Supporting Information
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Supporting Information

Materials and methods

**General.** All solvents were dried over molecular sieves, for at least 24 h prior to use. When dry conditions were required, the reaction was performed under Ar atmosphere. Thin-layer chromatography (TLC) was performed on silica gel 60F_{254} coated glass plates (Merck) with UV detection when possible, charring with a conc. H_{2}SO_{4}/EtOH/H_{2}O solution (10:45:45 v/v/v), or with a solution of (NH_{4})_{6}Mo_{7}O_{24} (21 g), Ce(SO_{4})_{2} (1 g), conc. H_{2}SO_{4} (31 mL) in water (500 mL) and then heating to 110°C for 5 min. Flash column chromatography was performed on silica gel 230-400 mesh (Merck). All reported compounds have been previously synthesised and characterized; here we present only selected NMR data.

Glucose and galactose C-glycosides were obtained from the corresponding methyl-α-D-2,3,4,6-tetra-O-benzylglycopyranoside, in a three steps sequence, involving the acid-catalysed C-glycosylation reaction with allyltrimethylsilane and boron trifluoride etherate in dry acetonitrile to compound 4 (a,b), followed by regiospecific hydroxylation with 9-BBN to the primary alcohol 5 (a,b), and final oxidation with TEMPO to the corresponding carboxylic acid 1 and 2 (Scheme S1).

![Scheme S1. Synthesis of galactose and glucose C-glycosides.](image1)

On the other hand, fucose C-glycoside 6 was obtained from 2,3,4-tri-O-benzyl-L-fucopyranose as reported in the literature. Introduction of the required carboxylic function was performed with the same reaction sequence as described before affording acid 3 (Scheme S2).

![Scheme S2 Synthesis of fucose C-glycosides.](image2)

**General procedure for hydroboration reaction:** To a stirred solution of α-allyl-C-glycoside (1.090 mmol) in anhydrous THF (3 ml) at 0°C and under argon was added a 0.5 M solution of 9-BBN in THF (6.6 mL, 3.3 mmol) via a syringe. The solution was allowed to warm to room temperature. After 2h the reaction mixture had cooled to 0°C, 0.186 mL ethanol was added, dropwise, followed by 0.478 mL of NaOH 4M. The aqueous 9-BBN THF(0.5M) 4a: X= OBn, Y= H 4b: X= H, Y=OBn 5a: X= OBn, Y= H 5b: X= H, Y=OBn 1: X= OBn, Y=H 2: X= H, Y=OBn

![9-BBN THF(0.5M)](image3)

35% hydrogen peroxide (0.478 ml) was added, dropwise, then to the resulting suspension was added brine and diethyl ether. The organic layer was collected, and the brine layer was re-extracted, carefully, into further diethyl ether. All organic layers were combined, washed with brine, dried and concentrated under vacuum to afford the corresponding primary alcohol.

**General procedure for TEMPO oxidation:** To a stirred suspension of primary alcohol (1.131 mmol) in NaHCO_{3} saturated solution (2.268 mL), were added a 0.5 M solution of KBr in H_{2}O (0.454 mL, 0.227 mmol) and a 0.1 M solution of TEMPO in CH_{3}CN (2.27 mL, 0.227 mmol). NaOCl (5.83 mL, 0.35 M) was added dropwise. The aqueous
layer was acidified with 5 mL of HCl 5% and extracted five times with EtOAc. The organic layer was dried on sodium sulfate, filtered and concentrated under vacuum to afford the corresponding carboxylic acid.

**Selected NMR data for compound 5a:**

\[ ^1H \text{ NMR (400 MHz, CDCl}_3\text{): } \delta = 1.65 \text{ (app. sex, 2 H, } J = 6.8 \text{ Hz), 1.79 (m, 2 H), 2.27 (br s, 1 H), 3.55 (m, 2 H), 3.65 - 3.70 (m, 1 H), 3.74 (dd, 1 H, } J = 3.0, 7.5 \text{ Hz), 3.83 (m, 2 H), 3.98 (t, 1 H, } J = 3.0 \text{ Hz), 4.00 - 4.03 (m, 2 H), 4.68 (d, 1 H, } J = 12.0 \text{ Hz), 4.67 - 4.78 (m, 6 H), 7.26 - 7.37 (m, 15 H). \]

**Selected NMR data for compound 5b:**

\[ ^1H \text{ NMR (500 MHz, CDCl}_3\text{): } \delta = 1.61 - 1.64 \text{ (m, 3 H), 1.72 (m, 1 H), 2.27 (br s, 1 H), 3.57 - 3.64 (m, 2 H), 3.65 - 3.70 (m, 1 H), 3.74 (dd, 1 H, } J = 3.0, 7.5 \text{ Hz), 3.83 (m, 2 H), 3.98 (t, 1 H, } J = 3.0 \text{ Hz), 4.00 - 4.03 (m, 2 H), 4.68 (d, 1 H, } J = 12.0 \text{ Hz), 4.54 (app d, 2 H, } J = 12.0 \text{ Hz), 4.58 (d, 1 H, } J = 11.5 \text{ Hz), 4.65 (app d, 2 H, } J = 12.5 \text{ Hz), 4.74 - 4.77 (m, 2 H), 7.28 - 7.35 (m, 20 H). \]

**Selected NMR data for compound 7:**

\[ ^1H \text{ NMR (500 MHz, CDCl}_3\text{): } \delta = 1.29 (d, 3 \text{ H, } J = 6.6 \text{ Hz), 1.60 (m, 4 H), 2.05 (brt, 1 H, } J = 5.6 \text{ Hz), 3.61 (m, 2 H), 3.77 (m, 3 H), 3.97 (m, 2 H), 4.49 - 4.78 (m, 6 H), 7.26 - 7.37 (m, 15 H). \]

