Supporting Information for:

meta-Bridged Calix[4]arenes Prepared by Friedel–Crafts Alkylation

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Table of Contents

Spectral characteristics of novel compounds

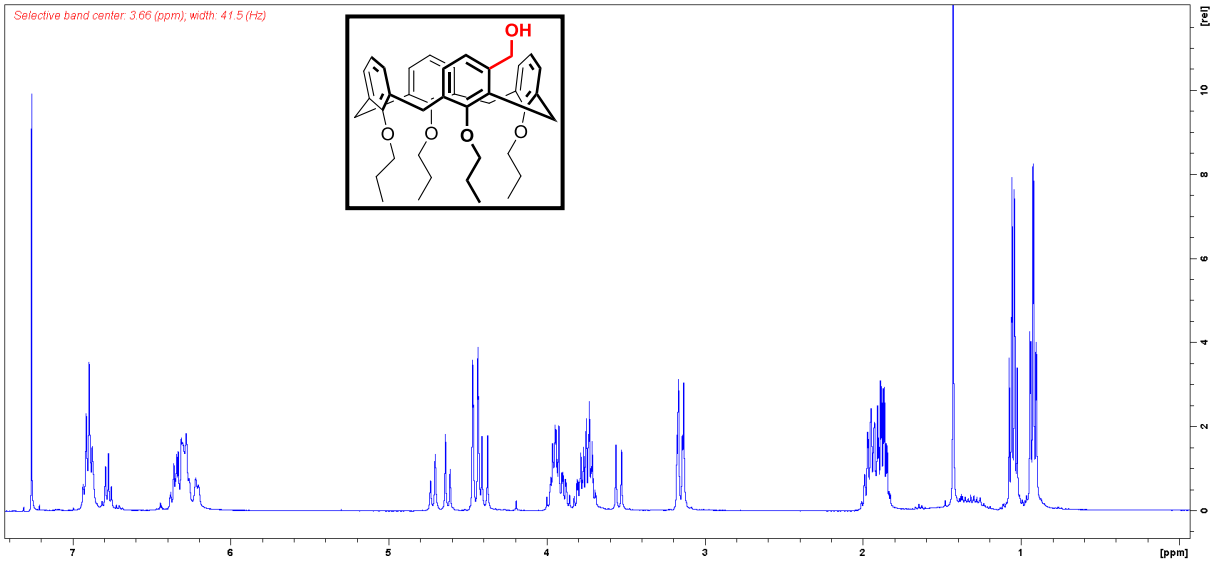

Figure 1. ^{1}H NMR of compound **5** ($CDCl_3$, 400 MHz, 293 K).

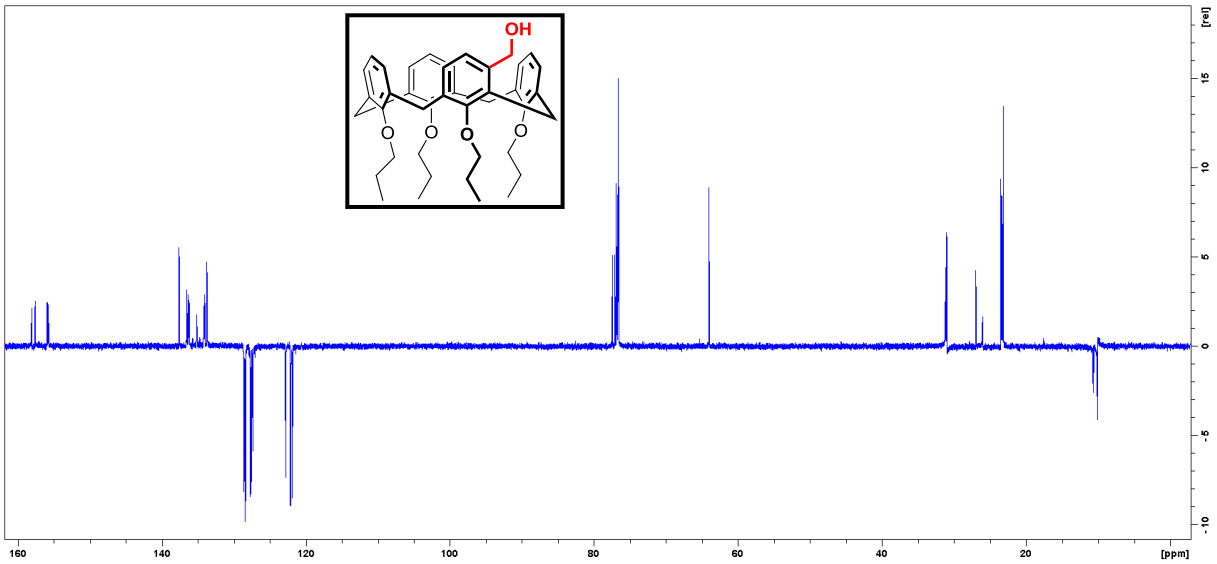

Figure 2. ^{13}C (APT) NMR of compound **5** ($CDCl_3$, 100 MHz, 293 K).

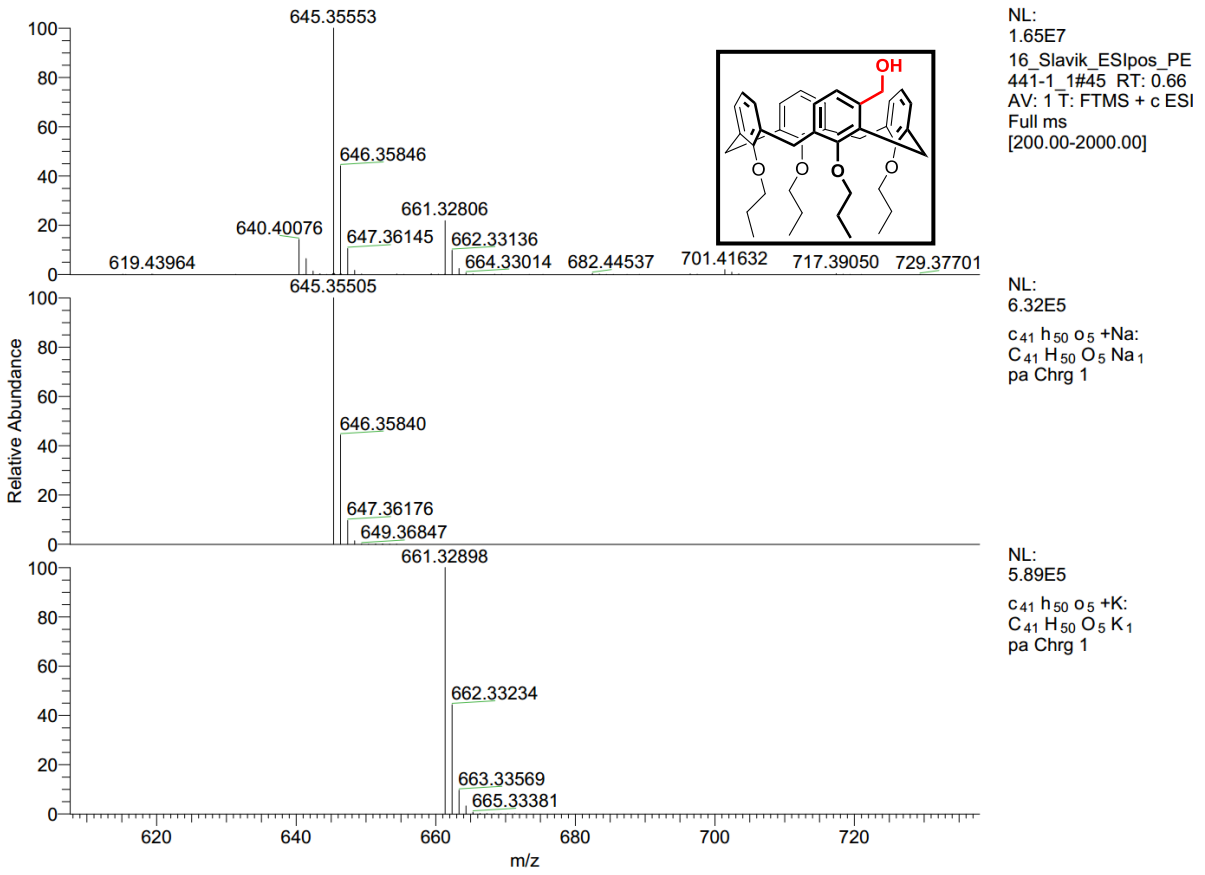

Figure 3. HRMS of compound **5** (ESI^+).

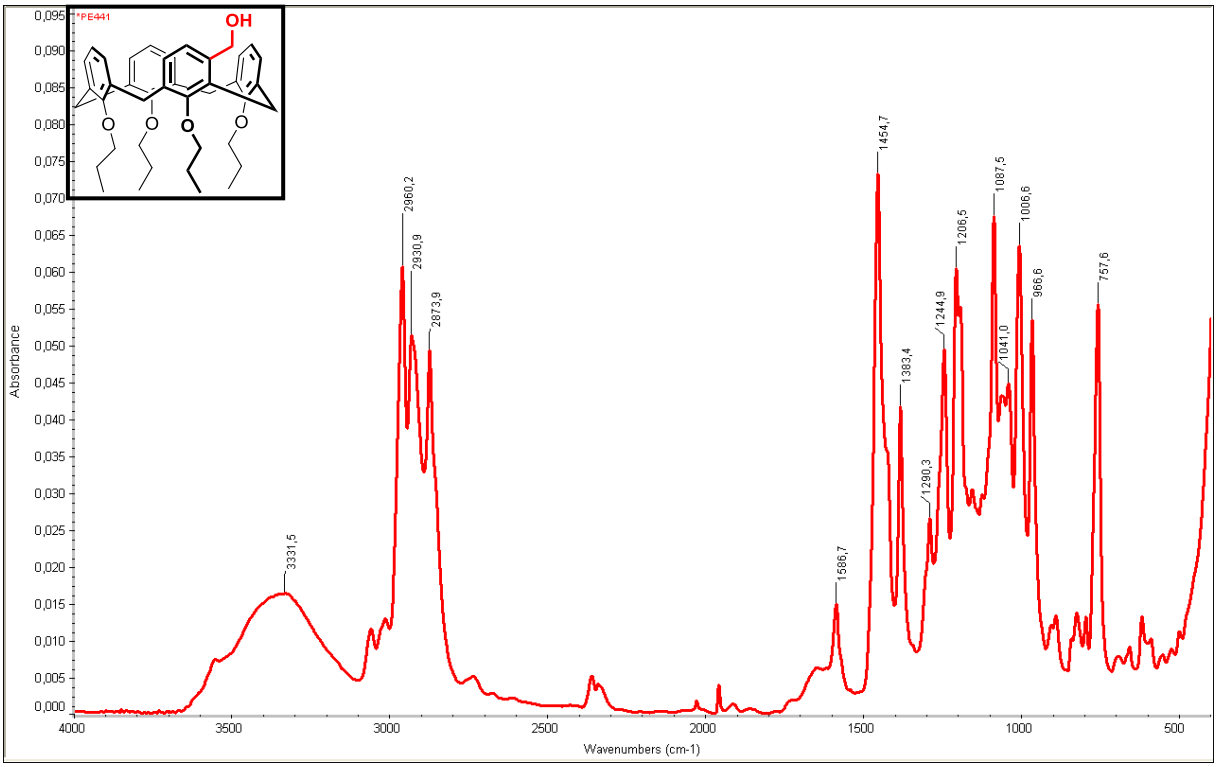

Figure 4. IR of compound **5** (KBr).

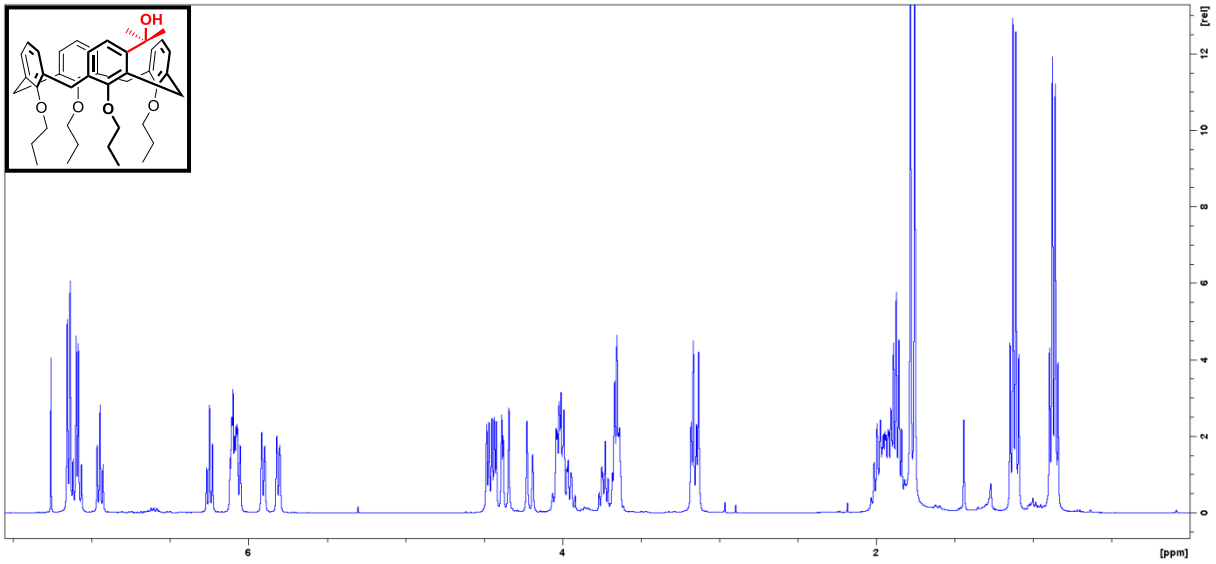

Figure 5. ^{1}H NMR of compound **7** ($CDCl_3$, 400 MHz, 293 K).

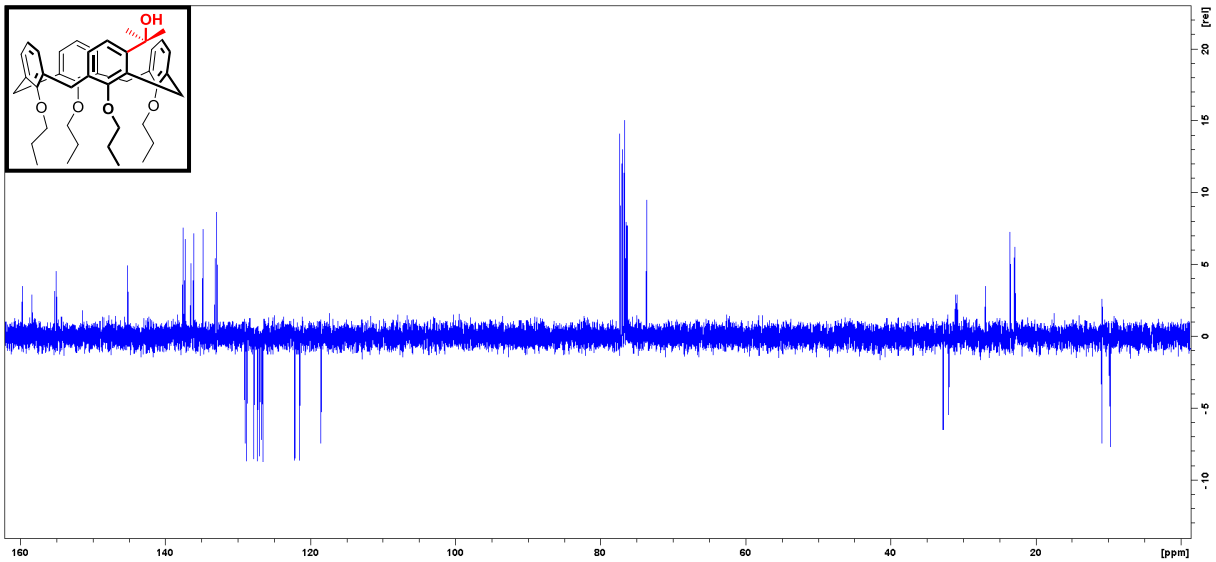

Figure 6. ^{13}C (APT) NMR of compound **7** ($CDCl_3$, 100 MHz, 293 K).

