Supporting Information for

Covalent Assembly of Molecular Ladders

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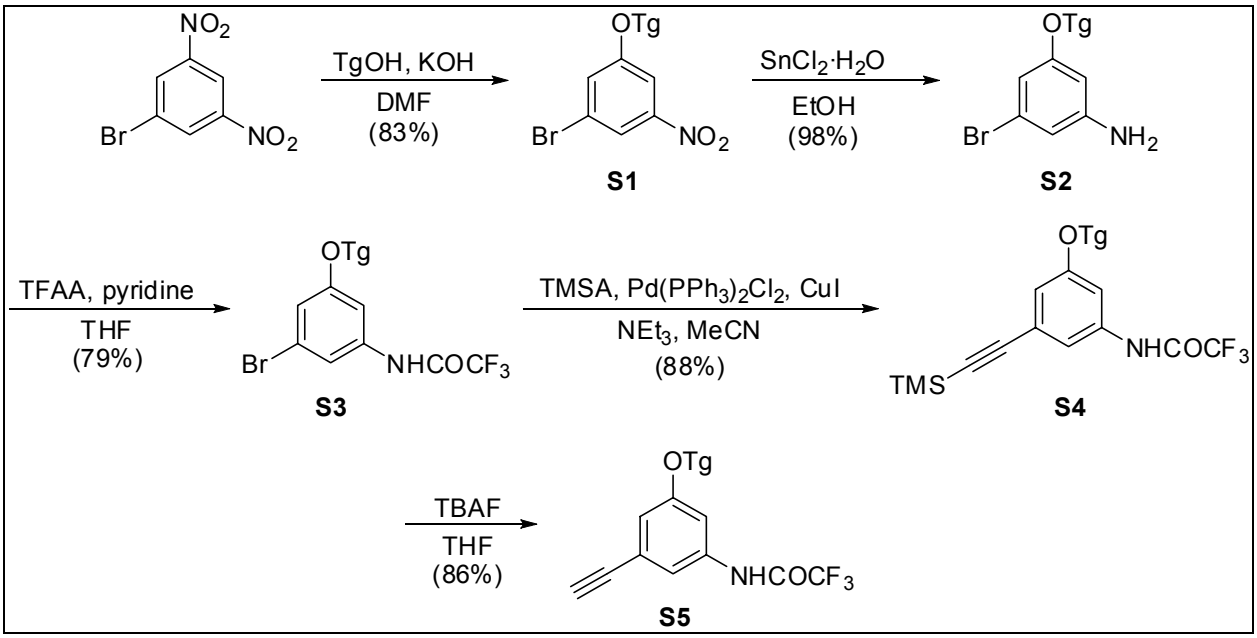
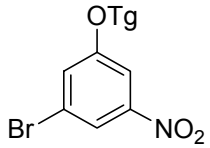
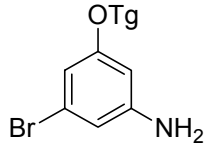
Experimental Procedures

General. Unless otherwise noted, all chemicals and reagents were purchased from commercial sources and used without further purification. Flash chromatography was performed using 60 Å silica gel from Silicycle, Inc. ^{1}H and ^{13}C NMR spectra were obtained on Varian Unity 400, Unity 500, and VXR 500 spectrometers. Chemical shifts are reported in δ (ppm) relative to the residual solvent protons ($CDCl_3$: 7.26 for ^{1}H, 77.16 for ^{13}C; $(CD_3)_2CO$: 2.05 for ^{1}H, 29.84 for ^{13}C). Low and high resolution EI, and low resolution FD mass spectra were recorded on Micromass 70-VSE spectrometers. High resolution ESI mass spectra were recorded on a Micromass Q-Tof Ultima spectrometer. MALDI mass spectra were recorded on an Applied Biosystems Voyager-DE STR spectrometer. MALDI analysis of oligomers **2**^{n} and **3**^{n}, and their precursors, was carried out using the HABA matrix (2-(4-hydroxyphenylazo)benzoic acid). The TCNQ matrix (7,7,8,8-tetracyanoquinodimethane)[1] was used for MALDI of the ladders **1**^{n}. In a typical sample preparation, 1 μL of a solution of the sample in chloroform (1 mg / 100 μL) was added to 10 μL of a 0.1 M mixture of the matrix in THF or MeCN. Elemental analysis was carried out by the University of Illinois School of Chemical Sciences Microanalytical Laboratory. Analytical gel permeation chromatography (GPC) was performed using a Waters 515 HPLC pump, a Thermo Separation Products Spectraseries AS100 autosampler, a Viscotek TDA Model 300 triple detector array, and a series of three Viscotek Viscogel columns (7.8 × 300 mm, 2 GMHXL16141 and 1 G3000HXL16136 columns) with 89:10:1 THF:MeOH:NEt_3 as the eluant at 30 °C. The analytical GPC was calibrated using monodisperse polystyrene standards. Preparatory GPC was carried out using a Waters 515 HPLC pump, a Waters 410 Differential Diffractometer, and a series of three Waters columns (19 × 300 mm, Ultrastyragel 10^4 Å THF, 10^3 Å THF, and 500 Å THF columns) with THF (HPLC grade, inhibitor-free) as the eluant.

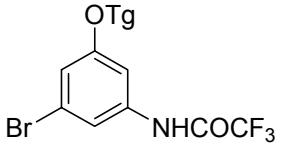




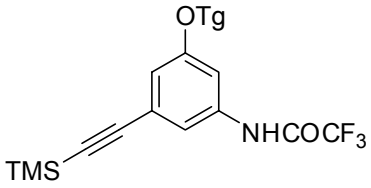
1-Bromo-3-{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}-5-nitrobenzene (S1). To a stirred mixture of powdered KOH (85%, 2.94 g, 44.5 mmol) and tri(ethylene glycol) monomethyl ether (95%, 13.5 mL, 74 mmol) in DMF (40 mL) was added, in one portion, a solution of 1-bromo-3,5-dinitrobenzene[2] (10.03 g, 40.6 mmol) in DMF (40 mL). The reaction mixture was stirred at 65 °C overnight, then cooled, poured into water (300 mL), and extracted with Et_2O (4×). The combined organic layers were washed with water (3×), dried ($MgSO_4$), filtered, and concentrated. Purification by Kugelrohr distillation (200–210 °C, 150 mtorr) gave 12.24 g (33.6 mmol, 83%) of **S1** as an orange oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.38 (s, 3H), 3.55 (m, 2H), 3.63-3.71 (m, 4H), 3.74 (m, 2H), 3.88 (m, 2H), 4.20 (m, 2H), 7.41 (t, J = 2.0 Hz, 1H), 7.71 (t, J = 2.2 Hz, 1H), 7.96 (t, J = 1.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 58.9, 68.5, 69.2, 70.47, 70.52, 70.8, 71.8, 108.4, 118.8, 122.8, 124.3, 149.2, 159.8; HRMS (ESI) calc'd for $C_{13}H_{19}BrNO_6$ ([M+H$^+$]) 364.0396, found 364.0387.



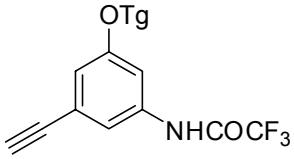
3-Bromo-5-{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}aniline (S2). A stirred mixture of **S1** (10.96 g, 29.3 mmol), $SnCl_2 \cdot 2H_2O$ (33.10 g, 146.7 mmol), and abs. EtOH (100 mL) was heated at reflux for 1 h, then cooled and poured into a 0 °C solution of NaOH (6 g) in water (100 mL). The mixture was basified with 10% NaOH, then diluted with water (to 500 mL) and extracted with Et_2O (4×). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated to 9.61 g (28.8 mmol, 98%) of **S2** as an orange oil: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.38 (s, 3H), 3.56 (m, 2H), 3.63-3.74 (m, 6H), 3.81 (m, 2H), 4.06 (m, 2H), 6.18 (t, J = 2.0 Hz, 1H), 6.45 (t, J = 1.7 Hz, 1H), 6.47 (t, J = 1.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 59.1, 67.6, 69.7, 70.6, 70.7, 70.9, 72.0, 100.6, 108.0, 111.1, 123.2, 148.8, 160.5; HRMS (ESI) calc'd for $C_{13}H_{21}BrNO_4$ ([M+H$^+$]) 334.0654, found 334.0663; anal. calc'd for $C_{13}H_{20}BrNO_4$ C 46.72, H 6.03, N 4.19, found C 46.37, H 6.03, N 4.58.



***N*-(3-Bromo-5-{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}phenyl)-2,2,2-trifluoro-acetamide (S3).** A stirred solution of **S2** (5.18 g, 15.5 mmol) and pyridine (1.9 mL) in THF (65 mL) was cooled to 0 °C and treated dropwise with a solution of trifluoroacetic anhydride (2.6 mL) in THF (15 mL). The reaction mixture was stirred at 0 °C for 1.5 h, then room temperature for 1.5 h, then quenched with brine. The organic layer was separated and the aqueous layer extracted with EtOAc (2×). The combined organic layers were then washed with 5% HCl, sat. $NaHCO_3$, and brine, then dried ($MgSO_4$), filtered, and concentrated. Purification by flash chromatography (1:1 *n*-hexane:EtOAc) gave 5.23 g (12.2 mmol, 79%) of **S3** as an off-white solid: m.p. 94-96 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.37 (s, 3H), 3.56 (m, 2H), 3.64-3.69 (m, 4H), 3.72 (m, 2H), 3.82 (m, 2H), 4.11 (m, 2H), 6.93 (t, J = 2.0 Hz, 1H), 7.18 (t, J = 2.1 Hz, 1H), 7.40 (t, J = 1.7 Hz, 1H), 8.27 (br s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 59.0, 68.2, 69.6, 70.6, 70.8, 70.9, 72.0, 106.3, 115.7 (q, J = 288.6 Hz), 116.1, 116.2, 123.0, 137.4, 155.1 (q, J = 37.7 Hz), 159.9; HRMS (ESI) calc'd for $C_{15}H_{20}BrF_3NO_5$ ([M+H$^+$]) 430.0477, found 430.0489; anal. calc'd for $C_{15}H_{19}BrF_3NO_5$ C 41.88, H 4.45, N 3.26, found C 41.73, H 4.34, N 3.26.

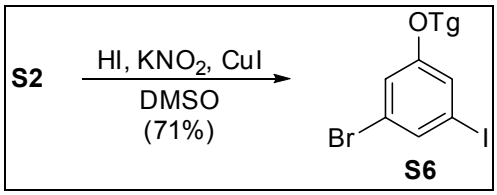


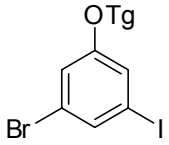
2,2,2-Trifluoro-*N*-{3-{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}-5-[(trimethylsilyl)-ethynyl]phenyl}acetamide (S4). In a heavy-walled sealed tube, a mixture of $Pd(PPh_3)_2Cl_2$ (183 mg, 0.26 mmol) and CuI (53 mg, 0.28 mmol) was evacuated and backfilled with nitrogen (3×). A solution of **S3** (2.22 g, 5.16 mmol) in MeCN (13 mL) was added, followed by NEt_3 (13 mL). The mixture was degassed by three freeze-pump-thaw cycles, then treated with degassed trimethylsilylacetylene (7.3 mL, 52 mmol), sealed, and heated at 70 °C overnight. The reaction mixture was then cooled, diluted with EtOAc, filtered, and concentrated. Purification by flash chromatography (3:2 EtOAc:*n*-hexane) gave 2.03 g (4.54 mmol, 88%) of **S4** as a brown oil: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.22 (s, 9H), 3.34 (s, 3H), 3.53 (m, 2H), 3.61-3.66 (m, 4H), 3.69 (m, 2H), 3.79 (m, 2H), 4.05 (m, 2H), 6.82 (dd, *J* = 1.2 Hz, *J* = 2.3 Hz, 1H), 7.19 (t, *J* = 2.2 Hz, 1H), 7.32 (dd, *J* = 1.2 Hz, *J* = 1.8 Hz, 1H), 8.56 (br s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 0.1, 59.0, 68.0, 69.6, 70.5, 70.7, 70.9, 72.0, 95.2, 104.0, 108.4, 115.6, 115.8 (q, *J* = 288.6 Hz), 116.7, 124.9, 136.5, 155.0 (q, *J* = 37.6 Hz), 159.1; HRMS (ESI) calc'd for $C_{20}H_{29}F_3NO_5Si$ ([M+H$^+$]) 448.1767, found 448.1760; anal. calc'd for $C_{20}H_{28}F_3NO_5Si$ C 53.68, H 6.31, N 3.13, found C 53.73, H 6.14, N 3.20.



