Electronic Supplementary Material (ESI) for RSC Advances.
This journal is © The Royal Society of Chemistry 2020

Electronic Supplementary Information

Tantalum(V) 1,3-Propanediolate β-Diketonate Solution as a Precursor to Sol-Gel Derived, Metal Oxide Thin Films

Christopher Beale,[a,b] Stefanie Hamacher,[a,b] Alexey Yakushenko,[c] Oumaima Bensaid,[a,b] Sabine Willbold,[d] Guillermo Beltramo,[e] Sören Möller,[f] Heinrich Hartmann,[d] Elmar Neumann,[g] Gregor Mussler,[h] Alexander Shkurmanov,[h] Dirk Mayer,[a] Bernhard Wolfrum,[a,i] and Andreas Offenhäusser[a]

[a] *IBI-3, Bioelectronics, Forschungszentrum Jülich GmbH, D-52425 Germany*
[b] *RWTH Aachen University, Templergraben 55, D-52062 Germany*
[c] *Fraunhofer Research Institute for Microsystems and Solid State Techologies, D-80686 Munich, Germany*
[d] *ZEA-3, Analytics, Forschungszentrum Jülich GmbH, D-52425 Germany*
[e] *IBI-2, Mechanobiology, Forschungszentrum Jülich GmbH, D-52425 Germany*
[f] *IEK-1, Materials Synthesis and Processing, Forschungszentrum Jülich GmbH, D-52425 Germany*
[g] *Helmholtz Nano Facility, Forschungszentrum Jülich GmbH, D-52425 Germany*
[h] *PGI-9, Semiconductor Nanoelectronics, Forschungszentrum Jülich GmbH, D-52425 Germany*
[i] *Neuroelectronics, Munich School of Bioengineering, Department of Electrical and Computer Engineering, Technical University of Munich (TUM), D-85748 Garching, Germany*

Table of Contents:

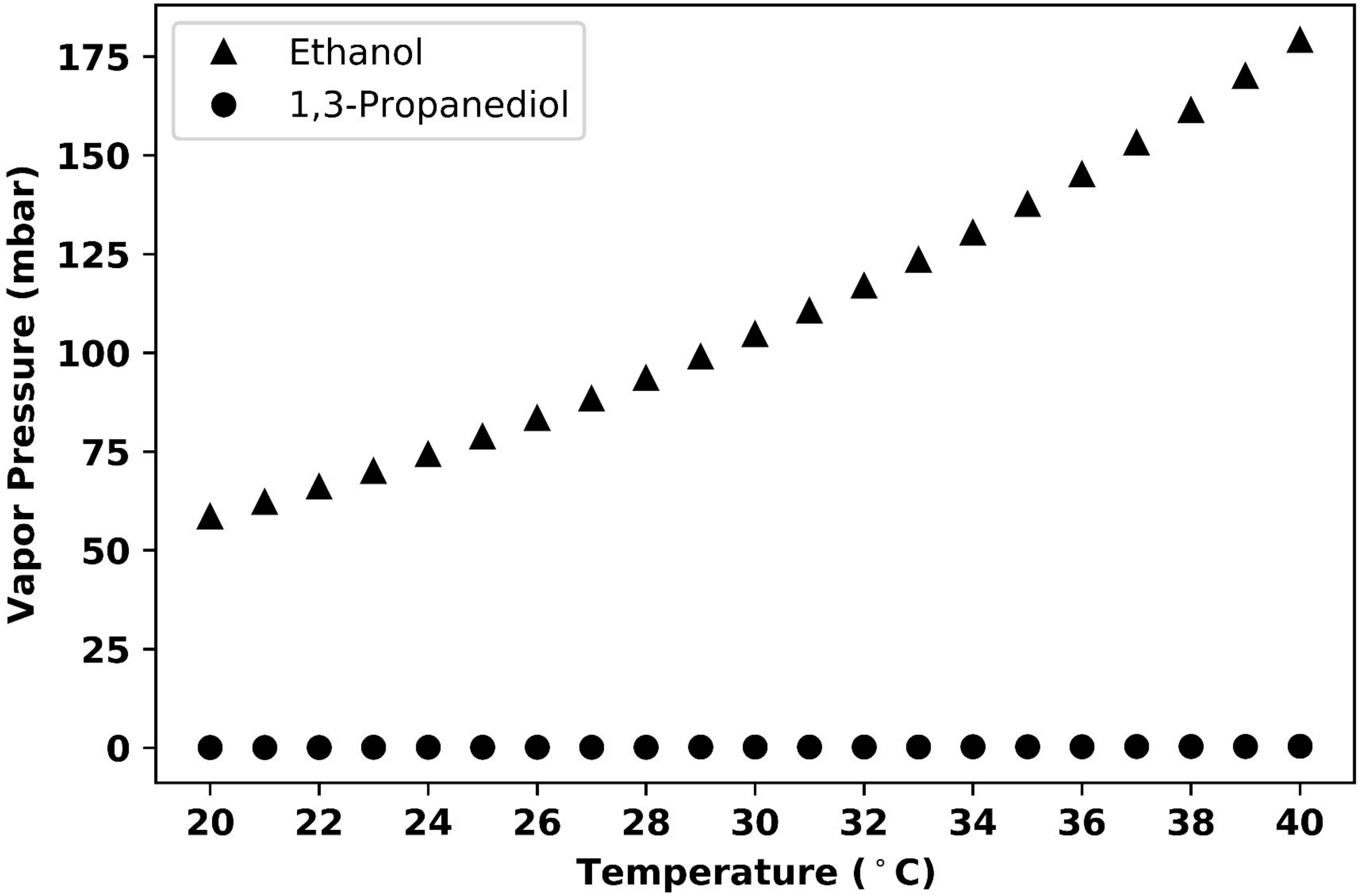


Figure S1: Temperature vs. vapor pressure as per the National Institute of Standards and Technology, U.S. Department of Commerce

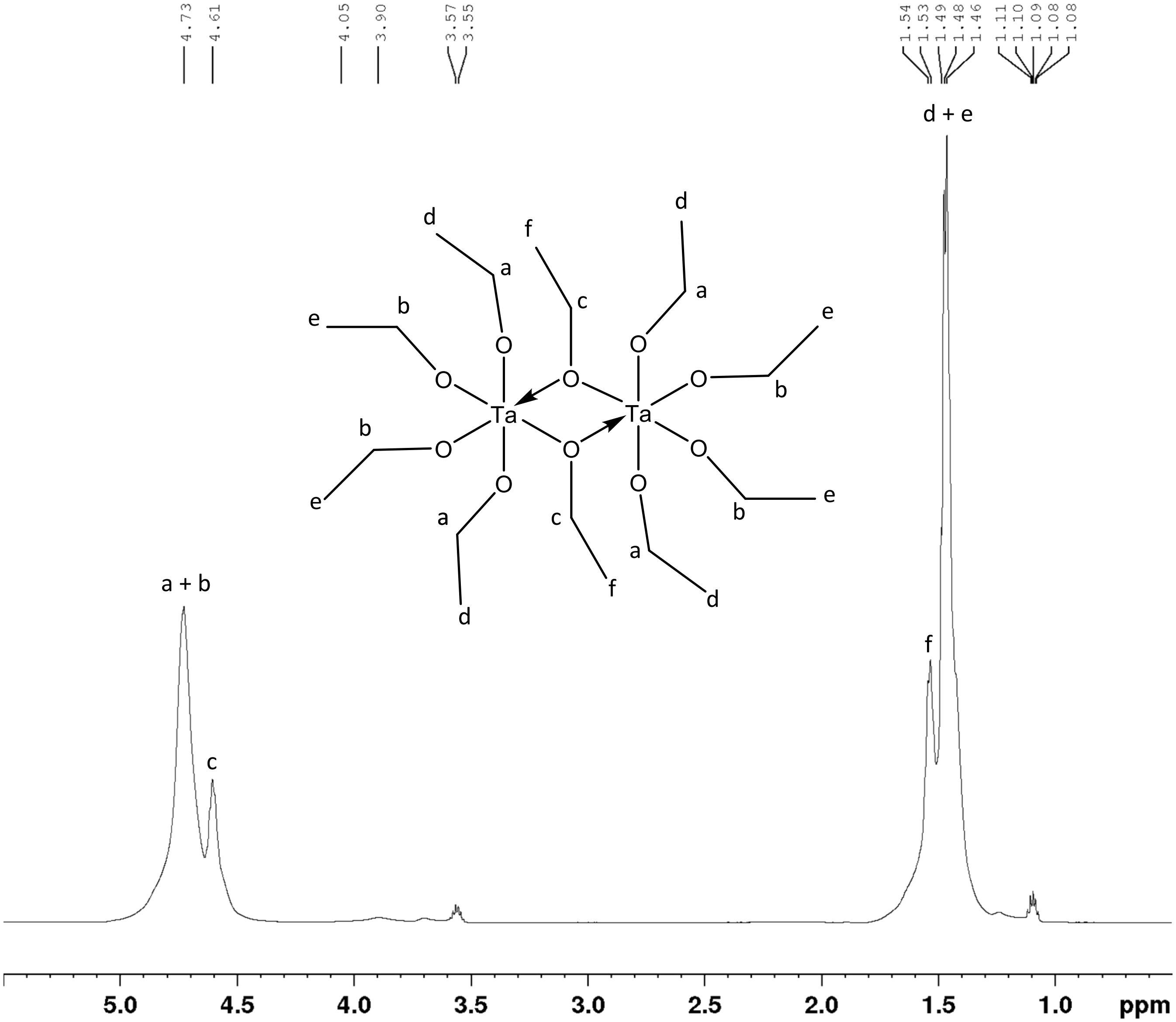


Figure S2: ^{1}H NMR [External D_2O]: Tantalum(V) Ethoxide (Alfa Aesar, 99+%)

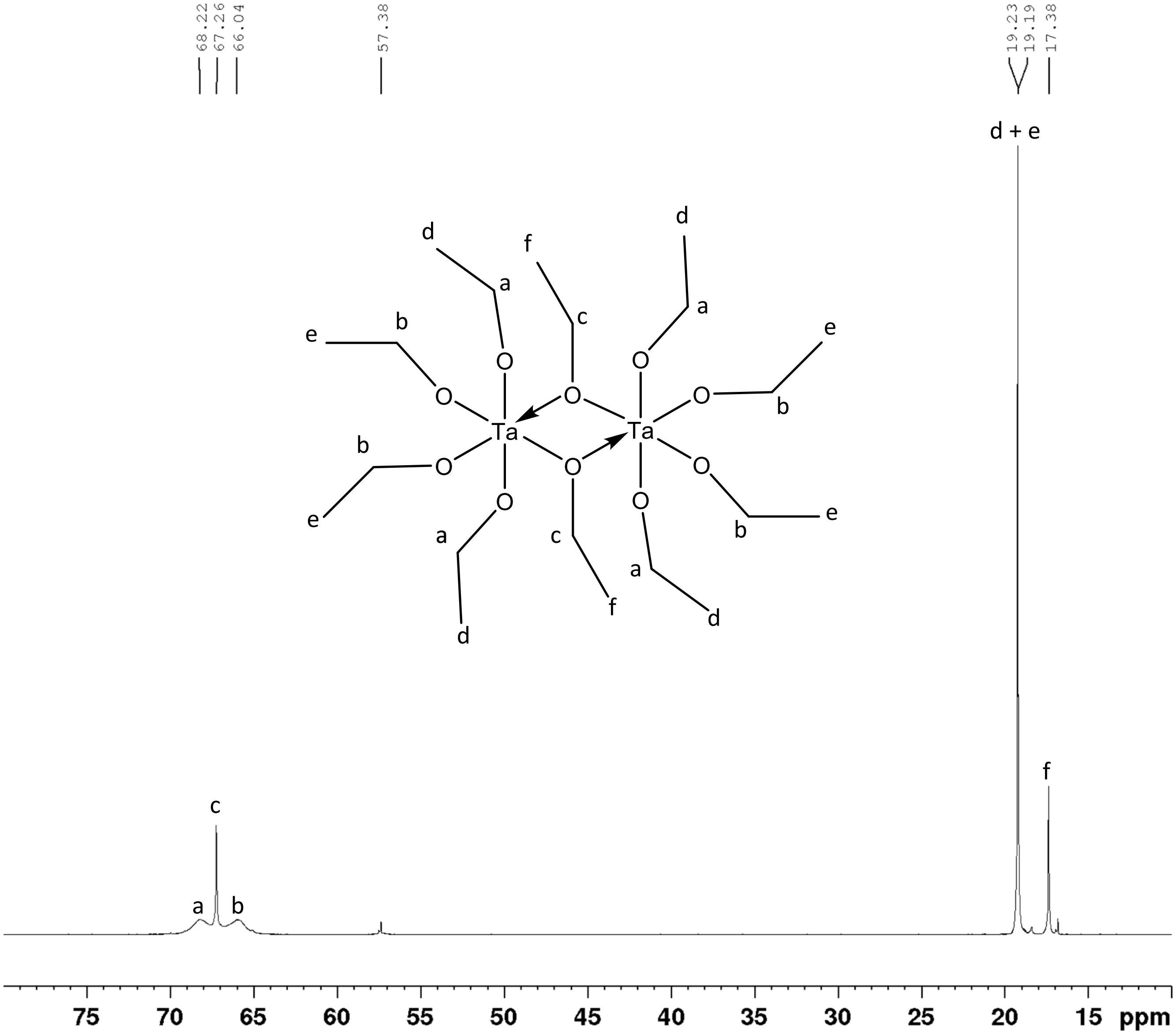


Figure S3: ^{13}C NMR [External D_2O]: Tantalum(V) Ethoxide (Alfa Aesar 99+%)

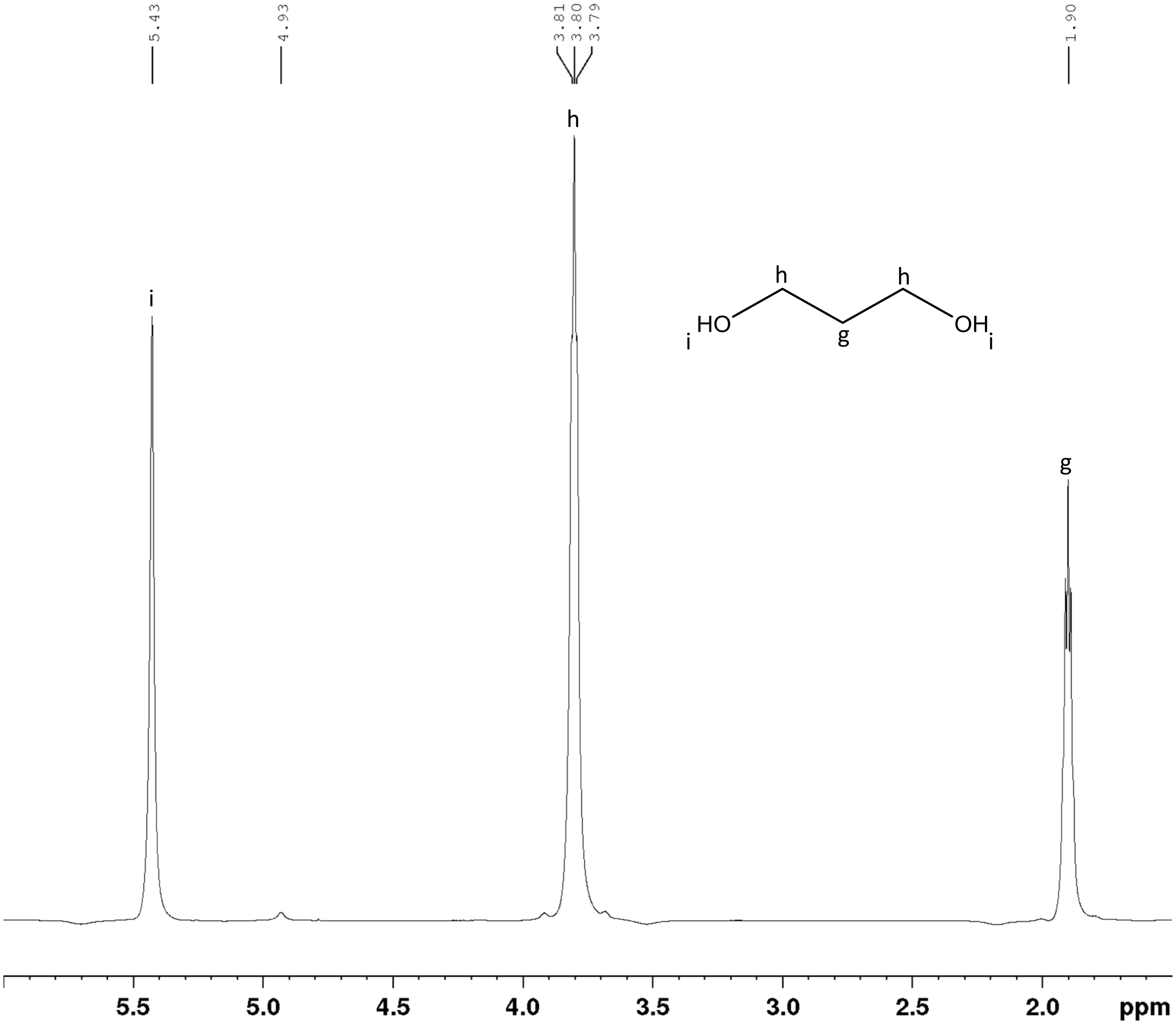


Figure S4: ^{1}H NMR [External D_2O]: 1,3-Propanediol (Sigma-Aldrich, for synthesis)

