Electronic Supplementary Information

α-Cyclodextrins reversibly capped with disulfide bonds

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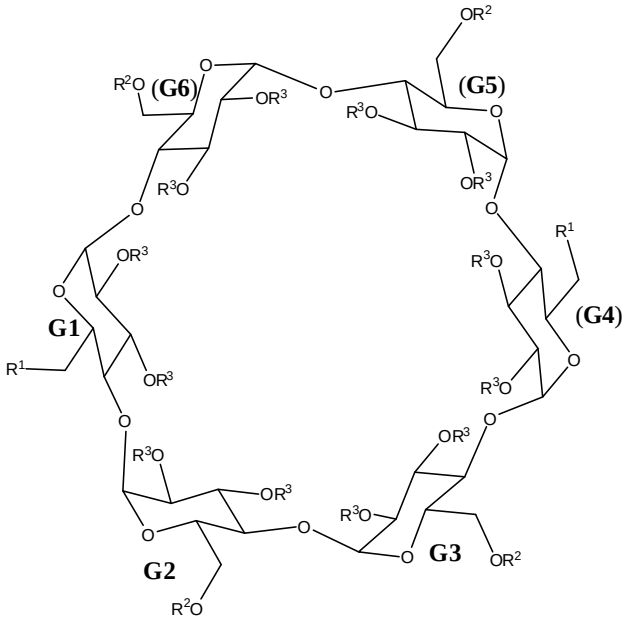


Figure S1. Numbering of glucose residues in cyclodextrin macrocycle used in Tables S1 and S2. **G4**-**G6** residues are related to the residues **G1**-**G3** by C_2-symmetry.

Table SI. ^{1}H NMR chemical shifts in compounds **1**-**9**.

Comp.	Solv.	Residue	H-1 (d)	H-2 (dd)	H-3 (dd)	H-4 (dd)	H-5 (ddd)	H-6a (dd)	H-6b (dd)
2 [a]	$CDCl_3$	G1 (G4)	5.70	3.55	4.19	3.92	3.95	3.71	3.64
		G2 (G5)	4.69	3.935	4.08	3.84	3.92	3.88	3.765
		G3 (G6)	4.71	3.40	4.01	3.74	3.93	3.99	3.71
3 [b]	$CDCl_3$	G1 (G4)	4.98	3.37	~4.15	~4.17	3.76	4.515	3.72
		G2 (G5)	5.14	3.48	~4.13	~4.12	4.035	4.13	3.55
		G3 (G6)	5.49	3.51	4.20	~4.16	3.91	3.98	3.52
4 [c]	CD_3OD	G1 (G4)	4.92	3.435	3.95	3.65	3.79	4.095	3.935
		G2 (G5)	4.945	3.48	3.95	3.62	3.79	3.92	3.77
		G3 (G6)	4.96	3.48	3.95	3.495	3.77	3.88	3.82
5 [d]	$CDCl_3$	G1 (G4)	4.99	3.08	~3.56	3.84	3.63	4.34	3.81
		G2 (G5)	5.07	3.16	~3.55	~3.56	~3.76	~3.75	~3.66
		G3 (G6)	5.10	3.16	~3.55	~3.56	~3.76	~3.75	~3.66
6 [e]	$CDCl_3$	G1 (G4)	5.042	3.165	3.56	3.55	3.80	3.92	3.92
		G2 (G5)	5.024	3.176	~3.54	3.62	3.79	3.87	3.68
		G3 (G6)	5.133	3.174	3.525	3.54	3.805	3.75	3.75
7 [f]	$CDCl_3$	G1 (G4)	5.07	3.18	~3.54	3.42	3.95	3.89	3.83
		G2 (G5)	5.06	3.165	~3.54	3.55	~3.82	3.75	3.71
		G3 (G6)	5.09	3.185	~3.54	3.69	~3.82	4.05	3.625
8 [g]	$CDCl_3$	G1 (G4)	4.99	3.135	3.515	3.27	3.995	3.615	3.16
		G2 (G5)	5.05	3.175	3.57	3.65	3.955	3.84	3.62
		G3 (G6)	5.07	3.18	3.555	3.66	3.82	3.98	3.65
9 [h]	$CDCl_3$	G1 (G4)	5.06	3.195	3.58	3.26	4.18	3.05	3.33
		G2 (G5)	5.42	3.20	3.65	3.975	3.97	4.13	3.555
		G3 (G6)	4.91	3.165	3.57	3.69	3.83	3.93	3.66

Proton signals of substituents:

[a] **16x OCH_2 (Bn)**: 5.42 d (2H) and 4.87 d (2H), J=10.4; 5.16 d (2H) and 4.74 d (2H), J=10.8; 4.86 d (2H) and 4.75 d (2H), J=11.8; 4.76 d (2H) and 4.44 d (2H), J=11.9; 4.54 d (2H) and 4.39 d (2H), J=12.0; 4.535 d (2H) and 4.40 d (2H), J=12.2; 4.52 d (2H) and 4.49 d (2H), J=12.6; 4.35 d (2H) and 4.30 d (2H), J=12.6; **16x C_6H_5 (Bn)**: 7.02 – 7.40 m (80H).
[b] **16x OCH_2 (Bn)**: 5.285 d (2H) and 4.78 d (2H), J=10.7; 5.235 d (2H) and 4.84 d (2H), J=10.7; 4.885 d (2H) and 4.825 d (2H), J=11.4; 4.645 d (2H) and 4.355 d (2H), J=11.7; 4.61 d (2H) and 4.415 d (2H), J=12.1; 4.58 d (2H) and 4.48 d (2H), J=12.0; 4.52 d (2H) and 4.36 d (2H), J=12.5; 4.43 d (2H) and 4.26 d (2H), J=12.2; **16x C_6H_5 (Bn)**: 7.02 – 7.28 m (80H); **2x OTIPS**: 0.97 um (42H).
[c] **2x OTIPS**: 1.11m (42H).
[d] **16x OCH_3**: 3.656 s (6H), 3.654 s (6H), 3.623 s (6H), 3.503 s (6H), 3.483 s (6H), 3.470 s (6H), 3.379 s (6H) and 3.362 s (6H); **2x OTIPS**: 1.065 b (36 H), 1.07 um (6H).
[e] **16x OCH_3**: 3.674 s (6H), 3.647 s (6H), 3.634 s (6H), 3.514 s (6H), 3.492 s (6H), 3.489 s (6H), 3.396 s (6H) and 3.393 s (6H).
[f] **16x OCH_3**: 3.654 s (6H), 3.645 s (6H), 3.626 s (6H), 3.504 s (6H), 3.500 s (6H), 3.493 s (6H), 3.414 s (6H) and 3.406 s (6H).
[g] **16x OCH_3**: 3.665 s (6H), 3.64 s (6H), 3.615 s (6H), 3.50 s (6H), 3.49 s (6H), 3.48 s (6H), 3.42 s (6H) and 3.39 s (6H); **2x $SCOCH_3$**: 2.35 s (6H).
[h] **16x OCH_3**: 3.805 s (6H), 3.677 s (6H), 3.597 s (6H), 3.573 s (6H), 3.499 s (6H), 3.456 s (6H), 3.403 s (6H) and 3.400 s (6H).

Table S2. ^{13}C NMR chemical shifts in compounds **1**-**9**.

Comp.	Solv.	Residue	C-1	C-2	C-3	C-4	C-5	C-6
2 [a]	$CDCl_3$	G1 (G4)	97.81	77.72	80.92	81.00	71.27	61.76
		G2 (G5)	98.27	79.81	81.60	74.31	72.01	69.70
		G3 (G6)	97.66	79.09	80.61	81.73	71.70	69.56
3 [b]	$CDCl_3$	G1 (G4)	97.52	78.62	80.61	75.87	71.33	62.43
		G2 (G5)	97.99	79.34	81.35	78.26	71.86	69.28
		G3 (G6)	98.03	79.78	81.53	80.32	72.95	69.33
4 [c]	CD_3OD	G1 (G4)	103.67	73.96	75.16	82.84	73.90	62.18
		G2 (G5)	103.49	73.95	75.12	82.78	73.73	61.64
		G3 (G6)	103.76	74.06	75.28	83.04	73.90	63.53
5 [d]	$CDCl_3$	G1 (G4)	100.14	82.21	81.29	81.14	72.81	62.32
		G2 (G5)	100.33	82.24	82.21	81.16	71.22	71.56
		G3 (G6)	99.39	82.27	82.58	81.27	71.26	71.56
6 [e]	$CDCl_3$	G1 (G4)	99.44	82.29	81.56	81.20	72.38	62.22
		G2 (G5)	99.54	81.81	81.35	82.06	71.43	71.58
		G3 (G6)	99.78	81.81	81.41	82.43	71.40	71.58
7 [f]	$CDCl_3$	G1 (G4)	99.43	81.92	81.02	84.71	71.42	34.27
		G2 (G5)	100.22	81.96	81.25	82.44	71.26	71.18
		G3 (G6)	99.86	82.03	81.28	82.09	71.12	71.18
8 [g]	$CDCl_3$	G1 (G4)	99.36	82.27	81.02	85.76	69.52	31.48
		G2 (G5)	100.53	82.10	81.19	82.27	71.29	70.80
		G3 (G6)	99.92	81.83	81.19	82.10	71.21	71.06
9 [h]	$CDCl_3$	G1 (G4)	98.14	80.56	82.50	79.54	70.60	48.16
		G2 (G5)	98.48	80.87	81.97	80.20	71.40	71.79
		G3 (G6)	96.52	82.50	82.05	81.55	71.35	71.03

[a] **16x OCH_2 (Bn)**: 76.42(2), 76.04(2), 73.97(2), 73.38(4), 73.33(2), 73.00(2) and 72.28(2); **16x C_6H_5 (Bn)**: 139.26(4), 139.20(2), 138.59(2), 138.27(2), 137.96(4), and 137.79(2); 128.34(4), 128.32(8), 128.26(4), 128.13(4), 128.05(8), 127.993(4), 127.984(4), 127.976(4), 127.958(4), 127.84(8), 127.76(4), 127.74(2), 127.64(2), 127.61(2), 127.60(2), 127.12(2), 127.10(2), 127.07(4), 127.00(2), 126.81(2) and 126.33(4).

[b] **16x OCH_2 (Bn)**: 76.28(2), 75.42(2), 74.69(2), 74.09(2), 73.28(2), 73.20(2), 72.99(2) and 72.08(2); **16x C_6H_5 (Bn)**: 139.32(2), 139.30(2), 139.27(2), 138.46(2), 138.34(2), 138.29(2), 138.28(2) and 138.16(2); 128.31(4), 128.21(4), 128.19(4), 128.13(4), 128.02(4), 127.99(4), 127.97(4), 127.92(4), 127.87(4), 127.80(4), 127.63(2), 127.48(8), 127.46(4), 127.41(2), 127.34(4), 127.32(2), 127.20(2), 127.14(4), 126.96 (2), 126.90(2), 126.83(4) and 126.80(4); **2x OTIPS:** 18.00(6), 17.86(6) and 11.88(6).

