

## Supplementary Information

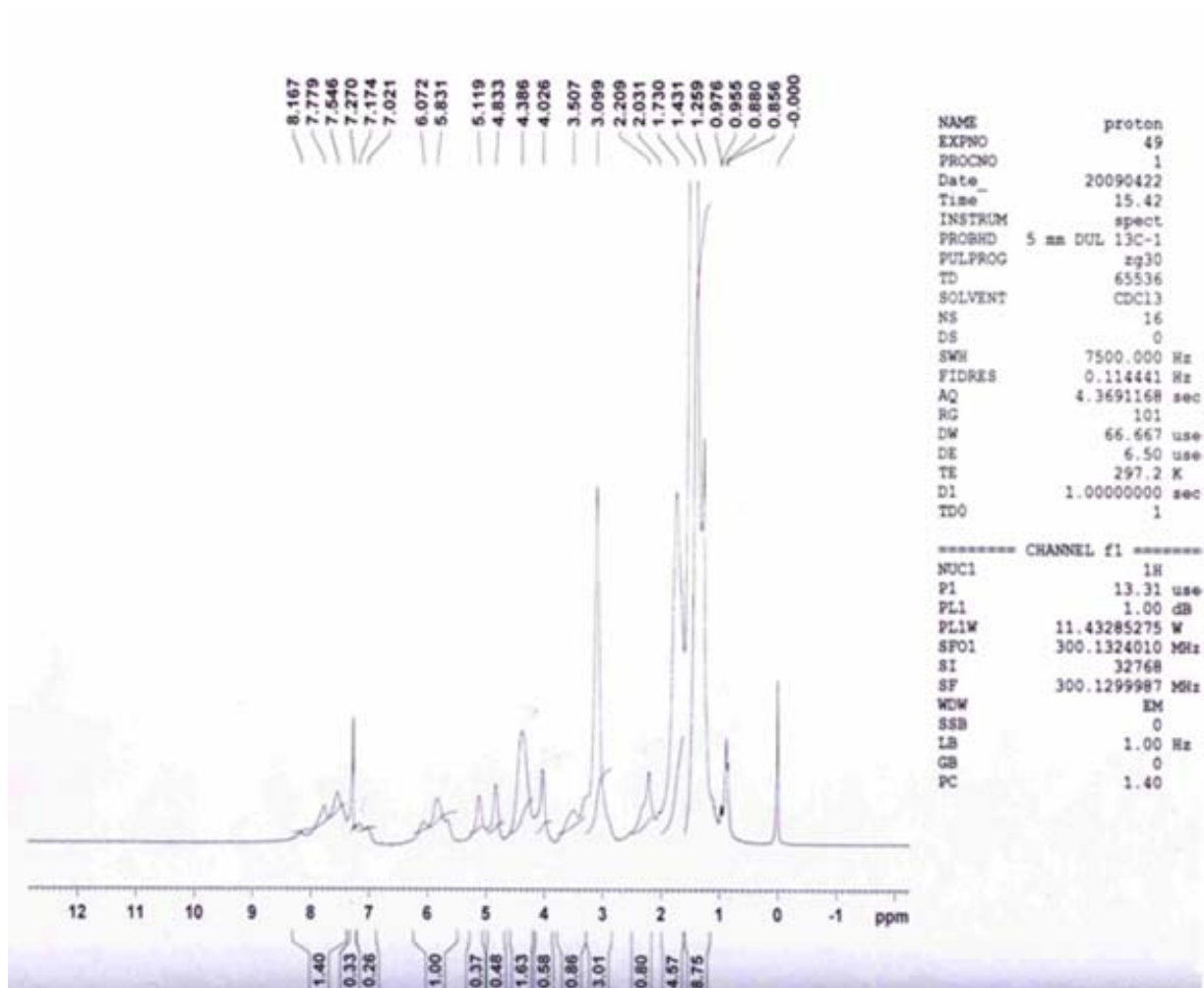
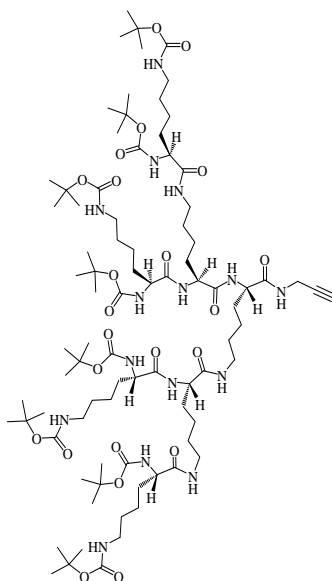
### Gelation and Topochemical Polymerization of Peptide Dendrimers

V. Haridas\*, Yogesh K. Sharma, Rhiannon Creasey, Srikanta Sahu, Christopher Gibson and  
Nicolas H. Voelcker\*

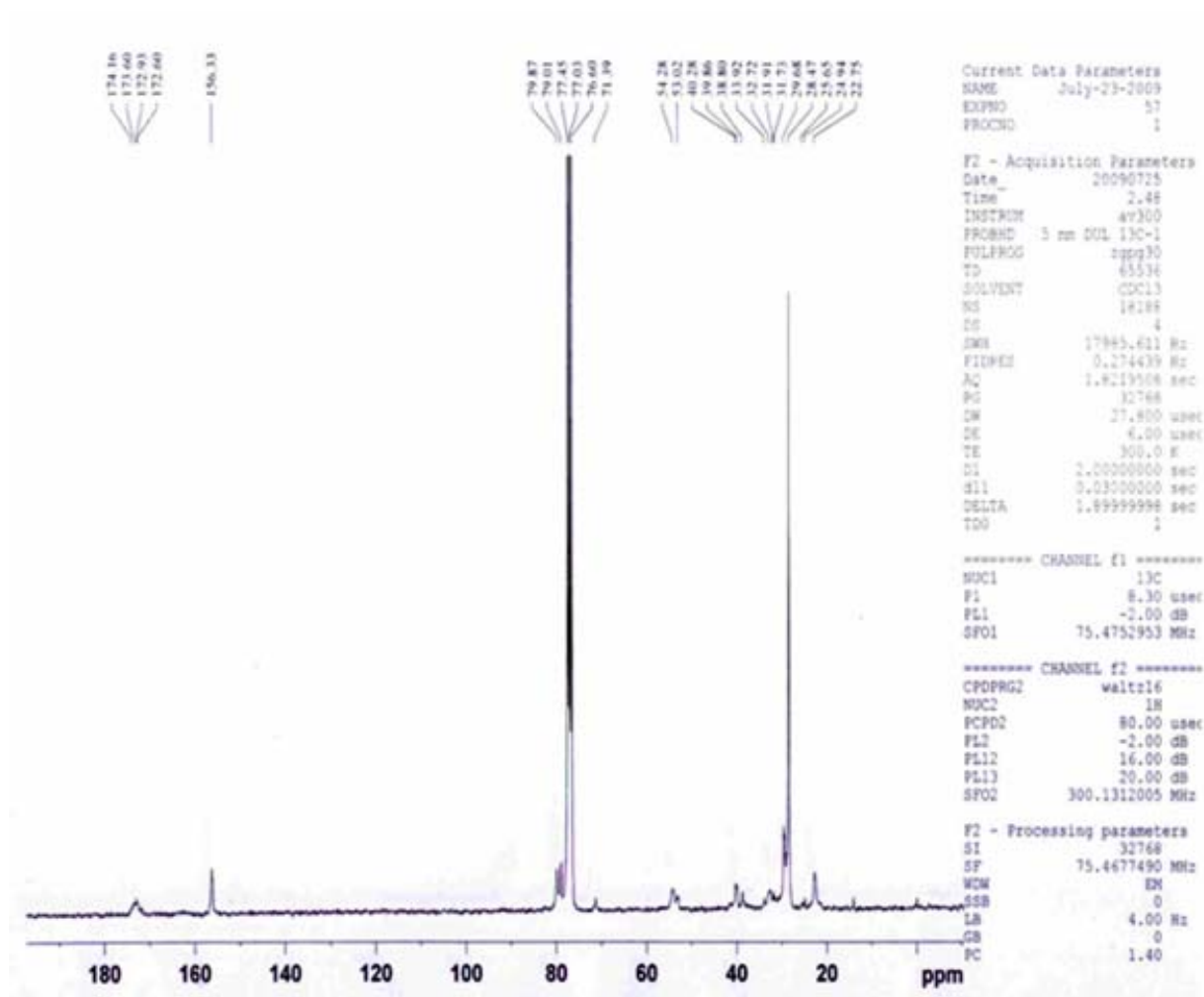
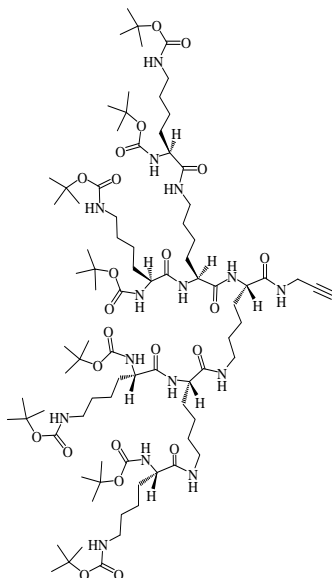
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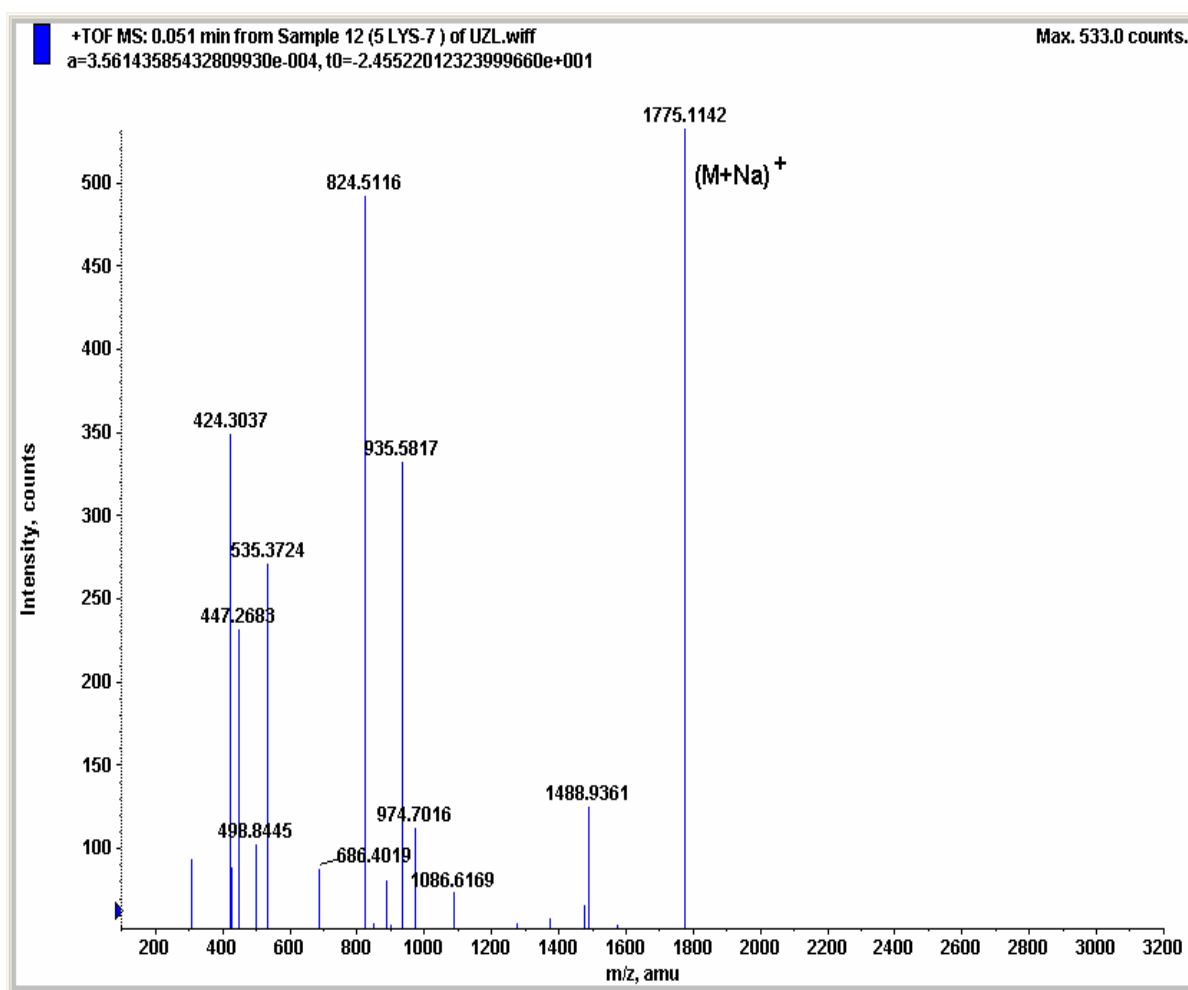
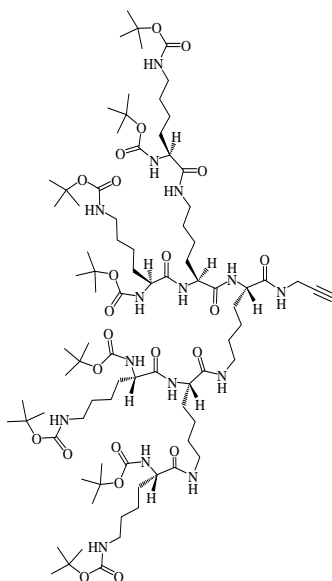
### <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) of 4



