SUPPORTING INFORMATION

The Long And The Short of It: Regiospecific Syntheses of Isomers of Dicarbomethoxydibenzo-27-Crown-9 and Binding Abilities of Their Pyridyl Cryptands

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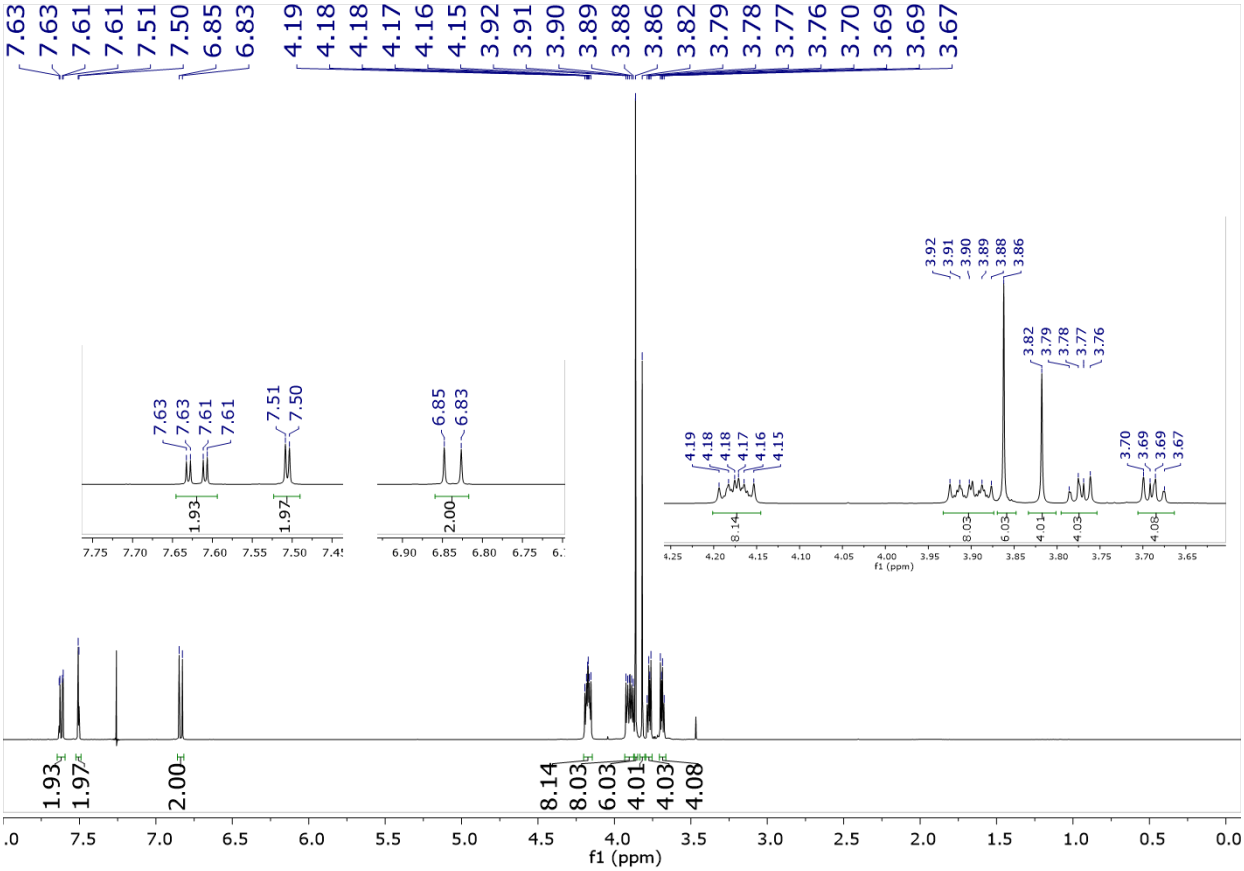

Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ^{o}C) of *cis*(4,4')-di(carbomethoxy)dibenzo-27-crown-9-short (**6**): δ 7.62 (dd, *J* = 8, 2 Hz, 2H), 7.51 (d, *J* = 2 Hz, 2H), 6.84 (d, *J* = 8 Hz, 2H), 4.20 – 4.15 (m, 8H), 3.93 – 3.87 (m, 8H), 3.86 (s, 6H), 3.82 (s, 4H), 3.79 – 3.76 (m, 4H), 3.71 – 3.66 (m, 4H).

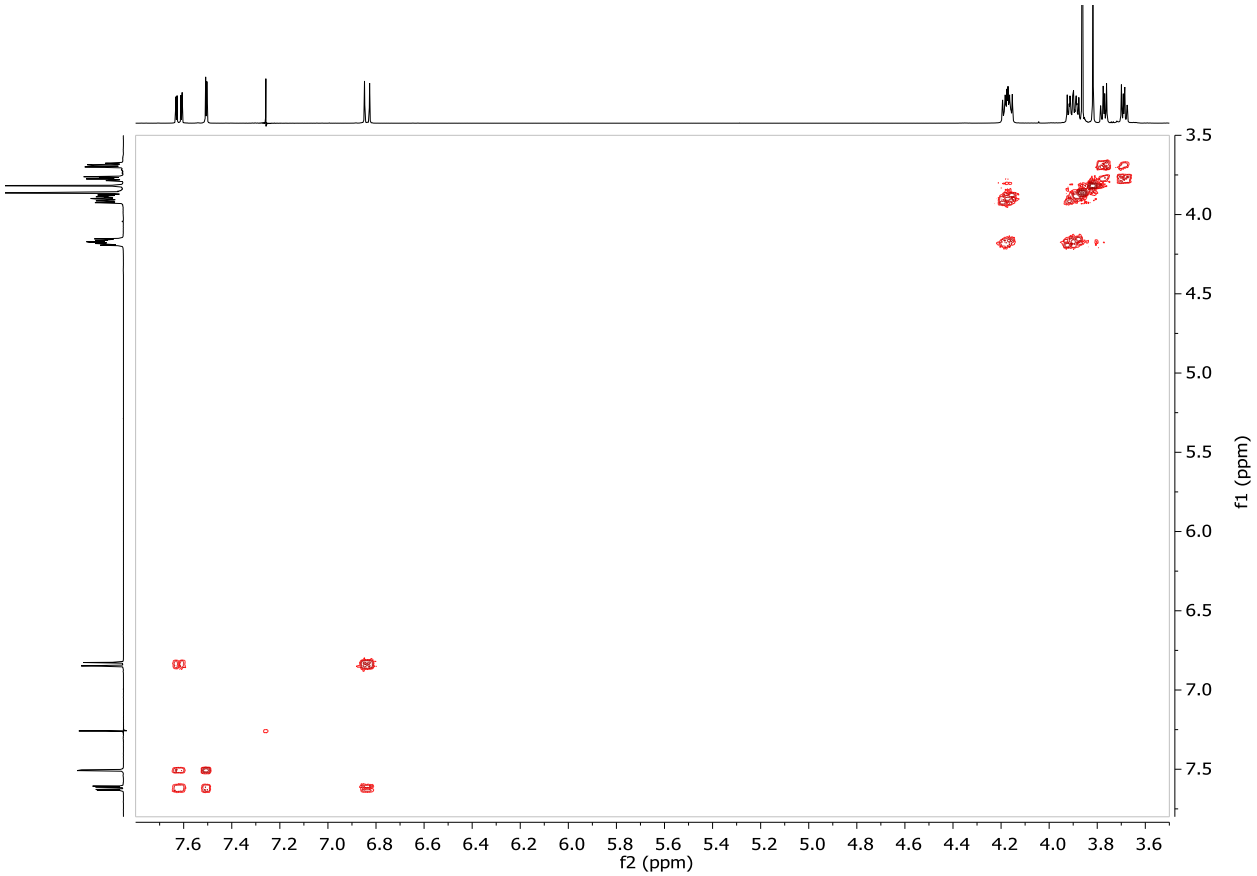

Figure S2. COSY NMR spectrum (400 MHz, $CDCl_3$, 23 ^{o}C) of *cis*(4,4')-di(carbomethoxy)dibenzo-27-crown-9-short (**6**).

