

Conformational Ordering of Apolar, Chiral *m*-Phenylene Ethynylene Oligomers

Luc Brunsveld,[†] Ryan B. Prince,[‡] E. W. Meijer,[†] Jeffrey S. Moore^{‡*}

[‡]*The Department of Chemistry and Materials Science & Engineering, 600 South Mathews Avenue
The University of Illinois at Urbana-Champaign Urbana, IL 61801 (USA)
moore@scs.uiuc.edu*

[†]*Laboratory of Macromolecular and Organic Chemistry
Eindhoven University of Technology
P.O. Box 513, 5600 MB Eindhoven (The Netherlands)*

Supporting Information

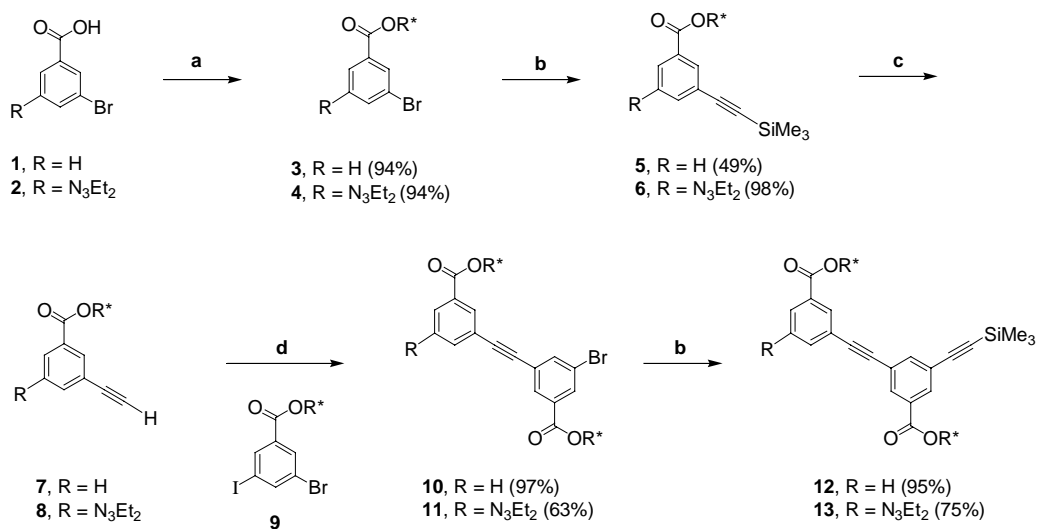
Experimental Procedures

General. Unless otherwise noted, all starting materials were obtained from commercial suppliers and were used without further purification. Analytical thin layer chromatography (TLC) was performed on precoated sheets of silica gel 60, and silica gel column chromatography was carried out with silica gel 60 (230-400 mesh). Dry triethylamine and acetonitrile were obtained by vacuum transfer from calcium hydride.

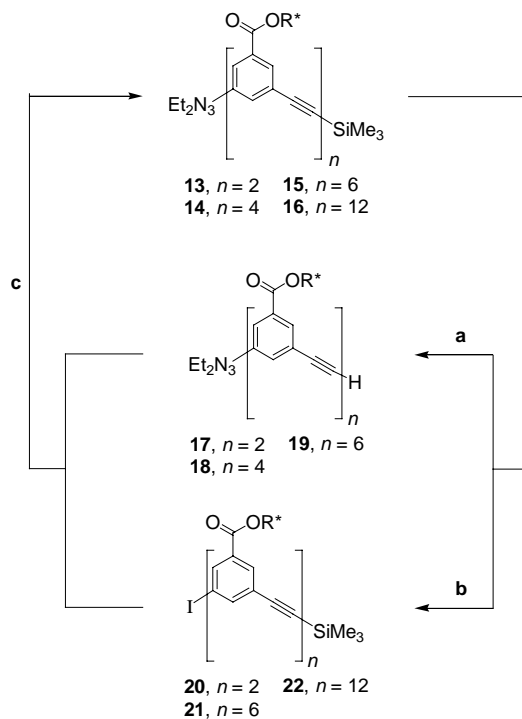
The ^1H NMR spectra were recorded at 400 MHz and ^{13}C NMR were recorded at 100 MHz. Chemical shifts are expressed in parts per million (δ) using residual solvent protons as internal standard. Coupling constants, J , are reported in Hertz (Hz). Splitting patterns are designated as s, singlet; br s, broad singlet; d, doublet; t, triplet; q, quartet; dd, doublet doublet; ddd, doublet doublet doublet; dt, doublet triplet; m, multiplet; quin, quintet. Low-resolution electron impact mass spectra were obtained on a Micromass ZAB-SE spectrometer. Low-resolution matrix assisted laser desorption mass spectra were obtained using IAA (indole acrylic acid) or 4-HMBN (4-hydroxybenzylidenemalononitrile) as the matrix on a PerSeptive BioSystems Voyager-DE STR spectrometer. Elemental analyses were performed by the University of Illinois Micro Analytical Service Laboratory using a Leeman Labs CE440. Analytical size-exclusion chromatography analysis was performed using a Waters 510 HPLC Pump, Waters 996 photodiode array, and a series of three Waters styragel HR 4E (7.8 x 300 mm) columns which were calibrated with narrow molecular weight polystyrene standards. Preparative size-exclusion chromatography was performed using Bio-Beads S-XI Beads (200-400 mesh) from Bio-Rad laboratories using toluene as the eluent. HPLC analysis was performed on a Rainin binary gradient system equipped with two SD-200 pumps, a Si 80-125-C5 analytical column (4.6 x 250 mm), and a UV detector operating at 275 nm.

UV-vis and Circular Dichroism Measurements. The UV absorption spectra were recorded on a Perkin-Elmer Lambda 900 spectrophotometer using 1-cm quartz cells. Circular dichroism spectra were recorded on a Jasco J-600 spectropolarimeter using 1-cm quartz cells. For both instruments, variable temperature spectra were obtained by equilibrating the sample at the desired temperature for 15 minutes with a temperature controllable cuvette holder. For the titration experiments, two stock solutions (100

mL each) of the appropriate oligomer in spectrophotometric grade CHCl_3 and heptane were prepared. Mixed solvent compositions from 0 to 100% CHCl_3 were obtained by adding the appropriate volume of the CHCl_3 solution into a volumetric flask and then diluting to a total volume of 5 mL with the heptane solution.



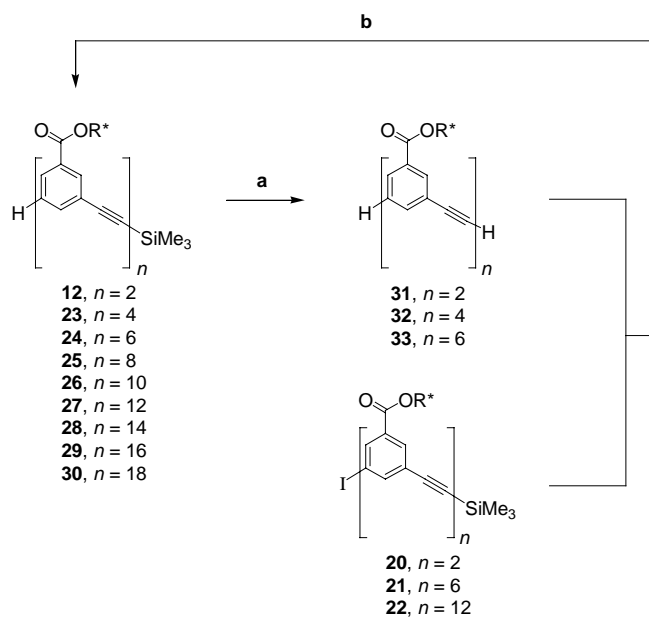
Scheme 1: (a) (*S*)-3,7-dimethyl-1-octanol (1.05 equiv), DCC, 4-DMAP, CH_2Cl_2 , 0 °C; (b) Trimethylsilylacetylene, $\text{Pd}_2(\text{dba})_3$, CuI, PPh_3 , Et_3N , 70 °C; (c) TBAF, THF, r.t.; (d) $\text{Pd}_2(\text{dba})_3$, CuI, PPh_3 , Et_3N , 70 °C. $\text{R}^* = -(S)\text{-3,7-dimethyloctane}$.



