Electronic Supplementary Material (ESI) for Green Chemistry.

Base free selective oxidation of pectin derived galacturonic acid to galactaric acid using gold catalysts

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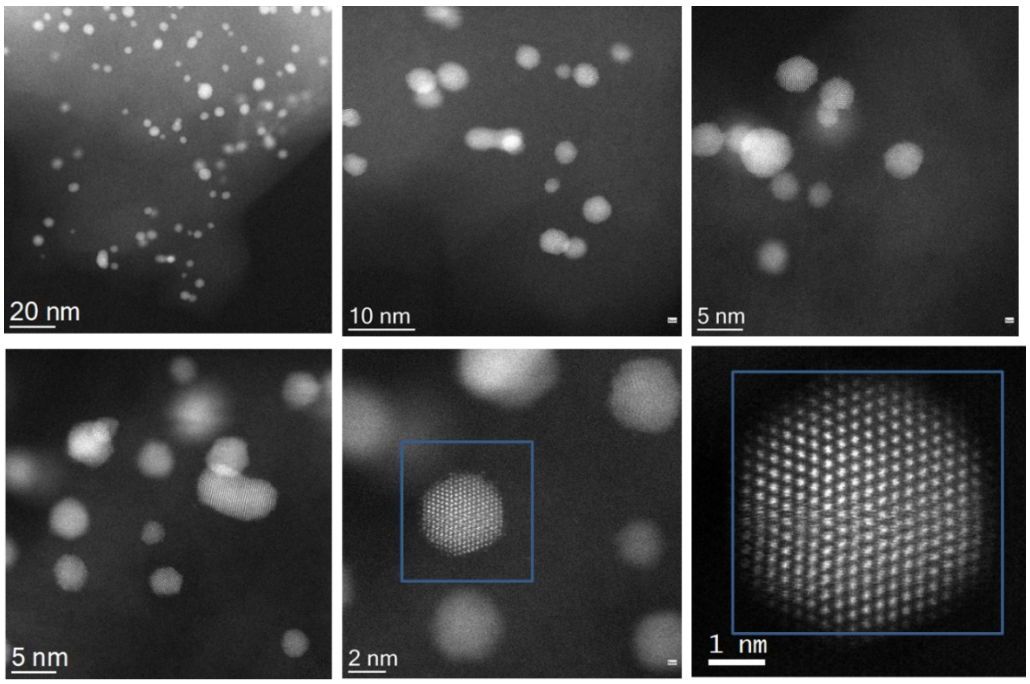
Supporting information



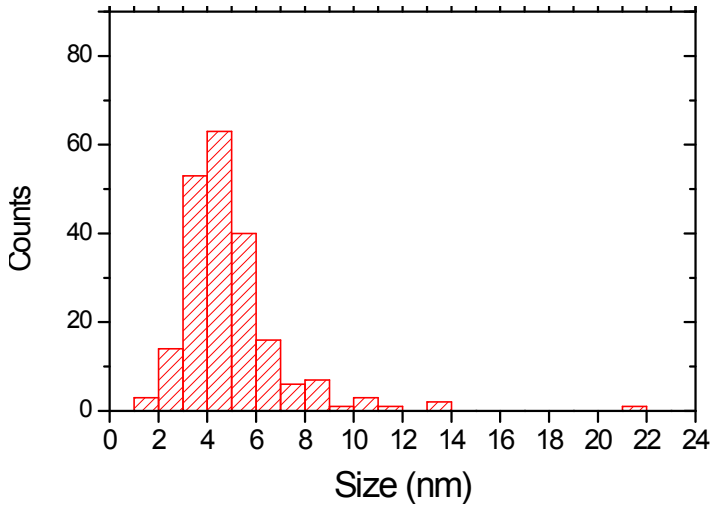
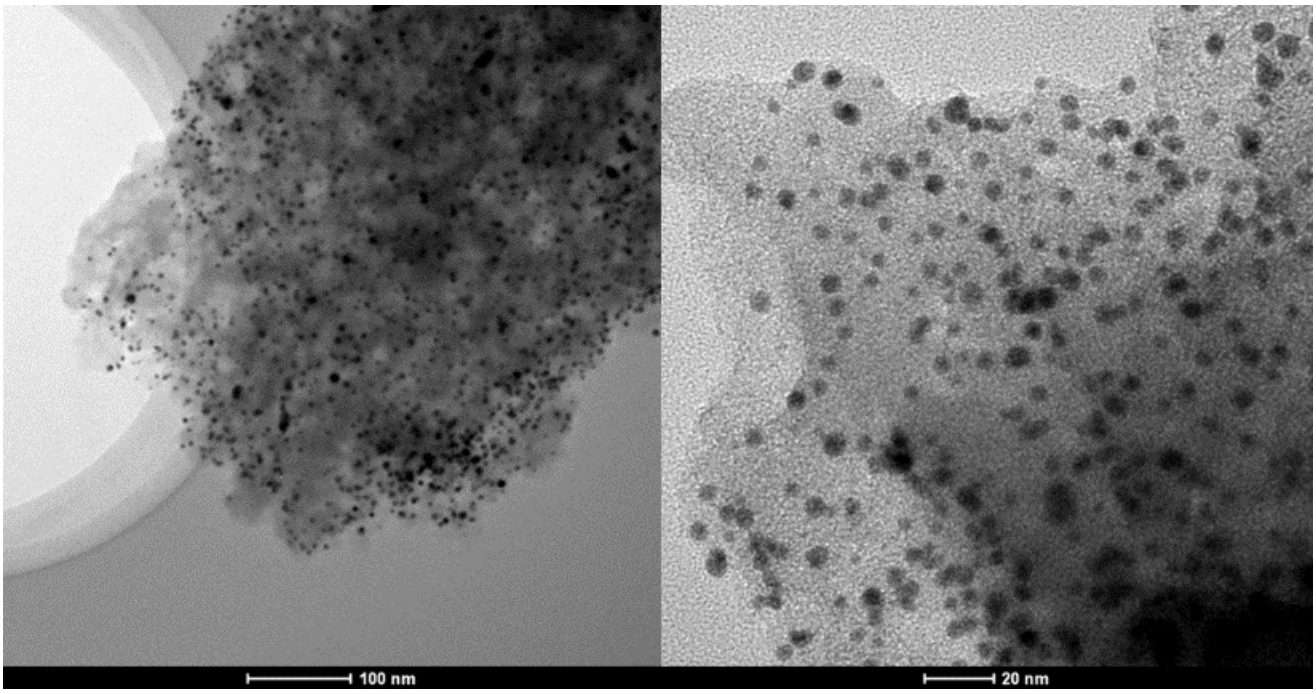


