Supporting information for:

Tuning Artificial Oxidase catalysis by cavity modification.

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Contents

Oxidation assays:

In a plate reader (Biotek Epoch 2) 8 samples (0.25 mL each) of the appropriate substrate at different concentrations (1.83-10.08 mM) in phosphate buffer solution (95 mM for benzyl alcohols, 50mM for anilines, pH = 7) containing cyclodextrin derivative **12** (0.45 mM) was simultaneously started by addition of 72 mM H_2O_2 for benzyl alcohols, 570mM H_2O_2 for anilines. The reactions were followed at 25 °C using UV absorption at an appropriate wavelength and typically monitored for 2-5 h. Velocities were determined as the slope of the progress curve of each reaction. The velocities of the uncatalyzed reactions were obtained directly from the control samples, those of the catalyzed reactions were calculated by subtracting the uncatalyzed rate from the total rate of the appropriate cyclodextrin-containing sample. The V_{cat} values were used to construct Hanes plots ([S]/V vs. [S]) to ensure that the reaction follows Michaelis–Menten kinetics. In that case K_m and V_{max} were determined using least-squares nonlinear regression fitting to the Vmax vs. [S] curve. k_{cat} was calculated as Vmax/[cyclodextrin]. The following previously published k_{uncat} values were used for the calculation of k_{cat}/k_{uncat}: k_{uncat} (2-aminophenol) = $1.9*10^{-5}s^{-1}$, k_{uncat} (2-amino-4-methylphenol) = $1.31*10^{-5}s^{-1}$, k_{uncat} (4-aminophenol) = $1.11*10^{-6}s^{-1}$, k_{uncat} (benzyl alcohol) = $1.59*10^{-8}s^{-1}$, k_{uncat} ((S)-1-Phenylethanol) = $4.11*10^{-9}s^{-1}$, k_{uncat} ((R)-1-Phenylethanol) = $4.11*10^{-9}s^{-1}$, k_{uncat} (3-methoxybenzyl alcohol) = $7.52*10^{-9}s^{-1}$, k_{uncat} (4-methoxybenzyl alcohol) = $1.42*10^{-9}s^{-1}$, k_{uncat} (2-hydrogen benzyl alcohol) = $1.59*10^{-8}s^{-1}$.

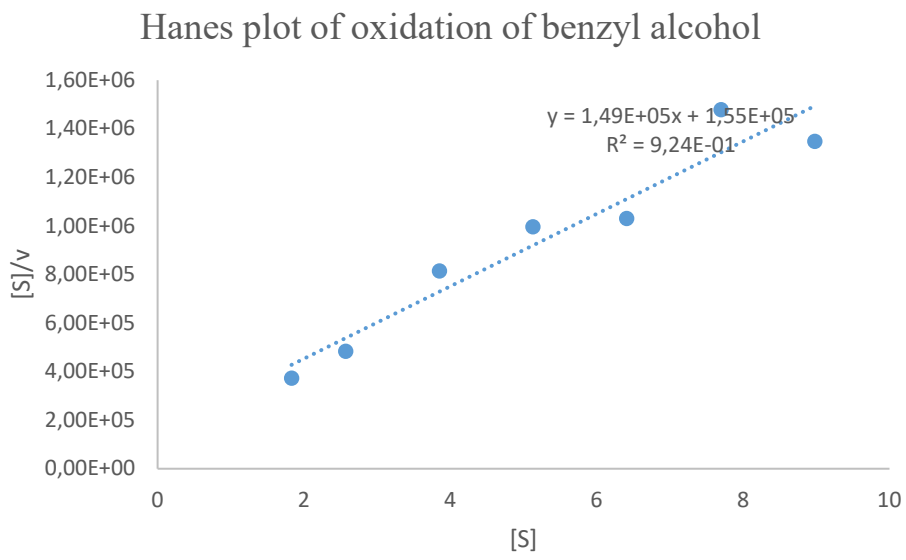
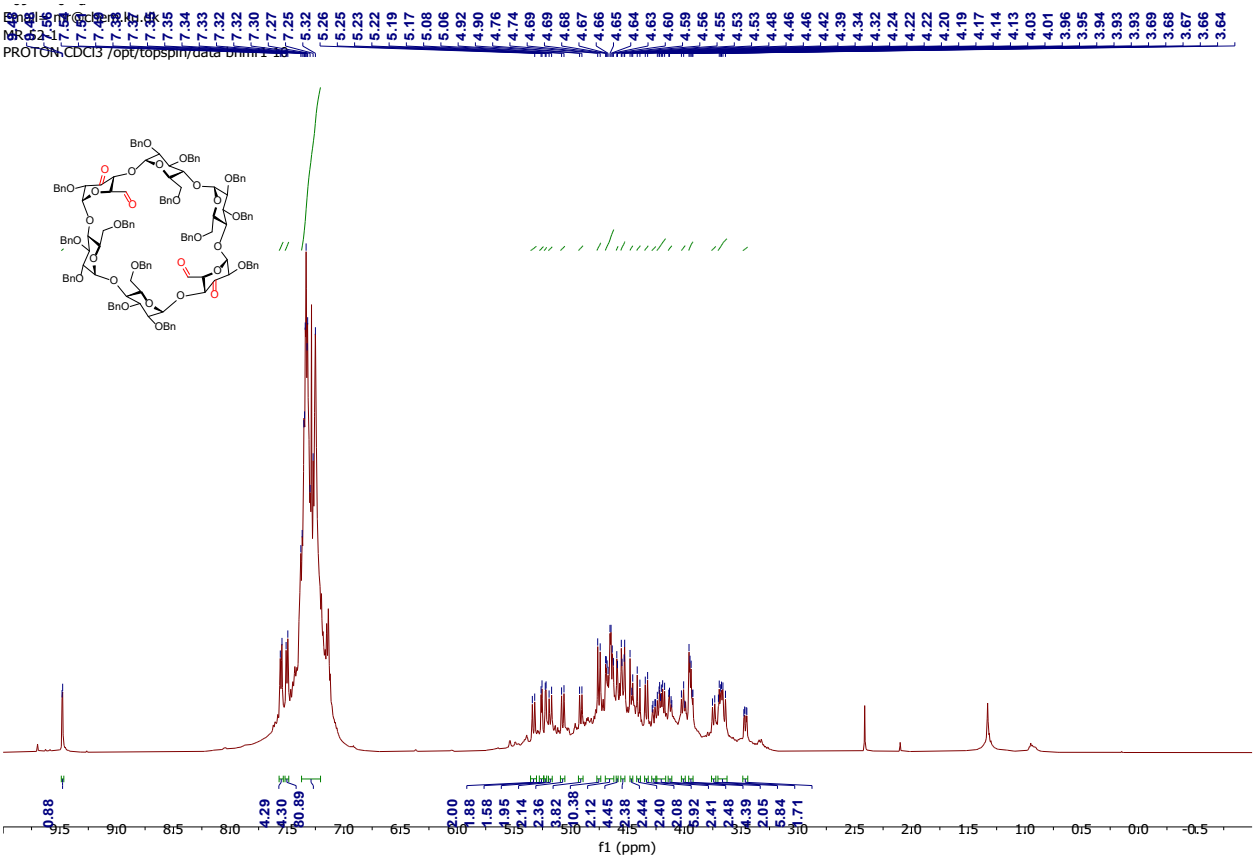
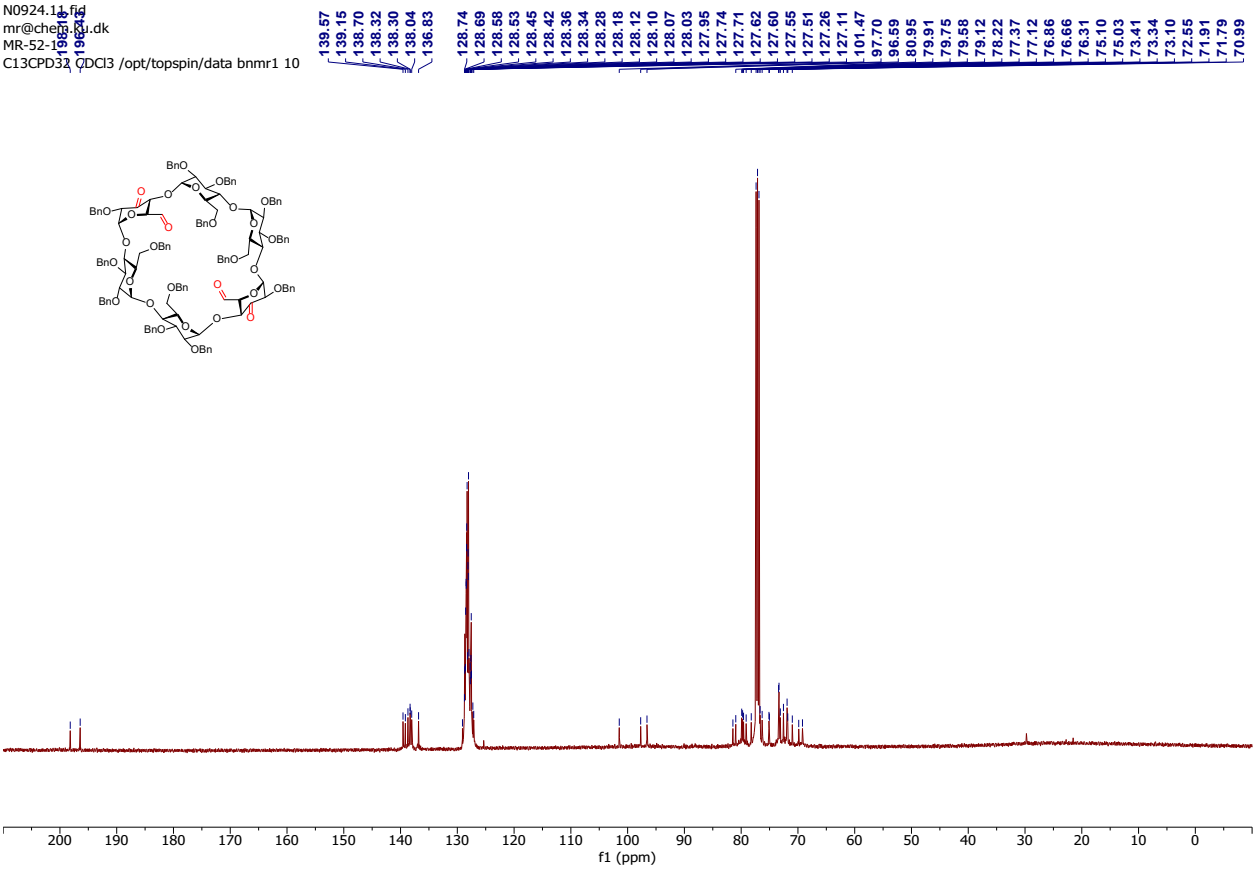


