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Supporting Information

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Supporting Information

for

Design of Triazole-Tethered Glycoclusters Exhibiting Three Different Spatial Arrangements and Comparative Study of their Affinity for PA-IL and RCA 120 by Using a DNA-Based Glycoarray

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General Experimental Section. All moisture-sensitive reactions were performed under a nitrogen atmosphere using oven-dried glassware. Anhydrous solvents were dried over standard drying agents[45] and freshly distilled prior to use. Reactions were monitored by TLC on silica gel 60 F_{254} with detection by charring with sulfuric acid. Flash column chromatography[46] was performed on silica gel 60 (40-63 μm). Melting points were determined with a capillary apparatus. Optical rotations were measured at 20 ± 2 ℃ in the stated solvent; $[\alpha]_D$ values are given in $deg \cdot mL \cdot g^{-1} \cdot dm^{-1}$. ^1H NMR (300 and 400 MHz) and ^{13}C NMR spectra (75 and 100 MHz) were recorded from $CDCl_3$ solutions at room temperature unless otherwise specified. Peak assignments were aided by ^1H-^1H COSY and gradient-HMQC experiments. In the ^1H NMR spectra reported below, the *n* and *m* values quoted in geminal or vicinal proton-proton coupling constants $J_{n,m}$ refer to the number of the corresponding sugar protons.

High performance liquid chromatography (HPLC) analyses and purifications were performed on a Waters-Millipore instrument equipped with a Rheodyne injector, a 600S controller and a model 996 photodiode array detector. For analyses, a reversed-phase C18 Nucleosil (5 μm) column (150 x 4.6 mm; Macherey-Nagel, Germany) was used at a flow rate of 1 $mL \cdot min^{-1}$ using a linear gradient of acetonitrile 5% to 60% in 0.05 M aqueous triethylammonium acetate (pH 7) for 25 min. For purifications, a reverse phase C18 Delta-Pak (15 μm) column (7.8 x 300 mm; Waters, Japan) was used at a flow rate of 2 $mL \cdot min^{-1}$ using a linear gradient of acetonitrile (24 to 48%) in 0.05 M aqueous triethylammonium acetate (pH 7) for 25 min.

ESI mass spectra were recorded in positive ion mode on a Waters-Micromass ZMD 2000 LC/MS spectrometer from CH_3CN-H_2O solutions containing ammonium formate (10 mM). For accurate mass measurements the compounds were analyzed in positive ion mode by electrospray hybrid quadrupole orthogonal acceleration time-of-flight mass spectrometer (Q-TOF) fitted with a Z-spray electrospray ion source (Waters, Manchester, UK). The capillary source voltage and the cone voltage were set at 3500 V and 35 V, respectively; the source temperature was kept at 80 ℃; nitrogen was used as a drying gas at a flow rate of ca. 50 L/h. The time-of-flight analyzer was externally calibrated with NaI from *m/z* 300 to 2000 to yield an accuracy near to 5 ppm. Accurate mass data were collected by directly infusing samples (10 pmol/μL in 1:1 CH_3CN-H_2O containing 10 mM ammonium formate) into the system at a flow rate of 5 μL/min. The acquisition and deconvolution of data were performed with

the MassLynx 4.1 software (Waters, Manchester, UK). MALDI-TOF mass spectra were recorded on a Voyager mass spectrometer (Perspective Biosystems, Framingham, MA) equipped with a nitrogen laser. MALDI conditions: accelerating voltage 24 kV; guide wire 0.05% of the accelerating voltage; grid voltage 94% of the accelerating voltage; delay extraction time 500 ns. The sample (1 μL) was mixed with a saturated solution (5 μL) of hydroxypicolinic acid (HPA) in 1:1 CH_3CN-H_2O containing 10% of ammonium citrate, then a few beads of DOWEX 50W-X8 ammonium sulfonic acid resin were added. The above mixture (1 μL) was placed on a plate and dried at room temperature and pressure.

5,11,17,23-Tetraallyl-25-(2,3:5,6-di-*O*-isopropylidene-β-D-mannofuranosyl)-26,27,28-tripropoxy-calix[4]arene (5). To a stirred solution of tetrol **3** (500 mg, 0.86 mmol) and triphenylphosphine (335 mg, 1.28 mmol) in anhydrous toluene (10 mL) was added diisopropyl azodicarboxylate (250 μL, 1.28 mmol) and, after 15 min, hemiacetal **4** (243 mg, 0.94 mmol). Stirring was continued for an additional 1.5 h, then the mixture was concentrated. To a stirred solution of the residue in DMF (20 mL) was added NaH (0.30 g, 7.7 mmol, of a 60% dispersion in oil) and, after 10 min, 1-iodopropane (0.75 mL, 7.7 mmol). The mixture was stirred at room temperature for 1.5 h, then diluted with CH_3OH (0.5 mL) and, after 30 min, diluted with 1 M phosphate buffer at pH 7 (80 mL) and extracted with Et_2O (2 x 100 mL). The combined organic phases were dried (Na_2SO_4) and concentrated. The residue was eluted from a column of silica gel with CH_2Cl_2-cyclohexane (from 1:1 to 3:1) to give **5** (652 mg, 80%) as a syrup; $[\alpha]_D$ = -19.2 (*c* 0.6, $CHCl_3$). ^{1}H NMR (400 MHz): δ 6.98-6.92 (m, 4H, Ar), 6.08 (ddt, 2H, *J* = 6.0, 12.0, 16.5 Hz, 2 CH_2=C*H*CH_2), 6.05-5.96 (m, 4H, Ar), 5.59-5.48 (m, 2H, 2 CH_2=C*H*CH_2), 5.12-5.01 (m, 4H, 2 C*H*$_2$=CHCH_2), 4.87-4.75 (m, 4H, 2 C*H*$_2$=CHCH_2), 4.78 (dd, 1H, $J_{1,2}$ = 3.0, $J_{2,3}$ = 6.3 Hz, H-2), 4.71 (dd, 1H, $J_{3,4}$ = 4.0 Hz, H-3), 4.69 (d, 1H, H-1), 4.63 and 3.01 (2d, 2H, *J* = 13.8 Hz, ArC*H*$_2$Ar), 4.48-4.43 (m, 1H, H-5), 4.42 (d, 1H, *J* = 13.0 Hz, H_{ax} of ArC*H*$_2$Ar), 4.40 (d, 1H, *J* = 13.0 Hz, H_{ax} of ArC*H*$_2$Ar), 4.35 (d, 1H, *J* = 13.0 Hz, H_{ax} of ArC*H*$_2$Ar), 4.23 and 3.88 (2dt, 2H, *J* = 5.5, 11.3 Hz, CH_3-CH_2C*H*$_2$O), 4.14-3.97 (m, 4H, 2 H-6, CH_3CH_2C*H*$_2$O), 3.65-3.57 (m, 2H, CH_3CH_2-C*H*$_2$O), 3.42-3.36 (m, 5H, H-4, 2 CH_2=CHC*H*$_2$), 3.08 (d, 1H, *J* = 13.0 Hz, H_{eq} of ArC*H*$_2$Ar), 3.07 (d, 1H, *J* = 13.0 Hz, H_{eq} of ArC*H*$_2$Ar), 3.05 (d, 1H, *J* = 13.0 Hz, H_{eq} of ArC*H*$_2$Ar), 2.77-2.72 (m, 4H, 2 CH_2=CHC*H*$_2$), 2.12-1.98 (m, 4H, 2 CH_3C*H*$_2$$CH_2$O), 1.94-1.82 (m, 2H, CH_3C*H*$_2$$CH_2$O), 1.60, 1.44, 1.39 (3s, 12H, 4 Me), 1.10 (t, 3H, *J* = 7.0 Hz, C*H*$_3$$CH_2CH_2$O), 0.87 (t, 6H, *J* = 7.0 Hz, 2 C*H*$_3$$CH_2CH_2$O). ^{13}C NMR (75 MHz):