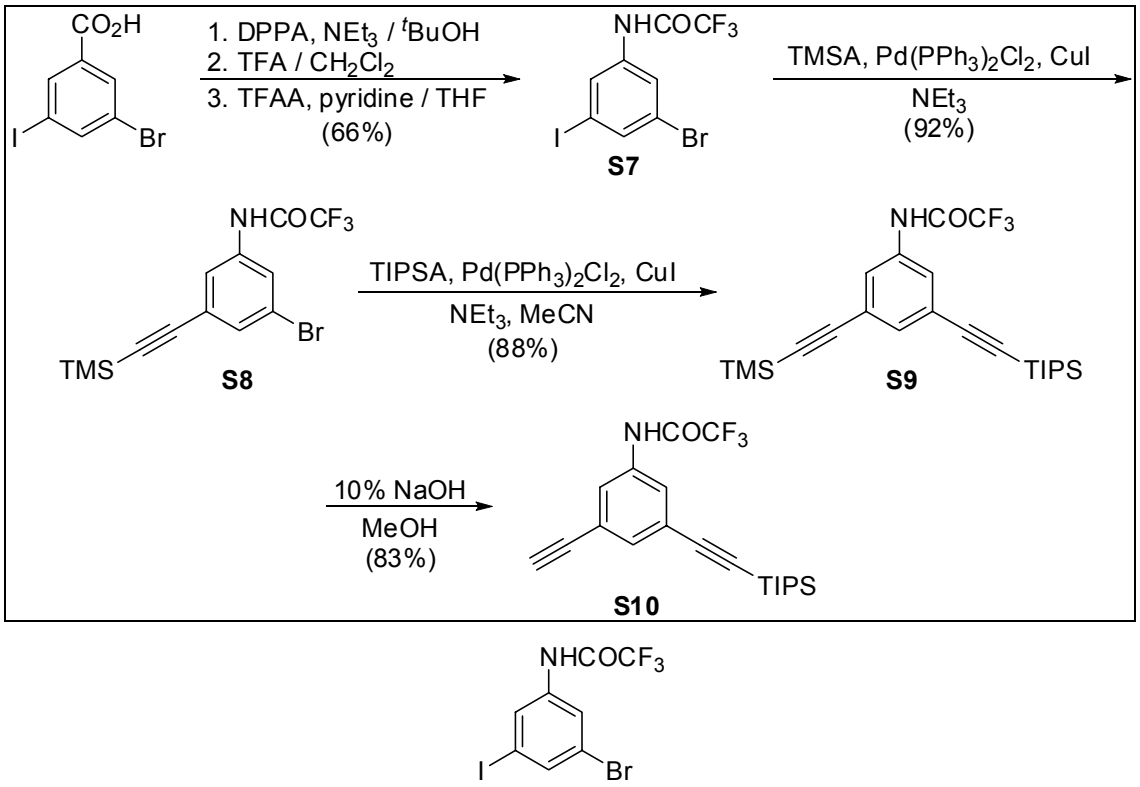
***N*-(3-Ethynyl-5-{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}phenyl)-2,2,2-trifluoro-acetamide (S5).** To a stirred solution of **S4** (1.86 g, 4.16 mmol) in THF (21 mL) was added dropwise a 1.0 M solution of TBAF in wet THF (4.6 mL, 4.6 mmol). The reaction mixture was stirred at room temperature for 5 min, then filtered through a silica plug, eluting with EtOAc, and concentrated. Purification by flash chromatography (3:2 EtOAc:*n*-hexane) gave 1.35 g (3.60 mmol, 86%) of **S5** as an orange solid: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.07 (s, 1H), 3.34 (s, 3H), 3.54 (m, 2H), 3.61-3.68 (m, 4H), 3.71 (m, 2H), 3.80 (m, 2H), 4.07 (m, 2H), 6.83 (dd, *J* = 1.2 Hz, *J* = 2.4 Hz, 1H), 7.24 (t, *J* = 2.2 Hz, 1H), 7.31 (dd, *J* = 1.3 Hz, *J* = 1.8 Hz, 1H), 8.57 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 59.0, 68.0, 69.6, 70.6, 70.7, 70.9, 72.0, 78.0, 82.7, 108.5, 115.8

(q, J = 288.6 Hz), 116.0, 116.8, 123.8, 136.6, 155.1 (q, J = 37.5 Hz), 159.1; HRMS (ESI) calc'd for $C_{17}H_{24}F_3N_2O_5$ ([M+NH_4^+]) 393.1637, found 393.1633; anal. calc'd for $C_{17}H_{20}F_3NO_5$ C 54.40, H 5.37, N 3.73, found C 54.39, H 5.26, N 3.71.



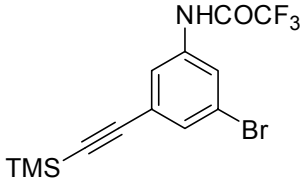


1-Bromo-3-iodo-5-{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}benzene (S6). To a stirred 35 °C mixture of **S2** (2.56 g, 7.66 mmol) and KNO_2 (8.37 g, 98.3 mmol) in DMSO (60 mL) was added dropwise a solution of CuI (0.52 g, 2.7 mmol) and 57% aq. HI (12.5 mL, 95 mmol) in DMSO (60 mL). The reaction mixture was stirred at 35 °C for 1 h, then poured into water (300 mL) containing K_2CO_3 (13 g) and extracted with Et_2O (3×100 mL). The combined organic layers were washed with water, sat. aq. Na_2SO_3 (2×), and brine, then dried ($MgSO_4$), filtered, and concentrated. Purification by flash chromatography (1:1 *n*-hexane:EtOAc) gave 2.41 g (5.41 mmol, 71%) of **S6** as a red oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.38 (s, 3H), 3.53-3.57 (m, 2H), 3.63-3.69 (m, 4H), 3.70-3.74 (m, 2H), 3.83 (m, 2H), 4.08 (m, 2H), 7.04 (dd, J = 1.8 Hz, J = 2.4 Hz, 1H), 7.21 (dd, J = 1.4 Hz, J = 2.4 Hz, 1H), 7.43 (t, J = 1.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 59.2, 68.1, 69.5, 70.69, 70.74, 71.0, 72.0, 94.2, 117.9, 123.0, 123.1, 132.2, 159.8; HRMS (ESI) calc'd for $C_{13}H_{19}BrIO_4$ ([M+H^+]) 444.9511, found 444.9514; anal. calc'd for $C_{13}H_{18}BrIO_4$ C 35.08, H 4.08, found C 35.05, H 3.91.

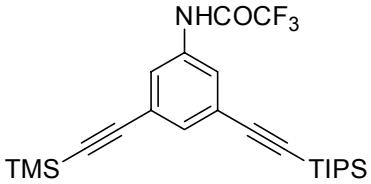


***N*-(3-Bromo-5-iodophenyl)-2,2,2-trifluoroacetamide (S7).** A stirred mixture of 3-bromo-5-iodobenzoic acid (4.71 g, 14.4 mmol), ^{t}BuOH (24 mL), NEt_3 (2.15 mL, 15.4 mmol), and diphenyl phosphoryl azide (3.30 mL, 14.8 mmol) was heated at reflux for 24 h. The reaction mixture was cooled, concentrated, and taken up in Et_2O, washed with 10% NaOH, water (2×), and brine, then dried ($MgSO_4$), filtered, and concentrated. The crude product was dissolved in CH_2Cl_2 (60 mL) and TFA (10 mL) and stirred at room temperature overnight. The reaction mixture was concentrated, taken up in EtOAc, and washed with sat. aq. $NaHCO_3$ (2×) and brine. The combined aqueous layers were extracted with EtOAc, and the organic layer washed with water. The combined organic layers were then dried ($MgSO_4$), filtered, and concentrated. Under a nitrogen atmosphere, a solution of the crude product and pyridine (1.7 mL, 21 mmol) in THF (60 mL) was cooled to 0 °C and treated dropwise with a solution of trifluoroacetic anhydride (2.3 mL, 17 mmol) in THF (10 mL). The reaction mixture was stirred for 1 h at 0 °C and 1 h at room temperature. The reaction was then quenched with brine and the organic layer separated. The aqueous layer was extracted with EtOAc, and the combined organic layers washed with 5% aq. HCl, sat. $NaHCO_3$, and brine, then dried ($MgSO_4$), filtered, and concentrated onto a silica plug. Purification by flash chromatography (9:1 *n*-hexane:EtOAc) gave 3.72 g (9.45 mmol, 66%) of **S7** as an off-white solid: m.p. 155-157 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.74 (t, J = 1.5 Hz, 1H),

7.79 (br s, 1H), 7.80 (t, J = 1.8 Hz, 1H), 7.88 (dd, J = 1.3 Hz, J = 2.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 94.4, 115.5 (q, J = 288.5 Hz), 123.0, 123.5, 127.9, 137.0, 137.8, 155.0 (q, J = 38.0 Hz); LRMS (EI) *m*/*z* 395 (96), 393 (100), 326 (18), 324 (19), 309 (45), 307 (44), 283 (10), 281 (9), 182 (20), 180 (20); HRMS (EI) calc'd for $C_8H_4BrF_3INO$ 392.8473, found 392.8478; anal. calc'd for $C_8H_4BrF_3INO$ C 24.39, H 1.02, N 3.56, found C 24.39, H 0.89, N 3.45.

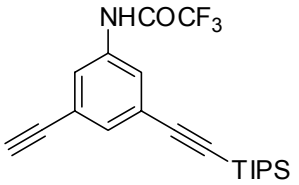


***N*-{3-Bromo-5-[(trimethylsilyl)ethynyl]phenyl}-2,2,2-trifluoroacetamide (S8).** A round bottom flask was charged with **S7** (4.36 g, 11.1 mmol), $Pd(PPh_3)_2Cl_2$ (233 mg, 0.332 mmol), and CuI (126 mg, 0.662 mmol) and evacuated and backfilled with nitrogen (3×). Degassed NEt_3 (35 mL) and trimethylsilylacetylene (17 mL, 120 mmol) were added, and the reaction mixture stirred at room temperature for 2 h. The reaction mixture was then diluted with EtOAc and filtered, then washed with sat. aq. NH_4Cl (2×), dried ($MgSO_4$), filtered, and concentrated onto a silica plug. Purification by flash chromatography (15:1 *n*-hexane:EtOAc) gave 3.70 g (10.2 mmol, 92%) of **S8** as a viscous orange oil: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.24 (s, 9H), 7.49 (dd, J = 1.4 Hz, J = 1.8 Hz, 1H), 7.58 (dd, J = 1.4 Hz, J = 2.0 Hz, 1H), 7.75 (br s, 1H), 7.79 (t, J = 2.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ -0.2, 97.5, 102.2, 115.6 (q, J = 288.9 Hz), 122.4, 122.7, 123.6, 126.2, 132.6, 136.1, 115.0 (q, J = 37.7 Hz); LRMS (EI) *m*/*z* 365 (59), 363 (59), 350 (100), 348 (100), 269 (18), 254 (83), 241 (34), 226 (16), 140.5 (17), 139.5 (17); HRMS (EI) calc'd for $C_{13}H_{13}BrF_3NOSi$ 362.9902, found 362.9902; anal. calc'd for $C_{13}H_{13}BrF_3NOSi$ C 42.87, H 3.60, N 3.85, found C 43.04, H 3.57, N 3.79.

