



2017

Use of Trispyrazolemethane in the Synthesis of Organometallic Compounds

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Intended date of commencement May 6, 2017

Read, approved, and signed by: Stacy O'Reilly 5/3/2017
Thesis adviser(s) Joe H 5/3/2017
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Use of Trispyrazolemethane in the Synthesis of Organometallic Compounds

A Thesis

Presented to the Department of Chemistry

College of Liberal Arts and Sciences

and

The Honors Program

of

Butler University

In Partial Fulfillment

of the Requirements for Graduation Honors

Claire Hazelton

May 3, 2017

Use of Trispyrazolemethane in the Synthesis of Organometallic Compounds

Claire Hazelton and Dr. Stacy O'Reilly

Abstract

Trispyrazoleborate is a negatively charged facially coordinating tridentate ligand that has been highly researched and used in many metal complexes. The related ligand trispyrazolemethane has not been widely studied due to its difficult synthesis. The objective of this project is to determine the effects of the neutral nature of the trispyrazolemethane on the metal carbonyl complexes of molybdenum and tungsten. Besides the ligand tricarbonyl complex, iodide and hydride derivatives were synthesized. All compounds were characterized with IR and HNMR.

Tpm'	Tris(3,5-dimethyl)pyrazolemethane	Molecular Mass: 298 g/mol
Tp	Trispyrazoleborate	212.8 g/mol
Tpm	Trispyrazolemethane	214 g/mol
TpmW(CO) ₃	Trispyrazolemethanetungsten tricarbonyl	482.12 g/mol
TpmMo(CO) ₃	Trispyrazolemethanemolybdenum tricarbonyl	393.96 g/mol
Tpm'W(CO) ₃	Tris(3,5-dimethyl)pyrazolemethanetungsten tricarbonyl	566.12 g/mol
Tpm'Mo(CO) ₃	Tris(3,5-dimethyl)pyrazolemethanemolybdenum tricarbonyl	477.96 g/mol
THF	Tetrahydrofuran	
IR	Infrared Spectroscopy	
HNMR	Hydrogen Nuclear Magnetic Resonance	
rbf	Round bottomed flask	
DMF	Dimethylformamide	

Table 1: Abbreviations for compounds

Introduction

Metal complexes can be used as models for metal containing catalysts, such as enzymes. Some of the roles of these metal-containing catalysts include an inhibitor of dehydrogenase as well as possibly affect antiallergic action and inhibit the start of mutations of carcinogens. Some of these metal-containing catalysts contain pyrazole ligands. The coordination of the ligand impacts that behavior of the catalyst. Therefore, the structure of the ligand does possibly affect the reactivity of the metal complex.

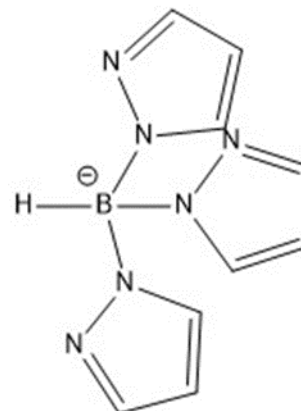


Figure 1: Trispyrazoleborate

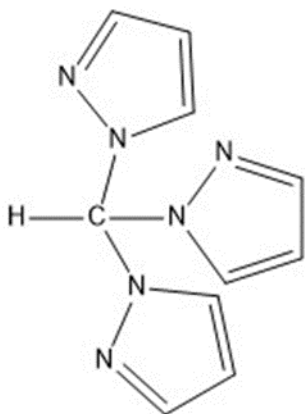


Figure 2: Trispyrazolemethane

The inorganic chemist Swiatoslaw Trofimenko⁷ prepared and began research of the metal complexes of the ligand trispyrazoleborate (Tp) in the late 1960s. Since that time, this specific ligand has been widely studied and is now one of the coordination ligands that has received the most attention in inorganic chemistry. Tp consists of a central boron atom bonded to three pyrazoles and a hydrogen atom. Tp (Fig. 1) is a negatively charged facially coordinating tridentate ligand that has been highly studied and used in many metal complexes (Fig. 3). It coordinates to the metal through electron donation from the nitrogen atoms in the ligand. This is depicted in Figure 4. The related ligand Tpm (Fig. 2) has not been widely studied due to its difficult synthesis. The central atom of Tpm is carbon with a neutral charge, unlike Tp which has a central atom of boron with a negative charge. If the ligand were more readily available, it could be used in a variety of metal complexes including transition metals such as molybdenum, and tungsten. Work has

shown that the ligand can be useful in synthesizing water-soluble metal complexes with nickel and cobalt. Complexes of the ligand are an excellent starting point to explore the general reactivity of transition metal species.

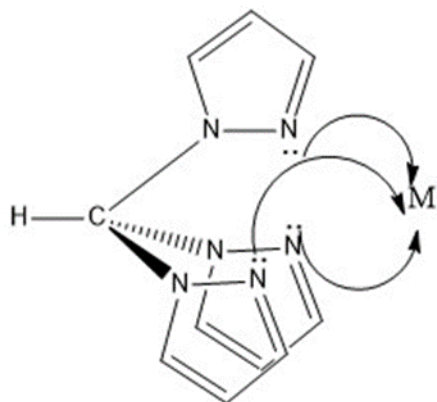


Figure 3: Reaction between Tpm and metal

In this paper, the ligand Tpm and its reactivity with Group IV carbonyls as well the addition of substrates was explored. Specifically, in this paper, the reactivity of Tpm with molybdenum hexacarbonyl and tungsten hexacarbonyl is studied. Also studied was Tpm' – a similar ligand to Tpm with the addition of a methyl on each of the pyrazoles – and its reactivity. After synthesis of the metal complex with a hexacarbonyl and the ligand, a halogen and alkyne addition were also attempted.

Experimental

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. HNMR was Bruker BioSpin Avance III HD 400 Nanobay System. H-NMR chemical shifts are reported in ppm versus TMS. IR used was Thermo Scientific, Nicolet iS10 FT-IR Spectrometer w/ATR capability. All reagents were purchased from Sigma Aldrich, except the tetra-n-butylammonium bromide, which was purchased from Eastman Organic Chemicals.

Trispyrazolemethane

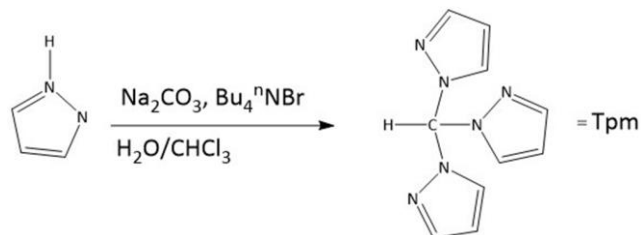


Figure 4: Synthesis of Tpm

The synthesis was conducted according to the literature (Dilsky). Pyrazole (24.0 mmols/1.6 g) and tetra-n-butylammonium bromide (1.20 mmols/0.39 g) were added to a 100 mL round bottom flask. Distilled water (50 mL) was then added. This solution was stirred vigorously while sodium carbonate (0.140 mols/14.8 g) was added *slowly* to the solution. The solution was allowed to cool to room temperature. Chloroform (11.7 mL) was added and the round bottom flask was equipped with a reflux condenser and refluxed for three days, resulting in a pale-yellow emulsion. The reflux was performed under the hood with a condensing system set up to allow for a constant flow of water. The solution was cooled to room temperature and filtered through a Buchner funnel to remove excess base, the sodium carbonate. Diethyl ether (40 mL) and deionized (DI) water (24 mL) was added to the solution. The organic layer was removed and the aqueous layer was extracted with diethyl ether (3 x 16 mL). The organic layers were combined and washed with the brine solution, a mixture of deionized water and sodium chloride. For further purification, activated carbon was added and the solution was then dried over magnesium sulfate and filtered. The solvent remaining was removed through rotary evaporation and dried under vacuum and put under nitrogen. The product was a pale yellow solid. A 60% yield was obtained. HNMR: 8.75, 7.8, 7.6, 6.4, 3.3, 2.1

Tris(3,5-dimethyl)pyrazolemethane

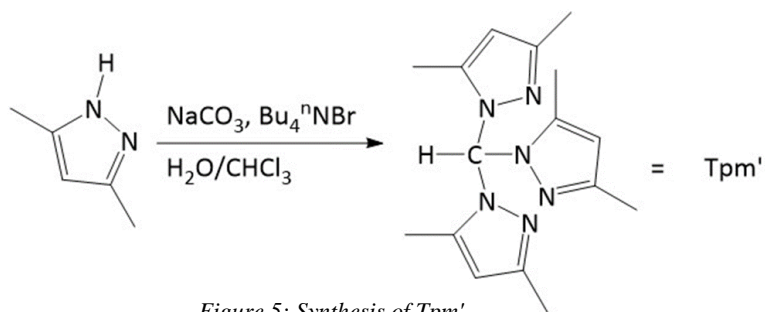


Figure 5: Synthesis of Tpm'

This ligand was also synthesized according to the literature (Dilsky). Distilled water (175 mL) was added to a rbf with 3,5-dimethyl pyrazole (0.177 mols/52.75 g) and tetra-n-butylammonium bromide (8.9 mmols/2.86 g). Sodium carbonate (1.41 mols/149.45 g) was added *very slowly* with vigorous stirring. The addition of sodium carbonate took about two hours to avoid clumping. An excess of DI water was also necessary to keep the solution stirring, approximately 100 mL. The solution was then cooled to room temperature and chloroform (87.5 mL) was added and then set up for a three-day reflux. The solution was cooled to room temperature and filtered through a Buchner funnel to remove the excess base, the sodium carbonate. The organic layer was separated from the aqueous layer and washed with DI water (3 x 12.5 mL) and dried over magnesium sulfate. The mixture was filtered and the solvent removed through rotary evaporation. Unreacted 3,5-dimethyl pyrazole was present. The product underwent sublimation in an oil bath, heated to 80 degrees Celsius, for about three hours. However, an error occurred with the sublimation and the adapter to the vacuum line became stuck. The product was obtained through dissolving the solid in methylene chloride and chloroform. The solvents were removed through rotary evaporation. The product still contained unreacted pyrazole and further purification was obtained through a silica gel column with hexanes followed by methylene chloride. The solvent was removed again through rotary evaporation. Product had lower concentration of unreacted pyrazole. Recrystallization occurred

in toluene and crashed out in ice and hexane, then filtered and washed with hexanes. HNMR revealed a clean product. A percent yield of approximately 30% was obtained. HNMR: 8.1. 5.9.

