Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Interactions between acyclic CB[n]-type receptors and nitrated explosive materials

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General experimental

Starting materials were purchased from commercial suppliers and used without further purification or were prepared according to literature procedures. NMR spectra were measured on a Bruker Ascend 400M instrument operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C using D_2O, $CDCl_3$, or DMSO-d_6 as solvents. Chemical shifts (δ) are referenced relative to the residual resonances for HOD (4.80 ppm), $CHCl_3$ (7.26 ppm for ^{1}H, 77.16 ppm for ^{13}C), and DMSO-d_6 (2.50 ppm for ^{1}H, 39.51 ppm for ^{13}C). Fluorescence studies were performed on Hitachi F-7000 fluorescence spectrophotometer.

Preparation of qualitative ^{1}H NMR samples

Qualitative ^{1}H NMR samples of hosts and energetic guests were prepared by mixing an excess amount of energetic guests as solid with a solution of a host (1 mM, 0.6 mL, D_2O) in a 1.5 mL centrifuge tube. The tube was then tightly capped and sealed with parafilm and then shaken and sonicated for 30 minutes and maintained at room temperature overnight to achieve equilibrium. Then the samples were filtered through a 0.45 μM syringe filter to obtain clear solutions for NMR measurements.

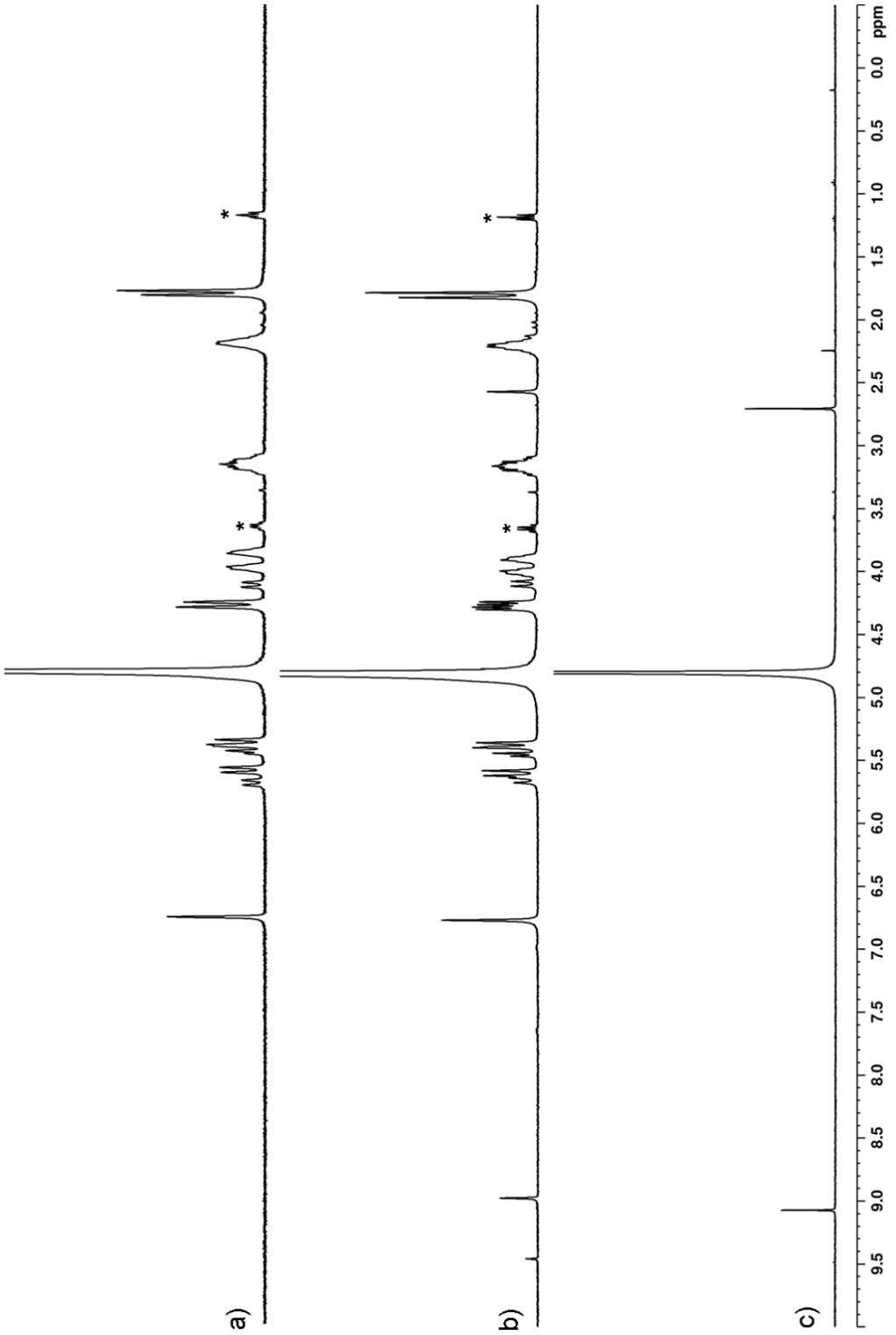

Figure S1. ^{1}H NMR spectra recorded (400 MHz, D_2O, RT) for: a) host **M1** (1.0 mM); b) a solution of host **M1** (1.0 mM) saturated with **TNT**; c) saturated solution of **TNT**. (* for residues of EtOH)

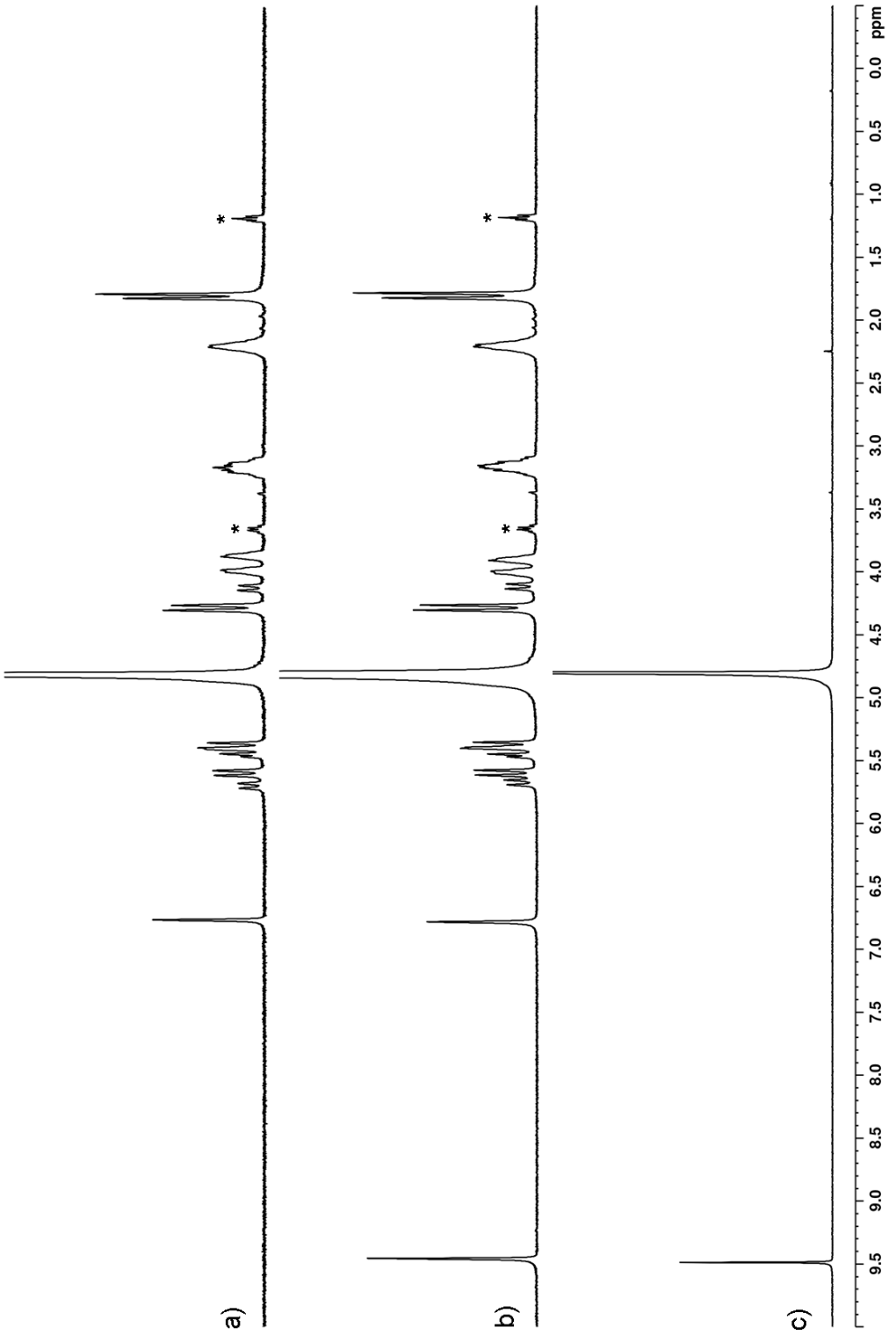

Figure S2. ^{1}H NMR spectra recorded (400 MHz, D_2O, RT) for: a) host **M1** (1.0 mM); b) a solution of host **M1** (1.0 mM) saturated with **TNB**; c) saturated solution of **TNB**. (* for residues of EtOH)

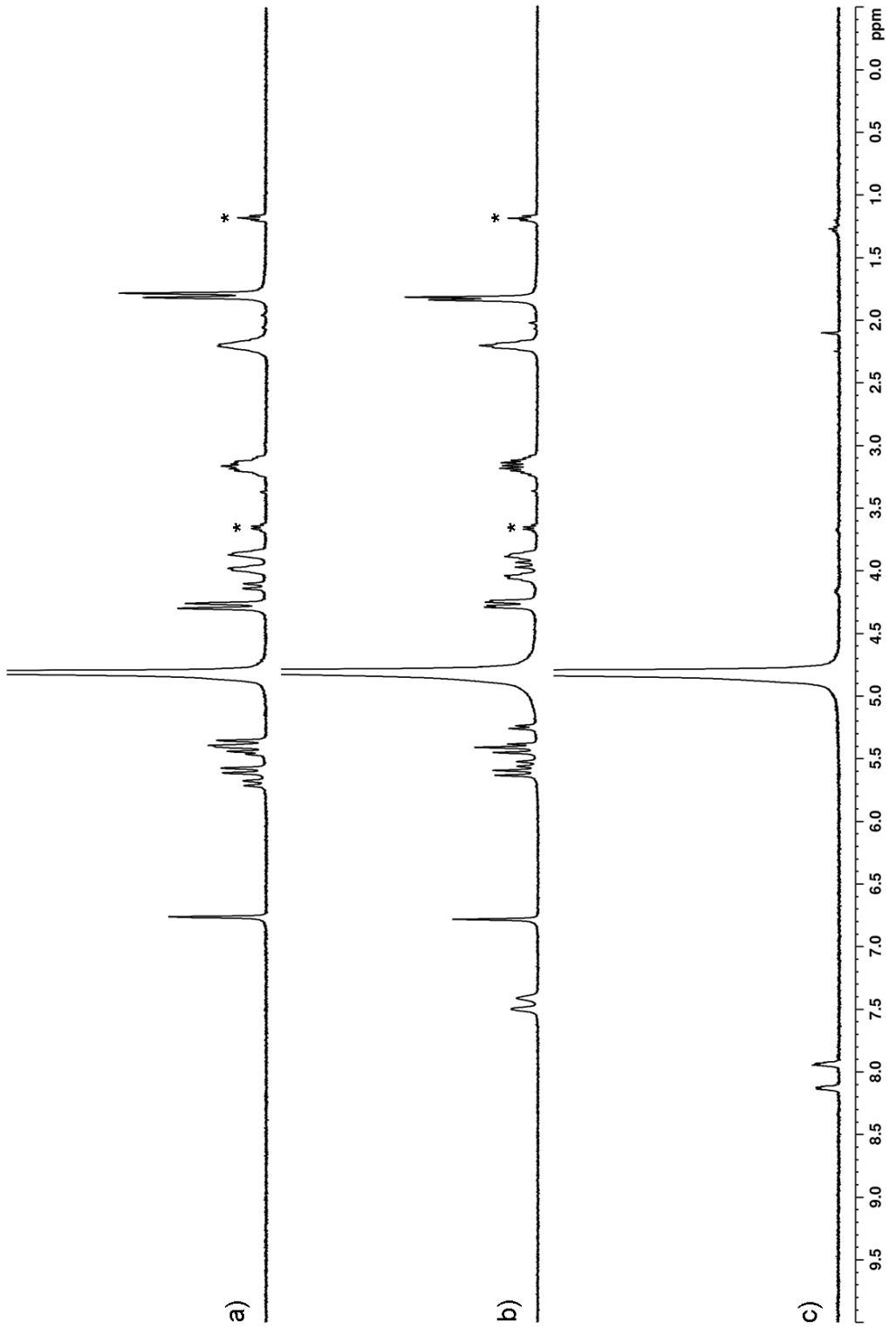

Figure S3. ^{1}H NMR spectra recorded (400 MHz, D_2O, RT) for: a) host **M1** (1.0 mM); b) a solution of host **M1** (1.0 mM) saturated with ***o*-DNB**; c) saturated solution of ***o*-DNB**. (* for residues of EtOH)

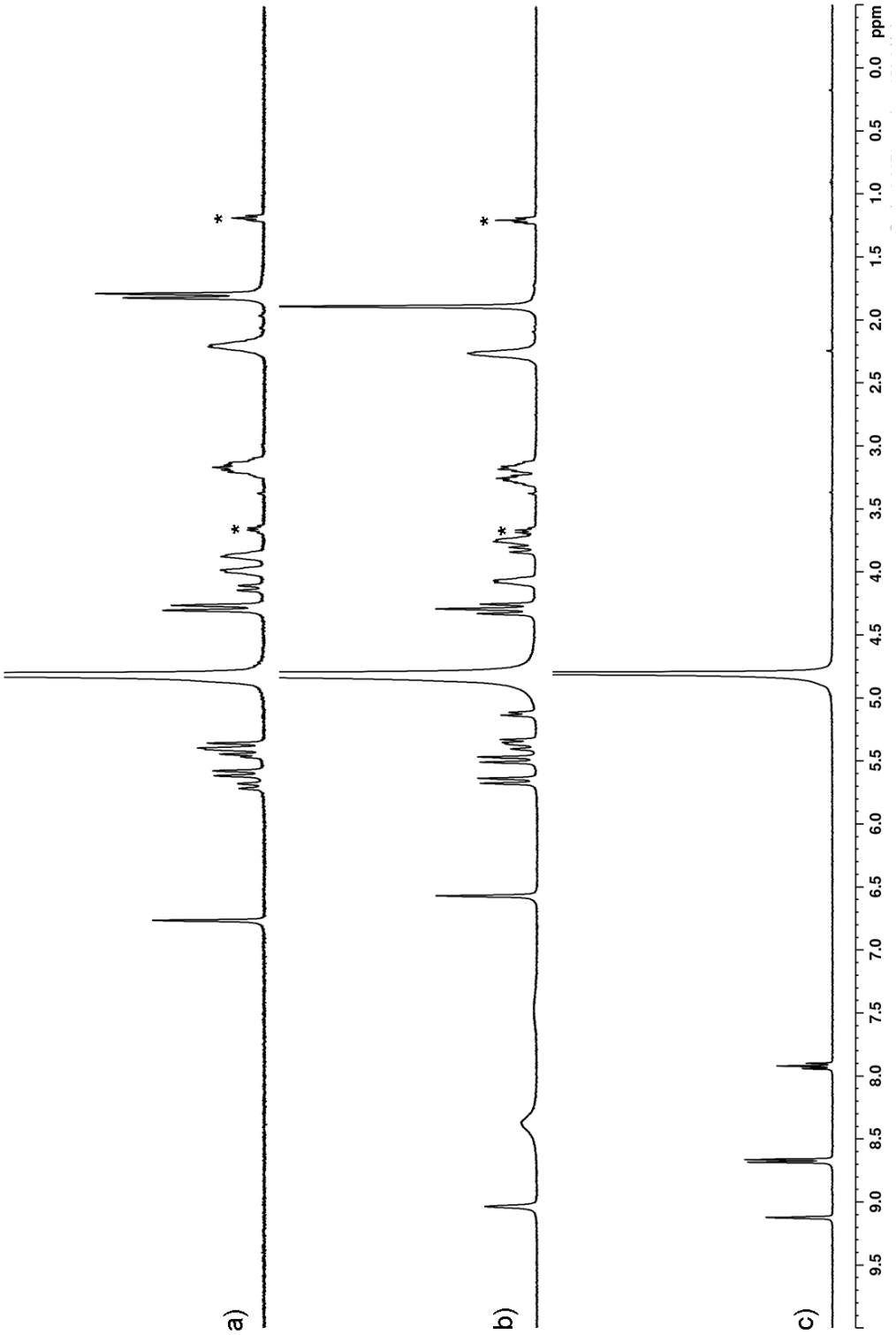

Figure S4. ^{1}H NMR spectra recorded (400 MHz, D_2O, RT) for: a) host **M1** (1.0 mM); b) a solution of host **M1** (1.0 mM) saturated with ***m*-DNB**; c) saturated solution of ***m*-DNB**. (* for residues of EtOH)

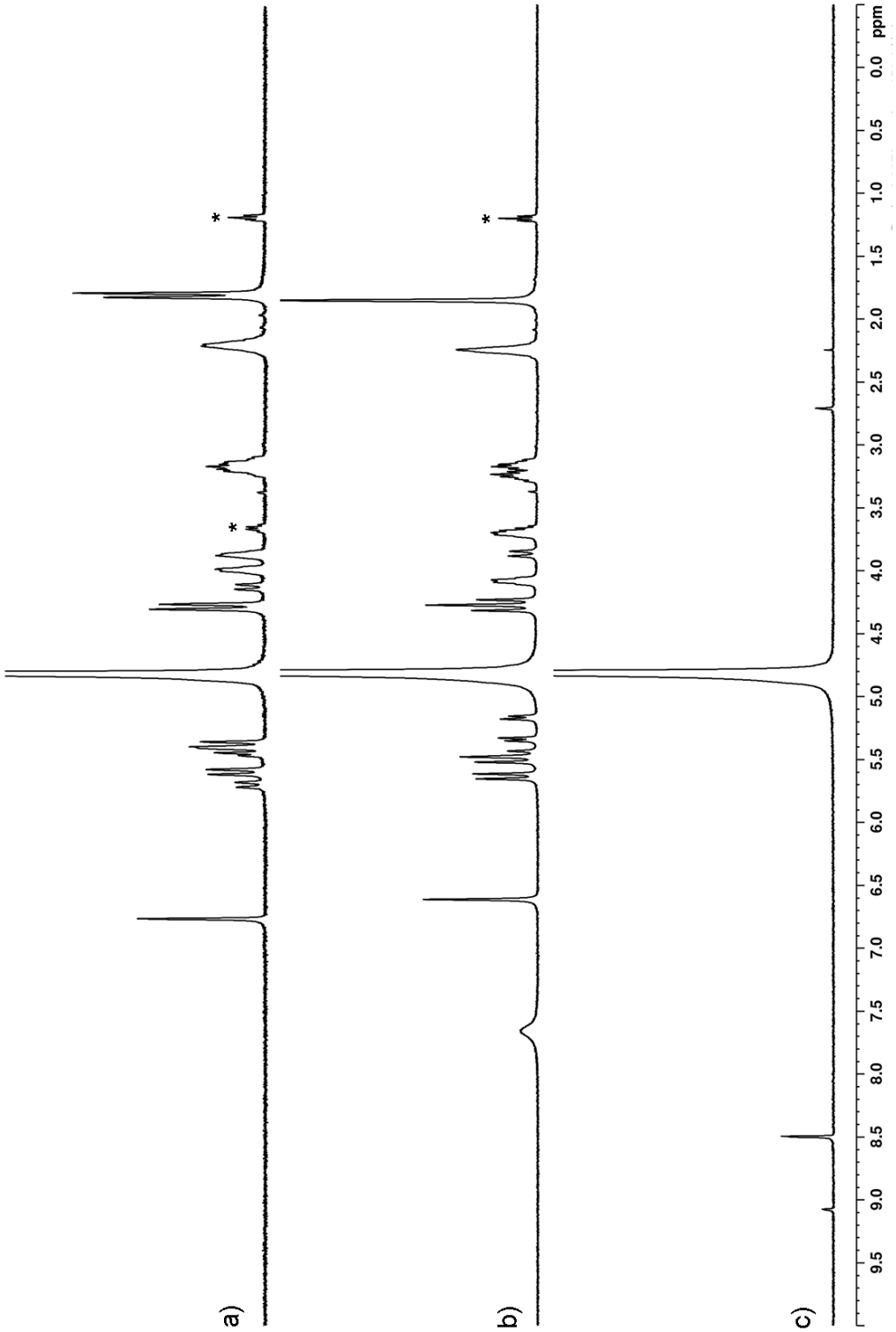

Figure S5. ^{1}H NMR spectra recorded (400 MHz, D_2O, RT) for: a) host **M1** (1.0 mM); b) a solution of host **M1** (1.0 mM) saturated with ***p*-DNB**; c) saturated solution of ***p*-DNB**. (* for residues of EtOH)