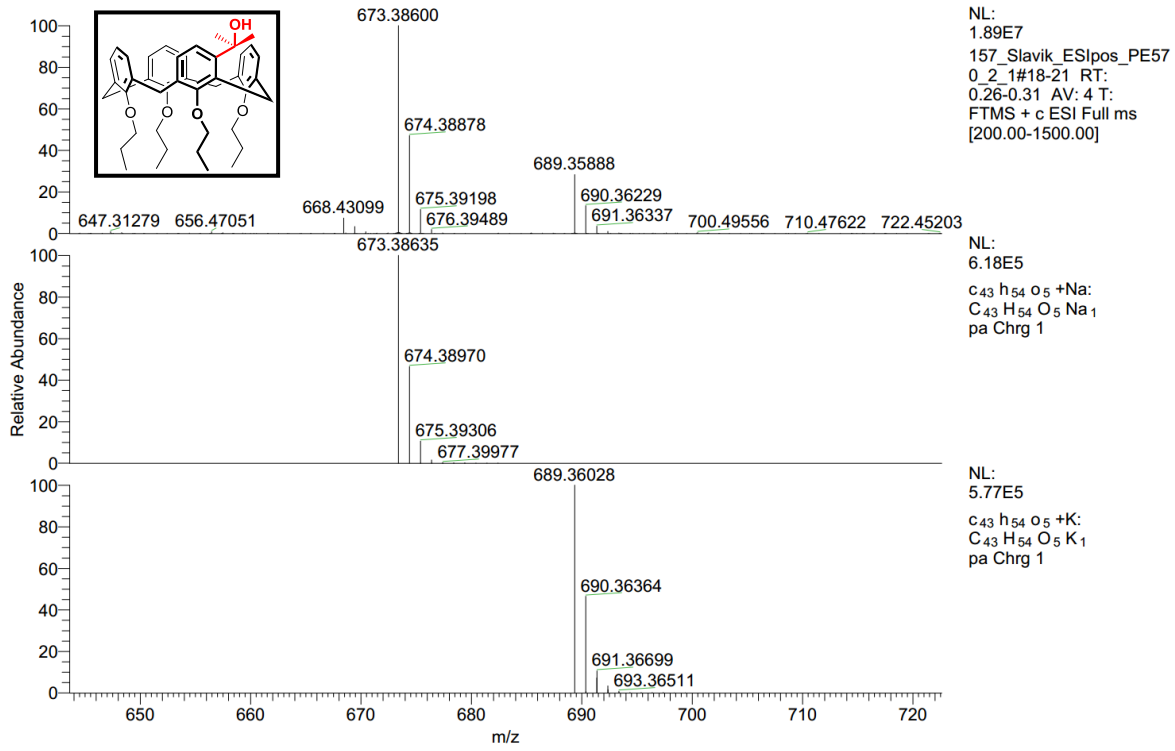

Figure 7. HRMS of compound **7** (ESI^+).

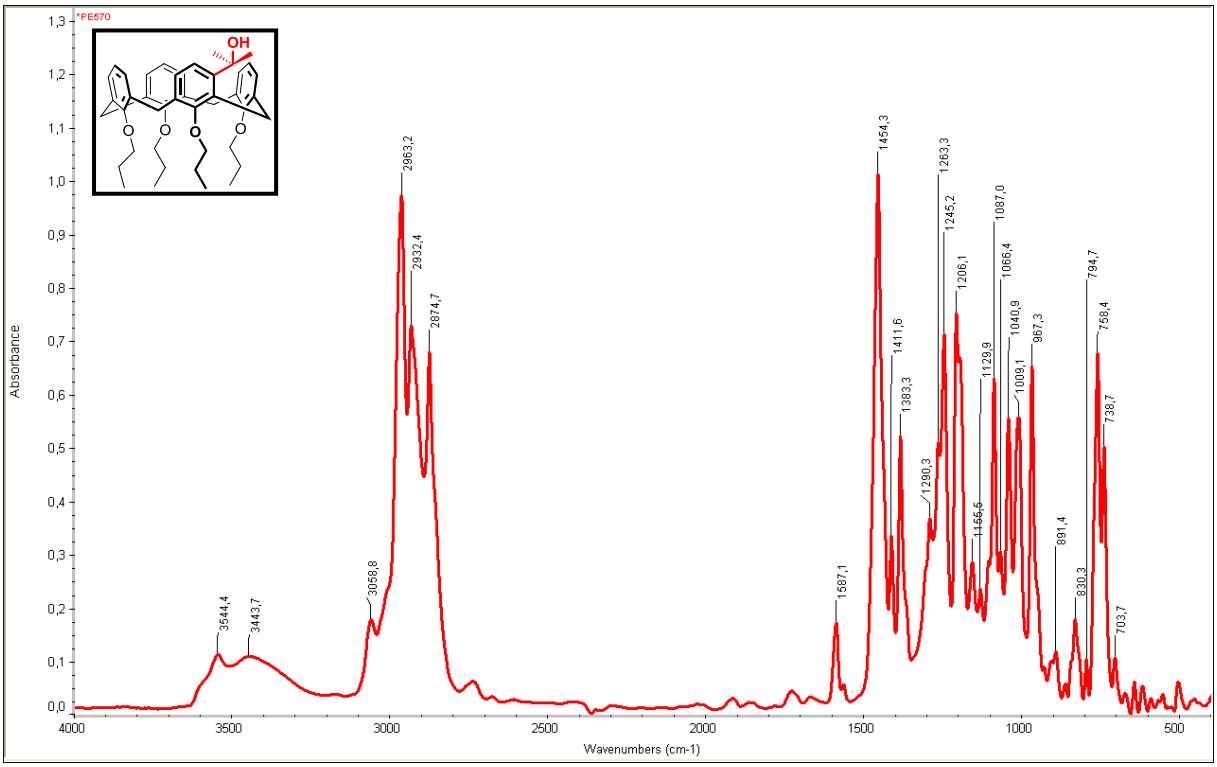

Figure 8. IR of compound **7** (KBr).

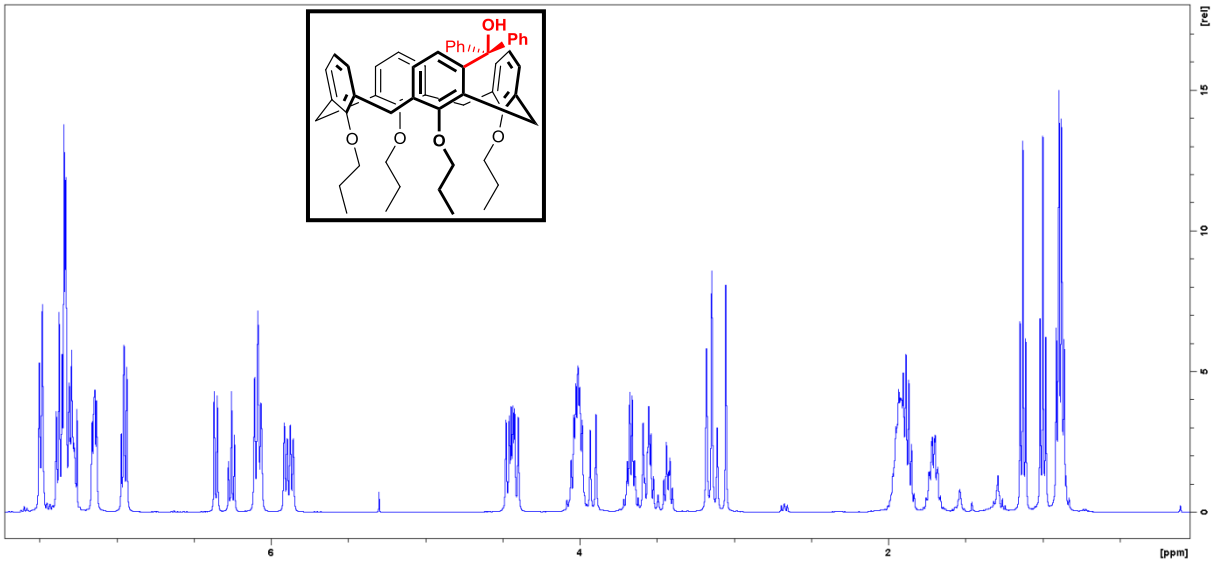

Figure 9. ^{1}H NMR of compound **8** ($CDCl_3$, 400 MHz, 293 K).

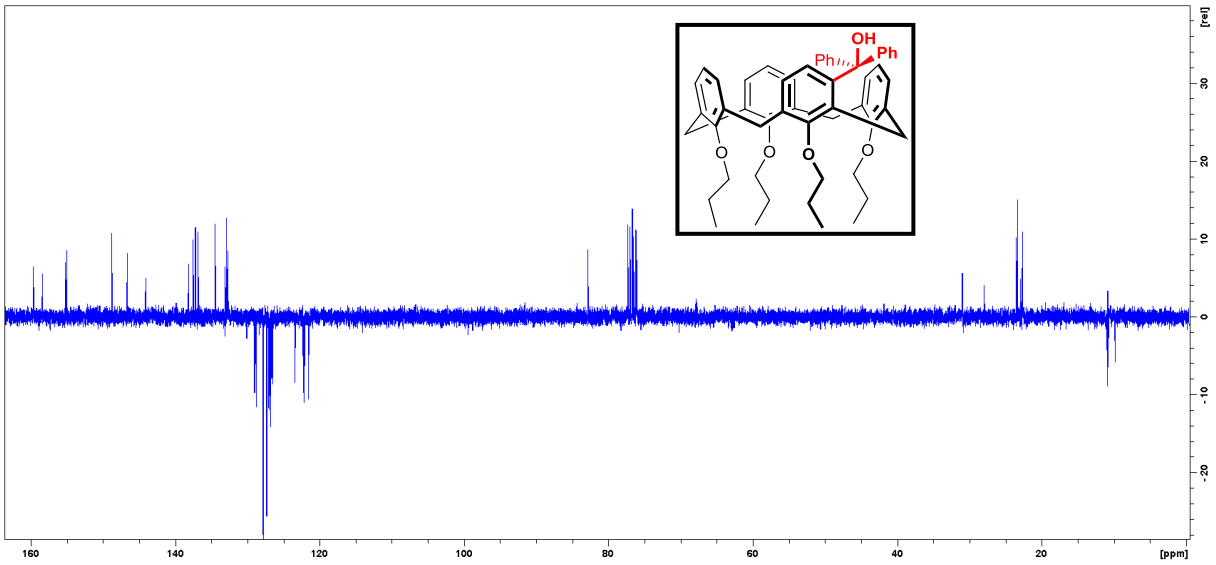

Figure 10. ^{13}C (APT) NMR of compound **8** ($CDCl_3$, 100 MHz, 293 K).

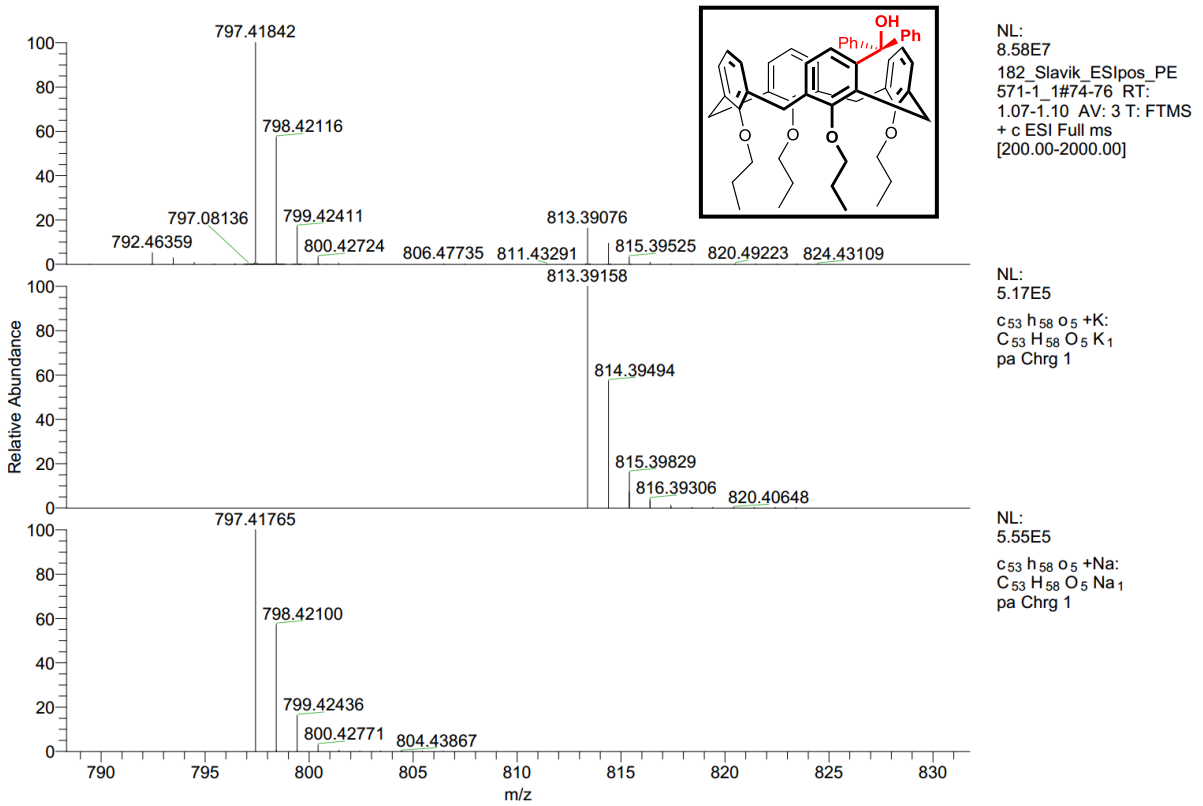

Figure 11. HRMS of compound **8** (ESI^+).

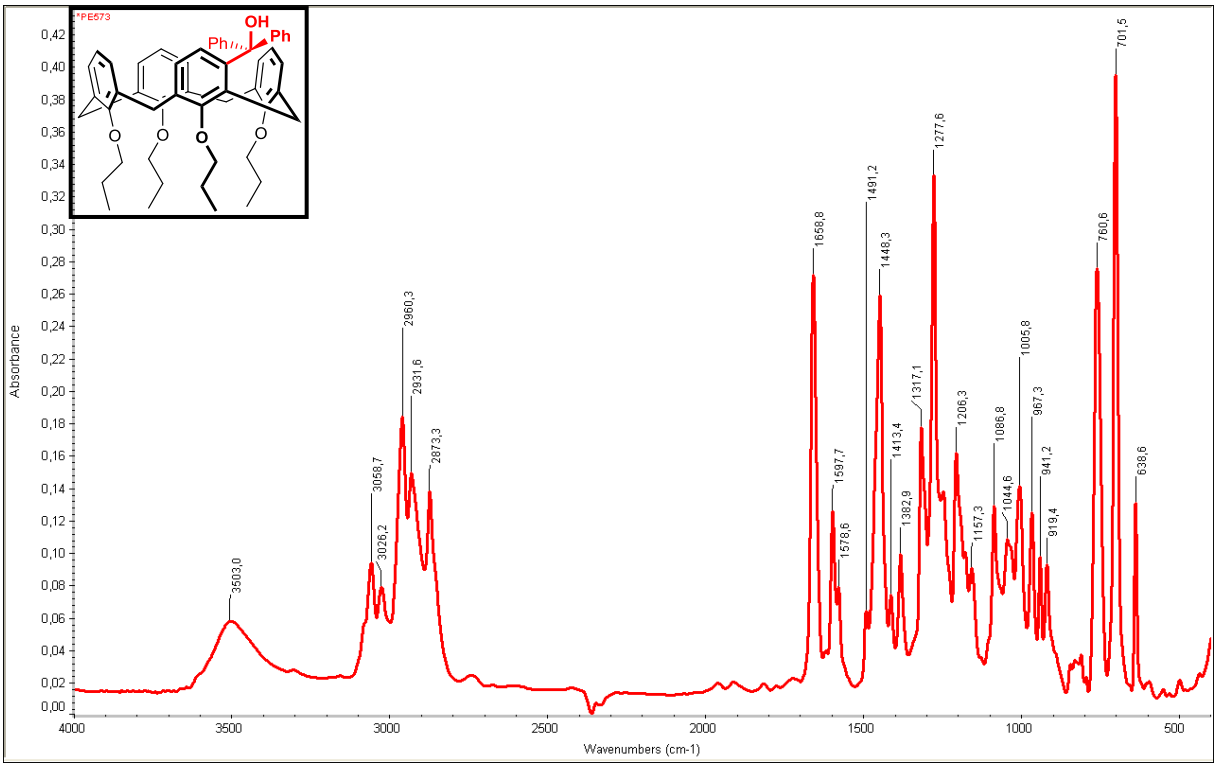

Figure 12. IR of compound **8** (KBr).

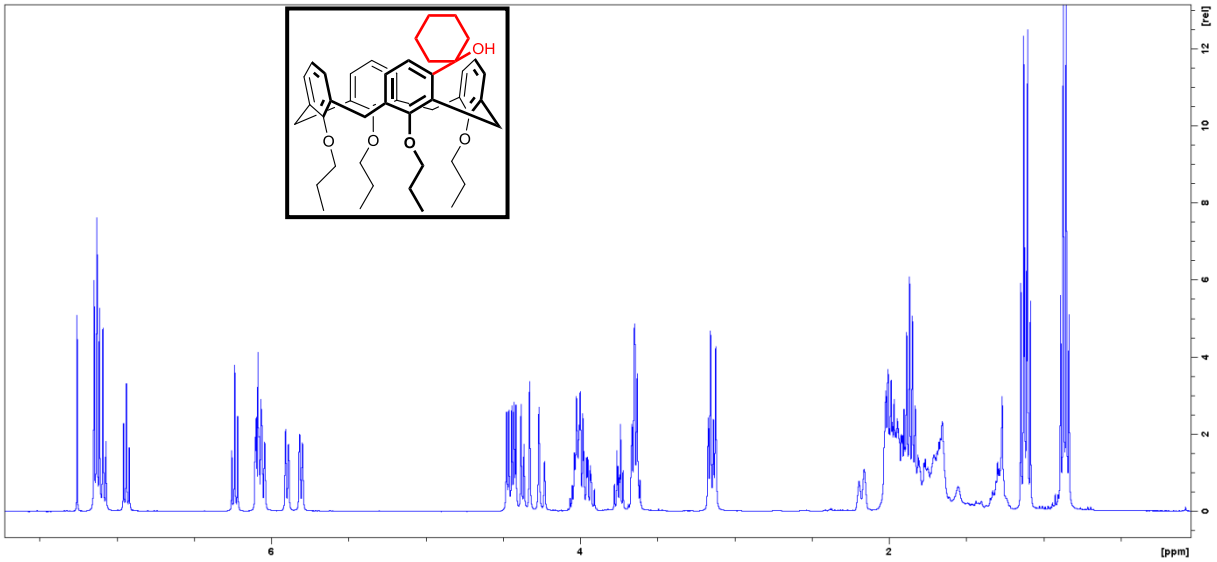

Figure 13. ^{1}H NMR of compound **9** ($CDCl_3$, 400 MHz, 293 K).

