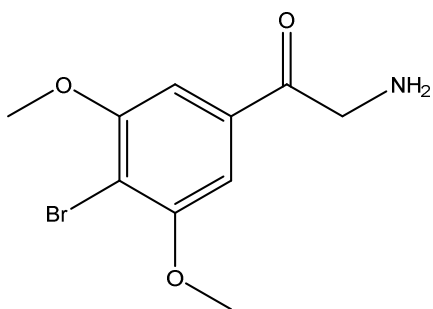
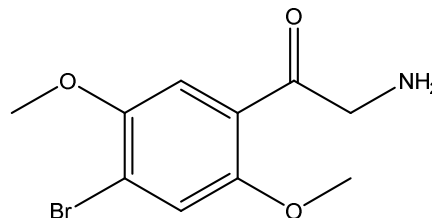


Report on NMR spectroscopy of BK-2CB

NMR spectra for BK-2CB, recorded in DMSO- d_6 , are enclosed. Rather than the structure proposed (**1**), the spectra appear to be more consistent with a structure where the methoxy groups are *para* to each other (**2**). In particular, the symmetry of structure **1** would be expected to make the two aromatic hydrogens chemically equivalent, the two OMe groups equivalent, and give rise to just four aromatic ^{13}C peaks (since the two C-OMe aromatic carbons and the two C-H carbons are identical); instead the spectra show two *inequivalent* aromatic protons, two *inequivalent* OMe groups, and six inequivalent aromatic carbons. This appears to suggest no plane of symmetry within the benzene ring.



1



2

The amine peak is observed as a broad singlet of relative area 3, suggesting that the compound exists in solution as an NH_3^+ salt

