Supporting Information

Solid state structure and solution phase self-assembly of clicked mannosylated diketopiperazines

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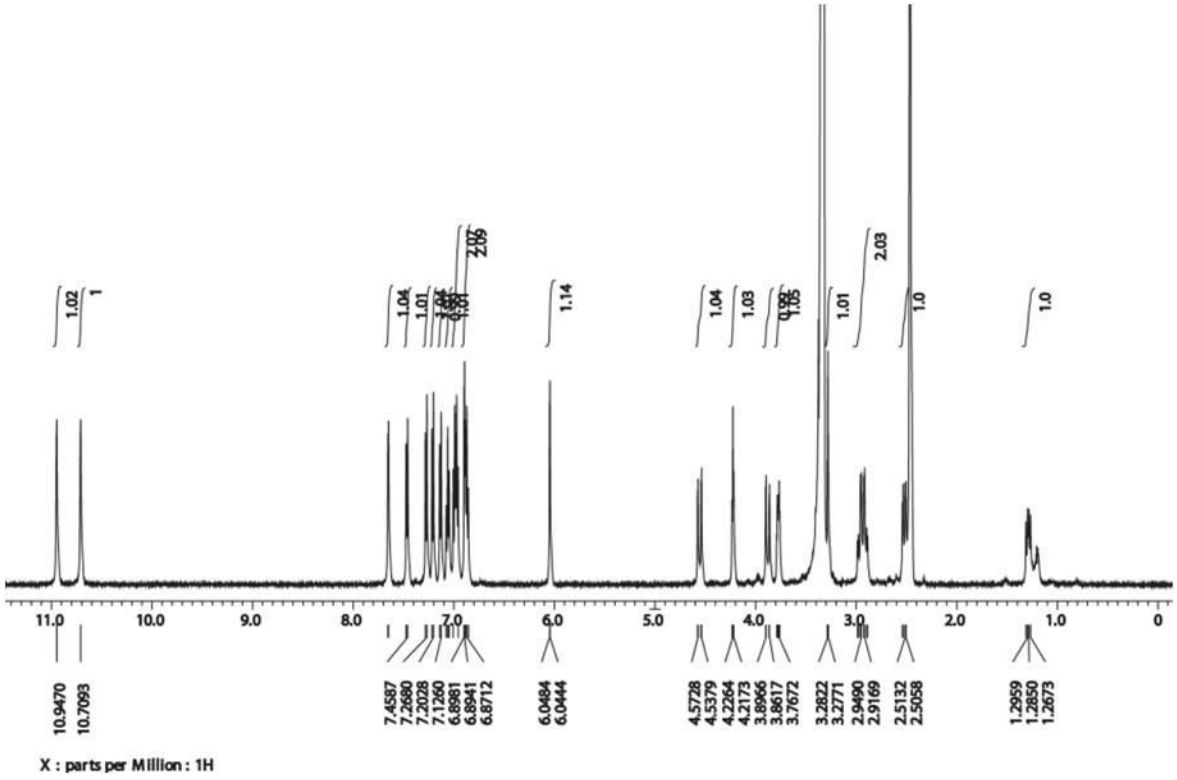
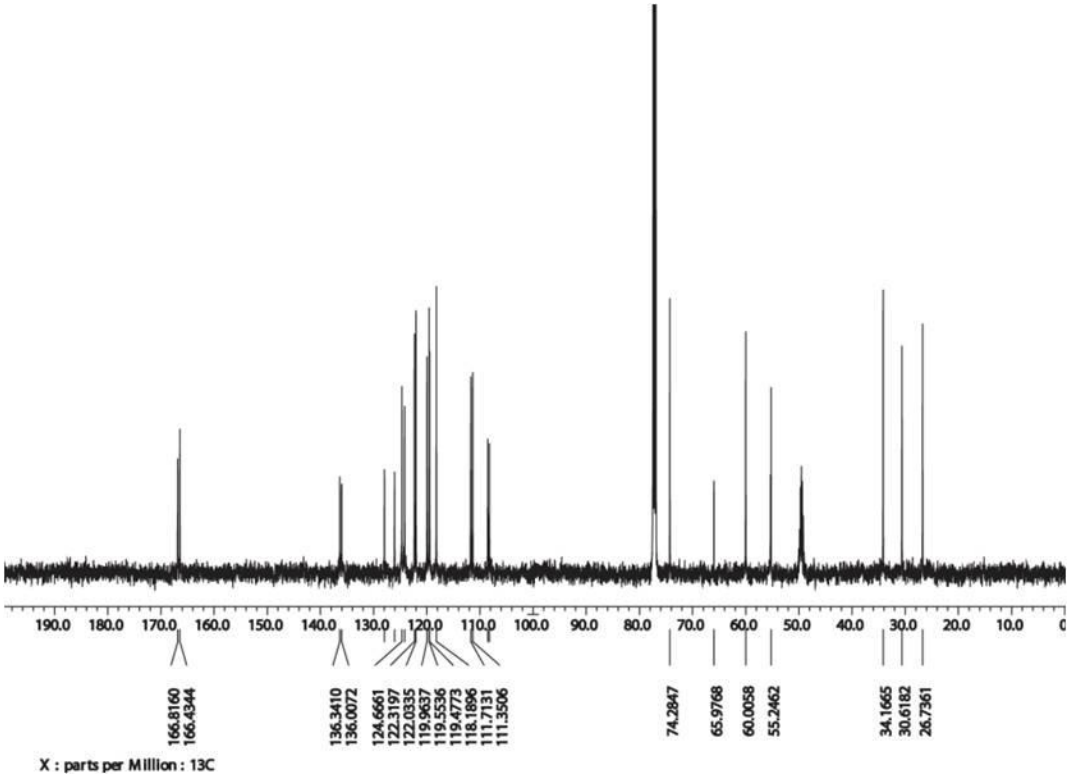
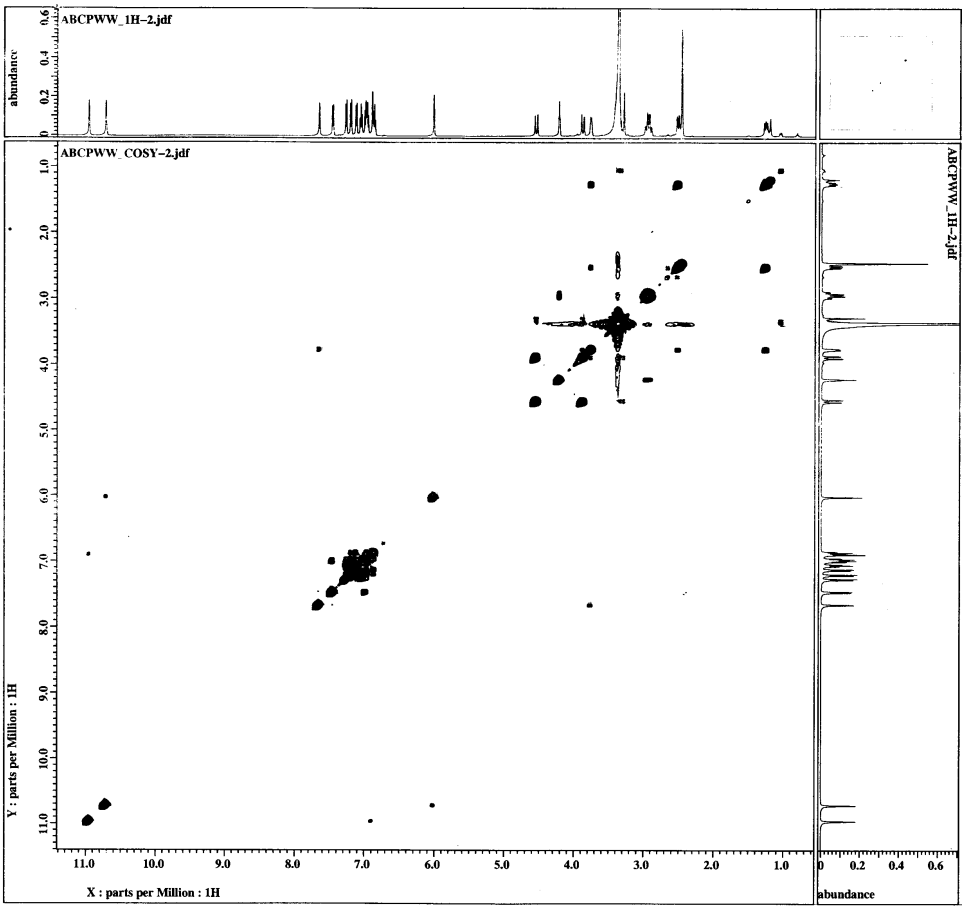
^{1}H NMR spectra of **6a** (DMSO-d_6):