[c] **2x OTIPS:** 18.56(6), 18.51(6) and 13.28(6).

[d] **16x OCH_3**: 61.85(2), 61.83(2), 61.70(2), 58.96(2), 58.88(2), 57.84(4) and 57.56(2); **2x OTIPS**: 17.99(6), 17.95(6) and 12.04(6).

[e] **16x OCH_3**: 61.87(2), 61.85(2), 61.54(2), 59.13(2), 59.07(2), 58.32(2), 57.86(2) and 57.80(2).

[f] **16x OCH_3**: 61.89(2), 61.77(2), 61.76(2), 59.19(2), 59.10(2), 58.02(4) and 57.96(2).

[g] **16x OCH_3**: 61.95(2), 61.83(2), 61.68(2), 59.05(2), 59.00(2), 58.17(2) and 57.76(4); **2x $SCOCH_3$**: 194.62(2) and 30.65(2).

[h] **16x OCH_3**: 61.99(2), 61.69(2), 60.75(2), 60.11(2), 59.35(2), 59.20(2), 57.75(2) and 57.68(2).

Table S3. Experimental *vs.* calculated values of ^{1}H NMR shifts.

compound	Residue	experiment vs. calculated	**H-1** (d)	**H-2** (dd)	**H-3** (dd)	**H-4** (dd)	**H-5** (ddd)	**H-6a** (dd)	**H-6b** (dd)
9	G1 (G4)	exp.[a]	5.06	3.195	3.58	3.26	4.18	3.05	3.33
		calc.[b]	4.4	2.8	3.3	3.2	4.1	2.5	3.4
	G2 (G5)	exp.[a]	5.42	3.20	3.65	3.975	3.97	4.13	3.555
		calc.[b]	5.2	2.8	3.5	2.9	3.8	4.1	2.8
	G3 (G6)	exp.[a]	4.91	3.165	3.57	3.69	3.83	3.93	3.66
		calc.[b]	4.6	2.8	3.4	2.8	4.3	3.6	2.8
10	G1 (G4)	exp.[a]	5.08	3.57	3.98	3.63	4.13	~3.25	~3.25
		calc.[b]	4.9	3.1	3.1	2.8	3.6	2.3	2.8
	G2 (G5)	exp.[a]	5.51	3.65	3.995	3.69	3.92	~3.93	~3.93
		calc.[b]	5.2	3.3	4.0	3.5	3.6	3.5	3.4
	G3 (G6)	exp.[a]	5.16	3.585	3.96	3.77	4.31	3.95	3.89
		calc.[b]	4.8	3.4	3.8	4.0	3.8	4.0	3.5

Table S4. Experimental *vs.* calculated values of ^{13}C NMR shifts.

compound	Residue	experiment vs. calculated	**C-1**	**C-2**	**C-3**	**C-4**	**C-5**	**C-6**
9	G1 (G4)	exp.[a]	98.14	80.56	82.50	79.54	70.60	48.16
		calc.[b]	102	88	86	81	75	56
	G2 (G5)	exp.[a]	98.48	80.87	81.97	80.20	71.40	71.79
		calc.[b]	103	84	86	90	75	75
	G3 (G6)	exp.[a]	96.52	82.50	82.05	81.55	71.35	71.03
		calc.[b]	101	87	84	89	76	77
10	G1 (G4)	exp.[a]	99.04	73.99	76.14	80.67	74.55	46.73
		calc.[b]	103	75	79	89	77	49
	G2 (G5)	exp.[a]	101.51	70.02	75.44	82.59	74.96	62.96
		calc.[b]	104	76	75	86	78	64
	G3 (G6)	exp.[a]	102.99	74.12	75.12	80.15	73.17	64.42
		calc.[b]	105	76	78	79	76	66

[a] Experimental values of ^{1}H and ^{13}C NMR shifts recorded for compounds **9** ($CDCl_3$, see Tables S1 and S2) and **10** (D_2O, see ref. 17 in the main text).
[b] Computed values of ^{1}H and ^{13}C NMR chemical shifts; calculated by Gaussian, at the BPW91/6-31G** level with the GIAO orbitals,[1] and referenced to the TMS standard.

[1] R. Ditchfield, *Mol. Phys.*, 1974, **27**, 789-807.

