

Supporting Information: DNP Solid-State NMR & Crystal Structure Prediction for the study of Polymorphs of Theophylline

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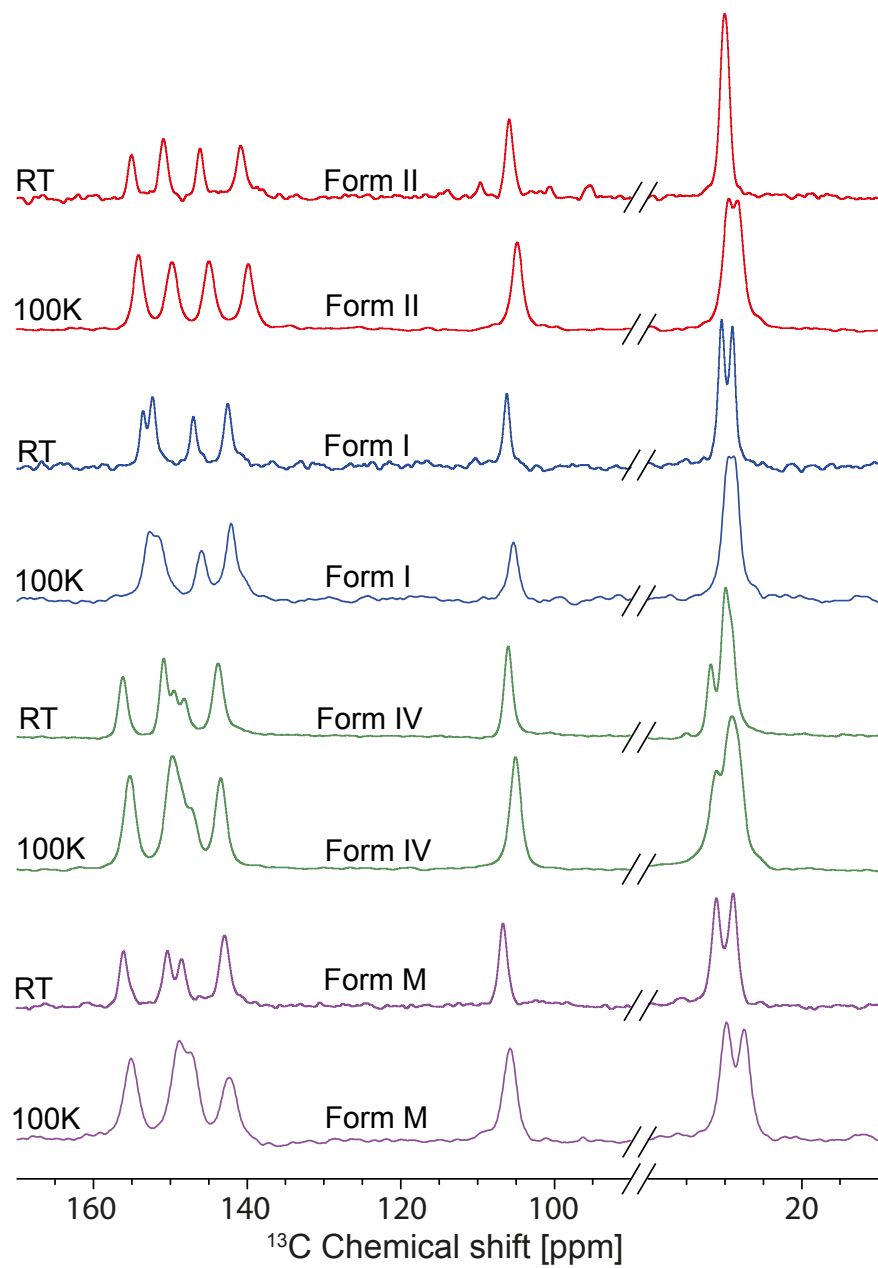


Figure S1: Comparison between ^{13}C chemical shifts at 105 K with a 9.4 T spectrometer and at RT with a 16.4 T spectrometer for different forms of theophylline in 64 scans. More details on CP parameters are given in the experimental section of the main text.

