

Supporting Information

Spatial Recognition Within Terpenes: Redox and H-bond Promoted Linkage Isomerizations and the Selective Binding of Complex Alkenes

Steven J. Dakermanji, Karl S. Westendorff, Emmit K. Pert, Katy B. Wilson, Jeffery T. Myers, Justin H. Wilde, Diane A. Dickie, Kevin D. Welch, and W. Dean Harman*

University of Virginia, Department of Chemistry, Charlottesville, VA 22904

Table of Contents

General Methods.....	S2
Compounds:	
MoTp(NO)(DMAP)(η^2-Trans-3-hexene) (3)	S3
(MoTp(NO-Me)(DMAP)(η^2-Trans-3-Hexene))(OTf) (3•CH₃)	S6
WTp(NO)(PMe₃)(η^2-Trans-3-hexene) (4)	S8
MoTp(NO)(DMAP)(η^2-<i>R</i>-limonene) (9)	S12
Mo_RTp(NO)(DMAP)(η^2-<i>R</i>-limonene) (<i>R,R</i>)- 9A	S14
Mo_STp(NO)(DMAP)(η^2-<i>R</i>-limonene) (<i>S,R</i>)- 9A	S15
WTp(NO)(PMe₃)(η^2-<i>R</i>-limonene) (<i>R,R</i>)- 10A and (<i>S,R</i>)- 10A	S16
MoTp(NO)(DMAP)(η^2-α-humulene) (12)	S20
(MoTp(NO-Me)(DMAP)(η^2-α-Humulene))(OTf) (12A•CH₃)	S23
WTp(NO)(PMe₃)(η^2 α-humulene) (13)	S25
MoTp(NO)(DMAP)(η^2-Cyclopentene) (14)	S28
Crystallography information (9a and 14)	S30

General Methods

NMR spectra were obtained on a 600 or 800 MHz spectrometer. All chemical shifts are reported in ppm, and proton and carbon shifts are referenced to tetramethylsilane (TMS) utilizing residual ^1H or ^{13}C signals of the deuterated solvents as an internal standard. Coupling constants (J) are reported in hertz (Hz). Infrared spectra (IR) were recorded as a glaze on a spectrometer fitted with a horizontal attenuated total reflectance (HATR) accessory or on a diamond anvil ATR assembly. Electrochemical experiments were performed under a nitrogen atmosphere. Cyclic voltammetry data were taken at ambient temperature ($\sim 25^\circ\text{C}$) at 100 mV/s in a standard three-electrode cell with a glassy-carbon working electrode, N,N-dimethylacetamide (DMA) or acetonitrile (CH_3CN) solvent (unless otherwise specified), and tetrabutylammonium hexafluorophosphate (TBAH) electrolyte (approximately 0.5 M). All potentials are reported versus NHE (normal hydrogen electrode) using cobaltocenium hexafluorophosphate ($E_{1/2} = -0.78$ V), ferrocene ($E_{1/2} = +0.55$ V), or decamethylferrocene ($E_{1/2} = +0.04$ V) as internal standard. The peak-to-peak separation was approximately 100 mV for all reversible couples. Unless otherwise noted, all synthetic reactions were performed in a glove box under a dry nitrogen atmosphere. Deuterated solvents were used as received. Pyrazole (Pz) protons of the hydrido tris(pyrazolyl)borate(Tp) ligand were uniquely assigned (e.g., "PzB3") using a combination of two-dimensional NMR data. When unambiguous assignments were not possible, Tp protons were labeled as "Pz3/5 or Pz4". All J values for Pz protons are $2(\pm 0.2)$ Hz. BH peaks (around 4–5 ppm) are not identified due to their quadrupole broadening; IR data are used to confirm the presence of a BH group (around 2500 cm^{-1}).

Figure S1. ^1H NMR of $\text{MoTp}(\text{NO})(\text{DMAP})(\eta^2\text{-trans-3-hexene})$ (**3**)

($\text{d}^6\text{-Acetone}$)

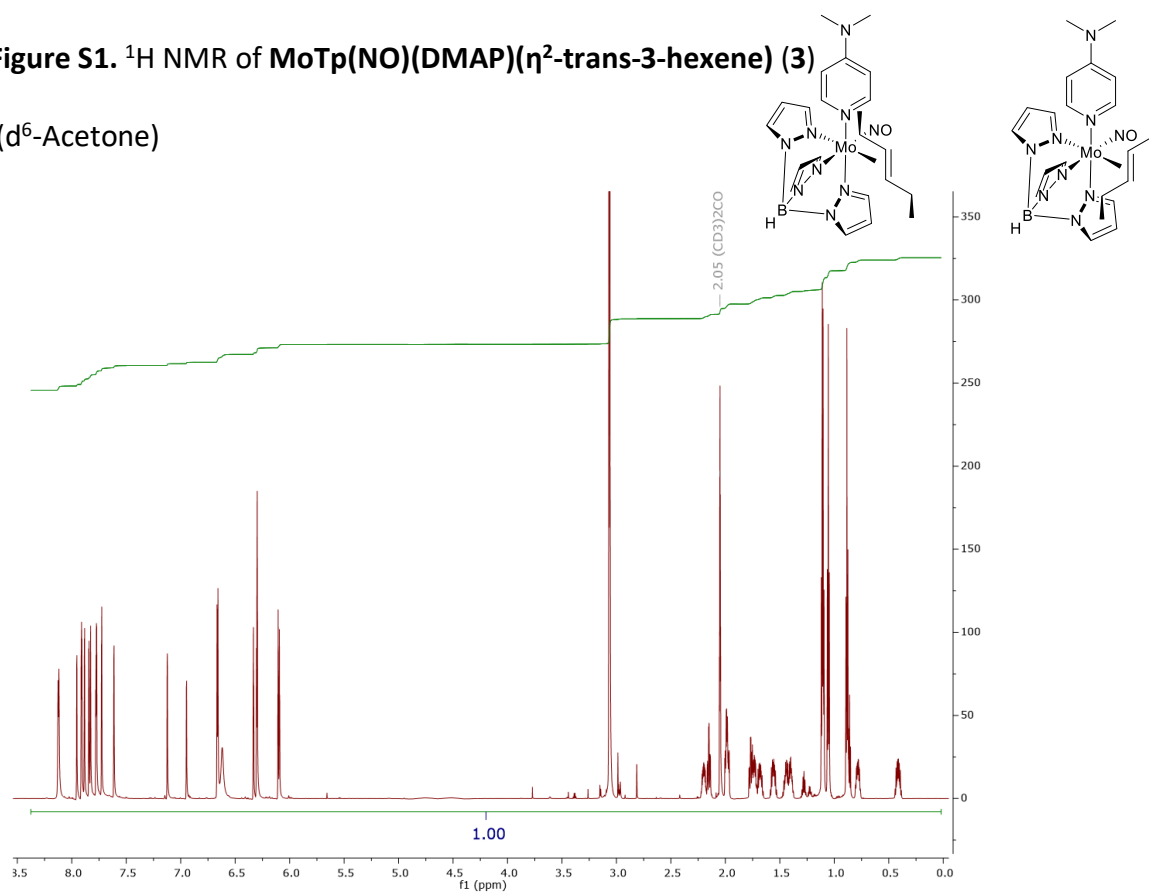


Figure S2. ^{13}C NMR ($\text{d}^6\text{-Acetone}$) of **3**

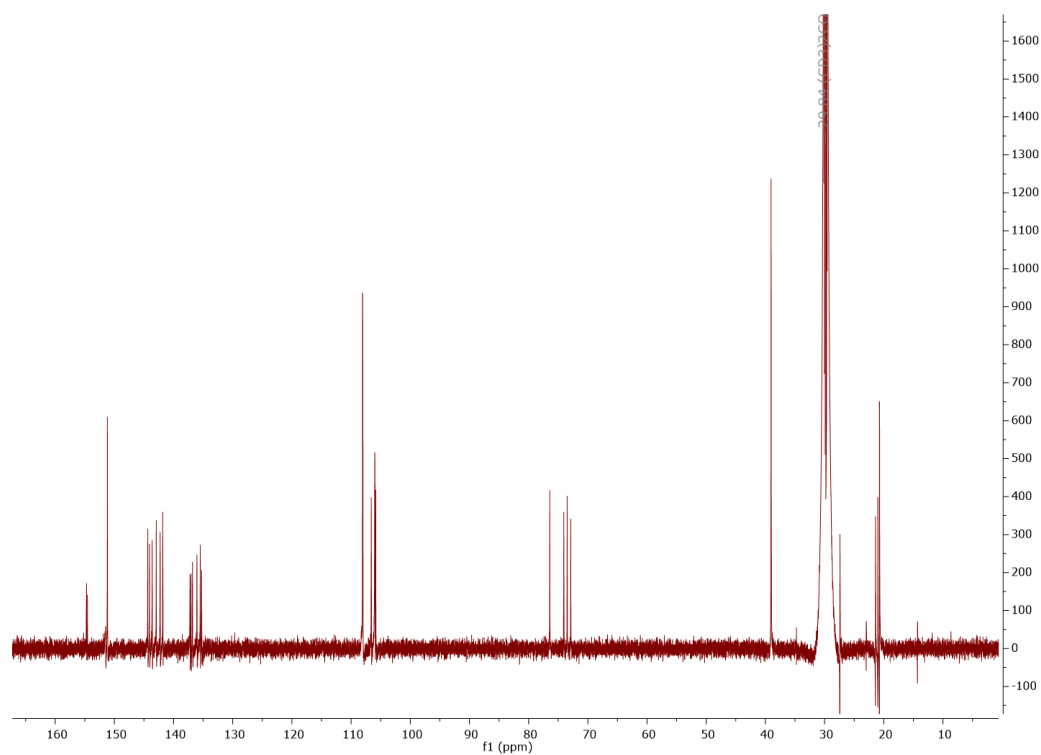


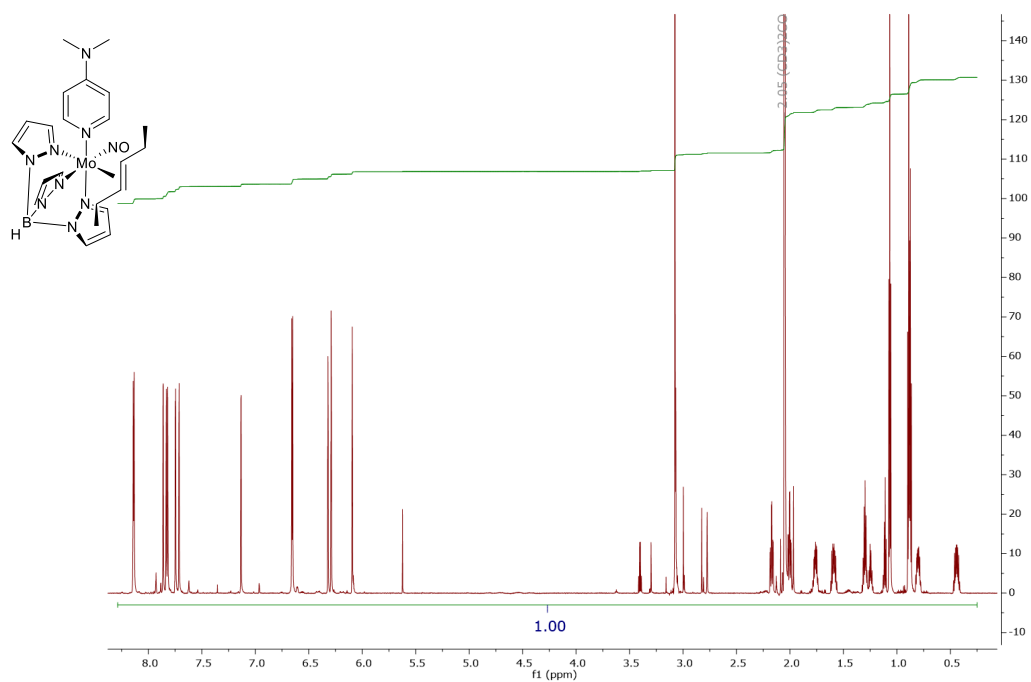
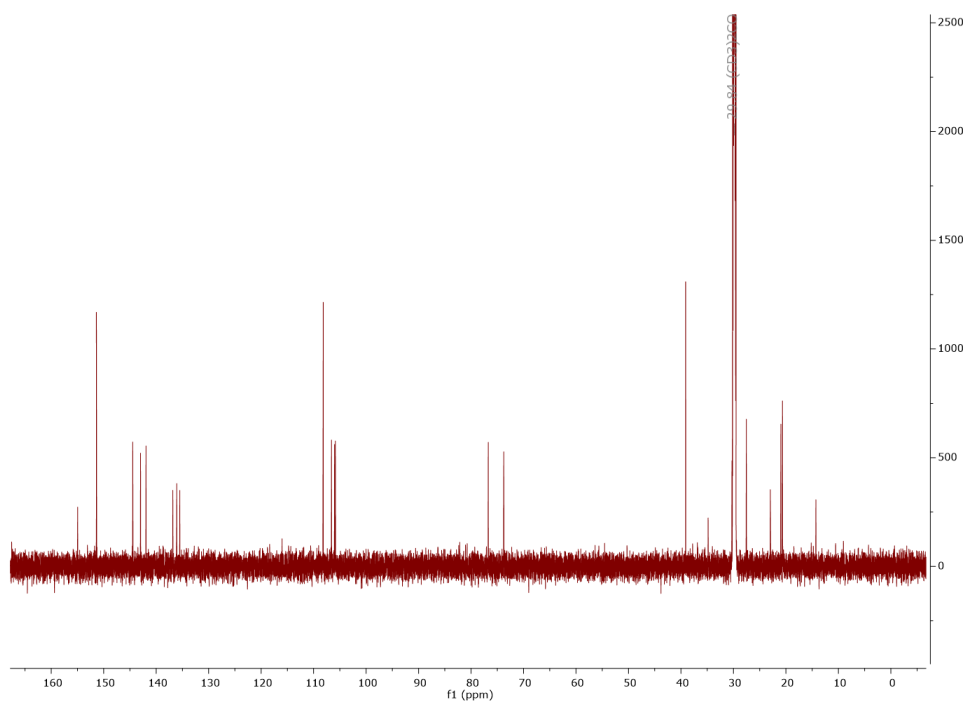
Figure S3. ^1H NMR (d^6 -Acetone) of **3B****Figure S4.** ^1H NMR ^{13}C NMR (d^6 -Acetone) of **3B**

Figure S5. CV of 3

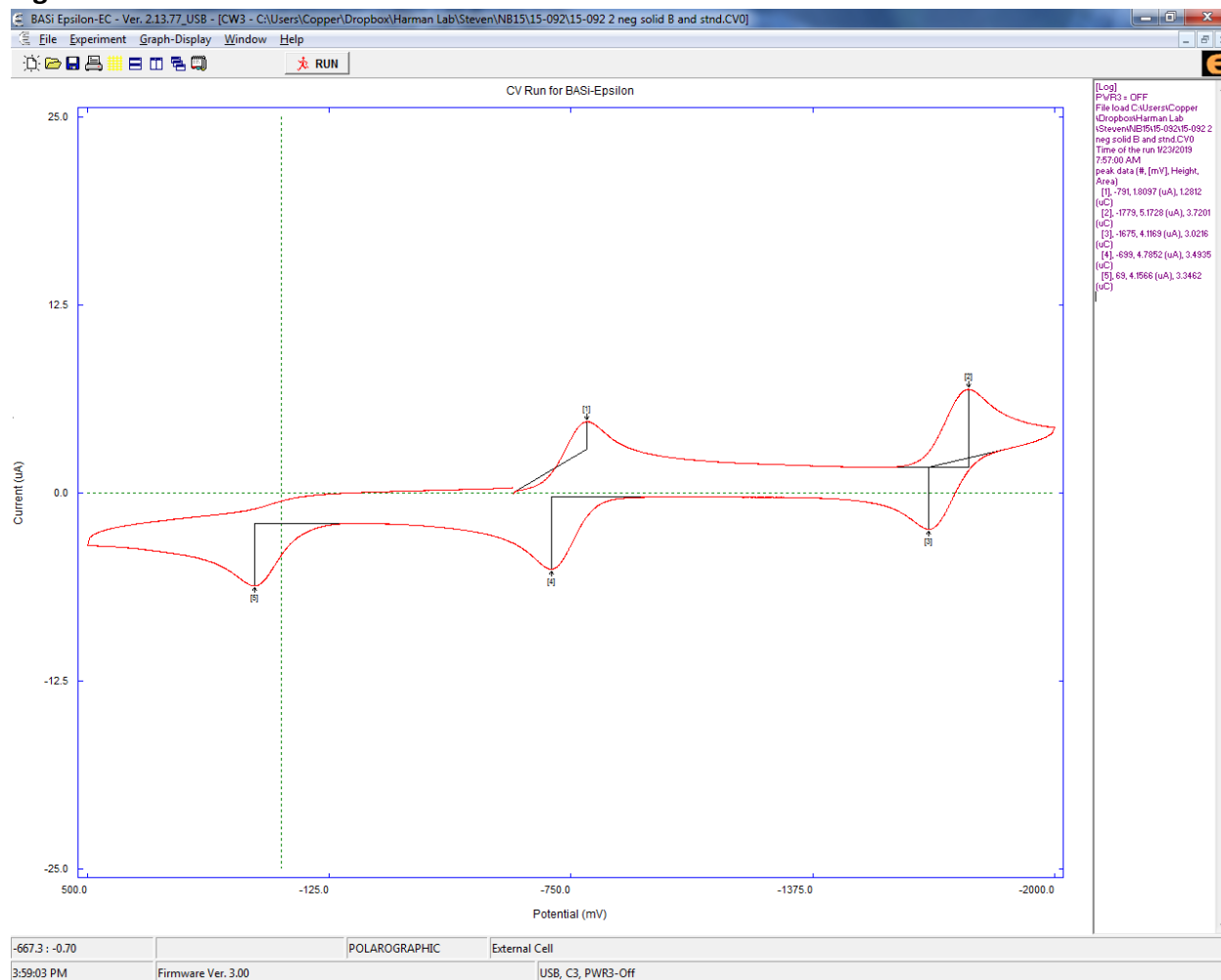
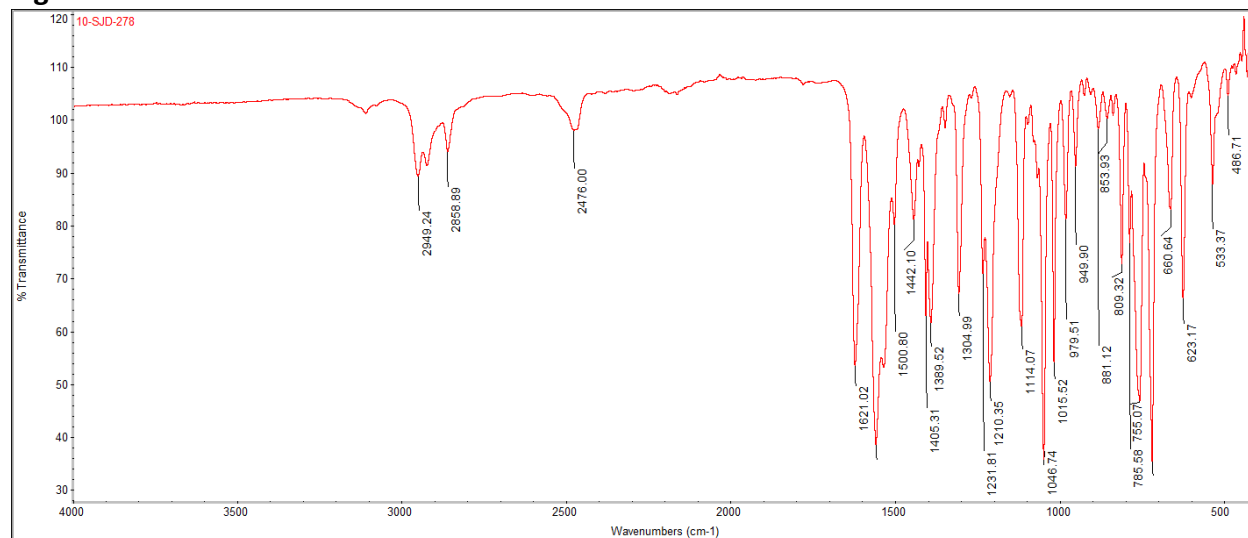