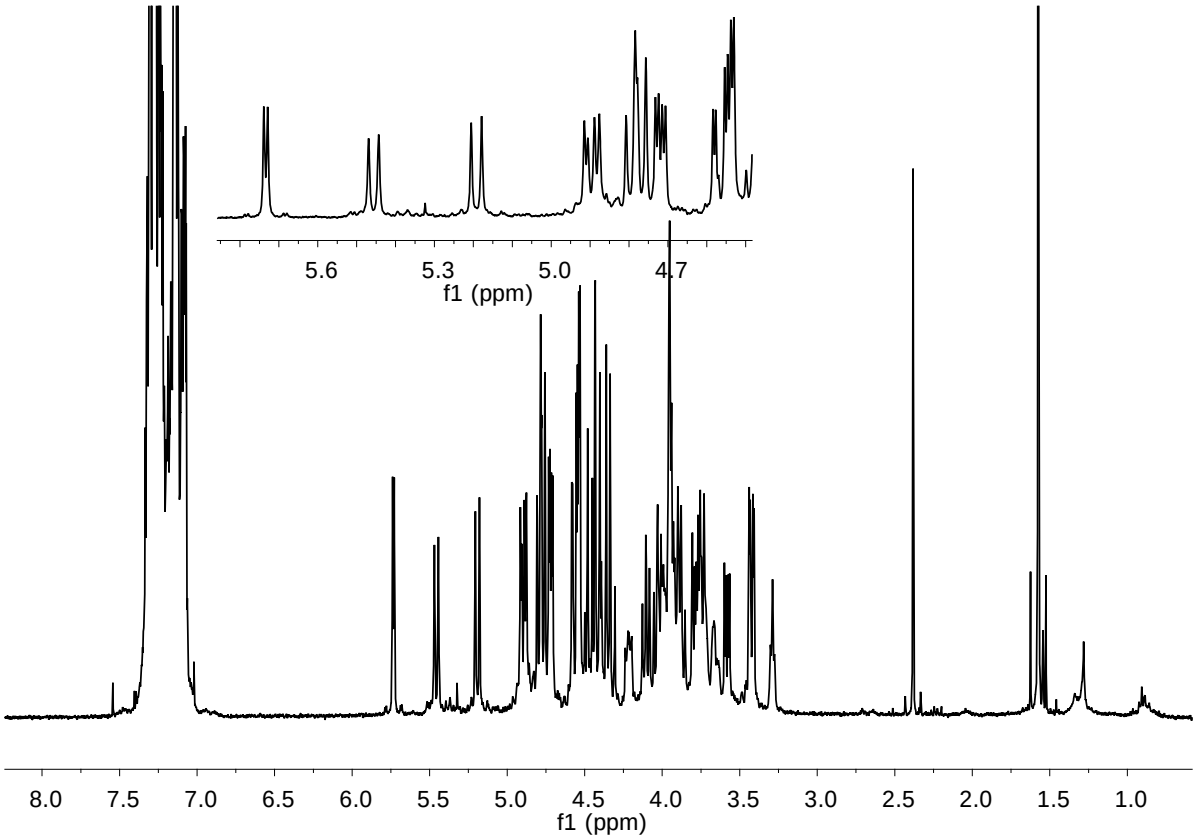
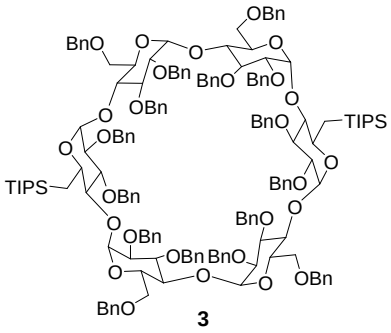
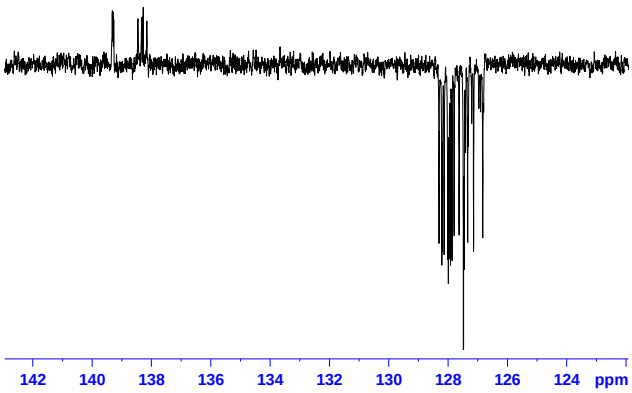


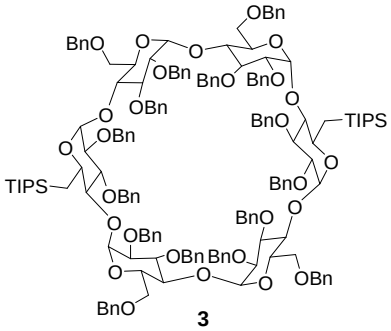
Figure S2. ^{1}H NMR spectrum of crude product **2**



3

^{1}H NMR (500.13 MHz; in $CDCl_3$)





