Supporting Information for

A Halogen- and Hydrogen-bonding [2]Catenane for Anion Recognition and Sensing

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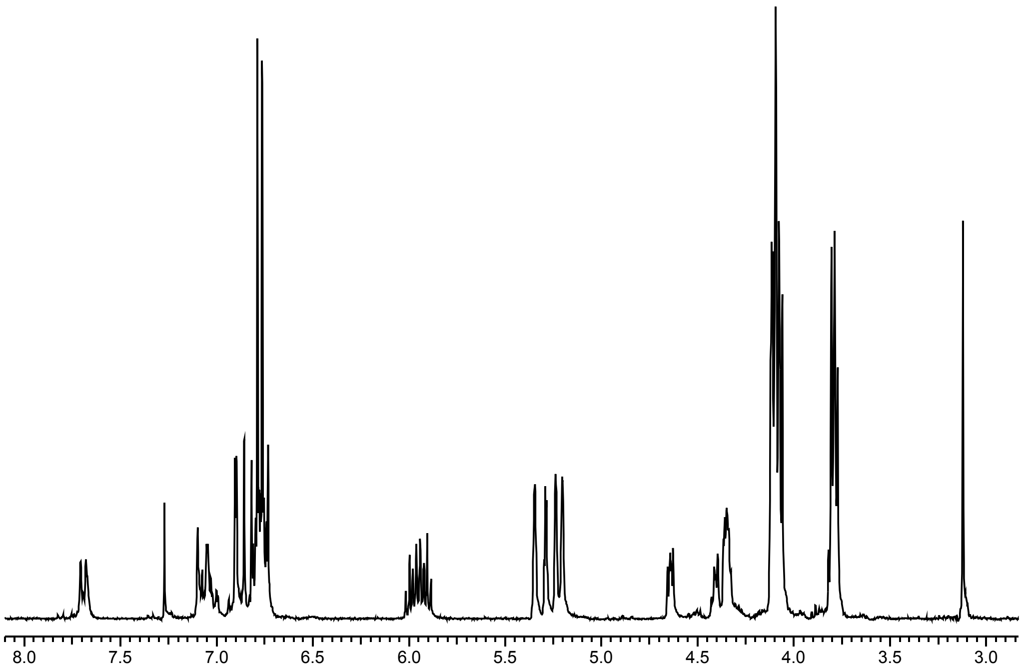
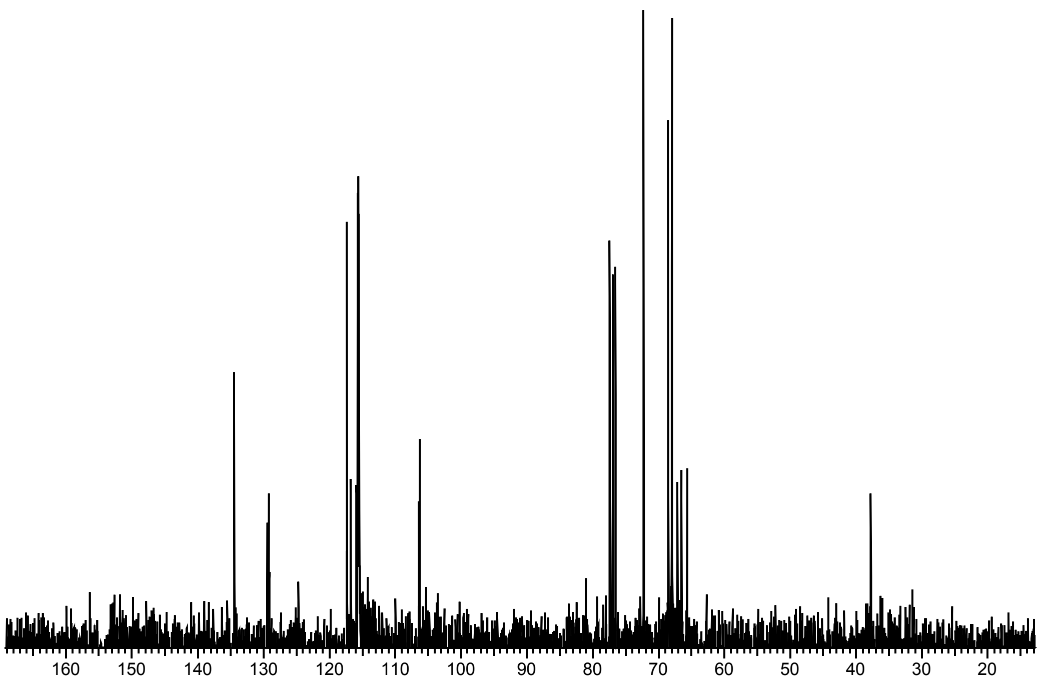
S.1 ^{1}H and ^{13}C NMR spectra of novel compounds

Vinyl-appended mesylate (6)

^{1}H NMR (300 MHz, 293 K, $CDCl_3$):

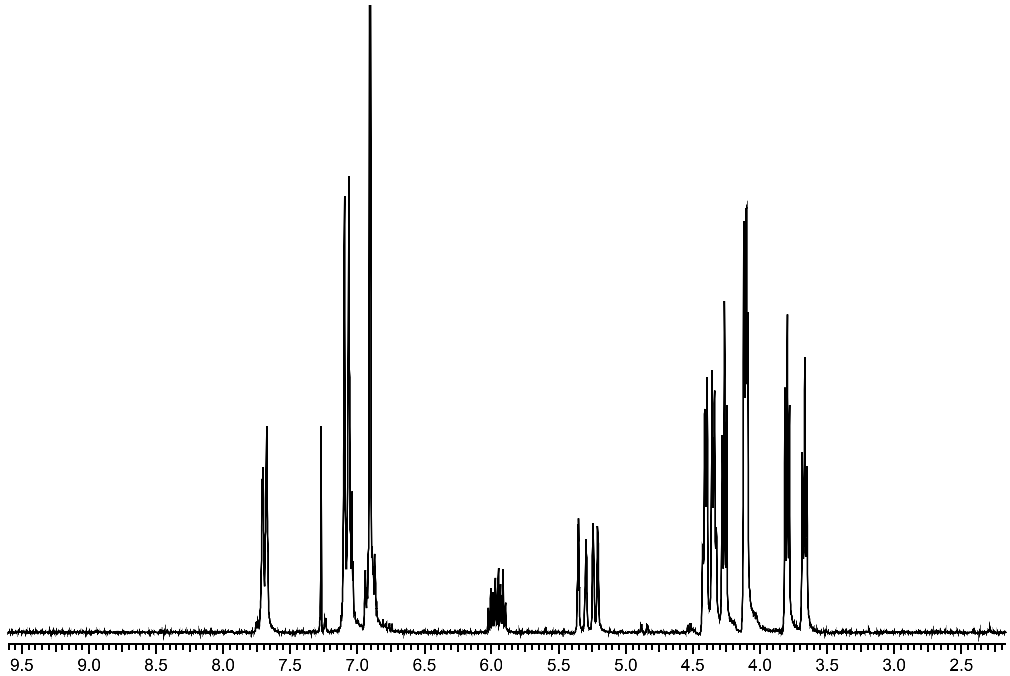


^{13}C NMR (75 MHz, 293 K, $CDCl_3$):