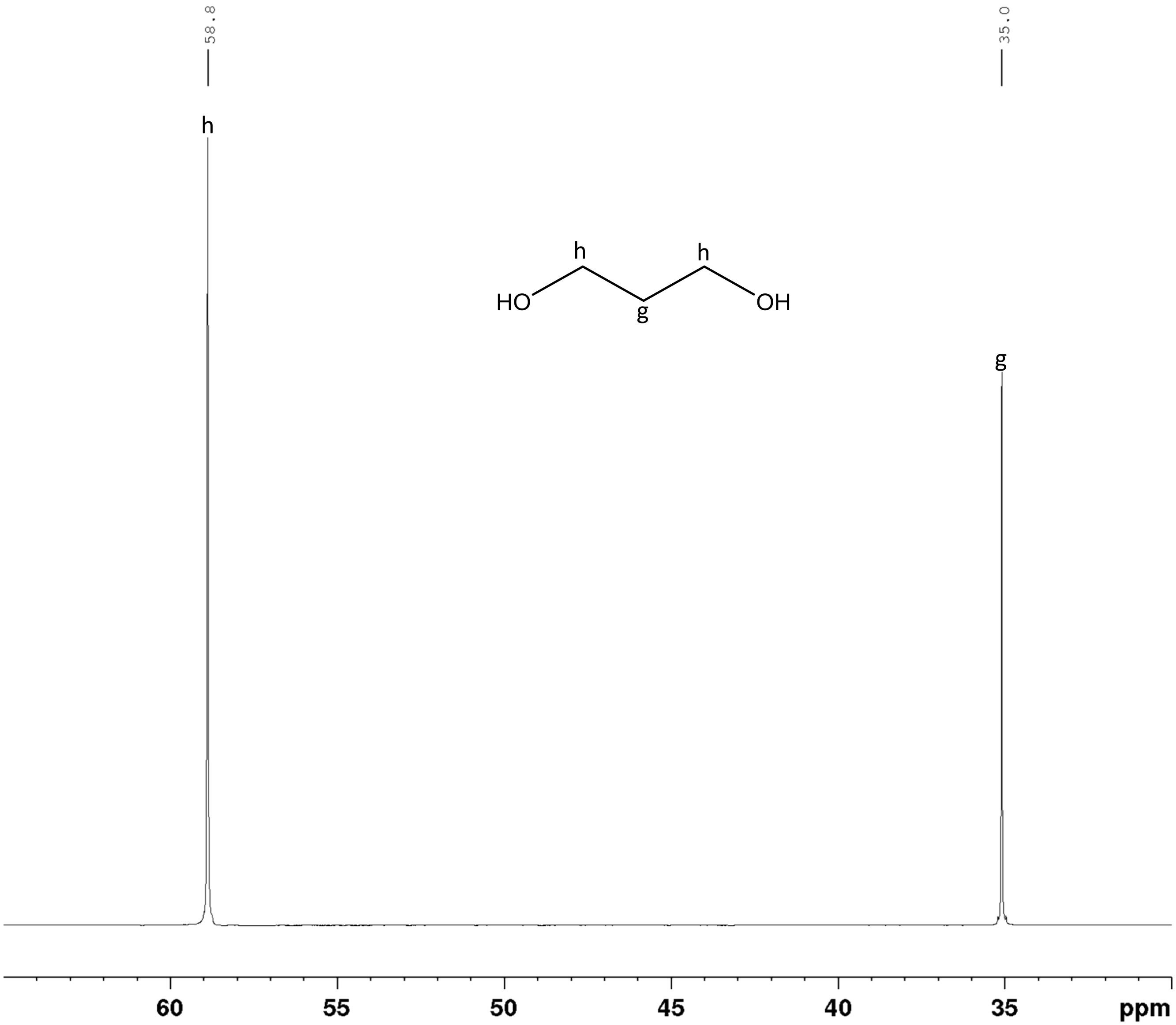


Figure S5: ^{13}C NMR [External D_2O]: 1,3-Propanediol (Sigma-Aldrich, for synthesis)

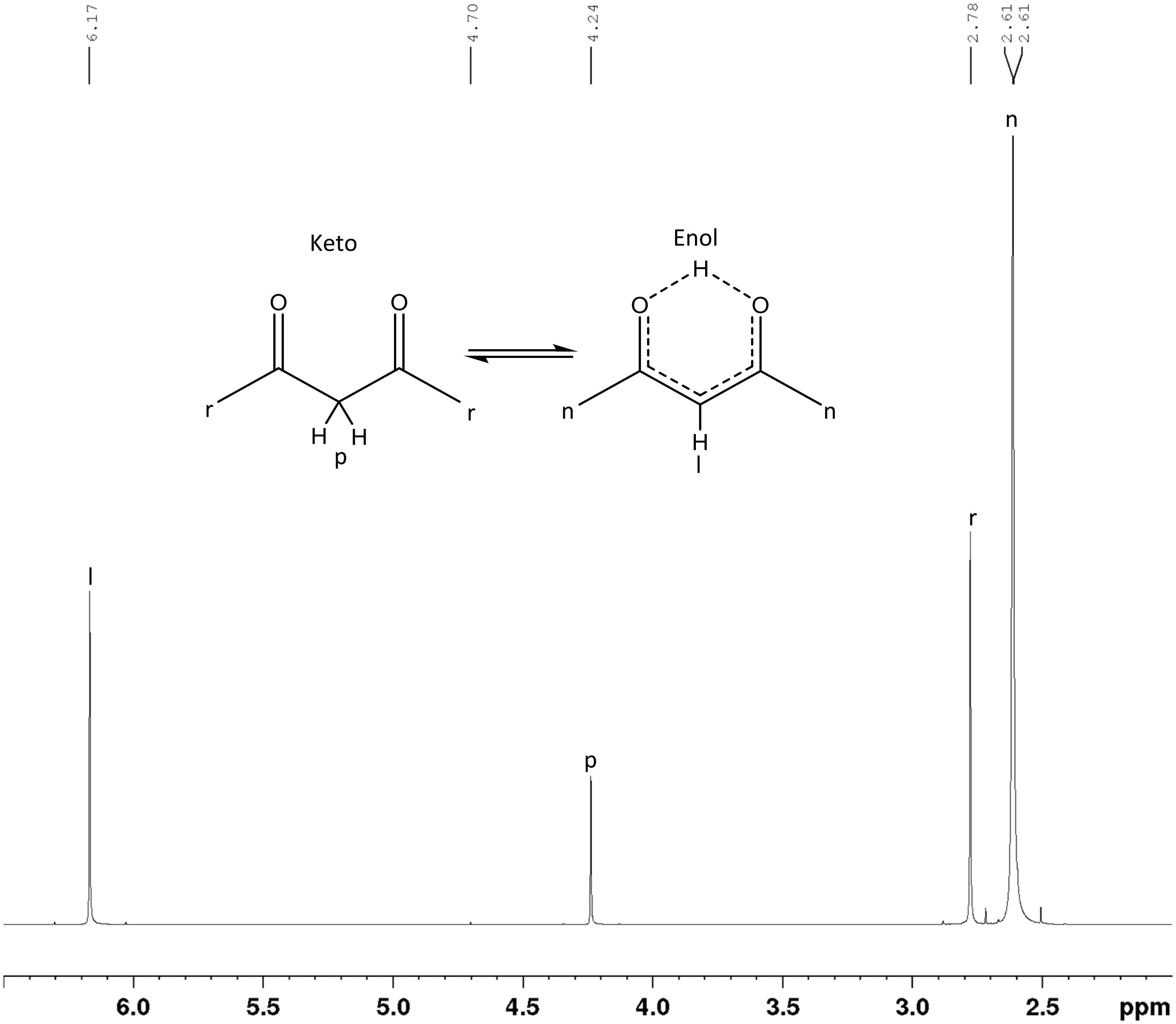


Figure S6: ^{1}H NMR [External D_2O]: Acetylacetone (Alfa Aesar, 95%)

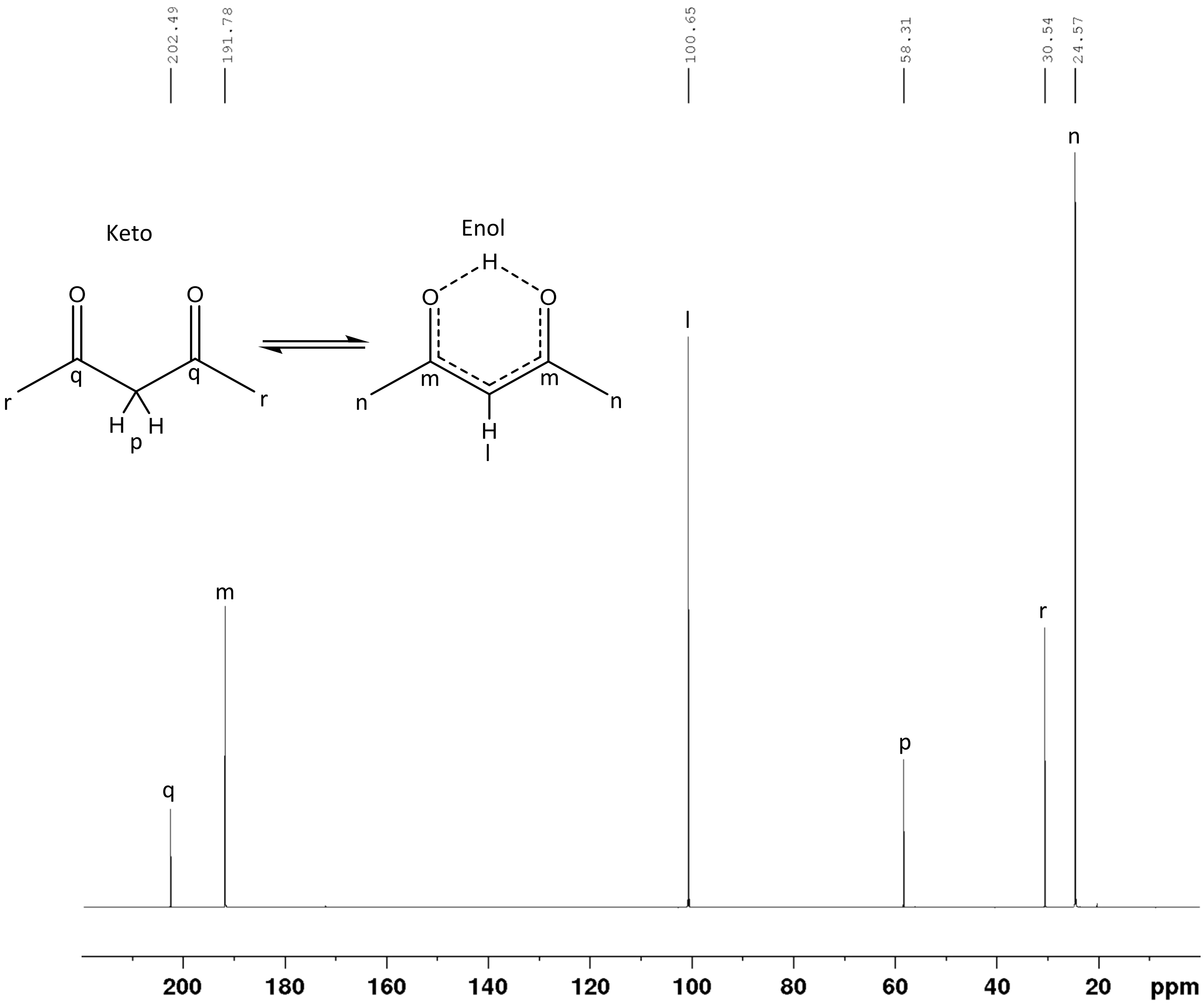


Figure S7: ^{13}C NMR [External D_2O]: Acetylacetone (Alfa Aesar, 95%)

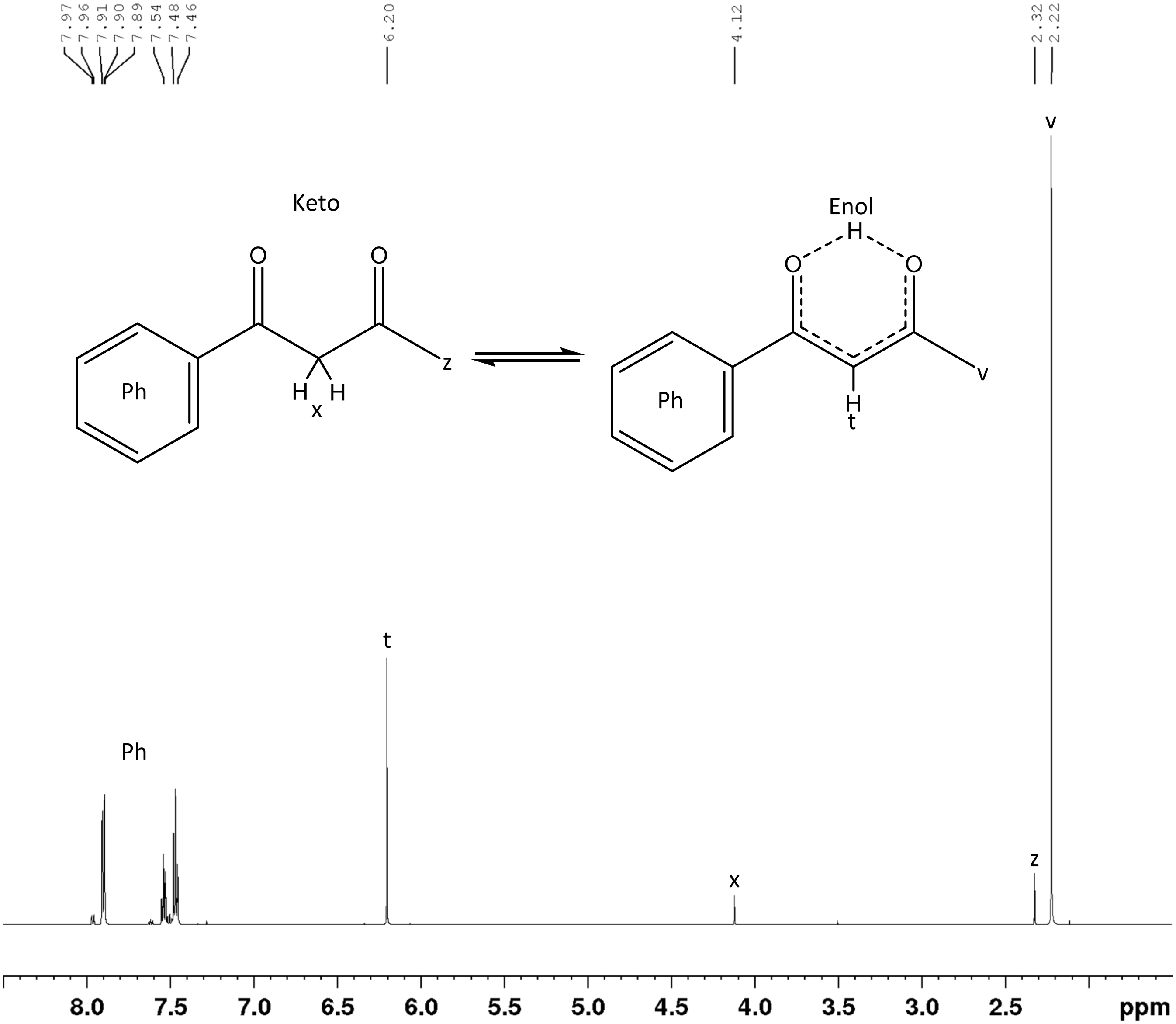


Figure S8: ^{1}H NMR [$CDCl_3$]: Benzoylacetone (Sigma Aldrich, 99%)

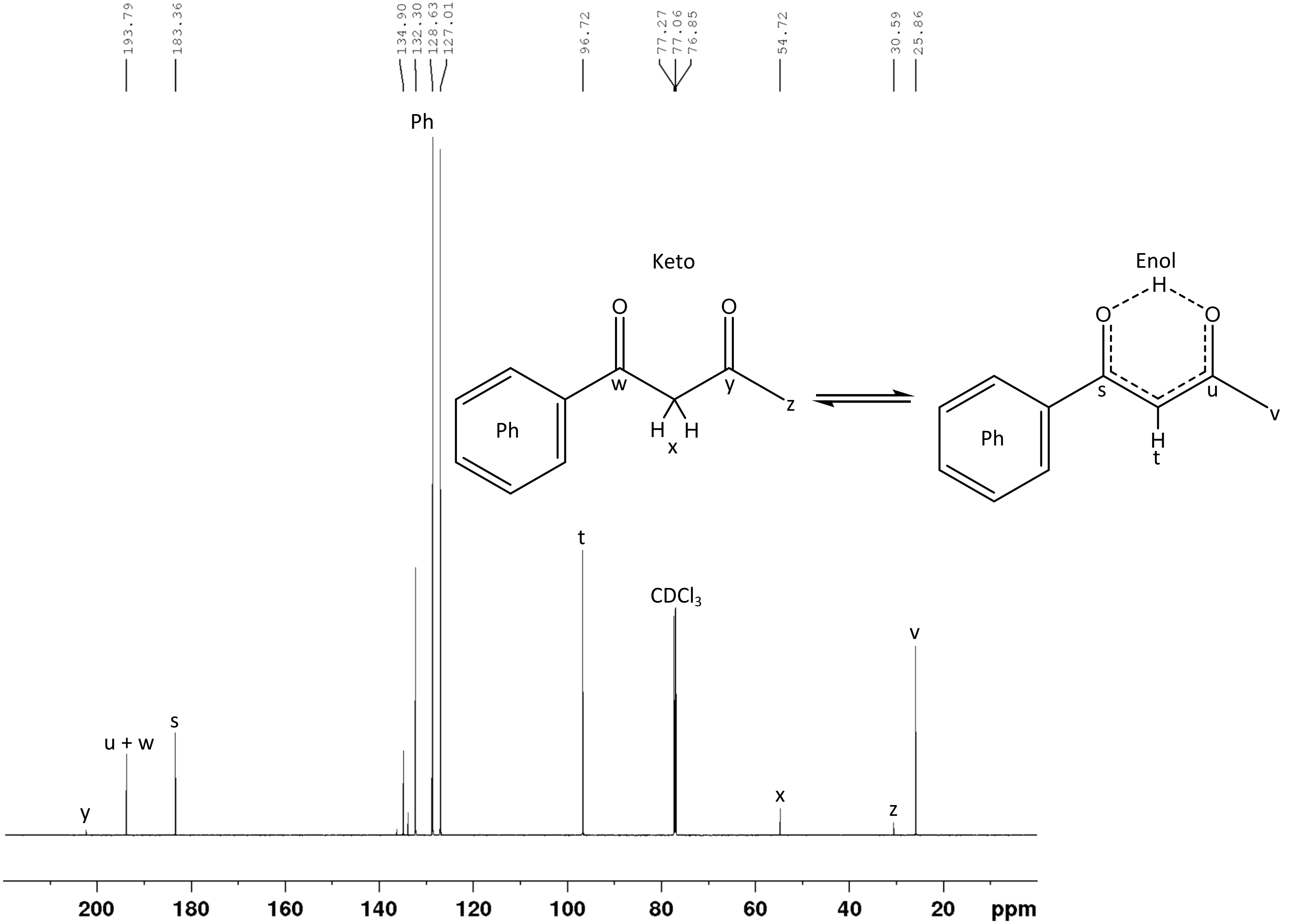


Figure S9: ^{13}C NMR [$CDCl_3$]: Benzoylacetone (Sigma Aldrich, 99%)

