Supplementary Material

New synthesis of heteroglycoclusters from p-^{t}Bu-calix[4]arene tetraalkoxyheterohalides as key intermediates

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1. MS-ESI follow-up of the one-pot sequential bromination with free Br^- and azidation of crud product

1.1. Experiment 1: MS-ESI follow-up from rt to 50 °C reaction temperature.

In 250 mL one necked flask flushed with argon was allowed to react 2g (3.08 mmol) of p-tBucalix[4]arene (**1**) and 1.48 g (37 mmol) of NaH(60%) in DMF (50 mL) as solvent for 1h at rt under stiring. 1-Bromo-5-chloropentane (**2**) (11.43g, 61.64 mmol) was added and the reaction progress are followed up by MS-ESI in times of 1h and 2h at rt (Figure 1 and 2). Only tetrachloroalkoxy calixarene **3** (MNa+ = 1089.9) was detected with a little formation of monobromotrichloralkoxycalixarene **4** (Mna+ = 1133.7). The temperature had subsequently reached 50 °C and a second follow-up at 10 min, 4h, 7h and 24h (Figures 3, 4, 5, 6) was realized.

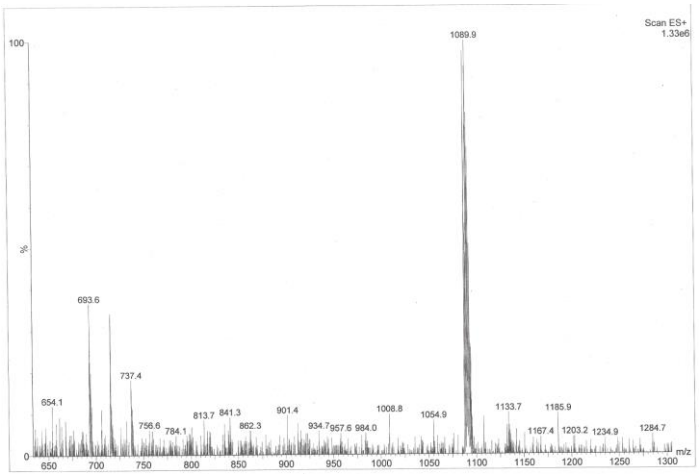

Figure 1. ES^+ (ESI-MS): 1h reaction time at rt

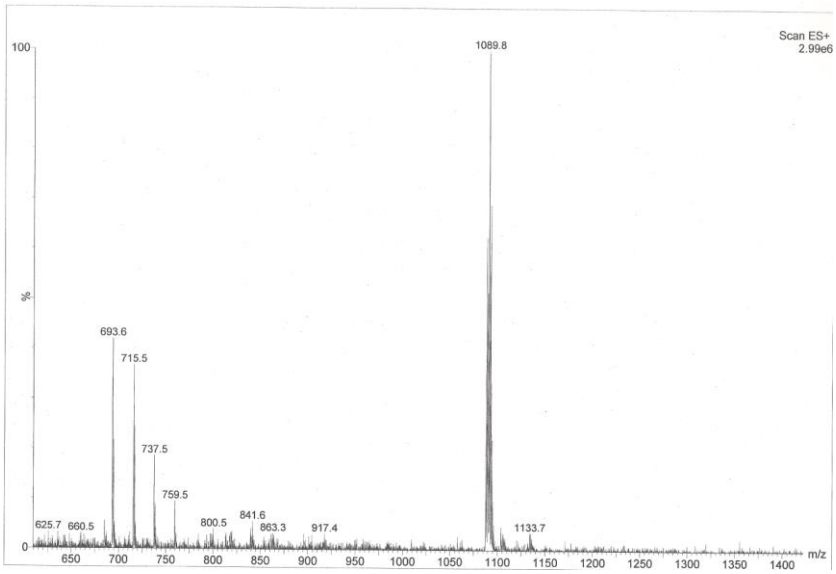

Figure 2. ES^+ (ESI-MS): 2h reaction time at rt

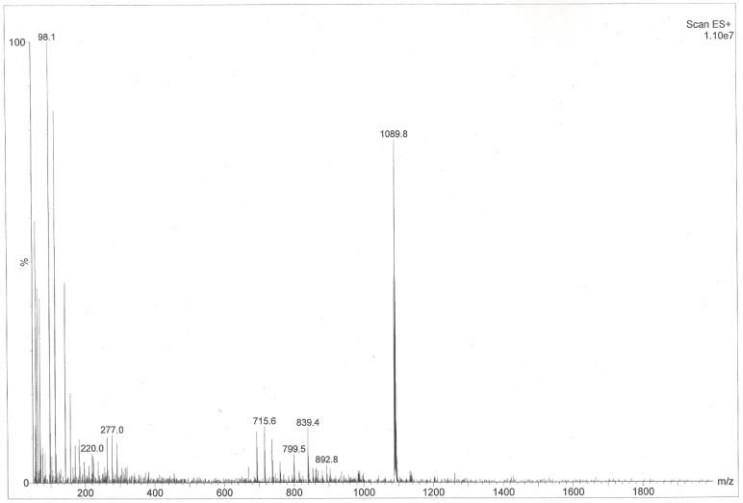

Figure 3. ES^+ (ESI-MS):10 min reaction time at 50°C

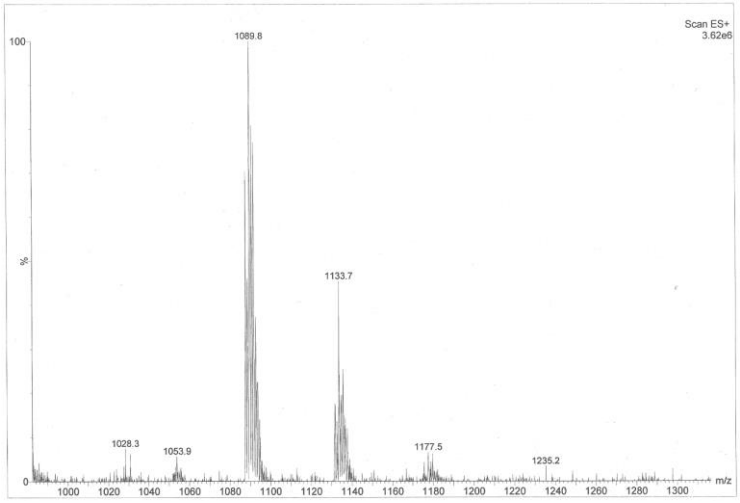

Figure 4. ES^+ (ESI-MS): 4h reaction time at 50°C

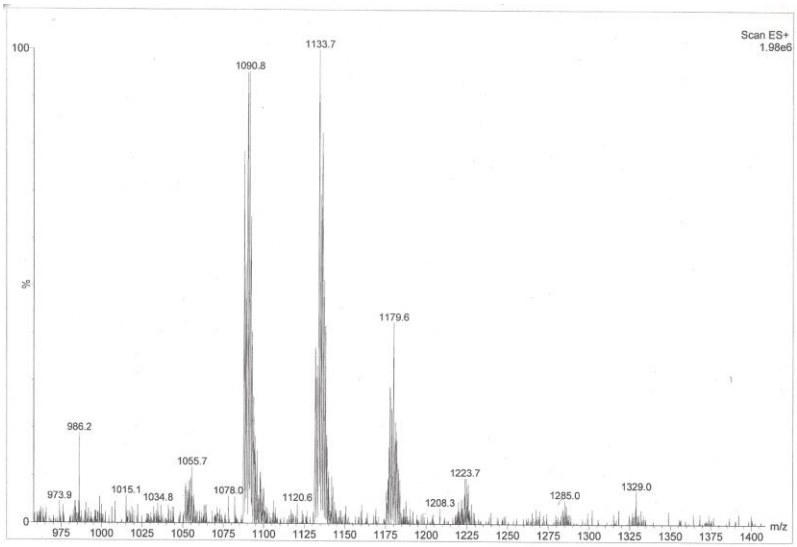

Figure 5. ES^+ (ESI-MS): 7h reaction time at 50°C

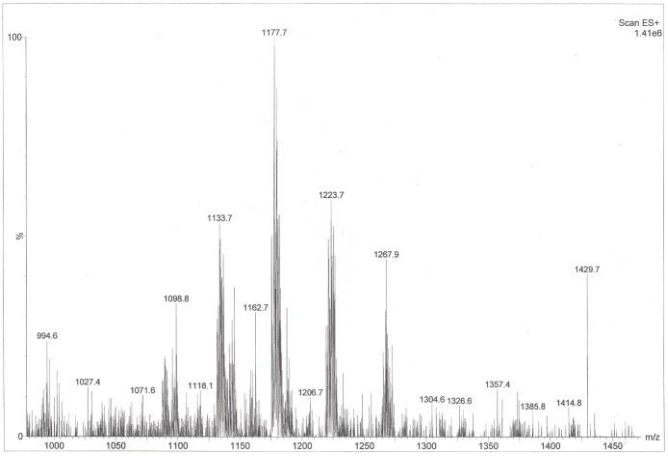

Figure 6. ES^+ (ESI-MS): 24h reaction time at 50°C

1.2 Experiment 2: MS-ESI follow-up at 90 °C reaction temperature

The reaction was reproduced at 90 °C with same amounts than experiment 1. The follow-up by MS-ESI at 5 min, 20 min and 2h times gave the spectrum of figures 7, 8 and 9 respectively.

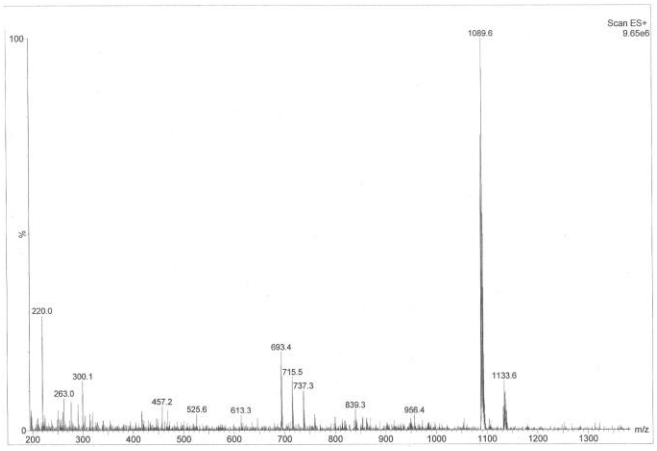

Figure 7. ES^+ (ESI-MS): 5 min reaction time at 90 °C

1.3. MS-ESI of the crud product from azidation of **3-7** mixture at rt.

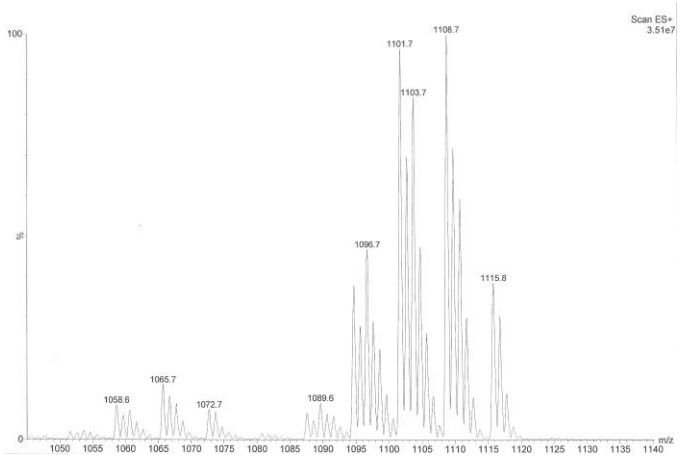

Figure 8. ES^+(ESI-MS) spectrum of the azido-chloro mixture **8-11** obtained from azidation of **3-7** crud product at rt.