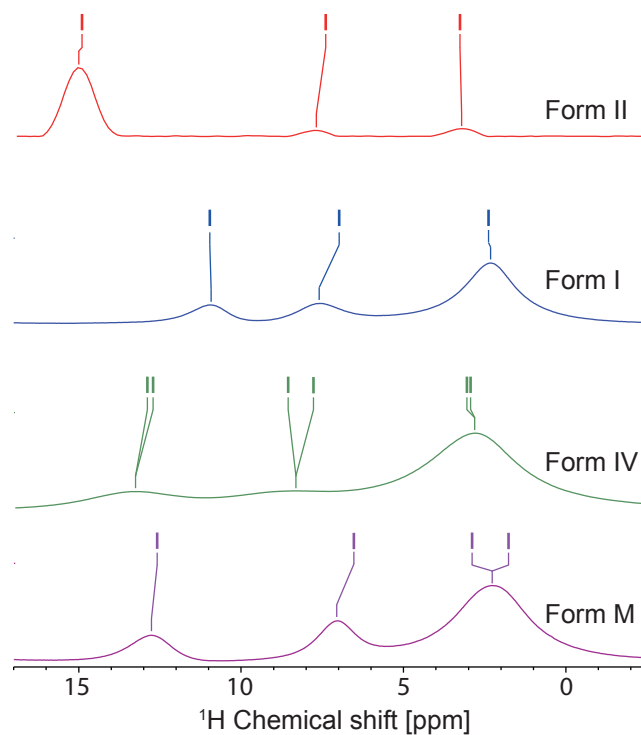


Figure S2: ^1H spectra obtained with a 9.4 T spectrometer at 105 K of each form of theophylline in 16 scans. The tick marks show the predicted shifts from GIPAW DFT calculations.