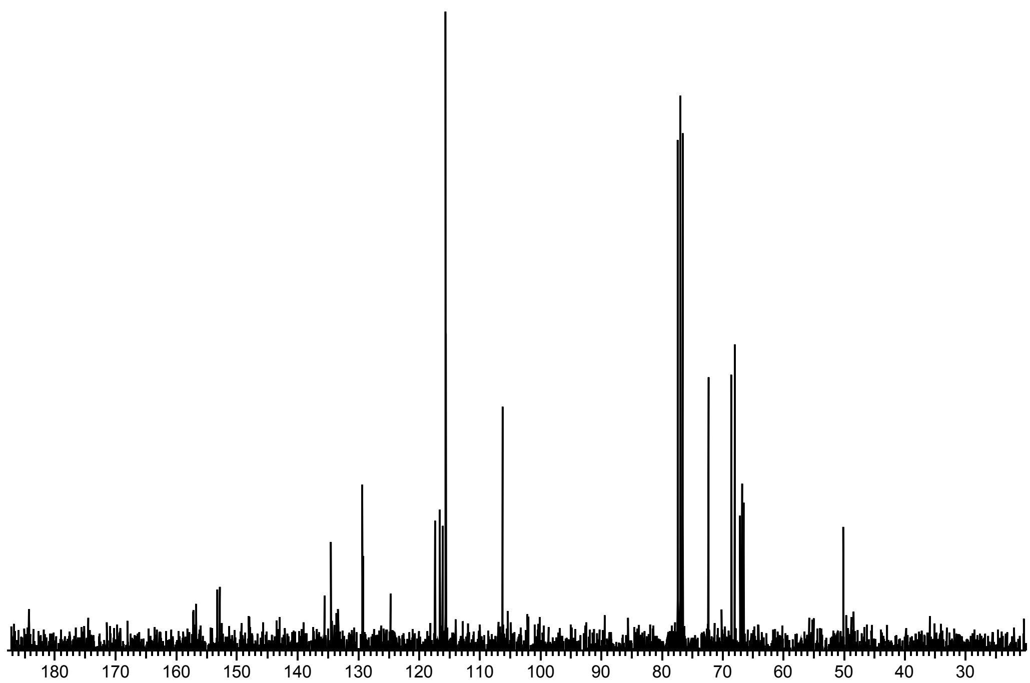


Vinyl-appended azide (7)

^{1}H NMR (300 MHz, 293 K, $CDCl_3$):

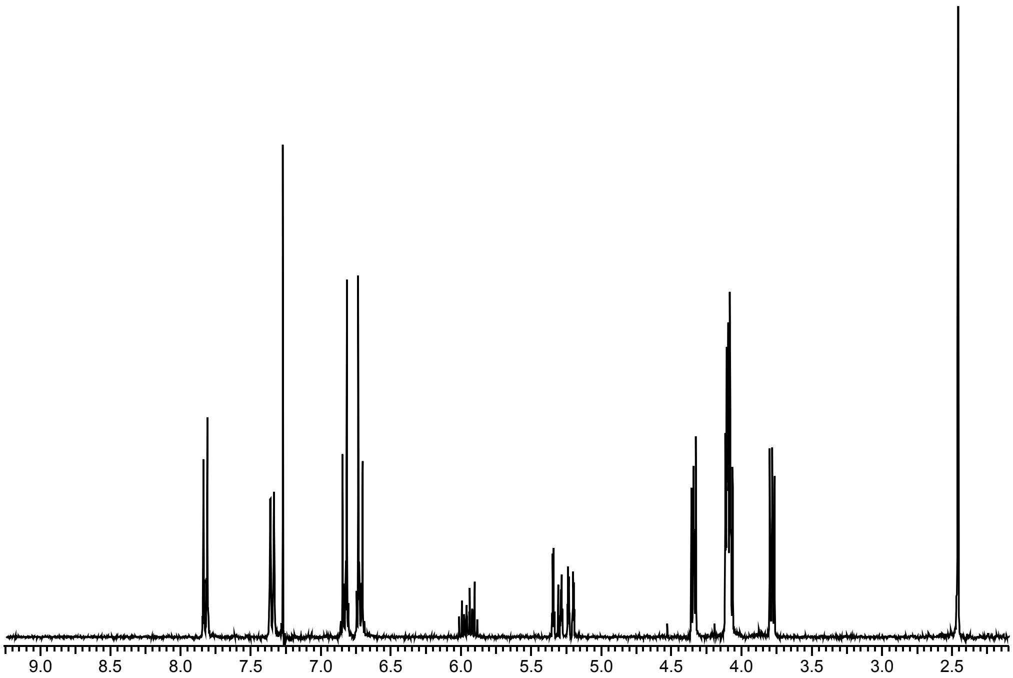


^{13}C NMR (75 MHz, 293 K, $CDCl_3$):

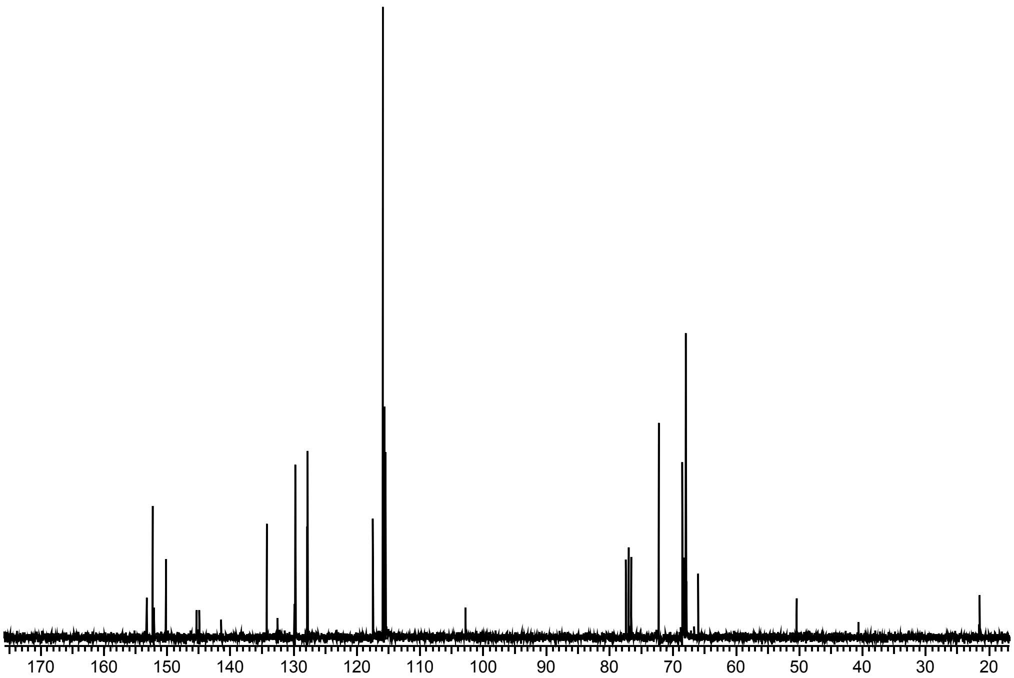


2-(4-(2-(Allyloxy)ethoxy)phenoxy)ethyl 4-methylbenzenesulfonate (9)

^{1}H NMR (300 MHz, 293 K, $CDCl_3$):

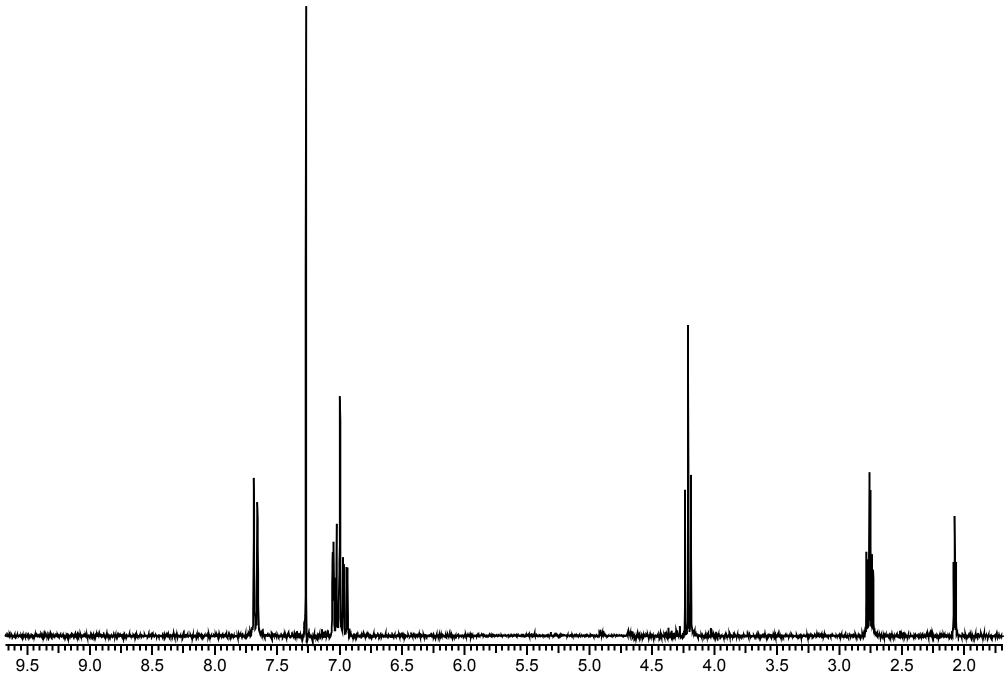


^{13}C NMR (75 MHz, 293 K, $CDCl_3$):