2. NMR data.

2.1. Spectra of crud product mixture **3-7**

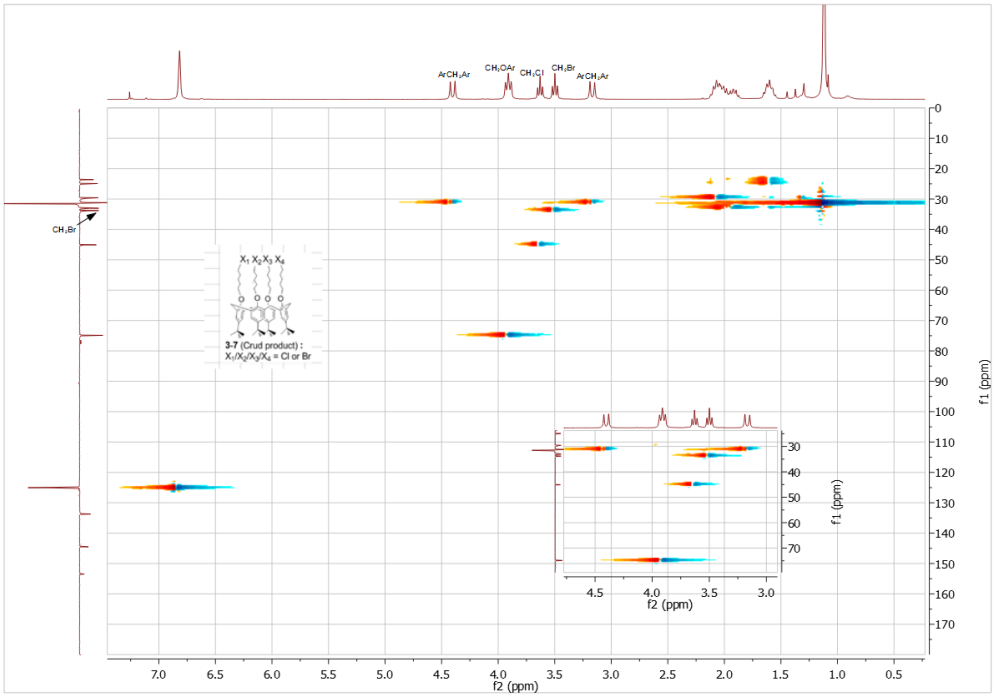

Figure 9. HSQC(600/150 MHz,$CDCl_3$) spectrum of crud mixture **3-7**.

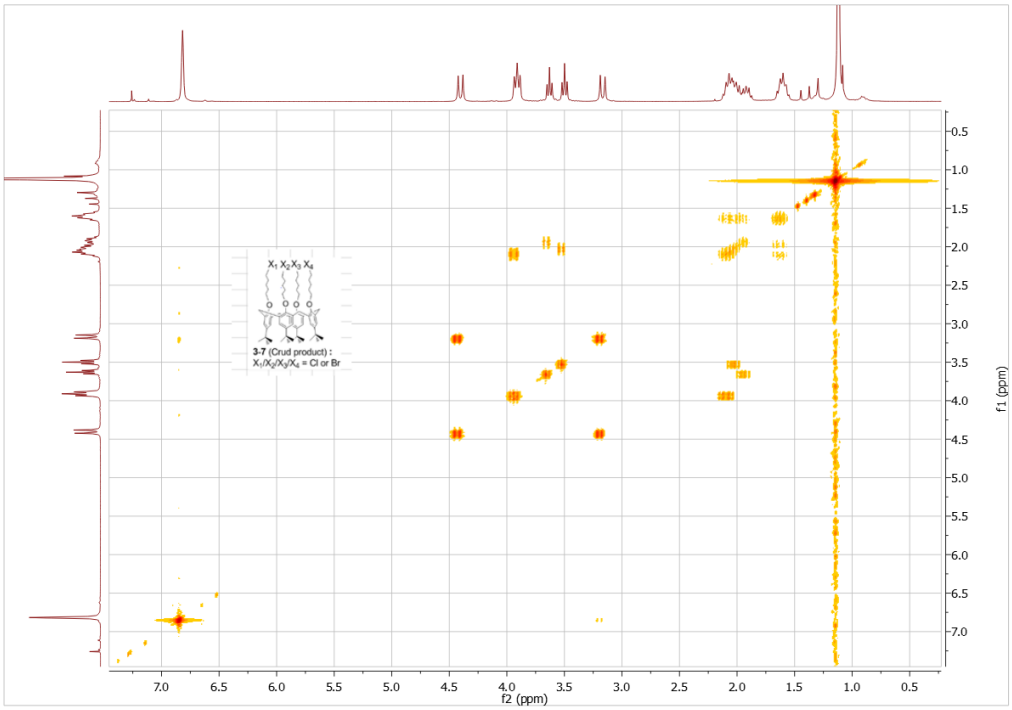

Figure 10. COSY H-H(600/600MHZ, $CDCl_3$) spectrum of crud mixture **3-7**.

2.2. Spectra of compounds **8**, **9**, **10**, **11**, **13**, **14**, **16**, **17**, **18**, **19**, **20** and **22**.

