catalysts

MDPI

Supplementary Materials

One-Pot Tandem Catalytic Epoxidation—CO_2 Insertion of Monounsaturated Methyl Oleate to the Corresponding Cyclic Organic Carbonate

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Characterization of Ionic Liquids

Trioctylmethylammonium-methyl carbonate $[N_{8,8,8,1}](CH_3OCOO)$

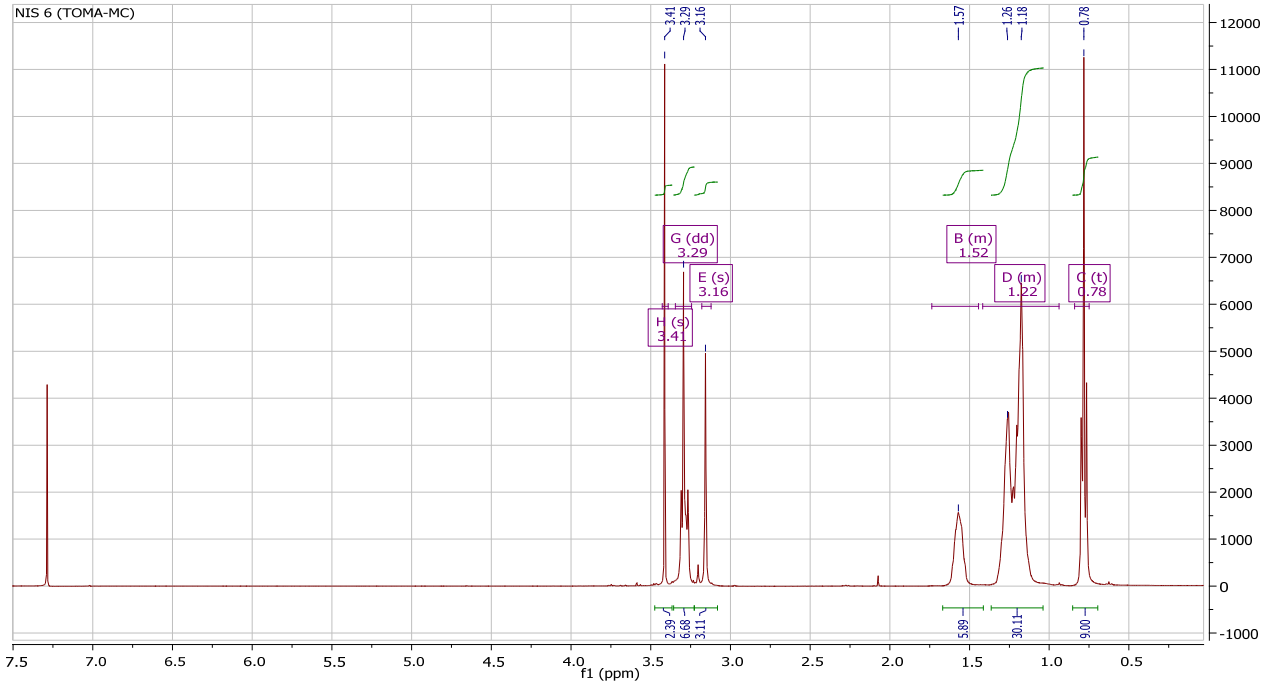

Figure S1. ^{1}H-NMR (400MHz, $CDCl_3$): δ = 0.78 (t, J=6.90, 9H), 1.18 (m, 30H), 1.57 (m, 6H), 3.16 (s, 3H), 3.29 (dd, J=5.56, 11.40hHz, 6H), 3.40 (s, 3H).

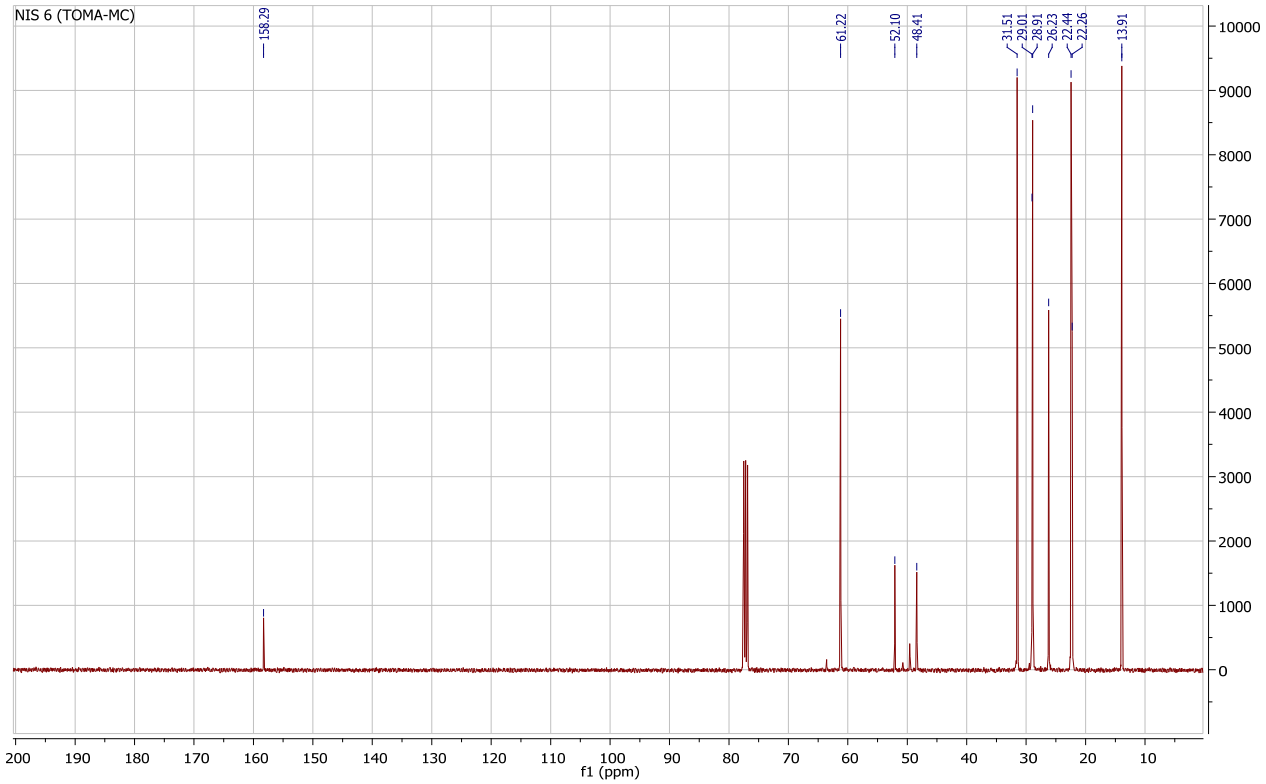

Figure S2. ^{13}C-NMR (100MHz, $CDCl_3$): δ = 13.91, 22.26, 22.44, 26.33, 28.91, 29.01, 31.51, 48.41, 52.10, 61.22, 158.29.

Trioctylmethylphosphonium-methyl carbonate [$P_{8,8,8,1}$](CH_3OCOO)

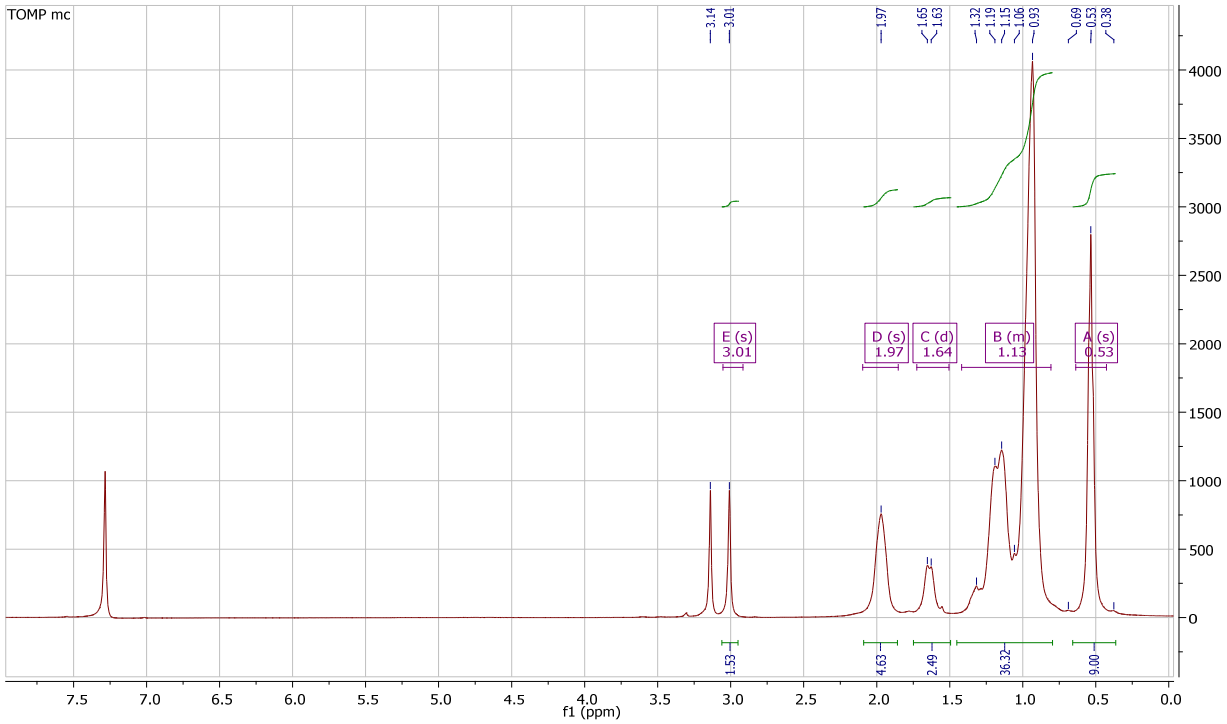

Figure S3. ^{1}H-NMR (400MHz, $CDCl_3$): δ = 0.53 (s, 9H), 0.93-1.32(m, 36H), 1.64 (d, 3H), 1.976 (s, 6H), 3.01 (s, 3H).

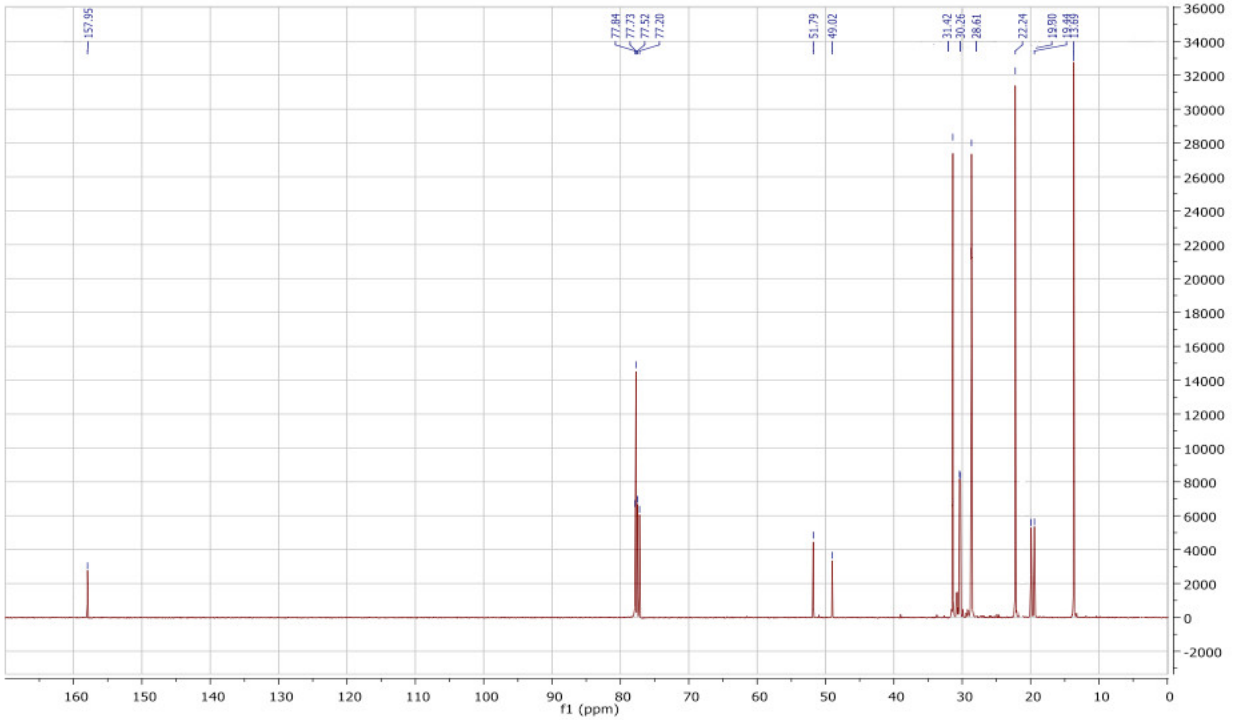

Figure S4. ^{13}C-NMR (100MHz, $CDCl_3$): δ = 13.69, 19.44, 19.90, 22.24, 28.61, 30.26, 31.42, 49.02, 51.79, 77.84, 157.95.

