Supplementary Material

ipso-Bromination of *tert*-butylcalix[4]arenes

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Spectroscopic Data

5,11,17-tribromo-23-*tert*-butylcalix[4]arene **8t**

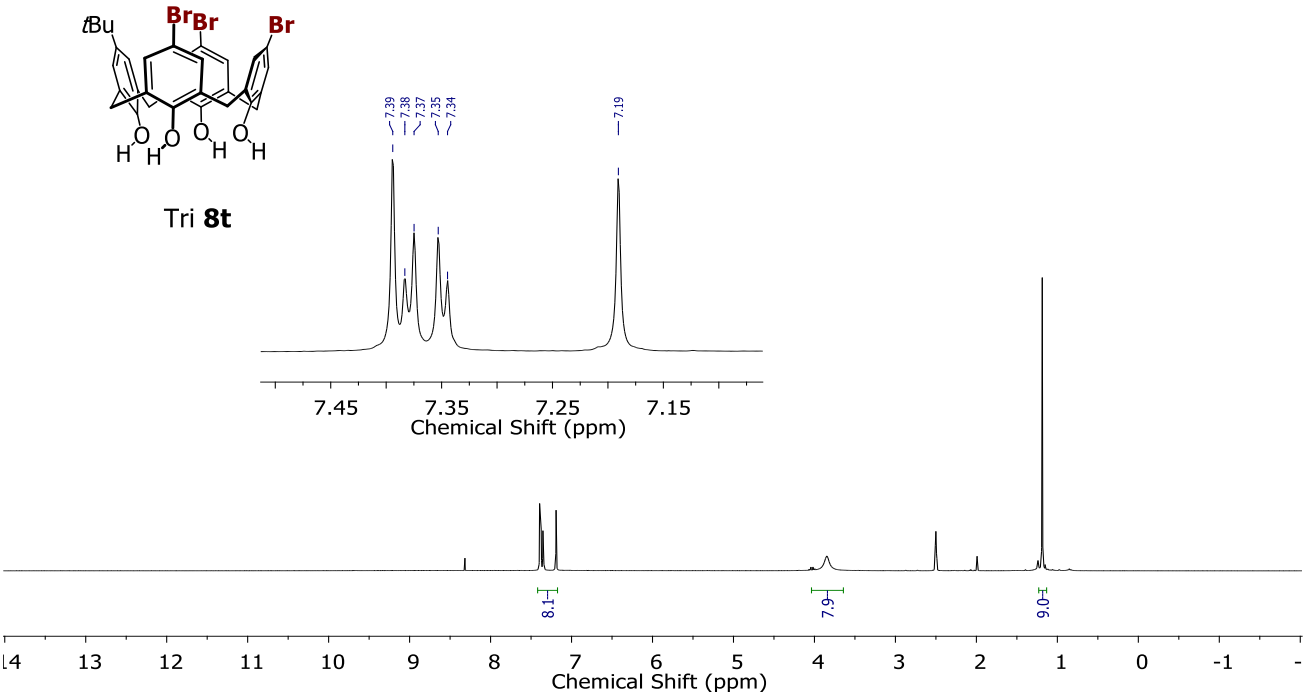

Figure S1. ^{1}H NMR Spectrum (400 MHz) of **8t** in DMSO-d_6

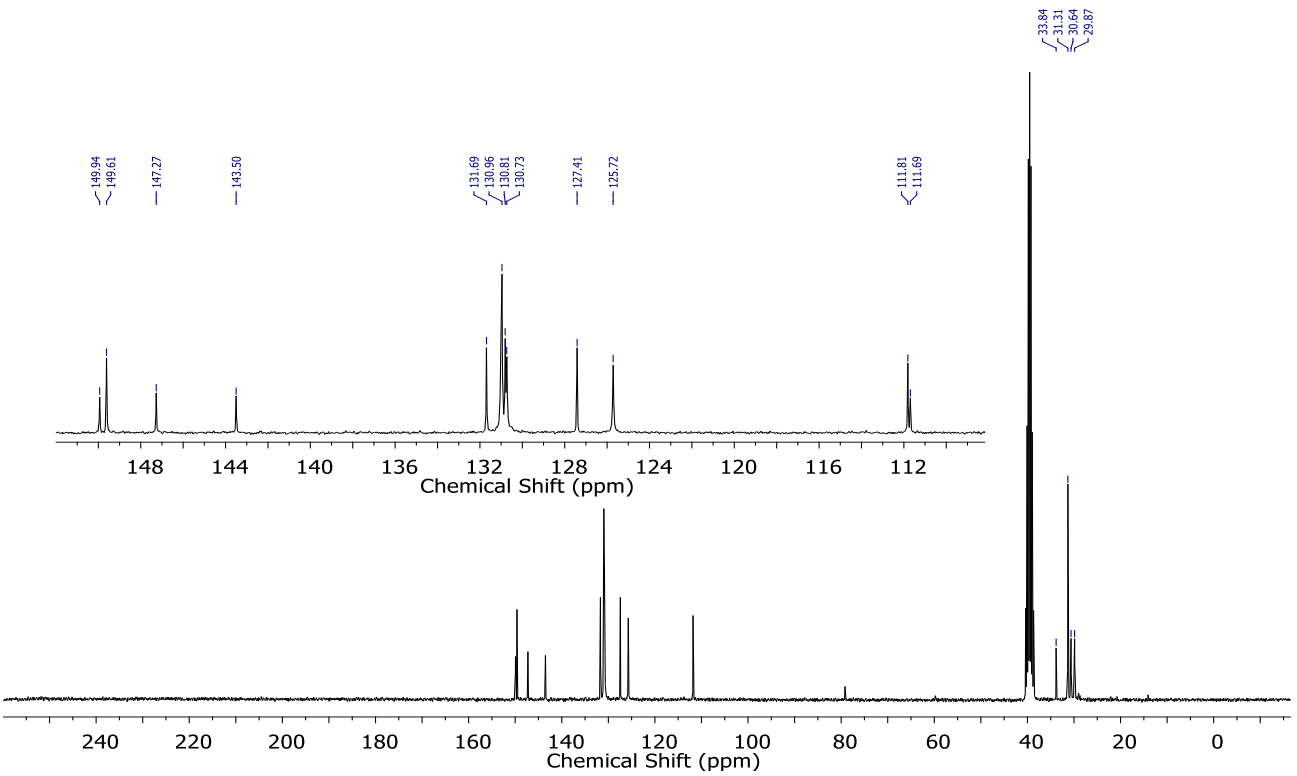

Figure S2. ^{13}C NMR spectrum (101 MHz) of **8t** in DMSO-d_6

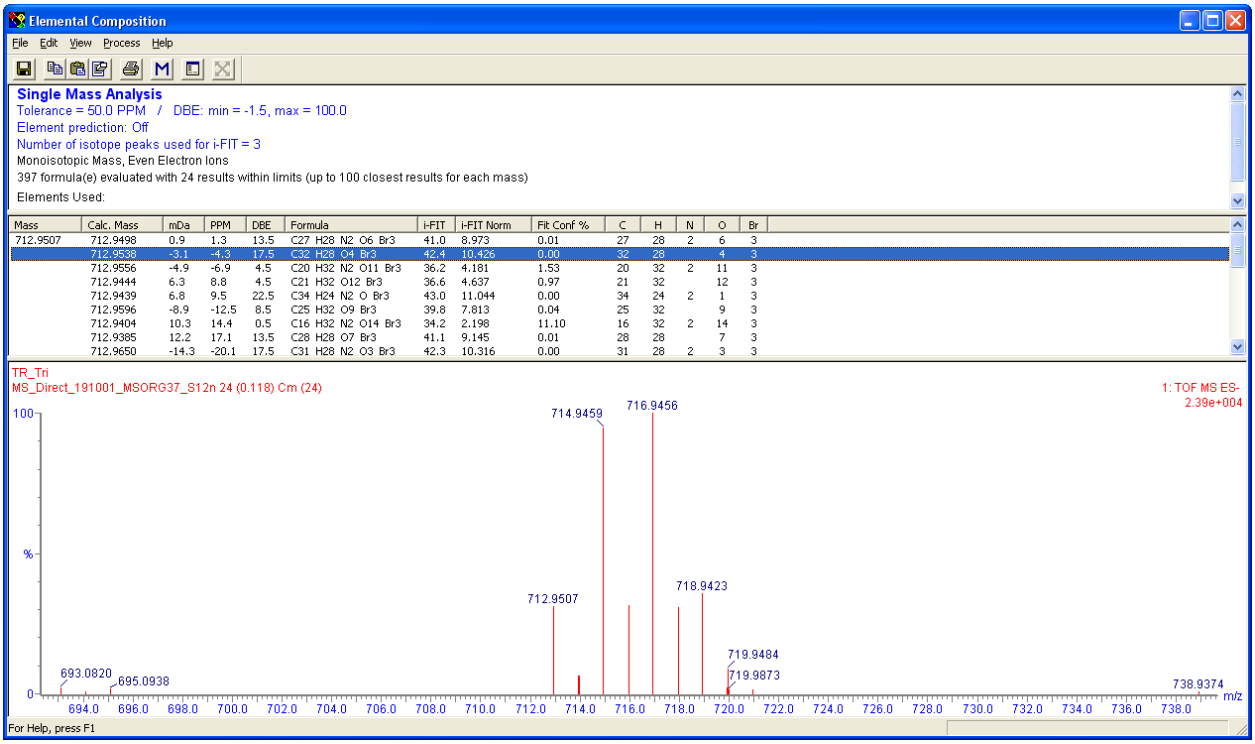

Figure S3. HRMS-ES- for **8t**

5,11,17,23-tetrabromocalix[4]arene **8q**

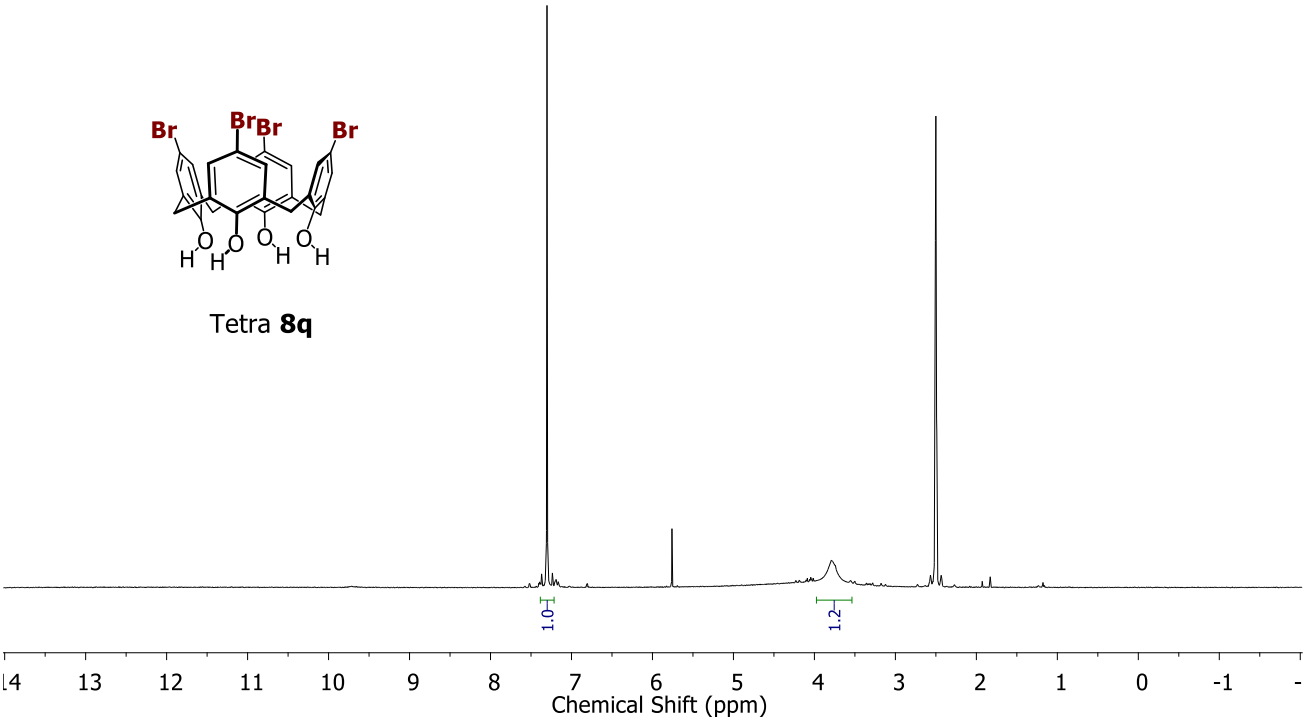

