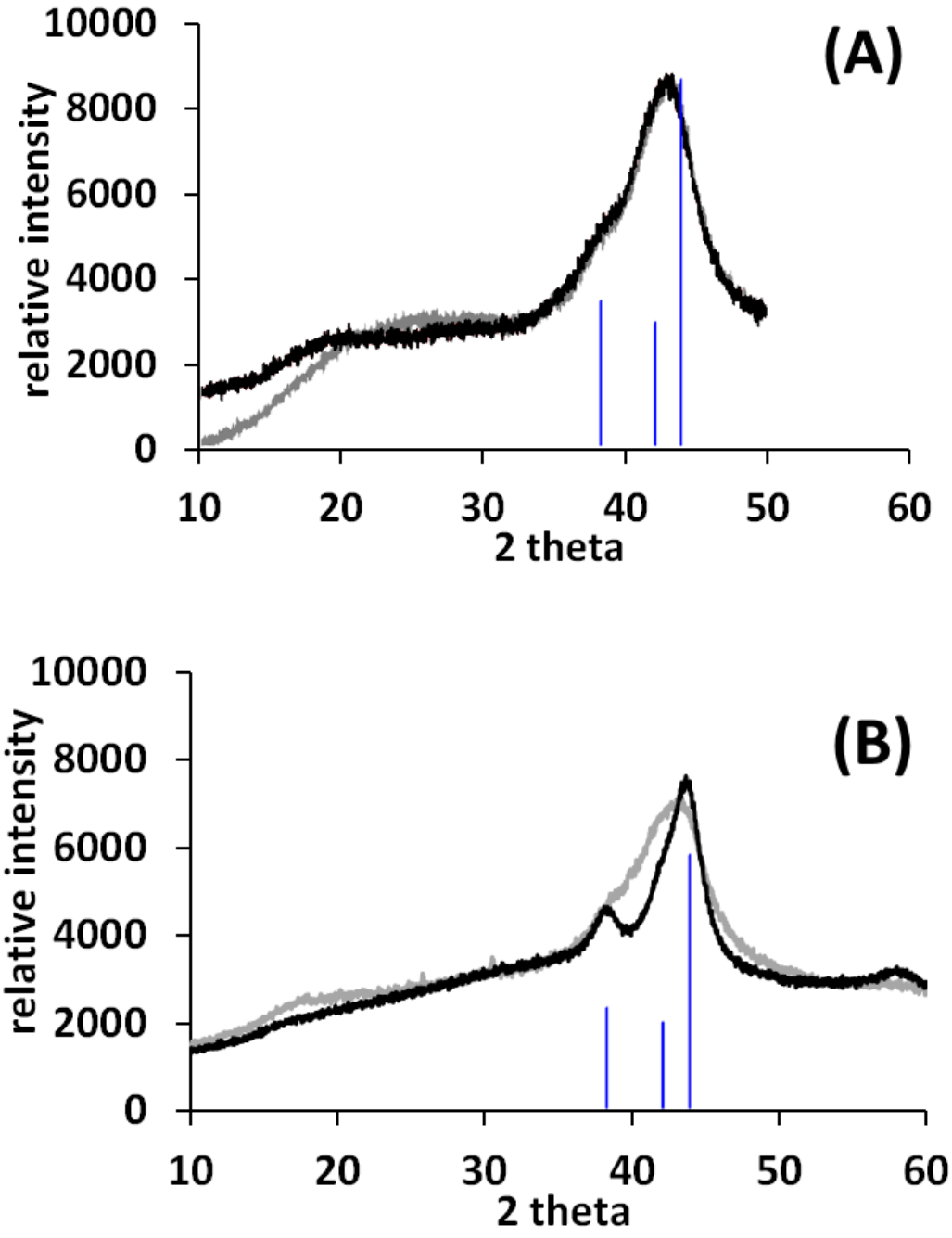


XPS analysis of Ru@3a nanocomposite.



Powder X-ray analysis of Ru@3a (A) and Ru@6a (B) nanocomposite before annealing (grey) and after annealing at 400°C (black). Theoretical peaks for Ru^0 are indicated in blue.



References for the ESI

1. L.-B. Xing, B. Yang, X.-J. Wang, J.-J. Wang, B. Chen, Q. Wu, H.-X. Peng, L.-P. Zhang, C.-H. Tung and L.-Z. Wu, *Langmuir*, 2013, **29**, 2843-2848.
2. A. R. Borges, M. Hyacinth, M. Lum, C. M. Dingle, P. L. Hamilton, M. Chruszcz, L. Pu, M. Sabat and K. L. Caran, *Langmuir*, 2008, **24**, 7421-7431.
3. O. Herd, A. Heßler, M. Hingst, M. Tepper and O. Stelzer, *J. Organomet. Chem.*, 1996, **522**, 69-76.
4. A. M. de Almeida, T. Nascimento, B. S. Ferreira, P. P. de Castro, V. L. Silva, C. G. Diniz and M. Le Hyaric, *Bioorg. Med. Chem. Lett.*, 2013, **23**, 2883-2887.