Figure S6. IR of 3



(MoTp(NO-Me)(DMAP)(η^2 -3-Trans-Hexene))(OTf) (3**•CH₃)**

Figure S7. ¹H NMR (d⁶-Acetone) of

Figure S8. ¹³C NMR (d⁶-Acetone) of

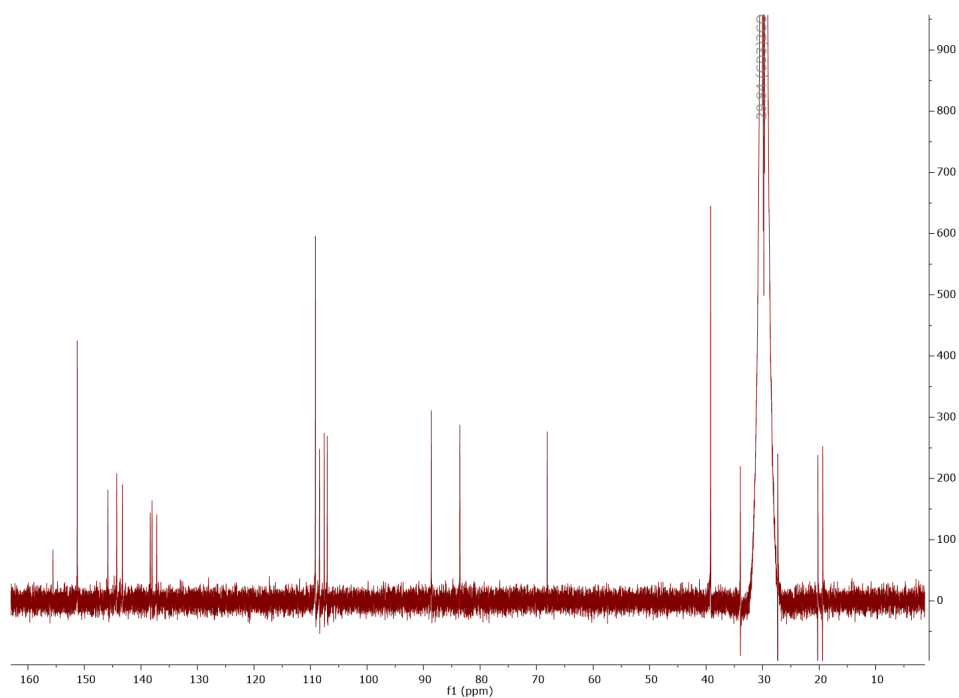
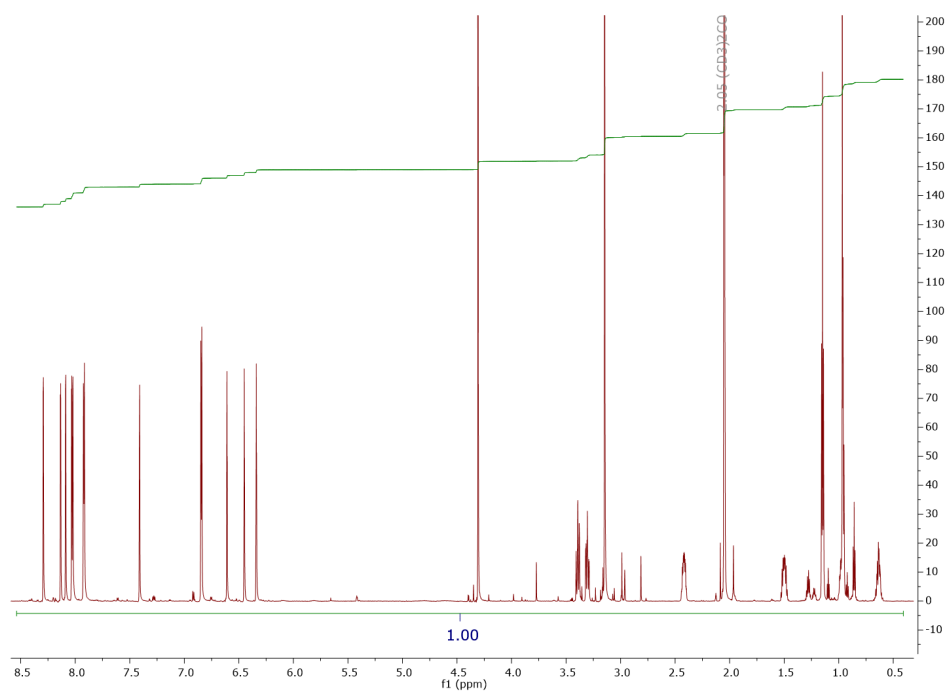
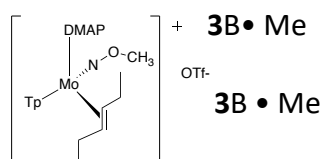
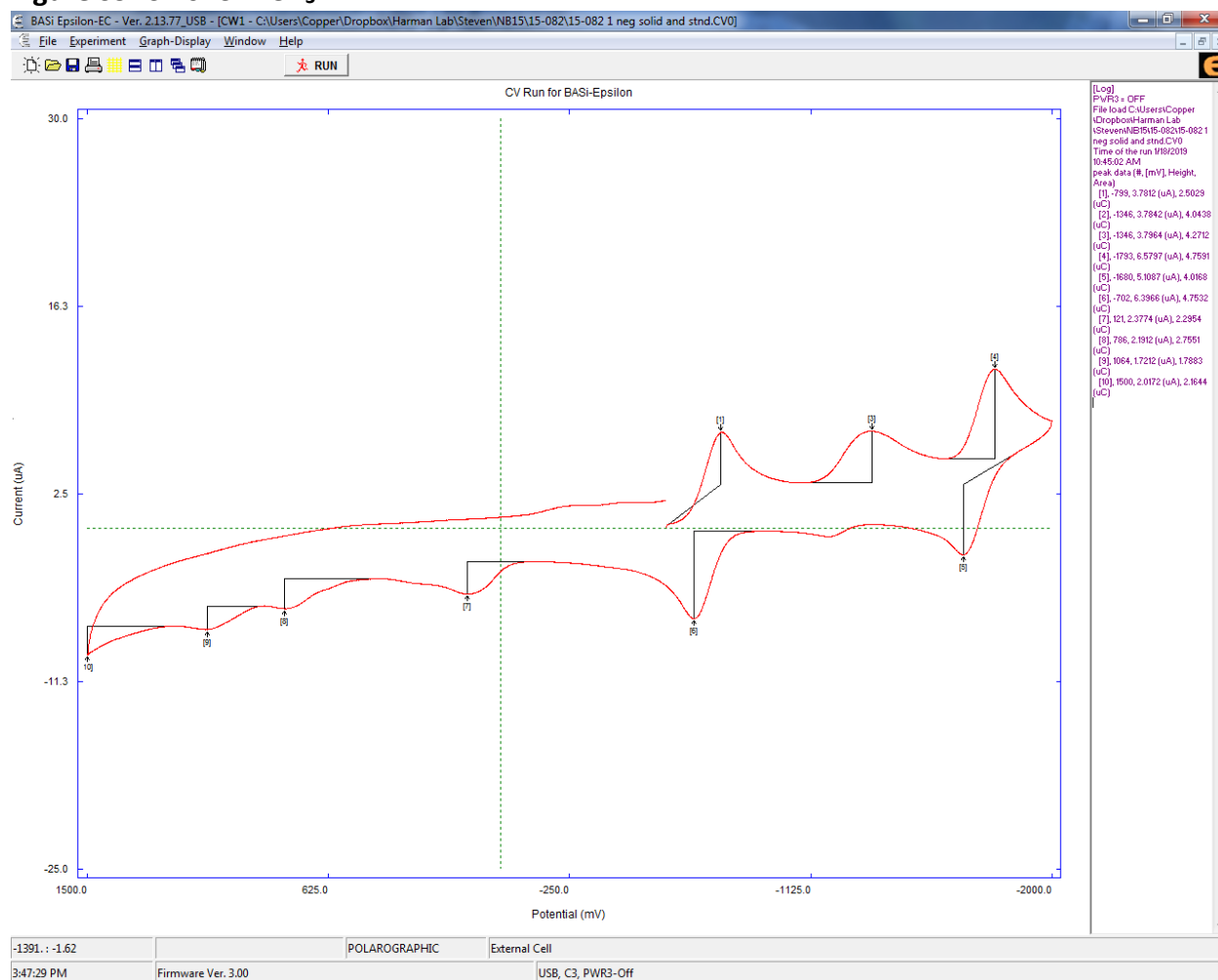
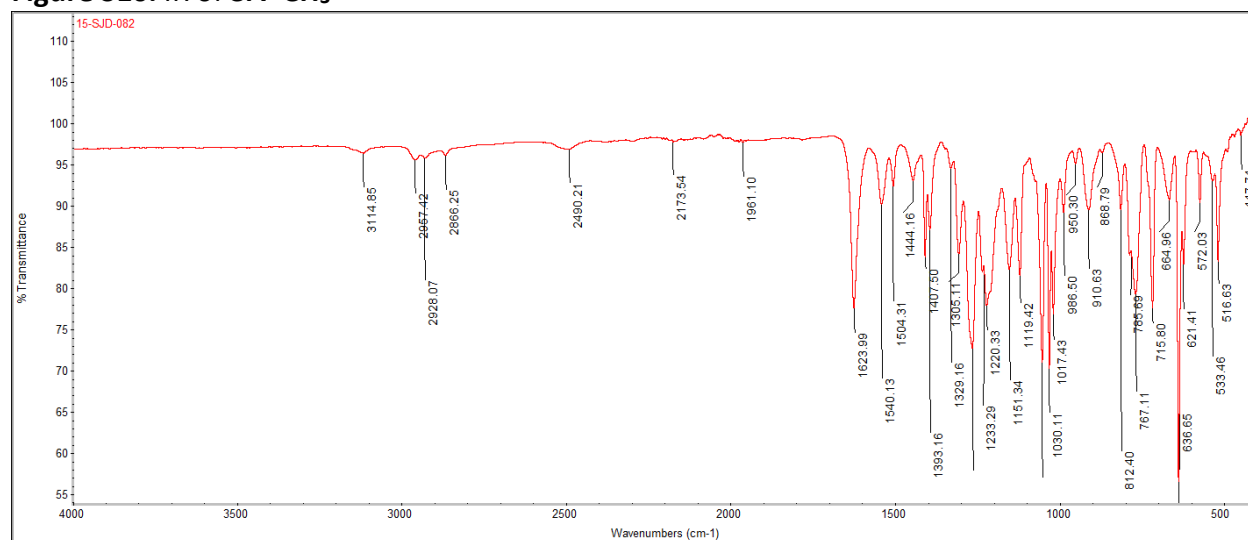


Figure S9. CV of $3A \bullet CH_3$ Figure S10. IR of $3A \bullet CH_3$ 

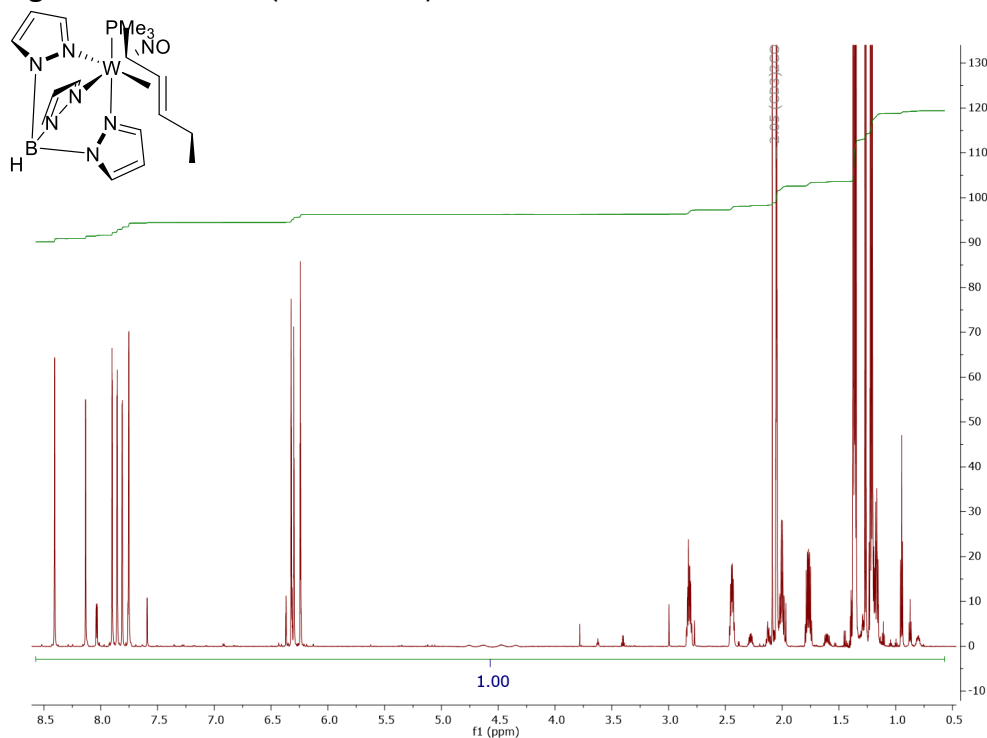
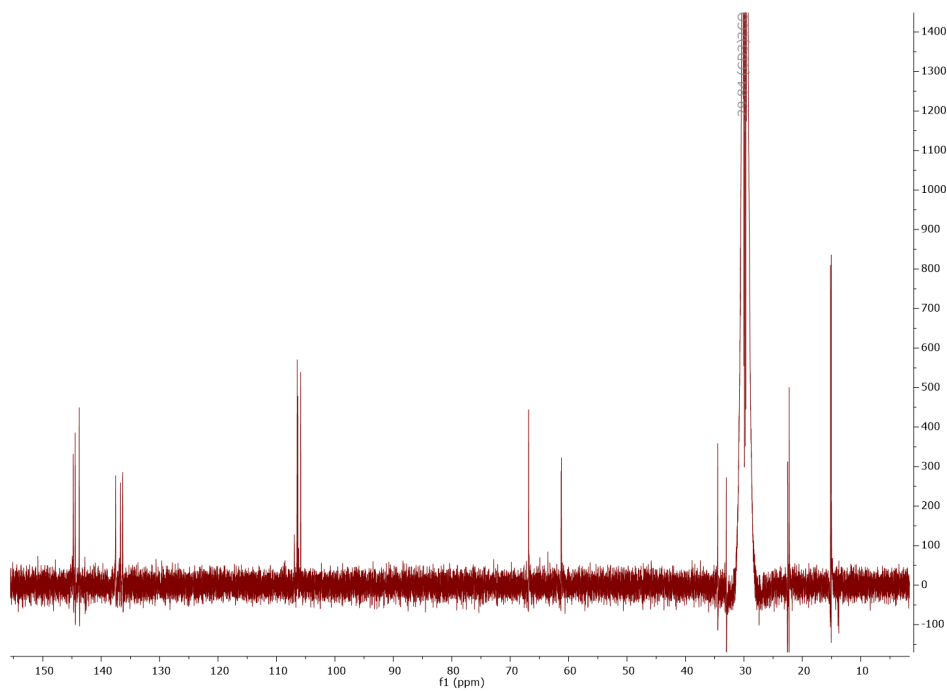
WTp(NO)(PMe₃)(η^2 -trans-3-hexene) (4)**Figure S11.** ¹H NMR (d⁶-Acetone) of 4A**Figure S12.** ¹³C NMR (d⁶-Acetone) of 4A

