Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

for

Angew. Chem. Int. Ed. Z51613

69451 Weinheim, Germany

First Synthesis and Characterization of Dendritic Necklaces: A New Class of Outer Sphere–Outer Sphere Connected Dendronized Organoplatinum Polymers

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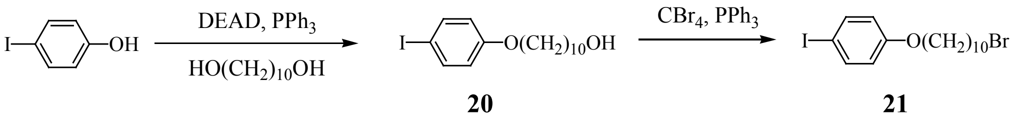
[**] We thank the Research Grants Council, HKSAR (CUHK4201/99P) for the financial support.

General Methods: All reagents were purchased from commercial suppliers (Acros or Aldrich) and used without further purification. Organic solvents were dried prior to use. All reactions were carried out under a nitrogen atmosphere. Thin layer chromatography (TLC) was performed on silica gel sheets 60 F_{254} (E. Merck). Column chromatography was performed on silica gel (Macherey Nagel Kieselgel 60M 230-400 mesh). All nuclear magnetic resonance (NMR) spectra were recorded either on a Brüker Advance DPX300 spectrometer (^{1}H: 300 MHz; ^{13}C: 75.5 MHz) or a Varian Unity INOVA400 spectrometer (^{31}P: 161.9 MHz) and chloroform-*d* was used as solvent unless otherwise stated. Chemical shifts are reported as parts per million (ppm) downfield from signal of Me_4Si as internal standard for ^{1}H and ^{13}C NMR or from signal of PPh_3 as external standard for ^{31}P NMR. Mass spectra were obtained by electron impact (EI) ionization on a Hewlett Packard 5989B mass spectrometer or liquid secondary ionization mass spectrometry (L-SIMS) method on a Brüker APEX 47e FTMS spectrometer or matrix-assisted laser desorption/ionization time of flight mass spectroscopy (MALDI-TOF-MS) on a Brüker Biflex TOF mass spectrometer. The reported molecular mass (*m/z*) values were the most abundant monoisotopic mass. Elemental analyses were carried out at MEDAC Ltd. (Egham, Surrey, UK). Gel permeation chromatography (GPC) analyses were performed on Waters® Styragel columns (HR1, HR2, HR3 and HR4 7.8 × 300 mm in serial) at 40 °C using THF as eluent (flow rate = 1.0 mL min^{-1}) on a Waters® HPLC 515 pump equipped with a Waters® 486 tunable UV absorbance detector. Molecular weights calculated from SEC measurements were based on a calibration curve derived from polystyrene (PS). Melting points were measured on an Electrothermal® 9100 digital melting point apparatus and are uncorrected.

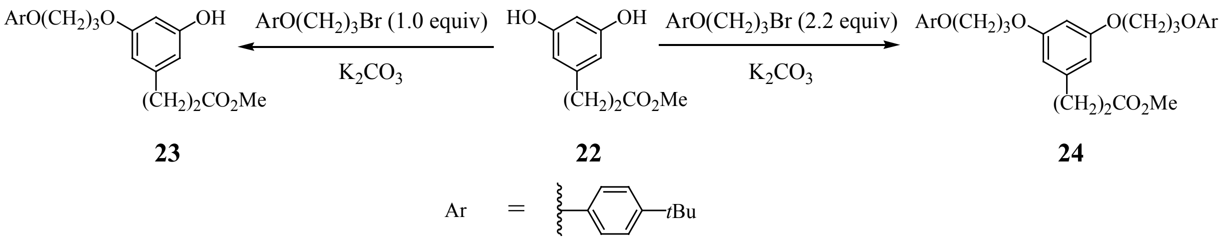
Synthesis



20: Diethyl azodicarboxylate (6.3 mL, 32 mmol) was added dropwise to a solution of PPh_3 (8.30 g, 32 mmol) in THF (70 mL) at 0 °C. After 30 min, a mixture of 1,10-decanediol (9.20 g, 53 mmol) and 4-iodophenol (5.80 g, 26 mmol) in THF (70 mL) was added dropwise. The reaction was stirred at 25 °C for 6 h. Excess THF was then evaporated under reduced pressure and a mixture of hexane/Et_2O (1:1, 30 mL) was added. The precipitate was filtered off and washed with Et_2O (20 mL). The filtrate was then concentrated under reduced pressure to give an oil which was purified by column chromatography (eluent: hexane/EtOAc, 5:1) to give compound **20** (8.70 g, 87%) as a white solid: R_f: 0.23 (hexane/EtOAc, 5:1); m.p. 59–60 °C; ^{1}H NMR: 1.20–1.50 (m, 13 H), 1.56 (quin, J = 6.6 Hz, 2 H), 1.76 (quin, J = 6.9 Hz, 2 H), 3.60–3.70 (m, 2 H), 3.90 (t, J = 6.6 Hz, 2 H), 6.68 (d, J = 6.9 Hz, 2 H), 7.53 (d, J = 6.9 Hz, 2 H); ^{13}C NMR: 25.7, 25.9, 29.1, 29.3, 29.37, 29.44, 29.5, 32.8, 63.1, 68.1, 82.4, 116.9, 138.1, 159.0; MS(EI): *m/z* 376 (M^+, 7); calcd (%) for $C_{16}H_{25}O_2I$: C, 51.07; H, 6.70; found: C, 50.89; H, 6.80.

21: PPh_3 (4.2 g, 16 mmol) was added to a mixture of the alcohol **20** (3.0 g, 8.0 mmol) and CBr_4 (4.0 g, 12 mmol) in THF (60 mL). The mixture was stirred at 25 °C for 1.5 h and then diluted with hexane/Et_2O (1:1, 30 mL). The precipitate formed was filtered off and washed with Et_2O (10 mL). The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography (eluent: hexane gradient to hexane/EtOAc, 10:1) to afford compound **21** (3.0 g, 86%) as a white solid; R_f: 0.25

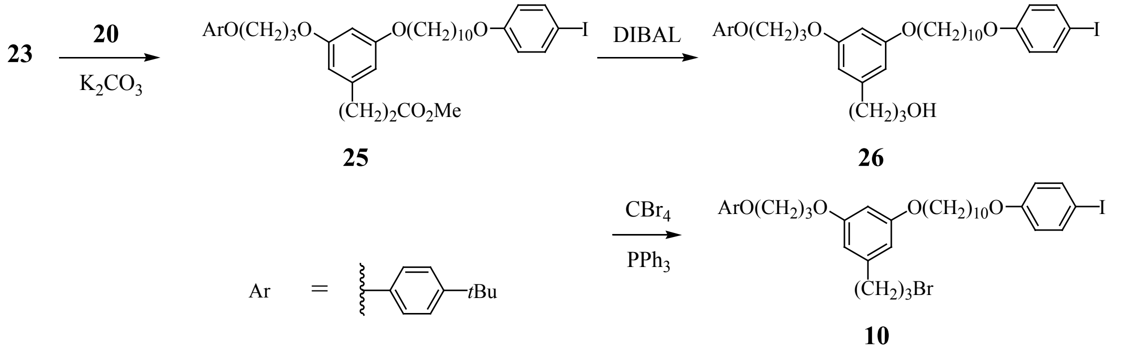
(hexane); m.p. 58–59 °C; ^{1}H NMR: 1.25–1.50 (m, 12 H), 1.76 (quin, J = 6.9 Hz, 2 H), 1.85 (quin, J = 6.9 Hz, 2 H), 3.41 (t, J = 6.9 Hz, 2 H), 3.91 (t, J = 6.3 Hz, 2 H), 6.67 (d, J = 6.6 Hz, 2 H), 7.53 (d, J = 6.6 Hz, 2 H); ^{13}C NMR: 25.9, 28.1, 28.7, 29.1, 29.28, 29.32, 29.4, 32.8, 34.0, 68.1, 82.4, 116.9, 138.1, 159.0; MS(EI): *m/z* 441 [M$^+$ (^{81}Br), 17]; calcd (%) for $C_{16}H_{24}OBrI$: C, 43.76; H, 5.51; found: C, 43.44; H, 5.59.



23: 3-Bromo-1-(4-*tert*-butylphenoxy)propane [1] (16.6 g, 60.0 mmol) was added dropwise to a mixture of methyl 3-(3,5-dihydroxyphenyl)propionate **22** [2] (12.0 g, 60.0 mmol), 18-crown-6 (1.0 g, 3.8 mmol) and K_2CO_3 (25.0 g, 180 mmol) in acetone (250 mL) at 56 °C. The mixture was then heated at 56 °C for 6 h. The solution was filtered and the filtrate obtained was evaporated under reduced pressure and the crude product was purified by column chromatography (eluent: hexane/EtOAc, 5:1 gradient to 3:1) to afford compound **23** (19.6 g, 83%) as a white solid; R_f: 0.10 (hexane/EtOAc, 5:1); m.p. 69–70 °C; ^{1}H NMR: 1.30 (s, 9 H), 2.22 (quin, J = 6.0 Hz, 2 H), 2.60 (t, J = 7.8 Hz, 2 H), 2.84 (t, J = 7.5 Hz, 2 H), 3.67 (s, 3 H), 4.10 (t, J = 6.3 Hz, 2 H), 4.12 (t, J = 6.3 Hz, 2 H), 5.10–5.25 (brs, 1 H), 6.27 (s, 2 H), 6.33 (s, 1 H), 6.85 (d, J = 8.7 Hz, 2 H), 7.29 (d, J = 8.7 Hz, 2 H); ^{13}C NMR: 29.9, 31.6, 32.1, 34.6, 36.2, 61.1, 64.9, 65.0, 100.4, 107.7, 108.4, 114.5, 126.8, 143.8, 144.0, 157.1, 157.3, 160.8, 173.6; MS(L-SIMS): *m/z* 386 (M$^+$, 1); calcd (%) for $C_{23}H_{30}O_5$: C, 71.48; H, 7.82; found: C, 71.27; H, 7.84.

24: A mixture of methyl 3-(3,5-dihydroxyphenyl)propionate **22** [2] (7.1 g, 36 mmol), 3-bromo-1-(4-*tert*-butylphenoxy)propane [1] (22.0 g, 80 mmol), 18-crown-6 (1.0 g, 3.8 mmol) and K_2CO_3 (25.0 g, 18 mmol) in acetone (200 mL) was heated at 56 °C for 6 h. The mixture was then filtered and the filtrate obtained was evaporated under reduced pressure. The residue was purified by column chromatography (eluent:

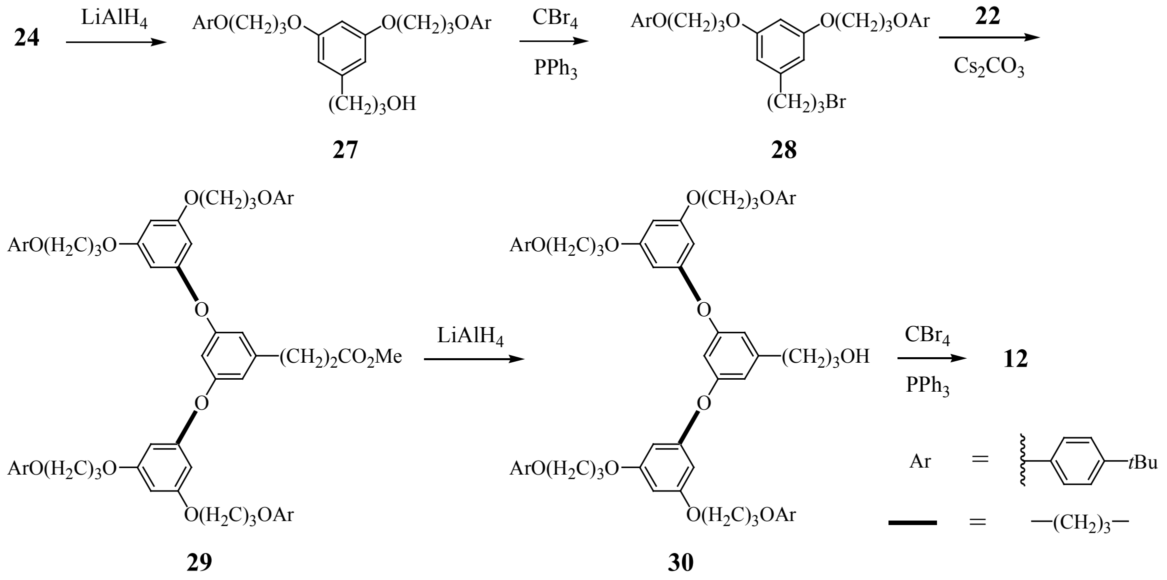
hexane/EtOAc, 8:1 gradient to 5:1) to afford compound **24** (16.5 g, 75%) as a white solid; R_f: 0.68 (hexane/EtOAc, 5:1); m.p. 59–61 °C; ^{1}H NMR: 1.32 (s, 18 H), 2.25 (quin, J = 6.0 Hz, 4 H), 2.62 (t, J = 7.5 Hz, 2 H), 2.89 (t, J = 7.5Hz, 2 H), 3.69 (s, 3 H), 4.13 (t, J = 6.0 Hz, 4 H), 4.15 (t, J = 6.0 Hz, 4 H), 6.34–6.40 (m, 3 H), 6.87 (d, J = 8.7 Hz, 4 H), 7.32 (d, J = 8.7 Hz, 4 H); ^{13}C NMR: 29.3, 31.2, 31.5, 34.0, 35.5, 51.6, 64.3, 64.4, 99.2, 107.0, 113.9, 126.2, 142.8, 143.3, 156.5, 160.1, 173.3; MS(L-SIMS): *m/z* 577 [$(M+H)^+$, 100]; calcd (%) for $C_{36}H_{48}O_6$: C, 74.97; H, 8.39; found: C, 75.25; H, 8.49.