2.15. 2.0

IR: 2071.16, 1973.03, 1828.46 cm^{-1}

Trispyrazolemethanetungsten tricarbonyl

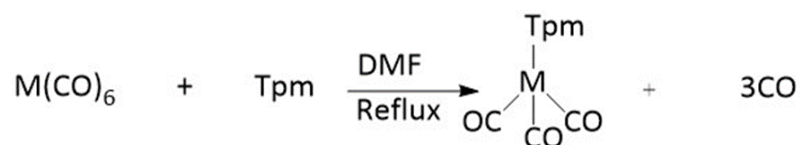


Figure 6: Synthesis of metal/ligand complex

Tungsten hexacarbonyl (12.1 mmols/4.26 g) and Tpm (12.1 mmols/2.59 g) were combined in a 2-neck Schlenk flask under nitrogen. DMF (50 mL) was added and the solution was refluxed approximately 16 hours. The solution was then filtered through a Buchner funnel and washed with methanol. The product was purified through sublimation. The resulting solid was pale yellow. A percent yield of 72% was obtained.

Trispyrazolemethanemolybdenum tricarbonyl

Molybdenum hexacarbonyl (27.9 mmols/7.37 g) and Tpm (21.0 mmols/4.49 g) were combined in a 2-neck Schlenk flask under nitrogen. DMF (50 mL) was added and the solution was refluxed approximately 10 hours. The solution was then filtered through a Buchner funnel and washed with methanol. The resulting solid was pale yellow. IR data revealed impurities, which were removed through sublimation in a sand bath. The product had a 85.9% yield.

HNMR: 7.25, 1.5

IR: 1983.27, 1817.23, 1793.63, 1648.56, 1559.43 cm^{-1}

Trispyrazolemethanechromium tricarbonyl-Attempted

Chromium hexacarbonyl (0.462 mmols/0.10 g) and Tpm (4.69 mmols/1.0 g) were added to Schlenk flask in excess acetonitrile. The solution was refluxed overnight, but the IR values did not match the literature values. Methylene chloride was used to bring the product into solution, as well as methanol, both of which were unsuccessful. The reflux was repeated and a product formed, however there were too many impurities to get a clear HNMR. The product was recrystallized in toluene and hexane. The HNMR of the purified solid determined the starting materials did not react.

Iodotrispyrazolemethanetungsten tricarbonyl Iodide

TpmW(CO)₃ (0.784 mmols/0.37 g) and iodide (0.788 mmols/0.20 g) were added to a Schlenk flask with methylenechloride (10 mL). The solution was stirred for approximately an hour. Diethyl ether (30 mL) was added to the solution and the product crashed out. The solution was filtered and had a 61 % yield. An orange solid was obtained. HNMR: 7.25, 5.3, 1.5

IR: 2155.43, 2125.72, 2035.71, 1961.42, 1926.47 cm⁻¹

Iodotrispyrazolemethanemolybdenum tricarbonyl iodide

TpmMo(CO)₃ (0.381 mmols/0.15 g) was added to Schlenk flask with iodide (0.449 mmols/0.11 g) and methylene chloride (20 mL). The mixture was gently stirred under nitrogen for approximately one hour. After an hour, an excess of diethyl ether was added to crash the product out of solution. It did not crash out, so the solution was left in the freezer overnight. The solution was filtered and product obtained with a 57 % yield. HNMR: 12.2, 9.1, 8.4, 7.2, 6.6, 3.5, 1.5 IR: 2045.32, 1981.52, 1950.06, 1817.23, 1923.63, 1646.82, 1601.37, 1560.30

Tris(3,5-dimethyl)pyrazolemethanetungsten tricarbonyl

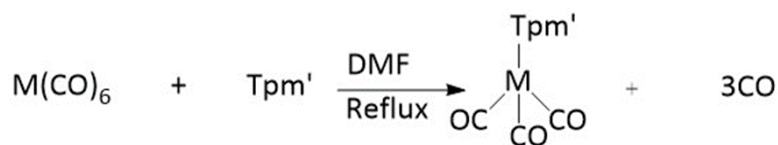


Figure 7: Synthesis of metal/ligand complex

Tpm' (12.1 mmols/3.6 g) and tungsten hexacarbonyl (12.1 mmols/4.26 g) were combined in a 2-neck Schlenk flask under nitrogen. DMF (50 mL) was added and the solution was refluxed approximately 16 hours. The solution was then filtered through a Buchner funnel and washed with methanol. The product was purified through sublimation. No percent yield obtained.

Iodotris(3,5-dimethyl)pyrazolemethanetungsten tricarbonyl iodide

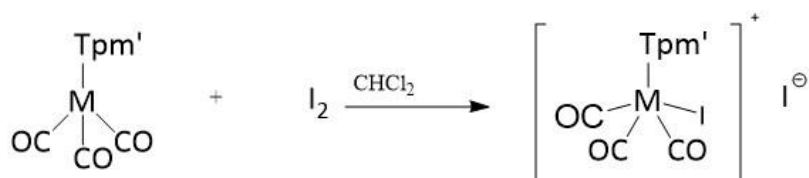


Figure 8: Reaction between metal complex and iodide

Tpm'W(CO)₃ (0.260 mmols/0.15 g) was added to Schlenk flask with iodide (0.176 mmols/0.045 g) and methylene chloride (20 mL). The mixture was gently stirred under nitrogen for approximately one hour. After an hour, an excess of diethyl ether was added to crash the product out of solution. However, the IR did not show enough IR peaks and THF was added to the product to see if there was a change in the peaks. This compound decomposed and the reaction was attempted again. The compound was determined to be air sensitive, so a nitrogen HNMR and IR was attempted. The reaction was attempted again with unpurified Tpm'W(CO)₃. This reaction was successful. HNMR: 8.15, 7.25, 6.4, 5.3, 2.9, 2.45, 1.7

IR: 2155.43, 2125.72, 2054.06, 2031.34, 1974.53, 1931.71

Trispyrazolemethanemolybdenum tricarbonyl iodide phenylpropyne-Attempted

Phenylpropyne (0.28 mL) was added to a Schlenk flask with TpmMo(CO)_3 iodide (0.617 mmols/0.24 g) and an excess of THF. This solution was refluxed for approximately 16-24 hours. IR revealed starting material was gone, but after rotary evaporation, the product was a sticky consistency. Hexanes were added to crash the product into solution. This was unsuccessful, as well as ether and dichloromethane, so it was left in the freezer overnight.

Trispyrazolemethanemolybdenum tricarbonyl iodide diphenylacetylene-Attempted

Iodo TpmMo(CO)_3 iodide (0.309 mmols/0.20 g) and diphenylacetylene (0.094 grams) were added to a Schlenk flask with DMF (approx. 25 mL). This solution was refluxed overnight under nitrogen. IR showed little change in materials, so the solution was left under nitrogen overnight. The solution was then put under rotary evaporation and the solid was analyzed using HNMR and IR, which showed decomposition.

Methylithium trispyrazolemethanemolybdenum tricarbonyl iodide-Attempted

THF (30 mL) was added to Iodo TpmMo(CO)_3 iodide (0.309 mmols/0.20 g) in a Schlenk flask under nitrogen and was left in an ice bath for approximately one hour. Then methylithium (0.4 mL) was added to the solution and was stirred. It was left in the freezer overnight. It was filtered and put under rotary evaporation. IR and HNMR showed the formation of some product, but it was exposed to air and decomposed.

Protonation of Tris(3,5-dimethyl)pyrazolemethanetungsten tricarbonyl

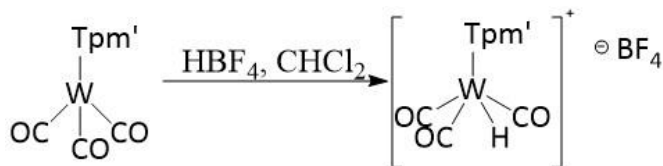


Figure 9: Protonation reaction of $\text{Tpm}'\text{W}(\text{CO})_3$

$\text{Tpm}'\text{W}(\text{CO})_3$ (0.26 mmols/0.150 g) was suspended in excess dichloromethane (5 mL) under nitrogen in a Schlenk flask. The flask was put in an ice bath for approximately 15 minutes, then HBF_4 in etherate (0.0357 mL) was added dropwise to the solution. The solution was stirred for approximately one hour. The solution was analyzed using IR and proved the reaction took place. The product was isolated after adding degassed hexanes (24 mL) and filtered using the canula method. The product was vacuumed dry, left under nitrogen, and stored in the freezer. The product was a pale yellow. HNMR: 7.2, 4.5, 2.5, 1.5, 2.7

IR: 2155.43, 2124.84, 2014.73, 1929.96, 1896.75

Results and Discussion

Ligand synthesis and explain NMR: The experimentation and analysis of this neutral ligand has yielded some success in learning about the difficulties in synthesis of both ligands and the reactivity of the ligands. The Tpm synthesis was successful and was replicated several times. The ligand requires an extensive purification process, but a clean product is obtained. In the HNMR, the hydrogen bonded to the central carbon atom is seen at 8.75, due to the strong electronegativity from the carbon atom bonded to three pyrazoles. The hydrogen on the pyrazoles follow after this hydrogen, according to the proximity to the nitrogen atoms. Compared to the HNMR spectrums of Tp, there is a downfield shift in the hydrogens of Tpm, most likely due to the oxidation state and/or seven coordination of the metal. Tpm' was also successfully synthesized, but with more difficulty. Tpm' has not produced a high yield, but the product has been obtained as well as purified. A simpler procedure for the synthesis of this ligand could be written as some of the language used to describe the synthesis was misleading and led to some missteps in the procedure. As was determined by the data gathered through the IR and HNMR spectra, the ligand reacted as predicted. The HNMR showed the hydrogen bonded to the central atom at about 8.1, with a large separation between the hydrogen at 5.9 and 2.15 and 2.0. The hydrogen at 5.9 is the hydrogen between the two methyl groups, resulting in the shift. The two hydrogen from the methyl groups are farther from electronegative atoms such as nitrogen and therefore are drastically different in shifts.