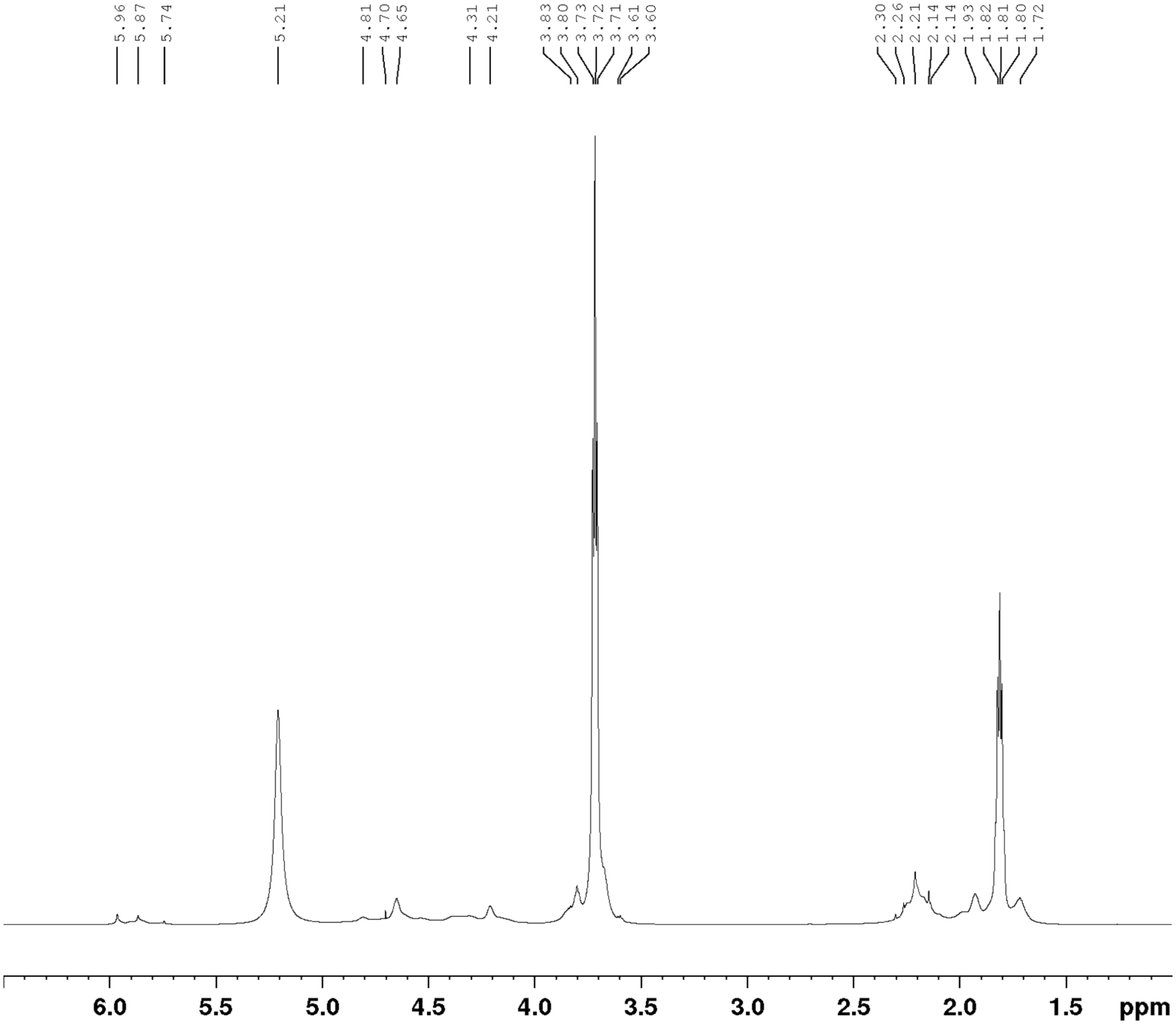


Figure S10: ^{1}H NMR [External D_2O]: Proposed synthesis – Tantalum(V) 1,3-propanediolate with acetylacetone

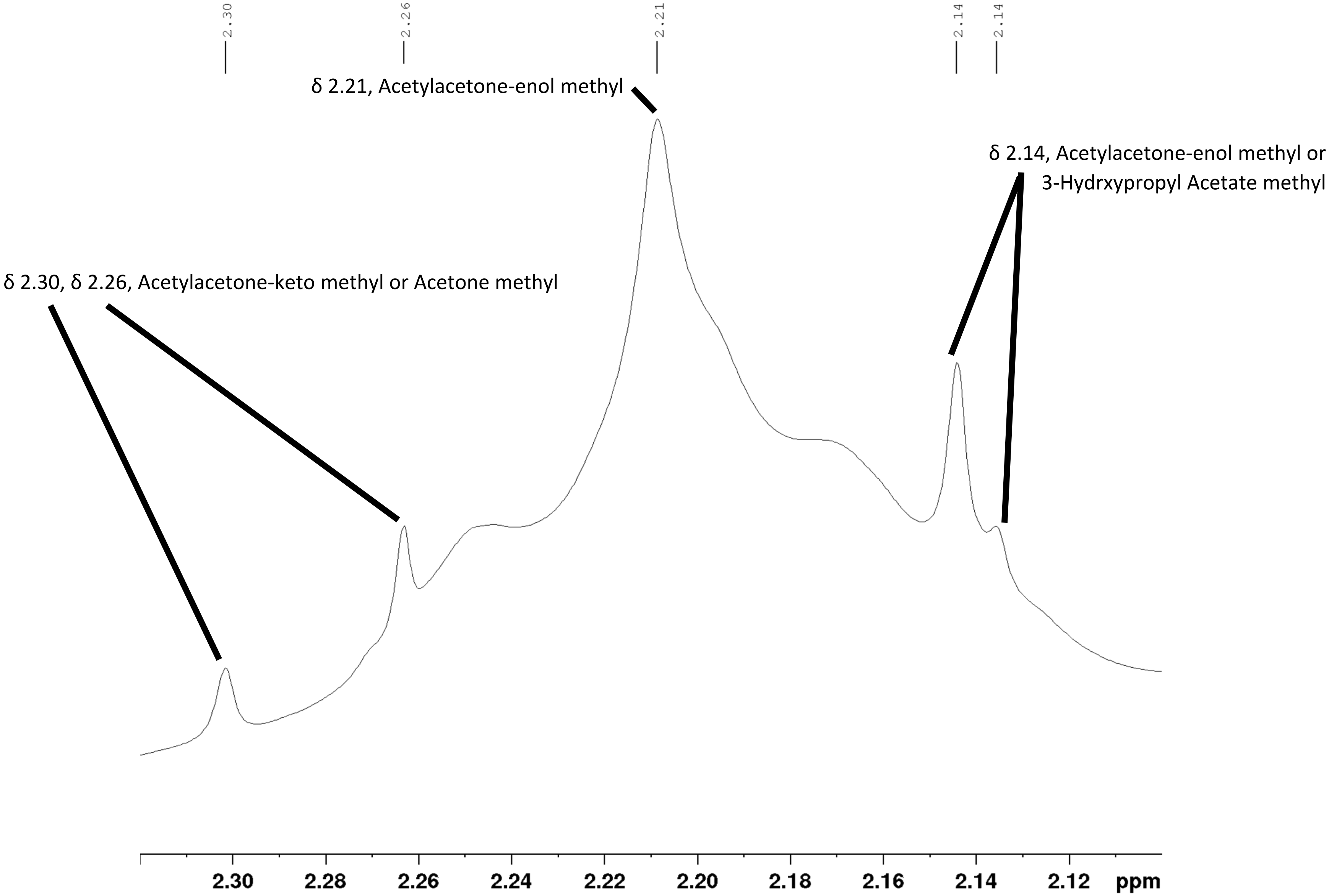


Figure S11: ^{1}H NMR [External D_2O]: Proposed synthesis – Tantalum(V) 1,3-propanediolate with acetylacetone (assigned with HMBC)

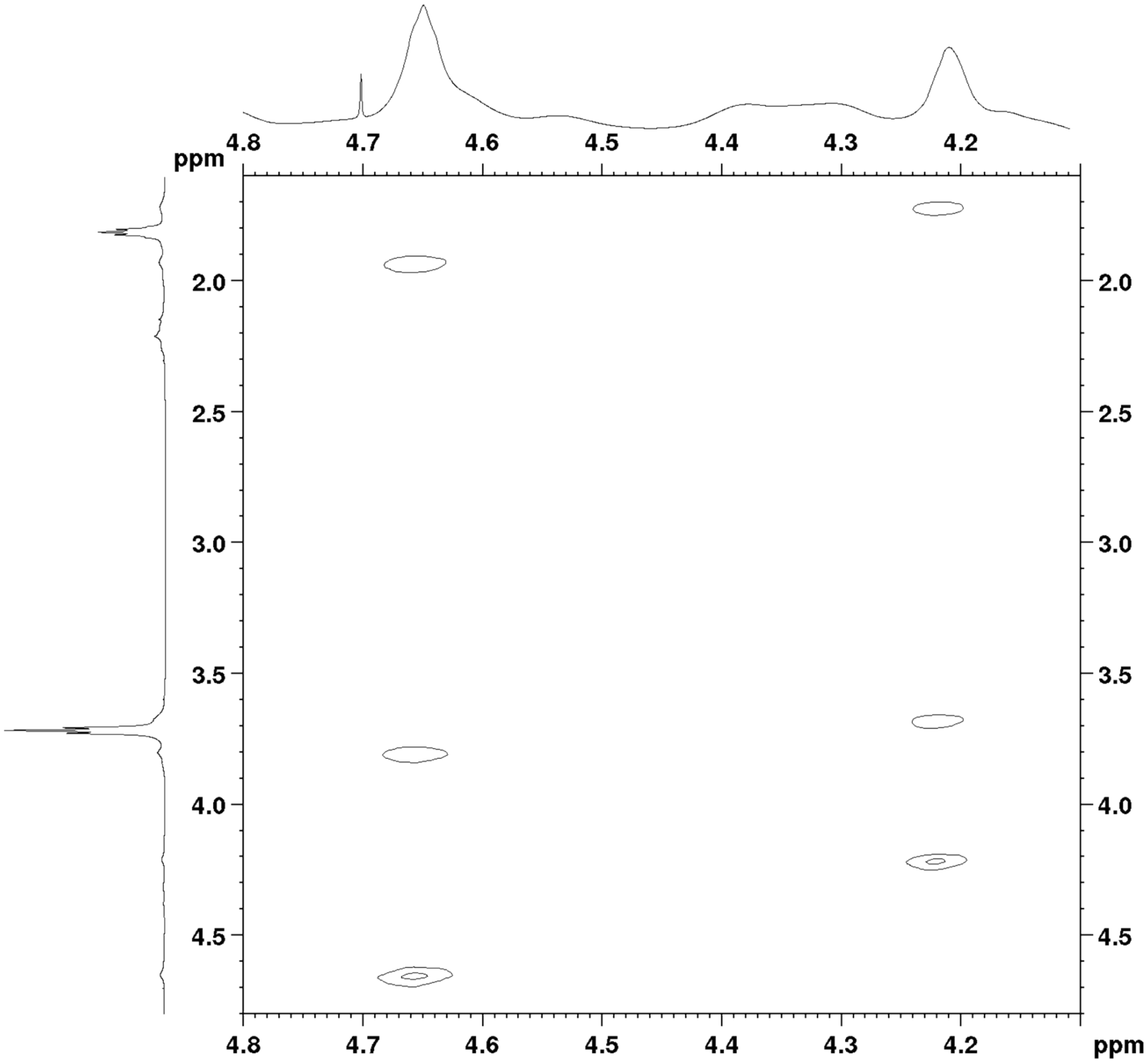


Figure S12: TOCSY [External D_2O]: Proposed synthesis – Tantalum(V) 1,3-propanediolate with acetylacetone

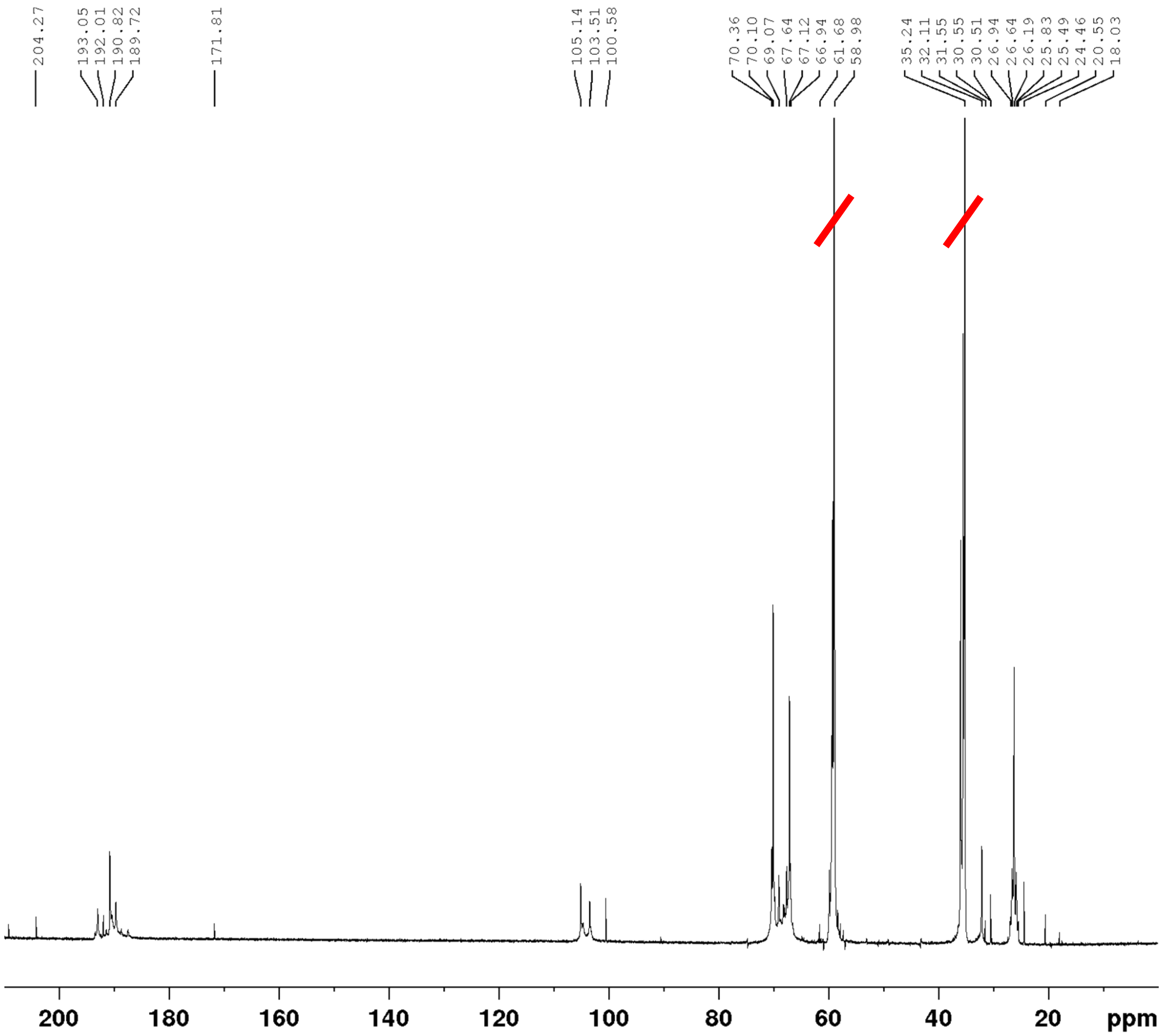


Figure S13: ^{13}C NMR [External D_2O]: Proposed synthesis – Tantalum(V) 1,3-propanediolate with acetylacetone

