Supporting Info for

Synthesis, Structure, Spectroscopy and Reactivity of New Heterotrinuclear Water Oxidation Catalysts

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Experimental Section

Preparations.

All reagents used in the present work were obtained from Aldrich Chemical Co. and were used without further purification. Solvents were purchased from SDS, and they were purified and dried either by passing them through an activated alumina purification system (M Braun SPS-800) or by conventional distillation techniques. Out-[Ru(μ-Cl)(bppy)(trpy)][PF$_6$], out-0, and Ru[bppy]$_2$[ClO$_4$]$_2$ were synthesized as reported in literature.¹

{(Ru$^{II}$(trpy))$_2$[μ-[Co$^{II}$(bpy)](PF$_6$)$_2$, Ru$_2$Co-Cl$_2$.

Out-[Ru(μ-Cl)(bppy)(trpy)][PF$_6$] (100 mg, 0.136 mmol) was placed in a 250 mL round-bottom flask and dissolved in 200 mL of methanol. A sample of NaOMe (8 mg, 0.142 mmol) was added and the solution stirred for 30 minutes. The reaction was then kept under 200 W light irradiation (tungsten lamp) overnight and after that 5 mL methanol/water (4:1) solution of CoCl$_2$ (25 mg, 0.190 mmol) and LiCl (57 mg, 1.344 mmol) were added. The reaction mixture was heated at 60 °C under 200 W tungsten lamp light for 5 h. It was then filtered and the volume was reduced to around 20 mL under reduced pressure. Saturated aqueous solution of KPF$_6$ (2 mL) was added, giving rise to a reddish-brown precipitate. The mixture was then cooled in an ice bath for 30 minutes and the solid filtered, washed with cold water (3 times) and then with diethyl ether (3 times), and finally dried under vacuum. Yield: 0.040 g (73.4%).

{(Ru$^{II}$(trpy))$_2$[μ-[Mn$^{II}$(Cl$_2$(bpy)](PF$_6$)$_2$, Ru$_2$Mn-Cl$_2$.

Out-[Ru(μ-Cl)(bppy)(trpy)][PF$_6$] (100 mg, 0.136 mmol) was placed in a 250 mL round-bottom flask and dissolved in 200 mL of methanol. A sample of NaOMe (15 mg, 0.278 mmol) was added and the solution stirred for 30 minutes. A solution of MnCl$_2$·4H$_2$O (27 mg, 0.136 mmol) and LiCl (57 mg, 1.344 mmol) in 5 mL of methanol/water (4:1) was added and the reaction mixture was heated at 60 °C for 4 hours. The solution was then filtered and the volume was reduced to around 20 mL under reduced pressure. Saturated aqueous solution of KPF$_6$ (2 mL) was added, giving rise to a reddish-brown precipitate. The reaction mixture was then cooled in an ice bath for 30 minutes and the solid filtered on a frit, washed with cold water (3 times) and then with diethyl ether (3 times), and finally dried under vacuum. Yield: 0.120 g (70.2%).

General Synthetic Procedure for Ru$_2$Co-OC$_2$ and Ru$_2$Mn-OC$_2$.

A sample of Ru$_2$Co-Cl$_2$ (50 mg, 0.033 mmol) or Ru$_2$Mn-Cl$_2$ (50 mg, 0.033 mmol), respectively, and NaOMe (0.030 g 0.365 mmol) was dissolved in 15 mL of an acetone/water (5:1) mixture and heated at 75°C for 3 h. After cooling at room temperature the resulting solution was filtered and few drops of saturated aqueous solution of KPF$_6$ were added. Upon reduction of the volume, a solid came out from the solution that was filtered and washed with cold water (3 times) and then with diethyl ether and finally dried under vacuum. The yields and characterizations of the complexes are given below:

{(Ru$^{II}$(trpy))$_2$[μ-[Co$^{II}$(Ac$_2$(bpy)](PF$_6$)$_2$, Ru$_2$Co-OC$_2$.

