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Supporting Information

A Saccharide-Based Crystalline Sponge for Hydrophilic Guests

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I. General Information

1. Reagents and equipment

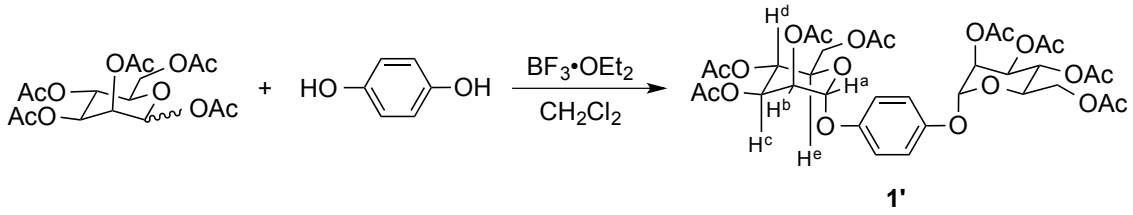
Solvents and reagents were purchased from TCI Co., Ltd., WAKO Pure Chemical Industries Ltd., and Sigma-Aldrich Co., and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on Bruker DRX-500 (500 MHz) NMR spectrometer or Bruker AVANCE 500 (500 MHz) NMR spectrometer with CP-TCI cryoprobe. All NMR spectral data were collected at 300 K and the chemical shifts are reported in parts per million (ppm) relative to an internal standard tetramethylsilane (δ = 0.00 ppm for ^{1}H and ^{13}C NMR) for $CDCl_3$. IR spectra for organic compounds were recorded with a JASCO FT/IR-6700 spectrometer. Elemental analysis was performed on a YANACO MT-6. Microscopic IR spectra were recorded on a Varian DIGILAB Scimitar instrument and are reported in frequency of absorption (cm^{-1}). For single crystal X-ray diffraction analysis and microscopic IR measurement, paratone®, fluorolube® and mineral oil were used as a protectant for the single crystals. Micro vials for this research were purchased from Waters (Deactivated Clear Glass 12 x 32 mm Screw Neck Max Recovery Vial, 1.5 mL Volume). An incubator Fine FF-12 was used to maintain the temperature during guest inclusion.

2. Single Crystal X-ray Analysis

Single crystal X-ray diffraction data were collected on a Rigaku VariMax RAPID/CS (CuK_α radiation λ= 1.5418 Å), BRUKER APEX-II CCD diffractometer equipped with a focusing mirror (MoK_α radiation λ= 0.71073 Å) and N_2 generator (Japan Thermal Eng. Co., Ltd.), BRUKER APEX-II CMOS diffractometer equipped with a focusing mirror (MoK_α radiation λ= 0.71073 Å) and N_2 generator (Japan Thermal Eng. Co., Ltd.). All structures were solved using a dual-space algorithm (SHELXT[1]) and refined using full-matrix least-squares method (SHELXL[2]). All the non-hydrogen atoms for host framework were refined anisotropically.

II. Synthesis

2-1. Synthesis of Ligand precursor 1'

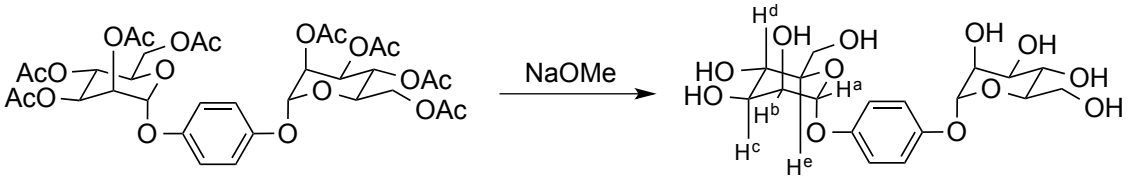


1'

