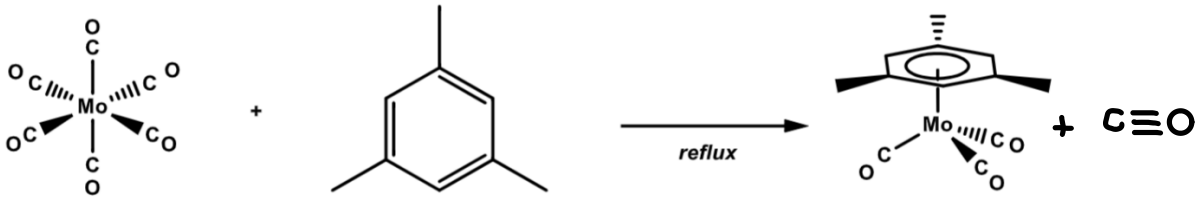
SYNTHESIS AND CHARACTERIZATION OF LIGAND-SUBSTITUTED $MO(CO)_3$(MESITYLENE) AND $MO(CO)_3$(ACETONITRILE) FROM $MO(CO)_6$

INTRODUCTION

Organometallic chemistry emerged as a distinct field in the mid 20th century and has since become central to both fundamental organic chemistry and industrial catalysis. Early studies of metal carbonyls and arene complexes by Fischer, Wilkinson and coworkers established key concepts about π-bonding, electron counting, and metal ligand synergic interactions.[1-2] Transition metal carbonyls, such as molybdenum hexacarbonyl, are particularly useful for model systems due to their well-defined structures and spectroscopic behavior. In this experiment, $Mo(CO)_6$ is converted into $(\eta^6\text{-}C_6H_3(CH_3)_3)Mo(CO)_3$ through substitution of carbonyl ligands by mesitylene.



Equation 1: Reaction between $Mo(CO)_6$ and mesitylene

Bonding in the molybdenum carbonyl and arene complexes is dominated by σ-donation from ligand to metal, and π-backbonding from filled molybdenum *d* orbitals into ligand π-anti-bonding orbitals. Carbon monoxide is a strong π-acceptor ligand, and because metal-ligand backbonding weakens the CO bond, CO stretching frequency decreases. When three CO ligands are replaced by mesitylene -- a weaker π-acceptor and stronger σ-donor -- electron density at the molybdenum center increases. This enhanced electron density strengthens π-backbonding to the remaining CO ligands, which results in further reduction of IR stretching frequencies.

IR is a primary diagnostic technique for this experiment. Both the number and position of Co stretching bands are sensitive to ligand substitution and molecular symmetry, so conversion from octahedral $Mo(CO)_6$ to C_{3v}-$(\eta^6\text{-}C_6H_3(CH_3)_3)Mo(CO)_3$ is expected to increase the number of observable CO stretches while shifting them to lower wavenumbers. Mesitylene coordination should also be evident in NMR spectroscopy. In the ^{1}H-NMR spectrum, η^6 binding to molybdenum alters the electronic and magnetic environment of the aromatic ring: this should result in significant upfield shifts of aromatic protons relative to free mesitylene protons due to increased shielding. Methyl protons are still expected to shift, but to a lesser extent due to greater distance from the metal center. Similar phenomena are expected in ^{13}C-NMR: aromatic carbons are expected to shift upfield relative to free mesitylene due to increased shielding. Together, these techniques help to identify products and allow insight into metal-ligand bonding in molybdenum complexes.

The proposed experiment substitutes the mesitylene ligand for acetonitrile. Compared to CO ligands, acetonitrile is more electron-rich, a stronger σ-donor, and a weaker π-acceptor. Similar to the changes seen in mesitylene substitution, the strong σ-donor will increase electron density at the molybdenum center. Π-backbonding between molybdenum and the remaining CO ligands in the IR spectrum of $Mo(CO)_3((CH_3)CN)_3$ is expected to result in lower stretching frequencies compared to the starting material. Nitrogen functions as an electron withdrawing group due to its high electronegativity, so electron density will be pulled away from the rest of the molecule, and the

protons/carbons will be deshielded. ^{1}H and ^{13}C chemical shifts of coordinated acetonitrile are expected to shift upfield compared to free acetonitrile.

RESULTS

39.14% yield of $(\eta^6\text{-}C_6H_3(CH_3)_3)Mo(CO)_3$. 12.94% yield of $Mo(CO)_3((CH_3)CN)_3$. Excluding spectra accompanying the synthesis of $Mo(CO)_3((CH_3)CN)_3$, all spectra provided were taken from other groups due to FID file errors or impure samples.

Table 1: FTIR tabulated data

Compound Spectrum	Region (cm^{-1})	Functional Groups	Comments
$Mo(CO)_6$	1983.91, 1454.55	C≡O, C-H	Strong CO stretching (characteristics of metal carbonyl stretch), CH stretch of hexanes or solvent
$(\eta^6\text{-}C_6H_3(CH_3)_3)Mo(CO)_3$	1962.70, 1875.92, 1213.49	C≡O, C≡O, n/a	CO stretching, CO stretching (two stretches due to reduced symmetry), background measurement
$Mo(CO)_3((CH_3)CN)_3$	2036.46, 1510.47, 996.16	C≡O, C-H, C-N?	CO stretch (higher than $Mo(CO)_6$ suggesting decomposition/reduced π-backbonding), CH bending of solvent/impurity, could be C-N stretch but absence of C≡N stretch is questionable

