

Supplementary material for Bendix, Bechgaard and Christensen: Synthesis and Properties of 2,4,7,9-Tetramethyl-1,6- dithiapyrene (TMDTP) and Structure of (TMDTP)₃(PF₆)₂·2THF and TMDTP-TCNQ.

Table of content:

S1-S18: Determination of composition of the mixture of 2,6- and 2,7-dimethylnaphthalene.

S19-S24: NMR of compound **4**.

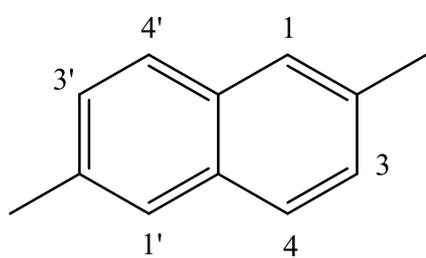
S25-S29: NMR of compound **5**.

S30-S35: NMR of compound **6**.

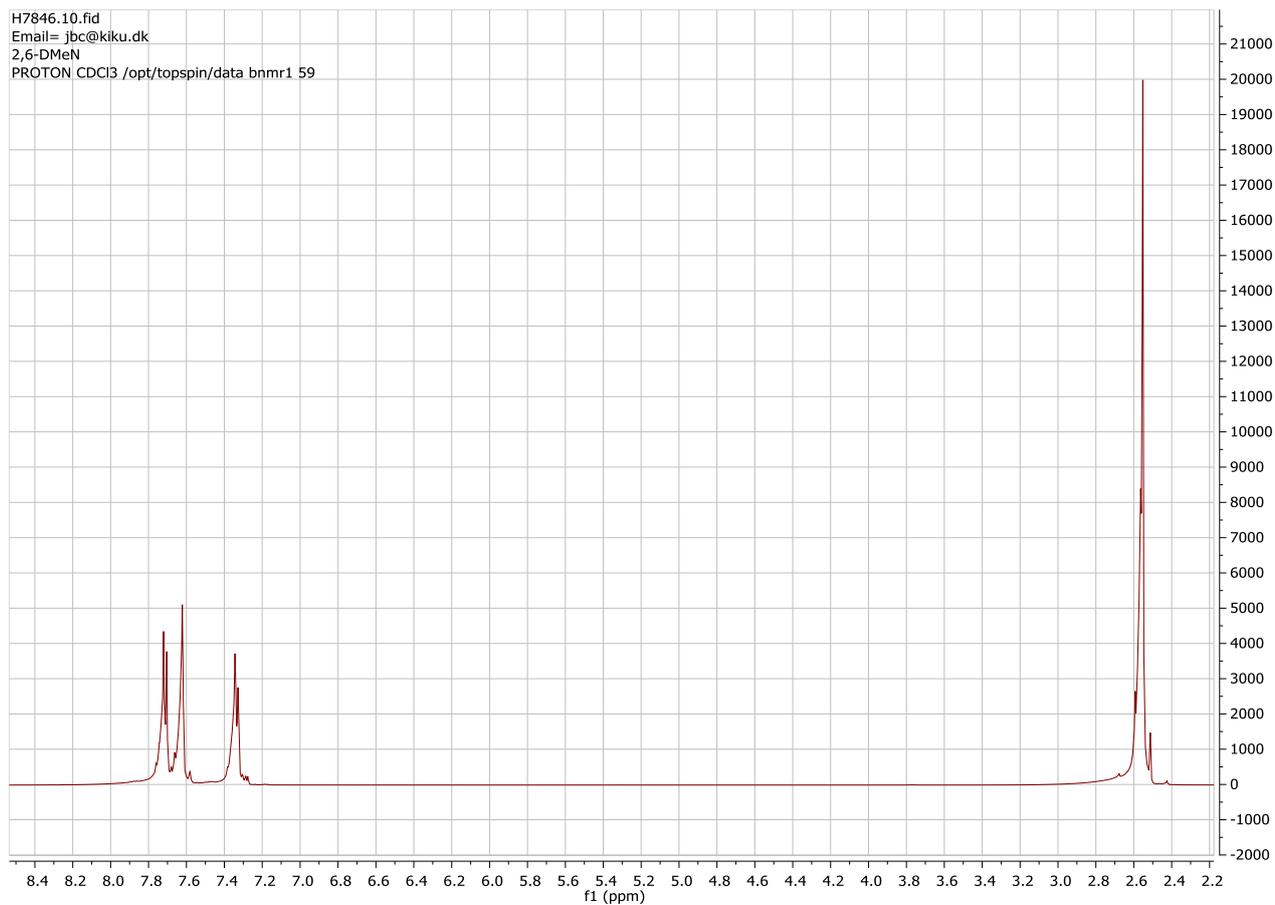
S36-S41: NMR of compound **7**.

S42-S47: NMR of compound **3**.

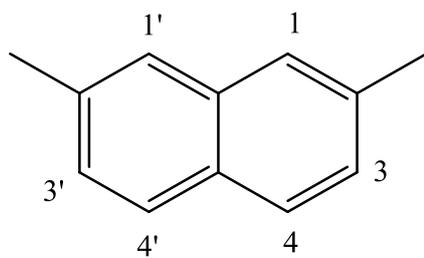
Full $^1\text{H-NMR}$ spectrum of 2,6-Dimethylnaphthalene in CDCl_3



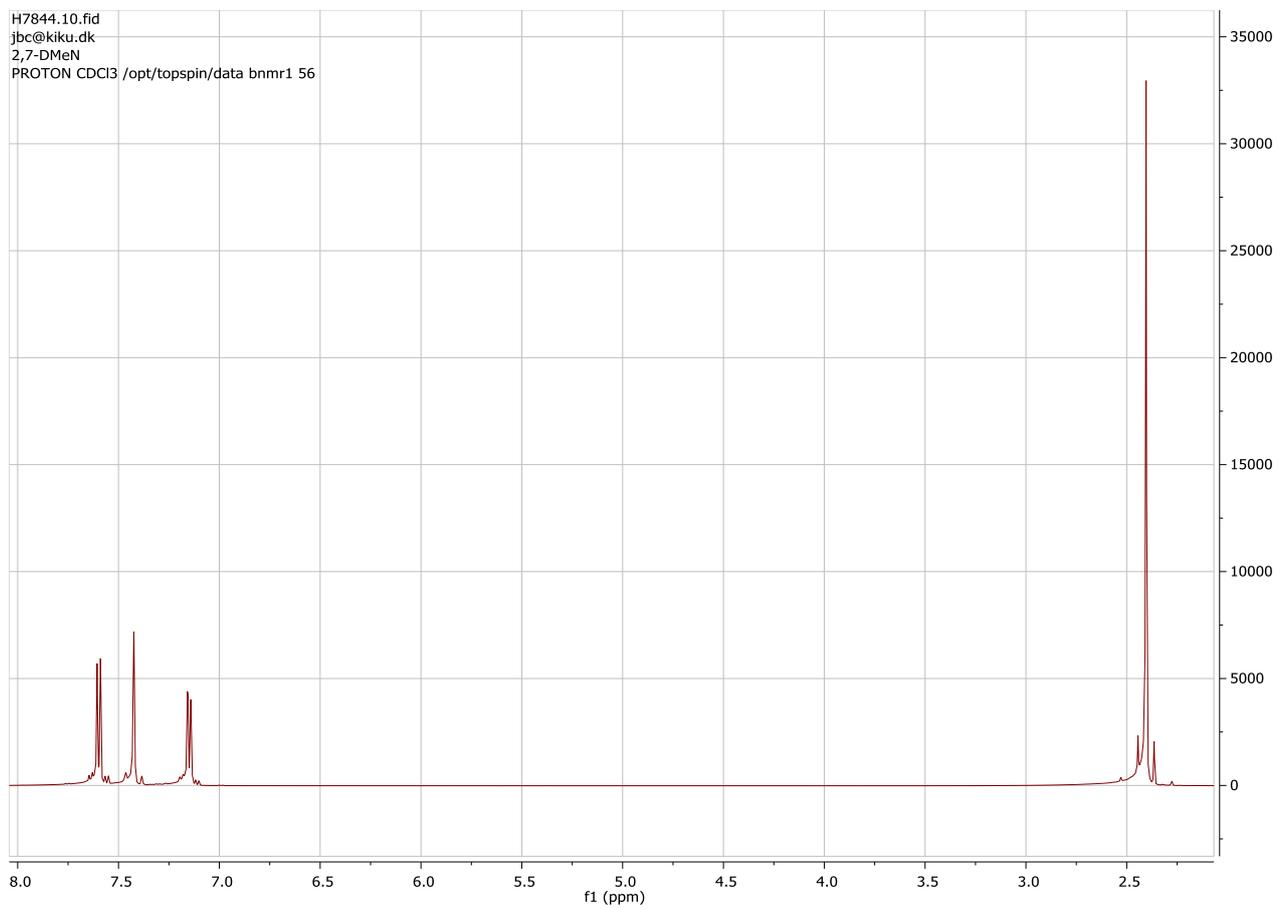
2,6-DMN



Full ^1H -NMR spectrum of 2,7-Dimethylnaphthalene (2,7-DMN) in CDCl_3

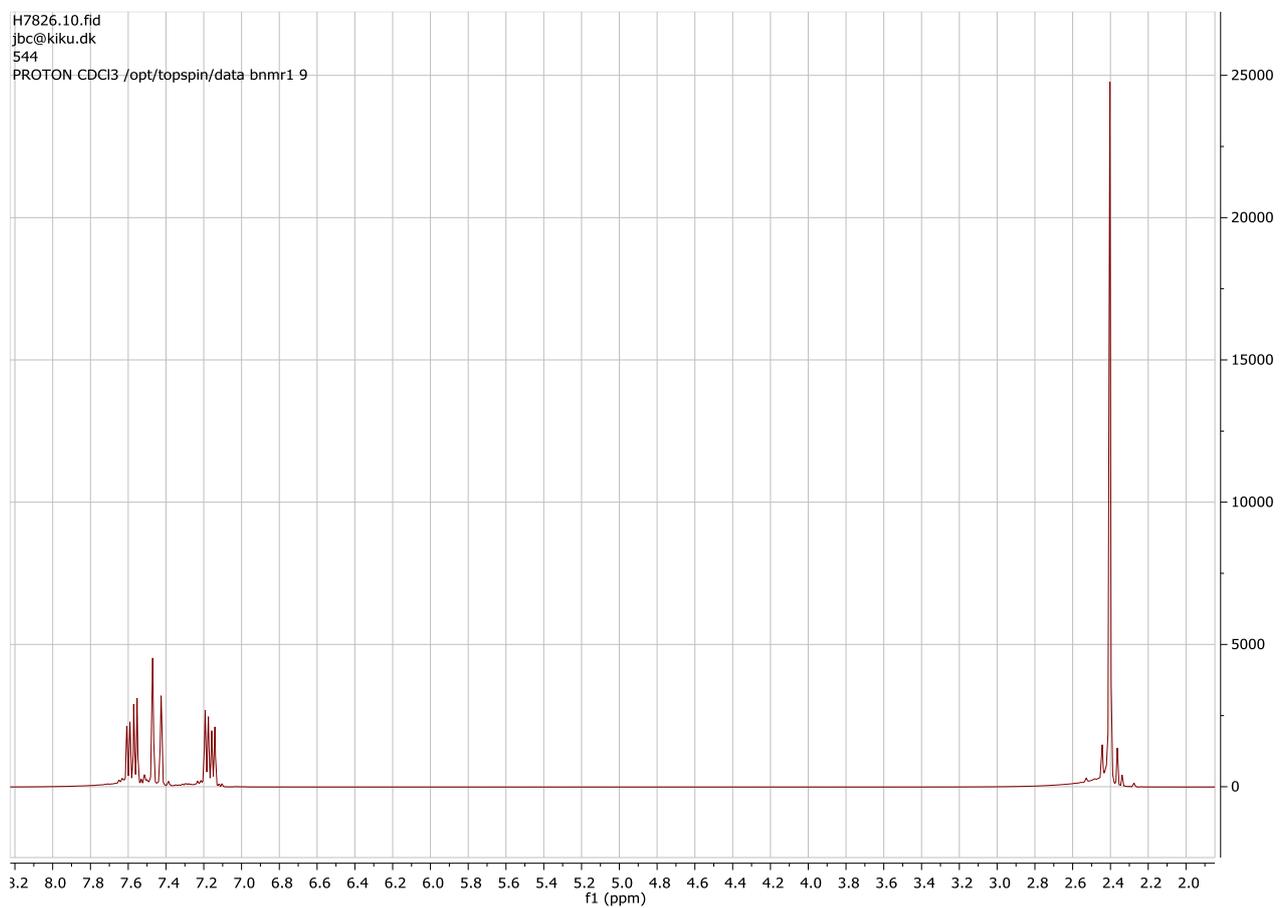


2,7-DMN

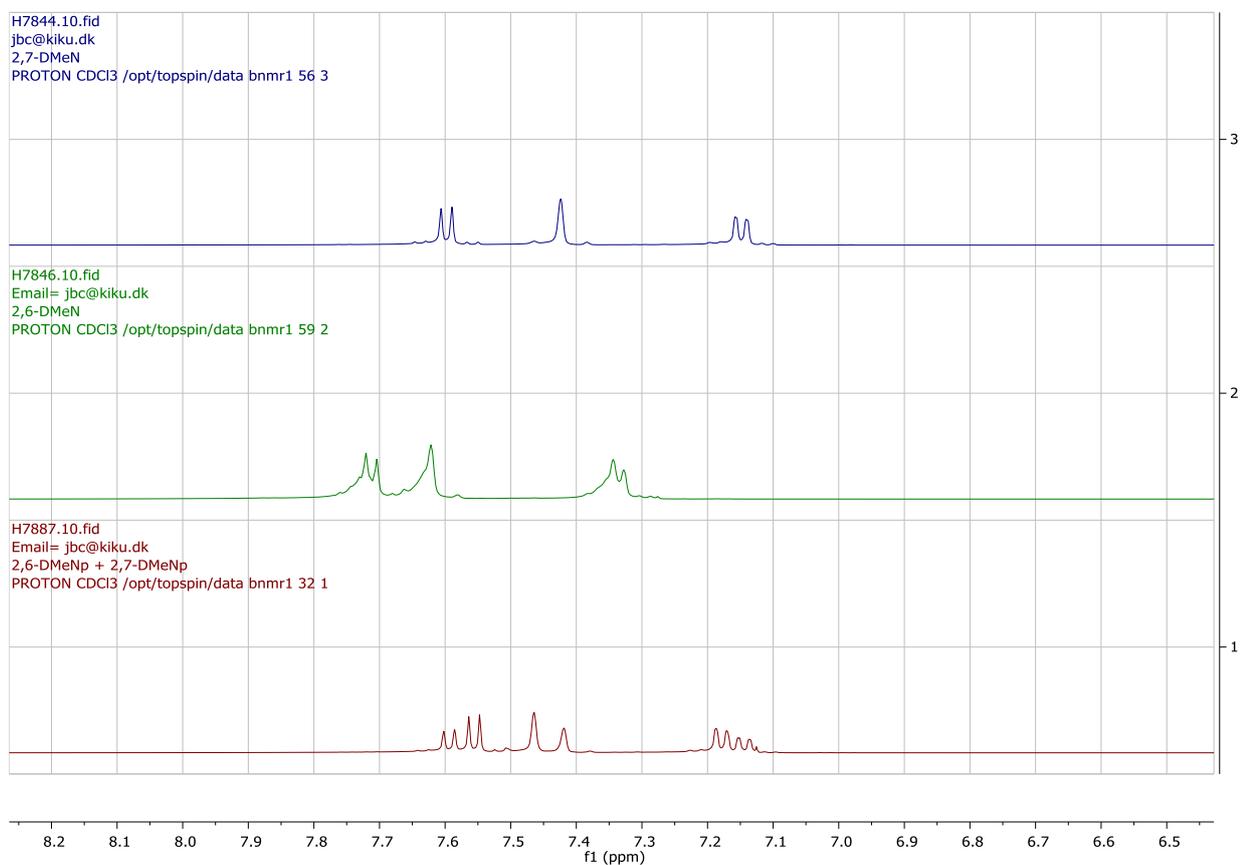


2,6-DMN and 2,7-DMN interacts in CDCl₃ as seen from the ¹H-NMR spectra:

Mixture of 2,6- and 2,7-DMN



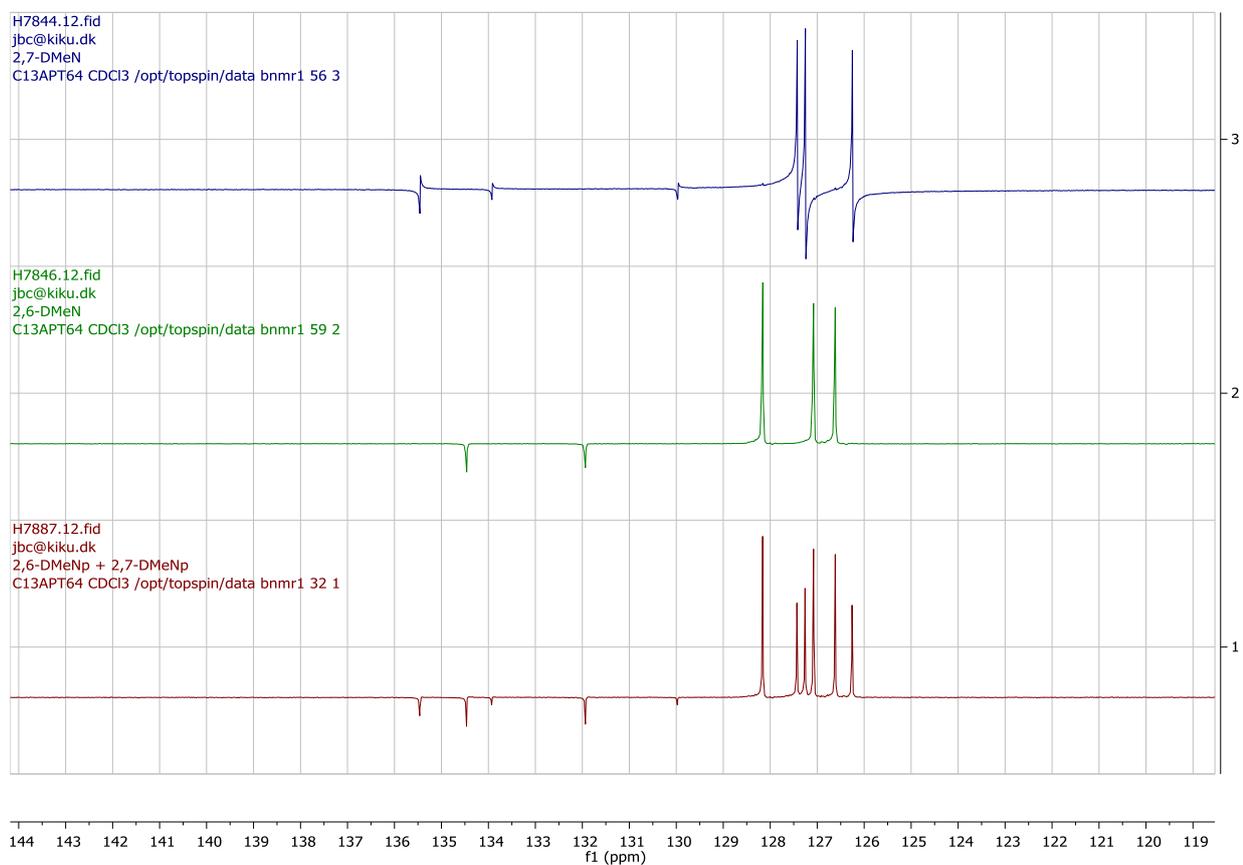
All 3 ^1H -spectra expanded in the aromatic area and stacked:



Legend: 2,7-DMN is blue, 2,6-DMN is green and the mixture of 2,6- and 2,7-DMN is red (formed by mixing the solutions of 2,6- and 2,7-DMN).