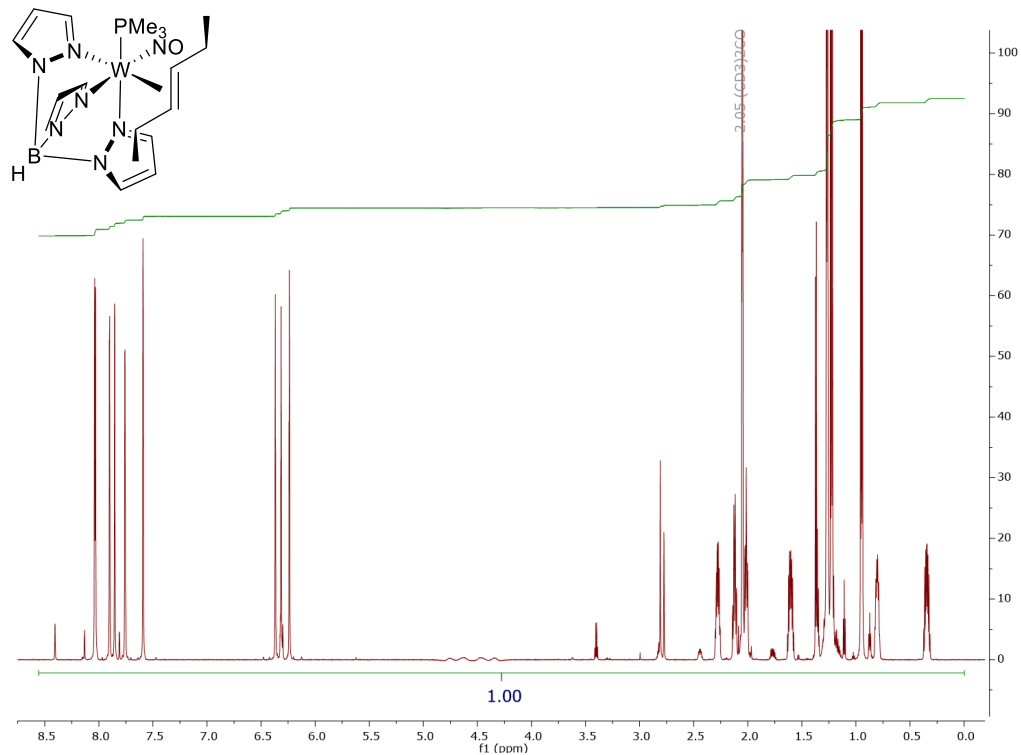
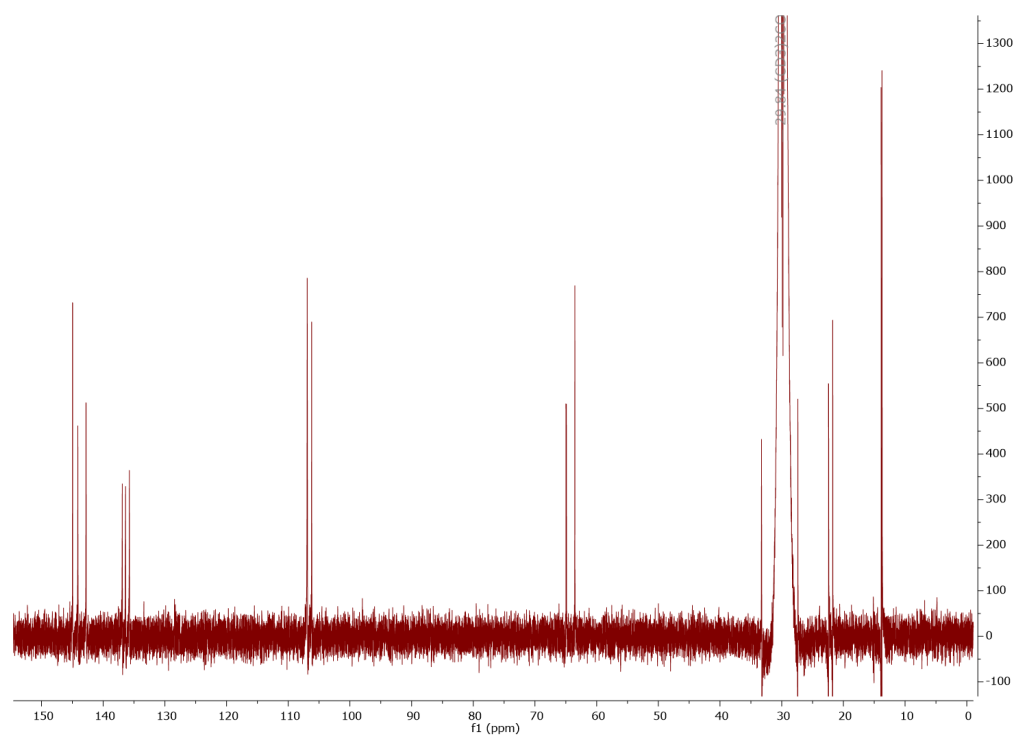
Figure S13. ^1H NMR (d^6 -Acetone) of **4B****Figure S14.** ^{13}C NMR (d^6 -Acetone) of **4B**

Figure S15. CV of 4A

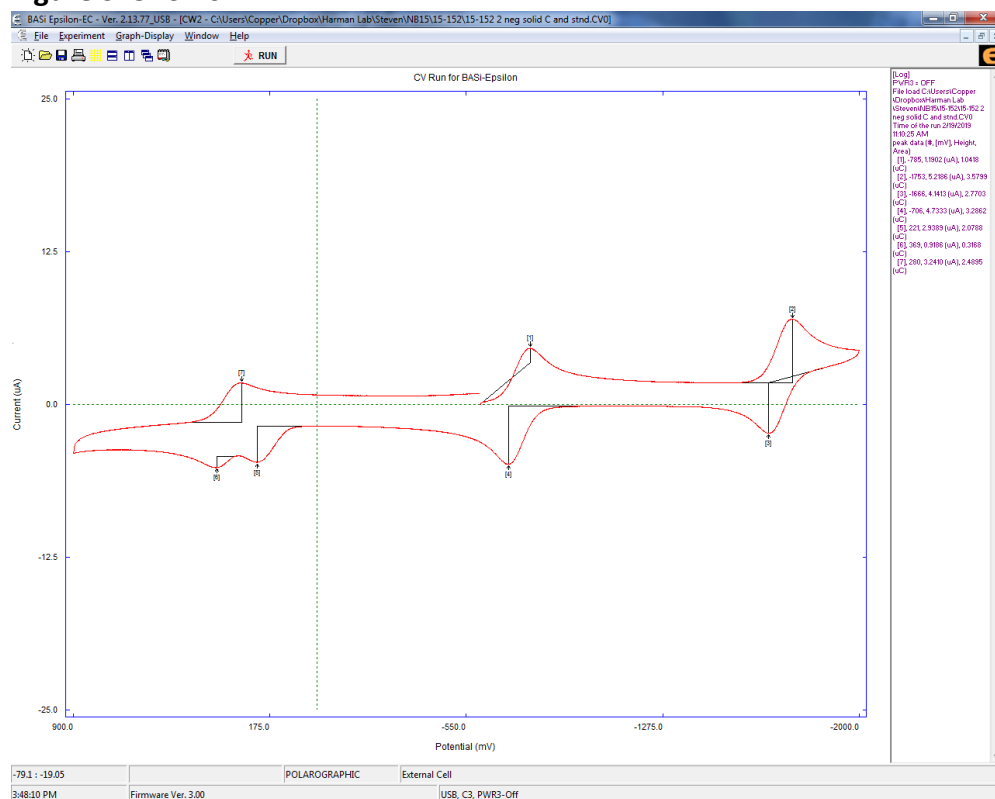


Figure S16. CV of 4B

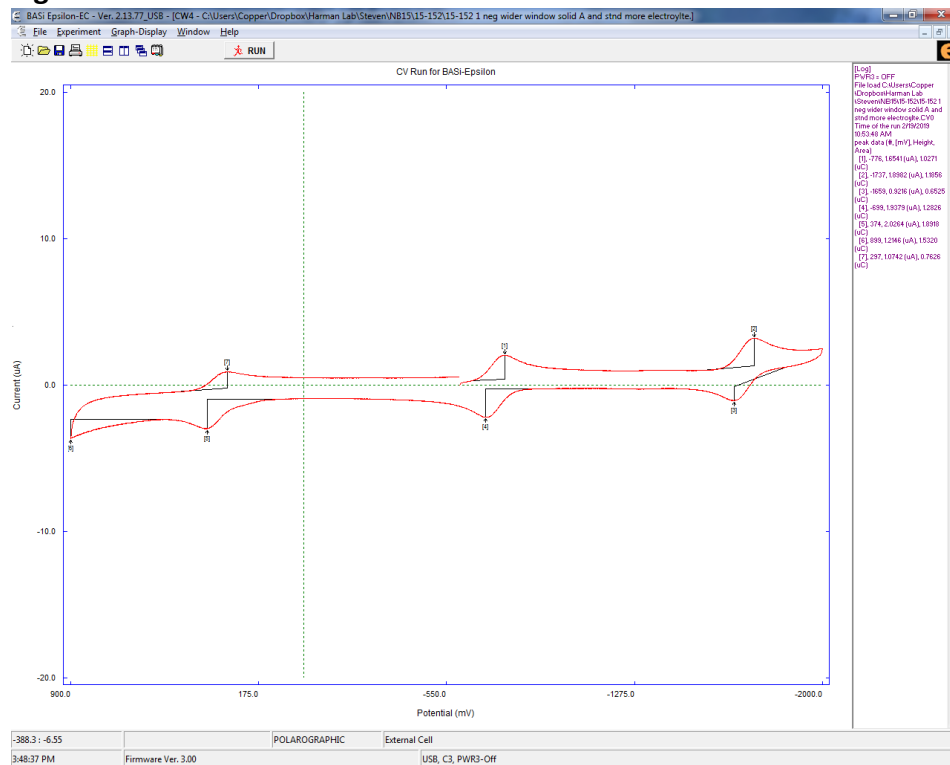


Figure S17. IR of 4A

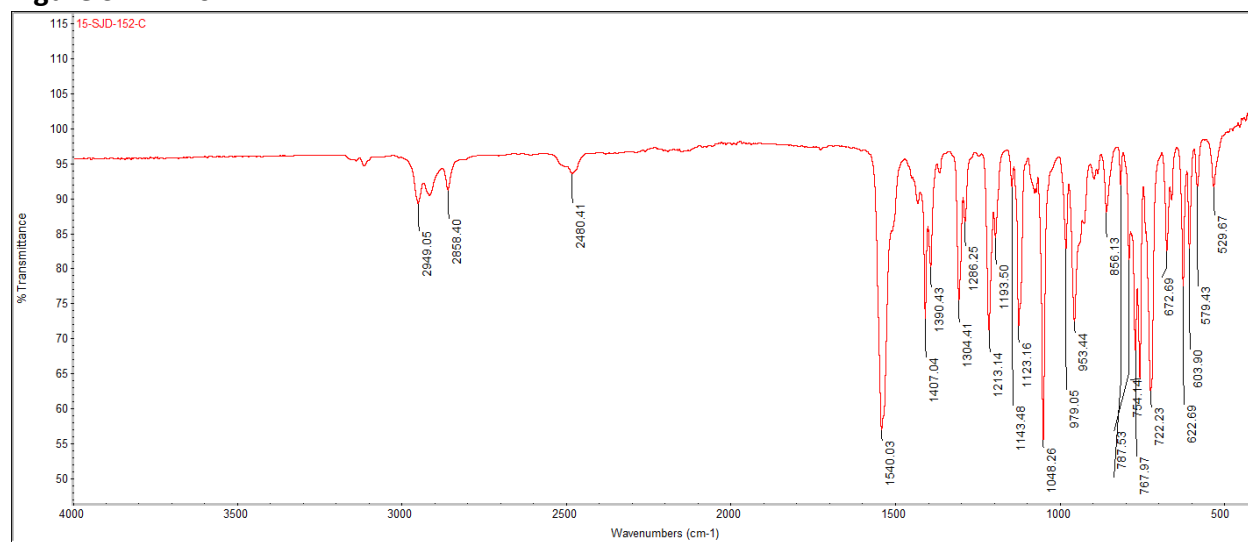
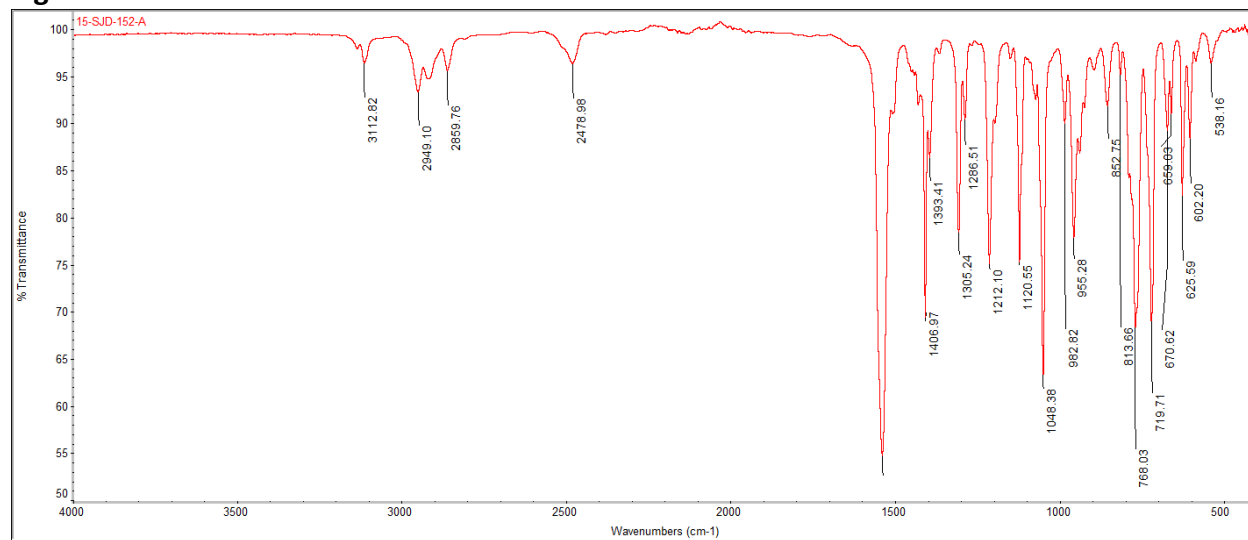


Figure S18. IR of 4B



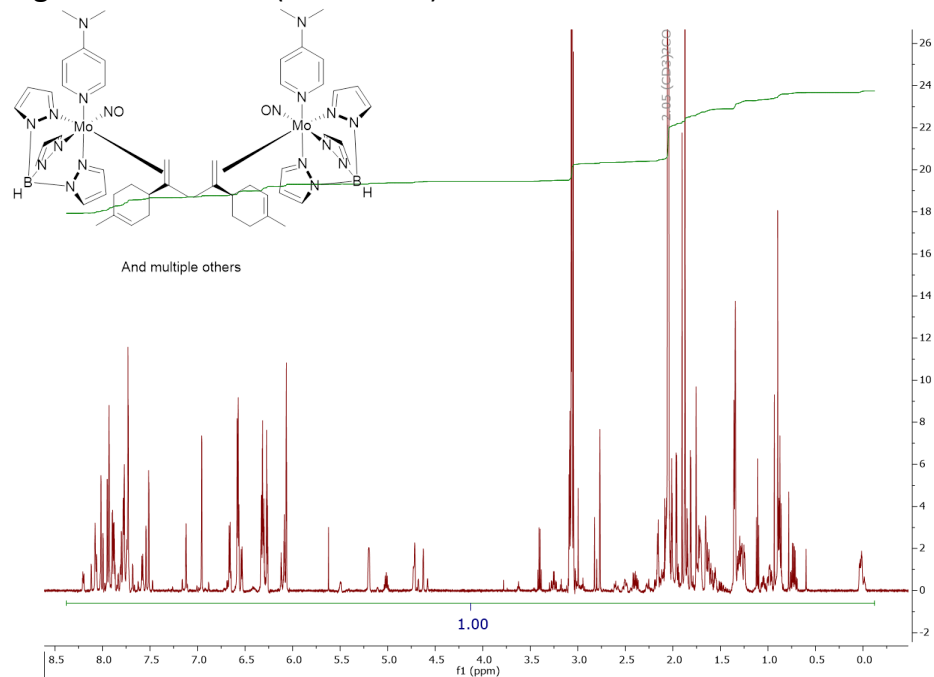
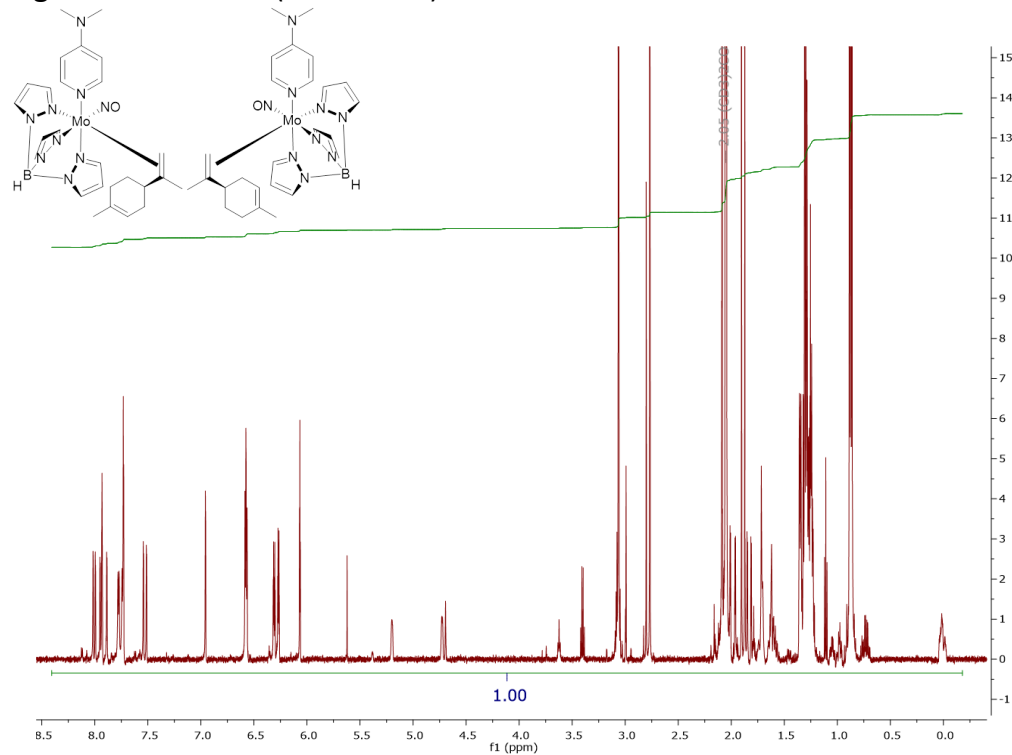
MoTp(NO)(DMAP)(η^2 -*R*-limonene) (9)**Figure S19.** ^1H NMR (d^6 -Acetone) of **9****Figure S20.** ^1H NMR (d^6 -Acetone) of **9A**

