Supplementary material (ESI) for Chemical Communications

Supramolecular One-pot Approach to Fluorescent Glycodendrimers

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1. General Information.

All chemicals used were reagent grade and used as supplied except where noted. Dichloromethane (CH_2Cl_2) was purified by a Cycle-Tainer solvent delivery system. Triethylamine was distilled over CaH_2 prior to use. Analytical thin layer chromatography (TLC) was performed on Merck silica gel 60 F_{254} plates (0.25 mm). Compounds were visualized by UV irradiation or by dipping the plate in CAN solution followed by heating. Flash column chromatography was carried out using force flow of the indicated solvent on Fluka Kieselgel 60 (230-400 mesh).

^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR-300 (300 MHz) or Bruker DRX500 (500 MHz) spectrometer. High-resolution mass spectra (HR MALDI MS) were performed by the Mass Spectrometry-service at the Laboratory for Organic Chemistry (ETH Zurich). ESI-MS were run on an Agilent 1100 Series LC/MSD instrument. IR spectra were recorded on a Perkin-

Elmer 1600 FTIR spectrometer. Optical rotation measurements were conducted using a Perkin-Elmer 241 polarimeter.

8-hydroxyquinaldine and 2,3,4,5,6-pentafluorophenol were purchased from Fluka-Chemie AG. ConcavalinA was purchased from Appli Chem (Axon Lab AG). Fluorescence emission spectra were recorded on a Perkin-Elmer LS-50B spectrofluorometer.

2. General Procedures:

General Procedure A: Synthesis of sugar-tripods.

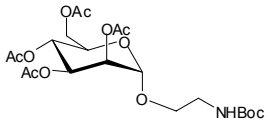
The Boc-protected amino-sugar (4.0 equiv) was dissolved in dichloromethane/trifluoroacetic acid (3:1, 10 mL) and stirred at room temperature for 1 h. The solvent was evaporated *in vacuo* and the residue redissolved in anhydrous dichloromethane (20 mL). 8-*O*-benzyl-quinoline-2-carbonyl-3-{*N*-{tris[3-[pentafluoro phenyl carboxyl-ethoxy) methyl]}methylamide}-3-*β*-alanine (1.0 equiv) was added, the pH was adjusted to pH 8 with triethylamine and stirred at room temperature for 12 h. The solvent was evaporated *in vacuo* and purified by flash silica column chromatography.

General Procedure B: Deacetylation and hydrogenolysis of sugar derivatives.

To a solution of sugar-substituted tripod (1.0 equiv) in methanol(10 mL) was added sodium methoxide (10%) and stirred for 2 h at rt. The mixture was neutralized with amberlite–acidic resin, filtered and then concentrated *in vacuo*. The residue was dissolved once more in methanol (10 mL), 10 % Pd/C (Pd/C, 10 mol % added) and hydrogen gas was bubbled through the solution for 12 h. The solution was filtered over celite and the filtrate concentrated *in vacuo* to afford the final compound.

General Procedure C: Synthesis of zinc complexes.

To a solution of dendron (**12**-**14** and **17**-**18)** (2 eq) in MeOH (10 mL) were added the appropriate metal salt (1 eq) and refluxed for 12 h. The solvent was evaporated to obtain yellow color oily residue, which was washed with CH_2Cl_2:MeOH (90:10) to remove starting materials and other other impurities. Then the oily residue was dried *in vacuo*.



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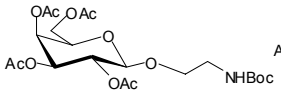

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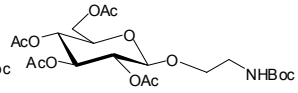

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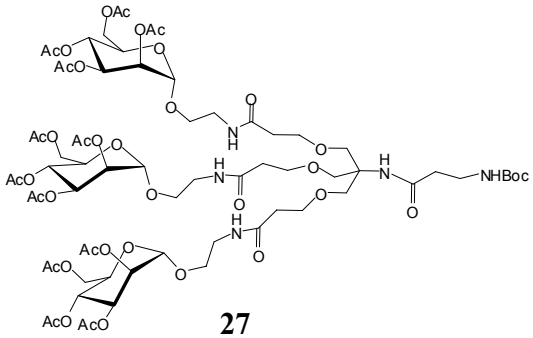

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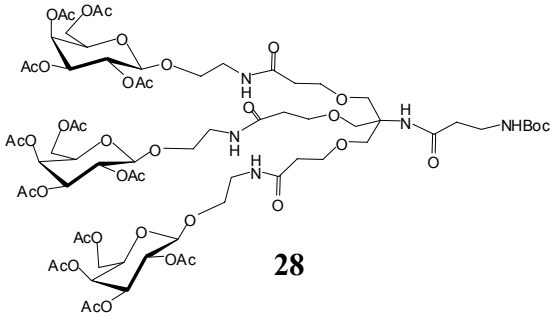

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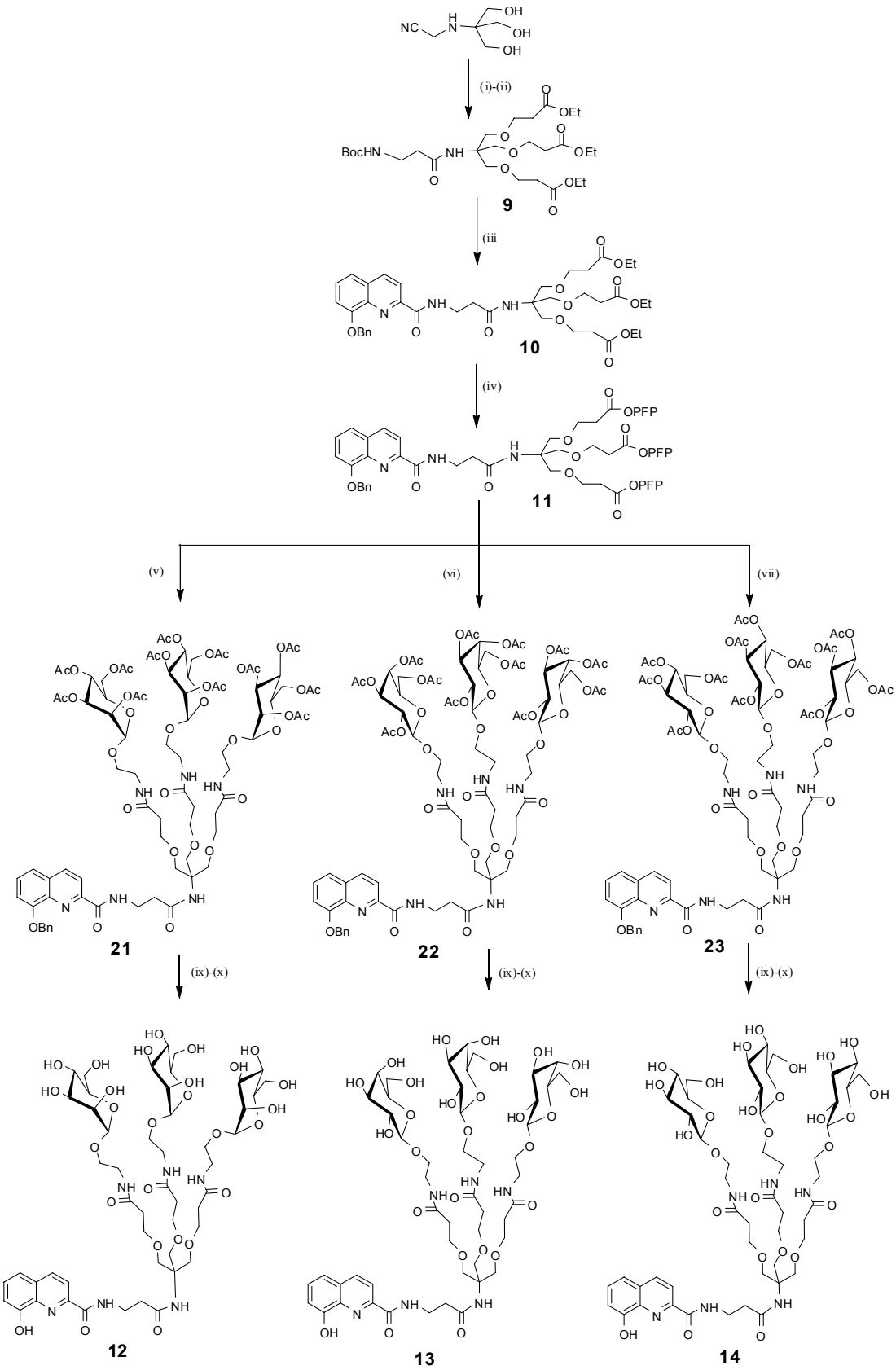
Carbohydrate Synthesis: 2-(*tert*-butoxycarbonylamino)ethoxy-2,3,4,6-tetra-*O*-acetyl-α-D-pyranoside (**24-26**) were synthesized according to published procedures.[1]



Scheme 1. Reagents and Conditions: (i) Acrylonitrile /NaOH (40%); (ii) Conc HCl/EtOH; (iii) Boc-*β*-ala/DIC/HOBT/DCM; (iv) 8-O-benzyl-quinoline-2-carboxylic acid, DIC/HOBT/DCM; (v) 1N NaOH/MeOH; pentafluorophenol (PFP)/DIC/DCM; (vi) Comp **24**/DCM/TEA; (vii) Comp **25**/DCM/TEA; (viii) Comp **26**/DCM/TEA; (ix) NaOMe/MeOH; (x) H_2/Pd-C/MeOH.