A full list of chemical shifts, and proposed assignments, are given below. The assignments are fully supported by PENDANT, COSY, NOESY, HSQC and HMBC experiments, some of which are commented on.

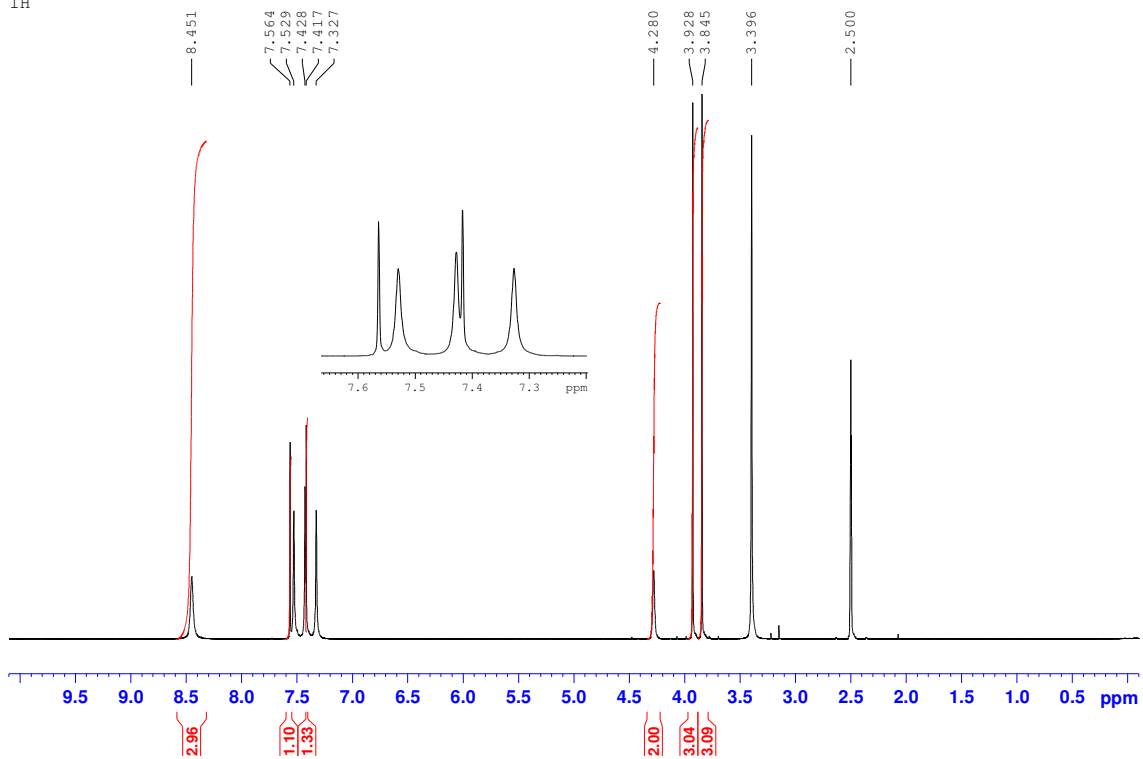
¹ H NMR (multiplicity, integration)	Assignment	Comments
8.40 (s, 3)	NH ₃	¹ H- ¹⁵ N correlation shows correlation to ¹⁵ N signal at ca 31 ppm, consistent with a primary amine or ammonium ion
7.56 (s, 1)	Aromatic CH	Shows weak COSY and NOESY correlations to OCH ₃ at 3.93 ppm
7.42 (s, 1)	Aromatic CH	Shows weak COSY and NOESY correlations to OCH ₃ at 3.84 ppm
4.28 (s, 2)	CH ₂	Shows COSY correlation to NH ₃ at 8.40
3.93 (s, 3)	OCH ₃	
3.84 (s, 3)	OCH ₃	
¹³ C NMR	Assignment	Comments
191.2	C=O	Shows HMBC peaks to the two aromatic protons
154.0	Aromatic C	Non-protonated
149.7	Aromatic C	Non-protonated
122.6	Aromatic C	Non-protonated
119.2	Aromatic C	Non-protonated
118.4	Aromatic CH	
111.8	Aromatic CH	
57.1	OCH ₃	
56.7	OCH ₃	
48.6	CH ₂	