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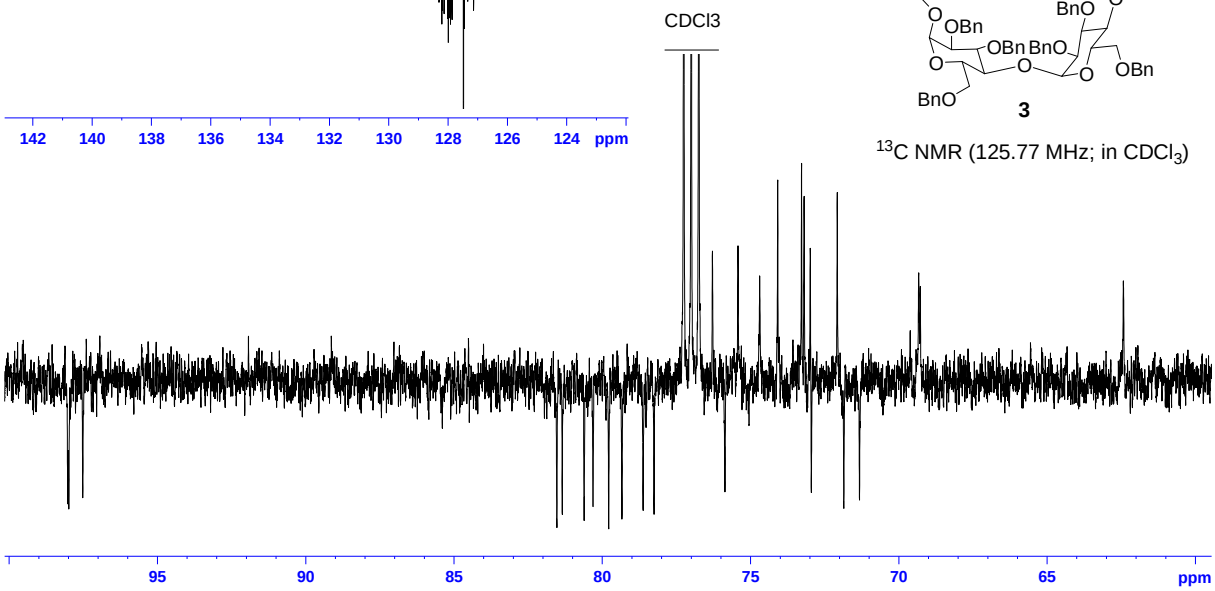
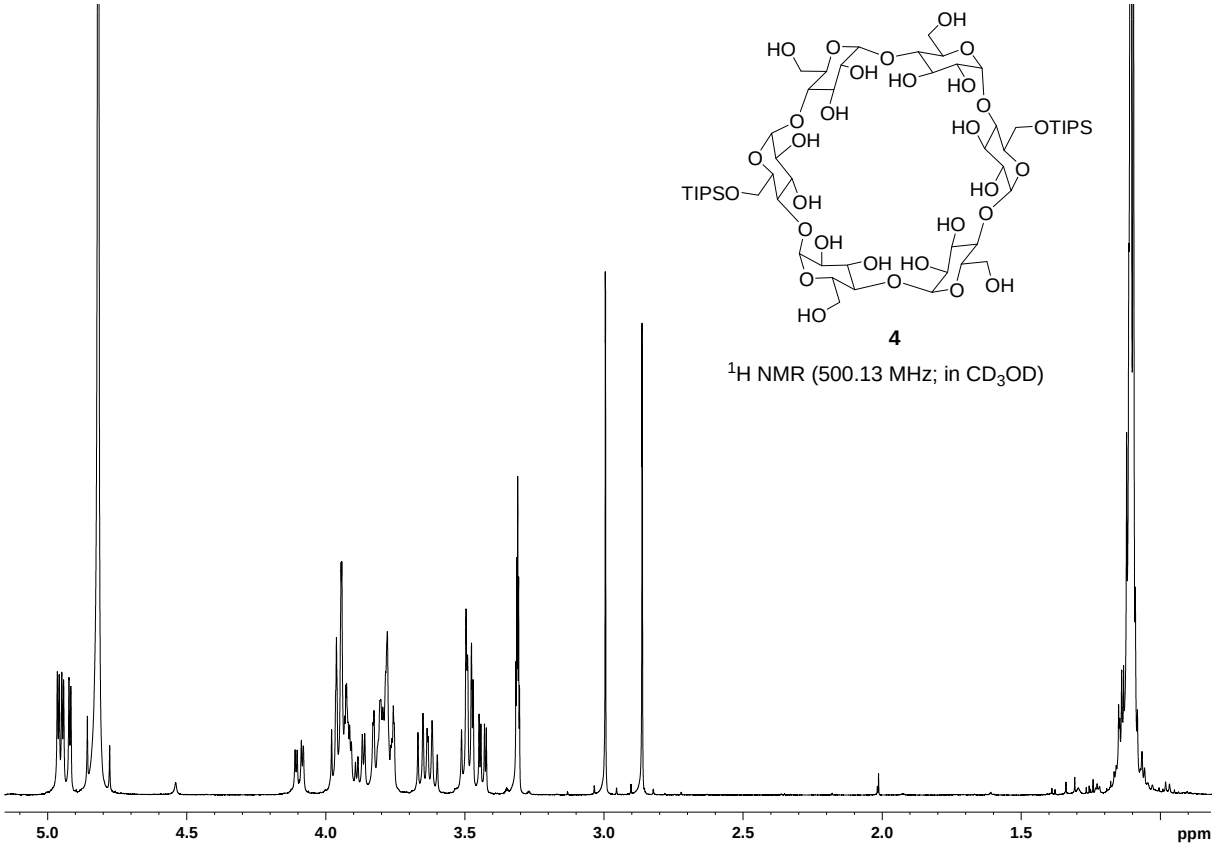
^{13}C NMR (125.77 MHz; in $CDCl_3$)