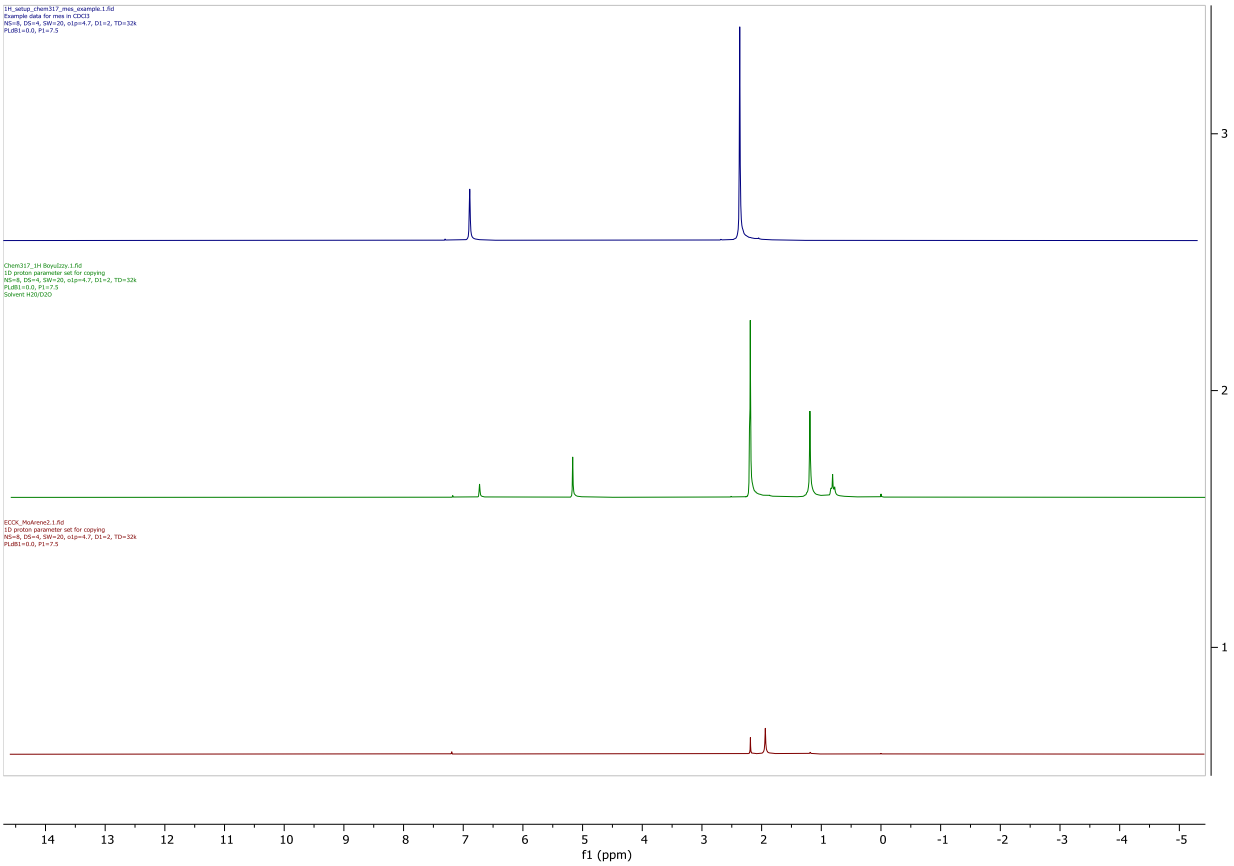


Figure 1: ^{1}H-NMR spectrums of Mesitylene (top), synthesized (η^{6}-$C_6H_3(CH_3)_3$)$Mo(CO)_3$ product (middle), and synthesized $Mo(CO)_3((CH_3)CN)_3$ product (bottom)

Table 2: ^{1}H-NMR tabulated data

Compound Spectrum	Peaks (ppm)	Multiplicity	Integration	Identity
Mesitylene	6.89, 2.36	s, s	1H, 3H	aryl protons, methyl protons,
(η^{6}-$C_6H_3(CH_3)_3$)$Mo(CO)_3$	6.73, 5.16, 2.19, 1.19, 0.81	s, s, d, s, s	1H, 4H, 12H, 9H, 4H	Unreacted mes., aryl protons, methyl protons, impurities/hexanes
$Mo(CO)_3((CH_3)CN)_3$	7.19, 2.19, 1.94, 1.18	n/a, s, n/a, s	n/a, 3H, n/a, 1H	$CDCl_3$, impurity, H_2O, impurity

