Electronic Supplementary Information

for

Self-Assembly of a Triple-Zwitterion in Polar Solutions: hierarchical Formation of Nanostructures

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1. ^{1}H NMR dilution studies

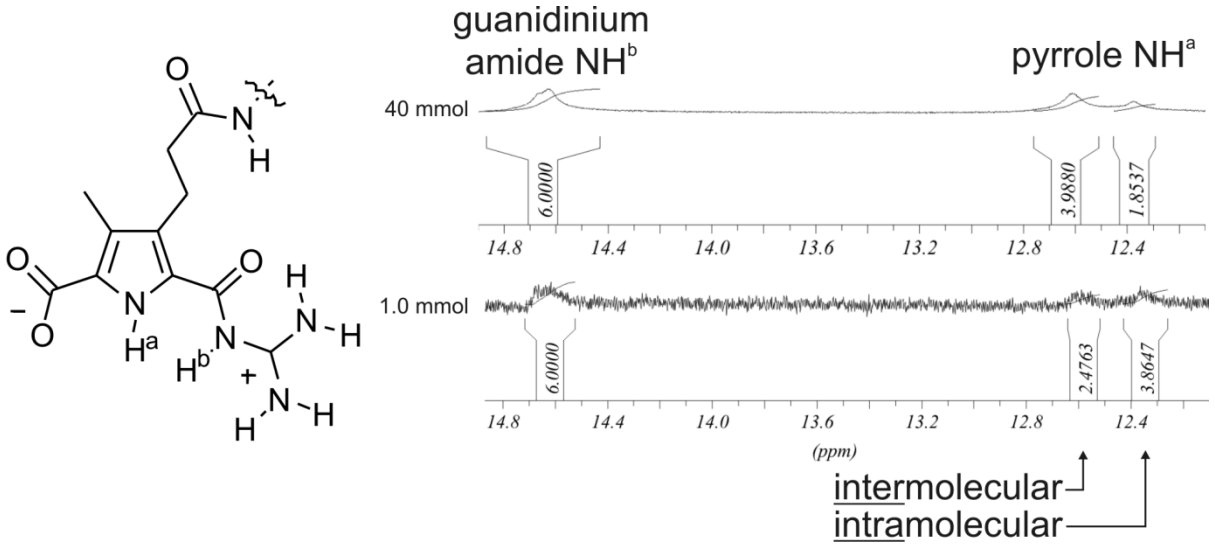


Figure S1. Inversion of the ^{1}H NMR signal integral by changing binding mode from *intra*- to *inter*molecular with increasing concentration: pyrrole NH_{intra} : pyrrole NH_{inter} ≈ 1.2 : 1.9 (1 mM) and 2 : 0.9 (40 mM).