3. Synthesis of 11:

(i) ***N*-{Tris[(2-ethylcarboxyl-ethoxy)methyl]}methylamine,** a known compound, was synthesized using different means to those available in literature.[3] *N*-{*tris*[(2-cyanoethoxy)methyl]} methylamine[2] (5 g, 17.6 mmol) was dissolved in HCl (5 mL, 36%) and refluxed for 4 h. The reaction mixture was dissolved in ethanol (30 mL) and refluxed for 12 h before the solvent was distilled off. NaOH (aqueous, 5N) was added to the white precipitate until the mixture reached pH 8. EtOAc (30 mL) was added and the organic layer washed ($3XH_2O$). Purification by flash silica column chromatography afforded (3.95 g, 51%) of *N*-{tris[(2-ethylcarboxyl-ethoxy) methyl]}methylamine. R_f = 0.5 (CH_2Cl_2/MeOH = 95:5); ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.15 (q, 6H, J = 7.2 Hz), 3.68 (t, 6H, J = 6.3 Hz), 3.30 (s, 6H), 2.54 (t, 6H, J = 6.3 Hz), 1.59 (br.s, 2H), 1.25 (t, 9H, J = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.4, 155.8, 72.7, 66.7, 60.3, 34.8, 14.1, LC-MS (*m/z*): 422.2 $(M+H)^+$; FTIR($CHCl_3$): 3379, 2982, 2873, 1736 cm^{-1}.

(iii) ***tert*-Butoxycarbonyl-3-{*N*-{tris[3-[ethylcarboxyl-ethoxy)methyl]}methylamide}-3-*β*-alanine**. To a solution of *N*-{tris[(3-[ethylcarboxyl-ethoxy)methyl]}methylamine (3 g, 7.12 mmol) and Boc-*β*-alanine (1.3 g, 7.14 mmol) in dichloromethane (10 mL) at 0°C, were added diisopropyl carbadiazime (1.35 ml, 8.56 mmol) and 1-hydroxybenzotriazole (9 mg, 0.71 mmol) The reaction mixture was stirred at room temperature for 12 h and concentrated *in vacuo*. The crude residue was purified by flash silica column chromatography to yield *tert*-butoxycarbonyl-3-{*N*-{tris[3-[ethylcarboxyl-ethoxy)methyl]}methylamide}-3-*β*-alanine (2.65 g, 63%). R_f = 0.5 (CH_2Cl_2/MeOH, 98:2); ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.05 (q, 6H, J = 6.9 Hz), 3.59 (br. s, 12H), 3.27 (q, 2H, J = 6.6 Hz), 2.44 (t, 6H, J = 6.0 Hz), 2.25 (t, 2H, J = 6.6 Hz), 1.33 (s, 9H); 1.16 (t, 9H, J = 6.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.1, 172.9, 79.5, 75.8, 70.9, 67.3, 61.5, 41.2, 36.8, 33.6, 28.5, 14.1, LC-MS (*m/z*): 593.4 $(M+H)^+$; FTIR($CHCl_3$): 3390, 2982, 2873, 1734, 1726, 1643, 1521 cm^{-1}.

(iv) 8-*O*-benzyl-quinoline-2-carbonyl-3-{*N*-{tris[3-[ethylcarboxyl-ethoxy)methyl]} methylamide}-3-*β*-alanine (10). *tert*-Butoxycarbonyl-3-{*N*-{tris[3-[ethylcarboxyl-ethoxy) methyl]}methylamide}-3-*β*-alanine (2.5 g, 4.22 mmol) was dissolved in dichloromethane/trifluoroacetic acid (3:1, 10 mL) and stirred at room temperature for 1 h. The solvent was evaporated *in vacuo*, the residue was re-dissolved in anhydrous dichloromethane (20 mL) and the pH adjusted to 8 using triethylamine. 8-*O*-benzyl-quinoline-2-carboxylic acid[4] (1.2 g, 4.3 mmol) and diisopropyl carbadiazine (0.81 ml, 5.1 mmol) were added to the above mixture and stirred for 12 h at rt. Finally, the mixture was concentrated *in vacuo* and purified by flash chromatography to afford 8-*O*-benzyl-quinoline-2-carbonyl-3-{*N*-{tris[3-[ethylcarboxyl-ethoxy)methyl]} methylamide}-3-*β*-alanine **10** (2.13 g, 66%). R_f = 0.5 (CH_2Cl_2/MeOH, 98:2); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.69 (t, 1H, J = 6.3 Hz), 8.20 (q, 2H, J = 6.9 Hz), 7.51 (d, 2H, J = 7.8 Hz), 7.34-7.32 (m, 4H), 7.23 (t, 1H, J = 7.8 Hz), 7.03 (d, 1H, J = 6.9 Hz), 5.29 (s, 2H), 4.00 (q, 6H, J = 7.2 Hz), 3.68 (q, 2H, J = 6.3 Hz), 3.60 (s, 6H), 3.50 (t, 6H, J = 6.0 Hz), 2.48 (dd, 2H, J = 6.3 Hz), 2.31 (t, 6H, J = 6.3 Hz), 1.10 (t, 9H, J = 7.2 Hz); ^{13}C NMR (75MHz, $CDCl_3$): δ 170.2, 167.3, 164.5, 154.4, 148.3, 142.6, 137.1, 136.8, 130.4, 128.5, 128.1, 127.6, 126.7, 119.8, 119.1, 110.9, 70.8, 66.0, 60.3, 53.5, 34.1, 24.4, 14.2; LC-MS (*m/z*): 754.3 $(M+H)^+$; FTIR($CHCl_3$): 3407, 2982, 2873, 1750, 1731, 1630, 1512 cm^{-1}.

(v) 8-*O*-benzyl-quinoline-2-carbonyl-3-{*N*-{tris[3-[pentafluoro phenyl carboxyl-ethoxy) methyl]}methylamide}-3-*β*-alanine (11). To a solution of 8-*O*-benzyl-quinoline-2-carbonyl-3-{*N*-{tris[3-[ethylcarboxyl-ethoxy)methyl]} methylamide}-3-*β*-alanine **10** (2.0 g, 2.66 mmol) in EtOH (10 mL) was added NaOH (aqueous, 1 N, 3 mL) The mixture was stirred at rt for 2 h, concentrated *in vacuo*, adjusted to pH 5 with HCl (aqueous, 1 N) and extracted with EtOAc. The organic layer was dried with Na_2SO_4, filtered and concentrated *in vacuo*. The residue was dissolved in DCM and 2,3,4,5,6-pentafluorophenol (1.94 g, 10.6 mmol) was added. After cooling to 0 $^\circ$C, diisopropyl carbadiazine (2.0 mL, 12.8 mmol) was added and the reaction mixture was stirred for 12 h at room temperature, concentrated *in vacuo* and purified by silica column flash chromatography to afford 8-*O*-benzyl-quinoline-2-carbonyl-3-{*N*-{tris[3-[pentafluoro phenyl carboxyl-ethoxy)methyl]}methylamide}-3-*β*-alanine (2.12 g, 71%). R_f = 0.5 (CH_2Cl_2/EtOH, 92:7); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.71 (t, 1H, J = 6.3 Hz), 8.26-8.24 (m, 2H, J = 6.9 Hz), 7.57 (d, 2H, J = 7.8 Hz), 7.40 (br.s, 5H), 7.29 (t, 1H, J = 7.8 Hz), 7.07 (d, 1H, J = 6.9 Hz), 5.22 (s, 2H), 3.71 (br.s, 14H), 2.73 (t, 6H, J = 6.0 Hz), 2.50 (t, 2H, J = 6.3 Hz); ^{13}C

NMR (75 MHz, $CDCl_3$): δ 170.1, 167.3, 164.5, 154.4, 148.3, 142.6, 139.4, 139.2, 137.1, 136.8, 130.4, 128.6, 128.0, 127.6, 126.7, 119.8, 119.2, 110.8, 70.8, 59.7, 53.5, 41.9, 36.4; FTIR($CHCl_3$): 3542, 3305, 1760, 1671, 1543, 1323 cm^{-1}; HRMS (MALDI-ToF) (*m/z*) calcd. for $C_{51}H_{36}F_{15}N_5O_{12}Na$ 1190.2063, found: 1190.6422 $[M+Na]^+$.

