

Supporting Information

Synthesis of Resorcin[4]arene Cavitands by Ring Closing Metathesis

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EXPERIMENTAL SECTION

General Methods: Elemental analyses were performed using a Carlo-Erba NA 2500 series 2carbon & Nitrogen analyzer. ^1H and ^{13}C NMR spectra were taken on Varian Inova 400 and 500MHz and Bruker DPX 250MHz spectrophotometers. Compounds were ionized by APCI-MS.

General procedure for synthesis of Octol-1:

Methyl resorcinol (10g, 0.081mol) was dissolved in ethanol (62.7mL, 775mL/mol) and 37% aqueous HCl (15.1mL, 185mL/mol). The solution was cooled in ice bath and heptaldehyde (11.3mL, 0.081mol) was added slowly over a period of 30 min. The reaction mixture was allowed to warm to room temperature and refluxed for 12 h. The yellow colored precipitate was filtered and washed several times with distilled water until it turns neutral to pH paper. Yield 10.7g (**88** %). MP: $>220^\circ\text{C}$ (decomposed). ^1H NMR (250 MHz, DMSO- d_6) δ : 0.84 (t, 12H, $J = 6.25\text{Hz}$), 1.23(m, 32H), 1.93(s, 12H), 2.21(s, 8H), 4.18 (t, 4H $J = 7.75\text{Hz}$), 7.21 (s, 4H), 8.69(bs, 8H).

^{13}C NMR (100 MHz, DMSO- d_6) δ : 10.7, 14.2, 22.9, 28.9, 29.8, 32.1, 35.4, 38.4, 73.0, 113.6, 122.0, 124.6, 154.0. Found: C, 72.81; H, 13.24. Calcd for $\text{C}_{56}\text{H}_{80}\text{O}_8 \cdot 2\text{H}_2\text{O}$: C, 72.99; H, 13.12..

General procedure for Synthesis of perallylated resorcinarenes (7-12)

In a pressure vessel, to the octahydroxy compound (**1-6**, 1g) in acetone (20mL/mol) potassium carbonate (30eq) was added and stirred for 30 minutes. To the reaction mixture allyl bromide (30eq) was added and the vessel was tightly capped. The reaction vessel was heated to temperature of 90°C for nearly 24-48 hrs in an oil bath. The reaction mixture was filtered and concentrated using a rotary evaporator. The product was recrystallized using 70% acetone -methanol mixture. NMR of the crystals was taken in CDCl_3 .

Compound **7**. MP: 71°C . ^1H NMR (400 MHz, CDCl_3) δ : 0.76(t, 12H, $J = 7.2\text{Hz}$), 1.2(m, 32H), 1.85(m, 8H), 2.15(s, 12H), 4.31(d, 16H, $J = 7.2\text{Hz}$), 5.06(t, 4H $J = 10.4\text{Hz}$), 5.2(d, 16H, $J = 14.8\text{Hz}$) 6.1(m, 8H), 6.55(s, 4H)

^{13}C NMR (100MHz, CDCl_3) δ : 10.7, 14.2, 22.9, 28.9, 29.8, 32.1, 35.4, 38.4, 73.3, 116.2, 124.0, 124.0, 124.6, 134.6.154.0. Found: C, 73.94; H, 16.13. Calcd for $\text{C}_{80}\text{H}_{112}\text{O}_8 \cdot \text{H}_2\text{O}$: C, 73.77; H, 16.41. HRMS-APCI calculated 1201.8430 ($\text{M} + \text{H}^+$); observed 1201.8401 ($\text{M} + \text{H}^+$).

Compound **8** ^1H NMR (400 MHz, CDCl_3) δ : 0.82 (t, 12H, $J = 7.2\text{ Hz}$), 1.26 (m, 56H), 1.85 (m, 8H), 2.15 (s, 12H), 4.25 (m, 16H), 4.55 (m, 4H), 5.25 (m, 16H), 6.13 (m, 8H), 6.55 (s, 4H)

^{13}C NMR (100MHz, CDCl_3) δ : 10.6, 10.9, 14.2, 22.8, 28.6, 28.9, 29.5, 30.2, 32.1, 33.5, 34.1, 35.4, 36.5, 37.4, 37.9, 38.4, 38.7, 40.0, 73.3, 73.7, 73.9, 74.5, 74.7, 116.2, 116.4, 116.7, 117.0, 117.3, 124.0, 124.5, 124.7, 124.9, 130.2, 131.7, 133.9, 134.4, 134.6, 134.7, 134.8, 136.8, 153.6, 153.9, 154.6, 155.2. Found: C, 74.87; H, 17.11. Calcd for

C₉₂H₁₃₆O₈.6H₂O: C, 74.11; H, 17.31. HRMS-APCI calculated 1369.0230 (M⁺); observed 1369.0263 (M⁺)

Compound **9**. MP: 114 °C. ¹H NMR (400 MHz, CDCl₃) δ: 0.77 (t, 12H, J= 6.75Hz), 1.16 (m, 32H), 1.48 (t, 8H, J= 8.25Hz), 1.82 (s, 4H), 4.36 (t, 16H, J= 7Hz), 5.14 (d, 16H, J = 9.5Hz), 5.92 (s, 8H).

¹³C NMR (400 MHz, CDCl₃) δ: 14.3, 22.8, 22.9, 28.8, 29.8, 32, 32.1, 35.0, 39.4, 74.1, 110.0, 117.4, 126, 133.9, 154. Found: C, 54.66; H, 18.12. Calcd for C₇₆H₁₀₀O₈Br₄.10H₂O: C, 54.9; H, 18.19. HRMS-APCI calculated 1457.4224 (M+H⁺); observed 1457.4213 (M+H⁺).

Compound **10** MP: 84 °C. ¹H NMR (400 MHz, CDCl₃) δ : 0.86 (t, 12H, J= 7Hz), 1.22 (m, 56H), 1.9 (s, 8H), 4.45 (t, 20H, J= 7Hz), 5.23 (d, 16H, J= 9.5Hz), 6.01 (s, 8H), 6.96 (s, 4H).

¹³C NMR (100 MHz, CDCl₃) δ: 14.3, 22.9, 28.8, 29.6, 29.9, 30.1, 32.2, 35.0, 39.4, 74.08, 110.0, 113.9, 117.3, 126.1, 133.9, 138.6, 157.1. Found: C, 64.88; H, 7.64. Calcd for C₈₈H₁₂₄O₈Br₄: C, 64.86; H, 7.67.

Compound **11** MP: 186 °C. ¹H NMR (400 MHz, CDCl₃) δ: 2.12 (d, J=9.2Hz, 6H), 2.25 (d, J=9.2Hz, 6H), 3.64 (m, 16H), 5.05-5.20(m, 16H), 5.60 (d, 2H, J=9.6Hz), 6.31 (d, 2H, J=9.6Hz), 5.85 (m, 8H), 5.93 (d, 4H), 6.60 (d, 8H, J= 7.6Hz), 6.84 (d, 8H, J= 7.6Hz), 6.86 (s, 4H).

¹³C NMR (100 MHz, CDCl₃) [10.71, 10.91], 44.47, [73.51, 73.76], [116.63, 116.99], 124.07, [125.23, 125.87], 127.78, 128.03, 129.09, 130.79, [132.85, 133.24], [134.17, 134.28], 143.13, [154.84, 154.93]. Found: C, 74.39; H, 15.24. Calcd for C₈₀H₈₀O₈.6H₂O: C, 74.46; H, 15.62. HRMS-APCI calculated 1169.5926 (M+H⁺); observed 1169.5912 (M+H⁺).

Compound **12** ¹H NMR (400 MHz, CDCl₃) δ: 2.12 (d, J=9.2Hz, 6H), 2.25 (d, J=9.2Hz, 6H), 3.64-4.42 (m, 16H), 5.05-5.20 (m, 16H), 5.60 (d, 2H, J=9.6Hz), 6.31 (d, 2H, J=9.6Hz), 5.85 (m, 8H), 5.93 (d, 4H), 6.60 (d, 8H, J= 7.6Hz), 6.84 (d, 4H, J= 7.6Hz), 6.86 (s, 4H).

¹³C NMR (100 MHz, CDCl₃) [10.71, 10.90], 43.84, [73.57, 73.87], [116.79, 117.43], 120.12, [130.68, 130.87], [132.39, 132.50], [133.79, 133.95], 142.35, [154.98, 155.06]. HRMS-APCI calculated 11484.2581 (M⁺); observed 1484.2541(M⁺).