δ 156.2 (C), 156.1 (C), 153.6 (C), 152.4 (C), 138.75 (CH), 138.66 (CH), 138.0 (CH), 137.8 (CH), 137.1 (C), 136.9 (C), 136.8 (C), 136.3 (C), 134.0 (C), 133.8 (C), 132.9 (C), 132.7 (C), 131.8 (C), 129.4 (CH), 129.0 (CH), 127.3 (CH), 127.1 (CH), 115.0 (CH_2), 114.9 (CH_2), 114.8 (CH_2), 114.6 (CH_2), 112.9 (C), 109.0 (C), 106.6 (CH), 79.1 (CH), 78.9 (CH), 76.2 (CH), 73.3 (CH), 77.1 (CH_2), 76.5 (CH_2), 76.4 (CH_2), 66.6 (CH_2), 39.5 (CH_2), 39.35 (CH_2), 39.30 (CH_2), 31.7 (CH_2), 31.0 (CH_2), 30.9 (CH_2), 26.9 (CH_3), 26.1 (CH_3), 25.5 (CH_3), 24.7 (CH_3), 23.5 (CH_2), 22.7 (CH_2), 10.8 (CH_3), 10.1 (CH_3), 9.7 (CH_3). HRMS (ESI/Q-TOF): calcd *m/z* for $C_{61}H_{80}NO_9$ $[M+NH_4]^+$: 970.5833; found: 970.5907.

5,11,17,23-Tetrakis(3-hydroxypropyl)-25-(2,3:5,6-di-*O*-isopropylidene-β-D-mannofuranosyl)-26,27,28-tripropoxy-calix[4]arene (6). To a cooled (0 ℃), stirred solution of **5** (950 mg, 1.00 mmol) in anhydrous THF (10 mL) was added dropwise 9-boracyclo[3.3.1]nonane (32 mL, 16.0 mmol, of a 0.5 M solution in hexane). The solution was allowed to reach room temperature in 3 h, then cooled to 0 ℃ and slowly diluted with 10 M NaOH (1 mL) and 35% H_2O_2 (3 mL). The mixture was stirred at room temperature for 15 min and then warmed to 60 ℃. Stirring was continued for an additional 2 h, then the mixture was cooled to room temperature, diluted with 1 M phosphate buffer at pH 7 (80 mL), concentrated to remove the organic solvents, and extracted with AcOEt (2 x 100 mL). The combined organic phases were dried (Na_2SO_4) and concentrated. The residue was eluted from a column of Sephadex LH 20 with 1:1 CH_2Cl_2-MeOH to give **6** (840 mg, 82%) as a white solid. An analytical sample was obtained by preparative TLC (silica gel 60, 0.5 mm, 10:1 $CHCl_3$-CH_3OH); $[\alpha]_D$ = -15.6 (*c* 0.3, $CHCl_3$). ^{1}H NMR (300 MHz): δ 7.01-6.95 (m, 4H, Ar), 6.18-6.07 (m, 4H, Ar), 4.82 (dd, 1H, $J_{1,2}$ = 3.0, $J_{2,3}$ = 5.6 Hz, H-2), 4.73 (dd, 1H, $J_{3,4}$ = 3.9 Hz, H-3), 4.71 (d, 1H, H-1), 4.66 and 3.03 (2d, 2H, *J* = 13.5 Hz, ArCH_2Ar), 4.50-4.45 (m, 1H, H-5), 4.46 (d, 1H, *J* = 13.0 Hz, H_{ax} of ArCH_2Ar), 4.43 (d, 1H, *J* = 13.0 Hz, H_{ax} of ArCH_2Ar), 4.38 (d, 1H, *J* = 13.0 Hz, H_{ax} of ArCH_2Ar), 4.26 and 3.89 (2dt, 2H, *J* = 5.9, 11.0 Hz, $CH_3CH_2CH_2O$), 4.16-3.98 (m, 4H, 2 H-6, $CH_3CH_2CH_2O$), 3.64 (t, 6H, *J* = 7.0 Hz, CH_3-CH_2CH_2O, 2 $CH_2CH_2CH_2OH$), 3.49 (t, 4H, *J* = 7.0 Hz, 2 $CH_2CH_2CH_2OH$), 3.42 (dd, 1H, $J_{4,5}$ = 6.8 Hz, H-4), 3.10 (d, 1H, *J* = 13.0 Hz, H_{eq} of ArCH_2Ar), 3.09 (d, 1H, *J* = 13.0 Hz, H_{eq} of ArCH_2Ar), 3.07 (d, 1H, *J* = 13.0 Hz, H_{eq} of ArCH_2Ar), 2.72 (t, 4H, *J* = 6.5 Hz, 2 $CH_2CH_2CH_2OH$), 2.19-1.98 (m, 16H, 4 $CH_2CH_2CH_2OH$, 2 $CH_2CH_2CH_2OH$, 2 $CH_3CH_2CH_2O$), 1.90 (tq, 2H, *J* = 7.0, 7.0 Hz, $CH_3CH_2CH_2O$), 1.60, 1.42, 1.40 (3s, 12H, 4 Me), 1.09 (t, 3H, *J* = 7.0 Hz, $CH_3CH_2CH_2O$), 0.89 (t, 6H, *J* = 7.0 Hz, 2 CH_3-