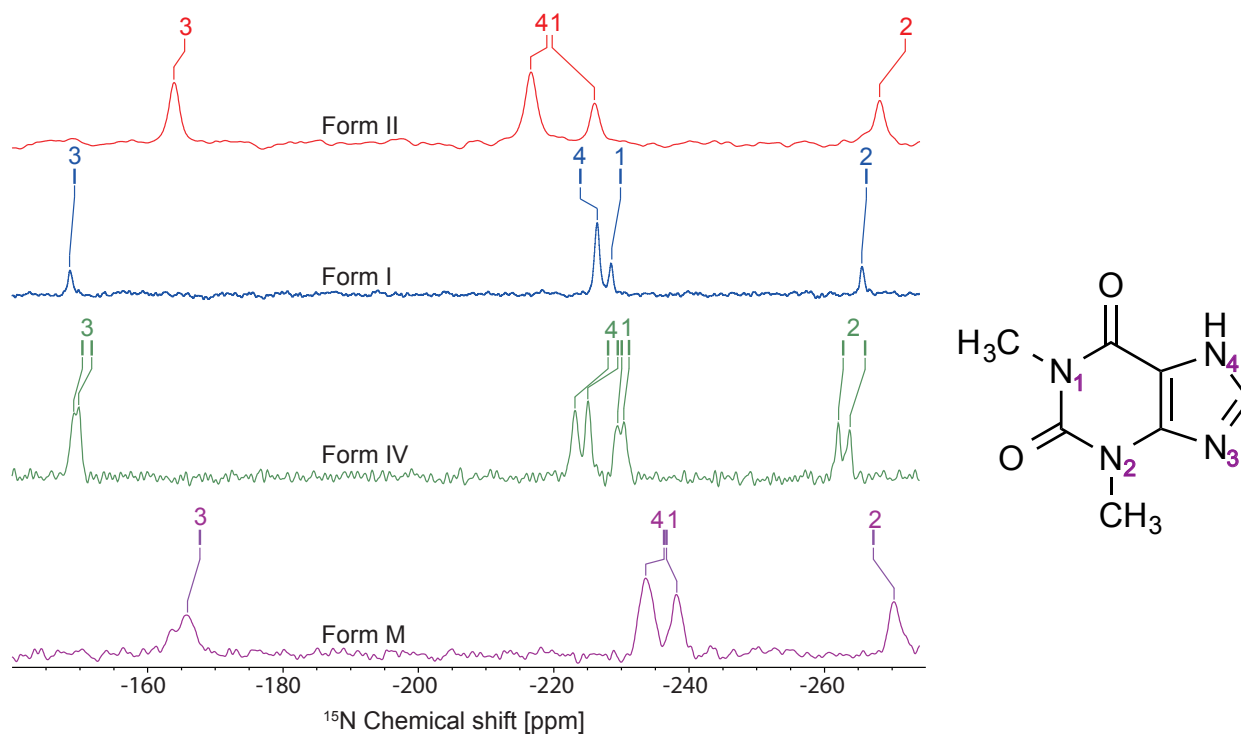


Figure S3: Left: DNP enhanced ^{15}N CPMAS spectra of theophylline Form II, IV, and M acquired with a 9.4 T spectrometer at 105 K. Form I spectra was acquired at 300 K with a 16.4 T spectrometer. The tick marks show the predicted shifts from GIPAW DFT calculations. **Right:** Molecular structure of theophylline. Purple numbers correspond to nitrogen peak labeling. More details on the CP parameters are given in the experimental section of the main text.

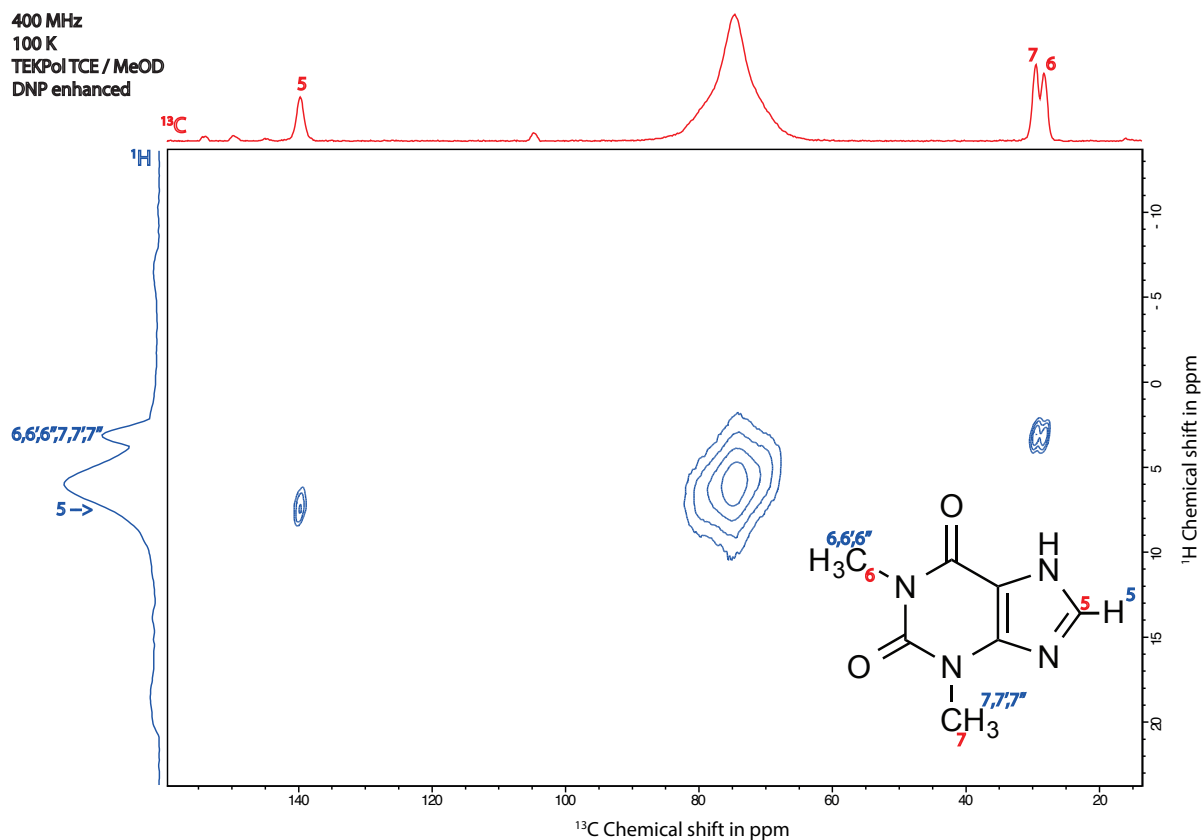


Figure S4: DNP enhanced ¹H-¹³C HETCOR CPMAS spectra recorded with a 9.4 T spectrometer at 105 K of theophylline Form II. More details on HETCOR parameters are given in the experimental section of the main text.

