Supporting Information

Molybdate Ionic Liquids as Halide-Free Catalysts for CO_2 Fixation into Epoxides

Nicola Bragato, Alvise Perosa, Maurizio Selva, Giulia Fiorani*, Roberto Calmanti*

Department of Molecular Sciences and Nanosystems, Università Ca' Foscari Venezia, Via Torino 155, 30172 Mestre–Venezia, Italia

* Correspondence: roberto.calmanti@unive.it; giulia.fiorani@unive.it

Table of Contents

1. Experimental Section

1.1 Materials and Methods

All reagents and solvents employed [ethyl acetate (EtOAc), diethyl ether (Et_2O), petroleum ether, methanol (MeOH), mesitylene (MES), dimethylcarbonate (DMC), trioctylammine (TOA), styrene oxide (SO), 1,2-epoxyhexane, butyl glycidyl ether, pheny glycidyl ether, limonene oxide, silica gel (70-230 mesh), chloroform-*d* ($CDCl_3$), CD_3CN-d_3 and dimethyl sulfoxide-d_6 (DMSO-d_6)] were purchased from Sigma Aldrich (now Merck) with ≥ 98 % purity, and used without further purification, unless otherwise specified. CO_2 (99.999 %) was supplied by SIAD.

Qualitative and quantitative analysis and characterization of reaction mixtures and pure products were performed with:

- GC-MS system consisting of an Agilent 6890N GC equipped with an HP-5 capillary column (30m·0.32mm, film thickness: 0.25mm), coupled with Agilent Technologies 5975 mass detector operating at 70 eV;
- Bruker Ascend 400 (AV400) NMR spectrometer, operating at 400 MHz for ^1H, 100 MHz for ^{13}C, 75 Hz for ^{31}P and 26 Hz for ^{95}Mo nuclei.
- Perkin-Elmer Spectrum One FT-IR spectrometer (PerkinElmer Italia, Milano, Italy) recording at wavenumbers ranging from 400 to 4000 cm^{-1} .
- Nexion ICP-MS 350XX coupled with seaFAST autosampler. KED mode (4.4 ml of He) using Pt 195 as internal standards.

GC-MS analyses were performed in EtOAc or Et_2O, while ^1H NMR and ^{13}C NMR samples were prepared using deuterated solvents ($CDCl_3$, CD_3CN-d^3 or DMSO-d_6, > 99.9 % D in all cases). For ^1H and ^{13}C NMR spectra, the deuterated solvent residual signal was selected as the spectrum reference. ^{95}Mo NMR spectra were referenced to a 2 M Na_2MoO_4 in D_2O external standard (δ = 0 ppm). The spectra were acquired on saturated DMSO-d_6 or CD_3CN-d_3 samples using a sweep width of 1000 ppm, an acquisition time of 2 s per scan, and, depending on the sample, acquiring 2000 to 5000 scans.

1.2 Method for the quantification of conversion, selectivity and yield by ^1H-NMR analysis.

The NMR samples used for quantitative determination were prepared by dissolving a few milligrams of the respective reaction mixture (*ca*. 10 mg) in *ca*. 0.8 ml of deuterated solvent ($CDCl_3$). Quantitative ^1H-NMR experiments were run recording 32 scans with a time delay of 30 s in order to ensure the maximum signal-to-noise ratio.

Quantifications were performed on 1D ^1H NMR spectra by proportional comparison of the peak areas integrated for both the selected signal from the internal standard (IS) and from the analyte (X) applying Eq. (1),:

$$Nmol_{(x)} = \frac{A_{(x)}}{nH_{(x)}} \cdot \frac{nH_{(IS)}}{A_{(IS)}} \cdot \frac{m_{(IS)}}{MW_{(IS)}} \cdot P_{(IS)} \qquad \text{(Eq. 1)}$$

Where $Nmol_{(x)}$ is the number of moles of the analyte, $nH_{(x)}$ and $nH_{(IS)}$ are the number of protons generating the selected signals for integration, $A_{(x)}$ and $A_{(IS)}$ are the areas for the selected peaks of the analyte (X) and the internal standard (IS), all respectively, $m_{(IS)}$ is the mass (weight) in grams of internal standard introduced, $MW_{(IS)}$ is the molecular weight (120.19 g·mol-1) of the IS, $P_{(IS)}$ is the purity (98 %) of the IS.

Conversion, selectivity and the yield were calculated using Eq. 2, Eq. 3 and Eq. 4 respectively.

$$Conv\ (\%) = \frac{N\ mol_i - N\ mol_f}{N\ mol_i} * 100 \qquad \text{(Eq. 2)}$$

Where *Nmol*$_i$ is the number of initial moles and *Nmol*$_f$ is the number of final moles.

$$Sel\ (\%) = \frac{N\ mol_x}{N\ mol_i - N\ mol_f} * 100 \qquad \text{(Eq. 3)}$$

Where *Nmol*$_x$ is the number of moles of product x forming during the reaction. In this specific case the selectivity is always expressed towards the COC product.

$$Yield\ (\%) = \frac{N\ mol_x}{N\ mol_{x\ teorical}} * 100 \qquad \text{(Eq. 4)}$$

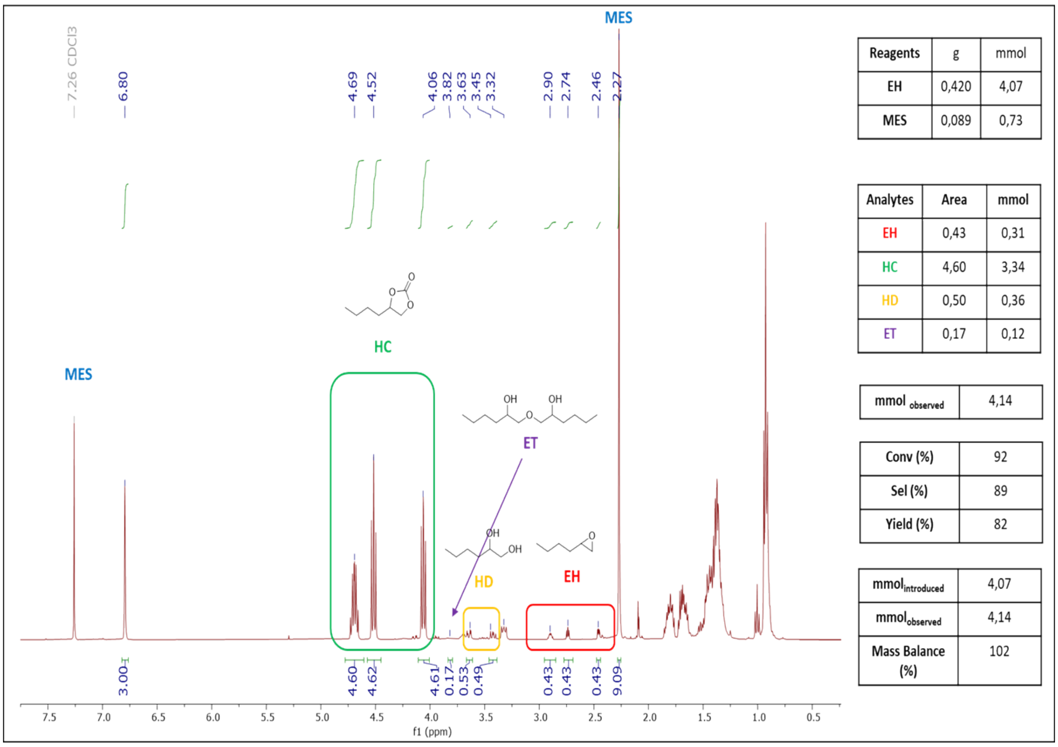
Where *Nmol*$_{x\ teorical}$ is the number of theorical moles of product x forming during the reaction.

In order to confirm the NMR quantification method we also reported the Mass Balance (Eq. 5)

$$Mass\ Balance\ (\%) = \frac{N\ mol_{\ observed\ (NMR)}}{N\ mol_{introduced\ (EH)}} * 100 \qquad \text{(Eq. 5)}$$

Where *Nmol*$_{observed\ (NMR)}$ is the total number of moles observed by ^{1}H-NMR analysis and *Nmol*$_{introduces\ (EH)}$ is the number of 1,2-epoxyhexane introduced at the beginning of the reaction.

In Figure S1 is reported an example of a crude ^{1}H NMR spectra of the reaction mixture of the CO_2 fixation reaction into epoxyhexane (Entry 2, Table S2) in order to show the method for quantification, mass balance calculation and the diagnostic signals of the epoxide, COC product , and main by-prodcuts (diol and polyethers) formed during the reaction.



Reagents	g	mmol
EH	0,420	4,07
MES	0,089	0,73

Analytes	Area	mmol
EH	0,43	0,31
HC	4,60	3,34
HD	0,50	0,36
ET	0,17	0,12

mmol $_{observed}$	4,14

Conv (%)	92
Sel (%)	89
Yield (%)	82

mmol$_{introduced}$	4,07
mmol$_{observed}$	4,14
Mass Balance (%)	102

Figure S1. ^{1}H NMR spectra of the crude reaction mixture of *the reaction reported in Entry 2, Table S2 (cat loading [N$_{4,4,4,4}$]$_2$MoO$_4$ 1.25 % mol).*

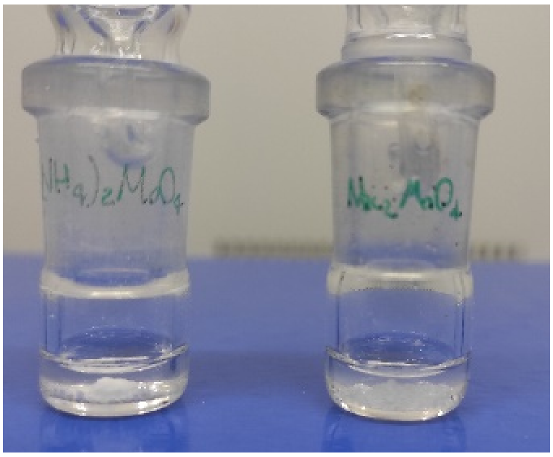


Figure S2. Pictures of crude reaction mixtures with insoluble catalysts: left, catalyst:$(NH_4)_2MoO_4$, Entry 5, Table 1; right: and 6 catalyst: Na_2MoO_4, Entry 6, Table 1.

2. Synthesis of Mo-ILs precursors

2.1 Trioctylmethylammonium methylcarbonate [N_{1888}][CH_3OCOO]

[N_{1888}][CH_3OCOO] was synthesized according to a published methodology.[1]

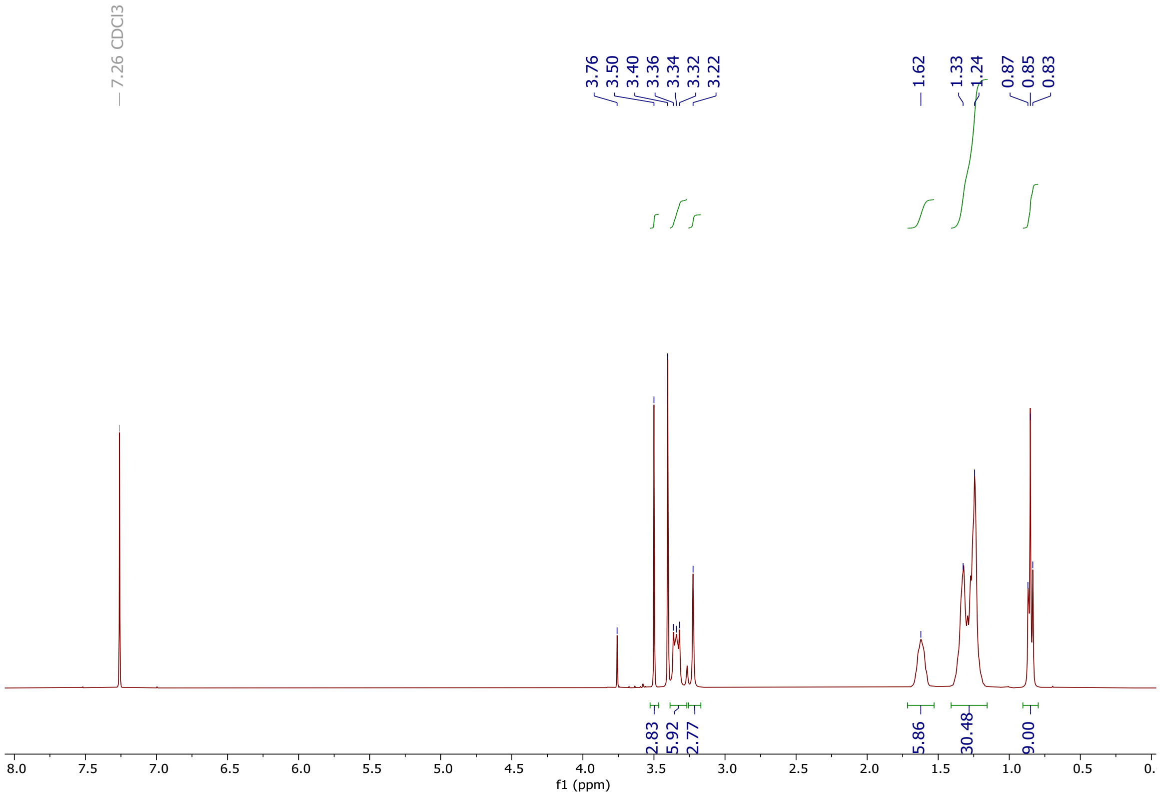


Figure S3. ^1H NMR (400 MHz, $CDCl_3$, 298 K) δ: 3.50 (s, 3H), 3.39 – 3.27 (m, 6H), 3.22 (s, 3H), 1.72 – 1.53 (m, 6H), 1.41 – 1.16 (m, 30H), 0.84 (t, *J* = 6.5 Hz, 9H).

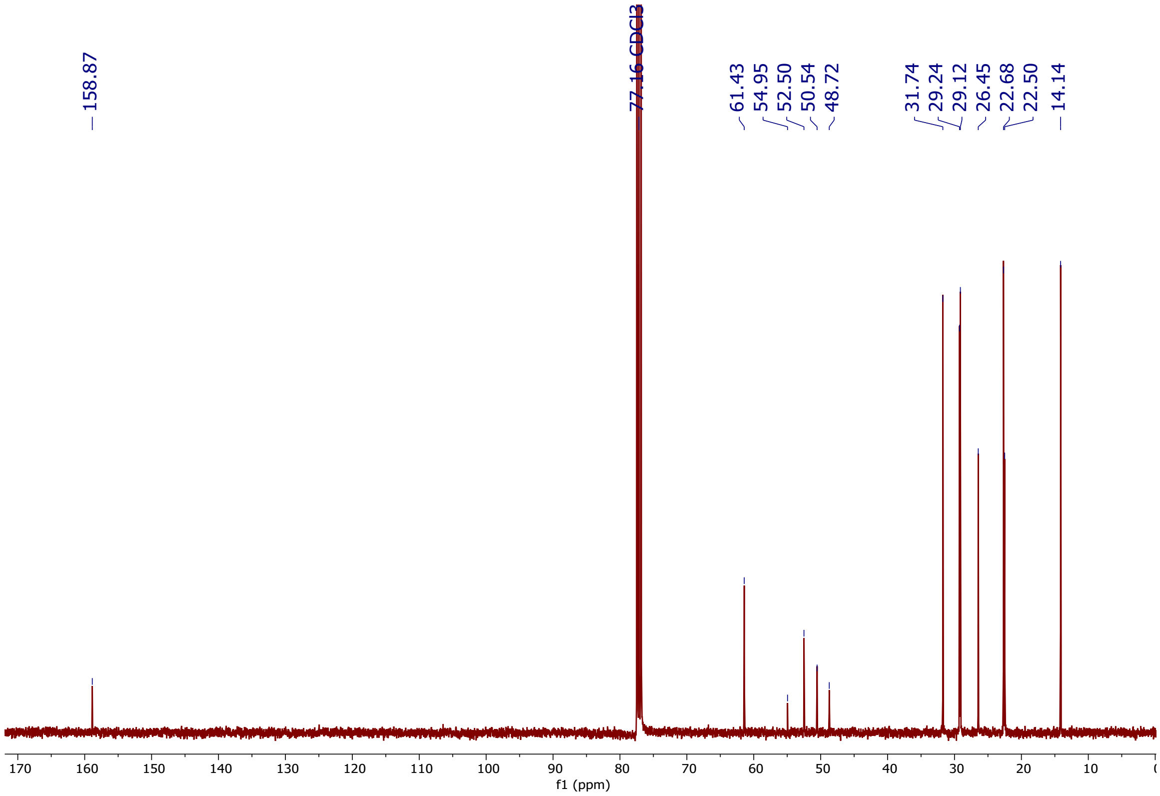


Figure S4. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ (ppm): 158.87; 61.43; 54.95; 52.50; 48.72; 31.74; 29.24; 29.12; 26.45; 22.68; 22.50; 14.14.

2.2 1-butyl-3-methylimidazolium methylcarbonate/1-butyl-3-methylimidazolium-2-carboxylate

The mixture was synthesised according to a published methodology.[2]

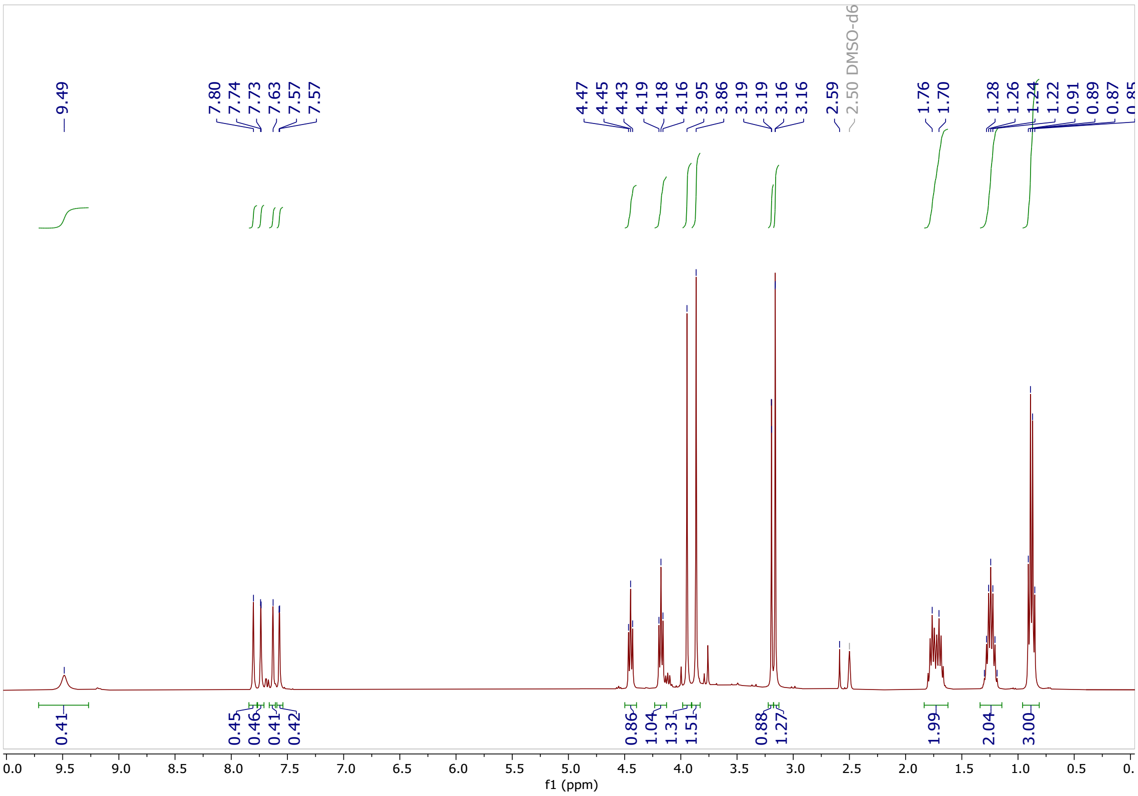


Figure S5. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K) δ (ppm): **(1-butyl-3-methyl-2-carboxyimidazolium)** 7.63 (d, *J* = 2.0 Hz, 1H), 7.57 (d, *J* = 1.9 Hz, 1H), 4.45 (t, *J* = 7.3 Hz, 2H), 3.95 (s, 3H), 1.83-1.62 (m, 2H), 1.24 (m, 2H), 0.88 (q, *J* = 7.7 Hz, 3H). **[C_4C_1Im][CH_3OCOO]** 9.49 (s, 1H), 7.80 (d, *J* = 1.9 Hz, 1H), 7.74 (d, *J* = 1.9 Hz, 1H), 4.18 (t, *J* = 7.2 Hz, 2H), 3.86 (s, 3H), 3.19 (s, 3H), 1.83-1.62 (m, 2H), 1.24 (m, 2H), 0.88 (q, *J* = 7.7 Hz, 3H).

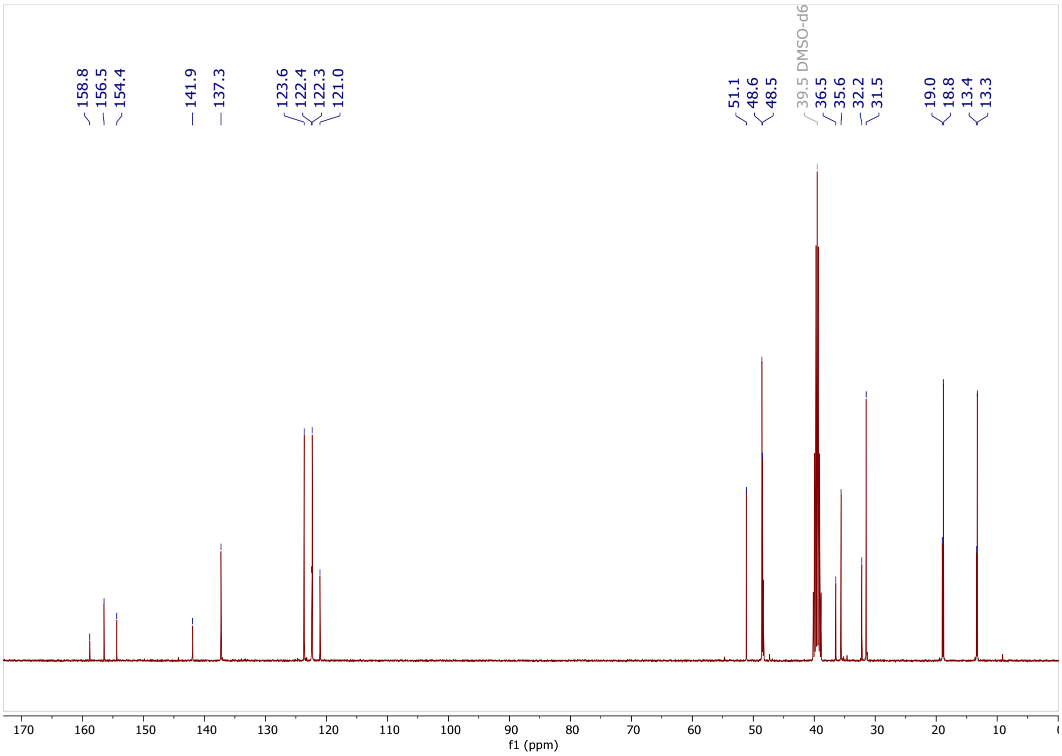


Figure S6. ^{13}C NMR (101 MHz, DMSO-d_6, 298 K) δ(ppm): **(1-butyl-3-methyl-2-carboxyimidazolium)** 158.8;141.9; 122.4; 121.0; 48.6; 36.5; 32.2; 19.0; 13.4.; **[C_4C_1im][CH_3OCOO]** 156.5; 137.3; 123.6; 122.3; 51.1; 48.5; 35.6; 31.5; 18.8; 13.3. .

3. Mo-ILs Characterization

3.1 Tetrabutylammonium molybdate(VI) $[N_{4444}]_2[MoO_4]$

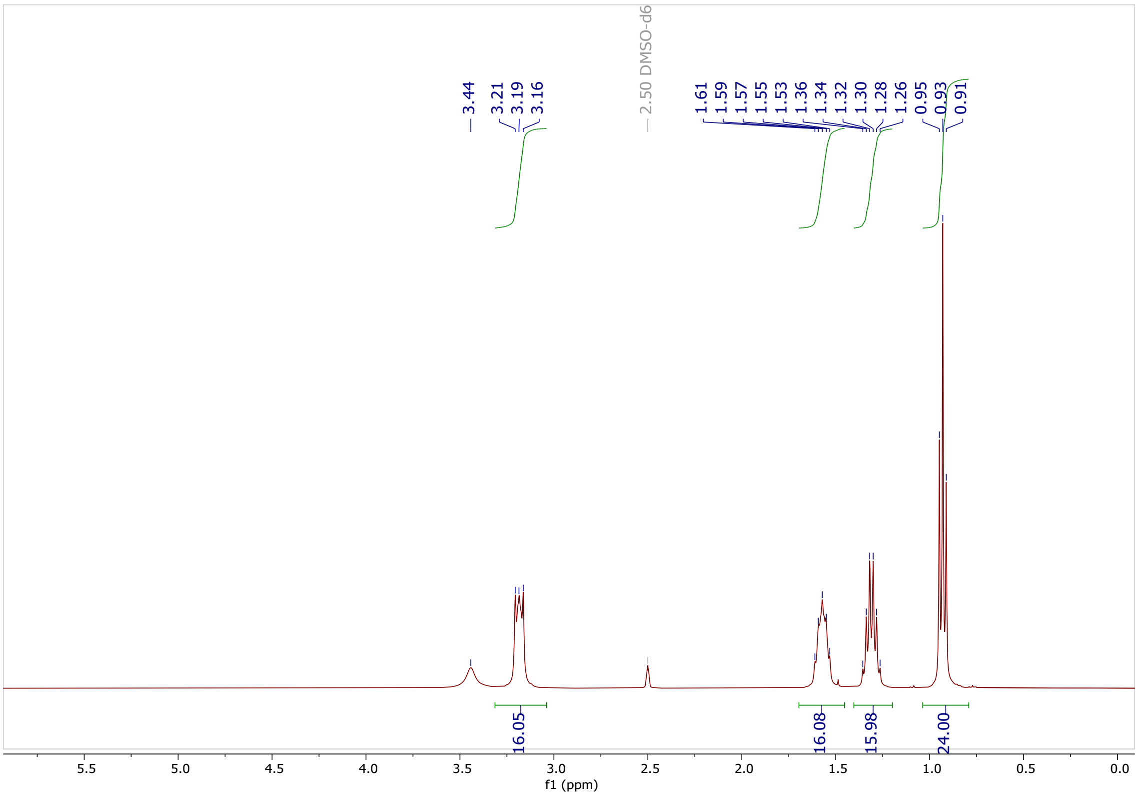


Figure S7. ^1H NMR (400 MHz, DMSO-d_6, 298 K) δ (ppm): 3.31 – 3.04 (m, 16H), 1.57 (m, 16H), 1.31 (m, 16H), 0.93 (t, *J* = 7.4 Hz, 24H).