4. Synthesis of 12,13 and 14 dendrons.

(vi) 8-*O*-benzyl-quinoline-2-carbonyl-3-{tris[3-[2-ethoxy-2,3,4,6-tetra-*O*-acetyl-*α*-D-mannopyranoside-ethoxy]methyl]methylamide}-3-*β*-alanine (21). General procedure A using 2-(*tert*-butoxycarbonylamino)ethoxy-2,3,4,6-tetra-*O*-acetyl-*α*-D-mannopyranoside **24** (1.34 g, 3.4 mmol) and 8-*O*-benzyl-quinoline-2-carbonyl-3-{*N*-{tris[3-[pentafluoro phenyl carboxyl-ethoxy) methyl]}methylamide}-3-*β*-alanine **11** (1 g, 0.86 mmol). Purification by flash chromatography yielded 8-*O*-benzyl-quinoline-2-carbonyl-3-{tris[3-[2-ethoxy-2,3,4,6-tetra-*O*-acetyl-*α*-D-mannopyranoside-ethoxy]methyl]methylamide}-3-*β*-alanine (0.87 g, 58%). R_f = 0.5 (CH_2Cl_2/MeOH, 92:8); $[\alpha]_D^{r.t}$ = +29.1 (c = 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, MeOD): δ 9.25 (t, 1H, *J* = 6.0 Hz), 8.43 (d, 1H, *J* = 8.4 Hz), 8.23 (d, 1H, *J* = 8.4 Hz), 8.06 (t, 4H, *J* = 5.4 Hz), 7.61 (d, 2H, *J* = 8.4 Hz), 7.54 (d, 2H, *J* = 8.4 Hz), 7.43 (t, 2H, *J* = 8.1 Hz), 7.36 (d, 1H, *J* = 7.2 Hz), 7.29 (t, 1H, *J* = 4.5 Hz), 7.24 (s, 1H), 5.45 (s, 2H), 5.26-5.21 (m, 9H), 4.23 (dd, 3H, *J* = 4.8, 7.2 Hz), 4.09 (dd, 3H, *J* = 2.4, 9.6 Hz), 4.02-4.01 (m, 3H), 3.73-3.71 (m, 6H), 3.65 (br.s, 6H), 3.61 (t, 6H, *J* = 6.0 Hz), 3.53-3.50 (m, 4H), 3.38 (t, 6H, *J* = 4.5 Hz), 2.62 (t, 2H, *J* = 6.9 Hz), 2.35 (t, 6H, *J* = 6.0 Hz), 2.10 (s, 9H), 2.03 (s, 9H), 2.01 (s, 9H), 1.91 (s, 9H); ^{13}C NMR (75 MHz, MeOD): δ 173.6, 173.3, 171.8, 171.1, 170.8, 166.2, 155.3, 149.4, 139.7, 138.6, 137.8, 131.6, 129.3, 128.7, 128.1, 120.9, 119.9, 112.2, 101.4, 73.8, 72.4, 71.6, 69.7, 69.3, 69.0, 68.1, 54.4, 40.0, 37.0, 20.4; HRMS (MALDI-ToF) (*m/z*); calcd. for $C_{81}H_{108}N_6O_{39}$ 1811.6650; found:1811.6544 $[M+Na]^+$.

(vii) 8-*O*-benzyl-quinoline-2-carbonyl-3-{tris[3-[2-ethoxy-2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranoside-ethoxy]methyl]methylamide}-3-*β*-alanine (22). General procedure A using 2-(*tert*-butoxycarbonylamino)ethoxy-2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranoside **25** (1.0 g, 2.56 mmol) and 8-*O*-benzyl-quinoline-2-carbonyl-3-{*N*-{tris[3-[pentafluoro phenyl carboxyl-ethoxy) methyl]}methylamide}-3-*β*-alanine **11** (0.80 g, 0.68 mmol). Purification column chromatography yielded 8-*O*-benzyl-quinoline-2-carbonyl-3-{tris[3-[2-ethoxy-2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranoside-ethoxy]methyl] methylamide}-3-*β*-alanine (0.64 g, 53%). R_f = 0.5

(CH_2Cl_2/MeOH, 92:8); $[\alpha]_D^{r.t}$ = +3.8 (c = 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, MeOD): δ 9.23 (t, 1H, *J* = 6.0 Hz), 8.40 (d, 1H, *J* = 8.4 Hz), 8.20 (d, 1H, *J* = 8.4 Hz), 8.10 (t, 3H, *J* = 5.4 Hz), 7.54 (d, 2H, *J* = 8.4 Hz), 7.51 (d, 2H, *J* = 8.4 Hz), 7.40 (t, 2H, *J* = 8.1 Hz), 7.31 (d, 1H, *J* = 7.2 Hz), 7.25 (t, 1H, *J* = 4.5 Hz), 7.20 (s, 1H), 5.42(s, 2H), 5.37 (d, 3H, *J* = 3.3 Hz), 5.37 (d, 3H, *J* = 3.3 Hz), 5.14 (t, 3H, *J* = 7.8 Hz), 4.99 (dd, 3H, *J*= 3.3, 4.2 Hz), 4.49 (d, 3H, *J* = 7.8 Hz), 4.12-4.10 (m, 6H), 3.92 (t, 3H, *J* = 6.2 Hz), 3.84 (d, 3H, *J* = 5.1 Hz), 3.70 (t, 6H, *J* = 5.4 Hz), 3.65 (br.s, 8H), 3.42 (t, 6H, *J* = 5.7 Hz), 3.34-3.31 (m, 2H), 2.39 (t, 6H, *J* = 5.4Hz), 2.14 (s, 9H), 2.04 (s, 9H), 2.02 (s, 9H), 1.96 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.1, 170.0, 169.8, 169.7, 155.7, 155.3, 149.4, 139.7, 138.6, 137.8, 131.6, 129.3, 128.7, 128.1, 120.9, 119.9, 112.2, 101.1, 70.6, 69.1, 68.7, 67.2, 66.7, 66.9, 61.2, 59.7, 45.7, 41.7, 39.1, 37.0, 36.4, 20.6; HRMS (MALDI-ToF) (*m/z*): $[M+Na]^+$ calcd. for $C_{81}H_{108}N_6O_{39}Na$ 1811.6544; found:1811.6541.

(viii) 8-*O*-benzyl-quinoline-2-carbonyl-3-{tris[3-[2-ethoxy-2,3,4,6-tetra-*O*-acetyl-*β*-D-glycopyranoside-ethoxy]methyl]methylamide}-3-*β*-alanine (23). General procedure A using 2-(*tert*-butoxycarbonylamino)ethoxy-2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranoside **26** (0.67 g, 1.72 mmol) and 8-*O*-benzyl-quinoline-2-carbonyl-3-{*N*-{tris[3-[pentafluoro phenyl carboxyl-ethoxy) methyl]}methylamide}-3-*β*-alanine **11** (0.5 g, 0.43 mmol). Purification by flash silica column chromatography yielded 8-*O*-benzyl-quinoline-2-carbonyl-3-{tris[3-[2-ethoxy-2,3,4,6-tetra-*O*-acetyl-*β*-D-glycopyranoside-ethoxy]methyl] methylamide}-3-*β*-alanine (0.46 g, 61%). R_f = 0.5 (CH_2Cl_2/MeOH, 92:8); $[\alpha]_D^{r.t}$ = -35.3 (c = 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, MeOD): δ 8.43 (d, 1H, *J* = 8.4 Hz), 8.25 (d, 1H, *J* = 8.4 Hz), 7.76 (t, 3H, *J* = 5.4 Hz), 7.62 (d, 2H, *J* = 8.4 Hz), 7.55 (d, 2H, *J* = 8.4 Hz), 7.44 (t, 2H, *J* = 8.1 Hz), 7.31 (d, 1H, *J* = 7.2 Hz), 7.29 (t, 2H, *J* = 4.5 Hz), 7.20 (s, 1H), 5.46 (s, 2H), 5.25 (t, 3H, *J* = 9.6 Hz), 5.00 (t, 3H, *J* = 9.6 Hz), 4.88 (t, 3H, *J* = 9.6 Hz), 4.67 (d, 3H, *J* = 8.1 Hz), 4.26 (dd, 3H, *J* = 4.8, 7.5 Hz), 4.12 (dd, 3H, *J* = 2.4, 10.2 Hz), 3.83-3.80 (m, 8H), 3.75 (t, 3H, *J* = 6.9 Hz), 3.65 (s, 6H), 3.59 (t, 6H, *J* = 5.7 Hz), 3.33 (br.s, 6H), 2.62 (t, 2H, *J* = 6.6 Hz), 2.32 (t, 6H, *J* = 5.7 Hz), 2.02 (s, 9H), 2.00 (s, 9H), 1.98 (s, 9H), 1.95 (s, 9H); ^{13}C NMR (75 MHz, MeOD): δ 171.5, 171.3, 170.4, 170.2, 170.1, 169.33, 164.6, 154.4, 148.4, 137.4, 136.7, 130.0, 128.6, 127.9,126.9, 120.0, 119.2, 111.1, 100.8, 72.7, 71.9, 71.0, 69.3, 69.0, 68.3, 67.3, 61.8, 39.2, 36.2, 20.7; HRMS (MALDI-ToF) (*m/z*): $[M+Na]^+$ calcd. for $C_{81}H_{108}N_6O_{39}Na$ 1811.6544; found:1811.6541.