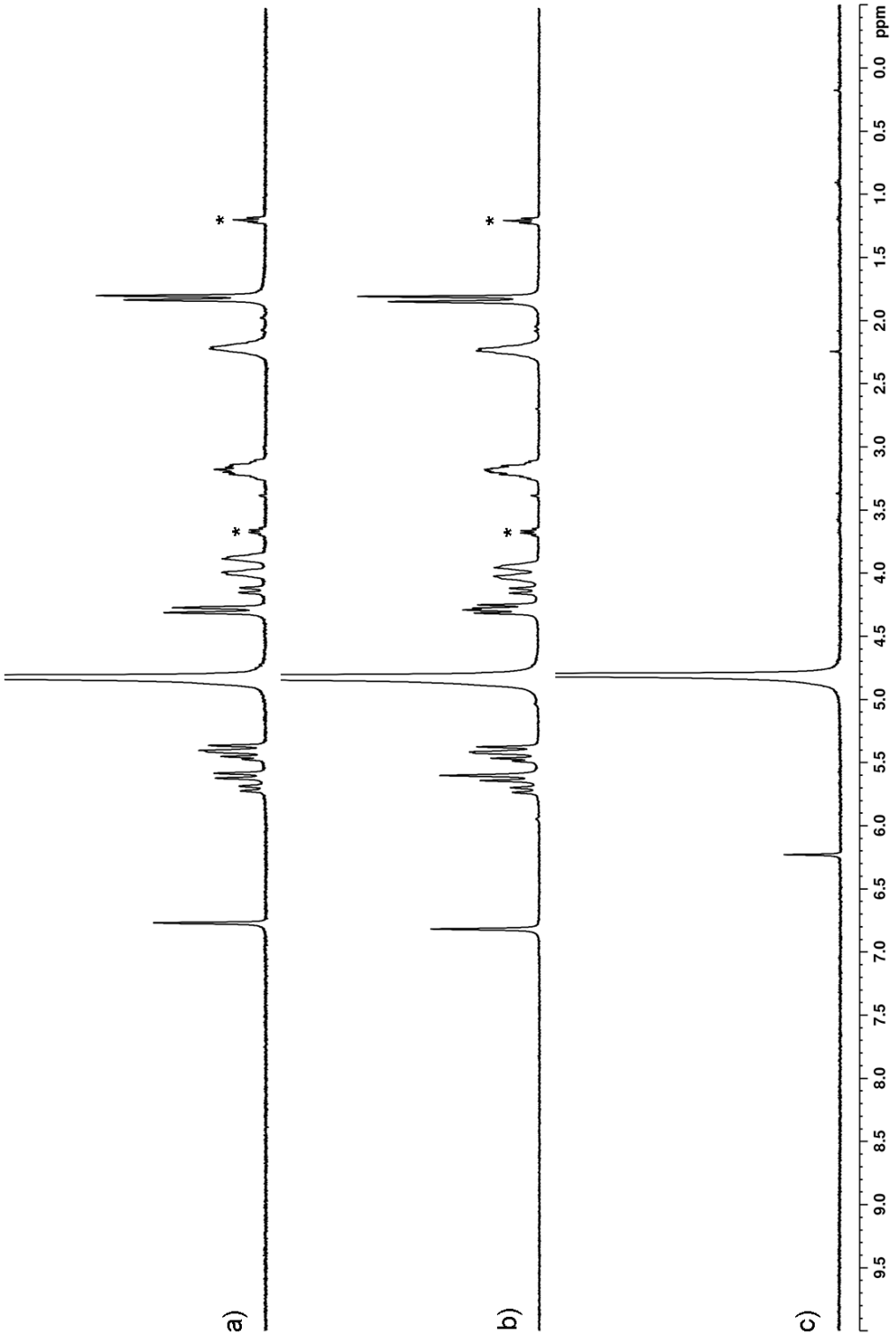

Figure S6. ^{1}H NMR spectra recorded (400 MHz, D_2O, RT) for: a) host **M1** (1.0 mM); b) a solution of host **M1** (1.0 mM) saturated with **RDX**; c) saturated solution of **RDX**. (* for residues of EtOH)

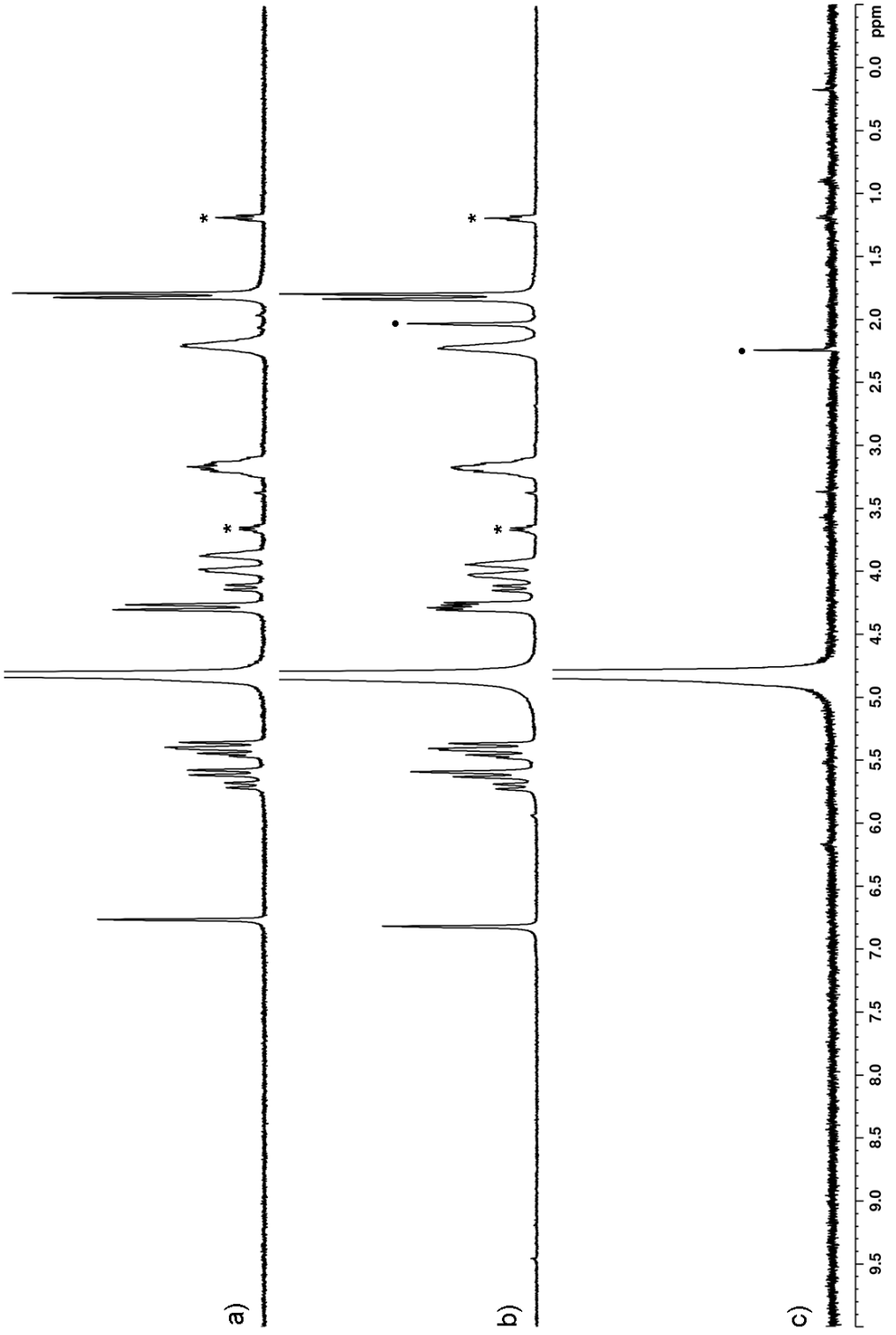

Figure S7. ^{1}H NMR spectra recorded (400 MHz, D_2O, RT) for: a) host **M1** (1.0 mM); b) a solution of host **M1** (1.0 mM) saturated with **HMX**; c) saturated solution of **HMX**. (* for residues of EtOH, • for unknown impurity in **HMX** solid sample)

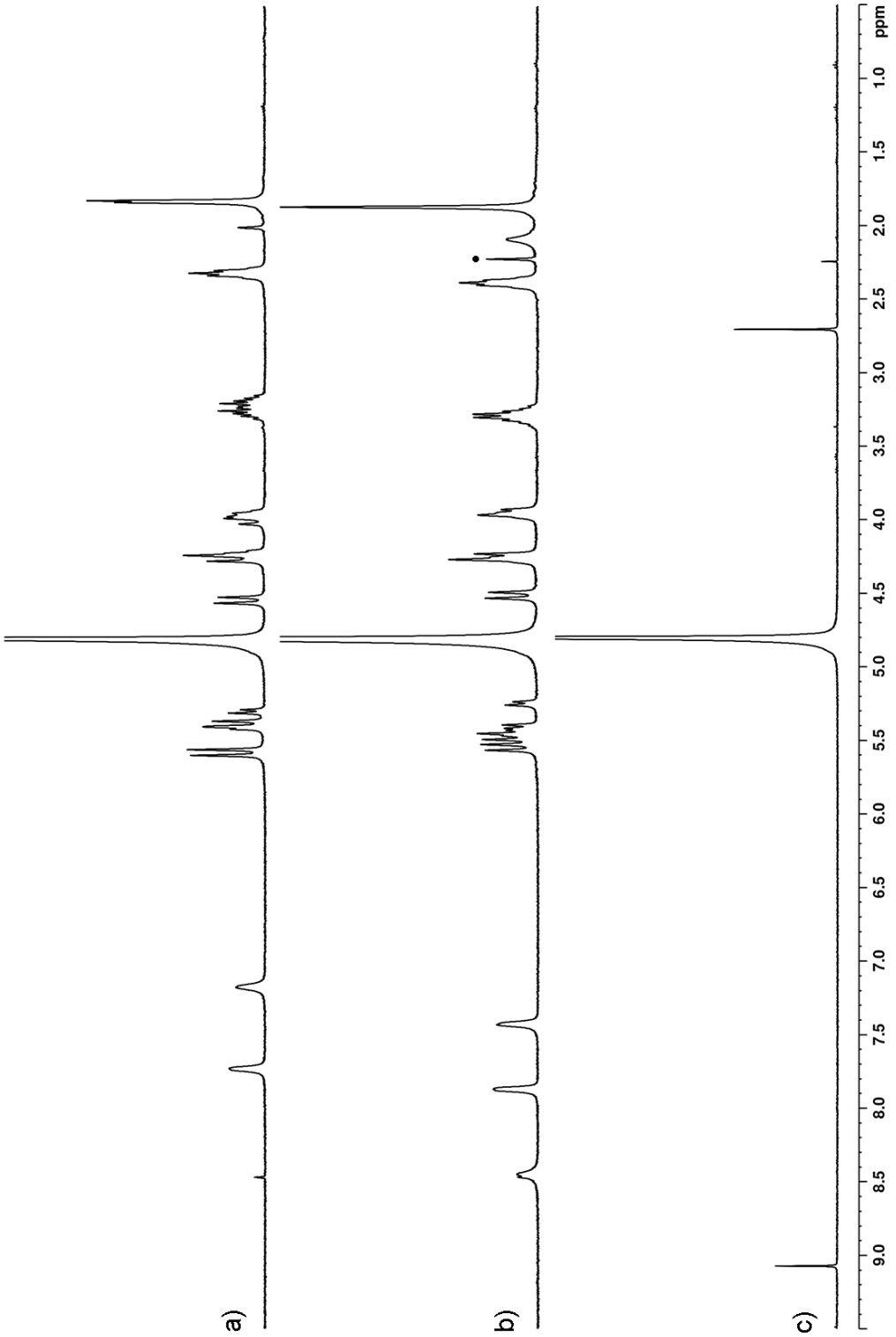

Figure S8. ^{1}H NMR spectra recorded (400 MHz, D_2O, RT) for: a) host **M2** (1.0 mM); b) a solution of host **M2** (1.0 mM) saturated with **TNT**; c) saturated solution of **TNT**. (• for unknown impurity in **TNT** solid sample)

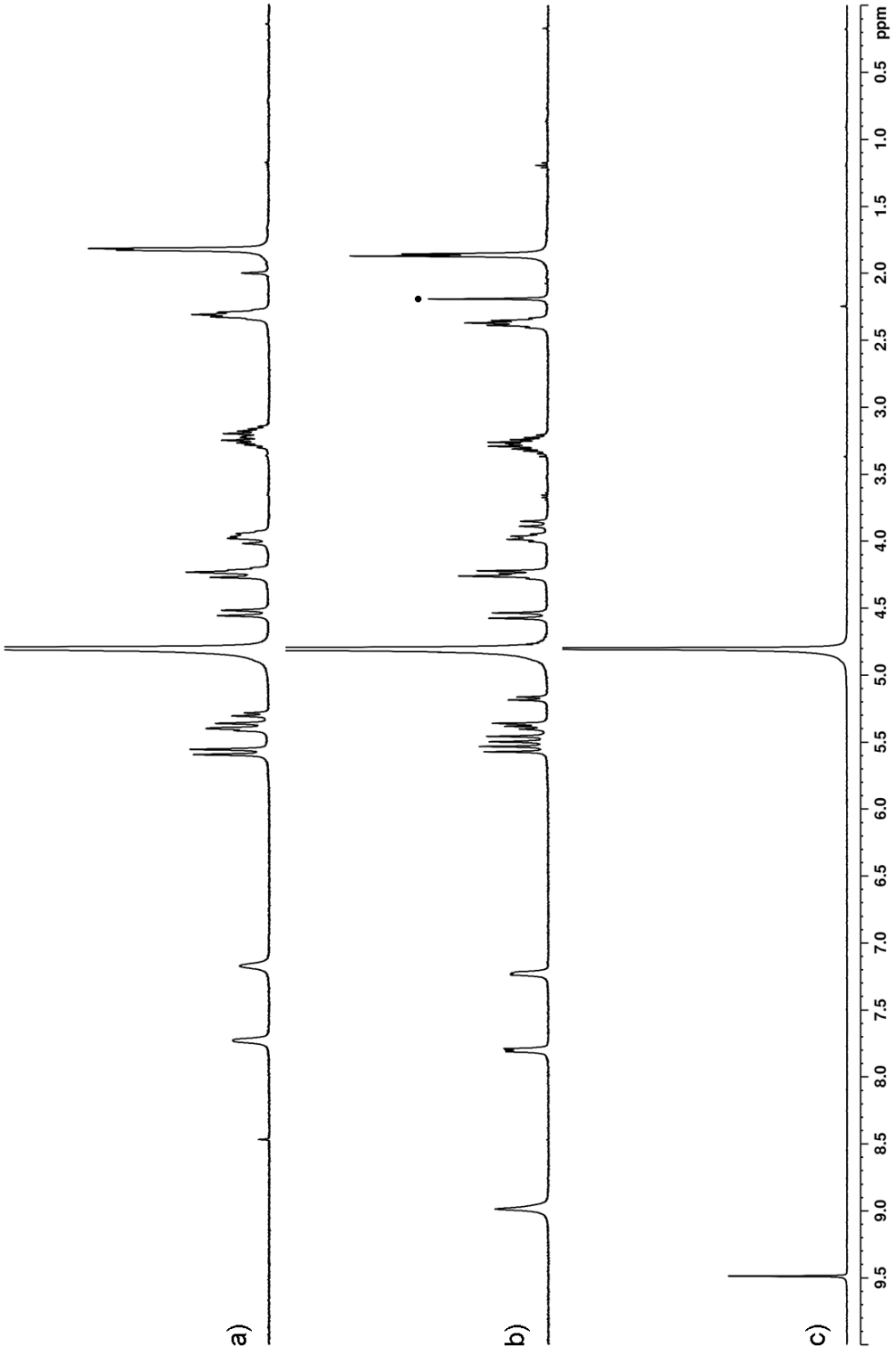

Figure S9. ^{1}H NMR spectra recorded (400 MHz, D_2O, RT) for: a) host **M2** (1.0 mM); b) a solution of host **M2** (1.0 mM) saturated with **TNB**; c) saturated solution of **TNB**. (• for unknown impurity in **TNB** solid sample)

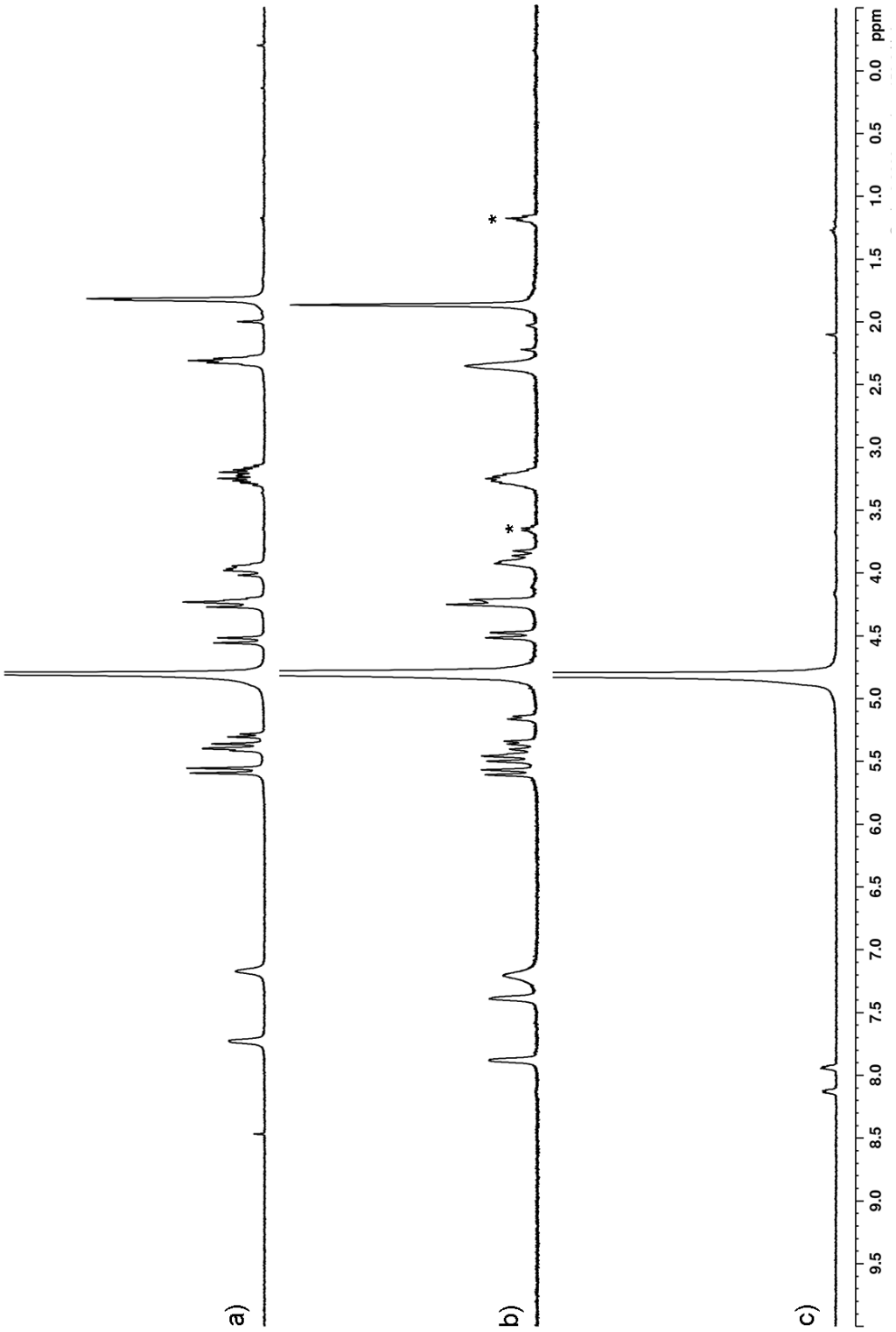

Figure S10. ^{1}H NMR spectra recorded (400 MHz, D_2O, RT) for: a) host **M2** (1.0 mM); b) a solution of host **M2** (1.0 mM) saturated with ***o*-DNB**; c) saturated solution of ***o*-DNB**. (* for residues of EtOH)