Figure S1. HR-STEM-HAADF image of fresh Au/C catalyst at different magnifications and Au particle size distribution



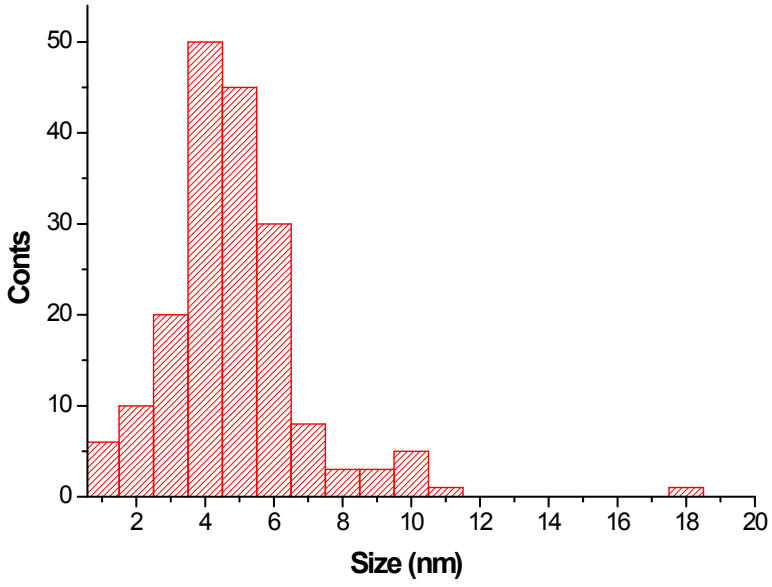
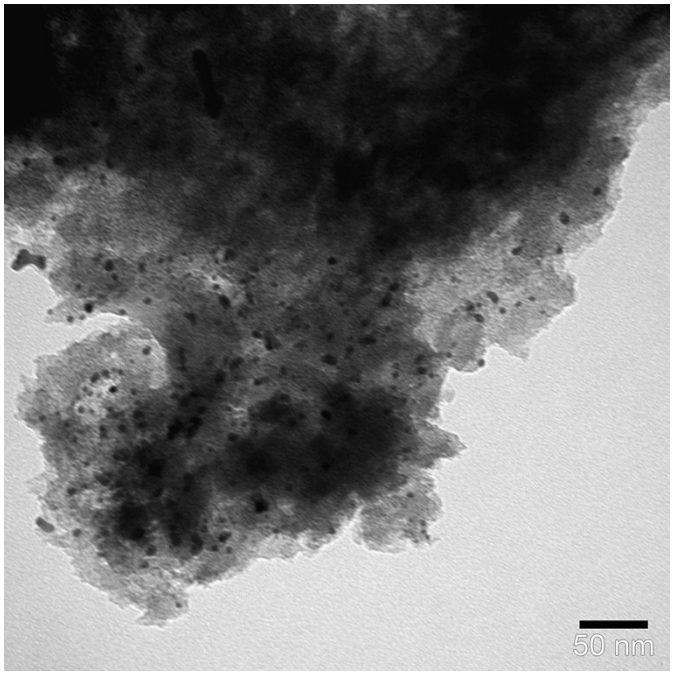
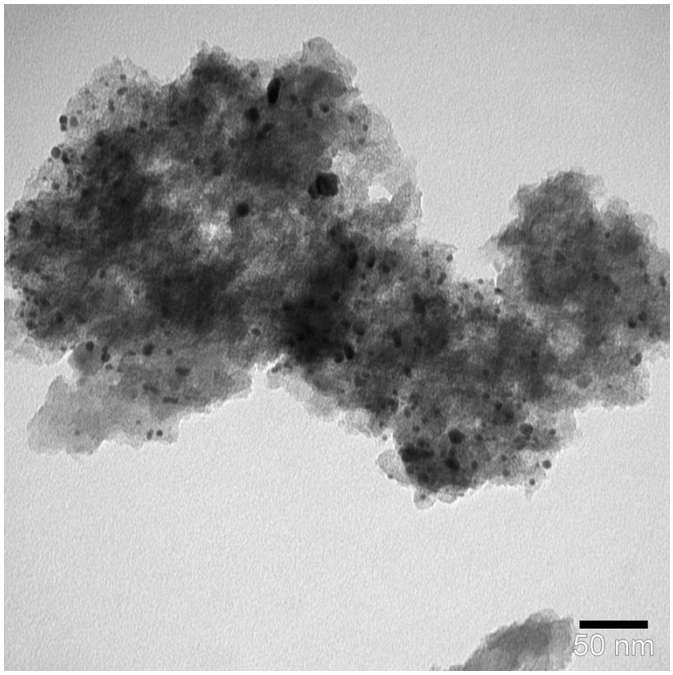