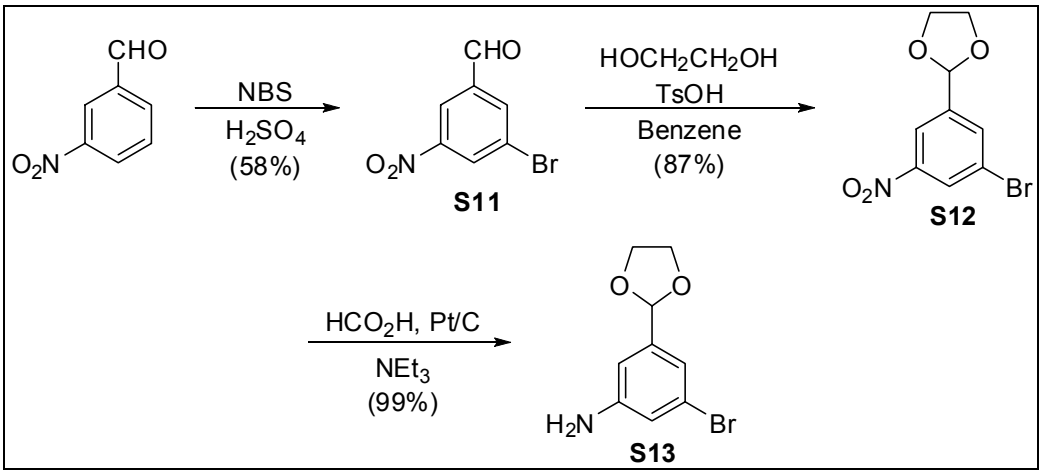


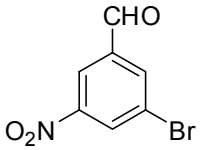
2,2,2-Trifluoro-*N*-{3-[(triisopropylsilyl)ethynyl]-5-[(trimethylsilyl)ethynyl]phenyl}-acetamide (S9). A heavy-walled tube was charged with $Pd(PPh_3)_2Cl_2$ (341 mg, 0.486 mmol) and CuI (93 mg, 0.488 mmol), then evacuated and back-filled with nitrogen. A solution of **S8** (3.56 g, 9.77 mmol) in MeCN (45 mL) and NEt_3 (5 mL) was added, and the reaction mixture degassed by three freeze-pump-thaw cycles. Degassed triisopropylsilylacetylene (7.0 mL, 30

mmol) was added, and the reaction mixture sealed and heated at 70 °C overnight. The mixture was then cooled, diluted with EtOAc, filtered, washed with sat. aq. NH_4Cl (2×), dried ($MgSO_4$), filtered, and concentrated. Purification by flash chromatography (25:1 *n*-hexane:EtOAc) gave 3.66 g (7.86 mmol, 80%) of **S9** as a viscous yellow oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.24 (s, 9H), 1.12 (s, 21H), 7.44 (t, *J* = 1.4 Hz, 1H), 7.58 (dd, *J* = 1.4 Hz, *J* = 2.1 Hz, 1H), 7.68 (dd, *J* = 1.5 Hz, *J* = 2.1 Hz, 1H), 7.75 (br s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ -0.1, 11.3, 18.8, 93.1, 96.6, 103.0, 104.9, 115.6 (q, *J* = 288.8 Hz), 123.56, 123.65, 124.8, 125.1, 133.3, 135.2, 155.0 (q, *J* = 37.8 Hz); LRMS (EI) *m*/*z* 465 (7), 450 (7), 422 (100), 394 (19), 380 (21), 366 (20), 352 (29), 176 (34); HRMS (EI) calc'd for $C_{24}H_{34}F_3NOSi_2$ 465.2131, found 465.2129; anal. calc'd for $C_{24}H_{34}F_3NOSi_2$ C 61.90, H 7.36, N 3.01; found C 62.25, H 7.61, N 3.00.

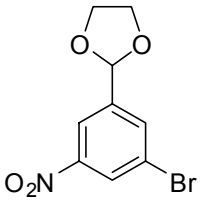


***N*-{3-Ethynyl-5-[(triisopropylsilyl)ethynyl]phenyl}-2,2,2-trifluoroacetamide (S10).** To a stirred solution of **S9** (3.55 g, 7.62 mmol) in MeOH (40 mL) was added 10% aq. NaOH (3.1 mL). The reaction mixture was stirred for 35 min, then poured in sat. aq. NH_4Cl and extracted with Et_2O (3×). The combined organic layers were washed with water, dried ($MgSO_4$), filtered, and concentrated. Purification by flash chromatography (12:1 *n*-hexane:EtOAc) gave 2.48 g (6.30 mmol, 83%) of **S10** as a yellowish oil that solidifies to an off-white solid when stored in the freezer: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.12 (s, 21H), 3.12 (s, 1H), 7.46 (t, *J* = 1.4 Hz, 1H), 7.63 (t, *J* = 1.8 Hz, 1H), 7.70 (t, *J* = 1.8 Hz, 1H), 7.90 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 11.3, 18.8, 79.1, 81.8, 93.4, 104.7, 115.6 (q, *J* = 288.8 Hz), 123.7, 123.8, 124.0, 125.2, 133.5, 133.2, 155.0 (q, *J* = 37.3 Hz); LRMS (EI) *m*/*z* 393 (13), 350 (100), 322 (33), 308 (32), 294 (41), 280 (46); HRMS (EI) calc'd for $C_{21}H_{26}F_3NOSi$ 393.1736, found 393.1742; anal. calc'd for $C_{21}H_{26}F_3NOSi$ C 64.09, H 6.66, N 3.56, found C 64.24, H 6.83, N 3.60.



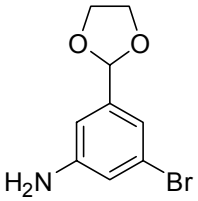


3-Bromo-5-nitrobenzaldehyde (S11).[3] To a stirred 80 °C solution of 3-nitrobenzaldehyde (28.1 g, 186 mmol) in conc. sulfuric acid (200 mL) was added solid NBS (43.0 g, 242 mmol) in 9 portions at 15 min intervals. The reaction mixture was stirred for an additional 40 min, then poured onto ice (300 g). The mixture was diluted with ice (to ~1 L), and the precipitate isolated by filtration, washing with water, then dissolved in EtOAc (500 mL) and washed with sat. aq. $NaHCO_3$, dried ($MgSO_4$), filtered, and concentrated. Recrystallization from *n*-hexane/toluene gave 24.95 g (108.5 mmol, 58%) of **S11** as an off-white powder: m.p. 98-100 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.35 (dd, J = 1.3 Hz, J = 1.8 Hz, 1H), 8.62 (t, J = 2.0 Hz, 1H), 8.65 (dd, J = 1.3 Hz, J = 2.1 Hz, 1H), 10.06 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 123.1, 124.2, 131.7, 137.6, 138.5, 149.3, 188.4; LRMS (EI) *m/z* 231 (97), 229 (100), 185 (37), 183 (37), 157 (32), 155 (35); HRMS (EI) calc'd for $C_7H_4BrNO_3$ 228.9374, found 228.9380; anal. calc'd for $C_7H_4BrNO_3$ C 36.55, H 1.75, N 6.09, found C 36.37, H 1.51, N 5.70.

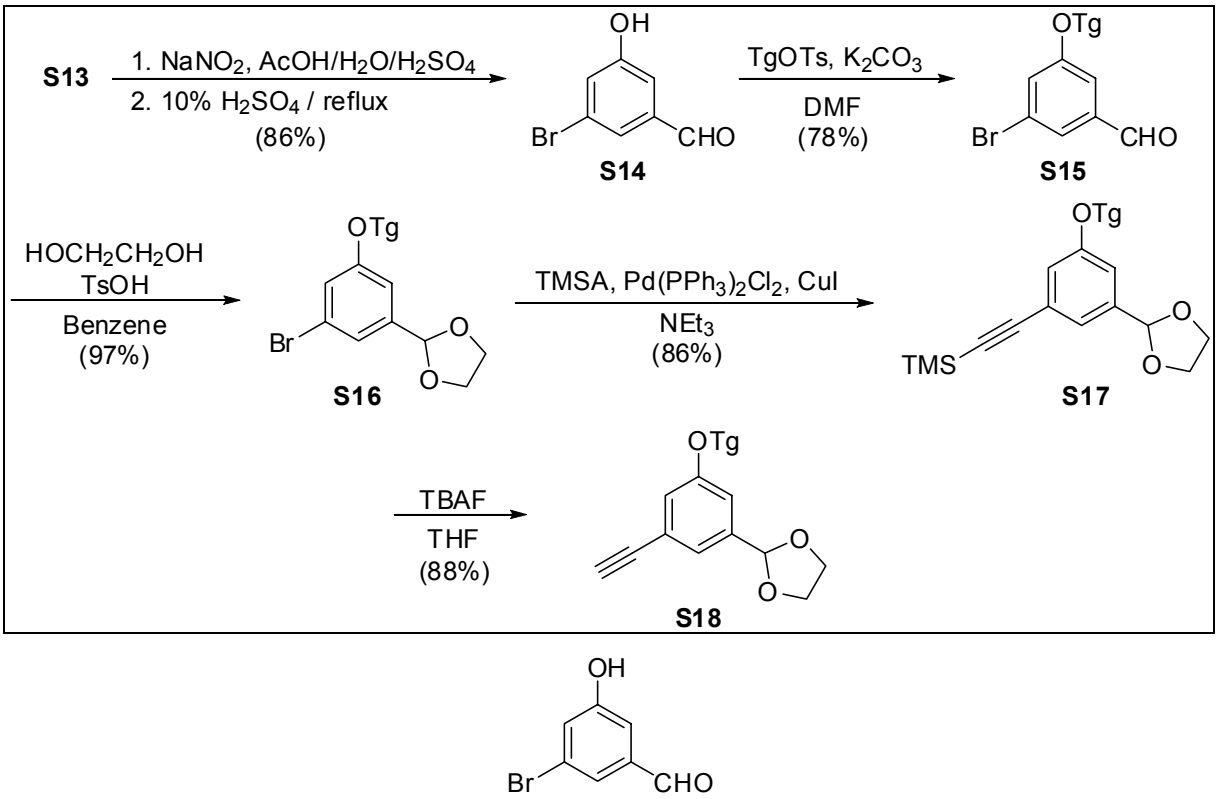


2-(3-Bromo-5-nitrophenyl)-1,3-dioxolane (S12). To a stirred solution of **S11** (15.49 g, 67.34 mmol) in benzene (200 mL) was added ethylene glycol (38 mL, 680 mmol) and *p*-TsOH·H_2O (390 mg, 1.42 mmol). The reaction mixture was heated at reflux overnight with a

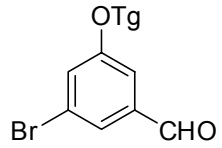
Dean-Stark trap, then cooled and washed with sat. aq. $NaHCO_3$ (2×), dried ($MgSO_4$), filtered, and concentrated. Purification by Kugelrohr distillation (150 °C, 190 mtorr) gave 16.01 g (58.42 mmol, 87%) of **S12** as a yellowish oil that solidifies on standing at room temperature: m.p. 48-51 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.05-4.15 (m, 4H), 5.87 (s, 1H), 7.95 (m, 1H), 8.28 (m, 1H), 8.36 (t, J = 2.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 65.6, 101.5, 120.5, 122.9, 127.1, 135.7, 142.3, 148.8; LRMS (EI) *m*/*z* 275 (17), 274 (44), 273 (17), 272 (44), 230 (16), 228 (22), 187 (16), 185 (23), 157 (14), 155 (14), 73 (100); HRMS (EI) calc'd for $C_9H_7BrNO_4$ ($[M-H]^+$) 271.9558, found 271.9555; anal. calc'd for $C_9H_8BrNO_4$ C 39.44, H 2.94, N 5.11; C 39.81, H 2.73, N 5.06.



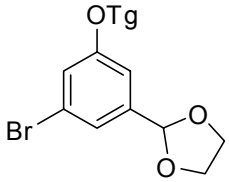
3-Bromo-5-(1,3-dioxolan-2-yl)aniline (S13). Under a nitrogen atmosphere, a mixture of **S12** (31.71 g, 115.7 mmol), 5% Pt/C (4.52 g, 1.2 mmol), and NEt_3 (70 mL, 500 mmol) was heated to reflux and treated dropwise over 20 min with 96% formic acid (15.0 mL, 382 mmol). Heating was continued for 2 h, then the reaction mixture was cooled and filtered through celite, washing the solids with CH_2Cl_2, and concentrated. The residue was dissolved in EtOAc, filtered through a silica plug, and concentrated to 27.92 g (99%) of crude **S13** that was used without further purification.