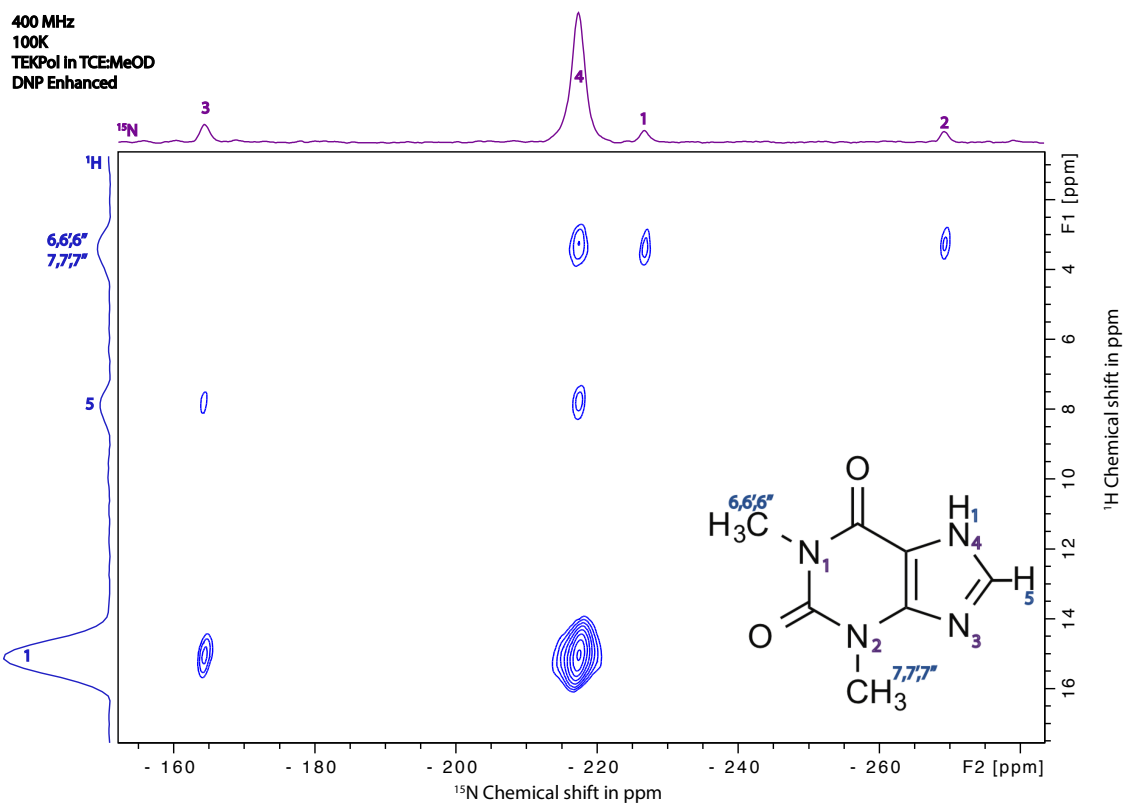


Figure S5: DNP enhanced ¹H-¹⁵N HETCOR CPMAS spectra recorded with a 9.4 T spectrometer at 105 K of theophylline Form II. More details on HETCOR parameters are given in the experimental section of the main text.