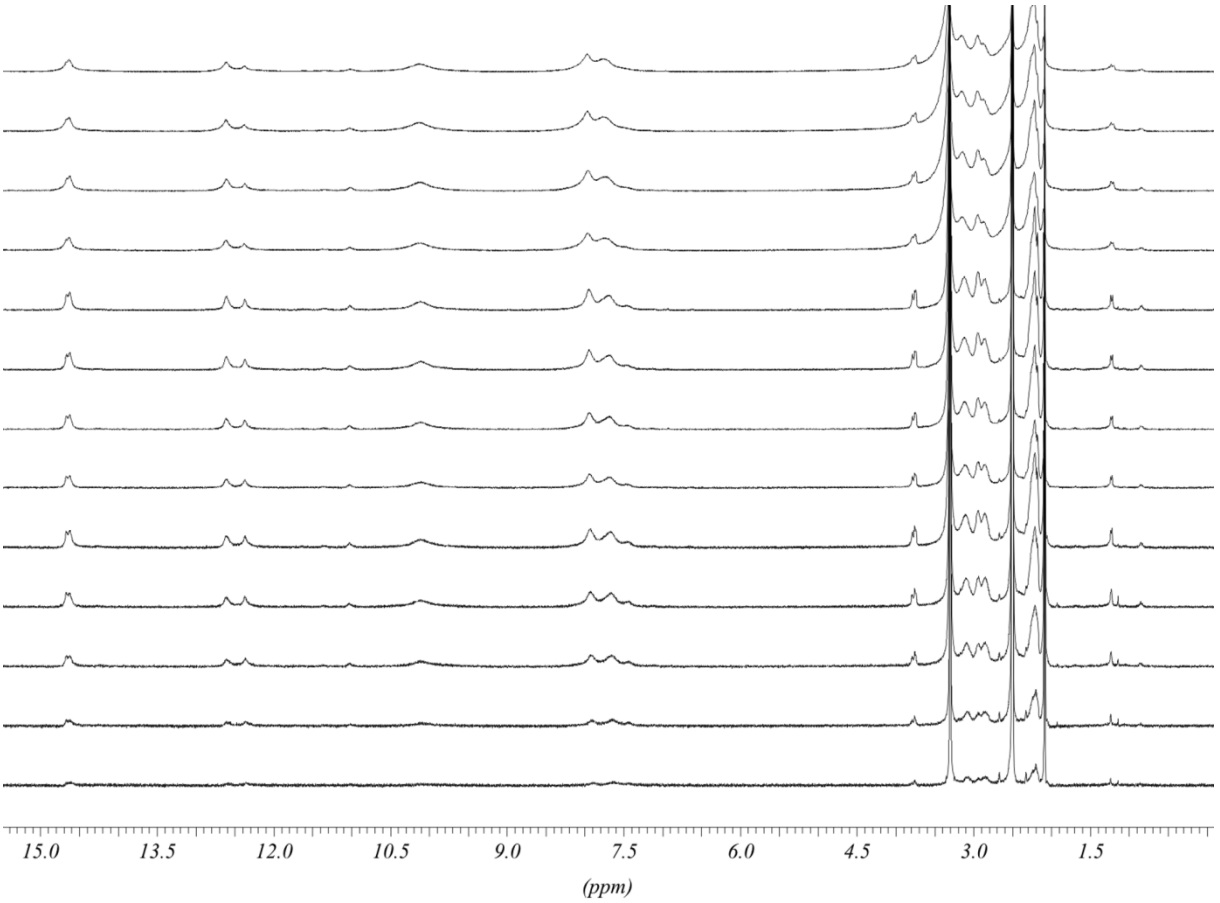


Figure S2. ^{1}H NMR dilution row for triple-zwitterion **1** in a concentrations range from 1 to 40 mM in DMSO-d_6 (from bottom to top).

2. ^{1}H DOSY NMR studies

Table S1. Acquisition parameters for the DOSY experiments

	1 (2 mM)	**1 (20 mM)**	**7 (2 mM)**
PULPROG	dstebpgp3s	dstebpgp3s	dstebpgp3s
TD[F2]	64K	64K	64K
TD[F1]	32	32	32
NS	384	128	512
DS	64	64	64
D20	50 ms	50 ms	100 ms
D21	5 ms	5 ms	5 ms
P30	5.4 ms	5.4 ms	5.4 ms
P19	1.1 ms	1.1 ms	1.1 ms
GPZ6	100 %	100 %	100 %
GPZ7	-13.17	-13.17	-13.17
GPZ8	-17.13	-17.13	-17.13

Table S2. **1** (2 mM, T = 303.4 K)

δ [ppm]	$D \cdot 10^{-11}$ [m^2/s]	log D	
14.673	8.905	-10.050	
12.628	9.131	-10.039	
12.371	9.042	-10.044	
11.069	7.150	-10.146	
3.758	7.937	-10.100	
3.326	$8.068 \cdot 10^{-10}$	-9.093	water
2.868	7.643	-10.117	
2.503	$6.196 \cdot 10^{-10}$	-9.208	DMSO
2.188	7.847	-10.105	
2.096	7.725	-10.112	
0.000	$6.029 \cdot 10^{-10}$	-9.220	TMS

Table S3. **1** (20 mM, T = 303.4 K)

δ [ppm]	$D \cdot 10^{-11}$ [m^2/s]	log D	
14.627	8.688	-10.061	
12.625	6.185	-10.209	
12.383	8.470	-10.072	
11.069	7.150	-10.146	
7.998	6.817	-10.166	
3.760	6.650	-10.177	
3.339	$7.820 \cdot 10^{-10}$	-9.107	water
2.870	6.320	-10.199	
2.504	$6.083 \cdot 10^{-10}$	-9.216	DMSO
2.179	6.050	-10.218	
0.000	$5.735 \cdot 10^{-10}$	-9.241	TMS

Table S4. **7** (2 mM, T = 303.4 K)