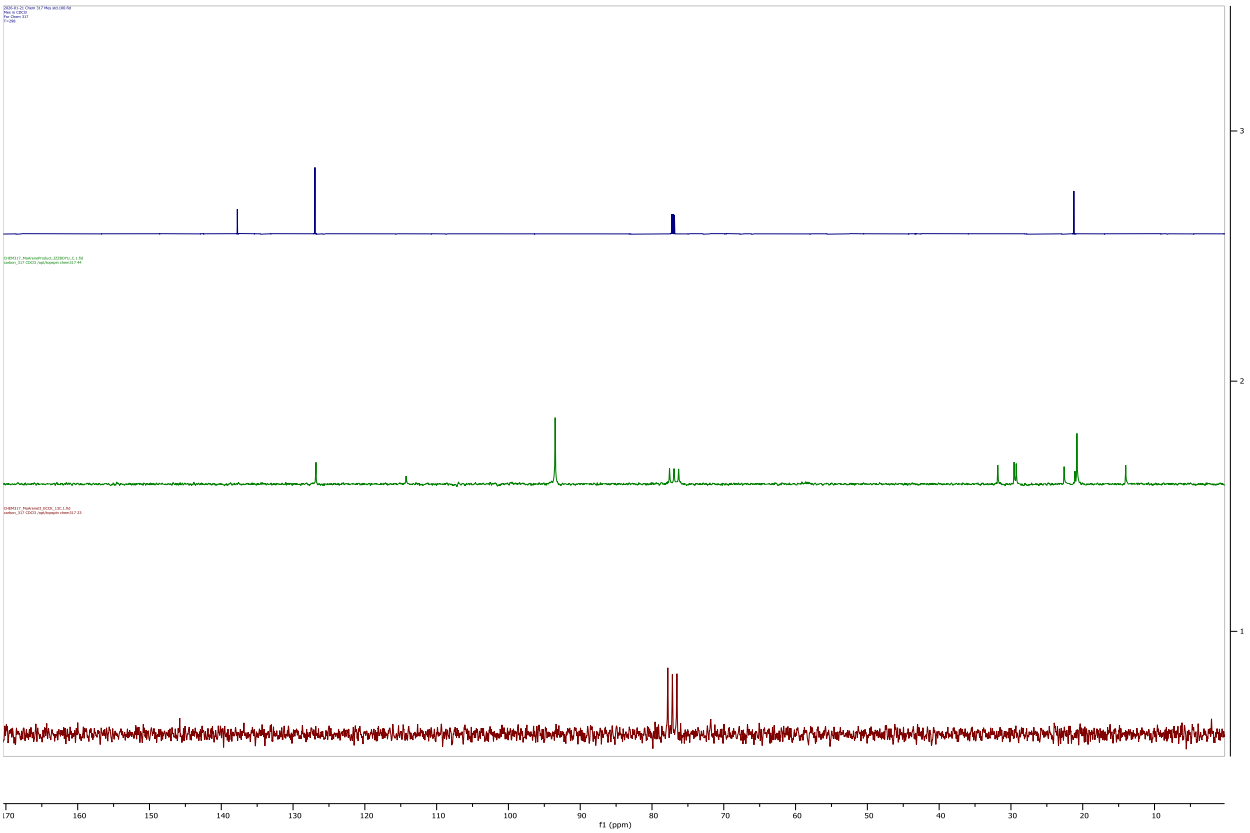


Figure 2: ^{13}C-NMR spectrums of Mesitylene (top), synthesized (η^6-$C_6H_3(CH_3)_3$)$Mo(CO)_3$ product (middle), and synthesized $Mo(CO)_3((CH_3)CN)_3$ product (bottom)

Table 3: ^{13}C-NMR tabulated data

Compound Spectrum	Notable Peaks (ppm)	Multiplicity	Identity
Mesitylene	137.77, 126.98, 77.21, 21.34	s, s, n/a, s	aryl carbons, aryl carbons, $CDCl_3$, methyl carbons
(η^6-$C_6H_3(CH_3)_3$)$Mo(CO)_3$	126.98, 114.14, 93.34, 77.06, 31.83, 29.56, 29.26, 22.59, 21.08, 20.94, 14.01	s, s, s, n/a, s, d, s, d, s	unreacted mes., aryl carbons, aryl carbons, $CDCl_3$, hexanes, hexanes, hexanes, hexanes, hexanes, methyl carbons, hexanes
$Mo(CO)_3((CH_3)CN)_3$	77.16	---	$CDCl_3$

DISCUSSION

IR and NMR spectroscopy were used to evaluate the formation of $(\eta^6\text{-}C_6H_3(CH_3)_3)Mo(CO)_3$ from $Mo(CO)_6$. The π-backbonding effect mentioned previously puts electron density into the CO antibonding orbital, which weakens the CO bond. This is represented in the IR, as the IR band of the CO stretch in the complex is lower than the frequency of the CO stretch for free carbon monoxide, which is closer to 2143 cm^{-1}. The starting material, $Mo(CO)_6$, has one CO stretch at 1996.9 cm^{-1}. In the synthesized product, $(\eta^6\text{-}C_6H_3(CH_3)_3)Mo(CO)_3$, there are two CO stretches at 1962.2 cm^{-1} and 1875.9 cm^{-1}, respectively. Both occur at lower wavenumbers than the CO stretch in Mo(CO)6, indicating enhanced π-backbonding. The reason for the appearance of two CO stretches instead of one is due to symmetry change about the molybdenum center: the conversion of $Mo(CO)_6$ to $(\eta^6\text{-}C_6H_3(CH_3)_3)Mo(CO)_3$ changes the molybdenum center symmetry from octahedral to C_{3v}. This shows up in IR due to quantum mechanical selection rules, which dictate that octahedral symmetry will see one CO stretch and C_{3v} point-group symmetry will see two.

NMR spectroscopy shows a semi-successful synthesis of $(\eta^6\text{-}C_6H_3(CH_3)_3)Mo(CO)_3$. In the starting material ^{1}H-NMR spectrum, free mesitylene shows an aromatic singlet at 6.89 ppm and a methyl singlet at 2.33 ppm. In the product spectrum, the aromatic singlet is shifted upfield to 5.16 ppm. This reflects the increased shielding of the aromatic ring upon coordination to molybdenum. The methyl protons show a small shift (2.36ppm to 2.18ppm) due to greater distance from the metal center. The small peak at 6.73ppm on the product spectrum likely corresponds to unreacted starting material due to low integration and close signal proximity. This is consistent with the moderate 39% yield.

In ^{13}C-NMR, the appearance of a peak at 126.98 ppm in both the starting material and product spectra indicates that there is still starting material present. The upfield shifts of aromatic proton peaks from mesitylene to $(\eta^6\text{-}C_6H_3(CH_3)_3)Mo(CO)_3$ (137.77ppm to 114.14ppm, and 126.98ppm to 93.34ppm) in Figure 2 reflect increased electron density on the molybdenum center. There is little to no shift of methyl protons (21.34ppm to 20.94ppm) because they are more shielded from the metal center. Overall, these spectral changes seem consistent with successful complex formation.

IR and NMR spectroscopy do not suggest a successful synthesis of the desired proposed compound, $Mo(CO)_3((CH_3)CN)_3$. The IR spectrum shows CO stretching at 2036.5 $cm^{-1,}$ which is higher than that of $Mo(CO)_6$. This increased CO stretching frequency indicates reduced π-backbonding, contrary to expected effects of substitution by a strong σ-donor. There should also be a nitrile C≡N stretch between 2200 cm^{-1} -2300 cm^{-1}, which is noticeably absent. ^{13}C-NMR shows no product peaks: only a $CDCl_3$ triplet. Similarly, ^{1}H-NMR shows only solvent impurity peaks. Visually, the product changed from a yellow crystalline powder to a brown/gray substance between lab sessions. Spectral data, observations of brown, decomposed products, and the low yield of 12.9% suggest that the acetonitrile complex may be air-sensitive or unstable without further workup.