1,2,3,4,6-Penta-*O*-acetyl-D-mannopyranose (2.00 g, 5.12 mmol) and hydroquinone (282 mg, 2.56 mmol) were dissolved in 20 mL of anhydrous dichloromethane. After addition of BF_3•Et_2O (1.47 g, 10.24 mmol), the resulting solution was stirred at room temperature for 1 d. The reaction was quenched by addition of sat. $NaHCO_3$ aq. (30 mL) and the organic layer was separated, washed with water (20 mL), and dried over anhydrous Na_2SO_4. After the evaporation of solvent, residual yellowish syrup was chromatographed on silica gel (eluent: *n*-hexane/AcOEt = 1/1, R_f = 0.21) to afford **1**' as a white solid (1.12 g, 57% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.03 (s, 4H, Ar-H), 5.54 (d, J = 10 Hz, 2H, H^c), 5.43 (br, 4H, H^a and H^b), 5.36 (t, J = 10 Hz, 2H, H^d), 4.28 (dd, J_{gem} = 5.5 Hz, J_{vic} = 12.5 Hz, 2H, methylene-H), 4.13-4.07 (m, 4H, H^e and methylene-H), 2.19-2.03 (m, 24H, acetyl); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.6, 170.1, 170.0, 169.8, 151.5, 117.9, 96.5, 69.5, 69.3, 68.9, 66.0 and 62.3. IR (cm^{-1}) 1741 (s), 1505 (s), 1436 (m), 1367 (s), 1203 (s), 1127 (m), 1032 (s), 978 (m), 821 (m), 755 (m) and 600 (m). HR-ESI-TOF MS: *m/z* = 793.2182 (calculated for $C_{34}H_{42}O_{20}Na$: 793.2162 $[M+Na]^+$). Elemental analysis (%): C 52.07, H 5.54, N 0.00 (calculated for $C_{34}H_{42}O_{20}$•H_2O: C 52.37, H 5.53, N 0.00).

2-2. Synthesis of Ligand 1



1' **1**

To a stirring solution of ligand precursor **1'** (200 mg, 0.26 mmol) in methanol (10 mL), was added sodium methoxide (1.5 mg, 0.028 mmol). After 1 d stirring at room temperature, the reaction was quenched by addition of ion exchanging resin Dowex 50w×2 100-200. After filtration of the resin, the solvent was removed by rotary evaporator to give ligand **1** as a white solid (110 mg, 97% yield).

^{1}H NMR (500 MHz, MeOD): δ (ppm) 7.05 (s, 4H, Ar-H), 5.37 (d, J = 1.5 Hz, 2H, H^a), 3.99 (dd, $J_{a\text{-}b}$ = 1.5 Hz, $J_{b\text{-}c}$ = 3.5 Hz, 2H, H^e), 3.88 (dd, $J_{b\text{-}c}$ = 3.5 Hz, $J_{c\text{-}d}$ = 9.5 Hz, 2H, H^c), 3.79-3.70 (m, 6H, H_c and methylene-H), 3.62 (ddd, J = 2.5 Hz, J = 4.5 Hz, J = 7 Hz, 2H, H^e); Note that OH protons were not observed because of H–D exchange with methanol-d_4. ^{13}C NMR (125 MHz, MeOD): δ 153.3, 119.0, 100.9, 75.3, 72.4, 72.1, 68.4 and 62.7. IR (cm^{-1}) 3327 (br), 1505 (s), 1434 (m), 1210 (s), 1117 (s), 1049 (m), 1005 (s), 975 (s), 883 (m), 824 (m), 776 (m), 721 (m) and 676 (m). HR-ESI-TOF MS: m/z = 457.1319 (calculated for $C_{18}H_{26}O_{12}Na$: 457.1316 $[M+Na]^+$). Elemental analysis (%):C 47.89, H 6.29, N 0.00 (calculated for $C_{18}H_{26}O_{12}\bullet H_2O$: C 47.79, H 6.24, N 0.00).

2-2. Synthesis of Sugar Sponge 2

A solution of disaccharide ligand **1** (8.7 mg, 0.02 mmol) in a mixture of water and ethanol (1 and 4 mL, respectively) was poured into a test tube (inner diameter 1 cm, height 10 cm). Diethyl ether (1 mL) was layered on the top of the solution as a buffer. A solution of NaOH (4.8 mg, 0.12 mmol) in water/ethanol (v/v= 1/40) (1 mL) was carefully layered on the top of the resultant solution, and the test tube was allowed to stand at room temperature for 1 week. Crystals of compound **2** grew on the glass surface around as colourless needles (~7 mg, 65% based on the elemental analysis result). The crystals were lightly scratched by a crystal remover so that they sink to the bottom. The mother liquid was removed by a pipet, and the crystals were washed with Et_2O shortly thereafter (5 mL × 5 times). After soaking in Et_2O (5 mL) at room temperature for 1 week, crystals were analyzed by IR, elemental, and X-ray analyses.

