Electronic Supplemental Information for

Electrostatic Polarization of Nonpolar Substrates: A Study of Interactions Between Simple Cations and Mo-bound N_2

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General Procedure

All manipulations were conducted under N_2, Ar or using high-vacuum line and glovebox techniques unless otherwise noted. All ambient-pressure chemistry was carried out under a pressure of approximately 590 torr (elevation ~7220 ft) and a temperature of 22±3 ºC unless otherwise stated; a table of pressure-corrected boiling points for the solvents used in this manuscript are reported in Table S1. All solvents were dried using an Innovative Technologies PureSolv Solvent Purification System. Deuterated solvents used in NMR studies were dried over activated 3 Å molecular sieves. NMR spectra were obtained with a Bruker DRX-400 instrument using 5 mm NMR tube fitted with re-sealable Teflon valves. ^{1}H and ^{13}C NMR spectra were referenced internally to either tetramethylsilane or residual protic solvent peaks. ^{31}P NMR spectra were referenced to an 85% H_3PO_4 external standard. Unless otherwise stated, reagents were purchased from Sigma-Aldrich, Fisher Scientific, Boulder Scientific, or Synquest and used without further purification. The starting materials $Ca(OTf)_2$,[1] was synthesized by a slight modification of literature procedures. Infrared spectra were recorded on a PerkinElmer Frontier FT-IR spectrometer (4 cm^{-1} resolution, 4000–450 cm^{-1} window) in a quartz-based liquid cell.

Experimental

S 1. Synthesis of n-Crown-R

For exact procedure, see Pap et al.[2]

S 2. Synthesis of $MoCl_3(THF)_3$

For exact procedure see Westland et al.[3]

S 3. Synthesis of MBF_{20} (M = Li, Na, Rb, Cs)

$[Li(thf)_4]BF_{20}$, $NaBF_{20}$, $RbBF_{20}$, $CsBF_{20}$ were synthesized from protonation of the anhydrous carbonate salts as described in a previous report.[4]

For exact synthetic procedure of $AgBF_{20}$ see: Zhang et al.[5]

Synthesis of $TlBF_{20}$

A 100 mL Schlenk flask was charged with 100 mg thallium acetate (0.38 mmol) then a solution of $H[Et_2O]_2BF_{20}$ (1.57 g, 1.89 mmol in 10 mL CH_2Cl_2) was added dropwisely. The solution was stirred for 24 hours at ambient temperature. After 24 hours, fine salt precipitation was observable, which was filtered and washed with CH_2Cl_2 excessively. The solid white powder was dried under *vacuo*. A 20 mL scintillation vial was charged with the dry powder and ~3 mL THF, then hexane was layered on the top of the transparent solution. After 96 hours, white powder precipitated out which was filtered and dried under *vacuo*. ^1H NMR spectrum was recorded to verify the absence of excess HBF_{20} and CH_3COOH side product. The salt was used without any further purification.

S 4. Synthesis of $Mo(N_2)_2(PPh_2Me)_4$

For exact procedure see Ning et al.[6]

S 5. Synthesis of (n-Crown-R)$MoCl_3$

In the glovebox, a 20 mL vial was charged with $MoCl_3(THF)_3$ (0.50 g, 1.19 mmol), a magnetic stir bar, and about 13 mL THF. The suspension was added dropwisely to the solution of n-Crown-R (1.19 mmol). After ~15 min, the yellow solution became dark brown, and it was stirred for an additional 3 h, followed by concentration *in vacuo* to get ~ 5 mL solution. Et_2O (15 mL) was then added slowly, and the product precipitated immediately. The Et_2O phase was decanted then the residue was washed with Et_2O (2 x 5 mL). Residual solvent was evaporated *in vacuo* resulting a pale yellow/orange/brown powder.

15-Crown-Ph)$MoCl_3$: Product is a pale brown powder, Yield: 78%,

(18-Crown-Ph)$MoCl_3$: Product is a pale brown powder, Yield: 75%,

(15-Crown-iPr)$MoCl_3$: Product is a yellowish brown powder, Yield: 72%,

(18-Crown-iPr)$MoCl_3$: Product is a yellowish brown powder, Yield: 68%.

Materials were used without any further purification.

S 6. Synthesis and spectroscopic characterization of (18-Crown[MCl_3]-P_3-Ph)$MoCl_3$

After successful synthesis, attempts were made to crystalize out the pure (n-Crown-P_3-R)$MoCl_3$, although no crystalline products were observed. Different spectroscopic and analytical methods were utilized to determine the purity of (n-Crown-P_3-R)$MoCl_3$. Attempts at measuring the magnetic moment via Evans method routinely gave values that were ~10% *higher* than expected and combustion analysis failed to produce that were within an acceptable range. In particular, carbon values were consistently ~5 percentage points lower than calculated (C: 53.02, H: 5.78, N: 1.55) despite a variety of combustion parameters:

Trial	*C/H/N Results*	*Conditions*
1	C: 47.05, H: 6.40, N: 1.51	*30mg WO_3 as combustion aide*
2	C: 48.01, H: 5.89, N: 1.25	*50mg WO_3 as combustion aide*
3	C: 48.90, H: 6.41, N: 1.61	*50mg WO_3 as combustion aide, mixed thoroughly with analyte*

Although the carbon, hydrogen and nitrogen amounts are independent measurements in an elemental analyzer (due to independent measurements of CO_2, H_2O and N_2), impurities that possess none of the elements will tend to lower all measured percentages proportionally. The hydrogen content (as %H) seems to be within the expected range (or slightly above), although the low elemental content results in less accuracy for %H and %N relative to the %C.

To test the hypothesis that the ligand was capable of binding multiple equivalents of $MoCl_3(THF)_3$, excess $MoCl_3(THF)_3$ was added to isolated [(18-Crown-P_3-Ph)$MoCl_3$] in an NMR-scale experiment. As shown in Figure 1, the $(CH_2)_2O$- protons of the crown ether (observable at δ3.65 ppm) shifting and broaden considerably upon addition of $MoCl_3(THF)_3$. The broadening (and not the complete disappearance as might be expected for coordination to a paramagnetic d^3 ion) and lack of observable free THF suggests a more complex equilibrium is present, but clearly establishes the possibility of excess Mo(III) coordination to the starting (n-Crown-P_3-R)$MoCl_3$ precursors. Although these experiments do not rule out other possible contaminants, they are at least consistent with the proposed $MoCl_3$ contamination.

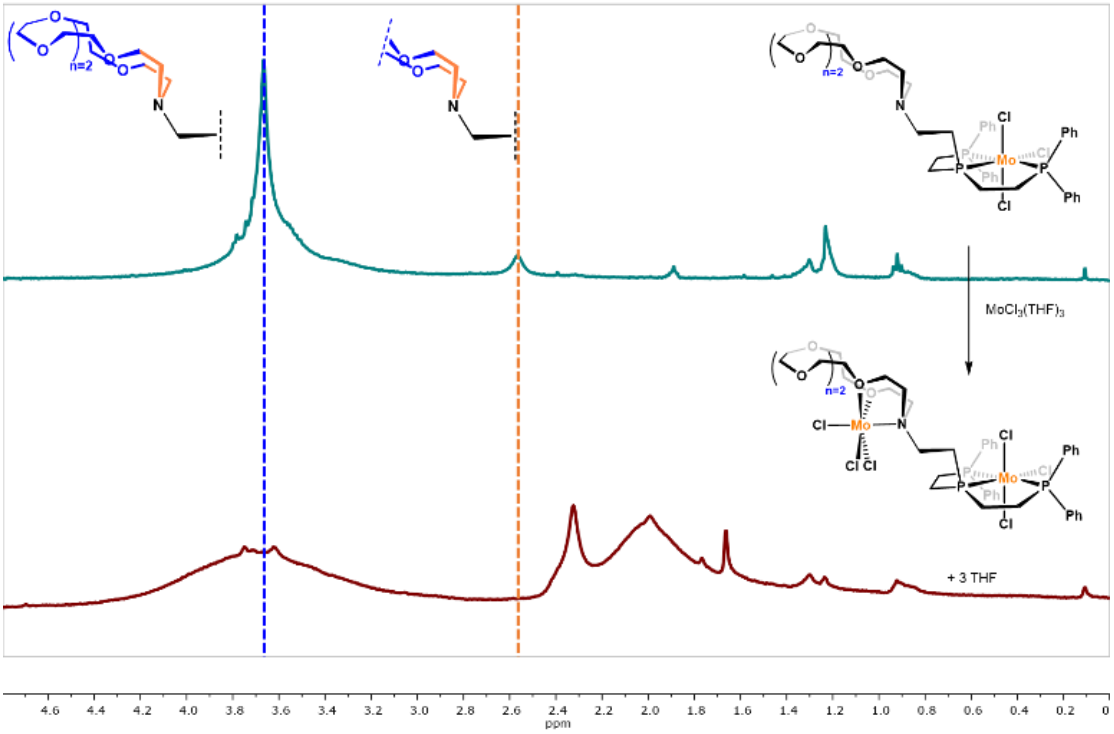


Figure 1. ^{1}H NMR of (18-Crown-P_3-Ph)$MoCl_3$ (top) and formation of (18-Crown[MCl_3]-P_3-Ph) $MoCl_3$ by the addition of $MoCl_3(THF)_3$ (bottom)

S 7. Synthesis of (18-Crown-iPr)$MoCl_2(PPh_2Me)$ and (18-Crown[$Ca(OTf)_2$]-iPr)$MoCl_2(PPh_2Me)$

In the glovebox, a 20 mL vial was charged with a magnetic stir bar, (18-Crown-iPr)$MoCl_3$ (0.198 g, 0.243 mmol), PPh_2Me (48.5 mg, 0.243 mmol), 0.92 m/m % Na/Hg amalgam (0.486 mmol Na) and about 5 mL THF. Note: The Na/Hg amalgam was shaken vigorously right before addition to ensure a homogeneous reducing agent. After 2 h the suspension became a green solution that was stirred for an additional 22 h, followed by a 0.45 µm PTFE syringe filtration. Solvent was evaporated *in vacuo* to get the greenish yellow crude product; efforts to purify this material failed. Et_2O (~5 mL) and 1.2 eq $Ca(OTf)_2$ (100 mg, 0.292 mmol) were added to the solution and stirred for ~15 min. Toluene was added dropwisely until the suspension became completely transparent. A crystallization tube was charged with the clear solution then it was placed into an empty 20 mL

vial. The slightly open vial was stood at ambient temperature and allowed the solvent to slowly evaporate under the N_2 atmosphere. Orange crystals deposited on the side of the tube within 72 h (0.115 g) that were amenable to X-Ray crystallographic analysis. Crystallization invariably produced small amounts of colorless crystals alongside the orange crystals of (18-Crown[$Ca(OTf)_2$]-iPr)$MoCl_2(PPh_2Me)$ that contaminated bulk isolation of the target Mo(III) complex. Elemental analysis revealed higher carbon and hydrogen content for bulk samples of (18-Crown[$Ca(OTf)_2$]-iPr)$MoCl_2(PPh_2Me)$ (C: 53.05, H: 6.98, N: 1.03) than would be expected based on the solid-state structure (C: 52.15, H: 5.34, N:0.83); at present we suspect contamination from solvated Ca salts is impeding satisfactory combustion analysis.

S 8. Synthesis of (18-Crown-Ph)MoN_2(dppm)[7]

In the glovebox, a 25 mL Schlenk flask was equipped with a magnetic stir bar, 50 mg (18-Crown-Ph)$MoCl_3$ (52.6 x 10^{-3} mmol), 922 mg, 0.92 m/m % Na/Hg amalgam (289 x 10^{-3} mmol), and 20 mg Bis(diphenylphosphino)methane (dppm) (52.6 x 10^{-3} mmol). The sealed system, was taken out from the box and cooled to 0°C under N_2 atmosphere. 5 mL of THF was added dropwisely under vigorous stirring and the reaction was running for 2h 45 min at 0°C then it was stirred for an additional 15 hours at ambient temperature. Solvent was evaporated *in vacuo* to get the brown crude product. Toluene was added (~3 mL) and filtered through a PTFE syringe filter. Solvent was evaporated *in vacuo* and material was used for further spectroscopic analysis without any further purification (50.2 mg, 76%).

^{1}H NMR (C_6D_6): δ 1.08 ppm (d, 4 H, $^2J_{H-P}$=1.35 Hz, ($Ph_2P(\mathbf{CH_2})_2PCH_2$-), δ 1.09 ppm (s, 2 H, $NCH_2C\mathbf{H_2}P$), δ 1.37 ppm (s, 2 H, -$PCH_2C\mathbf{H_2}N$), δ 1.45 ppm (s, 4 H, $Ph_2PC\mathbf{H_2}CH_2P$), δ 2.62 ppm (t, 2 H, $OCH_2C\mathbf{H_2}N$), δ 2.78 ppm (t, 2 H, $Ph_2PC\mathbf{H_2}PPh_2$), δ 3.54 ppm (m, 24 H, $OC\mathbf{H_2}C\mathbf{H_2}O$ and $OC\mathbf{H_2}CH_2N$), δ 6.75 ppm (m, Ph), δ 6.86 ppm (t, Ph), δ 7.01 ppm (m, Ph), δ 7.25 ppm (m, Ph), δ

7.44 ppm (m, Ph), δ 7.54 ppm (m, Ph); ^{31}P {^{1}H} NMR (C_6D_6): δ 10.2 ppm (m, 2 P, $^{2}J_{P-P}$=72.0 Hz, -(CH_2CH_2)**P**Ph_2); δ 66.3 ppm (m, 2 P, $^{2}J_{P-P}$=72.0 Hz, PCH_2**P**Ph_2).