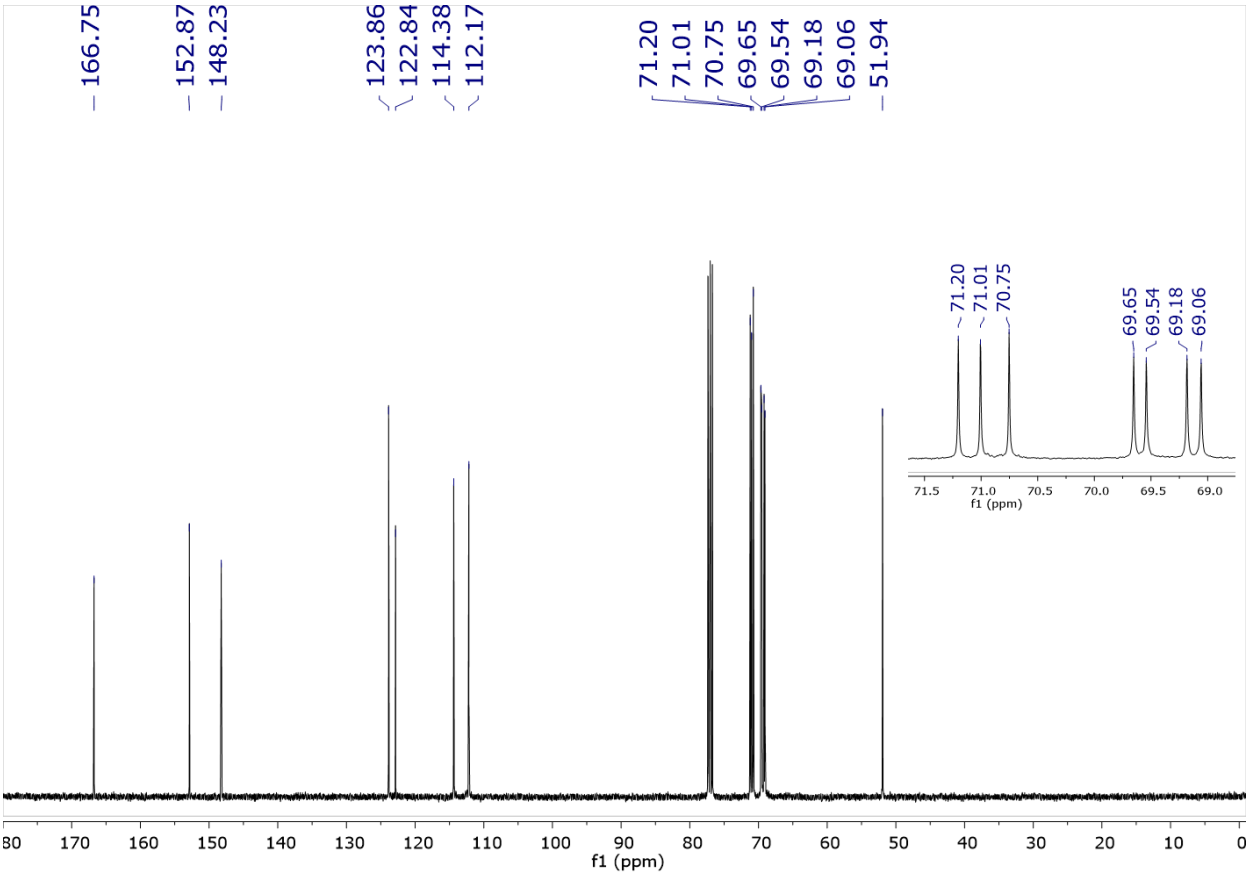

Figure S3. ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ^{o}C) of *cis*(4,4')-di(carbomethoxy)dibenzo-27-crown-9-short (**6**): δ 166.75, 152.87, 148.23, 123.86, 122.84, 114.38, 112.17, 71.20, 71.01, 70.75, 69.65, 69.54, 69.18, 69.06, 51.94.

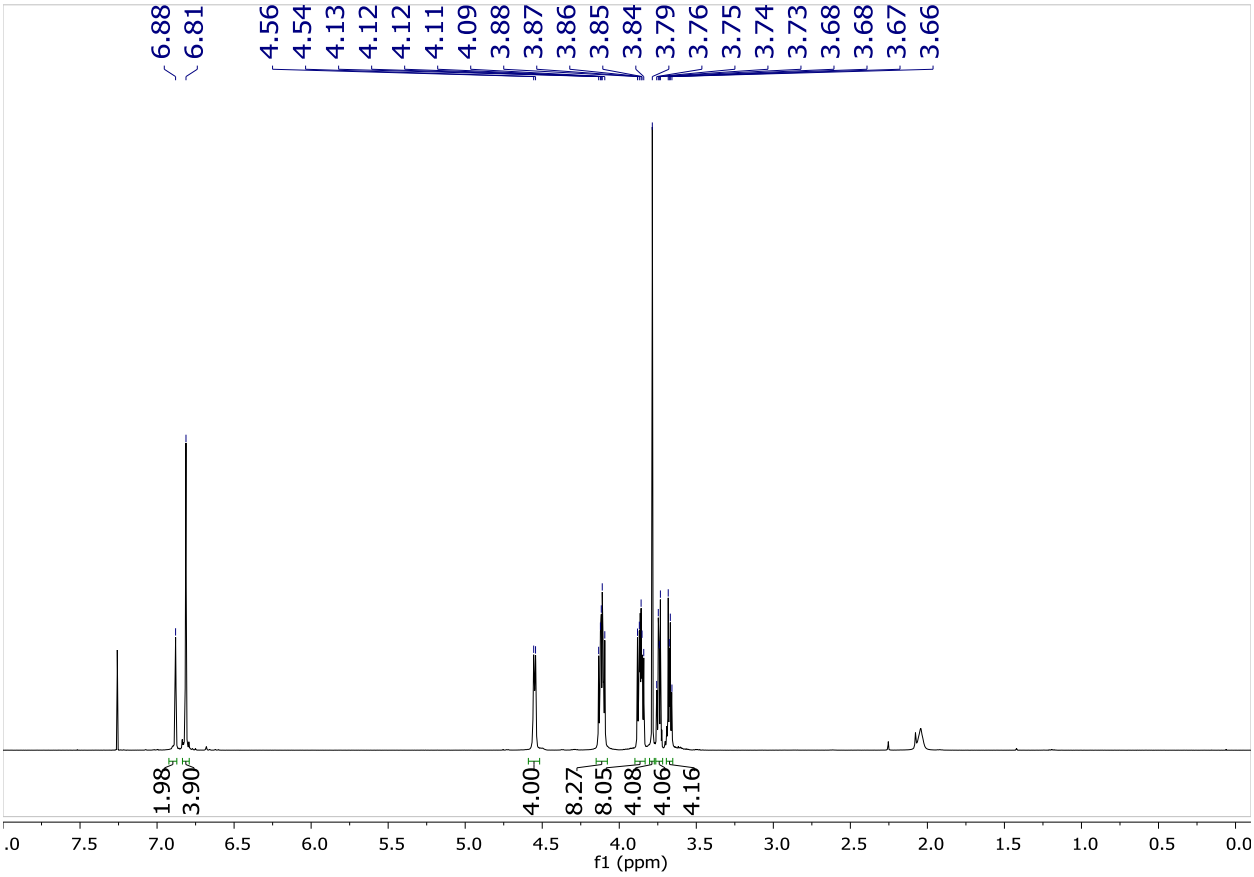

Figure S4. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ^{o}C) of *cis*-bis(hydroxymethyl)dibenzo-27-crown-9-short (**7**): δ 6.88 (s, 2H), 6.81 (s, 4H), 4.55 (d, *J* = 5 Hz, 4H), 4.15 – 4.08 (m, 8H), 3.90 – 3.83 (m, 8H), 3.79 (s, 4H), 3.76 – 3.72 (m, 4H), 3.69 – 3.65 (m, 4H).

