Supplementary Information

Type III-B Rotaxane Dendrimers

Watson K.-W. Ho,[a] Siu-Fung Lee,[a] Chi-Hin Wong,[b] Xiaoming Zhu,[b] Chak-Shing Kwan,[b] Chun-Pong Chak,[a] Paula M. Mendes,[c] Christopher H. K. Cheng,[d] and Ken Cham-Fai Leung*[b,e]

[a] Department of Chemistry, The Chinese University of Hong Kong, Shatin, NT, Hong Kong SAR, P. R. China
[b] Department of Chemistry and Institute of Creativity, The Hong Kong Baptist University, Kowloon Tong, Kowloon, Hong Kong SAR, P. R. China
[c] School of Chemical Engineering, The University of Birmingham, Birmingham, United Kingdom
[d] School of Biomedical Sciences, The Chinese University of Hong Kong, Shatin, NT, Hong Kong SAR, P. R. China
[e] Institute of Molecular Functional Materials, University Grants Committee, Hong Kong SAR, P. R. China

Correspondence:
Dr. Ken Cham-Fai Leung
E-mail: cfleung@hkbu.edu.hk
Tel: (+852) 3411 2319
Fax: (+852) 3411 7348

Experimental Section

General

All non-aqueous reactions were carried out under dry, high-purity N_2 with oven-dried (115 ºC) glassware. Unless otherwise specified, all solvents and reagents were purchased commercially with reagent quality and used without further purification. Tetrahydrofuran (THF) was freshly distilled from $LiAlH_4$ under N_2. Thin layer chromatography (TLC) was performed on silica gel 60 F_{254} (Merck). Column chromatography was performed on silica gel 60F (Merck 9385, 0.040–0.063 mm). ^1H and ^{13}C NMR spectra for structural characterization were recorded on Bruker Avance 400 (H: 400 MHz; C: 101 MHz) spectrometer at 298 K. NMR samples were dissolved in $CDCl_3$ unless otherwise stated. Chemical shifts were reported as parts per million (ppm) in δ scale and calibrated by using the solvent residual peak (e.g., for residual $CHCl_3$ in $CDCl_3$, ^1H: $\delta = 7.26$; ^{13}C: $\delta = 77.16$) as internal standard. Coupling constants (*J*) were reported in hertz. Electrospray ionization (ESI) mass spectra were obtained on a Thermo Finnigan MAT 95XL mass spectrometer using CH_2Cl_2 as mobile phase. The reported molecular mass (*m/z*) values correspond to the most abundant monoisotopic masses. Melting points were measured on an Electrothermal 9100 digital melting point apparatus. UV/Visible absorption spectra were obtained using a Cary 5G UV-Vis-NIR spectrophotometer. Contact angles were measured using a Face CA-X contact angle meter at ambient temperature with highly oriented pyrolytic graphite (HOPG). The samples were spin-coated (400 rpm) on a freshly cleaved HOPG surface at a concentration of 1 mg/mL according to different CH_2Cl_2/DMSO gradients.

*Acetylene **3***

To a solution of 3,5-bis(benzyloxy)benzoic acid[S1] (8.00 g, 17.39 mmol) in CH_2Cl_2 (30 mL), DCC (4.30 g, 20.87 mmol) and DMAP (0.2 g, 1.63 mmol) were added. The solution was allowed to stir at ambient temperature for 30 min. Then, propargyl alcohol (3.00 mL, 52.17 mmol) was added. The reaction mixture was stirred at ambient temperature for 24 h. Subsequently, the reaction mixture was filtered through a plug of silica gel. The silica gel was further washed with 500 mL CH_2Cl_2. The solvents were evaporated to dryness to give a white solid, which was then re-dissolved in 450 mL of hot EtOH. The solution was allowed to cool down to room temperature and then to ice water. Then, 10 mL of H_2O was added to facilitate recrystallization. After a filtration and subsequent removal of solvent in vacuo, acetylene compound **3** was obtained as a white solid (6.20 g, 74%). R*f*: 0.60 (hexane/EtOAc = 5:1). M.p. = 115.8–117.6 ºC. ^{1}H NMR: δ 1.33 (s, 18 H, aliphatic H), 2.51 (t, *J* = 2.44 Hz, 1 H, aliphatic H), 4.91 (d, *J* = 2.44 Hz, 2 H, CH_2O), 5.03 (s, 4 H, CH_2O), 6.82 (t, *J* = 2.24 Hz, 1 H, ArH), 7.32 (d, *J* = 2.24 Hz, 2 H, ArH), 7.36 (d, *J* = 8.28 Hz, 4 H, ArH), 7.42 (d, *J* = 8.28 Hz, 4 H, ArH). ^{13}C NMR: δ 31.3, 34.6, 52.6, 70.2, 75.0, 77.3, 77.6, 107.5, 108.5, 125.6, 127.6, 131.1, 133.3, 151.2, 159.9, 165.5. HRMS (ESI): $C_{32}H_{36}O_4$ $[M+H]^+$: calcd 458.2686; found 458.2687.

*G1 [2]rotaxane dendron **4**-H•PF$_6$*

Ammonium thread bis(4-azidomethylbenzyl) ammonium hexafluorophosphate **1**-H•PF6 (0.31 g, 0.68 mmol),[17a] crown ether **2** (0.49 g, 0.83 mmol),[S2] and acetylene **3** (0.71 g, 1.47 mmol), were dissolved in CH_2Cl_2 (7 mL). The resulting solution was degased by sonication for 3 min. $Cu(MeCN)_4PF_6$ (0.51 g, 1.47 mmol), AcOH (168 μL, 2.8 mmol) and DIPEA (240 μL, 1.4 mmol) were added to the solution. The reaction mixture was stirred at ambient temperature for three days. After that, a solution of AcOH (2 mL) and $CHCl_3$ (50 mL) and saturated Na_2CO_3 (30 mL) solution was added to the reaction mixture. The two layers were vigorously shaked in separatory funnel until the organic layer became pale yellow and the aqueous layer became blue. The aqueous layer was extracted with $CHCl_3$ (2 × 50 mL). The combined organic extracts were dried ($MgSO_4$) and the resulting solution was evaporated to dryness. Flash column chromatography with hexane/EtOAc (1:1) gradient to EtOAc, then to EtOAc/acetone (1:1) with NH_4PF_6 (0.3 gL^{-1}) on silica gel of the residue gave the G1 [2]rotaxane dendron **4**-H•PF$_6$ (0.70 g, 50%) as a glassy pale yellow solid. R*f*: 0.65 (EtOAc). M.p. = 148–149 ºC. ^{1}H NMR: δ 1.31 (s, 36 H, aliphatic H), 2.82 (s, 4 H, aliphatic H), 3.46 (m, 4 H, CH_2O), 3.54 (m, 4 H, CH_2O), 3.82 (m, 4 H, CH_2O), 3.91 (m, 4 H, CH_2O), 4.02 (m, 4 H, CH_2O), 4.07 (m, 4 H, CH_2O), 4.62 (s, 4 H, $CH_2NH_2^+$), 5.00 (s, 8 H, CH_2O), 5.38 (s, 4 H, CH_2N), 5.42 (s, 4 H, CH_2O), 6.58 (t, *J* = 9.32 Hz, 2 H, ArH), 6.74 (d, *J* = 8.6 Hz, 1 H, ArH), 6.80 (m, 4 H, ArH), 7.05 (d, *J* = 7.92 Hz, 4 H, ArH), 7.24 (m, 8 H, ArH), 7.31 (s, 1 H, ArH), 7.33 (d, *J* = 8.24 Hz, 8 H, ArH), 7.41 (d, *J* = 8.24 Hz, 8 H, ArH), 7.60 (s, 2 H, NH_2^+), 7.67 (d, *J* = 8.6 Hz, 1 H, ArH), 7.70 (s, 2 H, ArH). ^{13}C NMR: δ 25.70, 31.39, 34.65, 52.07, 53.69, 57.80, 67.83, 68.15, 68.37, 70.06, 70.26, 70.50, 77.36, 107.34, 108.54, 111.96, 112.18, 112.28, 113.26, 117.25, 121.59, 125.63, 127.68, 128.30, 129.57, 131.58, 131.93, 133.36, 135.69, 149.72, 146.77, 147.33, 151.27, 153.10, 159.97, 161.34, 169.68 (one peak is overlapping). HRMS (ESI): $C_{109}H_{125}N_8O_{20}PF_6$ [M–PF6]$^+$: calcd 1865.9005; found 1865.8979.

G1 [2]rotaxane dendron ***5****-H•*PF_6

To a solution of G1 [2]rotaxane dendron **4**-H•PF_6 (0.70 g, 0.35 mmol) in CH_2Cl_2 (3 mL), propargyl amine (0.35 mL, 6.25 mmol) was added. The reaction mixture was stirred at ambient temperature for 24 h. After that, the solution was diluted by 15 mL CH_2Cl_2. The solid was filtered and the solvents were evaporated to dryness. The resulting yellow oil was washed by EtOH (5 mL) twice to yield a pale yellow solid. The solvents were evaporated in vacuo to yield the G1 [2]rotaxane dendron **5**-H•PF_6 as a pale yellow glassy solid (0.52 g, 77%). R_f: 0.60 (EtOAc). M.p. = 140–142 ºC. ^{1}H NMR: δ 1.31 (s, 36 H, aliphatic H), 2.26 (t, J = 2.24 Hz, 1 H, aliphatic H), 3.48 (m, 8 H, CH_2O), 3.68 (m, 4 H, CH_2O), 3.74 (m, 4 H, CH_2O), 3.92 (m, 4 H, CH_2O), 4.00 (m, 2 H, CH_2O), 4.18 (dd, J_1 = 2.24 Hz, J_2 = 2.96 Hz, 2 H, CH_2O), 4.25 (br, 2 H, CH_2N), 4.63 (t, J = 5.32 Hz, 4 H, $CH_2NH_2^+$), 4.99 (s, 8 H, CH_2O), 5.38 (s, 4 H, CH_2N), 5.42 (s, 4 H, CH_2O), 6.51 (d, J = 8.4 Hz, 1 H, ArH), 6.61 (dd, J_1 = 6.72 Hz, J_2 = 2.4 Hz, 1 H, ArH), 6.67 (dd, J_1 = 7.24 Hz, J_2 = 1.92 Hz, 1 H, ArH), 6.80 (m, 4 H, ArH), 7.02 (m, 5 H, ArH), 7.19 (d, J = 8.08 Hz, 2 H, ArH), 7.25 (m, 8 H, ArH), 7.33 (d, J = 8.24 Hz, 8 H, ArH), 7.41 (d, J = 8.24 Hz, 8 H, ArH), 7.60 (s, 2 H, NH_2^+), 7.71 (s, 2 H, ArH). ^{13}C NMR: δ 29.54, 29.77, 31.15, 34.58, 52.21, 53.41, 58.31, 67.78, 67.84, 68.05, 68.17, 70.12, 70.29, 70.65, 70.74, 70.85, 80.49, 107.08, 108.42, 111.32, 111.60, 112.40, 120.56, 121,61, 124.55, 125.60, 127.29, 127.65, 128.15, 129.69, 131,89, 132.00, 133.56, 136.26, 147.21, 147.24, 149.95, 151.44, 160.09, 166.03, 166.26 (one peak is overlapping). HRMS (ESI): $C_{108}H_{125}N_8O_{17}PF_6$ [M–PF$_6$]$^+$: calcd 1805.9157; found 1805.9171.

