Electronic Supporting Information

Facile construction of organometallic rotaxane-terminated dendrimers using neutral platinum-acetylides as main scaffold

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Section A. Materials/General Methods/Instrumentation

All reagents were commercially available and used as supplied without further purification, organometallic [2]rotaxane **3**[S1] were prepared according to the published procedures. Deuterated solvents were purchased from Cambridge Isotope Laboratory (Andover, MA).

NMR spectra were recorded on a Bruker DRX 400 (400 MHz) spectrometer. ^{1}H and ^{13}C NMR chemical shifts are reported relative to residual solvent signals, and $^{31}P\{^{1}H\}$ NMR chemical shifts are referenced to an external unlocked sample of 85% H_3PO_4 (δ 0.0). The two-dimensional diffusion-ordered NMR spectroscopy (2D-DOSY) was recorded on a Bruker DRX500 spectrometer. The AFM samples were prepared by dropping the solutions onto a mica sheet. AFM images were obtained on a Dimension FastScan (Bruker) by using ScanAsyst mode under the ambient condition. The DLS samples were prepared in DCM at a concentration of 10^{-6} mol/L. DLS measurements were performed under a Malvern Zetasizer Nano-ZS light scattering apparatus (Malvern Instruments, U.K.) with a He-Ne laser (633 nm, 4 mW). TEM images were obtained using a Philips TECNAI-12 instrument with an accelerating voltage of 120 kV. UV−vis spectra were recorded in a quartz cell (light path 10 mm) on a Cary 50Bio UV-Visible spectrophotometer. Steady-state fluorescence spectra were recorded in a conventional quartz cell (light path 10 mm) on a Cary Eclipse fluorescence spectrophotometer.

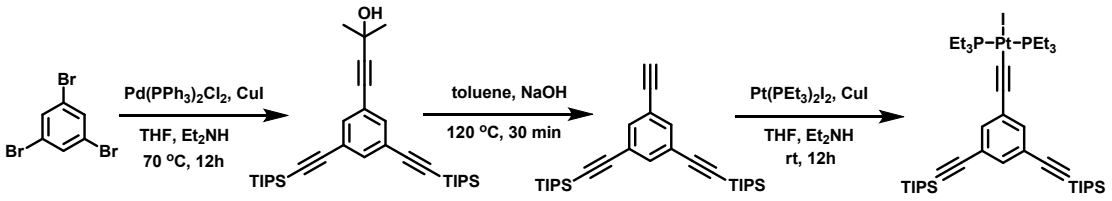
The MALDI MS experiments were carried out on a Bruker UltrafleXtreme MALDI TOF/TOF Mass Spectrometer (Bruker Daltonics, Billerica, MA), equipped with smartbeam-II laser. All spectra were measured in positive reflectron or linear mode. The instrument was

calibrated externally with BSA, myoglobin, cytochrom C and insulin standards prior to each measurement.*Trans*-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile(DCTB) dissolved in $CHCl_3$ at 5 mg/mL was used as matrix. The samples were dissolved in $CHCl_3$ at 5-10 mg/mL. Sample preparation involved depositing 0.5 μL of matrix on the wells of a 384-well ground-steel plate, allowing the spots to dry, depositing 0.5 μL of each sample on top of a dry matrix spot, and adding another 0.5 μL of matrix on top of the dry sample (sandwich method). Compared to the commonly used dry droplet method, in which a mixture of matrix and sample is deposited onto the target plate, the sandwich method minimizes the disintegration of large molecules and allows for facile variation of the matrix to maximize the signal intensity.

Section B. Synthetic Protocols and Characterization

1. Synthesis of key building block platinum-acetylide complex **2**.

Scheme S1: The synthesis route of platinum-acetylide complex 2.



Synthesis of 2: A Schlenk flask was charge with 1-ethynyl-3,5-bis-[(triisopropylsilanyl)-ethynyl]-benzene(**A**) (800 mg, 1.73 mmol) and $Pt(PEt_3)_2I_2$ (4.74 g, 6.92 mmol). The Schlenk flask was then evacuated via reduced pressure and backfilled with N_2 for three times. Next, THF (50 mL) and Et_2NH (25 mL) was added via syringe. The resultant solution was stirred for 5 min. Then CuI (33 mg, 0.173 mmol) was added to the mixture under N_2 atmosphere, and the mixture was allowed to stir overnight. The solvent was then removed by reduced pressure, and the compound was purified by column chromatography on silica gel (eluent: petroleum ether/dichloromethane, v/v, 50:1 to 10:1). A yellow solid was obtained (1.21 g, 68% yield). M.p. 94 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.34 (s, 1H), 7.28 (br, 2H), 2.21 (m, 12H), 1.16 (m, 18H), 1.12 (s, 42H); ^{31}P NMR ($CDCl_3$, 161.9 MHz): δ 9.18; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 134.1, 131.9, 128.9, 123.7, 106.3, 99.0, 92.3, 91.2, 18.8, 16.7, 11.4, 8.40; MS: simulated value for $C_{42}H_{75}IP_2PtSi_2$ (1019.36). (MALDI-TOF-MS) 894.5 ($[M - I]^+$).

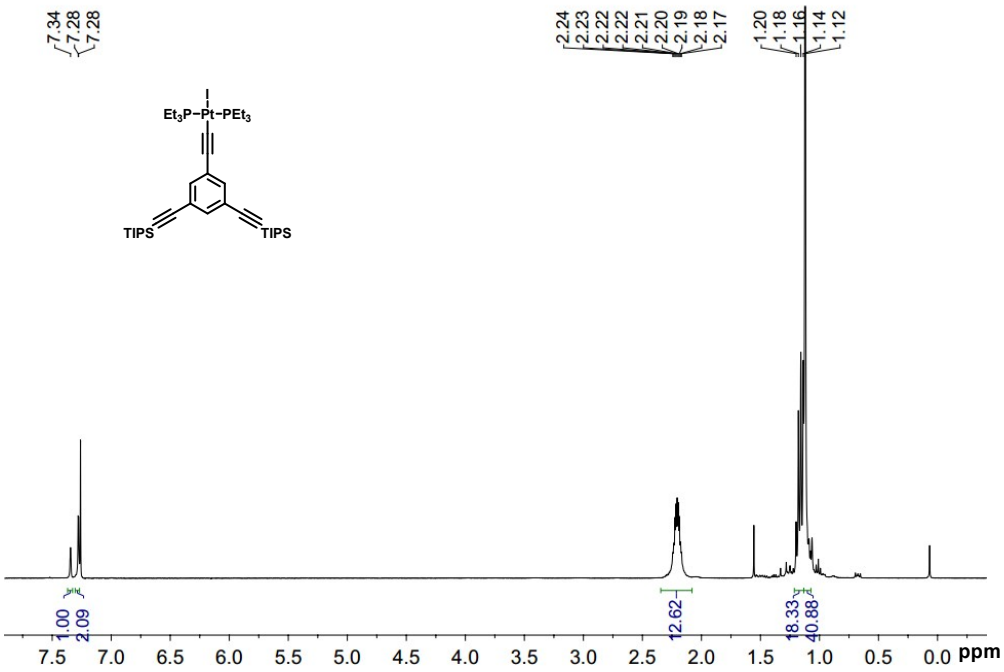


Figure S1. ^{1}H NMR spectrum ($CDCl_3$, room temperature, 400 MHz) of **2**.

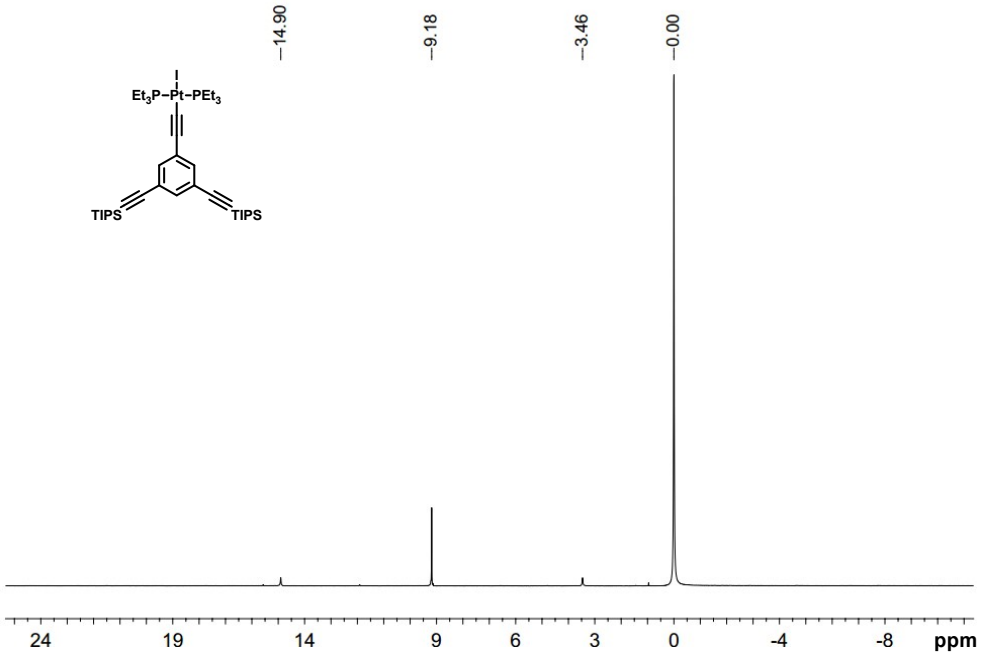


Figure S2. ^{31}P NMR spectrum ($CDCl_3$, room temperature, 161.9 MHz) of **2**.

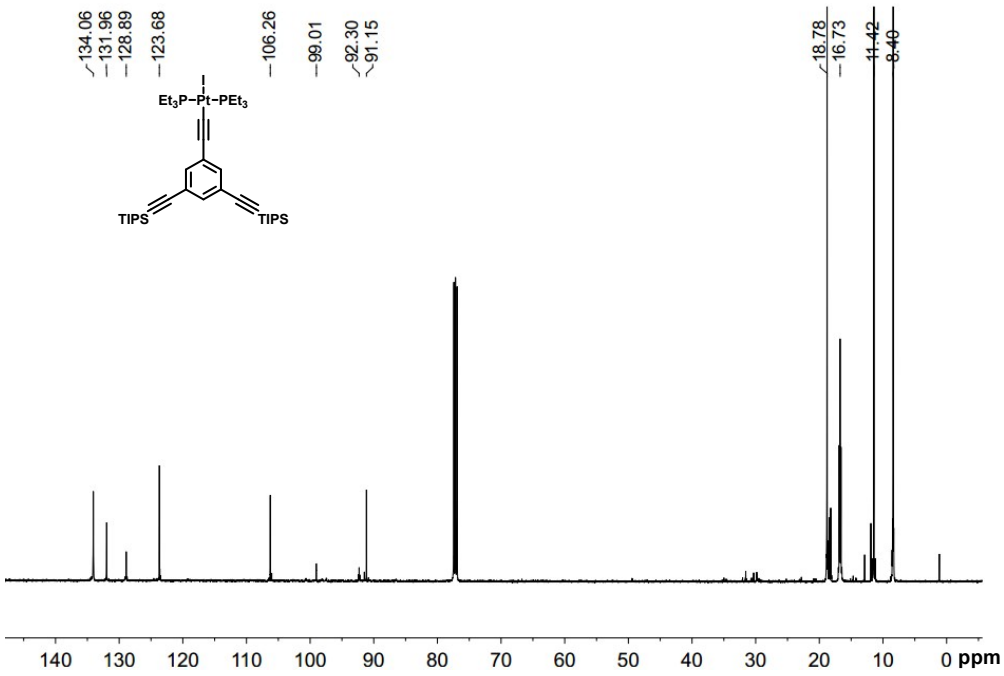


Figure S3. ^{13}C NMR spectrum ($CDCl_3$, room temperature, 100 MHz) of **2**.

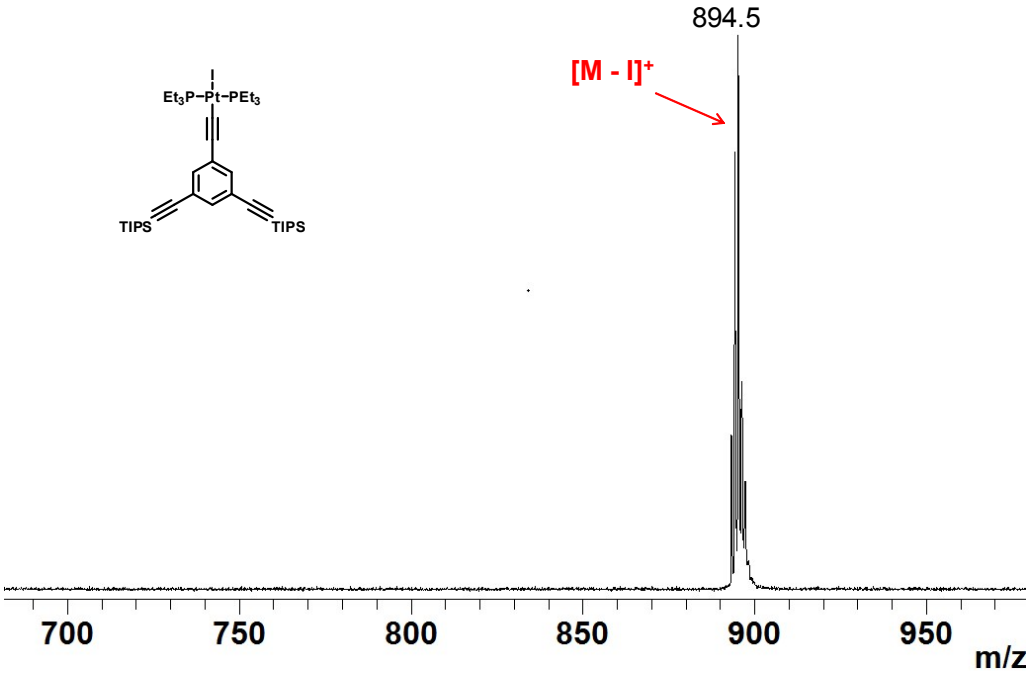
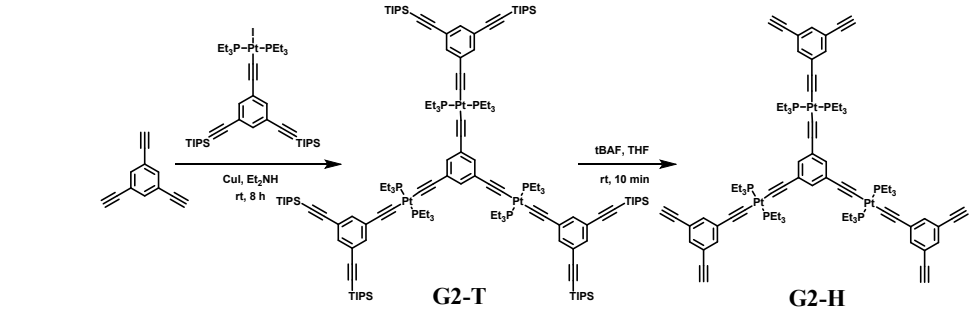
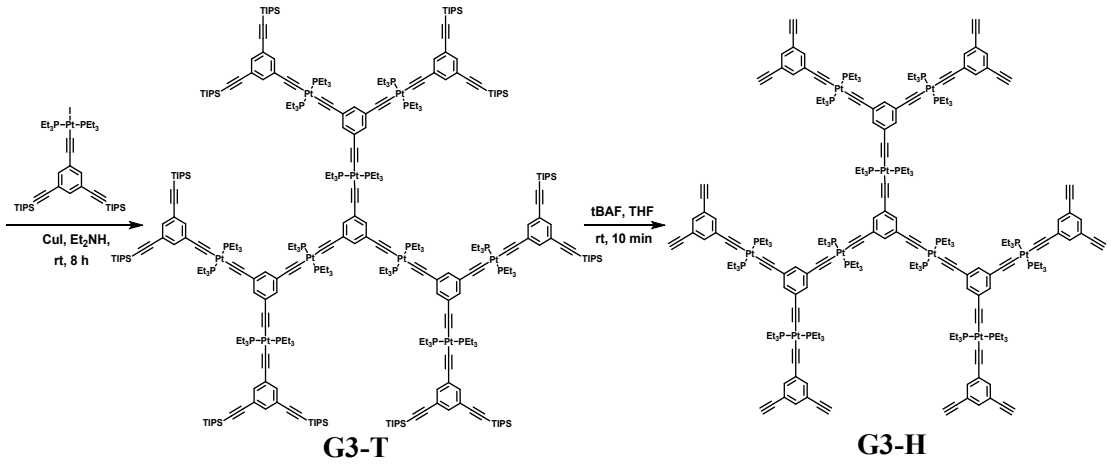


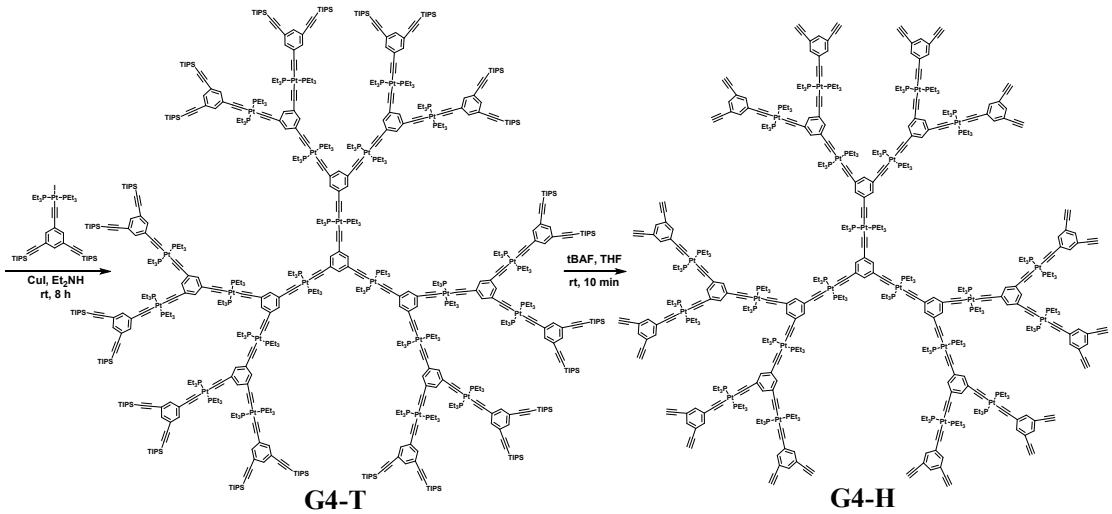
Figure S4. MALDI-TOF-MS spectrum of **2**.

2. Synthesis of dendrimers **Gn-T** and **Gn-H**.

Scheme S2: The synthesis route of Gn-T and Gn-H.







Synthesis of G2-T: Schlenk flask was charge with 1,3,5-triethynylbenzene (44.4 mg 0.296 mmol) and 2 (950 mg, 0.932 mmol). The Schlenk flask was then evacuated via reduced pressure and backfilled with N_2 for three times. Next, Et_2NH (2 mL) was added via syringe. The solution was stirred for 5 min. Then CuI (9.0 mg) was added into the mixture under N_2 atmosphere, and the mixture was allowed to stir overnight. The solvent was then removed by reduced pressure, and the compound was purified by alumina column chromatography (eluent: ether/dichloromethane (2:1)). A slight yellow solid was obtained (620 mg, 67% yield). M.p. 115 ^oC. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.30 (br, 3H), 7.28 (br, 6H), 7.00 (s, 3H), 2.15 (m, 36H), 1.20 (m, 54H), 1.12 (s, 126H); ^{31}P NMR ($CDCl_3$, 161.9 MHz): δ11.60; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 134.3, 131.4, 130.6, 129.1, 127.9, 123.4, 110.7, 109.7, 108.0, 106.4, 105.9, 90.7, 18.8, 16.4, 11.4, 8.4; MS: simulated value for $C_{138}H_{228}P_6Pt_3Si_6$ (2824.38). (MALDI-TOF-MS) 2824.4 ($[M]^+$).