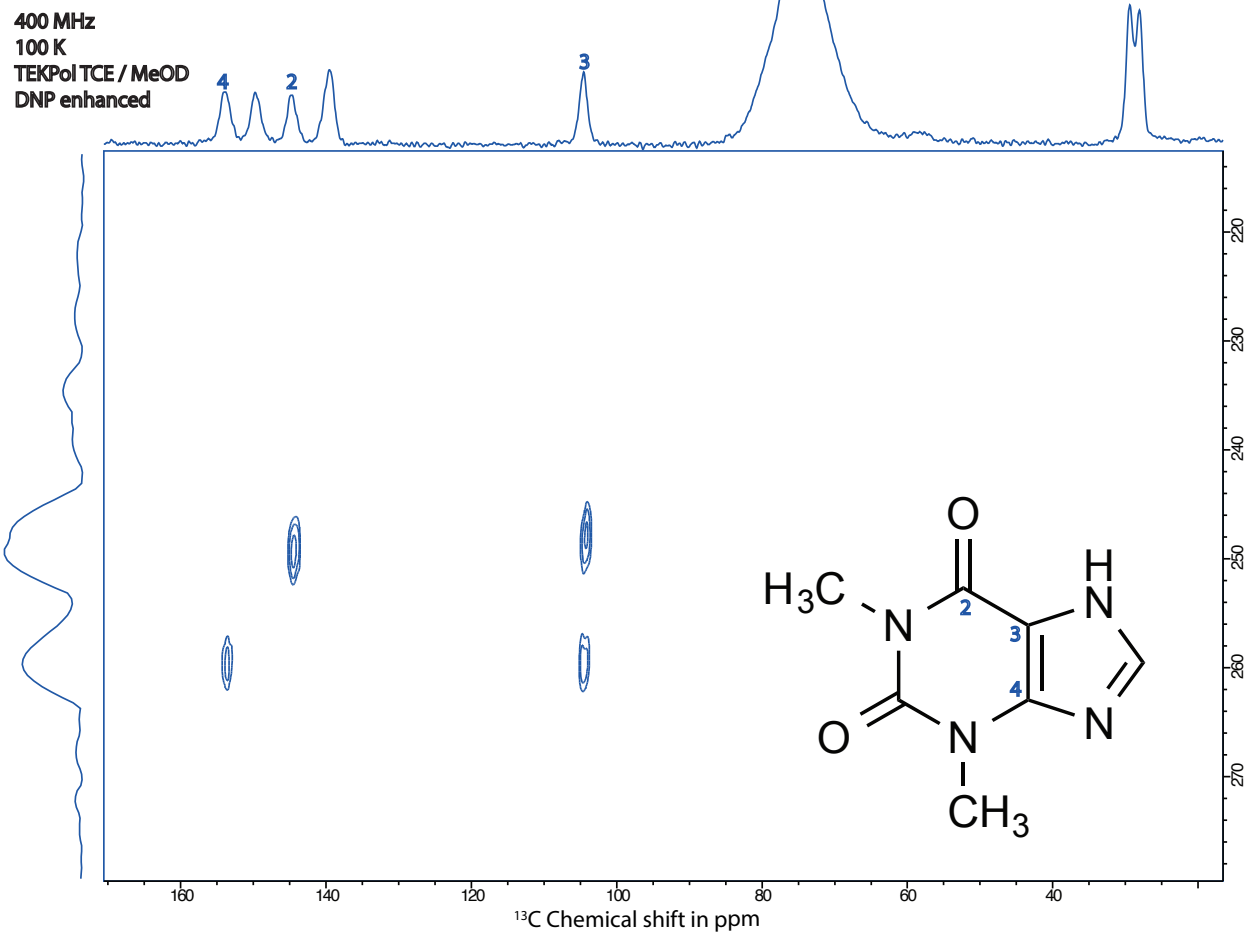


Figure S6: DNP enhanced ¹³C-¹³C INADEQUATE spectra recorded with a 9.4 T spectrometer at 105 K of theophylline Form II. More details on the sequence parameters are given in the experimental section of the main text.

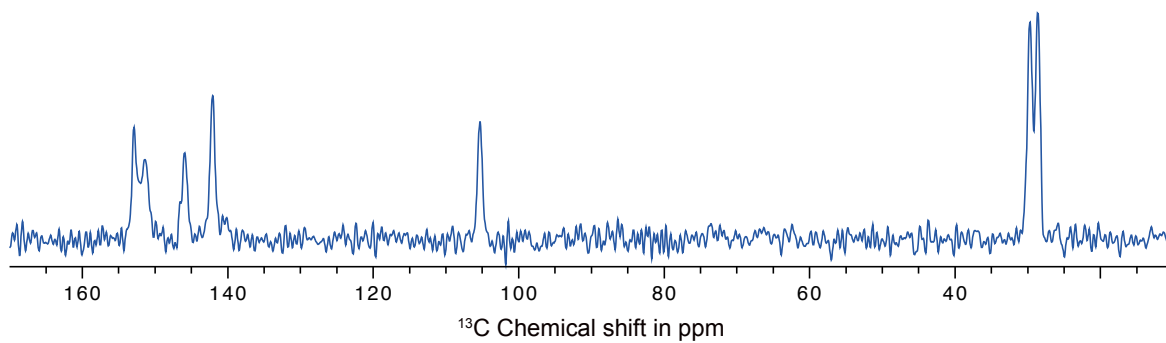


Figure S7: DNP enhanced ¹³C CPMAS spectra recorded with a 9.4 T spectrometer at 105 K of pure theophylline Form I with 64 scans. More details on the CP parameters are given in the experimental section of the main text.