25: A mixture of the phenol **23** (3.8 g, 9.9 mmol), the bromide **20** (5.2 g, 12 mmol), Cs_2CO_3 (6.5 g, 20 mmol) and dibenzo-24-crown-8 (0.9 g, 2.0 mmol) in DMF (60 ml) was stirred at 60 °C for 1.5 h. The reaction was then quenched with water and extracted with EtOAc (50 mL × 2). The organic layers were combined, washed with saturated NaCl solution (50 mL), dried ($MgSO_4$) and concentrated under reduced pressure. The crude product obtained was purified by column chromatography (eluent: hexane/EtOAc, 9:1 gradient to 7:1) to yield compound **25** (6.2 g, 84%) as a white solid; R_f: 0.59 (hexane/EtOAc, 5:1); m.p. 49–50 °C; ^{1}H NMR: 1.25–1.50 (m, 12 H), 1.30 (s, 9 H), 1.76-1.82 (m, 4 H), 2.23 (quin, J = 6.0 Hz, 2 H), 2.60 (t, J = 7.5 Hz, 2 H), 2.84 (t, J = 7.5 Hz, 2 H), 3.67 (s, 3 H), 3.85–3.93 (m, 4 H), 4.10–4.20 (m, 4 H), 6.20–6.40 (m, 3 H), 6.67 (d, J = 6.9 Hz, 2 H), 6.85 (d, J = 6.9 Hz, 2 H), 7.29 (d, J = 6.9 Hz, 2 H), 7.54 (d, J = 6.9 Hz, 2 H); ^{13}C NMR: 25.96, 26.02, 29.1, 29.25, 29.34, 29.5, 31.2, 31.5, 34.0, 35.8, 60.4, 64.3, 64.4, 67.9, 68.1, 82.4, 99.1, 106.8, 107.0, 113.9, 116.9, 126.2, 138.1, 142.8, 143.4, 156.6, 159.0, 160.1, 160.3, 172.9; MS(L-SIMS): *m/z* 745 [$(M+H)^+$, 100]; calcd (%) for $C_{39}H_{53}O_6I$: C, 62.90; H, 7.17; found: C, 62.92; H, 7.18.

26: A mixture of the ester **25** (6.2 g, 8.3 mmol) in toluene (50 ml) was treated with DIBAL (1.0 M in hexane) (34 mL, 33 mmol) at –60 °C to –10 °C for 1.5 h. The reaction was then quenched with EtOAc (5 mL) and water (5 mL). The resulting mixture was acidified to pH 6 by adding HCl solution (2 M) and then extracted with EtOAc (40 mL × 2). The combined organic layers were washed with brine (40 mL), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatographic purification of the crude product (eluent: hexane/EtOAc, 4:1) afforded compound **26** (5.7 g, 96%) as a colorless oil; R_f: 0.39 (hexane/EtOAc, 3:1); ^{1}H NMR: 1.20–1.50 (m, 13 H) 1.29 (s, 9 H), 1.70–1.80 (m, 4 H), 1.80–1.91 (m, 2 H), 2.23 (quin, *J* = 6.0 Hz, 2 H), 2.63 (t, *J* = 7.2 Hz, 2 H), 3.67 (q, *J* = 6.0 Hz, 2 H), 3.90 (t, *J* = 6.6 Hz, 4 H), 4.12 (t, *J* = 6.0 Hz, 2 H), 4.13 (t, *J* = 6.0 Hz, 2 H), 6.31 (t, *J* = 2.4 Hz, 1 H), 6.35 (d, *J* = 2.1 Hz, 2 H), 6.67 (d, *J* = 6.9 Hz, 2 H), 6.85 (d, *J* = 6.9 Hz, 2 H), 7.29 (d, *J* = 6.9 Hz, 2 H), 7.53 (d, *J* = 6.9 Hz, 2 H); ^{13}C NMR: 25.96, 26.03, 29.1, 29.3, 29.5, 31.5, 32.4, 33.9, 34.0, 62.3, 64.3, 64.4, 67.9, 68.1, 82.4, 98.7, 106.9, 107.2, 113.9, 116.9, 126.2, 138.1, 143.4, 144.1, 156.6, 159.0, 160.0, 160.3; MS(L-SIMS): *m/z* 717 [$(M+H)^+$, 100]; calcd (%) for $C_{38}H_{53}O_5I$: C, 63.68; H, 7.45; found: C, 63.77; H, 7.58.

10: A mixture of the alcohol **26** (1.9 g, 2.7 mmol), CBr_4 (1.4 g, 4.0 mmol) and PPh_3 (1.4 g, 5.3 mmol) in THF (25 ml) was stirred at 25 °C for 1.5 h. The mixture was diluted with hexane/Et_2O (1:1, 6 mL) and the precipitate formed was filtered off and washed with Et_2O (10 mL). The filtrate was concentrated under reduced pressure. Chromatographic purification of the crude product (eluent: hexane/EtOAc, 100:1 gradient to 8:1) afforded compound **10** (2.0 g, 97%) as a colorless oil; R_f: 0.70 (hexane/EtOAc, 5:1); ^{1}H NMR: 1.25–1.50 (m, 12 H), 1.32 (s, 9 H), 1.77 (quin, *J* = 6.9 Hz, 4 H), 2.15 (quin, *J* = 6.9 Hz, 2 H), 2.24 (quin, *J* = 6.0 Hz, 2 H), 2.70 (t, *J* = 7.2 Hz, 2 H), 3.39 (t, *J* = 6.6 Hz, 2 H), 3.91 (t, *J* = 6.3 Hz, 4 H), 4.13 (t, *J* = 6.0 Hz, 2 H), 4.14 (t, *J* = 6.0 Hz, 2 H), 6.30–6.40 (m, 3 H), 6.68 (d, *J* = 8.7 Hz, 2 H), 6.87 (d, *J* = 8.7 Hz, 2 H), 7.31 (d, *J* = 8.7 Hz, 2 H), 7.55 (d, *J* = 8.7 Hz, 2 H); ^{13}C NMR: 25.95, 26.02, 29.1, 29.25, 29.33, 29.4, 31.5, 33.1, 33.9, 34.0, 34.2, 64.3, 64.4, 67.9, 68.1, 82.4, 99.0, 107.0, 107.3, 113.9, 116.9, 126.3, 138.1, 142.7, 143.4, 156.5, 159.0, 160.1, 160.3; MS(L-SIMS): *m/z* 781 [$(M+H)^+$ (^{81}Br), 100]; calcd (%) for $C_{38}H_{52}O_4BrI$: C, 58.54; H, 6.72; found: C, 58.80; H, 6.57.



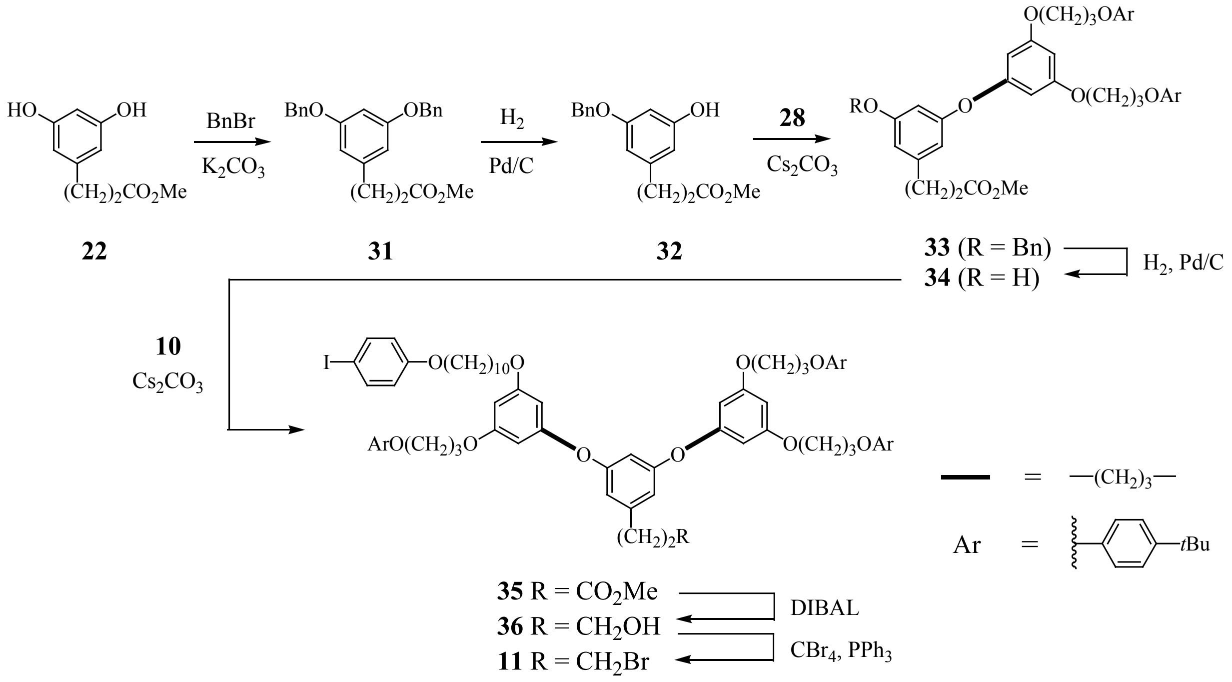
27: A mixture of the ester **24** (4.1 g, 7.1 mmol) and $LiAlH_4$ (0.4 g, 11 mmol) in THF (25 mL) was stirred from 0 °C to 25 °C for 1.5 h. The reaction was then quenched with EtOAc (5 mL) and water (5 mL). The mixture was acidified to pH 6 by adding HCl solution (2 M) and then extracted with EtOAc (35 mL × 2). The organic layers were combined, washed with brine (35 mL), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatographic purification of the crude product (eluent: hexane/EtOAc, 3:1) afforded compound **27** (3.8 g, 99%) as a white solid; R_f: 0.32 (hexane/EtOAc, 3:1); m.p. 60–61 °C; ^{1}H NMR (OH signal not observed): 1.30 (s, 18 H), 1.86 (quin, J = 6.9 Hz, 2 H), 2.22 (quin, J = 6.0 Hz, 4 H), 2.62 (t, J = 7.2 Hz, 2 H), 3.66 (q, J = 4.8 Hz, 2 H), 4.12 (t, J = 6.0 Hz, 4 H), 4.13 (t, J = 6.0 Hz, 4 H), 6.32 (t, J = 2.1 Hz, 1 H), 6.36 (d, J = 1.8 Hz, 2 H), 6.85 (d, J = 8.7 Hz, 4 H), 7.30 (d, J = 8.7 Hz, 4 H); ^{13}C NMR: 30.0, 32.1, 32.9, 34.5, 34.6, 62.9, 64.9, 65.1, 99.4, 107.8, 114.5, 126.8, 144.0, 144.8, 157.2, 160.7; MS(EI): *m/z* 549 [$(M+H)^+$, 100]; calcd (%) for $C_{35}H_{48}O_5$: C, 76.61; H, 8.82; found: C, 76.31; H, 8.89.

28: A mixture of the alcohol **27** (3.8 g, 6.9 mmol), CBr_4 (3.5 g, 10 mmol) and PPh_3 (3.7 g, 14 mmol) in THF (50 mL) was stirred at 25 °C for 1.5 h. The mixture was diluted with hexane/Et_2O (1:1, 20 mL) and the precipitate formed was filtered off and washed with Et_2O (20 mL). The filtrate was concentrated under reduced pressure and the residue was purified by chromatography (eluent: hexane/EtOAc, 100:1 gradient to 5:1) to give compound **28** (4.1 g, 97%) as a colorless oil; R_f: 0.84 (hexane/EtOAc, 5:1); ^1H NMR: 1.30 (s, 18 H), 2.13 (quin, *J* = 6.9 Hz, 2 H), 2.23 (quin, *J* = 6.0 Hz, 4 H), 2.69 (t, *J* = 7.2 Hz, 2 H), 3.38 (t, *J* = 6.6 Hz, 2 H), 4.12 (t, *J* = 6.0 Hz, 4 H), 4.13 (t, *J* = 6.0 Hz, 4 H), 6.32–6.37 (m, 3 H), 6.87 (d, *J* = 8.7 Hz, 4 H), 7.29 (d, *J* = 8.7 Hz, 4 H); ^{13}C NMR: 30.0, 32.1, 33.8, 34.5, 34.7, 34.8, 64.9, 65.1, 99.6, 107.9, 114.5, 126.8, 143.4, 144.0, 157.2, 160.7; MS(L-SIMS): *m/z* 612 [M^+(^{81}Br), 100]; calcd (%) for $C_{35}H_{47}O_4Br$: C, 68.73; H, 7.75; found: C, 68.54; H, 7.74.

29: A mixture of compound **22** (2.1 g, 11 mmol), the bromide **28** (14.0 g, 23 mmol), dibenzo-24-crown-8 (1.4 g, 3.1 mmol) and Cs_2CO_3 (10.0 g, 31 mmol) in DMF (20 mL) was stirred at 60 °C for 1.5 h. The reaction mixture was then quenched with water and extracted with EtOAc (50 mL × 2). The organic layers were combined, washed with brine (50 mL), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatographic purification of the crude product (eluent: hexane/EtOAc, 8:1 gradient to 3:1) gave compound **29** (10.0 g, 74%) as a colorless oil; R_f: 0.66 (hexane/EtOAc, 3:1); ^1H NMR: 1.29 (s, 36 H), 2.05 (quin, *J* = 5.4 Hz, 4 H), 2.21 (quin, *J* = 6.0 Hz, 8 H), 2.59 (t, *J* = 7.5 Hz, 2 H), 2.70 (t, *J* = 7.2 Hz, 4 H), 2.86 (t, *J* = 7.5 Hz, 2 H), 3.66 (s, 3 H), 3.90 (t, *J* = 6.0 Hz, 4 H), 4.09 (t, *J* = 6.3 Hz, 8 H), 4.11 (t, *J* = 6.3 Hz, 8 H), 6.31 (t, *J* = 2.1 Hz, 3 H), 6.36 (d, *J* = 1.8 Hz, 6 H), 6.85 (d, *J* = 8.7 Hz, 8 H), 7.29 (d, *J* = 8.7 Hz, 8 H); ^{13}C NMR: 29.3, 30.6, 31.2, 31.5, 32.4, 34.0, 35.5, 51.6, 64.3, 64.4, 66.9, 98.9, 99.2, 106.8, 107.2, 113.9, 126.2, 142.7, 143.3, 143.8, 156.5, 160.0, 160.3, 173.3; MS(L-SIMS): *m/z* 1258 (M^+, 100); calcd (%) for $C_{80}H_{104}O_{12}$: C, 76.39; H, 8.35; found: C, 76.54; H, 8.41.