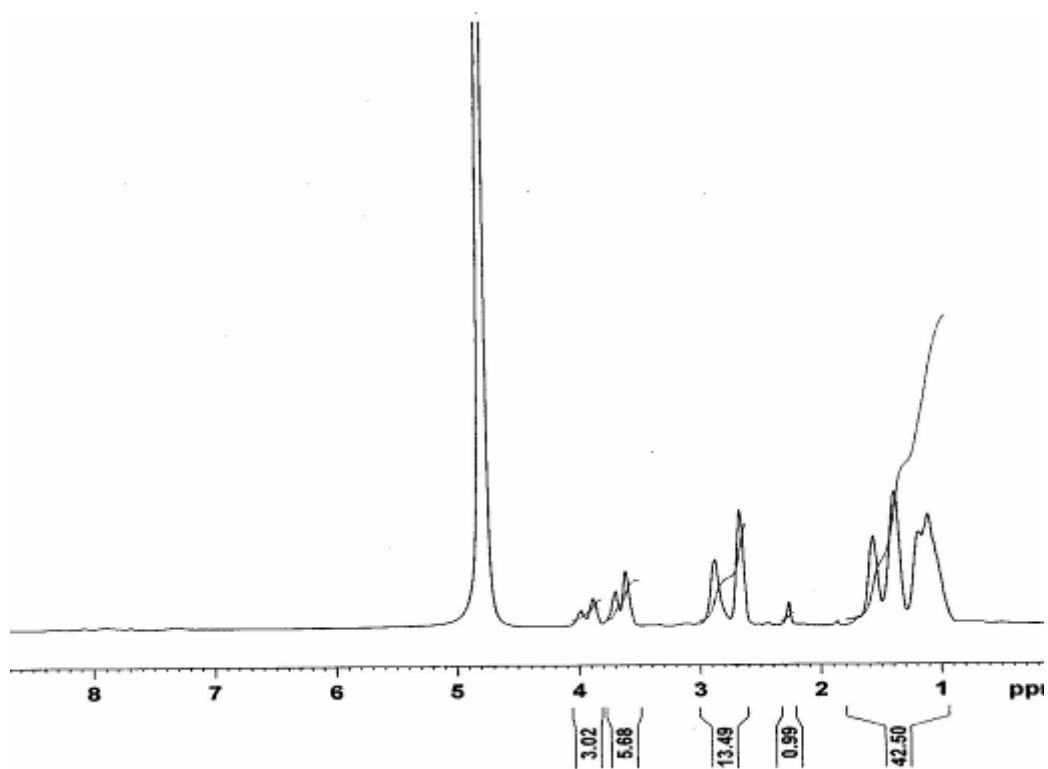
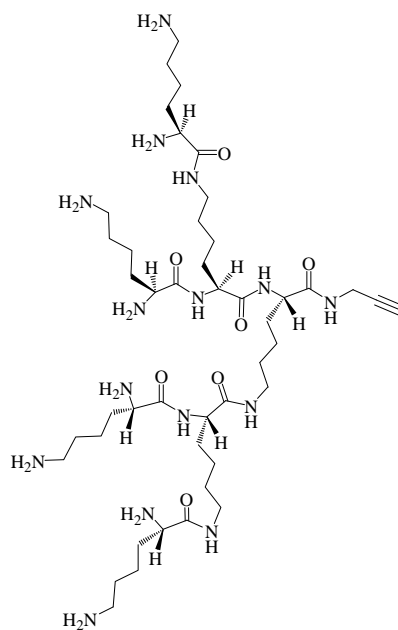
**$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ) of 4**



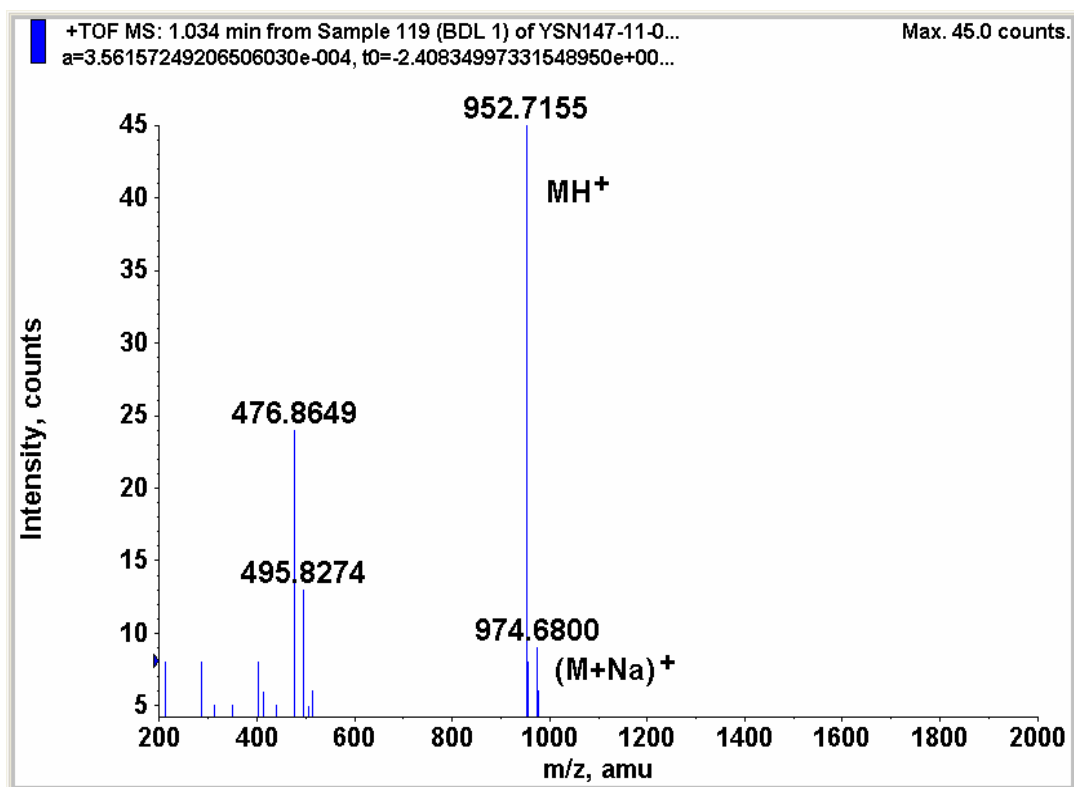
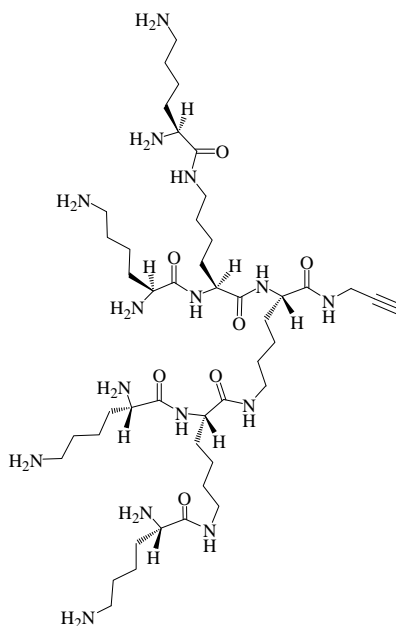
### HRMS of 4



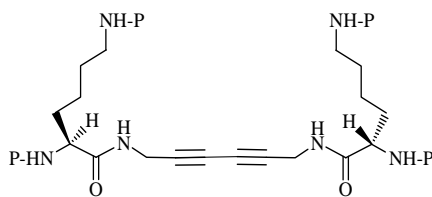
$^1\text{H}$  NMR ( $\text{D}_2\text{O}$ , 300 MHz) spectrum of deprotected **4**



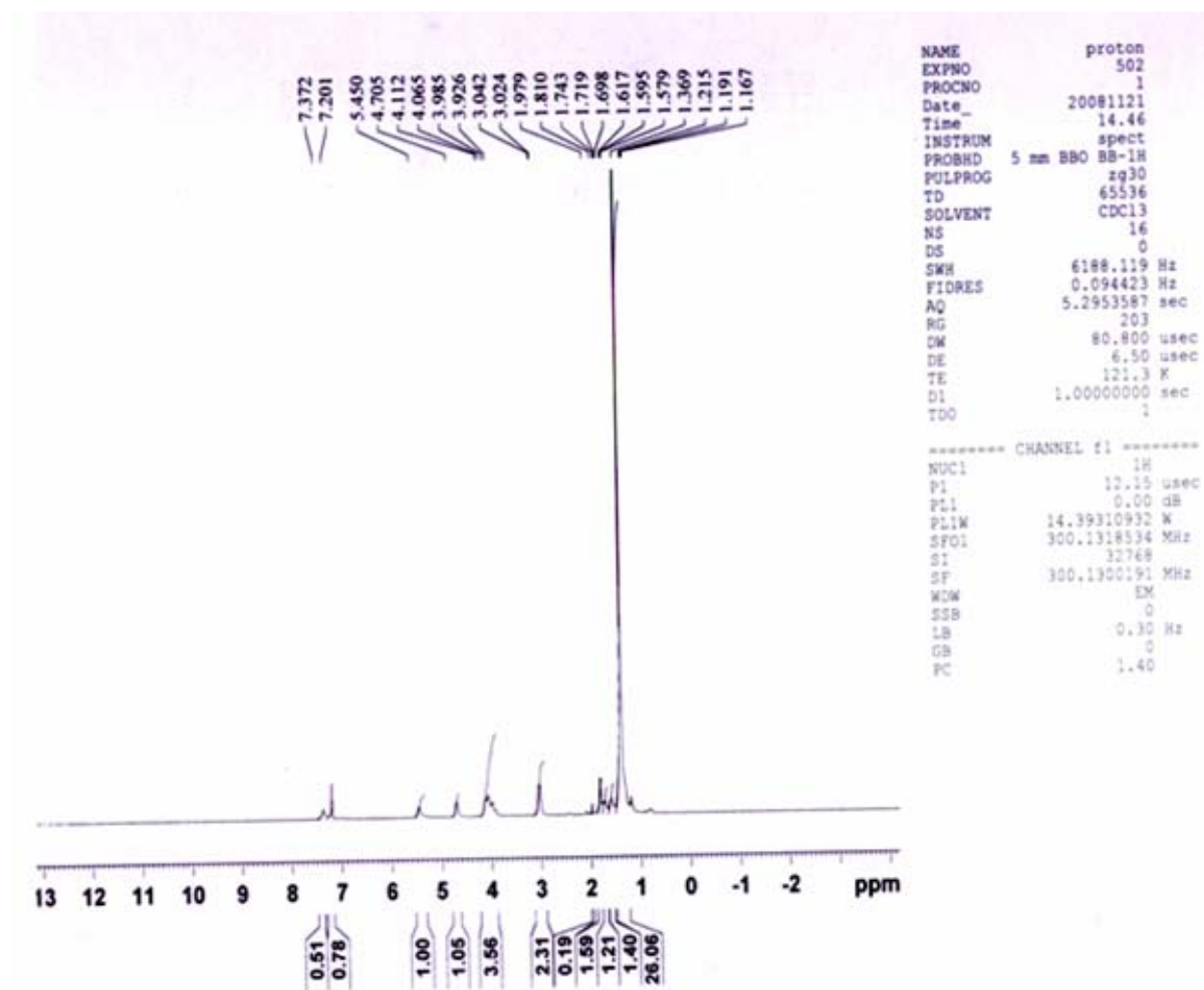
### ESI-MS of deprotected 4



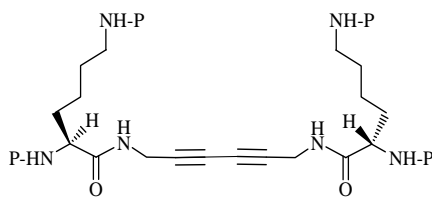
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) of **5a**