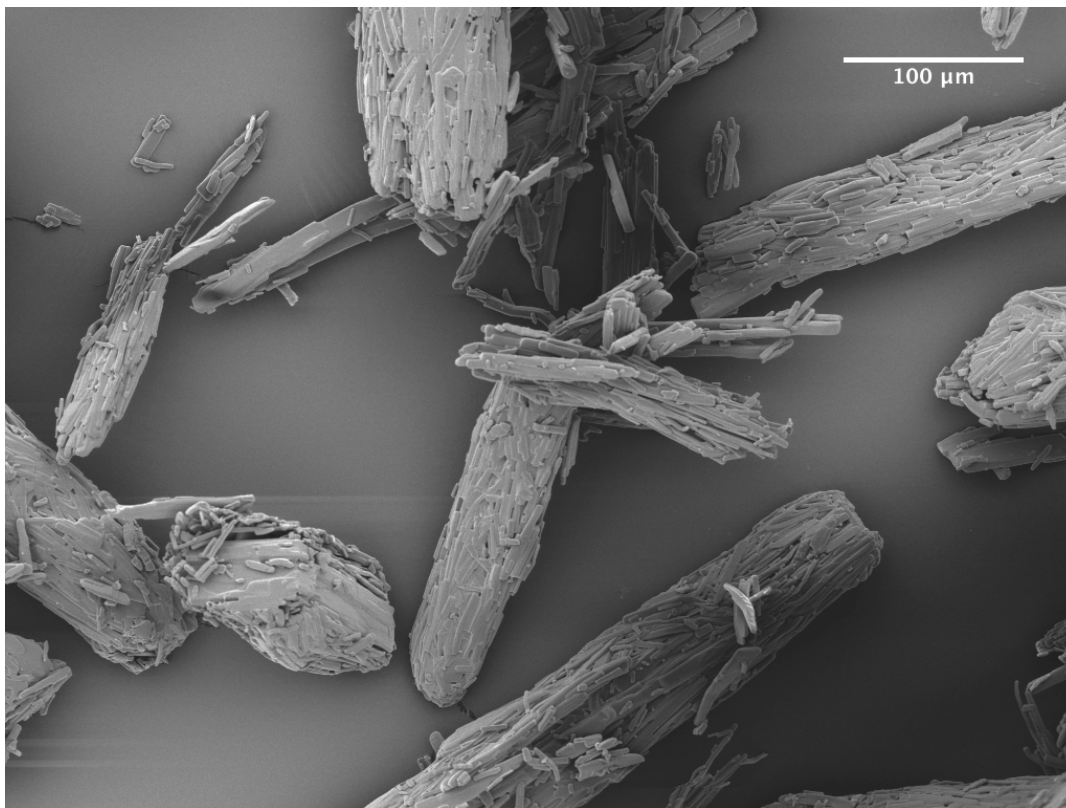


Figure S8: SEM image of commercially available theophylline Form II before any treatment. More details of the procedure are given in the experimental section of the main text.

