Biosourced Polymetallic Catalysts: An Efficient Means To Synthesize Underexploited Platform Molecules from Carbohydrates

Vincent Escande,^[a, b] Tomasz K. Olszewski,^[c] Eddy Petit,^[d] and Claude Grison*^[a, b]

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I. General remarks

Reagents and solvents were purchased from Sigma-Aldrich, and were used without further purification.

Flash column chromatography was performed using Chromagel Carlo Erba Reactifs SDS silica 60 A CC 35-70 μ m. Reactions were monitored using Merck Kieselgel 60 F254 aluminium. TLC's were visualized by UV fluorescence (254 nm) then one of the following: KMnO₄, ninhydrin, phosphomolybdic acid solution, phosphotungstic acid solution.

NMR spectra were recorded on a Brüker Avance 300 spectrometer at room temperature, ¹H frequency is at 300 MHz, ¹³C frequency is at 75 MHz. IR spectra were recorded on a PerkinElmer Spectrum 100 FT-IR spectrometer, in ATR mode. GC/MS analyses were performed on a Shimadzu QP2010 apparatus.

II. Preparation of polymetallic plant-based catalyst

Leaves of *Noccaea caerulescens* and *Anthyllis vulneraria* were harvested before flowering in Les Avinières, a former zinc mining site in Saint-Laurent-Le-Minier, southern France (same mass of the two plants), air-dried and crushed. The obtained solid (150 g) was calcinated at 400°C for 5 h and the resulting powder (24 g) was added to 100 mL of 1 M HCl solution. The solution was heated at 60°C and stirred for 2 h. The reaction mixture was filtered on celite. The resulting solution, composed of different metal chlorides, was then concentrated under vacuum. The catalyst was kept in a desiccator under vacuum.

III. General procedure for the synthesis of uncyclized polyhydroxyalkyl furans

Carbohydrate (10 mmol), plant-based catalyst (390 mg, amount corresponding to 0.40 mmol of Zn, 0.19 mmol Fe, 0.22 mmol Al following ICP-MS dosing) and silica (500 mg, Chromagel Carlo Erba Reactifs SDS silica 60 A CC 35-70 μ m) were mixed by grinding in a mortar. β -dicarbonyl compound (12 mmol) was added and the resulting solid was homogenized with a spatula. The solid was introduced in a sealed tube (Ace glass tube, 10.2 cm x 25.4 mm) with a magnetic stirring bar and heated to 50°C in oil bath for 24 h until completion of the reaction (TLC monitoring, toluene/acetone 1:1). The solid mixture was then

washed with ethyl acetate (2 x 5 mL) and filtered. The resulting solution was evaporated under reduced pressure to yield a grey powder. This powder was purified by crystallization in hot ethyl acetate, giving the uncyclized polyhydroxyalkyl furan as a white solid. The previous catalytic solid (mixture of plant-based catalyst and SiO₂) was recycled by washing with ethyl acetate and drying in an oven (120°C, 5 h), before being reused in the next run.

IV. General procedure for the synthesis of cyclized polyhydroxyalkyl furans

Carbohydrate (10 mmol), plant-based catalyst (390 mg, amount corresponding to 0.40 mmol of Zn, 0.19 mmol Fe, 0.22 mmol Al following ICP-MS dosing) and silica (500 mg, Chromagel Carlo Erba Reactifs SDS silica 60 A CC 35-70 μ m) were mixed by grinding in a mortar. β -dicarbonyl compound (12 mmol) was added and the resulting solid was homogenized with a spatula. The solid was introduced in a sealed tube (Ace glass tube, 10.2 cm x 25.4 mm) with a magnetic stirring bar and heated to 85°C in oil bath for 24 h until completion of the reaction (TLC monitoring, toluene/acetone 1:1). The solid mixture was then washed with ethyl acetate (2 x 5 mL) and filtered. The resulting solution was evaporated under reduced pressure to yield a brown oil. This oil was purified by flash column chromatography (toluene/acetone 1:1) to yield the cyclized polyhydroxyalkyl furan as an off-white solid, which was recrystallized in hot ethyl acetate. The previous catalytic solid (mixture of plant-based catalyst and SiO₂) was recycled by washing with ethyl acetate and drying in an oven (120°C, 5 h), before being reused in the next run.