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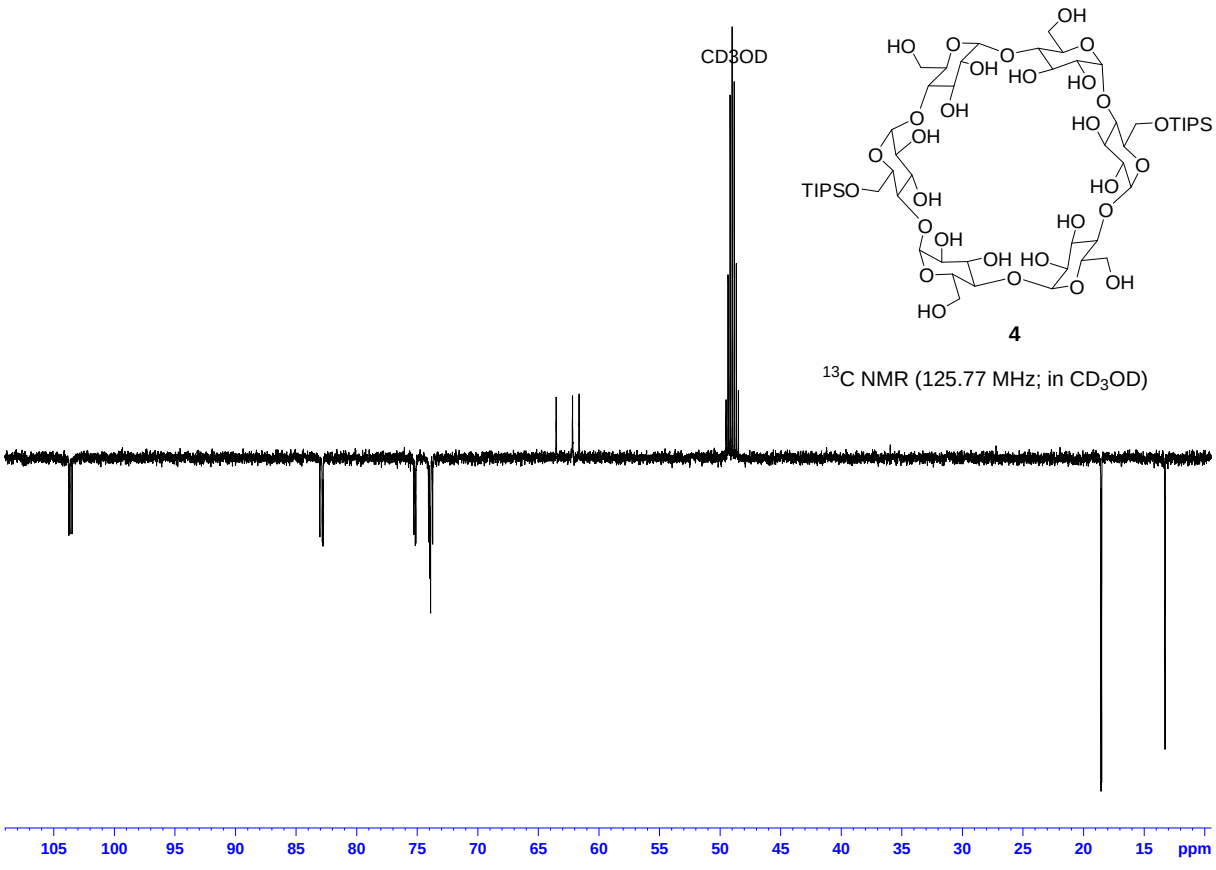
^{1}H NMR (500.13 MHz; in CD_3OD)



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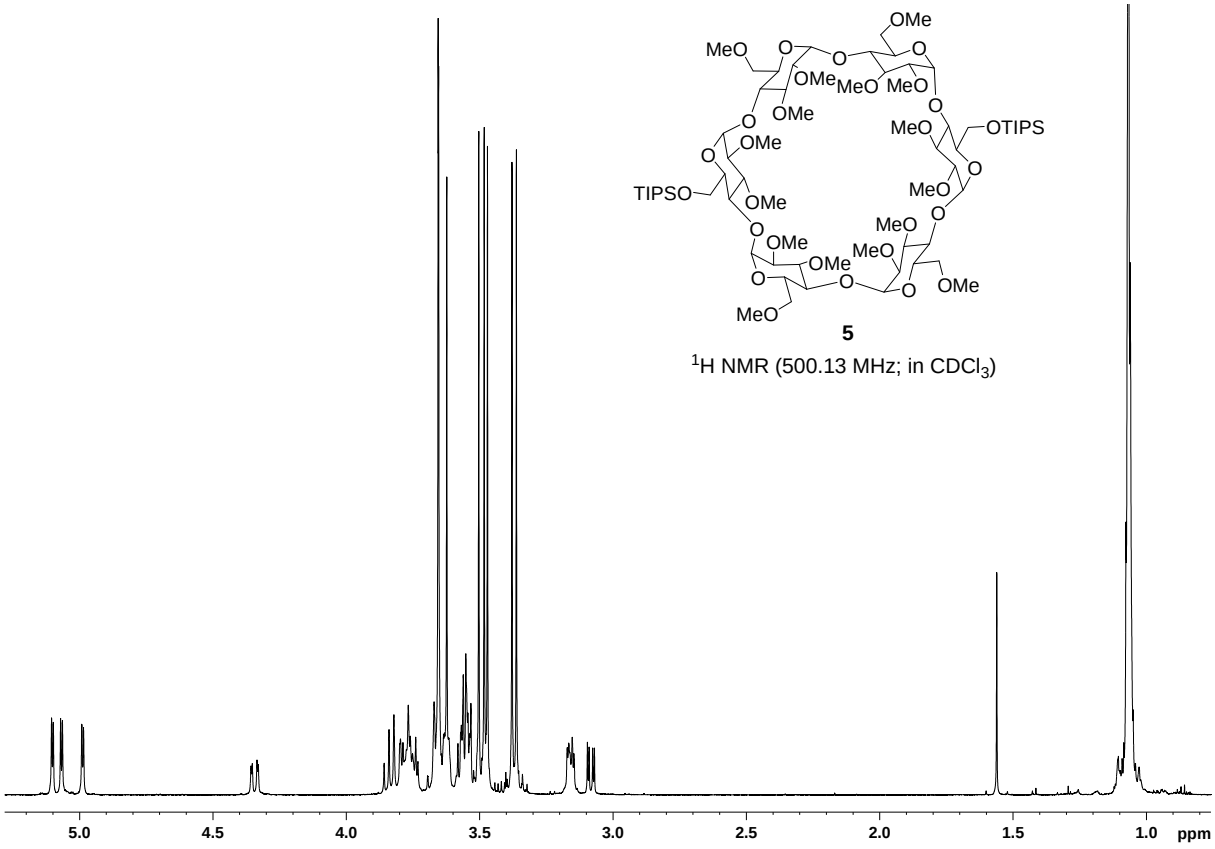
^{13}C NMR (125.77 MHz; in CD_3OD)