Figure S2. BF-TEM images of spent Au/C catalyst after first run in two different magnifications and Au particle size distribution


50 nm


50 nm

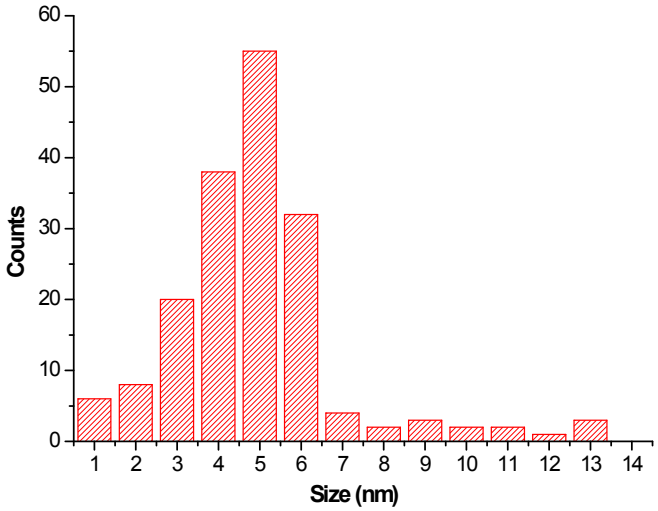
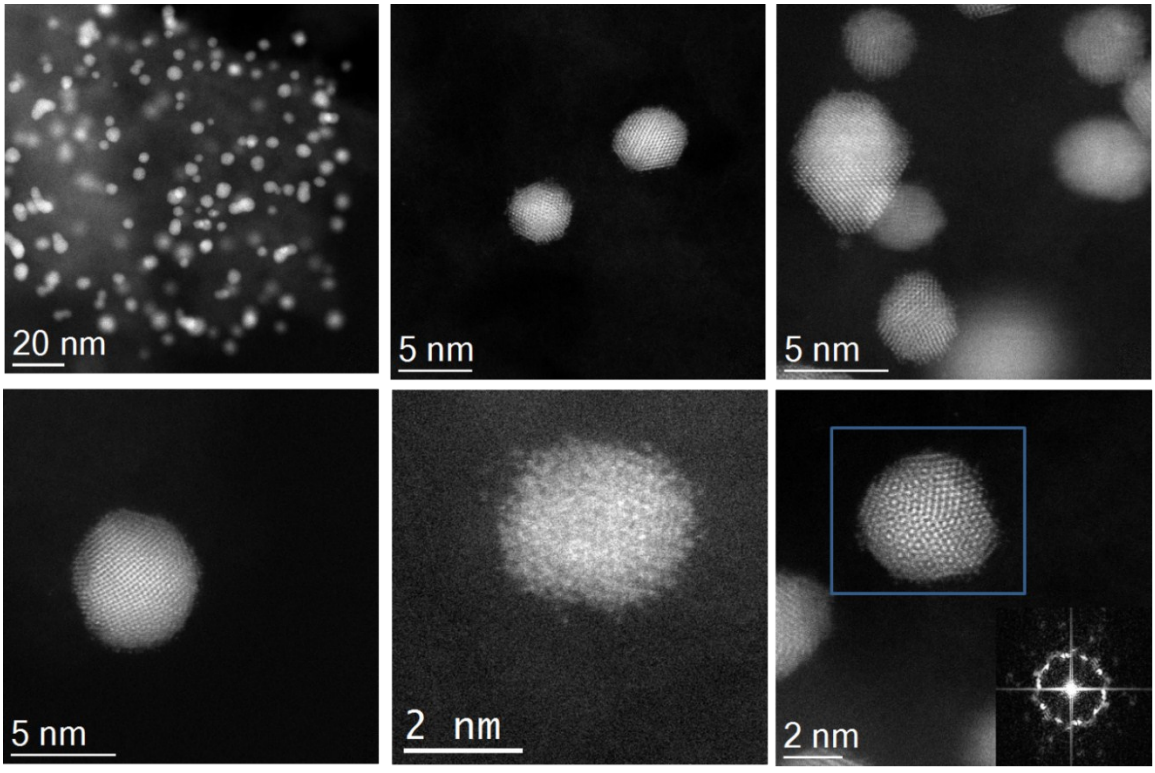


Figure S3. BF-TEM images of spent Au/C catalyst after second run and Au particle size distribution