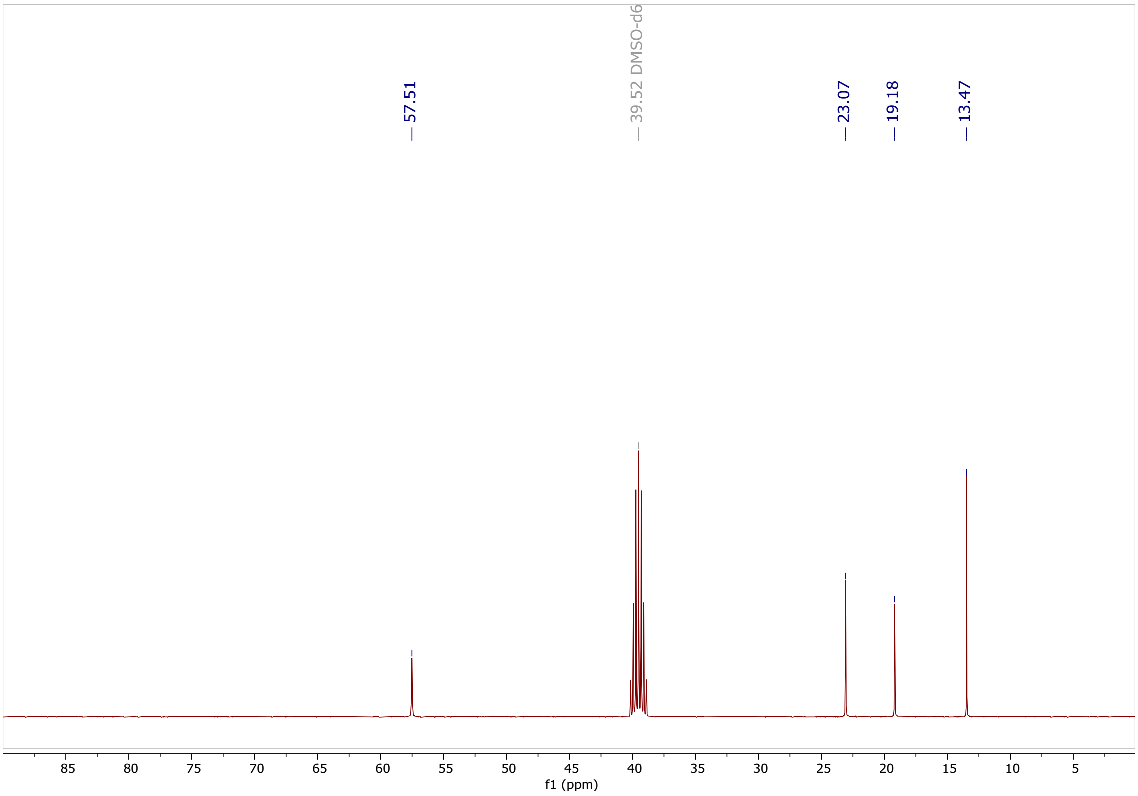


Figure S8. ^{13}C NMR (101 MHz, DMSO-d_6, 298 K) δ (ppm): 57.51; 23.07; 19.18; 13.47.

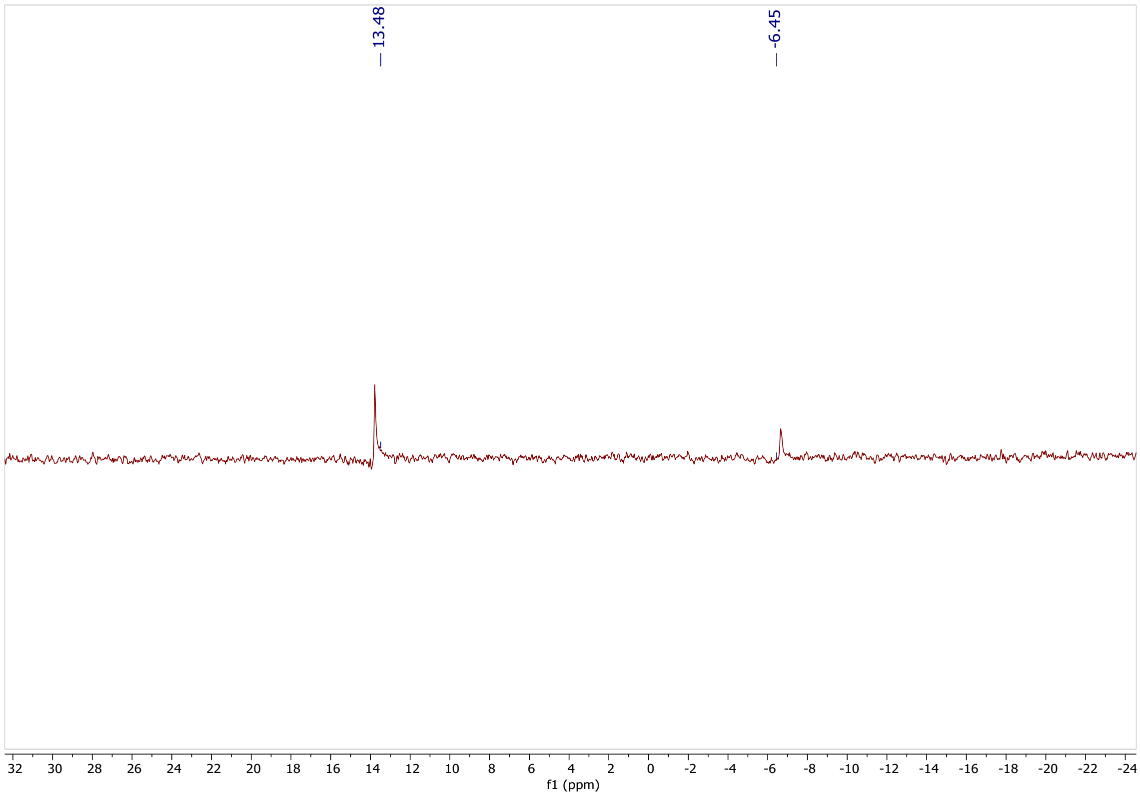


Figure S9. ^{95}Mo NMR (26 MHz, DMSO-d$_6$, 298 K) δ (ppm): 13.48.

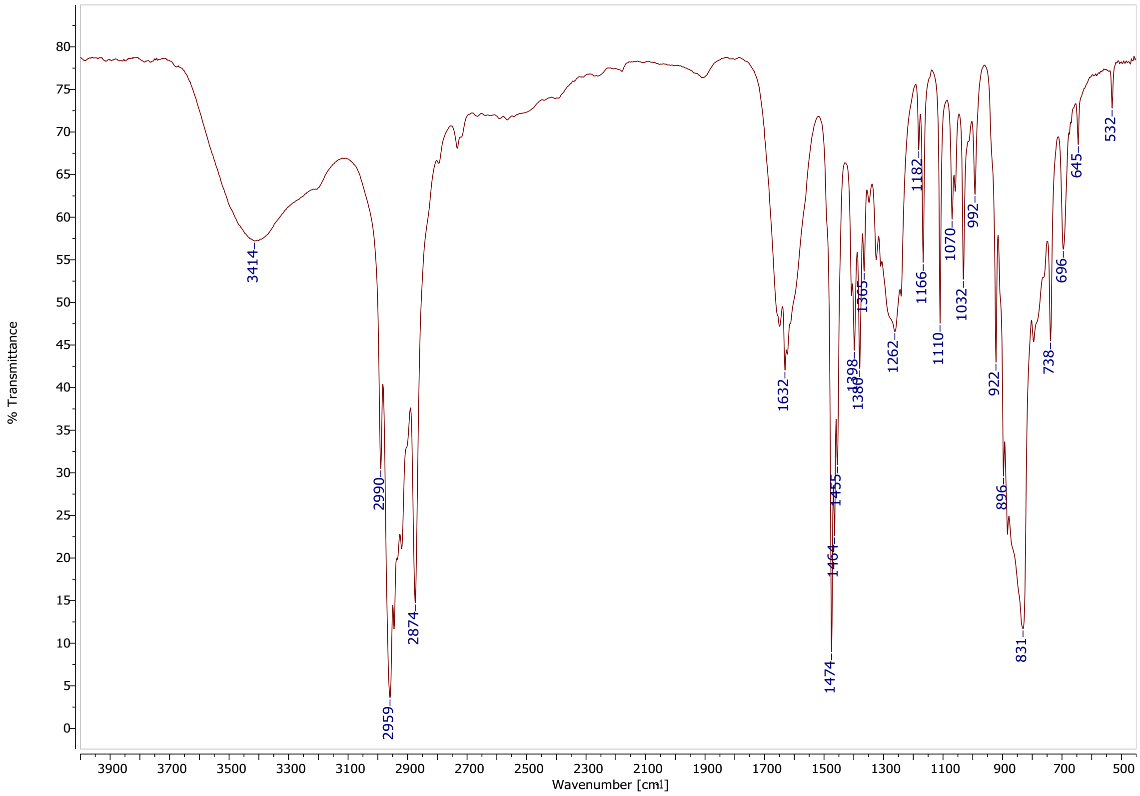


Figure S10. FT-IR spectrum of [N$_{4444}$]$_2$[MoO$_4$] (KBr).

3.2 Tetrabutylammonium dimolybdate(VI) $[N_{4444}]_2[Mo_2O_7]$

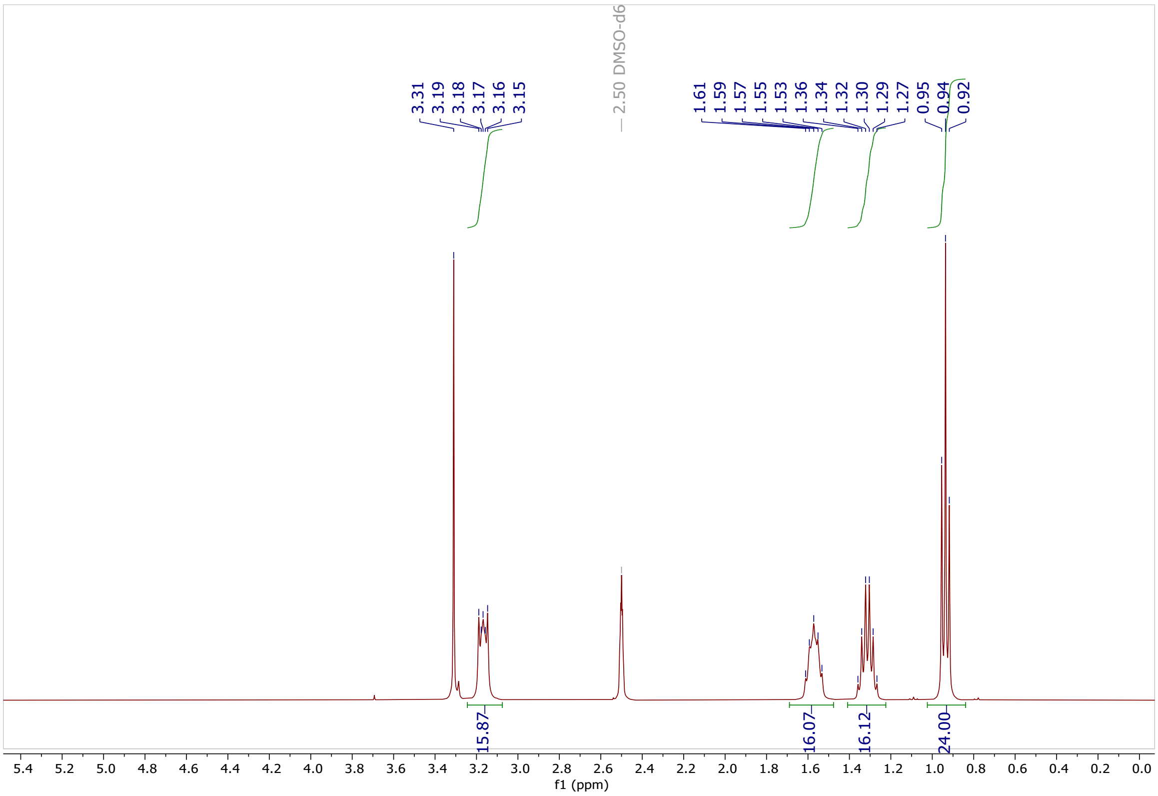


Figure S11. ^1H NMR (400 MHz, DMSO-d_6, 298 K) δ (ppm): 3.24 – 3.08 (m, 16H), 1.57 (m, 16H), 1.31 (m, 16H), 0.94 (t, *J* = 7.3 Hz, 24H).

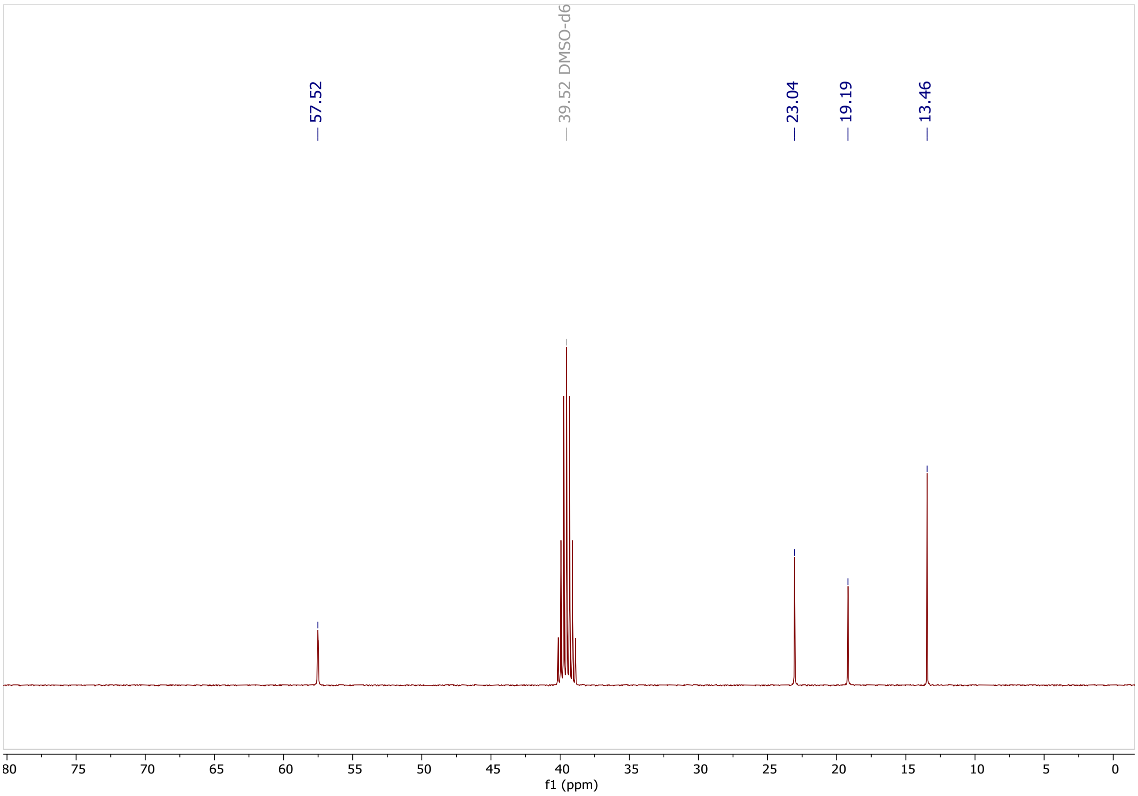


Figure S12. ^{13}C NMR (101 MHz, DMSO-d_6, 298 K) δ (ppm): 57.51; 23.04; 19.19; 13.46.

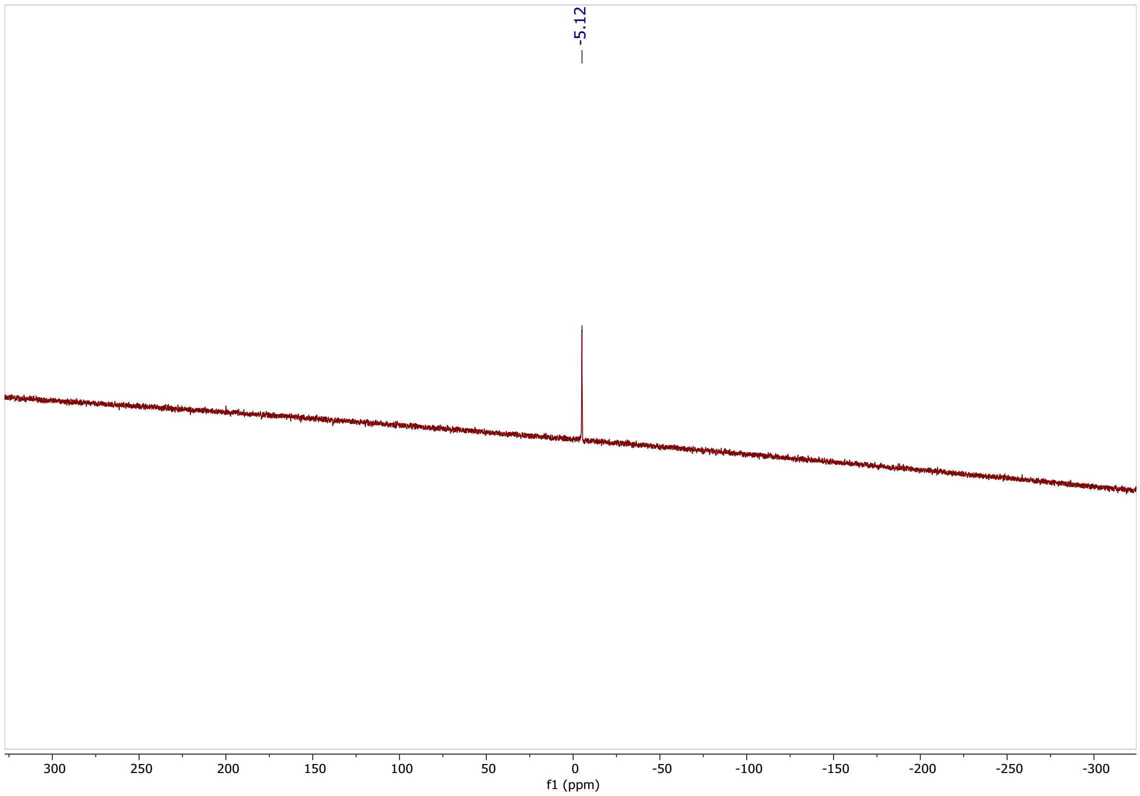


Figure S13. ^{95}Mo NMR (26 MHz, DMSO-d_6, 298 K) δ (ppm): -5.12.

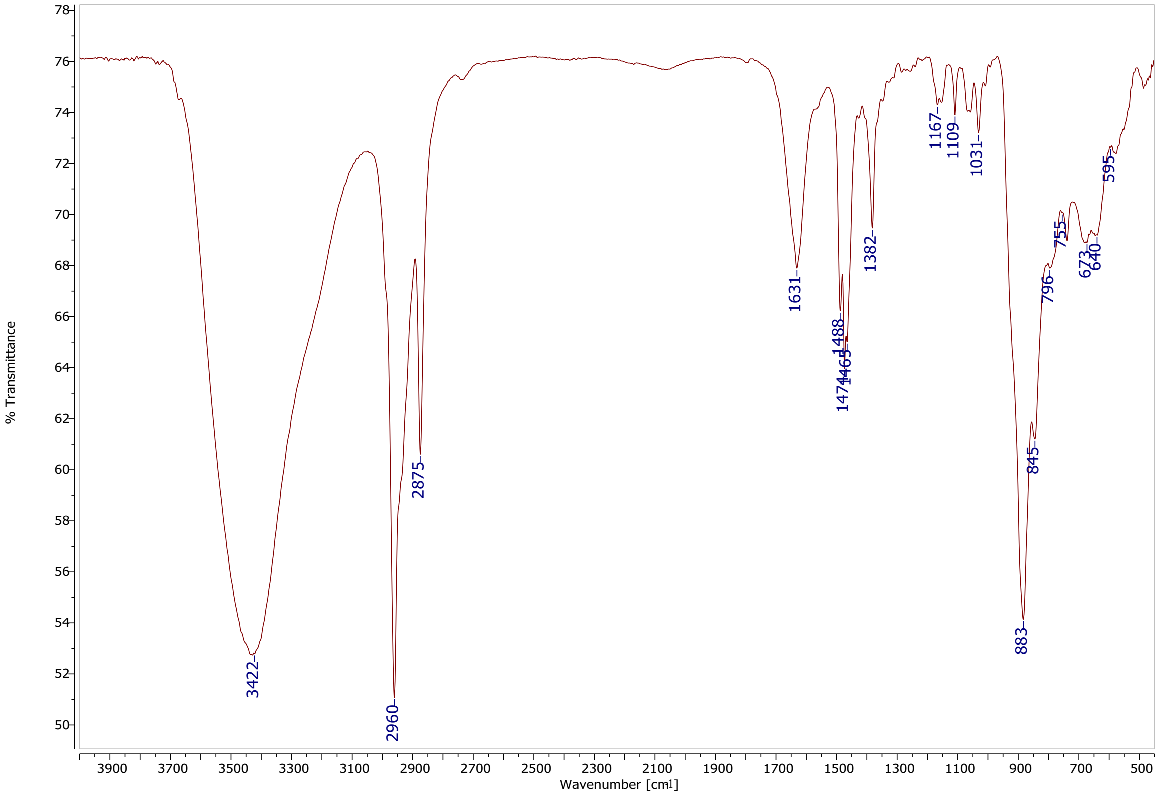


Figure S14. FT-IR spectrum of $[N_{4444}]_2[Mo_2O_7]$ (KBr).

3.3 Tetrabutylammonium hexamolybdate(VI) $[N_{4444}]_2[Mo_6O_{19}]$

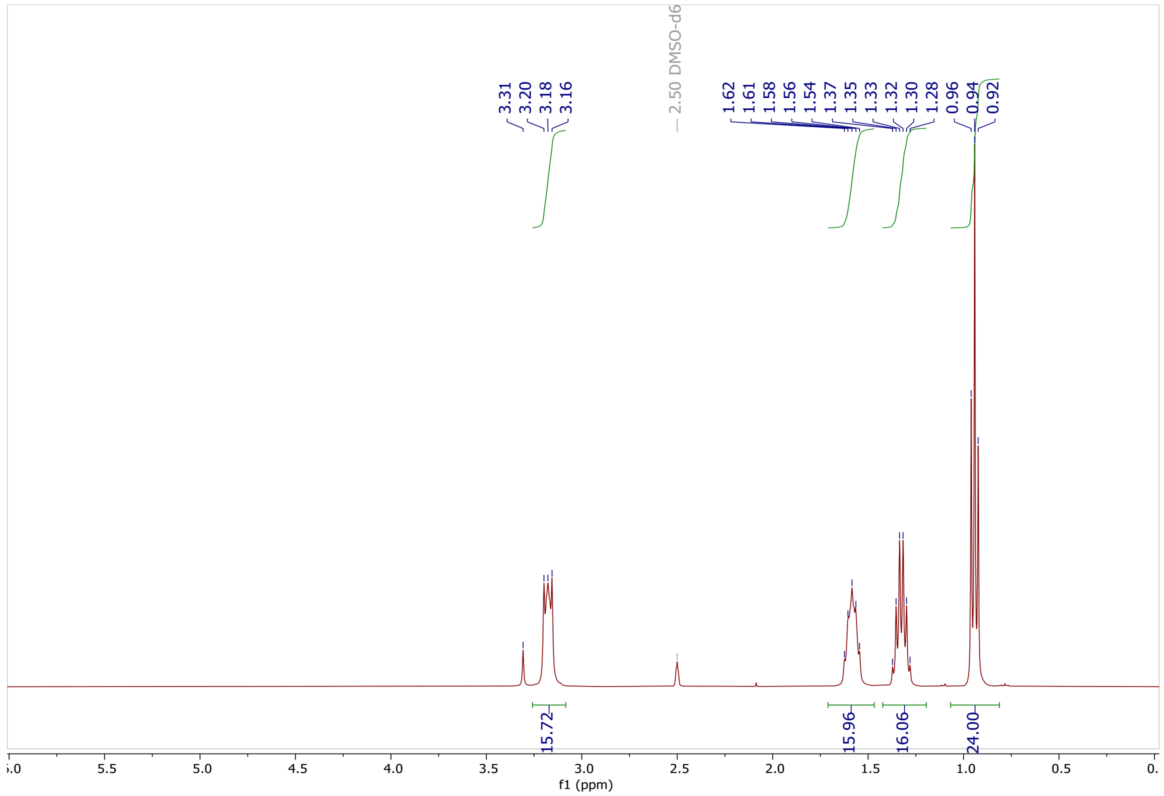


Figure S15. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K) δ (ppm): 3.26 – 3.08 (m, 16H), 1.58 (m, 16H), 1.33 (m, 16H), 0.94 (t, *J* = 7.3 Hz, 24H).

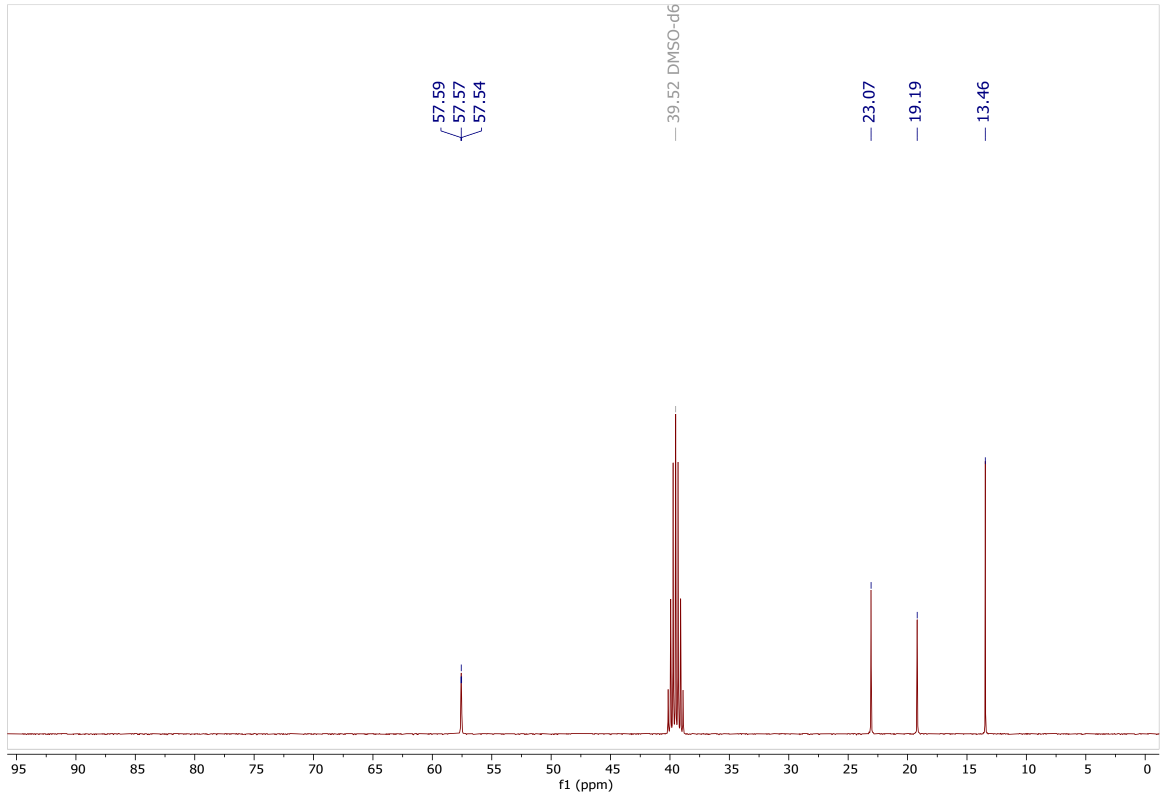


Figure S16. ^{13}C NMR (101 MHz, DMSO-d_6, 298 K) δ (ppm): 57.57; 23.07; 19.19; 13.46.

