Electronic Supplementary Material (ESI) for CrystEngComm

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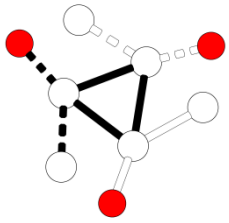
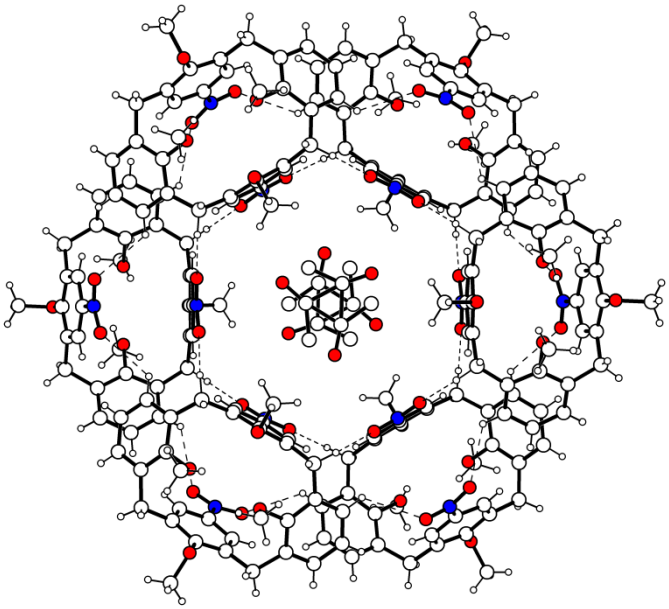


a)



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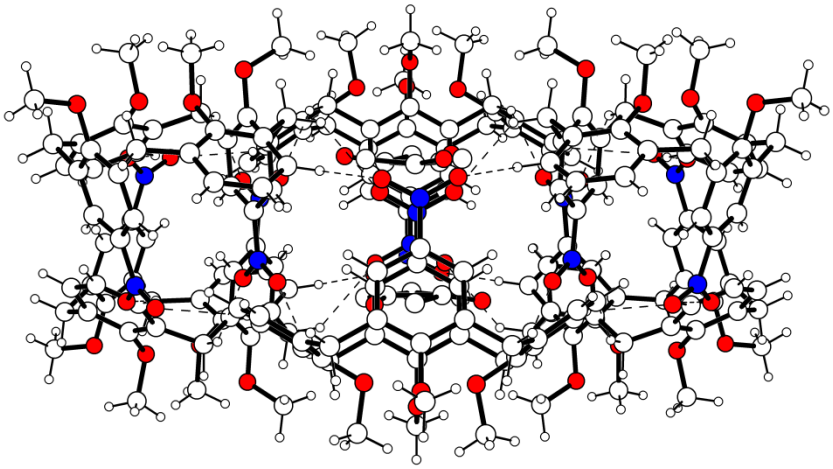

c)

Fig. S1. Representation of the acetone disorder in **1a** (a). Structure of the hexameric calixarene units found in the inclusion compound of **1** with acetone, viewed down the crystallographic *c*-axis (b) and *b*-axis (c), respectively. H-bond contacts are shown as broken lines.

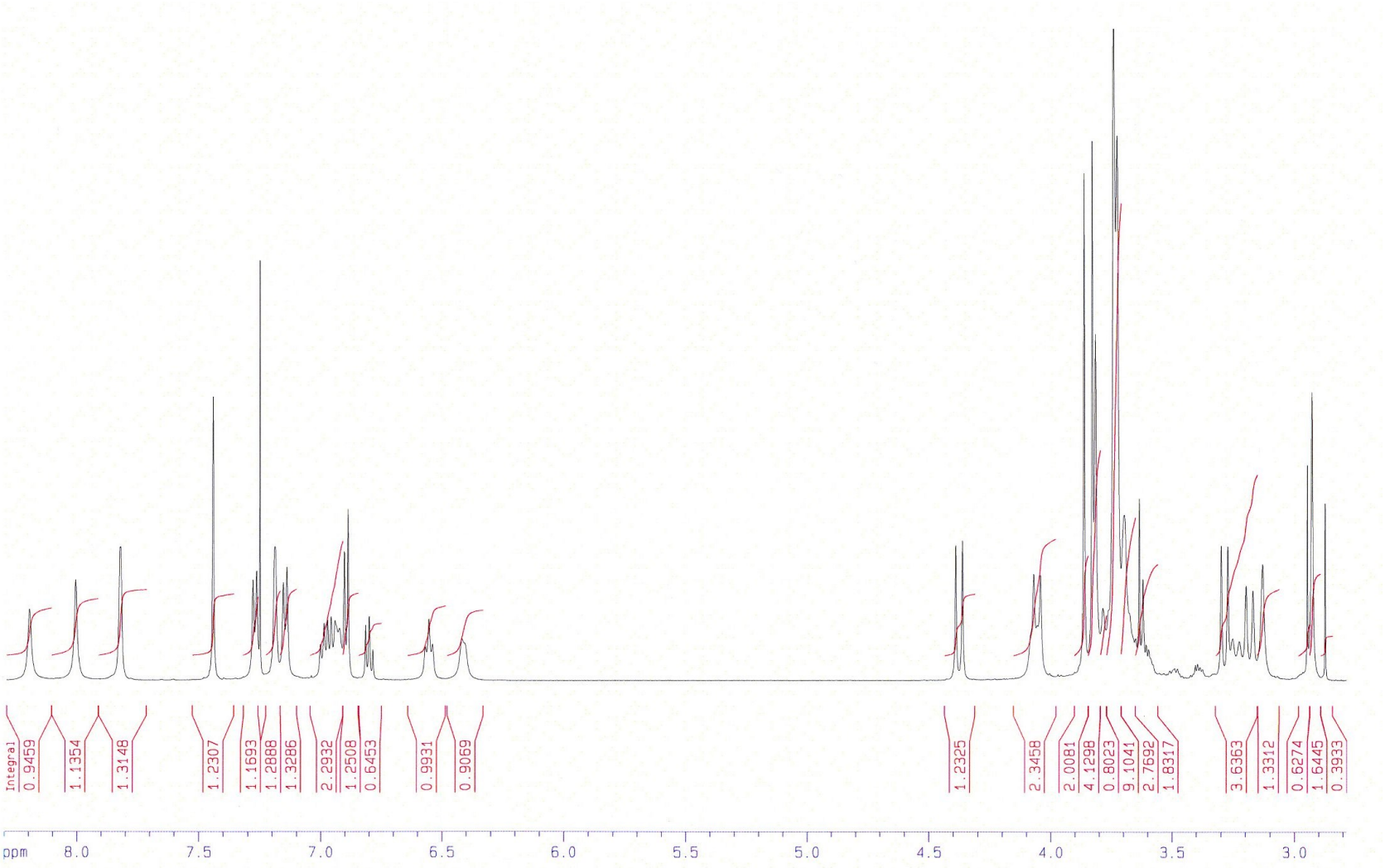

Fig. S2. ^{1}H NMR spectrum of **1** in $CDCl_3$ at T = 277 K.