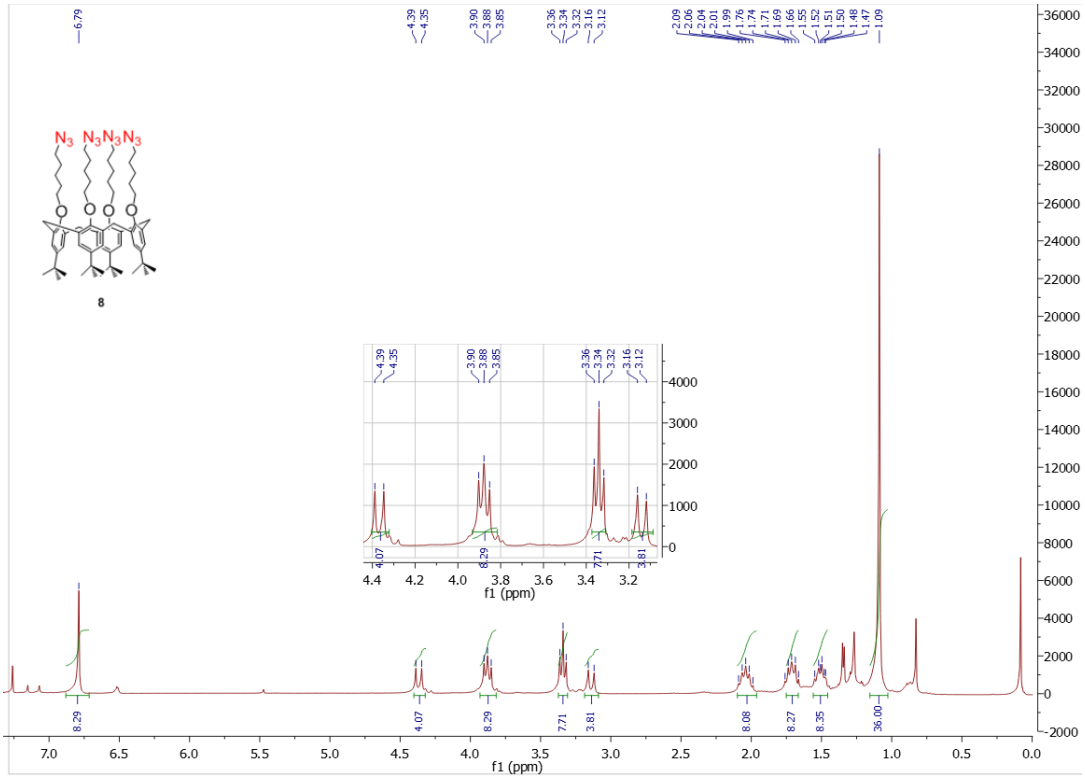

Figure 11. ^{1}H(300 MHz, $CDCl_3$) spectrum of compound **8.**

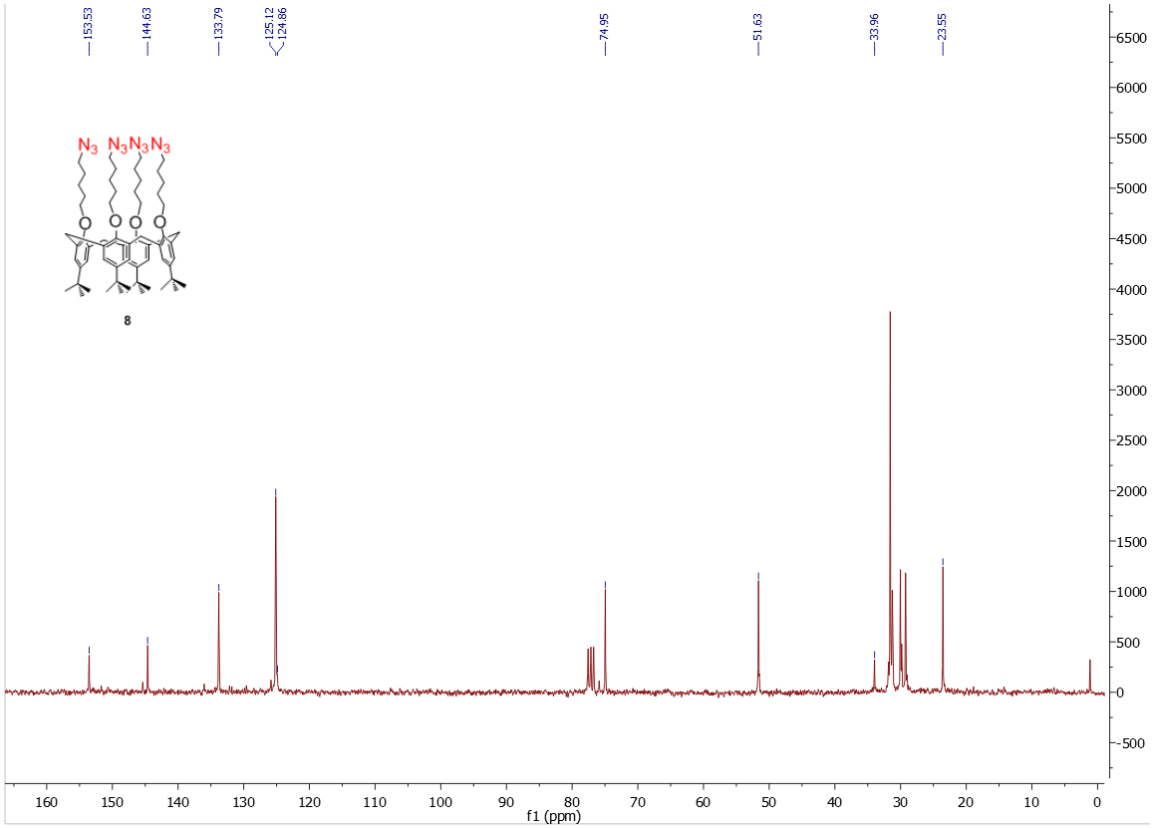

Figure 12. ^{13}C(75 MHz, $CDCl_3$) spectrum of compound **8.**

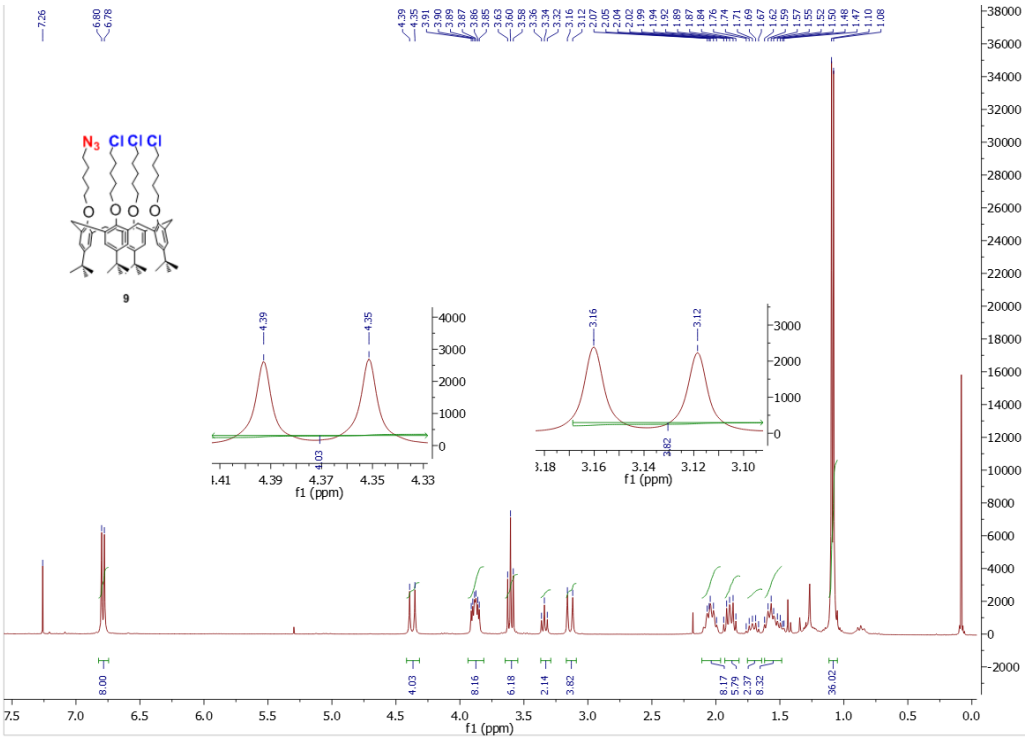

Figure 13. ^{1}H(300 MHz, $CDCl_3$) spectrum of compound **9.**

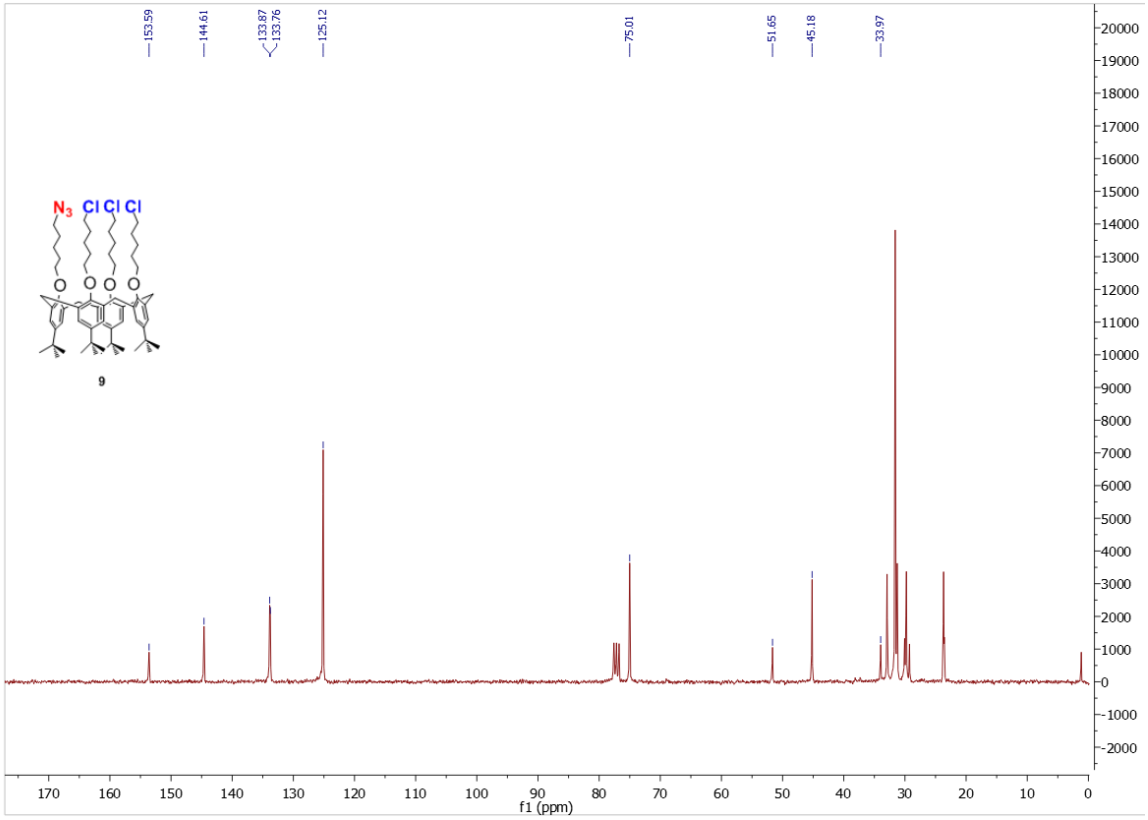

Figure 14. ^{13}C(75 MHz, $CDCl_3$) spectrum of compound **9**

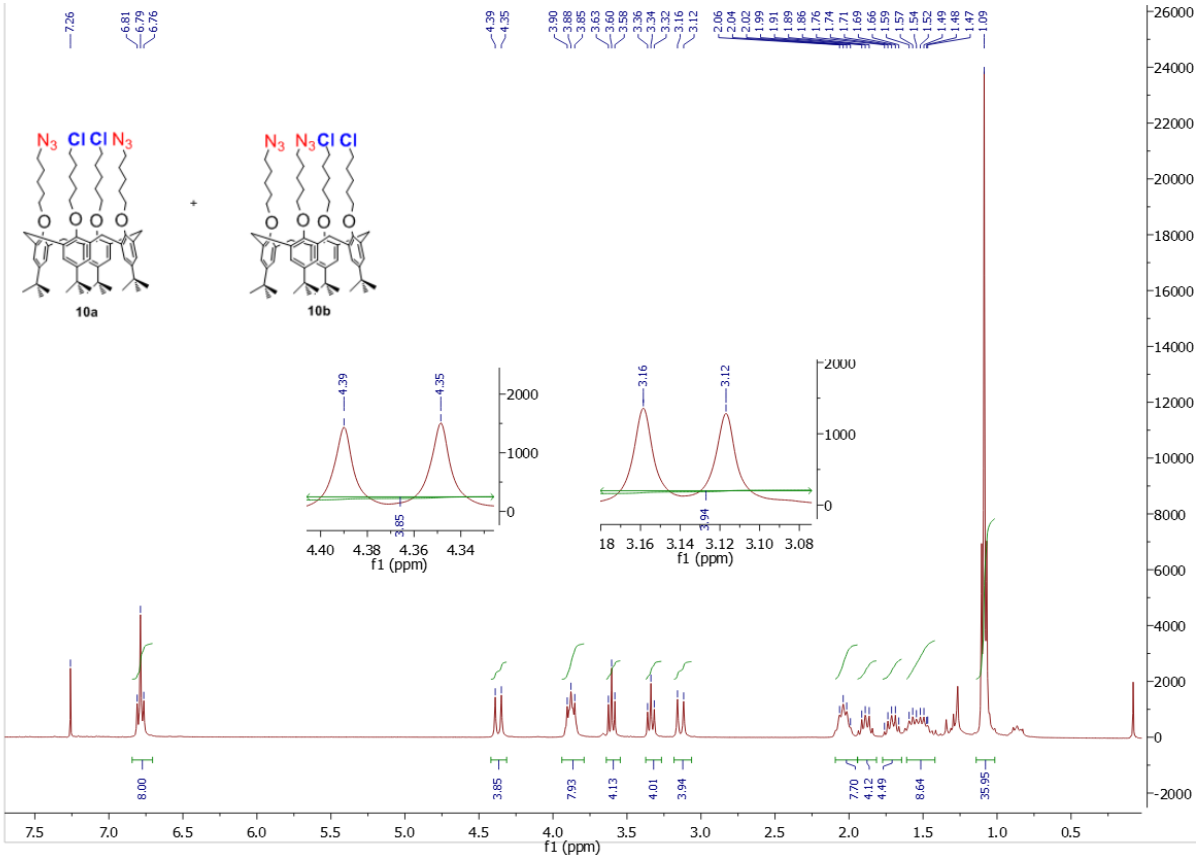

