Supplementary material

Process optimization by NMR-assisted investigation of chemical pathways during depolymerization of PET in subcritical water.

Antonio Jaime-Azuara (aja@energy.aau.dk) [a], Thomas Helmer Pedersen (thp@energy.aau.dk) *[a] and Reinhard Wimmer (rw@bio.aau.dk)*[b]

[a] Department of Energy, Aalborg University, Pontoppidanstræde 111, Aalborg Øst 9220, Denmark.

[b] Department of Chemistry and Bioscience, Aalborg University, Frederik Bajers vej 7H, 9220 Aalborg, Denmark.

Table of contents

1.- NMR quantification of solid and aqueous products from hydrothermal depolymerization of PET

PRODUCT SEPARATION PROCEDURE

After cooling, pressure was released, reactors were opened, and all products were collected in 50 mL vials together with any extra deionized water used during reactor cleaning. After centrifugation, the supernatant was decanted to a 100 mL volumetric flask and extra 25 mL of deionized water were added to the vial. Water and solids were shaken to transfer any water-soluble compound adsorbed to the solids into the aqueous phase fraction. Vials were centrifuged again, and the supernatant added to the volumetric flask. Finally, the volumetric flask was filled up to the ring graduation mark with deionized water. Solids left in the vial after centrifugation were lyophilized and weighed. Two reactors were run in parallel for every reaction condition. Analysis and calculations were done separately for each reactor and average values of both reactors were used just for graphical representation.

SOLID QUANTIFICATION

100 mg of dried solids were weighed off and dissolved in 2.5 mL of DMSO. Any undissolved residues were dried again and weighed. The NMR sample was prepared by diluting 25 µL of this solution with 475 µL of a stock solution of known concentration of maleic acid in DMSO-d_6. Concentrations of compounds were determined by quantitative NMR and normalized to the known concentration of maleic acid in the stock solution, taking into account its dilution. The number of moles of any compound *j* in the solid fraction could then be expressed as:

$$n_j^{solid} = c_{j,NMR}^{solid} \frac{V_{sample}^{solid}}{f_{dilution}^{solid}} \frac{m_{total}^{solid}}{m_{sample}^{solid}}$$

Where

$c_{j,NMR}^{solid}$ is the concentration of compound j in the NMR sample

V_{sample}^{solid} is the volume that was used to dissolve the solid sample (2.5 mL)

m_{sample}^{solid} is the mass of solid dissolved in the sample (0.1 g)

$f_{dilution}^{solid}$ is the dilution of solid sample in the NMR sample (25/500)

m_{total}^{solid} is the total amount of solids retrieved from the reactor

AQUEOUS PHASE QUANTIFICATION

500 µL of the combined aqueous phases obtained after product separation was added to 25 µL of a stock solution of sodium trimethylsilylpropanesulfonate (DSS) in D_2O. Concentrations of compounds were determined by quantitative NMR and normalized to the known concentration of DSS in the stock solution, taking into account its dilution. The number of moles of any compound *j* in the aqueous phase could then be expressed as:

$$n_j^{aq} = c_{j,NMR}^{aq} \frac{V^{aq}}{f_{dilution}^{aq}}$$

Where:

$c_{j,NMR}^{aq}$ is the concentration of compound *j* in the NMR sample

V^{aq} is the total volume of the aqueous phase (0.1 L)

$f_{dilution}^{aq}$ is the dilution factor of the aqueous phase in the NMR sample (500/525)

For each compound, the total number of moles in the reactor is defined as:

$$n_j = n_j^{solid} + n_j^{aq}$$

2.- Calculations for the environmental impact factors

Energy economy coefficient (ε)

$$\varepsilon = \frac{Y}{T \cdot t}$$

Where

Y is the yield of the product considered for each scenario as generated mass of product per unitary mass of processed PET (-)

T is the processing temperature during the reaction (°C)

t is the reaction time (min)

Environmental factor (E)

$$E = \frac{m_{waste}}{m_{product}}$$

Where

$m_{product}$ is the mass of product per unitary mass of processed PET (-)

m_{waste} is the mass of waste generated per unitary mass of processed PET (-)

m_{waste} is calculated as:

$$m_{waste} = \frac{f \cdot \lambda + m_{biproducts}}{m_{product}}$$

Where

f is the mass fraction of solvent waste in the process assuming 90% solvent recovery for industrial processes (0.1)

λ is the mass ratio m_{water}/m_{PET} loaded into the reactor (-)

$m_{biproducts}$ is the mass of useful products per unitary mass of processed PET, also expressed as $(1 - m_{product})$ (-)

3.- Values of x_j^{PA} and x_j^{EG} coefficients

Table S1. Coefficient x representing number of PA and EG subunits that make up or that were consumed to produce every quantified compound.

Compound	x_j^{PA}	x_j^{EG}
TPA	1	0
MHET	1	1
BHET	1	2
IPA	1	0
MHEI	1	1
BHEI	1	2
Benzoic Acid	1	0
DEG Ester	1	3
EG	0	1
DEG	0	2
Dioxane	0	2
Acetaldehyde	0	1
Crotonaldehyde	0	2

4.-Product yields for both reactors

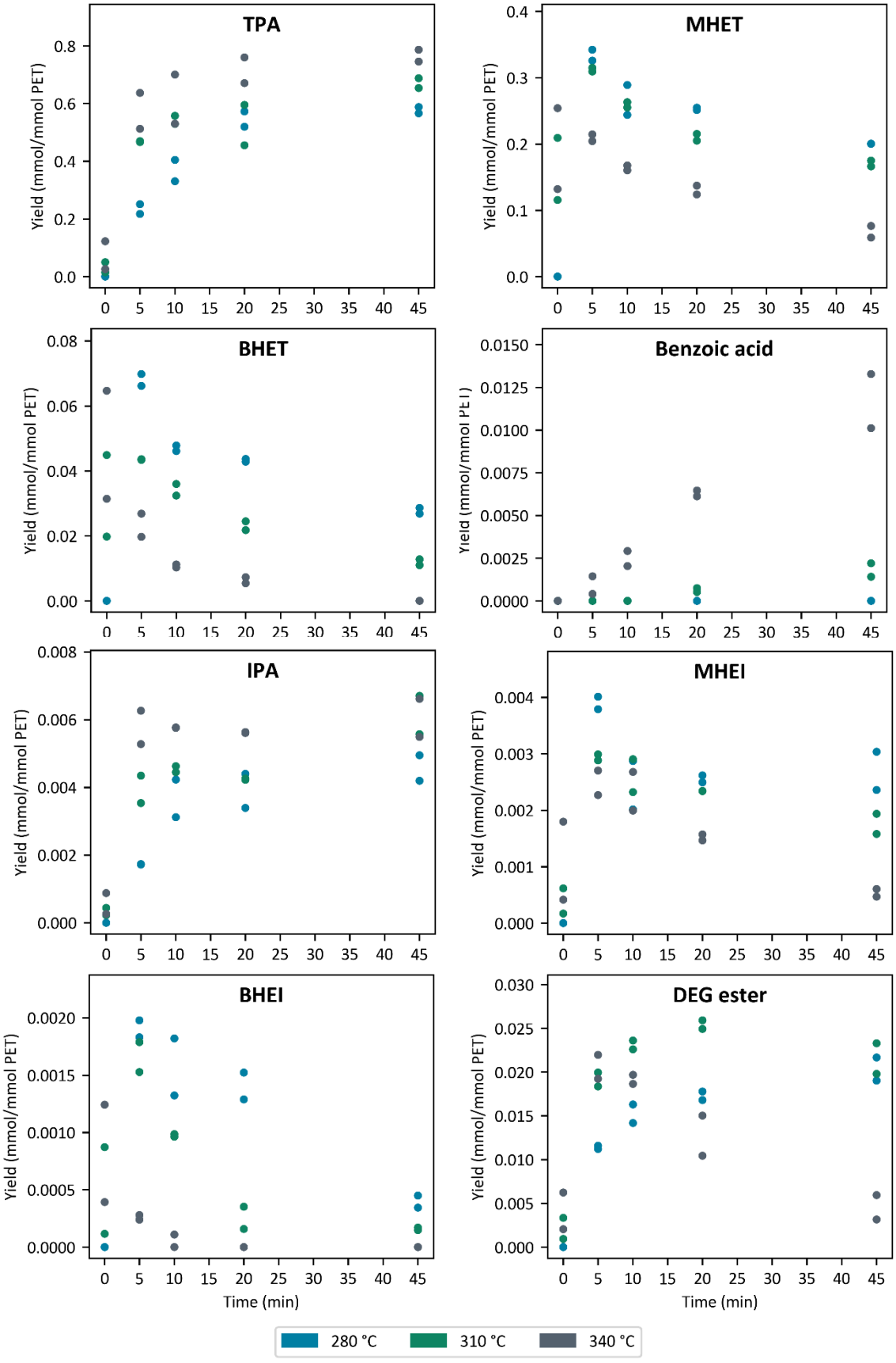


Figure S1. Yield of quantified products per mmol of PET as a function of time and temperature. Results from both reactors are shown for each time and temperature condition.

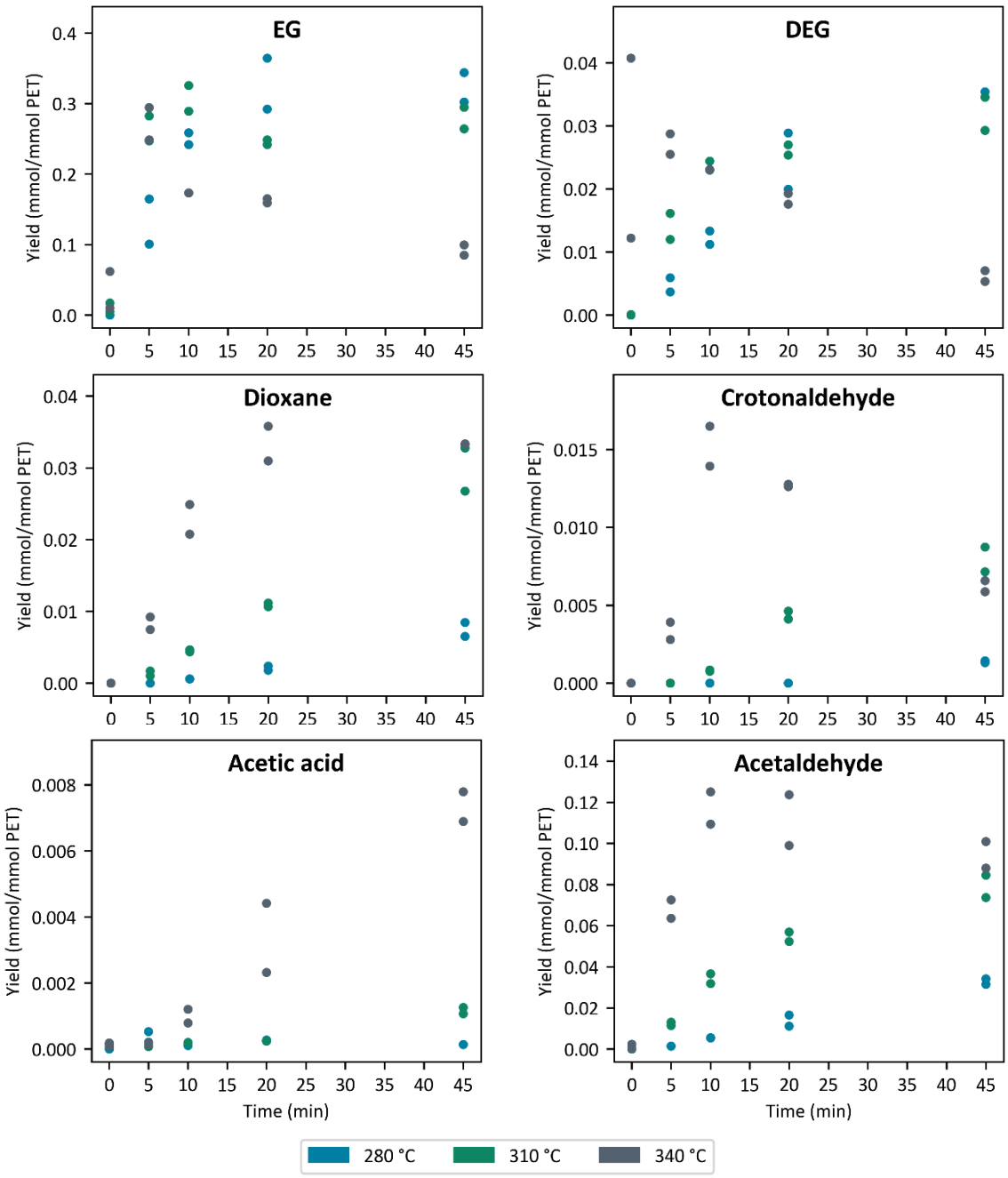


Figure S2. Yield of quantified products per mmol of PET as a function of time and temperature. Results from both reactors are shown for each time and temperature condition.