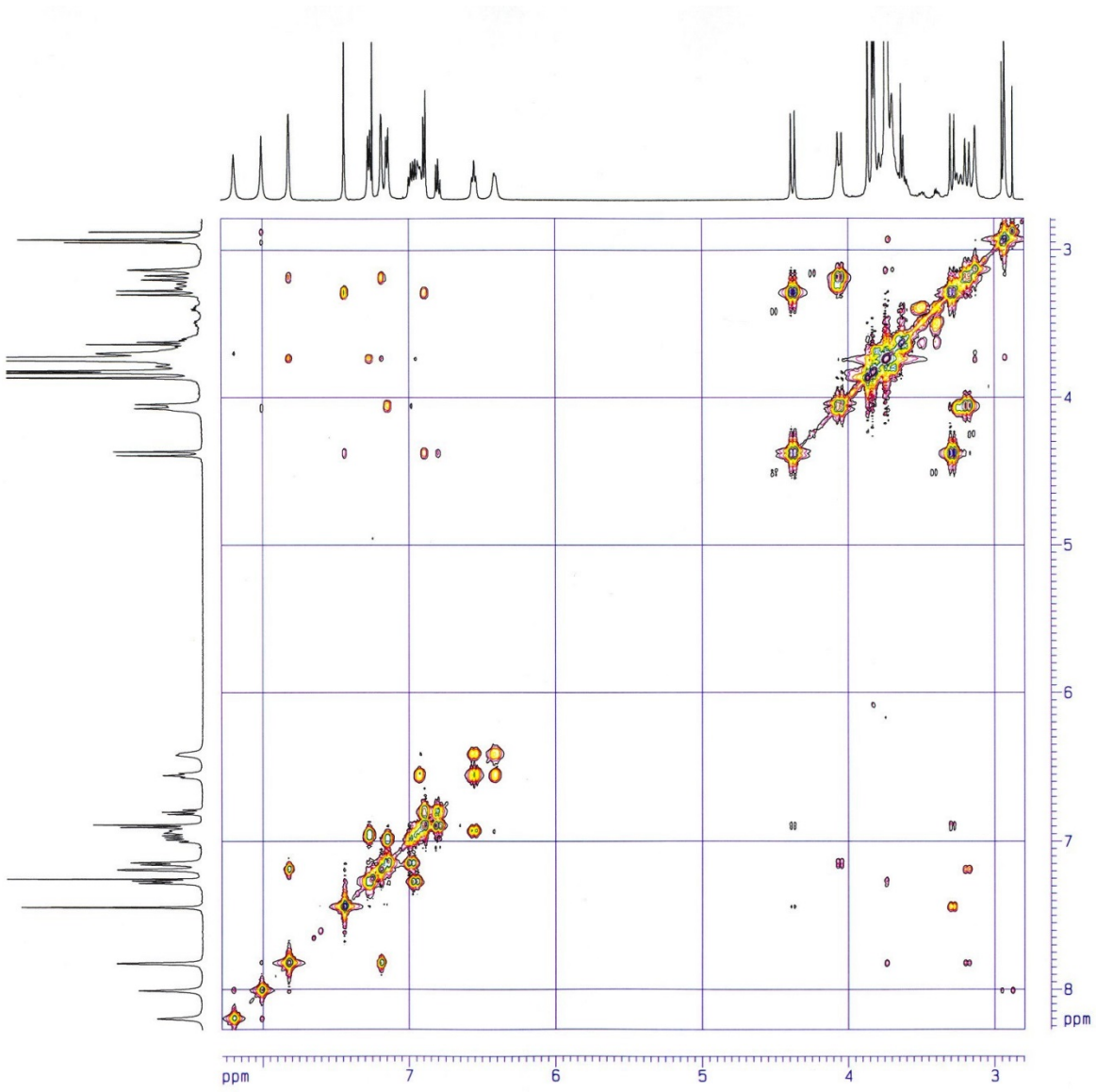

Fig. S3. COSY spectrum of **1** in $CDCl_3$ at 277 K.

