Supporting Information for

meta-Bridged Calix[4]arenes with Methylene Moiety Possessing In/Out Stereochemistry of Substituents

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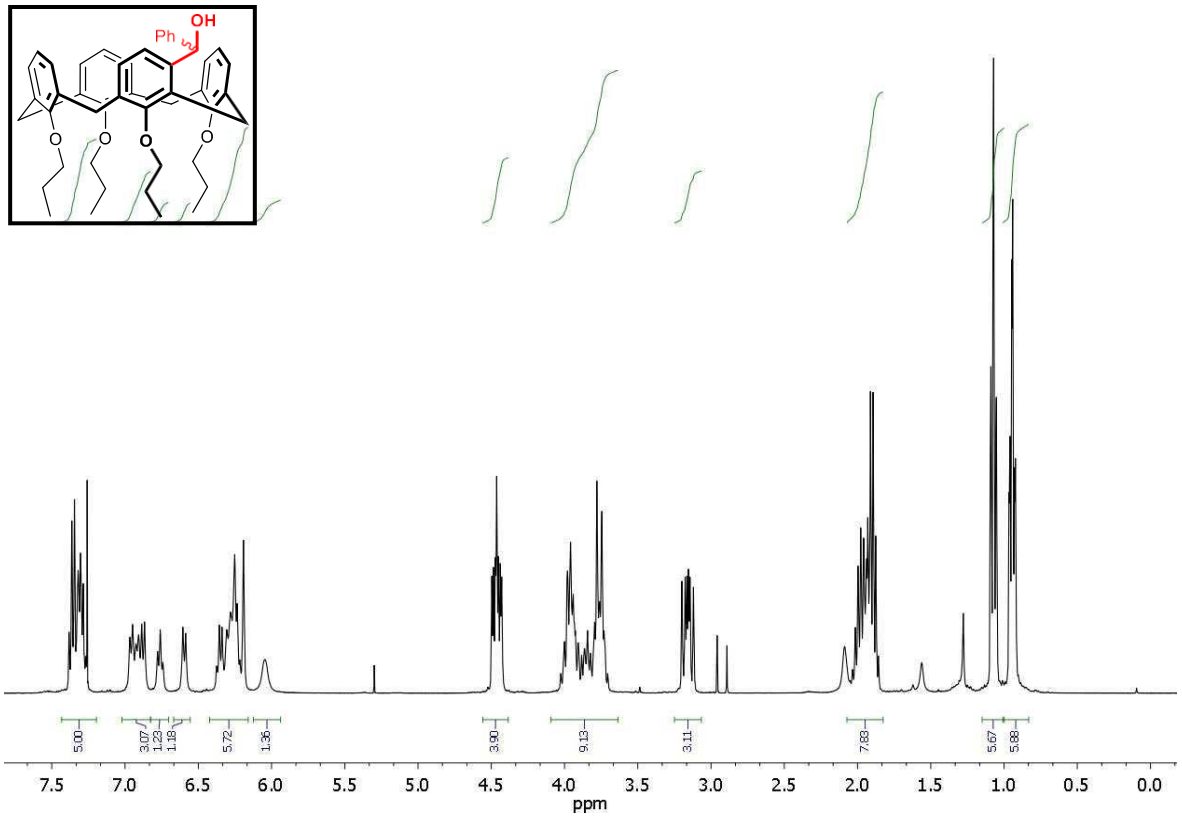


Figure S1. ^{1}H NMR of compound **4a** ($CDCl_3$, 400 MHz).

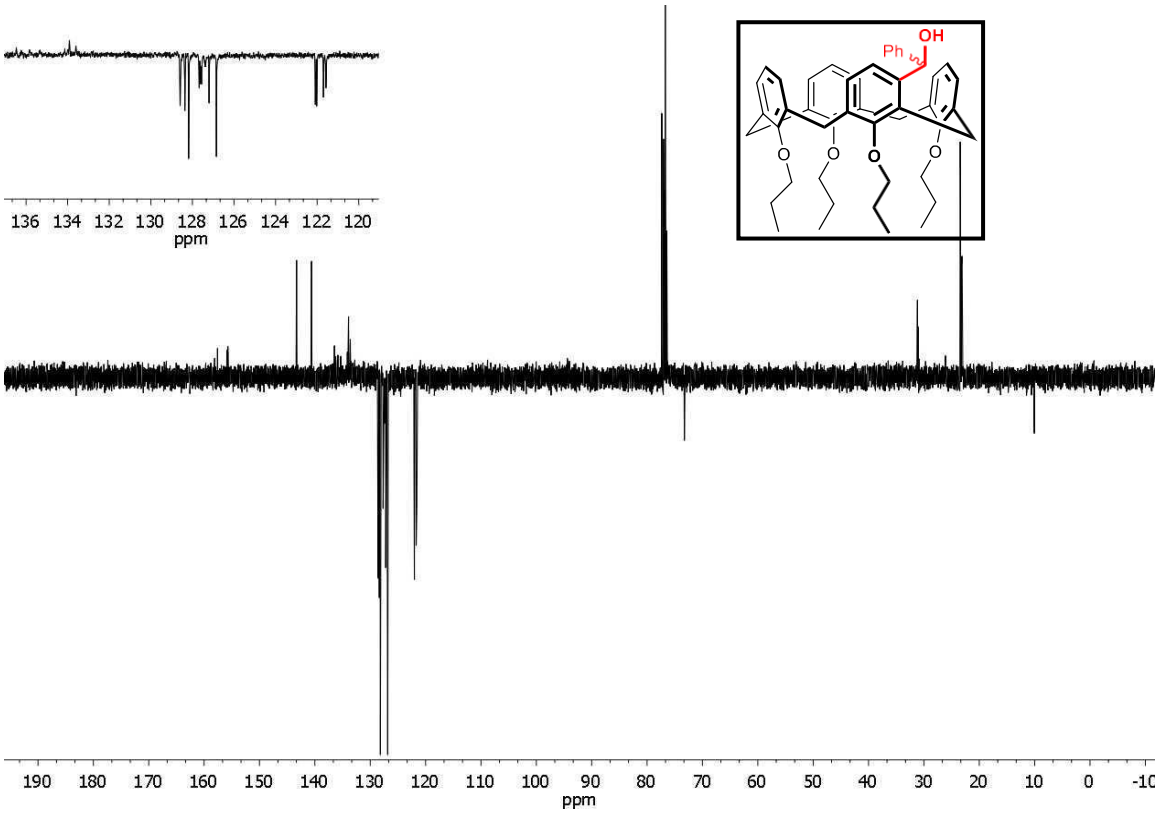


Figure S2. ^{13}C NMR (APT) of compound **4a** ($CDCl_3$, 100 MHz).

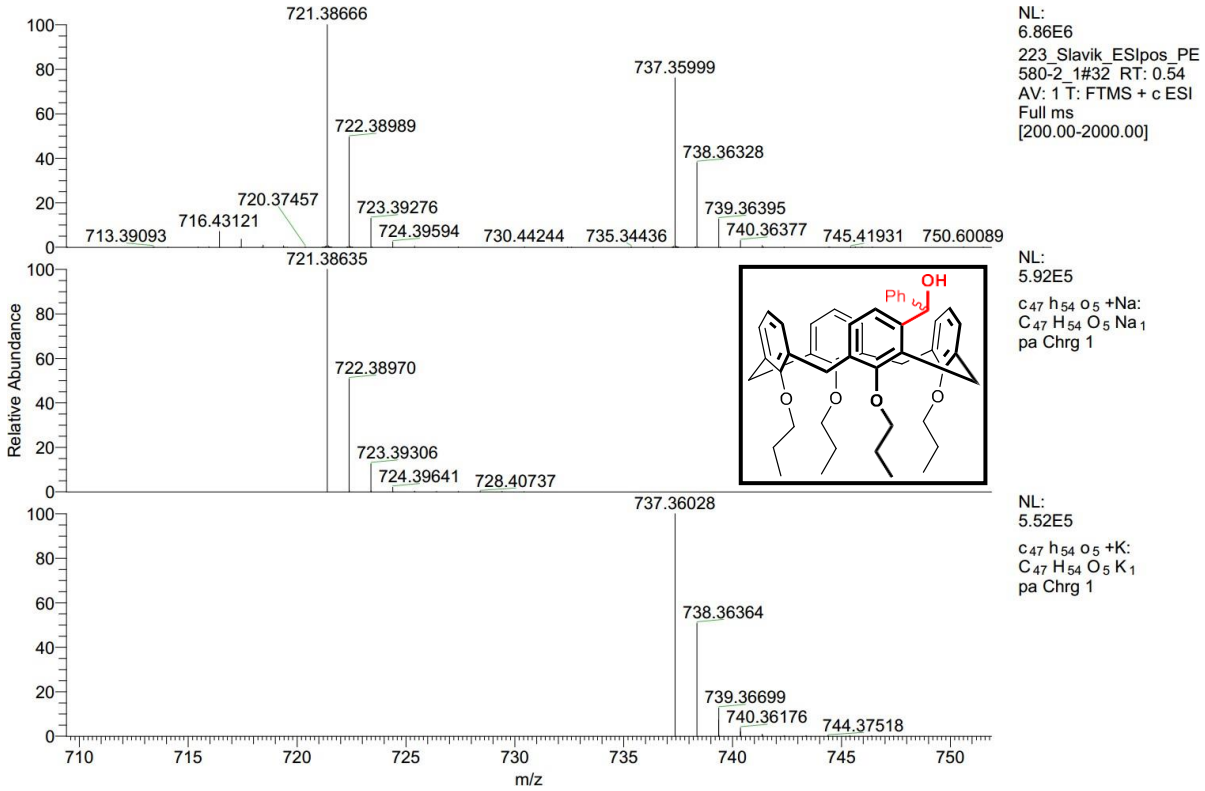


Figure S3. HRMS of compound **4a** (ESI^+).

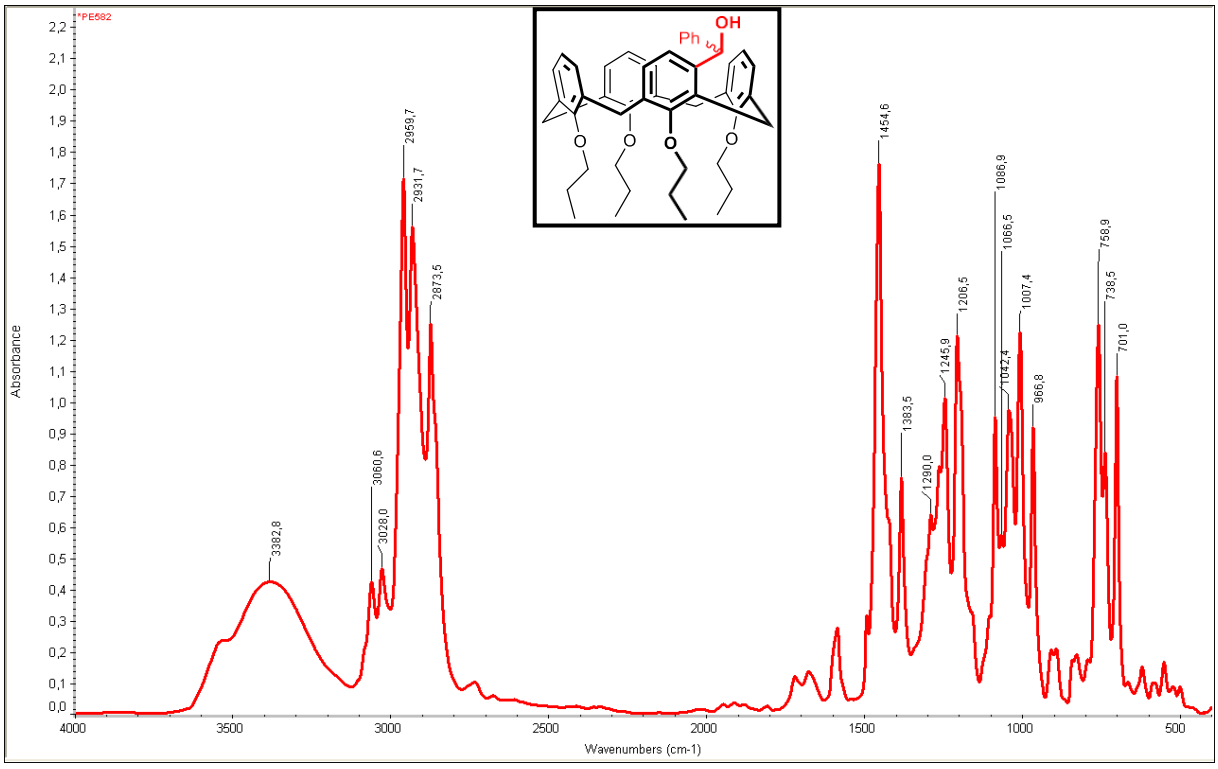


Figure S4. IR of compound **4a** (KBr).

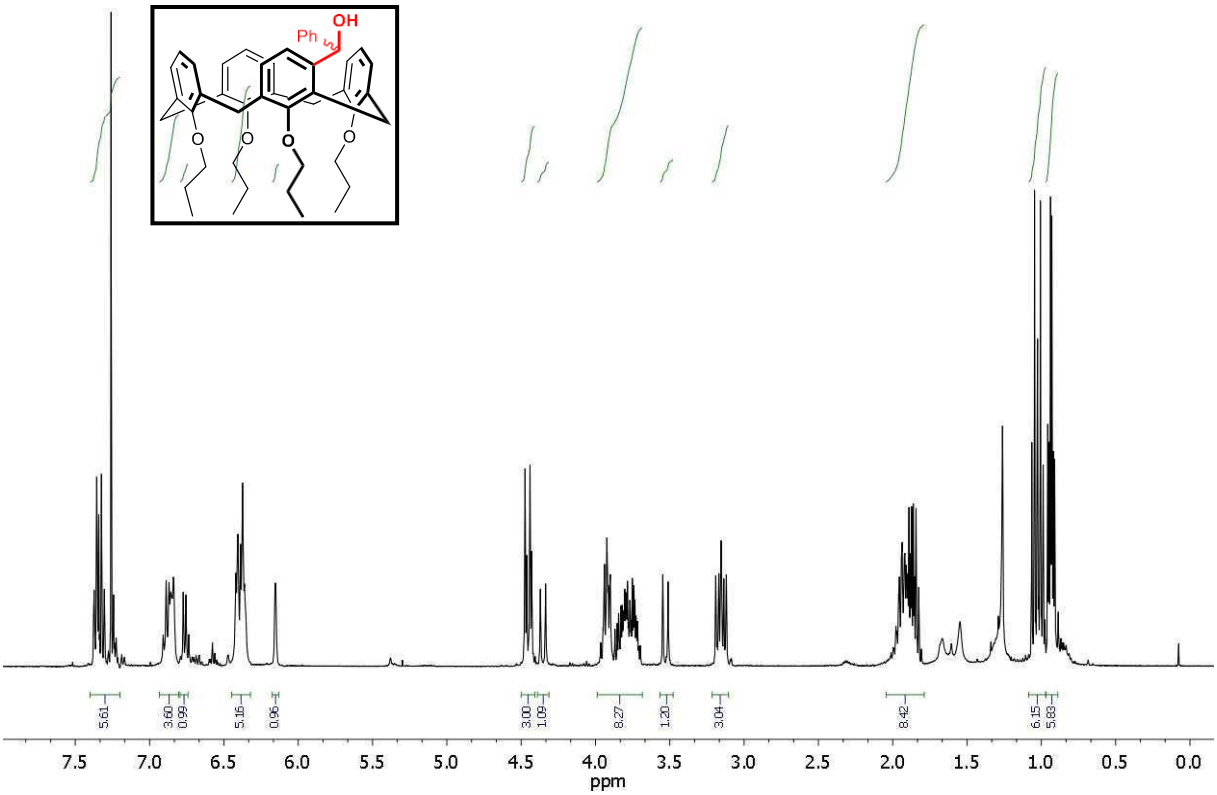


Figure S5. ^{1}H NMR of compound **4b** ($CDCl_3$, 400 MHz).