General procedure for Synthesis of bridged resorcinarenes (13-18)

To a stirred solution of octa-allyloxy resorcinarene in dry methylene chloride [108mL/mmol] was added Grubb's generation -I catalyst [8 mole%,] in dry methylene chloride [20mL] at room temperature. Reaction was continued for 4 days. Reaction mixture was then concentrated using a rotary evaporator and compound was isolated by column chromatography using 10% ethyl acetate and 90% hexane solvent system. Strural

analysis of the product was undertaken using ^1H NMR, COSY, ^{13}C , DEPT, HSQC, and Mass analysis.

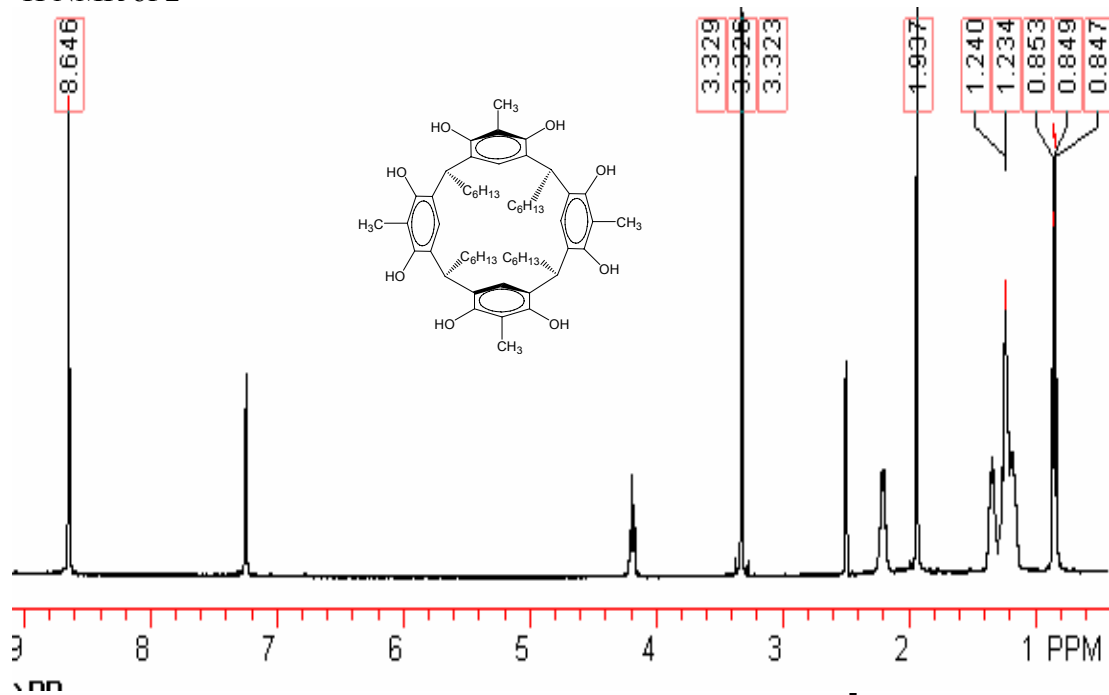
Compound **13**. MP: 162 $^{\circ}\text{C}$. ^1H NMR (400MHz, CDCl_3) δ : 0.82 (t, 12H, $J = 6.8$ Hz), 1.27-1.20 (m, 32H), 1.85 (m, 8H), 2.18 (s, 12H), 4.45 (d, 8H, $J = 12.4$ Hz), 4.73 (dd, 8H, $J = 2.4$ Hz, $J = 12.8$ Hz), 4.82 (t, 4H, $J = 8.0$ Hz), 5.88 (bs, 8H), 7.03 (s, 4H); ^{13}C NMR (100MHz, CDCl_3) δ : 11.5, 14.2, 22.9, 28.0, 29.6, 32.1, 36.1, 37.2, 71.0, 123.7, 129.14, 133.5, 154.9. Found: C, 79.57; H, 8.81. Calcd for $\text{C}_{72}\text{H}_{96}\text{O}_8$: C, 79.37; H, 8.88. HRMS-ESI calculated 1089.7178 ($\text{M}+\text{H}^+$); observed 1089.7182($\text{M}+\text{H}^+$)

Compound **14**. MP: 145 $^{\circ}\text{C}$. ^1H NMR (400MHz, CDCl_3) δ : 0.83 (t, 12H, $J = 6.8$ Hz), 1.24-1.12 (m, 32H), 1.82 (m, 8H), 2.14 (s, 12H), 4.41 (d, 8H, $J = 12.0$ Hz), 4.68 (dd, 8H, $J = 3.4$ Hz, $J = 12.5$ Hz), 4.76 (t, 4H, $J = 7.6$ Hz), 5.85 (bs, 8H), 7.01 (s, 4H); ^{13}C NMR (100MHz, CDCl_3) δ : 10.3, 13.0, 21.6, 26.9, 28.3, 28.6, 28.7, 28.8, 30.9, 34.9, 35.9, 69.7, 122.5, 127.9, 132.3, 153.6. Found: C, 75.97; H, 9.65. Calcd for $\text{C}_{84}\text{H}_{120}\text{O}_8$ $4\text{H}_2\text{O}$: C, 75.86; H, 9.7. HRMS-ESI Calculated $m/z=1274.9321$ ($\text{M}+\text{NH}_4^+$); Observed $m/z = 1274.9280$ ($\text{M}+\text{NH}_4^+$).

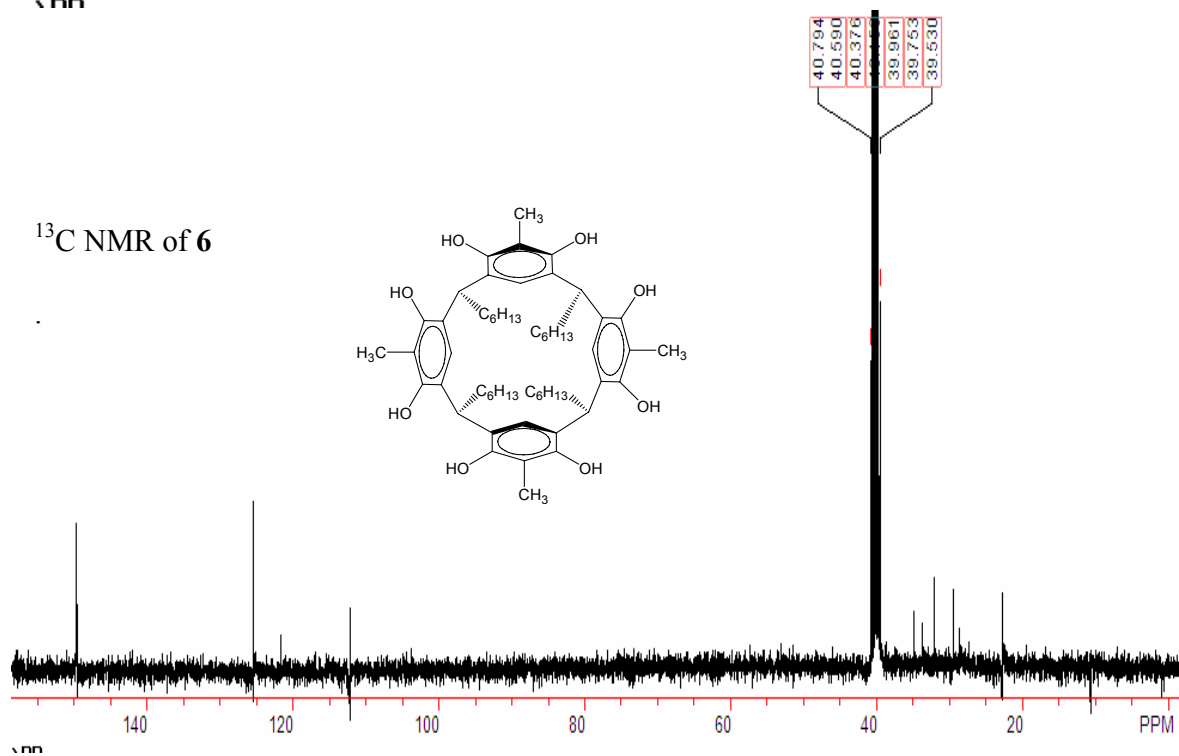
Compound **15** ^1H NMR (500MHz, CDCl_3) δ : 0.86 (t, 12H, $J=7\text{Hz}$), 1.23 (m, 56H), 1.9 (s, 8H), 4.82 (t, 20H, $J= 12.5\text{Hz}$), 5.95 (s, 8H), 6.96 (s, 4H). ^{13}C NMR (125MHz, CDCl_3) 14.3, 22.9, 27.8, 29.6, 29.8, 29.9, 32.2, 77.5, 109.9, 113.6, 117.3, 125.3, 130.1, 135.3, 154.2. Found: C, 58.48; H, 8.98. Calcd for $\text{C}_{68}\text{H}_{84}\text{O}_8\text{Br}_4.2\text{H}_2\text{O}$: C, 58.79; H, 9.00. HRMS-APCI Calculated $m/z=1345.2978$ ($\text{M}+\text{H}^+$); Observed $m/z = 1345.2918$ ($\text{M}+\text{H}^+$)

