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Supplementary Material for:

Enhanced Squaraine Rotaxane Endoperoxide Chemiluminescence in Acidic Alcohols

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Contents

A. Structural Elucidation of Squaraine Rotaxane Diol 6:

A drop of D_2O was added to an NMR tube containing **6** (1.0 mM) and the mixture was shaken vigorously. After allowing the mixture to stand for 15 minutes, the samples was cooled to -40°C and a spectrum was taken. At this time, the solvent was removed under reduced pressure. The dry film was dissolved in $CDCl_3$ and the process was repeated using H_2O.

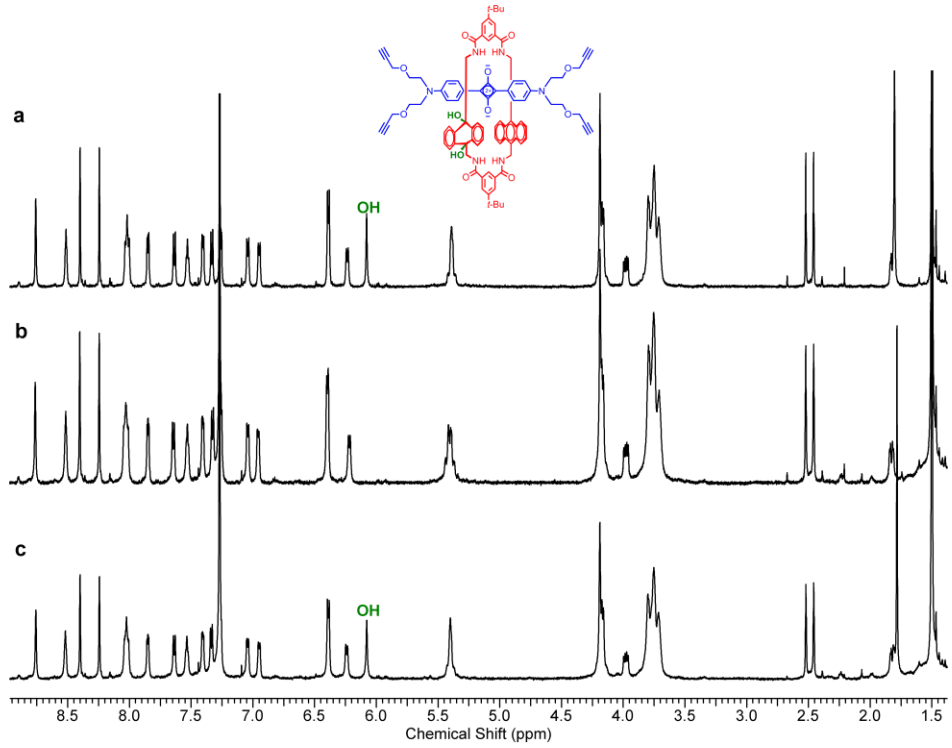


Figure S1: Deuterium exchange studies on **6** (600MHz, $CDCl_3$, -40°C). (a) Before addition of D_2O; (b) After addition of D_2O; (c) After removal of solvent and addition of H_2O.