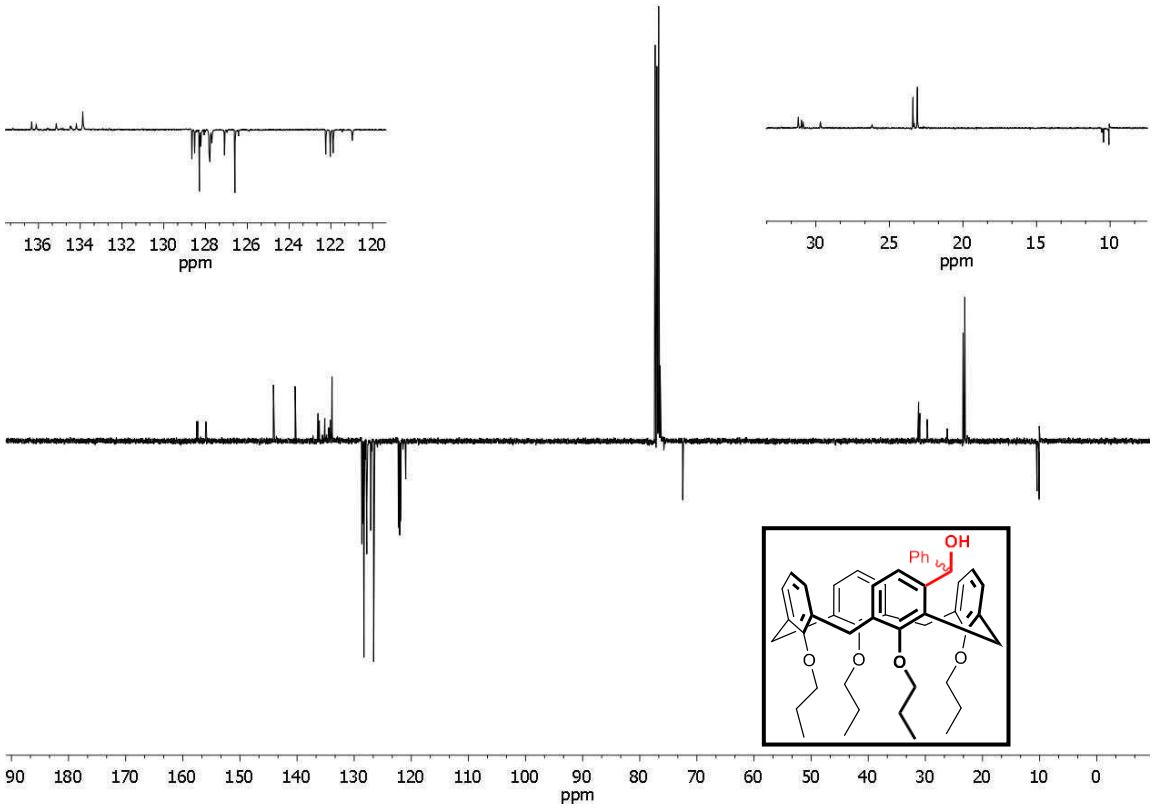


Figure S6. ^{13}C NMR (APT) of compound **4b** ($CDCl_3$, 100 MHz).

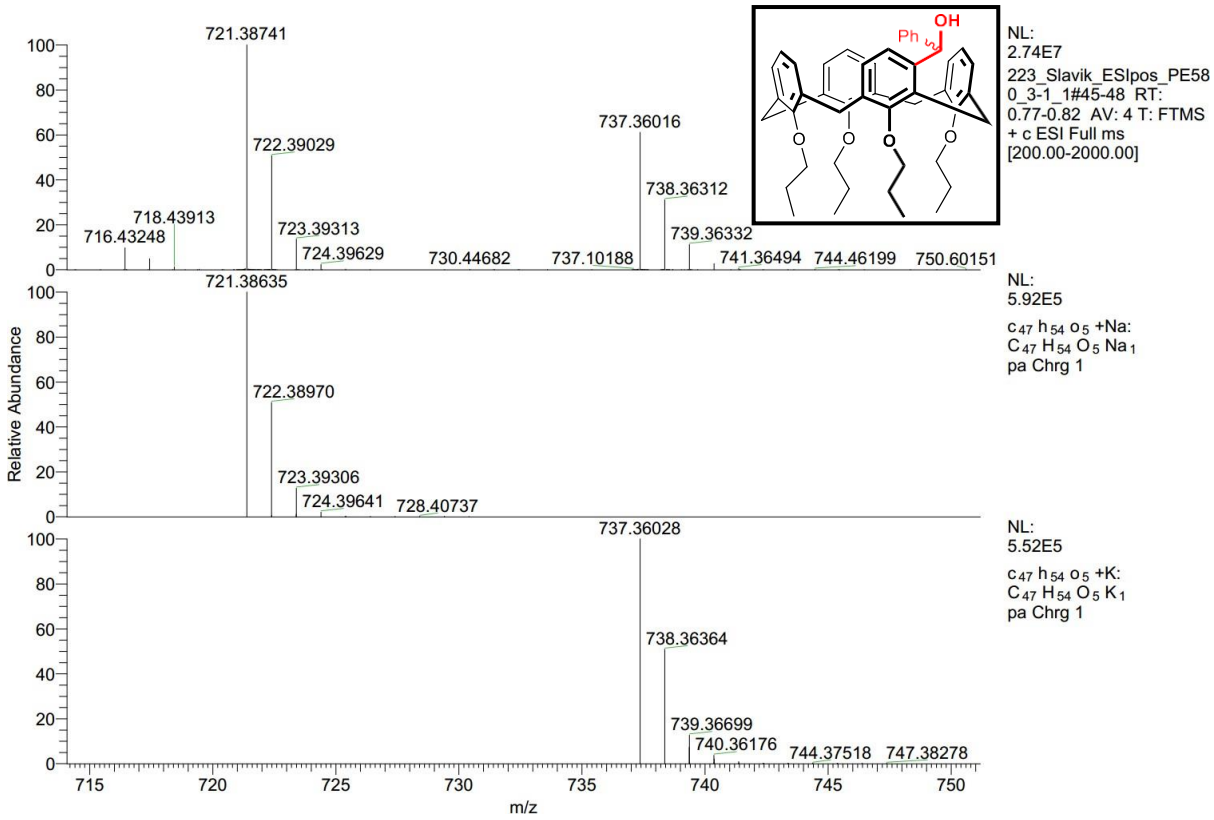


Figure S7. HRMS of compound **4b** (ESI^+).

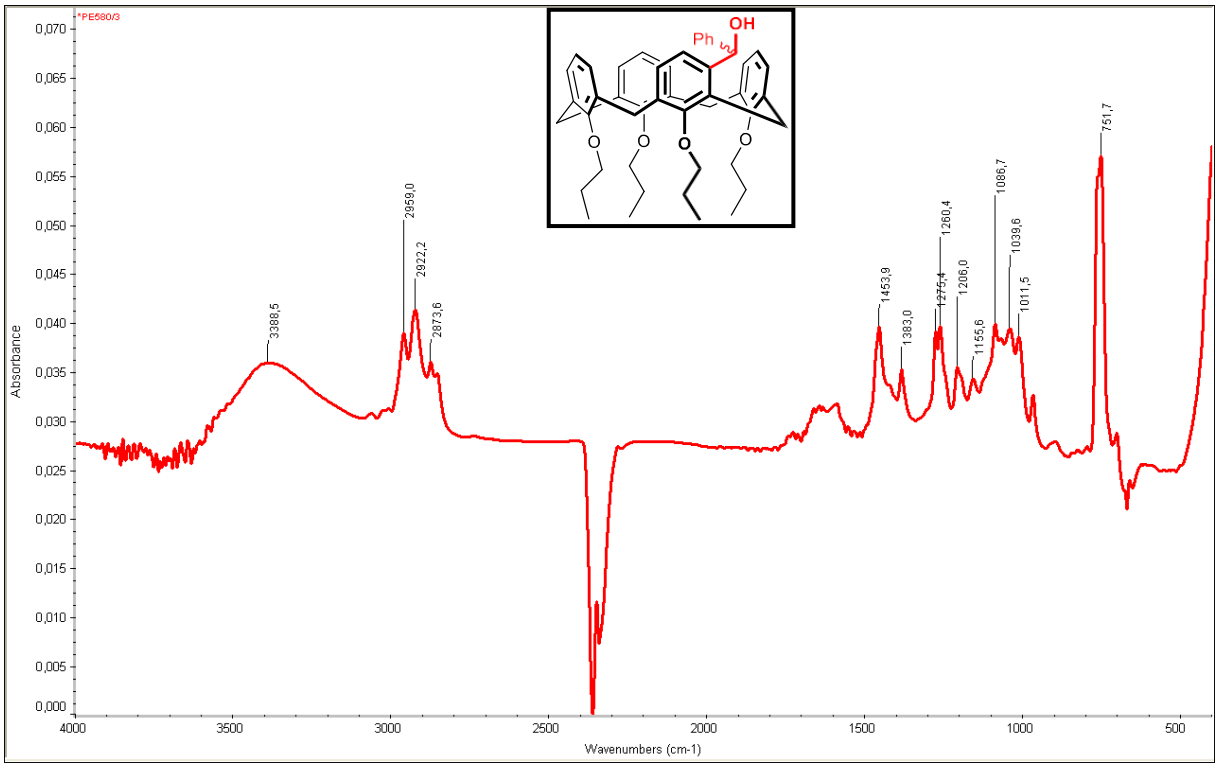


Figure S8. IR of compound **4b** (KBr).

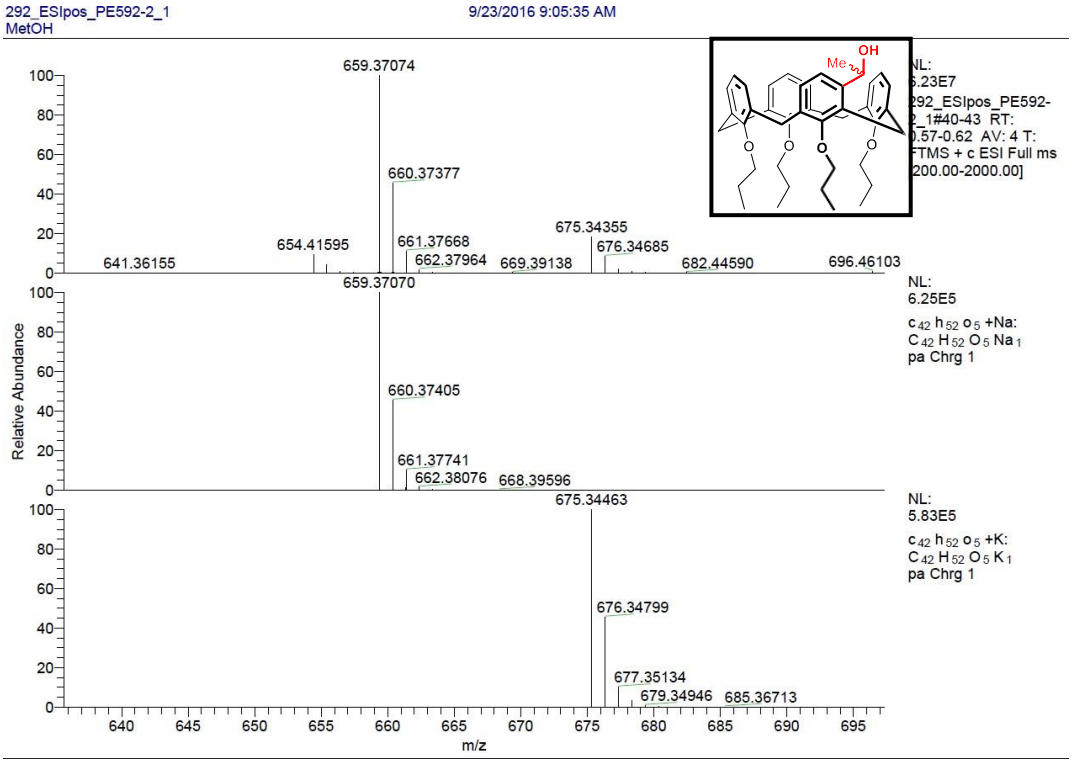


Figure S9. HRMS of mixture of **5a** and **5b** (ESI^+).

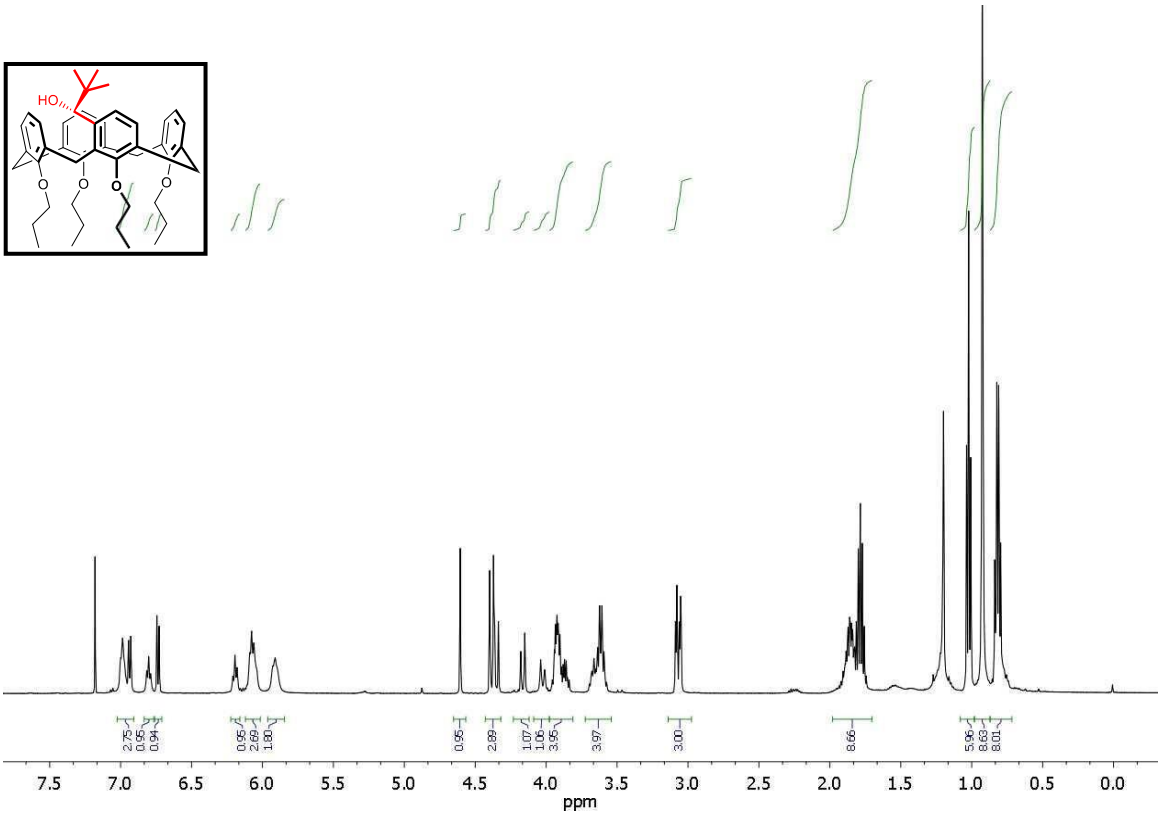


Figure S10. ^{1}H NMR of compound **6a** ($CDCl_3$, 500.1 MHz, 323 K).