(ix) 8-*O*-hydroxyquinoline-2-carbonyl-3-{tris[3-[2-ethoxy-*α*-D-mannopyranoside-ethoxy]methyl]methylamide}-3-*β*-alanine (12). General procedure B with 8-*O*-benzyl-

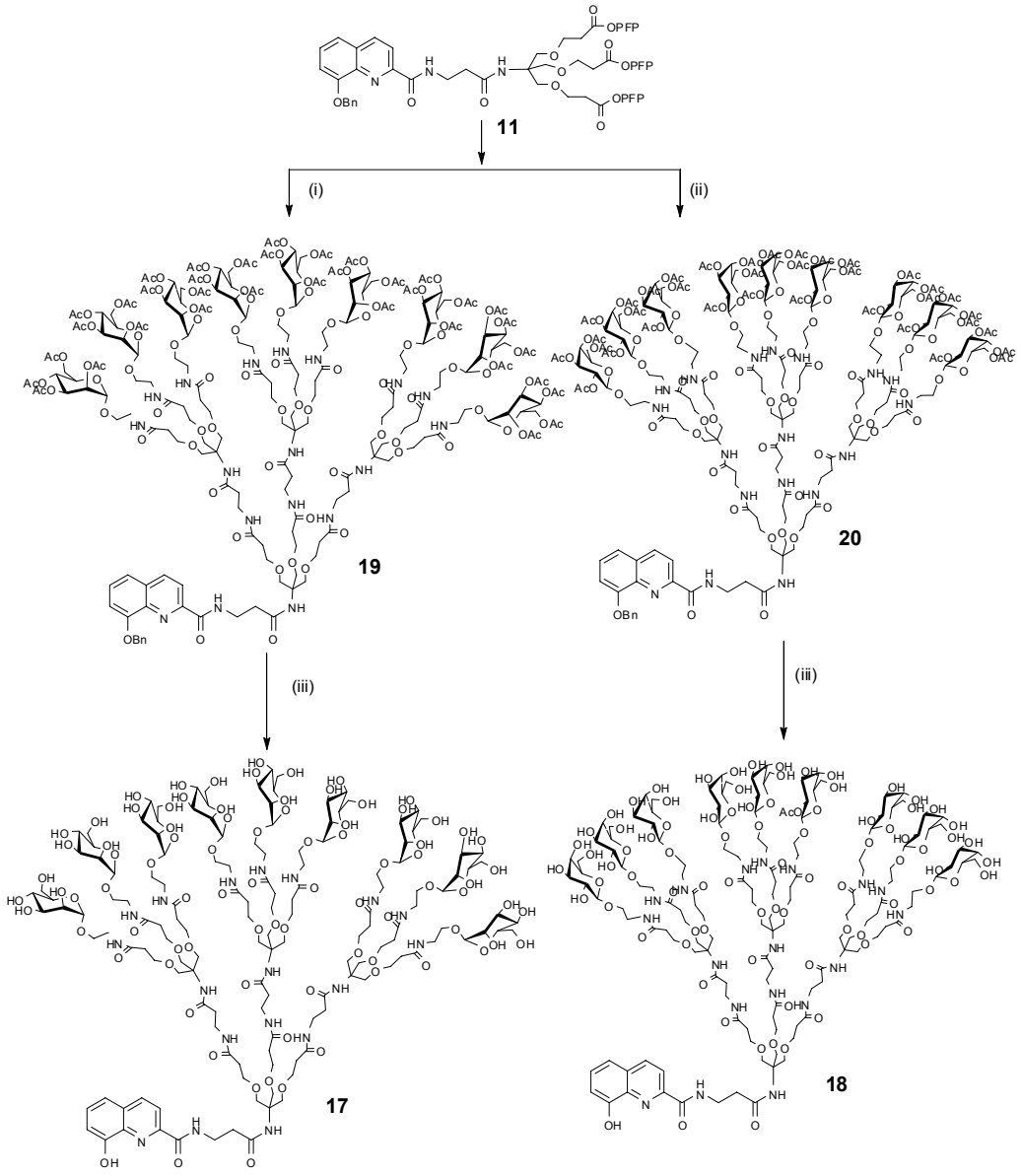
quinoline-2-carbonyl-3-{tris[3-[2-ethoxy-2,3,4,6-tetra-*O*-acetyl-*α*-D-mannopyranoside-ethoxy]methyl] methylamide}-3-*β*-alanine **21** (0.5 g, 0.27 mmol), sodium methoxide (50 mg, 27 μmol) and 10 % Pd/C (50 mg) yielded 8-*O*-hydroxyquinoline-2-carbonyl-3-{tris[3-[2-ethoxy-*α*-D-mannopyranoside-ethoxy]methyl]methylamide}-3-*β*-alanine **12** (0.14 g, 42%). $[\alpha]_D^{r.t}$ = +73.8 (c = 1.0, H_2O); ^{1}H NMR (300 MHz, MeOD): *δ* 8.35 (d, 1H, *J* = 7.8 Hz), 8.15 (d, 1H, *J* = 7.8 Hz), 7.50 (t, 1H, *J* = 6.3 Hz), 7.36 (d, 1H, *J* = 7.2 Hz), 7.10 (d, 1H, *J* = 6.3 Hz), 4.75 (s, 3H), 3.81 (d, 6H, *J* = 7.8 Hz), 3.72-3.67 (m, 12H), 3.64-3.54 (m, 18H), 3.53-3.49 (m, 8H), 2.62 (t, 2H, *J* = 6.9 Hz), 2.33 (t, 6H, *J* = 6.0 Hz); ^{13}C NMR (75 MHz, MeOD): *δ* 176.7, 173.7, 166.3, 138.6, 138.6, 130.3, 129.5, 128.6, 119.6, 118.6, 112.5, 101.2, 74.3, 71.6, 69.6, 68.2, 66.8, 62.31, 61.1, 39.9, 37.0; HRMS (MALDI-ToF) (*m/z*) $[M+Na]^+$ calcd. for $C_{50}H_{78}N_6O_{27}Na$ 1217.4807; found:1217.4801.

8-Hydroxyquinoline-2-carbonyl-3-{tris[3-[2-ethoxy-*β*-D-galactopyranoside-ethoxy]methyl]methylamide}-3-*β*-alanine (13) : General procedure B with 8-*O*-benzyl-quinoline-2-carbonyl-3-{tris[3-[2-ethoxy-2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranoside-ethoxy]methyl] methylamide}-3-*β*-alanine **22** (0.35 g, 0.19 mmol), sodium methoxide (35 mg, 65μmol) and 10% Pd/C (35 mg) yielded 8-Hydroxyquinoline-2-carbonyl-3-{tris[3-[2-ethoxy-*β*-D-galactopyranoside-ethoxy]methyl]methylamide}-3-*β*-alanine (93 mg, 40%). $[\alpha]_D^{r.t}$ = +12.6 (c = 1.0, H_2O); ^{1}H NMR (300 MHz, MeOD): *δ* 8.32 (d, 1H, *J* = 7.8 Hz), 7.92 (d, 1H, *J* = 7.8 Hz), 7.47 (t, 1H, *J* = 6.3 Hz), 7.17 (d, 1H, *J* = 7.2 Hz), 6.94 (d, 1H, *J* = 6.3 Hz), 4.29 (d, 3H, *J* = 7.5 Hz), 3.88 (s, 6H), 3.72-3.55 (m, 38H), 2.61 (t, 2H, *J* = 6.9 Hz), 2.33 (t, 6H, *J* = 6.0 Hz); ^{13}C NMR (75 MHz, MeOD): *δ* 176.7, 173.6, 166.3, 138.58, 138.55, 130.3, 129.5, 128.6, 119.6, 118.6, 112.5, 75.0, 72.6, 70.6, 68.5, 67.2, 60.9, 39.3, 35.8; HRMS (MALDI-ToF) (*m/z*); $[M+Na]^+$ calcd. for $C_{50}H_{78}N_6O_{27}Na$ 1217.4807; found:1217.4801.