Scheme 2: (a) TBAF, THF, r.t.; (b) MeI, 110 °C; (c) Pd₂(dba)₃, CuI, PPh₃, Et₃N, CH₃CN, 70 °C. R* = - (S)-3,7-dimethyloctane.

Table 3.3: Yields of triazene conversion and subsequent coupling reactions of the orthogonally protected oligomers.

oligomer length (n)	% Yield I-R	% Yield Coupling
2	90 (20)	-----
4	-----	93 (14 ⇒ 17 + 20)
6	91 (21)	94 (15 ⇒ 18 + 20)
12	90 (22)	71 (16 ⇒ 19 + 21)



Scheme 3: (a) TBAF, THF, r.t.; (b) $\text{Pd}_2(\text{dba})_3$, CuI, PPh_3 , Et_3N , 70°C . $\text{R}^* = -(S)\text{-}3,7\text{-dimethyloctane}$.

Table 3.4: Yields and purity for the capped oligomers **12**, **23-30**.

oligomer length (n)	% Yield Coupling	Purity (area %) ^a
2	-----	100
4	82 (23 \Rightarrow 31 + 20)	99.4
6	96 (24 \Rightarrow 32 + 20)	98.7
8	58 (25 \Rightarrow 31 + 21)	100
10	90 (26 \Rightarrow 32 + 21)	100
12	64 (27 \Rightarrow 33 + 21)	100
14	75 (28 \Rightarrow 31 + 22)	100
16	62 (29 \Rightarrow 32 + 22)	99.8
18	68 (30 \Rightarrow 33 + 22)	99.3

^aPurity determined by HPLC analysis.

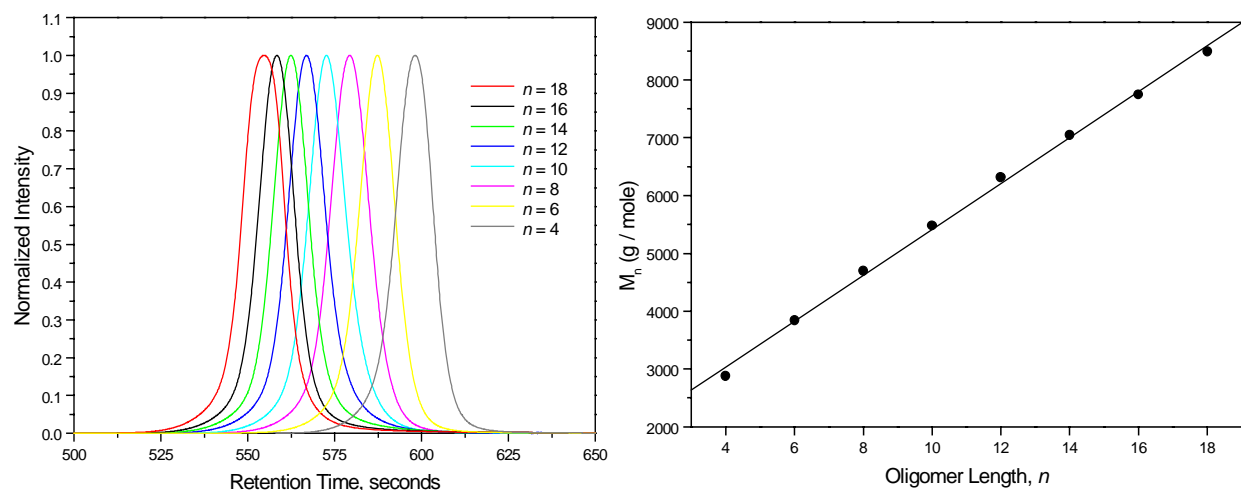


Figure 2: Size exclusion chromatograms of **23-30** in chloroform (left). All traces have been normalized to a constant intensity of 1.0. Plot of M_n against the oligomer length (right). The molecular weight was calibrated against narrow molecular weight polystyrene standards. The solid line is the least squares linear fit (correlation coefficient = 0.999).

Table 1. Size-exclusion chromatography data on oligomers **23-30**.

Compound		M_n (g/mol) ^a	M_w/M_n
Tetramer	23	2782	1.04
Hexamer	24	3728	1.03
Octamer	25	4552	1.03
Decamer	26	5298	1.03
Dodecamer	27	6075	1.04
Tetradecamer	28	6807	1.04
Hexadecamer	29	7493	1.03
Octadecamer	30	8207	1.03

^aNumber average molecular weight relative to polystyrene standards.

Experimental Procedures

(S)-3,7-dimethyloctyloxy-3-bromobenzoate (3). To an oven-dried 500 mL round bottom flask was added **1** (6.05 g, 31.6 mmol), (S)-1-hydroxy-3,7-dimethyloctane (5.00 g, 31.6 mmol), *N, N'*-dimethylaminopyridine (1.22 g, 1.00 mmol) and dry CH₂Cl₂ (150 mL). The homogeneous, yellow solution was placed under a N₂ atmosphere and cooled in a 0 °C bath. Dicyclohexylcarbodiimide (12.4 g, 60.0 mmol) was added in portions and the solution was stirred for 1 h at 0 °C, warmed to room temperature and stirred 12 h. The solution was cooled in a 0 °C ice bath, gravity filtered to remove the DCU and then concentrated in vacuo resulting in a yellow oil. The crude product was purified by silica gel column chromatography (heptane/dichloromethane, 1/0, 2/3) to afford 9.70 g (28.4 mmol, 94%) of analytically pure **3** as a colorless oil: ¹H NMR (400 MHz, CDCl₃) δ 8.16 (ddd, *J* = 1.86, 1.70, 0.39 Hz, 1H), 7.96 (ddd, *J* = 7.83, 1.65, 1.09 Hz, 1H), 7.66 (ddd, *J* = 8.02, 2.05, 1.10 Hz, 1H), 7.30 (ddd, *J* = 8.24, 7.97, 0.35 Hz, 1H), 4.38-4.32 (m, 2H), 1.82-1.78 (m, 1H), 1.61-1.50 (m, 3H), 1.36-1.13 (m, 6H), 0.95 (d, *J* = 6.5 Hz, 3H), 0.87 (d, *J* = 6.5 Hz, 3H), 0.87 (d, *J* = 6.5 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 165.2, 135.7, 132.5, 132.4, 129.6, 128.1, 122.4, 64.0, 39.1, 37.1, 35.5, 29.7, 27.9, 24.6, 22.6, 22.6, 19.6; MS (FAB) *m/z* 343.1 (40), 341.1 (47), 185.0 (74), 183.0 (76); Anal. Calcd for C₁₇H₂₅O₂Br (341.29): C, 59.83; H, 7.38; found: C, 60.11; H, 7.57.

(S)-3,7-dimethyloctyloxy 3-bromo-5-(3,3-diethyltriazenyl) benzoate (4). To an oven-dried 50 mL round bottom flask was added **2** (2.01 g, 6.71 mmol), (S)-1-hydroxy-3,7-dimethyloctane (1.13 g, 7.16 mmol), *N, N'*-dimethylaminopyridine (0.25 g, 2.07 mmol) and dry CH₂Cl₂ (40 mL). The homogeneous, yellow solution was placed under a N₂ atmosphere and cooled in a 0 °C bath. Dicyclohexylcarbodiimide (2.82 g, 13.7 mmol) was added in one portion and the solution was stirred for 1 h at 0 °C, warmed to room temperature and stirred 15 h. The solution was cooled in a 0 °C ice bath, gravity filtered to remove the DCU and then concentrated in vacuo resulting in a yellow oil. The crude product was purified by silica gel column chromatography (hexane/dichloromethane, 2/1) to afford 2.77 g (6.33 mmol, 94%) of analytically pure **4** as a light yellow oil: ¹H NMR (400 MHz, CDCl₃) δ 7.97 (dd, *J* = 1.89, 1.52 Hz, 1H), 7.88 (dd, *J* = 1.93, 1.46 Hz, 1H), 7.75 (t, *J* = 1.87 Hz, 1H), 4.30-4.40 (m, 2H), 3.76-3.82 (m, 4H), 1.76-1.85 (m, 1H), 1.50-1.68 (m, 4H), 1.10-1.37 (m, 13H), 0.95 (d, *J* = 6.49 Hz, 3H), 0.86 (d, *J* = 6.54, 6H);

^{13}C NMR (100 MHz, CDCl_3) δ 165.6, 152.6, 132.5, 128.3, 126.7, 122.5, 121.0, 63.9, 39.1, 37.1, 35.5, 29.9, 27.9, 24.6, 22.6, 22.5, 19.6; MS (FAB) m/z 440.2 (100), 442.2 (94.6); TLC R_f = 0.41 (hexane/dichloromethane, 2/1); Anal. Calcd for $\text{C}_{21}\text{H}_{34}\text{N}_3\text{O}_2\text{Br}$ (440.42): C, 57.27; H, 7.78; N, 9.54. Found: C, 57.27; H, 7.80; N, 9.50.