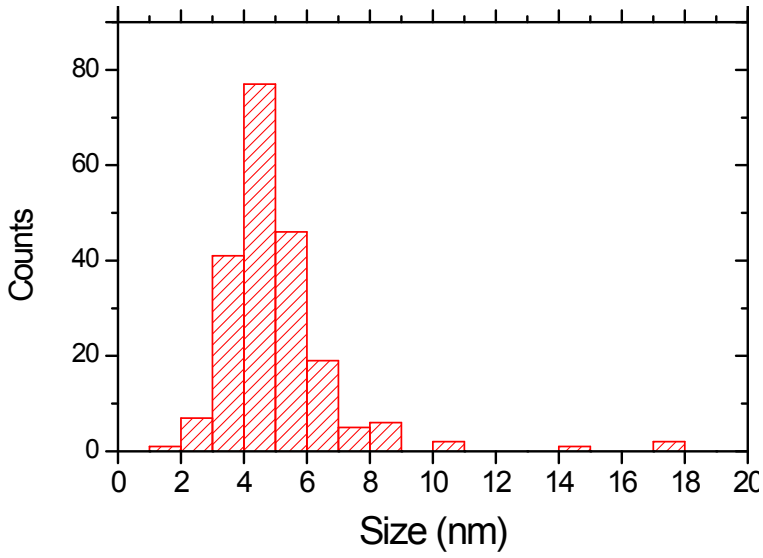
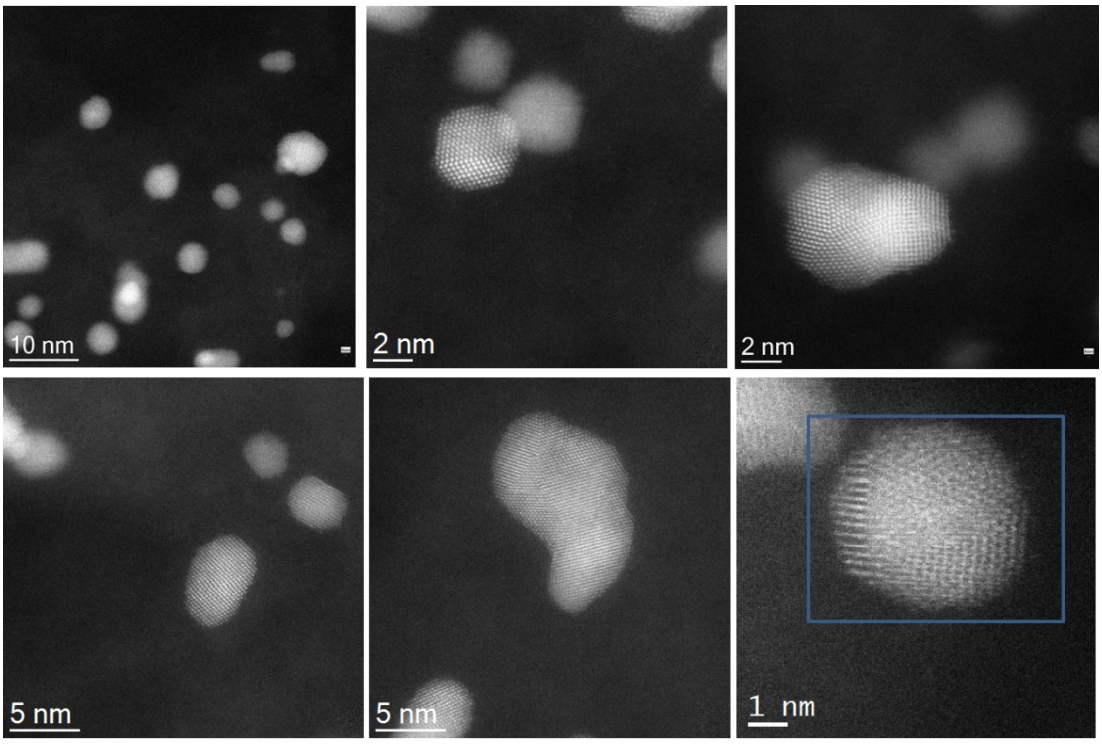


Figure S4. HR-STEM-HAADF image of spent Au/C catalyst after third run at different magnifications and Au particle size distribution



