Multifunctionalized Glycolurils—Supporting Information

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General. All reagents were purchased from Aldrich Chemical Company and were used without further purification except as noted. Amino acid esters, PyBOP, and EDC•MeI were acquired from Novabiochem (San Diego, CA). Deuterated solvents were obtained from Cambridge Isotopes Laboratories and deuterated chloroform was dried over 4Å molecular sieves. HCl refers to a 1N stock solution. NMR spectra were recorded on either a Bruker AC-250, a Bruker AM-300, or a Bruker DRX-600; TMS was used as a reference in some chloroform-*d* spectra, otherwise residual solvent was used as a reference. Either a Finnegan Mat 8200 (for EI) *m/z* or a VG ZAB-VSE (for FAB) mass spectrometer was used to ascertain masses. FT-IR spectra were obtained on a Perkin Elmer Paragon 1000 PC FT-IR Spectrometer. Silica gel chromatography was performed with Silica Gel 60 (EM Science or Bodman, 230–400 mesh). TLC analysis was performed using glass-bound Silica Gel 60 (F254) plates. DMAP = *N*,*N*-dimethyl-4-aminopyridine, DPPA = diphenylphosphoryl azide, DRAK = diffuse reflectance accessory kit, EDC·MeI = 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide methiodide, PyBOP = benzotriazole-1-yl-oxy-tris-pyrrolidino-phosphonium hexafluorophosphate.

Dibenzyl 4,4'-bis(methoxycarboxylate)-benzil (7). To a flame-dried 1000 mL round-bottom flask was added 4,4'-dihydroxybenzil (30.00 g, 123.8 mmol), benzyl bromoacetate (102.2 g, 446 mmol), and 500 mL dry acetonitrile. This solution was stirred vigorously and potassium carbonate (84.8 g, 614 mmol) was added. The resulting suspension was stirred and refluxed under nitrogen for 24 hours. The insoluble salts were removed from the solution by filtration, then the acetonitrile solution was poured into ~1900 mL stirring water. The brown precipitate was removed by filtration and was washed thoroughly with diethyl ether. The solids were partially taken up in methylene chloride and then were precipitated with ether, yielding **11** (43.22 g, 65%) as a bright white powder. m.p. 121 °C (dec.) ^{1}H-NMR (300 MHz, $CDCl_3$): δ 4.74 (s, 4H), 5.24 (s, 4H), 6.95 (d, *J* = 8.9 Hz, 4H), 7.30–7.35 (m, 10H), 7.92 (d, *J* = 8.9 Hz, 4H). ^{13}C-NMR (76 MHz, $CDCl_3$): δ 65.28, 67.50, 115.04, 127.20, 128.76, 128.88, 132.57, 135.00, 162.96, 168.01, 193.31. HRMS (FAB, NBA/CsI) *m/z* calcd for $[C_{32}H_{26}O_8 + Cs]^+$ 671.0682 found 671.0664. FT-IR (neat) 1755, 1665, 1597, 1508, 1422, 1161, 1075, 884, 834, 753, 698 cm^{-1}.

Benzyl hydantoate (8). Glycine benzyl ester tosylate (60.1 g, 178 mmol) was dissolved in 250 mL hot ethanol. To this solution was added a solution of potassium cyanate (14.50 g, 179 mmol) in 250 mL water. The resulting clear solution was stirred at room temperature for 15 hours, then ~3/5 of the solution was removed by rotary evaporation and the white product **8** (34.33 g, 93%) crystallized from the remaining solution upon cooling. m.p. 119–121 °C. ^{1}H-NMR (600 MHz, DMSO-d_6): δ 7.37–7.31 (m, 5H), 6.29 (t, *J* = 5.7 Hz, 1H), 5.71 (s, 2H), 5.11 (s, 2H), 3.80 (d, *J* = 6.1 Hz, 2H).

Glycoluril tetrakis(benzyl ester) (4). Dibenzyl 4,4'-bis(methoxycarboxylate)-benzil **7** (10.78 g, 20.0 mmol), benzyl hydantoate **8** (10.42 g, 50.0 mmol), and trifluoroacetic acid (5 mL) were dissolved in 100 mL benzene. The solution was raised to reflux under a Dean-Stark trap in a nitrogen atmosphere, and was held there for 28 h. The solvent was removed by rotary evaporation and the residue was dissolved in chloroform and was washed with water until achieving neutral pH in the aqueous phase (washing with base caused a difficult emulsion) then was washed with brine. The organic phase was dried over magnesium sulfate and filtered, and the solvent was reduced by rotary evaporation. Ethanol was added to the mixture and the resulting solids were isolated by filtration. Recrystallization from ethanol yielded **4** (6.73 g, 56%) as brilliant white crystals. m.p. 103–106 °C. ^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.33–7.24 (m, 20H), 7.06 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.54 (d, *J* = 9.0 Hz, 2H), 6.50 (d, *J* = 9.0 Hz, 2H), 6.38 (s, 2H), 5.17–5.15 (m, 4H), 5.07–5.05 (m, 4H), 4.50 (s, 2H), 4.46 (s, 2H), 3.91 (d, *J* = 17.5 Hz, 2H), 3.59 (d, *J* = 17.5 Hz, 2H). ^{13}C-NMR (151 MHz, $CDCl_3$): δ 135.41, 135.34, 135.31, 129.79, 129.00, 128.94, 128.91, 128.88, 128.78, 128.76, 128.73, 125.19, 114.91, 114.31, 89.20, 80.77, 67.64, 67.20, 67.14, 65.12, 64.87, 43.11. HRMS (FAB, NBA/CsI) *m/z* calcd for $[C_{52}H_{46}N_4O_{12} + Cs]^+$ 1051.2167 found 1051.2123. FT-IR (DRAK, KBr) 3364, 3033, 1752, 1609, 1586, 1512, 1456, 1388, 1306, 1178, 1118, 1081, 1006, 962, 881, 837, 753, 699, 666 cm^{-1}.