The reactions between the two ligands, Tpm and Tpm', and the metal hexacarbonyls was successful and produced high yields. The reaction was relatively simple, requiring a 1:1 mol ratio between the ligand and the metal hexacarbonyl suspended in DMF and refluxed for approximately 16 hours. The purification process was minimal, requiring filtration and

sublimation. The difficulties with the metal complexes arose with finding a solvent in which the metal complexes would be soluble. HNMR and IR spectrums were not obtained for all of the metal complexes as the compounds were insoluble in commonly used solvents, chloroform and acetone. This is most likely due to the complicated polarity of the metal complex.

The halogenation addition has been successful and has had high yields in product. The reaction is simple, requiring a 1:1 mol ratio of the metal complex and iodide suspended in methylene chloride and stirred under nitrogen for one hour. The product is a dark red solution. Ether was added to the solution to isolate the product and then filtered. HNMR and IR data was gathered, which was supported by the data from previous research. The CO stretches for all of the iodide complexes are from 2160 to 2120 cm^{-1} , as well as 2030, 1960, 1925 cm^{-1} , approximately. This data shows the carbonyls are still present. Though the presence of the iodide cannot be determined from the IR, the pattern seen in the spectrum is typical for a seven coordinated tricarbonyl complex.

The alkyne addition was unsuccessful. The first alkyne used was not chiral, which may have caused the failed reaction, as it may have produced stereoisomers and not reacted as predicted. However, the alkyne diphenylacetylene was chiral, and the reaction was still unsuccessful, as it originally showed an IR spectra similar to the previous alkyne addition. However, after allowing the solution to sit overnight, the product decomposed. This was most likely due to exposure after being left out overnight, so further attempts at this reaction may prove successful. The addition of a methyl group through methyl lithium was also unsuccessful, as well as the reaction between Tpm and chromium hexacarbonyl. The reaction between Tpm and chromium hexacarbonyl would go to full completion and would most likely need a strong

catalyst to aid it. The methyllithium reaction might have been successful, but it was exposed to air and therefore decomposed.

Overall, as a result of the reactions performed, it can be determined that this ligand is useful and further experimentation on it will only give more information as to its applicability in inorganic chemistry.

Conclusion

In the future, further attempts will be made to synthesis the Tpm' and metal complexes containing this ligand in higher yield. Also, more attempts will be made to react the metal complexes with alkynes and other substrates. As of yet, an alkyne addition has been unsuccessful and it would give a lot of information in the reactivity of this ligand.

Acknowledgements

I would like to acknowledge the Butler Summer Institute, for allowing me to conduct research over the summer, the Butler University Chemistry Department for providing lab equipment and chemicals, and of course Dr. O'Reilly for her guidance in this project.