δ [ppm]	$D \cdot 10^{-11}$ [m^2/s]	log D	
7.691	1.154	-9.953	
4.246	1.096	-9.960	
3.326	8.417	-9.075	water
3.057	1.098	-9.959	
2.924	1.082	-9.966	
2.505	6.535	-9.185	DMSO
2.432	1.112	-9.954	
2.262	1.089	-9.963	
2.160	1.093	-9.961	
1.469	1.091	-9.962	
1.290	1.105	-9.957	
0.003	6.213	-9.207	TMS

Table S5. Mean diffusion coefficients and corresponding hydrodynamic radii

	Ø D [m^2/s]	$r_H \cdot 10^{-9}$ [m]
1 (2 mM)	$8.15 \cdot 10^{-11}$	1.37
1 (20 mM)	$6.98 \cdot 10^{-11}$	1.60
7 (2 mM)	$1.59 \cdot 10^{-10}$	0.70

3. Molecular Modelling

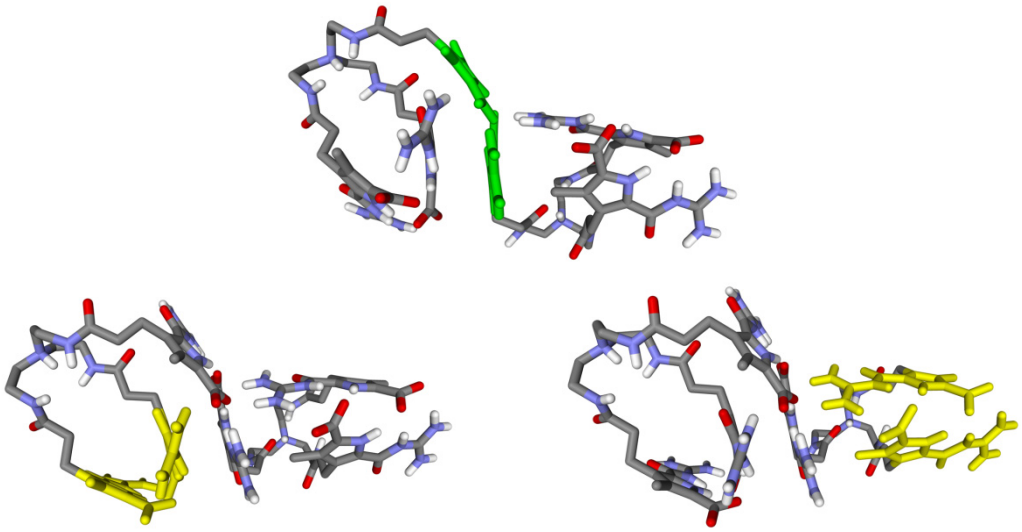


Figure S3. Calculated structure of dimeric **1**. The *intermolecular* binding motive is shown in green. Both *intramolecular* binding motives are shown in yellow. Non-polar hydrogen atoms are omitted for clarity.

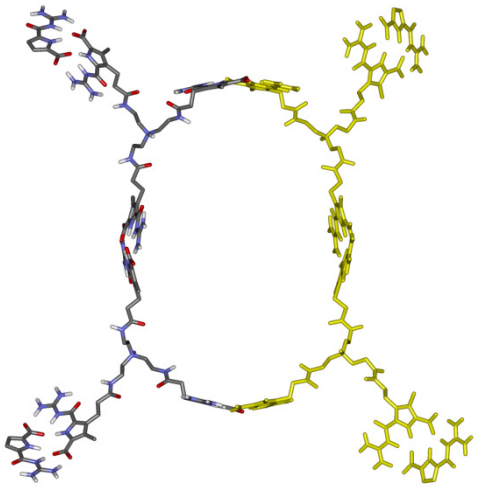


Figure S4. End-capped tetramer as repeating element for the self-assembly of **1** (one capped dimer is highlighted in yellow; non-polar hydrogen atoms are omitted for clarity).