Glycoluril tetraacid (1). Glycoluril tetrakis(benzyl ester) **4** (4.00 g, 4.35 mmol) was dissolved in 400 mL 1:1 EtOAc/MeOH and 10% palladium on activated carbon (412 mg, cat.) was added. The slurry was stirred under an atmosphere of hydrogen for 15 hours, and was then filtered through Celite. The filtrate was placed on a rotary evaporator and the solvent was removed, leaving a white foam. Compound **1** (2.53g, quant.) was isolated after further drying the foam under high vacuum. m.p. 126 °C (dec.) ^{1}H-NMR (600 MHz, DMSO-d_6): δ 12.65 (br. s, 4H), 8.09 (s, 2H), 6.96–6.93 (m, 4H), 6.65–6.62 m, 4H), 4.55 (s, 2H), 4.52 (s, 2H), 3.86 (d, *J* = 17.6 Hz, 2H), 3.59 (d, *J* = 17.6 Hz, 2H). ^{13}C-NMR (151 MHz, DMSO-d_6): δ 170.78, 170.01, 169.97, 159.14, 157.82, 157.52, 130.13, 129.31, 128.49, 126.09, 114.13, 113.40, 88.26, 79.66, 64.53, 64.47, 42.93. HRMS (FAB, NBA/CsI) *m/z* calcd for $[C_{24}H_{22}N_4O_{12} + Cs]^+$ 691.0289 found 691.0313. FT-IR (DRAK, KBr) 3375 (br., strong), 1720, 1513, 1479, 1305, 1228, 1075, 965, 838, 536 cm^{-1}.

Glycoluril bis(benzyl ester) (9). Dibenzyl 4,4'-bis(carboxymethoxy)benzil (43.82 g, 81.4 mmol) and urea (12.22 g, 203.5 mmol) were dissolved in 400 mL benzene. TFA (20 mL) was added and the solution was refluxed under a Dean-Stark trap in a nitrogen atmosphere for 16 h. EtOH was added to the cooled solution and the solid precipitate was isolated by filtration. The solids were purified by stirring overnight in boiling EtOH. The resulting solids were isolated by filtration and dried *in vacuo*, yielding **9** (36.97 g, 73%) as a white powder. m.p. 213–217 °C (dec.) ^{1}H-NMR (600 MHz, DMSO-d_6): δ 7.65 (s, 4H), 7.33–7.38 (m, 10H), 6.94 (d, *J* = 8.8 Hz, 4H), 6.65 (d, *J* = 8.8 Hz, 4H), 5.13 (s, 4H), 4.71 (s, 4H). ^{13}C-NMR (151 MHz, DMSO-d_6): δ 168.66, 160.79, 157.24, 135.82, 131.30, 128.60, 128.42, 128.34, 128.20, 113.55, 81.60, 65.98, 64.56. HRMS (FAB, NBA/CsI) *m/z* calcd for $[C_{34}H_{30}N_4O_8 + Cs]^+$ 755.1118 found 755.1148. FT-IR (neat) 3229.6, 1760.0, 1721.7, 1682.8, 1667.3, 1610.2, 1494.5, 1454.6, 1416.5, 1175.5, 1140.7, 1110.5, 1082.9, 1024.5, 955.0, 836.7, 736.1, 696.6 cm^{-1}.

Glycoluril diacid (2).

A. Saponification of bis(benzyl ester) **9**. To a stirred suspension of glycoluril bis(benzyl ester) **9** (1.00 g, 1.61 mmol) in 17.5 mL THF was added a solution of $LiOH \cdot H_2O$ (0.16 g, 3.9 mmol) in 3.5 mL water. The resulting mixture was vigorously stirred at RT for 17 h. The mixture was poured into 90 mL HCl. The resulting white solids were isolated by filtration and were dried at elevated temperature, yielding the diacid **2** (0.68 g, 96%). m.p. 287 °C (dec.) ^{1}H-NMR (600 MHz, DMSO-d_6): δ 12.92, (br. s, 2H), 7.66 (s, 4H), 6.95 (d, *J* = 8.8 Hz, 4H), 6.63 (d, *J* = 8.7 Hz, 4H), 4.53 (s, 4H). ^{13}C-NMR (151 MHz, DMSO-d_6): δ 170.00, 160.64, 157.23, 130.90, 128.28, 113.36, 81.59, 64.38. HRMS (FAB, NBA/NaI) *m/z* calcd for $[C_{20}H_{18}N_4O_8 + H]^+$ 443.1203 found 443.1233. FT-IR (DRAK, KBr) 3381, 3221 (br., v.s.), 2361, 1726, 1684, 1610, 1513, 1476, 1445, 1419, 1302, 1235, 1185, 1110, 1074, 954, 839, 780, 737, 634 cm^{-1}.

B. Condensation of 4,4'-bis(methoxycarboxylic acid) benzil **19** with urea. Benzil **19** (3.00 g, 8.37 mmol), urea (1.52 g, 25.3 mmol), and trifluoroacetic acid (2 mL) was dissolved in 40 mL benzene. The solution was refluxed under a Dean-Stark trap in a nitrogen atmosphere for 40 hours. Ethanol was added to the cooled solution and the undissolved white solids were removed by filtration. Drying at elevated temperatures overnight yielded **2** (3.42 g, 92%) as white solids.

***Cis*- and *trans*-glycoluril bis(benzyl esters) (10 and 11).** Benzyl hydantoate **8** (18.0 g, 86.4 mmol), benzil (6.00 g, 28.5 mmol), and trifluoroacetic acid (7.5 mL) were dissolved in 150 mL benzene. The solution was refluxed under a Dean-Stark trap in a nitrogen atmosphere for 20 hours. A precipitate was removed by filtration, then the filtrate was concentrated to a yellow oil by rotary evaporation, was taken up in chloroform, and was washed with brine until the aqueous phase was neutral. The organic layer was dried over magnesium sulfate, was filtered, and was concentrated again to a yellow oil. Sonication with methylene chloride/ether produced a yellow solution with white solids. The solids were isolated by filtration and were combined with the solids removed directly from the reaction solution and were recrystallized from hot ethanol. Upon cooling to room temperature, **10** (11.56 g, 69%) was isolated by filtration as white solids. Concentration of the mother liquor caused the precipitation of **11** (1.27 g, 8%). Compound **10**: m.p. 213–218 °C. ^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.31–7.27 (m, 10H), 7.20 (d, *J* = 6.8 Hz, 2H), 7.10–7.05 (m, 4H), 7.01 (d, *J* = 4.2 Hz, 4H), 6.28 (s, 2H), 5.15 (d, *J* = 12.0 Hz, 2H), 5.07 (d, *J* = 12.0 Hz, 2H), 3.97 (d, *J* = 17.5 Hz, 2H), 3.64 (d, *J* = 17.5 Hz, 2H). ^{13}C-NMR (151 MHz, $CDCl_3$): δ 136.34, 135.38, 132.15, 129.66, 129.26, 128.99, 128.91 (large), 128.78, 128.78, 128.53, 128.30, 127.56, 89.62, 81.04, 67.64, 43.30. HRMS (FAB, NBA/CsI) *m/z* calcd for $[C_{34}H_{30}N_4O_6 + Cs]^+$ 723.1220 found 723.1245. FT-IR (neat) 3252, 3064, 2248, 1707, 1450, 1388, 1307, 1191, 1144, 1012, 960, 940, 910, 877, 778, 734, 698 cm^{-1}. Compound **11**: ^{1}H-NMR (600 MHz, DMSO-d_6): δ 8.43 (s, 2H), 7.36–7.32 (m, 10H), 7.08–7.04 (m, 10H), 5.10 (d, *J* = 12.6 Hz, 2H), 3.90 (d, *J* = 17.8 Hz, 2H), 3.61 (d, *J* = 17.8 Hz, 2H). ^{13}C-NMR (151 MHz, DMSO-d_6): δ 168.82, 159.05, 136.07, 135.50, 128.62, 128.53, 128.15, 128.04, 127.87, 127.81, 83.92, 65.92, 42.24. HRMS (FAB, NBA/CsI) *m/z* calcd for $[C_{34}H_{30}N_4O_6 + Cs]^+$ 723.1220 found 723.1202.