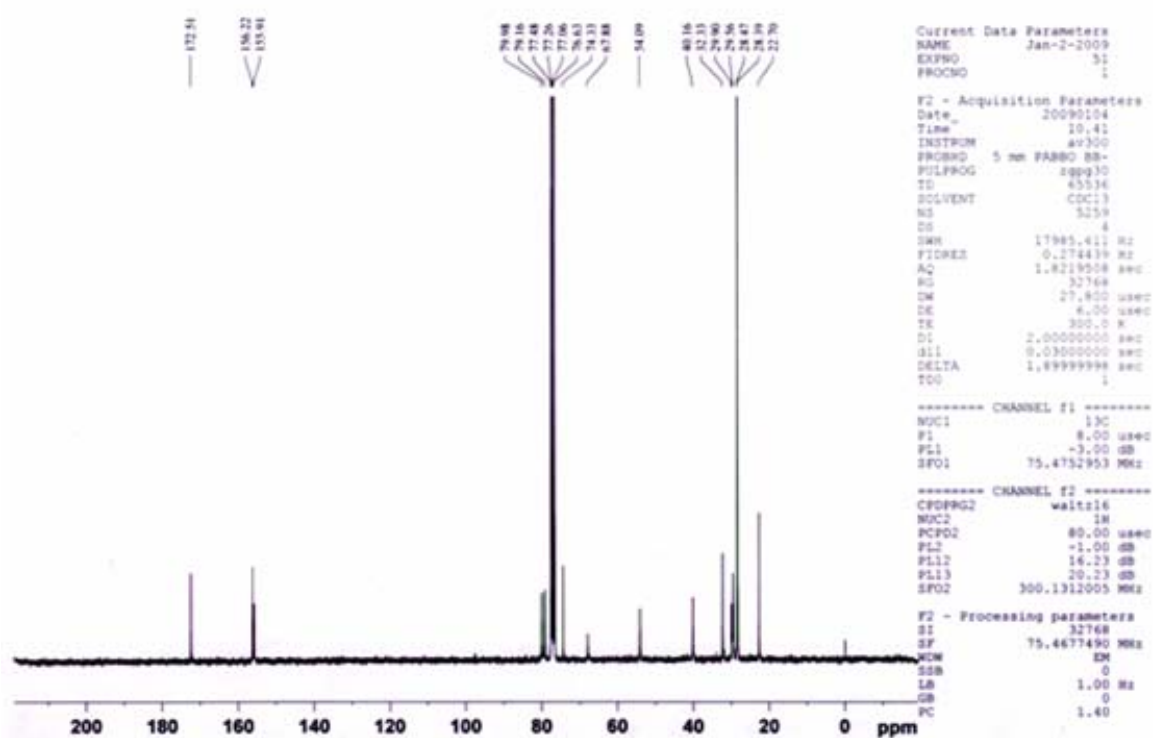
P = Boc



$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ) of **5a**

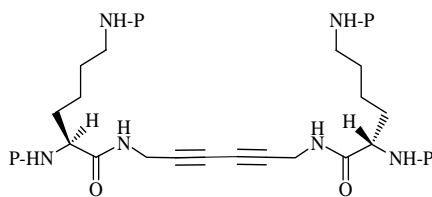


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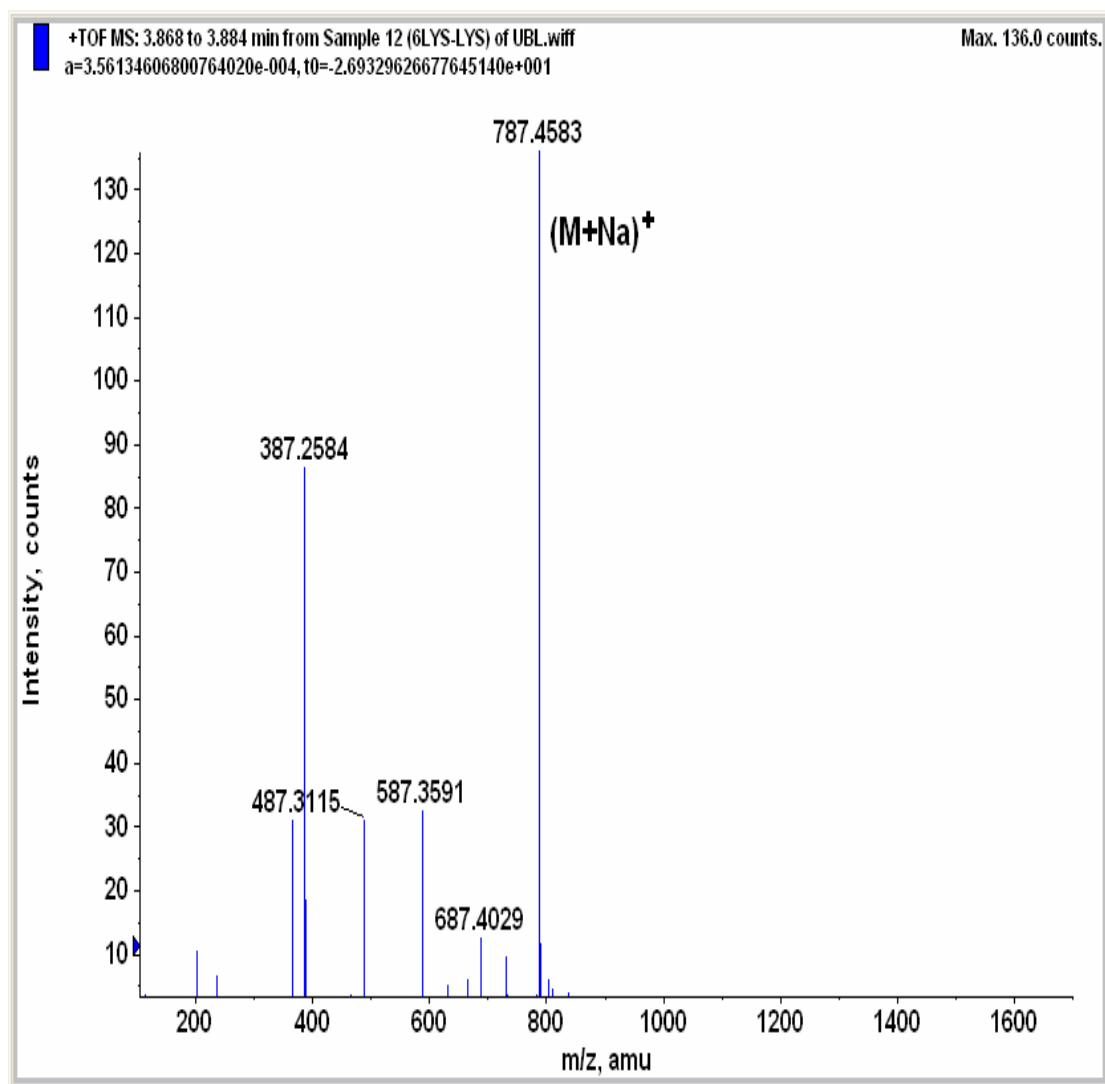




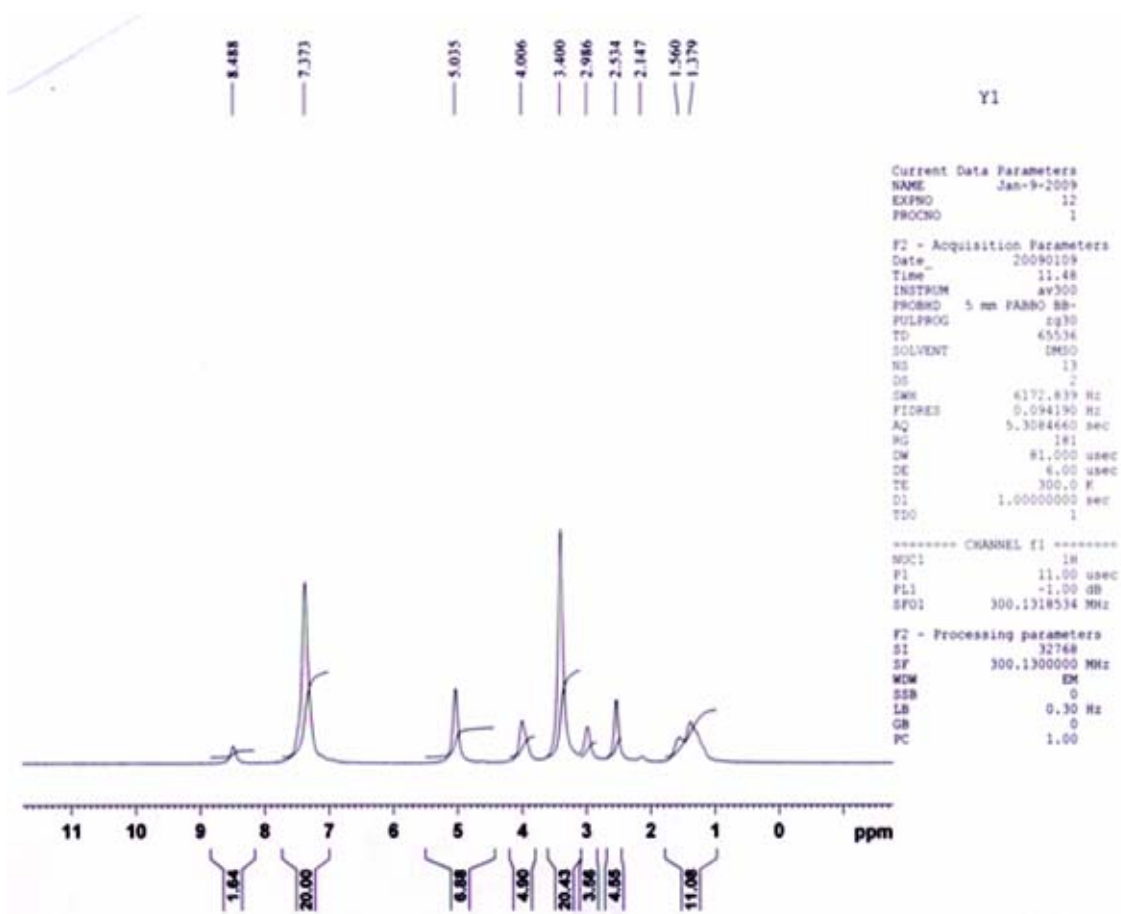
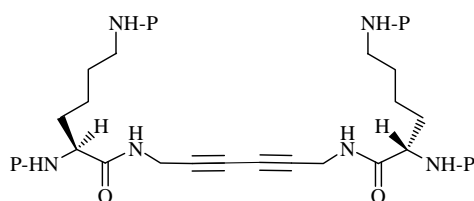
### HRMS of **5a**



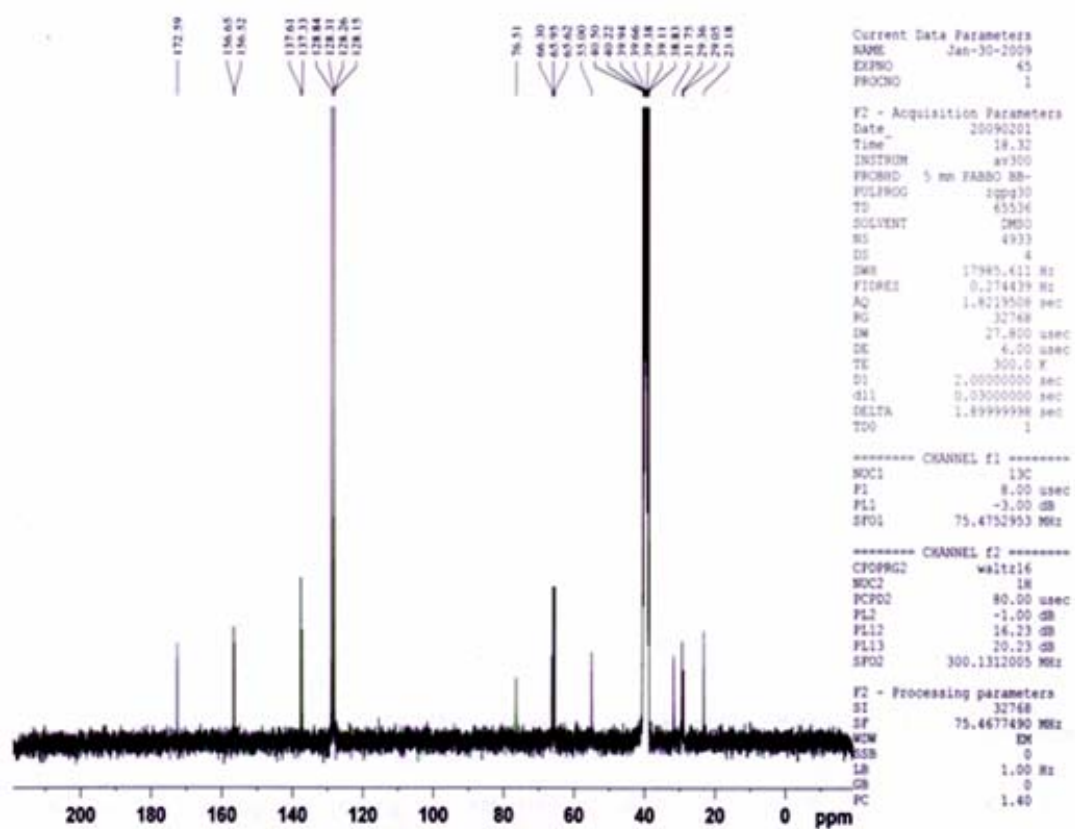
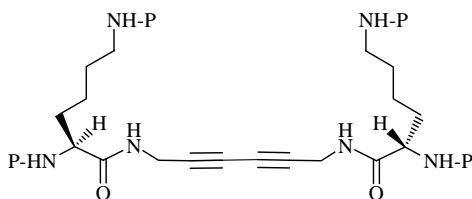
**P = Boc**