The ¹H spectrum contains additional peaks, most notably a 1:1:1 triplet (J = 50.8 Hz) at δ 7.43 ppm. This correlates to a signal in the ¹⁵N spectrum at ca. δ 27 ppm and can probably be assigned as NH₄⁺. The NOESY experiment shows clear chemical *exchange* of these protons with the NH₃ protons of the organic molecule in solution. There is also a ¹H resonance at δ 3.4 ppm, possibly due to water or an OH⁻ group (maybe NH₄OH?).

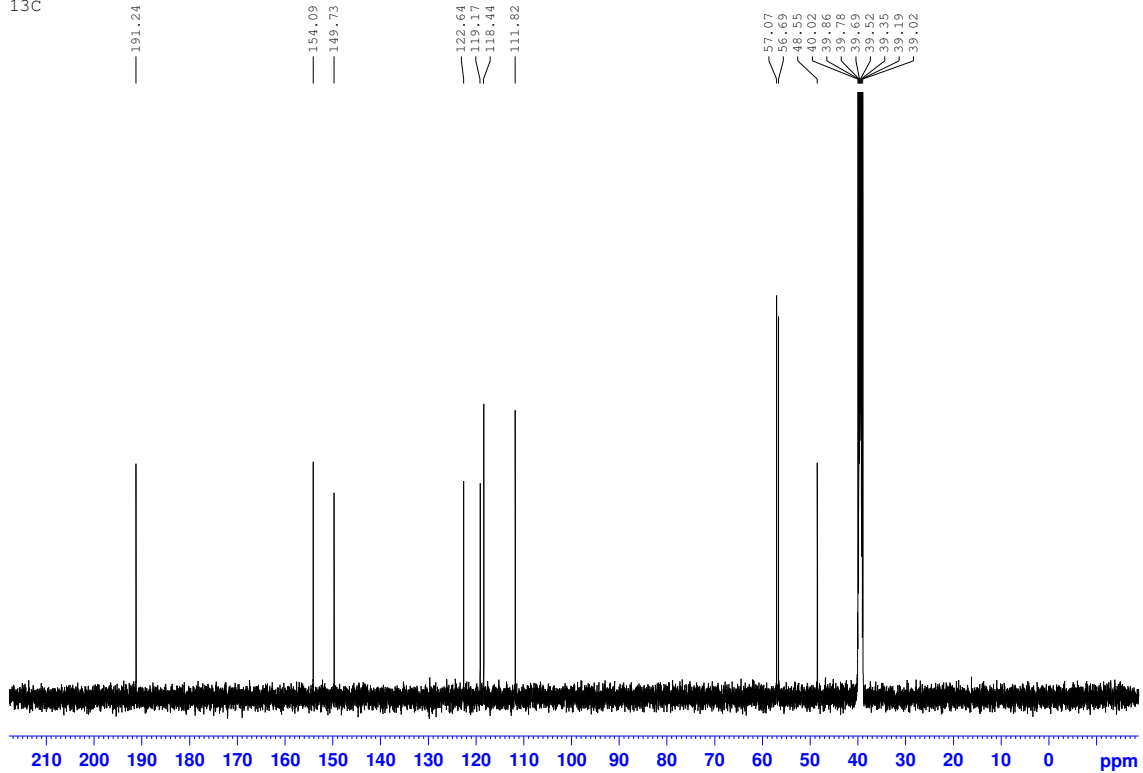
In summary, the spectra are consistent with sample BK-2CB being a protonated salt of structure **2**, and also containing substantial amounts of NH₄⁺X⁻. We cannot categorically rule out a stereoisomer of **2**, with a different arrangement of the groups on the benzene ring, but structure **2** seems the most likely.

NB in the following spectra “pendant” is shown with CH and CH₃ carbons pointing upwards, CH₂ and quaternary carbons downwards. “HSQC edited” shows CH and CH₃ groups in blue and CH₂ groups in red. In the NOESY spectrum, NOE peaks are red, peaks due to chemical exchange within the timescale of the pulse sequence (ca. 1 s) are blue.