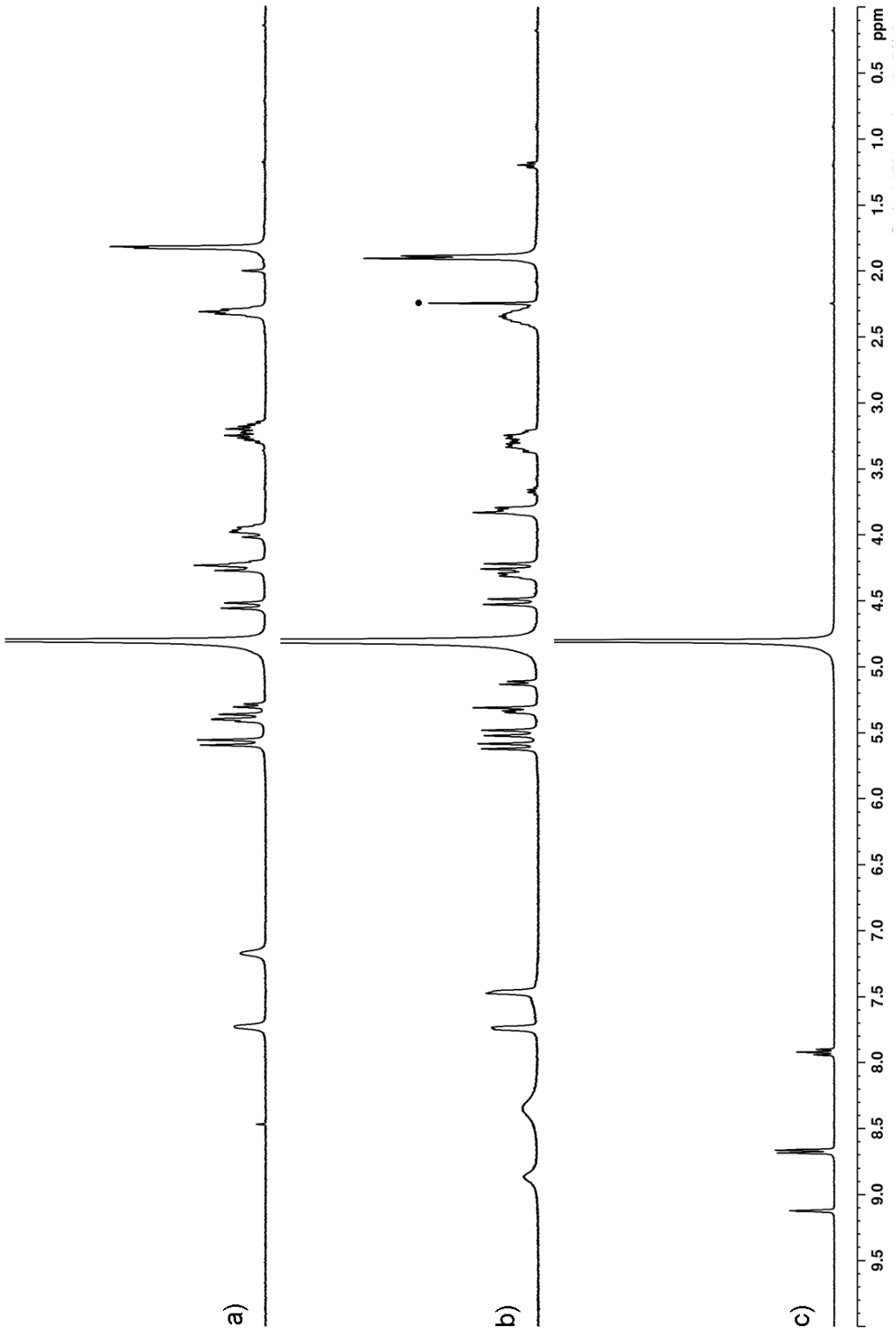

Figure S11. ^{1}H NMR spectra recorded (400 MHz, D_2O, RT) for: a) host **M2** (1.0 mM); b) a solution of host **M2** (1.0 mM) saturated with ***m*-DNB**; c) saturated solution of ***m*-DNB**. (• for unknown impurity in ***m*-DNB** solid sample)

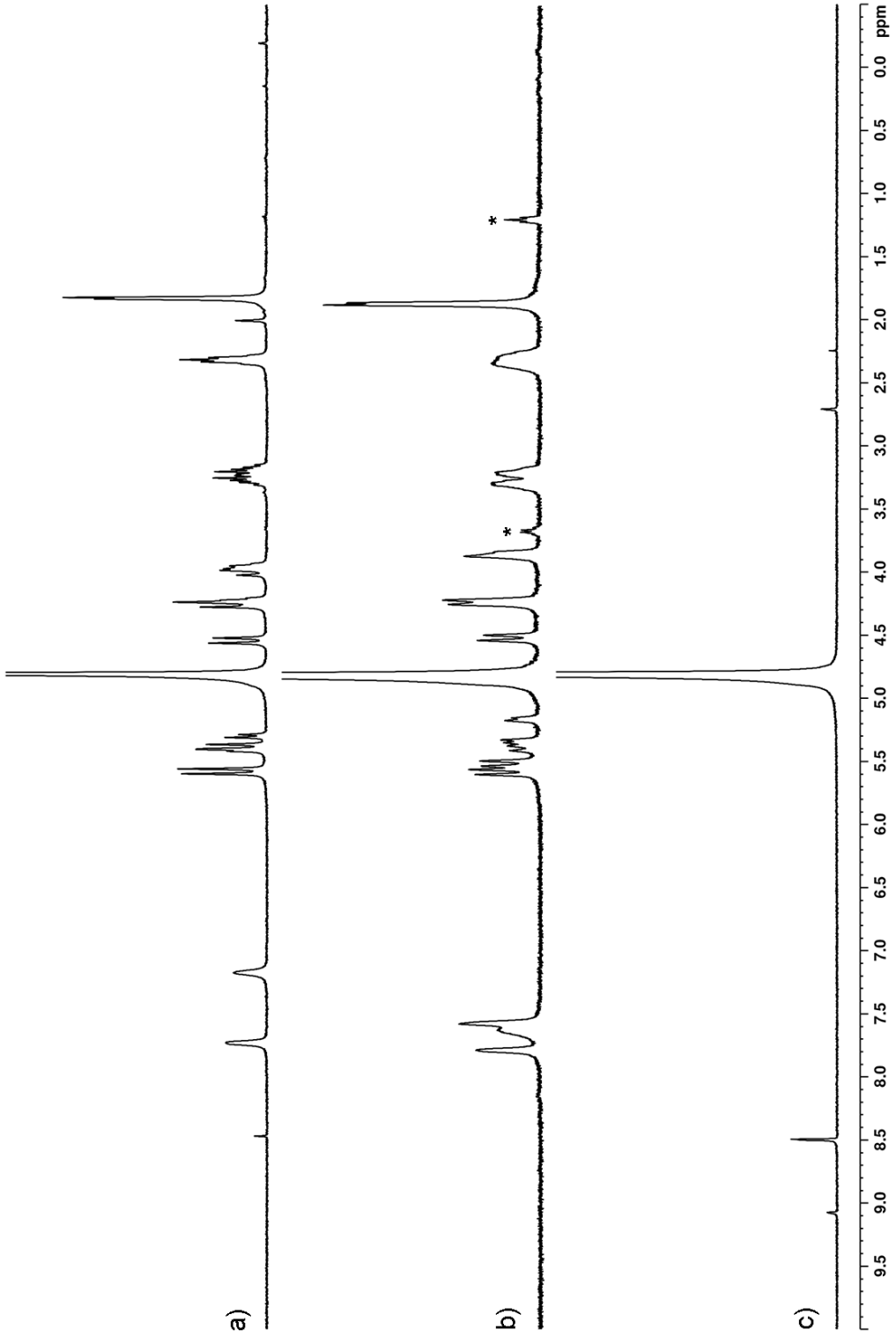

Figure S12. ^{1}H NMR spectra recorded (400 MHz, D_2O, RT) for: a) host **M2** (1.0 mM); b) a solution of host **M2** (1.0 mM) saturated with ***p*-DNB**; c) saturated solution of ***p*-DNB**. (* for residues of EtOH)

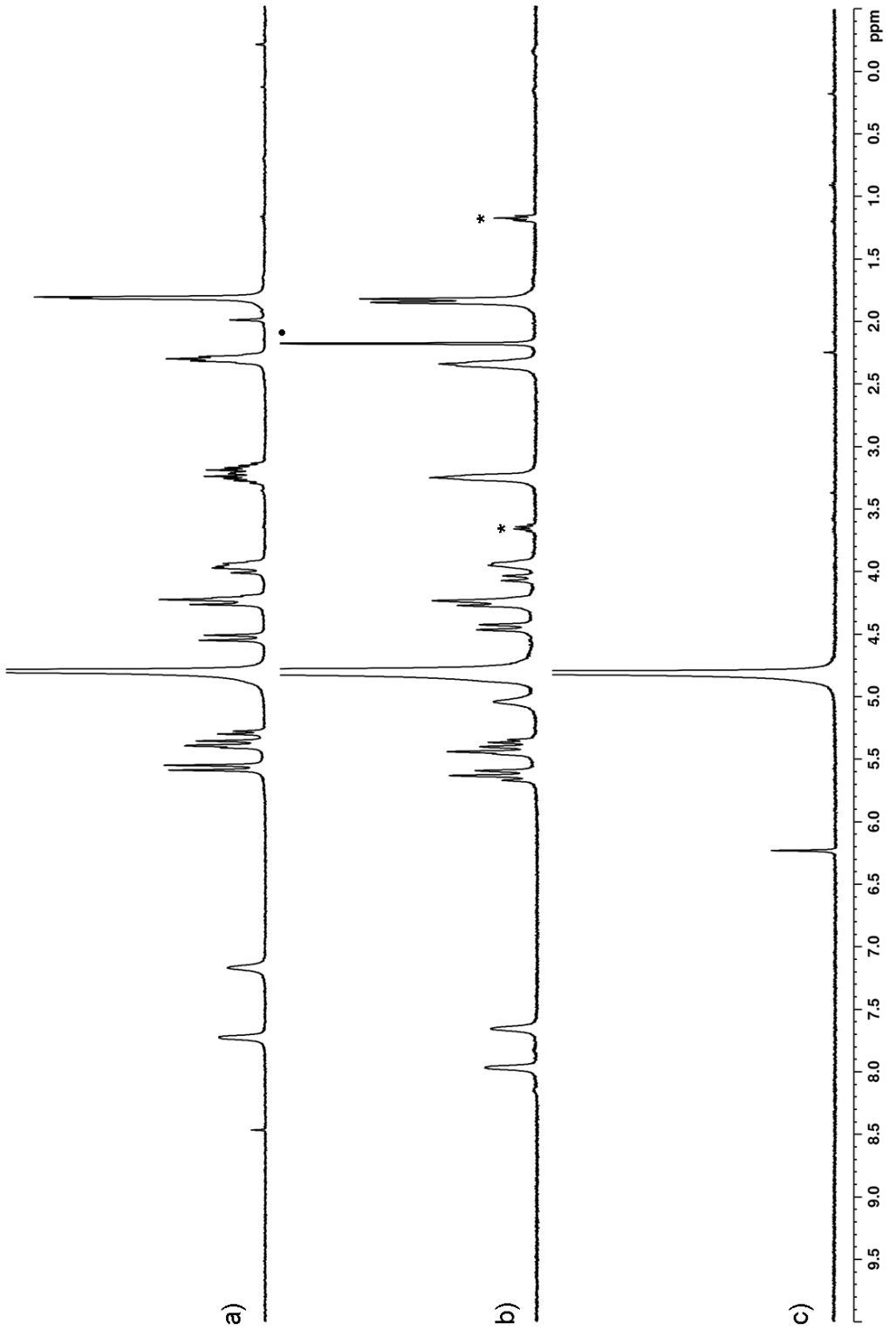

Figure S13. ^{1}H NMR spectra recorded (400 MHz, D_2O, RT) for: a) host **M2** (1.0 mM); b) a solution of host **M2** (1.0 mM) saturated with **RDX**; c) saturated solution of **RDX**. (* for residues of EtOH, • for unknown impurity in **RDX** solid sample)

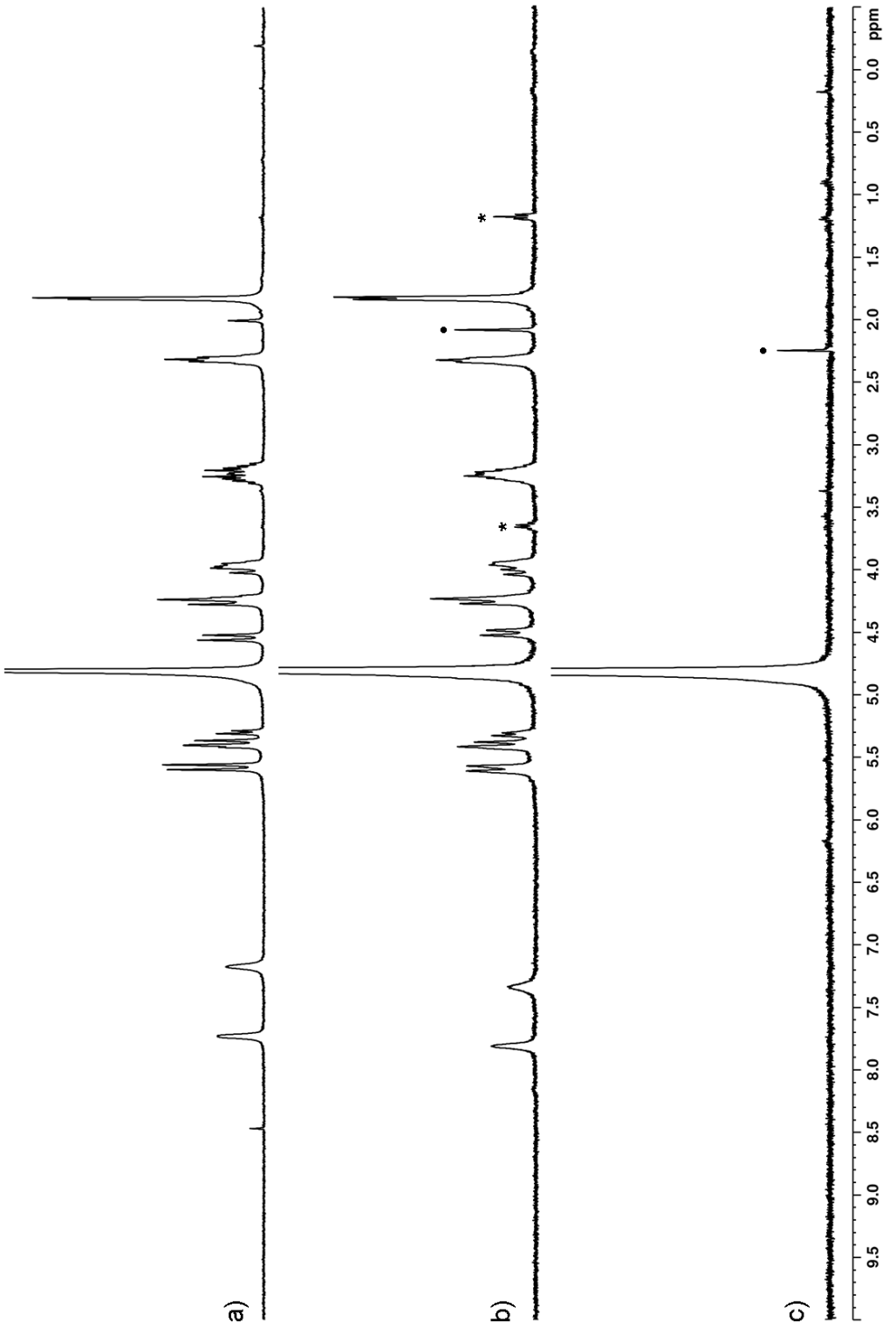

Figure S14. ^{1}H NMR spectra recorded (400 MHz, D_2O, RT) for: a) host **M2** (1.0 mM); b) a solution of host **M2** (1.0 mM) saturated with **HMX**; c) saturated solution of **HMX**. (* for residues of EtOH, • for unknown impurity in **HMX** solid sample)

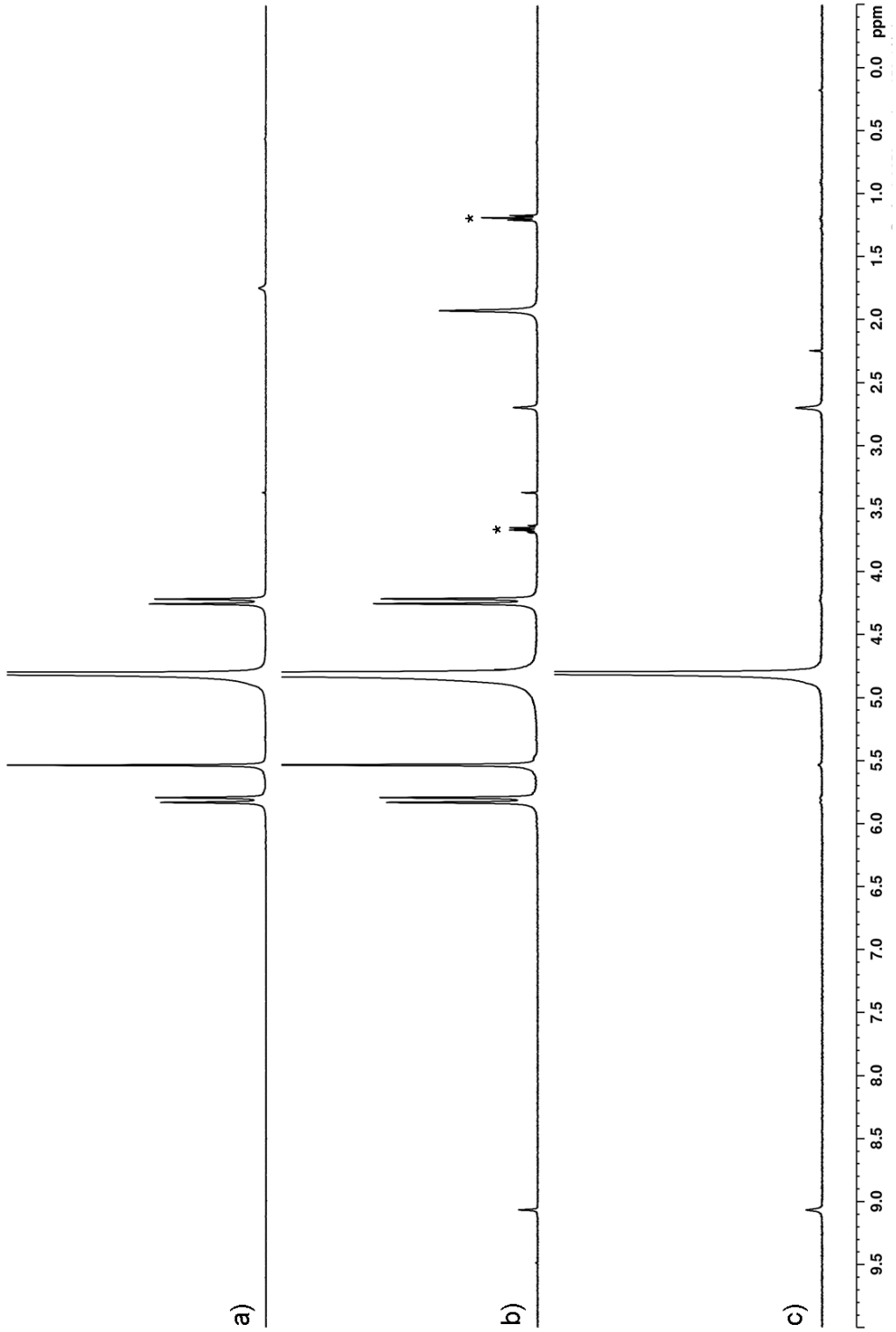

Figure S15. ^{1}H NMR spectra recorded (400 MHz, D_2O, RT) for: a) host CB[7] (1.0 mM); b) a solution of host CB[7] (1.0 mM) saturated with **TNT**; c) saturated solution of **TNT**. (* for residues of EtOH)