**Selected NMR data for compound 1:**

\[ ^1H \text{ NMR (300 MHz, CDCl}_3\text{): } \delta = 2.06 (m, 2 H), 2.52 (m, 2 H), 3.65 (m, 2 H), 3.75 (m, 2 H), 3.88 (m, 2 H), 4.05 (m, 1 H), 4.49 (d, 1 H, } J = 10.8 \text{ Hz), 4.52 (d, 1 H, } J = 12.3 \text{ Hz), 4.64 (d, 1 H, } J = 12.3 \text{ Hz), 4.66 (d, 1 H, } J = 11.4 \text{ Hz), 4.72 (d, 1 H, } J = 11.7 \text{ Hz), 4.83 (d, 1 H, } J = 10.8 \text{ Hz), 4.84 (d, 1 H, } J = 10.8 \text{ Hz), 4.96 (d, 1 H, } J = 10.8 \text{ Hz), 7.13 (m, 2 H), 7.20 - 7.55 (m, 18 H). \]

**Selected NMR data for compound 2:**

\[ ^1H \text{ NMR (400 MHz, CDCl}_3\text{): } \delta = 1.95 - 2.20 (m, 2 H), 2.37 - 2.44 (m, 1 H), 2.49 - 2.57 (m, 1 H), 3.65 - 3.69 (m, 1 H), 3.75 - 3.83 (m, 2 H), 3.91 (m, 1 H), 4.02 - 4.06 (m, 3 H), 4.48 - 4.63 (m, 4 H), 4.67 - 4.86 (m, 4 H), 7.32 - 7.36 (m, 20 H). \]

**Selected NMR data for compound 3:**

\[ ^1H \text{ NMR (400 MHz, CDCl}_3\text{): } \delta = 1.85 (d, 3 \text{ H, } J = 6.5 \text{ Hz), 2.42 - 2.69 (m, 2 H), 2.92 - 3.10 (m, 2 H), 4.33 - 4.39 (m, 2 H), 4.49 (brs, 2 H), 4.64 (dt, 1 H, } J = 3.7, 7.8 \text{ Hz), 5.15 - 5.43 (m, 6 H), 7.85 - 8.01 (m, 15 H). \]

**Hydroxyapatite functionalization (via APTES)**

General procedure for grafting hydroxyapatite : granules were heated at 160°C for 24 h and under vacuum at room temperature to remove any water attached to the surface. Silanisation of hydroxyapatite was carried out by immersing 0.400 mg of granules in a 1 M solution of APTES (0.900 mL, 3.846 mmol) in anhydrous hexane (4 ml; 1 ml of APTES solution per 0.1 g of hydroxyapatite) for 3 h while stirring. The resulting suspension was washed with EtOAc and hexane several times and granules were dried at mild heat under vacuum for 24 h. Carbohydrates were finally supported on hydroxyapatite samples (–NH\textsubscript{2} functionalised, CHA-APTES, see Scheme 1 in the main text) as follows: a 0.065 M solution of compounds 1-3 in dry THF was prepared (1 ml of solution per 0.1 g of hydroxyapatite), then NHS (5 equiv based on the carbohydrate) and DIC (5 equiv based on the carbohydrate) were sequentially added. The mixture was stirred for 1 hour, then added to CHA-APTES. The suspension was stirred overnight, then the functionalized CHA (CHA-1, CHA-2 and CHA-3 respectively) was washed thoroughly with EtOAc and hexane and finally essicated under vacuum.

**Material characterization**

Inductively coupled plasma - atomic emission spectrometry (ICP-AES) analysis (Liberty 200, Varian, Clayton South, Australia) and energy dispersion spectroscopy (EDS, Link, Oxford) with scanning electron microscopy (SEM; Stereoscopy 360, Leica Cambridge, UK), were used to assess the chemical composition of the materials. Fourier transformed infrared spectroscopy (Thermo Nicolet-Avatar 320 FTIR) was performed using the KBr method with sample dilution 1:100. X-ray diffraction analysis (XRD; Rigaku Miniflex, Cu K\textsubscript{α} radiation, Tokyo, Japan) permitted to check the crystallinity and the crystalline phase purity of the apatite. The specific surface area of the apatite was measured by Brunauer-Emmett-Teller (BET) method (Carlo Erba Sorpy 1750 Milan, Italy). Simultaneous thermal analysis (STA 409 Netzsch Geraetebau GmbH, Selb, Germany) was used to follow the thermal transformation of the granules and indirectly obtain informations concerning the starting composition of the apatite.

**FTIR spectroscopy**

FTIR spectra of solid Hap derivates were measured in Attenuated Total Reflection (ATR) using a single reflection diamond element (Golden Gate, Specac, USA). The FTIR spectrometer Varian 670-IR (Varian Australia Pty Ltd, Mulgrave VIC, Australia) - equipped with a nitrogen cooled mercury cadmium telluride detector and an air purging system - was employed under the following conditions: 25 kHz scan speed, 2 cm\textsuperscript{-1} spectral resolution, 512 scan co-addition, and triangular apodization. The second derivative of the absorption spectra was calculated following the
Savitsky–Golay procedure (5 points) after a binomial smoothing (11 points) of the spectra using the GRAMS/32 software (Galactic Industries Corporation, Salem, NH, USA).