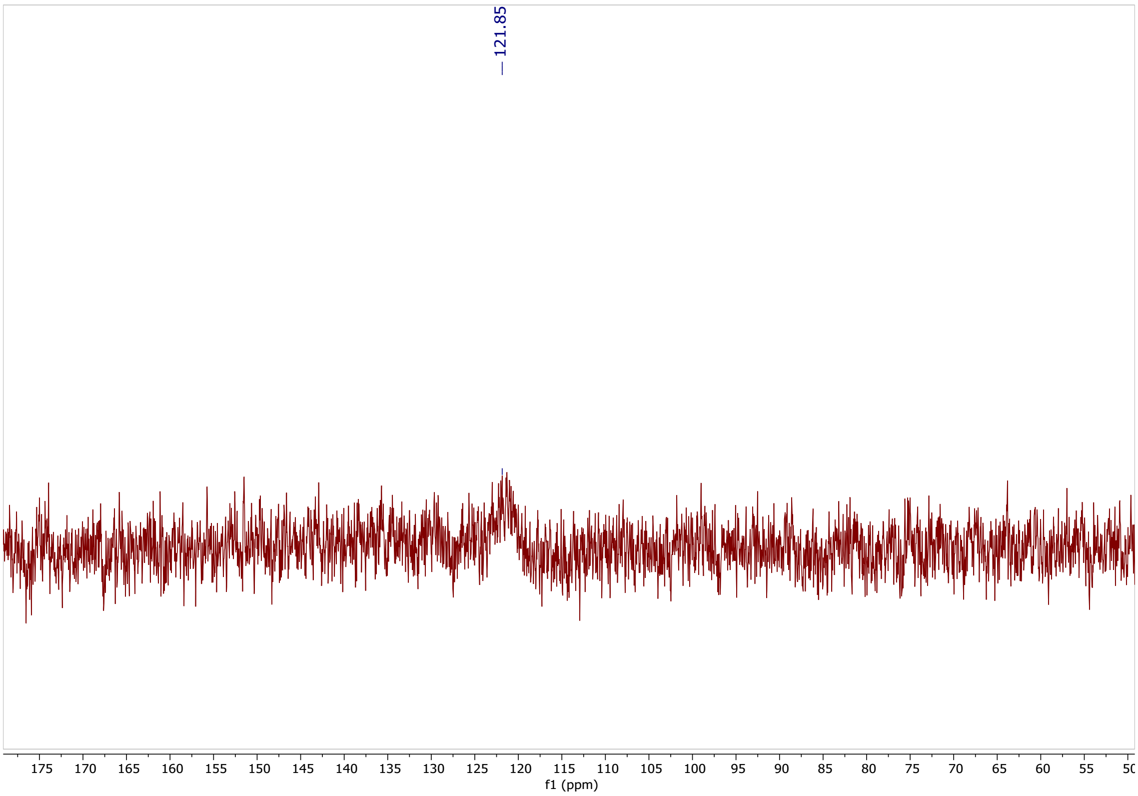


Figure S17. ^{95}Mo NMR (26 MHz, CD_3CN, 298 K) δ (ppm): 121.85.

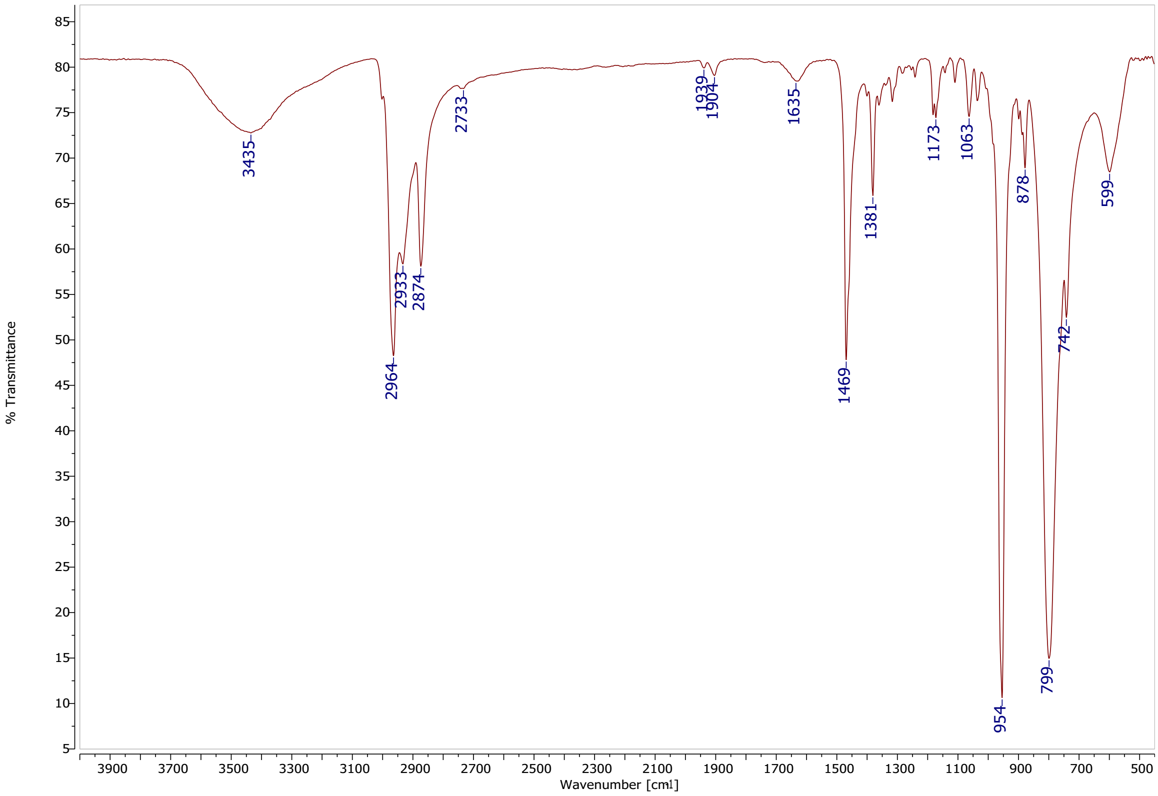


Figure S18. FT-IR spectrum of $[N_{4444}]_2[Mo_6O_{19}]$ (KBr).

3.4 Tetrabutylammonium octamolybdate(VI) $[N_{4444}]_4[Mo_8O_{26}]$

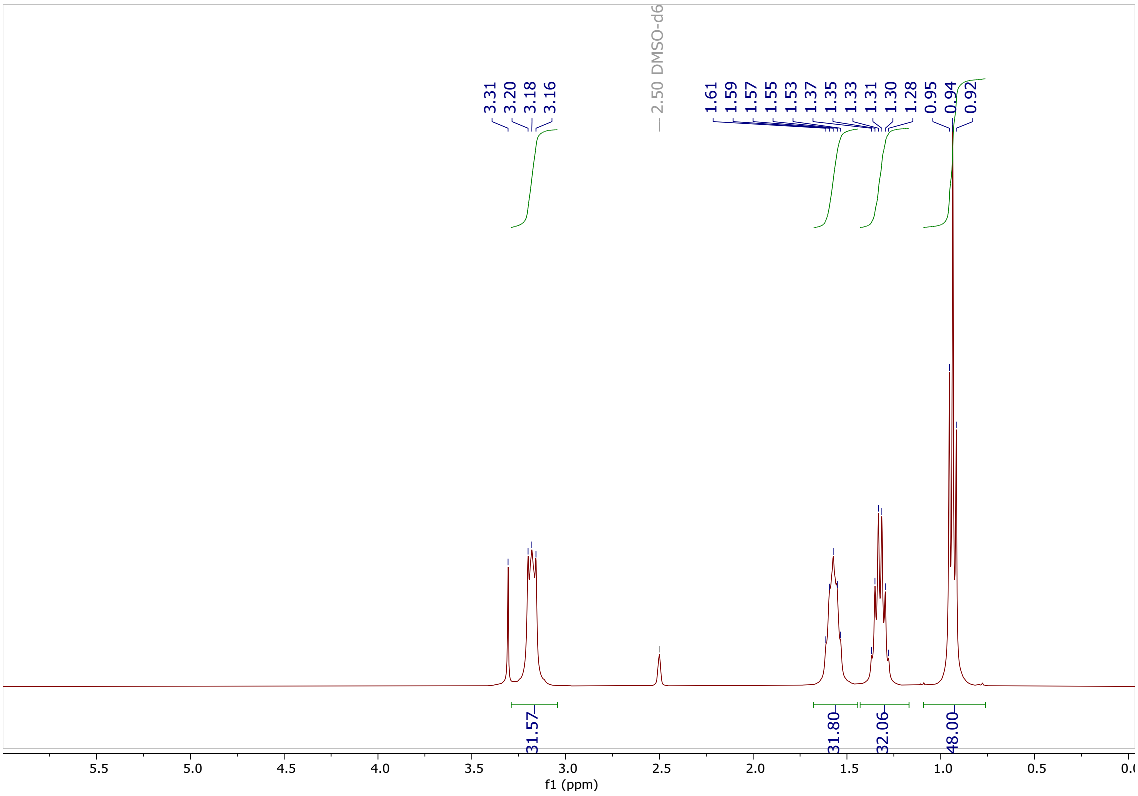


Figure S19. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K) δ (ppm): 3.29 – 3.04 (m, 32H), 1.57 (m, 32H), 1.32 (m, 32H), 0.94 (t, *J* = 7.3 Hz, 48H).

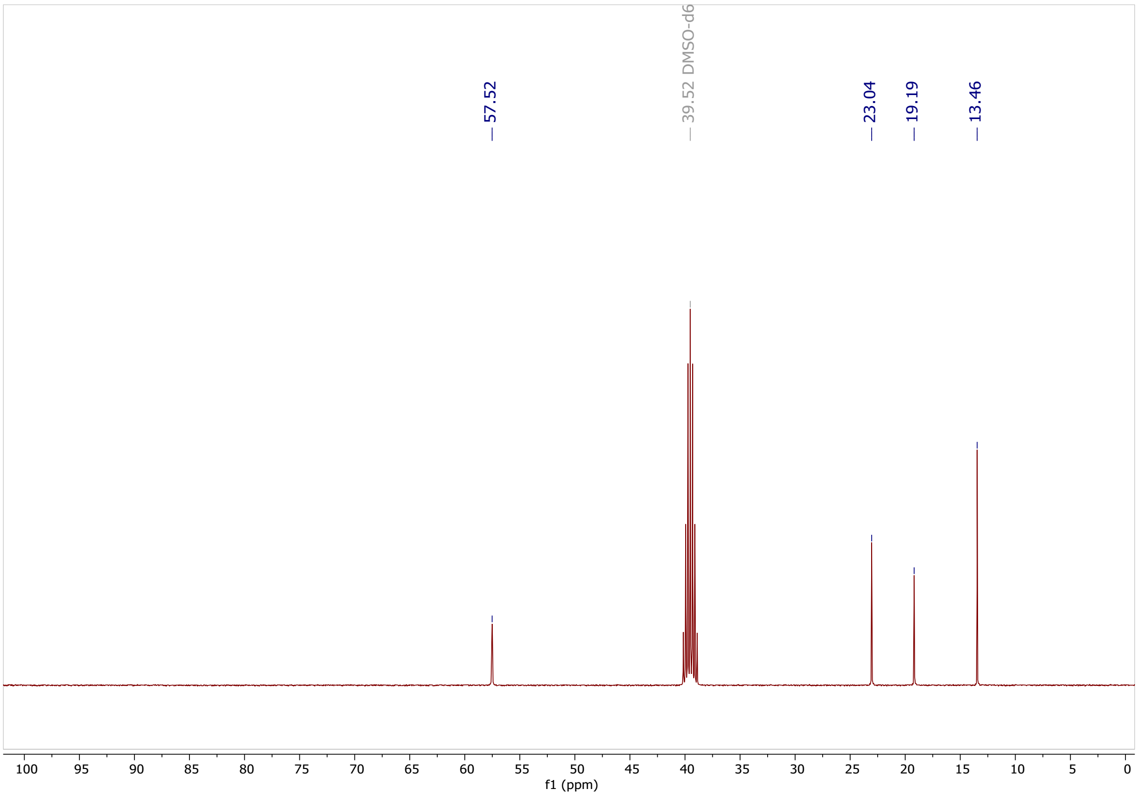


Figure S20. ^{13}C NMR (101 MHz, DMSO-d_6, 298 K) δ (ppm): 57.52; 23.04; 19.19; 13.46.

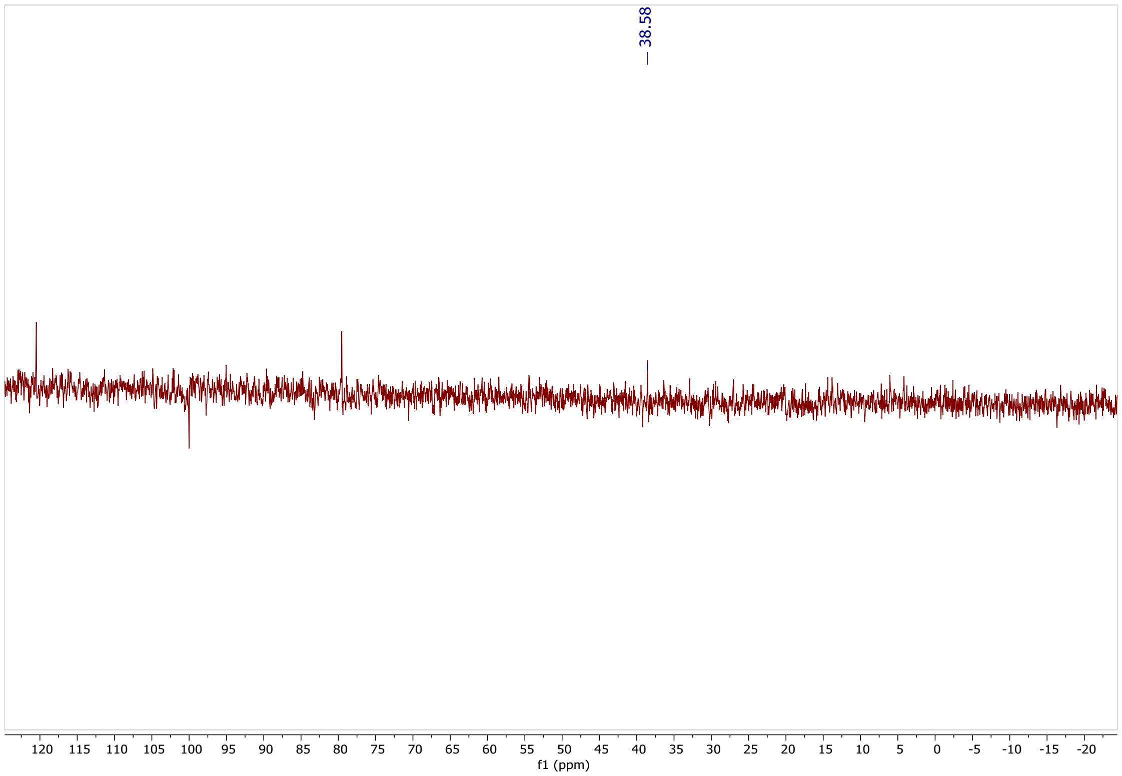


Figure S21. ^{95}Mo NMR (26 MHz, DMSO-d_6, 298 K) δ (ppm): 38.58; spike signals are present at 120, 100 and 80 ppm.

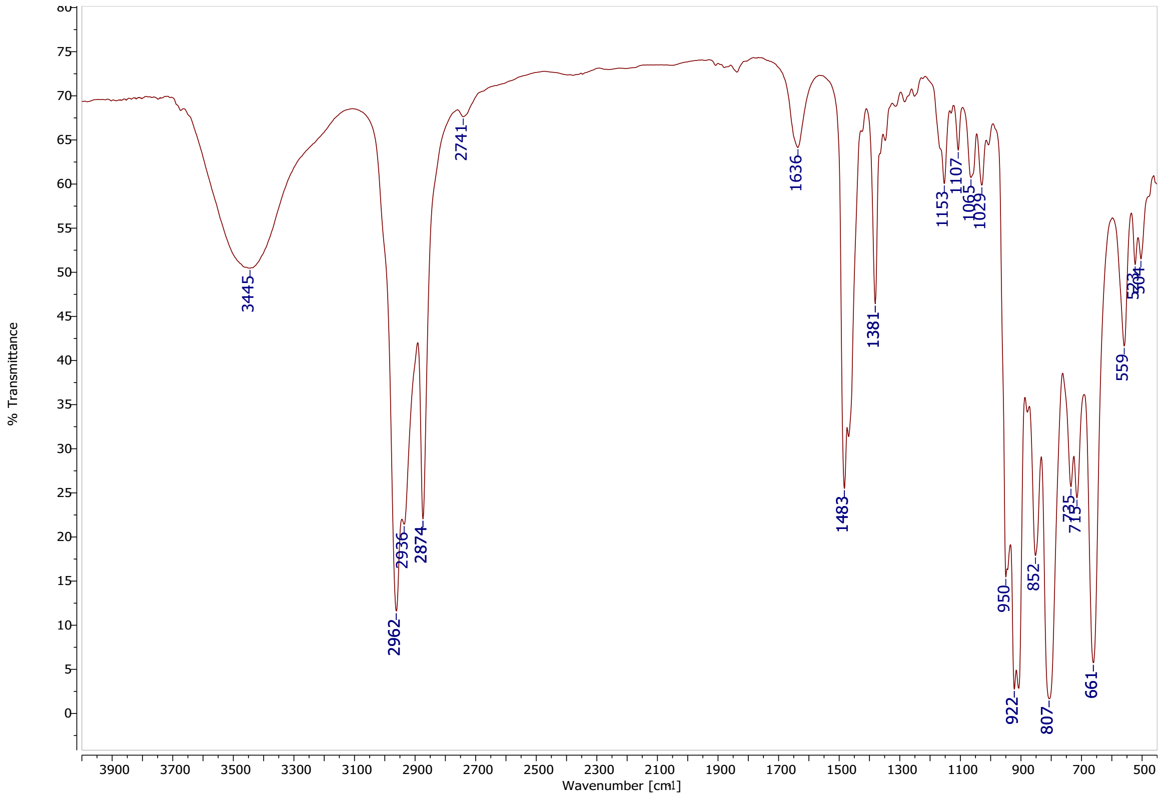


Figure S22. FT-IR spectrum of $[N_{4444}]_4[Mo_8O_{26}]$ (KBr).

3.5 Trioctylmethylammonium molybdate(VI) $[N_{1888}]_2[MoO_4]$

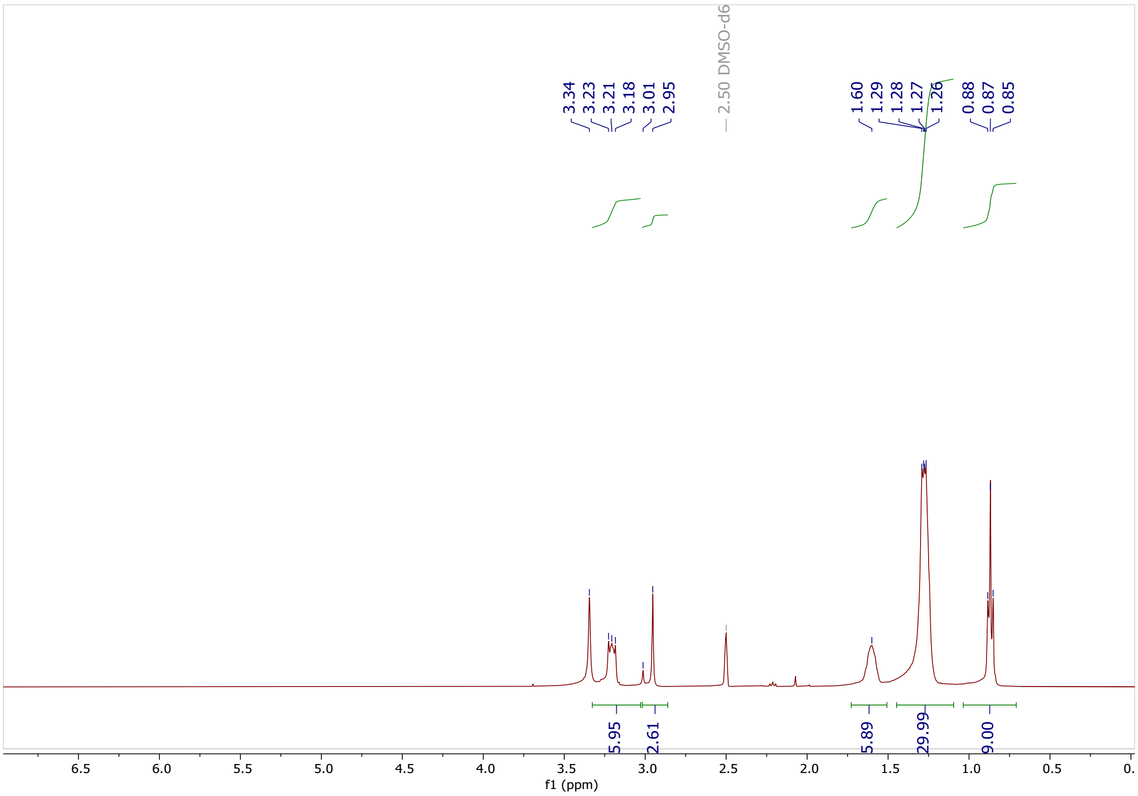


Figure S23. ^1H NMR (400 MHz, DMSO-d_6, 298 K) δ (ppm): 3.33 – 3.03 (m, 6H), 2.95 (s, 3H), 1.73-1.51 (m, 6H), 1.45 – 1.09 (m, 30H), 0.87 (t, *J* = 6.6 Hz, 9H).

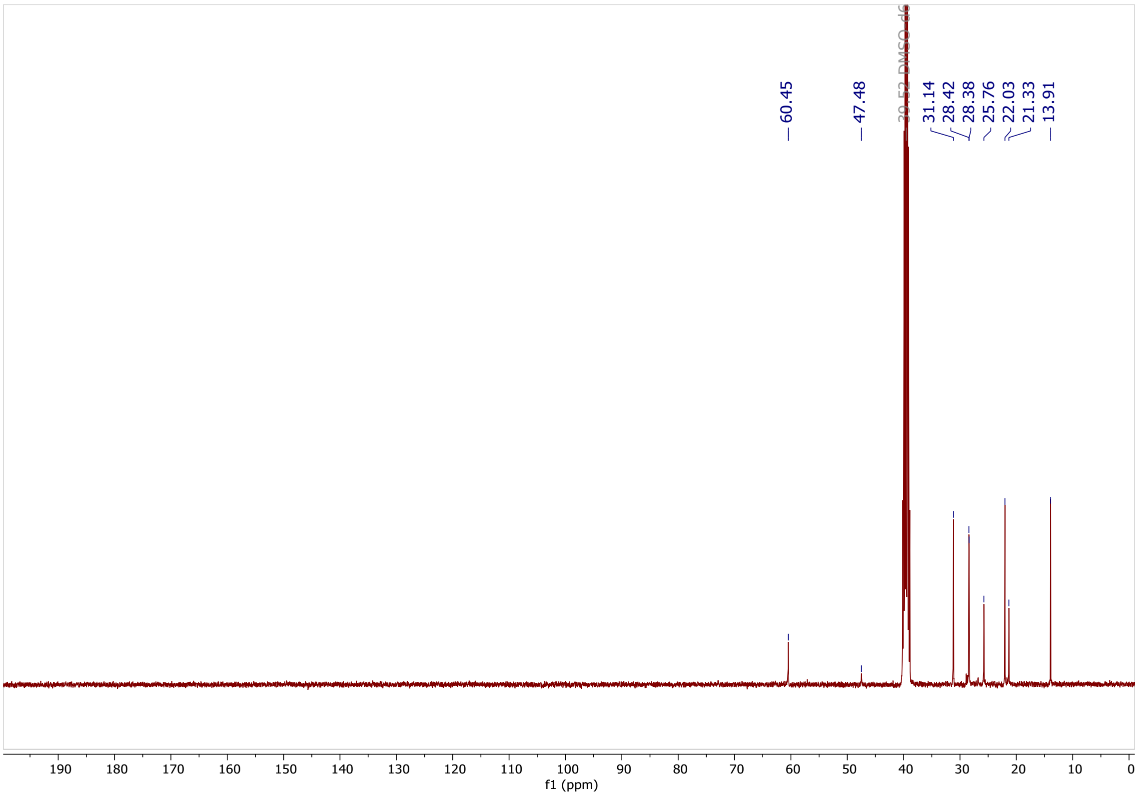


Figure S24. ^{13}C NMR (101 MHz, DMSO-d_6, 298 K) δ (ppm): 60.45; 47.48; 31.14; 28.42; 28.38; 25.76; 22.03; 21.33; 13.91.

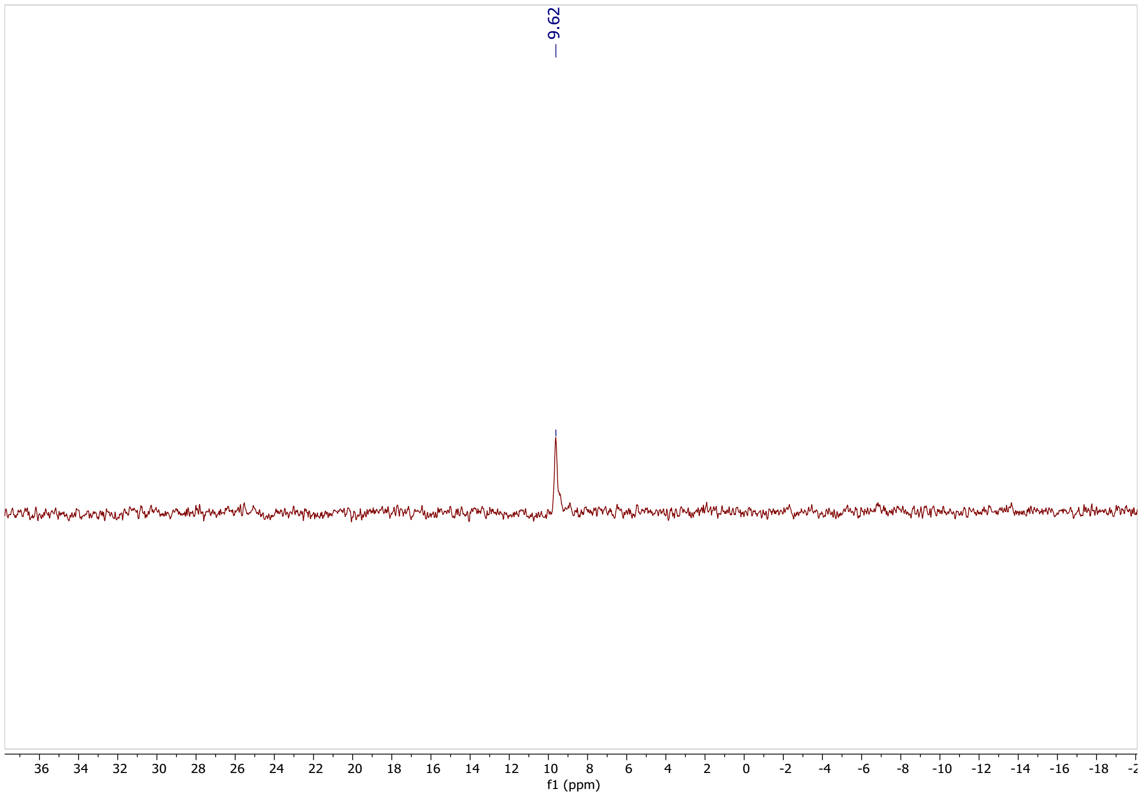


Figure S25. ^{95}Mo NMR (26 MHz, DMSO-d_6, 298 K) δ (ppm): 9.62.