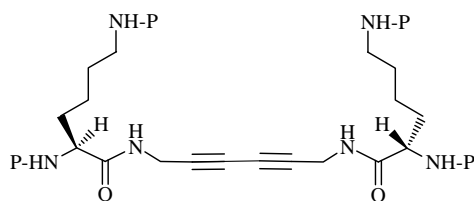
$^1\text{H}$  NMR (300 MHz,  $\text{DMSO-d}_6$ ) of **5b**



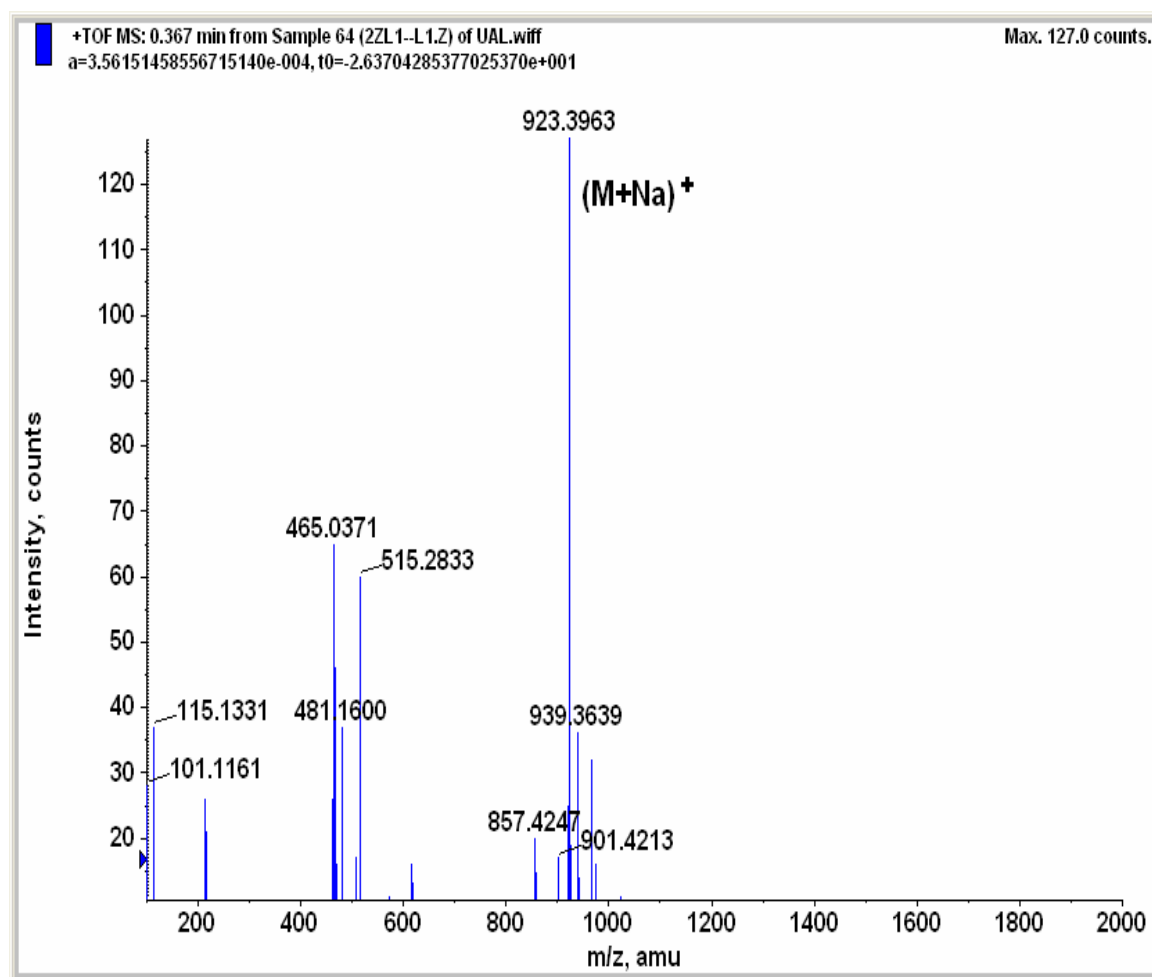
$^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ ) of **5b**



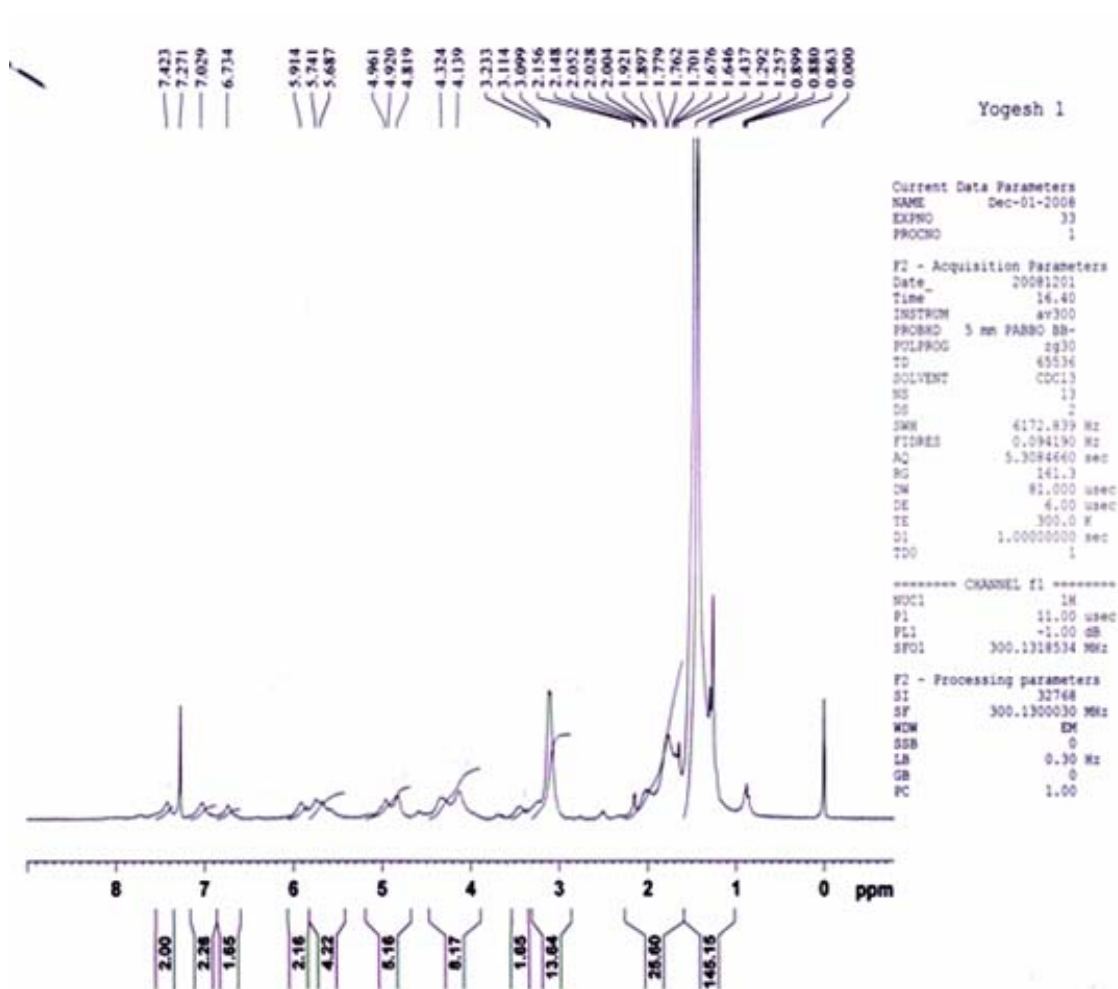
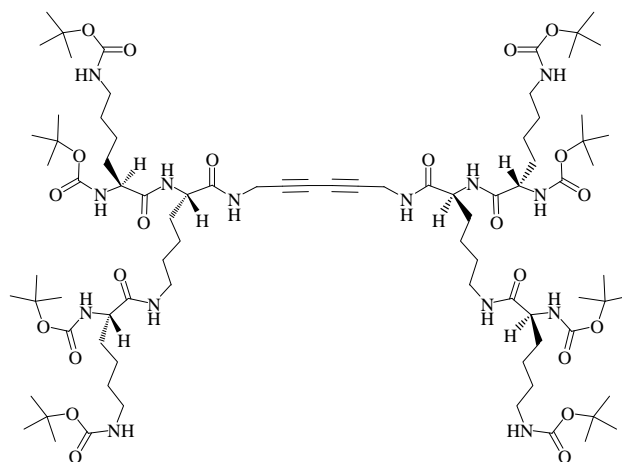
### HRMS of **5b**