Yield: 0.040 g (73.4%). Anal. Calcd for C$_{68}$H$_{42}$Co$_2$Ni$_2$O$_2$P$_2$Ru$_2$: C 46.57, H 2.94, N 12.43. Found: C 46.52, H 2.92, N 12.56. ESI-MS (in MeOH): 1434.1 ([M-PF$_6$]$: 644.5 ([M-2PF$_6$]$^+$. UV-vis $\lambda_{max}$ nm (ε, M$^{-1}$ cm$^{-1}$): (in CH$_3$CN) 540 (sh) (12697), 506 (15307), 412 (16614), 368 (26614), 314 (82077), 276 (75931), 234 (67057); (in CH$_3$Cl)$_2$ 540 (sh) (13587), 506 (16103), 412 (17771), 368 (27267), 314 (181785), 276 (75910), 236 (68229). IR (KBr, cm$^{-1}$, selected bands): 1604, 1568 (v$_{asym}$(O$_2$CMe)); 1447, 1437, 1416 (v$_{sym}$(O$_2$CMe)); 843 (v(PF$_6$)).

{(Ru$^{II}$(trpy))$_2$[μ-[Mn$^{II}$(Ac$_2$(bpy)](PF$_6$)$_2$, Ru$_2$Mn-OC$_2$.

Yield: 0.040 g (73.6%). Anal. Calcd for C$_{68}$H$_{42}$Mn$_2$Ni$_2$O$_2$P$_2$Ru$_2$: C 45.78, H 2.95, N 12.46. Found: C 45.90, H 2.99, N 12.51. ESI-MS (in MeOH): 1430.1 ([M-PF$_6$]$: 642.5 ([M-2PF$_6$]$^+$. UV-vis $\lambda_{max}$ nm (ε, M$^{-1}$ cm$^{-1}$): (in CH$_3$CN) 538 (sh) (12815), 504 (15384), 410 (sh) (17070), 365 (26520), 318 (71463), 306 (71388), 278 (68937), 234 (62473); (in CH$_3$Cl)$_2$ 538 (sh) (13620), 504 (16069), 410 (sh) (17862), 365 (27603), 318 (71381), 306 (72999), 278 (70850), 234 (64346). IR (KBr, cm$^{-1}$, selected bands): 1601, 1568 (v$_{asym}$(O$_2$CMe)); 1446, 1436, 1421 (v$_{sym}$(O$_2$CMe)); 843 (v(PF$_6$)).
Instrument and measurements.

Physical methods.

Elemental analysis were performed using a CHNS-O EA-1108 elemental analyser from Fisons. IR spectra of solid samples were taken in Bruker Vector 22 FT-IR spectrophotometer (in KBr, 4000–500 cm$^{-1}$). UV-vis spectra were recorded either in Agilent 8453 diode-array spectrophotometer or Cary 50 scan spectrometer (experimental errors on the measurement for extinction coefficients are less than 1%). This is now indicated in the experimental section. The cell path length was 1 mm. MS analyses were recorded on an esquire 6000 ESI ion trap LC/MS (Bruker Daltonics) equipped with an electrospray ion source and MALDI were recorded in Bruker Autoflex.

Electrochemistry.

The electrochemical measurements were run under an argon atmosphere at room temperature. When CH$_3$CN was used as solvent, the electrochemical measurements were performed in a dry-glove box. Cyclic voltammetry experiments were performed using an EG&G model 173 potentiostat/galvanostat equipped with a PAR model universal programmer and a PAR model 179 digital coulometer. A standard three-electrode electrochemical cell was used. Potentials were measured with an Ag/0.01 M AgNO$_3$ reference electrode in a solution 0.1 M ([nBu$_4$N]ClO$_4$) in CH$_3$CN, or with an aqueous Saturated Calomel Electrode (SCE) reference electrode in a pH = 7.0 phosphate buffer solution and CF$_3$CH$_2$OH mixture (19:1). Potentials referred to Ag/AgNO$_3$ system can be converted to the normal hydrogen electrode (NHE) by adding 548 mV. Potentials referred to SCE system can be converted to NHE electrode by adding 205 mV. The working electrodes, polished with 2 µm diamond paste (Mecaprex Presi), were a platinum disk (5 mm in diameter) or a carbon vitreous disk (3 mm in diameter) for cyclic voltammetry. For rotating disk electrode (RDE) experiments, a carbon disk (2 mm in diameter) was used. The auxiliary electrode was a Pt wire. All the potentials are reported against NHE, unless otherwise indicated.