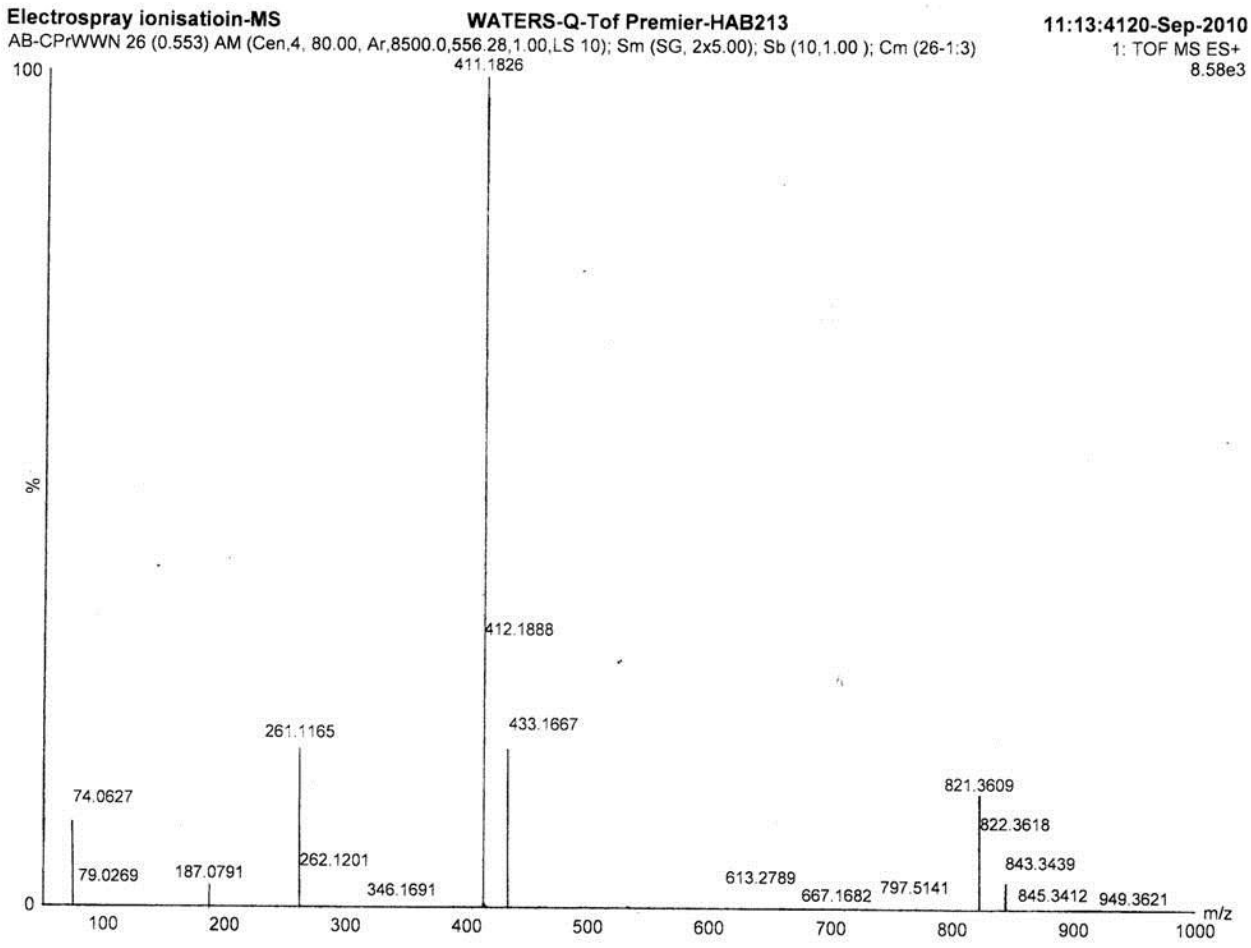
^{13}C NMR spectra of **6a**:



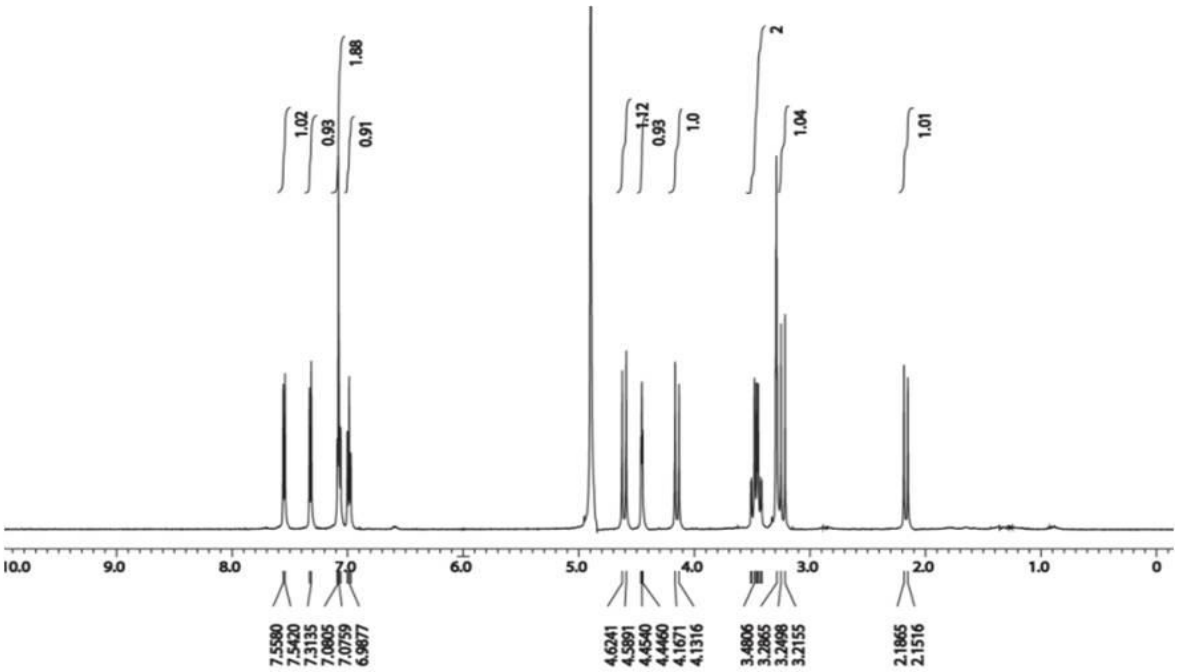
^{1}H-^{1}H COSY NMR spectra of **6a** (DMSO-d_6)

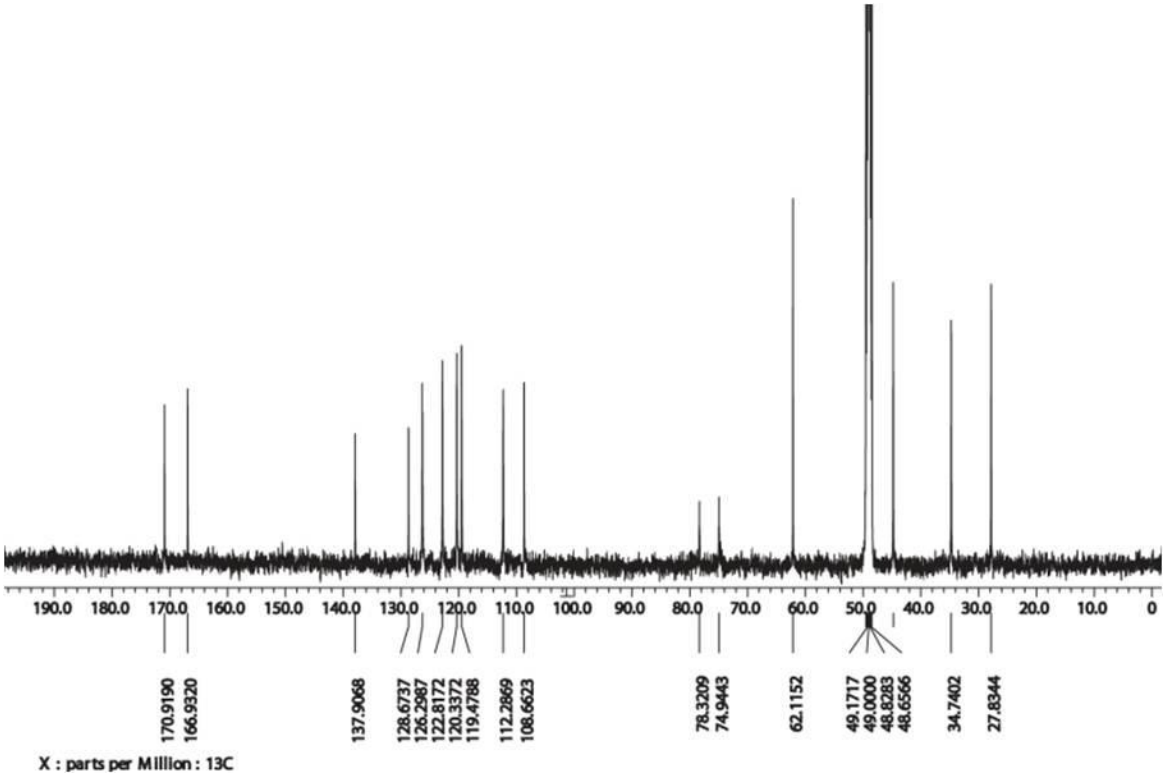


ESI-HRMS of **6a**:

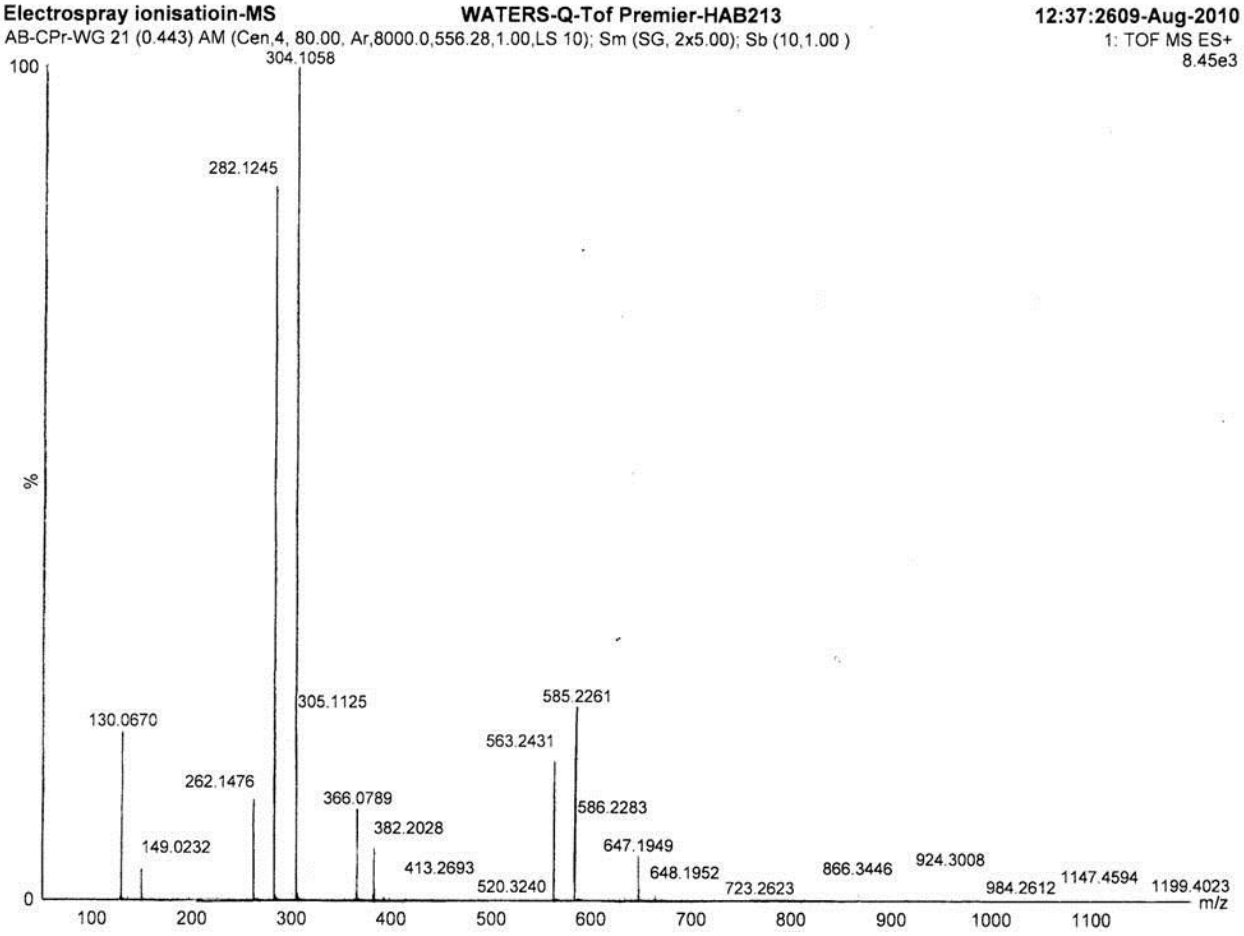


^{1}H and ^{13}C NMR spectra of **6b**:

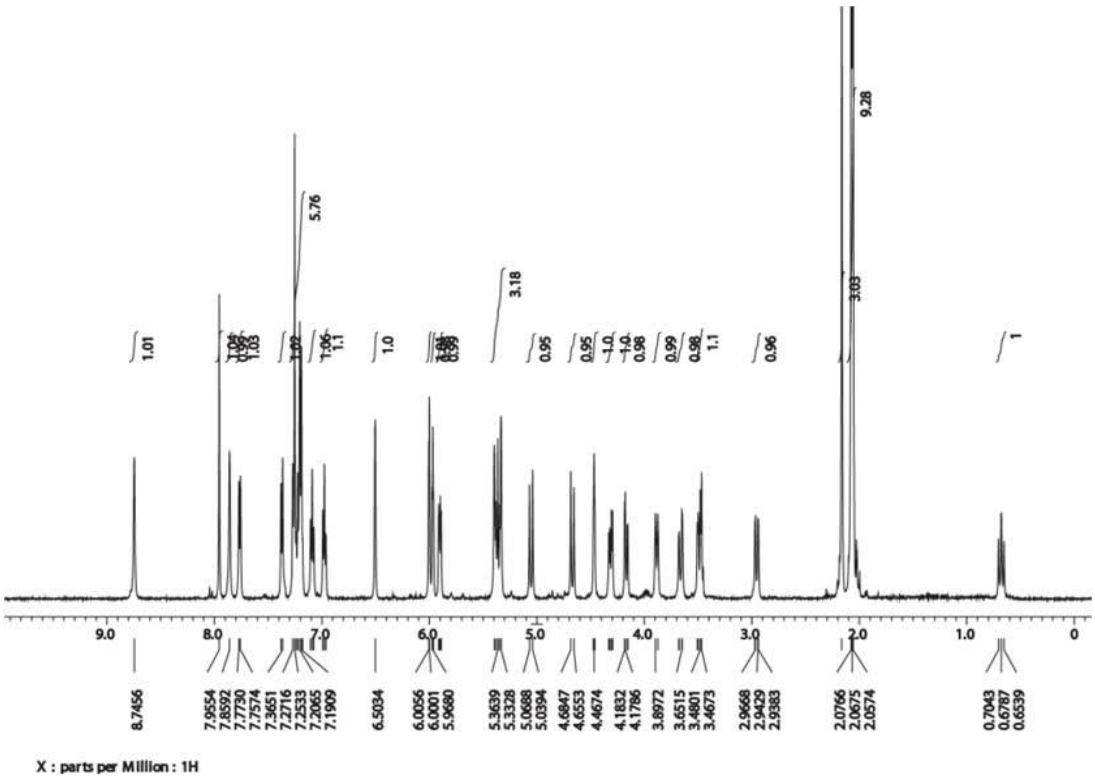


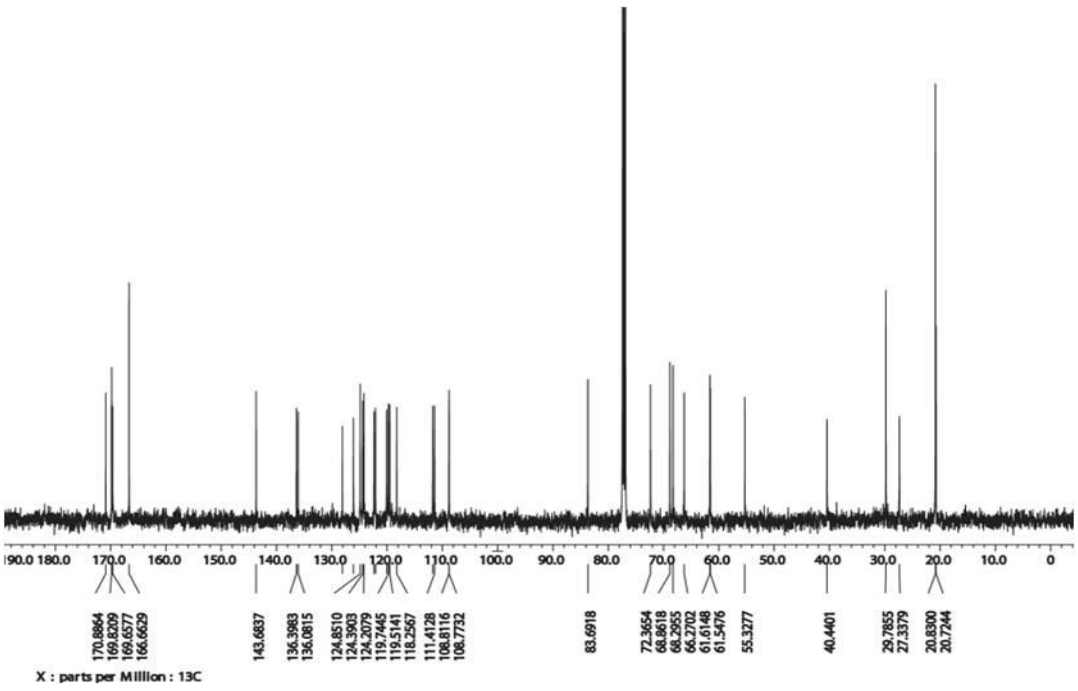


ESI-HRMS of **6b**:



^{1}H and ^{13}C NMR spectra of 7**a**:





ESI-

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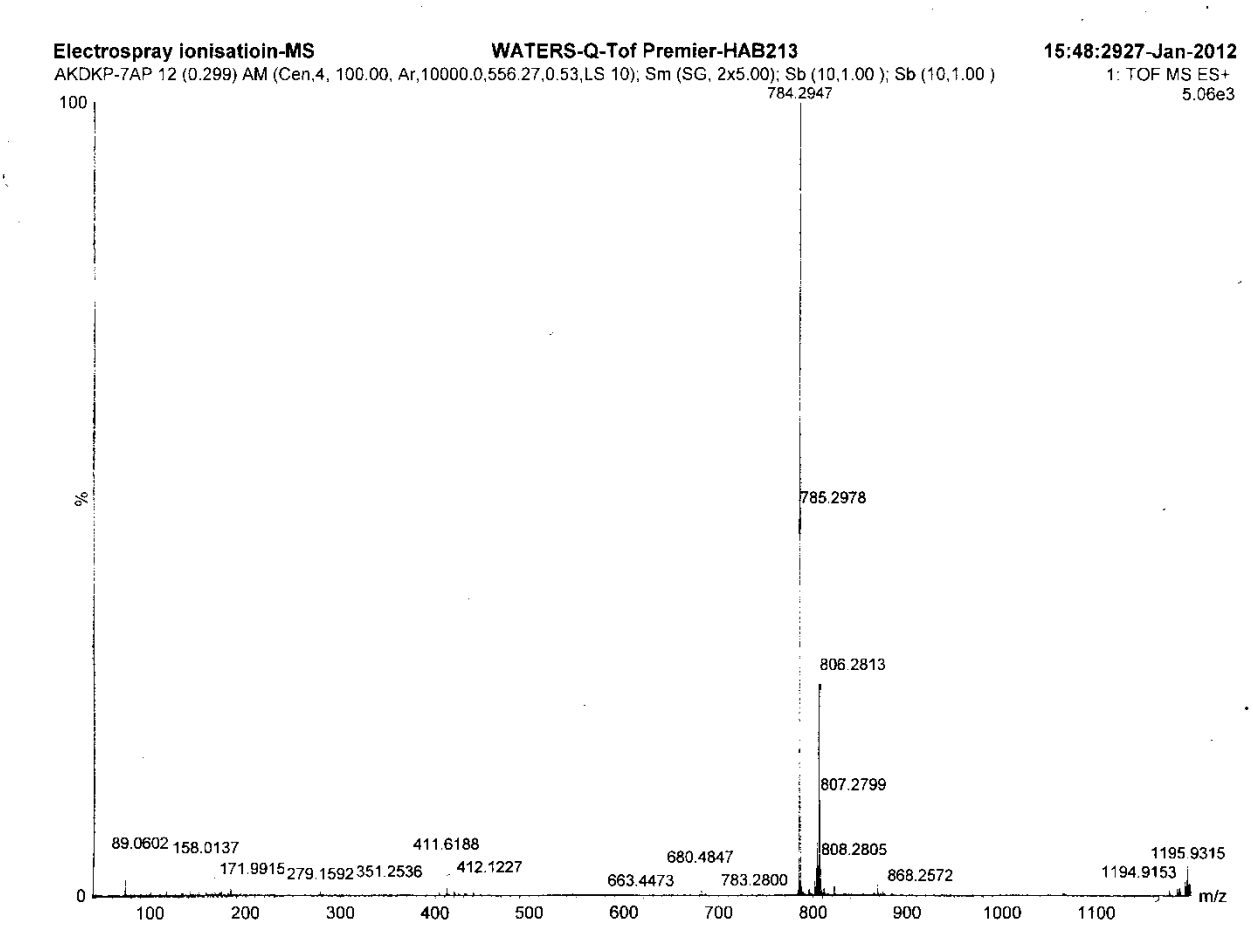
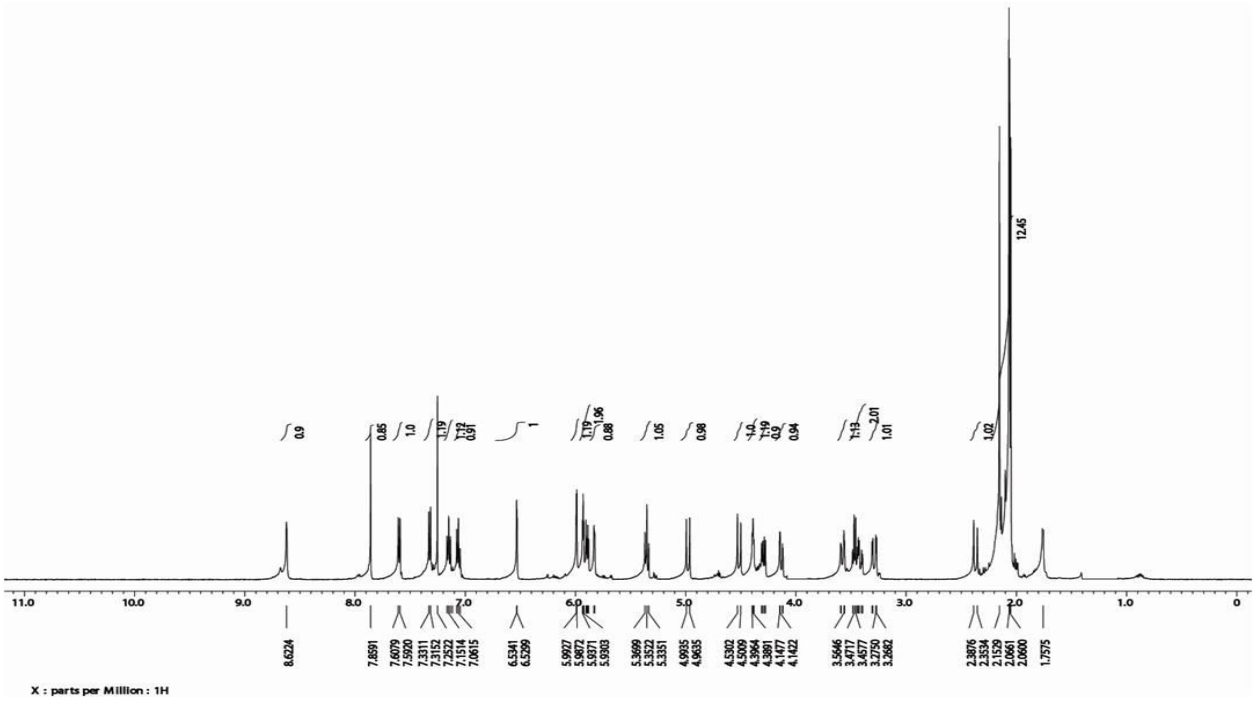
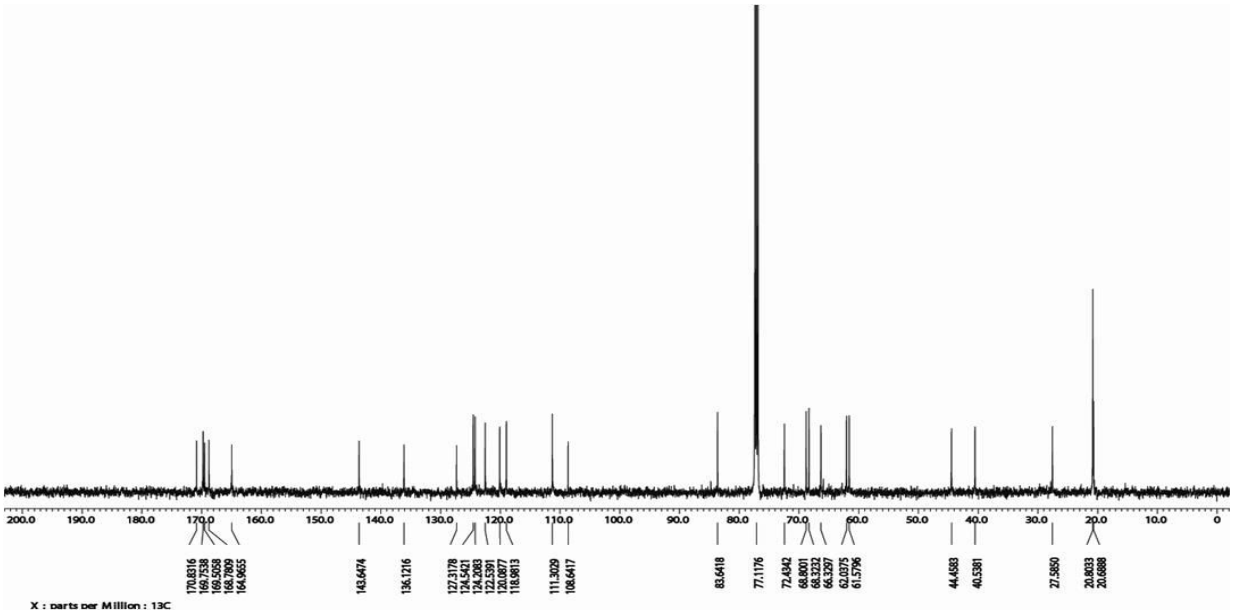


^{1}H and ^{13}C NMR spectra of **7b**:





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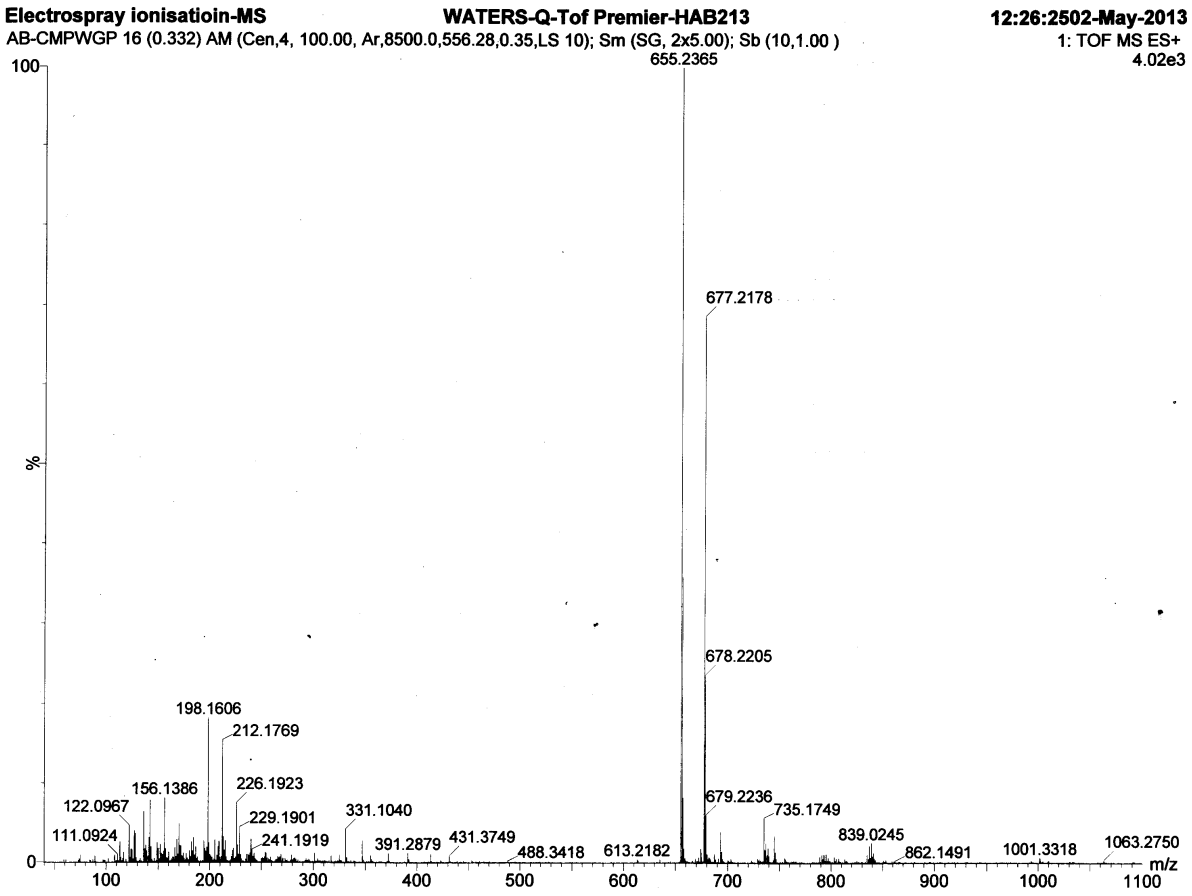
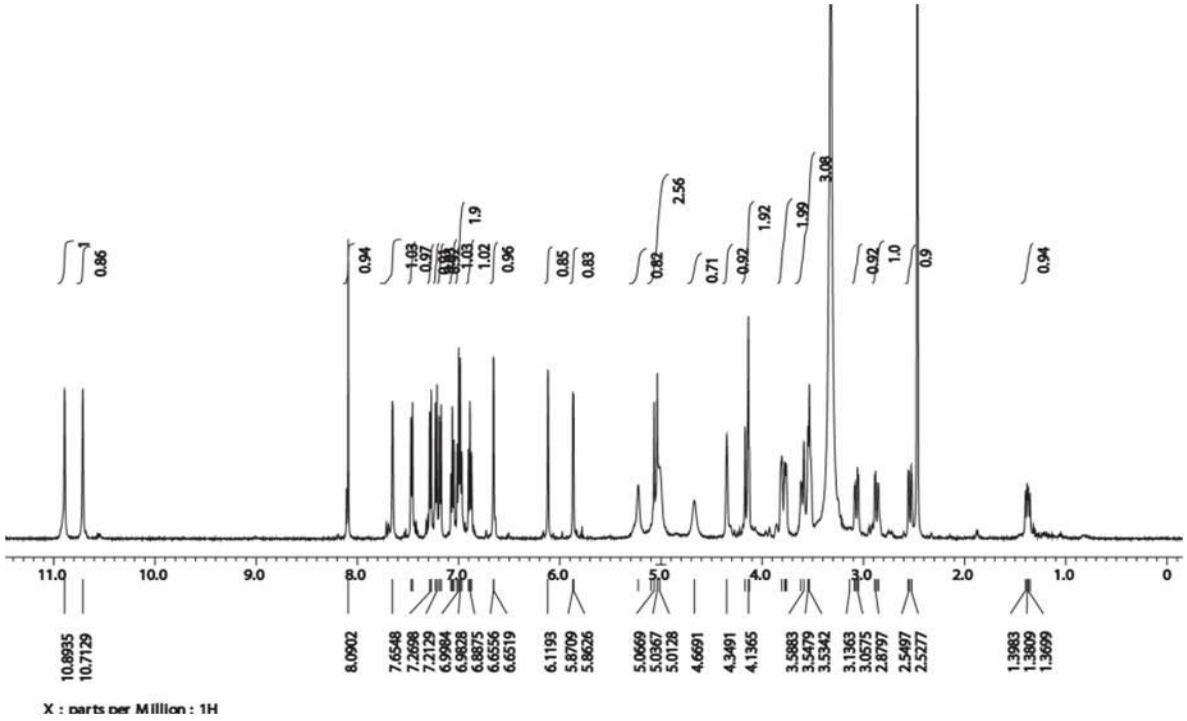
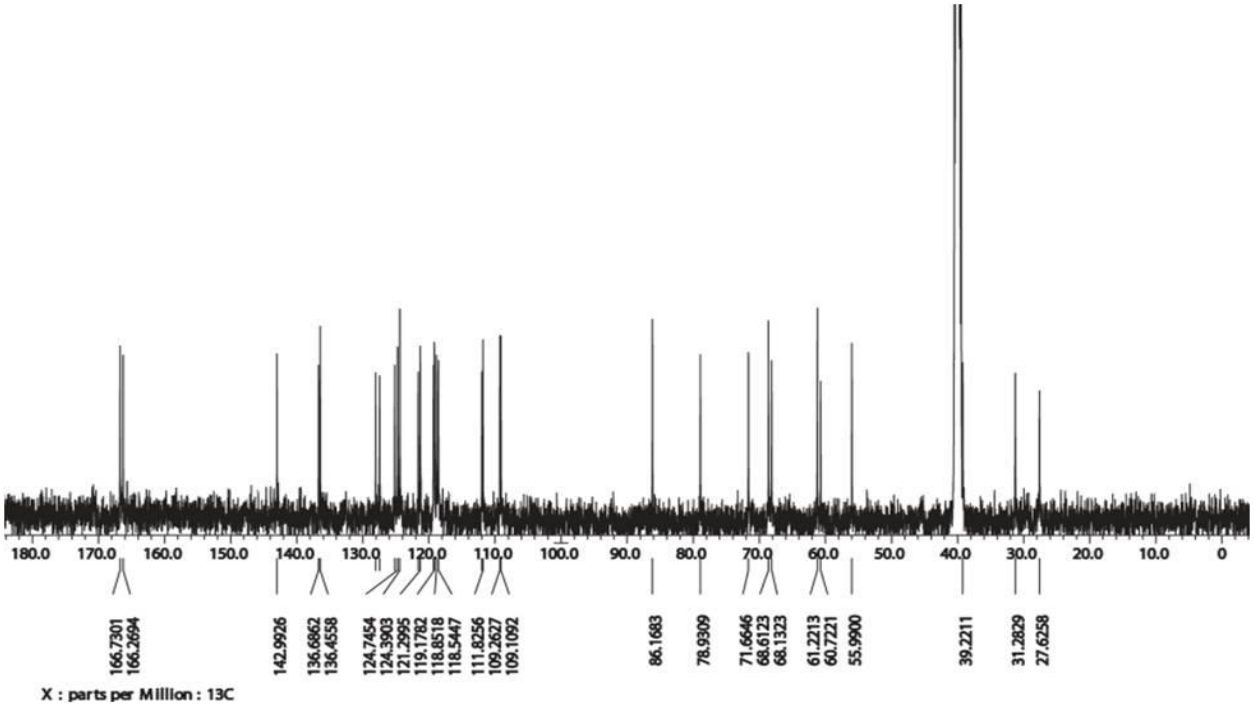


^{1}H and ^{13}C NMR spectra of **8a**:





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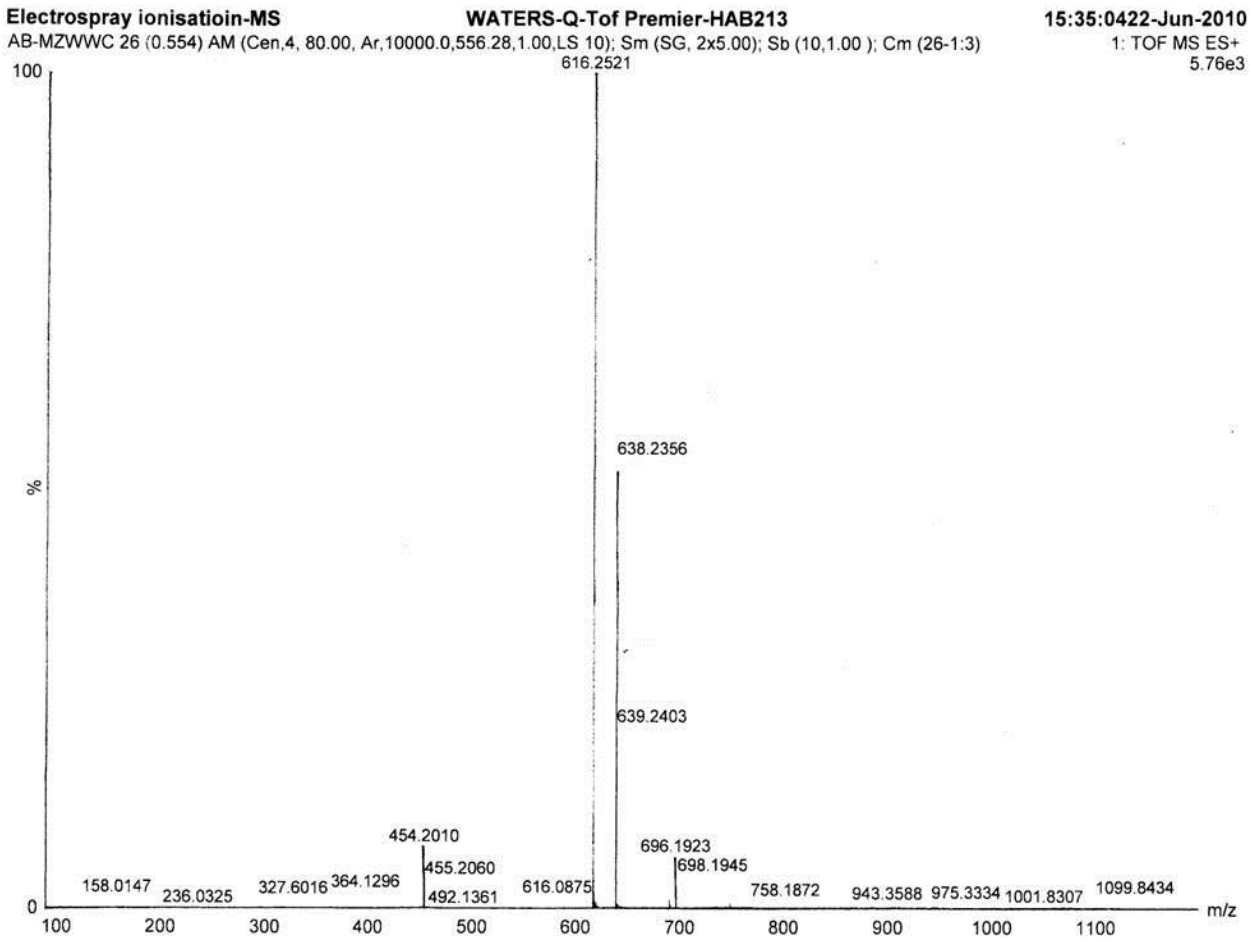