Synthesis of G2-H: A solution of the **G2-T** (150 mg, 0.053 mmol) in THF was cooled in ice bath, and a solution of Bu_4NF (0.48 mmol) in THF (1.0 M) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 10 min. The solvent was removed under reduced pressure and the residue was purified by alumina column chromatography with dichloromethane: 85 mg (85% yield) of a slight yellow solid was afforded. The related characterization was consistent with the literature.[S2]

Synthesis of G3-T: G2-H (60 mg 0.0318 mmol) and 2 (204 mg, 0.200 mmol) were reacted in a similar manner to that of the preparation of **G2-T**. Column chromatography on alumina was performed with dichloromethane as eluent: 78 mg (34% yield) of a slight yellow solid was afforded. M.p. 167 ^oC. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.30 (br, 6H), 7.28 (br, 12H), 7.00 (s, 12H), 2.15 (m, 108H), 1.20 (m, 162H), 1.12 (s, 252H); ^{31}P NMR ($CDCl_3$, 161.9 MHz): δ 11.40, 11.14; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 134.2, 131.4, 130.6, 129.1, 128.0, 127.9, 123.4, 109.7, 109.6, 108.8, 106.4, 106.2, 105.8, 91.0, 90.7, 18.7, 16.4, 11.3, 8.3; MS: simulated value for $C_{336}H_{552}P_{18}Pt_9Si_{12}$ (7236.25). (MALDI-TOF-MS) 7359.5 ($[M + Na]^+$).

Synthesis of G3-H: A solution of the **G3-T** (130 mg, 0.018 mmol) in THF was cooled in ice bath, and a solution of Bu_4NF (0.32 mmol) in THF (1.0 M) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 10 min. The solvent was removed under reduced pressure and the residue was purified by alumina column chromatography with dichloromethane: 87 mg (91% yield) of a slight yellow solid was afforded. M.p. >250 ^oC

(decomp). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36 (br, 6H), 7.33 (br, 12H), 6.99 (br, 12H), 3.05 (s, 12H), 2.15 (m, 108H), 1.20 (m, 162H); ^{31}P NMR ($CDCl_3$, 161.9 MHz): δ 11.68, 11.39; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 134.8, 132.0, 130.7, 129.5, 128.0, 122.2, 110.0, 107.6, 82.9, 29.8, 18.0, 16.5, 8.5; MS: simulated value for $C_{228}H_{312}P_{18}Pt_9$ (5362.65). (MALDI-TOF-MS) 5386.3 ($[M + Na]^+$).

Synthesis of G4-T: G3-H (50 mg 0.0093 mmol) and 2 (119 mg, 0.117 mmol) were reacted in a similar manner to that of the preparation of **G2-T**. Alumina column chromatography was performed with dichloromethane as eluent: 79 mg (53% yield) of a slight yellow solid was afforded. M.p. 190 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.29 (br,12H), 7.28 (br, 24H), 6.99 (s, 30H), 2.15 (m, 252H), 1.20 (m, 378H), 1.12 (s, 504H); ^{31}P NMR ($CDCl_3$, 161.9 MHz): δ 11.64, 11.38; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 134.2, 131.5, 130.5, 129.1, 128.0, 123.4, 106.5, 90.6, 37.1, 29.7, 27.1, 18.7, 16.5, 16.3, 12.8, 11.3, 8.3. MS: simulated value for $C_{732}H_{1200}P_{42}Pt_{21}Si_{24}$ (16059.99). (GPC) M_n 11463.

Synthesis of G4-H: G4-T (128 mg, 0.0080 mmol) was treated with a solution of Bu_4NF (0.29 mL) in THF (1.0 M) in a similar manner to that of preparation of the **G2-H**. The crude product was purified by alumina column chromatography with dichloromethane as eluent: 81 mg (82% yield) of a slight yellow solid was afforded. M.p. >250 ^{o}C (decomp). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36 (br, 12H), 7.33 (br, 24H), 6.99 (br, 30H), 3.05 (s, 24H), 2.15 (m, 252H) 1.20 (m, 378H); ^{31}P NMR ($CDCl_3$, 161.9 MHz): δ 11.65, 11.36; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 130.9, 130.6, 129.4, 128.8, 127.8, 112.1, 122.1, 82.8, 68.2, 38.7, 30.4, 28.9, 23.0, 17.9, 16.4, 14.0, 11.0, 8.4. MS: simulated value for $C_{516}H_{720}P_{42}Pt_{21}$ (12312.79). (GPC) M_n 9328.

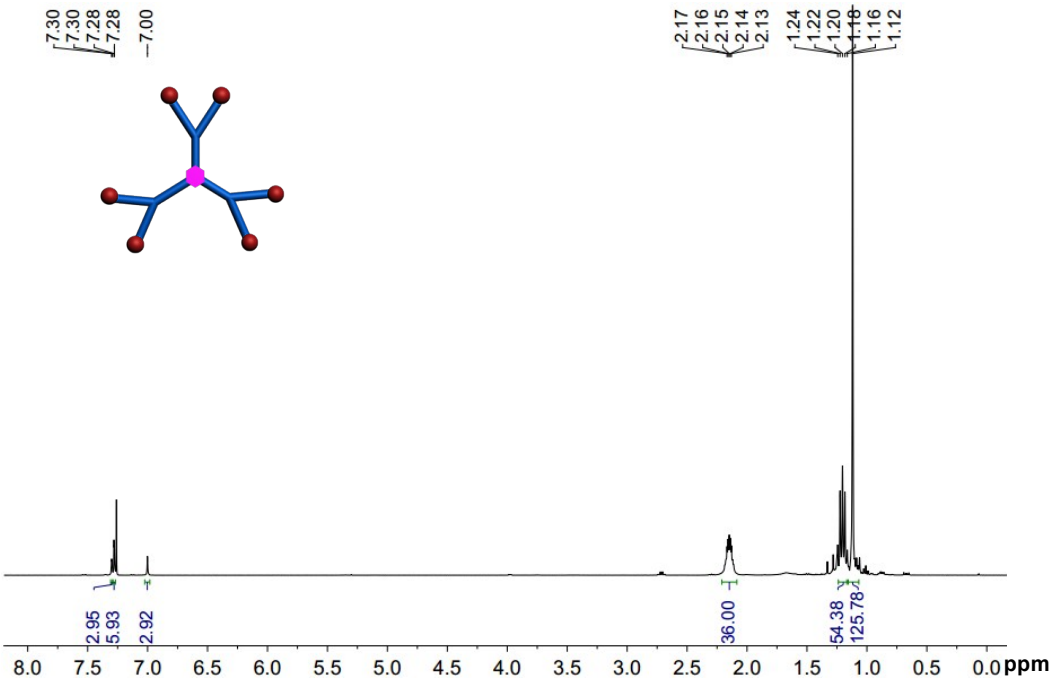


Figure S4. ^{1}H NMR spectrum ($CDCl_3$, room temperature, 400 MHz) of **G2-T**.

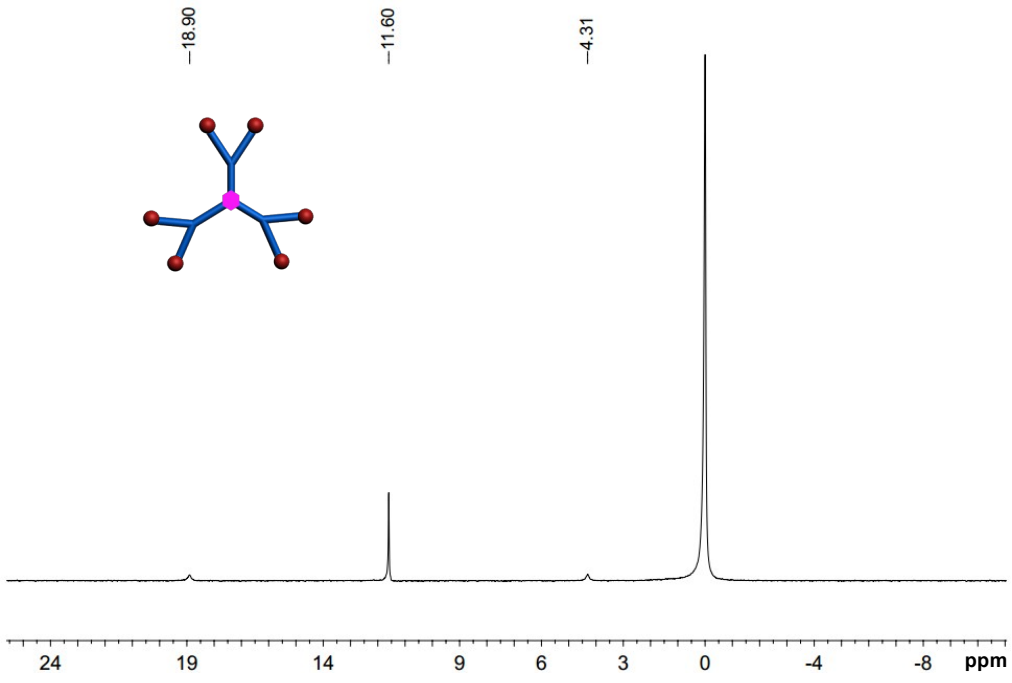


Figure S5. ^{31}P NMR spectrum ($CDCl_3$, room temperature, 161.9 MHz) of **G2-T**.

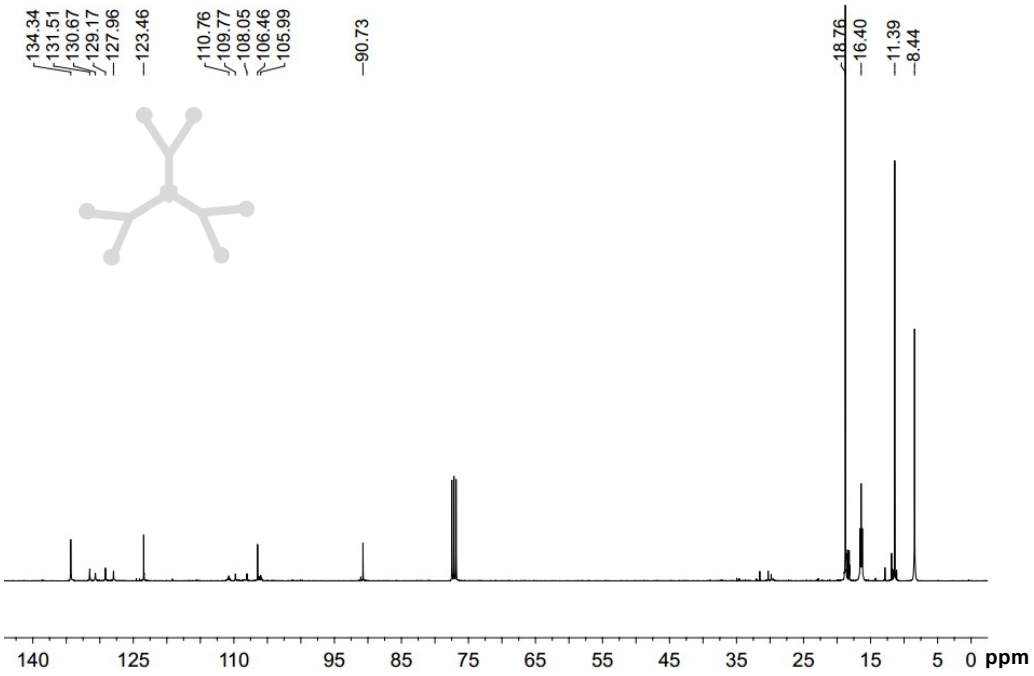


Figure S6. ^{13}C NMR spectrum ($CDCl_3$, room temperature, 125 MHz) of **G2-T**.

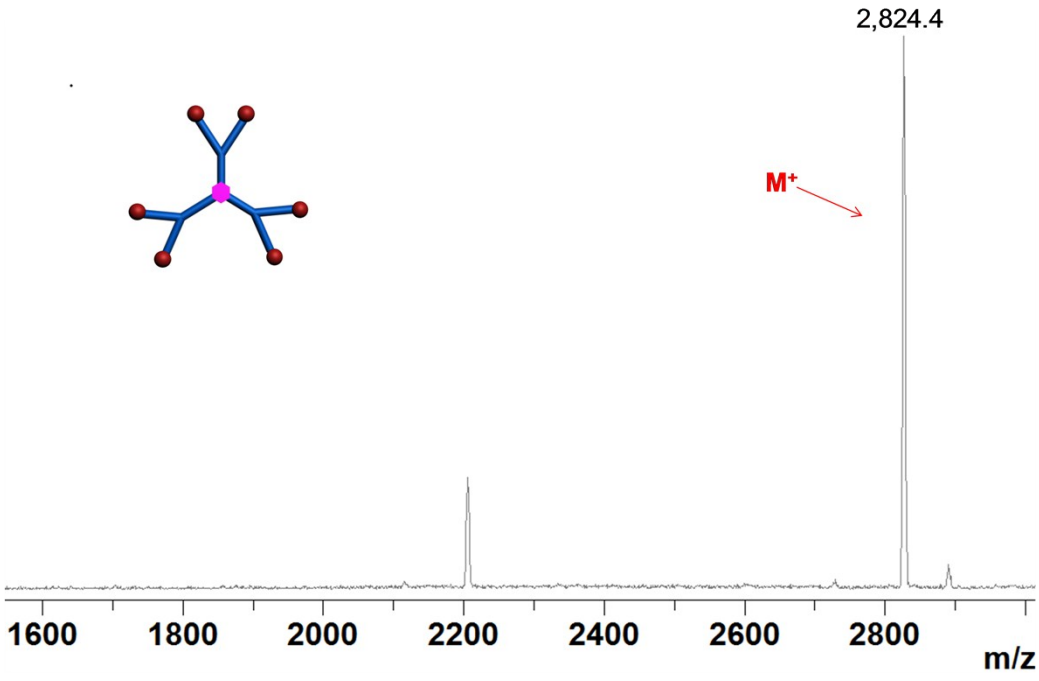


Figure S7. MALDI-TOF-MS spectrum of **G2-T**.

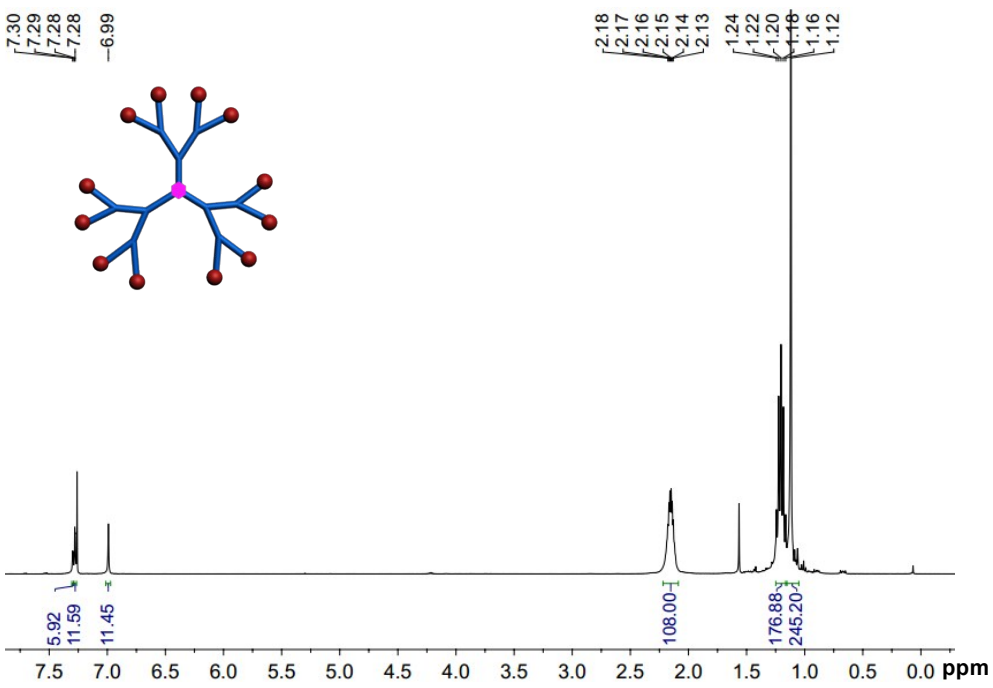


Figure S8. ^{1}H NMR spectrum ($CDCl_3$, room temperature, 400 MHz) of **G3-T**.

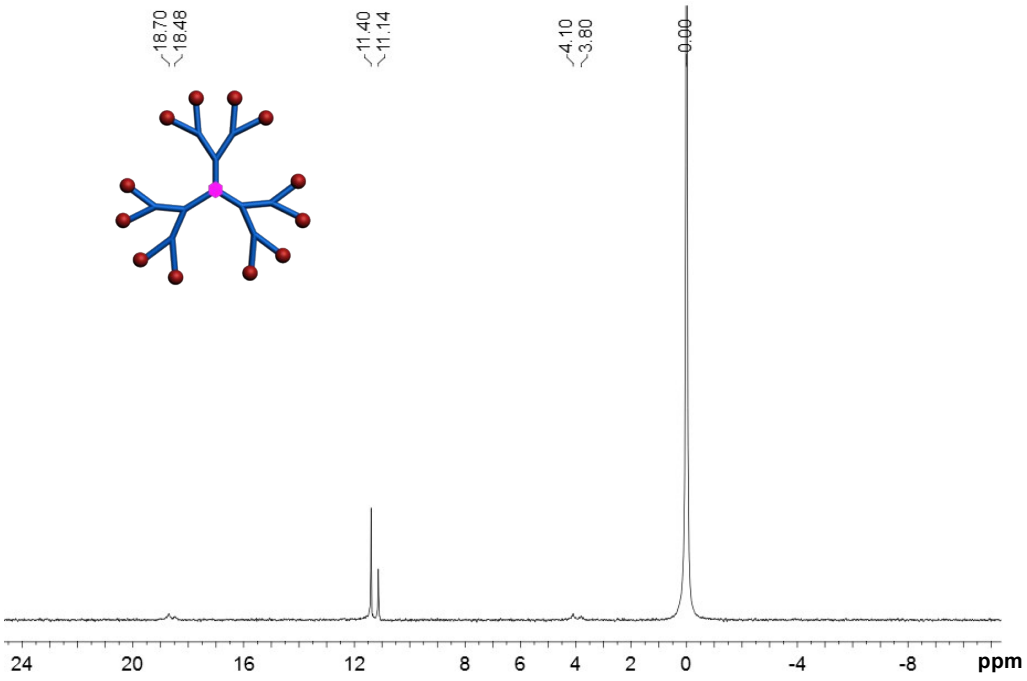


Figure S9. ^{13}P NMR spectrum ($CDCl_3$, room temperature, 161.9 MHz) of **G3-T**.

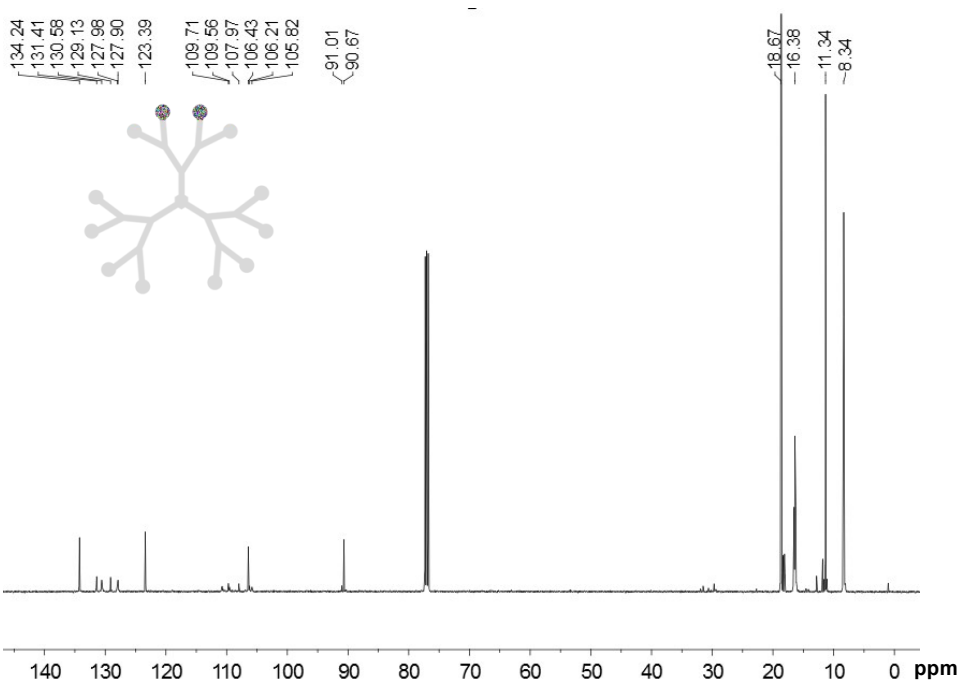


Figure S10. ^{13}C NMR spectrum ($CDCl_3$, room temperature, 125 MHz) of **G3-T**.