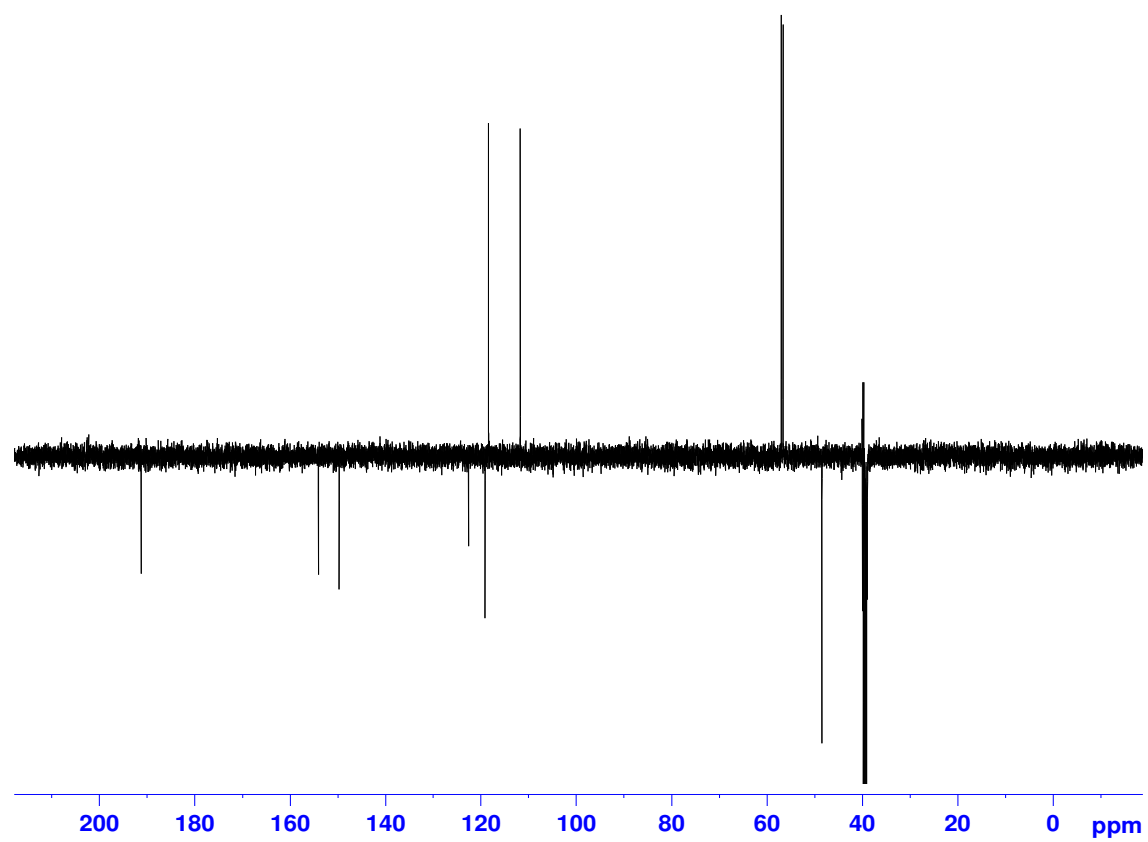
BK-2CB DMSO
1H



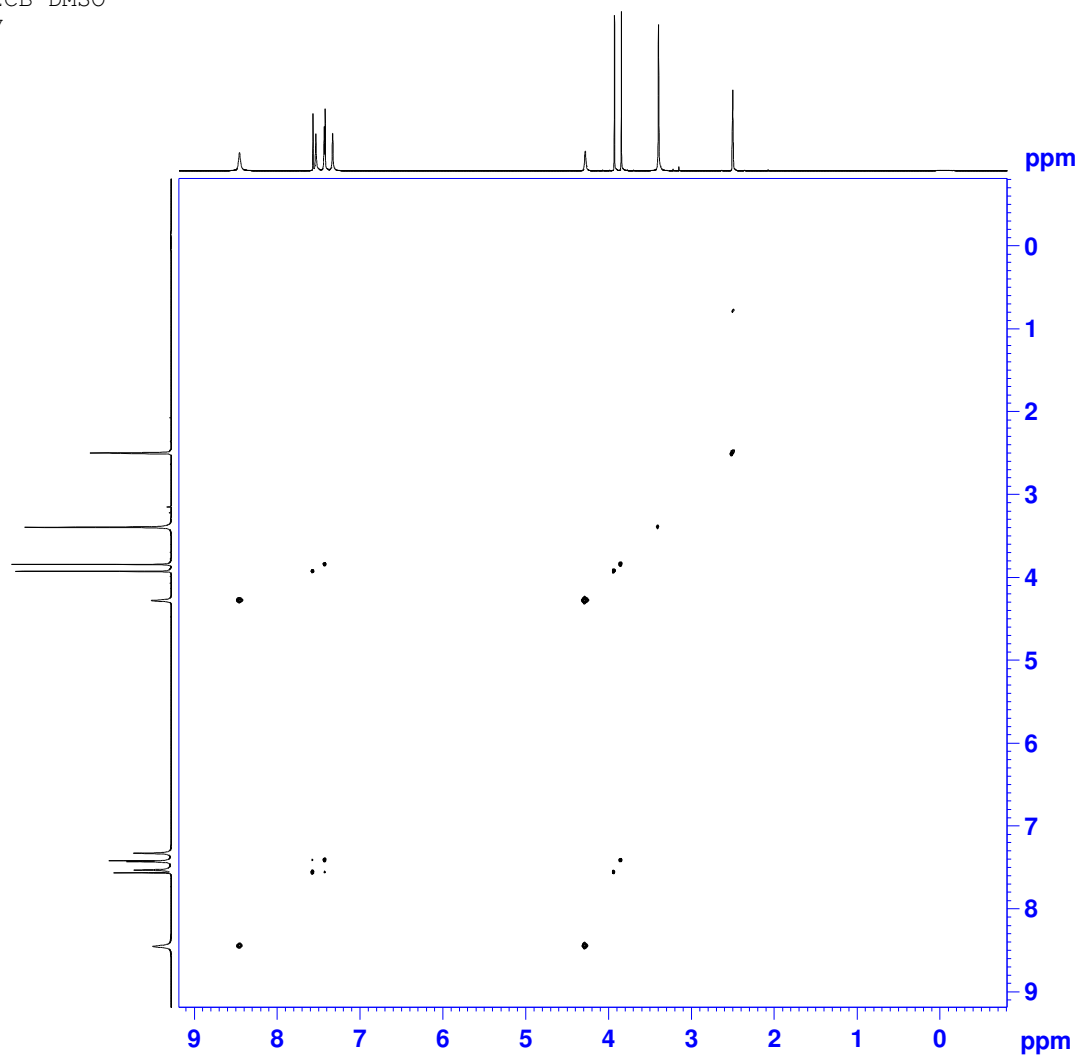