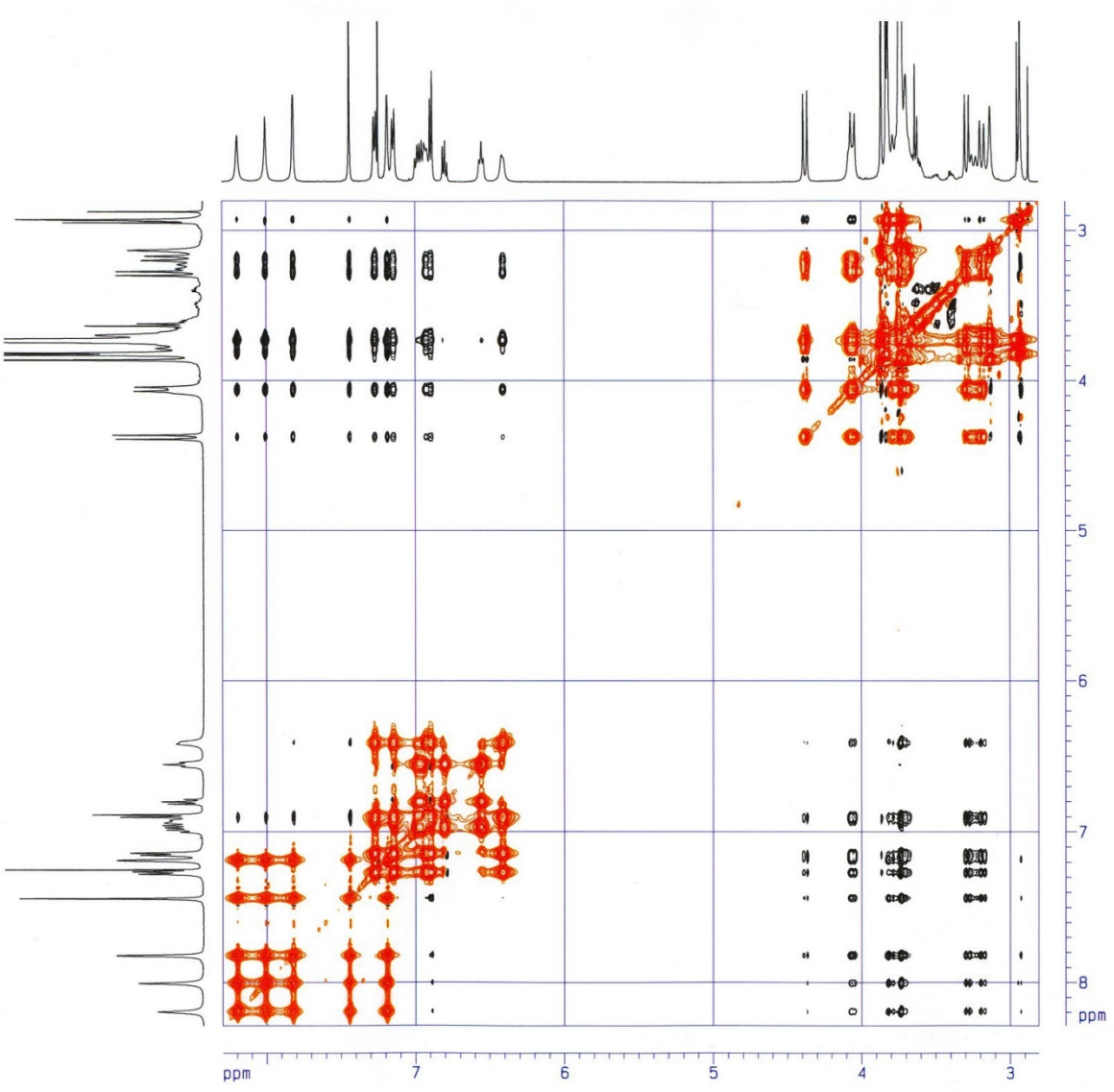

Fig. S4. NOESY spectrum of **1** in $CDCl_3$ at 277 K.

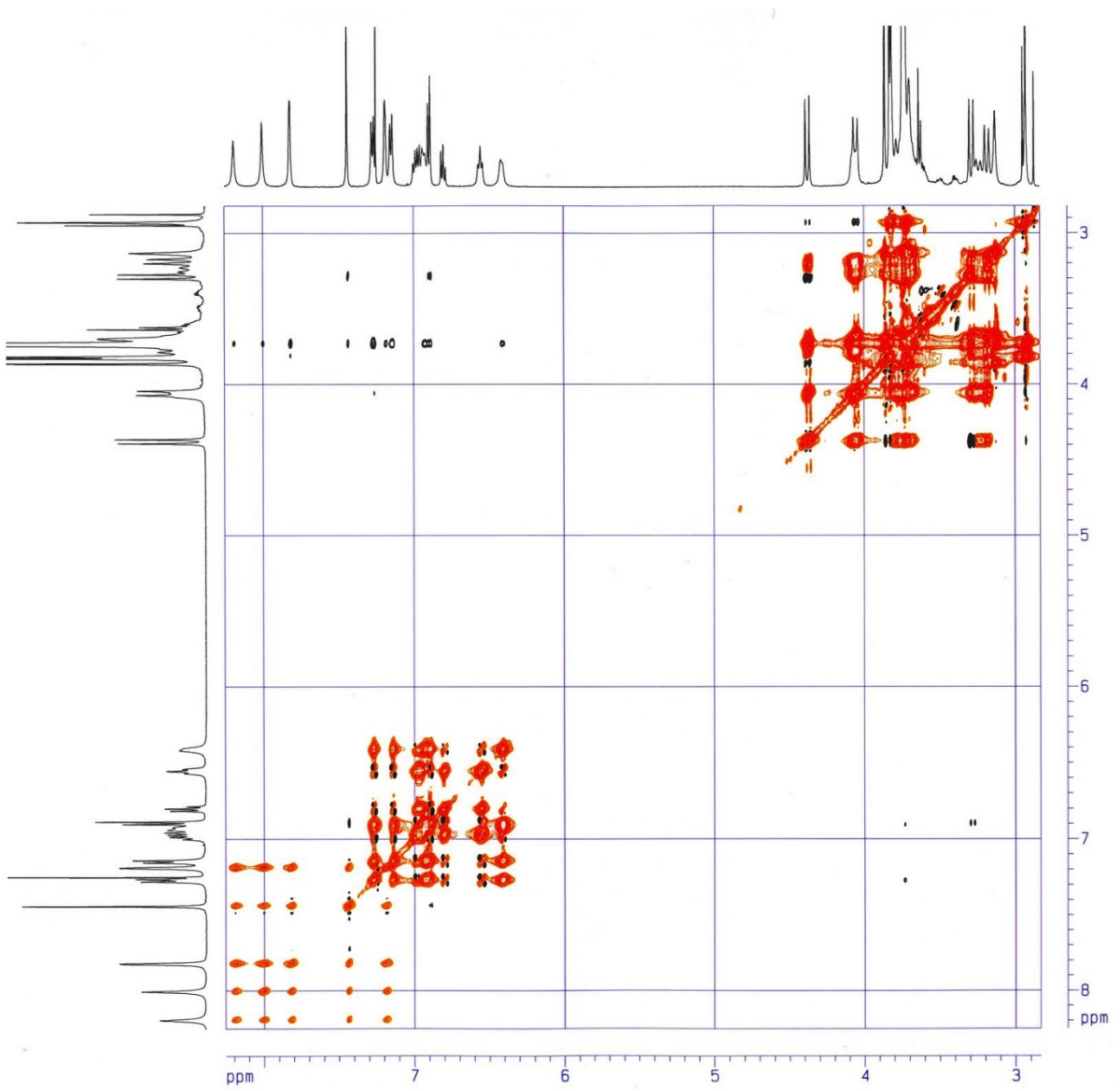

Fig. S5. ROESY spectrum of **1** in $CDCl_3$ at 277 K.