S 9. General synthesis of (n-Crown-Ph)MoN$_2$(PMe$_3$)$_2$

In the glovebox, a 50 mL Schlenk flask was equipped with a magnetic stir bar, 0.21 mmol (n-Crown-Ph)$MoCl_3$ an 9.0 g 0.92 m/m % Na/Hg amalgam (2.83 mmol). The sealed system, was taken out from the box and cooled to 0°C under N_2 atmosphere. 16 mg of PMe_3 in 2 mL (0.21 mmol, 8 mg/mL) was added dropwise under vigorous stirring. Another 12 mL THF was injected into the reaction flask and the reaction was running for 1 h at 0°C, then it was stirred for an additional 23 hours at ambient temperature. The flask was pumped into the glovebox, and the suspension was filtered through a 0.45 μm PTFE syringe filter. Solvent was evaporated *in vacuo*, resulting a dark brown crude product. Methanol was added (~15 mL) and the solution was transferred into a separatory funnel, ~15 mL hexane was added and the MeOH phase was extracted eight times. The MeOH phases were combined and solvent was evaporated *in vacuo.*

(15-Crown-Ph)$MoN_2(PMe_3)_2$: brown thick oil (144 mg, 70%);

(18-Crown-Ph)$MoN_2(PMe_3)_2$: brown thick oil (166 mg, 77%).

S 10. NMR data of (15-Crown-Ph)MoN$_2$(PMe$_3$)$_2$

^{1}H NMR (C_6D_6): δ 1.06 ppm (d, 9 H, $^{2}J_{H-P}$=4.95 Hz, **Me$_3$**P-), δ 1.67 ppm (d, 9 H, $^{2}J_{H-P}$=3.98 Hz, **Me$_3$**P-, trans to -PPh_2), δ 2.14 ppm (m, 6 H, PC**H$_2$**CH_2PPh_2 and PC**H$_2$**CH_2N), δ 2.31 ppm (m, 4 H, PCH_2C**H$_2$**PPh_2), δ 2.43 ppm (m, 2 H, PCH_2C**H$_2$**N), δ 2.84 ppm (t, 4 H, OCH_2C**H$_2$**N), δ 3.47 ppm (m, 16 H, OC**H$_2$**C**H$_2$**O and OC**H$_2$**CH_2N), δ 6.85 ppm (m, 8 H, ^{m}Ph), δ 7.09 ppm (m, 8 H, ^{o}Ph), δ 7.29 ppm (m, 4 H, ^{p}Ph); ^{13}C{^{1}H} NMR (C_6D_6): δ 17.2 ppm (d, 6 C, $^{1}J_{C-P}$=15.9 Hz, **C**H_3P), δ 23.0 ppm (d, 2 C, Ph_2P**C**H_2CH_2P), δ 25.5 ppm (m, **Me$_3$**P), δ 31.9 ppm (d, 1 C, Ph_2PCH_2**CH$_2$**P),δ 30.7 ppm (d, 1 C, Ph_2PCH_2**CH$_2$**P), δ 34.0 ppm (d, 1 C, NCH_2**CH$_2$**P), δ 54.9 ppm (s, 1 C, N**C**H_2CH_2P),

δ 67.4 ppm (s, 2 C, N**C**H_2CH_2O), δ 70.2 ppm (s, 2 C, O**C**H_2CH_2N), δ 70.5 ppm (s, 4 C, O**C**H_2**C**H_2O), δ 71.2 ppm (s, 2 C, O**C**H_2**C**H_2O), δ 126.8 ppm (m, 8 C, ^{m}Ph), δ 128.4 ppm (d, 4 C, ^{y}Ph), δ 130.8 ppm and 131.9 ppm (d, 8 C, ^{o}Ph), δ 133.1 ppm and 133.7 ppm (d, 4 C, ^{p}Ph); ^{31}P {^{1}H} NMR (C_6D_6): δ -11.8 ppm (dd(t), 1 P, $^{2}J_{P\text{-}Ptrans}$=104.2 Hz, $^{2}J_{P\text{-}P}$=21.1 Hz, -(**P**Me_3 trans to -PPh_2), δ -9.2 ppm (dm, 1 P, $^{2}J_{P\text{-}Ptrans}$=95.4 Hz, $^{2}J_{P\text{-}P}$=11.1 Hz, **P**Me_3 trans to P$(CH_2)_3$-), δ 65.7 ppm (m, 1 P, $^{2}J_{P\text{-}P}$=7.5 Hz, **P**Ph_2 trans to N_2), δ 72.0 ppm (ddd, 1 P, $^{2}J_{P\text{-}Ptrans}$=95.4 Hz, $^{2}J_{P\text{-}P}$=21.1 Hz, $^{2}J_{P\text{-}P}$=9.7 Hz, **P**$(CH_2)_3$- trans to PMe_3), δ 87.8 ppm (dd, 1 P, $^{2}J_{P\text{-}P}$=104.2 Hz, $^{2}J_{P\text{-}P}$=11.1 Hz, **P**Ph_2 trans to PMe_3).

S 11. NMR (18-Crown-Ph)MoN_2(PMe_3)$_2$

^{1}H NMR (C_6D_6): δ 1.08 ppm (d, 9 H, $^{2}J_{H\text{-}P}$=5.1 Hz, **Me**$_3$P-), δ 1.69 ppm (d, 9 H, $^{2}J_{H\text{-}P}$=4.28 Hz, **Me**$_3$P-, trans to -PPh_2), δ 2.16 ppm (m, 6 H, PC**H**$_2$$CH_2PPh_2$ and PC**H**$_2$$CH_2N$), δ 2.32 ppm (m, 4 H, PCH_2C**H**$_2$$PPh_2$), δ 2.46 ppm (m, 2 H, PCH_2C**H**$_2$N), δ 3.12 ppm (broad s, 4 H, OCH_2C**H**$_2$N), δ 3.52 ppm (m, 20 H, OC**H**$_2$C**H**$_2$O and OC**H**$_2$$CH_2N$), δ 6.65 ppm (m, 8 H, ^{m}Ph), δ 6.86 ppm (m, 8 H, ^{o}Ph), δ 7.3 ppm (m, 4 H, ^{p}Ph); ^{13}C{^{1}H} NMR (C_6D_6): δ 23.0 ppm (d, 3 C, $^{1}J_{C\text{-}P}$=15.4 Hz, **C**H_3P), δ 25.4 ppm (d, 3 C, $^{1}J_{C\text{-}P}$=14.7 Hz, **C**H_3P), δ 27.2 ppm (s, 1 C, NCH_2**C**H_2P), δ 29.1 ppm (d, 1 C, Ph_2PCH_2**C**H_2P), δ 30.7 ppm (d, 1 C, Ph_2PCH_2**C**H_2P), δ 34.1 ppm (d, 2 C, Ph_2P**C**H_2CH_2P), δ 49.9 ppm (s, 1 C, N**C**H_2CH_2P), δ 54.2 ppm (s, 2 C, N**C**H_2CH_2O), δ 70.4 ppm (s, 2 C, O**C**H_2CH_2N), δ 70.6 ppm (s, 4 C, O**C**H_2CH_2O), δ 70.8 ppm (s, 2 C, O**C**H_2**C**H_2O), δ 70.9 ppm (s, 2 C, O**C**H_2**C**H_2O), δ 71.0 ppm (s, 2 C, O**C**H_2**C**H_2O), δ 126.6 ppm (d, 4 C, ^{y}Ph), δ 126.9 ppm (m, 8 C, ^{m}Ph), δ 131.4 ppm (m, 8 C, ^{o}Ph), δ 133.4 ppm (d, 4 C, ^{p}Ph); ^{31}P {^{1}H} NMR (C_6D_6): δ -11.7 ppm (dd(t), 1 P, $^{2}J_{P\text{-}Ptrans}$=103.7 Hz, $^{2}J_{P\text{-}P}$=20.8 Hz, -(**P**Me_3 trans to -PPh_2), δ -9.2 ppm (dm, 1 P, $^{2}J_{P\text{-}Ptrans}$=95.3 Hz, $^{2}J_{P\text{-}P}$=10.8 Hz, **P**Me_3 trans to P$(CH_2)_3$-), δ 65.6 ppm (m, 1 P, $^{2}J_{P\text{-}P}$=8.6 Hz, **P**Ph_2 trans to N_2), δ 72.0

ppm (ddd, 1 P, $^{2}J_{P\text{-}P_{trans}}$=95.3 Hz, $^{2}J_{P\text{-}P}$=20.8 Hz, $^{2}J_{P\text{-}P}$=8.6 Hz, **P**$(CH_2)_3$- trans to PMe_3), δ 87.9 ppm (dd, 1 P, $^{2}J_{P\text{-}P}$=103.7 Hz, $^{2}J_{P\text{-}P}$=10.8 Hz, **P**Ph_2 trans to PMe_3).

S 12. General Synthetic procedure of (n-Crown-iPr)Mo$(N_2)_2$(PPh_2Me)

In the glovebox, a 20 mL glass vial was charged with $Mo(N_2)_2(PPh_2Me)_4$ (200 mg, 0.21 mmol), a magnetic stir bar, n-Crown-iPr (0.21 mmol, 15-Crown-iPr: 119 mg, 18-Crown-iPr: 129 mg) and 5 mL THF. The dark brown solution was stirred for 9 h, followed by concentration *in vacuo*. A glass frit funnel was charged with a silica gel / toluene suspension then the excess toluene was removed by *vacuo*. The crude product in 2-3 mL toluene was layered on the top of the silica (dried under vacuo and 150 °C for 24 h) and washed with toluene excessively (3 x 20 mL). The solid phase was washed with THF until all the dark brown/yellow material was washed off from the silica pad. THF phases were combined followed by concentration *in vacuo* resulting a dark orange/brown oil.

(15-Crown-iPr)Mo$(N_2)_2$(PPh_2Me): brown/orange thick oil (112 mg, 58 %);

(18-Crown-iPr)Mo$(N_2)_2$(PPh_2Me): brown/orange thick oil (91 mg, 45%).

S 13. NMR data of (15-Crown-iPr)Mo$(N_2)_2$(PPh_2Me)

^{1}H NMR (C_6D_6): δ 0.98 ppm (m, 12 H, (C**H**$_3$)$_2$CHP-), δ 1.10 ppm (m, 12 H, (C**H**$_3$)$_2$CHP-), δ 1.47 ppm (m, 4 H, (PC**H**$_2$$CH_2P^iPr_2$), δ 1.60 ppm (m, 4 H, ($PCH_2$C**H**$_2$$P^iPr_2$), δ 1.99 ppm (t, 2 H, ($NCH_2$C**H**$_2$P), δ 2.11 ppm (s, 3 H, PPh_2C**H**$_3$), δ 2.19 ppm (m, 2 H, NC**H**$_2$$CH_2$P), δ 2.28 ppm (d, 4 H, $^{2}J_{H\text{-}P}$=3.8 Hz, $(CH_3)_2$C**H**P-), δ 2.82 ppm (t, 4 H, $^{2}J_{H\text{-}H}$=5.81 Hz, (OCH_2C**H**$_2$N), δ 3.39 ppm (s, 4 H, NCH_2C**H**$_2$O), δ 3.68 ppm (m, 8 H, OC**H**$_2$C**H**$_2$O), δ 3.68 ppm (t, 4 H, $^{2}J_{H\text{-}H}$=5.89 Hz, OC**H**$_2$C**H**$_2$O), δ 7.03 ppm (m, 4 H, ^{m}Ph), δ 7.12 ppm (m, 4 H, ^{o}Ph), δ 7.77 ppm (t, 2 H, $^{2}J_{H\text{-}H}$=8.40 Hz, ^{p}Ph); ^{13}C{^{1}H} NMR (C_6D_6): δ 18.4 ppm (d, 1 C, $^{1}J_{C\text{-}P}$=17.5 Hz, **C**H_3P), δ 19.2 ppm, 19.4 ppm, 19.6 ppm (s, 8 C, (**C**H_3)$_2$CHP), δ 22.0 ppm (dt, 2 C, $^{1}J_{C\text{-}P}$=19.4 Hz, $^{2}J_{C\text{-}P}$=7.2 Hz, Ph_2PCH_2**C**H_2P),

δ 22.6 ppm (m, 2 C, $Ph_2P\mathbf{C}H_2CH_2P$), δ 25.2 ppm (m, 1 C, $P\mathbf{C}H_2CH_2N$), δ 29.7 ppm, 29.8 ppm, 29.82 ppm (s, 4 C, $(CH_3)_2\mathbf{C}HP$), δ 52.2 ppm (d, 1 C, $^2J_{C\text{-}P}$=3.81 Hz, $N\mathbf{C}H_2CH_2P$), δ 54.9 ppm (s, 2 C, $N\mathbf{C}H_2CH_2O$), δ 70.3 ppm (s, 2 C, $O\mathbf{C}H_2CH_2O$), δ 70.6 ppm (s, 2 C, $OCH_2\mathbf{C}H_2O$),δ 70.61 ppm (s, 2 C, $O\mathbf{C}H_2CH_2O$), δ 71.4 ppm (s, 2 C, $O\mathbf{C}H_2CH_2N$), δ 129.0 ppm (s, 2 C, ^{y}Ph), δ 128.2 ppm (m, 4 C, ^{m}Ph), δ 131.4 ppm (d, 4 C, $^2J_{C\text{-}P}$=11.3 Hz, ^{o}Ph), δ 132.1 ppm (d, 2 C, $^2J_{C\text{-}P}$=18.8 Hz, ^{p}Ph); ^{31}P {^{1}H} NMR (C_6D_6): δ 20.0 ppm (dt, 1 P, $^2J_{P\text{-}Ptrans}$=114.2 Hz, $^2J_{P\text{-}Pcis}$=11.8 Hz, -(**P**(-CH_2-)$_3$, δ 69.9 ppm (d, 2 P, $^2J_{P\text{-}Pcis}$=12.6 Hz, **P**Ph_2), δ 94.7 ppm (d, 1 P, $^2J_{P\text{-}P}$=114.2 Hz, **P**Ph_2Me).