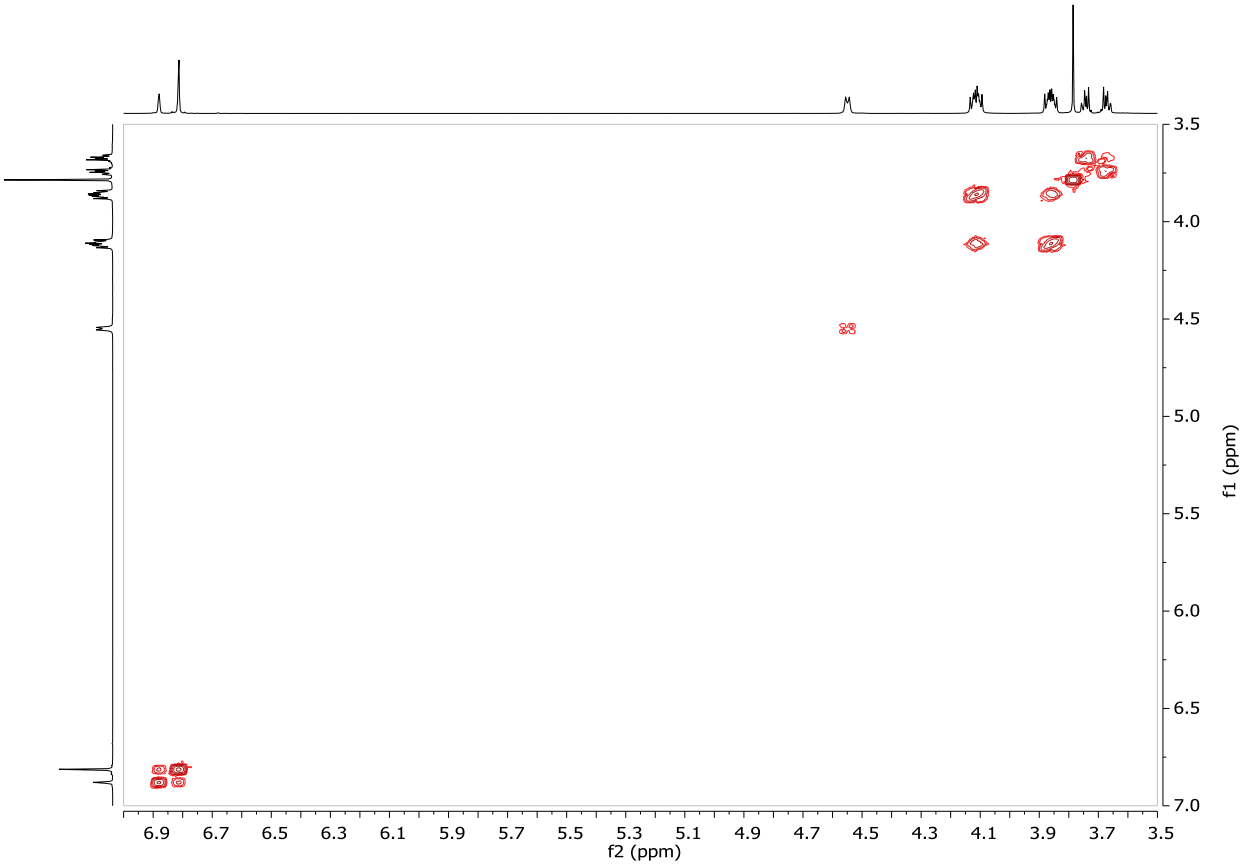

Figure S5. COSY NMR spectrum (400 MHz, $CDCl_3$, 23 ^{o}C) of *cis*-bis(hydroxymethyl)dibenzo-27-crown-9-short (**7**).

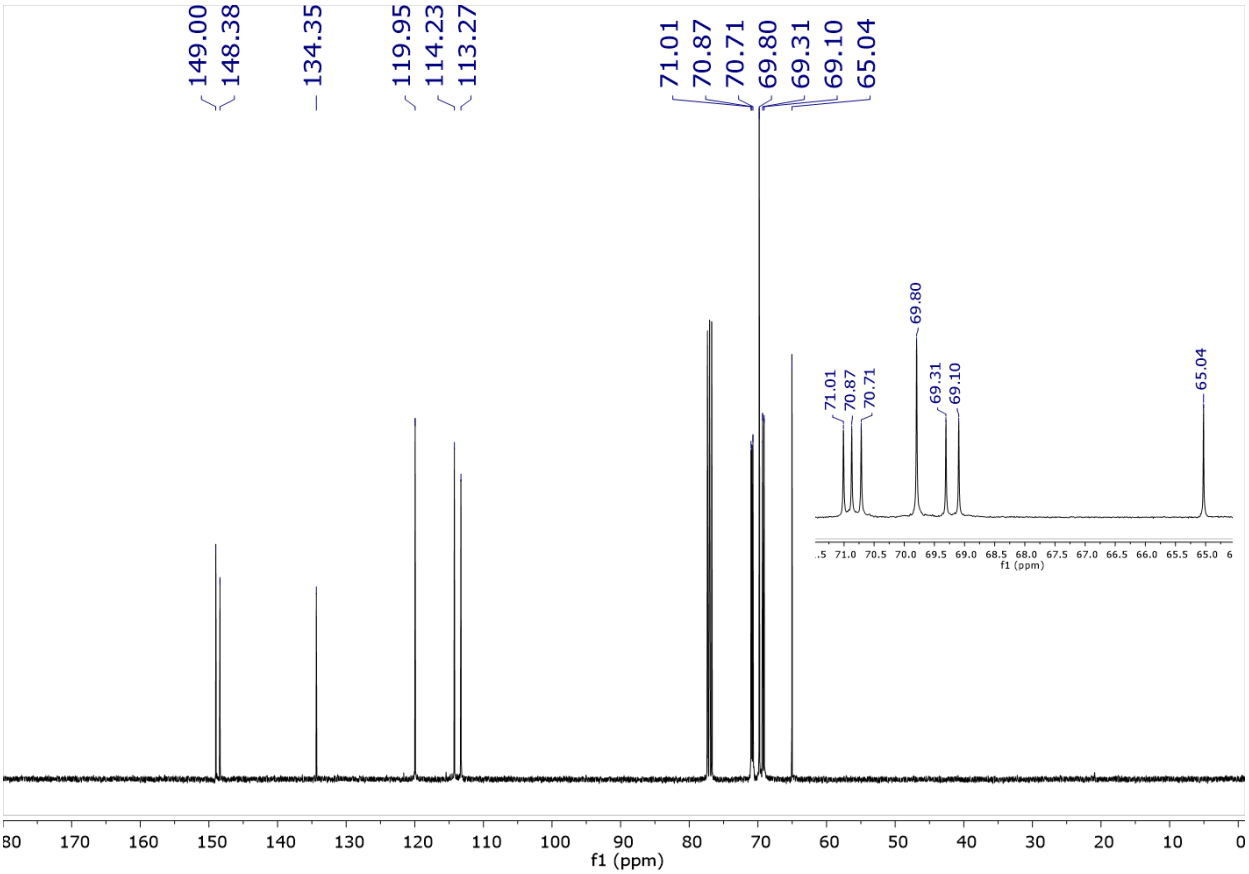

Figure S6. ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ^{o}C) of *cis*-bis(hydroxymethyl)dibenzo-27-crown-9-short (**7**): δ 149.00, 148.38, 134.35, 119.95, 114.23, 113.27, 71.01, 70.87, 70.71, 69.80, 69.31, 69.10, 65.04.