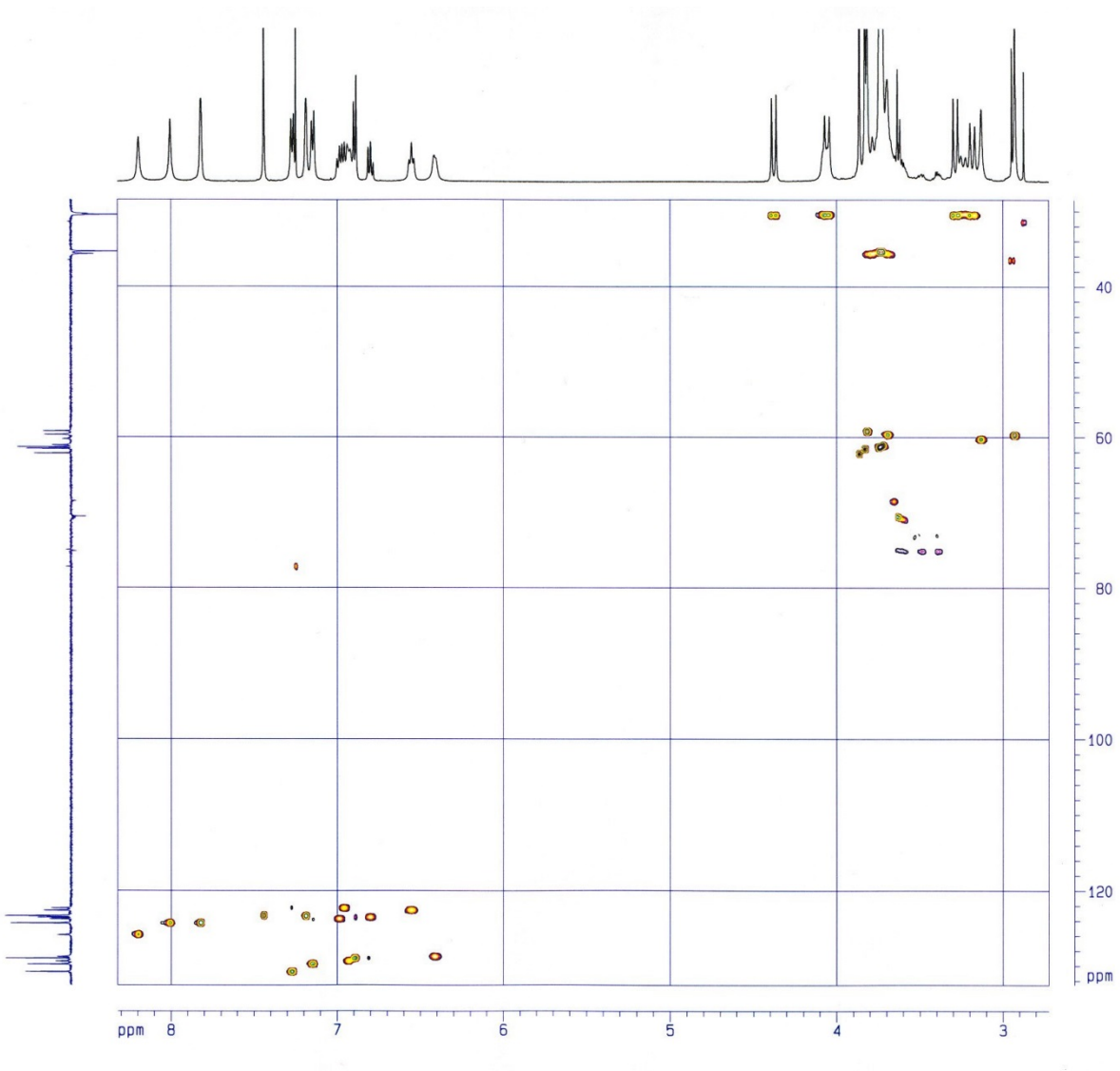

Fig. S6. HSQC spectrum of **1** in $CDCl_3$ at 277 K.