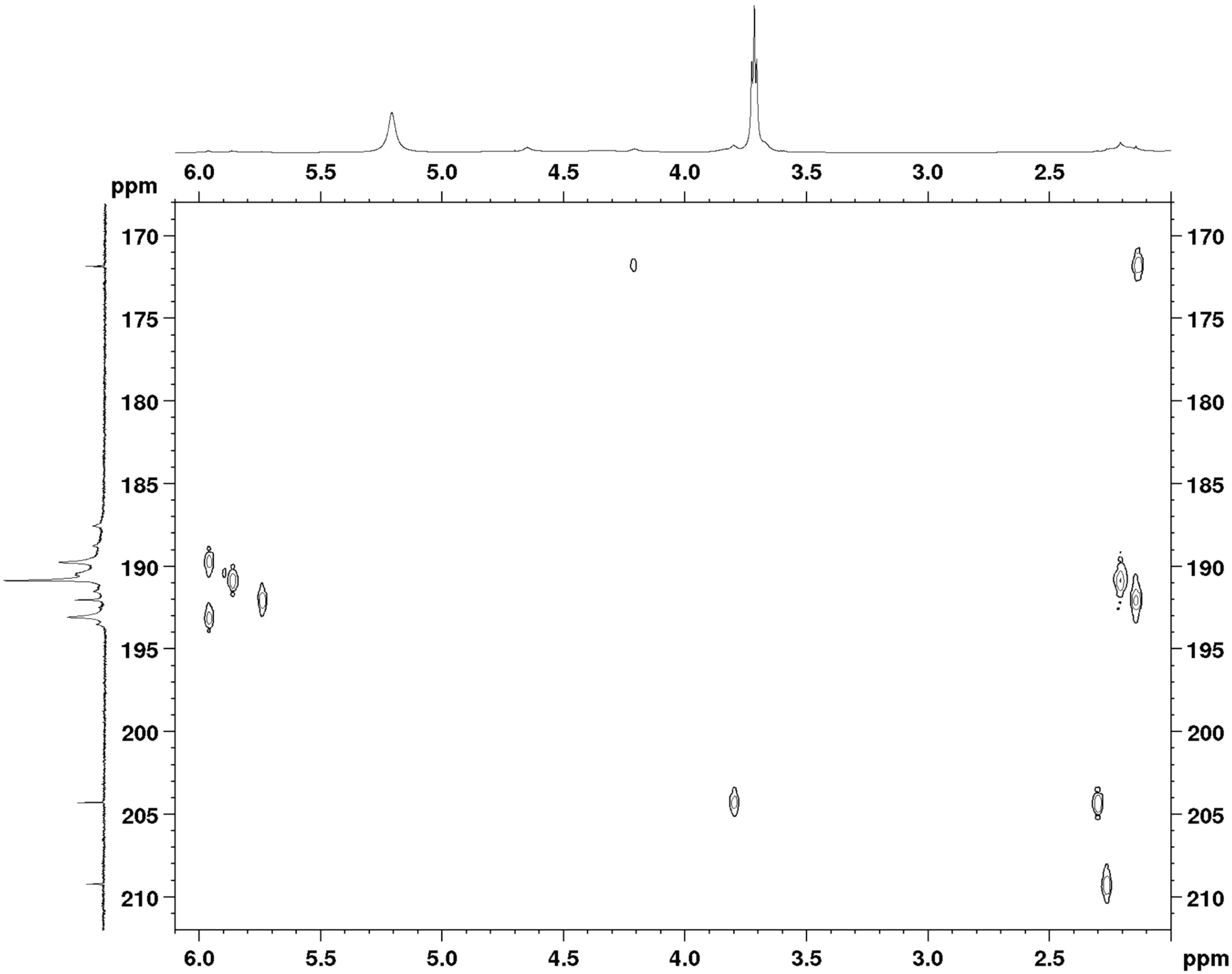


Figure S14: HMBC [External D_2O]: Proposed synthesis – Tantalum(V) 1,3-propanediolate with acetylacetone

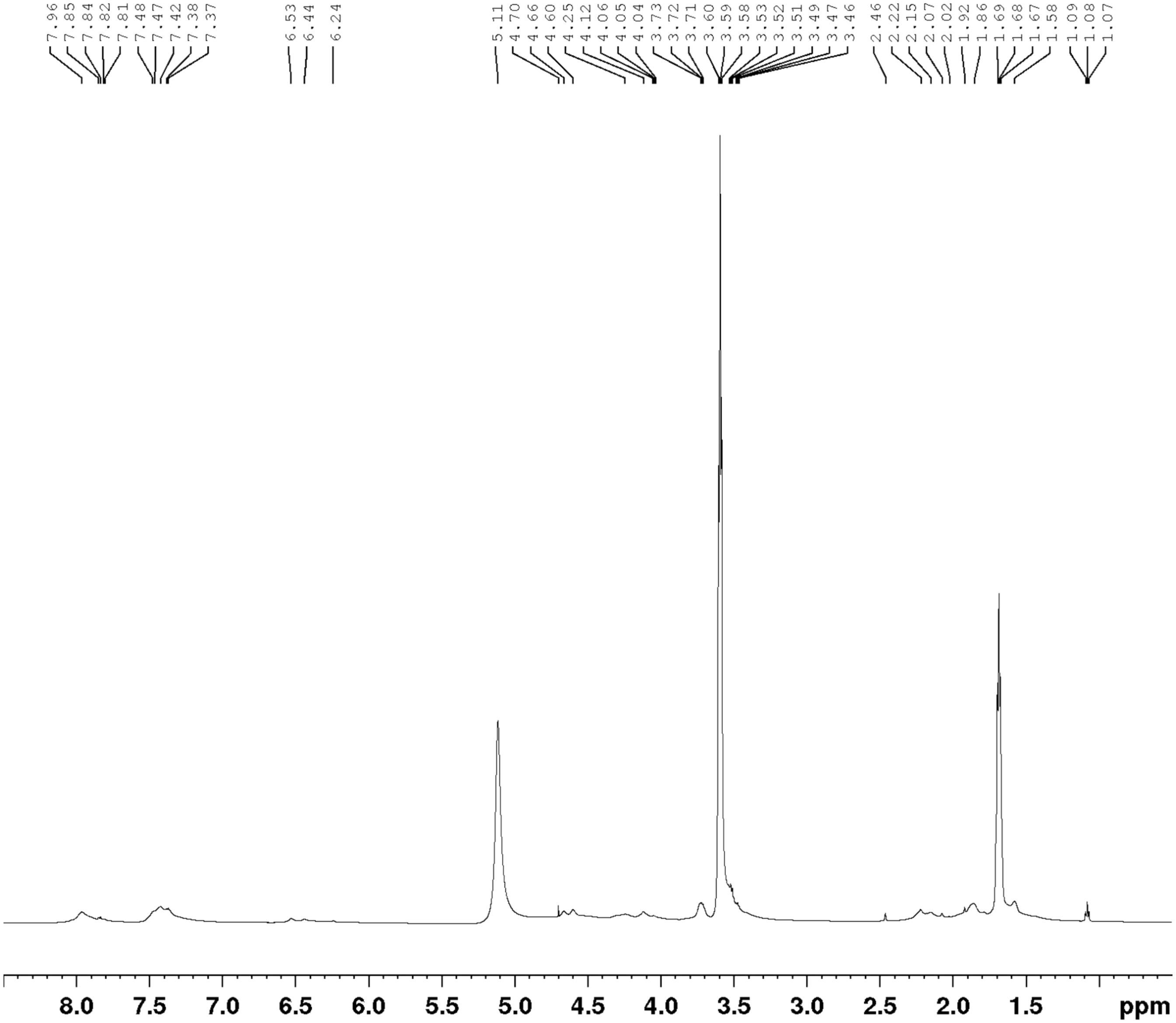


Figure S15: ${}^{1}H$ NMR [External D_2O]: Proposed synthesis – Tantalum(V) 1,3-propanediolate with benzoylacetone

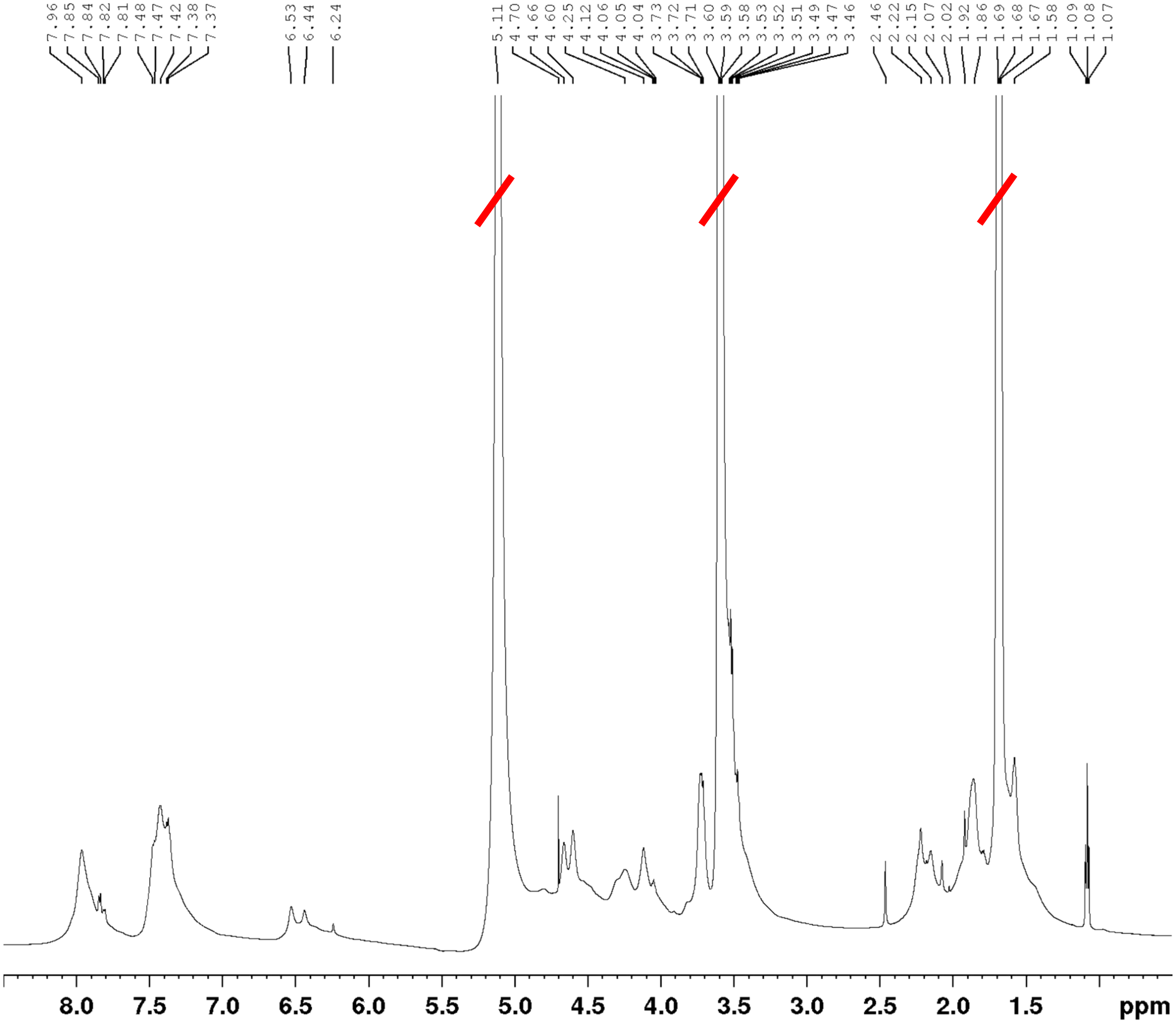


Figure S16: ^{1}H NMR [External D_2O]: Proposed synthesis – Tantalum(V) 1,3-propanediolate with benzoylacetone

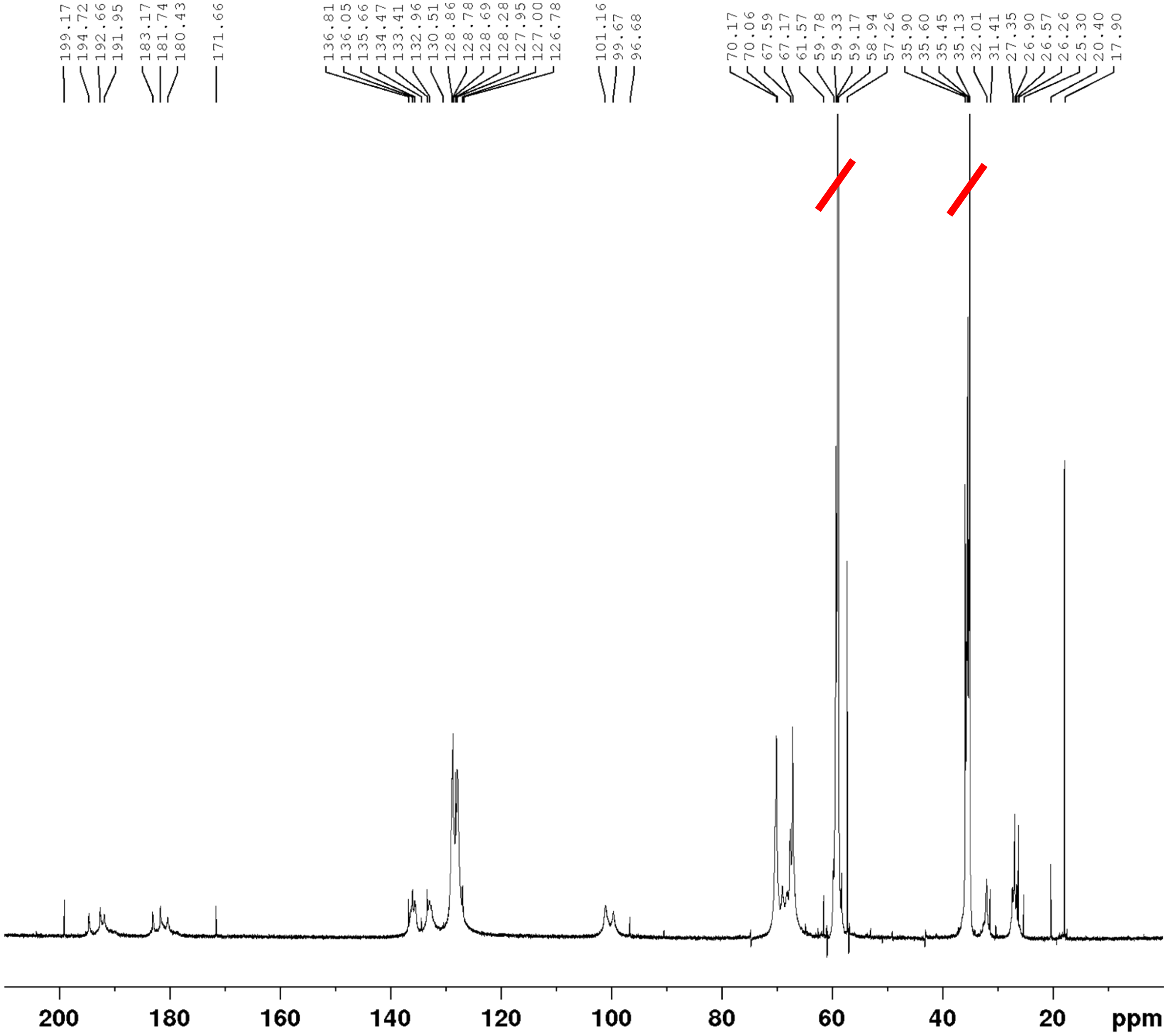
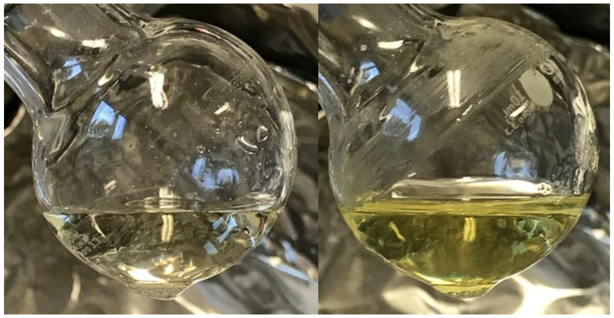


Figure S17: ^{13}C NMR [External D_2O]: Proposed synthesis – Tantalum(V) 1,3-propanediolate with benzoylacetone

Products



Repeated with Acetylacetone

Repeated with Benzoylacetone

<table>
<tr><th colspan="6"><u>Proposed Synthesis Reagents with Acetylactone</u></th></tr>
<tr><th colspan="2">Component</th><th colspan="2">Intended Amount</th><th colspan="2">Measured Amount</th></tr>
<tr><td colspan="2">Anhydrous Ethanol</td><td colspan="2">1935 (42 mmol)</td><td colspan="2">1965 mg (42.65 mmol)</td></tr>
<tr><td colspan="2">Acetylacetone</td><td colspan="2">601 mg (6 mmol)</td><td colspan="2">605 mg (6.04 mmol)</td></tr>
<tr><td colspan="2">Tantalum(V) Ethoxide</td><td colspan="2">2438 mg (6 mmol)</td><td colspan="2">2440 mg (6.01 mmol)</td></tr>
<tr><td colspan="2">1,3-Propanediol</td><td colspan="2">3196 mg (42 mmol)</td><td colspan="2">3204 mg (42.11 mmol)</td></tr>
<tr><th colspan="3">Expected Ethanol Loss from Vacuum Distillation</th><th colspan="3">Measured Ethanol Loss from Vacuum Distillation</th></tr>
<tr><td colspan="3">3349 mg</td><td colspan="3">3216 mg</td></tr>
</table>

<table>
<tr><th colspan="6"><u>Proposed Synthesis Reagents with Benzoylacetone</u></th></tr>
<tr><th colspan="2">Component</th><th colspan="2">Intended Amount</th><th colspan="2">Measured Amount</th></tr>
<tr><td colspan="2">Anhydrous Ethanol</td><td colspan="2">2500 mg (54.27 mmol)</td><td colspan="2">2500 mg (54.27 mmol)</td></tr>
<tr><td colspan="2">Benzoylacetone</td><td colspan="2">973 mg (6 mmol)</td><td colspan="2">973 mg (6.00 mmol)</td></tr>
<tr><td colspan="2">Tantalum(V) Ethoxide</td><td colspan="2">2438 mg (6 mmol)</td><td colspan="2">2445 mg (6.02 mmol)</td></tr>
<tr><td colspan="2">1,3-Propanediol</td><td colspan="2">3196 mg (42 mmol)</td><td colspan="2">3200 mg (42.06 mmol)</td></tr>
<tr><th colspan="3">Expected Ethanol Loss from Vacuum Distillation</th><th colspan="3">Measured Ethanol Loss from Vacuum Distillation</th></tr>
<tr><td colspan="3">3887 mg</td><td colspan="3">3577 mg</td></tr>
</table>

Figure S18: Tabulated Reagent Amounts for Repeated Synthesis – Used for Viscosity / Surface Tension Measurements