IR (cm^{-1}): 3312 (br), 1507 (s), 1365 (m), 1225 (s), 1116 (m), 1130 (m), 1057 (m), 976 (s), 822 (s), 669 (m) and 625 (m). Elemental analysis (%):C 46.12, H 6.48, N 0.00 (calculated for $[(C_{18}H_{26}O_{12})_2(NaOH)_2\bullet(Et_2O)(H_2O)]_n$: C 46.16, H 6.39, N 0.00).

Crystal Structure for as-synthesized 2

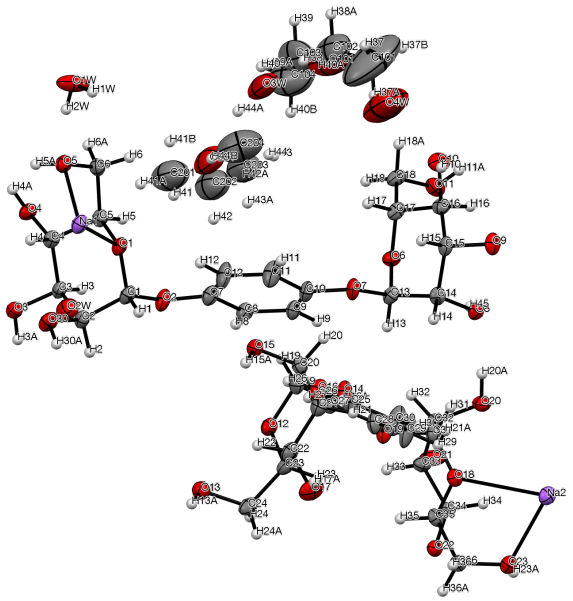


Fig. S1. ORTEP drawing (50% probability) of the asymmetric unit for as-synthesized **2**.

***Crystallographic Data for* as-synthesized 2:**

$2(C_{18}H_{25}NaO_{12})\bullet 1.042(C_4H_{10}O)\bullet(H_2O)\bullet 1.958(O)$, M_r = 1039.34, Monoclinic $P2_1$, a = 6.60580(10), b = 24.8860(4), c = 14.6272(3) Å, β = 102.224(7)°, V = 2350.08(9) Å^3, T = 90(2) K, Z = 2, ρ_{calcd} = 1.469, 6889 unique reflections out of 14173 with $I > 2\sigma(I)$, GoF = 1.063, final R factors R_1 = 0.0506, and wR_2= 0.1456 for all data, Flack parameter (Parsons) = 0.07(6). CCDC deposit number 1470809.

Hydrogen atoms for the hydroxyl groups of mannose ligand **1** were generated using HFIX command. From the elemental analysis result, it is suggested that mannose ligand **1** is partially deprotonated to preserve electroneutrality. Judging from the electron density map F_o–F_c and inter-hydrogen distances, O9 and O22 were refined as their deprotonated form. Hydrogen atoms for water oxygen atom (O1W) were modeled using DFIX and DANG commands with a normal standard deviation. Assignment of hydrogen atoms for other solvent water oxygen atoms was not successful. Disordered solvent Et_2O molecules were refined applying several restraints (RIGU, DANG, SAME) with a normal standard deviation.

III. Crystalline Sponge Analysis

3-1 Solvent soaking test

As-synthesized crystals **2** (*ca*. 10 mg) were soaked in a solvent (10 mL) at room temperature for 5 d. The resulting crystals were suction-filtrated and dried on a funnel for 10 min. Then the crystals were dissolved in MeOD/D_2O and analyzed by NMR spectroscopy.