8-Hydroxyquinoline-2-carbonyl-3-{tris[3-[2-ethoxy-*β*-D-glucopyranoside-ethoxy]methyl]methylamide}-3-*β*-alanine (14). General procedure B with 8-*O*-benzyl-quinoline-2-carbonyl-3-{tris[3-[2-ethoxy-2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranoside-ethoxy]methyl] methylamide}-3-*β*-alanine **23** (0.25 g, 0.14 mmol), sodium methoxide (25 mg, 46 μmol) and 10% Pd/C (25 mg) yielded 8-Hydroxyquinoline-2-carbonyl-3-{tris[3-[2-ethoxy-*β*-D-glucopyranoside-ethoxy]methyl]methylamide}-3-*β*-alanine (0.14 g, 42%). $[\alpha]_D^{r.t}$ = -15.9 (c = 1.0, H_2O); ^{1}H NMR (300 MHz, MeOD): *δ* 8.43 (d, 1H, *J* = 7.8 Hz), 8.21 (d, 1H, *J* = 7.8 Hz), 7.53 (t, 1H, *J* = 6.3 Hz), 7.44 (d, 1H, *J* = 7.2 Hz); 7.19 (d, 1H, *J* = 6.3 Hz), 4.29 (d, 3H, *J* = 7.8

Hz), 3.88 (d, 6H, *J* = 7.8 Hz), 3.66 (br.s, 22H), 3.44-3.34 (m, 16H), 3.25 (t, 6H, *J* = 8.1 Hz), 2.62 (t, 2H, *J* = 6.9 Hz), 2.33 (t, 6H, *J* = 6.0 Hz); ^{13}C NMR (75 MHz, MeOD): δ 176.8, 173.7, 166.3, 138.6, 138.5, 130.3, 129.5, 128.6, 119.9, 118.8, 112.5, 104.1, 77.6, 71.2, 69.4, 68.3, 62.3, 54.5, 40.4, 38.0, 35.7; HRMS (MALDI-ToF) (*m/z*); $[M+Na]^+$ calcd. for $C_{50}H_{78}N_6O_{27}Na$ 1217.4807; found:1217.4801.

5. Synthesis of dendrons 17 and 18.



Scheme 2. Reagents and Conditions: (i) Comp **27**/DCM/TEA; (ii) Comp **28**/DCM/TEA; (iii) NaOMe/MeOH; H_2/Pd-C/MeOH.

(v) *tert*-Butoxycarbonyl-3-{tris[3-[2-ethoxy-2,3,4,6-tetra-*O*-acetyl-*α*-D-mannopyranoside-ethoxy]methyl]methylamide}-3-*β*-alanine (27). General procedure A using 2-(*tert*-butoxycarbonylamino)ethoxy-2,3,4,6-tetra-*O*-acetyl-*α*-D-mannopyranoside **24** (0.97 g, 1.96 mmol), *tert*-butoxycarbonyl-3-{*N*-{tris[3-[pentafluoro-phenyl-carboxyl-ethoxy)methyl]}methyl amine}-3-*β*-alanine[5] (0.5 g, 0.49 mmol) and purified by flash chromatography to yield *tert*-butoxycarbonyl-3-{tris[3-[2-ethoxy-2,3,4,6-tetra-*O*-acetyl-*α*-D-mannopyranoside-ethoxy]methyl]methylamide}-3-*β*-alanine (0.37 g, 47%). R_f = 0.45 (CH_2Cl_2/MeOH, 93:7); $[\alpha]_D^{r.t}$ = +21.4 (c = 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.79 (br.s, 2H), 6.43 (br.s, 1H), 5.30 (br.s, 1H), 5.27-5.20 (m, 9H), 4.80 (s, 3H), 4.25 (dd, 3H, *J* = 9.0, 5.1 Hz), 4.10 (dd, 3H, *J* = 2.1, 9.9 Hz), 3.90 (br.s, 3H), 3.76 (dd, 3H, *J* = 4.5, 5.4 Hz), 3.68 (dd, 6H, *J* = 5.4, 6.0 Hz), 3.64 (s, 6H), 3.54-3.52 (m, 6H), 3.37 (br.s, 8H), 2.42 (t, 6H, *J* = 5.4Hz), 2.12 (s, 9H), 2.07 (s, 9H), 2.02 (s, 9H), 1.96 (s, 9H), 1.39 (s, 9H), ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.4, 170.5, 170.0, 169.5, 155.8, 97.6, 69.3, 69.2, 68.6, 67.3, 67.1, 66.0, 62.4, 59.8, 45.7, 39.0, 37.2, 36.9, 36.5, 28.5, 20.9; FTIR($CHCl_3$): 3376, 2918, 1751, 1663, 1515, 1457, 1250 cm^{-1}; HRMS (MALDI-ToF) (*m/z*) $[M+Na]^+$ calcd. for $C_{69}H_{105}N_5O_{39}Na$ 1650.6284; found: 1650.6252.

***tert*-Butoxycarbonyl-3-{tris[3-[2-ethoxy-2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranoside-ethoxy]methyl]methylamide}-3-*β*-alanine (28).** General procedure A with 2-(*tert*-butoxycarbonylamino)ethoxy-2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranoside **25** (0.85 g, 1.73 mmol), *tert*-butoxycarbonyl-3-{*N*-{tris[3-[pentafluoro-phenyl-carboxyl-ethoxy)methyl]}methyl amine}-3-*β*-alanine[5] (0.43 g, 0.43 mmol) and flash silica column chromatography yielded *tert*-butoxycarbonyl-3-{tris[3-[2-ethoxy-2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranoside-ethoxy]methyl]methylamide}-3-*β*-alanine (0.26g, 52%). R_f 0.4 (CH_2Cl_2/MeOH, 93:7); $[\alpha]_D^{r.t}$ = +10.2 (c =1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.90(br.s, 1H), 6.47 (br.s, 3H), 5.37 (d, 4H, *J* = 3.3 Hz), 5.14 (t, 3H, *J* = 7.8 Hz), 4.99 (dd, 3H, *J* = 3.3, 4.2 Hz), 4.49 (d, 3H, *J* = 7.8 Hz), 4.12-4.10 (m, 6H), 3.92 (t, 3H, *J* = 6.2 Hz), 3.84-3.83 (m, 3H), 3.70 (t, 8H, *J* = 5.4 Hz), 3.65 (s, 9H), 3.42 (t, 6H, *J* = 5.7 Hz), 3.33 (q, 2H, *J* = 5.7 Hz), 2.39 (t, 6H, *J* = 5.4Hz), 2.14 (s, 9H), 2.04 (s, 9H), 2.02 (s, 9H), 1.96 (s, 9H), 1.40 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.1; 170.0, 169.8, 169.7, 155.7, 101.1, 70.6, 69.1, 68.7, 67.2, 67.0, 66.9, 61.2, 59.7, 45.65, 41.67, 39.1, 37.0,

36.4, 28.3, 20.6; FTIR($CHCl_3$): 3343, 2945, 1751, 1560, 1458, 1350 cm^{-1}; HRMS (MALDI-ToF) (*m/z*): $[M+Na]^+$ calcd. for $C_{69}H_{105}N_5O_{39}Na$ 1650.6284; found: 1650.6252.

(i) 8-*O*-benzyl-quinoline-2-carbonyl-3-{tris[3-carboxyl ethoxy]methyl] 3'-{tris[2'-ethoxy-2,3,4,6-tetra-*O*-acetyl-*α*-D-mannopyranoside-ethoxy]methyl]methylamide}-3-*β*-alanine (18). General procedure A using *tert*-butoxycarbonyl-3-{tris[3-[2-ethoxy-2,3,4,6-tetra-*O*-acetyl-*α*-D-mannopyranoside-ethoxy]methyl]methylamide}-3-*β*-alanine **27** (0.2 g, 0.12 mmol), 8-*O*-benzyl-quinoline-2-carbonyl-3-{*N*-{tris[3-[pentafluoro phenyl carboxyl-ethoxy) methyl]}methylamide}-3-*β*-alanine (36 mg, 0.03 mmol) and flash silica column chromatography to afford 8-*O*-benzyl-quinoline-2-carbonyl-3-{tris[3-carboxylethoxy]methyl]3'-{tris[2'-ethoxy-2,3,4,6-tetra-*O*-acetyl-*α*-D-mannopyranoside-ethoxy]methyl]methylamide}-3-*β*-alanine (0.11 g, 73%). R_f = 0.5 (CH_2Cl_2/MeOH, 90:10); $[\alpha]_D^{r.t}$ = -9.8 (c = 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, MeOD): *δ* 8.46 (d, 1H, *J* = 8.4 Hz), 8.26 (d, 1H, *J* = 8.4 Hz), 7.62 (d, 2H, *J* = 8.4 Hz), 7.55 (d, 2H, *J* = 8.4 Hz), 7.43 (t, 2H, *J* = 8.1 Hz), 7.37 (d, 1H, *J* = 7.2 Hz), 7.30 (t, 1H, *J* = 4.5 Hz), 5.45 (s, 2H), 5.21-5.26 (m, 27H), 4.23 (dd, 9H, *J* = 4.8, 7.2 Hz), 4.09 (dd, 9H, *J* = 2.4, 9.6 Hz), 4.03-4.01 (m, 14H), 3.70-3.62 (br.s, 57H), 3.55 (s, 28H), 3.45 (br.s, 32H), 2.45 (t, 28H, *J* = 6.0 Hz), 2.13 (s, 27H), 2.05 (s, 27H), 2.03 (s, 27H), 1.95 (s, 27H); ^{13}C NMR (75 MHz, MeOD): *δ* 171.8, 171.6, 170.5, 167.0, 169.6, 166.2, 155.3, 149.4, 139.7, 138.6, 137.8, 131.6, 129.3, 128.6, 126.9, 120.9, 119.9, 112.2, 97.5, 69.2, 69.0, 68.9, 68.5, 67.2, 66.9, 65.9, 62.3, 59.8, 53.3, 38.8, 36.3, 20.8; HRMS-MALDI (*m/z*): calcd. for $C_{225}H_{324}N_{18}O_{120}Na$ 5220.9696; found: 5220.956 $[M+Na]^+$.