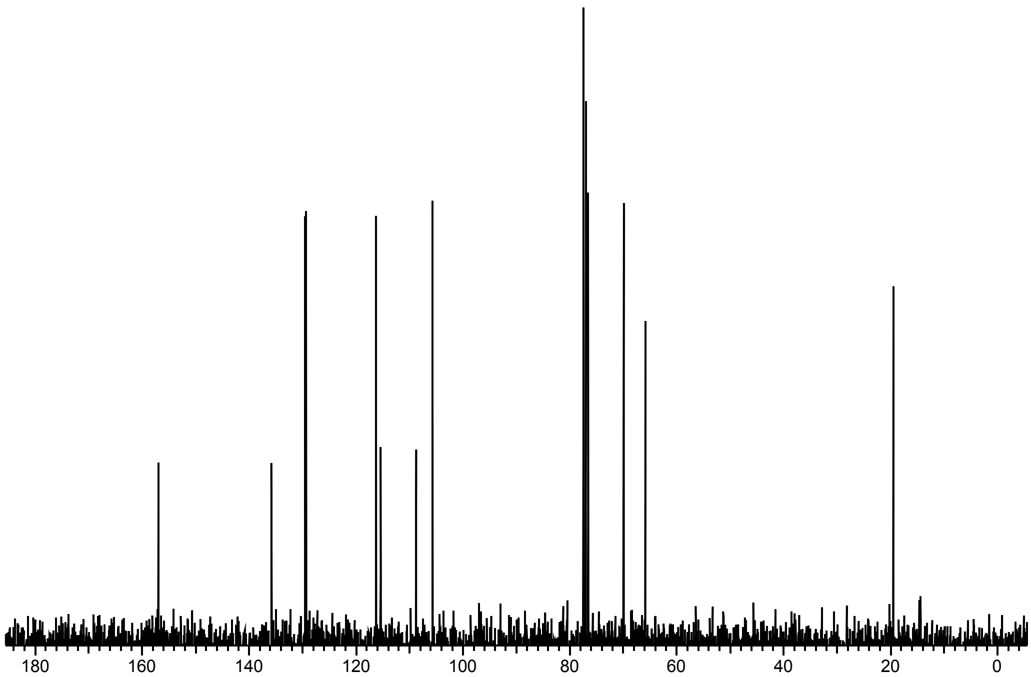


7-(But-3-yn-1-yloxy)naphthalen-2-ol (10)

^{1}H NMR (300 MHz, 293 K, $CDCl_3$):

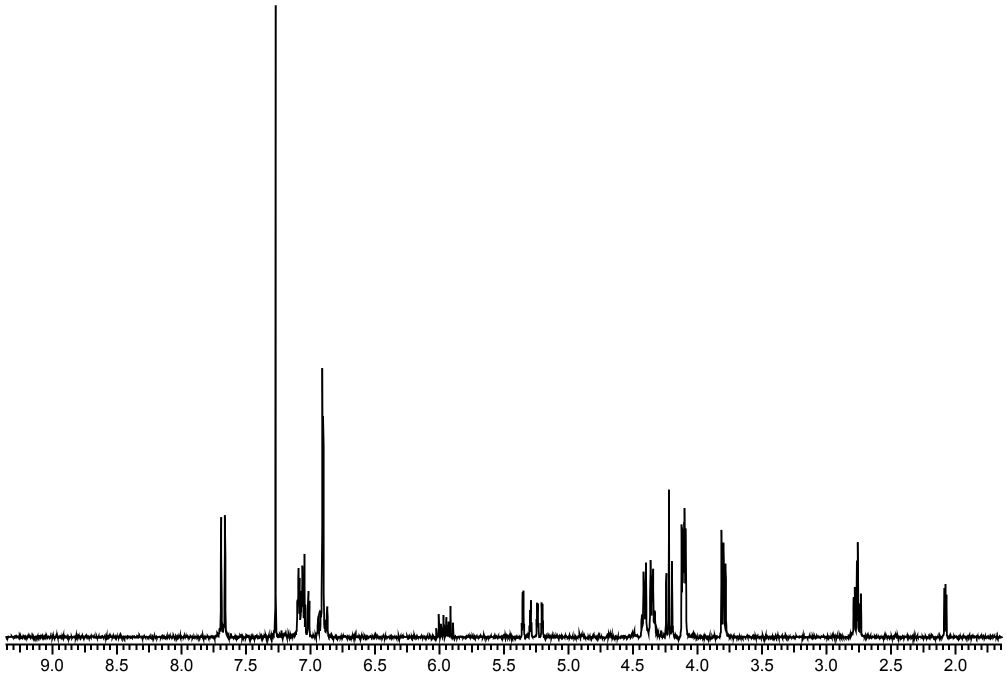


^{13}C NMR (75 MHz, 293 K, $CDCl_3$):

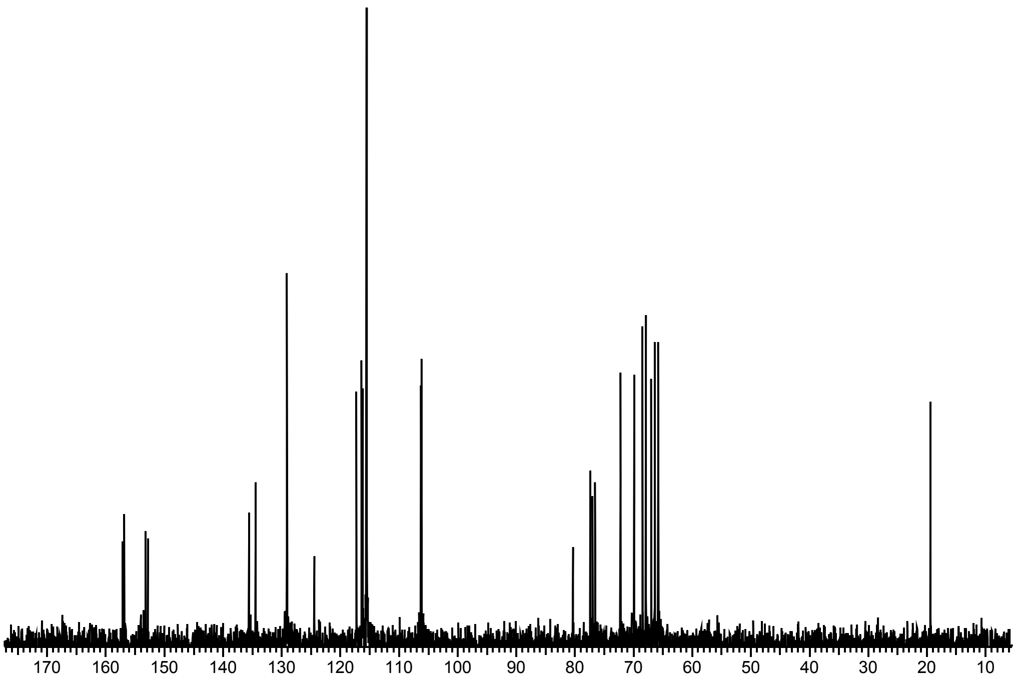


2-(2-(4-(2-(Allyloxy)ethoxy)phenoxy)ethoxy)-7-(but-3-yn-1-yloxy)naphthalene (11)

^{1}H NMR (300 MHz, 293 K, $CDCl_3$):