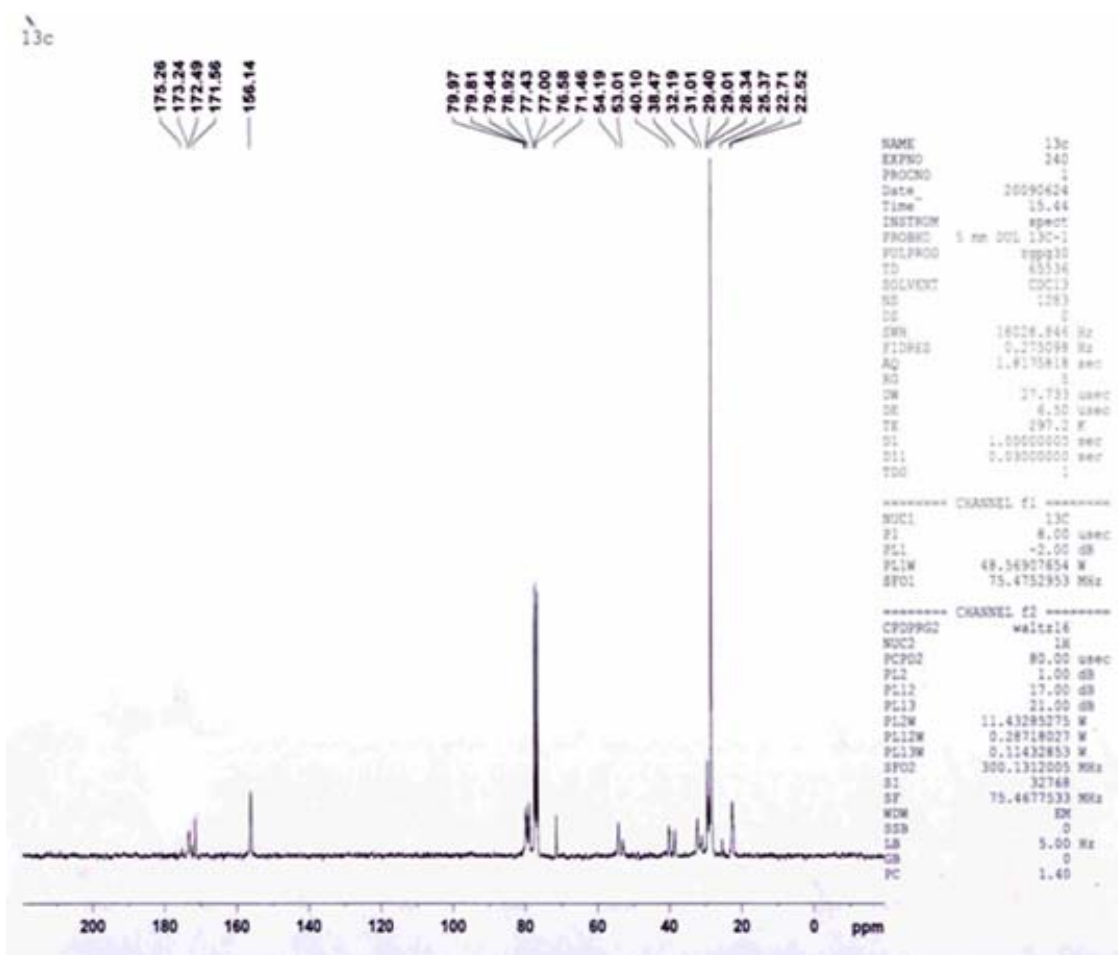
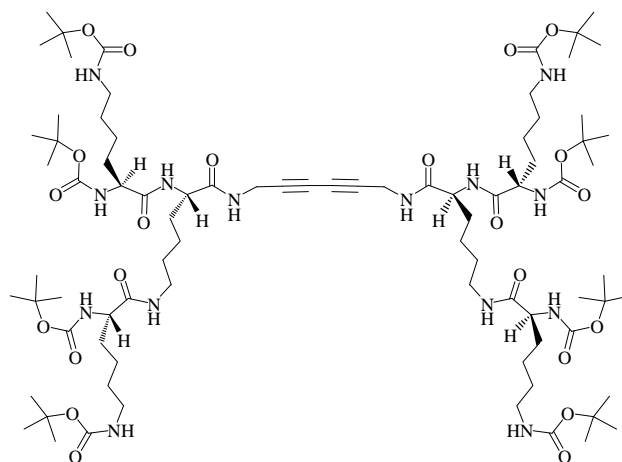
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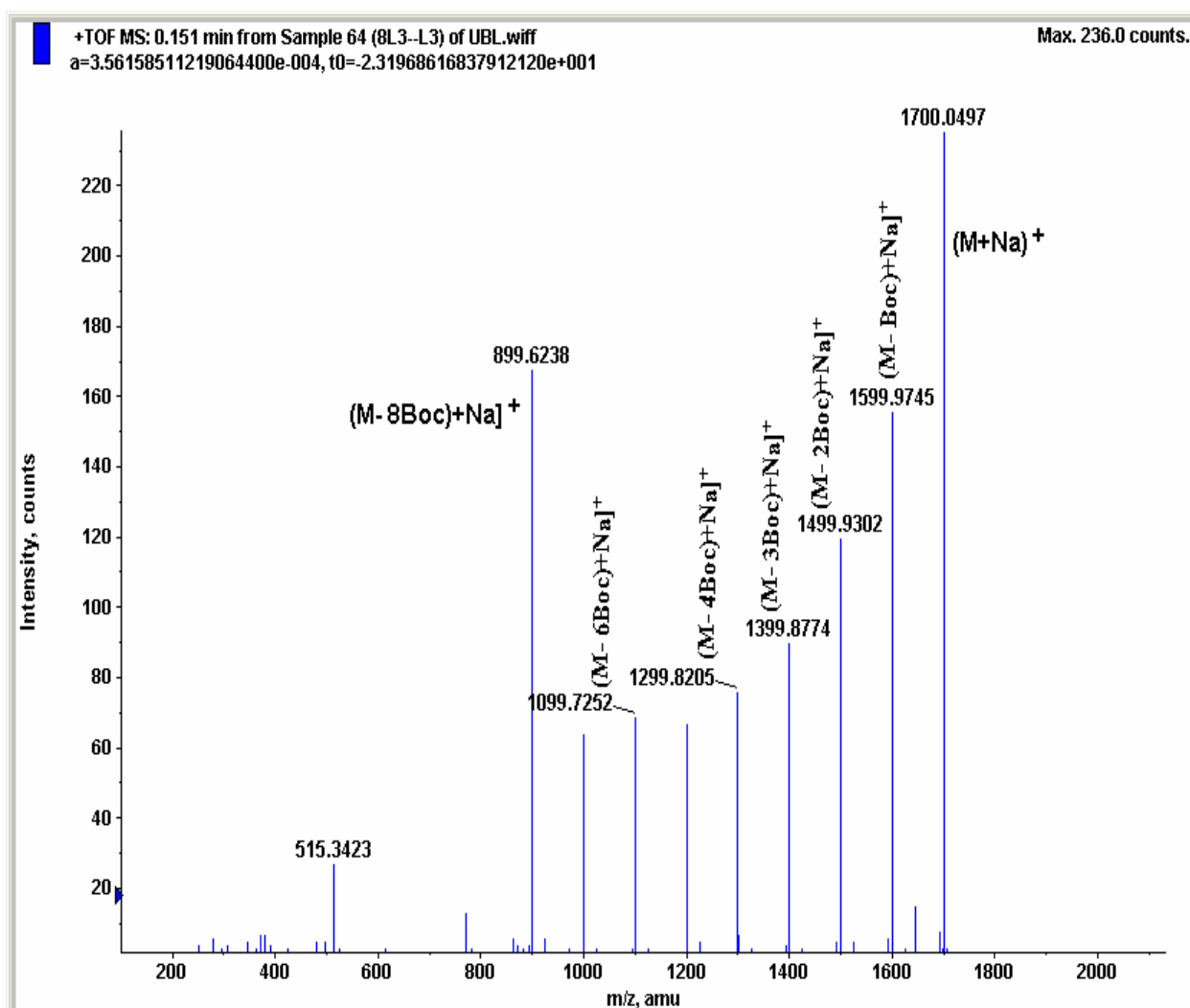
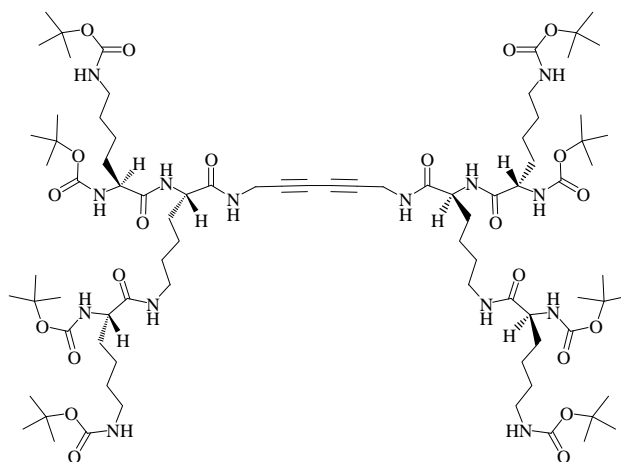
### <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) of 6



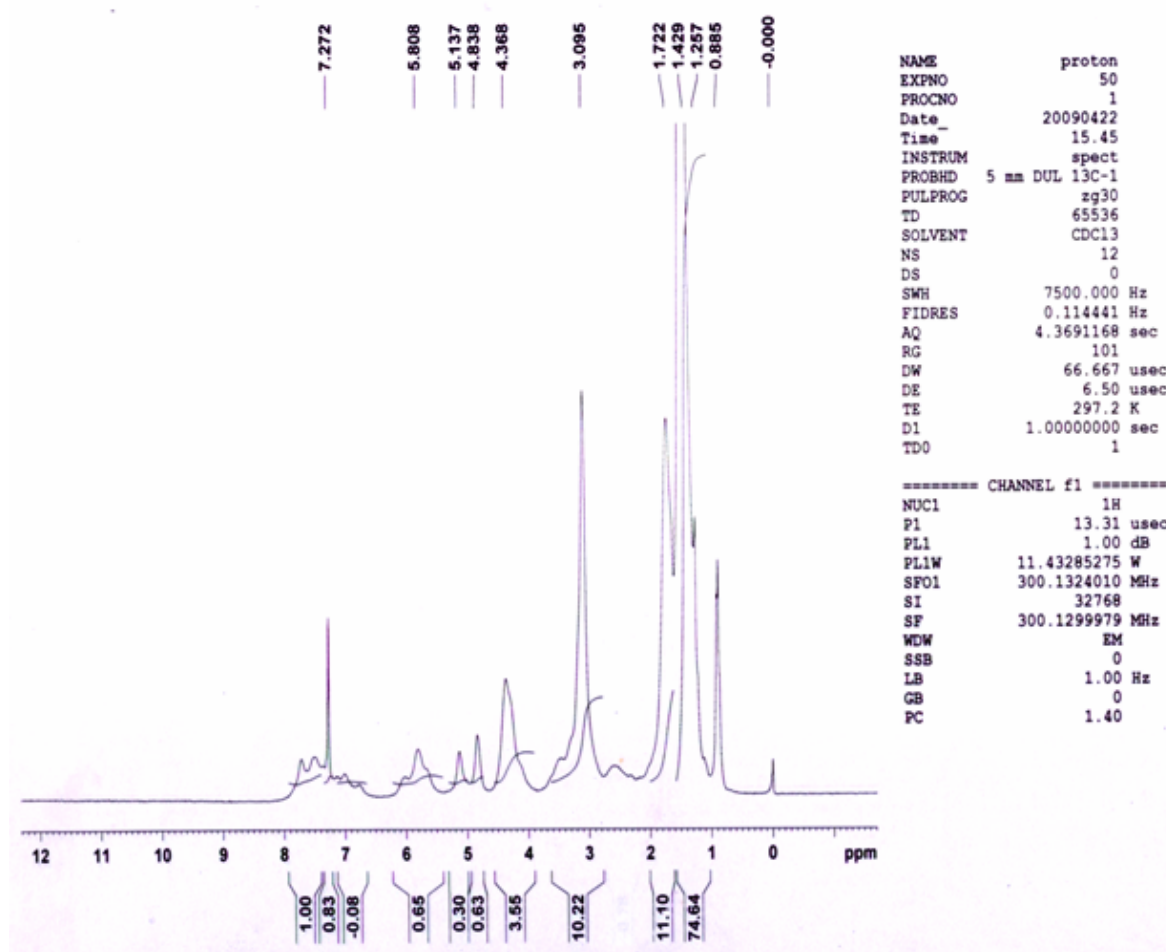
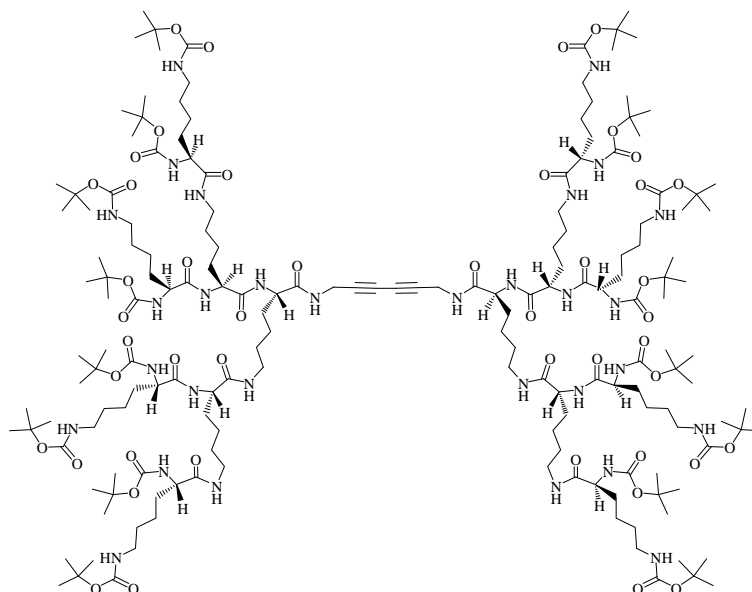
### $^{13}\text{C}$ NMR (75 MHz, $\text{CDCl}_3$ ) of 6