5.- ^{1}H and HSQC of standards in D_2O

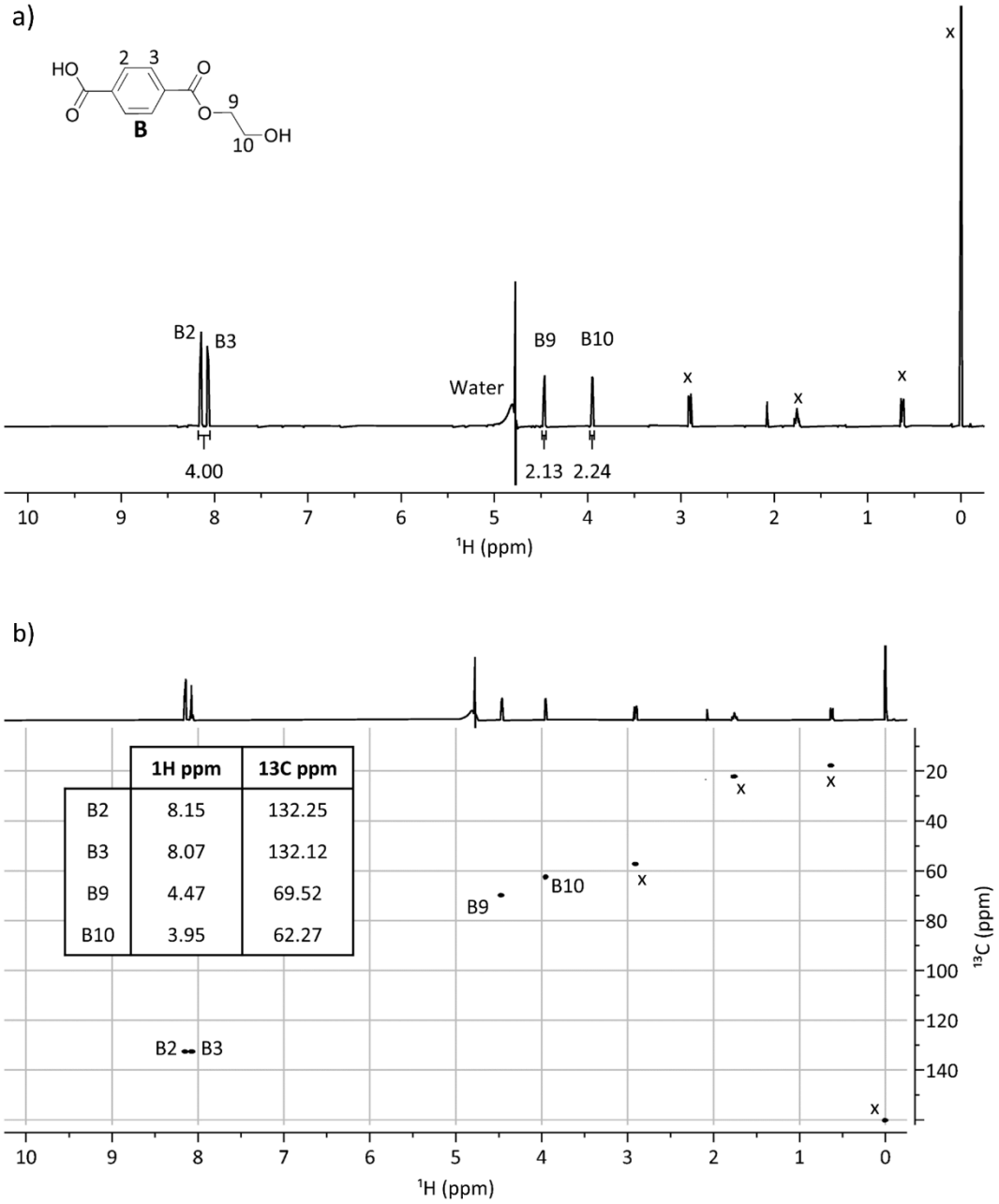


Figure S3. ^{1}H-NMR (a) and [^{1}H,^{13}C]-HSQC (b) of mono(2-hydroxyethyl) terephthalate (compound B) in D_2O. The DSS signals are labelled "x". In the ^{13}C-dimension of the HSQC, the methyl DSS signal appears at 150 ppm due to folding. Non-assigned peaks in the ^{1}H-NMR correspond to contaminants present in the standard sample.

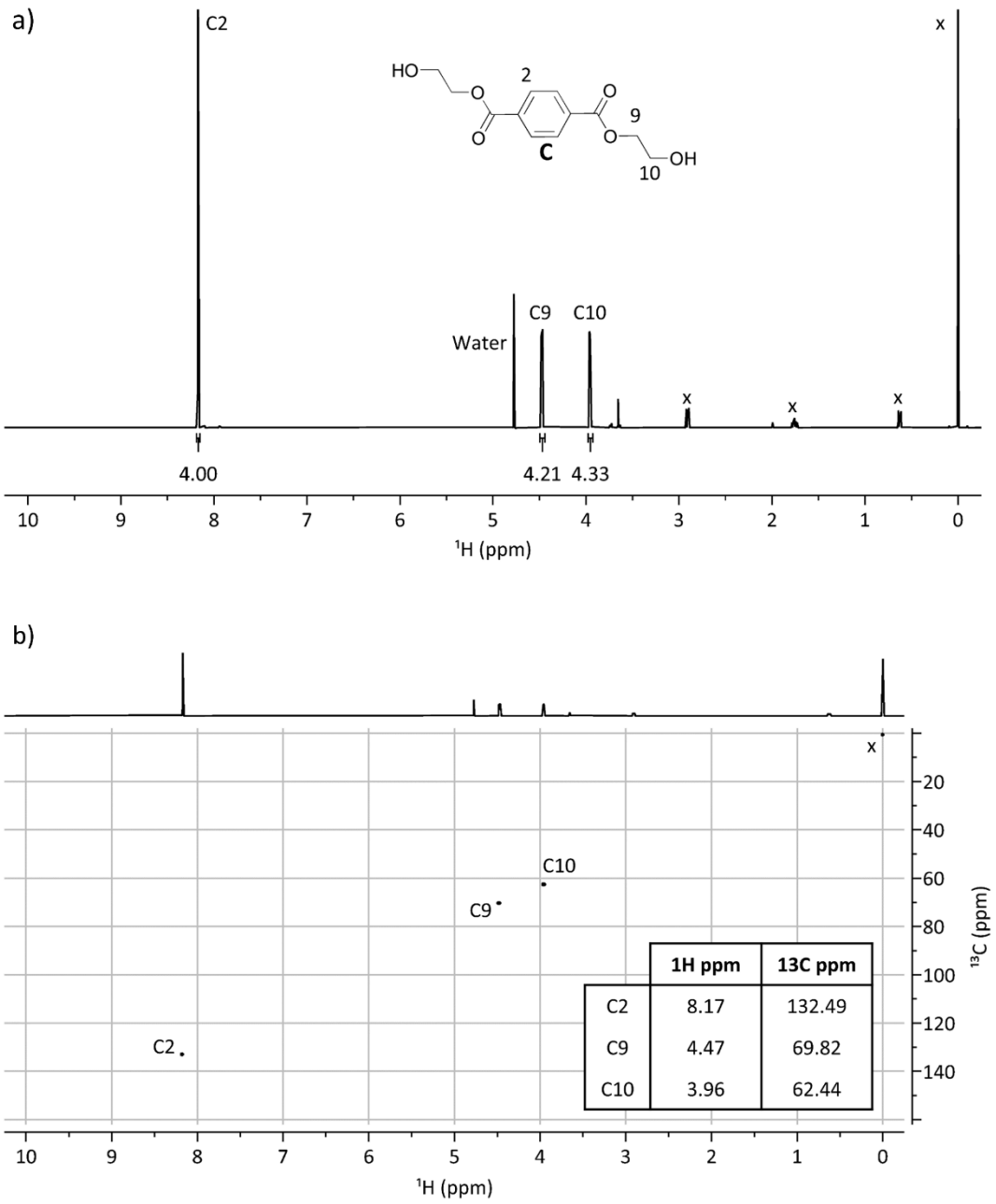


Figure S4. ^{1}H-NMR (a) and [^{1}H,^{13}C]-HSQC (b) of bis(2-hydroxyethyl) terephthalate (compound C) in D_2O. The methyl DSS signal is labelled ”x”. Non-assigned peaks in the ^{1}H-NMR correspond to contaminants present in the standard sample.

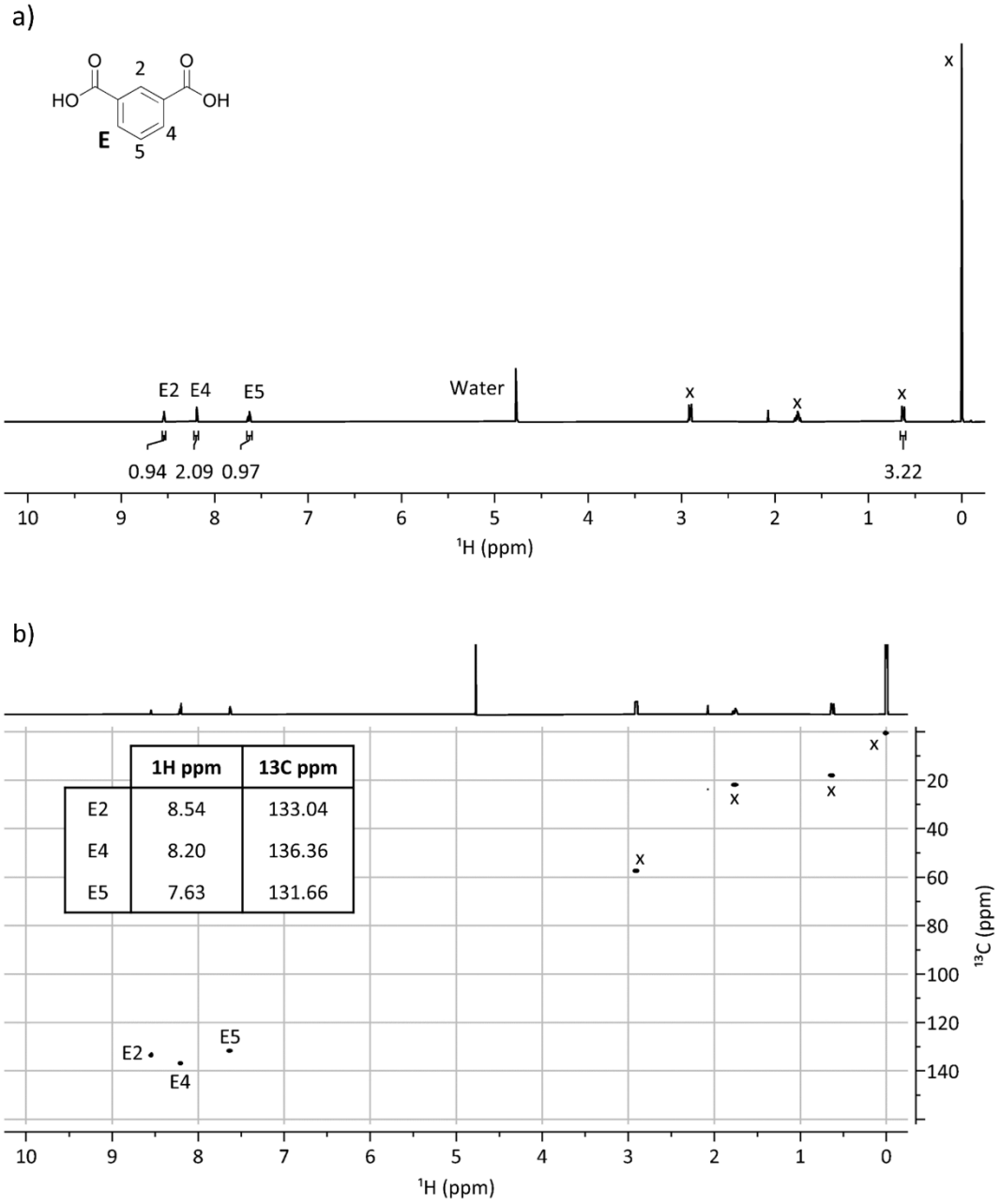


Figure S5. ^{1}H-NMR (a) and [^{1}H,^{13}C]-HSQC (b) of isophthalic acid (compound E) in D_2O. The DSS signals are labelled ”x”. Non-assigned peaks in the ^{1}H-NMR correspond to contaminants present in the standard sample.