Glycoluril diacid (3). To a stirred suspension of glycoluril bis(benzyl ester) **10** (0.590 g, 1.00 mmol) in 10 mL THF was added a solution of $LiOH{\bullet}H_2O$ (0.101 g, 2.40 mmol) in 2 mLH_2O. The mixture was stirred at RT for 15 h. The mixture was then poured into 50 mL HCl. The resulting solution was chilled at 5 °C for 24 hours, whereupon colorless crystals developed. The crystals were isolated by filtration and were dried at elevated temperature, yielding diacid **3** (0.388 g, 95%). m.p. 292–294 °C (dec.) ^{1}H-NMR (600 MHz, DMSO-d_6): δ 12.62 (br. s, 2H {integrated low}), 8.21 (s, 2H), 7.07 (s, 10H), 3.90 (d, *J* = 17.6 Hz, 2H), 3.62 (d, *J* = 17.6 Hz, 2H). ^{13}C-NMR (151 MHz, DMSO-d_6): δ 171.06, 159.54, 137.87, 133.96, 128.79, 128.38, 128.35, 128.19, 127.62, 127.51, 88.64, 79.90, 43.08. HRMS (FAB, NBA/NaI) *m/z* calcd for $[C_{20}H_{18}N_4O_6 + H]^+$ 411.1305 found 411.1317. FT-IR (DRAK, KBr) 3456.6, 3228.0 (br.), 1734.8, 1700.2, 1474.6, 1449.8, 1399.8, 1340.7, 1225.6, 1147.2, 985.8, 963.9, 944.5, 780.7, 703.7, 667.9 cm^{-1}.

Glycoluril bis(pentafluorophenyl ester) (13). To a stirred suspension of glycoluril diacid **3** (1.00 g, 2.44 mmol) in 100 mL THF was added pentafluorophenol (1.80 g, 9.76 mmol), EDC·MeI (3.12 g, 10.5 mmol) and catalytic DMAP. The mixture was stirred at RT for 14 h. The solvent was removed by rotary evaporation and the resulting paste was sonicated in EtOAc and filtered to remove insoluble material. The filtrate was run through a plug of silica gel with EtOAc. The filtrate was concentrated and sonicated in Et_2O to remove pentafluorophenol. The white powder was isolated by filtration, rinsed with Et_2O and dried *in vacuo*, yielding the diester **13** (1.42 g, 79%). ^{1}H-NMR (600 MHz, DMSO-d_6): δ 8.58 (s, 2H), 7.15–7.03 (m, 10H), 4.77 (d, *J* = 18.4 Hz, 2H), 4.38 (d, *J* = 18.4 Hz, 2H). ^{13}C-NMR (151 MHz, DMSO-d_6): δ 166.77, 159.03, 141.52 (m), 139.83 (m), 138.54 (m), 137.06, 136.89 (m), 133.31, 129.08, 128.55, 127.79, 127.69, 127.31, 88.34, 80.48, 42.39. ^{19}F-NMR (565 MHz, DMSO-d_6): δ -152.61 (d, *J* = 24 Hz), -157.44 (t, *J* = 24 Hz), -162.16 (t, *J* = 24 Hz). HRMS (FAB, NBA/CsI) *m/z* calcd for $[C_{32}H_{16}F_{10}N_4O_6 + Cs]^+$ 874.9964 found 875.0004. FT-IR (neat) 1788.7, 1714.4, 1521.7, 1450.0, 1103.7, 998.1 cm^{-1}.

Glycoluril bis(leucine t-butyl ester) adduct (14).

A. Reaction of bis(pentafluorophenyl ester) **13**. To a solution of leucine *t*-butyl ester hydrochloride (34.8 mg, 0.155 mmol) in 1 mL DMF and 0.5 mL Et_3N chilled in an ice bath was added a partial solution/suspension of glycoluril bis(pentafluorophenyl ester) **13** (50.4 mg, 0.0683 mmol) in 3.5 mL CH_2Cl_2. The solution warmed over 2.5 h, then was diluted with CH_2Cl_2 and was washed with water (3x) and brine (3x). The organic phase was dried over $MgSO_4$, was filtered, and was concentrated by rotary evaporation to pale yellow solids which were dried *in vacuo*, yielding **14** (53 mg, quant.). ^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.24–7.21 (m, 2H), 7.16–6.97 (m, 10H), 6.85 (br. s, 1H), 6.78 (br. s, 1H), 4.41–4.37 (m, 2H), 3.95 (d, *J* = 16.3 Hz, 1H), 3.82 (s, 2H), 3.65 (d, *J* = 16.5 Hz, 1H), 1.70–1.46 (m, 6H), 1.44 (s, 9H), 1.42 (s, 9H), 0.95 (d, *J* = 6.6 Hz, 3H), 0.93 (d, *J* = 6.5 Hz, 3H), 0.93 (d, *J* = 6.4 Hz, 3H), 0.88 (d, *J* = 6.4 Hz, 3H). ^{13}C-NMR (151 MHz, $CDCl_3$): δ 172.57, 172.41, 168.57, 168.52, 160.98, 160.59, 136.57, 131.90, 129.51, 129.38, 129.00, 128.82, 1283.63, 128.27, 127.57, 123.48, 120.50, 120.47, 90.79, 82.10, 82.02, 80.69, 51.93, 51.75, 45.96, 45.79, 41.46, 41.33, 28.08, 28.06, 25.00, 24.98, 22.83, 22.74, 22.33, 22.21. HRMS (FAB, NBA/CsI) *m/z* calcd for $[C_{40}H_{56}N_6O_8 + Cs]^+$ 881.3214 found 881.3236. FT-IR (neat) 3242.3, 2958.7, 1701.9, 1458.4, 1150.0 cm^{-1}.