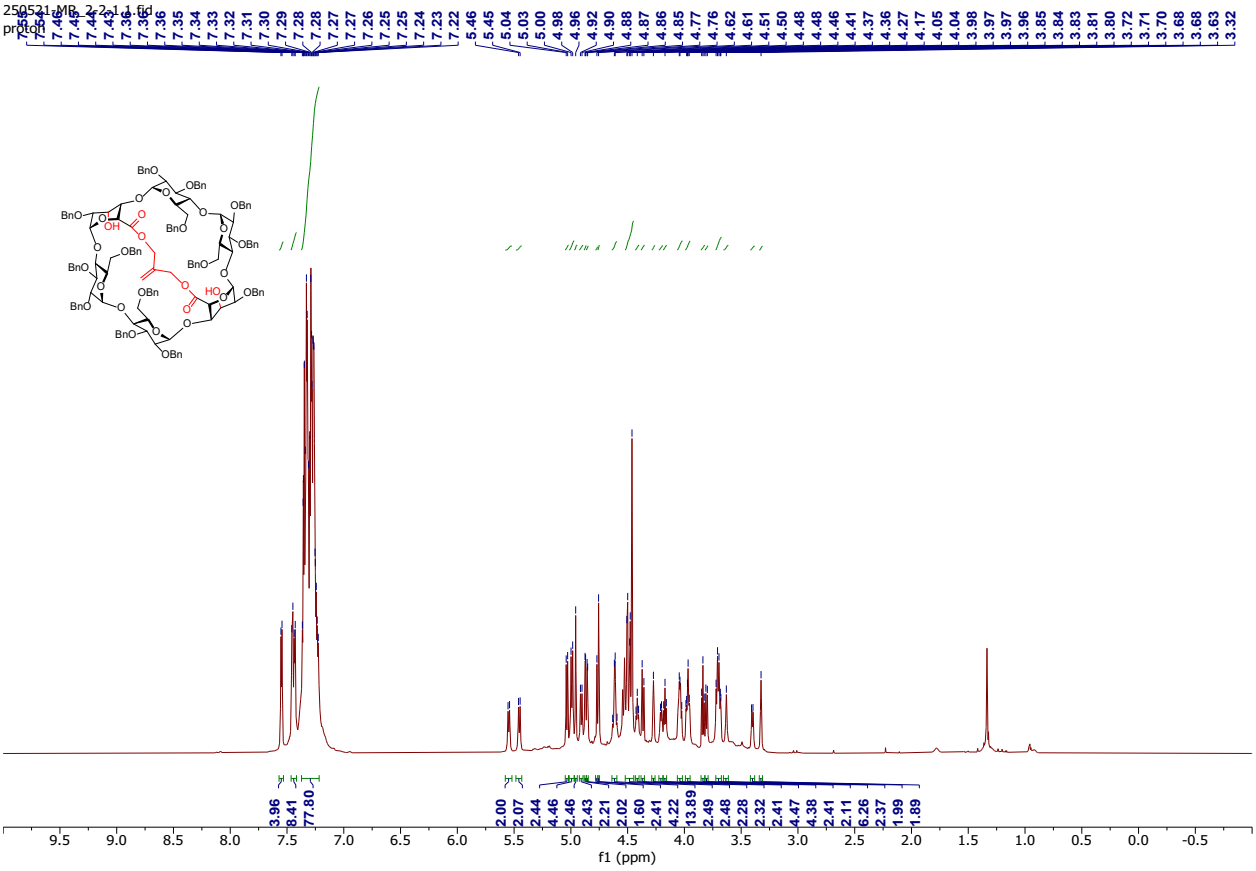
Figure S1: Hanes plot for the catalytic oxidation of benzyl alcohol by cyclodextrin derivative **12** at pH 7.0, 25 °C. The concentration of H_2O_2 was 72 mM and of **12** was 0.45 mM.



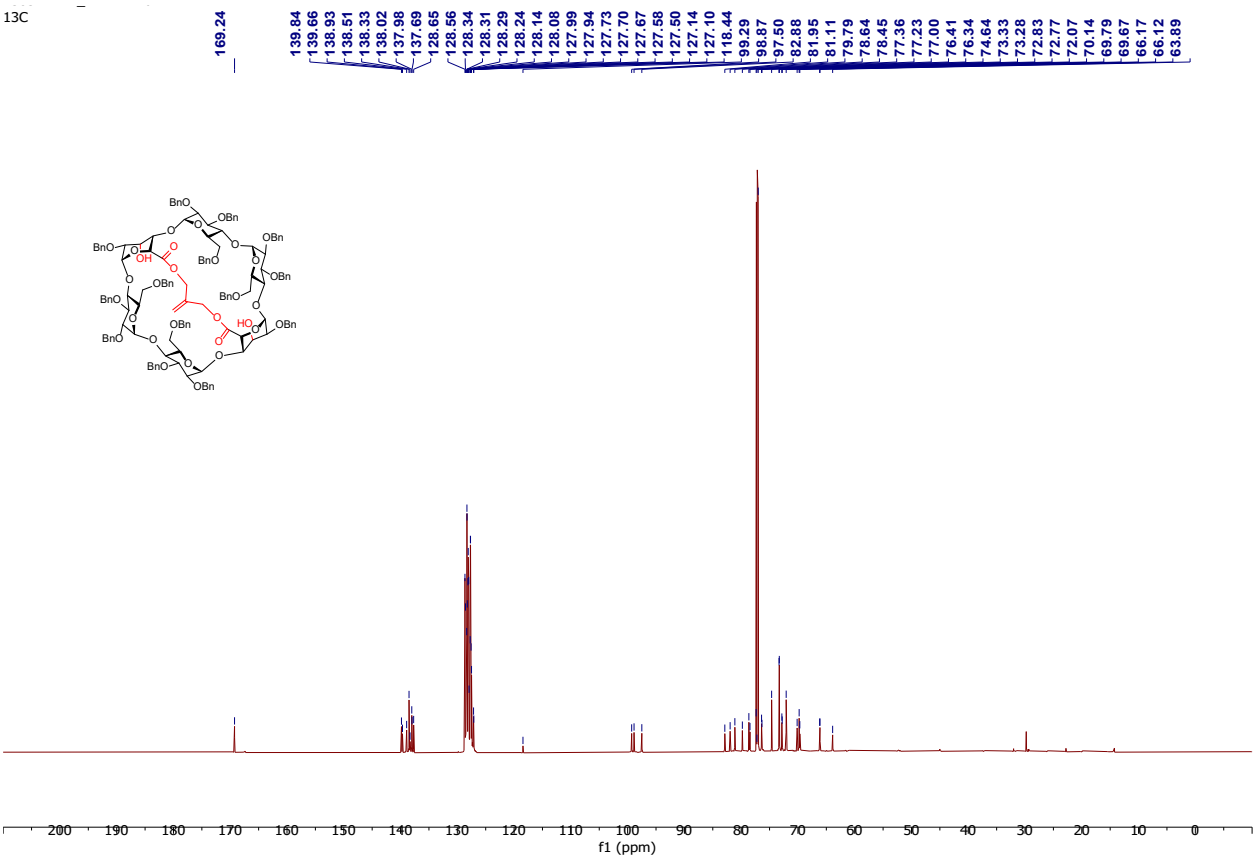
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound 7