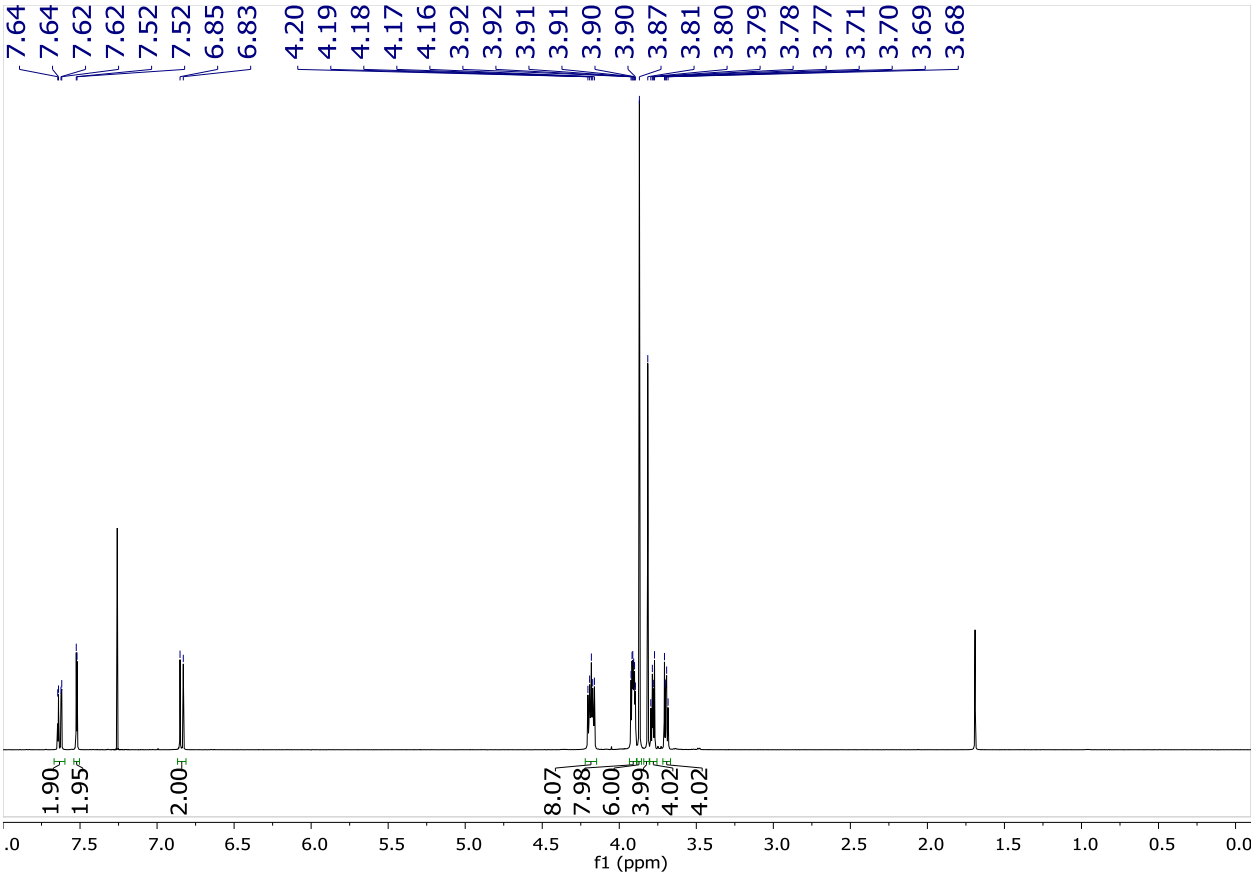

Figure S7. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ^{o}C) of *cis*-di(carbomethoxy)dibenzo-27-crown-9-long (**9**): δ 7.63 (dd, *J* = 8, 2 Hz, 2H), 7.52 (d, *J* = 2 Hz, 2H), 6.84 (d, *J* = 8 Hz, 2H), 4.20 – 4.16 (m, 8H), 3.93 – 3.89 (m, 8H), 3.87 (s, 6H), 3.81 (s, 4H), 3.80 – 3.77 (m, 4H), 3.71 – 3.68 (m, 4H).

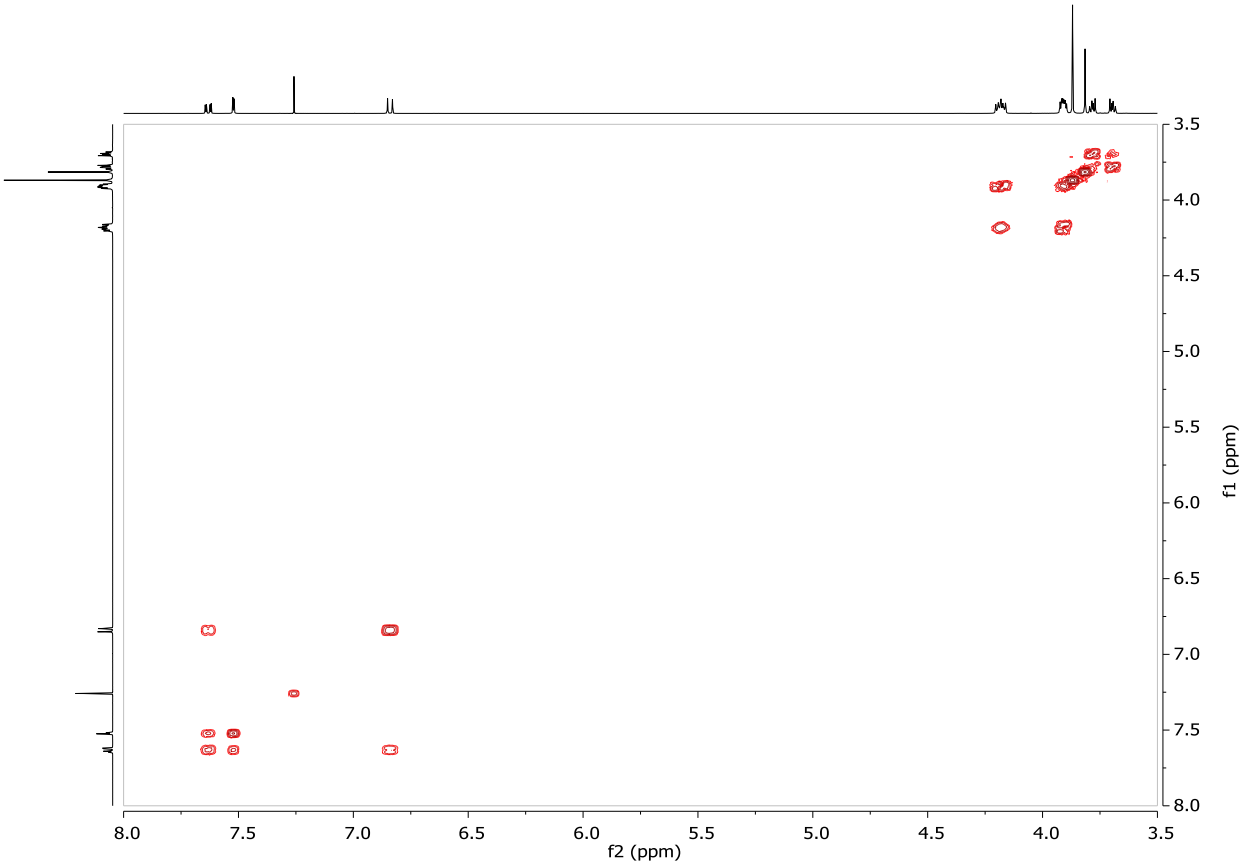

Figure S8. COSY NMR spectrum (400 MHz, $CDCl_3$, 23 ^{o}C) of *cis*-di(carbomethoxy)dibenzo-27-crown-9-long (**9**).