G1 [3]rotaxane dendrimer ***6****-*H_2*•2*PF_6

G1 [2]rotaxane dendron **5**-H•PF_6 (0.2 g, 0.04 mmol) was dissolved in THF. TMEDA (0.3 mL, 2 mmol) and $Cu(MeCN)_4PF_6$ (30 mg, 0.08 mmol) were added. The resulting solution was stirred in air for 5 min. After that, O_2 was pumped continuously to the solution for 15 min. The resulting solution was stirred in open air for 12 h. After that,

H_2O (15 mL) and 30 mL $CHCl_3$ (30 mL) were added to the reaction mixture. The two layers were shaked vigorously. The aqueous layer was extracted with $CHCl_3$ (2 × 10 mL). The organic extracts were dried ($MgSO_4$) and reprotonated by NH_4PF_6. The resulting solution was evaporated to dryness. The resulting yellow solid was washed with EtOH and G1 [3]rotaxane dendrimer **6**-H_2•$2PF_6$ (0.18 g, 60%) was obtained as a pale yellow solid. R_f: 0.20 (EtOAc). M.p. = 152–153 ºC. ^{1}H NMR: δ 1.33 (s, 72 H, aliphatic H), 3.35 (m, 16 H, CH_2O), 3.74 (m, 16 H, CH_2O), 4.00 (m, 16 H, CH_2O), 4.18 (br, 4 H, CH_2O), 4.58 (br, 8 H, $CH_2NH_2^+$), 4.99 (s, 16 H, CH_2O), 5.44 (br, 16 H, CH_2N/CH_2O), 6.68 (br, 5 H, ArH), 6.80 (br, 8 H, ArH), 7.07 (br, 8 H, ArH), 7.24 (d, *J* = 6.80 Hz, 7 H, ArH), 7.29 (br, 14 H, CONH/ArH), 7.35 (d, *J* = 8.24 Hz, 17 H, ArH), 7.41 (d, *J* = 8.24 Hz, 17 H, ArH), 7.60 (br, 4 H, NH_2^+), 7.83 (s, 4 H, ArH). ^{13}C NMR: δ 30.09, 30.83, 31.38, 34.64, 52.08, 53.38, 58.25, 66.92, 67.74, 68.01, 69.20, 70.20, 70.64, 74.73, 77.36, 107.28, 108.44, 111.37, 112.36, 121.02, 121,65, 125.62, 125.98, 126.31, 126.77, 127.65, 128.21, 129.59, 131.64, 131.79, 133.33, 136.05, 146.15, 146.76, 147.10, 147.16, 149.9, 151.25, 159.92, 166.18, 166.33. HRMS (ESI): $C_{216}H_{248}F_{12}N_{16}O_{34}P_2$ [M–2PF6]$^+$: calcd 1805.9111; found 1805.9099.

G2 [4]rotaxane dendrimer 7-H_3*•*$3PF_6$

G1 [2]rotaxane dendron **5**-H•PF_6 (0.40 g, 0.20 mmol), ammonium thread **1**-H•PF6 (46 mg, 0.10 mmol) and dibenzo[24]crown-8 (0.26 g, 0.60 mmol) were dissolved in CH_2Cl_2 (4 mL). The resulting solution was degased by sonication for 3 min. $Cu(MeCN)_4PF_6$ (69 mg, 0.20 mmol), AcOH (24 µL, 0.40 mmol) and DIPEA (36 µL, 0.20 mmol) were added to the solution. The reaction mixture was stirred at ambient temperature for 10 d. After that, a solution of AcOH (1 mL), $CHCl_3$ (30 mL) and saturated Na_2CO_3 (15 mL) solution was added to the reaction mixture. The two layers were vigorously shaked in separatory funnel until the organic layer became pale yellow and the aqueous layer became blue. The aqueous layer was extracted with $CHCl_3$ (2 × 30 mL). The combined organic extracts were dried ($MgSO_4$) and reprotonated by NH_4PF_6. The resulting solution was evaporated to dryness. Flash column chromatography with EtOAc on silica gel of the residue gave a white solid. Second Flash column chromatography on silica gel of the residue with hexane, gradient to EtOAc, to EtOAc/acetone (1:1), to acetone and then to acetone with NH_4PF_6 (0.3 gL^{-1}) gave the G2 [4]rotaxane dendrimer **7**-H_3•$3PF_6$ (0.19 g, 38%) as a white solid. M.p. = 156–157 ºC. ^{1}H NMR: δ 1.30 (s, 72 H, aliphatic H), 3.38 (m, 24 H, CH_2O), 3.68 (m, 24 H, CH_2O), 3.93 (m, 24 H, CH_2O), 4.53 (br, 12 H, $CH_2NH_2^+$), 4.74 (br, 4 H, CH_2N/CH_2O), 4.97 (s, 16 H, CH_2O), 5.39 (20 H, CH_2N/CH_2O), 6.58 (m, 8 H, ArH), 6.77 (m, 11 H, ArH), 7.06 (m, 16 H, ArH), 7.20 (m, 17 H, CONH/ArH), 7.32 (d, J = 8.24 Hz, 20 H, ArH), 7.38 (d, J = 8.24 Hz, 20 H, ArH), 7.58 (br, 6 H, NH_2^+), 7.77 (s, 6 H, ArH). ^{13}C NMR: δ 31.34, 34.59, 35.59, 52.05, 53.28, 58.17, 67.74, 68.03, 70.17, 70.49, 107.22, 108.45, 109.13, 111.24, 111.60, 112.32, 112.64, 120.99, 121.31, 121.68, 123.00, 124.69, 125.57, 126.20, 127.13, 127.60, 128.23, 128.95, 129.57, 131.63, 131.77, 132.00, 133.31, 136.02, 136.12, 145.87, 146.04, 146.68, 146.87, 147.03, 147.24, 147.67, 149.55, 149.77, 151.21, 159.88, 166.10, 166.74. HRMS (ESI): $C_{256}H_{300}F_{18}N_{23}O_{42}P_3$ $[M–3PF6]^+$: calcd 1457.0708; found 1457.0687.

Cytotoxicity

Mouse fibroblast L929 cells were obtained from American Type Culture Collection (ATCC, Manassas, VA, USA) and cultured with DMEM (Invitrogen, Carlsbad, CA, USA) containing 10% fetal bovine serum (FBS), 100 U/mL penicillin and 100 μg/mL streptomycin at 37 ºC and in a humidified 5% CO_2 atmosphere. 10,000 L929 cells were seeded into the wells of a 96-well plate. After 12 h incubation, the medium in the wells was replaced with 100 μL fresh medium containing different concentration of tested compounds. After 24 h incubation, medium was replaced with 100 μL fresh medium containing 0.5 mg/mL MTT (Sigma-Aldrich, St. Louis, MO, USA). After 3 h incubation, the medium was removed and formazan crystals were dissolved with 150 μL DMSO for 10 min on a shaker. The absorbance of each well was measured by a Multiskan GO UV/Vis microplate spectrophotometer (Thermo Fisher Scientific, Waltham, MA, USA) at a wavelength of 540 nm.

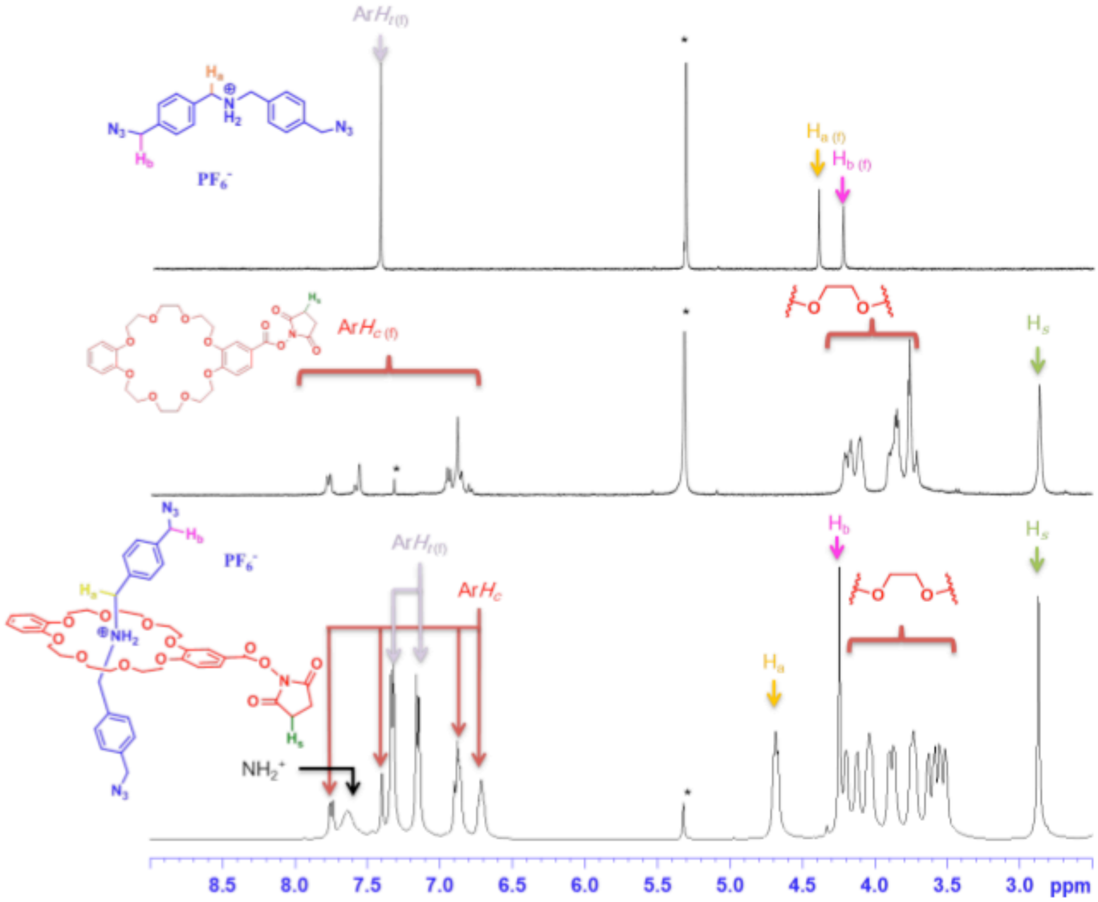

Figure S1. Partial ^{1}H NMR spectra (CD_2Cl_2, 2.5 to 9.0 ppm) of ammonium salt **1**-H•PF_6, crown ether **2**, and [2]pseudorotaxane **1**-H•PF_6⊂**2** (Asterisk: solvent residual signal, f = free). It is noticeable that benzylic methylene protons, H_a, that are adjacent to the ammonium centre, are remarkably shifted from δ = 4.4 ppm in **1**-H•PF_6 to δ = 4.7 ppm in (**1**-H•PF_6⊃**2**), indicating that complexation occurs and the H_a peak becomes triplet after complexation.