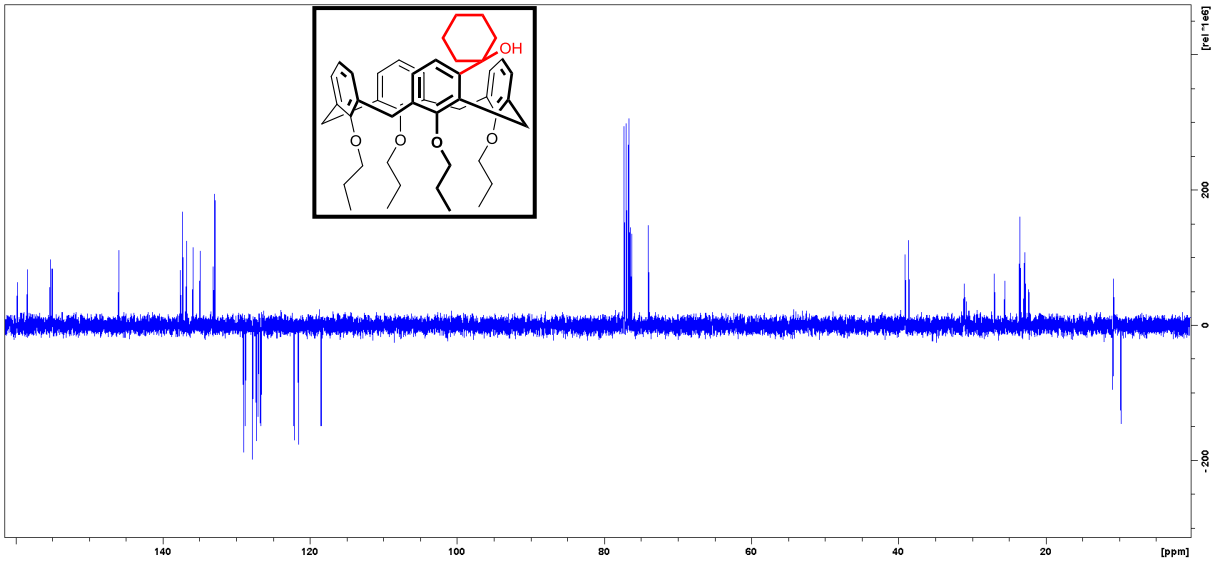

Figure 14. ^{13}C (APT) NMR of compound **9** ($CDCl_3$, 100 MHz, 293 K).

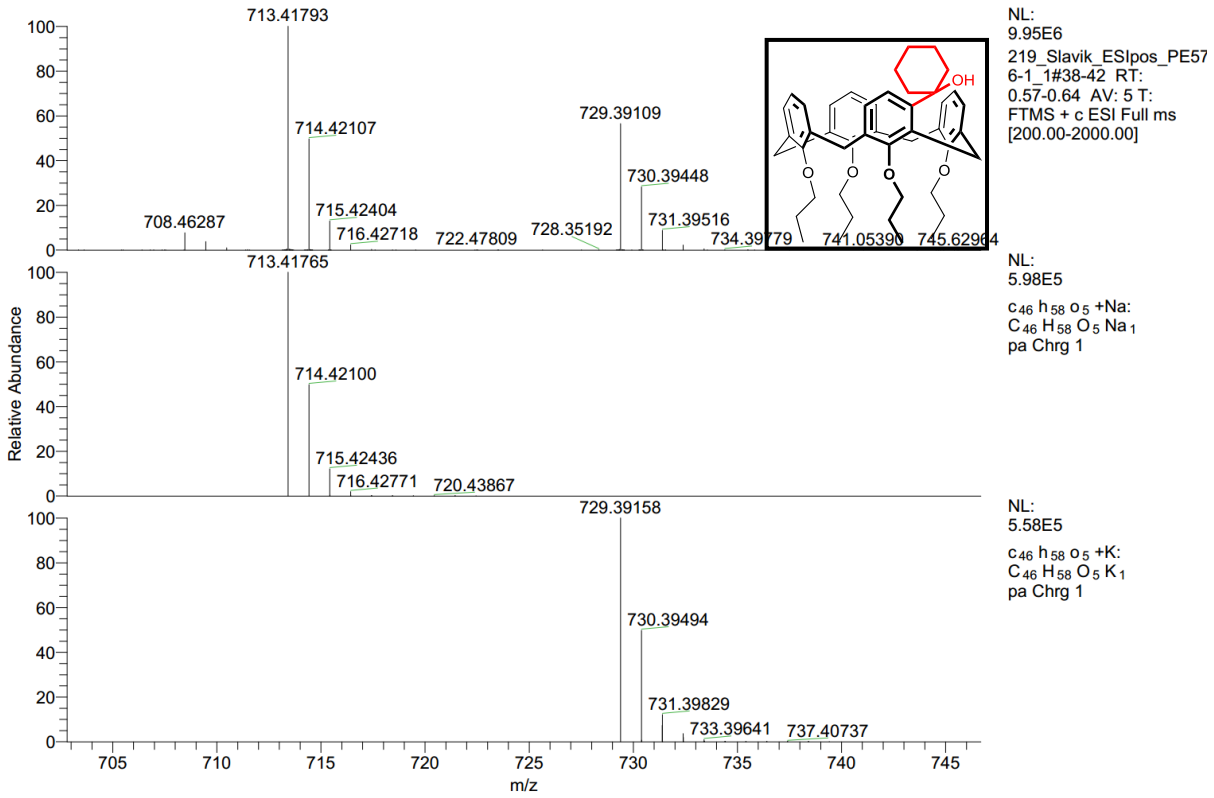

Figure 15. HRMS of compound **9** (ESI^+).

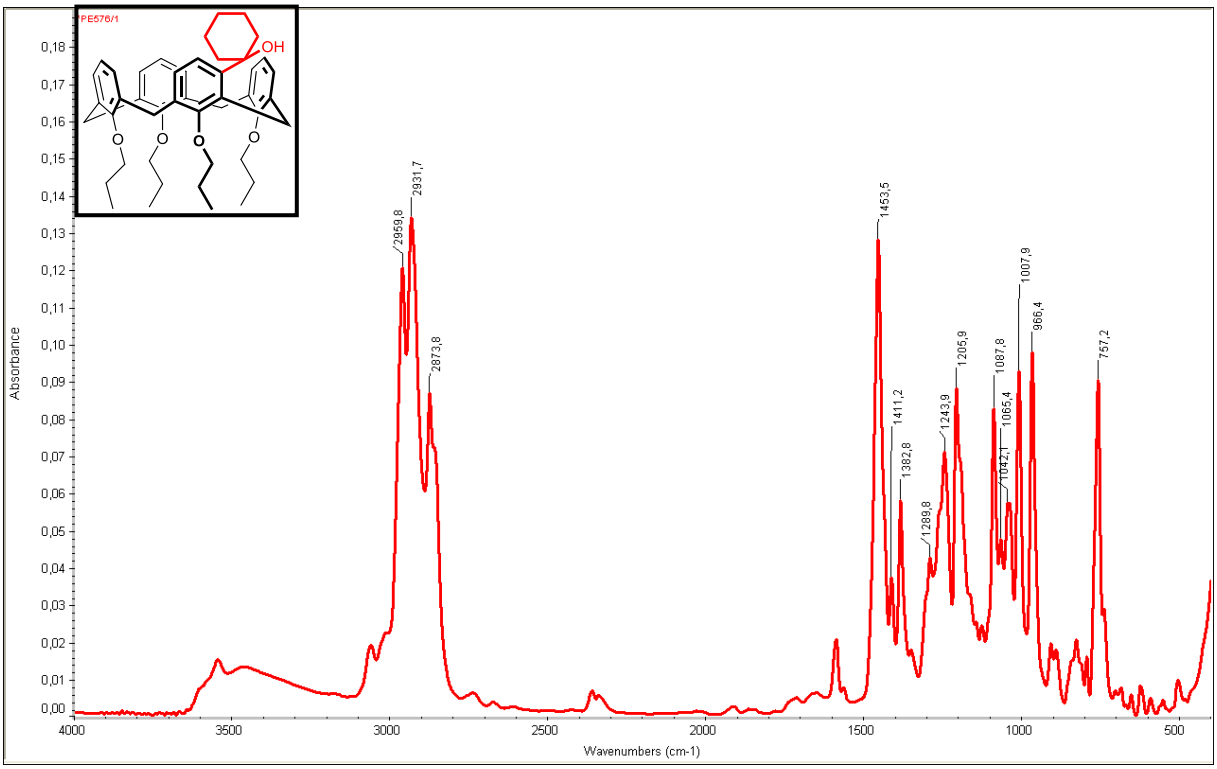

Figure 16. IR of compound **9** (KBr).

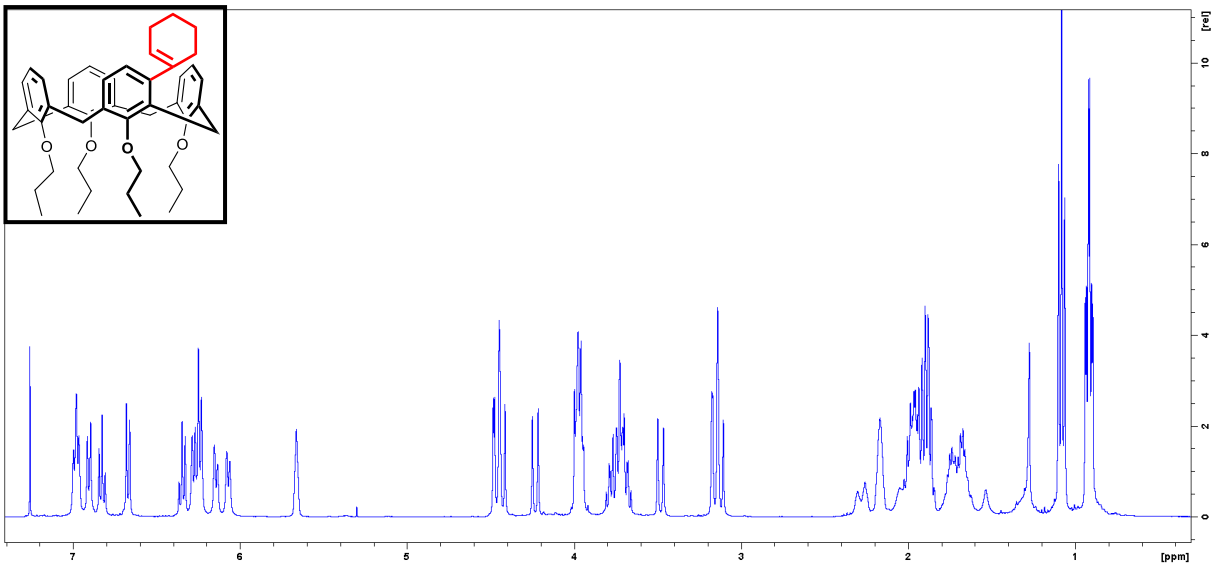

Figure 17. ^{1}H NMR of compound **10a** ($CDCl_3$, 400 MHz, 293 K).

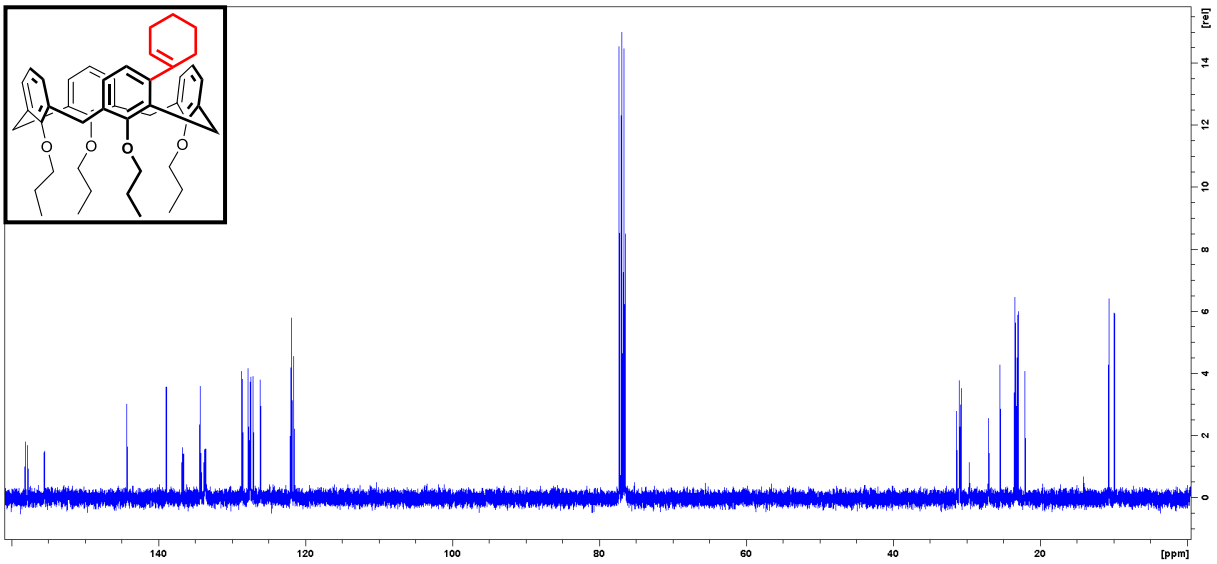

Figure 18. ^{13}C NMR of compound **10a** ($CDCl_3$, 100 MHz, 293 K).

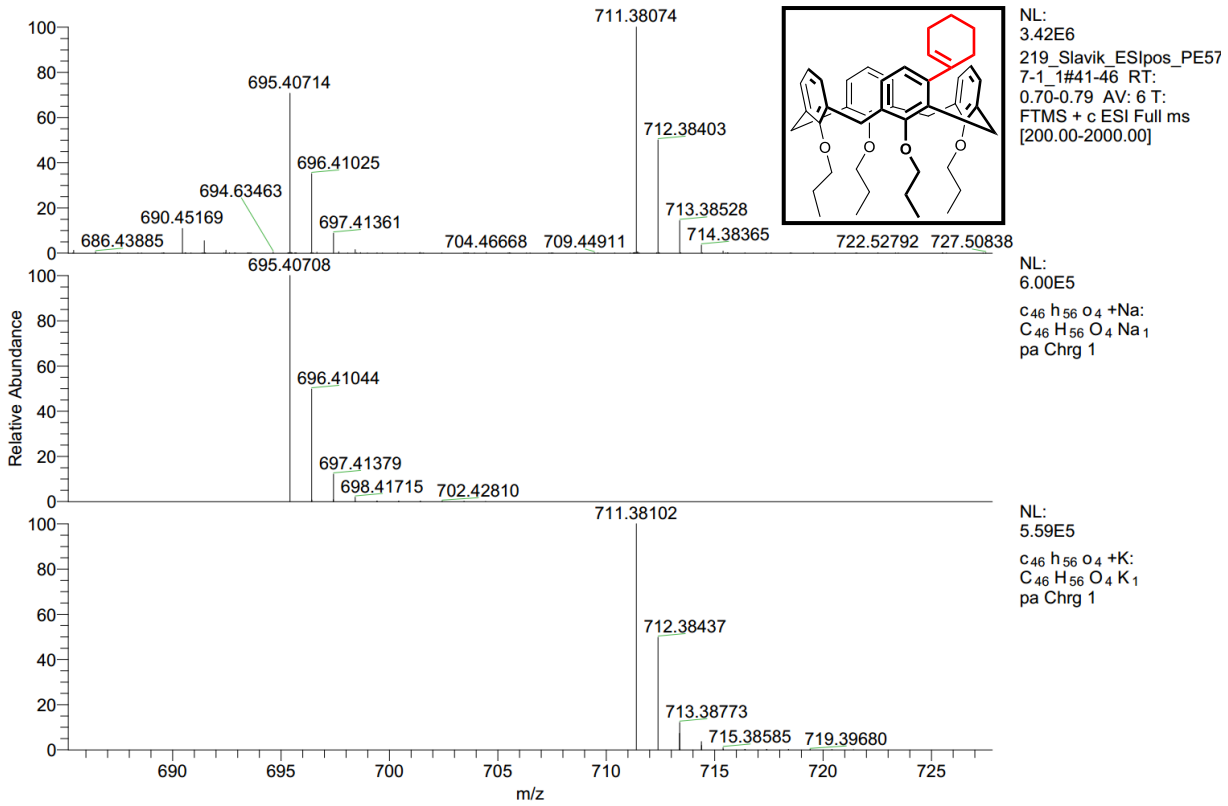

Figure 19. HRMS of compound **10a** (ESI^+).