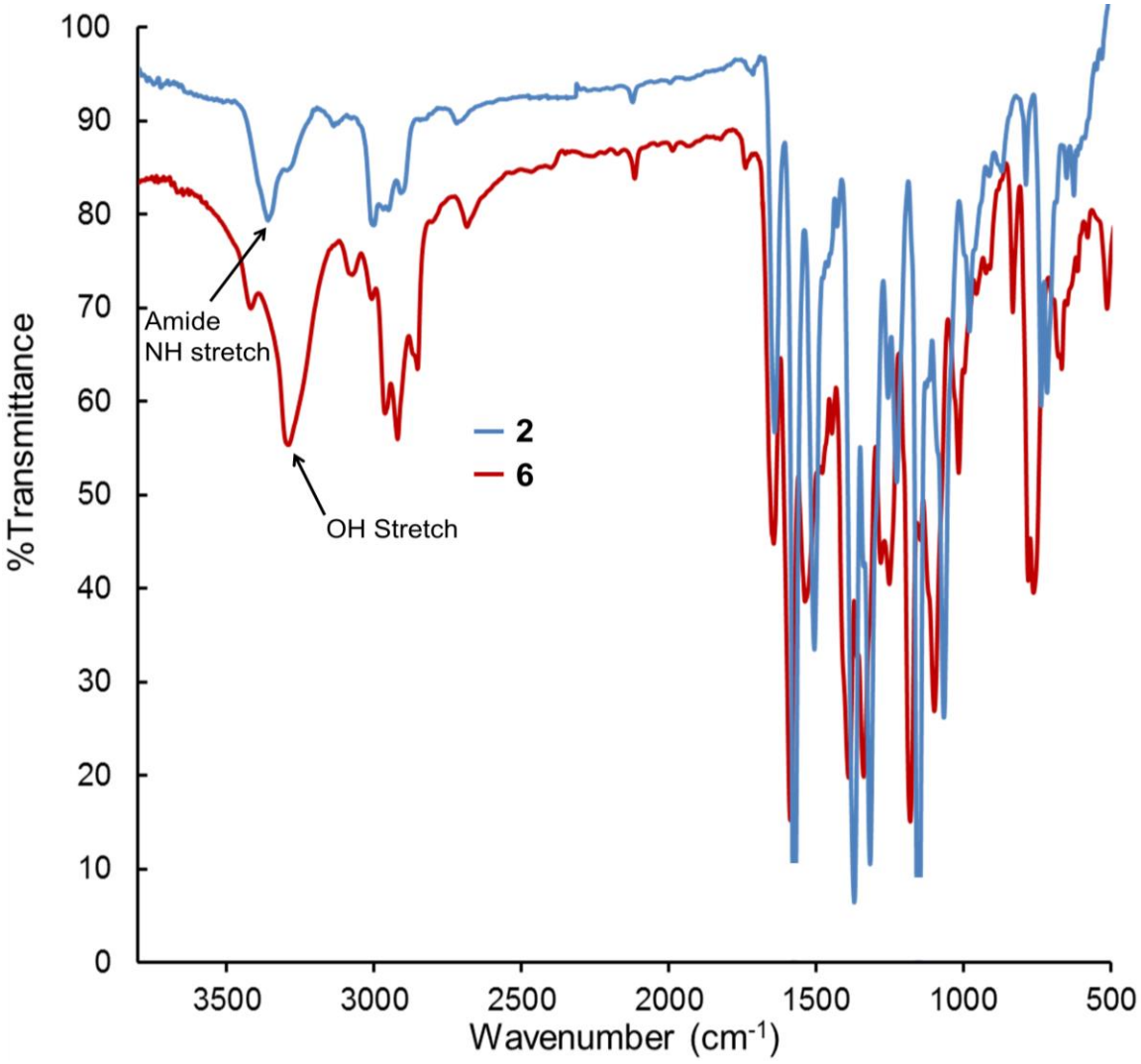


Figure S2: IR-spectrum of **2** and **6**, indicating the presence of an OH group. Amide N-H stretches are present in the parent squaraine rotaxane **2** at 3300 cm^{-1}, however the OH stretch in the diol-containing **6** appears at 3280 cm^{-1} and its signature is quite different from that of **2**. It is interesting to note that in both compounds the alkyne C-C and C-H stretches, although present, are much weaker than expected.