(ii) 8-*O*-benzyl-quinoline-2-carbonyl-3-{tris[3-carboxyl ethoxy]methyl] 3'-{tris[2'-ethoxy-2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranoside-ethoxy]methyl]methylamide}-3-*β*-alanine (19). General procedure A using *tert*-butoxycarbonyl-3-{tris[3-[2-ethoxy-2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranoside-ethoxy]methyl]methylamide}-3-*β*-alanine **28** (0.18 g, 0.11 mmol), 8-*O*-benzyl-quinoline-2-carbonyl-3-{*N*-{tris[3-[pentafluoro phenyl carboxyl-ethoxy) methyl]}methylamide}-3-*β*-alanine **14** (31 mg, 0.027 mmol) and purification by flash silica column chromatography afforded 8-*O*-benzyl-quinoline-2-carbonyl-3-{tris[3-carboxyl ethoxy]methyl] 3'-{tris[2'-ethoxy-2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranoside-ethoxy]methyl]methylamide}-3-*β*-alanine (95 g, 64%). R_f = 0.5 (CH_2Cl_2/MeOH, 90:10); $[\alpha]_D^{r.t}$ = -15.8 (c =1.0, $CHCl_3$); ^{1}H NMR (300 MHz, MeOD): *δ* 8.49 (d, 1H, *J* = 8.4 Hz), 8.29 (d, 1H, *J* = 8.4 Hz), 7.61 (dd, 4H, *J* = 5.4, 8.4 Hz), 7.44 (t, 2H, *J* = 8.1 Hz), 7.35 (d, 1H, *J* = 7.2 Hz), 7.25 (t, 1H, *J* = 4.5 Hz), 7.20 (s, 1H), 5.40 (s, 2H), 5.38 (d, 9H, *J* = 3.3 Hz), 5.10 (dd, 10H, *J* = 3.3,

7.8 Hz), 4.68 (d, 9H, *J* = 4.2 Hz), 4.13 (d, *J* = 6.9 Hz, 32H), 3.87 (br.s, 9H), 3.66 (br.s, 78H), 3.39-3.36 (m, 24H), 2.43 (t, 32H, *J* = 6.3 Hz), 2.13 (s, 27H), 2.05 (s, 27H), 2.01 (s, 27H), 1.94 (s, 27H); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 173.4, 171.5, 171.4, 170.9, 169.6 166.2, 155.3, 149.4, 139.7, 138.6, 137.8, 131.6, 129.3, 128.6, 126.9, 120.9, 119.9, 112.2, 101.8, 72.0, 71.5, 70.05, 68.5, 68.3, 62.3, 54.5, 40.3, 37.2, 32.5, 20.4; HRMS (MALDI-ToF) (*m/z*): $C_{225}H_{324}N_{18}O_{120}Na$ 5220.9696; found: 5220.956 $[M+Na]^+$.

(iii) **8-Hydroxyquinoline-2-carbonyl-3-{tris[3-carboxyl ethoxy]methyl] 3'-{tris[2'-ethoxy-*α*-D-mannopyranoside-ethoxy]methyl]methylamide}-3-*β*-alanine 5.** General procedure B using 8-*O*-benzyl-quinoline-2-carbonyl-3-{tris[3-carboxylethoxy]methyl]3'-{tris[2'-ethoxy-2,3,4,6-tetra-*O*-acetyl-*α*-D-mannopyranoside-ethoxy]methyl]methylamide}-3-*β*-alanine (0.1 g, 0.019 mmol), sodium methoxide (10 mg, 2 μmol) and Pd/C (20 mg, 2 μmol) yielded 8-*O*-hydroxyquinoline-2-carbonyl-3-{tris[3-[2-ethoxy-*α*-D-mannopyranoside-ethoxy]methyl]methylamide}-3-*β*-alanine (32 mg, 59%). $[\alpha]_D^{r.t}$ = +51.2 (c = 1.0, H_2O); ^{1}H NMR (300 MHz, MeOD): *δ* 8.35 (d, 1H, *J* = 7.8 Hz), 8.15 (d, 1H, *J* = 7.8 Hz), 7.50 (t, 1H, *J* = 6.3 Hz), 7.36 (d, 1H, *J* = 7.2 Hz), 7.10 (d, 1H, *J* = 6.3 Hz), 4.75 (s, 9H), 3.81 (d, 18H, *J* = 7.8 Hz), 3.72-3.67 (m, 40H), 3.64-3.54 (m, 54H), 3.53-3.49 (m, 24H), 2.80 (t, 2H, *J* = 6.0Hz), 2.45 (t, 30H, *J* = 6.0 Hz); ^{13}C NMR (75 MHz, MeOD): *δ* 176.7, 173.8, 166.3, 138.6, 138.6, 130.3, 129.5, 128.6, 119.6, 118.6, 112.5, 101.2, 74.3, 71.6, 69.6, 68.2, 66.8, 62.3, 61.1, 39.9, 37.0; HRMS (MALDI-ToF) (*m/z*); calcd. for $C_{146}H_{246}N_{18}O_{84}Na$ 3619.5423; found : 3618.532 $[M+Na]^+$.

8-Hydroxyquinoline-2-carbonyl-3-{*tris*[3-carboxylethoxy]methyl]3'-{*tris*[2'-ethoxy-*β*-D-galactopyranoside-ethoxy]methyl]methylamide}-3-*β*-alanine 6. General procedure B using 8-*O*-benzyl-quinoline-2-carbonyl-3-{tris[3-carboxyl ethoxy]methyl]3'-{tris[2'-ethoxy-2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranoside-ethoxy]methyl]methylamide}-3-*β*-alanine (65 mg, 0.012 mmol), sodium methoxide (12 mg, 2.4 μmol) and 10% Pd/C (12 mg) yielded 8-Hydroxyquinoline-2-carbonyl-3-{*tris*[3-carboxylethoxy]methyl]3'-{*tris*[2'-ethoxy-*β*-D-galactopyranoside-ethoxy]methyl]methylamide}-3-*β*-alanine **6** (22 mg, 57%). $[\alpha]_D^{r.t}$ = -28.3 (c = 1.0, H_2O); ^{1}H NMR (300 MHz, MeOD): *δ* 8.32 (d, 1H, *J* = 7.8 Hz), 7.91 (d, 1H, *J* = 7.8 Hz), 7.56 (t, 1H, *J* = 6.3 Hz), 7.27 (d, 1H, *J* = 7.2 Hz), 6.91 (d, 1H, *J* = 6.3 Hz), 4.35 (d, 9H, *J* = 7.5 Hz), 3.88 (s, 18H), 3.72-3.55 (m, 118H), 2.45 (t, 32H, *J* = 6.0 Hz); ^{13}C NMR (75 MHz, MeOD): *δ* 176.7, 173.6, 166.3, 138.58, 138.55, 130.3, 129.5, 128.6, 119.6, 118.6, 112.5, 75.0, 72.6, 70.6,

68.5, 67.2, 60.9, 39.3, 35.8; HRMS (MALDI-ToF) (*m/z*); $C_{146}H_{246}N_{18}O_{84}Na$ 3619.5423; found : 3618.532 $[M+Na]^+$.

6. Synthesis of 1-7 Complexes

Zinc(II) bis{8-*O*-hydroxyquinoline-2-carbonyl-3-{tris[3-[2-ethoxy-*α*-D-mannopyranoside-ethoxy]methyl]methylamide}-3-*β*-alanine} (1): General Procedure C using 8-*O*-hydroxyquinoline-2-carbonyl-3-{*tris*[3-[2-ethoxy-*α*-D-mannopyranoside-ethoxy]methyl] methylamide}-3-*β*-alanine **12** (20 mg, 0.017 moles) and zinc(II) acetate (2 mg, 8.0 mmoles) yielded zinc(II) bis{8-*O*-hydroxyquinoline-2-carbonyl-3-{*tris*[3-[2-ethoxy-*α*-D-mannopyranoside-ethoxy]methyl]methylamide}-3-*β*-alanine} (12 mg, 76%). $[\alpha]_D^{r.t}$ = -36.8 (c = 1.0, water); ^{1}H NMR (300 MHz, MeOD): δ 8.49 (dd, J = 9.0 Hz, 2H), 8.42 (dd, J = 9.0 Hz, 2H,), 7.39 (t, J = 6.3 Hz, 2H), 7.05 (br.s, 2H), 6.80 (dd, 2H, J = 6.3 Hz), 4.70 (br.s, 6H), 3.90-3.55 (m, 88H), 2.62 (br.s, 4H), 2.33 (br.s, 12H), HRMS (MALDI-ToF) (*m/z*) calcd for $C_{100}H_{155}N_{12}O_{54}Zn$ 2451.7865; found 2451.7811.