For experiments performed in glove box, progress of electrolysis was followed by the change in UV-Vis spectra with a MCS 501 UV-NIR (Carl Zeiss) spectrophotometer equipped with an automatic shutter. The light sources are halogen (CLH 500 20 W) and deuterium lamps (CLD 500) with optic fibers (041.002–UV SN 012105). For experiments performed in water, UV-visible spectra were recorded on a Variant Cary 300. The cell path length was 1 mm.

EPR spectroscopy.

X-band EPR spectra were recorded with a Bruker EMX, equipped with the ER-4192 ST Bruker cavity. The simulations were performed using the Bruker X-Sophe software (version 1.1.4.).

Magnetic susceptibility.

The variable-temperature magnetic susceptibility data of crystalline samples of Ru$_2$Mn-Cl$_2$, Ru$_2$Mn-OAc$_2$, Ru$_2$Co-Cl$_2$ and Ru$_2$Co-OAc$_2$ were collected with Quantum Design MPMS5 SQUID magnetometer at the Centres Científics i Tecnològics (CCiT) of the Universitat de Barcelona. Pascal’s constants were used to estimate diamagnetic corrections to the molar paramagnetic susceptibility, and a correction was applied for the sample holder. For sample Ru$_2$Mn-Cl$_2$ the data were also corrected for a very residual amount of Ru$^2+$ impurity, which introduced a slope to the χT vs T curve.

Photochemical oxidations.

The photochemical oxygen evolution was carried out under irradiation with 300 W xenon lamp (MAX 302) with band pass filter 440 nm in a custom-made glass vessel with a water jacket. The temperature of the cell was maintained at 298 K by continuous flow of water connected with a thermostat. Oxygen evolution was analysed with a gas phase Clark electrode, and successively calibrated with known additions of air. On-line mass
measurement of the gas evolution for labelling experiments was performed on a Pfeiffer Omnistar GSD 301C mass spectrometer, in the same conditions as the Chemical water oxidation.

X-ray Crystal Structure Determination.

Crystals of Ru$_2$Mn-Cl$_2$ were obtained by slow diffusion of diethyl ether into an acetonitrile solution of the complex. Crystals of Ru$_2$Mn-OAc$_2$ were obtained by slow evaporation of a methanol solution of the complex. The measured crystals were prepared under inert conditions immersed in perfluoropolyether as protecting oil for manipulation.

*Data collection:* Crystal structure determination for Ru$_2$Mn-Cl$_2$ and Ru$_2$Mn-OAc$_2$ was carried out using a Bruker-Nonius diffractometer equipped with an APPEX 2 4K CCD area detector, a FR591 rotating anode with MoK$_\alpha$ radiation, Montel mirrors as monochromator and an Oxford Cryosystems low temperature device Cryostream 700 plus ($T = -173 \, ^\circ C$). Full-sphere data collection was used with $\omega$ and $\phi$ scans. Programs used: Data collection APEX-2, data reduction Bruker Saint V/.60A and absorption correction SADABS.

*Structure Solution and Refinement:* Crystal structure solution was achieved using direct methods as implemented in SHELXTL$^5$ and visualized using the program XP. Missing atoms were subsequently located from difference Fourier synthesis and added to the atom list. Least-squares refinement on $F^2$ using all measured intensities was carried out using the program SHELXTL. All non hydrogen atoms were refined including anisotropic displacement parameters.

*Comments to the structures:* Ru$_2$Mn-Cl$_2$: The unit cell contains one molecule of the complex, two PF$_6$ anions, one diethyl ether molecule, one acetonitrile molecule and two water molecules. One of the water molecules is disordered in two positions (ratio: 56:44). Ru$_2$Mn-OAc$_2$: The unit cell contains one molecule of the complex, two PF$_6$ anions and one molecule of methanol. One of the PF$_6$ anions is disordered in two orientations. The methanol molecule is also disordered in two orientations (ratio 59:31). The measured sample was formed by two crystals with a ratio of 70:30. The collected data for both crystals were processed with TWINABS taking in account overlapping reflections.$^7$ The measured crystals were of extreme small dimensions and although the measured sample was formed by two crystals only a completeness of 92 % was reached. Not better data could be collected.

Notes and references

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**Figure S1.** Mass spectra (MALDI+) of [(RuII(trpy))2(μ-[CoII(Cl)2(bpp)2])][PF6]2, Ru2Co-Cl2, in dctb-CH2Cl2. The peak at 1386.0 corresponds to cation [M-PF6]+; experimental (left) and simulated (right).