(S)-3,7-dimethyloctyloxy-3-[2-(1,1,1-trimethylsilyl)-1-ethynyl] benzoate (5). To a sealed tube fitted with a magnetic stirrer was added Pd_2dba_3 (400 mg, 0.44 mmol), copper(I) iodide (170 mg, 0.88 mmol), triphenylphosphine (1.0 g, 3.81 mmol), **3** (5.00 g, 14.65 mmol), and dry triethylamine (50 mL). The mixture was evacuated and back-filled with nitrogen three times and dry, degassed trimethylsilylacetylene (12.9 mL, 77 mmol) was added. The tube was sealed and stirred at 75 °C for 60 h (during which time a white salt precipitate formed). The solution was diluted with hexane (300 mL), filtered to remove the precipitate and concentrated in vacuo leaving a brown oil. The residue was purified by silica gel column chromatography (hexane/dichloromethane, 1/0, 4/1) to give 2.55 g (7.11 mmol, 49%) of analytically pure **5** as a colorless oil: ^1H NMR (400 MHz, CDCl_3) δ 8.12 (t, J = 1.73 Hz, 1H), 7.98 (dt, J = 7.78, 1.73 Hz, 1H), 7.63 (dt, J = 7.77, 1.73 Hz, 1H), 7.37 (t, J = 7.68 Hz, 1H), 4.40-4.30 (m, 2H), 1.82-1.78 (m, 1H), 1.61-1.50 (m, 3H), 1.36-1.13 (m, 6H), 0.95 (d, J = 6.5 Hz, 3H), 0.87 (d, J = 6.5 Hz, 3H), 0.87 (d, J = 6.5 Hz, 3H), 0.27 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.9, 136.0, 132.9, 130.6, 129.4, 128.2, 123.5, 103.9, 95.2, 39.1, 37.1, 35.5, 29.9, 27.9, 24.6, 22.7, 19.6, -0.2; MS (FAB) m/z 359.2 (30), 219.1 (33), 201.1 (100); TLC R_f = 0.07 (hexane/dichloromethane, 9/1); Anal. Calcd for $\text{C}_{22}\text{H}_{34}\text{O}_2\text{Si}$ (358.60): C, 73.69; H, 9.56; found: C, 73.54; H, 9.48.

(S)-3,7-dimethyloctyloxy 3-(3,3-diethyltriazenyl)-5-[2-(1,1,1-trimethylsilyl) benzoate (6). To a sealed tube fitted with a magnetic stirrer was added **4** (3.51 g, 7.97 mmol), Pd_2dba_3 (0.23 g, 0.25 mmol), copper iodide (0.09 g, 0.48 mmol), triphenylphosphine (0.54 g, 2.1 mmol) and triethylamine (40 mL). The mixture was evacuated and back-filled with nitrogen three times. Trimethylsilylacetylene (2.5 mL, 14.2 mmol) was added to the flask and it was sealed, under a nitrogen atmosphere, with a Teflon[®] screw cap. The solution was stirred at 70 °C for 22 h. After being cooled to rt, the contents of the flask were added to diethyl ether (100 mL). The insoluble amine salts were filtered off and the resulting solution was concentrated in vacuo to provide an orange oil. The crude product was purified by silica gel

column chromatography (hexane/CH₂Cl₂, 5/2) to afford 3.58 g (7.82 mmol, 98%) of analytically pure **6** as a light yellow oil: ¹H NMR (400 MHz, CDCl₃) δ 8.00 (dd, *J* = 1.89, 1.52 Hz, 1H), 7.87 (t, *J* = 1.87 Hz, 1H), 7.68 (dd, *J* = 1.93, 1.46 Hz, 1H), 4.30-4.40 (m, 2H), 3.76-3.82 (m, 4H), 1.76-1.85 (m, 1H), 1.50-1.68 (m, 4H), 1.10-1.37 (m, 13H), 0.95 (d, *J* = 6.51 Hz, 3H), 0.86 (d, *J* = 6.63 Hz, 6H), 0.25 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.1, 151.3, 131.2, 129.1, 127.5, 123.6, 122.0, 104.4, 94.2, 63.7, 39.1, 37.1, 35.5, 29.9, 27.9, 24.6, 22.7, 22.6, 19.6, -0.1; MS (FAB) *m/z* 458.3 (49), 318.2 (19); TLC *R_f* = 0.20 (hexane/dichloromethane, 2/1); Anal. Calcd for C₂₆H₄₃N₃O₂Si (457.73): C, 68.22, H, 9.47, N, 9.18. Found: C, 68.11; H, 9.53; N, 9.22.

(S)-3,7-dimethyloctyloxy-5-bromo-3-iodobenzoate (9). To an oven-dried 500 mL round bottom flask was added 3-bromo-5-iodobenzoic acid (12.0 g, 36.7 mmol), (*S*)-1-hydroxy-3,7-dimethyloctane (6.1 g, 38.5 mmol), *N,N'*-dimethylaminopyridine (1.35 g, 11.0 mmol) and dry CH₂Cl₂ (200 mL). The heterogeneous, yellow solution was placed under a N₂ atmosphere and cooled in a 0 °C bath. Dicyclohexylcarbodiimide (15.2 g, 73.4 mmol) was added in small portions and the solution was stirred for 1 h at 0 °C, warmed to room temperature and stirred 12 h. The solution was cooled in a 0 °C ice bath, gravity filtered to remove the DCU and then concentrated in vacuo resulting in a yellow oil. The crude product was purified by silica gel column chromatography (heptane/dichloromethane, 1/0, 2/3) to afford 13.7 g (29.32 mmol, 80%) of analytically pure **9** as a colorless oil: ¹H NMR (400 MHz, CDCl₃) δ 8.29 (t, *J* = 1.5 Hz, 1H), 8.11 (dd, *J* = 1.8, 1.5 Hz, 1H), 8.03 (t, *J* = 1.8 Hz, 1H), 4.38-4.32 (m, 2H), 1.82-1.78 (m, 1H), 1.61-1.50 (m, 3H), 1.36-1.13 (m, 6H), 0.95 (d, *J* = 6.5 Hz, 3H), 0.87 (d, *J* = 6.5 Hz, 3H), 0.87 (d, *J* = 6.5 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.9, 143.6, 137.1, 133.6, 131.9, 123.0, 94.0, 64.5, 39.1, 37.1, 35.4, 29.9, 27.9, 24.6, 22.7, 22.6, 19.6; MS (FAB) *m/z* 469.0 (29), 467.0 (33), 310.8 (41), 308.8 (41); TLC *R_f* = 0.30 (heptane/dichloromethane, 2/3); Anal. Calcd for C₁₇H₂₄O₂BrI (467.19): C, 43.71; H, 5.18; found: C, 43.80; H, 5.28.