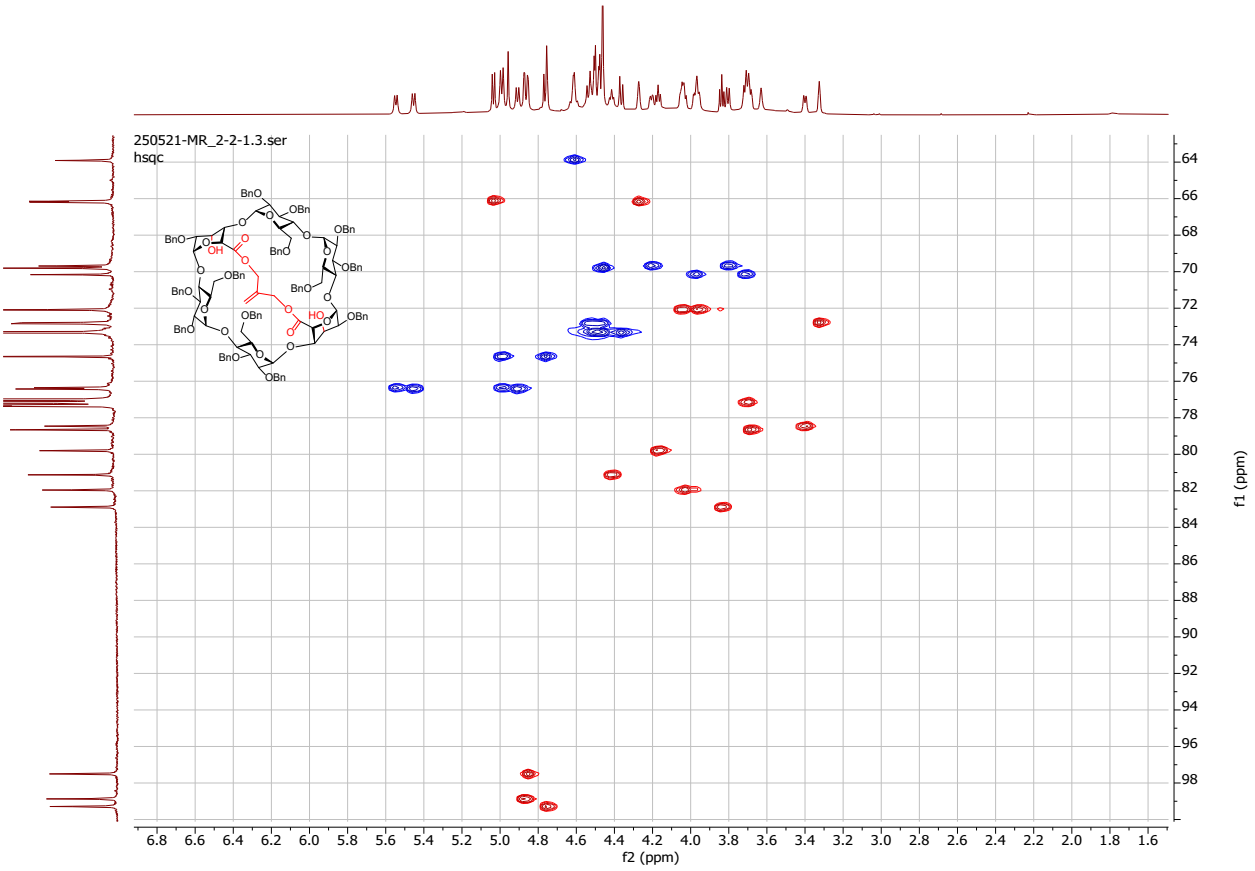
^{13}C NMR spectrum (126 MHz, $CDCl_3$) of compound **7**



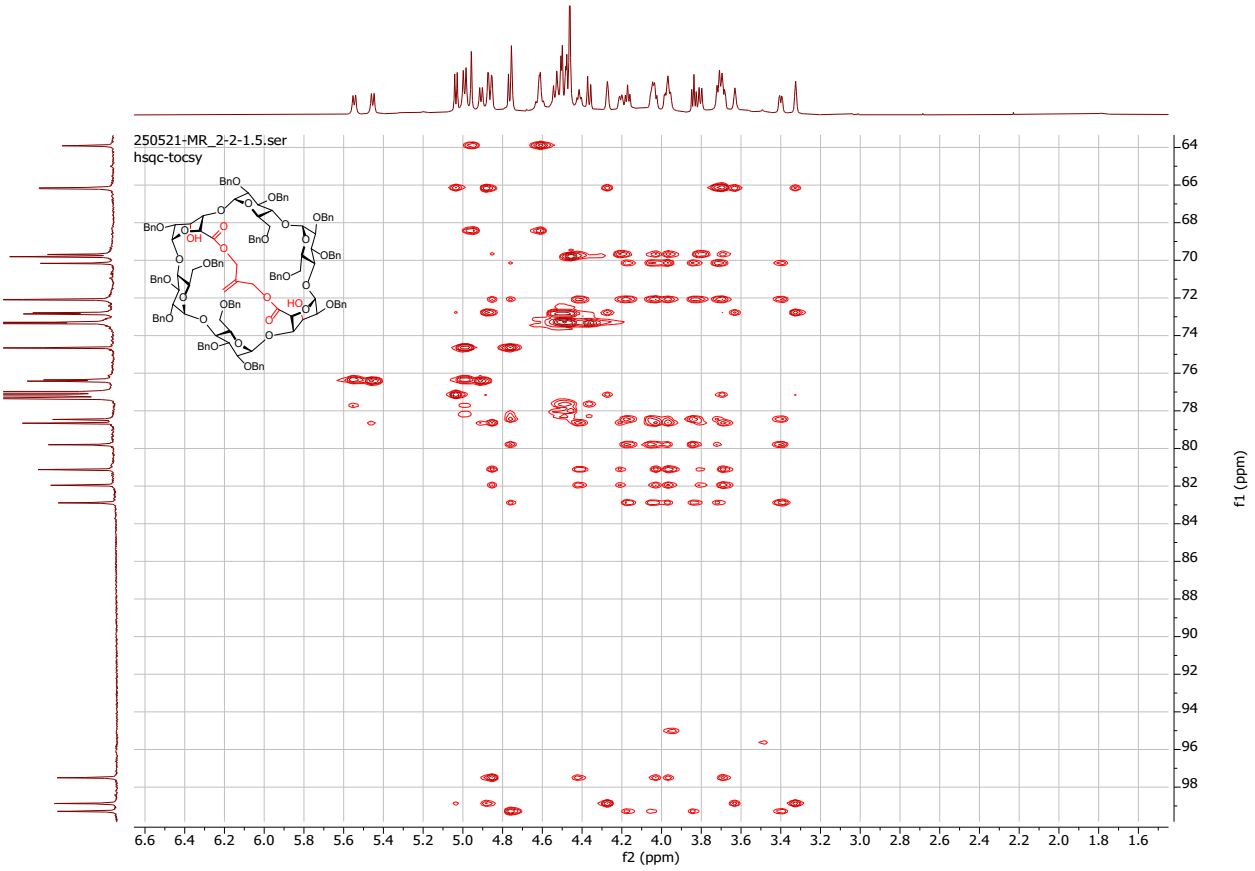
^{1}H NMR spectrum (800 MHz, $CDCl_3$) of compound **10**



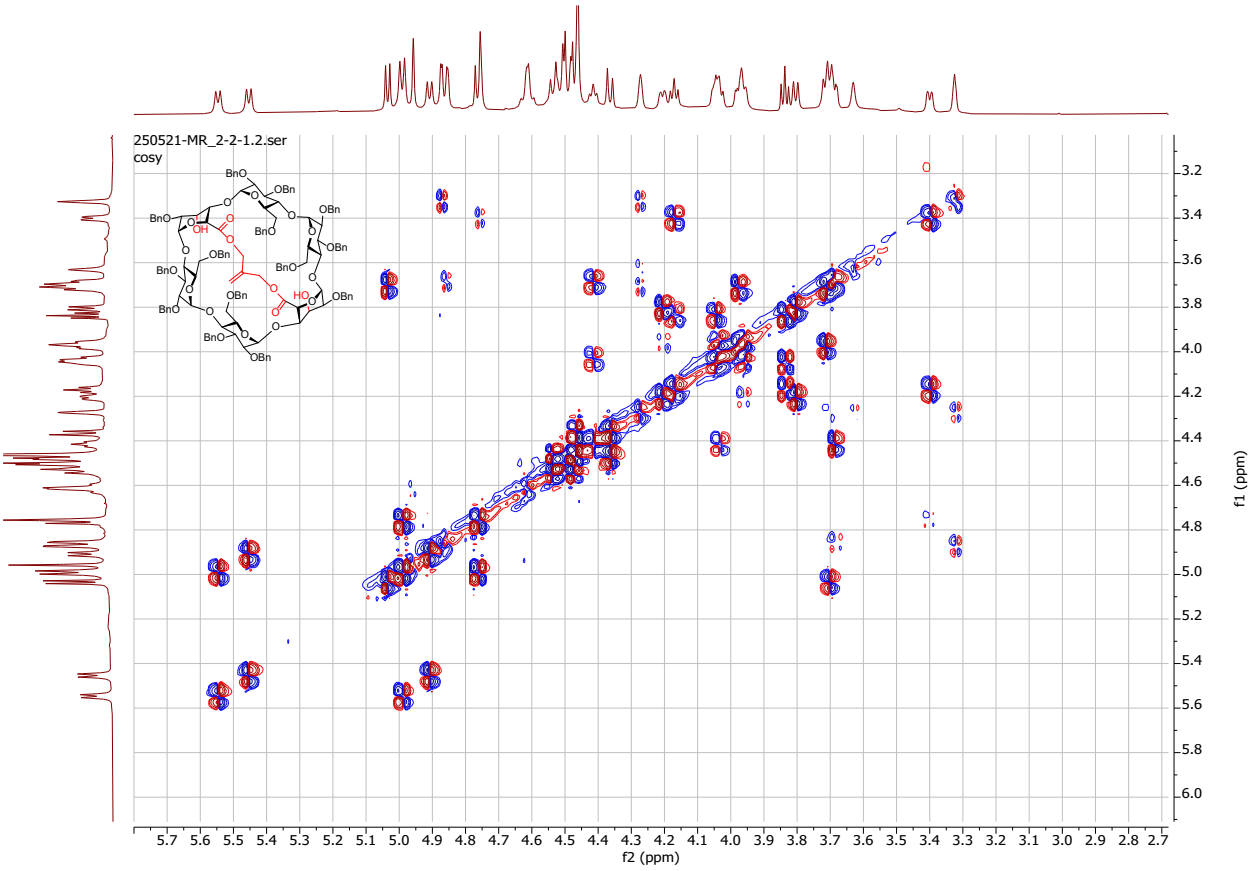
^{13}C NMR spectrum (201 MHz, $CDCl_3$) of compound **10**



