Supplementary Material (ESI) for Chemical Communications

Supplementary Information for *Chem. Commun.*

Macrocyclic aromatic tetrasulfonamides with a stable cone conformation

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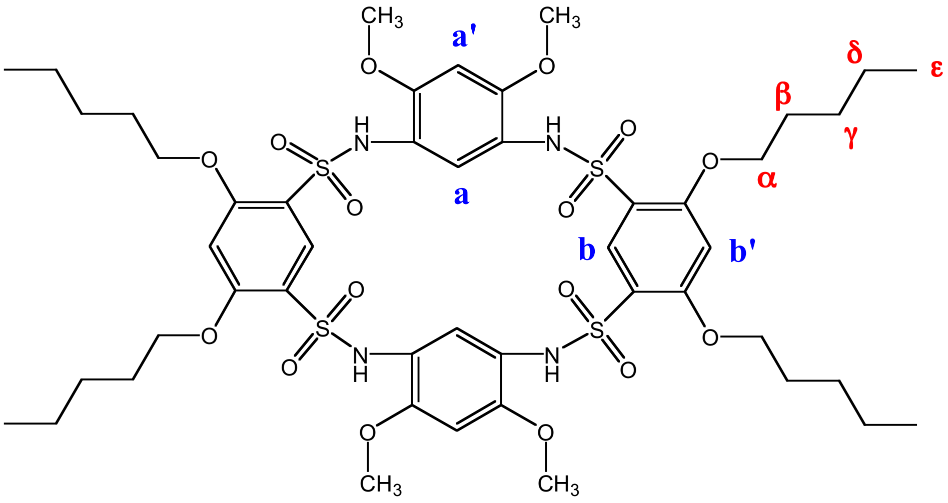
Experimental procedures

NMR analyses were carried out on Varian INOVA 500 spectrometer (500 MHz). Tetramethylsilane (TMS) or deuterated N, N-dimthyl formamide (DMF-d_7) was used as the internal standard for ^{1}H NMR and the deuterated solvent ($CDCl_3$) as standard for ^{13}C NMR. Chemical shifts are reported in ™ ppm values downfield from tetramethylsilane and *J* values are reported in Hz.

General procedure for preparing macrocycles 4. 1,3-Diamino-4,6-dimethoxybenzene (2.19mmol) was dissolved in CH_2Cl_2 (15mL) to give solution A. 4, 6-Dialkoxybenzene-1, 3-disulphonyl chloride was dissolved in CH_2Cl_2 (15mL) to give solution B. Solution A, solution B and triethylamine (4.38 mmol) were added at the same time to a flask at around –12 ºC. The reaction mixture was stirred until it gradually warmed up to room temperature (4-6 hrs), and was then heated and refluxed for 12-24 hrs. The reaction was quenched by addition of acetyl chloride followed by methanol. After evaporating the solvent, the crude product was washed with methanol, acetone, THF, and was then recrystallized with DMF to give the pure products as white solids.

I. NMR spectra of *4a-4d*



Compund **4b**

Table 1 Chemical shift of compound **4b** in DMF-d_6

Temp	Ar					Alkyl					
	b	a	b’	a’	OMe	α	β	γ	δ	ε	NH
60^0C	7.799	7.464	7.130	6.435	3.544	4.458	1.997	1.564	1.432	0.930	7.647
50^0C	7.801	7.460	7.139	6.438	3.546	4.462	2.001	1.562	1.430	0.930	7.693
30^0C	7.803	7.453	7.156	6.443	3.548	4.466	2.008	1.556	1.434	0.929	7.793
20^0C	7.806	7.449	7.164	6.445	3.550	4.469	2.013	1.553	1.431	0.929	7.857
0^0C	7.812	7.440	7.179	6.448	3.553	4.472	2.021	1.544	1.416	0.927	8.005
-10^0C	7.815	7.436	7.186	6.449	3.555	4.474	2.028	1.538	1.421	0.927	8.089
-20^0C	7.819	7.431	7.192	6.448	3.555	4.475	2.032	1.575	1.417	0.925	8.181
$\Delta\delta$*	0.02	0.033	0.062	0.013	0.011	0.017	0.035	0.011	-0.0015	–0.0005	0.534

