Supporting Information to Accompany

Synthesis and Characterization of 9-Phenylcarbazole Monodendrons: an Exploration of Peripheral Groups to Facilitate Purification

Contribution from the Roger Adams Laboratory
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Experiment Procedures

General

Unless otherwise indicated, all starting materials were obtained from commercial suppliers (Aldrich, Lancaster, Fischer) and were used without purification. Hexane, dichloromethane, and ethyl acetate were distilled before use. All atmosphere sensitive reactions were done under nitrogen using a vacuum line or in a drybox. Analytical TLC was performed on KIESELGEL F-254 precoated silica gel plates. Visualization was accomplished with UV light or iodine stain. Flash chromatography was carried out with Silica Gel 60 (230-400 mesh) from EM Science. 150-Å-pore-size silica gel (Davisil™, 200-425 mesh) was purchased from Aldrich. Dry THF was obtained by vacuum transfer from sodium and benzophenone.

^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity 400, 500, or INOVA 500NB spectrometer. Chemical shifts were recorded in parts per million (ppm), and

splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad). Coupling constants, J, are reported in Hertz (Hz). The residual proton signal of the solvent was used as an internal standard for spectra recorded in chloroform-d (7.26 for ^{1}H, 77.0 for ^{13}C), benzene-d_6 (7.15 for ^{1}H, 128 for ^{13}C). Low- and high-resolution electron impact mass spectra were obtained on either a Finnigan-MAT CH5 or Micromass 70-VSE spectrometer operating at 70 eV. Low- and high-resolution fast atom bombardment (FAB) mass spectra were obtained on VG ZAB-SE and VG 70-SE-4F spectrometers. Matrix-assisted laser desorption mass spectra (MALDI) were recorded on a Voyager (Starfleet Registry NCC 74656) or Micromass TofSpec matrix-assisted laser desorption time-of-flight mass spectrometer. Elemental analyses were performed by the University of Illinois Microanalytical Service Laboratory using a Leeman Labs CE440. Analytical HPLC was performed with a Rainin Dyanamax solvent delivery system, model SD-200, using a Microsorb Si-80-125-C5 silica column. GPC was performed using a Waters 510 HPLC pump, Waters 996 photodiode array detector, and a series of three Waters styragel HR 4E 7.8 X 300 mm columns which were calibrated with narrow molecular weight polystyrene standards. GPC data were obtained in THF at 35 °C. A blast shield should be used for all reactions conducted in sealed tubes.

Synthetic Procedures

General Procedure A1: The coupling of trimethylsilylacetylene or 2-methyl-3-butyn-2-ol with aryl iodide. A heavy-walled flask was charged with aryl iodide (1 equiv), $Pd(dba)_2$ (0.013 equiv), CuI (0.02 equiv), triphenylphosphine (0.1 equiv), and dry

triethylamine or piperidine. The concentration of the reactant varied from 0.3 M to 0.05 M depending on the solubility of the reactants and products. The flask was degassed and back-filled with nitrogen three times. Trimethylsilylacetylene or 2-methyl-3-butyn-2-ol was added through a syringe under a nitrogen atmosphere. The flask was then sealed and heated at 65-75 °C for 12-24 h when triethylamine was used as solvent. The reaction was allowed to stir at room temperature for 5-14 h when piperidine was used as solvent. Solvent was then evaporated under vacuum and the crude product purified by flash chromatography.

General Procedure A2: The coupling of terminal acetylene with aryl iodide. A heavy-walled flask was charged with aryl iodide (1 equiv), $Pd(dba)_2$ (0.013 equiv), CuI (0.02 equiv), triphenylphosphine (0.1 equiv), terminal acetylene (0.8-1 equiv) and dry triethylamine or piperidine. The concentration of the reactant varied from 0.3 M to 0.05 M depending on the solubility of the reactants and products. The flask was degassed and back-filled with nitrogen three times, then sealed. The reaction was heated to 65-75 °C for 12-24 h when triethylamine was used as solvent. The reaction was allowed to stir at room temperature for 5-14 h. Solvent was then evaporated under vacuum and the crude product purified by flash chromatography.

9-Benzylcarbazole (1).[33] To a stirred solution of carbazole (24.0 g, 143.7 mmol) in DMF (100 mL) cooled in an ice bath was added sodium hydride (60% suspension of in mineral oil, 6.0 g, 150 mmol) in small portions. Then benzyl chloride (30 mL) was slowly added. The mixture was allowed to stir at 70 °C for 14 h and

transferred into a beaker containing ice water. The precipitates were collected by filtration, washed with water, methanol and recrystallized from a mixed solvent of CH_2Cl_2 and methanol to give 9-benzylcarbazole (30.5 g, 83%) as white crystalline solid: R_f 0.43 (CH_2Cl_2 : hexane, 1 : 4); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (ddd, J = 7.8, 1.3, 0.8 Hz, 2H), 7.43 (ddd, J = 8.3, 7.0, 1.3 Hz, 2H), 7.37 (dt, J = 8.2, 1.0 Hz, 2H), 7.26 (m, 3H), 7.15 (m, 2H), 5.53 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.64, 137.16, 128.74, 127.41, 126.38, 125.82, 123.01, 120.36, 119.18, 108.87, 46.53; MS (EI) *m/z* 257.1 (M^+); Analysis calc'd for $C_{19}H_{15}N$: C, 88.68; H, 5.88; N, 5.44; found: C, 88.82; H, 5.92; N, 5.53.

9-Benzyl-3,6-bis(1,1,3,3-tetramethyl-butyl)-carbazole (2). To a stirred solution of 9-benzylcarbazole (**1**, 9.16 g, 35.4 mmol) in CS_2 (150 ml), cooled in an ice-acetone bath, was added $AlCl_3$ (100 mg) and 2,4,4-trimethyl-1-pentene (9.16 g, 81.6 mmol). The mixture was then allowed to warm to room temperature over 2 h and stir for 14 h. Water was added and the reaction was extracted with dichloromethnae. The organic layer was separated, washed with aqueous sodium bicarbonate, brine, and dried over anhydrous magnesium sulfate. Flash chromatography (CH_2Cl_2 : hexane, 1 : 6) followed by recrystallization from a mixed solvent of CH_2Cl_2 and methanol afforded 9-benzyl-3,6-bis(1,1,3,3-tetramethyl-butyl)-carbazole (**2**, 14.8 g, 86%) as white crystals.: R_f 0.47 (CH_2Cl_2 : hexane, 1 : 4); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 1.7 Hz, 2H), 7.43 (dd, J = 8.8, 2.0 Hz, 2H), 7.23 (m, 5H), 7.16 (d, J = 8.0 Hz, 2H), 5.46 (s, 2H), 1.84 (s, 4H), 1.51 (s, 12H), 0.74 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.85, 139.11, 137.66, 128.64, 127.26, 126.52, 124.40, 122.80, 117.01, 107.99, 57.42, 46.73, 38.58,

32.46, 32.13, 31.88; MS (EI) *m/z* 481.4 (M+, 14.4), 410.3 (100); Analysis calc'd for $C_{35}H_{47}N$: C, 87.26; H, 9.83; N, 2.91; found: C, 87.09; H, 9.93; N, 3.00.