Figure S4. ^{1}H NMR Spectrum (400 MHz) of **8q** in DMSO-d_6

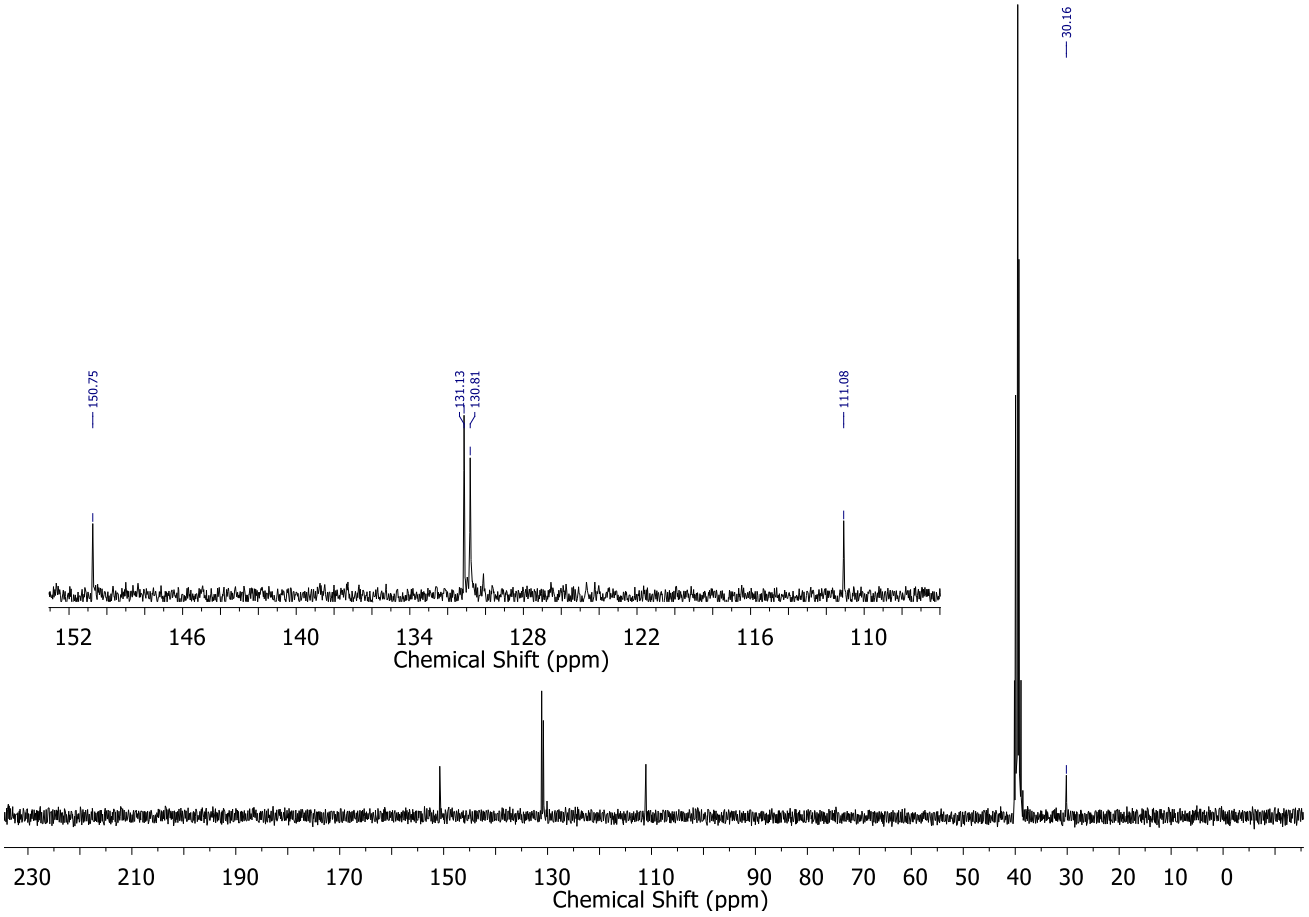

Figure S5. ^{13}C NMR Spectrum (101 MHz) of **8q** in DMSO-d_6