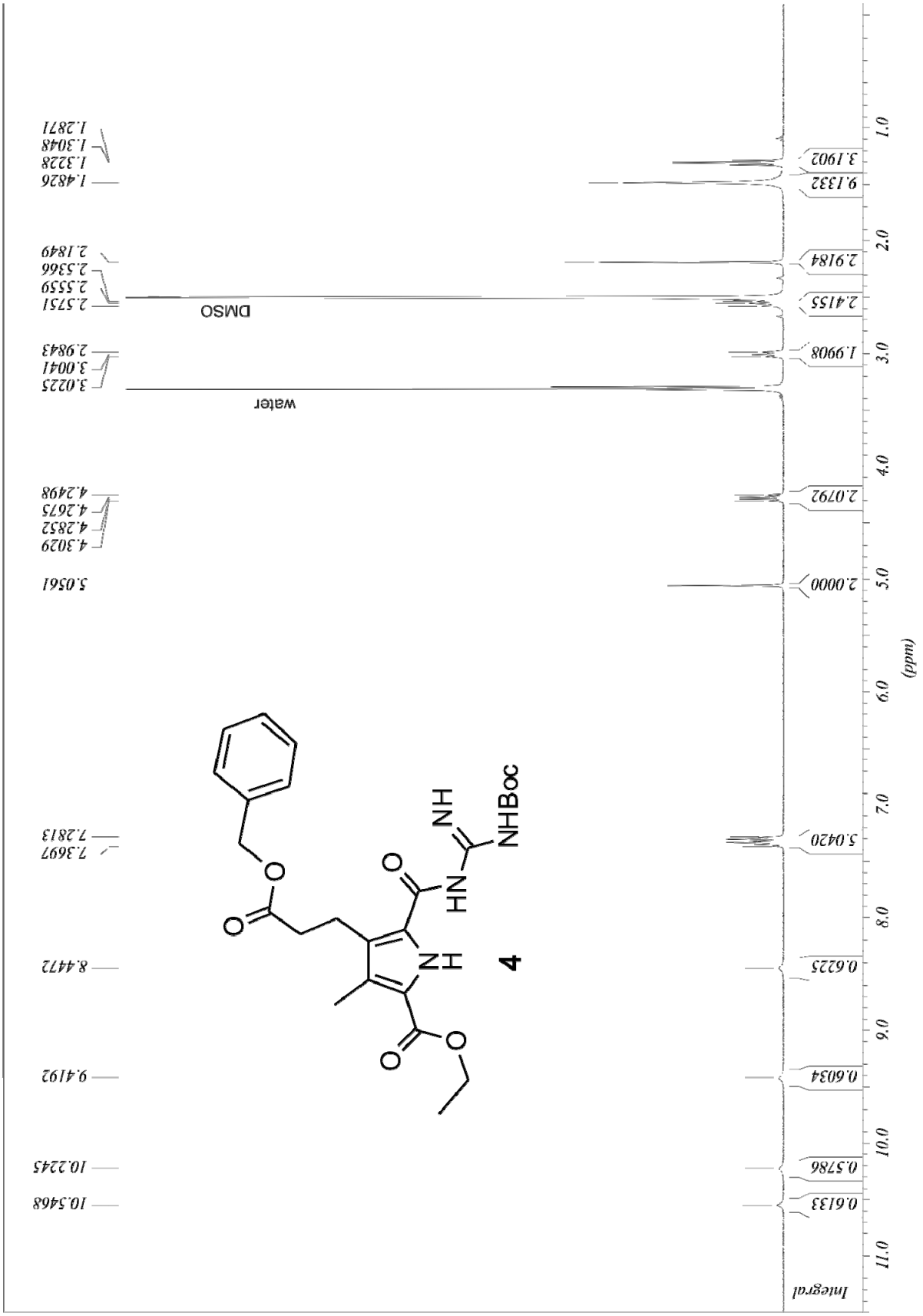
Table S6. Distances between the central nitrogen atoms of the *tren*-linker (A-A) and the maximum distance of the exterior binding motifs (B-B) as derived from the molecular mechanics calculations [Å].