B. Variable Temperature NMR Studies:

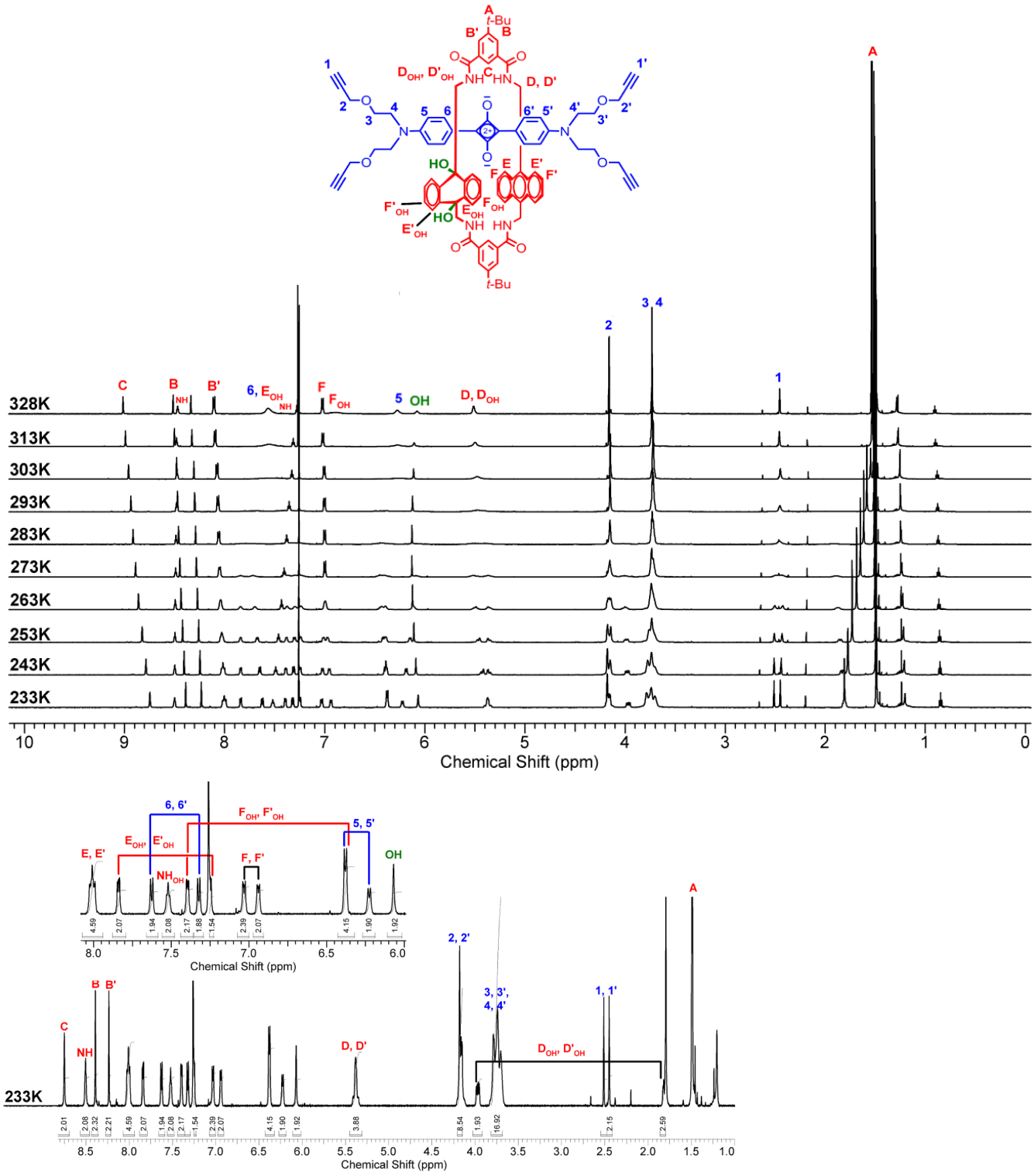


Figure S3: Variable temperature NMR of **6** ($CDCl_3$, 600MHz)

The exchange rate at the coalescence temperature was determined using:

$$k = \frac{\pi}{\sqrt{2}}\Delta v_0$$

Where Δv_0 is the limiting chemical shift difference of two exchanging protons (in Hz). To determine the free energy of activation (in kcal·mol^{-1}), the Eyring equation was simplified into the following form:

$$\Delta G^{\ddagger} = 4.57\, T_C \left[9.97 + log_{10}\left(\frac{T_C}{\Delta v_0}\right)\right]$$