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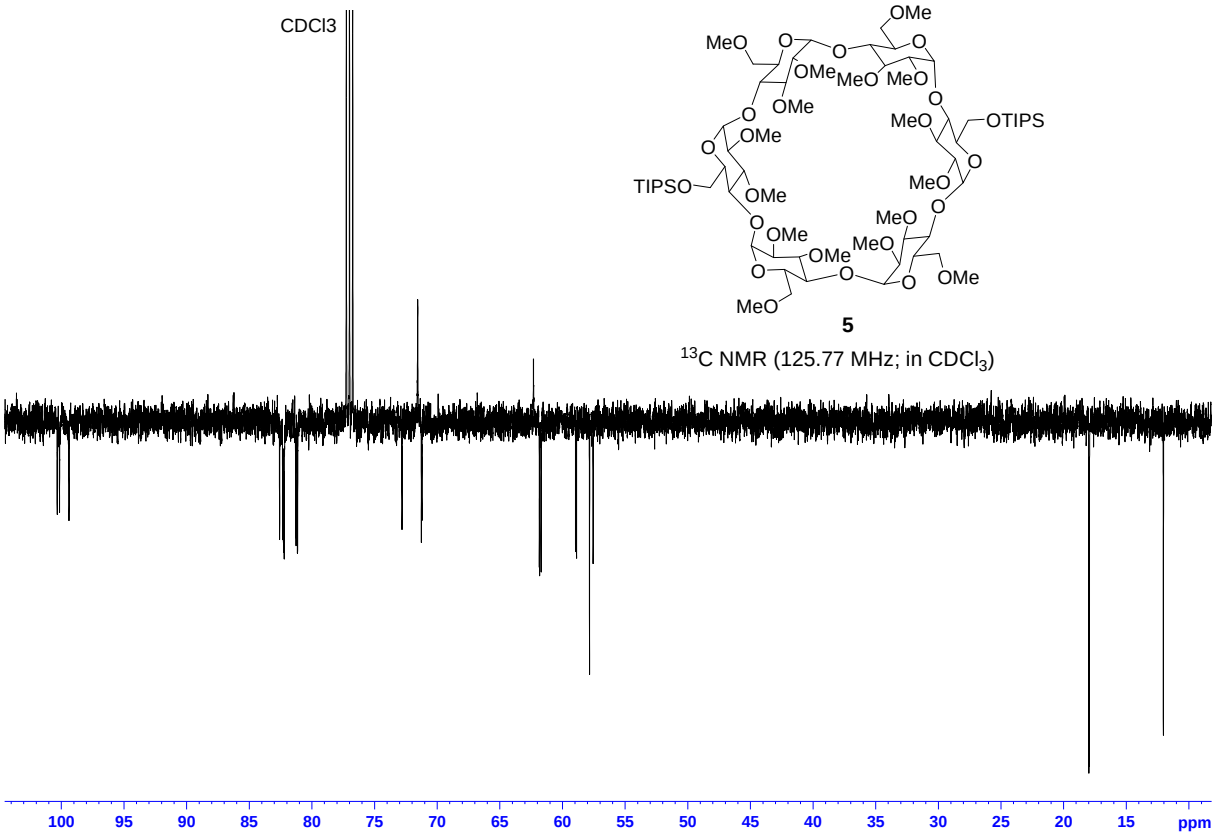
^{1}H NMR (500.13 MHz; in $CDCl_3$)



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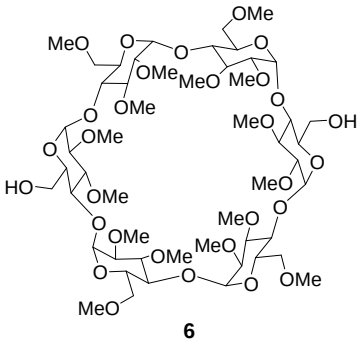
^{13}C NMR (125.77 MHz; in $CDCl_3$)



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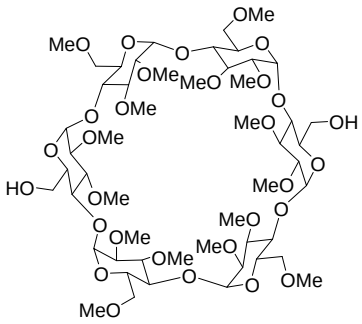

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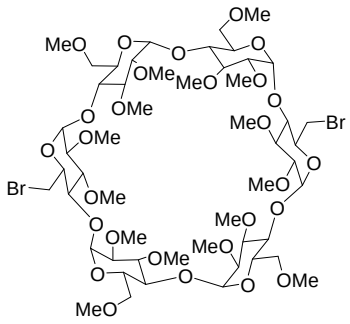
^{13}C NMR (125.77 MHz; in $CDCl_3$)