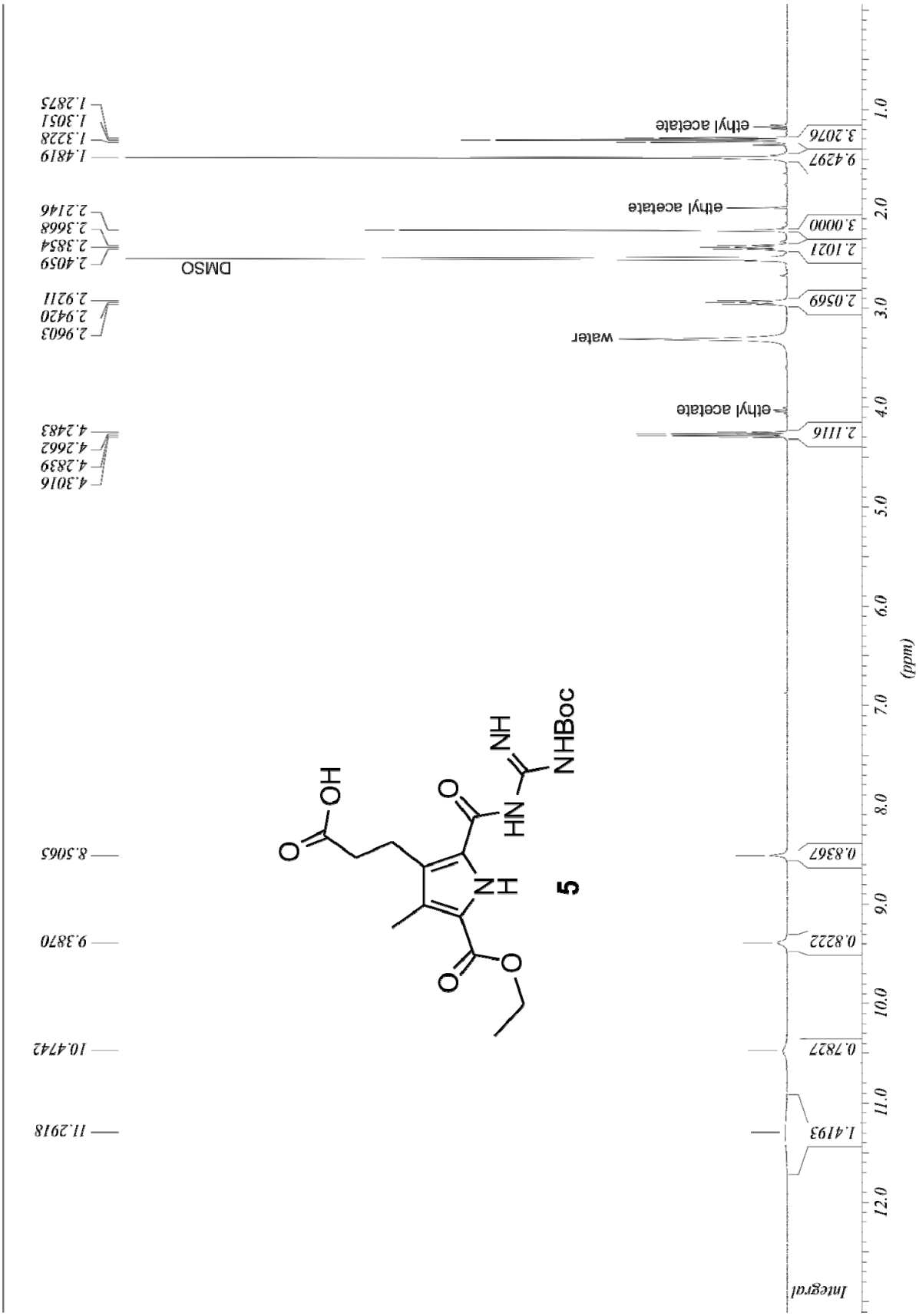
A-A	**B-B**
23,5	34,6
22,6	33,5
24,2	33,2
22,1	20,6
19,9	32,4
24,9	29,8