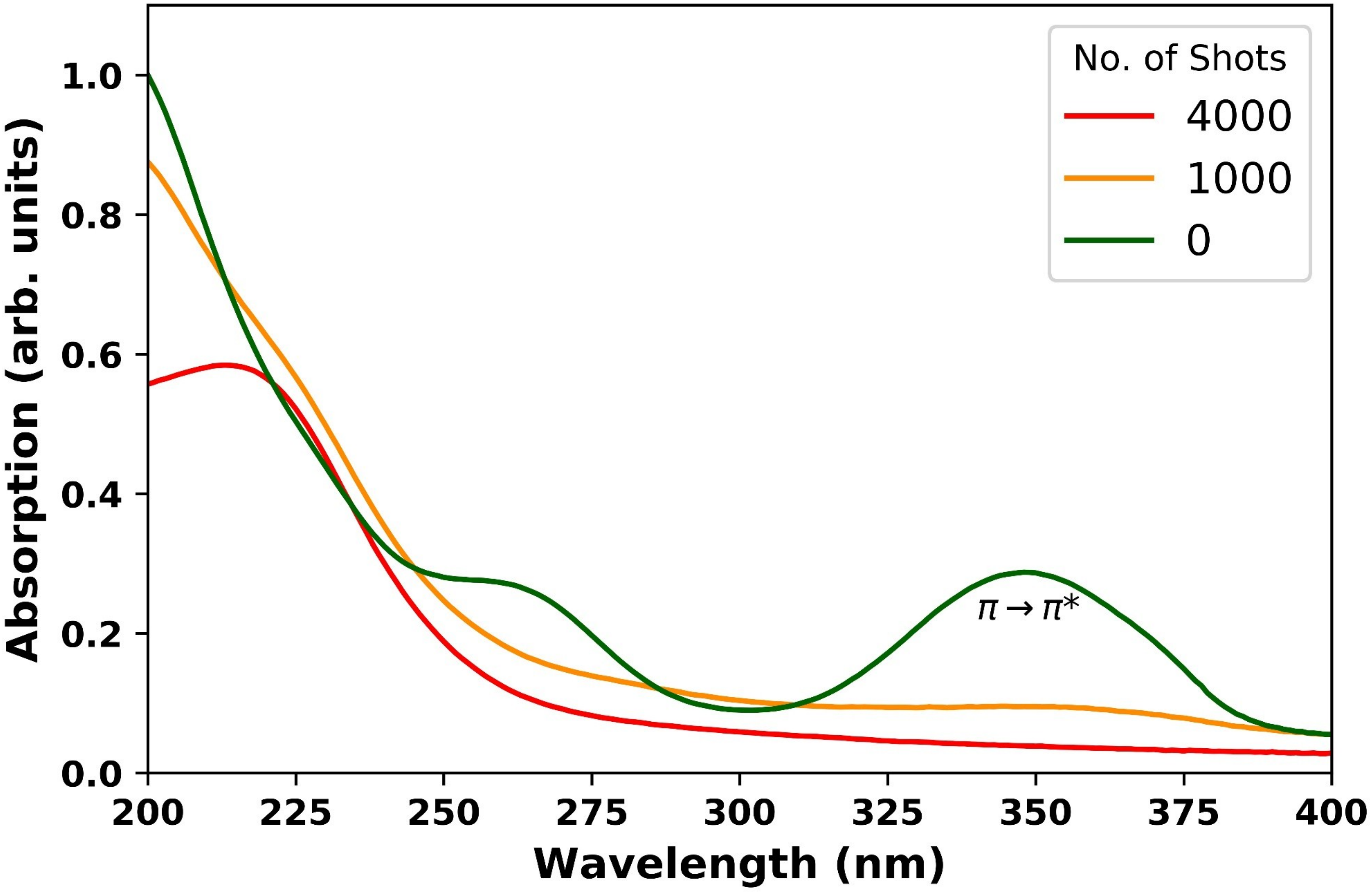


Figure S19: UV/Vis spectrum of inkjet printed, benzoylacetone based film

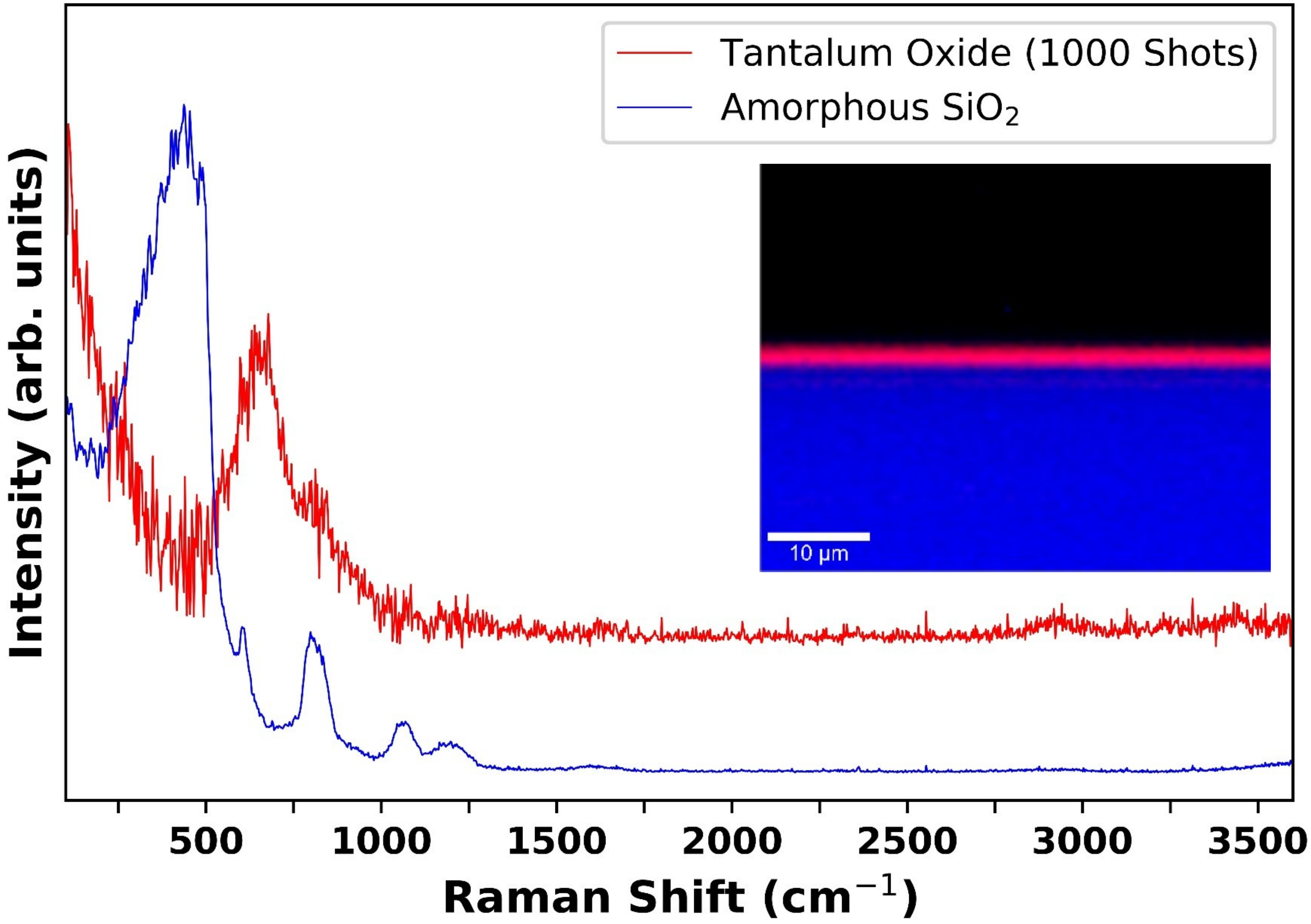


Figure S20: Shifted Raman spectra and depth scan of 1000 shot sample (red) on amorphous silica (blue). The layer thickness cannot be resolved.

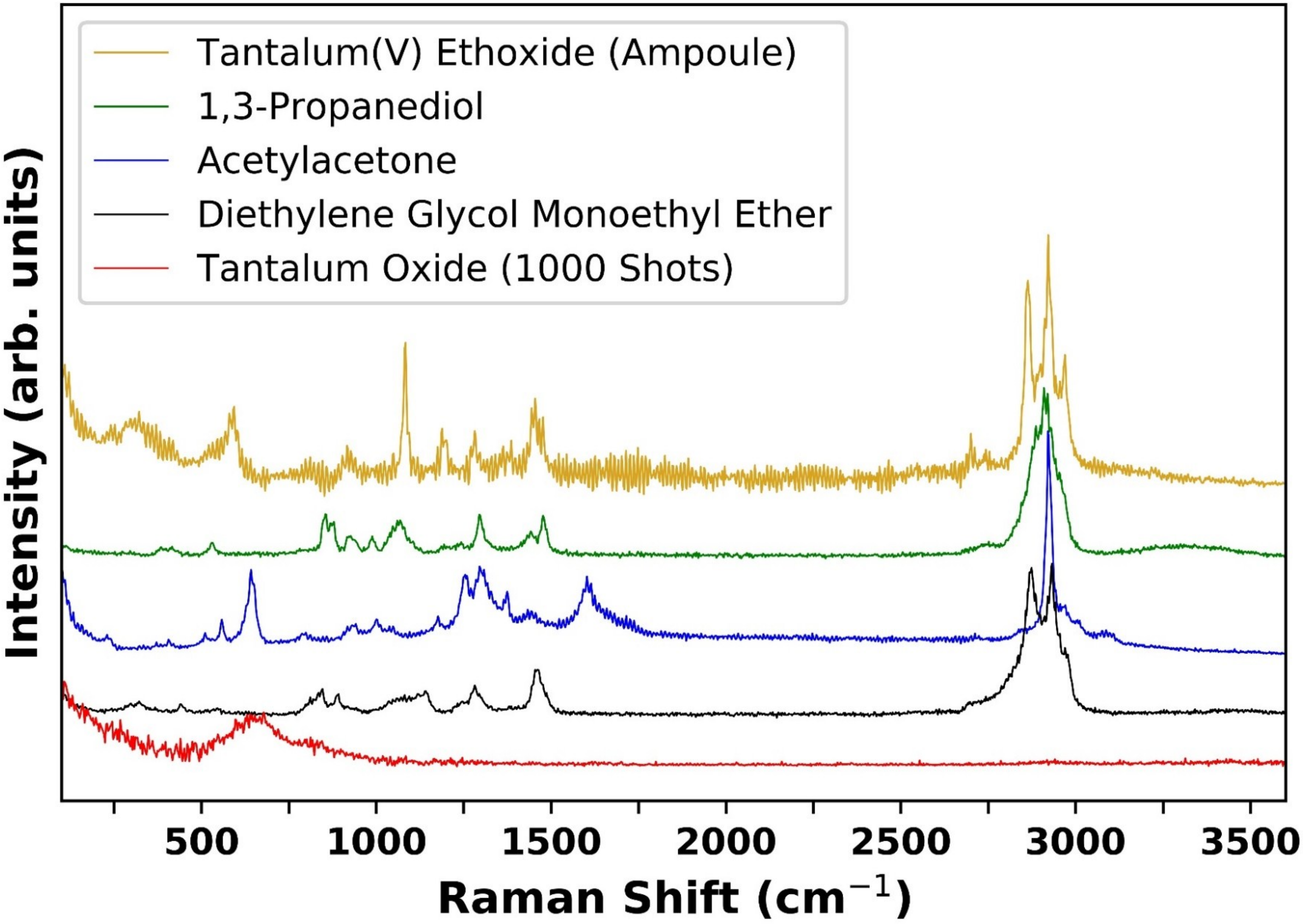


Figure S21: Shifted Raman spectra of precursor solutions, showing that most peaks are absent in the 1000 shot sample.

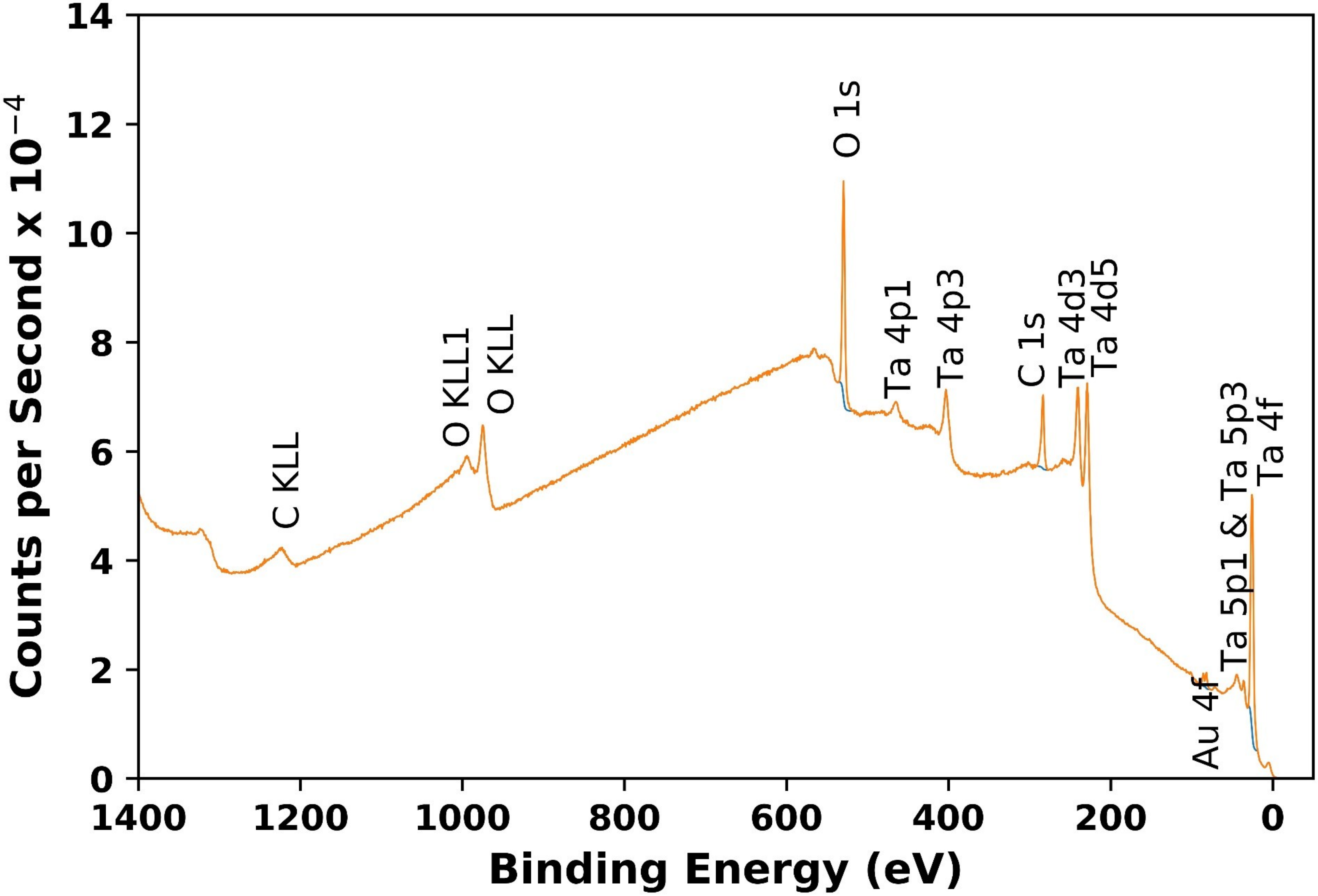


Figure S22: XPS survey spectrum of the 0 shot sample on wet etched Au/Ti/PET foil.

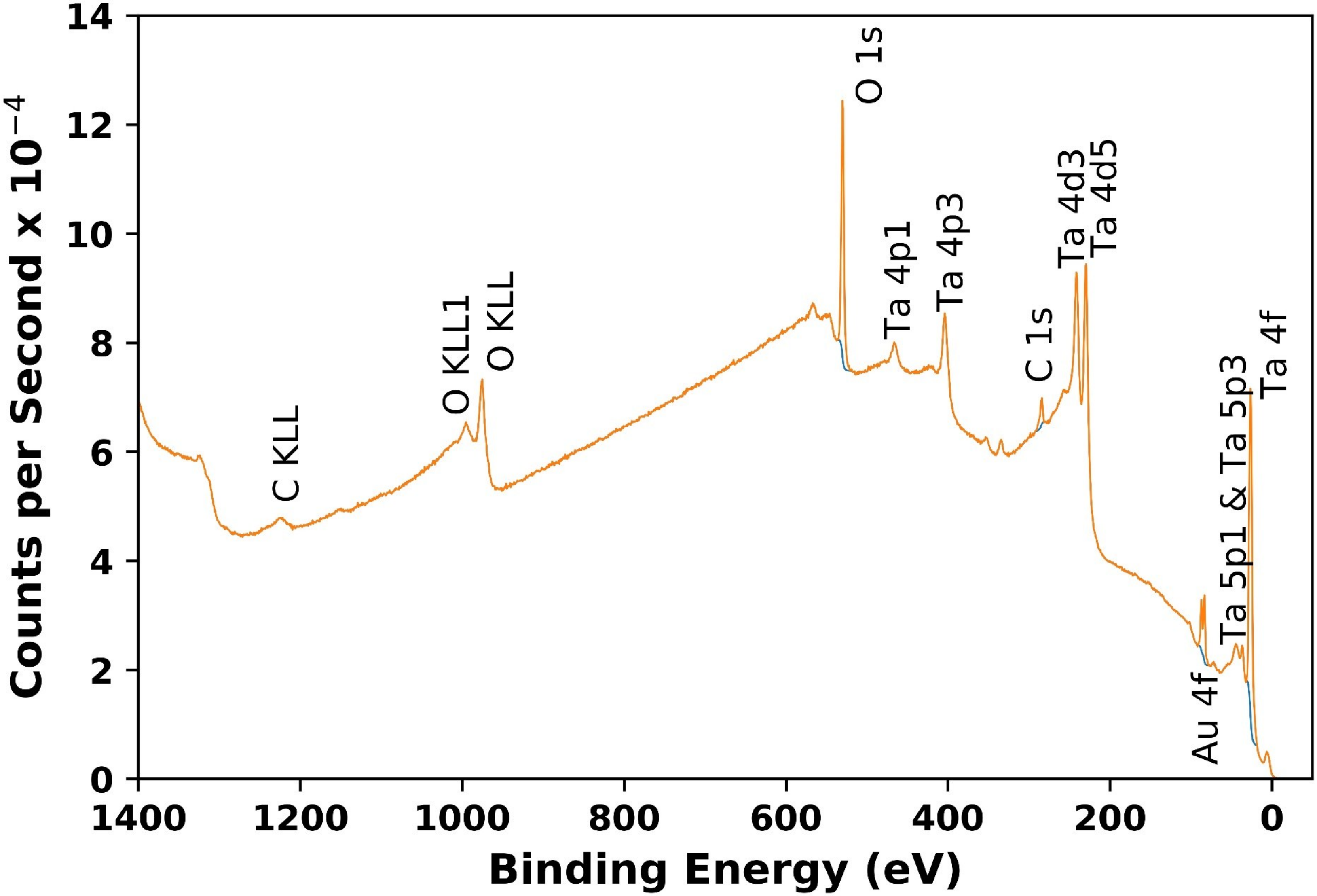


Figure S23: XPS survey spectrum of the 1000 shot sample on wet etched Au/Ti/PET foil.