CH_2CH_2O). ^{13}C NMR (75 MHz): δ 155.9 (C), 155.8 (C), 153.2 (C), 152.0 (C), 137.1 (C), 137.0 (C), 136.8 (CH), 136.3 (C), 135.8 (C), 134.8 (C), 134.6 (C), 133.8 (C), 132.7 (C), 132.5 (C), 131.6 (C), 129.0 (CH), 128.7 (CH), 127.0 (CH), 126.9 (CH), 126.8 (CH), 112.8 (C), 109.0 (C), 106.7 (CH), 79.1 (CH), 78.9 (CH), 77.4 (CH_2), 76.9 (CH_2), 76.5 (CH_2), 76.1 (CH), 73.3 (CH), 66.6 (CH_2), 62.45 (CH_2), 62.39 (CH_2), 62.2 (CH_2), 62.1 (CH_2), 34.2 (CH_2), 33.64 (CH_2), 33.57 (CH_2), 31.6 (CH_2), 31.1 (CH_2), 30.8 (CH_2), 26.9 (CH_3), 26.1 (CH_3), 25.5 (CH_3), 24.6 (CH_3), 23.5 (CH_2), 22.7 (CH_2), 10.8 (CH_3), 10.2 (CH_3), 9.8 (CH_3). HRMS (ESI/Q-TOF): calcd *m/z* for $C_{61}H_{85}O_{13}$ $[M+H]^+$: 1025.5990; found: 1025.6002.

5,11,17,23-Tetrakis(3-azidopropyl)-25-hydroxy-26,27,28-tripropoxy-calix[4]-arene (7). A mixture of calixarene tetrol **6** (774 mg, 0.76 mmol), sodium azide (390 mg, 6.00 mmol), diphenyl phosphoryl azide (980 μL, 4.53 mmol), 1,8-diazabicyclo-[5.4.0]undec-7-ene (450 μL, 3.02 mmol), and anhydrous DMF (4 mL) was stirred at 110 ℃ for 16 h then cooled to room temperature, di luted with Et_2O (100 mL), washed with H_2O (20 mL), dried (Na_2SO_4), and concentrated. A solution of the residue in 2:1 CH_2Cl_2-CF_3CO_2H (6 mL) was kept at room temperature for 3 h, then concentrated. The residue was eluted from a column of silica gel with 2:1 CH_2Cl_2-cyclohexane to give **7** (397 mg, 60%) as a syrup. ^1H NMR (300 MHz): δ 6.99 (s, 2H, Ar), 6.90 (s, 2H, Ar), 6.25-6.20 (m, 4H, Ar), 4.84 (s, 1H, OH), 4.38 and 3.36 (2d, 4H, *J* = 13.0 Hz, 2 ArC*H*$_2$Ar), 4.35 and 3.24 (2d, 4H, *J* = 13.6 Hz, 2 ArC*H*$_2$Ar), 3.86-3.80 (m, 2H, CH_3-CH_2C*H*$_2$O), 3.73 (t, 4H, *J* = 7.0 Hz, 2 CH_3CH_2C*H*$_2$O), 3.33 (t, 2H, *J* = 7.0 Hz, CH_2-CH_2C*H*$_2N_3$), 3.30 (t, 2H, *J* = 7.0 Hz, CH_2CH_2C*H*$_2N_3$), 2.96 (t, 4H, *J* = 6.8 Hz, 2 CH_2-CH_2C*H*$_2N_3$), 2.75 (t, 2H, *J* = 7.0 Hz, C*H*$_2CH_2CH_2N_3$), 2.68 (t, 2H, *J* = 7.0 Hz, C*H*$_2CH_2$-CH_2N_3), 2.37-2.24 (m, 2H, CH_3C*H*$_2CH_2O$), 2.14 (t, 4H, *J* = 7.5 Hz, 2 C*H*$_2CH_2CH_2N_3$), 2.04-1.82 (m, 12H, 2 CH_2C*H*$_2CH_2N_3$, 2 CH_3C*H*$_2CH_2O$), 1.45 (tt, 4H, *J* = 7.0, 7.0 Hz, 2 CH_2C*H*$_2CH_2N_3$), 1.13 (t, 6H, *J* = 7.5 Hz, 2 C*H*$_3CH_2CH_2O$), 0.94 (t, 3H, *J* = 7.5 Hz, C*H*$_3CH_2CH_2O$). ^{13}C NMR (75 MHz): δ 154.9 (C), 152.8 (C), 151.4 (C), 136.8 (C), 135.1 (C), 134.8 (C), 133.2 (C), 132.6 (C), 131.2 (C), 130.7 (C), 129.0 (CH), 128.3 (CH), 127.7 (CH), 127.6 (CH), 77.6 (CH_2), 76.6 (CH_2), 50.6 (CH_2), 50.3 (CH_2), 32.1 (CH_2), 31.9 (CH_2), 31.8 (CH_2), 30.8 (CH_2), 30.7 (CH_2), 30.5 (CH_2), 30.4 (CH_2), 23.4 (CH_2), 22.2 (CH_2), 10.8 (CH_3), 9.5 (CH_3). HRMS (ESI/Q-TOF): calcd *m/z* for $C_{49}H_{63}$-$N_{12}O_4$ $[M+H]^+$: 883.5095; found: 883.5152.