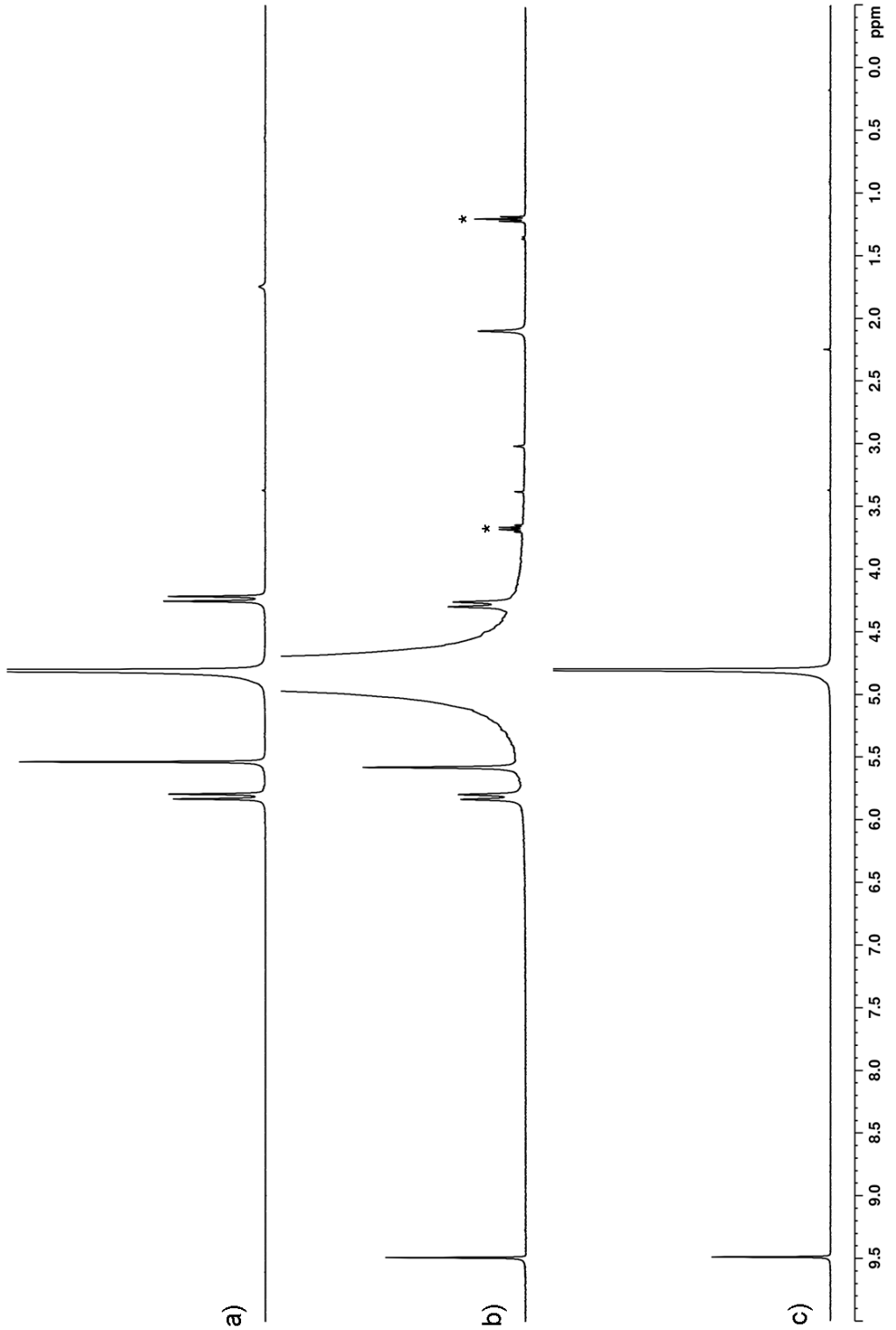

Figure S16. ^{1}H NMR spectra recorded (400 MHz, D_2O, RT) for: a) host CB[7] (1.0 mM); b) a solution of host CB[7] (1.0 mM) saturated with **TNB**; c) saturated solution of **TNB**. (* for residues of EtOH)

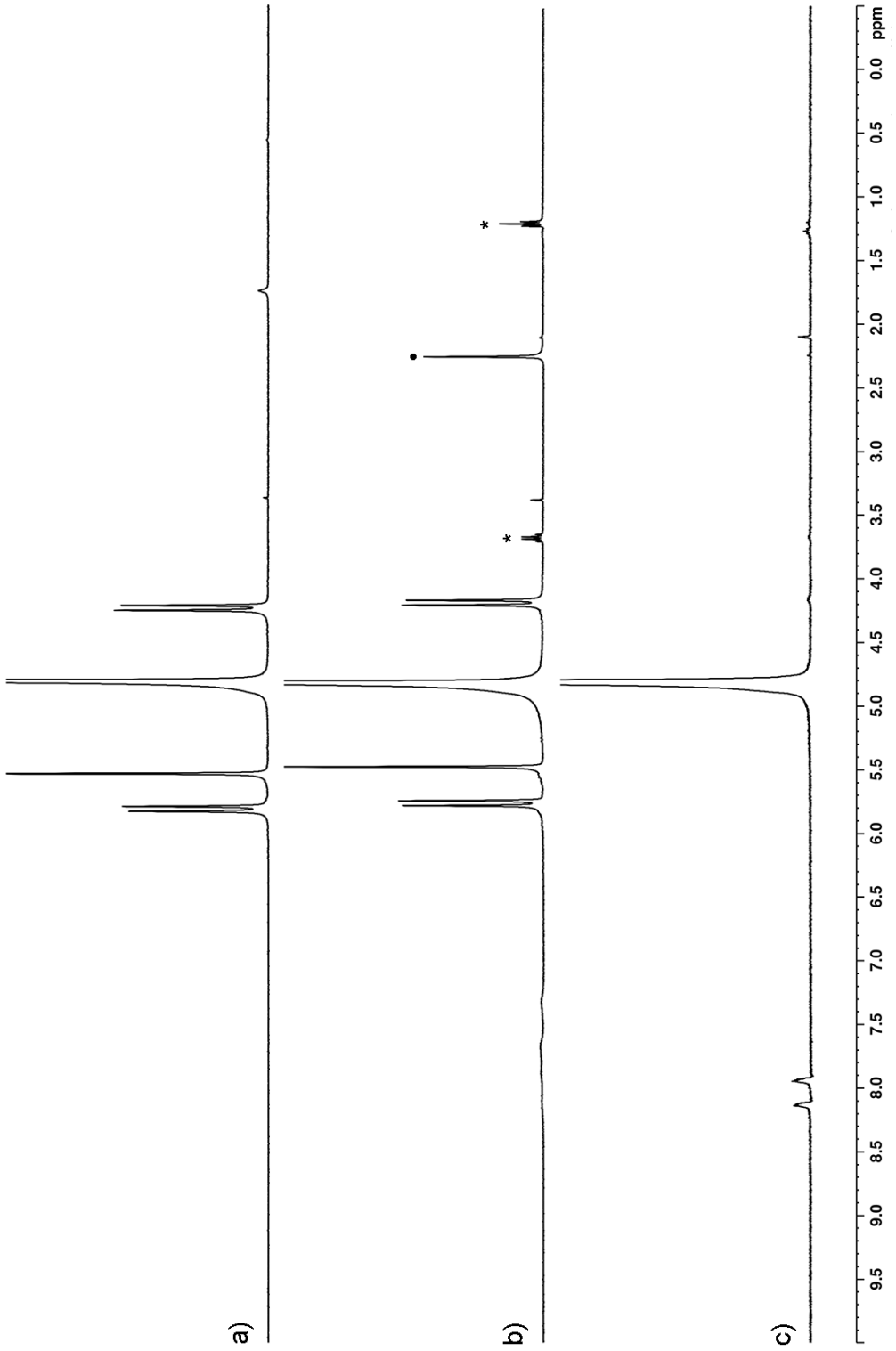

Figure S17. ^{1}H NMR spectra recorded (400 MHz, D_2O, RT) for: a) host CB[7] (1.0 mM); b) a solution of host CB[7] (1.0 mM) saturated with ***o*-DNB**; c) saturated solution of ***o*-DNB**. (* for residues of EtOH, • for unknown impurity in ***o*-DNB** solid sample)

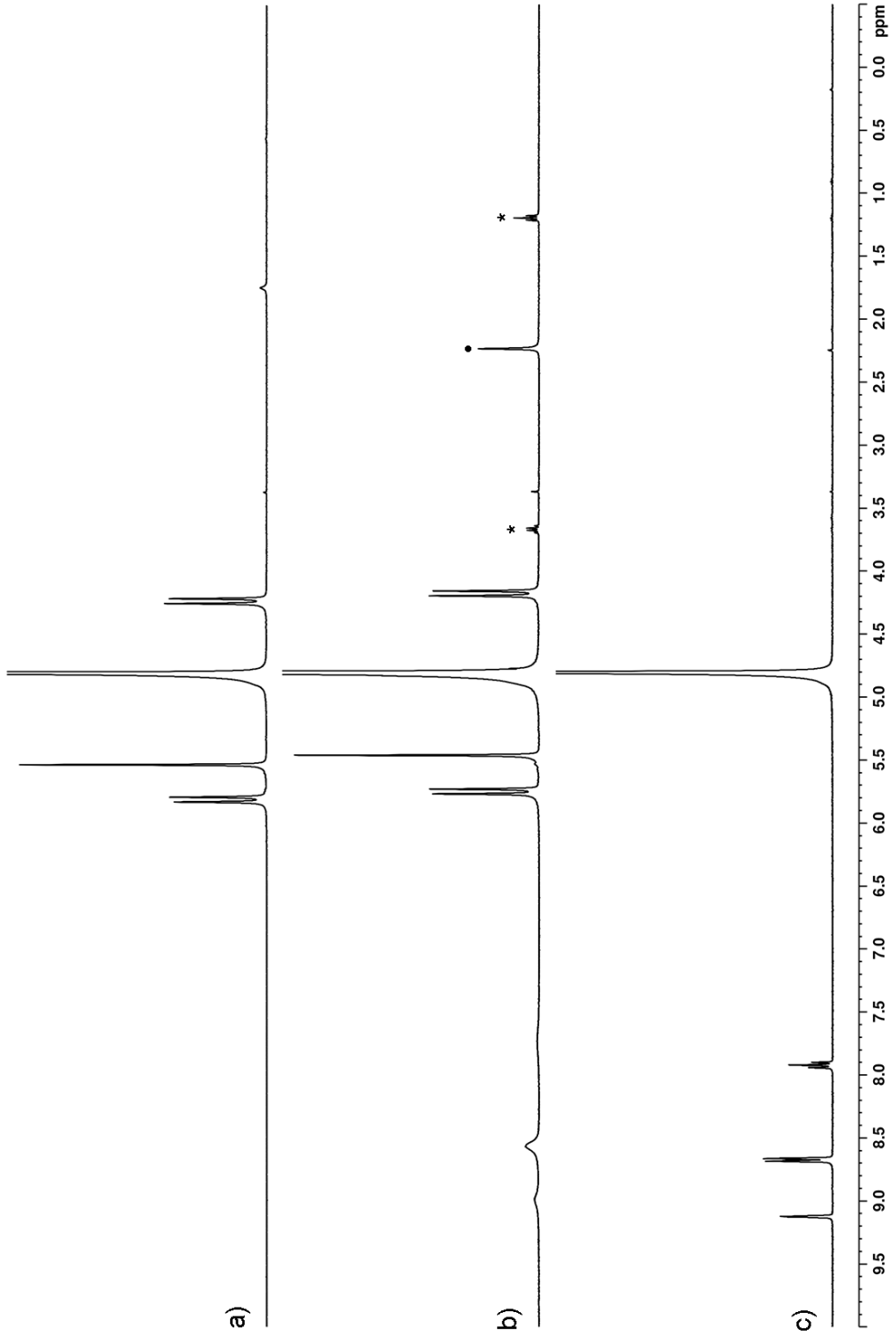

Figure S18. ^{1}H NMR spectra recorded (400 MHz, D_2O, RT) for: a) host CB[7] (1.0 mM); b) a solution of host CB[7] (1.0 mM) saturated with ***m*-DNB**; c) saturated solution of ***m*-DNB**. (* for residues of EtOH, • for unknown impurity in ***m*-DNB** solid sample)

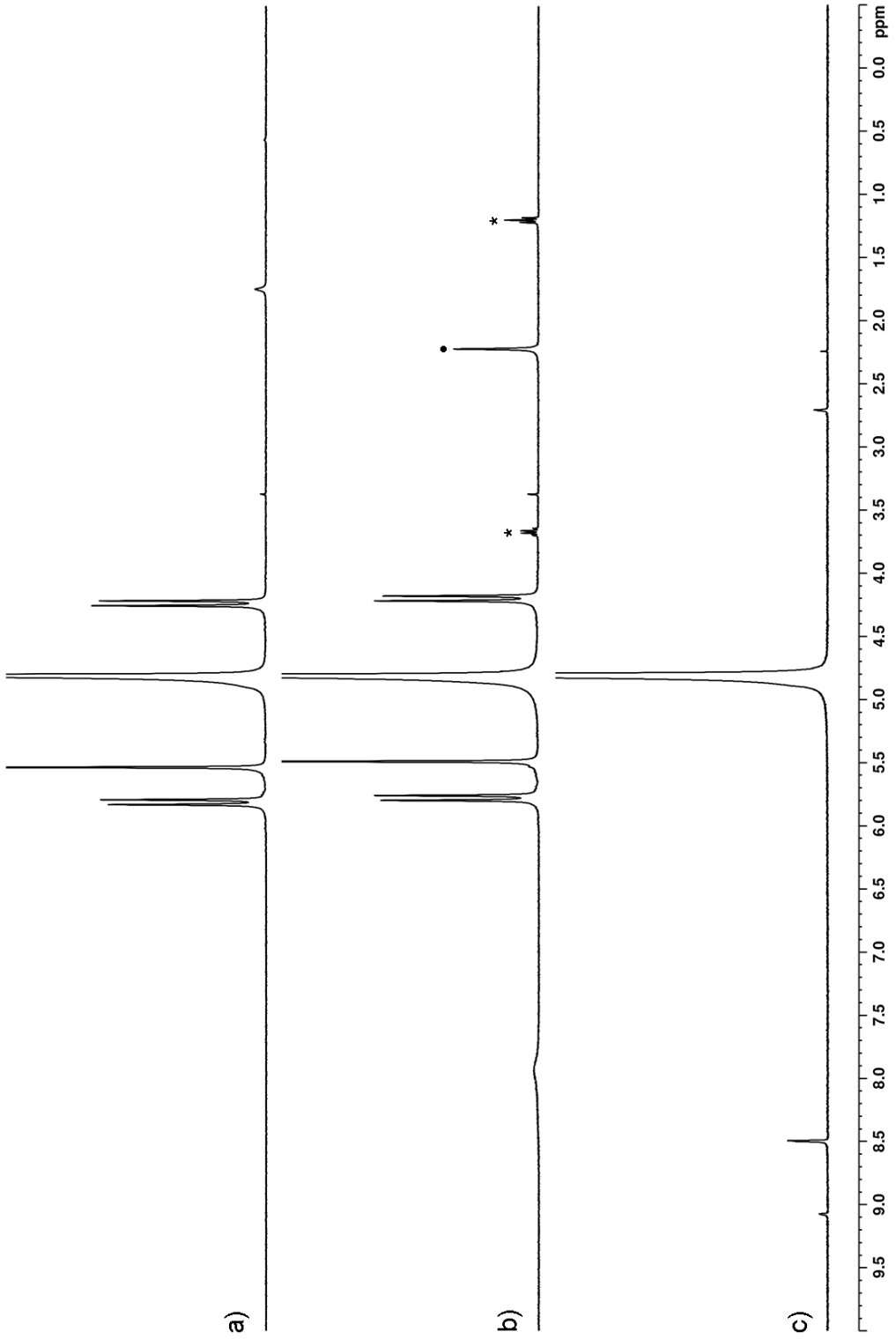

Figure S19. ^{1}H NMR spectra recorded (400 MHz, D_2O, RT) for: a) host CB[7] (1.0 mM); b) a solution of host CB[7] (1.0 mM) saturated with ***p*-DNB**; c) saturated solution of ***p*-DNB**. (* for residues of EtOH, • for unknown impurity in ***p*-DNB** solid sample)

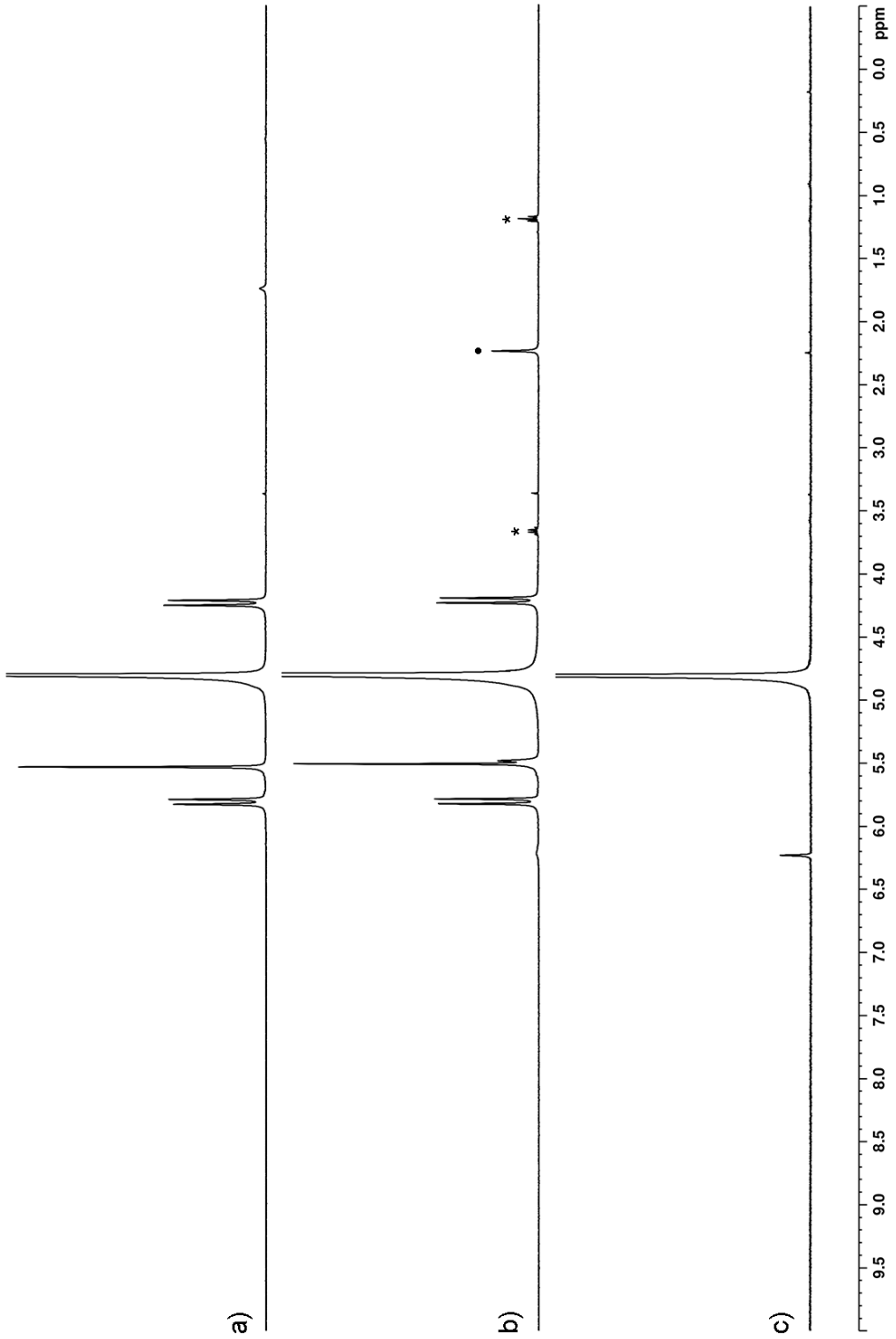

Figure S20. ^{1}H NMR spectra recorded (400 MHz, D_2O, RT) for: a) host CB[7] (1.0 mM); b) a solution of host CB[7] (1.0 mM) saturated with **RDX**; c) saturated solution of **RDX**. (* for residues of EtOH, • for unknown impurity in **RDX** solid sample)