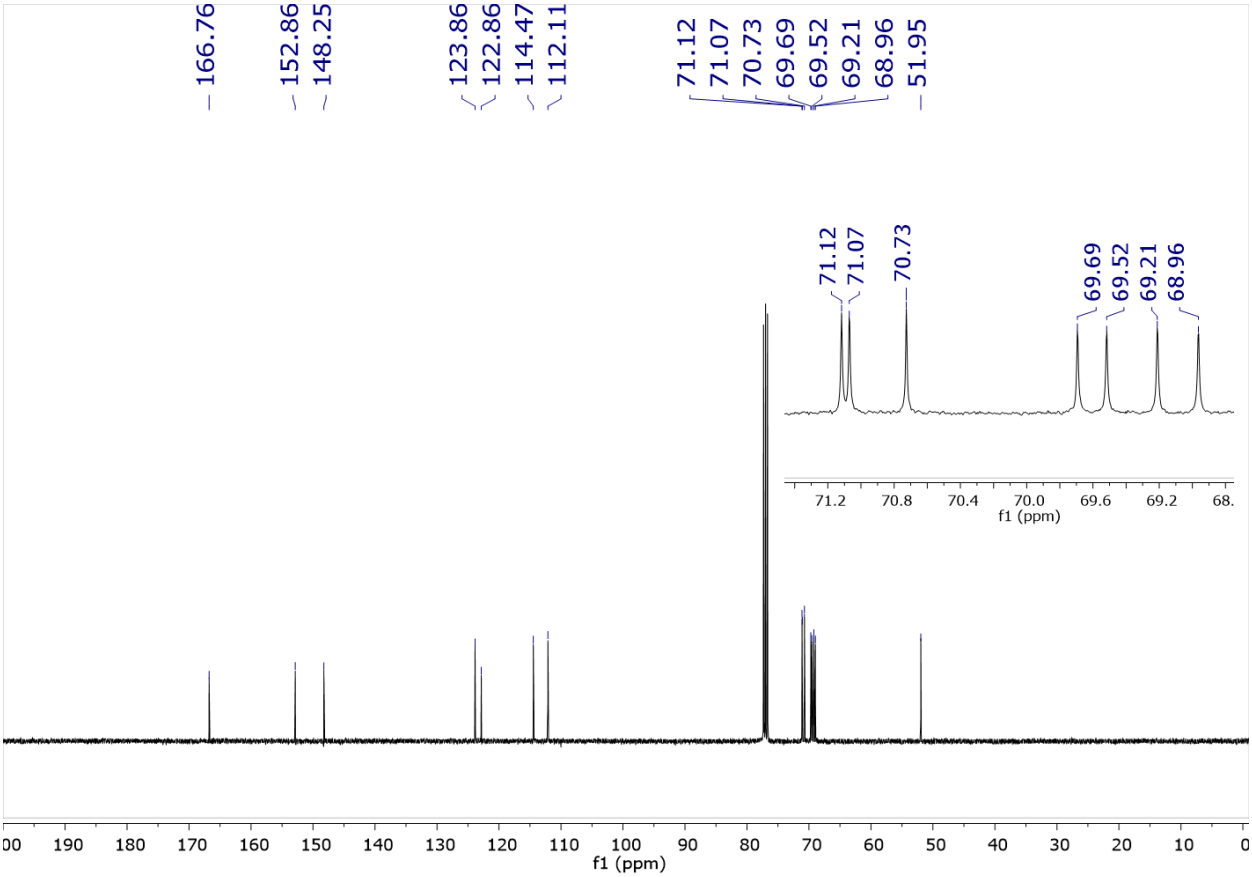

Figure S9. ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ^{o}C) of *cis*-di(carbomethoxy)dibenzo-27-crown-9-long (**9**): δ 166.76, 152.86, 148.25, 123.86, 122.86, 114.47, 112.11, 71.12, 71.07, 70.73, 69.69, 69.52, 69.21, 68.96, 51.95 (15 signals expected and 15 signals found).

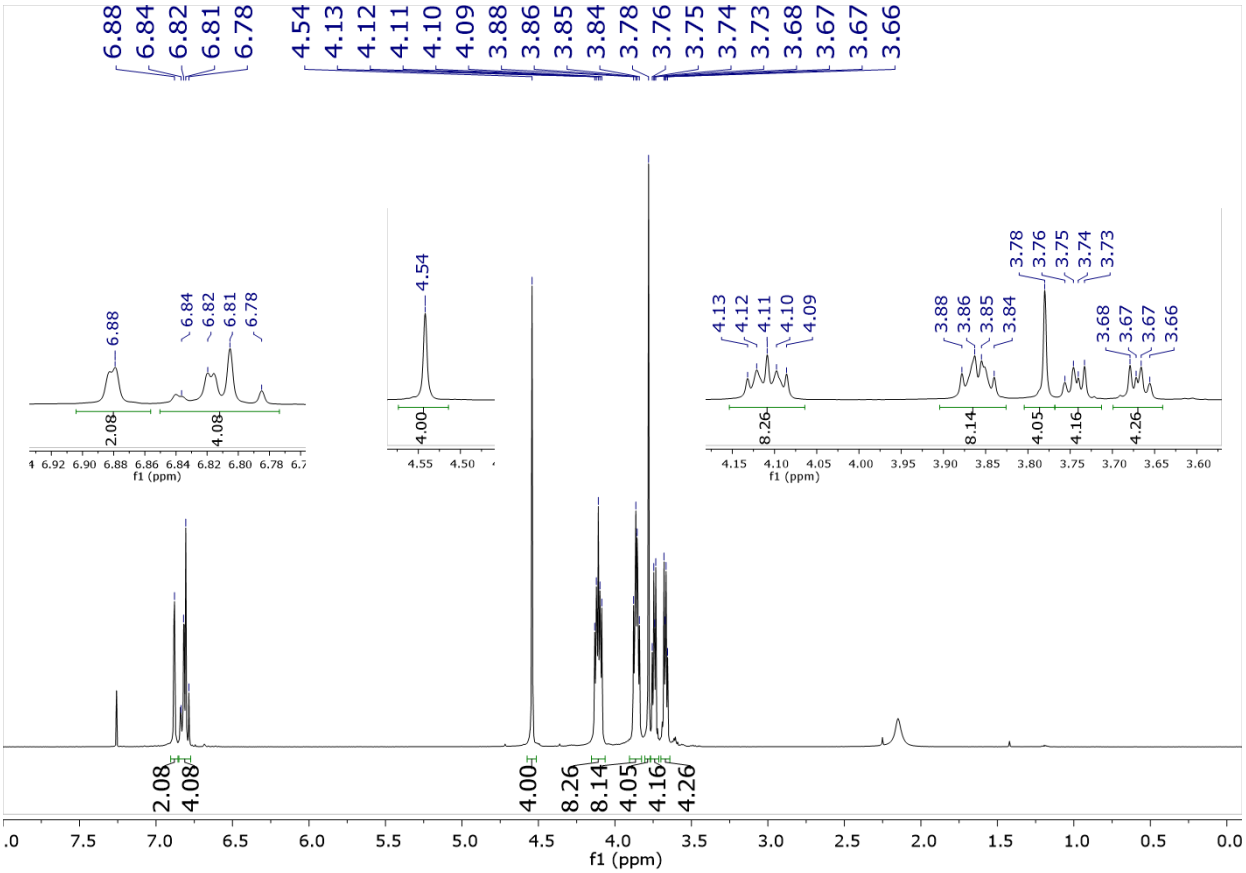

Figure S10. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ^{o}C) of *cis*-bis(hydroxymethyl)dibenzo-27-crown-9-long (**10**): δ 6.88 (s, 2H), 6.85 – 6.77 (m, 4H), 4.54 (s, 4H), 4.13 – 4.09 (m, 8H), 3.90 – 3.83 (m, 8H), 3.78 (s, 4H), 3.76 – 3.73 (m, 4H), 3.68 – 3.66 (m, 4H).