Figure S21. CV of 9

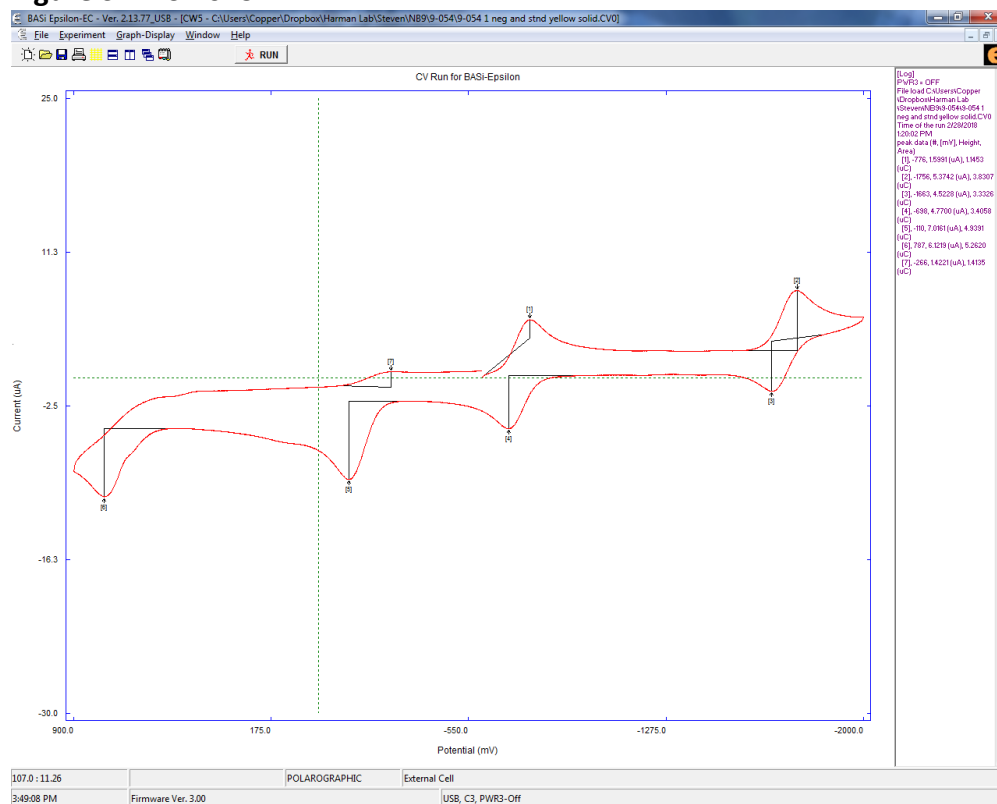
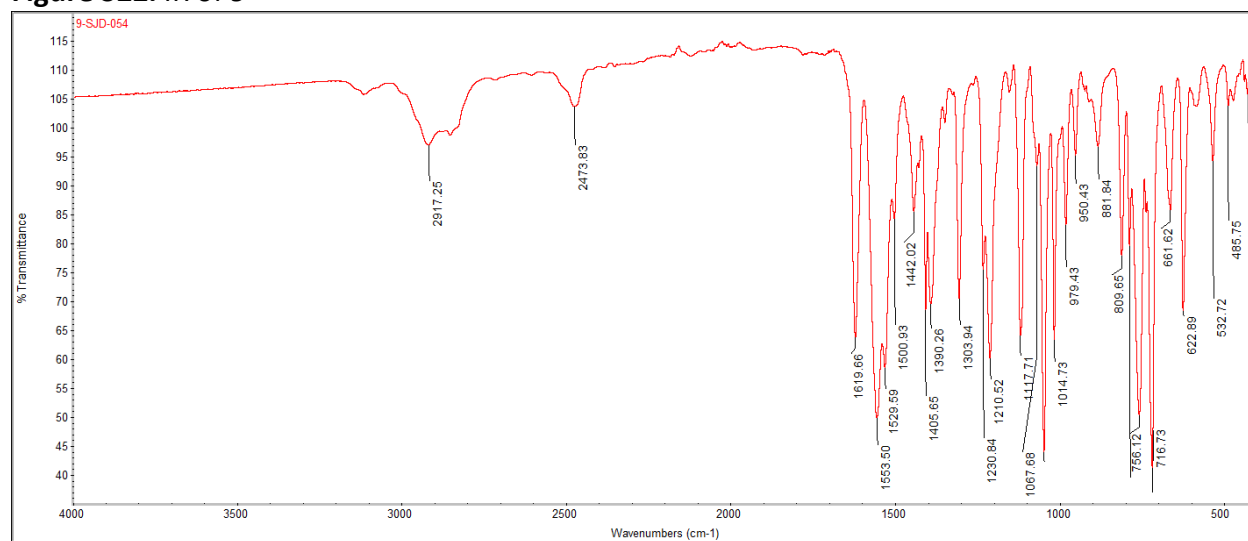


Figure S22. IR of 9



Mo_RTp(NO)(DMAP)(η^2 -*R*-limonene) (*R,R*)- 9A

Figure S23. ¹H NMR (CD₂Cl₂) of *R*_{Mo},*R*-9A (unidentified side product present)

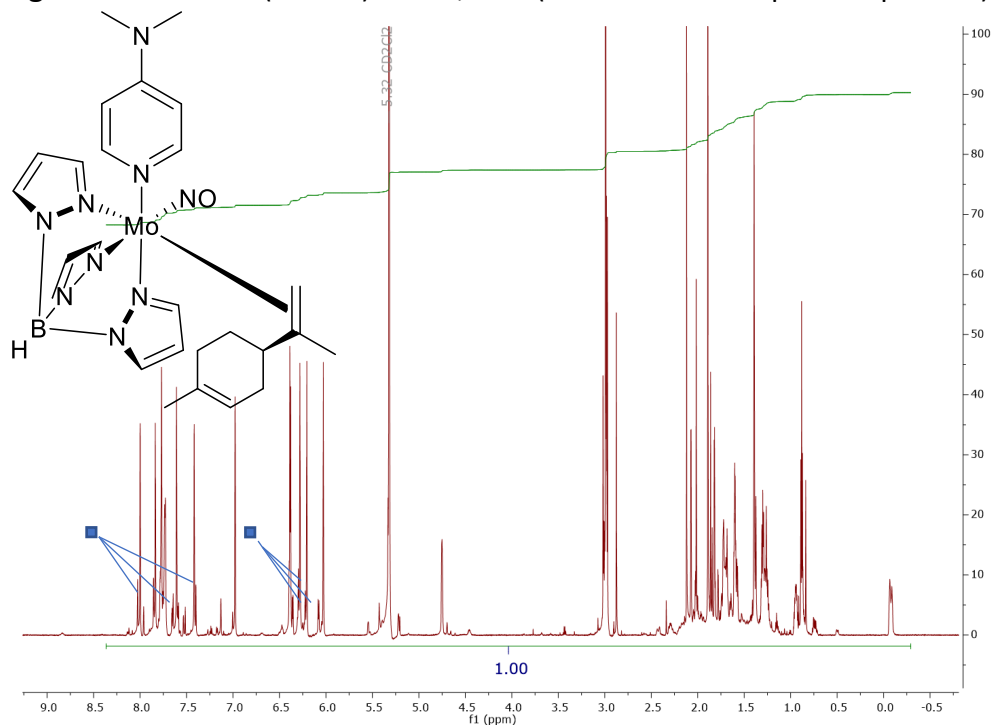
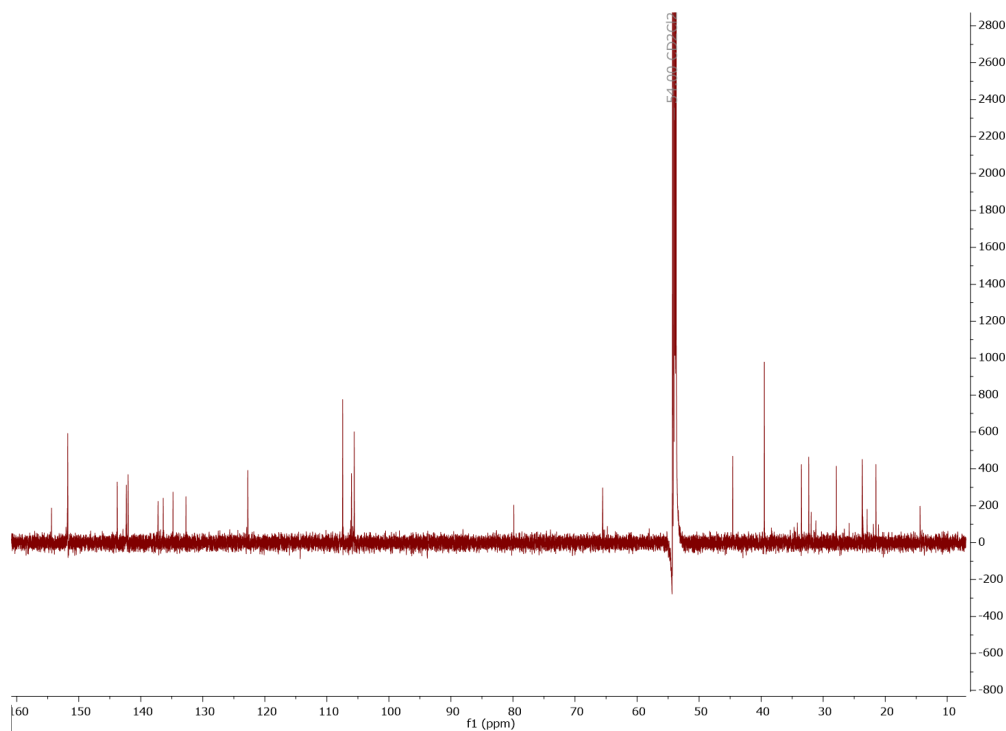


Figure S24. ¹³C NMR (CD₂Cl₂) of *R*_{Mo},*R*-9A (unidentified side product present)



Mo₅Tp(NO)(DMAP)(η^2 -*R*-limonene) (*S,R*)- 9A

Figure S25. ¹H NMR (CD₂Cl₂) of *S*_{Mo},*R*-9A (unidentified side product present)

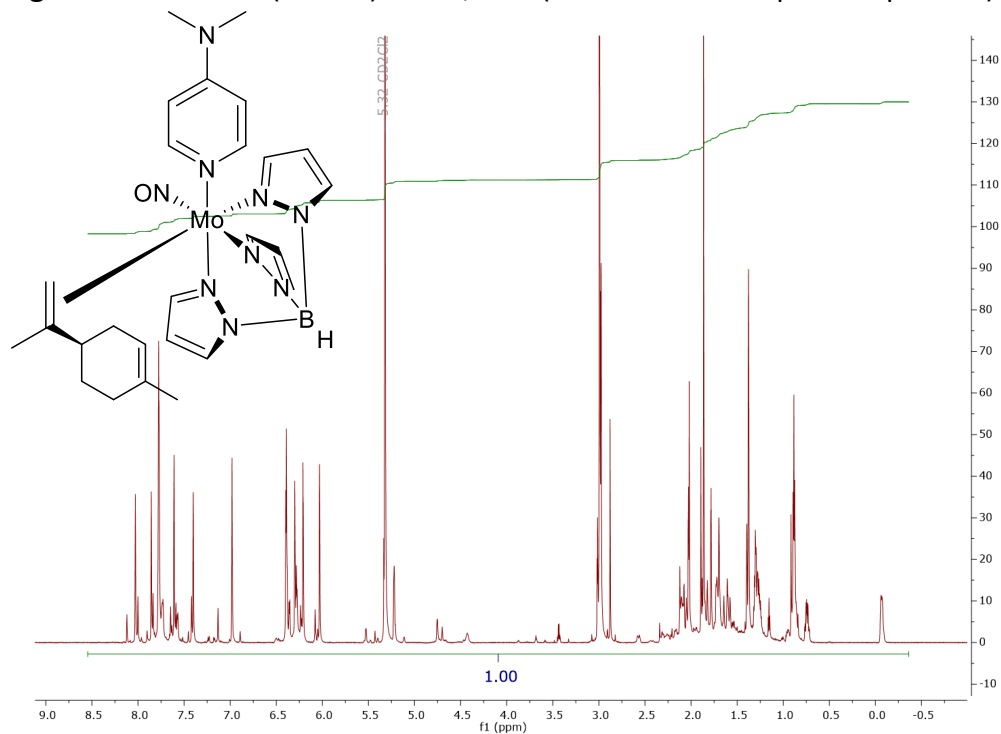
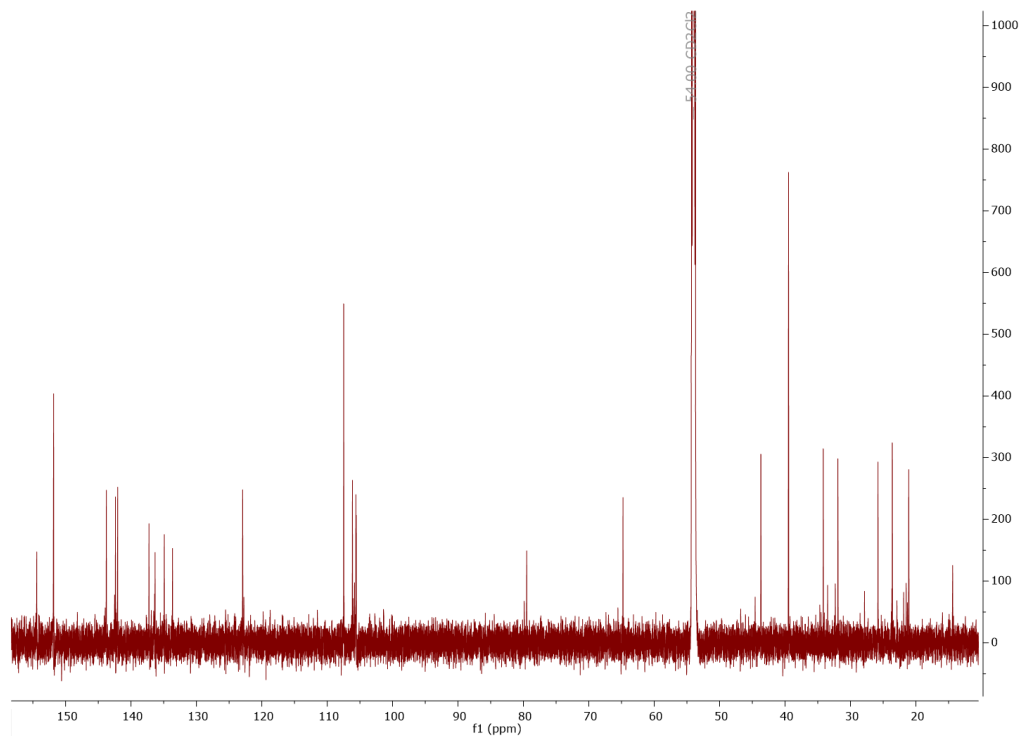


Figure S26. ¹³C NMR (CD₂Cl₂) of *S*_{Mo},*R*-9A (unidentified side product present)