Zinc(II) *bis*{8-Hydroxyquinoline-2-carbonyl-3-{*tris*[3-[2-ethoxy-*β*-D-galactopyranoside-ethoxy]methyl]methylamide}-3-*β*-alanine} (2): General Procedure C using 8-Hydroxyquinoline-2-carbonyl-3-{*tris*[3-[2-ethoxy-*β*-D-galactopyranoside-ethoxy]methyl] methylamide}-3-*β*-alanine (20 mg, 0.017 mmol) and zinc(II) acetate (2 mg, 8.0 μmol) yielded zinc(II) bis{8-Hydroxyquinoline-2-carbonyl-3-{*tris*[3-[2-ethoxy-*β*-D-galactopyranoside-ethoxy]methyl]methylamide}-3-*β*-alanine} (13 mg, 81%). $[\alpha]_D^{r.t}$ = +21.8 (c = 1.0, H_2O); ^{1}H NMR (300 MHz, MeOD): δ 8.45 (br.s, 2H), 8.34 (br.s, 2H), 7.50 (br.s, 2H), 7.09 (br.s, 2H), 6.90 (br.s, 2H), 4.29 (d, J = 6.8 Hz 6H), 3.80-3.55 (m, 88H), 2.61 (br.s, 4H), 2.33 (br.s, 12H), HRMS (MALDI-ToF) (*m/z*) calcd. for $C_{100}H_{155}N_{12}O_{54}Zn$ 2451.7865; found 2451.7811.

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Zinc(II) *bis*{8-Hydroxyquinoline-2-carbonyl-3-{tris[3-carboxyl ethoxy]methyl]3'-{*tris*[2'-ethoxy-*α*-D-mannopyranoside-ethoxy]methyl]methylamide}-3-*β*-alanine} (6). General Procedure C using 8-Hydroxyquinoline-2-carbonyl-3-{*tris*[3-carboxyl ethoxy]methyl]3'-{*tris*[2'-ethoxy-*α*-D-mannopyranoside-ethoxy]methyl]methylamide}-3-*β*-alanine **17** (15 mg, 4.2 μmol) and zinc(II) acetate (1 mg, 4 μmol) yielded zinc(II) *bis*{ 8-Hydroxyquinoline-2-carbonyl-3-{*tris*[3-carboxylethoxy]methyl]3'-{*tris*[2'-ethoxy-*α*-D-mannopyranoside-ethoxy]methyl]methylamide}-3-*β*-alanine} (10 mg, 82%). $[\alpha]_D^{r.t}$ = -49.8 (c = 1.0, H_2O); ^{1}H

NMR (300 MHz, MeOD): δ 8.43 (dd, 2H, J = 7.8 Hz), 8.34 (dd, 2H, J = 7.8 Hz), 7.50-7.48 (m, 2H), 6.97 (t, 2H, J = 7.2 Hz), 6.92 (t, 2H, J = 6.3 Hz), 4.72 (s, 18H), 3.82-3.54 (m, 278H), 2.52 (t, 54H, J = 6.0 Hz), 2.46 (t12H, J = 6.0 Hz), 2.26 (t 12H, J = 6.0 Hz), HRMS (MALDI-ToF) (*m/z*); calcd. for $C_{292}H_{491}N_{36}O_{168}Zn$ 7254.1597; found: 7254.153.

Zinc(II) bis{8-Hydroxyquinoline-2-carbonyl-3-{tris[3-carboxylethoxy]methyl]3'-{tris[2'-ethoxy-*β*-D-galactopyranoside-ethoxy]methyl]methylamide}-3-*β*-alanine} (7): General Procedure C using 8-Hydroxyquinoline-2-carbonyl-3-{tris[3-carboxylethoxy]methyl]3'-{tris[2'-ethoxy-*β*-D-galactopyranoside-ethoxy]methyl]methylamide}-3-*β*-alanine **18** (20 mg, 5.6 μmol) and Zinc(II) acetate (1 mg, 4 μmol) yielded of zinc(II) bis{8-Hydroxyquinoline-2-carbonyl-3-{*tris*[3-carboxylethoxy]methyl]3'-{*tris*[2'-ethoxy-*β*-D-galactopyranoside-ethoxy]methyl]methylamide}-3-*β*-alanine}(12 mg, 80%). $[\alpha]_D^{r.t}$ = +4.3 (c = 1.0, H_2O); 8.42 (dd, 2H, J = 7.8 Hz), 8.34 (dd, 2H, J = 7.8 Hz), 7.50 (br.s, 2H,), 6.97 (br.s, 2H), 6.91 (d, 2H, J = 6.3 Hz), 4.32 (d, J = 6.8 Hz, 18H), 3.80-3.50 (m, 292H), 2.80 (t, 6H, J = 6.0 Hz), 2.50 (t, 46H, J = 6.0 Hz), 2.20 (br.s, 12H); HRMS (MALDI-ToF) (*m/z*) calcd. for $C_{292}H_{491}N_{36}O_{168}Zn$ 7254.1597; found: 7254.153.

Aluminum(II)*tris*{8-Hydroxyquinoline-2-carbonyl-3-{*tris*[3-[2-ethoxy-*β*-D-galactopyranoside-ethoxy]methyl]methylamide}-3-*β*-alanine} (3): General Procedure C using 8-Hydroxyquinoline-2-carbonyl-3-{*tris*[3-[2-ethoxy-*β*-D-galactopyranoside-ethoxy]methyl] methylamide}-3-*β*-alanine (20 mg, 17 μmol) and aluminium(III) acetate (1 mg, 5.6 μmol) yielded aluminum(III) *tris*{8-Hydroxyquinoline-2-carbonyl-3-{*tris*[3-[2-ethoxy-*β*-D-galactopyranoside-ethoxy]methyl]methylamide}-3-*β*-alanine} (12 mg, 75%). (MALDI-ToF) (*m/z*); calcd. for $C_{150}H_{232}N_{18}O_{81}Al$ 3608.9169; found:3608.912.

Aluminum(III)*tris*{8-Hydroxyquinoline-2-carbonyl-3-{*tris*[3-[2-ethoxy-*β*-D-galactopyranoside-ethoxy]methyl]methylamide}-3-*β*-alanine} (4): General Procedure C using 8-Hydroxyquinoline-2-carbonyl-3-{*tris*[3-[2-ethoxy-*β*-D-galactopyranoside-ethoxy]methyl] methylamide}-3-*β*-alanine (20 mg, 17 μmol) and aluminum(II) acetate (1 mg, 6.0 μmol) yielded aluminum(III) *tris*{8-Hydroxyquinoline-2-carbonyl-3-{*tris*[3-[2-ethoxy-*β*-D-galactopyranoside-ethoxy]methyl]methylamide}-3-*β*-alanine} (12 mg, 75%). (MALDI-ToF) (*m/z*) calcd. for $C_{150}H_{232}N_{18}O_{81}Al$ 3608.9169; found:3608.912.

Gadolinium(II)*tris*{8-Hydroxyquinoline-2-carbonyl-3-{*tris*[3-[2-ethoxy-*β*-D-galactopyranoside-ethoxy]methyl]methylamide}-3-*β*-alanine} (5): General Procedure C using 8-Hydroxyquinoline-2-carbonyl-3-{*tris*[3-[2-ethoxy-*β*-D-galactopyranoside-ethoxy]methyl] methylamide}-3-*β*-alanine (20 mg, 17 μmol) and Gadolinium(III) chloride hexa hydrate (2 mg, 6 μmol) yielded gadolinium(III) *tris*{8-Hydroxyquinoline-2-carbonyl-3-{*tris*[3-[2-ethoxy-*β*-D-galactopyranoside-ethoxy]methyl]methylamide}-3-*β*-alanine} (12 mg, 75%). (MALDI-ToF) (*m/z*) $[M+H]^+$ calcd. for $C_{150}H_{231}N_{18}O_{81}GdH$ 3740.6351; found 3740.621.

Fluorescent spectra and Quantum Yield.

Comp No	λ_{max} (nm)	Quantum Yield
1	532	0.0270
3	528	0.0250
5	521	0.0030
6	532	0.0270
12	521	0.0040
17	520	0.0042

Quantum yields have been calculated using the equation,

$\mathbf{\Phi_{comp}/\Phi_{ref}=[A]_{comp} * [C]_{ref} / [A]_{ref} * [C]_{comp}}$

Where **[C]** refers to the concentration of the samples and [**A]** to the area of the emission spectra. Here, $Ru(bipy)_3(Cl)_2$ was used as a reference compound, exhibiting a quantum yield of 0.062[6] at the same concentration.

7. Tubidimetric analysis:

To a solution of lectin ConA (1.0 mg/ml, 0.1mL) in HEPES buffer (10 mM Hepes, pH 6.5, 1 mM $MgCl_2$, 1mM $CaCl_2$, 1% BSA) were added to complexes **1-7** (1.0 mM, H_2O). The time dependent turbidity kinetics was recorded by measuring the absorption coefficient at 500 nm at

intervals of 1 min. After 25 min, the solution was restored to its clear state by addition of mannose (100 mM, 0.01 mL) to the solution.