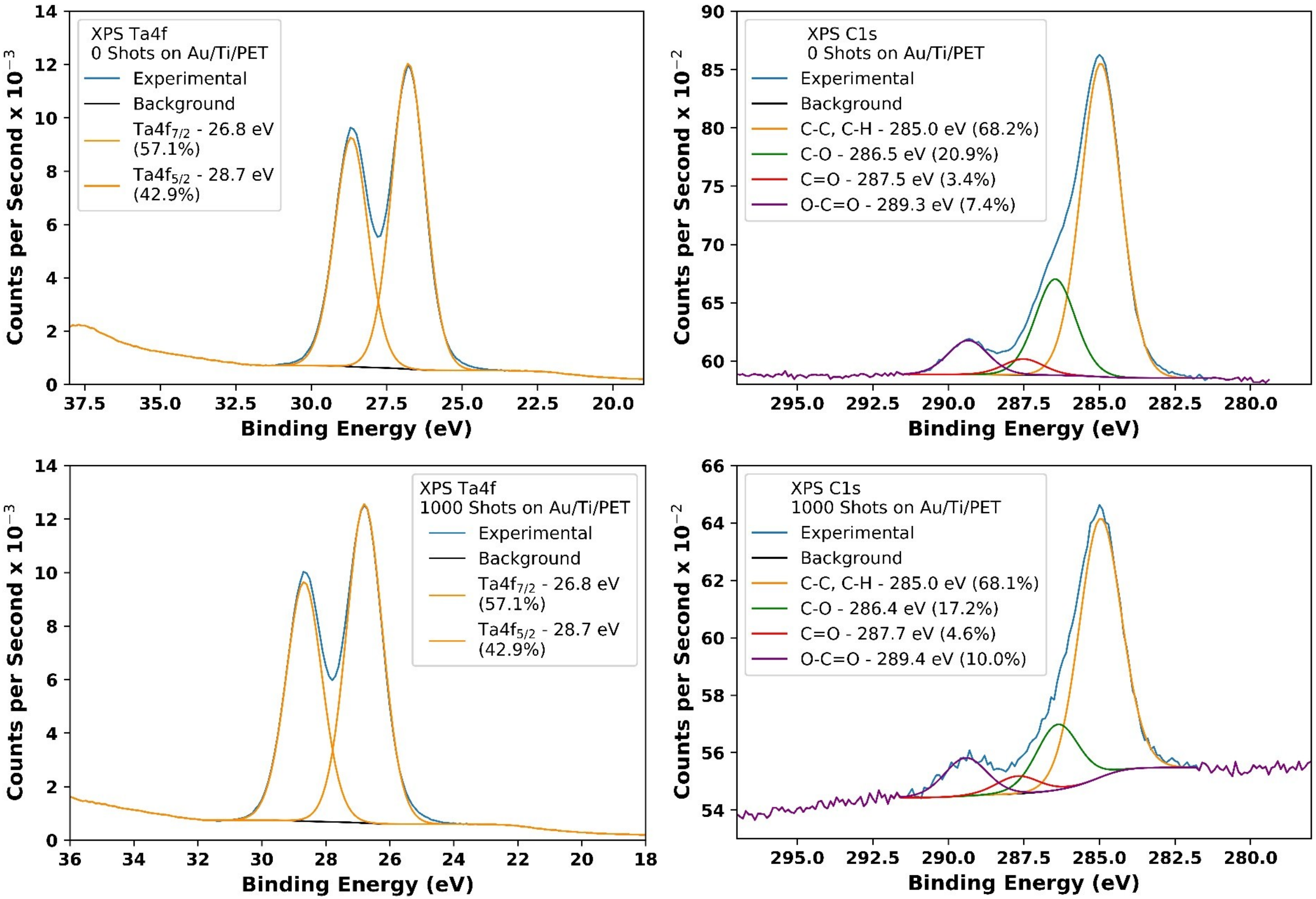


Figure S24: XPS scans of Ta4f and C1s peaks for both 0 shots and 1000 shots samples – percentages are calculated peak areas.

Synthesis with Calzada and González precursor and acetylacetone

A modified procedure from Calzada and González[1,2] was used in an attempt to create a tantalum(V) acetylacetonate 1,3-propanediolate solution, and see whether alcoholysis is possible in the absence of ethanol. 1,3-Propanediol (42.37 mmol, 3224 mg [Sigma-Aldrich, for synthesis]) and tantalum(V) ethoxide (6.02 mmol, 2445 mg [Alfa Aesar, 99+%]) were mixed together via magnetic stirring in a dry Schlenk flask in an argon filled glovebox, and were subsequently removed from the glovebox and connected to a Schlenk line. A short-path distillation setup was used, where the Schlenk flask containing the reagents (reaction flask) was immersed in silicone oil, with the oil temperature being held and maintained at 130°C. The reaction was carried out in argon, and the vertical condenser was pointed towards the distillation flask for 24 hours with mixing to distill the ethanol from the reactor flask.

The distillate was then collected and the system was then exposed to air for 5 hours to decrease the pressure above the reacting solution and to be sure the ethanol was removed from the reaction flask. After 5 hours, some of the product (710 mg) was removed from the reaction flask, and was sent along with the distillate for NMR measurements. Acetylacetone (5.05 mmol, 506 mg [Alfa-Aesar, 95%]) was then added to the reaction flask, followed by reconnecting the flask to the Schlenk line. The flask was then heated to 80°C and mixed for 72 hours in argon. Relatively long lengths of time have been used in past experiments to either improve solubility[3] of metal acetylacetonate complexes or their yield.[4] NMR was used to characterize the product.

NMR: Calzada and González tantalum(V) 1,3-propanediolate precursor with acetylacetone

In preparing the tantalum(V) 1,3-propanediolate product, distillate results show only the presence of ethanol; ^{1}H NMR (δ [ppm], Figure S26): δ 1.72 [$HOCH_2C\mathit{H}_3$], δ 4.15 [$HOC\mathit{H}_2CH_3$], δ 5.86 [$\mathit{H}OCH_2CH_3$]; ^{13}C NMR (δ [ppm], Figure S27): δ 15.8 [$HOCH_2\mathit{C}H_3$], δ 55.2 [$HO\mathit{C}H_2CH_3$]. Product results indicate the presence of 1,3-propanediol; ^{1}H NMR (δ [ppm], Figure S28): δ 1.77 [$HOCH_2C\mathit{H}_2CH_2OH$], δ 3.68 [$HOC\mathit{H}_2CH_2C\mathit{H}_2OH$], δ 5.41 [$\mathit{H}OCH_2CH_2CH_2O\mathit{H}$] (a relatively large D_2O peak at δ 4.54 is present due to the low sample volume); ^{13}C NMR (δ [ppm], Figure S29): δ 35.3 [$HOCH_2\mathit{C}H_2CH_2OH$], δ 59.0 [$HO\mathit{C}H_2CH_2\mathit{C}H_2OH$]. The results corroborate those obtained by Calzada and González.[1,2]

The ^{1}H NMR spectrum of the product with added acetylacetone (δ [ppm], Figures S30 and S31) shows the presence of the expected 1,3-propanediol peaks at δ 1.83 [$HOCH_2C\mathit{H}_2CH_2OH$], δ 3.74 [$HOC\mathit{H}_2CH_2C\mathit{H}_2OH$], and δ 5.18 [$\mathit{H}OCH_2CH_2CH_2O\mathit{H}$]. Two separate methine acetylacetone-enol peaks appear at δ 5.98 and δ 5.88 [$H_3C(CO)C\mathit{H}(CO)CH_3$]. An acetylacetone-keto methyl peak [$\mathit{H}_3C(CO)CH_2(CO)C\mathit{H}_3$] or acetone-methyl peak from alcoholysis[5,6] [$\mathit{H}_3C(CO)C\mathit{H}_3$] occurs at δ 2.28. An acetylacetone-enol methyl peak [$\mathit{H}_3C(CO)CH(CO)C\mathit{H}_3$] occurs at δ 2.23. The δ 4.23 peak occurs as a triplet and indicates coupling to two protons with the same coupling constant on neighboring carbon atom(s); the peak at δ 4.67 is difficult to assign with the available data. Due to the fact that the δ 4.23 peak resonates at a higher frequency than the alcoholic methylene 1,3-propanediol peak at δ 3.74, in addition to the large methyl peak at δ 2.15, likely indicates the acetylation of 1,3-propanediol and the creation of 3-hydroxypropyl acetate.[7] The δ 2.15 peak would then correspond to the methyl attached to the ester carbonyl [$HOCH_2CH_2CH_2O(CO)C\mathit{H}_3$],

Figure S25: Final solution products from method based on Calzada and González with acetylacetone (a), the proposed method with acetylacetone (b), and the proposed method with benzoylacetone (c). (a) has an enhanced color when compared to (b) – this may be caused by light scattering from nanoparticle formation by alcoholysis in (a). (c) appears redshifted relative to (b).

and the peak at δ 4.23 would be the protons on the methylene carbon bound to the ester oxygen $[\mathrm{HOCH_2CH_2C}\textit{H}_2\mathrm{O(CO)CH_3}]$. In support of this, the TOCSY spectrum in Figure S32 shows three distinct proton groups on three consecutive carbon atoms, and the ^{13}C NMR and HMBC spectra corroborate these findings, as well as the literature values for 3-hydroxypropyl acetate.[8]

The ^{13}C NMR spectrum of the product (δ [ppm], Figure S33) shows the expected 1,3-propanediol peaks at δ 35.3 $[\mathrm{HOCH_2}\textit{C}\mathrm{H_2CH_2OH}]$ and δ 59.0 $[\mathrm{HO}\textit{C}\mathrm{H_2CH_2}\textit{C}\mathrm{H_2OH}]$. Enol peaks around δ 191.0 $[\mathrm{H_3C(}\textit{C}\mathrm{O)CH(}\textit{C}\mathrm{O)CH_3}]$, around δ 104.0 $[\mathrm{H_3C(CO)}\textit{C}\mathrm{H(CO)CH_3}]$, and around δ 26.2 $[\mathrm{H_3}\textit{C}\mathrm{(CO)CH(CO)}\textit{C}\mathrm{H_3}]$ appear in the spectrum. Either acetylacetone-keto, or acetone from alcoholysis,[5,9] peaks are visible at δ 208.9 $[\mathrm{H_3C(}\textit{C}\mathrm{O)CH_2(}\textit{C}\mathrm{O)CH_3}]$ or $[\mathrm{H_3C(}\textit{C}\mathrm{O)CH_3}]$, and δ 30.5 $[\mathrm{H_3}\textit{C}\mathrm{(CO)CH_2(CO)}\textit{C}\mathrm{H_3}]$ or $[\mathrm{H_3}\textit{C}\mathrm{(CO)}\textit{C}\mathrm{H_3}]$. The peak at δ 171.7 $[\mathrm{HOCH_2CH_2CH_2O(}\textit{C}\mathrm{O)CH_3}]$, not associated with any of the reagents, is located in the range typically found for ester carbonyl carbons[7] and would support the idea that 1,3-propanediol has been acetylated to create 3-hydroxypropyl acetate. This is supported by literature[8] and by the HMBC spectrum in Figure S34, which shows cross-peaks at ^{1}H δ 2.15 – ^{13}C δ 171.7 and ^{1}H δ 4.23 – ^{13}C δ 171.7. HMBC also shows no visible cross-peak at ^{1}H δ 4.67 – ^{13}C δ 171.7, possibly indicating that the compound with the ^{1}H δ 4.67 peak does not contain an acetylated alcohol.

The yellow color of the solution in Figure S25 may be enhanced by light scattering from nanoparticle formation after alcoholysis.[10–12] However, this would need to be confirmed with dynamic light scattering experiments. Interesting to note is that no visible, insoluble precipitates form, unlike with Ti(IV) and Zr(IV) acetylacetonate complexes with 1,3-propanediol.[5] Furthermore, as 3-hydroxypropyl acetate appears to be present in the NMR spectra, efforts to minimize alcoholysis side reactions should be undertaken.