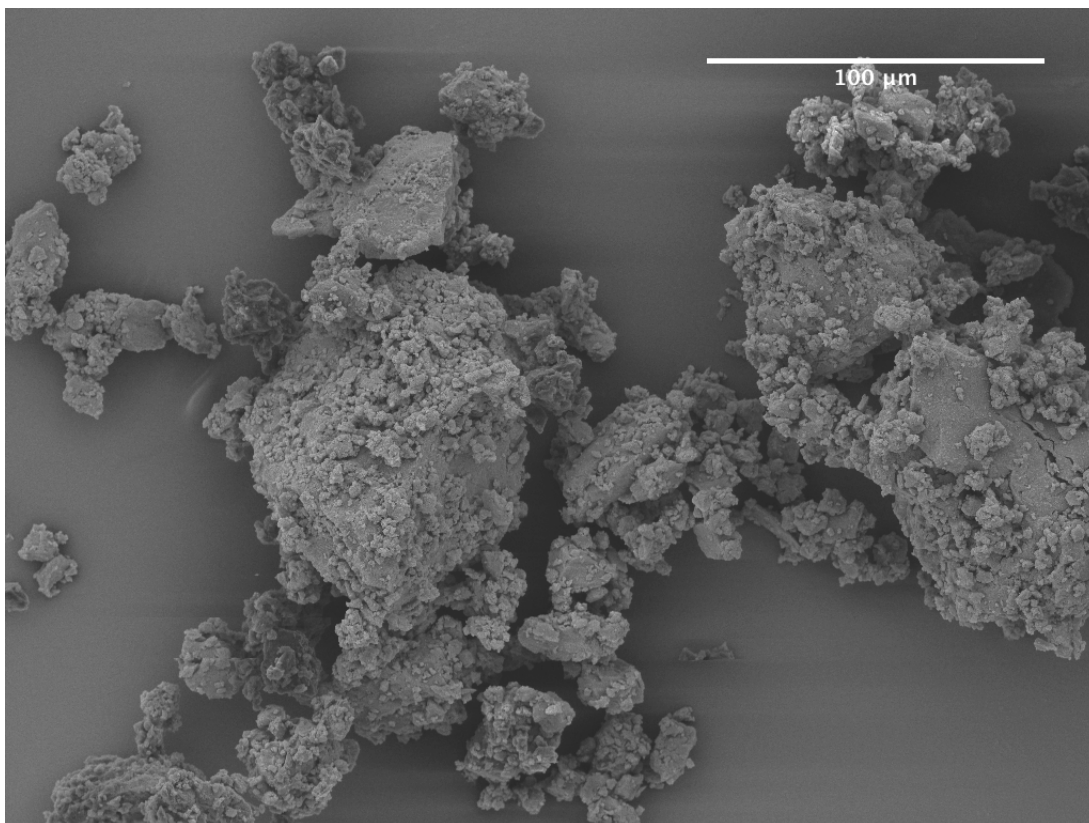


Figure S9: SEM image of theophylline Form II after being cryo-ground into an automatic cryo-grinder. More details of the procedure are given in the main text.