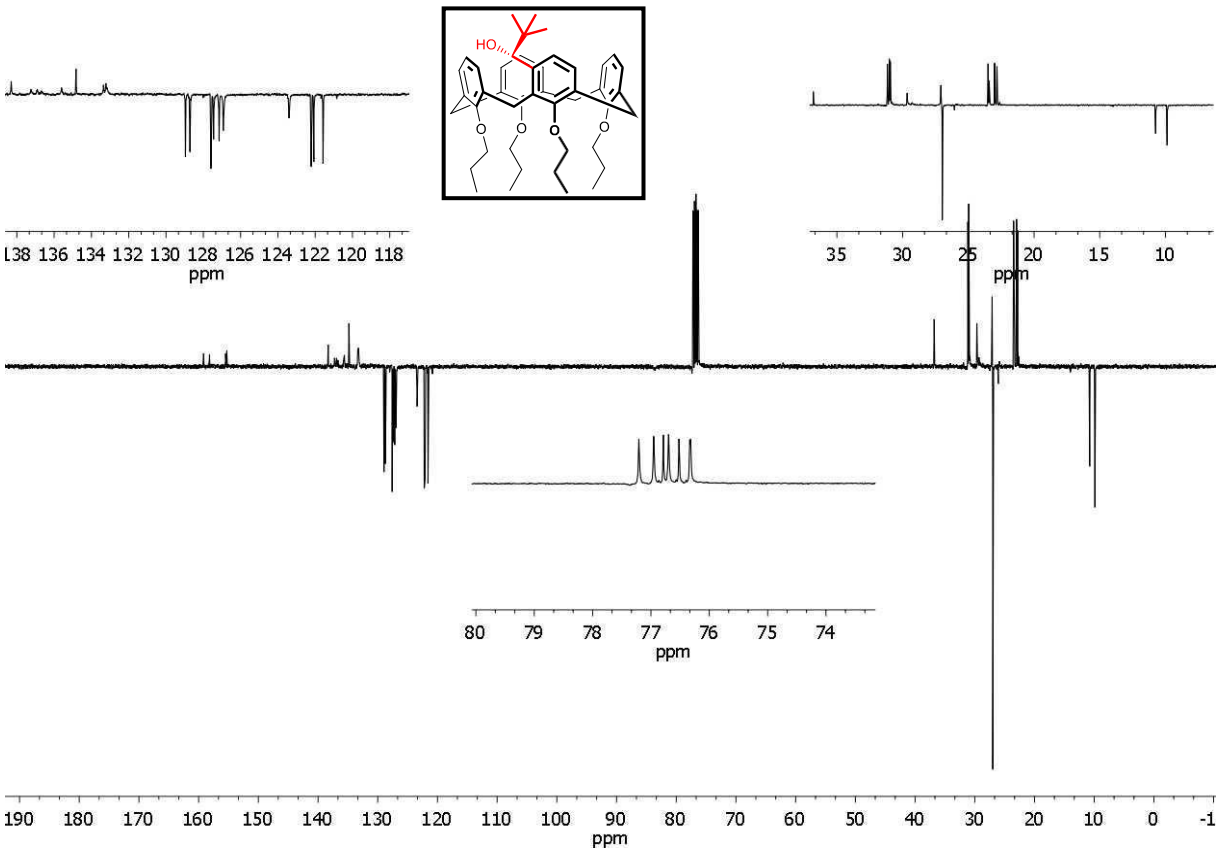


Figure S11. ^{13}C NMR (APT) of compound **6a** ($CDCl_3$, 125.8 MHz, 323 K).

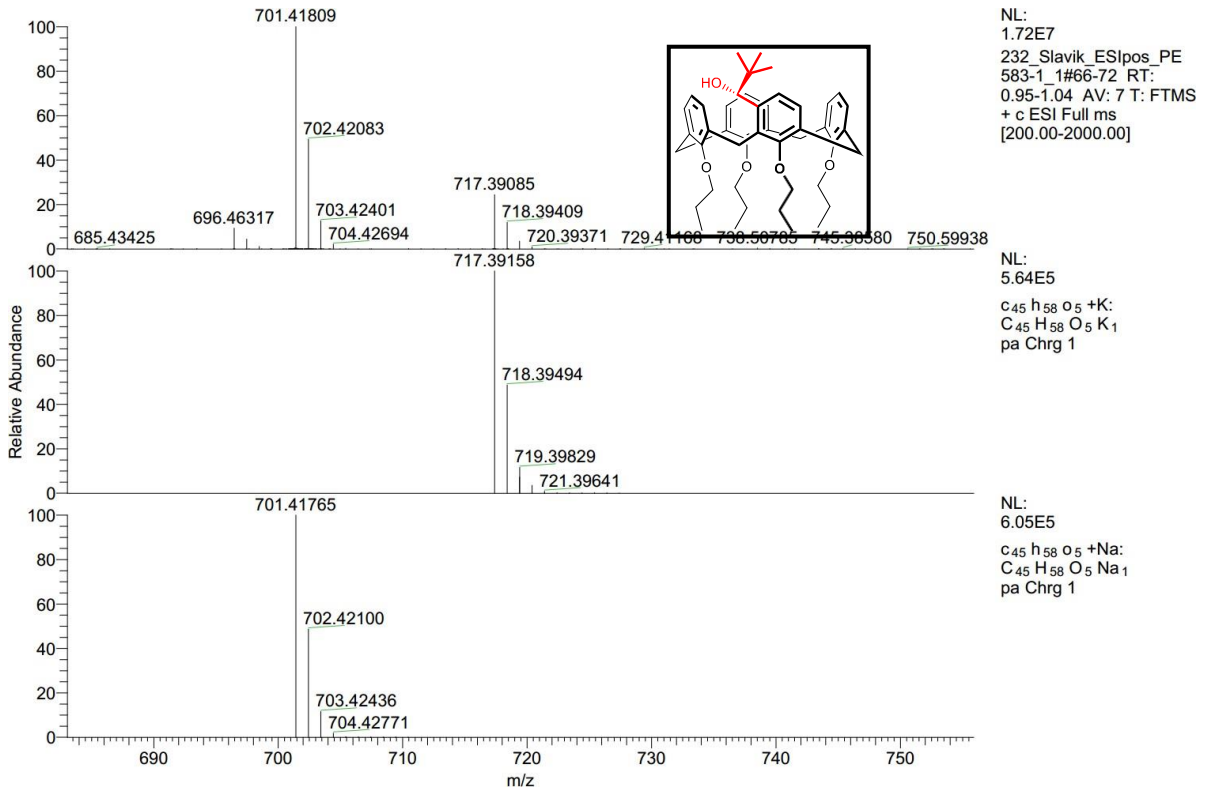


Figure S12. HRMS of compound **6a** (ESI^+).

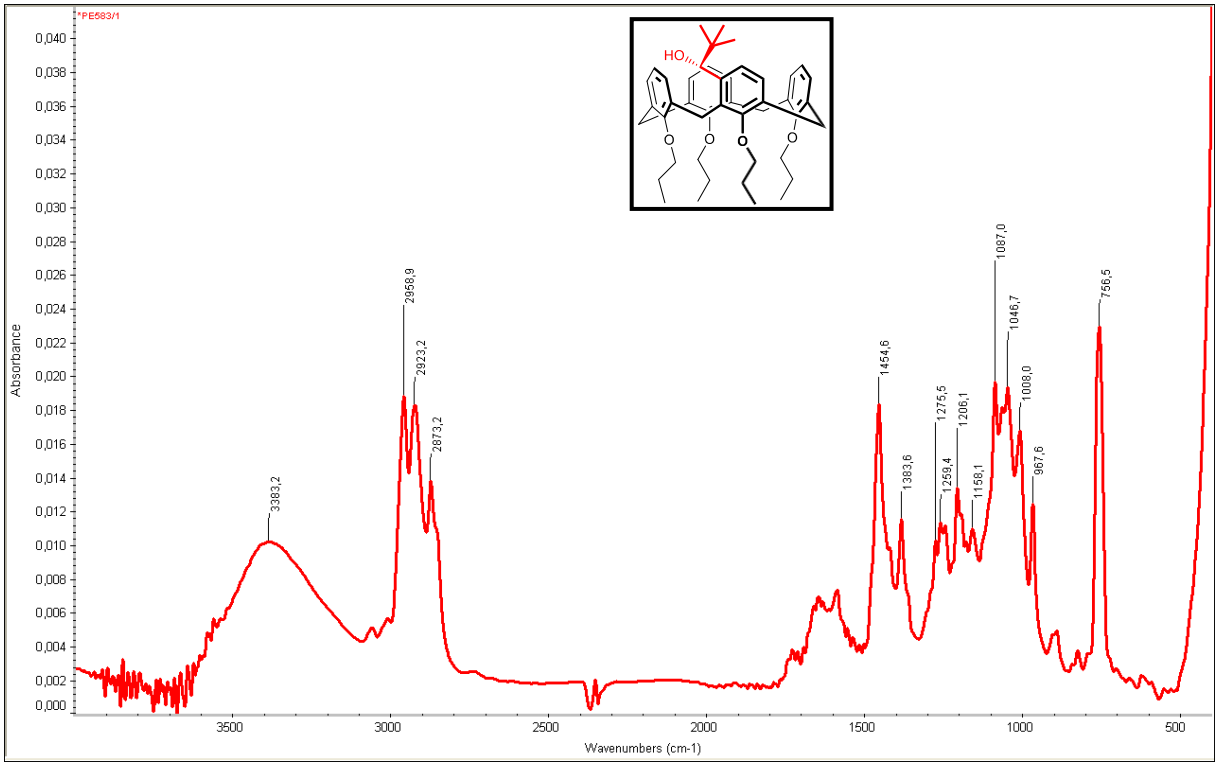


Figure S13. IR of compound **6a** (KBr).

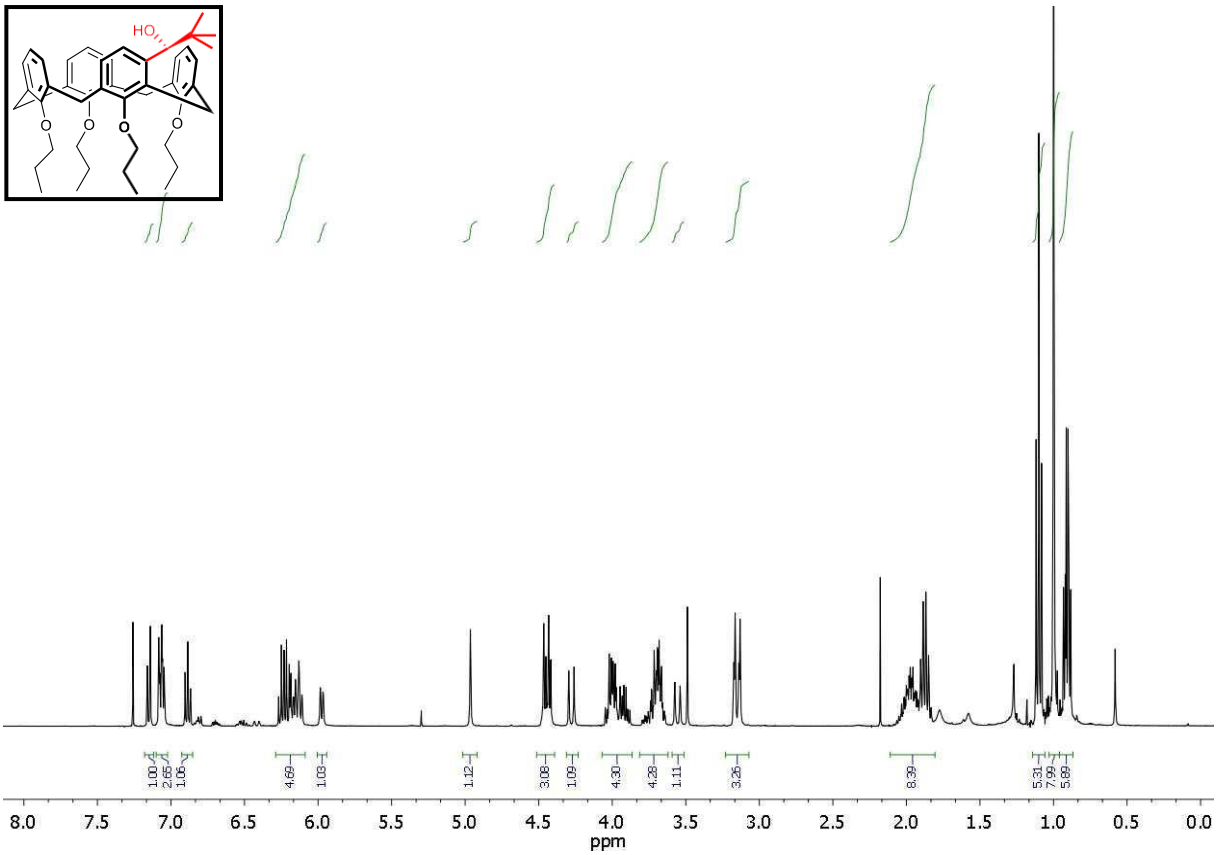


Figure S14. ^{1}H NMR of compound **6b** ($CDCl_3$, 400 MHz).

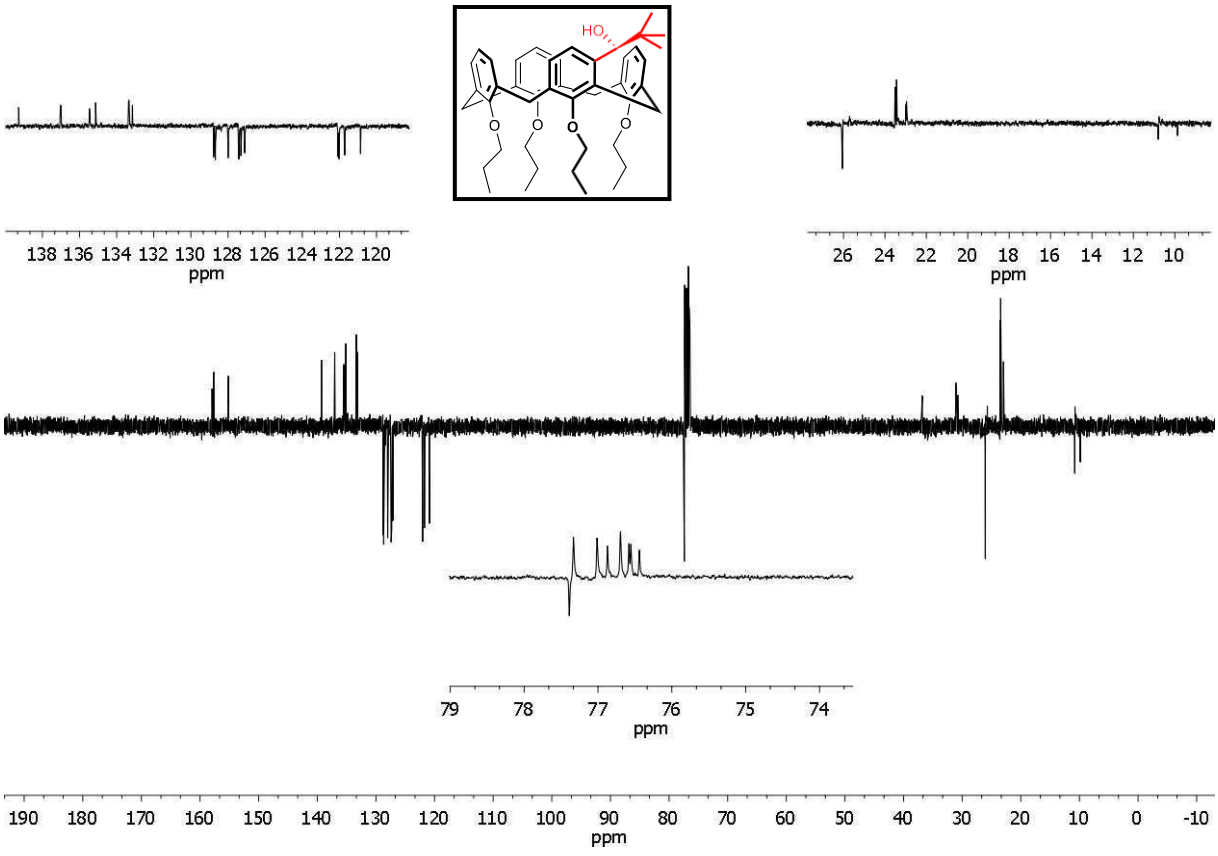


Figure S15. ^{13}C NMR (APT) of compound **6b** ($CDCl_3$, 100 MHz).