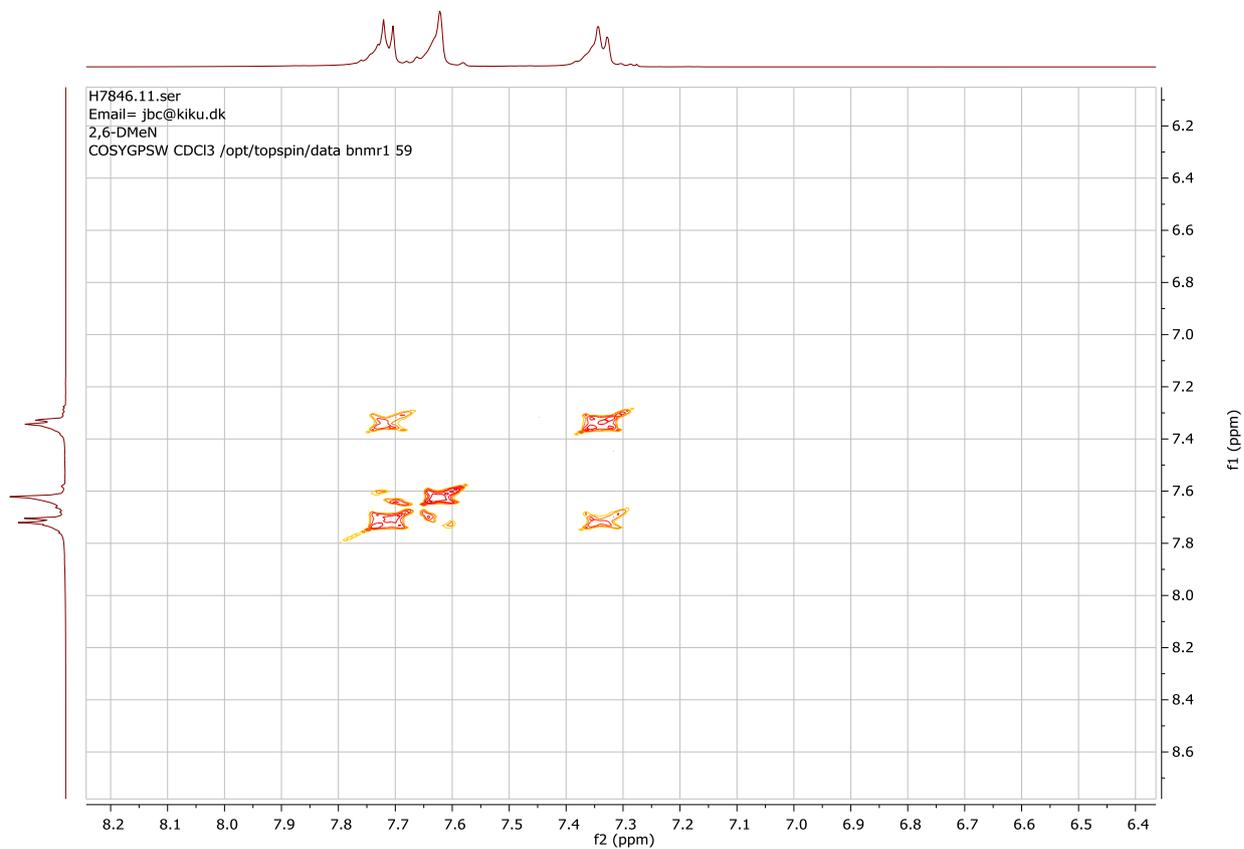
There is some interaction taking place between the 2,6- and the 2,7-DMN. The carbon-spectra are however unchanged:

All 3 ^{13}C -spectra expanded in the aromatic region and stacked:



Legend: 2,7-DMN is blue, 2,6-DMN is green and the mixture of 2,6- and 2,7-DMN is red. None of the carbon-signals are shifted upon mixing the two isomers.

Assigning the protons in 2,6-DMN by 1H-COSY in CDCl₃:

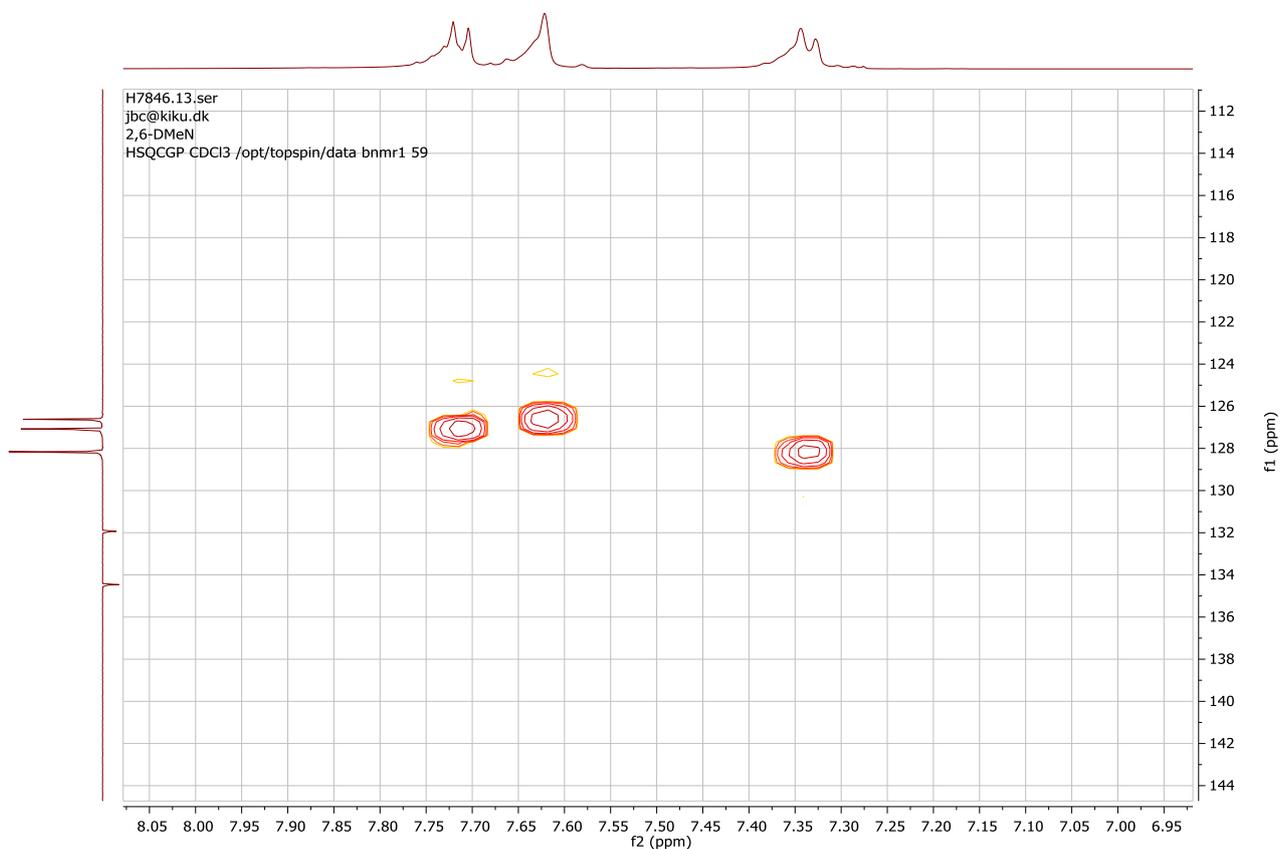


H 1 & H1': 7.33 ppm (s), but small meta-coupling to H3, H3'

H4, H4': 7.71 ppm (d, J = 10 Hz)

H3, H3': 7.34 ppm (d, J = 10 Hz)

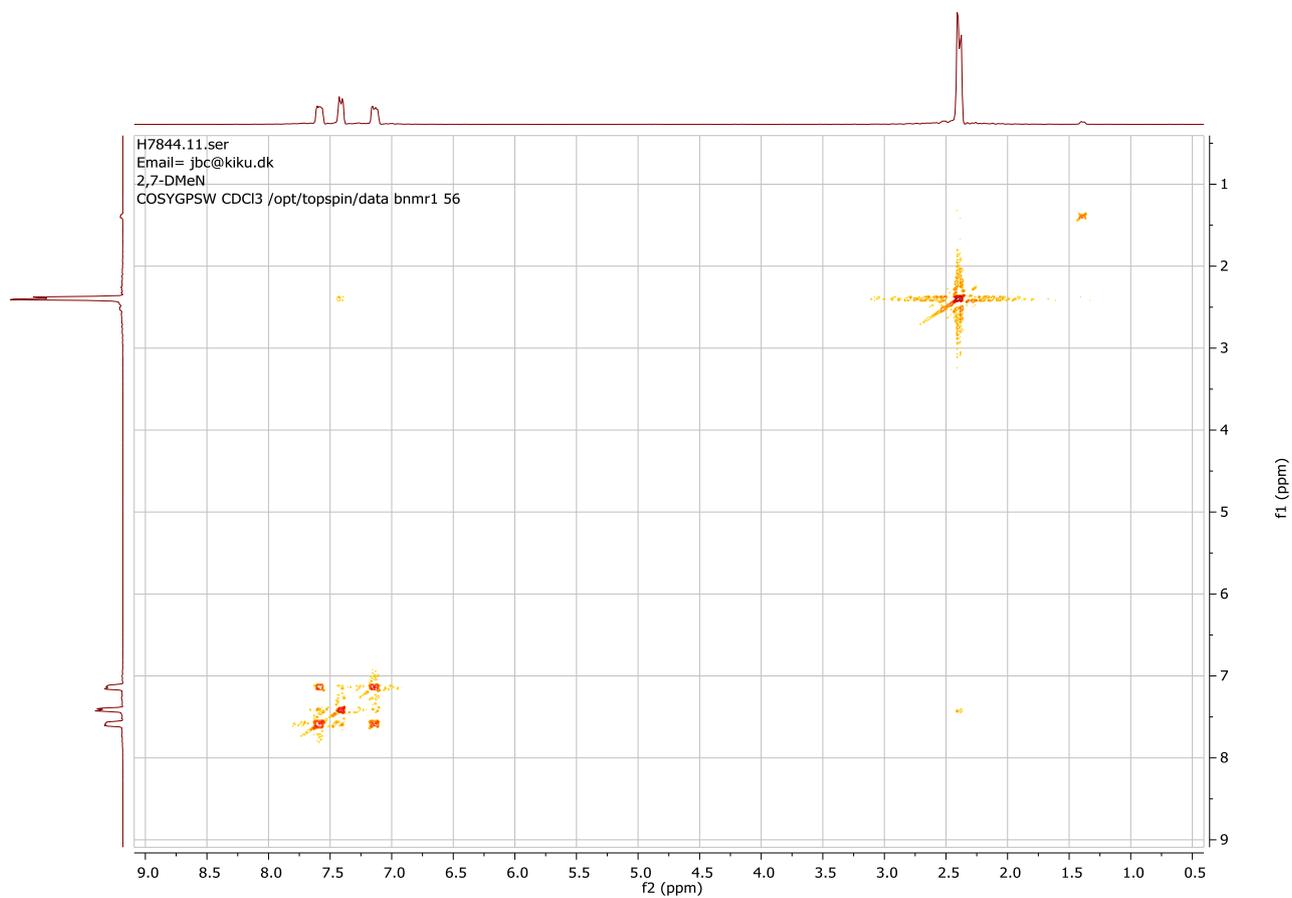
HSQC-spectrum of 2,6-DMN in CDCl₃ was used to find assign C1/C1' to H1/H1':



Shows that the carbon at 126.65 ppm is bound to proton 1 and 1'.

This allows identification of H1/H1' in the mixture of 2,6- and 2,7-DMN:

Assigning the protons in 2,7-DMN by 1H-COSY in CDCl₃:

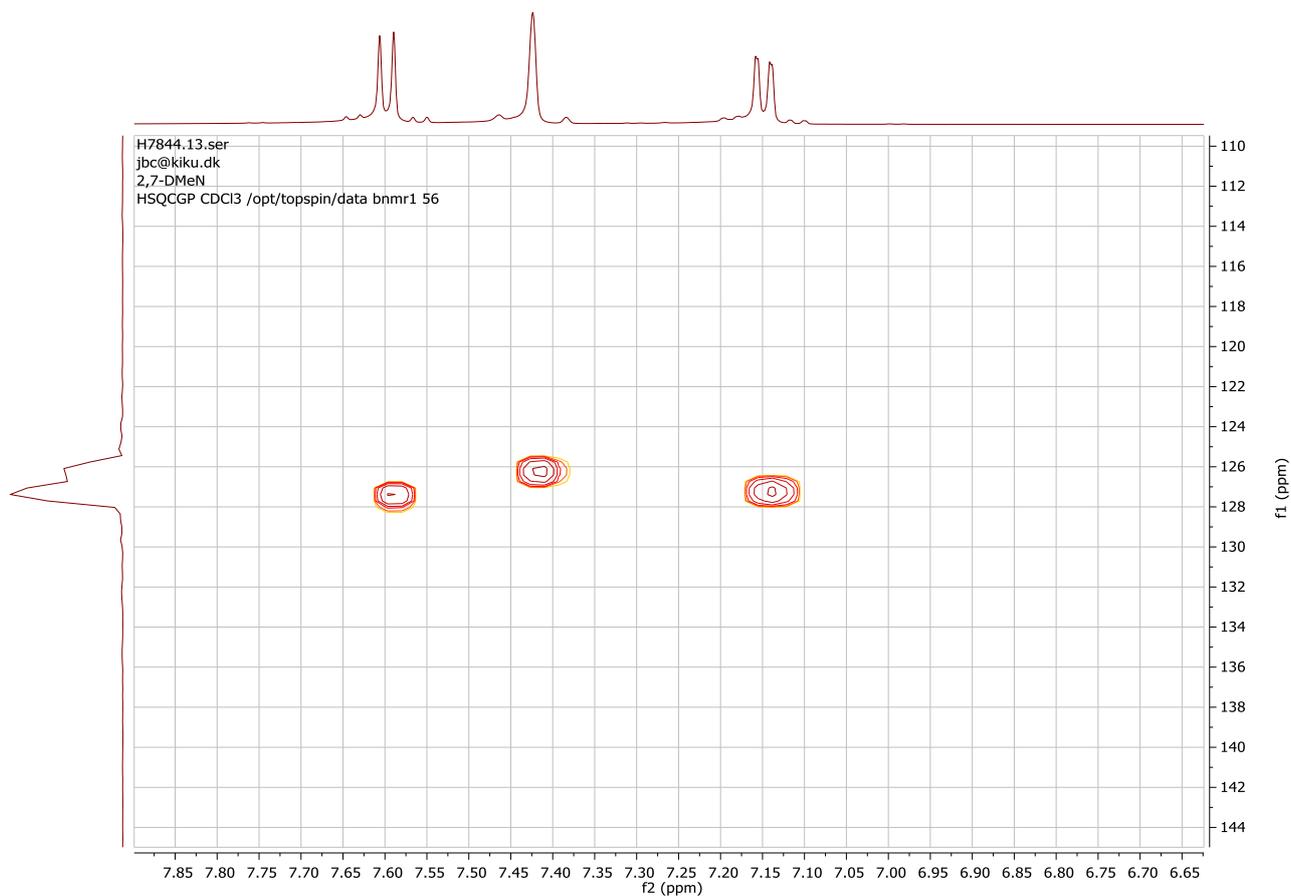


H 1 & H1': 7.42 ppm (s)

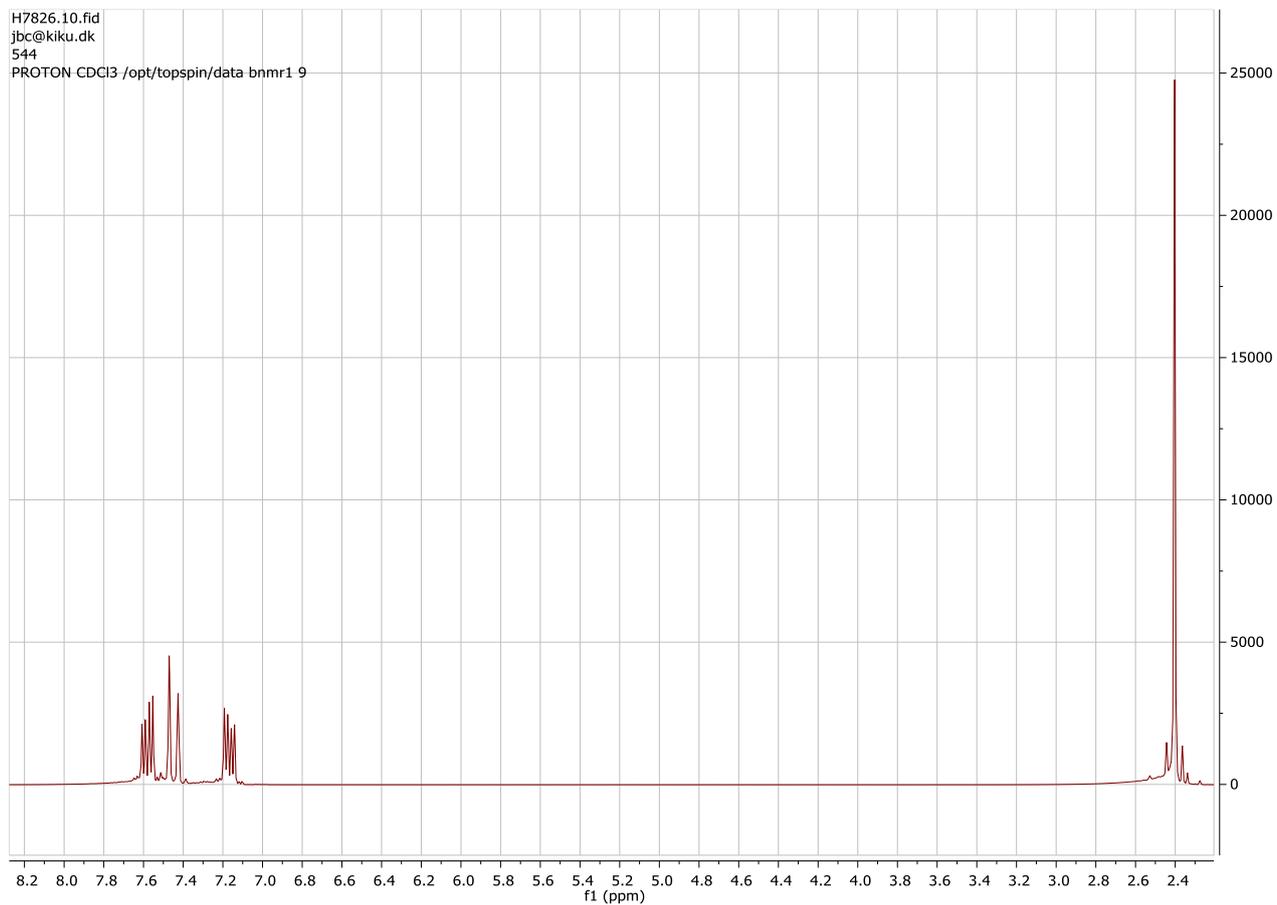
H4, H4': 7.60 ppm (d, J = 10 Hz)

H3, H3': 7.34 ppm (d, J = 10 Hz)

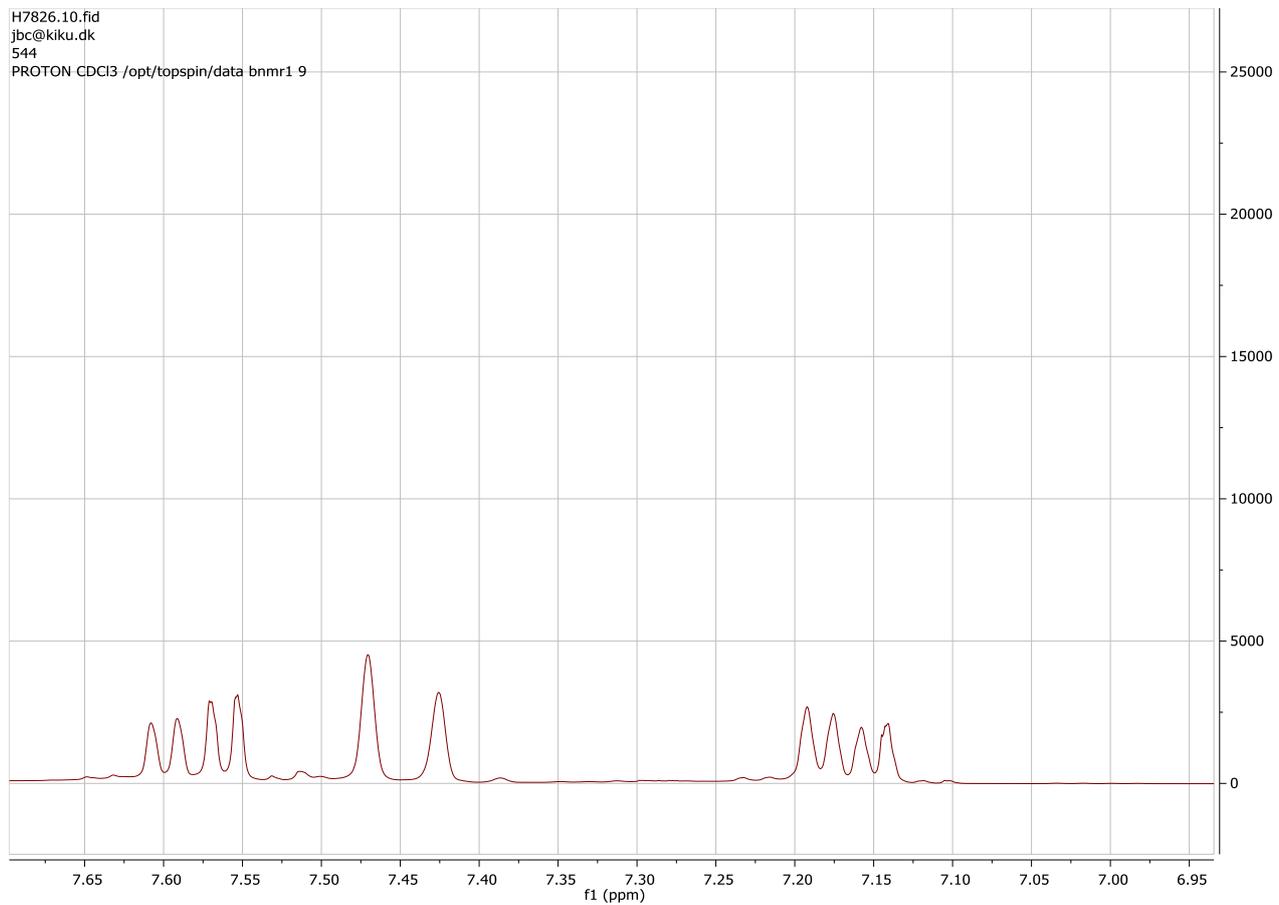
HSQC-spectrum of 2,7-DMN in CDCl₃ was used to find assign C1/C1' to H1/H1':