### HRMS of 6

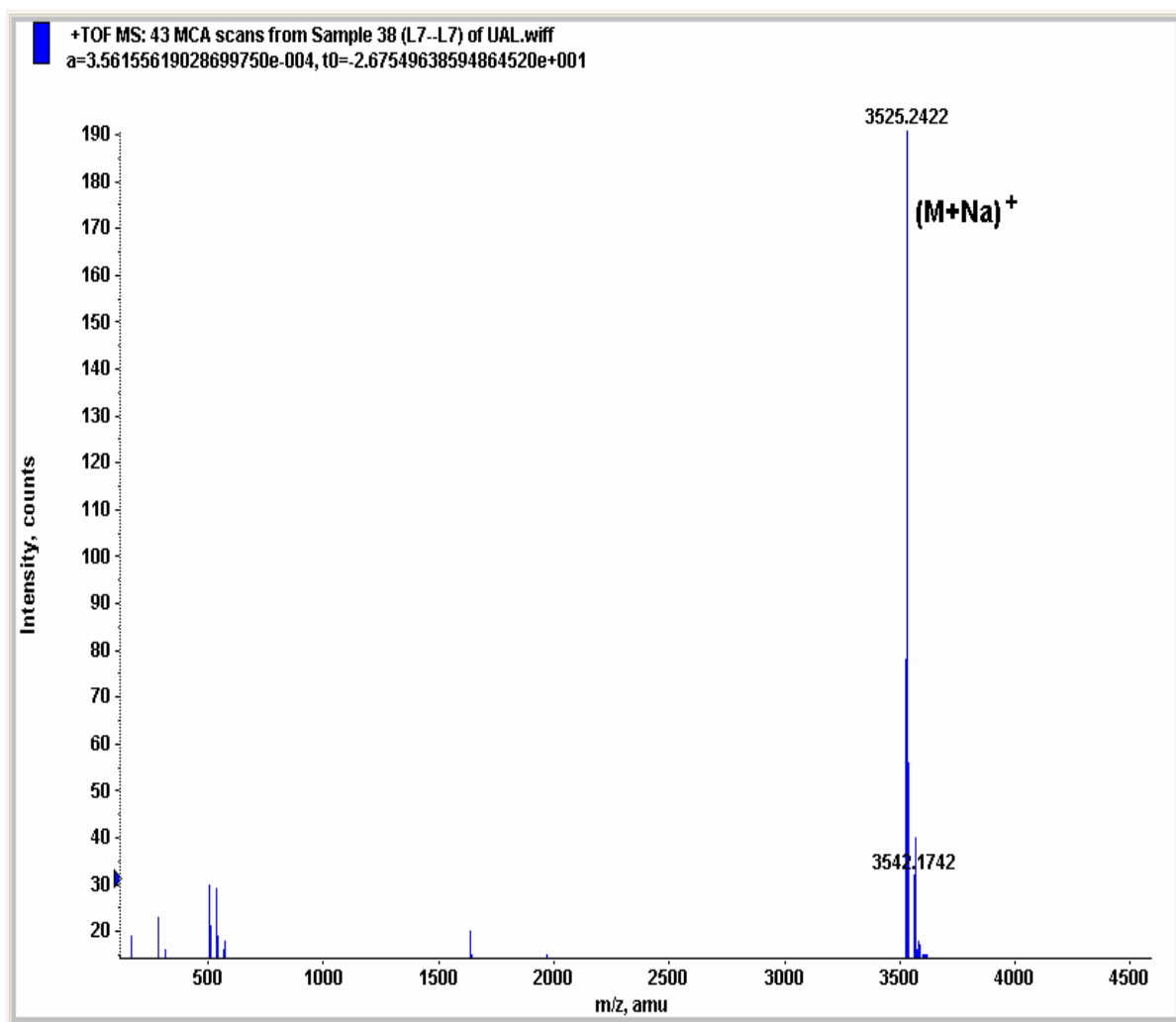
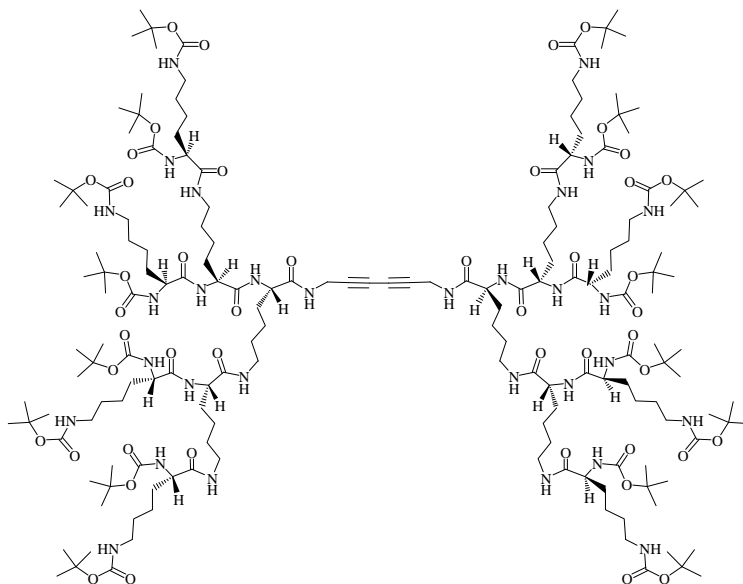


### <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) of 7

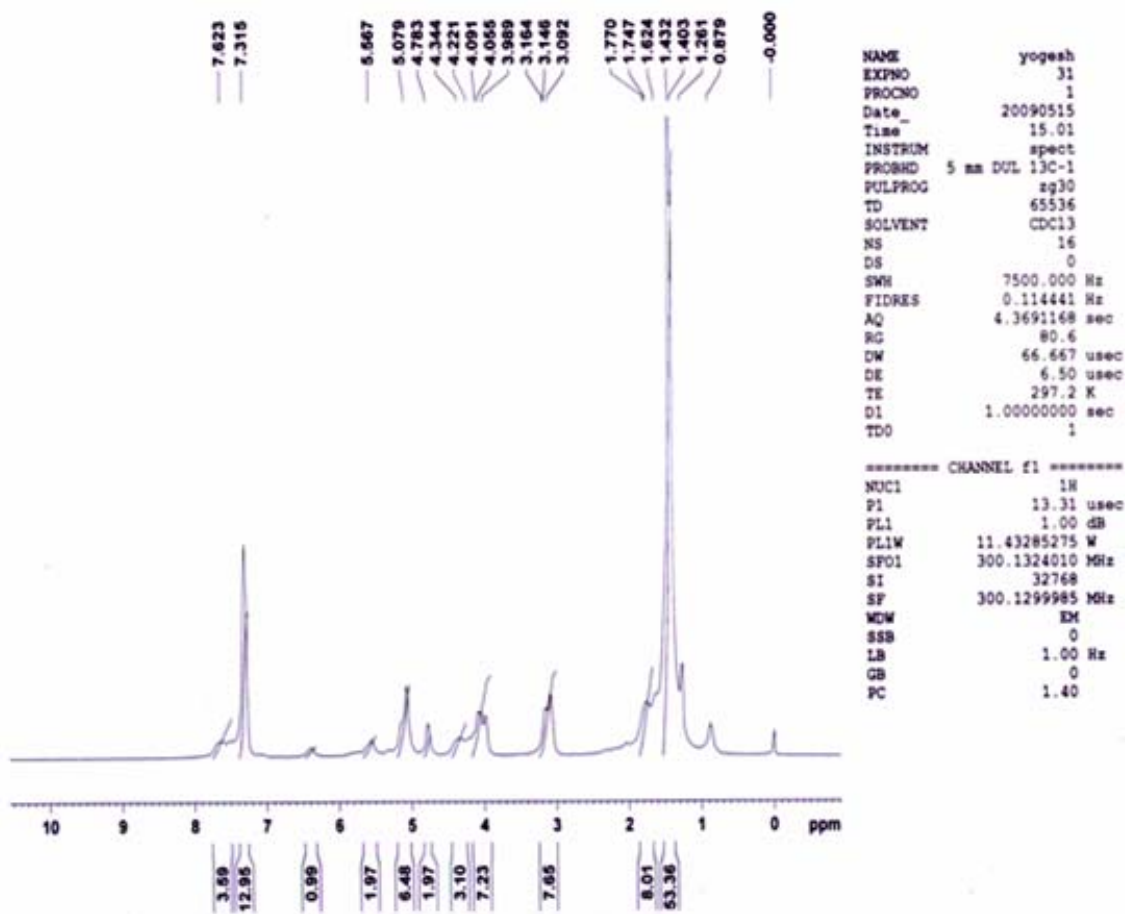
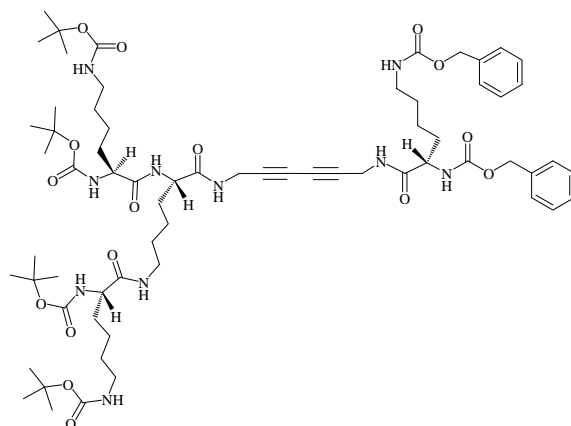




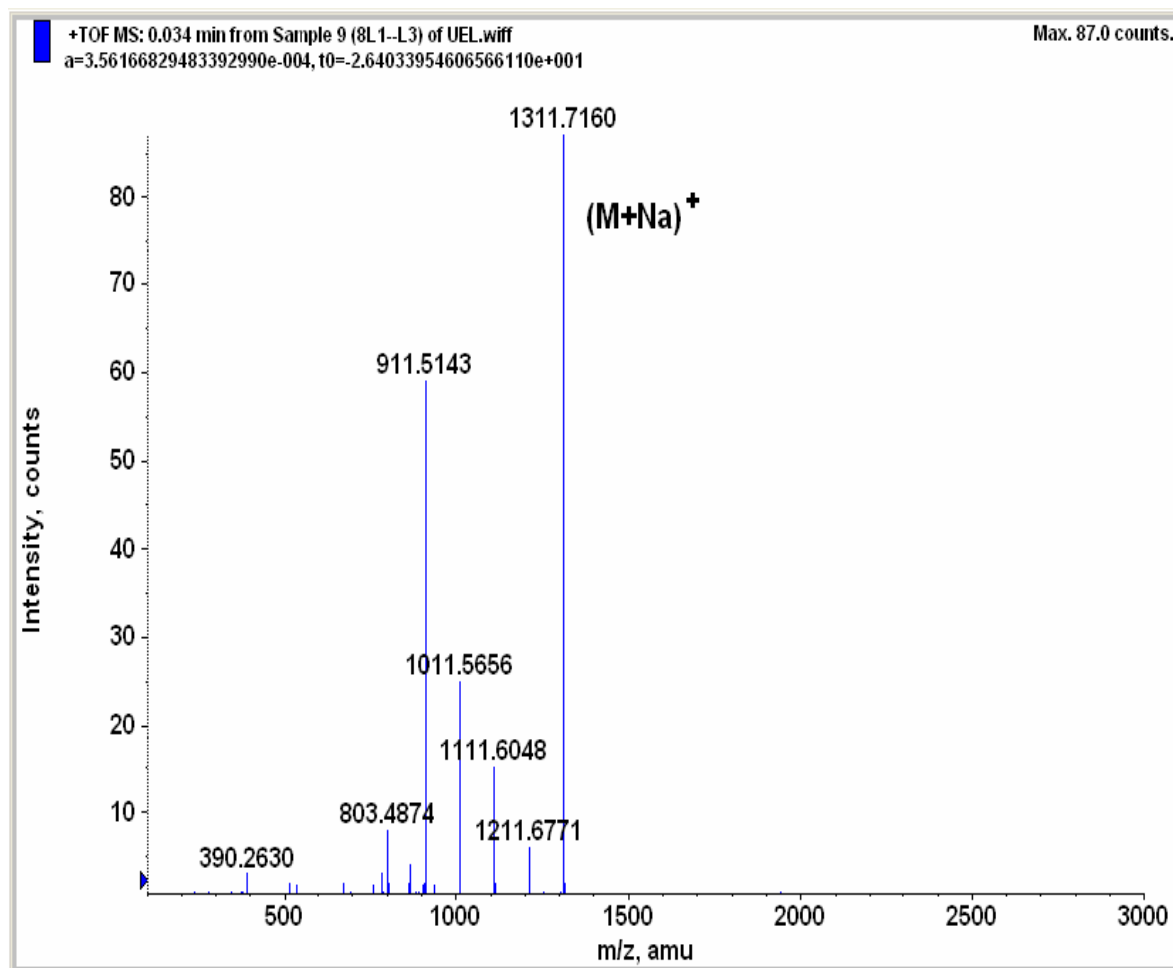
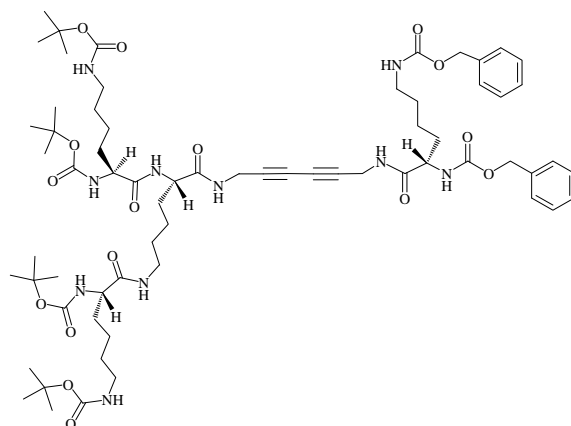
### HRMS of 7