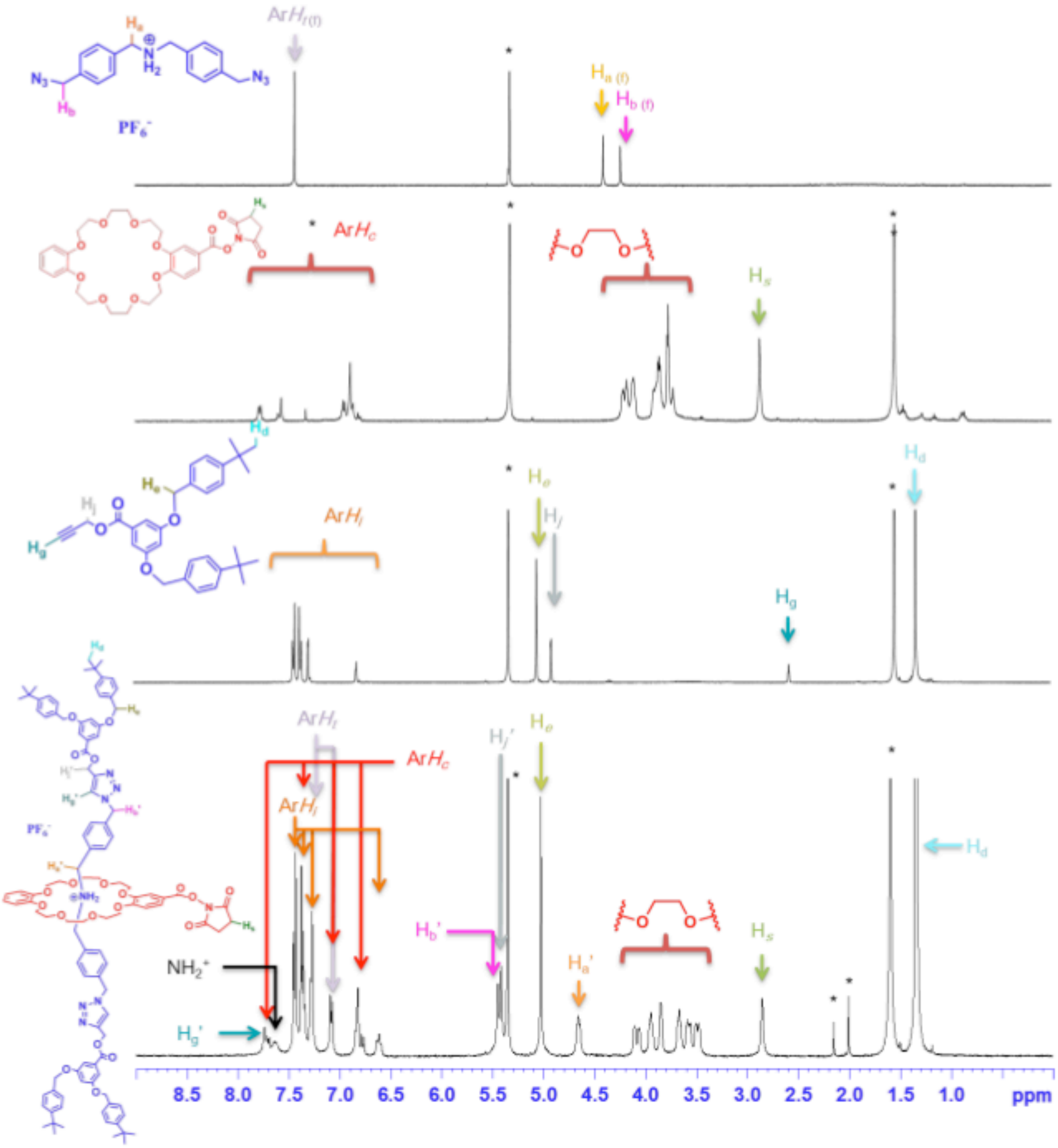

Figure S2. ^{1}H NMR spectra (CD_2Cl_2, 0 to 9 ppm) of ammonium salt **1**-H•PF_6, crown ether **2**, aryl ether surface **3**, and G1 [2]rotaxane dendron **4**-H•PF_6 (Asterisk: solvent residual signal). In the spectrum of aryl ether surface **3** and compared with the spectrum of G1 [2]rotaxane dendron **4**-H•PF_6, acetylene proton H_g, methylene proton H_j, and benzyl methylene proton H_b are observed up-field shifts from δ = 2.5 ppm in **3** greatly to δ = 7.7 ppm in **4**-H•PF_6, from δ = 4.9 ppm in **3** to δ = 5.4 ppm in **4**-H•PF_6 and from δ = 4.2 ppm in **1**-H•PF_6 to δ = 5.4 ppm in **4**-H•PF_6 respectively.

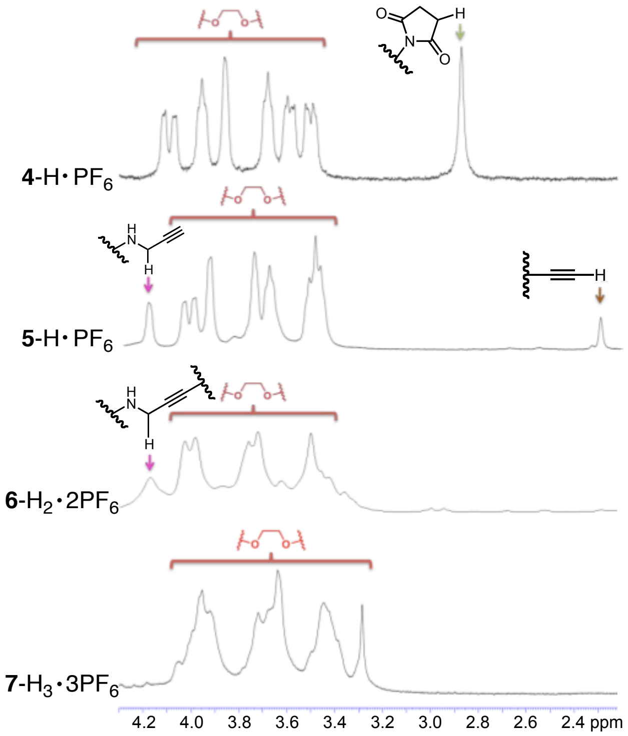

Figure S3. Partial ^{1}H NMR spectra (CD_2Cl_2, 2.2 to 4.3 ppm) of G1 [2]rotaxane dendron **4**-H•PF_6, G1 [2]rotaxane dendron **5**-H•PF_6, G1 [3]rotaxane dendrimer **6**-H_2•$2PF_6$, and G2 [4]rotaxane dendrimer **7**-H_3•$3PF_6$. The disappearance of succinimide proton (2.9 ppm) of **4**-H•PF_6 and appearance of propargyl protons (2.3 and 4.2 ppm) in **5**-H•PF_6 indicate the successful introduction of a terminal acetylene group of the G1 [2]rotaxane dendron. The disappearance of acetylenic proton (2.3 ppm) in **6**-H_2•$2PF_6$ reveals successful Glaser-Hay's acetyleneic oxidative homo-coupling between two molecules of **5**-H•PF_6. The disappearance of the propargyl proton signals (2.3 and 4.2 ppm) in G2 [4]rotaxane dendrimer **7**-H_3•$3PF_6$ reveals that the terminal acetylene group has been reacted with the modified CuAAC clicked condition.

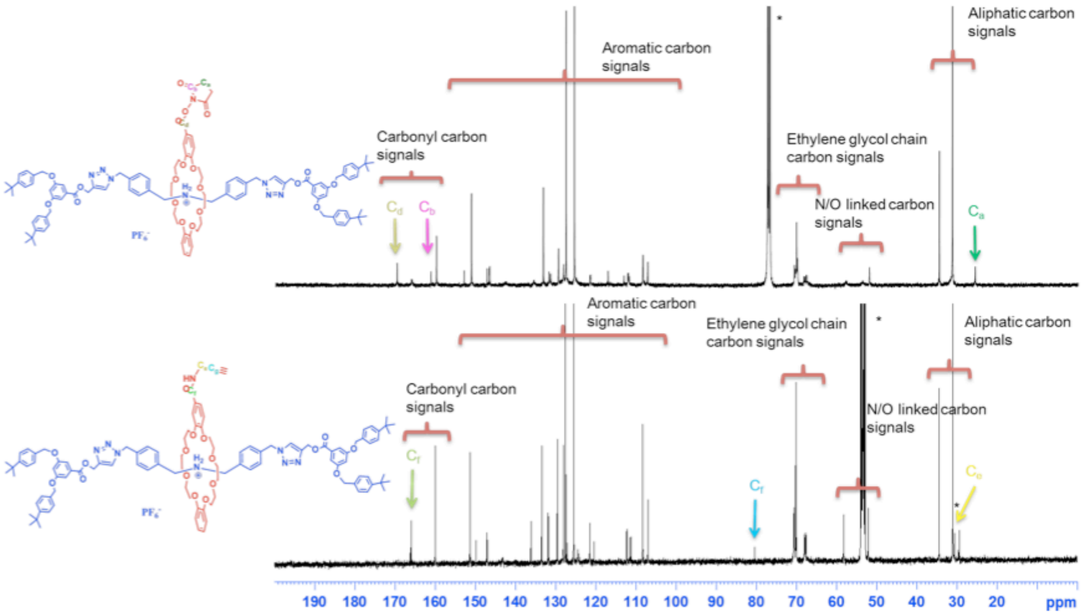

Figure S4. ^{13}C NMR spectra of G1 [2]rotaxane dendrons **4**-H•PF$_6$ (CDCl$_3$) and **5**-H•PF$_6$ (CD$_2$Cl$_2$) (Asterisk: solvent residual signal).