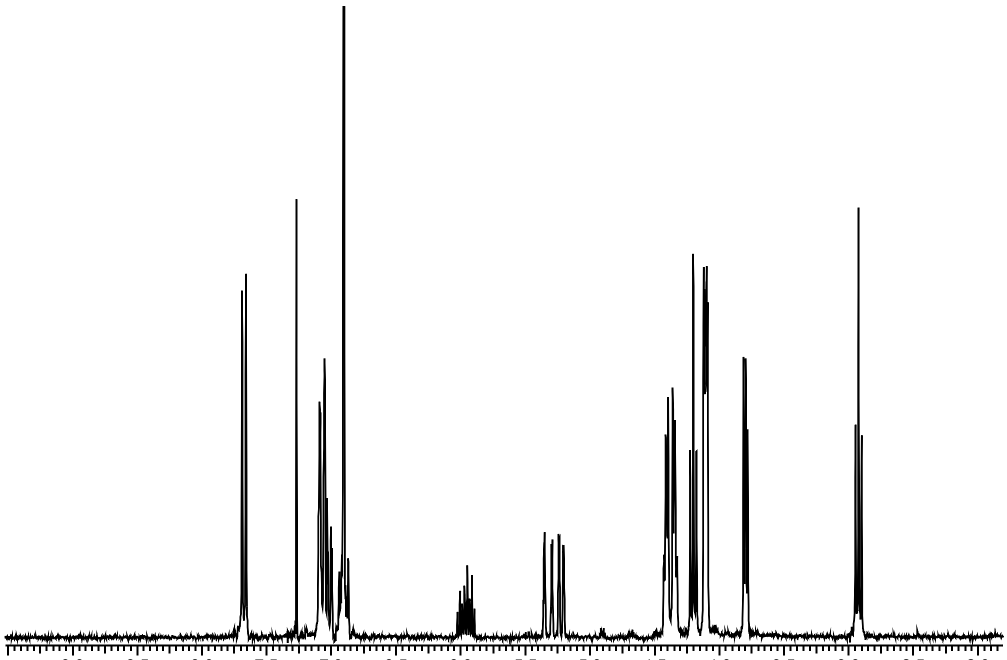


^{13}C NMR (75 MHz, 293 K, $CDCl_3$):

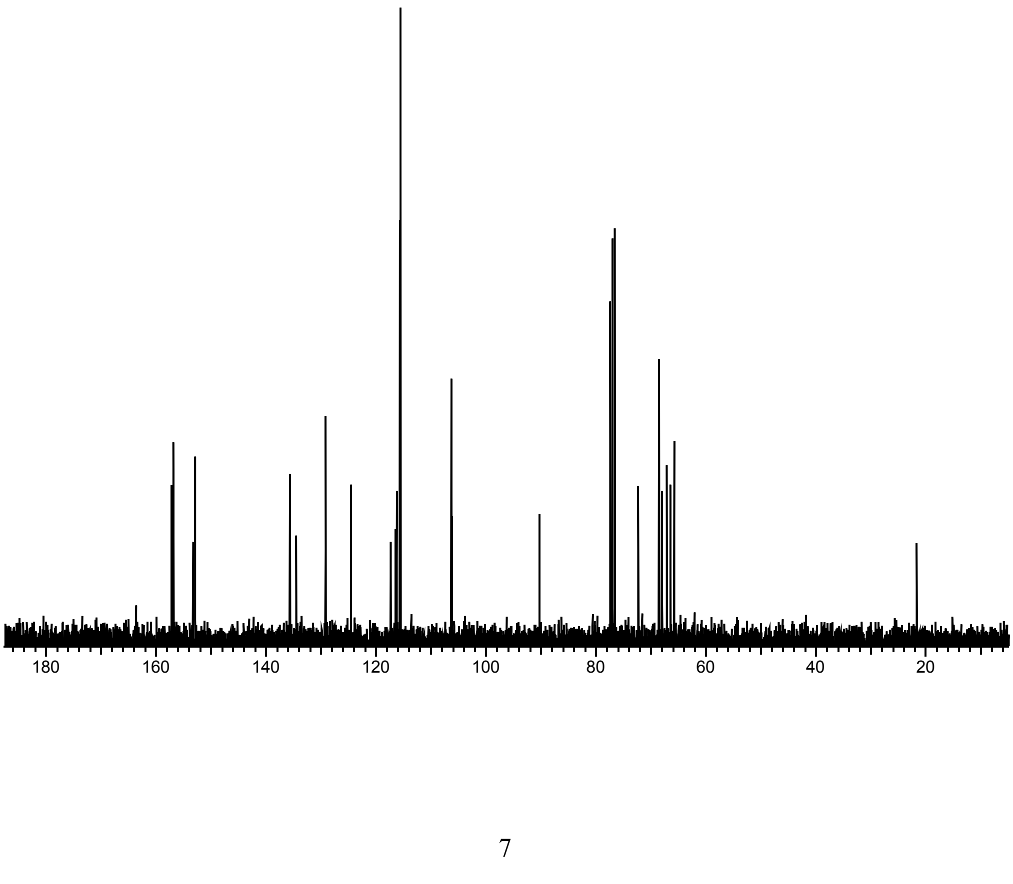


Vinyl-appended iodo-alkyne (12)

^{1}H NMR (300 MHz, 293 K, $CDCl_3$):

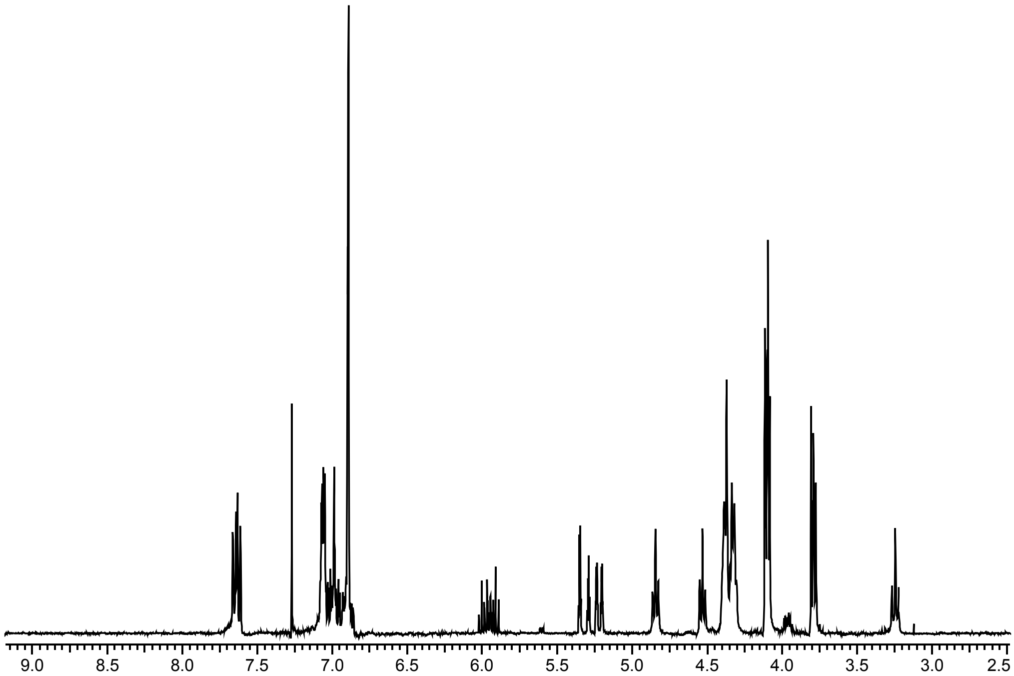


^{13}C NMR (75 MHz, 293 K, $CDCl_3$):