30: A mixture of the ester **29** (9.90 g, 7.9 mmol) and $LiAlH_4$ (0.50 g, 12 mmol) in THF (60 mL) was stirred from 0 °C to 25 °C for 1.5 h. The reaction was then quenched with EtOAc (5 mL) and water (5 mL). The resulting mixture was acidified to pH 6 by adding HCl solution (2 M) and extracted with EtOAc (40 mL × 2). The organic layers were combined, washed with brine (40 mL), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatographic purification of the crude product (eluent: hexane/EtOAc, 3:1 gradient to 2:1) afforded compound **30** (8.90 g, 92%) as a colorless oil; R_f: 0.25 (hexane/EtOAc, 3:1); ^{1}H NMR (OH signal not observed): 1.29 (s, 36 H), 1.86 (quin, J = 6.6 Hz, 2 H), 2.05 (quin, J = 5.7 Hz, 4 H), 2.21 (quin, J = 6.0 Hz, 8 H), 2.61 (t, J = 7.2 Hz, 2 H), 2.71 (t, J = 7.2 Hz, 4 H), 3.65 (q, J = 5.4 Hz, 2 H), 3.91 (t, J = 6.0 Hz, 4 H), 4.09 (t, J = 6.3 Hz, 8 H), 4.10 (t, J = 6.3 Hz, 8 H), 6.25–6.40 (m, 9 H), 6.84 (d, J = 8.7 Hz, 8 H), 7.29 (d, J = 8.7 Hz, 8 H); ^{13}C NMR: 29.3, 30.6, 31.5, 32.3, 32.4, 33.96, 34.03, 62.2, 64.35, 64.44, 66.8, 98.9, 107.1, 107.2, 113.9, 126.2, 143.4, 143.9, 144.1, 156.6, 160.0, 160.2; MS(L-SIMS): *m/z* 1230 (M^+, 100); calcd (%) for $C_{79}H_{104}O_{11}$: C, 77.16; H, 8.52; found: C, 76.90; H, 8.52.

12: A mixture of the alcohol **30** (3.0 g, 2.4 mmol), CBr_4 (1.2 g, 3.7 mmol) and PPh_3 (1.3 g, 4.9 mmol) in THF (30 mL) was stirred at 25 °C for 1.5 h. The reaction mixture was diluted with hexane/Et_2O (1:1, 5 mL) and the precipitate formed was filtered off and washed with Et_2O (10 mL). The filtrate was concentrated under reduced pressure and the residue was purified by chromatography (eluent: hexane/EtOAc, 100:1 gradient to 5:1) to furnish compound **12** (2.9 g, 93%) as a colorless oil; R_f: 0.73 (hexane/EtOAc, 3:1); ^{1}H NMR: 1.30 (s, 36 H), 2.06 (quin, J = 6.9 Hz, 4 H), 2.13 (quin, J = 6.0 Hz, 2 H), 2.22 (quin, J = 6.0 Hz, 8 H), 2.64–2.77 (m, 6 H), 3.38 (t, J = 6.3 Hz, 2 H), 3.93 (t, J = 6.0 Hz, 4 H), 4.10 (t, J = 7.8 Hz, 8 H), 4.13 (t, J = 7.8 Hz, 8 H), 6.30–6.40 (m, 9 H), 6.86 (d, J = 8.7 Hz, 8 H), 7.30 (d, J = 8.7 Hz, 8 H); ^{13}C NMR: 29.3, 30.6, 31.5, 32.4, 33.1, 33.9, 34.0, 34.2, 64.3, 64.4, 66.9, 98.9, 99.1, 107.2, 113.9, 126.2, 142.8, 143.3, 143.8, 156.5, 160.0, 160.3; MS(FAB): *m/z* 1294 [M^+(^{81}Br), 100]; calcd (%) for $C_{79}H_{103}O_{10}Br$: C, 73.41; H, 8.03; found: C, 73.46; H, 7.95.



31: A mixture of compound **22** (9.1 g, 46 mmol), benzyl bromide (12.0 mL, 97 mmol) and K_2CO_3 (19.2 g, 0.14 mol) in acetone (150 mL) was heated at 56 °C for 6 h. The solution was allowed to cool to room temperature and filtered. The filtrate was evaporated under reduced pressure and the residue was purified by column chromatography (eluent: hexane/EtOAc, 4:1) to afford compound **31** (17.0 g, 97%) as a colorless oil; *Rf*: 0.36 (hexane/EtOAc, 5:1); ^{1}H NMR: 2.62 (t, J = 7.2 Hz, 2 H), 2.90 (t, J = 7.5 Hz, 2 H), 3.68 (s, 3 H), 5.02 (s, 4 H), 6.42–6.52 (m, 3 H), 7.30–7.50 (m, 10 H); ^{13}C NMR: 31.2, 35.4, 51.7, 70.0, 99.9, 107.5, 127.5, 128.0, 136.9, 142.9, 160.0, 173.2; MS(EI): *m/z* 376 (M^+, 100); calcd (%) for $C_{24}H_{24}O_4$: C, 76.57; H, 6.43; found: C, 76.57; H, 6.45.

32: A mixture of the dibenzyl ether **31** (8.3 g, 22 mmol) and 10% palladium on charcoal (0.8 g) in EtOH/EtOAc (1:1, 100 mL) was stirred under hydrogen atmosphere (1 atm) at 25 °C for 2 h. The mixture was then filtered and the filtrate obtained was evaporated under reduced pressure. Chromatographic purification (eluent: hexane/EtOAc, 4:1) of the residue afforded compound **32** (3.0 g, 47%) as a colorless oil; *Rf*: 0.22 (hexane/EtOAc, 3:1); ^{1}H NMR (OH signal not observed): 2.61 (t, J = 7.8 Hz, 2 H), 2.86 (t, J = 7.5 Hz, 2 H), 3.68 (s, 3 H), 5.01 (s, 2 H), 6.29 (s, 1 H), 6.34 (s, 1 H), 6.42 (s, 1

H), 7.30–7.50 (m, 5 H); ^{13}C NMR: 30.9, 35.3, 51.7, 70.0, 100.2, 107.4, 108.0, 127.5, 128.0, 128.6, 136.8, 143.2, 156.7, 160.2, 173.4; MS(EI): *m/z* 286 (M^+, 46); calcd (%) for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34; found: C, 71.44; H, 6.29.

33: A mixture of the phenol **32** (1.6 g, 5.6 mmol), the bromide **28** (4.1 g, 6.7 mmol), Cs_2CO_3 (3.7 g, 11 mmol) and dibenzo-24-crown-8 (0.5 g, 1.1 mmol) in DMF (40 mL) was stirred at 60 °C for 1.5 h. The mixture was then quenched with water and extracted with EtOAc (80 mL × 2). The combined extracts were washed with brine (80 mL), dried ($MgSO_4$) and evaporated under reduced pressure. Column chromatographic purification of the crude product (eluent: hexane/EtOAc, 4:1) yielded compound **33** (4.0 g, 88%) as a colorless oil; R_f: 0.43 (hexane/EtOAc, 5:1); ^{1}H NMR: 1.29 (s, 18 H), 2.05 (quin, J = 6.6 Hz, 2 H), 2.21 (quin, J = 6.0 Hz, 4 H), 2.61 (t, J = 7.5 Hz, 2 H), 2.70 (t, J = 7.2 Hz, 2 H), 2.88 (t, J = 7.5 Hz, 2 H), 3.67 (s, 3 H), 3.91 (t, J = 6.3 Hz, 2 H), 4.09 (t, J = 6.3 Hz, 4 H), 4.12 (t, J = 6.3 Hz, 4 H), 5.01 (s, 2 H), 6.30–6.50 (m, 6 H), 6.83 (d, J = 8.7 Hz, 4 H), 7.28 (d, J = 8.7 Hz, 4 H), 7.30–7.45 (m, 5 H); ^{13}C NMR: 29.3, 30.5, 31.2, 31.5, 32.4, 34.0, 35.5, 51.6, 64.35, 64.45, 66.9, 70.0, 98.9, 99.5, 107.1, 107.2, 107.3, 113.9, 126.2, 127.5, 127.9, 128.6, 136.9, 142.8, 143.4, 143.8, 156.6, 160.0, 160.3, 173.3; MS(L-SIMS): *m/z* 817 [$(M+H)^+$, 100]; calcd (%) for $C_{52}H_{64}O_8$: C, 76.44; H, 7.90; found: C, 76.27; H, 7.88.

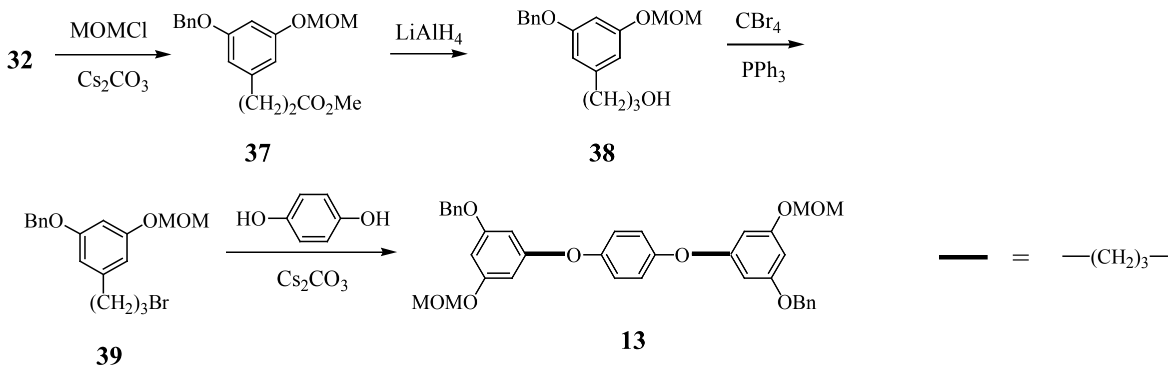
34: A mixture of the benzyl ether **33** (4.5 g, 5.5 mmol) and 10% palladium on charcoal (0.4 g) in EtOH/EtOAc (1:1, 30 mL) was stirred at 25 °C for 2 h under hydrogen atmosphere (1 atm). The reaction mixture was filtered and the filtrate was evaporated under reduced pressure. The crude product was purified by column chromatography (eluent: hexane/EtOAc = 4:1) to afford compound **34** (3.8 g, 96%) as a colorless oil; R_f: 0.25 (hexane/EtOAc, 3:1); ^{1}H NMR: 1.31 (s, 18 H), 2.05 (quin, J = 6.9 Hz, 2 H), 2.22 (quin, J = 6.0 Hz, 4 H), 2.60 (t, J = 7.8 Hz, 2 H), 2.71 (t, J = 7.5 Hz, 2 H), 2.85 (t, J = 7.8 Hz, 2 H), 3.68 (s, 3 H), 3.89 (t, J = 6.3 Hz, 2 H), 4.10 (t, J = 6.0 Hz, 4 H), 4.13 (t, J = 6.0 Hz, 4 H), 5.25 (s, 1 H), 6.25 (s, 2 H), 6.33 (s, 2 H), 6.37 (s, 2 H), 6.85 (d, J = 8.7 Hz, 4 H), 7.29 (d, J = 8.7 Hz, 4 H); ^{13}C NMR:

29.3, 30.5, 30.9, 31.5, 32.3, 34.0, 35.4, 51.7, 64.37, 64.44, 66.8, 99.0, 99.9, 107.2, 107.3, 107.6, 113.9, 126.2, 143.0, 143.4, 143.8, 156.6, 156.8, 160.0, 160.4, 173.5; MS(L-SIMS): *m/z* 727 [$(M+H)^+$, 100]; calcd (%) for $C_{45}H_{58}O_8$: C, 74.35; H, 8.04; found: C, 74.53; H, 8.13.

35: A mixture of the bromide **10** (2.9 g, 3.6 mmol), the phenol **34** (2.2 g, 3.0 mmol), Cs_2CO_3 (2.0 g 6.0 mmol) and dibenzo-24-crown-8 (0.3 g, 0.6 mmol) in DMF (30 ml) was stirred at 60 °C for 1.5 h. The reaction was then quenched with water, and extracted with EtOAc (20 mL × 2). The organic layers were combined, washed with brine (20 mL), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatographic purification of the crude product (eluent: hexane/EtOAc, 8:1) yielded compound **35** (4.2 g, 97%) as a colorless oil; R_f: 0.47 (hexane/EtOAc, 5:1); ^{1}H NMR: 1.25–1.50 (m, 12 H), 1.30 (s, 27 H), 1.70–1.80 (m, 4 H), 2.05 (quin, J = 6.6 Hz, 4 H), 2.22 (quin, J = 6.0 Hz, 6 H), 2.63 (t, J = 7.5 Hz, 2 H), 2.71 (t, J = 7.2 Hz, 4 H), 2.87 (t, J = 7.5 Hz, 2 H), 3.67 (s, 3 H), 3.80–4.00 (m, 8 H), 4.10 (t, J = 6.0 Hz, 6 H), 4.12 (t, J = 6.0 Hz, 6 H), 6.20–6.40 (m, 9 H), 6.67 (d, J = 8.7 Hz, 2 H), 6.85 (d, J = 8.4 Hz, 6 H), 7.30 (d, J = 8.7 Hz, 6 H), 7.54 (d, J = 8.4 Hz, 2 H); ^{13}C NMR: 25.96, 26.03, 29.1, 29.4, 29.5, 30.6, 31.2, 31.5, 32.5, 34.0, 35.5, 51.6, 64.4, 64.5, 66.9, 67.9, 68.1, 82.4, 98.9, 99.3, 106.9, 107.2, 113.9, 116.9, 126.2, 138.1, 142.8, 143.4, 143.8, 156.6, 160.0, 160.3, 173.3; MS(FAB): *m/z* 1425.5 (M^+, 100); calcd (%) for $C_{83}H_{109}O_{12}I$: C, 69.93; H, 7.71; found: C, 70.24; H, 7.89.