3,6-Bis(1,1,3,3-tetramethy-butyl)-carbazole (3). Finely cut sodium (900 mg, 39.1 mmol) was added to three-neck containing liquid ammonia (300 mL), fitted with a dry-ice-isopropanol condenser and placed in a dry-ice-isopropanol bath. A solution of 9-benzyl-3.6-bis(1,1,3,3-tetramethyl-butyl)-carbazole (**2**, 9.31 g, 19.3 mmol) in dry THF (100 mL) was slowly added. The mixture was stirred for 2 h and ammonium chloride (2.0 g) was added. The dry-ice-isopropanol bath and condenser were removed and the ammonia was allowed to evaporate. The residue was extracted with ether and washed with water. The organic layer was dried over anhydrous magnesium sulfate and solvent was removed under vacuum. Recrystallization from hexane yielded **3** (6.86 g, 90.6%) as white crystals.: R_f 0.32 (CH_2Cl_2 : hexane, 1 : 4); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 1.7 Hz, 2H), 7.83 (1, s, 1H), 7.44 (dd, J = 8.6, 1.7 Hz, 2H), 7.32 (d, 8.3H), 1.85 (s, 4H), 1.51 (s, 12H), 0.74 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.08, 137.68, 124.46, 123.24, 116.92, 109.72, 57.38, 38.58, 32.46, 32.18, 31.86; MS (EI) *m/z* 391.3 (M+, 9.83), 320.2 (100); Analysis calc'd for $C_{28}H_{41}N$: C, 85.88; H, 10.55; N, 3.58; found: C, 85.87; H, 10.57; N, 3.71.

9-(4-Nitrophehyl)-3,6-bis(1,1,3,3-tetramethylbutyl)-carbazole (4). To a solution of 3,6-bis(1,1,3,3-tetramethy-butyl)carbazole (**3**, 3.20 g, 8.17 mmol) in DMF (50 mL) was added sodium hydride (60% suspension in mineral oil, 600 mg, 15.0 mmol). Then 4-fluoro-nithrobenzene (2.16 g, 16.3 mmol) was added. The mixture was stired at

rt under dry nitrogen for 12 h and poured into ice water. The yellow precipitates were collected by filtration and recrystallized from a mixed solvent of CH_2Cl_2 and methanol to afford **4** (3.65 g, 87.1%) as a yellow solid: R_f 0.33 (CH_2Cl_2 : hexane, 1 : 4); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (m, 2H), 8.09 (dd, J = 8.6, 0.7 Hz, 2H), 7.82 (m, 2H), 7.47 (dd, J = 8.8, 1.7 Hz, 2H), 7.44 (dd, J = 8.6, 0.6 Hz, 2H), 1.87 (s, 4H), 1.52 (s, 12H), 0.76 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.12, 144.42, 143.37, 137.90, 125.91, 125.41, 125.03, 124.22, 117.29, 108.89, 57.22, 38.70, 32.46, 32.11, 31.89; MS (EI) *m/z* 512.4 (M^+), 441.3 (100); Analysis calc'd for $C_{34}H_{44}N_2O_2$: C, 79.65; H, 8.65; N, 5.46; found: C, 79.36; H, 8.43; N, 5.56.

9-(4-Aminophenyl)-3,6-bis(1,1,3,3-tetramethybutyl)carbazole (5). 9-(4-Nitrophenyl)-3,6-bis(1,1,3,3-tetramethybutyl)carbazole (**4**, 3.65 g, 7.12 mmol) and stannous chloride dihydrate (8.7 g, 38.6 mmol) in ethanol (200 mL) were heated to reflux for 14 h. Ethanol was evaporated under vacuum. To the residue was added aqueous NaOH and ether. The organic layer was separated and washed with water until neutral, and then dried with anhydrous sodium sulfate. Solvents were removed under reduced pressure and the residue recrystallized from a mixed solvent of methanol and dichloromethane to yield **5** (3.09 g, 90%) as a white solid.: R_f 0.23 (CH_2Cl_2 : hexane, 2 : 3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (dd, J = 2.0, 0.6 Hz, 2H), 7.41 (dd, J = 8.7, 1.9 Hz, 2H), 7.35 (m, 2H), 7.24 (dd, J = 8.5, 0.6 Hz, 2H), 6.91 (m, 2H), 1.85 (s, 4H), 1.51 (s, 12H), 0.74 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.23, 139.66, 128.14, 124.36, 122.87, 116.82, 115.98, 108.85, 57.34, 38.59, 32.44, 32.18, 31.89; MS (EI) *m/z* 482.4

(M^+, 21.8), 411.3 (100); Analysis calc'd for $C_{34}H_{46}N_2$: C, 84.60; H, 9.60; N, 5.80; found: C, 84.61; H, 9.47; N, 5.81.

9-(3,3-Diethyltriazenylphenyl)-3,6-bis(1,1,3,3-tetramethybutyl)carbazole (6). 9-(4-aminophenyl)-3,6-bis(1,1,3,3-tetramethybutyl)carbazole (**5**, 3.96 g, 8.22 mmol) was dissolved in THF (50 mL). To this solution, cooled to -15 °C, was slowly added BF_3•Et_2O (2.01 mL), and *tert*-butyl nitrite (1.6 mL). The reaction was allowed to stir at that temperature for 30 min and allowed to warm to 0 °C. Diethyl amine (5.36 mL) and potassium carbonate (5.36 g) were then added. The reaction was allowed to stir for 20 min before H_2O was added. The reaction was extracted with dichloromethane and the combined organic layers were washed with water and dried over anhydrous magnesium sulfate. Solvent was removed under vacuum, and the residue purified by flash chromatography (hexane : CH_2Cl_2, 1 : 10) to afford **6** (3.77 g, 81%): R_f 0.36 (CH_2Cl_2 : hexane, 1 : 4); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 1.5 Hz, 2H), 7.62 (m, 2H), 7.52 (m, 2H), 7.42 (dd, J = 8.5, 2.0 Hz, 2H), 7.34 (d, J = 8.8 Hz, 2H), 3.83 (q, J = 7.1 Hz, 4H), 1.86 (s, 4H), 1.52 (s, 12H), 1.32 (t, J = 7.1 Hz, 6H), 0.76 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.85, 141.49, 139.22, 134.90, 127.13, 124.42, 123.12, 121.38, 116.84, 108.98, 57.33, 38.62, 32.46, 32.18, 31.91; MS (EI) *m/z* 566.4 (M^+, 14.6), 495.4 (52.3), 396.3 (100); Analysis calc'd for $C_{38}H_{34}N_4$: C, 80.52; H, 9.60; N, 9.88; found: C, 80.50; H, 9.53; N, 9.69.