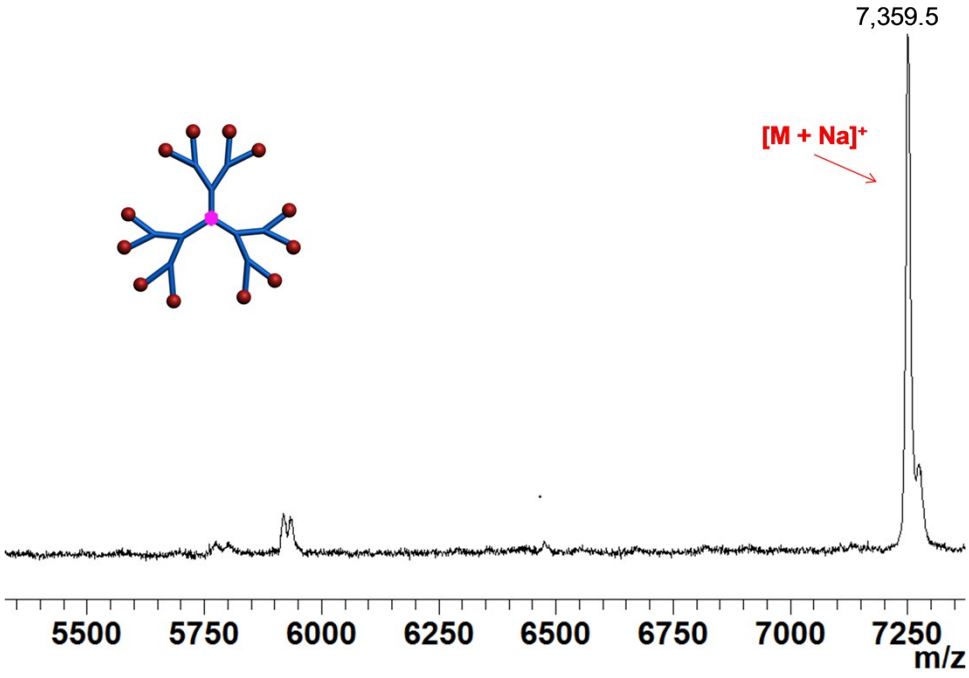


Figure S11. MALDI-TOF-MS spectrum of **G3-T**.

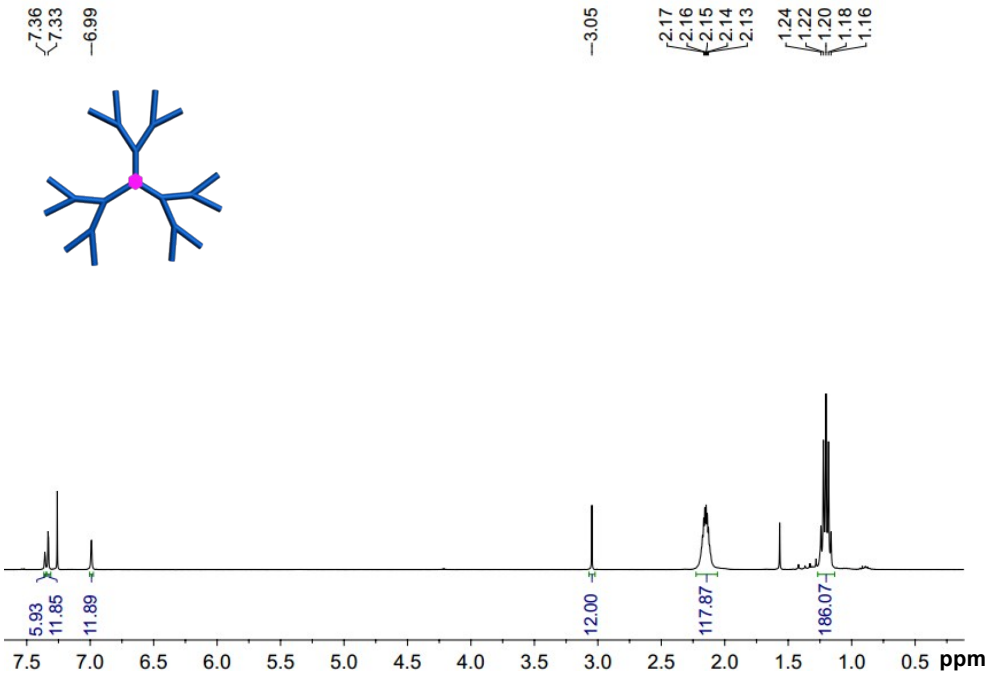


Figure S12. ^{1}H NMR spectrum ($CDCl_3$, room temperature, 400 MHz) of **G3-H**.

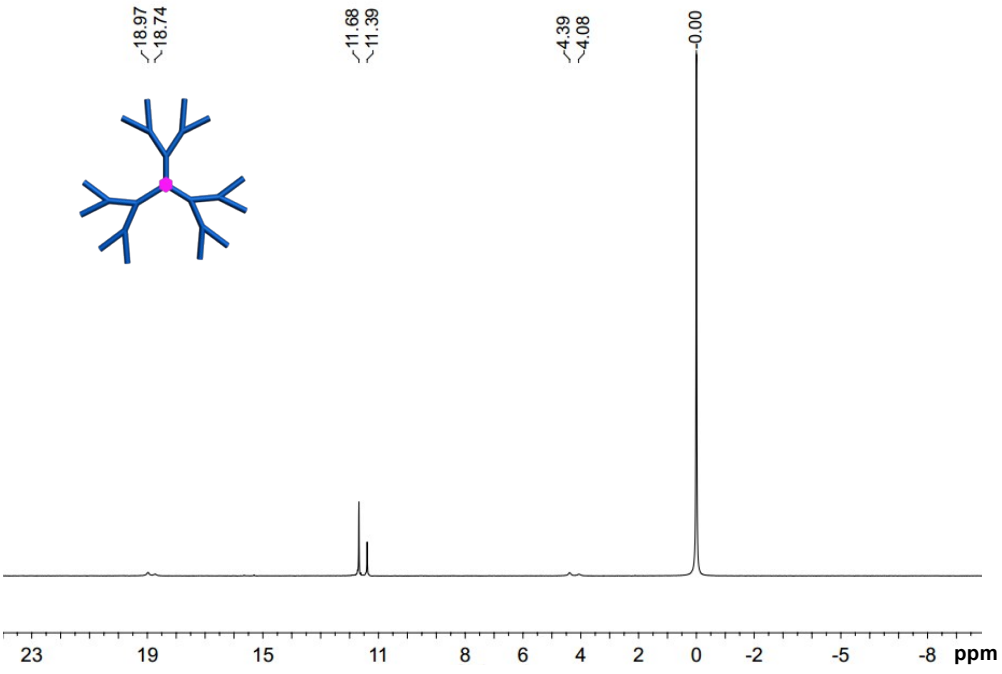


Figure S13. ^{31}P NMR spectrum ($CDCl_3$, room temperature, 161.9 MHz) of **G3-H**.

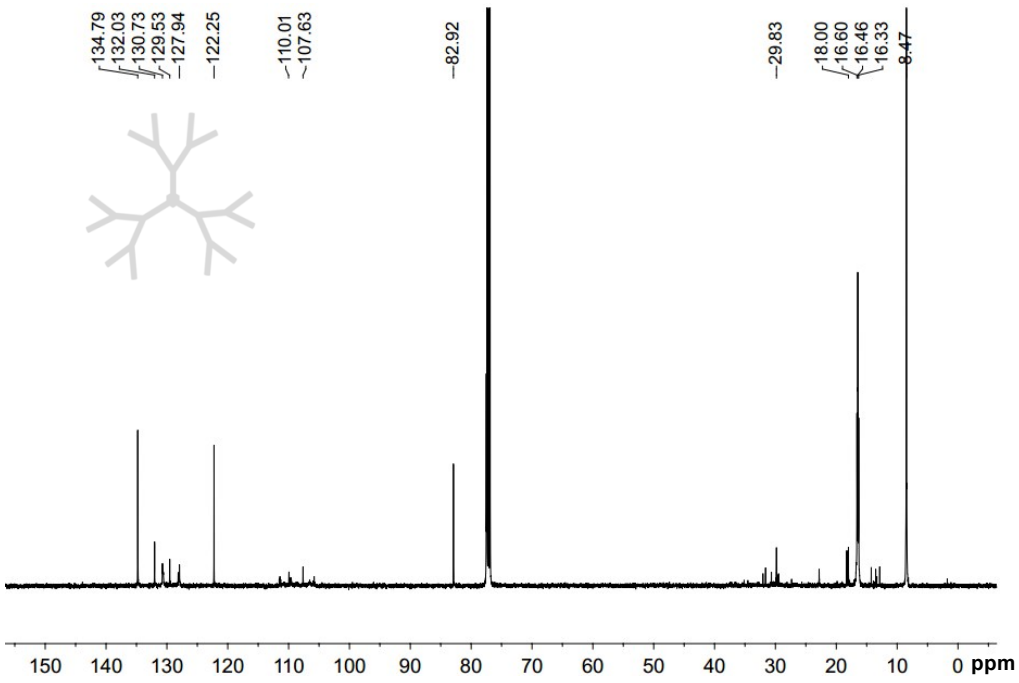


Figure S14. ^{13}C NMR spectrum ($CDCl_3$, room temperature, 125 MHz) of **G3-H**.

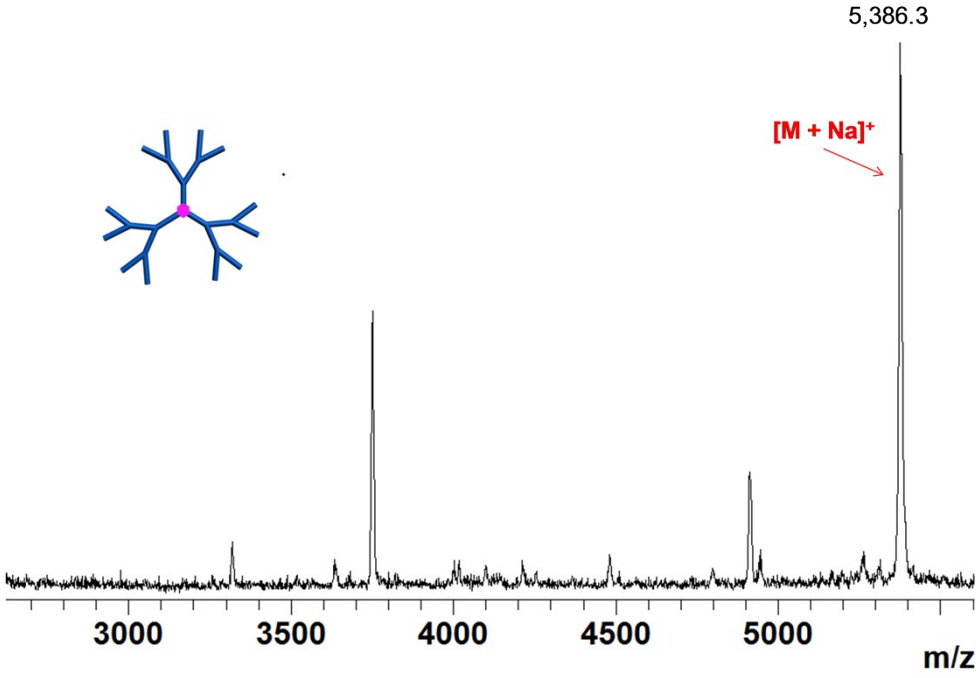


Figure S15. MALDI-TOF-MS spectrum of **G3-H**.

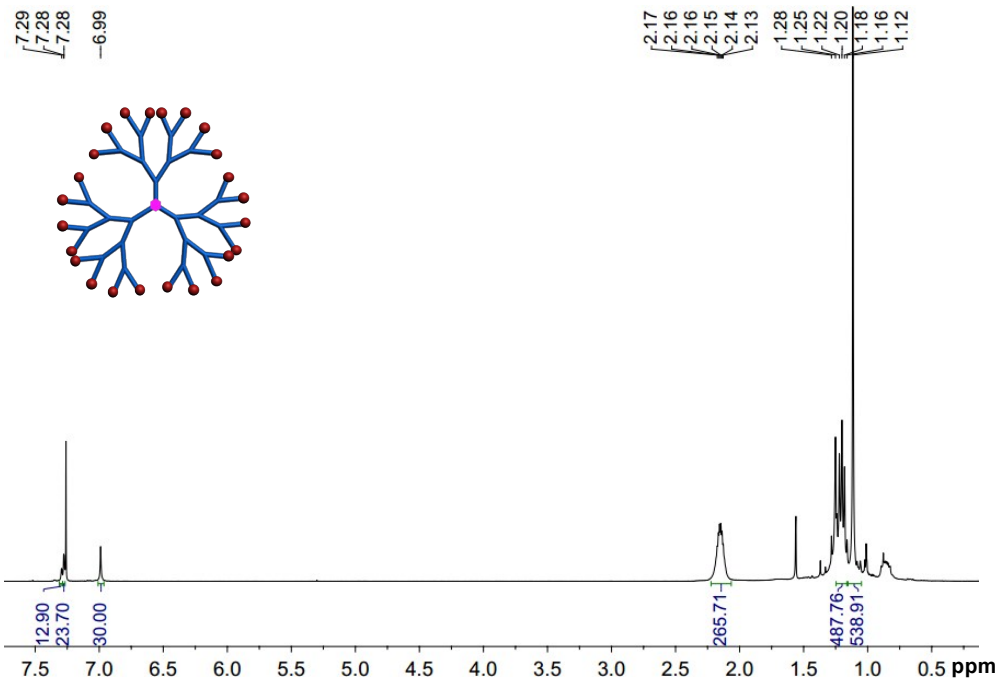


Figure S16. ^{1}H NMR spectrum ($CDCl_3$, room temperature, 400 MHz) of **G4-T**.

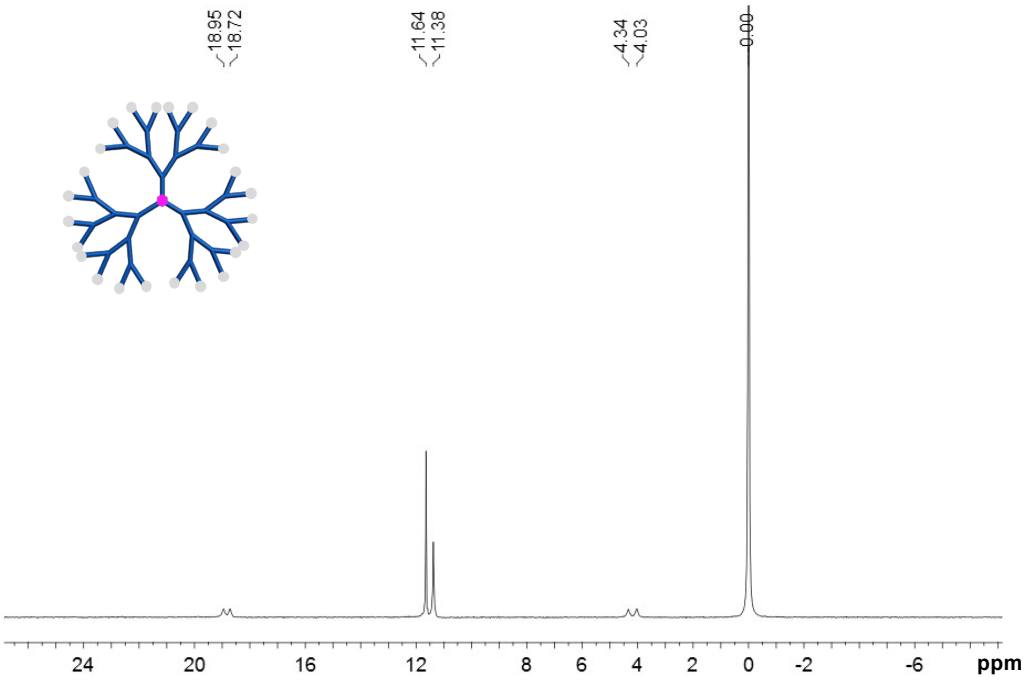


Figure S17. ^{31}P NMR spectrum ($CDCl_3$, room temperature, 161.9 MHz) of **G4-T**.

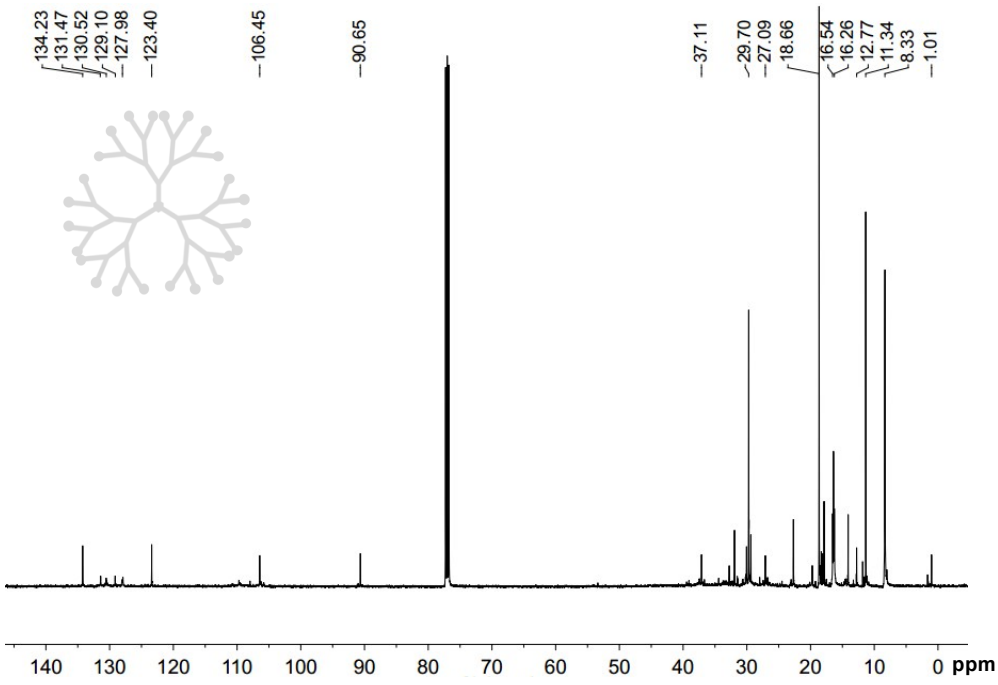
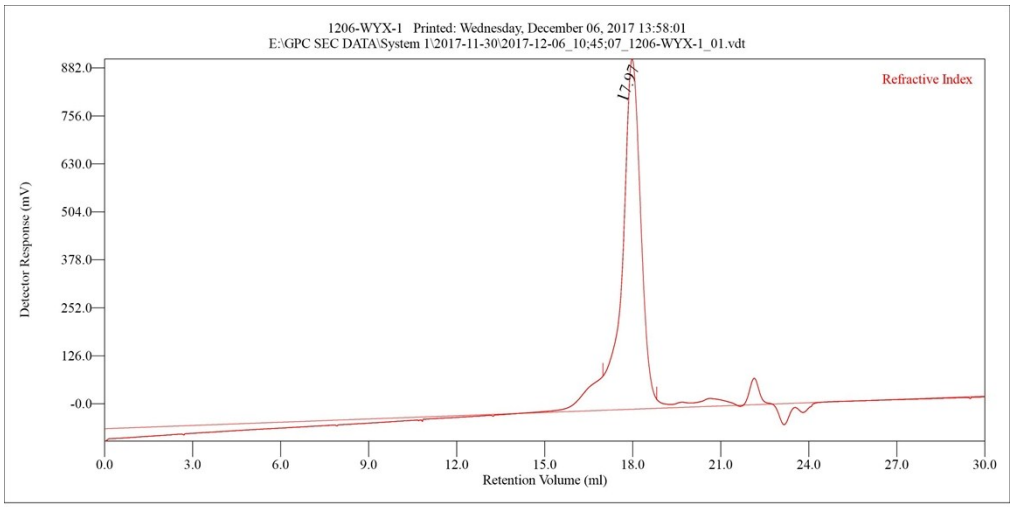


Figure S18. ^{13}C NMR spectrum ($CDCl_3$, room temperature, 125 MHz) of **G4-T**.