V. Analytical Data



Yield: 65 %. White solid, recrystallized in hot ethyl acetate.

IR 3400, 1730 cm⁻¹

¹**H NMR** (300 MHz, CDCl₃) δ 6.60 (s, 1H), 4.28 (q, *J* = 7.3 Hz, 2H), 3.82-3.62 (m, 5H), 2.56 (s, 3H), 1.35 (t, *J* = 7.3 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 165.8, 160.9, 151.3, 111.7, 102.6, 73.9, 71.2, 68.0, 63.5, 60.3, 16.5, 14.1.



Yield: 72 %. White solid, recrystallized in hot ethyl acetate.

IR 3395, 1690 cm⁻¹

¹**H NMR** (300 MHz, CDCl₃) δ 6.67 (s, 1H), 3.90-3.62 (m, 5H), 2.55 (s, 3H), 2.39 (s, 3H).

¹³**C NMR** (75 MHz, CDCl₃) δ 196.9, 159.3, 155,2, 108.7, 108.5, 74.6, 72.8, 67.9, 64.8, 30.2, 14.9.



Yield: 70 %. Brown syrup

IR 3411, 1669 cm⁻¹

¹**H NMR** (300 MHz, CDCl₃) δ 6.62 (s, 1H), 3.70-3.41 (m, 4H), 2.60 (s, 3H), 2.42 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 194.5, 158.2, 155.7, 109.4, 108,9, 76,8, 65.3, 61.5, 28,7, 14.2.

нο OH 3e'

Yield: 70 %. Brown syrup

IR 3419, 1669 cm⁻¹

¹H NMR (300 MHz, CDCl₃) δ 6.61 (s, 1H), 3.70-3.41 (m, 4H), 2.59 (s, 3H), 2.41 (s, 3H).
¹³C NMR (75 MHz, CDCl₃) δ 194.5, 158.3, 155.5, 109.4, 108,7, 76,9, 65.2, 61.4, 28,7, 14.3.



Yield: 97 %. White solid, recrystallized in hot ethyl acetate.

IR 3412, 1710 cm⁻¹

¹**H** NMR (300 MHz, CDCl₃) δ 6.60 (s, 1H), 4.68 (d, J = 7.0 Hz, 1H), 4.31-4.15 (m, 5H), 3.82 (dd, J = 2.4, 9.0 Hz, 1H), 2.60 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 163.8, 159.2, 149.6, 113.6, 109.1, 76.5, 74.3, 72.4, 70.7, 60.1, 29.1, 14.0.



Yield: 91 %. White solid, recrystallized in hot ethyl acetate.

IR 3411, 1670 cm⁻¹

¹**H NMR** (300 MHz, CDCl₃) δ 6.59 (s, 1H), 4.67 (d, J = 7.0 Hz, 1H), 4.31-4.15 (m, 3H), 3.82 (dd, J = 2.4, 9.0 Hz, 1H), 2.60 (s, 3H), 2.40 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 194.5, 156.9, 150.7, 122.4, 106.7, 79.3, 77.3, 76.8, 28.8, 14.2.



Yield: 38 %. White solid, recrystallized in hot ethyl acetate.

IR 3357, 1659 cm⁻¹

¹**H** NMR (300 MHz, MeOD) δ 6.63 (s, 1H), 4.68 (d, J = 7.0 Hz, 1H), 4.32-4.16 (m, 3H), 3.82 (dd, J = 9.8, 2.2 Hz, 1H), 2.92 (t, J = 6.3 Hz, 2H), 2.50 (t, J = 6.7 Hz, 2H), 2.19 (m, 2H).