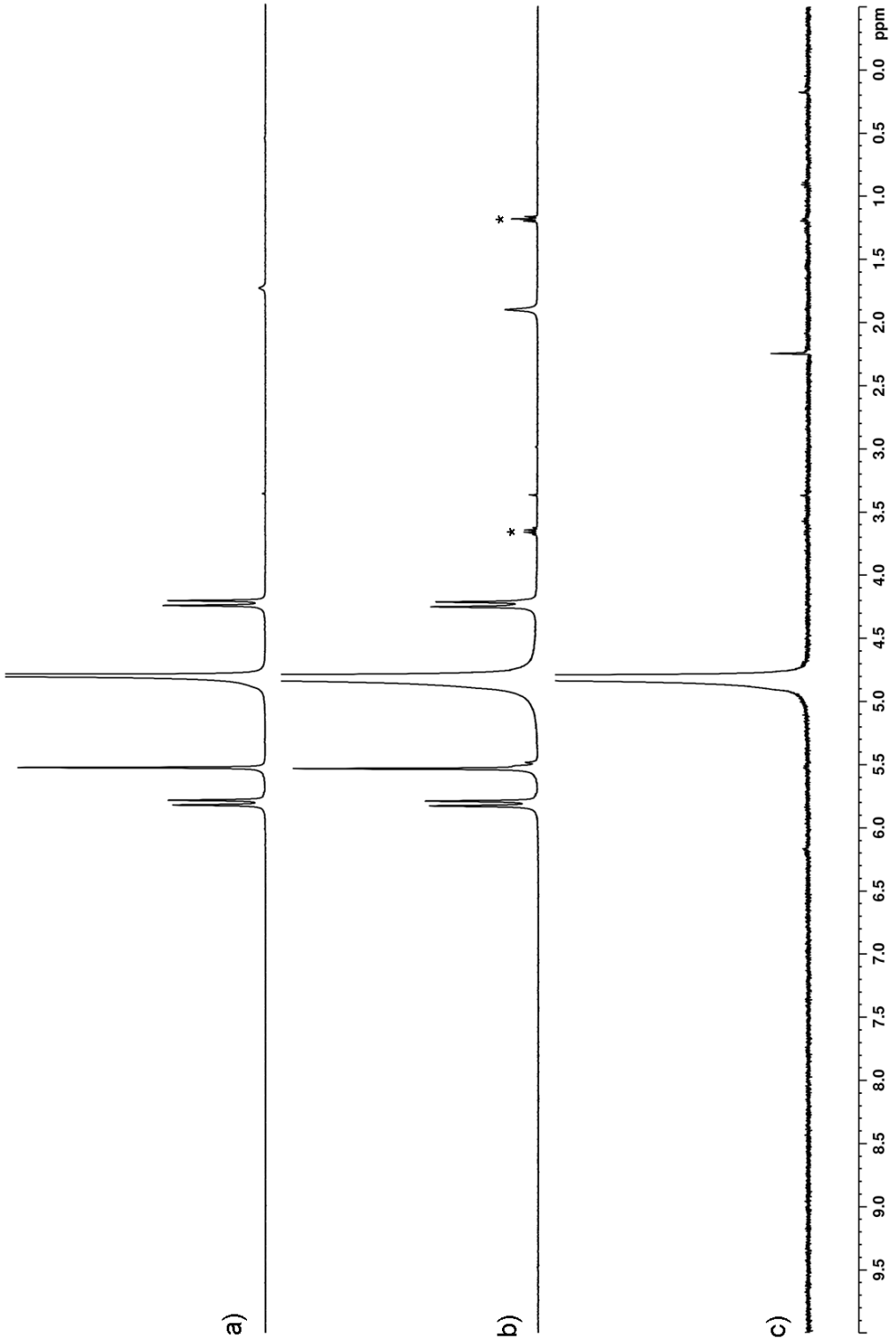

Figure S21. ^{1}H NMR spectra recorded (400 MHz, D_2O, RT) for: a) host CB[7] (1.0 mM); b) a solution of host CB[7] (1.0 mM) saturated with **HMX**; c) saturated solution of **HMX**. (* for residues of EtOH)

Quantitative measurements of K_a by PSDs

Excess amount of energetic guests were added into host solutions of known concentration (1-8 mM) in D_2O in 1.5 mL centrifuge tubes. The tubes were tightly sealed with parafilm and then shaken and sonicated for 30 minutes and were allowed to stand at room temperature overnight to achieve equilibrium. Subsequently, the samples were filtered through a 0.45 μM syringe filter and the obtained clear solutions were mixed with $MeSO_3H$ solutions as internal standard (4.0 mM, 2.83 ppm) for ^1H NMR measurements. The concentrations of the dissolved energetic guests can be calculated from the ratio of integrals of energetic guest peak relative to the internal standard peak. Plotting and fitting the concentrations of energetic guests versus the concentrations of hosts give the PSDs and slope values. Eventually, the K_a values were determined according to Equation (1). Uncertainty of the slope values were obtained as standard deviation and the uncertainty of K_a values were related to the uncertainty of slope values.

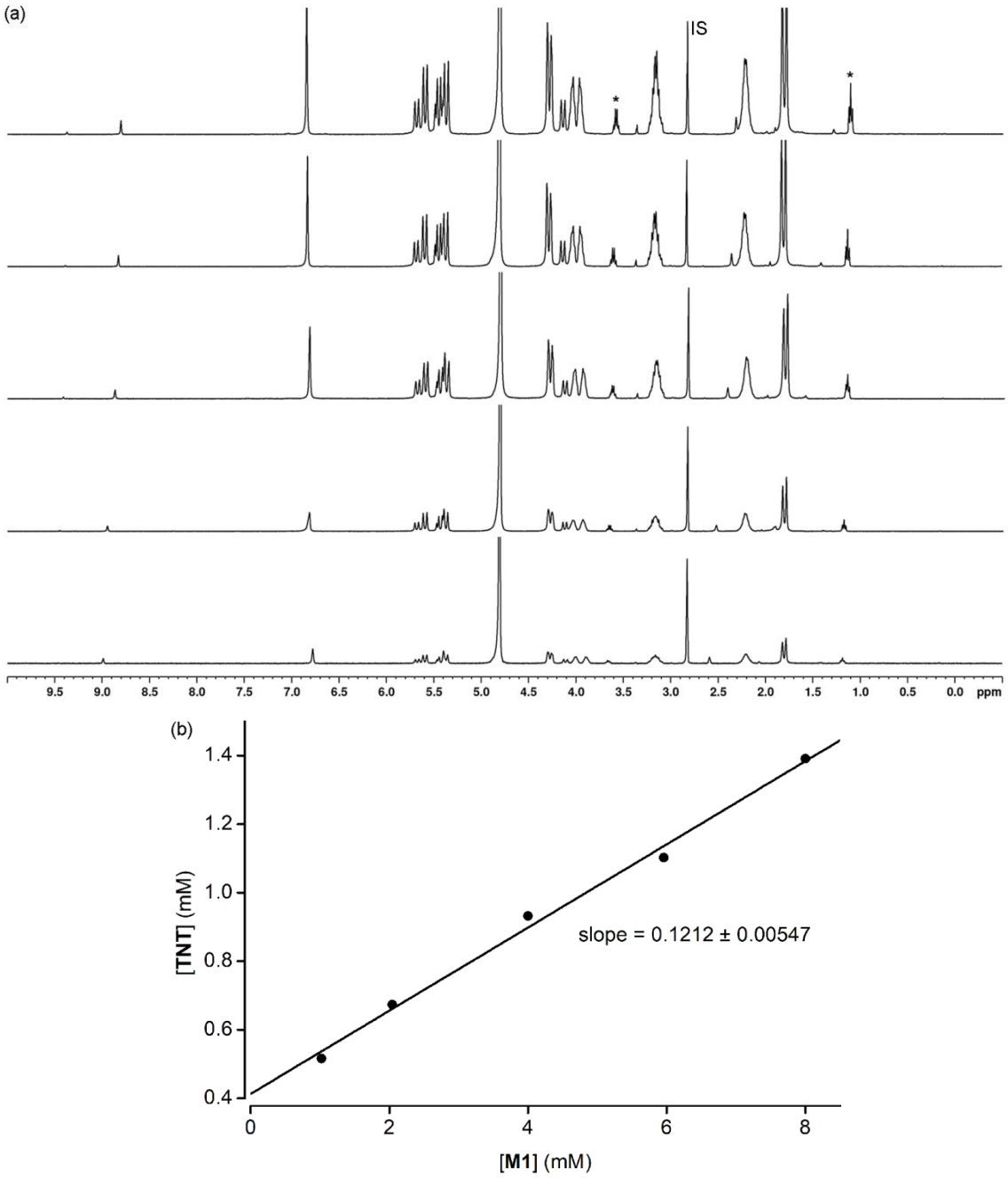

Figure S22 a) ^{1}H NMR spectra recorded (400 MHz, D_2O) for **TNT** in the presence of various concentrations of **M1**. (IS for internal standard, * for residues of EtOH); b) plot of the concentration of **TNT** *versus* the concentration of **M1**.

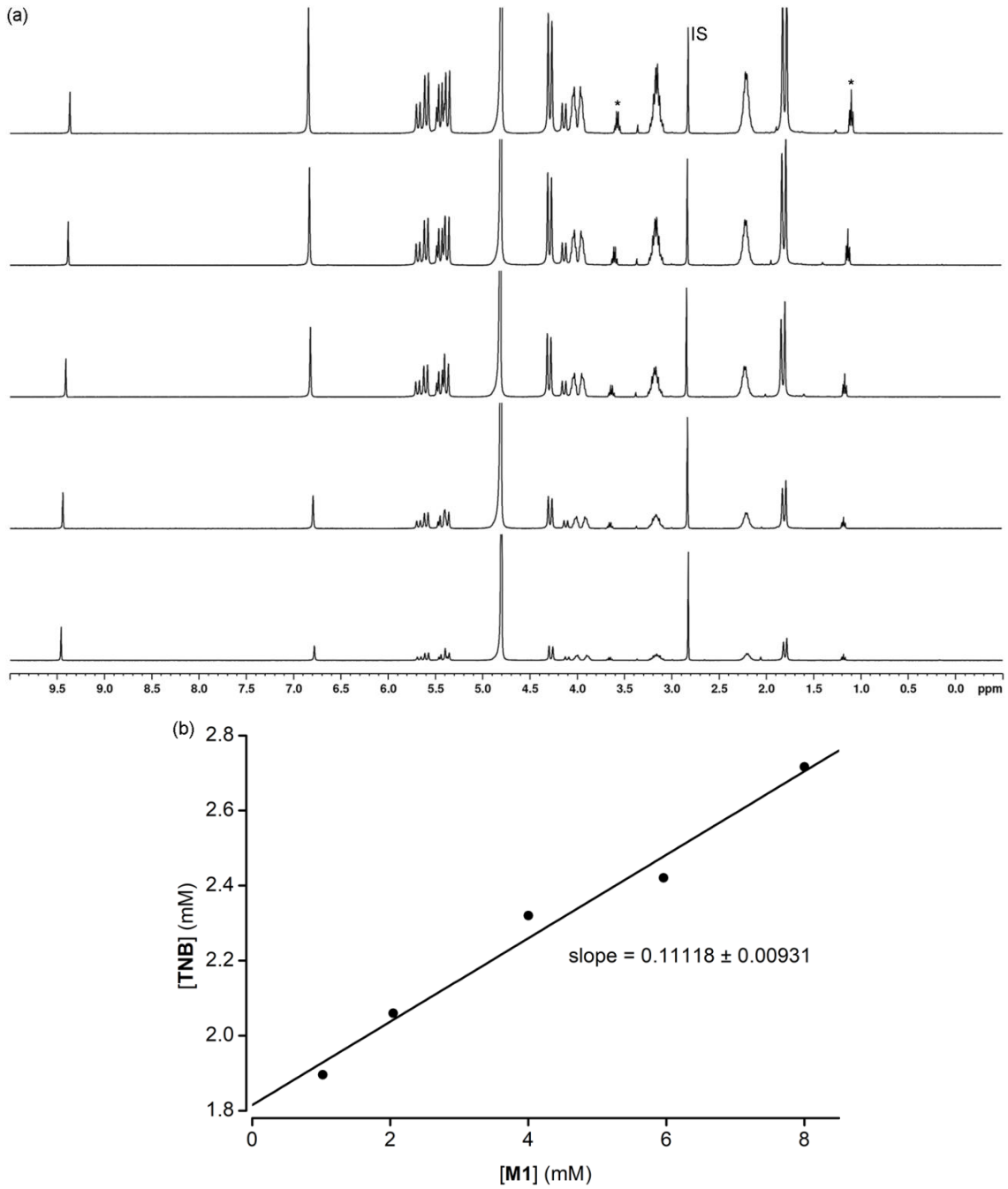

Figure S23 a) ^{1}H NMR spectra recorded (400 MHz, D_2O) for **TNB** in the presence of various concentrations of **M1**. (IS for internal standard, * for residues of EtOH); b) plot of the concentration of **TNB** *versus* the concentration of **M1**.

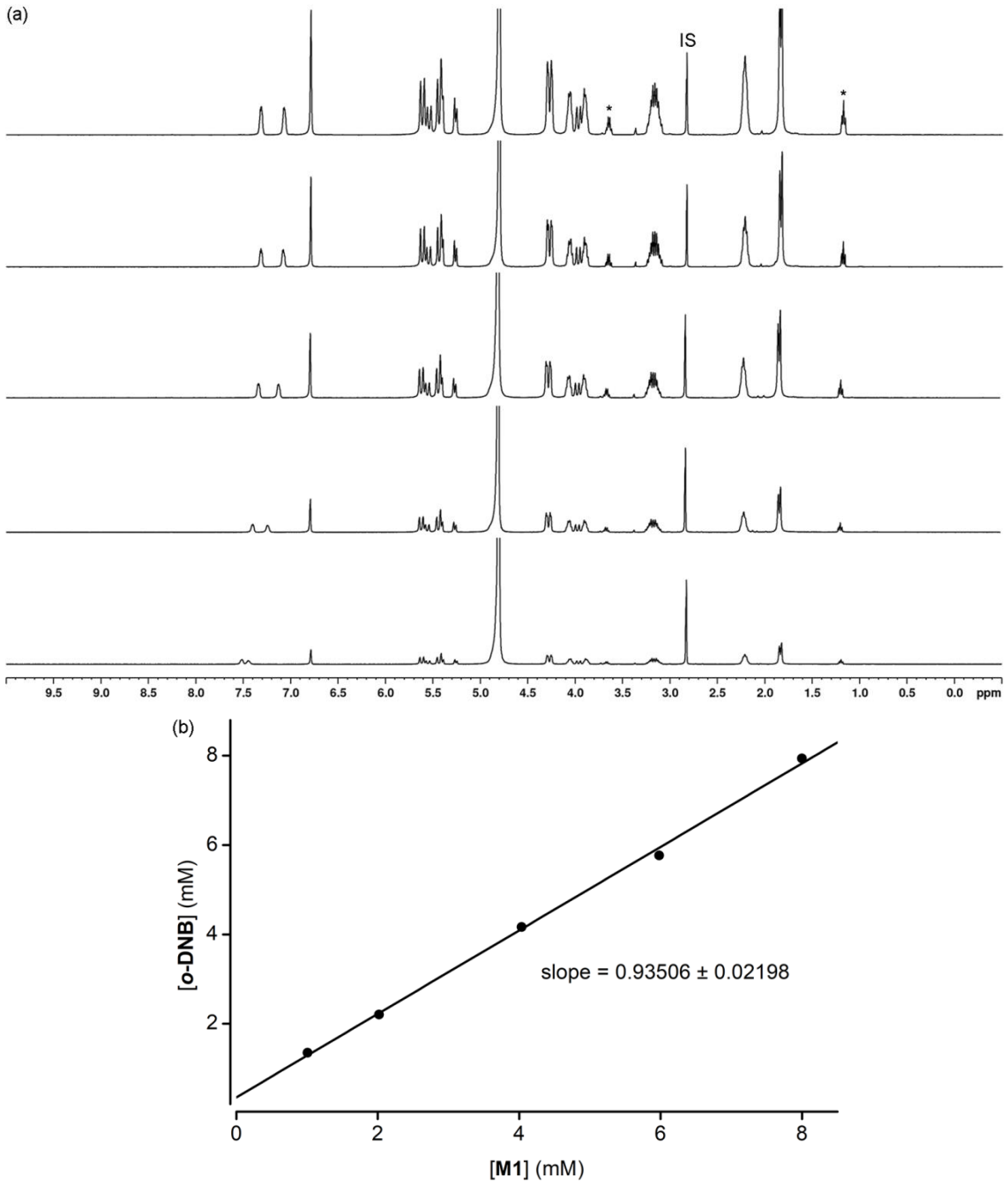

Figure S24 a) ^{1}H NMR spectra recorded (400 MHz, D_2O) for ***o*-DNB** in the presence of various concentrations of **M1**. (IS for internal standard, * for residues of EtOH); b) plot of the concentration of ***o*-DNB** *versus* the concentration of **M1**.

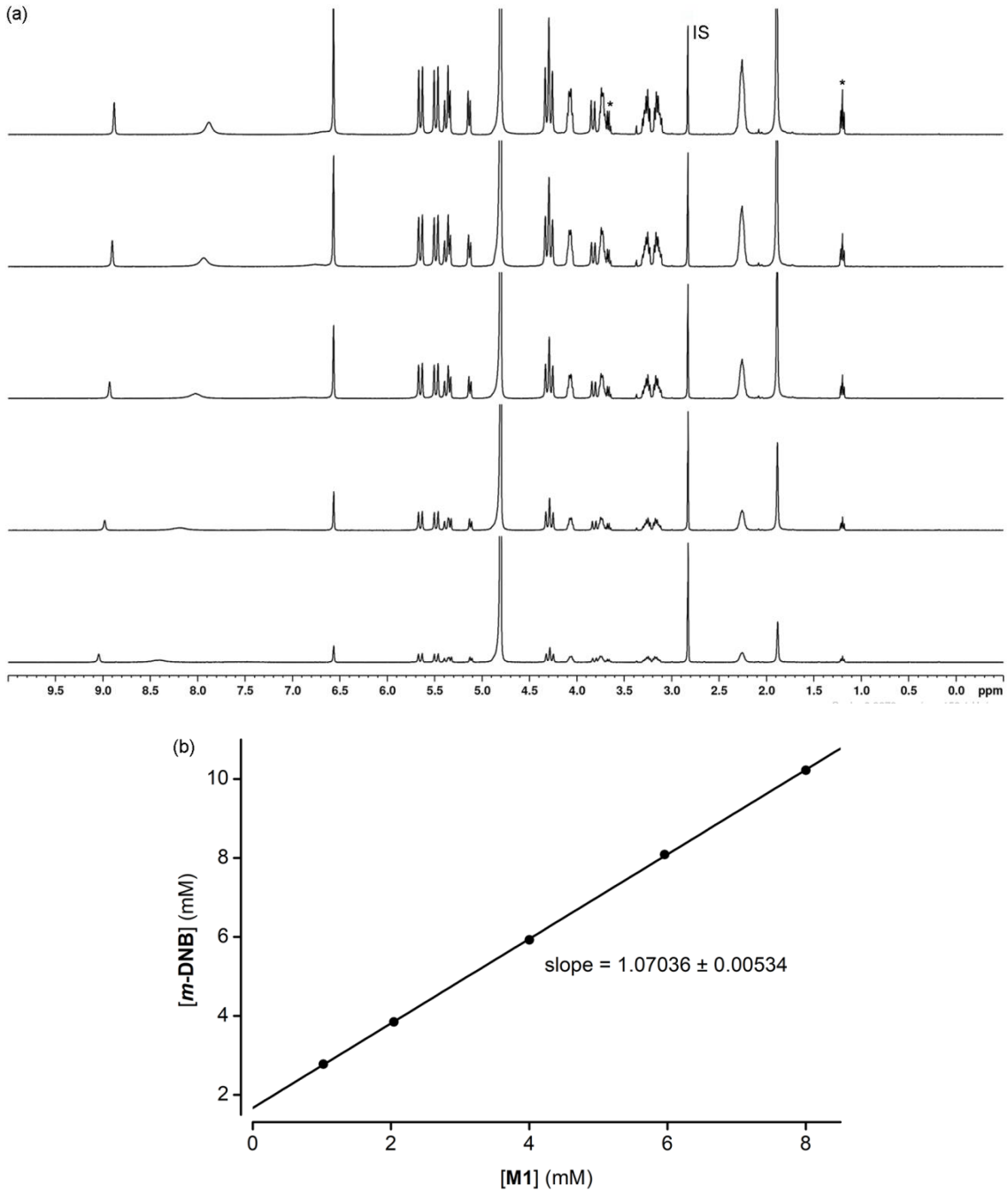

Figure S25 a) ^{1}H NMR spectra recorded (400 MHz, D_2O) for ***m*-DNB** in the presence of various concentrations of **M1**. (IS for internal standard, * for residues of EtOH); b) plot of the concentration of ***m*-DNB** *versus* the concentration of **M1**.