EXPERIMENTAL:

General Considerations: Unless otherwise specified, all reactions were conducted under an inert nitrogen atmosphere using Schlenk line techniques. NMR was collected on a Bruker-Avance 200 MHz instrument. Solution cell and ATR-IR were collected on a Thermo Scientific FTIR spectrometer.

Synthesis of $(\eta^6\text{-}C6H_3(CH_3)_3)Mo(CO)_3$

$Mo(CO)_6$ (1.01 g, 3.83 mmol) was added to 10 mL mesitylene and 10 mL decane in a 100 mL Schlenk flask attached to a reflux condenser (with no water flowing). The apparatus was flushed with N_2 for 5 minutes to remove air. The solution was stirred and refluxed at a moderate boil (mesitylene bp: 165C, decane bp: 174 C) for 30 minutes. After the mixture cooled to room temperature, 15 mL hexane was added to induce precipitation of yellow crystals. No longer air-sensitive, the crystals were vacuum filtered and washed with minimal hexane. Crude yield of 39.14% (0.45 g, 1.5 mmol). NMR samples were prepared in $CDCl_3$. Solution cell IR samples were prepared in $CHCl_3$.

Synthesis of $Mo(CO)_3((CH_3)CN)_3$

This procedure was adapted from two established procedures in literature.[3-4] 2.00 g $Mo(CO)_6$ (7.58 mmol) and excess acetonitrile (approx. 10 mL) were placed in a dry 50 mL Schlenk flask attached to a reflux condenser (no water flowing). The apparatus was flushed with N_2 for 10 minutes to remove air. The reaction mixture was heated to a moderate boil (120C) and allowed to reflux for 2.5 hours. After the mixture cooled to room temperature, ether was added to complete the precipitation. The mixture was filtered through a Buchner funnel to yield a yellow solid with gray/brown particles of decomposed molybdenum. The resulting solid was washed with cold ether. Around ½ of the product filtered through the funnel and into the filter flask; minimal ether was added to the flask to dissolve the solid and poured into a scintillation vial. The solid on the filter paper was allowed to dry on a watch glass inside a lab drawer, and the solid in the scintillation vial was left uncapped in the fume hood to allow ether evaporation. Crude $Mo(CO)_3((CH_3)CN)_3$ yield of 12.94% (0.315 g, 0.98 mmol). No further purification was performed due to time constraints. NMR sample was prepared in $CDCl_3$. No sample prep necessary for ATR-IR.

SPECTRAL DATA

C_9H_{12}: ^{1}H-NMR ($CDCl_3$): δ_H 6.89 (s, 1H), 2.33 (s, 3H). ^{13}C-NMR ($CDCl_3$): δ_C 137.77. 126.98, 77.21, 21.34. $(\eta^6\text{-}C_6H_3(CH_3)_3)Mo(CO)_3$: ^{1}H-NMR ($CDCl_3$): δ_H 6.73 (s, 1H), 5.16 (s, 4H), 2.19 (d, 12H), 1.19 (s, 9H), 0.81 (s, 4H). ^{13}C-NMR ($CDCl_3$): δ_C 126.98, 114.14, 93.34, 77.06, 31.83, 29.56, 29.26, 22.59, 21.08, 20.94, 14.01. IR ($CHCl_3$): 1962.22, 1875.92, 1213.49. $Mo(CO)_6$: IR ($CHCl_3$): 1996.93, 1453.58. $Mo(CO)_3(HCN)_3$: ^{1}H-NMR ($CDCl_3$): δ_H 7.19, 2.19 (s, 3H), 1.94, 1.18 (s, 1H).^{13}C-NMR ($CDCl_3$): δ_C 77.16. IR ($CHCl_3$): 2036.46, 1510.47, 966.16.

CONCLUSION:

The reaction of $Mo(CO)_6$ with mesitylene successfully produced $(\eta^6\text{-}C_6H_3(CH_3)_3)Mo(CO)_3$ with 39% yield. IR spectroscopy showed the expected decrease in CO stretching frequencies and the appearance of two bands consistent with a change in symmetry. ^1H and ^{13}C NMR spectra demonstrated significant upfield shifts of aromatic resonances, characteristic of η^6-arene coordination. Minor impurities and residual starting material were observed, but overall spectroscopic data confirms formation of $(\eta^6\text{-}C_6H_3(CH_3)_3)Mo(CO)_3$.

Attempts to synthesize $Mo(CO)_3((CH_3)CN)_3$ were unsuccessful. The absence of a diagnostic C≡N stretch near 2200–2300 cm^{-1}, combined with the upward shift of the CO stretching frequency relative to $Mo(CO)_6$, indicates that the proposed $Mo(CO)_3((CH_3)CN)_3$ complex was not successfully formed. The observed IR and NMR data do not match expectations for the proposed structure, and the low yield alongside visible decomposition suggests instability under the reaction or workup conditions. More rapid purification and strictly air-free procedure could improve future attempts.

REFERENCES

1. Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; Wiley: New York, 1999.
2. Fischer, E. O.; Hafner, W. *Z. Naturforsch. B* **1955**, *10*, 665–668
3. Angelici, R. J. Preparation and Characterization of Mesitylene Tricarbonyl Molybdenum(0): An Experiment in Organometallic Chemistry. *J. Chem. Educ.* 1968, *45*, 119. DOI: 10.1021/ed045p119.
4. “Tate, D. P.; Knipple, W. R.; Augl, J. M. *Nitrile Derivatives of Chromium Group Metal Carbonyls.* Inorg. Chem. 1962, *1* (2), 433–434. https://doi.org/10.1021/ic50002a052