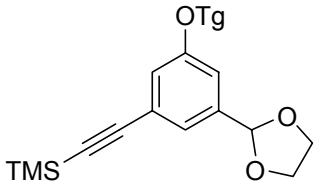
3-Bromo-5-hydroxybenzaldehyde (S14). To a stirred 0 °C solution of **S13** (5.50 g, 22.5 mmol) in 8:1:1 AcOH:H_2O:H_2SO_4 (25 mL) was added dropwise a solution of $NaNO_2$ (1.71 g, 24.8 mmol) in water (3 mL). The reaction mixture was stirred at 0 °C for 30 min, then added dropwise to a boiling 10% aq. H_2SO_4 solution (150 mL). The mixture was heated at reflux for 5 min, then cooled and extracted with Et_2O (3×). The combined organic layers were then washed with water (3×), dried ($MgSO_4$), filtered, and concentrated onto a silica plug. Purification by flash chromatography (3:2 *n*-hexane:EtOAc) gave 3.89 g (19.4 mmol, 86%) of **S14** as an orange solid: m.p. 134-138 °C; ^{1}H NMR ($(CD_3)_2CO$, 400 MHz) δ 7.32 (t, J = 2.1 Hz, 1H), 7.34 (dd, J = 2.3 Hz, J = 1.3 Hz, 1H), 7.54 (t, J = 1.5 Hz, 1H), 9.30 (br s, 1H), 9.92 (s, 1H); ^{13}C NMR ($(CD_3)_2CO$, 100 MHz) δ 115.4, 123.8, 124.4, 124.8, 140.3, 159.8, 191.6; LRMS (EI) *m*/*z* 202 (98), 201 (83), 200 (100), 199 (79), 173 (30), 171 (30), 145 (14), 143 (14); HRMS calc'd for $C_7H_5BrO_2$ 199.9473, found 199.9469; anal. calc'd for $C_7H_5BrO_2$ C 41.82, H 2.51, found C 41.78, H 2.38.



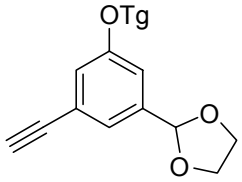
3-Bromo-5-{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}benzaldehyde (S15). To a stirred mixture of **S14** (3.13 g, 15.6 mmol) and K_2CO_3 (3.23 g, 23.4 mmol) in DMF (40 mL) was added TsOTg[4] (4.46 g, 14.0 mmol) and additional DMF (5 mL). The reaction mixture was stirred under nitrogen at 60-70 °C for 3 d, then cooled, poured into water (300 mL), and extracted with Et_2O (4×). The combined organic layers were washed with water (2×) and brine, then dried ($MgSO_4$), filtered, and concentrated. Purification by Kugelrohr distillation (180-185 °C, 60 mtorr) gave 3.77 g (10.9 mmol, 78%) of **S15** as a yellow oil: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.38 (s, 3H), 3.55 (m, 2H), 3.63-3.71 (m, 4H), 3.73 (m, 2H), 3.88 (m, 2H), 4.18 (m, 2H), 7.33-7.36 (m, 2H), 7.58 (t, *J* = 1.5 Hz, 1H), 9.89 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 59.1, 68.2, 69.5, 70.67, 70.73, 71.0, 72.0, 113.0, 115.1, 123.5, 124.5, 125.9, 138.7, 160.1, 190.7; HRMS (ESI) calc'd for $C_{14}H_{20}BrO_5$ ([M+H$^+$]) 347.0494, found 347.0511; anal. calc'd for $C_{14}H_{19}BrO_5$ C 48.29, H 5.79, found C 48.59, H 5.40.



2-(3-Bromo-5-{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}phenyl)-1,3-dioxolane (S16). A mixture of **S15** (2.60 g, 7.49 mmol), TsOH·H_2O (48 mg, 0.25 mmol), ethylene glycol (4.5 mL, 81 mmol), and benzene (40 mL) was heated at reflux overnight with a Dean-Stark trap. The reaction mixture was then cooled, washed with sat. aq. $NaHCO_3$ (2×), dried ($MgSO_4$), filtered, and concentrated to give 2.84 g (7.26 mmol, 97%) of **S16** as a slightly yellowish oil: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.38 (s, 3H), 3.55 (m, 2H), 3.64-3.69 (m, 4H), 3.72 (m, 2H), 3.84 (m, 2H), 3.99-4.14 (m, 6H), 5.75 (s, 1H), 6.96 (dd, *J* = 1.2 Hz, *J* = 1.8 Hz, 1H), 7.06 (t, *J* = 2.1 Hz, 1H), 7.21 (t, *J* = 1.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 58.8, 65.1, 67.6, 69.3, 70.38, 70.45, 70.7, 71.7, 102.4, 111.5, 118.4, 121.8, 122.4, 141.1, 159.4; HRMS (ESI) calc'd for $C_{16}H_{24}BrO_6$ ([M+H$^+$]) 391.0756, found 391.0763; anal. calc'd for $C_{16}H_{23}BrO_6$ C 49.12, H 5.93, found C 48.98, H 5.93.

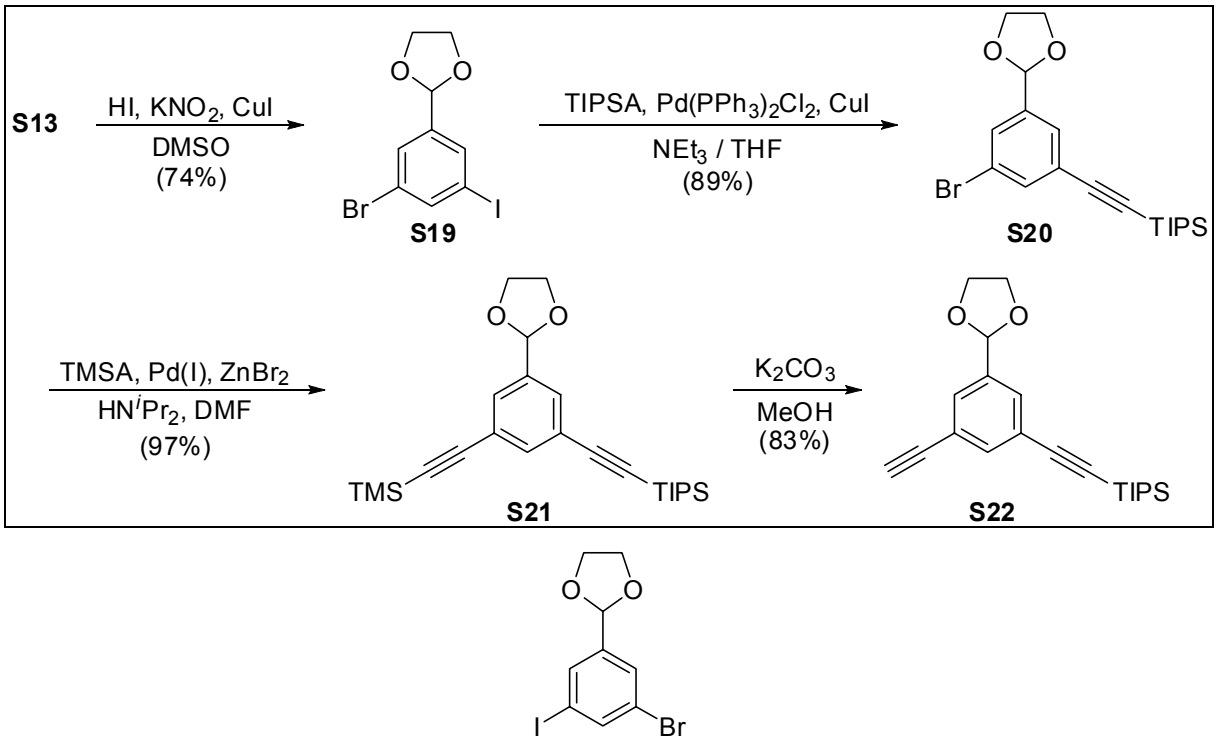


[(3-(1,3-Dioxolan-2-yl)-5-{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}phenyl)ethynyl]-(trimethyl)silane (S17). A heavy-walled sealed tube was charged with $Pd(PPh_3)_2Cl_2$ (199 mg, 0.284 mmol) and CuI (54 mg, 0.28 mmol) and evacuated and backfilled with nitrogen (3×). A solution of **S16** (2.22 g, 5.67 mmol) in NEt_3 (28 mL) was added, and the reaction mixture degassed by three freeze-pump-thaw cycles. Degassed trimethylsilylacetylene (8.0 mL, 57 mmol) was added, and the reaction mixture sealed and heated at 75–80 °C overnight. The mixture was then cooled, diluted with EtOAc, filtered, and concentrated. Purification by flash chromatography (1:1 *n*-hexane:EtOAc) gave 2.00 g (4.90 mmol, 86%) of **S17** as an orange oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.24 (s, 9H), 3.38 (s, 3H), 3.55 (m, 2H), 3.64-3.69 (m, 4H), 3.76 (m, 2H), 3.84 (m, 2H), 3.99-4.09 (m, 4H), 4.12 (m, 2H), 5.75 (s, 1H), 6.98 (dd, *J* = 1.4 Hz, *J* = 2.6 Hz, 1H), 7.00 (ddd, *J* = 0.4 Hz, *J* = 1.6 Hz, *J* = 2.6 Hz, 1H), 7.18 (td, *J* = 0.5 Hz, *J* = 1.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 0.0, 59.1, 65.3, 67.7, 69.7, 70.6, 70.7, 70.9, 72.0, 94.2, 103.0, 104.7, 113.8, 118.1, 122.8, 124.2, 139.8, 158.6; HRMS (ESI) calc'd for $C_{21}H_{33}O_6Si$ ($[M+H^+]$) 409.2046, found 409.2030; anal. calc'd for $C_{21}H_{32}O_6Si$ C 61.73, H 7.89, found C 61.37, H 7.91.

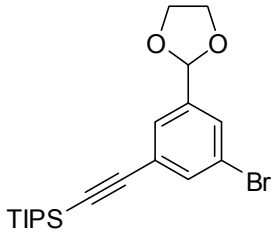


2-(3-Ethynyl-5-{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}phenyl)-1,3-dioxolane (S18). To a stirred solution of **S17** (1.07 g, 2.73 mmol) in THF (14 mL) was added dropwise a wet 1.0 M solution of TBAF in THF (3.0 mL, 3.0 mmol). The reaction mixture was stirred at room temperature for 5 min, then filtered through a silica plug, eluting with EtOAc, and concentrated. Purification by flash chromatography (7:3 EtOAc:*n*-hexane) gave 0.81 g (2.41 mmol, 88%) of **S18** as a slightly yellowish oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.04 (s, 1H), 3.38 (s, 3H), 3.55 (m, 2H), 3.64-3.70 (m, 4H), 3.73 (m, 2H), 3.85 (m, 2H), 4.00-4.15 (m, 6H), 5.76 (s, 1H), 7.02 (dd, *J* = 1.4 Hz, *J* = 2.5 Hz, 1H), 7.04 (m, 1H), 7.21 (br t, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 59.2, 65.4, 67.7, 69.7, 70.7, 70.8, 71.0, 72.0, 83.3, 103.0, 113.8, 118.7, 123.0, 123.2, 140.0, 158.7;

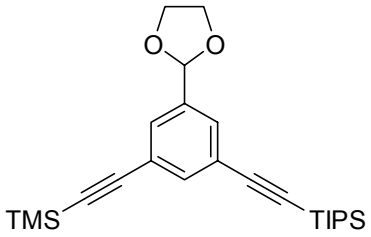
HRMS (ESI) calc'd for $C_{18}H_{25}O_6$ ([M+H$^+$]) 337.1651, found 337.1645; anal. calc'd for $C_{18}H_{24}O_6$ C 64.27, H 7.19, found C 63.96, H 7.13.