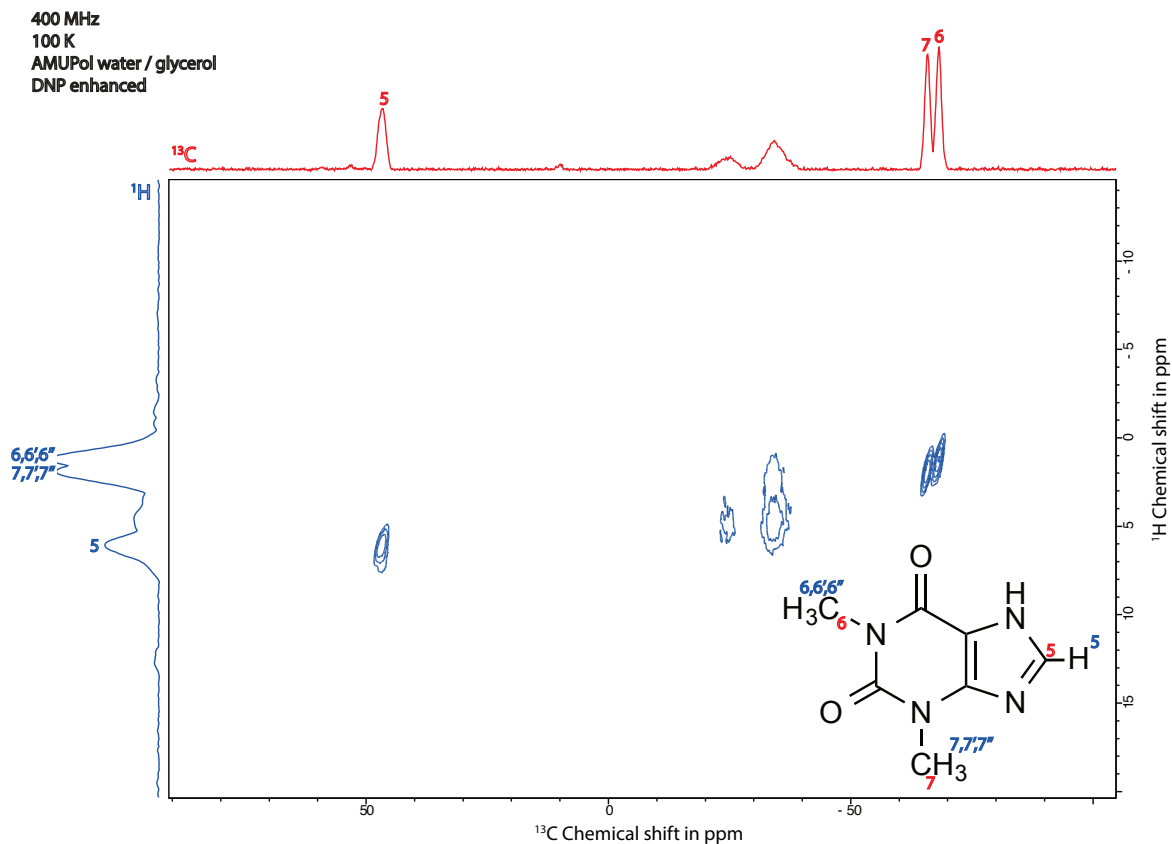


Figure S10: DNP enhanced ¹H-¹³C HETCOR spectra recorded with a 9.4 T spectrometer at 105 K of theophylline Form M. More details on HETCOR parameters are given in the experimental section of the main text.

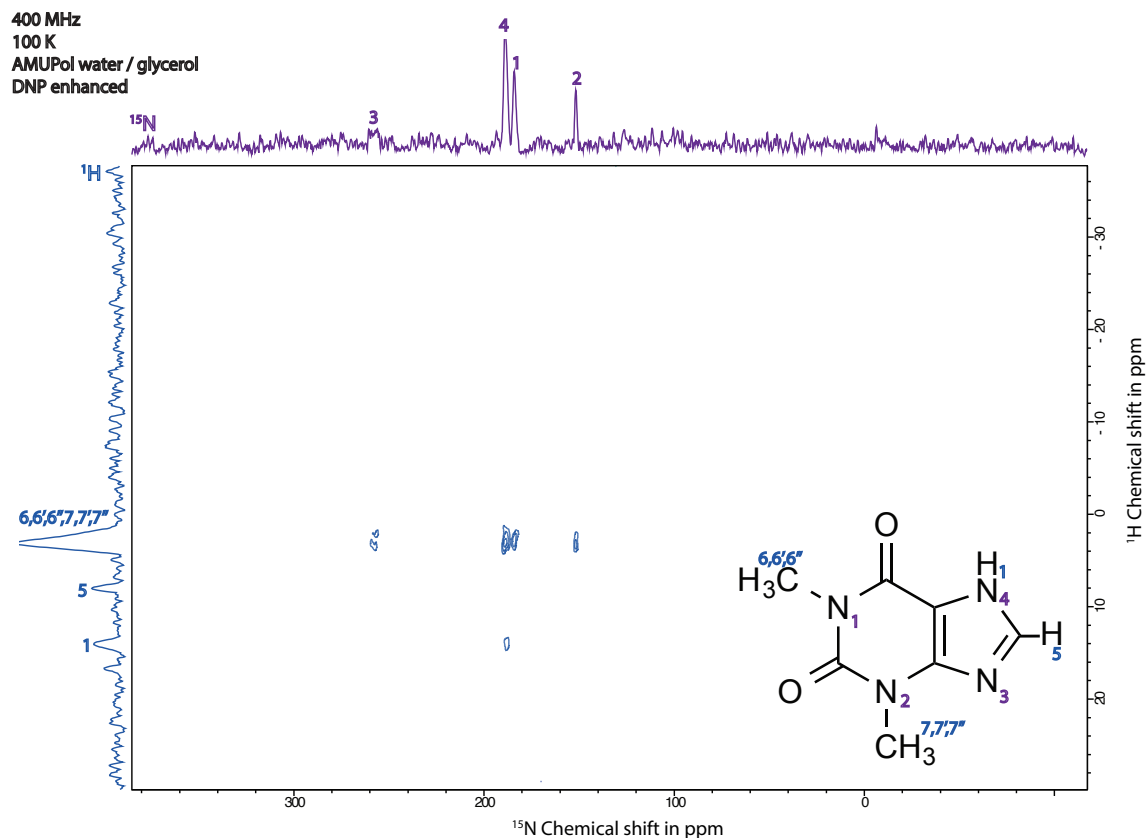


Figure S11: DNP enhanced ¹H-¹⁵N HETCOR spectra recorded with a 9.4 T spectrometer at 105 K of theophylline Form M. More details on HETCOR parameters are given in the experimental section of the main text.