Compound **16**. MP:111 $^{\circ}\text{C}$. ^1H NMR (500MHz, CDCl_3) δ : 0.86 (t, 12H, $J= 6.8\text{Hz}$), 1.22 (m, 56H), 1.9 (s, 8H), 4.76 (d, 12H, $J=12.0\text{Hz}$), 6.01 (s, 8H), 6.9 (s, 4H). ^{13}C NMR (125MHz, CDCl_3) 14.3, 22.9, 28.8, 29.6, 29.9, 30.1, 32.2, 35.0, 39.4, 74.08, 113.9, 117.4, 126.1, 133.9, 138.6, 157.1. Found: C, 63.69; H, 7.20. Calcd for $\text{C}_{80}\text{H}_{108}\text{O}_8\text{Br}_4$: C, 63.33; H, 7.17. HRMS-APCI Calculated $m/z=1513.4856$ ($\text{M}+\text{H}^+$); Observed $m/z = 1513.4900$ ($\text{M}+\text{H}^+$).

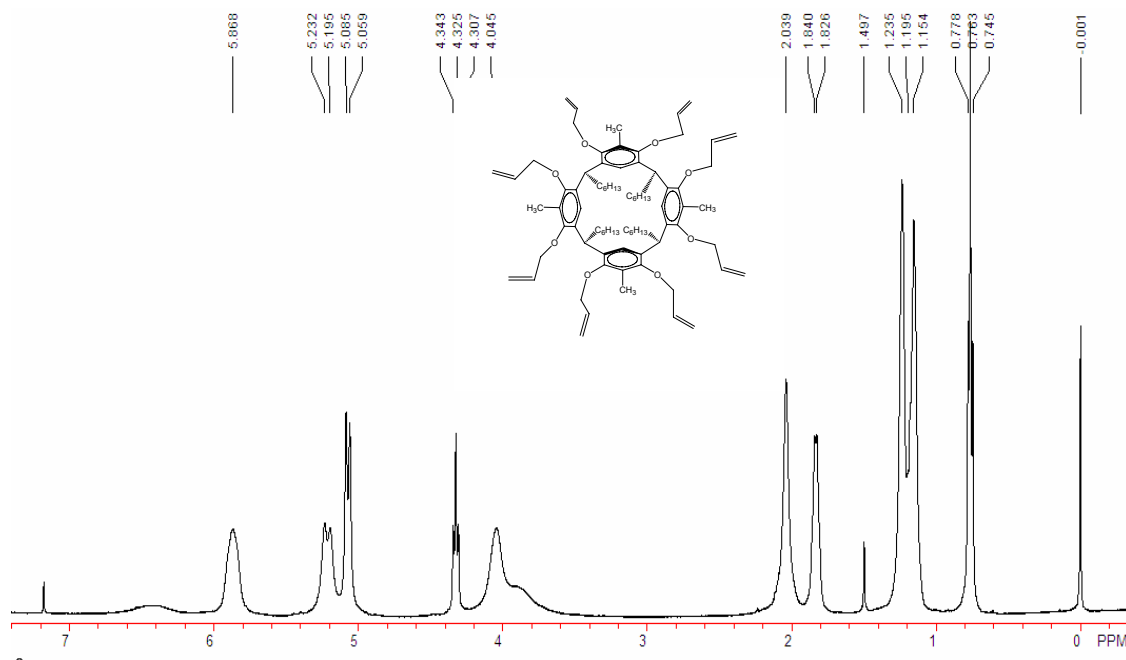
^1H NMR of **2**



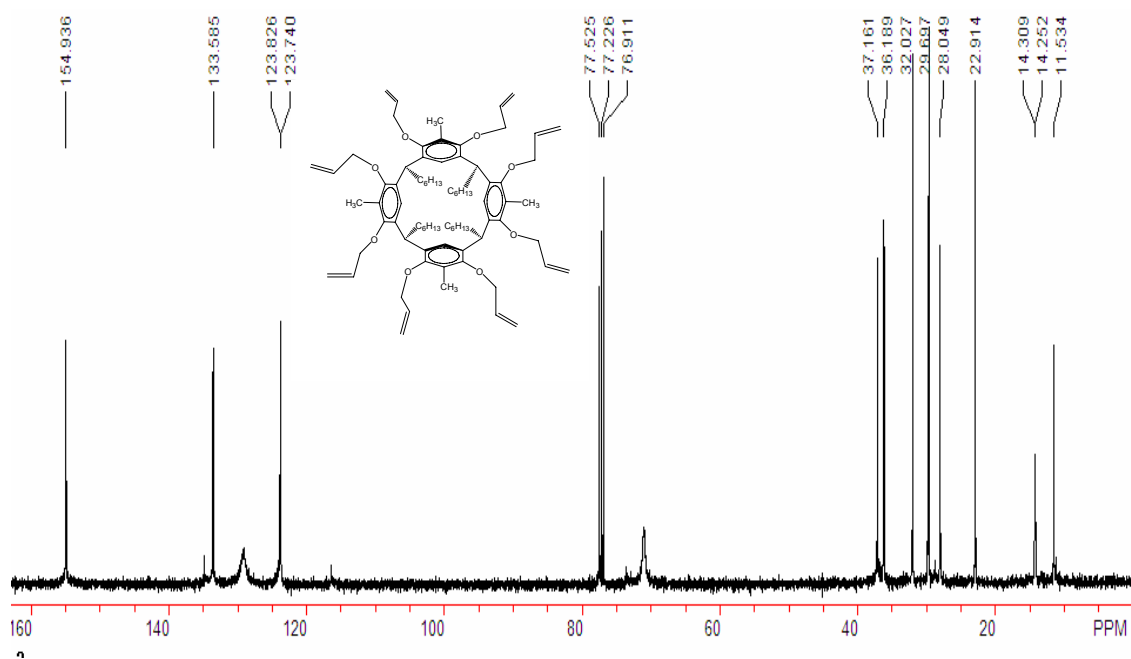
^{13}C NMR of **6**



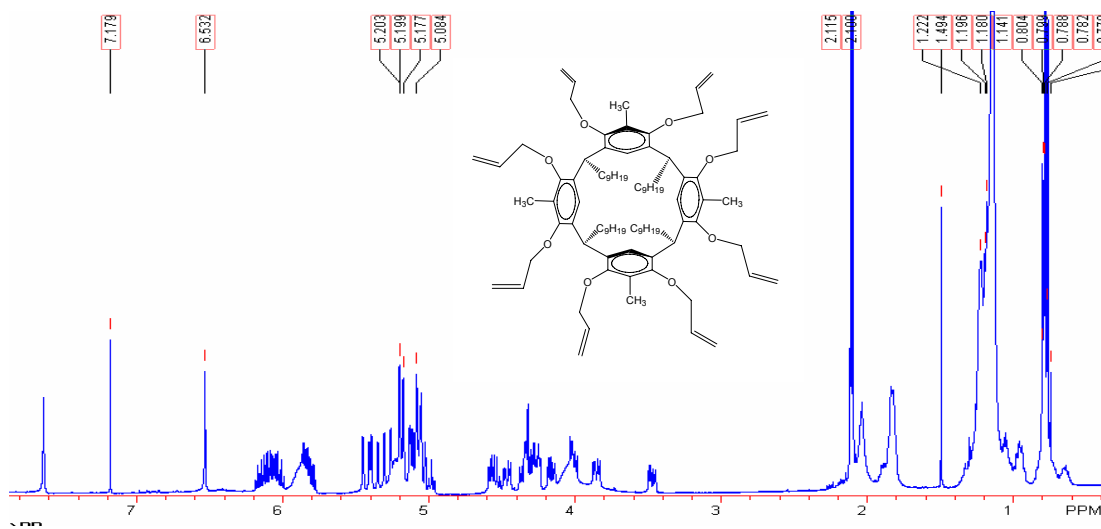
^1H NMR of 7



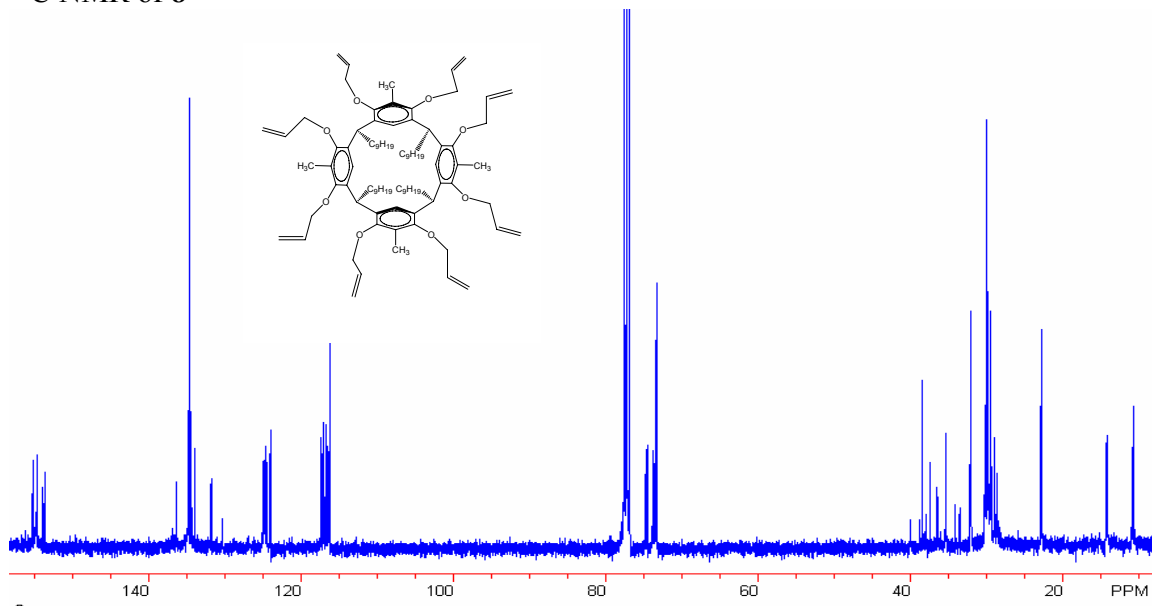