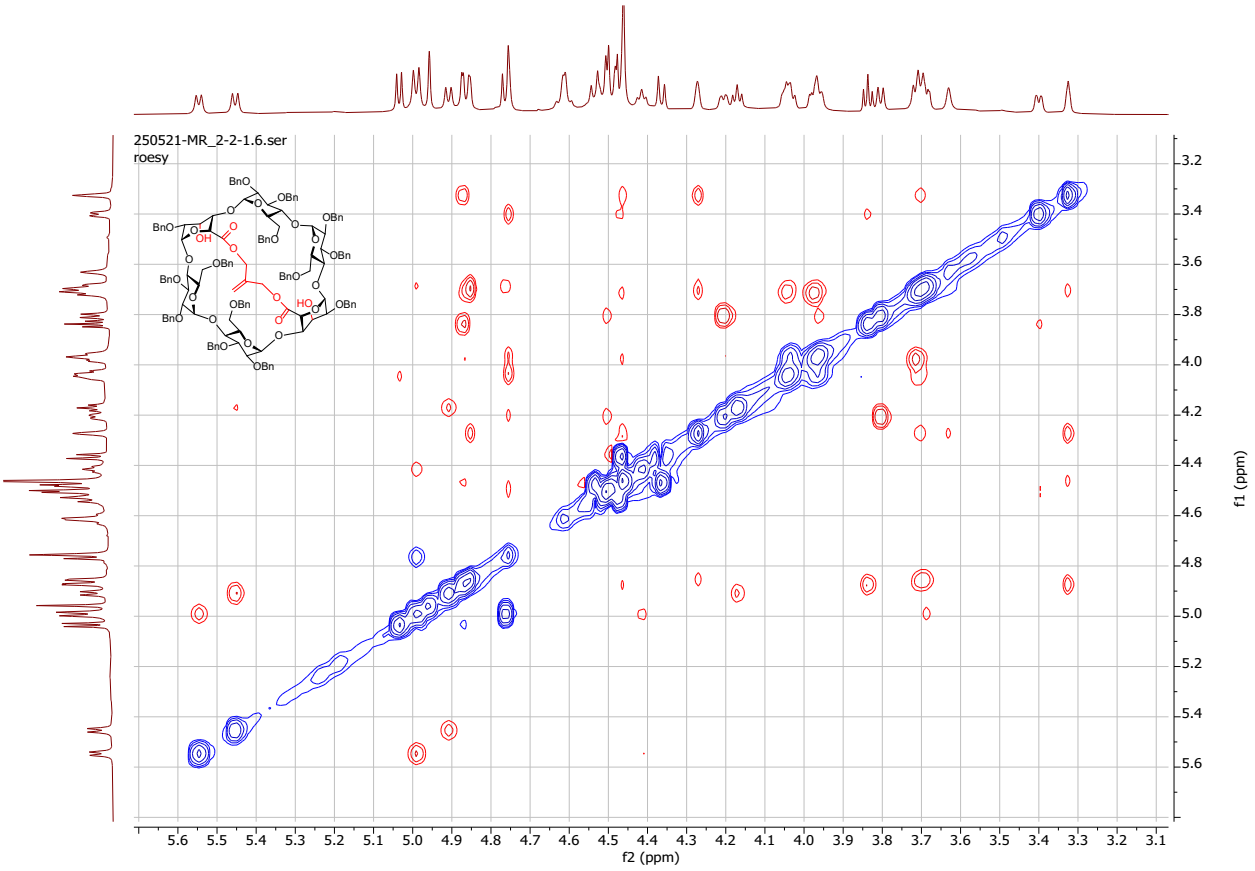
HSQC spectrum (800 MHz, $CDCl_3$) of compound **10**



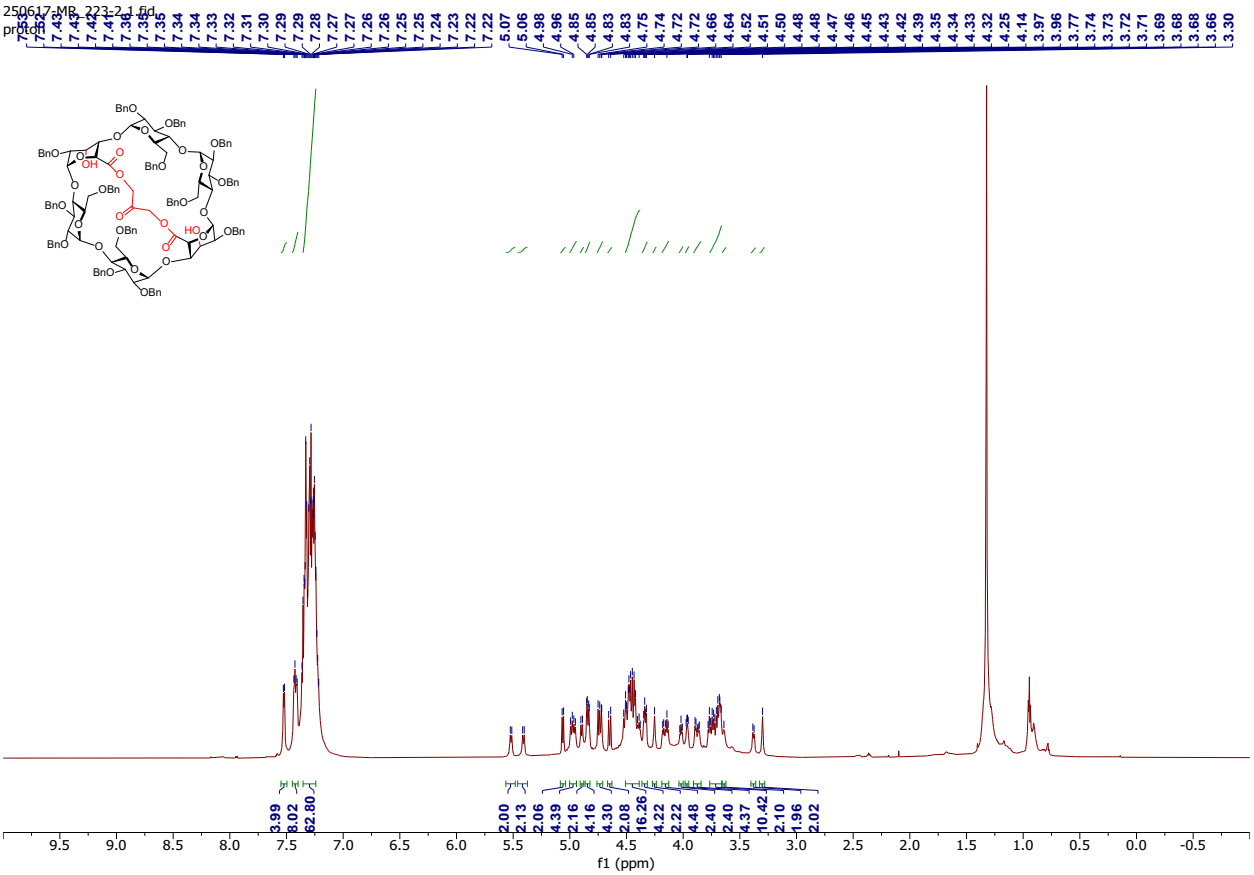
HSQC-Tocsy spectrum (800 MHz, $CDCl_3$) of compound **10**