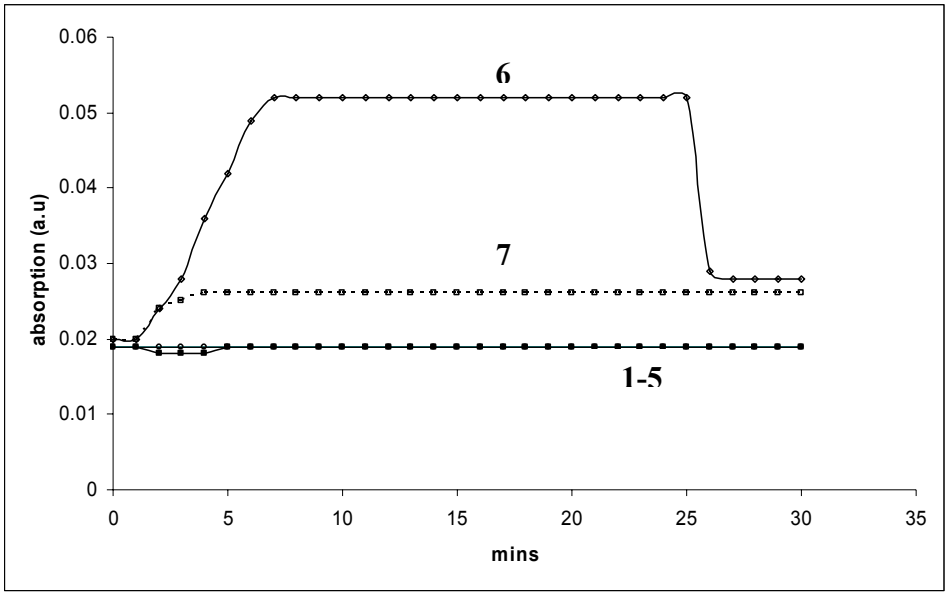

Figure 1. Turbidity analysis: Absorption change of compound **1-7** at 500 nm, upon additon of ConA. After 25 min, mannose (100 mM, 0.01 mL) was added to **6**.

Fluorescent spectra: To a solution of lectin (1.0 mg/ml, 0.1ml) in HEPES buffer (10 mM Hepes pH 6.5, 1mM $MgCl_2$, 1mM $CaCl_2$, 1% BSA) and was added complex **1-7** (1.0 mM, H_2O). The fluorescence spectra was recorded after 20 min.

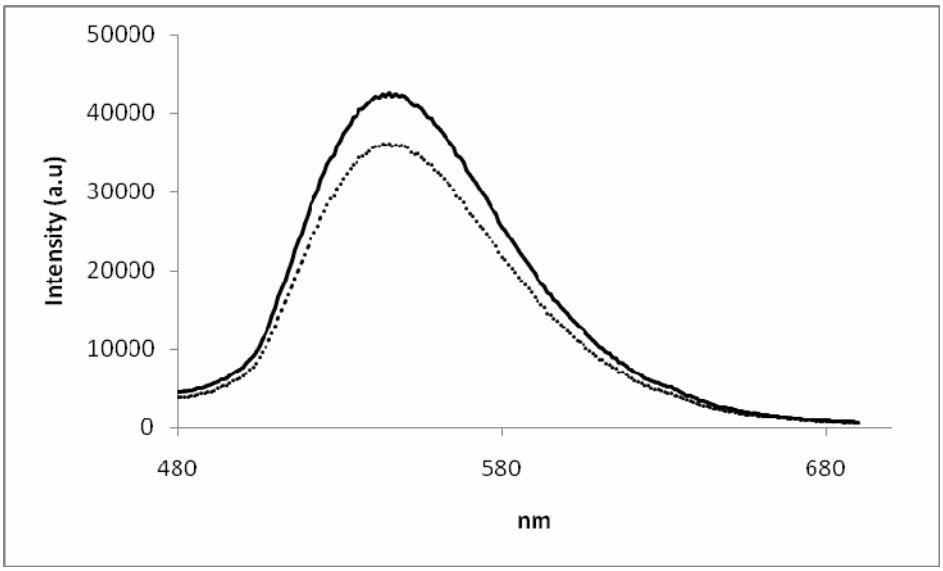

Figure 2. Fluorescent spectra of **6** (dark line) and **6** with ConA (dotted line) after 20 min, stirring at room temperature.

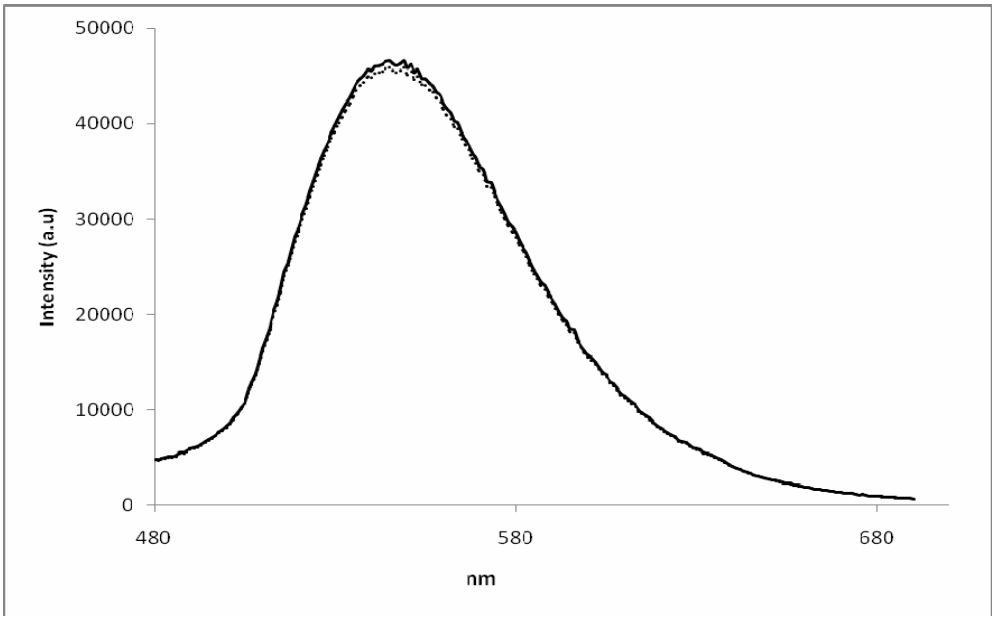

Figure 3. Fluorescent spectra of **7** (dark line) and **7** with ConA (dotted line) after 20 min stirring at room temperature.

Imaging Experiment :

The snapshot experiment was performed with 1 mM of **6** and **7** complex and 1 mg/mL (0.1 ml) of ConA lectin in HEPES buffer solution (10 mM Hepes pH 6.5, 1mM $MgCl_2$, 1mM $CaCl_2$, 1% BSA). Complex **6** showed turbidity with ConA after 10 mins. From Figure **3** it is quite clear

that visible view of the ConA with complex **6** clearly showed turbidity compared to other samples. However, the particles size was very small to see a significant differences in fluorescent view.

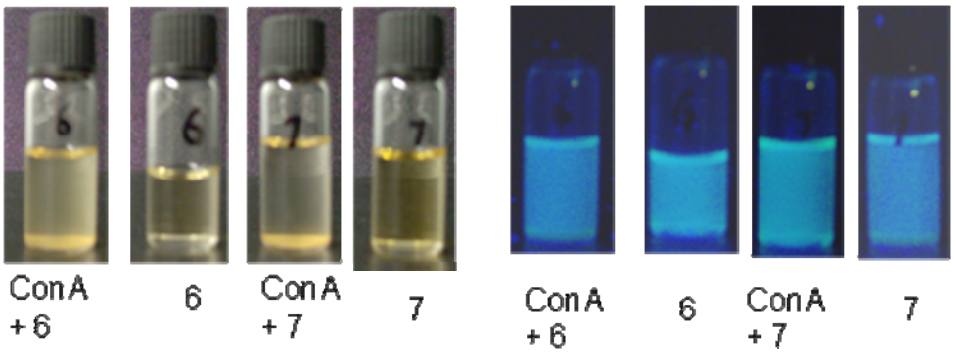

Figure 4. Visible and fluorescent images of the complex **6** & **7** in presence and absence of ConA lectin. Complex was excited by UV lamp at 365 nm.

8. References

1. Kieburg, C.; Sadalapure, K.; Lindhorst, T. K. *Eur. J. Org. Chem*. **2000**, 11, 2035.
2. Basu, P.; Nemykin, V.N.; Sengar, R. S. *Inorg. Chem.* **2003**, 42, 23, 7489.
3. Kikkeri, R.; Traboulsi, H.; Humbert, N.; Gumienna-K.E.; Arad-Yellin, R.; Melman, G.; Elhabiri, M.; Albrecht-Gary, A-M.; Shanzer, A. *Inorg. Chem.* **2007**, 46, 7, 2485.
4. C. Caris, P. Baret, J-L. Pierre, G. Serrtrice, *Tetrahedron,* 1996, **52,** 4659.
5. R.Kikkeri, K. Faustin, P.H.Seeberger, *J. Am. Chem. Soc.* Submitted
6. J. V. Caspar, T. J. Meyer, *J. Am. Chem. Soc.* **1983**, 105, 5583.