5,11,17,23-Tetrakis(3-azidopropyl)-25-(2-*t*-butoxycarbonyl-aminoethoxy)-26,27,28-tripropoxy-calix[4]arene (8). To a stirred solution of alcohol **7** (110 mg, 0.12 mmol) in anhydrous DMF (2 mL) was added NaH (15 mg, 0.37 mmol, of a 60% dispersion in oil) and, after 15 min, 1-bromo-2-*t*-butoxycarbonylaminoethane (84 mg, 0.38 mmol). The mixture was stirred at 50 °C for 18 h, then cooled to room temperature, diluted with 1 M phosphate buffer at pH 7 (15 mL) and extracted with Et_2O (2 x 50 mL). The combined organic phases were dried (Na_2SO_4) and concentrated. The residue was eluted from a column of silica gel with 1:1 CH_2Cl_2/cyclohexane (containing 0.3% of Et_3N) to give **8** (64 mg, 50%) as a syrup; ^{1}H NMR (400 MHz): δ 6.98 (bt, 1H, *J* = 6.0 Hz, NH), 6.85 (s, 4H, Ar), 6.08 (s, 2H, Ar), 6.05 (s, 2H, Ar), 4.40 and 3.06 (2d, 4H, *J* = 12.8 Hz, 2 ArC*H*$_2$Ar), 4.25 and 3.09 (2d, 4H, *J* = 13.2 Hz, 2 ArC*H*$_2$Ar), 3.99 (t, 2H, *J* = 4.5 Hz, OC*H*$_2$CH$_2$N), 3.98-3.92 (m, 2H, $CH_3CH_2CH_2O$), 3.86-3.79 (m, 2H, $CH_3CH_2CH_2O$), 3.77-3.71 (m, 2H, $CH_3CH_2CH_2O$), 3.64 (dt, 2H, *J* = 4.5, 6.0 Hz, OCH$_2$C*H*$_2$N), 3.28 (t, 4H, *J* = 6.8 Hz, 2 $CH_2CH_2CH_2N_3$), 3.04 (t, 4H, *J* = 7.2 Hz, 2 $CH_2CH_2CH_2N_3$), 2.67 (t, 4H, *J* = 6.8 Hz, 2 $CH_2CH_2CH_2N_3$), 2.07 (t, 4H, *J* = 7.2 Hz, 2 $CH_2CH_2CH_2N_3$), 1.93 (tt, 4H, *J* = 6.8, 6.8 Hz, 2 $CH_2CH_2CH_2N_3$), 1.87-1.76 (m, 6H, 3 $CH_3CH_2CH_2O$), 1.52 (s, 9H, *t*-Bu), 1.47 (tt, 4H, *J* = 7.2, 7.2 Hz, 2 $CH_2CH_2CH_2N_3$), 0.94 (t, 6H, *J* = 7.5 Hz, 2 $CH_3CH_2CH_2O$), 0.86 (t, 3H, *J* = 7.5 Hz, $CH_3CH_2CH_2O$). ^{13}C NMR (75 MHz): δ 156.5 (C), 155.3 (C), 154.9 (C), 153.1 (C), 136.3 (C), 136.2 (C), 134.8 (C), 134.1 (C), 133.9 (C), 133.2 (C), 133.0 (C), 129.0 (CH), 128.7 (CH), 127.6 (CH), 127.4 (CH), 78.9 (C), 77.2 (CH_2), 76.5 (CH_2), 75.2 (CH_2), 50.6 (CH_2), 50.5 (CH_2), 41.0 (CH_2), 32.0 (CH_2), 31.0 (CH_2), 30.9 (CH_2), 30.6 (CH_2), 30.4 (CH_2), 28.7 (CH_3), 22.7 (CH_2), 22.5 (CH_2), 10.2 (CH_3). HRMS (ESI/Q-TOF): calcd *m/z* for $C_{56}H_{76}N_{13}O_6$ [*M*+H]$^+$: 1026.6041; found: 1026.6030.

5,11,17,23-Tetrakis{3-[4-(2,3,4,6-tetra-*O*-acetyl-β-D-galacto-pyranosyl)-1*H*-1,2,3-triazol-1-yl]propyl}-25-(2-*t*-butoxycarbonyl-aminoethoxy)-26,27,28-tripropoxy-calix[4]arene (10). A mixture of calix[4]arene tetra-azide **8** (34 mg, 0.03 mmol), ethynyl *C*-galactoside **9** (47 mg, 0.12 mmol), freshly distilled *N,N*-diisopropylethylamine (105 μL, 0.60 mmol), CuI (6 mg, 0.03 mmol), and anhydrous toluene (1 mL) was stirred in the dark at room temperature for 18 h, then concentrated. The residue was eluted from a column of silica gel with AcOEt (containing 0.3% of Et_3N) to give **10** (55 mg, 75%), a white foam; $[\alpha]_D$ = -8.8 (*c* 0.7, $CHCl_3$). ^{1}H NMR (400 MHz): δ 7.72 (s, 1H, H-5 Tr.), 7.71 (s, 1H, H-5 Tr.), 7.58 (s, 2H, 2 H-5 Tr.), 6.90 (bt, 1H, *J* = 5.5 Hz, NH), 6.84 (s, 4H, Ar), 6.07 (s, 2H, Ar), 6.04 (s, 2H, Ar), 5.53-5.51 (4dd, 4H, 4 H-4),