1.-. Butyl-3-methylimidazolium–methyl carbonate / 1-butyl-3-methylimidazolium-2-carboxylate

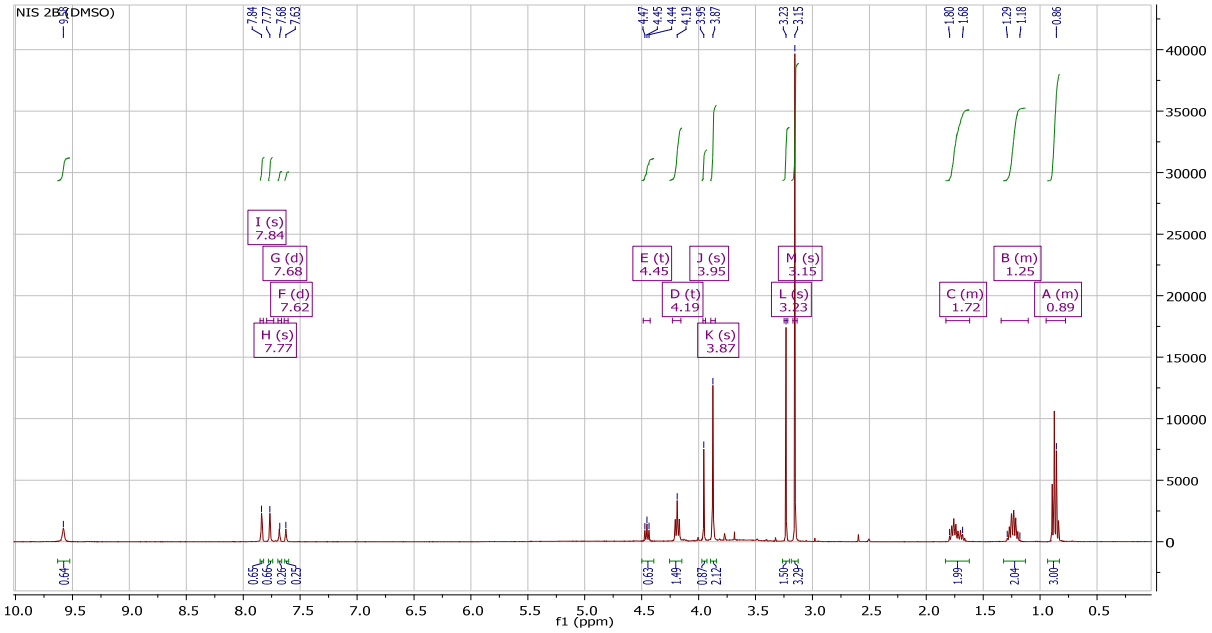

Figure S5. ^{1}H-NMR (400MHz, DMSO) (1-Butyl-3-Methyl-2-Carboxy-Imidazolium): δ = 0.89 (m, 3H), 1.25 (m, 2H), 1.72 (m, 2H), 3.95 (s, 3H), 4.45 (t, J= 7.3, 2H), 7.62 (d, J=1.68Hz, 1H), 7.68 (d, J=1.57Hz, 1H); **^{1}H-NMR (400MHz, DMSO) (BMIM-CH3OCOO):** δ = 0.88 (t, 3H), 1.25 (m, 2H), 1.76 (m, 2H), 3.23 (s, 3H), 3.87 (s, 3H), 4.19 (t, J=7.2Hz, 2H), 7.77 (s, 1H), 7.84 (s, 1H), 9.58 (bs, 1H).

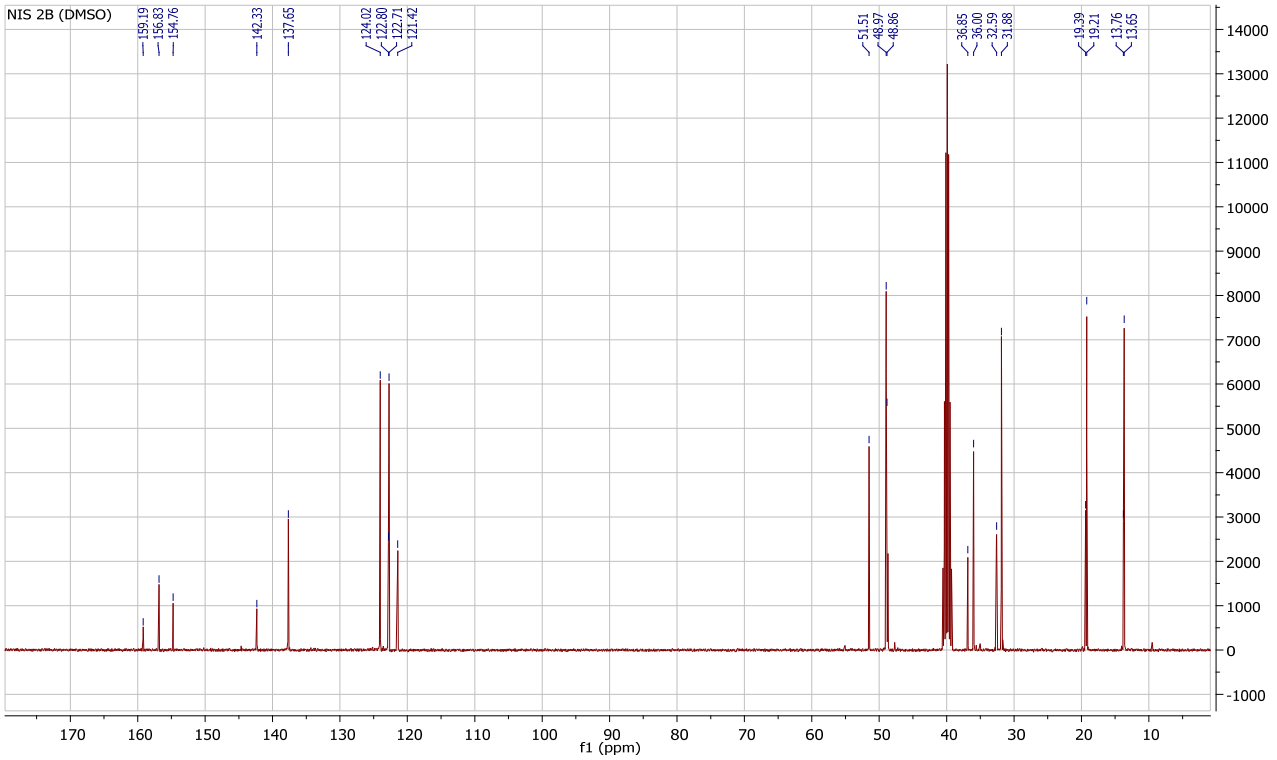

Figure S6. ^{13}C-NMR (100MHz, DMSO) (1-Butyl-3-Methyl-2-Carboxy-Imidazolium): δ = 13.76, 19.39, 32.59, 36.85, 48.97, 112.8, 121.42, 122.8, 159.19; **^{13}C-NMR (100MHz, DMSO) (BMIM-CH$_3$COO):** δ = 13.65, 19.21, 31.88, 36.00, 48.97, 51.51, 122.71, 124.02, 137.65, 156.83.

Trioctylmethylammonium-tungstate ([N$_{8,8,8,1}$]$_2$(WO$_4$), 1)

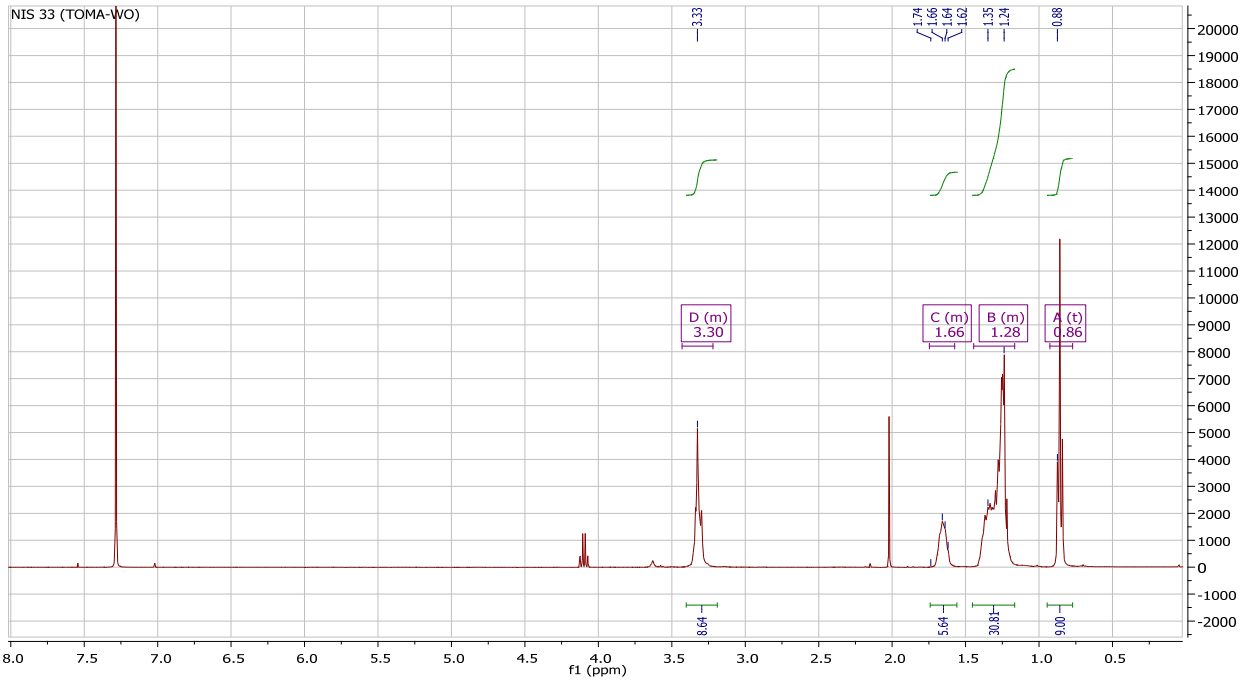

Figure S7. ^{1}H-NMR (400MHz, CDCl$_3$): δ = 0.86 (t, J=6.9Hz, 9H), 1.17-1.45 (m, 30H), 1.67 (m, 6H), 3.36(s, 3H), 3.38 (m, 6H).

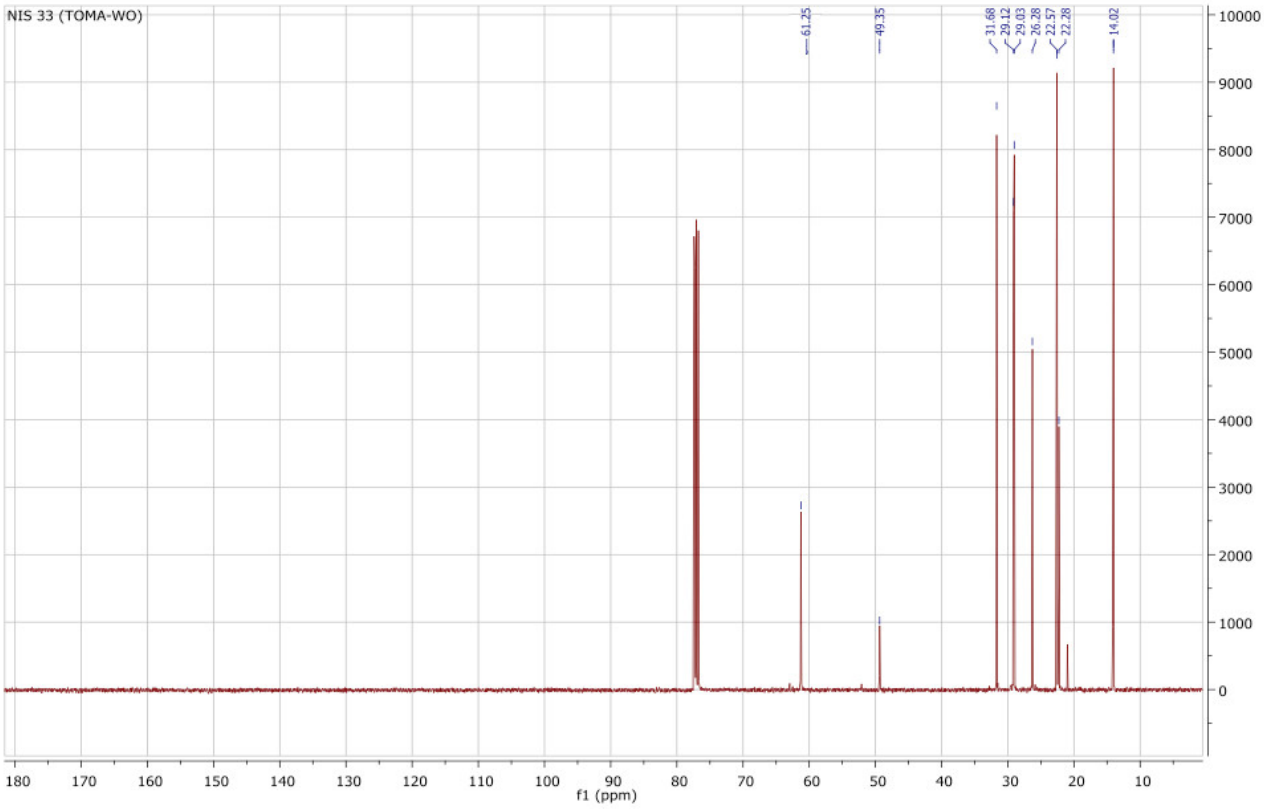

Figure S8. ^{13}**C-NMR (100MHz, CDCl$_3$):** δ = 61.25, 49.35, 31.68, 29.12, 29.03, 26.28, 22.57, 22.28, 14.02.