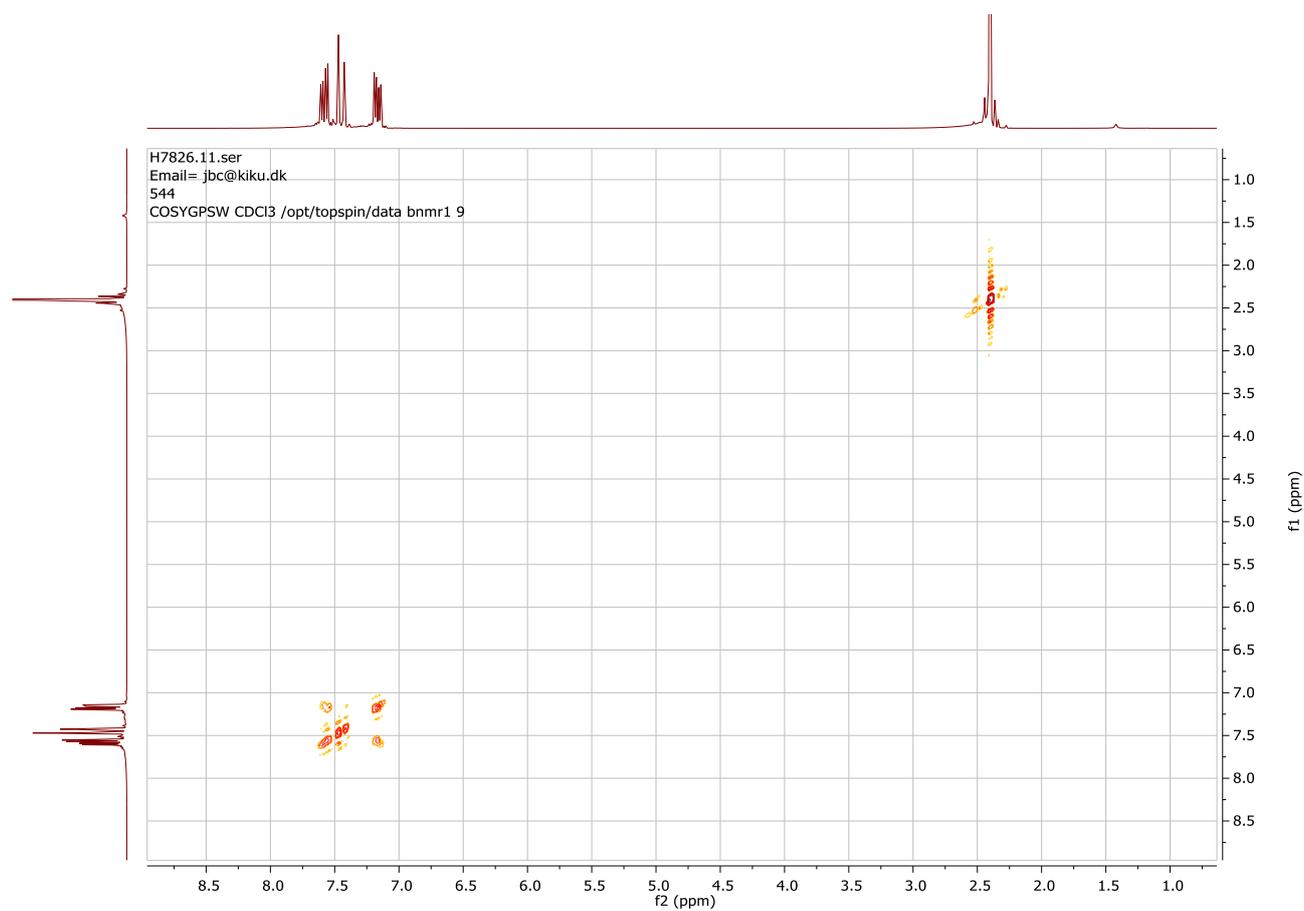
The NMR-spectra in CDCl₃ of the eutectic mixture isolated by crystallization looks:



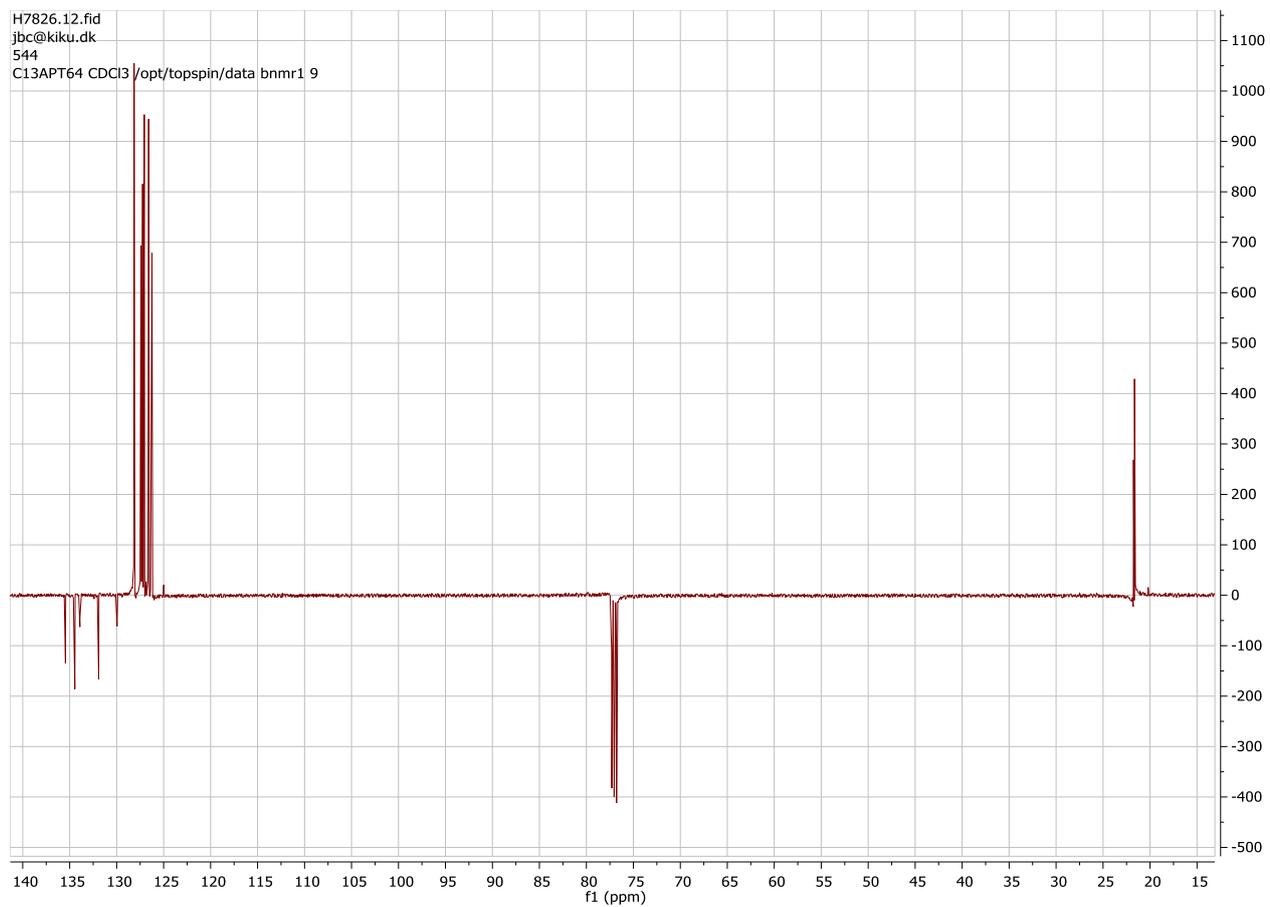
Expanded:



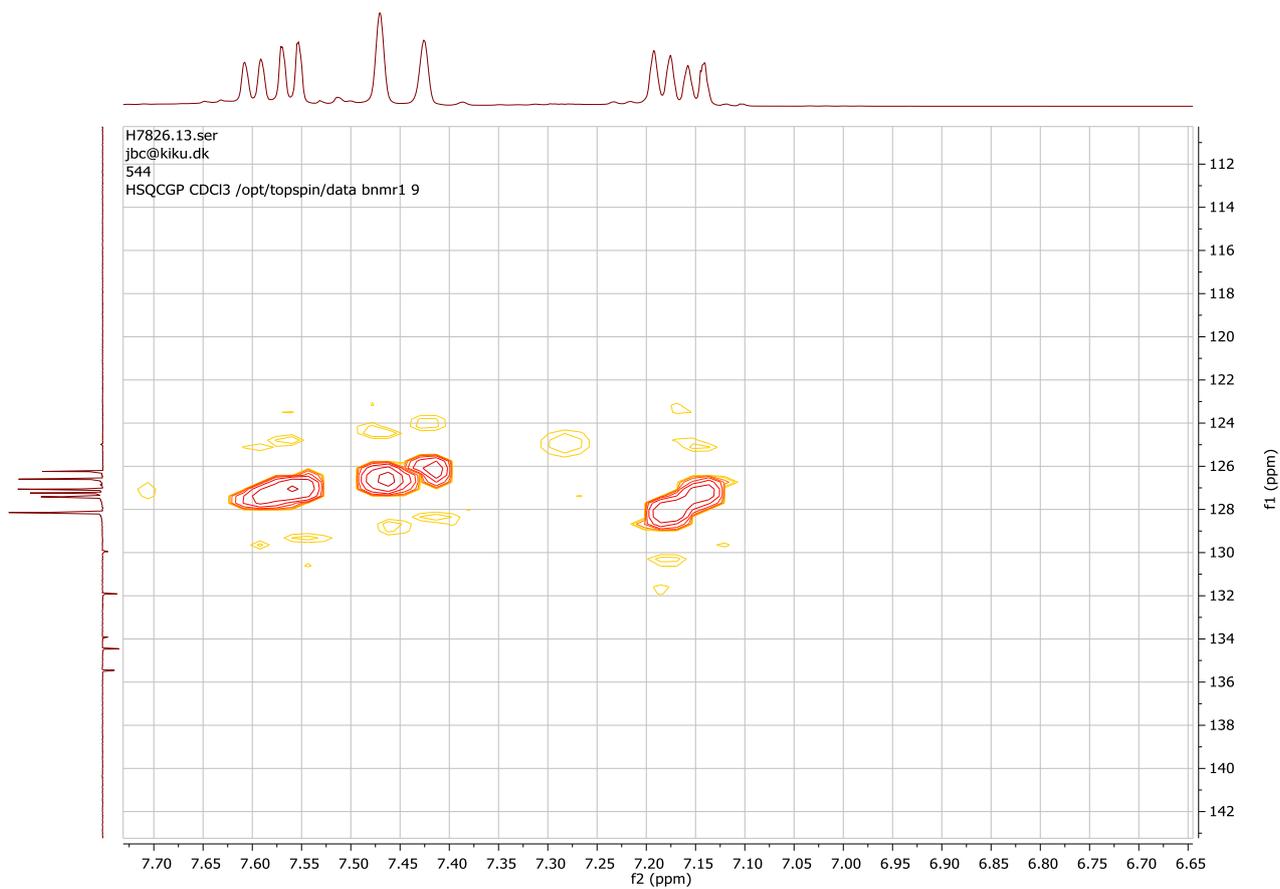
¹H-COSY:



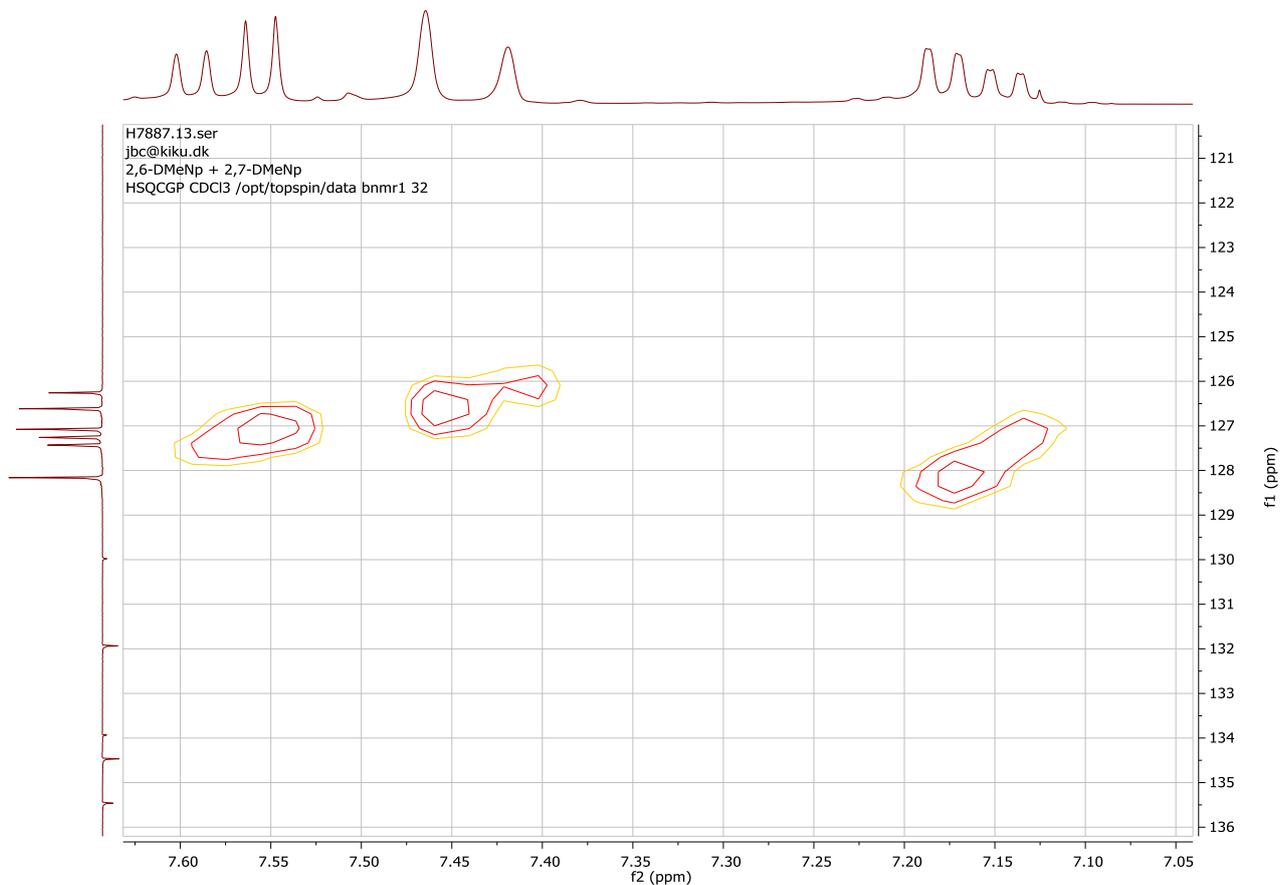
¹³C-NMR:



HSQC-NMR:

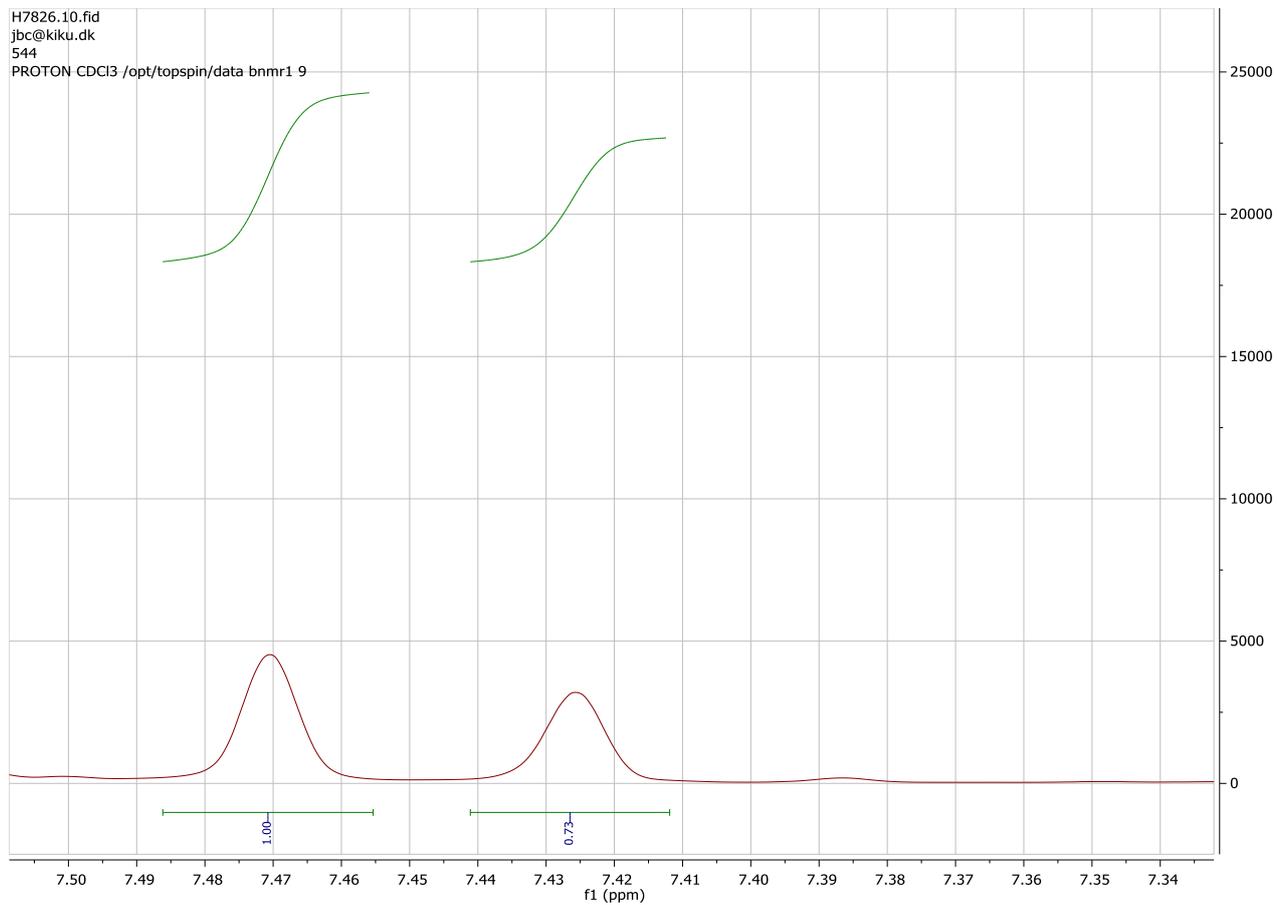


HSQC-spectrum of the mixture of 2,6- and 2,7-DMN in CDCl₃. Finding H1/H1' in 2,6-DMN:



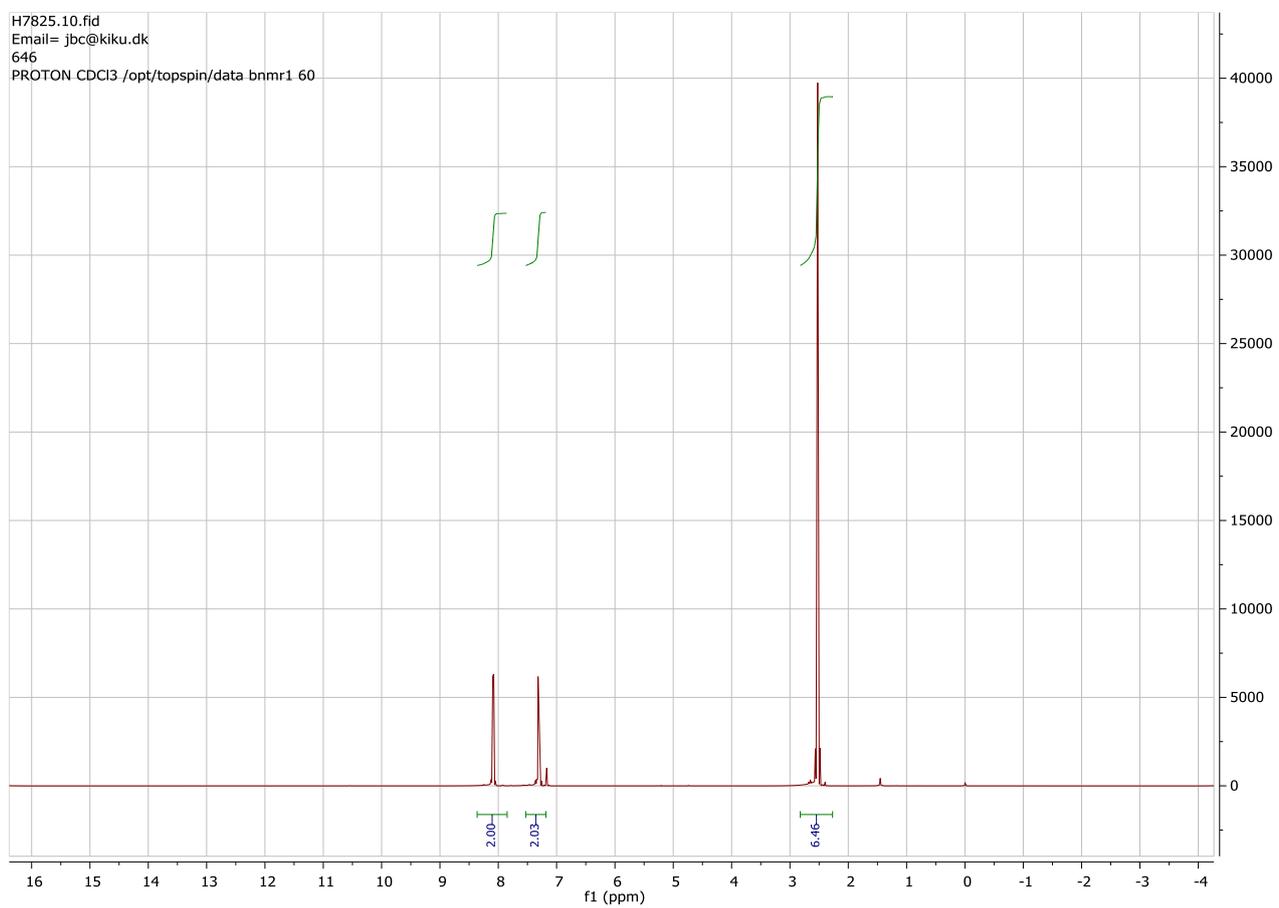
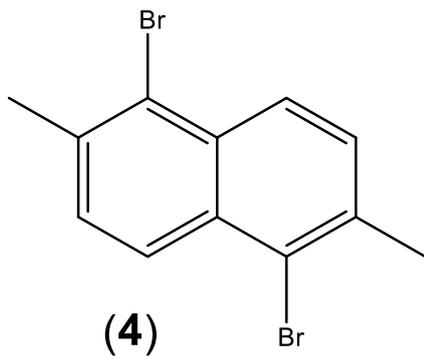
The peak at 7.46 ppm corresponds to H1/H1' in 2,6-DMN and the peak at 7.42 ppm corresponds to H1/H1' in 2,7-DMN.