5.47-5.38 (4dd, 4H, 4 H-2), 5.21-5.17 (4dd, 4H, 4 H-3), 4.76 (d, 2H, $J_{1,2}$ = 10.0 Hz, 2 H-1), 4.72 (d, 2H, $J_{1,2}$ = 10.0 Hz, 2 H-1), 4.40 and 3.07 (2d, 4H, J = 13.2 Hz, 2 ArCH_2-Ar), 4.36-4.30 (4ddd, 4H, 4 H-5), 4.27 and 3.09 (2d, 4H, J = 13.2 Hz, 2 ArCH_2Ar), 4.14-4.07 (m, 16H, 8 H-6, 4 $ArCH_2CH_2CH_2$), 4.01-4.00 (m, 2H, OCH_2CH_2N), 3.97-3.93 (m, 2H, $CH_3CH_2CH_2O$), 3.85-3.81 (m, 2H, $CH_3CH_2CH_2O$), 3.76-3.72 (m, 2H, $CH_3CH_2CH_2O$), 3.63-3.60 (m, 2H, OCH_2CH_2N), 2.63-2.58 (m, 4H, 2 $ArCH_2CH_2CH_2$), 2.24-2.19 (m, 4H, 2 $ArCH_2CH_2CH_2$), 2.17, 2.16, 2.03, 2.02, 1.99, 1.91, and 1.88 (7s, 48H, 16 Ac), 2.04-1.85 (m, 8H, 4 $ArCH_2CH_2CH_2$), 1.85-1.74 (m, 6H, 3 $CH_3CH_2CH_2O$), 1.52 (s, 9H, *t*-Bu), 0.95 (t, 6H, J = 7.5 Hz, 2 $CH_3CH_2CH_2O$), 0.86 (t, 3H, J = 7.5 Hz, $CH_3CH_2CH_2O$). ^{13}C NMR (75 MHz): δ 170.4 (C), 170.1 (C), 170.0 (C), 169.7 (C), 169.6 (C), 156.4 (C), 155.3 (C), 155.1 (C), 153.3 (C), 144.4 (C), 144.1 (C), 136.3 (C), 136.2 (C), 134.0 (C), 133.4 (C), 133.1 (C), 129.0 (CH), 128.9 (CH), 128.7 (CH), 128.6 (CH), 128.4 (CH), 128.3 (CH), 128.2 (CH), 127.7 (CH), 127.6 (CH), 127.3 (CH), 122.1 (CH), 78.9 (C), 77.5 (CH_2), 76.7 (CH_2), 75.2 (CH_2), 74.7 (CH), 73.7 (CH), 71.8 (CH), 68.7 (CH), 67.6 (CH), 61.5 (CH_2), 49.7 (CH_2), 49.5 (CH_2), 40.9 (CH_2), 31.8 (CH_2), 31.0 (CH_2), 28.6 (CH_3), 22.7 (CH_2), 20.65 (CH_3), 20.57 (CH_3), 10.2 (CH_3). HRMS (ESI/Q-TOF): calcd *m/z* for ($C_{120}H_{157}N_{13}O_{42}$)/2 [$M$+2H]$^{2+}$: 1226.0275; found: 1226.0211.

5,11,17,23-Tetrakis{3-[4-(2,3,4,6-tetra-*O*-acetyl-β-D-*galacto*-pyranosyl)-1*H*-1,2,3-triazol-1-yl]propyl}-25-(2-azidoethoxy)-26,27,28-tripropoxy-calix[4]arene (11). A solution of **10** (196 mg, 0.08 mmol) in CH_2Cl_2 (8 mL) and CF_3CO_2H (4 mL) was kept at room temperature for 1 h, then concentrated. To a mixture of the crude ammonium salt, K_2CO_3 (60 mg, 0.44 mmol), $CuSO_4{\cdot}5H_2O$ (2 mg, 8 μmol), CH_3OH (4 mL), and CH_3CN (1 mL), was added imidazole-1-sulfonyl azide hydrochloride[29] (40 mg, 0.20 mmol). The mixture was stirred at room temperature for 6 h, then concentrated, diluted with acetic anhydride (2 mL) and pyridine (2 mL), stirred for an additional 3 h, and concentrated. The residue was diluted with H_2O (10 mL) and extracted with AcOEt (2 x 50 mL). The combined organic phases were dried (Na_2SO_4) and concentrated. The residue was eluted from a column of silica gel with AcOEt to give **11** (132 mg, 69%) as a white foam; $[\alpha]_D$ = -10.2 (*c* 0.7, $CHCl_3$). ^{1}H NMR (400 MHz): δ 7.69 (s, 1H, H-5 Tr.), 7.67 (s, 1H, H-5 Tr.), 7.59 (s, 2H, 2 H-5 Tr.), 6.71 (s, 4H, Ar), 6.22 (s, 2H, Ar), 6.17 (s, 2H, Ar), 5.54-5.51 (4dd, 4H, 4 H-4), 5.44 (dd, 2H, $J_{1,2}$ = $J_{2,3}$ = 10.0 Hz, 2 H-2), 5.42 (dd, 2H, $J_{1,2}$ = $J_{2,3}$ = 10.0 Hz, 2 H-2), 5.22-5.16 (4dd, 4H, 4 H-3), 4.76 (d, 2H, 2 H-1), 4.73 (d, 2H, 2 H-1), 4.40 and 3.07 (2d, 4H, J = 13.1 Hz, 2 Ar-

C*H*$_2$Ar), 4.34 and 3.10 (2d, 4H, *J* = 13.1 Hz, 2 ArC*H*$_2$Ar), 4.32-4.25 (m, 4H, 2 ArCH$_2$-CH$_2$C*H*$_2$), 4.18-4.07 (m, 18H, 4 H-5, 8 H-6, 2 ArCH$_2$CH$_2$C*H*$_2$, OCH$_2$C*H*$_2$N$_3$), 3.92-3.86 (m, 4H, OC*H*$_2$CH$_2$N$_3$, CH$_3$CH$_2$C*H*$_2$O), 3.78-3.69 (m, 4H, 2 CH$_3$CH$_2$C*H*$_2$O), 2.53-2.47 (m, 4H, 2 ArC*H*$_2$CH$_2$CH$_2$), 2.17, 2.16, 2.03, 2.02, 1.99, 1.90, and 1.88 (7s, 48H, 16 Ac), 2.18-2.08 (m, 8H, 2 ArC*H*$_2$CH$_2$CH$_2$, 2 ArCH$_2$C*H*$_2$CH$_2$), 1.94-1.84 (m, 10H, 2 Ar-CH$_2$C*H*$_2$CH$_2$, 3 CH$_3$C*H*$_2$CH$_2$O), 1.04 (t, 6H, *J* = 7.4 Hz, 2 C*H*$_3$CH$_2$CH$_2$O), 0.94 (t, 3H, *J* = 7.4 Hz, C*H*$_3$CH$_2$CH$_2$O). ^{13}C NMR (75 MHz): δ 170.4 (C), 170.1 (C), 170.0 (C), 169.7 (C), 155.6 (C), 155.0 (C), 154.1 (C), 144.4 (C), 144.2 (C), 135.8 (C), 135.6 (C), 134.0 (C), 133.8 (C), 133.6 (C), 133.4 (C), 128.5 (CH), 127.8 (CH), 127.5 (CH), 122.1 (CH), 77.2 (CH$_2$), 76.5 (CH$_2$), 74.7 (CH), 73.8 (CH), 71.9 (CH), 71.3 (CH$_2$), 68.6 (CH), 67.6 (CH), 61.5 (CH$_2$), 50.7 (CH$_2$), 49.7 (CH$_2$), 49.6 (CH$_2$), 31.9 (CH$_2$), 30.9 (CH$_2$), 30.8 (CH$_2$), 29.6 (CH$_2$), 23.3 (CH$_2$), 23.0 (CH$_2$), 20.7 (CH$_3$), 20.6 (CH$_3$), 10.5 (CH$_3$), 10.0 (CH$_3$). HRMS (ESI/Q-TOF): calcd *m/z* for (C$_{115}$H$_{145}$N$_{15}$O$_{40}$)/2 [*M*+2H]$^{2+}$: 1188.9965; found: 1188.9915.