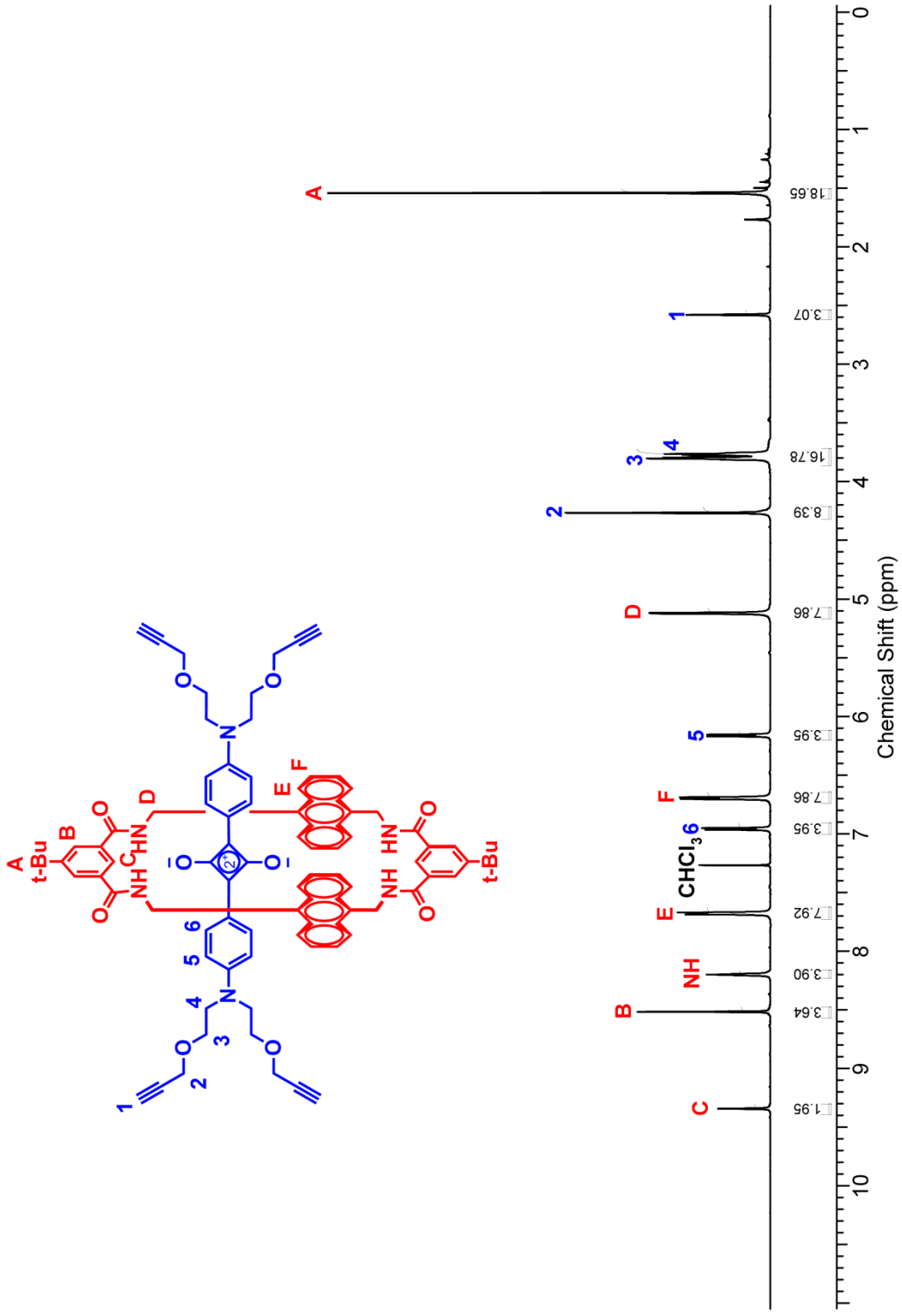
Where T_C is the coalescence temperature (in K).

Table S1: Summary of DNMR data from *Figure S3.*

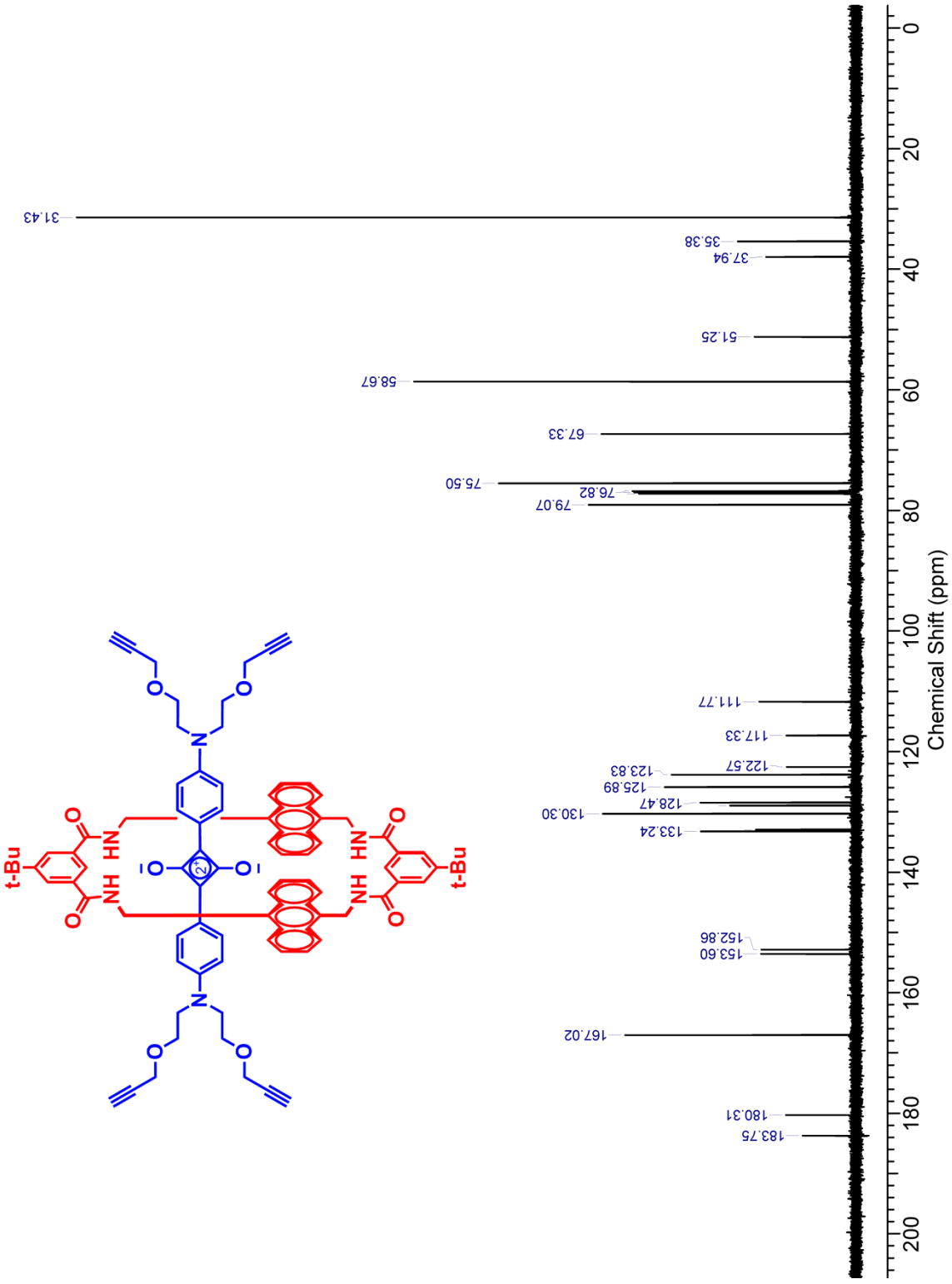
Proton	Δv_0 (Hz)[a]	T_C (K)[b]	$\Delta G^{\ddagger}$(kcal·mol^{-1})[c]
E_{OH}	267	283	14.4
F	55	268	13.1
1	38	278	13.7