Determining the composition:

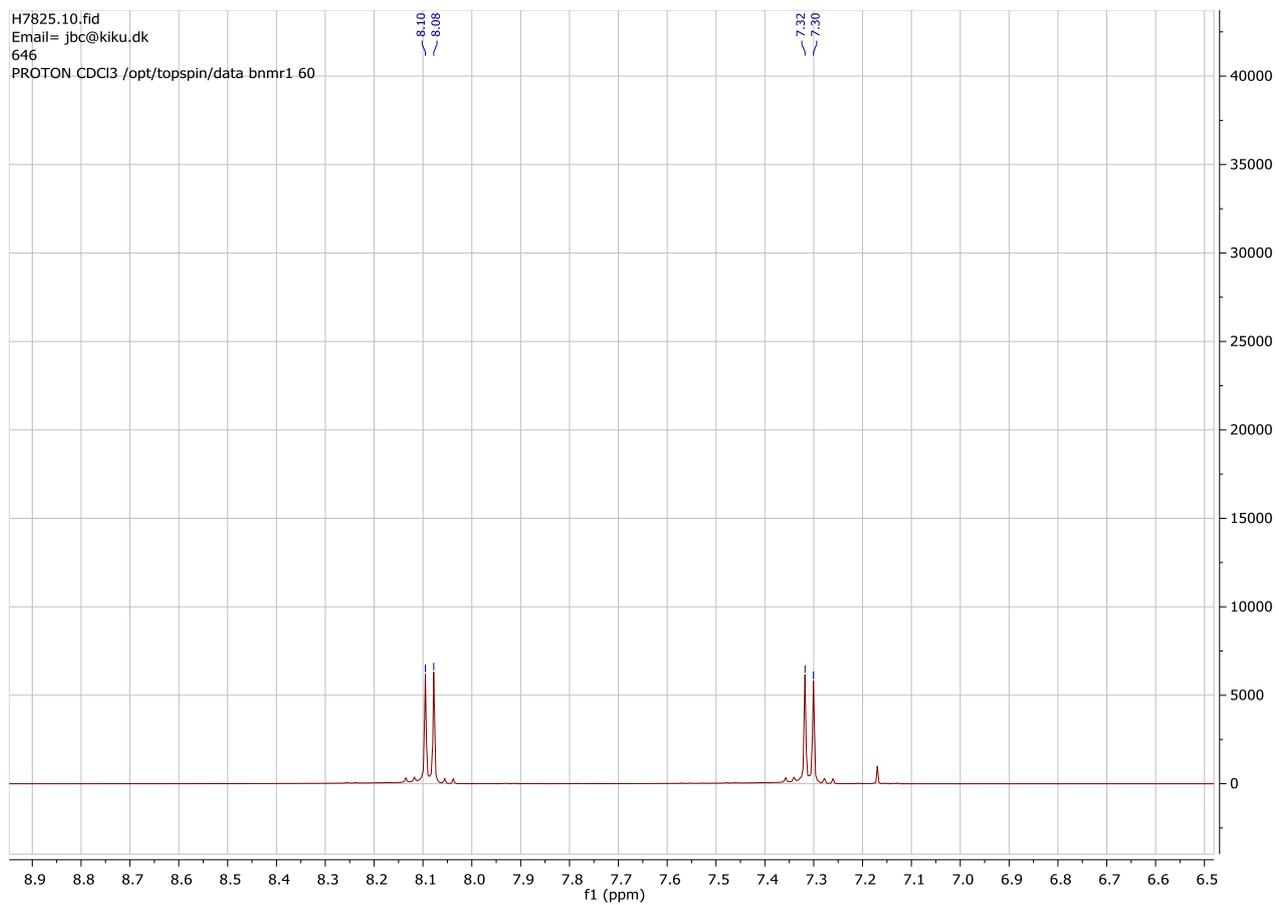


Gives a 1:0.73 ratio between 2,6- and 2,7-DMN corresponding to 58 % 2,6-DMN in the mixture.

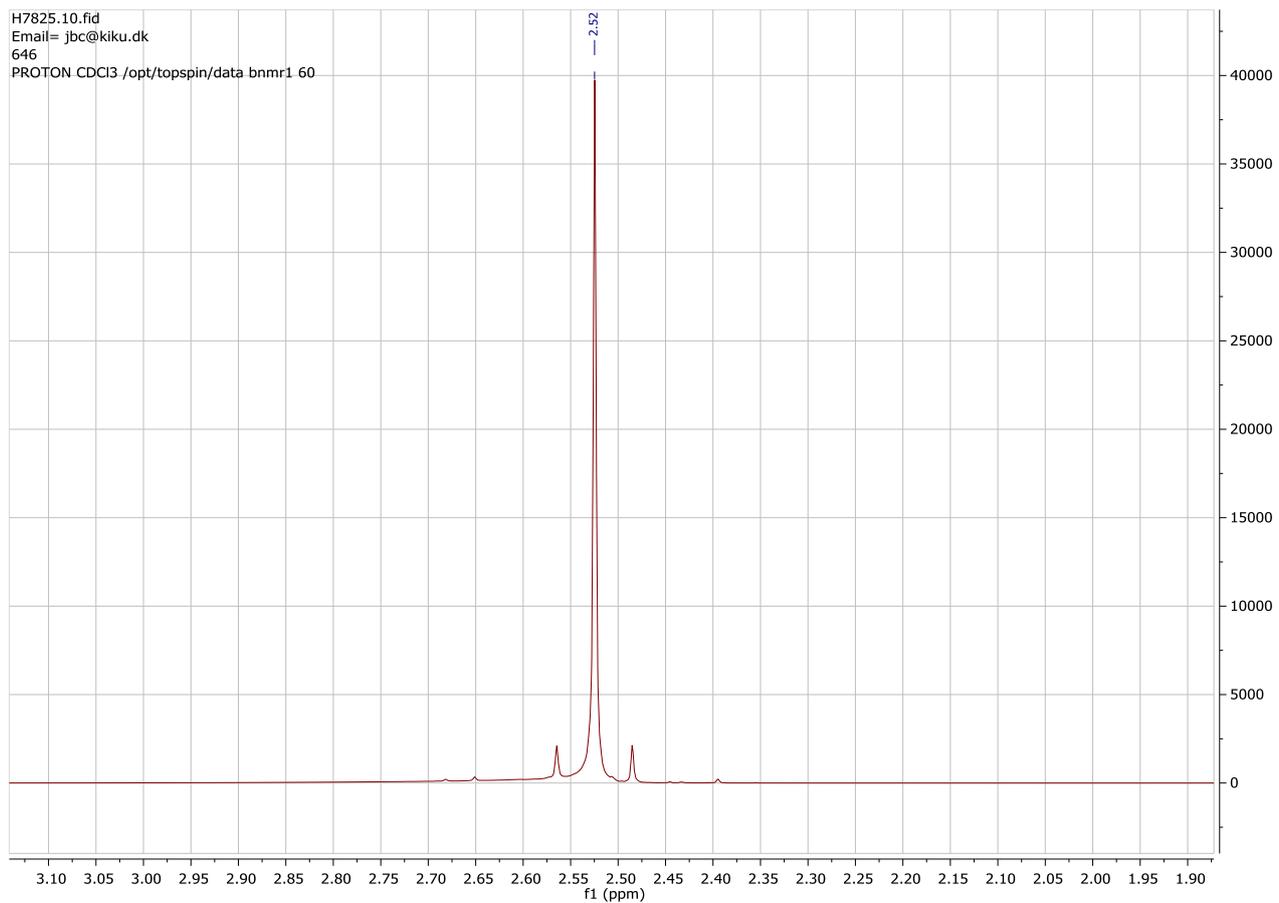
NMR-spectra of compound **4** in CDCl₃



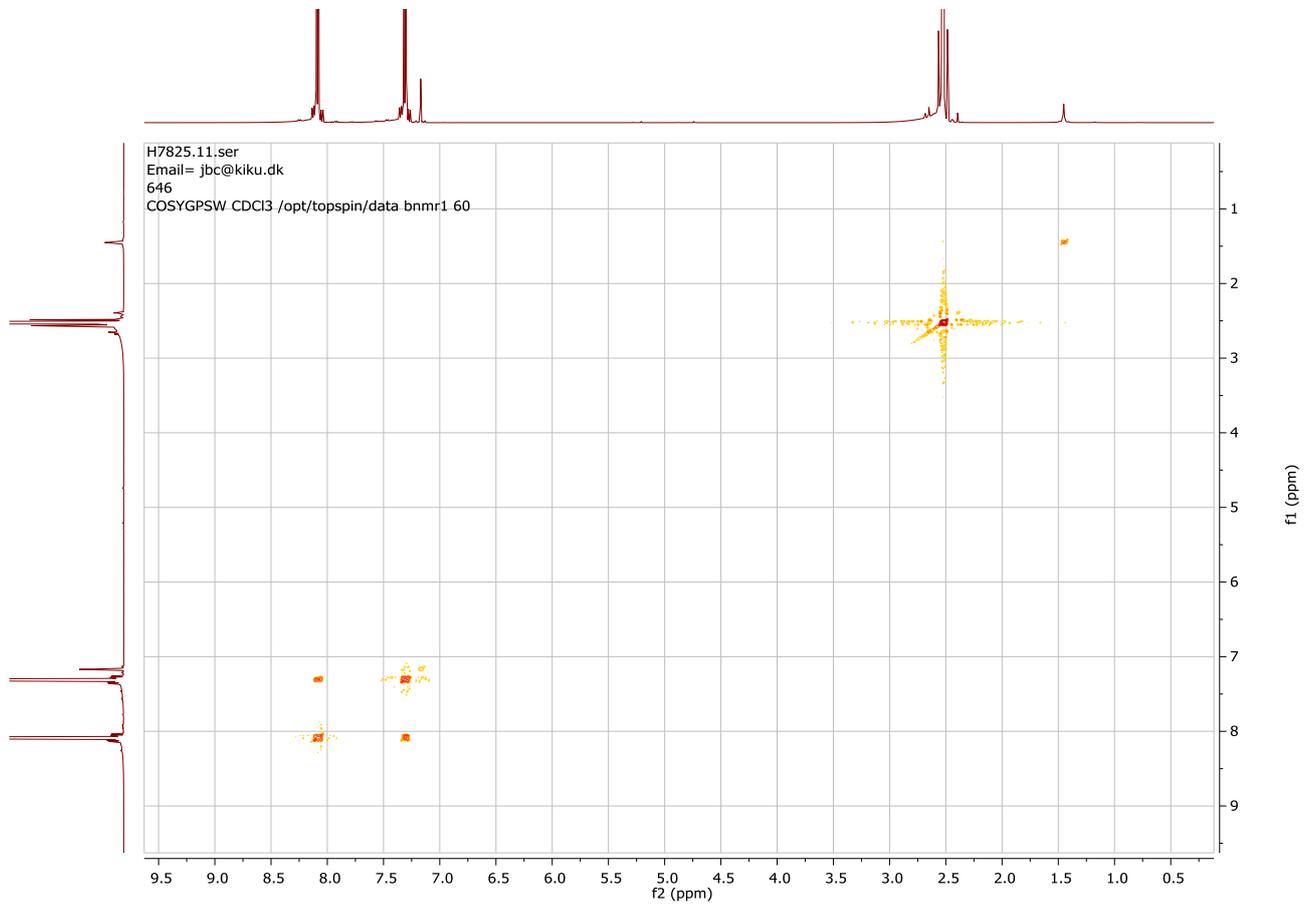
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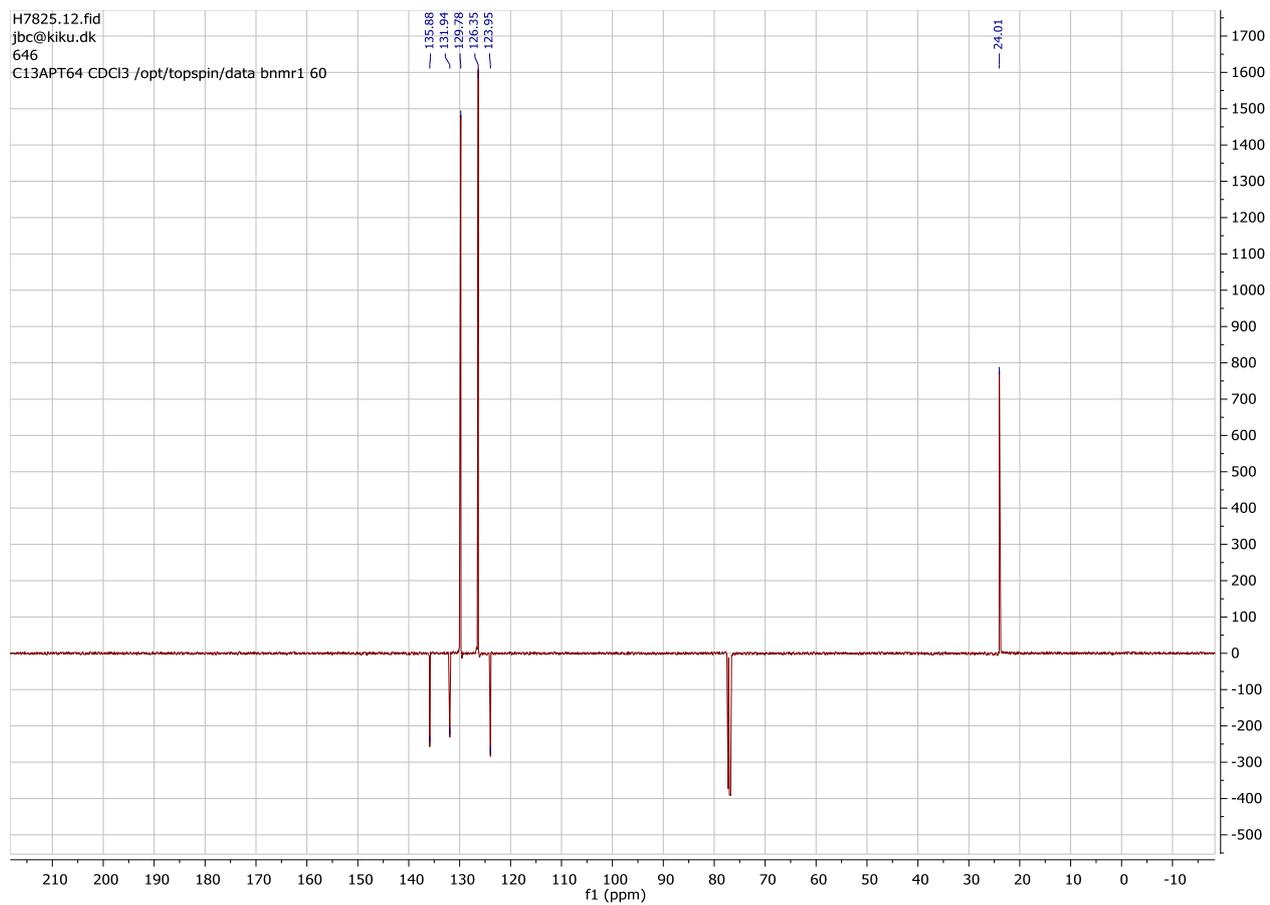
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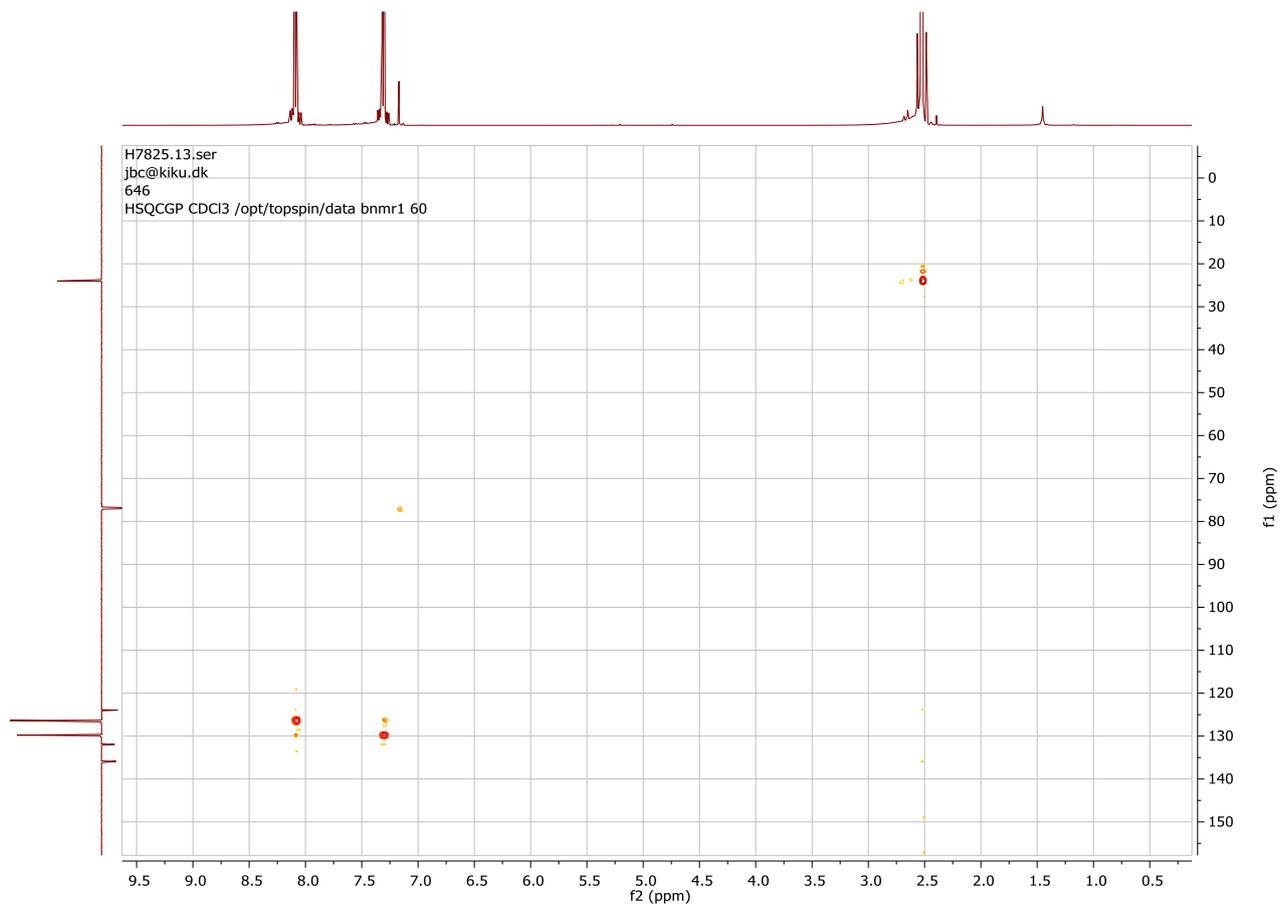