H-[A]₂-Br (10). To a solution of **5** (2.32 g, 6.47 mmol) and THF (50 mL) was added a solution of tetrabutylammonium fluoride in wet THF (8.4 mL, 1.0 M). The solution was stirred for 60 seconds, filtered through silica (eluting with hexane/dichloromethane, 1/1), and the solvent was removed in vacuo to leave a yellow oil. The crude acetylene was used without further purification. To a sealed tube fitted

with a magnetic stirrer was added Pd₂dba₃ (127 mg, 0.13 mmol), copper(I) iodide (50 mg, 0.26 mmol), triphenylphosphine (300 mg, 1.15 mmol), **7** (1.80 g, 6.3 mmol), **9** (4.2 g, 9.0 mmol), and dry triethylamine (30 mL). The mixture was evacuated and back-filled with nitrogen three times and heated at 55 °C for 36 h (during which time a white salt precipitate formed). The solution was diluted with hexane (300 mL), filtered to remove the precipitate and concentrated in vacuo leaving a yellow residue. The residue was purified by silica gel column chromatography (hexane/EtOAc, 1/0, 10/1) to give 3.81 g (6.09 mmol, 97%) of analytically pure **10** as a light yellow oil: ¹H NMR (400 MHz, CDCl₃) δ 8.21 (td, *J* = 1.69, 0.58 Hz, 1H), 8.14 (dd, *J* = 1.88, 1.56 Hz, 1H), 8.13 (t, *J* = 1.48 Hz, 1H), 8.05 (ddd, *J* = 7.83, 1.74, 1.19 Hz, 1H), 7.86 (dd, *J* = 1.90, 1.49 Hz, 1H), 7.71 (ddd, *J* = 7.72, 1.60, 1.28 Hz, 1H), 7.45 (td, *J* = 7.78, 0.62 Hz, 1H), 4.43-4.32 (m, 4H), 1.85-1.78 (m, 2H), 1.68-1.47 (m, 6H), 1.39-1.11 (m, 12H), 0.97 (d, *J* = 6.5 Hz, 3H), 0.95 (d, *J* = 6.5 Hz, 3H), 0.87 (m, 12H); ¹³C NMR (100 MHz, CDCl₃) δ 165.8, 164.7, 138.1, 135.7, 132.7, 132.5, 132.4, 131.2, 130.9, 129.8, 128.6, 125.1, 122.7, 122.2, 90.4, 87.6, 64.3, 63.9, 39.1, 37.1, 37.1, 35.5, 35.4, 29.9, 29.9, 27.9, 24.6, 22.7, 22.6, 19.6, 19.6; MS (FAB) *m/z* 626.2 (76), 624.2 (66); TLC R_f = 0.35 (hexane/EtOAc, 20/1); Anal. Calcd for C₃₆H₄₉O₄Br (625.69): C, 69.11; H, 7.89; found: C, 68.71; H, 7.87.

Et₂N₃-[A]₂-Br (11). To a solution of **6** (2.58 g, 5.64 mmol) and THF (35 mL) was added a solution of tetrabutylammonium fluoride in wet THF (7.3 mL, 1.0 M). The solution was stirred for 60 seconds, filtered through silica (eluting with hexane/dichloromethane, 1/1), and the solvent was removed in vacuo to leave a brown oil. The crude acetylene was used without further purification. To a sealed tube fitted with a magnetic stirrer was added Pd₂dba₃ (103 mg, 0.11 mmol), copper(I) iodide (43 mg, 0.23 mmol), triphenylphosphine (265 mg, 1.00 mmol), **8** (2.16 g, 5.60 mmol), **9** (3.40 g, 7.28 mmol), and dry triethylamine (30 mL). The mixture was evacuated and back-filled with nitrogen three times and heated at 55 °C for 14 h (during which time a white salt precipitate formed). The solution was diluted with hexane (250 mL), filtered to remove the precipitate and concentrated in vacuo leaving a brown residue. The residue was purified by silica gel column chromatography (hexane/EtOAc, 1/0, 20/1) to give 2.57 g (3.55 mmol, 63%) of analytically pure **11** as a colorless oil: ¹H NMR (400 MHz, CDCl₃) δ 8.13 (t, *J* = 1.6 Hz, 1H), 8.12 (t, *J* = 1.4 Hz, 1H), 8.06 (dd, *J* = 1.9, 1.7 Hz, 1H), 7.93 (t, *J* = 1.5 Hz, 1H), 7.85 (t, *J* =

1.5 Hz, 1H), 7.76 (dd, $J = 1.9, 1.6$ Hz, 1H), 4.41-4.32 (m, 4H), 3.84-3.76 (q, 4H), 1.87-1.78 (m, 2H), 1.68-1.48 (m, 6H), 1.37-1.10 (m, 18H), 0.95 (d, $J = 6.5$ Hz, 3H), 0.95 (d, $J = 6.5$ Hz, 3H), 0.86 (d, $J = 6.6$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.1, 164.7, 151.5, 138.1, 132.4, 132.2, 131.5, 131.2, 128.9, 127.2, 125.3, 122.9, 122.5, 122.2, 91.1, 86.9, 64.3, 63.8, 39.1, 37.1, 37.0, 35.5, 35.4, 29.9, 29.9, 27.9, 24.6, 24.5, 22.7, 22.6, 19.6, 19.6; MS (FAB) m/z 726.3 (96), 724.3 (100); TLC $R_f = 0.15$ (hexane/EtOAc, 33/1); Anal. Calcd for $\text{C}_{40}\text{H}_{58}\text{O}_4\text{N}_3\text{Br}$ (724.83): C, 66.28; H, 8.07; N, 5.80; found: C, 65.95; H, 8.16; N, 5.64.

H-[A]₂-SiMe₃ (12). To a sealed tube fitted with a magnetic stirrer was added Pd_2dba_3 (100 mg, 0.11 mmol), copper(I) iodide (62 mg, 0.33 mmol), triphenylphosphine (373 mg, 1.42 mmol), **10** (3.41 g, 5.45 mmol), and dry triethylamine (18 mL). The mixture was evacuated and back-filled with nitrogen three times and dry, degassed trimethylsilylacetylene (2.6 mL, 18.5 mmol) was added. The tube was sealed and stirred at 75 °C for 36 h (during which time a white precipitate formed). The solution was diluted with hexane (300 mL), filtered to remove the precipitate and concentrated in vacuo leaving a yellow residue. The residue was purified by silica gel column chromatography (hexane/dichloromethane, 1/0, 1/1) to give 3.34 g (5.18 mmol, 95%) of analytically pure **12** as a colorless oil: ^1H NMR (400 MHz, CDCl_3) δ 8.18 (td, $J = 1.65, 0.5$ Hz, 1H), 8.12 (t, $J = 1.6$ Hz, 1H), 8.07 (t, $J = 1.6$ Hz, 1H), 8.03 (ddd, $J = 7.9, 1.7, 1.2$ Hz, 1H), 7.8 (t, $J = 1.6$ Hz, 1H), 7.70 (ddd, $J = 7.7, 1.5, 1.2$ Hz, 1H), 7.45 (td, $J = 7.8, 0.6$ Hz, 1H), 4.42-4.35 (m, 4H), 1.86-1.78 (m, 2H), 1.68-1.47 (m, 6H), 1.40-1.12 (m, 12H), 0.98 (d, $J = 6.48$ Hz, 3H), 0.97 (d, $J = 6.47$ Hz, 3H), 0.86 (m, 12H), 0.27 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.8, 165.2, 138.6, 135.6, 132.7, 132.6, 132.3, 131.1, 130.9, 129.6, 128.5, 124.0, 123.66, 123.0, 102.9, 96.2, 89.7, 88.3, 64.1, 63.9, 39.17, 39.15, 37.10, 37.09, 35.50, 35.48, 29.91, 29.87, 27.93, 24.59, 24.58, 22.68, 22.59, 19.62, 19.60, -0.2; MS (FAB) m/z 642 (53), 345 (68); TLC $R_f = 0.05$ (hexane/dichloromethane, 7/1); Anal. Calcd for $\text{C}_{41}\text{H}_{58}\text{O}_4\text{Si}$: C, 76.59; H, 9.09; found: C, 76.27; H, 9.29.