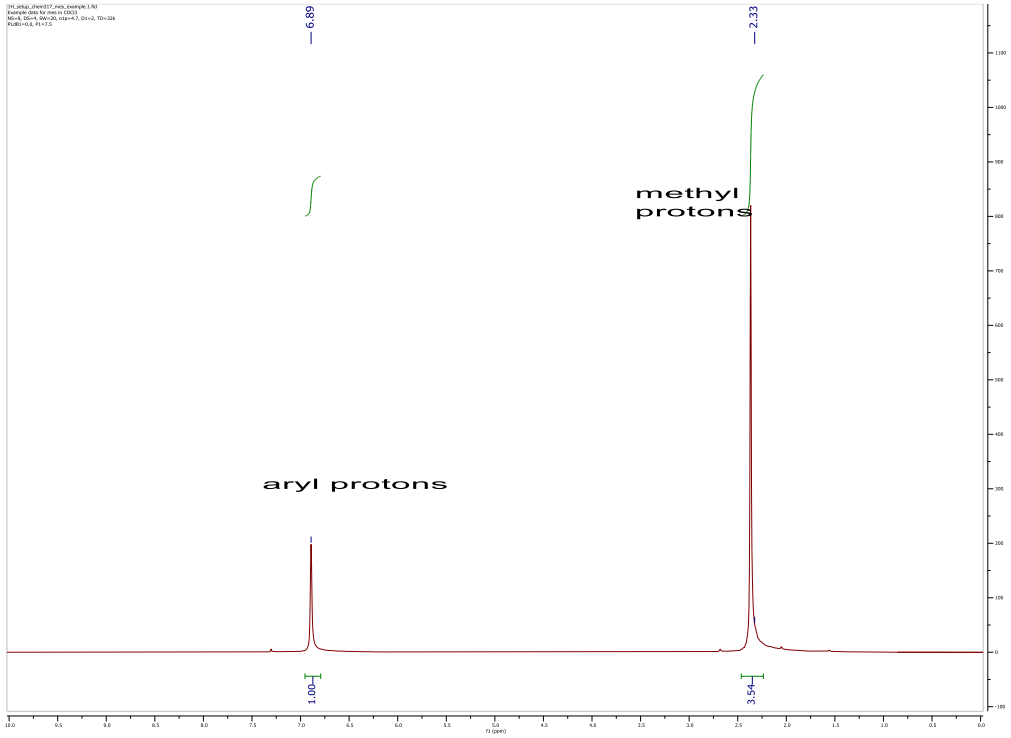


Figure 3: ^{1}H-NMR spectrum of mesitylene

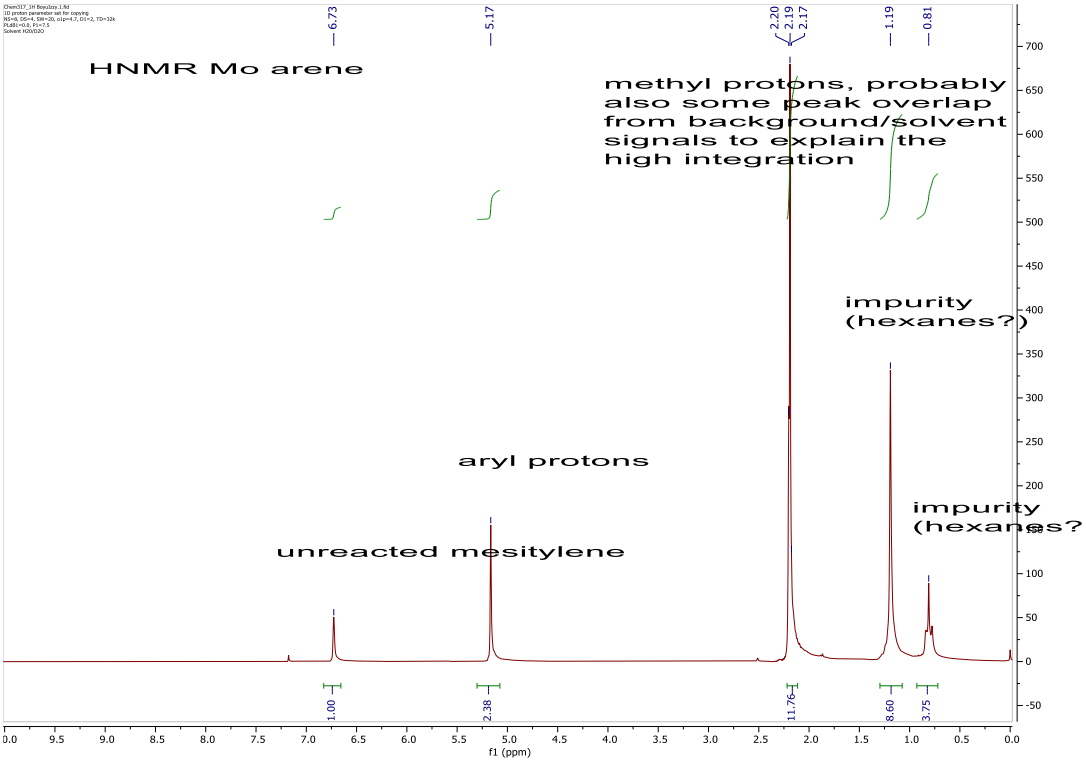


Figure 4: ^{1}H-NMR spectrum of synthesized (η^6-$C_6H_3(CH_3)_3$)$Mo(CO)_3$ product