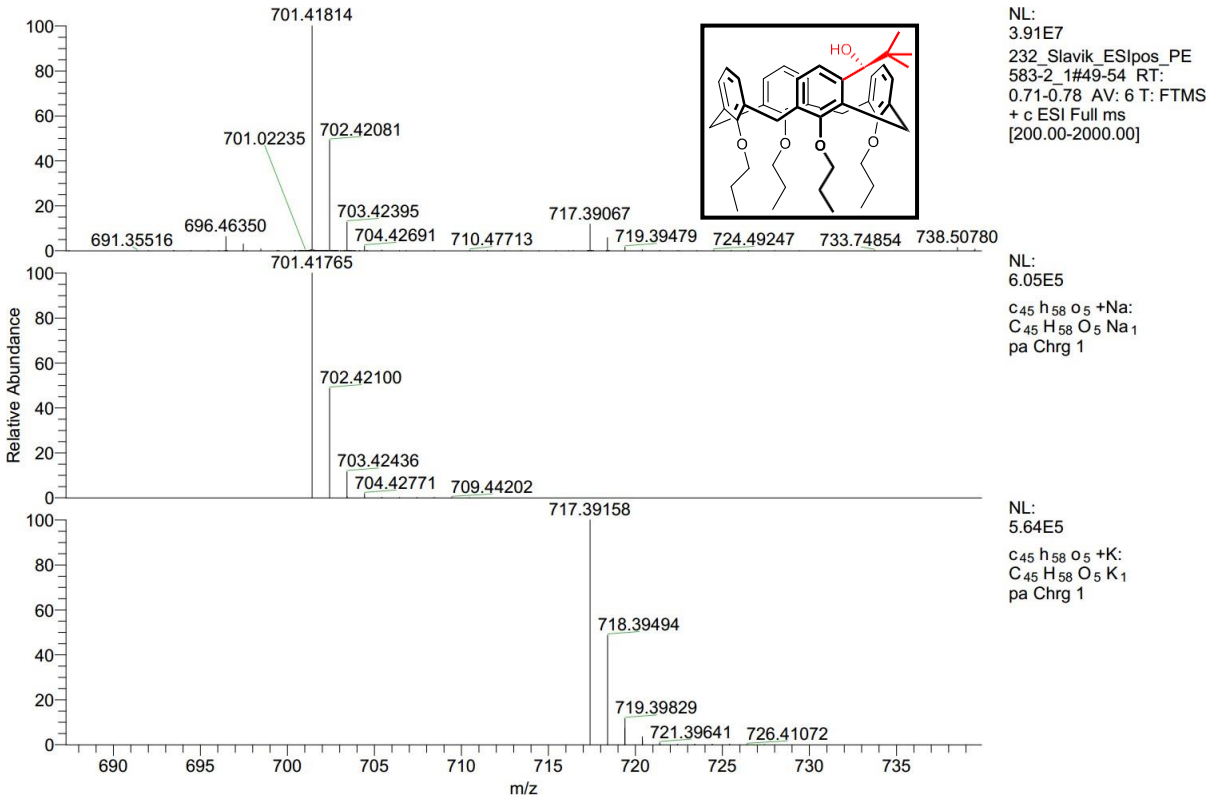


Figure S16. HRMS of compound **6b** (ESI^+).

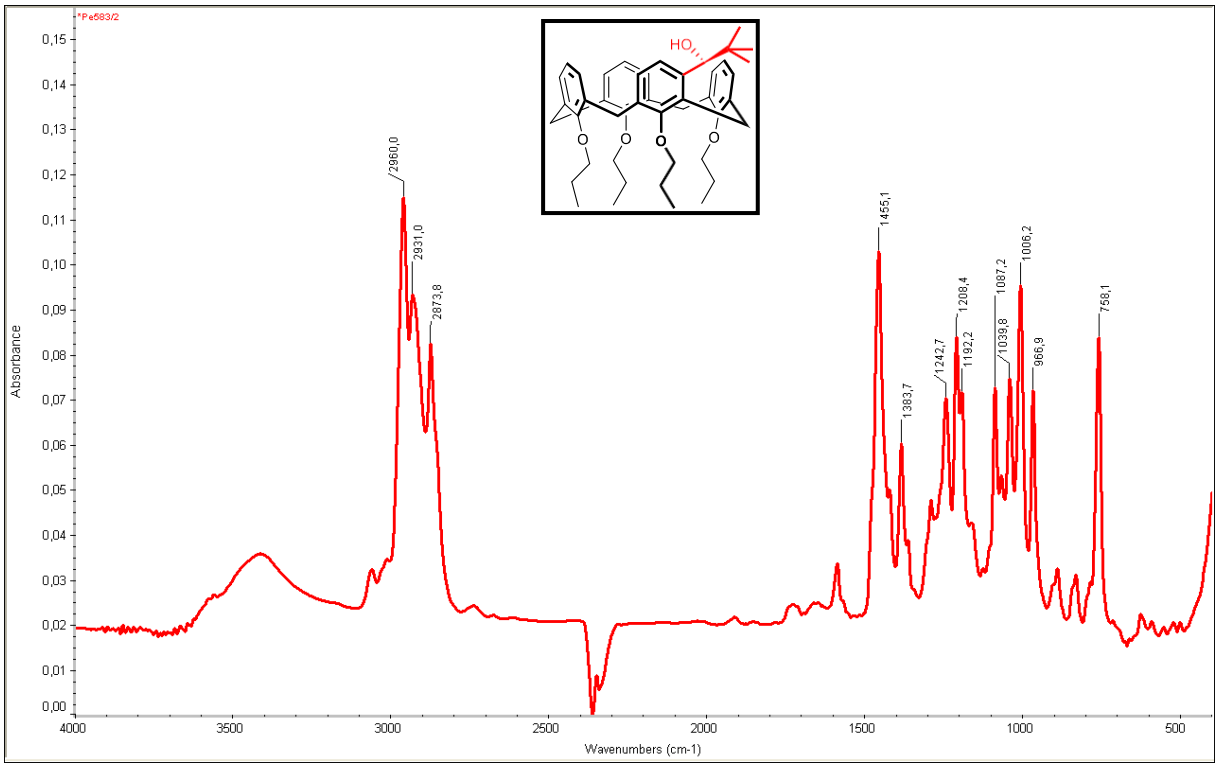


Figure S17. IR of compound **6b** (KBr).

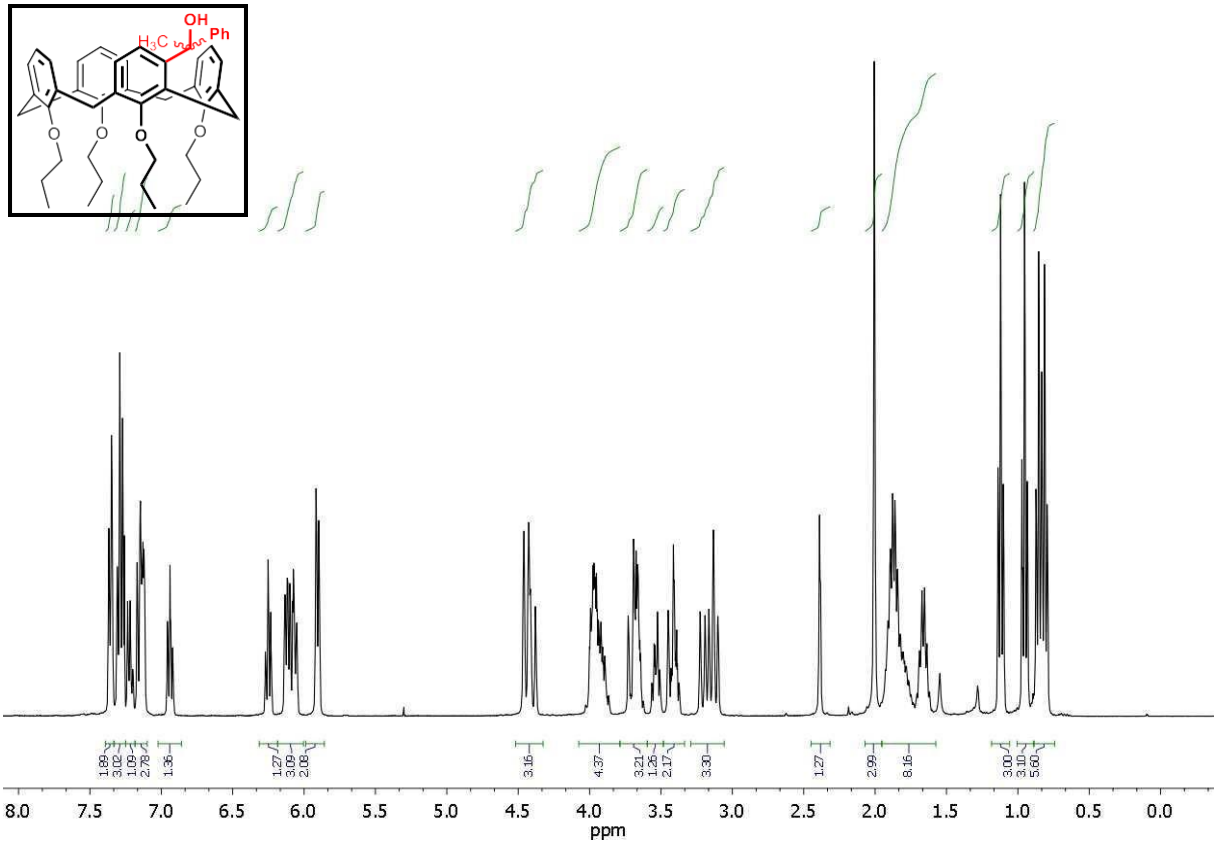


Figure S18. ^{1}H NMR of mixture of **7a** and **7b** ($CDCl_3$, 400 MHz).

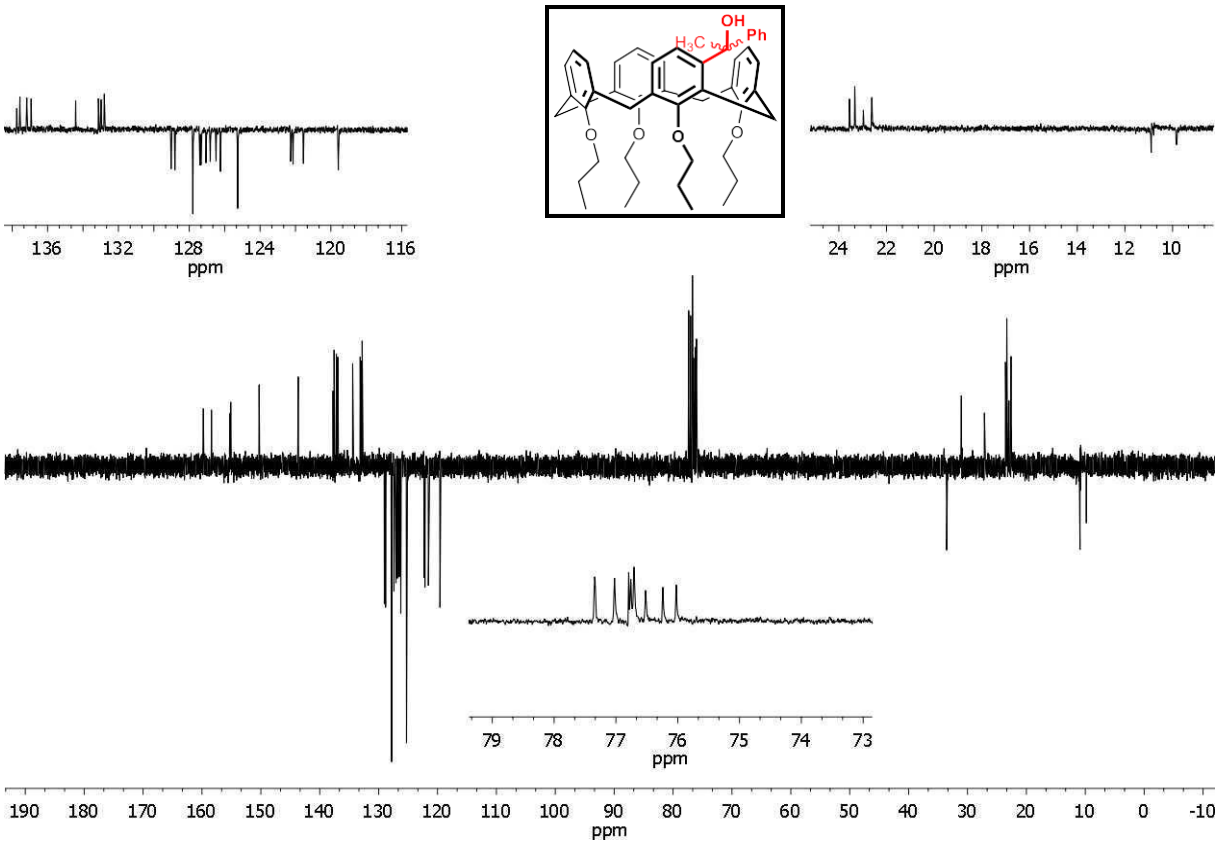


Figure S19. ^{13}C NMR (APT) of **7a** and **7b** ($CDCl_3$, 100 MHz).

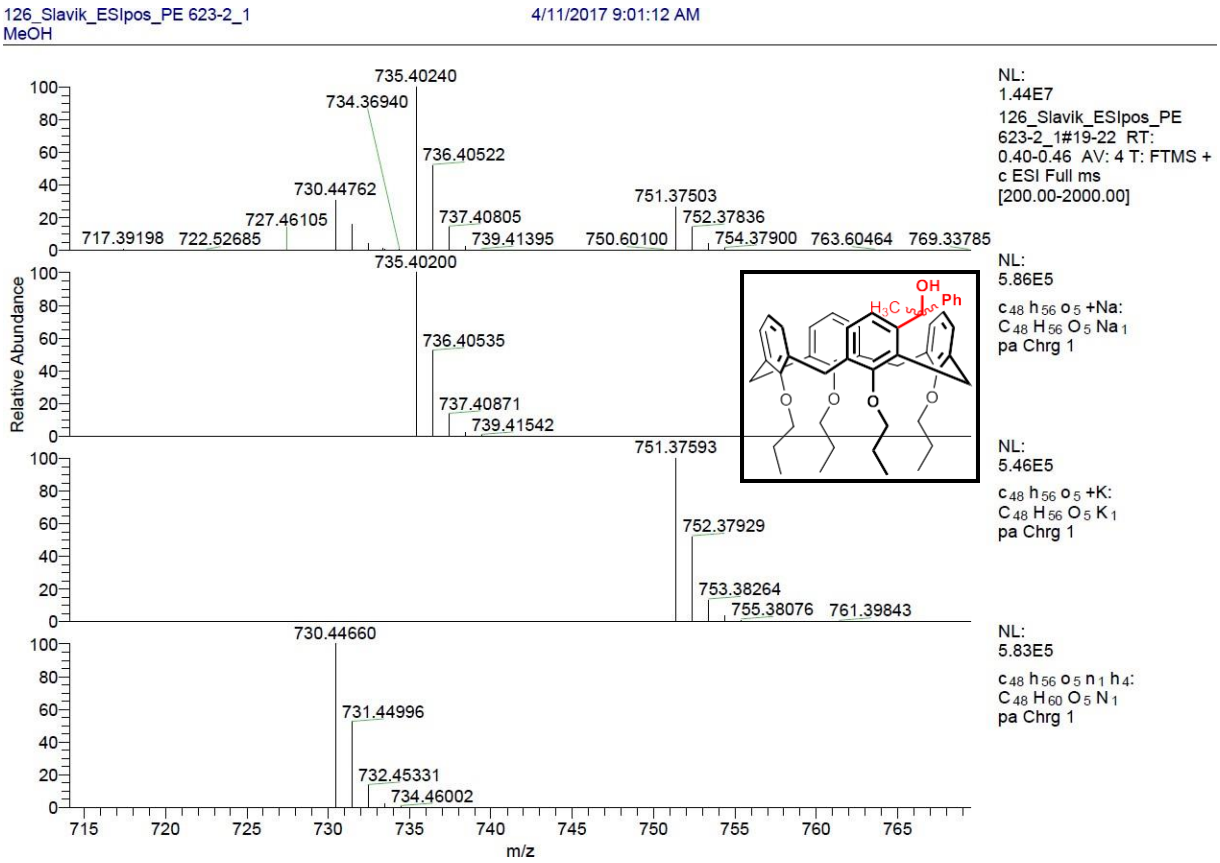


Figure S20. HRMS of mixture **7a** and **7b** (ESI^+).

