Supporting information

Selective oxidation of uronic acids into aldaric acids over gold catalyst

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1. Catalyst characterization

Thermogravimetric analysis (Mettler Toledo TGA850) was carried out for 10 mg of both fresh and spent catalyst. The temperature was increased 10 °C/min to 1000 °C under air flow. The calcination resulted in weight loss of ca. 5% for the fresh catalyst and 6% for the spent catalyst.

2. Product analysis by NMR spectroscopy

NMR spectra were measured directly from the reaction solution using Varian 500 MHz for ^{1}H-NMR and Varian 300 MHz for ^{13}C-NMR measurements. Filtered samples from the reaction mixture were diluted with deionized water if necessary to concentration 10-20 mg/ml. The sample (0.4 ml) was mixed with 0.1 ml D_2O in NMR tube. For ^{1}H-NMR, water signal of the sample solvent was suppressed using a low power pulse. The chemical shift values and coupling constants of the products are listed in Table S1 (see Figure S1 for carbon atom numbering). As an example, NMR spectra of glucarate (Figures S2 & S3) and galactarate (Figures S4 & S5) are shown after oxidation of the corresponding uronic acids at pH 9 using 0.09 mol% Au/Al_2O_3.

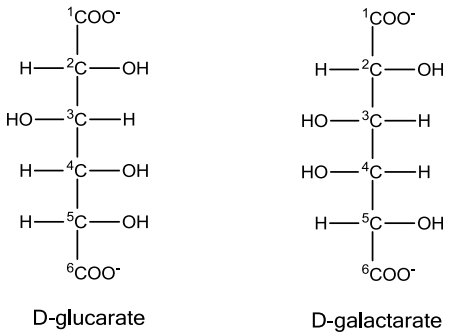

Figure S1. Structures of glucarate and galactarate.

Table S1. ^{13}C and ^{1}H chemical shifts (ppm) of the products, assignments according to van Duin *et al.*[1] for glucarate and Lakatos *et al.*[2] for galactarate.

Carbon no.	Glucarate			Galactarate	
	C	H	*J*(H,H)/Hz	C	H
1	178.53	-	-	181.40	-
2	73.78	4.17	3.0	73.41	4.14
3	71.70	4.10	4.5, 3.1	73.70	3.83
4	73.78	3.96	4.6	73.70	3.83
5	73.60	4.15	4.6	73.41	4.14
6	178.41	-	-	181.40	-

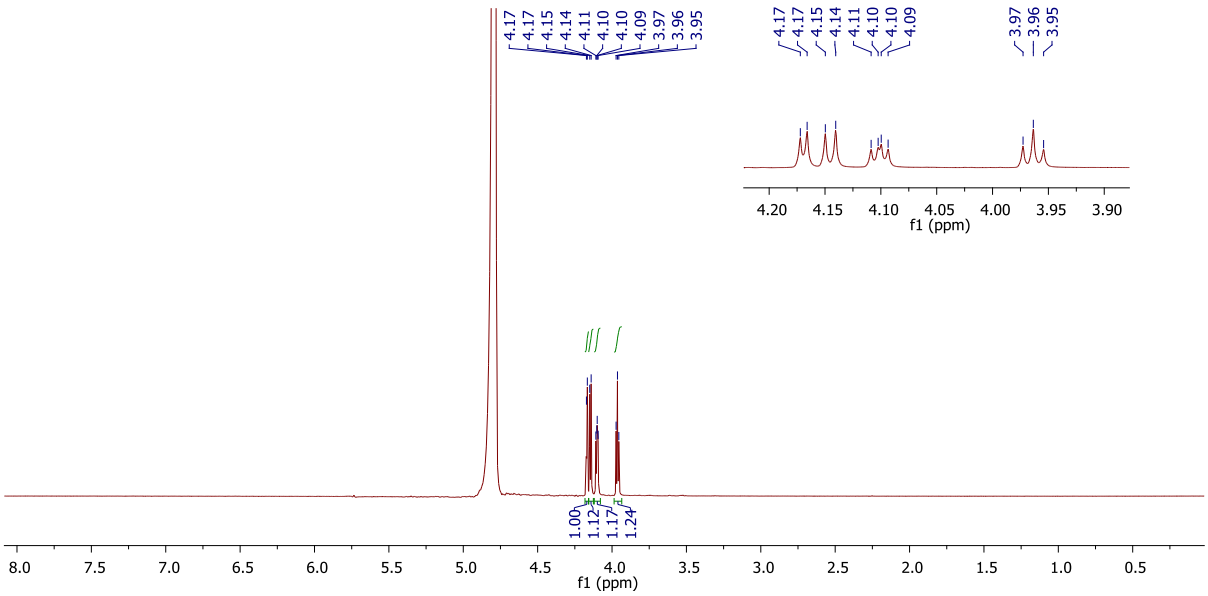

Figure S2. ^{1}H-NMR spectrum of glucarate at pH 9. Water signal is suppressed.