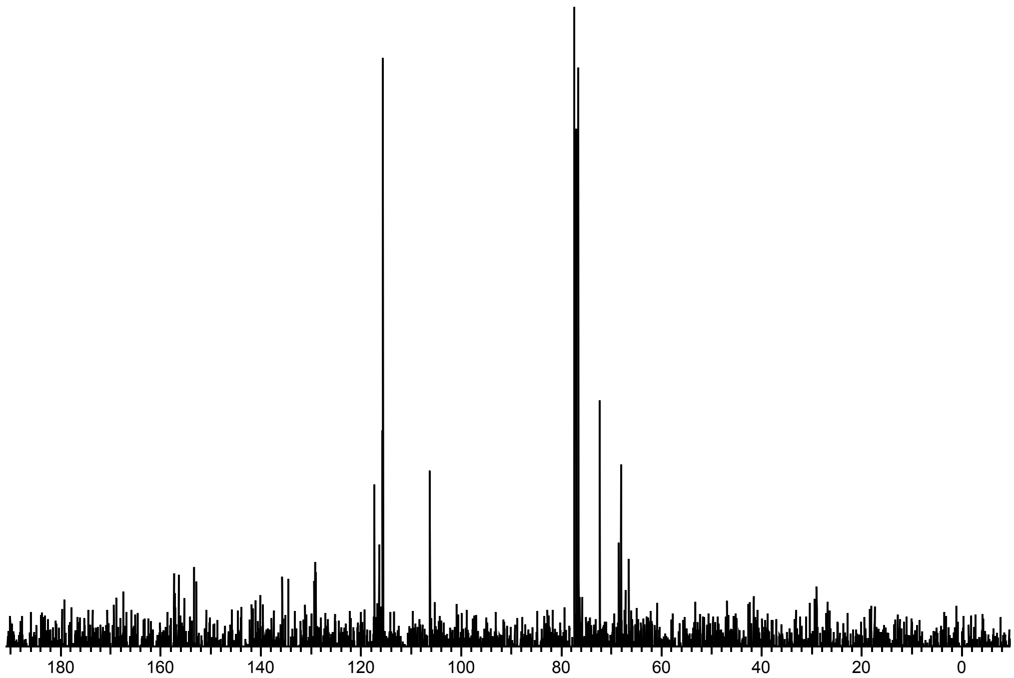


Iodo-triazole containing bis-vinyl appended precursor (13)

^{1}H NMR (300 MHz, 293 K, $CDCl_3$):

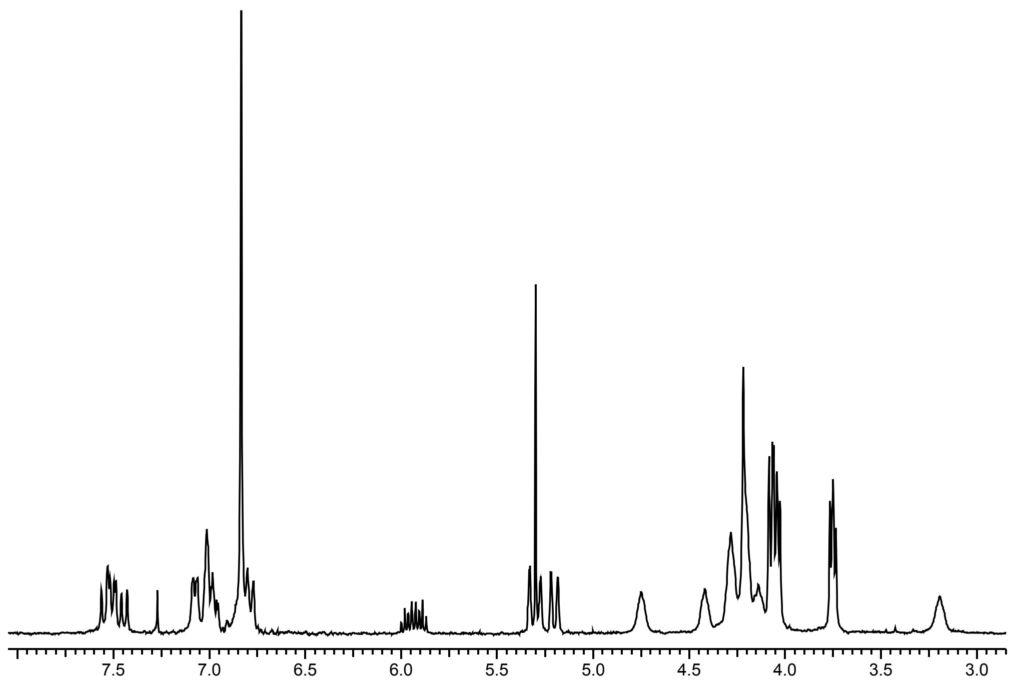


^{13}C NMR (75 MHz, 293 K, $CDCl_3$):

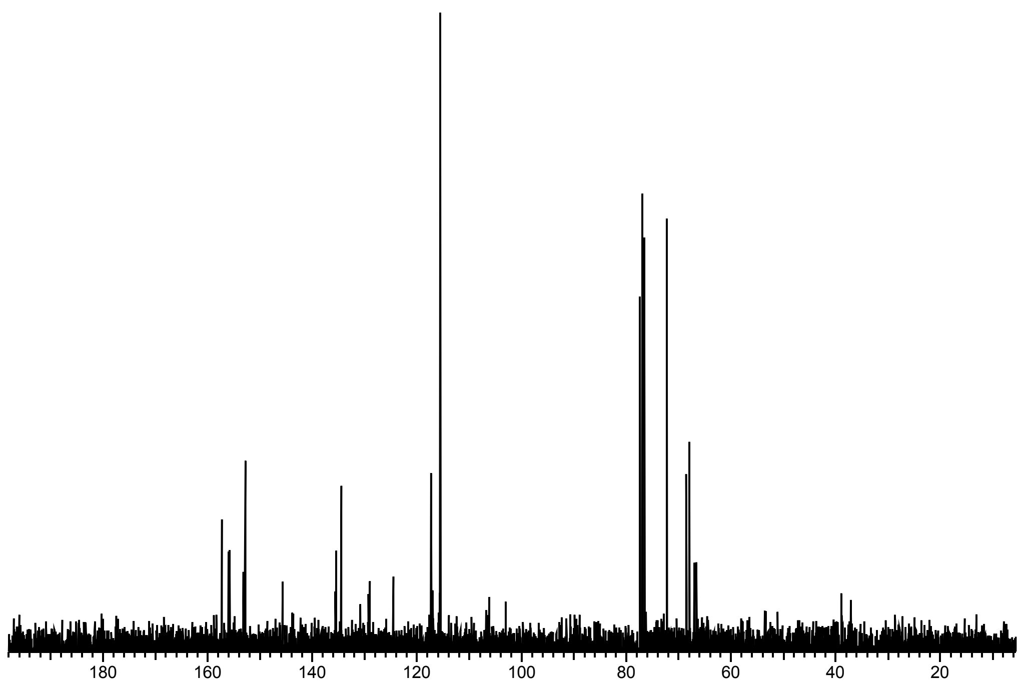


Iodo-triazolium containing bis-vinyl appended precursor tetrafluoroborate salt ($14{\cdot}BF_4$)

^{1}H NMR (300 MHz, 293 K, $CDCl_3$):

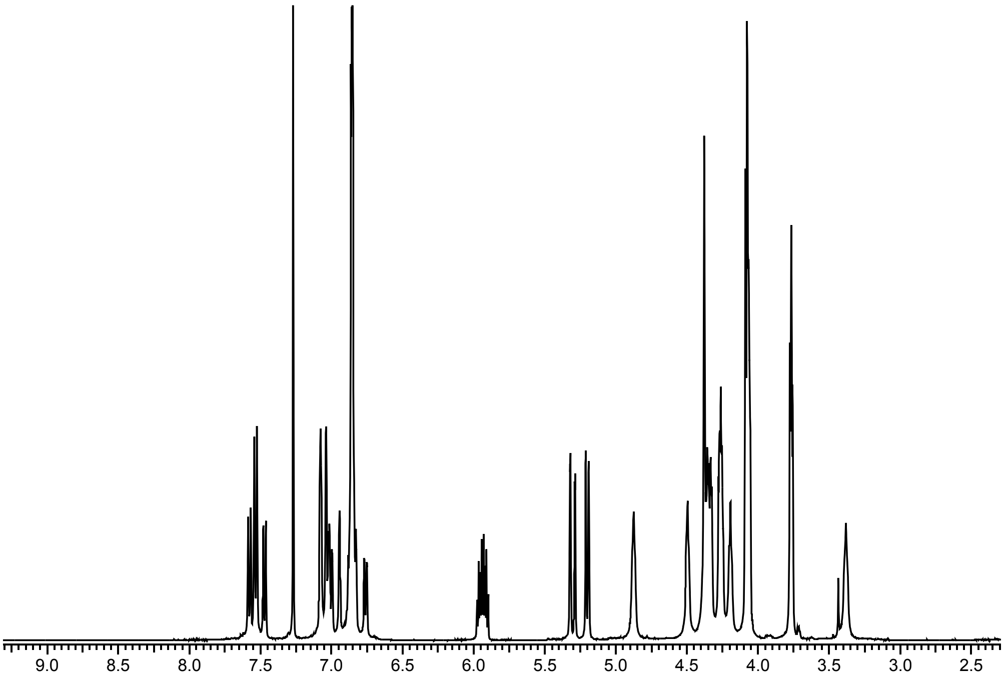


^{13}C NMR (75 MHz, 293 K, $CDCl_3$):