S 14. NMR data of (18-Crown-iPr)Mo(N_2)$_2$(PPh_2Me)

^{1}H NMR (C_6D_6): δ 1.00 ppm (m, 12 H, (C**H$_3$**)$_2$CHP-), δ 1.11 ppm (m, 12 H, (C**H$_3$**)$_2$CHP-), δ 1.50 ppm (m, 4 H, (PC**H$_2$**$CH_2P^iPr_2$), δ 1.64 ppm (m, 4 H, ($PCH_2C\mathbf{H_2}P^iPr_2$), δ 1.99 ppm (m, 2 H, ($NCH_2C\mathbf{H_2}P$), δ 2.11 ppm (s, 3 H, $PPh_2C\mathbf{H_3}$), δ 2.21 ppm (m, 2 H, NC**H$_2$**CH_2P), δ 2.30 ppm (d, 4 H, $^2J_{H\text{-}P}$=3.71 Hz, $(CH_3)_2C\mathbf{H}P$-), δ 2.82 ppm (t, 4 H, $^2J_{H\text{-}H}$=5.43 Hz, ($OCH_2C\mathbf{H_2}N$), δ 3.49 ppm (s, 4 H, $NCH_2C\mathbf{H_2}O$), δ 3.51 ppm (m, 12 H, OC**H$_2$**C**H$_2$**O), δ 3.66 ppm (t, 4 H, $^2J_{H\text{-}H}$=5.60 Hz, OC**H$_2$**C**H$_2$**O), δ 7.04 ppm (m, 4 H, ^{m}Ph), δ 7.13 ppm (m, 4 H, ^{o}Ph), δ 7.79 ppm (t, 2 H, $^2J_{H\text{-}H}$=7.98 Hz, ^{p}Ph); ^{13}C{^{1}H} NMR (C_6D_6): δ 18.5 ppm (d, 1 C, $^1J_{C\text{-}P}$=17.6 Hz, **C**H_3P), δ 19.3 ppm, 19.5 ppm, 19.7 ppm (s, 8 C, (**C**H_3)$_2$CHP), δ 22.0 ppm (dt, 2 C, $^1J_{C\text{-}P}$=19.0 Hz, $^2J_{C\text{-}P}$=8.1 Hz, $Ph_2PCH_2\mathbf{C}H_2P$), δ 22.7 ppm (m, 2 C, $Ph_2P\mathbf{C}H_2CH_2P$), δ 24.6 ppm (d, 1 C, $^1J_{C\text{-}P}$=9.88 Hz, $P\mathbf{C}H_2CH_2N$), δ 29.8 ppm, 29.86 ppm, 29.9 ppm (s, 4 C, $(CH_3)_2\mathbf{C}HP$), δ 51.3 ppm (d, 1 C, $^2J_{C\text{-}P}$=4.33 Hz, $N\mathbf{C}H_2CH_2P$), δ 54.3 ppm (s, 2 C, $N\mathbf{C}H_2CH_2O$), δ 70.65 ppm (s, 2 C, $O\mathbf{C}H_2CH_2O$), δ 70.72 ppm (s, 2 C, $OCH_2\mathbf{C}H_2O$), δ 70.90 ppm (s, 2 C, $O\mathbf{C}H_2CH_2O$), δ 71.0 ppm (s, 4 C, $O\mathbf{C}H_2CH_2O$), δ 71.20 ppm (s, 2 C, $O\mathbf{C}H_2CH_2N$), δ 127.7 ppm (s, 2 C, ^{y}Ph), δ 128.2 ppm (m, 4 C, ^{m}Ph), δ 131.5 ppm (d, 4 C, $^2J_{C\text{-}P}$=11.7 Hz, ^{o}Ph), δ 132.2 ppm (d, 2 C, $^2J_{C\text{-}P}$=18.6 Hz, ^{p}Ph); ^{31}P {^{1}H} NMR (C_6D_6): δ 20.1 ppm (dt,

1 P, $^2J_{P\text{-}Ptrans}$=113.8 Hz, $^2J_{P\text{-}Pcis}$=12.0 Hz, -(**P**(-CH_2-)$_3$, δ 70.0 ppm (d, 2 P, $^2J_{P\text{-}Pcis}$=12.0 Hz, **P**Ph_2), δ 95.0 ppm (d, 1 P, $^2J_{P\text{-}P}$=113.8 Hz, **P**Ph_2Me).

S 15. Synthesis and spectroscopic characterization of (15-Crown[M^+]-P_3-Ph)MoN_2(PMe_3)$_2$[BF_{20}]$^-$

A 10 mL Teflon cap glass vial was charged with 48 mg of (15-Crown-P_3-Ph)MoN_2(PMe_3)$_2$ and 4.0 mL of PhF_2 (1,2-difluorobenzene). Eppendorf tubes (1.5 mL) were charged with the solution (0.2 mL, 12 mg/mL, 2.45 x 10^{-3} mmol), then 1.1 eq MBF_{20} salts (specified below) were added to the Eppendorf tubes via a Hamilton 100 µL glass syringe. After vigorous shaking (~5-10 s) a quartz FTIR liquid cell was charged with the corresponding MoN_2-salt adduct and FTIR spectra were acquired for each adduct. Before spectrum acquisition a baseline was recorded by using the same quartz FTIR liquid cell filled with PhF_2.

Concentration and volume of the used MBF_{20} salt solutions in PhF_2:

$LiBF_{20}$: (MW: 686 g/mol), 16.5 mg/mL, 112 µL, 2.69 × 10^{-3} mmol, 1.1 eq

$NaBF_{20}$: (MW: 702 g/mol), 16.8 mg/mL, 113 µL, 2.70 × 10^{-3} mmol, 1.1 eq

KBF_{20}: (MW: 718 g/mol), 16.0 mg/mL, 120 µL, 2.67 × 10^{-3} mmol, 1.1 eq

$RbBF_{20}$: (MW: 765 g/mol), 16.0 mg/mL, 129 µL, 2.70 × 10^{-3} mmol, 1.1 eq

$CsBF_{20}$: (MW: 813 g/mol), 15.2 mg/mL, 144 µL, 2.69 × 10^{-3} mmol, 1.1 eq

$AgBF_{20}$: (MW: 787 g/mol), 15.7 mg/mL, 135 µL, 2.69 × 10^{-3} mmol, 1.1 eq

$TlBF_{20}$: (MW: 883 g/mol), 15.0 mg/mL, 158 µL. 2.68 × 10^{-3} mmol, 1.1 eq

S 16. Synthesis and spectroscopic characterization of (18-Crown[M^+]-P_3-Ph)MoN_2(PMe_3)$_2$[BF_{20}]$^-$

A 10 mL Teflon cap glass vial was charged with 78 mg of (18-Crown-P_3-Ph)MoN_2(PMe_3)$_2$ and 4.0 mL of PhF_2 (1,2-difluorobenzene). Eppendorf tubes (1.5 mL) were charged with the solution (0.2 mL, 19.5 mg/mL, 3.81 x 10^{-3} mmol), then 1.1 eq MBF_{20} salts (specified below) were added to the Eppendorf tubes

via a Hamilton 100 µL glass syringe. After vigorous shaking (~5-10 s) a quartz FTIR liquid cell was charged with the corresponding MoN_2-salt adduct and FTIR spectra were acquired for each adduct. Before spectrum acquisition a baseline was recorded by using the same quartz FTIR liquid cell filled with PhF_2.

Concentration and volume of the used MBF_{20} salt solutions in PhF_2:

$LiBF_{20}$: (MW: 686 g/mol), 16.5 mg/mL, 174 µL, 4.18×10^{-3} mmol, 1.1 eq

$NaBF_{20}$: (MW: 702 g/mol), 16.8 mg/mL, 175 µL, 4.19×10^{-3} mmol, 1.1 eq

KBF_{20}: (MW: 718 g/mol), 16.0 mg/mL, 188 µL, 4.19×10^{-3} mmol, 1.1 eq

$RbBF_{20}$: (MW: 765 g/mol), 16.0 mg/mL, 201 µL, 4.20×10^{-3} mmol, 1.1 eq

$CsBF_{20}$: (MW: 813 g/mol), 15.2 mg/mL, 224 µL, 4.19×10^{-3} mmol, 1.1 eq

$AgBF_{20}$: (MW: 787 g/mol), 15.7 mg/mL, 210 µL, 4.19×10^{-3} mmol, 1.1 eq

$TlBF_{20}$: (MW: 883 g/mol), 15.0 mg/mL, 247 µL. 4.20×10^{-3} mmol, 1.1 eq

S 17. Synthesis and spectroscopic characterization of (15-Crown[M^+]-P_3-^{i}Pr)Mo(N_2)$_2$(PPh_2Me)[BF_{20}]$^-$

A 10 mL Teflon cap glass vial was charged with 88.5 mg of (15-Crown-P_3-^{i}Pr)Mo(N_2)$_2$(PPh_2Me) and 4.0 mL of PhF_2 (1,2-difluorobenzene). Eppendorf tubes (1.5 mL) were charged with the solution (0.2 mL, 22.1 mg/mL, 4.8 x 10^{-3} mmol), then 1.1 eq MBF_{20} salts (specified below) were added to the Eppendorf tubes via a Hamilton 100 µL glass syringe. After vigorous shaking (~5-10 s) a quartz FTIR liquid cell was charged with the corresponding MoN_2-salt adduct and FTIR spectra were acquired for each adduct. Before spectrum acquisition a baseline was recorded by using the same quartz FTIR liquid cell filled with PhF_2.

Concentration and volume of the used MBF_{20} salt solutions in PhF_2:

$LiBF_{20}$: (MW: 686 g/mol), 16.5 mg/mL, 220 µL, 5.29×10^{-3} mmol, 1.1 eq

$NaBF_{20}$: (MW: 702 g/mol), 16.8 mg/mL, 217 µL, 5.19×10^{-3} mmol, 1.1 eq

KBF_{20}: (MW: 718 g/mol), 16.0 mg/mL, 233 µL, 5.19×10^{-3} mmol, 1.1 eq

$RbBF_{20}$: (MW: 765 g/mol), 16.0 mg/mL, 249 µL, 5.21×10^{-3} mmol, 1.1 eq

$CsBF_{20}$: (MW: 813 g/mol), 15.2 mg/mL, 278 µL, 5.20×10^{-3} mmol, 1.1 eq

$AgBF_{20}$: (MW: 787 g/mol), 15.7 mg/mL, 261 µL, 5.21×10^{-3} mmol, 1.1 eq

$TlBF_{20}$: (MW: 883 g/mol), 15.0 mg/mL, 306 µL. 5.20×10^{-3} mmol, 1.1 eq

S 18. Synthesis and spectroscopic characterization of (18-Crown[M^+]-P_3-^{i}Pr)Mo(N_2)$_2$(PPh_2Me)[BF_{20}]$^-$

A 10 mL Teflon cap glass vial was charged with 82.8 mg of (18-Crown-P_3-^{i}Pr)Mo(N_2)$_2$(PPh_2Me) and 4.0 mL of PhF_2 (1,2-difluorobenzene). Eppendorf tubes (1.5 mL) were charged with the solution (0.2 mL, 20.7 mg/mL, 4.3 x 10^{-3} mmol), then 1.1 eq MBF_{20} salts (specified below) were added to the Eppendorf tubes via a Hamilton 100 µL glass syringe. After vigorous shaking (~5-10 s) a quartz FTIR liquid cell was charged with the corresponding MoN_2-salt adduct and FTIR spectra were acquired for each adduct. Before spectrum acquisition a baseline was recorded by using the same quartz FTIR liquid cell filled with PhF_2.

Concentration and volume of the used MBF_{20} salt solutions in PhF_2:

$LiBF_{20}$: (MW: 686 g/mol), 16.5 mg/mL, 196 µL, 4.71×10^{-3} mmol, 1.1 eq

$NaBF_{20}$: (MW: 702 g/mol), 16.8 mg/mL, 197 µL, 4.71×10^{-3} mmol, 1.1 eq

KBF_{20}: (MW: 718 g/mol), 16.0 mg/mL, 211 µL, 4.70×10^{-3} mmol, 1.1 eq

$RbBF_{20}$: (MW: 765 g/mol), 16.0 mg/mL, 225 µL, 4.71×10^{-3} mmol, 1.1 eq

$CsBF_{20}$: (MW: 813 g/mol), 15.2 mg/mL, 252 µL, 4.71×10^{-3} mmol, 1.1 eq

$AgBF_{20}$: (MW: 787 g/mol), 15.7 mg/mL, 236 µL, 4.71×10^{-3} mmol, 1.1 eq

$TlBF_{20}$: (MW: 883 g/mol), 15.0 mg/mL, 277 µL. 4.71×10^{-3} mmol, 1.1 eq

S 19. X-Ray Crystallography – Experimental Details

X-ray diffraction data were measured for [(18-Crown-[H^+]-P_3-^{i}Pr)$MoCl_3$]Cl·2Et_2O and [(18-Crown-[$Ca(OTf)_2$]-P_3-Ph)$MoCl_2(PPh_2Me)$·(1½Toluene) at 100 K on a Bruker SMART APEX II CCD area detector system equipped with a graphite monochromator and a Mo Kα fine-focus sealed tube operated at 1.2 kW power (40 kV, 30 mA). For each of the crystals, a series of narrow frames of data were for collected with a scan width of 0.5˚ in ω or ϕ and an exposure time of 10 s per frame. The frames were integrated with the Bruker SAINT Software package[8] using a narrow-frame integration algorithm. The data were corrected for absorption effects by the multi-scan method (SADABS). The structure was solved by the direct methods using the Bruker SHELXTL (V2014.11-0) Software Package.[8] All non-hydrogen atoms were located in successive Fourier maps and refined anisotropically.