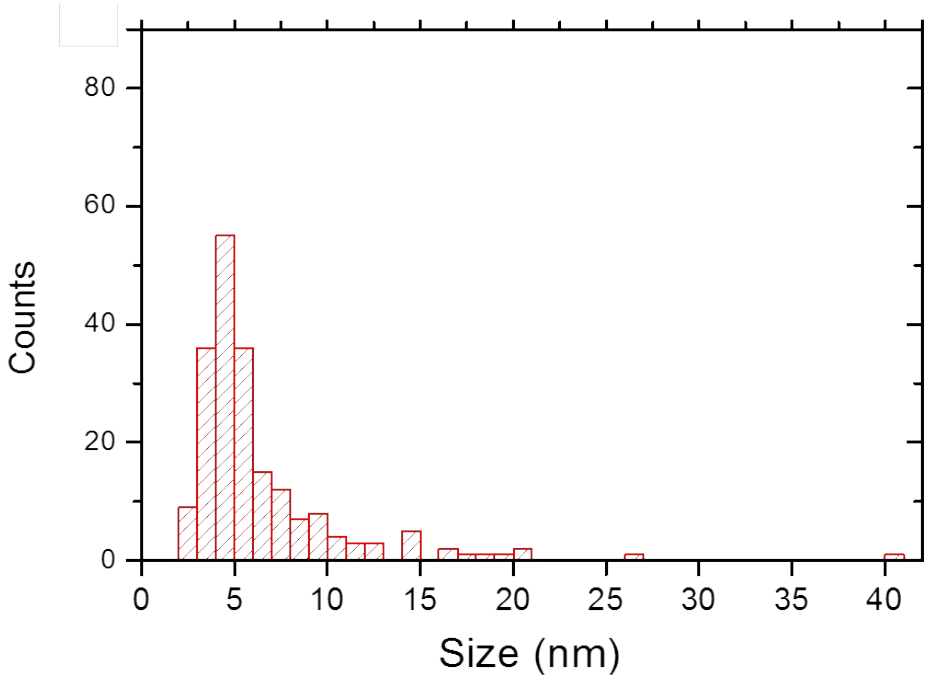


Figure S5. HR-STEM-HAADF image of spent Au/C catalyst after fourth run at different magnifications and Au particle size distribution

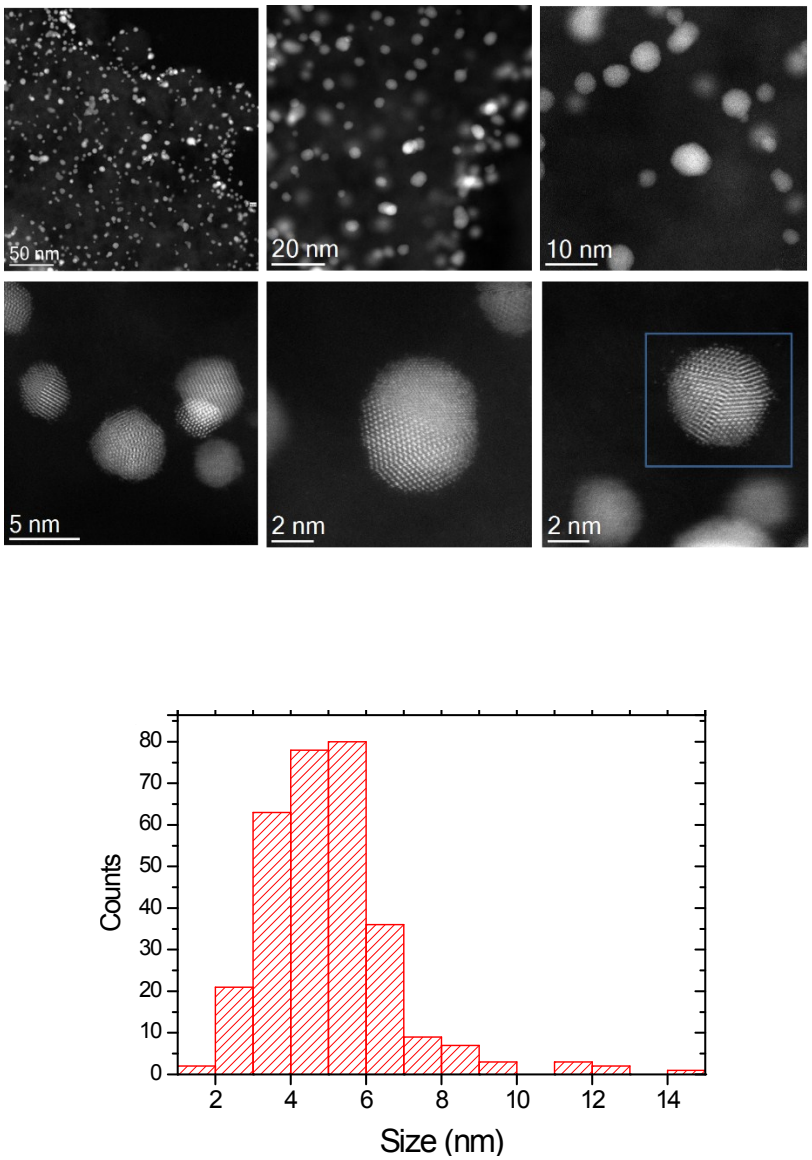


Figure S6. HR-STEM-HAADF image of spent Au/C catalyst after fifth run at different magnifications and Au particle size distribution