BK-2CB DMSO
13C



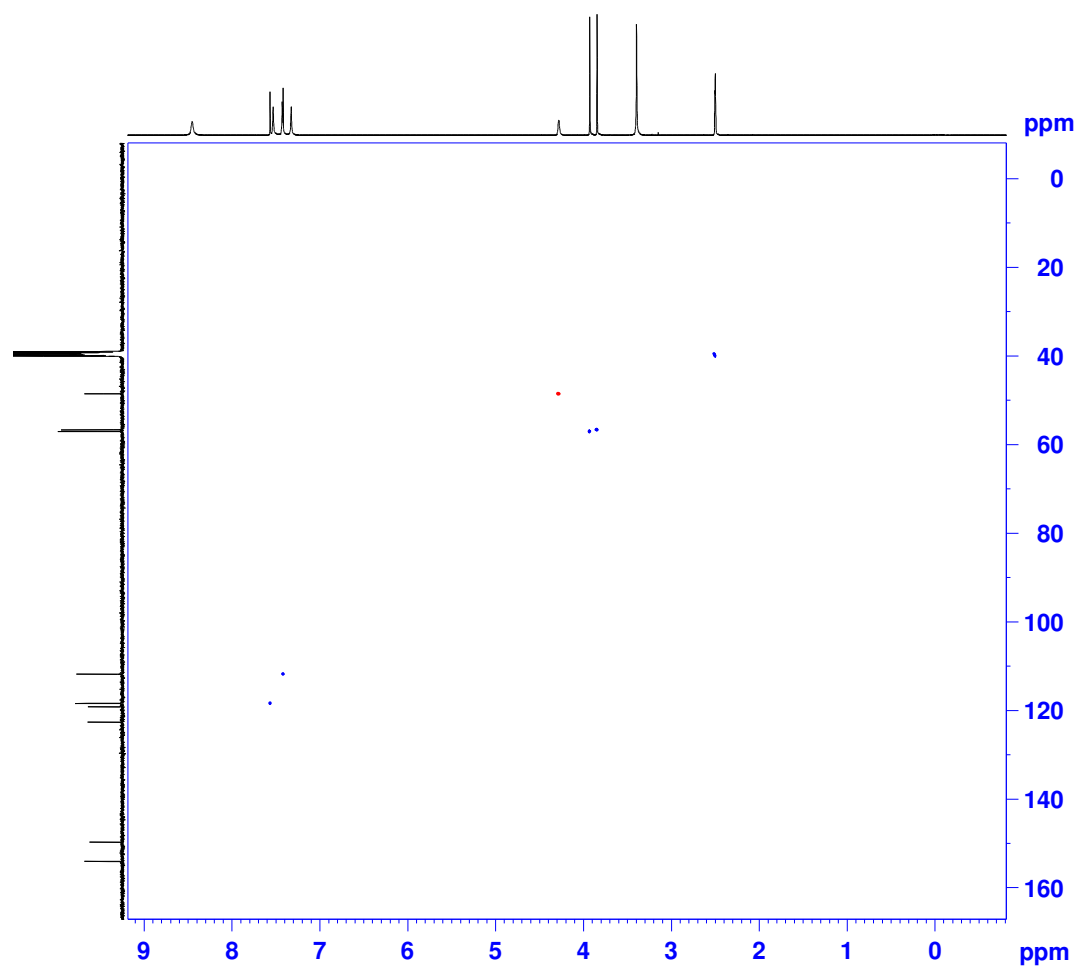
BK-2CB DMSO
pendant



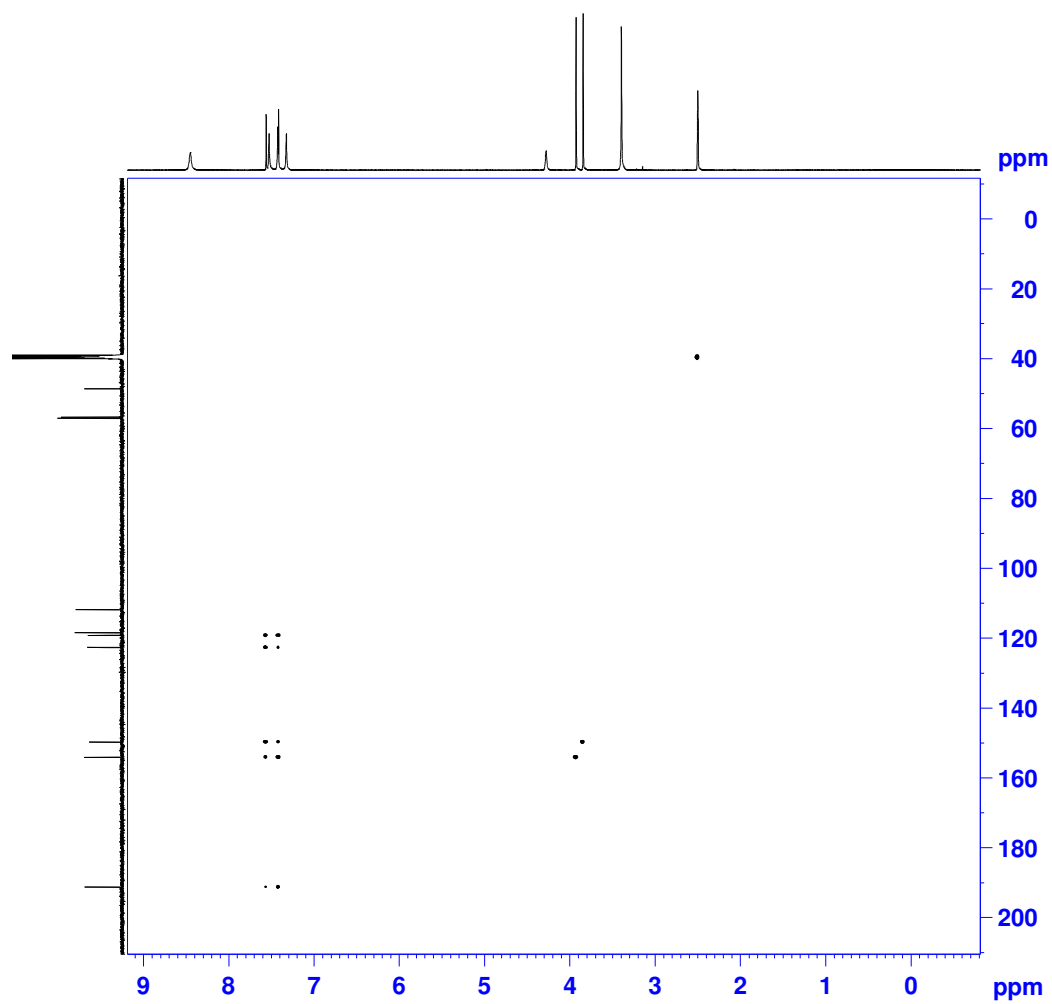