[(18-Crown-[H^+]-P_3-^{i}Pr)$MoCl_3$]Cl·2Et_2O. A yellow rectangular plate of approximate dimensions 0.226 × 0.216 × 0.209 mm^3 was used for the measurement of diffraction data. The integration of the data using a monoclinic unit cell yielded a total of 63254 reflections in the θ range of 1.733 to 33.563° of which 8219 were independent with $I \geq 2\sigma(I)$ (R_{int} = 0.0711). All non-hydrogen atoms were located in successive Fourier maps and refined anisotropically. The asymmetric unit consists of a half of the [(18-Crown-[H^+]-P_3-^{i}Pr)$MoCl_3$]$^+$ cation and a chloride anion located on a two-fold symmetry plane. The central P atom, the C atoms of the bridging ethylene group, the bridging N atom, one of the O atoms of the cyclic ether, and the Mo and Cl atoms are located on the plane of symmetry. The cation is highly disordered with high thermal parameters observed for all atoms of the cyclic ether. The disorder associated with one of the ethylene linkages is treated with a model consisting of two sites for the C atoms. The ethylene

group which links the central P to the terminal P atom is also disordered and treated similarly. Free variable refinement of the site occupancies of the two sets of sites settle close to 0.5. In addition, the two isopropyl substituents of the terminal P atom also exhibit disorder. One of the isopropyl groups is refined by assigning two sites for one of the methyl C atoms and the other with two sets of sites for all three C atoms. All non-hydrogen atoms of the ions were located in successive Fourier maps and refined anisotropically. The hydrogen atom of the protonated tertiary amine group was located and refined isotropically. The rest of the H atoms were placed in calculated in positions and refined isotropically using a riding model with fixed thermal parameters. Substantial electron density was observed in the asymmetric unit away from the ions, and could not be assigned to any solvent molecules. Therefore, SQUEEZE/PLATON was applied.[9] The program calculated 113 electrons in a void-space volume of 422 $Å^3$, and the values are interpreted as diffused electron density resulting from four diethyl ether molecules in the unit cell. The final refinement parameters are R_1 = 0.0900 and wR_2 = 0.1790 for data with $F > 4\sigma(F)$ giving the data to parameter ratio of 29.6. The refinement data for all data are R_1 = 0.1065 and wR_2 = 0.1863.

The overall refinement of the structure is severely impacted by the extensive disorders of the cation and the solvent molecules. Therefore, the structure obtained is only useful for the verification of the identity of the compound, and the metric parameters associated with the bonds must be treated with caution.

[(18-Crown-[Ca(OTf)$_2$]-P$_3$-Ph)MoCl$_2$(PPh$_2$Me)]·(1½Toluene). The compound forms large orange crystals from toluene solutions. Attempts to cut the crystals into a suitable size led to multiple fractures, and therefore, we used a crystal of 0.627 × 0.366 × 0.280 was used for the data

collection. The air sensitive orange crystal used in the data acquisition diffracted well but there were some shadow reflections possibly due to the partial damage the crystal. The integration of the data using a monoclinic unit cell yielded a total of 63254 reflections in the θ range of 1.733 to 33.563 of which 8219 were independent with $I \geq 2\sigma(I)$ ($R_{int} = 0.0711$).

The asymmetric unit contains one [(18-Crown-[$Ca(OTf)_2$]-P_3-Ph)$MoCl_2(PPh_2Me)$ complex molecule and 1½ molecules of solvated toluene. One of the toluene solvates is located on a two folded axis of symmetry, while all other atoms are located on general positions. The methyl group of the toluene molecule on the symmetry axis is disordered over two sites. One of the –OCH_2CH_2O– linkages also exhibits positional disorder. A model with two sets of sites for the atoms leads to satisfactory refinement of the whole structure.

Table 1. Crystal data and structure refinement for [(18-Crown-[Ca(OTf)$_2$]-P$_3$-Ph)MoCl$_2$(PPh$_2$Me) × (1 ½ Toluene).

Identification code	lp11a	
Empirical formula	C135 H159 Ca2 Cl4 F12 Mo2 N2 O22 P8 S4	
Formula weight	3179.47	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	*C2/c*	
Unit cell dimensions	a = 34.2085(8) Å	α= 90°.
	b = 9.9862(2) Å	β= 110.165(1)°.
	c = 44.8955(10) Å	γ = 90°.
Volume	14396.8(6) Å^3	
Z	4	
Density (calculated)	1.467 Mg/m^3	
Absorption coefficient	0.548 mm^{-1}	
F(000)	6572	
Crystal size	0.627 × 0.366 × 0.280 mm^3	
Theta range for data collection	1.841 to 28.699°.	
Index ranges	$-46 \le h \le 46$, $-13 \le k \le 13$, $-60 \le l \le 60$	
Reflections collected	158953	
Independent reflections	18605 [R(int) = 0.0462]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7469 and 0.6689	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	18605 / 0 / 865	
Goodness-of-fit on F^2	1.290	
Final R indices [I>2sigma(I)]	R1 = 0.0791, wR2 = 0.1721	
R indices (all data)	R1 = 0.0878, wR2 = 0.1767	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.898 and -1.528 e.Å^{-3}	

S 21. Crystal Structure Data of [(18-Crown-[H^+]-P_3-^{i}Pr)$MoCl_3$]$^+$[Cl]$^-$ × 2Et_2O

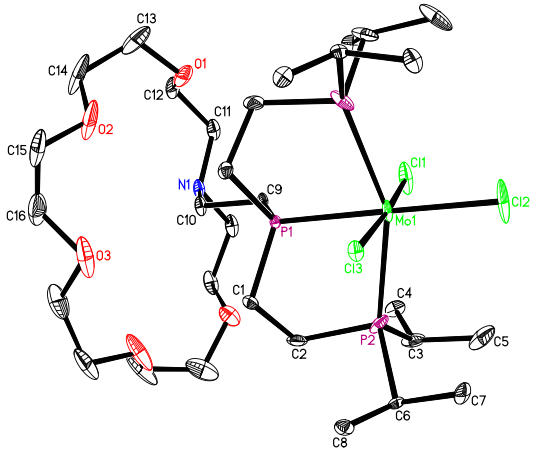


Figure 2. View of the [(18-Crown-[H^+]-P_3-^{i}Pr)$MoCl_3$]$^+$ cation. Symmetric equivalents are unlabeled, the second sites of the disordered atoms are not shown, and H atoms are omitted for clarity. The thermal parameters are drawn at 20% probability.

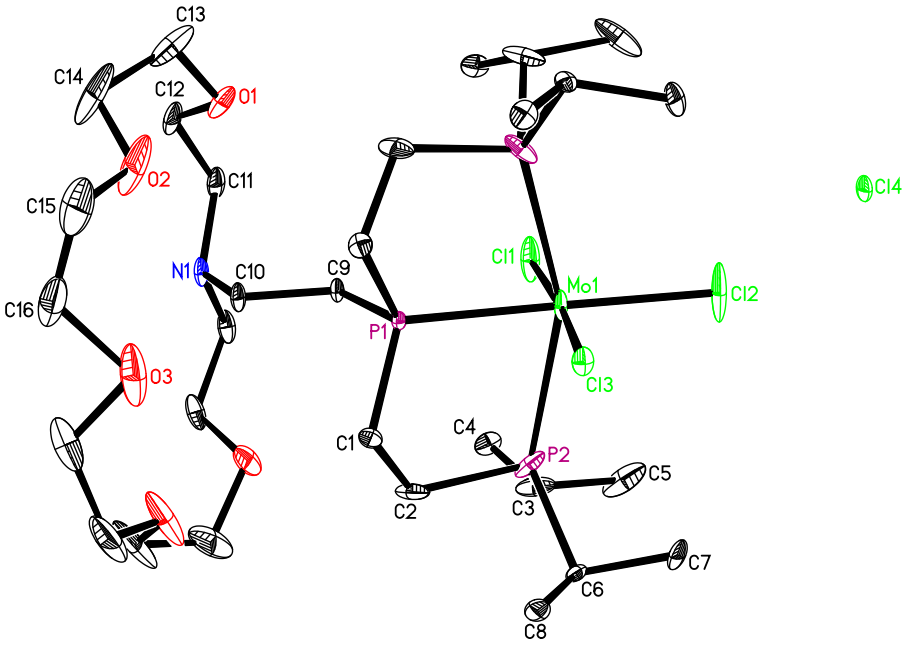


Figure 3. View of [(18-Crown-[H^+]-P_3-^{i}Pr)$MoCl_3$]$^+$[Cl]$^-$

Table 2. Crystal data and structure refinement for [*mer*-(18-Crown[H^+]-P_3)$MoCl_3$]$Cl \cdot ½Et_2O$.

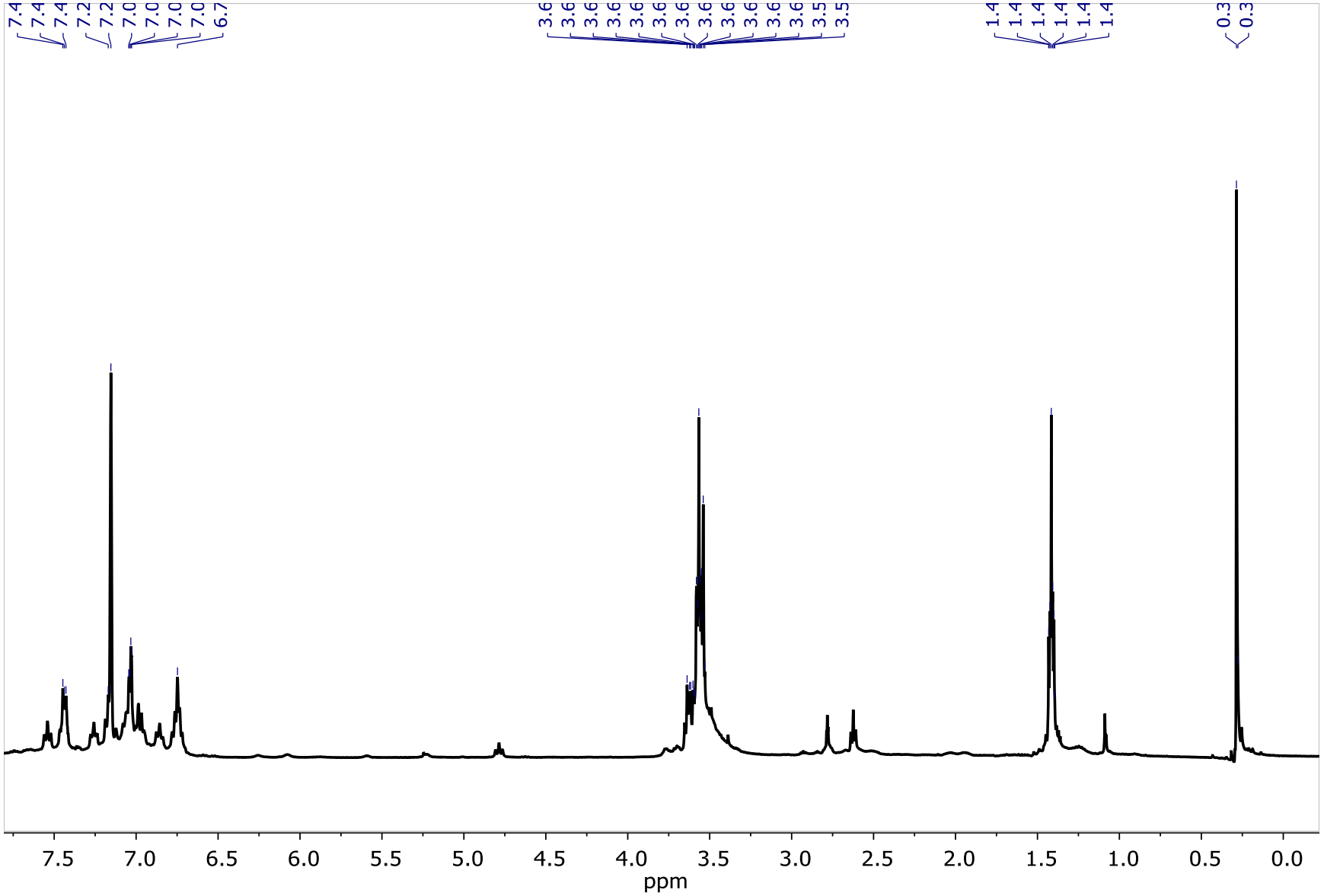
Identification code	lp39_sqd	
Empirical formula	C32 H66 Cl4 Mo N O5.50 P3	
Formula weight	883.50	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/m	
Unit cell dimensions	a = 24.6809(12) Å	α= 90°.
	b = 11.9759(6) Å	β= 117.310(1)°.
	c = 16.5785(8) Å	γ = 90°.
Volume	4354.0(4) $Å^3$	
Z	4	
Density (calculated)	1.348 Mg/m^3	
Absorption coefficient	0.694 mm^{-1}	
F(000)	1856	
Crystal size	0.226 × 0.216 × 0.209 mm^3	
Theta range for data collection	1.733 to 32.563°.	
Index ranges	$-37 \leq h \leq 37$, $-18 \leq k \leq 17$, $-24 \leq l \leq 25$	
Reflections collected	64254	
Independent reflections	8219 [R(int) = 0.0711]	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7462 and 0.6550	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8219 / 36 / 278	
Goodness-of-fit on F^2	1.114	
Final R indices [I>2sigma(I)]	R1 = 0.0900, wR2 = 0.1790	
R indices (all data)	R1 = 0.1065, wR2 = 0.1863	
Extinction coefficient	n/a	
Largest diff. peak and hole	3.172 and -2.849 $e.Å^{-3}$	

Table 3. Hydrogen bonds for [*mer*-(18-Crown[H^+]-P_3)$MoCl_3$]$Cl \cdot ½Et_2O$.