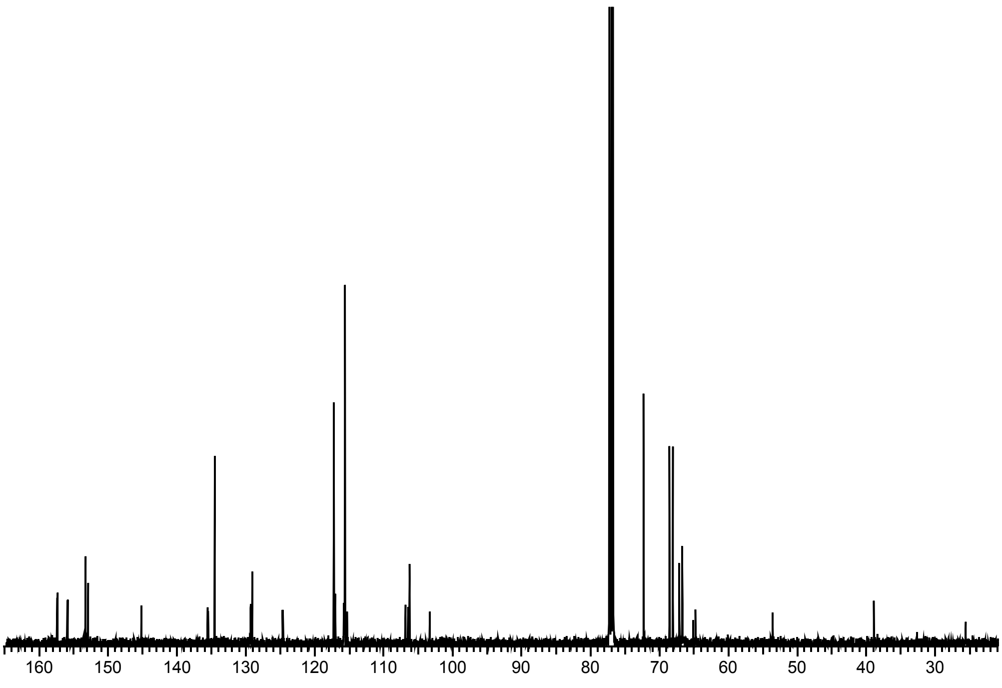


Iodo-triazolium containing bis-vinyl appended precursor chloride salt (14·Cl)

^{1}H NMR (500 MHz, 293 K, $CDCl_3$):

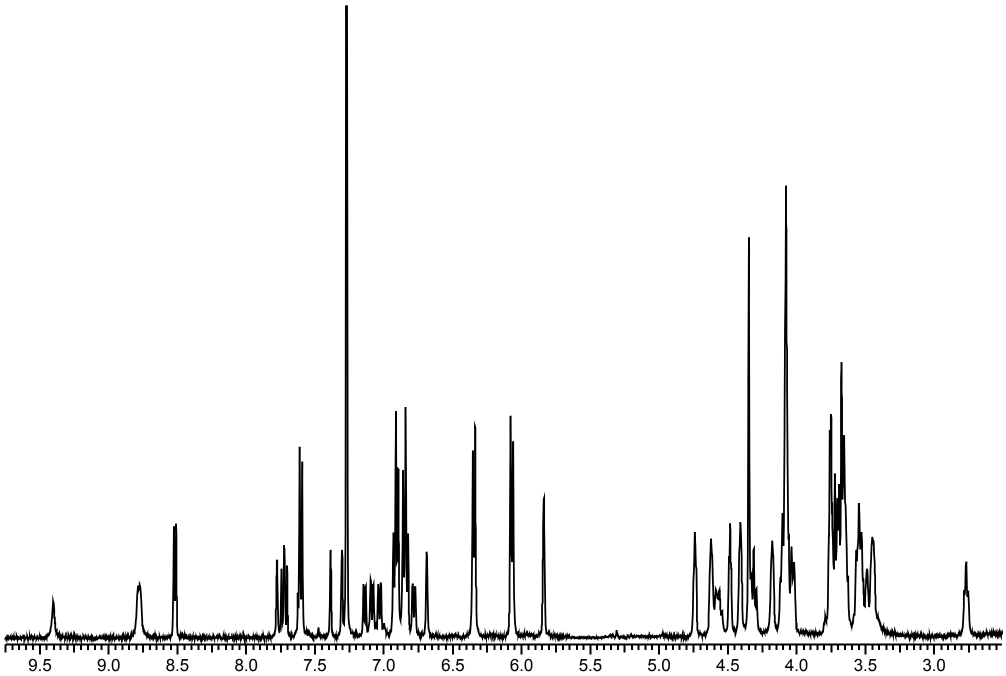


^{13}C NMR (126 MHz, 293 K, $CDCl_3$):

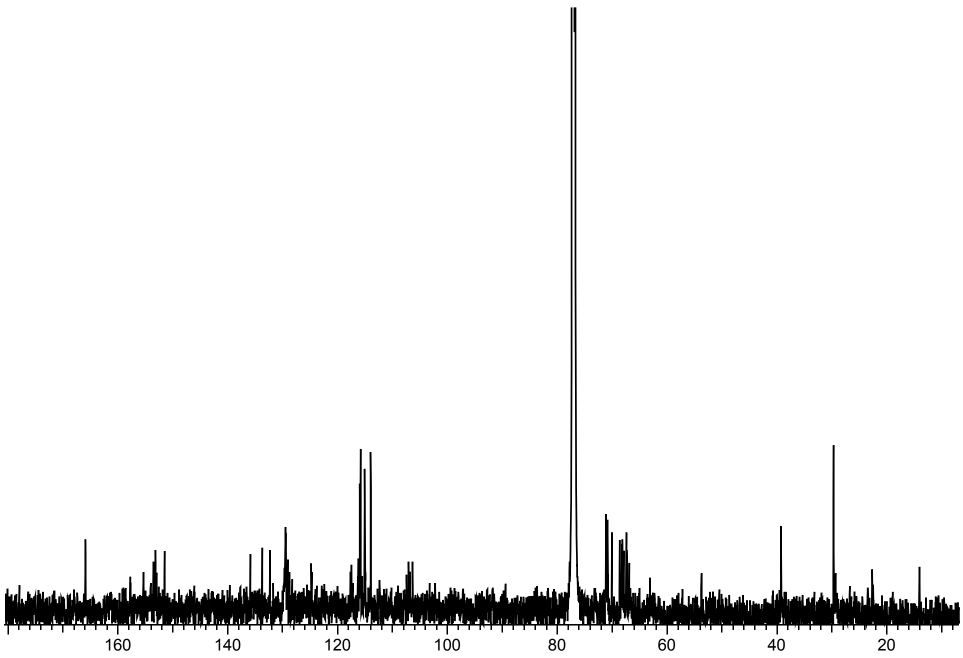


Iodo-triazolium functionalised [2]catenane chloride salt (16·Cl)

^{1}H NMR (500 MHz, 293 K, $CDCl_3$):