* $\Delta\delta = \delta(-20^0\text{C}) - \delta(60^0\text{C})$

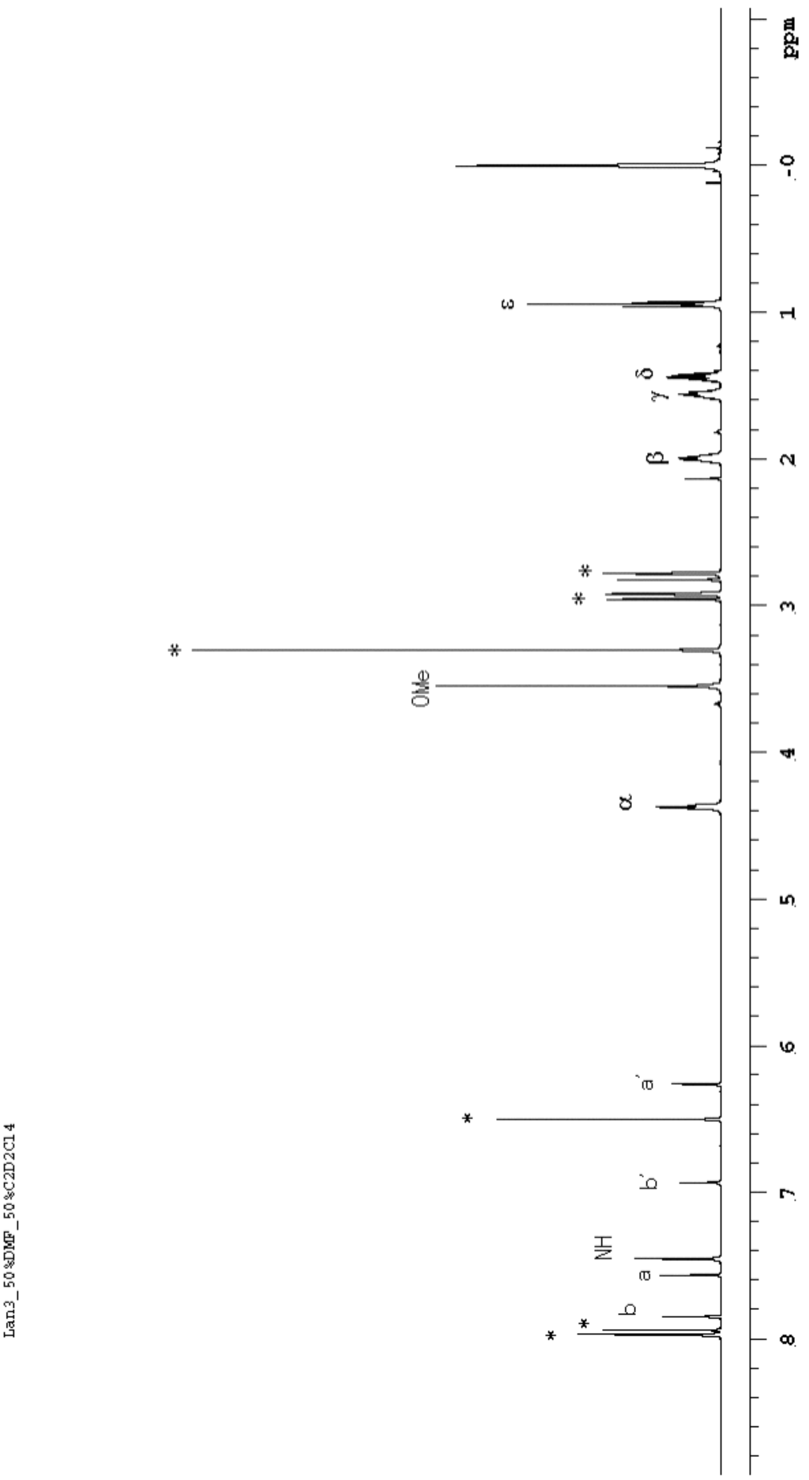


Fig.1 ^{1}H NMR spectrum of compound **4b** (R=-n-C_5H_{11}) in 50%DMF-d_7-50%$CDCl_2CDCl_2$ at 294 K (* from solvents).

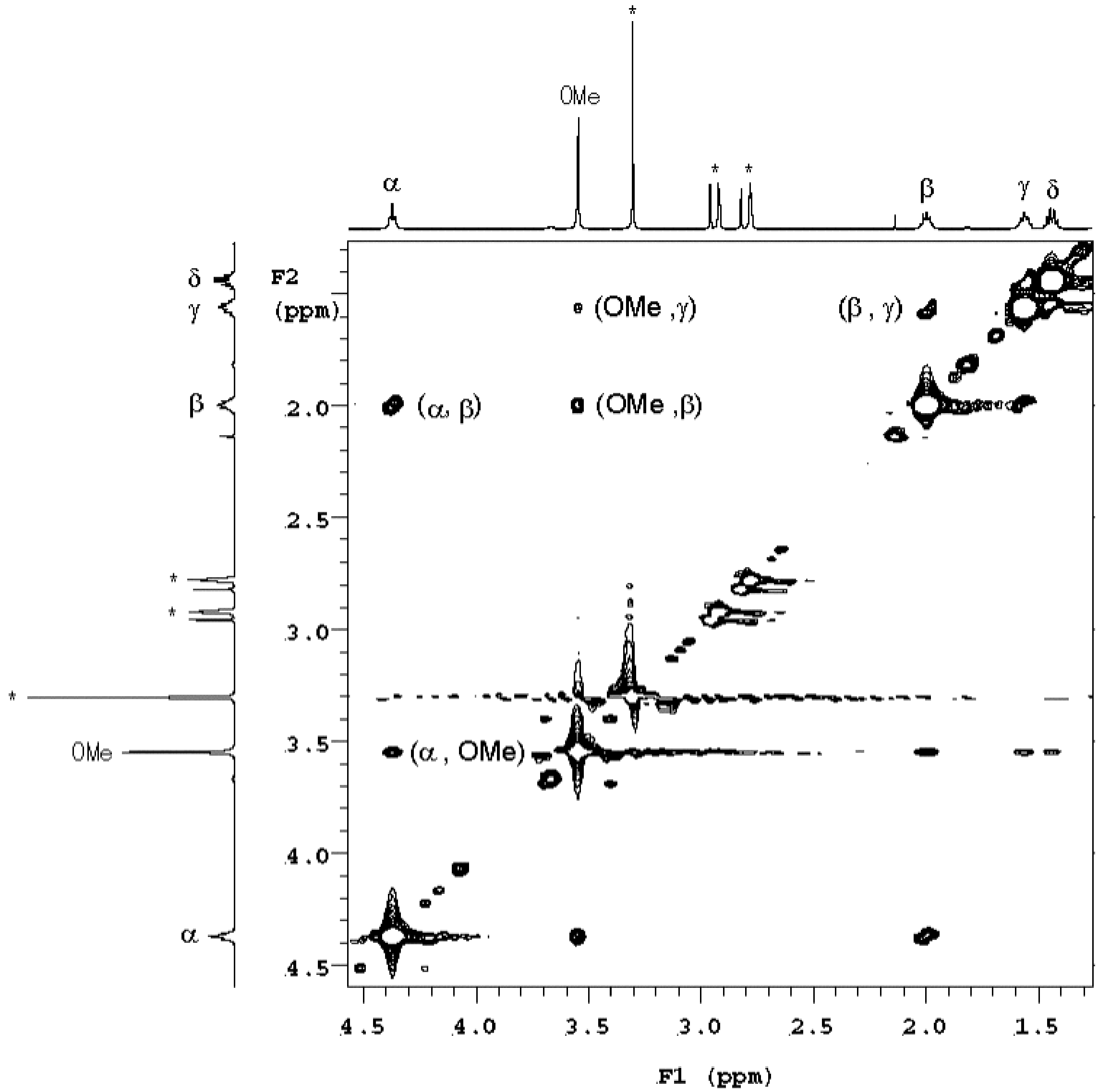


Fig.2 Partial 2D NOE spectrum of compound **4b** (R=-n-C_5H_{11}) in 50%DMF-d_7-50%$CDCl_2CDCl_2$ at 294 K (* from solvents).