2-(3-Bromo-5-iodophenyl)-1,3-dioxolane (S19). To a stirred 35 °C mixture of **S13** (5.42 g, 22.2 mmol) and KNO_2 (15.68 g, 184 mmol) in DMSO (110 mL) was added dropwise a solution of CuI (0.85 g, 4.5 mmol) and 57% aq. HI (23.5 mL, 180 mmol) in DMSO (110 mL). The reaction mixture was stirred at 35 °C for 1 h, then poured into ice water (600 mL) containing K_2CO_3 (45 g). The mixture was extracted with Et_2O (3×), and the combined organic layers washed with water (2×), sat. aq. $Na_2S_2O_3$, and brine, then dried ($MgSO_4$), filtered, and concentrated. Purification by flash chromatography (9:1 *n*-hexane:EtOAc) gave 5.84 g (16.5 mmol, 74%) of **S19** as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.00-4.11 (m, 4H), 5.73 (s, 1H), 7.58 (td, J = 0.4 Hz, J = 1.6 Hz, 1H), 7.74 (td, J = 0.5 Hz, J = 1.4 Hz, 1H), 7.84 (t, J = 1.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 65.5, 94.4, 101.8, 123.0, 129.2, 134.3, 140.3, 142.2; LRMS (FD) *m*/*z* 355.9 [M$^+$]; anal. calc'd for $C_9H_8BrIO_2$ C 30.45, H 2.27, found C 30.44, H 2.06.

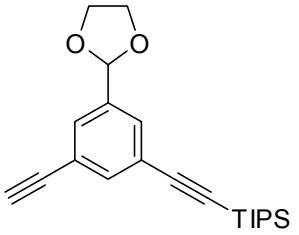


{[3-Bromo-5-(1,3-dioxolan-2-yl)phenyl]ethynyl}(triisopropyl)silane (S20). A round bottom flask fitted with a stir bar was charged with CuI (0.098 g, 0.51 mmol) and $Pd(PPh_3)_2Cl_2$ (0.096 g, 0.14 mmol). **S19** (3.25 g, 9.16 mmol) was dissolved in THF (11 mL) and transferred to the reaction mixture. NEt_3 (19 mL, 137.4 mmol) and triisopropylsilylacetylene (10.2 mL, 45.8 mmol) were then added to the reaction mixture. The reaction was then stirred for an additional hour after which time the reaction mixture was poured into a separatory funnel containing sat. aq. NH_4Cl (20 mL). The reaction mixture was then washed with sat. aq. NH_4Cl (3×20 mL) and finally with brine (20 mL). The organic layer was then dried ($MgSO_4$), filtered, and concentrated to produce a reddish black oil. Purification using flash chromatography (1:1 *n*-hexane:CH_2Cl_2) gave 3.31 g (8.08 mmol, 89%) of **S20** as a yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (t, J = 1.5 Hz, 1H), 7.58 (t, J = 1.8 Hz, 1H), 7.51 (t, J = 1.5 Hz, 1H), 5.75 (s, 1H), 4.04 (m, 4H), 1.14 (s, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.6, 135.4, 129.7, 128.9, 125.7, 122.2, 105.3, 102.5, 92.8, 65.5, 18.9, 11.5; LRMS (FD) *m*/*z* 408.1 [M^+]; anal. calc'd for $C_{20}H_{29}BrO_2Si$ C 58.67, H 7.14, found C 58.44, H 6.96.



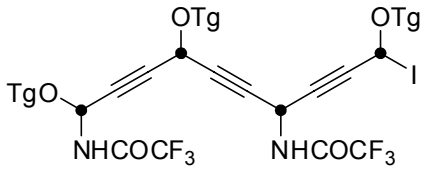
({3-(1,3-Dioxolan-2-yl)-5-[(triisopropylsilyl)ethynyl]phenyl}ethynyl)(trimethyl)silane (S21). In a glove box, a round bottom flask fitted with a stir bar was charged with **S20** (2.47g, 6.02 mmol) and dissolved in DMF (25 mL). To **S20** was added in the following order: Pd(I) dimer pre-catalyst[5] (0.064g, 0.18 mmol), HN^iPr_2 (1.69 mL, 12.04 mmol), $ZnBr_2$ (2.71 g, 12.04 mmol) and finally trimethysilylacetylene (3 mL, 30.10 mmol). The reaction mixture was stirred for 12 h, then removed from the glove box and washed with sat. aq. NH_4Cl (2×10 mL). The organic layer was then dried ($MgSO_4$), filtered, and concentrated to a dark oil. Purification using flash chromatography (1:1 *n*-hexane:CH_2Cl_2) gave 2.50 g (5.86 mmol, 97%) of **S21** as a yellow

oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (t, *J* = 1.4 Hz, 1H), 7.51 (m, 2H), 5.76 (s, 1H), 4.06 (m, 4H), 1.12 (s, 21H), 0.24 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.8, 136.1, 130.1, 130.0, 124.2, 123.7, 105.9, 104.0, 102.9, 95.4, 91.8, 65.5, 18.8, 11.4, 0.1; LRMS (FD) *m*/*z* 426.3 [M^+].



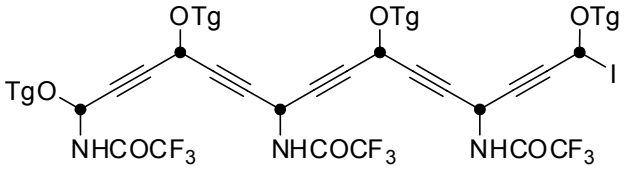
{[3-(1,3-Dioxolan-2-yl)-5-ethynylphenyl]ethynyl}(triisopropyl)silane (S22). A scintillation vial was charged with **S21** (0.91 g, 2.13 mmol), CH_2Cl_2 (5 mL), methanol (5 mL) and K_2CO_3 (0.030 g, 0.21 mmol) and stirred for 2 h. After this time the reaction mixture was washed with sat. aq. NH_4Cl (2×5 mL) and brine (2×5 mL). The organic layer was then dried ($MgSO_4$), filtered, and concentrated to give 0.63 g (1.77 mmol, 83%) of **S22** as a clear oil which solidified upon freezing: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (t, *J* = 1.7 Hz, 1H), 7.55 (m, 2H), 5.76 (s, 1H), 4.05 (m, 4H), 3.09 (s, 1H), 1.13 (s, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.0, 136.3, 130.5, 130.1, 124.3, 122.7, 105.8, 102.8, 92.1, 82.7, 78.2, 65.5, 18.8, 11.4; LRMS (FD) *m*/*z* 354.5 [M^+].

General Procedure for the Solid Phase Synthesis of Oligomers S23–S26. A previously reported solid phase method[5] was applied to monomers **S5**, **S6**, **S10**, **S18**, **S22**. Oligomers **S23**–**S26** were purified by prep. GPC.



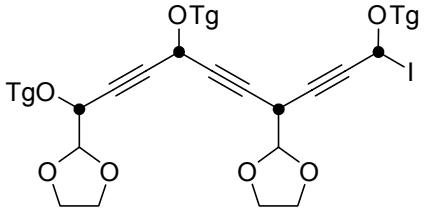
S23

Oligomer S23. 0.129 g (0.107 mmol, 89%) of **S23** was obtained as an off-white solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.51 (s, 1H), 9.29 (s, 1H), 7.79 (t, *J* = 1.7 Hz, 1H), 7.73 (t, *J* = 1.7 Hz, 1H), 7.40 (t, *J* = 1.5 Hz, 1H), 7.38 (t, *J* = 1.6 Hz, 1H), 7.37 (t, *J* = 1.4 Hz, 1H), 7.28 (t, *J* = 2.07 Hz, 1H), 7.19 (m, 1H), 7.14 (t, *J* = 1.3 Hz, 1H), 6.89 (m, 3H), 6.78 (m, 1H), 3.83-3.80 (m, 6H), 3.75-3.63 (m, 24H), 3.55-3.53 (m, 6H), 3.338 (s, 3H), 3.335 (s, 3H), 3.318 (s, 3H); GPC (oligomer too small to accurately determine PDI); MS (MALDI) calc'd for $C_{55}H_{59}F_6IN_2NaO_{14}$ ([M+Na^+]) 1235.95, found 1236.29.



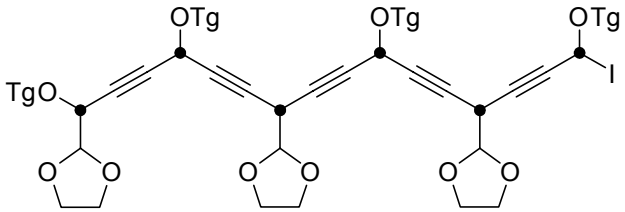
S24

Oligomer S24. 0.105 g (0.062 mmol, 52%) of **S24** was obtained as a yellow wax: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.79 (s, 1H), 9.71 (s, 1H), 9.42 (s, 1H), 7.77 (m, 2H), 7.73 (m, 2H), 7.39 (t, *J* = 1.3 Hz, 1H), 7.37 (br, 1H), 7.30 (t, *J* = 1.3 Hz, 1H), 7.28 (t, *J* = 2.0 Hz, 1H), 7.26 (m, 1H), 7.15 (m, 3H), 6.85-6.81 (m, 5H), 6.75 (m, 1H), 4.05-3.96 (m, 8H), 3.82-3.63 (m, 32H), 3.62-3.52 (m, 8H), 3.52 (s, 3H), 3.34 (s, 3H), 3.29 (s, 3H), 3.28 (s, 3H); GPC PDI = 1.04; MS (MALDI) calc'd for $C_{80}H_{81}F_9IN_3NaO_{19}$ ([M+Na^+]) 1709.39, found 1709.17.



S25

Oligomer S25. 0.132g (0.116 mmol, 86%) of **S25** was obtained as an off-white solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (t, *J* = 1.4 Hz, 1H), 7.61 (t, *J* = 1.6 Hz, 1H), 7.58 (t, *J* = 1.6 Hz, 1H), 7.46 (t, *J* = 1.5 Hz, 1H), 7.28 (t, *J* = 1.4 Hz, 1H), 7.27 (m, 1H), 7.24 (m, 1H), 7.04 (m, 4H), 7.01 (m, 1H), 5.81(s, 1H), 5.78 (s, 1H), 4.09 (m, 8H), 3.87-3.83 (m, 6H), 3.76-3.71 (m, 6H), 3.69-3.64 (m, 18H), 3.56-3.53 (m, 6H), 3.37 (s, 9H); GPC (oligomer too small to accurately determine PDI); MS (MALDI) calc'd for $C_{57}H_{67}INaO_{16}$ ([M+Na^+]) 1158.03, found 1158.27.



S26

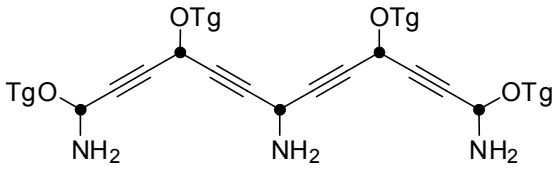
Oligomer S26. 0.140 g (0.089 mmol, 74%) of **S26** was obtained as a yellow wax: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (t, *J* = 1.5 Hz, 1H), 7.66 (t, *J* = 1.5 Hz, 1H), 7.61 (m, 3H), 7.59 (t, *J* = 1.5 Hz, 1H), 7.46 (t, *J* = 1.3 Hz, 1H), 7.30 (m, 2H), 7.26 (m, 1H), 7.24 (br,1H), 7.04 (m, 5H), 7.03 (m, 1H), 7.01 (m, 1H), 5.82 (s, 1H), 5.81 (s, 1H), 5.78 (s, 1H), 4.18-4.01 (m, 12H),

3.88- 3.82 (m, 8H), 3.76-3.71 (m, 8H), 3.70-3.64 (m, 24H), 3.56-3.53 (m, 8H), 3.37 (m, 12H); GPC PDI = 1.07; MS (MALDI) calc'd for $C_{83}H_{93}INaO_{22}$ ([M+Na^+]) 1592.51, found 1592.45.