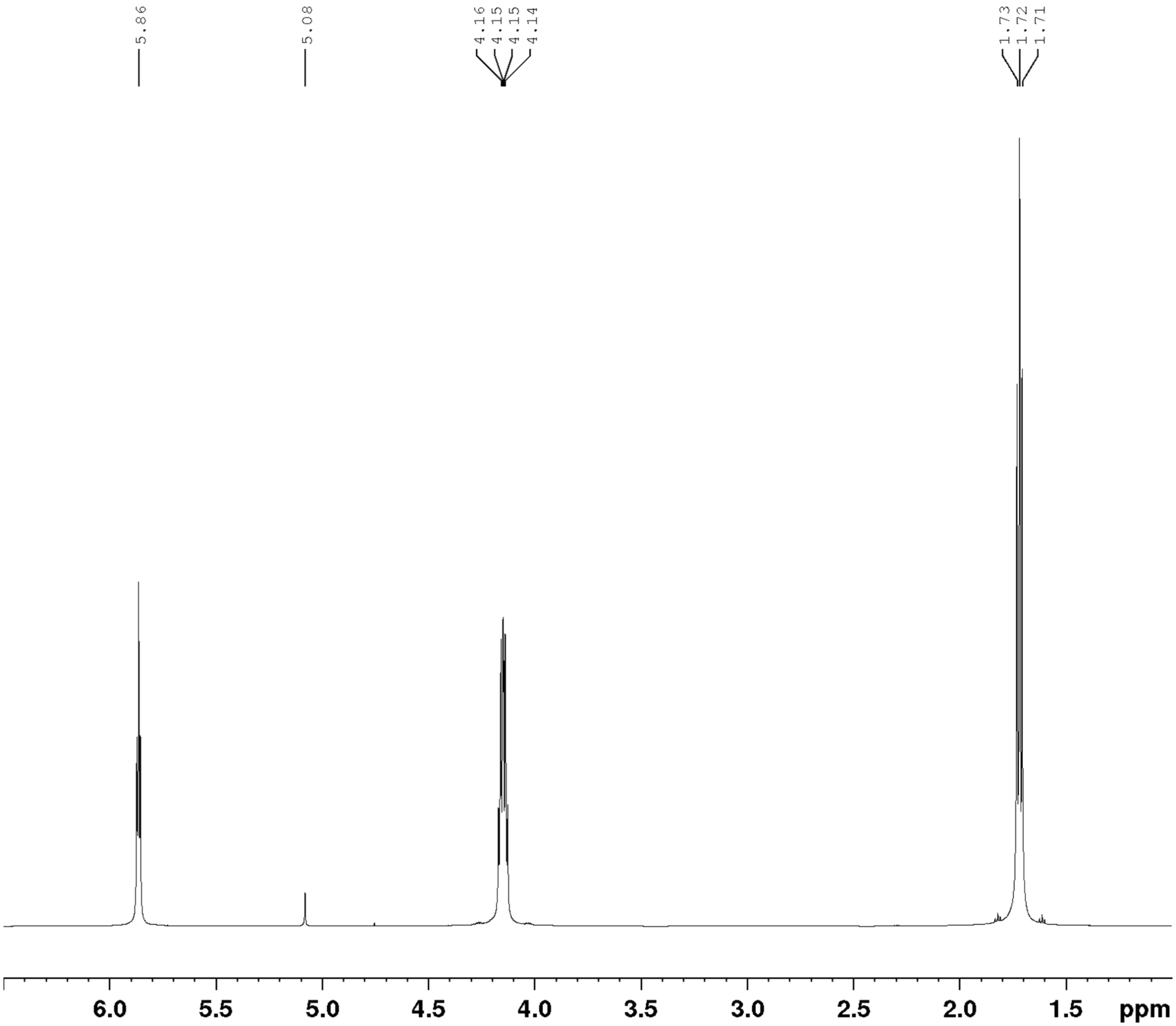


Figure S26: ^{1}H NMR [External D_2O]: Calzada and González – Distillate

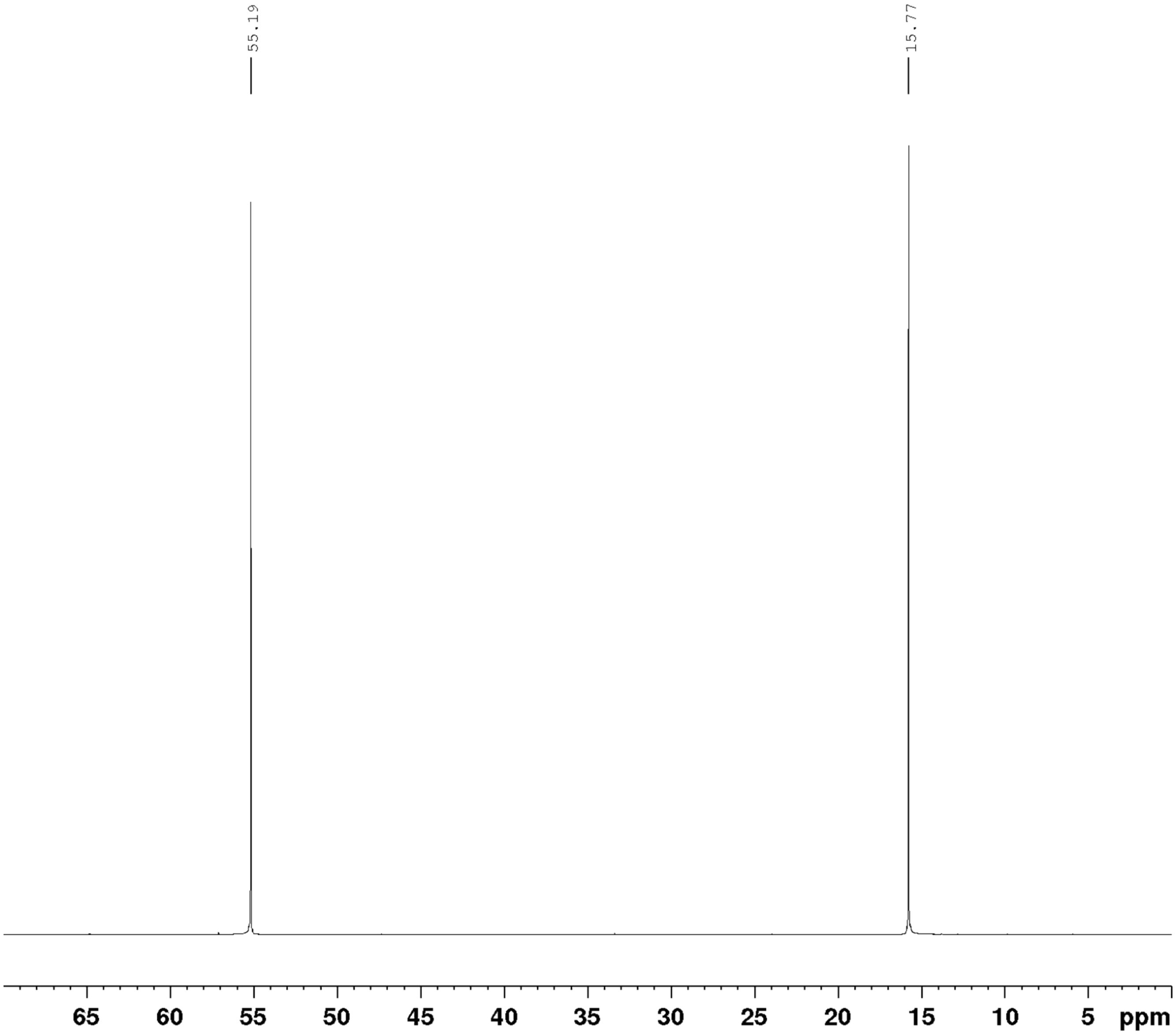


Figure S27: ^{13}C NMR [External D_2O]: Calzada and González – Distillate

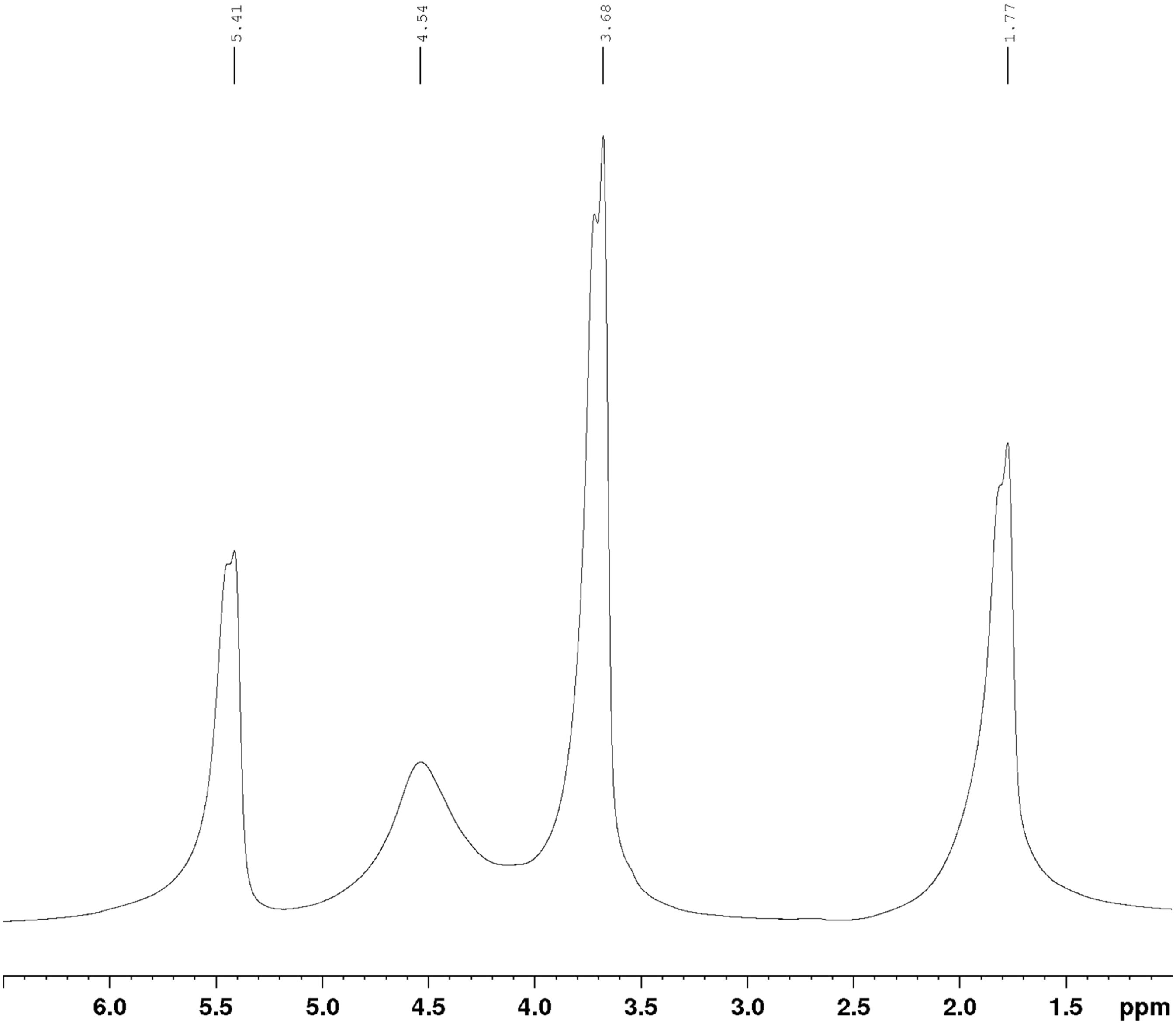


Figure S28: ^{1}H NMR [External D_2O]: Calzada and González – Tantalum(V) 1,3-propanediolate

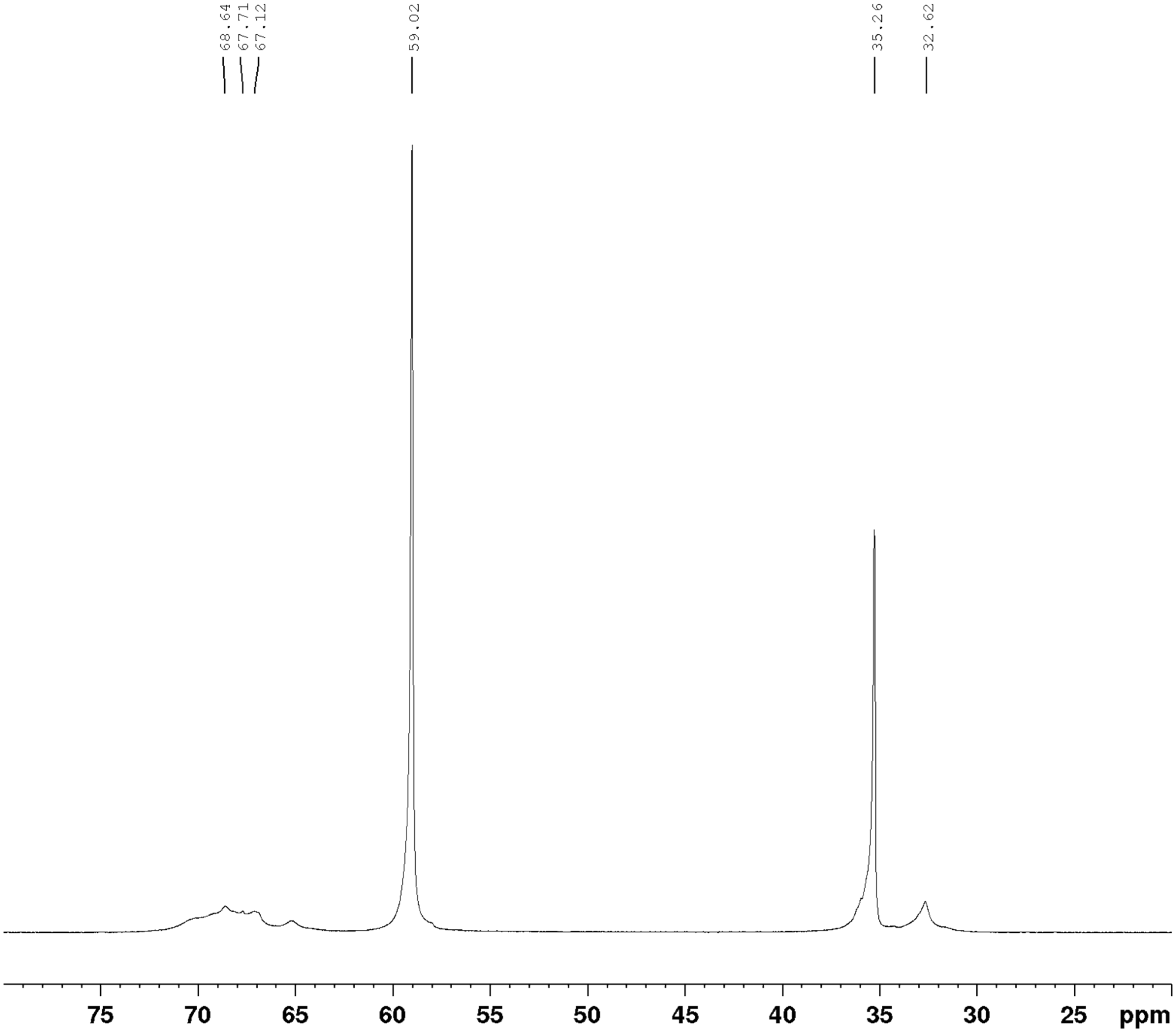


Figure S29 ^{13}C NMR [External D_2O]: Calzada and González – Tantalum(V) 1,3-propanediolate

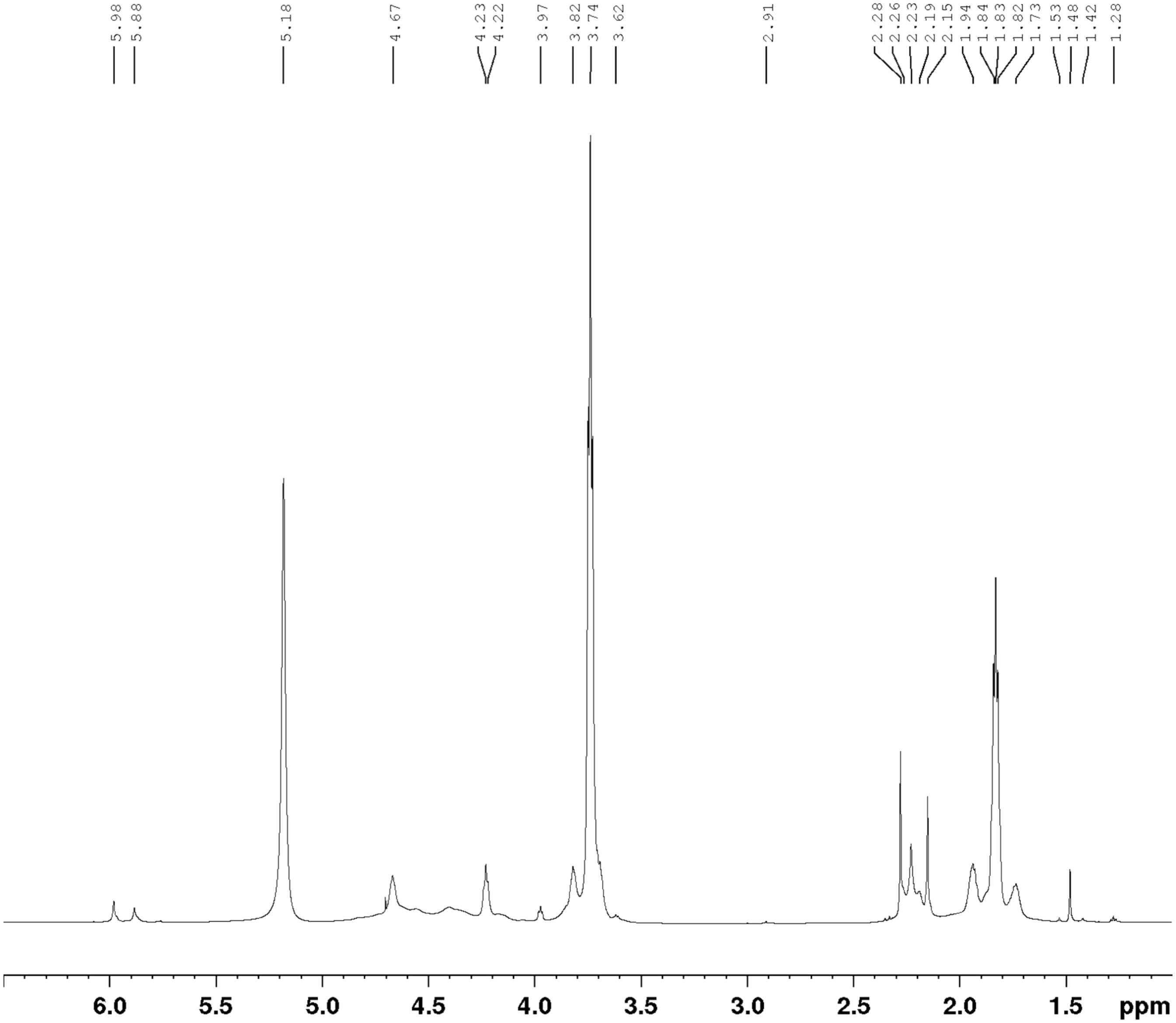


Figure S30: ^{1}H NMR [External D_2O]: Calzada and González – Tantalum(V) 1,3-propanediolate with acetylacetone

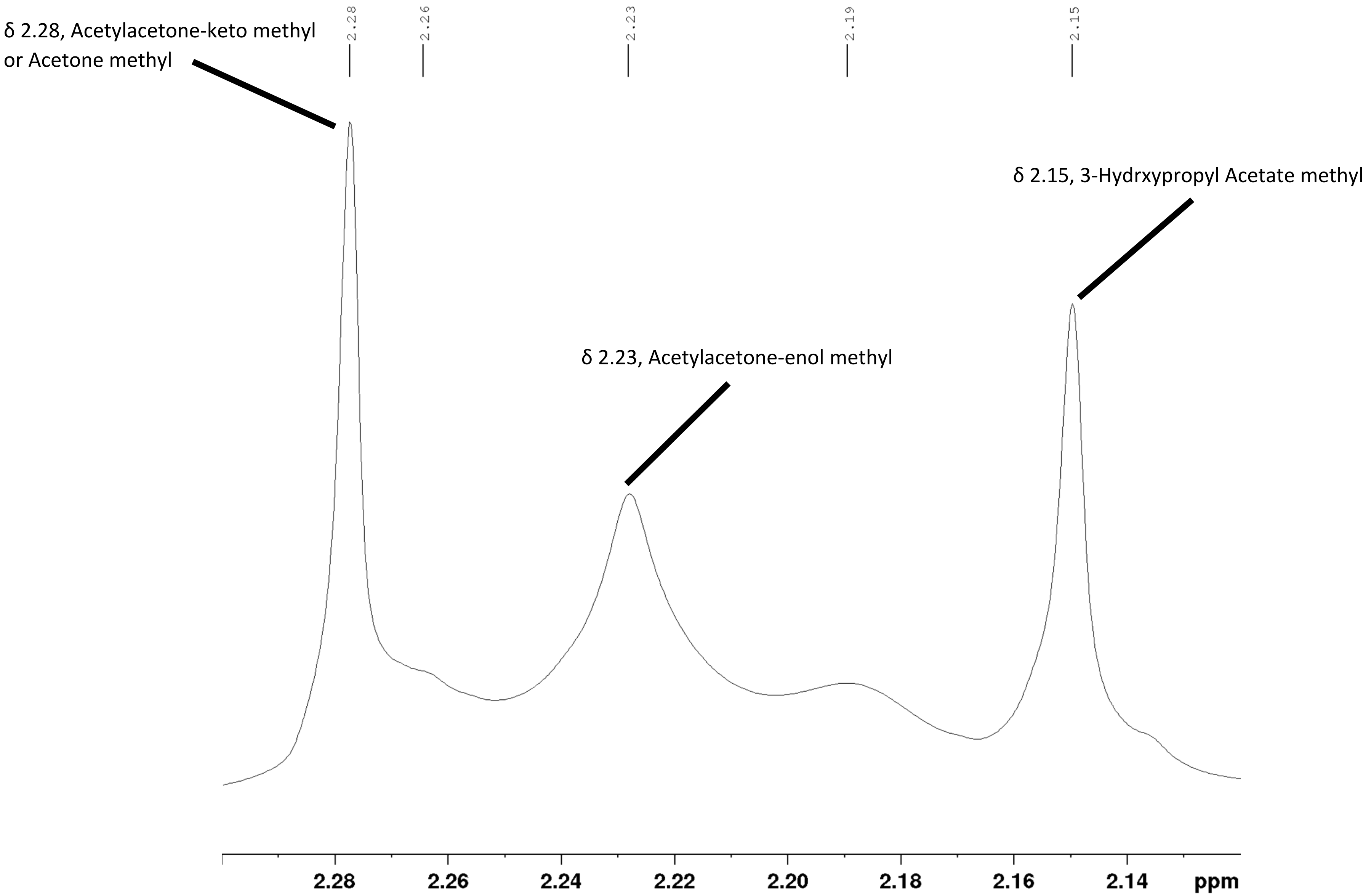


Figure S31: ^{1}H NMR [External D_2O]: Calzada and González – Tantalum(V) 1,3-propanediolate with acetylacetone