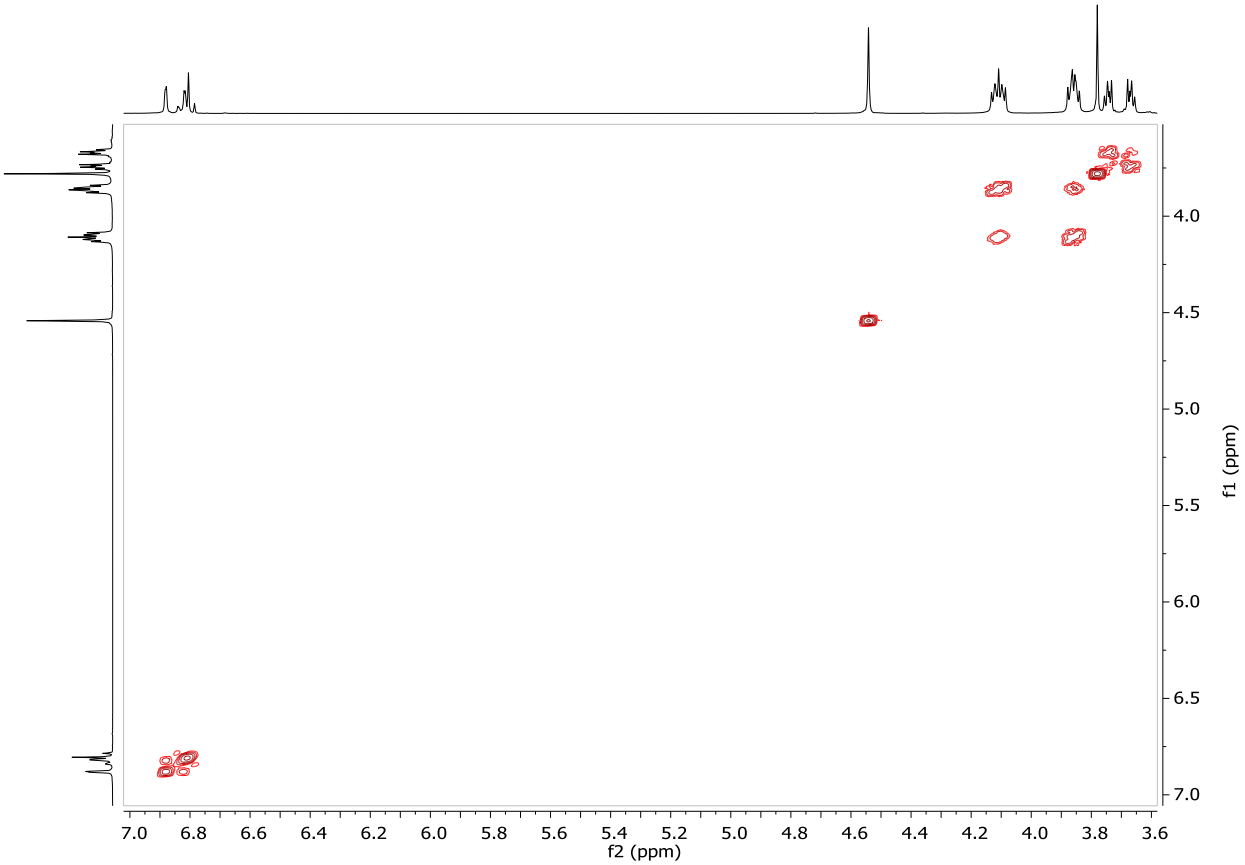

Figure S11. COSY NMR spectrum of of *cis*-bis(hydroxymethyl)dibenzo-27-crown-9-long (**10**).

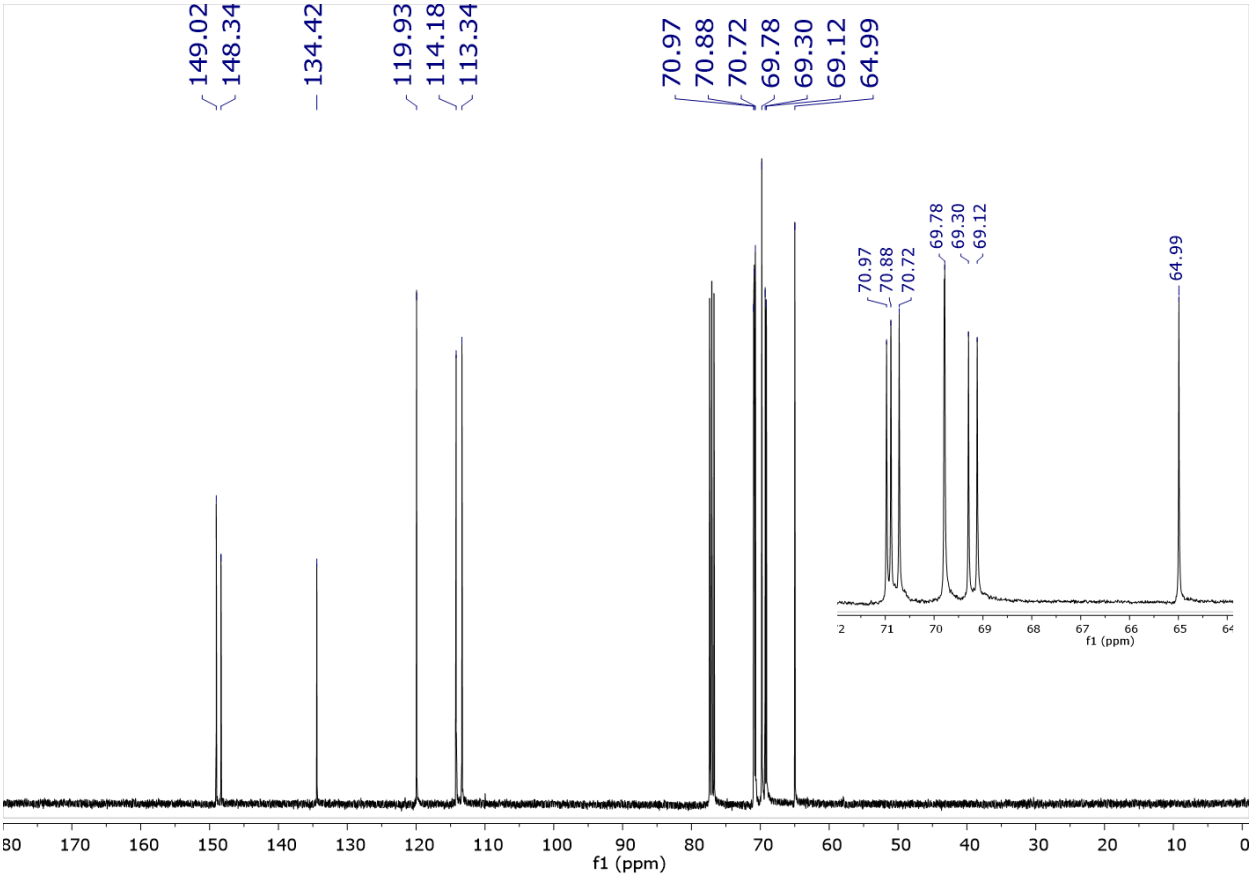

Figure S12. ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ^{o}C) of *cis*-bis(hydroxymethyl)dibenzo-27-crown-9-long (**10**): δ 149.02, 148.34, 134.42, 119.93, 114.18, 113.34, 70.97, 70.88, 70.72, 69.78, 69.30, 69.12, 64.99 (13 signals expected and 13 signals found).