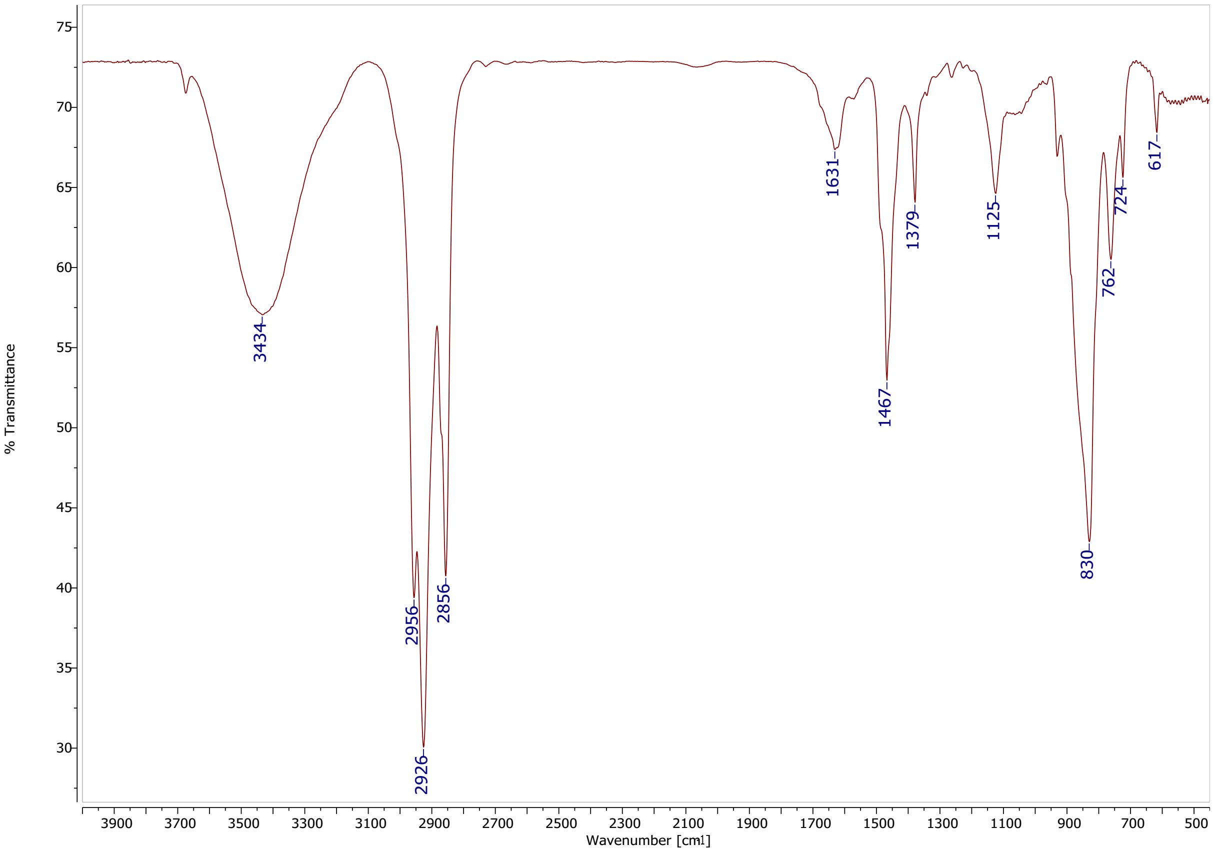


Figure S26. FT-IR spectrum of $[N_{1888}]_2[MoO_4]$ (KBr).

3.6 Tetrabutylphosphonium molybdate(VI) $[P_{4444}]_2[MoO_4]$

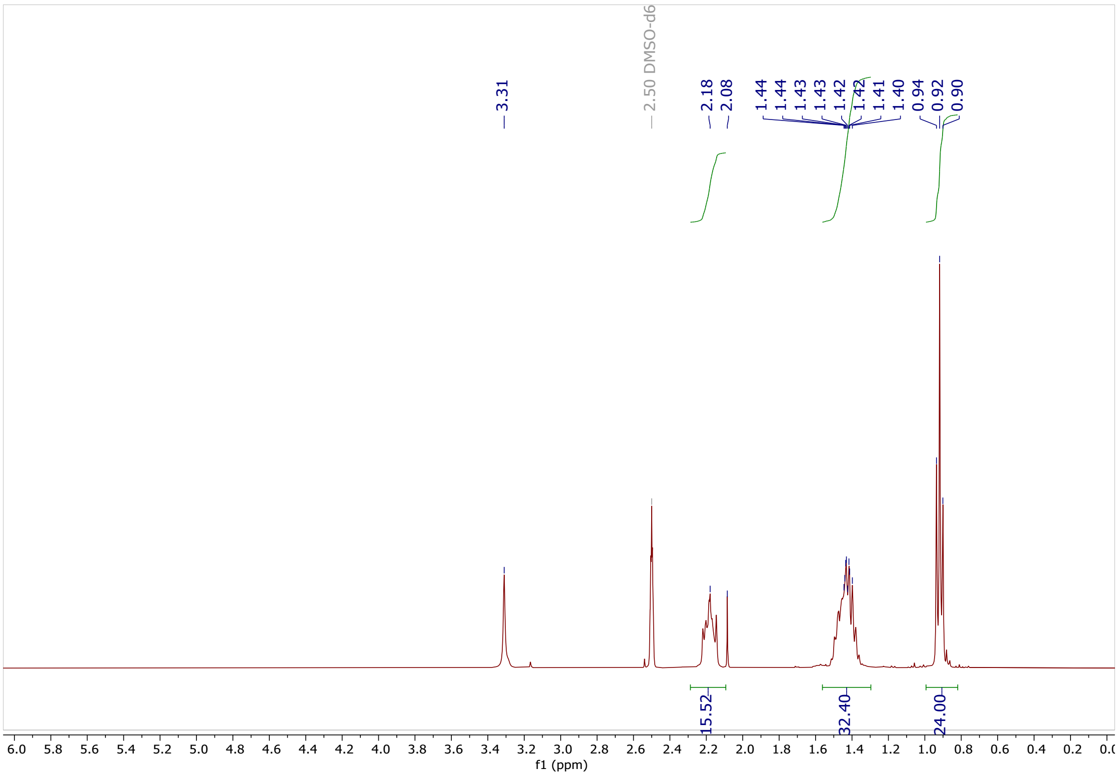


Figure S27. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K) δ (ppm): 2.18 (m, 16H), 1.56 – 1.30 (m, 32H), 0.92 (t, *J* = 7.0 Hz, 24H).

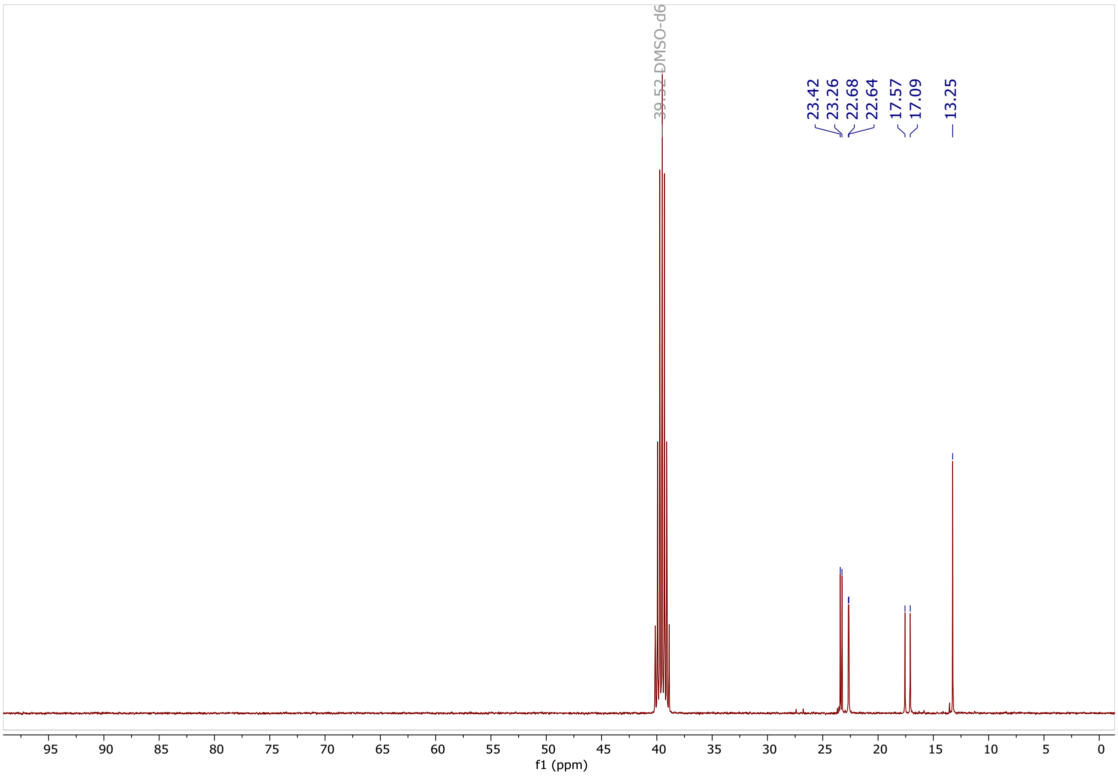


Figure S28. ^{13}C NMR (101 MHz, DMSO) δ 23.42, 23.26, 22.68, 22.64, 17.57, 17.09, 13.25.

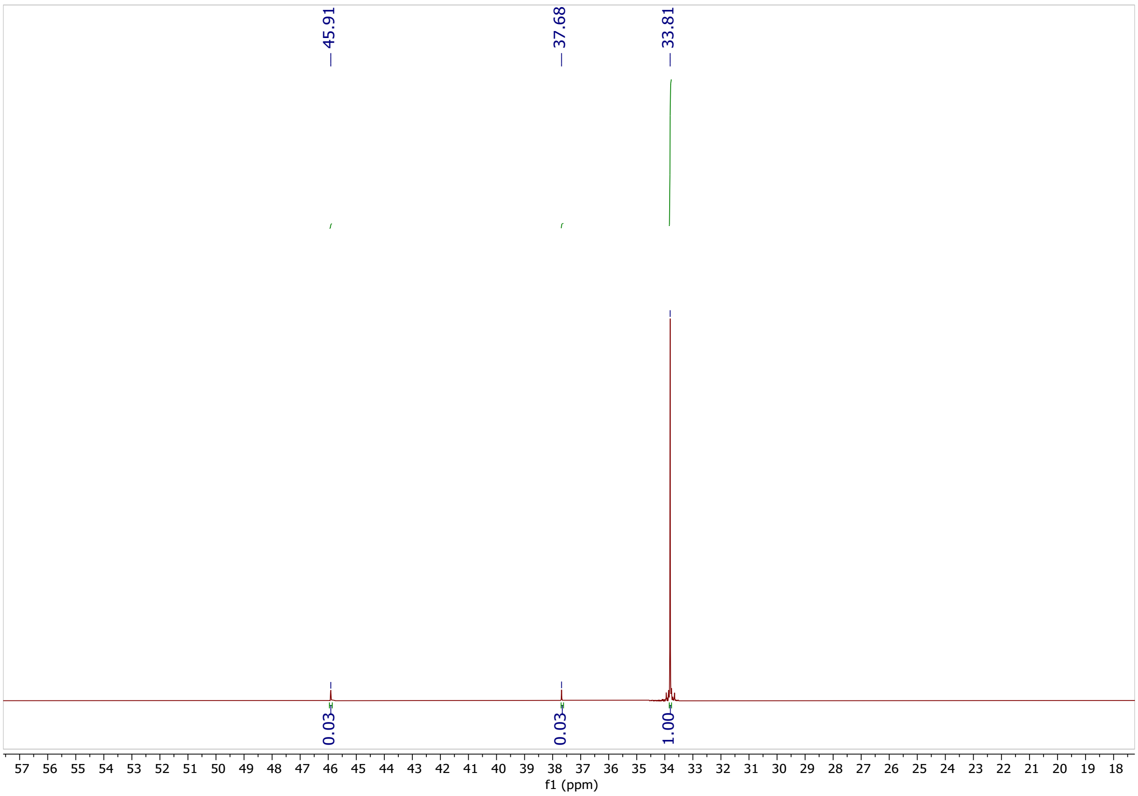


Figure S29. ^{31}P NMR (75 MHz, DMSO-d_6, 298 K) δ (ppm): 33.81.

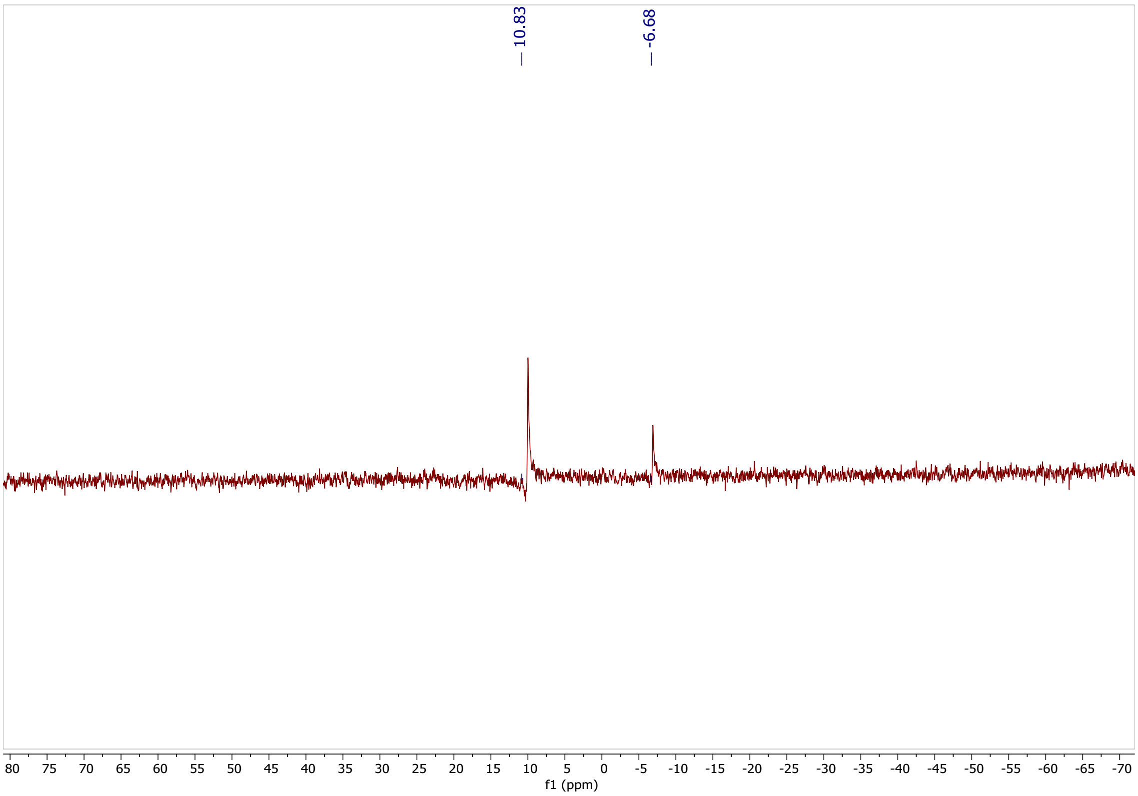


Figure S30. ^{95}Mo NMR (26 MHz, DMSO-d_6, 298 K) δ (ppm): 10.83.

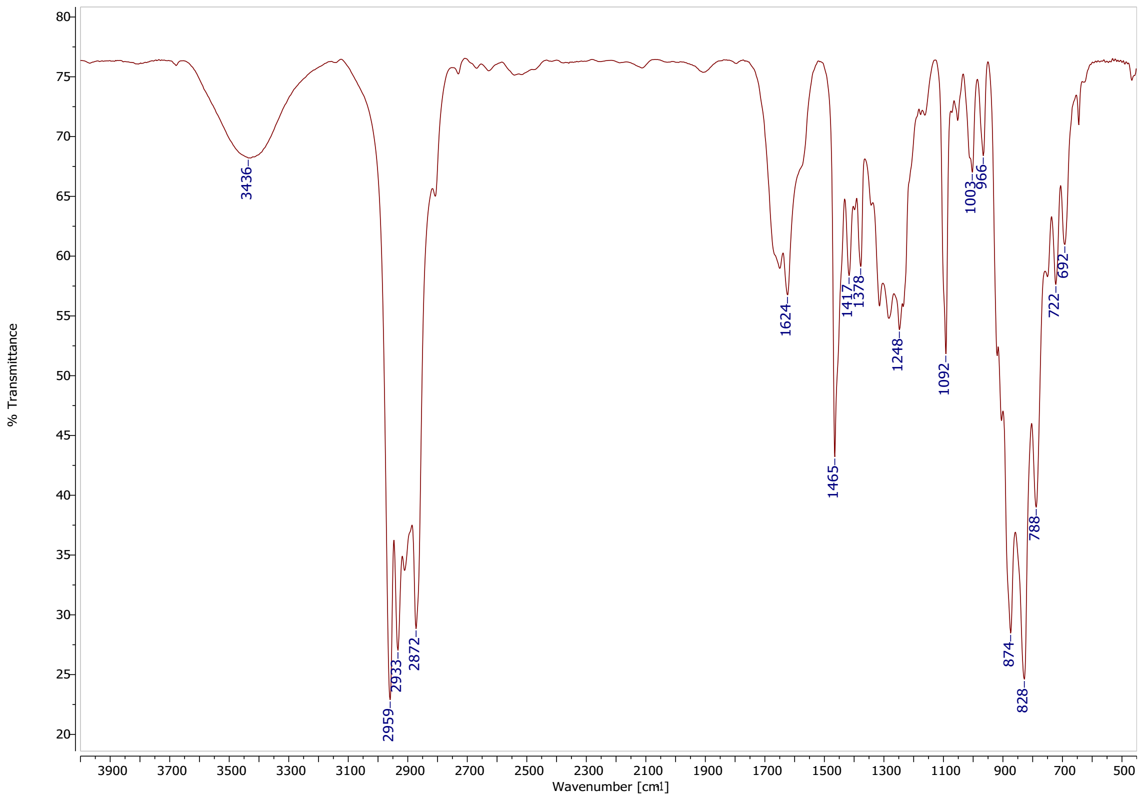


Figure S31. FT-IR spectrum of $[P_{4444}]_2[MoO_4]$ (KBr).

3.7 1-butyl-3-methylimidazolium molybdate(VI) $[C_4C_1im]_2[MoO_4]$

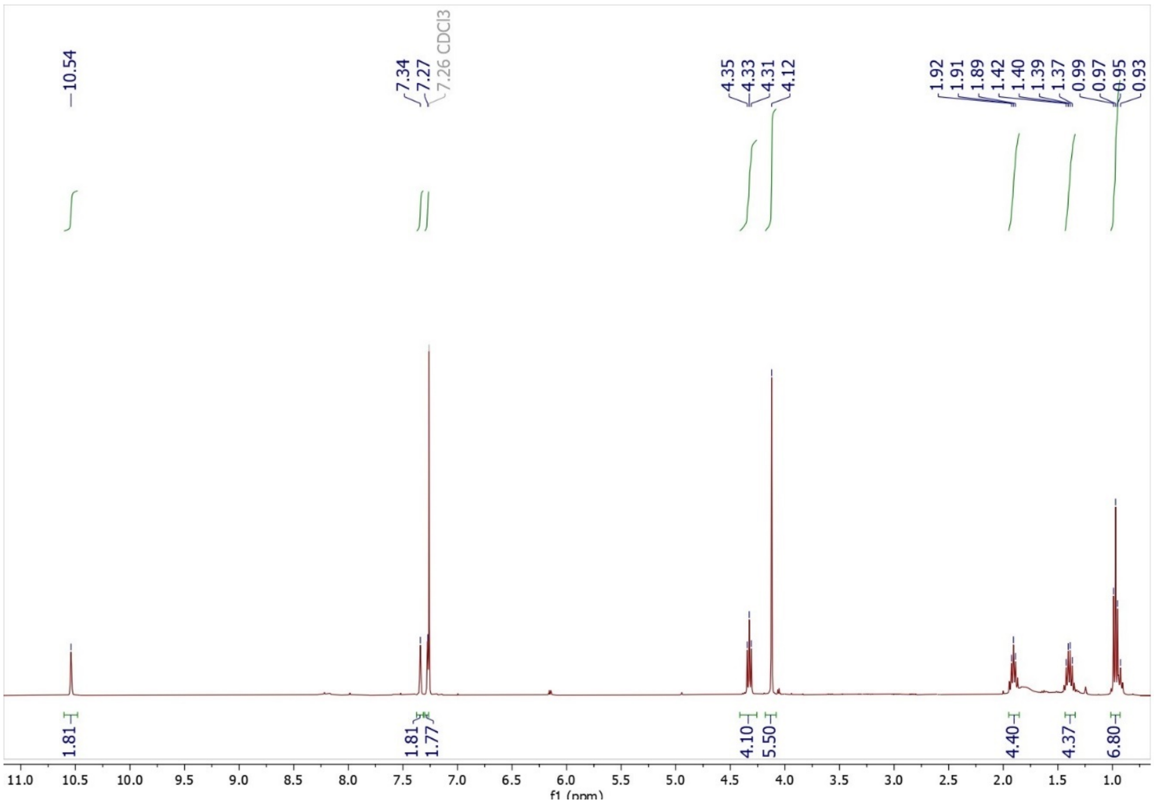


Figure S32. ^1H NMR (400 MHz, DMSO-d_6, 298 K) δ (ppm): 10,54 (s, 2H), 7.34, (d, 2H), 7.27 (d, 2H), 4.33 (m, 4H), 4.12 (s, 6H), 1.91 (m, 4H), 1.39 (m, 4H), 0.95 (t, *J* = 7.1 Hz, 6H).

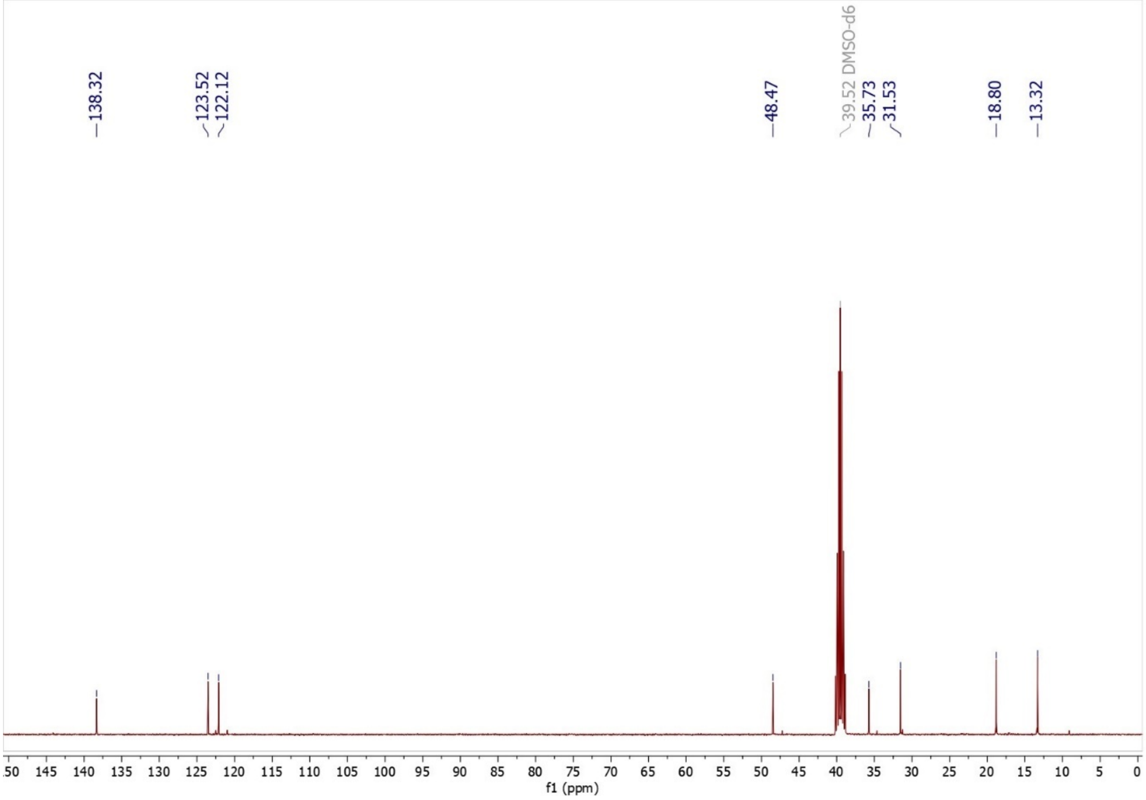


Figure S33. ^{13}C NMR (101 MHz, DMSO-d_6, 298 K) δ: 138.32; 123.53; 122.12; 48.47; 35.73; 31.53; 18.80; 13.32.