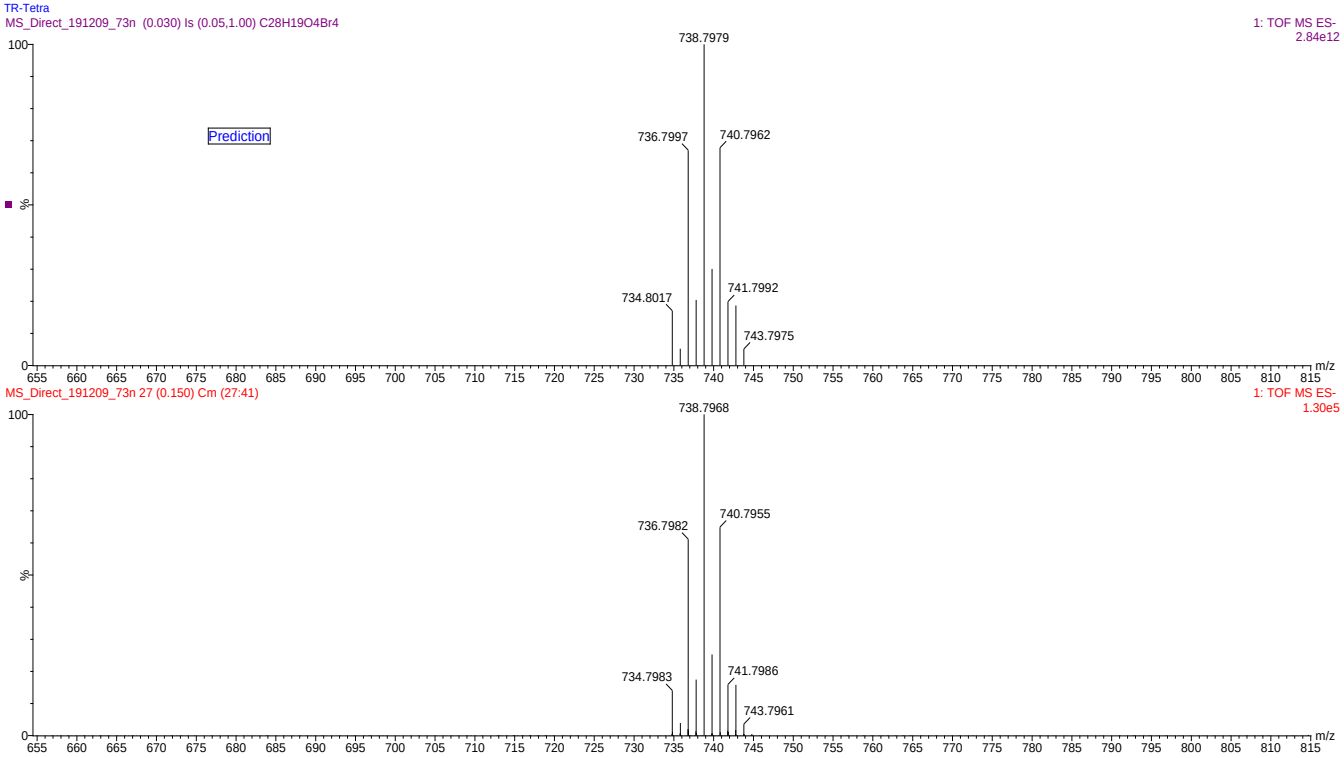

Figure S6. HRMS-ESI– spectrum for **8q**. Predicted (top) and measured (bottom)

^{1}H NMR spectroscopic method for determining the ratio of brominated products.