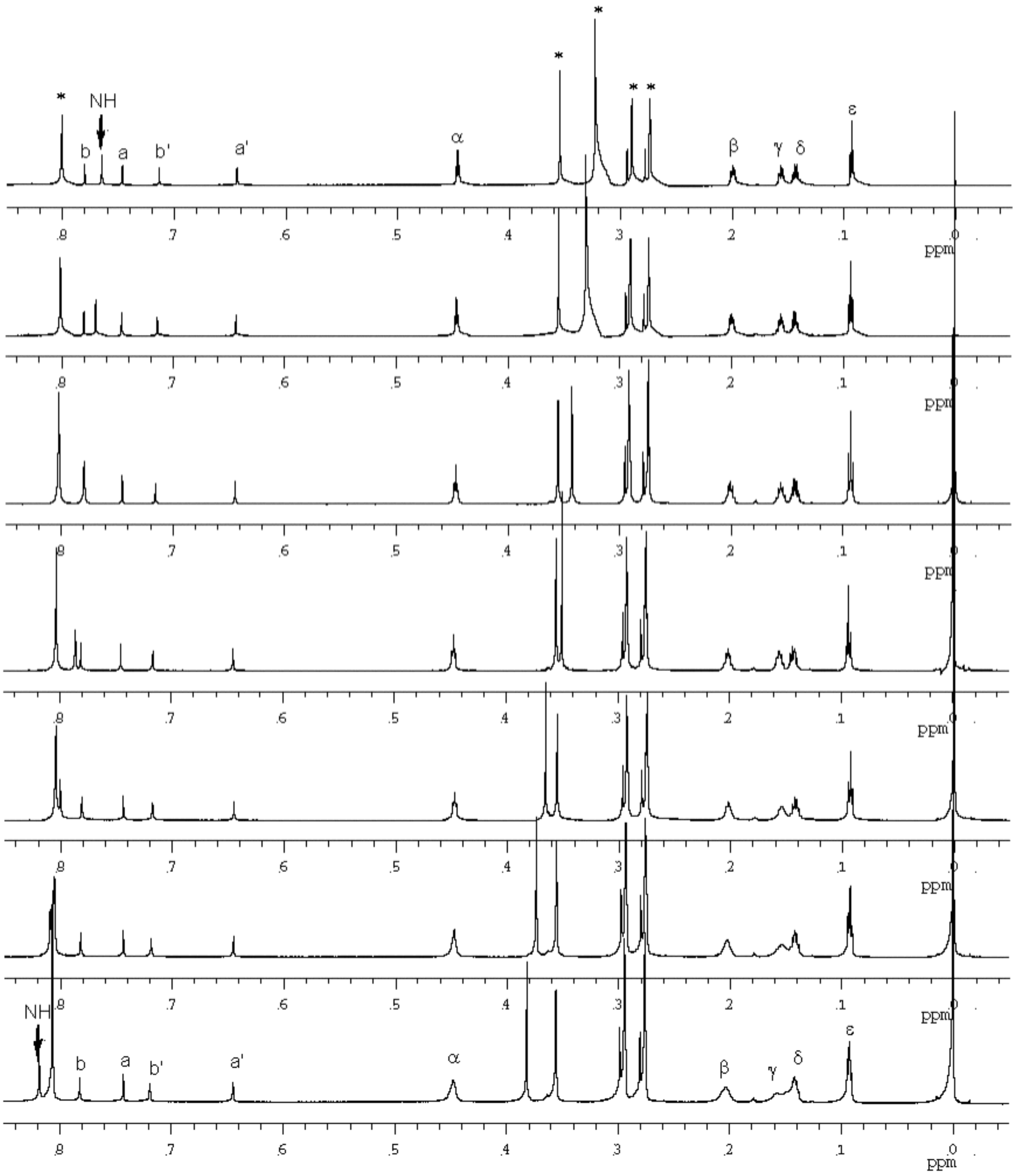


Fig.3 Variable temperature 1D NMR spectra of compound **4b** (R= -n-C_5H_{11}) in DMF-d_7 at 294 K (* from solvents).