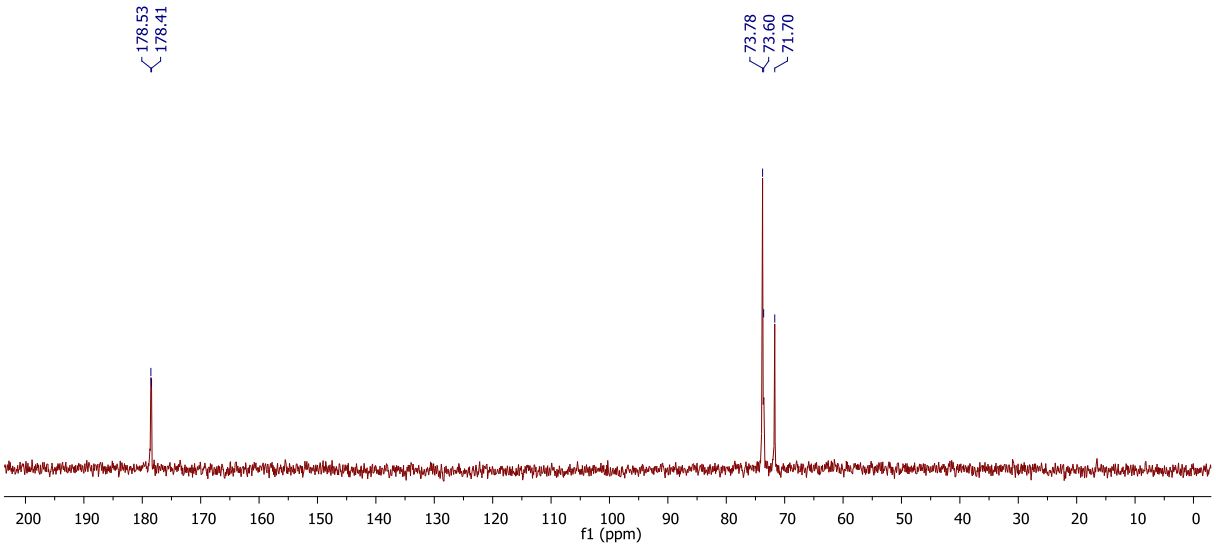

Figure S3. ^{13}C-NMR spectrum of glucarate.