WTp(NO)(PMe₃)(η^2 -*R*-limonene) (*R,R*)- **10A** and (*S,R*)- **10A**

Figure S27. ¹H NMR (d⁶-Acetone) of **10**

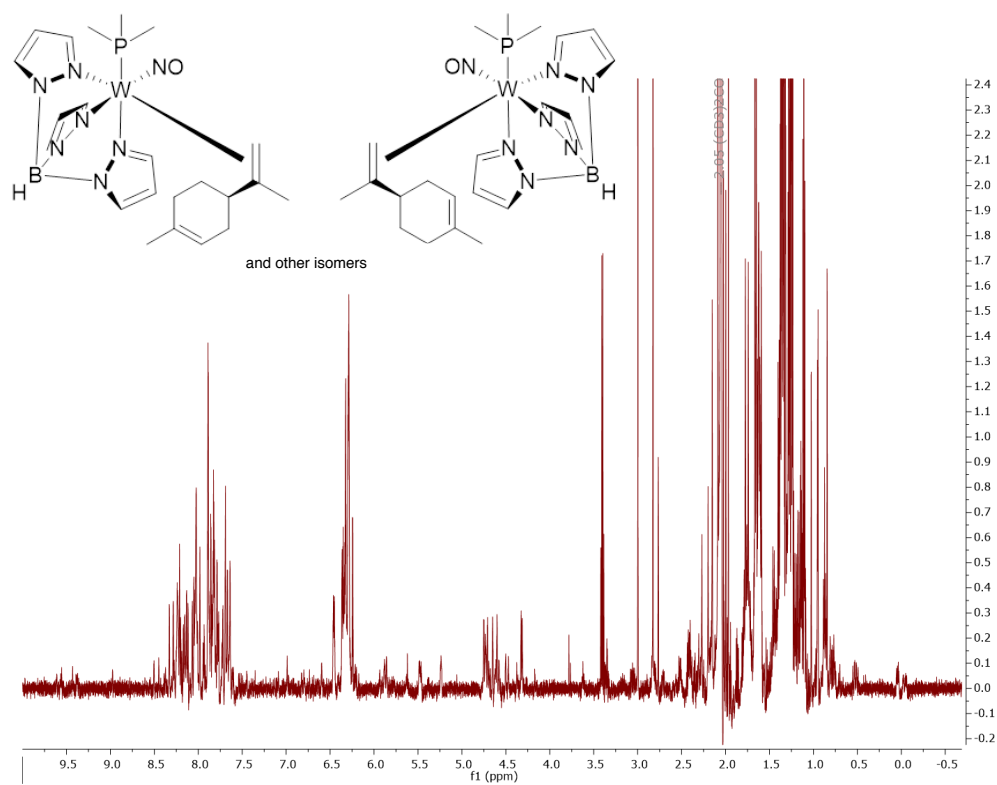


Figure S28. CV of 10

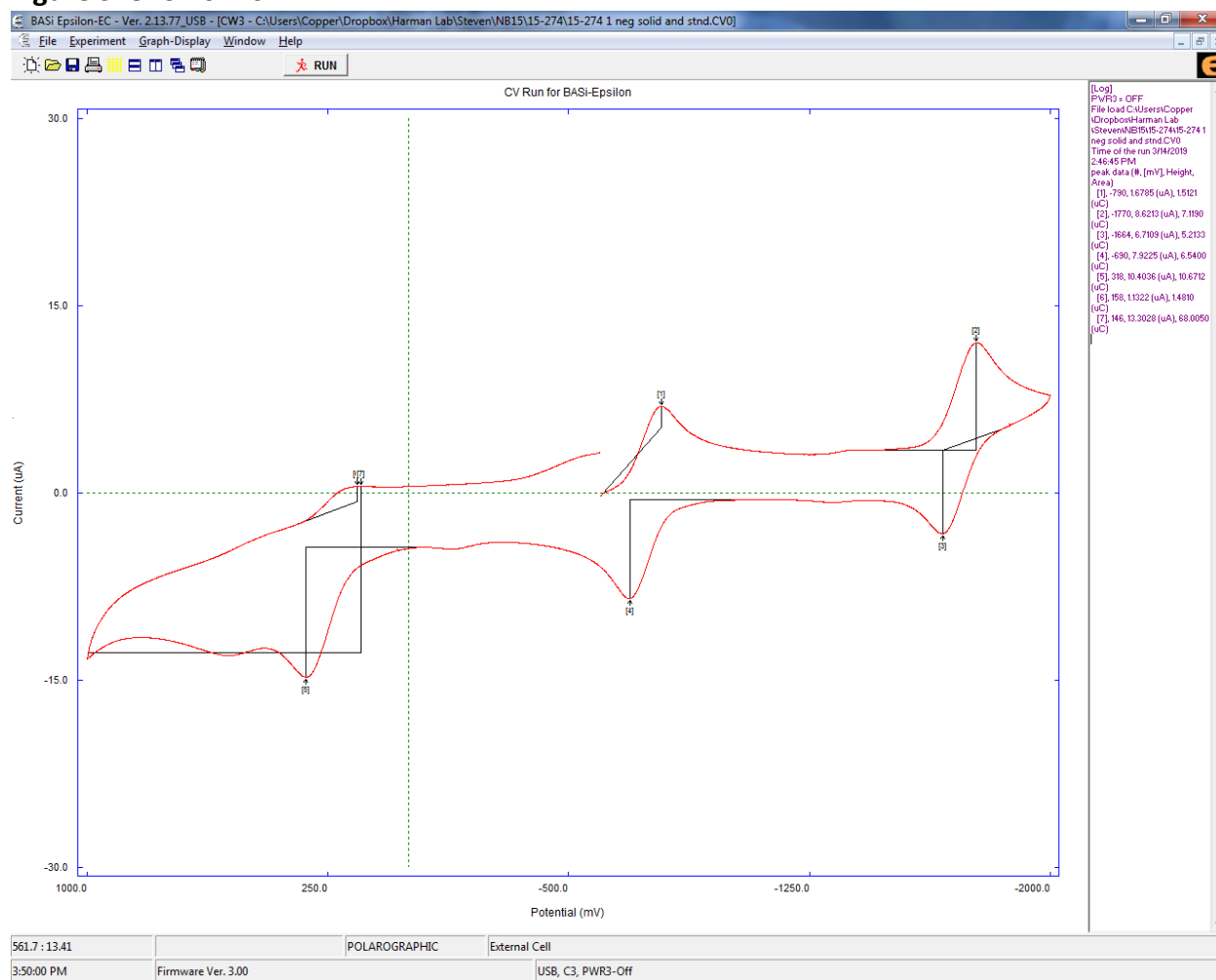


Figure S29. IR of 10

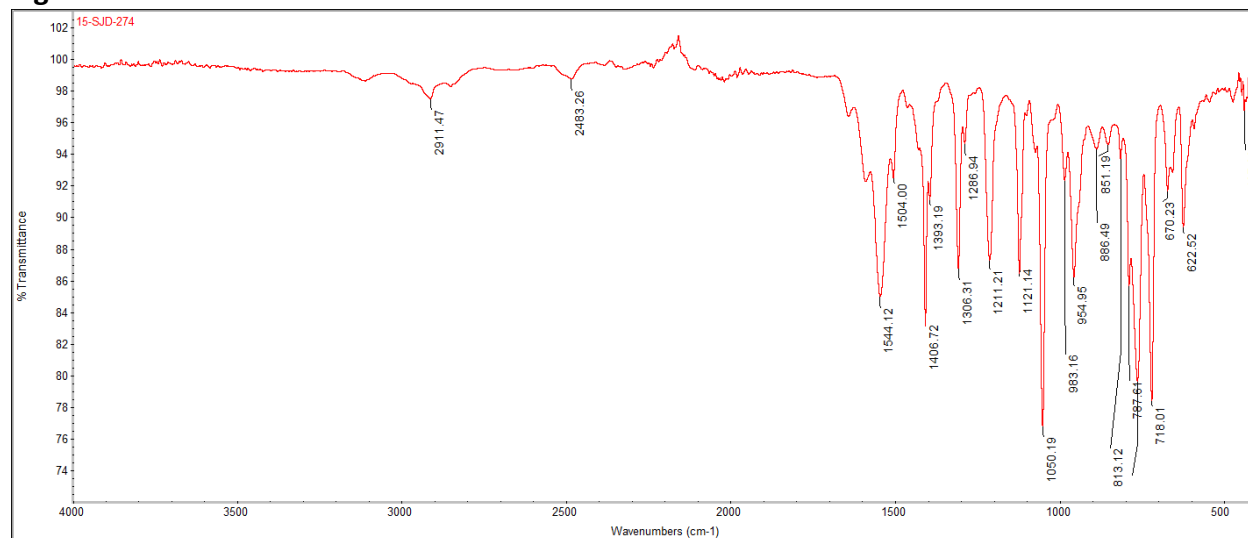


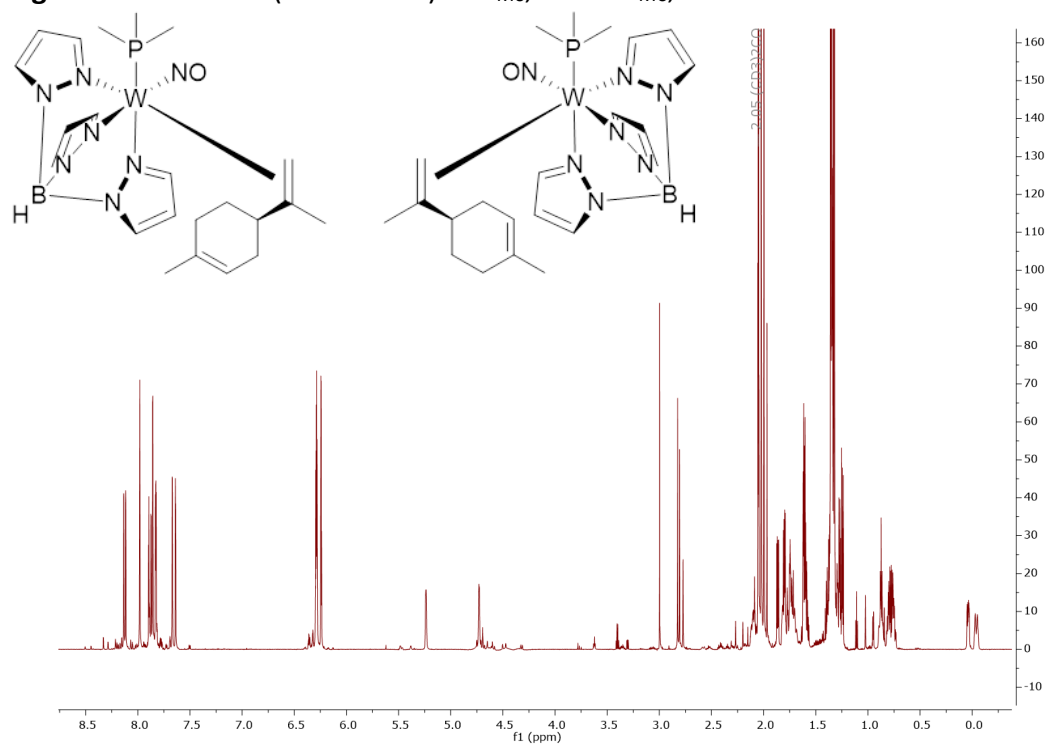
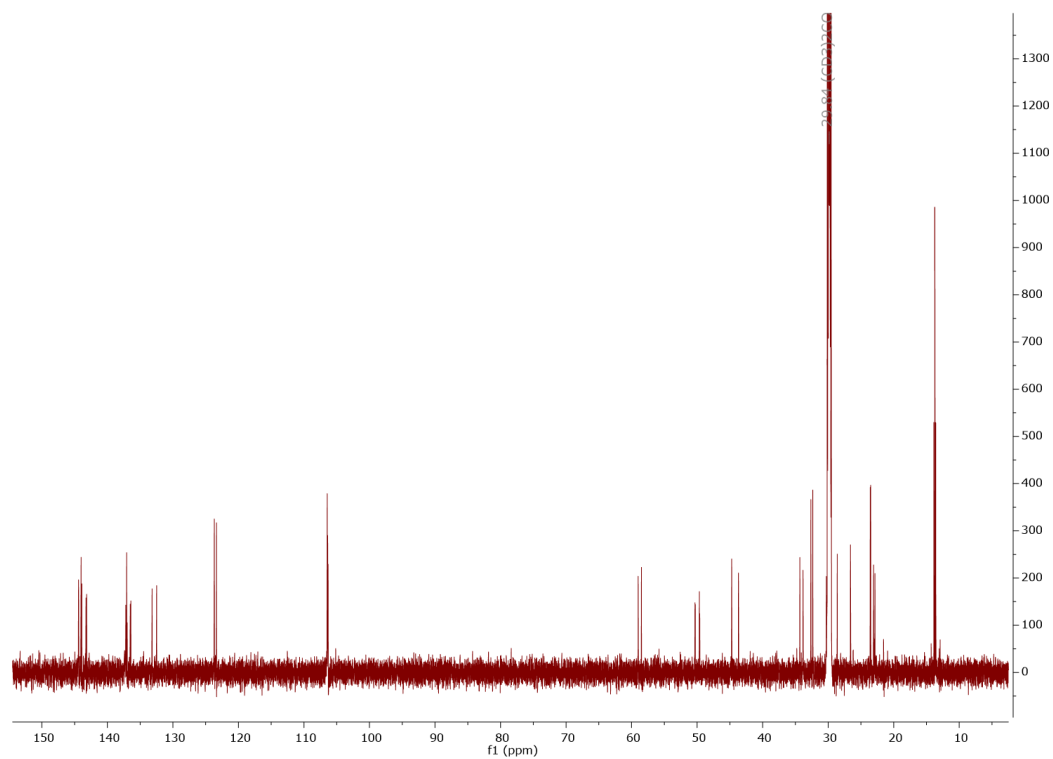
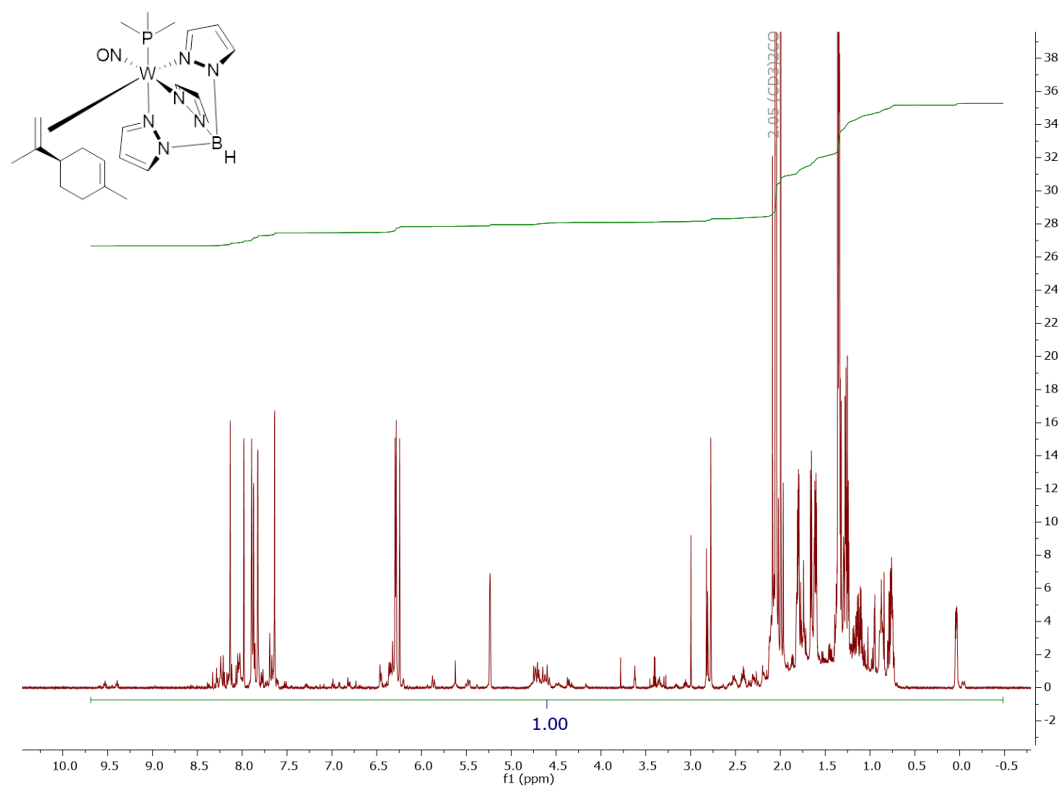
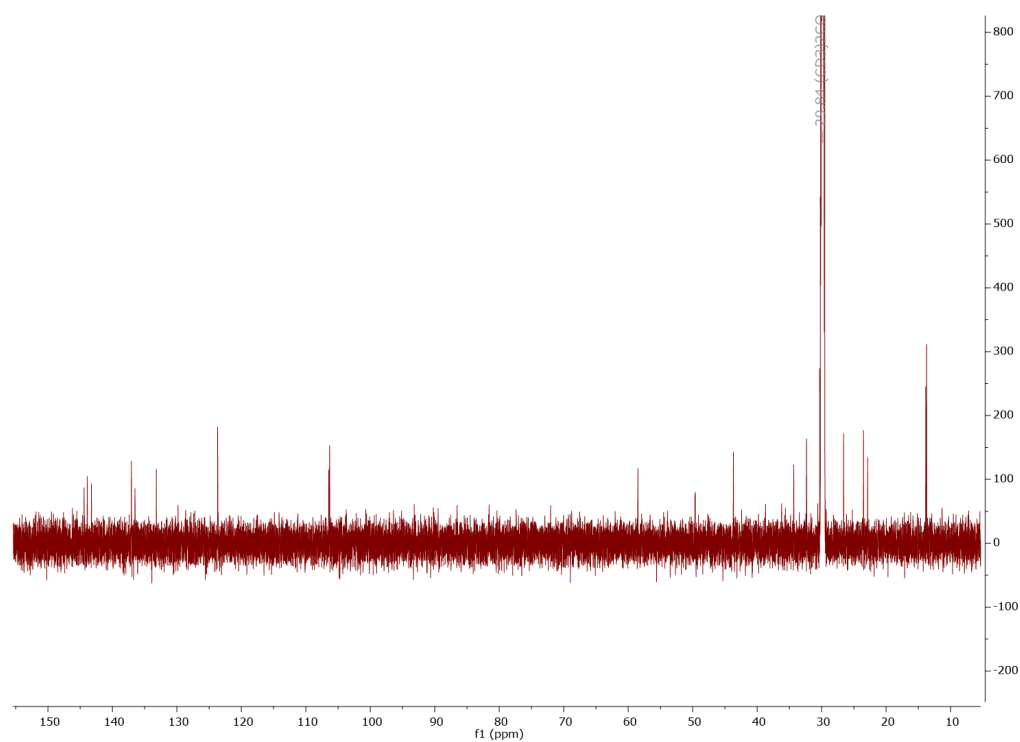
Figure S30. ^1H NMR (d^6 -Acetone) of R_{Mo},R - and S_{Mo},R - **10A****Figure S31.** ^{13}C NMR (d^6 -Acetone) of R_{Mo},R - and S_{Mo},R - **10A**

Figure S32. ^1H NMR (d^6 -Acetone) of S_{Mo},R - **10A****Figure S33.** ^{13}C NMR (d^6 -Acetone) of S_{Mo},R - **10A**