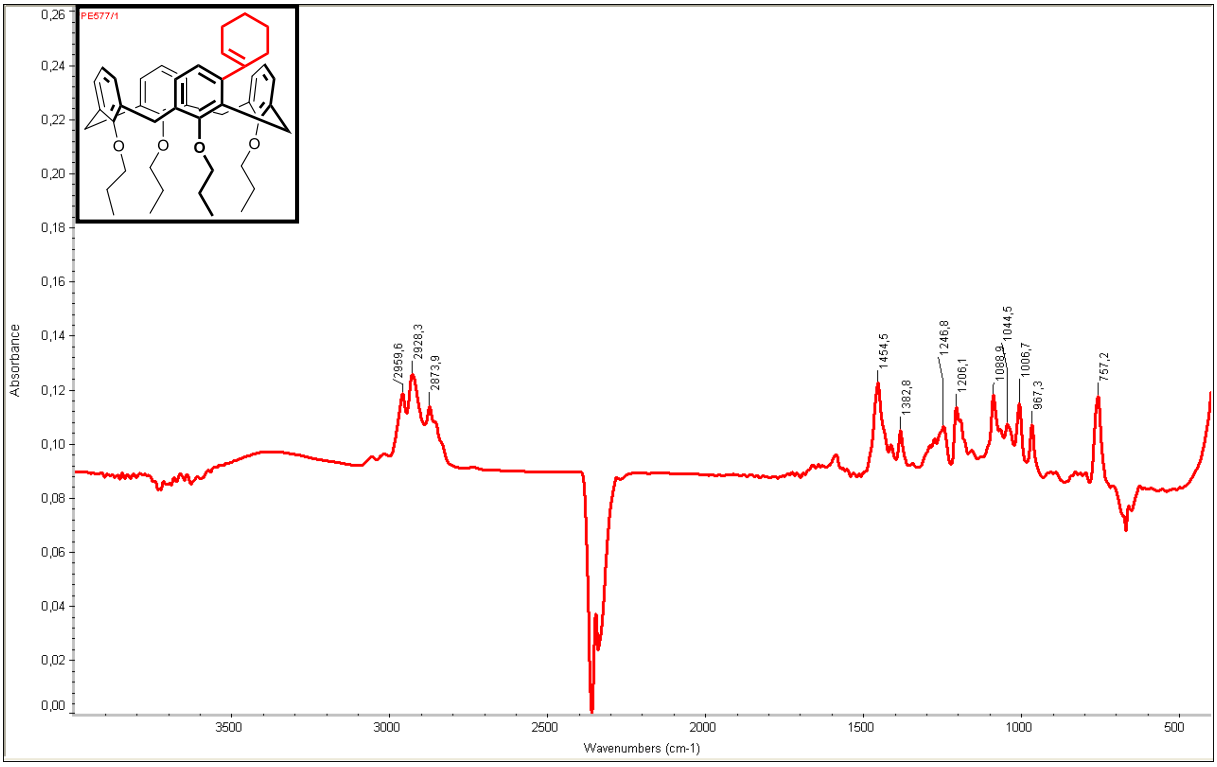

Figure 20. IR of compound **10a** (KBr).

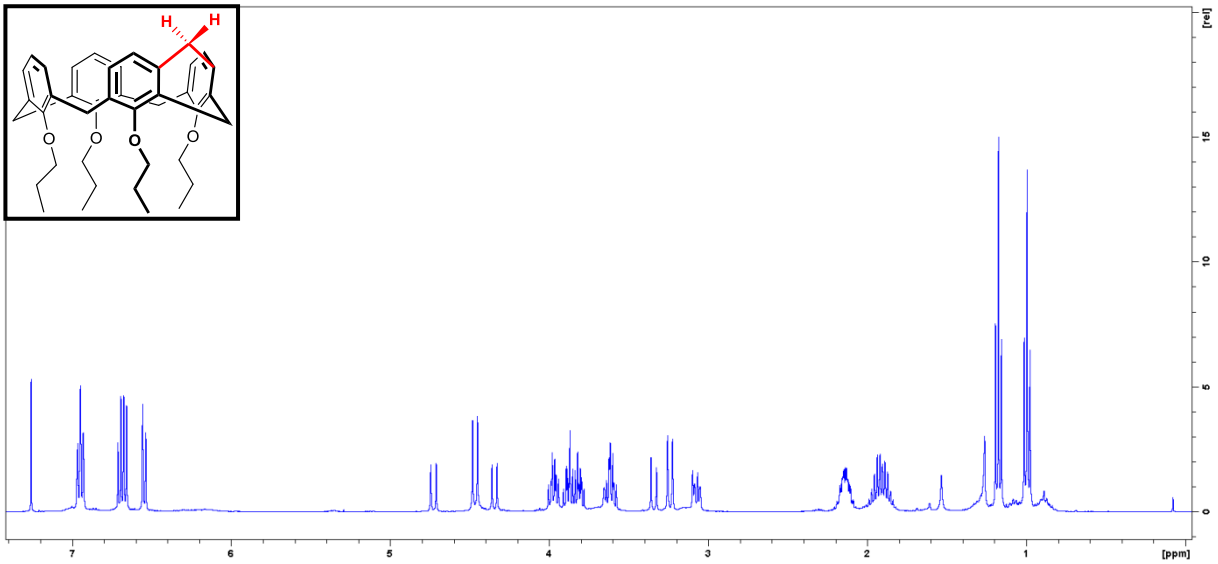

Figure 21. ^{1}H NMR of compound **11** ($CDCl_3$, 400 MHz, 293 K).

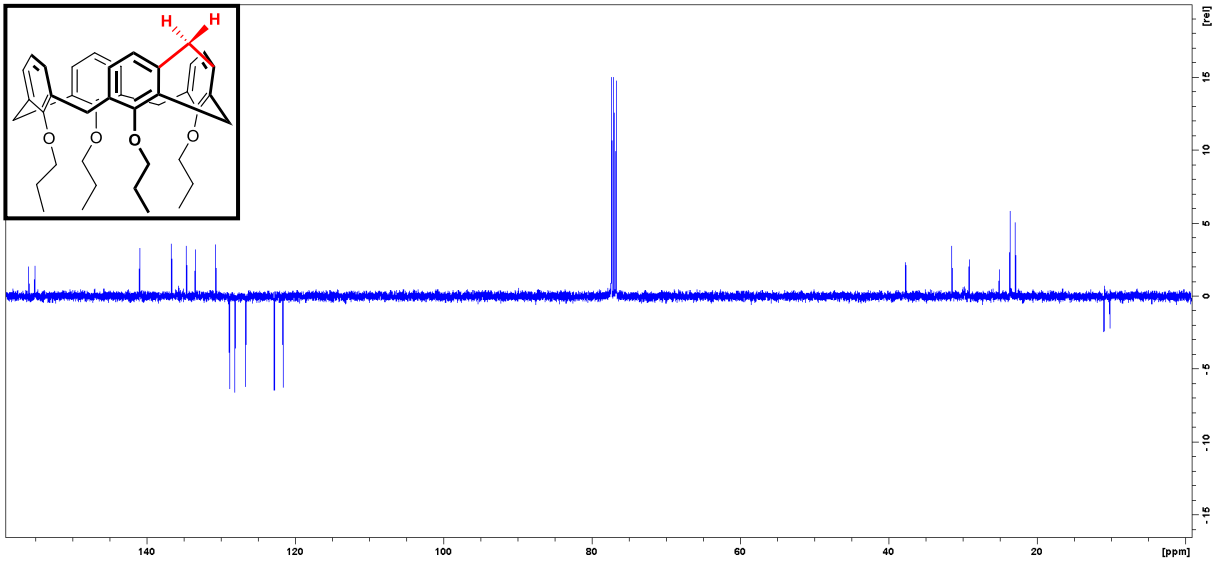

Figure 22. ^{13}C (APT) NMR of compound **11** ($CDCl_3$, 100 MHz, 293 K).

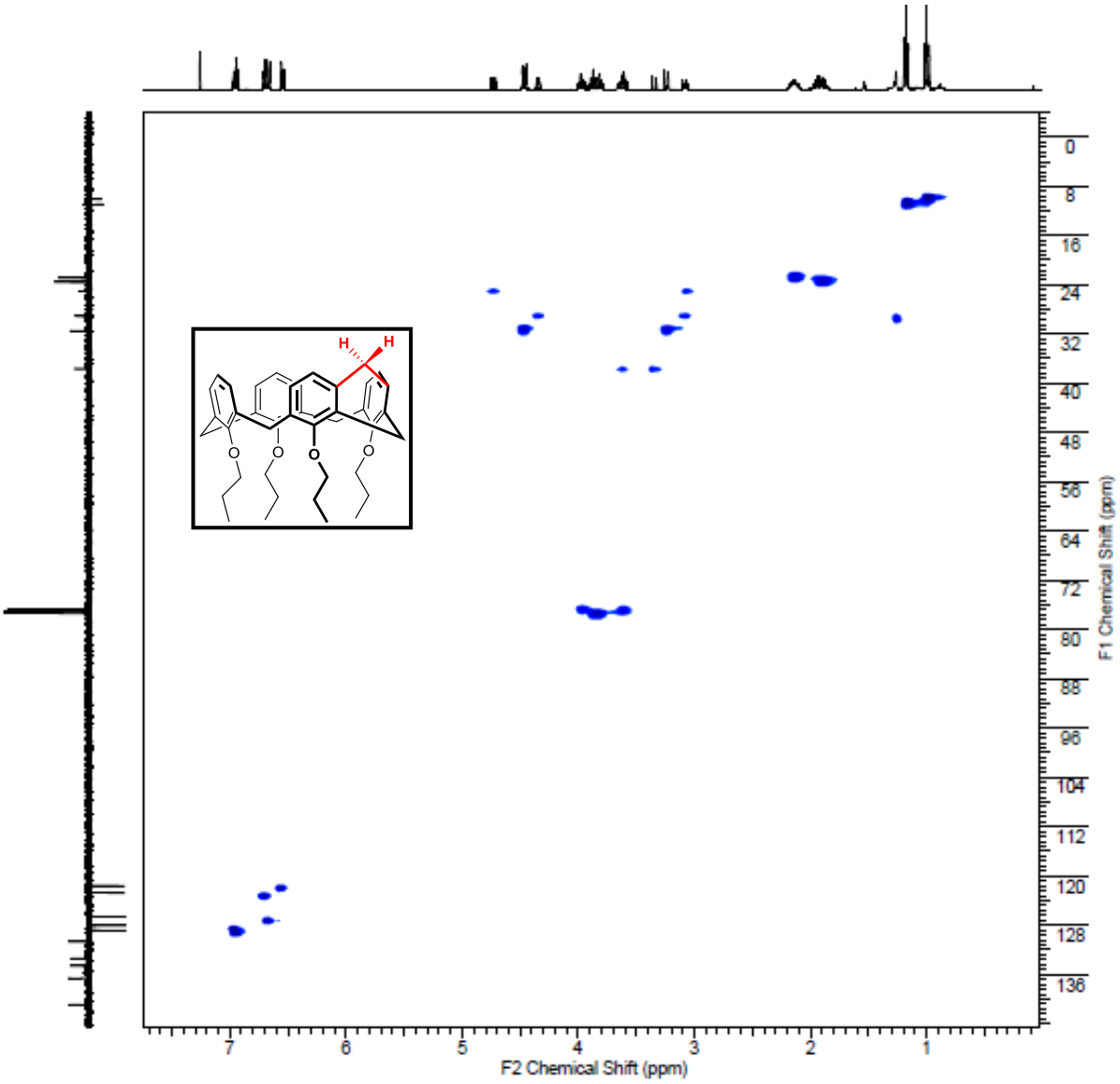

Figure 23. 2D NMR (ASAPHMQC) of compound **11** ($CDCl_3$, 400 MHz, 293 K).

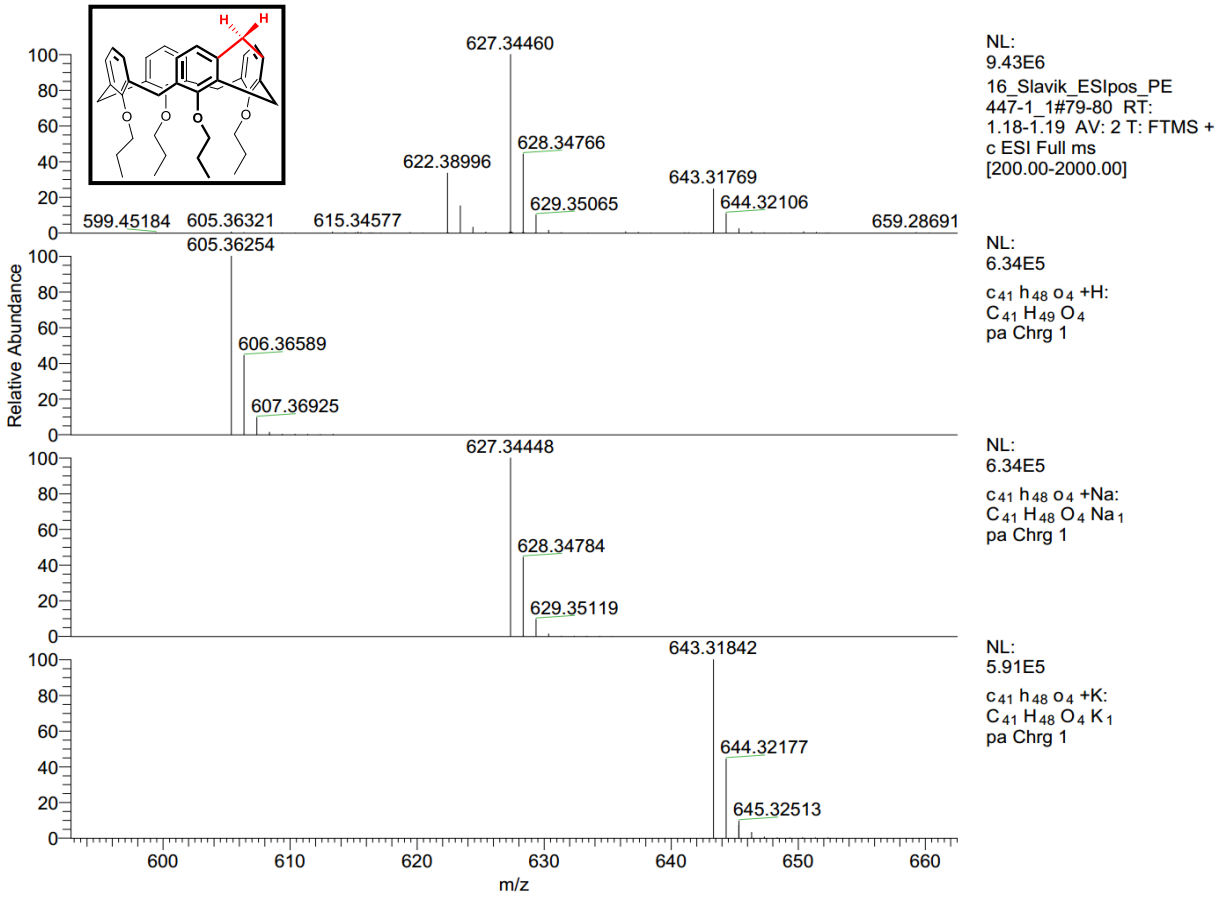

Figure 24. HRMS of compound **11** (ESI^+).

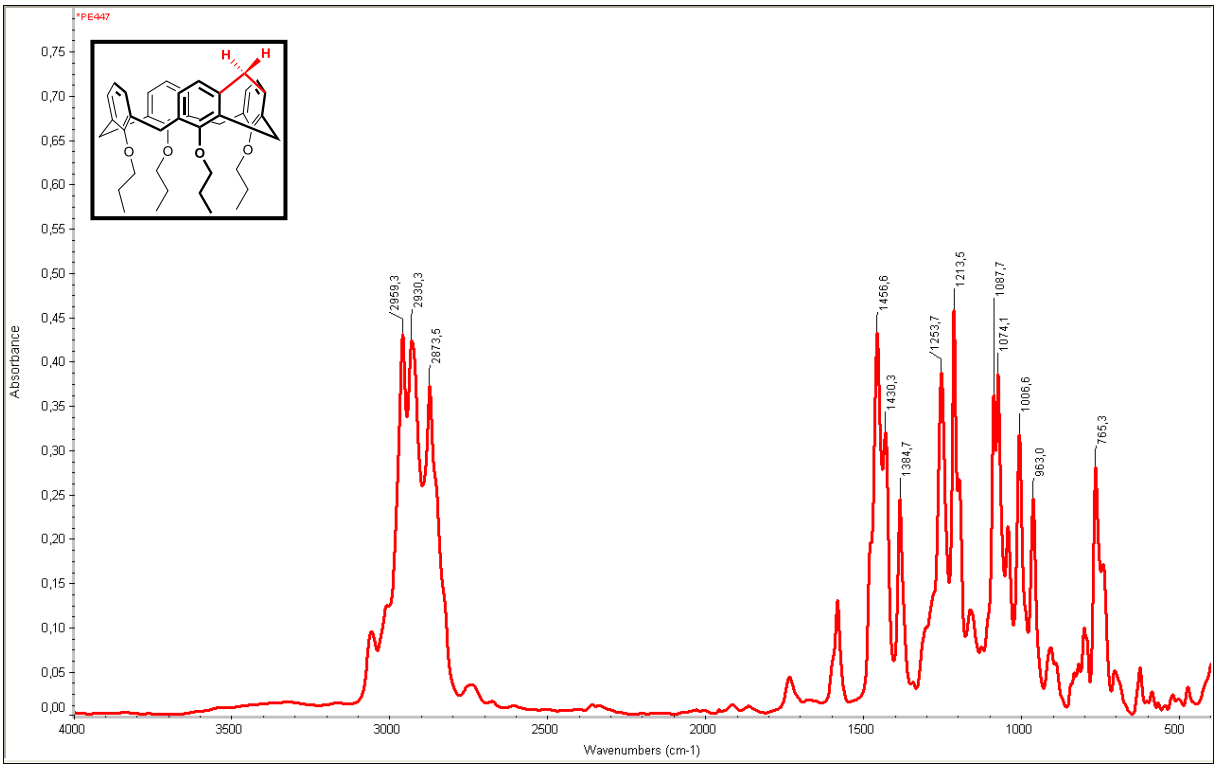

Figure 25. IR of compound **11** (KBr).