BK-2CB DMSO
cosy



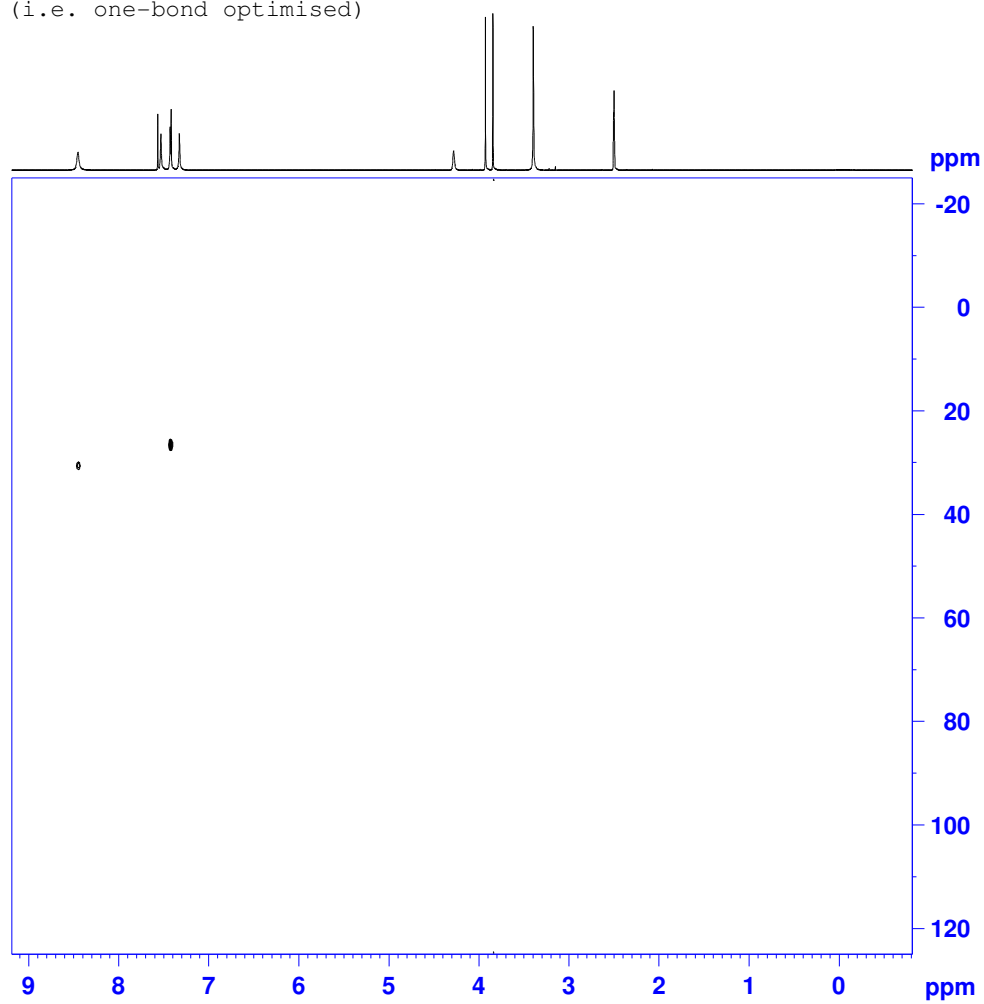
BK-2CB DMSO
HSQC edited



BK-2CB DMSO
HMBC



BK-2CB DMSO
15N-1H HSQC
cnst2 = 50 (i.e. one-bond optimised)



BK-2CB DMSO
noesy