9-(4-Iodophenyl)-3,6-bis(1,1,3,3-tetramethybutyl)carbazole (7). A heavy-walled flask charged with 9-(4-(3,3-diethyltriazenyl)phenyl)-3,6-bis(1,1,3,3-

tetramethybutyl)carbazole (**6**, 1.31 g, 2.31 mmol), iodine (0.588 g, 2.31 mmol), and methyl iodide (10 mL) was degassed and back-filled with nitrogen three times, and then heated to 80 °C for 4.5 h. Solvent was removed under vacuum, and the residue dissolved in dichloromethane, washed with saturated aqueous sodium thiosulfate. The organic layer was collected, and dried over anhydrous magnesium sulfate. Solvent was removed and the residue purified by flash chromatography (hexane) followed by recrystallization from a mixed solvent of dichloromethane and methanol to afford **7** (1.22 g, 89%): R_f 0.78 (CH_2Cl_2 : hexane, 1 : 4); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (dd, J = 1.9, 0.6 Hz, 2H), 7.89 (m, 2H), 7.43 (dd, J = 8.8, 1.9 Hz, 2H), 7.35 (m, 2H), 7.32 (dd, J = 8.7, 0.6 Hz, 2H), 1.86 (s, 4H), 1.51 (s, 12H), 0.75 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.15, 138.82, 138.59, 138.04, 128.42, 124.65, 123.46, 117.03, 108.72, 91.09, 57.28, 38.63, 32.46, 32.16, 31.89; MS (EI) *m/z* 593.3 (M^+, 16.6), 522.2 (100); Analysis calc'd for $C_{34}H_{44}NI$: C, 68.79; H, 7.47; N, 2.36; I, 21.38; found: C, 68.65; H, 7.51; N, 2.31; I, 21.55.

9-(4-(3-Hydroxy-3-methyl-butynyl)-phenyl)-3,6-bis(1,1,3,3-tetramethybutyl)-carbazole (8). 9-(4-Iodophenyl)-3,6-bis(1,1,3,3-tetramethybutyl)carbazole (**7**, 13.1 g, 22.07 mmol) was coupled with 2-methyl-3-butyn-2-ol (4.3 mL) according to general procedure A1. Piperidine was used as solvent and the reaction was carried out at room temperature. The crude product was purified by flash chromatography eluting with 3 : 1, CH_2Cl_2 : hexane to afford **8** (11.98 g, 99%): R_f 0.43 (CH_2Cl_2 : hexane, 4 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 1.5 Hz, 2H), 7.62 (m, 2H), 7.54 (m, 2H), 7.43 (dd, J = 8.8, 2.0 Hz, 2H), 7.34 (d, J = 8.5 Hz, 2H), 1.86 (s, 4H), 1.67 (s, 6H), 1.52 (s, 12H), 0.75 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.10, 138.60, 138.15, 132.98, 126.19, 124.62,

123.47, 120.85, 116.99, 108.83, 94.35, 81.63, 65.68, 57.28, 38.62, 32.45, 32.15, 31.89, 31.51; MS (EI) *m/z* 549.4 (M^+), 478.3, 420.3; Analysis calc'd for $C_{39}H_{51}NO$: C, 85.19; H, 9.35; N, 2.55; found: C, 84.18; H, 9.39; N, 2.52.

9-(4-Ethynylphenyl)-3,6-bis(1,1,3,3-tetramethybutyl)carbazole (9). 9-(4-(3-Hydroxy-3-methyl-butynyl)-phenyl)-3,6-bis(1,1,3,3-tetramethybutyl)carbazole (**8**, 3.06 g, 5.56 mmol) was dissolvend in toluene (150 mL). To this solution was added a solution of KOH (1.56 g) in butanol (20 mL). The reaction was heated to 110 °C for 1.5 h under nitrogen, and allowed to cool to rt. Water was added, and the reaction was extracted with dichloromethane. The organic layer was separated and dried over anhydrous magnesium sulfate. Solvent was removed, and the residue was purified by flash chromatography (hexane) to afford **9** (2.55 g, 93%): R_f 0.68 (CH_2Cl_2 : hexane, 1 : 4); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (dd, J = 1.7, 0.6 Hz, 2H), 7.69 (m, 2H), 7.56 (m, 2H), 7.43 (dd, J = 8.6, 2.0 Hz, 2H), 7.35 (dd, J = 8.6, 1.7 Hz, 2H), 3.16 (s, 1H), 1.86 (s, 4H), 1.51 (s, 12H), 0.75 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.09, 138.70, 138.57, 133.52, 126.22, 124.67, 123.54, 120.19, 117.03, 108.88, 83.13, 77.79, 57.29, 38.65, 32.46, 32.17, 31.90; MS (EI) *m/z* 471.4 (M^+), 420.3; Analysis calc'd for $C_{36}H_{45}N$: C, 87.93; H, 9.22; N, 2.85; found: C, 87.77; H, 9.17; N, 2.94.

2-Cascade:9-(4-(3-hydroxy-3-methyl-but-1-ynyl)phenyl)carbazole[2-3,6]:9-(4-ethynylphenyl)-3,6- bis(1,1,3,3-tetramethyl-butyl)carbazole (11). 9-(4-ethynylphenyl)-3,6-bis(1,1,3,3-tetramethybutyl)carbazole (**9**, 617 mg, 1.25 mmol) was coupled to 3,6-diodo-9-(4-(3-hydroxy-3-methyl-but-1-ynyl)-phenyl)-carbazole (**10**, 329

mg, 0.57 mmol) according to general procedure A2. Piperidine (40 mL) was used as solvent. The crude product was purified by flash chromatography eluting with 1 : 1, hexane : CH_2Cl_2 to afford trimer monodendron **11** (548 mg, 74%): R_f 0.41 (CH_2Cl_2 : hexane, 3 : 2); ^1H NMR (400 MHz, $CDCl_3$) δ 8.41 (dd, J = 1.7, 0.7 Hz, 2H), 8.12 (dd, J = 2.0, 0.7 Hz, 4H), 7.80 (m, 4H), 7.71 (m, 2H), 7.68 (dd, J = 8.6, 1.6 Hz, 2H), 7.63 (m, 4H), 7.55 (m, 2H), 7.47 (dd, J = 8.8, 1.8 Hz, 4H), 7.42 (dd, J = 8.6, 0.4 Hz, 4H), 7.41 (dd, J = 8.5, 0.6 Hz, 2H), 1.89 (s, 8H), 1.70 (s, 6H), 1.54 (s, 24H), 0.77 (s, 36H); MS (FD) *m/z* 1304.3 (M^+); Analysis calc'd for $C_{95}H_{105}N_3O$: C, 87.44; H, 8.11; N, 3.22; found: C, 87.17; H, 8.04; N, 3.21.

2-Cascade:9-(4-ethynylphenyl)carbazole[2-3,6]:9-(4-ethynylphenyl)-3,6-bis(1,1,3,3-tetramethyl-butyl)carbazole (12). To a solution of **11** (950 mg, 0.728 mmol) in toluene (50 mL) was added a solution of KOH (204 mg, 3.64 mmol) in butanol. The reaction was heated to 110 °C for 1.5 h under nitrogen, and the solvent was removed under vacuum. Crude product was purified by flash chromatography eluting with 1 : 3, dichloromethane : hexane to afford **12** (793 mg, 87%) as a white powder: R_f 0.68 (CH_2Cl_2 : hexane, 2 : 3); ^1H NMR (400 MHz, $CDCl_3$) δ 8.40 (dd, J = 1.5, 0.6 Hz, 2H), 8.10 (dd, J = 1.9, 0.6 Hz, 4H), 7.79 (m, 6H), 7.67 (dd, J = 8.6, 1.6 Hz, 2H), 7.62 (m, 4H), 7.58 (m, 2H), 7.44 (dd, J = 8.8, 1.9 Hz, 4H), 7.42 (dd, J = 8.5, 0.7 Hz, 2H), 7.41 (dd, J = 8.7, 0.6 Hz, 4H), 3.23 (s, 1H), 1.88 (s, 8H), 1.53 (s, 24H), 0.76 (s, 36H); MS (FD) *m/z* 1246.6 (M^+); Analysis calc'd for $C_{92}H_{99}N_3$: C, 88.63; H, 8.00; N, 3.37; found: C, 88.48; H, 7.84; N, 3.79.