Conventional Calibration - Homopolymers : Results

Peak RV - (ml)	17.967
Mn - (Daltons)	11,463
Mw - (Daltons)	12,288
Mz - (Daltons)	13,227
Mp - (Daltons)	11,555
Mw / Mn	1.072
Percent Above Mw: 0	100.000
Percent Below Mw: 0	0.000
Mw 10.0% Low	7,617
Mw 10.0% High	19,817
Wt Fr (Peak)	1.000
RI Area - (mvml)	659.28
UV Area - (mvml)	0.00

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Limits File	
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Calculation Operator	admin : Administrator
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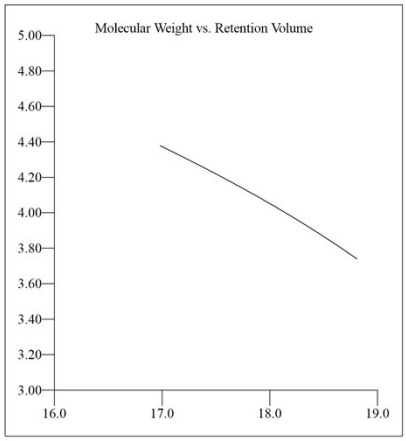
Detector Temp. - (deg C)	35.0
Column Temp. - (deg C)	35.0
OmniSEC Build Number	467



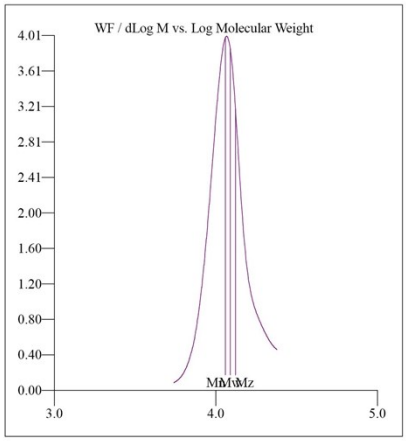


Figure S19. GPC data of **G4-T**.

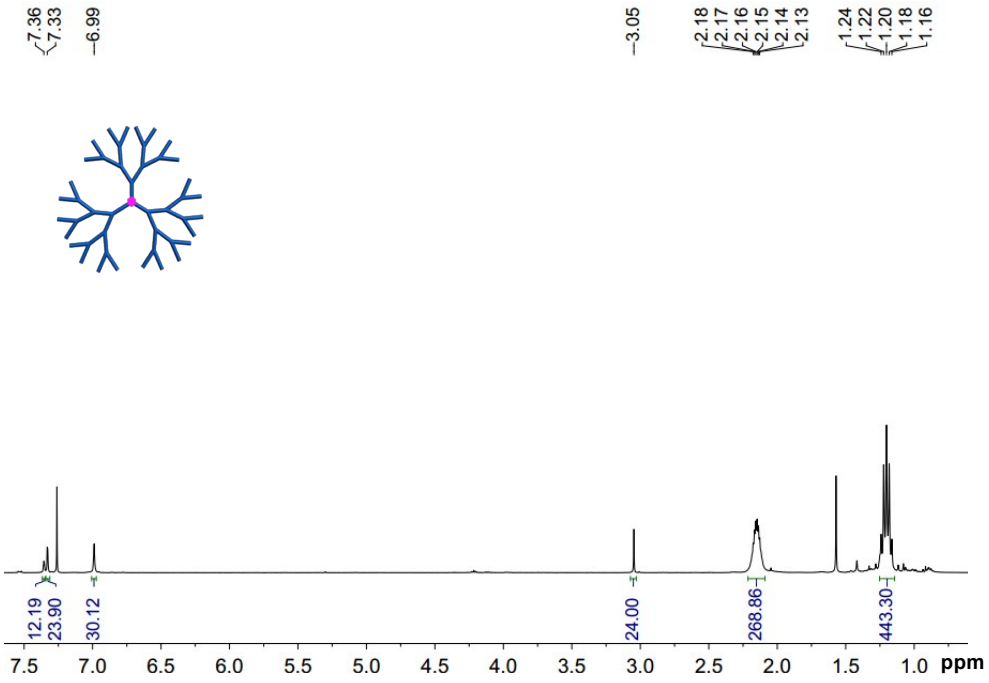


Figure S20. ^{1}H NMR spectrum ($CDCl_3$, room temperature, 400 MHz) of **G4-H**.

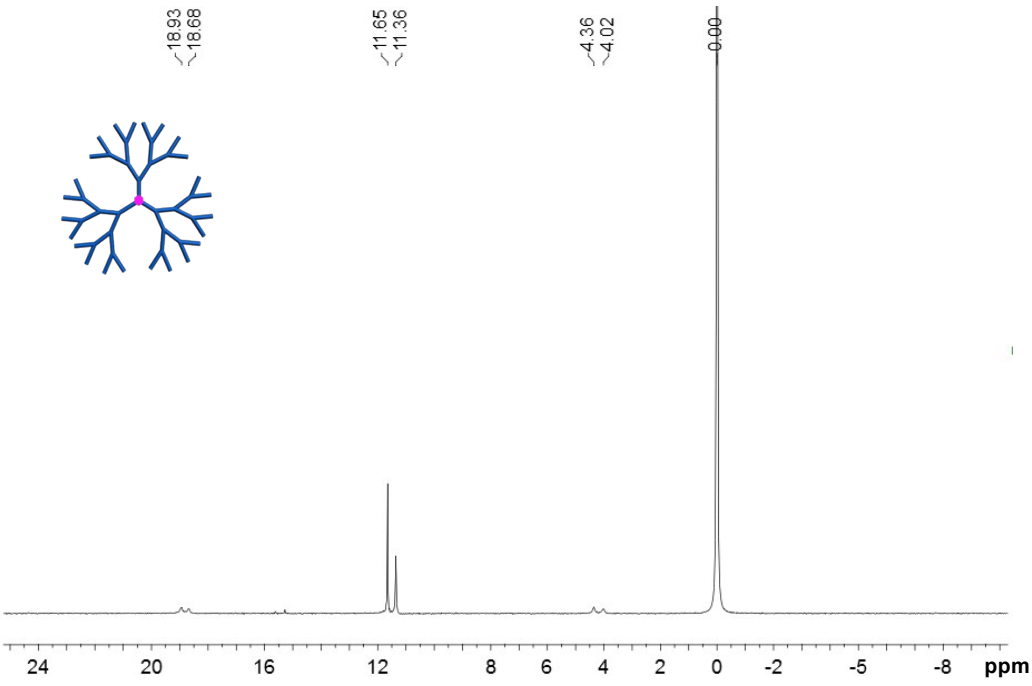


Figure S21. ^{31}P NMR spectrum ($CDCl_3$, room temperature, 161.9 MHz) of **G4-H**.

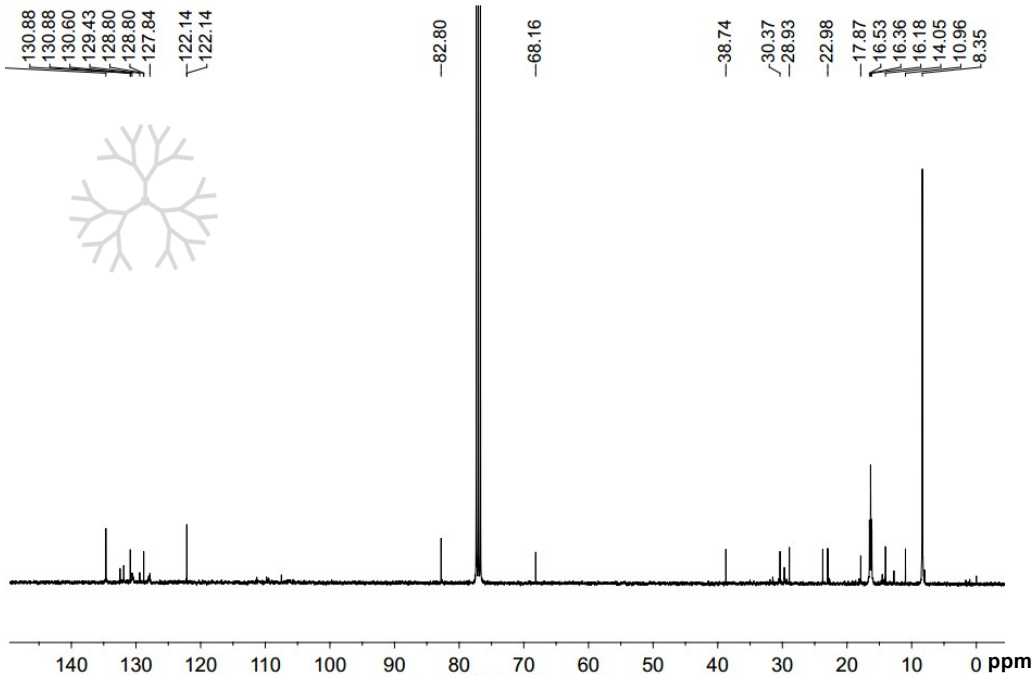
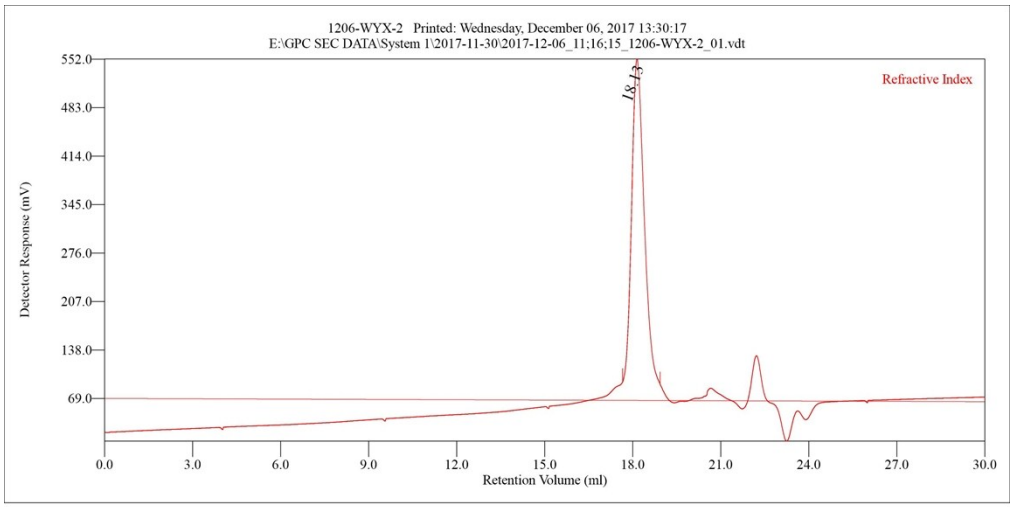


Figure S22. ^{13}C NMR spectrum ($CDCl_3$, room temperature, 125 MHz) of **G4-H**.



Conventional Calibration - Homopolymers : Results

Peak RV - (ml)	18.133
Mn - (Daltons)	9,328
Mw - (Daltons)	9,696
Mz - (Daltons)	10,033
Mp - (Daltons)	10,092
Mw / Mn	1.039
Percent Above Mw: 0	100.000
Percent Below Mw: 0	0.000
Mw 10.0% Low	6,411
Mw 10.0% High	12,804
Wt Fr (Peak)	1.000
RI Area - (mvml)	254.18
UV Area - (mvml)	0.00

Annotation	
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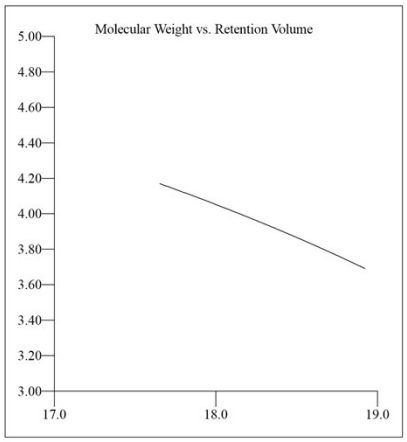
Limits File	
Date Acquired	Dec 06, 2017 - 11:16:15
Solvent	THF
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	G+T6000M
System	System 1
Flow Rate - (ml/min)	1.000
Inj Volume - (ul)	100.0
Volume Increment - (ml)	0.00333
Detector Temp. - (deg C)	35.0
Column Temp. - (deg C)	35.0
OmniSEC Build Number	467



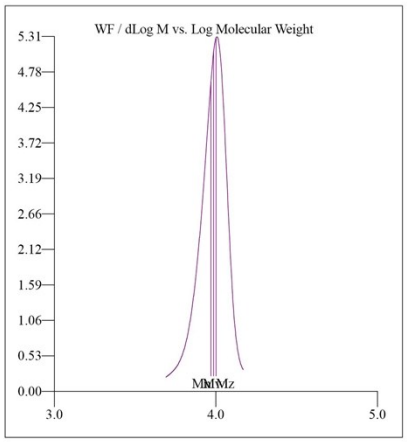
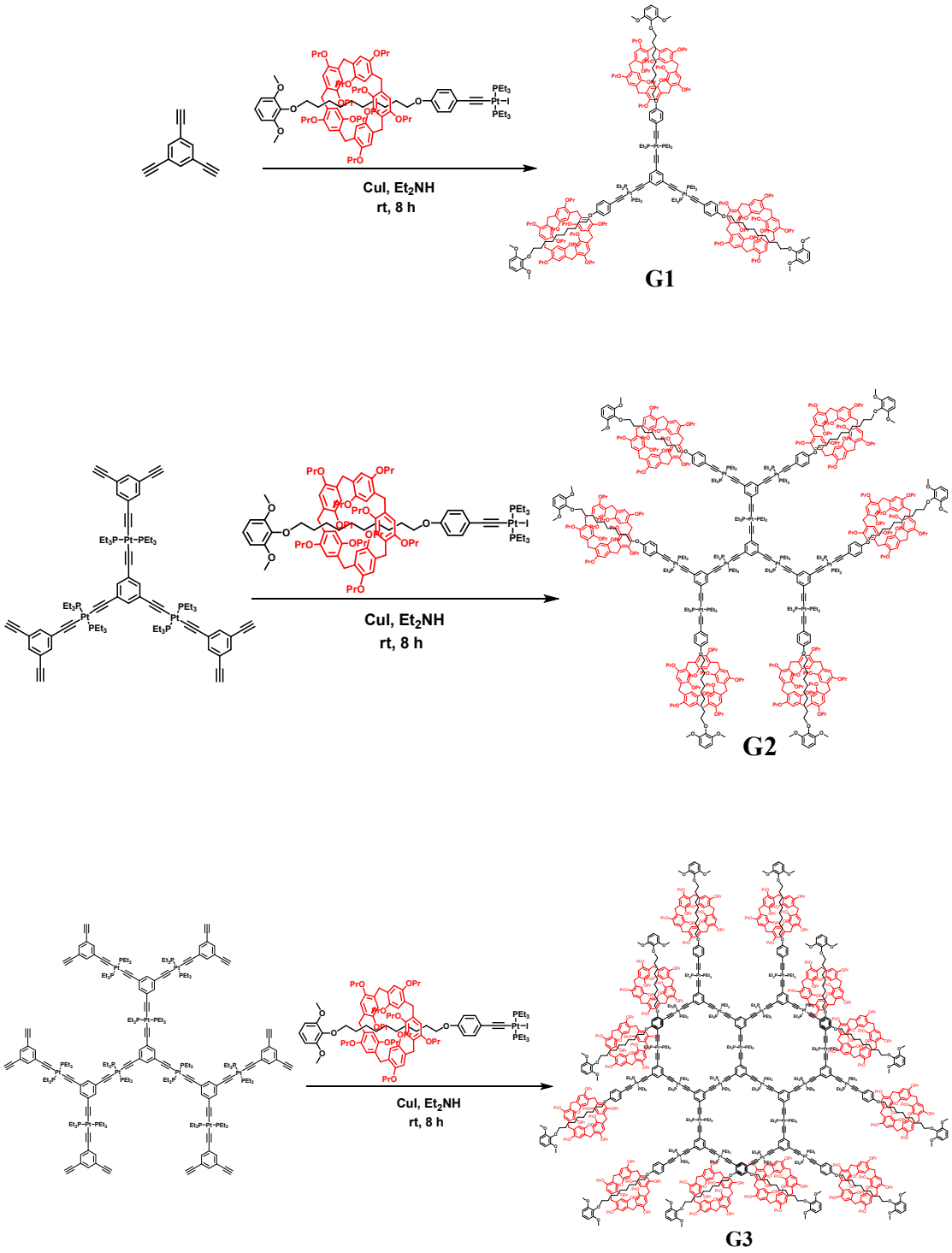
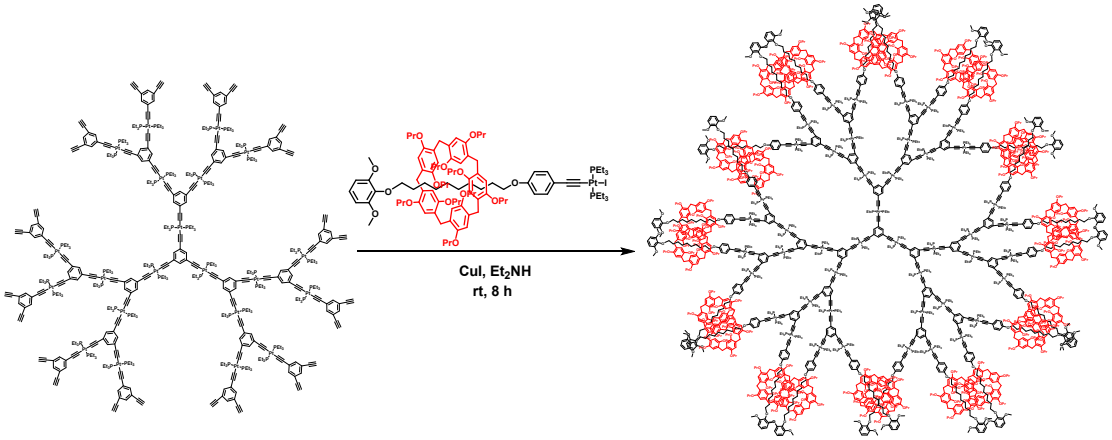


Figure S23. GPC data of **G4-H**.

3. Synthesis of rotaxane-terminated dendrimers **Gn**.

Scheme S3: The synthesis route of Gn.





G4

Synthesis of G1: A Schlenk flask was charge with 1,3,5-triethynylbenzene (3.60 mg 0.024 mmol) and **3** (153 mg, 0.0756 mmol). The Schlenk flask was then evacuated via reduced pressure and backfilled with N_2 for three times. Next, Et_2NH (2 mL) was added via syringe. The solution was stirred for 5 min. Then CuI (9 mg) was added to the mixture under N_2 atmosphere, and the mixture was allowed to stir overnight. The solvent was then removed by reduced pressure, and the compound was purified by alumina column chromatography (eluent: dichloromethane): 80 mg (58% yield) of a slight yellow solid was afforded. M.p. 102 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.18 (d, J = 8.4 Hz, 6H), 7.02 (m, 6H), 6.93 (s, 15H), 6.87 (s, 15H), 6.65 (d, J = 8.4 Hz, 6H), 6.62 (d, J = 8.4 Hz, 6H), 3.64-4.00 (m, 114H), 2.47 (m, 6H), 2.23 (m, 36H), 1.67-1.91 (m, 66H), 1.27 (m, 60H), 1.12 (m, 51H), 0.97 (m, 45H), 0.63 (m, 6H), -0.25 (m, 6H), -0.72 (m, 6H), -1.54 (m, 6H), -2.23 (m, 6H); ^{31}P NMR ($CDCl_3$, 161.9 MHz): δ 11.26; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 157.8 (Ar C_{ipso}-OCH_3), 153.8 (Ar C_{ipso}-OCH_2), 149.8 (Pillararene, Ar C_{ipso}-OPr), 149.7 (Pillararene, Ar C_{ipso}-OPr), 137.6, (Ar C_{ipso}-OCH_3), 131.7 (Ar C_{meta}), 130.6 (Ar C_{meta}), 128.3 (Pillararene, Ar C_{meta}), 128.1 (Pillararene, Ar C_{meta}), 124.8 (Ar C_{meta}), 123.6 (Ar C_{meta}), 120.2 (Ar C_{para}), 114.5 (Pillararene, Ar C_{ortho}), 114.0 (Pillararene, Ar C_{ortho}), 113.7 (Ar C_{ortho}), 109.7 (C-Pt), 109.5 (C-Pt), 105.4 (Ar C_{ortho}), 73.8 (ArO-CH_2), 70.0 (Pillararene, O-CH_2), 69.6 (Pillararene, O-CH_2), 68.5 (ArO-CH_3), 56.2 (Pillararene, Ar-CH_2-Ar), 31.6 (O-C_nH_{2n}), 31.3 (O-C_nH_{2n}), 30.9 (O-C_nH_{2n}), 30.5 (O-C_nH_{2n}), 29.2 (O-C_nH_{2n}), 28.6 (O-C_nH_{2n}), 28.1 (O-C_nH_{2n}), 27.1 (O-C_nH_{2n}), 23.4 (Pillararene, OCH_2-CH_2), 23.3 (Pillararene, OCH_2-CH_2), 22.4 (O-C_nH_{2n}), 16.5 (PCH_2), 10.9 (Pillararene, OCH_2CH_2-CH_3), 10.7 (Pillararene, OCH_2CH_2-CH_3), 8.5 (PCH_2 CH_3).; MS: simulated value for

$C_{321}H_{462}O_{42}P_6Pt_3$ (5,760.14). (MALDI-TOF-MS) 5,880.1 ([M + Na]$^+$).