^{13}C NMR spectrum of 7



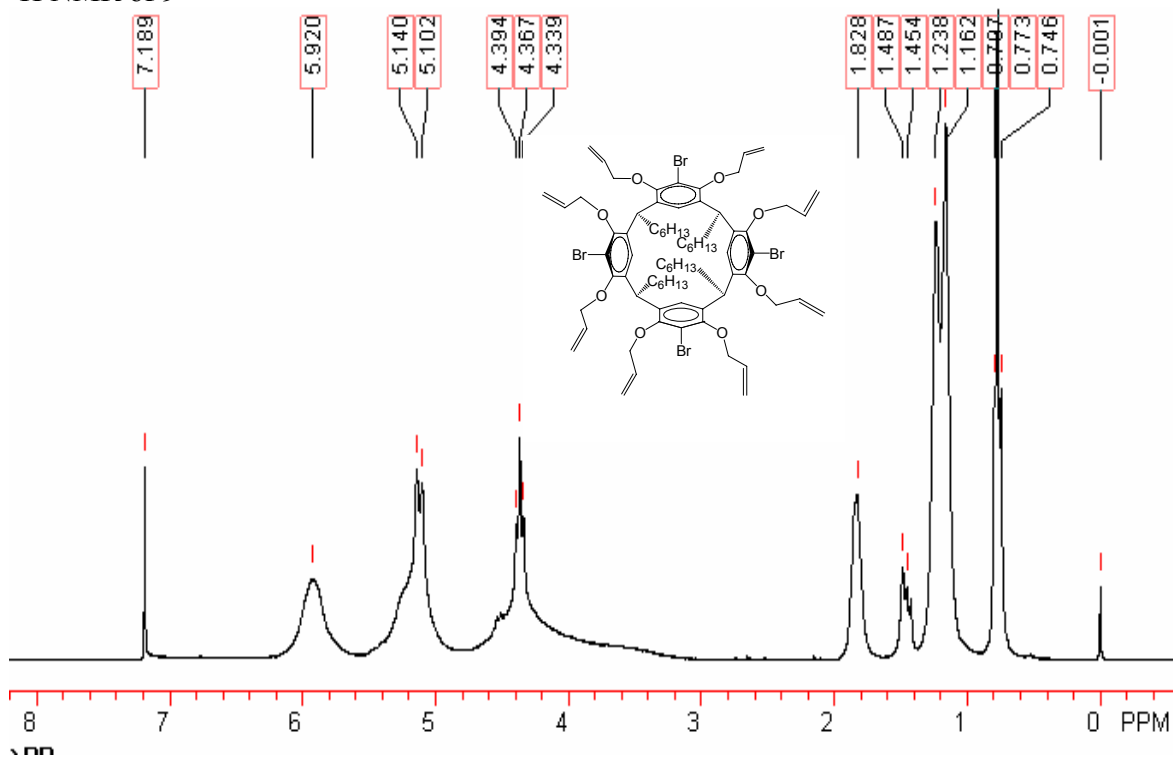
^1H NMR of **8**



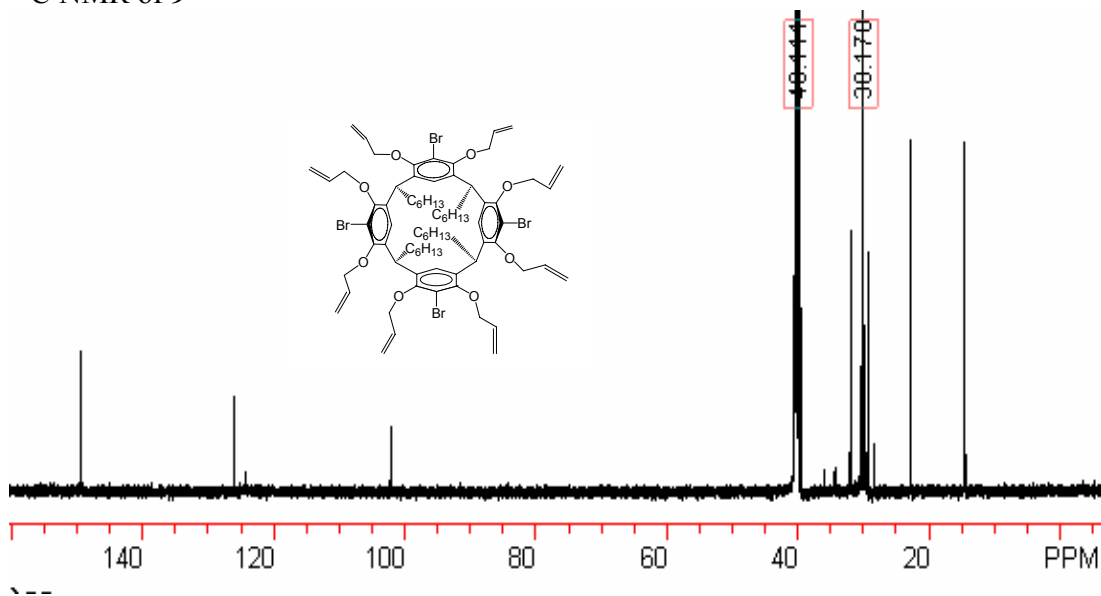
^{13}C NMR of **8**



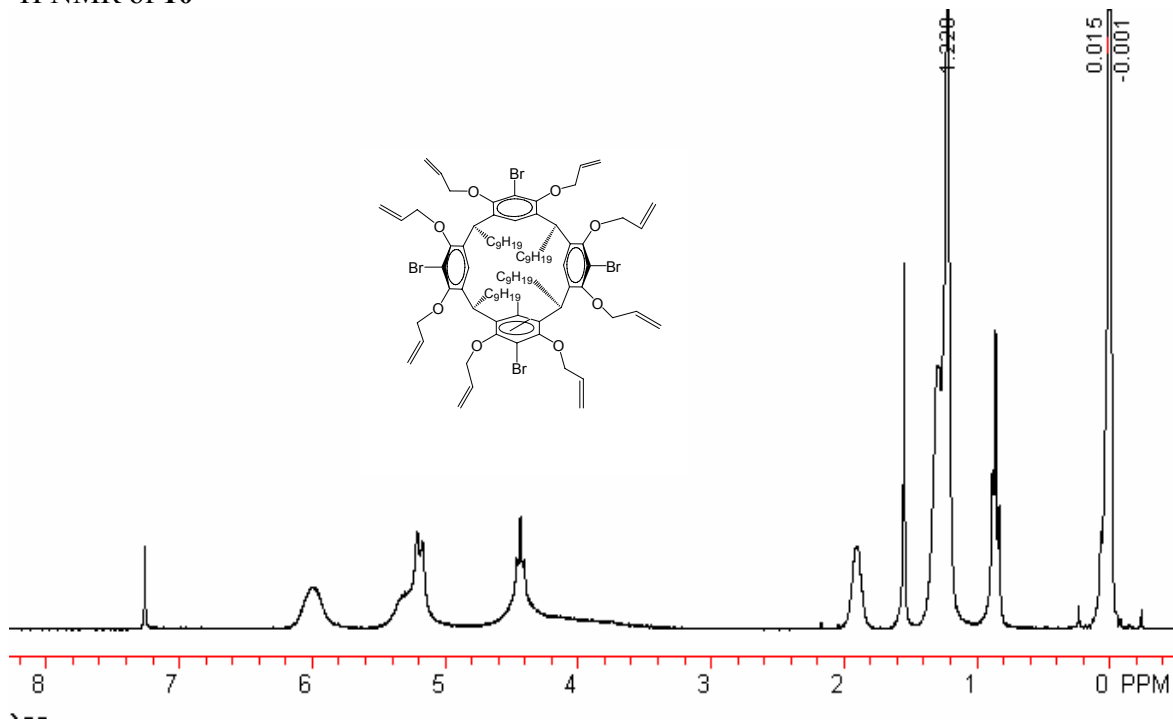
^1H NMR of **9**



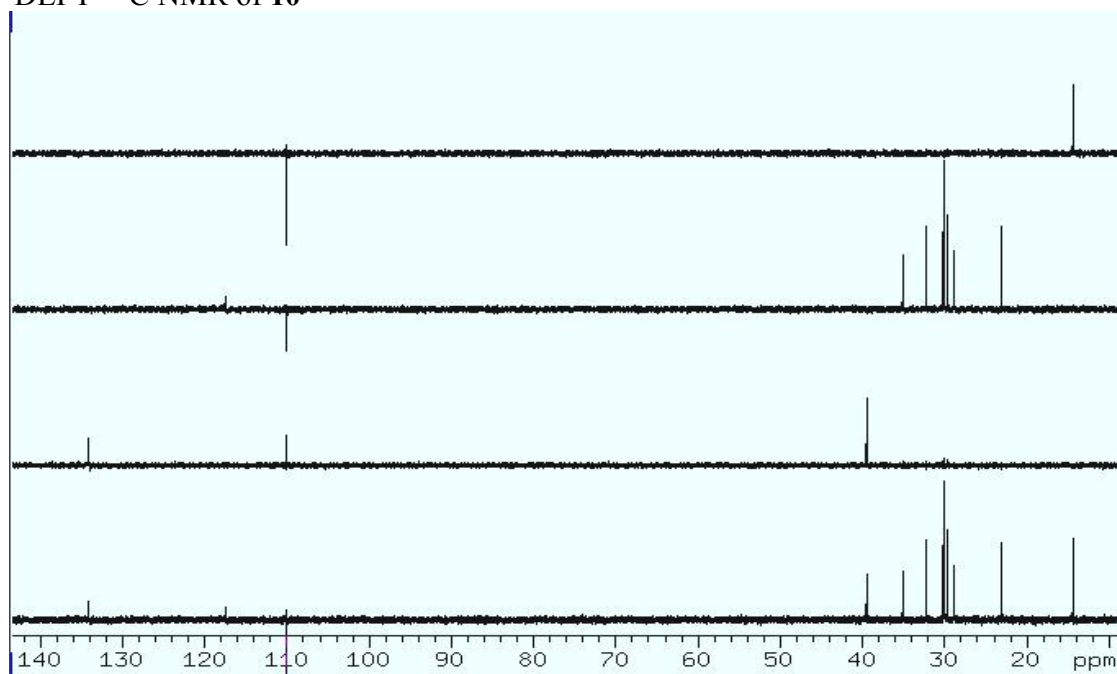
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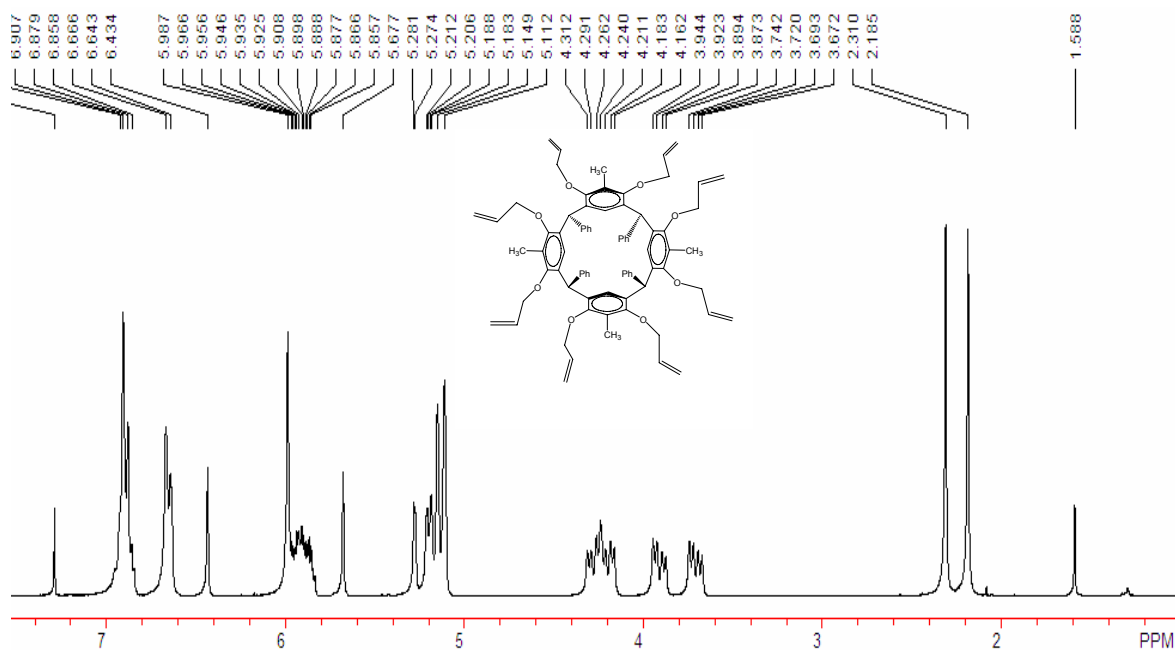
^1H NMR of **10**