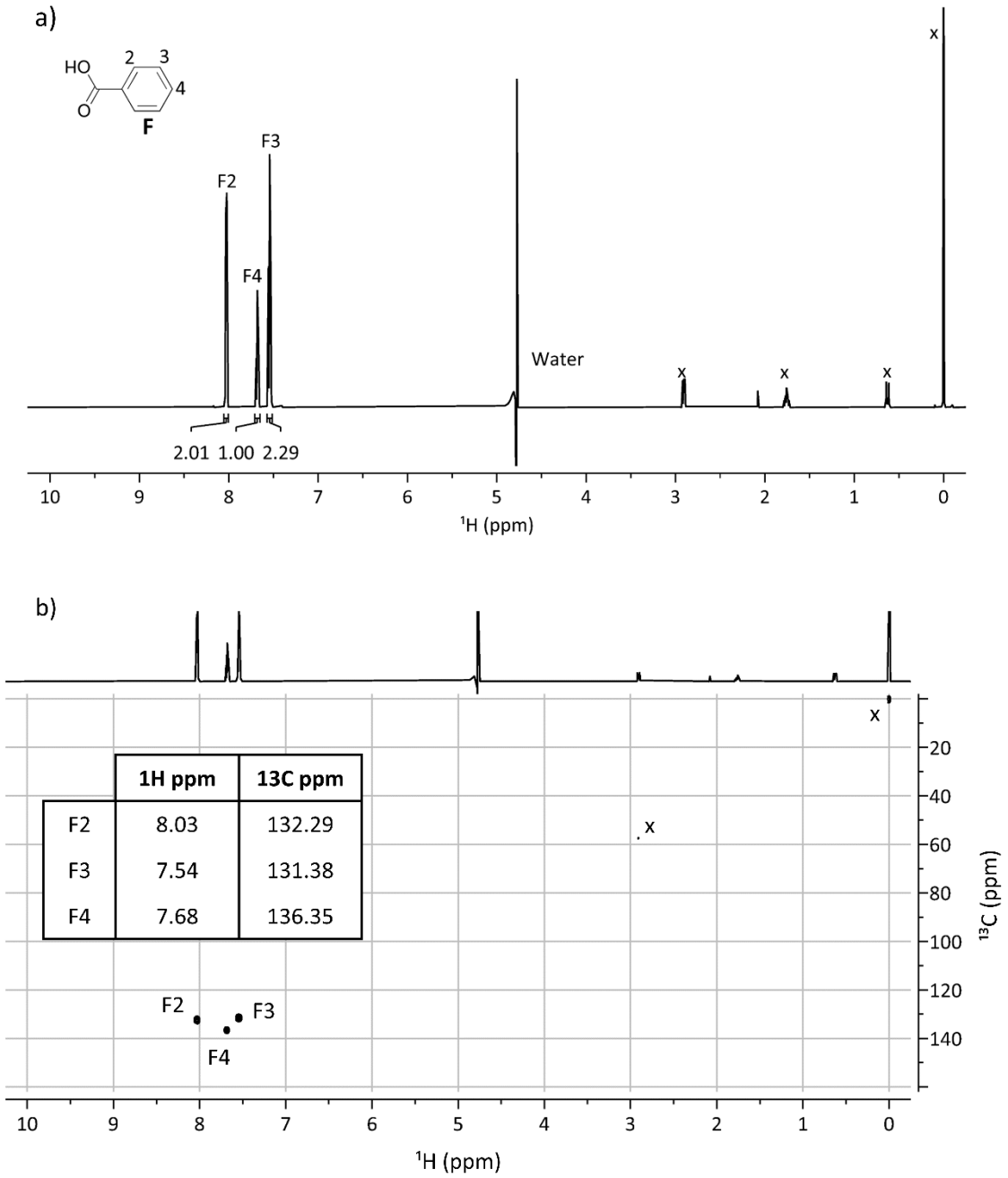


Figure S6. ^{1}H-NMR (a) and [^{1}H,^{13}C]-HSQC (b) of benzoic acid (compound F) in D_2O. The DSS signals are labelled "x". Non-assigned peaks in the ^{1}H-NMR correspond to contaminants present in the standard sample.

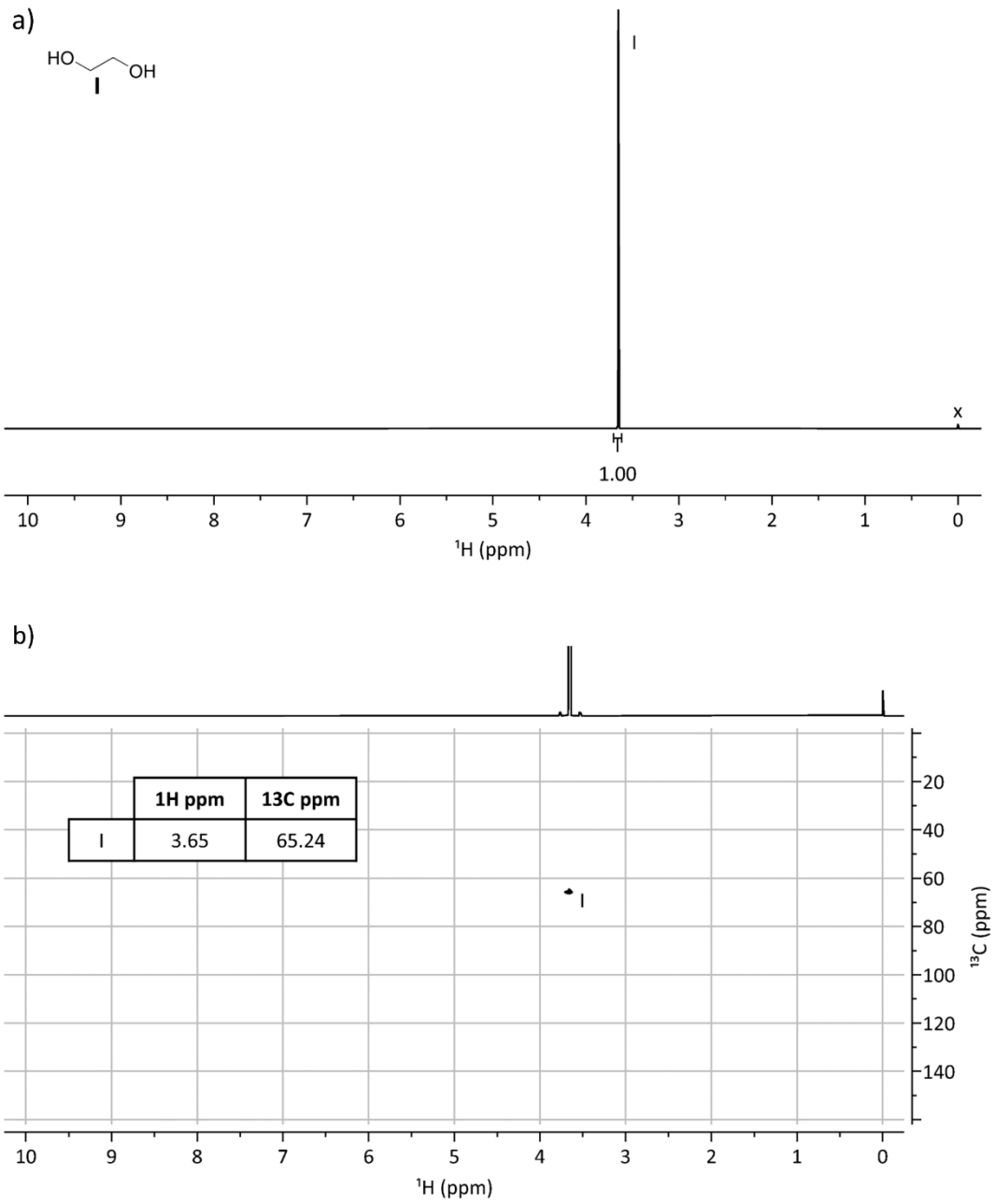


Figure S7. ^{1}H-NMR (a) and [^{1}H,^{13}C]-HSQC (b) of ethylene glycol (compound I) in D_2O. The DSS methyl signal is labelled ”x”.

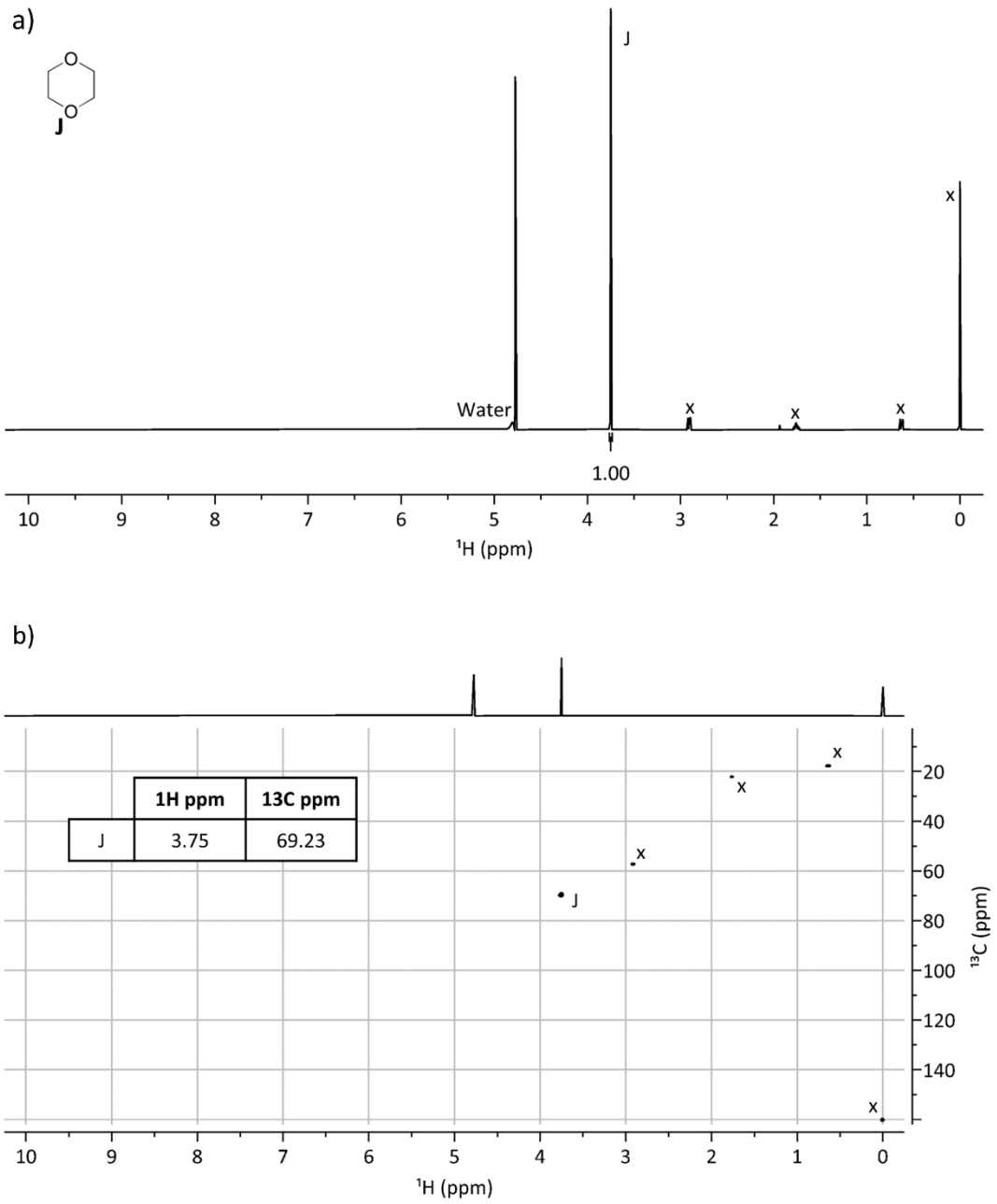
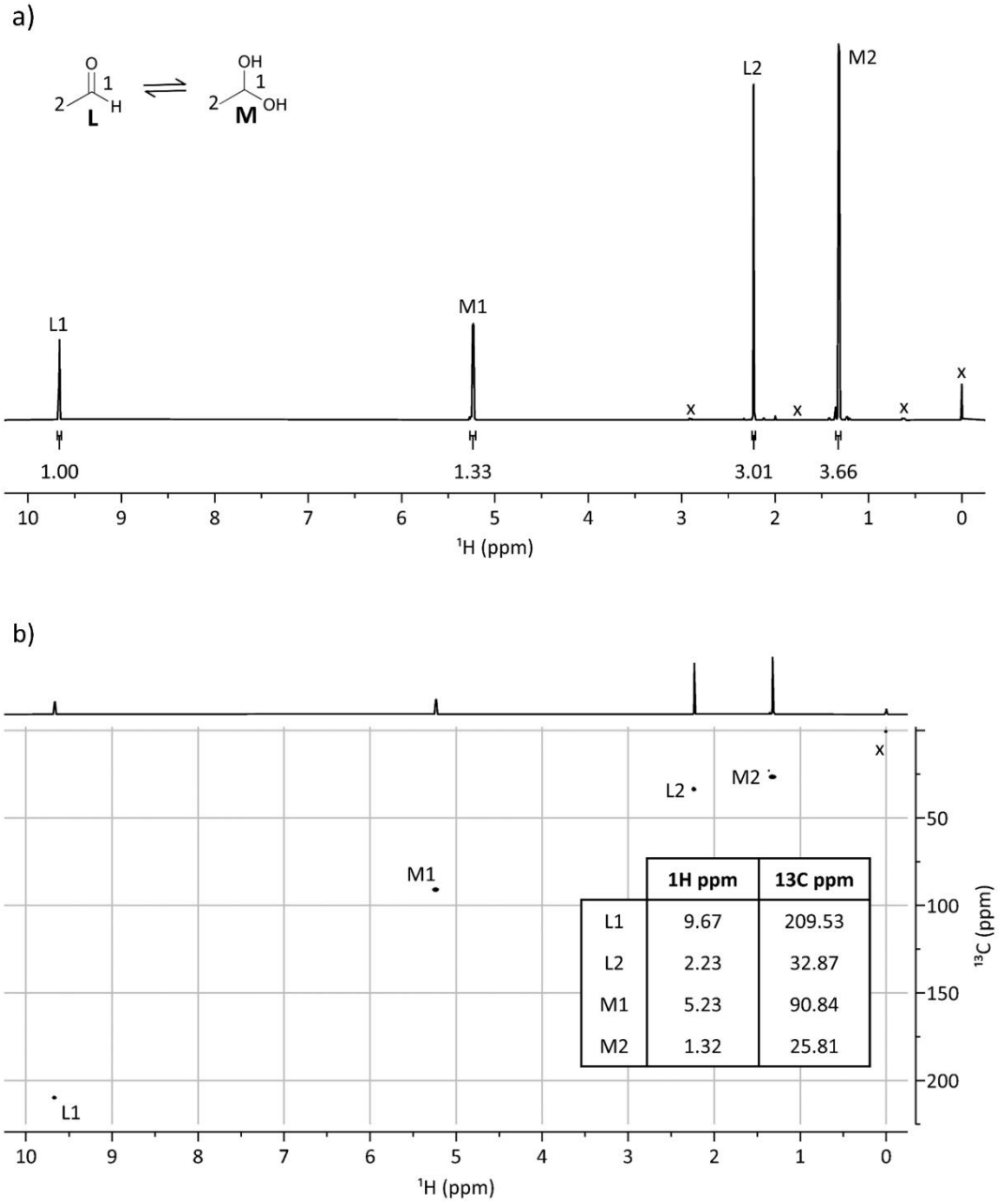


Figure S8. ^{1}H-NMR (a) and [^{1}H,^{13}C]-HSQC (b) of dioxane (compound J) in D_2O. The DSS signals are labelled ”x”. In the ^{13}C-dimension of the HSQC, the methyl DSS signal appears at 150 ppm due to folding. Non-assigned peaks in the ^{1}H-NMR correspond to contaminants present in the standard sample.