4-Cascade:9-(4-(3-hydroxy-3-methyl-but-1-ynyl)phenyl)carbazole[2-3,6]:9-(4-ethynylphenyl)-3,6-carbazole:9-(4-ethynylphenyl)-3,6-bis(1,1,3,3-tetramethyl-butyl)carbazole (13). Terminal acetylene functionalized trimer monodendron (**12**, 776 mg, 0.622 mmol) was coupled with focal point monomer **22** (175 mg, 0.303 mmol) according to general procedure A2. Piperidine (60 mL) was used as solvent. Solvent was removed under vacuum and crude product was purified by flash chromatography eluting first with 2 : 3, followed by 1 : 1, dichloromethane : hexane to give **13** as a pale yellow solid (712 mg, 83%): R_f 0.42 (CH_2Cl_2 : hexane, 3 : 2); ^1H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, J = 1.4 Hz, 2H), 8.42 (d, J = 1.7 Hz, 4H), 8.10 (d, J = 1.7 Hz, 8H), 7.87 (m, 4H), 7.80 (m, 8H), 7.73-7.68 (m, 8H), 7.64-7.61 (m, 12H), 7.57 (m, 2H), 7.48-7.44 (m, 14H), 7.40 (d, J = 8.8 Hz, 8H), 1.87 (s, 16H), 1.70 (s, 6H), 1.52 (s, 48H), 0.76 (s, 72H); MS (MALDI, dithranol/AgTFA as matrix) *m/z* calc'd for $C_{207}H_{213}N_7O$: 2815.01; found: 2921.86 ($M + Ag^+$); Analysis calc'd for $C_{207}H_{213}N_7O$: C, 88.32; H, 7.63; N, 3.48; found: C, 87.96; H, 7.62; N, 3.40.

4-Cascade:9-(4-ethynylphenyl)carbazole[2-3,6]:9-(4-ethynylphenyl)-3,6-carbazole:9-(4-ethynylphenyl)-3,6-bis(1,1,3,3-tetramethyl-butyl)carbazole (14).

To a solution of **13** (700 mg, 0.248 mmol) in toluene (100 mL), was added a solution of KOH (69.6 mg, 1.24 mmol) in butanol (10 mL). The reaction was heated to 110 °C for 1.5 h under nitrogen atmosphere, and the solvent was removed under vacuum. The crude product was purified by flash chromatography eluting with 1 : 3, dichloromethane : hexane to afford the terminal acetylene functionalized 7-mer monodendron **14** as white powder (620 mg, 90%): R_f 0.69 (CH_2Cl_2 : hexane, 2 : 3); 1H

NMR (500 MHz, $CDCl_3$) δ 8.44 (dd, J = 1.6, 0.7 Hz, 2H), 8.42 (dd, J = 1.7, 0.7 Hz, 4H), 8.10 (d, J = 1.7 Hz, 8H), 7.88 (m, 4H), 7.80 (m, 8H), 7.72-7.69 (6), 7.64-7.59 (m, 14H), 7.48-7.44 (m, 14H), 7.41 (d, 8.5H), 3.24 (s, 1H), 1.87 (s, 16H), 1.53 (s, 48H), 0.76 (s, 72H); MS (MALDI, IAA as matrix) *m/z* calc'd for $C_{204}H_{207}N_{93}$: 2756.93; found: 2757.9 (M^+); Analysis calc'd for $C_{204}H_{207}N_{93}$: C, 88.88; H, 7.57; N, 3.56; found: C, 88.91; H, 7.66; N, 3.45.

8-Cascade:9-(4-(3-hydroxy-3-methyl-but-1-ynyl)phenyl)carbazole[2-3,6]:(9-(4-ethynylphenyl)-3,6-carbazole)^2:9-(4-ethynylphenyl)-3,6-bis(1,1,3,3-tetramethyl-butyl)carbazole (15). Terminal acetylene functionalized 7-mer monodendron (**14**, 770 mg, 0.279 mmol) was reacted with focal point monomer **10** (73.0 mg, 0.126 mmol) using general procedure A2. The crude product was purified by flash chromatography eluting with 3 : 2, benzene : cyclohexane to give **15** as white solid (530 mg, 72%): R_f 0.48 (CH_2Cl_2 : hexane, 3 : 2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46-8.45 (m, 6H), 8.42 (dd, J = 1.7, 0.6 Hz, 8H), 8.10 (d, J = 1.5 Hz, 16H), 7.91-7.87 (m, 12H), 7.80 (m, 16H), 7.74-7.60 (m, 44H), 7.52-7.39 (m, 48H), 1.87 (s, 32H), 1.70 (s, 6H), 1.52 (s, 96H), 0.76 (s, 144H); MS (MALDI, dithranol/AgTFA as matrix) *m/z* calc'd for $C_{431}H_{429}N_{15}O$: 5835.24; found: 5935.86 ($M + Ag^+$); Analysis calc'd for $C_{431}H_{429}N_{15}O$: C, 88.72; H, 7.41; N, 3.60; found: C, 89.10; H, 7.63; N, 3.53.

8-Cascade:9-(4-ethynylphenyl)carbazole[2-3,6]:(9-(4-ethynylphenyl)-3,6-carbazole)^2:9-(4-ethynylphenyl)-3,6-bis(1,1,3,3-tetramethyl-butyl)carbazole (16).

To a solution of **15** (575 mg, 0.0985 mmoL) in toluene (50 mL) was added a

solution of KOH (28 mg) in butanol (10 mL). The reaction was heated to 110 °C for 1.5 h, and the solvent was removed under vacuum. The crude product was purified flash chromatography eluting with 2 : 3, followed by 1 : 1, dichloromethane : hexane to give **16** as a white powder (525 mg, 92%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46-8.45 (m, 6H), 8.42 (dd, J = 1.7, 0.6 Hz, 8H), 8.10 (d, J = 2.0 Hz, 16H), 7.91-7.87 (m, 12H), 7.80-7.78 (m, 18H), 7.74-7.68 (m, 14H), 7.66-7.58 (m, 30H), 7.50-7.39 (m, 46H), 3.25 (s, 1H), 1.88 (s, 32H), 1.53 (s, 96H), 0.77 (s, 144H); MS (MALDI, dithranol/AgTFA as matrix) *m/z* calc'd for $C_{428}H_{423}N_{15}$: 5777.12; found: 5886.33 ($M + Ag^+$); MS (MALDI, *t*-retinoic acid as matrix) *m/z* 5796.9 (M^+), 11567 ($2M^+$).