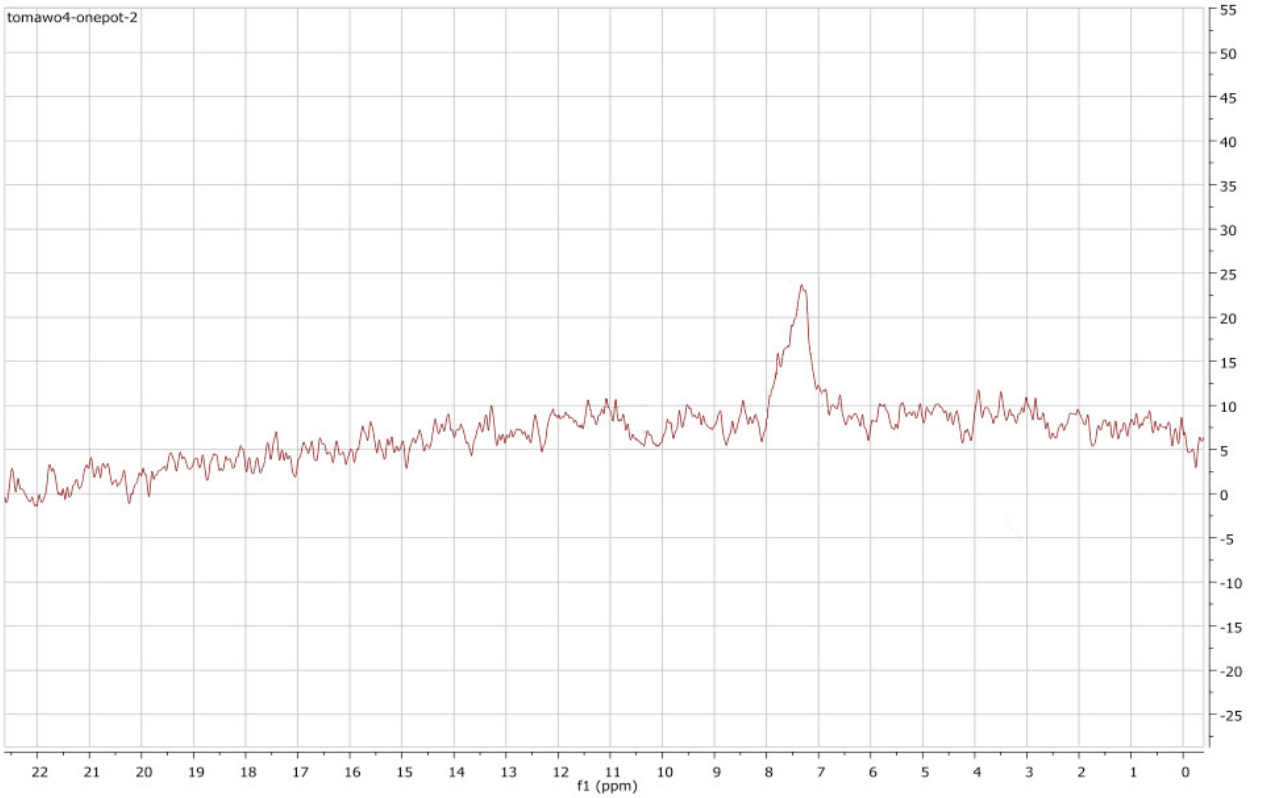

Figure S9. ^{183}W NMR spectra of $[N_{8,8,8,1}]_2WO_4$ in D_2O.

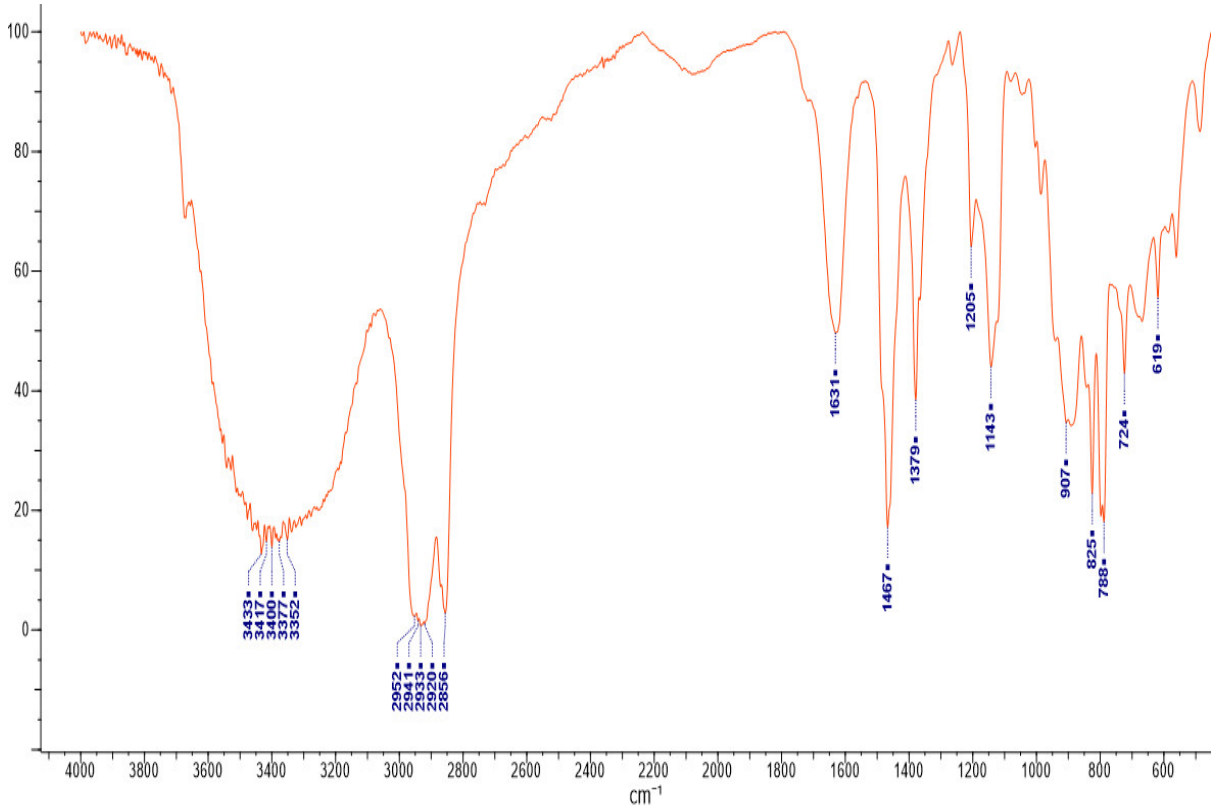

Figure S10. FT-IR spectra of $[N_{8,8,8,1}]_2WO_4$ (KBr pellets).

Trioctylmethylphosphonium-tungstate ($[P_{8,8,8,1}]_2(WO_4)$, 2)

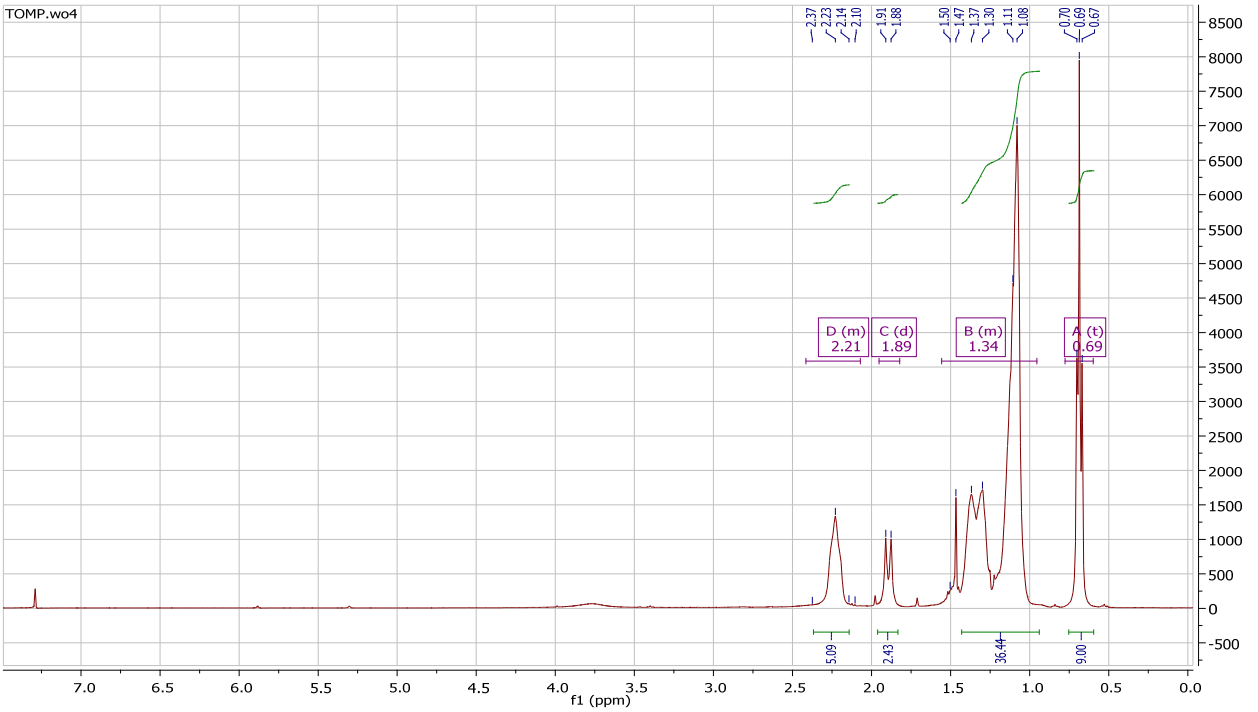

Figure S11. ^{1}H-NMR (400MHz, $CDCl_3$): δ = 0.69 (t, J=6.7Hz, 9H), 1.00-1.50 (m, 36H), 1.85-1.95(d, J=13.3Hz, 3H), 2.21 (m, 6H).

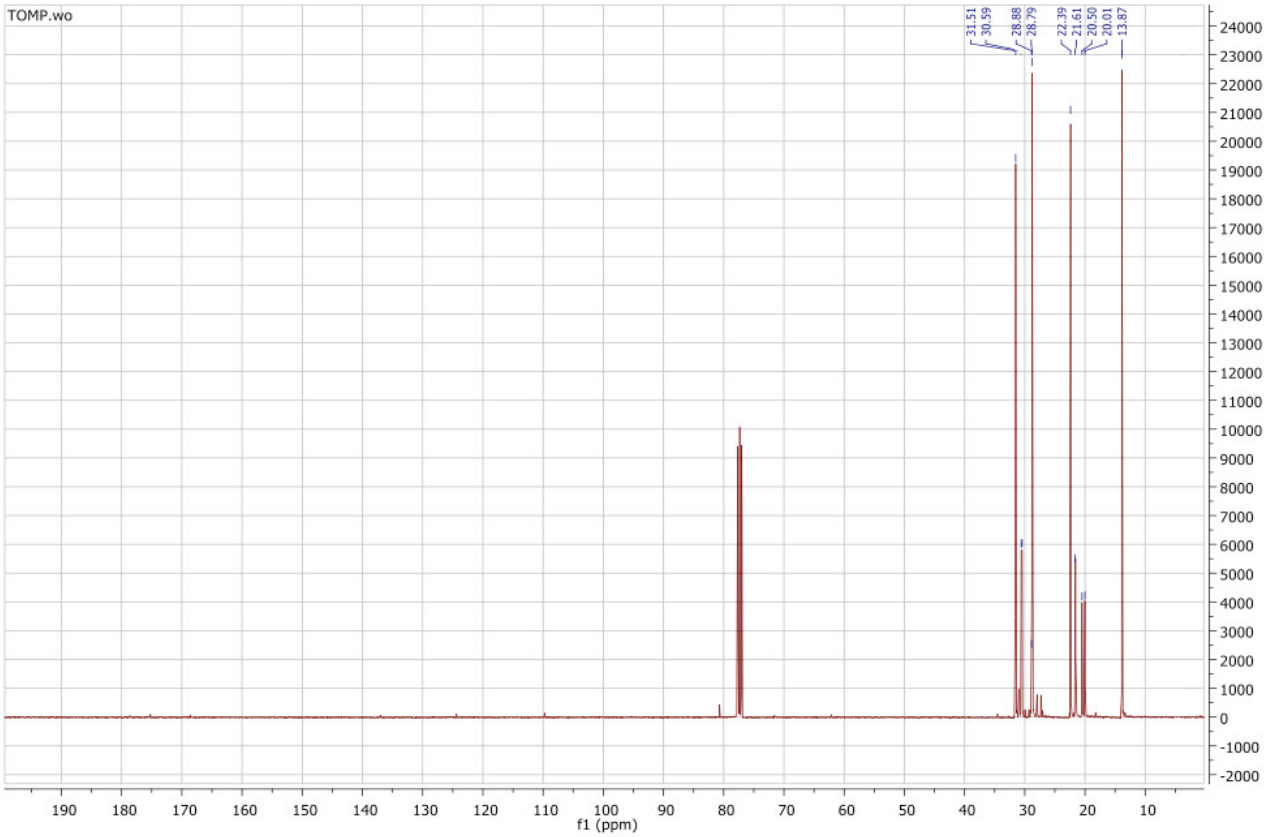

Figure S12. ^{13}C-NMR (100MHz, $CDCl_3$): δ = 13.87, 20.01, 20.50, 21.61, 22.39, 28.79, 28.88, 30.59, 31.51.

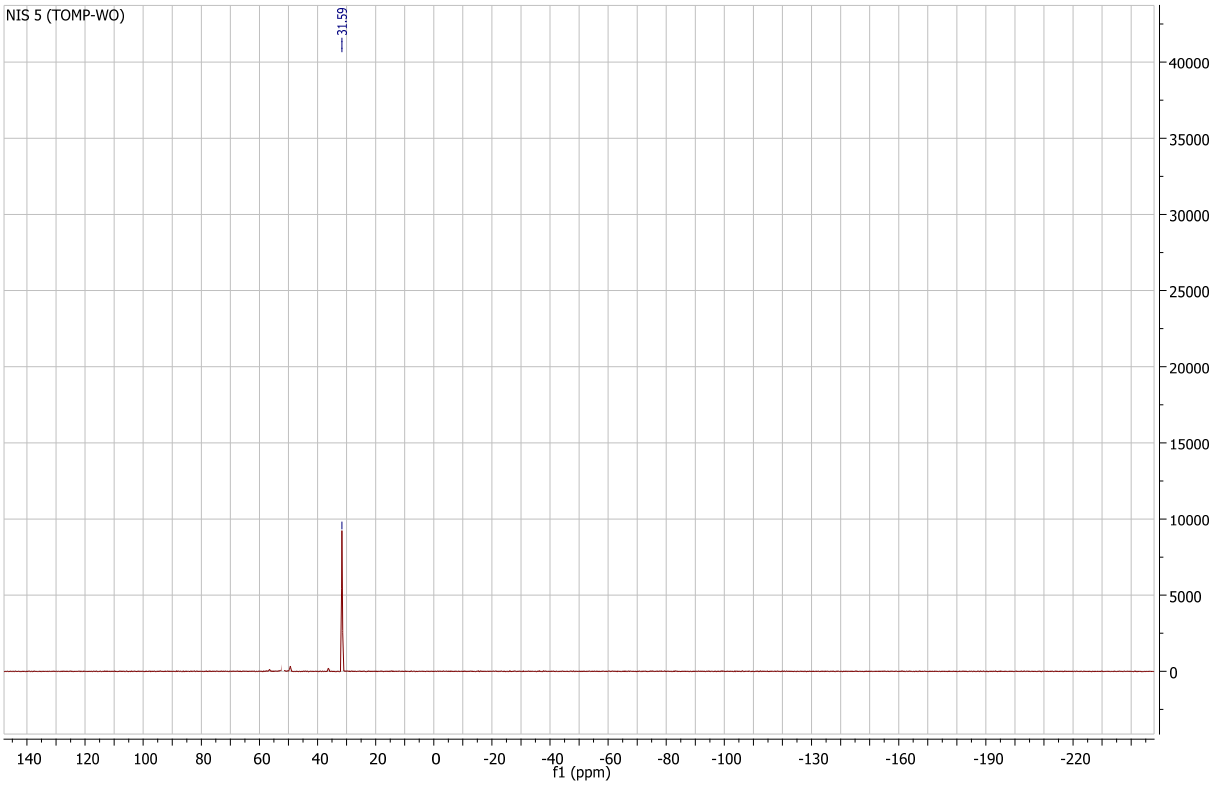

Figure S13. ^{31}P-NMR (162MHz, $CDCl_3$): δ = 31.53.

