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Figure S1. Structure of compound 8', the linear precursor of compound 8.

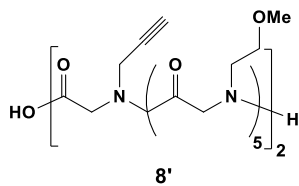


Figure S2. Full structure of cluster 1.

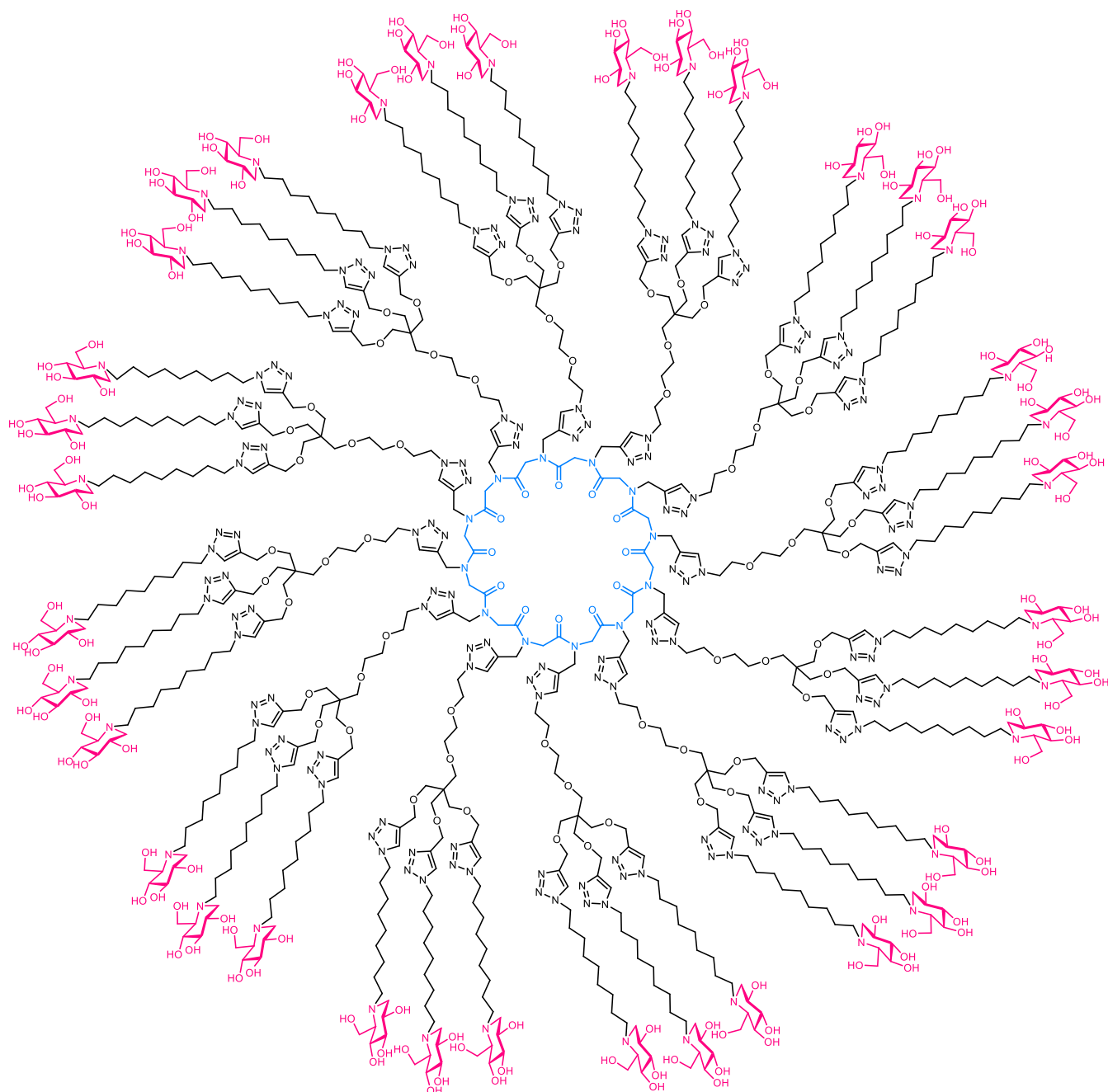


Figure S3. Full structure of cluster 4.

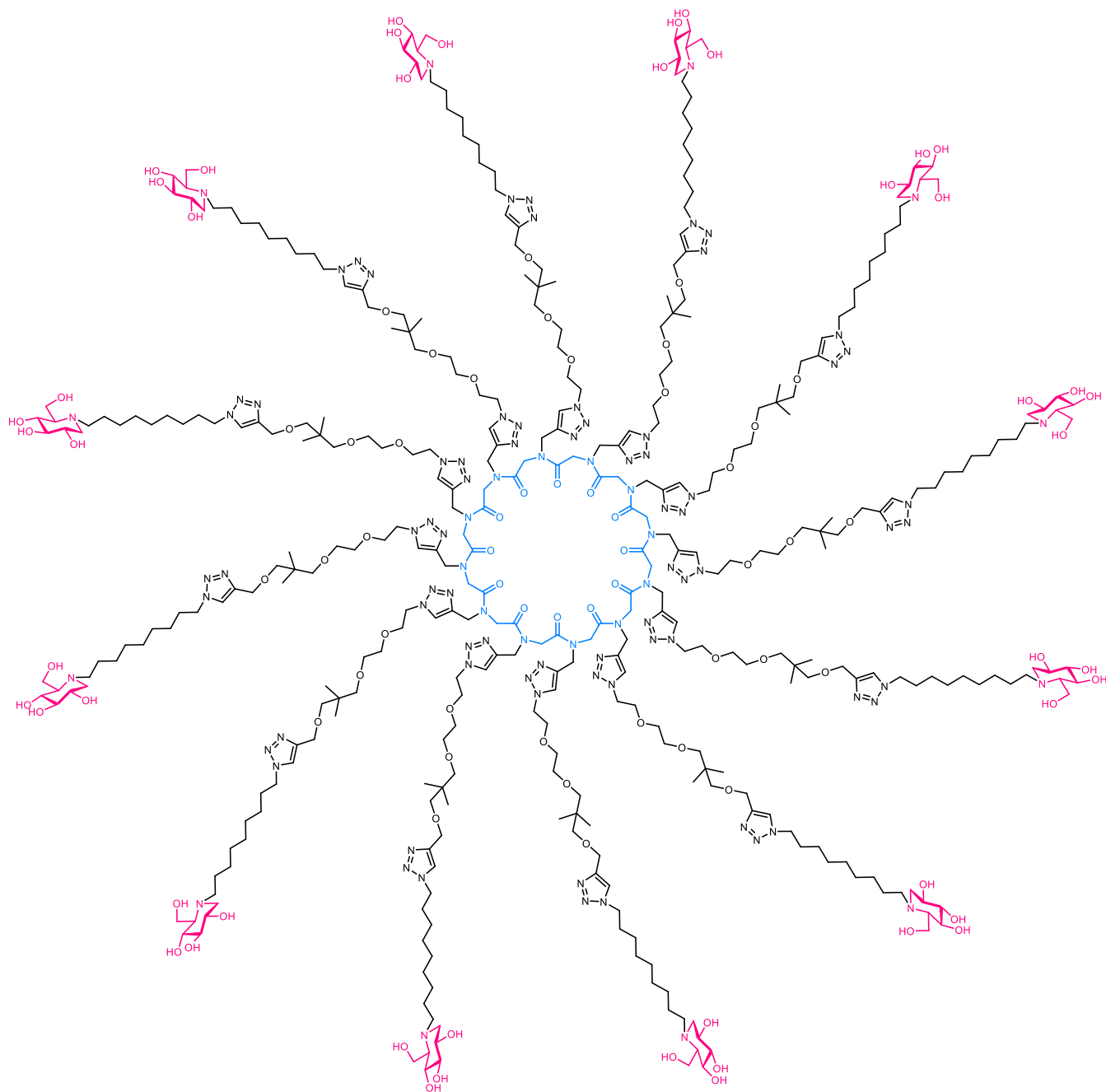
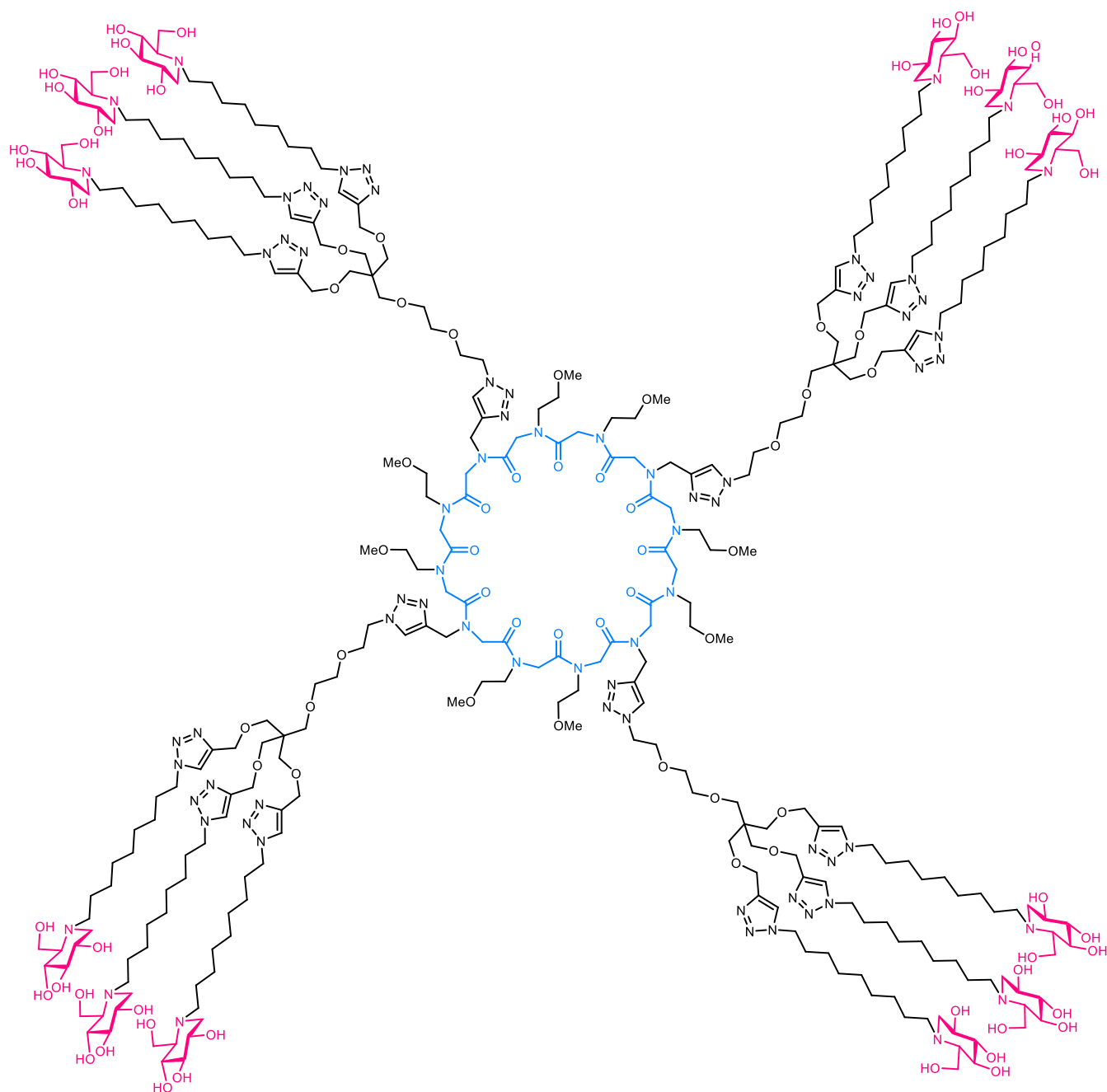


Figure S4. Full structure of cluster 5c.



Inhibition assays against Jack Bean α -mannosidase.

Figure S5. Lineweaver-Burk plot and replot for K_i determination of compound 7 against JB α -man at pH 5. $K_i = 54 \pm 5 \mu\text{M}$.

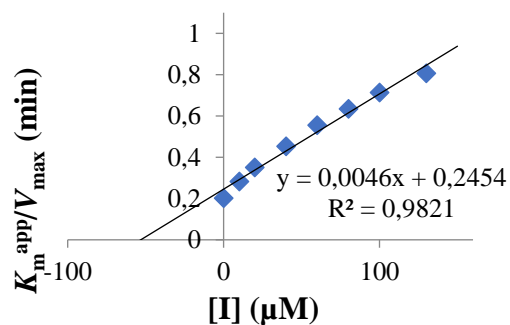
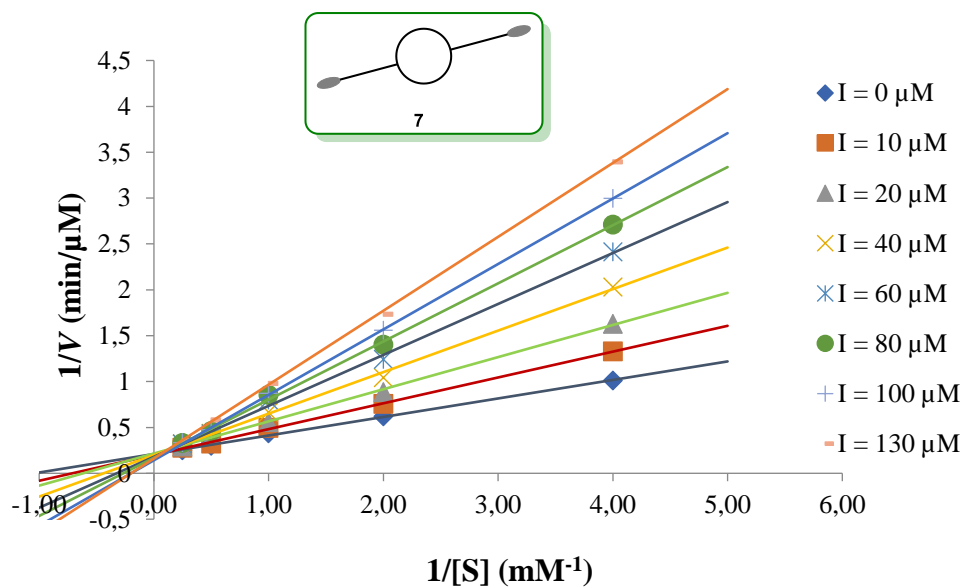
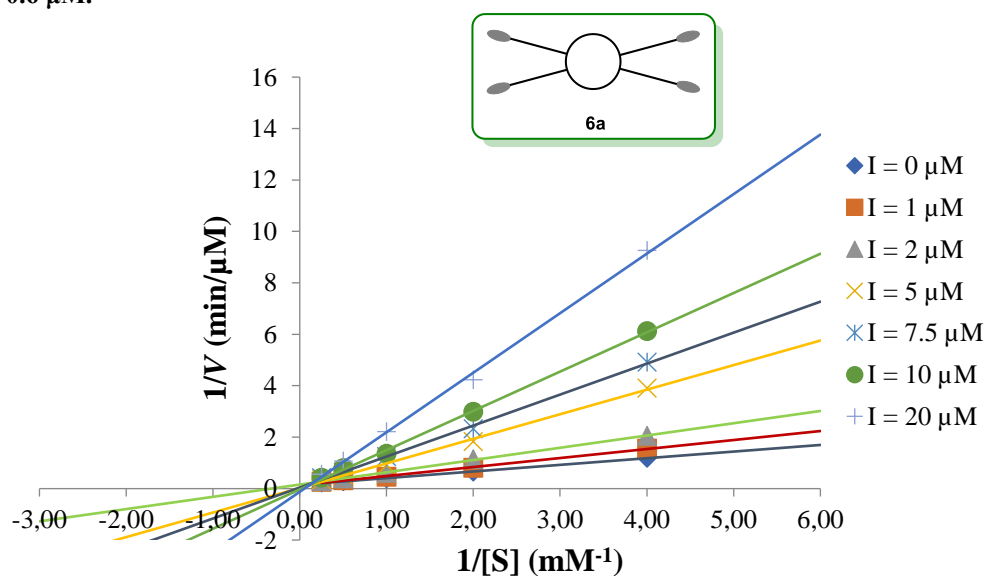


Figure S6. Lineweaver-Burk plot and replot for K_i determination of compound 6a against JB α -man at pH 5. $K_i = 3.1 \pm 0.6 \mu\text{M}$.



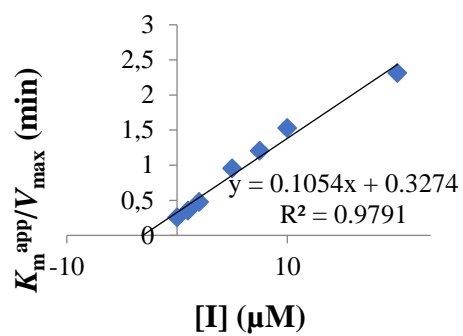


Figure S7. Lineweaver-Burk plot and replot for K_i determination of compound 6b against JBa-man at pH 5. $K_i = 2.2 \pm 0.1 \mu\text{M}$.

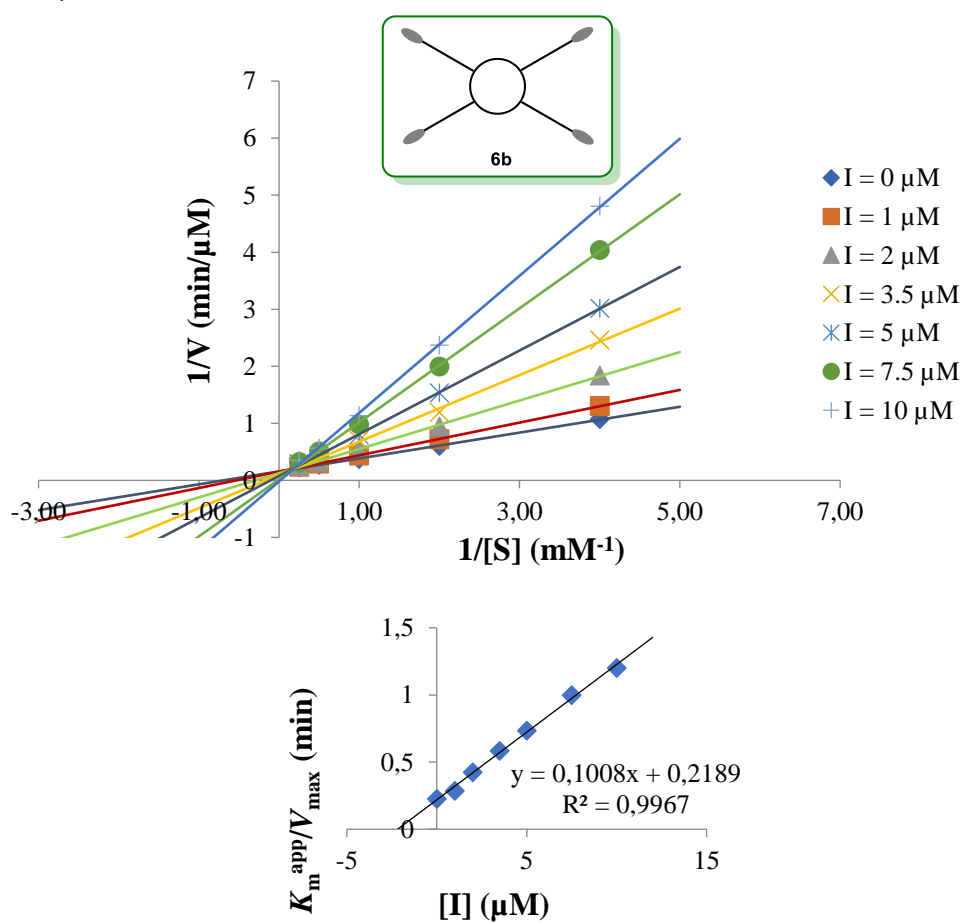


Figure S8. Lineweaver-Burk plot and replot for K_i determination of compound 6c against JB α -man at pH 5. $K_i = 2.3 \pm 0.3 \mu\text{M}$.

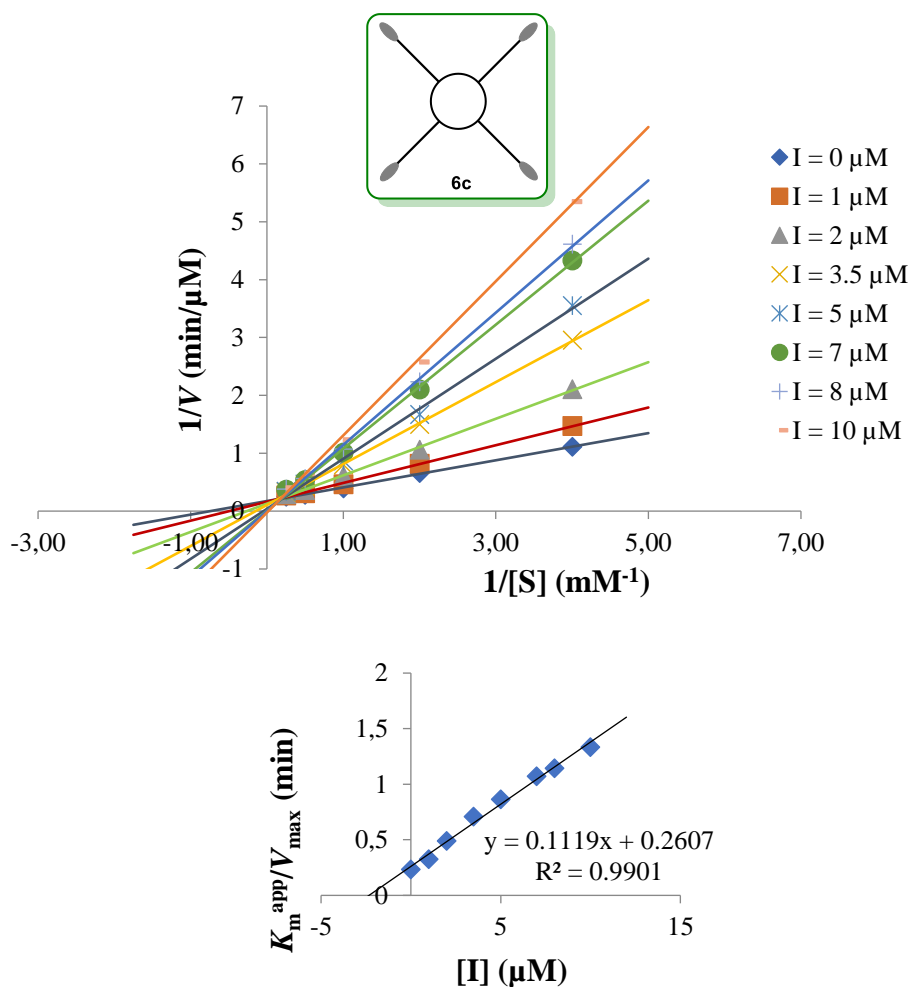


Figure S9: Plot of enzyme velocity as a function of inhibitor 5a concentration. The solid curves drawn through the data points represent the best fit to the Morrison equation used to obtain K_i value ($0.084 \pm 0.029 \mu\text{M}$) for competitive inhibitor 5a against JB α -man at pH 5.

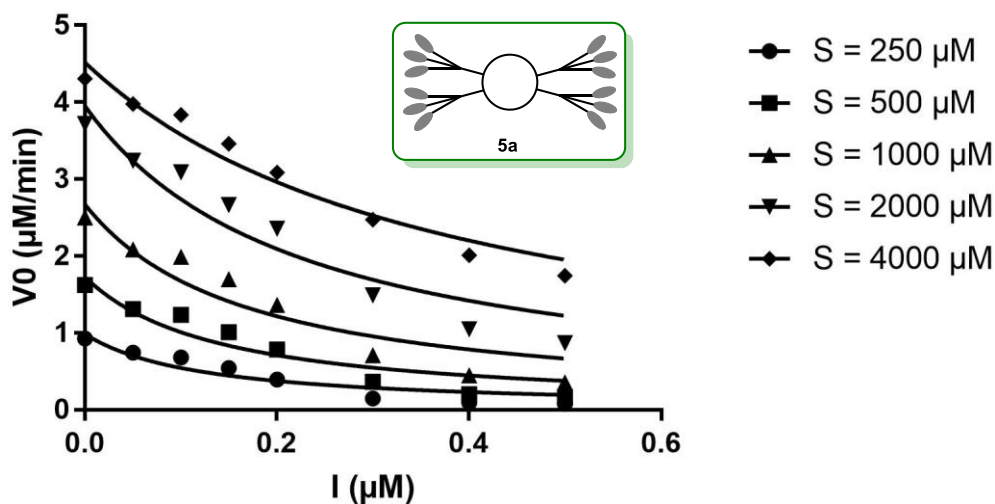


Figure S10: Plot of enzyme velocity as a function of inhibitor 5b concentration. The solid curves drawn through the data points represent the best fit to the Morrison equation used to obtain K_i value ($0.12 \pm 0.024 \mu\text{M}$) for competitive inhibitor 5b against JBA-man at pH 5.

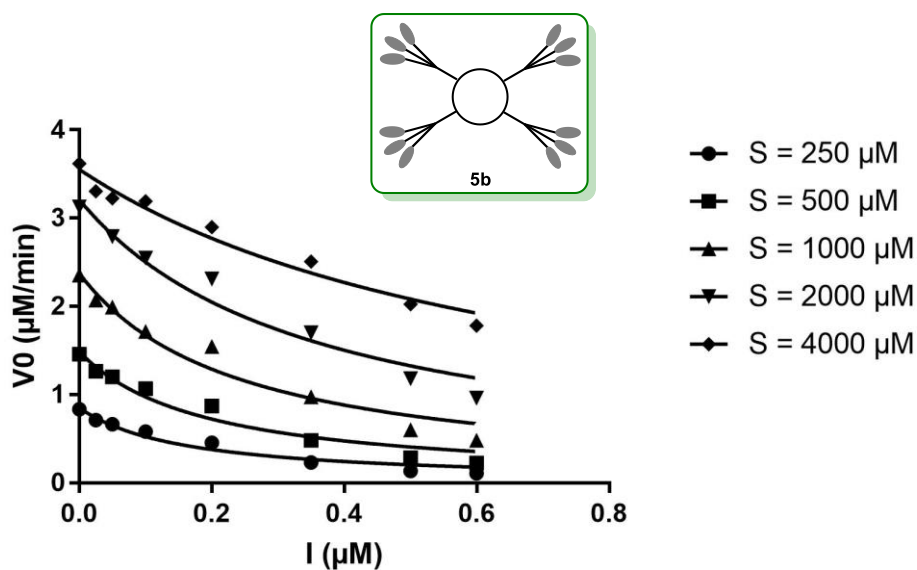


Figure S11: Plot of enzyme velocity as a function of inhibitor 5c concentration. The solid curves drawn through the data points represent the best fit to the Morrison equation used to obtain K_i value ($0.097 \pm 0.025 \mu\text{M}$) for competitive inhibitor 5c against JBA-man at pH 5.

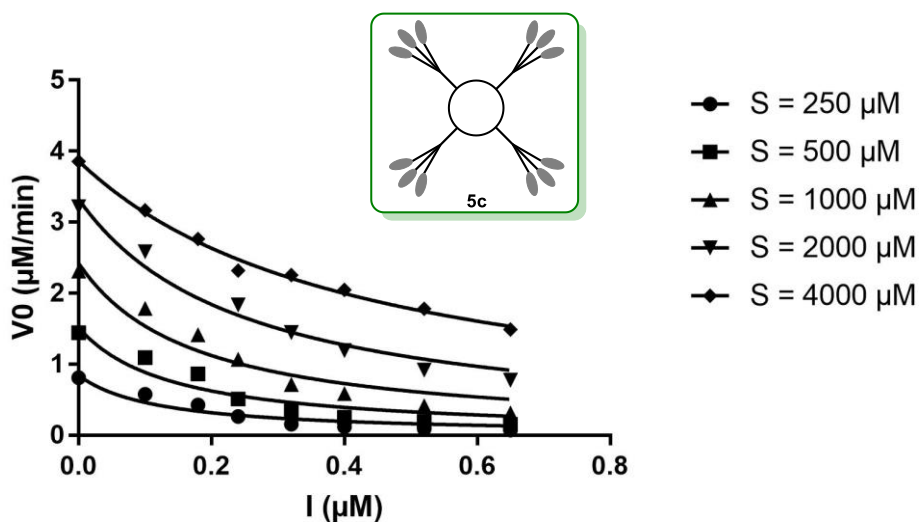


Figure S12: Plot of enzyme velocity as a function of inhibitor 4 concentration. The solid curves drawn through the data points represent the best fit to the Morrison equation used to obtain K_i value ($0.042 \pm 0.005 \mu\text{M}$) for competitive 4 against JB α -man at pH 5.

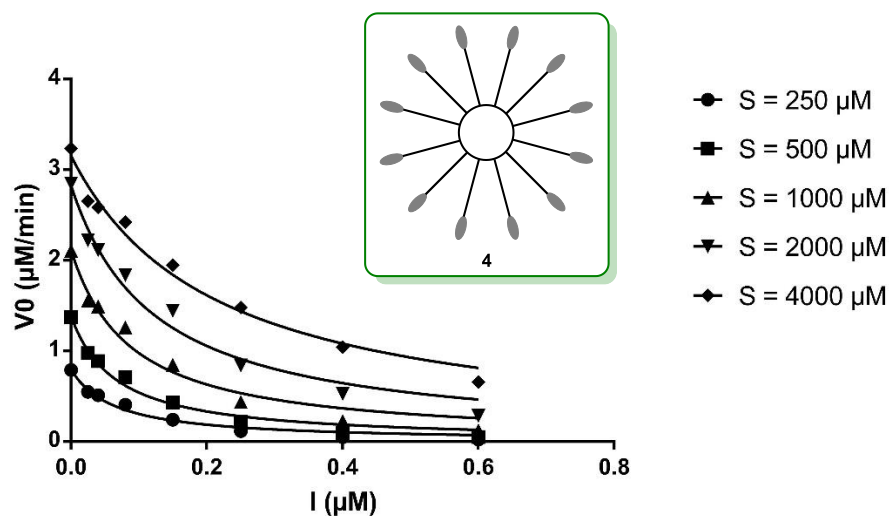


Figure S13. Lineweaver-Burk plot and replot for K_i determination of compound 3 against JB α -man at pH 5. $K_i = 0.074 \pm 0.009 \mu\text{M}$.