[a]Frequency difference of limiting chemical shifts at 233 K.
[b]Coalescence temperature, error ± 5 K.
[c]Calculated free energy of activation

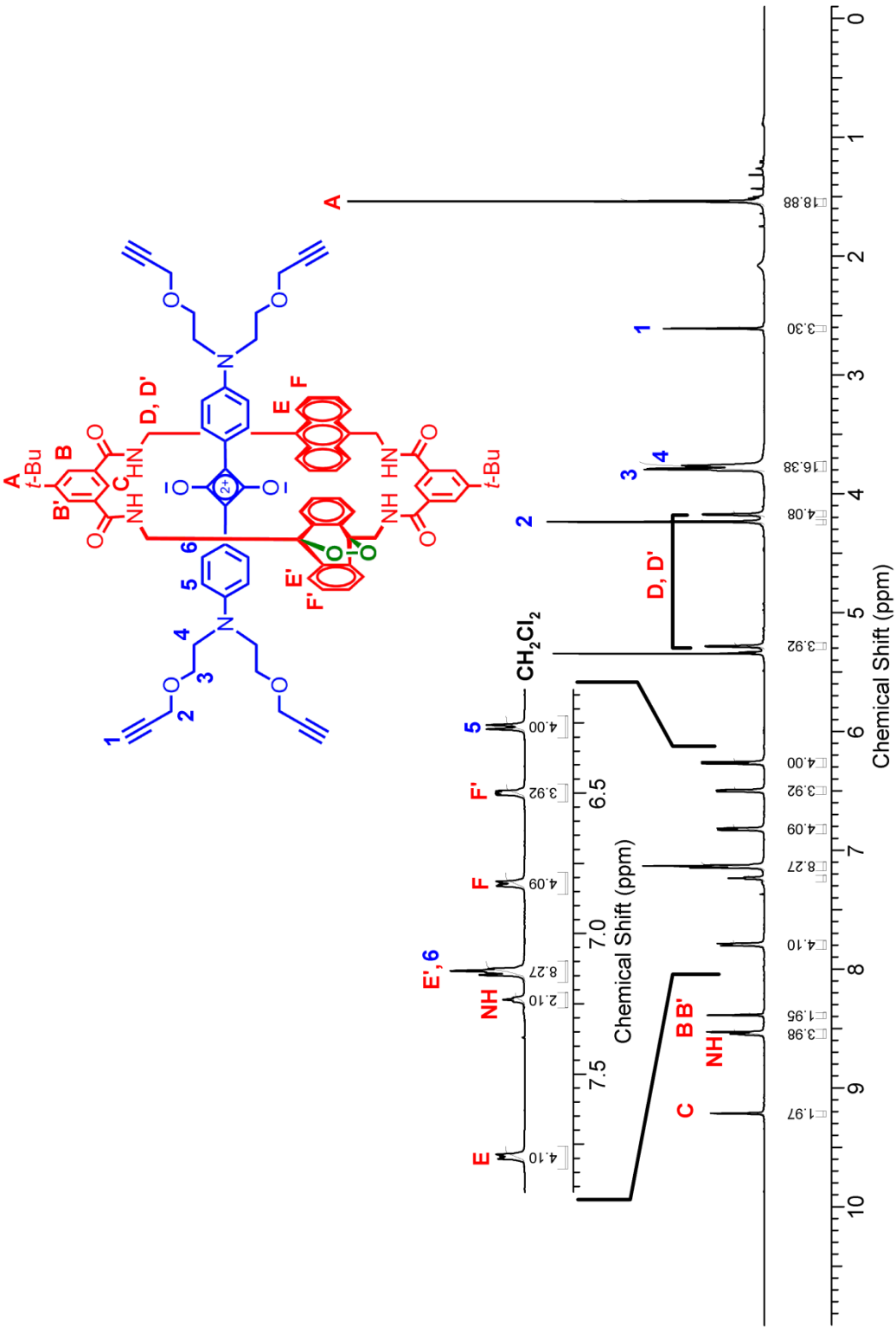
C. ^{1}H and ^{13}C NMR Spectra:



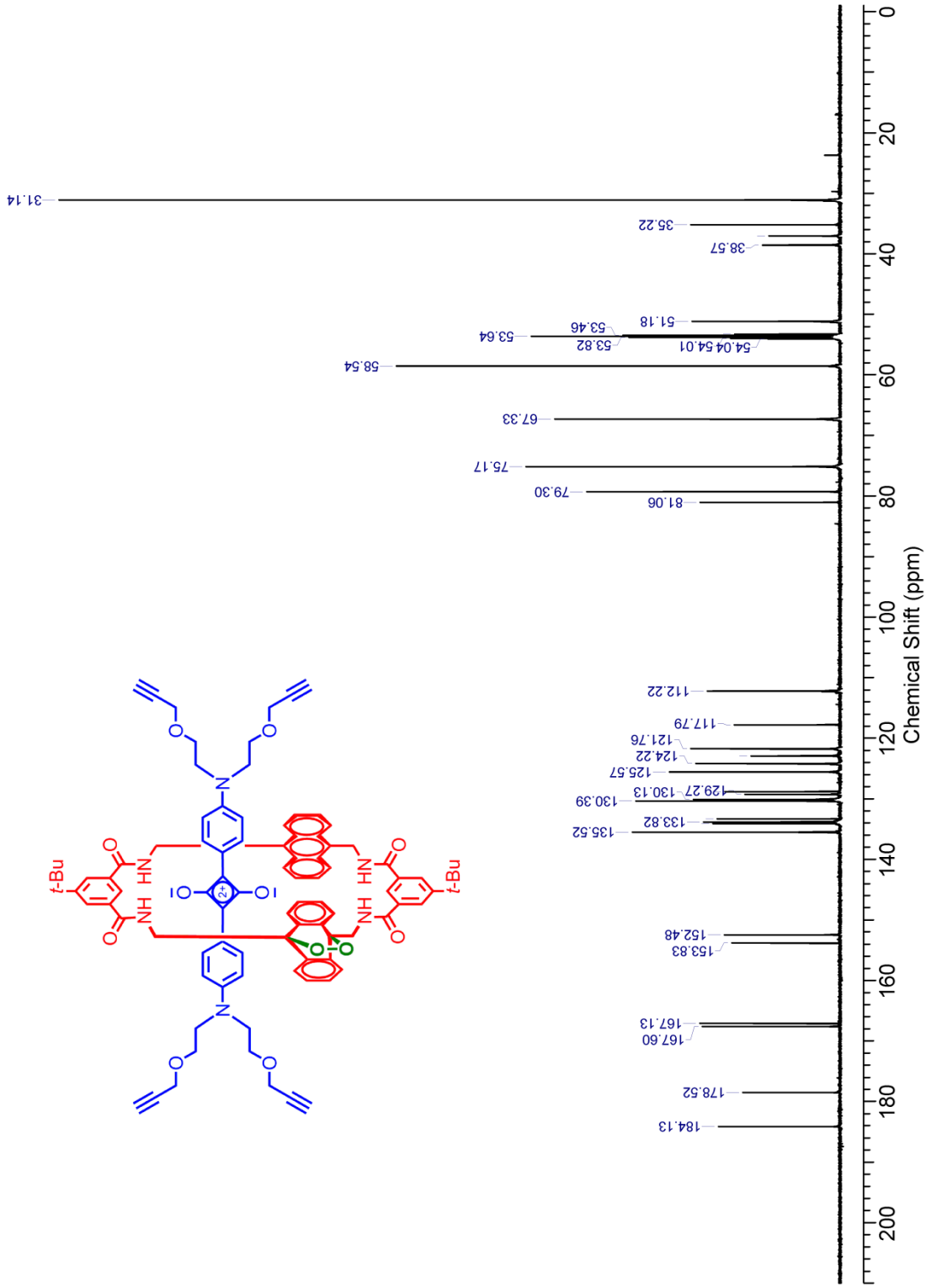
^{1}H NMR (500 MHz, $CDCl_3$, 23°C) spectrum of squaraine rotaxane, **2**.