Et₂N₃-[A]₂-SiMe₃ (13). To a sealed tube fitted with a magnetic stirrer was added Pd_2dba_3 (176 mg, 0.19 mmol), copper(I) iodide (132 mg, 0.70 mmol), triphenylphosphine (793 mg, 3.0 mmol), **11** (8.40 g, 11.59 mmol), and dry triethylamine (70 mL). The mixture was evacuated and back-filled with nitrogen three times and dry, degassed trimethylsilylacetylene (12 mL, 84 mmol) was added. The tube was sealed

and stirred at 75 °C for 72 h (during which time a white salt precipitate formed). The solution was diluted with hexane (400 mL), filtered to remove the precipitate and concentrated in vacuo leaving a brown oil. The crude product was purified by silica gel column chromatography (hexane/dichloromethane, 1/0, 1/1) to give 6.45 g (8.69 mmol, 75%) of analytically pure **13** as a light brown oil: ¹H NMR (400 MHz, CDCl₃) δ 8.12 (t, *J* = 1.6 Hz, 1H), 8.06 (t, *J* = 1.6 Hz, 1H), 8.05 (dd, *J* = 2.0, 1.6 Hz, 1H), 7.93 (t, *J* = 1.6 Hz, 1H), 7.80 (t, *J* = 1.6 Hz, 1H), 7.75 (dd, *J* = 2.1, 1.5 Hz, 1H), 4.41-4.35 (m, 4H), 3.80 (q, *J* = 7.2 Hz, 4H), 1.87-1.78 (m, 2H), 1.69-1.45 (m, 6H), 1.42-1.11 (m, 18H), 0.98 (d, *J* = 6.5 Hz, 3H), 0.97 (d, *J* = 6.5 Hz, 3H), 0.85 (m, 12H) 0.26 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 166.1, 165.2, 151.5, 138.6, 132.4, 132.3, 131.4, 131.0, 128.8, 127.1, 123.9, 123.8, 123.1, 122.3, 103.0, 96.1, 90.3, 87.6, 64.1, 63.8, 39.16, 39.14, 37.12, 37.07, 35.52, 35.46, 29.90, 29.85, 27.9, 24.59, 24.56, 22.67, 22.58, 19.62, 19.60, -0.2; MS (FAB) *m/z* 742.4 (100); TLC *R_f* = 0.35 (hexane/dichloromethane, 1/1); Anal. Calcd for C₄₅H₆₇N₃O₄Si (742.14): C, 72.83; H, 9.10; N, 5.66; found: C, 72.62; H, 9.10; N, 5.46.

Et₂N₃-[A]₄-SiMe₃ (14). To a solution of **13** (1.37 g, 1.85 mmol) and THF (13 mL) was added a solution of tetrabutylammonium fluoride in wet THF (2.5 mL, 1.0 M). The solution was stirred for 60 seconds, filtered through silica (eluting with dichloromethane), and the solvent was removed in vacuo to leave a yellow oil. The crude product was used without further purification. To a sealed tube fitted with a magnetic stirrer was added Pd₂dba₃ (34 mg, 0.037 mmol), copper(I) iodide (16 mg, 0.083 mmol), triphenylphosphine (80 mg, 0.31 mmol), **20** (1.50 g, 1.95 mmol), **17** (1.30 g, 1.85 mmol) and dry triethylamine (10 mL). The mixture was evacuated and back-filled with nitrogen three times. The tube was sealed and stirred at 65 °C for 15 h (during which time a white salt precipitate formed). The solution was diluted with hexane (100 mL), filtered to remove the precipitate and concentrated in vacuo leaving a yellow oil. The crude product was purified by silica gel column chromatography (hexane/EtOAc, 1/0, 20/1) to give 2.26 g (1.72 mmol, 93%) of **14** as a colorless oil: ¹H NMR (400 MHz, CDCl₃) δ 8.19 (t, *J* = 1.6 Hz, 1H), 8.18 (t, *J* = 1.7 Hz, 1H), 8.17 (t, *J* = 1.6 Hz, 2H), 8.14 (t, *J* = 1.5 Hz, 1H), 8.09 (t, *J* = 1.6 Hz, 1H), 8.06 (dd, *J* = 1.75, 1.67 Hz, 1H), 7.95 (t, *J* = 1.6 Hz, 1H), 7.88 (t, *J* = 1.6 Hz, 1H), 7.87 (t, *J* = 1.7 Hz, 1H), 7.81 (t, *J* = 1.6 Hz, 1H), 7.78 (dd, *J* = 1.9, 1.7 Hz, 1H), 4.44-4.35 (m, 8H), 3.81 (q, *J* = 7.2 Hz, 4H), 1.86-1.78 (m, 4H), 1.68-1.47 (m, 12H), 1.40-1.12 (m, 30H), 0.99-0.96 (m, 12H), 0.86 (m, 24H), 0.26

(s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.1, 165.2, 165.1, 165.0, 151.5, 138.6, 138.2, 132.7, 132.5, 132.4, 132.3, 132.2, 131.4, 131.3, 131.2, 131.0, 128.9, 127.2, 124.1, 124.0, 123.6, 123.6, 123.4, 123.2, 123.1, 122.3, 102.9, 96.3, 90.6, 89.1, 89.1, 88.8, 88.7, 87.5, 64.21, 64.17, 64.12, 63.80, 39.17, 39.14, 37.12, 37.08, 35.56, 35.49, 31.55, 29.93, 29.91, 29.88, 27.91, 24.59, 24.56, 22.66, 22.62, 22.57, 22.47, 19.63, 19.59, 14.08, -0.3; MS (MALDI) m/z 1311.8 (calcd $[\text{M} + \text{H}]^+ = 1311.9$); TLC $R_f = 0.10$ (hexane/dichloromethane, 2/1).

$\text{Et}_2\text{N}_3\text{-[A]}_6\text{-SiMe}_3$ (15). To a solution of **14** (2.02 g, 1.54 mmol) and THF (10 mL) was added a solution of tetrabutylammonium fluoride in wet THF (2.0 mL, 1.0 M). The solution was stirred for 60 seconds, filtered through silica (eluting with dichloromethane), and the solvent was removed in vacuo to leave a yellow oil. The crude product was used without further purification. To a sealed tube fitted with a magnetic stirrer was added Pd_2dba_3 (28 mg, 0.03 mmol), copper(I) iodide (13 mg, 0.07 mmol), triphenylphosphine (67 mg, 0.25 mmol), **20** (1.25 g, 1.63 mmol), **18** (1.90 g, 1.54 mmol) and dry triethylamine (12 mL). The mixture was evacuated and back-filled with nitrogen three times. The tube was sealed and stirred at 65 °C for 15 h. The solution was diluted with hexane (150 mL), filtered to remove the precipitate and concentrated in vacuo leaving a yellow oil. The crude product was purified by silica gel column chromatography (hexane/EtOAc, 1/0, 20/1) to give 2.71 g (1.44 mmol, 94%) of **15** as a colorless oil: ^1H NMR (400 MHz, CDCl_3) δ 8.20-8.15 (m, 8H), 8.12 (t, $J = 1.6$ Hz, 1H), 8.08 (t, $J = 1.5$ Hz, 1H), 8.06 (t, $J = 1.6$ Hz, 1H), 7.95 (t, $J = 1.5$ Hz, 1H), 7.90-7.85 (m, 4H), 7.81 (t, $J = 1.6$ Hz, 1H), 7.77 (t, $J = 1.6$ Hz, 1H), 4.46-4.35 (m, 12H), 3.80 (q, $J = 7.2$ Hz, 4H), 1.86-1.78 (m, 6H), 1.68-1.47 (m, 18H), 1.40-1.12 (m, 42H), 0.99-0.96 (m, 18H), 0.86 (m, 36H), 0.26 (s, 9H); MS (MALDI) m/z 1879.15 (calcd $[\text{M}]^+ = 1879.20$); TLC $R_f = 0.20$ (hexane/dichloromethane, 1/1).

$\text{Et}_2\text{N}_3\text{-[A]}_{12}\text{-SiMe}_3$ (16). To a solution of **15** (800 mg, 0.43 mmol) and THF (5 mL) was added a solution of tetrabutylammonium fluoride in wet THF (0.55 mL, 1.0 M). The solution was stirred for 1 minute, filtered through silica (eluting with CH_2Cl_2), and the solvent was removed in vacuo to leave a yellow oil. The crude product was used without further purification. To a sealed tube fitted with a magnetic stirrer was added **21** (750 mg, 0.39 mmol), **19** (677 mg, 0.38 mmol), $\text{Pd}_2(\text{dba})_3$ (7 mg, 0.008 mmol), CuI (3.2 mg, 0.017 mmol), PPh_3 (16 mg, 0.06 mmol), and dry triethylamine (8 mL). The mixture

was evacuated and back-filled with nitrogen three times. The tube was sealed and stirred at 65 °C for 15 h. The solution was diluted with hexanes (100 mL), filtered to remove the precipitate and concentrated in vacuo leaving a yellow solid. The crude product was purified by silica gel column chromatography (hexanes/CH₂Cl₂, 1/0, 1/4) to give 960 mg (0.27 mmol, 71%) of **16** as an off-white solid: ¹H NMR (400 MHz, CDCl₃) δ 8.20-8.15 (m, 20H), 8.12 (t, *J* = 1.5 Hz, 1H), 8.08 (t, *J* = 1.5 Hz, 1H), 8.05 (t, *J* = 1.8 Hz, 1H), 7.95 (t, *J* = 1.5 Hz, 1H), 7.90-7.87 (m, 9H), 7.86 (t, *J* = 1.6 Hz, 1H), 7.81 (t, *J* = 1.6 Hz, 1H), 7.78 (dd, *J* = 2.0, 1.6 Hz, 1H), 4.46-4.33 (m, 24H), 3.80 (q, *J* = 7.2 Hz, 4H), 1.86-1.78 (m, 12H), 1.68-1.47 (m, 36H), 1.40-1.12 (m, 78H), 0.99-0.96 (m, 36H), 0.88-0.84 (m, 72H), 0.26 (s, 9H); MS (MALDI) *m/z* 3588.9 (calcd [M + H]⁺ = 3586.3); TLC R_f = 0.15 (hexanes/CH₂Cl₂, 1/4); GPC 6092 (M_n), 1.04 (M_w/M_n), 100%.