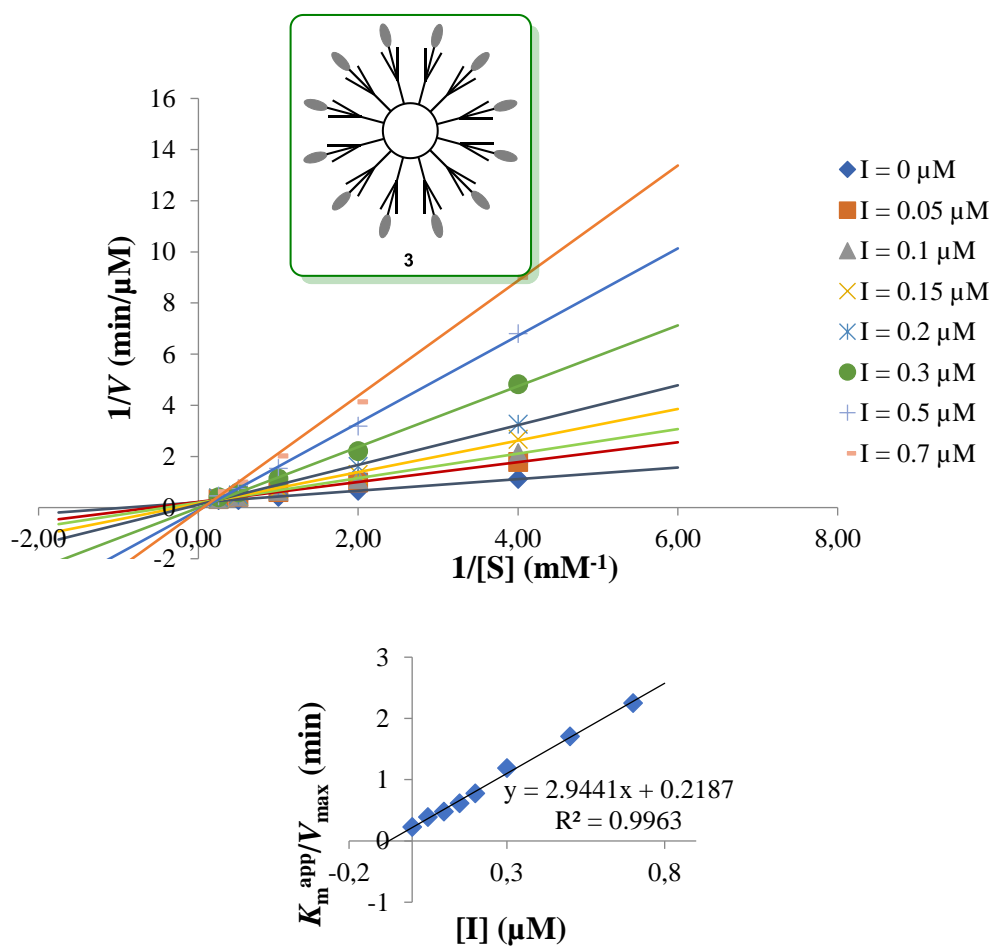


Figure S14. Lineweaver-Burk plot and replot for K_i determination of compound 5c against JB α -man at pH 4. $K_i = 42 \pm 14 \mu\text{M}$.

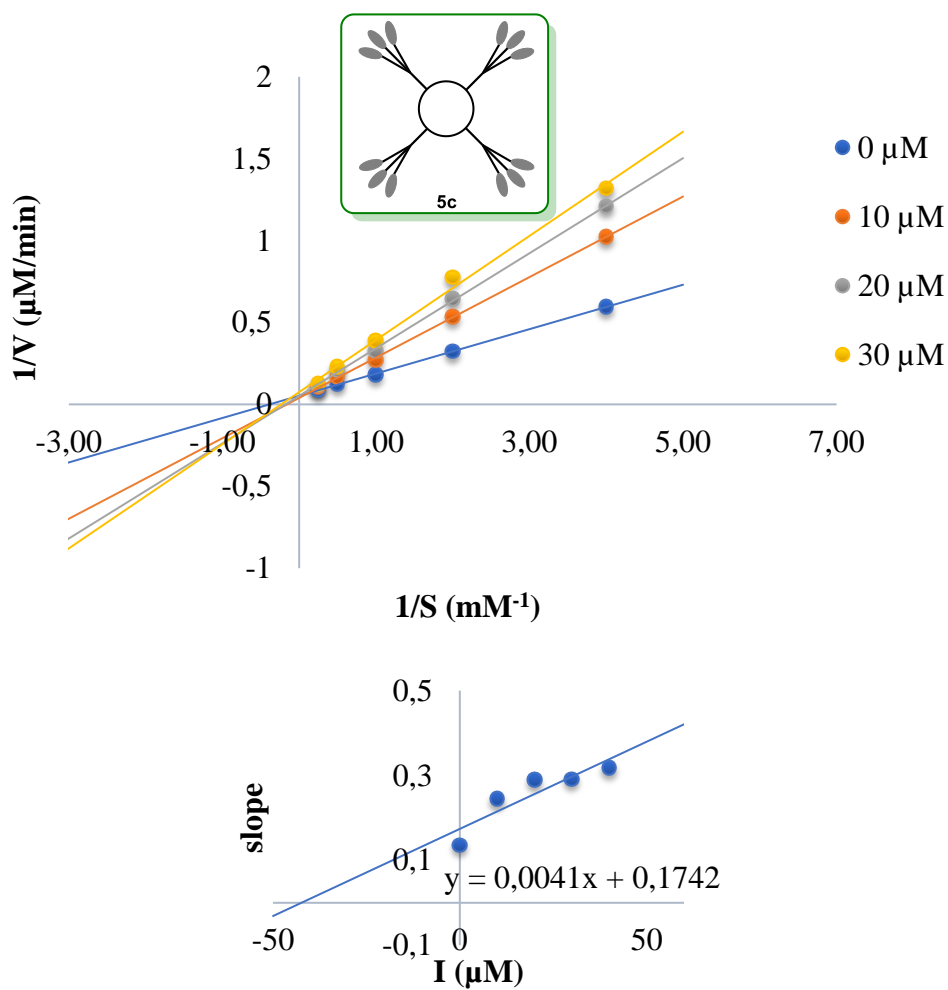
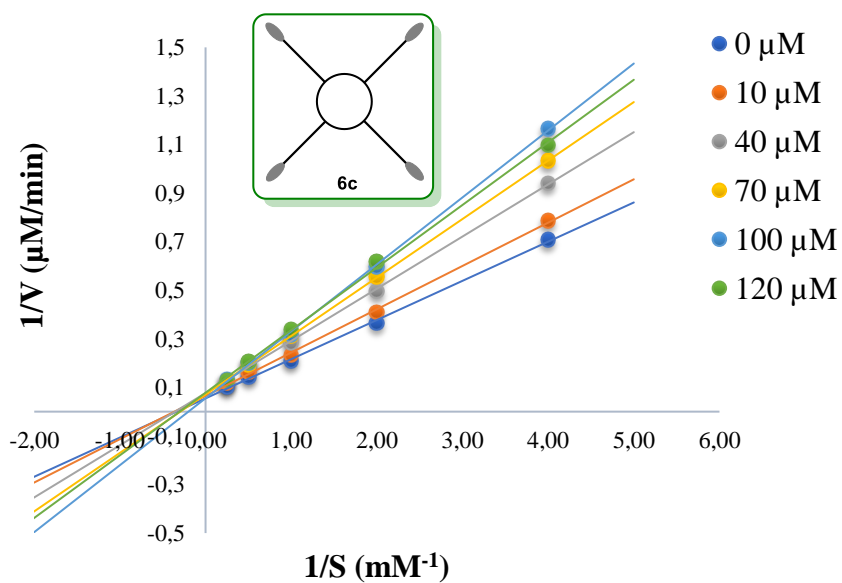


Figure S15. Lineweaver-Burk plot and replot for K_i determination of compound 6c against JB α -man at pH 4. $K_i = 184 \pm 15 \mu\text{M}$.



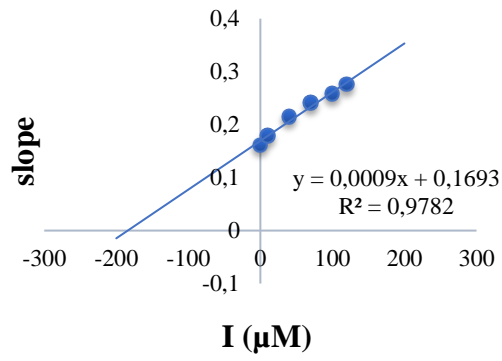


Figure S16. Sedimentation coefficient distributions $c(s)$ of JB α -man alone and with compounds 1, 3, 4, 5c, 6c, 7.

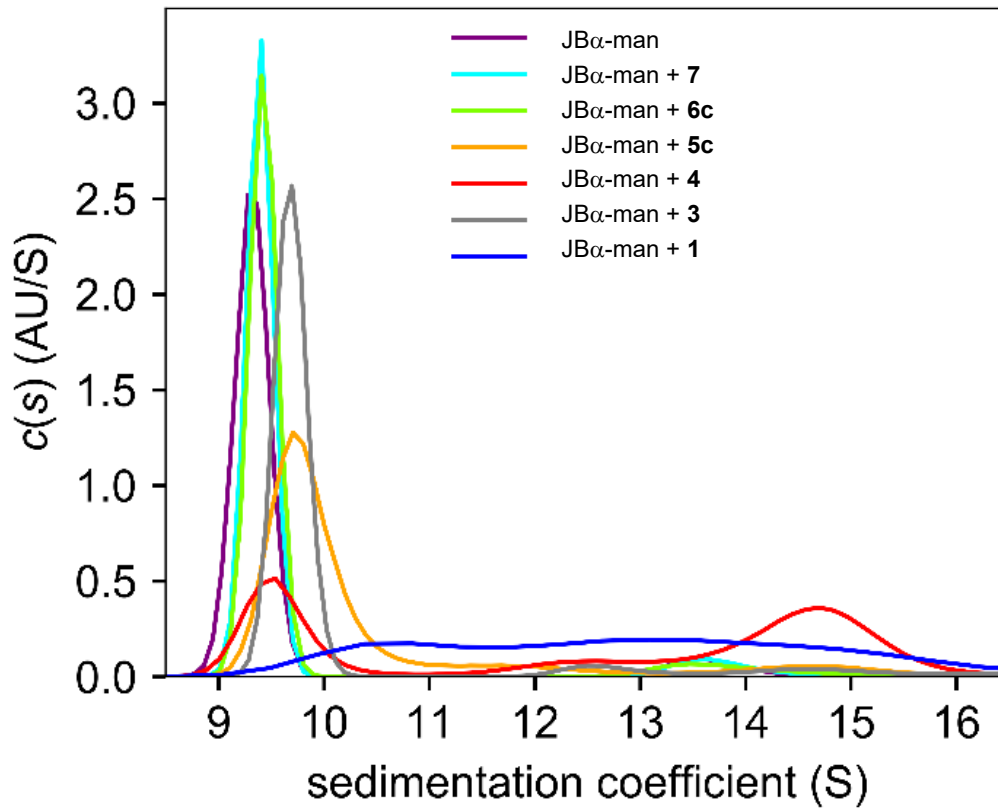


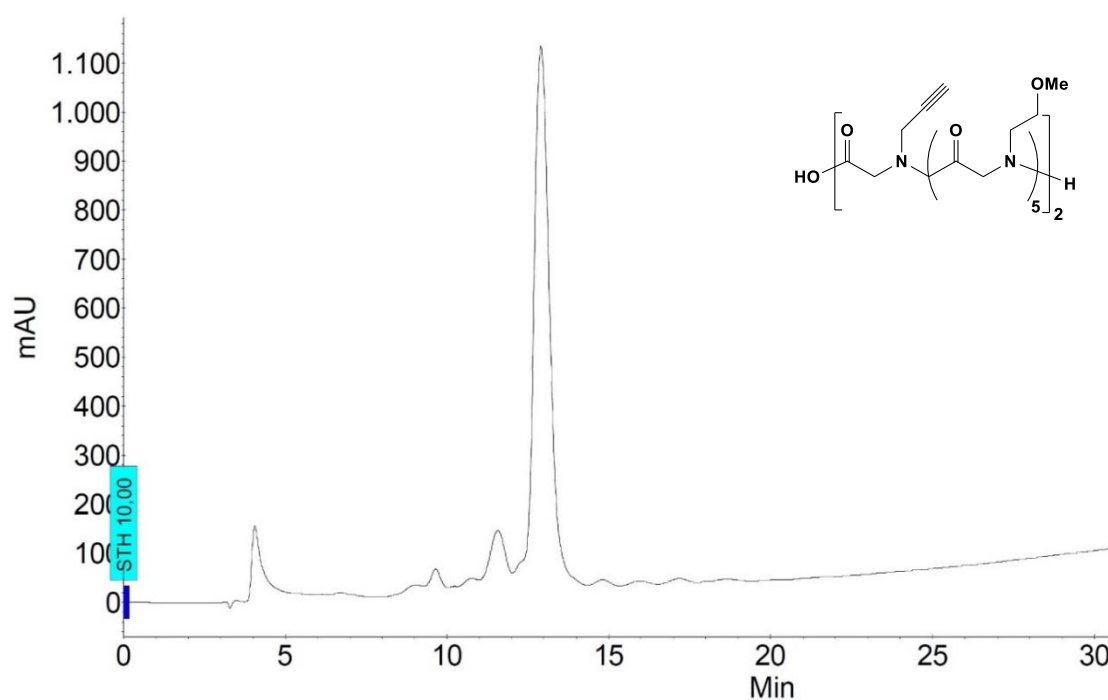
Table S1: Analytical ultracentrifugation results for JB α -man alone and with compounds 1, 3, 4, 5c, 6c, 7.

Frictional ratios, size distribution between three sedimentation ranges obtained by integration of the area under the curve for sedimentation coefficients ranges relative to the total signal and normalized with the signal integration from 8.45 S to 16.6 S, mean value of sedimentation coefficient (sw) is given under brackets with predominant species in red. For sake of results analysis, inhibition constants and rp/n are also given.

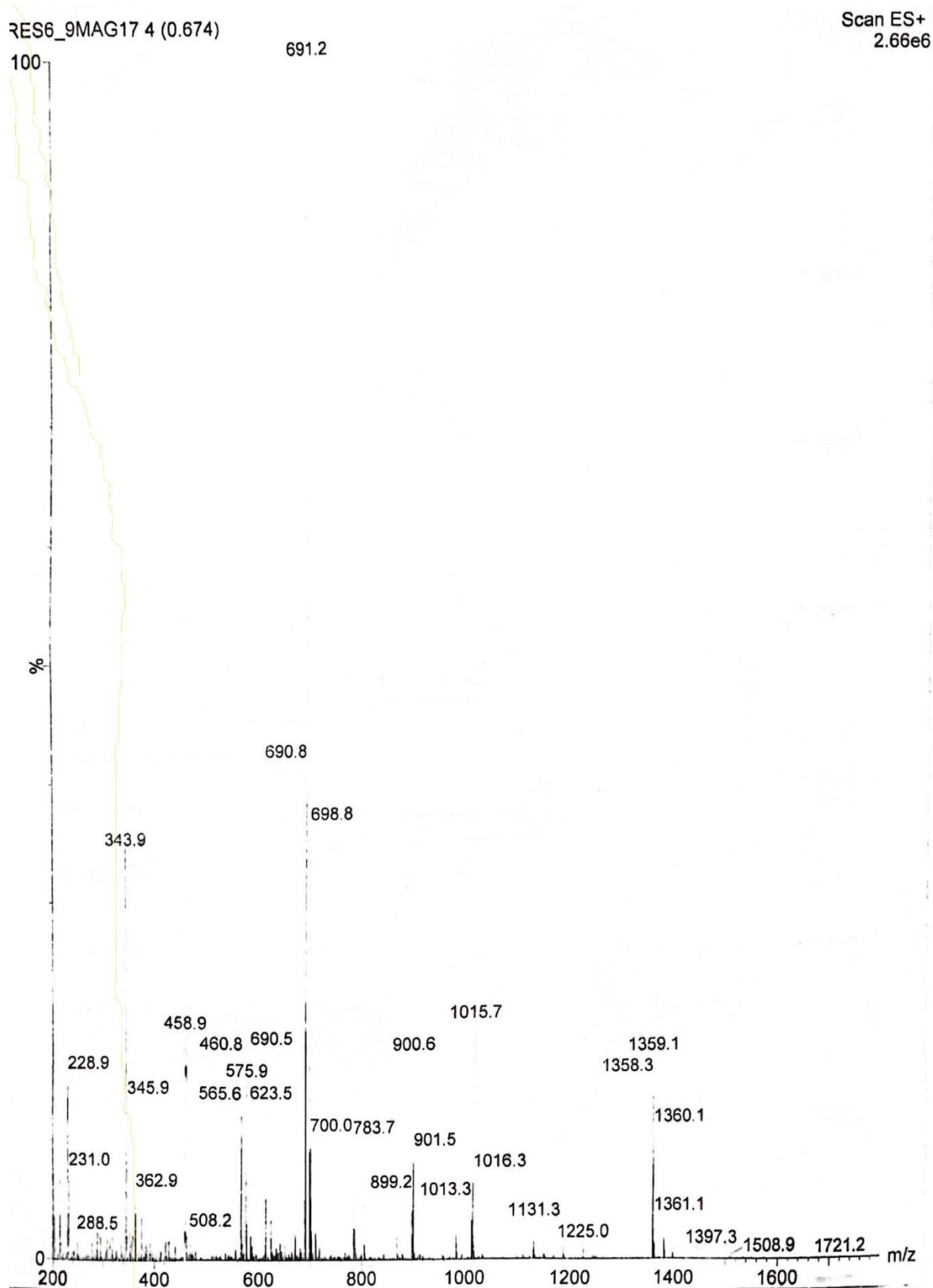
sample	valency	Frictional ratio	percentage integration (%) for sedimentation range and (sw)			K_i (nM)	rp/n
			8.45 S -11 S	11 S -13 S	13 S -16.6		
JB α -man	/	1.35	92 (9.3 S)	0 (12.8 S)	8 (13.8 S)	/	/
JB α -man + 7	2	1.31	92 (9.4 S)	0	8 (13.9 S)	54000	1.7
JB α -man + 6c	4	1.32	92 (9.4 S)	0	8 (14.0 S)	2300	20
JB α -man + 5c	4*3	1.09	83 (9.8 S)	8 (11.8 S)	9 (14.6 S)	97	161
JB α -man + 4	12	1.09	36 (9.6 S)	10 (12.3 S)	54 (14.6 S)	42	373
JB α -man + 3	12	1.35	89 (9.7 S)	4 (12.5 S)	7 (14.6 S)	74	212
JB α -man + 1	36	0.85	21 (10.3 S)	33 (12.0 S)	46 (14.4 S)	1.1	4747

Characterization data:

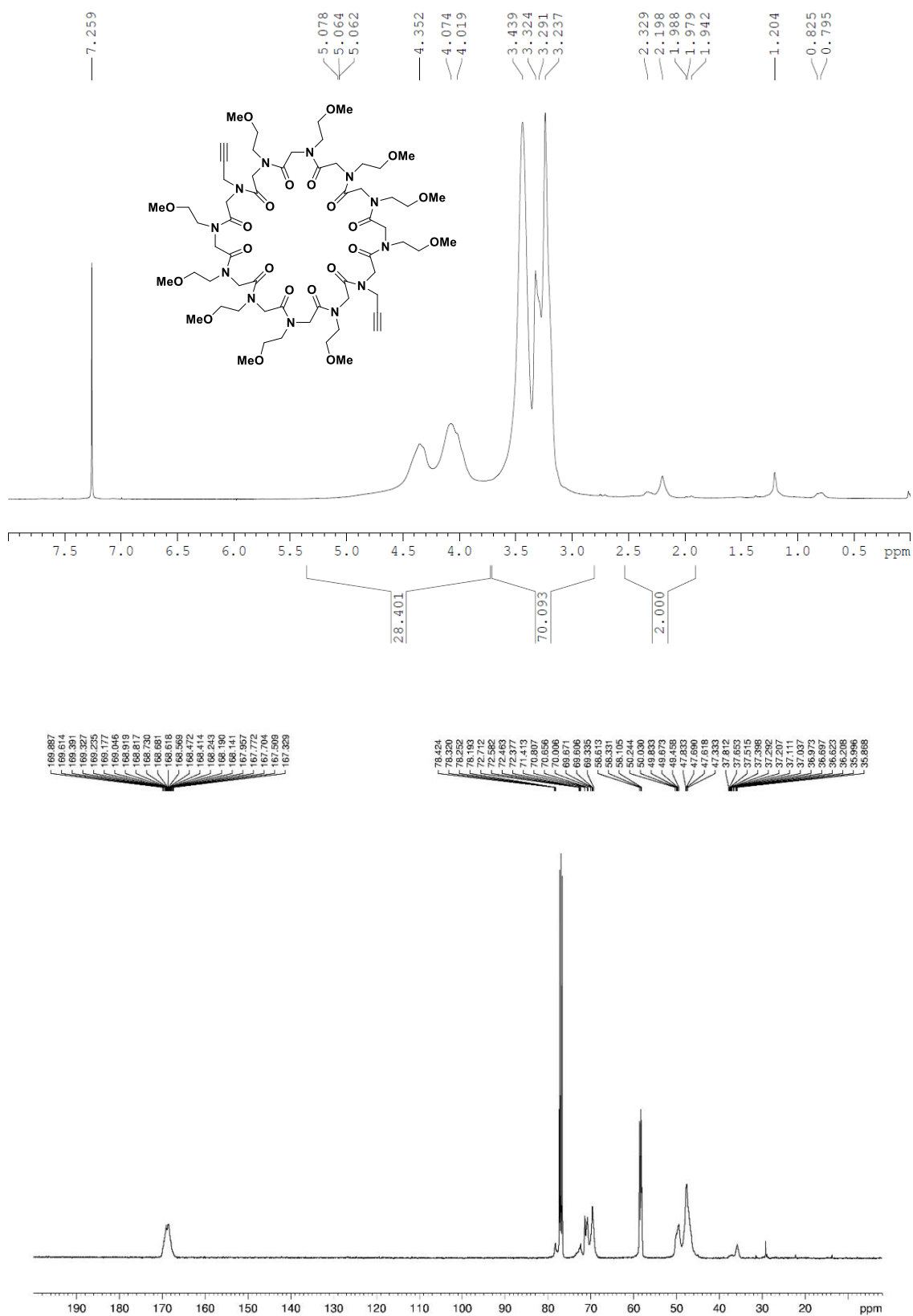
RP-HPLC of compound **8'**:



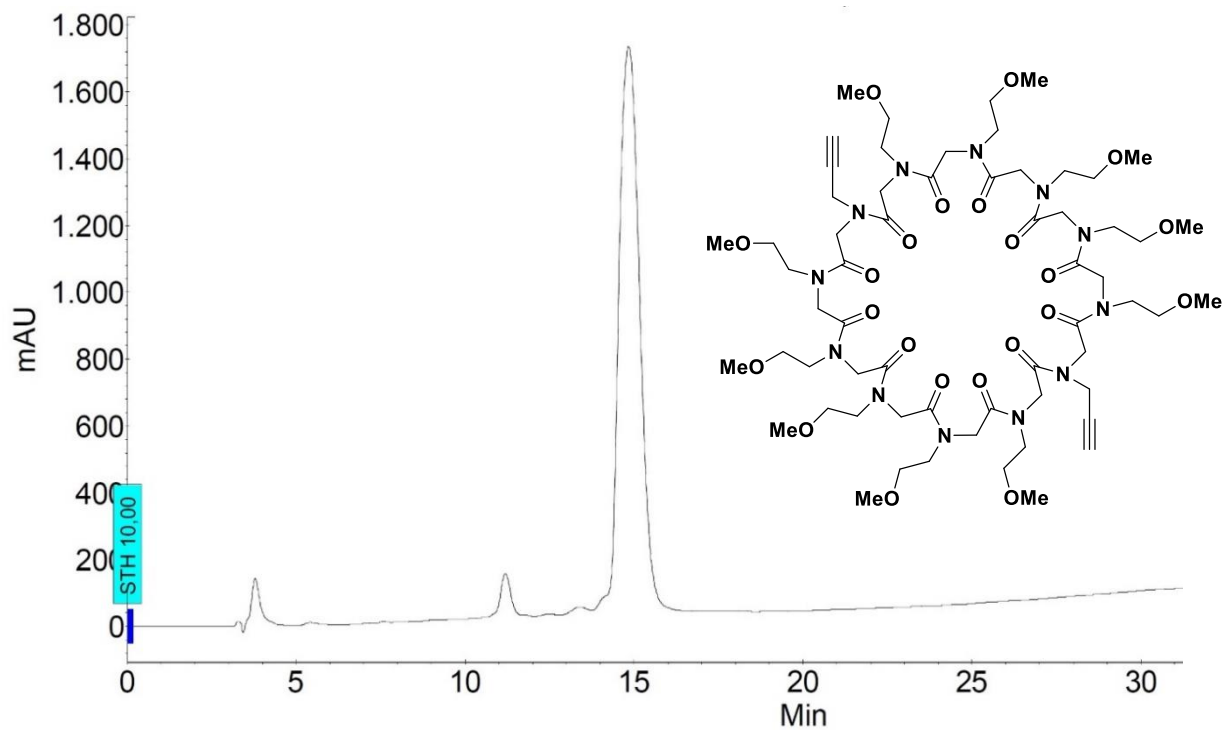
MS-ESI spectrum of compound 8'



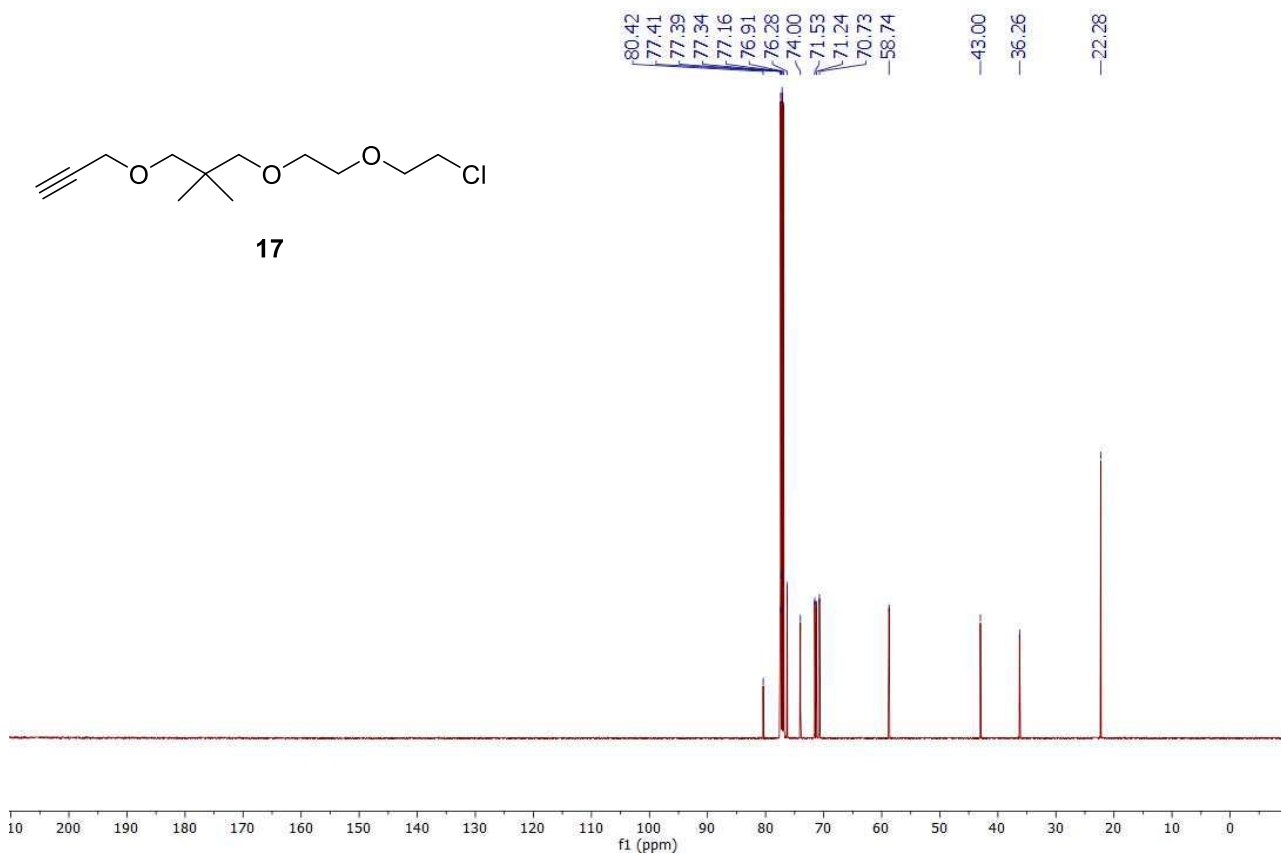
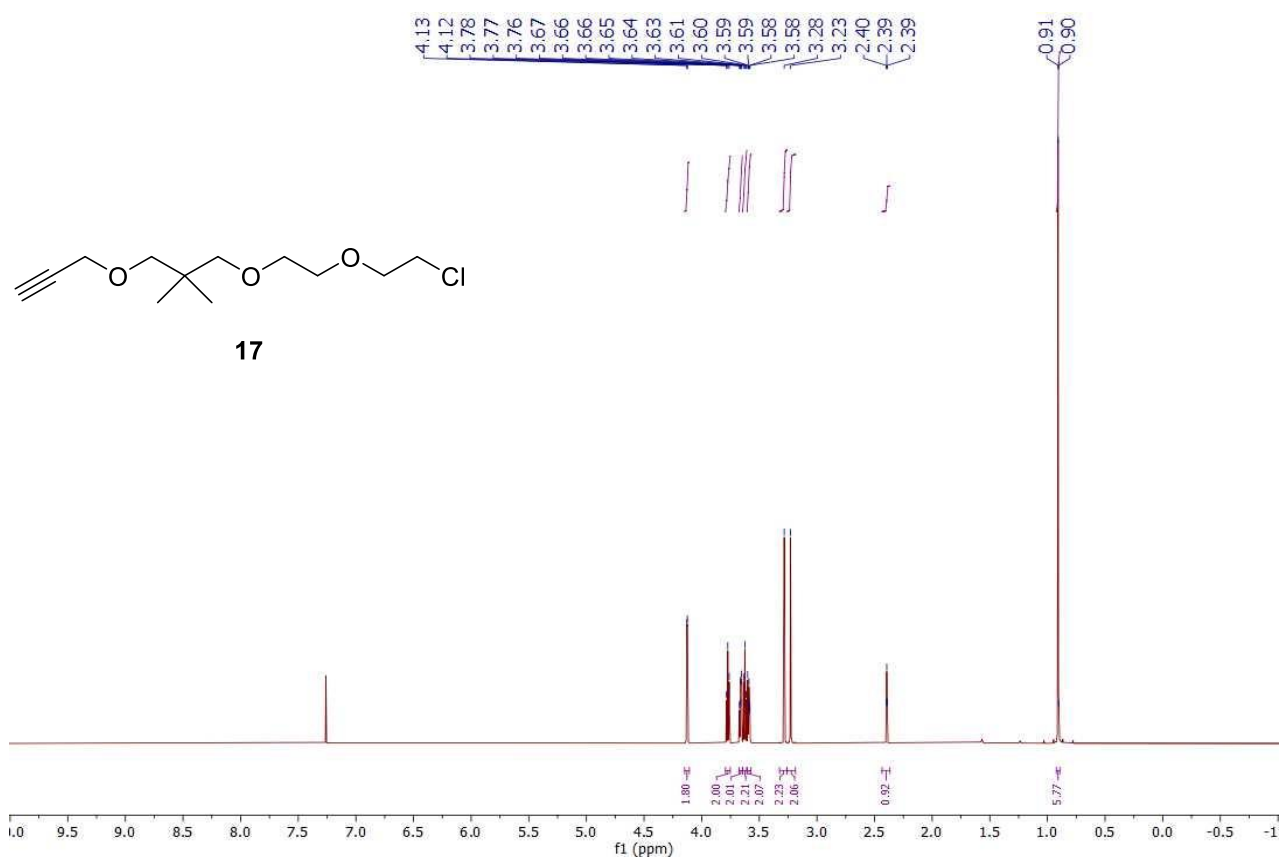
^1H NMR spectrum (CDCl_3 , 400 MHz) and ^{13}C NMR spectrum (CDCl_3 , 100 MHz) of compound **8**