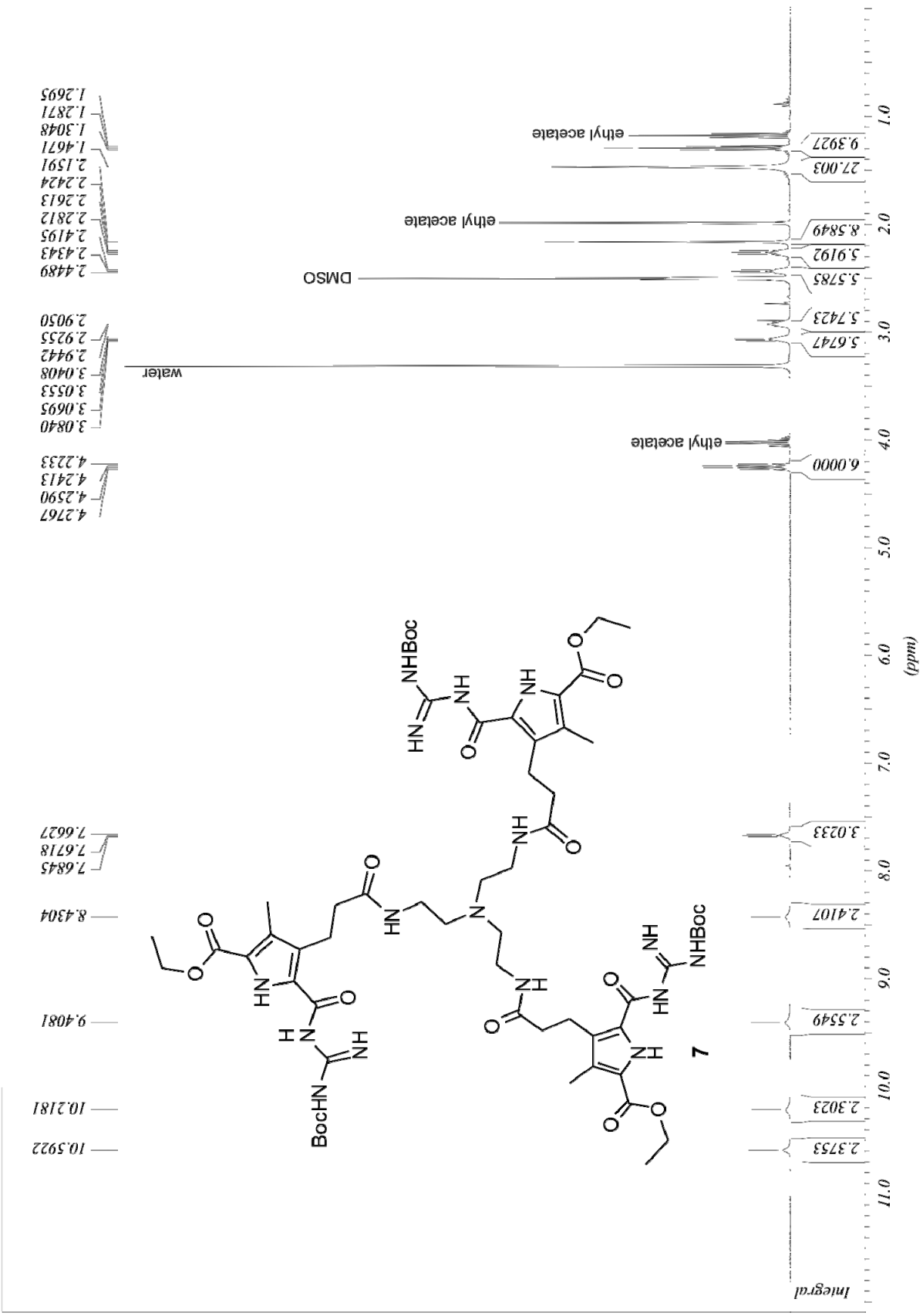
24,5	29,5
20,5	27,1
24,7	28,5
22,5	26,8
24,3	29,7
26,5	27,3
22,3	33,4
23,9	33,9
25	34,6
23,2	30,5
25,4	36,4
23,7	37,2
22,8	30
24,3	35,4
18,2	27,8
24,4	26
22,2	34,8
23,2	32,9
19,1	27,1
23,4	34,4
22	34,4
24,1	22,1
22,3	31,9
20,9	30
21,7	24,3
24,5	33,4
22,7	35,7
20,9	23,9
22,8	32,8
21,1	30,1
19,4	25,5
22,9	21,7
23,5	37,5
23,6	27,8
23,3	33,8
16,5	34,7
21	27,6
24,1	32,7
23,6	36,7
23	24,7
33,4	33,5
17,6	30,3
20,5	28,9
22,6	28,9
23,5	34,9
23,1	26