Appendix A: HNMR

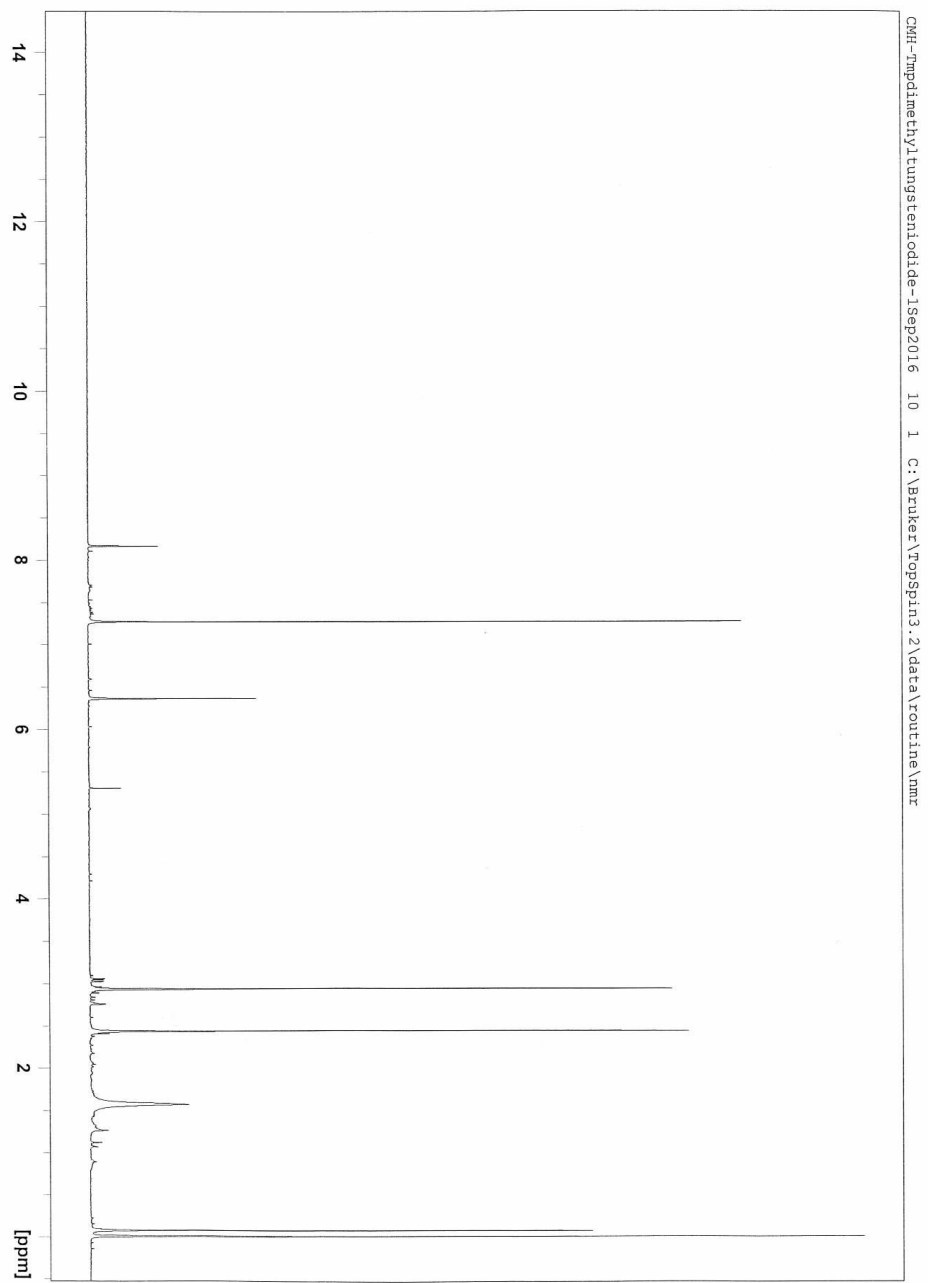


Figure 10: HNMR of $\text{Cp}^*\text{W}(\text{CO})_3\text{I}_2$

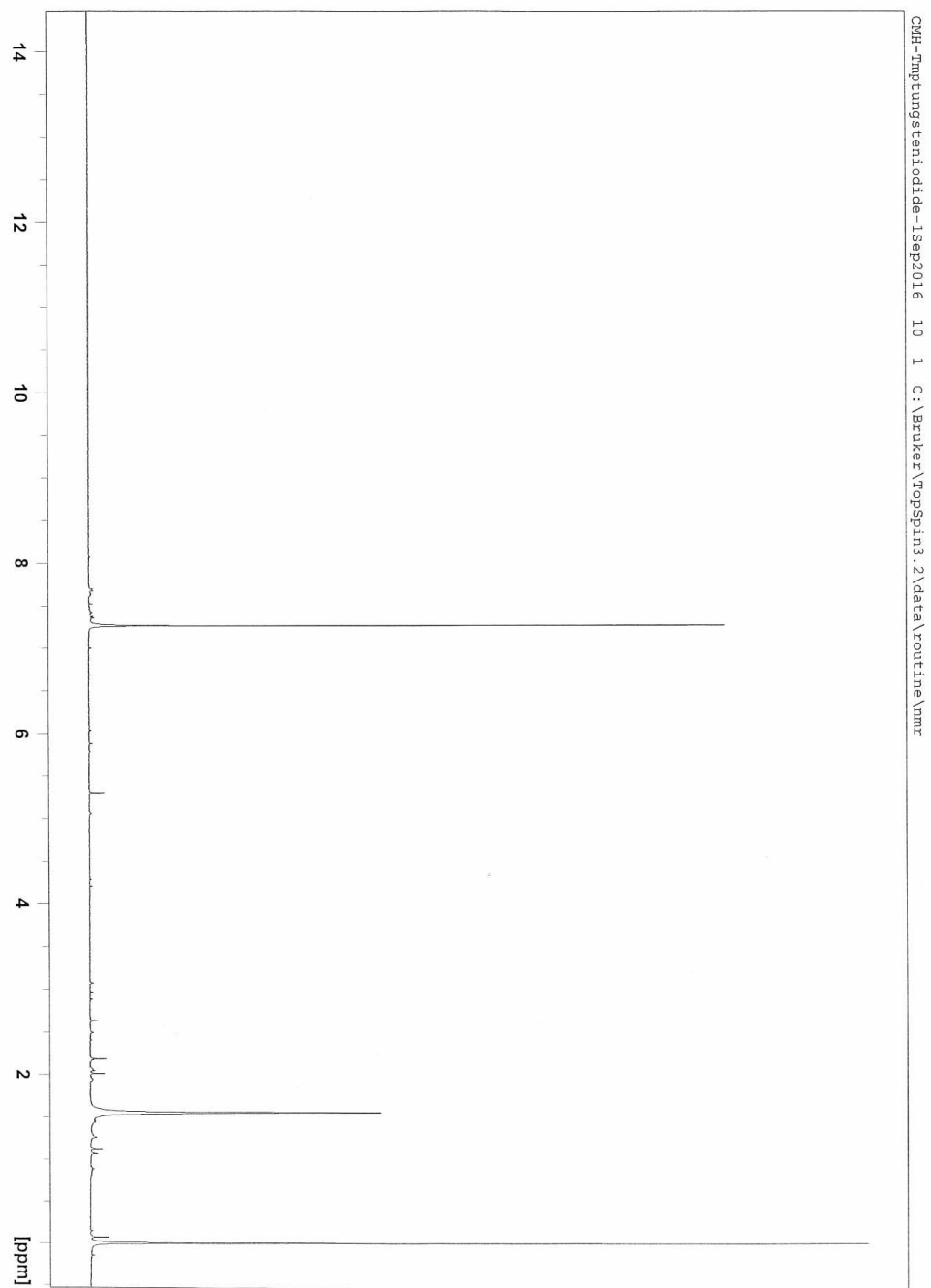


Figure 11: ^1H NMR of $\text{TmpW}(\text{CO})_3\text{I}_2$

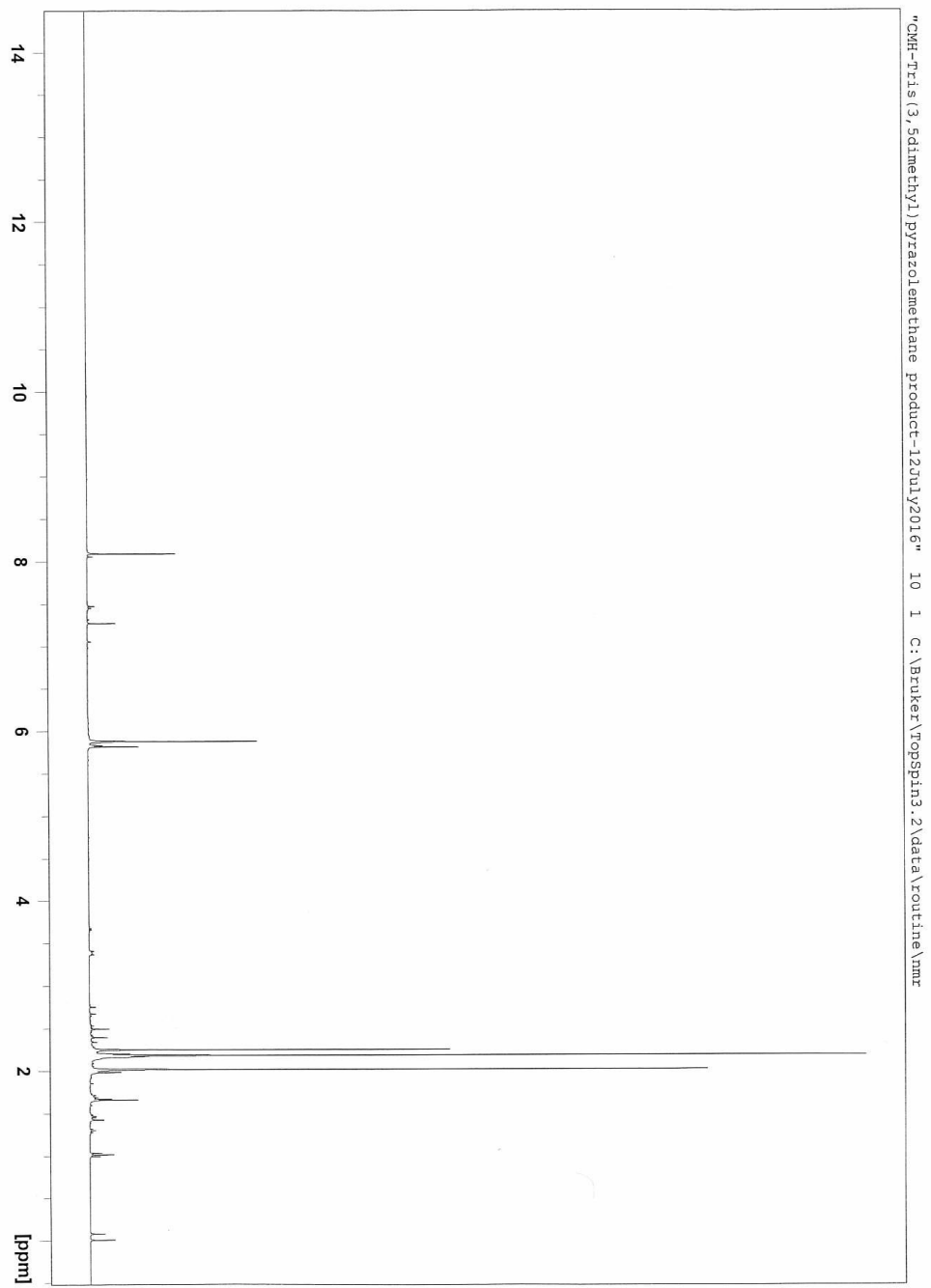


Figure 12: ¹H NMR of Tpm'