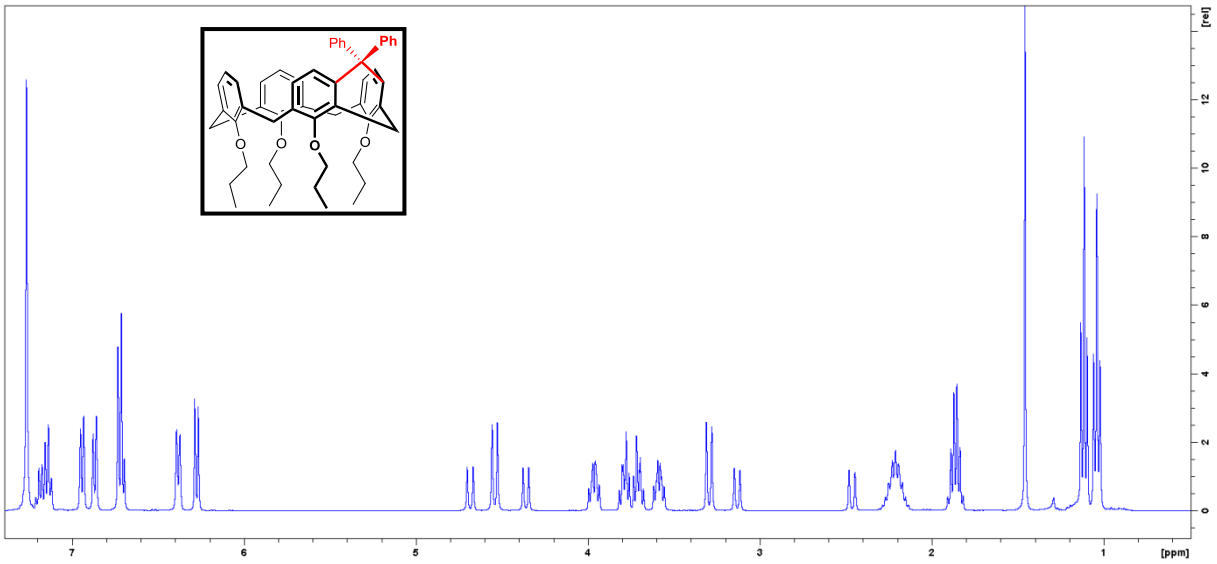

Figure 26. ^{1}H NMR of compound **12**($CDCl_3$, 400 MHz, 293 K).

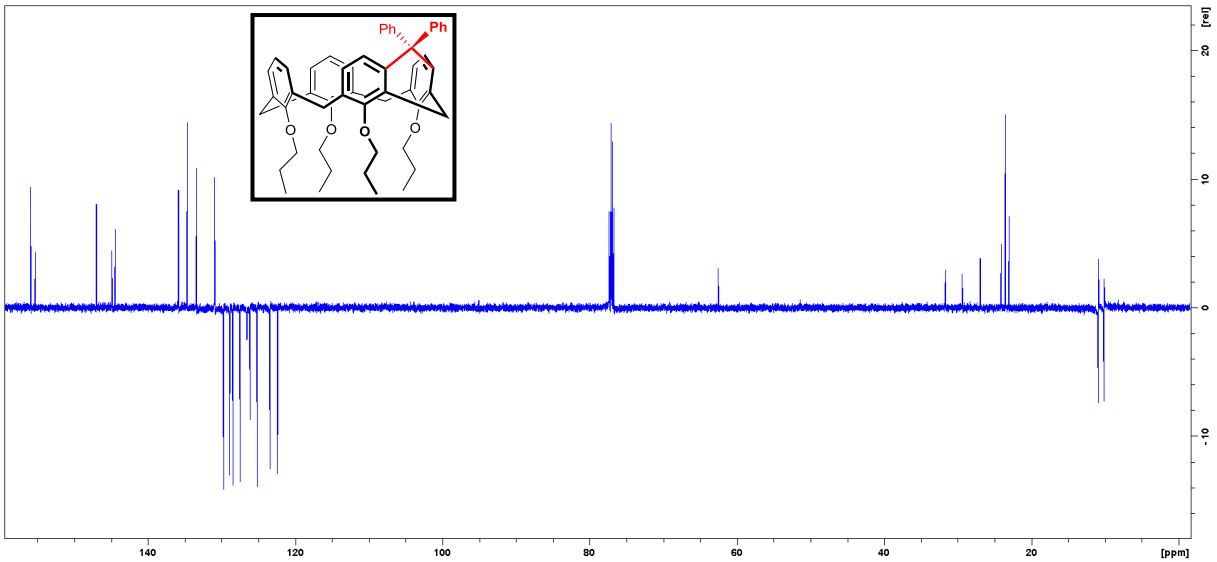

Figure 27. ^{13}C (APT) NMR of compound **12** ($CDCl_3$, 100 MHz, 293 K).

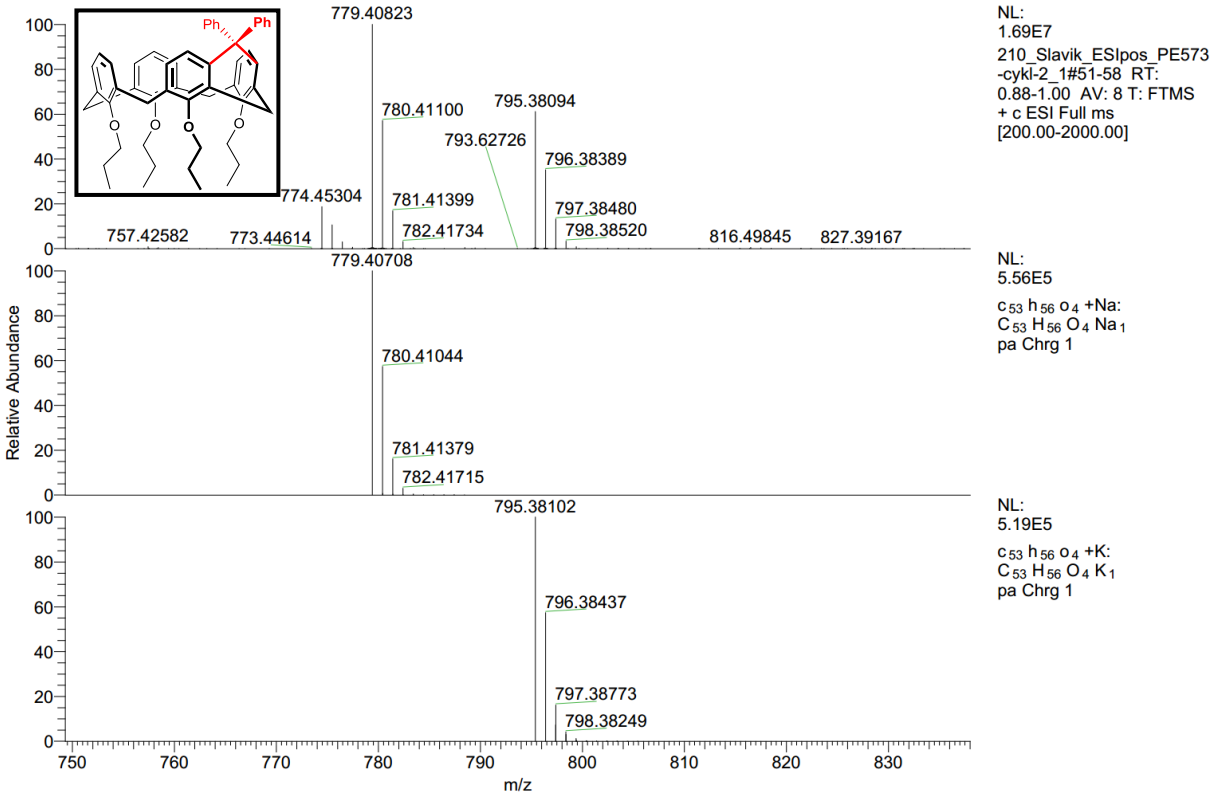

Figure 28. HRMS of compound **12** (ESI^+).

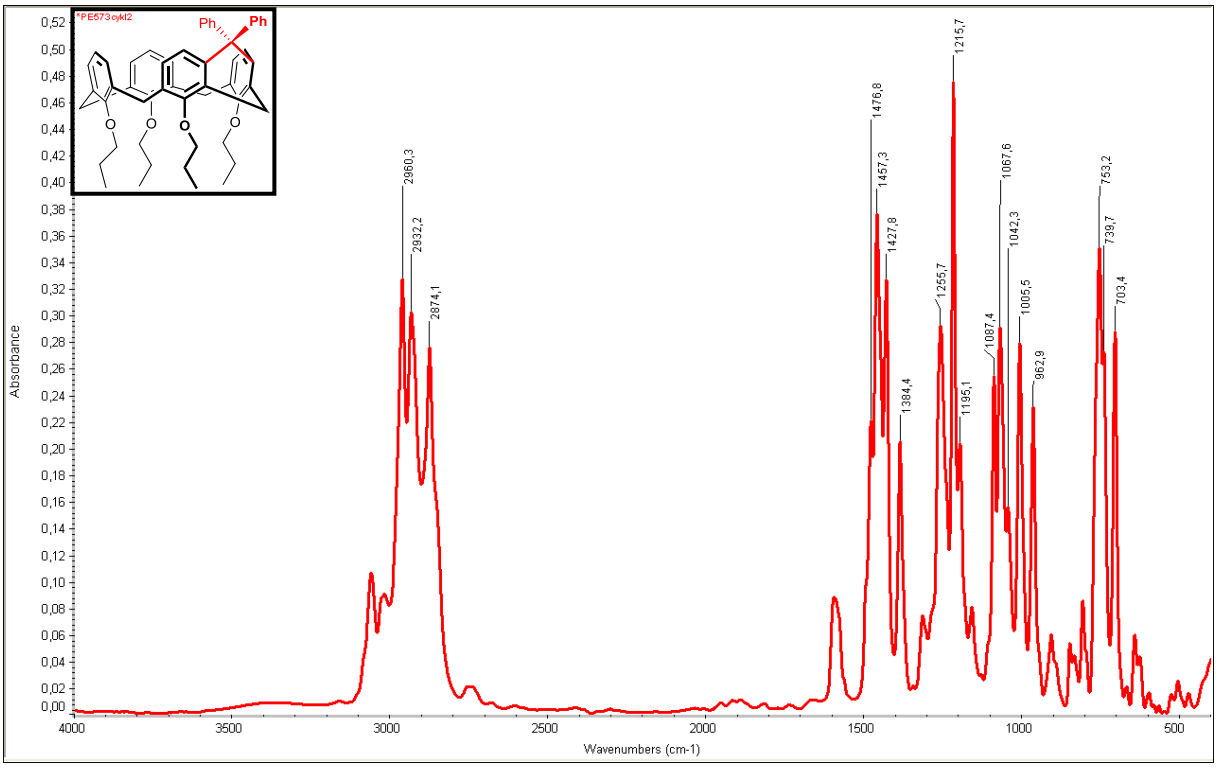

Figure 29. IR of compound **12** (KBr).

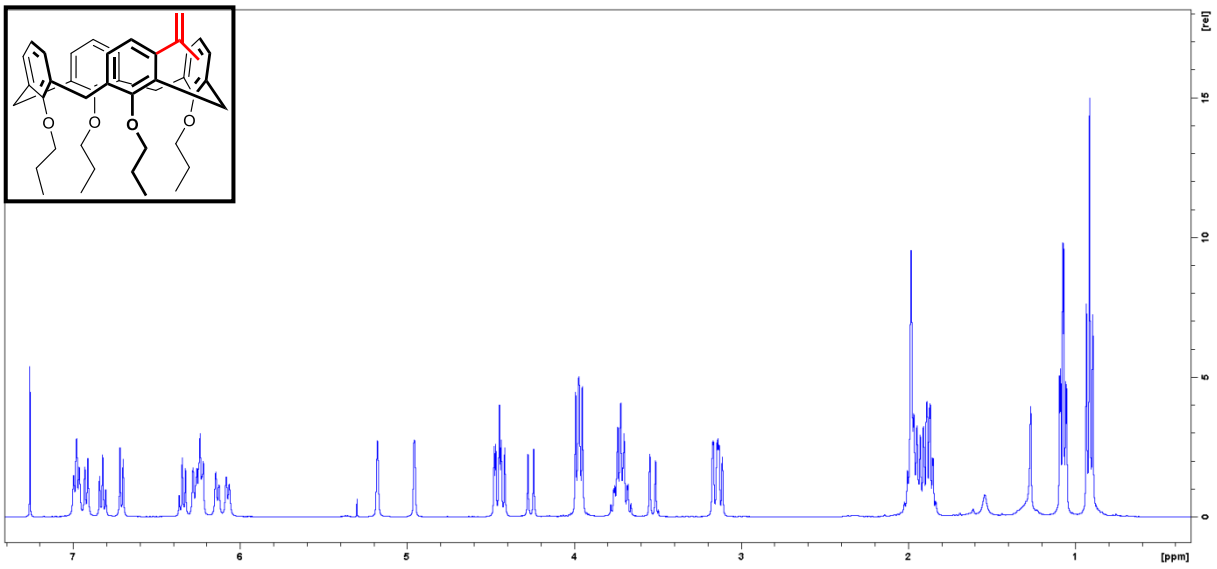

Figure 30. ^{1}H NMR of compound **13a** ($CDCl_3$, 400 MHz, 293 K).

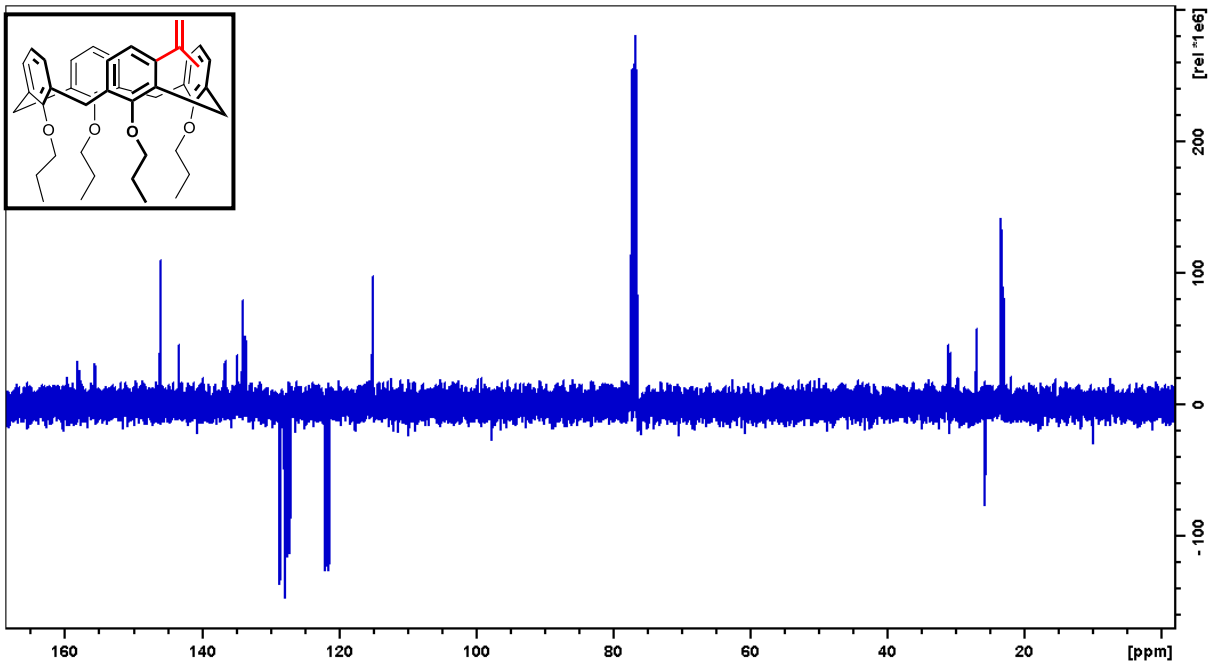

Figure 31. ^{13}C (APT) NMR of compound **13a** ($CDCl_3$, 100 MHz, 293 K).