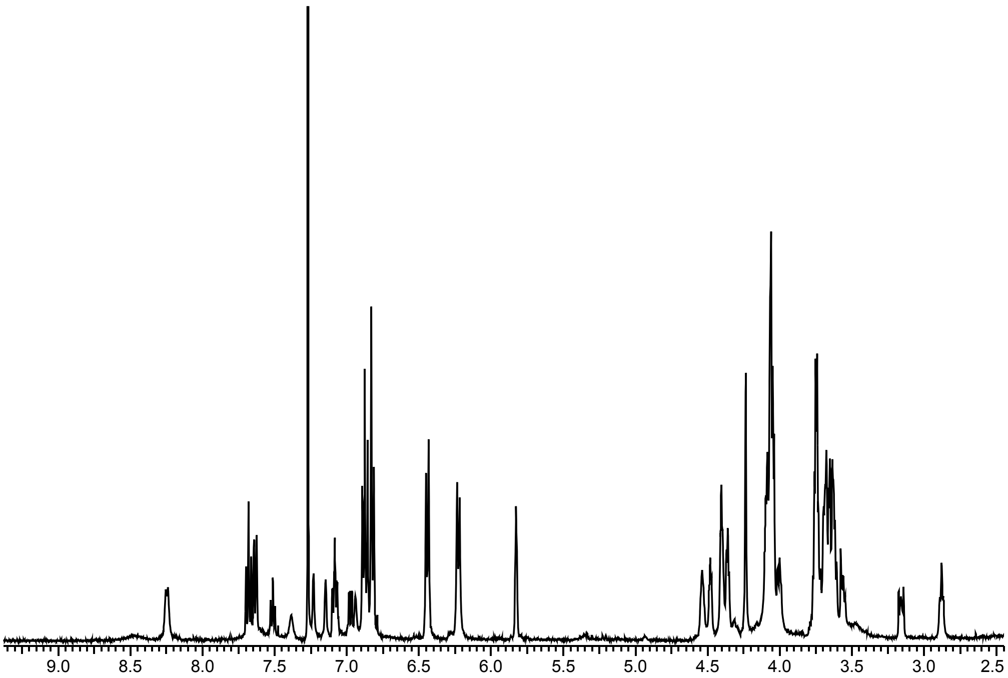


^{13}C NMR (126 MHz, 293 K, $CDCl_3$):



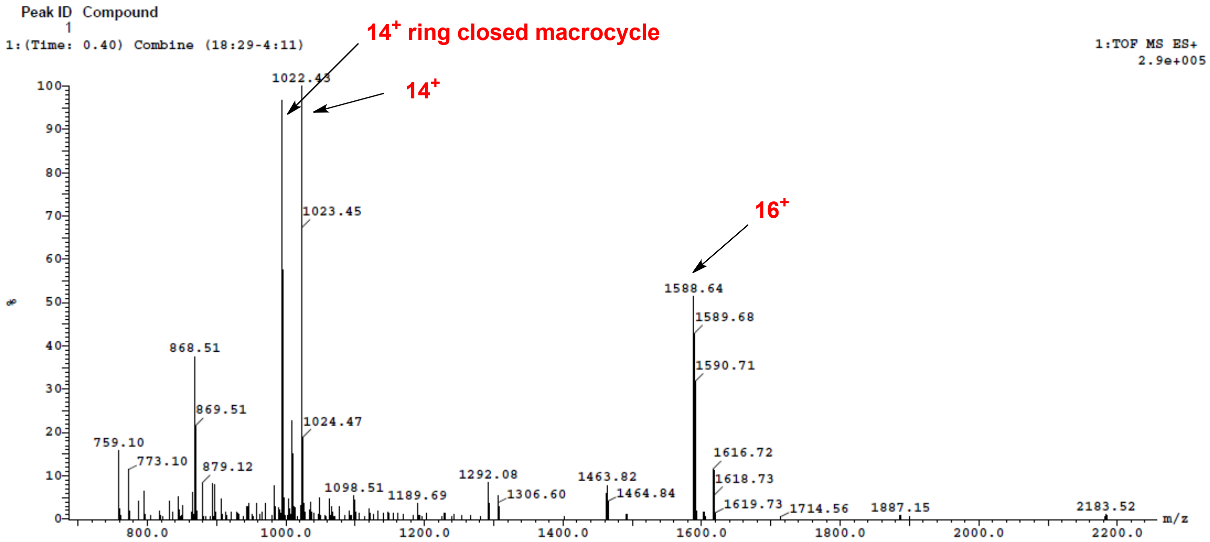
Iodo-triazolium functionalised [2]catenane hexafluorophosphate salt ($16 \cdot PF_6$)

^{1}H NMR (500 MHz, 293 K, $CDCl_3$):



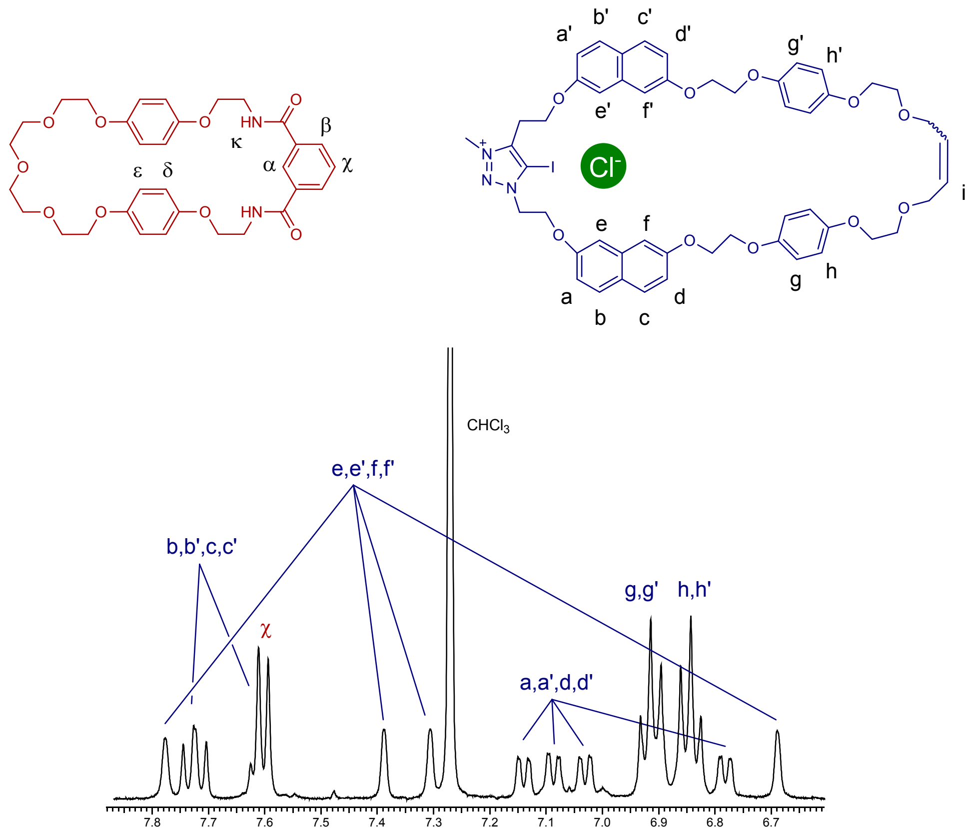
Note: insufficient material was isolated to obtain a ^{13}C NMR spectrum.

S.2 Crude ESI-MS spectrum of catenane 16·Cl reaction mixture



ESI-MS spectrum of crude catenane reaction mixture showing formation of the ring closed form of ***14***$^+$.