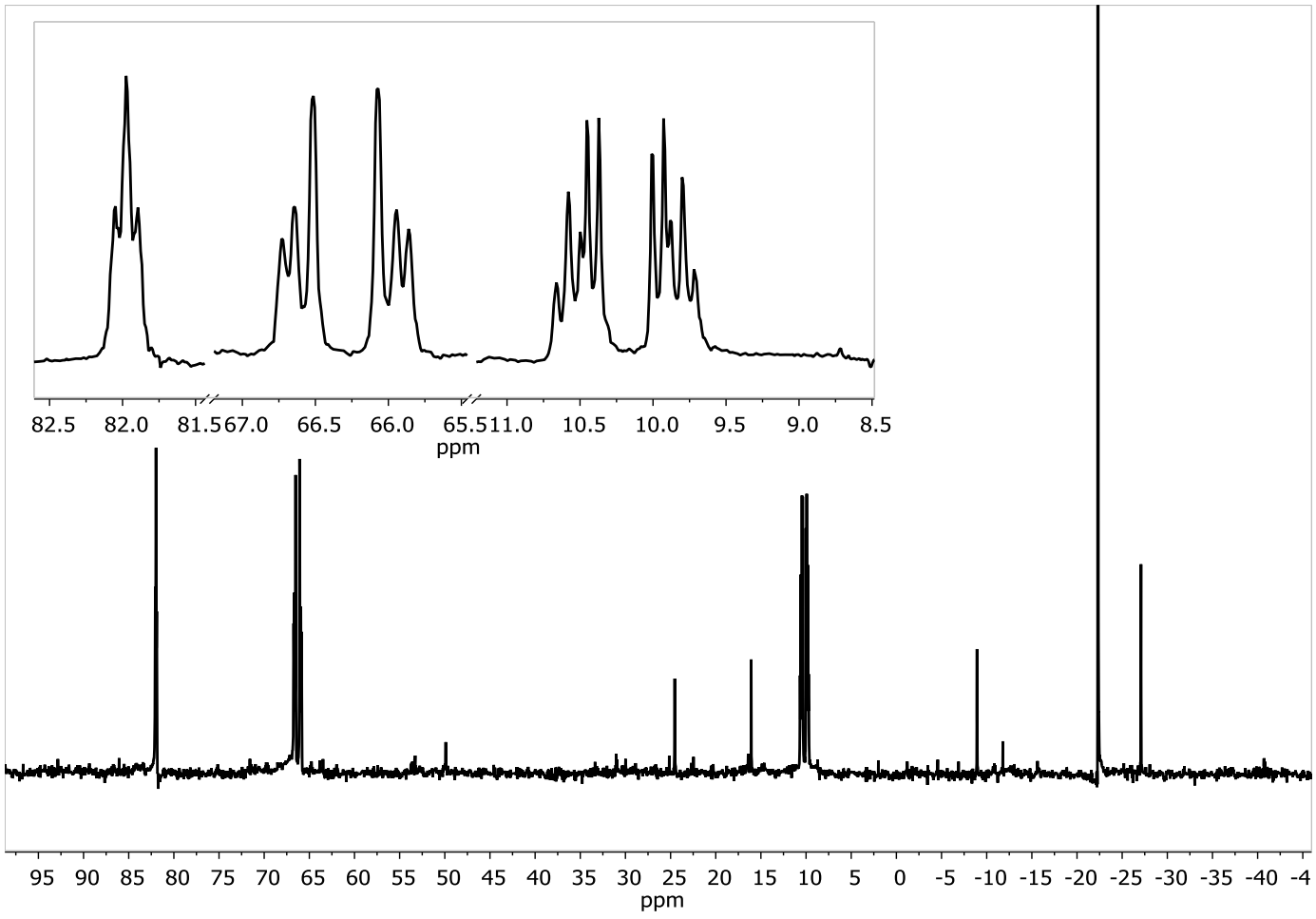
D-H...A	d(D-H, Å)	d(H...A, Å)	d(D...A, Å)	∠(DHA, degrees)
C(1)-H(1B)...O(2)#1	0.99	2.47	3.379(6)	152.8
C(2)-H(2A)...O(1)#1	0.99	2.51	3.418(7)	152.0
C(4)-H(4B)...Cl(1)	0.98	2.39	3.271(10)	148.8
C(8)-H(8C)...Cl(3)	0.98	2.93	3.767(9)	144.5
C(6A)-H(6AA)...Cl(3)	1.00	2.79	3.285(9)	111.3
C(7A)-H(7AA)...Cl(2)	0.98	2.60	3.382(12)	136.4
C(7A)-H(7AA)...Cl(3)	0.98	2.78	3.430(10)	124.4
C(10)-H(10)...O(1)#1	0.87(10)	2.50(10)	3.005(4)	118(8)
N(1)-H(1)...Cl(4)#2	1.04(9)	1.96(9)	2.997(5)	175(7)
C(11)-H(11A)...Cl(1)#2	0.99	2.81	3.542(5)	131.7
C(12)-H(12B)...Cl(4)#2	0.99	2.92	3.719(6)	138.3
C(16A)-H(16D)...Cl(3)#3	0.99	2.93	3.919(12)	176.3

Symmetry transformations used to generate equivalent atoms:
#1 x,-y+1,z #2 -x+1,-y+1,-z+1 #3 -x+1,-y+1,-z

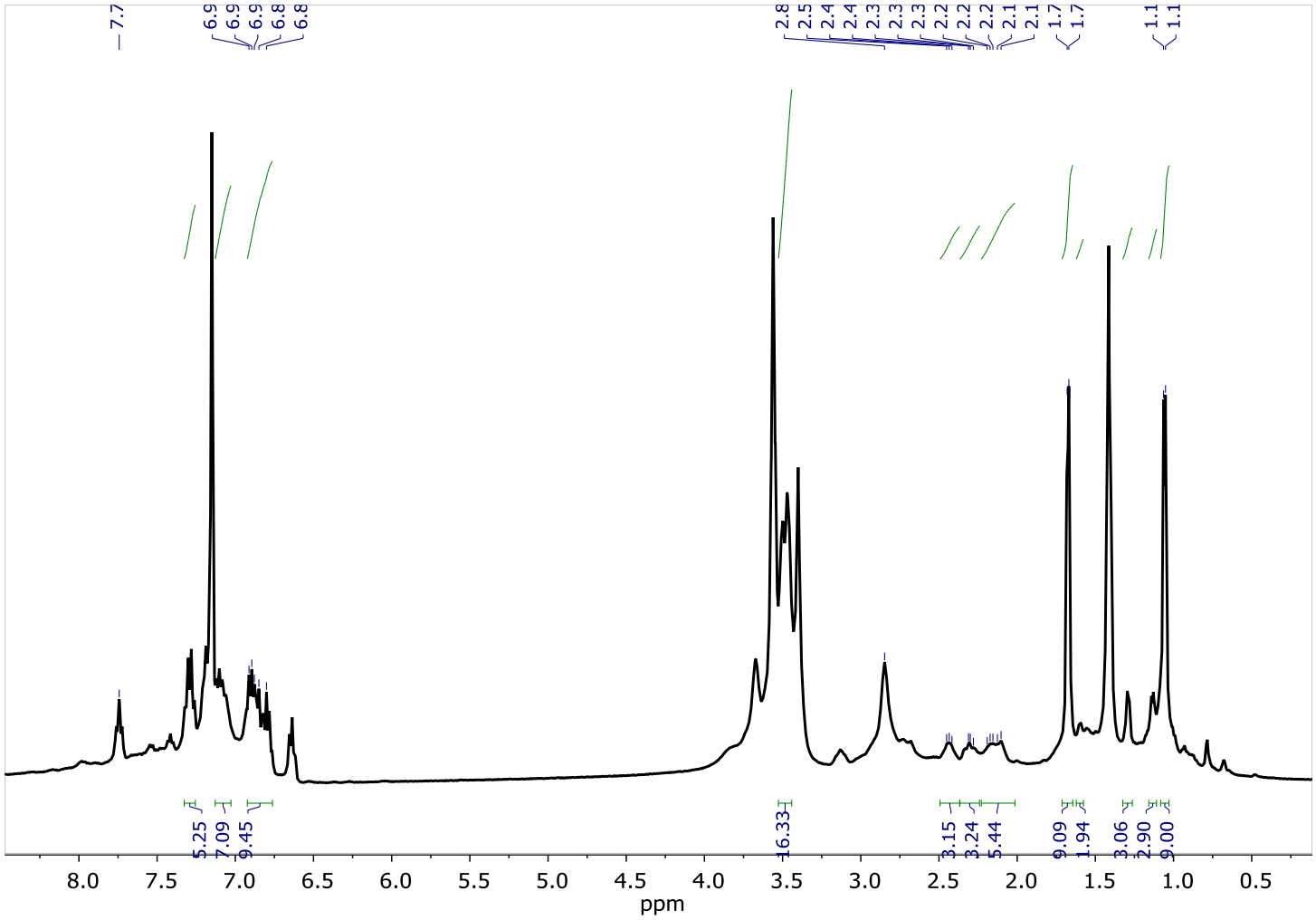
S 22. ^{1}H NMR of (18-Crown-Ph)MoN_2(dppm) in C_6D_6



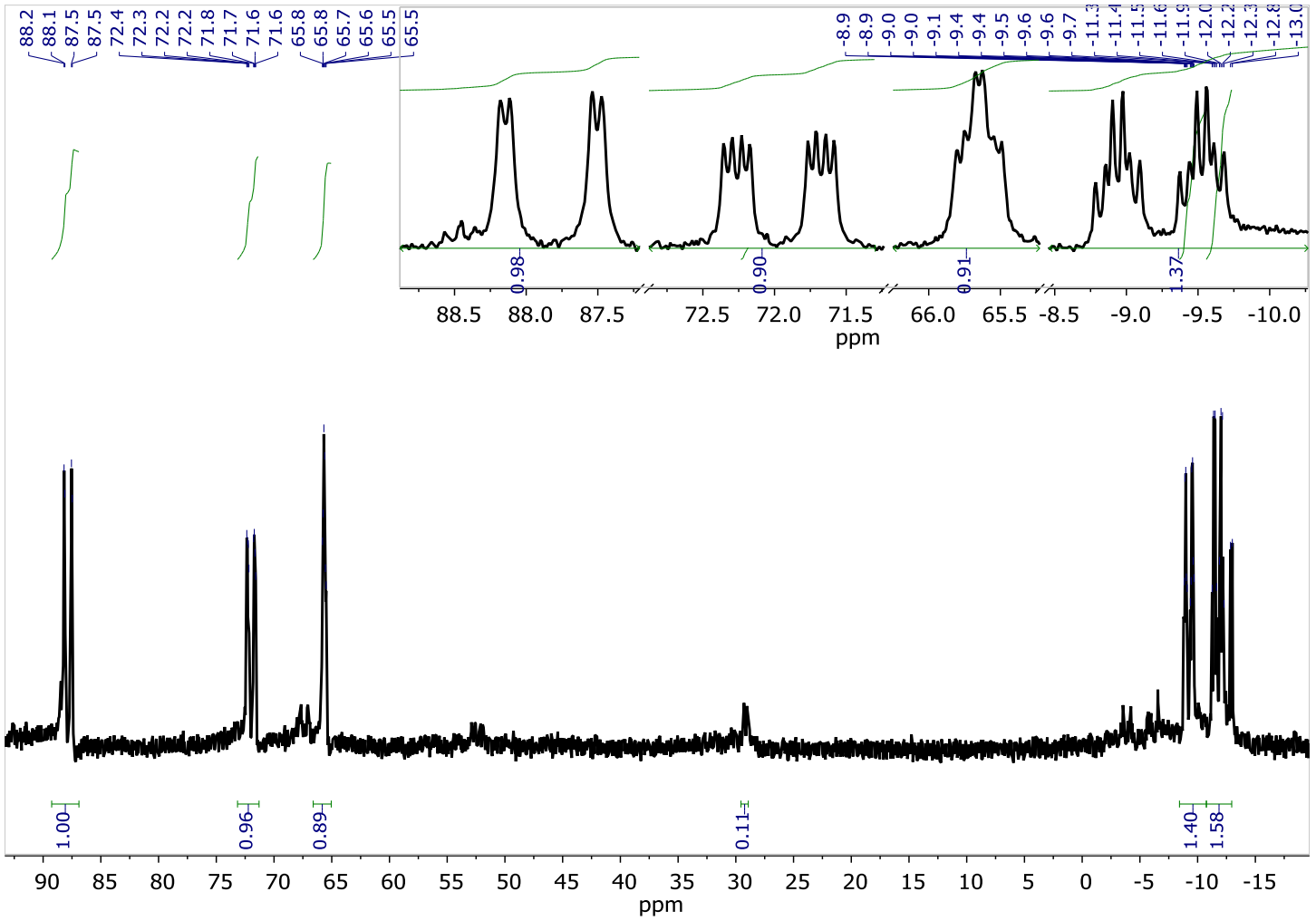
S 23. $^{31}P\{^{1}H\}$ NMR of (18-Crown-Ph)MoN_2(dppm) in C_6D_6