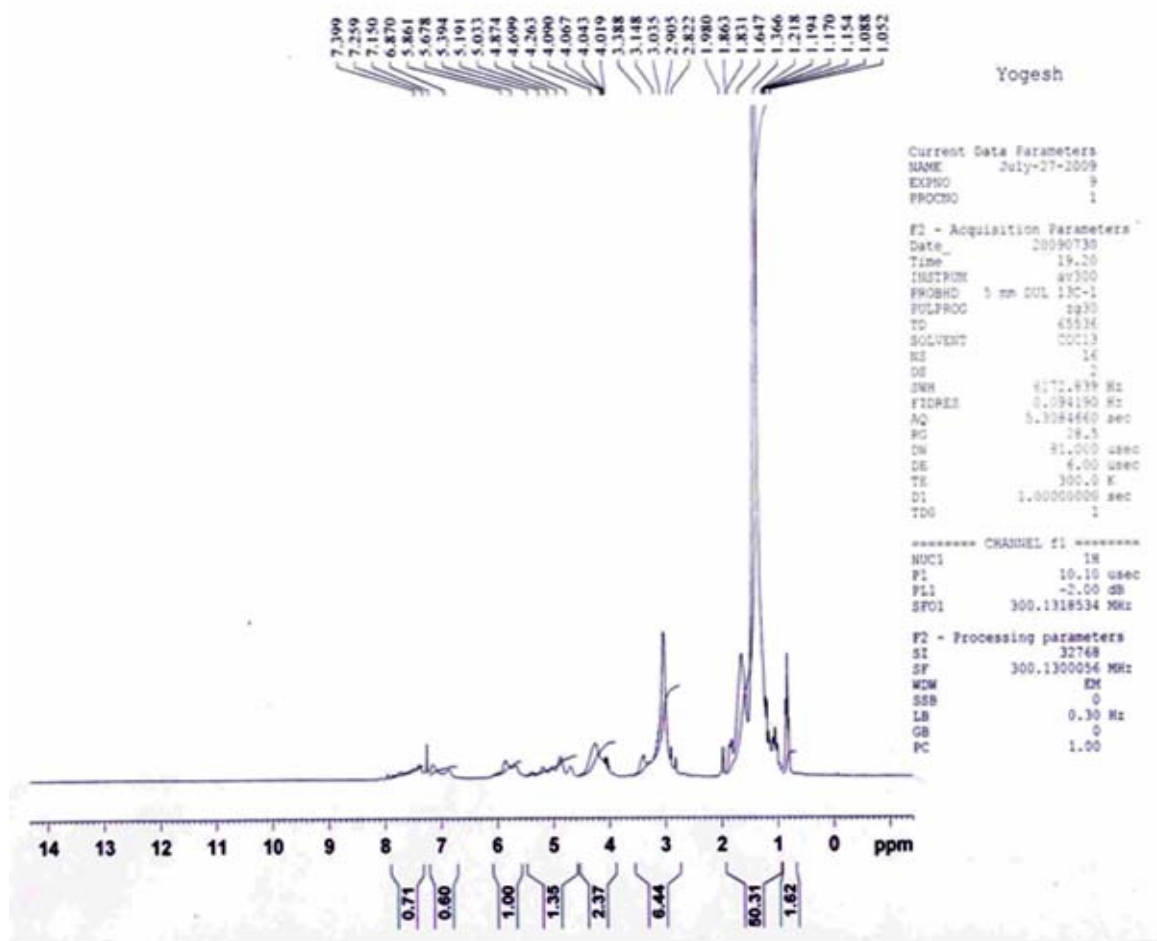
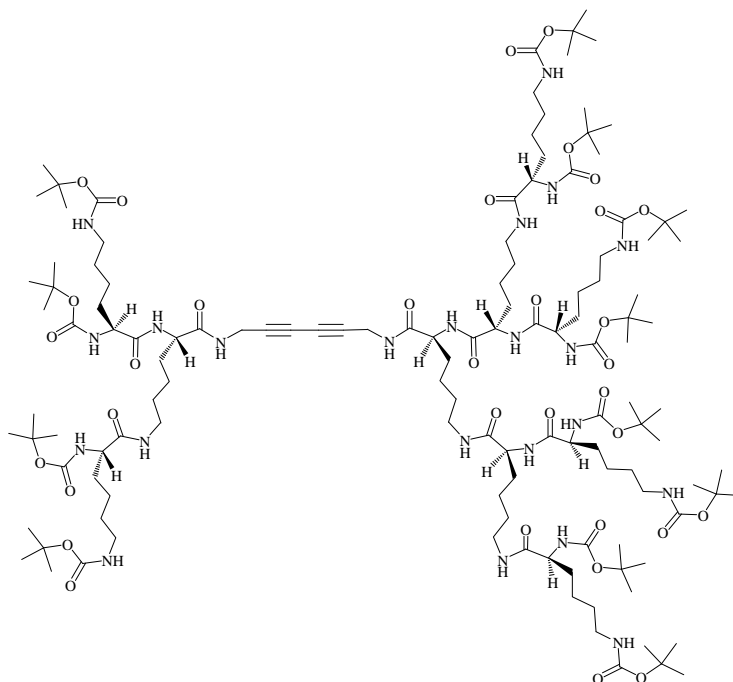
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) of **8**



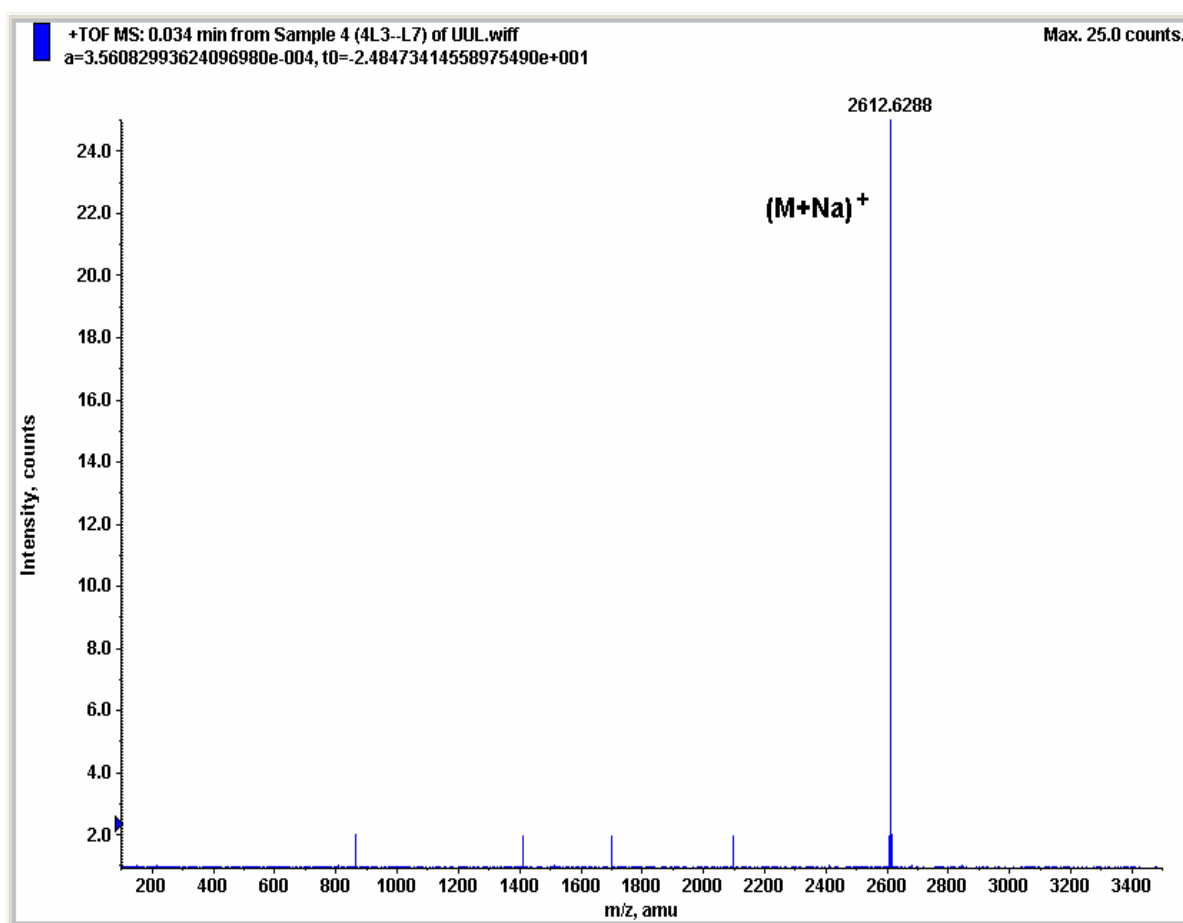
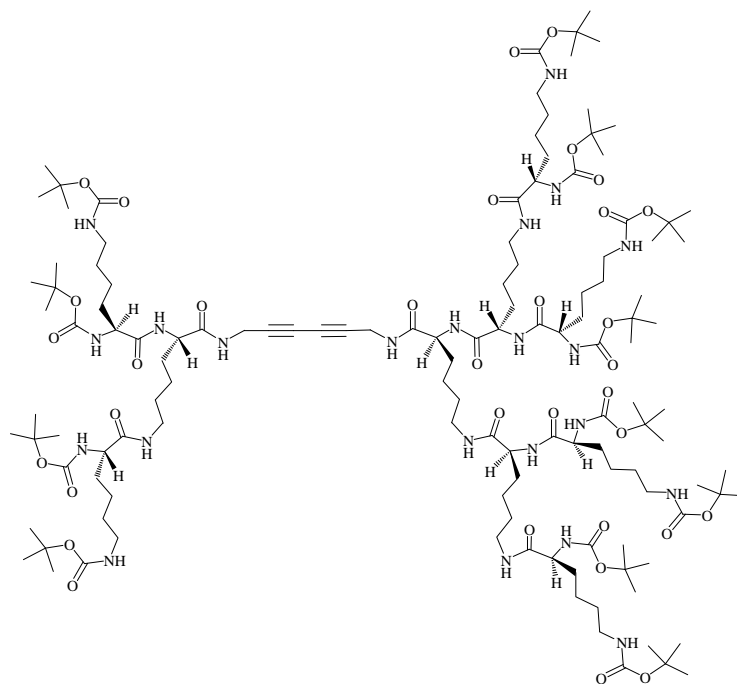
### HRMS of **8**



### $^1\text{H}$ NMR (300 MHz, $\text{CDCl}_3$ ) of **9**



### HRMS of 9



### Supplementary Table

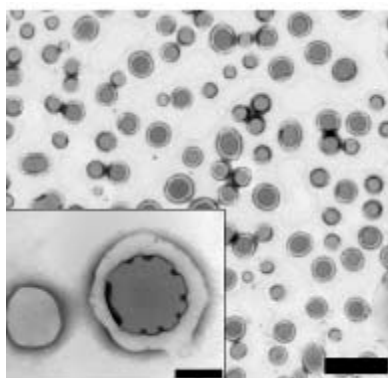
**Table S1.** Gelation study in various solvent mixtures. The dendrons (**3** and **4**) or dendrimers (**5a** and **5b**) were dissolved in the more polar solvent and the less polar solvent was then added to initiate gel formation. The gel formation is assessed by the tube inversion method. The symbol ✓ in the table corresponds to formation of the gel and X denotes that no gel formation in that particular solvent has taken place. This table shows only mixture of solvents, because none of the compounds gelled in a single solvent.