**Figure S2.** Mass spectra (MALDI+) of [(RuII(trpy))2(μ-[MnII(Cl)2(bpp)2])][PF6]2, Ru2Mn-Cl2, in dctb-CH2Cl2. The peak at 1382.1 corresponds to cation [M-PF6]+; experimental (left) and simulated (right).
Figure S3. ESI Mass spectra of ([Ru^II(trpy)]_2(μ-[Co^II(AcO)]_2(bpp)_2)])(PF_6)_2, Ru_2Co-OAc_2, in MeOH. (a) the peak at 1434 corresponds to cation [M-PF_6]^+; Experimental (left) and simulated (right); the peak at 644.5 corresponds to cation [M-2PF_6]^{2+}; Experimental (left) and simulated (right).

(a)

(b)
Figure S4. ESI Mass spectra of \( [\text{Ru}^{II}(\text{trpy})_2(\mu-\text{[Mn}^{II}(\text{AcO})_2(bpp)_2)])(\text{PF}_6)_3 \), \( \text{Ru}_2\text{Mn-OAc}_2 \), in MeOH. (a) The peak at 1430 corresponds to cation \([\text{M-PF}_6]^+\); Experimental (left) and simulated (right); (b) the peak at 642.5 corresponds to cation \([\text{M-2PF}_6]^{2+}\); Experimental (left) and simulated (right).
Figure S5. UV-vis spectra of \([\{\text{Ru}^{II}(\text{trpy})\}_2(\mu-\text{[Co}^{II}(\text{Cl})_2(\text{bpp})_2)\}](\text{PF}_6)_2, \text{Ru}_2\text{Co-Cl}_2\), in (a) CH$_3$CN and (b) CH$_2$Cl$_2$.

![Graph](image1)

Figure S6. UV-vis spectra of \([\{\text{Ru}^{II}(\text{trpy})\}_2(\mu-\text{[Mn}^{II}(\text{Cl})_2(\text{bpp})_2)\}](\text{PF}_6)_2, \text{Ru}_2\text{Mn-Cl}_2\), in (a) CH$_3$CN and (b) CH$_2$Cl$_2$.

![Graph](image2)

Figure S7. UV-vis spectra of \([\{\text{Ru}^{II}(\text{trpy})\}_2(\mu-\text{[Co}^{II}(\text{AcO})_2(\text{bpp})_2)\}](\text{PF}_6)_2, \text{Ru}_2\text{Co-OAc}_2\), in (a) CH$_3$CN and (b) CH$_2$Cl$_2$.

![Graph](image3)
Figure S8. UV-vis spectra of \([\text{Ru}^{II}(\text{trpy})_2(\mu-[\text{Mn}^{II}(\text{AcO})_2(\text{bpp})_2])\text{(PF}_6)_2, \text{Ru}_2\text{CMn-OAc}_2\], in (a) CH₃CN and (b) CH₂Cl₂.

Figure S9. UV-visible absorption spectra of \(\text{Ru}_2\text{Co-OAc}_2\) (red) in CH₃CN and of \(\text{Ru}_2\text{Mn-OAc}_2\) (black) in CH₃CN.
Figure S10. IR spectra (KBr) of \([\text{Ru}^{II}(\text{trpy})]_2(\mu-\text{[Co}^{II}(\text{Cl})_2(\text{bpp})_2])\)(PF_6)_3, Ru_2Co-Cl_2.

Figure S11. IR spectra (KBr) of \([\text{Ru}^{II}(\text{trpy})]_2(\mu-\text{[Mn}^{II}(\text{Cl})_2(\text{bpp})_2])\)(PF_6)_2, Ru_2Mn-Cl_2.
Figure S12. IR spectra (KBr) of \([\text{Ru}^\text{II}(\text{trpy})_2(\mu-\text{Co}^\text{II}(\text{OAc})_2(\text{bpp})_2)](\text{PF}_6)_2\), Ru$_2$Co-OAc$_2$.