COSY



APC-¹³C

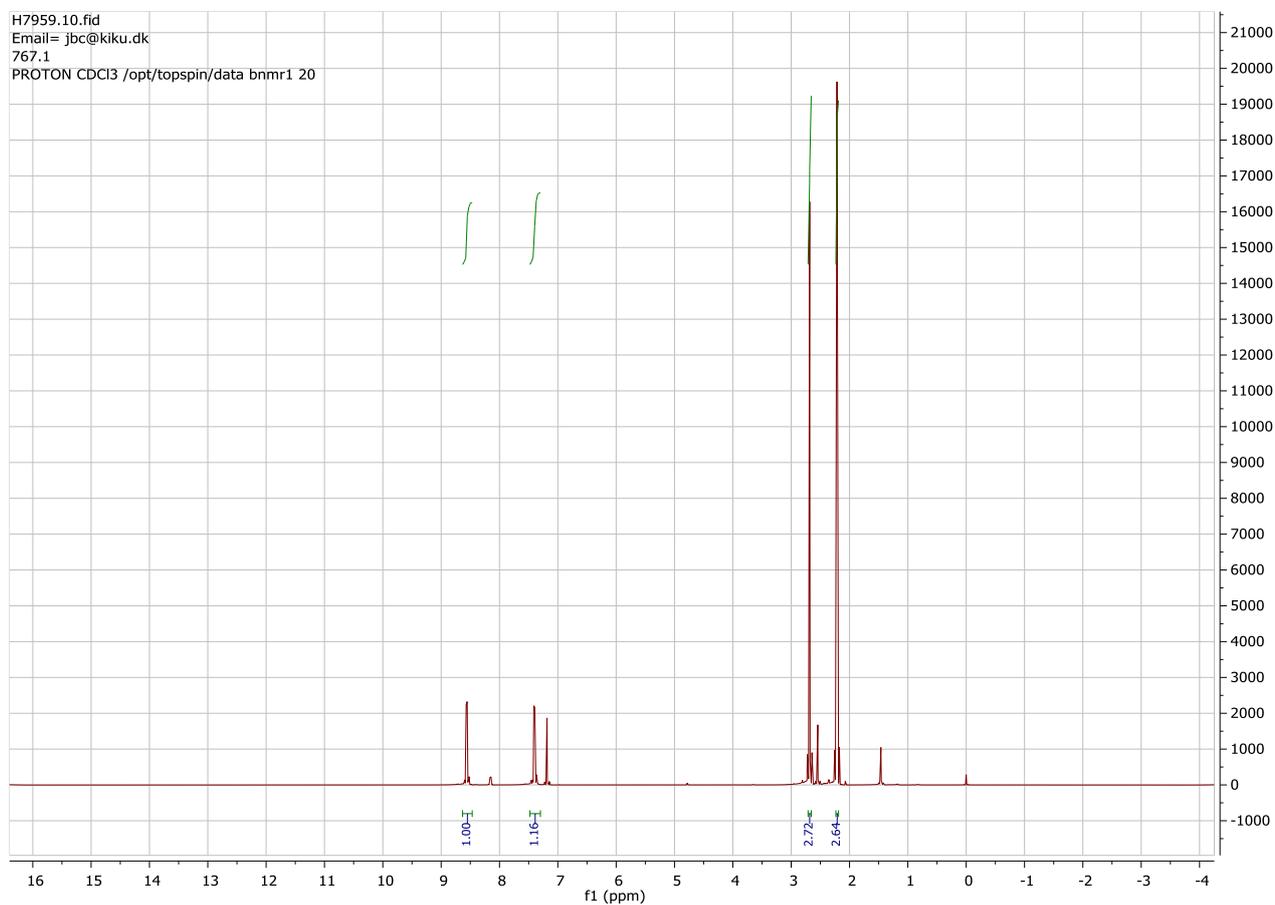
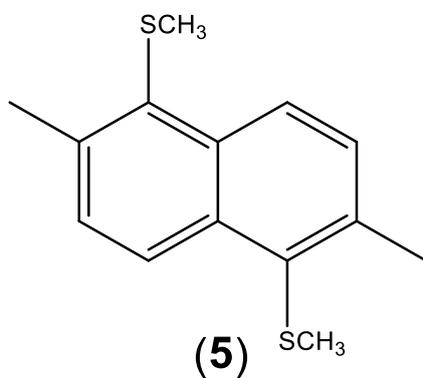




HSQC-NMR

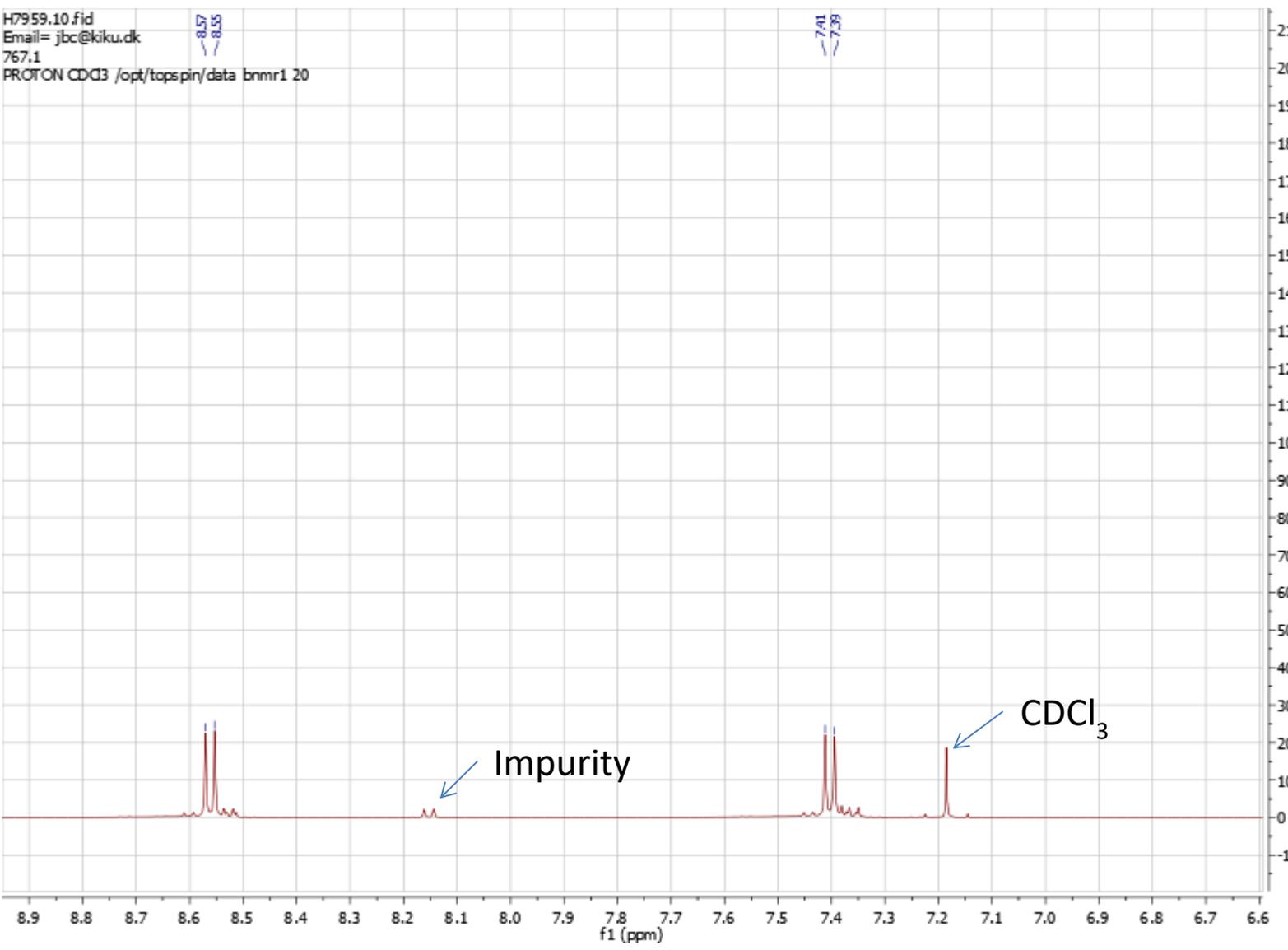
NMR-spectra of compound **5** in CDCl₃

¹H-NMR

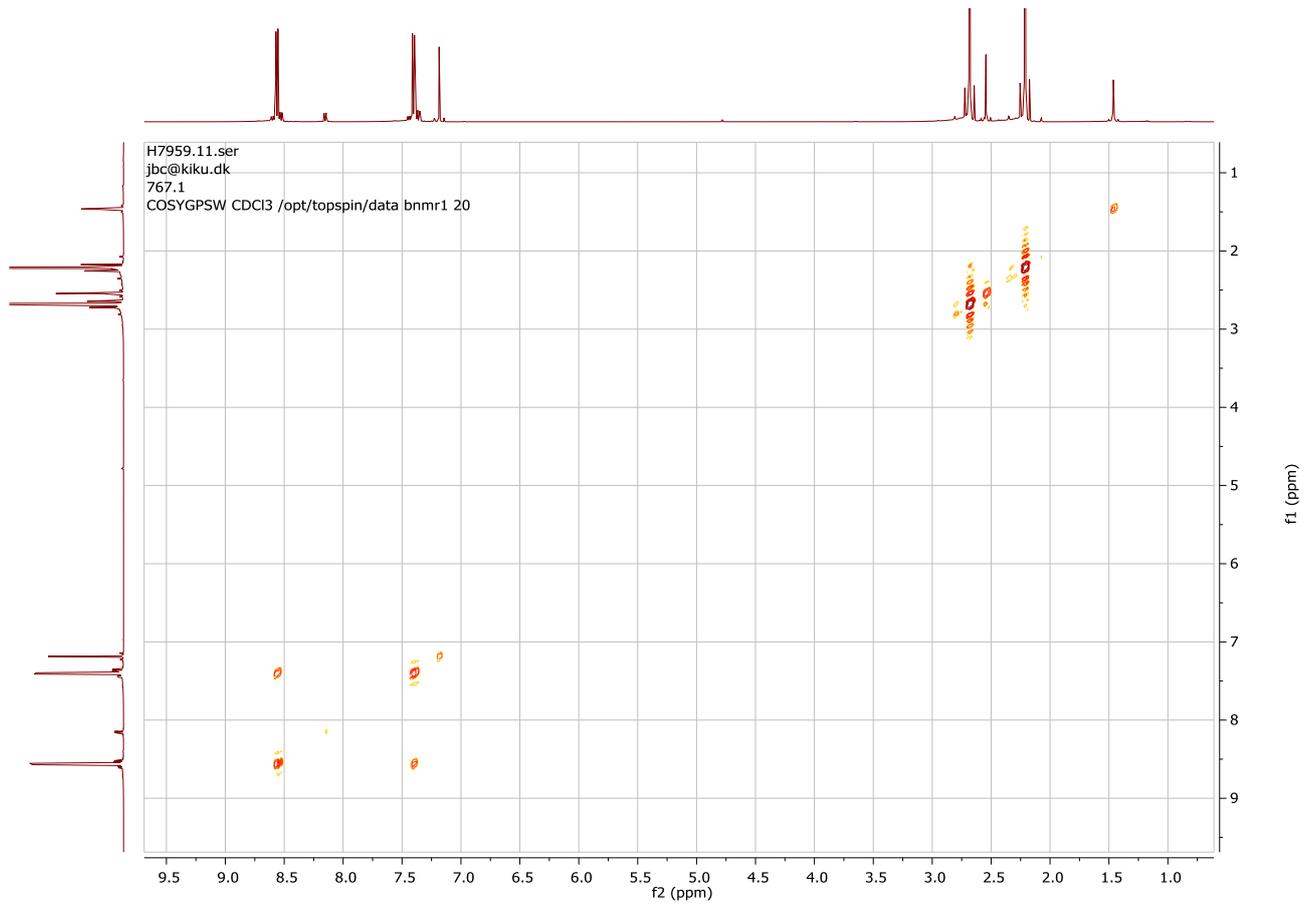


8.57
8.58

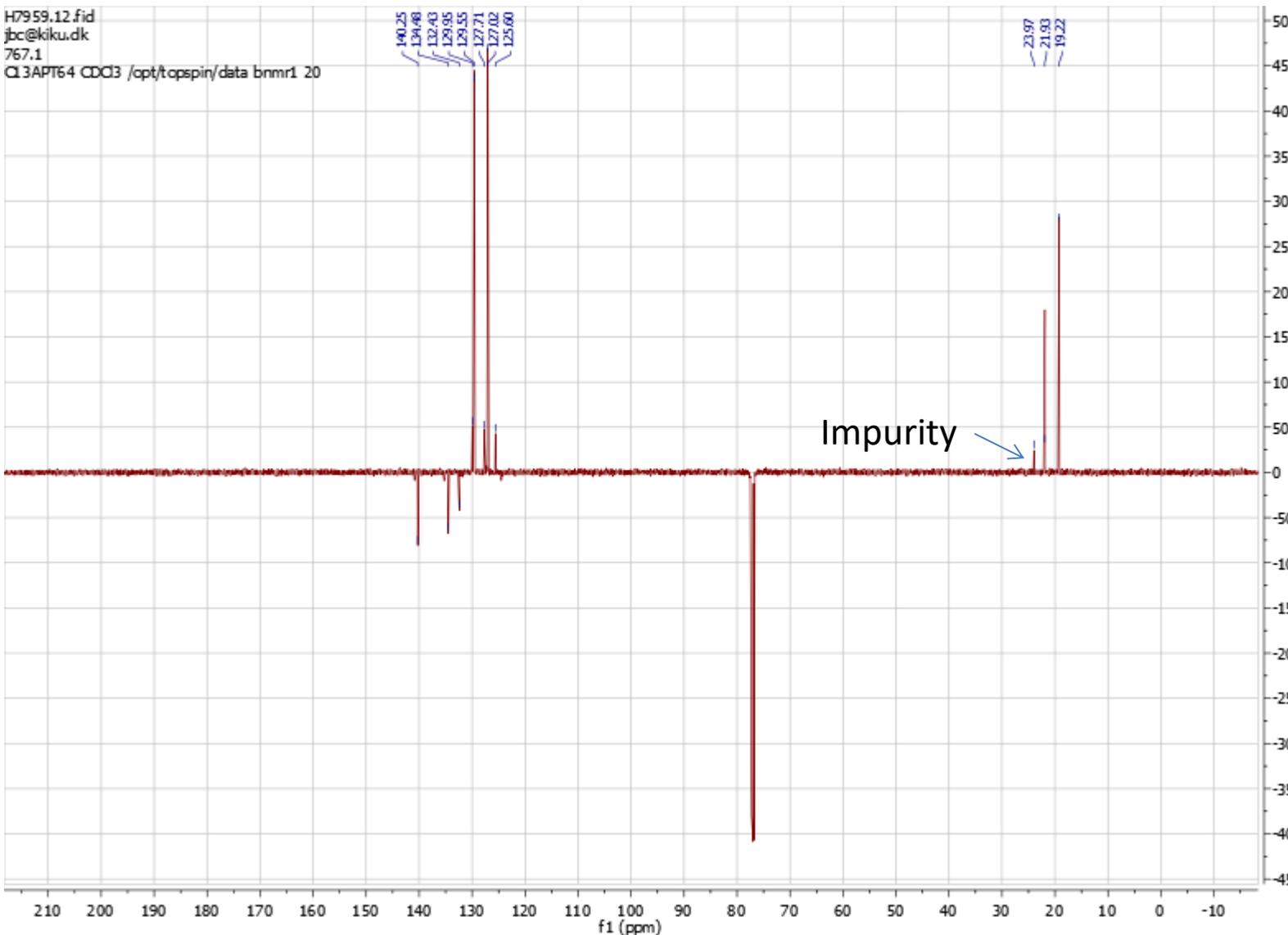
7.41
7.39



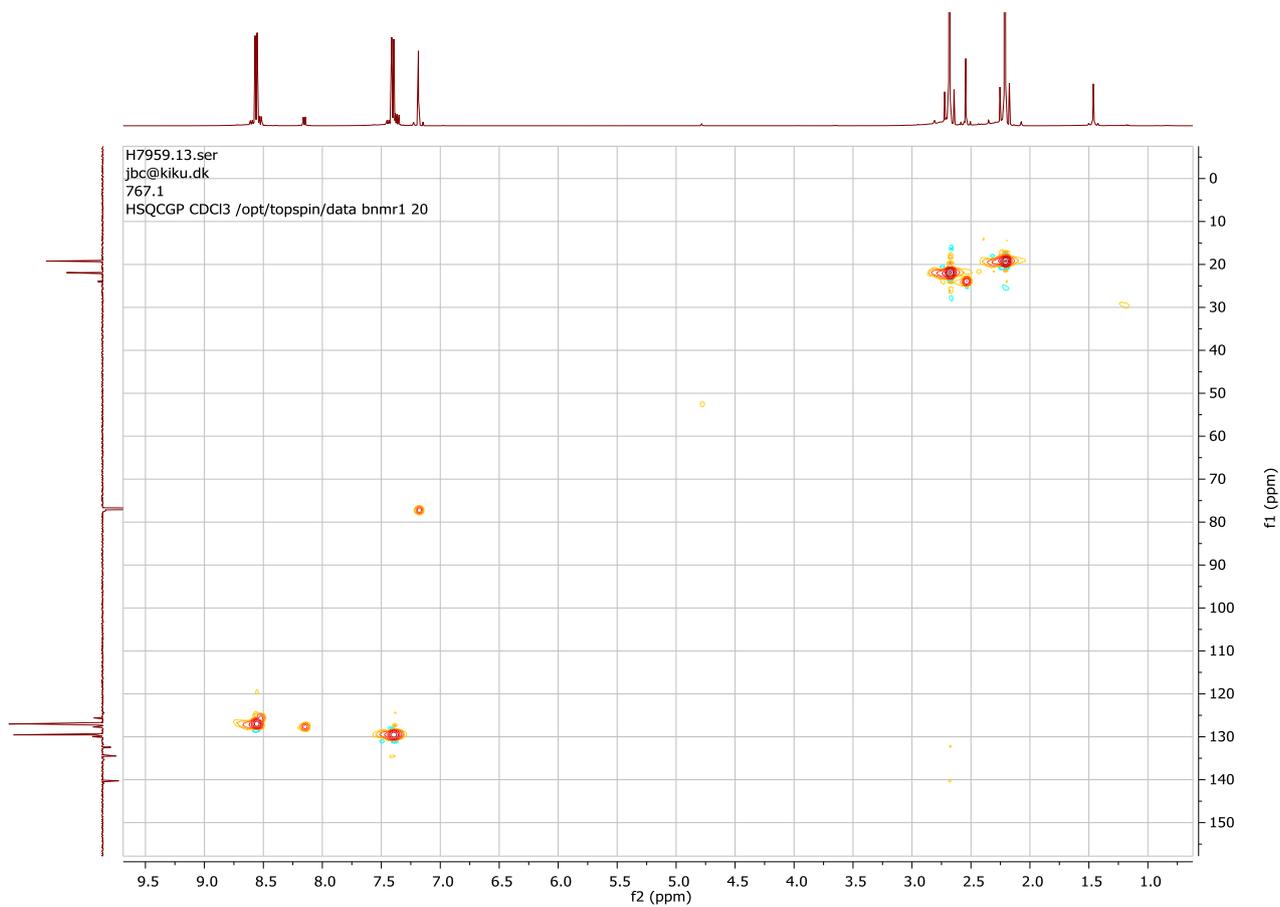
COSY-NMR



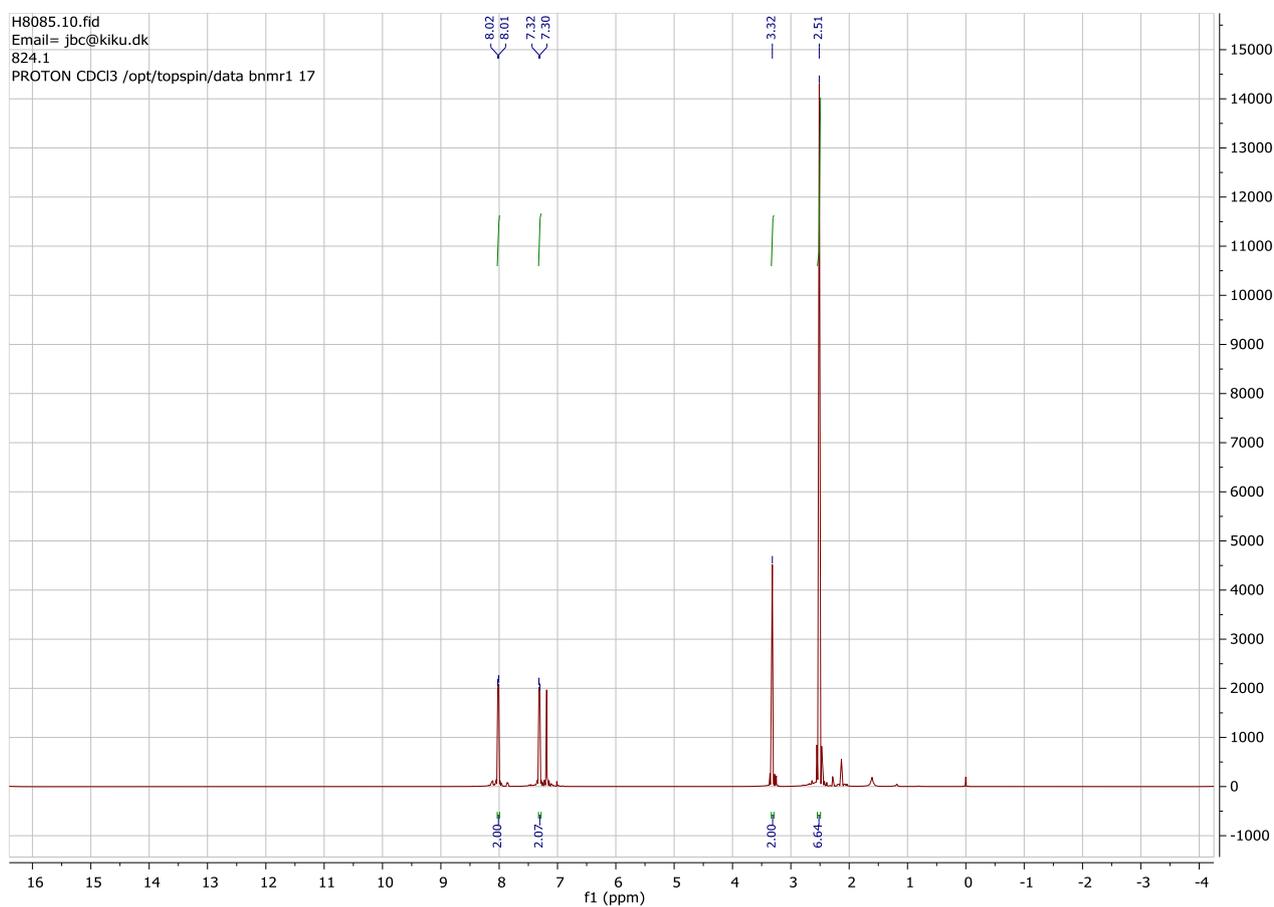
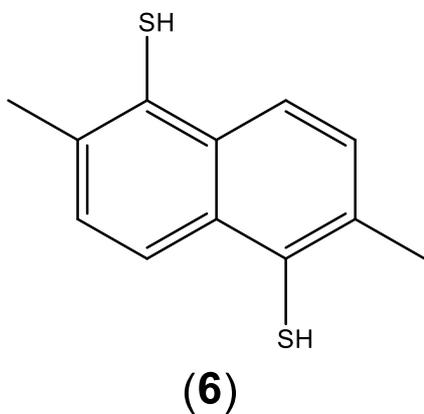
APT-¹³C-NMR