B. Reaction of diacid **3** with DPPA. A stirred solution of glycoluril diacid **3** (200 mg, 0.487 mmol) and leucine *t*-butyl ester hydrochloride (240 mg, 1.07 mmol) in 2 mL DMF was chilled in a salt/ice bath. To this solution was added diphenylphosphoryl azide (231 μL, 294 mg, 1.07 mmol) and Et_3N, (298 μL, 217 mg, 2.14 mmol) and the solution was stirred 17 h, warming to RT. The solvent was removed by rotary evaporation and the residue was taken up in EtOAc and was washed with water (2x) and brine (3x). The organic phase was dried over $MgSO_4$, was filtered, and was concentrated by rotary evaporation to an off-white foam (323 mg, 88%).

Glycoluril bis(leucine) adduct (15). Glycoluril bis(leucine t-butyl ester adduct) **14** (45 mg, 0.060 mmol) was stirred in 5 mL TFA for 15 h. The TFA was removed by rotary evaporation and the resulting oil was sonicated in 1:1 Et_2O:hexane. The resulting precipitate was isolated by filtration and was rinsed with Et_2O, yielding a white powder (34 mg, 86%). ^{1}H-NMR (600 MHz, DMSO-d_6): δ 8.27 (s, 1H), 8.25 (s, 1H), 7.96 (d, *J* = 7.9 Hz, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.09–7.02 (m, 10H), 4.28–4.26 (m, 2H), 3.85 (d, *J* = 16.6 Hz, 1H), 3.66 (d, *J* = 16.8 Hz, 1H), 3.53 (d, *J* = 16.7 Hz, 1H), 3.52 (d, *J* = 16.8 Hz, 1H), 1.79–1.70 (m, 1H), 1.70–1.62 (m, 1H), 1.55–1.48 (m, 4H), 0.92–0.85 (m, 12H). ^{13}C-NMR (151 MHz, DMSO-d_6): δ 174.42, 174.19, 168.47, 168.39, 159.73, 159.69, 137.62, 133.37, 128.72, 128.26, 127.49, 127.36, 89.12, 79.61, 50.30, 45.77, 44.22, 44.05, 40.28, 24.21, 22.85, 22.79, 21.41, 8.58. LRMS (FAB, NBA/CsI) *m/z* calcd for $[C_{32}H_{40}N_6O_8 + Cs]^+$ 769 found 769.

Diethyl 4,4’-bis(methoxycarboxylate)-benzil (18). To a flame-dried 1000 mL round-bottom flask was added 4,4’-dihydroxybenzil (29.0 g, 120 mmol), ethyl bromoacetate (101.1 g, 598 mmol), and 500 mL dry acetonitrile. This solution was stirred vigorously and potassium carbonate (83.1 g, 601 mmol) was added. The resulting suspension was stirred and refluxed under nitrogen for 24 hours. The insoluble salts were removed from the solution by filtration, then the acetonitrile solution was poured into ~1400 mL stirring water. The orange precipitate was removed by filtration and was washed thoroughly with diethyl ether. The solids were crystallized from EtOH, yielding **18** (39.59 g, 80%) as pale yellow crystals. ^{1}H-NMR (600 MHz, CDCl$_3$): δ 7.96–7.94 (m, 4H), 6.99–6.96 (m, 4H), 4.70 (s, 4H), 4.28 (q, *J* = 7.1 Hz, 4H), 1.30 (t, *J* = 7.1 Hz, 6H). ^{13}C-NMR (151 MHz, CDCl$_3$): δ 193.33, 168.14, 163.09, 132.60, 127.24, 115.05, 65.37, 61.93, 14.35. HRMS (FAB, NBA/CsI) *m/z* calcd for [C$_{22}$H$_{22}$O$_8$ + Na]$^+$ 437.1212 found 437.1206. FT-IR (neat) 2983.8, 1755.0, 1667.3, 1597.7, 1576.1, 1509.1, 1205.7, 1162.1, 1076.1, 885.6, 843.9, 607.3 cm^{-1}.

4,4'-bis(Methoxycarboxylic acid) benzil (19). Diester **18** (12.0 g, 29.0 mmol) was dissolved in 250 mL THF. To this solution was added a solution of lithium hydroxide monohydrate (2.92 g, 70.0 mmol) in 50 mL water. The resulting biphasic solution was vigorously stirred for 15 h. After this period, solids had developed. The slurry was poured into 1400 mL 1M HCl and bright yellow solids formed. This material was removed by filtration and dried at 50 °C overnight, yielding **19** as a dry yellow powder (9.99 g, 96%). m.p. 225–227 °C. ^{1}H NMR (DMSO-*d*$_6$, 600 MHz): δ 13.22 (br. s, 2H), 7.86 (d, *J* = 9.0 Hz, 4H), 7.11 (d, *J* = 9.0 Hz, 4H), 4.85 (s, 4H). ^{13}C NMR (DMSO-*d*$_6$, 151 MHz): δ 193.85, 169.83, 163.56, 132.22, 125.98, 115.53, 64.76. FT-IR (KBr pellet) 2913.5, 1748.0, 1709.9, 1663.0, 1601.5, 1577.1, 1507.4, 1419.7, 1312.9, 1252.6, 1171.7, 882.9, 846.4 cm^{-1}. HRMS (FAB in NBA/NaI) *m/z* calcd for [C$_{18}$H$_{15}$O$_8$ +H]$^+$ 359.0767 found 359.0756.

4,4'-bis(Methoxy carboxylic acid chloride) benzil (20). Diacid **19** (6.00 g, 16.7 mmol) and oxalyl chloride (5.8 mL, 8.4 g, 66 mmol) were stirred in 240 mL methylene chloride. To the stirred suspension was added 8 drops of a 4% solution of DMF in methylene chloride. The mixture was refluxed for 9 h. The resulting solution was filtered through Celite and the solvent was removed by rotary evaportation. The residue was taken up in toluene and the solvent was again removed. Drying under high vacuum for 2 h yielded **20** as a yellow powder (6.18 g, 93%). m.p. 99–102 °C. ^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.99 (d, *J* = 8.8 Hz, 4H), 6.99 (d, *J* = 8.7 Hz, 4H), 5.05 (s, 4H). ^{13}C NMR (CDCl$_3$, 151 MHz): δ 193.06, 169.68, 162.01, 132.84, 128.02, 115.18, 72.08. FT-IR (neat) 2908.6, 2359.2, 1804.6, 1667.4, 1597.6, 1578.5, 1508.6, 1418.0, 1309.7, 1269.6, 1222.6, 1164.6, 945.8, 884.7, 840.8, 766.9, 736.8 cm^{-1}. Sample too labile for mass spectral analysis.