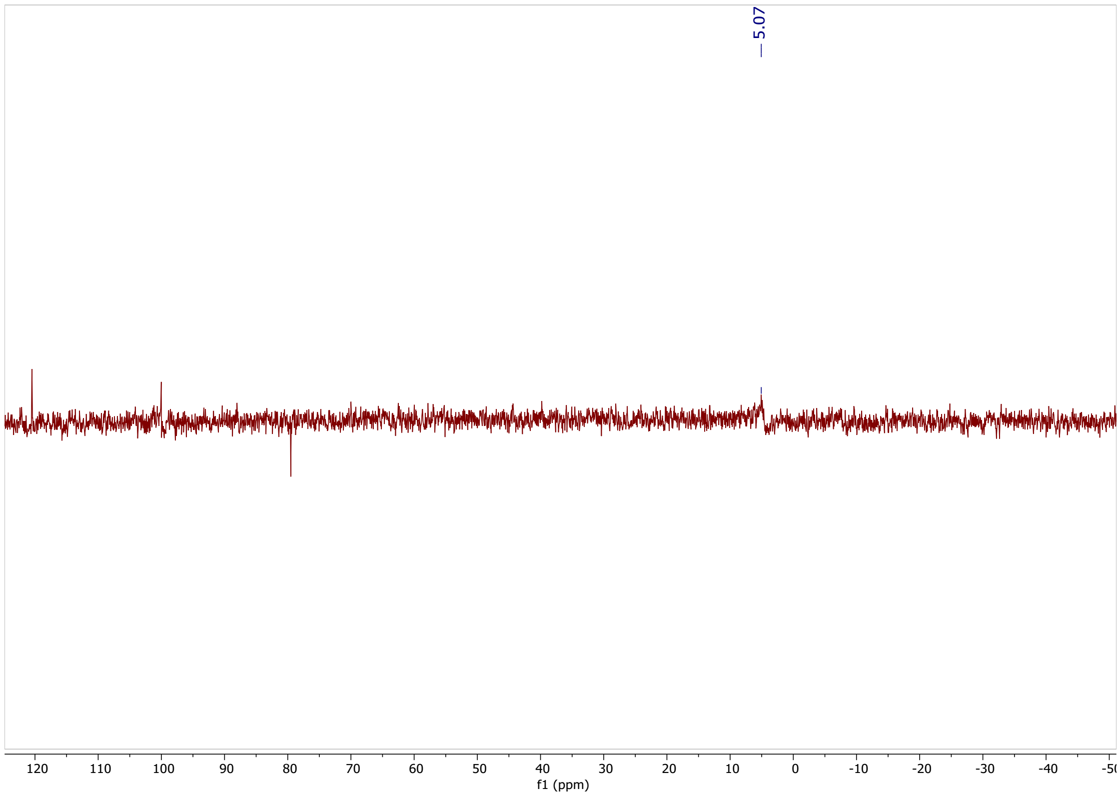


Figure S34. ^{95}Mo NMR (26 MHz, DMSO-d_6, 298 K) δ (ppm): 5.07; spike signals at 120, 100 and 80 ppm.

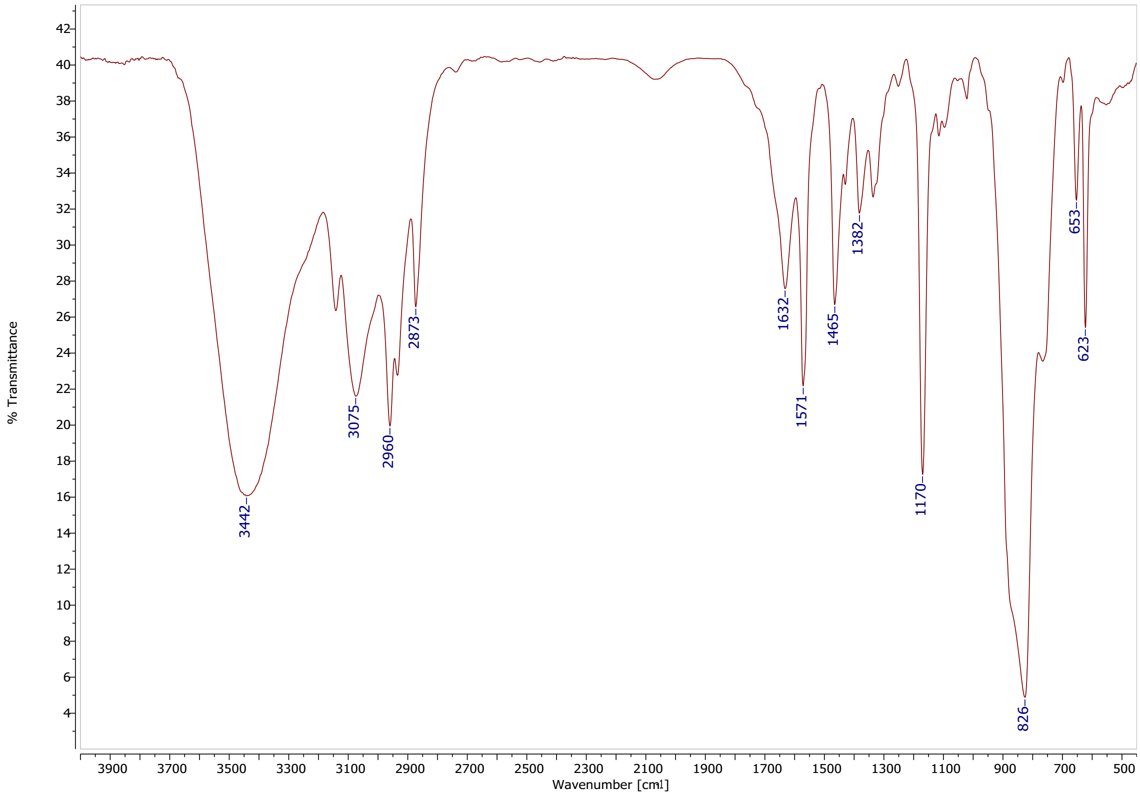


Figure S35. FT-IR spectrum of $[C_4C_1im]_2[MoO_4]$ (KBr).

3.8 Diazabicycloundecene molybdate(VI) $[DBUH]_2[MoO_4]$

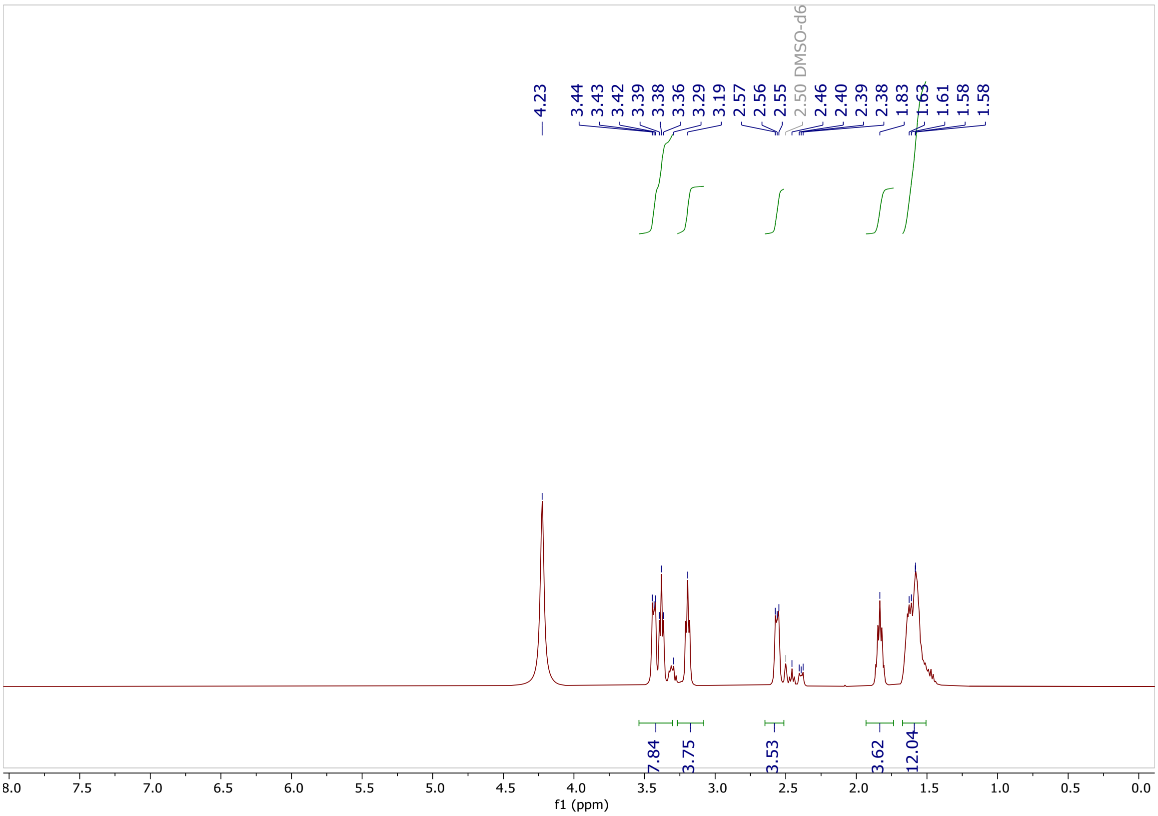


Figure S36. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K) δ (ppm): 3.59 – 3.39 (m, 4H), 3.27 (t,2H), 2.65 – 2.54 (m, 2H), 2.00 – 1.88 (m, 2H), 1.63 (m, 6H).

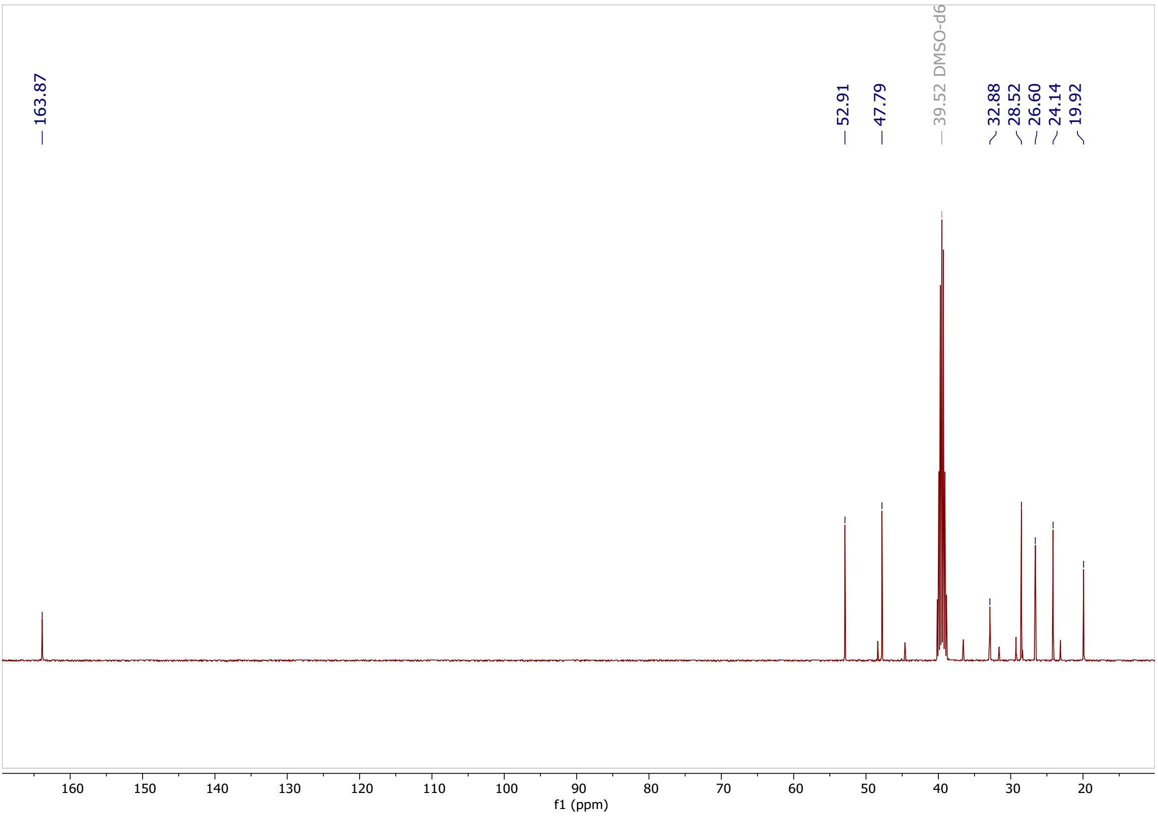


Figure S37. ^{13}C NMR (101 MHz, DMSO-d_6, 298 K) δ (ppm): 163.87; 52.91; 47.79; 32.88; 28.52; 26.60; 24.14; 19.92.

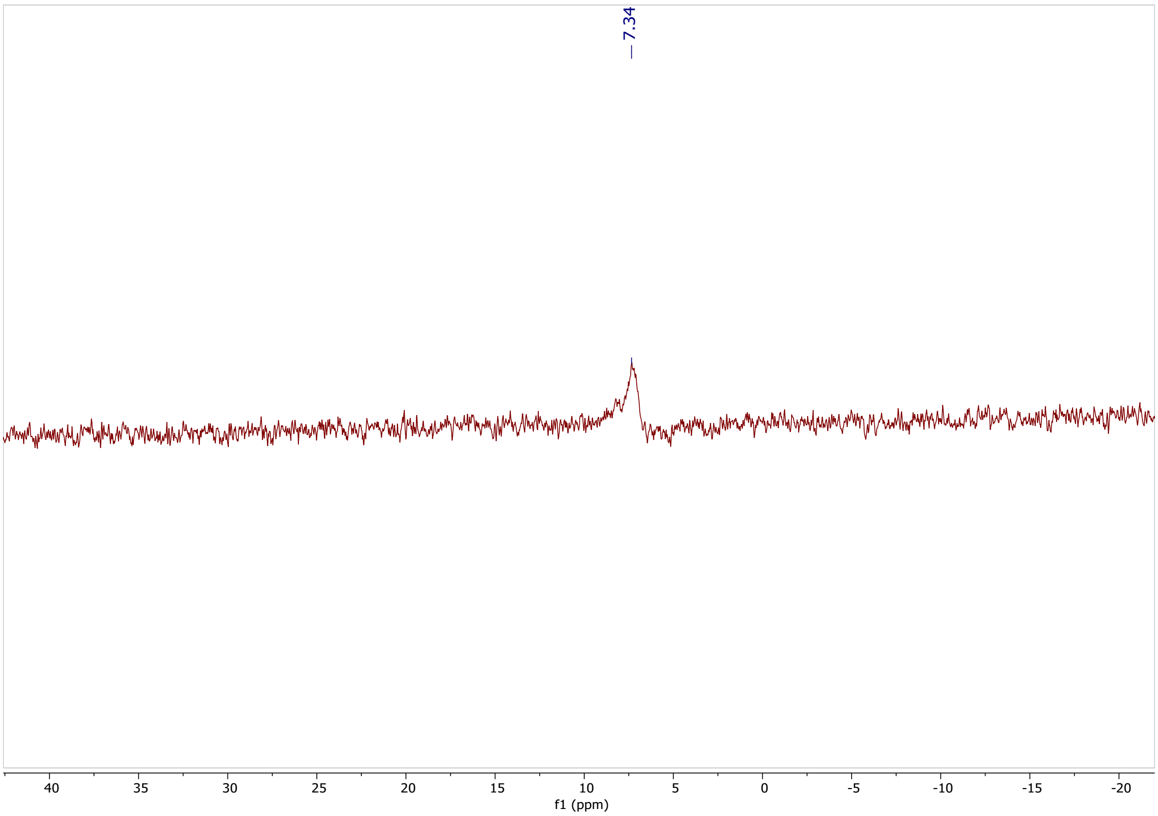


Figure S38. ^{95}Mo NMR (26 MHz, DMSO-d$_6$, 298 K) δ (ppm): 7.54.

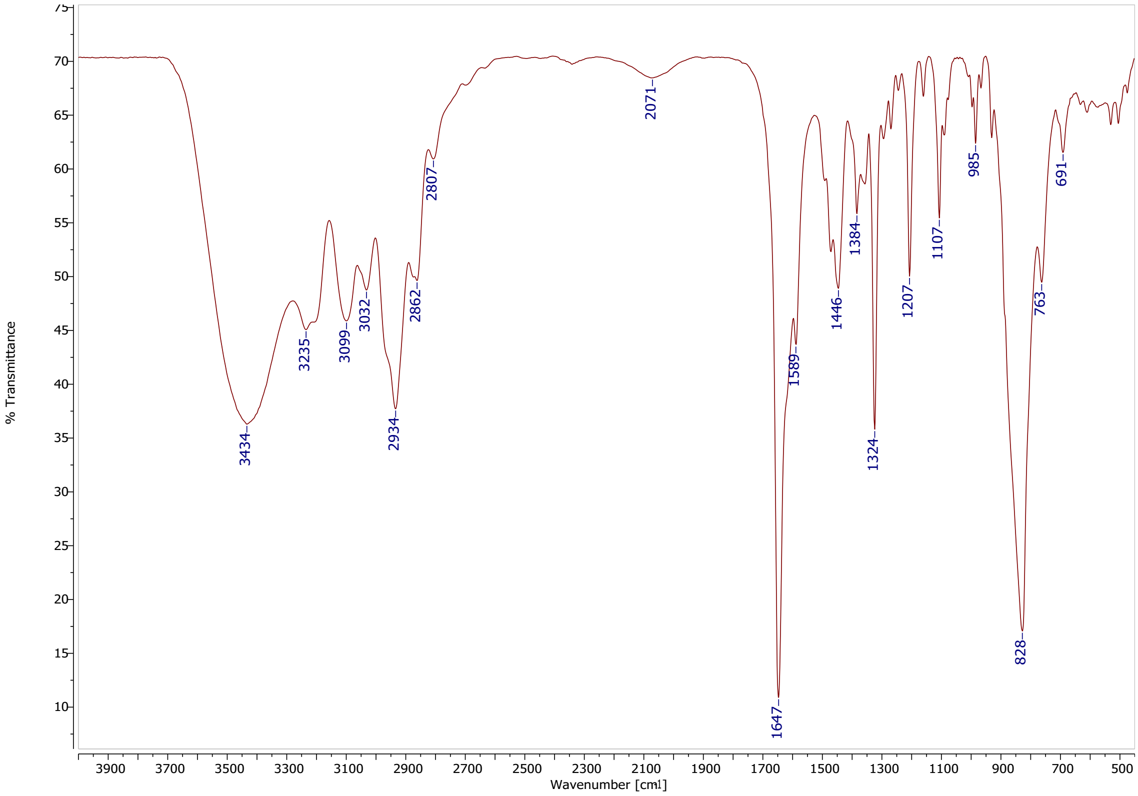


Figure S39. FT-IR spectrum of [DBUH]$_2$[MoO$_4$] (KBr).

4. Isolated Products and by-products

4.1 4-butyl-1,3-dioxolan-2-one

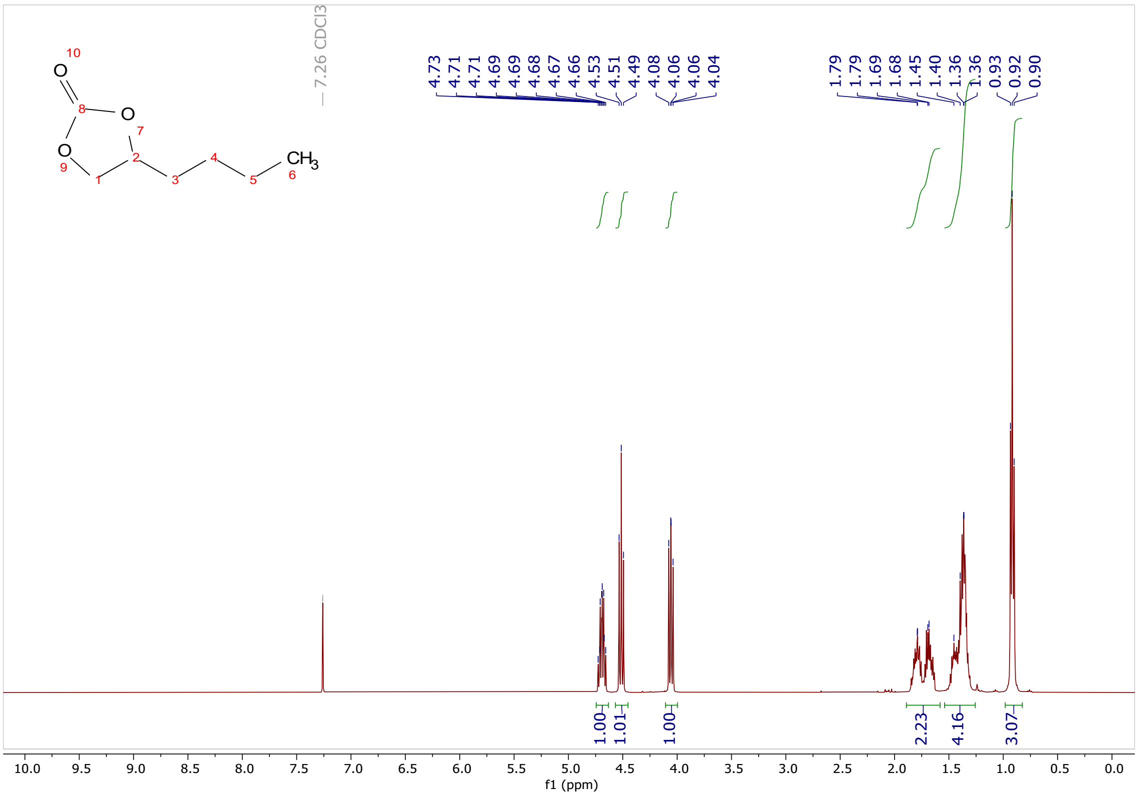


Figure S40. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 4.69 (m, 1H), 4.51 (t, *J* = 8.1 Hz, 1H), 4.06 (dd, *J* = 8.4, 7.2 Hz, 1H), 1.89 – 1.58 (m, 2H), 1.54 – 1.26 (m, 4H), 0.92 (t, *J* = 7.0 Hz, 3H).

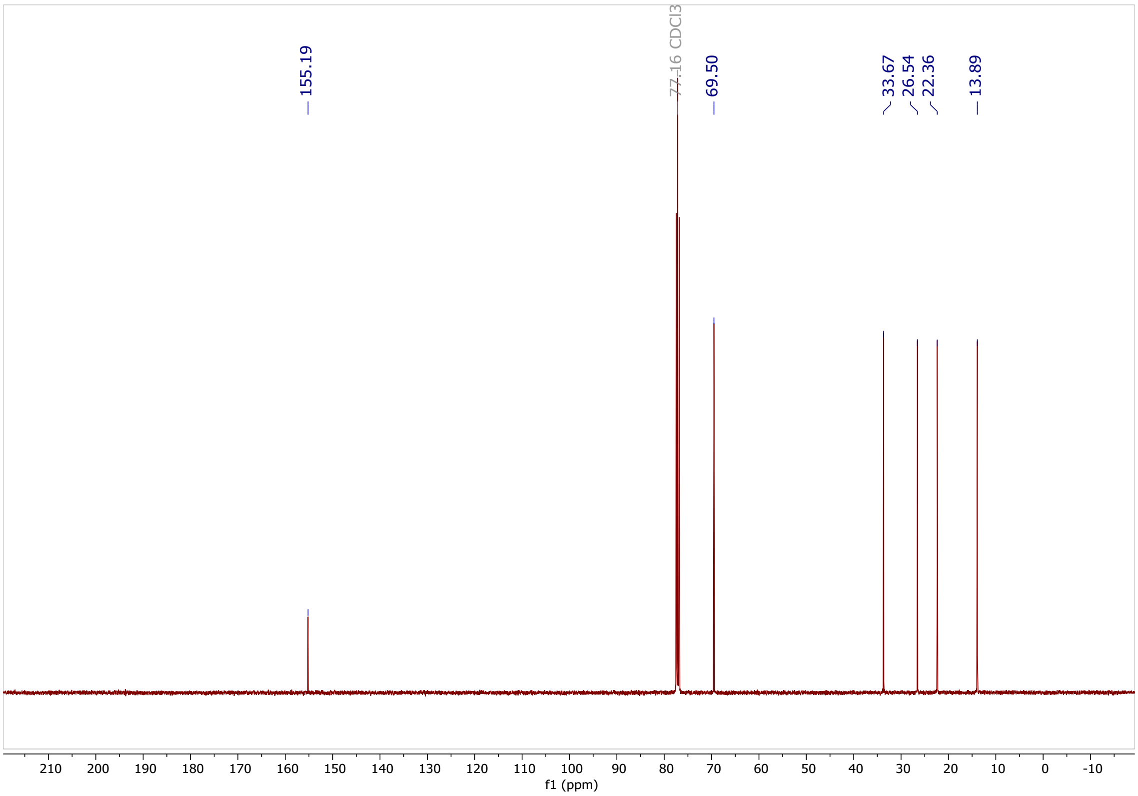


Figure S41. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ (ppm): 155.19; 69.50; 33.67; 26.54; 22.36; 13.89.

4.2 Hexane-1,2-diol

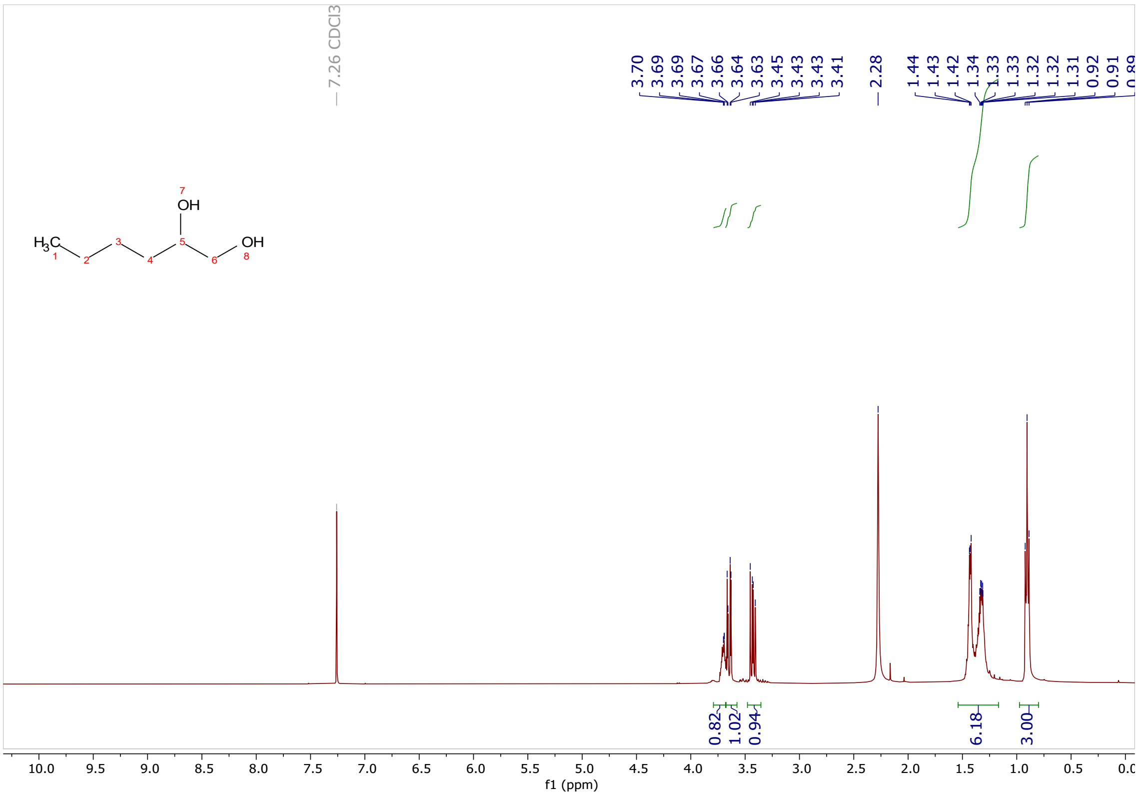


Figure S42. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 3.79 – 3.68 (m, 1H), 3.65 (dd, *J* = 11.1, 3.0 Hz, 1H), 3.43 (dd, *J* = 11.0, 7.6 Hz, 1H), 2.28 (s, OH), 1.54 – 1.17 (m, 6H), 0.90 (t, *J* = 7.1 Hz, 3H).