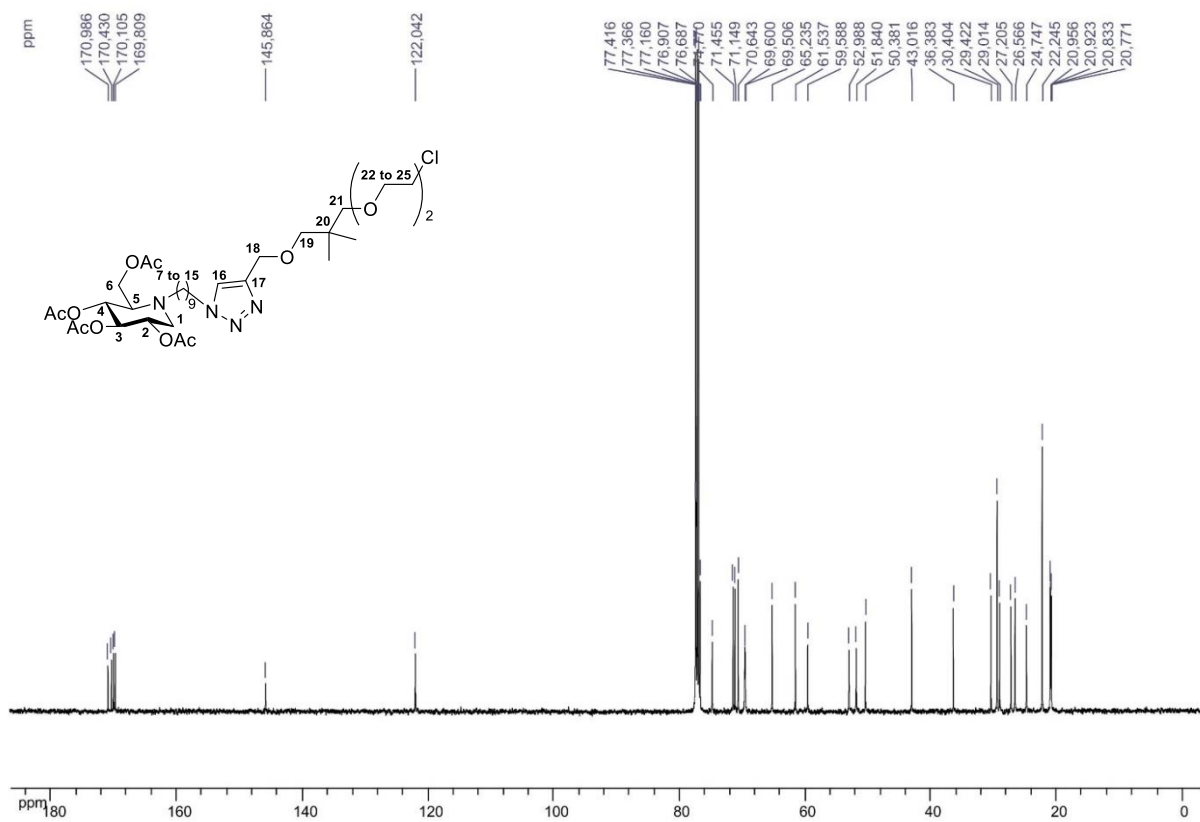
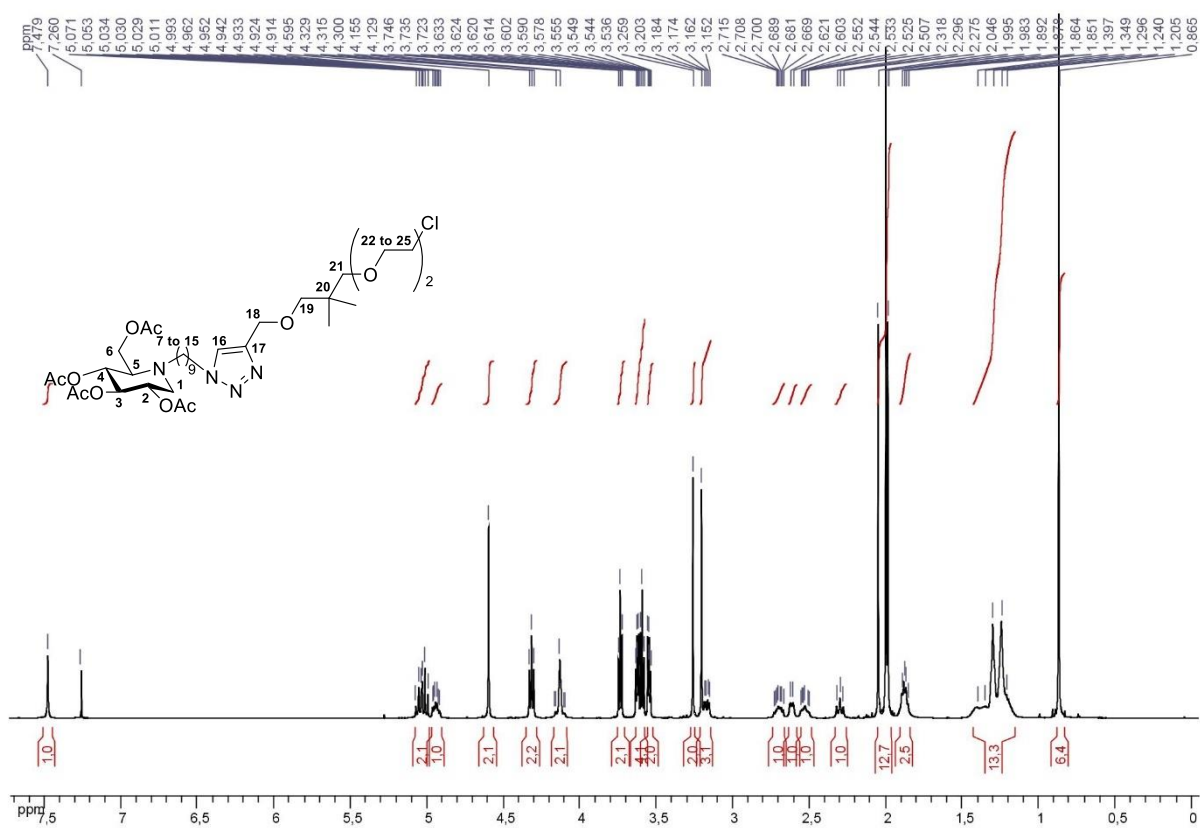
RP-HPLC of compound **8**:



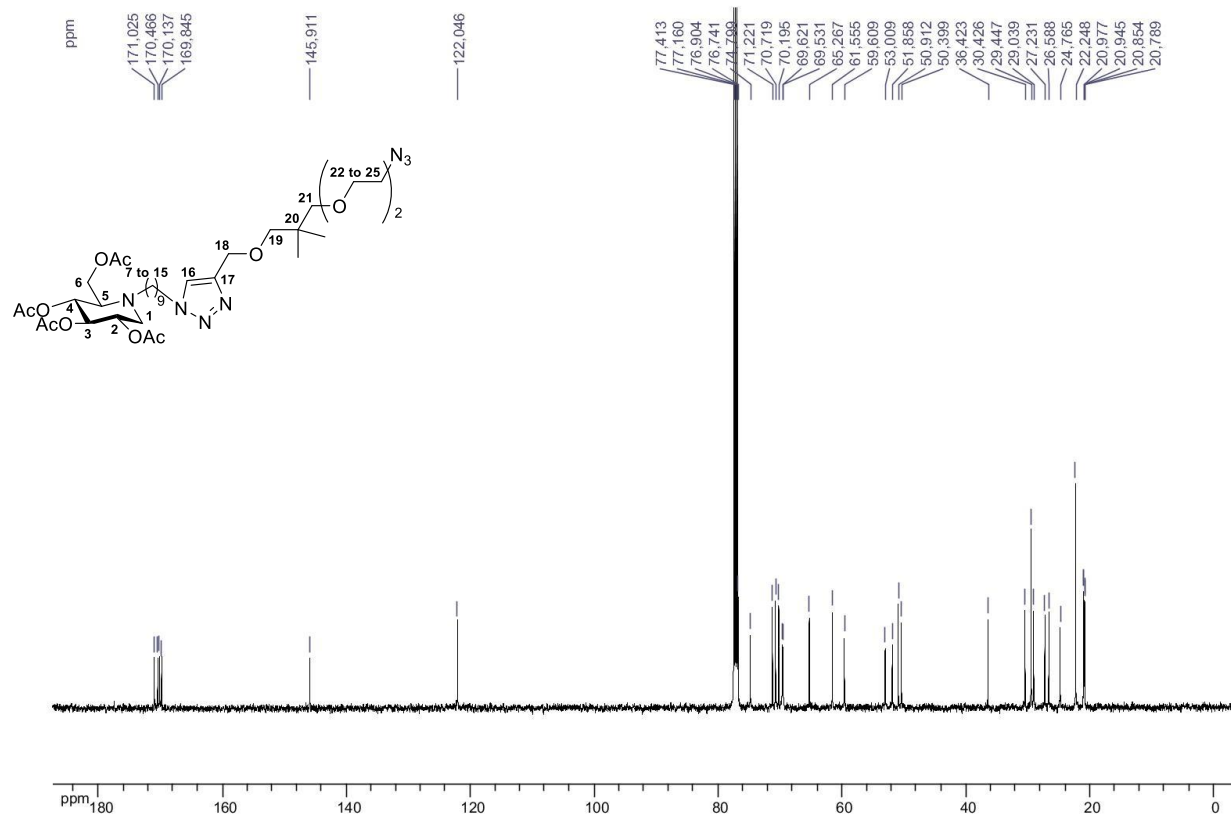
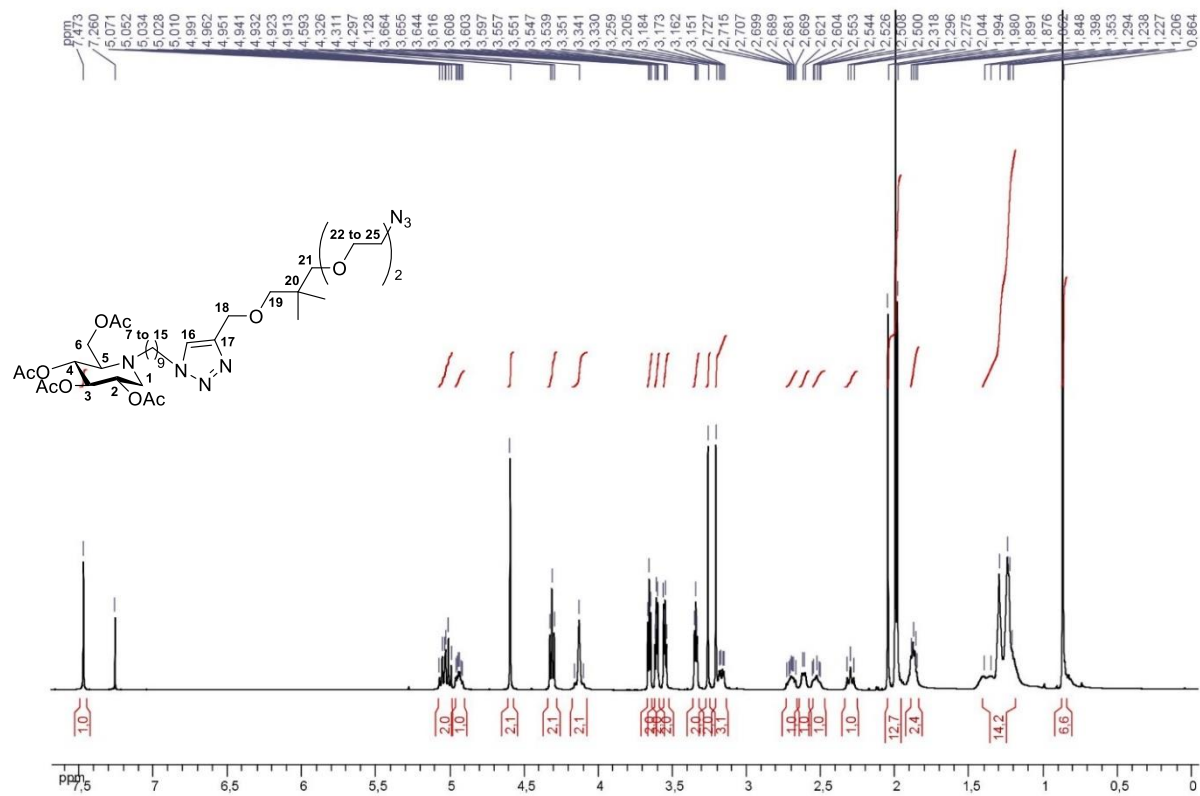
^1H NMR spectrum (CDCl_3 , 500 MHz) and ^{13}C NMR spectrum (CDCl_3 , 125 MHz) for compound **17**



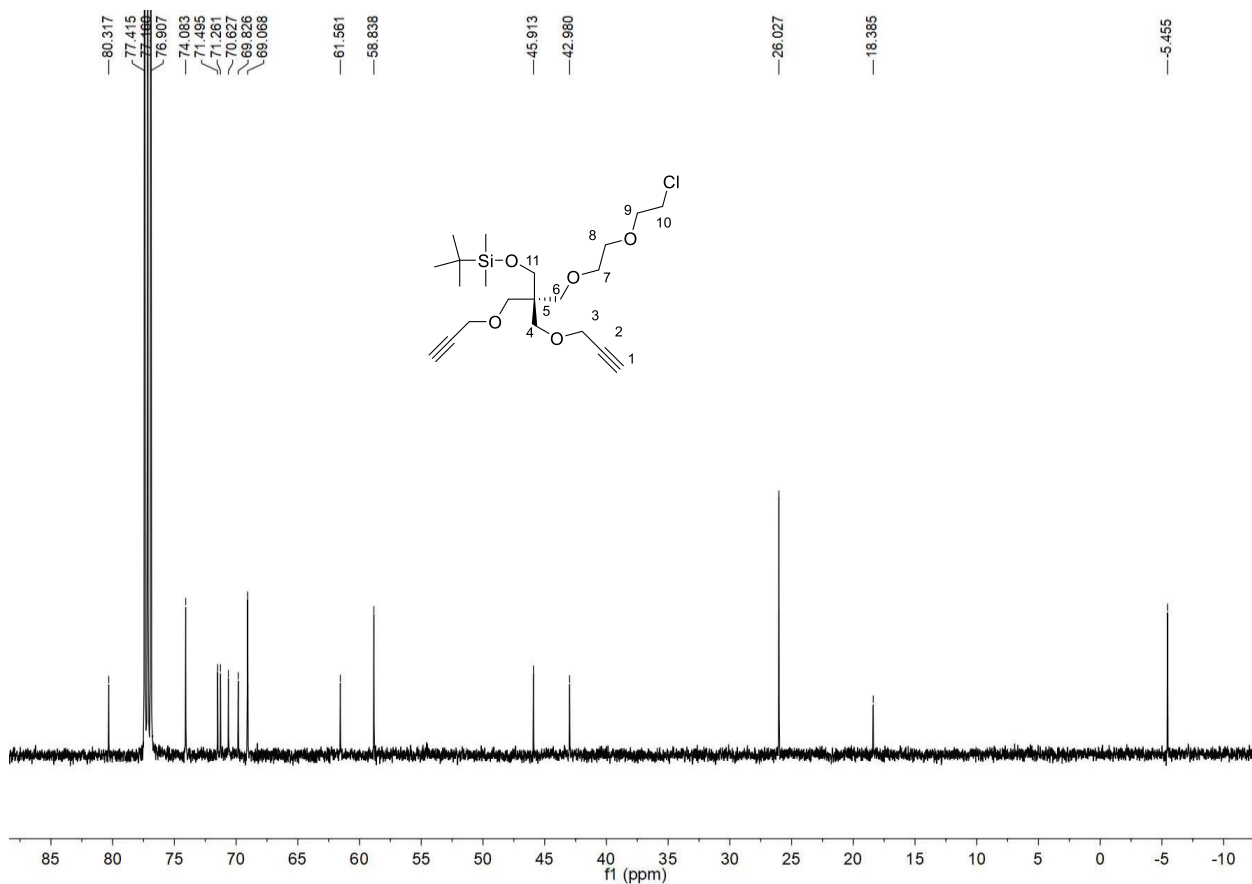
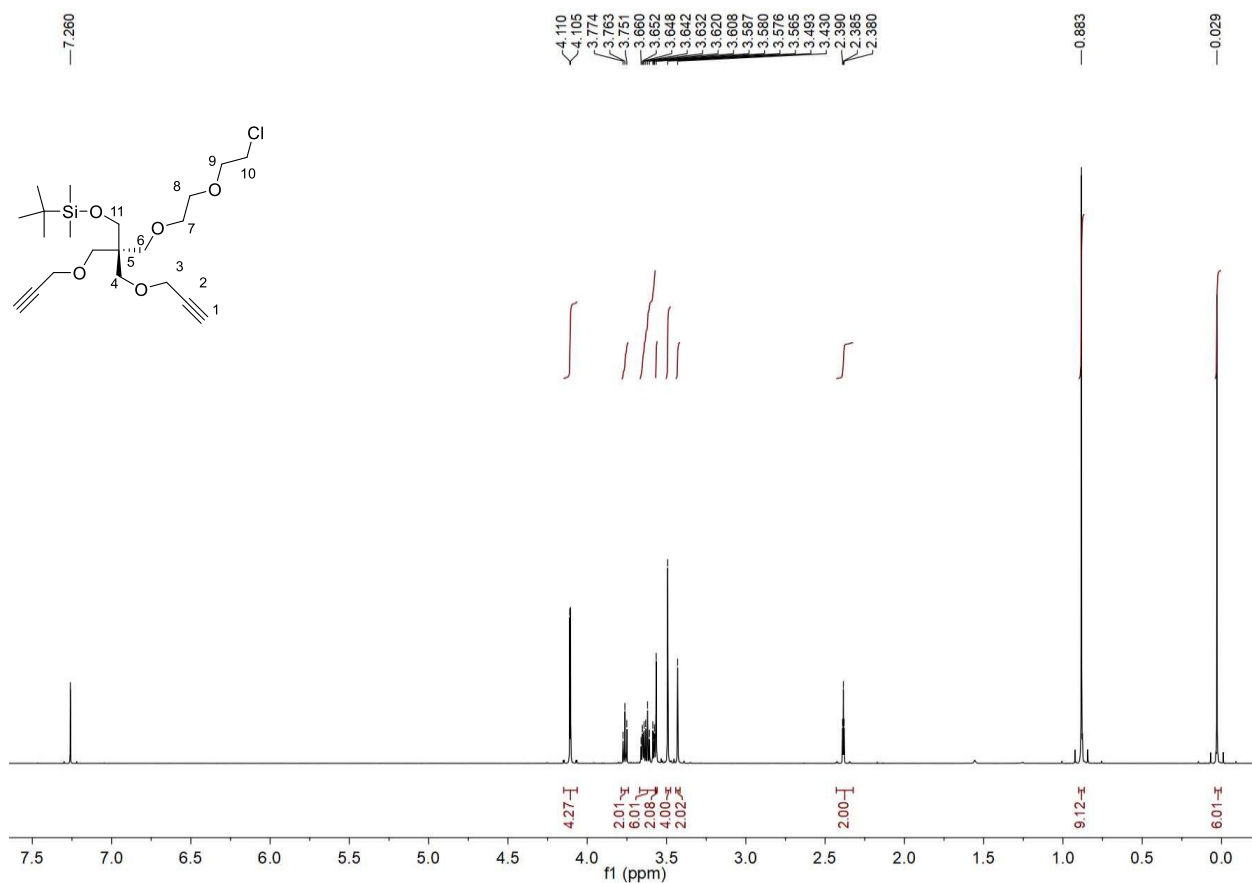
¹H NMR spectrum (CDCl₃, 500 MHz) and ¹³C NMR spectrum (CDCl₃, 125 MHz) for compound **19**



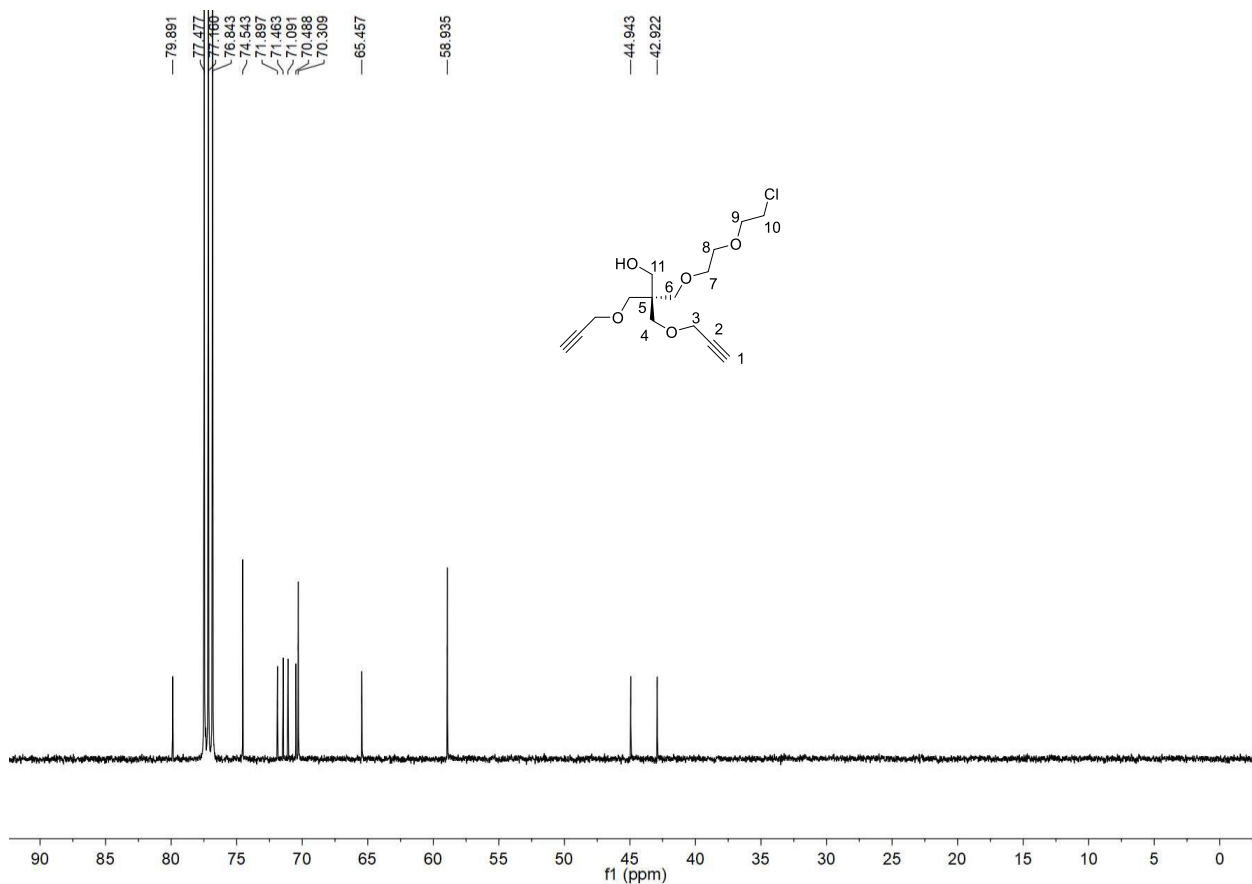
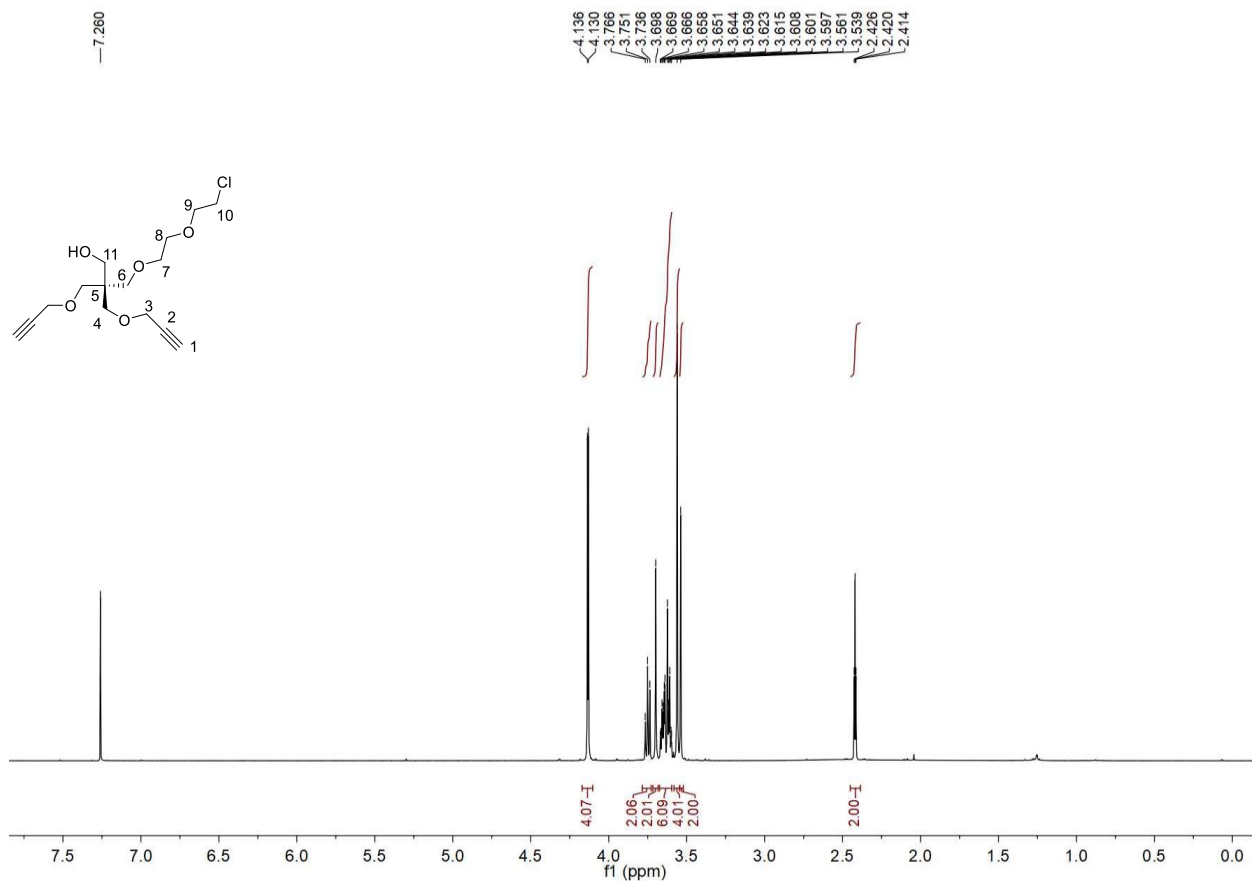
¹H NMR spectrum (CDCl₃, 500 MHz) and ¹³C NMR spectrum (CDCl₃, 125 MHz) for compound **15**



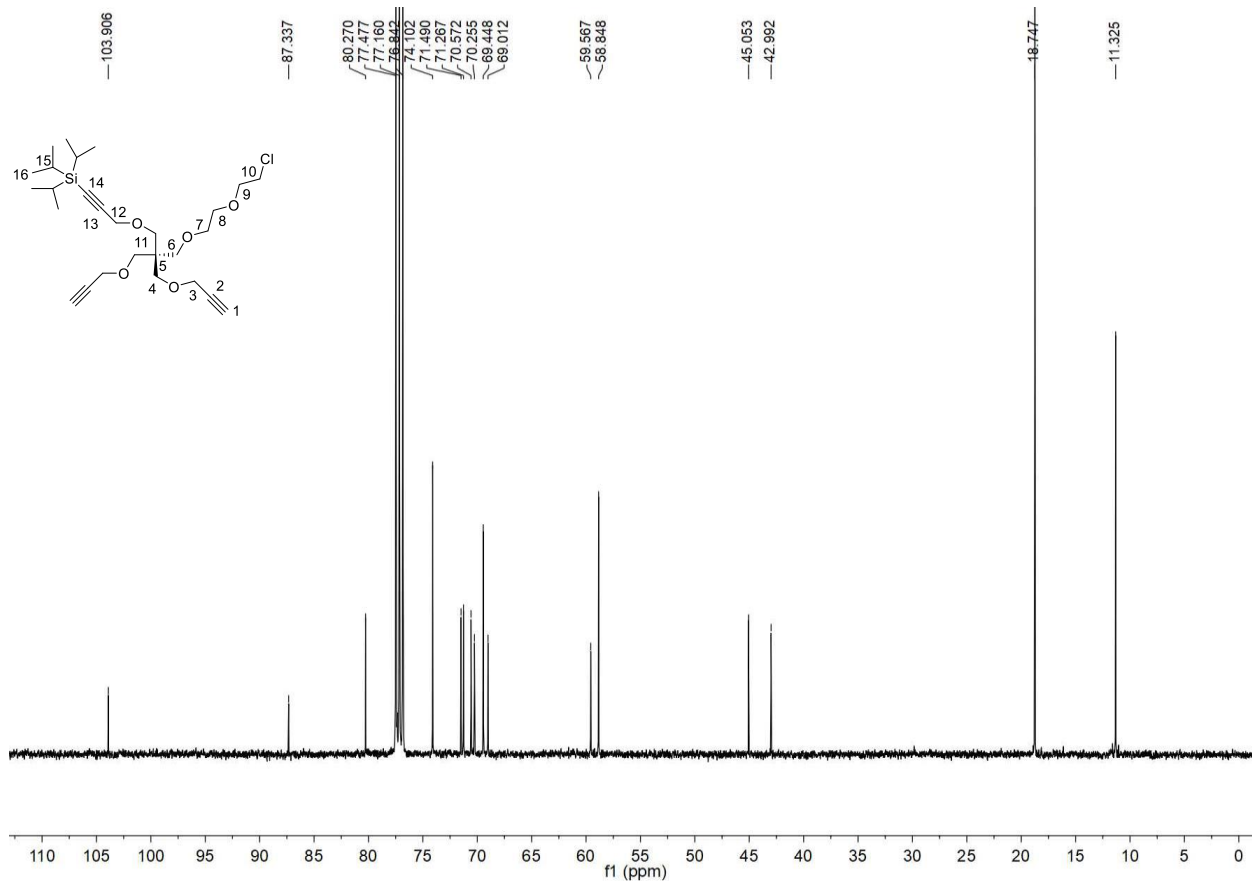
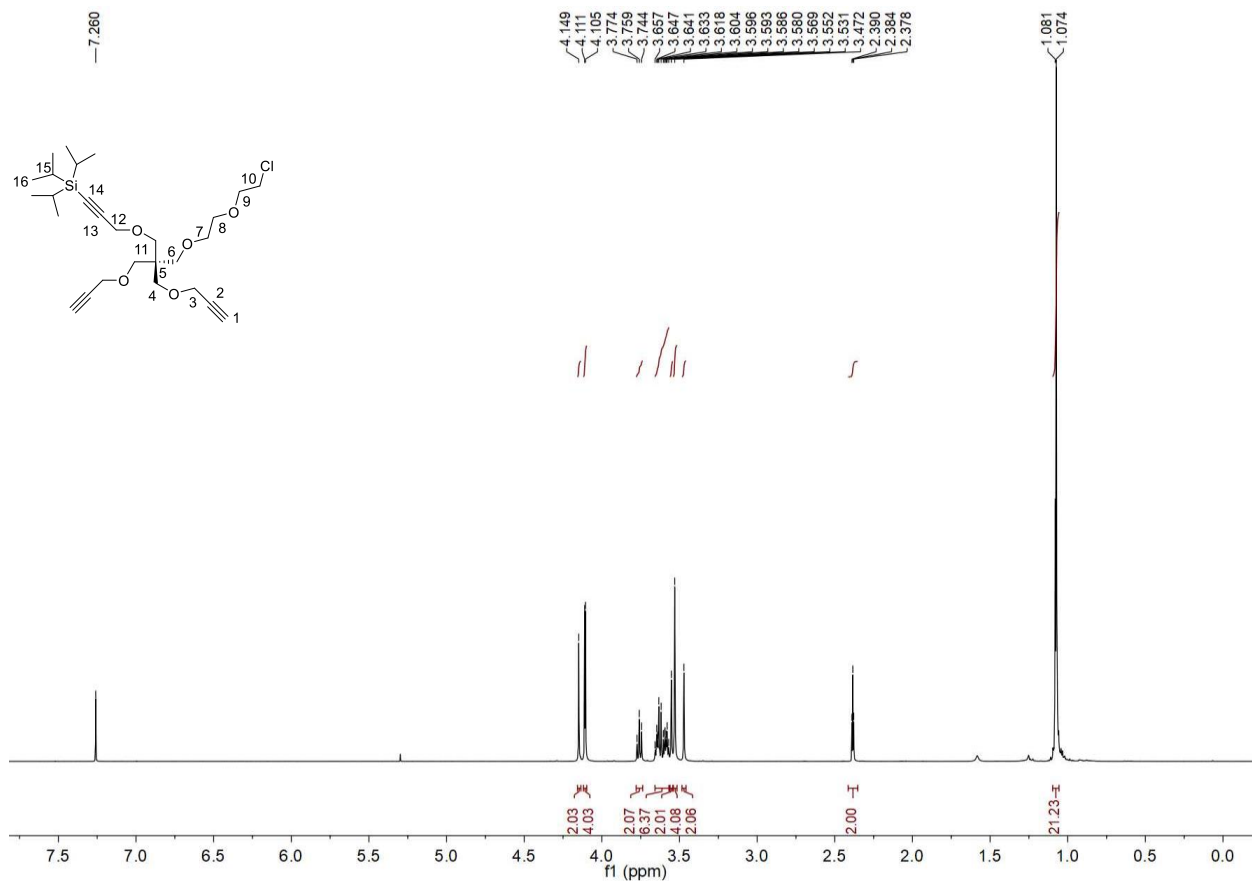
^1H NMR spectrum (CDCl_3 , 500 MHz) and ^{13}C NMR spectrum (CDCl_3 , 125 MHz) for compound **21**