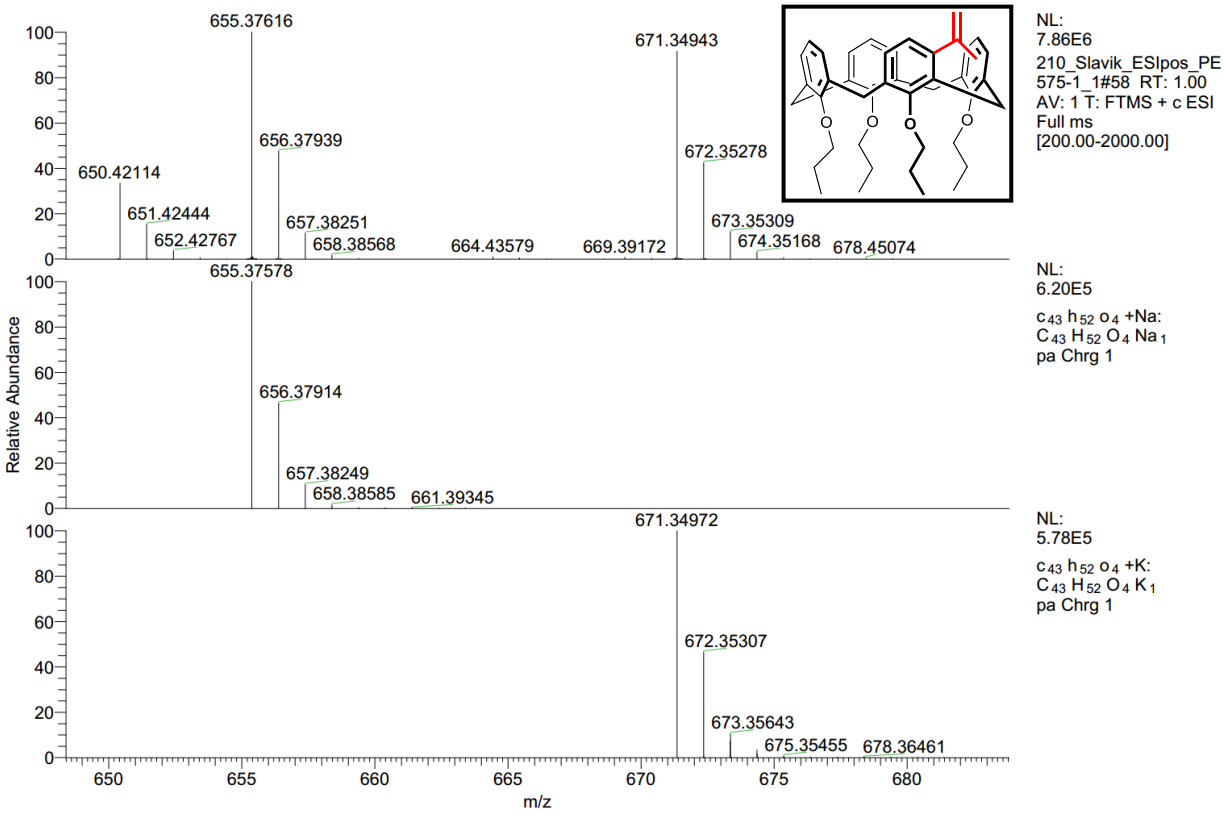

Figure 32. HRMS of compound **13a** (ESI^+).

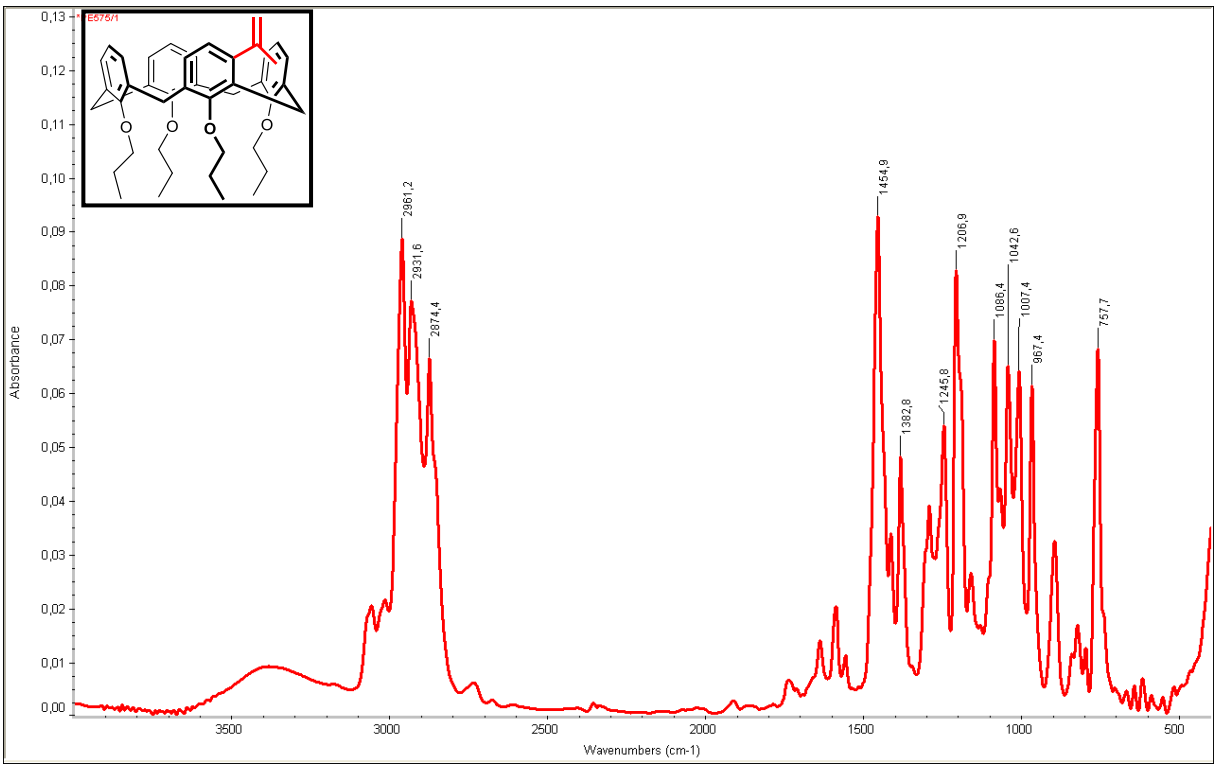

Figure 33. IR of compound **13a** (KBr).

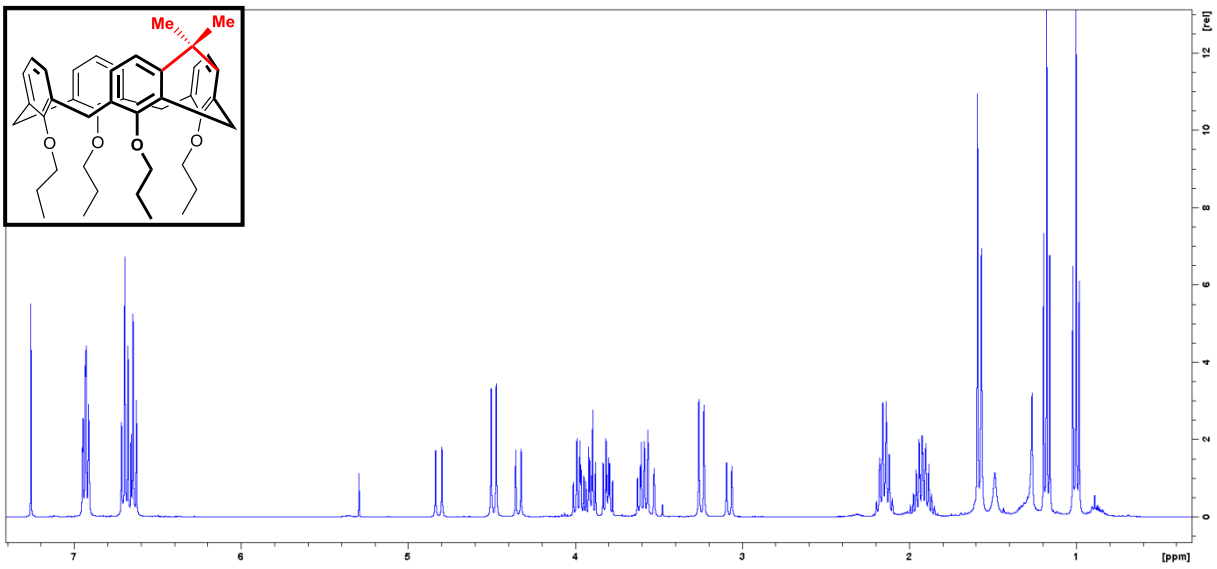

Figure 34. ^{1}H NMR of compound **13** ($CDCl_3$, 400 MHz, 293 K).

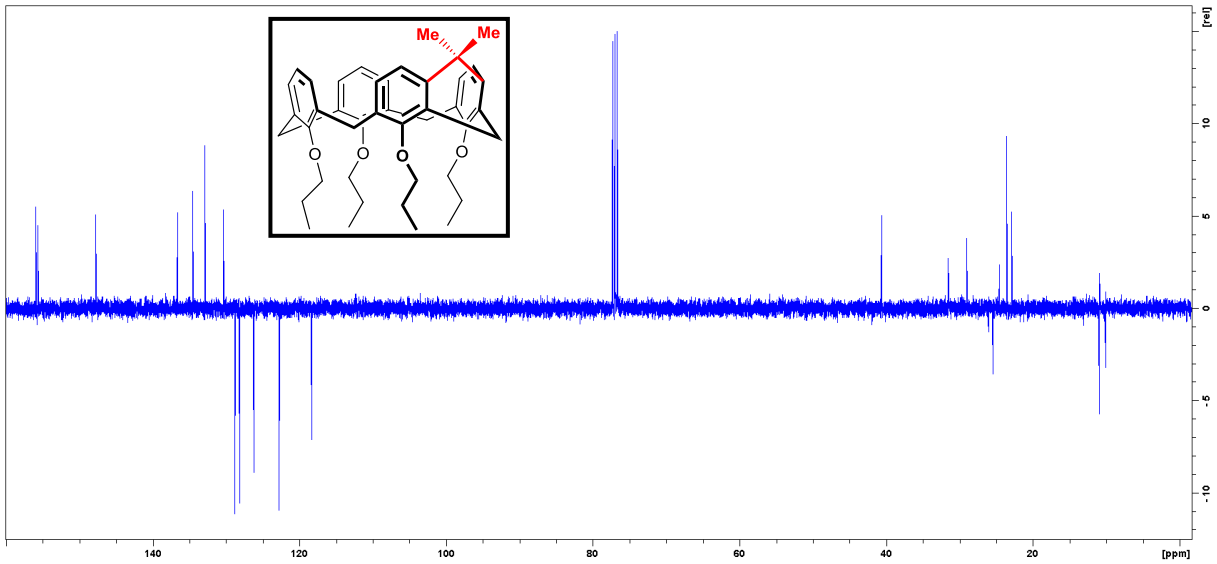

Figure 35. ^{13}C (APT) NMR of compound **13** ($CDCl_3$, 100 MHz, 293 K).

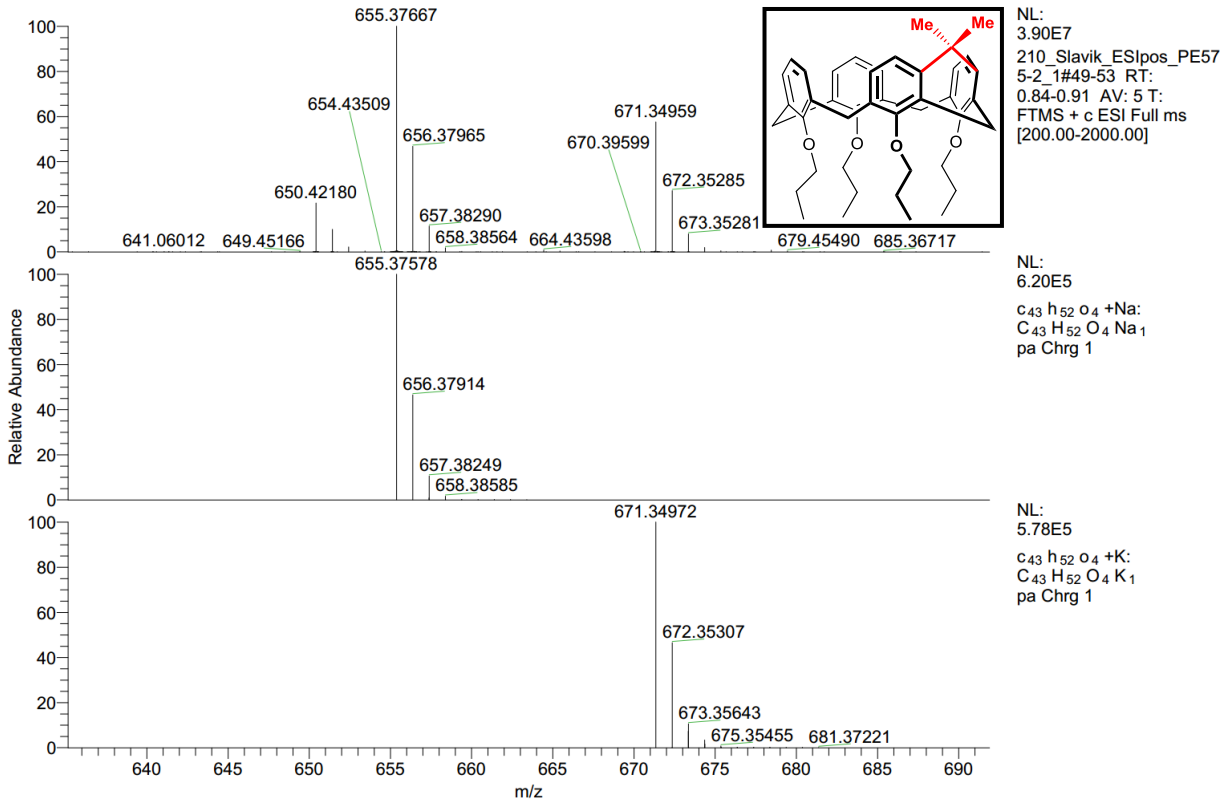

Figure 36. HRMS of compound **13** (ESI^+).

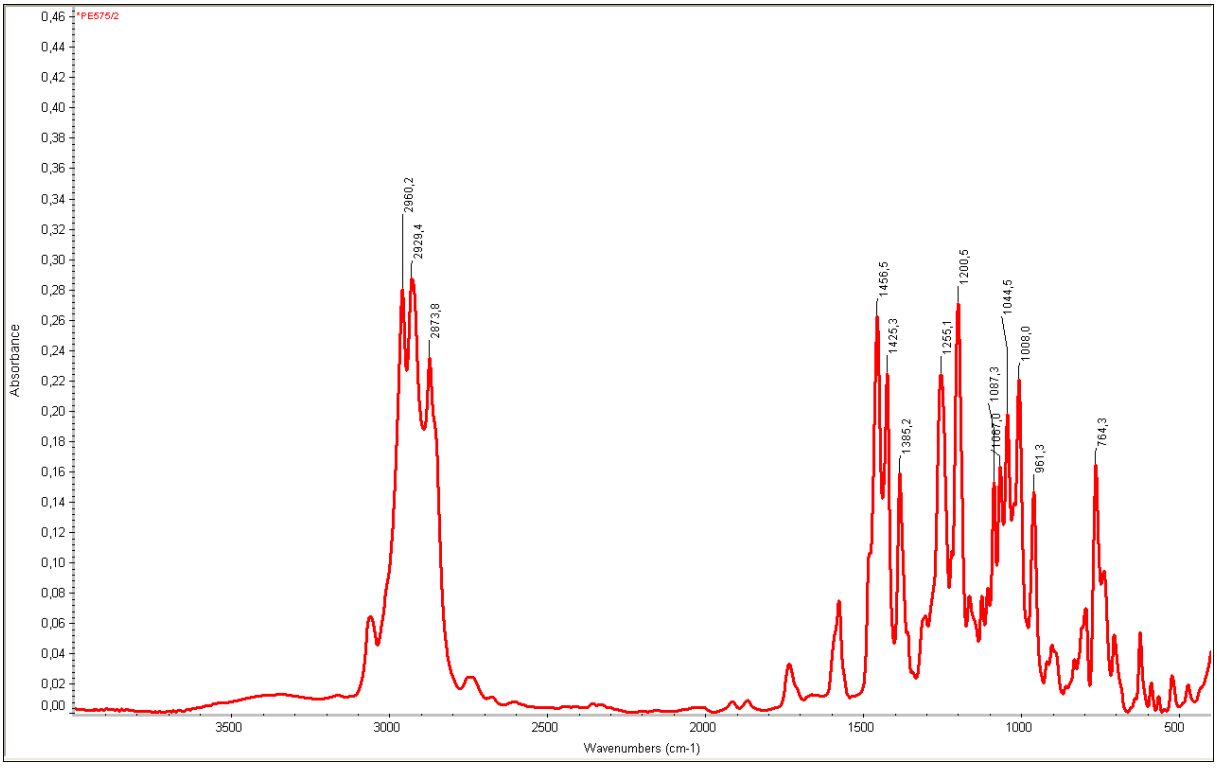

Figure 37. IR of compound **13** (KBr).