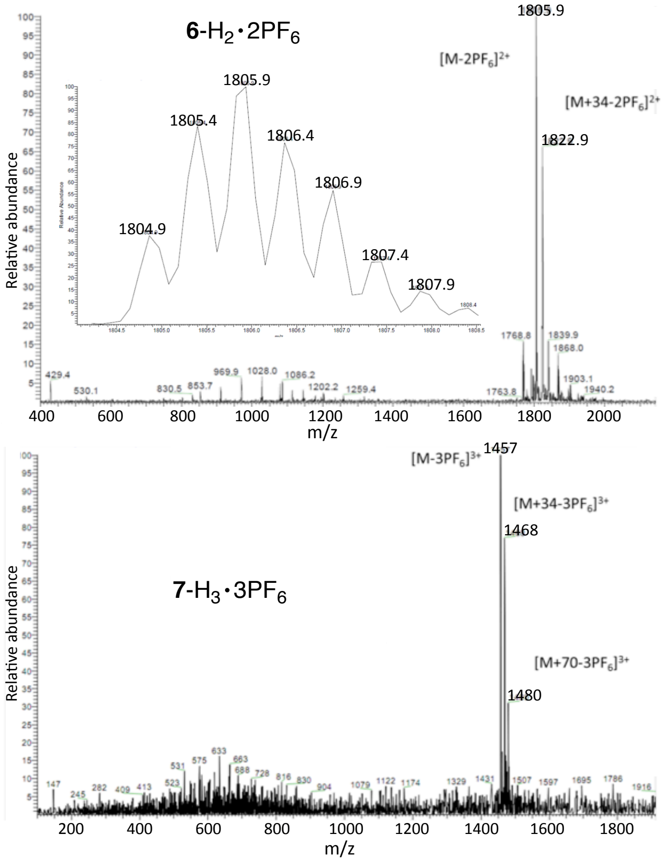

Figure S5. ESI-MS spectra of G1 [3]rotaxane dendrimer **6**-H_2•$2PF_6$, and G2 [4]rotaxane dendrimer **7**-H_3•$3PF_6$. For ESI-MS spectrum of **6**-H_2•$2PF_6$, it reveals two doubly charged peaks (m/z=1805.9, 100% and m/z=1822.9, 70%) which are corresponding to $[M–2PF_6]^{2+}$ and $[M+34–2PF_6]^{2+}$, respectively. On the other hand, for ESI-MS spectrum of **7**-H_3•$3PF_6$, it reveals three triply charged peaks (m/z=1457; 100%, m/z=1468; 75%, and m/z=1480; 35%) which are corresponding to $[M–3PF_6]^{3+}$, $[M+34–3PF_6]^{3+}$, and $[M+70–3PF_6]^{3+}$, respectively.

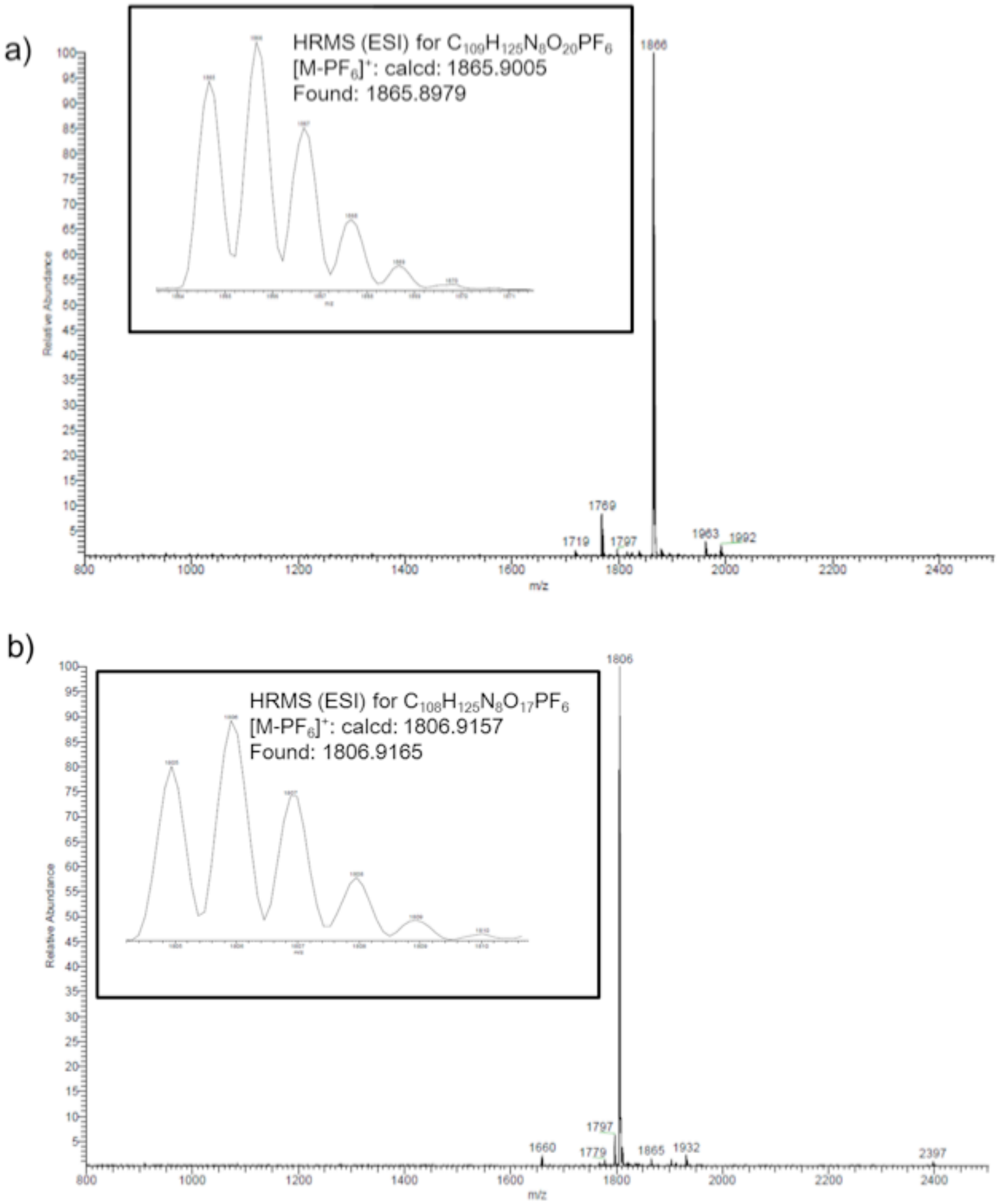

Figure S6. ESI-MS spectra of G1 [2]rotaxane dendrons (a) **4**-H•PF_6 and (b) **5**-H•PF_6, showing their $[M–PF_6]^+$ molecular ion peaks.

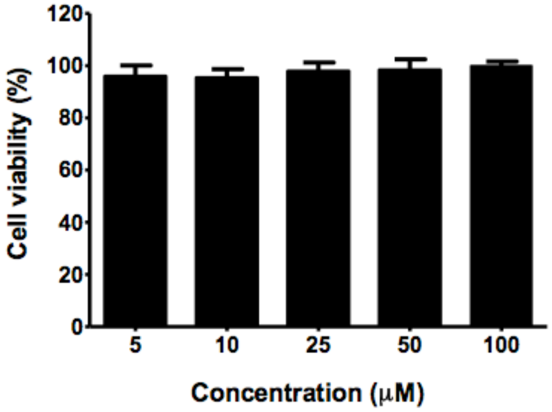

Figure S7. Cell viability of L929 fibroblast cells as determined by MTT assay after incubation with G1 [2]rotaxane dendron **4**-H•PF_6 at different concentrations for 24 h. Data are expressed as means with standard derivations from four experiments.

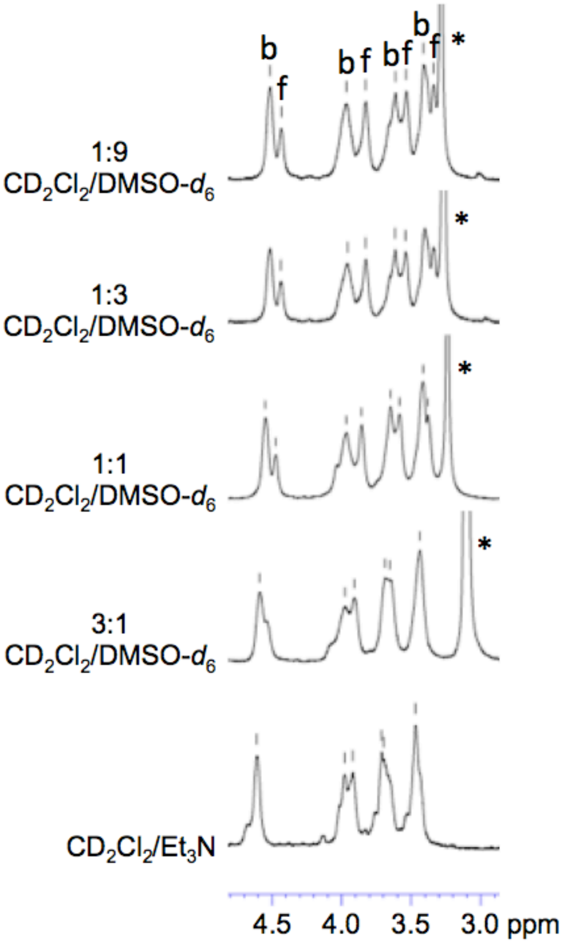

Figure S8. Partial ^{1}H NMR spectra (CD_2Cl_2, 2.9 to 4.8 ppm) of G2 [4]rotaxane dendrimer treated with triethylamine or DMSO-d_6 (*solvent residue signal, f=free, and b=bound). For the G2 [4]rotaxane dendrimer, the ammonium centres could not be deprotonated by triethylamine. This result confirms by observing the N^+CH proton signal (4.6 ppm) encircling with (bound) crown ether after triethylamine treatment.