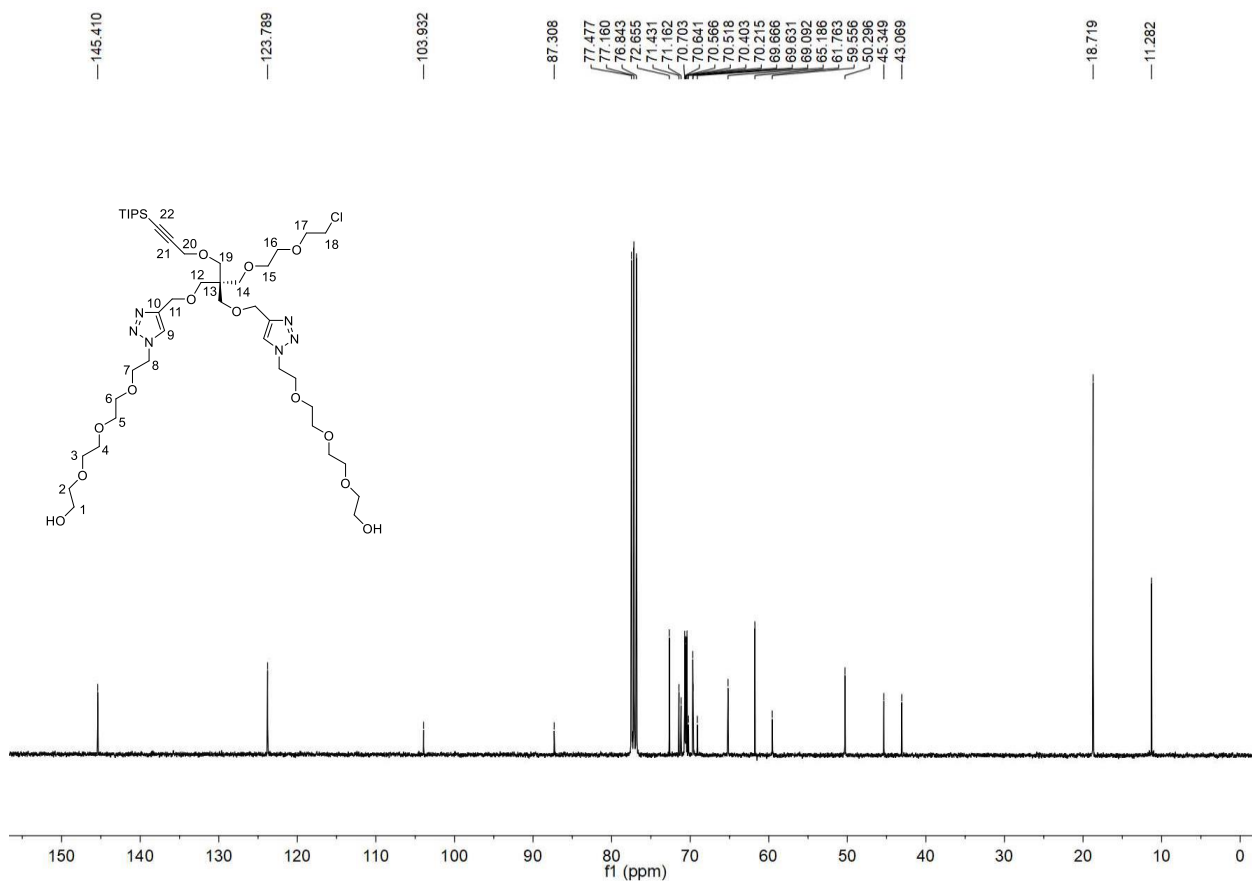
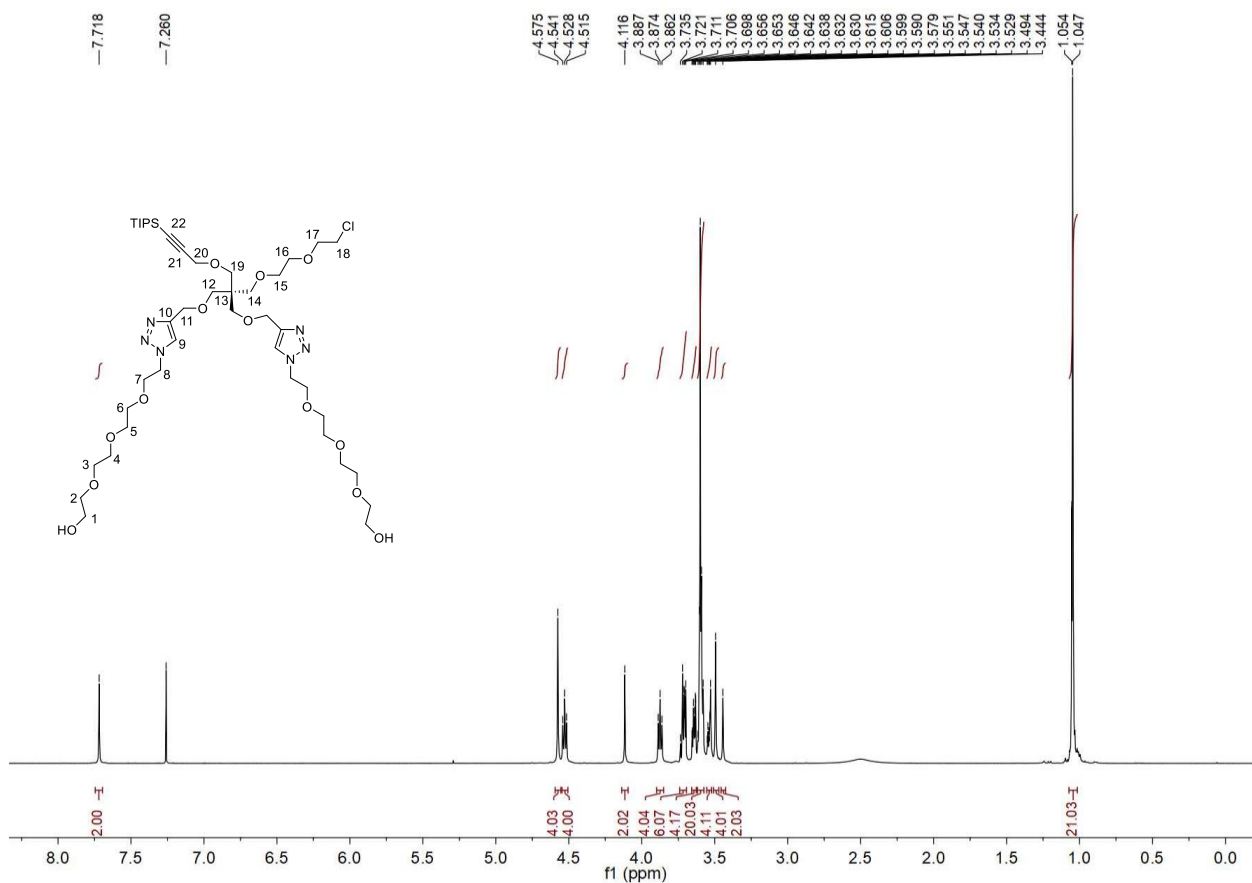
^1H NMR spectrum (CDCl_3 , 400 MHz) and ^{13}C NMR spectrum (CDCl_3 , 100 MHz) for compound **22**



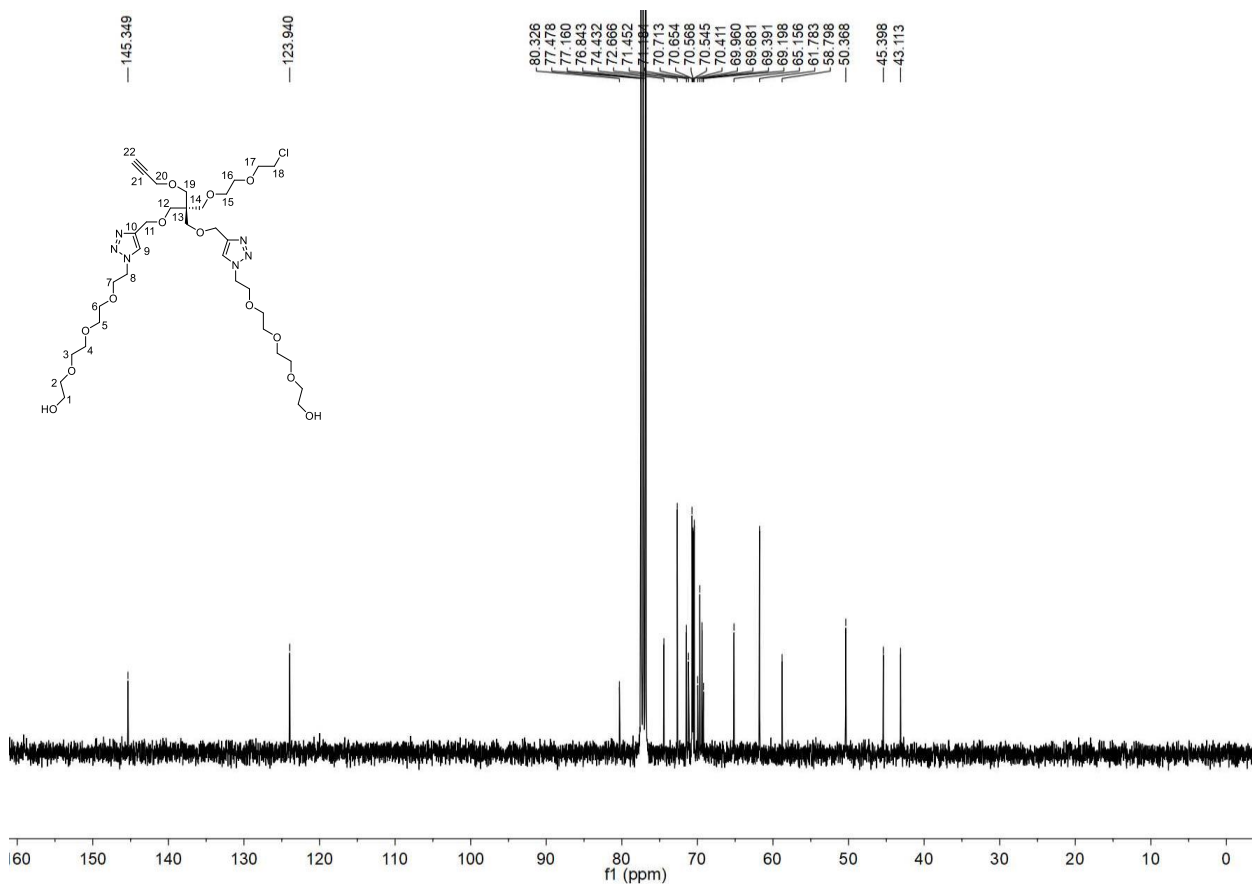
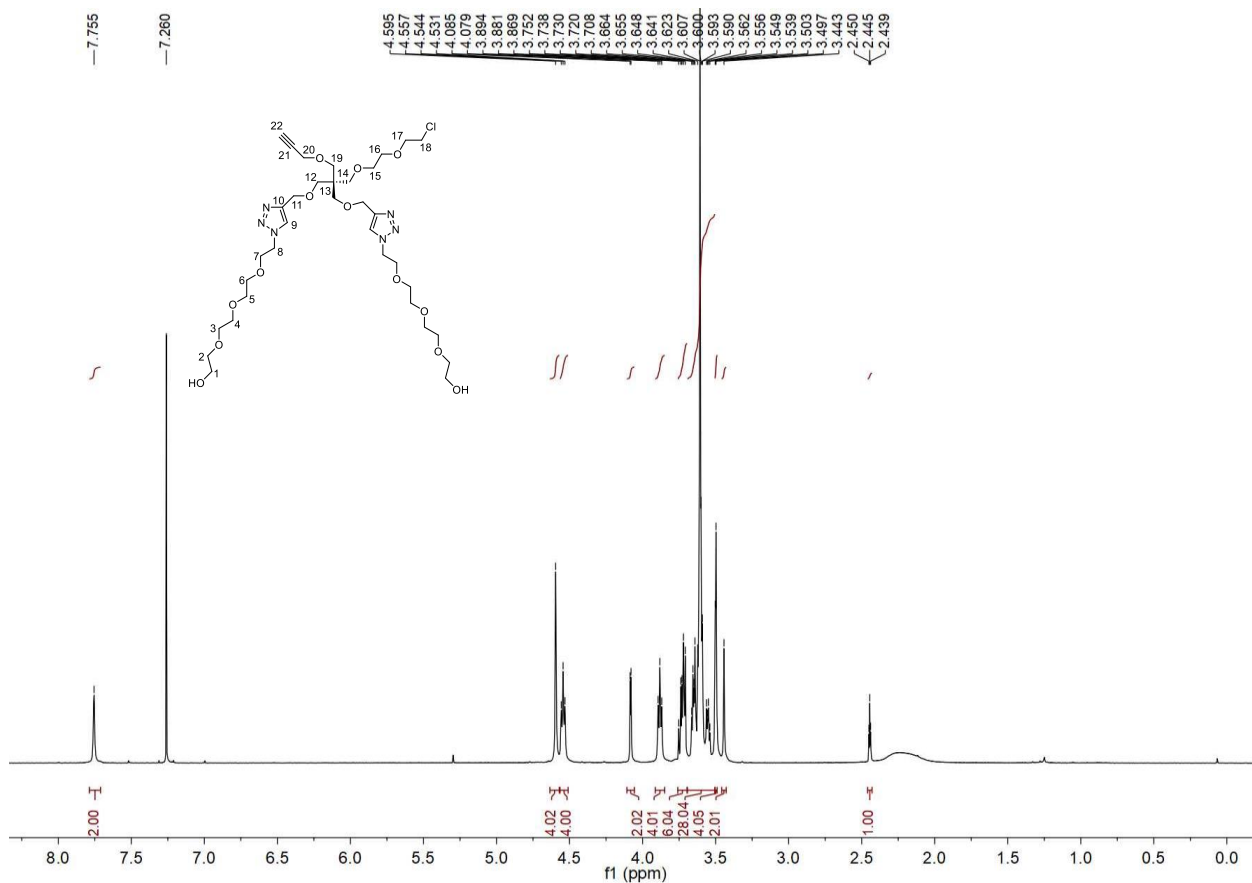
^1H NMR spectrum (CDCl_3 , 400 MHz) and ^{13}C NMR spectrum (CDCl_3 , 100 MHz) for compound **23**



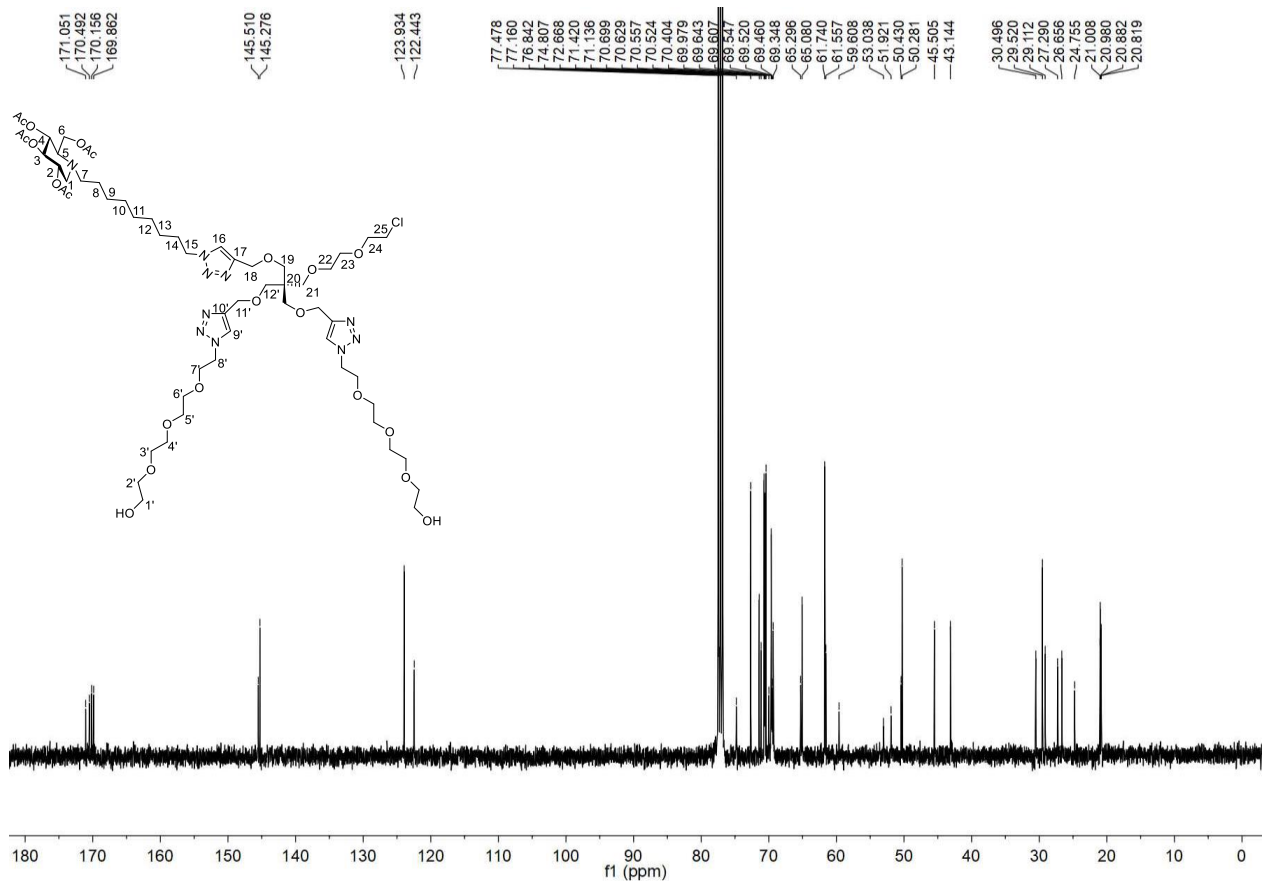
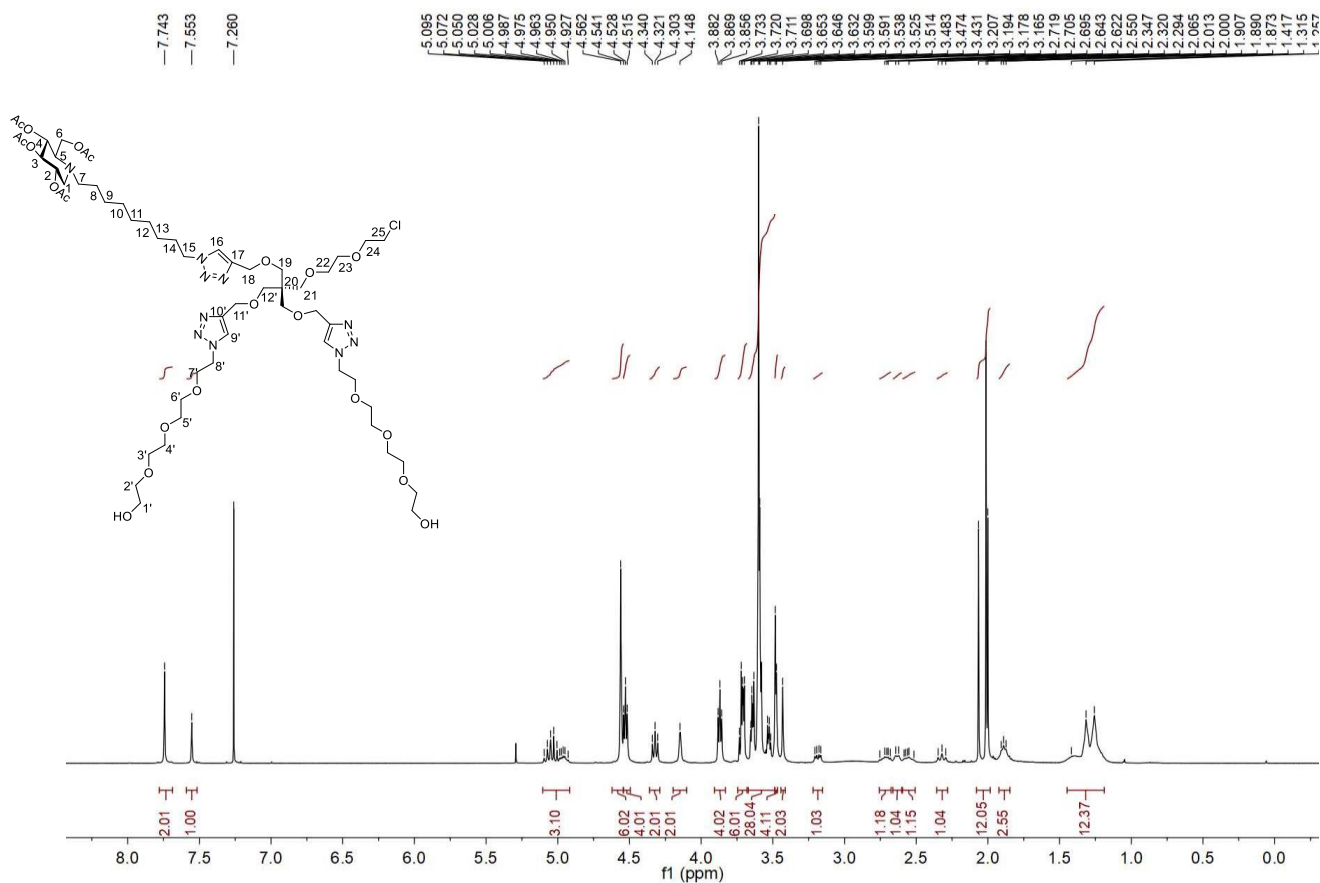
¹H NMR spectrum (CDCl₃, 400 MHz) and ¹³C NMR spectrum (CDCl₃, 100 MHz) for compound **24**



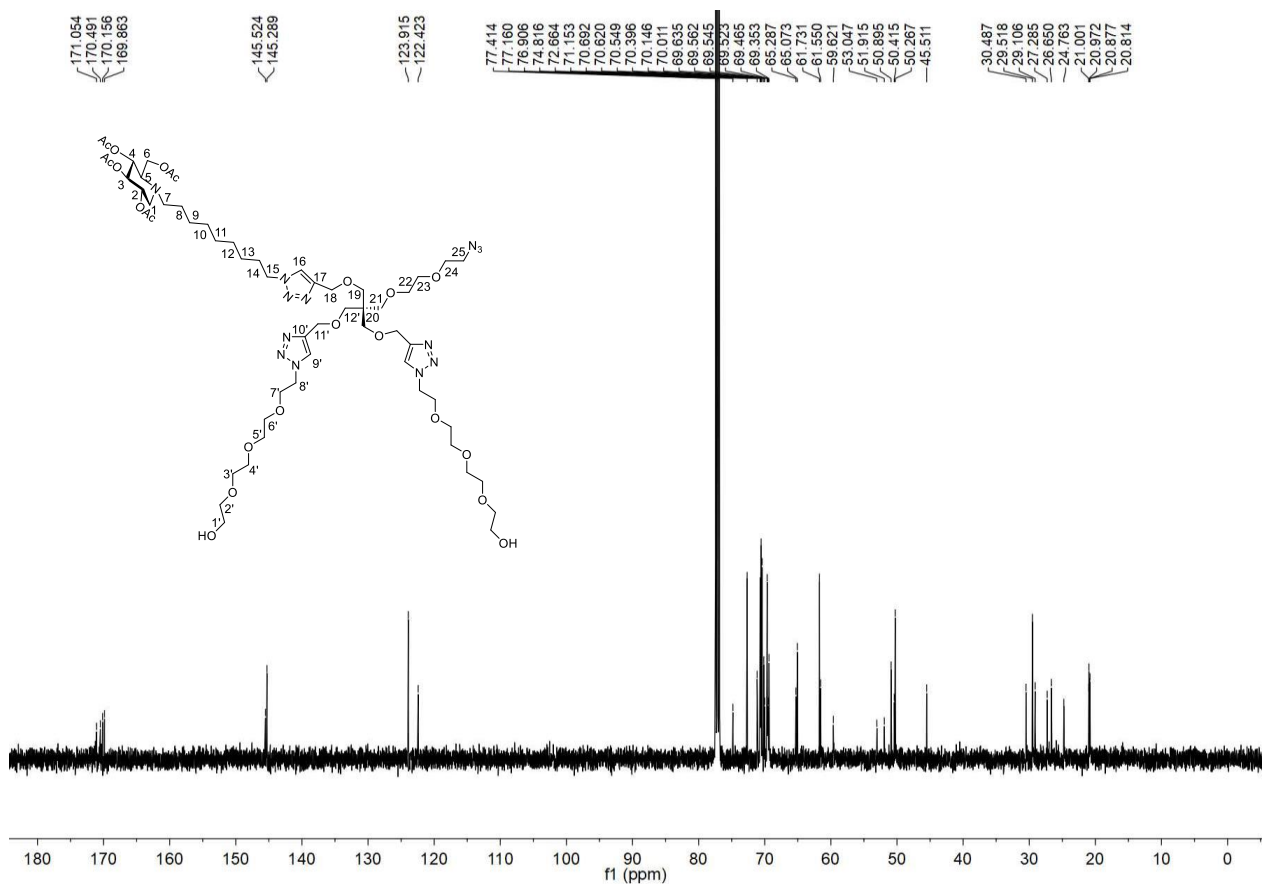
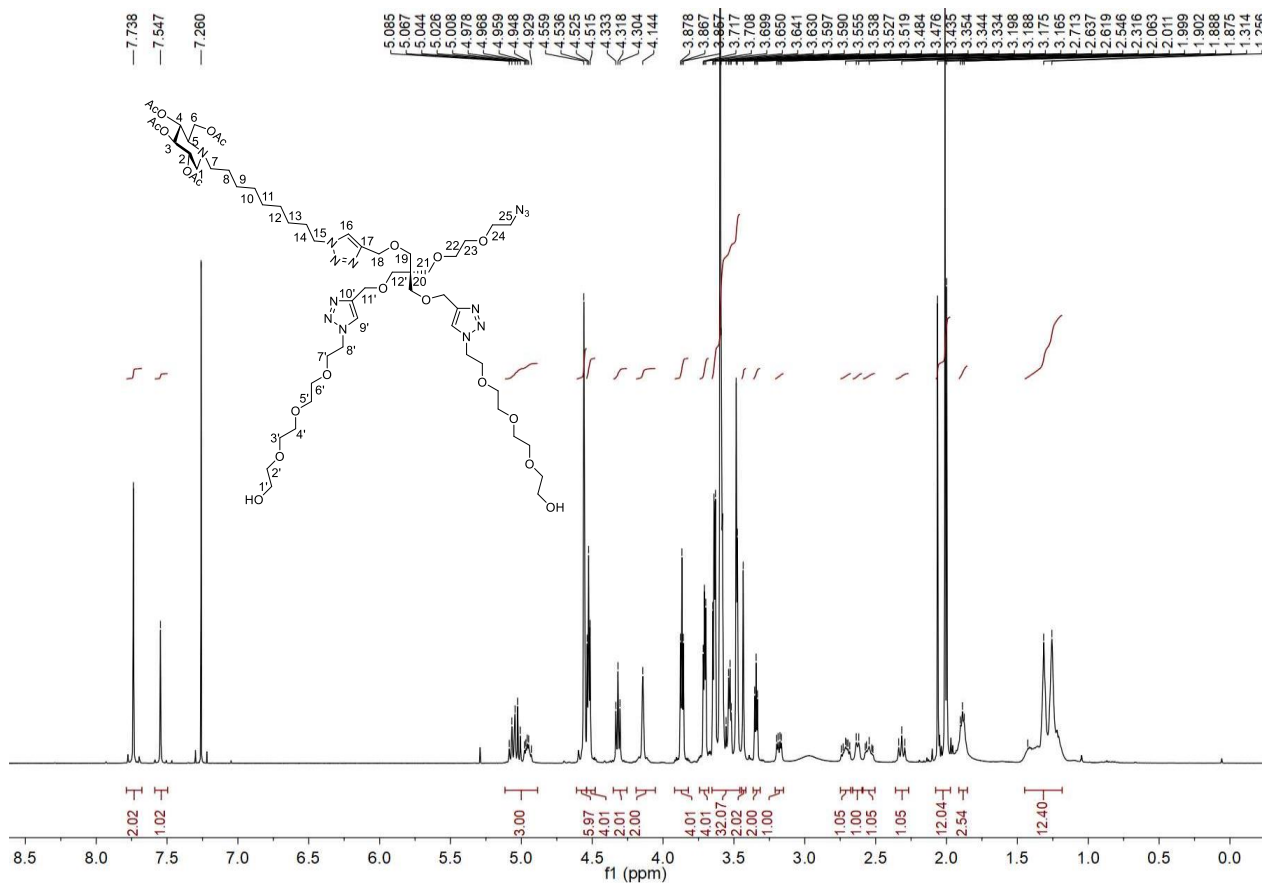
^1H NMR spectrum (CDCl_3 , 400 MHz) and ^{13}C NMR spectrum (CDCl_3 , 100 MHz) for compound **25**