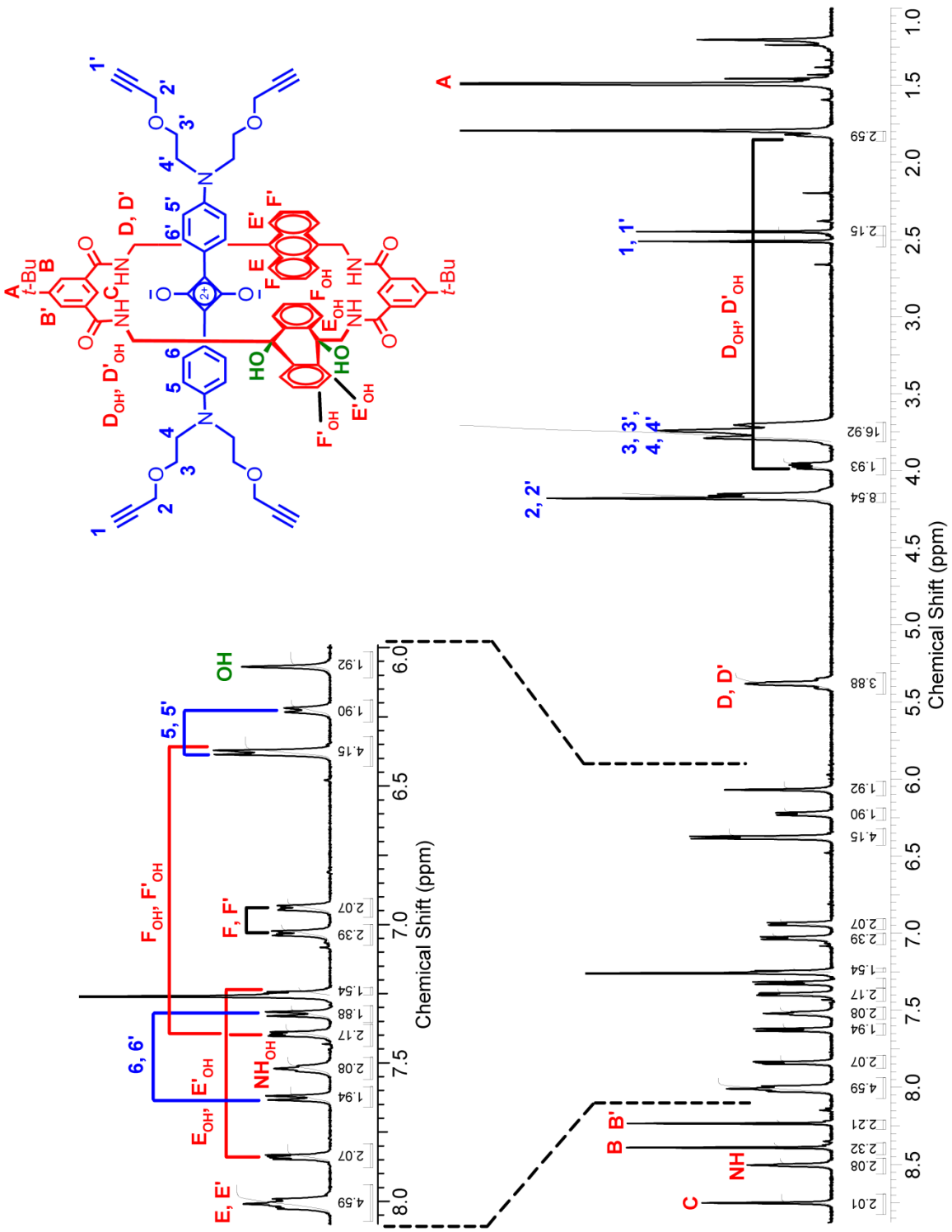
^{13}C NMR (150 MHz, $CDCl_3$, 23°C) spectrum of squaraine rotaxane **2**.