Figure 15. ^{1}H (300 MHz, $CDCl_3$) spectrum of compound **10a/10b.**

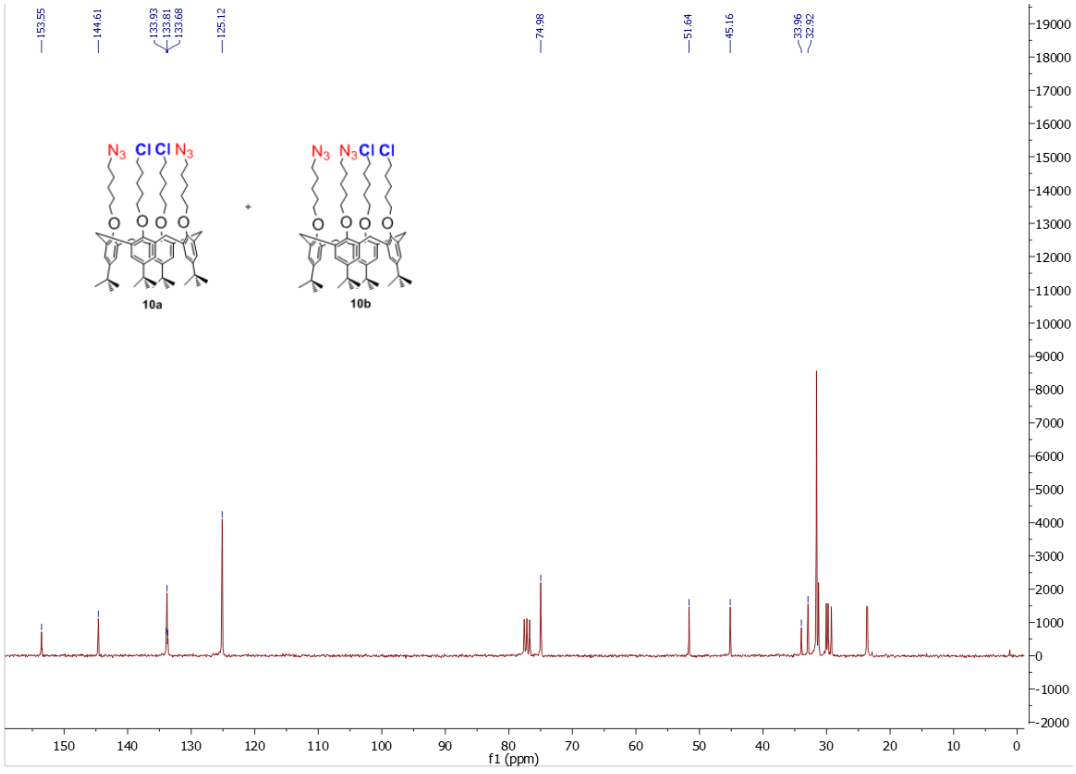

Figure 16. ^{13}C(75 MHz, $CDCl_3$) spectrum of compound **10a/10b.**

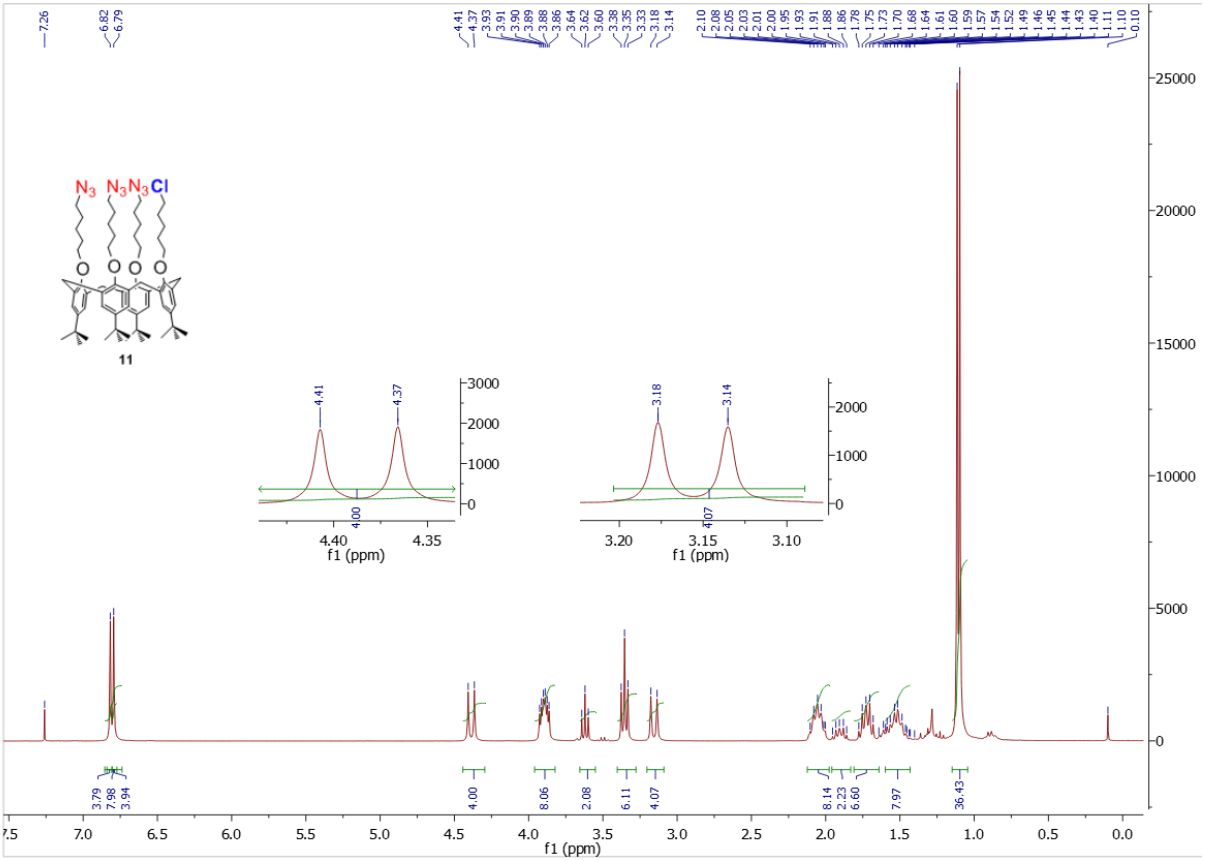

Figure 17. ^{1}H (300 MHz, $CDCl_3$) spectrum of compound **11.**

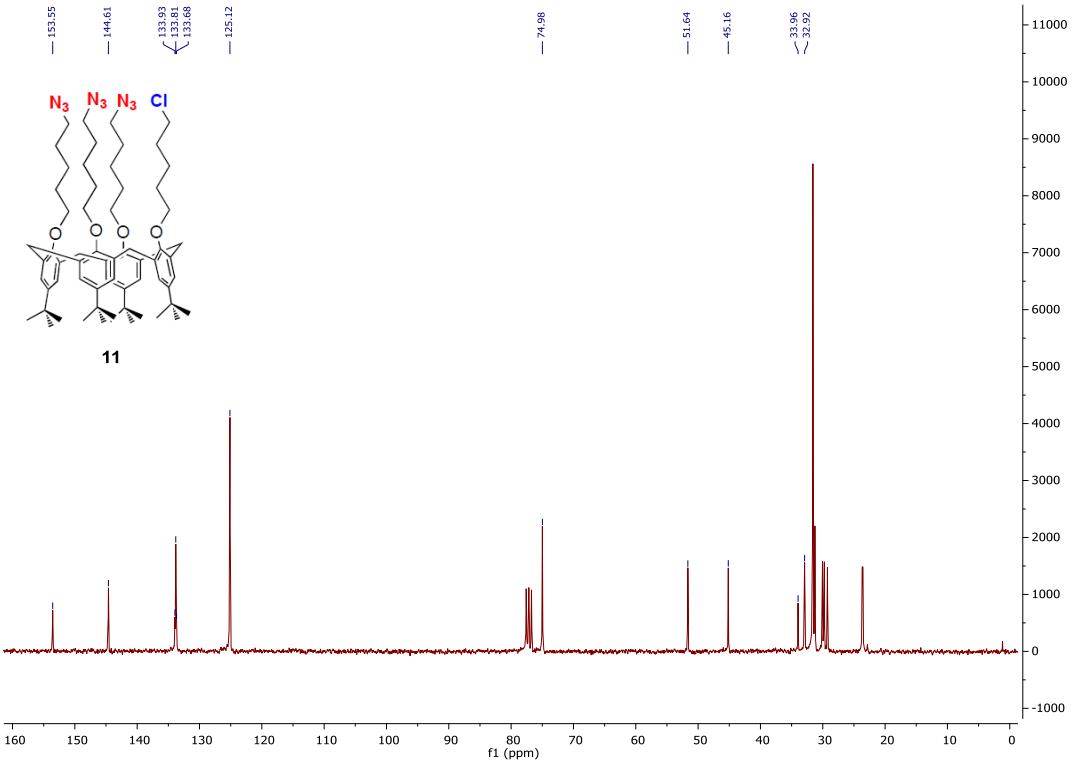

Figure 18. ^{13}C (75 MHz, $CDCl_3$) spectrum of compound **11**

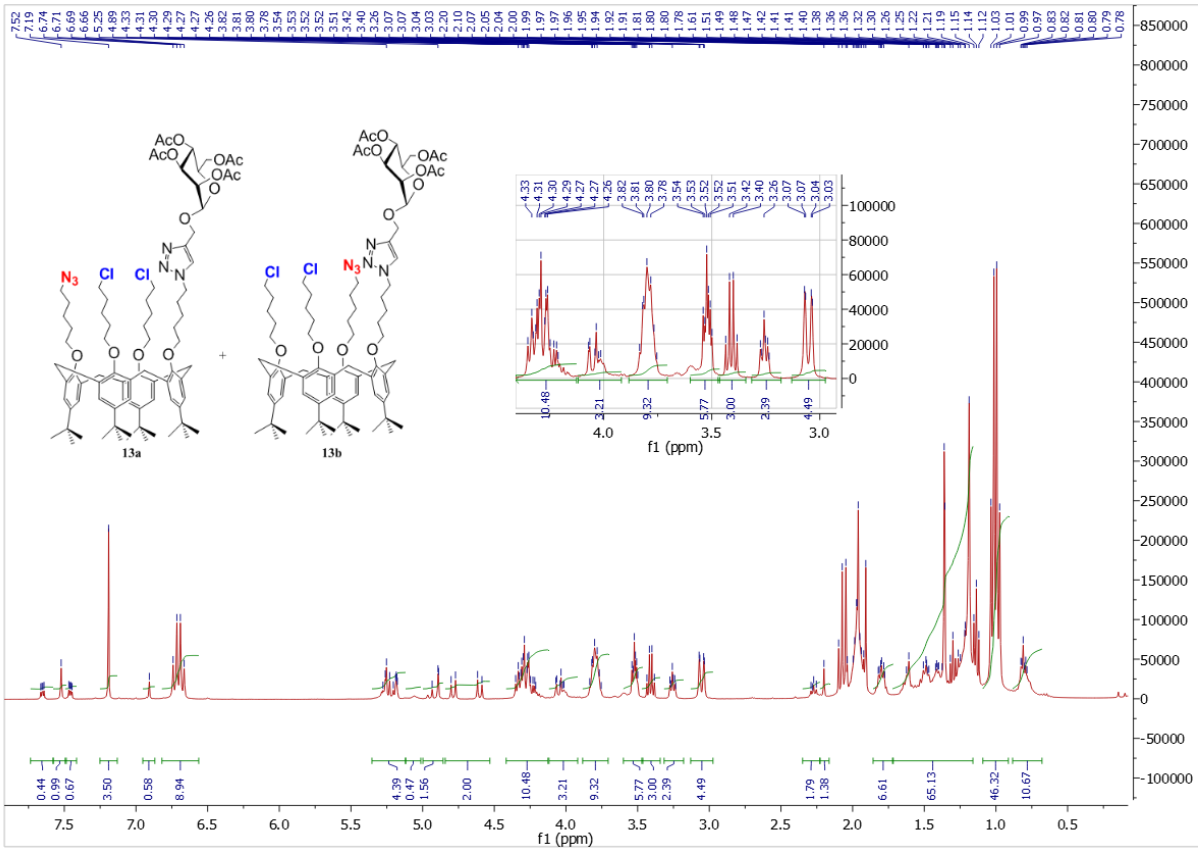

Figure 19. ^{1}H (400 MHz, $CDCl_3$) spectrum of compound **13a/13b.**