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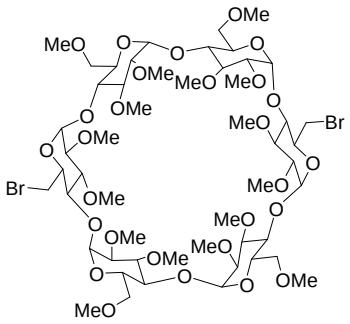
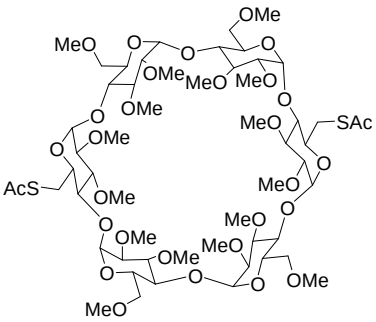
^{1}H NMR (500.13 MHz; in $CDCl_3$)



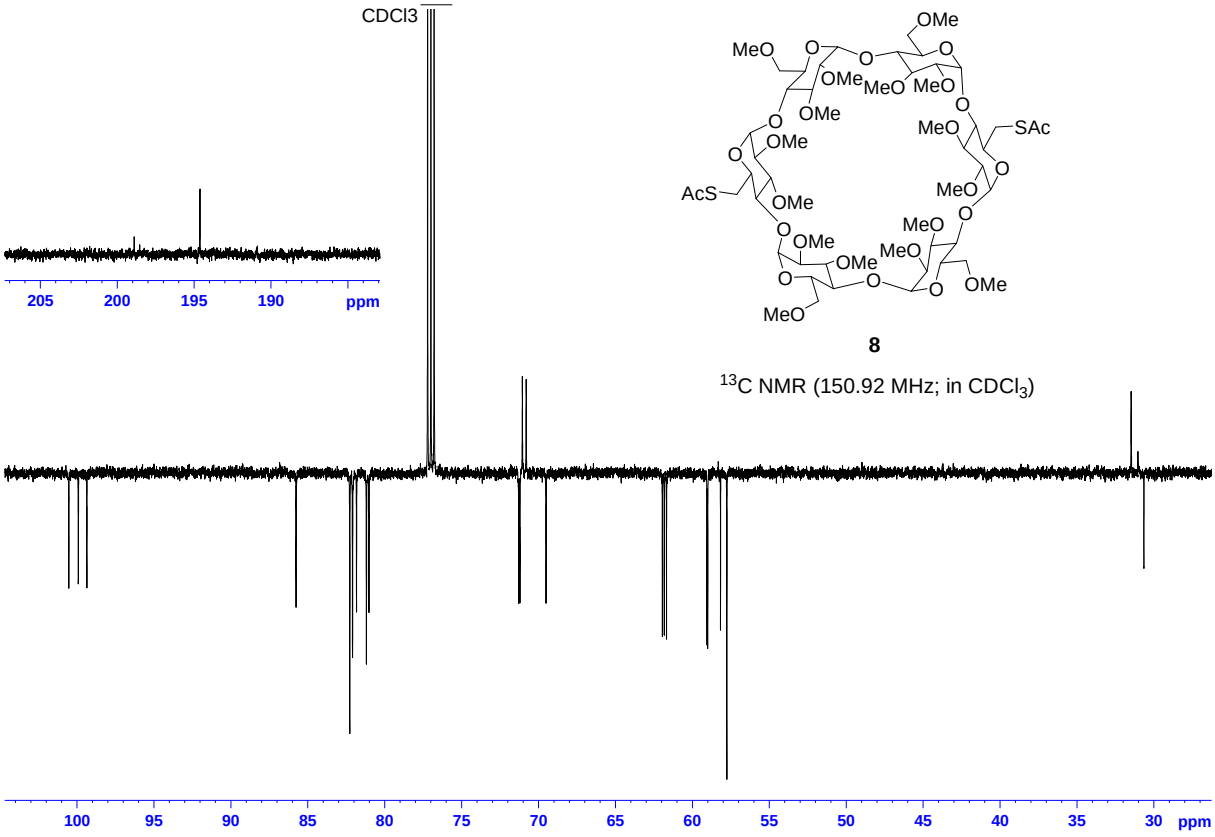
7

^{13}C NMR (125.77 MHz; in $CDCl_3$)



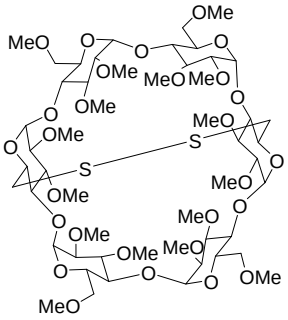
8

^{1}H NMR (600.13 MHz; in $CDCl_3$)



8

^{13}C NMR (150.92 MHz; in $CDCl_3$)



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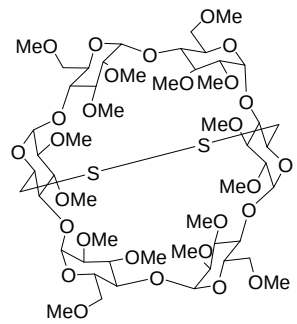
^{1}H NMR (600.13 MHz; in $CDCl_3$)



9

^{13}C NMR (150.92 MHz; in $CDCl_3$)