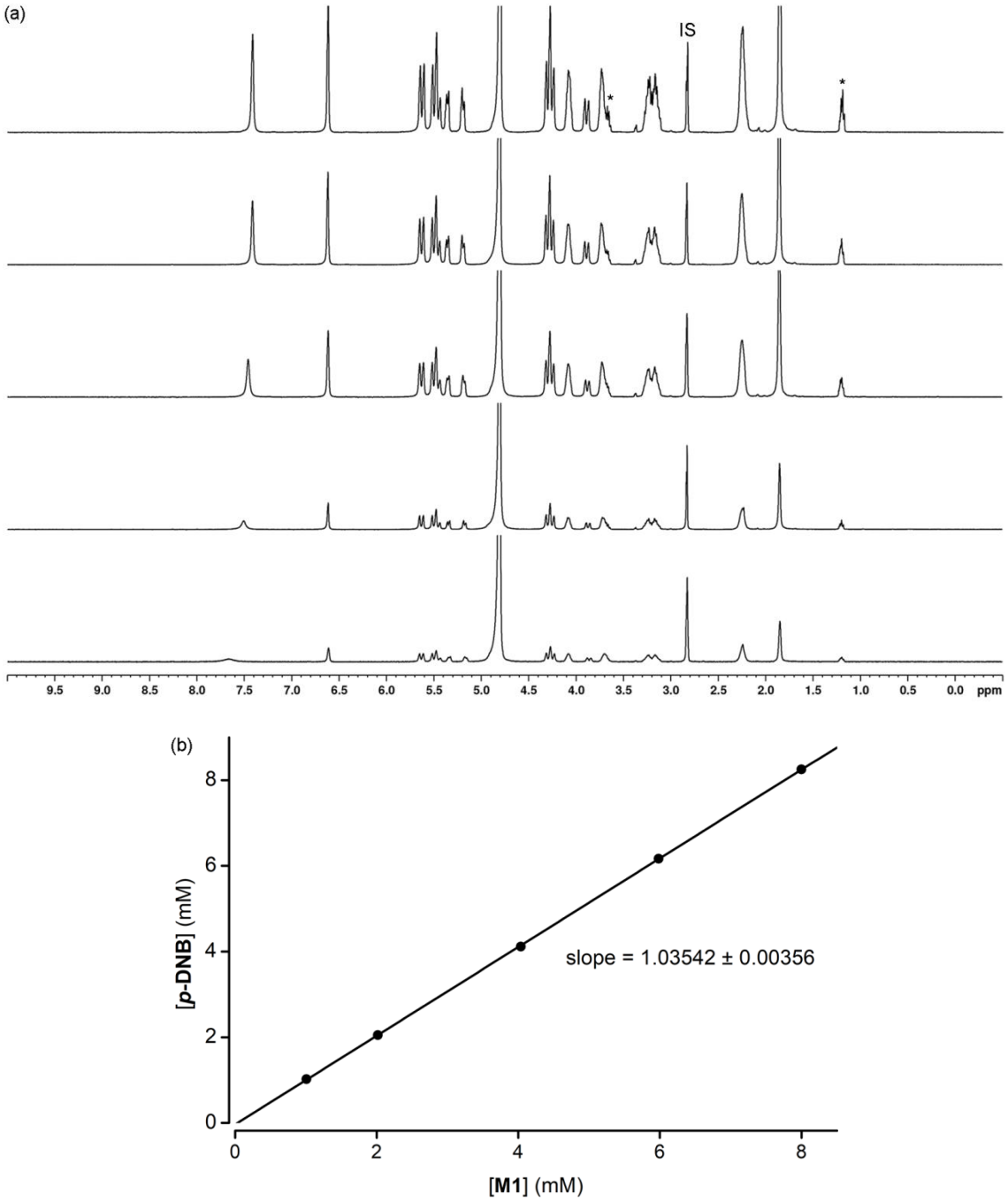

Figure S26 a) ^{1}H NMR spectra recorded (400 MHz, D_2O) for ***p*-DNB** in the presence of various concentrations of **M1**. (IS for internal standard, * for residues of EtOH); b) plot of the concentration of ***p*-DNB** *versus* the concentration of **M1**.

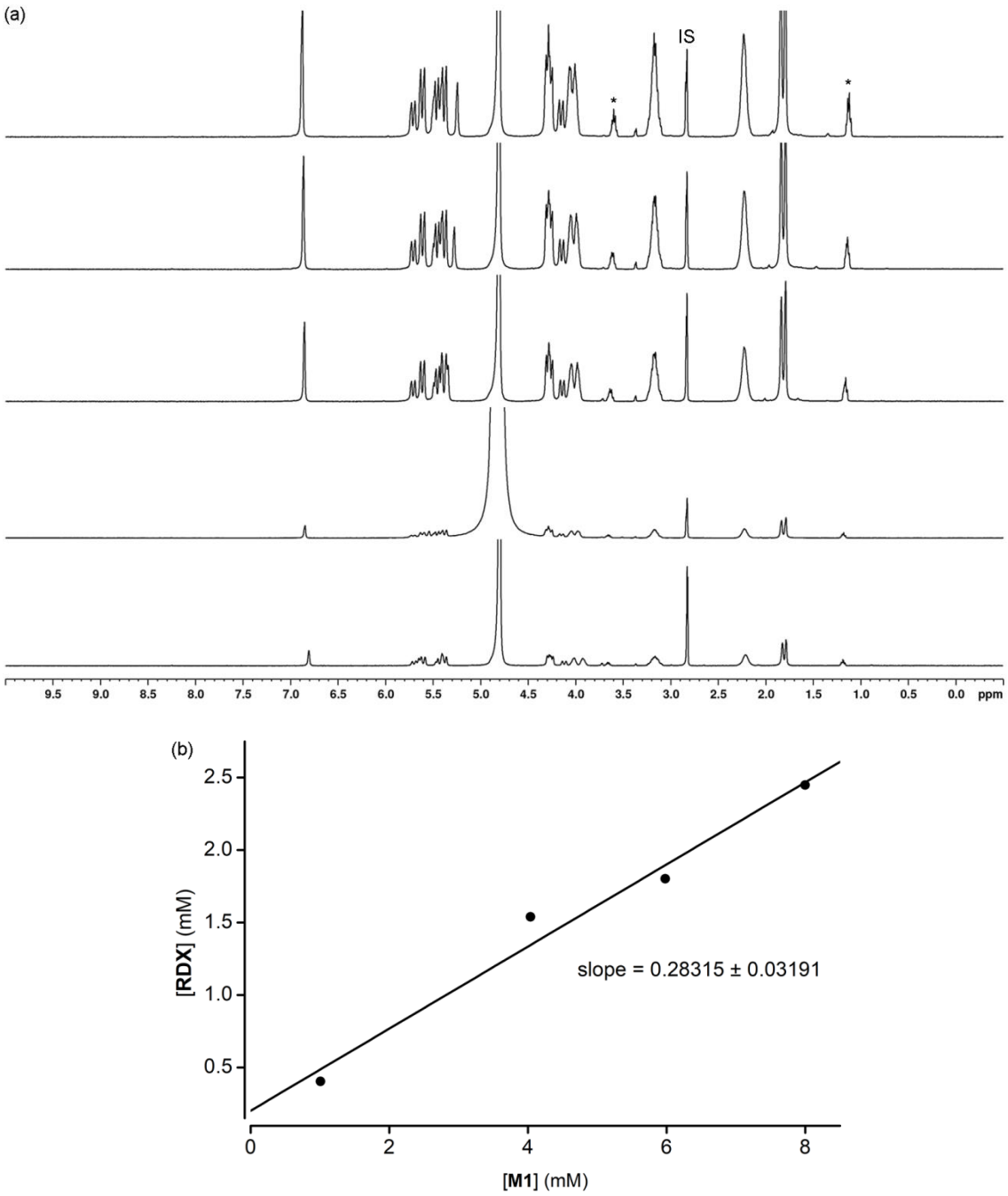

Figure S27 a) ^{1}H NMR spectra recorded (400 MHz, D_2O) for **RDX** in the presence of various concentrations of **M1**. (IS for internal standard, * for residues of EtOH); b) plot of the concentration of **RDX** *versus* the concentration of **M1**.

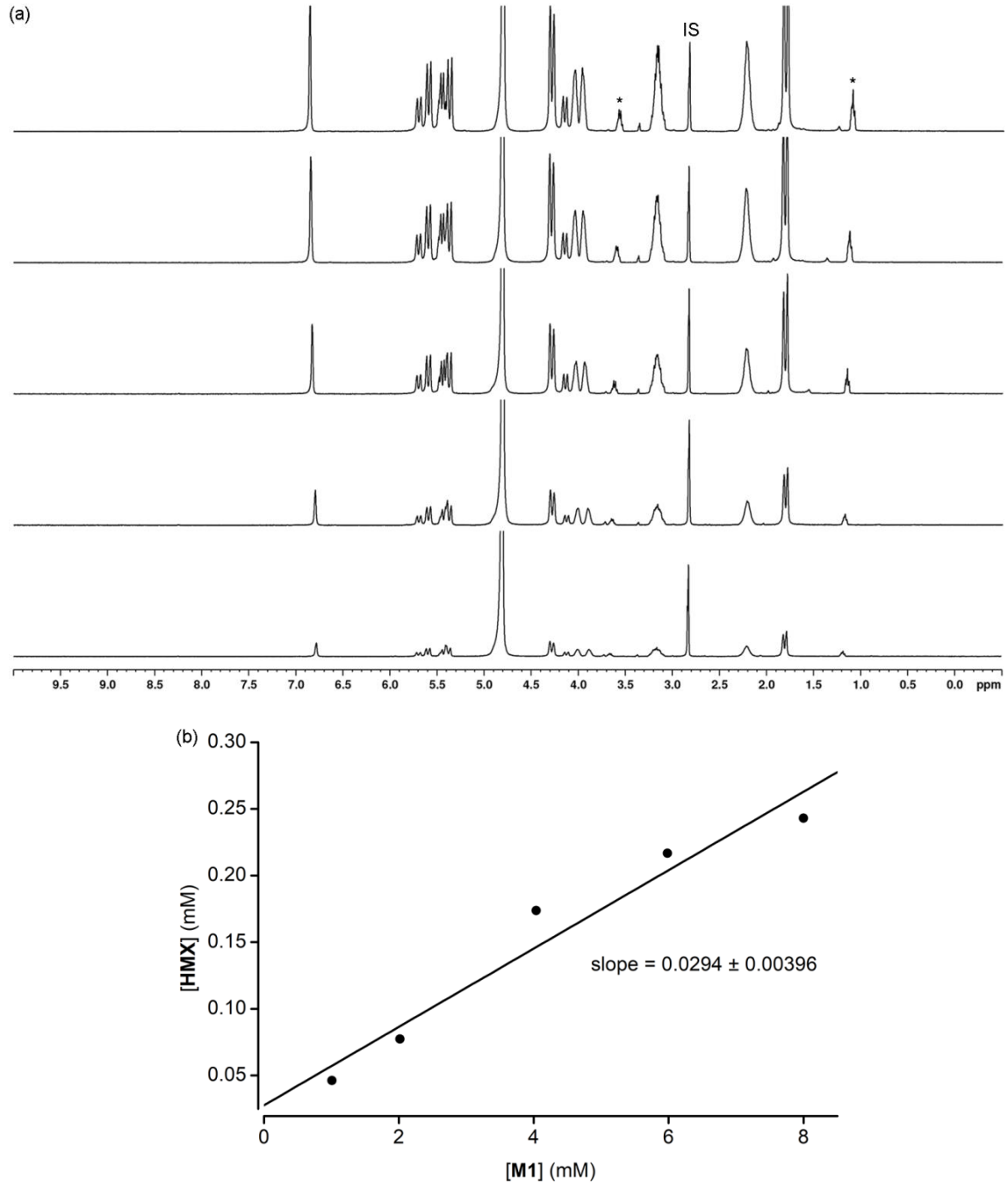

Figure S28 a) ^{1}H NMR spectra recorded (400 MHz, D_2O) for **HMX** in the presence of various concentrations of **M1**. (IS for internal standard, * for residues of EtOH); b) plot of the concentration of **HMX** *versus* the concentration of **M1**.

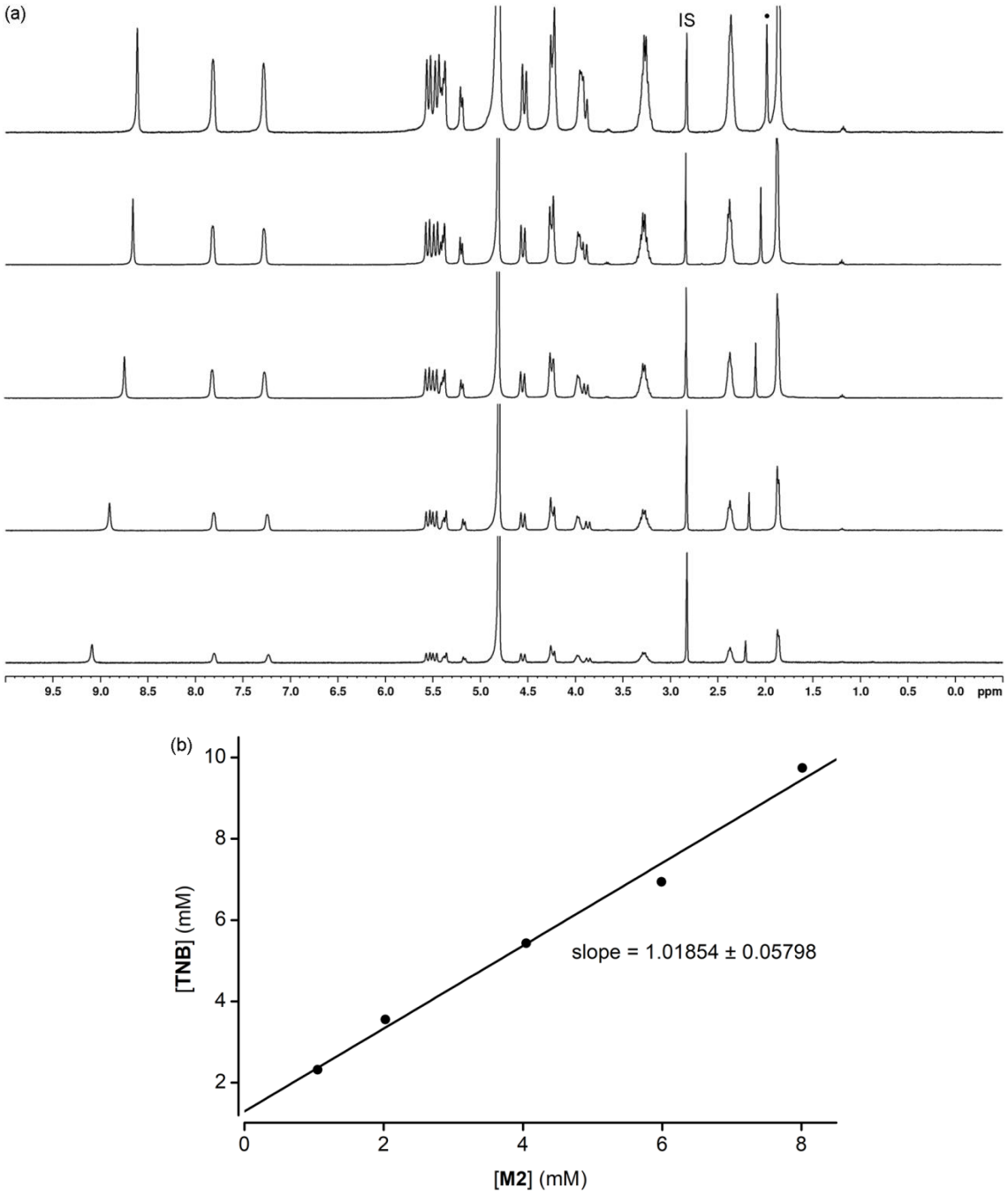

Figure S29 a) ^{1}H NMR spectra recorded (400 MHz, D_2O) for **TNB** in the presence of various concentrations of **M2**. (IS for internal standard, • for unknown impurity in **TNB** solid sample); b) plot of the concentration of **TNB** *versus* the concentration of **M2**.

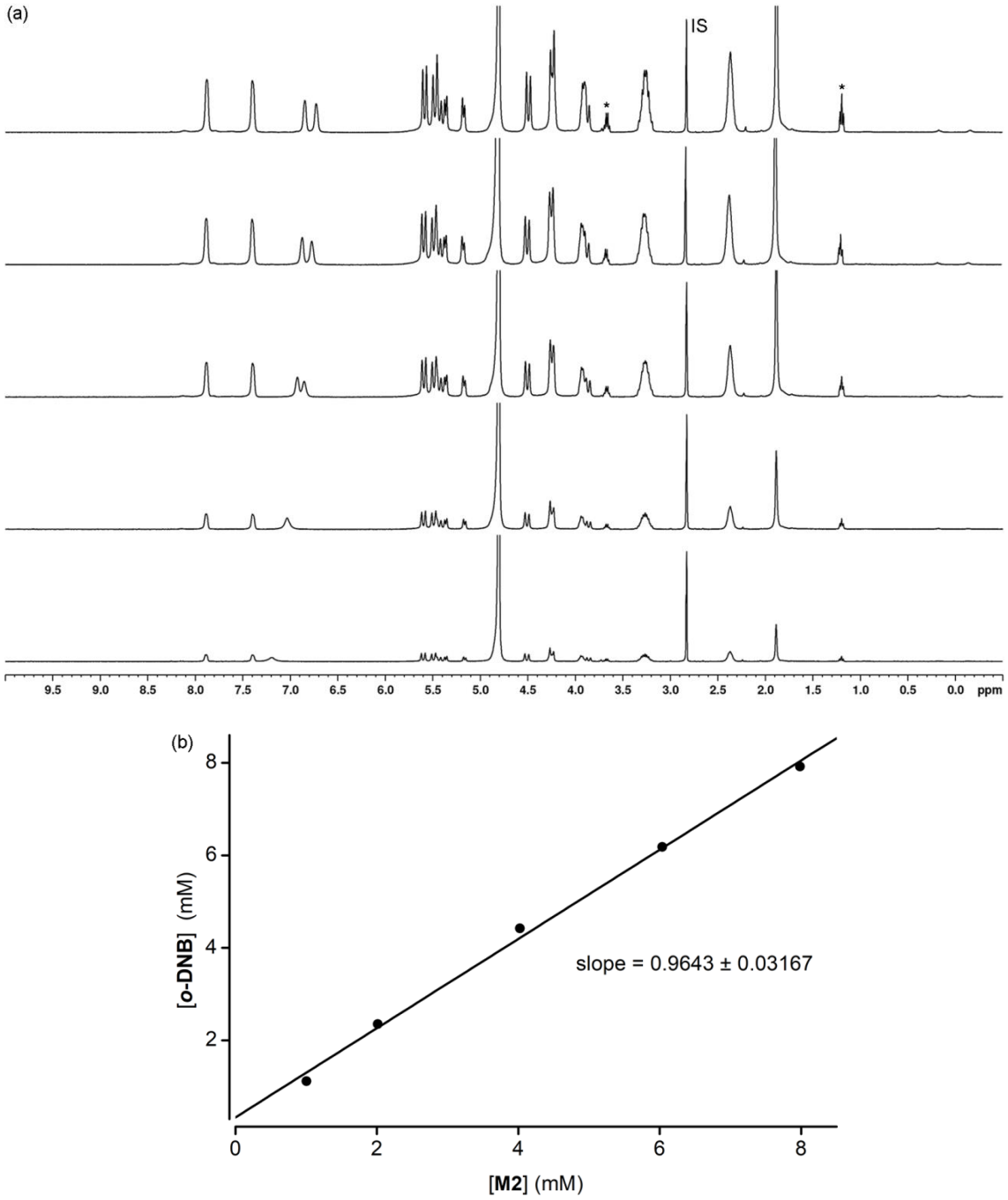

Figure S30 a) ^{1}H NMR spectra recorded (400 MHz, D_2O) for ***o*-DNB** in the presence of various concentrations of **M2**. (IS for internal standard, * for residues of EtOH); b) plot of the concentration of ***o*-DNB** *versus* the concentration of **M2**.