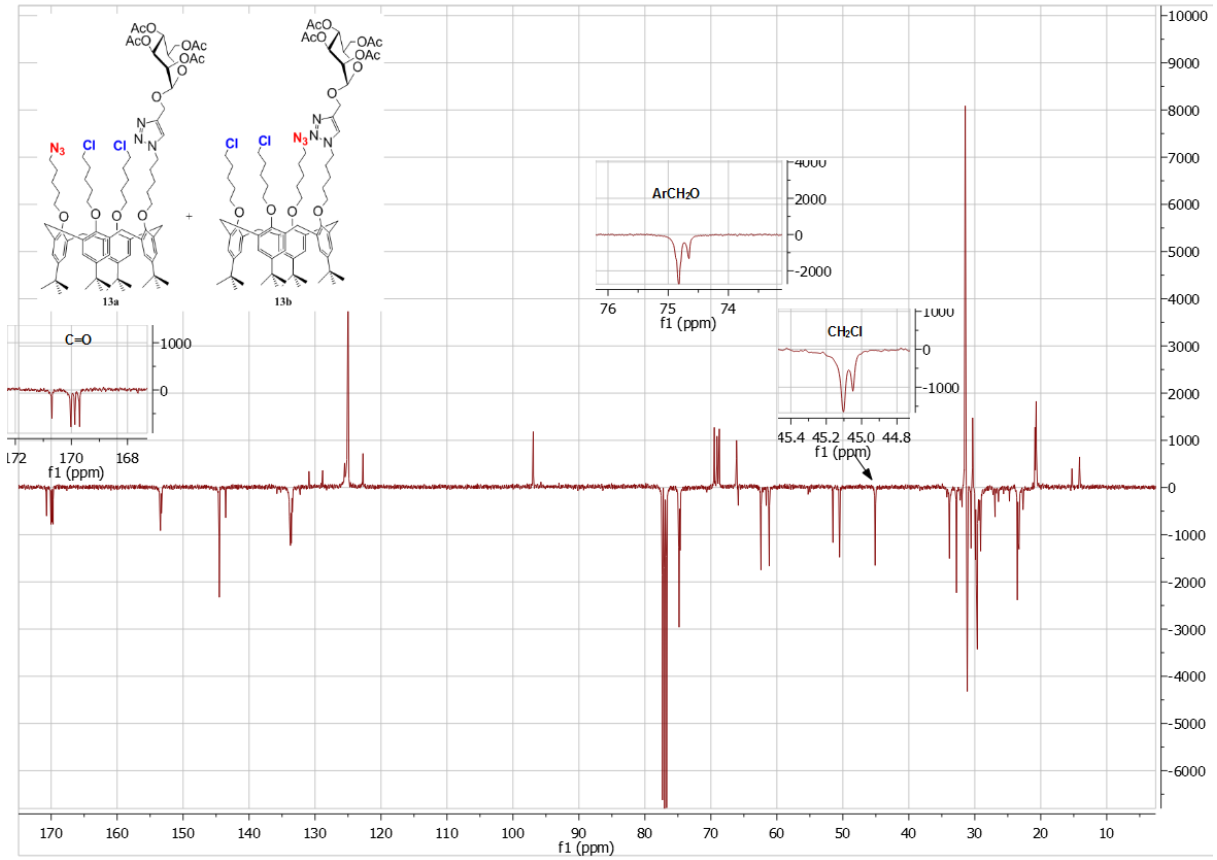

Figure 20. DeptQ(100MHz, $CDCl_3$) spectrum of compound **13a/13b.**

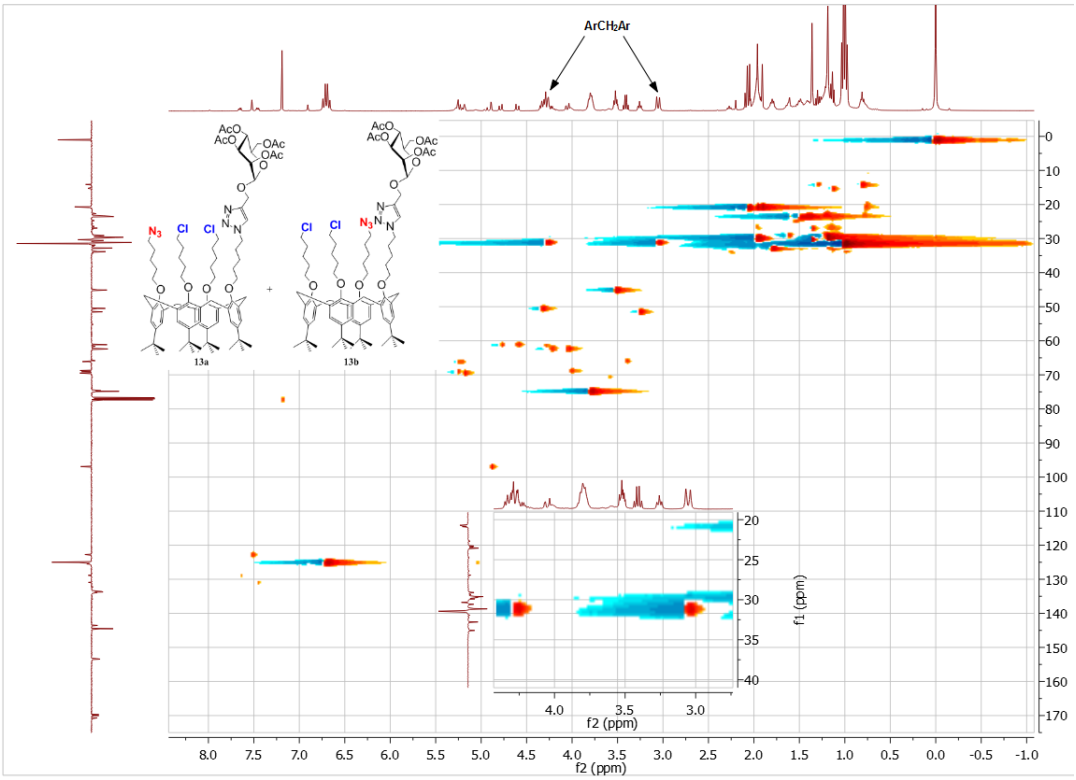

Figure 21. HSQC(400/100MHz, $CDCl_3$) spectrum of compound **13a/13b.**

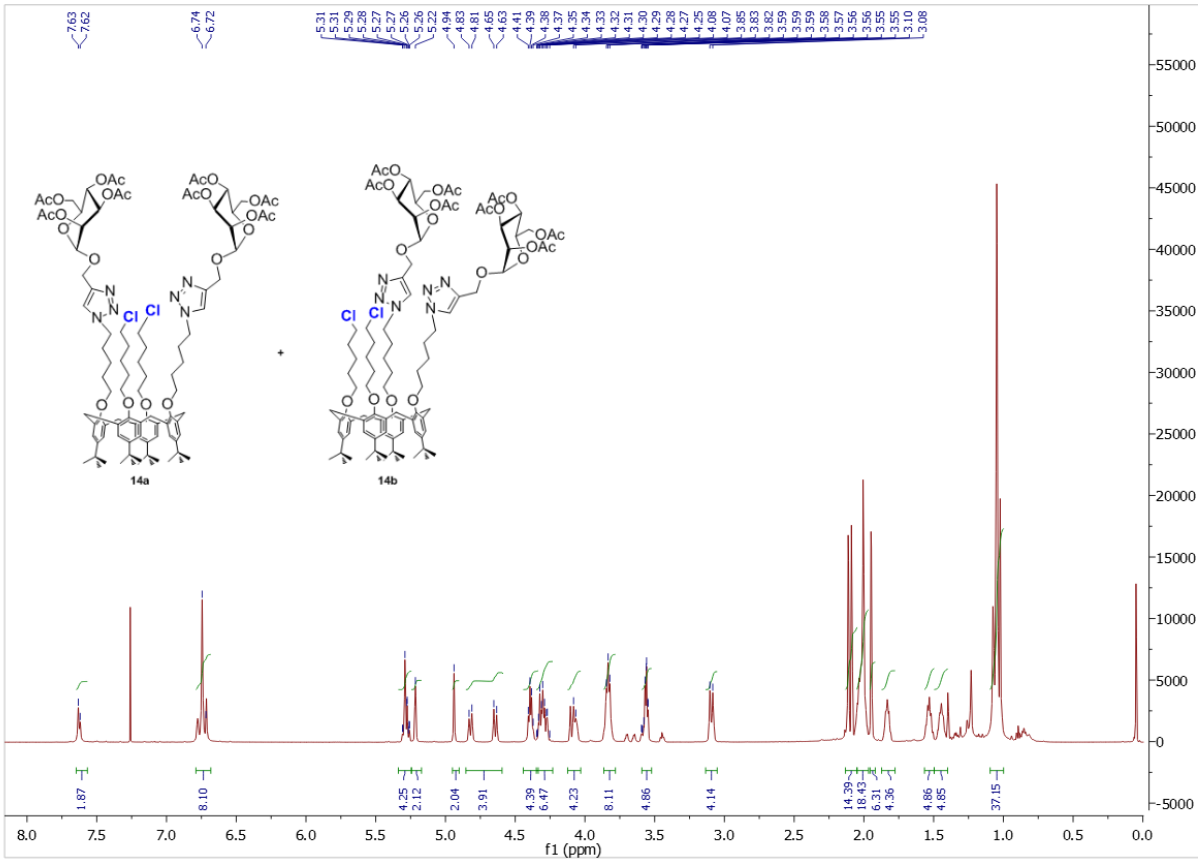

Figure 22. ^1H(600MHz, $CDCl_3$) spectrum of compound **14a/14b.**

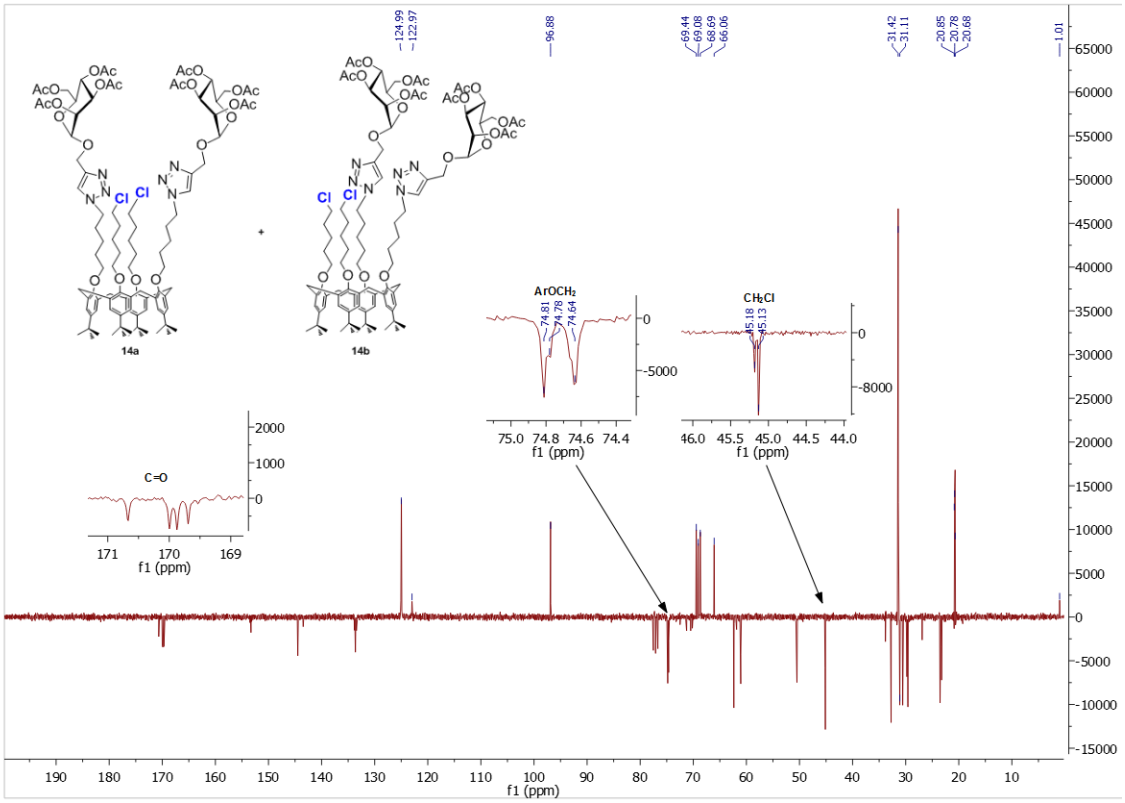

Figure 23. DeptQ(75 MHz, $CDCl_3$) spectrum of compound **14a/14b.**

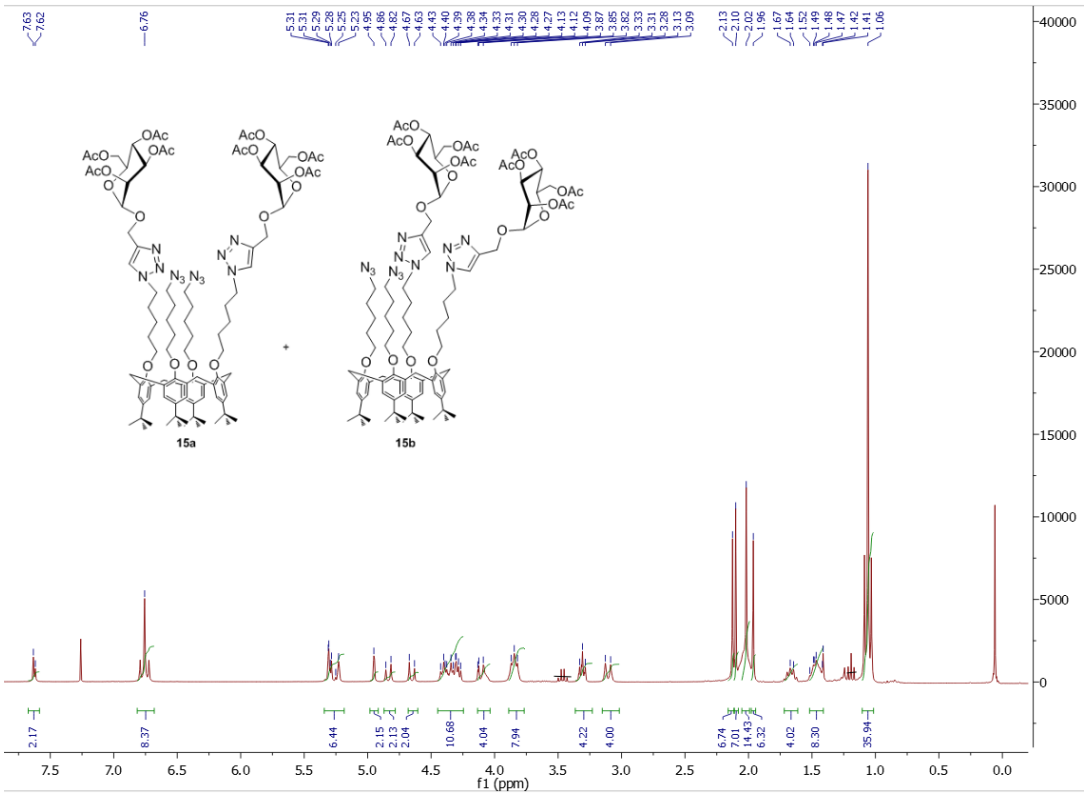