36: A solution of the ester **35** (2.0 g, 1.4 mmol) in toluene (20 ml) was treated with DIBAL (1.0 M in hexane) (5.6 mL, 5.6 mmol) at –60 °C. The reaction mixture was stirred for 1.5 h and allowed to warm to –10 °C. The reaction was then quenched with EtOAc (5 mL) and water (5 mL). The resulting mixture was acidified to pH 6 by adding HCl solution (2 M) and then extracted with EtOAc (10 mL × 2). The combined organic layers were washed with brine (10 mL), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatographic purification of the crude product (eluent: hexane/EtOAc, 3:1) yielded compound **36** (1.6 g, 81%) as a colorless oil; R_f: 0.36 (hexane/EtOAc, 3:1) ^{1}H NMR (OH signal not observed): 1.20–1.50 (m, 12 H), 1.29 (s, 27 H), 1.70–1.80 (m, 4 H), 1.87 (quin, J = 7.5 Hz, 2 H), 2.05 (quin, *J* = 6.9 Hz, 4 H), 2.21 (quin, *J* = 6.0 Hz, 6 H), 2.62 (t, *J* = 7.5 Hz, 2 H), 2.71 (t, *J* = 6.3 Hz, 4 H), 3.66 (q, *J* = 5.4 Hz, 2 H), 3.80–3.95 (m, 8 H), 4.09 (t, *J* = 6.6 Hz, 6 H), 4.12 (t, *J* = 6.6 Hz, 6 H), 6.25–6.40 (m, 9 H), 6.67 (d, *J* = 8.7 Hz, 2 H), 6.85 (d, *J* = 8.7 Hz, 6 H), 7.30 (d, *J* = 8.7 Hz, 6 H), 7.54 (d, *J* = 8.7 Hz, 2 H); ^{13}C NMR: 25.96, 26.03, 29.1, 29.3, 29.5, 30.6, 31.5, 32.35, 32.44, 33.96, 34.03, 62.2, 64.35, 64.44, 66.9, 67.9, 68.1, 82.4, 98.9, 107.0, 107.1, 107.2, 113.9, 116.9, 126.2, 138.1, 143.4, 143.8, 144.1, 156.6, 159.0, 160.0, 160.2, 160.3; MS(L-SIMS): *m/z* 1397.8 [$(M+H)^+$, 100]; calcd (%) for $C_{82}H_{109}O_{11}I$: C, 70.47; H, 7.86; found: C, 70.99; H, 8.00.

11: A mixture of the alcohol **36** (1.50 g, 1.0 mmol), CBr_4 (0.60 g, 1.6 mmol) and PPh_3 (0.6 g, 2.2 mmol) in THF (15 ml) was stirred at 25 °C for 1.5 h. The reaction mixture was diluted with hexane/Et_2O (1:1, 2 mL) and the precipitate formed was filtered off and washed with Et_2O (3 mL). The filtrate was concentrated under reduced pressure. Chromatographic purification of the crude product (eluent: hexane gradient to hexane/EtOAc, 10:1) gave compound **11** (1.40 g, 89%) as a colorless oil; R_f: 0.61 (hexane/EtOAc, 5:1); ^{1}H NMR: 1.20–1.50 (m, 12 H), 1.29 (s, 27 H), 1.70–1.80 (m, 4 H), 2.05 (quin, *J* = 6.9 Hz, 4 H), 2.10–2.17 (m, 2 H), 2.21 (quin, *J* = 6.0 Hz, 6 H), 2.62–2.76 (m, 6 H), 3.37 (t, *J* = 6.6 Hz, 2 H), 3.83–3.93 (m, 8 H), 4.09 (t, *J* = 6.3 Hz, 6 H), 4.11 (t, *J* = 6.3 Hz, 6 H), 6.30–6.40 (m, 9 H), 6.67 (d, *J* = 8.7 Hz, 2 H), 6.85 (d, *J* = 8.7 Hz, 6 H), 7.29 (d, *J* = 8.7 Hz, 6 H), 7.53 (d, *J* = 8.7 Hz, 2 H); ^{13}C NMR: 25.95, 26.02, 29.1, 29.3, 29.4, 30.6, 31.5, 32.4, 33.1, 33.9, 34.0, 34.2, 64.3, 64.4, 66.9, 67.9, 68.1, 82.4, 98.9, 99.1, 106.9, 107.2, 113.9, 116.9, 126.2, 138.1, 142.8, 143.3, 143.8, 156.5, 159.0, 160.0, 160.3; MS(FAB): *m/z* 1461.4 [$M^+(^{81}Br)$, 100]; calcd (%) for $C_{82}H_{108}O_{10}BrI$: C, 67.43; H, 7.45; found: C, 67.45; H, 7.54.

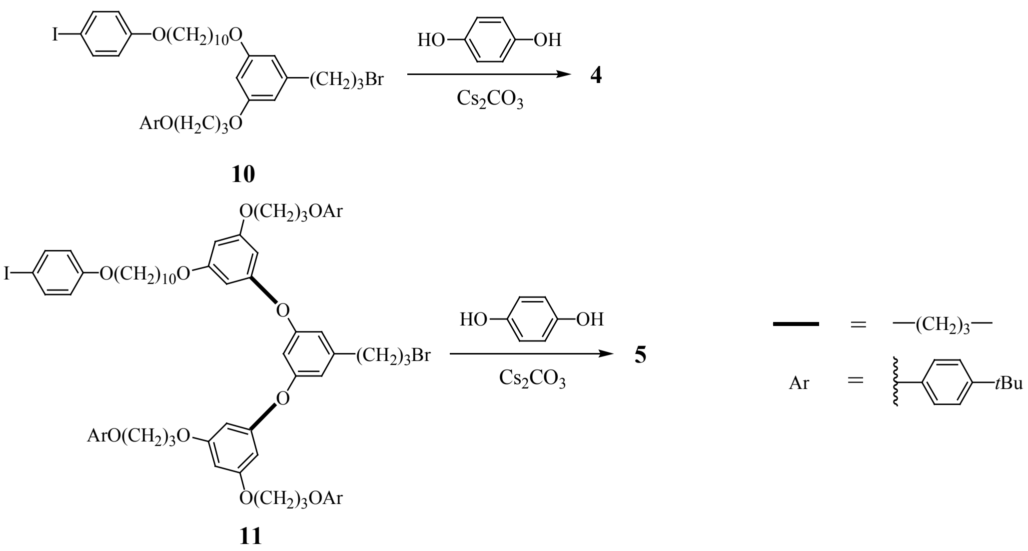


37: Chloromethyl methyl ether (1.7 mL, 22 mmol) was added dropwise to a mixture of compound **32** (3.1 g, 11 mmol), dibenzo-24-crown-8 (1.0 g, 2.2 mmol) and cesium carbonate (7.1 g, 22 mmol) in DMF (40 mL) at 25 °C. After 2 h, the mixture was quenched with water and extracted with dichloromethane (80 mL × 2). The combined extracts were washed with brine (80 mL), dried ($MgSO_4$) and evaporated to dryness under reduced pressure followed by chromatographic purification of the crude product (eluent: hexane/EtOAc, 4:1) to afford compound **37** (2.1 g, 58%) as a colorless oil; R_f: 0.59 (hexane/EtOAc, 3:1); ^{1}H NMR: 2.62 (t, J = 7.5 Hz, 2 H), 2.90 (t, J = 7.5 Hz, 2 H), 3.47 (s, 3 H), 3.68 (s, 3 H), 5.02 (s, 2 H), 5.12 (s, 2 H), 6.50 (d, J = 2.1 Hz, 2 H), 6.56 (t, J = 2.1 Hz, 1 H), 7.30–7.50 (m, 5 H); ^{13}C NMR: 31.1, 35.4, 51.6, 56.0, 70.0, 94.5, 101.2, 108.4, 108.8, 127.5, 127.9, 128.5, 136.8, 142.9, 158.4, 159.9, 173.2; MS(EI): m/z 330 (M^+, 17); calcd (%) for $C_{19}H_{22}O_5$: C, 69.07; H, 6.71; found: C, 68.93; H, 6.78.

38: A solution of the ester **37** (2.0 g, 6.1 mmol) in THF (5 mL) was added dropwise to a slurry of $LiAlH_4$ (0.4 g, 9.1 mmol) in THF (10 mL) at 0 °C. The mixture was stirred at 25 °C for 1.5 h and then quenched with EtOAc and water. The mixture was extracted with EtOAc (30 mL × 2). The combined extracts were washed with brine (30 mL), dried ($MgSO_4$) and evaporated under reduced pressure. Chromatographic purification of the crude product (eluent: hexane/EtOAc, 2:1) afforded compound **38** (1.8 g, 97%) as a colorless oil; R_f: 0.16 (hexane/EtOAc, 3:1); ^{1}H NMR: 1.31 (brs, 1 H), 1.88 (quin, J = 6.3 Hz, 2 H), 2.65 (t, J = 7.2 Hz, 2 H), 3.50 (s, 3 H), 3.66 (t, J = 5.7 Hz, 2 H), 5.03 (s, 2 H), 5.17 (s, 2 H), 6.49–6.57 (m, 3 H), 7.30–7.50 (m, 5 H); ^{13}C NMR: 32.3, 33.9, 56.0, 62.2, 70.0, 94.5, 100.8, 108.6, 108.9, 127.5, 127.9, 128.5, 136.9, 144.3, 158.4, 159.8; MS(EI): *m/z* 302 (M^+, 5); calcd (%) for $C_{18}H_{22}O_4$: C, 71.50; H, 7.33; found: C, 71.22; H, 7.09.

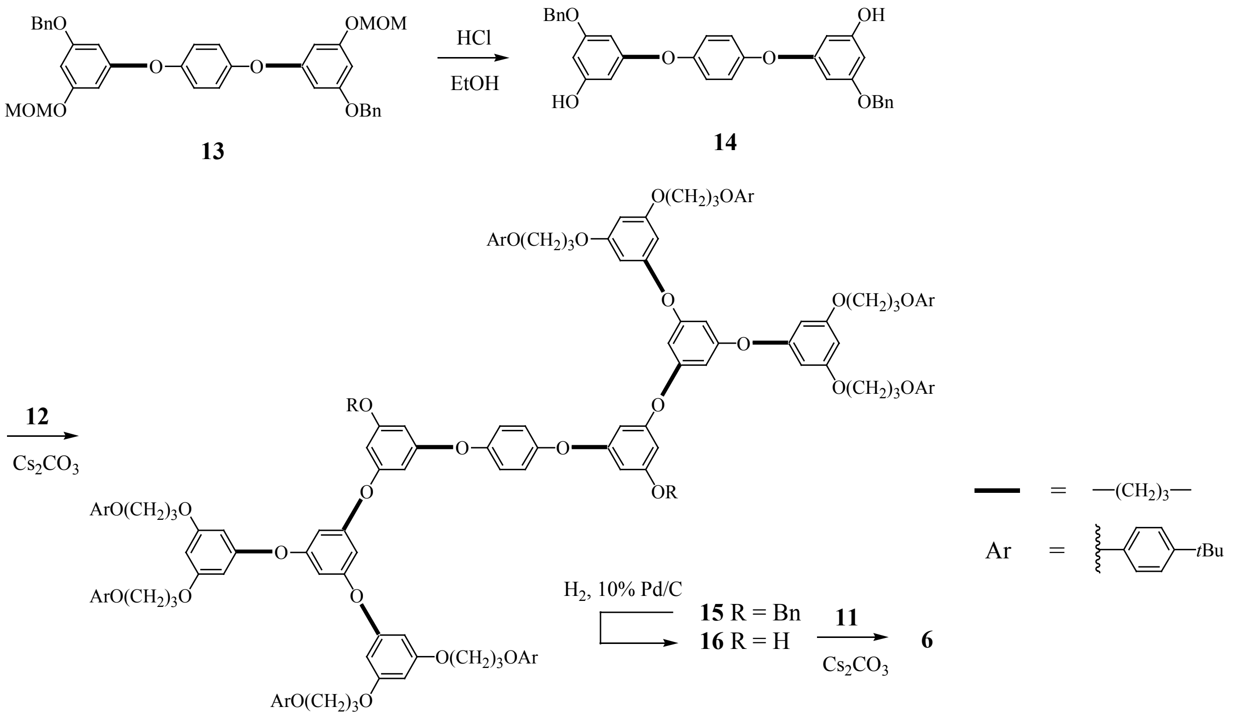
39: A mixture of the alcohol **38** (1.7 g, 5.6 mmol), CBr_4 (2.8 g, 8.4 mmol) and PPh_3 (3.0 g. 11 mmol) in THF (40 mL) was stirred at 25 °C for 1.5 h. The reaction mixture was diluted with hexane/Et_2O (1:1, 20 mL) and the precipitate formed was filtered off and washed with Et_2O (10 mL). The filtrate was evaporated under reduced pressure and the residue was purified by chromatography (eluent: hexane/EtOAc, 100:1 gradient to 10:1) to produce compound **39** (1.7 g, 82%) as a colorless oil; R_f: 0.73 (hexane/EtOAc, 3:1); ^{1}H NMR: 2.14 (quin, *J* = 6.6 Hz, 2 H), 2.71 (t, *J* = 7.2 Hz, 2 H), 3.39 (t, *J* = 6.6 Hz, 2 H), 3.48 (s, 3 H), 5.03 (s, 2 H), 5.15 (s, 2 H), 6.51 (d, *J* = 2.4 Hz, 2 H), 6.56 (t, *J* = 2.1 Hz, 1 H), 7.30–7.50 (m, 5 H); ^{13}C NMR: 33.0, 33.9, 34.2, 56.0, 70.0, 94.5, 101.1, 108.8, 109.1, 127.6, 128.0, 128.6, 136.8, 143.0, 158.5, 159.9; MS(L-SIMS): *m/z* 366 [M^+ (^{81}Br), 100]; calcd (%) for $C_{18}H_{21}O_3Br$: C, 59.19; H, 5.79; found: C, 59.25; H, 5.88.

13: A mixture of the bromide **39** (1.70 g, 4.6 mmol), hydroquinone (0.23 g, 2.1 mmol), dibenzo-24-crown-8 (0.3 g, 0.62 mmol) and Cs_2CO_3 (2.0 g, 6.2 mmol) in DMF (20 mL) was heated at 110 °C for 1 h. The reaction was then quenched with water and extracted with EtOAc (40 mL × 2). The combined extracts were washed with brine (40 mL), dried ($MgSO_4$) and evaporated to dryness under reduced pressure. Chromatographic purification of the crude product (eluent: hexane/EtOAc, 4:1) afforded compound **13** (0.84 g, 59%) as a colorless oil; R_f: 0.59 (hexane/EtOAc, 3:1); ^{1}H NMR: 2.05 (quin, *J* = 6.6 Hz, 4 H), 2.74 (t, *J* = 7.2 Hz, 4 H), 3.46 (s, 6 H), 3.89 (t, *J* = 6.0 Hz, 4 H), 4.98 (s, 4 H), 5.12 (s, 4 H), 6.45–6.55 (m, 6 H), 6.82 (s, 4 H), 7.30–7.50 (m, 10 H); ^{13}C NMR: 30.6, 32.4, 56.0, 67.4, 69.9, 94.4, 101.0, 108.6, 109.0, 115.4, 127.5, 127.9, 128.5, 136.9, 144.0, 153.1, 158.3, 159.8; MS(L-SIMS): *m/z* 678 (M^+, 100); calcd (%) for $C_{42}H_{46}O_8$: C, 74.31; H, 6.83; found: C, 74.34; H, 6.95.