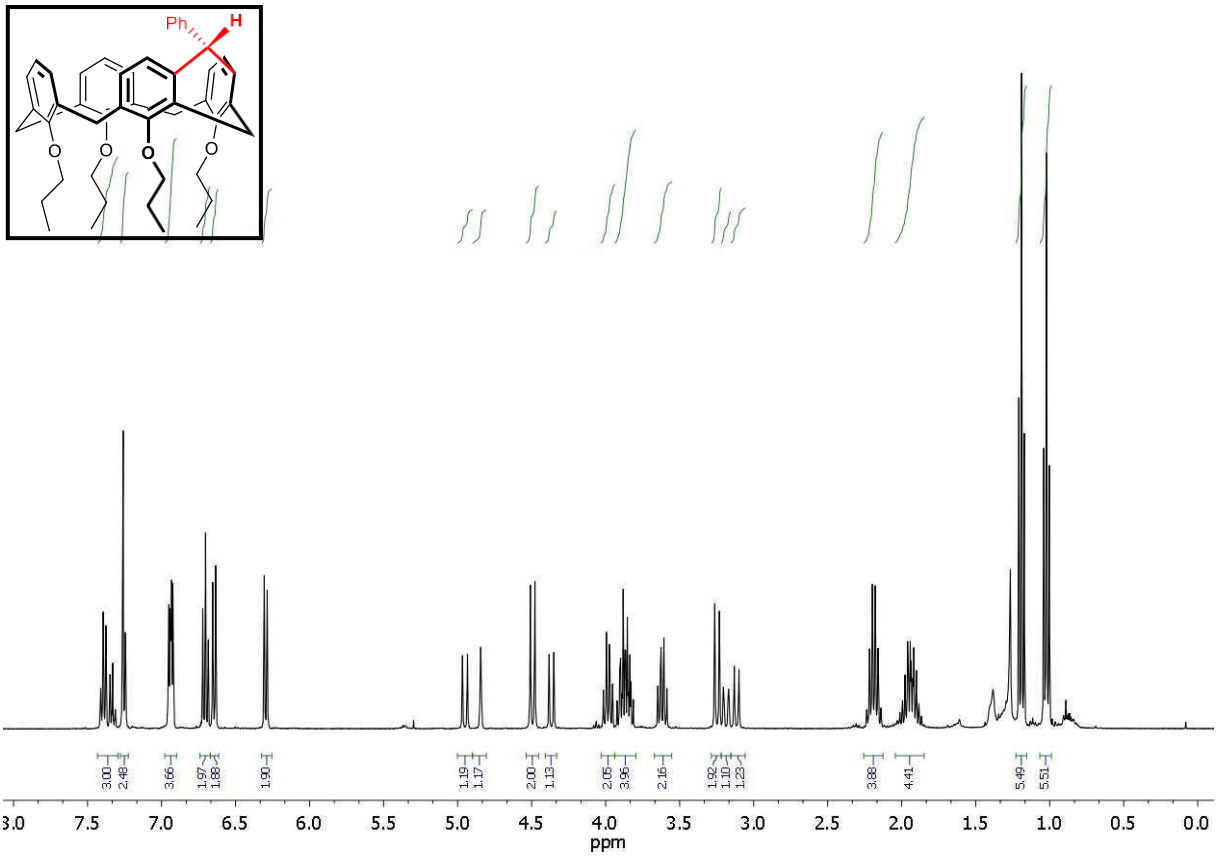


Figure S21. ^{1}H NMR of compound **8a** ($CDCl_3$, 400 MHz).

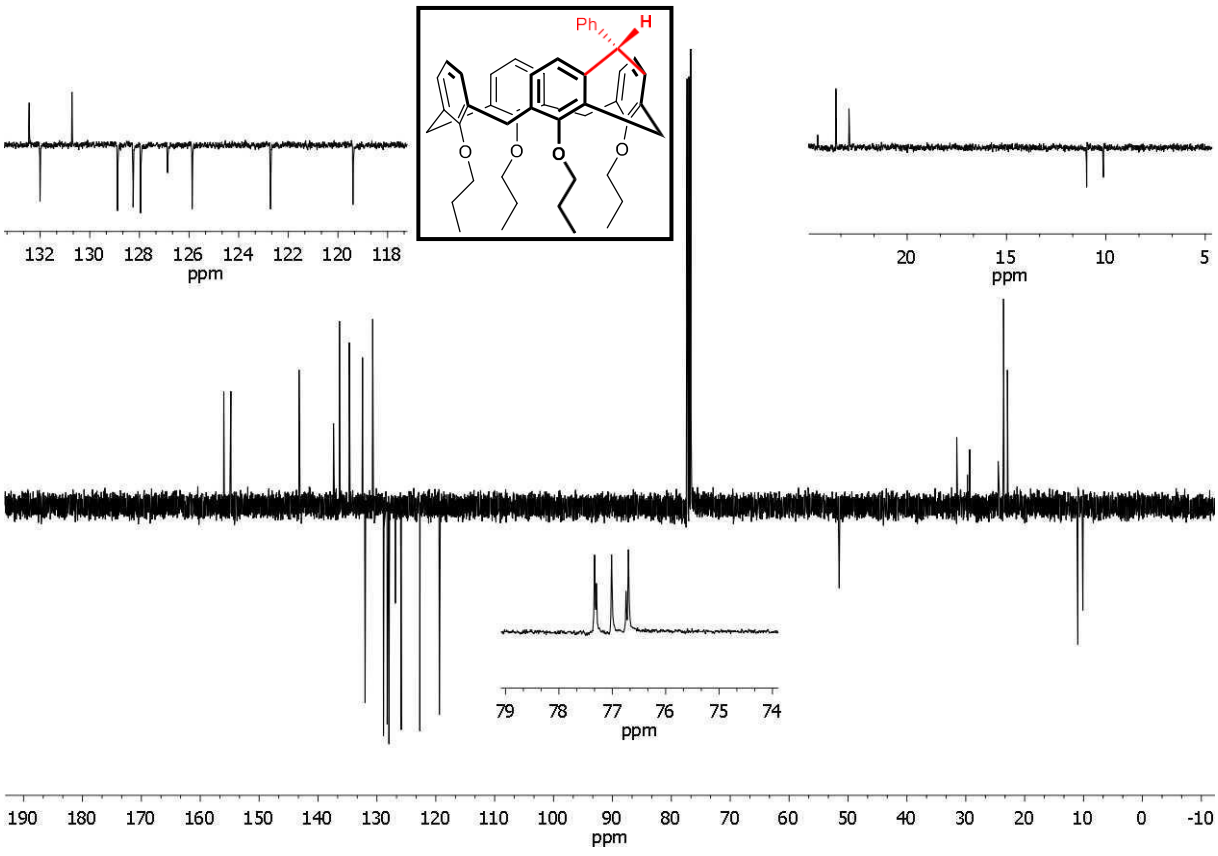


Figure S22. ^{13}C NMR (APT) of compound **8a** ($CDCl_3$, 100 MHz).

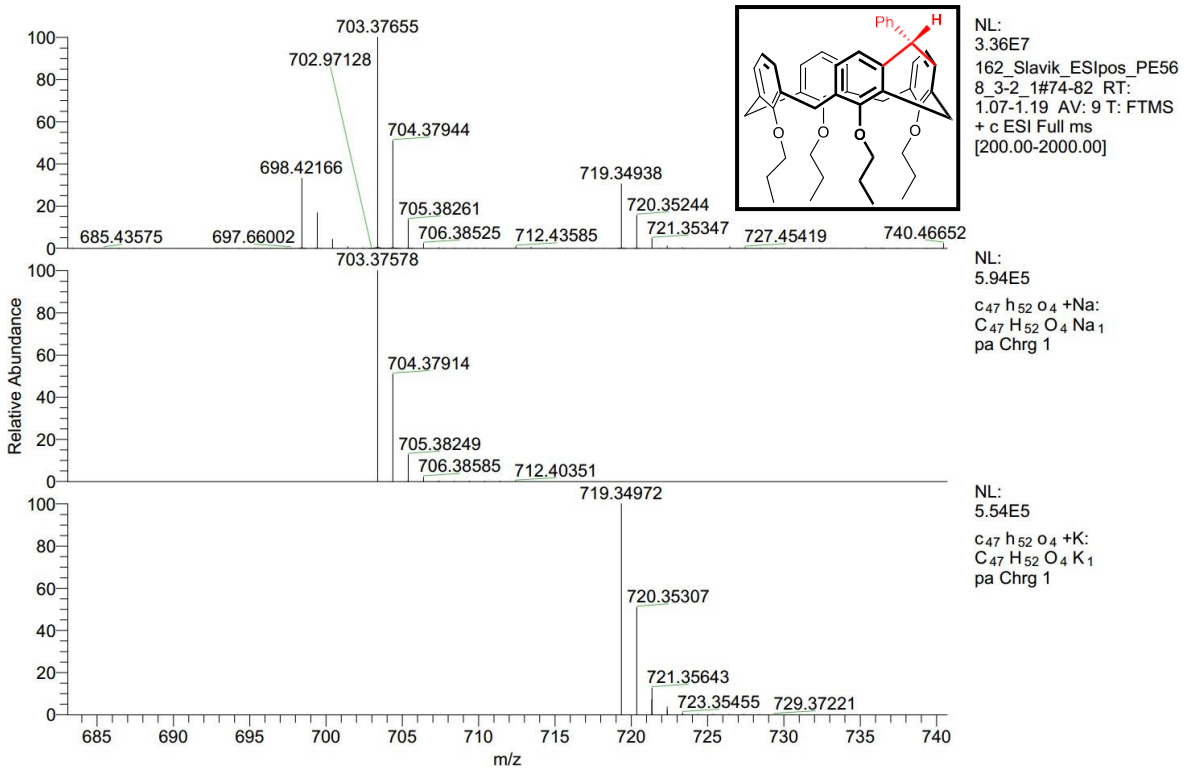


Figure S23. HRMS of compound **8a** (ESI^+).

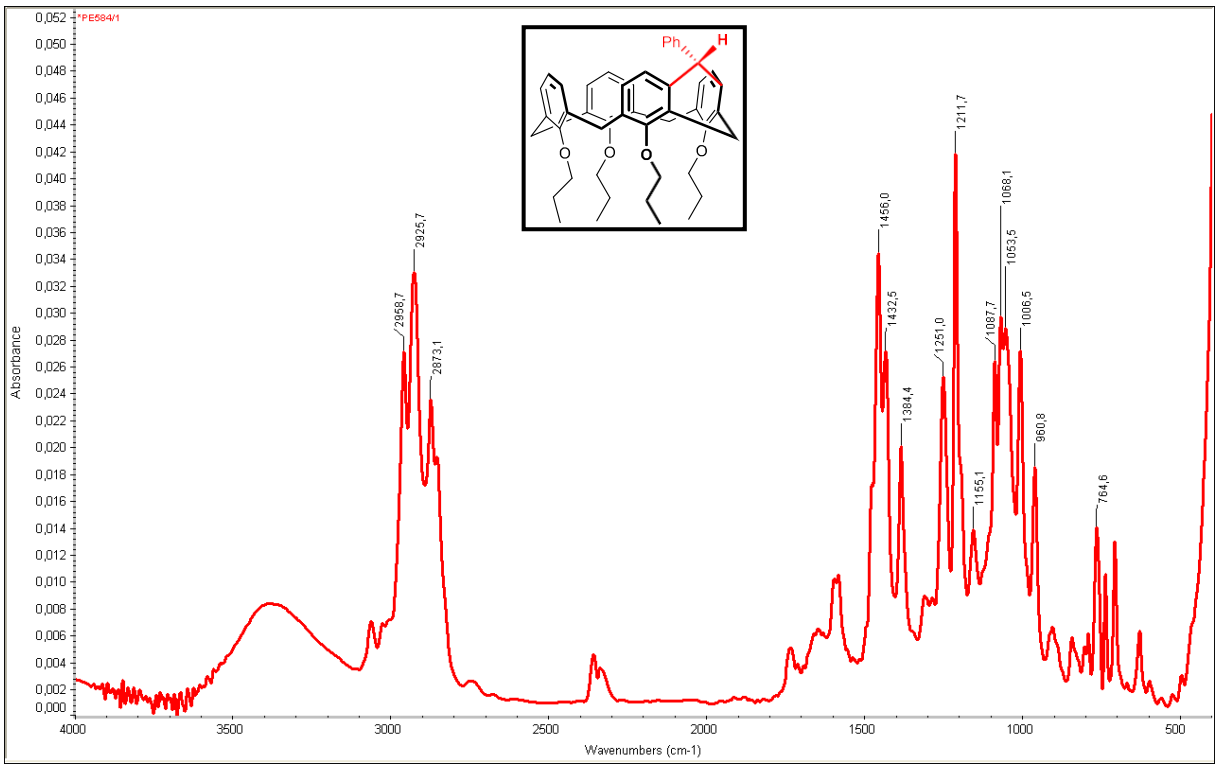


Figure S24. IR of compound **8a** (KBr).

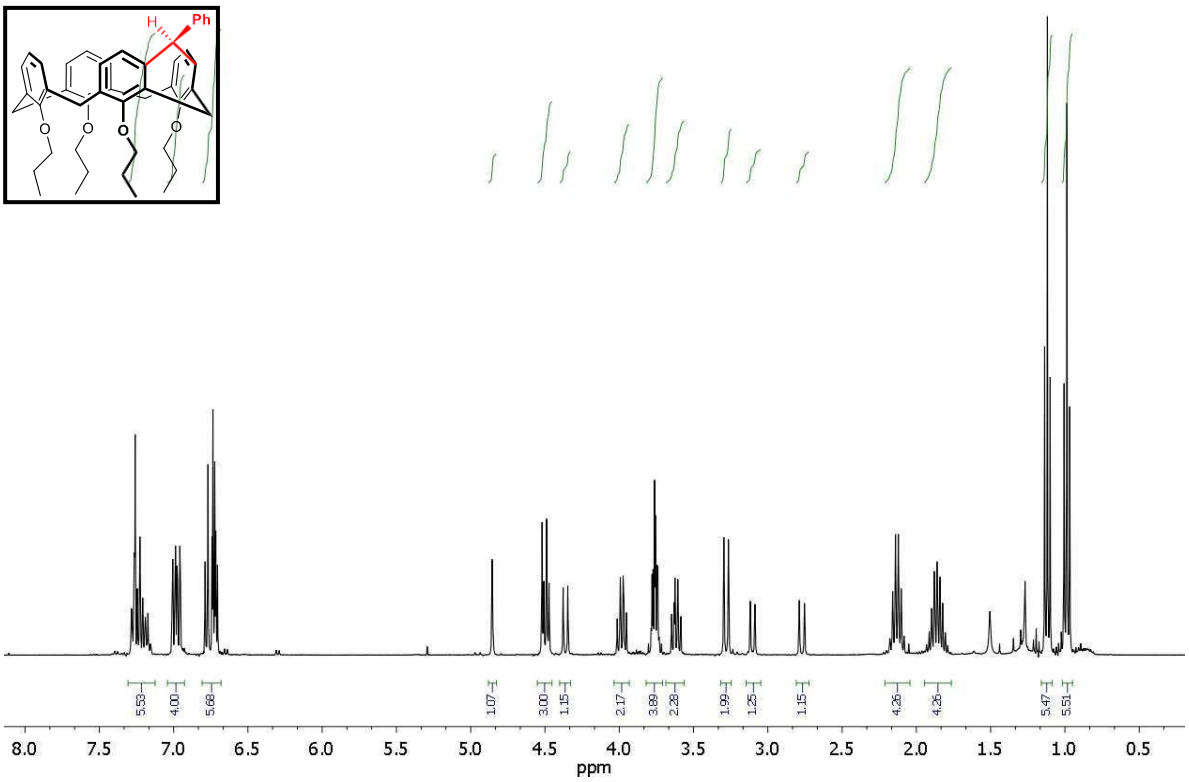


Figure S25. ^{1}H NMR of compound **8b** ($CDCl_3$, 400 MHz).