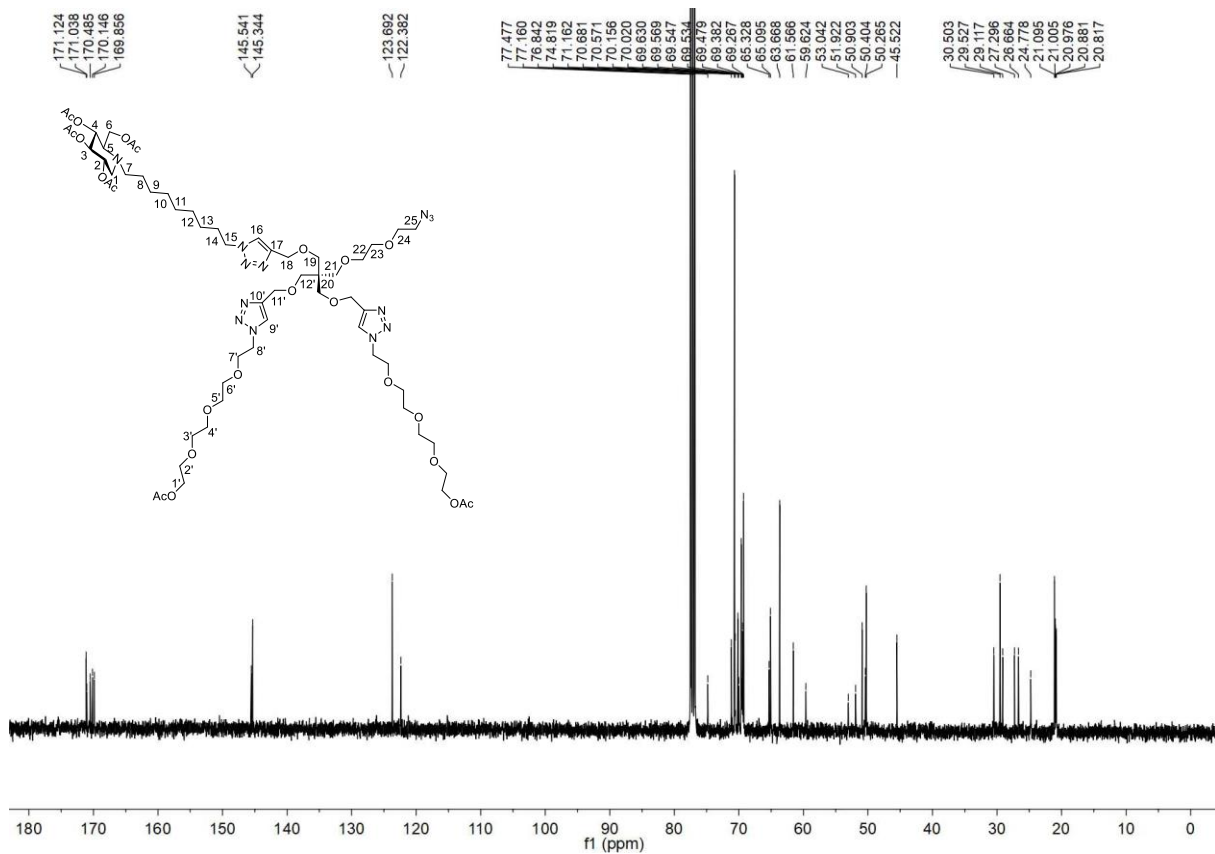
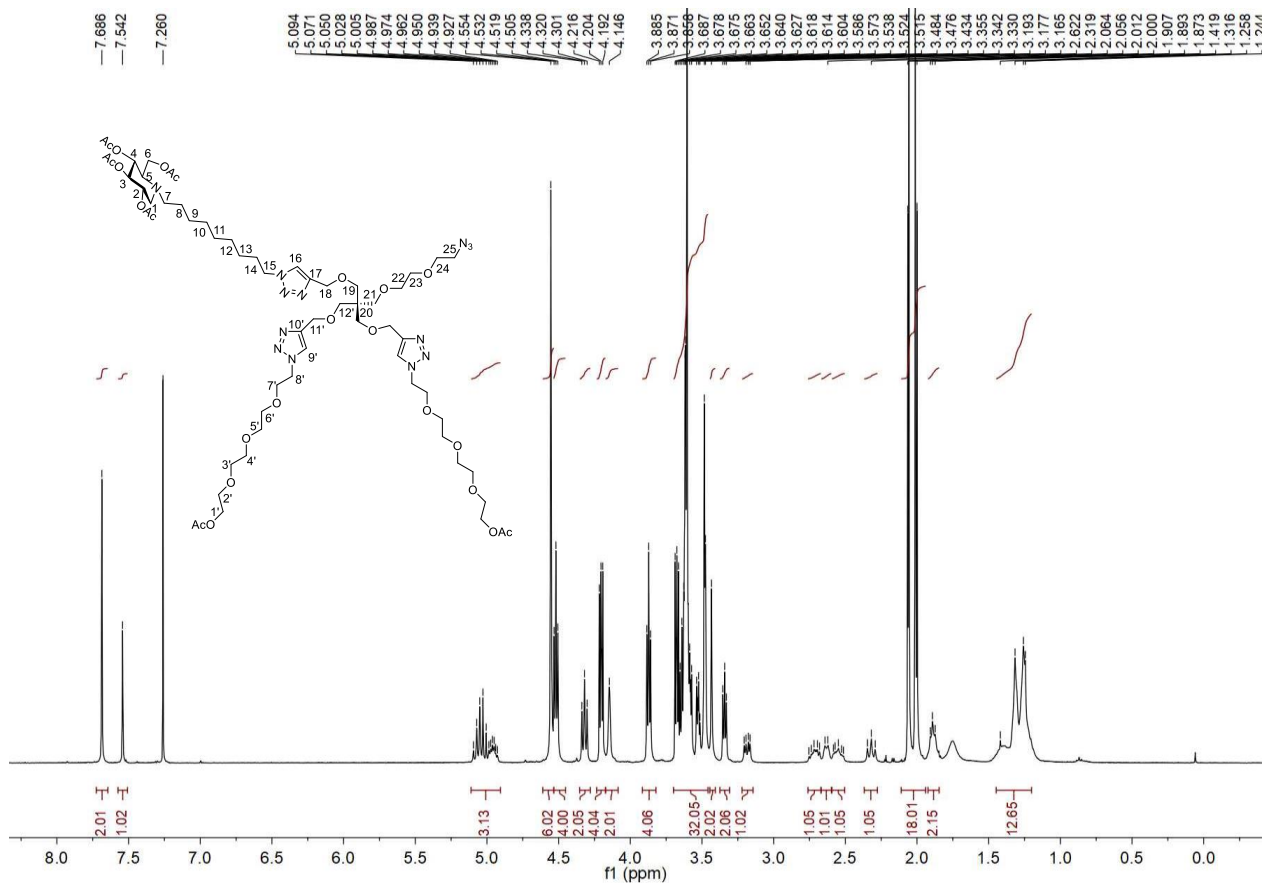
¹H NMR spectrum (CDCl₃, 400 MHz) and ¹³C NMR spectrum (CDCl₃, 100 MHz) for compound **26**



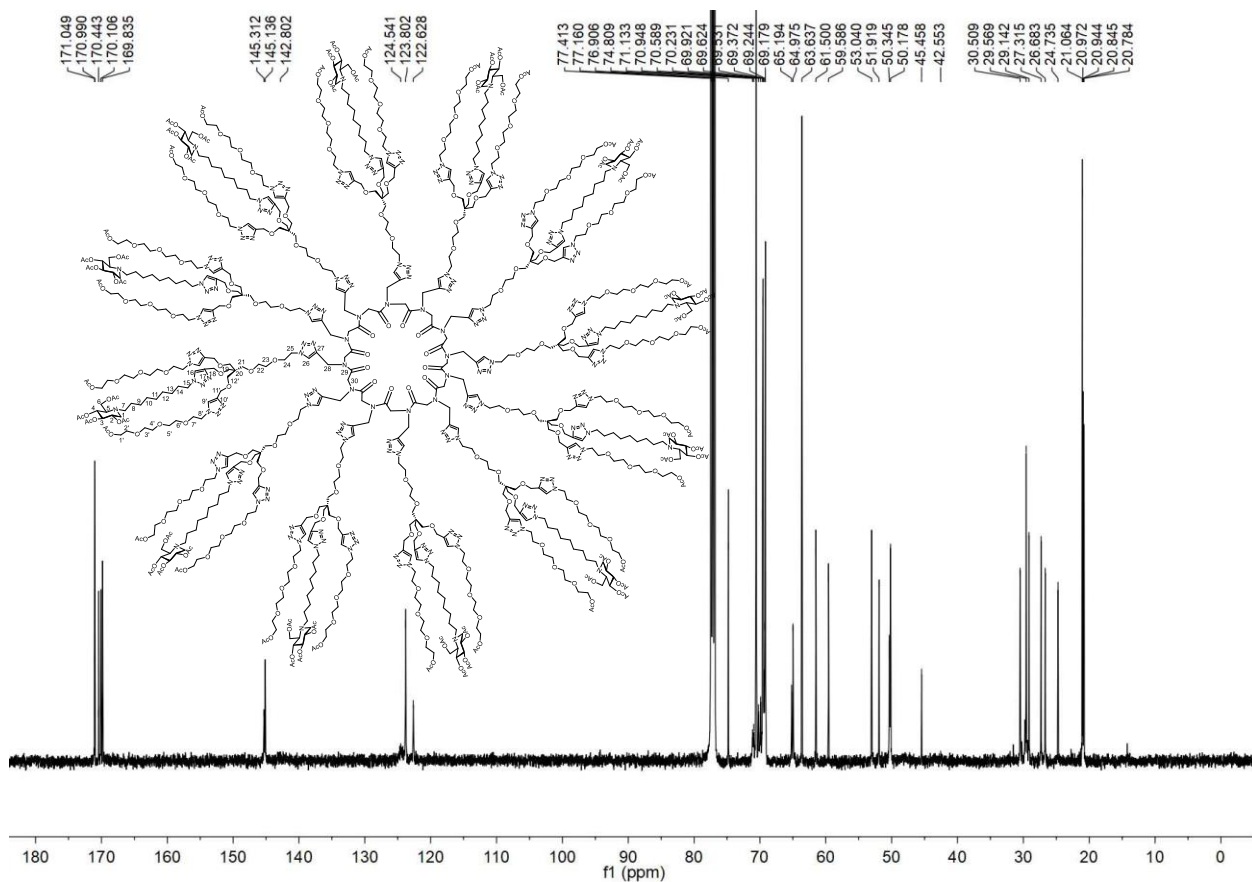
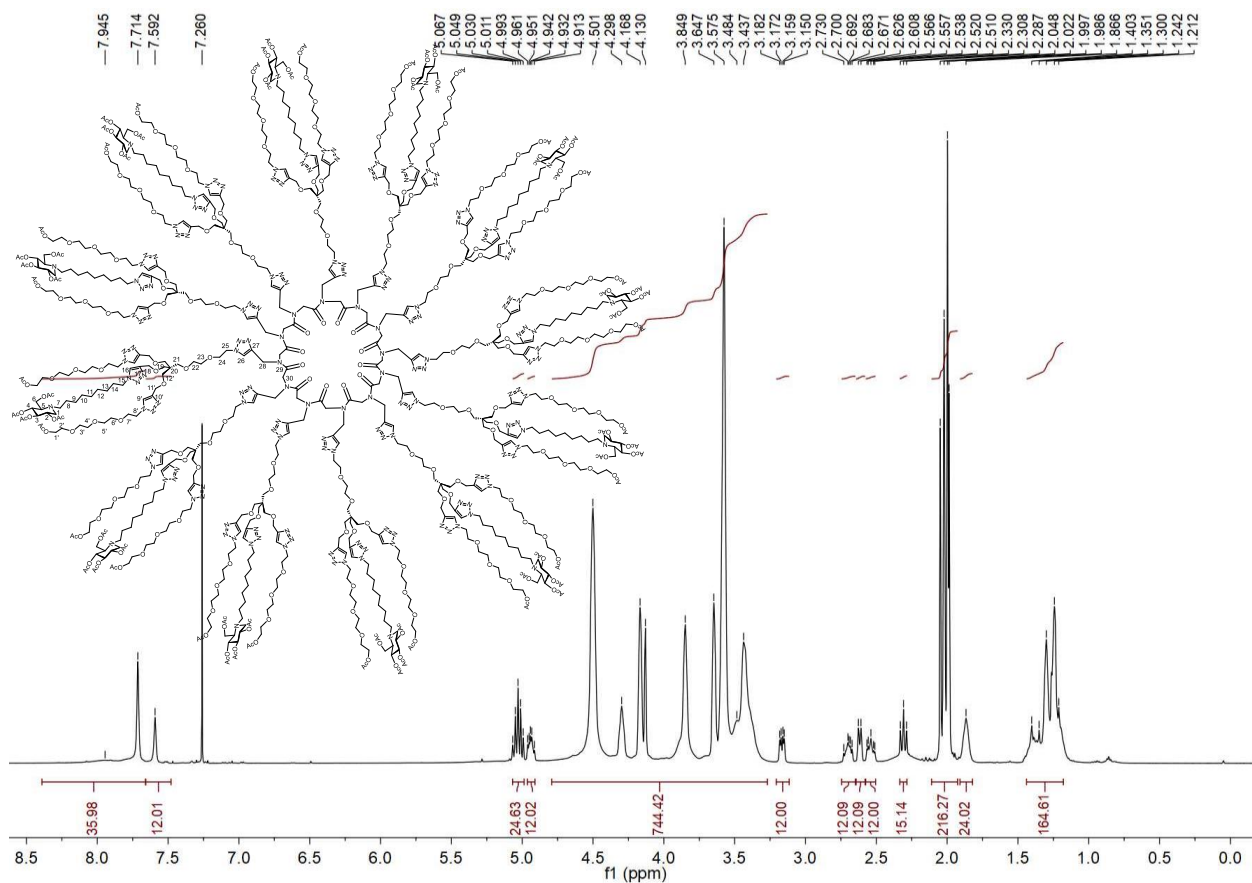
¹H NMR spectrum (CDCl₃, 500 MHz) and ¹³C NMR spectrum (CDCl₃, 125 MHz) for compound **27**



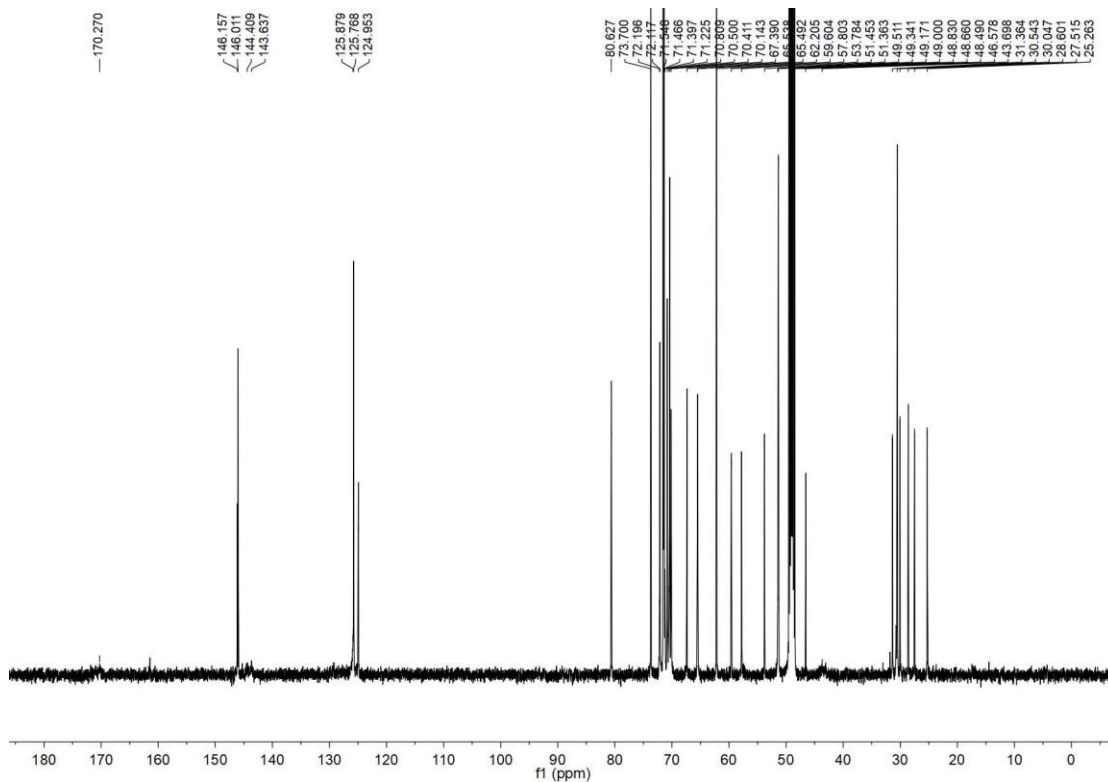
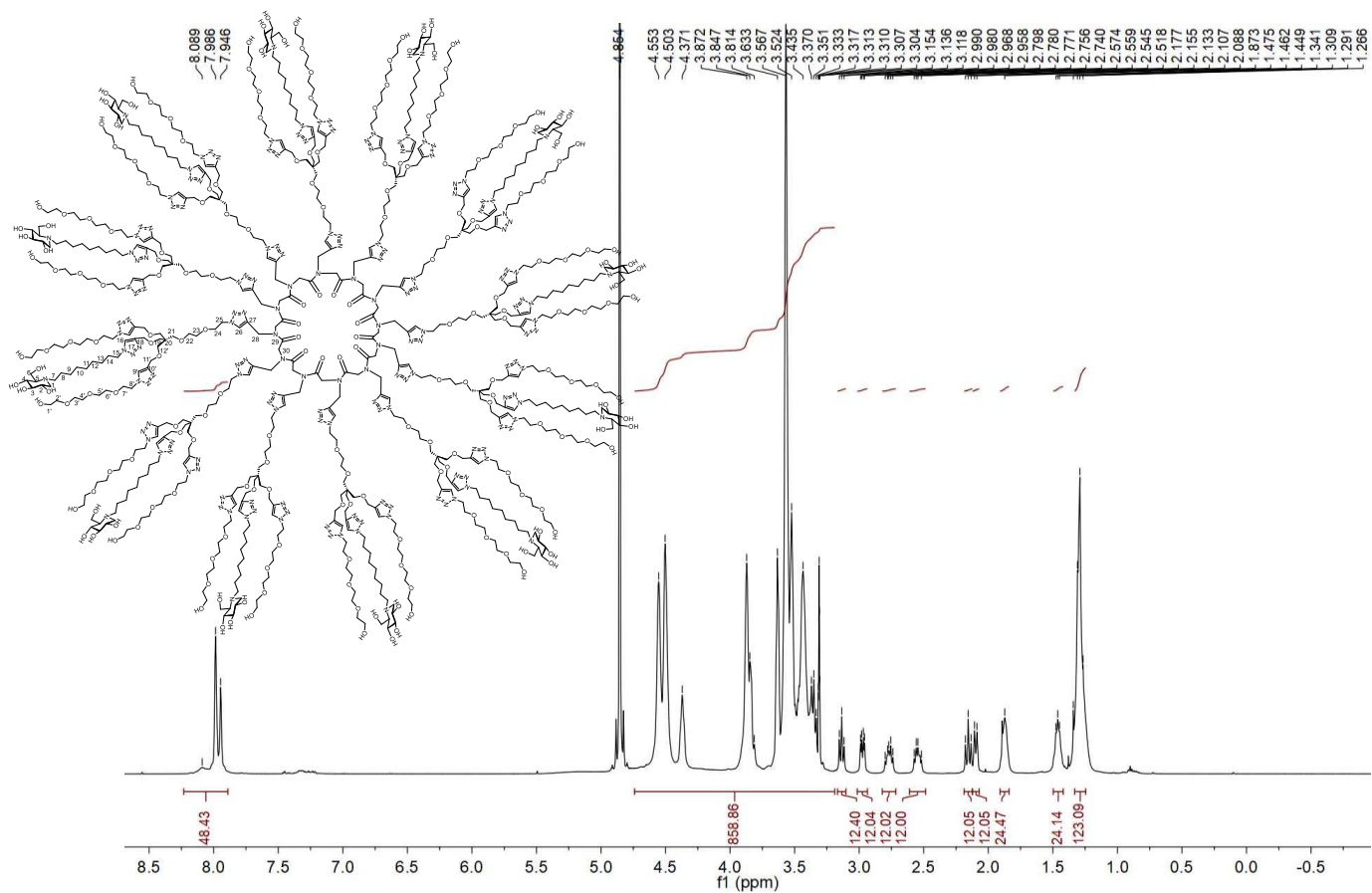
¹H NMR spectrum (CDCl₃, 500 MHz) and ¹³C NMR spectrum (CDCl₃, 125 MHz) for compound **14**



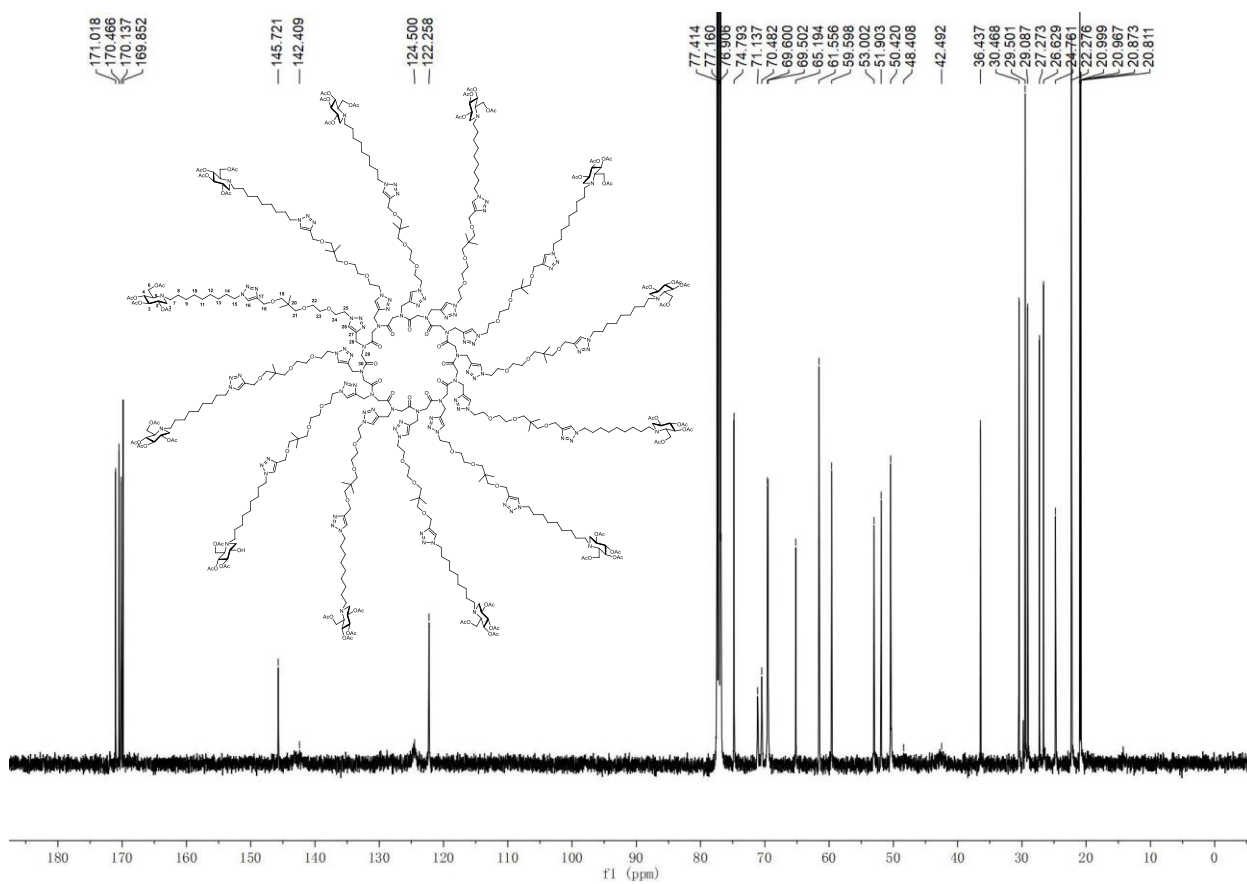
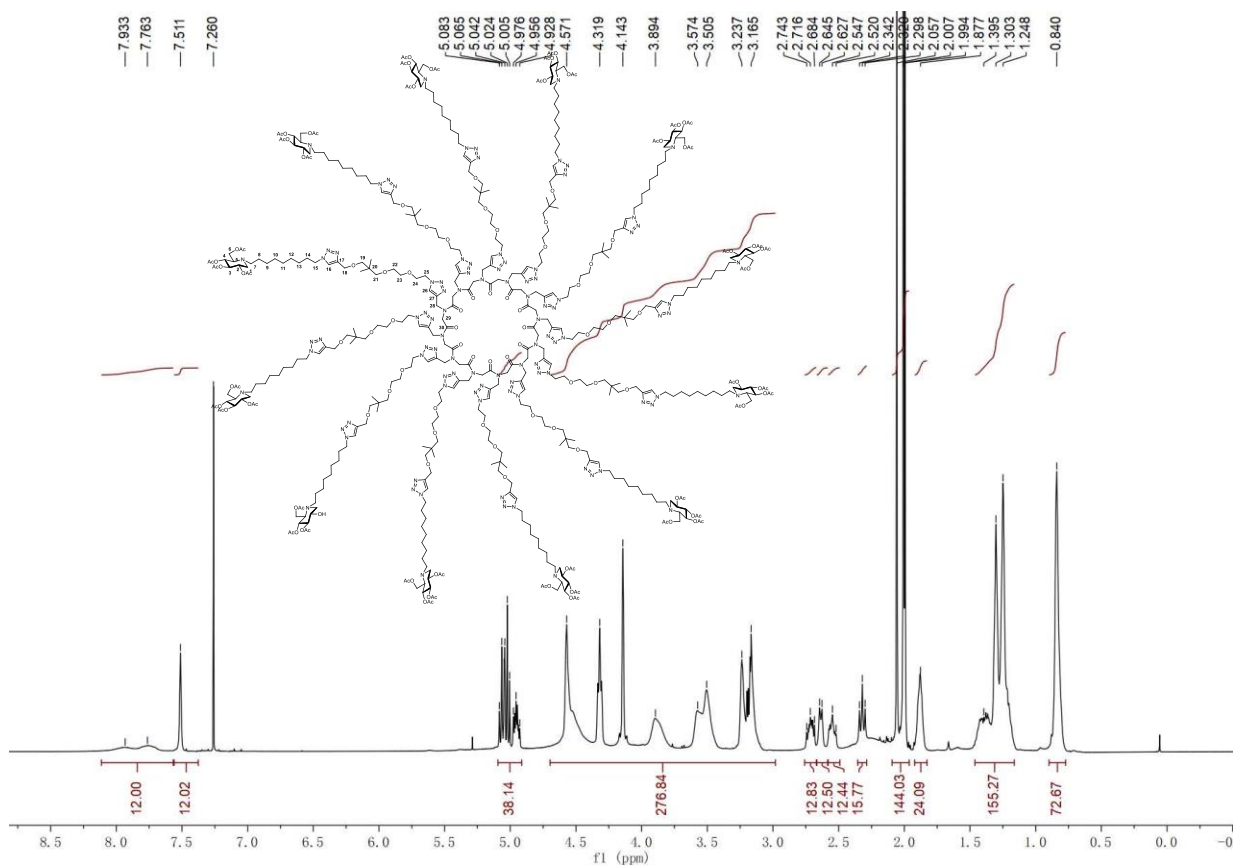
¹H NMR spectrum (CDCl₃, 500 MHz) and ¹³C NMR spectrum (CDCl₃, 125 MHz) for compound **28**