4: A mixture of hydroquinone (0.45 g, 4.0 mmol), the bromide **10** (6.8 g, 8.7 mmol), Cs_2CO_3 (3.9 g, 12 mmol) and dibenzo-24-crown-8 (0.5 g, 1.2 mmol) in DMF (40 mL) was heated at 110 °C for 2 h. The mixture was then quenched with water and extracted with EtOAc (50 mL × 2). The combined extracts were washed with brine (50 mL), dried ($MgSO_4$) and evaporated under reduced pressure. Chromatographic purification of the crude product (eluent: hexane/EtOAc, 7:1) afforded compound **4** (4.8 g, 78%) as a white solid; R_f: 0.41 (hexane/EtOAc, 5:1); m.p. 89–93 °C; ^{1}H NMR: 1.20–1.50 (m, 24 H), 1.29 (s, 18 H), 1.70–1.80 (m, 8 H), 2.05 (quin, J = 7.5 Hz, 4 H), 2.21 (quin, J = 6.0 Hz, 4 H), 2.71 (t, J = 6.9 Hz, 4 H), 3.82–3.92 (m, 12 H), 4.09 (t, J = 6.0 Hz, 4 H), 4.11 (t, J = 6.0 Hz, 4 H), 6.31 (t, J = 2.1 Hz, 2 H), 6.35 (d, J = 2.1 Hz, 4 H), 6.69 (d, J = 8.7 Hz, 4 H), 6.81 (s, 4 H), 6.85 (d, J = 6.9 Hz, 4 H), 7.29 (d, J = 6.9 Hz, 4 H), 7.54 (d, J = 9.0 Hz, 4 H); ^{13}C NMR: 25.97, 26.03, 29.1, 29.4, 29.5, 29.9, 30.7, 31.5, 32.5, 34.0, 64.36, 64.43, 67.5, 67.9, 68.1, 82.4, 98.9, 107.0, 107.2, 113.9, 115.4, 116.9, 126.2, 138.1, 143.4, 143.9, 153.2, 156.6, 159.0, 160.0, 160.3; MS(L-SIMS): *m/z* 1506.7 (M^+, 100); calcd (%) for $C_{82}H_{108}O_{10}I_2$: C, 65.33; H, 7.22; Found: C, 65.15; H, 7.29.

5: A mixture of hydroquinone (60 mg, 0.50 mmol), the bromide **11** (1.60 g, 1.1 mmol), Cs_2CO_3 (0.5 g, 1.5 mmol) and dibenzo-24-crown-8 (0.07 g, 0.15 mmol) in DMF (10 mL) was heated at 110 °C for 2 h. The mixture was then quenched with water and extracted with EtOAc (30 mL × 2). The combined extracts were washed with brine (30 mL), dried ($MgSO_4$) and evaporated under reduced pressure. Chromatographic purification of the crude product (eluent: hexane/EtOAc, 8:1 gradient to 5:1) afforded compound **5** (0.60 g, 42%) as a colorless oil; R_f: 0.80 (hexane/EtOAc, 3:1); ^{1}H NMR: 1.20–1.50 (m, 24 H), 1.29 (s, 54 H), 1.70–1.80 (m, 8 H), 2.04 (quin, J = 6.9 Hz, 12 H), 2.20 (quin, J = 6.0 Hz, 12 H), 2.70 (t, J = 7.5 Hz, 12 H), 3.80–4.00 (m, 20 H), 4.09 (t, J = 6.0 Hz, 12 H), 4.11 (t, J = 6.0 Hz, 12 H), 6.30–6.40 (m, 18 H), 6.65 (d, J = 9.0 Hz, 4 H), 6.80 (s, 4 H), 6.84 (d, J = 8.7 Hz, 12 H), 7.28 (d, J = 8.7 Hz, 12 H), 7.53 (d, J = 8.7 Hz, 4 H); ^{13}C NMR: 25.97, 26.04, 29.1, 29.4, 29.5, 30.7, 30.8, 31.5, 32.5, 34.0, 64.36, 64.45, 66.9, 67.3, 67.6, 67.9, 68.1, 82.4, 98.9, 107.0, 107.1, 107.2, 113.9, 115.4, 116.9, 126.2, 138.1, 143.4, 143.9, 153.2, 156.6, 159.0, 160.0, 160.2, 160.3; MS(MALDI-TOF): *m/z* 2890.7 [(M+Na)$^+$, 100]; calcd (%) for $C_{170}H_{220}O_{22}I_2$: C, 71.16; H, 7.73; found: C, 71.31; H, 7.94.



14: A solution of hydrogen chloride in ethanol (2.0 M, 10 mL) was added dropwise to a solution of compound **13** (0.80 g, 1.2 mmol) in THF (5 mL) at 0 °C. After 1 h, the mixture was quenched with water and extracted with EtOAc (10 mL × 2). The combined extracts were washed with brine (10 mL), dried ($MgSO_4$) and evaporated to dryness under reduced pressure. Chromatographic purification of the crude product (eluent: hexane/EtOAc, 2:1) afforded compound **14** (0.58 g, 83%) as a white solid; *R_f*: 0.27 (hexane/EtOAc, 2:1); m.p. 92–94 °C; ^{1}H NMR: 2.04 (quin, *J* = 6.6 Hz, 4 H), 2.71 (t, *J* = 7.2 Hz, 4 H), 3.88 (t, *J* = 6.0 Hz, 4 H), 4.84 (s, 2 H), 4.97 (s, 4 H), 6.25–6.35 (m, 4 H), 6.43 (s, 2 H), 6.81 (s, 4 H), 7.30–7.50 (m, 10 H); ^{13}C NMR: 31.1, 32.8, 67.9, 70.5, 100.5, 108.3, 108.9, 116.0, 128.1, 128.5, 129.2, 137.5, 144.9, 153.7, 157.2, 160.7; MS(L-SIMS): *m/z* 590 (M^+, 100); calcd (%) for $C_{38}H_{38}O_6$: C, 77.27; H, 6.48; found: C, 77.04; H, 6.64.

15: A mixture of the bisphenol **14** (0.80 g, 1.4 mmol), the bromide **12** (3.70 g, 3.0 mmol), dibenzo-24-crown-8 (0.20 g, 0.41 mmol) and Cs_2CO_3 (1.4 g, 4.1 mmol) in DMF (25 mL) was stirred at 60 °C for 3 h. The mixture was then quenched with water and extracted with EtOAc (50 mL × 2). The combined extracts were washed with brine (50 mL), dried ($MgSO_4$) and evaporated to dryness under reduced pressure. Chromatographic purification of the crude product (eluent: hexane/EtOAc, 6:1 gradient to 4:1) afforded compound **15** (3.30 g, 81%) as a colorless oil; R_f: 0.40 (hexane/EtOAc, 3:1); ^{1}H NMR: 1.30 (s, 72 H), 2.00–2.15 (m, 16 H), 2.22 (quin, *J* = 6.0 Hz, 16 H), 2.67–2.78 (m, 16 H), 3.85–3.93 (m, 16 H), 4.09 (t, *J* = 7.8 Hz, 16 H), 4.12 (t, *J* = 7.8 Hz, 16 H), 4.97 (s, 4 H), 6.30–6.50 (m, 24 H), 6.82 (s, 4 H), 6.86 (d, *J* = 6.9 Hz, 16 H), 7.27 (d, *J* = 6.9 Hz, 16 H), 7.30–7.50 (m, 10 H); ^{13}C NMR: 29.3, 30.7, 31.5, 32.5, 34.0, 64.3, 64.4, 66.9, 67.5, 69.9, 98.9, 99.3, 107.2, 107.6, 113.9, 115.4, 126.2, 127.5, 127.9, 128.5, 137.0, 143.3, 143.9, 153.2, 156.6, 160.0, 160.2; MS(MALDI-TOF) *m/z* 3038 [$(M+Na)^+$, 100]; calcd (%) for $C_{196}H_{242}O_{26}$: C, 78.11; H, 8.09; found: C, 77.98; H, 8.16.

16: A mixture of compound **15** (2.00 g, 0.66 mmol) and 10% palladium on charcoal (0.2 g) in EtOAc/EtOH (1:1, 20 mL) was stirred under hydrogen atmosphere (1 atm) at 25 °C for 6 h. The mixture was then filtered and the filtrate was evaporated under reduced pressure. Chromatographic purification of the crude product (eluent: hexane/EtOAc, 3:1) afforded compound **16** (1.70 g, 90%) as a colorless oil; R_f: 0.27 (hexane/EtOAc, 3:1); ^{1}H NMR: 1.29 (s, 72 H), 1.95–2.10 (m, 16 H), 2.22 (quin, *J* = 6.0 Hz, 16 H), 2.60–2.80 (m, 16 H), 3.80–4.00 (m, 16 H), 4.08 (t, *J* = 5.7 Hz, 16 H), 4.11 (t, *J* = 5.7 Hz, 16 H), 5.06

(s, 2 H), 6.20–6.40 (m, 24 H), 6.79 (s, 4 H), 6.84 (d, *J* = 7.8 Hz, 16 H), 7.28 (d, *J* = 7.8 Hz, 16 H); ^{13}C NMR: 29.3, 30.6, 31.5, 32.2, 32.4, 34.0, 64.4, 64.5, 66.7, 66.9, 67.4, 98.9, 99.5, 107.3, 107.4, 107.9, 113.9, 115.4, 126.2, 143.4, 143.7, 143.9, 144.2, 153.1, 156.5, 156.7, 160.0, 160.2; MS(MALDI-TOF) *m/z* 2830.5 (M$^+$, 100); calcd (%) for $C_{182}H_{230}O_{26}$: C, 77.14; H, 8.18; found: C, 77.25; H, 8.25.

6: A mixture of the bromide **11** (1.50 g, 1.0 mmol), the bisphenol **16** (1.30 g, 0.47 mmol), Cs_2CO_3 (1.0 g, 2.8 mmol) and dibenzo-24-crown-8 (70 mg, 0.14 mmol) in DMF (15 ml) was stirred at 60 °C for 3 h. The reaction was then quenched with water and extracted with EtOAc (30 mL × 2). The organic extracts were combined, washed with brine (30 mL), dried ($MgSO_4$) and concentrated under reduced pressure. Column chromatographic purification of the crude product (eluent: hexane/EtOAc, 8:1 gradient to 2:1) afforded compound **6** (2.50 g, 97%) as a colorless oil; R_f: 0.64 (hexane/EtOAc, 3:1); ^{1}H NMR: 1.20–1.50 (m, 24 H), 1.28 (s, 126 H), 1.65–1.80 (m, 8 H), 1.95–2.05 (m, 28 H), 2.20 (quin, *J* = 6.0 Hz, 28 H), 2.69 (t, *J* = 6.9 Hz, 28 H), 3.80–3.95 (m, 36 H), 4.07 (t, *J* = 6.3 Hz, 28 H), 4.09 (t, *J* = 6.3 Hz, 28 H), 6.31 (brs, 14 H), 6.35 (brs, 28 H), 6.65 (d, *J* = 8.7 Hz, 4 H), 6.80 (s, 4 H), 6.83 (d, *J* = 7.8 Hz, 28 H), 7.27 (d, *J* = 7.8 Hz, 28 H), 7.52 (d, *J* = 8.7 Hz, 4 H); ^{13}C NMR: 25.96, 26.03, 29.1, 29.3, 29.5, 29.7, 30.7, 30.9, 31.5, 32.5, 34.0, 64.3, 64.4, 66.9, 67.7, 67.9, 68.1, 82.4, 98.9, 107.0, 107.2, 113.9, 115.4, 116.9, 126.2, 138.1, 143.3, 143.9, 153.2, 156.6, 159.0, 160.0, 160.3; MS(MALDI-TOF): *m/z* 5617.6 [(M+Na)$^+$, 100]; calcd (%) for $C_{346}H_{444}O_{46}I_2$: C, 74.30; H, 8.00; found: C, 74.37; H, 8.19.

$$\begin{array}{ccccc} \mathbf{4} & & \mathbf{7} & & \mathbf{1} \\ \mathbf{5} & \xrightarrow[\text{CuI, NEt}_3\text{, PPh}_3]{\text{TMSCCH, Pd(PPh}_3)_2\text{Cl}_2} & \mathbf{8} & \xrightarrow[\text{MeOH}]{\text{K}_2\text{CO}_3} & \mathbf{2} \\ \mathbf{6} & & \mathbf{9} & & \mathbf{3} \end{array}$$

7: A mixture of the diiodide **4** (160 mg, 0.11 mmol), TMSC≡CH (0.2 mL, 1.1 mmol), $Pd(PPh_3)_2Cl_2$ (40 mg, 53 μmol), PPh_3 (10 mg, 21 μmol), CuI (10 mg, 21 μmol) and NEt_3 (0.2 mL, 1.1 mmol) in toluene (4.0 mL) was placed inside a sealed tube equipped with a stirrer bar. The reaction mixture was degassed and stirred at 60 °C for 24 h. The mixture was filtered and then washed with Et_2O (10 mL). The combined filtrates were concentrated under reduced pressure. Chromatographic purification of the crude product (eluent: hexane gradient to hexane/EtOAc, 10:1) afforded compound **7** (120 mg, 78%) as a yellow oil; R_f: 0.34 (hexane/EtOAc, 8:1); ^{1}H NMR: 0.24 (s, 18 H), 1.20–1.50 (m, 24 H), 1.30 (s, 18 H), 1.70–1.82 (m, 8 H), 2.05 (quin, *J* = 6.6 Hz, 4 H), 2.21 (quin, *J* = 5.7 Hz, 4 H), 2.71 (t, *J* = 7.5 Hz, 4 H), 3.80–4.00 (m, 12 H), 4.09 (t, *J* = 6.3 Hz, 4 H), 4.11 (t, *J* = 6.3 Hz, 4 H), 6.29–6.37 (m, 6 H), 6.70–6.90 (m, 12 H), 7.29 (d, *J* = 8.4 Hz, 4 H), 7.39 (d, *J* = 8.4 Hz, 4 H); ^{13}C NMR: 0.1, 25.99, 26.04, 29.2, 29.3, 29.4, 29.5, 30.7, 31.5, 32.5, 34.0, 64.38, 64.43, 67.6, 67.9, 68.0, 92.3, 98.8, 105.3, 107.0, 107.3, 113.9, 114.3, 115.0, 115.4, 126.2, 133.4, 143.4, 143.9, 153.1, 156.6, 159.3, 160.0, 160.3; MS(MALDI-TOF): *m/z* 1470 [$(M+Na)^+$, 100]; calcd (%) for $C_{92}H_{126}O_{10}Si_2$: C, 76.30; H, 8.77; found: C, 76.35; H, 8.55.