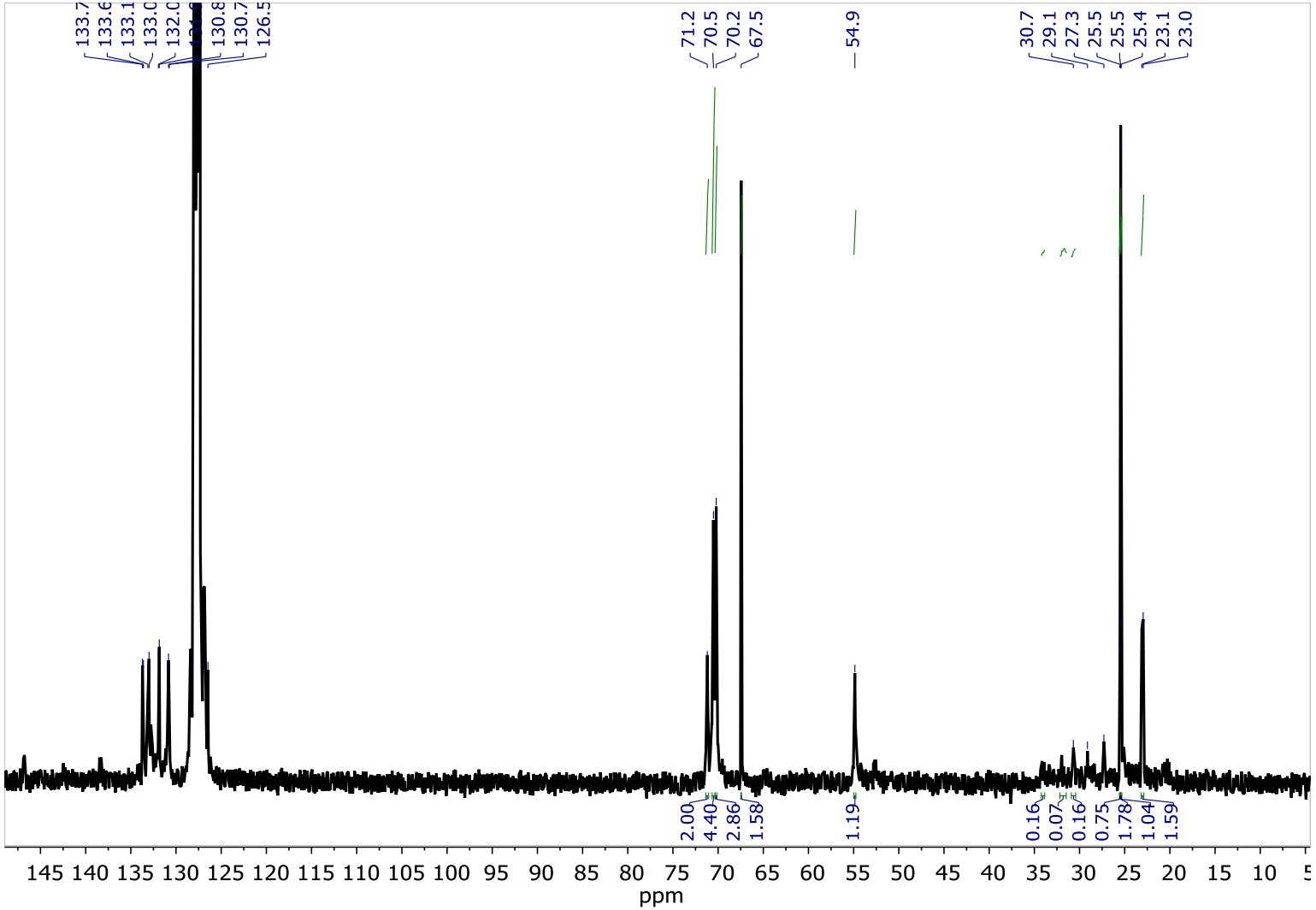
S 24. ^{1}H NMR of (15-Crown-Ph)$MoN_2(PMe_3)_2$ in C_6D_6



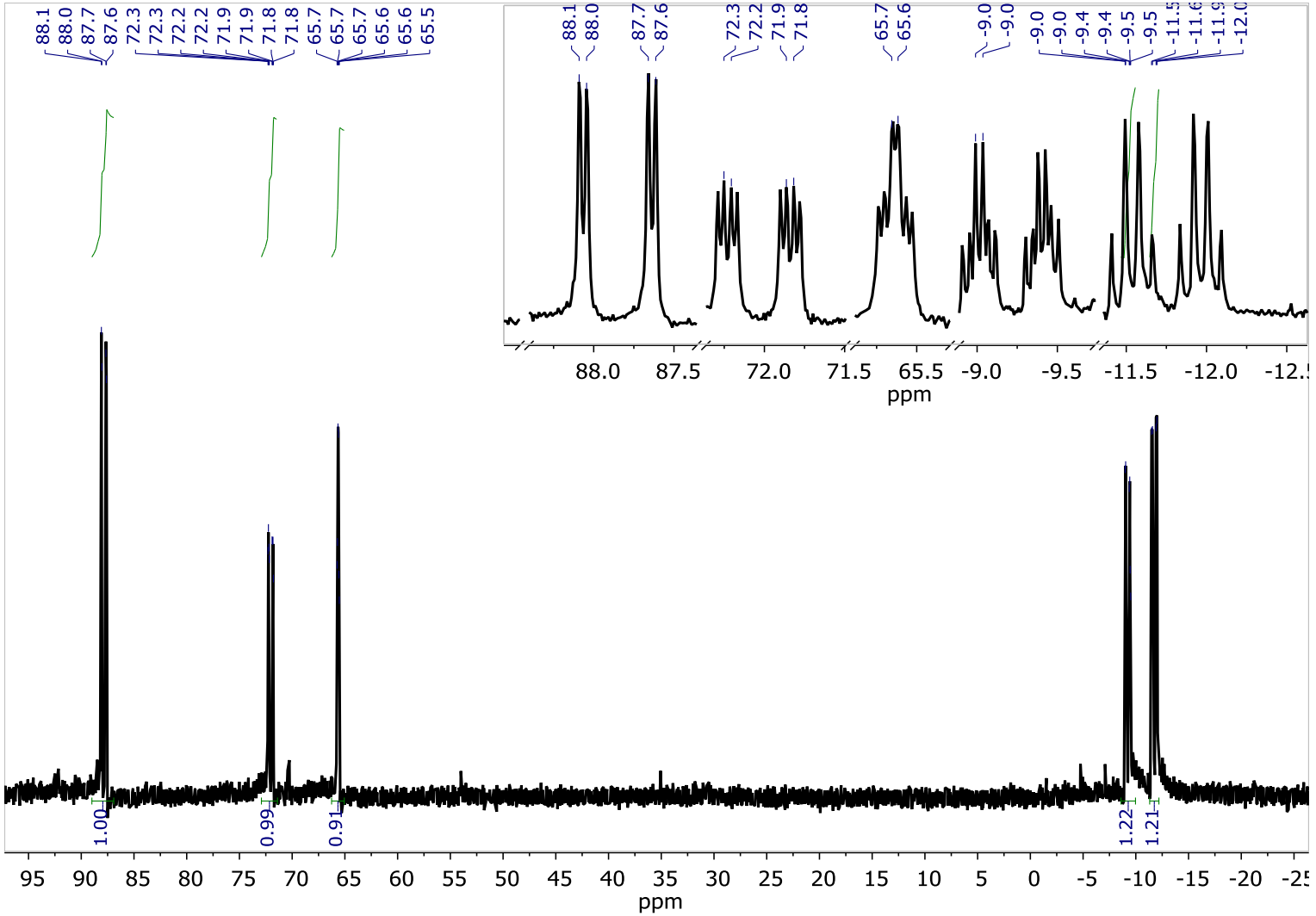
S 25. $^{31}P\{^{1}H\}$ NMR of (15-Crown-Ph)$MoN_2(PMe_3)_2$ in C_6D_6



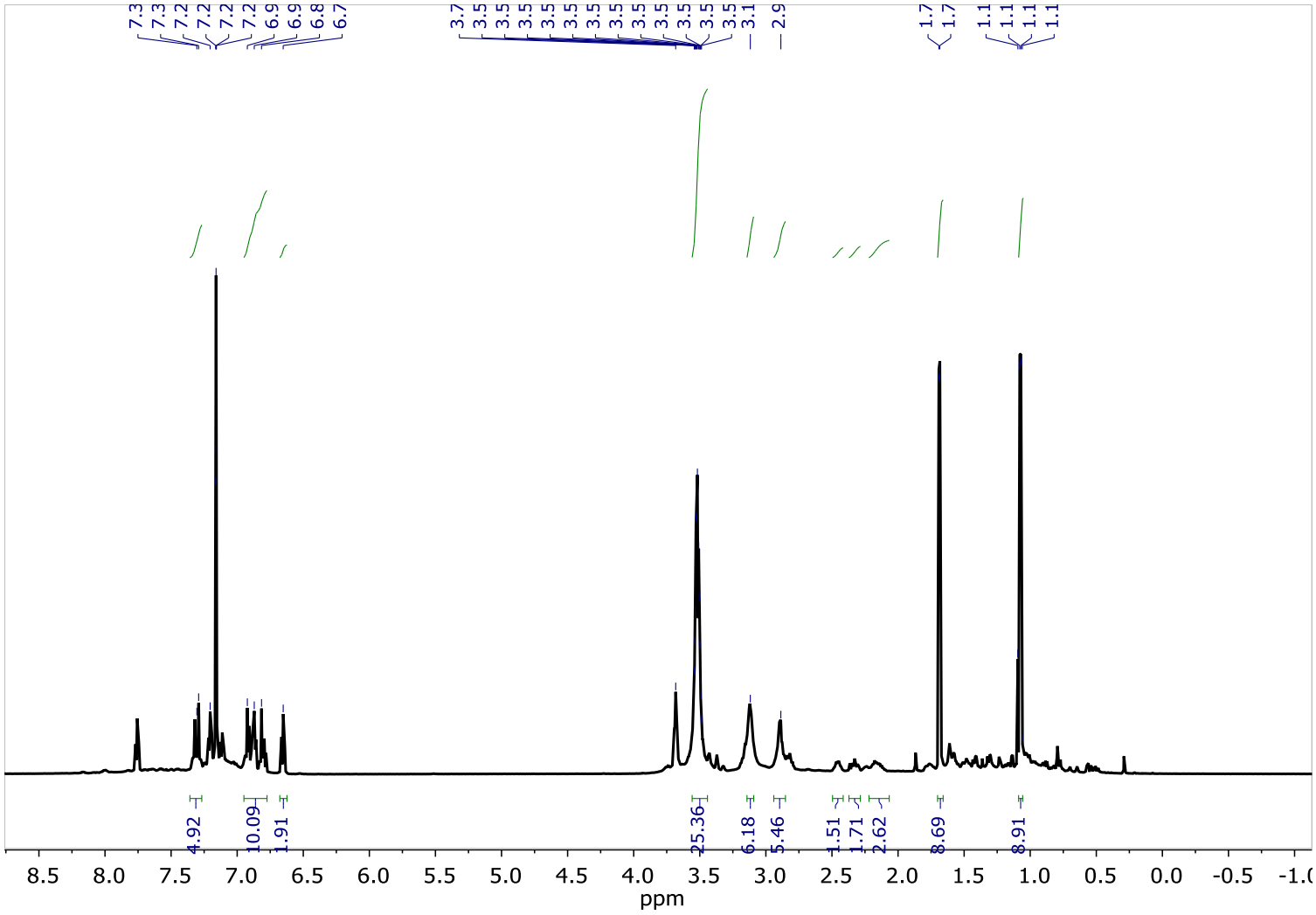
S 26. $^{13}C\{^{1}H\}$ NMR of (15-Crown-Ph)$MoN_2(PMe_3)_2$ in C_6D_6



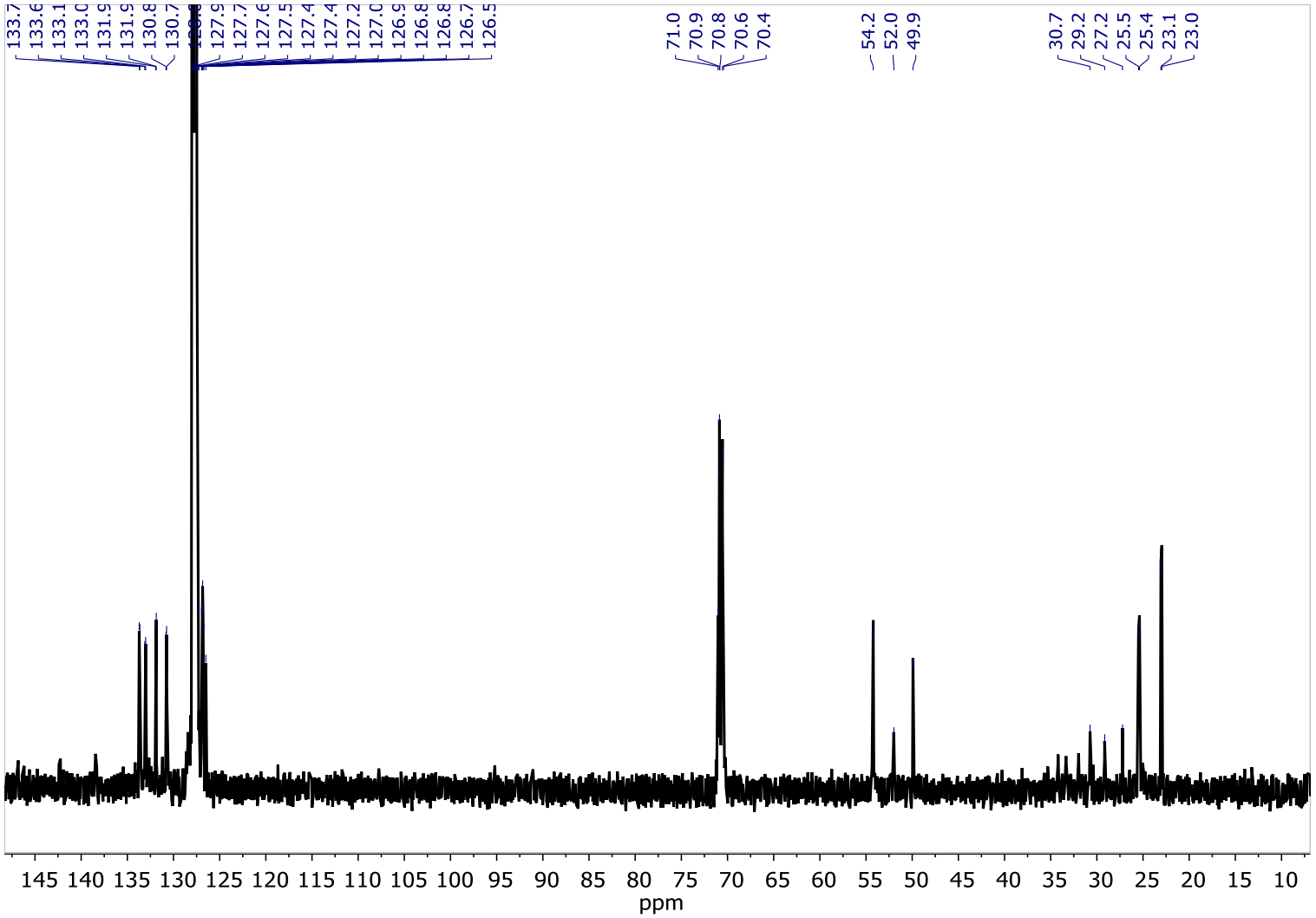
S 27. $^{31}P\{^{1}H\}$ NMR of (18-Crown-Ph)$MoN_2(PMe_3)_2$ in C_6D_6