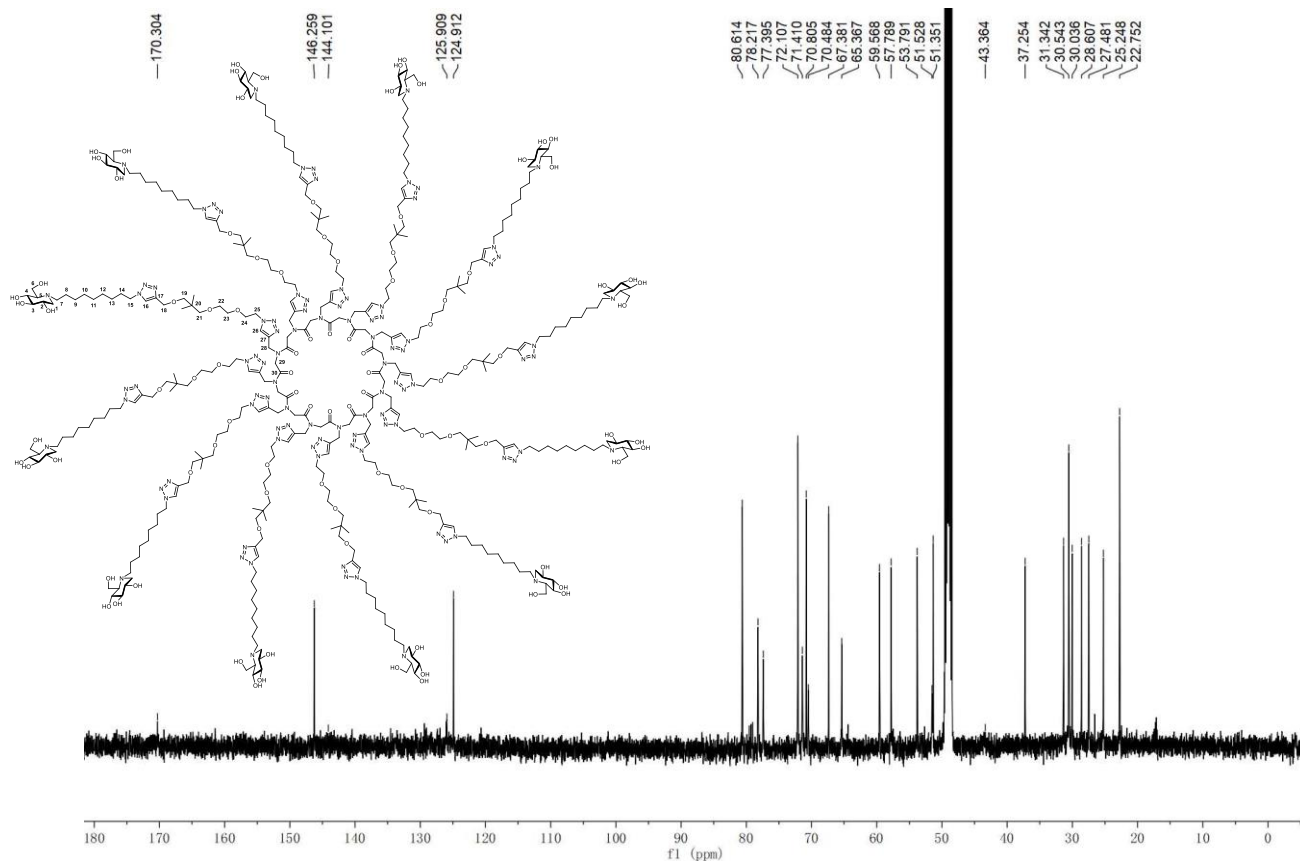
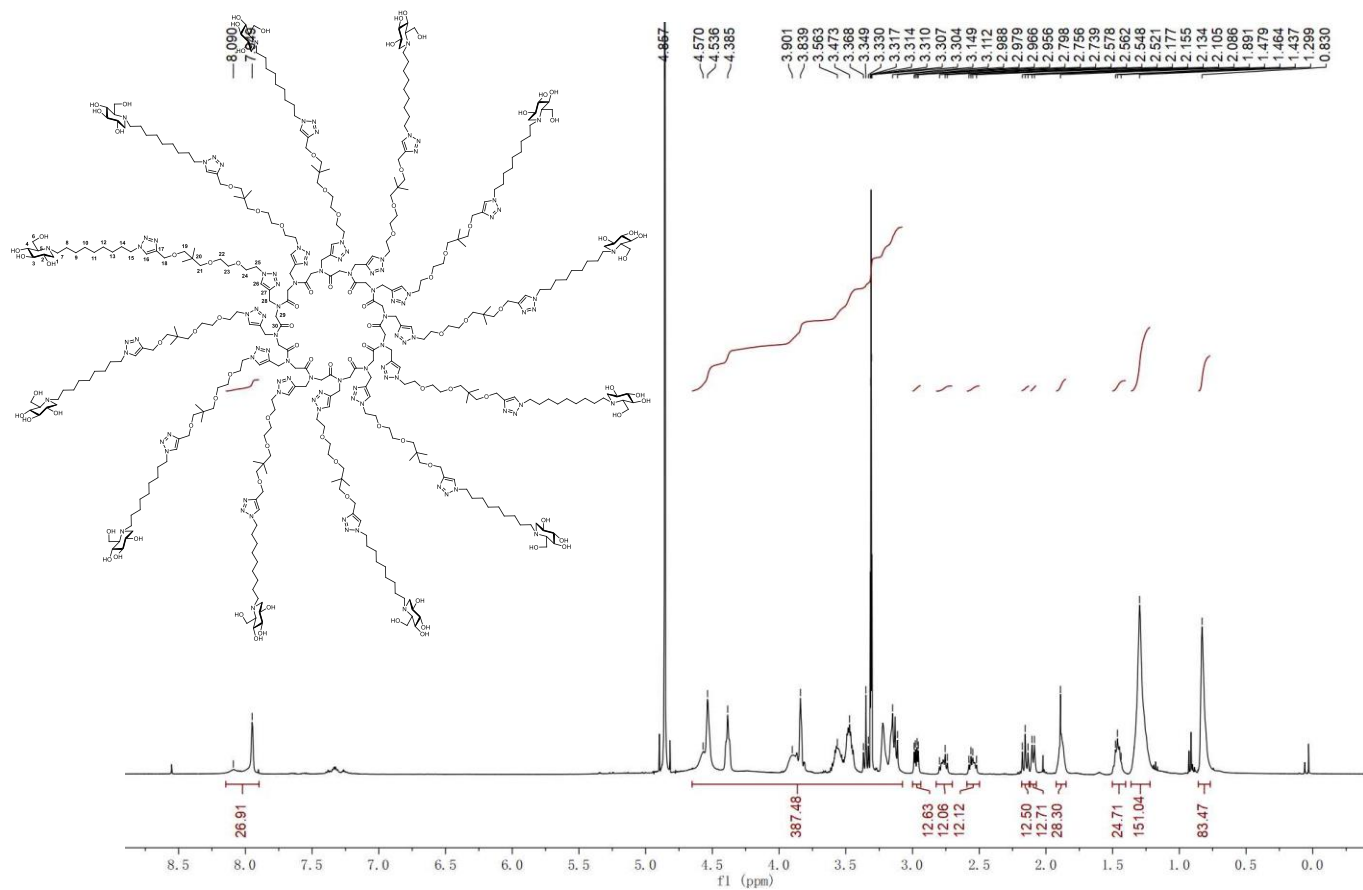
¹H NMR spectrum (MeOD, 500 MHz) and ¹³C NMR spectrum (MeOD, 125 MHz) for compound **3**



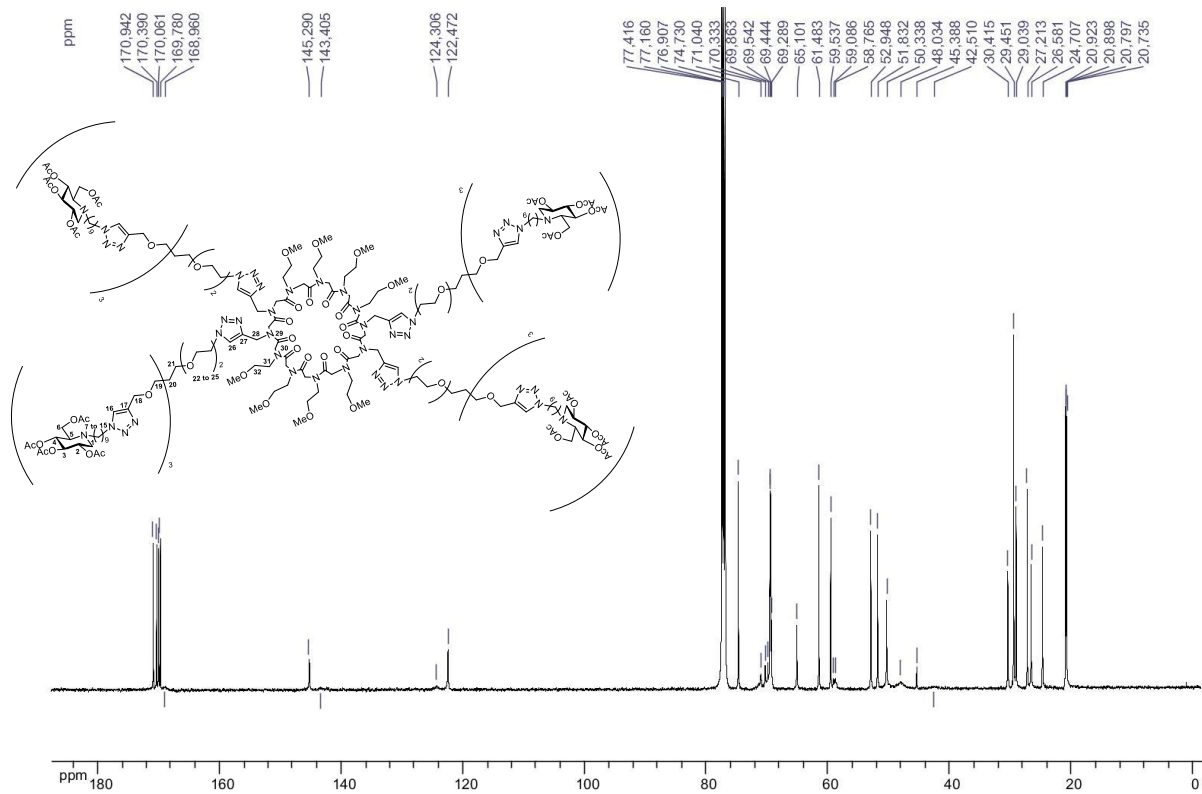
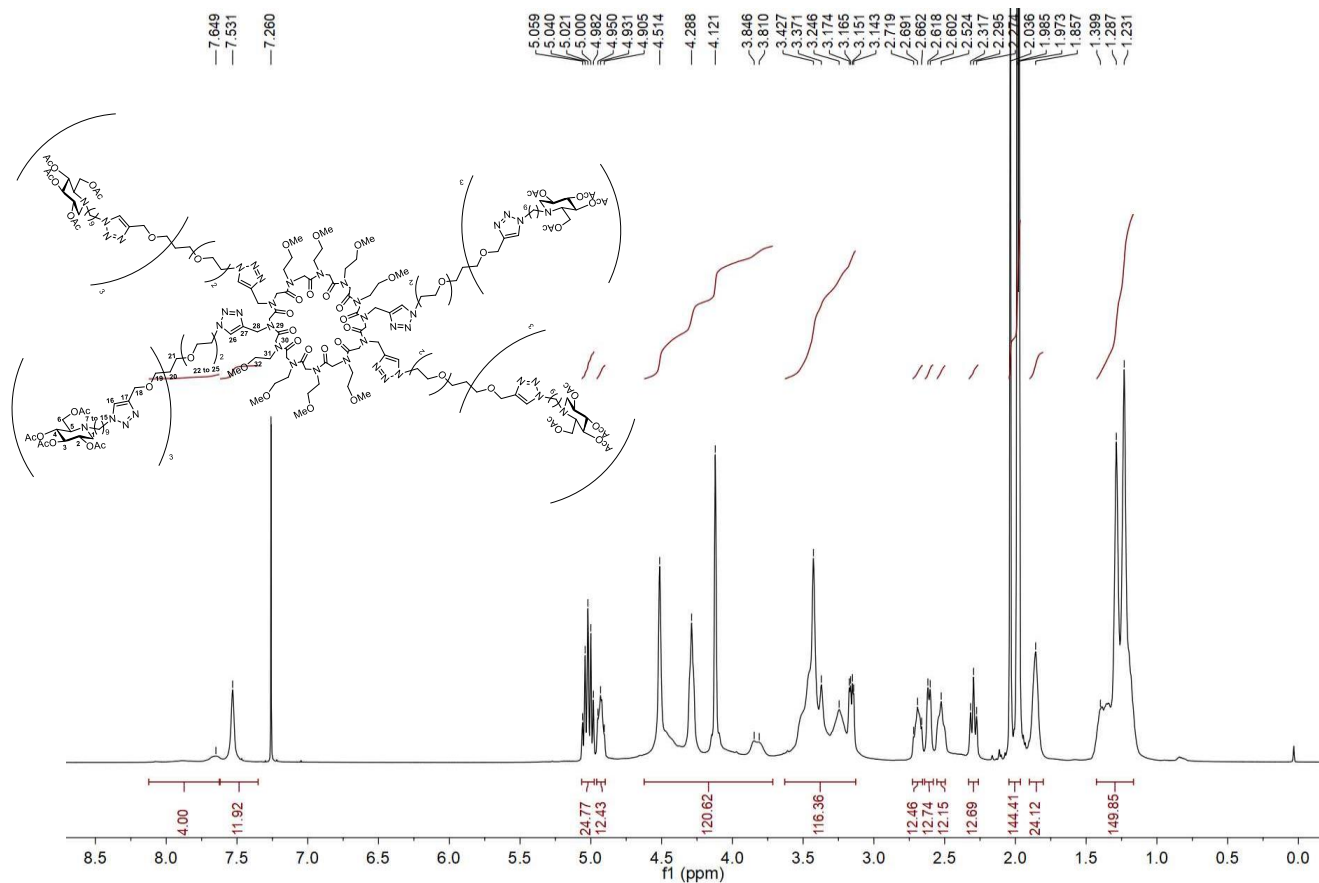
¹H NMR spectrum (CDCl₃, 500 MHz) and ¹³C NMR spectrum (CDCl₃, 125 MHz) for compound **29**



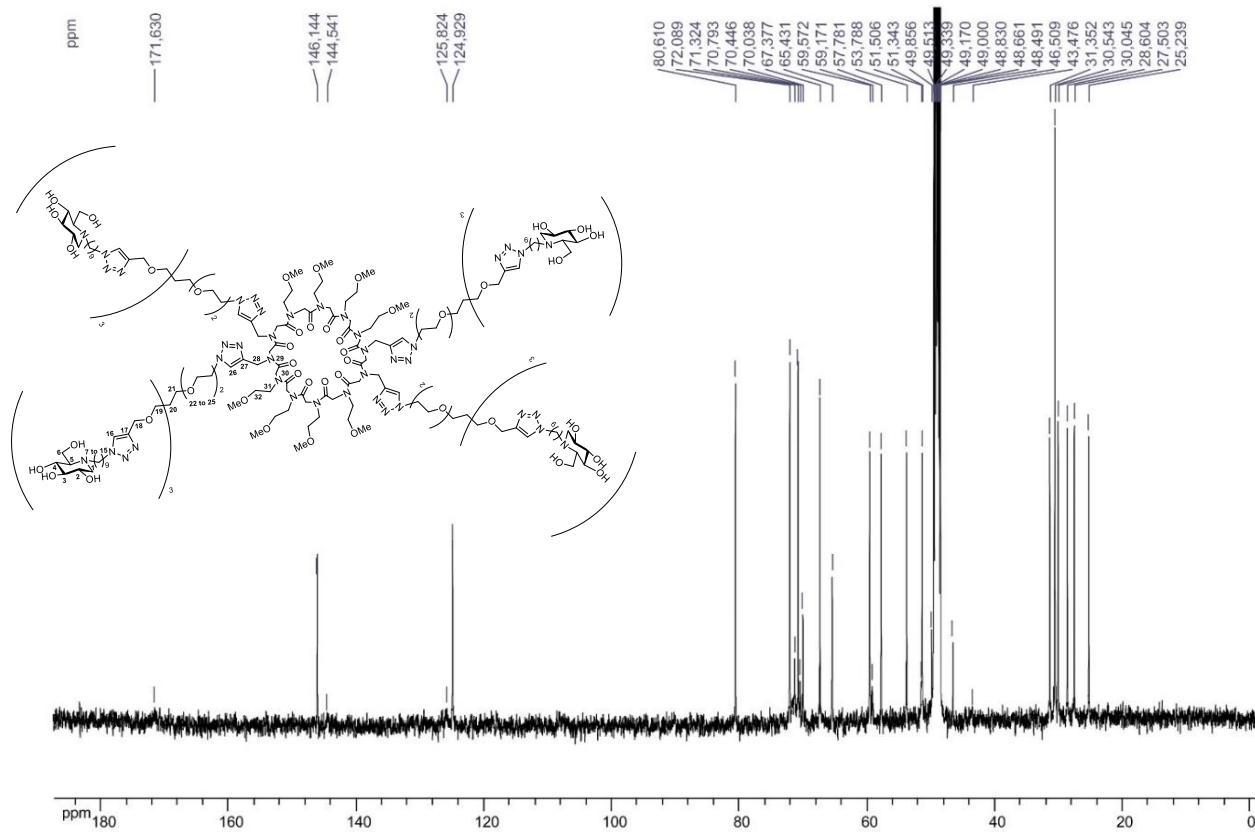
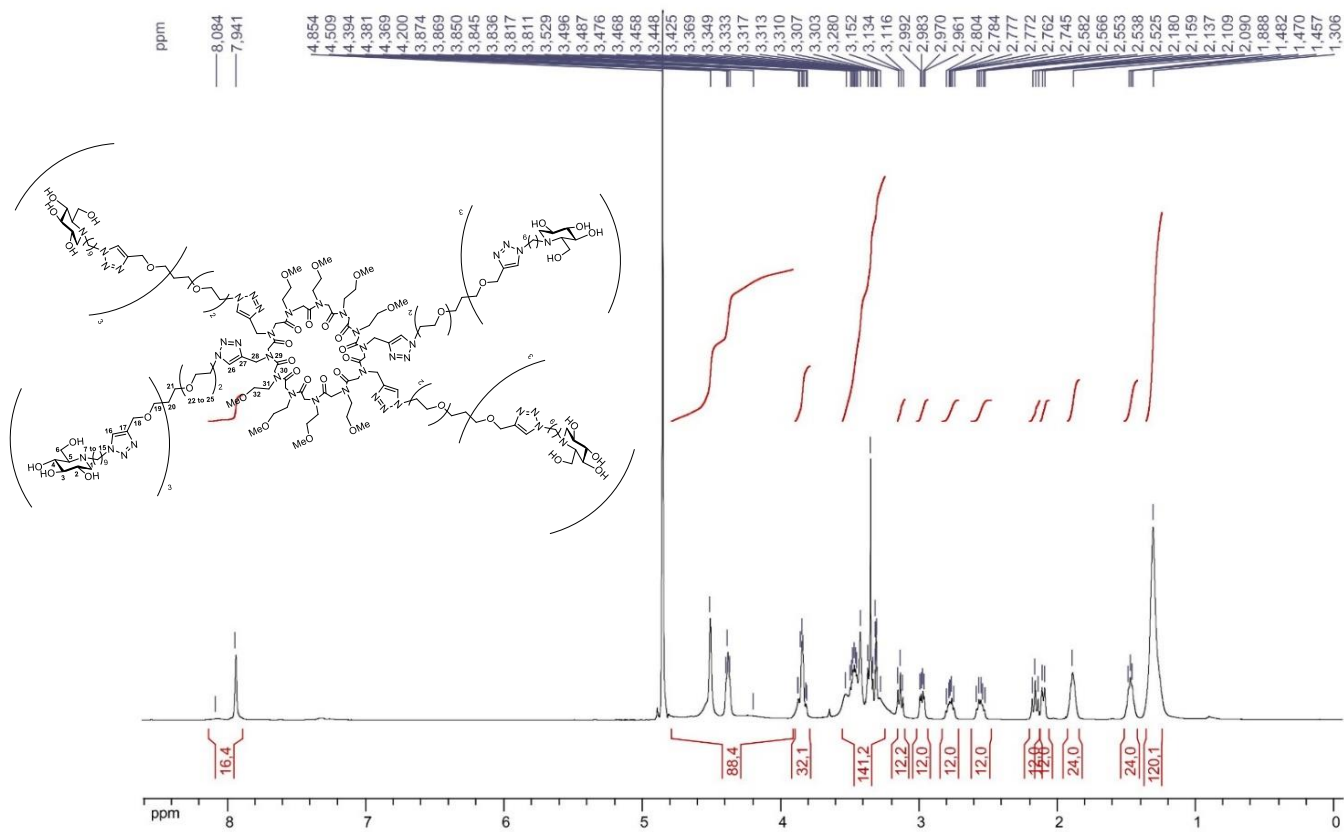
^1H NMR spectrum (MeOD, 500 MHz) and ^{13}C NMR spectrum (MeOD, 125 MHz) for compound **4**



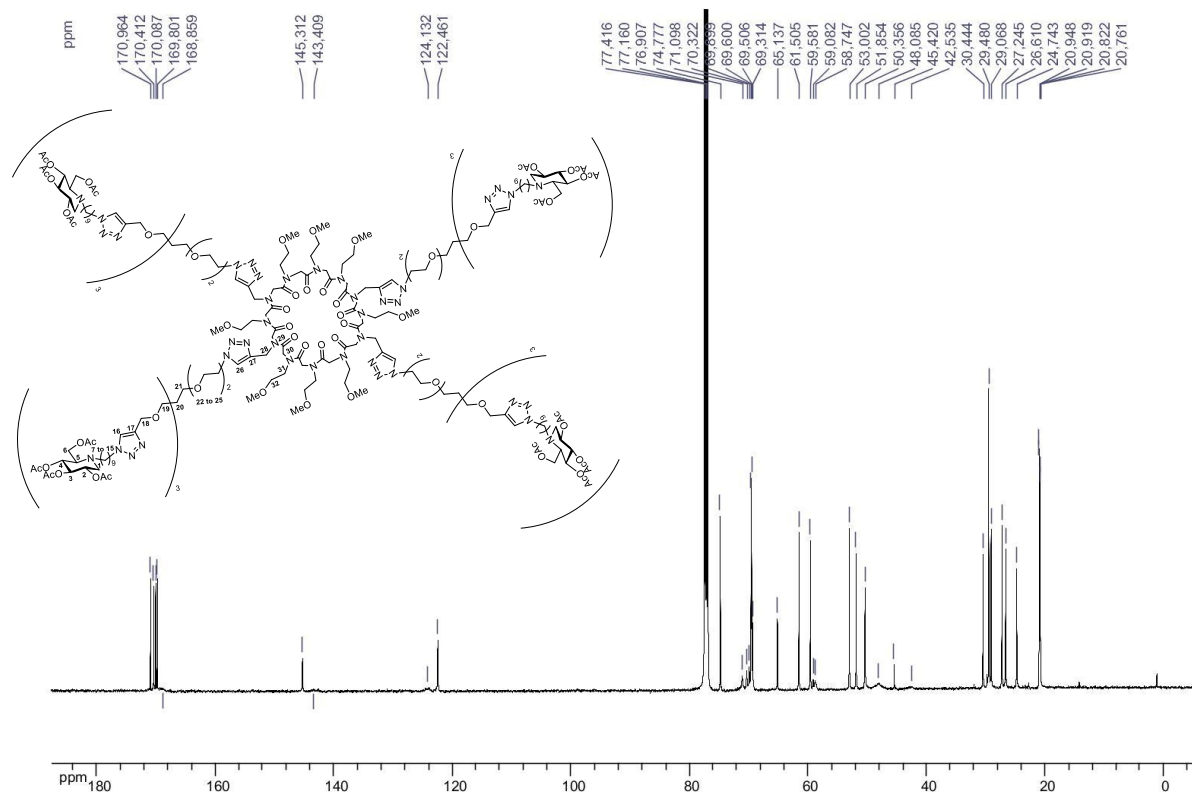
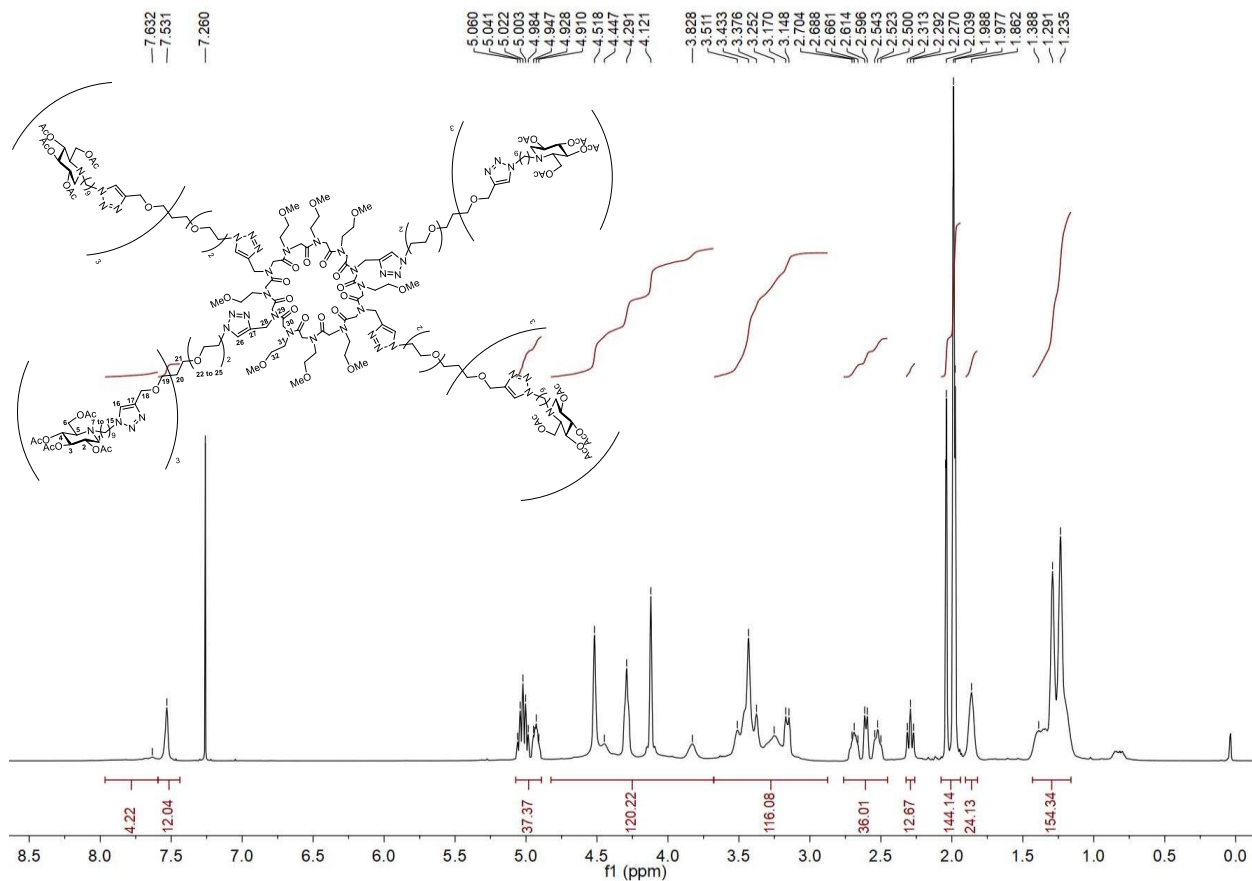
¹H NMR spectrum (CDCl₃, 500 MHz) and ¹³C NMR spectrum (CDCl₃, 125 MHz) for compound **30a**



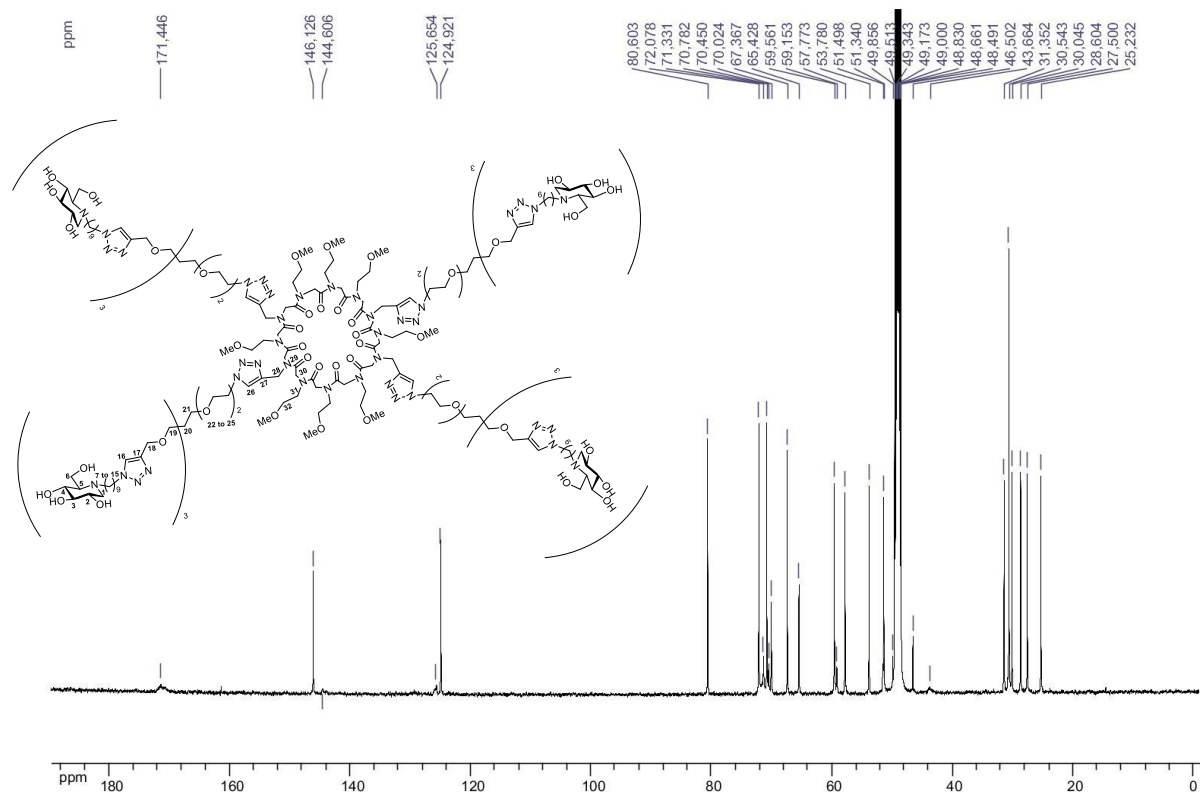
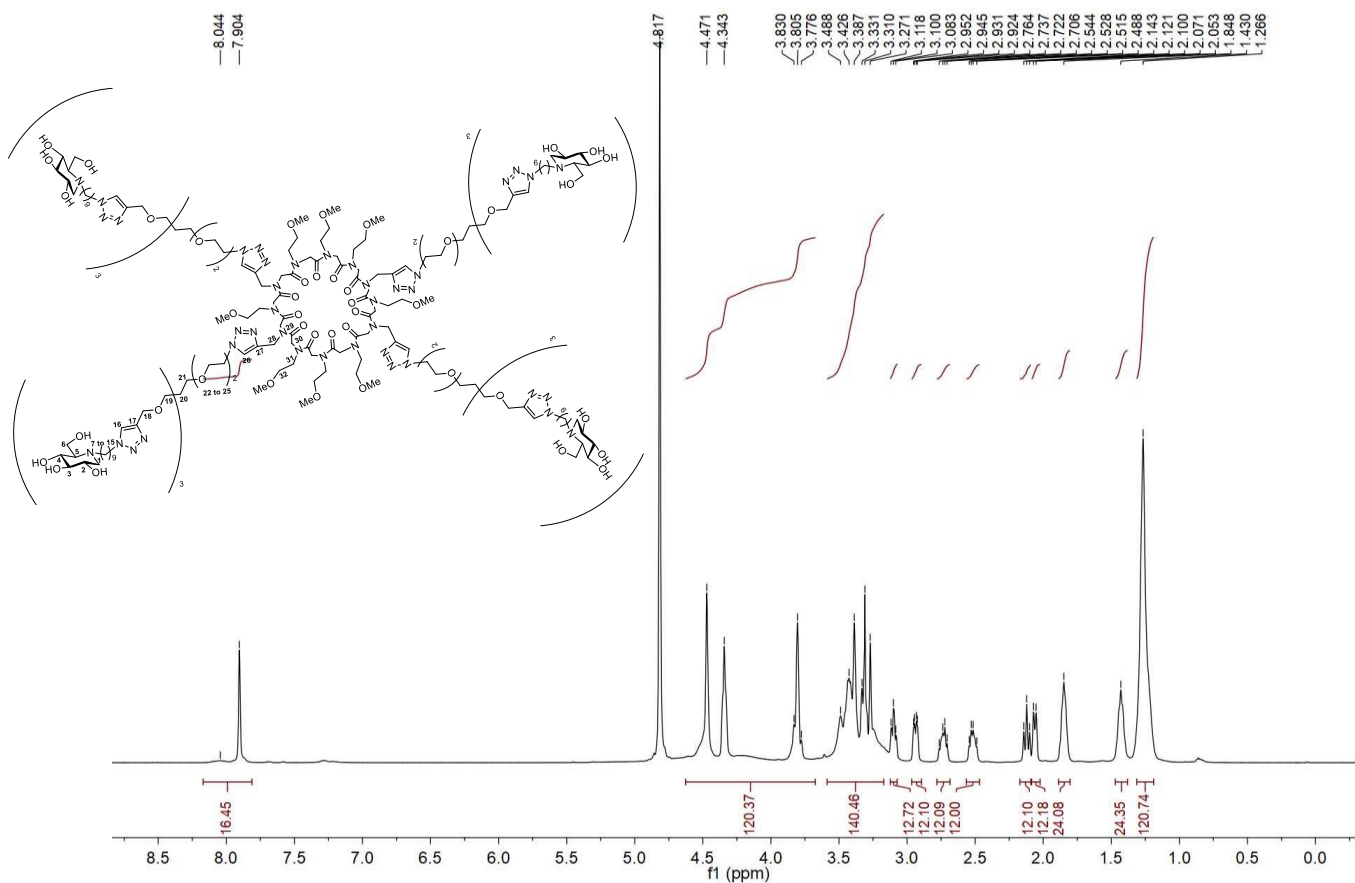
^1H NMR spectrum (MeOD, 500 MHz) and ^{13}C NMR spectrum (MeOD, 125 MHz) for compound **5a**