5,11,17,23-Tetrakis{3-[4-(β-D-galactopyranosyl)-1*H*-1,2,3-triazol-1-yl]propyl}-25-(2-azidoethoxy)-26,27,28-tripropoxy-calix[4]arene (1). A solution of **11** (15 mg, 0.006 mmol) in a 2 M solution of NH$_3$ in CH$_3$OH (1 mL) was kept at room temperature for 16 h, then concentrated. The residue was eluted from a C18 silica gel cartridge with H$_2$O-CH$_3$OH (from 1:1 to 1:5), then CH$_3$OH, to give **1** (9.7 mg, 90%) as an amorphous solid; [α]$_D$ = +14.2 (*c* 0.4, CH$_3$OH). ^{1}H NMR (400 MHz, CD$_3$OD): δ 8.06, 8.03, 7.92, and 7.91 (4s, 4H, 4 H-5 Tr.), 6.79 (s, 4H, Ar), 6.47-6.45 (m, 2H, Ar), 6.40 (bs, 2H, Ar), 4.44 and 3.12 (2d, 4H, *J* = 12.7 Hz, 2 ArC*H*$_2$Ar), 4.39-4.34 (3d, 4H, 4 H-1), 4.37 and 3.14 (2d, 4H, *J* = 12.8 Hz, 2 ArC*H*$_2$Ar), 4.19 (t, 4H, *J* = 7.3 Hz, 2 ArCH$_2$-CH$_2$C*H*$_2$), 4.10-4.05 (m, 6H, 2 ArCH$_2$CH$_2$C*H*$_2$, OC*H*$_2$CH$_2$N$_3$), 3.99-3.87 (m, 12H, 4 H-4, 4 H-2, CH$_3$CH$_2$C*H*$_2$O, OCH$_2$C*H*$_2$N$_3$), 3.79-3.64 (m, 16H, 4 H-5, 8 H-6, 2 CH$_3$CH$_2$-C*H*$_2$O), 3.64-3.59 (3d, 4H, $J_{2,3}$ = 9.5, $J_{3,4}$ = 3.2 Hz, 4 H-3), 2.42-2.36 (m, 4H, 2 ArC*H*$_2$-CH$_2$CH$_2$), 2.11-2.04 (m, 8H, 2 ArC*H*$_2$CH$_2$CH$_2$, 2 ArCH$_2$C*H*$_2$CH$_2$), 2.02-1.90 (m, 6H, 3 CH$_3$C*H*$_2$CH$_2$O), 1.84-1.76 (m, 4H, 2 ArCH$_2$C*H*$_2$CH$_2$), 1.08 (t, 6H, *J* = 7.5 Hz, 2 C*H*$_3$-CH$_2$CH$_2$O), 1.00 (t, 3H, *J* = 7.5 Hz, C*H*$_3$CH$_2$CH$_2$O). ^{13}C NMR (75 MHz, CD$_3$OD): δ 155.3 (C), 147.5 (C), 136.7 (C), 135.3 (C), 130.0 (CH), 129.3 (CH), 124.9 (CH), 80.9 (CH), 78.3 (CH$_2$), 76.3 (CH), 72.1 (CH), 71.0 (CH), 62.9 (CH$_2$), 52.2 (CH$_2$), 50.3 (CH$_2$), 33.0 (CH$_2$), 31.7 (CH$_2$), 24.6 (CH$_2$), 11.1 (CH$_3$), 10.6 (CH$_3$). HRMS (ESI/Q-TOF): calcd *m/z* for (C$_{83}$H$_{115}$N$_{15}$O$_{24}$)/2 [*M*+2H]$^{2+}$: 852.9120; found: 852.9095.

5,11,17,23-Tetrakis(3-azidopropyl)-25-(ethoxycarbonylmethoxy)-26,27,28-tripropoxy-calix[4]arene (12). To a stirred solution of alcohol **7** (159 mg, 0.18 mmol) in anhydrous DMF (3 mL) was added NaH (15 mg, 0.37 mmol, of a 60% dispersion in oil) and, after 15 min, ethyl bromoacetate (60 μL, 0.54 mmol). The mixture was stirred at 55 ℃ for 18 h, then cooled to room temp erature, diluted with 1 M phosphate buffer at pH 7 (15 mL) and extracted with Et_2O (2 x 50 mL). The combined organic phases were dried (Na_2SO_4) and concentrated. The residue was eluted from a column of silica gel with 8:1 cyclohexane-AcOEt to give **12** (144 mg, 82%) as a syrup; ^{1}H NMR (400 MHz): δ 6.67 (s, 2H, Ar), 6.65 (s, 2H, Ar), 6.23 (s, 4H, Ar), 4.77 (s, 2H, OCH_2CO_2), 4.60 and 3.12 (2d, 4H, *J* = 13.5 Hz, 2 ArC*H*$_2$Ar), 4.39 and 3.07 (2d, 4H, *J* = 13.0 Hz, 2 ArC*H*$_2$Ar), 4.19 (q, 2H, *J* = 7.2 Hz, $CO_2CH_2CH_3$), 3.88-3.83 (m, 2H, CH_3-CH_2CH_2O), 3.80-3.70 (m, 4H, 2 $CH_3CH_2CH_2O$), 3.23 (t, 2H, *J* = 6.8 Hz, $ArCH_2CH_2$-CH_2), 3.22 (t, 2H, *J* = 6.8 Hz, $ArCH_2CH_2CH_2$), 3.10 (t, 4H, *J* = 6.8 Hz, 2 $ArCH_2CH_2$-CH_2), 2.55-2.50 (m, 4H, 2 $ArCH_2CH_2CH_2$), 2.22 (t, 4H, *J* = 7.5 Hz, 2 $ArCH_2CH_2CH_2$), 2.01-1.78 (m, 10H, 3 $CH_3CH_2CH_2O$, 2 $ArCH_2CH_2CH_2$), 1.66-1.56 (m, 4H, 2 $ArCH_2$-CH_2CH_2), 1.30 (t, 3H, *J* = 7.2 Hz, $CO_2CH_2CH_3$), 1.04 (t, 6H, *J* = 7.5 Hz, 2 CH_3CH_2-CH_2O), 0.98 (t, 3H, *J* = 7.5 Hz, $CH_3CH_2CH_2O$). ^{13}C NMR (75 MHz): δ 170.4 (C), 155.3 (C), 154.3 (C), 135.5 (C), 135.2 (C), 134.4 (C), 134.0 (C), 133.8 (C), 128.6 (CH), 128.3 (CH), 127.7 (CH), 127.6 (CH), 77.0 (CH_2), 70.3 (CH_2), 60.2 (CH_2), 50.6 (CH_2), 32.0 (CH_2), 31.3 (CH_2), 30.8 (CH_2), 30.5 (CH_2), 23.2 (CH_2), 14.2 (CH_3), 10.5 (CH_3), 10.1 (CH_3). ESI MS (969.18): 987.4 $[M + NH_4]^+$.