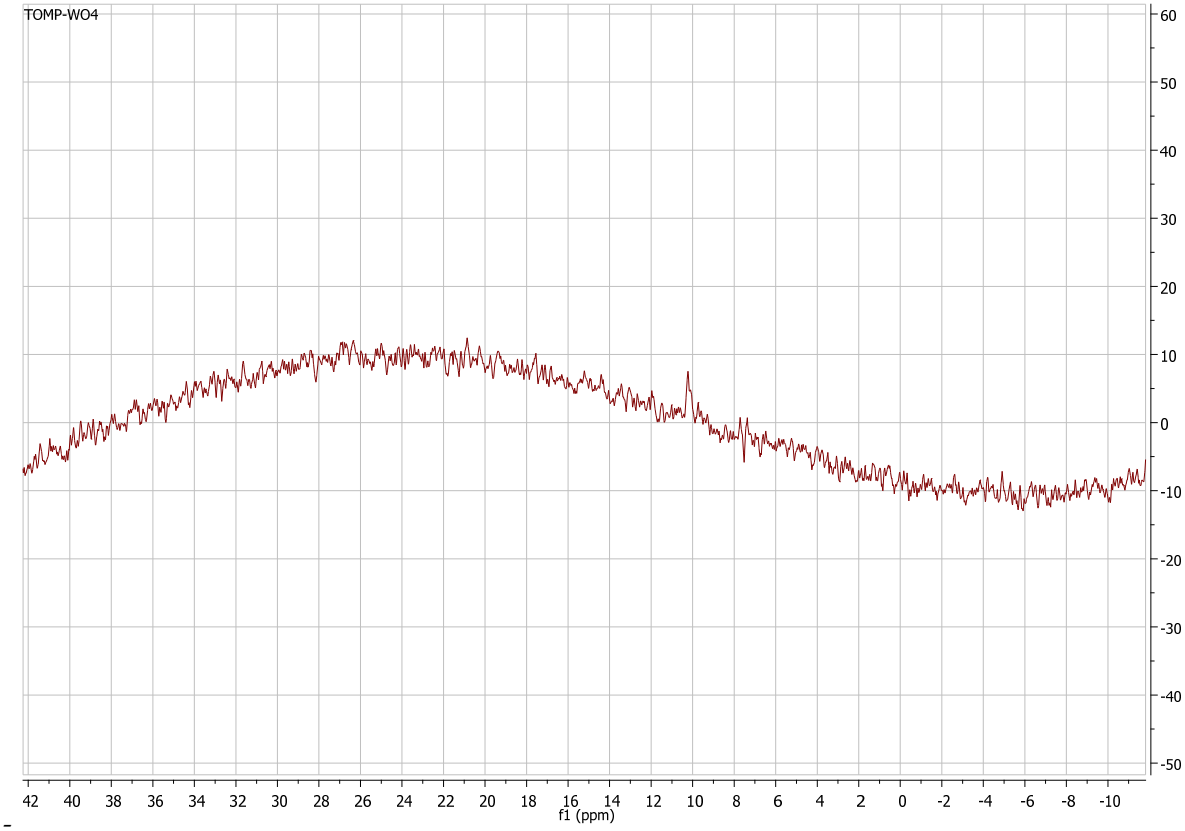

Figure S14. ^{183}W NMR spectra of $[P_{8,8,8,1}]_2WO_4$ in D_2O.

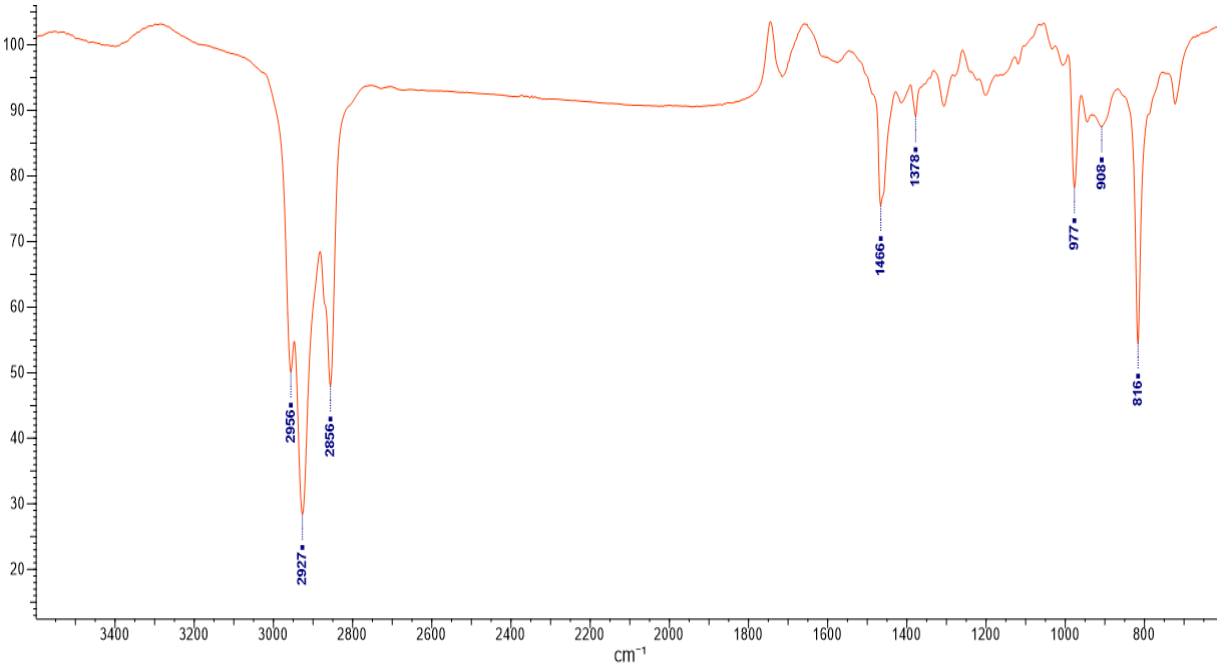

Figure S15. FT-IR spectra of $[P_{8,8,8,1}]_2WO_4$ (KBr pellets).

Trioctylmethylammonium-phosphotungstate ($[N_{8,8,8,1}]_3(PW_{12}O_{40})$, 3)

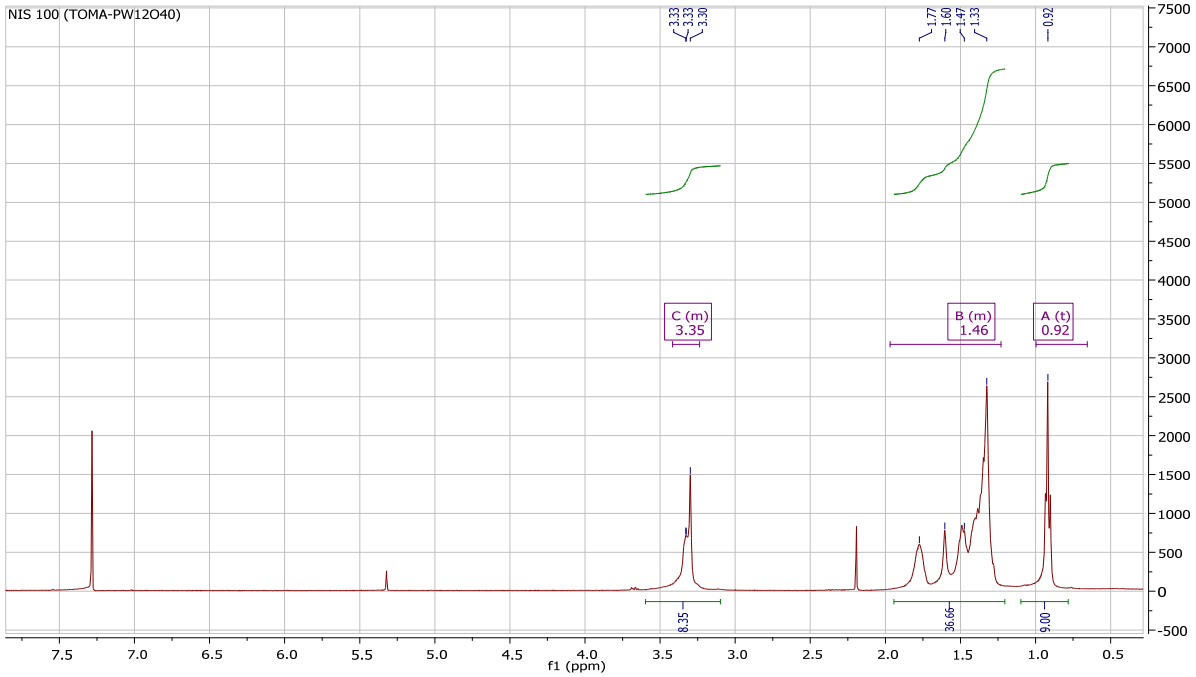

Figure S16. ^{1}H-NMR (400MHz, $CDCl_3$): δ = 0.87 (t, 9H), 1.25-1.72 (m, 36H), 3.37-3.75(m, 9H).

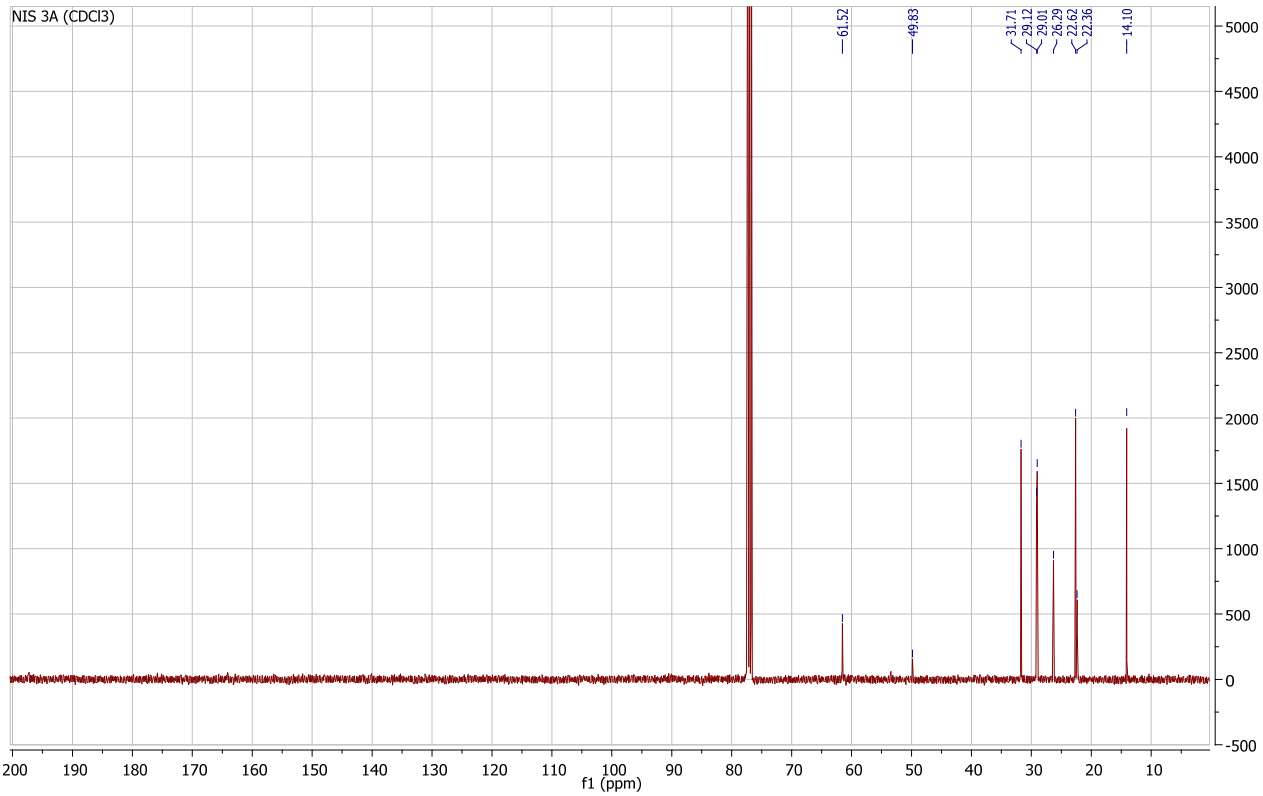

Figure S17. ^{13}C-NMR (100MHz, $CDCl_3$): δ = 14.1, 22.36, 22.62, 26.29, 29.01, 29.12, 31.71, 49.83, 61.52.