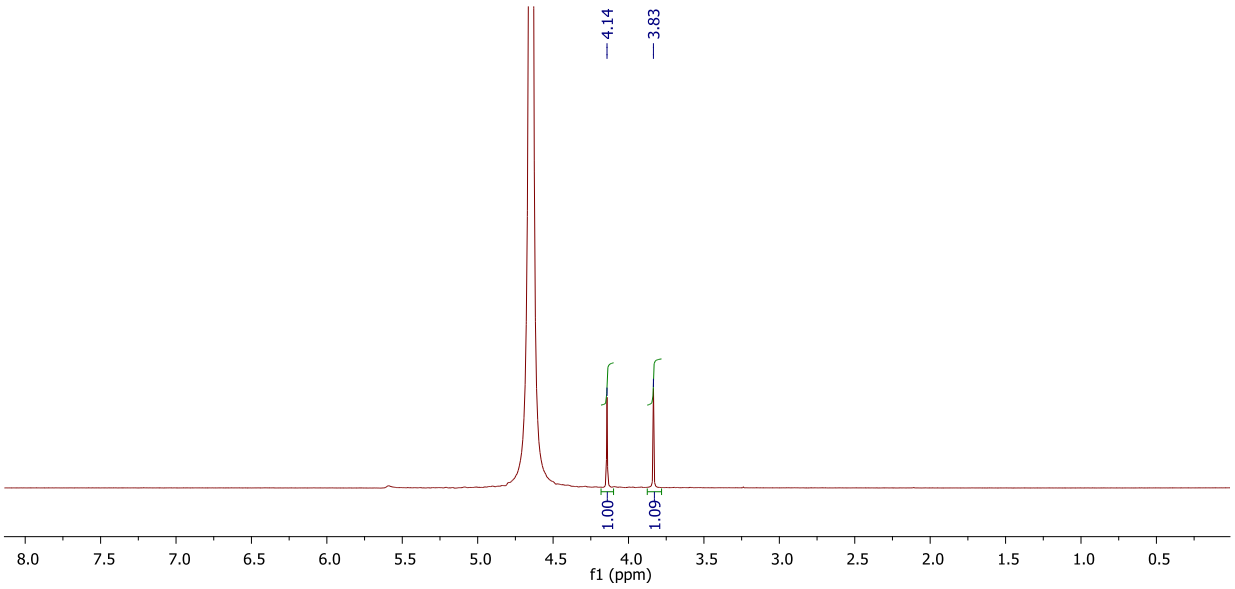

Figure S4. ^{1}H-NMR spectrum of galactarate at pH 9. Water signal is suppressed.

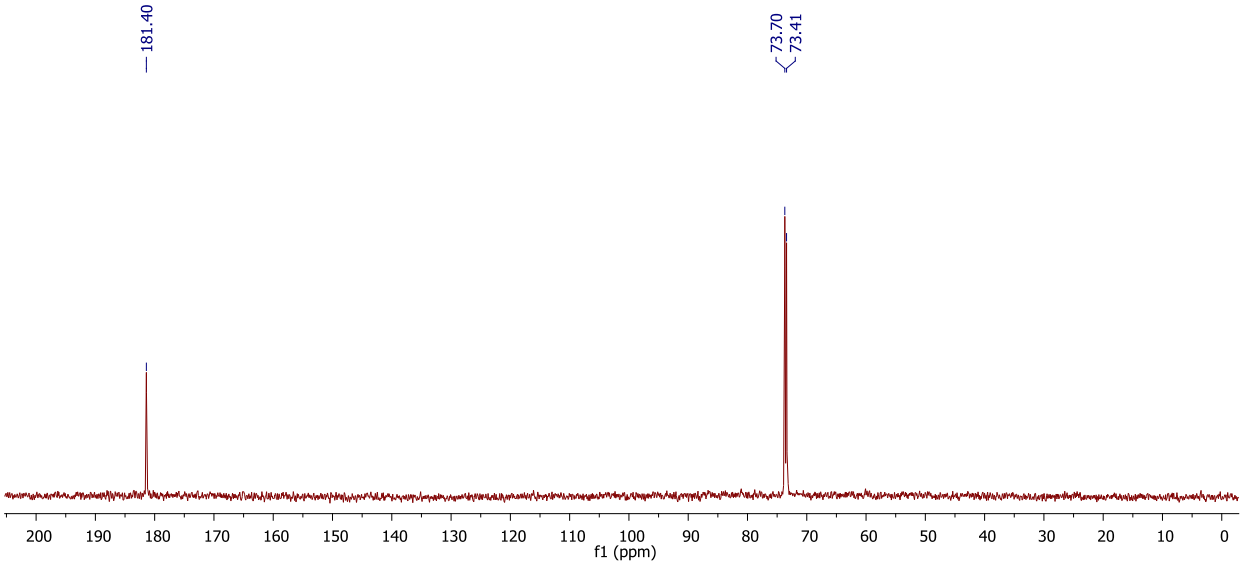

Figure S5. ^{13}C-NMR spectrum of galactarate.

3. Product analysis by GC/MS

For the GC/MS analyses, the reaction samples were treated according to the procedure reported.[3] Typically, the samples (1 ml) were cation-exchanged to H^+ and filtered, and 0.2 ml of the filtrates evaporated to dryness and trimethylsilylated with a mixture (1:1) of BSTFA and TMCS. Known amount of xylitol was added as internal standard to the samples before the cation-exchange. The GC/MS runs were performed with an Agilent 6890 Series GC System, equipped with an Agilent 5973 Mass Selective Detector and a Phenomenex ZB-5HT Inferno capillary column (30 m

x 0.25 mm, film thickness 0.25 µm). The temperature programme was 3 min at 200 °C, followed by 8 °C/min increase to 320 °C (for 15 min). A sample chromatogram of glucuronic acid oxidation at 60 °C and pH 9 is shown in Fig. S6. Glucaric acid lactones shown in the chromatogram are formed during the sample preparation.