Synthesis of G2: G2-H (23 mg 0.012 mmol) and **3** (153 mg, 0.076 mmol) were reacted in a similar manner to that of the preparation of **G1**. Alumina column chromatography was performed with dichloromethane as eluent: 94 mg (60% yield) of a slight yellow solid was afforded. M.p. 140 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.17 (d, J = 8.4 Hz, 12H), 7.02 (br, 18H), 6.92 (s, 30H), 6.86 (s, 30H), 6.65 (d, J = 8.8 Hz, 12H), 6.61 (d, J = 8.0 Hz, 12H), 3.65-3.97 (m, 228H), 2.47 (m, 12H), 2.23 (m, 108H), 1.67-1.91 (m, 132H), 1.27 (m, 174H), 1.11 (m, 102H), 0.94 (m, 90H), 0.61 (m, 12H), -0.26 (m, 12H), -0.73 (m, 12H), -1.55 (m, 12H), -2.24 (m, 12H); ^{31}P NMR ($CDCl_3$, 161.9 MHz): δ 11.17, 11.05; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 157.8, 153.9, 149.8, 149.7, 137.6, 131.8, 129.2, 123.6, 114.5,114.1, 113.7, 105.5, 73.8, 70.0, 69.6, 68.5, 56.2, 31.0, 30.5, 29.2, 28.6, 27.1, 23.3, 16.3, 10.8, 8.5, 8.2; MS: simulated value for $C_{702}H_{1020}O_{84}P_{18}Pt_9$ (13,107.77). (MALDI-TOF-MS) 13,106.1 (M^+).

Synthesis of G3: G3-H (37 mg 0.007 mmol) and **3** (178 mg, 0.088 mmol) were reacted in a similar manner to that of the preparation of **G1**. Alumina column chromatography was performed with dichloromethane as eluent: 95 mg (49% yield) of a slight yellow solid was afforded. M.p. 151 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.18 (d, J = 8.4 Hz, 24H), 7.02 (br, 42H), 6.92 (s, 60H), 6.86 (s, 60H), 6.65 (d, J = 8.4 Hz, 24H), 6.61 (d, J = 8.4 Hz, 24H), 3.60-3.79 (m, 456H), 2.47 (m, 24H), 2.23 (m, 252H), 1.67-1.91 (m, 264H), 1.27 (m, 402H), 1.11 (m, 204H), 0.96 (m, 180H), 0.61 (m, 24H), -0.26 (m, 24H), -0.73 (m, 24H), -1.54 (m, 24H), -2.23 (m, 24H); ^{31}P NMR ($CDCl_3$, 161.9 MHz): δ11.12, 11.01; ^{13}C NMR ($CDCl_3$, 125 MHz): δ157.8, 153.9, 149.8, 149.7, 137.6, 131.8, 128.3, 120.3, 114.5, 114.1, 113.7, 105.5, 73.8, 70.0, 69.6, 68.5, 56.2, 31.0, 30.5, 29.2, 28.6, 28.1, 27.1, 22.4, 16.3, 10.8, 8.4, 8.2; MS: simulated value for $C_{1464}H_{2136}O_{168}P_{42}Pt_{21}$ (27,803.02). (MALDI-TOF-MS) 27,839.4 ([M + K]$^+$).

Synthesis of G4: G4-H (42 mg 0.0034 mmol) and **3** (173 mg, 0.086 mmol) were reacted in a similar manner to that of the preparation of **G1**. Alumina column chromatography was performed with dichloromethane as eluent: 80 mg (41% yield) of a slight yellow solid was afforded. M.p. 175 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.18 (d, J = 8.0 Hz, 48H), 7.01 (br, 114H), 6.92 (s, 120H), 6.86 (s, 120H), 6.64 (d, J = 8.4 Hz, 48H), 6.60 (d, J = 8.4 Hz, 48H), 3.65-3.97 (m, 912H), 2.44 (m, 48H), 2.23 (m, 540H), 1.67-1.91 (m, 528H), 1.27 (m, 858H), 1.11 (m, 408H), 0.96 (m, 360H), 0.61 (m, 48H), -0.26 (m, 48H), -0.73 (m, 48H), -1.55 (m, 48H), -2.23 (m, 48H); ^{31}P NMR ($CDCl_3$,

161.9 MHz): δ 11.36, 11.23; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 157.6, 153.8, 149.7, 149.6, 137.5, 131.8, 128.3, 123.5, 114.4, 114.1, 113.7, 105.4, 73.7, 69.8, 69.5, 68.4, 56.1, 30.8, 30.5, 29.2, 28.6, 28.1, 27.0, 23.2, 16.3, 10.8, 8.4, 8.2. MS: simulated value for $C_{2988}H_{4368}O_{336}P_{90}Pt_4$ (57,193.52). (GPC) M_n 52,117.

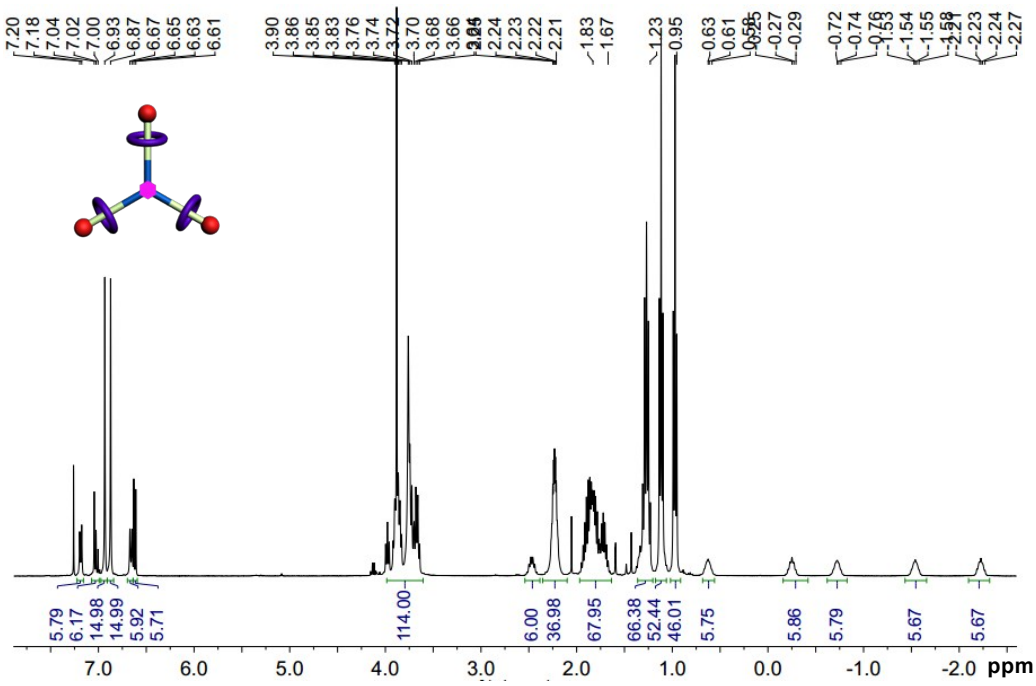


Figure S24. ^{1}H NMR spectrum ($CDCl_3$, room temperature, 400 MHz) of **G1**.

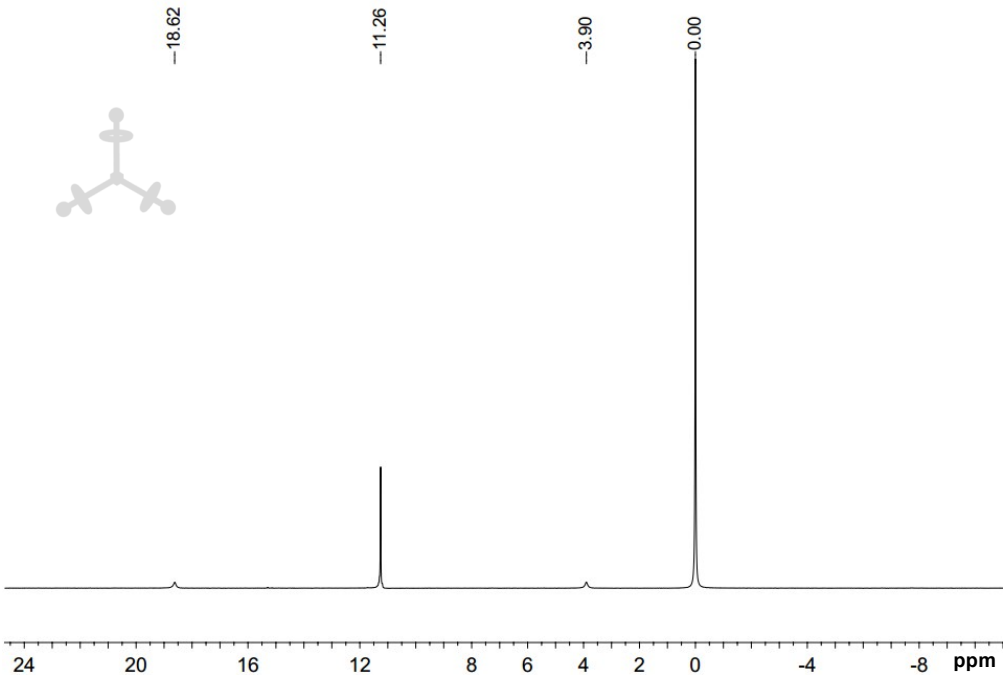


Figure S25. ^{31}P NMR spectrum ($CDCl_3$, room temperature, 161.9 MHz) of **G1**.

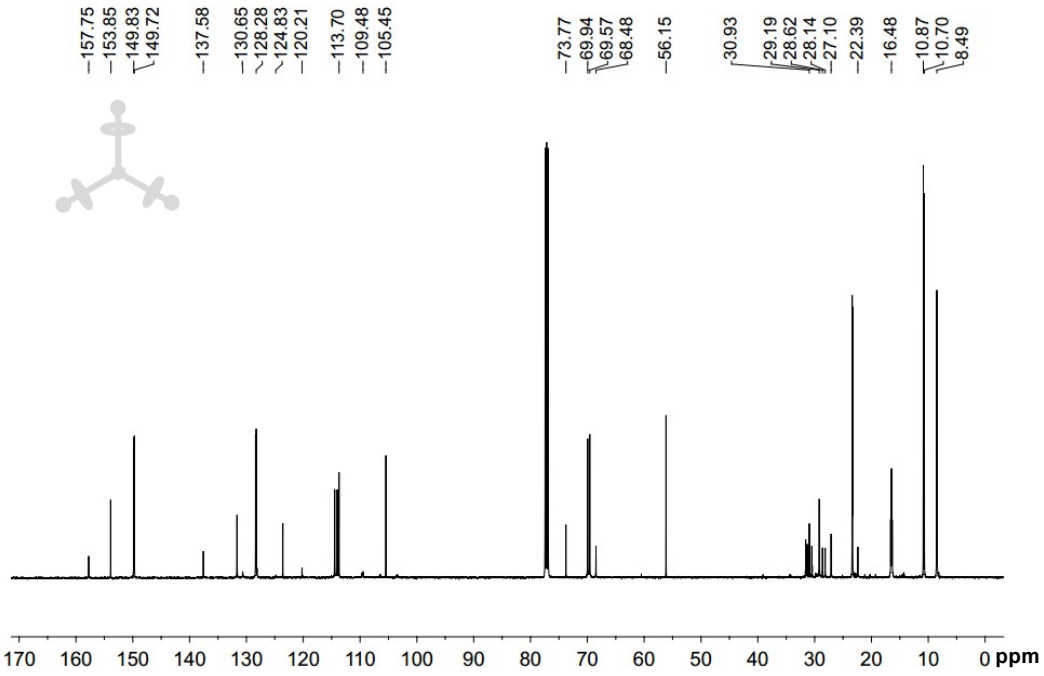


Figure S26. ^{13}C NMR spectrum ($CDCl_3$, room temperature, 125 MHz) of **G1**.

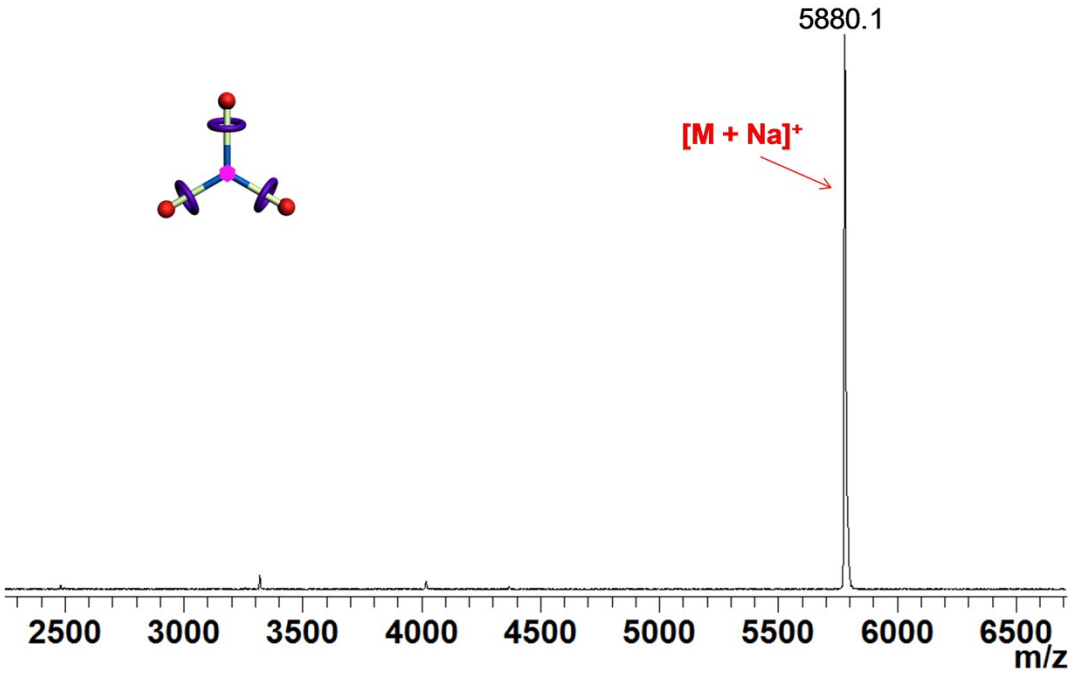


Figure S27. MALDI-TOF-MS spectrum of **G1**.

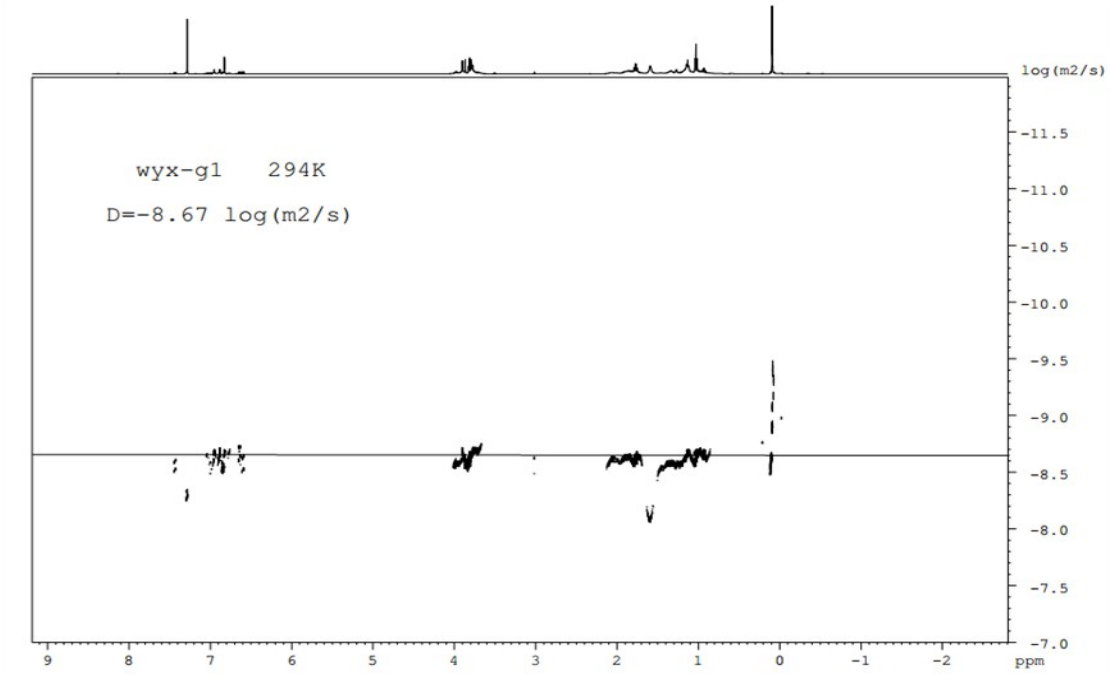


Figure S28. DOSY spectrum ($CDCl_3$, 294 K) of **G1**.

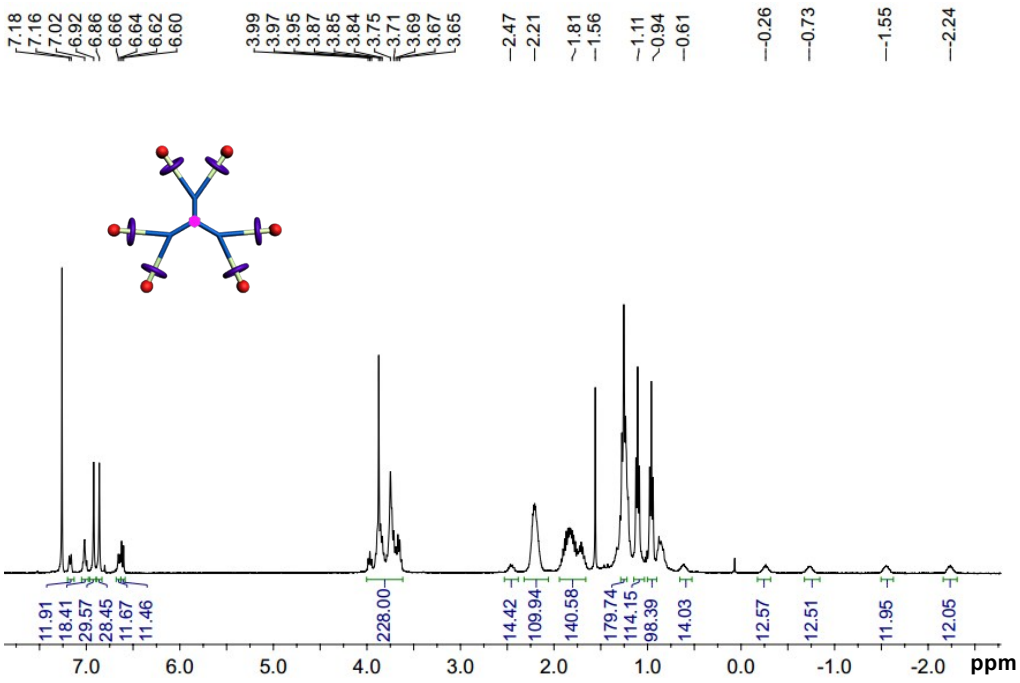


Figure S29. ^{1}H NMR spectrum ($CDCl_3$, room temperature, 400 MHz) of **G2**.