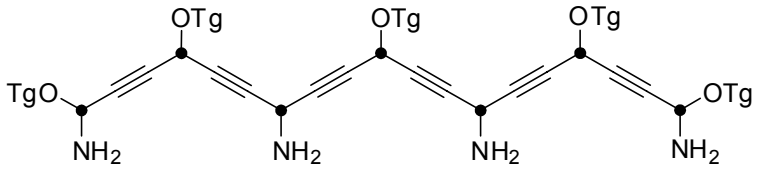
General Procedure for the Sonogashira Coupling of Oligomers S23–S26 with Monomer Units. In a glove box under an atmosphere of argon, a scintillation vial containing the oligomer was treated with $Pd(tfp)_4$ (10 mol% per coupling), CuI (10 mol% per coupling), and piperidine (10 eq.). A solution of the ethynyl or bisethynyl monomer (1 or 0.5 eq., respectively) in DMF was then added, and the mixture stirred at room temperature overnight. The reaction mixture was then removed from the glove box and partitioned between sat. aq. NH_4Cl and $CHCl_3$. The aqueous layer was extracted with $CHCl_3$ (3×), and the combined organic layers dried ($MgSO_4$), filtered, and concentrated. The crude product was then deprotected without purification, or purified by flash chromatography or prep. GPC.

General Procedure for the Deprotection of Acetal-Functionalized Oligomers. A ~0.05 M solution of the protected oligomer in THF was treated with conc. aq. HCl (3 drops) and stirred at room temperature for 24–48 h. The reaction mixture was then partitioned between sat. aq. $NaHCO_3$ and EtOAc, and the aq. layer extracted with EtOAc (2×). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated. The crude product was purified by prep. GPC.

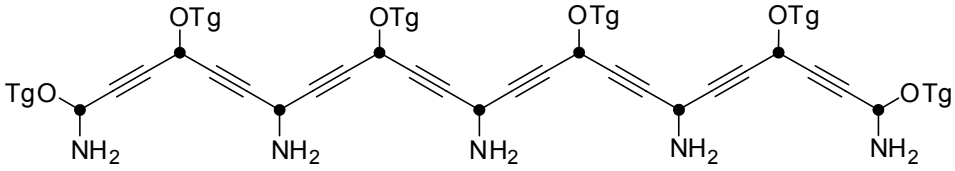
General Procedure for the Deprotection of Trifluoroacetamide-Functionalized Oligomers. A solution of the oligomer (50–100 mg) in THF (2.0 mL) was treated with 10% aq. NaOH (0.20 mL) and heated at reflux overnight. The reaction mixture was then cooled, poured into sat. aq. NH_4Cl, and extracted with $CHCl_3$ (4×). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated. The crude products were then purified by flash chromatography or prep. GPC. Note: in some cases, we observed (NMR and MALDI) scavenging of THF oxidation products when the materials were purified by GPC; this process is reversible (*e.g.*, by hydrolysis), and does not appear to affect the self-assembly to ladder structures. Alternatively, freshly distilled THF (sodium/benzophenone) has been used and reaction carried out under N_2; in this case, the material is quite pure after workup (*i.e.*, by ^1H NMR, MALDI, and GPC which indicates only a trace amount of higher MW impurity) and can be used without further purification.



Oligomer 2[3]. The trifluoroacetamide-protected oligomer was purified by flash chromatography (3:1 CH_2Cl_2:acetone). After deprotection and purification by flash chromatography (60:40:5 CH_2Cl_2:acetone:NEt_3) and prep. GPC, 49 mg (0.042 mmol, 57%) of **2**[3] was obtained as an light orange oil: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.38 (s, 12H), 3.56 (m, 8H), 3.65-3.76 (m, 30H), 3.84 (m, 4H), 3.87 (m, 4H), 4.11 (m, 4H), 4.16 (m, 4H), 6.27 (t, *J* = 2.2 Hz, 2H), 6.48 (dd, *J* = 1.2 Hz, *J* = 2.0 Hz, 2H), 6.49 (dd, *J* = 1.2 Hz, *J* = 2.2 Hz, 2H), 6.82 (d, *J* = 1.3 Hz, 2H), 7.03 (d, *J* = 1.3 Hz, 4H), 7.11 (t, *J* = 1.4 Hz, 1H), 7.27 (t, *J* = 1.3 Hz, 2H); GPC indicated >95% purity (PDI unavailable due to low MW); MS (MALDI) calc'd for $C_{66}H_{81}N_3NaO_{16}$ ([M+Na^+]) 1195.35, found 1195.05.

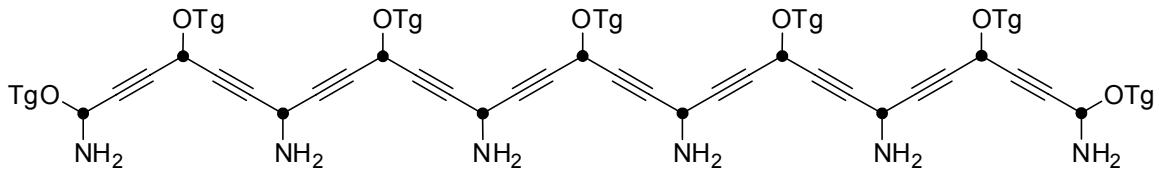


Oligomer 2[4]. After deprotection and purification by flash chromatography (60:40:5 CH_2Cl_2:acetone:NEt_3), 39 mg (0.025 mmol, 43%) of **2**[4] was obtained as a cloudy yellow oil: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.37 (s, 15H), 3.55 (m, 10H), 3.6-3.9 (m, 48H), 4.09 (m, 4H), 4.15 (m, 6H), 6.26 (t, *J* = 2.2 Hz, 2H), 6.46 (dd, *J* = 1.3 Hz, *J* = 2.0 Hz, 2H), 6.48 (dd, *J* = 1.3 Hz, *J* = 2.2 Hz, 2H), 6.81 (d, *J* = 1.4 Hz, 4H), 7.02 (d, *J* = 1.3 Hz, 4H), 7.03 (d, *J* = 1.4 Hz, 2H), 7.10 (t, *J* = 1.4 Hz, 2H), 7.26 (m, 2H), 7.27 (t, *J* = 1.3 Hz, 1H); GPC PDI = 1.02; MS (MALDI) calc'd for $C_{89}H_{104}N_4NaO_{20}$ ([M+Na^+]) 1572.78, found 1573.15.

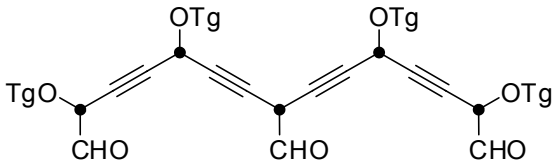


Oligomer 2[5]. The trifluoroacetamide-protected oligomer was purified by prep. GPC. After deprotection using distilled THF under nitrogen, 25 mg (0.042 mmol, 57%) of **2**[5] was obtained as a cloudy orange oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.37 (s, 18H), 3.55 (m, 12H), 3.6-3.9 (m, 58H), 4.09 (m, 4H), 4.15 (m, 8H), 6.28 (t, *J* = 2.2 Hz, 2H), 6.48 (d, *J* = 2.2 Hz, 4H), 6.81 (m, 6H), 7.00 (d, *J* = 1.3 Hz, 4H), 7.02 (d, *J* = 1.4 Hz, 4H), 7.10 (t, *J* = 1.4 Hz, 2H), 7.11 (t, *J* =

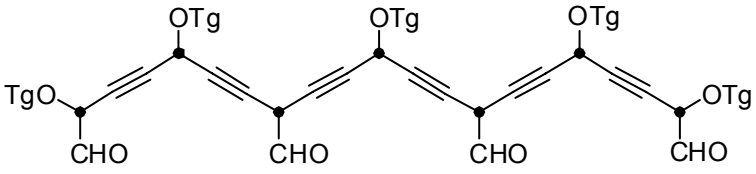
1.4 Hz, 1H), 7.25 (m, 2H), 7.28 (t, J = 1.4 Hz, 2H); GPC PDI = 1.05; MS (MALDI) calc'd for $C_{112}H_{127}N_5NaO_{24}$ 1950.22, found 1950.53.



Oligomer 2^6. The Sonogashira coupling was carried out in two steps using the TIPS-protected monomer **S10**, purifying by prep. GPC after each step. After deprotection using distilled THF under nitrogen, 31 mg (0.013 mmol, 66%) of $\mathbf{2}^6$ was obtained as a cloudy orange oil: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.37 (s, 21H), 3.54 (m, 14H), 3.6-3.9 (m, 68H), 4.09 (m, 4H), 4.14 (m, 10H), 6.25 (t, J = 2.1 Hz, 2H), 6.46 (d, J = 1.7 Hz, 2H), 6.47 (d, J = 2.1 Hz, 2H), 6.81 (m, 8H), 7.01 (d, J = 1.2 Hz, 4H), 7.02 (s, 6H), 7.09 (d, J = 1.7 Hz, 2H), 7.10 (d, J = 2.1 Hz, 2H), 7.26 (m, 2H), 7.27 (m, 3H); GPC PDI = 1.04; MS (MALDI) calc'd for $C_{135}H_{150}N_6NaO_{28}$ ([M+Na^+]) 2327.65, found 2327.48.

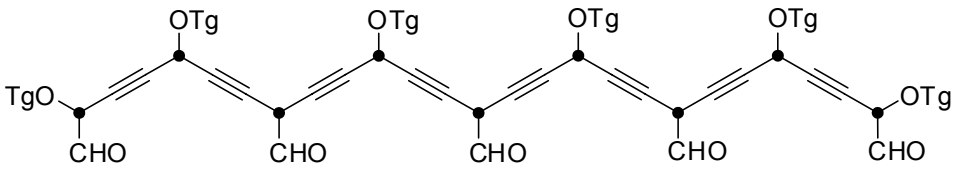


Oligomer 3^3. After deprotection and purifcation by prep. GPC and flash chromatography (7:3 CH_2Cl_2:acetone), 40.2 mg (0.033 mmol, 50%) of $\mathbf{3}^3$ was obtained as a yellow wax: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.380 (s, 6H), 3.383 (s, 6H), 3.55 (m, 8H), 3.63-3.73 (m, 16H), 3.76 (m, 8H), 3.90 (m, 8H), 4.19 (m, 4H), 4.22 (m, 4H), 7.10 (d, J = 1.3 Hz, 4H), 7.34 (m, 4H), 7.41 (dd, J = 1.4 Hz, J = 2.6 Hz, 2H), 7.62 (t, J = 1.4 Hz, 2H), 7.92 (t, J = 1.6 Hz, 1H), 7.99 (d, J = 1.6 Hz, 2H), 9.96 (s, 2H), 10.03 (s, 1H); GPC indicated >95% purity (PDI unavailable due to low MW); MS (MALDI) calc'd for $C_{69}H_{78}NaO_{19}$ ([M+Na^+]) 1234.34, found 1234.35.

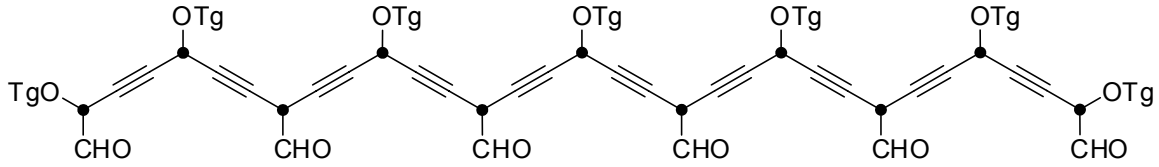


Oligomer 3^4. After deprotection and purification by prep. GPC and flash chromatography (3:1 CH_2Cl_2:acetone), 89.8 mg (0.056 mmol, 64%) of $\mathbf{3}^4$ was obtained as a yellow wax: ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.02 (s, 2H), 9.95 (s, 2H), 7.98 (br, 4H), 7.91 (br, 2H), 7.61 (br, 2H), 7.39 (br, 2H), 7.32 (br, 5H), 7.09 (br, 6H), 4.20-4.17 (m, 10H), 3.89-3.87 (m,

10H), 3.76-3.64 (m, 30H), 3.56-3.53 (m, 10H), 3.37 (s, 15H); GPC PDI = 1.01; MS (MALDI) calc'd for $C_{93}H_{100}NaO_{24}$ ([M+Na^+]) 1624.76, found 1624.48.