8: A mixture of the diiodide **5** (0.50 g, 0.17 mmol), TMSC≡CH (0.3 mL, 1.7 mmol), $Pd(PPh_3)_2Cl_2$ (70 mg, 87 μmol), PPh_3 (10 mg, 35 μmol), CuI (10 mg, 35 μmol) and NEt_3 (0.3 mL, 1.7 mmol) in toluene (15 mL) was placed inside a sealed tube equipped with a stirrer bar. The reaction mixture was degassed, and stirred at 60 °C for 24 h. The mixture was filtered and then washed with Et_2O (10 mL). The combined filtrates were concentrated under reduced pressure. Chromatographic purification of the crude product (eluent: hexane gradient to hexane/EtOAc, 5:1) afforded compound **8** (0.43 g, 88%) as a yellow oil; R_f: 0.50 (hexane/EtOAc, 5:1); ^{1}H NMR: 0.23 (s, 18 H), 1.20–1.50 (m, 24 H), 1.28 (s, 54 H), 1.70–1.80 (m, 8 H), 2.04 (quin, *J* = 6.9 Hz, 12 H), 2.20 (quin, *J* = 6.0 Hz, 12 H), 2.69 (t, *J* = 7.2 Hz, 12 H), 3.80–4.00 (m, 20 H), 4.08 (t, *J* = 6.3 Hz, 12 H), 4.10 (t, *J* = 6.3 Hz, 12 H), 6.29–6.38 (m, 18 H), 6.78–6.85 (m, 20 H), 7.28 (d, *J* = 8.4 Hz, 12 H), 7.38 (d, *J* = 8.4 Hz, 4 H); ^{13}C NMR:[3] 0.1, 26.0, 26.1, 29.2, 29.4, 29.5, 30.7, 30.8, 31.5, 32.5, 34.0, 64.37, 64.45, 66.9, 67.6, 67.9, 68.0, 98.9, 107.1, 107.2, 113.9, 114.3, 115.4, 126.2, 133.4, 143.4, 143.9, 153.2, 156.6, 160.0, 160.2, 160.3; MS(MALDI-TOF): *m/z* 2833.6 [$(M+Na)^+$, 100]; calcd (%) for $C_{180}H_{238}O_{22}Si_2$: C, 76.94; H, 8.54; found: C, 76.87; H, 8.39.

9: A mixture of the diiodo compound **6** (0.90 g, 0.16 mmol), TMSC≡CH (0.3 mL, 1.6 mmol), $Pd(PPh_3)_2Cl_2$ (0.10 g, 0.16 mmol), PPh_3 (10 mg, 32 μmol), copper(I) iodide (10 mg, 32 μmol) and NEt_3 (0.3 mL, 1.6 mmol) in toluene (10 mL) was placed inside a sealed tube equipped with a stirrer bar. The reaction mixture was degassed and stirred at 60 °C for 24 h. The mixture was filtered and then washed with Et_2O (10 mL). The combined filtrates were concentrated under reduced pressure. Chromatographic purification of the crude product (eluent: hexane/EtOAc, 8:1 gradient to 5:1) gave compound **9** (0.63 g, 71%) as a yellow oil; R_f: 0.34 (hexane/EtOAc, 5:1); ^{1}H NMR: 0.22 (s, 18 H), 1.20–1.50 (m, 24 H), 1.28 (s, 126 H), 1.70–1.80 (m, 8 H), 2.00–2.10 (br, 28 H), 2.21 (quin, *J* = 6.0 Hz, 28 H), 2.69 (t, *J* = 6.9 Hz, 28 H), 3.80–4.00 (m, 36 H), 4.07 (t, *J* = 6.6 Hz, 28 H), 4.10 (t, *J* = 6.6 Hz, 28 H), 6.31, (t, *J* = 2.1 Hz, 14 H), 6.36 (d, *J* = 2.1 Hz, 28 H), 6.70–6.90 (m, 36 H), 7.28 (d, *J* = 8.4 Hz, 28 H), 7.38 (d, *J* = 8.7 Hz, 4 H); ^{13}C NMR:[4] 0.1, 26.0, 29.2, 29.3, 29.5, 30.7, 31.5, 32.5, 34.0, 64.3, 64.4, 66.9, 67.0, 67.7, 67.9, 68.0, 98.9, 105.3, 107.1, 107.2, 113.9, 114.3, 115.4, 126.2, 133.4, 143.3, 143.9, 153.2, 156.6, 159.3, 160.0, 160.2; MS(MALDI-TOF): *m/z* 5558.0 [$(M+Na)^+$, 100]; calcd (%) for $C_{356}H_{462}O_{46}Si_2$: C, 77.27; H, 8.41; found: C, 77.24; H, 7.99.

General synthetic procedure for bis(ethynyl) Gn-dendrimers (n = 1–3) **1**–**3**: Anhydrous K_2CO_3 (5.0 equiv) was added to a solution of bis(trimethylsilylethynyl) surface functionalized Gn-dendrimers **7**–**9** (1.0 equiv) in methanol/THF (1:1) (2 mL/mmol). The mixture was stirred at 25 °C for 1.5 h and then quenched with water and extracted with ethyl acetate (25 mL × 2). The combined organic layers were washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by silica column chromatography eluting with hexane/EtOAc = 8/1.

1: Starting from compound **7** (100 mg, 69 μmol) and after chromatographic purification, compound **1** was obtained (90 mg, 98%) as a white solid; R_f: 0.50 (hexane/EtOAc, 5:1); m.p. 86–89 °C; ^{1}H NMR: 1.20–1.50 (m, 24 H), 1.29 (s, 18 H), 1.70–1.80 (m, 8 H), 2.04 (quin, *J* = 6.6 Hz, 4 H), 2.21 (quin, *J* = 6.3 Hz, 4 H), 2.71 (t, *J* = 7.2 Hz, 4 H), 2.98 (s, 2 H), 3.80–4.00 (m, 12 H), 4.09 (t, *J* = 6.3 Hz, 4 H), 4.11 (t, *J*

= 6.3 Hz, 4 H), 6.30 (s, 2 H), 6.35 (s, 4 H), 6.80–6.90 (m, 12 H), 7.29 (d, *J* = 8.7 Hz, 4 H), 7.41 (d, *J* = 8.7 Hz, 4 H); ^{13}C NMR: 25.96, 26.01, 29.1, 29.26, 29.33, 29.5, 30.7, 31.5, 32.4, 34.0, 64.4, 67.5, 67.9, 68.0, 75.6, 77.2, 83.7, 98.8, 106.9, 107.2, 113.9, 114.4, 115.4, 126.2, 133.5, 143.3, 143.8, 153.1, 156.6, 159.5, 160.0, 160.3; MS(MALDI-TOF): *m/z* 1326.1 [(M+Na)$^+$, 100]; calcd (%) for $C_{86}H_{110}O_{10}$: C, 79.22; H, 8.50; found: C, 79.05; H, 8.52.

2: Starting from compound **8** (60 mg, 21 μmol) and after chromatographic purification, compound **2** (50 mg, 88%) was obtained as a colorless oil; R_f: 0.41 (hexane/EtOAc, 5:1); ^{1}H NMR: 1.20–1.50 (m, 24 H), 1.28 (s, 54 H), 1.70–1.80 (m, 8 H), 2.04 (quin, *J* = 6.9 Hz, 12 H), 2.20 (quin, *J* = 6.0 Hz, 12 H), 2.69 (t, *J* = 7.5 Hz, 12 H), 2.98 (s, 2 H), 3.80–4.00 (m, 20 H), 4.09 (t, *J* = 6.0 Hz, 12 H), 4.11 (t, *J* = 6.0 Hz, 12 H), 6.30–6.40 (m, 18 H), 6.80–6.90 (m, 20 H), 7.28 (d, *J* = 8.7 Hz, 12 H), 7.41 (d, *J* = 8.7, 4 H); ^{13}C NMR: 26.0, 29.1, 29.4, 29.5, 30.7, 31.5, 32.5, 34.0, 64.36, 64.44, 66.9, 67.6, 67.9, 68.0, 75.6, 77.2, 83.9, 98.9, 107.1, 107.2, 113.9, 114.4, 115.4, 126.2, 133.5, 143.3, 143.9, 153.2, 156.6, 159.5, 160.0, 160.2; MS(MALDI-TOF): *m/z* 2689.5 [(M+Na)$^+$, 100]; calcd (%) for $C_{174}H_{222}O_{22}$: C, 78.40; H, 8.39; found: C, 78.21; H, 8.25.

3: Starting from compound **9** (0.25 g, 45 μmol) and after chromatographic purification, compound **3** (0.16 g, 66%) was obtained as a colorless oil; R_f: 0.27 (hexane/EtOAc, 5:1); ^{1}H NMR: 1.20–1.50 (m, 24 H), 1.28 (s, 126 H), 1.70–1.80 (m, 8 H), 2.00–2.10 (m, 28 H), 2.20 (quin, *J* = 6.0 Hz, 28 H), 2.69 (t, *J* = 6.6 Hz, 28 H), 2.98 (s, 2 H), 3.80–4.00 (m, 36 H), 4.08 (t, *J* = 6.6 Hz, 28 H), 4.10 (t, *J* = 6.6 Hz, 28 H), 6.31 (brs, 14 H), 6.36 (brs, 28 H), 6.75–6.90 (m, 36 H), 7.25–7.30 (m, 28 H), 7.42 (d, *J* = 8.7 Hz, 4 H); ^{13}C NMR: 26.0, 29.2, 29.3, 30.7, 30.9, 31.5, 32.5, 34.0, 64.3, 64.4, 66.9, 67.7, 67.9, 68.0, 68.1, 75.7, 77.2, 82.9, 98.9, 107.1, 107.2, 113.9, 114.4, 114.6, 115.4, 126.2, 128.4, 128.6, 133.5, 134.0, 143.3, 143.9, 153.2, 156.6, 159.8, 160.0, 160.2; MS(MALDI-TOF): *m/z* 5415.3 [(M+Na)$^+$, 100]; calcd (%) for $C_{350}H_{446}O_{46}$: C, 77.92; H, 8.38; found: C, 77.72; H, 8.33.

General synthetic procedure for Gn-dendritic necklaces (n = 1–3) **17–19**. A catalytic amount of CuI (5 mg) was added to a mixture of the bis(ethynyl) surface-functionalized Gn-dendrimer **1**–**3** (1.0 equiv) and *trans*-[$(Et_3P)_2PtCl_2$] (1.0 equiv) in CH_2Cl_2/diisopropylamine (1:1) (20 mL/mmol) at 25 °C. The mixture was stirred for 12 h and the solvent was evaporated under reduced pressure. The residue was re-dissolved in dichloromethane and filtered through a short pad of alumina. The filtrate collected was concentrated to about 1 mL under reduced pressure and then precipitated successively to acetone and to methanol (200 mL each). The dendritic polymer was collected by filtration.

G1-dendritic necklace **17**: Starting from compound **1** (500 mg, 77 μmol) and *trans*-[$(Et_3P)_2PtCl_2$] (190 mg, 38 μmol), the dendritic polymer **17** (600 mg, 88%) was obtained as a yellow solid; T_d: 500 °C; ^{1}H NMR: 1.10–1.20 (m, 18 H), 1.20–1.50 (m, 24 H), 1.29 (s, 18 H), 1.65–1.80 (m, 8 H), 1.98–2.20 (m, 20 H), 2.60–2.80 (m, 4 H), 3.80–4.00 (m, 12 H), 4.09 (t, *J* = 6.6 Hz, 4 H), 4.11 (t, *J* = 6.6 Hz, 4 H), 6.30 (s, 2 H), 6.35 (s, 4 H), 6.74 (d, *J* = 8.7 Hz, 4 H), 6.81 (s, 4 H), 6.84 (d, *J* = 8.7 Hz, 4 H), 7.19 (d, *J* = 8.7 Hz, 4 H), 7.29 (d, *J* = 8.7 Hz, 4 H); ^{13}C NMR[5]: 8.4 (PCH_2CH_3), 16.3 (pseudo quin, *J* = 17 Hz; PCH_2), 26.0, 29.1, 29.4, 29.5, 30.7, 31.5, 32.5, 34.0, 64.4, 67.6, 67.9, 98.8, 107.0, 107.2, 108.7 (s, $C\equiv CPt$), 113.9, 114.1, 114.5, 115.4, 126.2, 131.9, 143.3, 143.9, 153.2, 156.6, 156.8, 160.0, 160.3; $^{31}P\{^1H\}$ NMR: 17.58 [^1J(Pt,P) = 2375 Hz]; UV (CH_2Cl_2, 25 °C): λ_{max} (logε) = 268 (4.05), 344 nm (3.93).

G2-dendritic necklace **18**: Starting from compound **2** (380 mg, 0.14 mmol) and *trans*-[$(Et_3P)_2PtCl_2$] (72 mg, 0.14 mmol), the dendritic polymer **18** (350 mg, 78%) was obtained as a yellow solid; T_d: 500 °C; ^{1}H NMR: 1.10–1.30 (m, 18 H), 1.20–1.50 (m, 24 H), 1.28 (s, 54 H), 1.65–1.80 (m, 8 H), 1.95–2.30 (m, 36 H), 2.60–2.80 (m, 12 H), 3.80–4.00 (m, 20 H), 4.08 (t, *J* = 6.6 Hz, 12 H), 4.10 (t, *J* = 6.6 Hz, 12 H), 6.30 (s, 6 H), 6.35 (s, 12 H), 6.75 (d, *J* = 8.7 Hz, 4 H), 6.80 (s, 4 H), 6.84 (d, *J* = 8.7 Hz, 12 H), 7.17 (d, *J* = 8.7 Hz, 4 H), 7.28 (d, *J* = 8.7 Hz, 12 H); ^{13}C NMR[5]: 8.4 (PCH_2CH_3), 16.3 (pseudo quin, *J* = 17 Hz; PCH_2), 26.1, 29.4, 30.7, 31.5, 32.5, 34.0, 64.3, 64.4, 66.9, 68.0, 98.9, 107.2, 113.9, 114.1, 115.4, 126.2, 131.9, 143.3, 143.9, 156.6, 160.0, 160.2; $^{31}P\{^1H\}$ NMR: 17.51 [^1J(Pt,P) = 2381 Hz]; UV (CH_2Cl_2, 25 °C): λ_{max} (logε) = 272 (3.94), 343 nm (3.83).