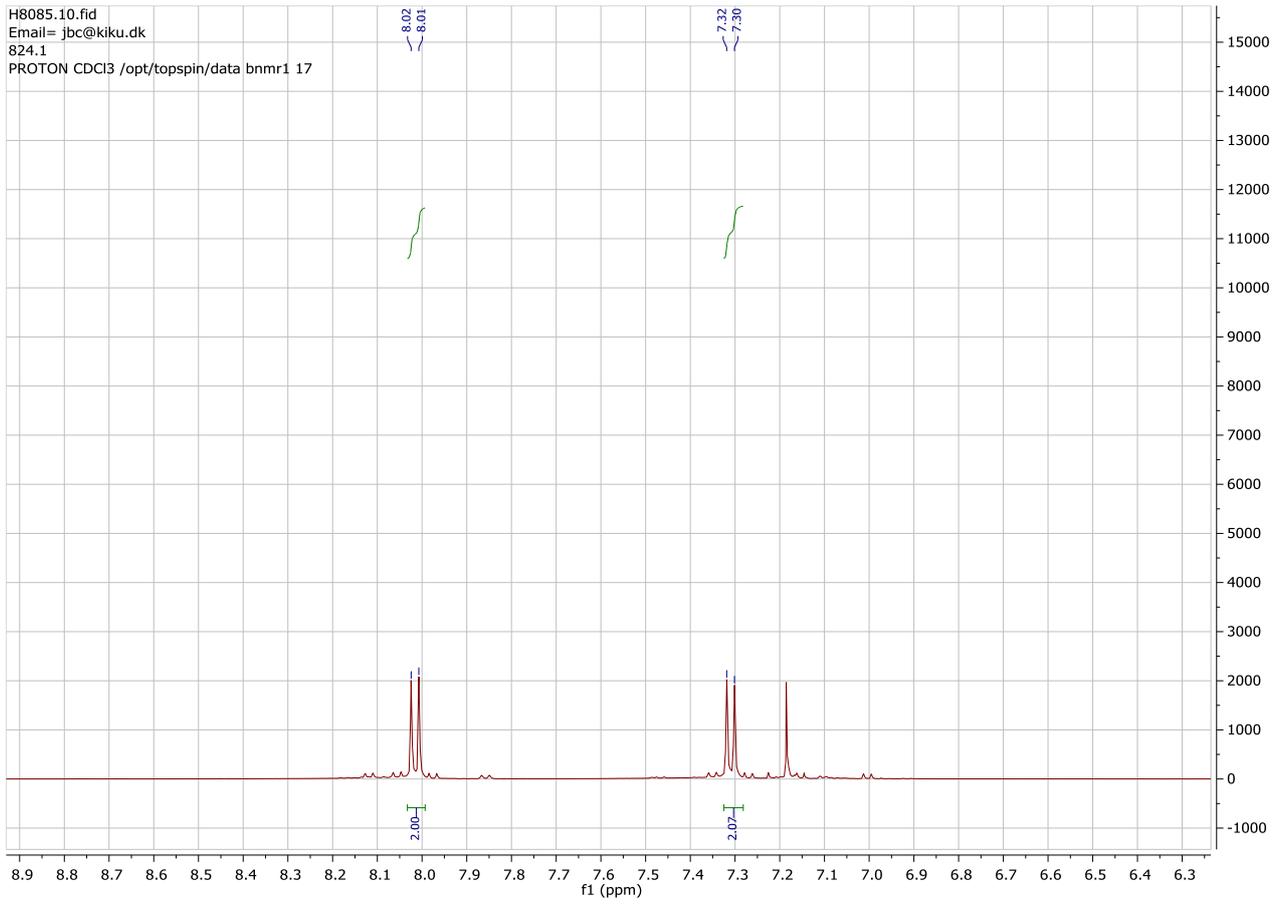
HSQC-NMR



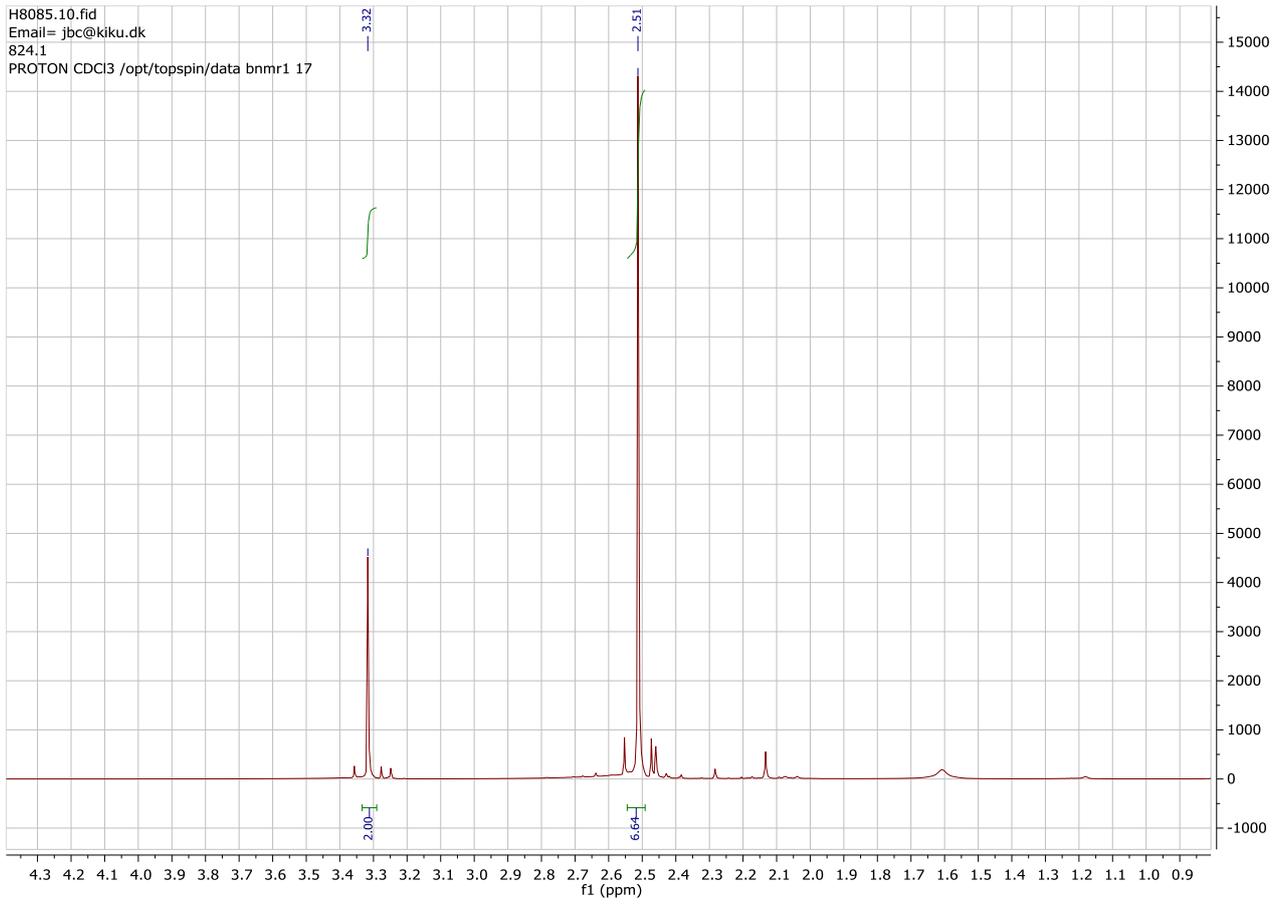
NMR-spectra of compound **6** in CDCl₃



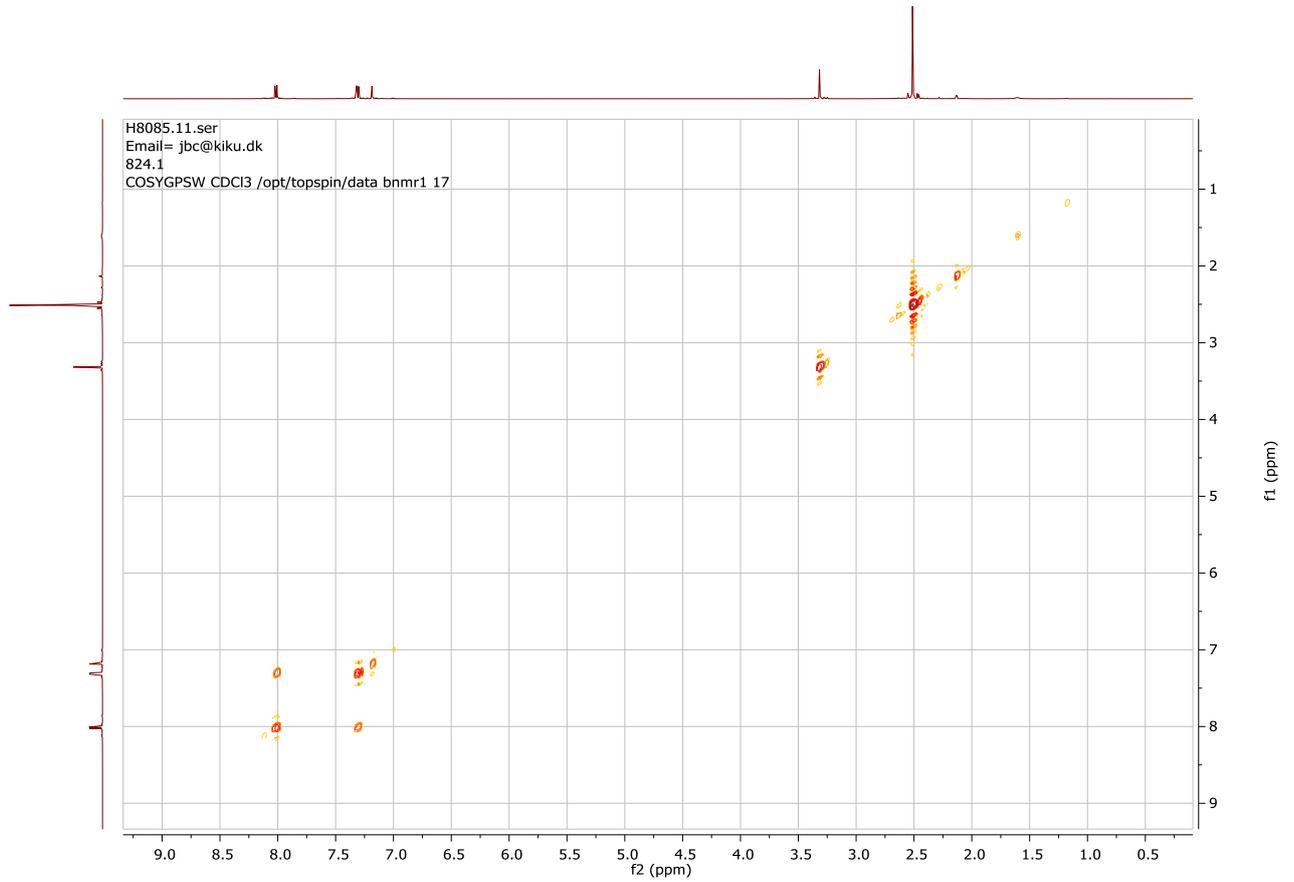
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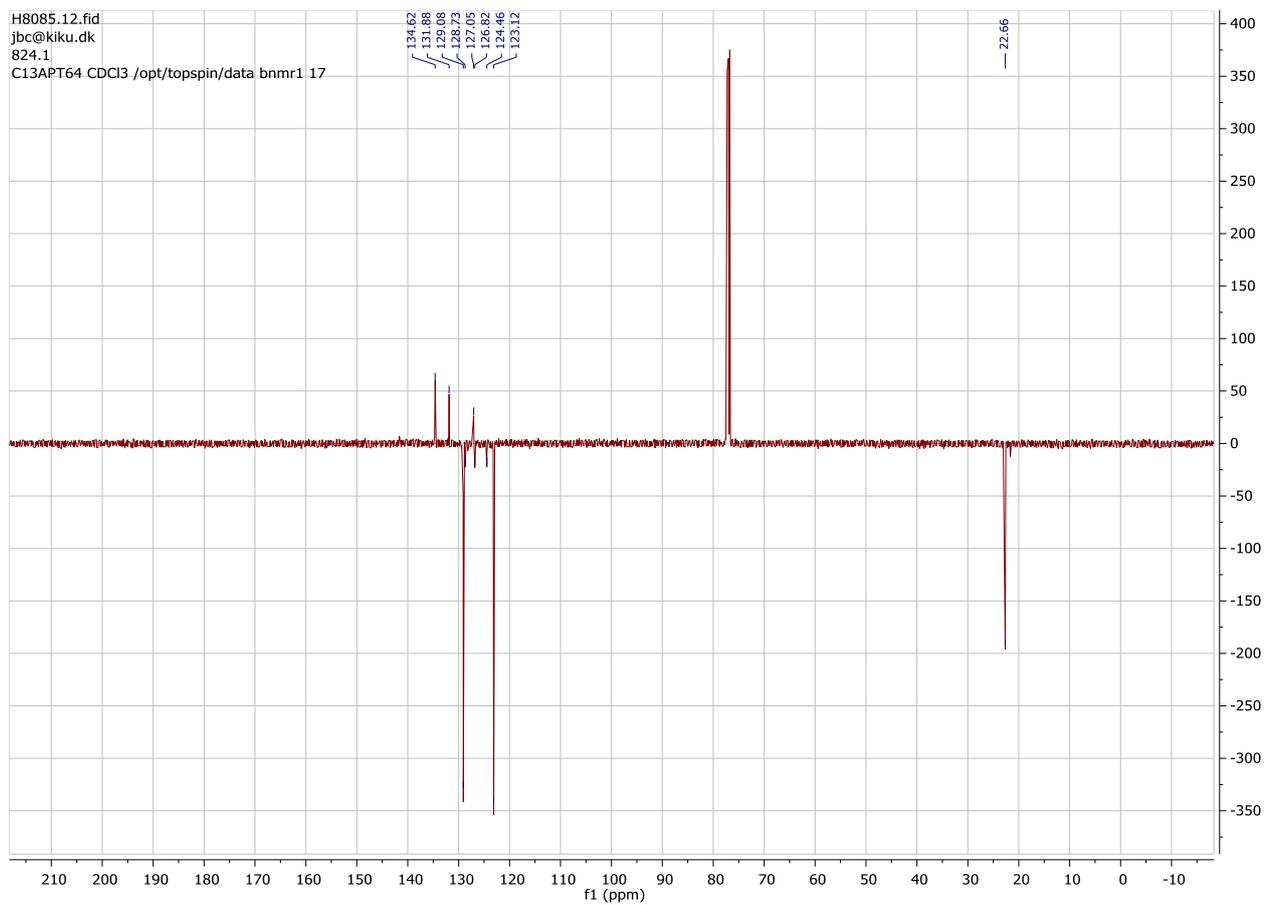
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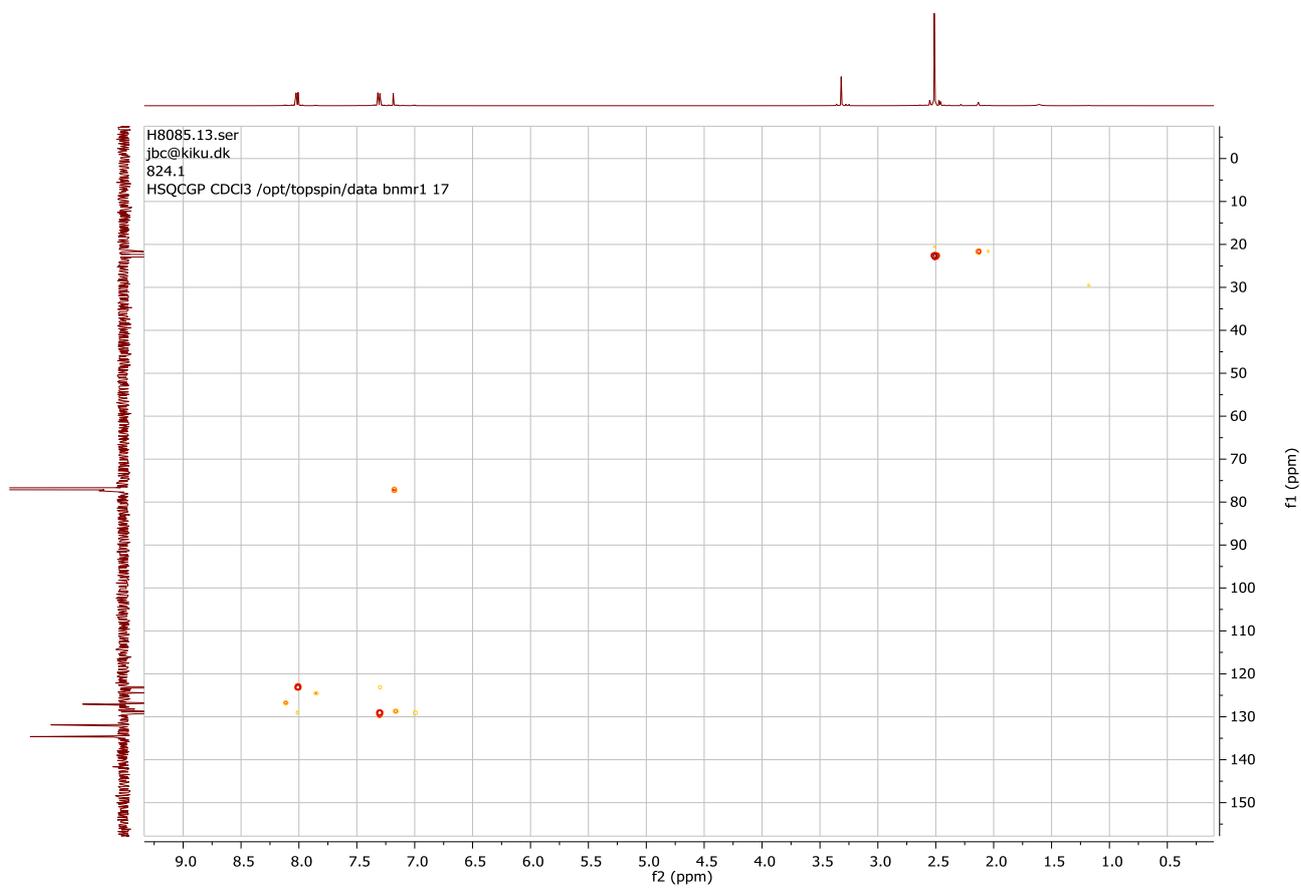
COSY-NMR