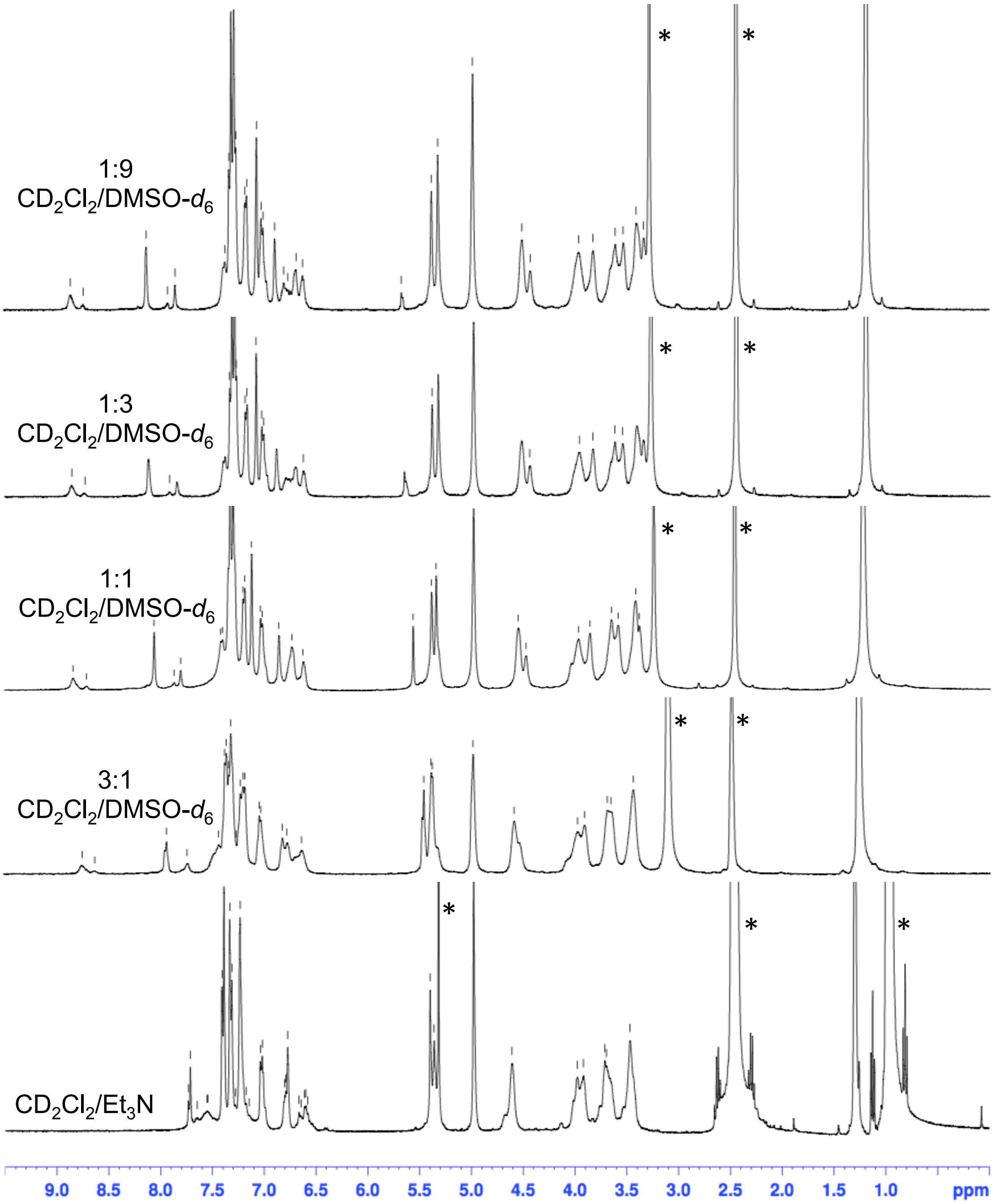

Figure S9. ^{1}H NMR spectra (CD_2Cl_2, 0 to 9.5 ppm) of G2 [4]rotaxane dendrimer treated with triethylamine or DMSO-d_6 (Asterisk: solvent residual signal).

Table S1. Contact angle measurements of bare HOPG with different solvent mixture droplets. Based on these control experiments, the determined contact angles with CH_2Cl_2/DMSO gradients are significantly lowered compared to the results showing in Table 1 (water contact angles of dendrimer coating on HOPG with different solvent mixture pre-treatments).

Solvent gradient (CH_2Cl_2/DMSO)	Contact angle (º)
3:1	19.2 ± 1.0
1:1	22.4 ± 1.0
1:3	26.4 ± 1.3
1:9	32.2 ± 0.4

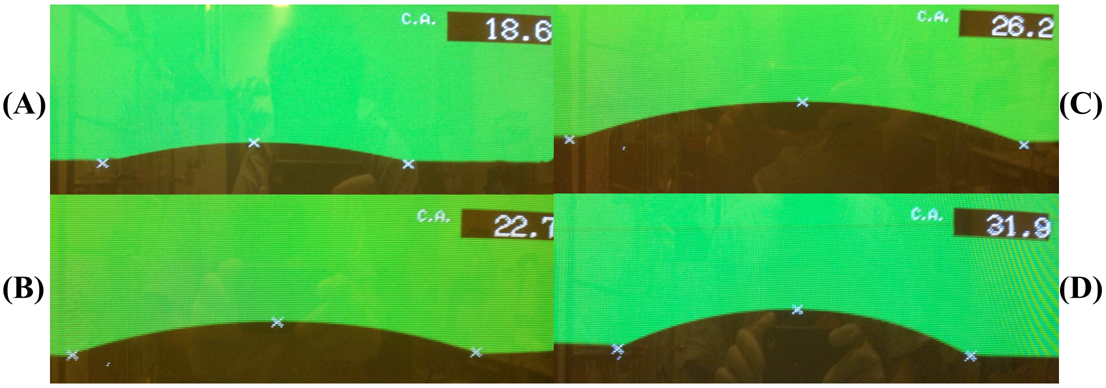

Figure S10. Images of contact angle measurements of CH_2Cl_2/DMSO gradient droplet on HOPG. (A): 3:1, (B): 1:1, (C): 1:3, and (D) 1:9.

References

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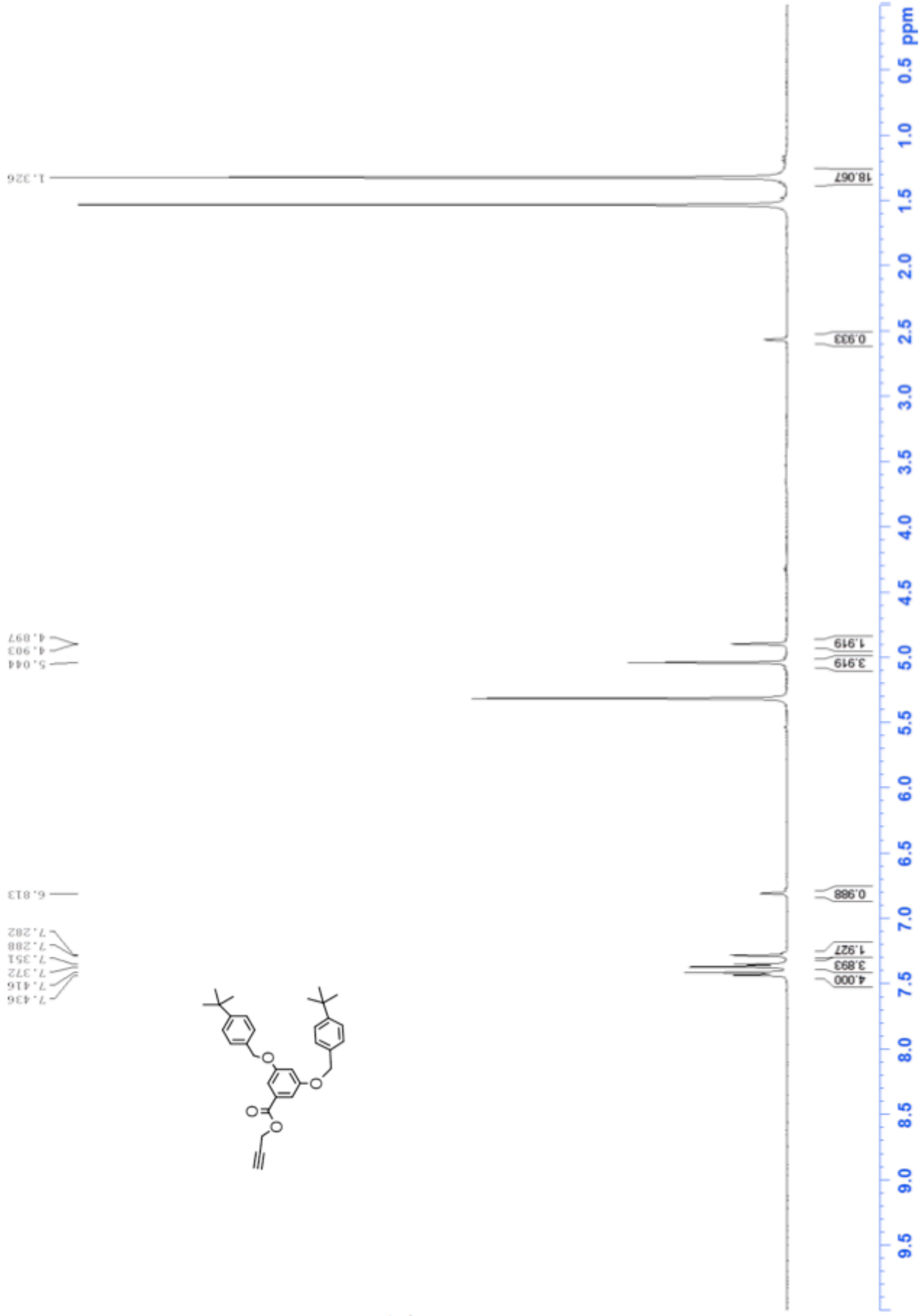
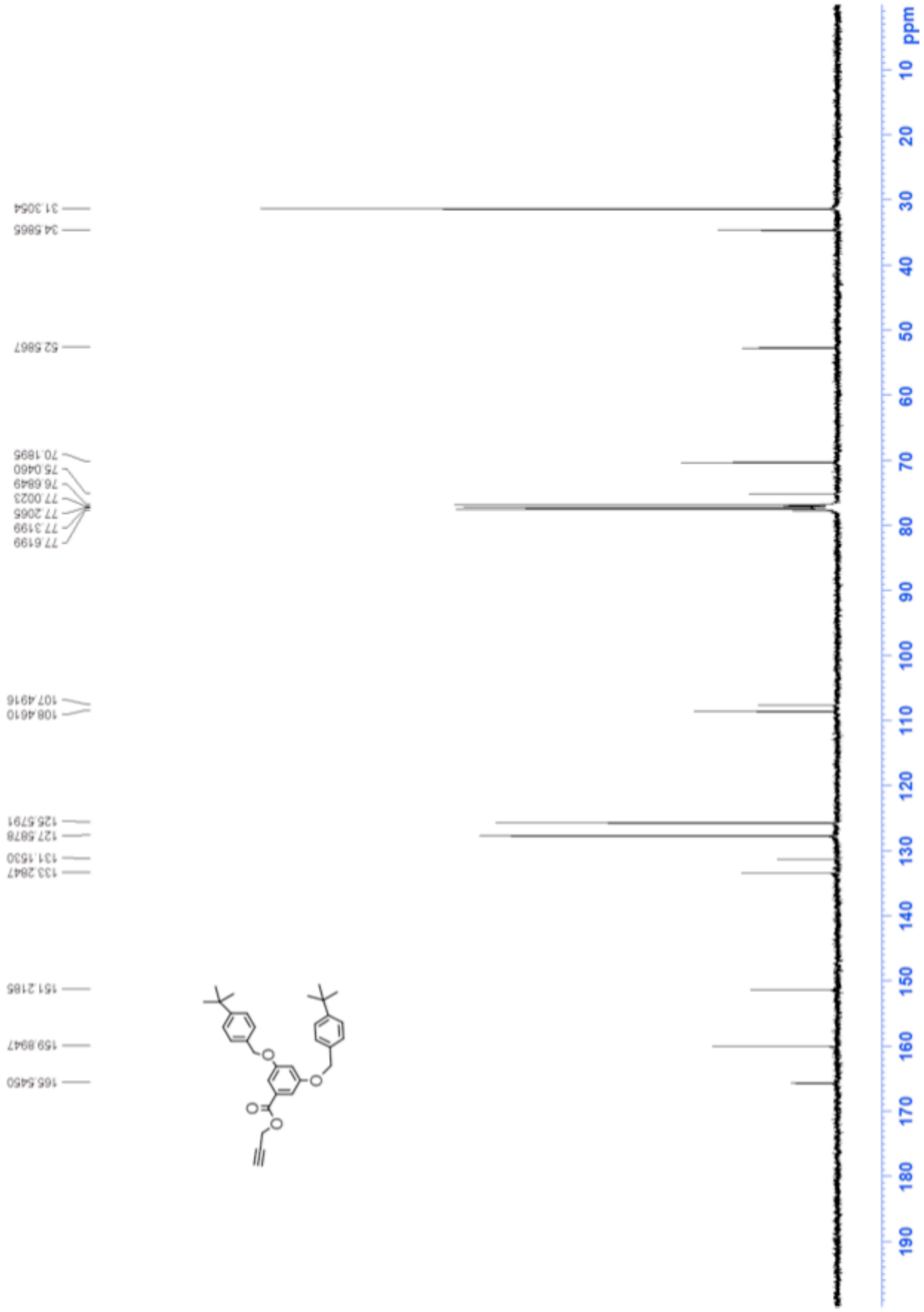
S2. J. W. Jones, W. S. Bryant, A. W. Bosman, R. A. J. Janssen, E. W. Meijer and H. W. Gibson, *J. Org. Chem.*, 2003, **68**, 2385-2389.