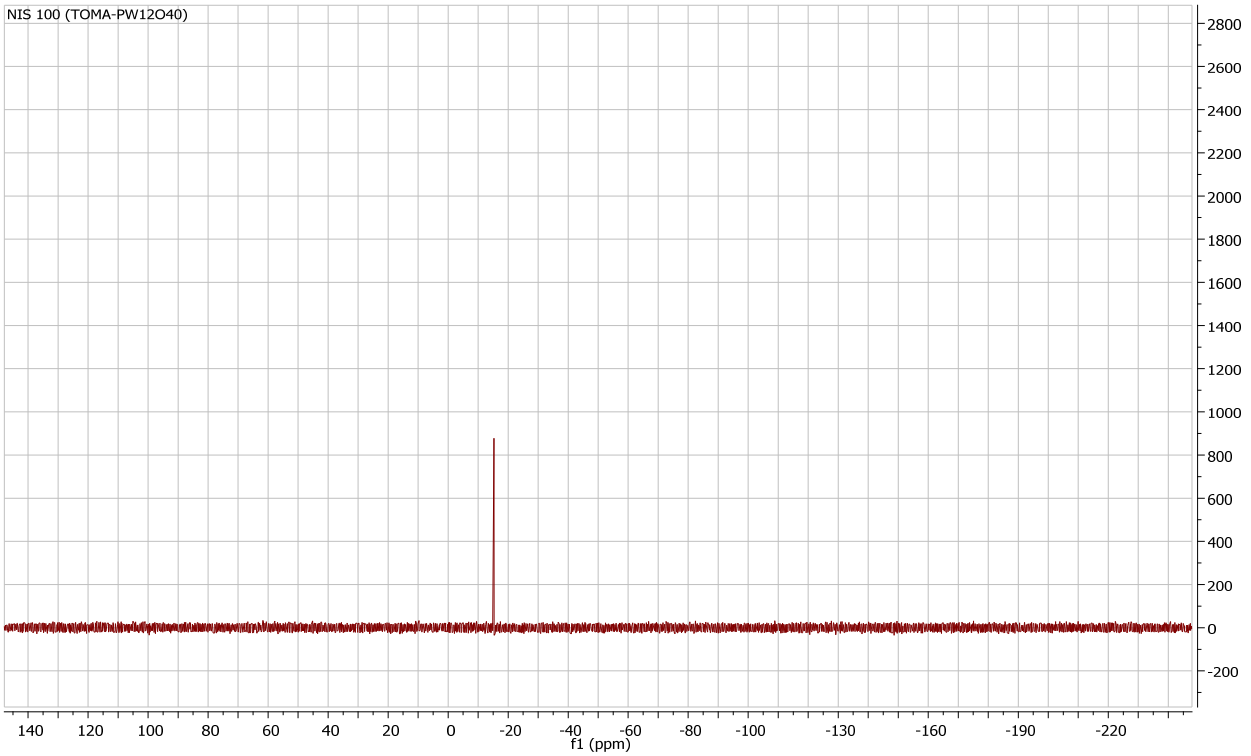

Figure S18. ^{31}P-NMR (162MHz, $CDCl_3$): δ = -15.29.

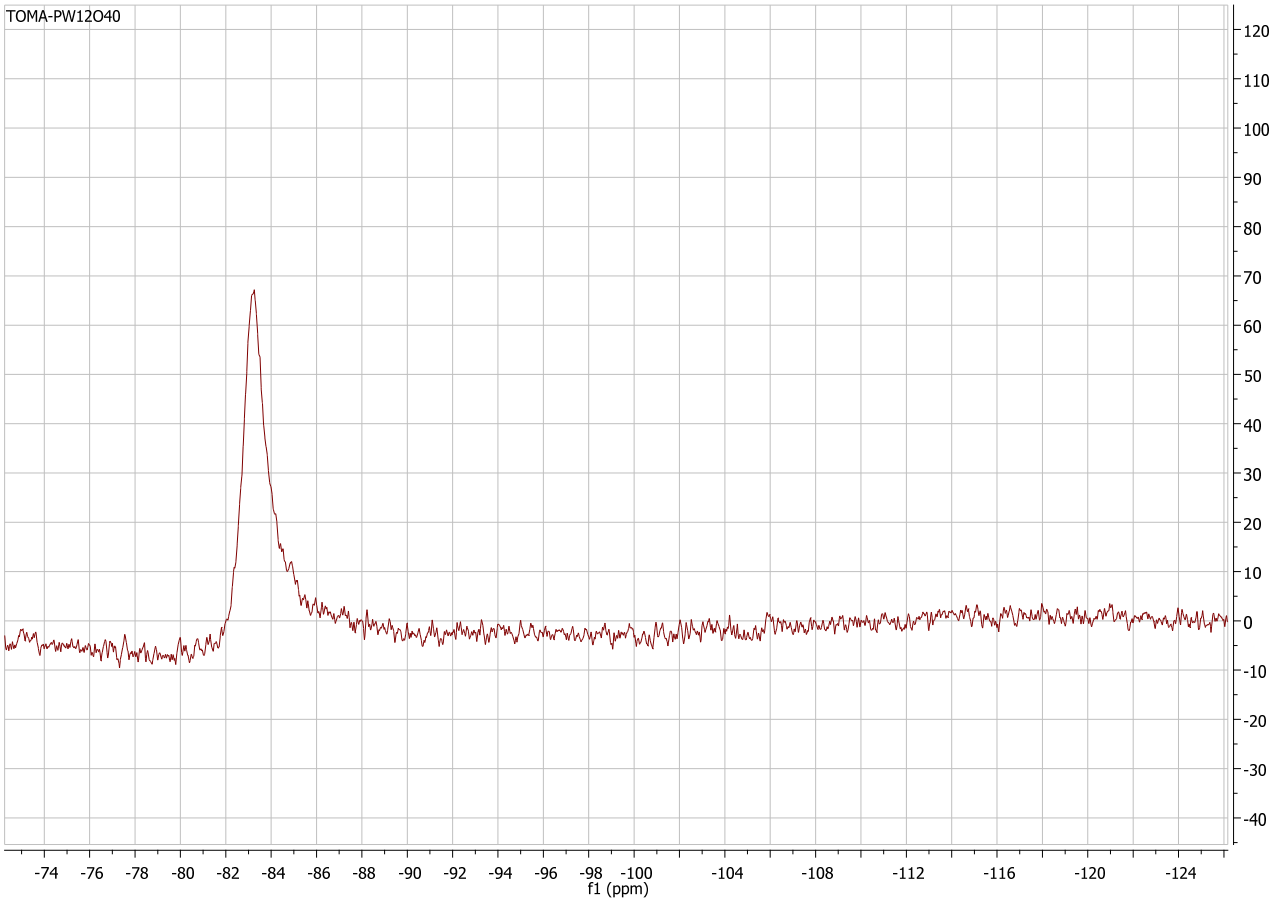

Figure S19. ^{183}W NMR spectra of $([N_{8,8,8,1}]_3(PW_{12}O_{40})$.

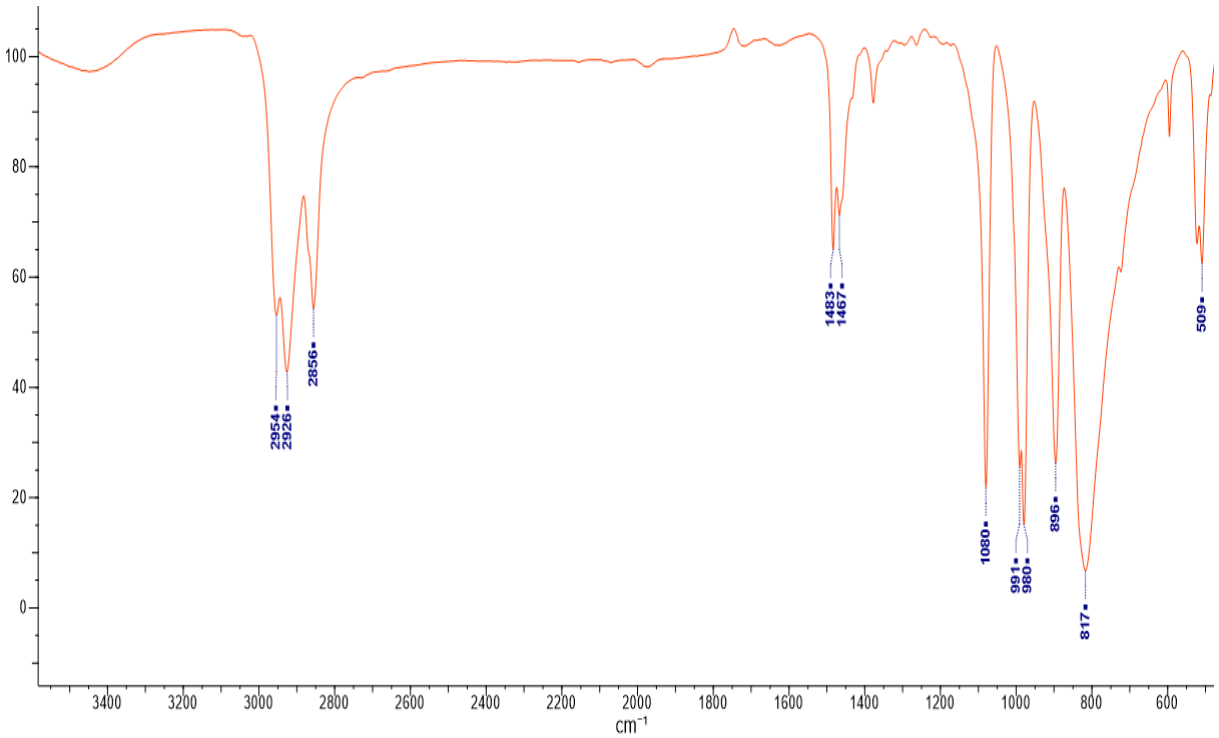

Figure S20. FT-IR spectra of ($[N_{8,8,8,1}]_3(PW_{12}O_{40})$) (KBr pellets).

1.-. butyl-3-methyl-ammonium tungstate ($[BMIM]_2(WO_4)$, 4)

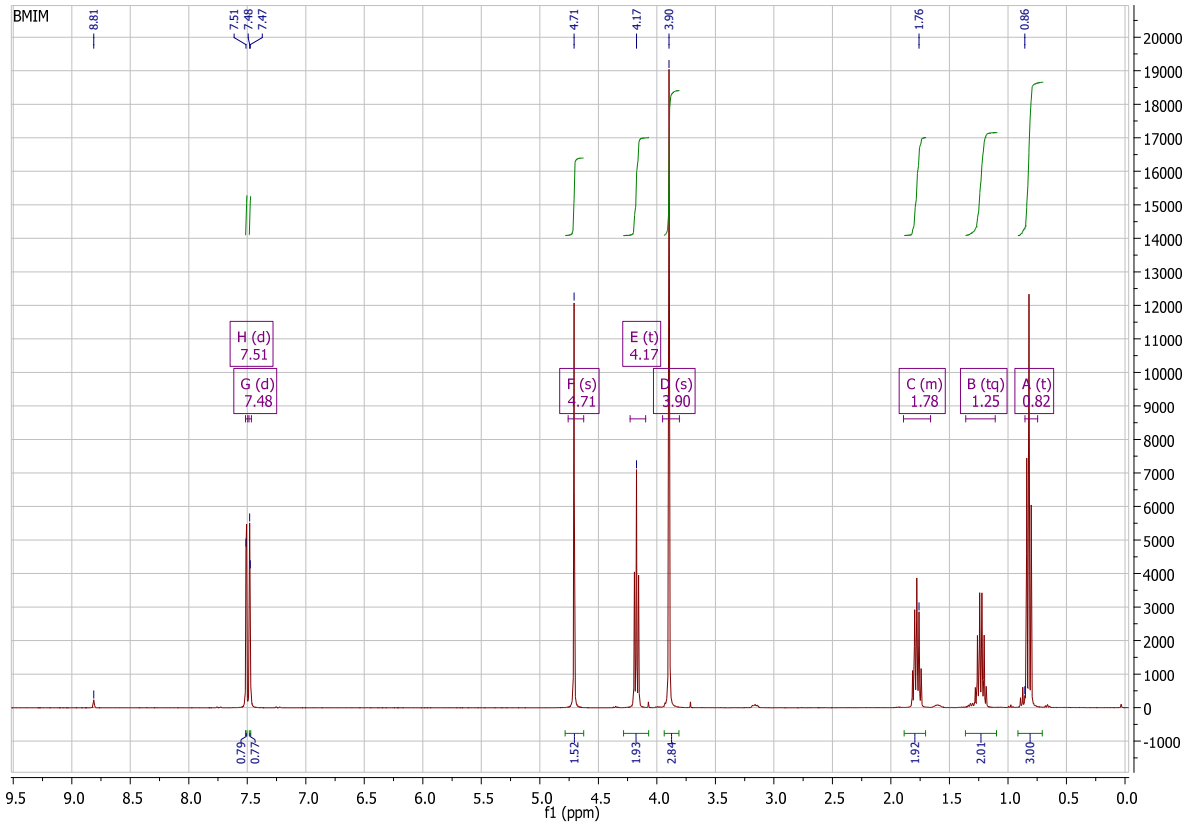

Figure S21. **^{1}H-NMR (400MHz, D_2O):** δ = 0.82 (t, J=7.4Hz, 3H), 1.18-1.29 (tq, J=14.8, 7.3Hz, 2H), 1.74-1.81(m, 2H), 3.90 (s, 3H), 4.17 (t, J=7.2Hz, 2H), 4.71 (s, 1H), 7.48 (d, J=2.0Hz, 1H), 7.51 (d, J=2.0Hz, 1H), 8.81 (bs, 1H).