4,4'-bis[(2,2,2-Trichloroethyl)methoxycarboxylate] benzil (21). In an ice bath at 0 °C, diacid chloride **20** (5.00 g, 12,7 mmol) was dissolved in 150 mL methylene chloride. To this chilled solution was added a solution of 2,2,2-trichloroethanol (2.7 mL, 4.2 g, 28 mmol) and triethylamine (7.1 mL, 5.2 g, 51 mmol) in 100 mL methylene chloride. The resulting solution was stirred under nitrogen, slowly warming to room temperature over the course of 14 h. The solution was then diluted with more methylene chloride and was washed thrice with HCl and once with brine. The organic phase was dried over magnesium sulfate, filtered, and the solvent was removed by rotary evaporation. Sonication of the resulting amber oil in 1:1 ether/hexane yielded, upon filtration, **21** as a pale yellow powder (6.67 g, 85%). m.p. 101–103 °C. ^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.95 (d, *J* = 8.5 Hz, 4H), 7.01 (d, *J* = 8.8 Hz, 4H), 4.89 (s, 4H), 4.86 (s, 4H). ^{13}C NMR (CDCl$_3$, 151 MHz): δ 193.33, 166.94, 162.85, 132.71, 127.55, 115.16, 94.44, 74.36, 64.79. HRMS (FAB in NBA/CsI) *m/z* calcd for [C$_{22}$H$_{16}$Cl$_6$O$_8$ + Cs]$^+$ 750.8031, found 750.8001. FT-IR (neat) 2958.7, 1775.1, 1770.8, 1667.7, 1598.6, 1509.1, 1276.0, 1224.2, 1159.5, 1071.1, 728.7 cm^{-1}.

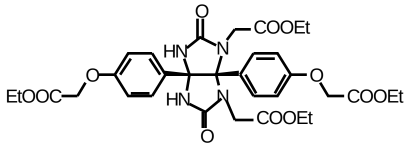
bis(Trichloroethyl ester)/bis(benzyl ester) glycoluril (16). Diketone **21** (7.00 g, 11.3 mmol) and benzyl hydantoate **8** (7.03 g, 33.8 mmol) were stirred in 120 mL benzene. The addition of 6 mL trifluoroacetic acid caused all solids to dissolve. The solution was refluxed under a Dean-Stark trap for 46 h. The hydantoin byproduct was removed from the raw reaction mixture by filtration and the solvent and trifluoroacetic acid was removed by rotary evaporation. Purification of the yellow oil by silica gel chromatography (40:1 methylene chloride/methanol) yielded **16** as a white powder (3.98 g, 35%). m.p. 141–144 °C. ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.35–7.29 (m, 10H), 7.13 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 6.65 (d, *J* = 9.0 Hz, 2H), 6.59 (d, *J* = 8.9 Hz, 2H), 6.09 (s, 2H), 5.19 (d, *J* = 12.0 Hz, 2H), 5.11 (d, *J* = 12.1 Hz, 2H), 4.84 (s, 2H), 4.76 (s, 2H), 4.69 (s, 4H), 3.96 (d, *J* = 17.5 Hz, 2H), 3.64 (d, *J* = 17.5 Hz, 2H). ^{13}C NMR (CDCl$_3$, 151 MHz): δ 169.11, 167.64, 167.37, 159.55, 158.37, 158.02, 135.37, 130.00, 129.89, 129.07, 128.91 (2 peaks), 128.78, 125.51, 115.02, 114.43, 94.63, 94.59, 89.21, 80.84, 74.22, 74.16, 67.67 (2 peaks), 64.70, 64.46, 43.12. HRMS (FAB , NBA/CsI) *m/z* calcd for [C$_{42}$H$_{36}$Cl$_6$N$_4$O$_{12}$ + Cs]$^+$ 1132.9486 found 1132.9428. FT-IR (neat) 3366.4, 3255.2, 1735.0, 1609.9, 1512.4, 1457.4, 1175.9, 729.3 cm^{-1}.

bis(Benzyl ester) diacid glycoluril (17). Glycoluril **16** (1.33 g, 1.33 mmol) was dissolved in 40 mL acetic acid, 9 mL THF, and 4.5 mL water. As the solution was stirred in an ice bath at 0 °C, zinc dust (0.67 g, 10.2 mmol) was added. The suspension was stirred at 0 °C for 2.5 h, then the zinc was removed by filtration. The filtrate was poured into 300 mL water. A white precipitate developed and was isolated by filtration after the mixture was chilled in a refrigerator overnight. The filter cake was dried under high vacuum, yielding **17** as a white powder (0.83 g, 85%). m.p. 235–237 °C (dec). ^{1}H NMR (DMSO-*d*$_6$, 600 MHz): δ 12.95 (br. s, 2H), 8.23 (s, 2H), 7.40–7.31 (m, 10H), 6.91 (d, *J* = 9.0 Hz, 2H), 6.90 (d, *J* = 9.0 Hz, 2H), 6.59 (d, *J* = 8.8 Hz, 2H), 6.58 (d, *J* = 8.8 Hz, 2H), 5.20 (d, *J* = 12.6 Hz, 2H), 5.13 (d, *J* = 12.6 Hz, 2H), 4.55 (s, 2H), 4.52 (s, 2H), 4.11 (d, *J* = 17.7 Hz, 2H), 3.79 (d, *J* = 17.7 Hz, 2H). ^{13}C NMR (DMSO-*d*$_6$, 151 MHz): δ 170.20, 170.17, 169.65, 159.28, 158.04, 157.75, 136.08, 129.98, 129.36, 128.60 (overlapping peaks), 128.20, 128.04 (two peaks), 127.53, 125.93, 114.22, 113.49, 88.24, 80.02, 66.04, 64.45, 42.95. HRMS (FAB in NBA/CsI) *m/z* calcd for $[C_{38}H_{34}N_4O_{12} + Cs]^+$ 871.1228 found 871.1265. FT-IR (neat) 1717.2, 1511.4, 1472.5, 1213.5, 1181.2, 1071.7, 836.1, 699.4 cm^{-1}.