Oligomer 3^5. After deprotection and purification by prep. GPC and flash chromatography (7:3 CH_2Cl_2:acetone), 27.4 mg (0.014 mmol, 43%) of $\mathbf{3}^5$ was obtained as a yellow wax: ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.02 (s, 1H), 10.01 (s, 2H), 9.94 (s, 2H), 7.97 (br, 6H), 7.91 (br, 2H), 7.61 (br, 2H), 7.39 (br, 2H), 7.32 (br, 7H), 7.08 (br, 8H), 4.21-4.16 (m, 12H), 3.90-3.87 (m, 12H), 3.76-3.72 (m, 12H), 3.70-3.64 (m, 24H), 3.56-3.53 (m, 12H), 3.37 (s, 18H); GPC PDI = 1.06; MS (MALDI) calc'd for $C_{117}H_{122}NaO_{29}$ ([M+Na^+]) 2015.19, found 2015.04.



Oligomer 3^6. After deprotection and purification by prep. GPC, 21.8 mg (0.009 mmol, 35%) of $\mathbf{3}^6$ was obtained as a yellow wax: ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.01 (s, 4H), 9.94 (s, 2H), 7.97 (br, 8H), 7.91 (br, 2H), 7.59 (br, 2H), 7.38 (br, 2H), 7.32 (br, 9H), 7.08 (br, 10H), 4.18 (br, 14H), 3.88 (br, 14H), 3.77-3.73 (m, 14H), 3.71-3.64 (m, 28H), 3.57-3.54 (m, 14H), 3.37 (s, 21H); GPC PDI = 1.04 (a small amount of high molecular weight peak was observed by anal. GPC which was not observed in repeated prep. GPC runs and attributed to aggregation or crosslinking by impurities in the anal. GPC solvent system); MS (MALDI) calc'd for $C_{141}H_{144}NaO_{34}$ ([M+Na^+]) 2405.62, found 2405.50. NOTE: Several peaks at +60 a.u. intervals were observed in the MALDI spectrum. Based on the relatively clean ^{1}H NMR spectrum (which indicates complete deprotection, Figure S1) and the absence of these peaks in the MALDI spectrum of the acetal-protected precursor, we presume that these are either aggregates/adducts formed in the MALDI process, or minor impurities that are more easily detected than the desired structure.

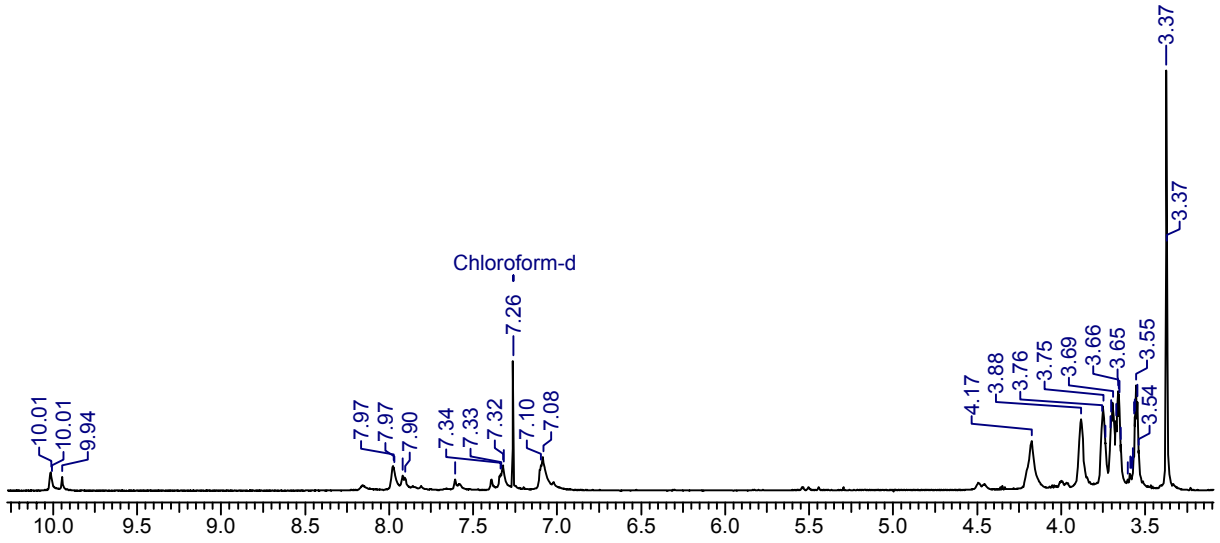
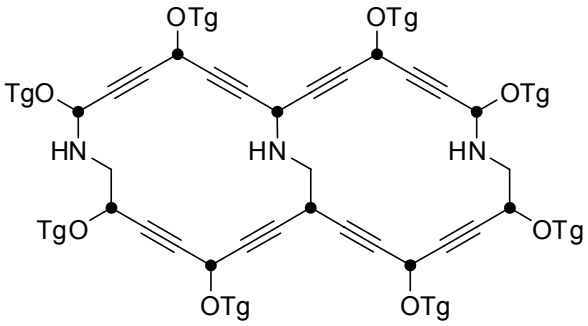


Figure S1. ^{1}H NMR spectrum of **3**^{6} (500 MHz, $CDCl_3$).

General Procedure for the Self-Assembly of Molecular Ladders 1^n. A 3 mM solution of **2**^{n} (1.05 eq.) and **3**^{n} (1.0 eq.) in $CHCl_3$ was treated with $Sc(OTf)_3$ (0.04 eq. per imine bond) dissolved in MeCN (such that the final solution was 5% MeCN by volume). After 5 h at room temperature, the reaction was quenched with $NaBH(OAc)_3$ (10 eq. per imine bond). The mixture was stirred overnight, then treated with sat. aq. $NaHCO_3$. After a few minutes, the mixture was extracted with $CHCl_3$ (4×), dried ($MgSO_4$), filtered, and concentrated. The crude products were then analyzed by GPC and MALDI, or purified by preparatory GPC. NOTE: Prior to use, the reaction $CHCl_3$ was passed through a short column of basic alumina to remove trace quantities of HCl.



Ladder 1^3. After purification by prep. GPC, 7.6 mg (3.3 μmol, 56%) of **1**^{3} was obtained as a colorless film: ^{1}H NMR ($CDCl_3$, 500 MHz, Figure S2) δ 3.37 (m, 24H), 3.55 (m, 16H), 3.62-3.77 (m, 50H), 3.81-3.91 (m, 16H), 4.07-4.19 (m, 16H), 4.35 (br s, 4H), 4.48 (br s, 3H), 6.20 (t, J = 2.0 Hz, 2H), 6.36 (br t, 2H), 6.43 (br t, 2H), 6.73 (d, J = 1.1 Hz, 2H), 6.89 (br t, 2H),

6.93 (br t, 2H), 7.00 (t, J = 1.2 Hz, 4H), 7.03 (t, J = 1.1 Hz, 4H), 7.05 (br t, 1H), 7.10 (br s, 2H), 7.31 (t, J = 1.2 Hz, 2H), 7.36 (t, J = 1.1 Hz, 2H), 7.44 (d, J = 0.7 Hz, 2H), 7.57 (br t, 1H); GPC PDI = 1.03; MS (MALDI) calc'd for $C_{135}H_{159}N_3NaO_{32}$ ([M+Na$^+$]) 2357.08, found 2358.57.

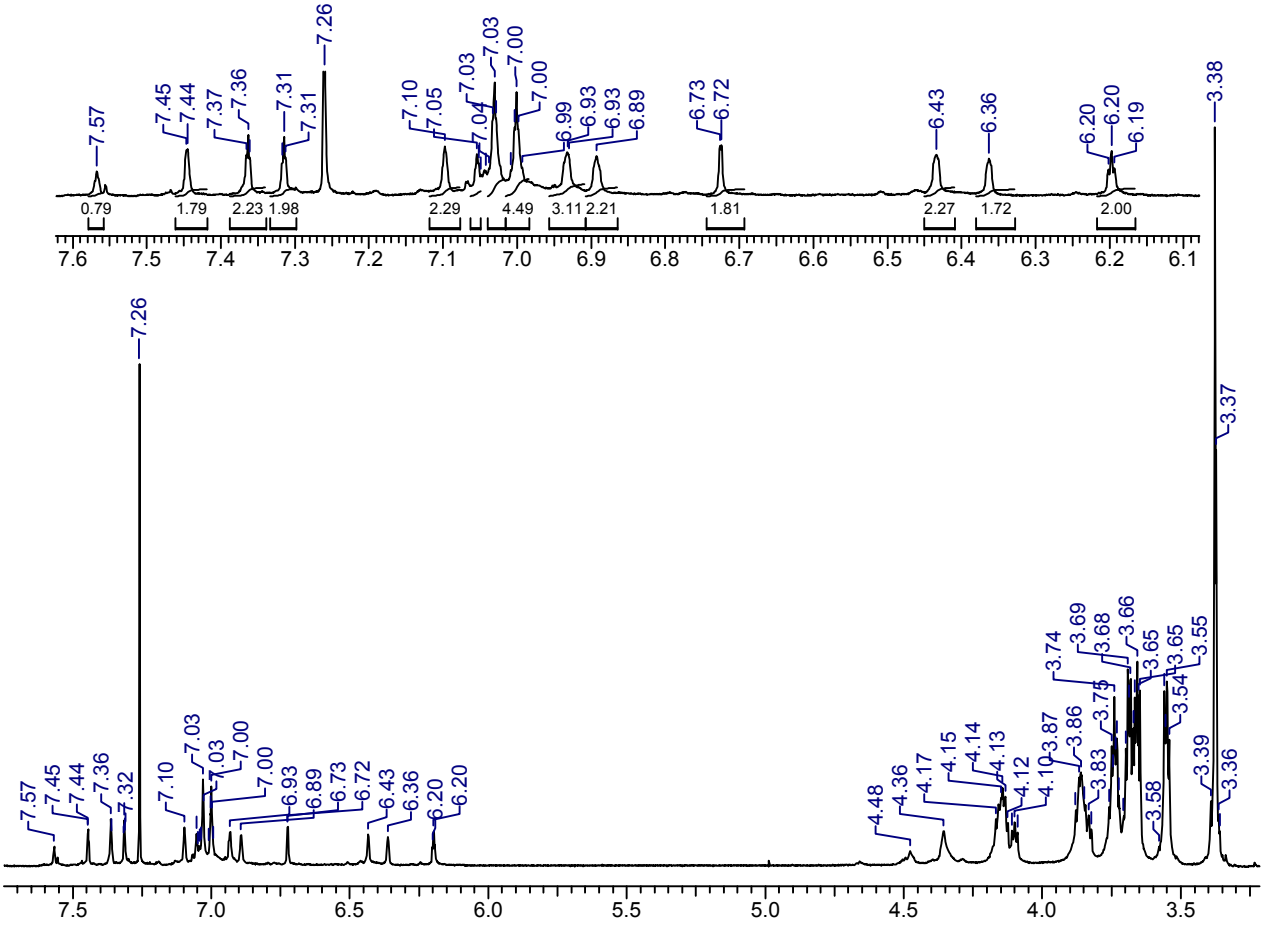
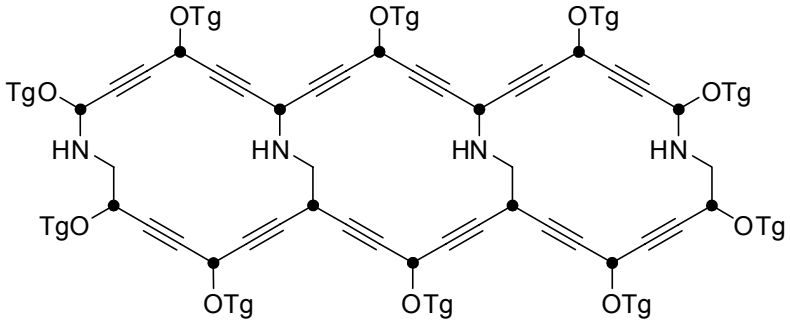


Figure S2. ^{1}H NMR spectrum of **1**[3] after purification by prep. GPC (500 MHz, $CDCl_3$).