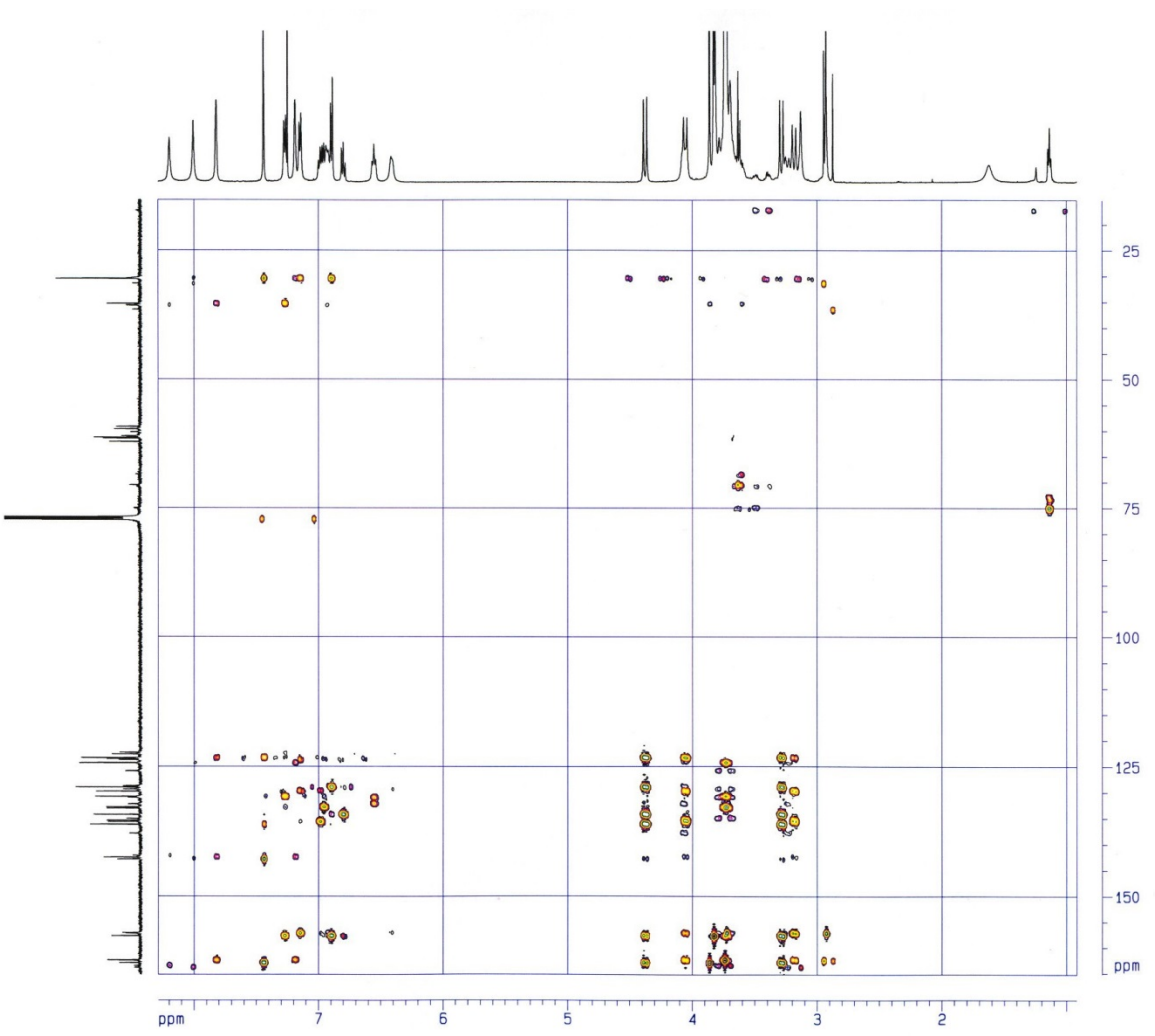

Fig. S7. HMBC spectrum of **1** in $CDCl_3$ at 277 K.

Table S1. Distances (Å) and angles (°) of hydrogen bonds and contacts of **1** and its inclusion compounds with acetone (**1a**) and chloroform (**1b**)

Atoms	Symmetry	Distances (Å)		Angles (°)
		D···A	H···A	D–H···A
1				
C(9)-H(9A)...O(2)	0.33+*y*, 0.66-*x*+*y*, 0.66-*z*	3.451(2)	2.63	140
C(1)-H(1B)...O(3)	0.33+*x*-*y*, -0.33+*x*, 0.66-*z*	3.439(2)	2.63	139
C(29)-H(29)...O(5)	0.33+*x*-*y*, -0.33+*x*, 0.66-*z*	3.282(2)	2.61	128
C(11)-H(11)...O(6)	0.33+*y*, 0.33-*x*+*y*, 0.66-*z*	3.349(2)	2.70	127
1a				
C(9)-H(9A)...O(1)	1+*x*, 1-*x*+*y*, 2-*z*	3.416(3)	2.61	138
C(1)-H(1B)...O(2)	*x*-*y*, -1+*x*, 2-*z*	3.428(3)	2.62	139
C(29)-H(29)...O(5)	*x*-*y*, -1+*x*, 2-*z*	3.343(3)	2.70	126
C(11)-H(11)...O(6)	1+*x*, 1-*x*+*y*, 2-*z*	3.264(3)	2.60	127
1b				
C(17)-H(17A)...O(5)	0.5+*x*, *y*, 0.5-*z*	3.414(4)	2.49	156
C(1G)-H(1G)...O(5)	-0.5+*x*, *y*, 0.5-*z*	3.106(5)	2.44	123
C(1H)-(H1H)...O(5)	-0.5+*x*, *y*, 0.5-*z*	3.361(4)	2.56	137
C(25)-H(25B)...O(6)	2-*x*, -0.5+*y*, 0.5-*z*	3.263(5)	2.51	133
C(11)-(H11)...O(8)	2-*x*, 0.5+*y*, 0.5-*z*	3.378(5)	2.64	135
C(1G)-(H1G)...O(8)	-0.5+*x*, *y*, 0.5-*z*	3.332(5)	2.61	130
C(1H)-C(1H)...O(8)	-0.5+*x*, *y*, 0.5-*z*	3.420(5)	2.64	135
C(27)-H(27)...Cl(2H)	1.5-*x*, -0.5+*y*, 1-*z*	2.686(5)	1.84	147
C(1H)-Cl(3H)...Cl(3H)	1-*x*, *y*, 1-*z*	4.387(5)	2.90[a]	142

[a] Distance between the Cl atoms.

Table S2. ^{13}C NMR data of **1** in $CDCl_3$ at T=295 K

cone (*)	**paco1 (+)**	**paco2 (Δ)**
162.95 (C-15, C-31) 157.73 (C-7, C-23)	162.42 (C-15, C-31) 157.72 (C-23) 157.10 (C-7)	63.86 (C-31) 163.51 (C-15) 157.22 (C-7, C-23)
142.86 (C-12, C-28) -	142.45 (C-12, C-28) -	142.78 (C-28) 142.15 (C-12)
136.13 (C-10, C-14, C-26,C-30) 134.26 (C-2, C-6, C-18, C-22) - -	135.62 (C-10, C-30) 135.37 (C-2, C-6) 133.02 (C-14, C-26) 132.81 (C-18, C-22)	137.84 (C-26, C-30) 134.98 (C-10, C-14) 132.21 (C-2, C-22) 130.96 (C-6, C-18)
128.99 (C-3, C-5, C-19, C-21) 123.56 (C-4, C-20) 123.31 (C-11, C-13, C-27, C-29) - - -	130.78 (C-19, C-21) 129.75 (C-3, C-5) 124.30 (C-13, C-27) 123.76 (C-4) 123.37 (C-11, C-29) 122.31 (C-20)	129.36 (C-5, C-19) 128.74 (C-3, C-21) 125.86 (C-11, C-13) 124.30 (C-27, C-29) 122.61 (C-4, C-20) -
62.17 (C-16, C-32) 59.21 (C-8, C-24) -	61.55 (C-24) 61.37 (C-16, C-32) 61.07 (C-8)	60.27 (C-16) 59.70 (C-8, C-24) 59.69 (C-32)
30.51 (C-1, C-9, C-17, C-25) -	35.57 (C-17, C-25) 30.50 (C-1, C-9)	35.69 (C-9, C-17) 30.36 (C-1, C-25)