OMH-pyrazole-3-31-16 10 1 C:\Bruker\Topspin3.2\data\routine\mmr

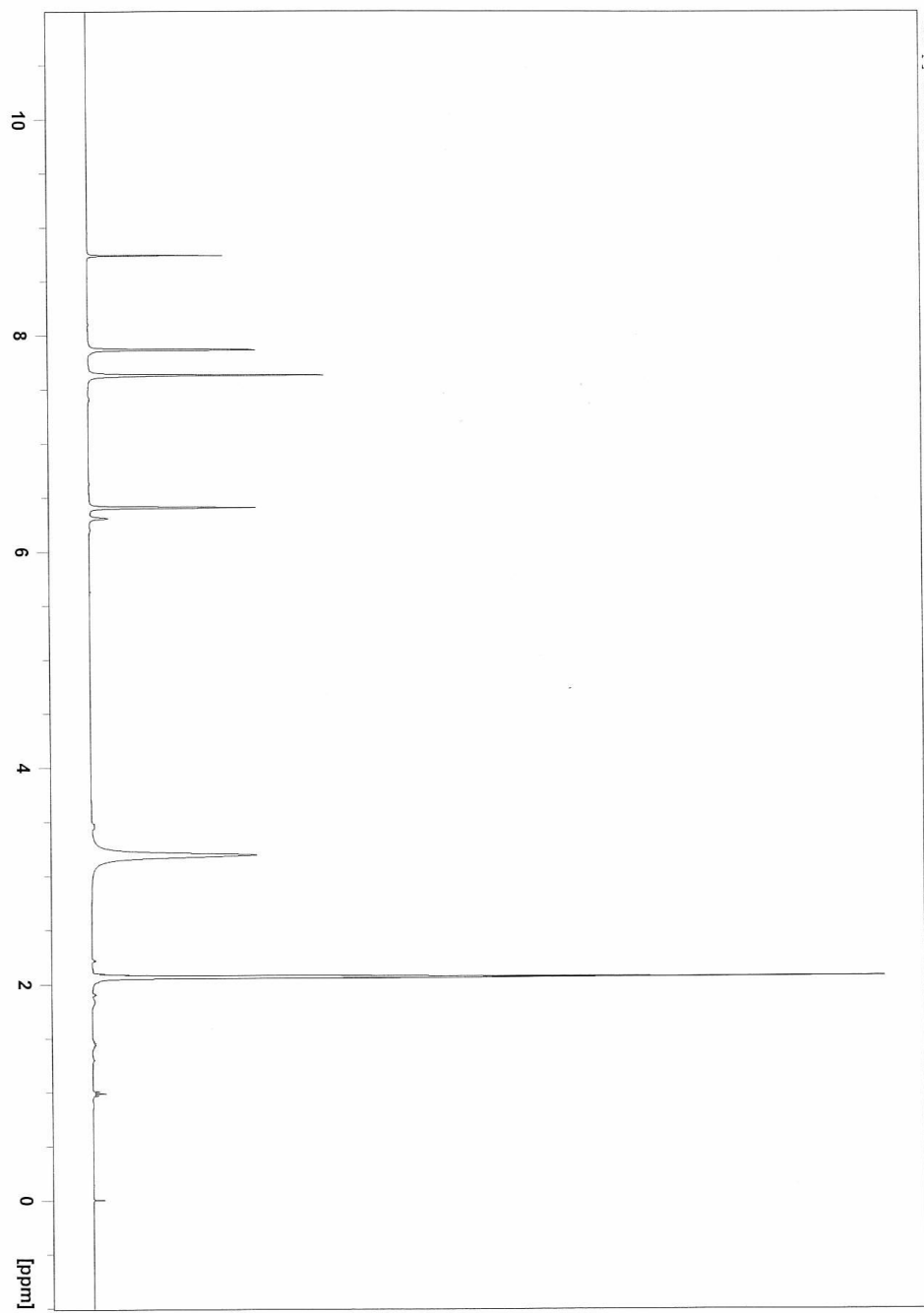


Figure 13: ¹H NMR of Tpm

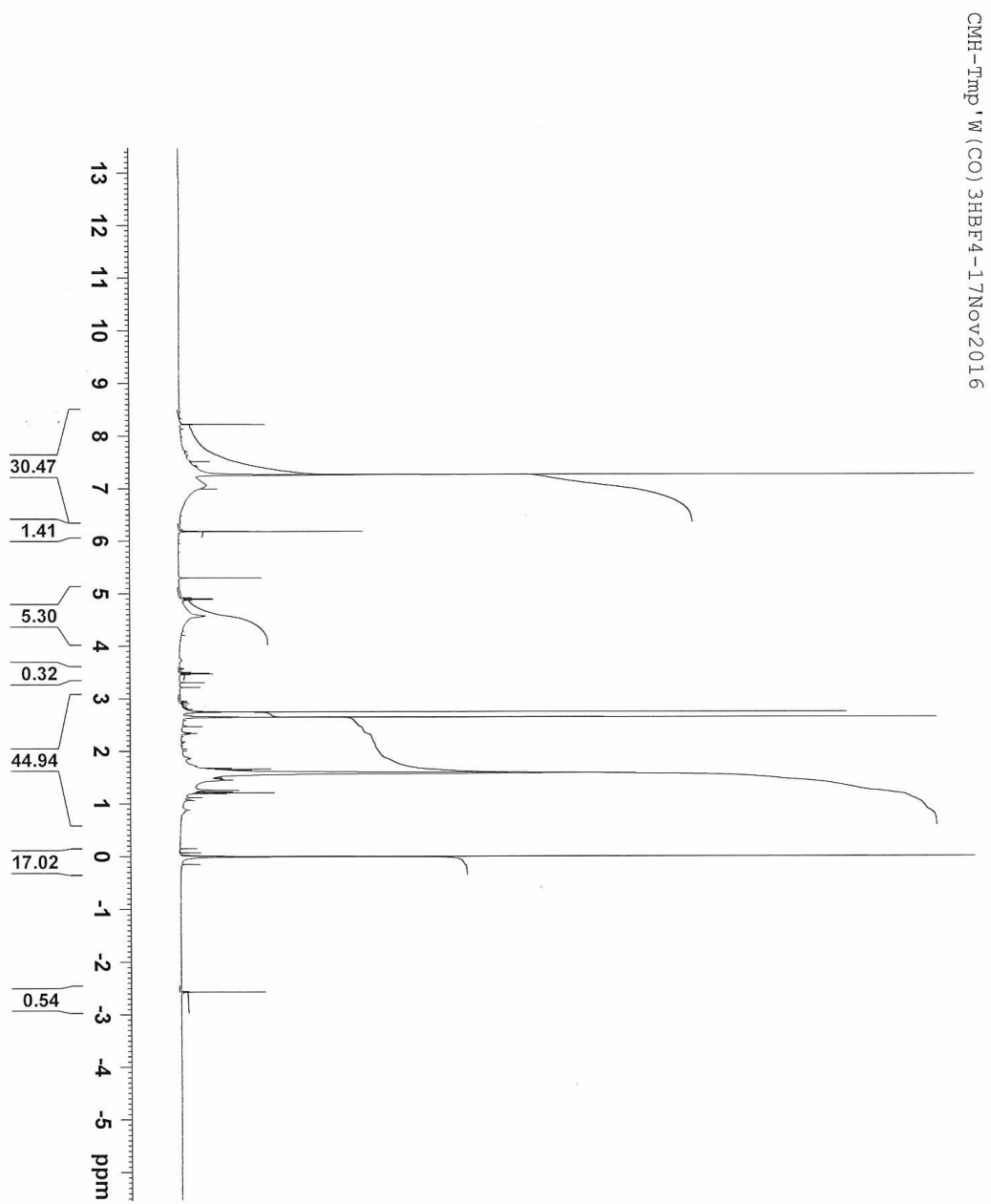


Figure 14: ¹H NMR of Tpm'W(CO)₃HBF₄