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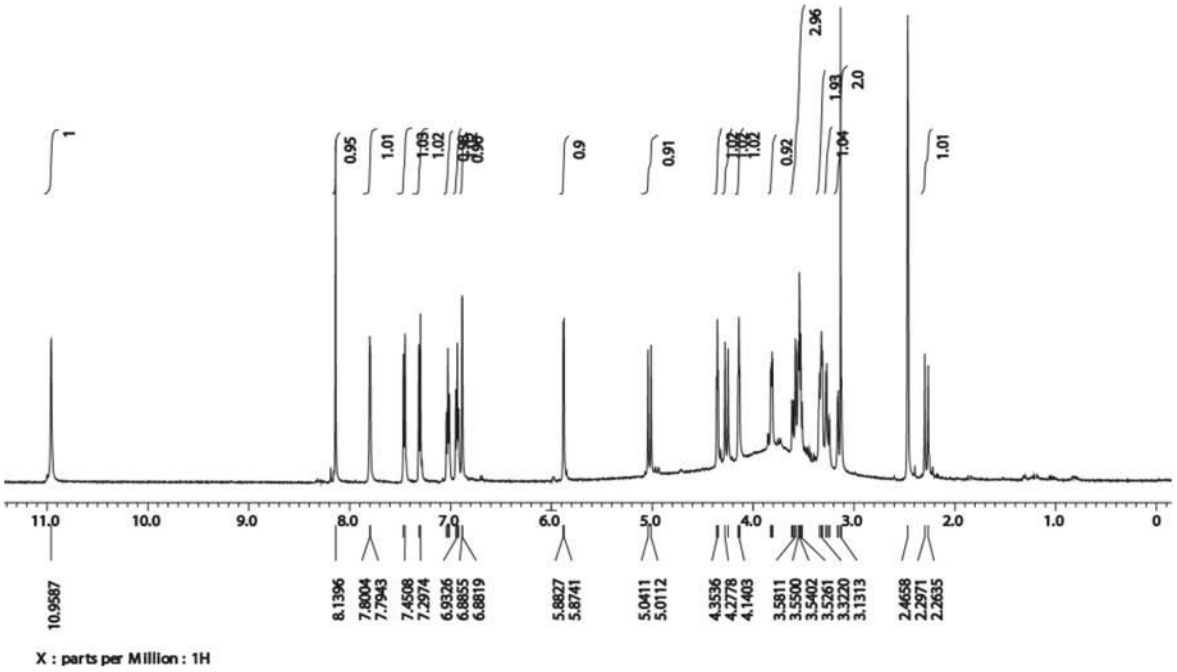
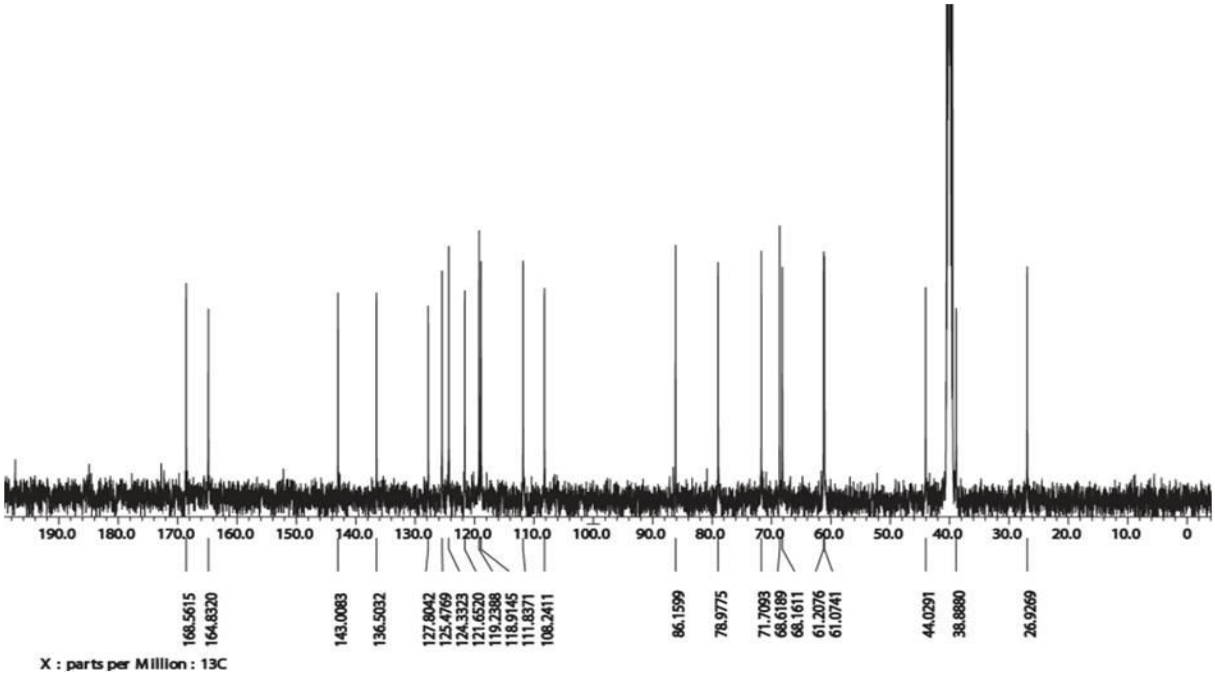
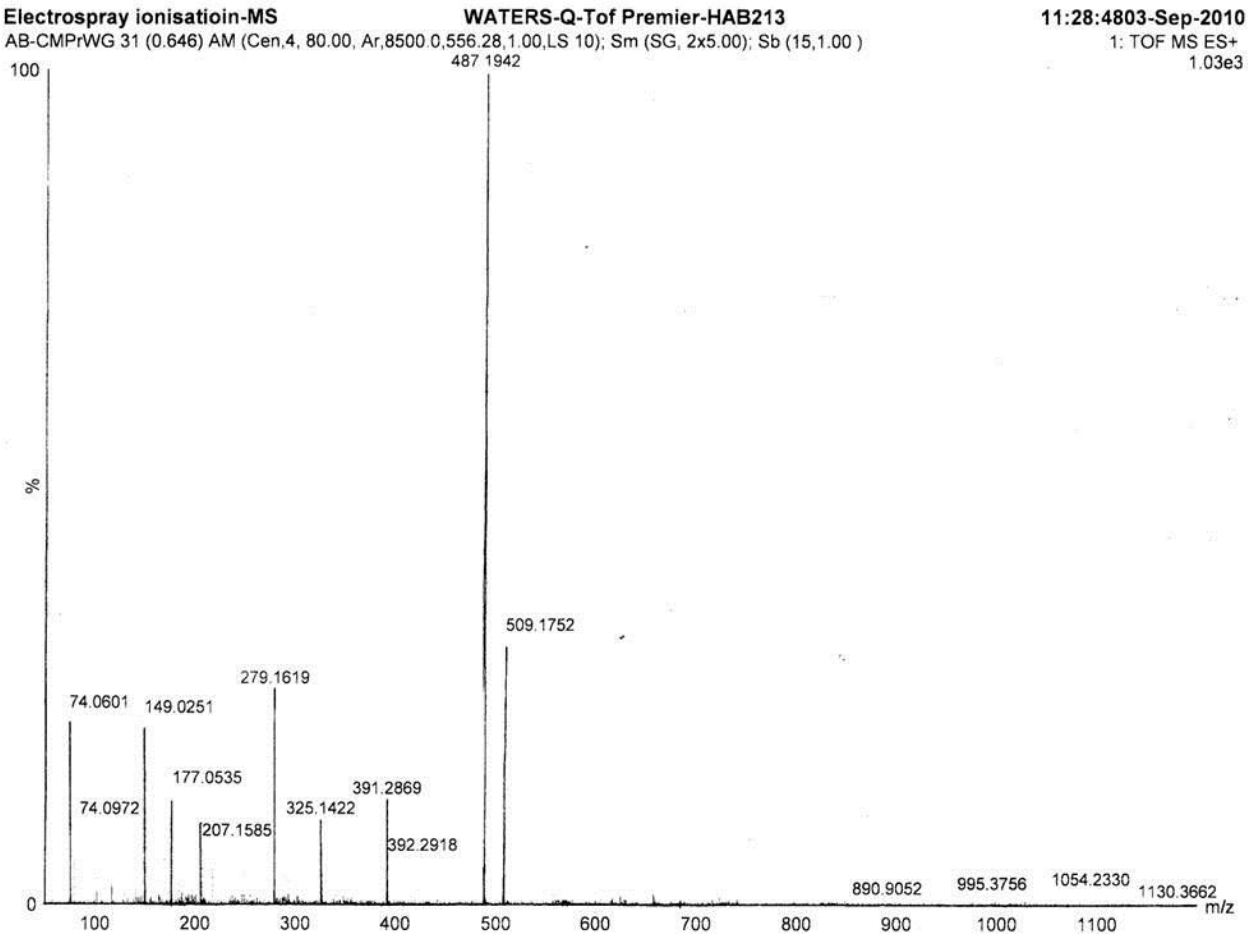
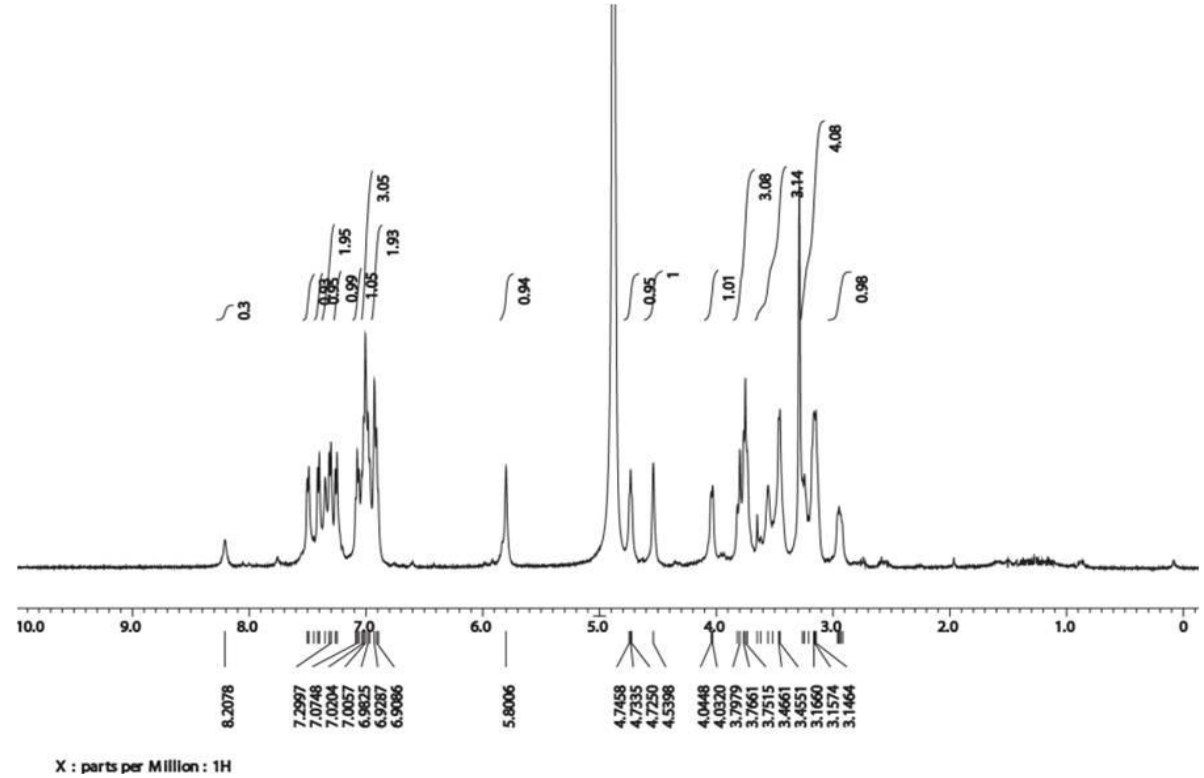