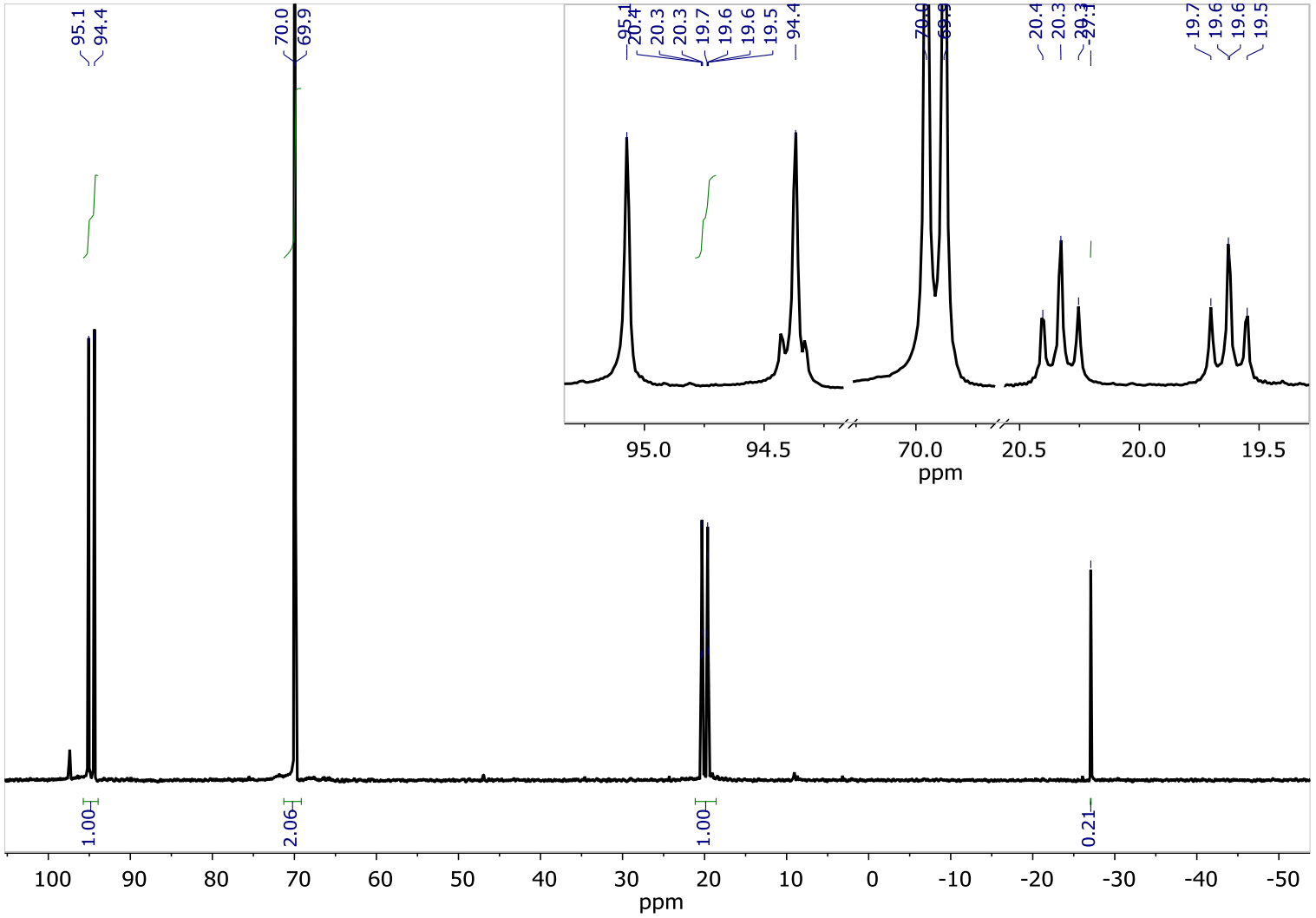
S 28. ^{1}H NMR of (18-Crown-Ph)MoN$_2$(PMe$_3$)$_2$ in C$_6$D$_6$



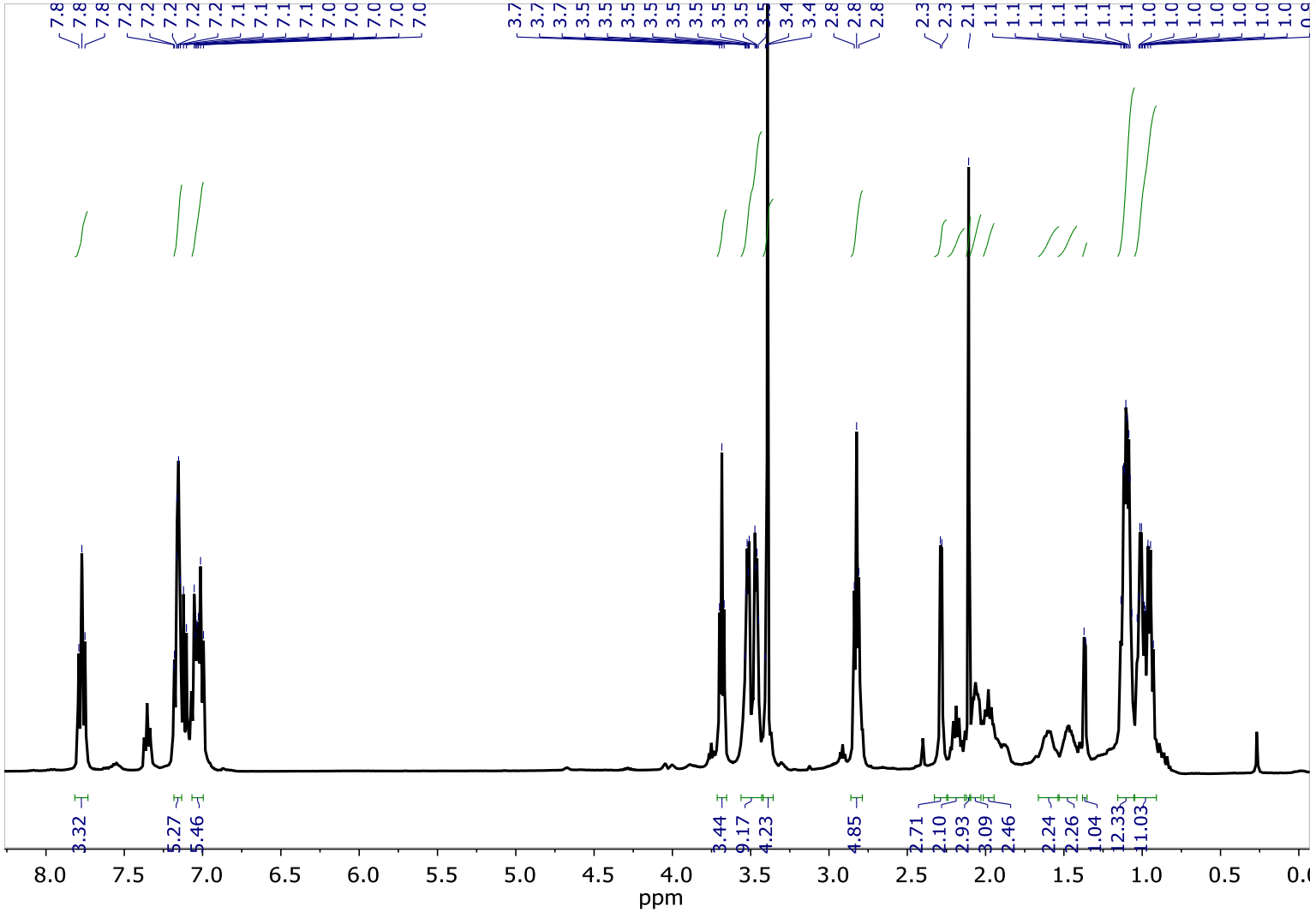
S 29. ^{13}C {^{1}H} NMR of (18-Crown-Ph)$MoN_2(PMe_3)_2$ in C_6D_6


133.7
133.6
133.1
133.0
131.9
131.9
130.8
130.7
127.9
127.7
127.6
127.5
127.4
127.4
127.2
127.0
126.9
126.8
126.8
126.7
126.5
71.0
70.9
70.8
70.6
70.4
54.2
52.0
49.9
30.7
29.2
27.2
25.5
25.4
23.1
23.0
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10
ppm

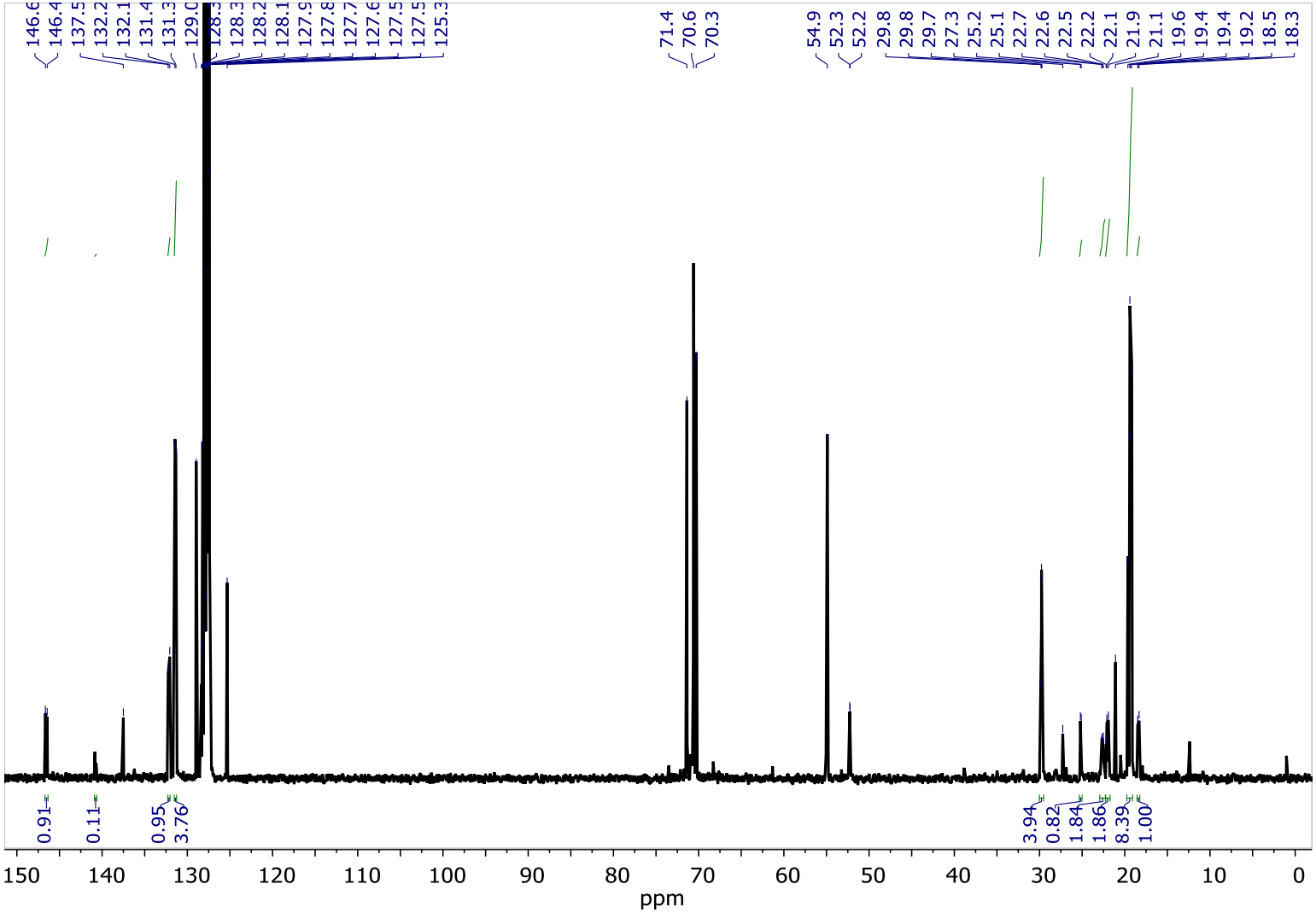
S 30. ^{31}P {^{1}H} NMR of (15-Crown-iPr)Mo(N_2)$_2$(PPh_2Me) in C_6D_6