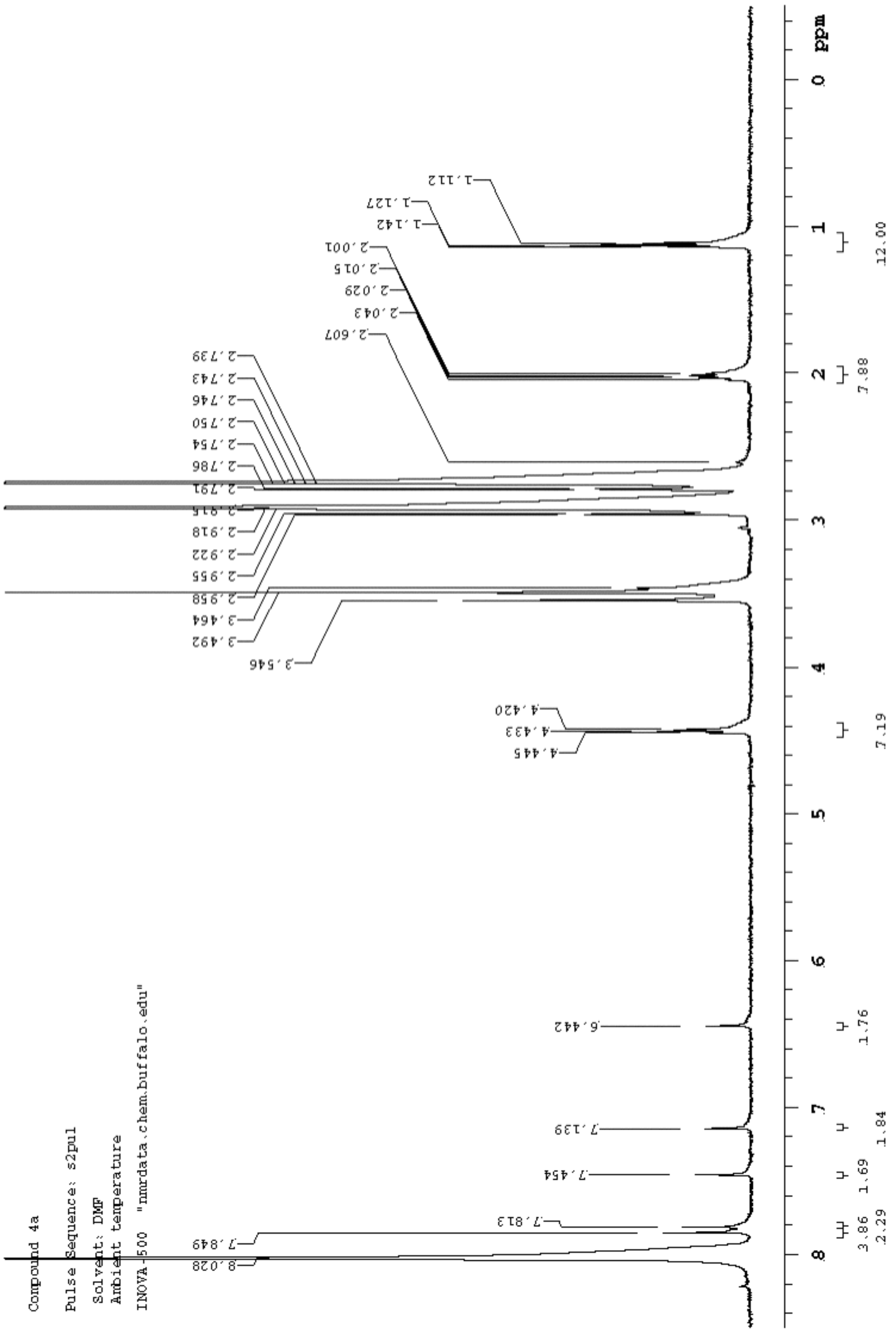


Fig.4 ^{1}H NMR spectrum of compound **4a** (R= -n-C_3H_7) in DMF-d_7 at 294 K.

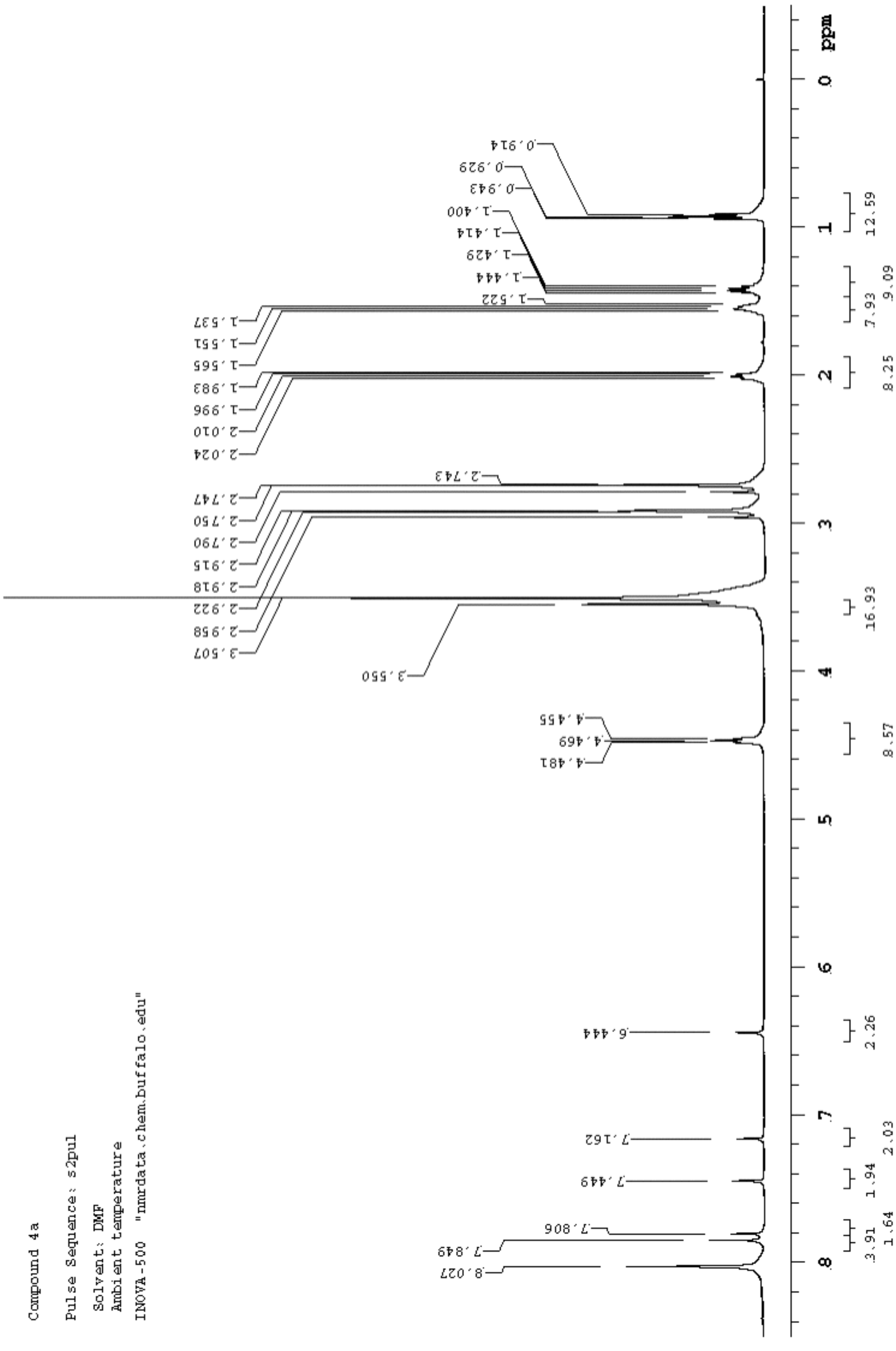


Fig.5 ^{1}H NMR spectrum of compound **4b** (R= -n-C_5H_{11}) in DMF-d_7 at 294 K.