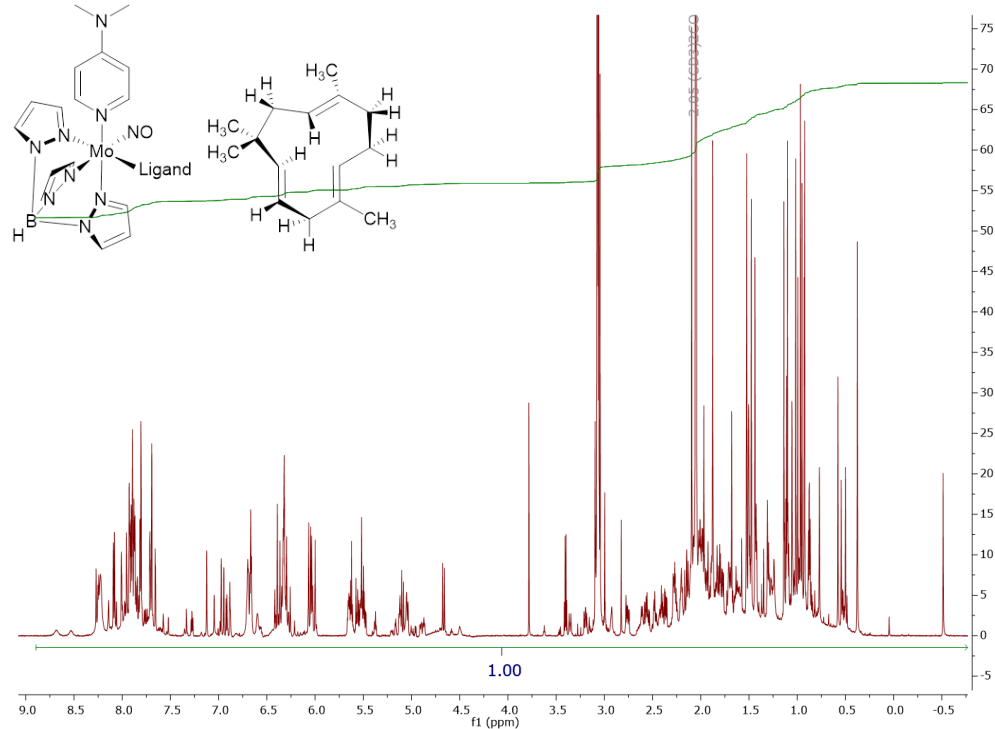
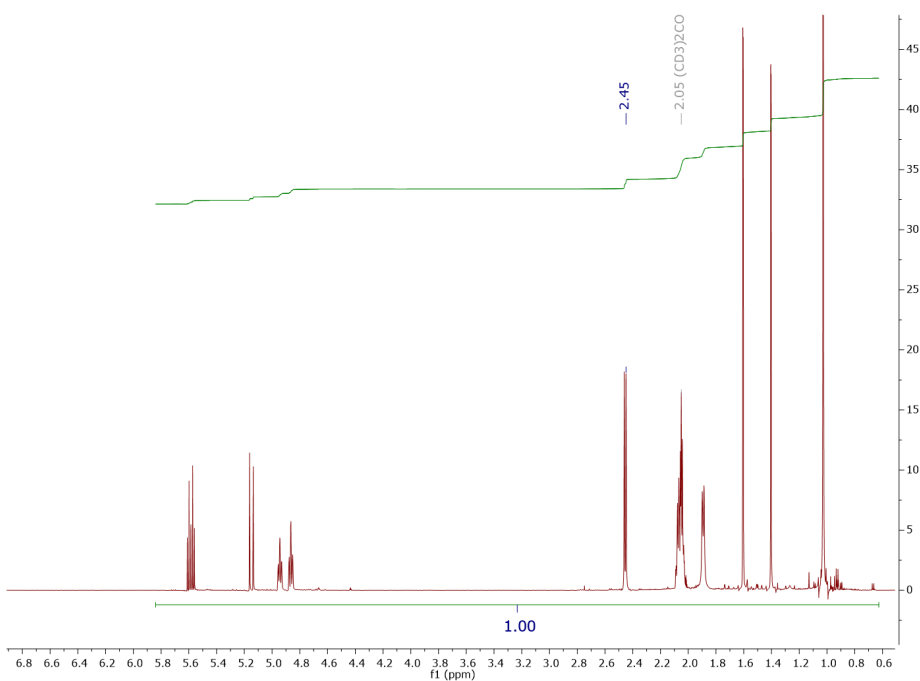
MoTp(NO)(DMAP)(η^2 - α -humulene) (12)**Figure S34.** ^1H NMR (d^6 -Acetone) of **12** mixture of Isomers**Figure S35.** ^1H NMR (d^6 -Acetone) of α -Humulene

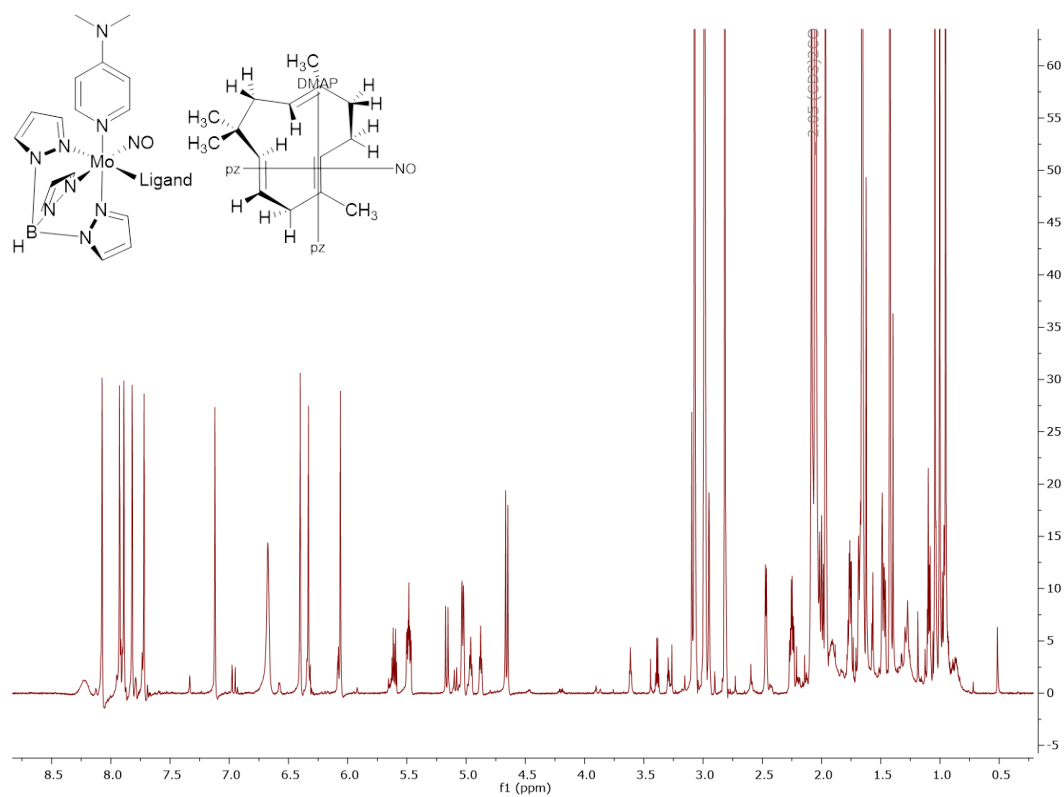
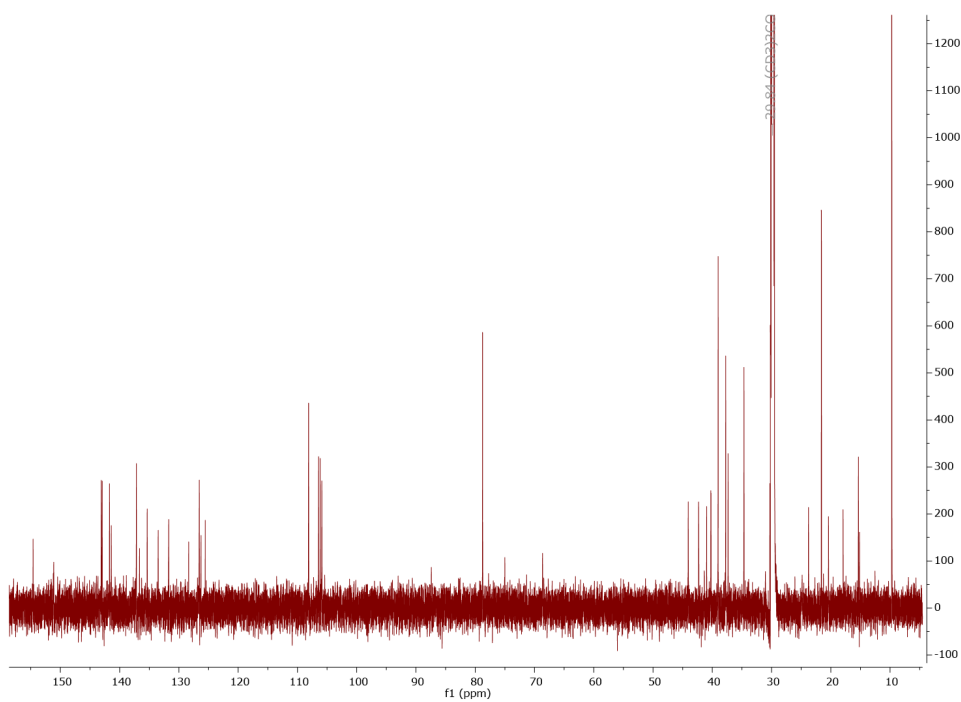
Figure S36. ^1H NMR (d^6 -Acetone) of **12A** (Free ligand impurity in sample)**Figure S37.** ^{13}C NMR (d^6 -Acetone) of **12A** (Free ligand impurity in sample)

Figure S38. CV of 12

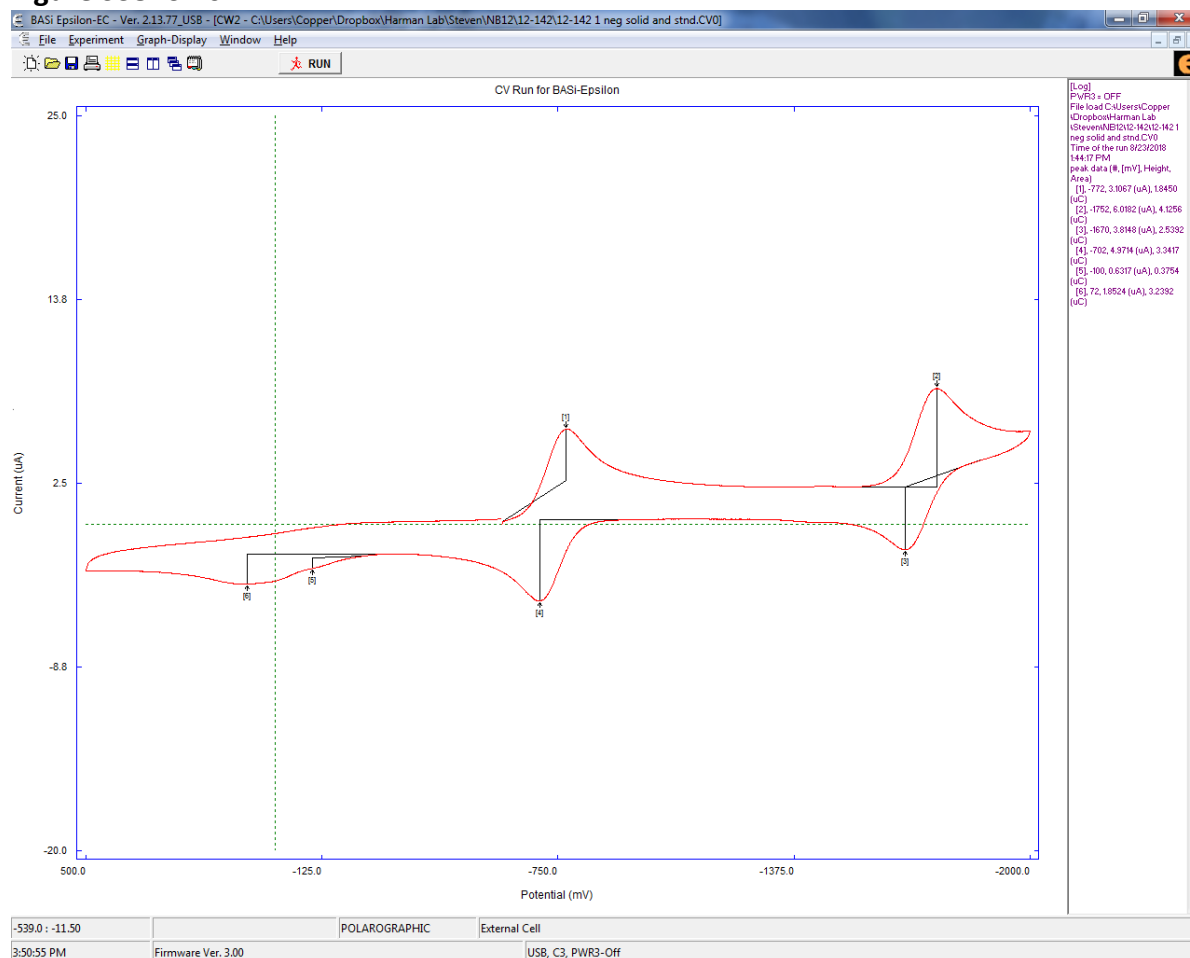
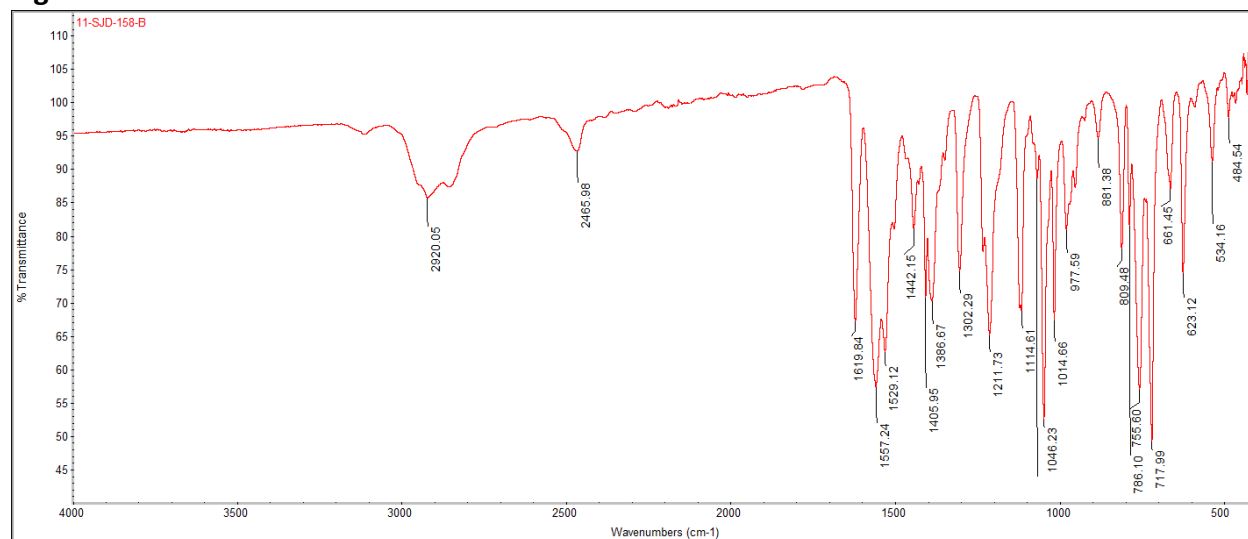


Figure S39. IR of 12



(MoTp(NO-Me)(DMAP)(η^2 - α -Humulene))(OTf) (12A**•CH₃)**

Figure S40. ¹H NMR (d⁶-Acetone) of **12A** • Me (impure due to decomposition and free ligand ejection)

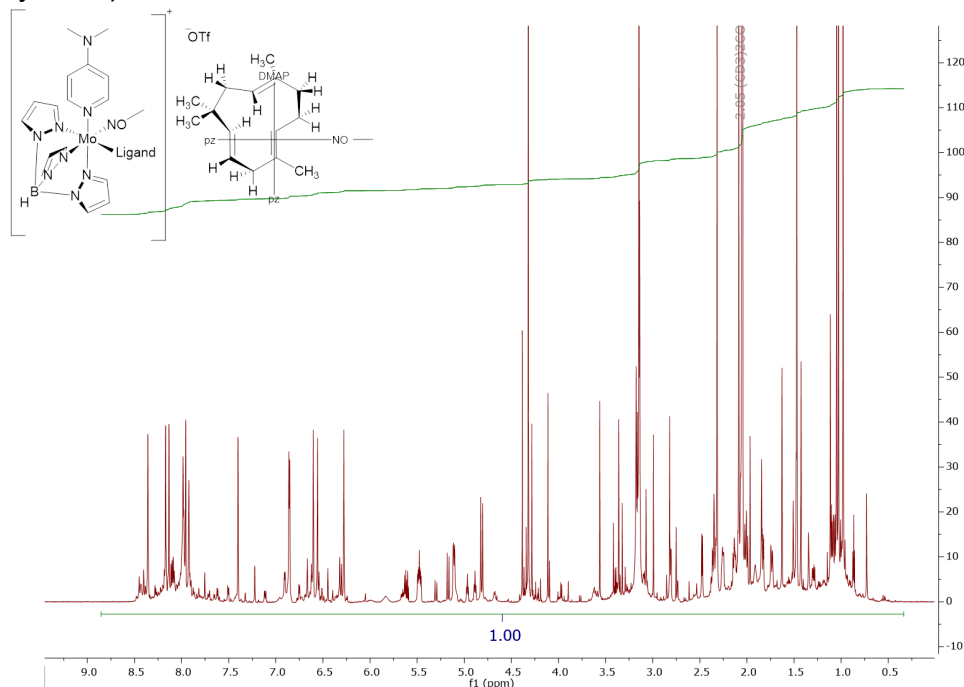


Figure S41. ¹³C NMR (d⁶-Acetone) of **12A** • Me (Marked peaks are complex, Free ligand impurity in sample)