Figure S7 shows how the signals within the crude ^{1}H NMR spectrum could be identified and correlated to the different brominated products.

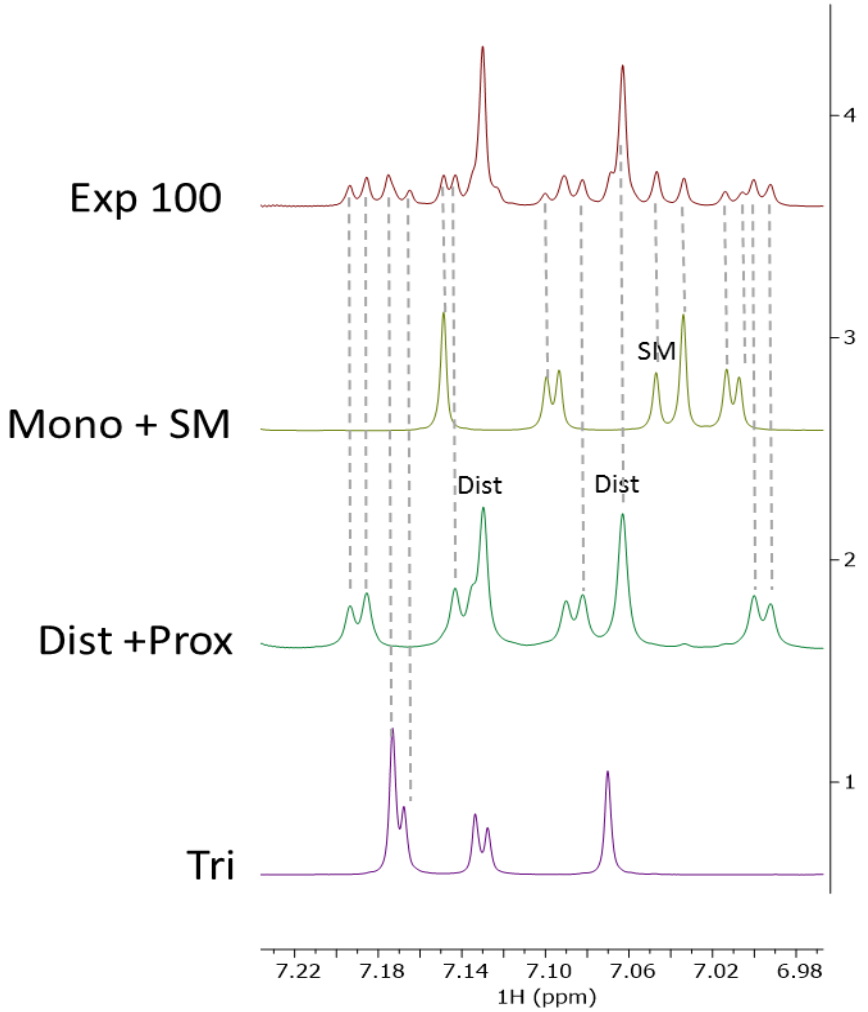

Figure S7. Stacked ^{1}H NMR spectrum showing signals that could be used for % conversion calculations

A typical workflow operated as follows:

1. The crude spectrum was analysed with peak fitting software (MNOVA v12.0.4) to generate fitted spectrum (see Figure S8 for an example for experiment 100).
2. The peak areas could then be extracted and were transferred to an MS Excel spreadsheet for further analysis.
3. Peak areas were then summed and normalised to 1H, and a ratio of these resulted in the relative % yields/conversions being calculated (Figure S9).
4. Errors could be estimated by using the normalised 1H area as a reference. For example, the 11% error (yellow highlight in Figure S9) was arrived at this way:

$$error = \frac{measured - average}{average} = \frac{2556 - 2285}{2285} = 0.11\ or\ 11\%$$