2,6-Di-*tert*-butyl-(2-methoxy-ethoxy)-benzene, (17). 2,6-Di-*tert*-butyl-phenol (20.0 g, 97.1 mmol) was dissolved in DMF (150 mL). Sodium hydride (60% suspension in mineral oil, 5.8 g, 145 mmol) was added in small portions. The reaction was allowed to stir at room temperature for 30 min, and 1-bromo-2-methoxy-ethane (30.0 g, 230 mmol) and tetrabutylammonium iodide (1.0 g, 2.7 mmol) were added. The reaction was heated to 110 °C for 48 h under nitrogen. Water was thenadded and the reaction was extracted with hexane. Solvent was removed and the crude product was purified by flash chromatography eluting with 1 : 10, dichloromethane : hexane to afford **17** (12.6 g, 49%) as colorless oil which solidifies over time.: R_f = 0.38 (CH_2Cl_2 : hexane, 1 : 4); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, J = 7.7 Hz, 2H), 6.98 (t, J = 7.8 Hz, 1H), 3.91 (t, J = 5.45 Hz, 2H), 3.79 (t, J = 5.6 Hz, 2H), 3.46 (s, 3H), 1.43 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.55, 143.63, 126.71, 122.95, 74.68, 71.48, 59 (43), 35.77, 32.11; MS (EI)

m/z 264.2 (M^+, 25), 150.1 (32), 59.1 (100); Analysis calc'd for $C_{17}H_{28}O_2$: C, 77.2; H, 10.67; found: C, 77.0; H, 10.67.

2,6-Di-*tert*-butyl-4-bromo-(2-methoxy-ethoxy)-benzene, (18). 2,4-Di-*tert*-butyl-(2-methoxy-ethoxy)-benzene (**17** , 12.3 g, 46.7 mmol) was dissolved dichloromethane (100 mL) and the solution was cooled to 0 °C and allowed to stir. Bromine (7.47 g, 46.7 mmol) was slowly added. The reaction was allowed to stir at that temperature for 2 h and saturated sodium thiosulfate was added. The reaction was extracted with dichloromethane and the organic layer was collected, washed with water, and dried over anhydrous magnesium sulfate. Solvent was removed and the crude product was purified by flash chromatography eluting with 1 : 10, dichloromethane : hexane to afford **18** as an oil (15.5 g, 97%): R_f 0.38 (CH_2Cl_2 : hexane, 1 : 4); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (s, 2H), 3.88 (t, J = 5.4 Hz, 2H), 3.77 (t, J = 5.5 Hz, 2H), 1.40 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.99, 135.62, 129.06, 125.12, 73.97, 58.22, 35.90, 34.06, 30.18; MS (EI) *m/z* 342.2 (M^+ - H, 13.5); Analysis calc'd for $C_{17}H_{17}BrO_2$: C, 59.48; H, 7.93; found: C, 59.51; H, 7.85.

2,6-Di-*tert*-butyl-4-(4,4,5,5-tetramethyl-(1,3,2)dioxaborolan-2-yl)-(2-methoxy-ethoxy)-benzene (19). 2,6-Di-*tert*-butyl-4-bromo-(2-methoxy-ethoxy)-benzene (**18**, 10.25 g, 29.86 mmol) was dissolved in dry THF (50 mL). The solution was cooled to -78 °C, and butyl lithium (1.6 M in hexanes, 22.5 mL, 36.0 mmol) was slowly added. The reaction was allowed to stir at that temperature for 2 h and then warmed to rt. Dichloromethane was added and the reaction mixture was passed through a plug of silica

gel, which was rinsed several times with more dichloromethane. The solution containing the crude product was collected and concentrated. Flash chromatography eluting with 1 : 4, followed by 3 : 2, dichoromethane : hexane afforded **19** as white solid (8.52 g, 73%): R_f 0.50 (CH_2Cl_2 : hexane, 3 : 2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 2H), 3.89 (t, J = 5.2 Hz, 2H), 3.80 (t, J = 5.2 Hz, 2H), 1.44 (s, 18H), 1.32 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.60, 142.95, 133.48, 83.48, 74.63, 71.46, 59.45, 35.73, 32.11, 24.86; MS (EI) *m/z* 390.4 (37.2, M^+), 276.2 (60.6); Analysis calc'd for $C_{23}H_{39}BO_4$: C, 70.77; H, 10.07; found: C, 71.07; H, 10.23.

9-(4-(3,3-Diethyltriazenyl)phenyl)-3,6-bis(3,5-di-*tert*-butyl-4-(2-methoxy-ethoxy)phenyl)carbazole (21). A heavy-walled flask was charged with 2,6-di-*tert*-butyl-4-(4,4,5,5-tetramethyl-(1,3,2)dioxaborolan-2-yl)-(2-methoxy-ethoxy)-benzene (**19** , 2.50 g, 6.17 mmol), triazene dibromide **20** (1.47 g, 2.94 mmo), tri-*o*-toly-phosphine (130 mg, 0.43 mmol), $Pd(dba)_2$ (56 mg, 0.097 mmoL), Na_2CO_3 (2 M aqueous solution, 6 mL, 12 mmoL), ethanol (16 mL) and toluene (50 mL). The flask was degassed and back-filled with nitrogen three times, and heated to 90 °C for 3 h. Solvents were removed under vacuum and the crude product purified by flash chromatography eluting with 2 : 50, ethyl acetate : hexane to afford **21** as yellow solid (2.07 g, 81%): R_f = 0.19 (ethyl acetate : hexane, 1 : 10); ^{1}H NMR (400 MHz, CD_2Cl_2/CS_2) δ 8.22 (d, J = 1.5 Hz, 2H), 7.64 (m, 2H), 7.56 (dd, J = 8.5, 1.5 Hz, 2H), 7.53 (m, 2H), 7.50 (s, 4H), 7.45 (d, J = 8.5 Hz, 2H), 3.95 (t, J = 5.4 Hz, 4H), 3.87 (q, J = 7.1 Hz, 4H), 3.80 (t, J = 5.4 Hz, 4H), 3.67 (s, 6H), 1.54 (s, 18H), 1.38 (s, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2/CS_2) δ 157.17, 150.56, 143.96, 140.92, 136.91, 134.56, 134.53, 127.50, 126.41, 126.23, 124.25, 122.19, 119.10,

110.54, 75.41, 72.00, 59.51, 36.20, 92.65; MS (EI) *m/z* 866.6 (M^+, 8.9), 767.5 (100); Analysis calc'd for $C_{56}H_{74}N_4O_4$: C, 77.56; H, 8.60; N, 6.46; found: C, 77.80; H, 8.61; N, 6.42.

9-(4-Iodophenyl)-3,6-bis(3,5-di-*tert*-butyl-4-(2-methoxy-ethoxy)phenyl)-carbazole (22). A heavy-walled flask was charged with **21** (2.4 g, 2.77 mmol), and methyl iodide (20 mL). The flask was degassed, back-filled with nitrogen three times and heated to 110 °C for 14 h. The solvent was removed and the crude product was purified by flash chromatography eluting with 2 : 3, follwed by 1 : 1, dichloromethane : hexane to afford **22** as a white solid (2.31 g, 93%): R_f 0.61 (CH_2Cl_2 : hexane, 3 : 2); ^1H NMR (400 MHz, CD_2Cl_2/CS_2) δ 8.25 (d, J = 1.5 Hz, 2H), 8.00 (m, 2H), 7.59 (dd, J = 8.6, 1.2 Hz, 2H), 7.51 (s, 4H), 7.46 (d, J = 8.6 Hz, 2H), 7.44 (m, 2H), 3.96 (t, J = 5.4 Hz, 4H), 3.81 (t, J = 5.4 Hz, 4H), 3.47 (s, 6H), 1.54 (s, 36H); ^{13}C NMR (100 MHz, CD_2Cl_2/CS_2) δ 157.32, 144.10, 140.33, 139.60, 137.90, 136.64, 135.15, 128.95, 126.39, 124.57, 116.24, 110.22, 95.77, 92.85, 75.43, 71.98, 59.52, 36.21, 32.60; MS (EI) *m/z* calc'd for $C_{52}H_{64}NOI$: 893.388, found 893.3887.