Solvent	Sample			
	3	4	5a	5b
Ethyl acetate + hexane (2:3)	✓	X	✓	X
Dichloromethane + hexane (2:3)	X	X	X	X
Chloroform + hexane (2:3)	X	X	X	X
Methanol + hexane (2:3)	X	X	X	X
Acetonitrile + hexane (2:3)	X	X	X	X
Ethanol + hexane (2:3)	X	X	X	X
Acetone + hexane (2:3)	X	X	X	X
Tetrahydrofuran + hexane (2:3)	X	X	X	X
Methanol + ethyl acetate (1:9)	X	✓	X	X
Methanol + dichloromethane (1:9)	X	X	X	X
Methanol + chloroform (1:9)	X	X	X	X
Methanol + acetonitrile (1:9)	X	X	X	X
Methanol + ethanol (1:9)	X	X	X	X
Methanol + acetone (1:9)	X	X	X	X
Methanol + ethyl acetate + hexane (1:2:2)	X	X	X	X
Methanol + chloroform + hexane (1:2:2)	X	X	X	✓

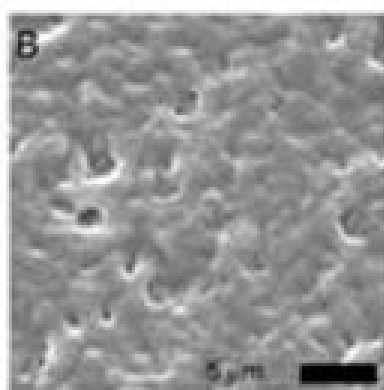
## Supplementary Figures



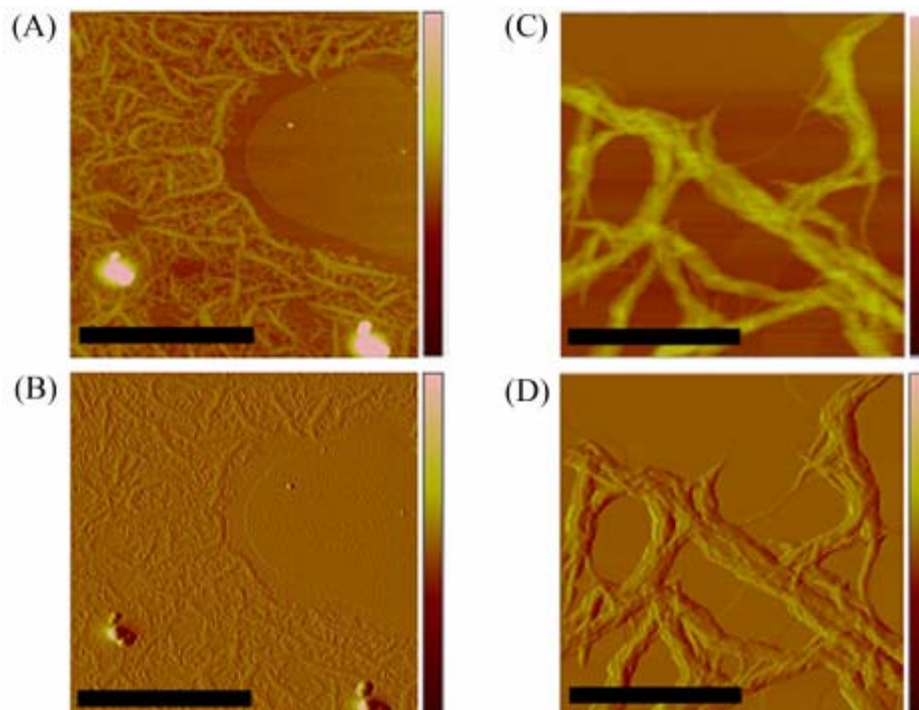
**Figure S1.** Photographs of a gel of **3** in an inverted glass tube.



**Figure S2.** TEM image of vesicles of **3** on a Cu and stained with phosphotungstate (Scale bar 2  $\mu\text{m}$ ; inset scale bar 200 nm).



**Figure S3.** SEM image of a gel of **4**

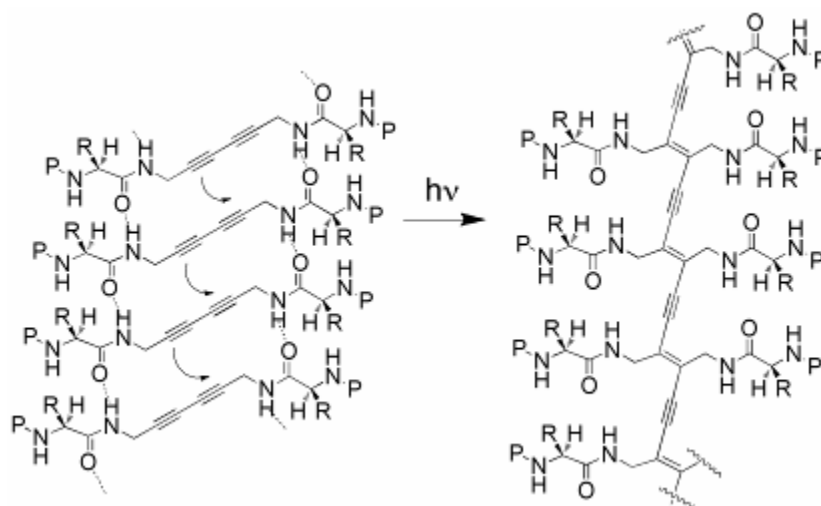


**Figure S4.** AFM topography images of **5b** gel before irradiation (scale bar 1  $\mu\text{m}$ ; z scale = 20 nm) [(A) and (B)] and after irradiation with an Hg lamp (scale bar 1  $\mu\text{m}$ ; z scale = 100 nm) [(C) and (D)], with (B) and (D) the corresponding AFM amplitude images to (A) and (C), respectively (z scale 0.25 V and 1 V correspondingly).

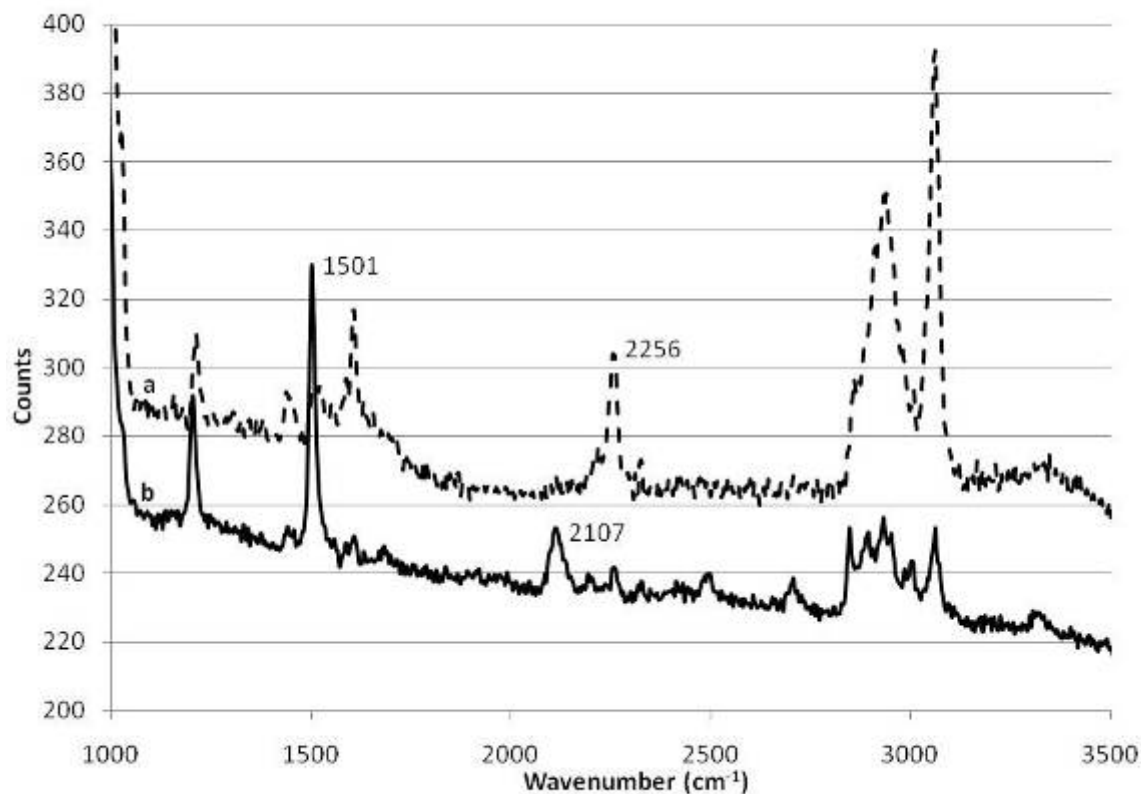


**Figure S5.** Photographs of a gel of **5b** in an inverted glass tube.





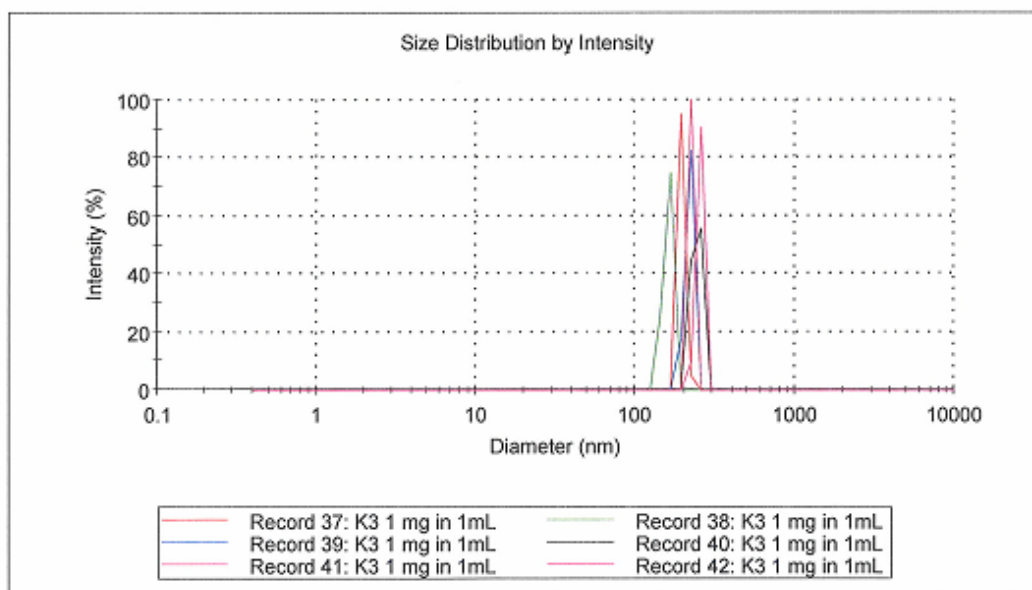
**Figure S6.** Schematic of the topochemical polymerization of diacetylene-core dendrimers.



**Figure S7.** (A) Raman spectra of the gel before UV irradiation (dotted line). The samples were dropped onto silicon and dried before recording. (B) Raman spectra of the gel after UV irradiation (solid line). The samples were dropped onto silicon and dried before recording.

Results

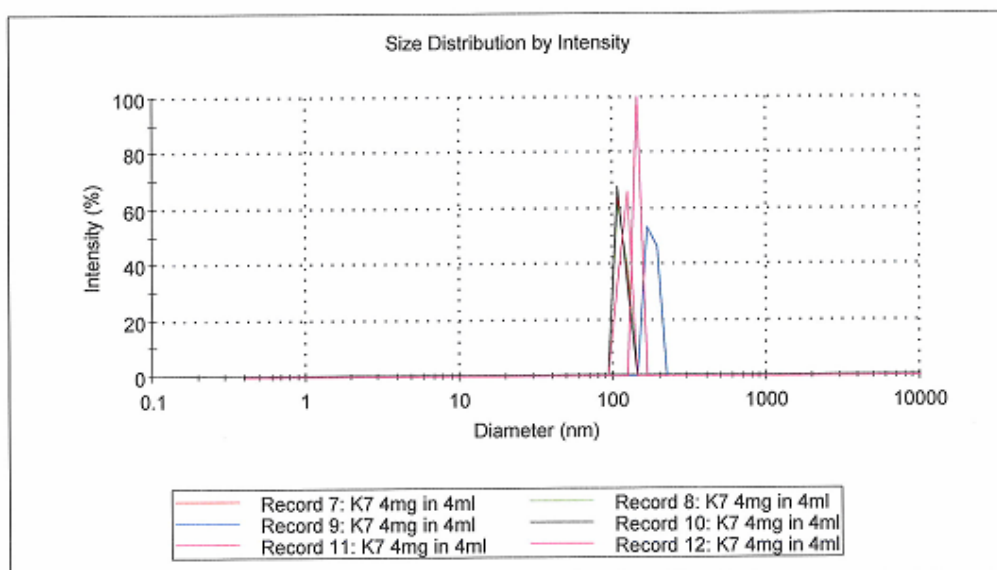
	Diam (nm)	% Int	Width (nm)
<b>Z-Average size (nm): 934.4</b>	<b>Peak 1:</b> 251.7	100	10.26
<b>Polydispersity index: 0.611</b>	<b>Peak 2:</b> 0	0	0
	<b>Peak 3:</b> 0	0	0



**Figure S8.** Dynamic light scattering measurement on dendron **3** (1 mg / mL) in Ethyl Acetate (data collected using a Zetasizer Nano-ZS , Malvern Instruments).

Results

	Diam (nm)	% Int	Width (nm)
<b>Z-Average size (nm): 1525</b>	<b>Peak 1:</b> 141.8	100	1.907e-006
<b>Polydispersity index: 1.000</b>	<b>Peak 2:</b> 0	0	0
	<b>Peak 3:</b> 0	0	0



**Figure S9.** Dynamic light scattering measurement on dendron **4** (1 mg / mL) in methanol (data collected using a Zetasizer Nano-ZS , Malvern Instruments)