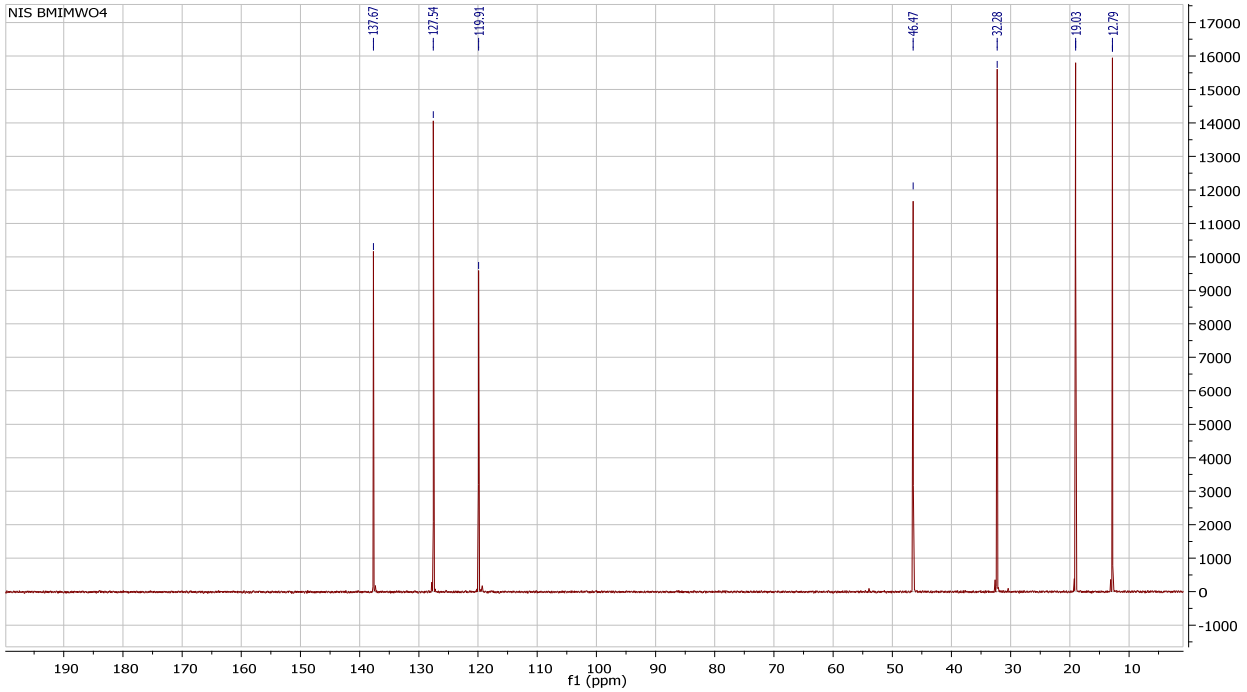

Figure S22. C-NMR (100MHz, D_2O): δ = 12.79, 19.03, 32.28, 46.47, 119.91, 127.54, 137.67.

13

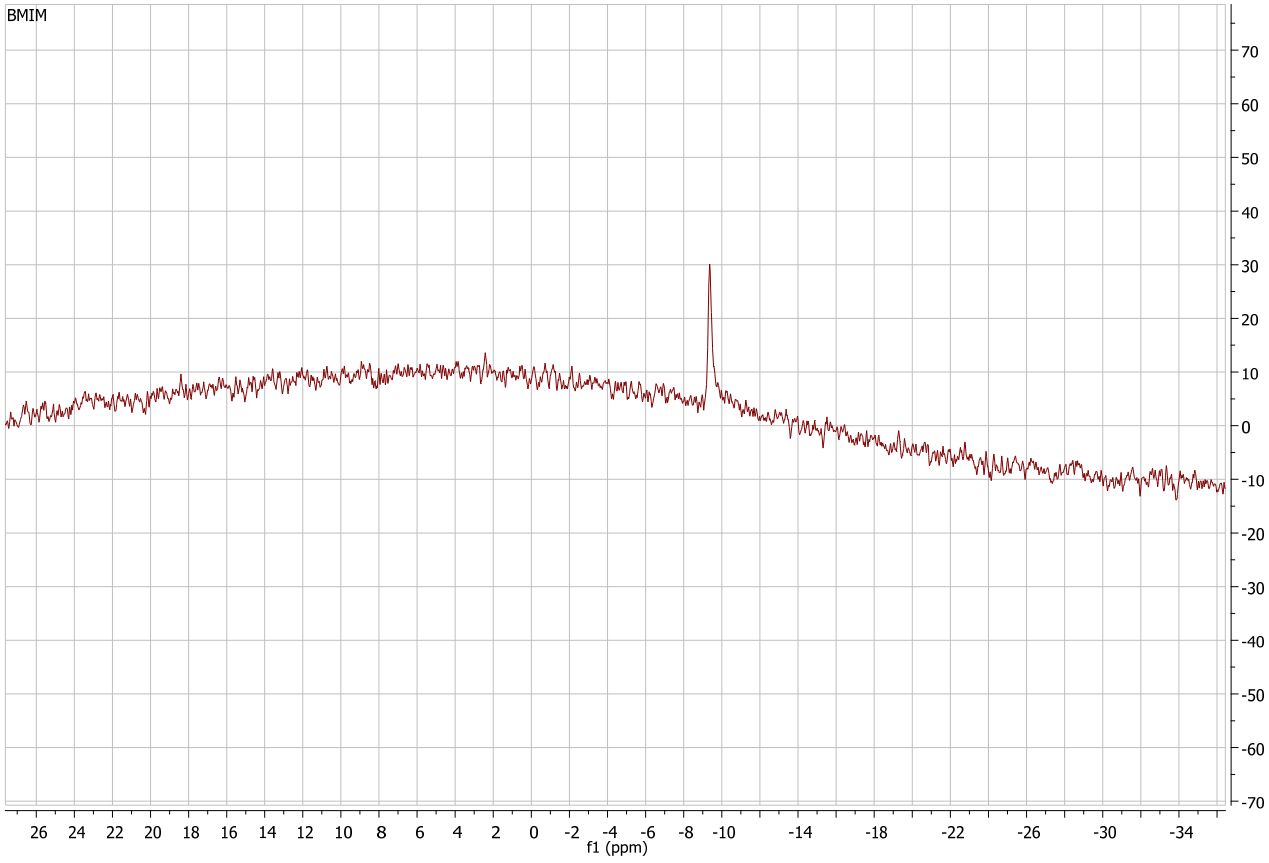

Figure S23. ^{183}W NMR spectra of $[BMIM]_2(WO_4)$ in D_2O.

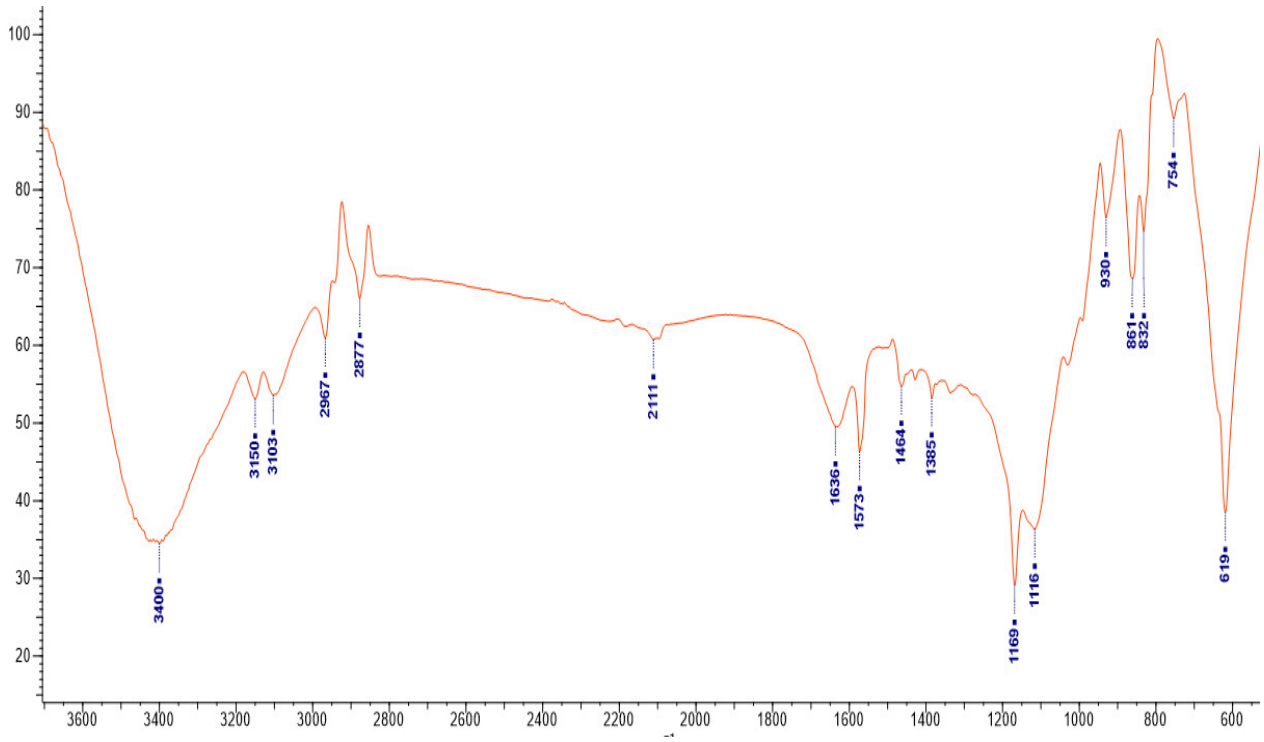

Figure S24. FT-IR spectra of $[BMIM]_2(WO_4)$ (KBr pellets).

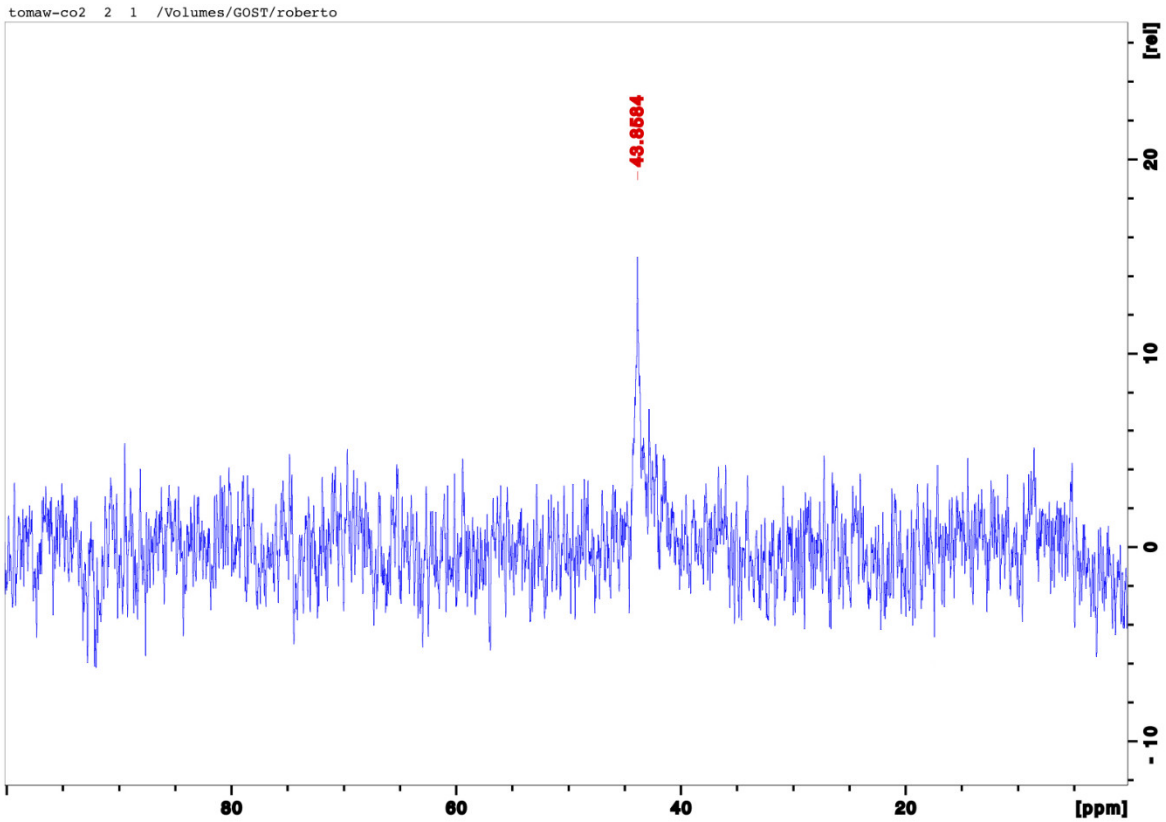

Figure S25. ^{183}W NMR spectra of the adduct $WO_4 \cdot CO_2$. A NMR tube was charged with $[N_{8,8,8,1}]_2WO_4$ (0.2 g), D_2O (0.4 ml) and placed in an autoclave that was sealed, degassed via two vacuum-CO_2 cycles and pressurized with 10 bar of CO_2. The mixture was placed at 85°C for 5 hours, then the autoclave was slowly vented and the NMR spectra was recorded.

Products Characterization

Methyl Oleate (MO)

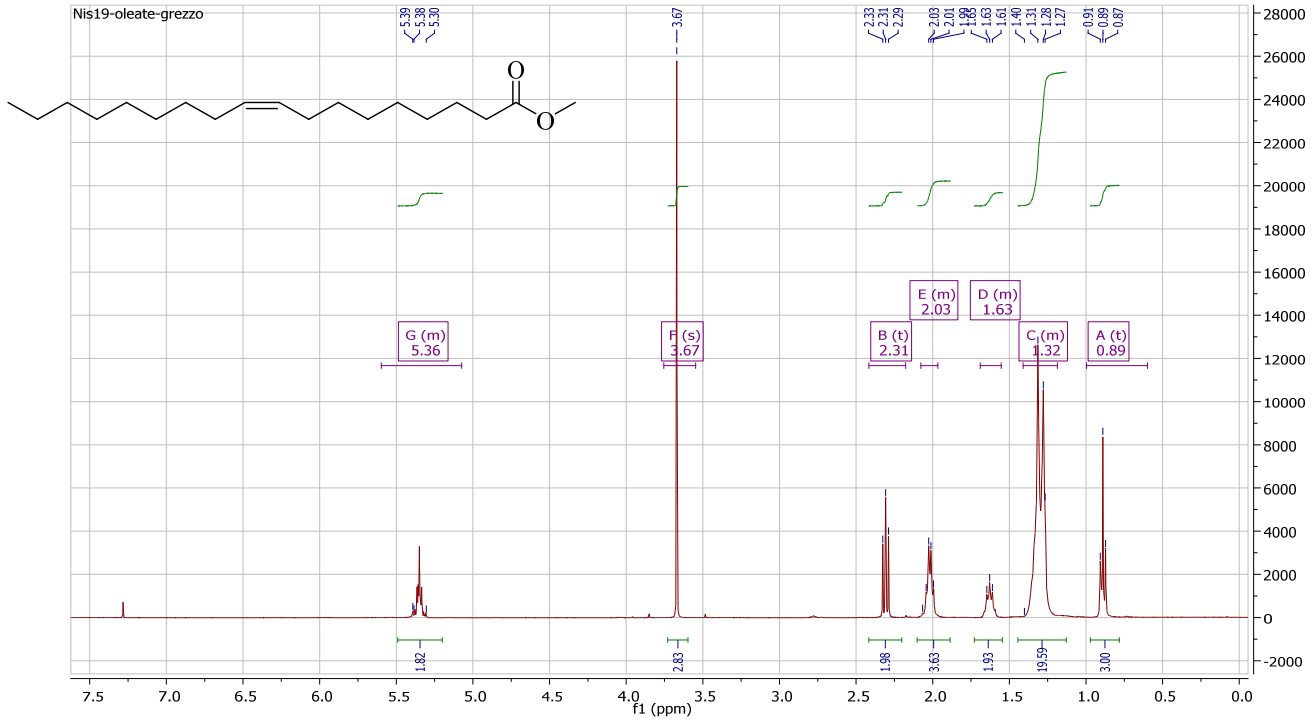

Figure S26. ^{1}H-NMR (400MHz, $CDCl_3$): δ = 0.89 (t, J=6.9Hz, 3H), 1.25-1.40 (m, 20H), 1.63 (m, 2H), 2.03 (m, 4H), 2.31 (t, J=7.6Hz, 2H), 3.67 (s, 3H), 5.30-5.39 (m, 2H).