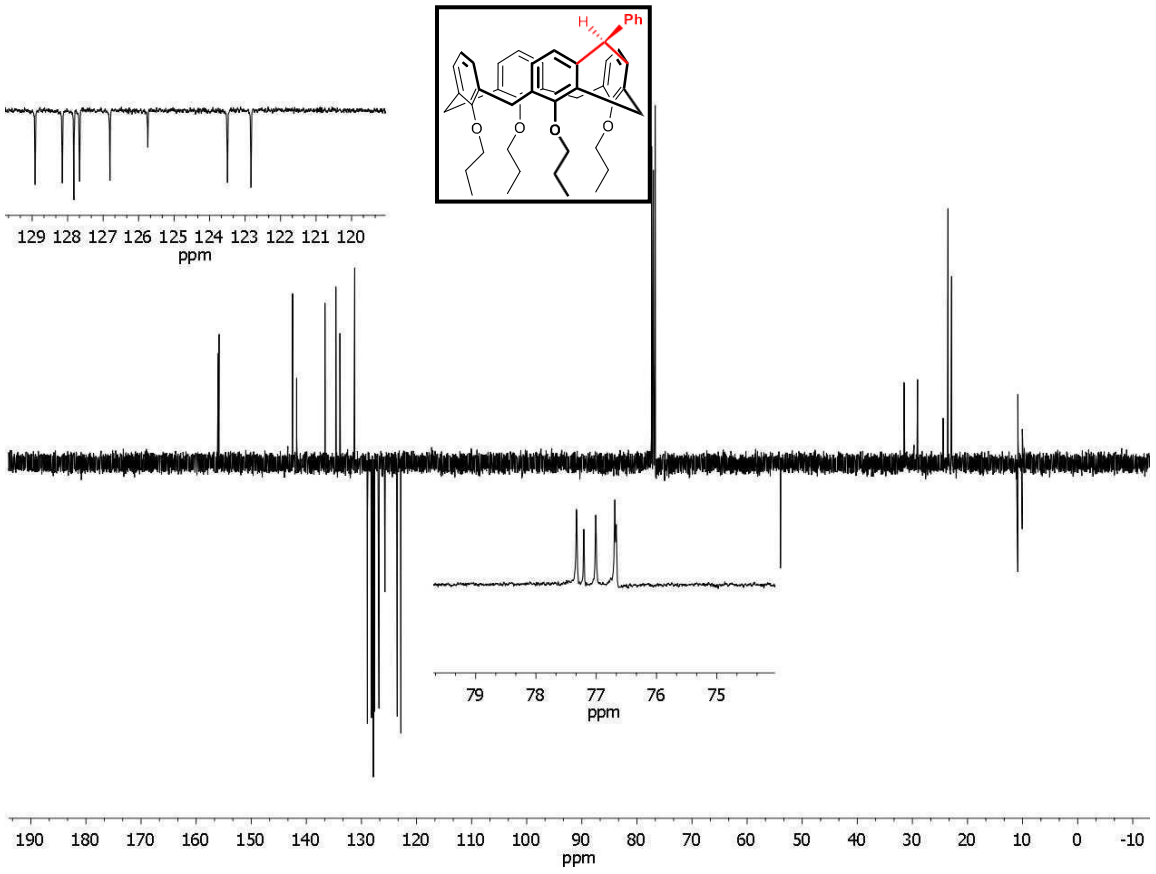


Figure S26. ^{13}C NMR (APT) of compound **8b** ($CDCl_3$, 100 MHz).

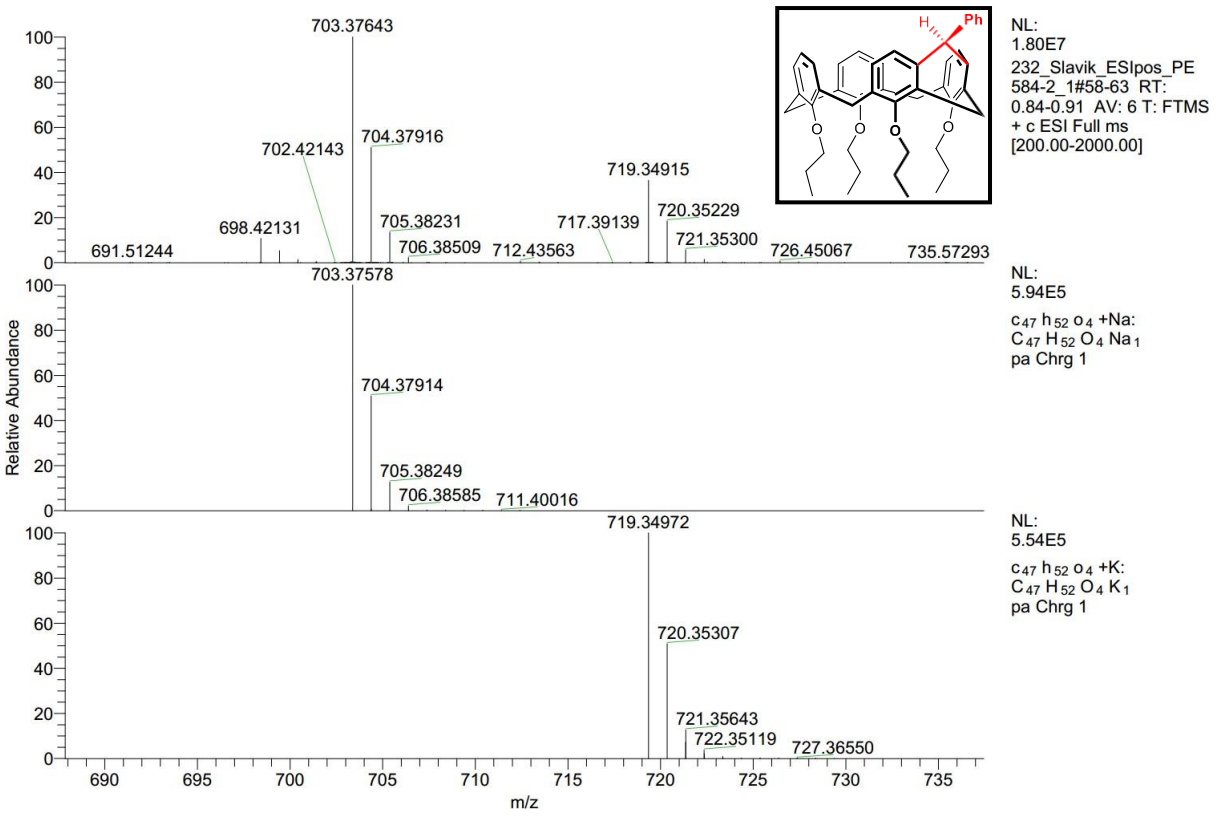


Figure S27. HRMS of compound **8b** (ESI^+).

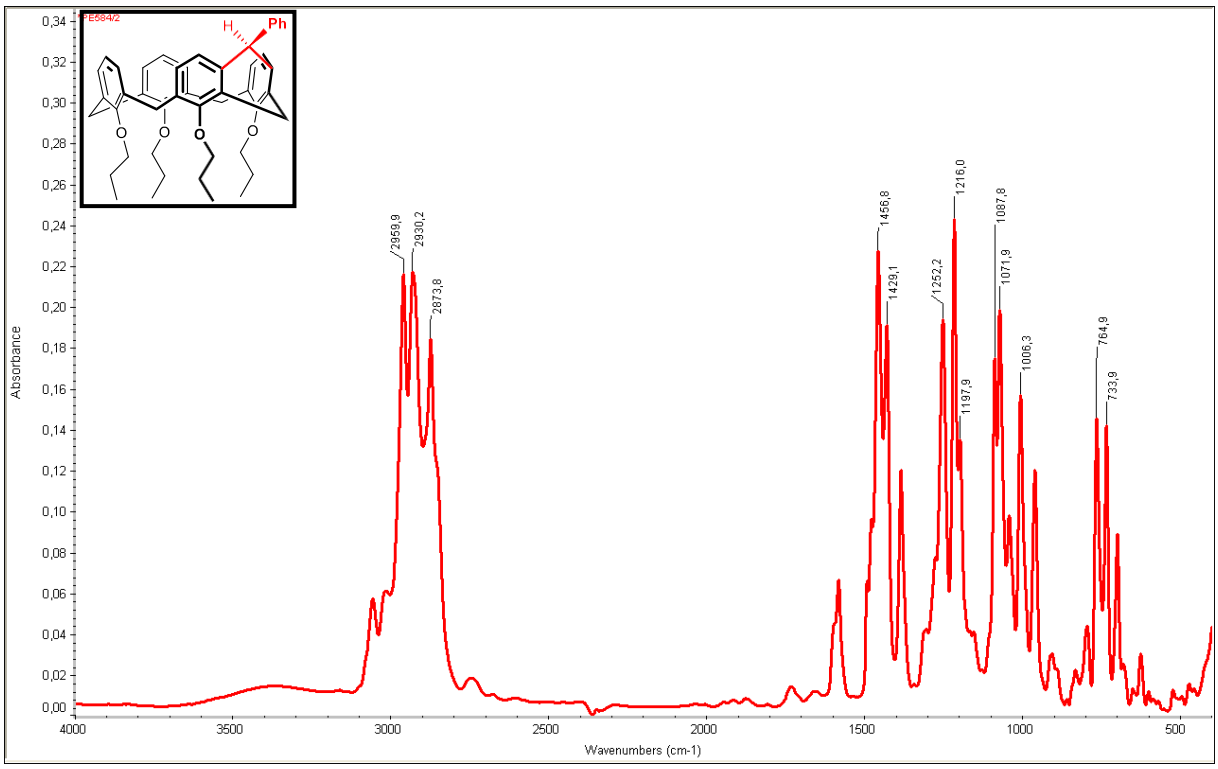


Figure S28. IR of compound **8b** (KBr).

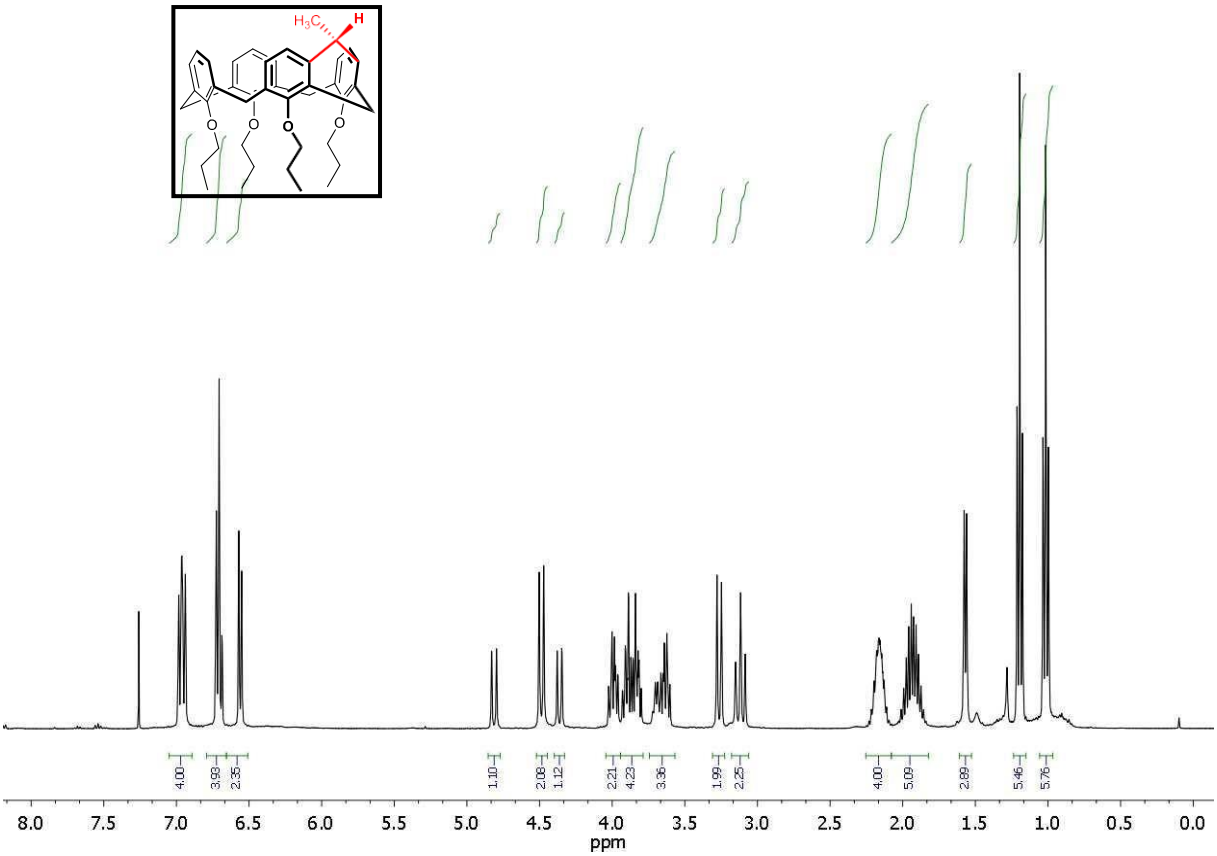


Figure S29. ^{1}H NMR of compound **9** ($CDCl_3$, 400 MHz).

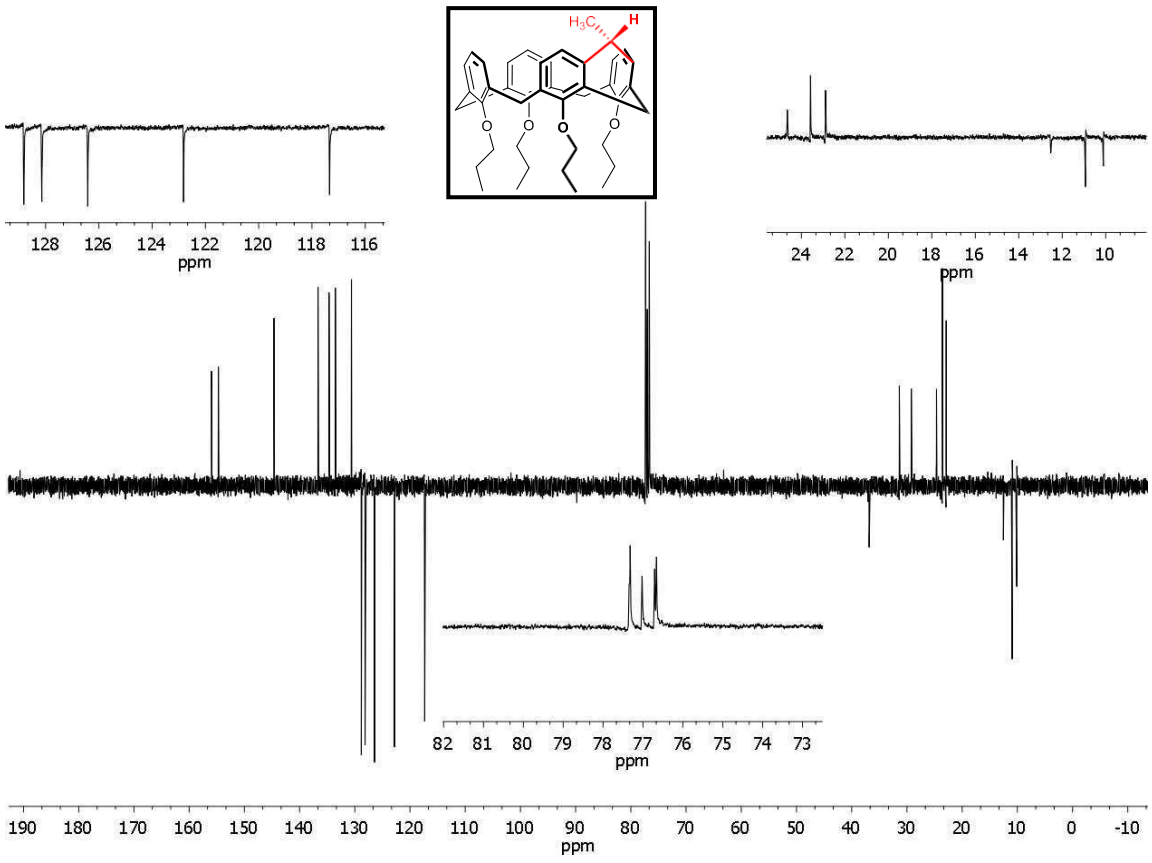


Figure S30. ^{13}C NMR (APT) of compound **9** ($CDCl_3$, 100 MHz).