Table S3. ^{1}H NMR data of **1** in $CDCl_3$ at T=295 K

cone (*)	**paco1** (+)	**paco2** (Δ)
7.44 (s, 4H, H-11, H-13, H-27, H-29)	7.82 (d, ^{4}J=1.4 Hz, 2H, H-13, H-27)	8.20 (s, br, 2H, H-11, H-13)
6.89 (d, ^{3}J=7.5 Hz, 4H, H-3, H-5, H-19, H-21)	7.27 (d, ^{3}J=7.4 Hz, 2H, H-19, H-21)	8.01 (s,br, 2H, H-27, H-29)
6.80 (t, ^{3}J=7.5 Hz, 2H, H-4, H-20)	7.19 (s, br, 2H, H-11, H-29	6.93 (d,^{3}J=7.4 Hz, 2H, H-5, H-19)
-	7.14 (d, ^{3}J=7.4 Hz, 2H, H-3, H-5)	6.55 (t, ^{3}J=7.4 Hz, 2H, H-4, H-20)
-	6.97 (t, ^{3}J=7.4 Hz, 1H, H-4)	6.42 (d, ^{3}J=7.4Hz, 2H, H-3, H-21)
-	6.96 (t, ^{3}J=7.4 Hz, 1H, H-20)	-
4.38 (d, ^{2}J=13.5 Hz, 4H, H-1a, H-9a, H-17a, H-25a)	4.06 (d,^{2}J=13.9 Hz,2H,H-1a, H-9a)	4.07 (d,^{2}J=13.6 Hz, 2H, H-1a, H-25a)
3.29 (d, ^{2}J=13.5 Hz, 4H, H-1b, H-9b, H-17b, H-25b)	3.75 (m, 4H, H-17a,b, H-25a,b)	3.78 (m, br, 2H, H-9a, H-17a)
-	3.19 (d,^{2}J=14.0 Hz, 2H, H-1b, H-9b)	3.68 (m, br, 2H, H-9b, H-17b)
-	-	3.24 (d,^{2}J=13.6 Hz, 2H, H-1b, H-25b)
3.86 (s, 6H, H-16, H-32)	3.83 (s, 3H, H-24)	3.70 (s, br, 3H, H-32)
3.82 (s, 6H, H-8, H-24)	3.74 (s, 6H, H-16, H-32)	3.13 (s, br, 3H, H-16)
	3.73 (s, 3H, H-8)	2.93 (s, br, 6H, H-8, H-24)

Table S4. Calculation of the conformer distribution of **1**

Conformer	Atoms	Integral		Number of atoms		Weighted integral	Ratio
cone	11* (5*, 19*, 21*)	1.242	:	4	=	0.311	0.20
partial cone 1	13+ (27+)	1.348	:	2	=	0.674	0.43
partial cone 2	27Δ (29Δ)	1.132	:	2	=	0.566	0.37
						1.551	

Determination of the conformer distribution of **1** in solution by NMR spectroscopy

(discussed here for the solution of **1** in $CDCl_3$ at T = 295 K as an example)

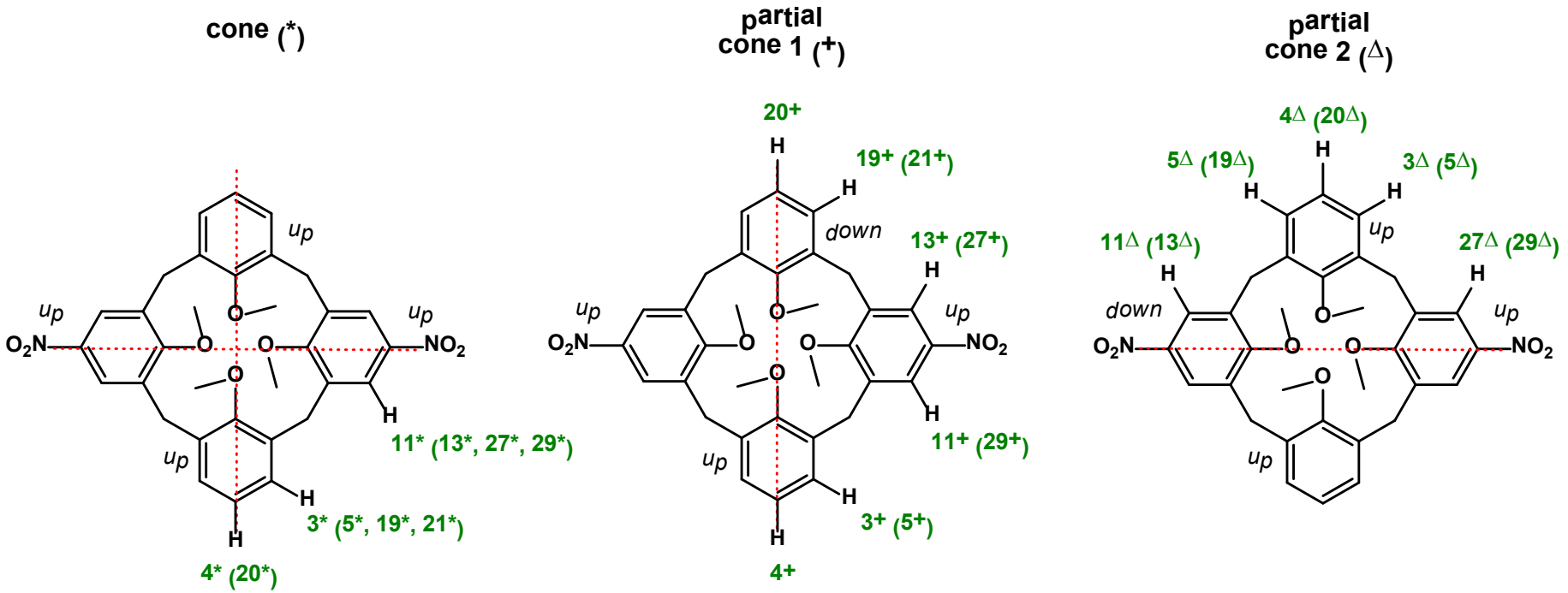

Fig. S8. Assignment of the non-equivalent aromatic protons in the three conformers of **1** with the respective numbering of H atoms. The dotted lines symbolize mirror planes through the respective molecule.