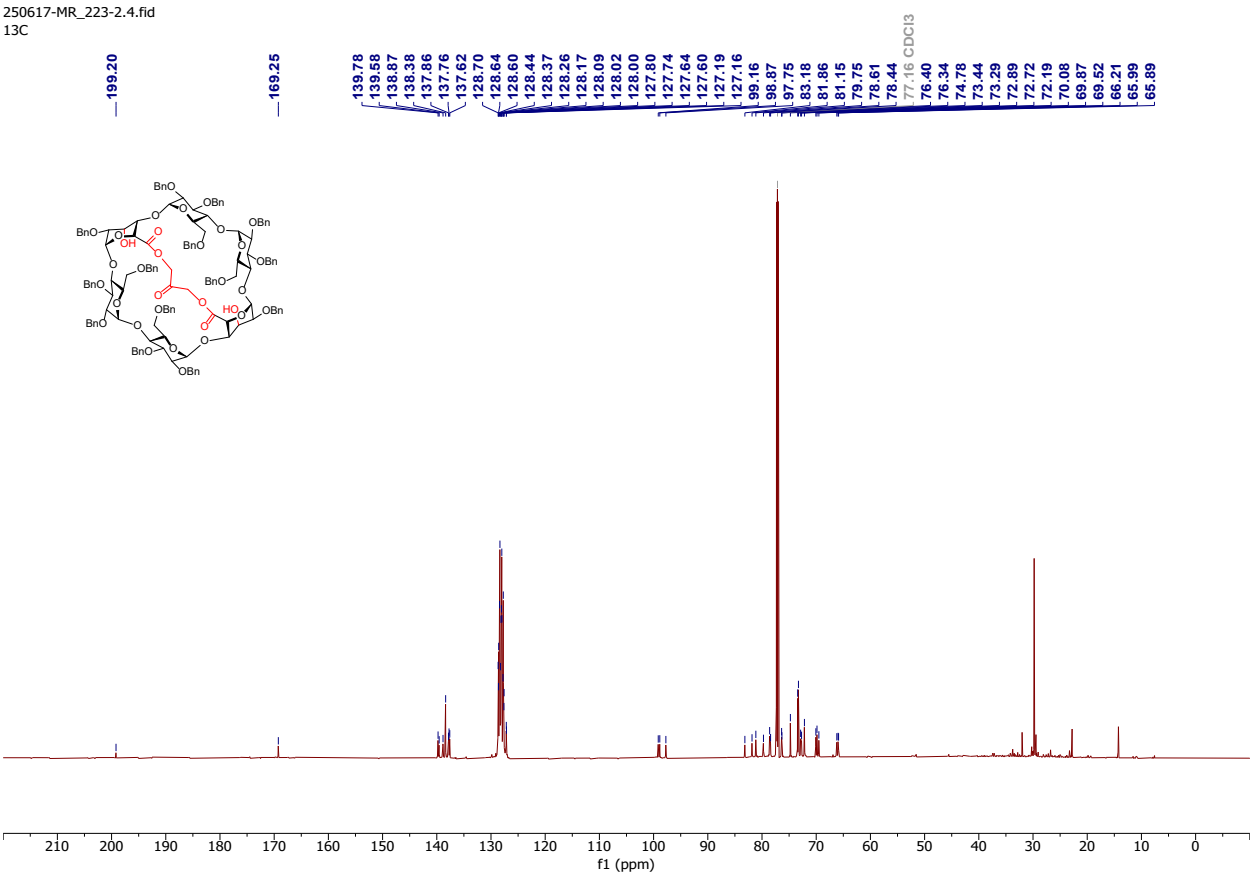
Cosy NMR spectrum (800 MHz, $CDCl_3$) of compound **10**



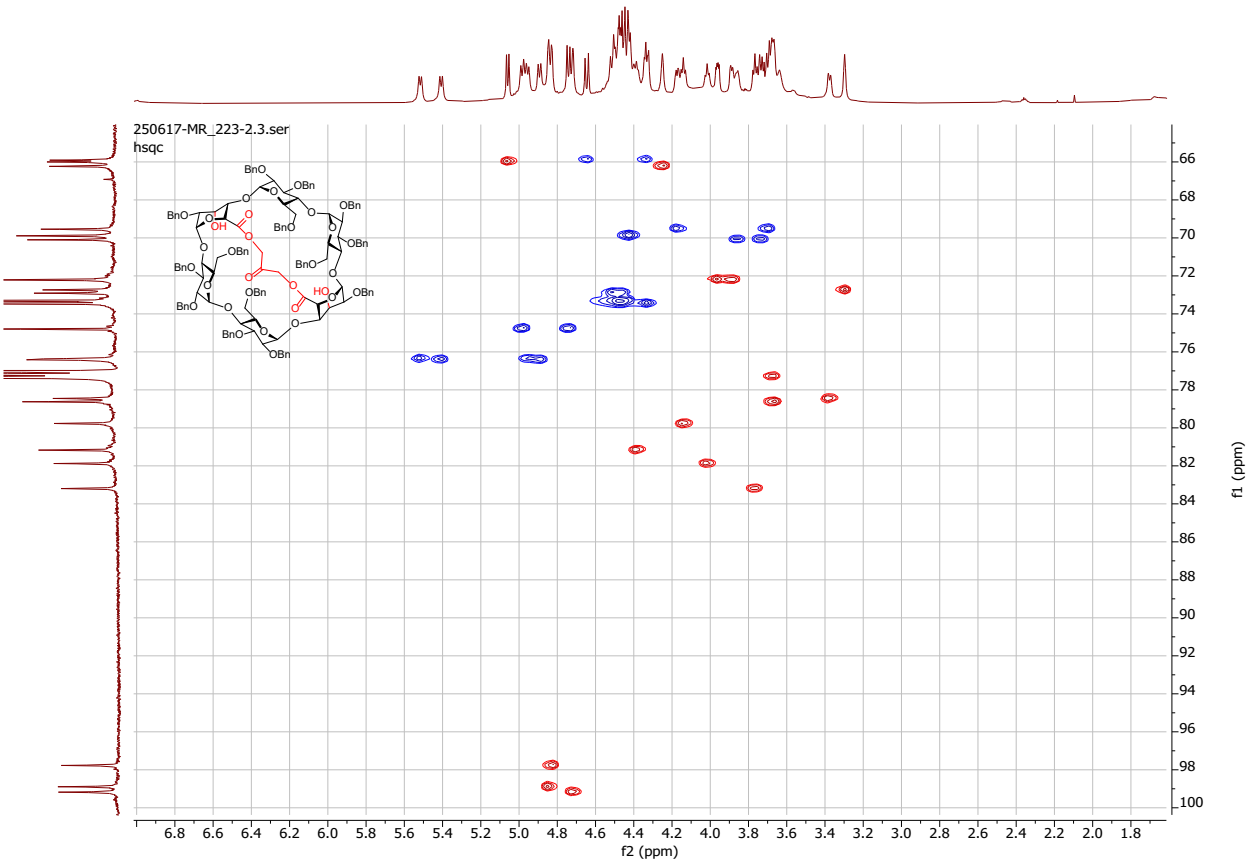
Roesy NMR spectrum (800 MHz, $CDCl_3$) of compound **10**



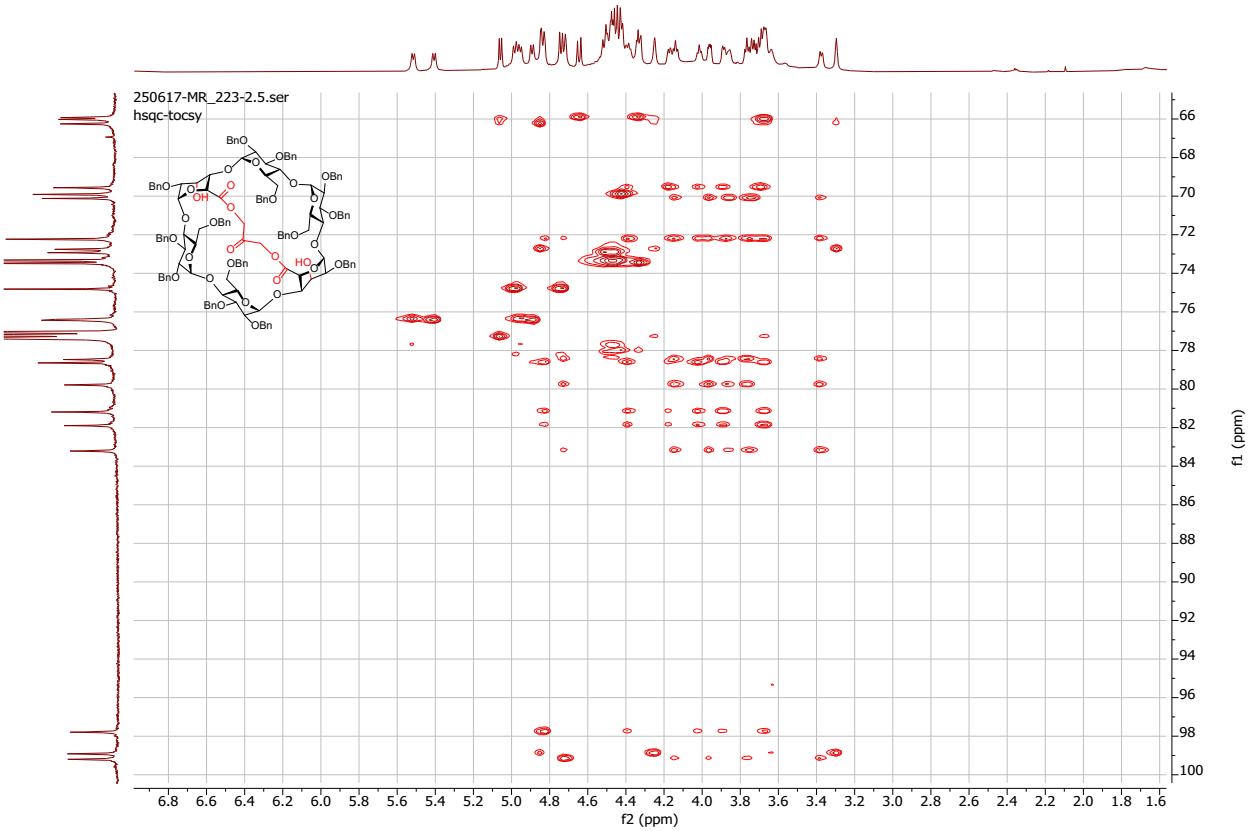
^{1}H NMR spectrum (800 MHz, $CDCl_3$) of compound **11**