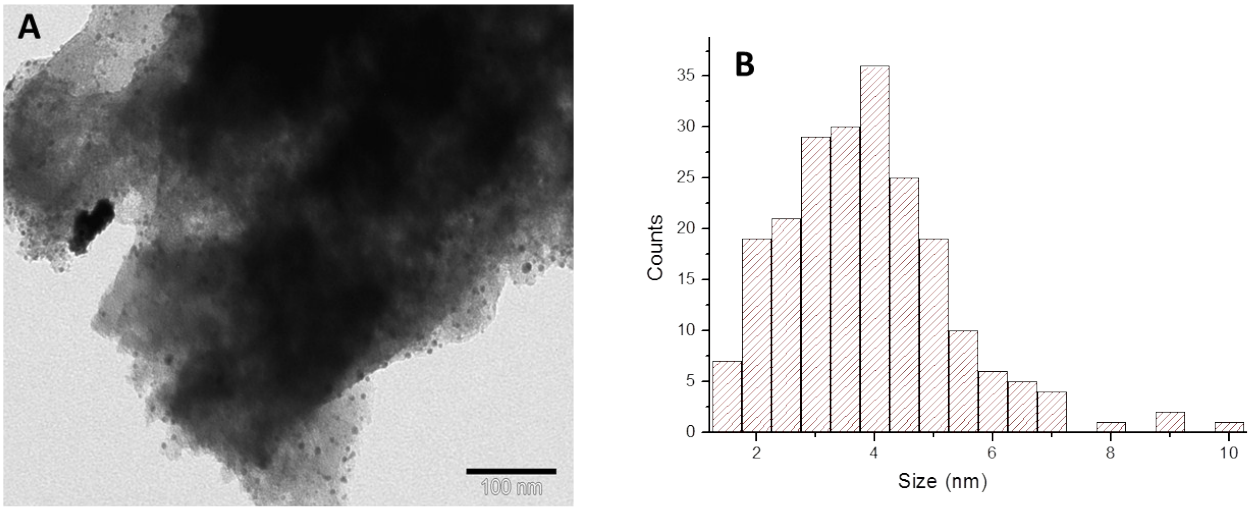


Figure S7. (A) BF-TEM image of Pd/C (B) Pd particle size distribution

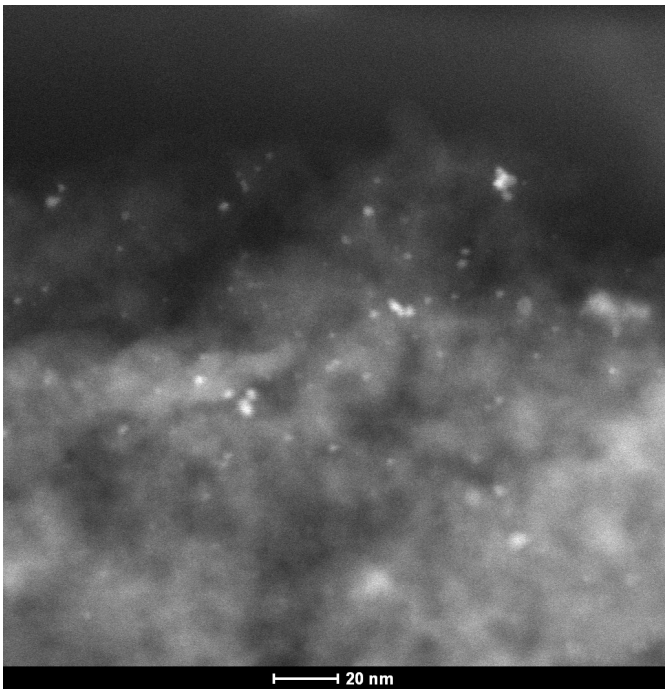


Figure S8: STEM-HAADF image of fresh Pt/C catalyst

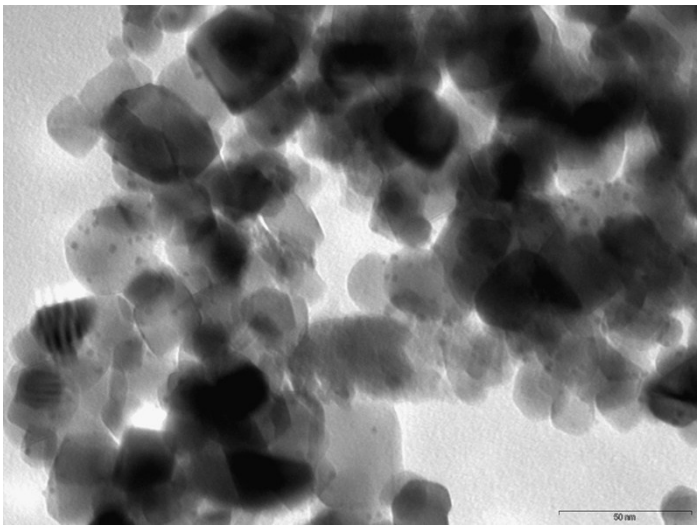


Figure S9: BF-TEM image of fresh Au/TiO_2 commercial catalyst

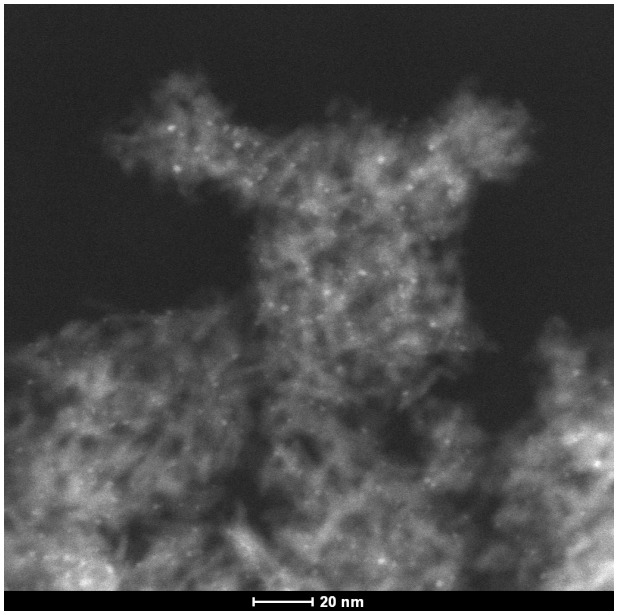


Figure S10: (A) STEM-HAADF image of fresh Au/Al_2O_3 commercial catalyst

Table S1. Base-free oxidation of galacturonic acid over commercial Ru and Rh catalysts [a]