I-[A]₂-SiMe₃ (20). To a 25 mL sealed tube was added **13** (2.00 g, 2.69 mmol), and iodomethane (15 mL). The mixture was degassed three times by evacuation, sealed and stirred at 110 °C for 14 h. The iodomethane was removed in vacuo to give a dark brown oil. The crude product was purified by silica gel column chromatography (hexane/dichloromethane, 1/0, 1/2) to give 1.86 g (2.42 mmol, 90%) of analytically pure **20** as a colorless oil: ¹H NMR (400 MHz, CDCl₃) δ 8.34 (t, *J* = 1.6 Hz, 1H), 8.13 (t, *J* = 1.5 Hz, 1H), 8.11 (t, *J* = 1.6 Hz, 1H), 8.09 (t, *J* = 1.6 Hz, 1H), 8.05 (t, *J* = 1.6 Hz, 1H), 7.80 (t, *J* = 1.6 Hz, 1H), 4.41-4.35 (m, 4H), 1.86-1.78 (m, 2H), 1.68-1.47 (m, 6H), 1.40-1.12 (m, 12H), 0.97 (d, *J* = 6.5 Hz, 3H), 0.96 (d, *J* = 6.5 Hz, 3H), 0.86 (m, 12H), 0.27 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 165.1, 164.4, 143.9, 138.7, 138.4, 132.9, 132.3, 132.2, 131.8, 131.1, 124.8, 124.0, 123.1, 102.8, 96.5, 93.3, 89.6, 88.0, 64.23, 64.18, 39.15, 37.09, 35.47, 35.44, 29.89, 29.87, 27.93, 24.58, 22.69, 22.60, 19.60, -0.2; MS (FAB) *m/z* 769.2 (6), 307.0 (15); TLC R_f = 0.45 (hexane/dichloromethane, 1/2); Anal. Calcd for C₄₁H₅₇O₄Si (768.40): C, 64.05; H, 7.47; found: C, 63.81; H, 7.52.

I-[A]₆-SiMe₃ (21). To a 15 mL sealed tube was added **15** (1.00 g, 0.53 mmol), and iodomethane (4 mL). The mixture was degassed three times by evacuation, sealed and stirred at 110 °C for 14 h. The iodomethane was removed in vacuo to give a dark brown oil. The crude product was purified by silica gel column chromatography (hexane EtOAc, 1/0, 33/1) to give 922 mg (0.484 mmol, 91%) of **21** as a waxy, white solid: ¹H NMR (400 MHz, CDCl₃) δ 8.35 (t, *J* = 1.5 Hz, 1H), 8.19-8.15 (m, 9H), 8.13 (t, *J* =

1.4 Hz, 1H), 8.09 (t, $J = 1.4$ Hz, 1H), 8.08 (t, $J = 1.4$ Hz, 1H), 7.91 (t, $J = 1.6$ Hz, 2H), 7.89-7.87 (m, 2H), 7.81 (t, $J = 1.5$ Hz, 1H), 4.44-4.35 (m, 12H), 1.86-1.78 (m, 6H), 1.68-1.47 (m, 18H), 1.40-1.12 (m, 36H), 0.99-0.96 (m, 18H), 0.86 (m, 36H), 0.27 (s, 9H); MS (FAB) m/z 1906.3 (28); TLC $R_f = 0.25$ (hexane/dichloromethane, 1/1).

I-[A]₁₂-SiMe₃ (22). To a 25 mL sealed tube was added **16** (900 mg, 0.25 mmol), and iodomethane (8 mL). The mixture was degassed three times by evacuation, sealed and stirred at 110 °C for 14 h. The iodomethane was removed in vacuo to give a dark brown oil. The crude product was purified by silica gel column chromatography (hexanes/CH₂Cl₂, 9/1, 1/2) to give 819 mg (0.23 mmol, 90%) of **22** as a white solid: ¹H NMR (400 MHz, CDCl₃) δ 8.34 (t, $J = 1.6$ Hz, 1H), 8.20-8.14 (m, 21H), 8.12 (t, $J = 1.6$ Hz, 1H), 8.08 (t, $J = 1.6$ Hz, 1H), 8.06 (t, $J = 1.6$ Hz, 1H), 7.91-7.88 (m, 8H), 7.86 (m, 2H), 7.81 (t, $J = 1.6$ Hz, 1H), 4.46-4.33 (m, 24H), 1.90-1.78 (m, 12H), 1.70-1.47 (m, 36H), 1.40-1.12 (m, 72H), 0.99-0.96 (m, 36H), 0.88-0.84 (m, 72H), 0.27 (s, 9H); MS (MALDI) m/z 3636.5 (calcd [M + Na]⁺ = 3636.1); TLC $R_f = 0.15$ (hexanes/CH₂Cl₂, 1/1); GPC 6004 (M_n), 1.04 (M_w/M_n), 100%.

H-[A]₄-SiMe₃ (23). To a solution of **12** (0.71 g, 1.10 mmol) and THF (7 mL) was added a solution of tetrabutylammonium fluoride in wet THF (1.4 mL, 1.0 M). The solution was stirred for 60 seconds, filtered through silica (eluting with hexane/dichloromethane, 1/1), and the solvent was removed in vacuo to leave a yellow oil. The crude product was used without further purification. To a sealed tube fitted with a magnetic stirrer was added Pd₂dba₃ (20 mg, 0.02 mmol), copper(I) iodide (9.2 mg, 0.05 mmol), triphenylphosphine (47 mg, 0.18 mmol), **20** (875 mg, 1.14 mmol), **31** (620 mg, 1.08 mmol) and dry triethylamine (6 mL). The mixture was evacuated and back-filled with nitrogen three times. The tube was sealed and stirred at 65 °C for 36 h (during which time a white salt precipitate formed). The solution was diluted with hexane (50 mL), filtered to remove the precipitate and concentrated in vacuo leaving a yellow oil. The crude product was purified by silica gel column chromatography (hexane/dichloromethane, 2/1, 1/1) to give 1.07 g (0.88 mmol, 82%) of **23** as a colorless oil: ¹H NMR (400 MHz, CDCl₃) δ 8.22 (td, $J = 1.6, 0.48$ Hz, 1H), 8.19-8.16 (m, 4H), 8.12 (t, $J = 1.6$ Hz, 1H), 8.09 (t, $J = 1.6$ Hz, 1H), 8.03 (ddd, $J = 7.8, 1.7, 1.2$ Hz, 1H), 7.88 (t, $J = 1.6$ Hz, 1H), 7.86 (t, $J = 1.6$ Hz, 1H), 7.81 (t, $J = 1.6$ Hz, 1H), 7.72 (ddd, $J = 7.7, 1.6, 1.3$ Hz, 1H), 7.46 (td, $J = 7.7, 0.55$ Hz, 1H), 4.44-4.35 (m, 8H),

1.86-1.78 (m, 4H), 1.68-1.47 (m, 12H), 1.40-1.12 (m, 24H), 0.99-0.96 (m, 12H), 0.86 (m, 24H), 0.27 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.7, 165.1, 165.0, 165.0, 138.7, 138.2, 138.2, 135.7, 135.7, 132.8, 132.7, 132.6, 132.5, 132.4, 132.3, 132.3, 131.4, 131.3, 131.2, 130.9, 129.7, 129.7, 128.6, 128.5, 124.1, 123.9, 123.7, 123.6, 123.5, 123.2, 122.9, 102.9, 96.4, 89.9, 89.2, 89.1, 88.9, 88.8, 88.3, 64.23, 64.24, 64.15, 63.90, 39.19, 39.17, 37.13, 37.11, 35.54, 35.52, 31.61, 29.94, 29.91, 29.89, 29.87, 27.95, 24.62, 22.71, 22.67, 22.62, 22.49, 19.66, 19.64, 14.14, -0.2; MS (FAB) m/z 1211.7 (2), 1053.5 (2); TLC R_f = 0.15 (hexane/dichloromethane, 2/1). Anal. Calcd for $\text{C}_{79}\text{H}_{106}\text{O}_8\text{Si}$: C, 78.30; H, 8.82; found: C, 78.28; H, 8.75.