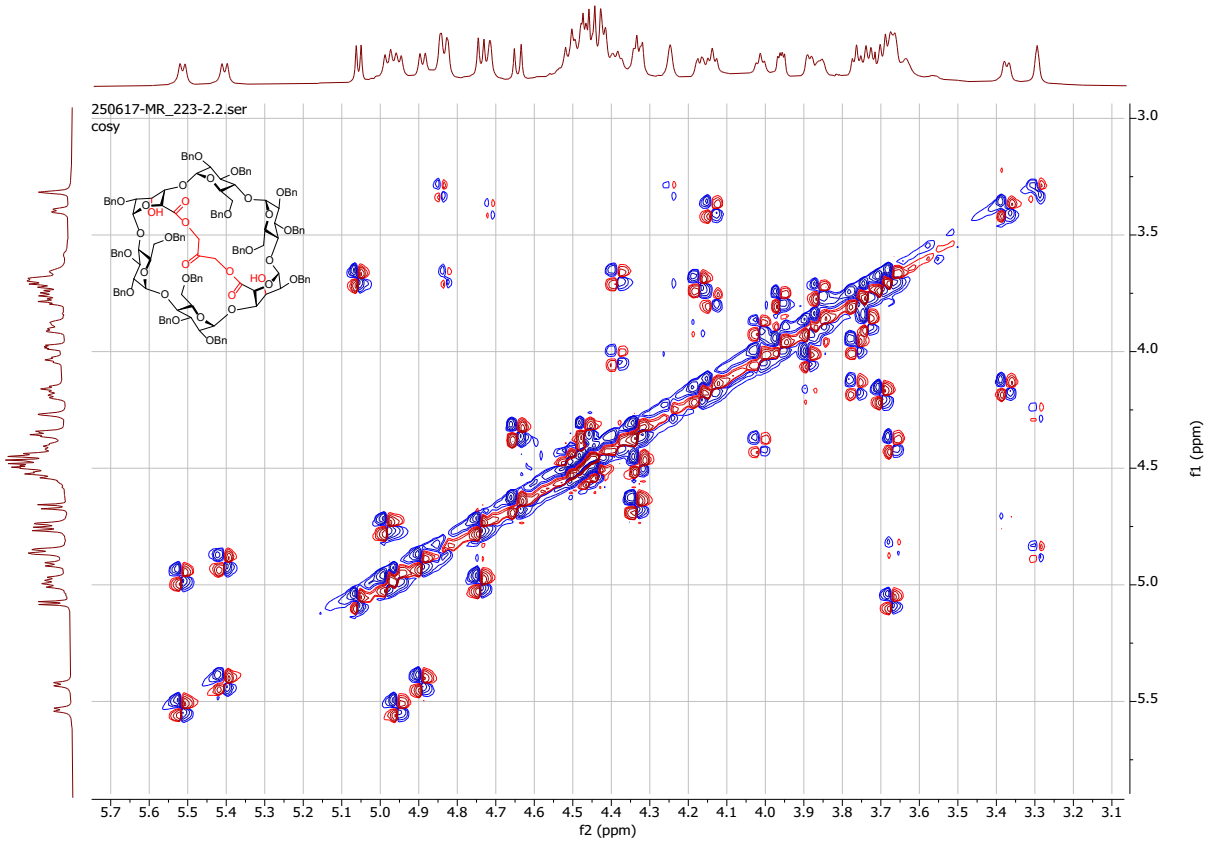
^{13}C NMR spectrum (201 MHz, $CDCl_3$) of compound **11**



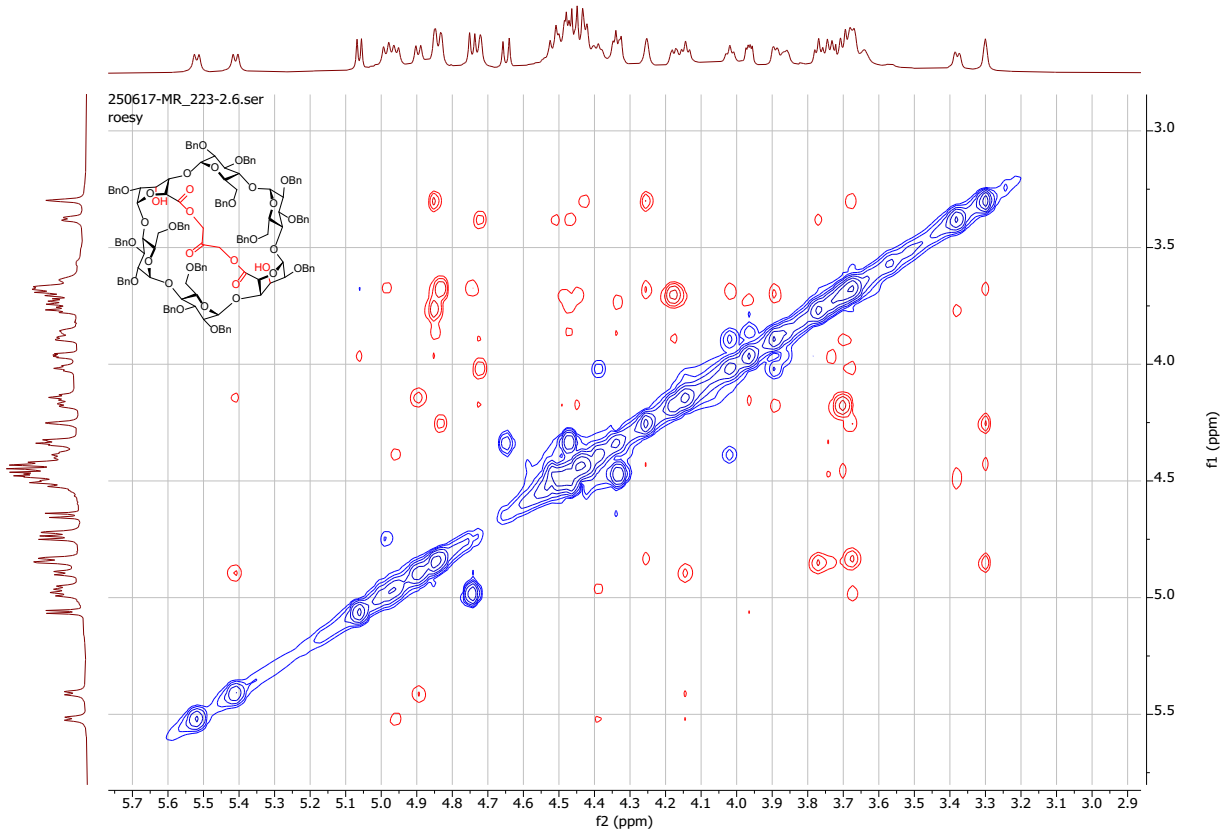
HSQC spectrum (800 MHz, $CDCl_3$) of compound **11**



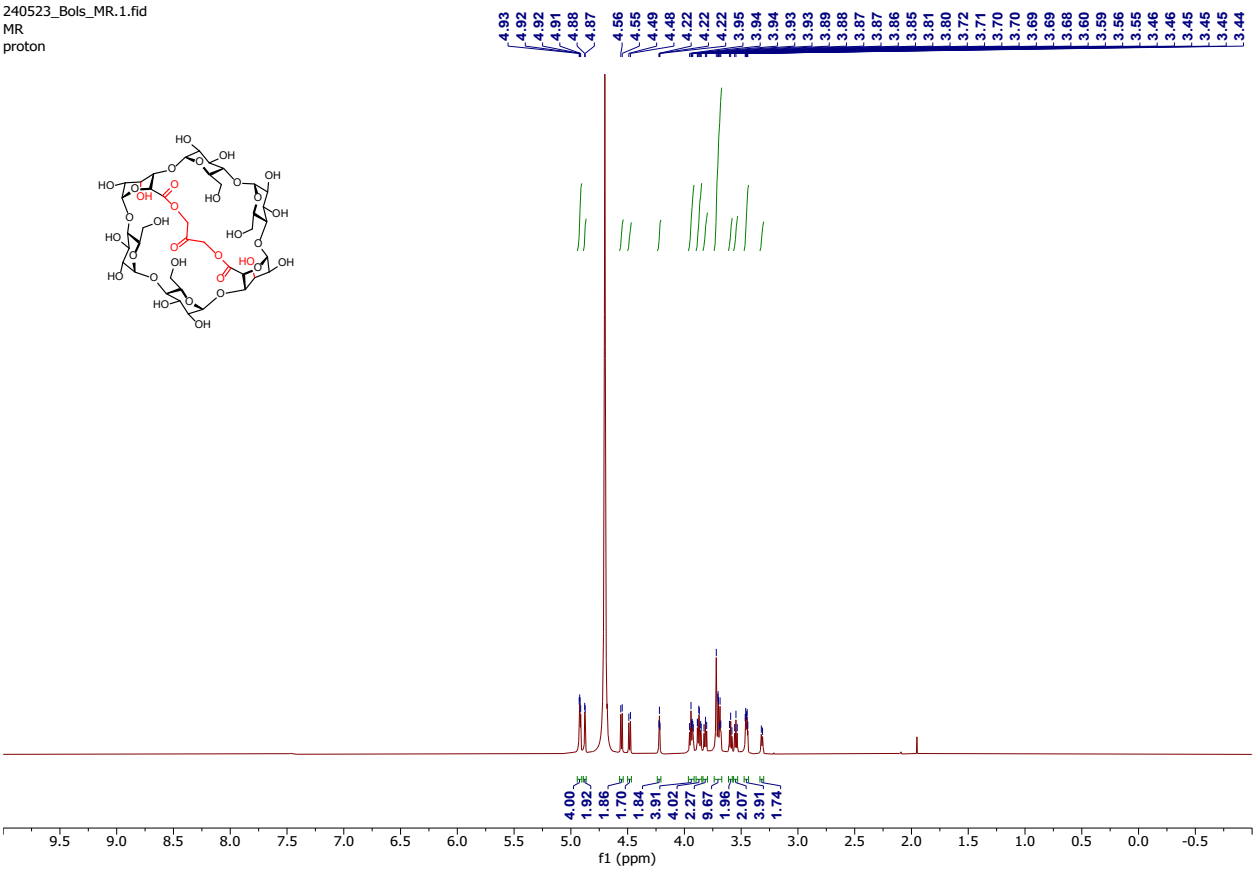
HSQC-Tocsy spectrum (800 MHz, $CDCl_3$) of compound **11**