Entry	Catalyst	Conv. (%) [(b)]	Selectivity (%) [(b)]
1	5wt% Rh/C	0	-
2	5wt% Ru/C	0	-
3	0.5wt% Ru/Al_2O_3	2	98

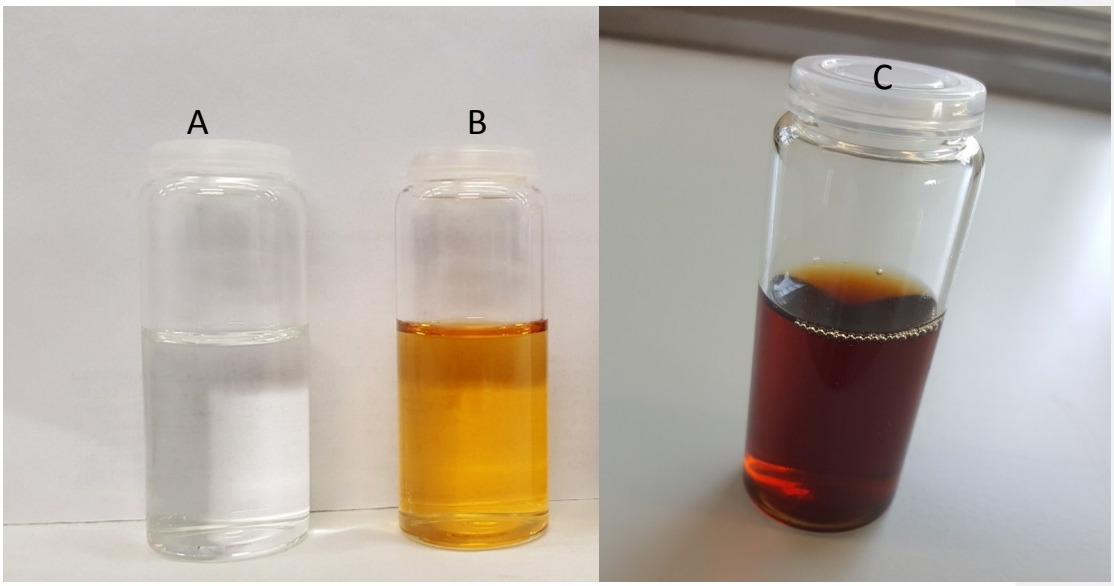
[a] **Reaction conditions** : 2 mmol of galacturonic acid in 20 mL of deionised water, $p(O_2)$ = 3 bar, stirring speed = 800 rpm, t = 21 h, T = 333 K, galacturonic acid/(bulk)metal = 448 mol/mol, initial pH= 2.2; [b] = determined by HPLC.

Table S2. Reactivity of galacturonic acid in the presence and absence of Au/C catalyst – effect of temperature [a]

Comment [EDv]: Check fonts!

Entry	Substrate	Temp. (K)	Catalyst	Conv. [b] (%)	Selectivity (%) [b]									C mass balance (%)
					GalA	GA	GlA	GlyA	TarT	GlyC	OxaL	AceT	ForM	
1	GalA	333	None	0	100	-	-	-	-	-	-	-	-	100
2	GalA	333	Au/C	76	24	76	0	0	0	0	0	0	0	100
3	GalA	353	None	<2.0	-	b.q	b.q	b.q	b.q	b.q	b.q	b.q	b.q	≥98
4	GalA	353	Au/C	100	-	95	-	-	b.q.	b.q.	-	-	b.q.	95
5	GalA	373	None	85	15	10	1	<1	2.5	2.5	4	1	1	37 [c]
6	GalA	373	Au/C	100	-	49	-	-	-	-	-	-	-	49 [d]

[a]**Reaction conditions:** 2 mmol of substrate in 20mL of deionized water, 126mg of catalyst, $p(O_2)$ = 3bar, GalA = galacturonic acid, GalacT = galactaric acid, GlA = glyceraldehyde, GlyA = glyceric acid, TarT = tartronic acid, GlyC = glycolic acid, OxaL = oxalic acid, AceT = acetic acid, ForM = formic acid; [b] = determined by HPLC; [c] No visible solid particles, dark brown transparent solution; [d] Colourless solution, pH 3.7 after 21h, 0.8 bar oxygen pressure drop; b.q = below quantification limit.



A = Aq.GalA at 333K for 21h + oxygen
B = Aq.GalA at 353K for 21h + oxygen
C = Aq.GalA at 373K for 21h + oxygen

Figure S11: Galacturonic acid in water at different temperature for 21h in oxygen atmosphere in the absence of catalyst illustrating browning