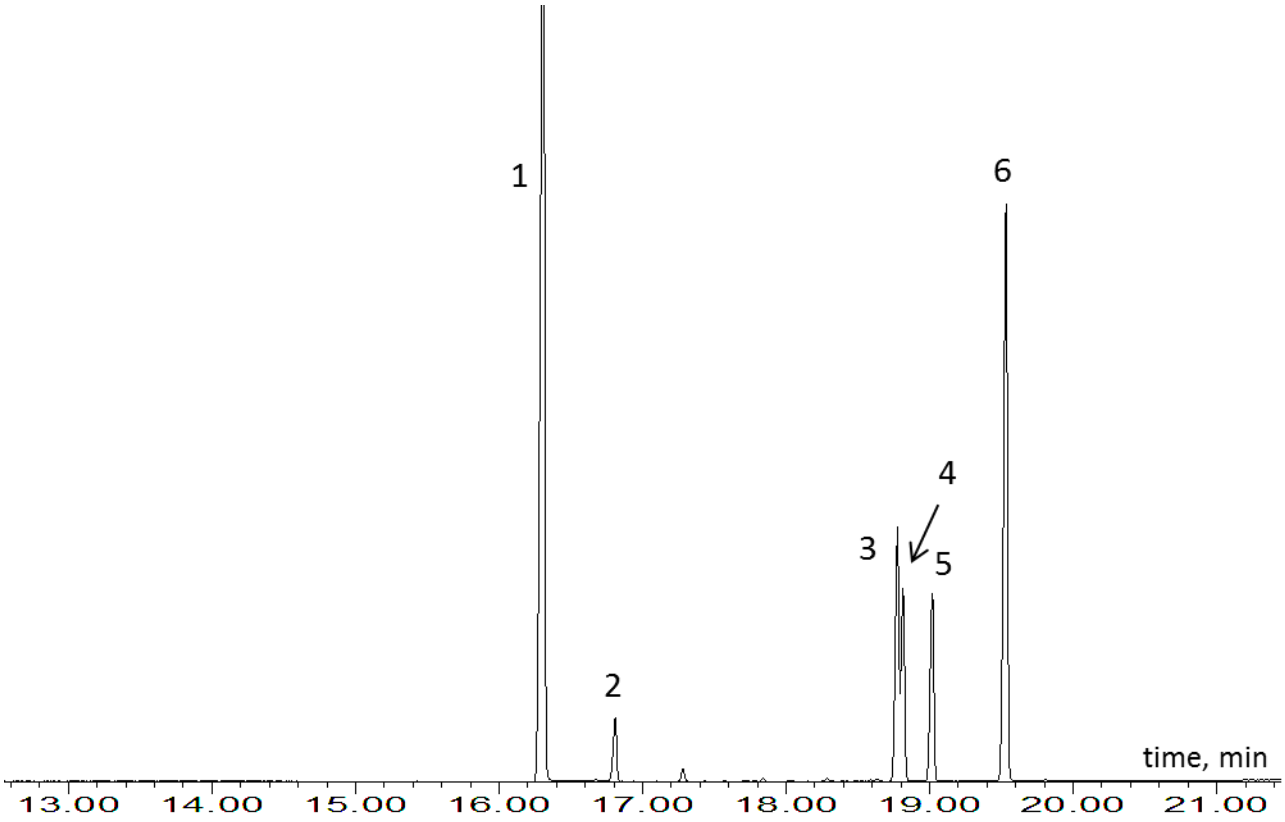

Figure S6. Separation of trimethylsilylated glucuronic acid oxidation products (at 60 °C and pH 9) on a Phenomenex Inferno capillary column: 1, xylitol (internal standard); 2, a dilactone of glucaric acid; 3-5, monolactones of glucaric acid; and 6, glucaric acid. The lactones are formed during acidification and evaporation of the reaction mixtures.

4. Product analysis by HPLC

Filtered samples were diluted to 0.5 mg/ml concentration using 0.25 mM H_2SO_4, and cation exchanged with Phenomenex strata-X X-C sorbents. HPLC runs were performed using Agilent 1200 HPLC system equipped with a Phenomenex Rezex ROA (300 x 7.8 mm) column at 40 °C. The eluent was 0.25 mM H_2SO_4 at a flow rate 0.35 ml/min. Detection was carried out by RID. Chromatograms for products of glucuronic acid and galacturonic acid oxidation are shown in Fig. S7 and S8, respectively. Aldaric acid lactones formed during acidification cause tailing of the product peak. As the peaks of substrate and product overlap, HPLC analysis was performed to determine possible side products in the oxidation.