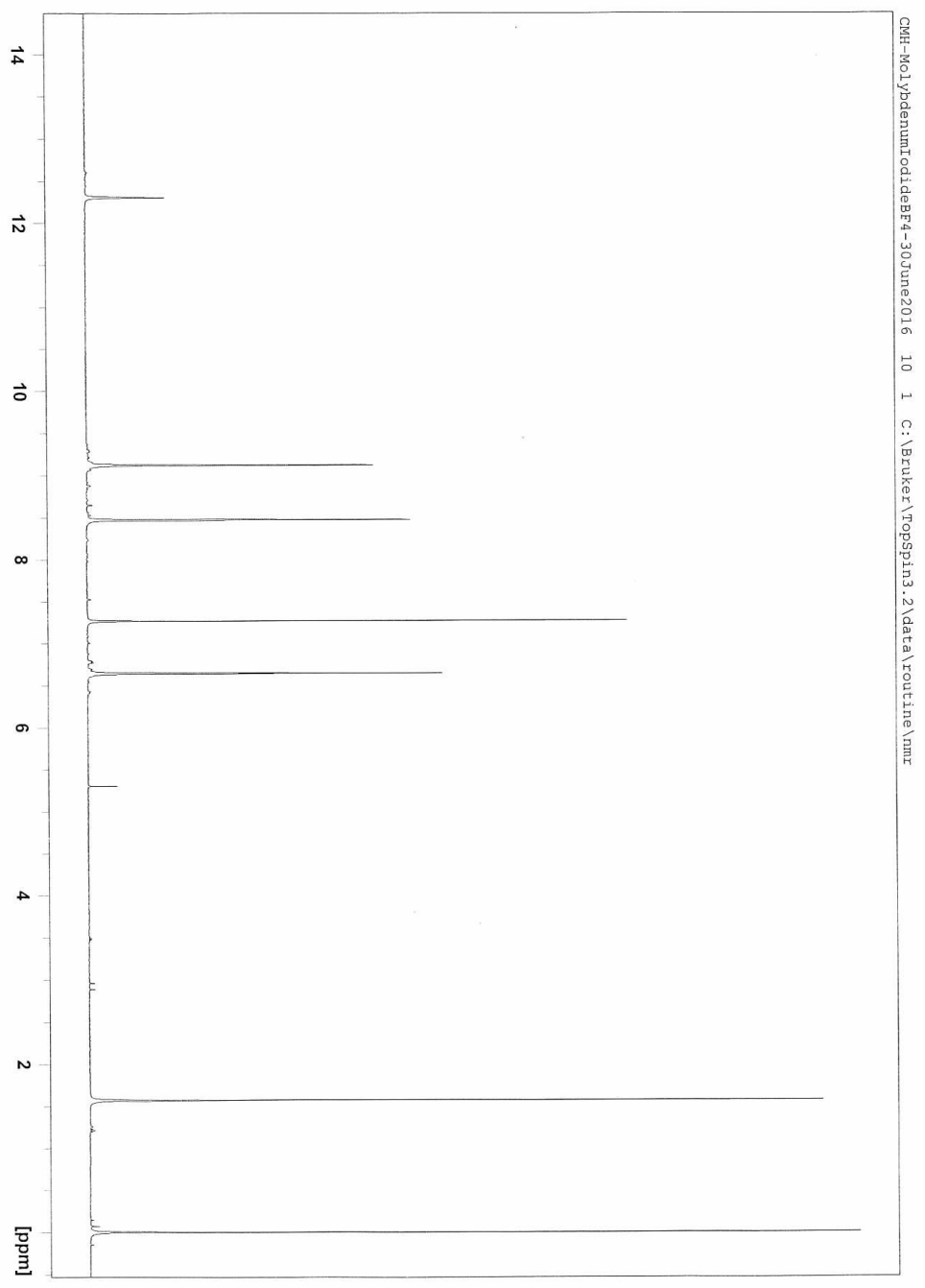


Figure 15: $TpmMo(CO)_3I_2$

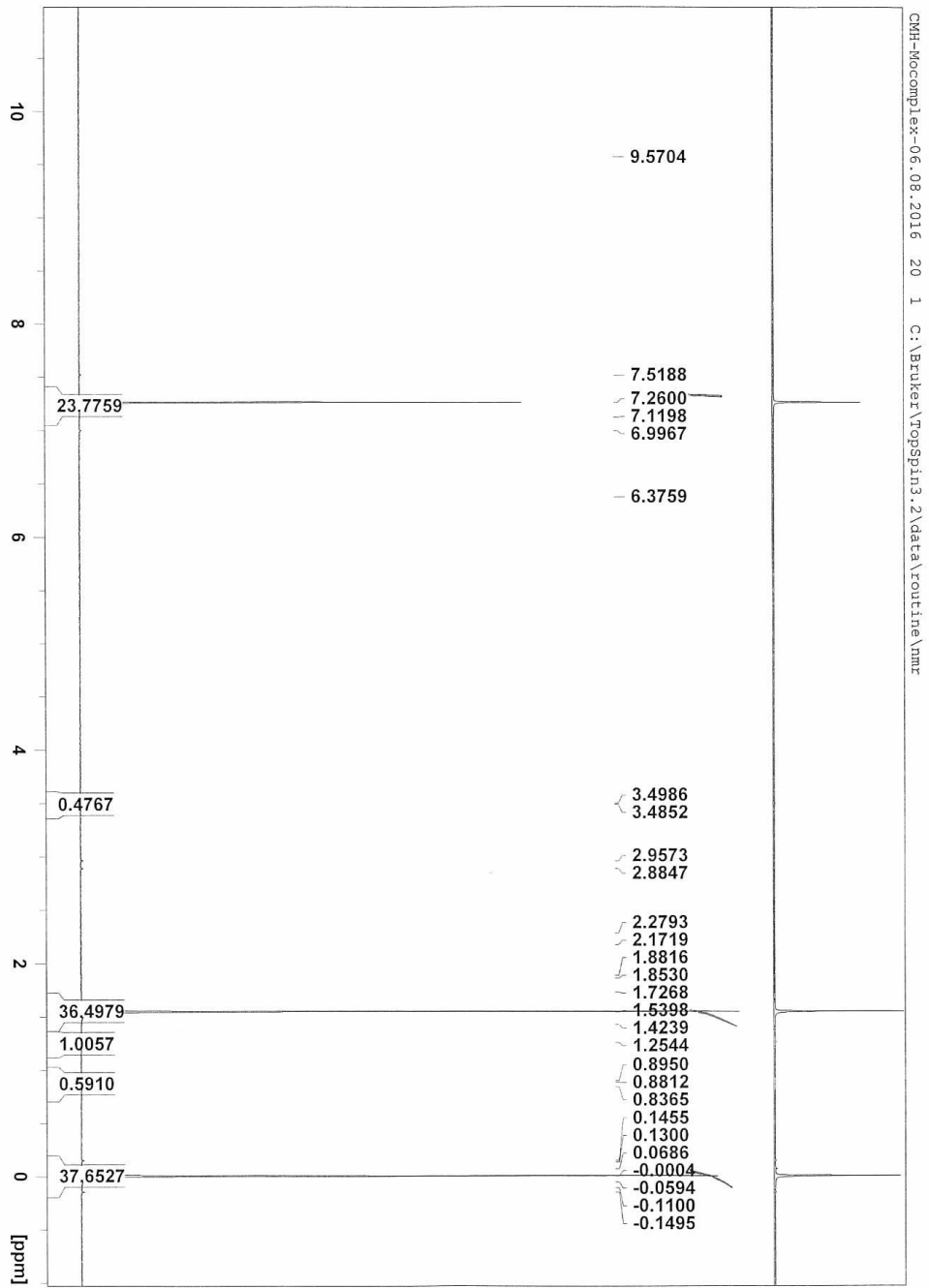


Figure 16: $TpmMo(CO)_3$

Appendix B: IR

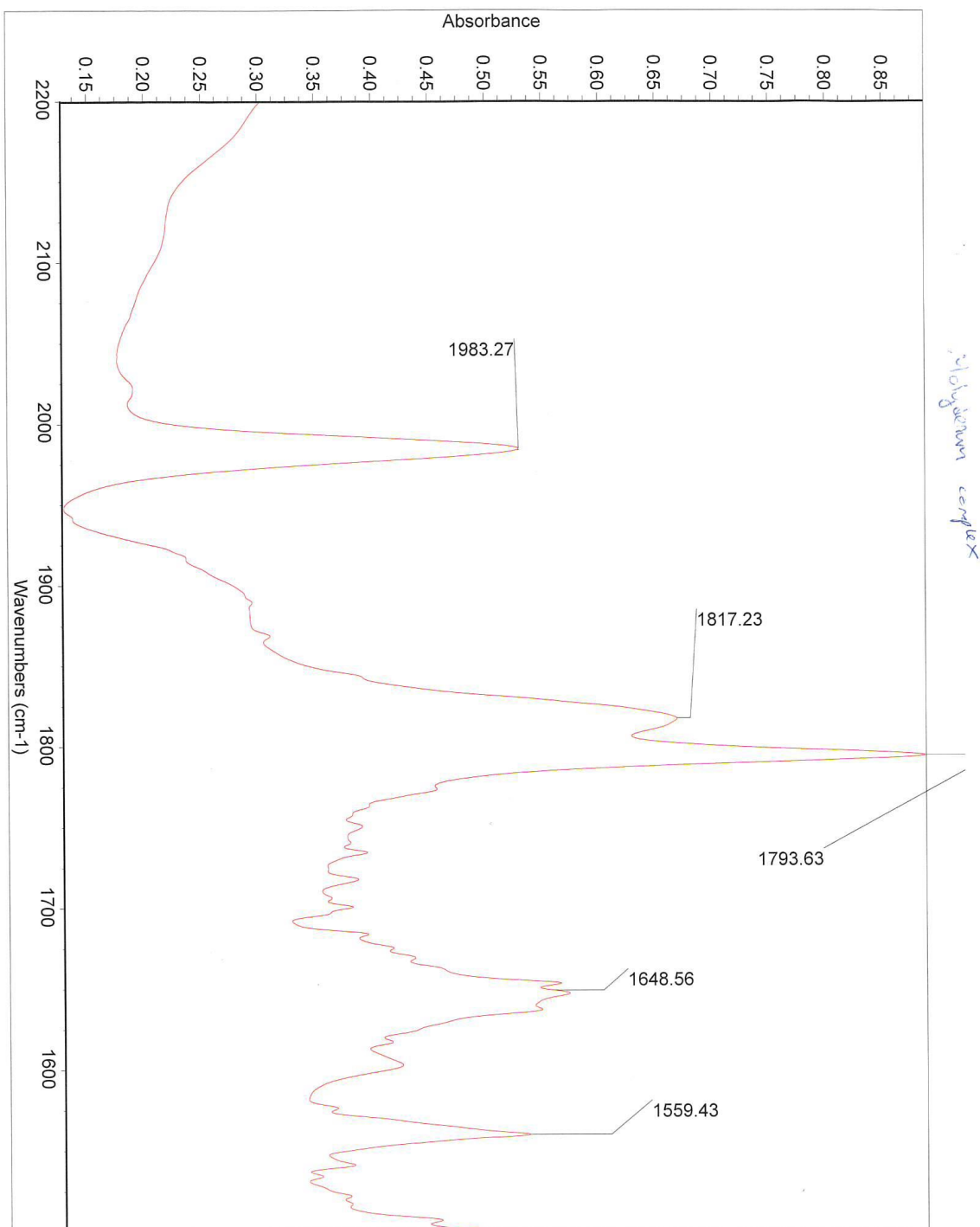


Figure 17: IR of $TpmMo(CO)_3$