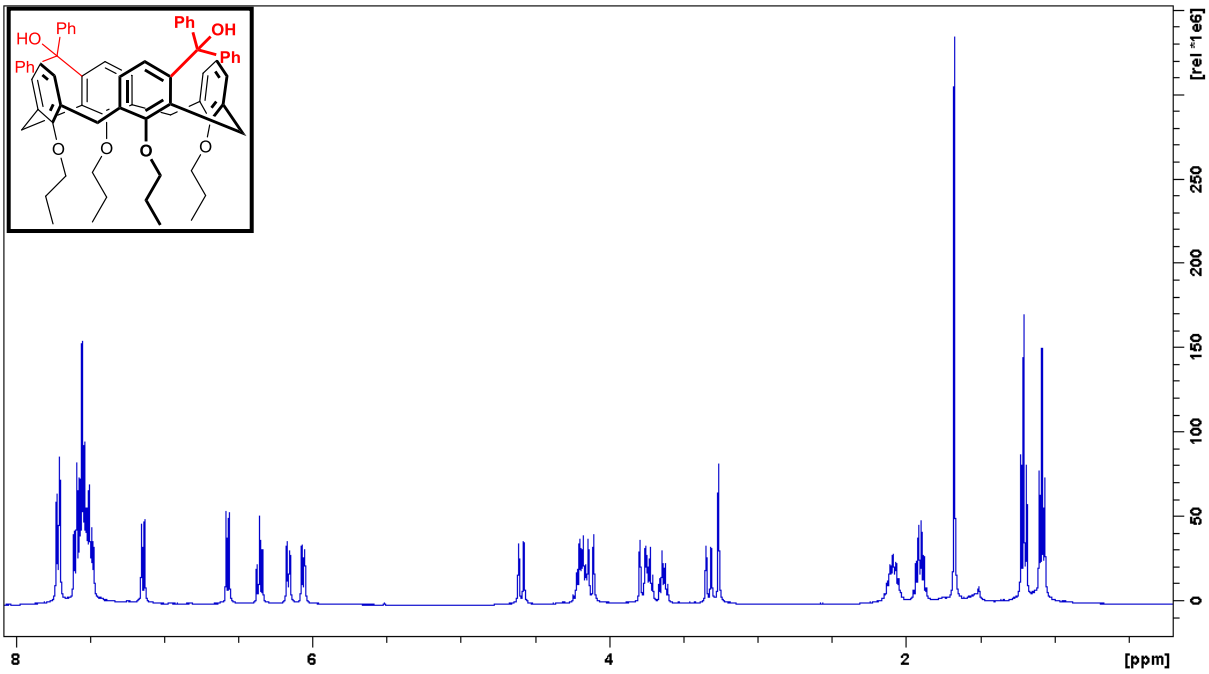

Figure 38. ^{1}H NMR of compound **15** ($CDCl_3$, 400 MHz, 293 K).

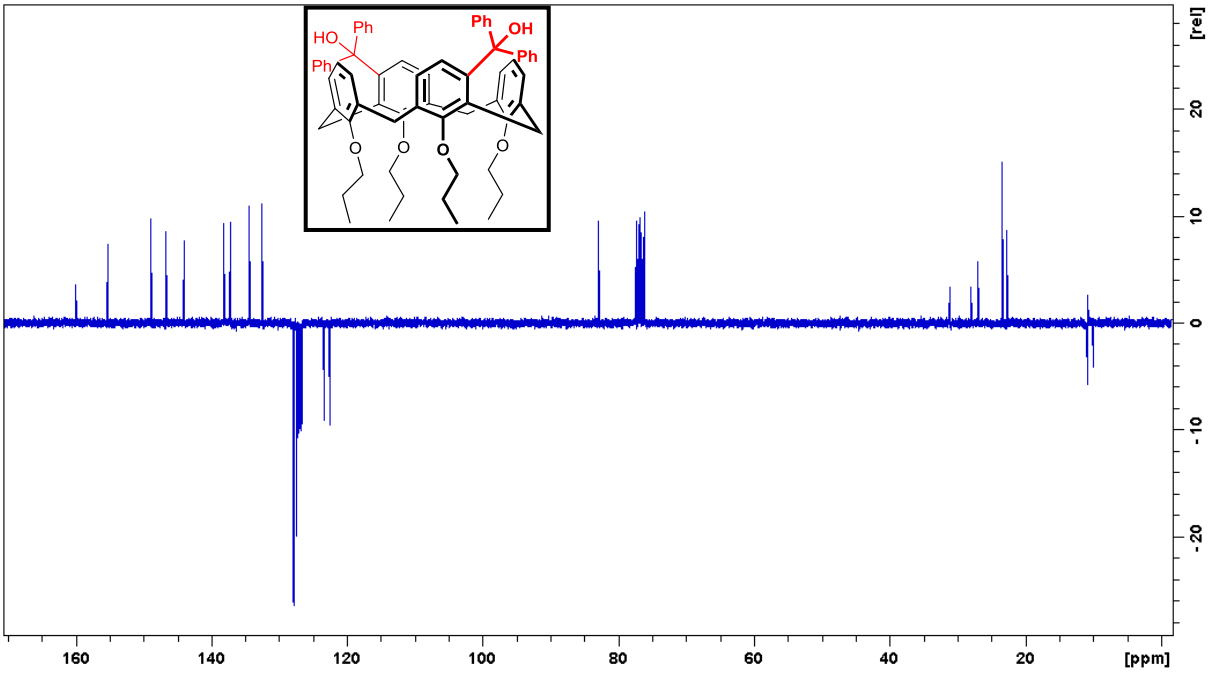

Figure 39. ^{13}C (APT) NMR of compound **15** ($CDCl_3$, 100 MHz, 293 K).

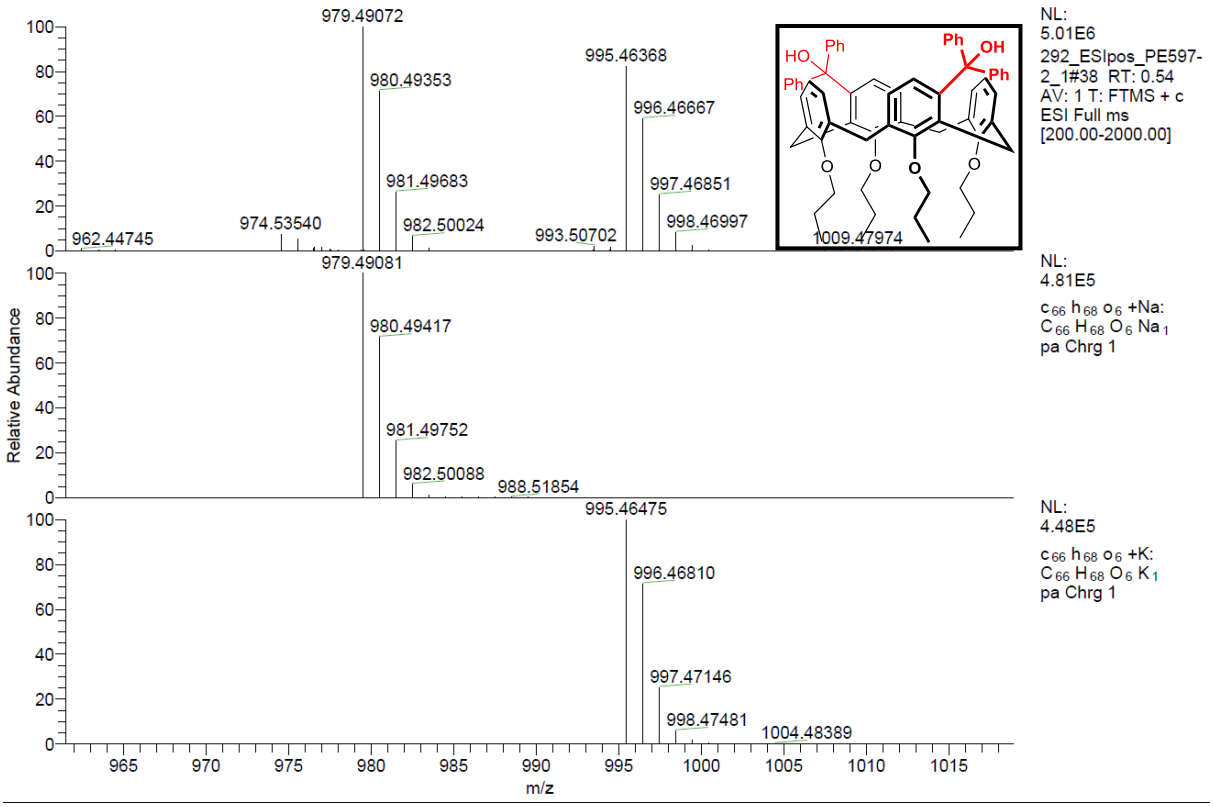

Figure 40. HRMS of compound **15** (ESI^+).

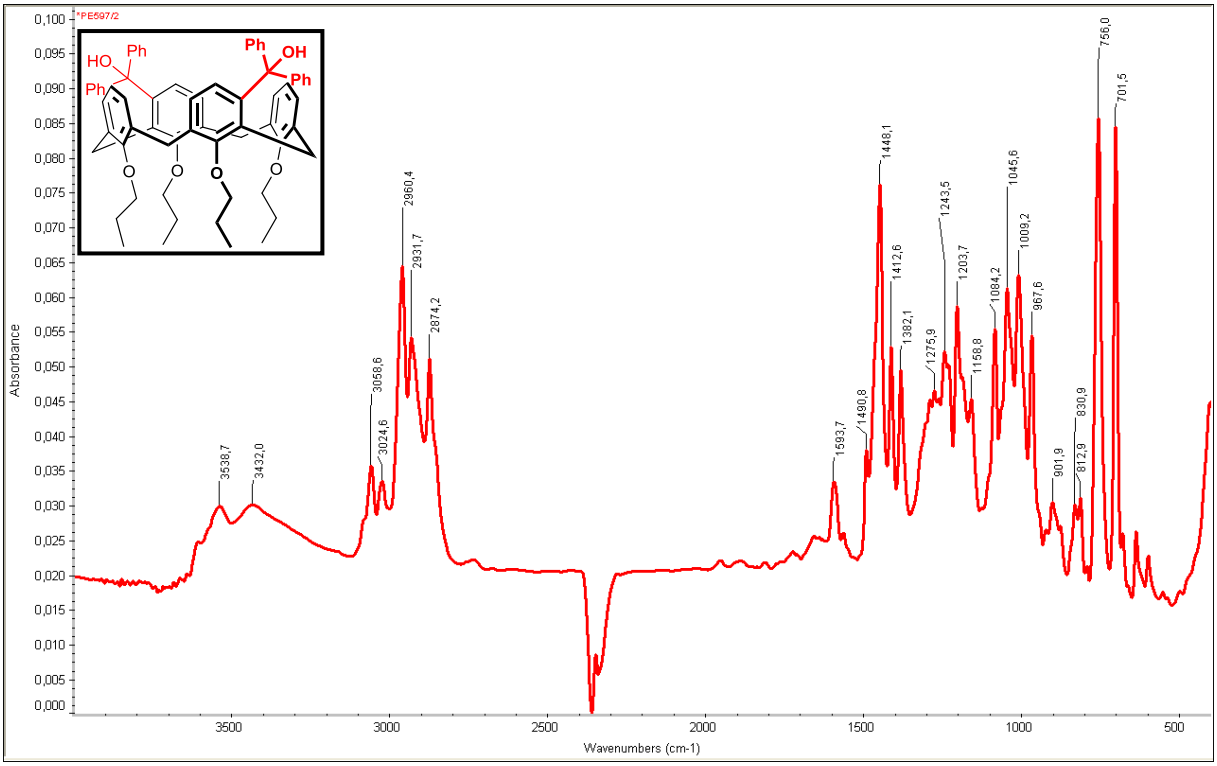

Figure 41. IR of compound **15** (KBr).

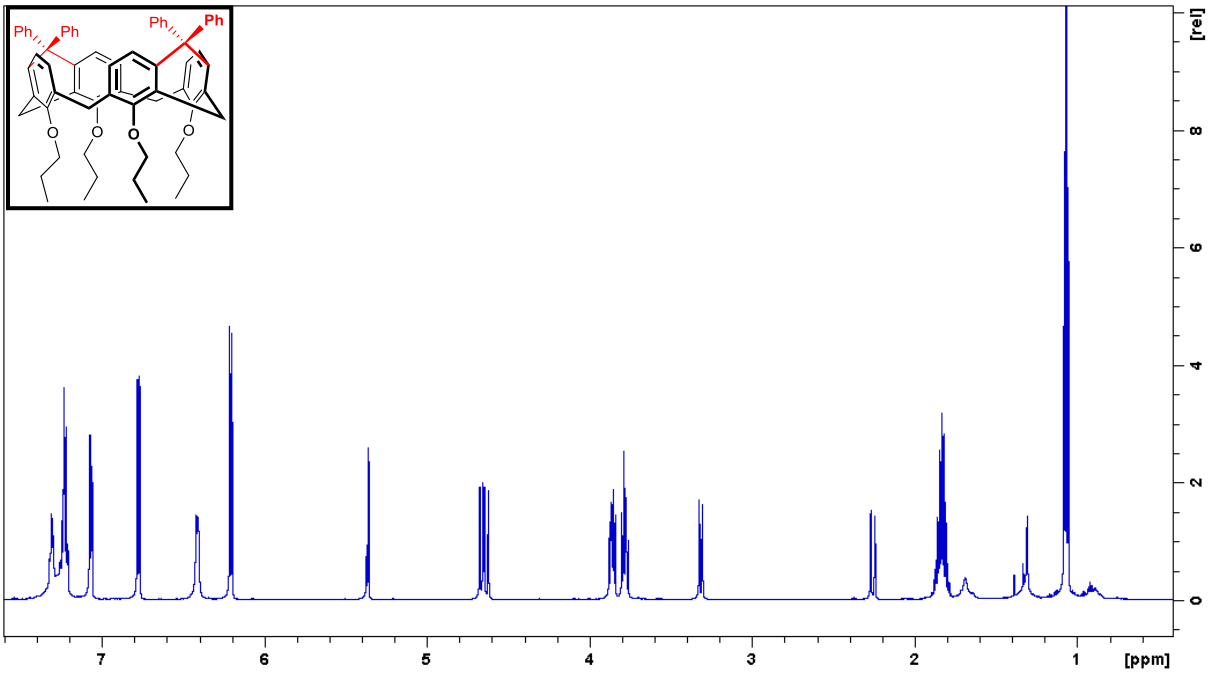

Figure 42. ^{1}H NMR of compound **16** (CD_2Cl_2, 600.1 MHz, 293 K).

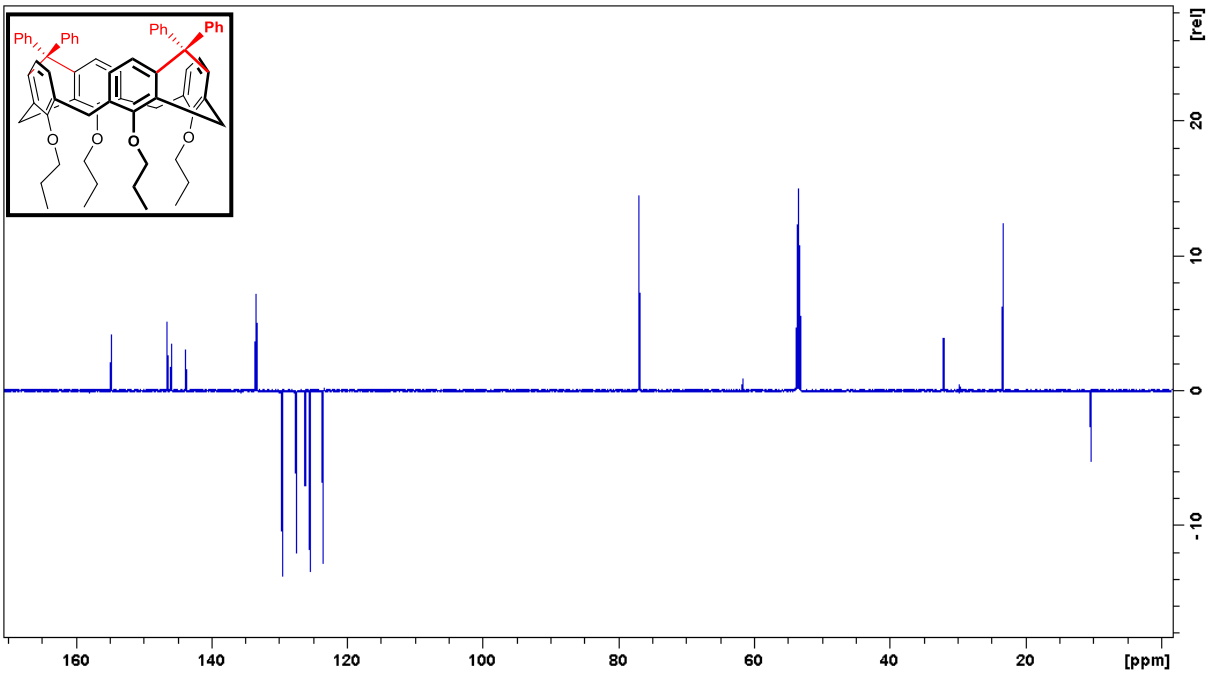

Figure 43. ^{13}C (APT) NMR of compound **16** (CD_2Cl_2 150.9 MHz, 293 K).