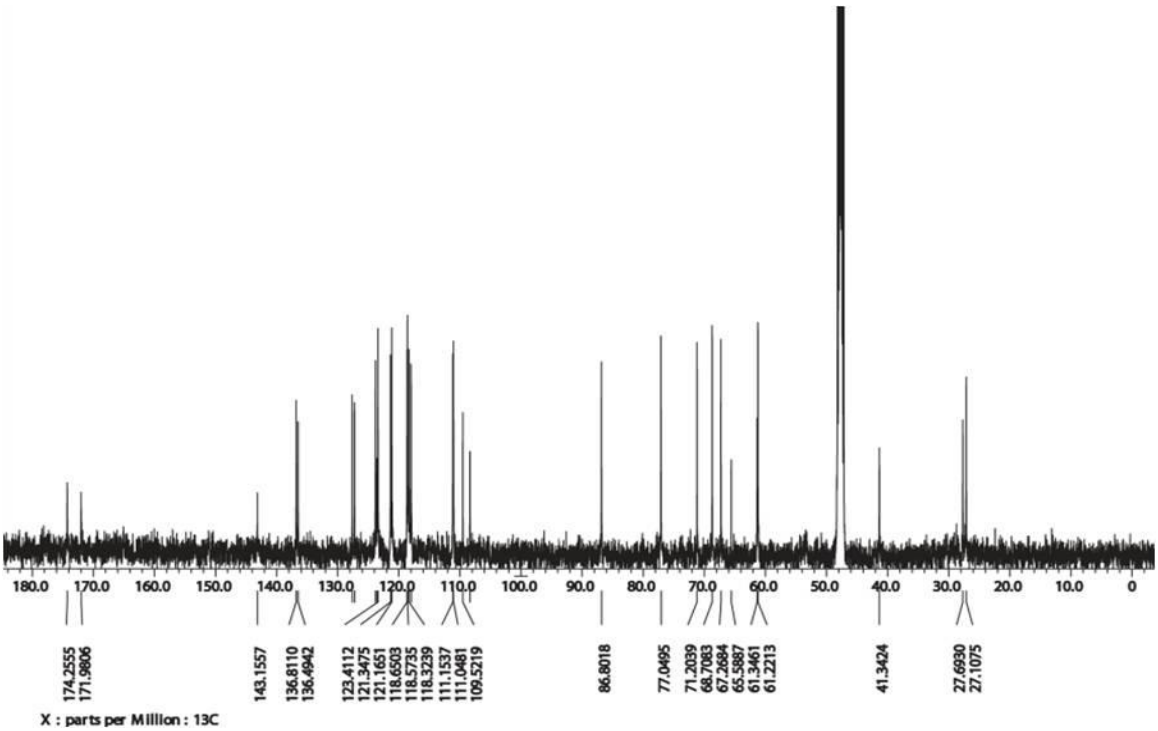


ESI-HRMS of **8b**:



^{1}H and ^{13}C NMR spectra of **10**:





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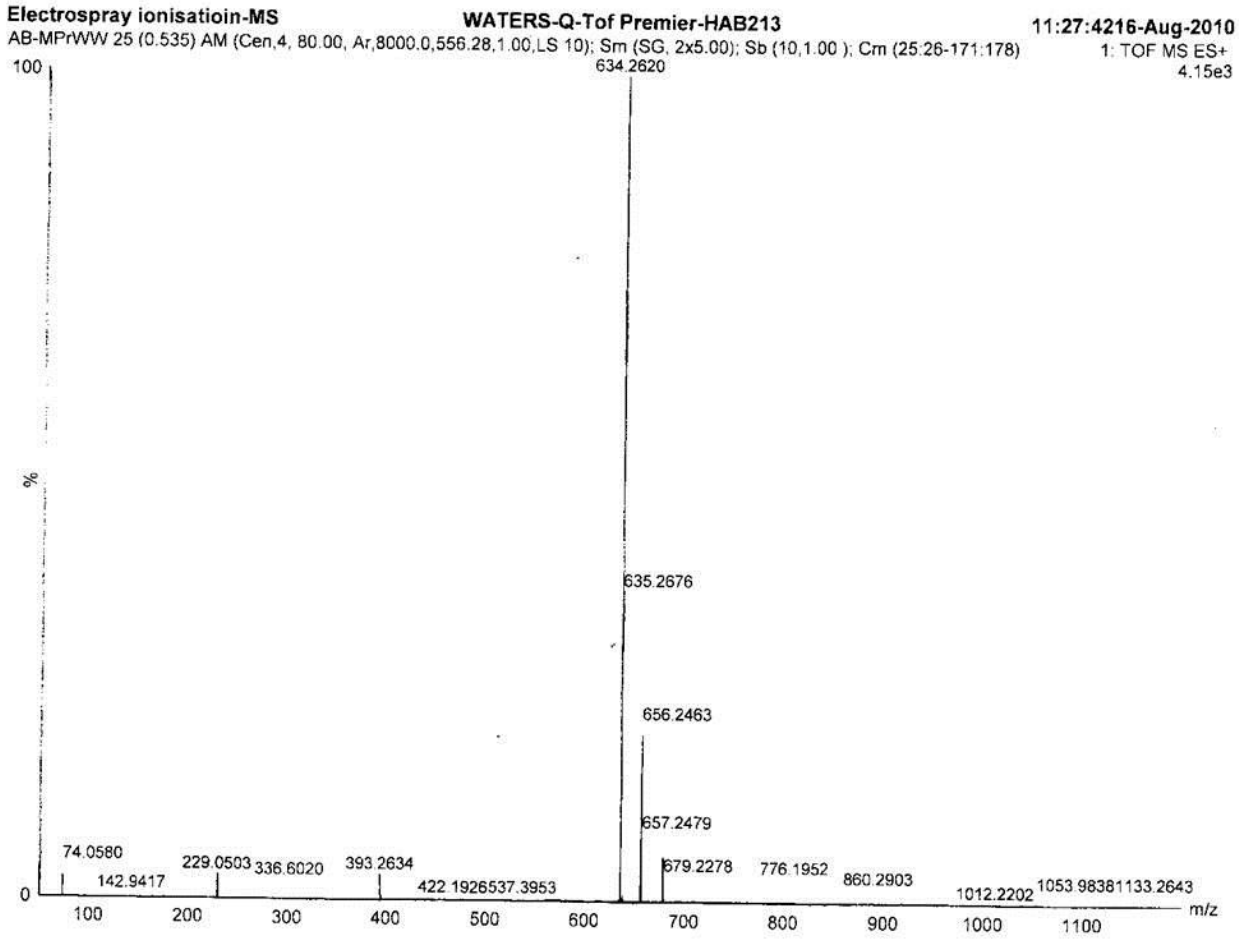