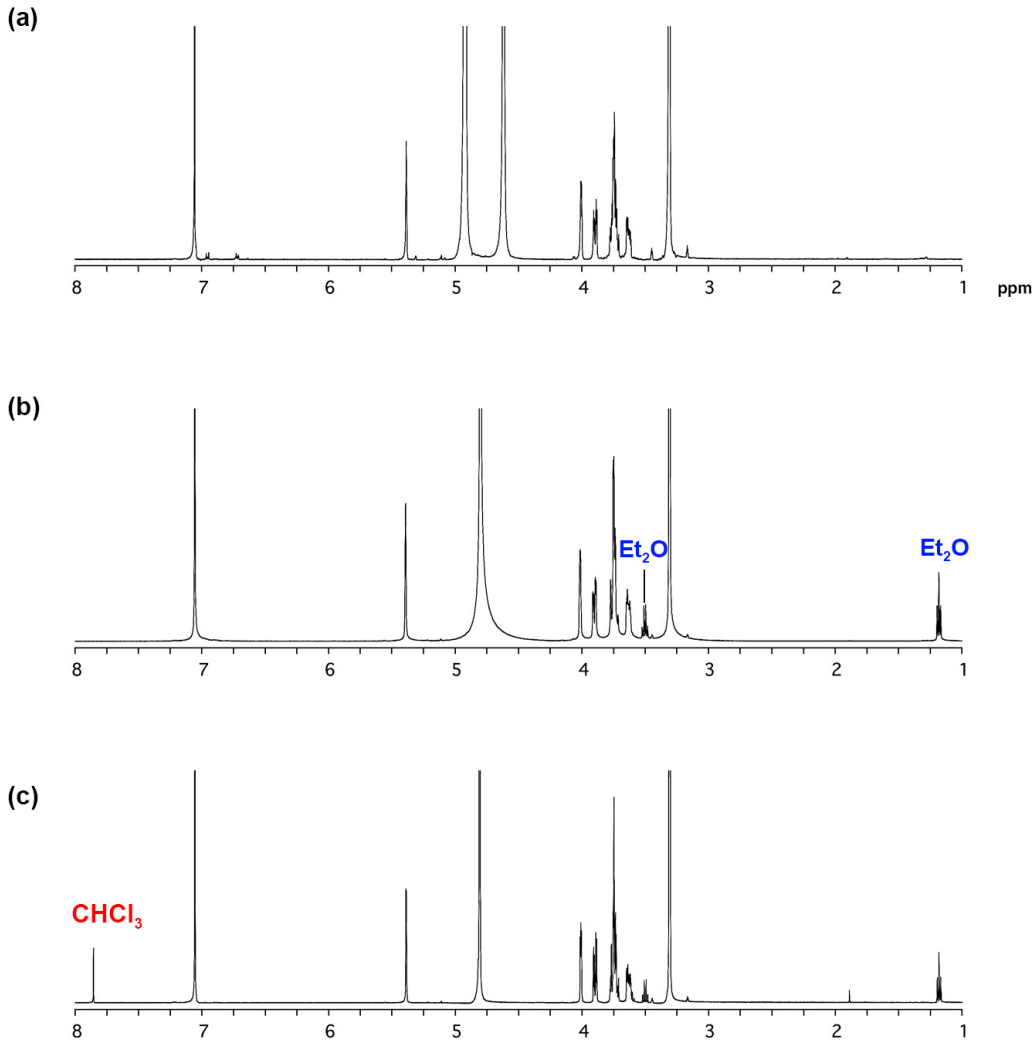


Fig. S2. ^{1}H NMR spectra (500 MHz, MeOD/D_2O) of (a) ligand **1**, (b) diisopropyl ether-soaked, and (c) $CHCl_3$-soaked crystals **2**.

3-2 Guest inclusion and structural analysis of *n*-propyl alcohol (3)

Guest soaking

To a test tube containing diisopropyl ether (100 μL) and 1-propanol (100 μL), as-synthesized crystals **2** (*ca*. 15 mg) were added. Then the test tube was sealed with a screw cap and allowed to stand at 50 °C for 2 d.

NMR analysis for determination of ligand/guest ratio

After filtration of guest-soaked crystals, the crystals were quickly washed with MeOH (1 mL × 3 times) on a funnel. Then the crystals were completely dissolved in MeOD/D_2O (v/v = 9/1) and analyzed by ^{1}H NMR spectroscopy.

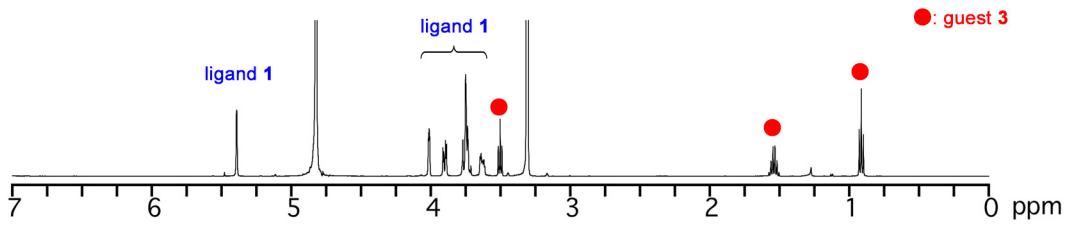


Fig. S3. ^{1}H NMR spectrum (500 MHz, MeOD/D_2O) of inclusion crystals **2•3** prepared as described above.