	1H ppm	13C ppm
L1	9.67	209.53
L2	2.23	32.87
M1	5.23	90.84
M2	1.32	25.81

Figure S9. ^{1}H-NMR (a) and [^{1}H,^{13}C]-HSQC (b) of acetaldehyde (compound L) and acetaldehyde hydrate (compound M) in D_2O. The DSS signals are labelled "x".

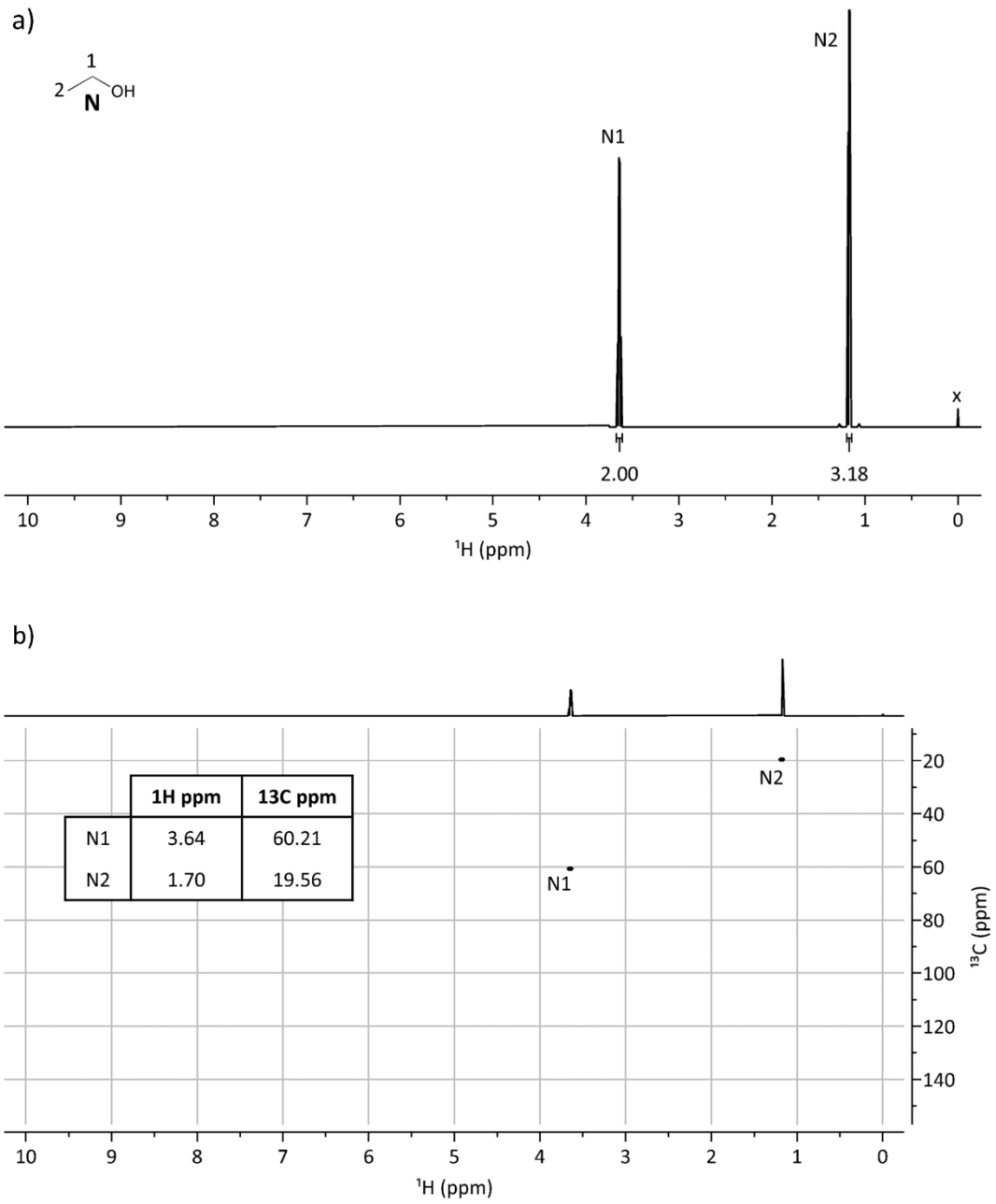


Figure S10. ^{1}H-NMR (a) and [^{1}H,^{13}C]-HSQC (b) of ethanol (compound N) in D_2O. The DSS methyl signal is labelled ”x”.

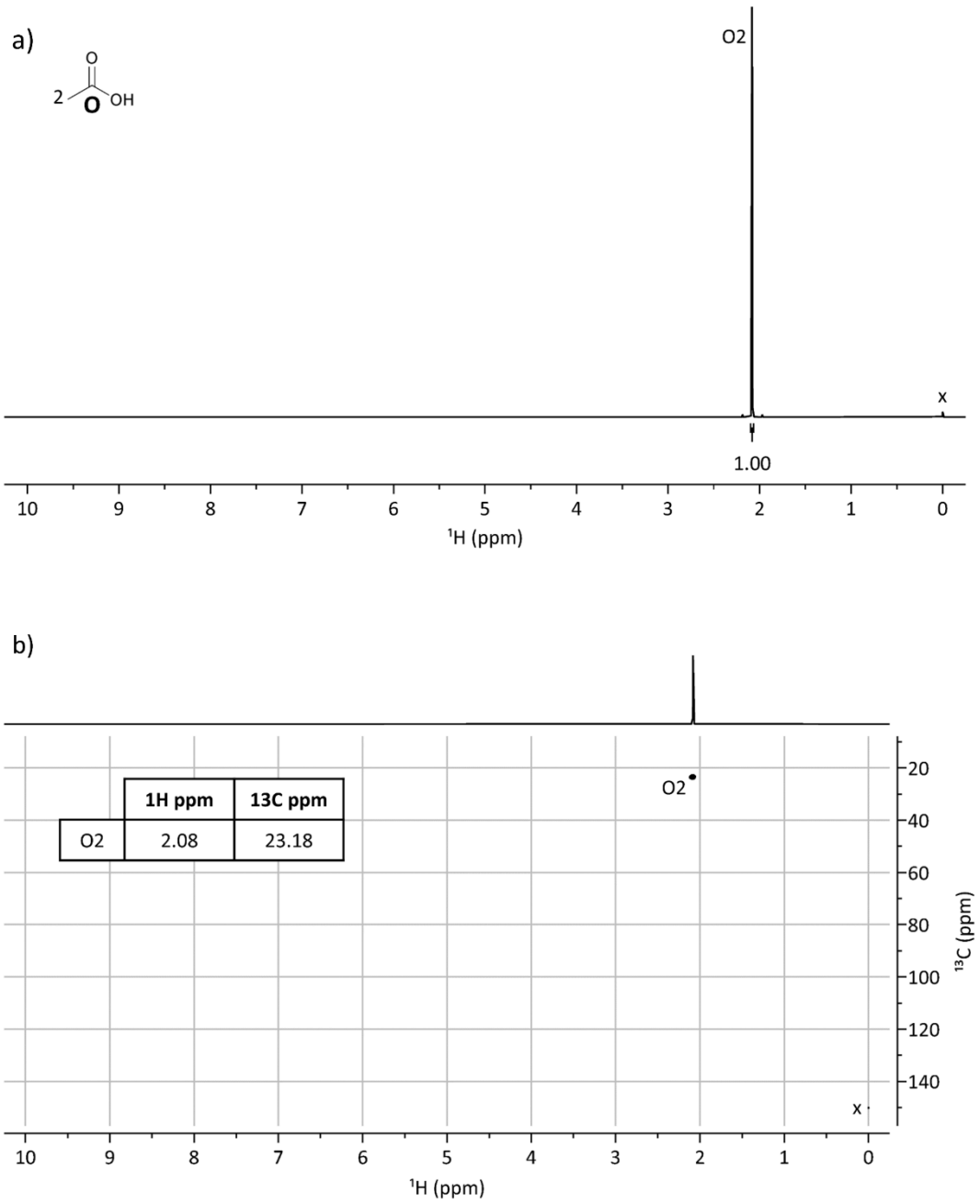


Figure S11. ^{1}H-NMR (a) and [^{1}H,^{13}C]-HSQC (b) of acetic acid (compound O) in D_2O. The methyl DSS signal is labelled ”x”. In the ^{13}C-dimension of the HSQC, the methyl DSS signal appears at 150 ppm due to folding.