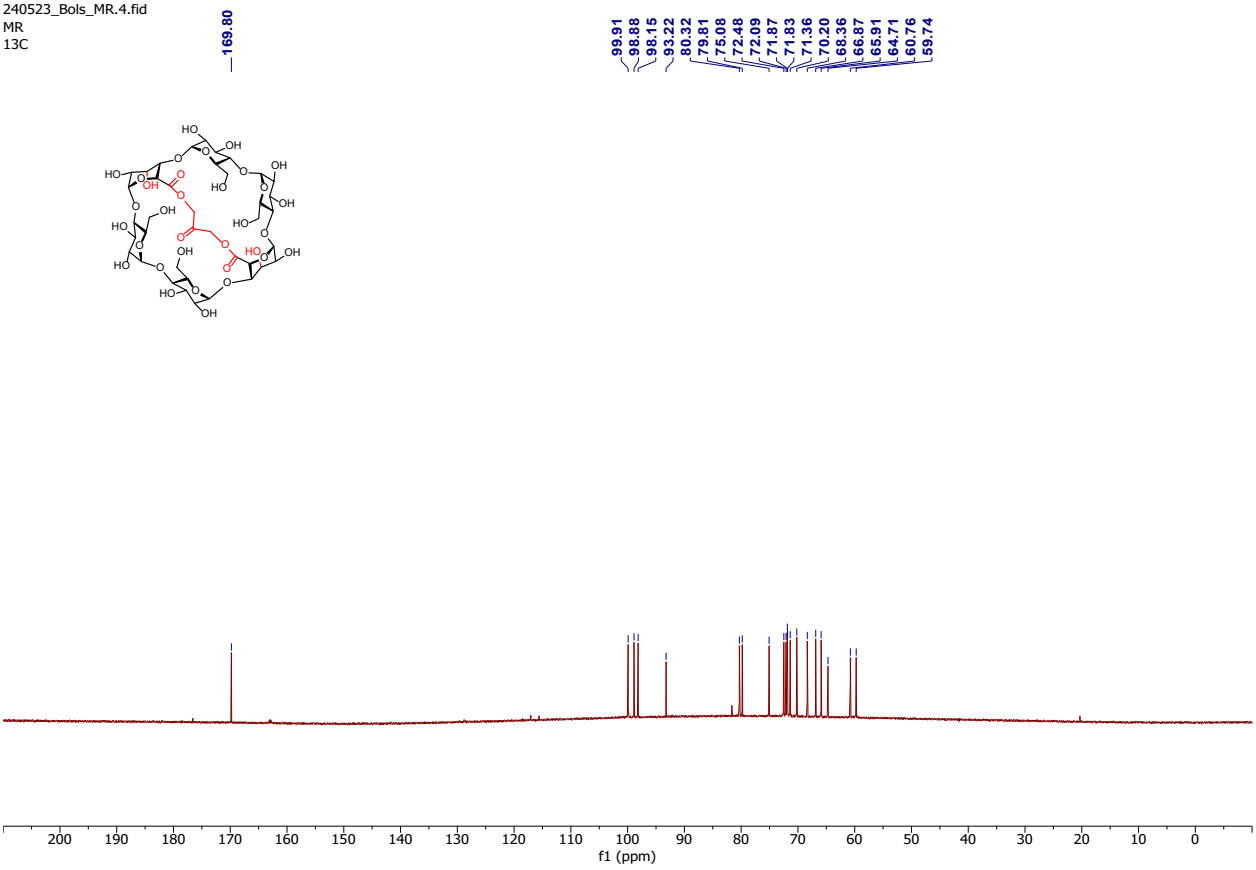
Cosy NMR spectrum (800 MHz, $CDCl_3$) of compound **11**



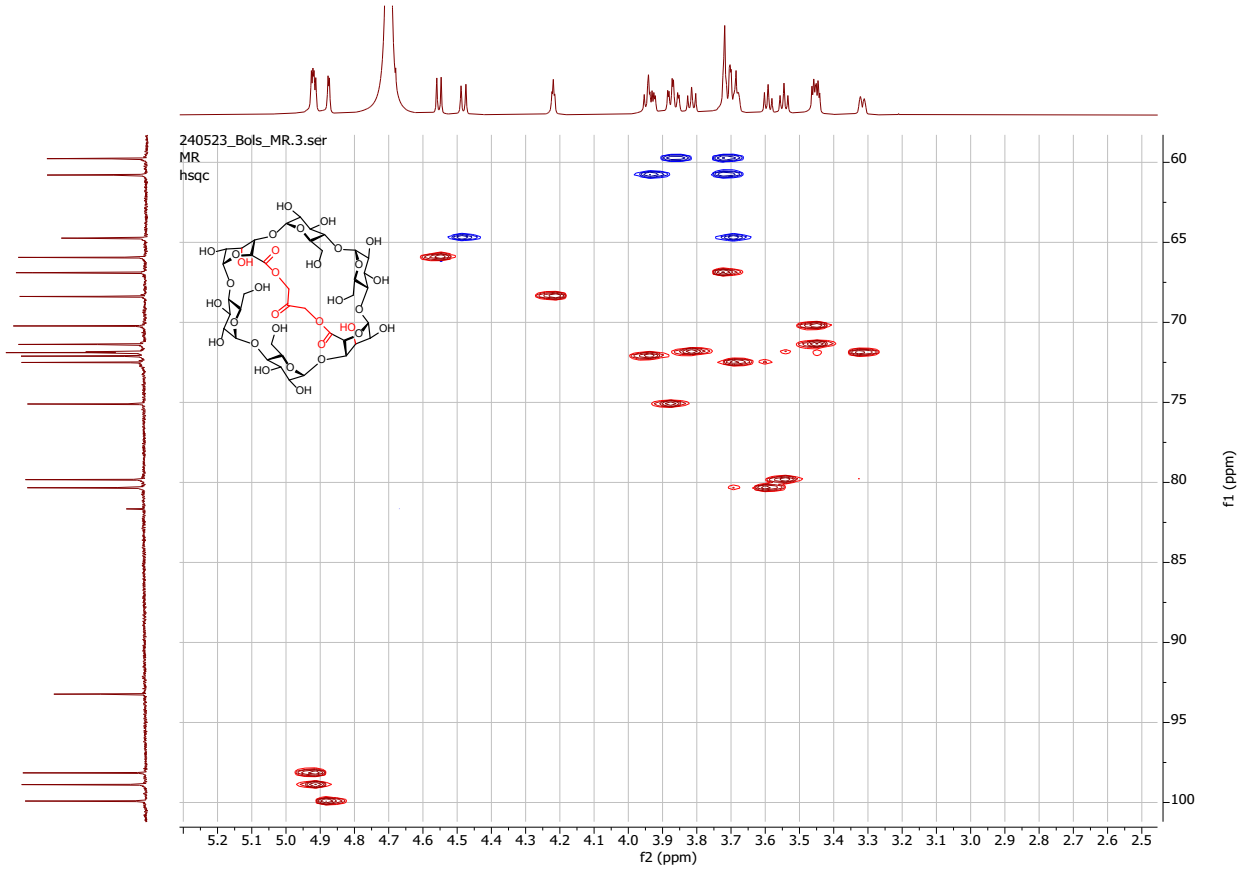
Roesy NMR spectrum (800 MHz, $CDCl_3$) of compound **11**