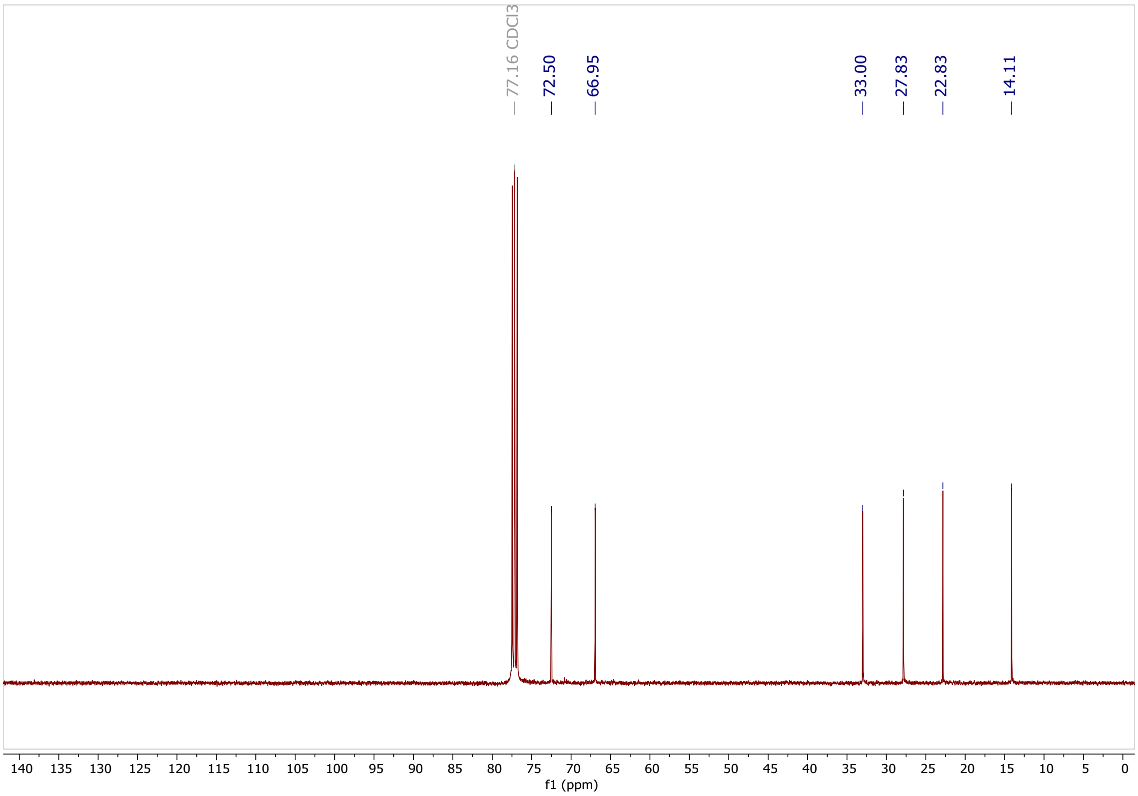


Figure S43. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ (ppm): 72.50; 66.95; 33.00; 27.83; 22.83; 14.11.

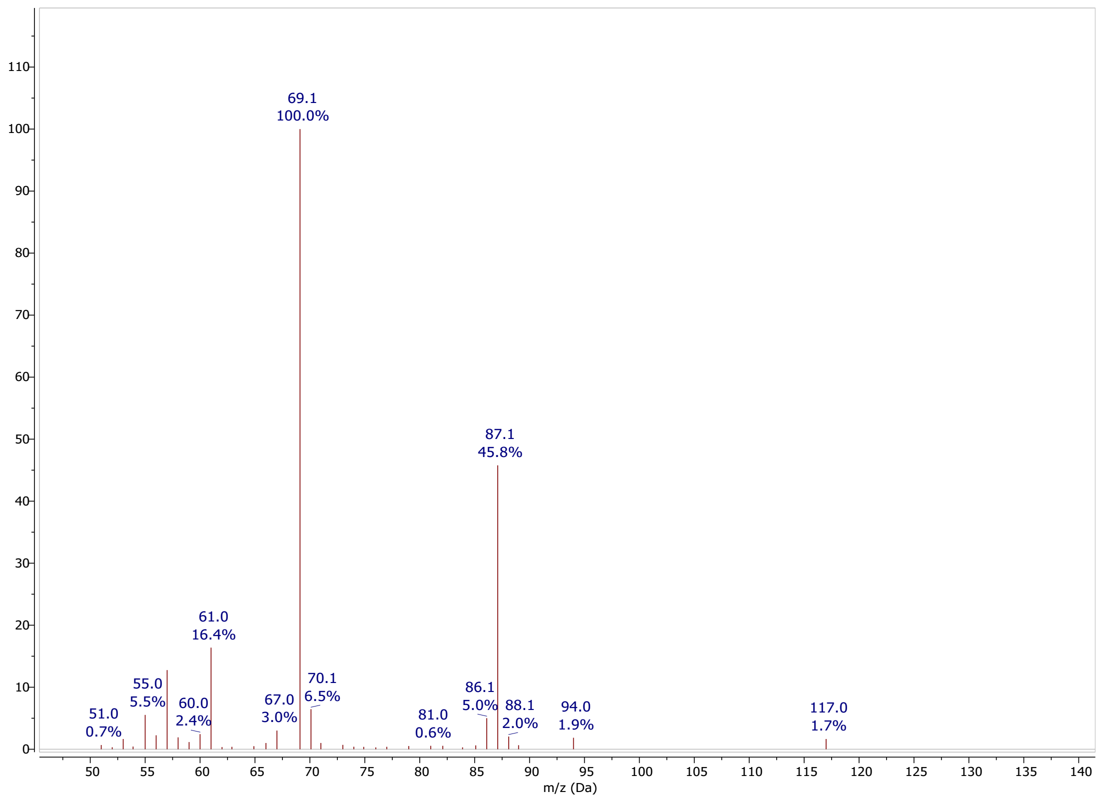


Figure S44. Mass fragmentation (EI, 70 eV) for hexane-1,2-diol.

4.3 1-(2-hydroxyhexoxy)hexan-2-ol

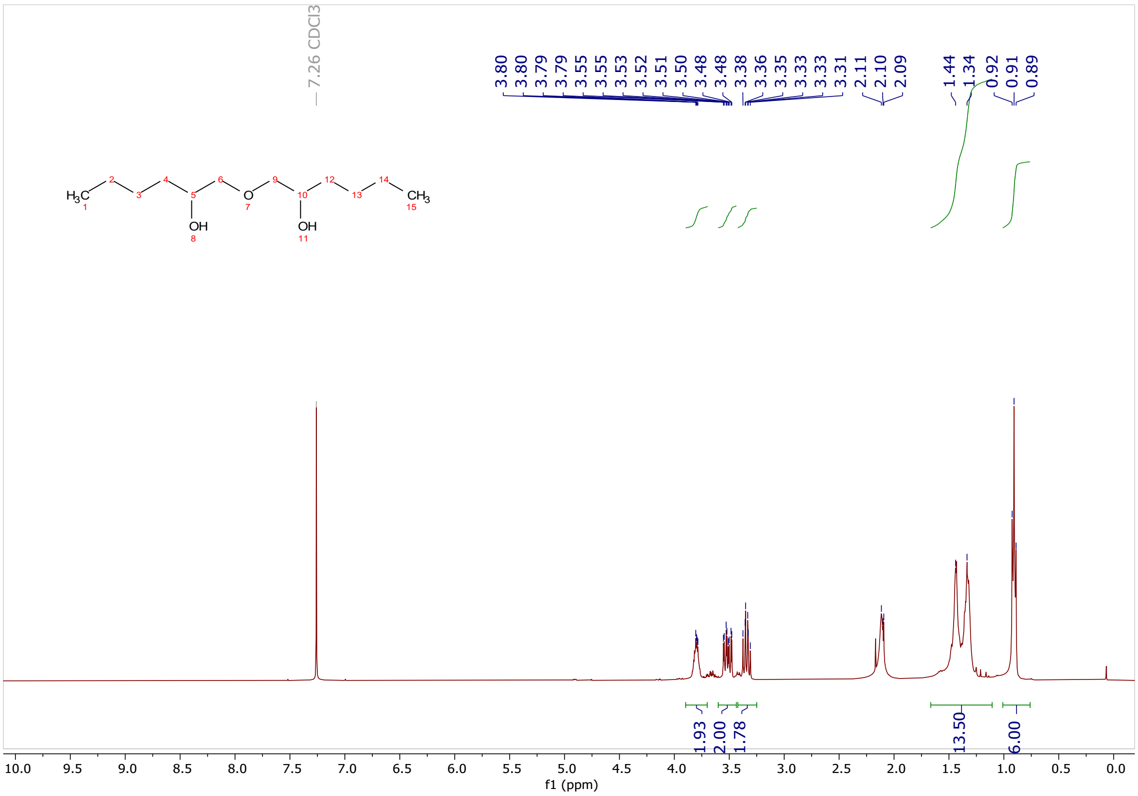


Figure S45. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ(ppm): 3.79 (m, 2H), 3.51 (m, 2H), 3.34 (m, 2H), 2.10 (OH, 2H), 1.67 – 1.13 (m, 14H), 0.91 (t, *J* = 7.2 Hz, 6H).

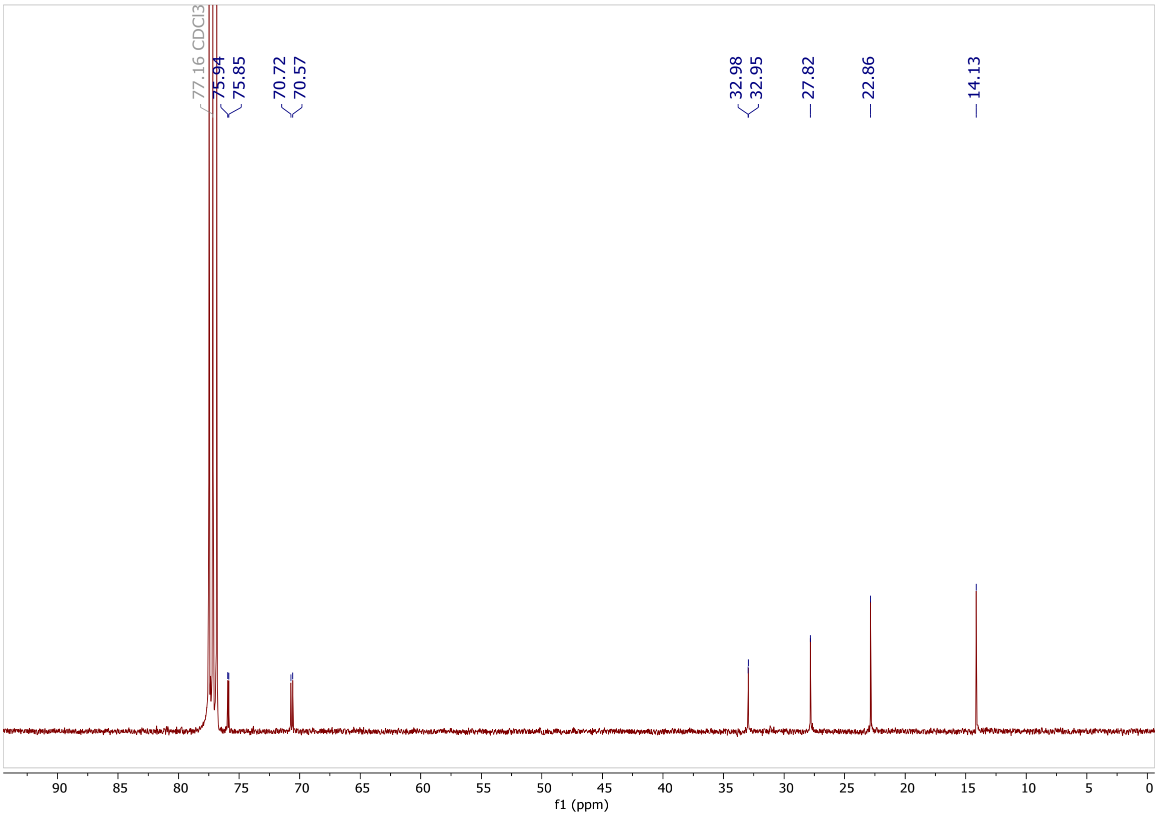


Figure S46. ^{13}C NMR (101 MHz, CDCl$_3$, 298 K) δ (ppm): 75.94; 75.85; 70.72; 70.57; 32.98; 32.95; 27.82; 22.86; 14.13.

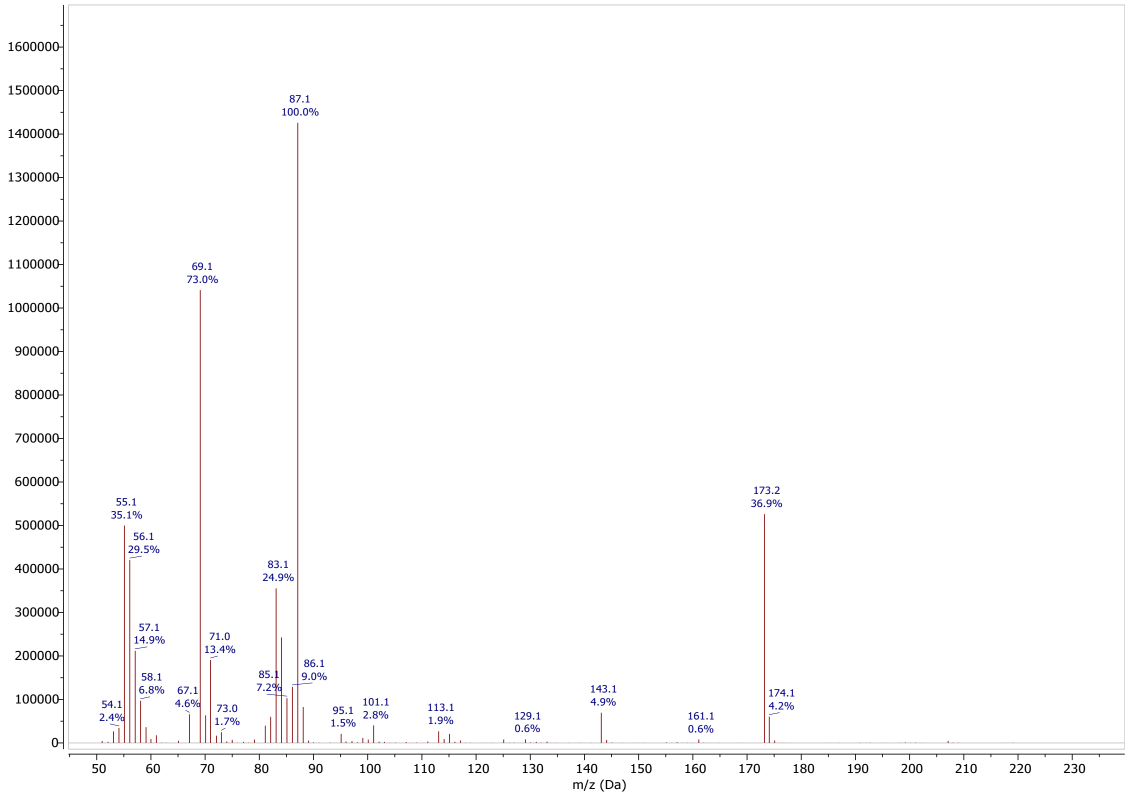


Figure S47. Mass fragmentations (EI, 70 eV) for 1-(2-hydroxyhexoxy)hexan-2-ol.

4.4 4-Phenyl-1,3-dioxolan-2-one

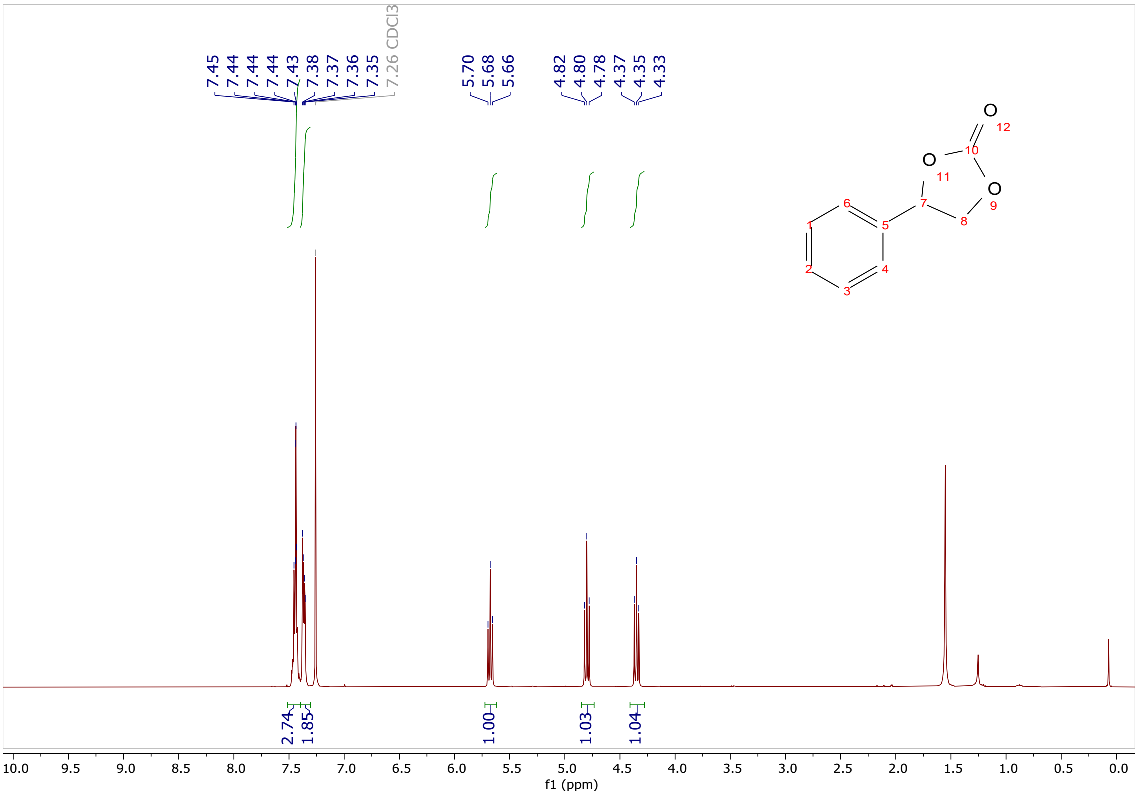


Figure S48. ^1H NMR (400 MHz, $CDCl_3$, 298 K) δ(ppm): 7.52 – 7.40 (m, 3H), 7.36 (m, 2H), 5.68 (t, *J* = 8.0 Hz, 1H), 4.80 (t, *J* = 8.4 Hz, 1H), 4.35 (t, *J* = 8.2 Hz, 1H).

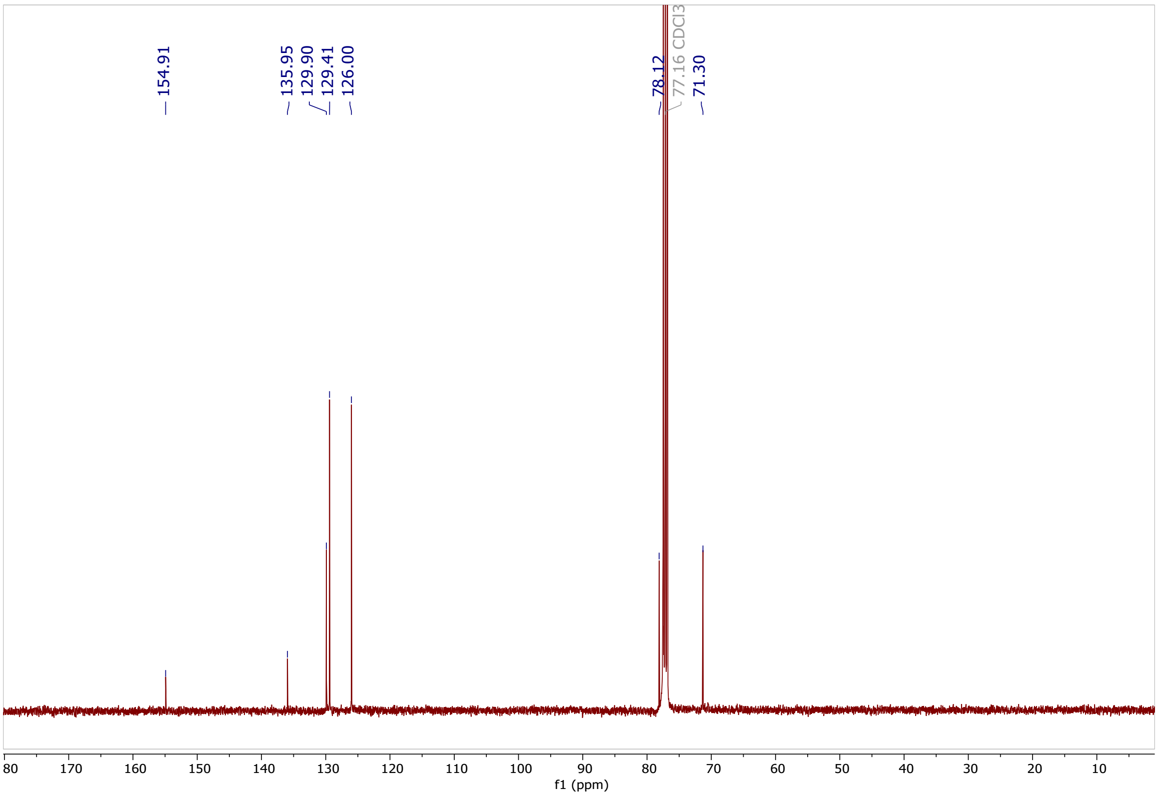


Figure S49. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ(ppm): 154.91; 135.95; 129.90; 129.41; 126.00; 78.12; 71.30.

4.5 4-(phenoxy)methyl-1,3-dioxolane-2-one

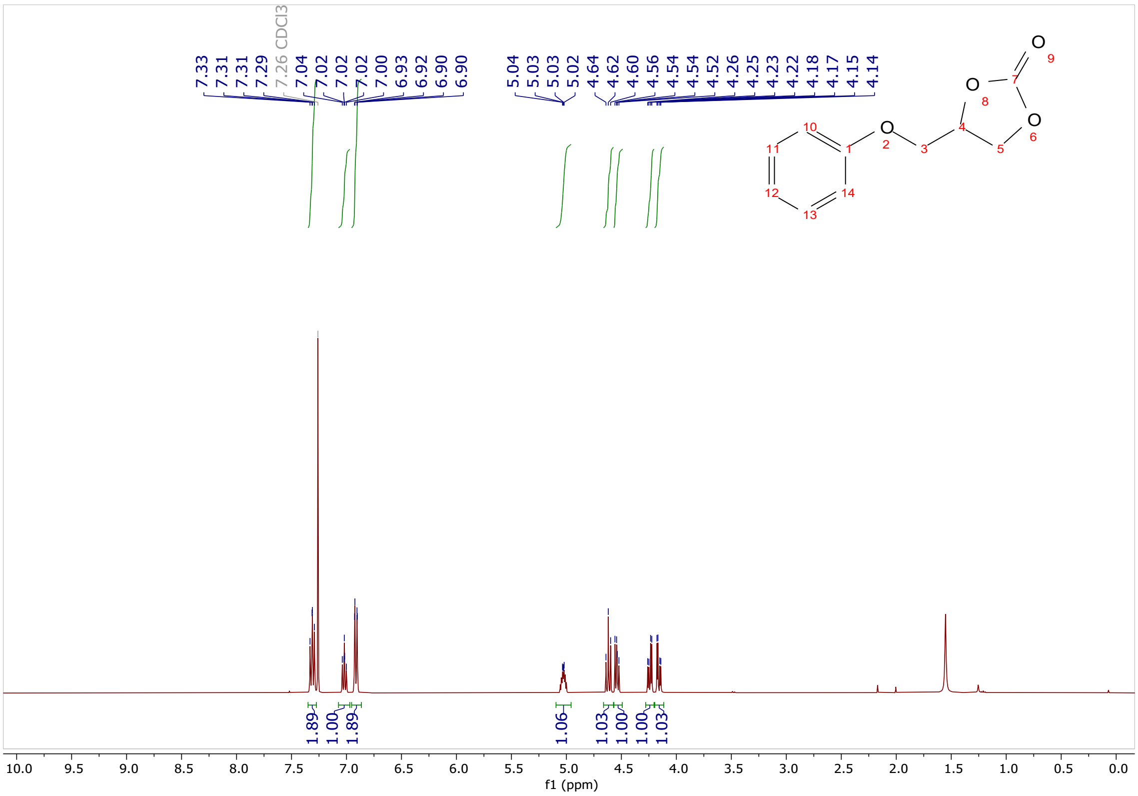


Figure S50. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ(ppm): 7.31 (dd, *J* = 8.7, 7.3 Hz, 2H), 7.07 – 6.97 (m, 1H), 6.91 (dd, *J* = 8.7, 1.0 Hz, 2H), 5.03 (dd, *J* = 4.2, 1.8 Hz, 1H), 4.62 (t, *J* = 8.4 Hz, 1H), 4.54 (dd, *J* = 8.5, 6.0 Hz, 1H), 4.24 (dd, *J* = 10.5, 4.4 Hz, 1H), 4.16 (dd, *J* = 10.5, 3.6 Hz, 1H).

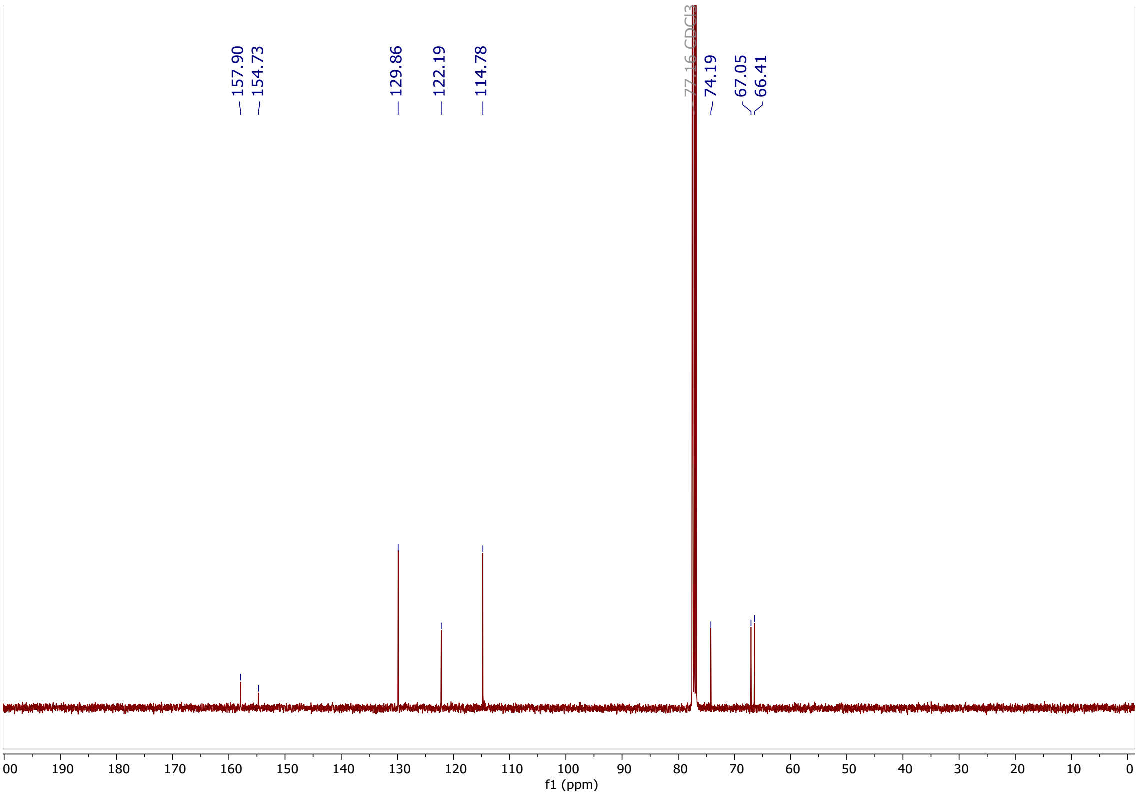


Figure S51. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ(ppm): 157.90; 154.73; 129.86; 122.19; 114.78; 74.19; 67.05; 66.41.