9-(4-(Trimethylsilylethynyl)phenyl)-3,6-bis(3,5-di-*tert*-butyl-4-(2-methoxy-ethoxy)phenyl)carbazole (23). Iodide **22** (7.0 g, 7.83 mmo) was coupled with trimethylsilylacetylene (2.4 mL, 1.67 g, 17.0 mmol) according to general procedure A1. Piperidine (60 mL) was used as solvent and the reaction was carried out at room temperature. The crude product was purified by flash chromatography eluting with 1 : 100, ethylacetale : hexane to afford **23** as a white solid (6.21 g, 92%): R_f 0.62 (CH_2Cl_2 :

hexane, 3 : 2); ^{1}H NMR (400 MHz, CD_2Cl_2/CS_2) δ 8.25 (d, J = 1.5 Hz, 2H), 3.73 (m, 2H), 7.62 (m, 2H), 7.60 (dd, J = 8.6, 1.5 Hz, 2H), 7.52 (s, 4H), 7.50 (d, J = 8.6 Hz, 2H), 3.96 (t, J = 5.4 Hz, 4H), 3.81 (t, J = 5.4 Hz, 4H), 3.48 (s, 6H), 1.52 (s, 36H), 0.36 (s, 9H); ^{13}C NMR (100 MHz, CD_2Cl_2/CS_2) δ 157.32, 144.09, 140.32, 138.11, 136.68, 135.16, 133.89, 126.78, 126.41, 124.63, 122.63, 119.23, 110.38, 104.92, 96.05, 75.44, 71.99, 59.53, 54.34, 36.22, 32.63, 0.37; MS (EI) *m/z* 863.5 (M^+, 100), 791.5 (47.4); Analysis calc'd for $C_{57}H_{73}NO_4SI$: C, 79.21; H, 8.51; N, 1.62; found: C, 79.19; H, 8.55; N, 1.57.

9-(4-Ethynylphenyl)-3,6-bis(3,5-di-*tert*-butyl-4-(2-methoxy-ethoxy)phenyl)-carbazole (24). Compound **23** (5.42 g, 6.27 mmol) was treated with tetrabutylammonium fluoride (1.0 M in THF, 6.3 mL, 6.3 mmol). The crude product was purified by flash chromatography eluting with 1 : 100, ethyl acetate : hexane, followed by 2 : 100, ethyl acetate : hexane to afford **24** as a white solid (4.30g, 86%): R_f 0.48 (CH_2Cl_2 : hexane, 3 : 2); ^{1}H NMR (400 MHz, CD_2Cl_2/CS_2) δ 8.23 (d, J = 1.7 Hz, 2H), 7.77 (m, 2H), 7.64 (m, 2H), 7.58 (dd, J = 8.6, 2.0 Hz, 2H), 7.50 (s, 4H), 7.49 (d, J = 8.6 Hz, 2H), 3.95 (t, J = 5.4 Hz, 4H), 3.80 (t, J = 5.4 Hz, 4H), 3.48 (s, 6H), 3.22 (s, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2/CS_2) δ 157.32, 144.03, 140.27, 138.47, 136.69, 135.24, 134.21, 126.83, 126.47, 126.44, 124.68, 121.59, 119.29, 110.34, 83.61, 79.03, 75.46, 72.00, 59.53, 36.20, 32.67; MS (EI) *m/z* 791.5 (M^+, 100), 732.5 (22.6); Analysis calc'd for $C_{54}H_{65}NO_4$: C, 81.88; H, 8.27; N, 1.77; found: C, 81.88; H, 8.28; N, 1.64.

2-Cascade:9-(4-(3-hydroxy-3-methyl-but-1-ynyl)phenyl)carbazole[2-3,6]:9-(4-ethynylphenyl)-3,6-bis(3,5-di-*tert*-butyl-4-(2-methoxy-ethoxy)phenyl)carbazole

(25). Peripheral monomer **24** (1.54 g, 1.94 mmol) was coupled with focal point monomer **10** (560 mg, 0.97 mmol) using general procedure A2. Piperidine (75 mL) was used as solvent and the reaction was carried out at room temperature. The crude product was purified by flash chromatography eluting with 100% dichloromethane, ramping up to 1 : 50, ethyl acetate : dichloromethane to afford **25** as white solid (1.74 g, 94%): R_f 0.79 (CH_2Cl_2 : ethyl acetate, 50 : 1); ^{1}H NMR (400 MHz, CD_2Cl_2/CS_2) δ 8.38 (d, J = 1.0 Hz, 2H), 8.22 (d, J = 1.2 Hz, 4H), 7.84 (m, 4H), 7.72 (m, 2H), 7.68 (m, 4H), 7.67 (dd, J = 8.6, 1.5 Hz, 2H), 7.61 (m, 2H), 7.59 (dd, J = 8.5 Hz, 1.7H), 7.53 (d, J = 8.5 Hz, 4H), 7.50 (s, 8H), 7.45 (d, J = 8.6 Hz, 2H), 3.95 (t, J = 5.4 Hz, 8H), 3.80 (t, J = 5.4 Hz, 8H), 3.47 (s, 12H), 1.83 (s, 1H), 1.67 (s, 6H), 1.54 (s, 72H); ^{13}C NMR (100 MHz, CD_2Cl_2/CS_2) δ 157.31, 144.01, 140.97, 140.37, 137.70, 136.82, 136.77, 135.18, 133.82, 133.50, 130.80, 127.05, 126.94, 126.46, 124.78, 124.67, 123.97, 123.36, 123.14, 119.31, 116.03, 110.56, 110.44, 96.42, 92.35, 88.88, 81.61, 75.46, 72.01, 65.52, 59.54, 36.51, 36.13, 32.71, 31.86; MS (MALDI, IAA as matrix) *m/z* calc'd for $C_{131}H_{145}N_3O_9$: 1905.60, found 1905.6; Analysis calc'd for $C_{131}H_{145}N_3O_9$: C, 82.57; H, 7.67; N, 2.21; found: C, 82.41; H, 7.65; N, 2.14.

2-Cascade:9-(4-ethynylphenyl)carbazole[2-3,6]:9-(4-ethynylphenyl)-3,6-bis(3,5-di-*tert*-butyl-4-(2-methoxy-ethoxy)phenyl)carbazole (26). Trimer monodendron **25** (1.72 g, 0.90 mmol) was dissolved in toluene and a solution of KOH (60 mg, 1.07 mmol) in methanol (15 mL) was added. The reaction was heated to 110 °C for 1.5 h and solvents were removed under vacuum. The crude product was purified by flash chromatography eluting with 1 : 4, hexane :dichloromethane ramped up to 100%

dichloromethane to afford **26** as a white solid (1.45 g, 87%): R_f 0.76 (CH_2Cl_2); ^{1}H NMR (400 MHz, C_6D_6/CS_2) δ 8.20 (dd, J = 1.7, 0.6 Hz, 2H), 8.05 (dd, J = 1.6, 0.5 Hz, 4H), 7.66 (m, 4H), 7.61 (m, 2H), 7.51 (m, 4H), 7.41 (m, 6H), 7.36 (dd, J = 8.4, 0.6 Hz, 4H), 7.33 (s, 8H), 7.27 (dd, J = 8.5, 0.7 Hz, 2H), 3.78 (t, J = 5.5 Hz, 8H), 3.61 (t, J = 5.4 Hz, 8H), 3.29 (s, 12H), 3.04 (s, 1H), 1.40 (s, 72H); MS (MALDI, IAA as matrix) *m/z* calc'd for $C_{128}H_{139}N_3O_8$: 1846.52; found: 1847.01; Analysis calc'd for $C_{128}H_{139}N_3O_8$: C, 83.21; H, 7.58; N, 2.27; found: C, 83.39; H, 7.57; N, 2.33.