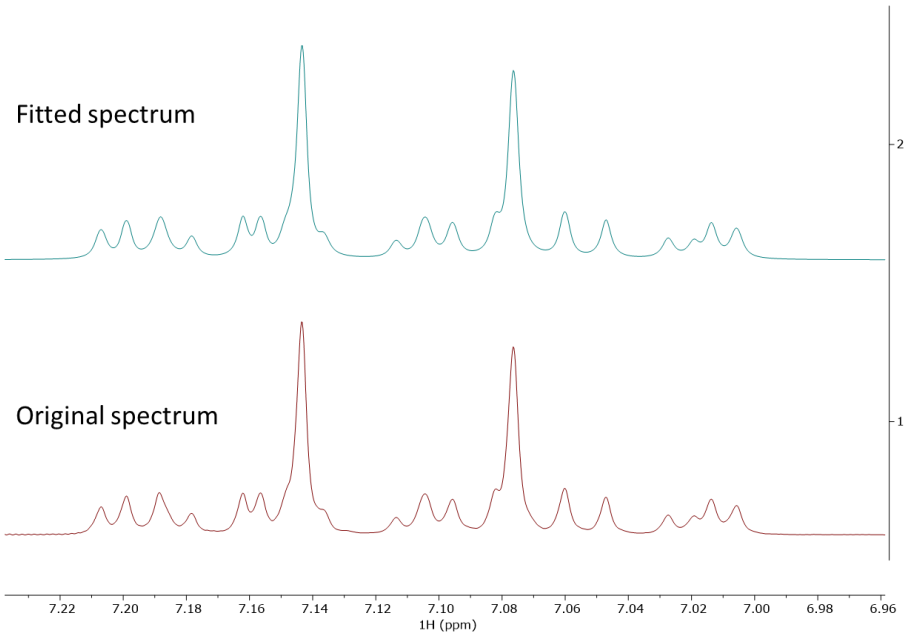

Figure S8. View of original and fitted spectrum for experiment 100 (Table 1, entry 2a)

Collated data from spectrum

Exp 100

#	ppm	Area	Error	Assignment
d	7.20	4188.37	2%	proximal (2)
m	7.18	4666.87	2%	tri (4)
s	7.16	2227.97	3%	mono (2)
part d	7.15	2286.74	7%	proximal (1)
m	7.14	13058.36	8%	distal (4) + tri (2) + proximal (1)
part d	7.13	1228.19	7%	mono (1)
m	7.11	3009.90	9%	mono (1) + proximal (1)
d	7.10	2242.50	5%	proximal (1)
m	7.08	13130.45	9%	distal (4) + tri (2)
s	7.06	2792.65		SM
s	7.05	2361.81	3%	mono (2)
d	7.02	2555.70	11%	mono (2)
d	7.01	4388.86	3%	proximal (2)

Raw data from spectrum

#	ppm	Area
1	7.2072	1891.849
2	7.1991	2296.525
3	7.1884	3220.482
4	7.1785	1446.388
5	7.1622	2227.969
6	7.1565	2286.743
7	7.1436	13058.355
8	7.1136	1228.188
9	7.1045	3009.902
10	7.0958	2242.501
11	7.0819	2443.839
12	7.0765	10686.611
13	7.0602	2792.652
14	7.0472	2361.808
15	7.0275	1322.727
16	7.0194	1232.969
17	7.0137	2269.177
18	7.0058	2119.678

		total area	protons	area/H	%	% error
	Starting Material	2792.652	8	349.082	5%	
	Mono	9141.062	8	1142.633	16%	1%
	Distal	19235.192	8	2404.399	33%	3%
	Proximal	14888.187	7	2126.884	30%	1%
	Tri	9493.599	8	1186.700	16%	1%
	Total Area			7209.697		

< 5%	
5-9%	
10-14%	
15-19%	
> 20%	

Figure S9. MS Excel processing of data for experiment 100

Raw data for Table 1 in manuscript.