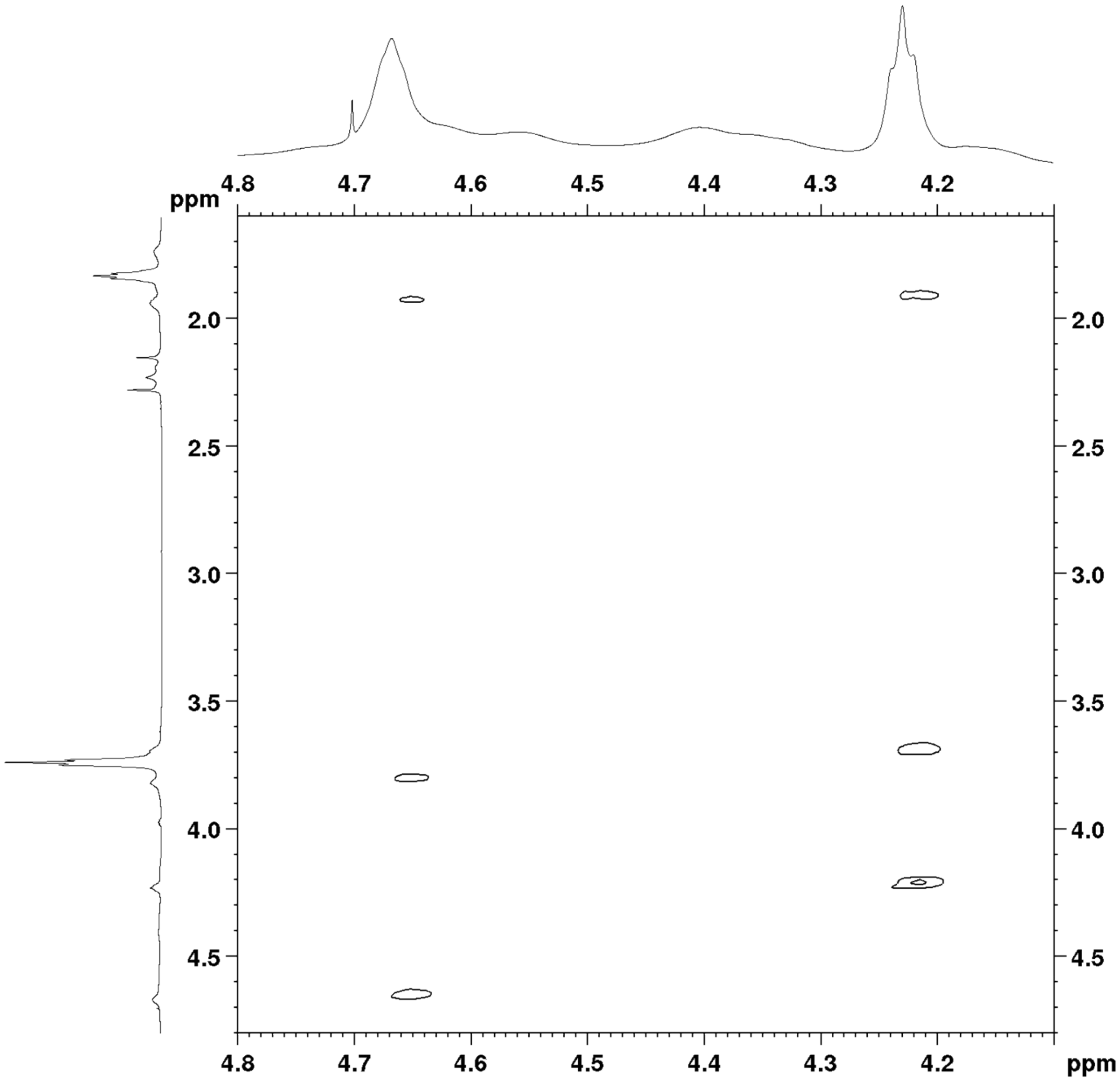


Figure S32: TOCSY [External D_2O]: Calzada and González – Tantalum(V) 1,3-propanediolate with acetylacetone

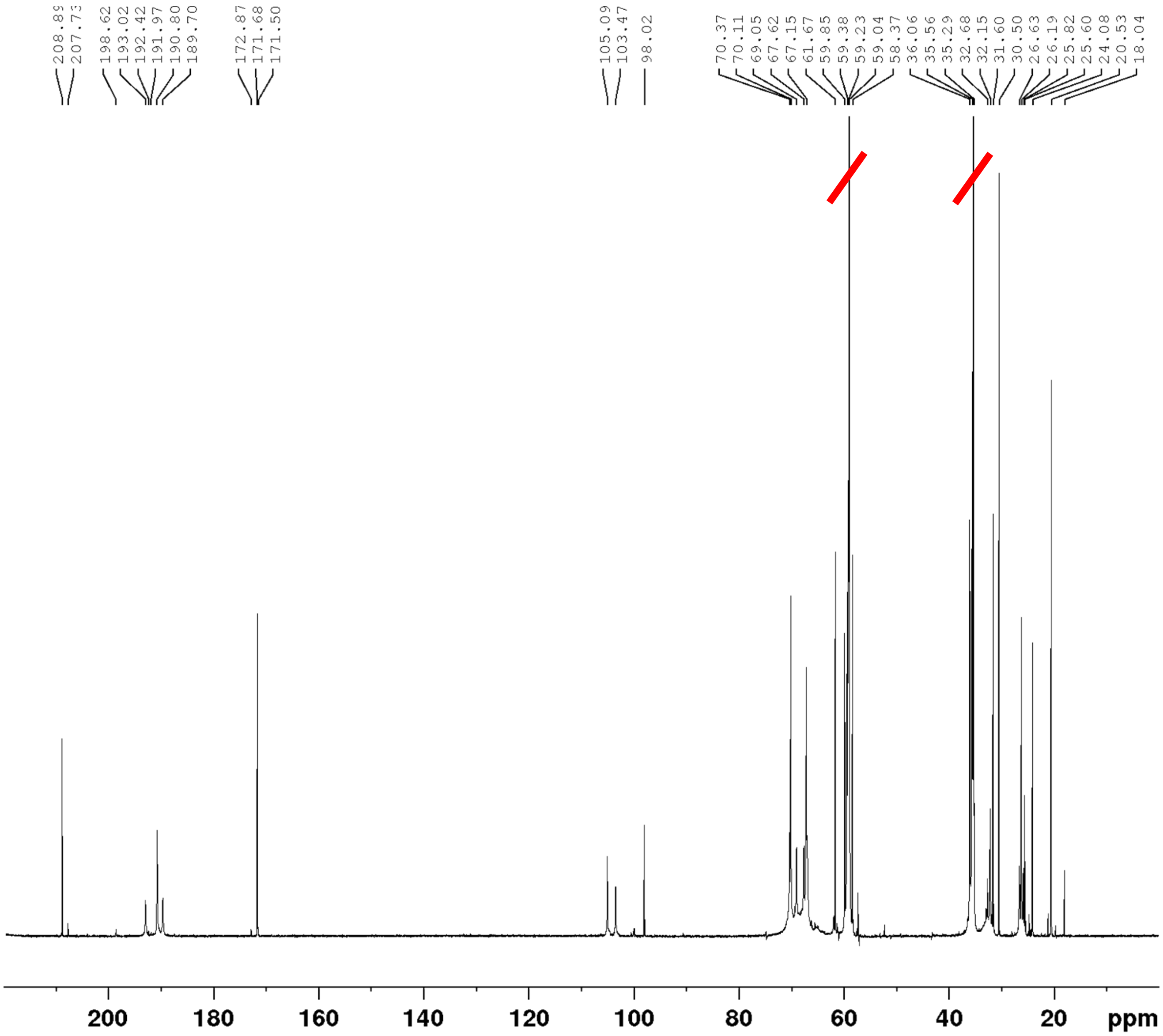


Figure S33: ^{13}C NMR [External D_2O]: Calzada and González – Tantalum(V) 1,3-propanediolate with acetylacetone

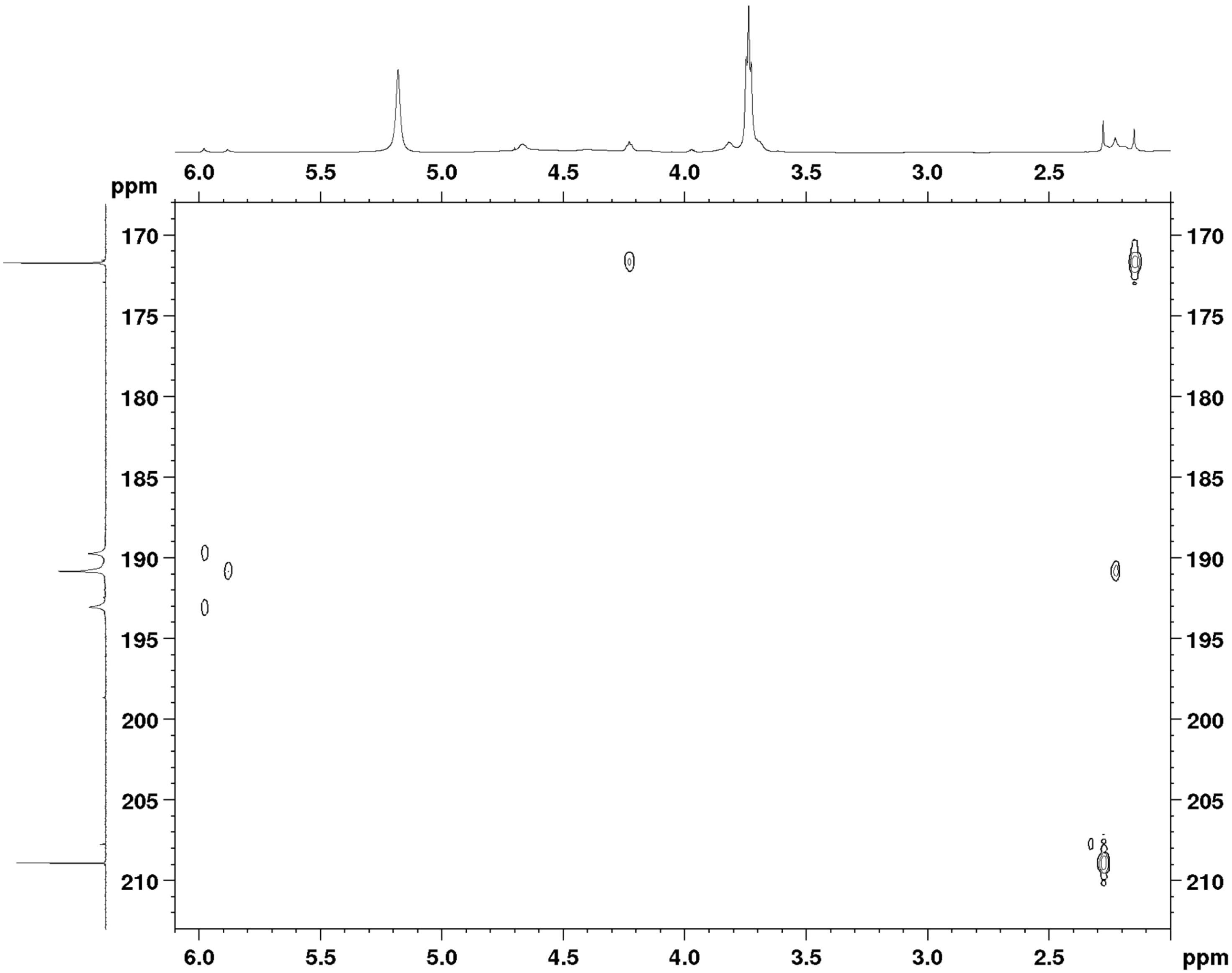


Figure S34: HMBC [External D_2O]: Calzada and González – Tantalum(V) 1,3-propanediolate with acetylacetone

Proposed Synthesis (Acetylacetone) – Replacing Ta(V) Ethoxide with Ti(IV) Isopropoxide

Anhydrous ethanol (42.00 mmol, 1935 mg [AcrosOrganics, 99.5%, ExtraDry, absolute]), acetylacetone (6.00 mmol, 601 mg, [Alfa-Aesar, 95%]), and titanium(IV) isopropoxide (6.01 mmol, 1708 mg [Sigma-Aldrich, 97%]) were mixed together via magnetic stirring in a dry Schlenk flask in an argon filled glovebox, and were subsequently removed from the glovebox and connected to a Schlenk line. The Schlenk flask containing the reagents (reaction flask) was immersed in silicone oil, with the oil temperature being held and maintained at 80°C to promote chelation of acetylacetone and match the preparation of the tantalum(V) ethoxide acetylacetonate precursor. The reaction was carried out in argon, and reflux was conducted for 8 hours with mixing to allow enough time for complexation of acetylacetone to titanium; the reaction time was minimized as much as possible in order to prevent decomposition of the complex.[5]

After 8 hours, the flask was cooled to 23°C over a 2 hour period. 1,3-Propanediol (36.38 mmol, 2768 mg [Sigma-Aldrich, for synthesis]) was then added via syringe through the Schlenk flask valve and mixed, where bubbles appeared for a short time but eventually disappeared. After 12 hours of mixing at a reduced temperature, the Schlenk flask was removed from the Schlenk line. The product was subsequently transferred from the Schlenk flask to a round bottom flask, and the round bottom flask was then connected to a rotary evaporator. The rotation speed was set to 95 rpm, the pressure was set to 30 mbar, and the water bath temperature was set to 40°C. Vigorous bubbling was present at the beginning, but the bubbling eventually dissipated. The flask remained attached for 8 hours, where afterward it was found that the mass loss (3030 mg) was close to the calculated ethanol and isopropanol loss (3380 mg).

After adding 1,3-propanediol at room temperature, the Ti(IV) acetylacetonate solution turns turbid over time as shown in Figure S35, in contrast to the Ta(V) solutions in Figure S25. This may be due to the formation of a Ti(IV)$(OC_3H_6O)_2$ precipitate, with both terminal oxygens on the diol bound to the cation as reported by Kemmitt and Daglish.[5] In contrast to the even valency of +4 for Ti(IV), Ta(V) has an odd valency of +5 and suggests that the proposed synthesis may only work for Ta(V),[1,2,13] and possibly Nb(V),[14] glycolate β-diketonate solutions.

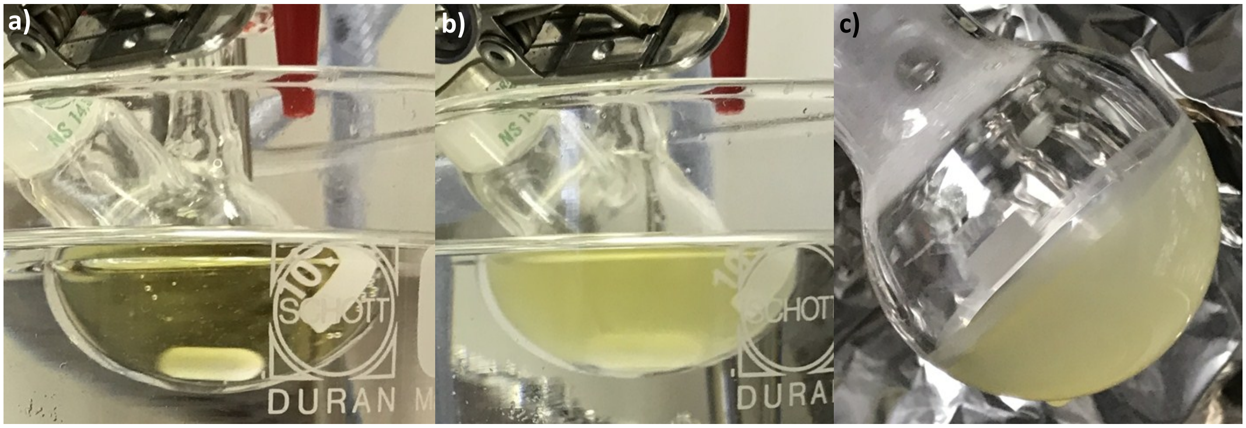


Figure S35: After addition of 1,3-propanediol to the Ti(IV) acetylacetonate solution (a), 12 hours after 1,3-propanediol addition (b), and after removal of isopropanol and ethanol (c). In contrast to the Ta(V) solutions, the Ti(IV) solution turns turbid over time at room temperature.

References

1 A. González García, Autonomous University of Madrid, 2002.

2 M. L. Calzada and A. González, *J. Am. Ceram. Soc.*, 2005, **88**, 2702–2708.

3 M. T. Colomer and J. R. Jurado, *Chem. Mater.*, 2000, **12**, 923–930.

4 N. Noma and M. Hamano, *J. Sol-Gel Sci. Technol.*, 2012, **64**, 297–303.

5 T. Kemmitt and M. Daglish, *Inorg. Chem.*, 1998, **37**, 2063–2065.

6 S. S. Likhodii and W. M. Burnham, *Med. Sci. Monit.*, 2002, **8**, HY19-24.

7 J. B. Lambert, E. P. Mazzola and C. D. Ridge, *Nuclear Magnetic Resonance Spectroscopy: An Introduction to Principles, Applications, and Experimental Methods*, John Wiley & Sons, Inc., Hoboken, 2nd edn., 2019.

8 Y. Zhao, J. Q. L. Ang, A. W. T. Ng and Y.-Y. Yeung, *RSC Adv.*, 2013, **3**, 19765.

9 Y. Takebayashi, S. Yoda, T. Sugeta, K. Otake, T. Sako and M. Nakahara, *J. Chem. Phys.*, 2004, **120**, 6100–6110.

10 M. Staniuk, D. Zindel, W. van Beek, O. Hirsch, N. Kränzlin, M. Niederberger and D. Koziej, *CrystEngComm*, 2015, **17**, 6962–6971.

11 G. Ambrožič, S. D. Škapin, M. Žigon and Z. C. Orel, *J. Colloid Interface Sci.*, 2010, **346**, 317–323.

12 R. K. Sodhi and S. Paul, *Catal. Surv. from Asia*, 2018, **22**, 31–62.

13 R. C. Mehrotra and P. N. Kapoor, *J. Less-Common Met.*, 1965, **10**, 237–245.

14 R. C. Mehrotra and P. N. Kapoor, *J. Less Common Met.*, 1965, **8**, 419–427.