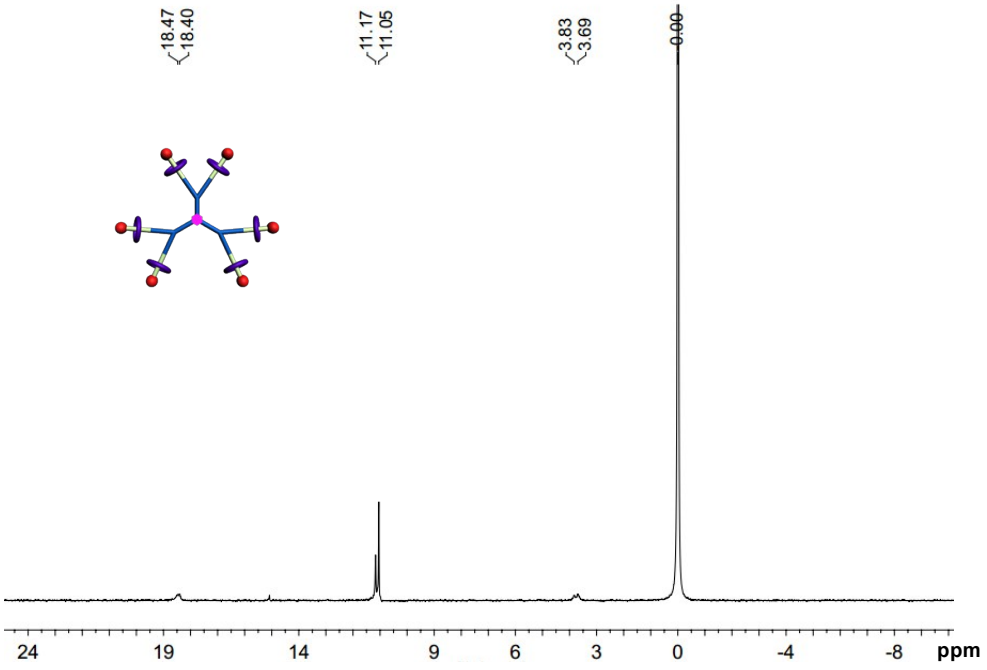


Figure S30. ^{31}P NMR spectrum ($CDCl_3$, room temperature, 161.9 MHz) of **G2**.

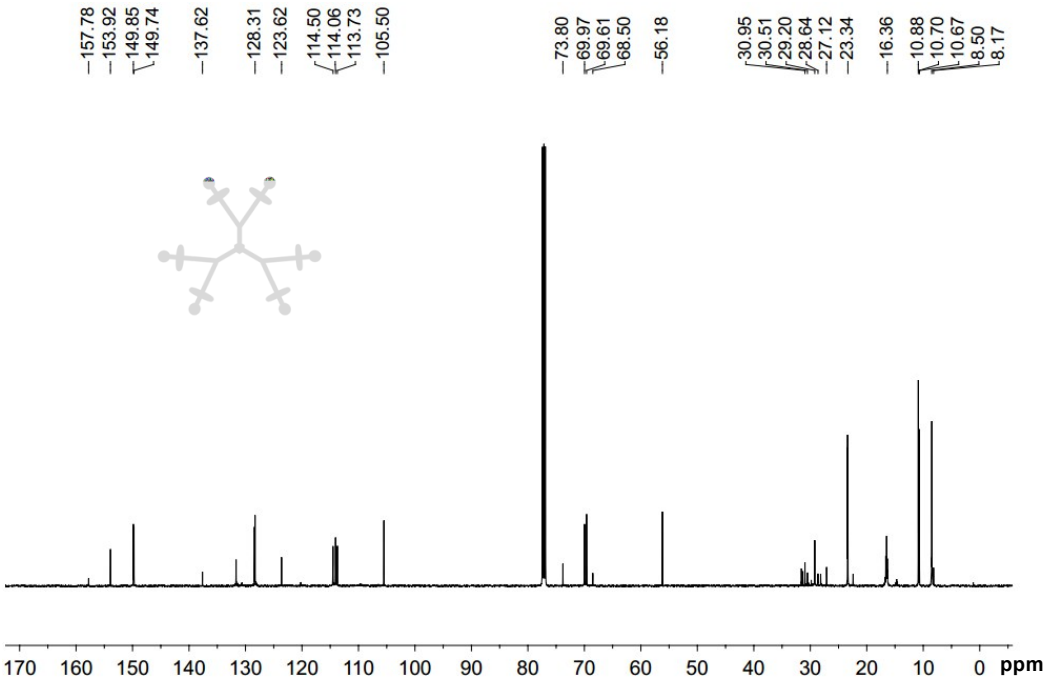


Figure S31. ^{13}C NMR spectrum ($CDCl_3$, room temperature, 125 MHz) of **G2**.

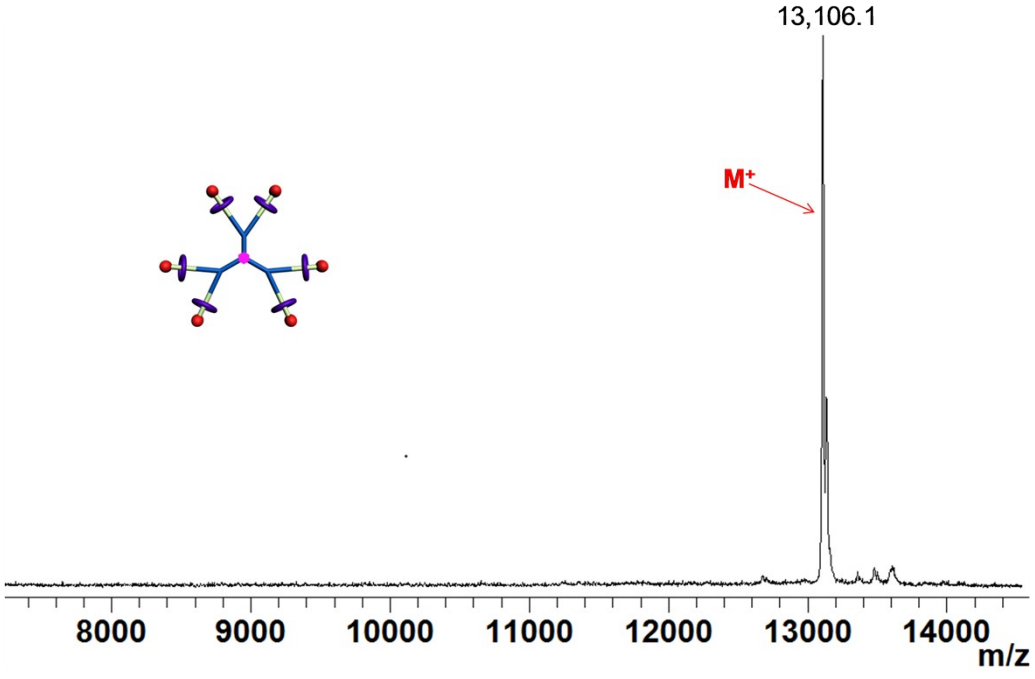


Figure S32. MALDI-TOF-MS spectrum of **G2**.

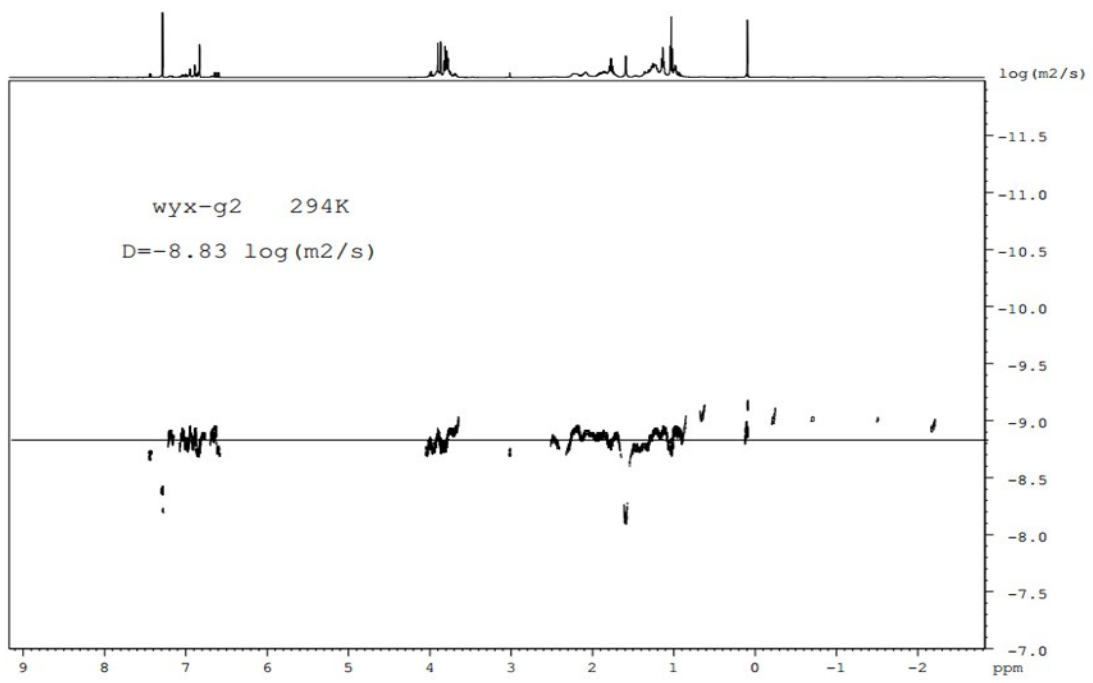


Figure S33. DOSY spectrum ($CDCl_3$, 294 K) of **G2**.

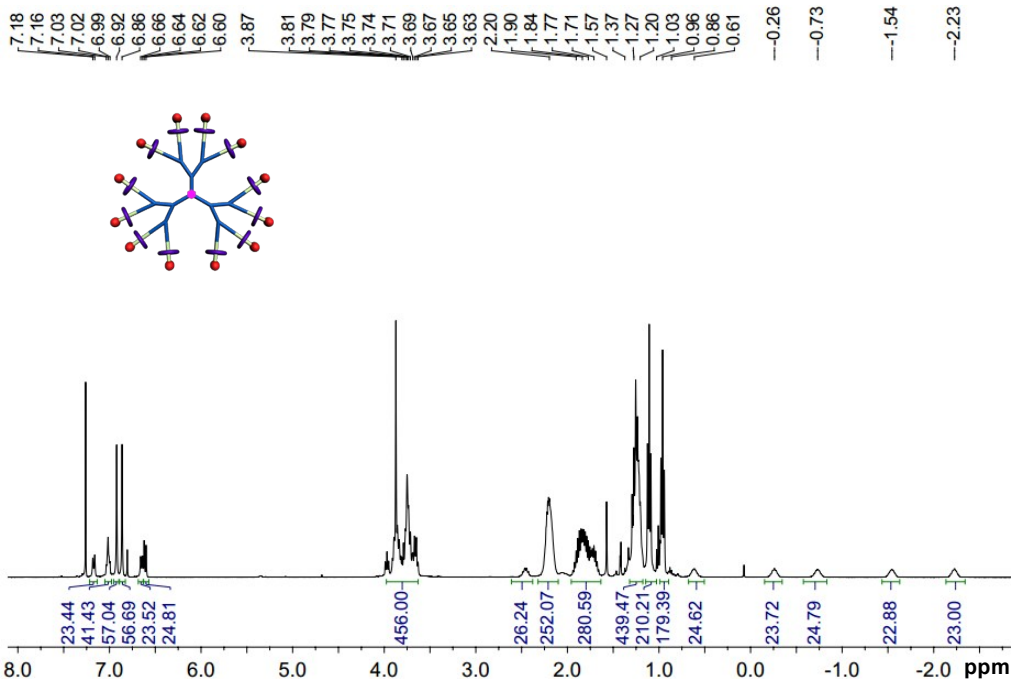


Figure S34. ^1H NMR spectrum ($CDCl_3$, room temperature, 400 MHz) of **G3**.

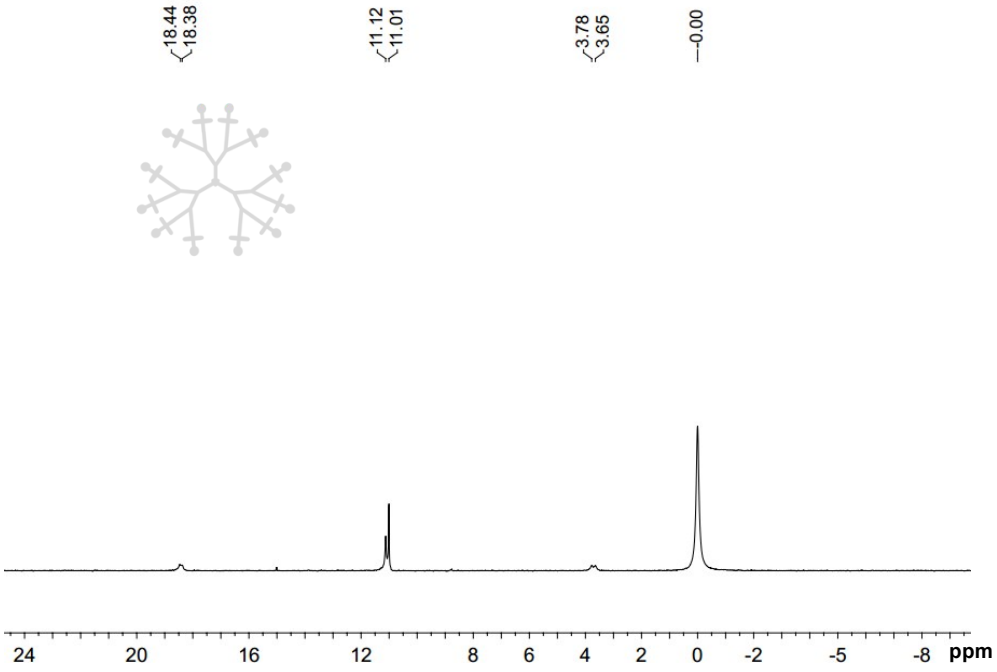


Figure S35. ^{31}P NMR spectrum ($CDCl_3$, room temperature, 161.9 MHz) of **G3**.

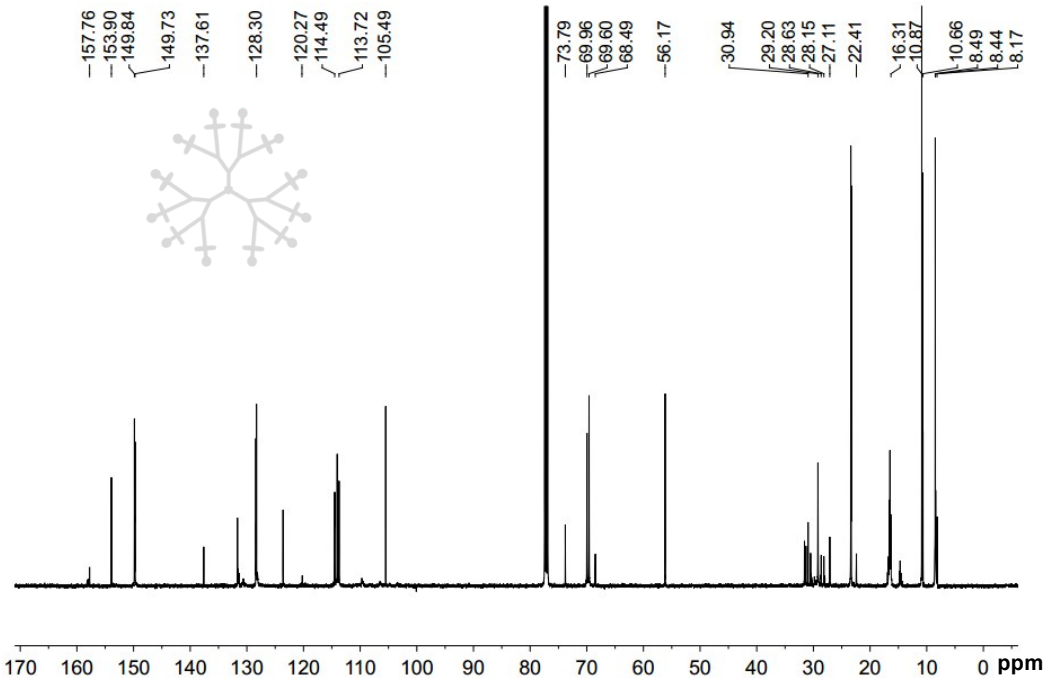


Figure S36. ^{13}C NMR spectrum ($CDCl_3$, room temperature, 125 MHz) of **G3**.

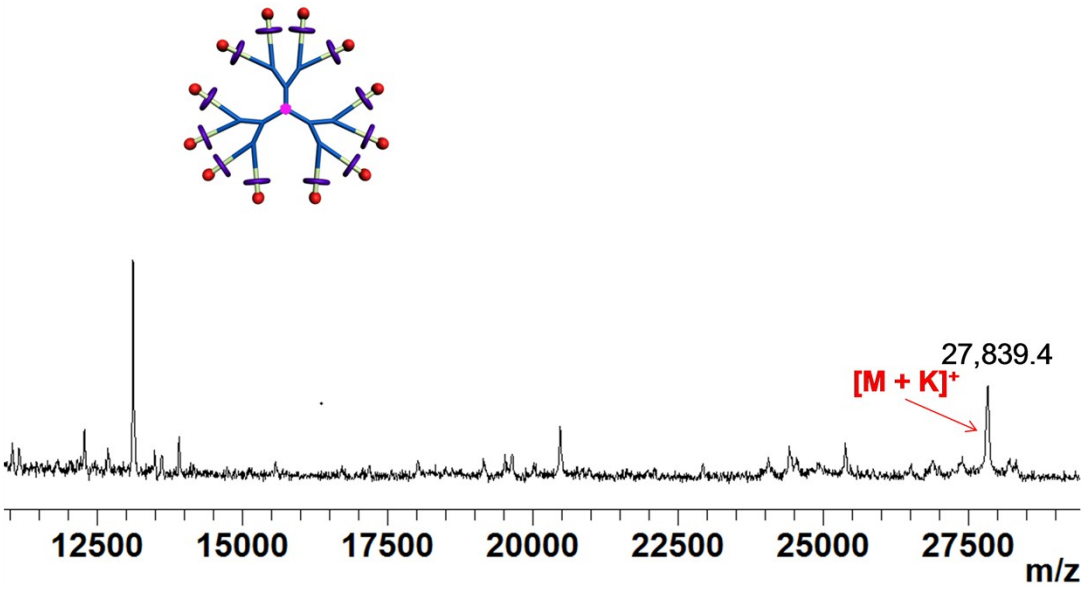


Figure S37. MALDI-TOF-MS spectrum of **G3**.

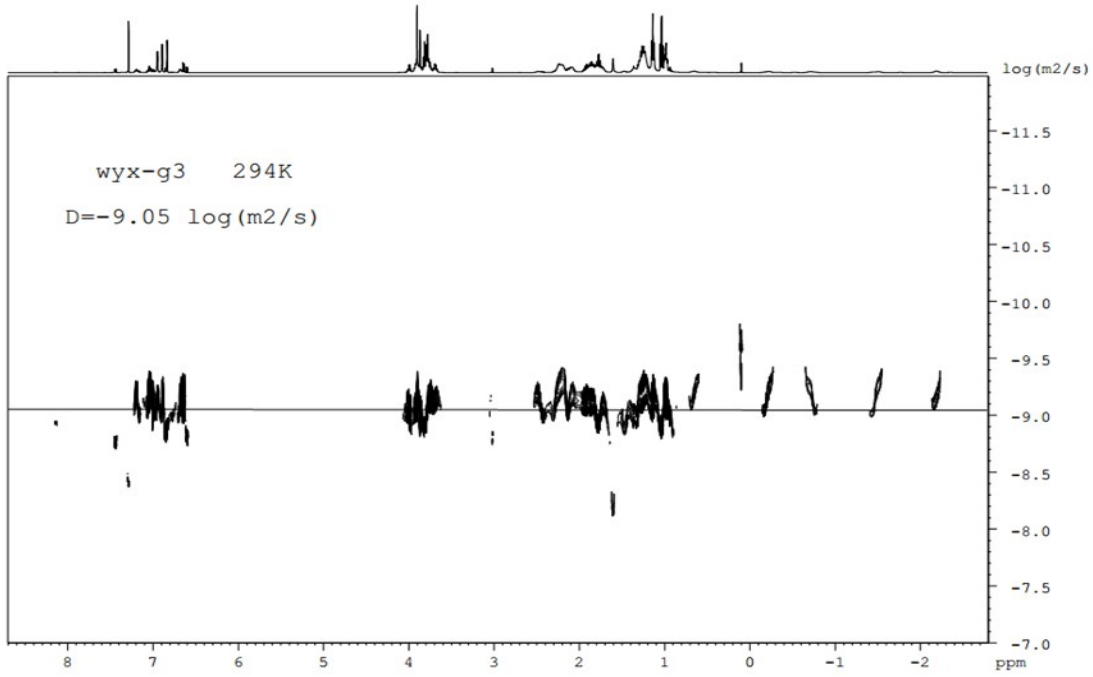


Figure S38. DOSY spectrum ($CDCl_3$, 294 K) of **G3**.