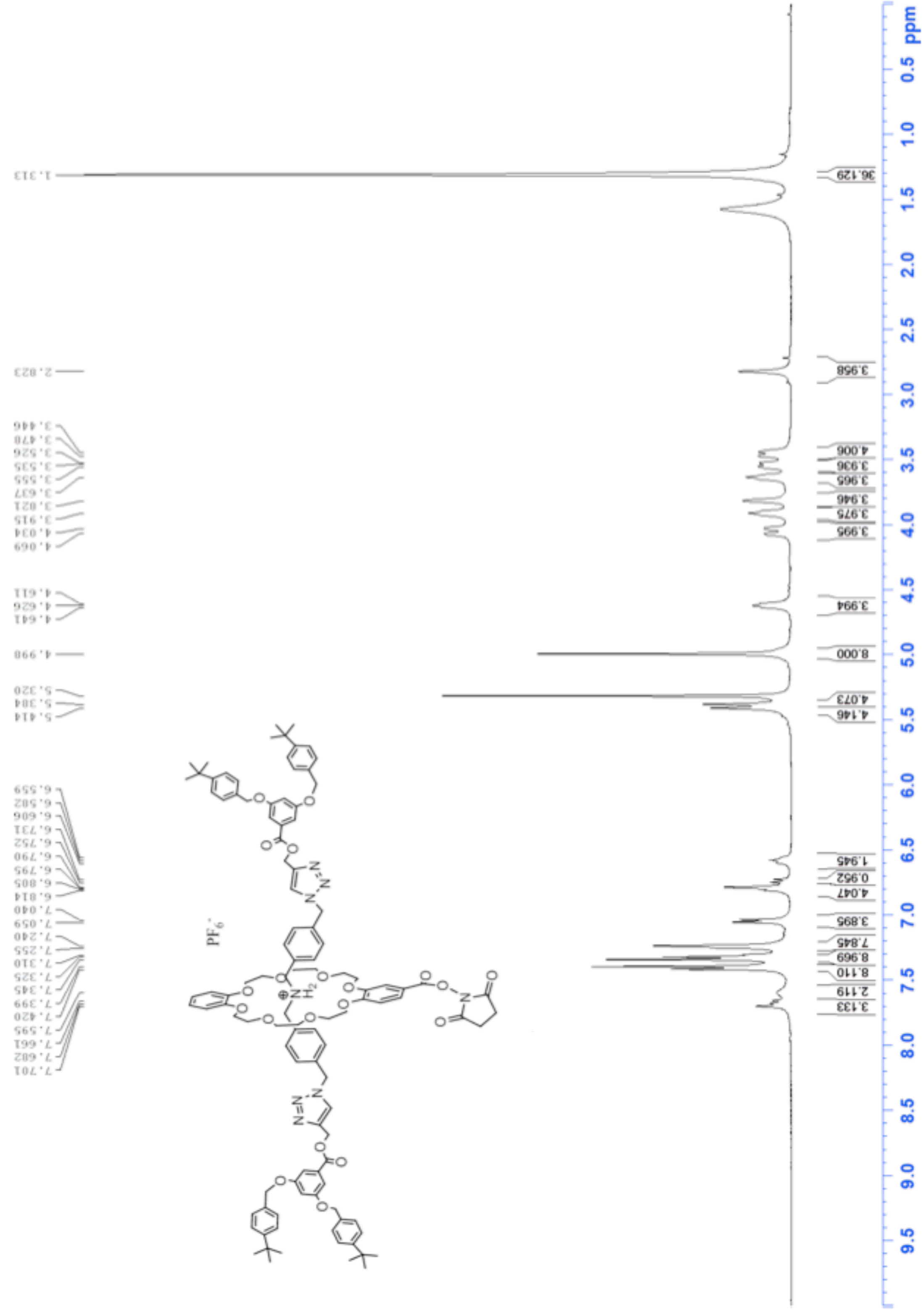
^{1}H NMR spectrum of compound **3** (CD_2Cl_2)



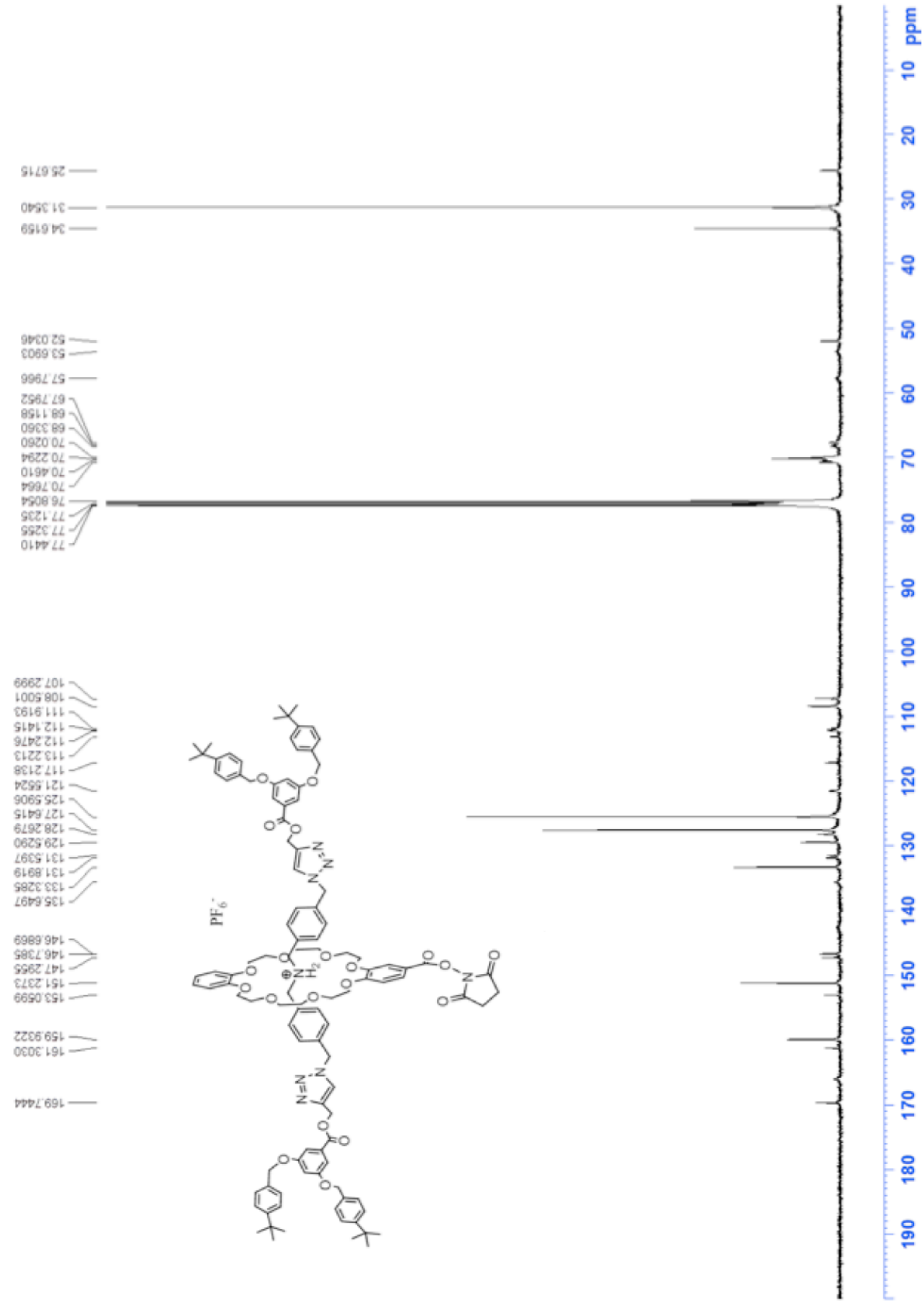
^{13}C NMR spectrum of compound **3** ($CDCl_3$)