G3-dendritic necklace **19**: Starting from compound **3** (400 mg, 0.074 mmol) and *trans*-[$(Et_3P)_2PtCl_2$] (37 mg, 0.074 mmol), the dendritic polymer **19** (250 mg, 58%) was obtained as a yellowish green solid; T_d: 500 °C; ^1H NMR: 1.10–1.30 (m, 18 H), 1.20–1.50 (m, 24 H), 1.27 (s, 126 H), 1.65–1.80 (m, 8 H), 1.95–2.30 (m, 68 H), 2.60–2.80 (m, 28 H), 3.80–4.00 (m, 36 H), 4.07 (t, *J* = 6.6 Hz, 28 H), 4.09 (t, *J* = 6.6 Hz, 28 H), 6.30 (s, 14 H), 6.35 (s, 28 H), 6.71 (d, *J* = 8.7 Hz, 4 H), 6.80 (s, 4 H), 6.83 (d, *J* = 8.7 Hz, 28 H), 7.20 (d, *J* = 8.7 Hz, 4 H), 7.27 (d, *J* = 8.7 Hz, 28 H); ^{13}C NMR[5]: 8.4 (PCH_2CH_3), 16.3 (pseudo quin, *J* = 17 Hz; PCH_2), 26.1, 29.3, 30.7, 30.9, 31.5, 32.5, 34.0, 64.3, 64.4, 66.9, 67.7, 67.9, 98.9, 107.1, 107.2, 113.9, 114.1, 115.4, 126.2, 131.9, 143.3, 143.9, 153.2, 156.6, 160.0, 160.2; $^{31}P\{^1H\}$ NMR: 16.28 [^1J(Pt,P) = 2393 Hz]; UV (CH_2Cl_2, 25 °C): λ_{max} (logε) = 276 (3.93), 343 nm (3.56).

References:

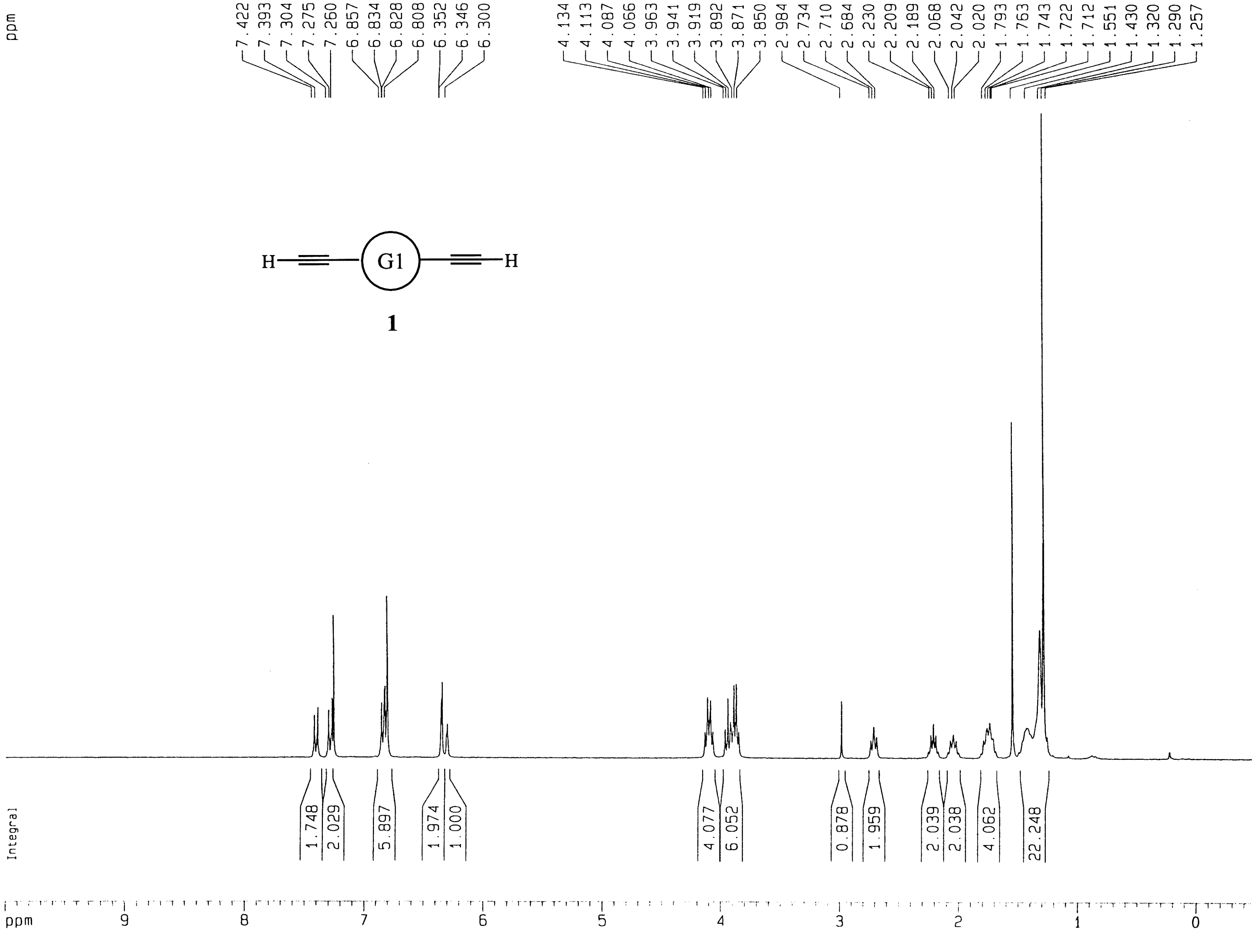
[1] H.-F. Chow, I. Y.-K. Chan, C. C. Mak, M.-K. Ng, *Tetrahedron* **1996**, *52*, 4277–4290.

[2] F. Lotz, U. Kraatz, F. Korte, *Liebigs Ann. Chem.* **1977**, 1132–1140.

[3] The intensities of the ^{13}C signals (δ ~ 92 and 105) of the two acetylenic carbons were too weak to be observed.

[4] One of the ^{13}C signals of the acetylenic carbons (δ ~ 92) was too weak to be observed.

[5] One of the ^{13}C signals of the acetylenic carbons of the G1- **17** dendritic necklace and both the ^{13}C signals of the two acetylenic carbons of the G2- **18** and G3- **19** dendritic necklaces are too weak to be observed.



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PROCNO               1

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SOLVENT          CDCl3
NS                   8
DS                   0
SWH           8992.806 Hz
FIDRES        0.274439 Hz
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RG                 512
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TE               300.0 K
D1          1.00000000 sec

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F2 - Processing parameters
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1D NMR plot parameters
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HZCM         137.01587 Hz/cm
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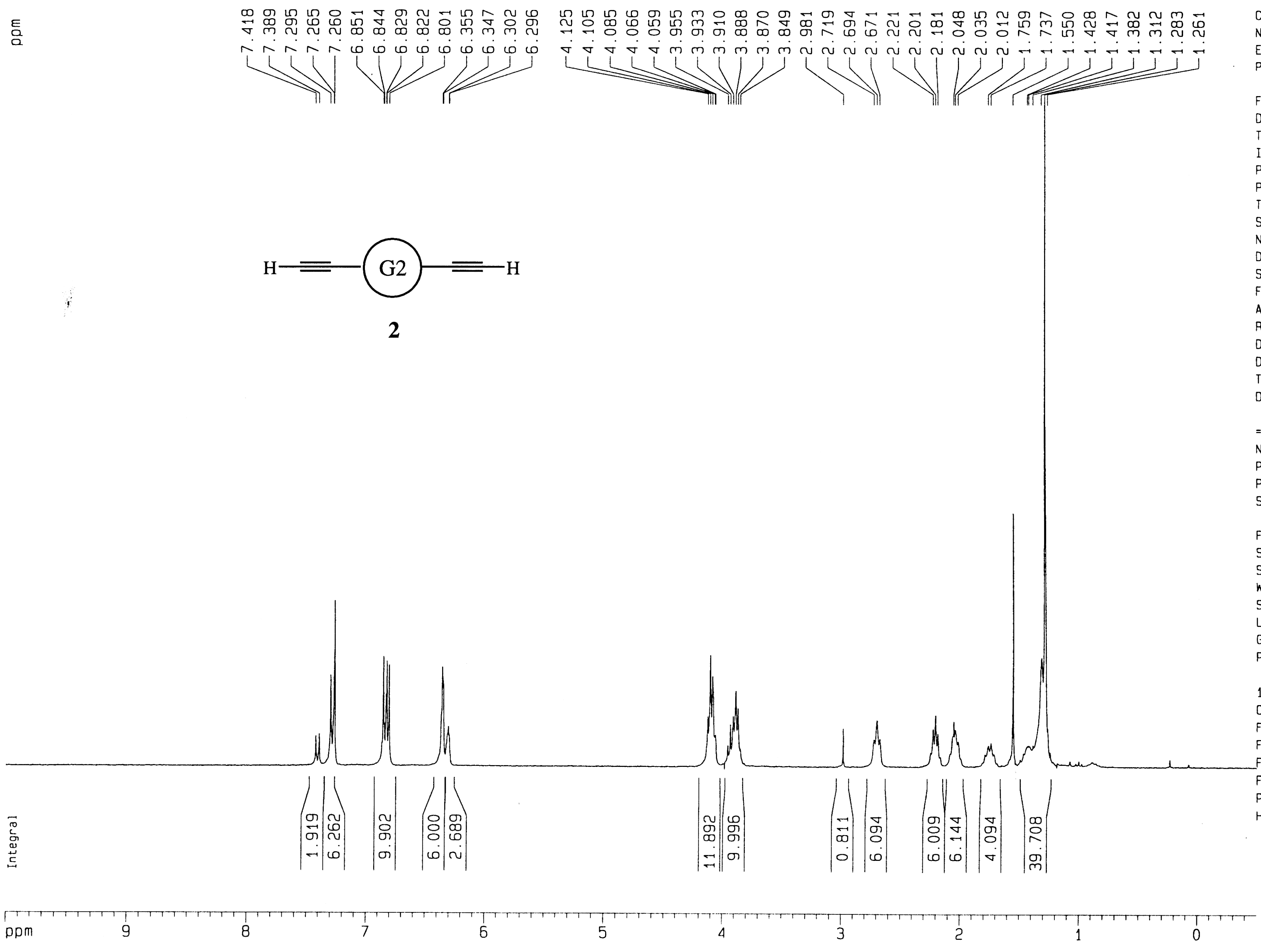

2

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PROCNO              1

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PULPROG            zg
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SOLVENT        Aceton
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SWH          8992.806 Hz
FIDRES       0.274439 Hz
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TE              300.0 K
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1D NMR plot parameters
CX              23.00 cm
F1P            10.000 ppm
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F2P            -0.500 ppm
F2            -150.07 Hz
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HZCM        137.01587 Hz/cm
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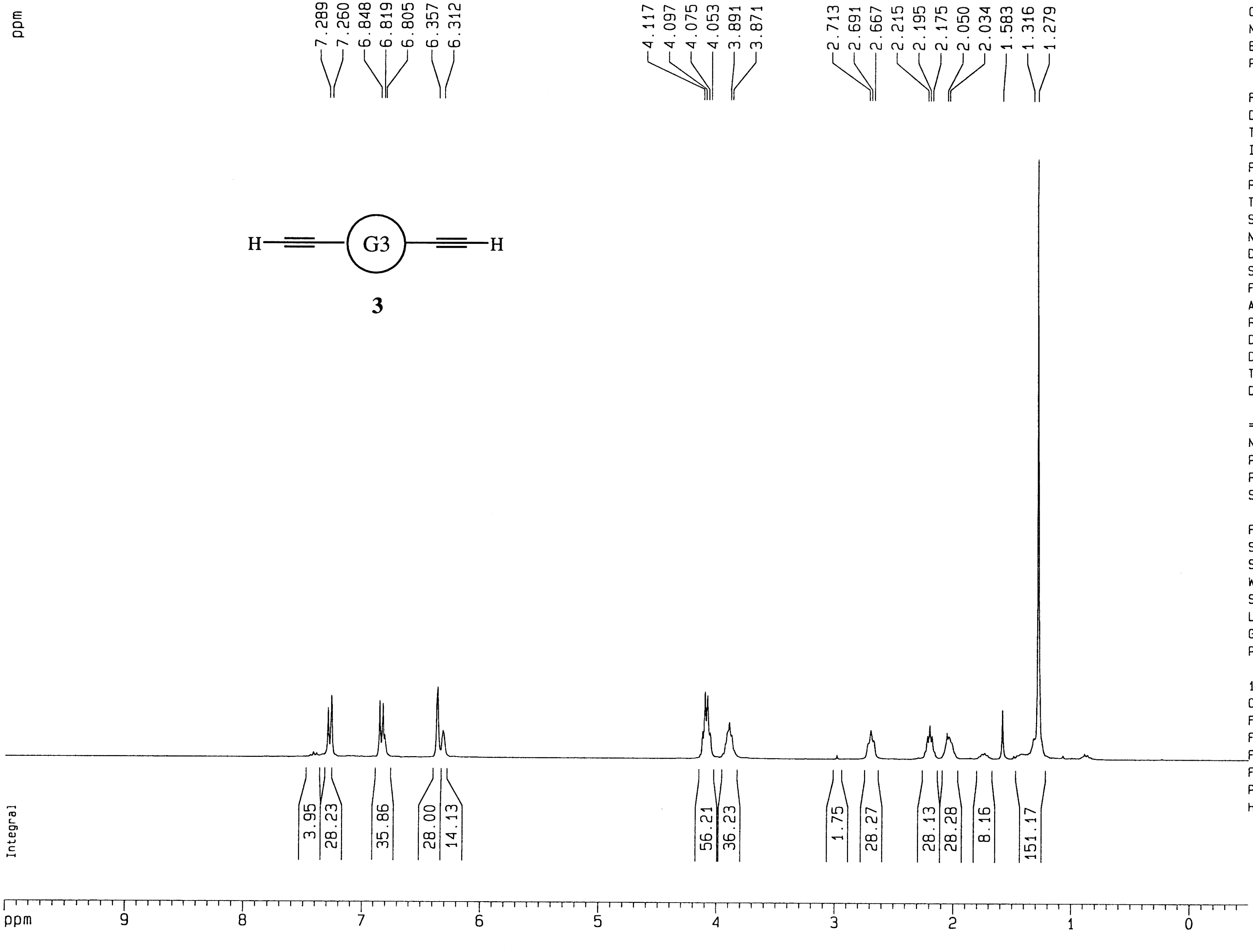