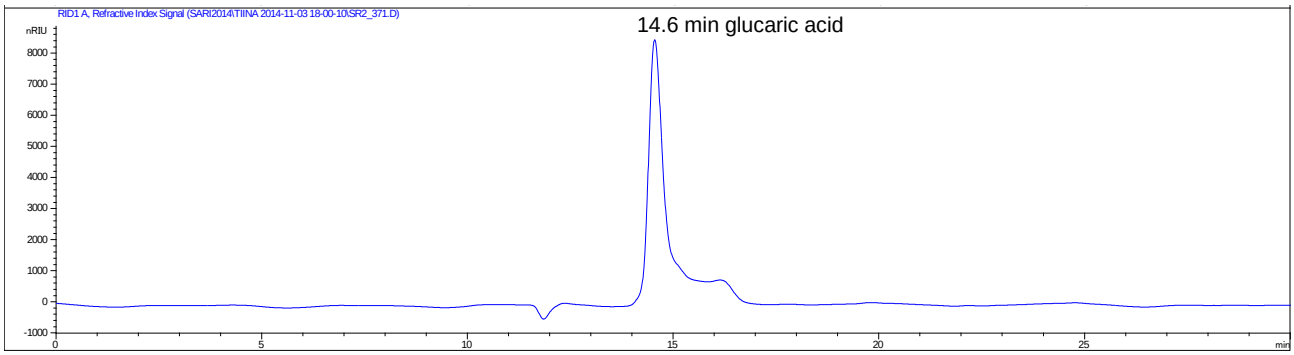

Figure S7. HPLC chromatogram of products of glucuronic acid oxidation (at 60 °C and pH 10). The negative peak at 12 min is caused by the eluent.

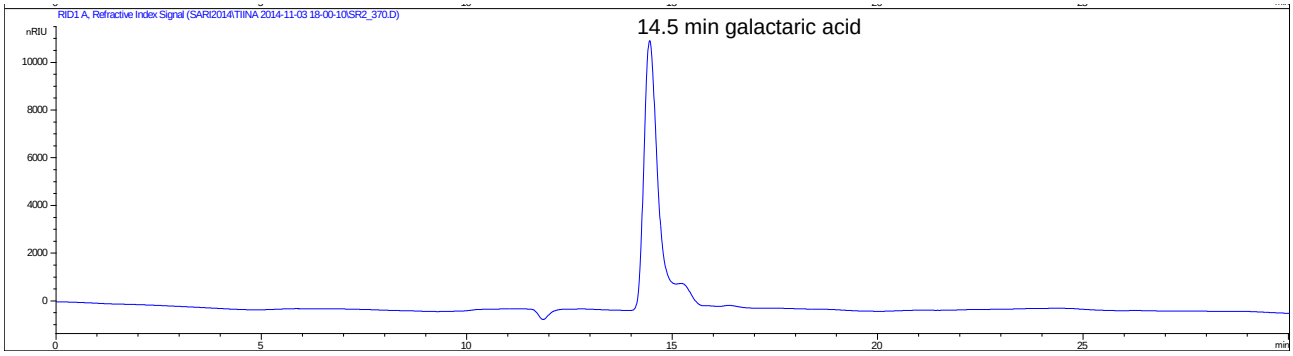

Figure S8. HPLC chromatogram of products of galacturonic acid oxidation (at 60 °C and pH 10). The negative peak at 12 min is caused by the eluent.

5. Activation energy determination

Activation energies E_a for the oxidations were determined based on the Arrhenius equation,

$$k = Ae^{-\frac{E_a}{RT}}$$

where k is the reaction rate, A the pre-exponential factor, E_a the activation energy ($Jmol^{-1}$), R the universal gas constant (8.314 $Jmol^{-1}K^{-1}$), and T the reaction temperature (K). Taking natural log on both sides of the equation,

$$\ln k = \ln A - \frac{E_a}{R}\frac{1}{T}$$

The apparent activation energy can be determined from the experimental data by plotting ln k [reacted substrate (mol)/total$_{Au}$ (mol)/time (s)] vs. 1/T. The Arrhenius plot gives a straight line with a slope - E_a/R (Fig. S9).