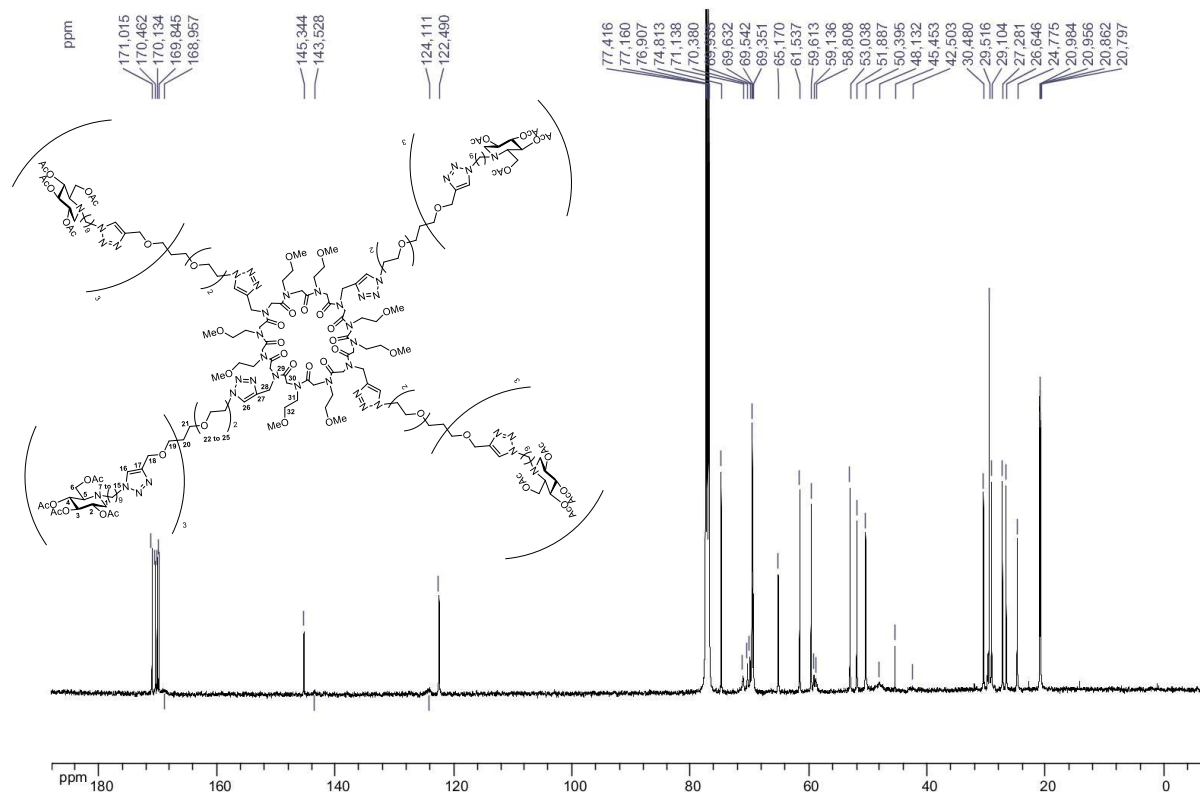
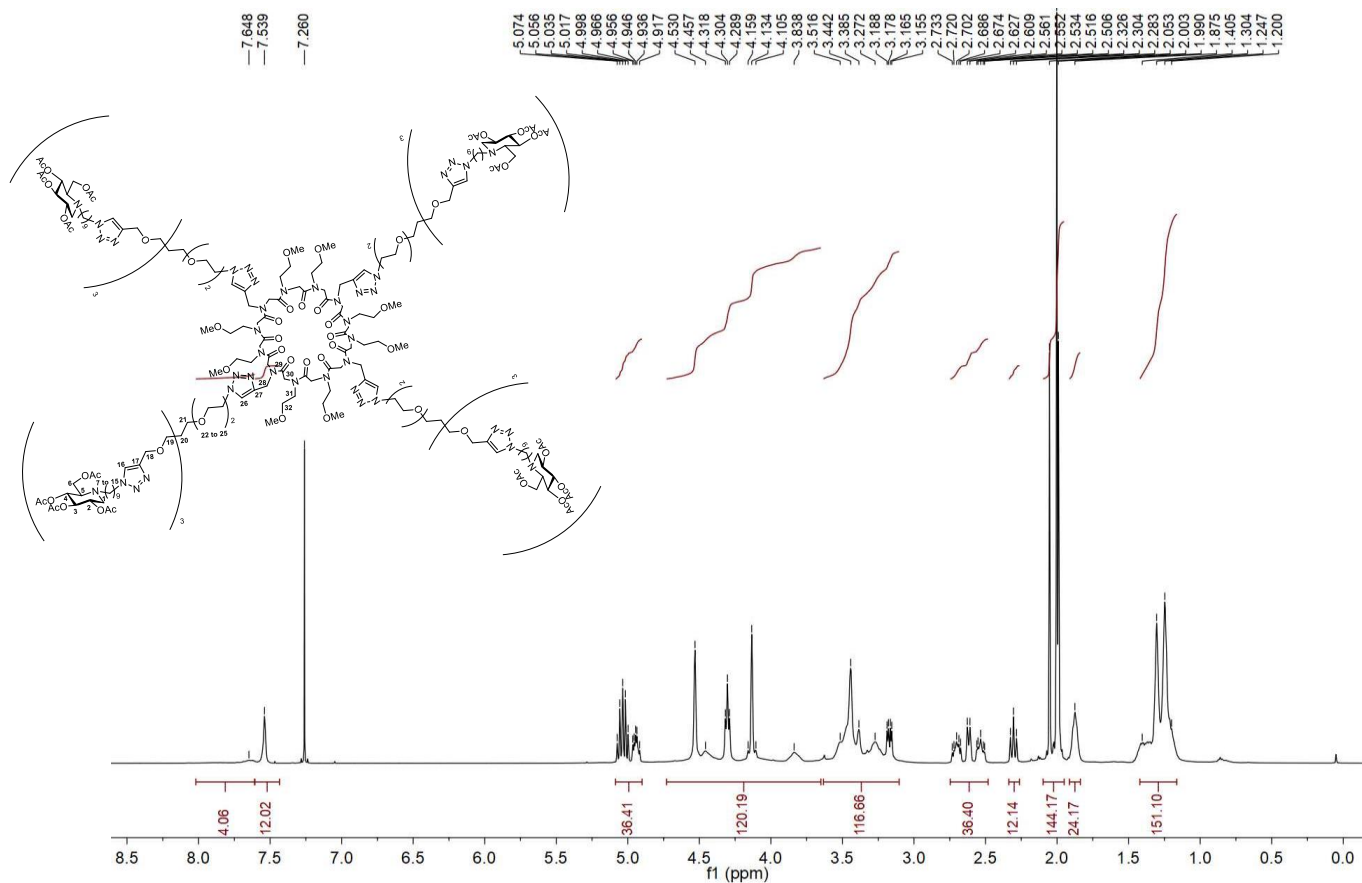
¹H NMR spectrum (CDCl₃, 500 MHz) and ¹³C NMR spectrum (CDCl₃, 125 MHz) for compound **30b**



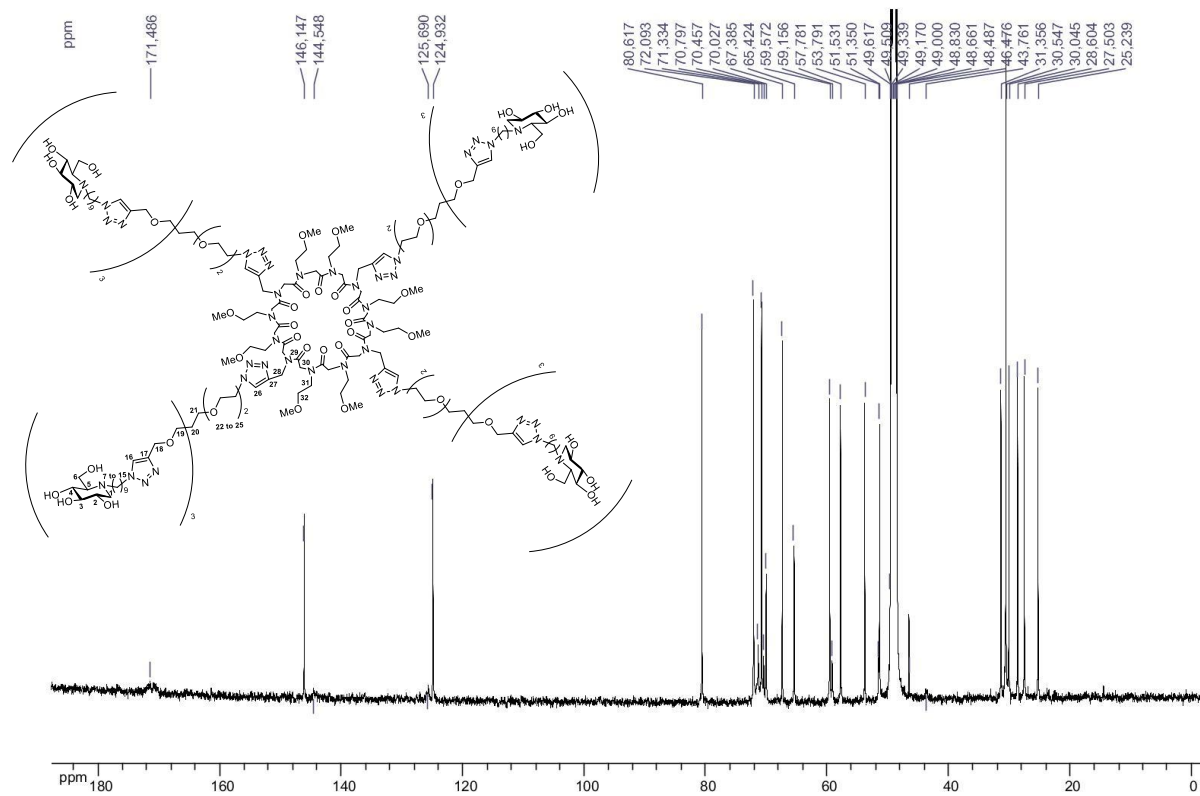
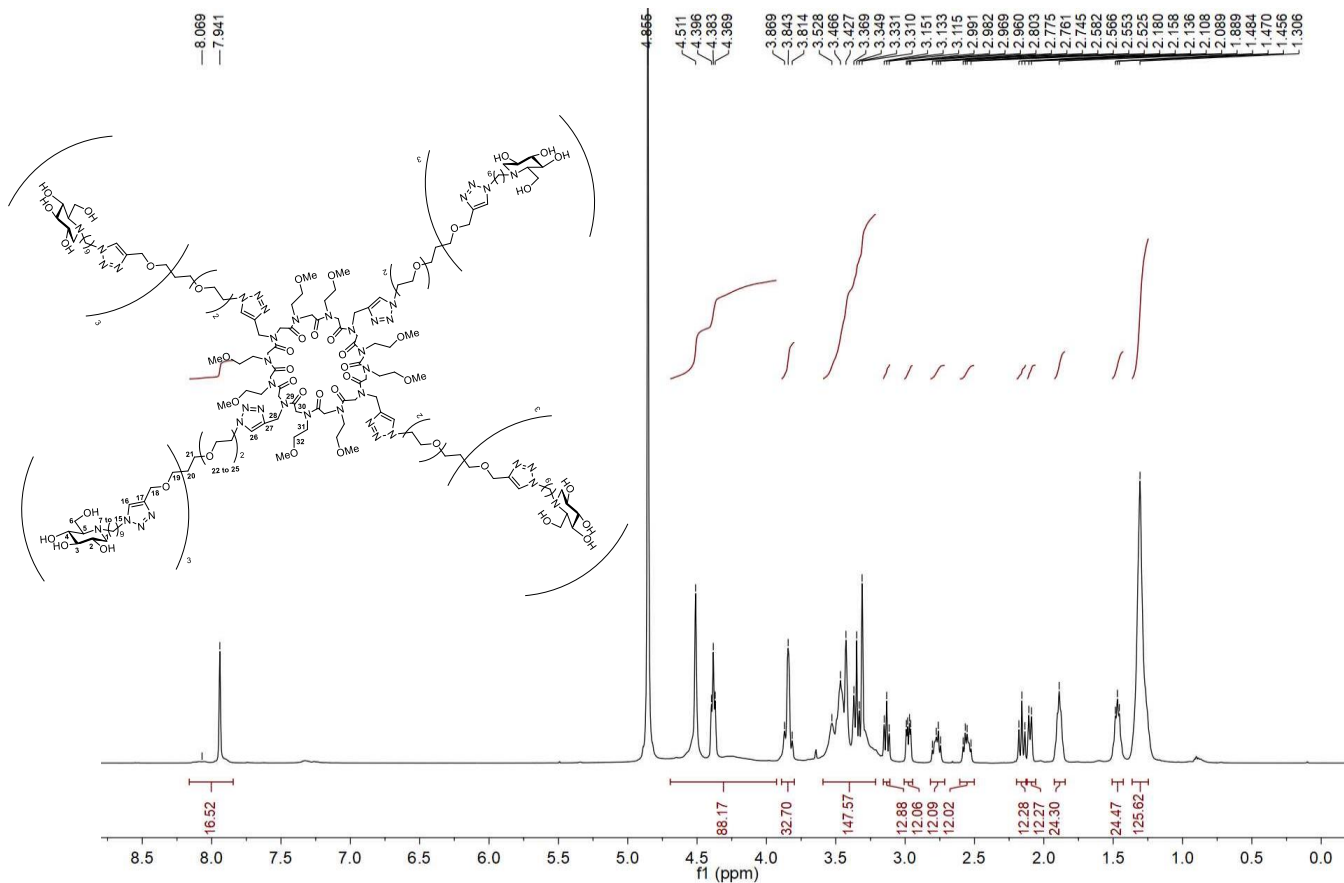
^1H NMR spectrum (MeOD, 500 MHz) and ^{13}C NMR spectrum (MeOD, 125 MHz) for compound **5b**



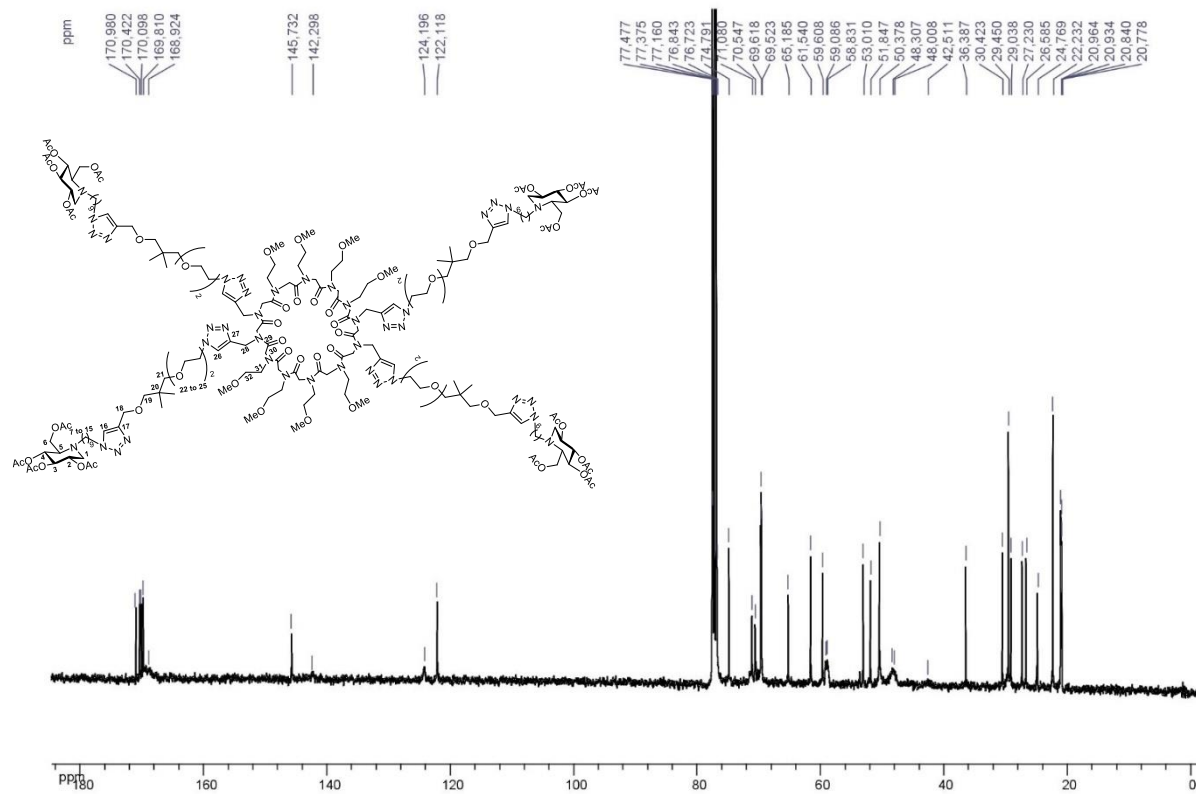
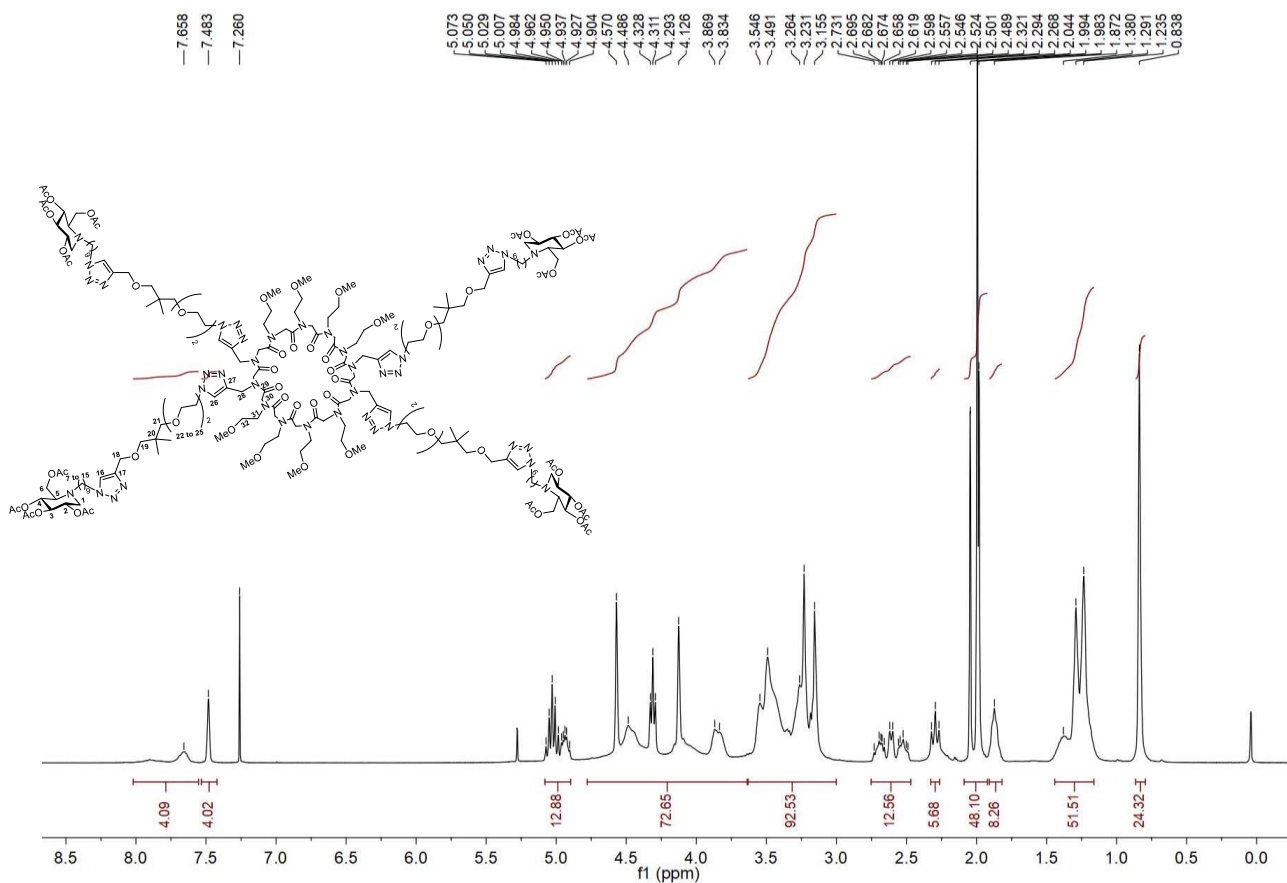
¹H NMR spectrum (CDCl₃, 500 MHz) and ¹³C NMR spectrum (CDCl₃, 125 MHz) for compound **30c**



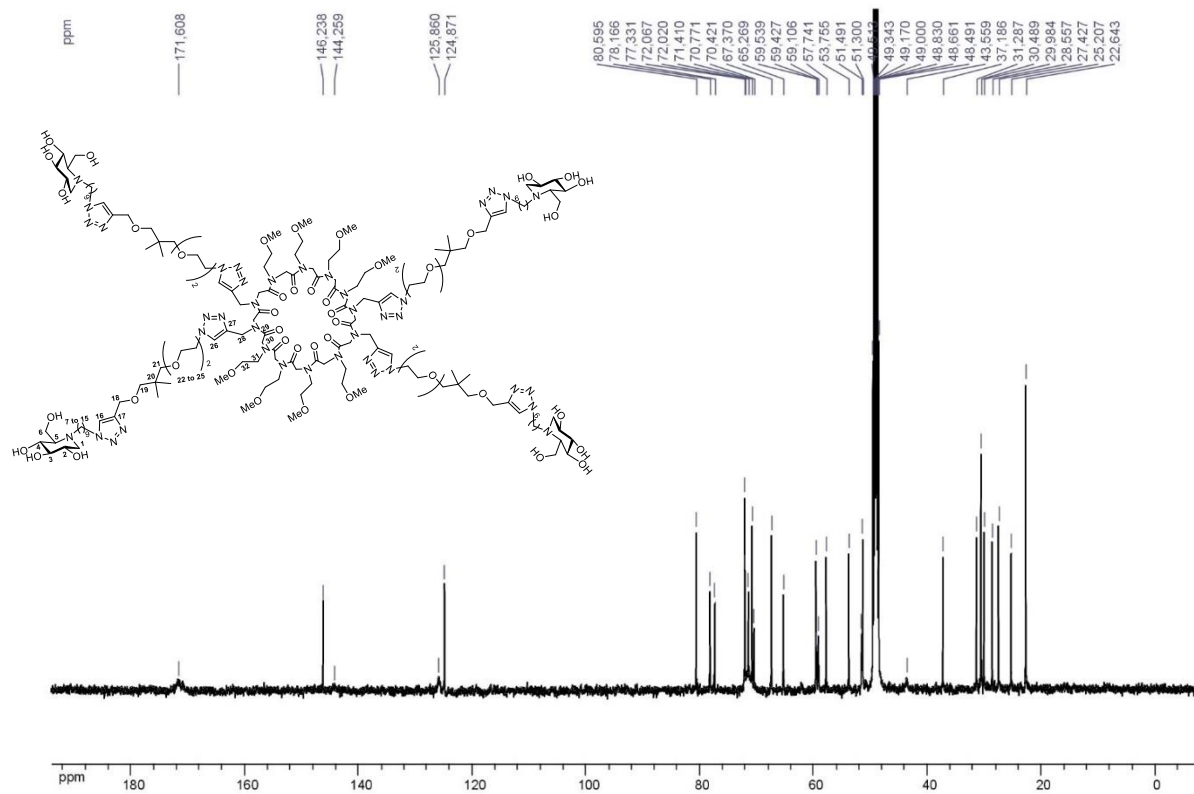
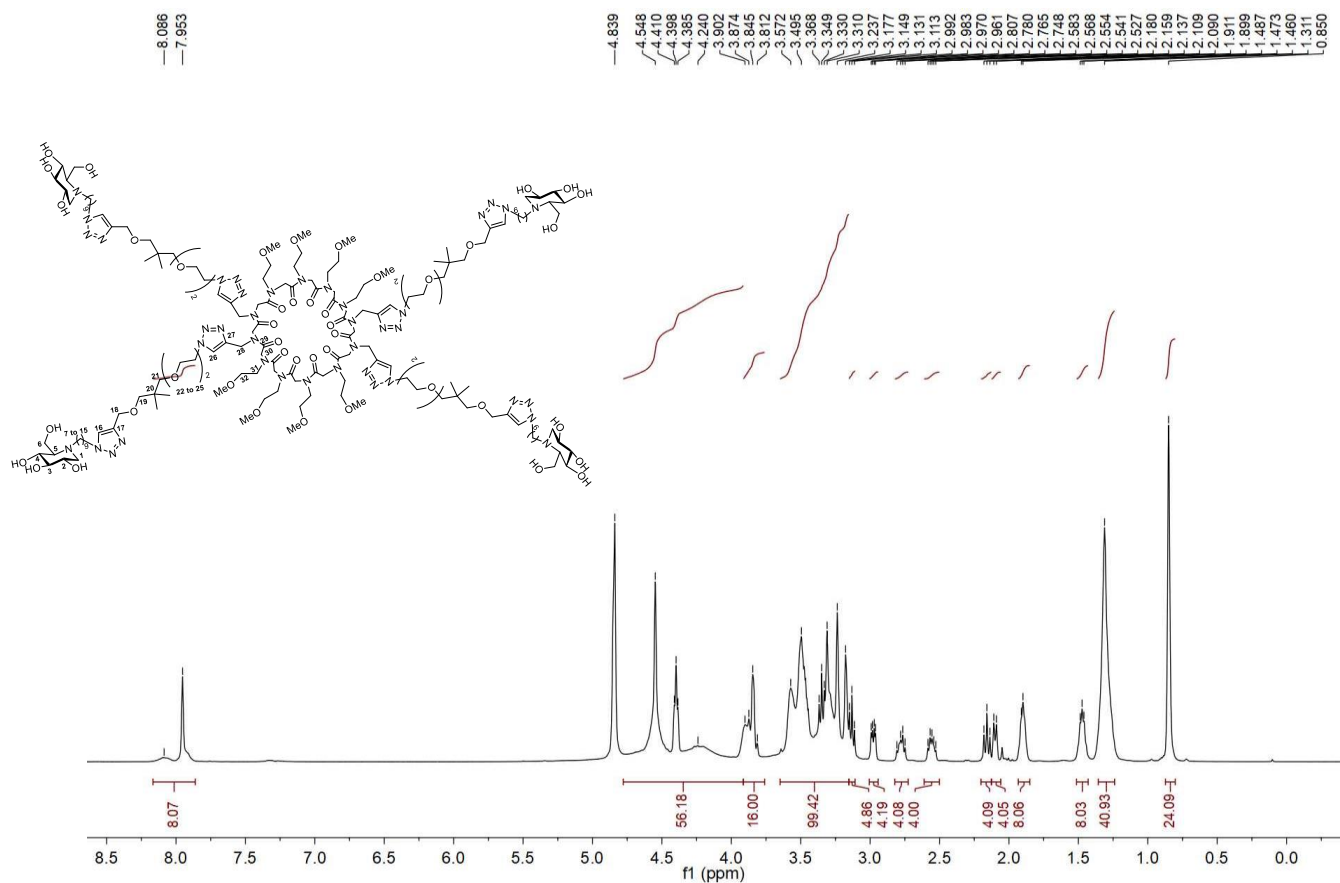
^1H NMR spectrum (MeOD, 500 MHz) and ^{13}C NMR spectrum (MeOD, 125 MHz) for compound **5c**



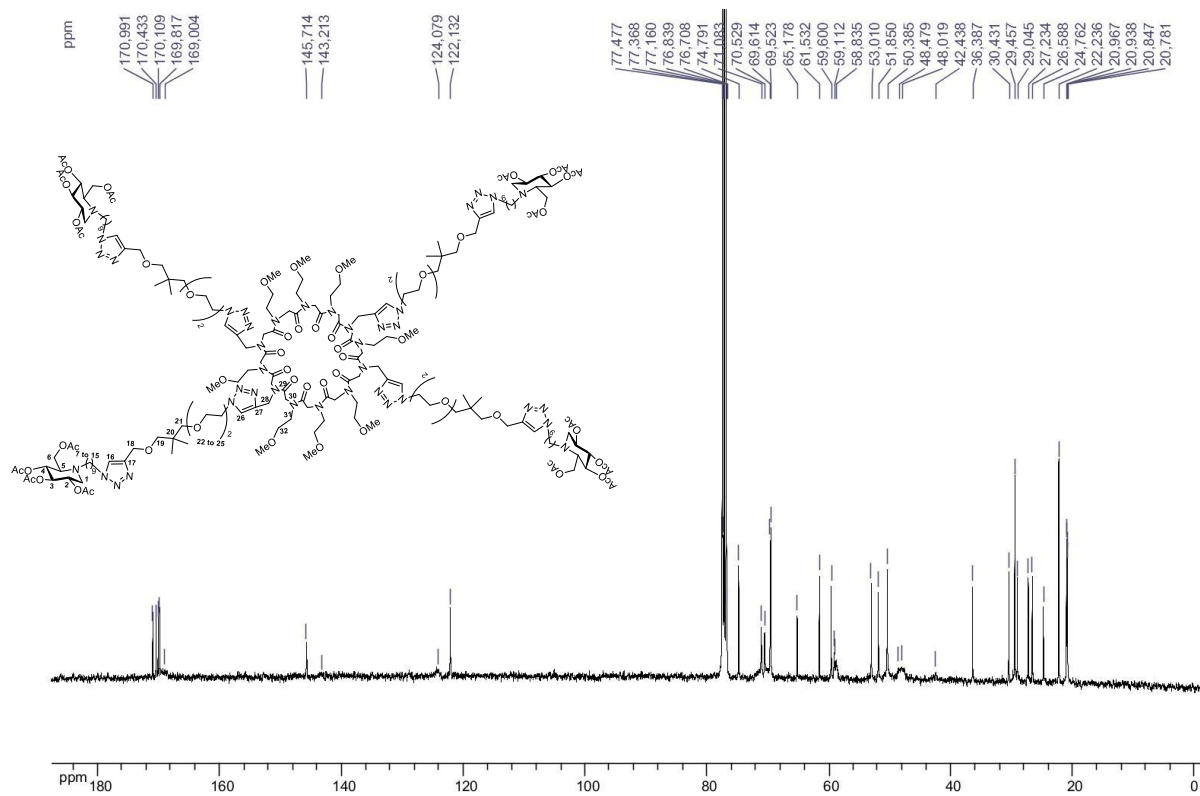
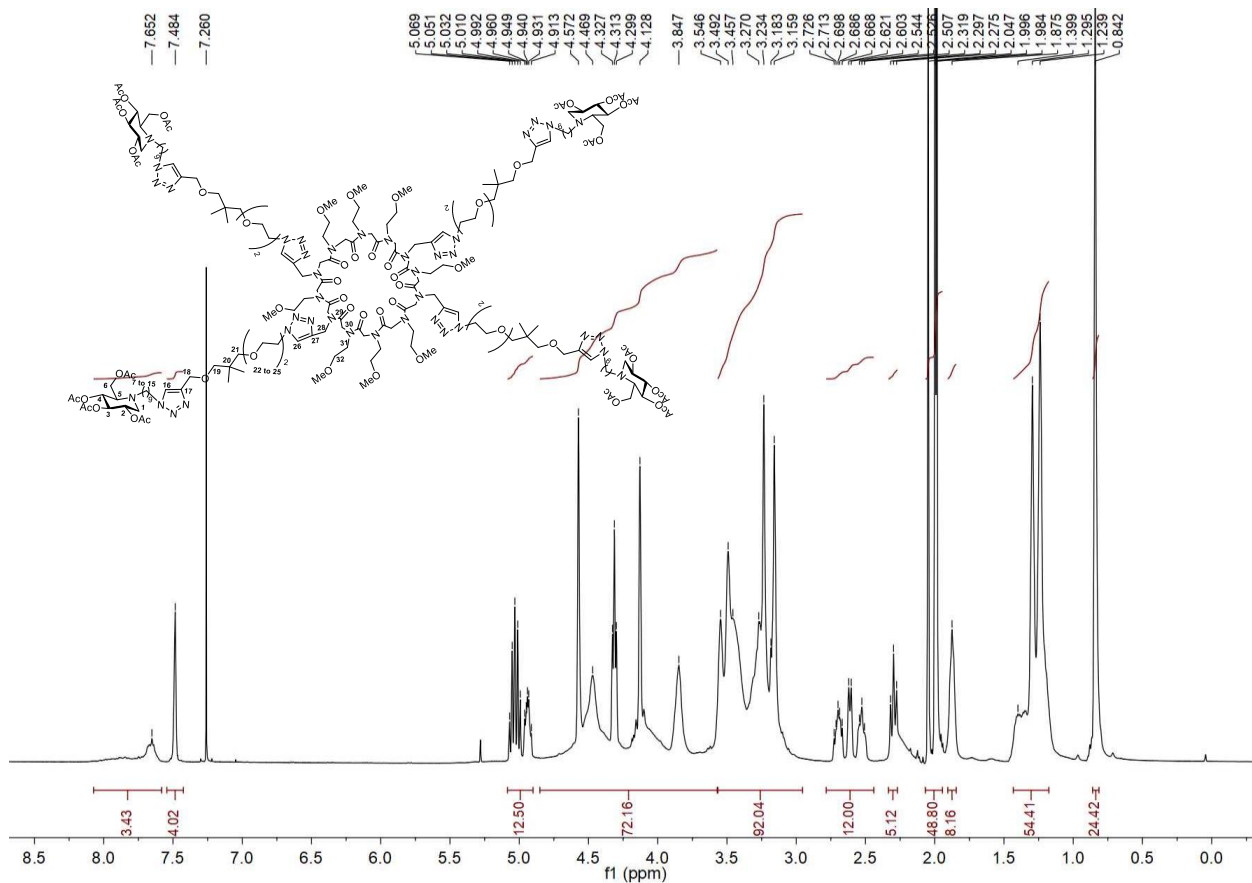
¹H NMR spectrum (CDCl₃, 400 MHz) and ¹³C NMR spectrum (CDCl₃, 100 MHz) for compound **31a**