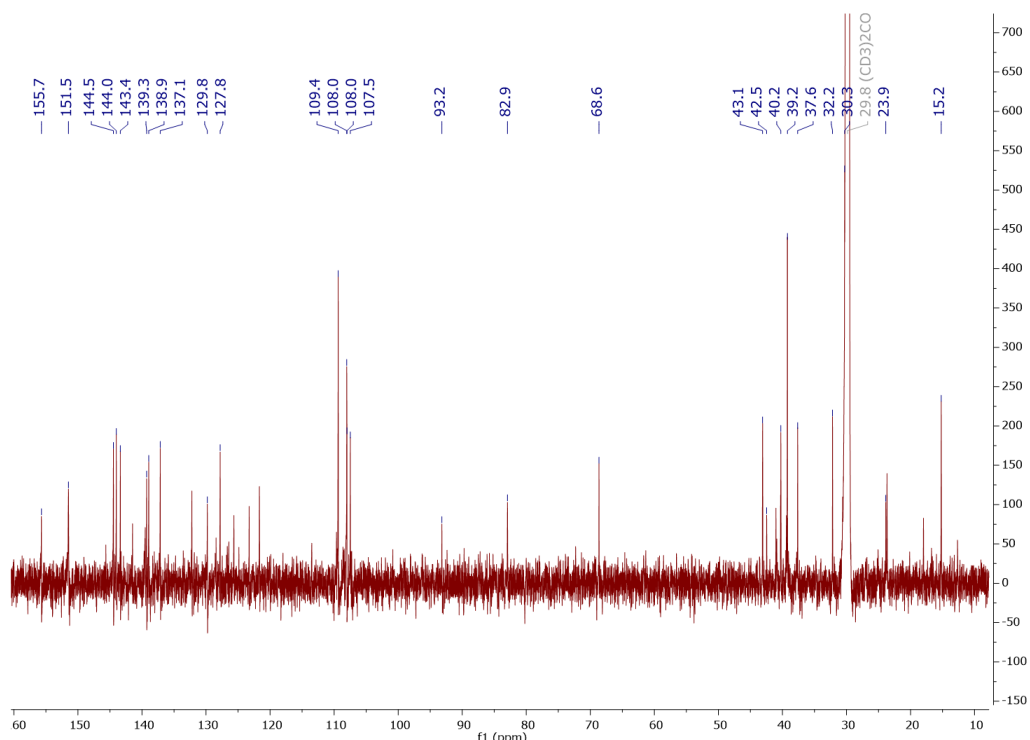


Figure S42. CV of 12A • Me

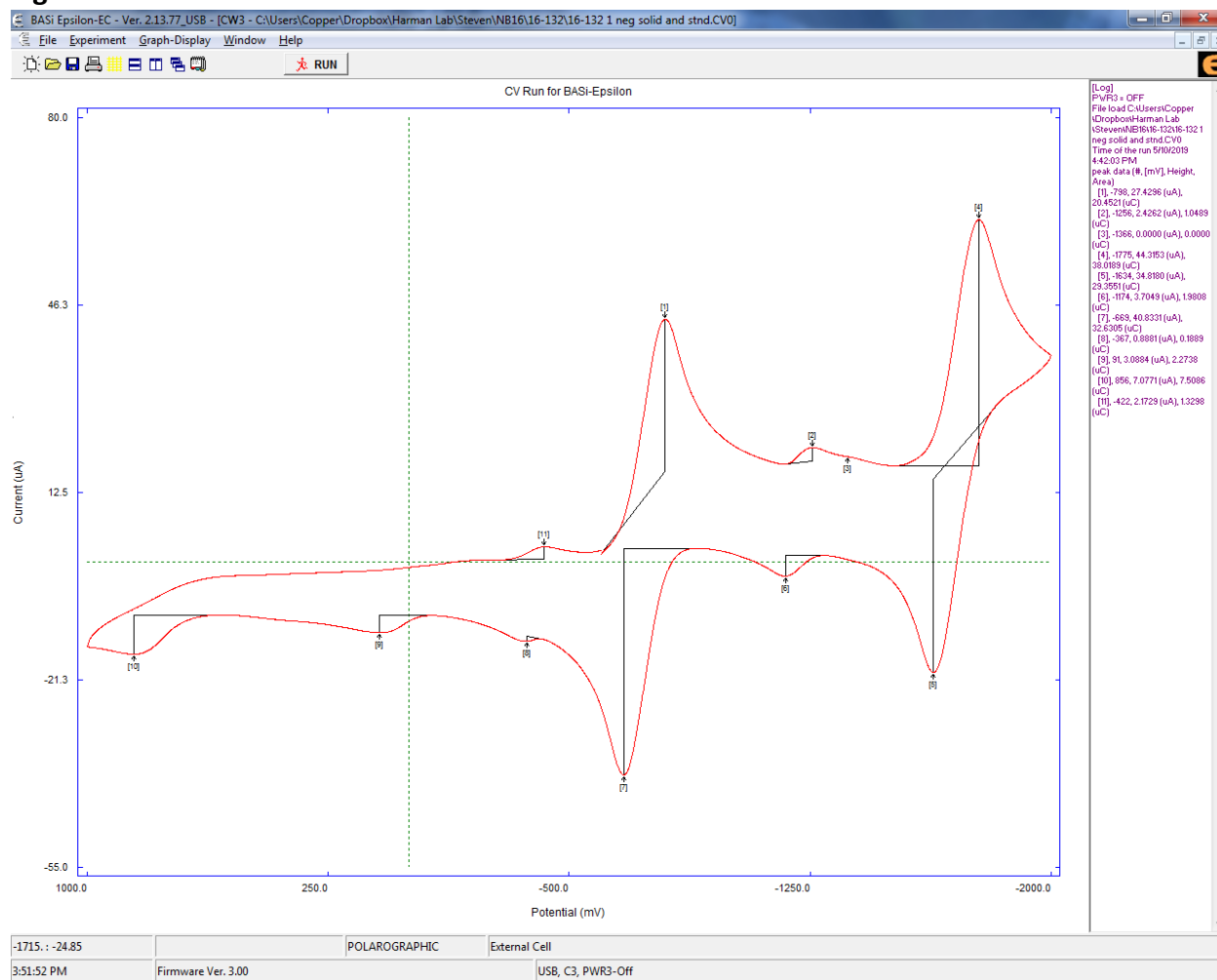
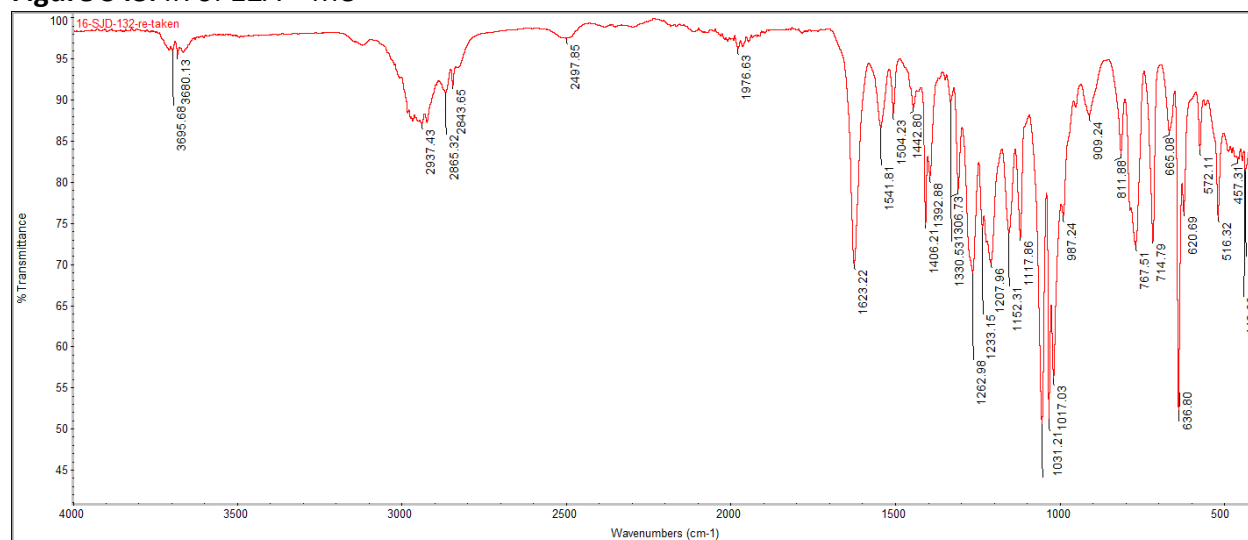


Figure S43. IR of 12A • Me



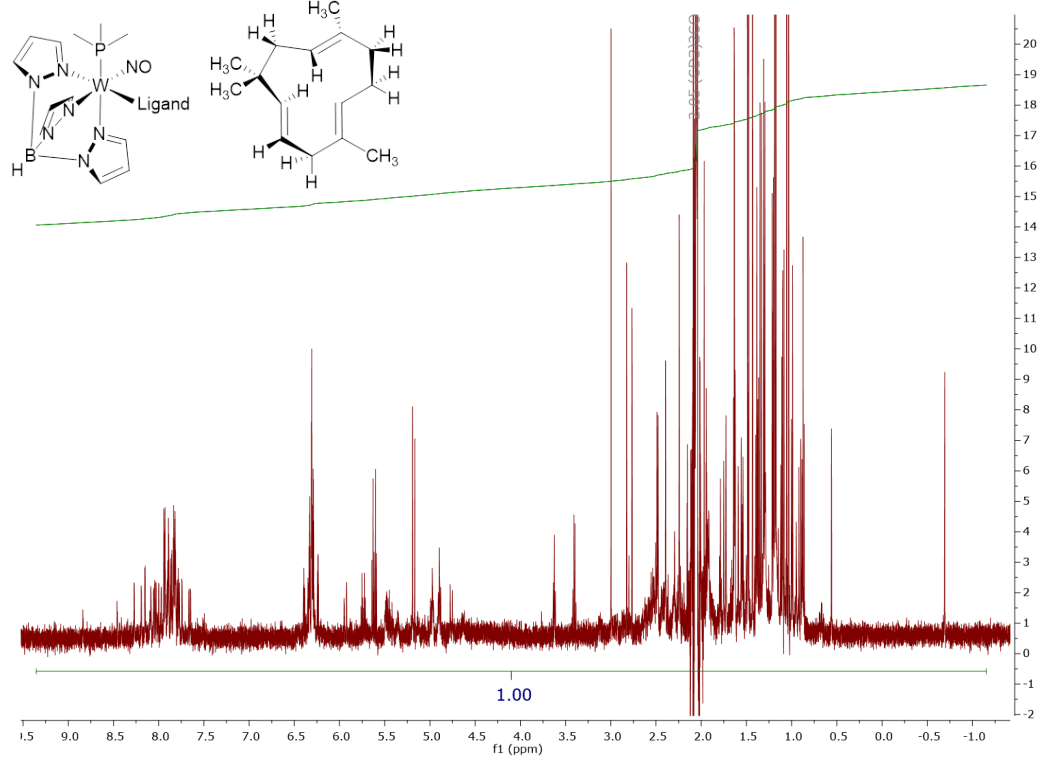
WTP(NO)(PMe₃)(η^2 α -humulene) (13)**Figure S44.** ¹H NMR (d⁶-Acetone) of **13**, mix of isomers

Figure S45. CV of 13

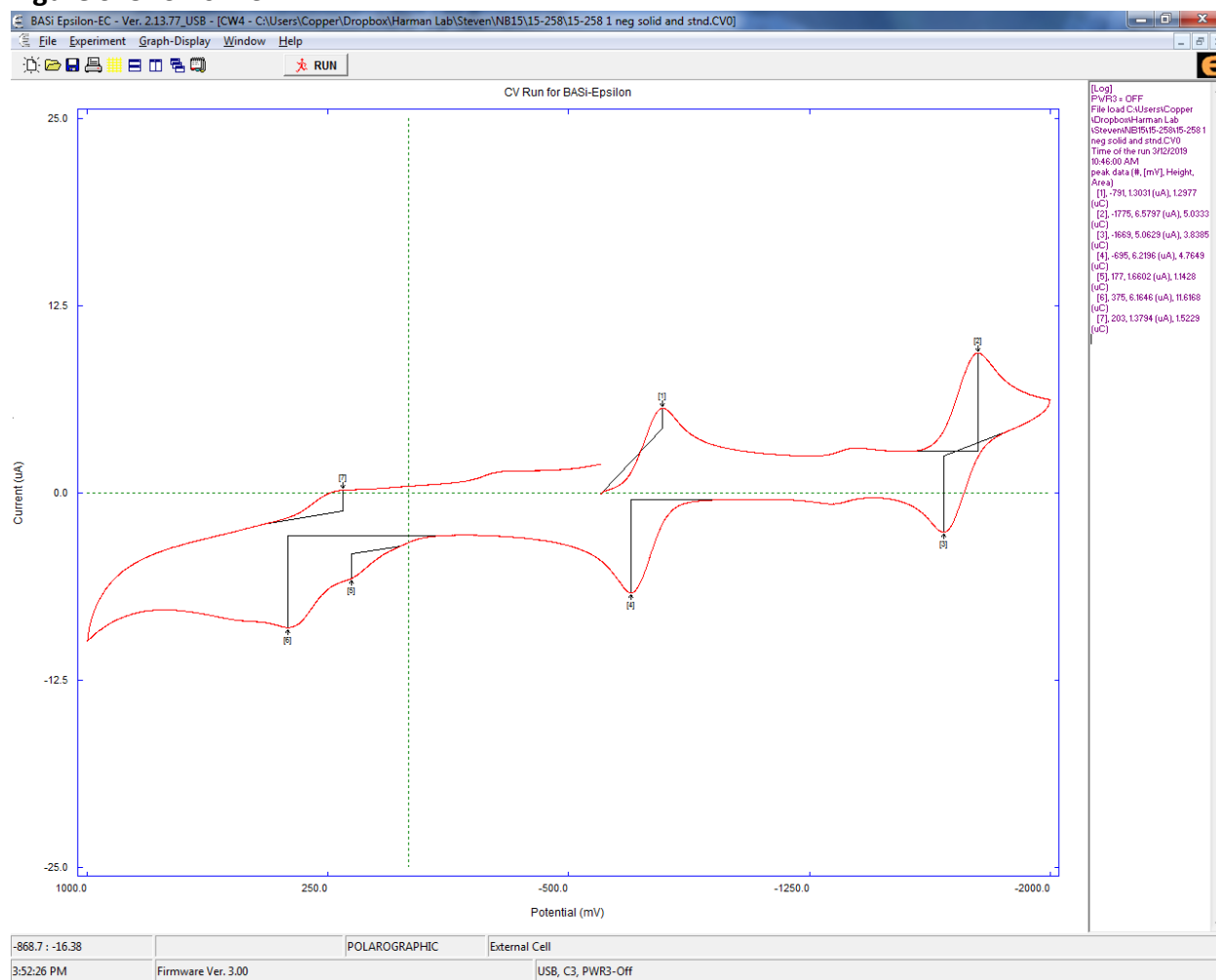


Figure S46. IR of 13

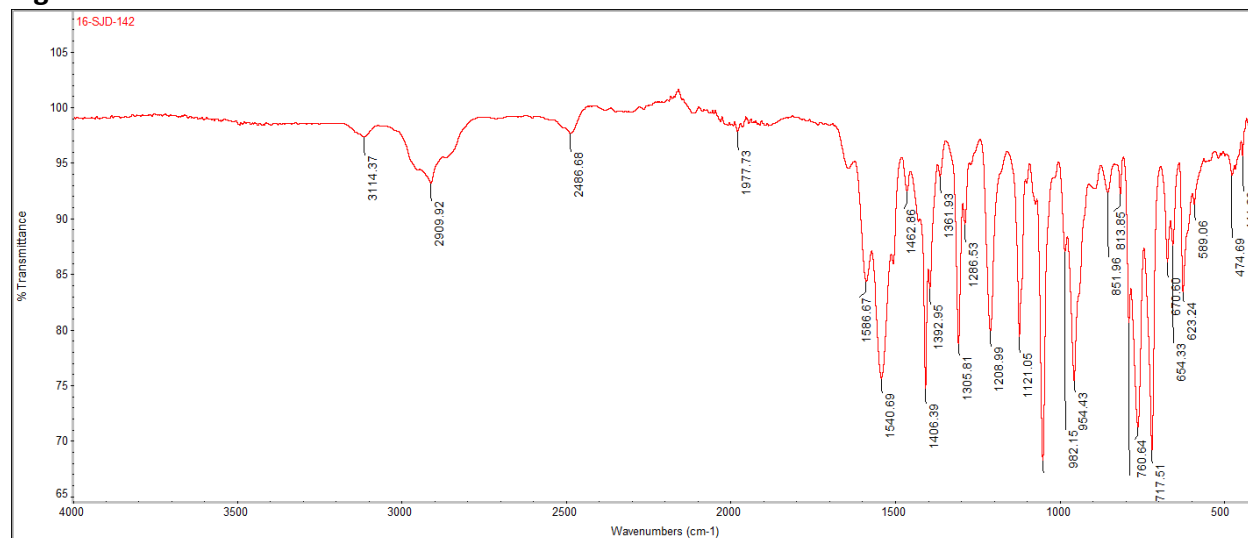


Figure S47. ^1H NMR (d^6 -Acetone) of **13A** (Singlet at 1.65 is permethylferrocene impurity and some free ligand is present)