As shown in Fig. S8, the three conformers of **1** differ in the number of non-equivalent protons. For our purposes we focused on the aromatic protons in *meta* position to the OMe groups. By using the respective NMR shifts, coupling constants and appropriate 2D NMR experiments (Fig. S9 - S11), we were able to fully assign the conformers. In order to calculate the conformer ratio, we used the well separated signals of H atoms 11* (5*, 19*, 21*), 13+ (27+) and 27Δ (29Δ), each neighboring the nitro group (Table S4).

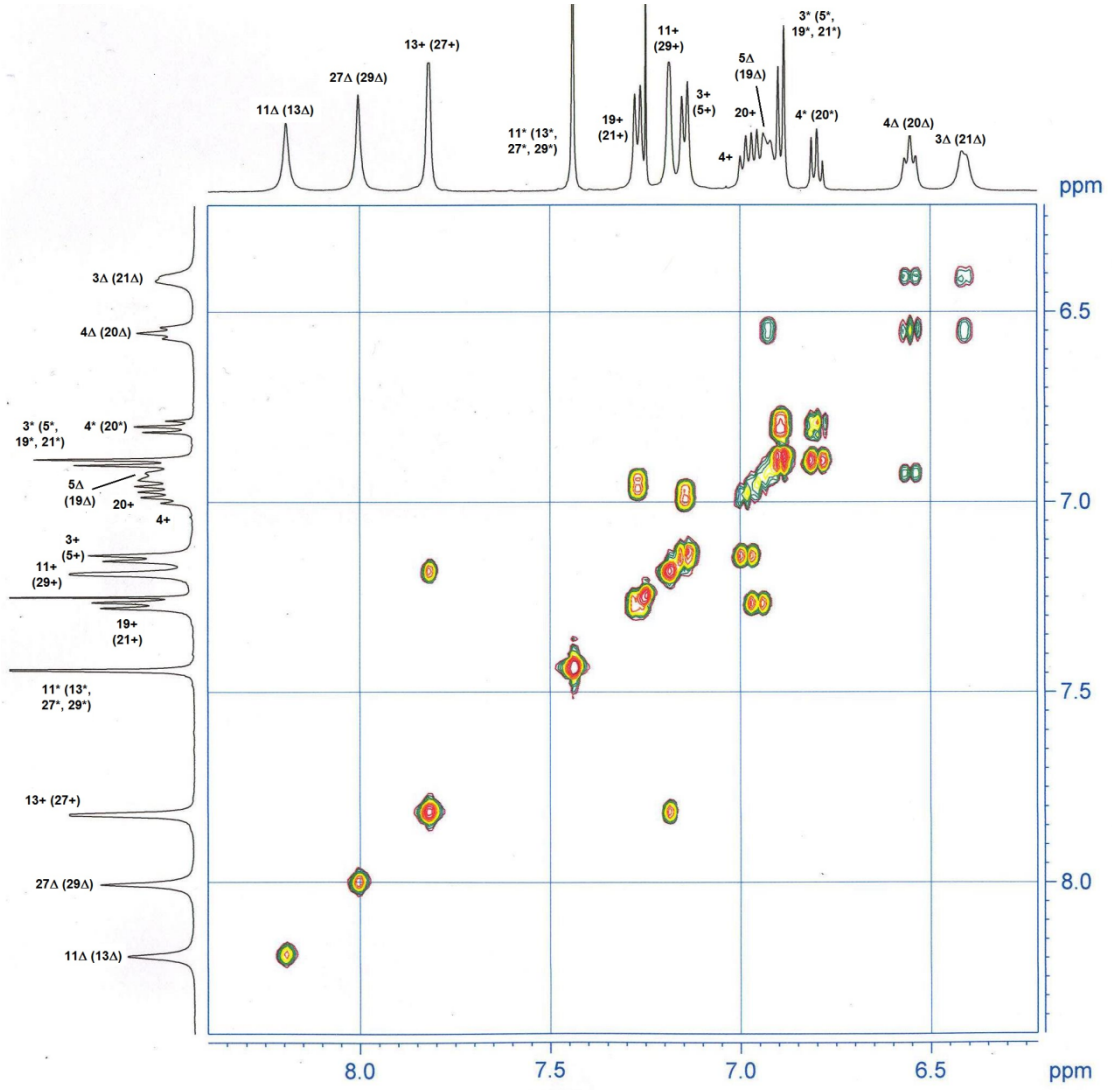

Fig. S9. Part of the COSY spectrum of **1** in $CDCl_3$ at 295 K. (Conformer assignment: cone = *, partial cone 1 = +, partial cone 2 = Δ)