¹³C NMR (75 MHz, MeOD) δ 193.9, 166.7, 155.7, 119.2, 102.3, 74.6, 72.9, 70.2, 69.6, 35.0, 20.8, 20.3.



Yield: 98 %. White solid, recrystallized in hot ethyl acetate.

IR 3410, 1668 cm⁻¹

¹**H NMR** (300 MHz, CDCl₃) δ 6.59 (s, 1H), 4.66 (d, J = 7.0 Hz, 1H), 4.31-4.15 (m, 3H), 3.82 (dd, J = 2.4, 9.0 Hz, 1H), 2.60 (s, 3H), 2.39 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 194.3, 156.9, 150.7, 122.2, 106.8, 79.3, 77.0, 76.8, 28.8, 14.5.

NMR spectra for new compound 4cc:



Figure S1. ¹H NMR spectrum of compound **4cc**



Figure S2. ¹³C NMR spectrum of compound **4cc**



Figure S3. COSY NMR spectrum of compound 4cc

VI. Spectroscopic characterization of the plant-based catalyst

Chemical analysis of the plant extract samples after calcinations(400°C for 3 h) was performed by X-ray fluorescence spectrometry (XRF) using a BRUKER AXS S4 Explorer wavelength dispersive spectrometer. The quantitative analysis of major and expected elements was performed on beaded samples for overcoming problems of particle size variation as well as mineralogy effects: the powdered sample is mixed with a $Li_2B_4O_7$ flux with a flux/sample ratio equal to 8, heated in a crucible between 400 and 600°C, then cast in a platinum dish to produce a homogeneous glass-like bead. Three analyzes were performed for each sample in order to determine the standard deviation of the measurement.

ICP-MS analyses were performed using the metal analysis of total dissolved solutes in water. The samples were acidified with nitric acid 2.5% and stirred for 30 min. The digestates were diluted to 0.005 g.L⁻¹. Three blanks were recorded for each step of the digestion and dilution procedure on a HR-ICP-MS Thermo Scientific Element XR. Three analyzes were performed for each sample in order to determine the standard deviation of the measurement.

X-ray diffraction (XRD) data measurements on the samples dried at 110°C for 2 h were performed by using a BRUKER diffractometer (D8 advance, with a Cu K α radiation $\lambda = 1.54086$ °A) equipped with a Lynxeyes detector.



Figure S4. Characterization of the plant-based catalyst by XRD

Electrospray ionization mass spectrometry (ESI-MS) was performed with a Waters Alliance e2695 Chain coupled to a Quattro Micro mass spectrometer. Electrospray ionization mass spectrometry was acquired in negative ion mode and recorded by direct infusion of the sample diluted in water, with a syringe pump at a flow rate of 1 mL.min⁻¹. Conditions: capillary voltage 3000 V; dry gas temperature, 120°C; dry gas flow, 400 L.h⁻¹ and nitrogen as nebulizer gas. 0.1% phosphoric acid was used as standard for internal calibration.



Figure S5. Direct infusion in ESI-MS (ES-) of the catalyst. (Mass range between 100 and 230 has been magnified x24 for readability)

Identification of the ions was performed with MassLynx software (Waters) by comparison between experimentally observed and predicted isotopic distribution.



Figure S6. Comparison between predicted and experimentally observed isotopic distribution for Fe^{II}Cl₃⁻



Figure S7. Comparison between predicted and experimentally observed isotopic distribution for Zn^{II}Cl₃⁻



Figure S8. Comparison between predicted and experimentally observed isotopic distribution for Fe^{III}Cl₄⁻



Figure S9. Comparison between predicted and experimentally observed isotopic distribution for Cd^{II}Cl₃⁻



Figure S10. Comparison between predicted and experimentally observed isotopic distribution for MgNa₃Cl₆⁻



Figure S11. Comparison between predicted and experimentally observed isotopic distribution for Pb^{II}Cl₃⁻