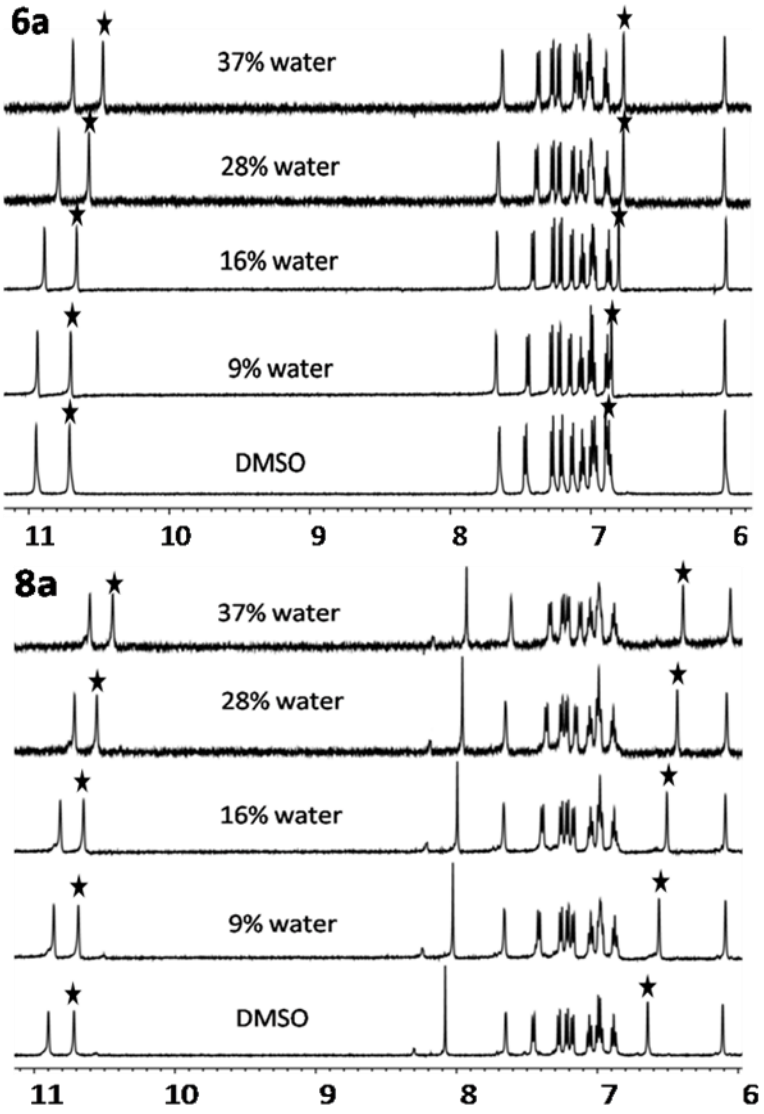

Figure S1: ^{1}H NMR of **6a** and **8a** in varying amounts of water (aromatic region). Concentration of **6a** and **8a** was 2.0×10^{-2}M.

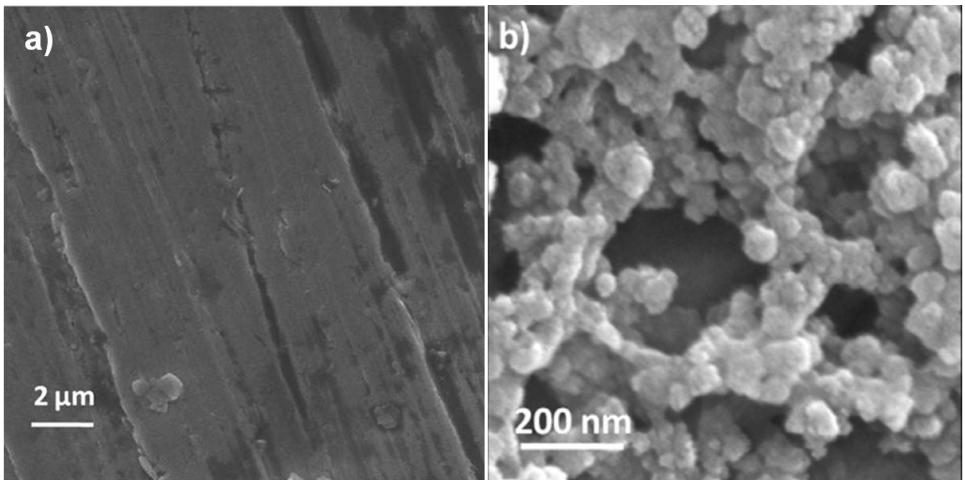

Figure S2: SEM images of a) **8b** & b) **10** in 50% aqueous methanol (2 mM) after 24 h ageing.

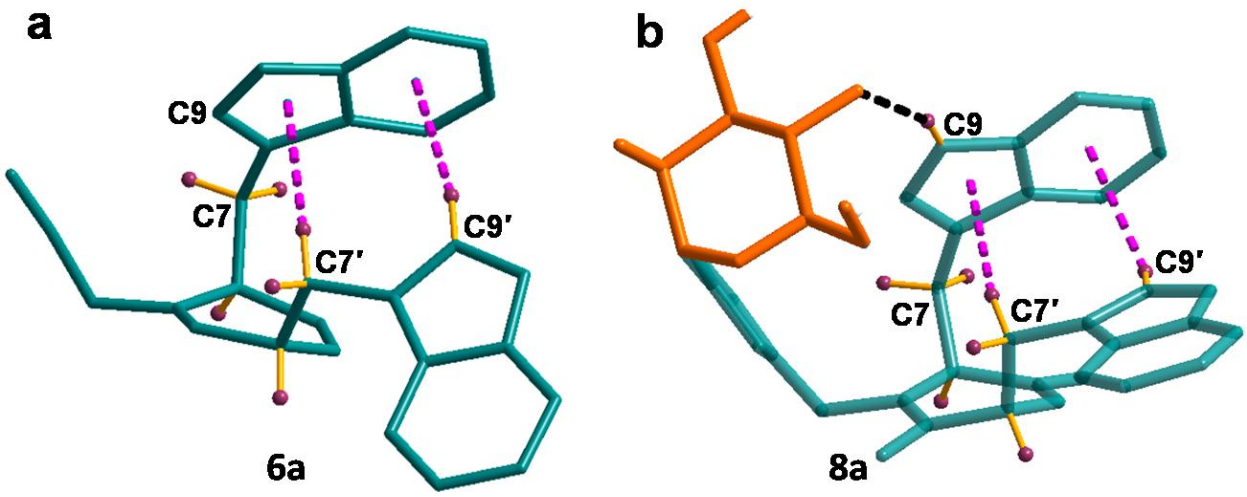

Figure S3: Crystal structures of a) **6a** and b) **8a** showing relationship of $-CH_2$ β hydrogens of Trp with vicinal hydrogens (-CH α hydrogens). Trans relationship could be seen for C7′H engaged in CH-π bond with the respective vicinal hydrogens.

Table S1. Crystal structure refinement parameters for **6a** and **8a**.

Identification code	**Compound 8a**	**Compound 6a**
Empirical formula	$C_{32}H_{33}N_7O_9$	$C_{25}H_{22}N_4O_2$
*M*r	659.65	410.47
crystal system	orthorhombic	tetragonal
space group	*P 21 21 21*	*P 43*
a/A	8.505 (2)	19.7959(19)
b/A	8.030(5)	19.7959(19)
c/A	24.601(5)	11.155(2)
α/°	90.000	90
β/°	90.000	90
γ/°	90.000	90
Volume/ A^3	2957.9	4371.4(11)
Z	4	8
Dx /Mg m^{-3}	1.481	1.247
F(000)	1384	1728
μ/ mm^{-1}	1.481	0.081
θ range for data collection/ °	2.19 - 28.36	2.30 - 26.00
Limiting indices	-10 → h → 11, -18 → k →10, -32 → l → 32	-24 → h → 23, -24 → k → 21, -13 → l → 13
Reflections collected	19274	24249
unique reflections	7246	8484
R(int)	0.0521	0.0652
Completeness to *θ*	28.36, 98.9	26.00, 99.2
T_{max} / T_{min}	0.9912/0.9782	0.9903/0.9839
Data / restraints / parameters	7246 / 1 / 441	8484 / 1 / 559
Goodness-of-fit on F^2	1.086	1.001
*R*1 and *R*2 [$I>2\sigma(I)$]	0.0638, 0.1573	0.0553, 0.1149
*R*1 and *R*2 (all data)	0.0891, 0.1822	0.0745, 0.1237
Absolute structure parameter	-1.5(14)	0.2(11)
Largest diff. peak and hole/e.A^{-3}	0.537 and -0.534	0.217 and -0.191
CCDC No.	864568	864569

Table S2. H-bonding of **6a** and **8a** in crystal structure.

D—H…A[a]	H...A	D...A	D—H...A
Compound 8a			
O4…H4'…O5	2.43	2.754(3)	105
O4…H4'…N8''	2.10	2.887(4)	160
O5…H5'…O6	2.54	2.867(4)	105
O5…H5…O1^{ii}	2.09	2.869(3)	159
O6…H6'…O5	2.56	2.867(4)	104
O6…H6'…O1W^{ii}	2.57	2.980(4)	112
O7…H7'…O1W ^{iii}	1.96	2.770(4)	169
N8…H8…O6	2.17(4)	2.911(4)	157(4)
N8'…H8'…O4^{iv}	2.03	2.887(4)	174
C3…H3...O5^{v}	2.58	3.355(4)	136
C7…H7A...O1A^{ii}	2.50	3.367(7)	148
C12…H12...O1A ^{iv}	2.41	3.178(8)	140
C13'…H13'...N8'^{vi}	2.62	3.516(5)	161
C19…H19...O	2.35	2.902(4)	118
C26…H26...O1A	2.54	3.430(8)	150
C27…H27...N20	2.54	2.897(4)	101
Compound 6a			
N4…H4...N8B^{vii}	2.41	3.061(3)	133
N4A…H4A...O2^{viii}	2.44	3.282(3)	165
N8…H8...O1A	1.99	2.837(3)	167
N8A…H8A...O1	2.00	2.812(3)	158
C17…H17A...O1A^{ix}	2.24	3.002(4)	135
C17A…-H17D...O2^{x}	2.29	3.198(4)	156

[a]**Symmetry of A:** (i)1/2-x,1-y,-1/2+z (ii)1- x,1/2+y,1/2-z (iii) -1+x,y,z (iv) 1/2-x,1-y,1/2+z(v) 1-x,-1/2+y,1/2-z (vi)-1/2+x,1/2-y,1-z (vii) y,-x,1/4+z (viii) -y,x,-1/4+z (ix) 1-y,x,-1/4+z (x) y,1-x,-3/4+z, where A= acceptor and D=donor