N-α-Boc-L-glycine-α-2,2,2-trichloroethyl ester (25). N-Boc-glycine-*p*-nitrophenyl ester (15.39 g, 51.9 mmol) (NovaBiochem) and 2,2,2-trichloroethanol (7.5 mL, 11.7 g, 77.9 mmol) were dissolved in 200 mL dichloromethane. Upon the addition of triethylamine (11 mL, 8.0 g, 79 mmol) a deep yellow color formed, and the solution was stirred for 15 hours. The solution was then extracted with saturated sodium bicarbonate solution until the yellow color disappeared. The organic phase was dried over magnesium sulfate and filtered, then the solvent was removed by rotary evaporation. Upon drying the resulting oil by exposure to high vacuum, **25** (14.14 g, 89%) was isolated as an off white solid. ^{1}H-NMR (600 MHz, $CDCl_3$): δ 5.11 (br. t, 1H), 4.80 (s, 2H), 4.07 (d, *J* = 5.8 Hz, 2H), 1.46 (s, 9H). LRMS (FAB, NBA/NaI) *m/z* calcd for $[C_9H_{14}Cl_3NO_4 + H]^+$ 306/308, $[C_9H_{14}Cl_3NO_4 + Na]^+$ 328/330 found 306/308, 328/330.

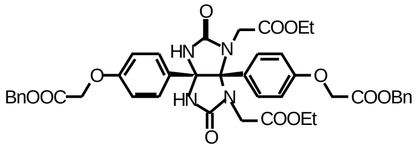
Glycine-α-2,2,2-trichloroethyl ester, trifluoroacetic acid adduct (26). Compound **25** (14.14 g, 46.13 mmol) was dissolved in a solution of 50 mL trifluoroacetic acid and 50 mL dichloromethane and the solution was stirred for 40 minutes. The solvent was removed by rotary evaporation and the resulting oil was crystallized from cold ether/hexane, yielding **26** (13.36 g, 90%) as white crystals. m.p. 85–86 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.50 (br. s, 3H), 4.83 (s, 2H), 4.04 (s, 2H).

2,2,2-Trichloroethyl-glycylurea (23). A solution of **26** (10.00 g, 31.2 mmol) in 25 mL ethanol was added to a solution of potassium cyanate (2.61 g, 32.2 mmol) in 50 mL water. The solution was stirred at room temperature for 16 hours. White solids formed after 2 hours. Most of the ethanol was removed by rotary evaporation; at the elevated temperatures of the water bath the solids redissolved. Upon cooling in a refrigerator the compound again crystallized. Isolation of this material by filtration followed by rinsing with water and drying at elevated temperatures yielded **23** (6.68 g, 86%) as white, mica-like crystals. m.p. 91–93 °C. ^{1}H-NMR (600 MHz, DMSO-d_6): δ 6.40 (t, *J* = 5.8 Hz, 1H), 5.76 (s, 2H), 4.89 (s, 2H), 3.91 (d, *J* = 6.2 Hz, 2H). ^{13}C-NMR (151 MHz, DMSO-d_6): δ 170.41, 158.83, 95.33, 73.36, 41.22. HRMS (FAB, NBA/NaI) *m/z* : calcd for $[C_5H_7Cl_3N_2O_3 + H]^+$ 250.9517 found 250.9579. FT-IR (neat) 3445.4, 3397.1, 3222.5, 2360.2, 2341.5, 1756.9, 1654.7, 1618.2, 1526.9, 1380.4, 1341.3, 1270.1, 1167.1, 877.2, 800.8, 720.3, 668.0 cm^{-1}.



27

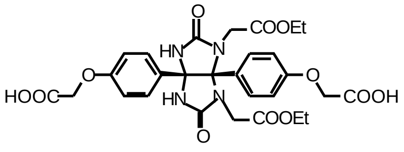
Glycoluril tetrakis(ethyl ester) (27). To 200 mL benzene was added diethyl 4,4’-bis(methoxycarboxylate)-benzil **18** (20.00 g, 48.30 mmol) and ethyl hydantoate (20.0 g, 137 mmol). Trifluoroacetic acid (10 mL) was added and the solution was refluxed with a Dean-Stark trap for 48 hours. The solvent was removed by rotary evaporation, then the residue was taken up in a minimum of chloroform and was washed with water (3x) and brine (1x). The organic phase was dried over $MgSO_4$, filtered, and the solvent was removed by rotary evaporation. The resulting orange oil was crystallized from hot EtOH/EtOAC (2:1) to yield **27** (14.51 g, 45%) as colorless microcrystalls in two crops. ^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.11 (d, *J* = 9.0 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 6.62 (d, *J* = 8.9 Hz, 2H), 6.60 (d, *J* = 9.0 Hz, 2H), 6.35 (s, 2H), 4.52 (s, 2H), 4.50 (s, 2H), 4.25–4.12 (m, 8H), 3.92 (d, *J* = 17.5 Hz, 2H), 3.60 (d, *J* = 17.5 Hz, 2H), 1.30–1.23 (m, 12H). ^{13}C-NMR (151 MHz, $CDCl_3$): δ 169.11, 168.88, 168.59, 159.36, 158.49, 158.12, 129.74, 129.69, 128.91, 125.14, 114.82, 114.16, 89.14, 80.76, 65.19, 64.96, 62.02, 61.61, 43.16, 14.33, 14.30, 14.26. HRMS (FAB, NBA/CsI) *m/z* : calcd for $[C_{32}H_{38}N_4O_{12} + Cs]^+$ 803.1541 found 803.1521. FT-IR (neat): 3351.7, 2983.0, 2252.4, 1731.8, 1609.9, 1512.7, 1462.8, 1305.6, 1204.3, 1182.9, 1082.4, 1027.6, 835.9, 730.5 cm^{-1}.