4.6 4-(butoxymethyl)-1,3-dioxolan-2-one

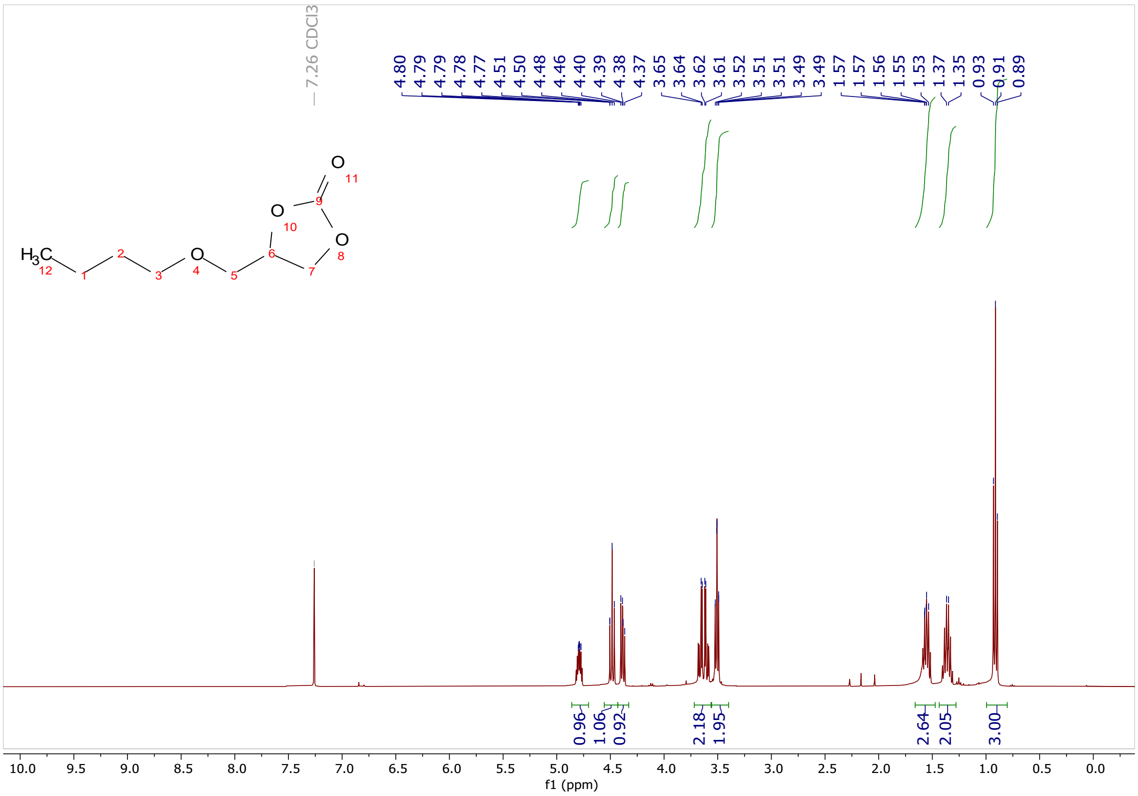


Figure S52. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ(ppm): 4.86 – 4.70 (m, 1H), 4.48 (t, *J* = 8.3 Hz, 1H), 4.38 (dd, *J* = 8.3, 6.1 Hz, 1H), 3.63 (dd, *J* = 13.6, 3.9 Hz, 2H), 3.56 – 3.40 (m, 2H), 1.66 – 1.47 (m, 2H), 1.36 (d, *J* = 7.6 Hz, 2H), 0.91 (t, *J* = 7.4 Hz, 3H).

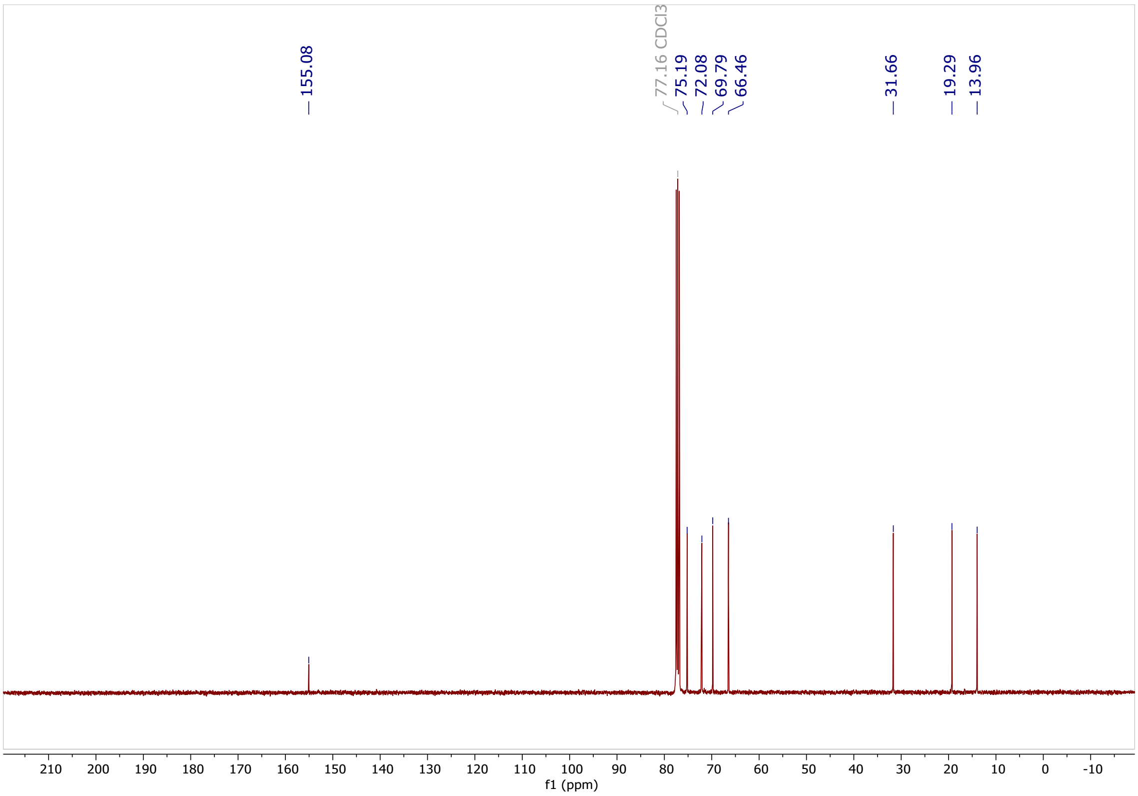


Figure S53. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ(ppm): 155.08; 75.19; 72.08; 69.79; 66.46; 31.66; 19.29, 13.96.

4.7 4-methyl-1,3-dioxolan-2-one

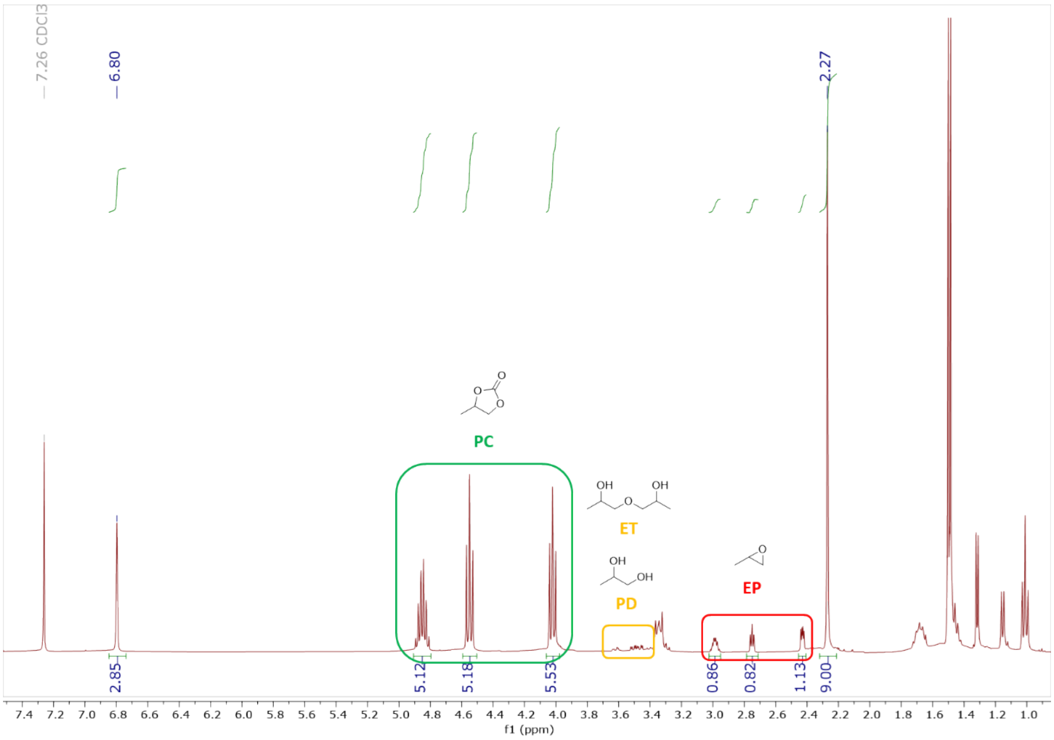


Figure S54. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$, 298 K) of the crude reaction mixture for CO_2 fixation into 1,2-epoxypropane.

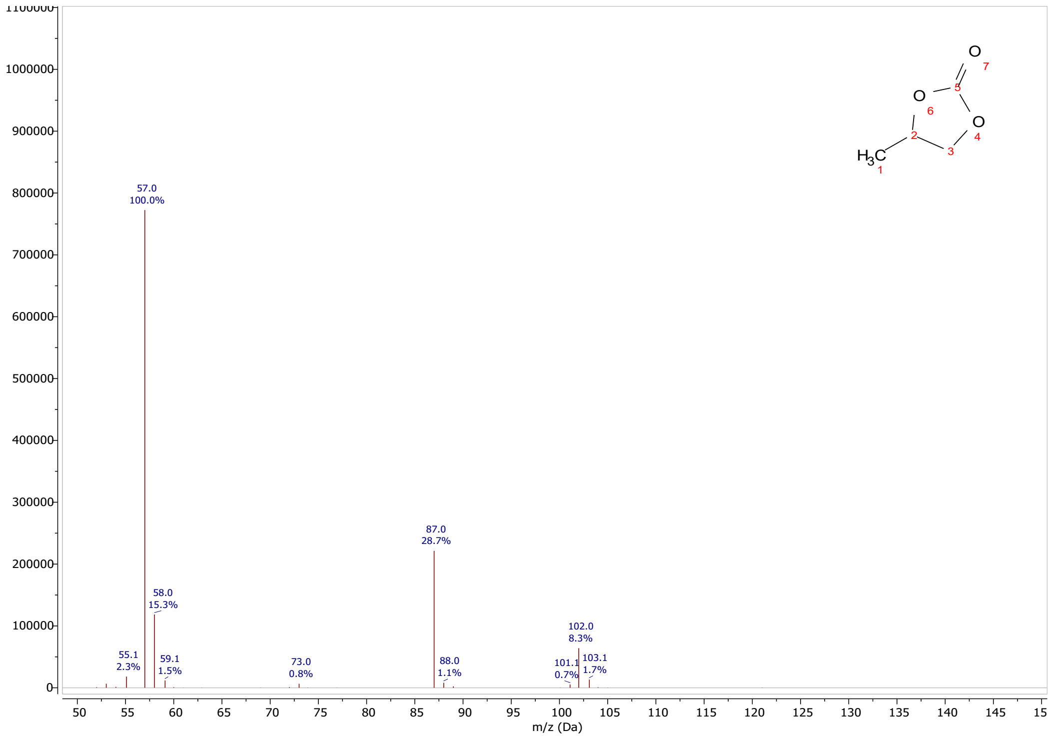


Figure S55. Mass fragmentations (EI; 70 eV) for 4-methyl-1,3-dioxolan-2-one.

4.8 4-chloromethyl-[1,3]dioxolan-2-one

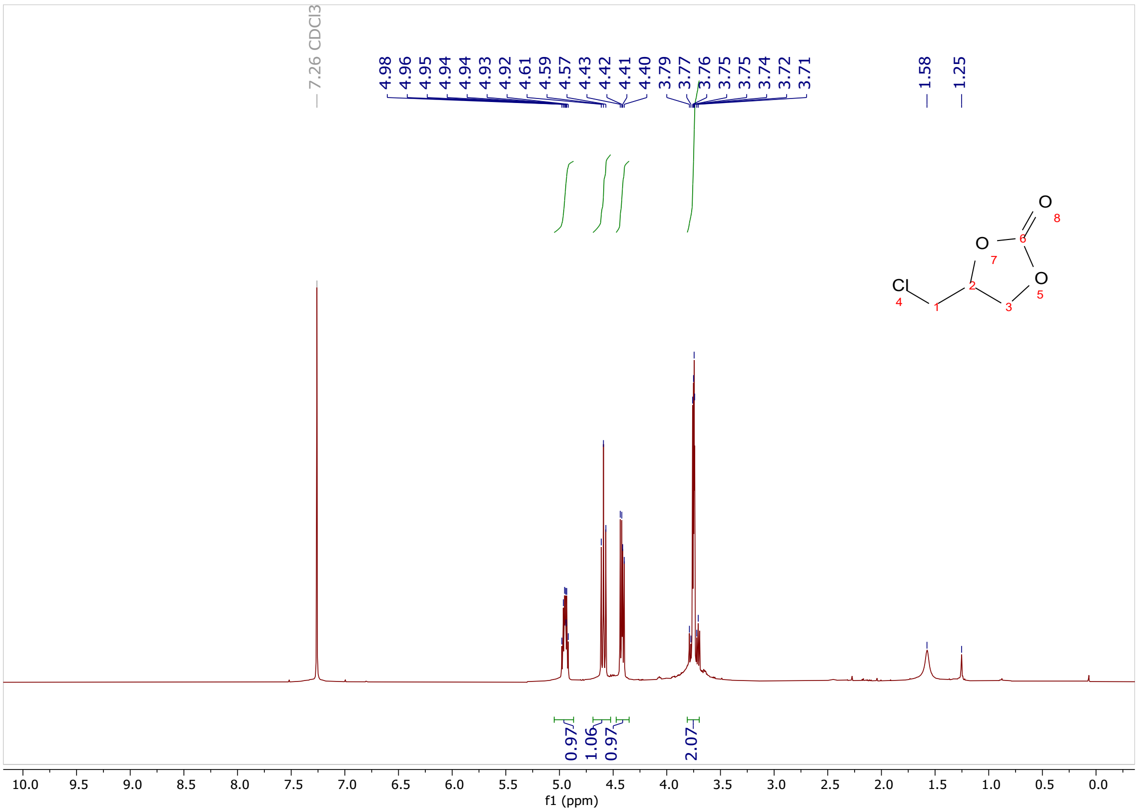


Figure S56. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ (ppm): 5.05 – 4.87 (m, 1H), 4.69 – 4.52 (m, 1H), 4.42 (dd, *J* = 8.9, 5.7 Hz, 1H), 3.81 – 3.70 (m, 2H).

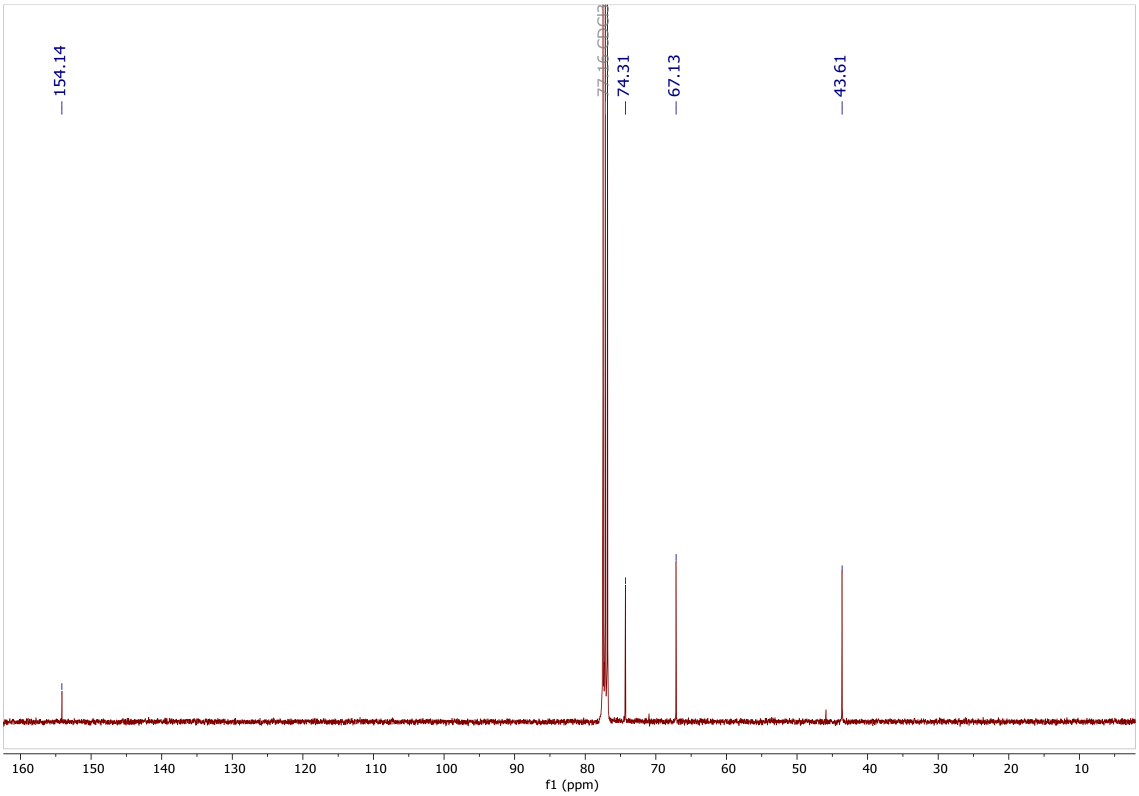


Figure S57. ^{13}C NMR (101 MHz, CDCl$_3$, 298 K) δ(ppm): 154.14; 74.31; 67.13; 43.61.

4.9 4-[(prop-2-yn-1-yloxy)methyl]-1,3-dioxolan-2-one

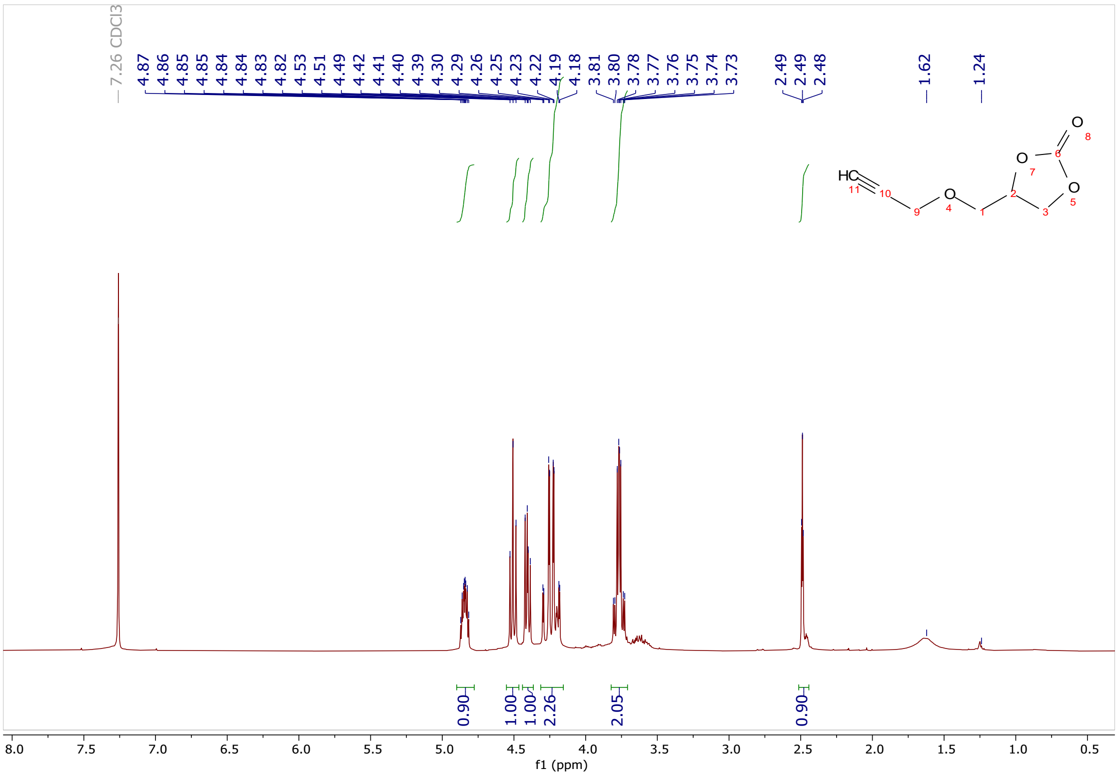


Figure S58. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ(ppm): 4.90 – 4.78 (m, 1H), 4.51 (t, *J* = 8.4 Hz, 1H), 4.40 (dd, *J* = 8.4, 6.0 Hz, 1H), 4.31 – 4.16 (m, 2H), 3.82 – 3.71 (m, 2H), 2.49 (t, *J* = 2.4 Hz, 1H).

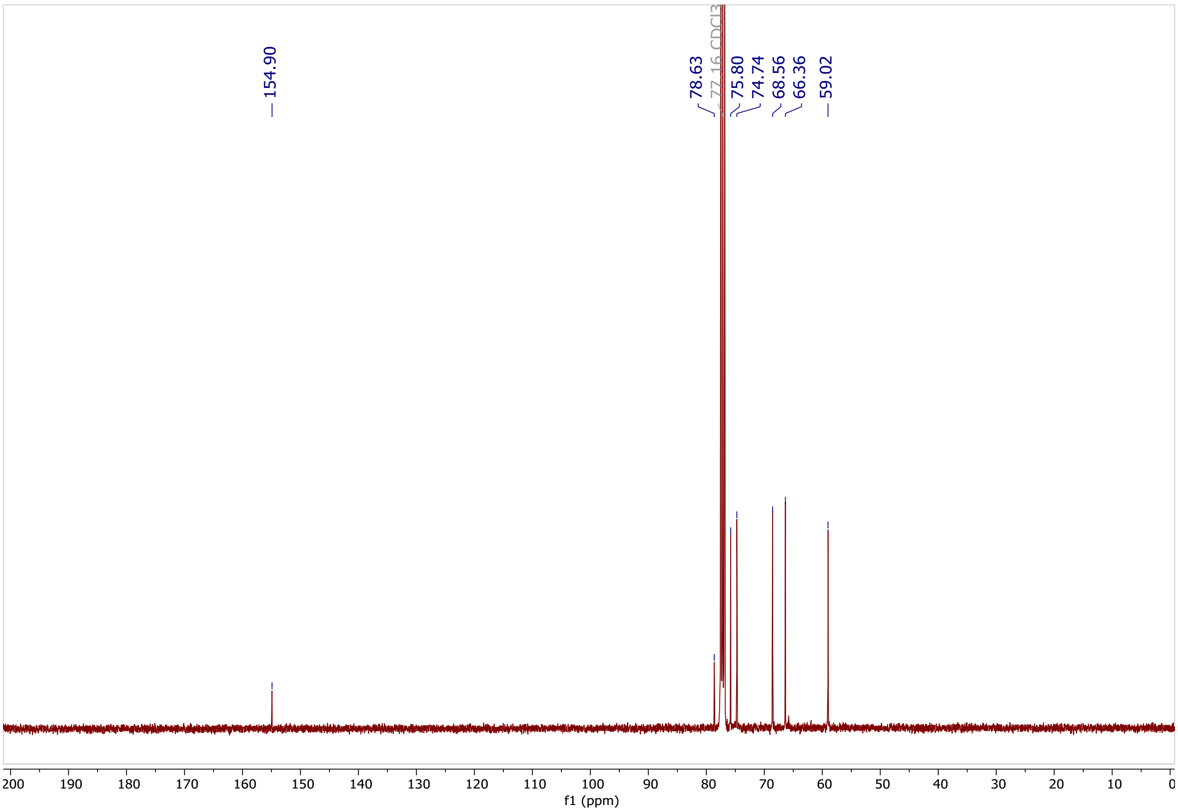


Figure S59. ^{13}C NMR (101 MHz, CDCl$_3$) δ 154.90, 78.63, 75.80, 74.74, 68.56, 66.36, 59.02.

4.10 4,4'-**{**[butane-1,4-diylbis(oxy)]bis(methylene)**}**bis(1,3-dioxolan-2-one)

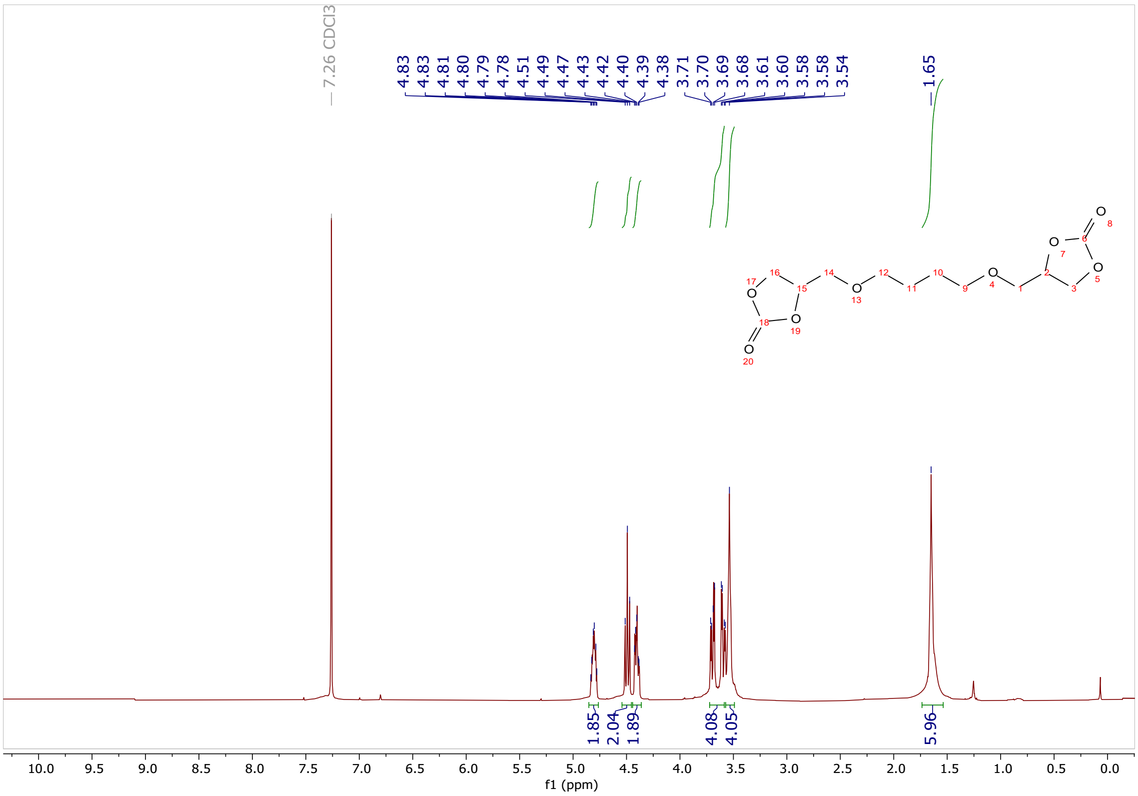


Figure S60. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ(ppm): 4.85 – 4.76 (m, 2H), 4.49 (t, J = 8.4 Hz, 2H), 4.44 – 4.36 (m, 2H), 3.72 – 3.59 (m, 4H), 3.57 – 3.49 (m, 4H), 1.74 – 1.54 (m, 6H).