Figure S13. IR spectra (KBr) of \([\text{Ru}^\text{II}(\text{trpy})_2(\mu-\text{Mn}^\text{II}(\text{OAc})_2(\text{bpp})_2)](\text{PF}_6)_2\), Ru$_2$Mn-OAc$_2$. 
**Figure S14.** CV (black) and DPV (red) of $\{[\text{Ru}^{II}(\text{trpy})]_2(\mu-[\text{Co}^{II}(\text{Cl})_2(\text{bpp})_2])\}(\text{PF}_6)_2$, Ru$_2$Co-Cl$_2$, in CH$_2$Cl$_2$. All redox potentials in this and the subsequent figures are reported vs. NHE.

**Figure S15.** CV (black) and DPV (red) of $\{[\text{Ru}^{II}(\text{trpy})]_2(\mu-[\text{Mn}^{II}(\text{Cl})_2(\text{bpp})_2])\}(\text{PF}_6)_2$, Ru$_2$Mn-Cl$_2$, in CH$_2$Cl$_2$. 
Figure S16. CV (black) and DPV (red) of \([\text{Ru}^{II}(\text{trpy})]_2(\mu-\text{[Co}^{II}(\text{AcO})_2(\text{bpp})_2])\)(\text{PF}_6)_2, \text{Ru}_2\text{Co-OAc}_2\), in CH$_3$CN.

![Graph showing CV and DPV for Ru$_2$Co-OAc$_2$](image1)

Figure S17. CV (black) and DPV (red) of \([\text{Ru}^{II}(\text{trpy})]_2(\mu-\text{[Mn}^{II}(\text{AcO})_2(\text{bpp})_2])\)(\text{PF}_6)_2, \text{Ru}_2\text{Mn-OAc}_2\), in CH$_3$CN.

![Graph showing CV and DPV for Ru$_2$Mn-OAc$_2$](image2)
**Figure S18.** Cyclic voltammograms at a vitreous carbon electrode (diameter 3 mm) in CH$_3$CN, 0.1 M [($^n$Bu$_4$N)ClO$_4$] of (A) a 0.25 mM solution of Ru$_2$Co-OAc$_2$, (B) after exhaustive oxidation at 0.85 V vs NHE (0.30 vs Ag/Ag$^+$) of the previous solution (formation of Ru$_2$(II)Co(III)), (C) after exhaustive oxidation at 1.40 vs NHE (0.85 vs Ag/Ag$^+$) of the previous solution (formation of Ru$_2$(III)Co(III)); scan rate 100 mV·s$^{-1}$. $E$ vs NHE = $E$ vs Ag/Ag$^+$ + 0.548.

**Figure S19.** Voltammograms at a carbon Rotating Disk Electrode (2 mm diameter) of a 0.25 mM solution of Ru$_2$Co-OAc$_2$ in CH$_3$CN, 0.1 M [($^n$Bu$_4$N)ClO$_4$]: (A) initial solution, (B) after oxidation at 0.85 V vs NHE (0.30 vs Ag/Ag$^+$), (C) after oxidation at 1.40 V vs NHE (0.85 vs Ag/Ag$^+$), rotation rate: $\omega = 600$ rot/min, scan rate: $v = 10$ mV·s$^{-1}$. $E$ vs NHE = $E$ vs Ag/Ag$^+$ + 0.548.
Figure S20. Cyclic voltammograms at a vitreous carbon electrode (diameter 3 mm) in CH$_3$CN, 0.1 M [($^n$Bu$_4$N)ClO$_4$] of a 0.25 mM solution of Ru$_2$Co-OAc$_2$ (black) and after two successive oxidations at 0.85 and 1.40 V vs NHE (0.30 and 0.85 V vs Ag/Ag$^+$), respectively, and one reduction at 0.35 V vs NHE (-0.20 V vs Ag/Ag$^+$) (red). $E$ vs NHE = $E$ vs Ag/Ag$^+$ + 0.548.
**Figure S21.** Cyclic voltammograms at a vitreous platinum electrode (diameter 5 mm) in CH$_3$CN, 0.1 M \((\text{[Bu}_4\text{N})\text{ClO}_4\) of (A) a 0.41 mM solution of \text{Ru}_2\text{Mn-OAc}_2\, (B) after exhaustive oxidation at 1.11 V vs NHE (0.56 vs Ag/Ag$^+\)) of the previous solution (formation of \text{Ru}_2\text{(III)Mn(II)}), (C) after exhaustive oxidation at 1.69 vs NHE (1.14 vs Ag/Ag$^+\)) of the previous solution (formation of \text{Ru}_2\text{(III)Mn(III)}); scan rate 50 mV·s$^{-1}$. \(E\) vs NHE = \(E\) vs Ag/Ag$^+\) + 0.548.
Figure S22. Cyclic voltammograms at a vitreous platinum electrode (diameter 5 mm) in CH$_3$CN, 0.1 M (["Bu$_4$N]ClO$_4$) of a 0.41 mM solution of Ru$_2$Mn-OAc$_2$ (black) and after two successive oxidations at 1.11 and 1.69 V vs NHE (0.56 and 1.14 V vs Ag/Ag$^+$), respectively, and one reduction at 0.35 V vs NHE (-0.20 V vs Ag/Ag$^+$) (red). $E_{\text{vs NHE}} = E_{\text{vs Ag/Ag}^+} + 0.548$
Figure S23. Reduced Magnetization versus field plots for compounds \textit{Ru}_2\textit{Mn-Cl}_2\ (black) and \textit{Ru}_2\textit{Mn-AcO}_2\ (red), measured at 2 K and variable field. Solid lines are just eye guides.