28

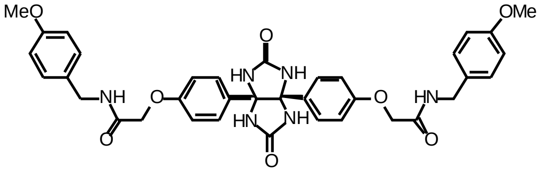
Glycoluril bis(ethyl ester) bis(benzyl ester) (28). Dibenzyl 4,4’-bis(methoxycarboxylate)-benzil (**5**) (5.00 g, 9.29 mmol), ethyl hydantoate (4.06 g, 27.8 mmol), and trifloroacetic acid (2.5 mL) were dissolved in 50 mL benzene. The solution was refluxed under a Dean-Stark trap in a nitrogen atmosphere for 14 hours. The solution was diluted with 200 mL chloroform and was extracted with water, saturated sodium bicarbonate solution (caused a bad emulsion), and brine. The organic layer was dried over magnesium sulfate and was filtered. The solvent was removed by rotary evaporation and the residue was crystallized from 2:1 EtOH/EtOAc, yielding **28** (4.46 g, 60%) as white microcrystals. m.p. 146–149 °C. ^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.36–7.31 (m, 10H), 7.09 (d, *J* = 9.0 Hz, 2H), 6.93 (d, *J* = 9.0 Hz, 2H), 6.61 (d, *J* = 9.0 Hz, 2H), 6.58 (s, *J* = 9.0 Hz, 2H), 6.39 (s, 2H), 5.17 (s, 2H), 5.07 (s, 2H), 4.53 (s, 2H), 4.52 (s, 2H), 4.20–4.14 (m, 4H), 3.91 (d, *J* = 17.5 Hz, 2H), 3.59 (d, *J* = 17.5 Hz, 2H), 1.23 (t, *J* = 7.1 Hz, 6H). ^{13}C-NMR (151 MHz,

$CDCl_3$): δ 169.10, 168.70, 168.45, 159.39, 158.42, 158.06, 135.21, 135.19, 129.72, 129.70, 128.90, 128.83, 128.78, 128.68, 128.63, 125.15, 114.84, 114.22, 89.15, 80.75, 67.22, 67.17, 65.12, 64.92, 62.04, 43.15, 14.25. HRMS (FAB, NBA/CsI) *m/z* calcd for $[C_{42}H_{42}N_2O_{12} + Cs]^+$ 927.1854 found 927.1819. FT-IR (neat): 3356.8, 2982.16, 2252.3, 1731.9, 1609.9, 1512.6, 1455.9, 1306.3, 1180.0, 1081.9, 1028.0, 912.5, 835.7, 733.6, 698.8 cm^{-1}.



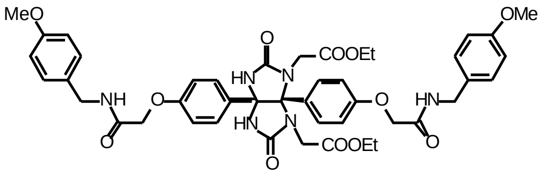
29

Glycoluril bis(ethyl ester) diacid (29). To a solution of **28** (1.00 g, 1.26 mmol) in 80 mL ethyl acetate and 20 mL ethanol was added 10% palladium on carbon (0.125 g). The flask was evacuated and backfilled with hydrogen three times, then the suspension was stirred under hydrogen overnight. The solution was filtered through Celite, then the solvent was removed by rotary evaporation. The resulting clear foamy oil was redissolved in ethyl acetate, and precipitation with hexane yielded **29** (0.72 g, 93%) as white powder. ^{1}H-NMR (600 MHz, DMSO-d_6): δ 12.95 (br. s, 2H), 8.18 (s, 2H), 6.94–6.91 (m, 4H), 6.65 (d, *J* = 9.0 Hz, 2H), 6.63 (d, *J* = 9.0 Hz, 2H), 4.56 (s, 2H), 4.53 (s, 2H), 4.13–4.09 (m, 4H), 4.39 (d, *J* = 17.6 Hz, 2H), 3.68 (d, *J* = 17.6 Hz, 2H), 1.20 (t, *J* = 7.1 Hz, 2H). ^{13}C NMR (DMSO-d_6, 151 MHz): δ 169.96, 169.93, 169.41, 159.01, 157.85, 157.60, 129.84, 129.18, 128.45, 125.74, 114.13, 113.41, 88.08, 79.97, 64.45, 60.64, 42.90, 14.03. HRMS (FAB, NBA/CsI) *m/z* calcd for $[C_{28}H_{30}N_4O_{12} + Cs]^+$ 747.0915 found 747.0935. FT-IR (DRAK, KBr) 3588.2, 3204.0, 1718.7, 1609.9, 1512.6, 1309.2, 1231.8, 1069.7, 1025.1, 885.7, 835.3, 774.5 cm^{-1}.



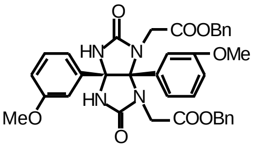
30

Glycoluril bis(4-methoxybenzyl amide) (30). To a suspension of glycoluril diacid **2** (0.200 g, 0.452 mmol) in 10 mL DMF was added N-methylmorpholine (104 µL, 0.096 g, 0.97 mmol), PyBOP (0.470 g, 0.903 mmol), and 4-methoxybenzylamine (124 µL, 0.130 g, 0.949 mmol). The resulting solution was stirred under nitrogen for 15 h. The solvent was removed by rotary evaporation and the residue was taken up in methylene chloride and insoluble material was isolated by filtration, yielding **30** (0.286 g, 93%) as white solids. ^{1}H-NMR (600 MHz, DMSO-d_6): δ 8.51 (t, *J* = 5.9 Hz, 2H), 7.69 (s, 4H), 7.16 (d, *J* = 8.6 Hz, 4H), 6.97 (d, *J* = 8.8 Hz, 4H), 6.86 (d, *J* = 8.6 Hz, 4H), 6.68 (d, *J* = 8.9 Hz, 4H), 4.67 (s, 4H), 4.22 (d, *J* = 5.9 Hz, 4H), 3.72 (s, 6H). ^{13}C NMR (DMSO-d_6, 151 MHz): δ 167.29, 160.63, 158.23, 157.12, 131.25, 131.12, 128.70, 128.29, 113.65, 81.56, 66.87, 55.08, 41.24. HRMS (FAB in NBA/CsI) *m/z* calcd for $[C_{36}H_{36}N_6O_8 + Cs]^+$ 813.1649 found 813.1628. FT-IR (DRAK, KBr: 3234.2, 1722.5, 1671.8, 1611.1, 1512.9, 1302.6, 1248.7, 1179.3, 110.6, 837.4, 778.4, 526.8 cm^{-1}.