H-[A]₆-SiMe₃ (24). To a solution of **23** (0.50 g, 0.41 mmol) and THF (4 mL) was added a solution of tetrabutylammonium fluoride in wet THF (0.54 mL, 1.0 M). The solution was stirred for 60 seconds, filtered through silica (eluting with dichloromethane), and the solvent was removed in vacuo to leave a yellow oil. The crude product was used without further purification. To a sealed tube fitted with a magnetic stirrer was added Pd_2dba_3 (7.0 mg, 0.008 mmol), copper(I) iodide (3.4 mg, 0.017 mmol), triphenylphosphine (17 mg, 0.064 mmol), **20** (312 mg, 0.41 mmol), **32** (440 mg, 0.39 mmol) and dry triethylamine (4 mL). The mixture was evacuated and back-filled with nitrogen three times. The tube was sealed and stirred at 65 °C for 14 h (during which time a white salt precipitate formed). The solution was diluted with hexane (30 mL), filtered to remove the precipitate and concentrated in vacuo leaving a yellow oil. The crude product was purified by silica gel column chromatography (hexane/dichloromethane, 1/0, 1/2) to give 657 mg (0.37 mmol, 96%) of **24** as a light yellow oil: ^1H NMR (400 MHz, CDCl_3) δ 8.21 (td, J = 1.68, 0.47 Hz, 1H), 8.20-8.15 (m, 7H), 8.12 (t, J = 1.7 Hz, 1H), 8.08 (t, J = 1.7 Hz, 1H), 8.03 (ddd, J = 7.8, 1.64, 1.14 Hz, 1H), 7.90-7.88 (m, 4H), 7.88 (t, J = 1.6 Hz, 1H), 7.81 (t, J = 1.6 Hz, 1H), 7.72 (ddd, J = 7.7, 1.58, 1.26 Hz, 1H), 7.46 (td, J = 7.83, 0.55 Hz, 1H), 4.44-4.35 (m, 12H), 1.86-1.78 (m, 6H), 1.68-1.47 (m, 18H), 1.40-1.12 (m, 36H), 0.99-0.96 (m, 18H), 0.86 (m, 36H), 0.27 (s, 9H); MS (MALDI) m/z 1781.3 (calcd $[\text{M} + \text{H}]^+ = 1781.1$); TLC R_f = 0.25 (hexane/dichloromethane, 1/1).

H-[A]₈-SiMe₃ (25). To a sealed tube fitted with a magnetic stirrer was added **31** (92 mg, 0.16 mmol), **21** (213 mg, 0.11 mmol), $\text{Pd}_2(\text{dba})_3$ (11 mg, 0.012 mmol), CuI (6 mg, 0.034 mmol), PPh_3 (36 mg,

0.098 mmol) and dry triethylamine (6 mL). The mixture was evacuated and back-filled with nitrogen three times. The tube was sealed and stirred at 70 °C for 18 h. The solution was diluted with hexanes (50 mL), filtered to remove the precipitate and concentrated in vacuo leaving a yellow solid. The crude product was purified by silica gel column chromatography (hexanes/CH₂Cl₂, 1/0, 1/1) and size exclusion chromatography (toluene) to give 152 mg (0.065 mmol, 58%) of **25** as a white solid: ¹H NMR (400 MHz, CDCl₃) δ 8.21 (td, *J* = 1.6, 0.5 Hz, 1H), 8.20-8.15 (m, 11H), 8.13 (t, *J* = 1.7 Hz, 1H), 8.09 (t, *J* = 1.7 Hz, 1H), 8.04 (ddd, *J* = 7.8, 1.6, 1.1 Hz, 1H), 7.91-7.88 (m, 6H), 7.87 (t, *J* = 1.6 Hz, 1H), 7.82 (t, *J* = 1.6 Hz, 1H), 7.72 (ddd, *J* = 7.7, 1.6, 1.3 Hz, 1H), 7.46 (td, *J* = 7.8, 0.6 Hz, 1H), 4.46-4.34 (m, 16H), 1.86-1.78 (m, 8H), 1.68-1.47 (m, 24H), 1.40-1.12 (m, 48H), 0.99-0.96 (m, 24H), 0.86 (m, 48H), 0.27 (s, 9H); MS (MALDI) *m/z* 2371.78 (calcd [M + Na]⁺ = 2371.42); TLC *R_f* = 0.20 (hexanes/CH₂Cl₂, 1/1); GPC 4552 (M_n), 1.03 (M_w/M_n), 100%.

H-[A]₁₀-SiMe₃ (26). To a solution of **23** (0.35 g, 0.29 mmol) and THF (4 mL) was added a solution of tetrabutylammonium fluoride in wet THF (0.38 mL, 1.0 M). The solution was stirred for 1 minute, filtered through silica (eluting with CH₂Cl₂), and the solvent was removed in vacuo to leave a yellow oil. The crude product was used without further purification. To a sealed tube fitted with a magnetic stirrer was added **21** (180 mg, 0.094 mmol), **32** (129 mg, 0.113 mmol), Pd₂(dba)₃ (8.6mg, 0.009 mmol), CuI (4.3 mg, 0.02 mmol), PPh₃ (21 mg, 0.08 mmol), and dry triethylamine (4 mL). The mixture was evacuated and back-filled with nitrogen three times. The tube was sealed and stirred at 65 °C for 15 h. The solution was diluted with hexanes (50 mL), filtered to remove the precipitate and concentrated in vacuo leaving a yellow solid. The crude product was purified by silica gel column chromatography (hexanes/CH₂Cl₂, 1/0, 1/1) and size exclusion chromatography (toluene) to give 244 mg (0.085 mmol, 90%) of **26** as a white wax: ¹H NMR (400 MHz, CDCl₃) δ 8.21 (td, *J* = 1.6, 0.4 Hz, 1H), 8.21-8.16 (m, 15H), 8.12 (t, *J* = 1.7 Hz, 1H), 8.08 (t, *J* = 1.6 Hz, 1H), 8.03 (ddd, *J* = 7.9, 1.7, 1.2 Hz, 1H), 7.91-7.88 (m, 8H), 7.86 (t, *J* = 1.6 Hz, 1H), 7.81 (t, *J* = 1.6 Hz, 1H), 7.71 (ddd, *J* = 7.7, 1.6, 1.3 Hz, 1H), 7.45 (td, *J* = 7.8, 0.6 Hz, 1H), 4.46-4.34 (m, 20H), 1.88-1.78 (m, 10H), 1.68-1.47 (m, 30H), 1.40-1.12 (m, 60H), 0.99-0.96 (m, 30H), 0.88-0.84 (m, 60H), 0.27 (s, 9H); MS (MALDI) *m/z* 2940.9 (calcd [M + Na]⁺ = 2940.8); TLC *R_f* = 0.15 (hexanes/CH₂Cl₂, 1/1); GPC 5298 (M_n), 1.03 (M_w/M_n), 100%.