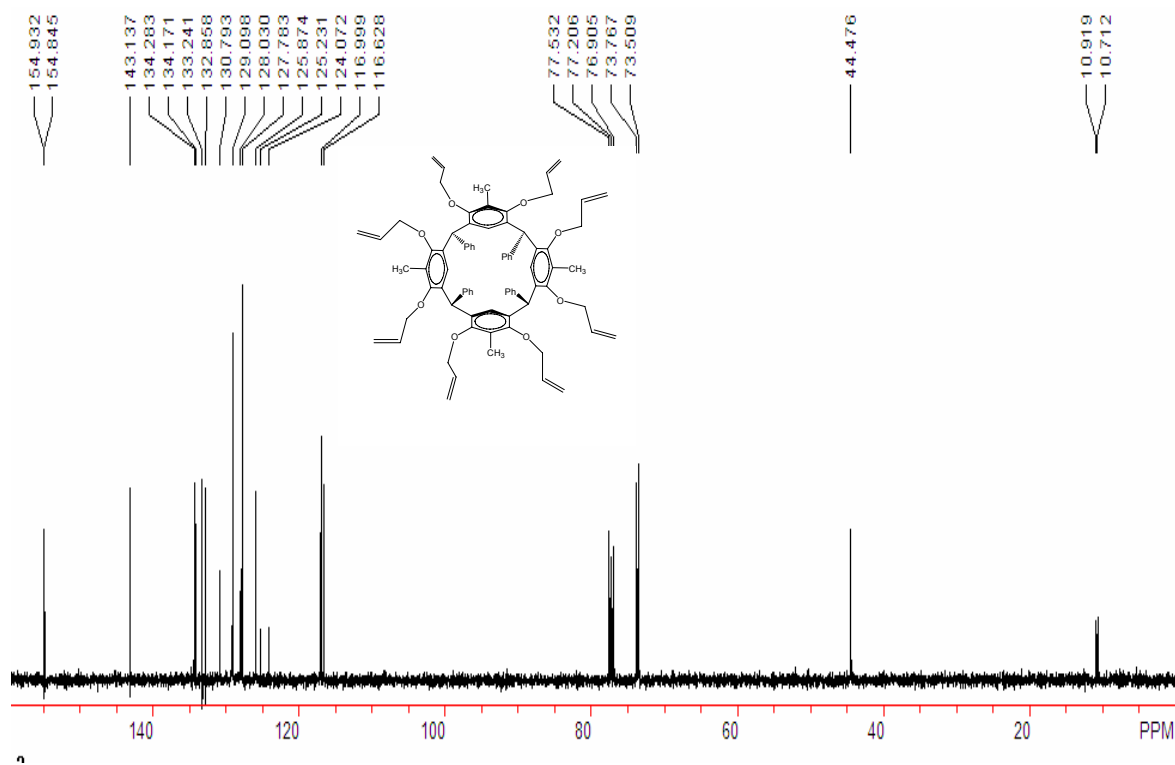
DEPT ^{13}C NMR of **10**



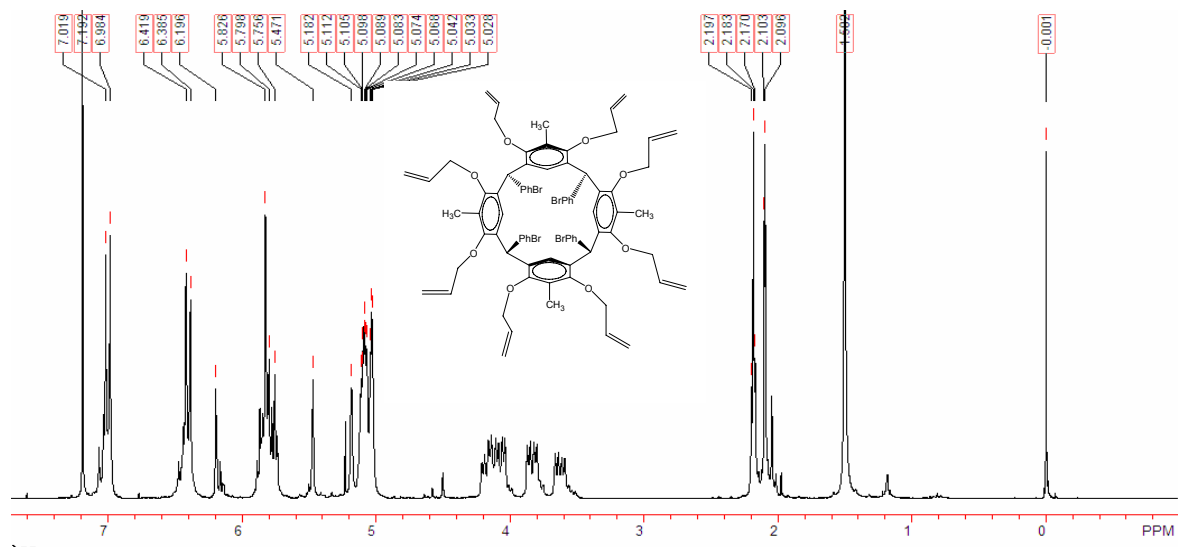
^1H NMR of **11**



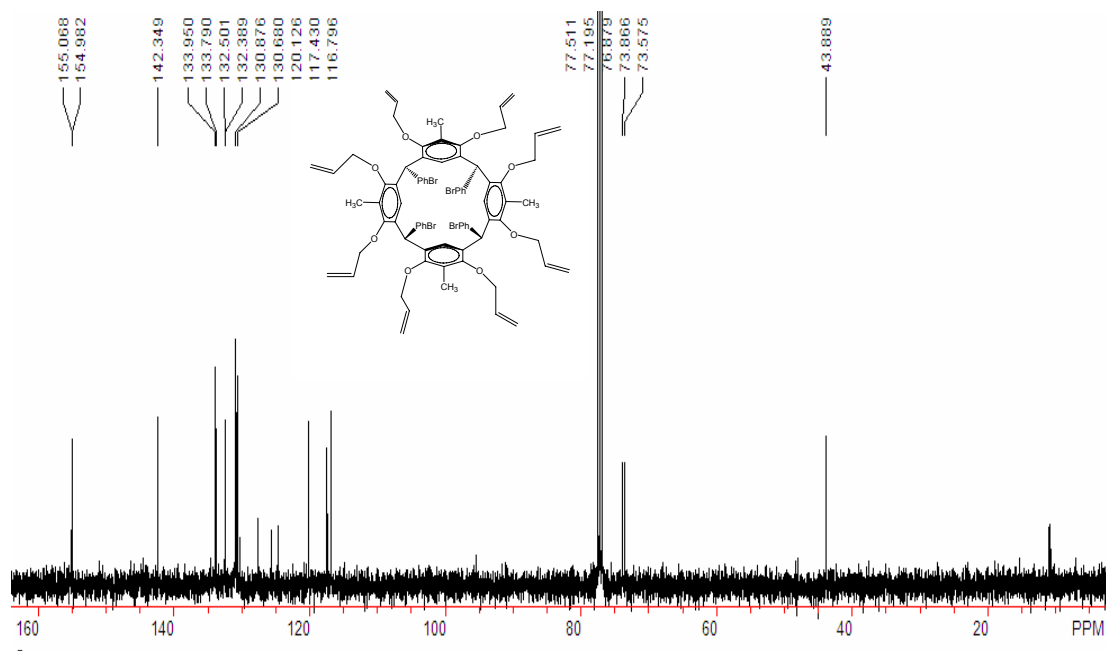
^{13}C NMR of **11**



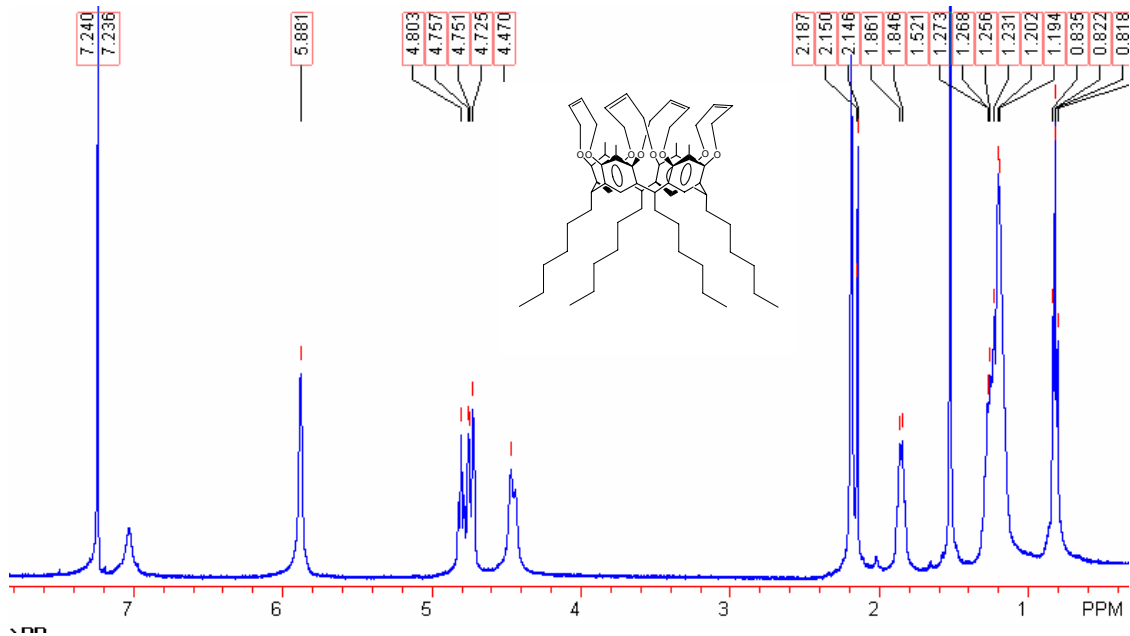
^1H NMR of **12**