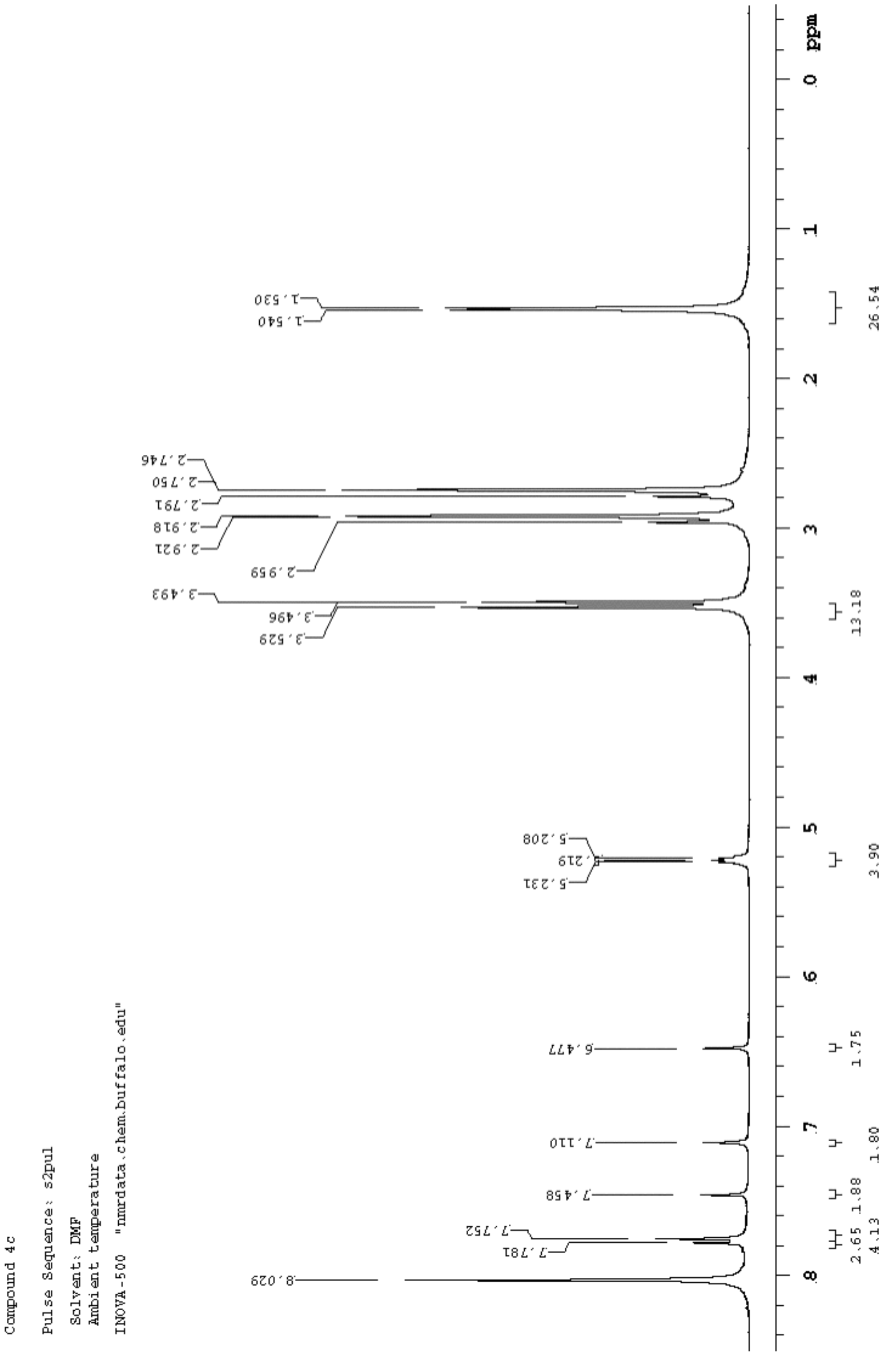


Fig.6 ^{1}H NMR spectrum of compound **4c** (R= -i-C_3H_7) in DMF-d_7 at 294 K.