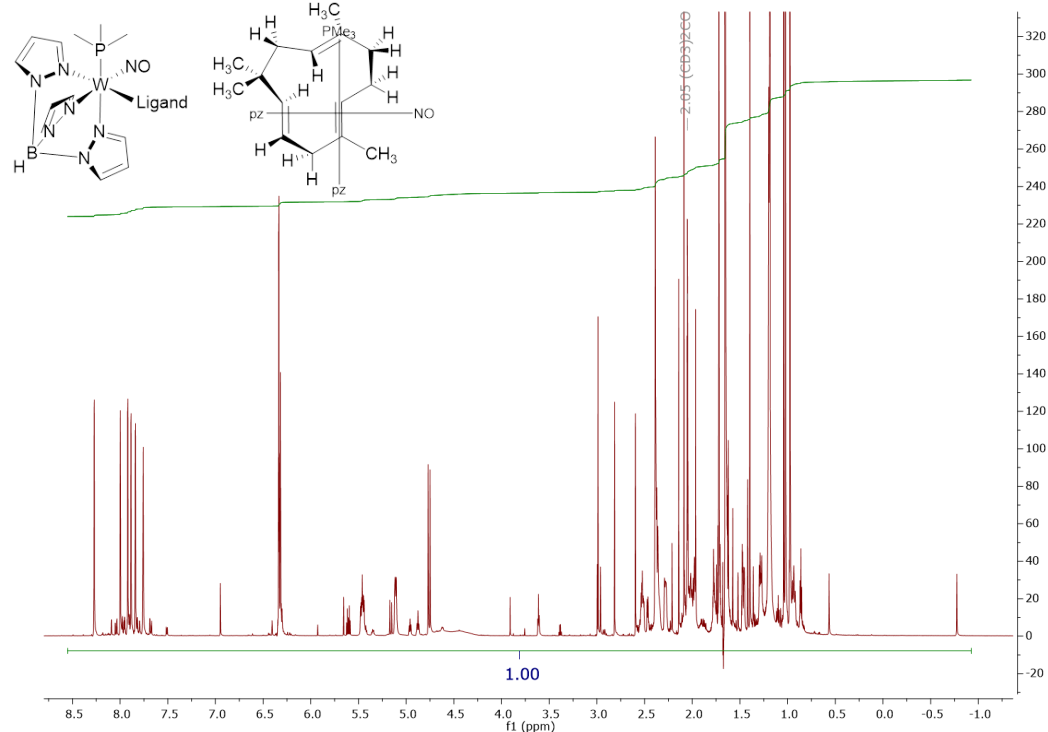
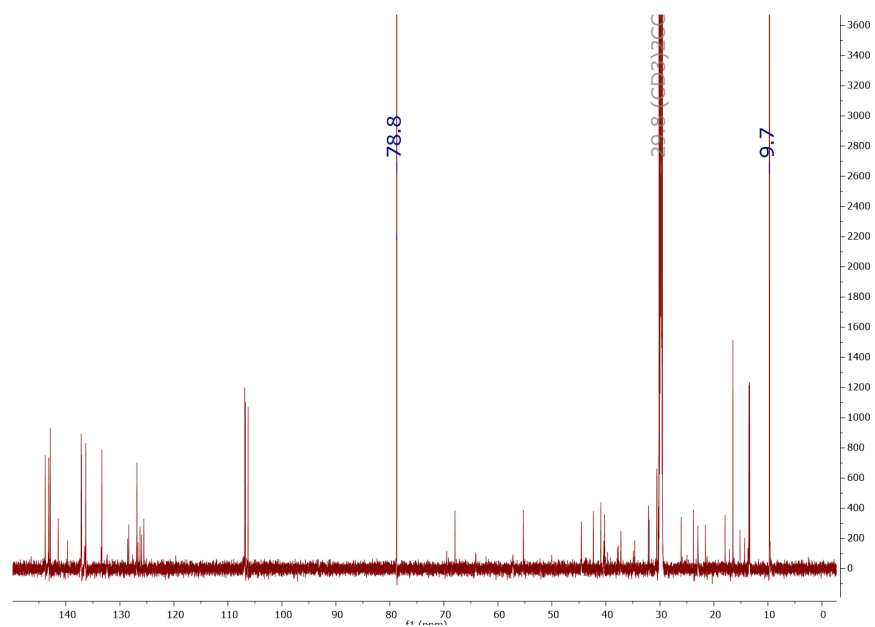
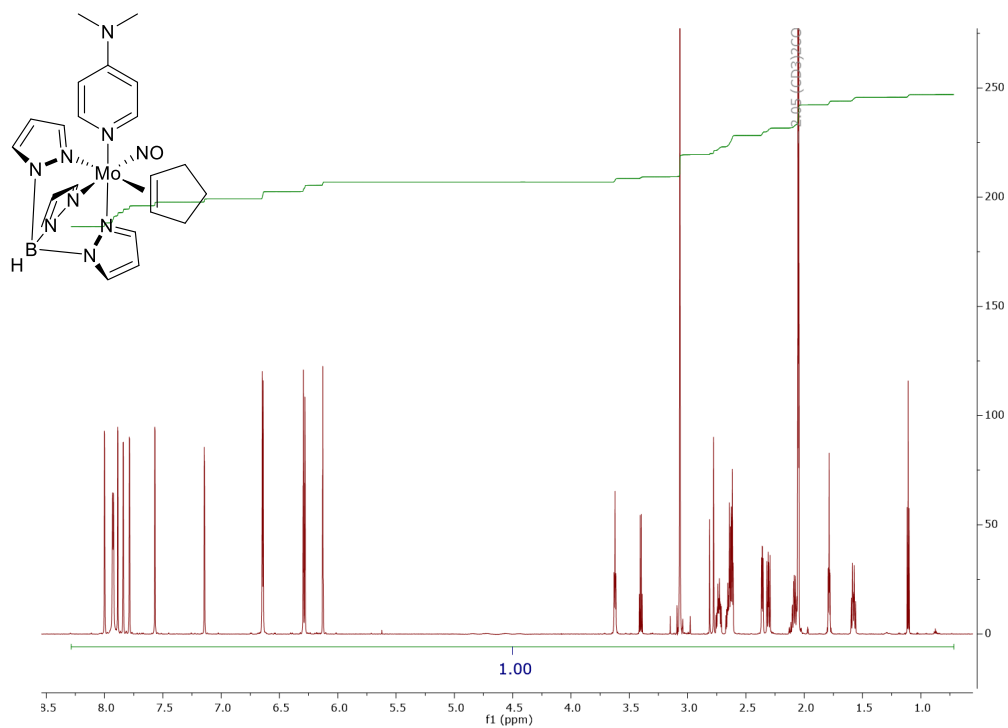
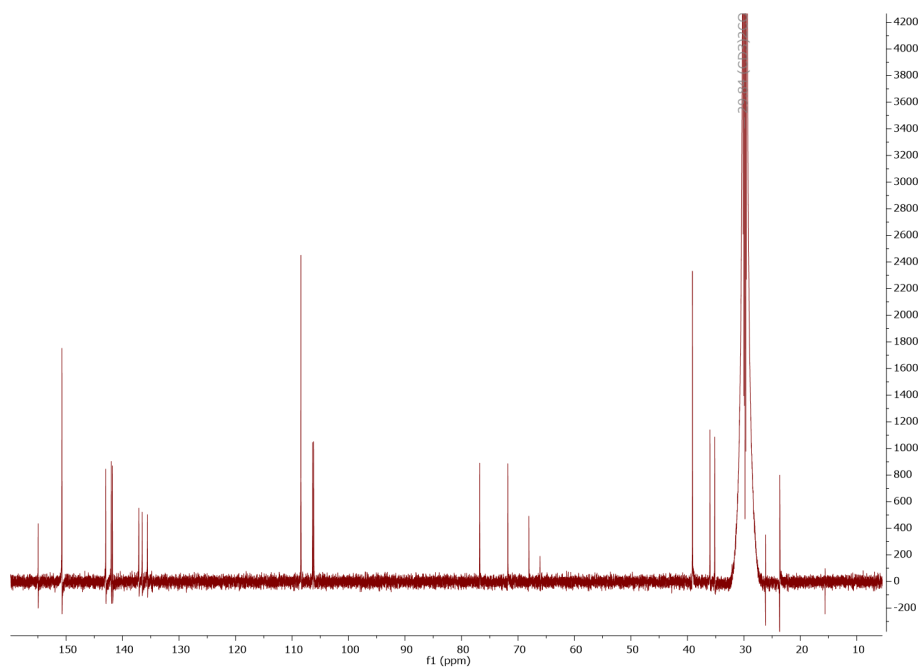
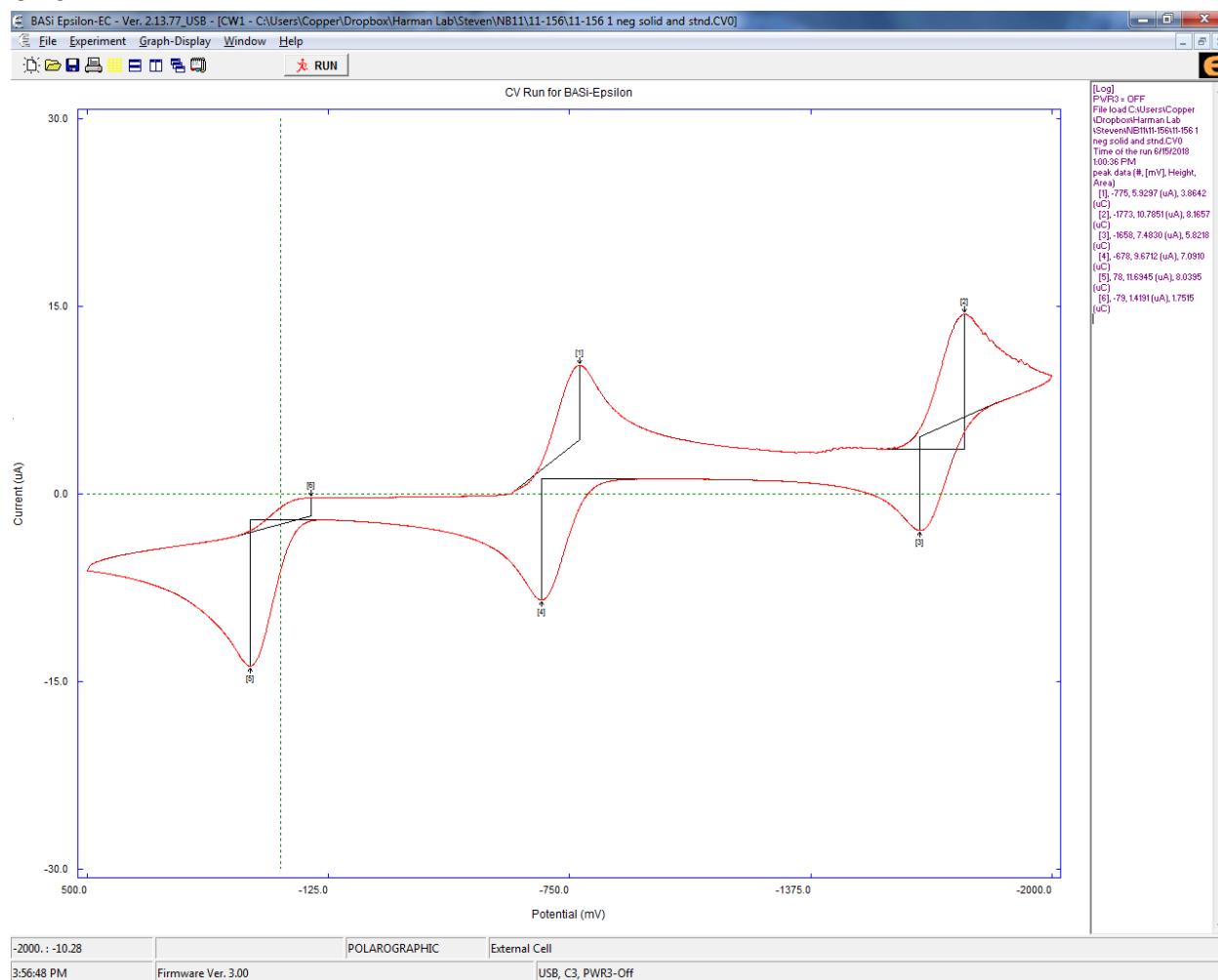


Figure S48. ^{13}C NMR (d^6 -Acetone) of **13A** (Signals marked are permethylferrocene impurity and some free ligand is present)

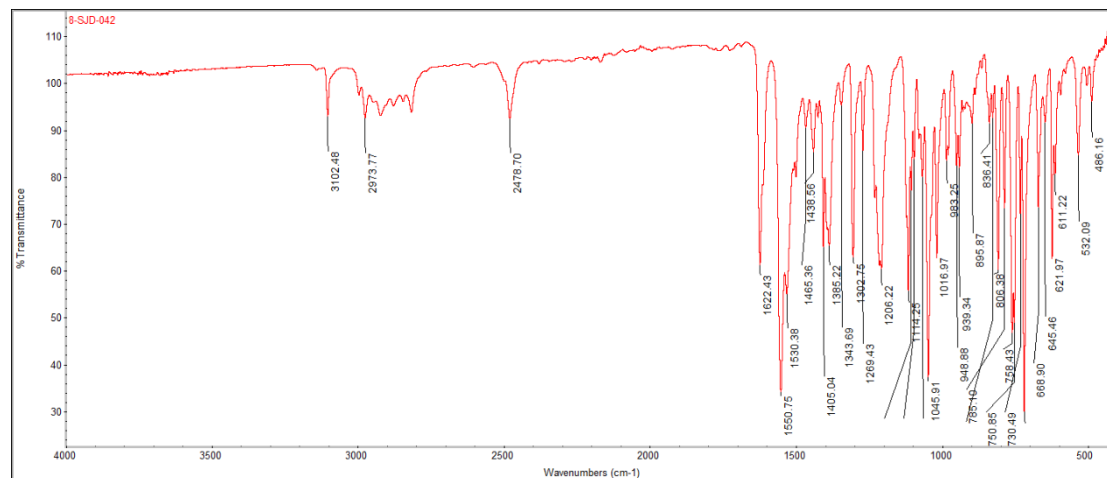


MoTp(NO)(DMAP)(η^2 -Cyclopentene) (14)**Figure S49.** ^1H NMR (d^6 -Acetone) of **14****Figure S50.** ^{13}C NMR (d^6 -Acetone) of **14**

CV of 14



IR of 14



Crystallography supporting information

Single crystals of **9a** and **14** were coated with Paratone oil and mounted on a MiTeGen MicroLoop. The X-ray intensity data were measured on a Bruker Kappa APEXII Duo system equipped with a graphite monochromator and a Mo K α fine-focus sealed tube ($\lambda = 0.71073$ Å). The frames were integrated with the Bruker SAINT software package¹ using a narrow-frame algorithm. Data were corrected for absorption effects using the Multi-Scan method (SADABS).¹ The structure was solved and refined using the Bruker SHELXTL Software Package² within APEX3¹ and OLEX2.³ Non-hydrogen atoms were refined anisotropically. The B-H hydrogen atom in **9a-centro** and **14** were located in the diffraction map and refined isotropically. All other hydrogen atoms were placed in geometrically calculated positions with $U_{iso} = 1.2U_{equiv}$ of the parent atom ($U_{iso} = 1.5 U_{equiv}$ for methyl).

In **9Acentro**, two carbon atoms of the limonene fragment were found to be disordered. The relative occupancies were freely refined, converging at 52/48 for the major and minor orientations of the limonene respectively. No constraints or restraints were used. The co-crystallized pentane solvent in **9Acentro** was disordered by symmetry and was refined with constraints on the thermal displacement parameters of the disordered atoms and restraints on the disordered bond lengths. In **9A-noncentro**, Non-hydrogen atoms were refined anisotropically with EADP constraints on most of the pseudo-symmetrically related atoms. During the refinement of **14**, electron density difference maps revealed that there was disordered solvent that could not be successfully modeled with or without restraints. Thus, the structure factors were modified using the PLATON SQUEEZE⁴ technique, in order to produce a “solvate-free” structure factor set. PLATON reported a total electron density of 88 e⁻ and total solvent accessible volume of 221 Å³, likely representing one dichloromethane molecule per asymmetric unit.

¹ Bruker (2012). *Saint*; *SADABS*; *APEX3*. Bruker AXS Inc., Madison, Wisconsin, USA.

² Sheldrick, G. M. (2015). *Acta Cryst.* **A71**, 3-8.

³ Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* (2009). **42**, 339-341.

⁴ Spek, A. L. *Acta Crystallogr. Sect C: Struct. Chem.* **2015**, *C71*, 9-18.

Crystal Data **Table S1.**

	9A (centrosymmetric)	9A (non-centrosym)	14
CCDC	1971582	1971583	1971584
Chemical formula	C ₅₇ H ₈₄ B ₂ Mo ₂ N ₁₈ O ₂	C ₅₇ H ₈₄ B ₂ Mo ₂ N ₁₈ O ₂	C ₂₁ H ₂₈ BMoN ₉ O
FW (g/mol)	1266.92	1266.92	529.27
T (K)	100(2)	100(2)	150(2)
Crystal size (mm)	0.060 x 0.106 x 0.285	0.040 x 0.076 x 0.202	0.254 x 0.488 x 0.548
Crystal habit	yellow rod	yellow plate	yellow block
Crystal system	triclinic	triclinic	monoclinic
Space group	P -1	P 1	P 2 ₁ /n
a (Å)	8.8194(6)	8.8141(7)	11.4512(8)
b (Å)	9.6136(7)	9.6056(8)	17.1393(12)
c (Å)	20.2847(16)	20.2594(16)	12.8859(9)
α (°)	85.461(2)	85.485(2)	90
β (°)	78.641(2)	78.635(2)	99.6970(10)
γ (°)	66.511(2)	66.512(2)	90
V (Å³)	1546.5(2)	1542.3(2)	2492.9(3)
Z	1	1	4
ρ_{calc} (g/cm³)	1.360	1.364	1.410
μ (mm⁻¹)	0.462	0.463	0.557
θ range (°)	2.05 to 26.41	2.05 to 28.34	2.00 to 29.60
Index ranges	-11 ≤ h ≤ 11 -12 ≤ k ≤ 12 -25 ≤ l ≤ 25	-11 ≤ h ≤ 11 -12 ≤ k ≤ 12 -27 ≤ l ≤ 26	-15 ≤ h ≤ 15 -23 ≤ k ≤ 22 -17 ≤ l ≤ 17
Reflns coll.	29888	57234	29694
Ind. rflns	6336 [R(int) = 0.0420]	15322 [R(int) = 0.0691]	6992 [R(int) = 0.0380]
Data / restraints / parameters	6336 / 28 / 413	15322 / 3 / 464	6992 / 0 / 304
Goodness-of-fit on F²	1.116	1.030	1.137
R₁ [I > 2σ(I)]	0.0303	0.0465	0.0319
wR₂ [all data]	0.0610	0.0877	0.0805