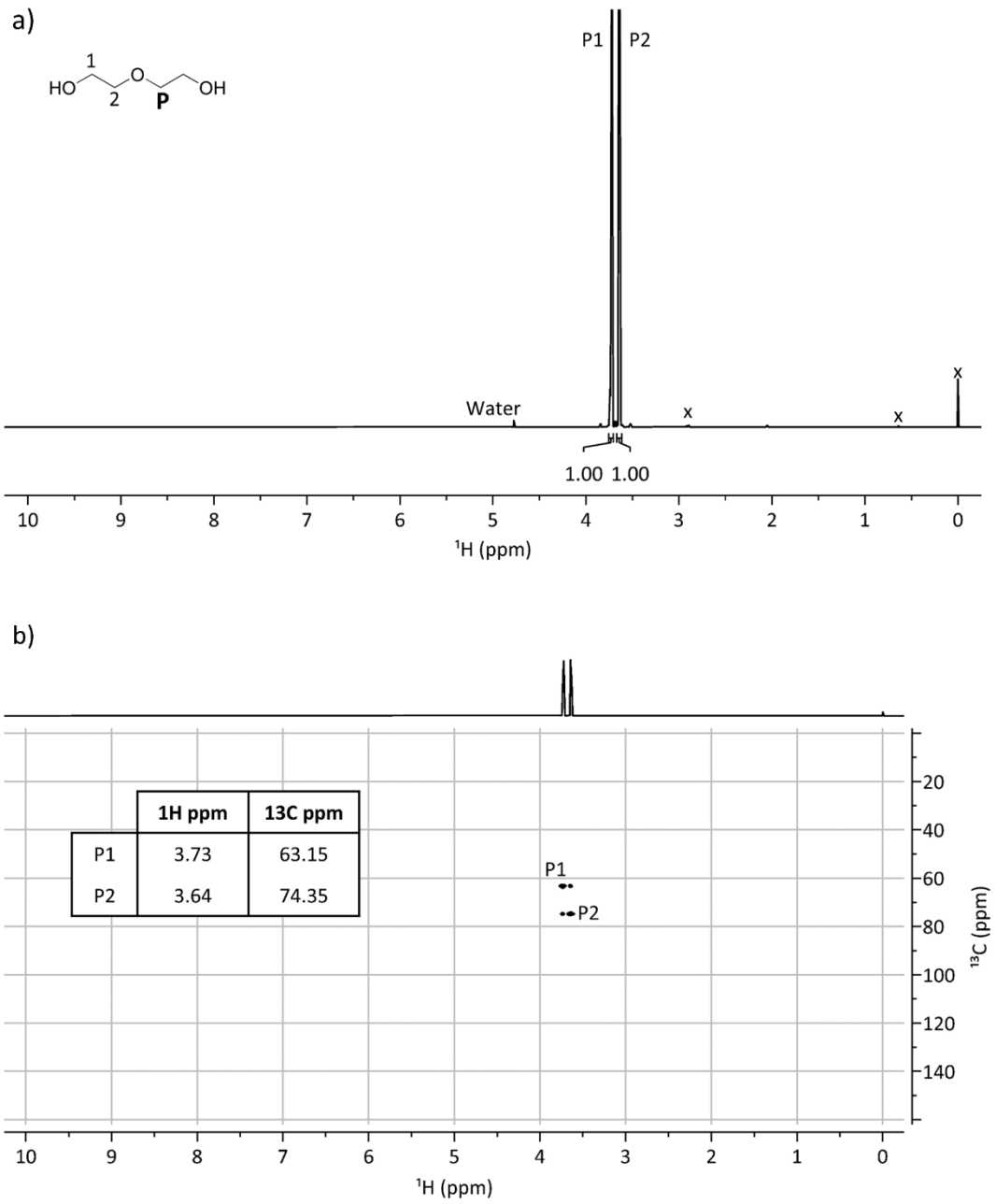
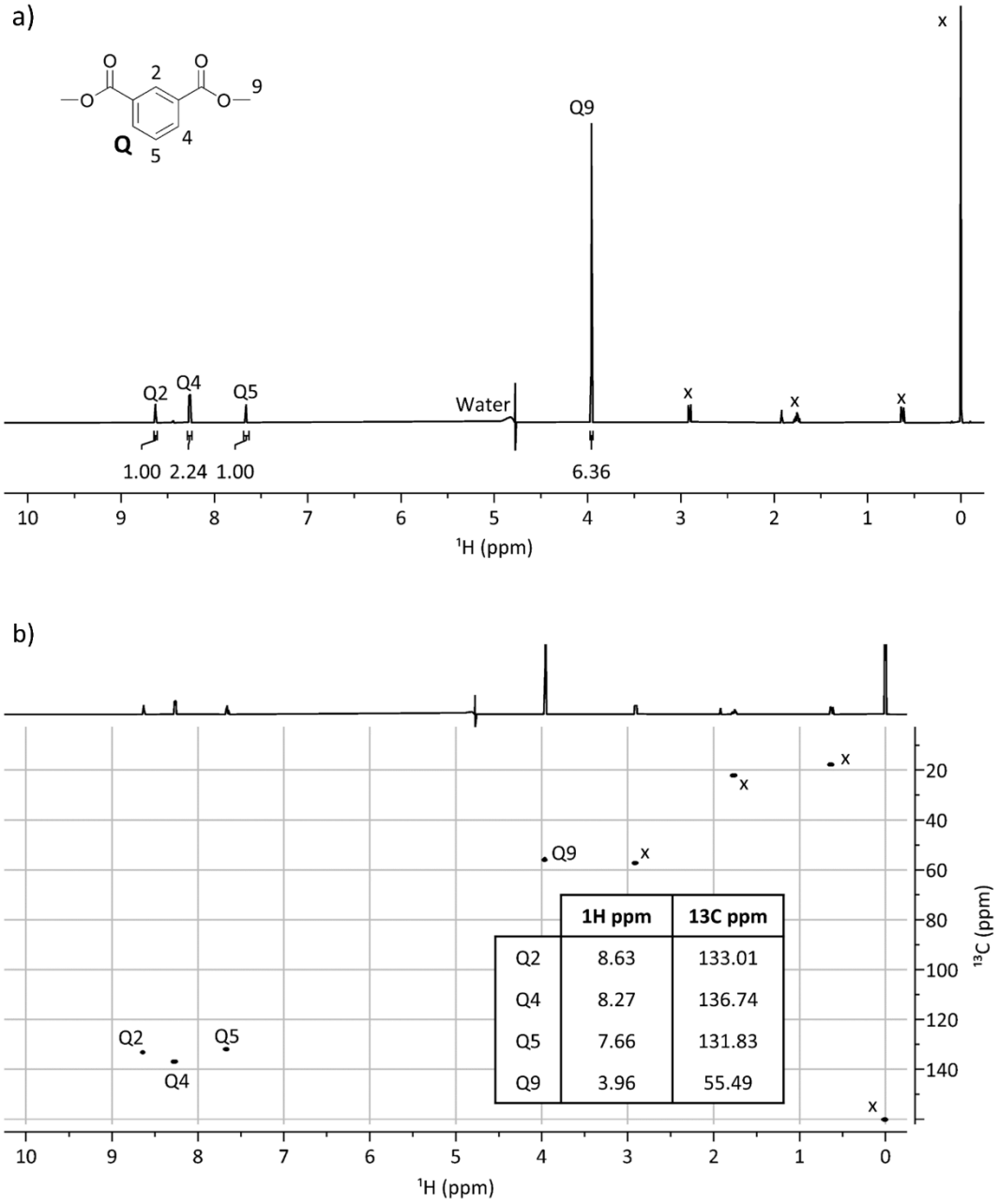


Figure S12. ^{1}H-NMR (a) and [^{1}H,^{13}C]-HSQC (b) of diethylene glycol (compound P) in D_2O. The DSS signals are labelled ”x”. Non-assigned peaks in the ^{1}H-NMR correspond to contaminants present in the standard sample.



	1H ppm	13C ppm
Q2	8.63	133.01
Q4	8.27	136.74
Q5	7.66	131.83
Q9	3.96	55.49

Figure S13. ^{1}H-NMR (a) and [^{1}H,^{13}C]-HSQC (b) of dimethyl isophthalate (compound Q) in D_2O. The DSS signals are labelled ”x”. In the ^{13}C-dimension of the HSQC, the methyl DSS signal appears at 150 ppm due to folding. Non-assigned peaks in the ^{1}H-NMR correspond to contaminants present in the standard sample.

6.- ^{1}H and HSQC of standards in DMSO

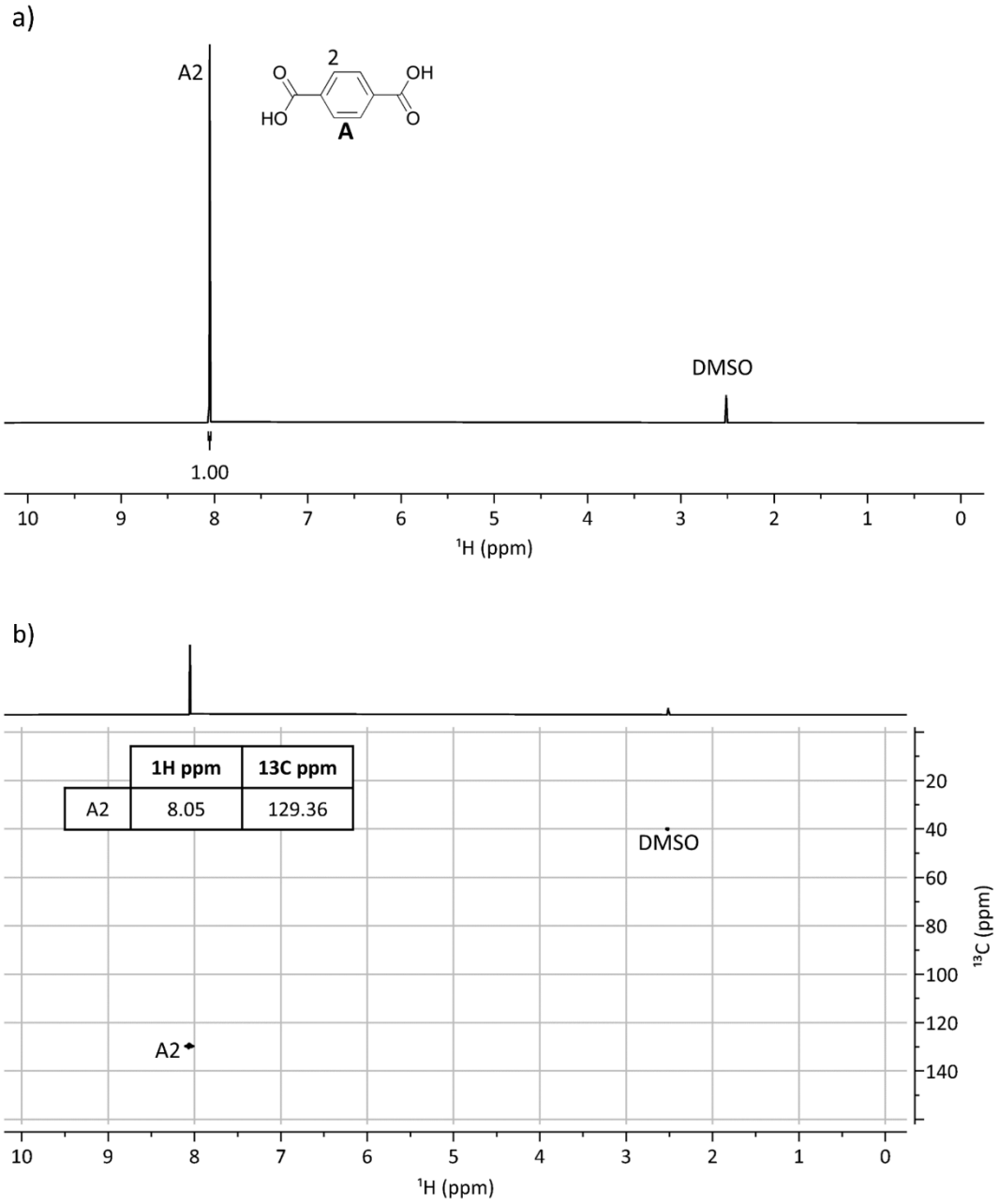


Figure S14. ^{1}H-NMR (a) and [^{1}H,^{13}C]-HSQC (b) of terephthalic acid (compound A) in DMSO-d6.

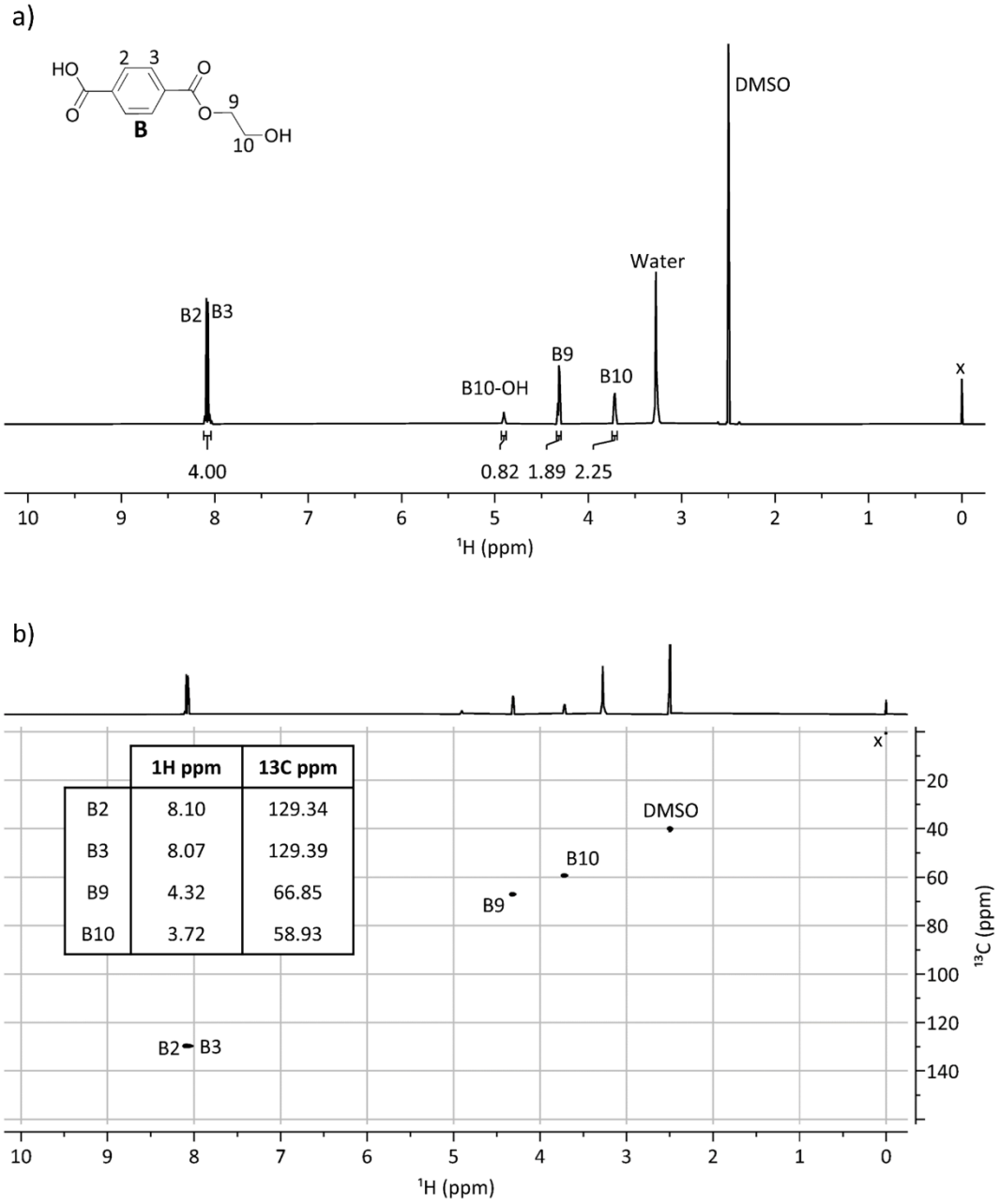


Figure S15. ^{1}H-NMR (a) and [^{1}H,^{13}C]-HSQC (b) of mono(2-hydroxyethyl) terephthalate (compound B) in DMSO-d6. The TMS signal is labelled ”x”.