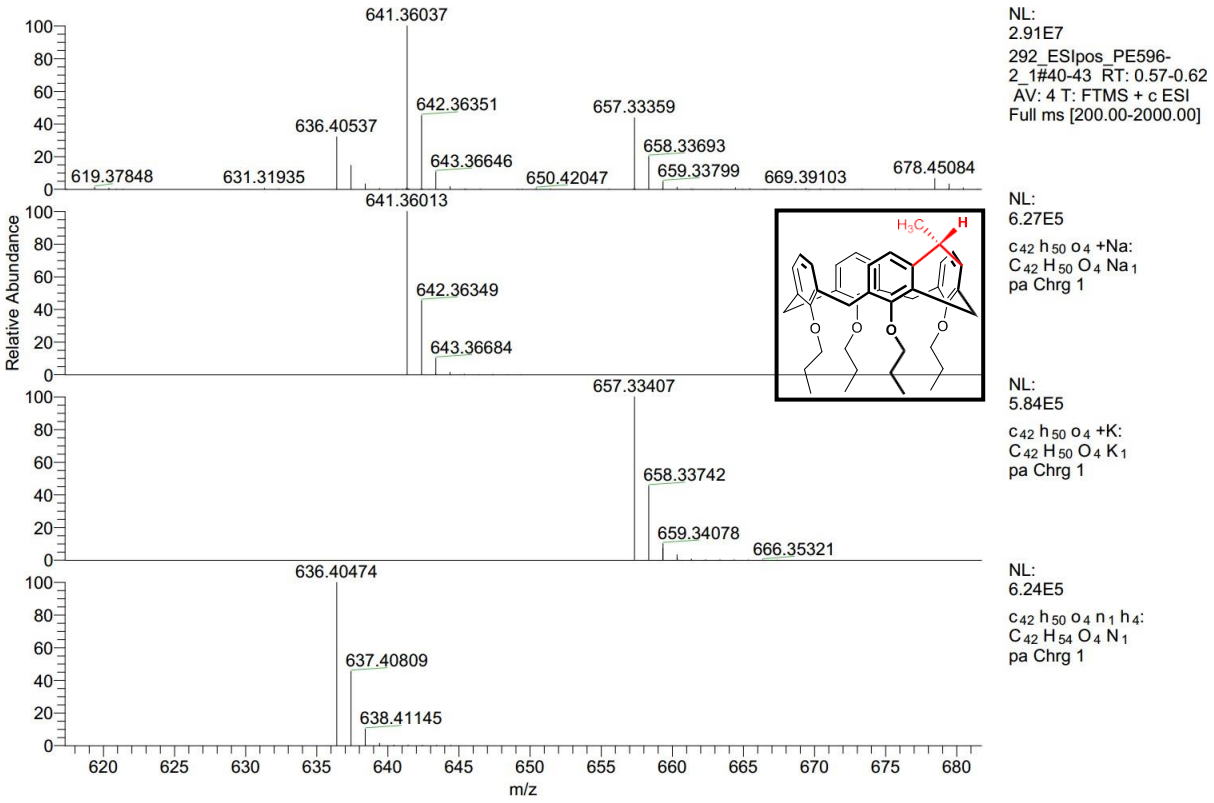


Figure S31. HRMS of compound **9** (ESI^+).

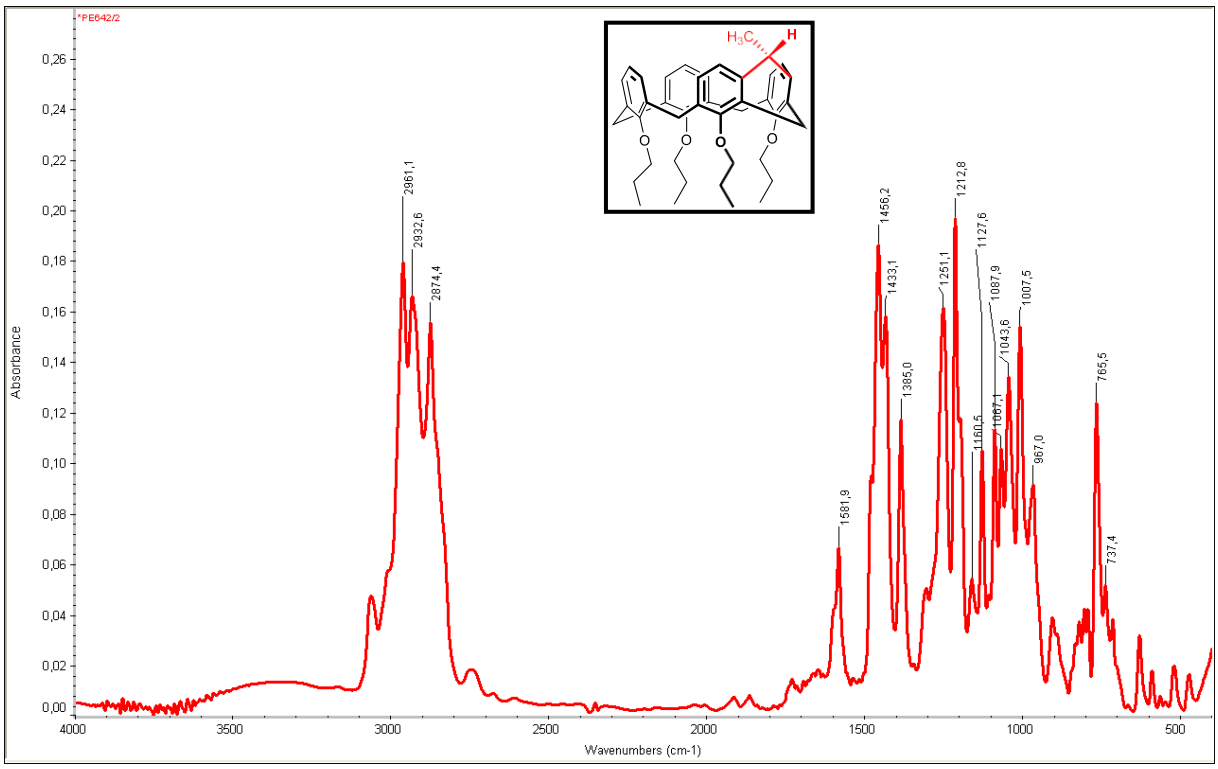


Figure S32. IR of compound **9** (KBr).

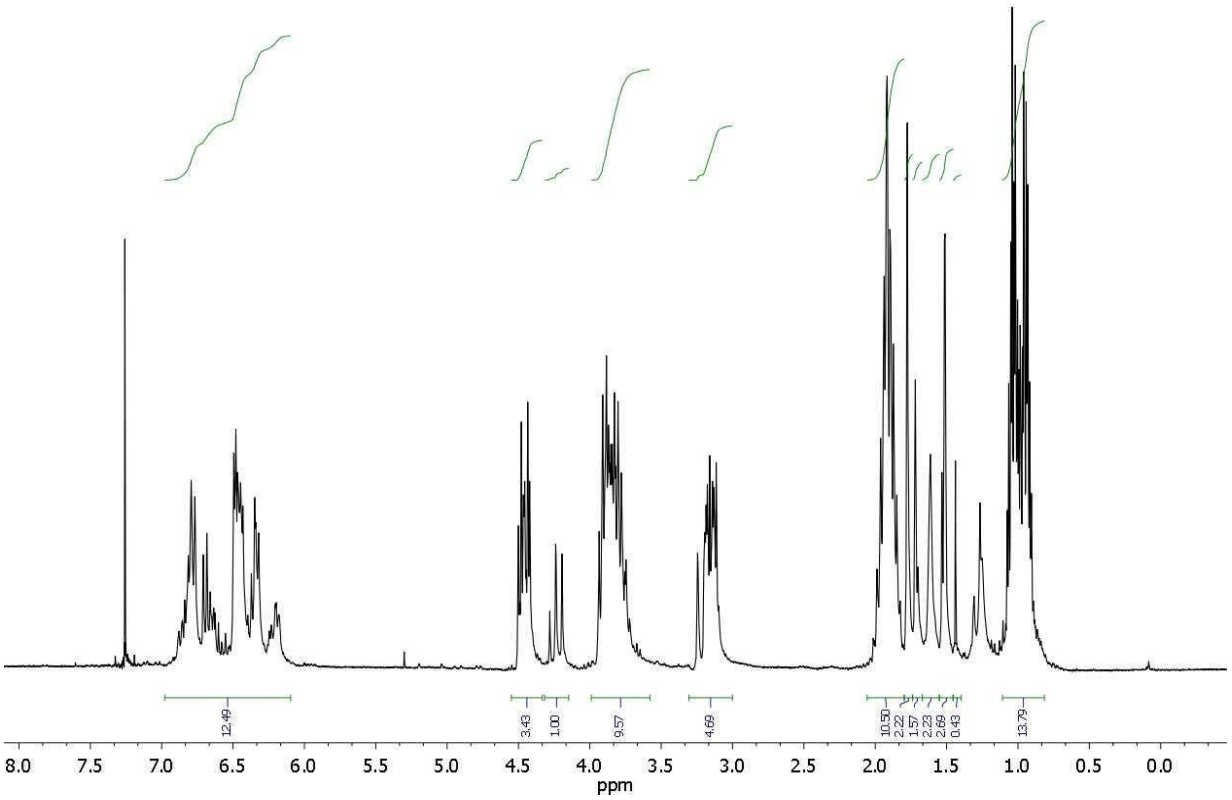


Figure S33. ^{1}H NMR of mixture of **10** ($CDCl_3$, 400 MHz).

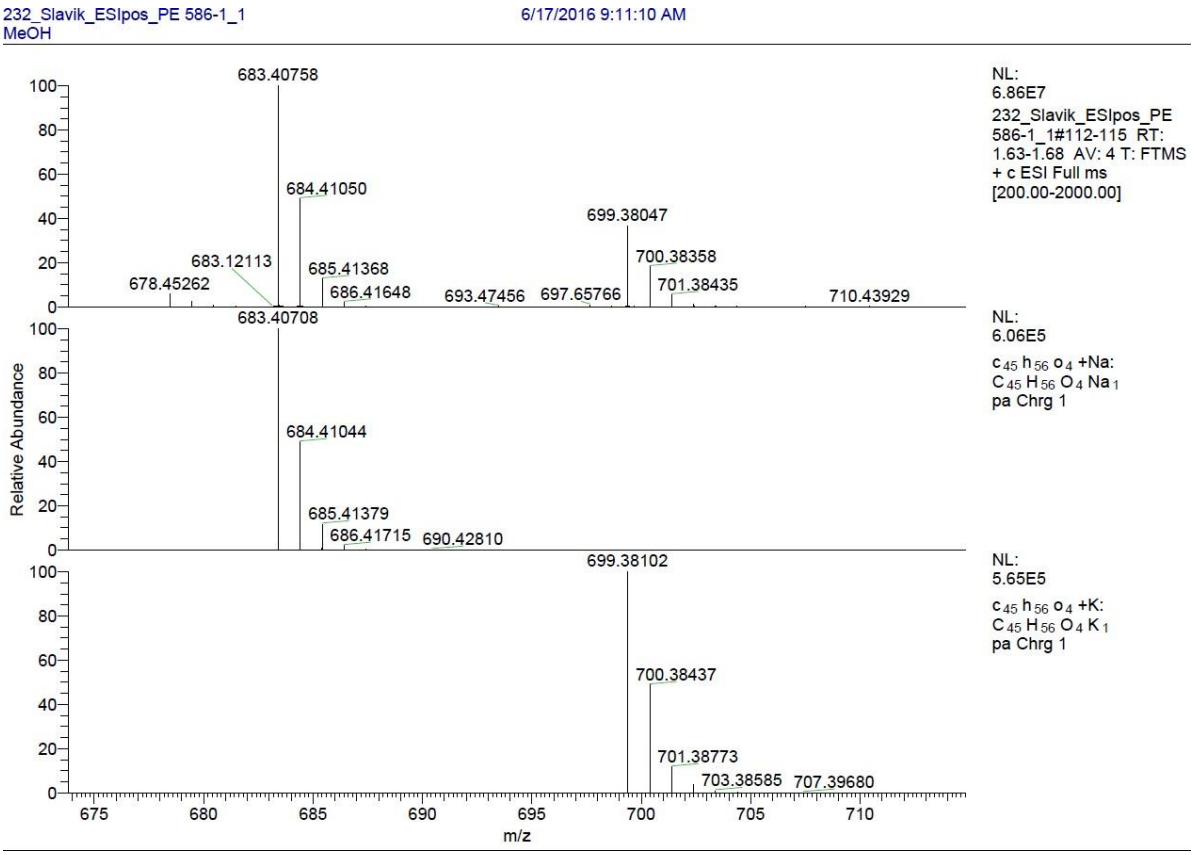


Figure S34. HRMS of mixture of **10** (ESI^+).

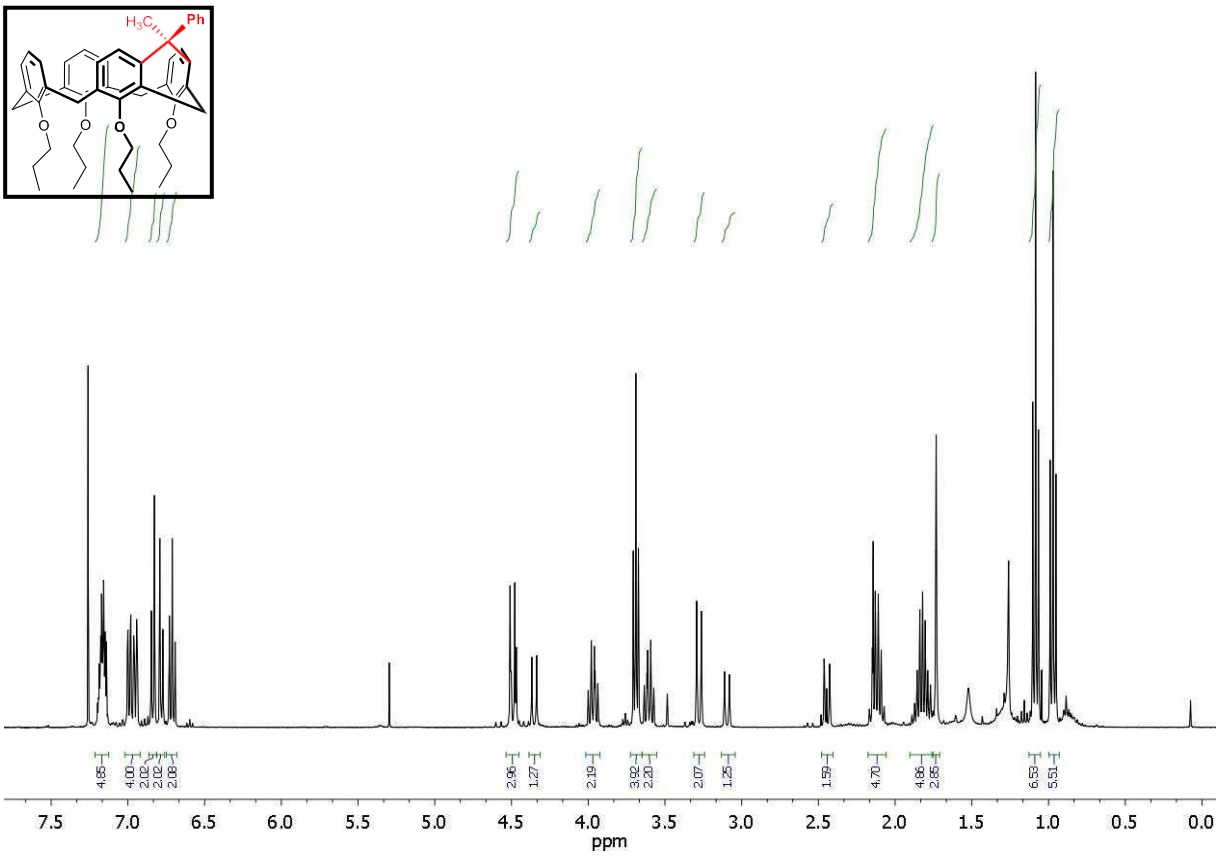


Figure S35. ^{1}H NMR of compound **11** ($CDCl_3$, 400 MHz).