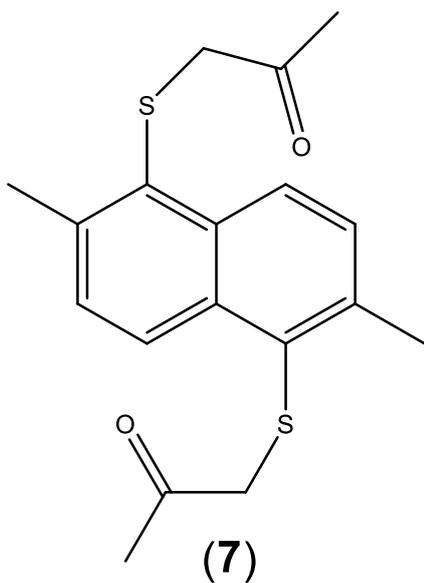
APT-¹³C-NMR



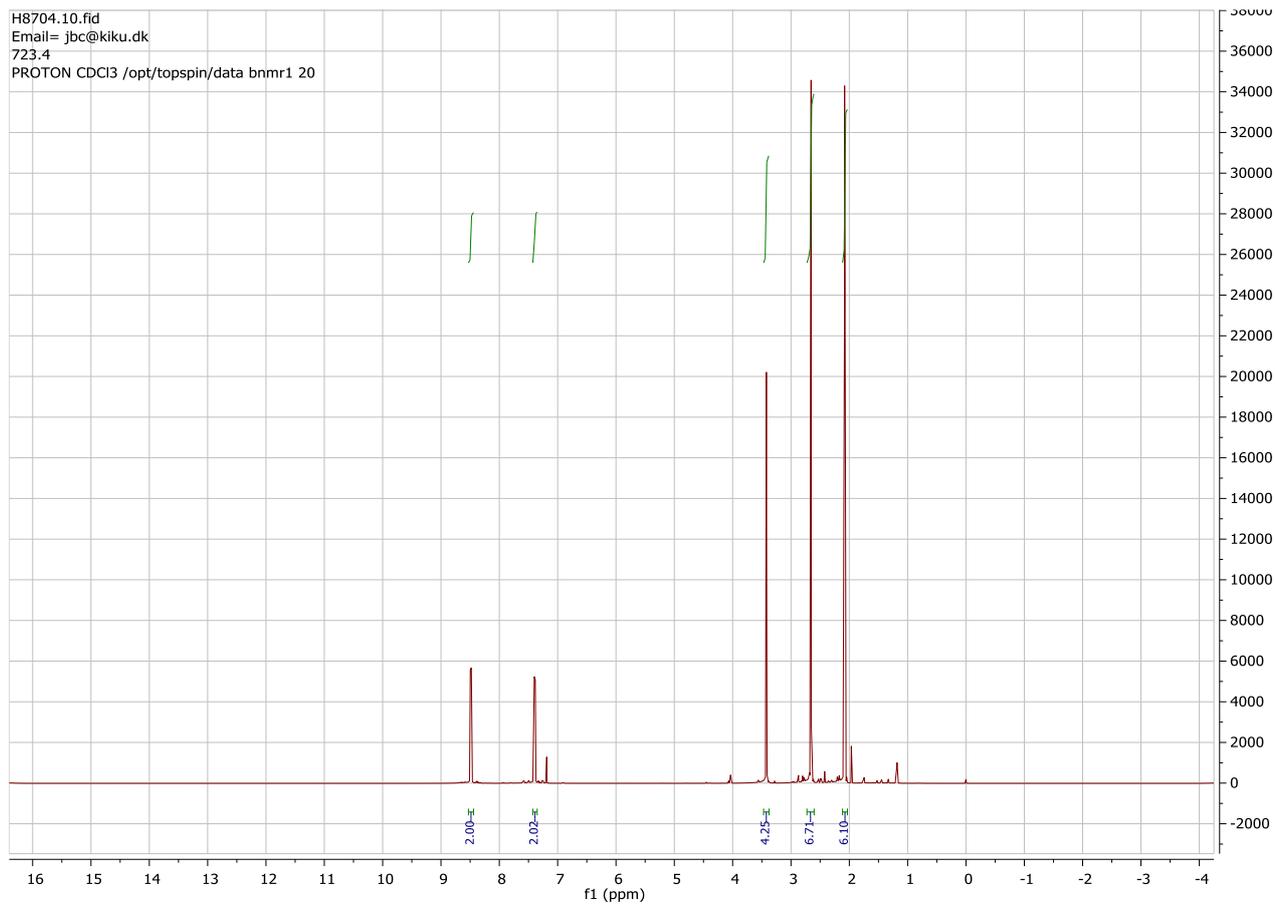
HSQC-NMR



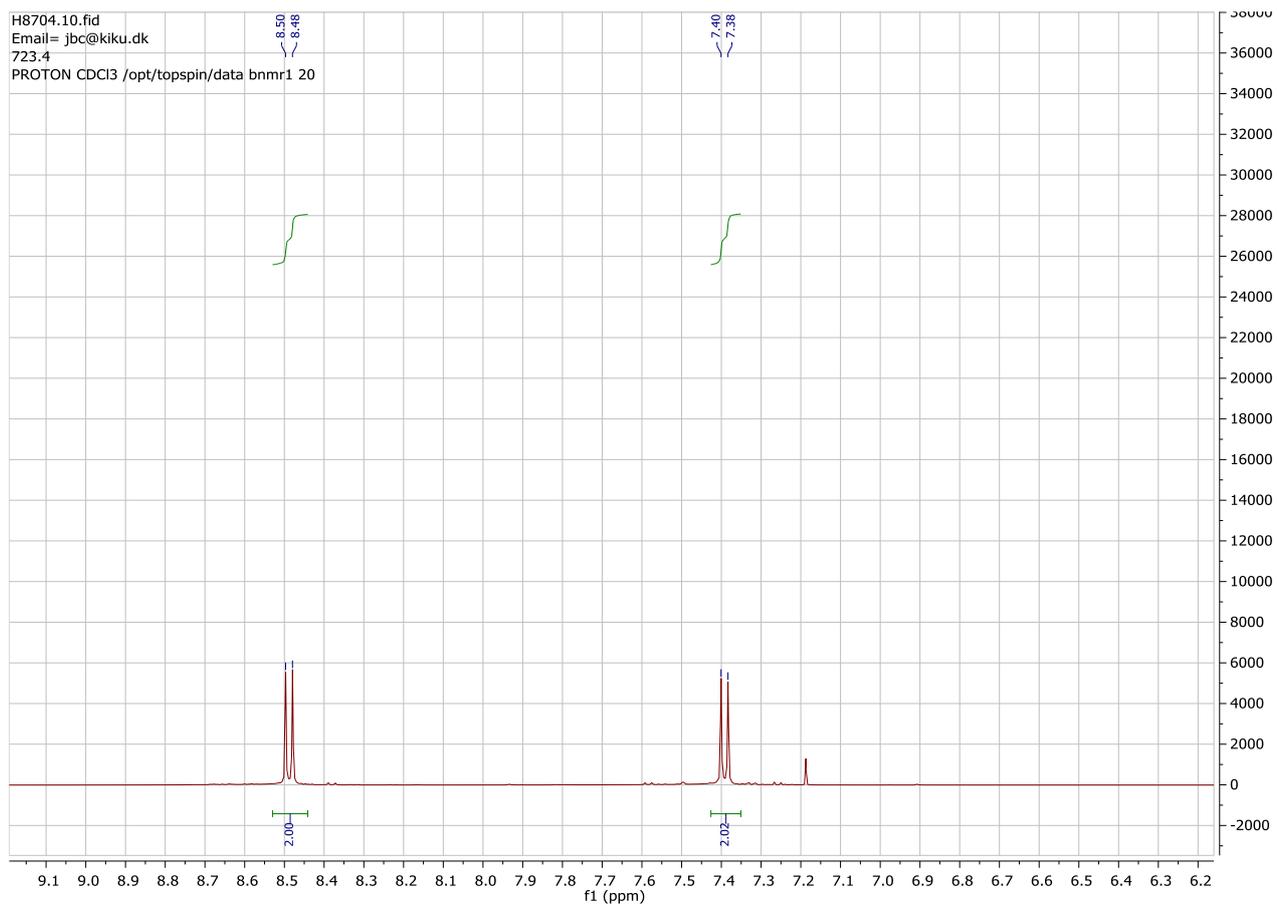
NMR of compound **7** in CDCl₃



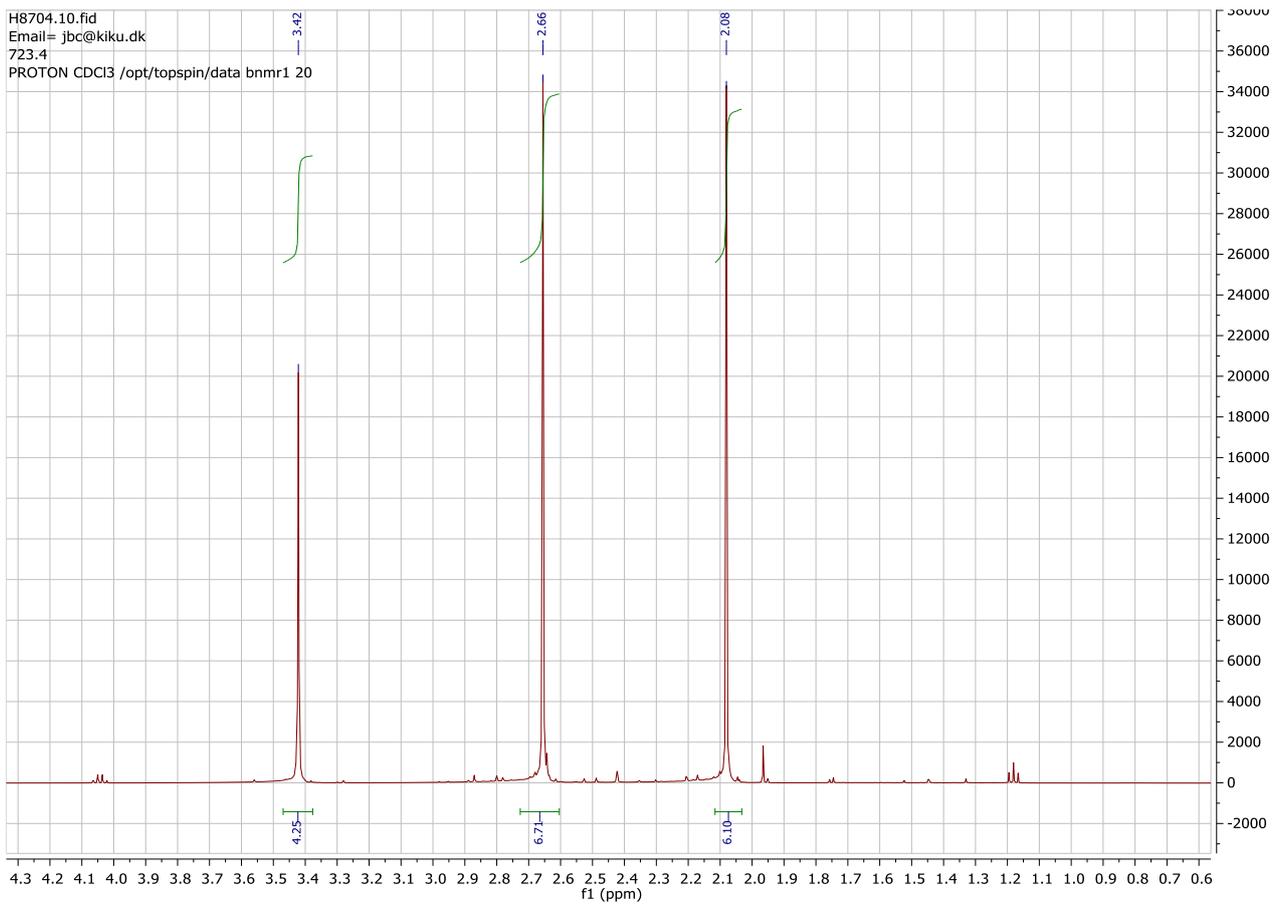
¹H-NMR



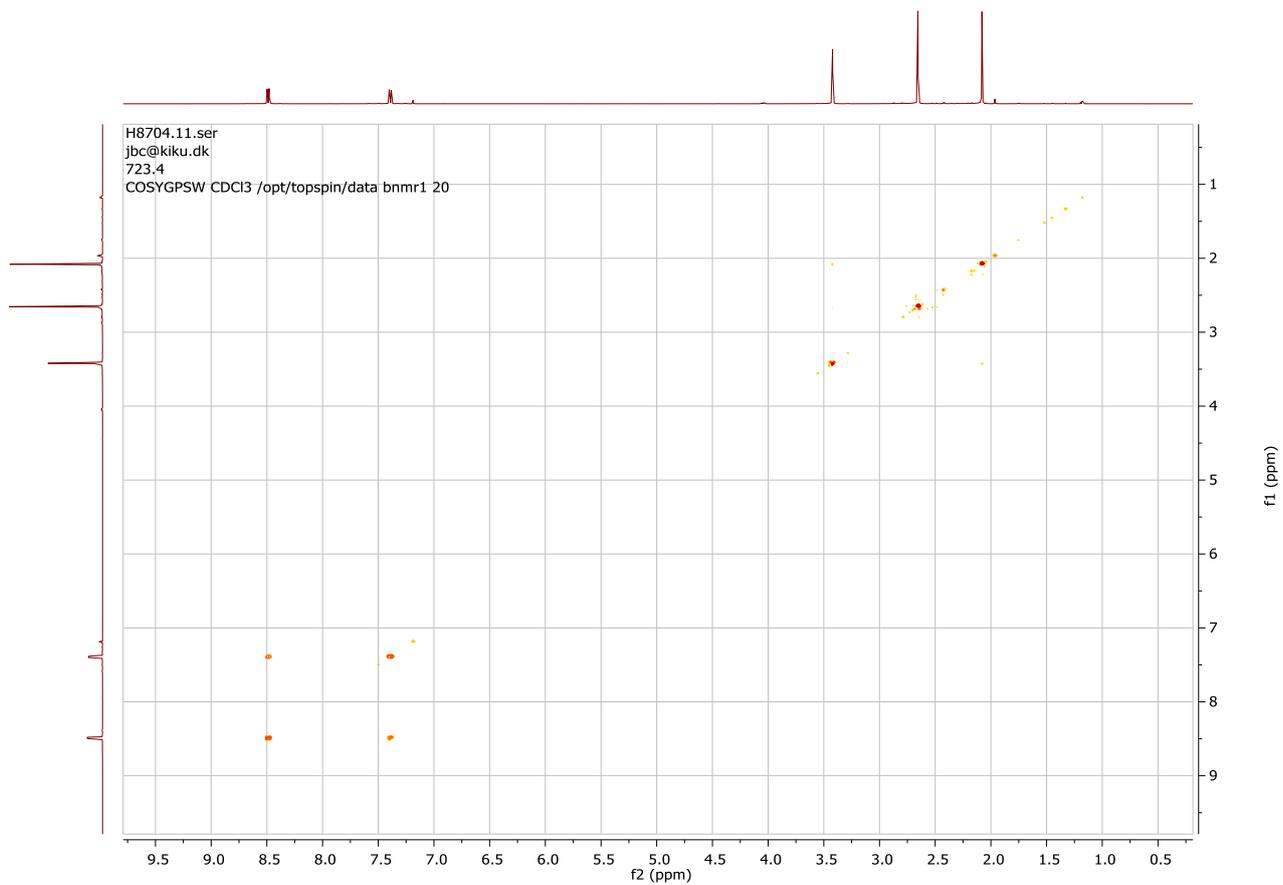
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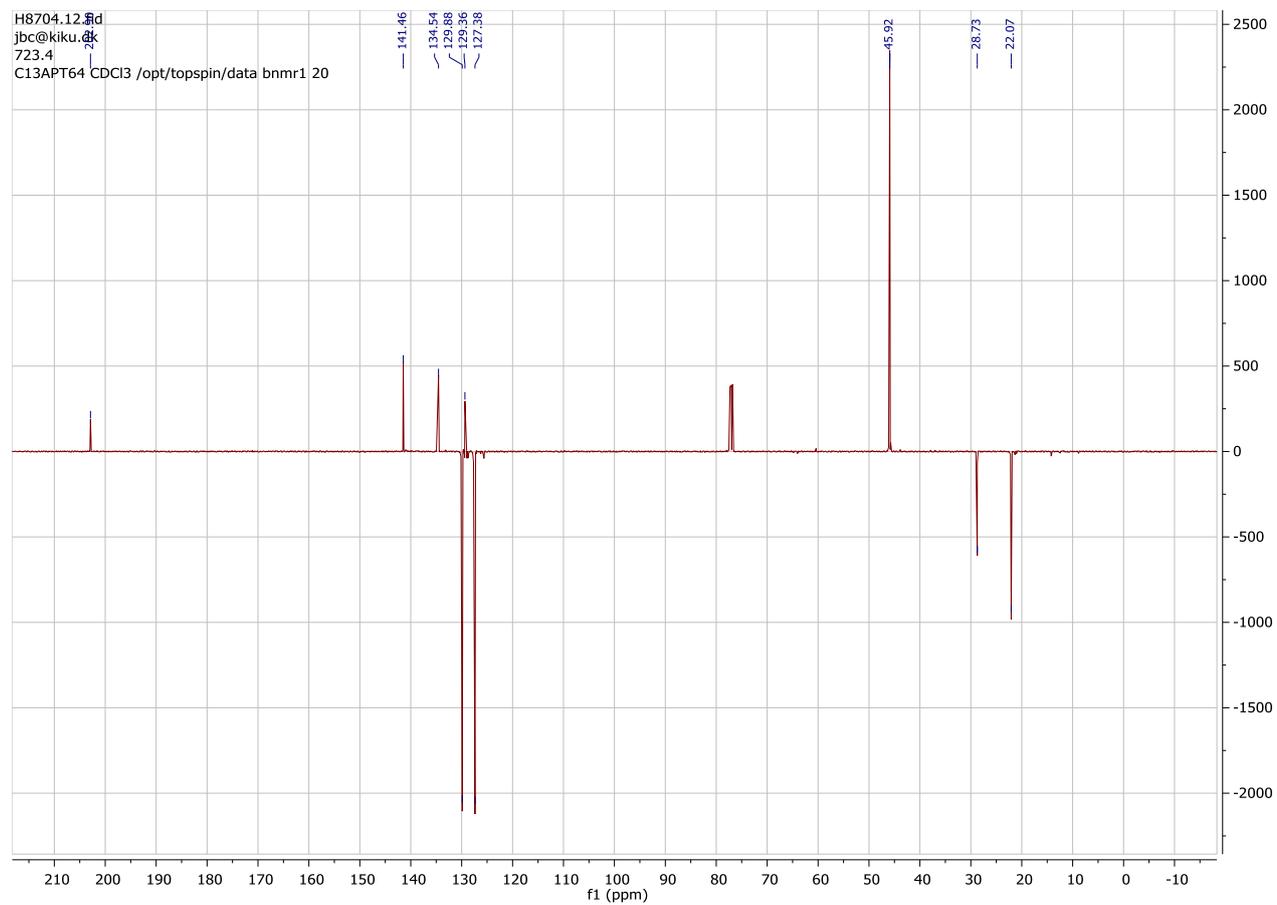
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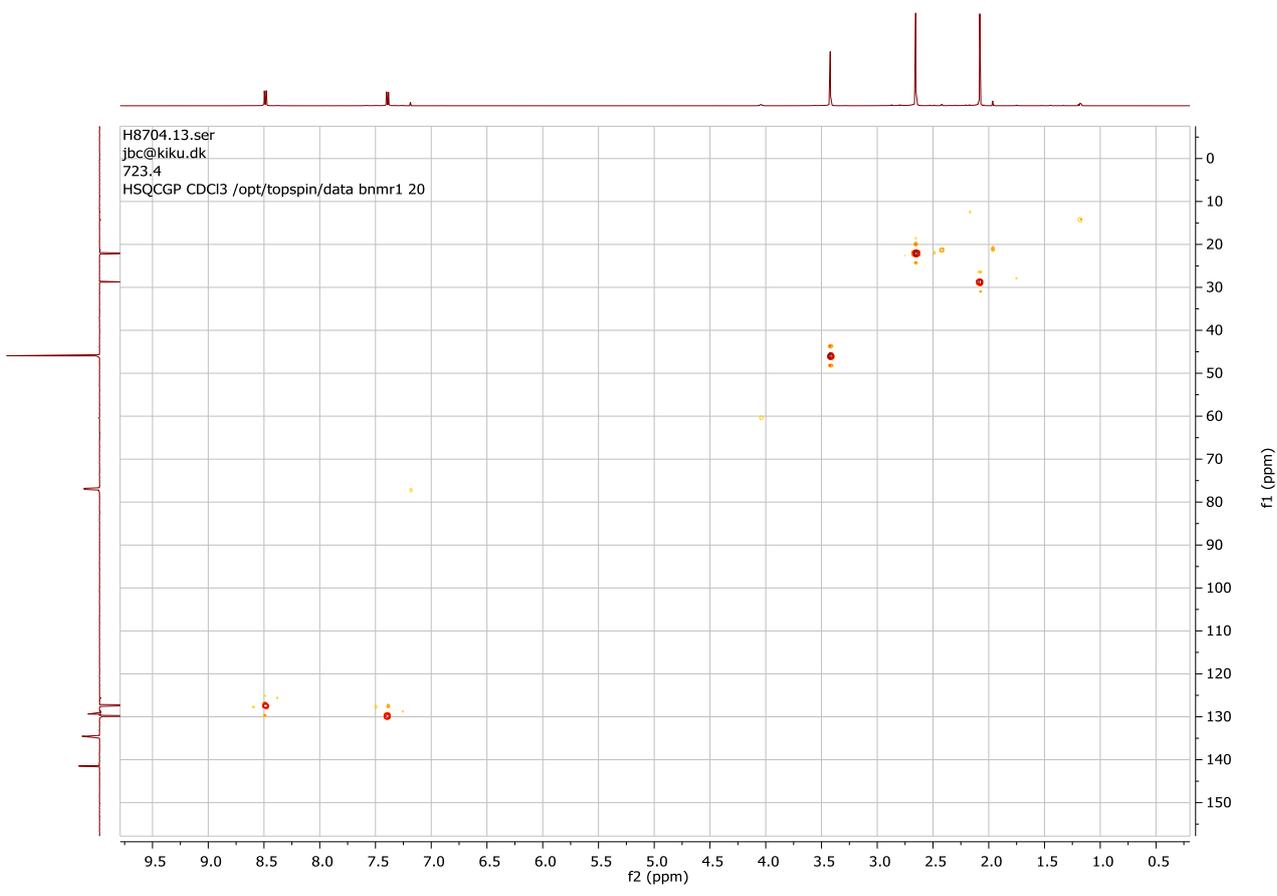
COSY-NMR