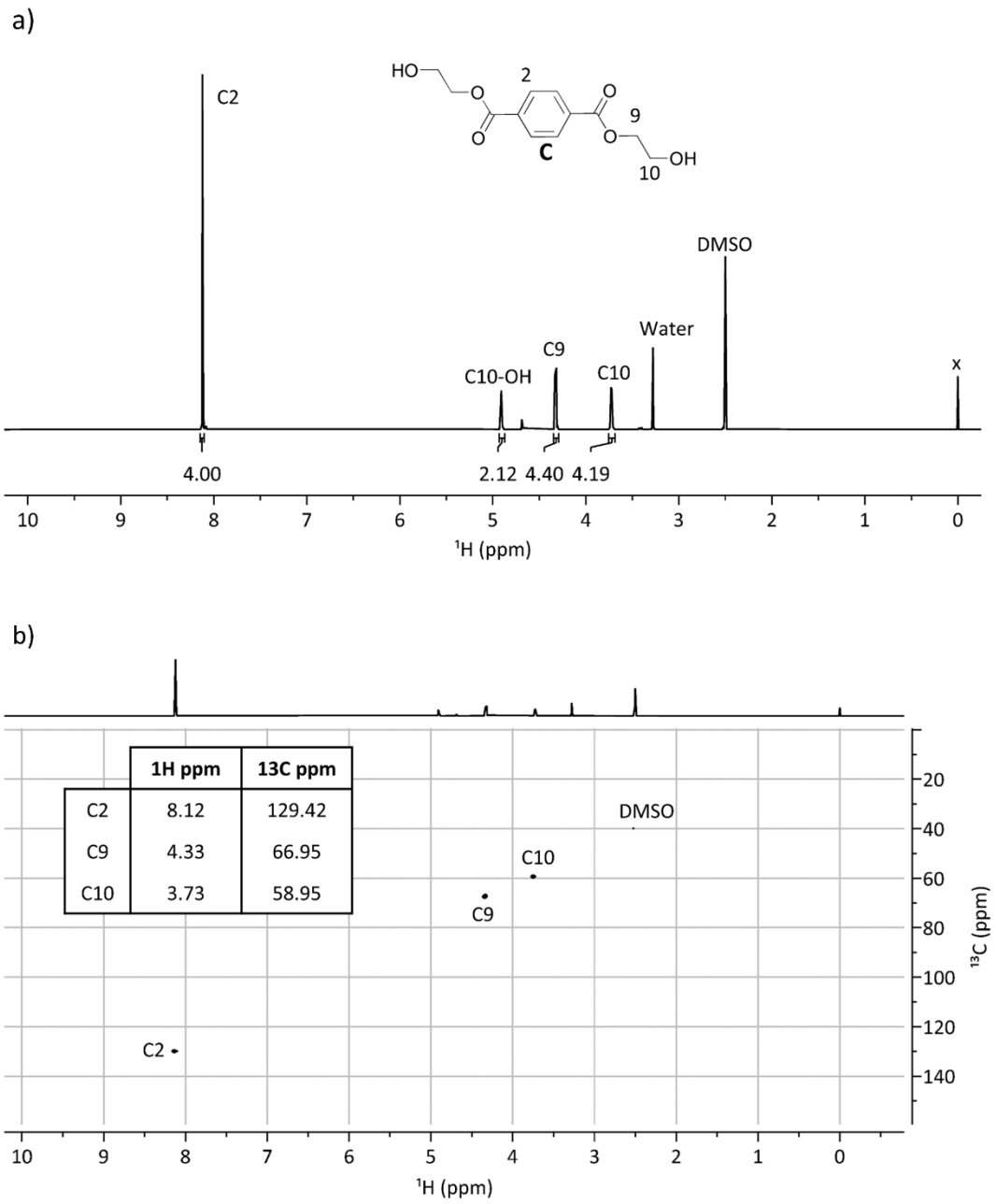


Figure S16. ^{1}H-NMR (a) and [^{1}H,^{13}C]-HSQC (b) of bis(2-hydroxyethyl) terephthalate (compound C) in DMSO-d6. The TMS signal is labelled ”x”. Non-assigned peaks in the ^{1}H-NMR correspond to contaminants present in the standard sample.

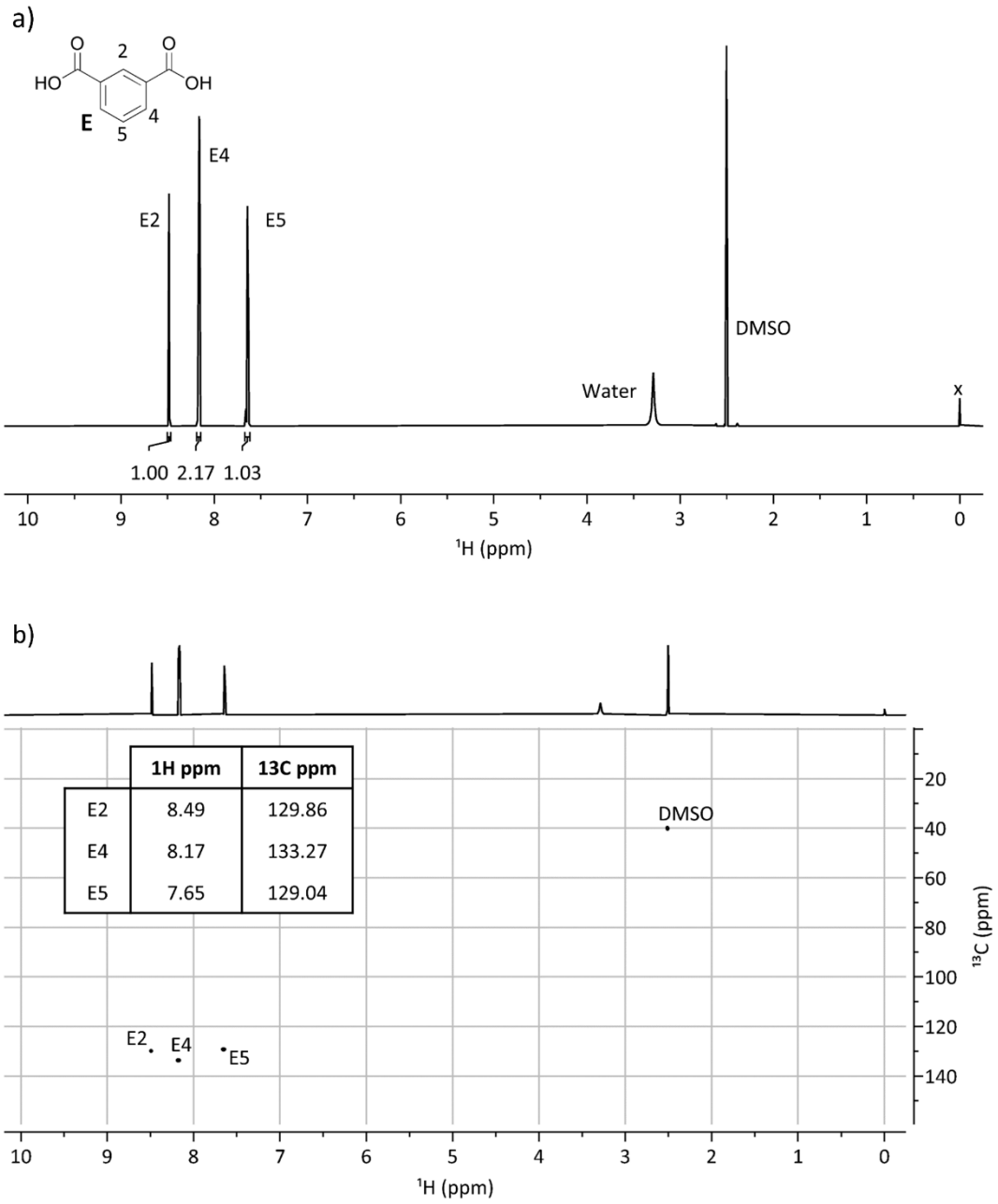


Figure S17. ^{1}H-NMR (a) and [^{1}H,^{13}C]-HSQC (b) of isophthalic acid (compound E) in DMSO-d6. The TMS signal is labelled ”x”.

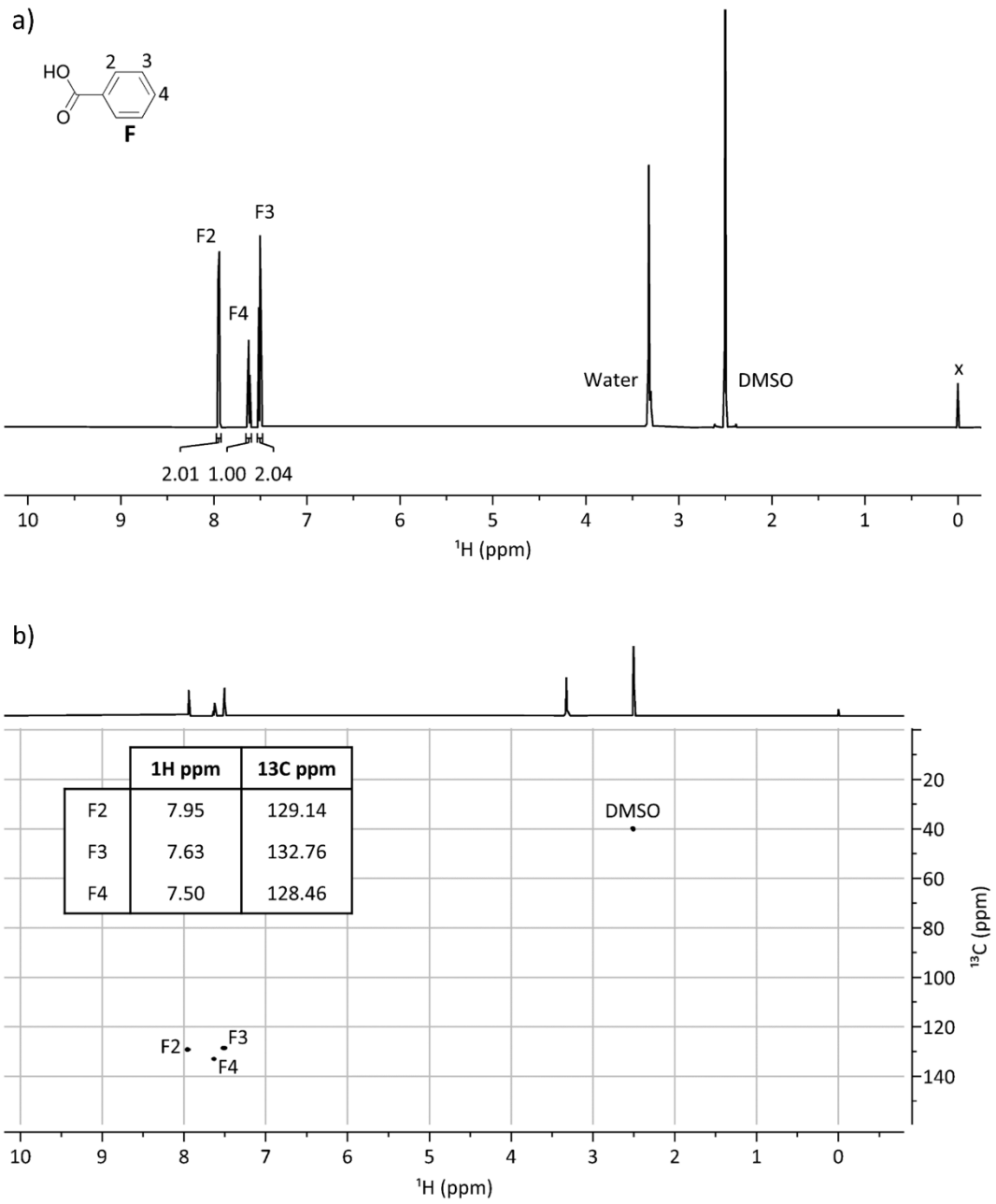


Figure S18. ^{1}H-NMR (a) and [^{1}H,^{13}C]-HSQC (b) of benzoic acid (compound F) in DMSO-d6. The TMS signal is labelled ”x”.