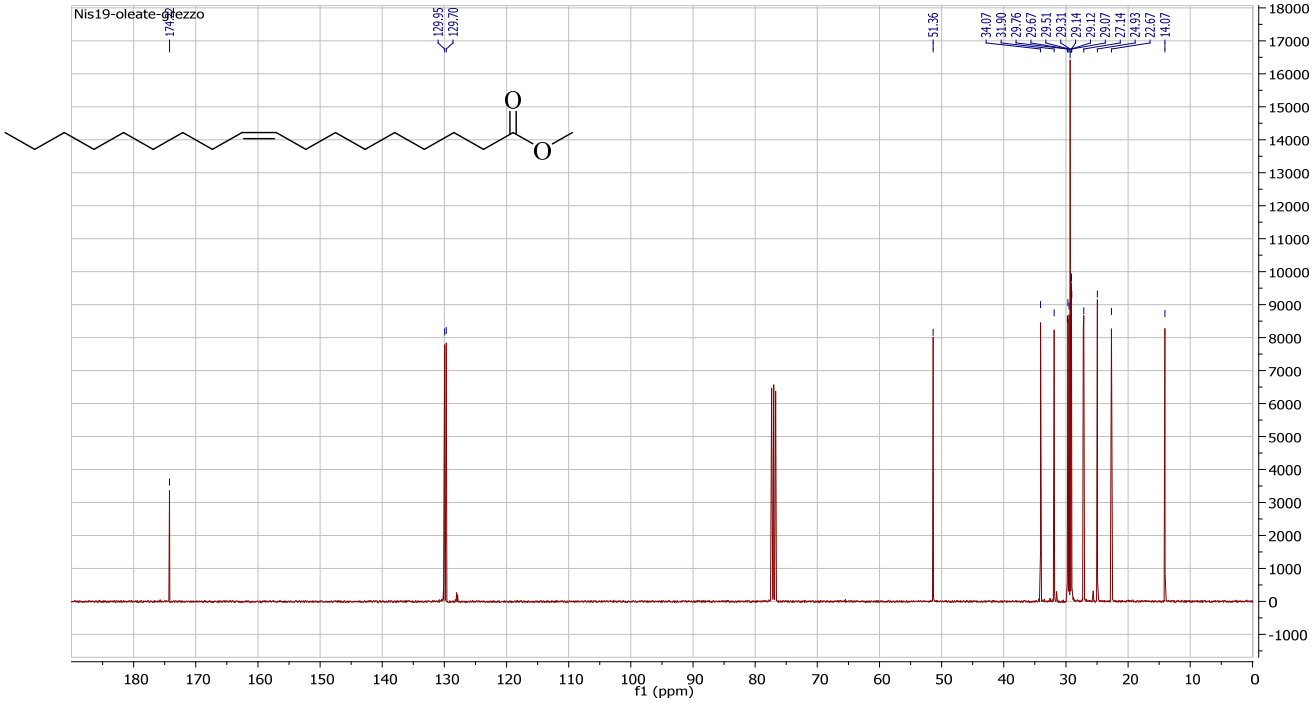

Figure S27. ^{13}C-NMR (100MHz, $CDCl_3$): δ = 14.07, 22.67, 24.93, 27.14, 27.20, 29.07, 29.12, 29.14, 29.31, 29.51, 29.67, 29.76, 31.90, 34.07, 51.36, 129.70, 129.95, 174.42.

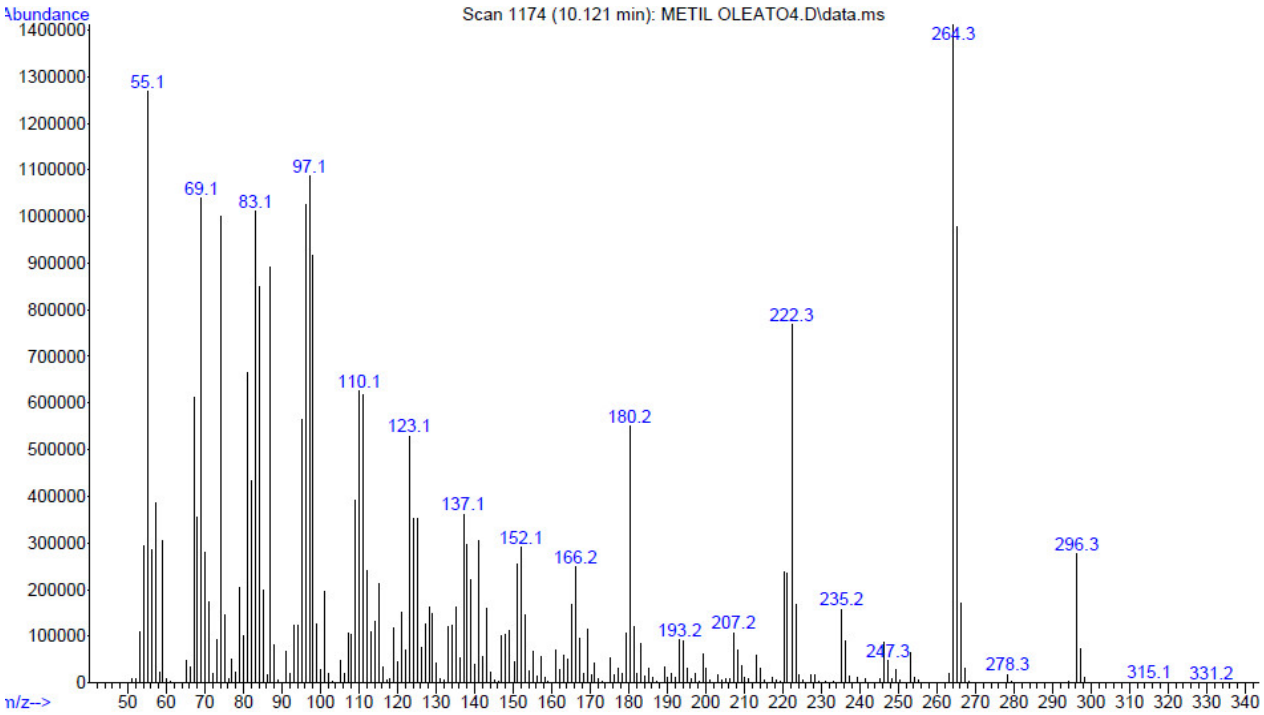

Figure S28. MS spectra of methyl oleate.

Methyl 8-((2R,3S)-3-octyloxiran-2-yl) octanoate – Epoxidized methyl oleate (EMO)

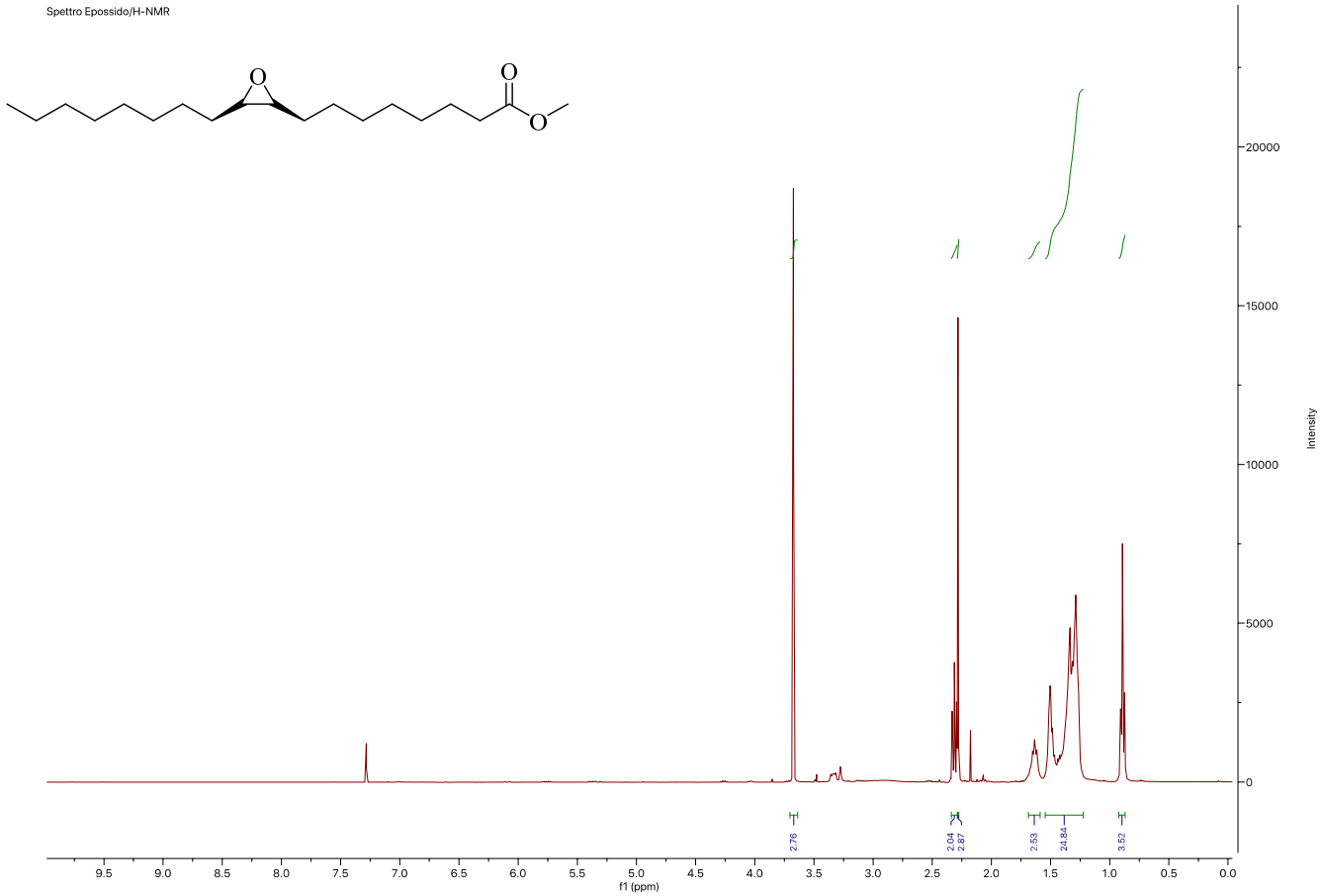

Figure S29. ^{1}H-NMR (400MHz, $CDCl_3$): δ = 3.75 – 3.49 (s, 3H), 2.35 – 2.29 (m, 2H), 2.30 – 2.25 (m, 2H), 1.72 – 1.55 (m, 2H), 1.54 – 1.18 (m, 24H), 0.94 – 0.81 (m, 3H).

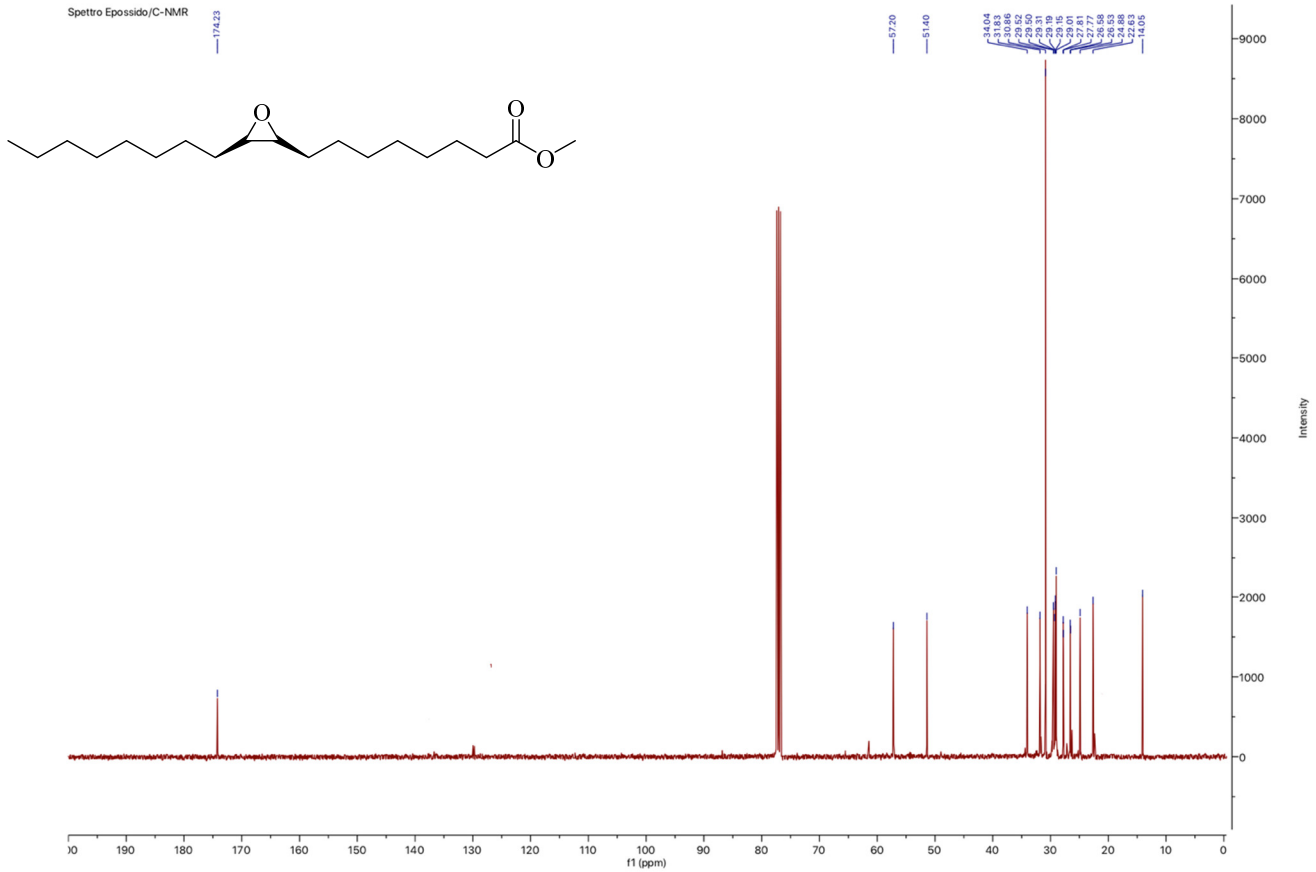

Figure S30. ^{13}C-NMR (100MHz, $CDCl_3$): δ = 174.23, 57.20, 51.40, 34.04, 31.83, 30.86, 29.52, 29.50, 29.31, 29.19, 29.15, 29.01, 27.81, 27.77, 26.58, 26.53, 24.88, 22.63, 14.05.