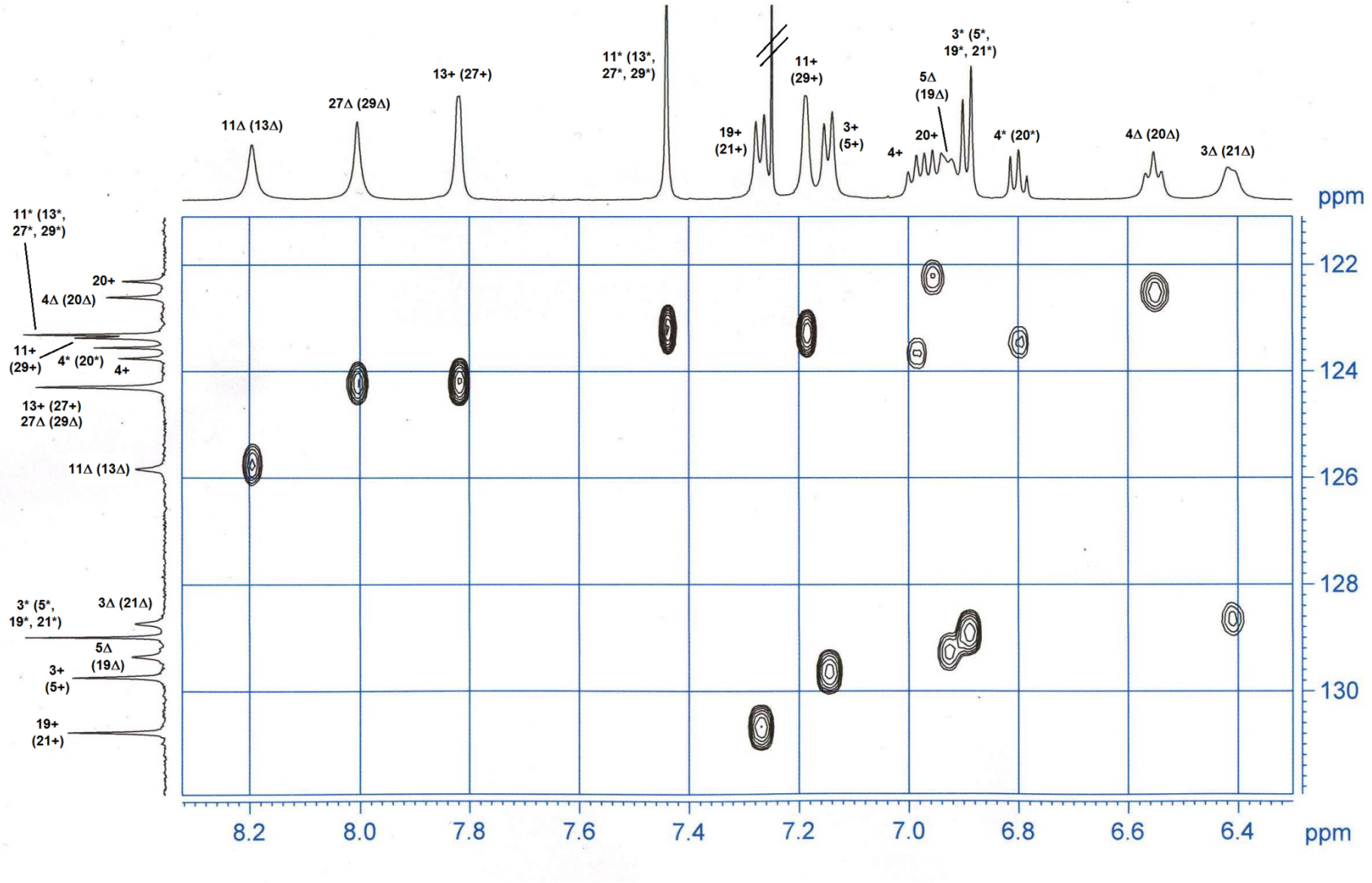

Fig. S10. Part of the HSQC spectrum of **1** in $CDCl_3$ at 295 K. (Conformer assignment: cone = *, partial cone 1 = +, partial cone 2 = Δ)

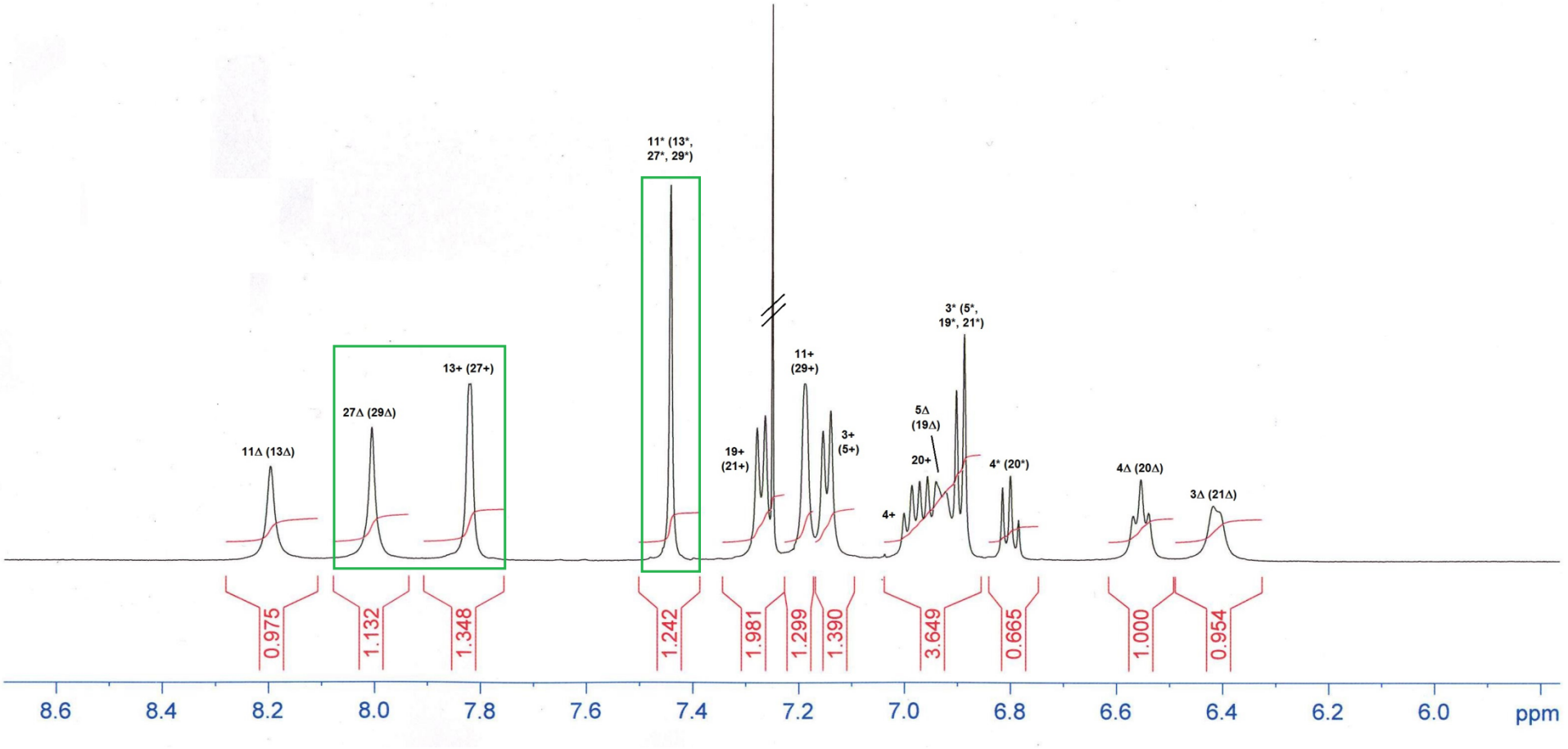

Fig. S11. Part of the ^{1}H NMR spectrum of **1** in $CDCl_3$ at T = 295 K. The integrals used for calculating the conformer ratio are framed. (Conformer assignment: cone = *, partial cone 1 = +, partial cone 2 = Δ)