5,11,17,23-Tetrakis{3-[4-(2,3,4,6-tetra-*O*-acetyl-β-D-*galacto*-pyranosyl)-1*H*-1,2,3-triazol-1-yl]propyl}-25-(ethoxycarbonyl-methoxy)-26,27,28-tripropoxy-calix[4]arene (13). The cycloaddition between the tetra-azide **12** (140 mg, 0.14 mmol) and the ethynyl *C*-galactoside **9** (226 mg, 0.63 mmol) was carried out as described for the preparation of **10** to give, after column chromatography of silica gel (AcOEt), **13** (277 mg, 80%) as a white foam; $[\alpha]_D$ = -8.6 (*c* 0.9, $CHCl_3$). ^{1}H NMR (400 MHz): δ 7.68 (s, 1H, H-5 Tr.), 7.66 (s, 1H, H-5 Tr.), 7.59 (s, 2H, 2 H-5 Tr.), 6.66 (s, 2H, Ar), 6.65 (s, 2H, Ar), 6.23 (s, 2H, Ar), 6.22 (s, 2H, Ar), 5.53-5.51 (4dd, 4H, 4 H-4), 5.44 (dd, 2H, $J_{1,2}$ = $J_{2,3}$ = 10.0 Hz, 2 H-2), 5.42 (dd, 2H, $J_{1,2}$ = $J_{2,3}$ = 10.0 Hz, 2 H-2), 5.19 (dd, 2H, $J_{3,4}$ = 3.2 Hz, 2 H-3), 5.18 (dd, 2H, $J_{3,4}$ = 3.2 Hz, 2 H-3), 4.76 (s, 2H, OCH_2CO_2), 4.75 (d, 2H, 2 H-1), 4.73 (d, 2H, 2 H-1), 4.61 and 3.11 (2d, 4H, *J* = 13.5 Hz, 2 ArC*H*$_2$Ar), 4.39 and 3.06 (2d, 4H, *J* = 13.0 Hz, 2 ArC*H*$_2$Ar), 4.30-4.25 (m, 4H, 2 $ArCH_2CH_2CH_2$), 4.18 (q, 2H, *J* = 7.0 Hz, $CO_2CH_2CH_3$), 4.16-4.08 (m, 16H, 4 H-5, 8

H-6, 2 $ArCH_2CH_2CH_2$), 3.87-3.86 (m, 2H, $CH_3CH_2CH_2O$), 3.79-3.69 (m, 4H, 2 CH_3-CH_2CH_2O), 2.50-2.43 (m, 4H, 2 $ArCH_2CH_2CH_2$), 2.17-2.09 (m, 8H, 2 $ArCH_2CH_2CH_2$, 2 $ArCH_2CH_2CH_2$), 2.16, 2.02, 2.01, 1.99, 1.90, and 1.87 (6s, 48H, 16 Ac), 1.96-1.84 (m, 10H, 2 $ArCH_2CH_2CH_2$, 3 $CH_3CH_2CH_2O$), 1.27 (t, 3H, *J* = 7.0 Hz, $CO_2CH_2CH_3$), 1.01 (t, 6H, *J* = 7.5 Hz, 2 $CH_3CH_2CH_2O$), 0.94 (t, 3H, *J* = 7.5 Hz, $CH_3CH_2CH_2O$). ^{13}C NMR (75 MHz): δ 170.3 (C), 170.1 (C), 170.0 (C), 169.6 (C), 155.5 (C), 154.5 (C), 144.3 (C), 144.1 (C), 135.6 (C), 135.3 (C), 133.9 (C), 133.7 (C), 133.2 (C), 128.3 (CH), 127.6 (CH), 122.1 (CH), 76.9 (CH_2), 74.6 (CH), 73.7 (CH), 71.8 (CH), 70.2 (CH_2), 68.6 (CH), 67.5 (CH), 61.4 (CH_2), 60.2 (CH_2), 49.6 (CH_2), 31.8 (CH_2), 31.3 (CH_2), 30.8 (CH_2), 23.1 (CH_2), 20.6 (CH_3), 20.5 (CH_3), 14.1 (CH_3), 10.4 (CH_3), 10.0 (CH_3). HRMS (ESI/Q-TOF): calcd *m/z* for ($C_{117}H_{150}N_{12}O_{42}$)/2 $[M+2H]^{2+}$: 1197.4985; found: 1197.5017.