Cis-methyl 8-(5-octyl-2-oxo-1,3-dioxolan-4-yl) octanoate – cis carbonated methyl oleate (-cis CMO)

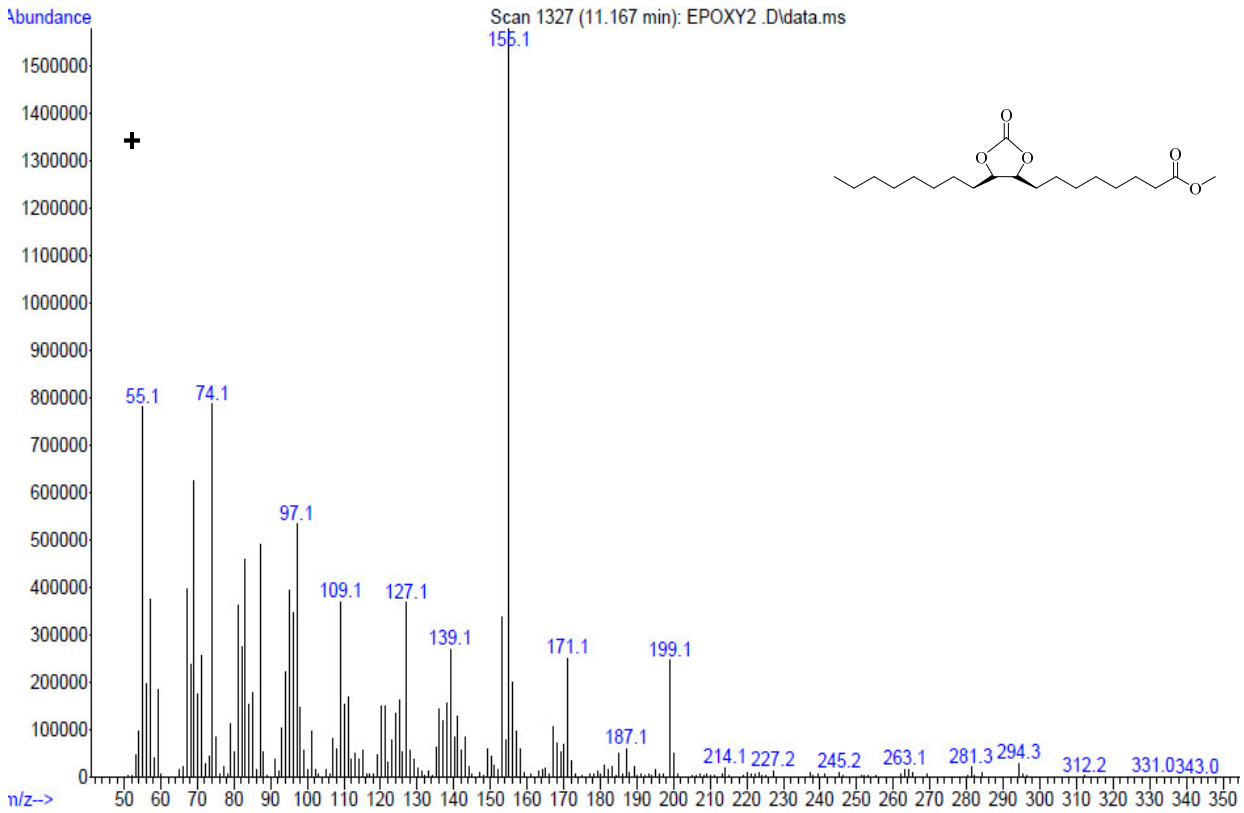

Figure S31. MS spectra of Epoxidized Methyl Oleate (EMO).

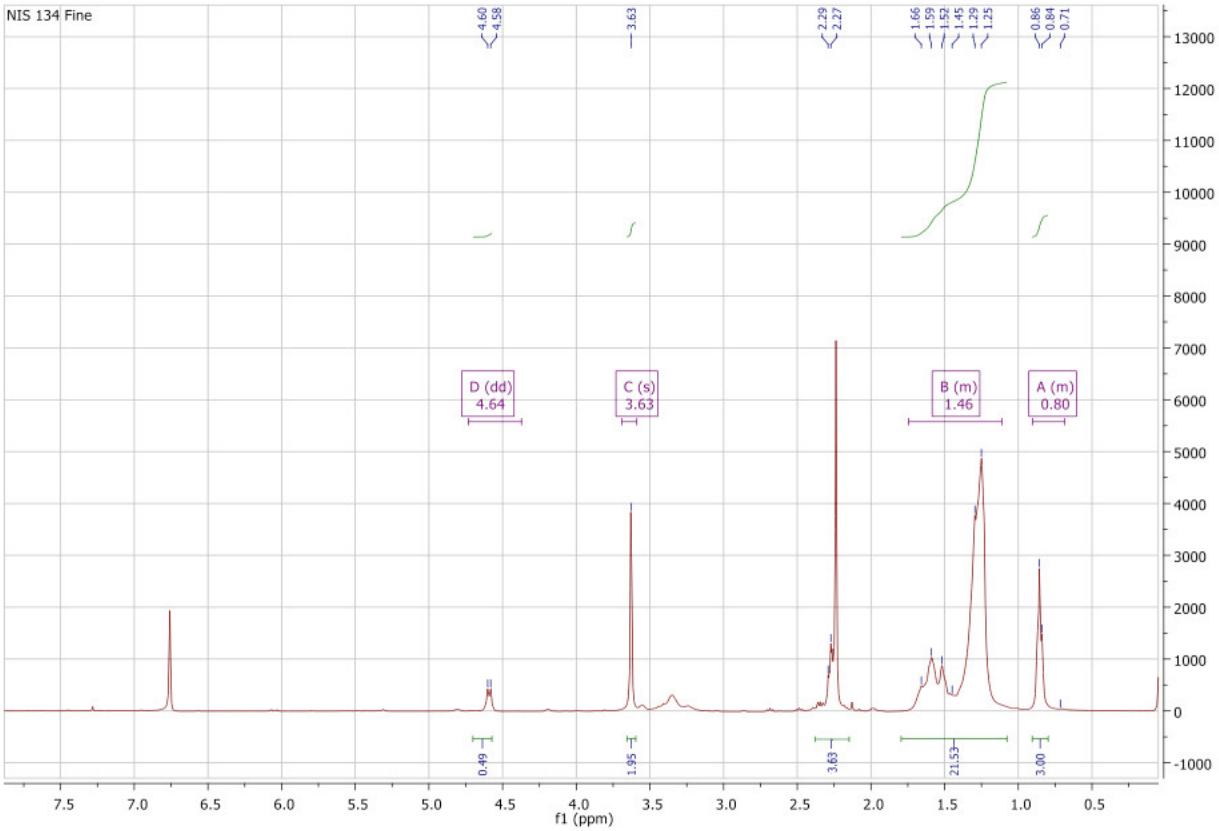

Figure S32. ^{1}H-NMR (400MHz, $CDCl_3$): δ = 0.80 (m, 3H), 1.25-1.66 (m, 24H), 2.27 (m, 4H), 3.63 (s, 3H), 4.64 (m, 2H).

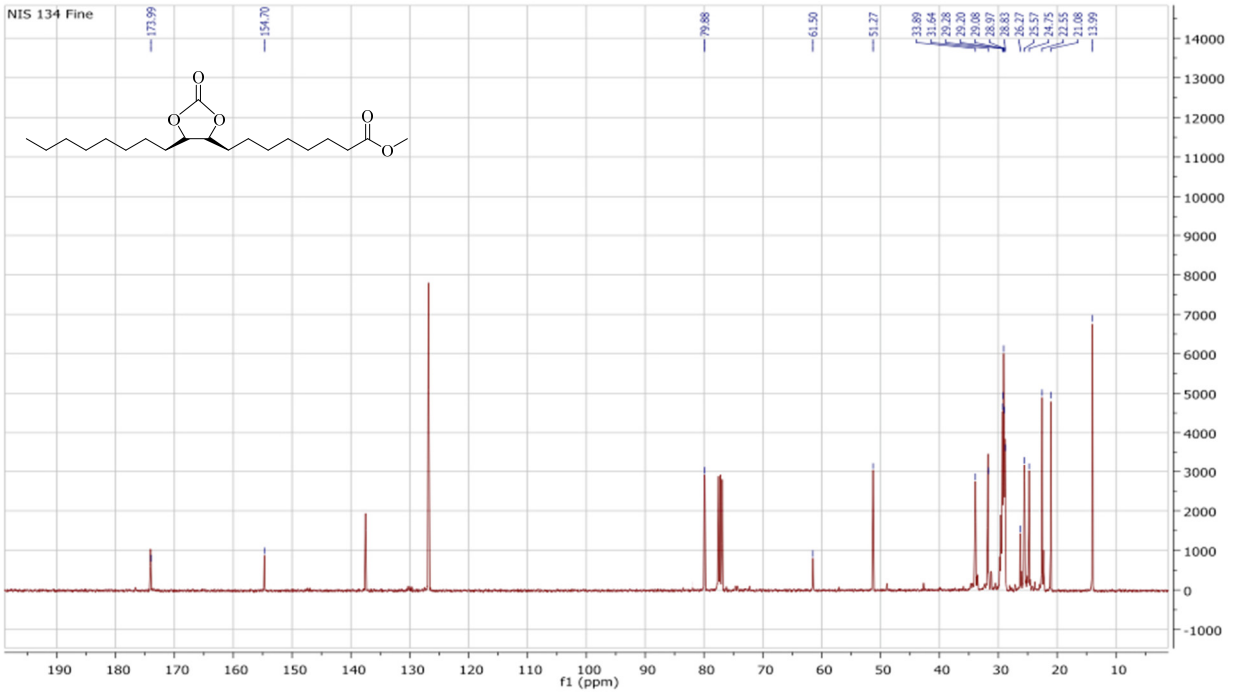

Figure S33. ^{13}**C-NMR (100MHz, CDCl$_3$):** δ = 13.99, 21.08, 22.25, 22.57, 24.75, 25.57, 26.27, 28.83, 28.97, 29.01, 29.08, 29.20, 29.28, 31.64, 33.89, 51.27, 61.50, 79.88, 154.70, 173.99.

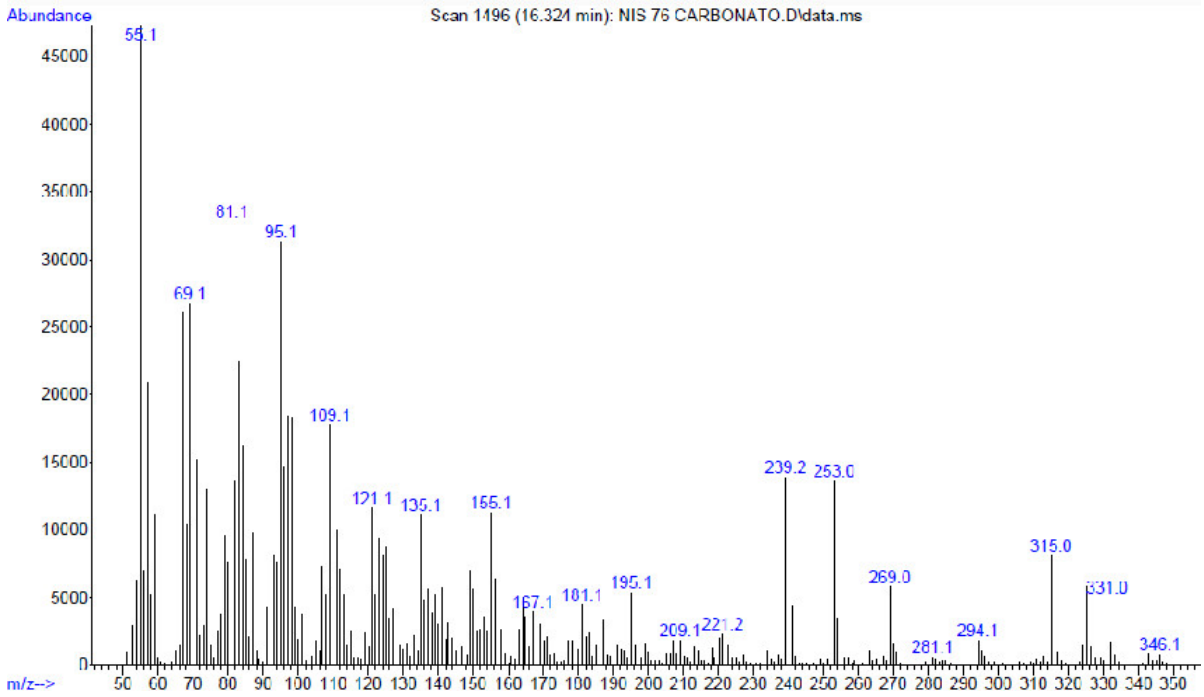

Figure S34. MS spectra of Carbonated Methyl Oleate (CMO).