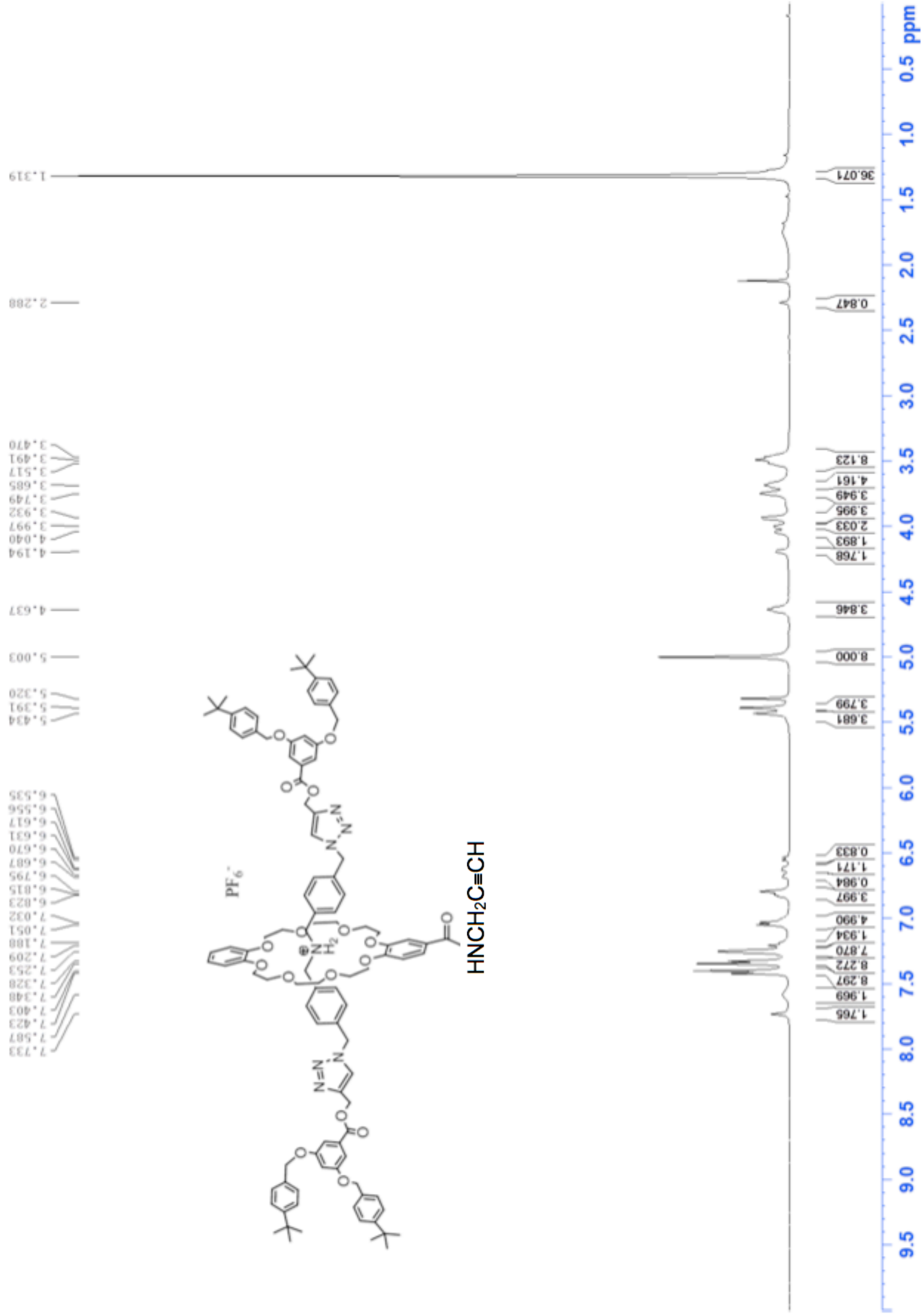
^{1}H NMR spectrum of G1 [2]rotaxane dendron **4**-H•PF$_6$ (CD$_2$Cl$_2$)



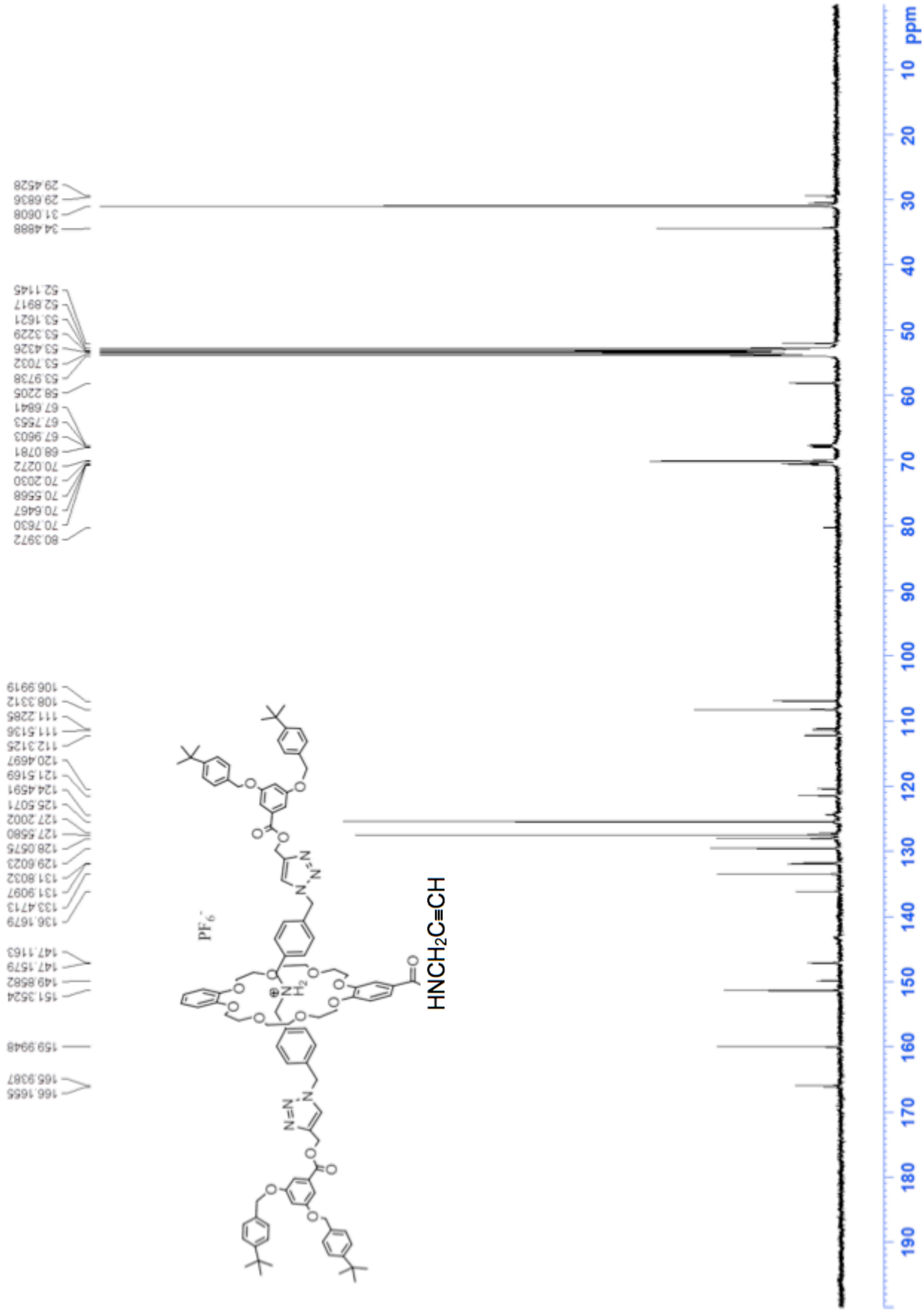
^{13}C NMR spectrum of G1 [2]rotaxane dendron **4**-H•PF_6 ($CDCl_3$)