4-Cascade:9-(4-ethynylphenyl)carbazole[2-3,6]:9-(4-ethynylphenyl)-3,6-carbazole:9-(4-ethynylphenyl)-3,6-bis(3,5-di-*tert*-butyl-4-(2-methoxy-ethoxy)phenyl)carbazole (27). Trimer monodendron **26** (1.41 g, 0.763 mmo) was coupled with focal point monomer **22** (220 mg, 0.381 mmol) using general procedure A2. Benzene (25 mL) and piperidine (25 mL) were used as solvents, and the reaction was carried out at room temperature. The crude product was purified by flash chromatography eluting with 1 : 5, ethyl acetate : dichloromethane to afford the 3-hydroxy-3-methyl-butynyl- functionalized 7-mer monodendron (1.32 g). Part of this 3-hydroxy-3-methyl-butynyl- functionalized 7-mer monodendron (1.21 g, 0.301 mmol) was dissolved in toluene (50 mL), and a solution of KOH (21 mg, 0.38 mmol) in methanol (25 mL) was added. The reaction was heated to 110 °C for 1.5 h and methanol allowed to evaporate. Solvents were removed under vacuum, and the crude product was purified by flash chromatography eluting with 3 : 500, ethyl acetate : dichloromethane to afford the terminal acetylene functionalized 7-mermonodendron **27** as a white solid: R_f 0.86 (CH_2Cl_2 : ethyl acetate, 100 : 1); ^{1}H NMR (400 MHz, C_6D_6/CS_2) δ 8.22 (m, 6), 8.06 (dd,

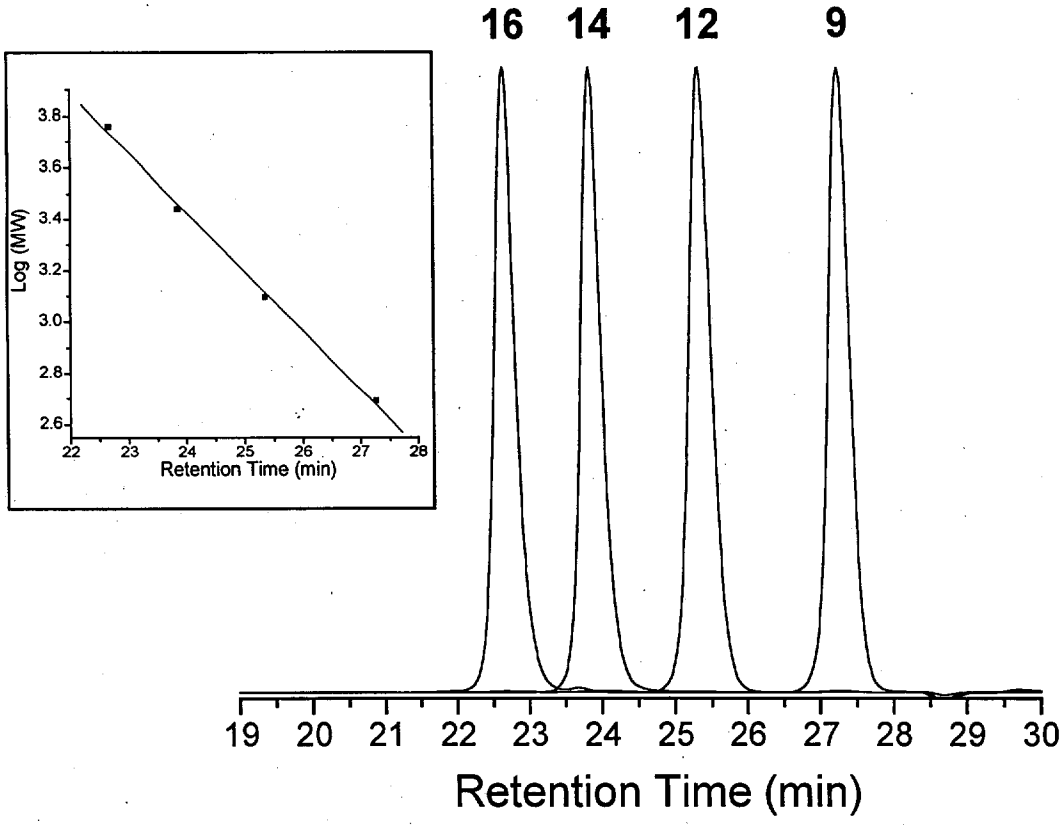
J = 1.8, 0.7 Hz, 8H), 7.70 (m, 4H), 7.68 (m, 8H), 7.62 (m, 2H), 7.55-7.49 (m, 18), 7.44-7.41 (m, 10), 7.37 (dd, J = 8.5, 0.6 Hz, 8H), 7.34 (s, 16H), 7.33-7.32 (m, 20H), 7.29 (dd, J = 8.4, 06 Hz, 2H), 3.78 (t, J = 5.4 Hz, 16H), 3.61 (t, J = 5.4 Hz, 16H), 3.28 (s, 24H), 3.05 (s, 1H), 1.40 (s, 144H); MS (MALDI, IAA as matrix) *m/z* calc'd for $C_{276}H_{287}N_7O_{16}$: 3955.35; found: 3957.64 (M+), 3900.64 (M^+ - *tert*-Bu); 3843.18 (M^+ - 2*tert*-Bu); Analysis calc'd for $C_{276}H_{287}N_7O_{16}$: C, 83.75; H, 7.31; N, 2.48; found: C, 84.07; H, 7.41; N, 2.21.

8-Cascade:9-(4-ethynylphenyl)carbazole[2-3,6]:(9-(4-ethynylphenyl)-3,6-carbazole)^2:9-(4-ethynylphenyl)-3,6-bis(3,5-di-*tert*-butyl-4-(2-methoxy-ethoxy)phenyl)carbazole (28). Seven-mer monodendron **27** (1.17 g, 0.295 mmo) was coupled with focal point monomer **10** (85.3 mg, 0.147 mmol) using general procedure A2. Benzene (30 mL) and piperidine (20 mL) was used as solvents, and the reaction was carried out at room temperature. The crude product was purified by flash chromatography eluting with 100% dichloromethane ramping up to 1 : 5, ethyl acetate : dichloromethane to afford the 3-hydroxy-3-methyl-butynyl- functionalized 15-mer monodendron (855 mg). Part of this 3-hydroxy-3-methyl-butynyl- functionalized 15-mer monodendron (850 mg, 0.103 mmol) was dissolved in toluene (40 mL), and a solution of KOH (20 mg, 0.36 mmol) in methanol (25 mL) was added. The reaction was heated to 110 °C for 1.5 under nitrogen, and methanol was allowed to evaporate. The reaction was passed through a plug of silica gel, eluting with 1 : 50, ethyl acetate : dichloromethane. Solvents were removed under vacuum, and the crude product was purified by flash chromatography eluting with 1 : 100, ramping up to 1.5 : 100, ethyl acetate :