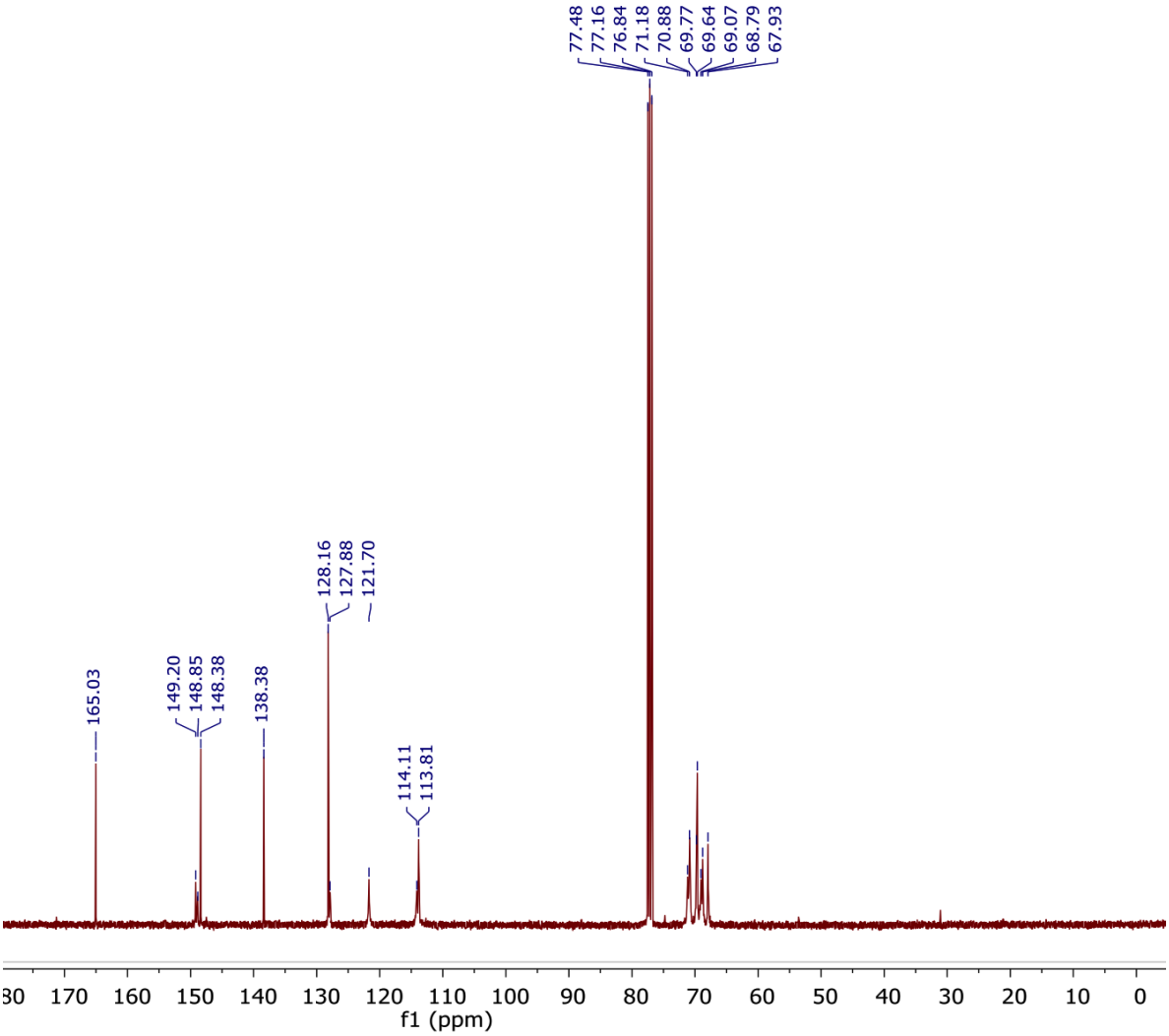

Figure S13. ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ^{o}C) of *cis*-dibenzo-27-crown-9-short pyridyl cryptand **3**: δ (ppm): 165.0, 149.2, 148.8, 148.3, 138.3, 128.1, 127.8, 121.7, 114.1, 113.8, 71.1, 70.8, 69.7, 69.6, 69.0, 68.7, 67.9 (18 peaks expected and 17 peaks found).