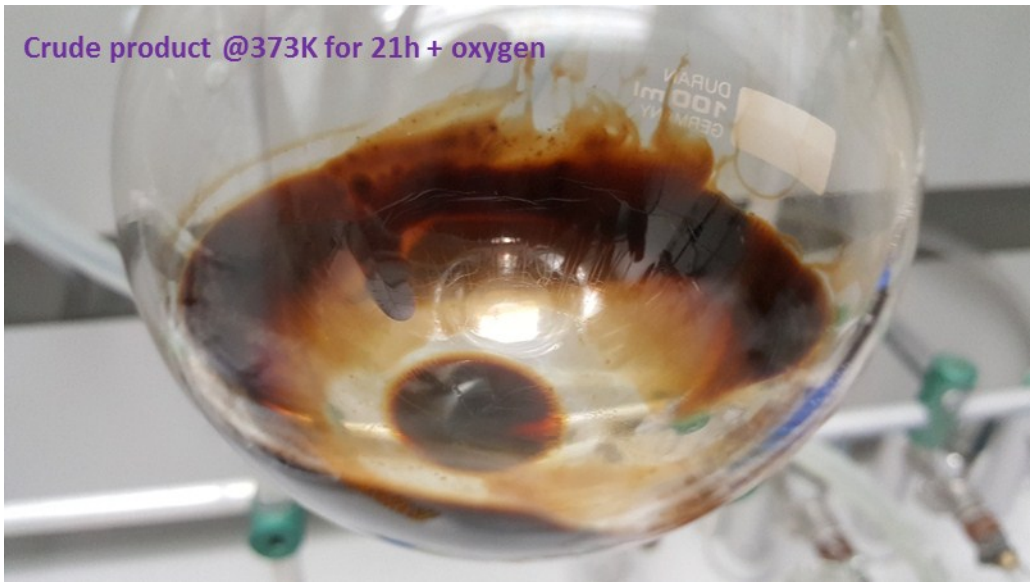


Figure S12: Crude product obtained from the reaction of galacturonic acid at 373K in oxygen atmosphere in the absence of catalyst

GPC analysis: GPC analyses were performed on a Waters Alliance system (Waters® e2695 Separations Module) equipped with a pre-column (TOSOH Bioscience; TSK gel® PW_{XL} Guard 12µm; 6.0×40mm), a column (TOSOH Bioscience; TSK gel® $GMPW_{XL}$ Guard 13µm; 7.8×300mm) and a UV detector (Waters 2487, dual λ absorbance) operating at 280 nm. The measurements were performed at 40°C using 0.15M NaOH (Emsure® analytical reagent) as the eluent at a flow rate of 1mL/min. Poly(styrene sulphonate) sodium salts were used for the calibration (obtained from Polymer Standard Services, GmbH). Before analyses, the samples at a concentration of 2mg/mL were dissolved in 0.15M NaOH solution at room temperature by gently shaking for 12h.

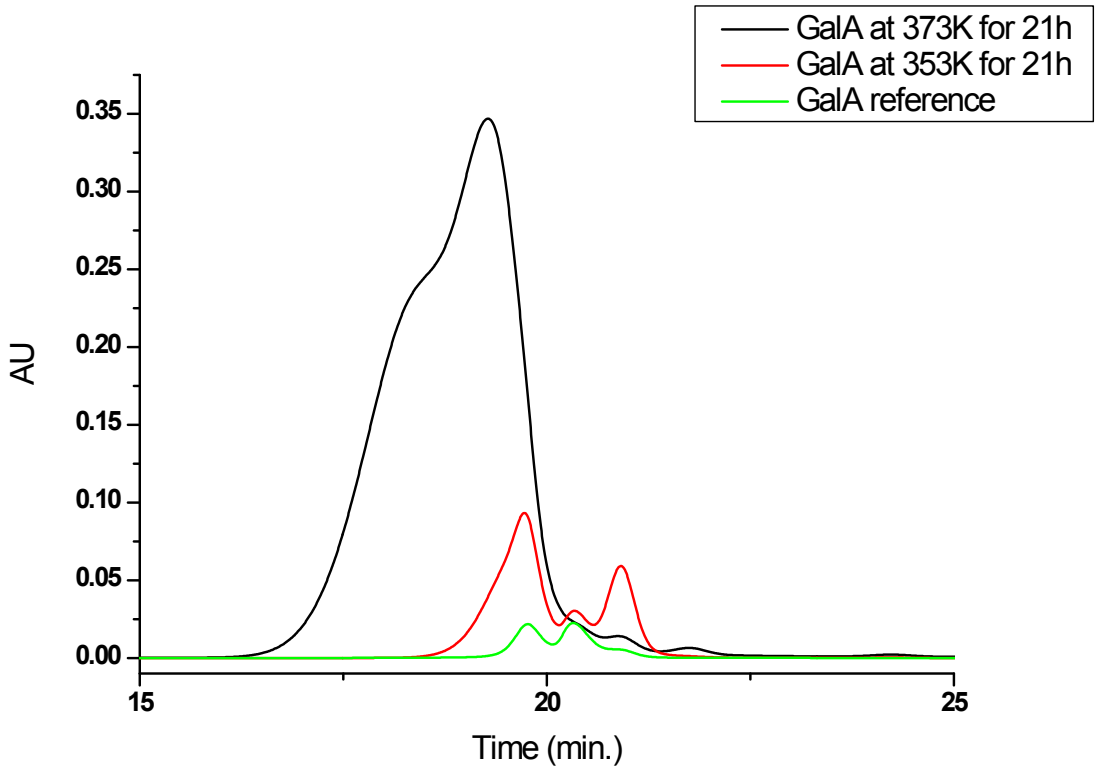


Figure S13: GPC Chromatogram of galacturonic acid treated at different temperature in oxygen atmosphere for 21h in the absence of catalyst