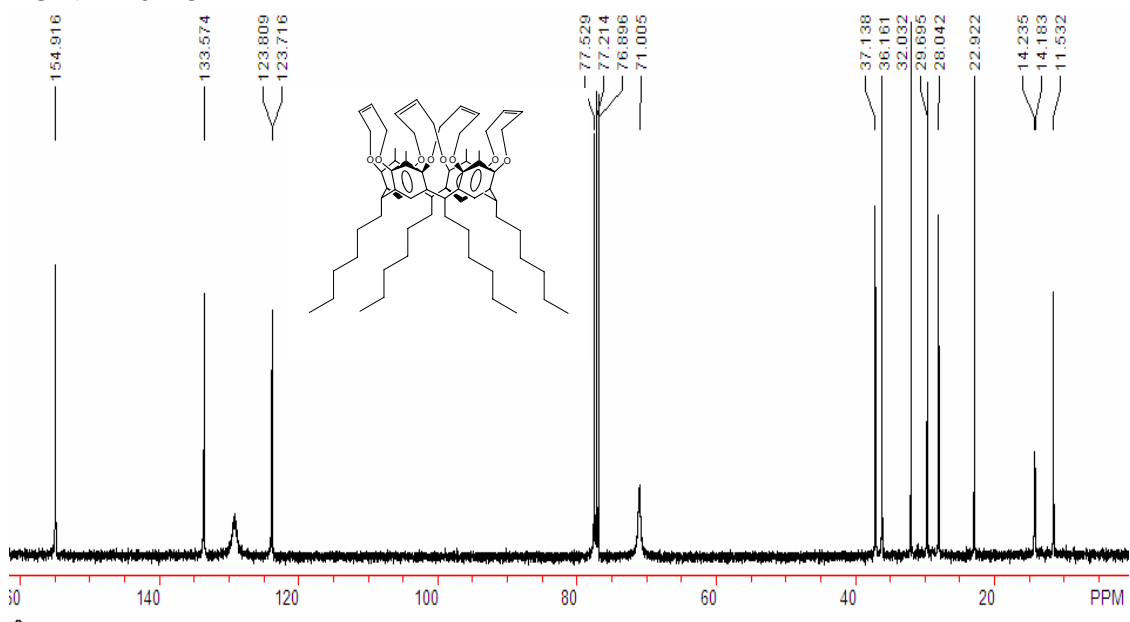
^{13}C NMR of **12**



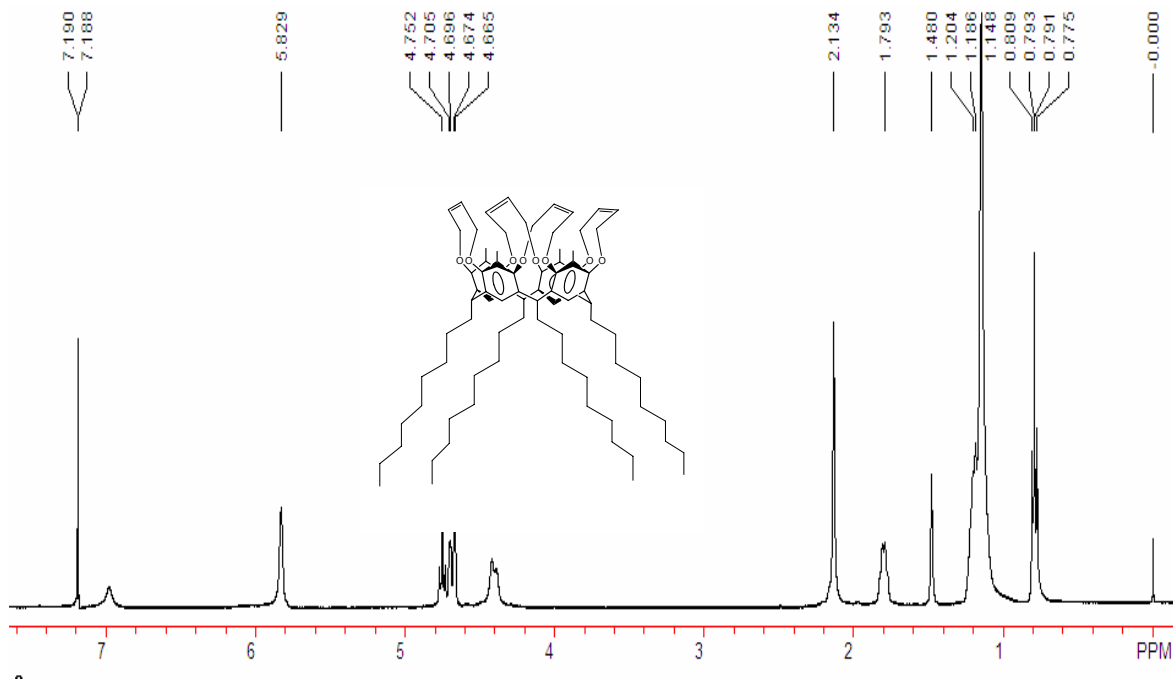
^1H NMR of **13**



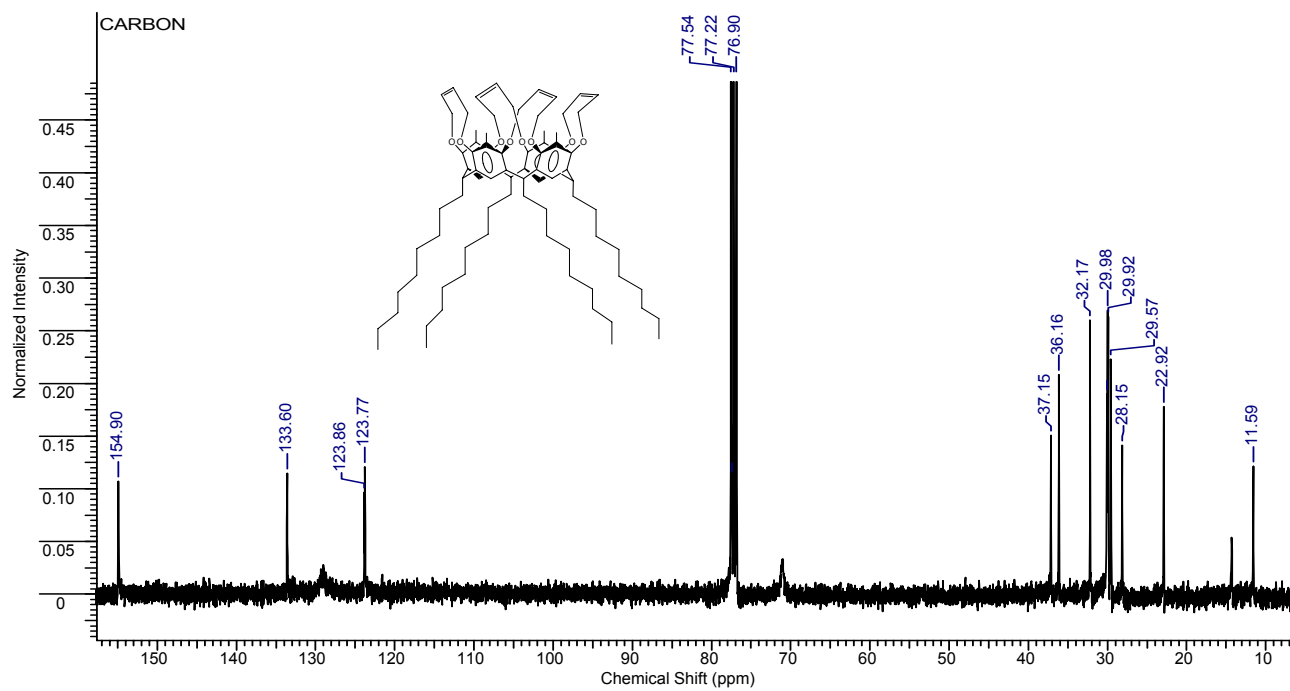
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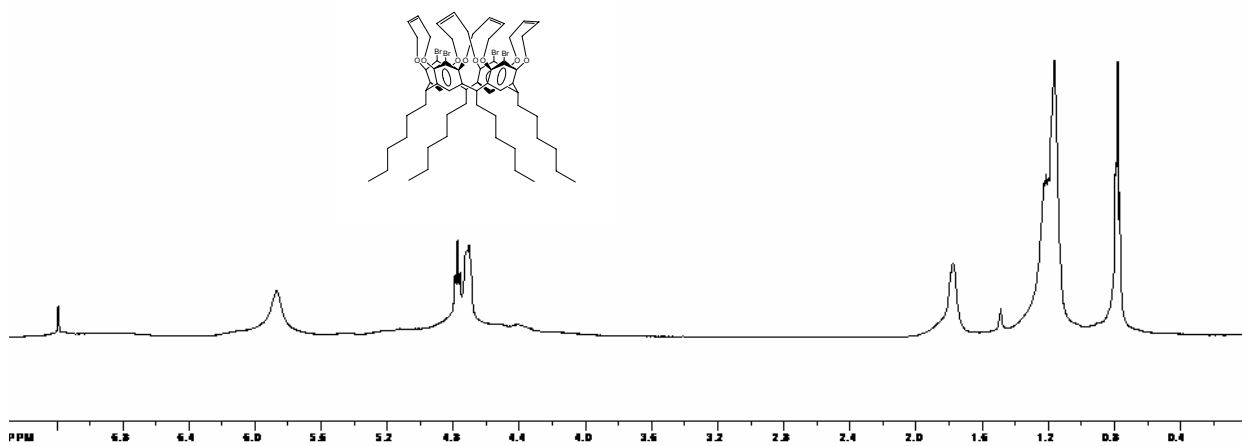
^1H NMR of **14**