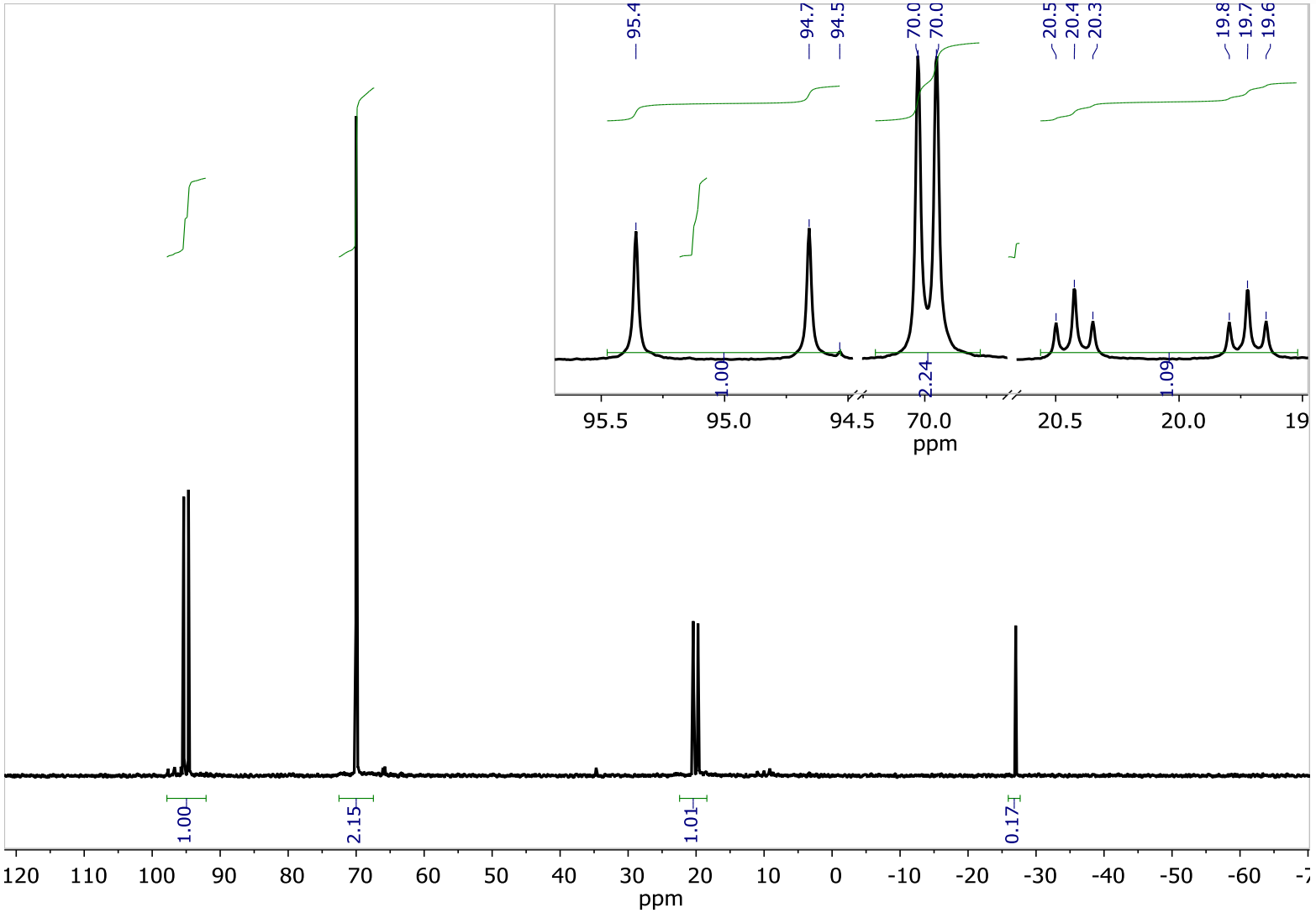
S 31. ^{1}H NMR of (15-Crown-iPr)Mo$(N_2)_2$(PPh_2Me) in C_6D_6



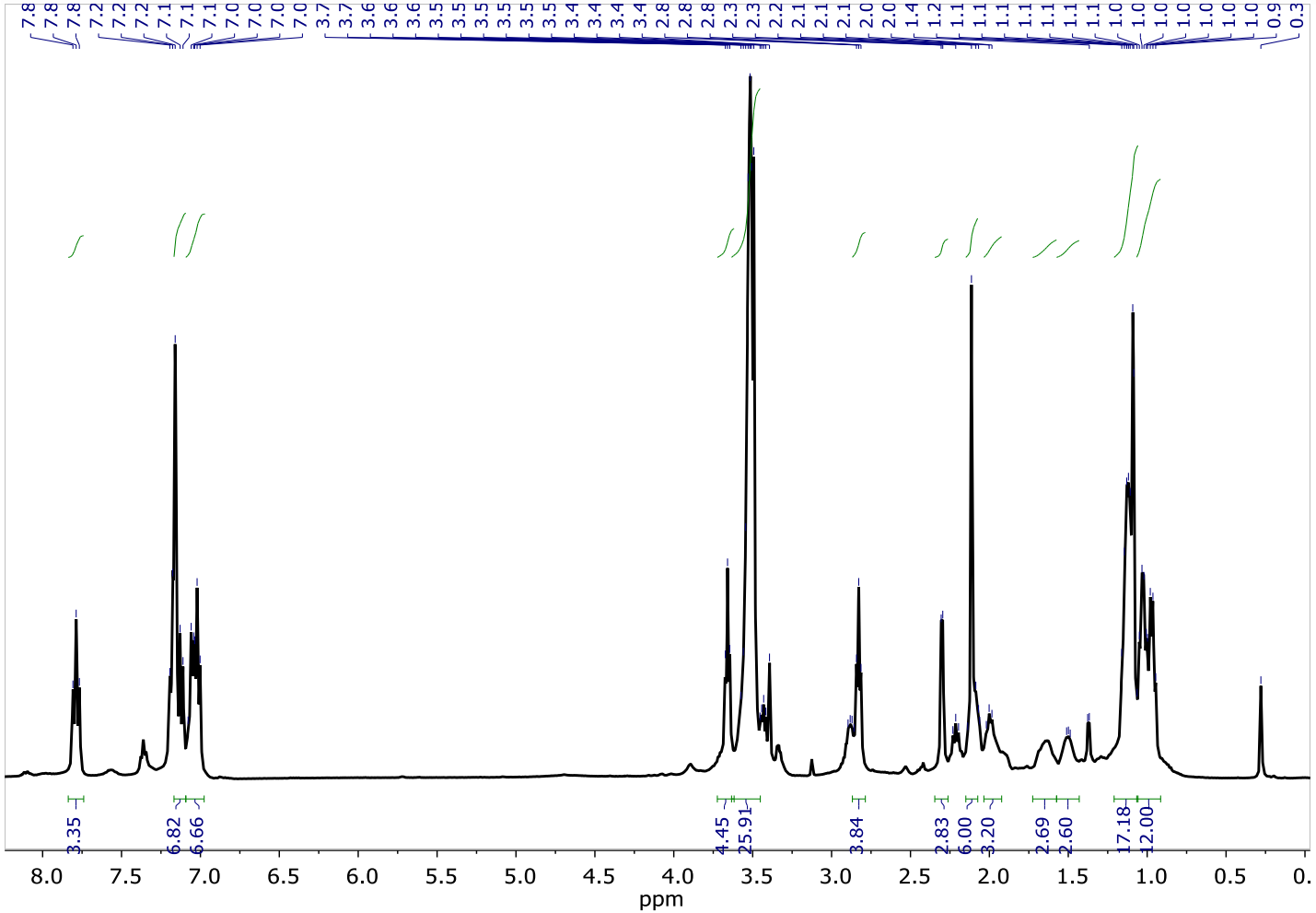
S 32. ^{13}C {^{1}H} NMR of (15-Crown-iPr)Mo$(N_2)_2$(PPh_2Me) in C_6D_6


146.6
146.4
137.5
132.2
132.1
131.4
131.3
129.0
128.3
128.3
128.2
128.1
127.9
127.8
127.7
127.6
127.5
127.5
125.3
71.4
70.6
70.3
54.9
52.3
52.2
29.8
29.8
29.7
27.3
25.2
25.1
22.7
22.6
22.5
22.2
22.1
21.9
21.1
19.6
19.4
19.4
19.2
18.5
18.3
0.91
0.11
0.95
3.76
3.94
0.82
1.84
1.86
8.39
1.00
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

S 33. ^{31}P {^{1}H} NMR of (18-Crown-iPr)Mo(N_2)$_2$(PPh_2Me) in C_6D_6



S 34. ^{1}H NMR of (18-Crown-iPr)Mo(N_2)$_2$(PPh_2Me) in C_6D_6



S 35. ^{13}C {^{1}H} NMR of (18-Crown-iPr)Mo(N_2)$_2$(PPh_2Me) in C_6D_6

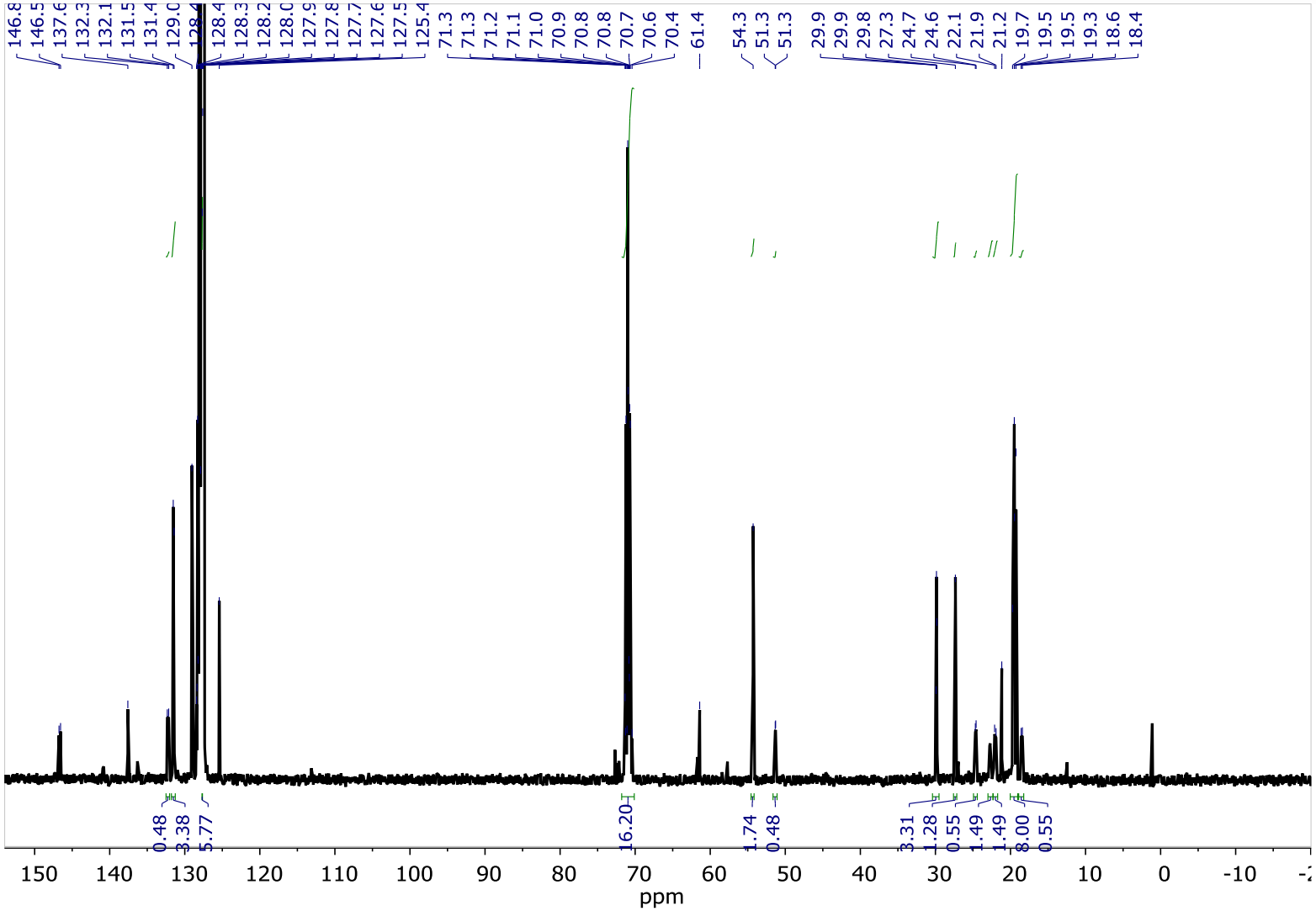


Table 4. Pressure Corrected Boiling Points for Selected Solvents and Reagents

Solvent	ΔH_{vap} (kJ/mol)	T_{boil} (ºC, 1 atm)	T_{boil} (K, 1 atm)	T_{boil} (ºC, 0.77 atm)	T_{boil} (K, 0.77 atm)
dichloromethane	29.2	39.6	312.75	32	305.5
diethyl ether	28.1	34.6	307.75	27	300.4
THF	30.8	66	339.15	58	331.0
toluene	33.5	111	384.15	101	374.6
hexane	31.52	69	342.15	61	334.1
pentane	26.42	36	309.15	28	301.3
water	43.99	100	373.15	93	366.2
ethanol	40.5	78.37	351.52	72	344.9
methanol	35.4	64.7	337.85	58	330.8
chloroform	30.9	61.15	334.3	53	326.4

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