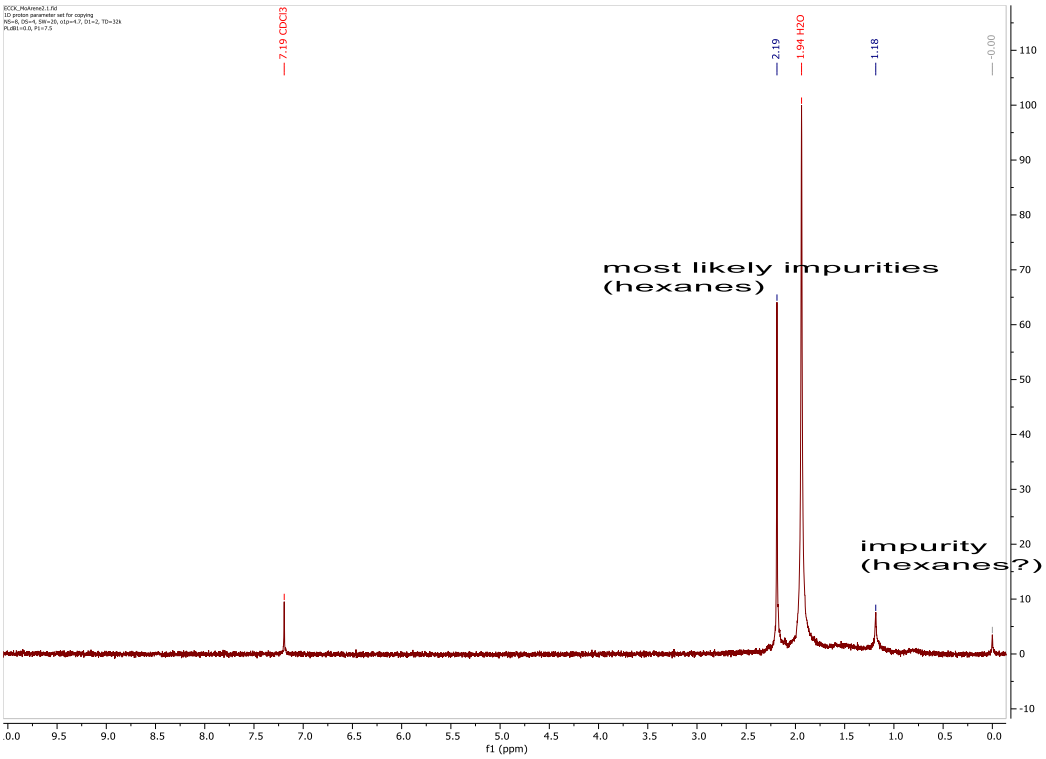


Figure 5: ^{1}H-NMR spectrum of synthesized $Mo(CO)_3((CH_3)CN)_3$ product

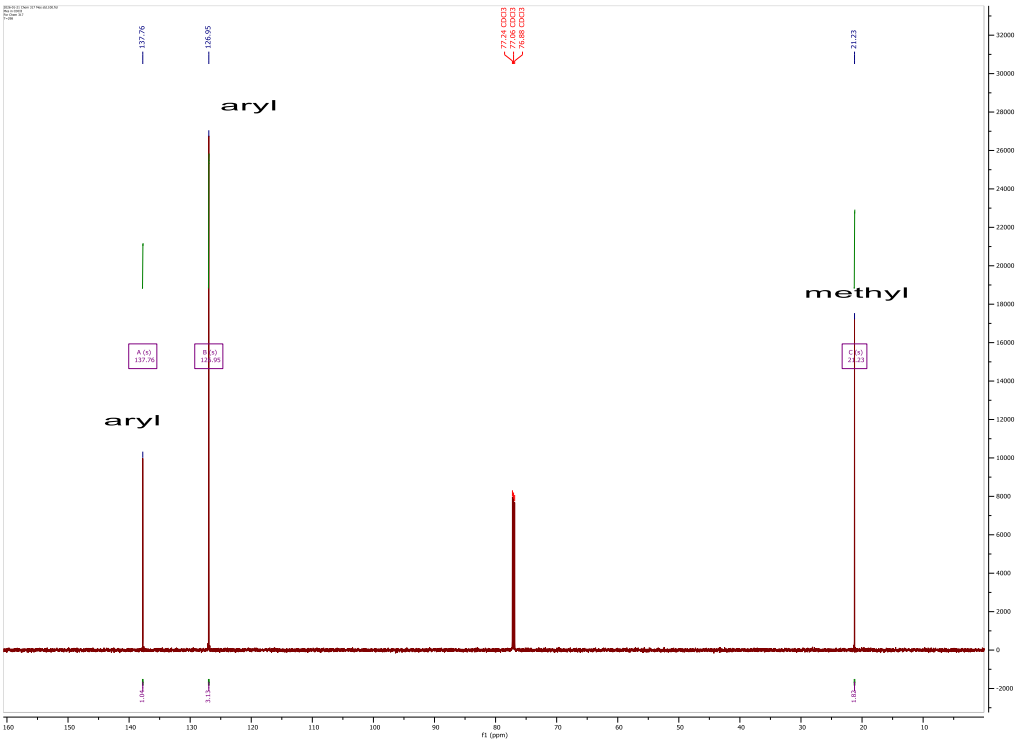


Figure 6: ^{13}C-NMR spectrum of mesitylene

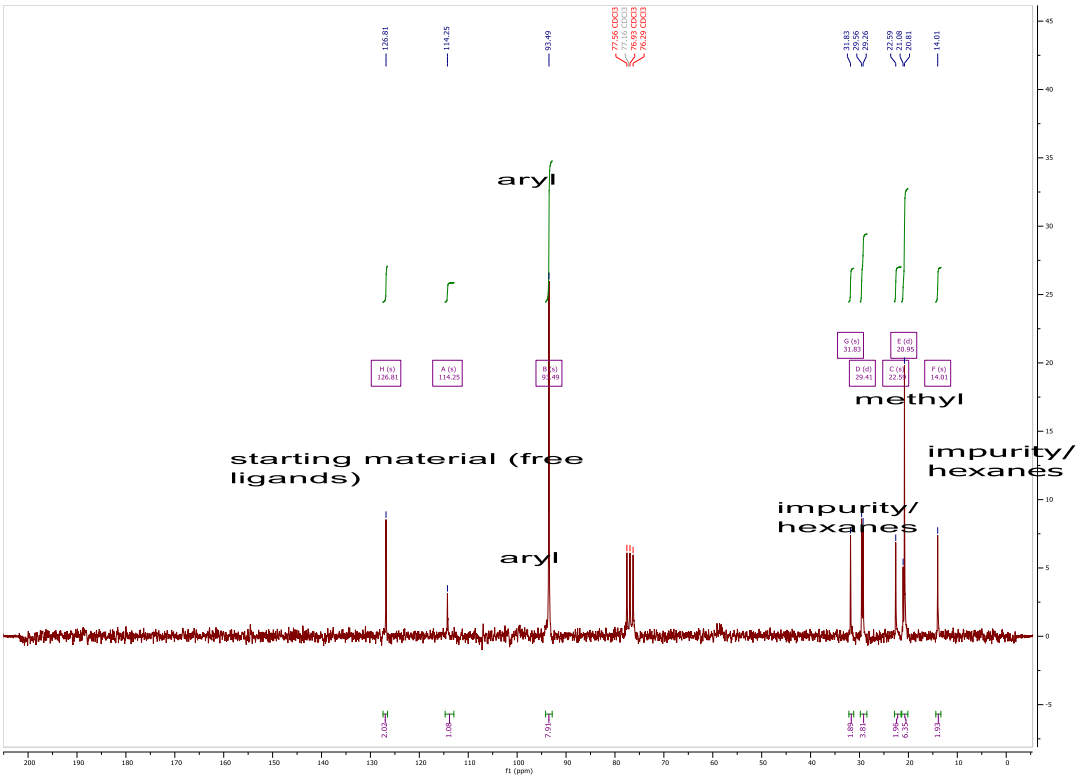


Figure 5: ^{13}C-NMR spectrum of synthesized (η^6-$C_6H_3(CH_3)_3$)$Mo(CO)_3$ product