Figure S24. Isofield reduced Magnetization versus \(H/T\) plots for compounds \textit{Ru}_2\textit{Mn-Cl}_2\ (left) and \textit{Ru}_2\textit{Mn-AcO}_2\ (right), in the 1.8 to 6.8 K temperature range, for fields of 0.5, 1, 2, 3, 4 and 5 T.
Figure S25. Reduced Magnetization versus field plots for compounds Ru$_2$Co-Cl$_2$ (black) and Ru$_2$Co-AcO$_2$ (red), measured at 2 K and variable field. Solid lines are just eye guides.

Figure S26. Isofield reduced magnetization versus $H/T$ plots for compounds Ru$_2$Co-Cl$_2$ (left) and Ru$_2$Co-AcO$_2$ (right), in the 1.8 to 6.8 K temperature range, for fields of 0.5, 1, 2, 3, 4 and 5 T (only up to 4 T for Ru$_2$Co-AcO$_2$).
Figure S27. CV in a mixture (19:1) of pH = 1 CF$_3$SO$_3$H and CF$_3$CH$_2$OH, of (red) Ru$_2$Co-OAc$_2$, (black) Ru$_2$Mn-OAc$_2$, and (blue) in-1.

Figure S28. CV in a mixture (19:1) of pH = 7.0 (50 mM) phosphate buffer and CF$_3$CH$_2$OH, of (red) Ru$_2$Co-OAc$_2$, (black) Ru$_2$Mn-OAc$_2$, and (blue) in-1.
Figure S29. Photochemically induced oxidation of (black) \( \text{Ru}_2\text{Co}-(\text{H}_2\text{O})_6 \), (red) \( \text{Co(CH}_3\text{COO})_2\cdot4\text{H}_2\text{O} \) and (blue) \( \text{[Ru(bpy)}_3]\text{[ClO}_4\text{]}_2 \). Reaction conditions: \([\text{catalyst}]_0 = 50 \mu\text{M}, [\text{[Ru(bpy)}_3]\text{[ClO}_4\text{]}_2]_0 = 0.5 \text{ mM; } [\text{Na}_2\text{S}_2\text{O}_8]_0 = 20 \text{ mM; total volume } = 2 \text{ mL in a pH } = 7.0 (50 \text{ mM}) \text{ phosphate buffer solution and CF}_3\text{CH}_2\text{OH mixture (19:1). A 300 W Xenon lamp was used to illuminate the sample through a band pass filter of 440 nm at 298 K.}

Figure S30. rRaman spectra of a mixture of 400 μL of a 0.5 M solution of Oxone in pH = 7.0 phosphate buffer mixed with 400 μL of H\(_2^{16}\)O (red) and mixed with 400 μL of H\(_2^{18}\)O (orange), after 30 minutes (yellow), 1 hour (green), 2 hours (blue) and 10 hours (purple).
Figure S31. Ratios $^{32}\text{O}_2/^{34}\text{O}_2$ obtained from the on-line mass analysis. Top: isotopiclabelling at 97% of $\text{H}_2^{18}\text{O}$. Bottom: isotopic labelling at 15% of $\text{H}_2^{18}\text{O}$. 