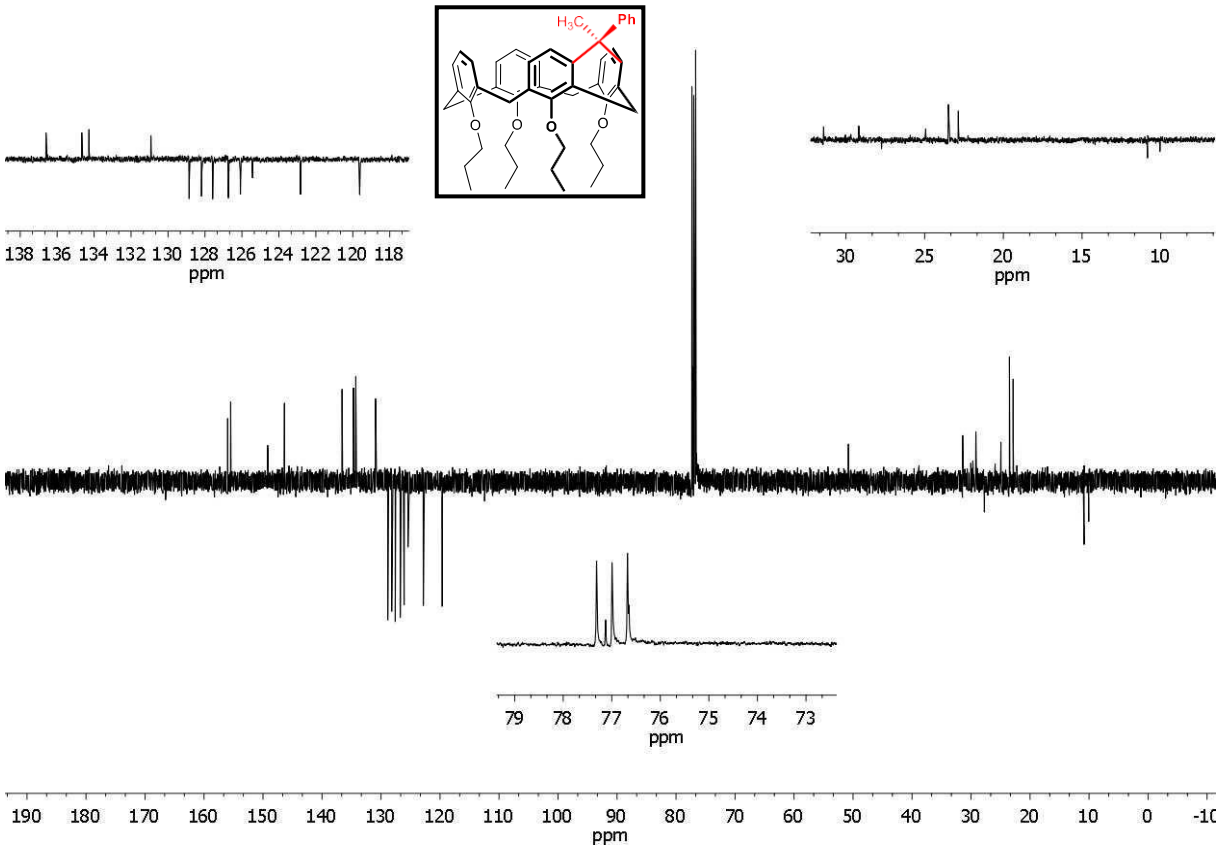


Figure S36. ^{13}C NMR (APT) of compound **11** ($CDCl_3$, 100 MHz).

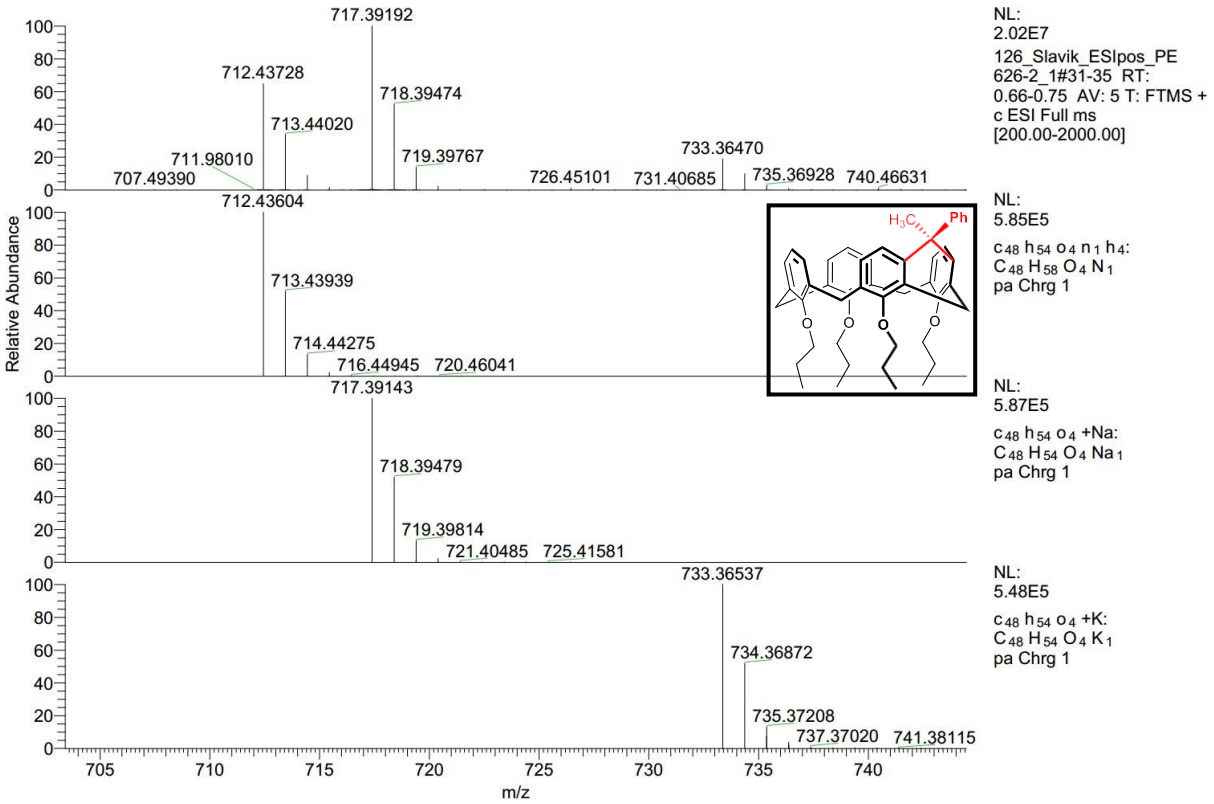


Figure S37. HRMS of compound **11** (ESI^+).

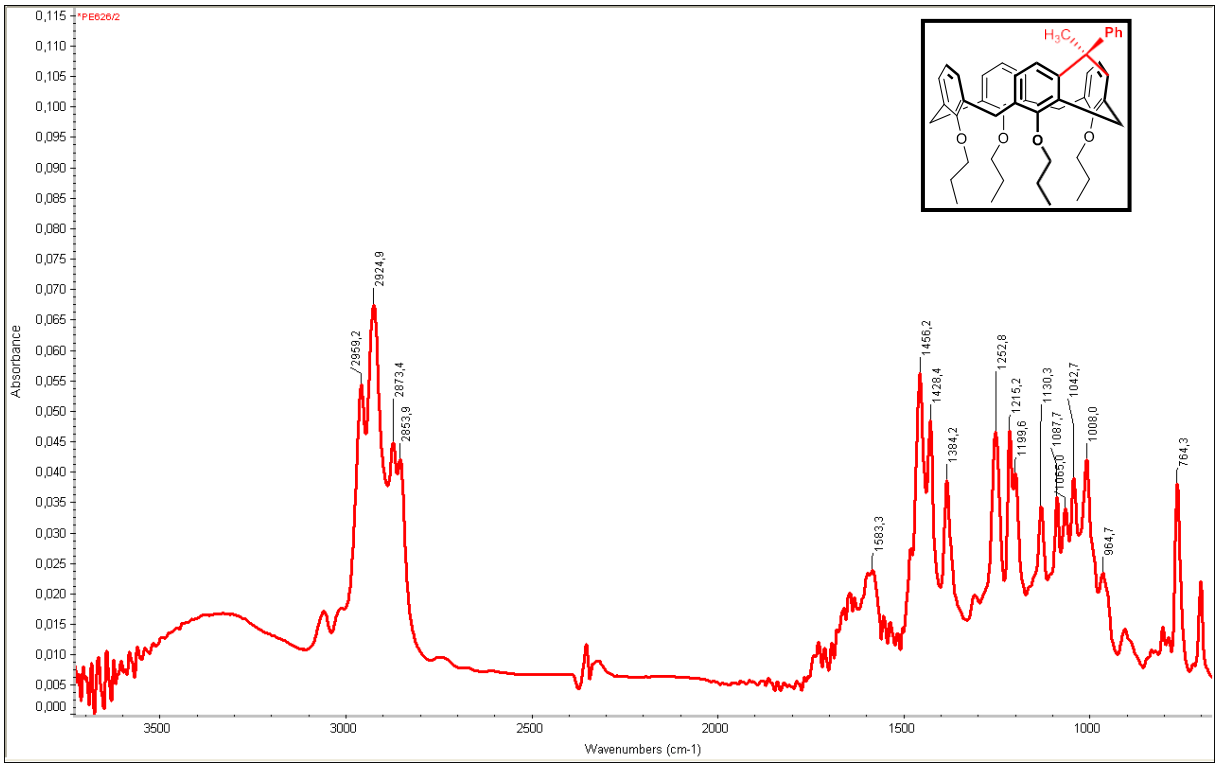


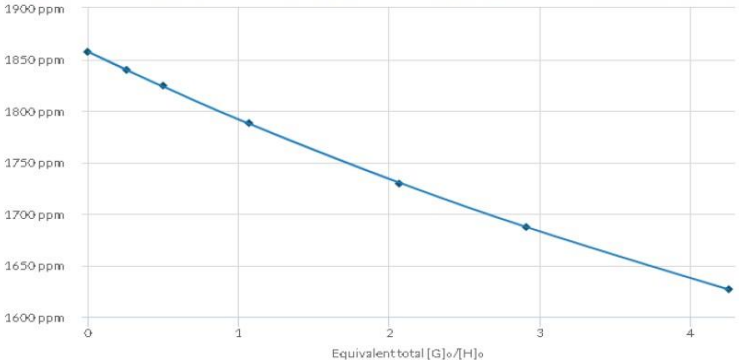
Figure S38. IR of compound **11** (KBr).

^{1}H NMR titration experiments

In the experiment a specified amount of *N*-methylpyridinium iodide was dissolved in specified amount of solvent ($C_2D_2Cl_4$). One half of the sample was put in NMR tube and to the rest was added specified amount of calixarene **8a** or **8b**. The aliquots of calixarene **8a** or **8b** were gradually added to NMR tube to achieve different calixarene/guest rations (1:0-7), ensuring a constant guest concentration during the whole experiment. The complexation constants were determined by analysing CIS of protons in position 2 of the host molecule. The values of the complexation constants were determined by analysing the binding isotherms for the 1:1 stoichiometry (using the online application Bindfit).

		Calixarene	**8a**	
		guest	NMPI	
		solvent	$C_2D_2Cl_4$	
m(calixarene) [g]	0.0144		m(NMPI) [g]	0.00078
$V(C_2D_2Cl_4)$	0.0005		c(NMPI) [mol/l]	0.003272424
c(calixarene) [mol/l]	0.042295096			

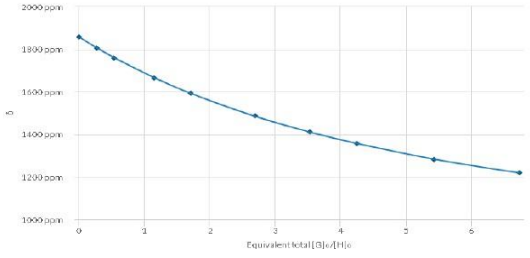
V(total) [l]	V(addition) [l]	V(calix) [l]	c(calixarene) [mol/l]	c(NMPI) [mol/l]	C(calixarene)/c(NMPI)	shift [Hz]	n(calixarene) [mol]
0.0005	0		0	0.003272424	0	1857.35	0
0.00051	0.00001	0.00001	0.000829316	0.003272424	0.253425476	1839.74	4.22951E-07
0.00052	0.00001	0.00002	0.001626734	0.003272424	0.497103819	1824.48	8.45902E-07
0.000545	0.000025	0.000045	0.003492256	0.003272424	1.067177005	1788.09	1.90328E-06
0.000595	0.00005	0.000095	0.006752999	0.003272424	2.063607449	1729.4	4.01803E-06
0.000645	0.00005	0.000145	0.0095082	0.003272424	2.905552552	1687.14	6.13279E-06
0.000745	0.0001	0.000245	0.013909126	0.003272424	4.250404463	1626.74	1.03623E-05



K	K error (%)
24.170554	0.762195535

		Calixarene	**8b**	
		guest	NMPI	
		solvent	$C_2D_2Cl_4$	
m(calixarene) [g]	0.01548		m(NMPI) [g]	0.00217
$V(C_2D_2Cl_4)$	0.0005		c(NMPI) [mol/l]	0.003272424
c(calixarene) [mol/l]	0.045467229			

V(total) [l]	V(addition) [l]	V(calix) [l]	c(calixarene) [mol/l]	c(NMPI) [mol/l]	C(calixarene)/c(NMPI)	shift [Hz]	n(calixarene) [mol]
0.0005	0		0	0.003272424	0	1857.35	0
0.00051	0.00001	0.00001	0.000891514	0.003272424	0.272432387	1804.92	4.54672E-07
0.00052	0.00001	0.00002	0.00174874	0.003272424	0.534386605	1757.96	9.09345E-07
0.000545	0.000025	0.000045	0.003754175	0.003272424	1.147215281	1664.84	2.04603E-06
0.00057	0.000025	0.00007	0.005583695	0.003272424	1.706287055	1593.63	3.18271E-06
0.00062	0.00005	0.00012	0.008800109	0.003272424	2.689171303	1487.59	5.45607E-06
0.00067	0.00005	0.00017	0.011536461	0.003272424	3.525356409	1412.08	7.72943E-06
0.00072	0.00005	0.00022	0.013892764	0.003272424	4.245404696	1356.91	1.00028E-05
0.00082	0.0001	0.00032	0.017743309	0.003272424	5.422068968	1282.09	1.45495E-05
0.00097	0.00015	0.00047	0.022030513	0.003272424	6.732169395	1219.96	2.13696E-05



K	K error (%)
62.30778	0.736292815