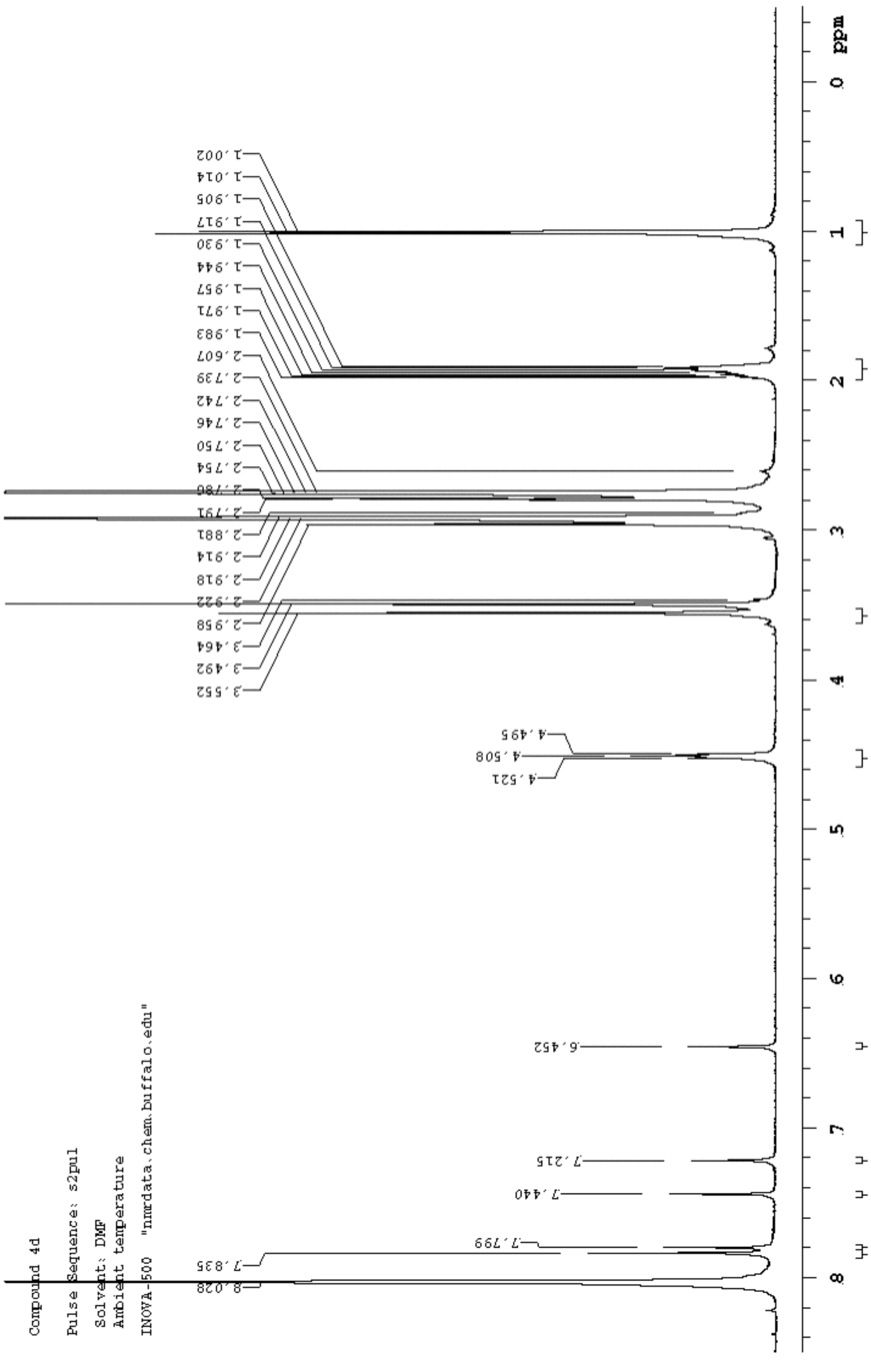


Fig.7 ^{1}H NMR spectrum of compound **4b** (R=n-C_5H_{11}) in DMF-d_7 at 294 K.

II. MALDI-TOF spectra of *4a-4d*

Sample was prepared by post-mix method. Dithranol (2 μl) dissolved in CH_2Cl_2 (20 g/L) was spotted on the target and air dried, then analyte solution in DMF was spotted on the thin layer of matrix. MALDI TOF MS spectra were recorded on a Bruker Biflex IV MS spectrometer with reflector mode.

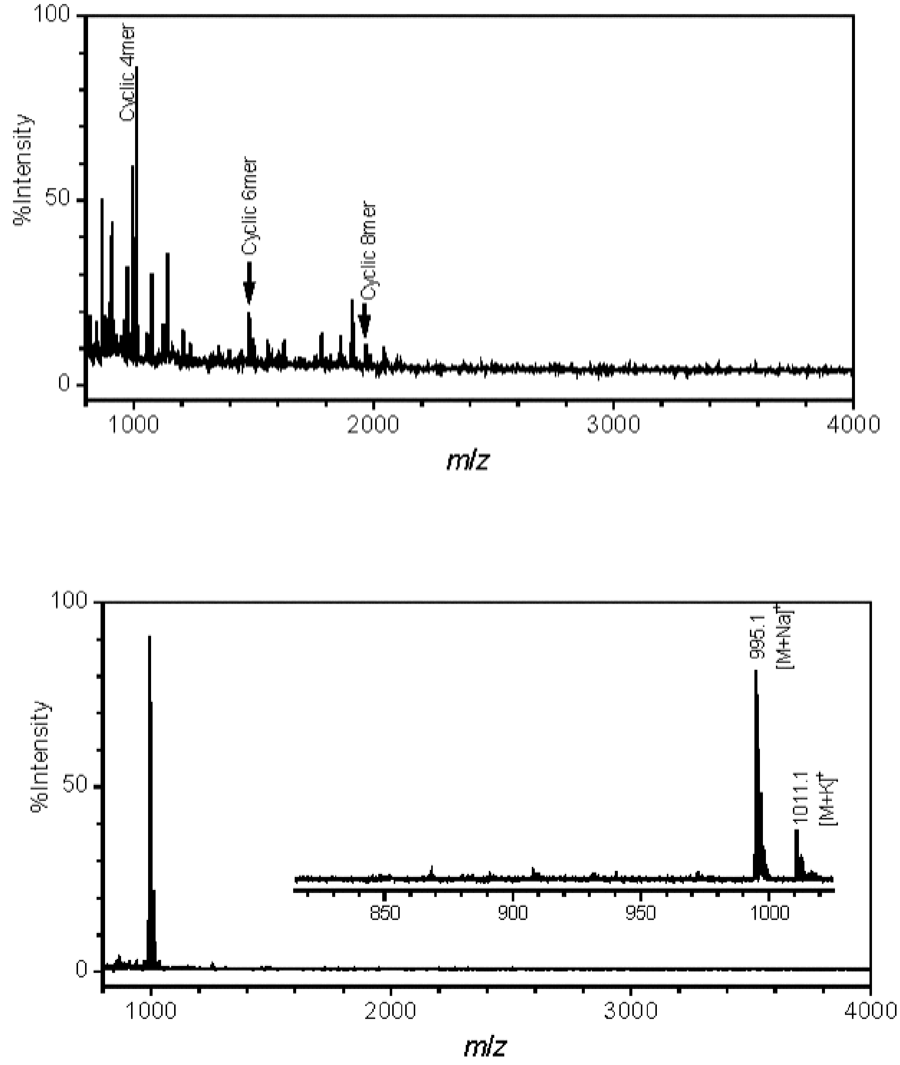


Fig.8 MALDI TOF MS Spectra of **4a** (R= -*n*-C_3H_7). (Upper: crude, Lower: Purified).