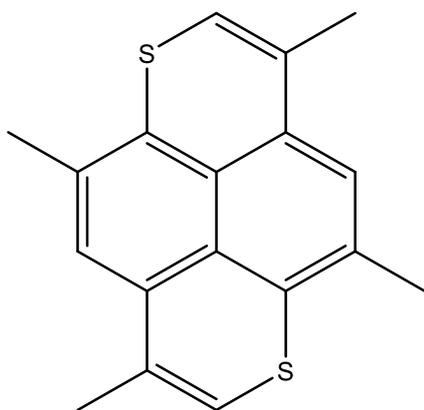
APT-¹³C-NMR



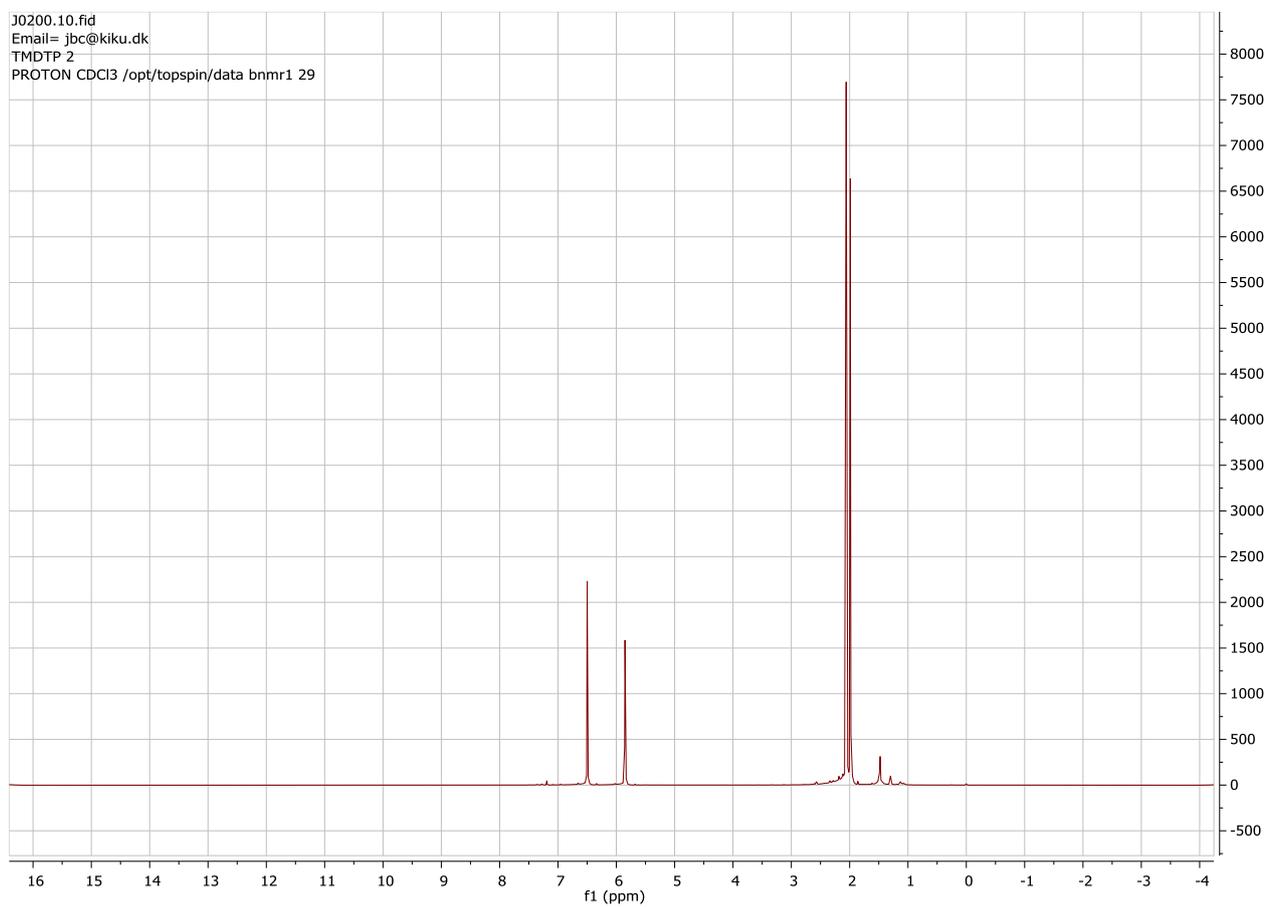
HSQC-NMR



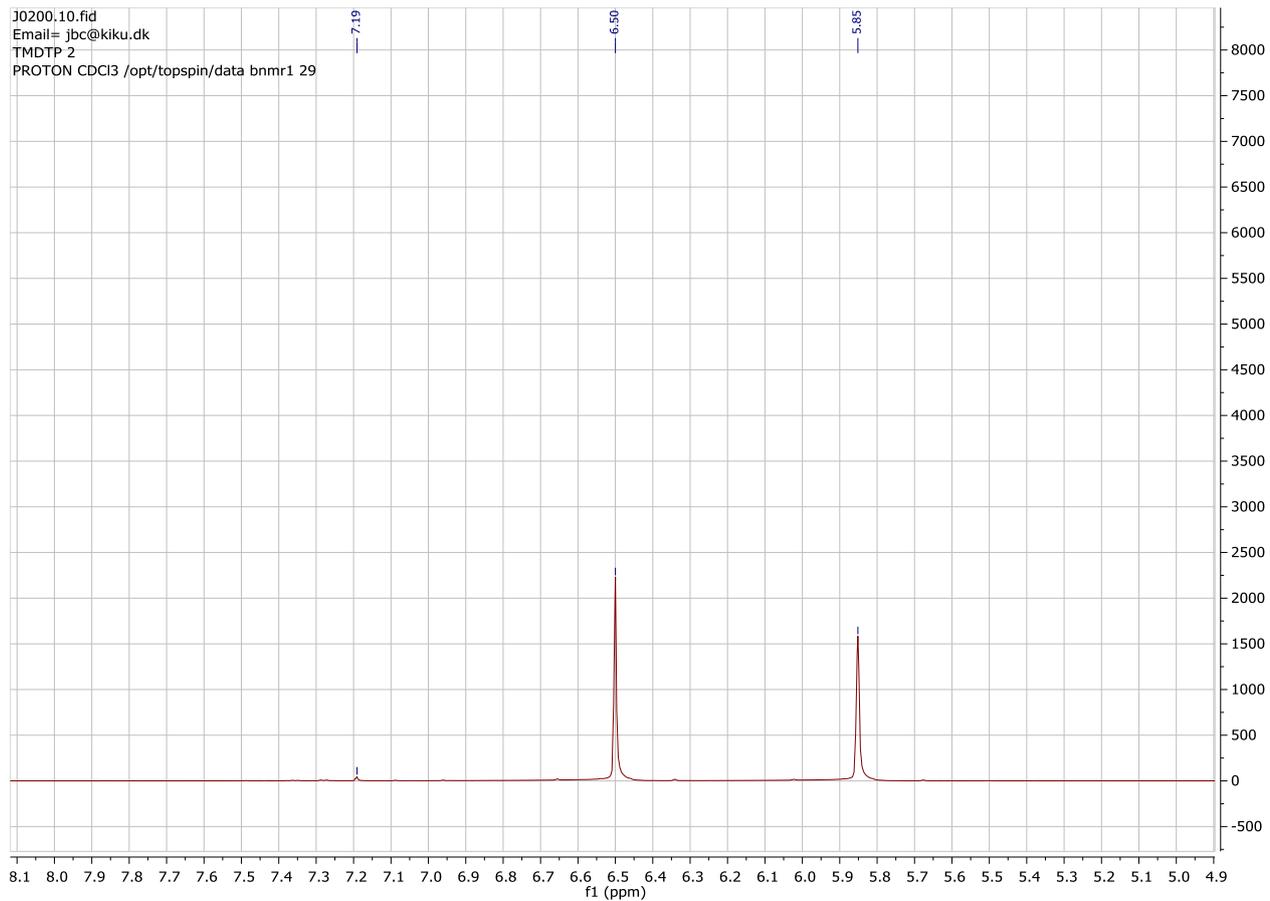
NMR-data on compound **2** in CS₂ with a CDCl₃-lock tube



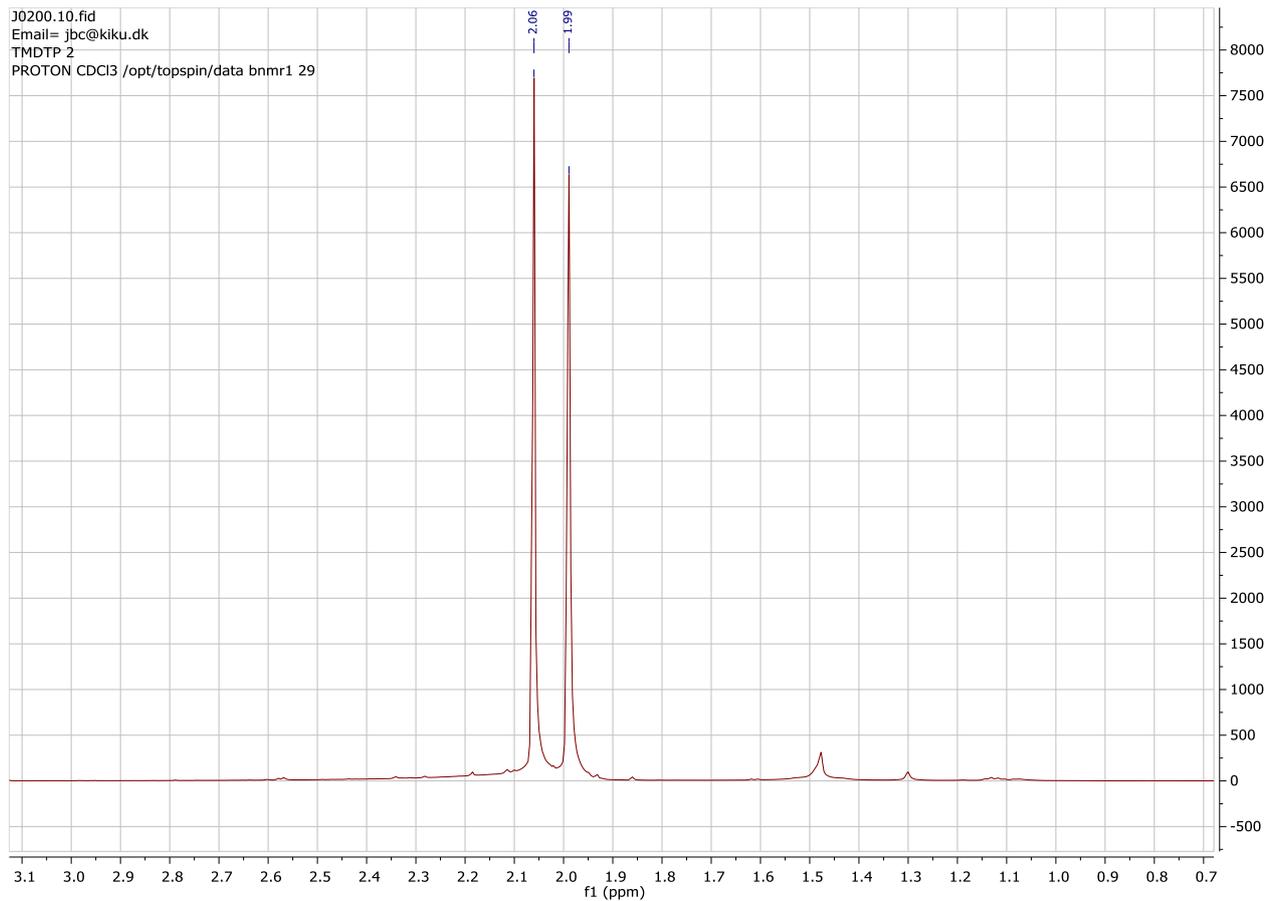
(2)



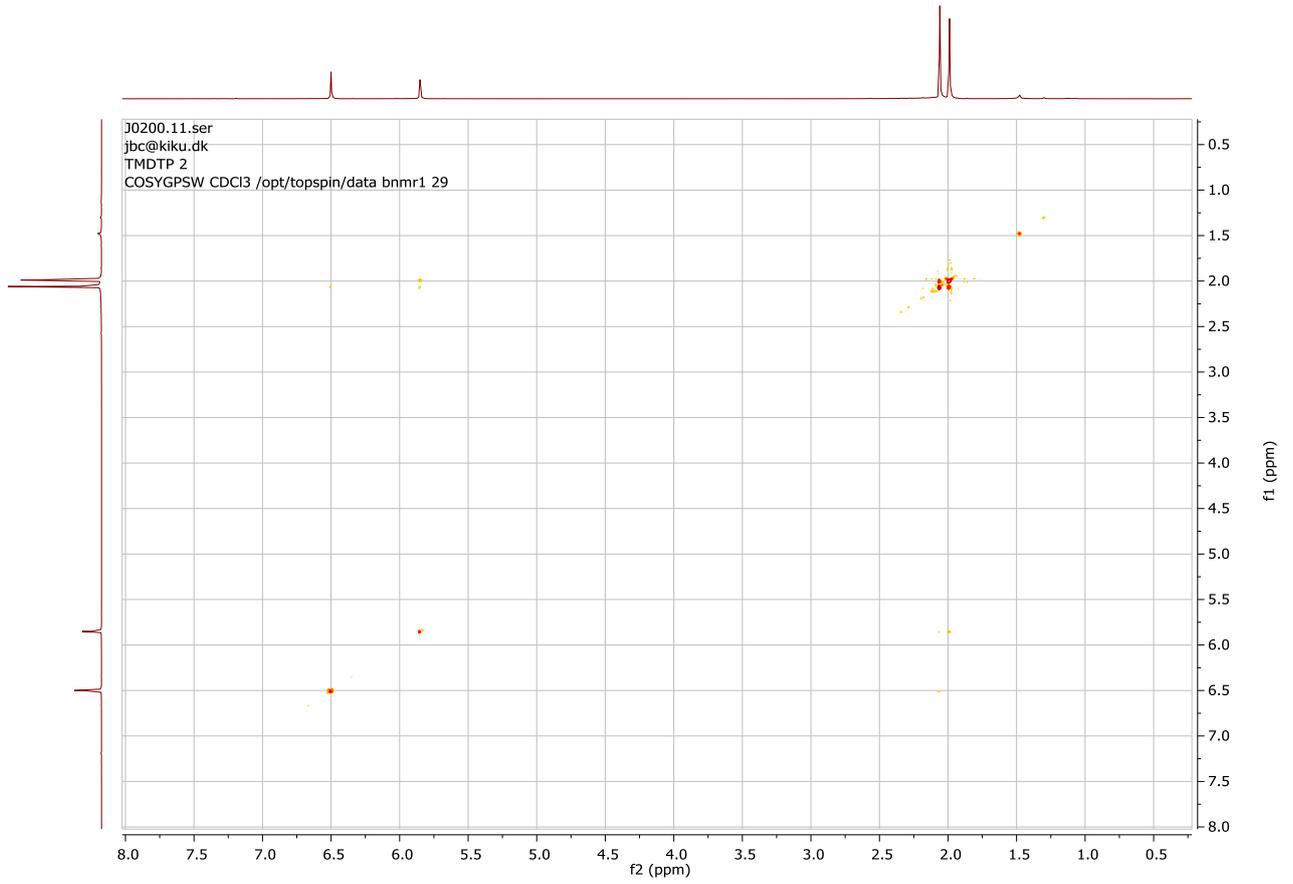
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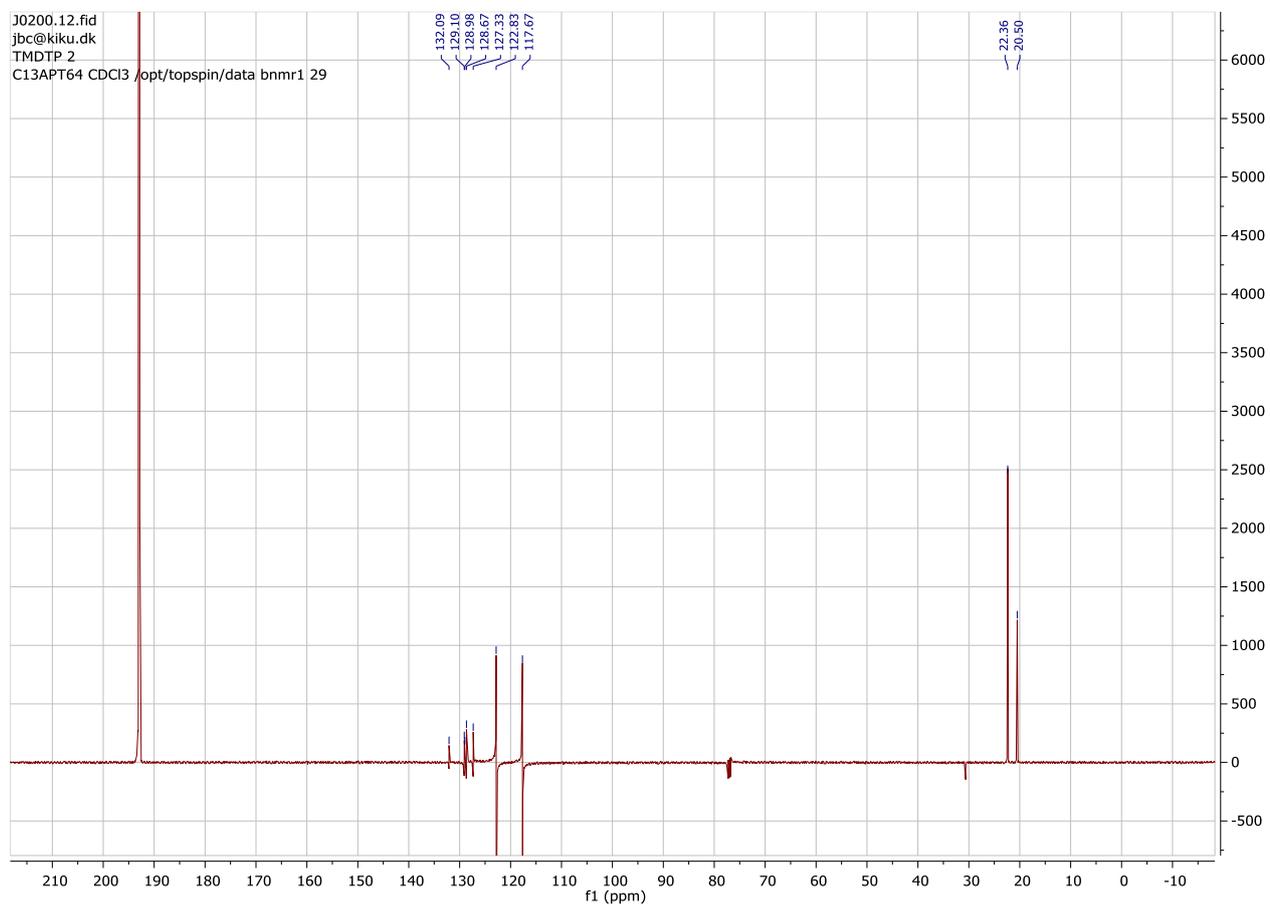
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COSY-NMR



APT-¹³C-NMR



HSQC-NMR