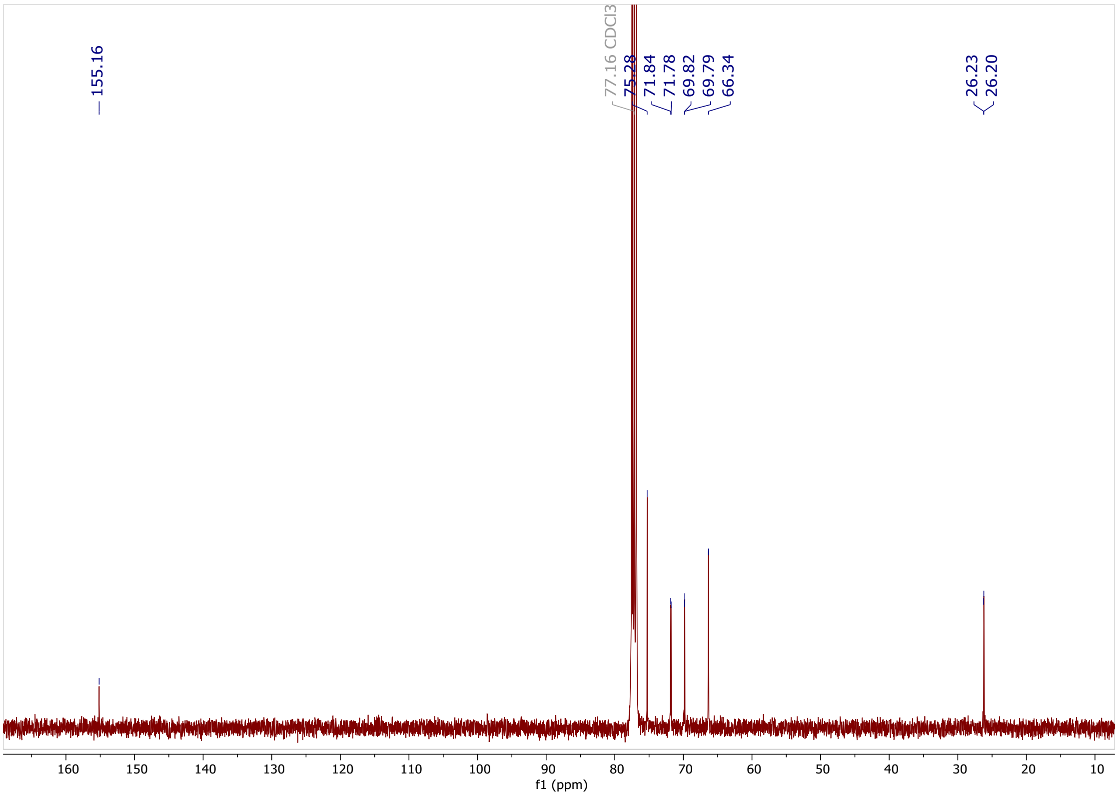


Figure S61. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ(ppm): 155.16; 75.28; 71.84; 71.78; 69.82; 69.79; 66.34; 26.23; 26.20.

4.11 Hexahydrobenzo[*d*][1,3]dioxol-2-one

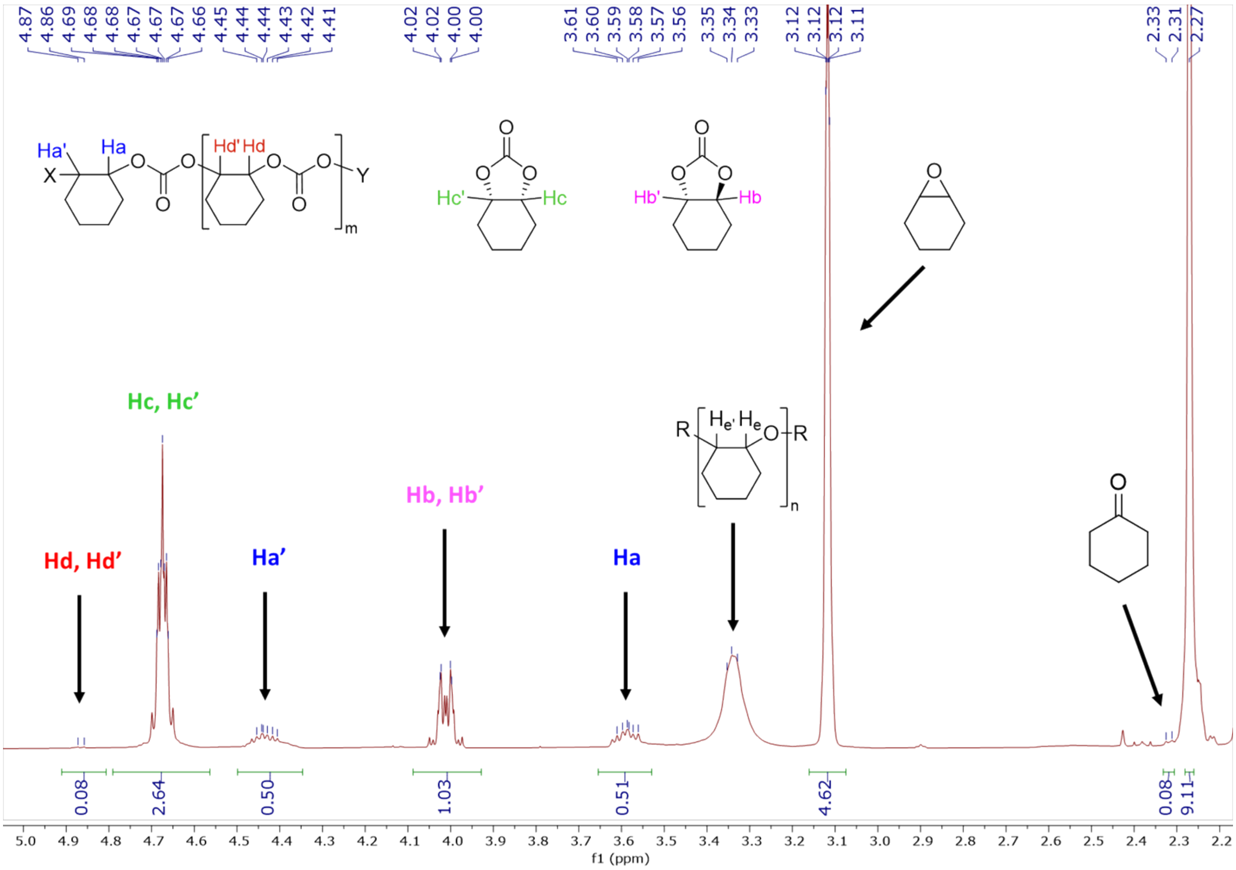


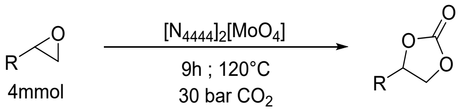
Figure S62. ^{1}H NMR spectrum of the crude reaction mixture of CO_2 fixation into cyclohexene oxide (Entry 11, Table 3).

5. Control experiments of the catalyst precursors

Entry	**Catalytic System**	**Conversion (%)[a]**	**Selectivity (%)[a]**	**Yield (%)[a]**
1	H_2MoO_4	0	n.d.	n.d.
2	$[N_{4444}][OH]$	84	75	63
3	$[P_{4444}][OH]$	24	39	9
4	$[N_{1888}][CH_3OCOO]$	78	80	62
5	$[C_4C_1im][CH_3OCOO]$	67	68	46
6	DBU	10	14	1

Table S1.Reaction conditions: 1,2-epoxyhexane (4 mmol), $p^0(CO_2)$ = 30 bar, T = 120 °C, t = 9 h, solventless.[a] Conversion, selectivity and yield determined by ^1H NMR.

6. Catalyst loading experiments



Entry	Loading (mol %)	Conversion (%)[a]	Selectivity (%)[a]	Yield (%)[a]
1	0.25	53	73	39
2	1.25	92	89	82
3	2.50	100	86	86
4	5.00	100	84	84

Table S2. Reaction conditions: 1,2-epoxyhexane (4 mmol), $p^0(CO_2)$ = 30 bar, T = 120 °C, t = 9 h, solventless.[a] Conversion, selectivity and yield determined by ^1H NMR.

7. Catalyst Recycle

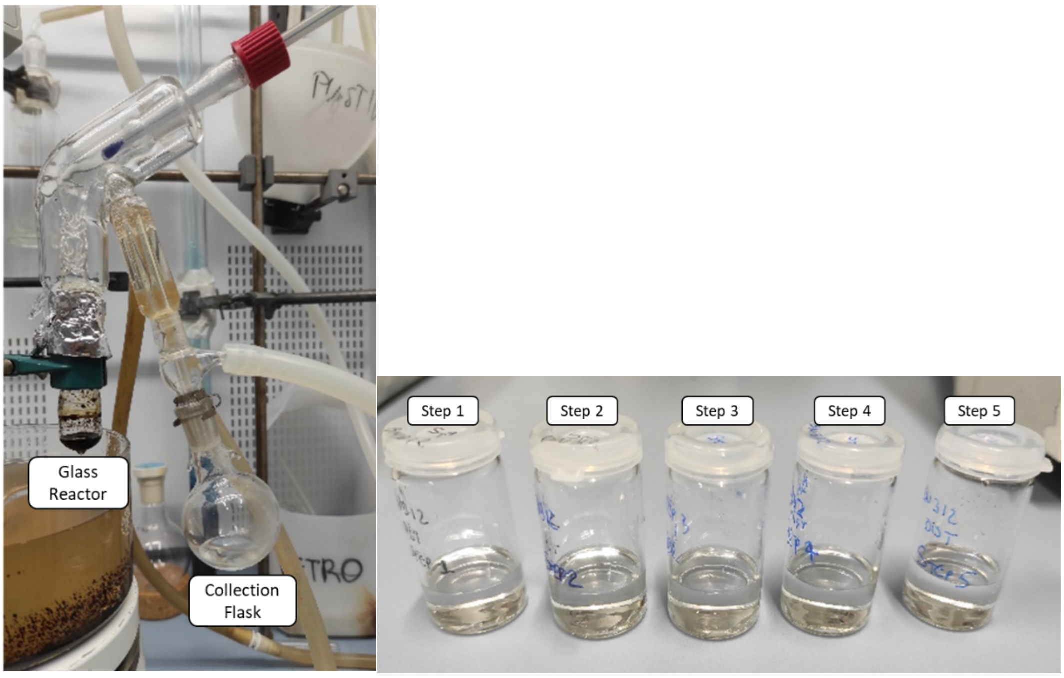


Figure S63. Short path distillation setup for catalytic recycles (left); product mixtures obtained after each recycle (right).

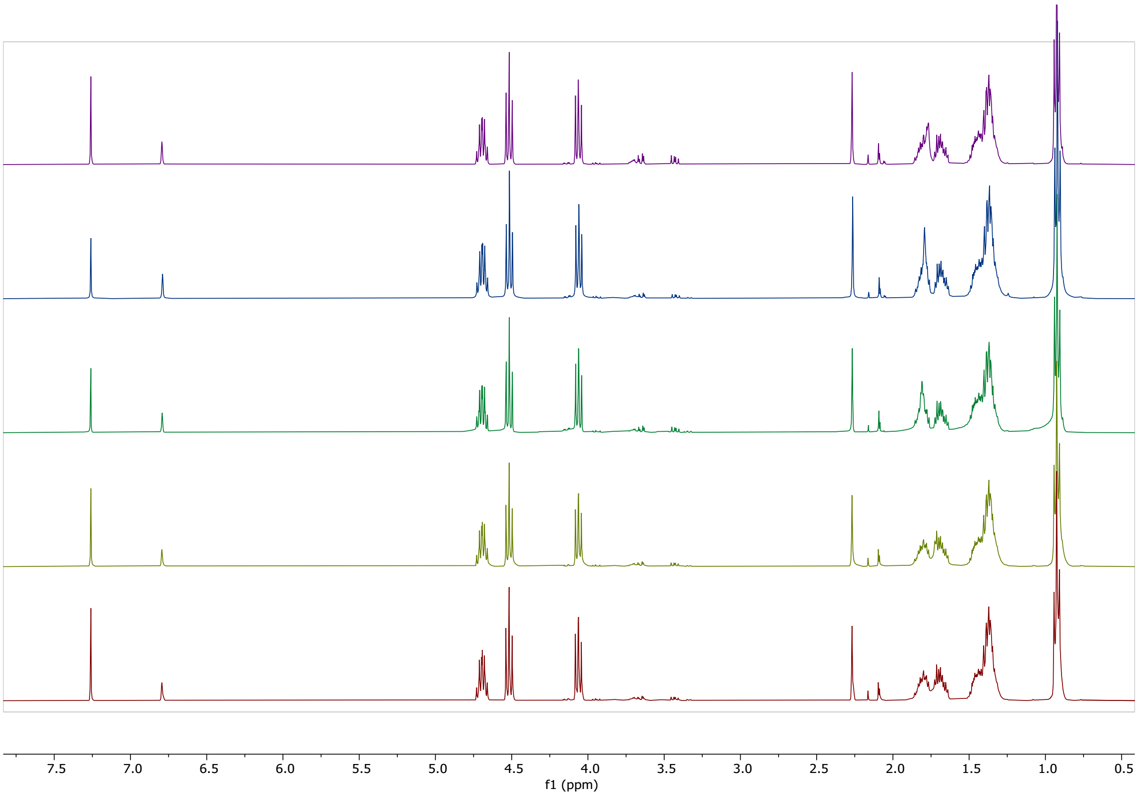


Figure S64. ^{1}H NMR spectra of the COC products obtained from the recycle runs from the first (top) to the fifth (bottom) recycle.

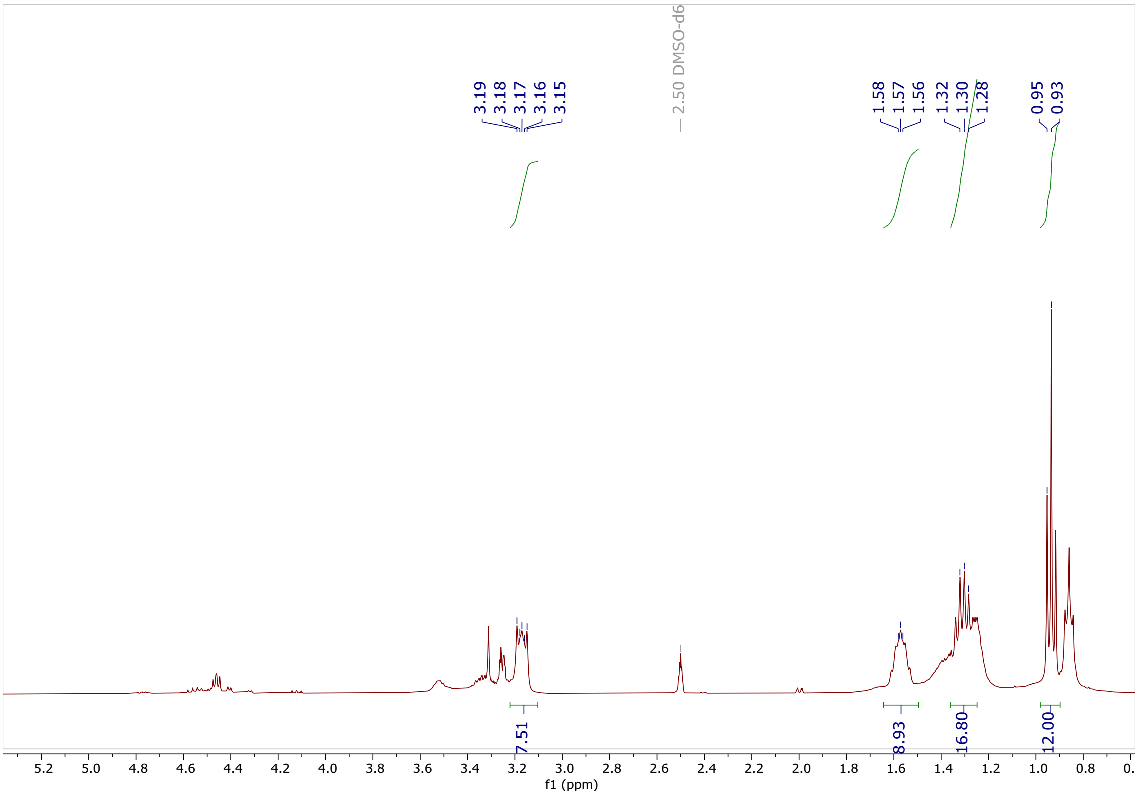


Figure S65. ^{1}H NMR (400 MHz, DMSO-d$_6$, 298 K) of the catalyst after the fifth recycle run.

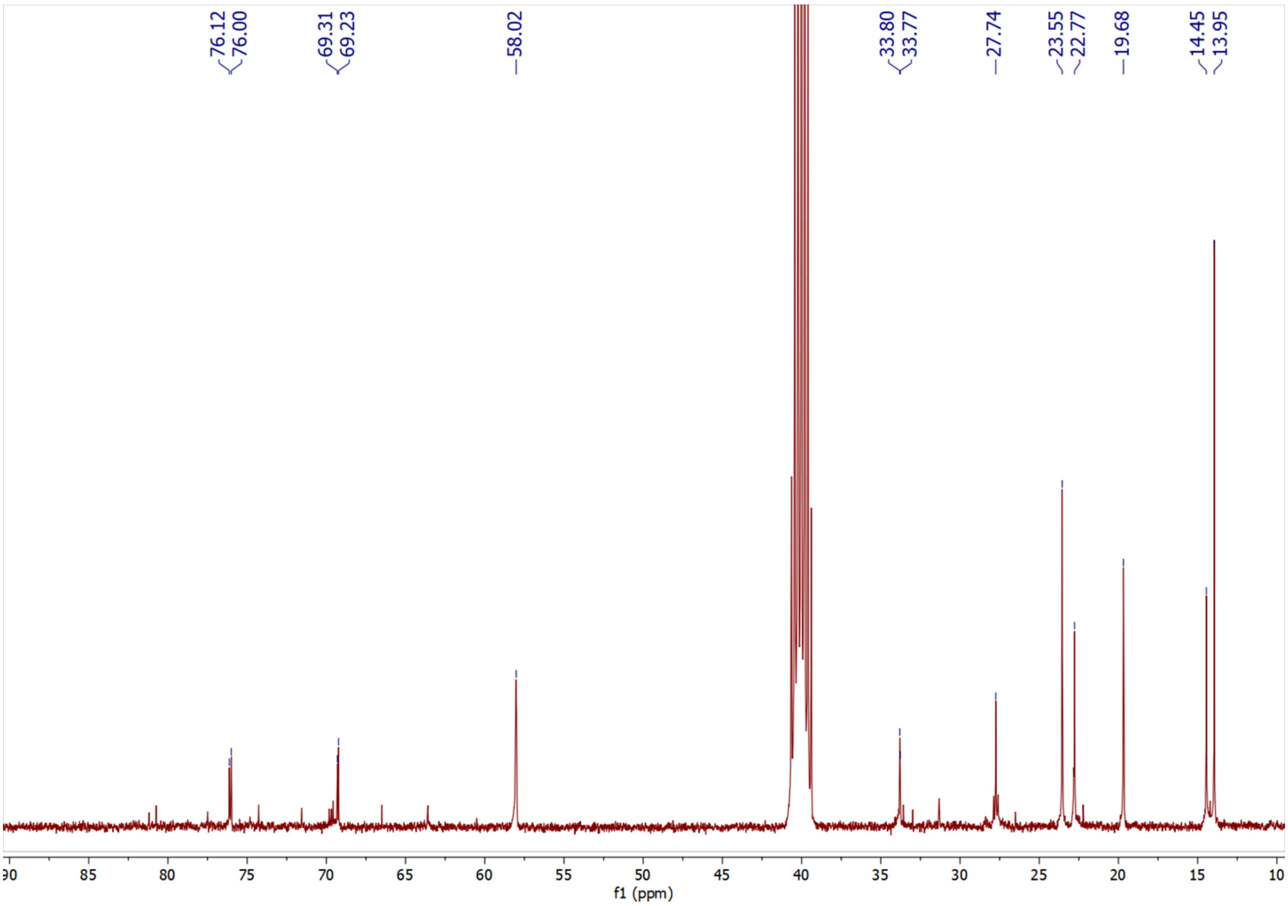


Figure S66. ^{13}C NMR (101 MHz, DMSO-d$_6$, 298 K) of the catalyst after the fifth recycle run. The peaks relative to $[N_{4444}]_2[MoO_4]$ are: 58.02, 23.55, 19.68, 13.95 ppm. The other peaks (76.12, 76.00, 69.31, 69.23, 33.80, 33.77, 27.74, 22.77, 14.45 ppm) are relative to the by-product (1-(2-hydroxyhexoxy)hexan-2-ol) which was accumulated during the cycles and it was not possible to separate from the catalyst with the recycle procedure used. No degradation of the [N_{4444}] cation was observed during the recycle of the catalyst

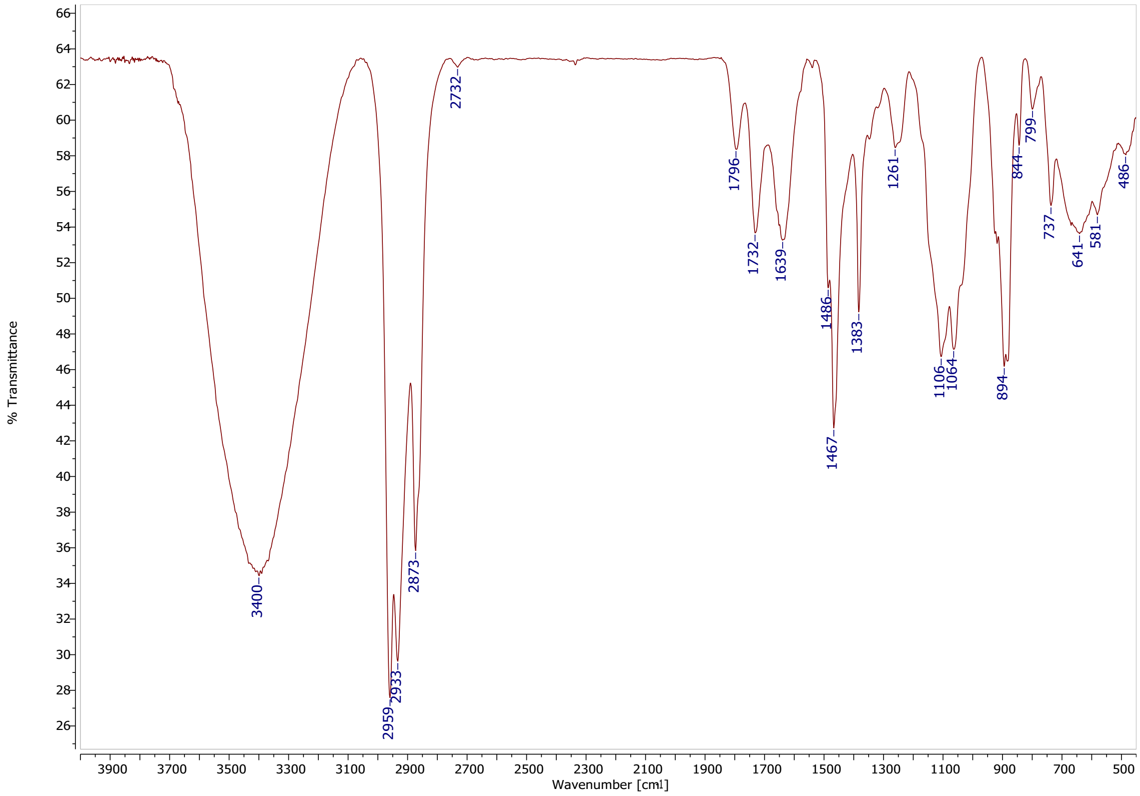


Figure S67. FT-IR spectrum of the catalyst after the fifth recycle run.

8. ICP analysis

Sample Preparation

Around 10 mg of each compound were weighted into a separate Teflon vessels and 6 ml of aqua regia was added. The vessels were than sealed and microwave-heated by means of a Milestone Ethos Up, following a previously reported temperature ramp. Samples were than diluted to 50 mL in MilliQ water and analyzed by ICP-MS. The instrument Nexion 350XX coupled with seaFAST autosampler was optimized in KED mode (4.4 ml of He) using Pt 195 as internal standards. For the quantification of Mo, the mass 95 was selected, and a 5-points calibration curve was used for the mass estimation.

Compound	MW (g/mol)	(mg) weighed	Mo theorical contribution (mg/g)	Mo detected (mg/g)	recovery (%)	RSD (%)
$[N_{4444}]_2[MoO_4]$	644	6.90	206	158	77	1.7
$[N_{4444}]_2[Mo_2O_7]$	788	10.35	252	246	97	1.0
$[N_{4444}]_2[Mo_6O_{19}]$	1364	10.36	437	417	95	0.1
$[N_{4444}]_4[Mo_8O_{26}]$	2153	10.71	382	352	92	0.9

Table S3. ICP data analysis collection.

9. Biblography

1 M. Fabris, V. Lucchini, M. Noè, A. Perosa and M. Selva, Ionic Liquids Made with Dimethyl Carbonate: Solvents as well as Boosted Basic Catalysts for the Michael Reaction, *Chemistry - A European Journal*, 2009, **15**, 12273–12282.

2 R. Calmanti, N. Sargentoni, M. Selva and A. Perosa, One-Pot Tandem Catalytic Epoxidation—CO2 Insertion of Monounsaturated Methyl Oleate to the Corresponding Cyclic Organic Carbonate, *Catalysts*, 2021, **11**, 1477.