5,11,17,23-Tetrakis{3-[4-(β-D-galactopyranosyl)-1*H*-1,2,3-triazol-1-yl]propyl}-25-carboxylmethoxy-26,27,28-tripropoxy-calix[4]arene (14). A solution of **13** (100 mg, 0.04 mmol) in a 0.2 M solution of NaOEt in EtOH (2 mL, prepared from Na and EtOH immediately before the use) was kept at room temperature for 3 h in a nitrogen atmosphere, then neutralized with Dowex 50 X2-400 resin (H^+ form, activated and washed with H_2O and EtOH immediately before the use), and filtered through a sintered glass filter. The resin was washed with H_2O and DMF, and the solution was concentrated. A solution of the residue in 0.2 M aqueous NaOH (2 mL) was kept at room temperature for 24 h in a nitrogen atmosphere, then neutralized with Dowex 50 x 2-400 resin (H^+ form, activated and washed with H_2O and EtOH immediately before the use), and filtered through a sintered glass filter. The resin was washed with H_2O and DMF, and the solution was concentrated. The residue was eluted from a C18 silica gel cartridge with 1:1 H_2O-CH_3OH, then CH_3OH, to give **14** (44 mg, 62%) as an amorphous solid; $[\alpha]_D$ = +14.2 (*c* 0.5, DMF). ^1H NMR (300 MHz, [D_6]DMSO + D_2O) selected data: δ 8.04 (s, 2H, 2 H-5 Tr.), 7.96 (s, 2H, 2 H-5 Tr.), 6.76 (s, 4H, Ar), 6.50 (s, 2H, Ar), 6.47 (s, 2H, Ar), 4.60 (s, 2H, OCH_2CO_2), 4.45 and 3.14 (2d, 4H, *J* = 13.0 Hz, 2 $ArCH_2Ar$), 4.31 and 3.14 (2d, 4H, *J* = 13.0 Hz, 2 $ArCH_2Ar$), 2.37-2.26 (m, 4H, 2 $ArCH_2CH_2CH_2$), 2.18-2.08 (m, 4H), 2.04-1.75 (m, 14H), 0.96 (t, 6H, *J* = 7.5 Hz, 2 $CH_3CH_2CH_2O$), 0.93 (t, 3H, *J* = 7.5 Hz, $CH_3CH_2CH_2O$). ^{13}C NMR (75 MHz, DMSO-d_6 + D_2O) selected data: δ 146.9 (C), 135.5 (C), 134.7 (C), 128.5 (CH), 124.0 (CH), 80.0 (CH), 79.9 (CH), 75.5 (CH), 70.8 (CH), 69.5 (CH), 61.4 (CH_2), 49.3 (CH_2), 31.9

(CH_2), 23.3 (CH_2), 11.0 (CH_3). HRMS (ESI/Q-TOF): calcd *m/z* for ($C_{83}H_{114}N_{12}O_{26}$)/2 [*M*+2H]$^{2+}$: 847.3984; found: 847.3996.

5,11,17,23-Tetrakis{3-[4-(β-D-galactopyranosyl)-1*H*-1,2,3-triazol-1-yl]propyl}-25-[(11-azido-3,6,9-trioxaundecan-1-amino)carbonyl-methoxy]-26,27,28-tripropoxy-calix[4]arene (2). A mixture of **14** (21 mg, 0.012 mmol), 1-hydroxybenzotriazole hydrate (HOBT, 3 mg, 0.024 mmol), and *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide (EDC, 14 mg, 0.072 mmol) in anhydrous DMF (2 mL) was stirred at room temperature for 30 min, then commercially available 11-azido-3,6,9-trioxaundecan-1-amine **15** (10 μL, 0.036 mmol) was added. Stirring was continued for an additional 48 h, then the solvent was removed under vacuum. The residue was eluted from a C18 silica gel cartridge with H_2O-CH_3OH (from 1:1 to 1:5), then CH_3OH, to give **2** (12 mg, 51%) as an amorphous solid; $[\alpha]_D$ = +14.5 (*c* 0.4, CH_3OH). ^{1}H NMR (400 MHz, CD_3OD): δ 8.11, 8.10, 7.90, and 7.89 (4s, 4H, 4 H-5 Tr.), 6.94 (s, 2H, Ar), 6.91 (s, 2H, Ar), 6.30-6.26 (m, 4H, Ar), 4.82 (s, 2H, OCH_2CO_2), 4.43 and 3.27 (2d, 4H, *J* = 13.5 Hz, 2 ArC*H*$_2$Ar), 4.40 and 3.14 (2d, 4H, *J* = 13.0 Hz, 2 ArC*H*$_2$Ar), 4.39 (d, 2H, $J_{1,2}$ = 9.8 Hz, 2 H-1), 4.34 (d, 2H, $J_{1,2}$ = 9.8 Hz, 2 H-1), 4.28-4.22 (m, 4H, 2 $ArCH_2$-CH_2C*H*$_2$), 4.11-4.06 (m, 4H, 2 $ArCH_2CH_2C$*H*$_2$), 3.99-3.91 (8 dd, 8H, 4 H-2, 4 H-4), 3.91-3.78 (m, 6H, 3 CH_3CH_2C*H*$_2$O), 3.76-3.56 (m, 30H), 3.31-3.29 (m, 2H), 2.58-2.51 (m, 4H, 2 ArC*H*$_2CH_2CH_2$), 2.27-2.16 (m, 4H, 2 $ArCH_2C$*H*$_2CH_2$), 2.05-1.97 (m, 4H, 2 ArC*H*$_2CH_2CH_2$), 1.95-1.72 (m, 10H, 2 $ArCH_2C$*H*$_2CH_2$, 3 CH_3C*H*$_2CH_2$O), 1.02 (t, 6H, *J* = 7.5 Hz, 2 C*H*$_3CH_2CH_2$O), 0.92 (t, 3H, *J* = 7.5 Hz, C*H*$_3CH_2CH_2$O). ^{13}C NMR (75 MHz, CD_3OD): δ 173.3 (C), 157.2 (C), 156.3 (C), 154.4 (C), 147.7 (C), 147.2 (C), 137.5 (C), 135.9 (C), 135.7 (C), 135.4 (C), 134.9 (C), 134.0 (C), 131.1 (CH), 130.3 (CH), 129.3 (CH), 128.9 (CH), 125.1 (CH), 124.9 (CH), 80.9 (CH), 78.9 (CH_2), 77.8 (CH_2), 76.3 (CH), 76.2 CH), 75.0 (CH_2), 72.2 (CH), 72.0 (CH), 71.8 (CH_2), 71.7 (CH_2), 71.6 (CH_2), 71.2 (CH_2), 71.0 (CH), 70.9 (CH_2), 62.9 (CH_2), 51.7 (CH_2), 50.8 (CH_2), 50.4 (CH_2), 33.0 (CH_2), 32.5 (CH_2), 32.1 (CH_2), 24.2 (CH_2), 24.0 (CH_2), 10.8 (CH_3), 10.4 (CH_3). HRMS (ESI/Q-TOF): calcd *m/z* for ($C_{91}H_{130}N_{16}O_{28}$)/2 [*M*+2H]$^{2+}$: 947.4620; found: 947.4687.

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