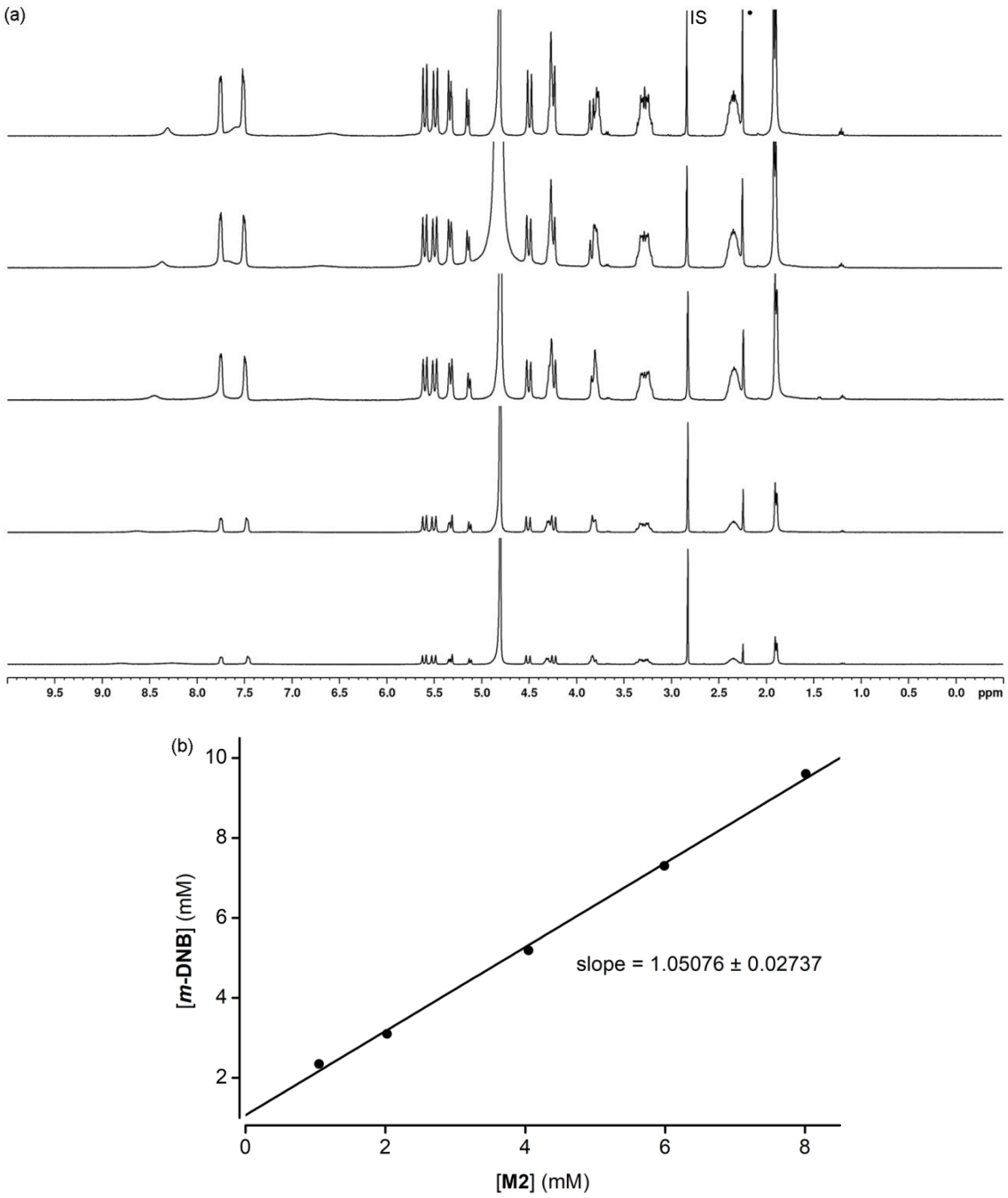

Figure S31 a) ^{1}H NMR spectra recorded (400 MHz, D_2O) for ***m*-DNB** in the presence of various concentrations of **M2**. (IS for internal standard, • for unknown impurity in ***m*-DNB** solid sample); b) plot of the concentration of ***m*-DNB** *versus* the concentration of **M2**.

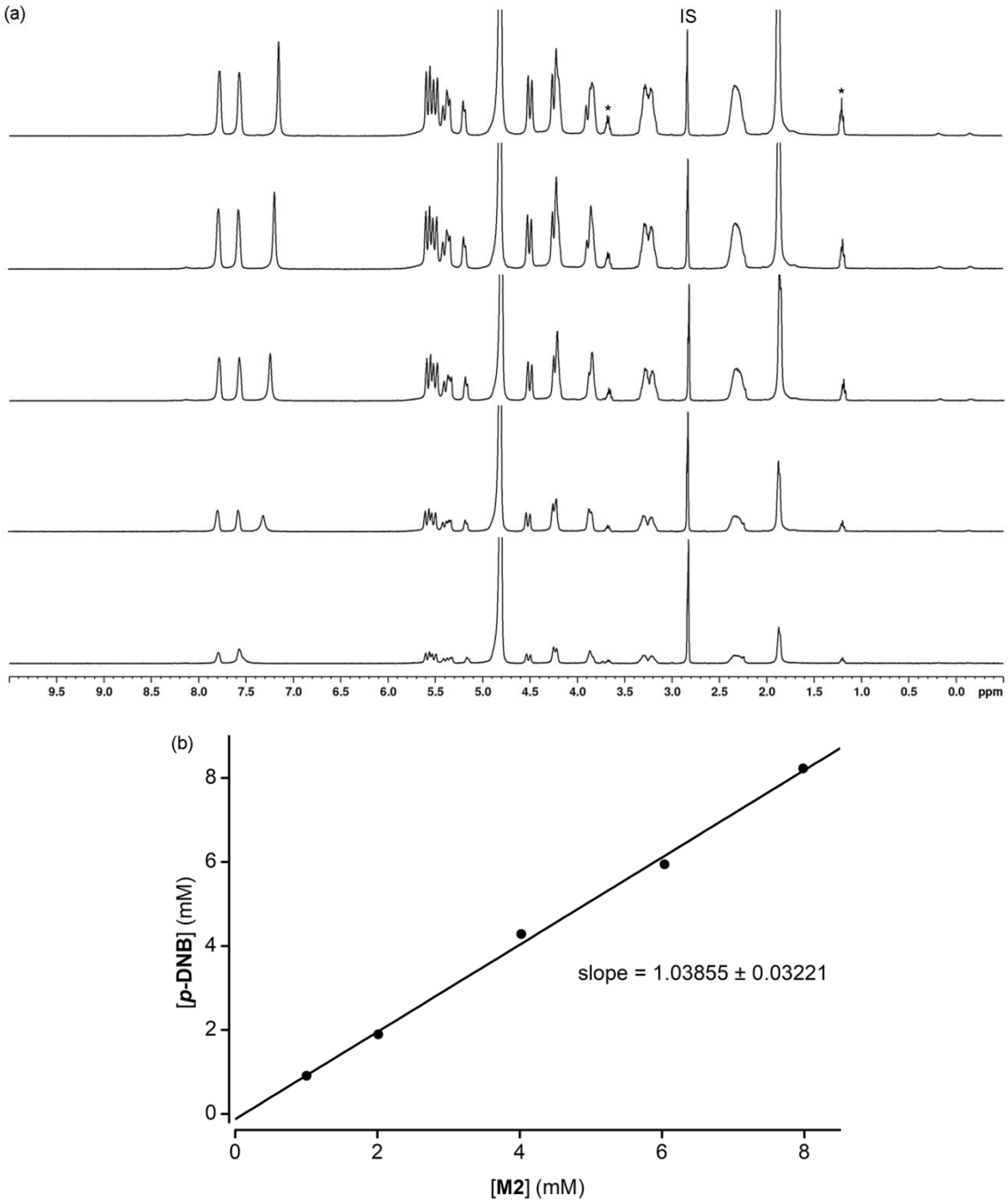

Figure S32 a) ^{1}H NMR spectra recorded (400 MHz, D_2O) for ***p*-DNB** in the presence of various concentrations of **M2**. (IS for internal standard, * for residues of EtOH); b) plot of the concentration of ***p*-DNB** *versus* the concentration of **M2**.

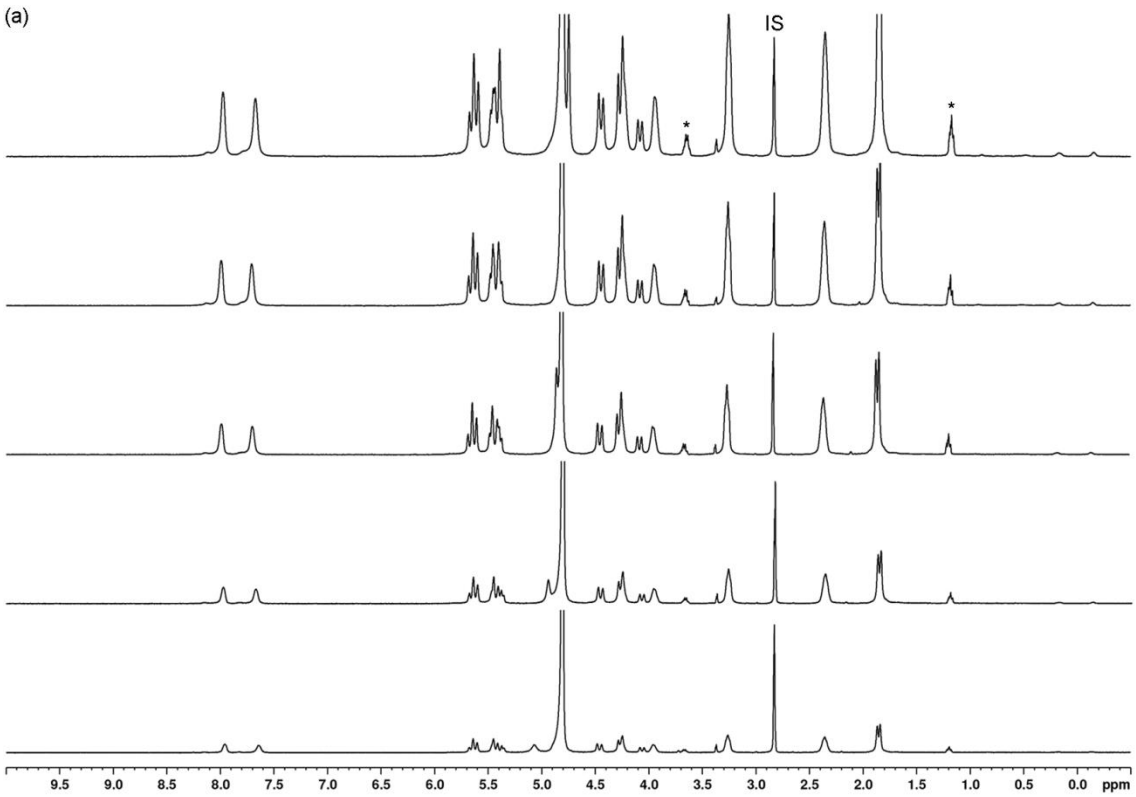

Figure S33 a) ^{1}H NMR spectra recorded (400 MHz, D_2O) for **RDX** in the presence of various concentrations of **M2**. (IS for internal standard, * for residues of EtOH).

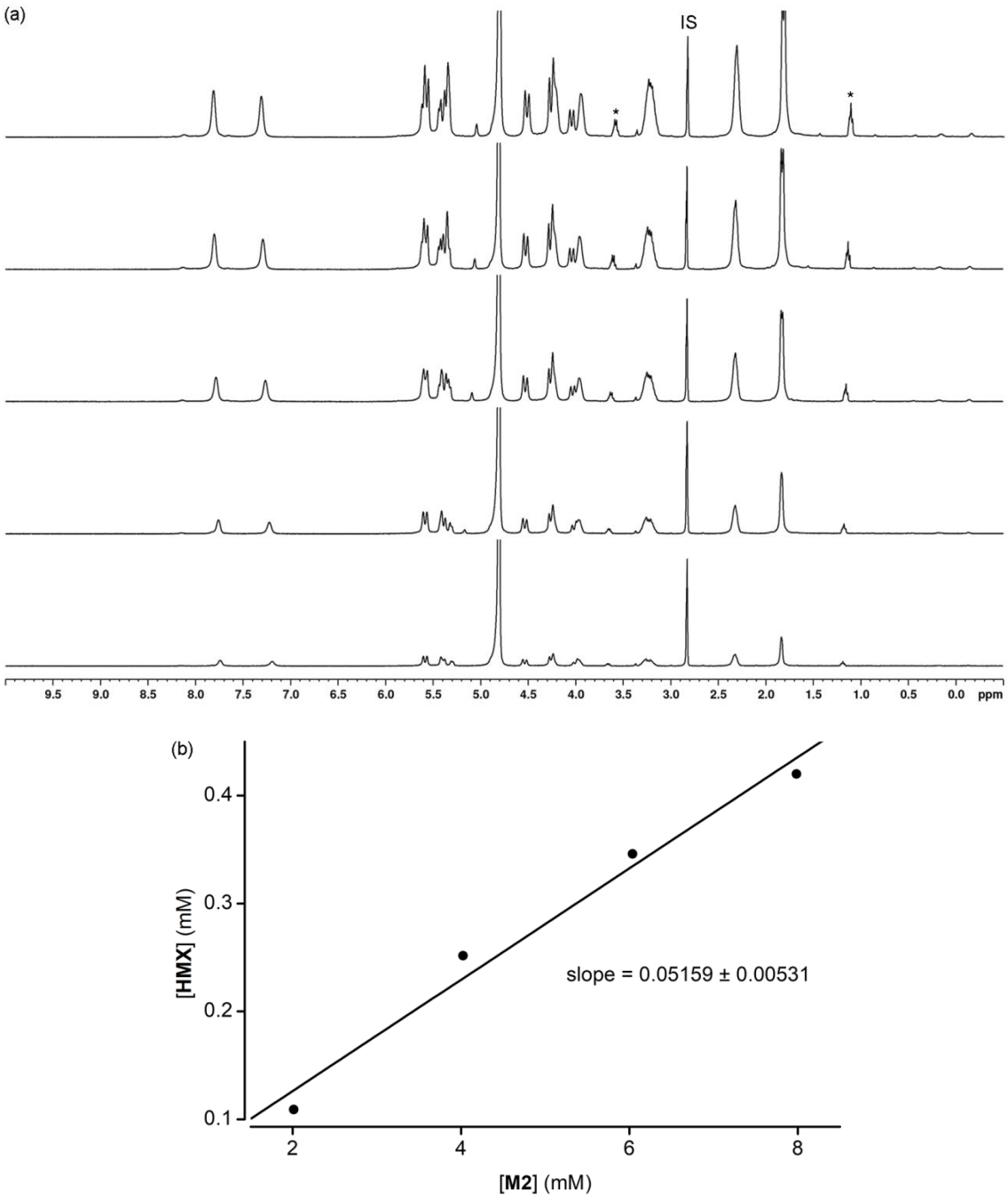

Figure S34 a) ^{1}H NMR spectra recorded (400 MHz, D_2O) for **HMX** in the presence of various concentrations of **M2**. (IS for internal standard, * for residues of EtOH); b) plot of the concentration of **HMX** *versus* the concentration of **M2**.

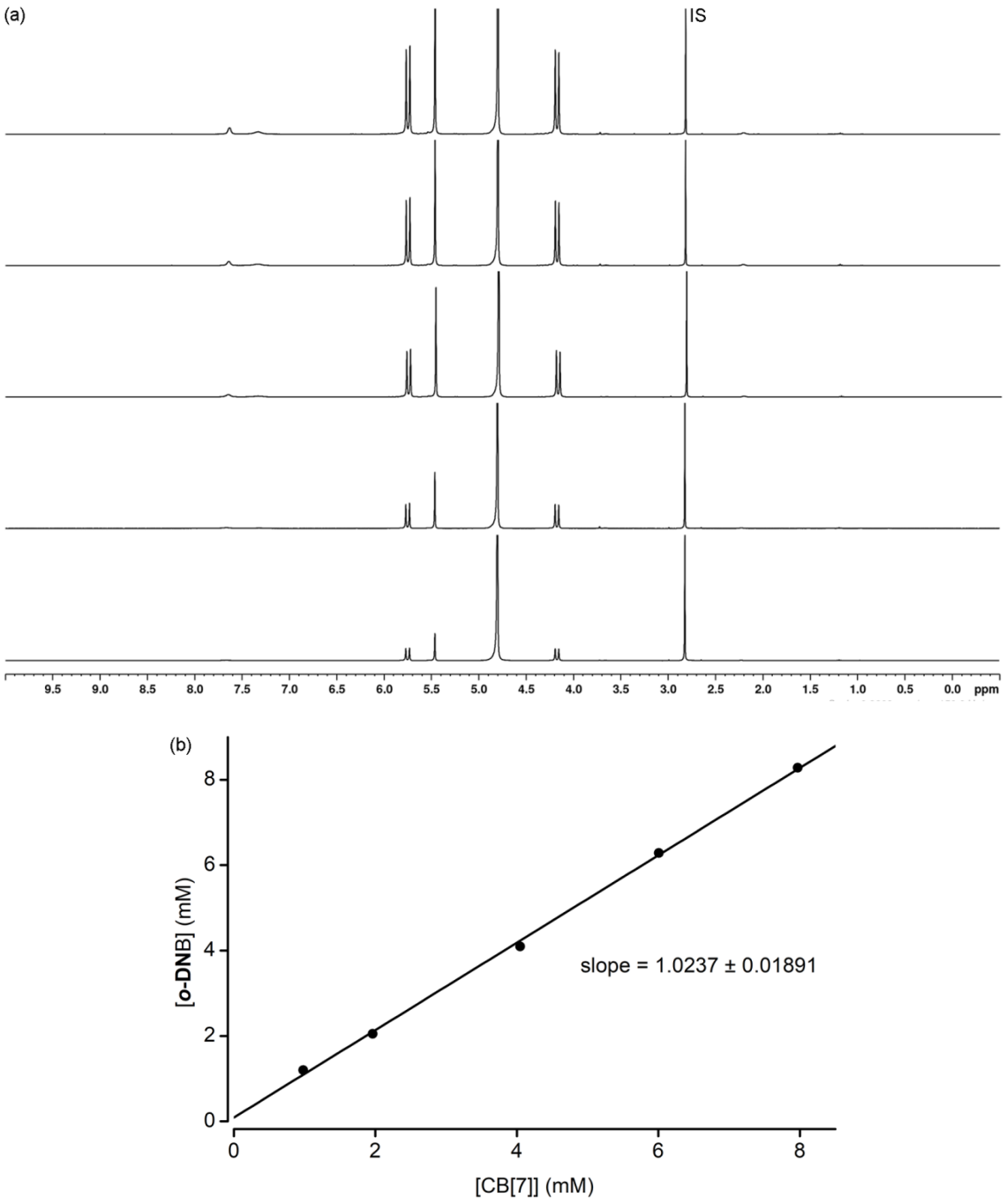

Figure S35 a) ^{1}H NMR spectra recorded (400 MHz, D_2O) for ***o*-DNB** in the presence of various concentrations of CB[7]. (IS for internal standard); b) plot of the concentration of ***o*-DNB** *versus* the concentration of CB[7].