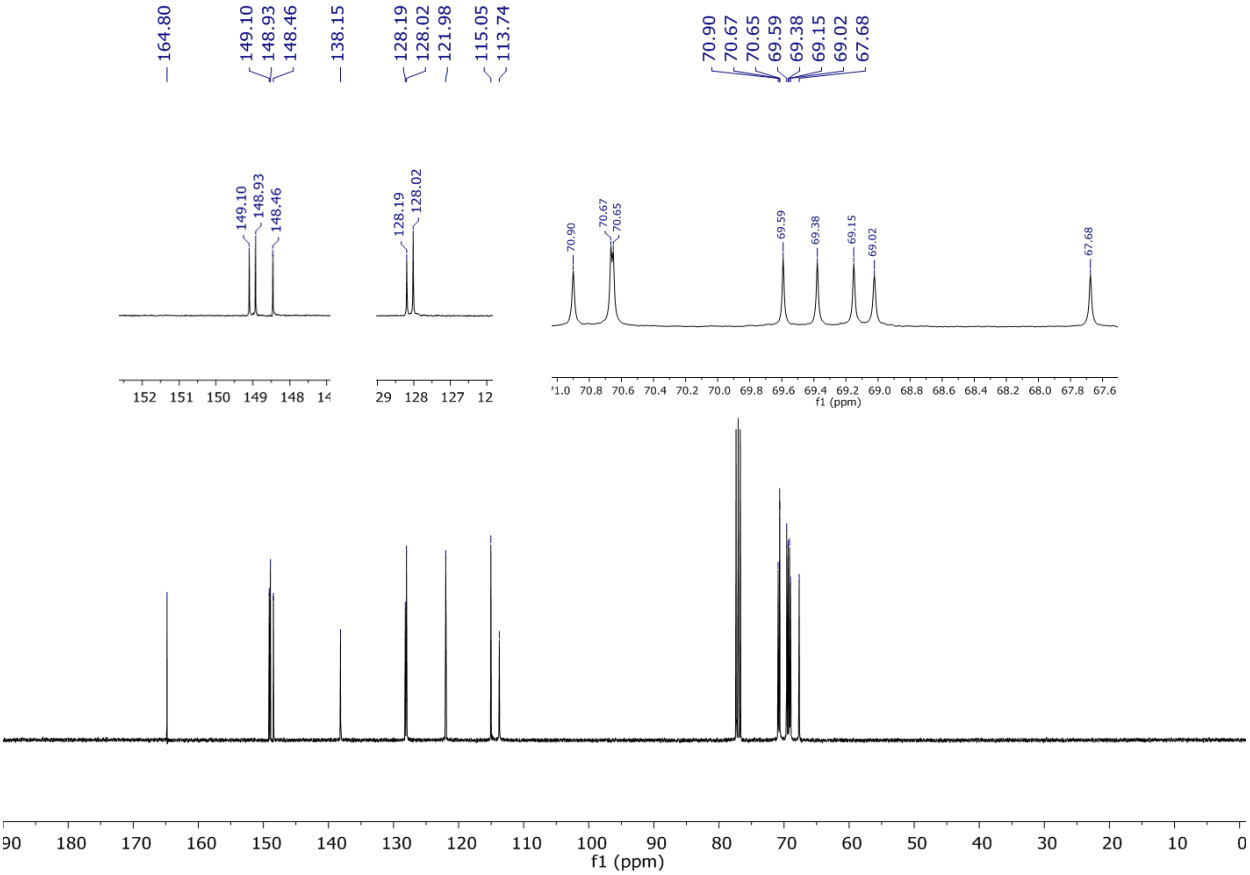

Figure S14. ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ^{o}C) of *cis*-dibenzo-27-crown-9-long pyridyl cryptand **4**: δ (ppm): 164.8, 149.1, 148.9, 148.5, 138.2, 128.2, 128.0, 122.0, 115.0, 113.7, 70.9, 70.7, 70.6, 69.6, 69.4, 69.2, 69.0, 67.7 (18 signals expected and 18 found).

Crystallographic Data for the complex 3•DQ(PF_6)$_2$.

Experimental

A yellow rod (0.089 x 0.148 x 0.376 mm^3) was centered on the goniometer of a Rigaku Oxford Diffraction Gemini S Ultra diffractometer operating with MoKα radiation. The data collection routine, unit cell refinement, and data processing were carried out with the program CrysAlisPro.[S1] The diffraction pattern showed evidence of a minor satellite crystal (<10%). Processing and refining as a twin did not improve the refinement, so the sample was treated as a single crystal. The Laue symmetry and systematic absences were consistent with the orthorhombic space group *Pbca*. The structure was solved using SHELXS-2014 [S2] and refined using SHELXL-2014 [S2] via Olex2. [S3] The final refinement model involved anisotropic displacement parameters for non-hydrogen atoms and a riding model for all hydrogen atoms. A 2-position disorder model was used for one of the polyether arms of the cryptand and for the diquat. Relative occupancies refined to 0.615(15) / 0.385(15) and 0.732(14) / 0.268(14), respectively. Disordered solvent at Wyckoff positions 8*c* (coordinates 0.009 0.237 0.674; point symmetry 1) could not be modeled effectively; therefore the solvent mask feature of OLEX2 was used. A total of 34.3 e^- (approx. 1 acetone) was subtracted from a void of 129.9 Å^3 (corresponding to 274.6 e^- subtracted from 1039.4 Å^3 total void space per unit cell).

Table 1. Crystal data and structure refinement for **3•DQ(PF_6)$_2$**.

Identification code	AMP006
Empirical formula	$[C_{35}H_{41}NO_{13} \bullet C_{12}H_{12}N_2][PF_6]_2 \bullet C_3H_6O$
Formula weight	1215.94
Temperature	100.05(10) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	*Pbca*
Unit cell dimensions	*a* = 20.9890(5) Å □= 90°.
	b = 21.5927(6) Å □= 90°.
	c = 23.4837(5) Å □ = 90°.
Volume	10643.0(5) Å^3
Z	8
Density (calculated)	1.518 Mg/m^3
Absorption coefficient	0.193 mm^{-1}
F(000)	5040
Crystal size	0.376 x 0.148 x 0.089 mm^3
Theta range for data collection	4.069 to 26.371°.
Index ranges	-26<=h<=22, -23<=k<=26, -29<=l<=29
Reflections collected	74416
Independent reflections	10831 [R(int) = 0.1081]
Completeness to theta = 25.242°	99.5 %
Absorption correction	Gaussian
Max. and min. transmission	0.984 and 0.946
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10831 / 225 / 741
Goodness-of-fit on F^2	1.212
Final R indices [I>2sigma(I)]	R1 = 0.1245, wR2 = 0.3188
R indices (all data)	R1 = 0.1744, wR2 = 0.3567
Extinction coefficient	n/a
Largest diff. peak and hole	1.701 and -0.508 e.Å^{-3}

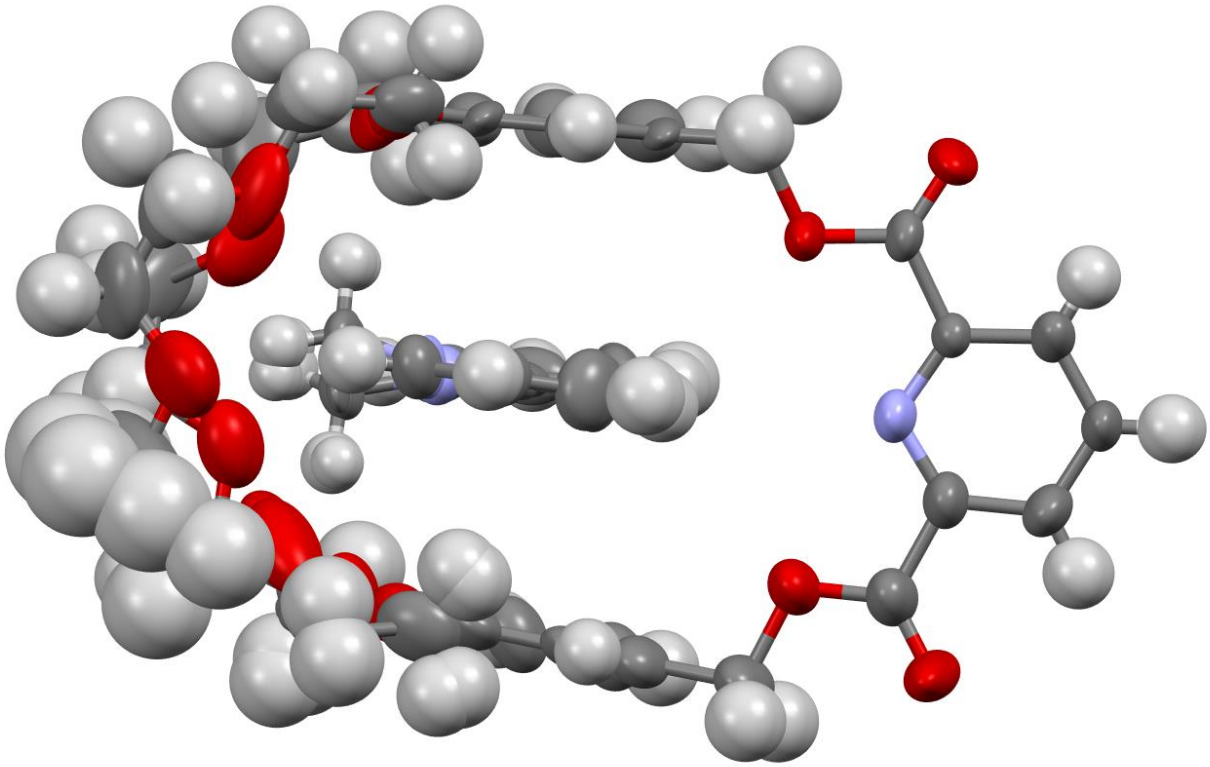

Figure S15. Thermal ellipsoid representation of **3**·**DQ(PF$_6$)$_2$** at the 90% confidence level.

REFERENCES

S1. CrysAlisPro Software System, v1.171.38.43, Rigaku Oxford Diffraction, **2017**, Rigaku Corporation, Oxford, UK.

S2. Sheldrick, G. M. "A short history of SHELX." *Acta Cryst.* **2008**, *A64*, 112-122.

S3. Dolomanov, O.V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* **2009**, *42***,** 339–341.