Figure 24. ^1H (300 MHz, $CDCl_3$) spectrum of compound **15a/15b.**

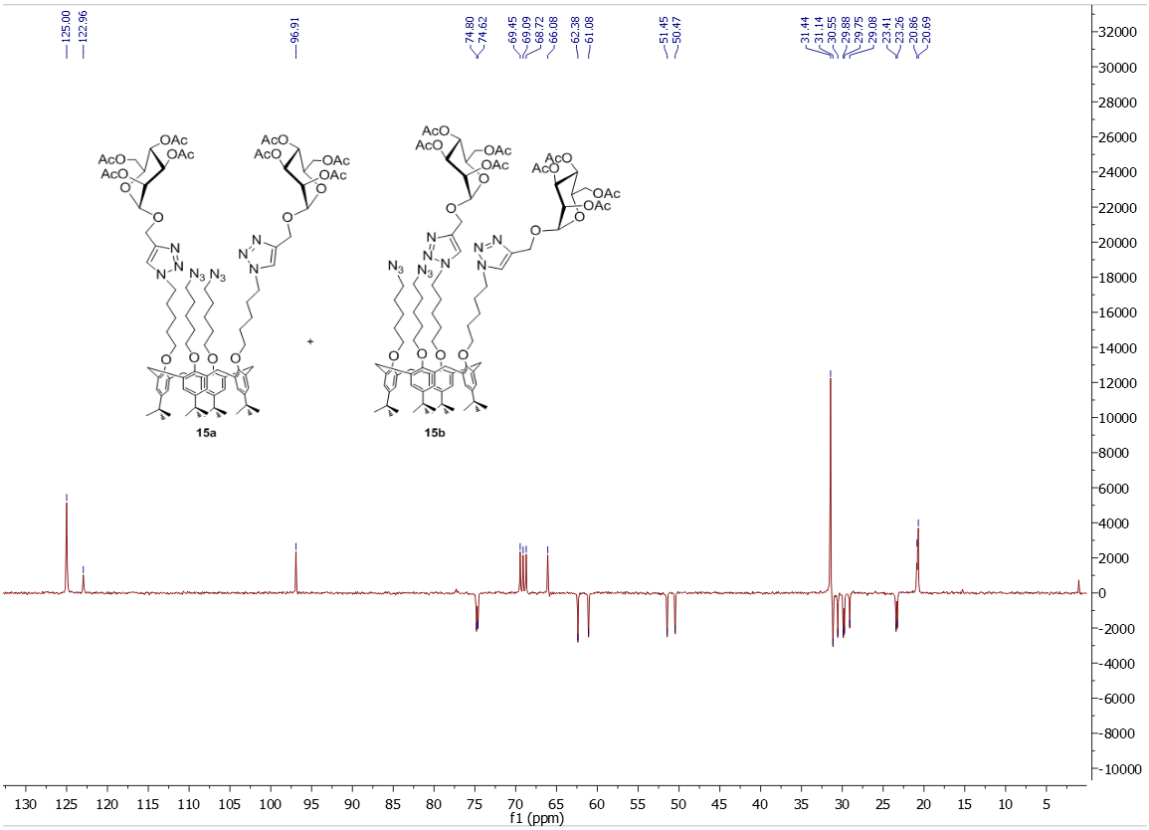

Figure 25. DEPT 135 (75 MHz, $CDCl_3$) spectrum of compound **15a/15b.**

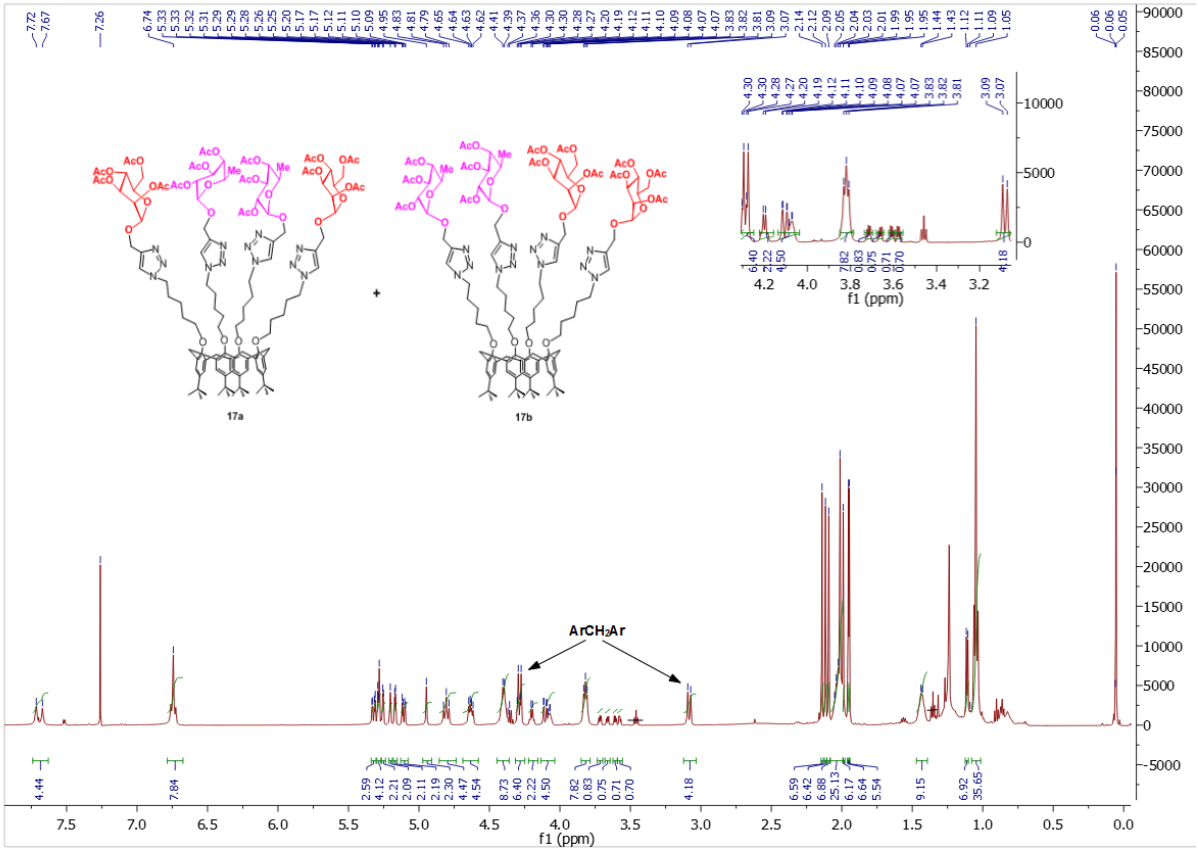

Figure 26. ^1H (600 MHz, $CDCl_3$) spectrum of compound **17a/17b.**

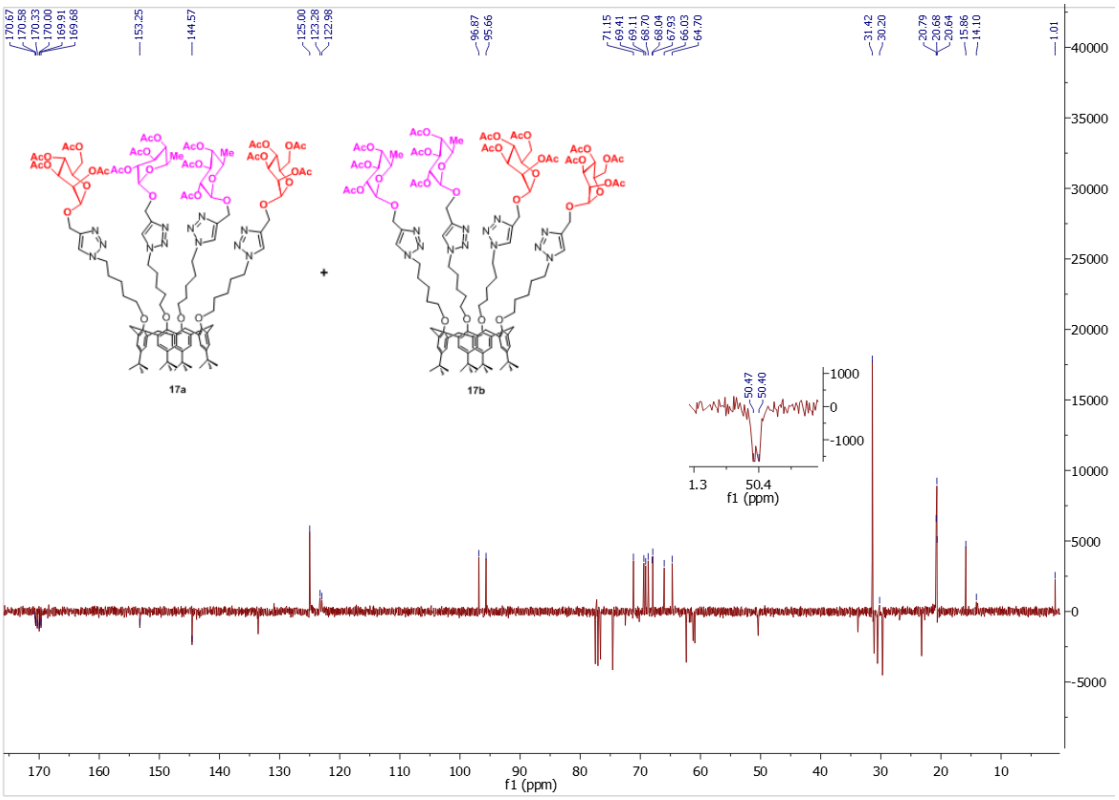

Figure 27. DEPTQ (75 MHz, $CDCl_3$) spectrum of compound **17a/17b.**

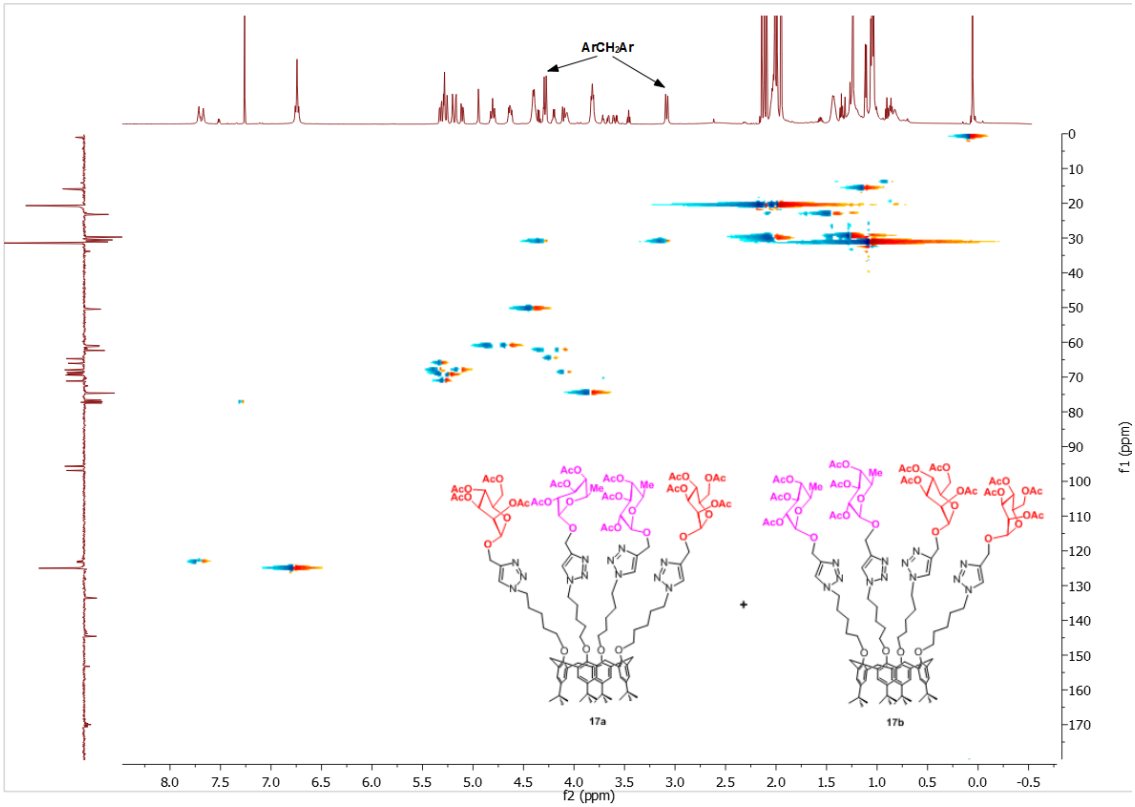

Figure 28. HSQC(600/150 MHz, $CDCl_3$) spectrum of compound **17a/17b.**