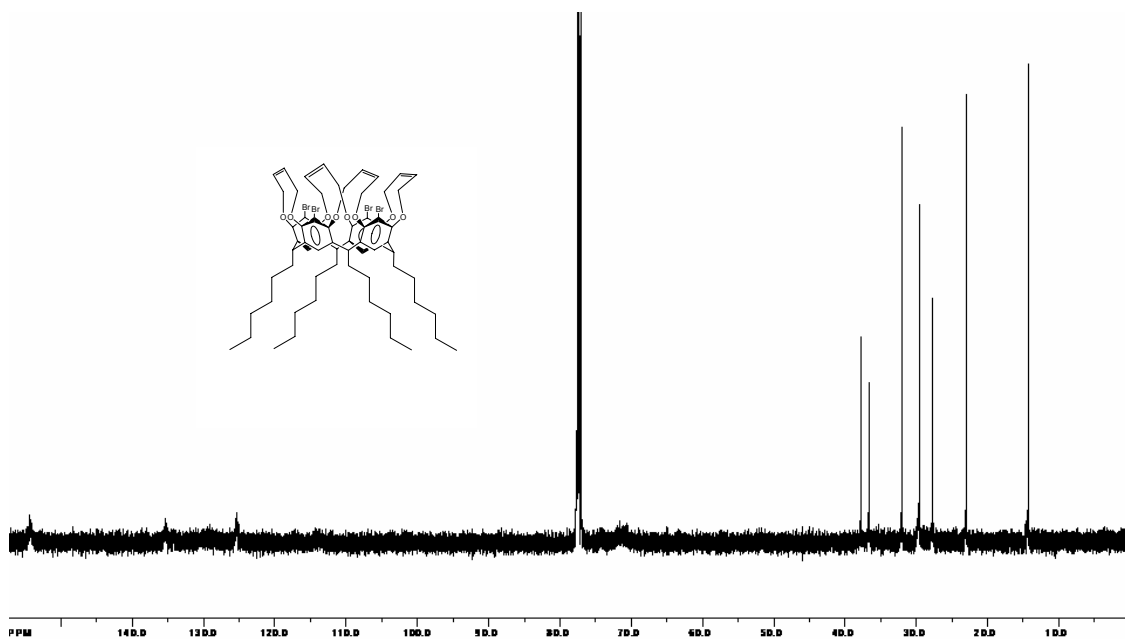
^{13}C NMR of **14**



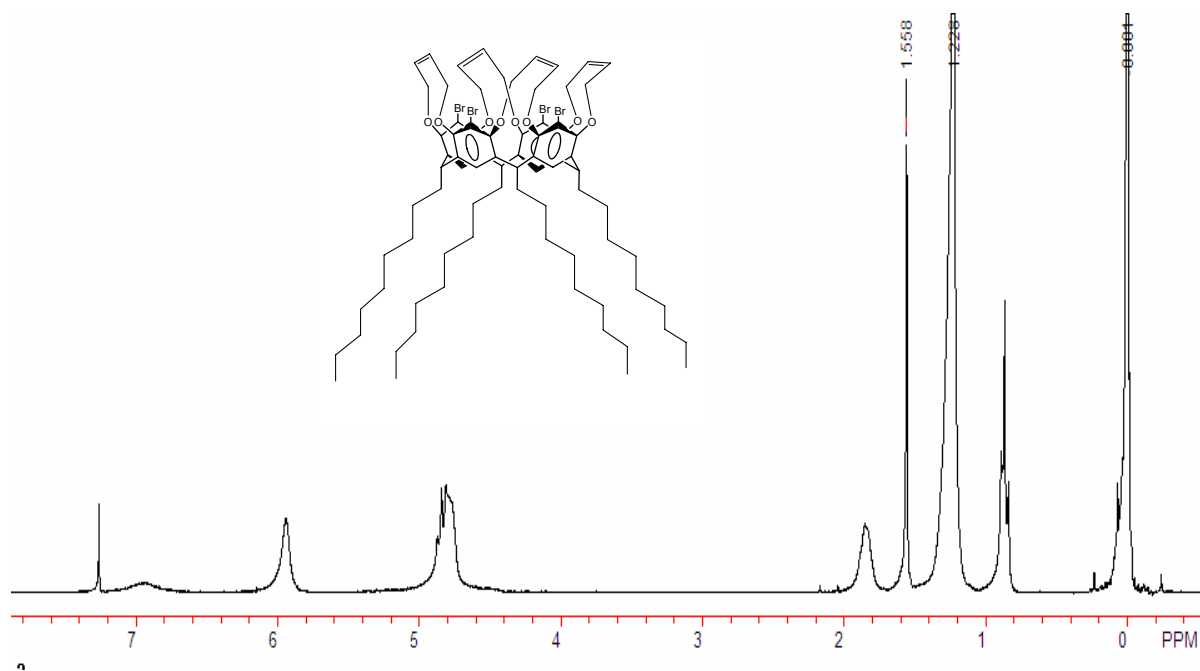
^1H NMR of **15**



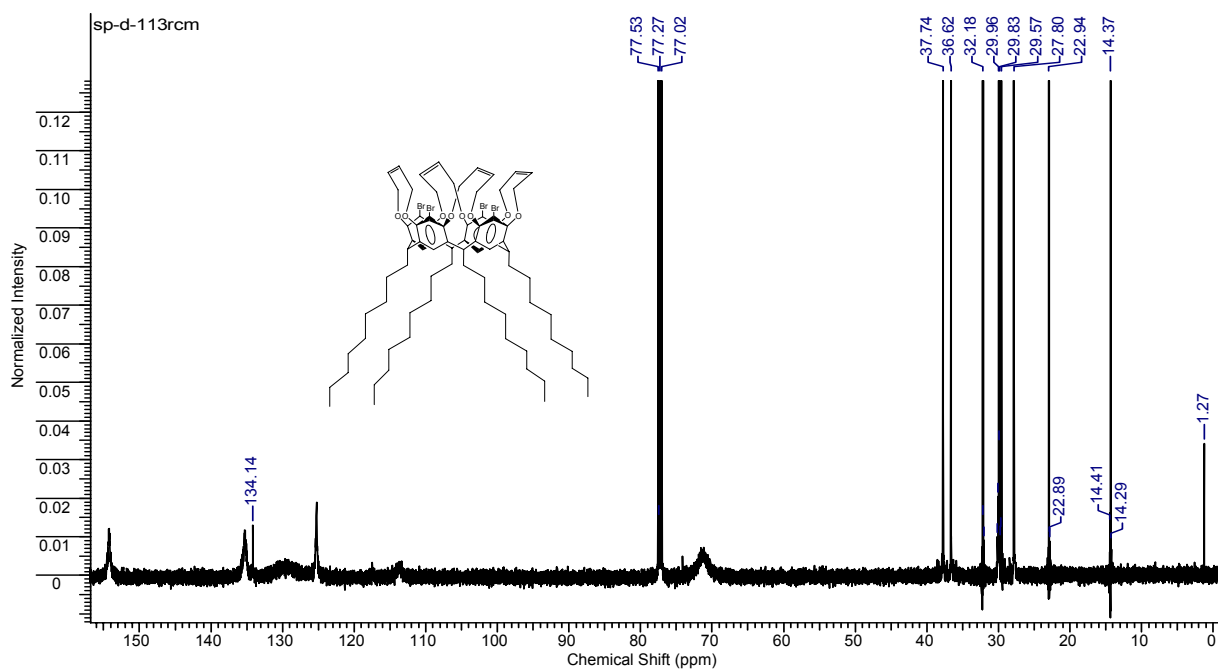
¹³C NMR of Compound 15



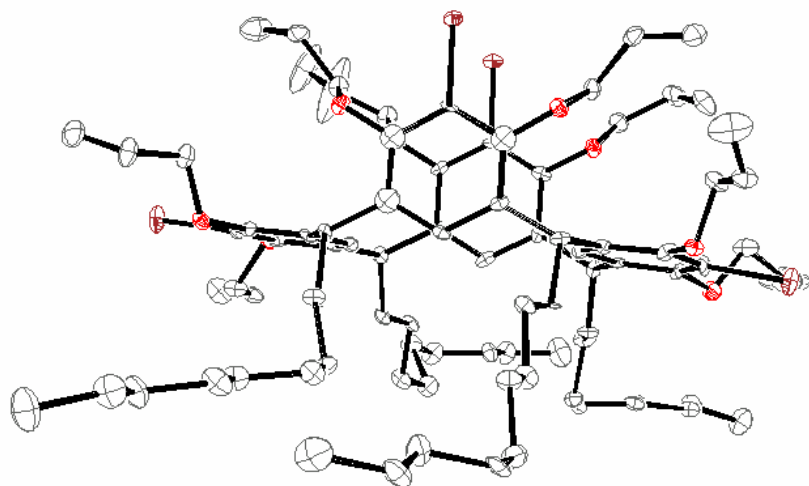
^1H NMR of **16**



^{13}C NMR of **16**



Crystal structure of compound **10**



Crystal structure of compound **11**