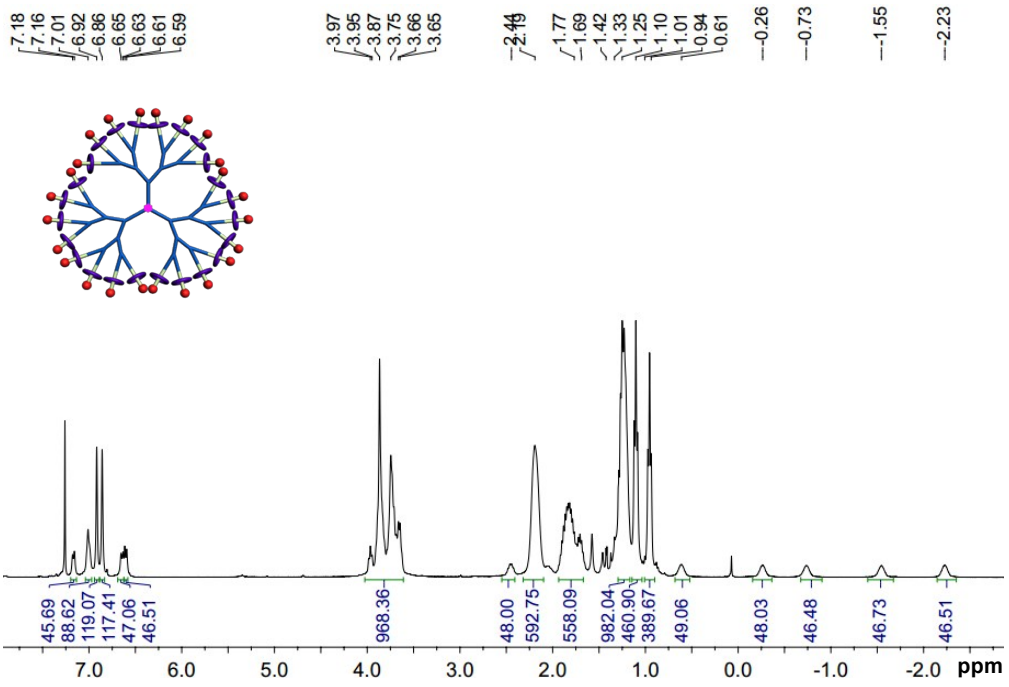


Figure S39. ^{1}H NMR spectrum ($CDCl_3$, room temperature, 400 MHz) of **G4**.

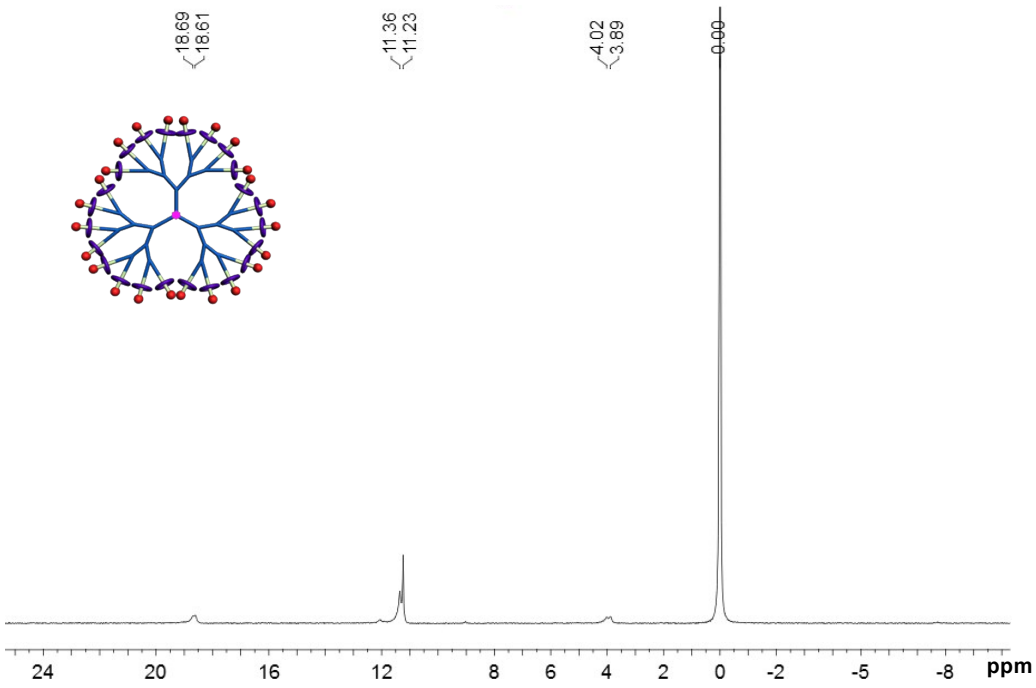


Figure S40. ^{31}P NMR spectrum ($CDCl_3$, room temperature, 161.9 MHz) of **G4**.

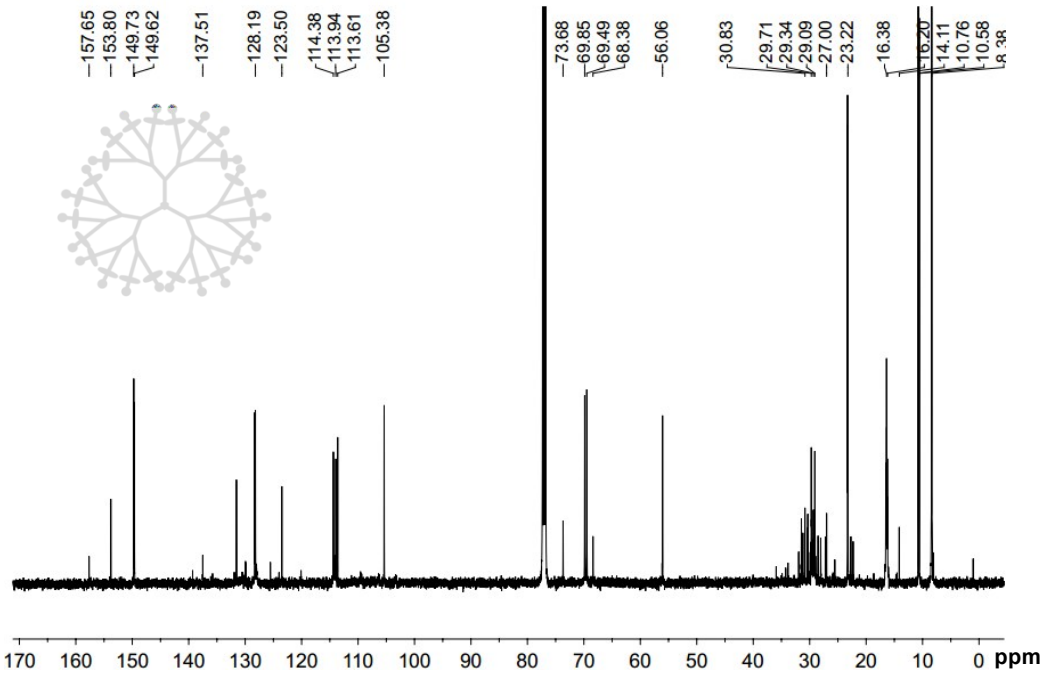
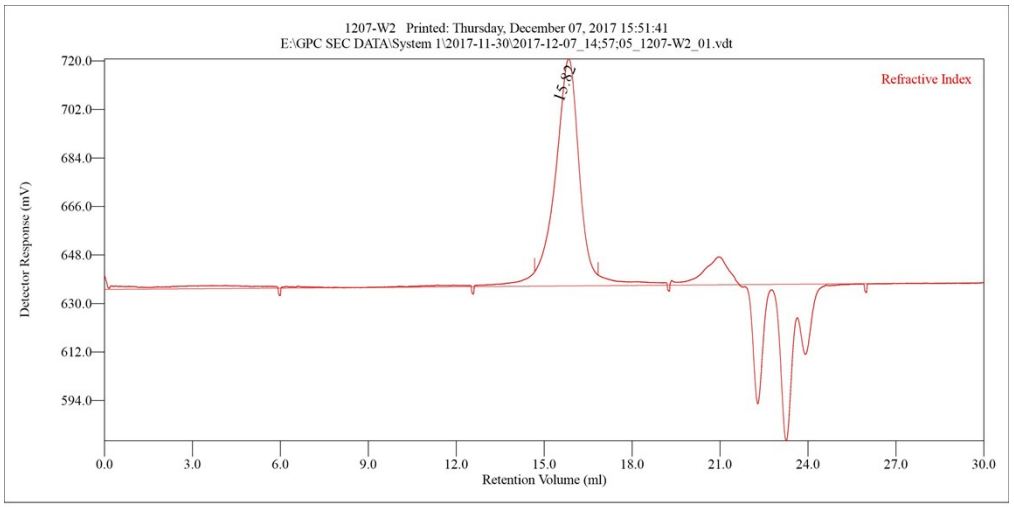


Figure S41. ^{13}C NMR spectrum ($CDCl_3$, room temperature, 125 MHz) of **G4**.



Conventional Calibration - Homopolymers : Results

Peak RV - (ml)	15.820
Mn - (Daltons)	52,117
Mw - (Daltons)	55,955
Mz - (Daltons)	60,341
Mp - (Daltons)	51,563
Mw / Mn	1.074
Percent Above Mw: 0	100.000
Percent Below Mw: 0	0.000
Mw 10.0% Low	34,629
Mw 10.0% High	89,929
Wt Fr (Peak)	1.000
RI Area - (mvml)	77.34
UV Area - (mvml)	0.00

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Limits File	
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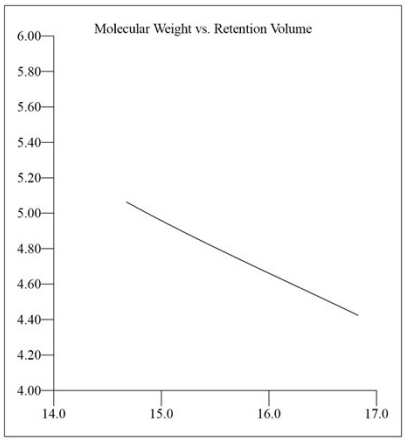
Solvent	THF
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	G+T6000M
System	System 1
Flow Rate - (ml/min)	1.000
Inj Volume - (ul)	100.0
Volume Increment - (ml)	0.00333
Detector Temp. - (deg C)	35.0
Column Temp. - (deg C)	35.0
OmniSEC Build Number	467



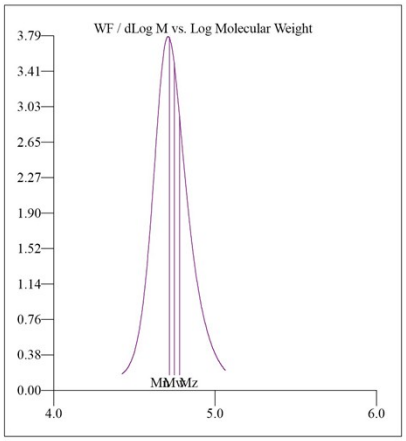


Figure S42. GPC data of **G4**.

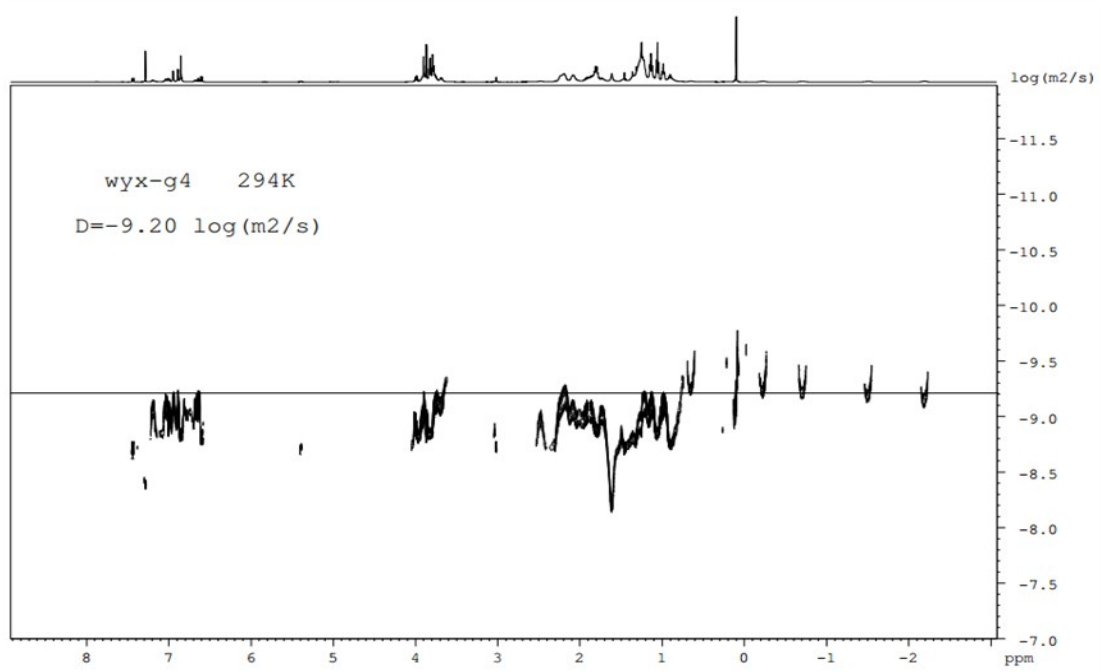


Figure S43. DOSY spectrum ($CDCl_3$, 294 K) of **G4**.

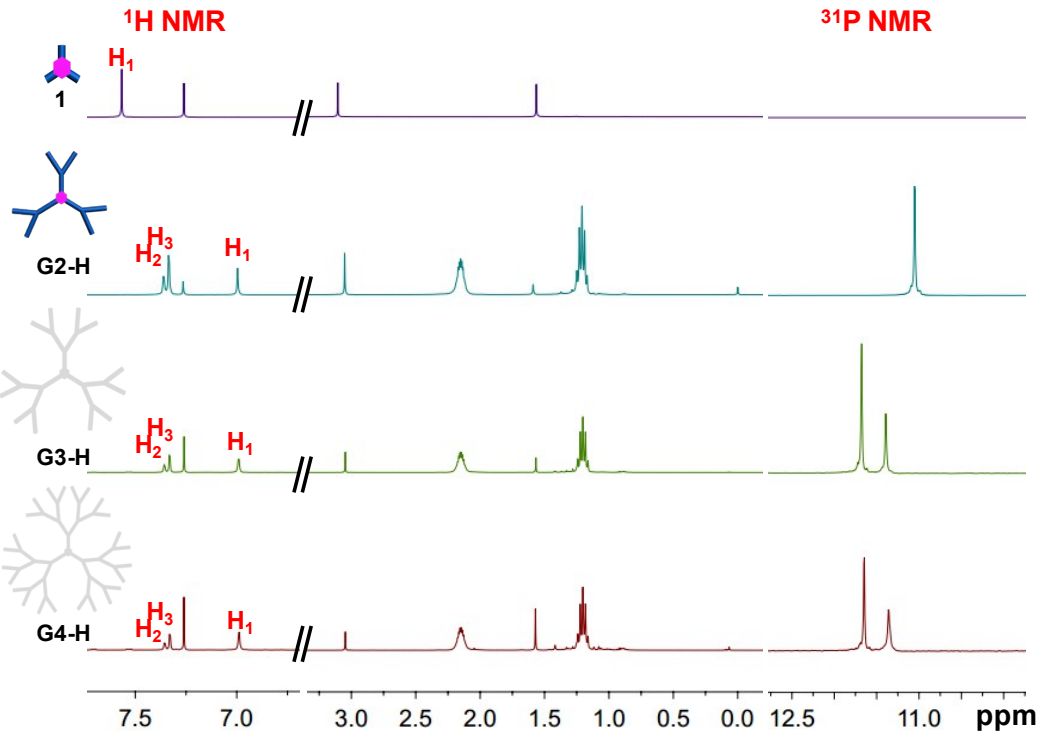


Figure S44. Partial ^{1}H and ^{31}P NMR spectra ($CDCl_3$, room temperature) of **Gn-H**.

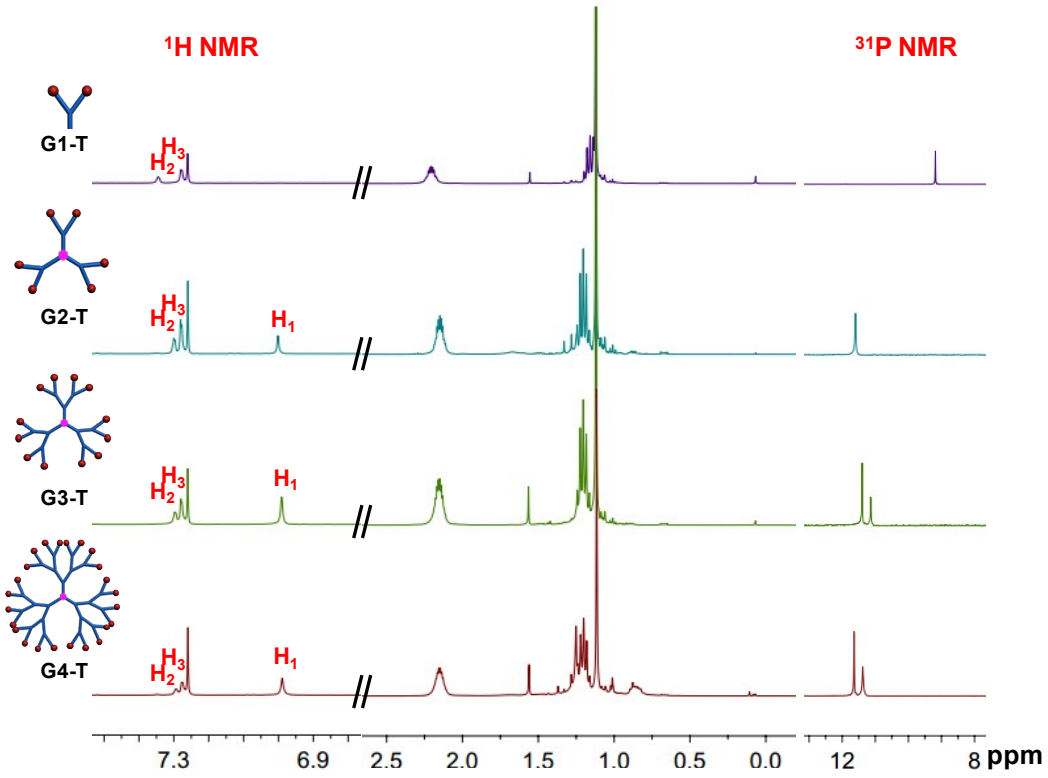


Figure S45. Partial ^{1}H and ^{31}P NMR spectra ($CDCl_3$, room temperature) of **Gn-T**.

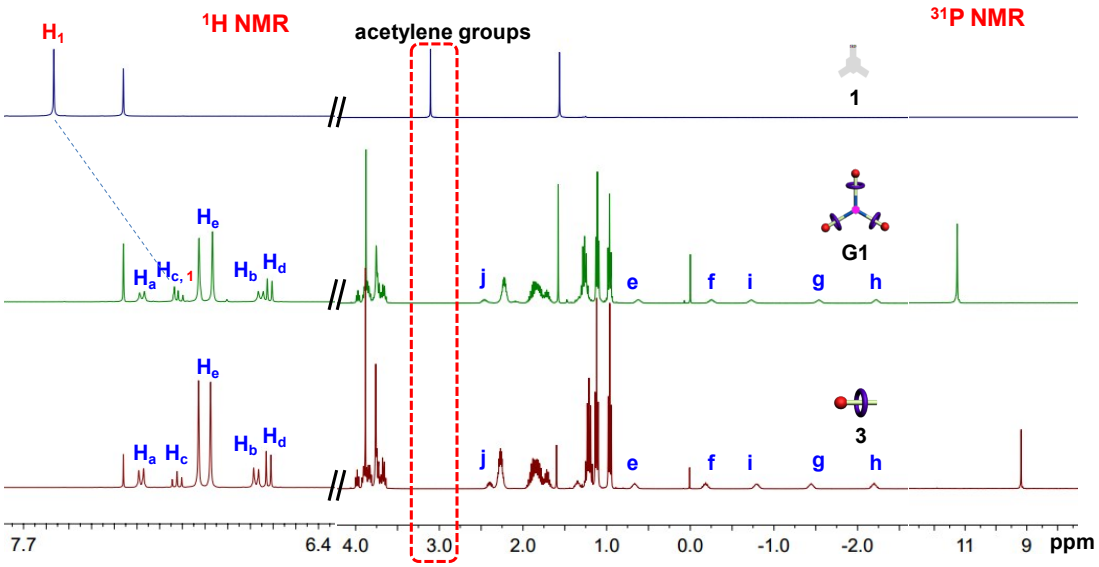


Figure S46. Partial ^{1}H and ^{31}P NMR spectra ($CDCl_3$, room temperature) of **1**, **G1** and **3**.