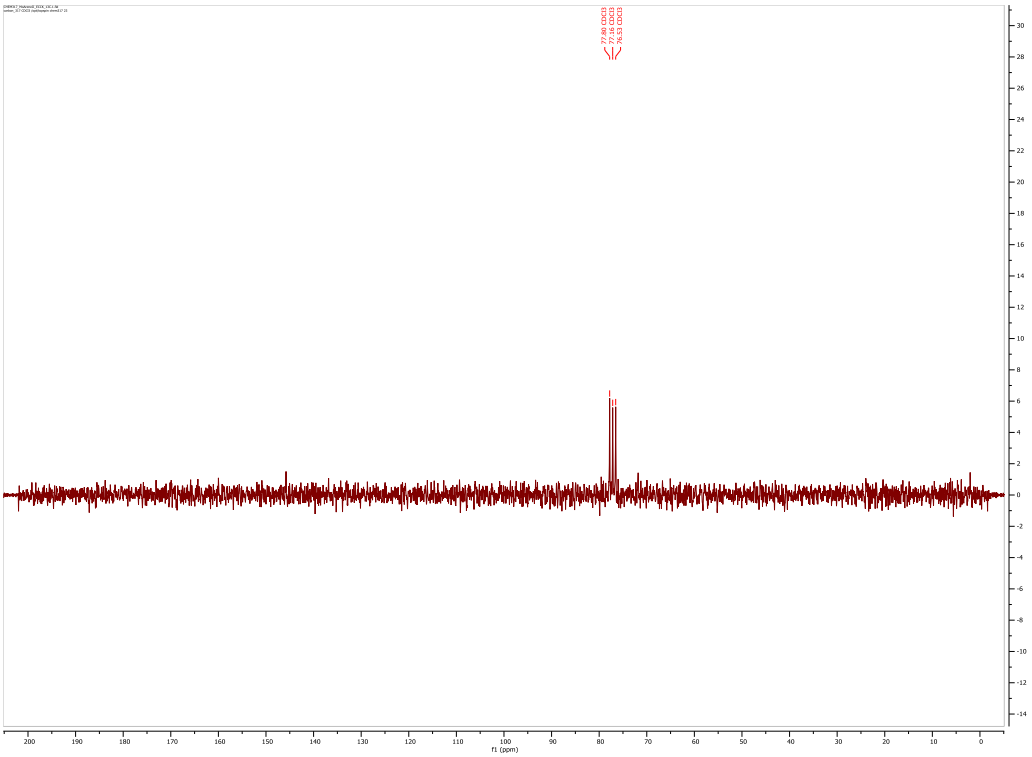


Figure 6: ^{13}C-NMR spectrum of synthesized $Mo(CO)_3((CH_3)CN)_3$ product

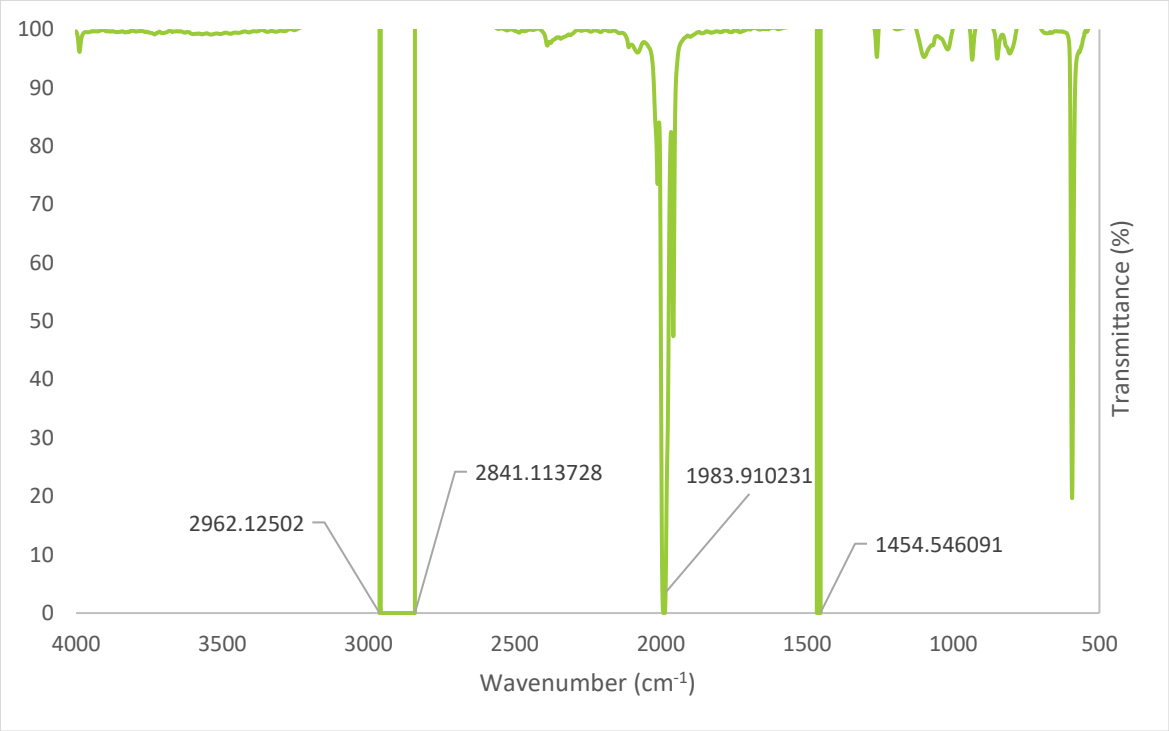


Figure 7: Solution-IR of Mo(CO)6