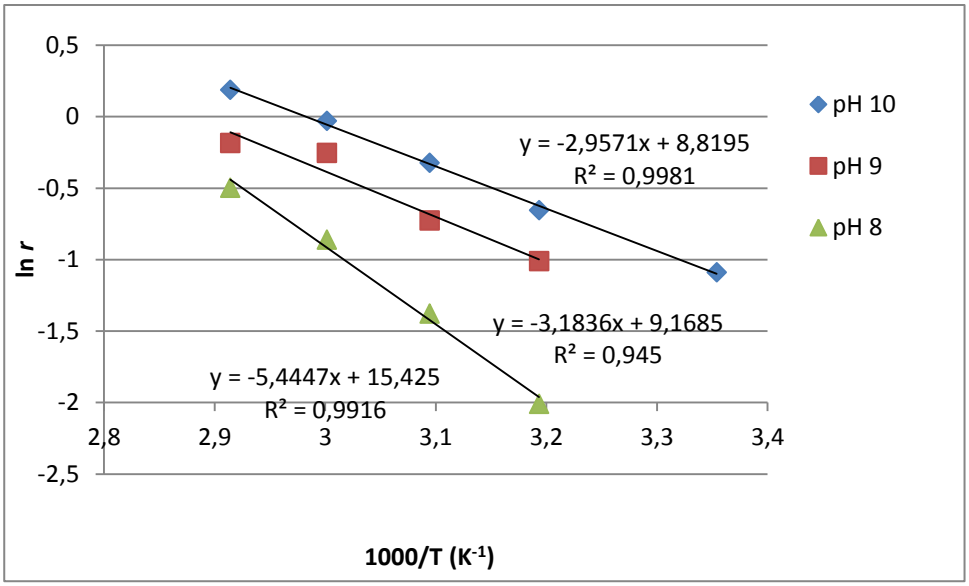

Figure S9. Arrhenius plots for glucuronic acid oxidation.

6. Catalyst recycling

Several washing treatments were applied to the spent catalyst to remove possible weakly adsorbed molecules from the catalyst surface (Fig. S10). After the reaction, the catalyst was washed four times with deionized water and dried at 80 °C. In case of base or acid wash, the catalyst was first washed with the solution in question, then three times with water and finally dried at 80 °C.

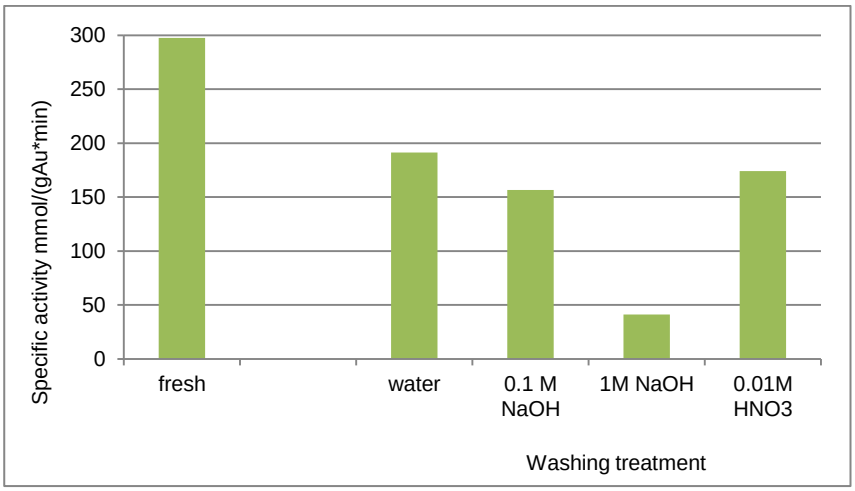

Figure S10. Specific activity for the fresh and recycled Au/Al_2O_3 with different washing treatments.

References

1 M. van Duin, J. A. Peters, A. P. G. Kieboom and H. van Bekkum, *Journal of the Chemical Society, Perkin Transactions 2*, 1987, 473-478.

2 A. Lakatos, R. Bertani, T. Kiss, A. Venzo, M. Casarin, F. Benetollo, P. Ganis and D. Favretto, *Chemistry – A European Journal*, 2004, **10**, 1281-1290.
3 M. Borrega, K. Niemelä and H. Sixta, *Holzforschung*, 2013, **67**, 871-879.