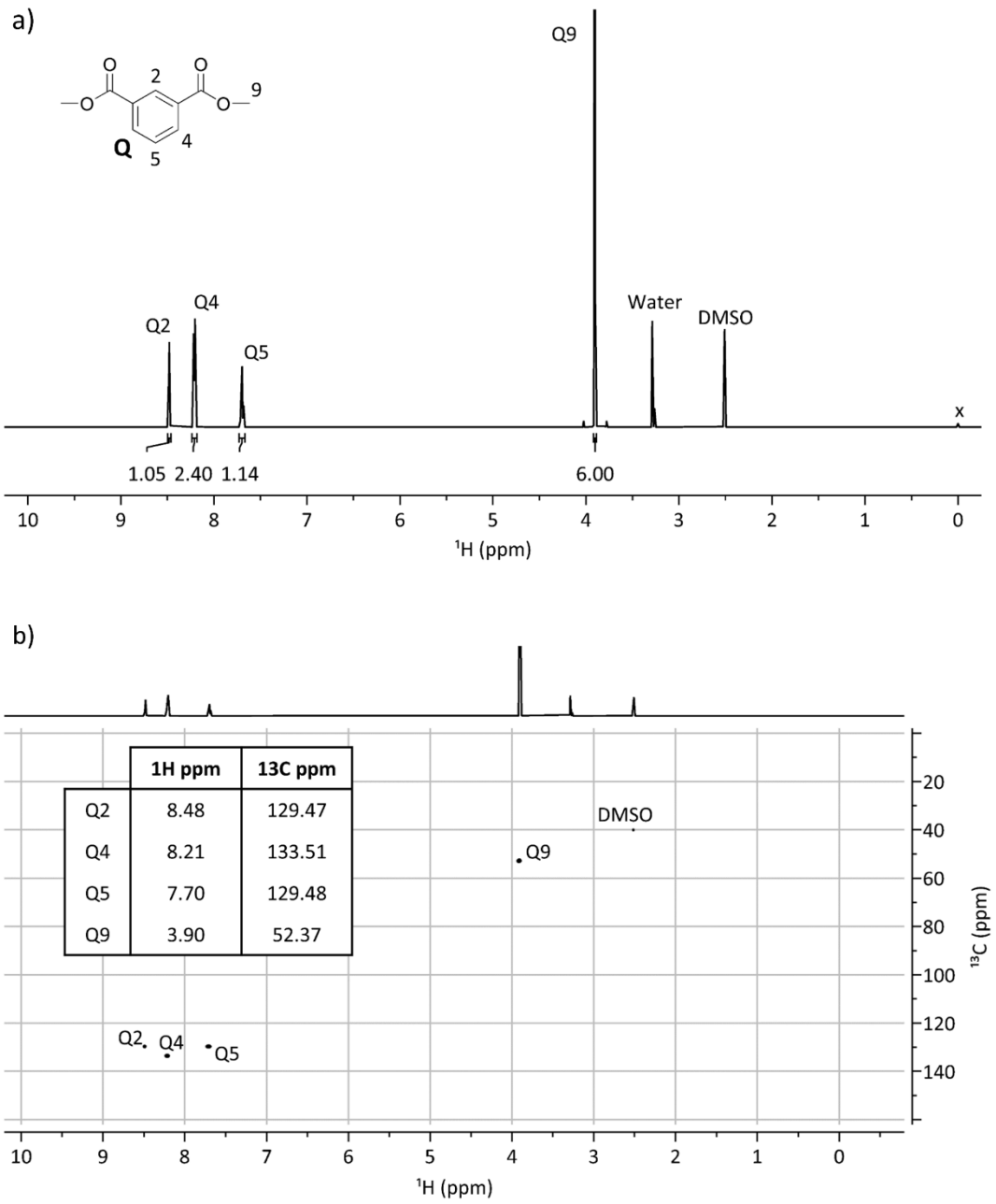


Figure S19. ^{1}H-NMR (a) and [^{1}H,^{13}C]-HSQC (b) of dimethyl isophthalate (compound Q) in DMSO-d6. The TMS signal is labelled ”x”.

7.- Identification of bis(2-(2-hydroxyethoxy)ethyl) terephthalate and other esters.

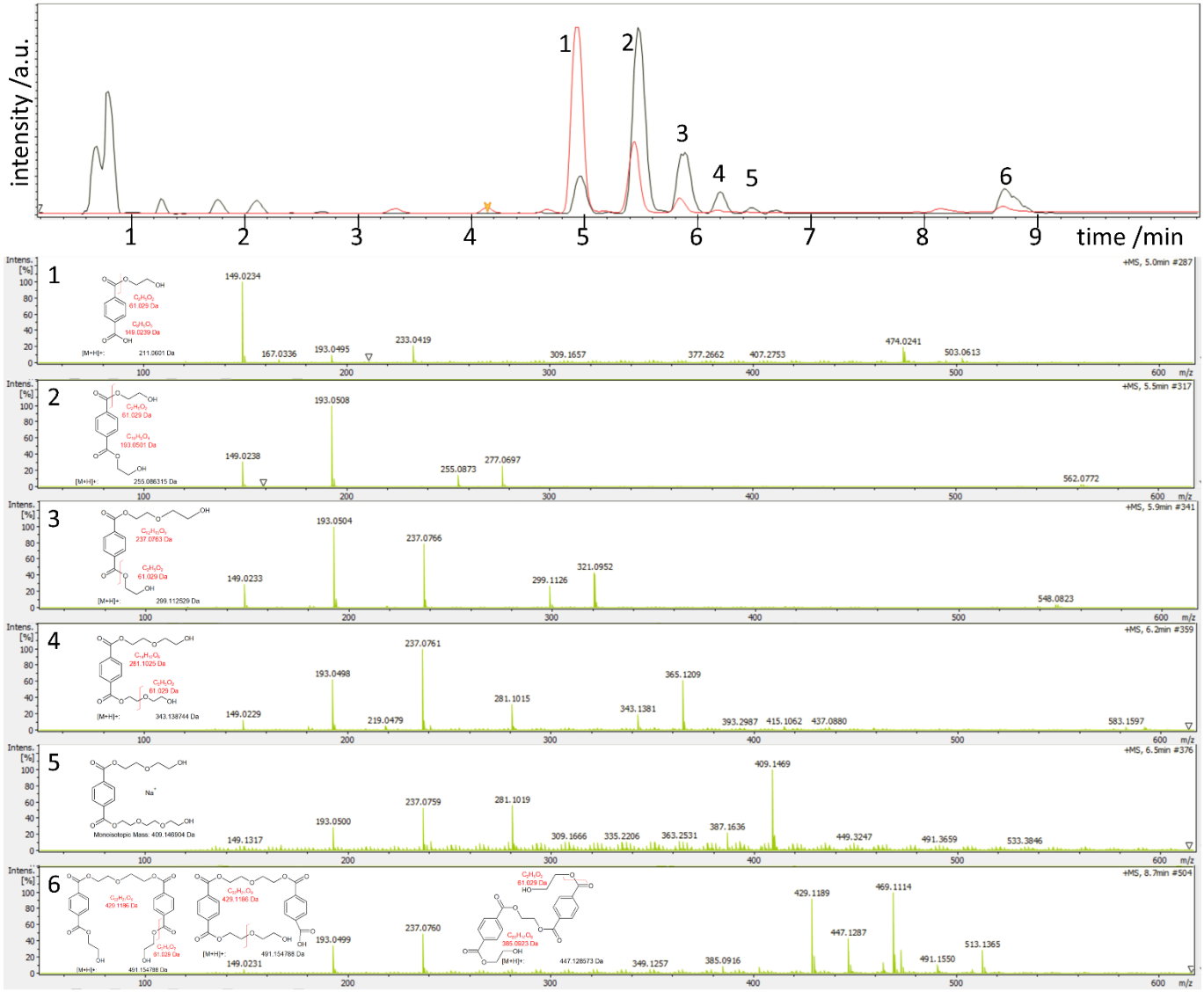


Figure S20. HPLC-UV/MS chromatogram of reaction product (aqueous phase) after hydrolysis at 340 °C for 10 min (reactor 1). Red: UV-chromatogram at 243 nm, black: base peak chromatogram (MS, positive mode). The mass spectra at the six indicated peaks are shown below with possible structures to fit the observed masses. Peak no. 1 corresponds to MHET, peak no. 2 corresponds to BHET. Peak no. 3 contains a mixed ester of TPA with ethylene glycol and diethylene glycol. Peak no. 5 features a mass that can only be explained by a triethylene glycol ester, something that we did not observe elsewhere in this study. Peak no. 6 contains several compounds: the peaks at 447.1287 and 469.1114 m/z corresponds to a molecule containing two PA and three EG subunits, the peaks at 429.1189, 491.155 and 513.1365 belong to a molecule consisting of two PA and four EG subunits. Possible structures are shown.

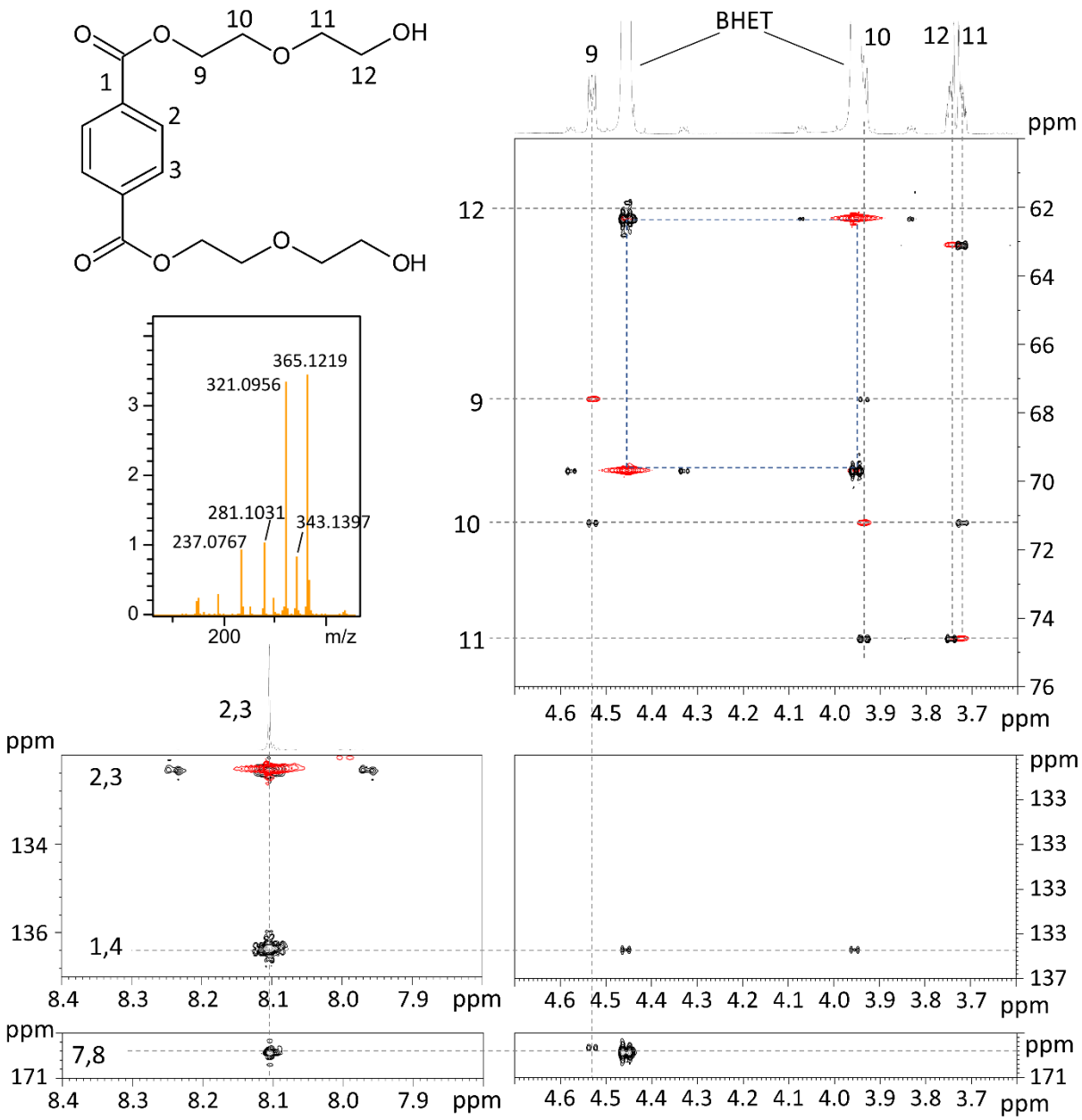


Figure S21. HR-MS, [^{1}H,^{13}C]-HMBC (black) and [^{1}H,^{13}C]-HSQC (red) fingerprint of bis(2-(2-hydroxyethoxy)ethyl) terephthalate ([M+H]$^{+}$=343.138744, [M+Na]$^{+}$=365.120689) in H_2O/D_2O (90/10 v/v). There is a large amount of BHET present in the sample.

8.- 2D NMR identification of PET depolymerization products in the aqueous phase mixture

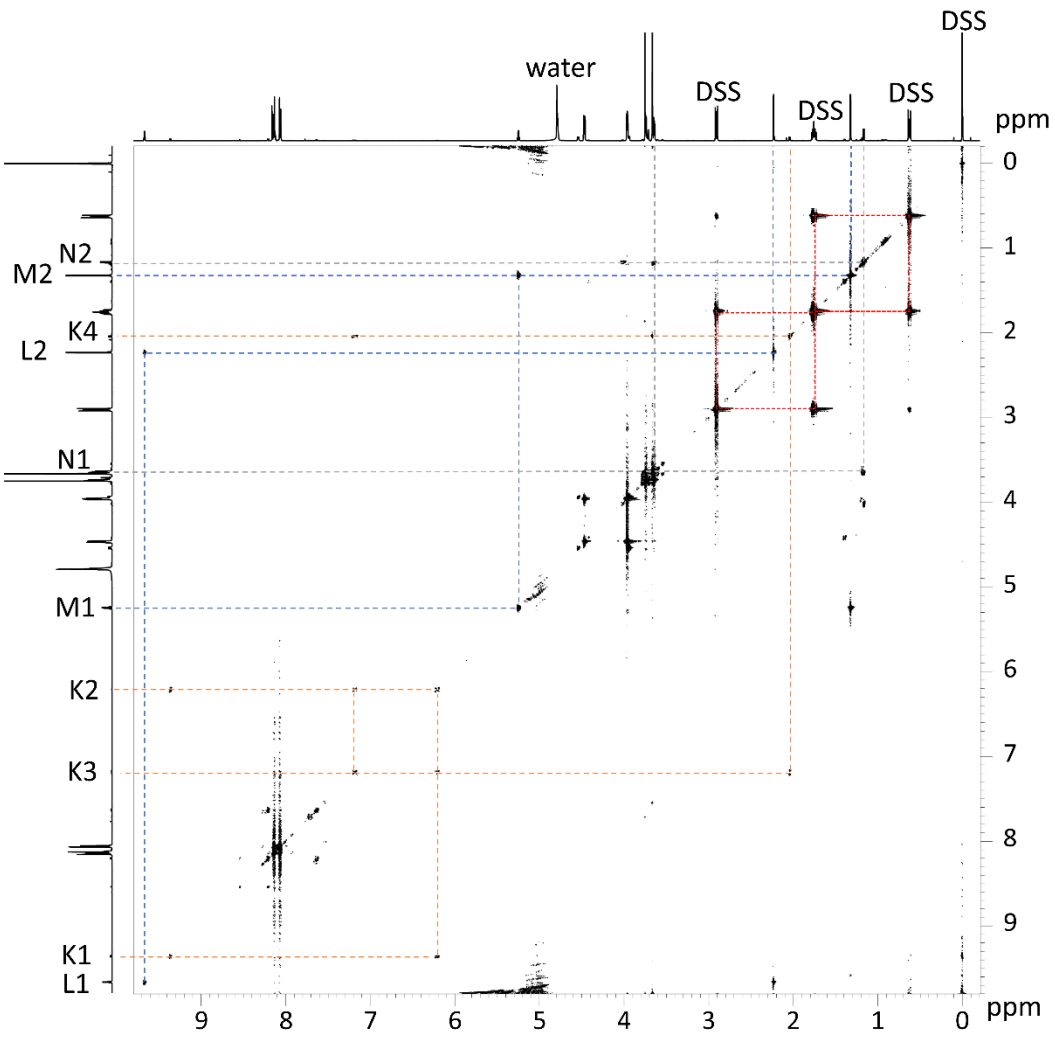


Figure S22. Aqueous phase after PET depolymerization at 310C for 45 min. DQF-COSY spectrum showing correlations of acetaldehyde (L), crotonaldehyde (K), acetaldehyde hydrate (M), ethanol (N) and DSS.