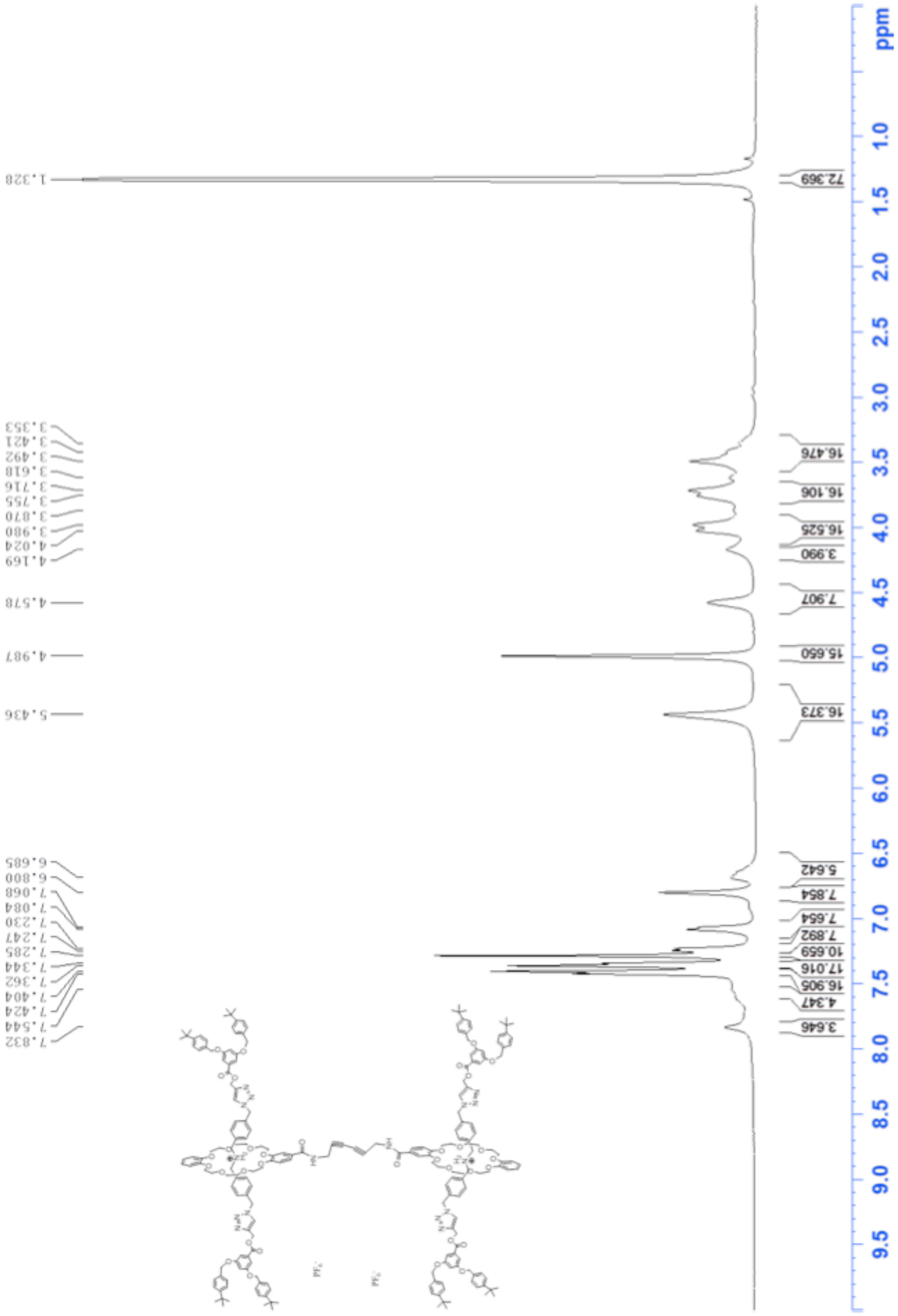
^{1}H NMR spectrum of G1 [2]rotaxane dendron **5**-H•PF$_6$ (CD$_2$Cl$_2$)



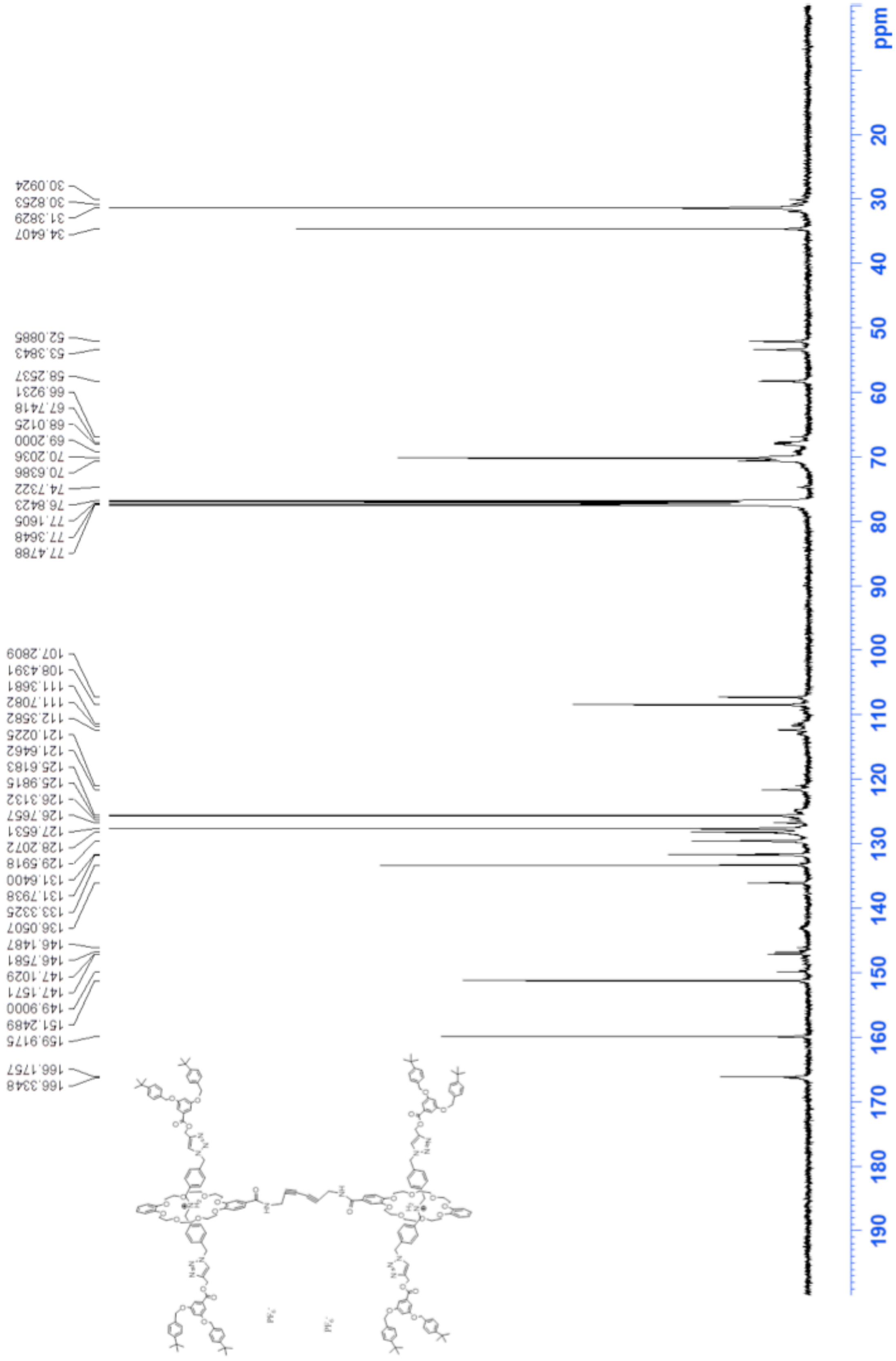
^{13}C NMR spectrum of G1 [2]rotaxane dendron **5**-H•PF$_6$ (CD$_2$Cl$_2$)



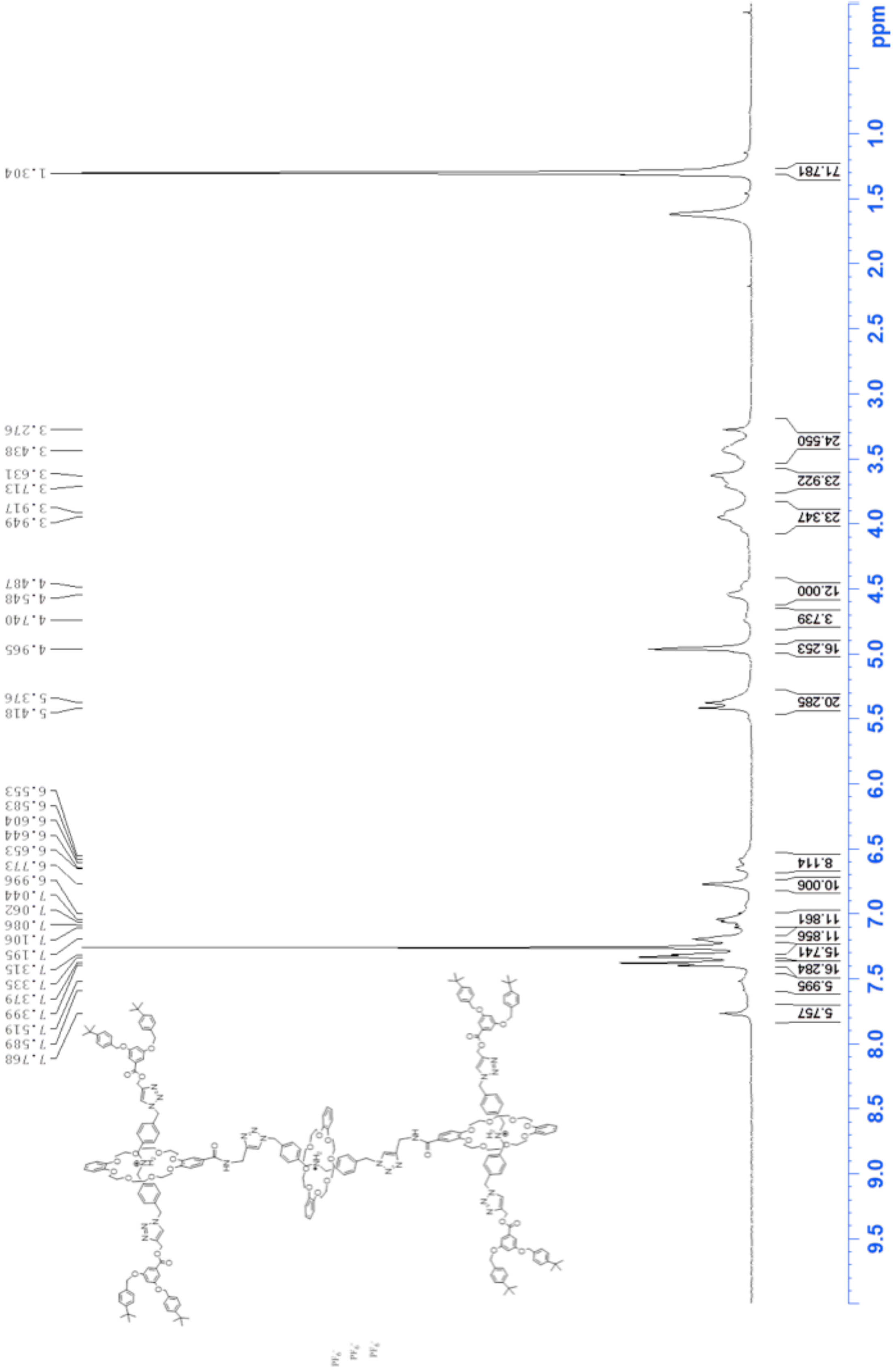
^{1}H NMR spectrum of G1 [3]rotaxane dendrimer **6**-H_2•$2PF_6$ ($CDCl_3$)



^{13}C NMR spectrum of G1 [3]rotaxane dendrimer **6**-H_2•$2PF_6$ ($CDCl_3$)



^{1}H NMR spectrum of G2 [4]rotaxane dendrimer **7**-H_3•3PF_6 ($CDCl_3$)



^{13}C NMR spectrum of G2 [4]rotaxane dendrimer **7**-H_3•$3PF_6$ ($CDCl_3$)