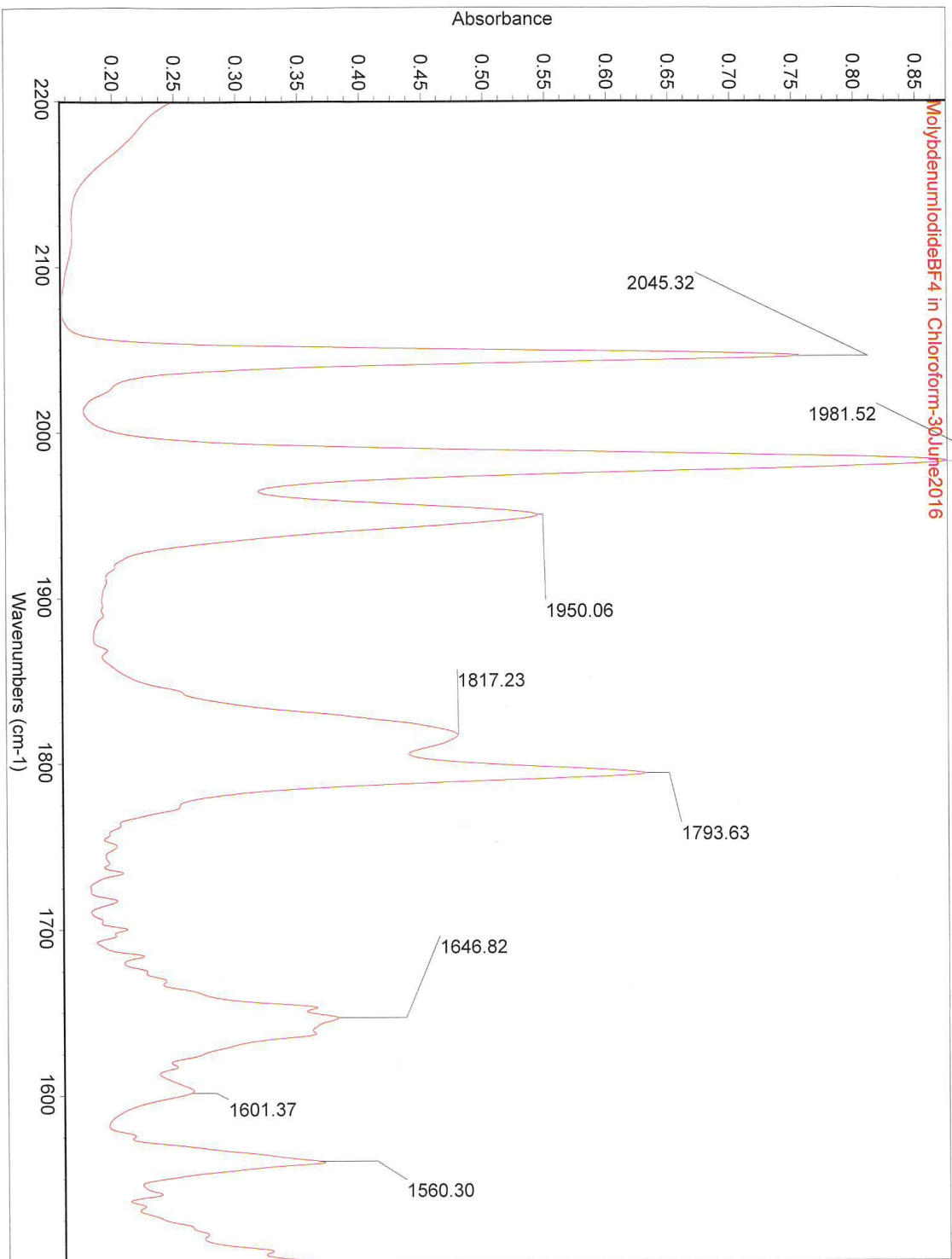


Figure 182: IR of $TpmmMo(CO)_3I_2$

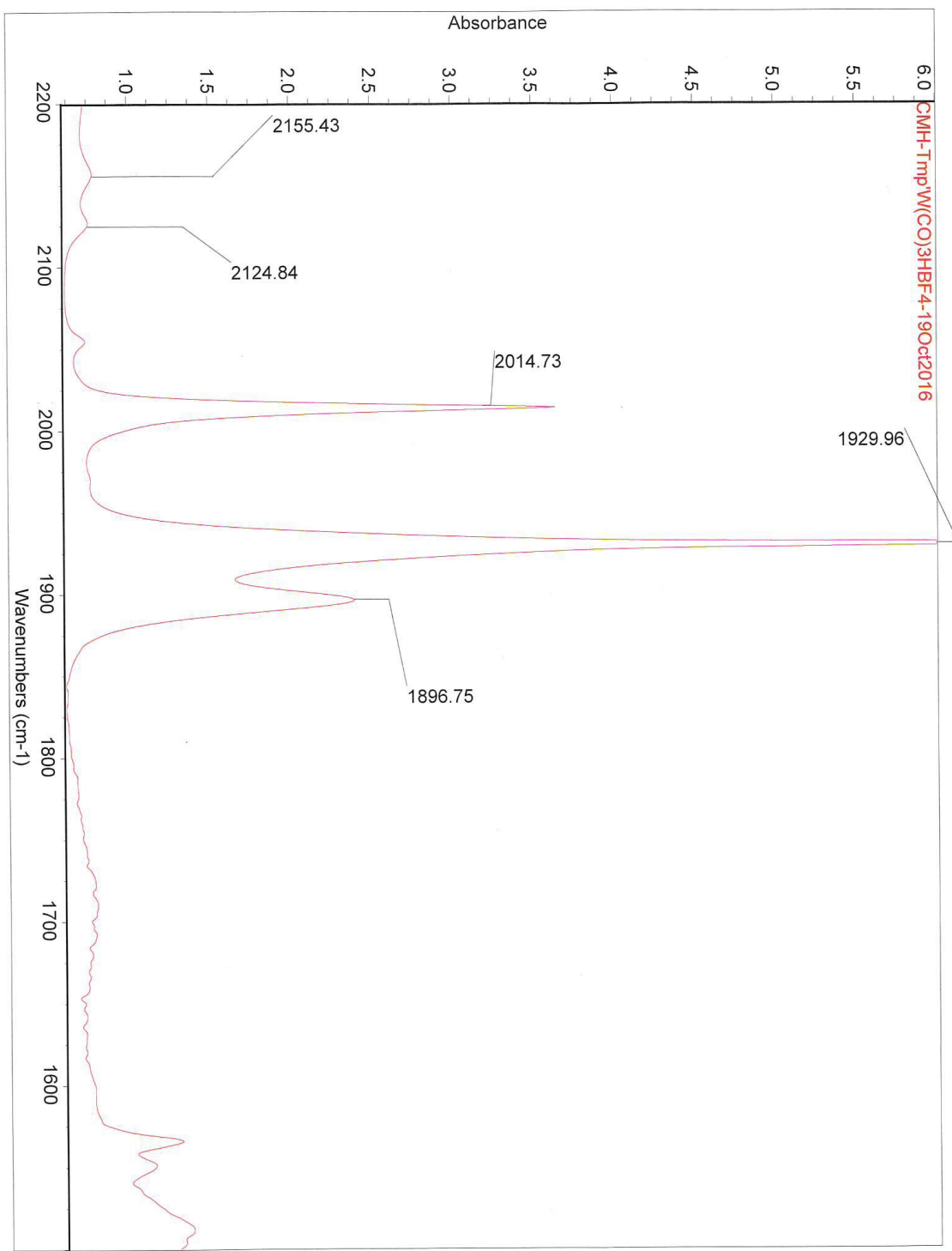


Figure 19: $Tpm'W(CO)_3HBF_4$

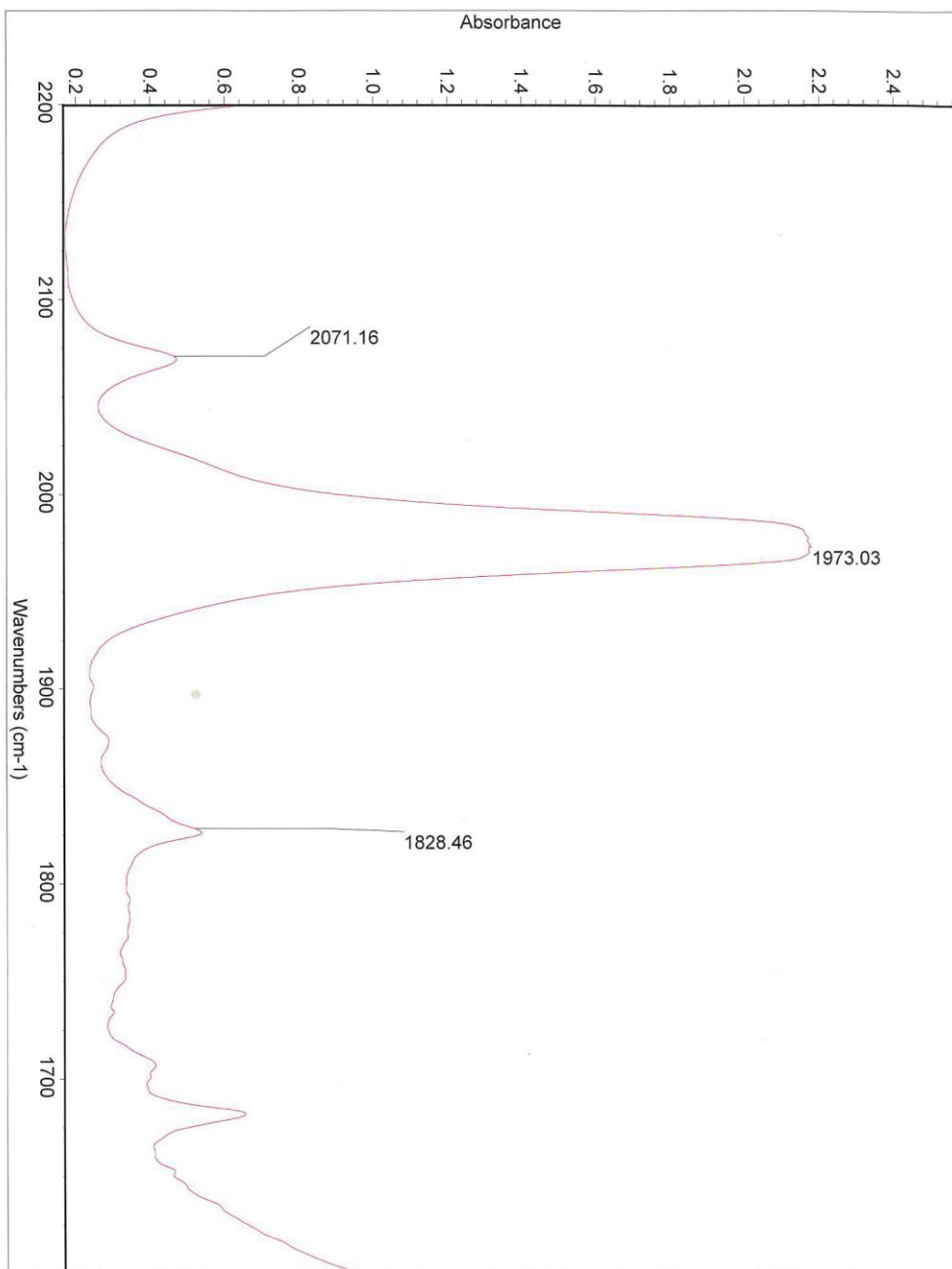


Figure 20: Tpm'