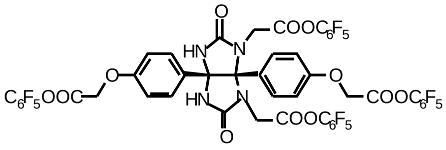
31

Glycoluril bis(ethyl ester) bis(4-methoxybenzyl amide) (31). To a solution of glycoluril diacid **29** (0.100 g, 0.163 mmol), in 5 mL DMF was added PyBOP (0.170 g, 0.327 mmol), N-methylmorpholine (37 µL, 34 mg, 0.336 mmol), and 4-methoxybenzylamine (43 µL, 45 mg, 0.329 mmol). The resulting clear solution was stirred at RT under nitrogen for 6 h. The solution was then poured into HCl and a white precipitate formed. The suspension was extracted with three portions of EtOAc, then the organic was washed with 1M NaOH (3x) and brine (3x). Solids insoluble in either layer after the final wash were removed by filtration, yielding **31** (0.096 g, 70%) as a white powder. ^{1}H-NMR (600 MHz, DMSO-d_6): δ 8.50 (t, *J* = 6.0 Hz, 2H), 8.20 (s, 2H), 7.15 (dd, *J* = 8.3, 6.6 Hz, 4H), 6.95 (dd, *J* = 11.0, 8.6 Hz, 4H), 6.87–6.84 (m, 4H), 6.69 (dd, *J* = 13.9 Hz, 8.7 Hz, 4H), 4.39 (br. s, 2H), 4.37 (br. s, 2H), 4.23–4.22 (m, 4H), 4.13–4.09 (m, 4H), 3.99 (d, *J* = 17.6 Hz, 2H), 3.72 (s, 6H), 3.67 (d, *J* = 17.6 Hz, 2H), 1.21–1.16 (m, 6H). LRMS (FAB, NBA/CsI) *m/z* calcd for $[C_{44}H_{48}N_6O_{12} + Cs]^+$ 985 found 985.



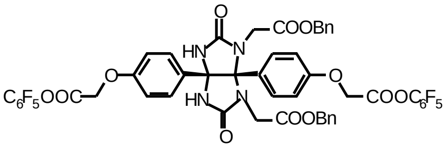
32

bis(3-Methoxyphenyl)/dibenzyl ester glycoluril (32). Benzyl hydantoate **8** (9.22 g, 44.3 mmol) and 3,3'-dimethoxybenzil (4.00 g, 14.8 mmol) were refluxed in a solution of 120 mL benzene and 6 mL trifluoroacetic acid under a Dean-Stark trap for 24 h. After cooling, the solution was filtered to remove hydantoin byproduct and the solvent was removed by rotary evaporation. The residue was taken up in methylene chloride and the solution was washed thrice with water and once with satd. NaCl soln. The organic layer was dried over magnesium sulfate, filtered, and the solvent was removed by rotary evaporation. Sonication of this yellow oil in ethyl acetate caused the release of a white solid. Isolation by filtration followed by drying at elevated temperature yielded **32** (4.25 g, 44%) as a white powder. m.p. 177–181 °C. ^{1}H NMR (DMSO-d_6, 600 MHz): δ 8.37, (br. s, 2H), 7.39–7.31 (m, 10H), 7.05 (t, *J* = 7.9 Hz, 1H), 6.97 (t, *J* = 8.0 Hz, 1H), 6.73–6.58 (m, 6H), 5.17 (br. s, 4H), 4.16 (b., 2H), 3.84 (b., 2H), 3.55 (s, 3H), 3.36 (s, 3H). ^{13}C NMR (DMSO-d_6, 151 MHz): δ 169.69, 159.31, 158.67, 139.12, 136.04, 135.28, 129.30, 128.57, 128.54, 128.18, 128.01, 119.92, 119.77, 115.77, 114.26, 112.99, 112.64, 88.38, 80.06, 66.08, 54.87, 54.62, 43.00. HRMS (FAB, NBA/CsI) *m/z* calcd for $[C_{36}H_{35}N_4O_8 + Cs]^+$ 651.2455 found 651.2478. FT-IR (neat): 3245.4, 1706.2, 1602.8, 1465.5, 1265.5, 1187.6, 946.7, 734.3 cm^{-1}.



33

Glycoluril tetrakis(pentafluorophenyl ester) (33). A solution of glycoluril tetraacid (200 mg, 0.358 mmol), pentafluoro-phenol (527 mg, 2.86 mmol), EDC·MeI (847 mg, 2.85 mmol), and catalytic DMAP in 20 mL THF was stirred at RT for 8 h. The solvent was removed by rotary evaporation and the residue was taken up in EtOAc and shaken. Insoluble material was removed by filtration and the filtrate was concentrated and purified by silica gel chromatography (100% EtOAc). Product-containing fractions were combined and concentrated by rotary evaporation. Excess pentafluorophenol co-eluted with the product and was removed by sonicating the resulting oil in Et_2O. White solids were isolated by filtration and were dried *in vacuo* (62 mg, 15%). ^{1}H-NMR (600 MHz, DMSO-d_6): δ 8.53 (s, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 6.98 (d, *J* = 8.7 Hz, 2H), 6.76 (d, *J* = 8.3 Hz, 4H), 5.22 (s, 2H), 5.21 (s, 2H), 4.77 (d, *J* = 18.3 Hz, 2H), 4.37 (d, *J* = 18.3 Hz, 2H). HRMS (FAB, NBA/CsI) *m/z* calcd for $[C_{48}H_{18}F_{20}N_4O_{12} + H]^+$ 1223.0680 found 1223.0609.



34

Glycoluril bis(benzyl ester)/bis(pentafluorophenyl ester) (34). Glycoluril diacid **17** (148 mg, 0.200 mmol) and pentafluorophenol (155 mg, 0.842 mmol) were dissolved in 18 mL THF and 2 mL DMF. To this stirred solution were added EDC·MeI (256 mg, 0.861 mmol) and DMAP (cat.). After stirring under nitrogen at RT for 17 h the solvent was removed by rotary evaporation. The resulting oil was taken up in EtOAc and was washed with water (2x) and brine (1x). The organic phase was dried over $MgSO_4$, filtered, and concentrated to a pale yellow oil *in vacuo*. The oil was purified by silica gel column chromatography (1:1 hexane:EtOAc). A clear oil crystallized upon sitting to give **34** (59 mg, 28%) as colorless crystals. ^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.30–7.27 (m, 10H), 7.13 (d, *J* = 8.9 Hz, 2H), 6.97 (d, *J* = 8.9 Hz, 2H), 6.64 (d, *J* = 8.9 Hz, 2H), 6.59 (d, *J* = 8.9 Hz, 2H), 6.23 (s, 2H), 5.15 (d, *J* = 12.0 Hz, 2H), 5.07 (d, *J* = 12.0 Hz, 2H), 4.83 (s, 2H), 4.82 (s, 2H), 3.96 (d, *J* = 17.5 Hz, 2H), 3.64 (d, *J* = 17.6 Hz, 2H). HRMS (FAB, NBA/CsI) *m/z* calcd for $[C_{50}H_{32}F_{10}N_4O_{12} + Cs]^+$ 1203.0911 found 1203.0961.