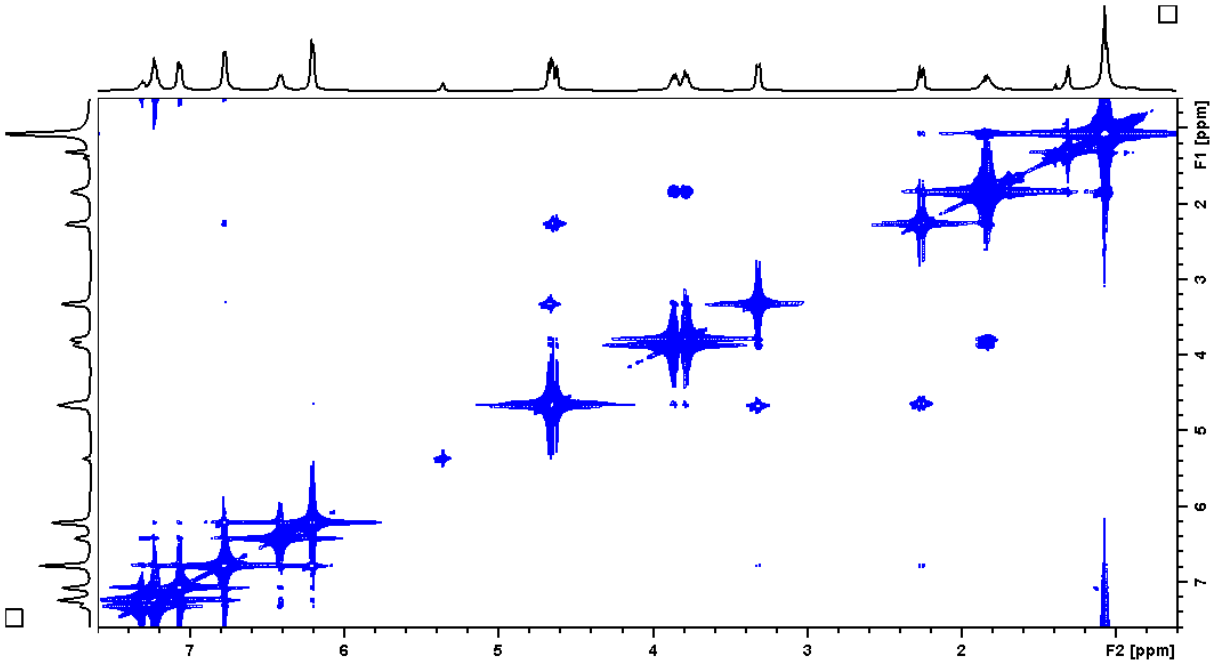

Figure 44. 2D NMR (COSY) of compound **16** (CD_2Cl_2 600.1 MHz, 293 K).

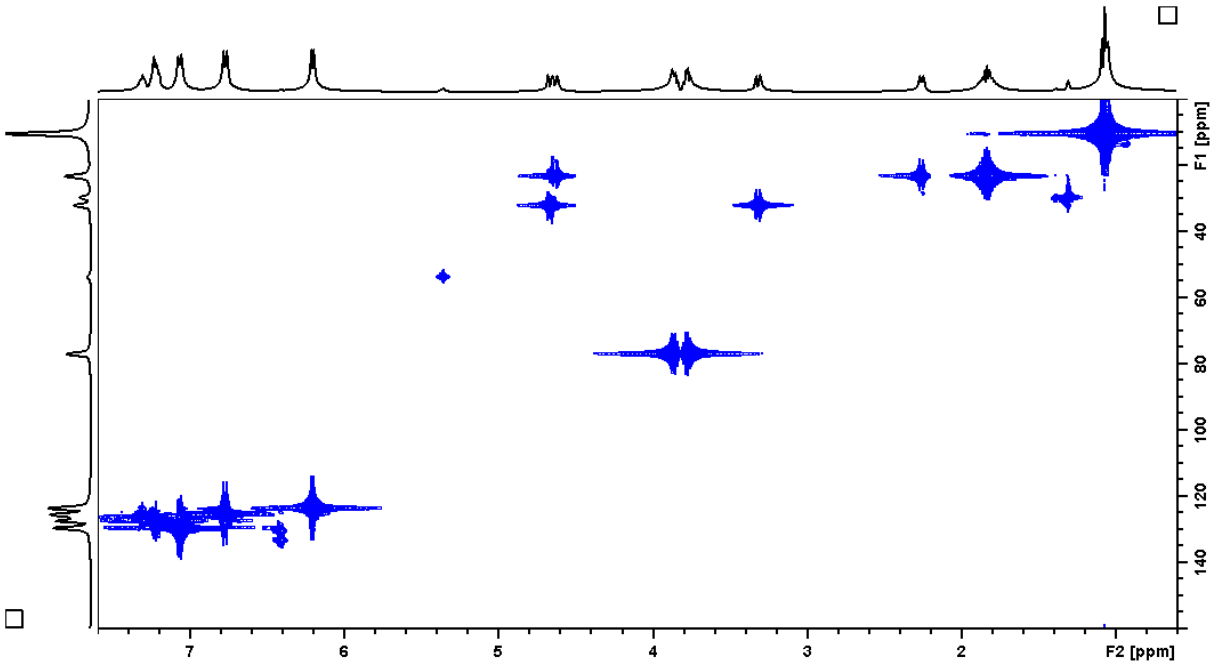

Figure 45. 2D NMR (HMQC) of compound **16** (CD_2Cl_2 600.1 and 150.9 MHz, 293 K).

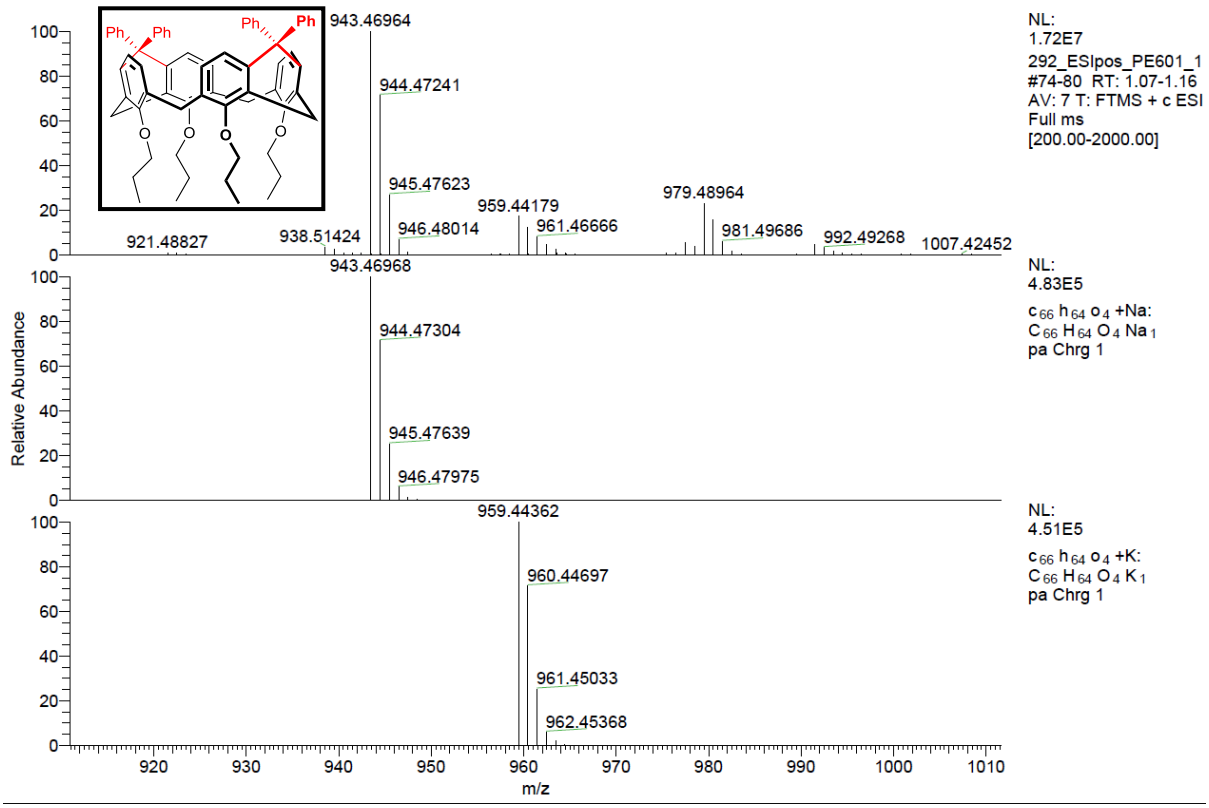

Figure 46. HRMS of compound **16** (ESI^+).

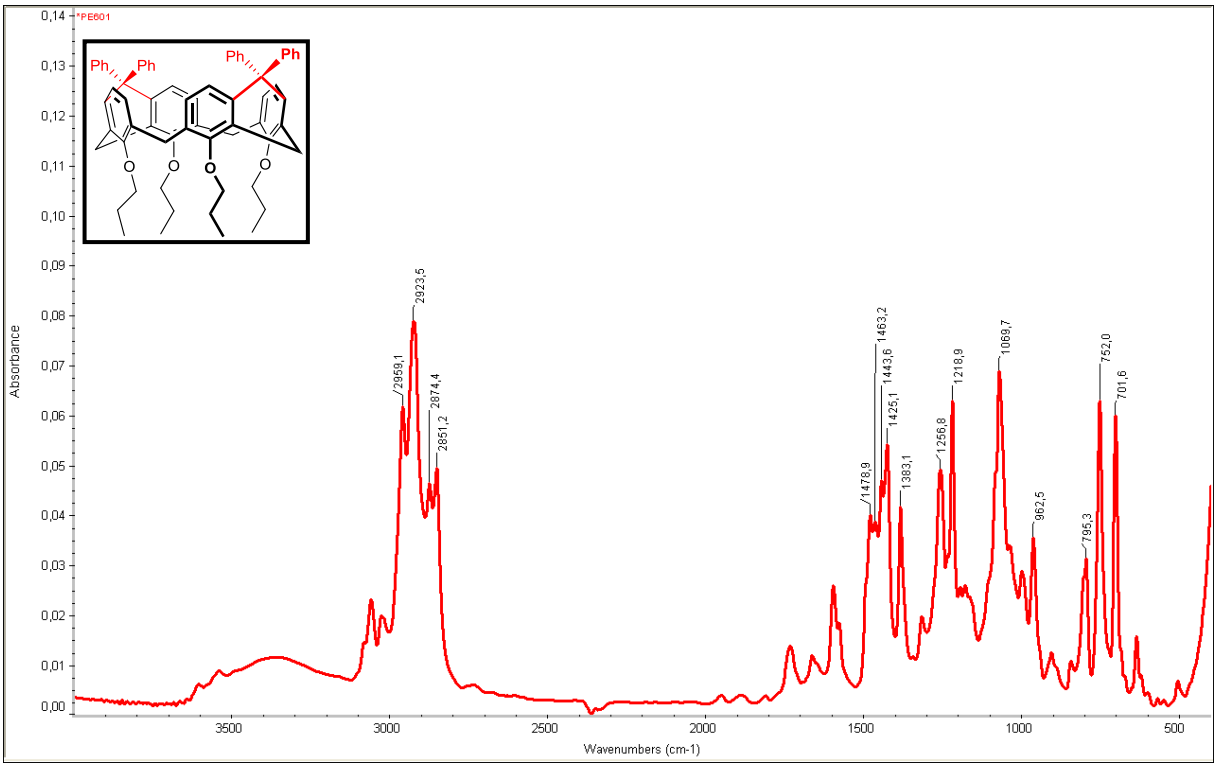

Figure 47. IR of compound **16** (KBr).

Titration experiments

Table 1. Complexation of MeCN with calixarene **11** in CCl_4

		M(calixarene) [g/mol]	V(MeCN) [l]			
m(calixarene) [g]	0.00795	604.83	m(MeCN) [g]	0.0103		
V(CCl_4) [l]	0.0005		c(MeCN) [mol/l]	0.002509135		
c(calixarene) [mol/l]	0.026288379					
V(total) [l]	V(addition) [l]	V(calixarene) [l]	c(calixarene) [mol/l]	c(MeCN) [mol/l]	C(calixarene)/c(guest)	shift [Hz]
0.0005	0		0	0.002509135	0	460.18
0.00055	0.000025	0.00005	0.002389853	0.002509135	0.95246067	428.49
0.000575	0.000025	0.000075	0.003428919	0.002509135	1.366574005	414.8
0.0006	0.000025	0.0001	0.004381396	0.002509135	1.746177896	402.67
0.00065	0.00005	0.00015	0.006066549	0.002509135	2.417784779	381.93
0.0007	0.00005	0.0002	0.007510965	0.002509135	2.993447821	363.93
0.00085	0.0001	0.00035	0.010824626	0.002509135	4.314086566	328.33
0.000925	0.000075	0.000425	0.012078444	0.002509135	4.813787713	317.77

Table 2. Complexation of NMPI with calixarene **11** in $C_2H_2Cl_4$

	M(calixarene) [g/mol]					
m(calixarene) [g]	0.0074	604.83	m(NMPI) [g]	0.00078		221.039
V($C_2D_2Cl_4$) [mol/l]	0.0005		c(NMPI) [mol/l]	0.001764395		
c(calixarene) [mol/l]	0.024469686					
V(total) [l]	V(addition) [l]	V(calixarene) [l]	c(calixarene) [mol/l]	c(MeCN) [mol/l]	C(calixarene)/c(guest	shift [Hz]
0.0005	0		0	0.001764395	0	952.77
0.00051	0.00001	0.00001	0.000479798	0.001764395	0.271933376	923.03
0.00052	0.00001	0.00002	0.000941142	0.001764395	0.533407777	896.04
0.00053	0.00001	0.00003	0.001385077	0.001764395	0.785015219	870.21
0.000555	0.000025	0.000055	0.002424924	0.001764395	1.374365983	819.74
0.00058	0.000025	0.00008	0.003375129	0.001764395	1.912910648	777.1
0.000605	0.000025	0.000105	0.004246805	0.001764395	2.406947489	741.1
0.000655	0.00005	0.000155	0.005790536	0.001764395	3.281882963	684.37
0.000705	0.00005	0.000205	0.007115299	0.001764395	4.032714114	639.61
0.000805	0.0001	0.000305	0.009271123	0.001764395	5.254563565	580.3

Crystallographic data

*Crystallographic data for **12***

M = 796.17 g.mol^{-1}, triclinic system, space group P-1, a = 10.0427 (3) Å, b = 11.1946 (3) Å, c = 21.0233 (4) Å, α = 96.2914 (18) °, β = 92.4769 (18) °, γ = 109.769 (2) °, Z = 2, V = 2202.68 (10) Å^3, D_c = 1.200 g.cm^{-3}, μ(Cu-Kα) = 0.61 mm^{-1}, crystal dimensions of 0.59 × 0.22 × 0.07 mm. Data were collected at 120 (2) K on Gemini Atlas2 CCD diffractometer with mirror collimated Cu-Kα radiation. The structure was solved by charge flipping methods[1] and anisotropically refined by full matrix least squares on F squared using the CRYSTALS suite of programs[2] to final value R = 0.056 and wR = 0.168 using 7769 independent reflections (Θ_{max} = 67.1°), 650 parameters and 95 restrains. The hydrogen atoms present in structure model were placed in calculated positions and refined with a riding constrains. The disordered functional groups positions were found in difference electron density maps and refined with restrained geometry. The occupancy was constrained to full for each functional group. The disordered water molecule was found in the structure, its hydrogen atoms could not be found in difference Fourier maps and therefore they are absent in the structure model. The disordered water molecule occupancy was refined and not constrained. The MCE program[3] was used for visualization of residual electron density maps. The structure was deposited into Cambridge Structural Database under number CCDC 1556075.

*Crystallographic data for **13***

M = 632.88 g.mol^{-1}, monoclinic system, space group $P2_1/c$, a = 12.6881 (2) Å, b = 19.1234 (3) Å, c = 14.91023 (19) Å, β = 93.0810 (13) °, Z = 4, V = 3612.58 (9) Å^3, D_c = 1.164 g.cm^{-3}, μ(Cu-Kα) = 0.57 mm^{-1}, crystal dimensions of 0.34 × 0.19 × 0.12 mm. Data were collected at 95 (2) K on a Supernova Atlas2 CCD diffractometer with mirror collimated microfocus sealed tube Cu-Kα radiation. The structure was solved by charge flipping methods[1] and anisotropically refined by full matrix least squares on F squared using the CRYSTALS suite of programs[2] to final value R = 0.043 and wR = 0.083 using 7259 independent reflections (Θ_{max} = 75.5°), 424 parameters and 0 restrains. The hydrogen atoms were placed in calculated positions and refined with a riding constrains. The structure was deposited into Cambridge Structural Database under number CCDC 1556077.

*Crystallographic data for **16***

M = 971.29 g.mol^{-1}, triclinic system, space group P-1, a = 11.4179 (5) Å, b = 11.8579 (5) Å, c = 23.594 (1) Å, α = 77.2299 (19) °, β = 79.1729 (18) °, γ = 72.4389 (18) °, Z = 2, V = 2944.9 (2) Å^3, D_c = 1.095 g.cm^{-3}, μ(Cu-Kα) = 0.54 mm^{-1}, crystal dimensions of 0.47 × 0.32 × 0.17 mm. Data were collected at 180 (2) K on a D8 Venture Photon CMOS diffractometer with Incoatec microfocus sealed tube Cu-Kα radiation. The structure was solved by charge flipping methods[1] and anisotropically refined by full matrix least squares on F squared using the CRYSTALS suite of programs[2] to final value R = 0.079 and wR = 0.213 using 10721 independent reflections (Θ_{max} = 68.5°), 768 parameters

and 129 restrains. The disordered functional group positions were found in difference electron density maps and refined with restrained geometry. The occupancy of disordered functional group was constrained to full. The hydrogen atoms attached to carbon atoms were placed in calculated positions the hydrogen atoms attached to oxygen atoms were found in difference electron density maps and refined with soft restrains. In both cases hydrogen atoms were refined with a riding constrains after initial refinement of geometry. The MCE program[3] was used for visualization of residual electron density maps. The structure contained severely disordered solvent molecules and any attempts on its refinement were unsuccessful; therefore it was removed from the structure using PLATON squeeze[4]. The structure was deposited into Cambridge Structural Database under number CCDC 1556076.

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