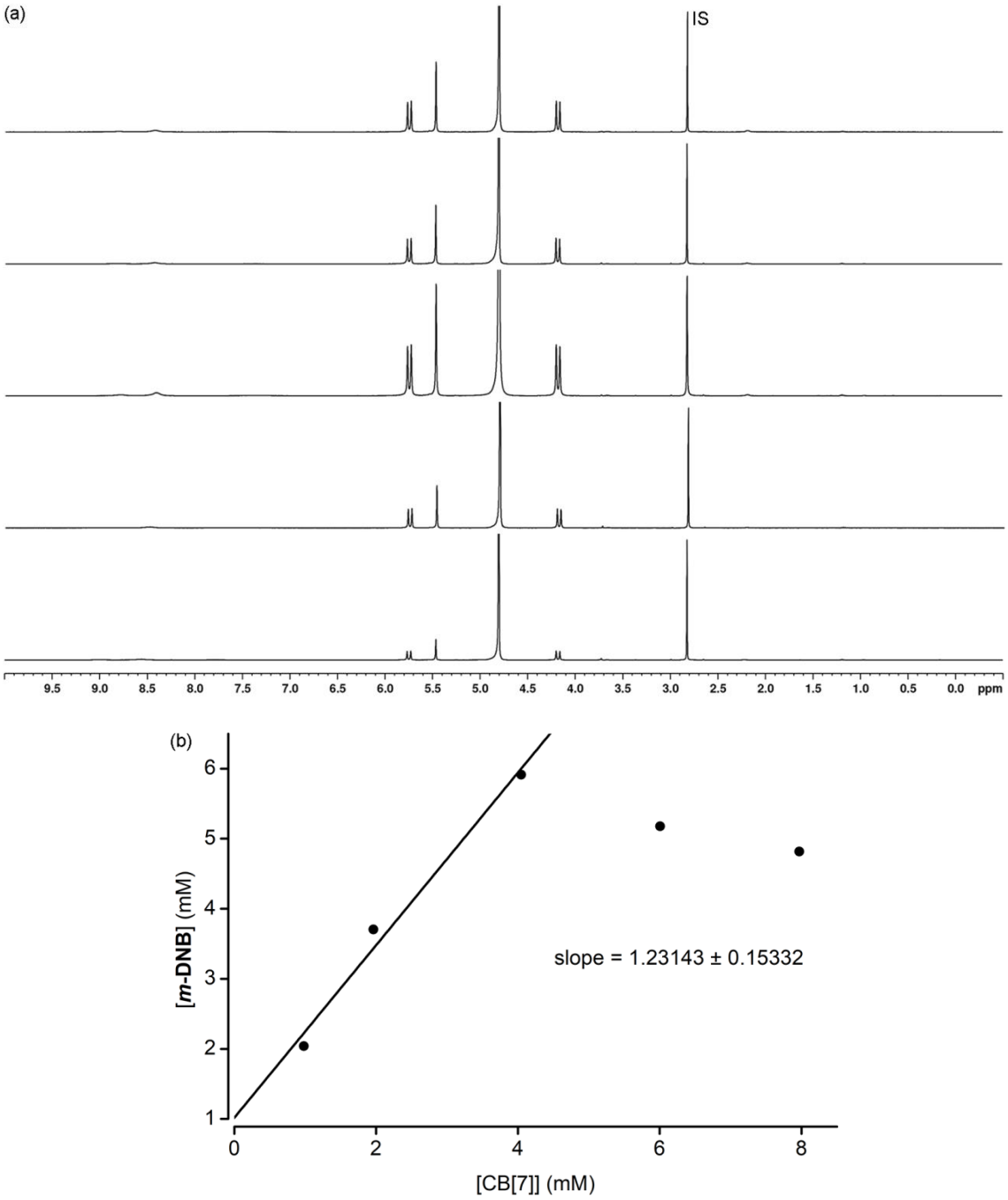

Figure S36 a) ^{1}H NMR spectra recorded (400 MHz, D_2O) for ***m*-DNB** in the presence of various concentrations of CB[7]. (IS for internal standard); b) plot of the concentration of ***m*-DNB** *versus* the concentration of CB[7].

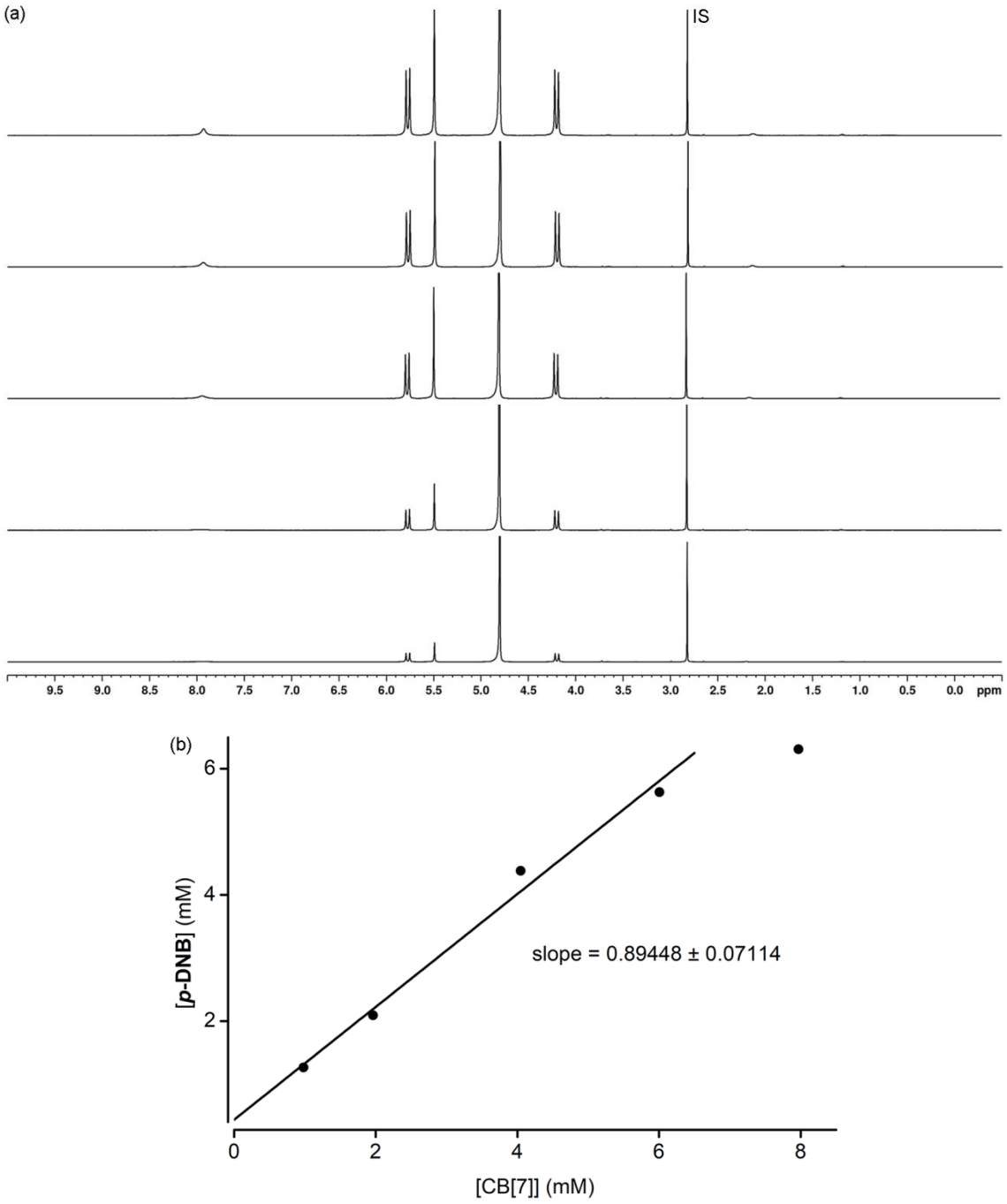

Figure S37 a) ^{1}H NMR spectra recorded (400 MHz, D_2O) for ***p*-DNB** in the presence of various concentrations of CB[7]. (IS for internal standard); b) plot of the concentration of ***p*-DNB** *versus* the concentration of CB[7].

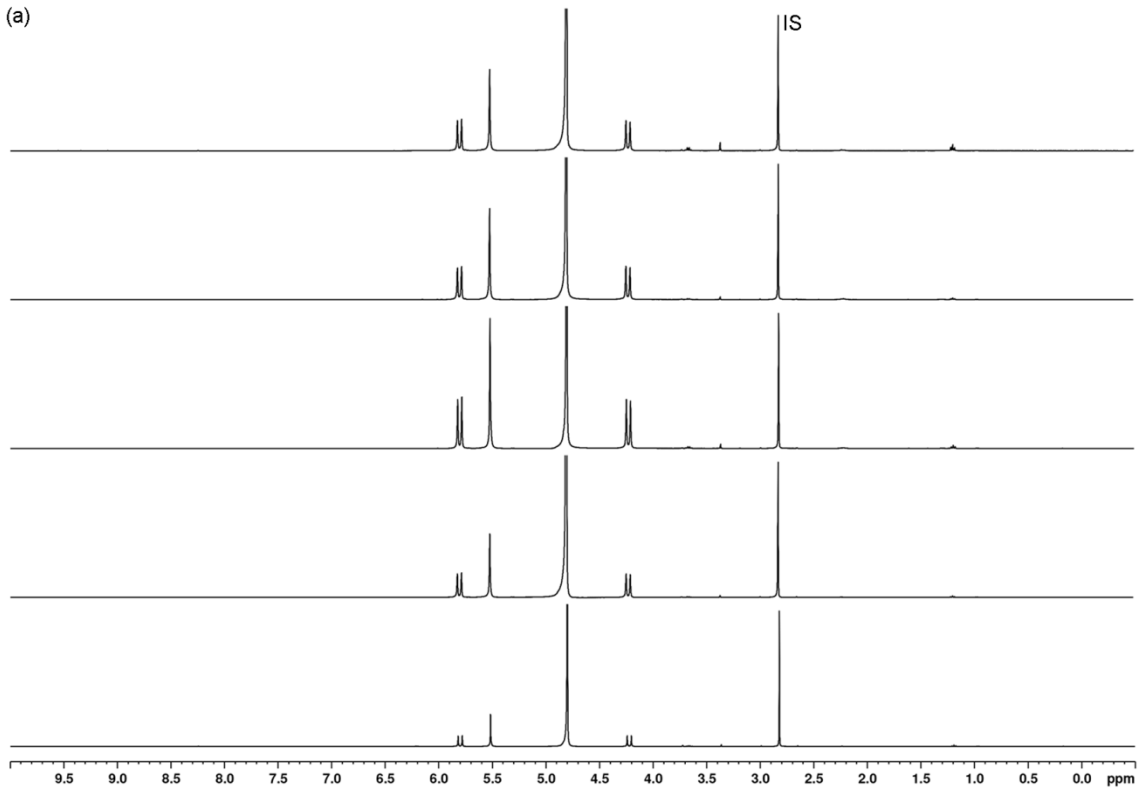

Figure S38 a) ^{1}H NMR spectra recorded (400 MHz, D_2O) for **RDX** in the presence of various concentrations of CB[7]. (IS for internal standard).

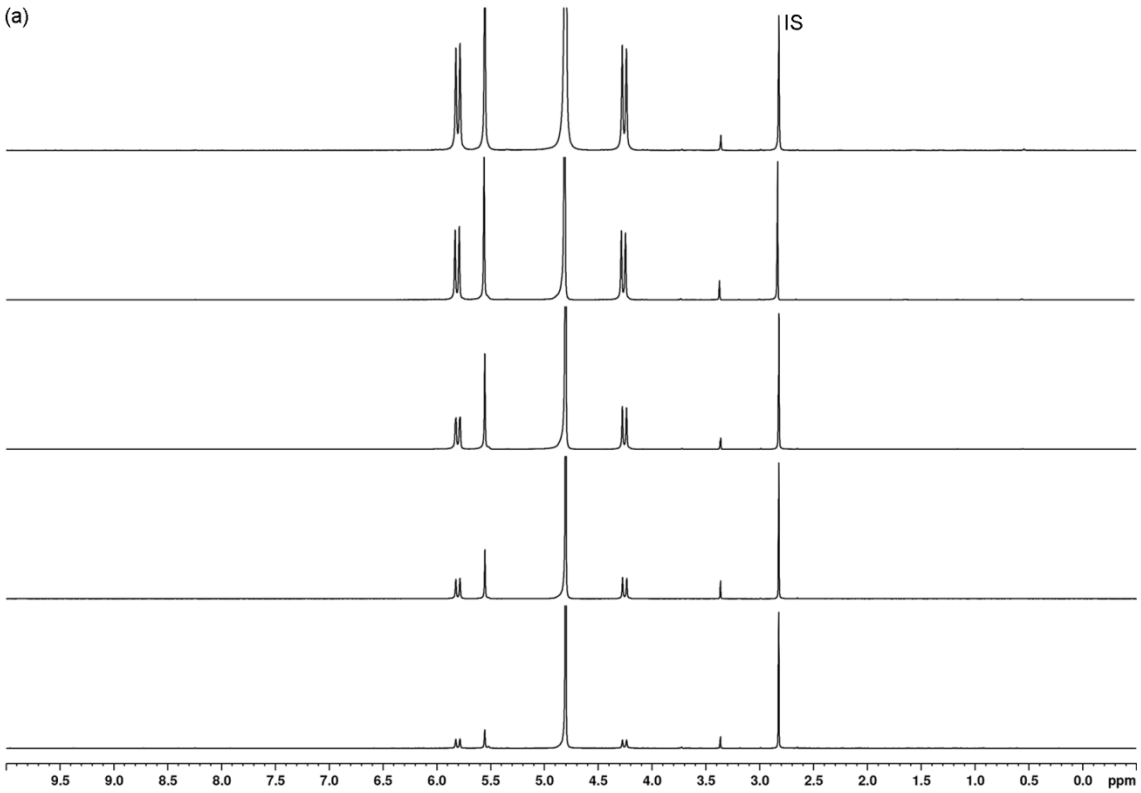

Figure S38 a) ^{1}H NMR spectra recorded (400 MHz, D_2O) for **HMX** in the presence of various concentrations of CB[7]. (IS for internal standard).

Fluorescence titration between M2 and aromatic energetic guests

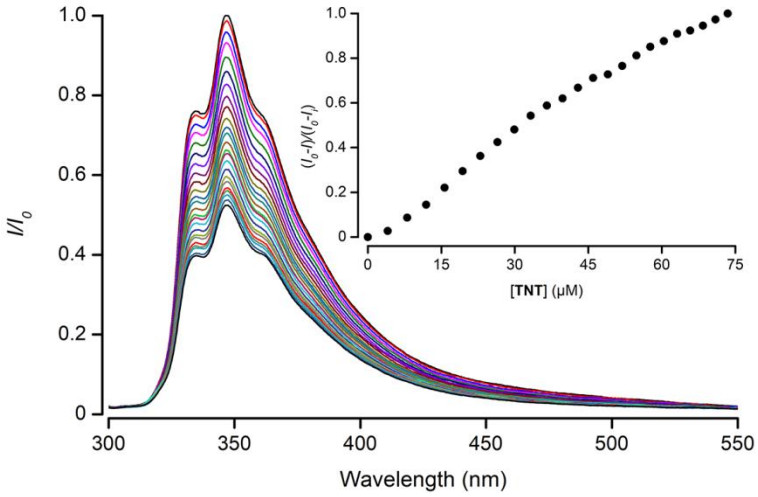

Figure 39 Fluorescence spectra of **M2** (5 μM) at 25 °C in water upon addition of incremental amounts of **TNT** (0 – 74 μM), λ_{ex} = 290 nm. Insets: Normalized titration isotherm corresponding to the guest-induced change of fluorescence intensity at maximum wavelength.

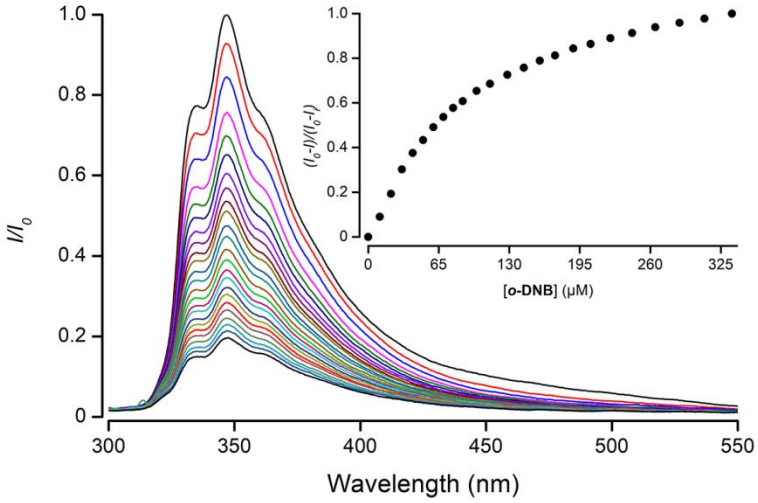

Figure 40 Fluorescence spectra of **M2** (5 μM) at 25 °C in water upon addition of incremental amounts of ***o*-DNB** (0 – 335 μM), λ_{ex} = 290 nm. Insets: Normalized titration isotherm corresponding to the guest-induced change of fluorescence intensity at maximum wavelength.

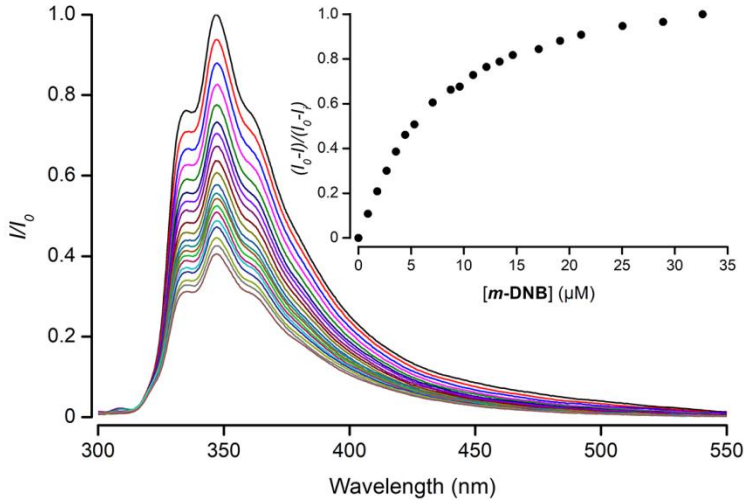

Figure 41 Fluorescence spectra of **M2** (5 μM) at 25 °C in water upon addition of incremental amounts of ***m*-DNB** (0 – 33 μM), λ_{ex} = 290 nm. Insets: Normalized titration isotherm corresponding to the guest-induced change of fluorescence intensity at maximum wavelength.

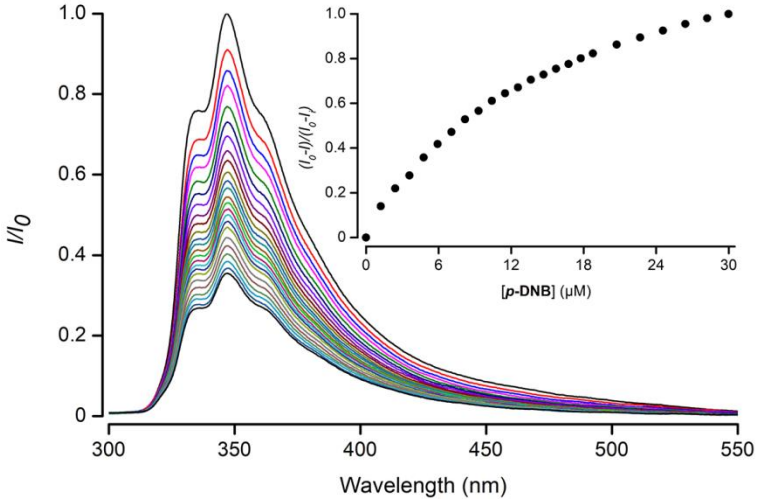

Figure 42 Fluorescence spectra of **M2** (5 μM) at 25 ℃ in water upon addition of incremental amounts of ***p*-DNB** (0 – 30 μM), λ_{ex} = 290 nm. Insets: Normalized titration isotherm corresponding to the guest-induced change of fluorescence intensity at maximum wavelength.

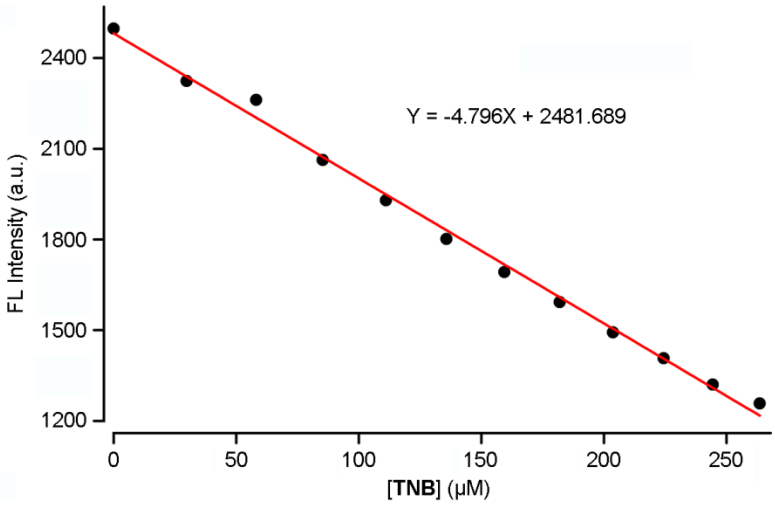

Figure 43 Regression line for the determination of LOD of **M2** toward **TNB**.