X-ray analysis

A crystal of host **2** (170 × 40 × 30 μm^3) was soaked in a mixture of diisopropyl ether and 1-propanol (1:1) as described above. After 6 d soaking at 50 ºC, the crystal was subjected to X-ray diffraction analysis.

Crystal Structure for inclusion crystal 2•3

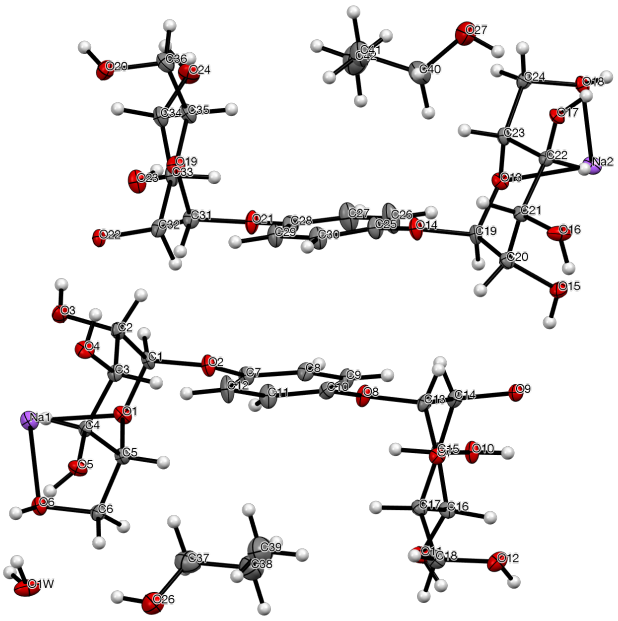


Fig. S4. ORTEP drawing (50% probability) of the asymmetric unit for inclusion crystal **2•3**.

***Crystallographic Data for* inclusion crystal 2•3:**

$2(C_{18}H_{25}O_{12}Na)•2(C_3H_7OH)•(H_2O)$, M = 1050.94, Monoclinic $P2_1$, a = 6.6503(15), b = 24.440(6), c = 14.717(3) Å, β = 101.390(2)°, V = 2344.9(9) Å^3, T = 93(2) K, Z = 2, ρ_{calcd} = 1.488, 9458 unique reflections out of 19037 with $I > 2\sigma(I)$, GoF = 1.022, final R factors R_1 = 0.0387, and wR_2= 0.0912 for all data, Flack parameter (Parsons) = –0.03(16). CCDC deposit number 1470810.

3-3 Guest inclusion and structural analysis of *S*-propylene oxide (4)

Guest soaking

A crystal of **2** (200 × 90 × 60 μm^3) was soaked in *S*-propylene oxide (10 μL) under the neat conditions. After incubation at 50 °C for 1 d in a sealed micro vial, the crystal was subjected to single crystal X-ray analysis.

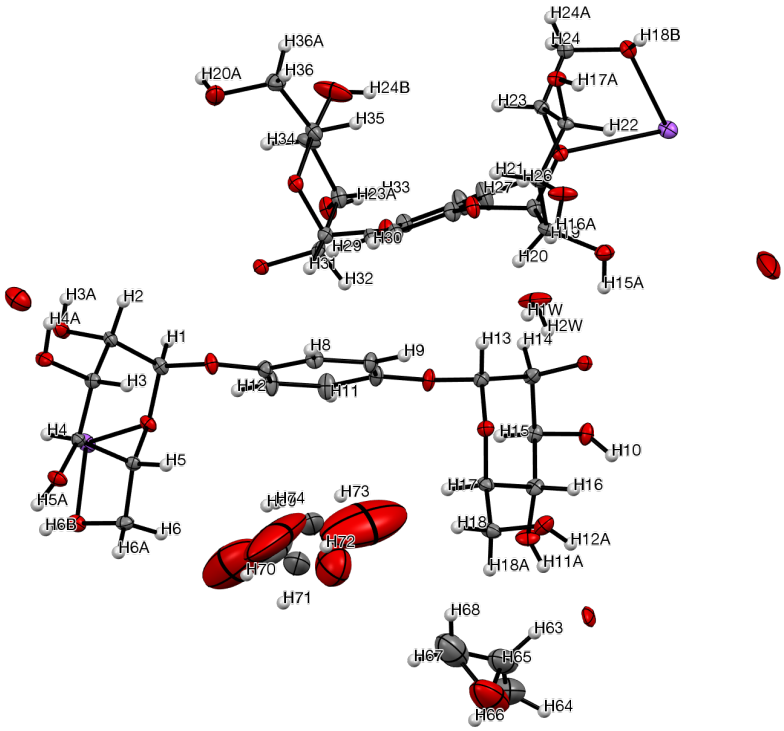


Fig. S5. ORTEP drawing (50% probability) of the asymmetric unit for inclusion crystal **2**•(*S*)-**4**.