Ladder 1[4]. After purification by prep. GPC, 5.0 mg (1.6 μmol, 37%) was obtained as a cloudy colorless film: ^{1}H NMR ($CDCl_3$, 500 MHz, Figure S3) δ 3.38 (m, 30H), 3.55 (m, 20H), 3.63-3.78 (m, 64H), 3.81-3.91 (m, 20H), 4.08-4.18 (m, 20H), 4.35 (br s, 4H), 4.46 (br s, 4H),

6.19 (t, J = 1.9 Hz, 2H), 6.36 (br s, 2H), 6.43 (br s, 2H), 6.72 (s, 3H), 6.89 (br s, 2H), 6.93 (br s, 2H), 6.99-7.08 (m, 16H), 7.09 (s, 2H), 7.31 (t, J = 1.2 Hz, 2H), 7.32 (t, J = 1.4 Hz, 1H), 7.36 (t, J = 1.2 Hz, 2H), 7.37 (m, 1H), 7.44 (s, 3H), 7.57 (s, 2H); GPC PDI = 1.03; MS (MALDI) calc'd for $C_{182}H_{204}N_4NaO_{40}$ ([M+Na$^+$]) 3110.56, found 3104.05.

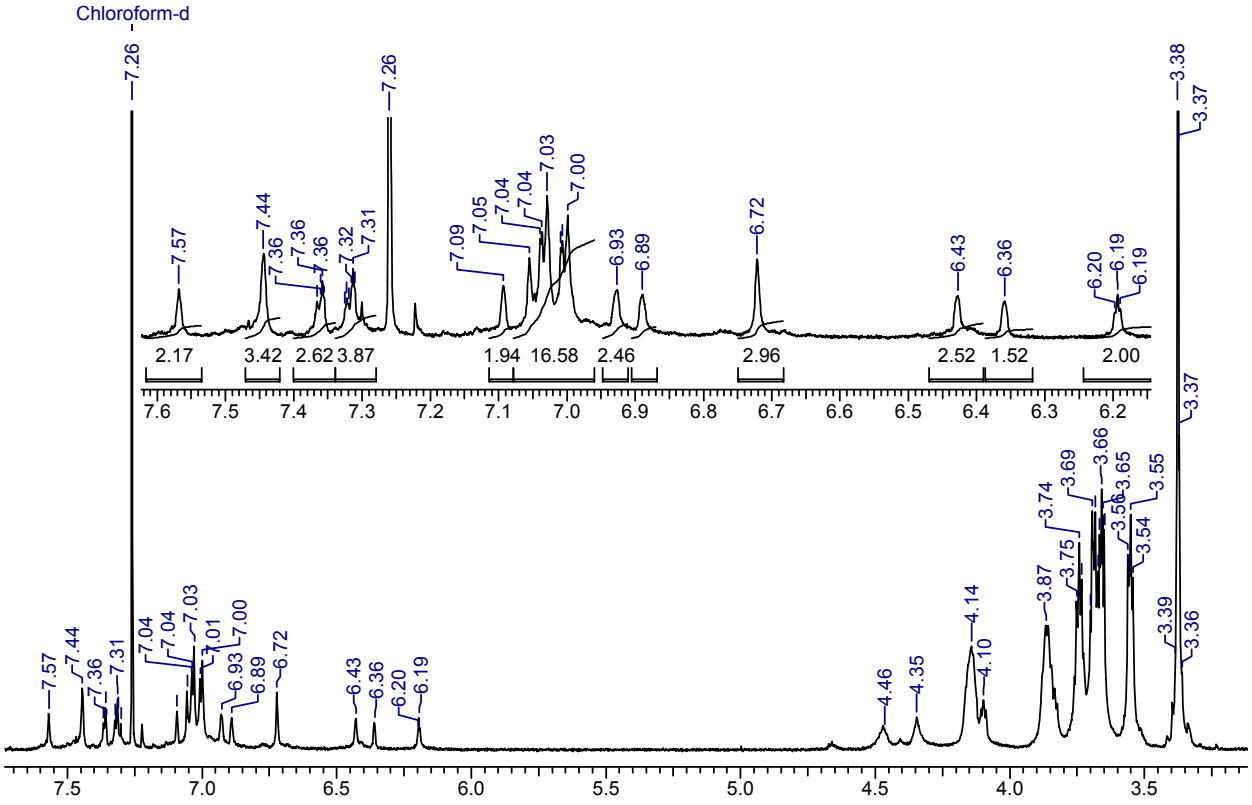


Figure S3. ^{1}H NMR spectrum of **1**[4] after purification by prep. GPC (500 MHz, $CDCl_3$).

Deconvolution of GPC Traces

GPC traces of $\mathbf{1}^n$ were deconvoluted using the program PeakFit v. 4.12 (Systat Software Inc.) using half-gaussian modified gaussian (GMG) functions to simulate the peaks. In each case, the spectra were fit using 4–5 simulated peaks. Yields were estimated by comparing the area of the peak assigned to $\mathbf{1}^n$ to the total area of the peaks for starting oligomers $\mathbf{2}^n/\mathbf{3}^n$, $\mathbf{1}^n$, and high molecular weight byproducts.

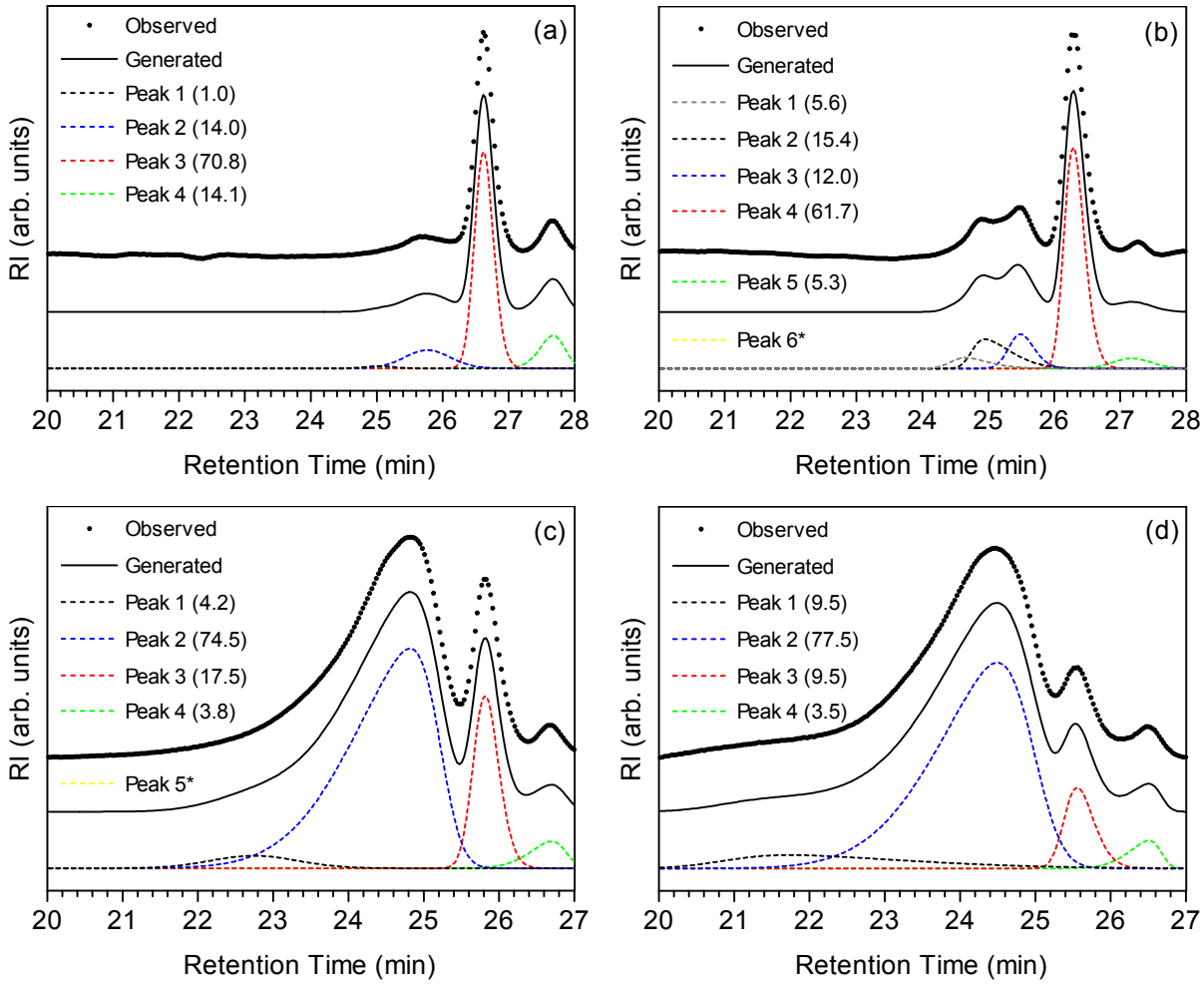


Figure S4. Deconvoluted GPC traces of (a) $\mathbf{1}^3$, (b) $\mathbf{1}^4$, (c) $\mathbf{1}^5$, and (d) $\mathbf{1}^6$ (unpurified reaction mixtures). The area (yield) of each peak is given in parentheses in the legends. The peaks marked * represent small amounts of unassigned low molecular weight impurities (*i.e.*, smaller than the peaks assigned to the starting oligomers $\mathbf{2}^n/\mathbf{3}^n$) that were included in the deconvolution but not considered in determining yield.

GPC Concentration Dependence of $\mathbf{1}^5$

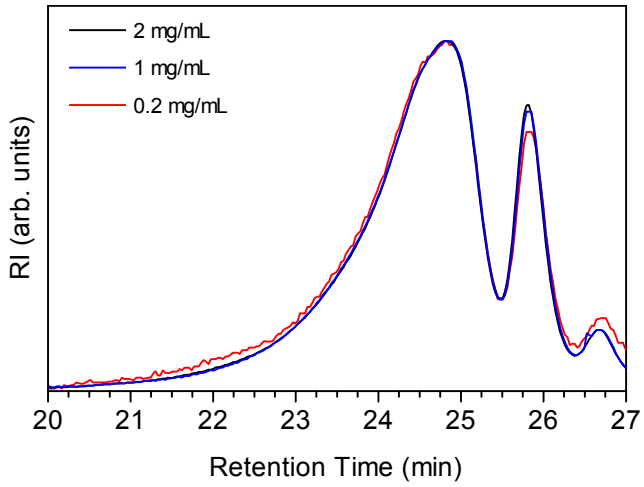


Figure S5. GPC traces of $\mathbf{1}^5$ as a function of initial sample concentration.

Self-Assembly of $\mathbf{1}^5$ at Elevated Temperature

The general procedure for the self-assembly of $\mathbf{1}^5$ was followed with two changes: the reaction was carried out in a sealed tube at 75 °C, and 2,6-di-*tert*-butyl-4-methylphenol (5 eq.) was added to inhibit trifluoromethylation. After workup, the crude product was analyzed by GPC (Figure S6) and MALDI (calc'd for $C_{229}H_{249}N_5NaO_{48}$ 3862.42, found 3854.61).

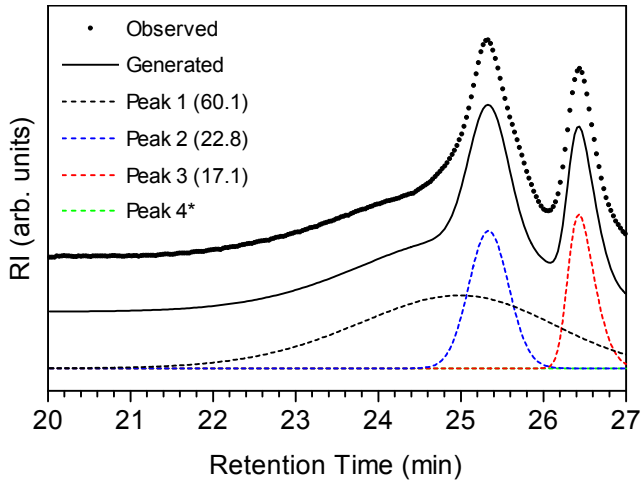


Figure S6. Observed and generated GPC traces for the formation of $\mathbf{1}^5$ at elevated temperature: t_r = 26.4 min, M_n = 5120, PDI = 1.04. Please note that the calibration of the analytical GPC had changed compared to the earlier runs (Figure 3), hence t_r cannot be directly compared.

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