3

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EXPNO                  1
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FIDRES          0.274439 Hz
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RG                   114
DW                55.600 usec
DE                  6.00 usec
TE                 300.0 K
D1            1.00000000 sec

============ CHANNEL f1 ======
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P1                  4.50 usec
PL1                -2.00 dB
SFO1         300.1312000 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300066 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 23.00 cm
F1P               10.000 ppm
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HZCM           137.01587 Hz/cm
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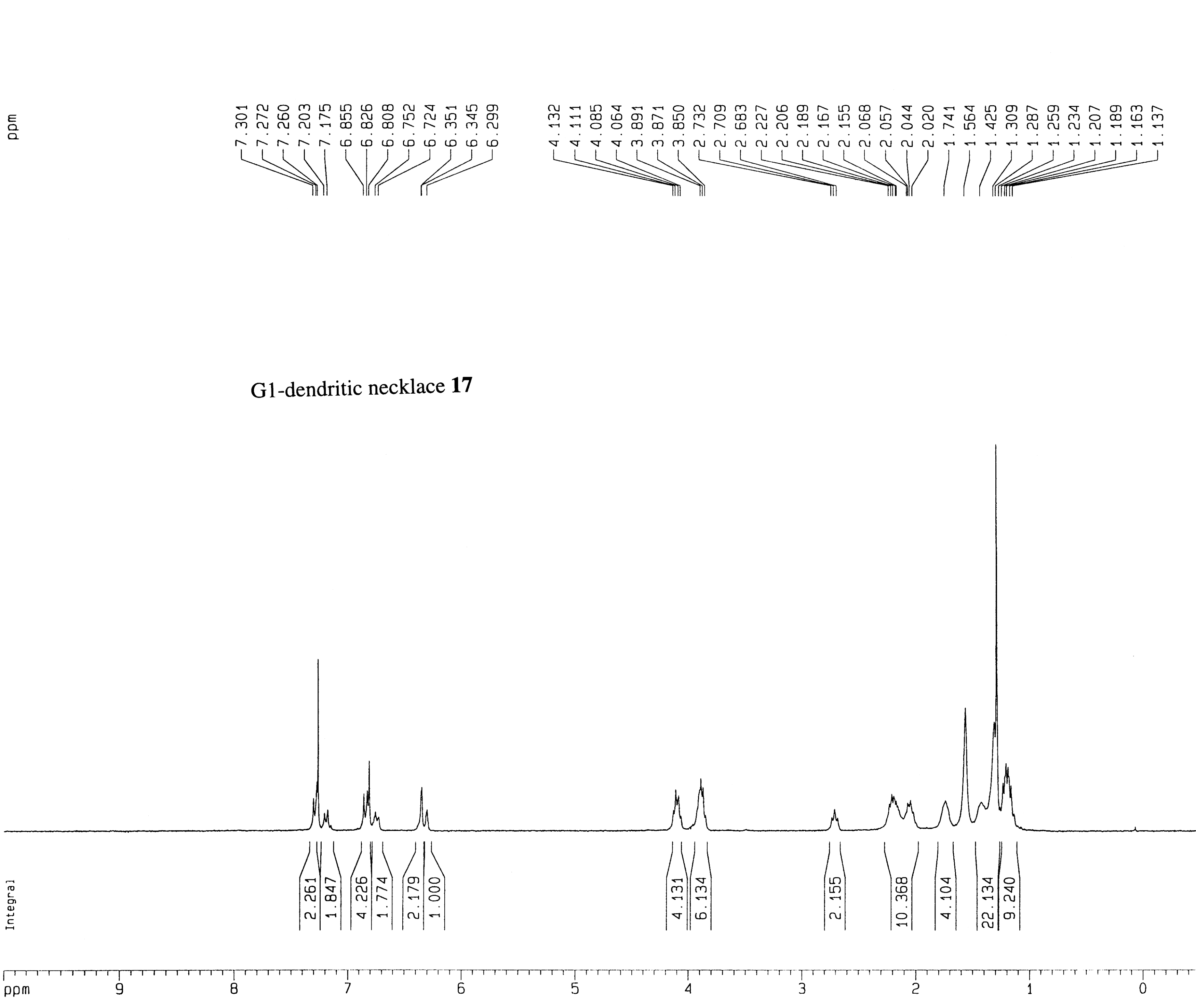

G1-dendritic necklace **17**

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EXPNO                   1
PROCNO                  1

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Time                15.52
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PULPROG                zg
TD                  32768
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DS                      0
SWH              8992.806 Hz
FIDRES           0.274439 Hz
AQ              1.8219508 sec
RG                  724.1
DW                 55.600 usec
DE                   6.00 usec
TE                  300.0 K
D1             1.00000000 sec

============ CHANNEL f1 ======
NUC1                   1H
P1                   4.50 usec
PL1                 -2.00 dB
SFO1          300.1312000 MHz

F2 - Processing parameters
SI                  32768
SF            300.1300057 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  23.00 cm
F1P                10.000 ppm
F1                3001.30 Hz
F2P                -0.500 ppm
F2                -150.07 Hz
PPMCM             0.45652 ppm/cm
HZCM            137.01587 Hz/cm
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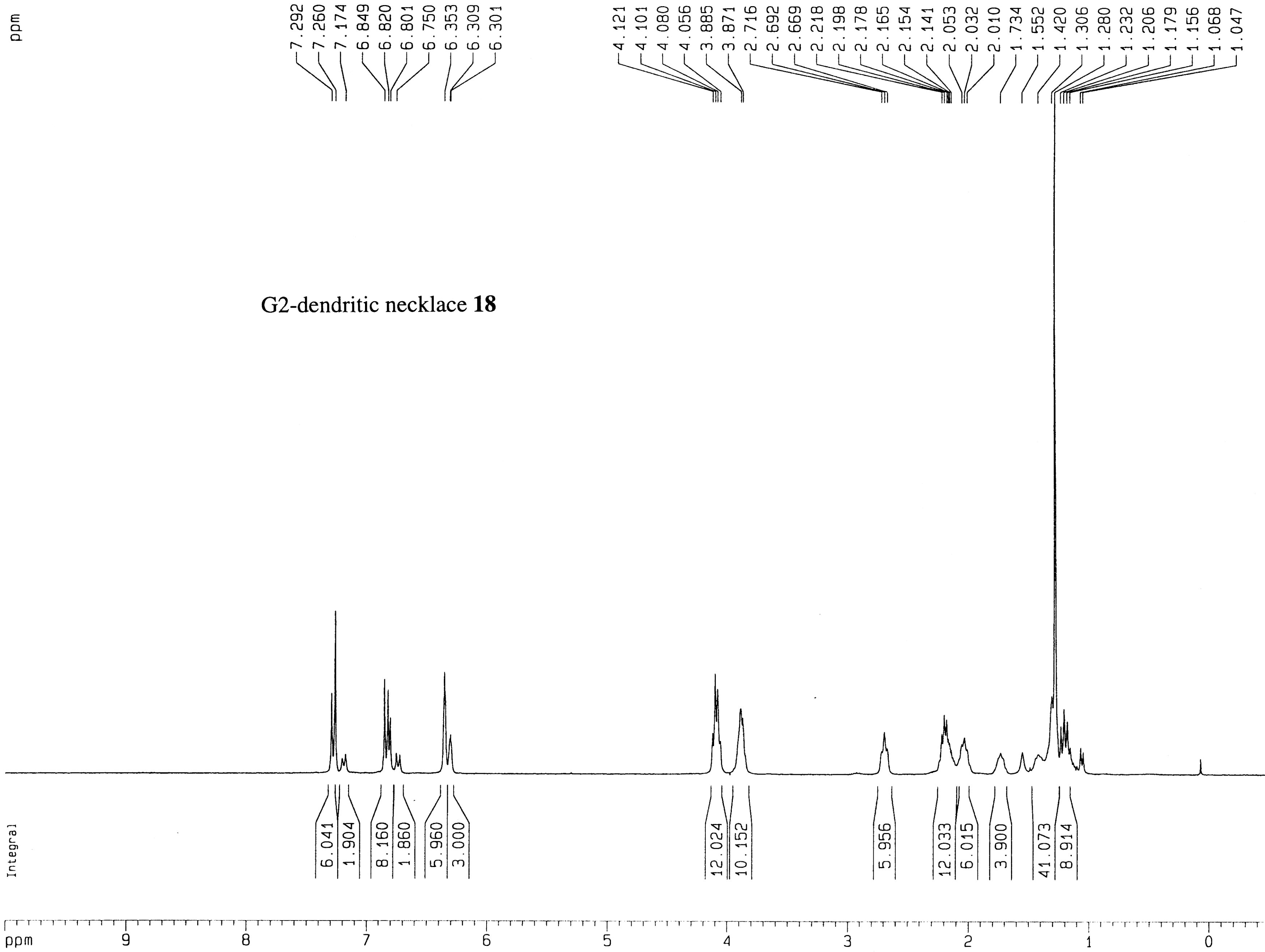
G2-dendritic necklace **18**

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EXPNO                  1
PROCNO                 1

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INSTRUM           dpx300
PROBHD      5 mm Dual 13
PULPROG               zg
TD                 32768
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             8992.806 Hz
FIDRES          0.274439 Hz
AQ             1.8219508 sec
RG                 406.4
DW                55.600 usec
DE                  6.00 usec
TE                 300.0 K
D1            1.00000000 sec

============ CHANNEL f1 ======
NUC1                  1H
P1                  4.50 usec
PL1                -2.00 dB
SFO1         300.1312000 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300060 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 23.00 cm
F1P               10.000 ppm
F1               3001.30 Hz
F2P               -0.500 ppm
F2               -150.07 Hz
PPMCM            0.45652 ppm/cm
HZCM           137.01587 Hz/cm
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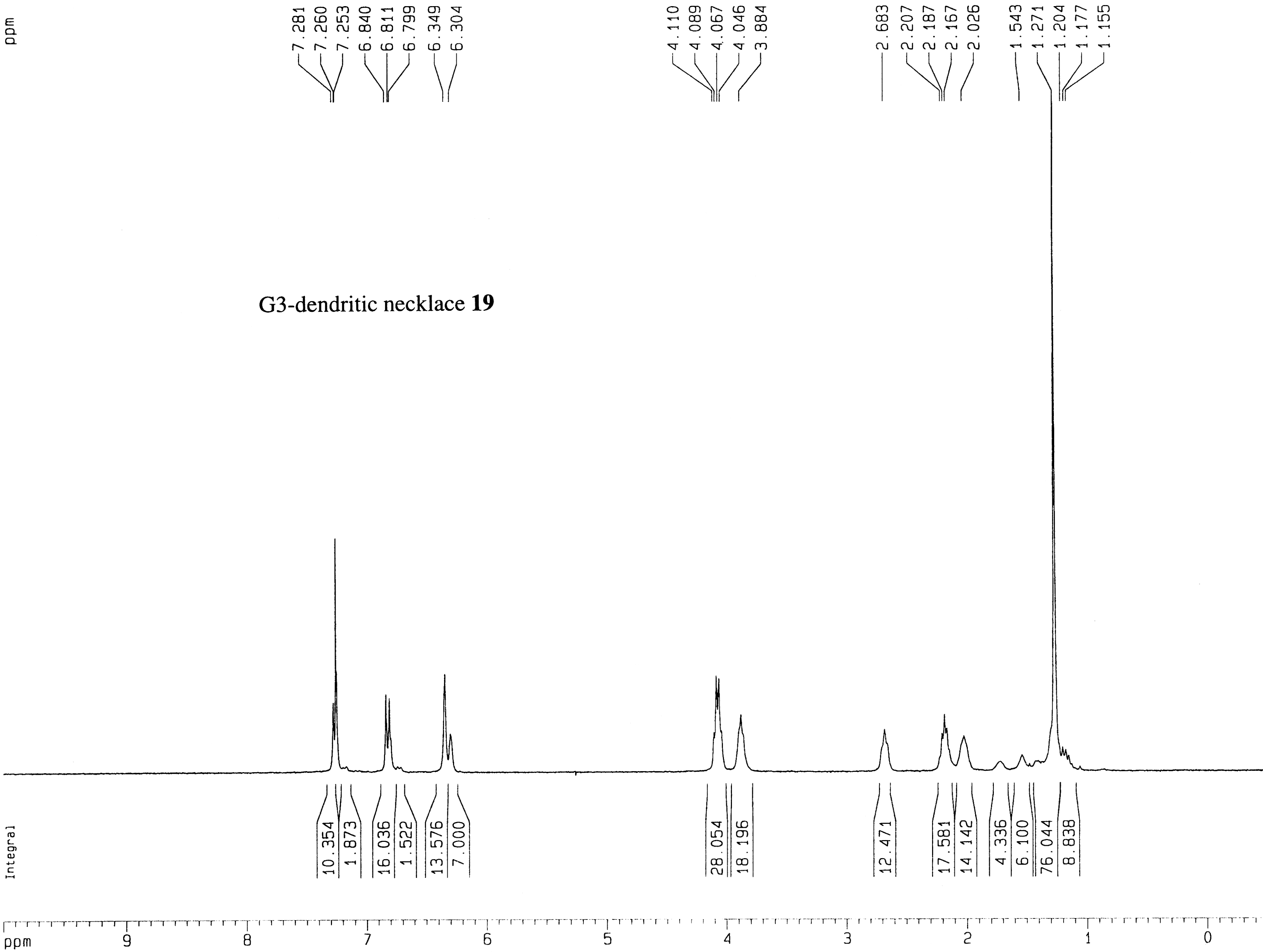
G3-dendritic necklace **19**



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PROCNO                 1

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PULPROG               zg
TD                 32768
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             8992.806 Hz
FIDRES          0.274439 Hz
AQ             1.8219508 sec
RG                 724.1
DW                55.600 usec
DE                  6.00 usec
TE                 300.0 K
D1            1.00000000 sec

============ CHANNEL f1 ======
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P1                  4.50 usec
PL1                -2.00 dB
SFO1         300.1312000 MHz

F2 - Processing parameters
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SF           300.1296207 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 23.00 cm
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F1               3001.30 Hz
F2P               -0.500 ppm
F2               -150.06 Hz
PPMCM            0.45652 ppm/cm
HZCM           137.01569 Hz/cm
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