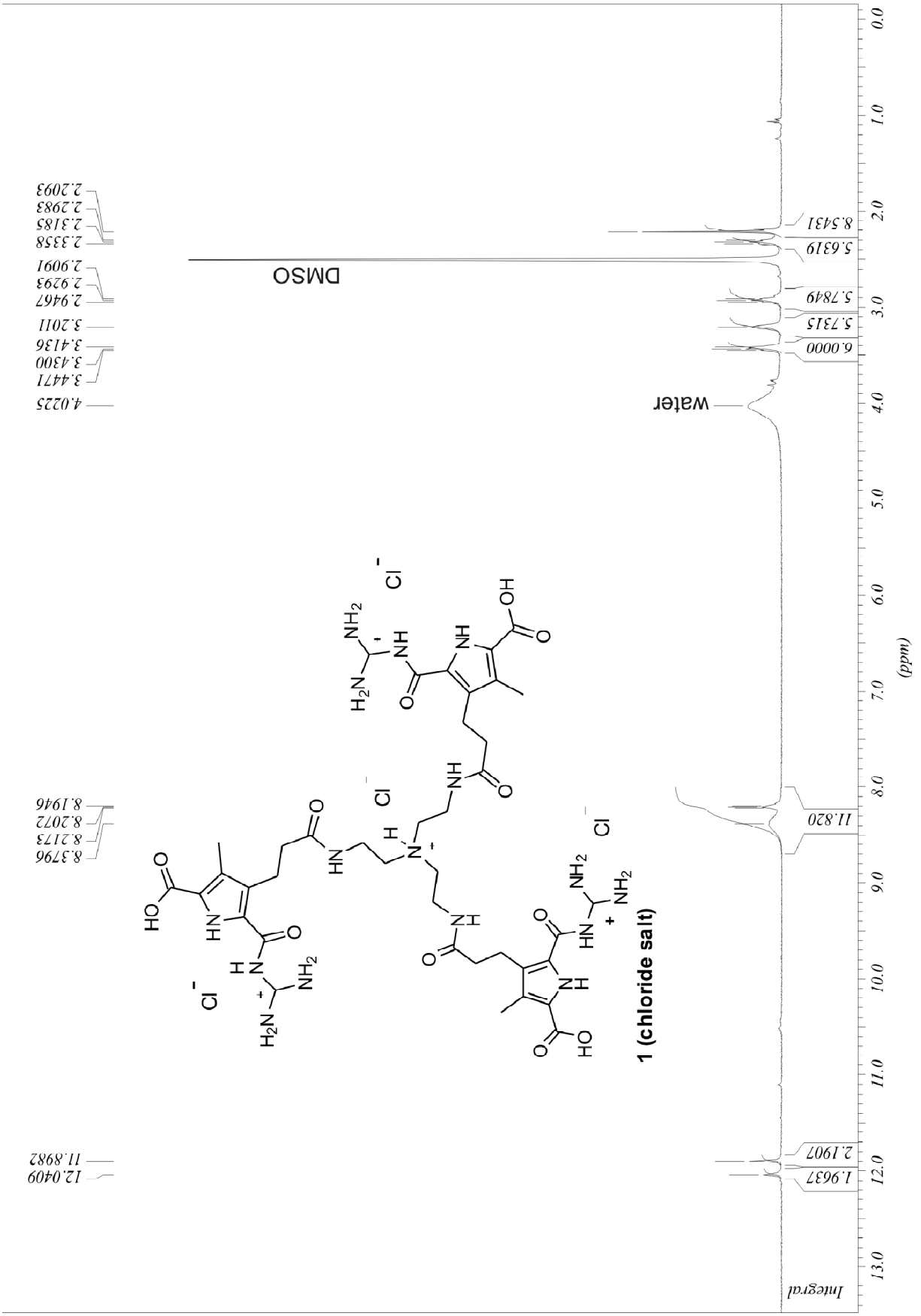
22,2	34,6
19,9	30,4
23,3	31,1
23,4	32,8
19,6	28,6
22,8	24,4
23,3	33,2
24,1	31,9
Ø 22,7	**Ø 30,6**