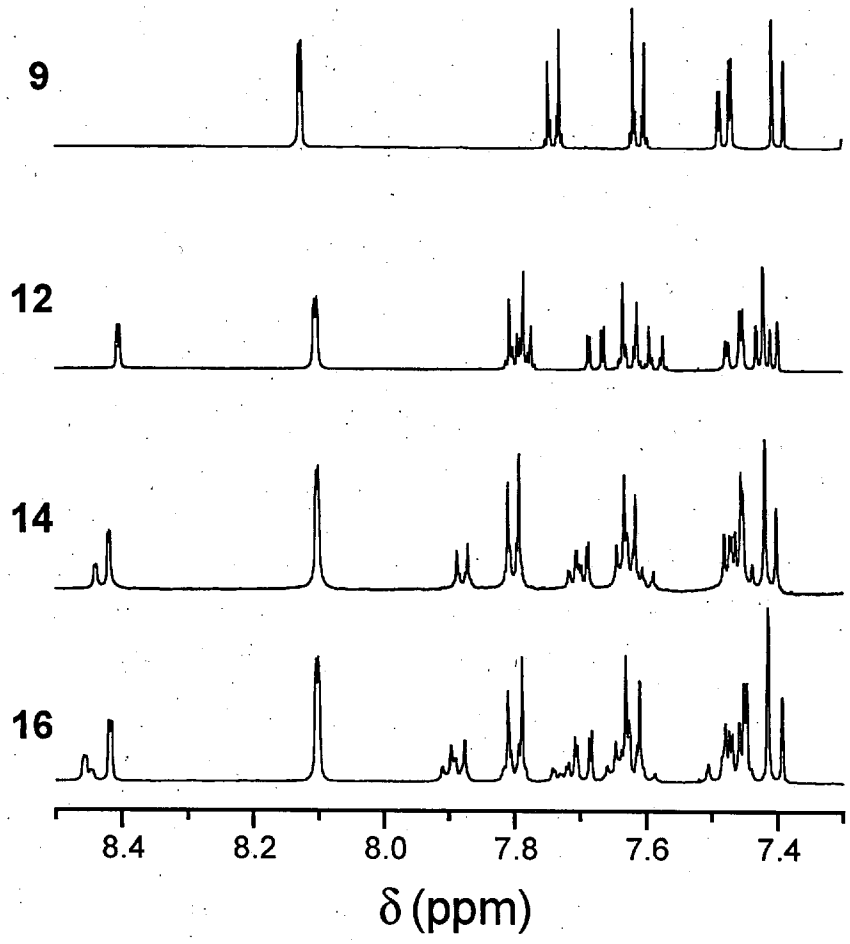
dichloromethane to afford the terminal acetylene functionalized 15-mermonodendron **28** as a white solid (756 mg, 63%over two steps) : ^{1}H NMR (400 MHz, C_6D_6/CS_2) δ 8.24 (dd, J = 1.5, 0.8 Hz, 4H), 8.22 (dd, J = 1.6, 0.6 Hz, 2H), 8.21 (dd, J = 1.5, 0.7 Hz, 8H), 8.04 (dd, J = 1.7, 0.7 Hz, 16H), 7.74-7.66 (m, 30H), 7.57-7.49 (m, 44H), 7.42-7.32 (m, 78H), 3.77 (t, J = 5.4 Hz, 32H), 3.61 (t, J = 5.4 Hz, 32H), 3.28 (s, 64H), 3.05 (s, 1H), 1.40 (s, 288H); MS (MALDI, *t*-retinoic acid as matrix) *m/z* calc'd for $C_{572}H_{583}N_{15}O_{32}$: 8180.0; found: 8189.2 (M^+); Analysis calc'd for $C_{572}H_{583}N_{15}O_{32}$: C, 83.99; H, 7.18; N, 2.57; found: C, 84.17; H, 7.44; N, 2.29.

16-Cascade:9-(4-ethynylphenyl)carbazole[2-3,6]:(9-(4-ethynylphenyl)-3,6-carbazole)^3:9-(4-ethynylphenyl)-3,6-bis(3,5-di-*tert*-butyl-4-(2-methoxy-ethoxy)phenyl)carbazole (29) Fifteen-mer monodendron **28** (325.7 mg, 0.0398 mmol) was coupled with focal point monomer **10** (11.49 mg, 0.0199 mmol) using general procedure A2. Benzene (20 mL) and piperidine (20 mL) was used as solvents, and the reaction was carried out at room temperature. The crude product was purified by flash chromatography eluting with 1 : 50, ramping up to 2 : 50, ethyl acetate : dichloromethane to afford the 3-hydroxy-3-methyl-butynyl- functionalized 31-mer monodendron (117.3 mg). Part of this 3-hydroxy-3-methyl-butynyl- functionalized 15-mer monodendron (65.0 mg, 0.00390 mmol) was dissolved in toluene (30 mL) and a solution of KOH (133 mg, 2.37 mmol) in methanol (10 mL) was added. The reaction was heated to 110 °C for 1.5 under nitrogen, and methanol allowed evaporating. The reaction was passed through a plug of silica gel, eluting with 2 : 50, ethyl acetate : dichloromethane. Solvents were removed under vacuum, and the crude product was

purified by flash chromatography eluting with 1 : 100, ramping up to 3 : 100, ethyl acetate : dichloromethane to afford the terminal acetylene functionalized 31-mermonodendron **29** as a white solid (48.7 mg, 26% over two steps) : ^{1}H NMR (500 MHz, CS_2/C_6D_6) δ 8.27-8.22 (m, 30H), 8.11 (m, 16H), 7.72-7.64 (m, 62H), 7.60-7.26 (m, 250H), 3.80 (t, J = 5.4 Hz, 64H), 3.60 (t, J = 5.4 Hz, 64H), 3.24 (s, 96H), 3.01 (s, 1H), 1.40 (s, 576H); MS (MALDI, *t*-retinoic acid as matrix) *m/z* calc'd for $C_{11164}H_{1175}N_{31}O_{64}$: 16623.3; found: 16633.2 (M^+), 16575.7 (M^+ - *tert*-Bu), 16518.1 (M^+ - 2*tert*-Bu); Analysis calc'd for $C_{11164}H_{1175}N_{31}O_{64}$: C, 84.10; H, 7.12; N, 2.61; found: C, 84.27; H, 7.25; N, 2.66.



Overlaid normalized GPC chromatograms of terminal acetylene functionalized monomer and monodendrons. The inset shows the linear correlation between log of theoretical molecular weights versus retention time: $[Log(MW) = -0.23\langle t + 8.97; R = 0.999]$.



Stacked plot of aromatic regions of ^{1}H NMR spectra of peripheral monomer **24** (400MHz, 3 : 2, CS_2 : CD_2Cl_2) and monodendrons **26** (400 MHz, 10 : 1, CS_2 : C_6D_6), **27** (400MHz, 10 : 1, CS_2 : C_6D_6), **28** (400MHz, 10 : 1, CS_2 : C_6D_6) and **29** (500 MHz, 5 : 1, CS_2 : C_6D_6) with terminal acetylene at the focal point.