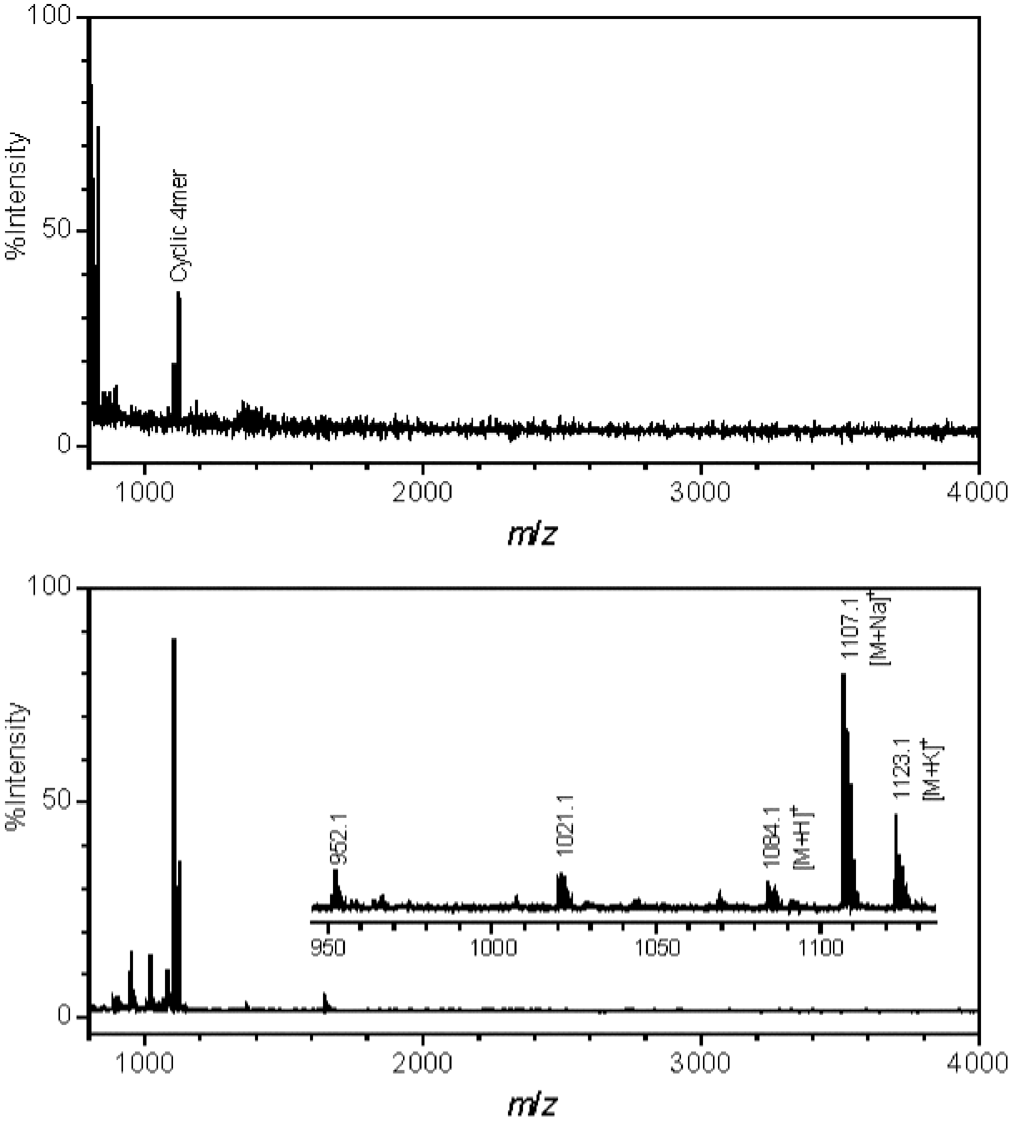


Fig.9 MALDI TOF MS Spectra of **4b** (R= -*n*-C_5H_{11}). (Upper: crude, Lower: Purified).