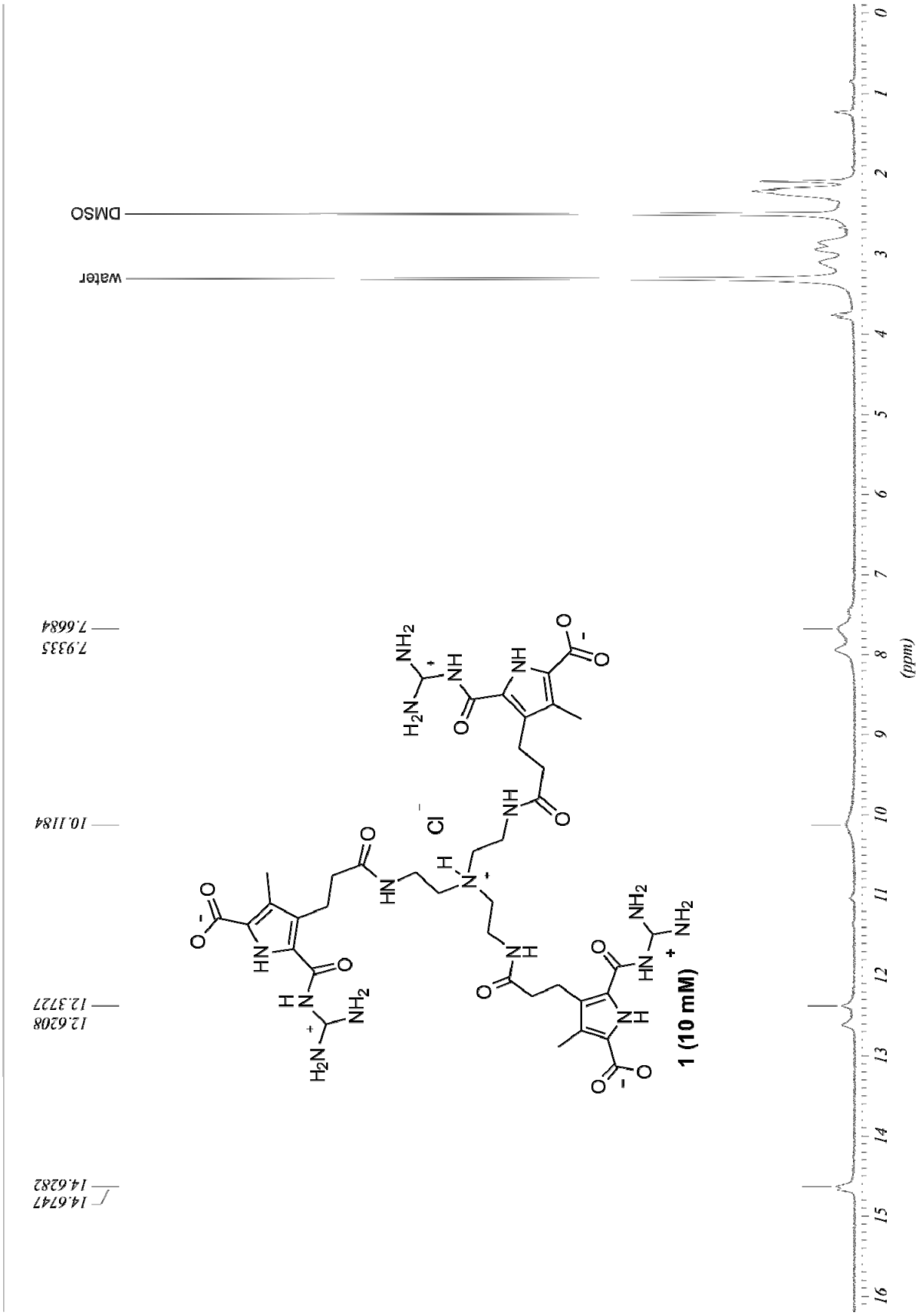
10. ^{1}H NMR spectra of the compounds 4, 5 and 7, and 1 as chloride salt or zwitterionic (10 mM) in DMSO-d_6




1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
(ppm)
Integral
1.4193
0.7827
0.8222
0.8367
2.1116
2.0569
2.1021
3.0000
3.2076
9.4297
1.4819
1.3228
1.3051
1.2875
2.2146
2.3668
2.3854
2.4059
2.9211
2.9420
2.9603
4.2483
4.2662
4.2839
4.3016
8.5065
9.3870
10.4742
11.2918
ethyl acetate
ethyl acetate
water
DMSO
ethyl acetate
NHBoc
NH
HN
N
H
O
O
HO
O
O
5


ethyl acetate
DMSO
ethyl acetate
water
ethyl acetate
7
(ppm)
Integral


DMSO
water
1 (chloride salt)
Integral
(ppm)
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
8.5431
5.6319
5.7849
5.7315
6.0000
4.0225
3.4471
3.4300
3.4136
3.2011
2.9467
2.9293
2.9091
2.3358
2.3185
2.2983
2.2093
8.3796
8.2173
8.2072
8.1946
11.820
12.0409
11.8982
2.1907
1.9637


DMSO
water
14.6747
14.6282
12.6208
12.3727
10.1184
7.9335
7.6684
1 (10 mM)
(ppm)