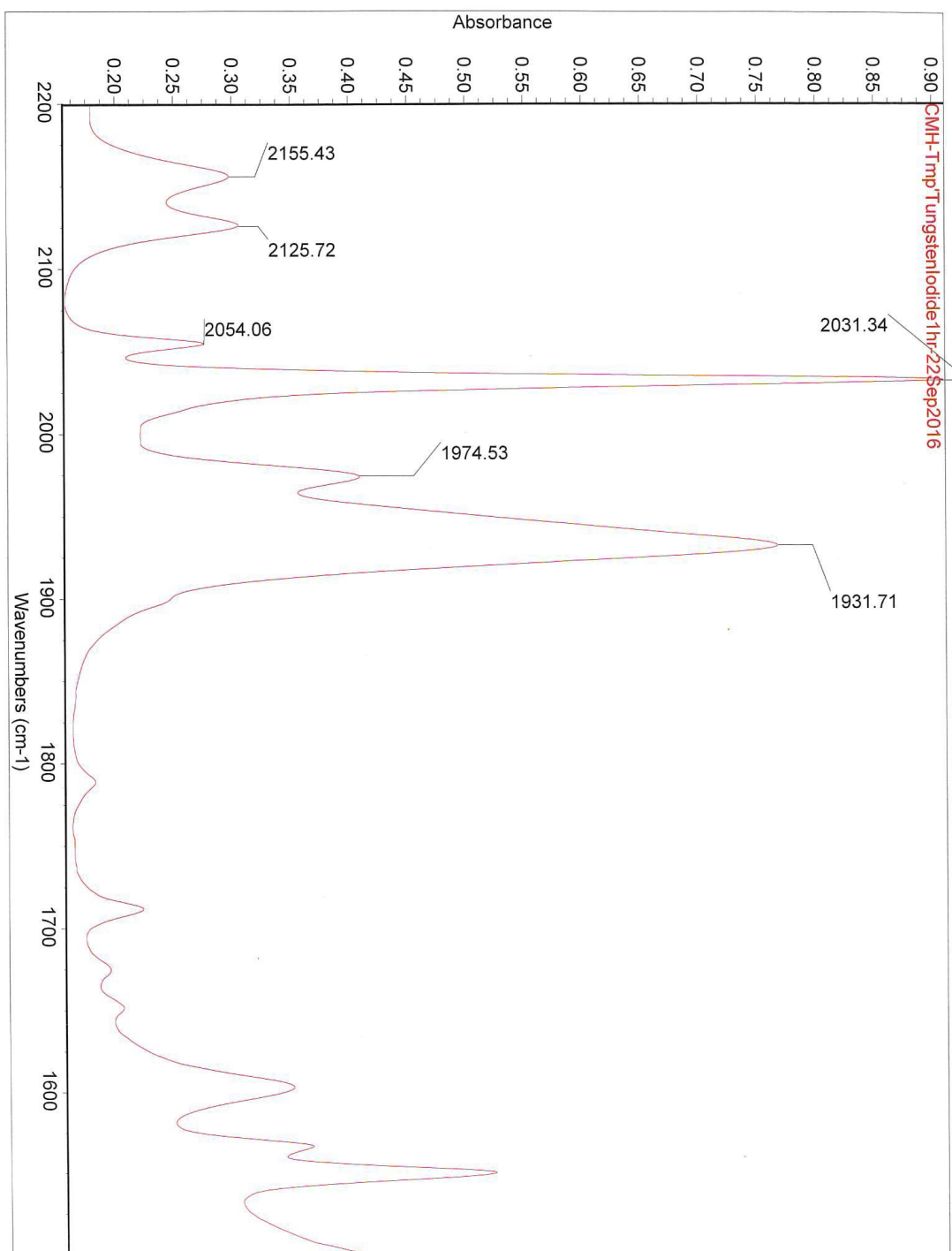
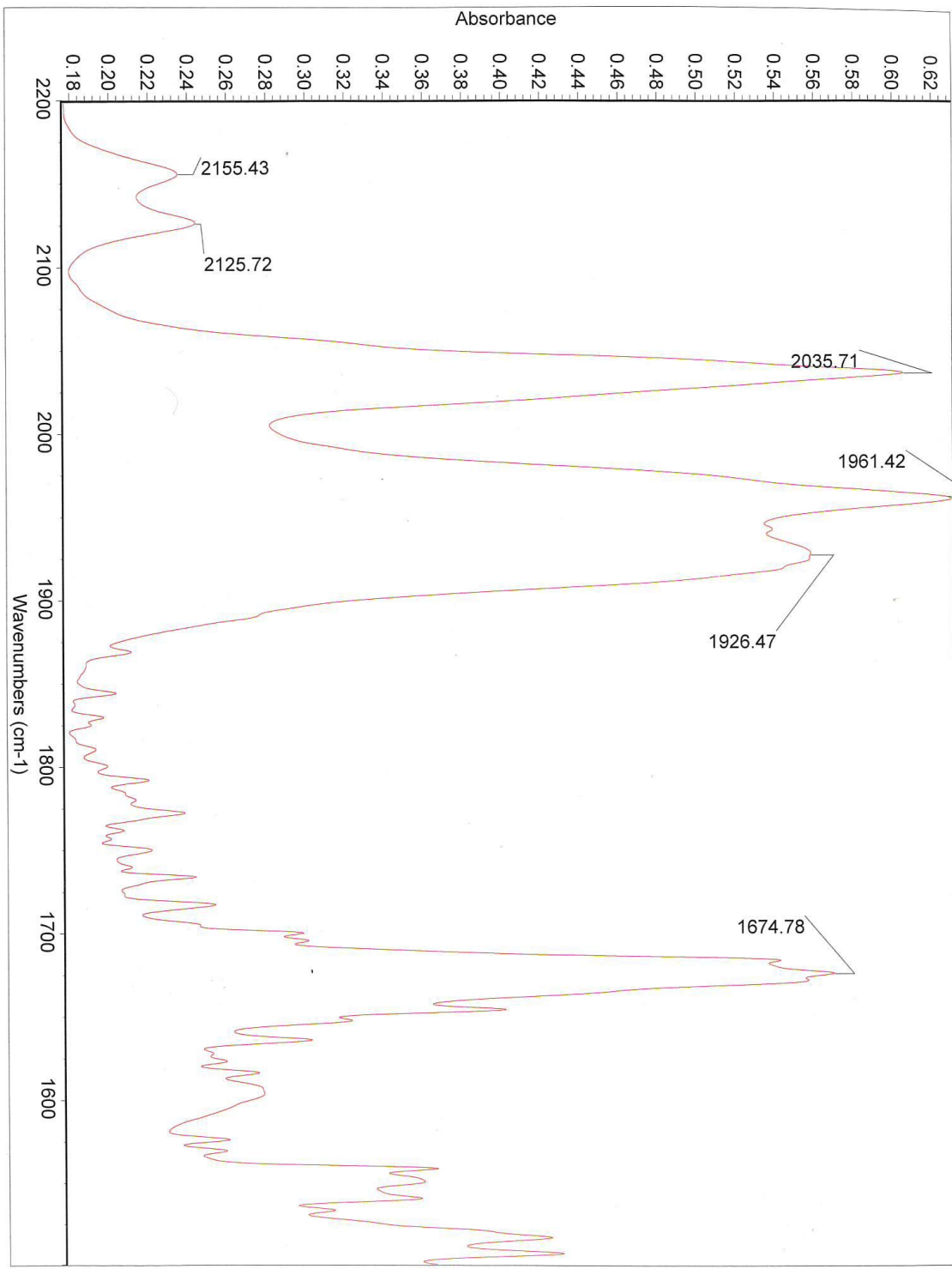


Figure 21: $Tpm^*W(CO)_3I_2$



TpmW(CO)₃I₂ - 6/12/17

Figure 22: TpmW(CO)₃I₂

References

1. Cameron, Charles J.; Fanwick, Phillip E.; Leeaphon, Malee; Walton, Richard A. (1989). Reactions of the Polyhydrides $\text{Re}_2\text{H}_8(\text{PPh}_3)_4$ and $\text{ReH}_7(\text{PPh}_3)_2$ with Acetic Acid/Acetic Anhydride. Isolation and Characterization of the Rhenium(I) Carbonyl Complexes $\text{Re}(\text{O}_2\text{CCH}_3)(\text{CO})_{1+x}(\text{PPh}_3)_{3+x}$ ($x=0,1$) and the Homoleptic Dirhenium(III) Carboxylate Complex $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_4(\text{O}_2\text{CCH}_3)_2$
2. Dilsky, Stefan. (2007). Molybdenum and tungsten complexes of the neutral tripod ligands $\text{HC}(\text{pz})_3$ and $\text{MeC}(\text{CH}_2\text{PPh}_2)_3$. *Journal of Organometallic Chemistry*, 692, 2887-2896.
3. Jacimovic, Zeljko K.; Bogdanovic, Goran A.; Hollo, Berta; Leovac, Vukadin M.; Szecsenyi, Katalin Meszaros (2009). Transition metal complexes with pyrazole-based ligands. Part 29. Reactions of zinc(II) and mercury(II) thiocyanate with 4-acetyl-3-amino-5-methylpyrazole. *Journal of the Serbian Chemical Society*, 74(11), 1259-1271.
4. Reger, Daniel L.; Grattan, T. Christian; Brown, Kenneth J.; Little, Christine A.; Lamba, Jaydeep J.S.; Rheingold, Arnold L.; Sommer, Roger D. (2000). Syntheses of tris(pyrazolyl) methane ligands and {[tris(pyrazolyl)methane] $\text{Mn}(\text{CO})_3$ } SO_3CF_3 complexes: comparison of ligand donor properties. *Journal of Organometallic Chemistry*, 607, 120-128.
5. Szecsenyi, K. Meszaros; Leovac, V. M.; Jacimovic, Z. K.; Cesljevic, V. I.; Kovacs, A.; Pokol, G.; Gal, S (2001). Transition Metal Complexes with Pyrazole-based Ligands. Part 8. Characterization and thermal decomposition of zinc(II) complexes with di- and trisubstituted pyrazoles. *Journal of Thermal Analysis and Calorimetry*, 63(3), 723-732.
6. Trofimenko, Swiatoslaw; Calabrese, Joseph C.; Domaille, Peter J.; Thompson, Jeffery S. (1989). Steric Effects in Polypyrazolylborate Ligands. Poly(3-isopropylpyrazolyl) borates: Ligands of Intermediate Steric Requirements. *Inorganic Chemistry*, 28, 1091-1101.
7. Trofimenko, S. (1970). Geminal Poly(1-pyrazolyl) alkanes and Their Coordination Chemistry. *Journal of the American Chemical Society*, 92(17), 5118-5126.