S.3 Expanded ^{1}H NMR spectrum for catenane 16·Cl

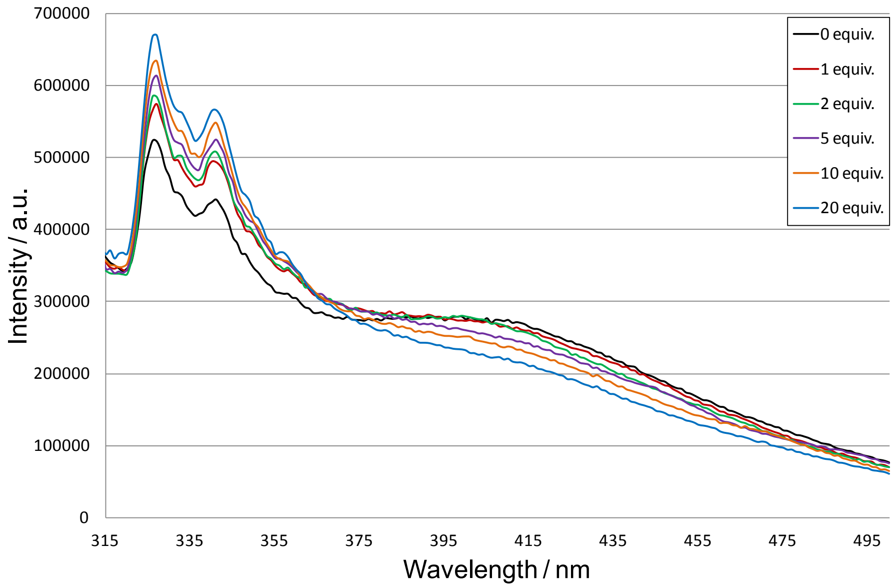


*Expanded aromatic region of the ^{1}H NMR spectrum of catenane **16·Cl** (500 MHz, CDCl3, 293 K).*

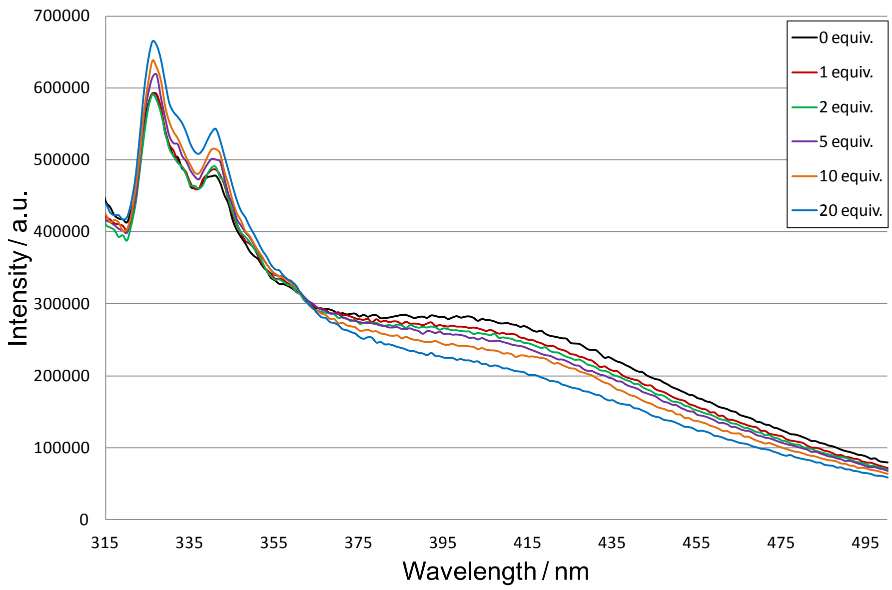
S.4 Fluorescence titration protocols

Fluorescence emission spectra were recorded on a Horiba Jobin Yvon Fluorlog spectrometer using a Hellma Quartz cuvette of pathlength 10 mm at 293 K. An excitation wavelength of 280 nm was used and the concentration of the host was 1 x 10^{-5} M. A starting volume of 2.5 mL was used in each titration to which aliquots of a 5 x 10^{-4} M guest solution were added up to the point where 20 equivalents of guest had been added. The concentration of the host was maintained at 1 x 10^{-5} M throughout the titration experiments, with this achieved by making the guest stock solutions using the host stock solution. The changes of intensity of each of the bands were determined by summing the intensity values across the entire band. This gave titration data which were analysed using the DynaFit[1] computer program to determine $\log K_a$ values and confidence intervals, with the parameters refined using a non-linear least-squares method.

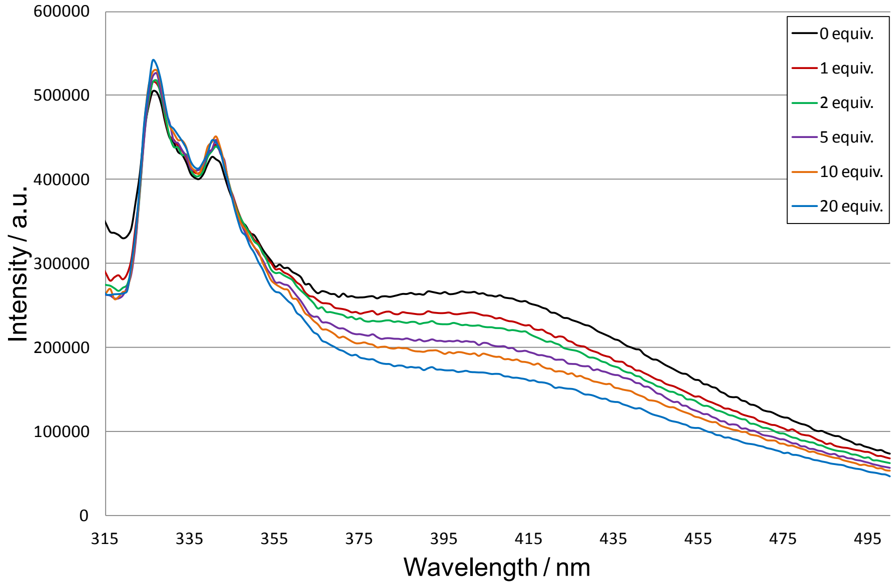
S.5 Fluorescence titration spectra



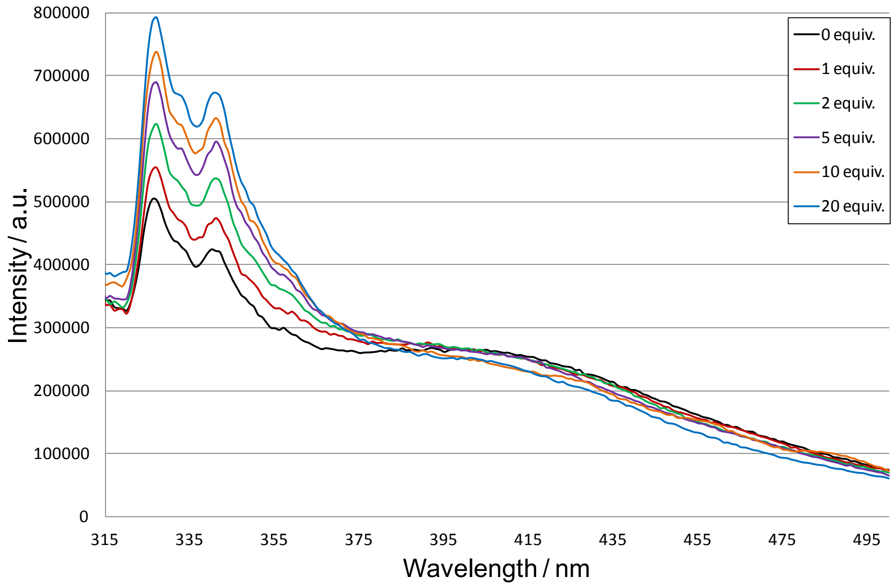
Changes in the emission spectrum of catenane ***16·PF$_6$*** *in acetonitrile upon addition of increasing amounts of TBA·Cl ([host] = 1 x 10^{-5} M, λexc = 280 nm, 293 K).*



Changes in the emission spectrum of catenane ***16·PF$_6$*** *in acetonitrile upon addition of increasing amounts of TBA·Br ([host] = 1 x 10^{-5} M, λexc = 280 nm, 293 K).*



Changes in the emission spectrum of catenane ***16·PF$_6$*** *in acetonitrile upon addition of increasing amounts of TBA·I ([host] = 1 x 10^{-5} M, λexc = 280 nm, 293 K).*



Changes in the emission spectrum of catenane ***16·PF$_6$*** *in acetonitrile upon addition of increasing amounts of TBA·H_2PO_4 ([host] = 1 x 10^{-5} M, λexc = 280 nm, 293 K).*

S.6 References

1. P. Kuzmič, *Anal. Biochem.*, 1996, **237**, 260-273.