H-[A]₁₂-SiMe₃ (27). To a solution of **24** (414 mg, 0.23 mmol) and THF (10 mL) was added a solution of tetrabutylammonium fluoride in wet THF (0.4 mL, 1.0 M). The solution was stirred for 1 minute, filtered through silica (eluting with CH₂Cl₂), and the solvent was removed in vacuo to leave a light yellow oil. The crude product was used without further purification. To a sealed tube fitted with a magnetic stirrer was added **21** (186 mg, 0.098 mmol), **33** (204 mg, 0.119 mmol), Pd₂(dba)₃ (8.6 mg, 0.01 mmol), CuI (4.2 mg, 0.02 mmol), PPh₃ (21 mg, 0.08 mmol), and dry triethylamine (5 mL). The mixture was evacuated and back-filled with nitrogen three times. The tube was sealed and stirred at 65 °C for 18 h. The solution was diluted with hexanes (80 mL), filtered to remove the precipitate and concentrated in vacuo leaving a yellow solid. The crude product was purified by silica gel column chromatography (hexanes/CH₂Cl₂, 2/1, 2/3) and size exclusion chromatography (toluene) to give 217 mg (0.062 mmol, 64%) of **27** as a white solid: ¹H NMR (400 MHz, CDCl₃) δ 8.21 (td, *J* = 1.7, 0.4 Hz, 1H), 8.21-8.16 (m, 19H), 8.12 (t, *J* = 1.8 Hz, 1H), 8.08 (t, *J* = 1.6 Hz, 1H), 8.03 (ddd, *J* = 7.7, 1.7, 1.2 Hz, 1H), 7.91-7.88 (m, 10H), 7.86 (t, *J* = 1.6 Hz, 1H), 7.81 (t, *J* = 1.6 Hz, 1H), 7.72 (ddd, *J* = 7.7, 1.6, 1.3 Hz, 1H), 7.45 (td, *J* = 7.8, 0.6 Hz, 1H), 4.46-4.34 (m, 24H), 1.90-1.78 (m, 12H), 1.68-1.47 (m, 36H), 1.40-1.12 (m, 72H), 0.99-0.96 (m, 36H), 0.88-0.84 (m, 72H), 0.27 (s, 9H); MS (MALDI) *m/z* 3510.56 (calcd [M + Na]⁺ = 3510.18); TLC R_f = 0.15 (hexanes/CH₂Cl₂, 1/1); GPC 6075 (M_n), 1.04 (M_w/M_n), 100%.

H-[A]₁₄-SiMe₃ (28). To a sealed tube fitted with a magnetic stirrer was added **31** (58 mg, 0.10 mmol), **22** (212 mg, 0.06 mmol), Pd₂(dba)₃ (6.5 mg, 0.007 mmol), CuI (2.9 mg, 0.015 mmol), PPh₃ (21 mg, 0.08 mmol) and dry triethylamine (7 mL). The mixture was evacuated and back-filled with nitrogen three times. The tube was sealed and stirred at 70 °C for 23 h. The solution was diluted with hexanes (100 mL), filtered to remove the precipitate and concentrated in vacuo leaving a yellow solid. The crude product was purified by silica gel column chromatography (hexanes/CH₂Cl₂, 2/1, 2/3) and size exclusion chromatography (toluene) to give 179 mg (0.044 mmol, 75%) of **28** as a white solid: ¹H NMR (400 MHz, CDCl₃) δ 8.21 (td, *J* = 1.7, 0.4 Hz, 1H), 8.20-8.15 (m, 24H), 8.12 (t, *J* = 1.8 Hz, 1H), 8.08 (t, *J* = 1.6 Hz, 1H), 8.03 (ddd, *J* = 7.7, 1.7, 1.2 Hz, 1H), 7.90-7.88 (m, 11H), 7.86 (t, *J* = 1.6 Hz, 1H), 7.81 (t, *J* = 1.6 Hz, 1H), 7.71 (ddd, *J* = 7.7, 1.6, 1.3 Hz, 1H), 7.45 (td, *J* = 7.8, 0.6 Hz, 1H), 4.46-4.33 (m, 28H), 1.90-1.78 (m, 14H), 1.70-1.47 (m, 42H), 1.40-1.12 (m, 84H), 0.99-0.96 (m, 42H), 0.88-0.84 (m, 84H), 0.27 (s, 9H); MS

(MALDI) m/z 4077.87 (calcd $[M + Na]^+ = 4078.54$); TLC $R_f = 0.20$ (hexanes/ CH_2Cl_2 , 1/2); GPC 6807 (M_n), 1.04 (M_w/M_n), 100%.

H-[A]₁₆-SiMe₃ (29). To a sealed tube fitted with a magnetic stirrer was added **32** (89 mg, 0.08 mmol), **22** (199 mg, 0.055 mmol), Pd₂(dba)₃ (9.3 mg, 0.01 mmol), CuI (3.6 mg, 0.02 mmol), PPh₃ (27 mg, 0.10 mmol) and dry triethylamine (7 mL). The mixture was evacuated and back-filled with nitrogen three times. The tube was sealed and stirred at 70 °C for 21 h. The solution was diluted with hexanes (80 mL), filtered to remove the precipitate and concentrated in vacuo leaving a yellow solid. The crude product was purified by silica gel column chromatography (hexanes/ CH_2Cl_2 , 2/1, 2/3) and size exclusion chromatography (toluene) to give 159 mg (0.034 mmol, 62%) of **29** as a white solid: ¹H NMR (400 MHz, CDCl₃) δ 8.21 (td, $J = 1.7, 0.4$ Hz, 1H), 8.20-8.15 (m, 28H), 8.13 (t, $J = 1.8$ Hz, 1H), 8.08 (t, $J = 1.6$ Hz, 1H), 8.04 (ddd, $J = 7.7, 1.7, 1.2$ Hz, 1H), 7.90-7.88 (m, 13H), 7.86 (t, $J = 1.6$ Hz, 1H), 7.81 (t, $J = 1.6$ Hz, 1H), 7.71 (ddd, $J = 7.7, 1.6, 1.3$ Hz, 1H), 7.45 (td, $J = 7.8, 0.6$ Hz, 1H), 4.46-4.33 (m, 32H), 1.90-1.78 (m, 16H), 1.70-1.47 (m, 48H), 1.40-1.12 (m, 96H), 0.99-0.96 (m, 48H), 0.88-0.84 (m, 96H), 0.27 (s, 9H); MS (MALDI) m/z 4644.2 (calcd $[M + Na]^+ = 4646.90$); TLC $R_f = 0.25$ (hexanes/ CH_2Cl_2 , 1/2); GPC 7493 (M_n), 1.03 (M_w/M_n), 99.8%.

H-[A]₁₈-SiMe₃ (30). To a sealed tube fitted with a magnetic stirrer was added **33** (126 mg, 0.074 mmol), **22** (196 mg, 0.054 mmol), Pd₂(dba)₃ (2.9 mg, 0.003 mmol), CuI (1.1 mg, 0.006 mmol), PPh₃ (69 mg, 0.026 mmol) and dry triethylamine (8 mL). The mixture was evacuated and back-filled with nitrogen three times. The tube was sealed and stirred at 70 °C for 18 h. The solution was diluted with hexanes (90 mL), filtered to remove the precipitate and concentrated in vacuo leaving a yellow solid. The crude product was purified by silica gel column chromatography (hexanes/ CH_2Cl_2 , 2/1, 2/3) and size exclusion chromatography (toluene) to give 192 mg (0.037 mmol, 68%) of **30** as a white solid: ¹H NMR (400 MHz, CDCl₃) δ 8.22 (td, $J = 1.7, 0.4$ Hz, 1H), 8.21-8.16 (m, 32H), 8.13 (t, $J = 1.8$ Hz, 1H), 8.09 (t, $J = 1.6$ Hz, 1H), 8.05 (ddd, $J = 7.7, 1.7, 1.2$ Hz, 1H), 7.92-7.90 (m, 15H), 7.88 (t, $J = 1.6$ Hz, 1H), 7.82 (t, $J = 1.6$ Hz, 1H), 7.73 (ddd, $J = 7.7, 1.6, 1.3$ Hz, 1H), 7.45 (td, $J = 7.8, 0.6$ Hz, 1H), 4.46-4.33 (m, 36H), 1.90-1.78 (m, 18H), 1.70-1.47 (m, 54H), 1.40-1.12 (m, 108H), 0.99-0.96 (m, 54H), 0.88-0.84 (m, 108H), 0.27 (s, 9H);

MS (MALDI) m/z 5214.6 (calcd $[M + Na]^+ = 5216.26$); TLC $R_f = 0.30$ (hexanes/ CH_2Cl_2 , 1/2); GPC 8207 (M_n), 1.03 (M_w/M_n), 100%.