Table 1 Entry	Exp Code	Calix Type	Calix solublity	Mass Calix (mg)	mmol Calix	Solvent	Vol Solvent (mL)	Calix Conc. (mM)	Br2 (eq)	mmol Br2	Temp (°C)	Light	Time (hours)	Crude Recovery	SM	Mono	Distal	Proximal	Tri	Tetra
1	61	R	A	200	0.31	DCM	16	19	3	0.92	Room	Yes	20	108%			12%		88%	
1	68	R	A	200	0.31	DCM	16	19	3	0.92	Room	Yes	24	114%	2%		33%	23%	42%	
1	246	R	A	100	0.15	DCM	8	19	3	0.46	Room	Yes	24	108%	3%	49%	25%	19%	4%	
1	250	R	U	100	0.15	DCM	8	19	3	0.46	Room	Yes	20	92%	21%	54%	14%	11%		
2	100	R	A	100	0.15	DCM	8	19	3	0.46	30	Yes	19	100%	5%	16%	33%	30%	16%	
2	103	R	A	100	0.15	DCM	8	19	3	0.46	30	Yes	17	106%			34%	19%	47%	
2	106	R	A	100	0.15	DCM	8	19	3	0.46	30	Yes	19	112%			30%	13%	57%	
3	110	R	A	100	0.15	DCM	8	19	3	0.46	30	No	19	107%			33%	9%	58%	
3	111	R	A	100	0.15	DCM	8	19	3	0.46	30	No	19	108%			32%	18%	50%	
4	114	R	A	100	0.15	DCM	8	19	3	0.46	30	No	48	100%			27%		68%	5%
4	115	R	A	100	0.15	DCM	8	19	3	0.46	30	No	48	100%			28%		68%	4%
5	118	R	A	100	0.15	DCM	8	19	4	0.62	30	No	48	100%			16%		68%	16%
5	119	R	A	100	0.15	DCM	8	19	4	0.62	30	No	48	107%			11%		70%	19%
6	281	R	A	100	0.15	DCM	8	19	1	0.15	30	No	48	92%	43%	49%	8%			
6	282	R	A	100	0.15	DCM	8	19	1	0.15	30	No	48	102%	47%	47%	6%			
7	283	R	A	100	0.15	DCM	8	19	2	0.31	30	No	48	104%	2%	49%	28%	21%		
7	284	R	A	100	0.15	DCM	8	19	2	0.31	20	No	48	98%	1%	45%	26%	23%	5%	
8	116	R	A	100	0.15	DCM	8	19	10	1.54	30	No	23.5	110%						100%
8	117	R	A	100	0.15	DCM	8	19	10	1.54	30	No	23.5	145%					14%	86%
8	123	R	A	100	0.15	DCM	8	19	10	1.54	30	No	24	119%					16%	84%
9	153	R	A	100	0.15	DCM	8	19	10	1.54	30	No	72	119%					24%	76%
10	155	R	A	100	0.15	DCM	8	19	10	1.54	Reflux	No	24	41%						100%
10	161	R	A	500	0.77	DCM	40	19	10.2	7.86	Reflux	No	24	113%						100%
11	157	R	A	100	0.15	DCM	8	19	10	1.54	40 MV	No	24	118%						100%
11	261	R	A	300	0.46	DCM	24	19	10	4.62	40 MV	No	24	107%						100%
11	268	R	A	1000	1.54	DCM	80	19	10	15.4	40 ST	No	24	119%						100%
12	218	R	A	100	0.15	DCM	8	19	10	1.54	60 MV	No	12	108%					32%	68%
12	223	R	A	200	0.31	DCM	16	19	10	3.08	60 MV	No	12	137%						100%
12	227	R	A	50	0.08	DCM	4	19	10	0.77	60 MV	No	12	114%					18%	82%