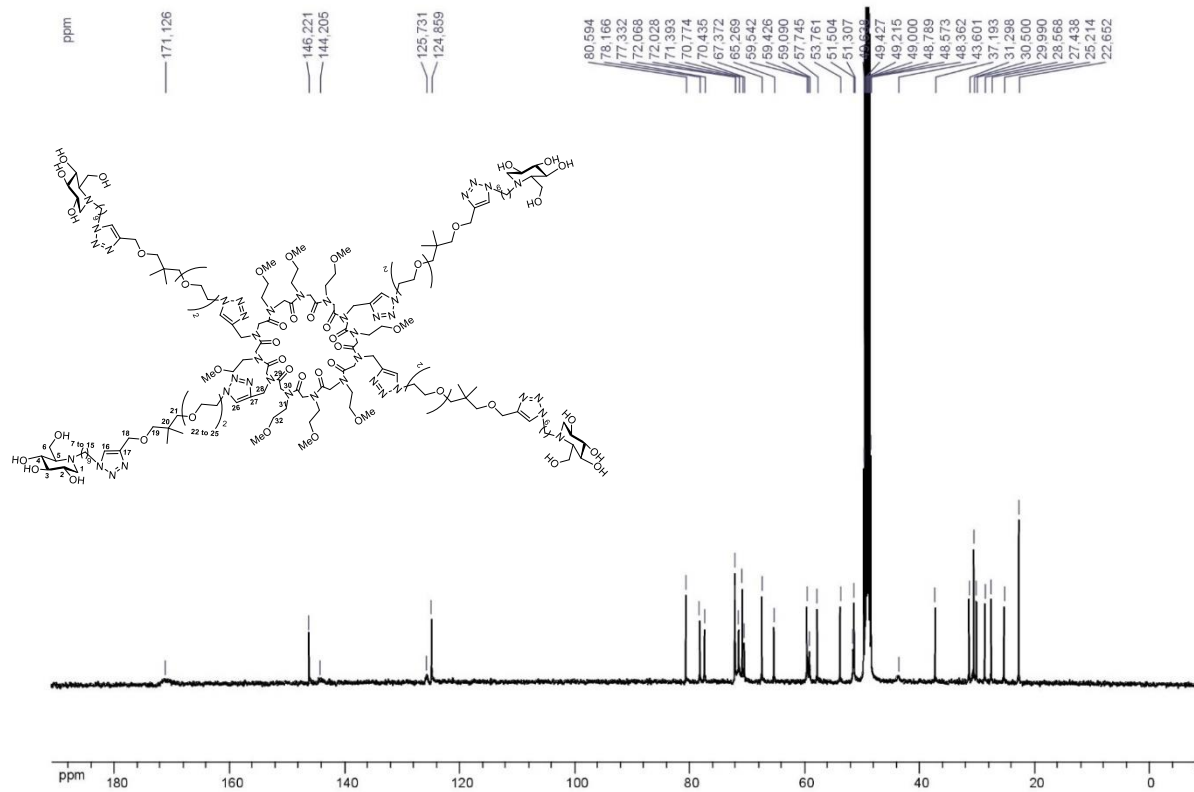
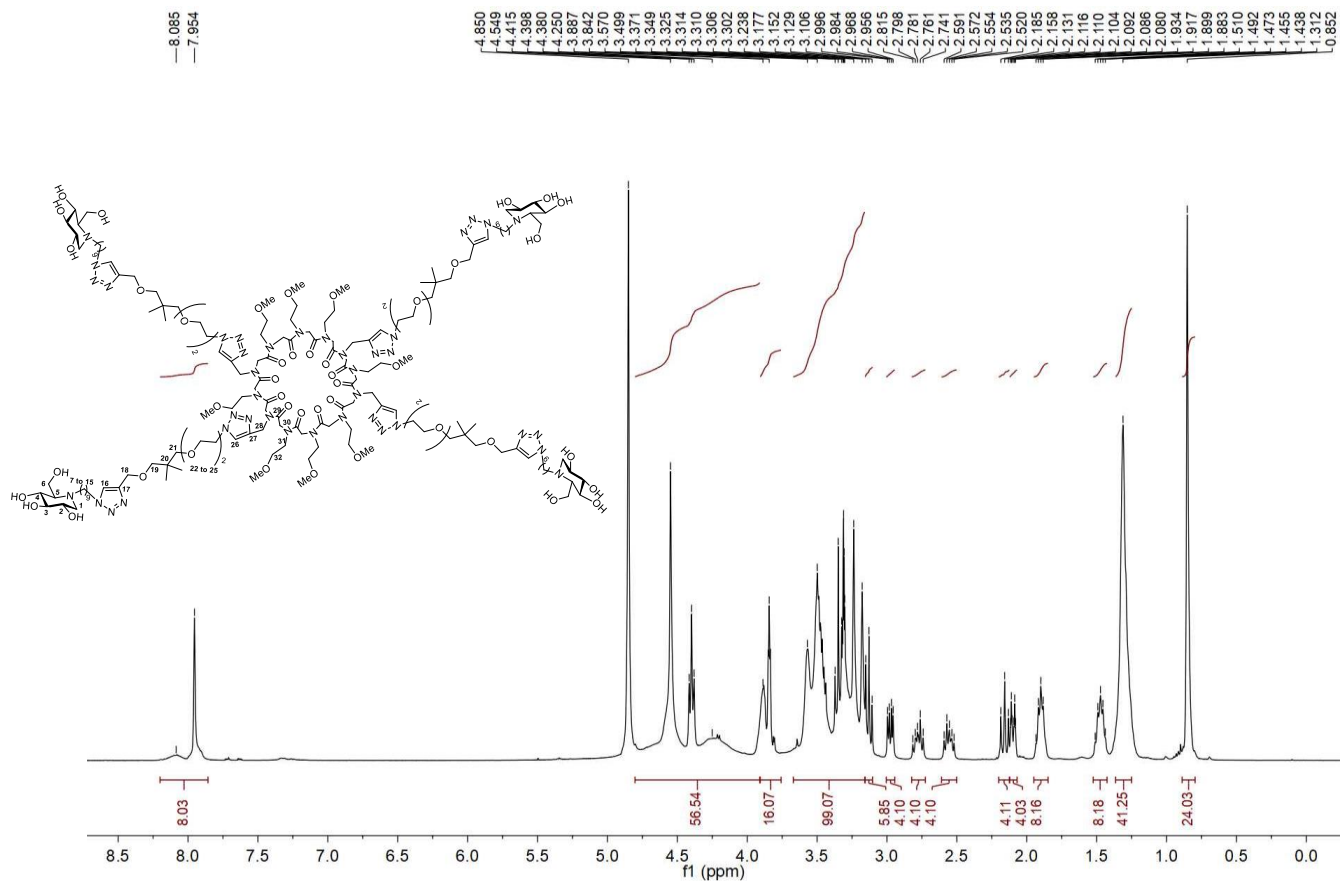
^1H NMR spectrum (MeOD, 500 MHz) and ^{13}C NMR spectrum (MeOD, 125 MHz) for compound **6a**



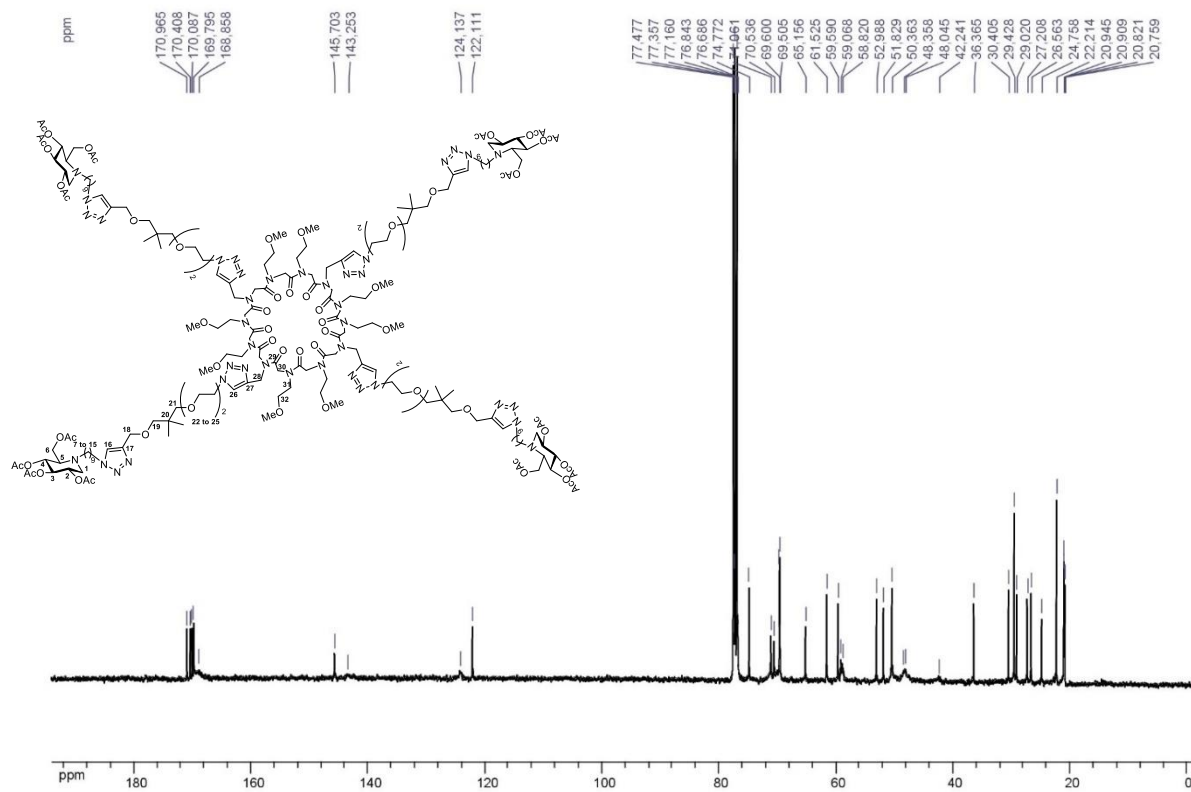
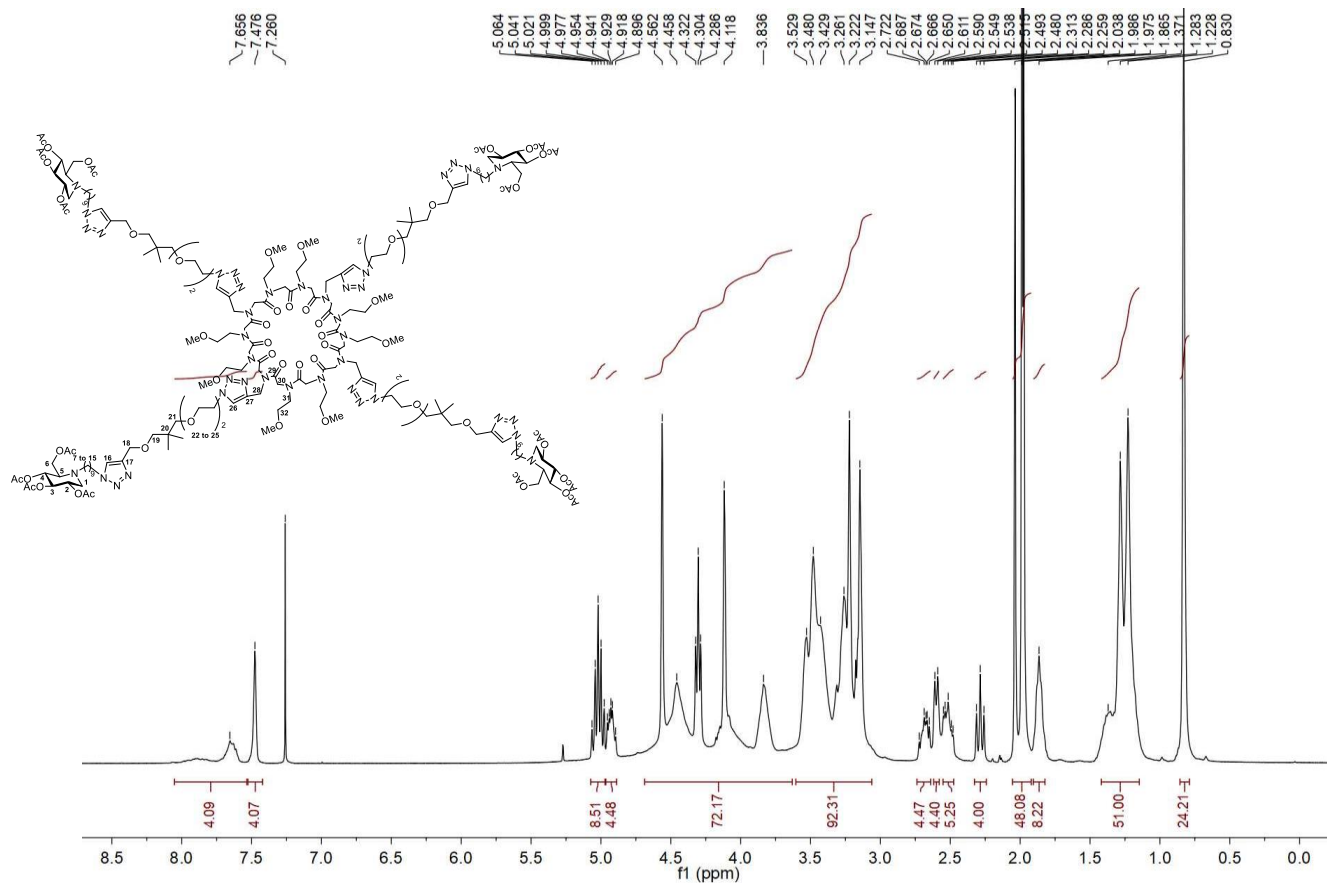
¹H NMR spectrum (CDCl₃, 500 MHz) and ¹³C NMR spectrum (CDCl₃, 100 MHz) for compound **31b**



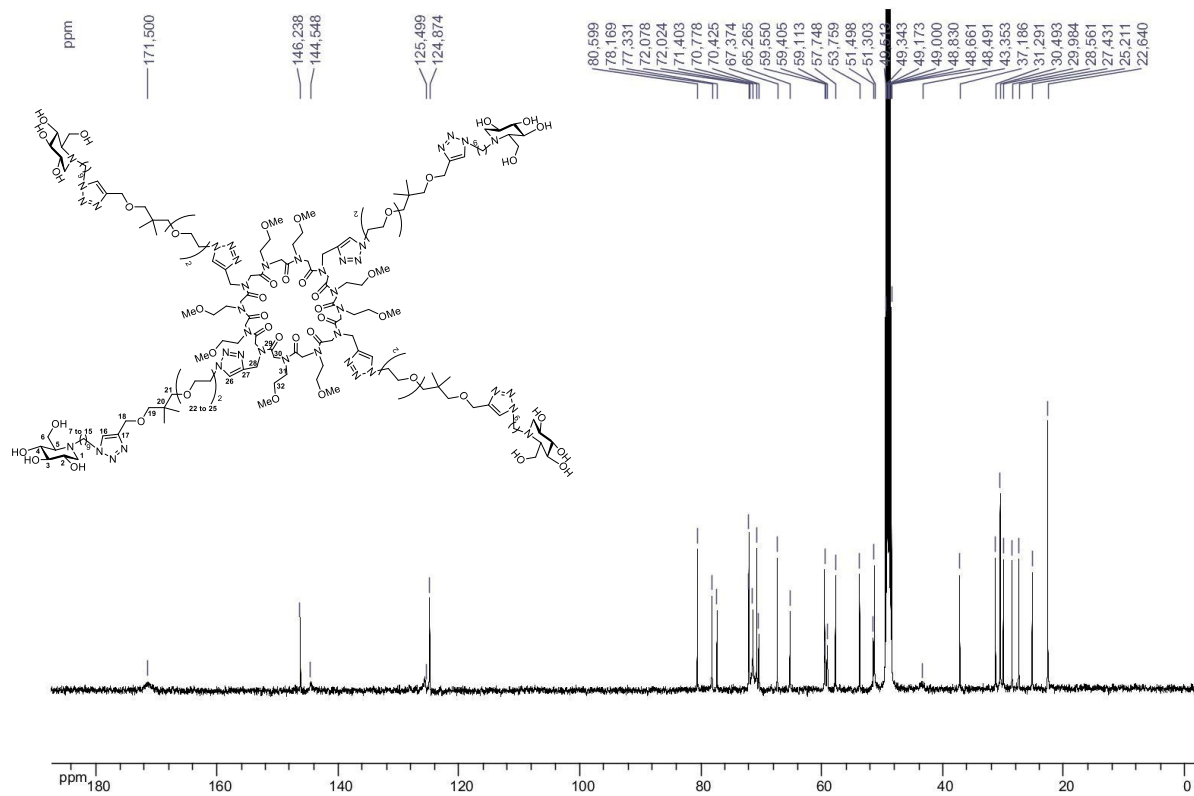
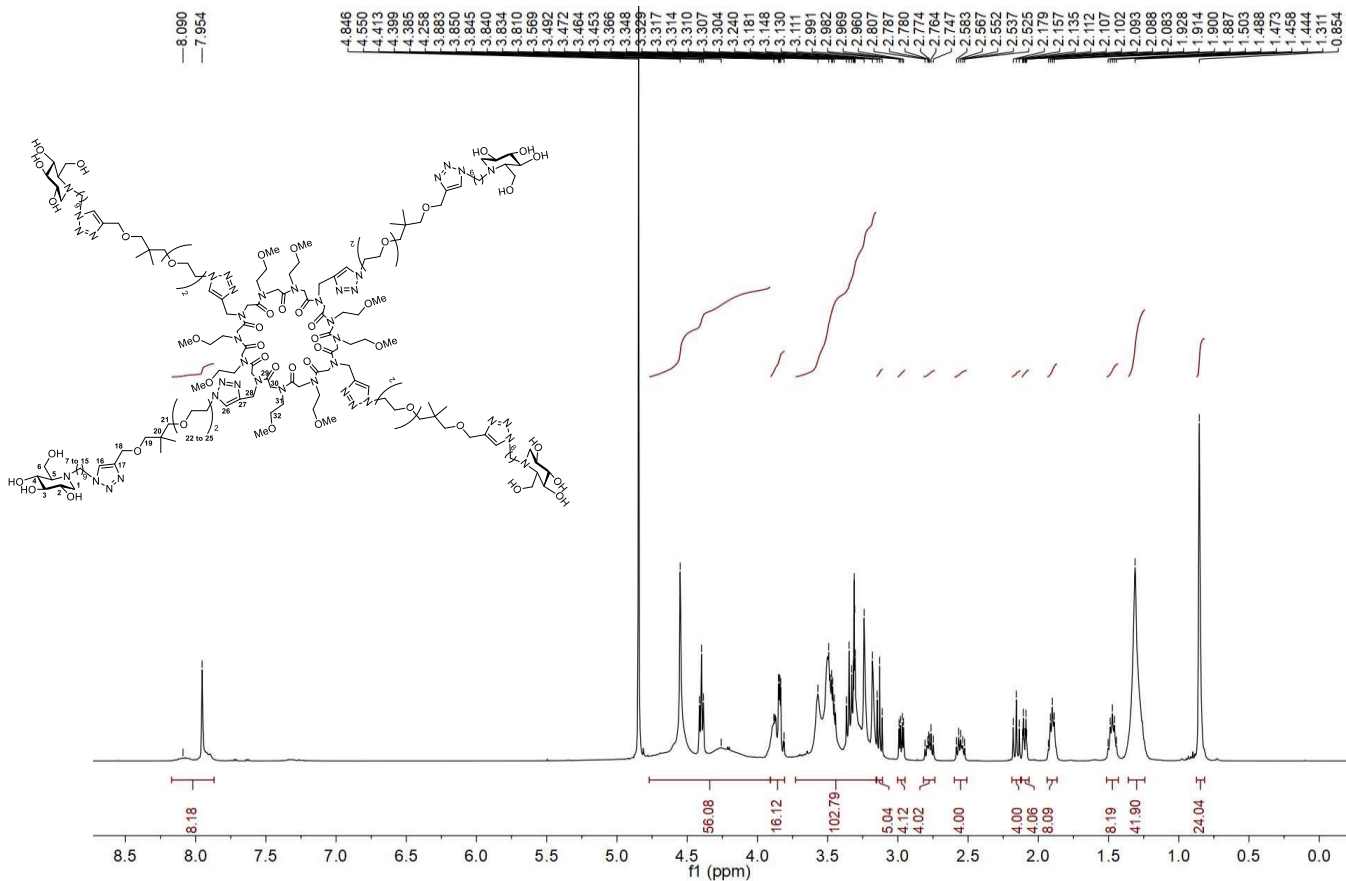
¹H NMR spectrum (MeOD, 400 MHz) and ¹³C NMR spectrum (MeOD, 100 MHz) for compound **6b**



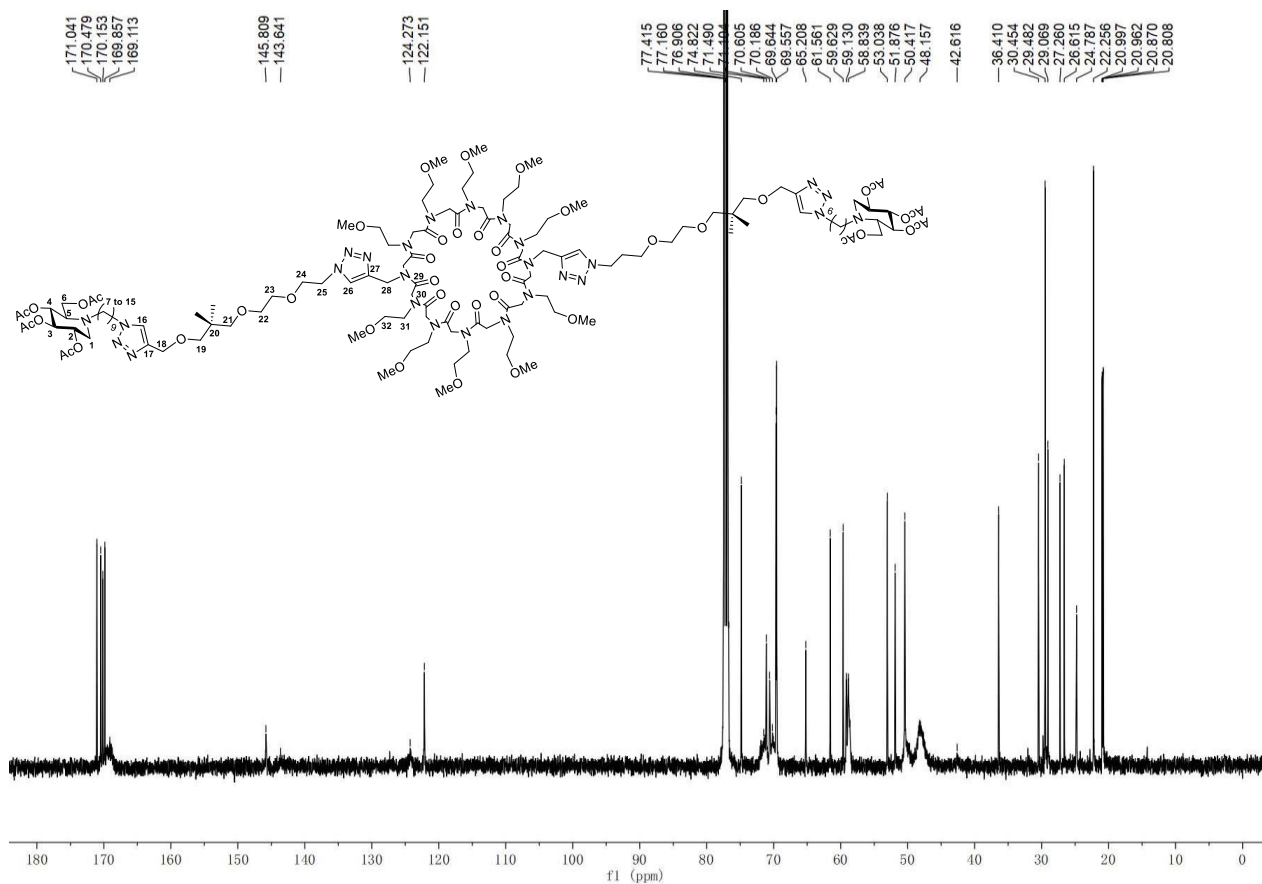
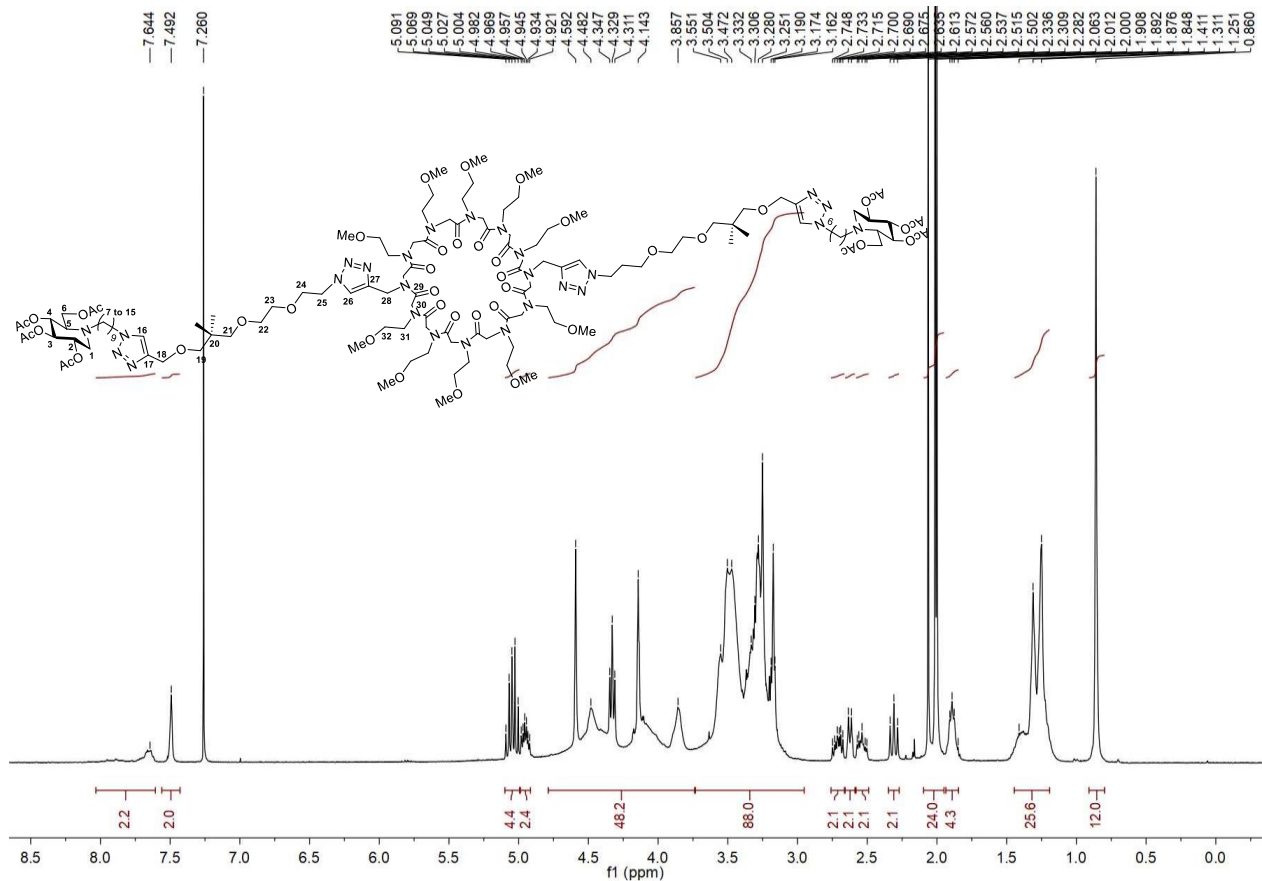
¹H NMR spectrum (CDCl₃, 400 MHz) and ¹³C NMR spectrum (CDCl₃, 100 MHz) for compound **31c**



¹H NMR spectrum (MeOD, 500 MHz) and ¹³C NMR spectrum (MeOD, 125 MHz) for compound **6c**



¹H NMR spectrum (CDCl₃, 400 MHz) and ¹³C NMR spectrum (CDCl₃, 125 MHz) for compound **32**



^1H NMR spectrum (MeOD, 500 MHz) and ^{13}C NMR spectrum (MeOD, 125 MHz) for compound **7**