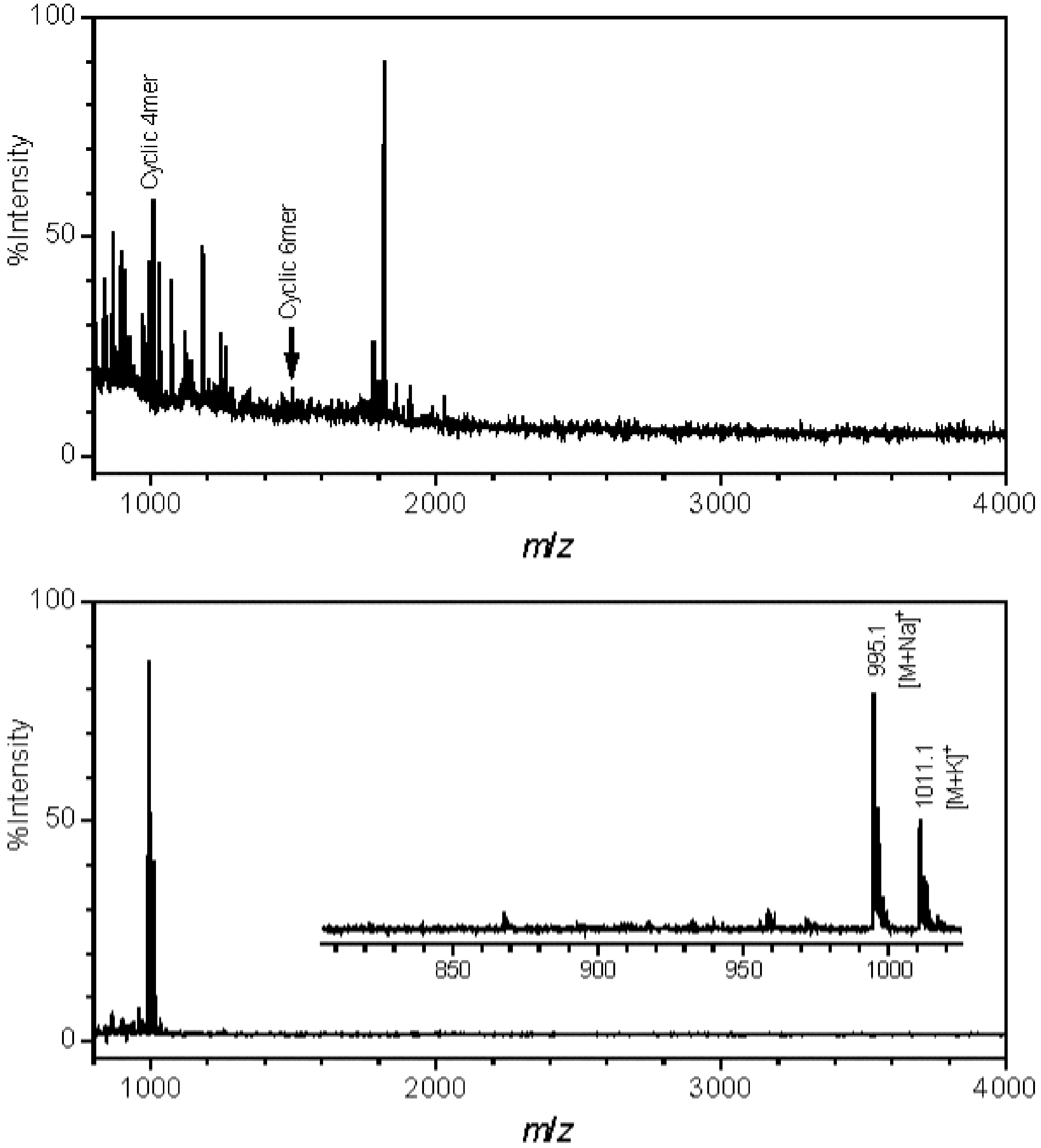


Fig.10 MALDI TOF MS Spectra of **4c** (R= -*i*-C_3H_7). (Upper: crude, Lower: Purified).

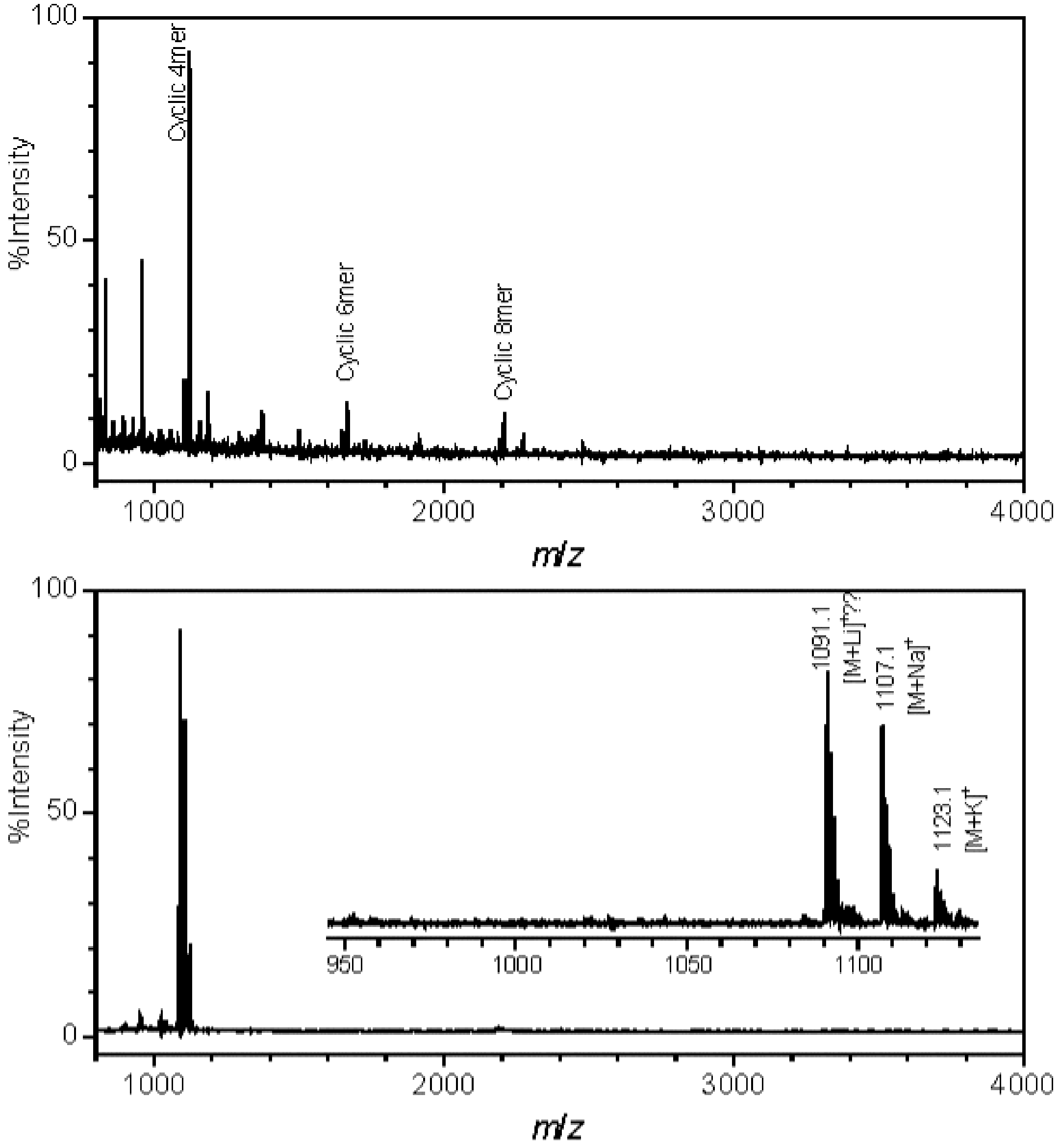


Fig. 11 MALDI TOF MS Spectra of **4d** (R= -*i*-C_5H_{11}). (Upper: crude, Lower: Purified).

III. Energy-Minimized Model of an Alternative Conformation

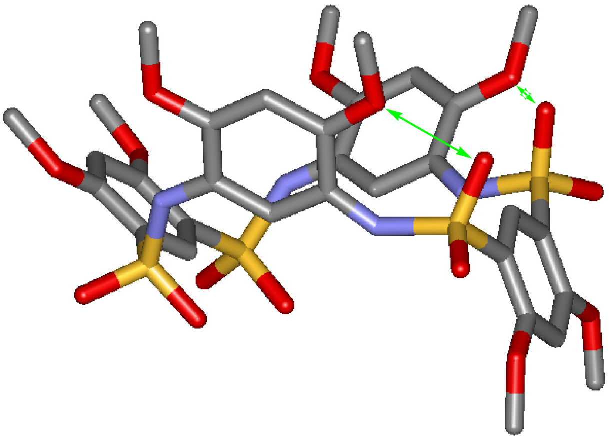


Fig. 12 The energy-minimized (MM3 force field) partial cone conformation of macrocycle **4** (side chain = methoxy). Placing one of the benzene rings downward brings two of the sulfonamide oxygens and the methoxy oxygens into close proximity (green arrows; ~2.5 Å).