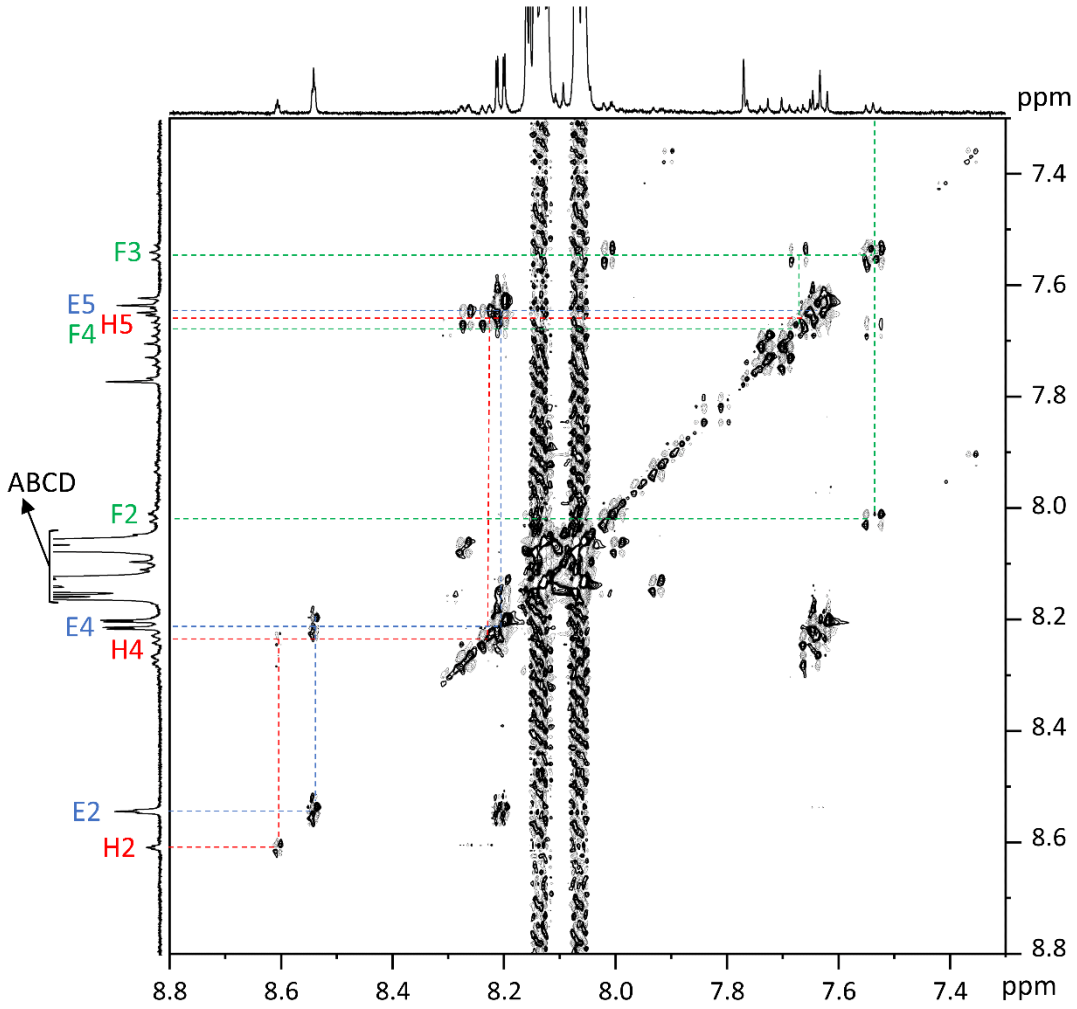


Figure S23. Aqueous phase after PET depolymerization at 310C for 45 min. Aromatic region of DQF-COSY spectrum showing correlations of IPA (E), MHEI (H) and benzoic acid (F).

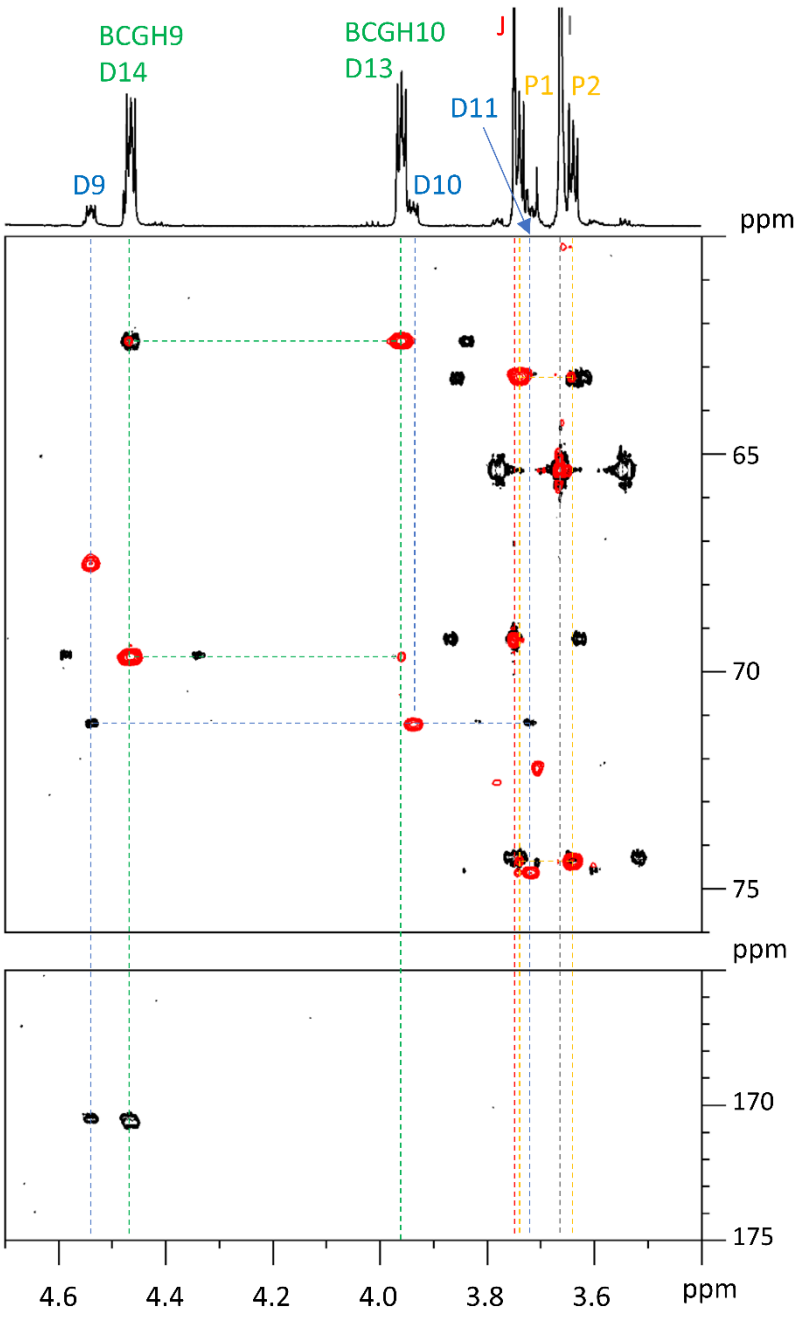


Figure S24. Aqueous phase after PET depolymerization at 310C for 45 min. Aliphatic regions of [^{1}H,^{13}C]-HMBC (black) and [^{1}H,^{13}C]-HSQC (red) showing signals of ethylene glycol (I), diethylene glycol (P), and their terephthalate (B,C,D) and isophthalate (G,H) esters.

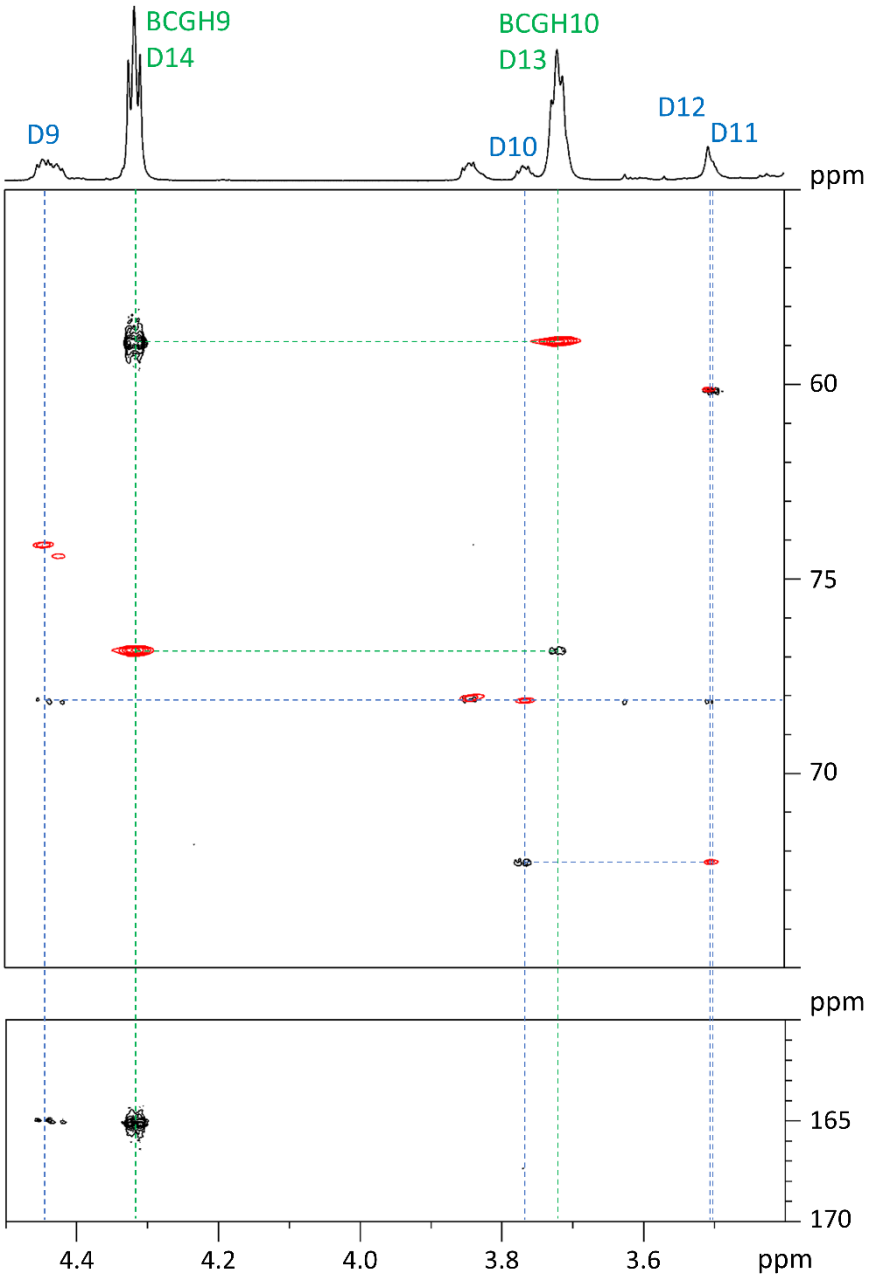


Figure S25. Solid phase after PET depolymerization at 310C for 20 min dissolved in DMSO-d_6. Aliphatic regions of [^{1}H,^{13}C]-HMBC (black) and [^{1}H,^{13}C]-HSQC (red) showing signals of ethylene glycol and diethylene glycol terephthalate (B,C,D) and isophthalate (G,H) esters.