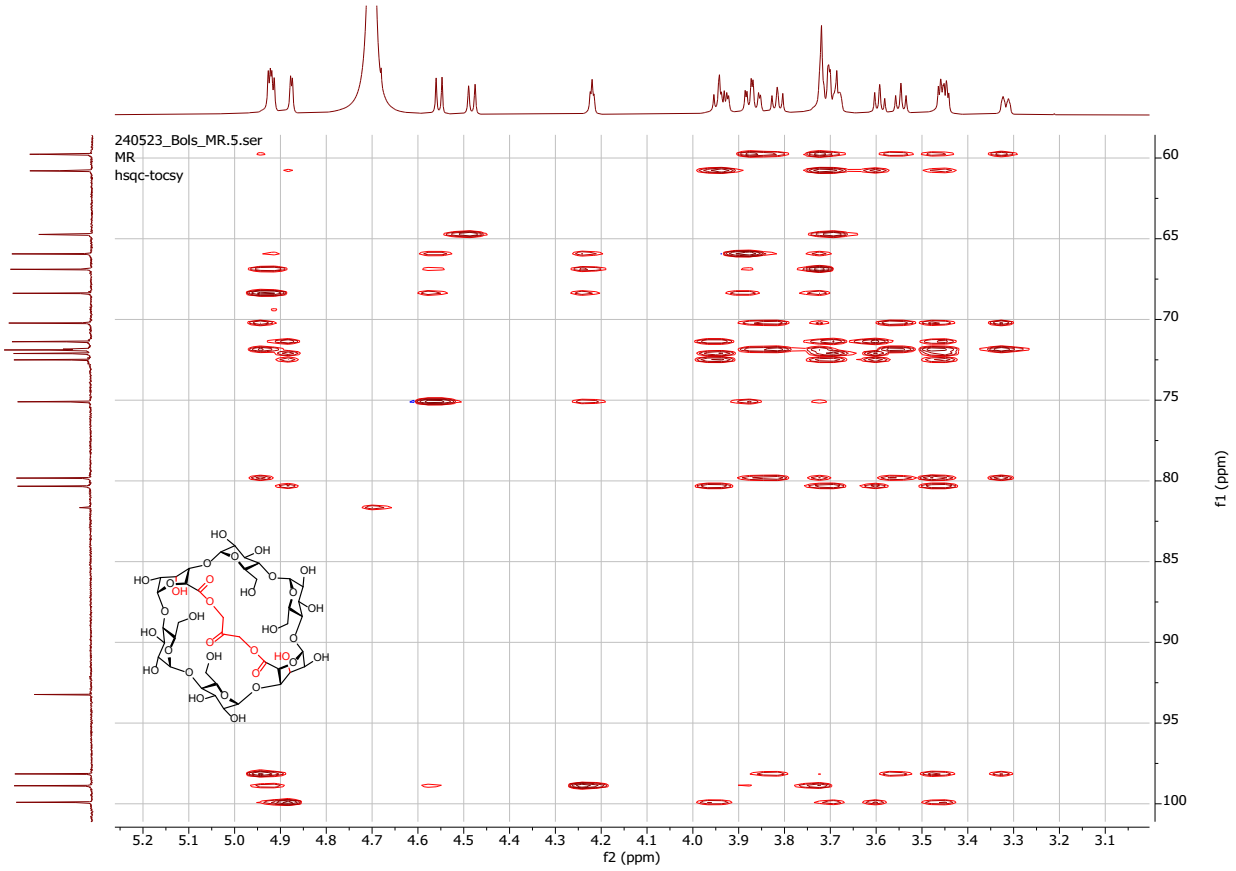
^{1}H NMR spectrum (800 MHz, D_2O) of compound **12**



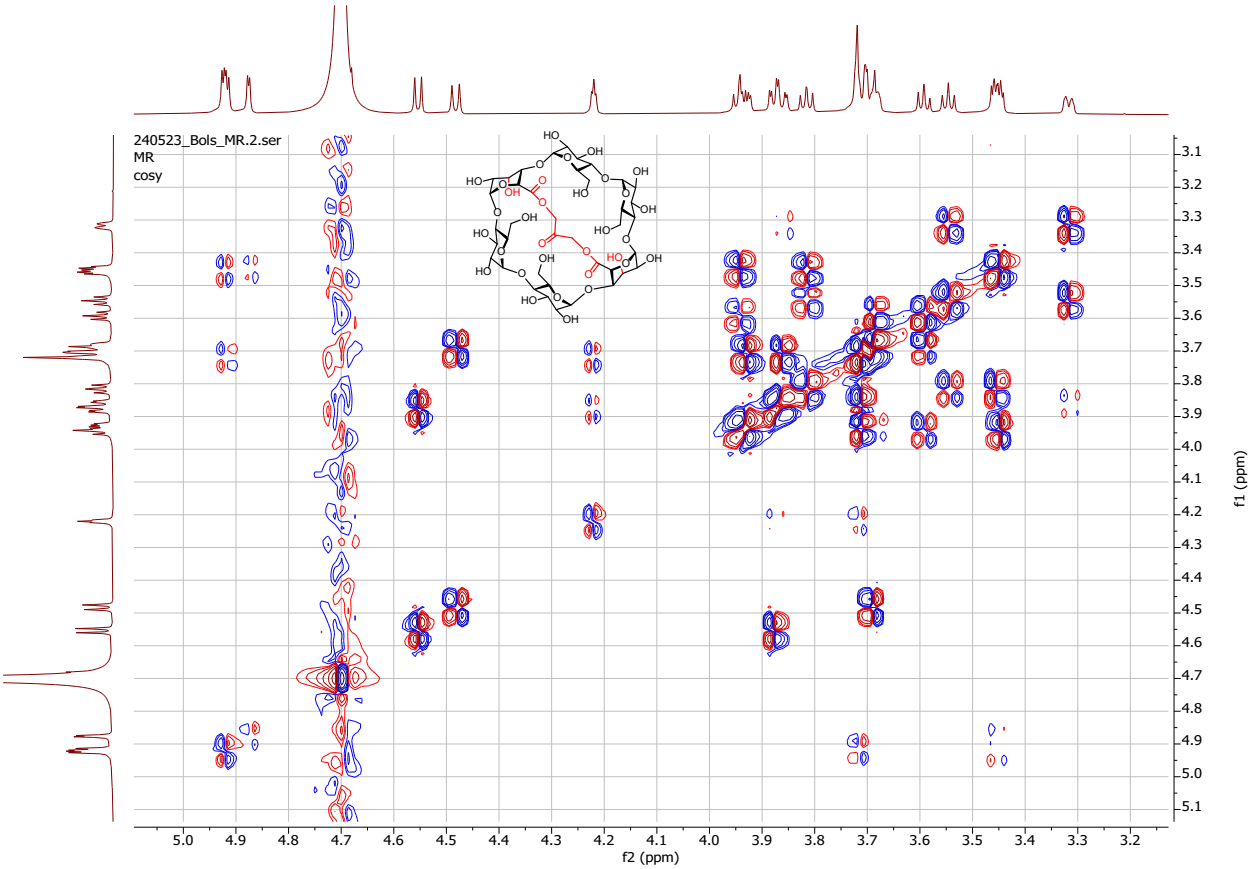
^{13}C NMR spectrum (201 MHz, D_2O) of compound **12**



HSQC spectrum (800 MHz, D_2O) of compound **12**



HSQC-Tocsy NMR spectrum (800 MHz, D_2O) of compound **12**



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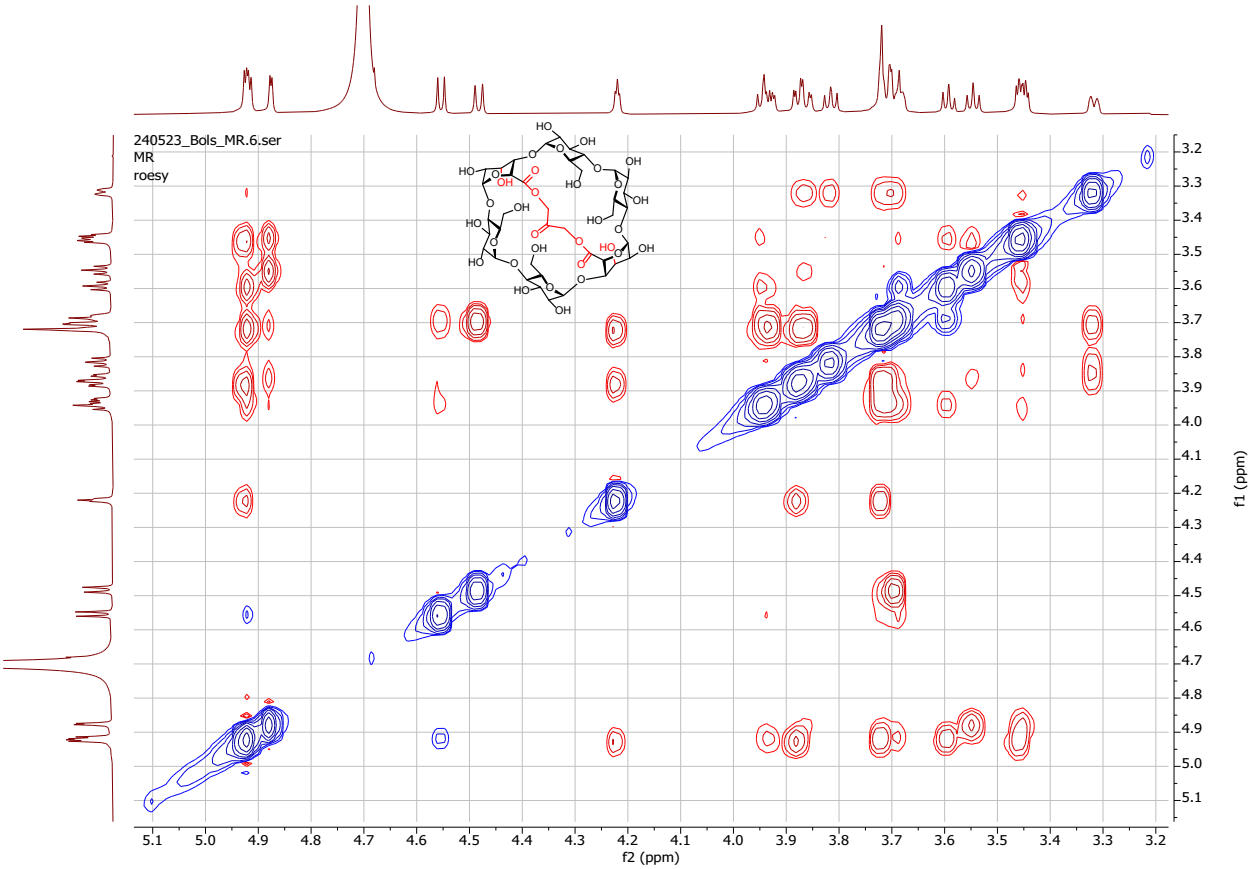

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