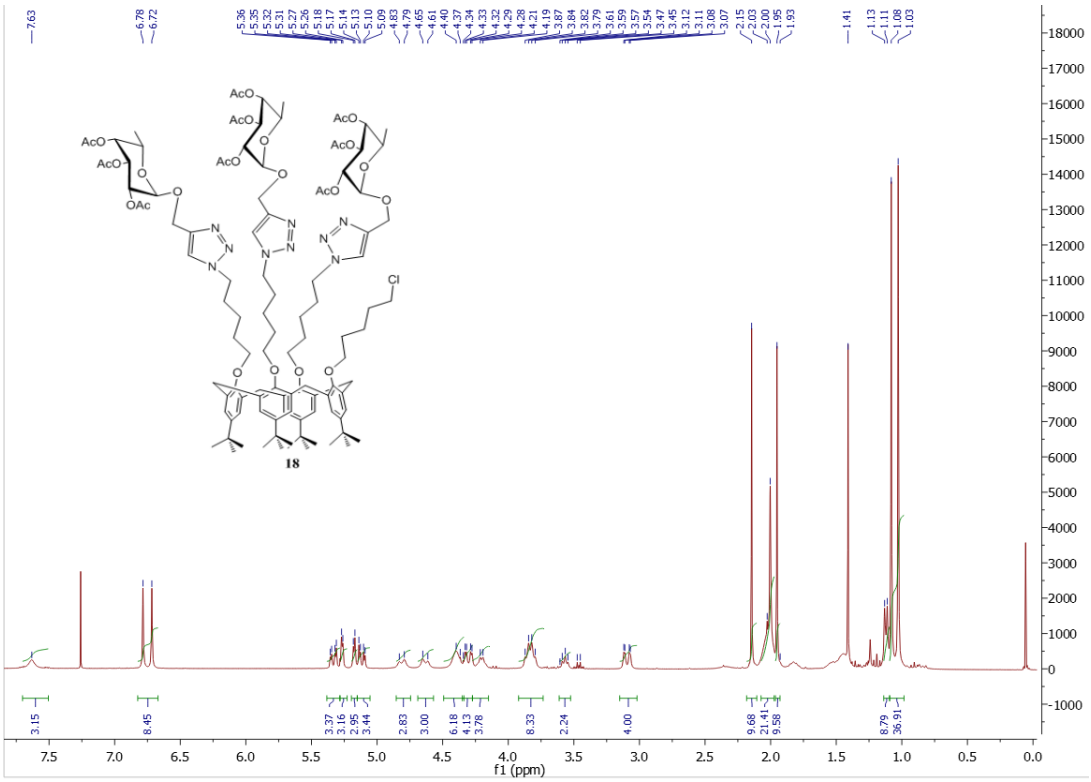

Figure 29. ^{1}H (300 MHz, $CDCl_3$) spectrum of compound **18.**

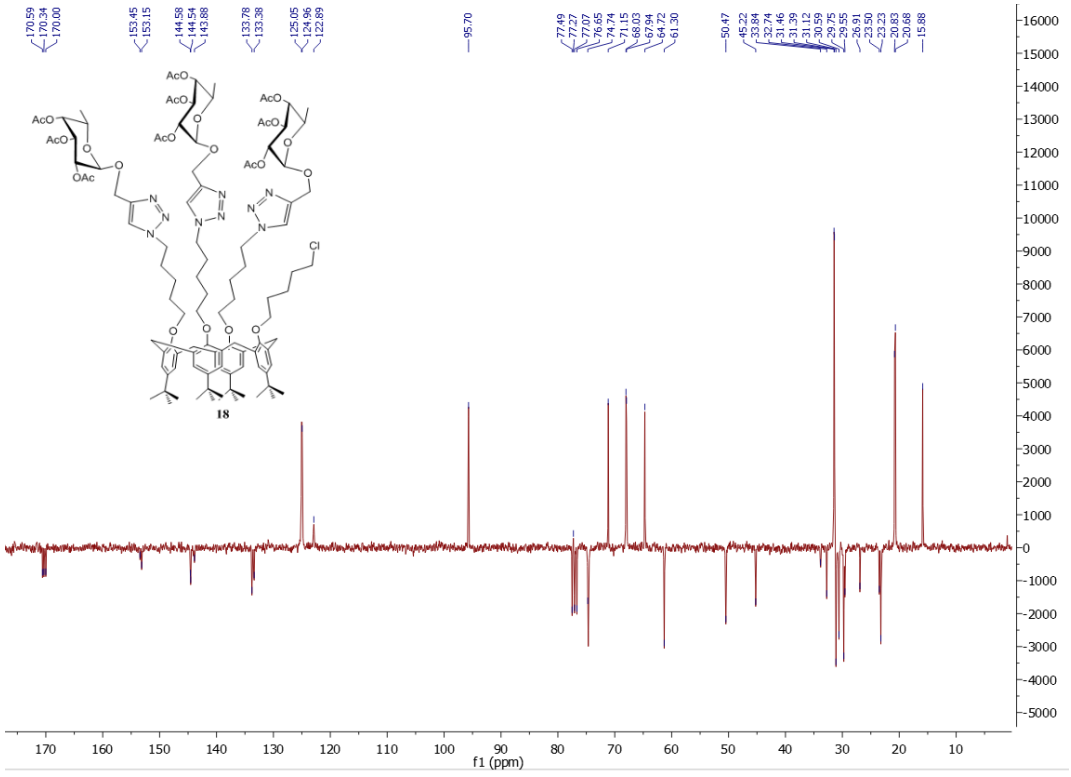

Figure 30. DeptQ (75 MHz, $CDCl_3$) spectrum of compound **18.**

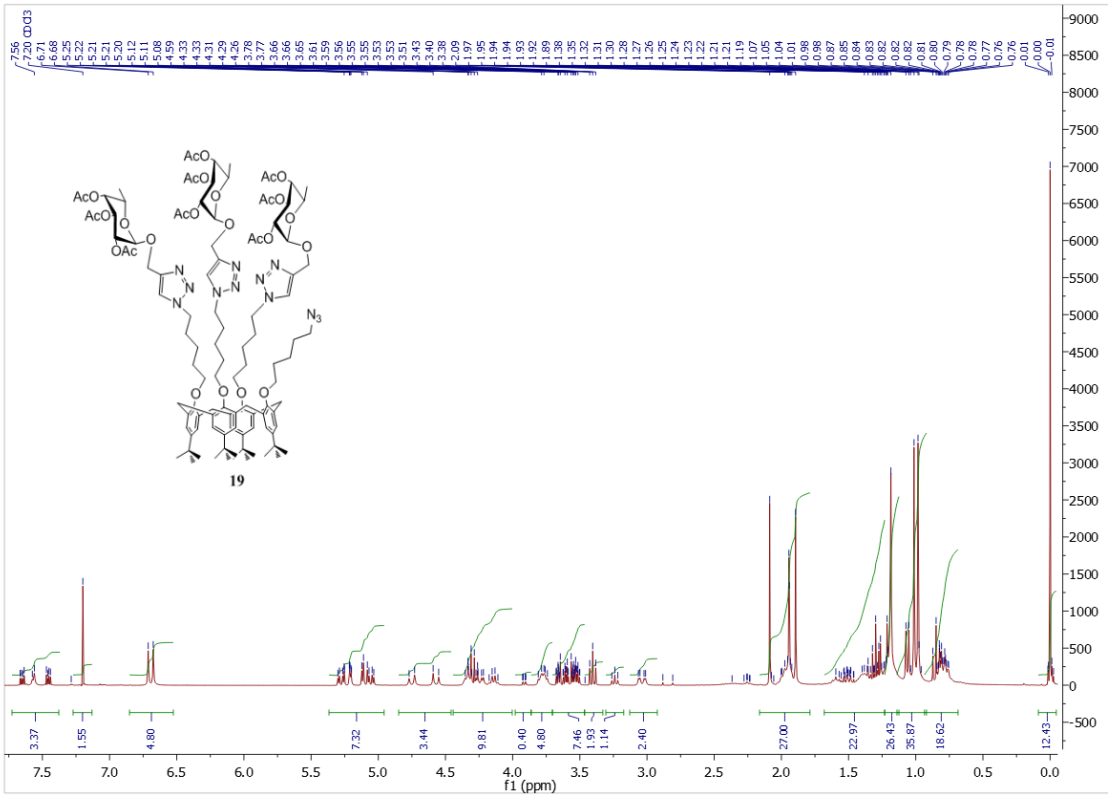

Figure 31. ^{1}H (300 MHz, $CDCl_3$) spectrum of compound **19.**

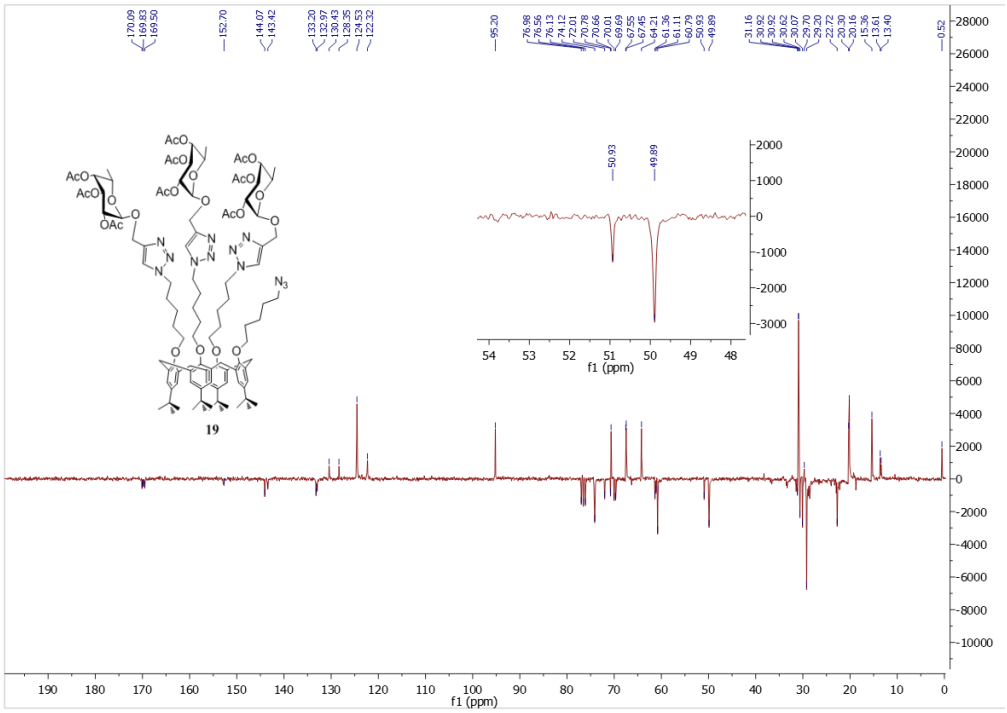

Figure 32. DeptQ (75 MHz, $CDCl_3$) spectrum of compound **19.**

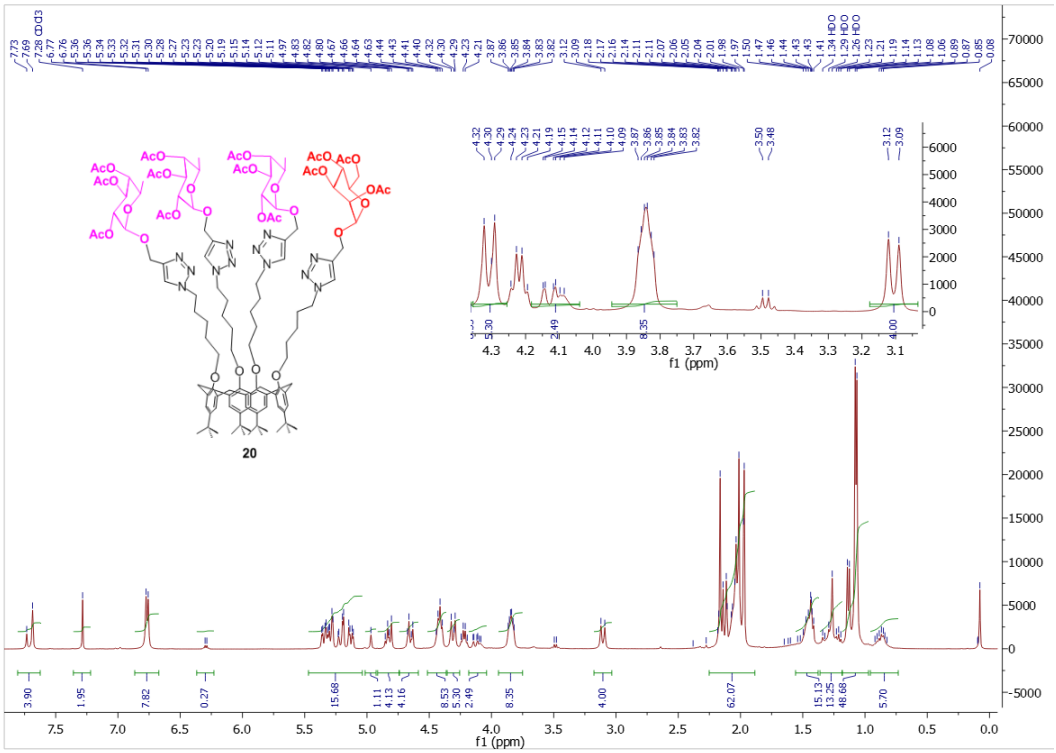