Crystallographic Data for **inclusion crystal 2•(*S*)-4:**

$2(C_{18}H_{25}NaO_{12})$•$1.636(C_3H_6O)$•(H_2O)•2.286(O), M = 1062.33, Monoclinic $P2_1$, a = 6.6481(5), b = 24.625(2), c = 14.7560(12) Å, β = 102.7980(9)°, V = 2355.7(3) Å^3, T = 93(2) K, Z = 2, ρ_{calcd} = 1.498, 11057 unique reflections out of 27369 with $I > 2\sigma(I)$, GoF = 1.096, final R factors R_1 = 0.0436, and wR_2= 0.1160 for all data, Flack parameter (Parsons) = 0.01(7). CCDC deposit number 1470811.

Structure determination of *R*-propylene oxide

A single crystal of **2**·(Et_2O) (230 × 130 × 80 μm^3) was putted into a microvial and soaked in *R*-propylene oxide (10 μL). The microvial was sealed with a screw cap and stand at 50 °C for 7 d. The resulting crystal was subjected to single crystal X-ray analysis.

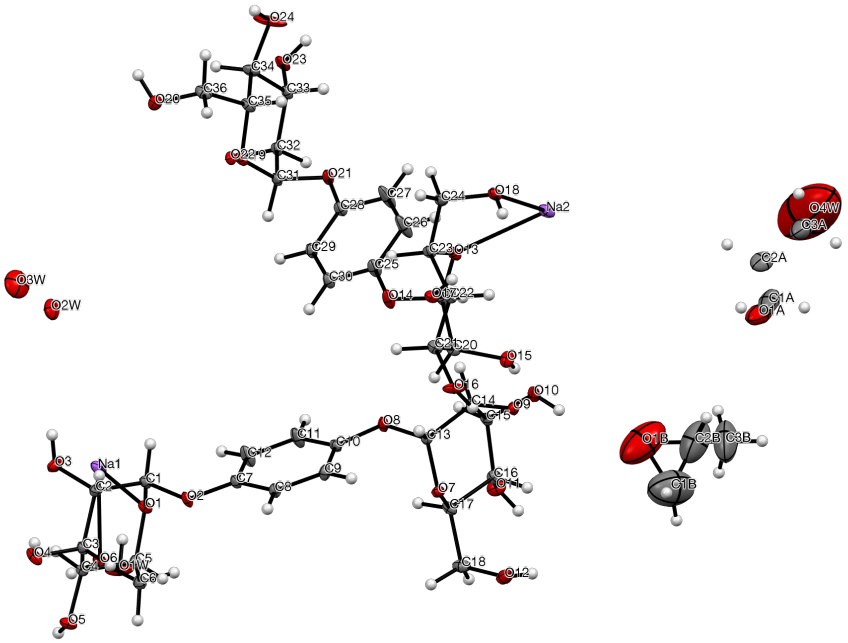


Fig. S6. ORTEP drawing (50% probability) of the asymmetric unit for inclusion crystal **2**•(*R*)-**4**.

Crystallographic Data for **inclusion crystal 2•(*R*)-4:**

2($C_{18}H_{25}NaO_{12}$) •1.531(C_3H_6O)•(H_2O)•1.469(O), M = 1062.33, Monoclinic $P2_1$, a = 6.6239(5), b = 24.7720(17), c = 14.6783(10) Å, β = 102.4297(15)^o, V = 2352.1(3) Å^3, T = 93(2) K, Z = 2, ρ_{calcd} = 1.498, 18582 unique reflections out of 48209 with $I > 2\sigma(I)$, GoF = 1.170, final R factors R_1 = 0.0645, and wR_2= 0.1648 for all data, Flack parameter (Parsons) = 0.00(5). CCDC deposit number 1470812.

IV. References

1. G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2015**, 71, 3-8.
2. G. M. Sheldrick, *Acta Crystallogr. Sect. C* **2015**, 71, 3-8.