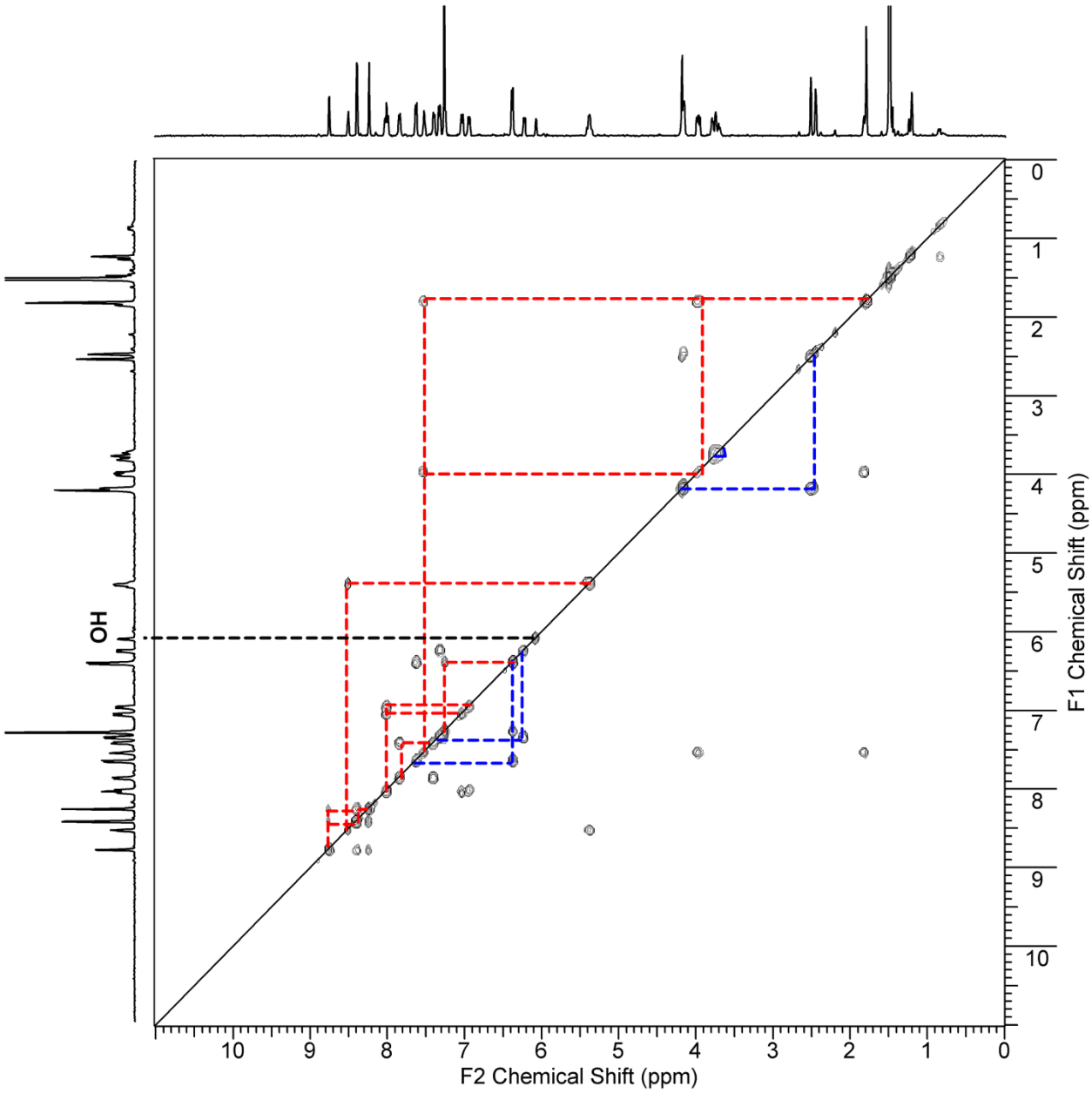
^{1}H NMR (600 MHz, CD_2Cl_2, 0°C) spectrum of SREP, **2EP**.



^{13}C NMR (150 MHz, CD_2Cl_2, 0°C) spectrum of SREP **2EP**.



^{1}H NMR (600 MHz, $CDCl_3$, -40°C) spectrum of squaraine rotaxane, **6**.



COSY-NMR of squaraine rotaxane diol **6**.