Figure 33. ^{1}H (400 MHz, $CDCl_3$) spectrum of compound **20.**

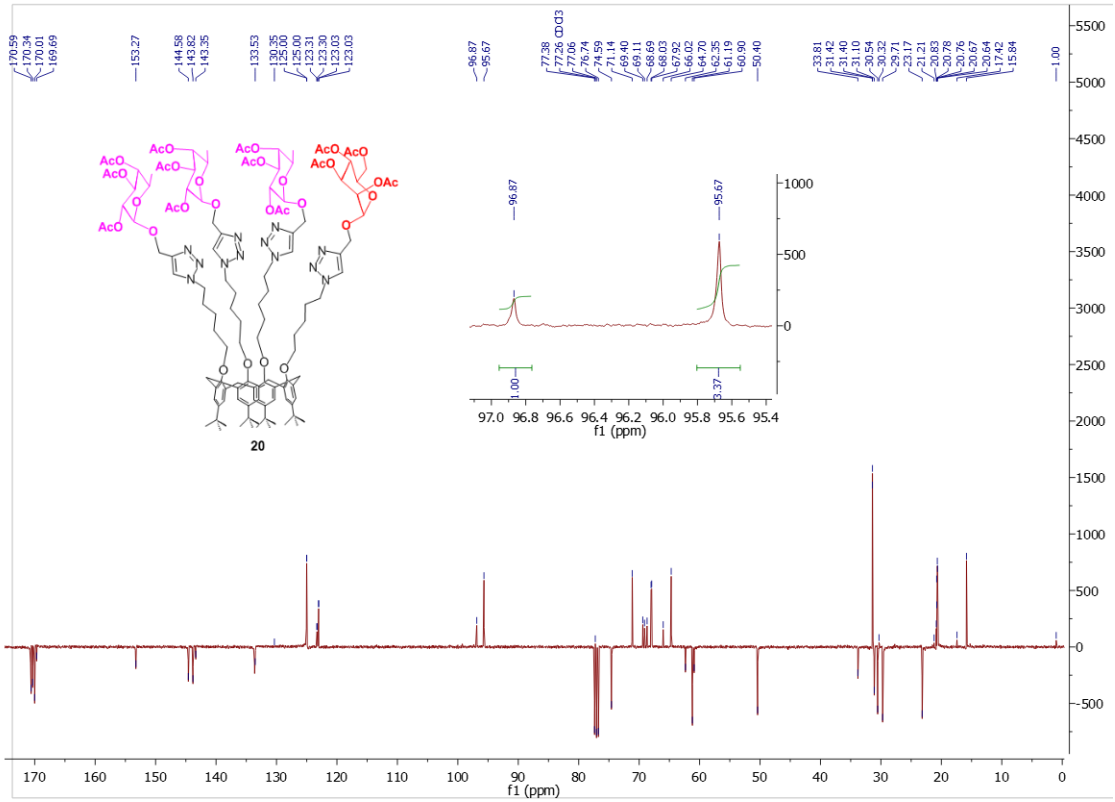

Figure 34. DeptQ (100 MHz, $CDCl_3$) spectrum of compound **20.**

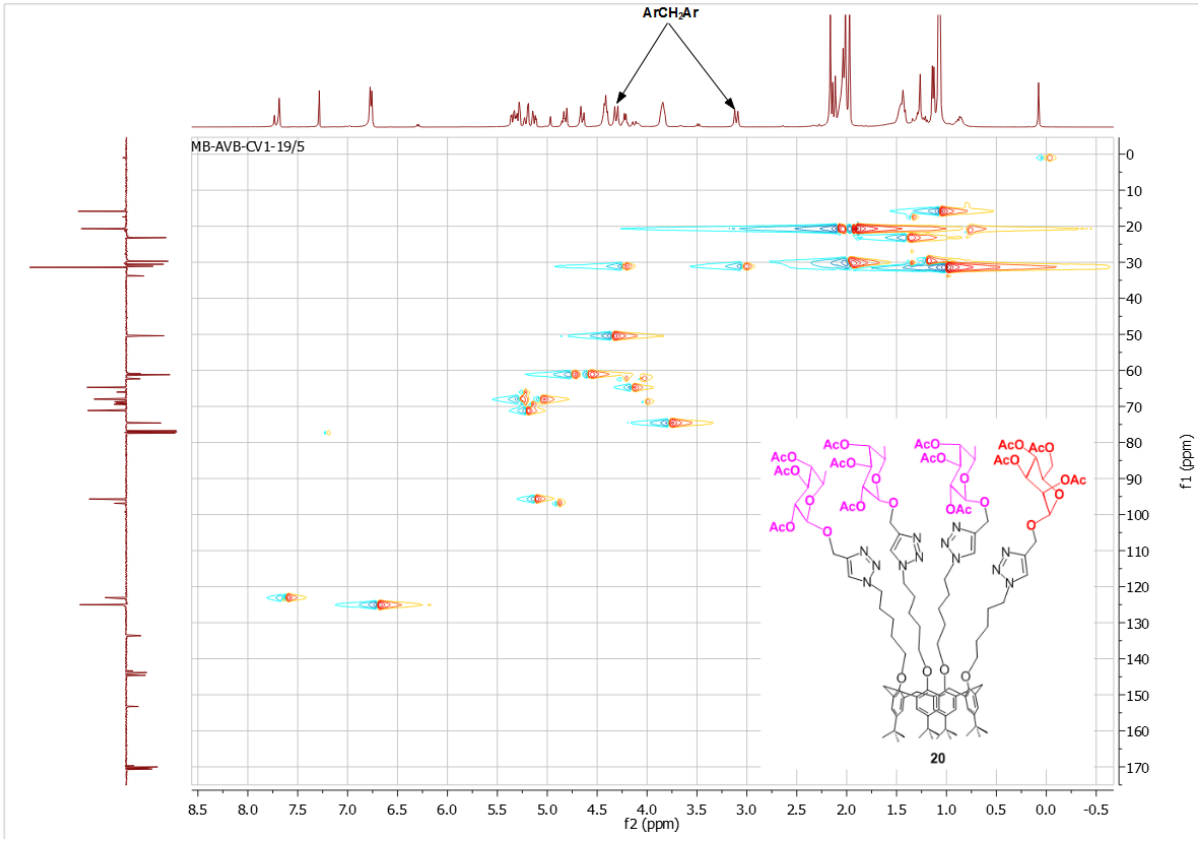

Figure 35. HSQC (400/100 MHz, $CDCl_3$) spectrum of compound **20.**

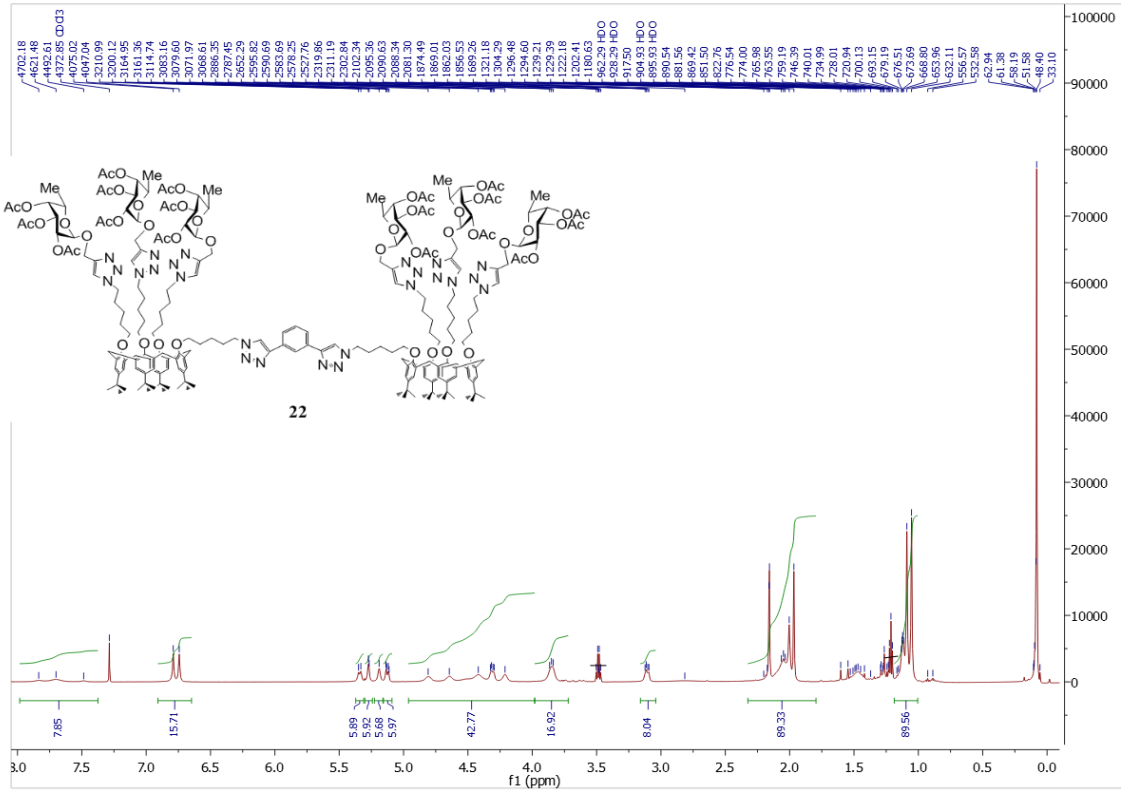

Figure 36. ^1H (600 MHz, $CDCl_3$) spectrum of compound **22.**

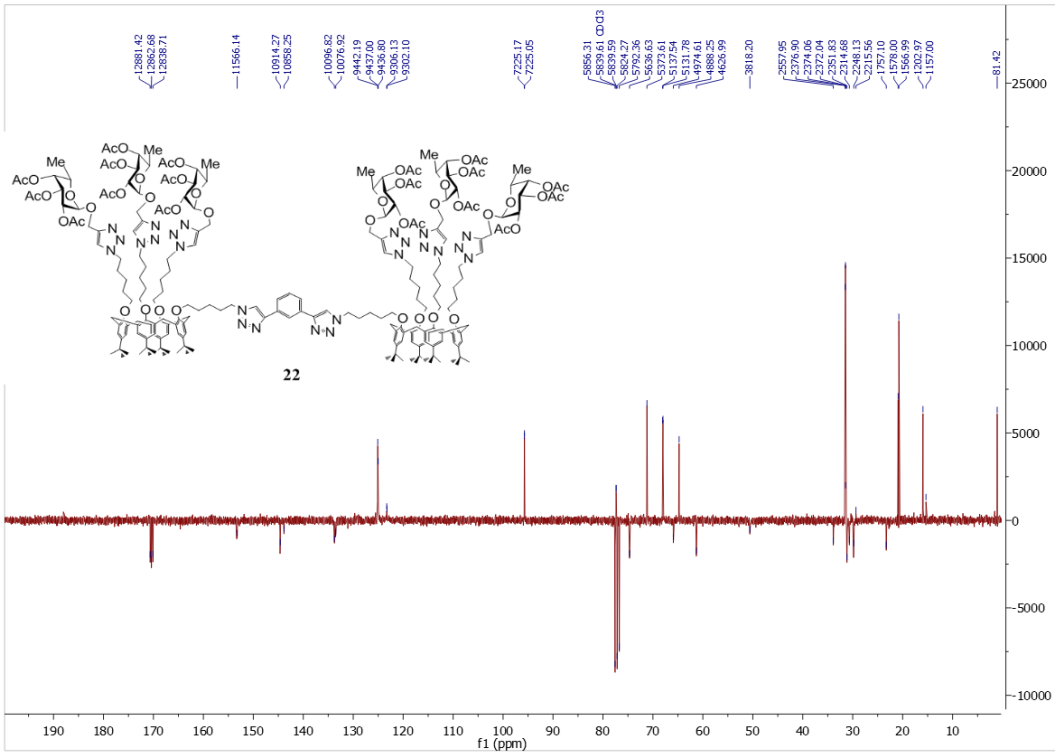

Figure 37. DeptQ (75 MHz, $CDCl_3$) spectrum of compound **22.**