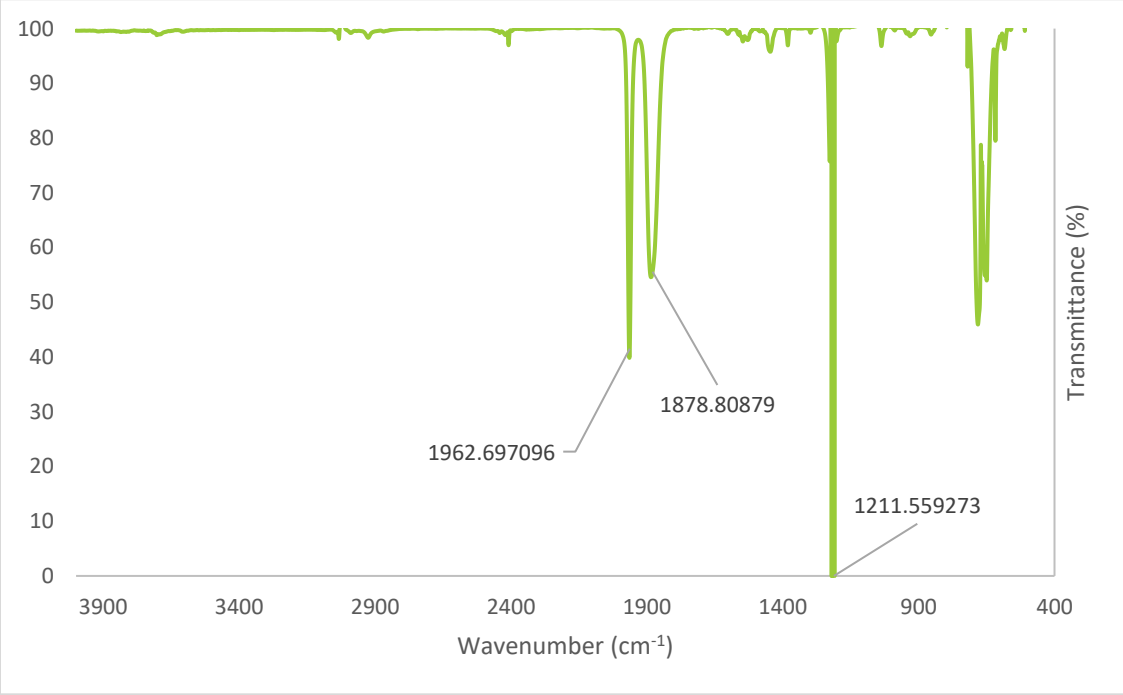


Figure 8: Solution-IR of synthesized (η^6-$C_6H_3(CH_3)_3$)$Mo(CO)_3$ product

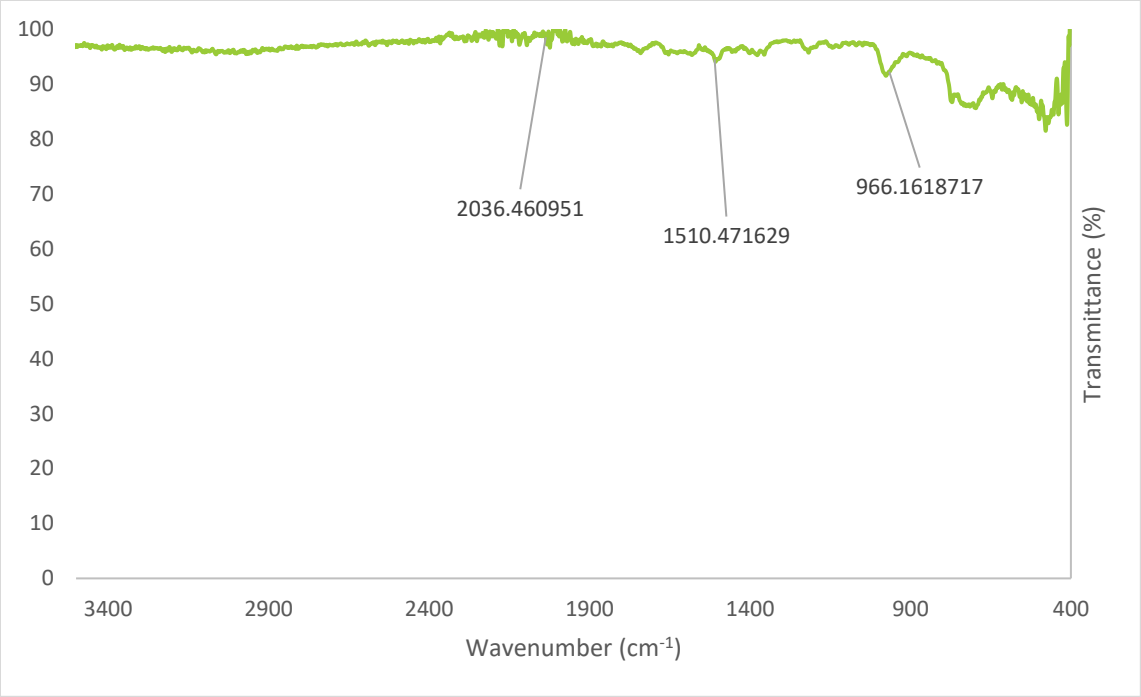


Figure 9: Solution-IR of synthesized $Mo(CO)_3((CH_3)CN)_3$ product