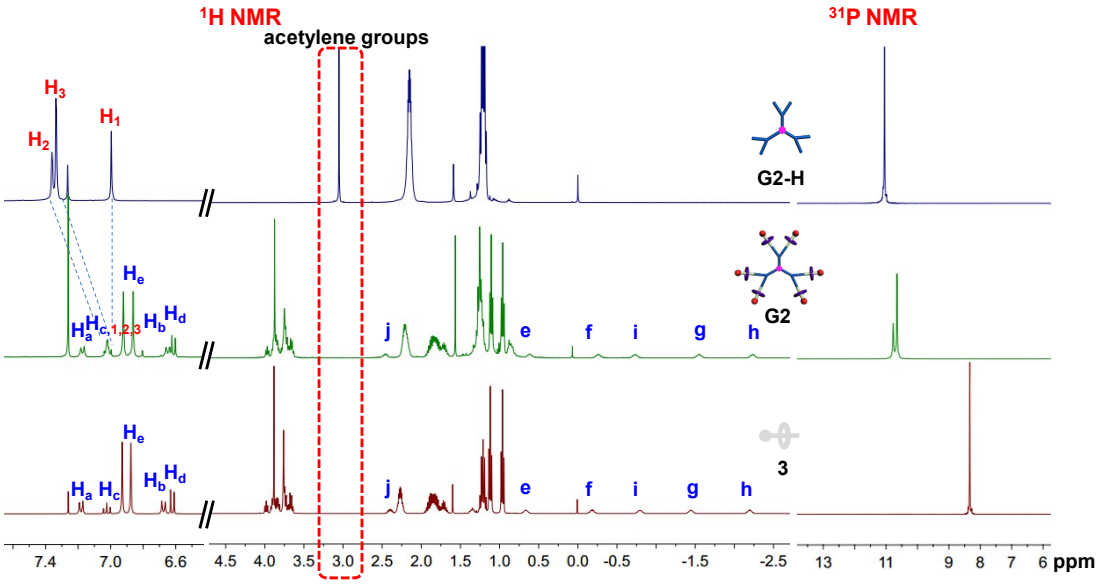


Figure S47. Partial ^{1}H and ^{31}P NMR spectra ($CDCl_3$, room temperature) of **G2-H**, **G2** and **3**.

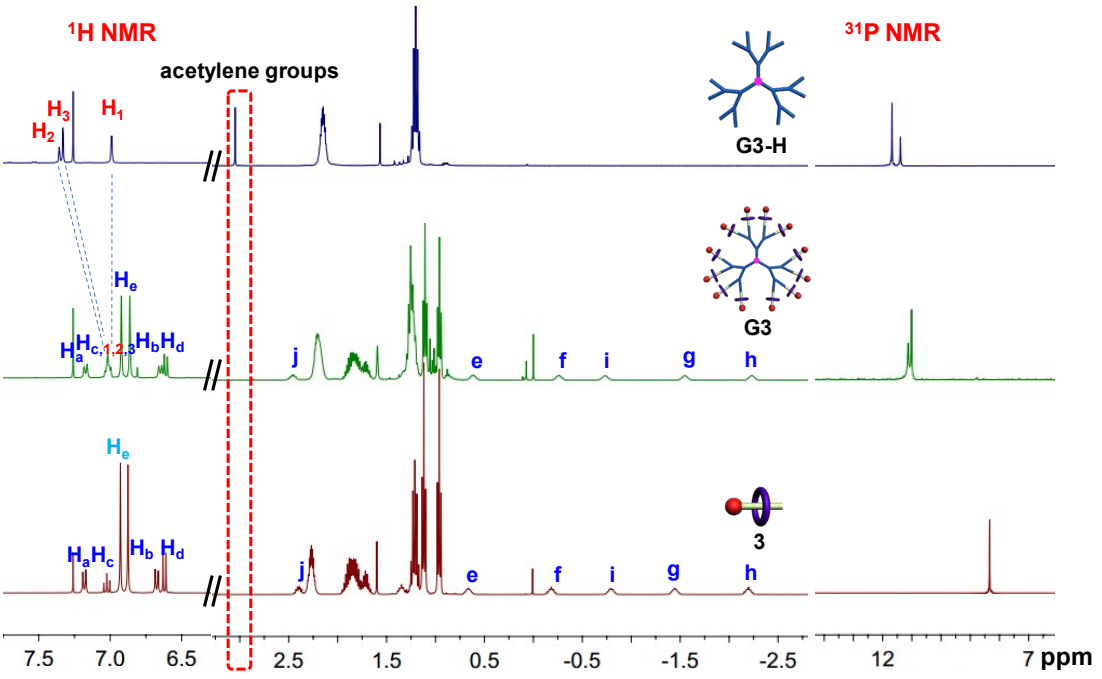


Figure S48. Partial ^{1}H and ^{31}P NMR spectra ($CDCl_3$, room temperature) of **G3-H**, **G3** and **3**.

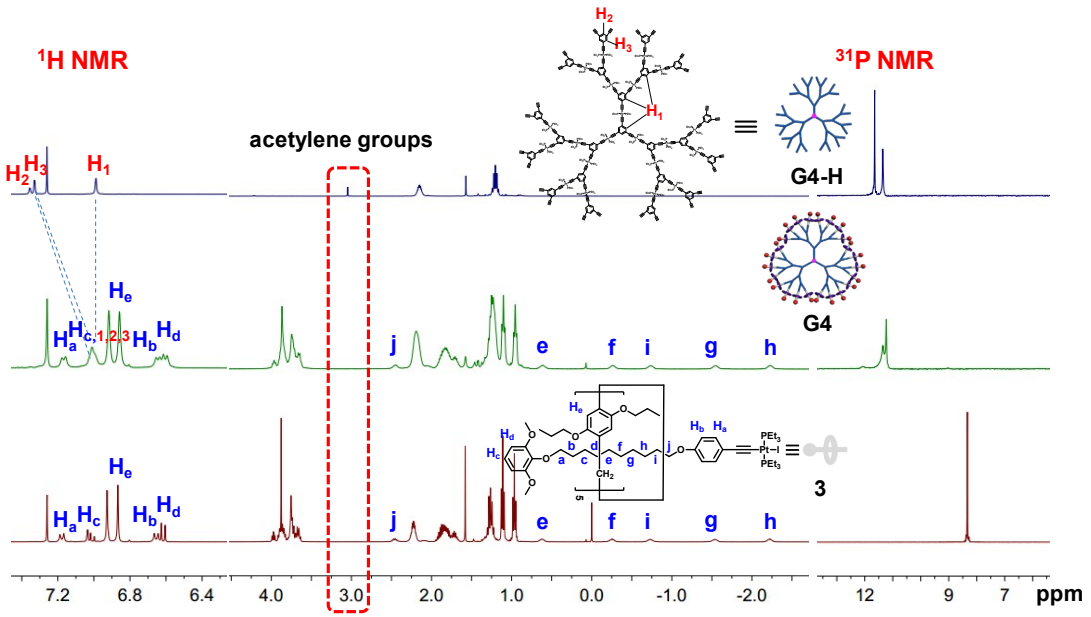


Figure S49. Partial ^{1}H and ^{31}P NMR spectra ($CDCl_3$, room temperature) of **G4-H**, **G4** and **3**.

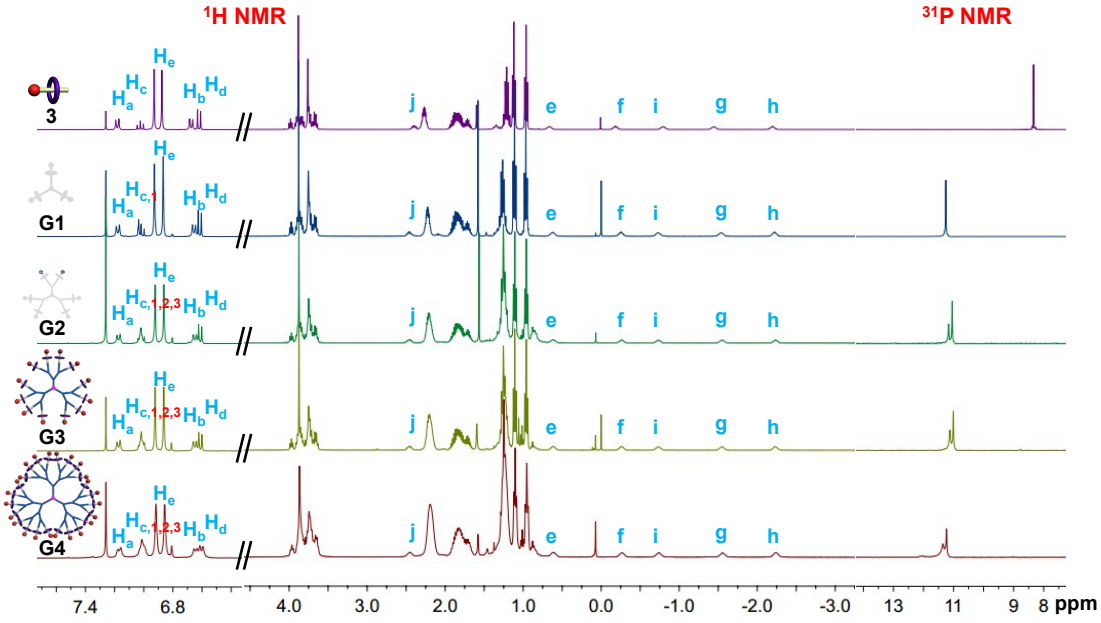


Figure S50. Partial ^{1}H and ^{31}P NMR spectra ($CDCl_3$, room temperature) of **3** and **Gn**.

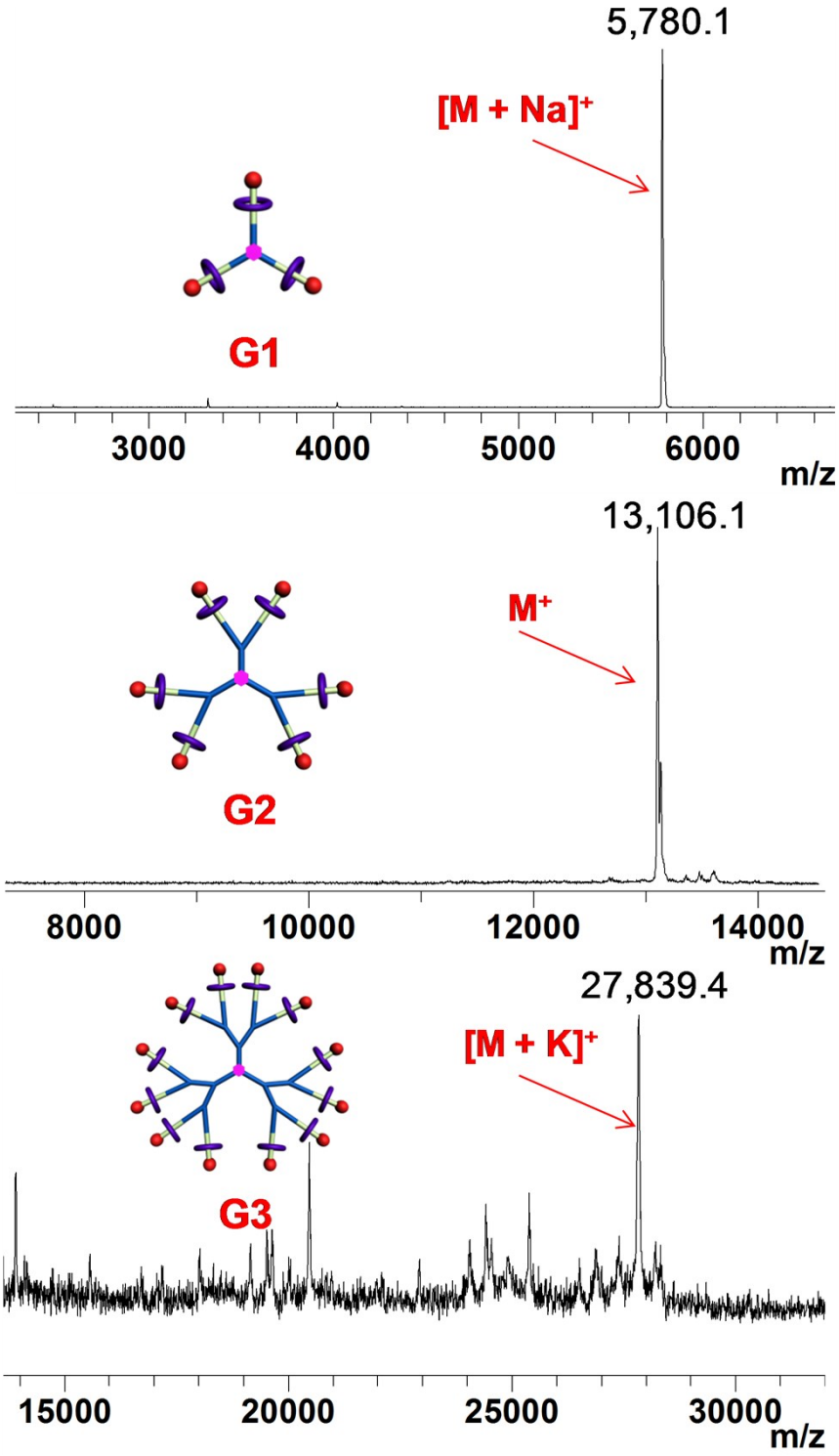


Figure S51. MALDI-TOF-MS spectra of **G1**, **G2** and **G3**.

Section C. Additional Characterization of Rotaxane-terminated Dendrimers

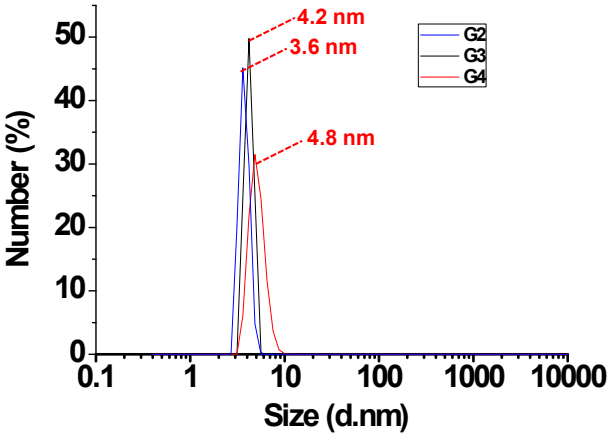


Figure S52. Dynamic light scattering (DLS) measurements of the hydrodynamic radius (R_h) of rotaxane-terminated dendrimers **G2-G4**. (It was not possible to obtain the hydrodynamic radius (R_h) of G1 by DLS because its size is below the limit for this technique.)

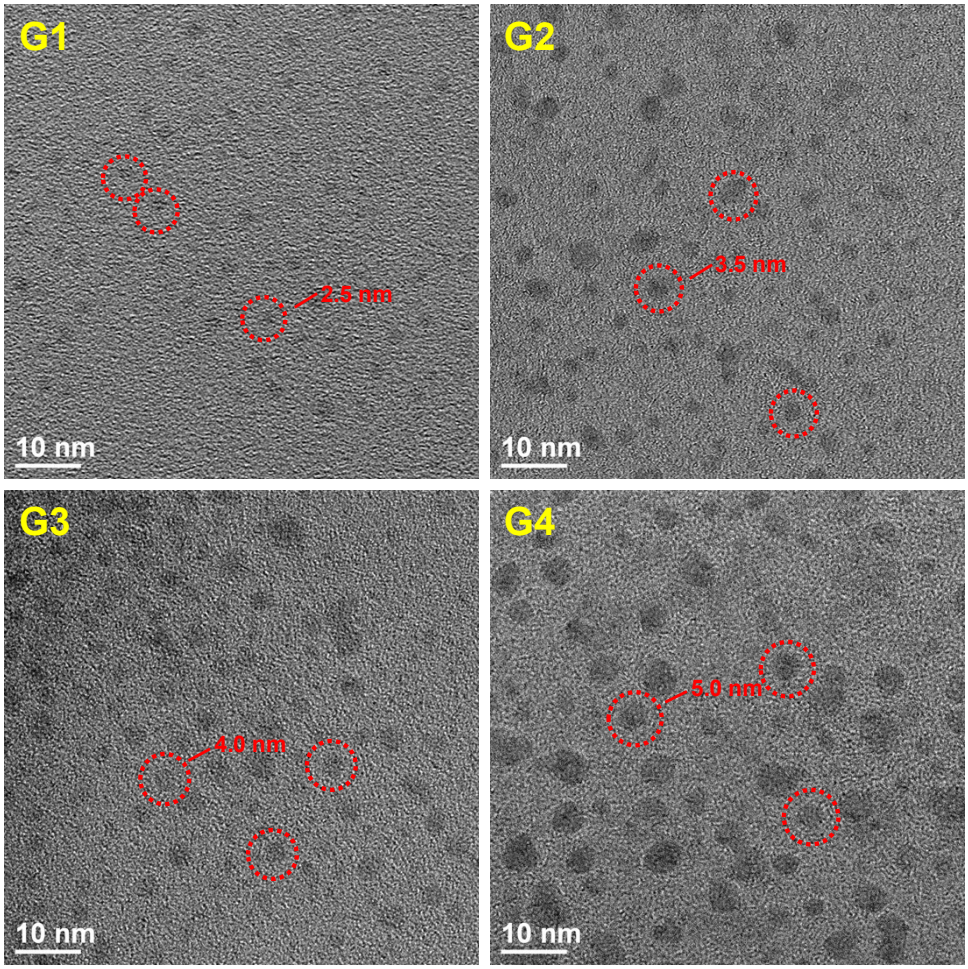


Figure S53. TEM image of the rotaxane-terminated dendrimers **Gn**.

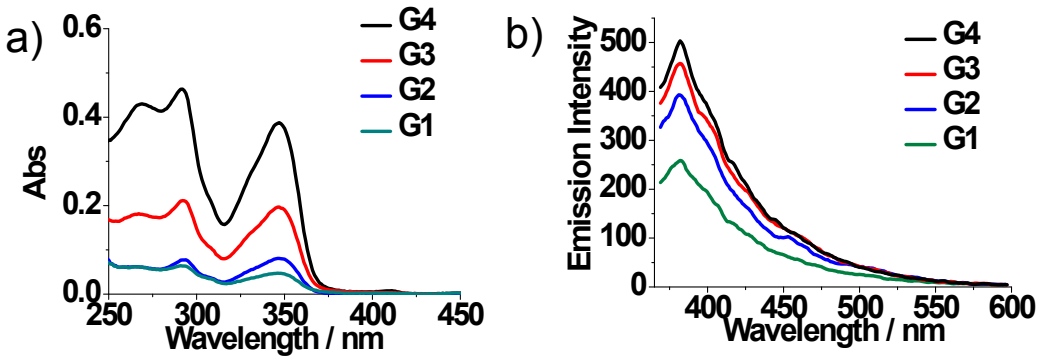


Figure S54. (a) UV-vis absorption spectra of rotaxane-terminated dendrimers **Gn** (n = 1, 2, 3, and4) in $CHCl_3$; (b) emission spectra of rotaxane-terminated dendrimers **Gn** (n = 1, 2, 3, and 4) in THF.

	absorption	emission
compound	λ_{abs}/nm (ε/dm^3 mol^{-1} cm^{-1})	λ_{em}/nm
G1	269 (30715), 292 (31695), 347 (23555)	380
G2	269 (30570), 292 (38600), 347 (40365)	380
G3	269 (90270), 292 (105765), 347 (98450)	380
G4	269 (2150350), 292 (2317150), 347 (1938800)	380

Table S1. Photophysical Properties of rotaxane-terminated dendrimers **Gn**.

References

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S2. S. Leininger, P. J. Stang and S. Huang, *Organometallics*, 1998, **17**, 3981.