

Supporting Information

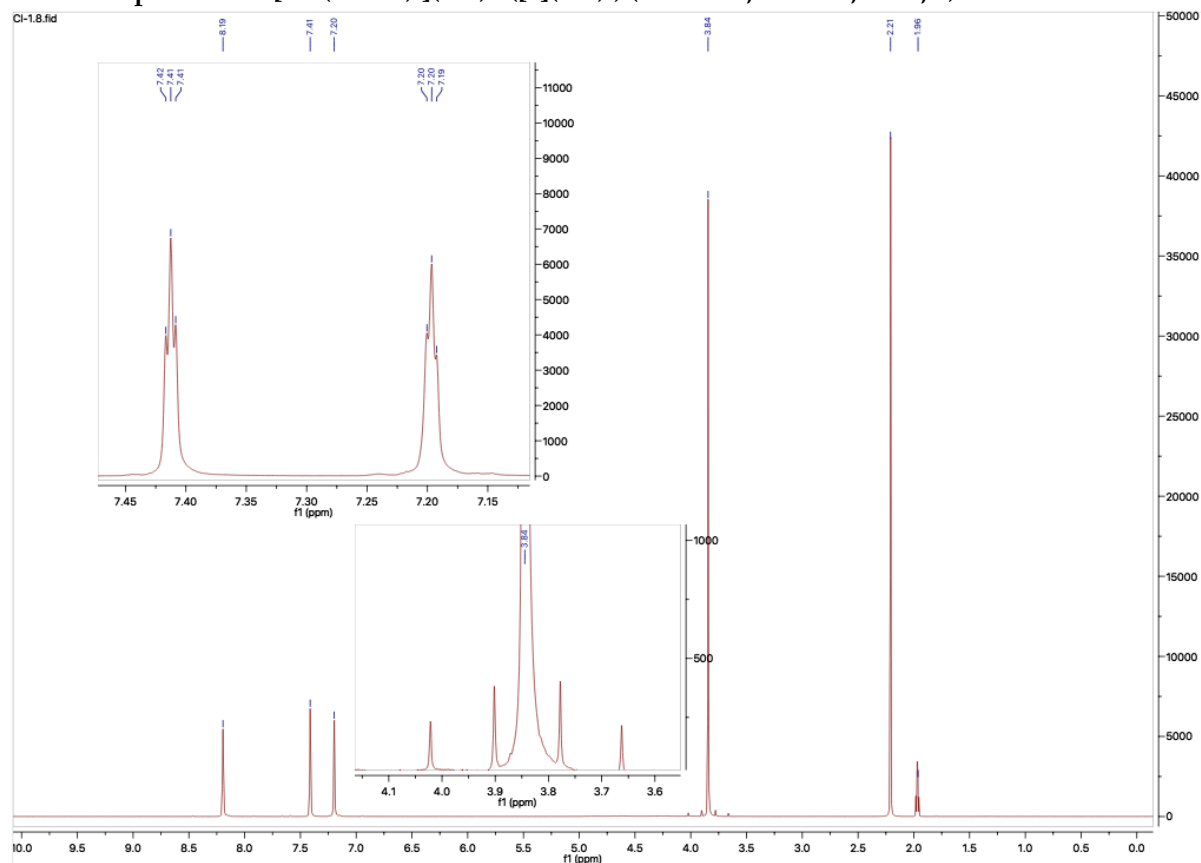
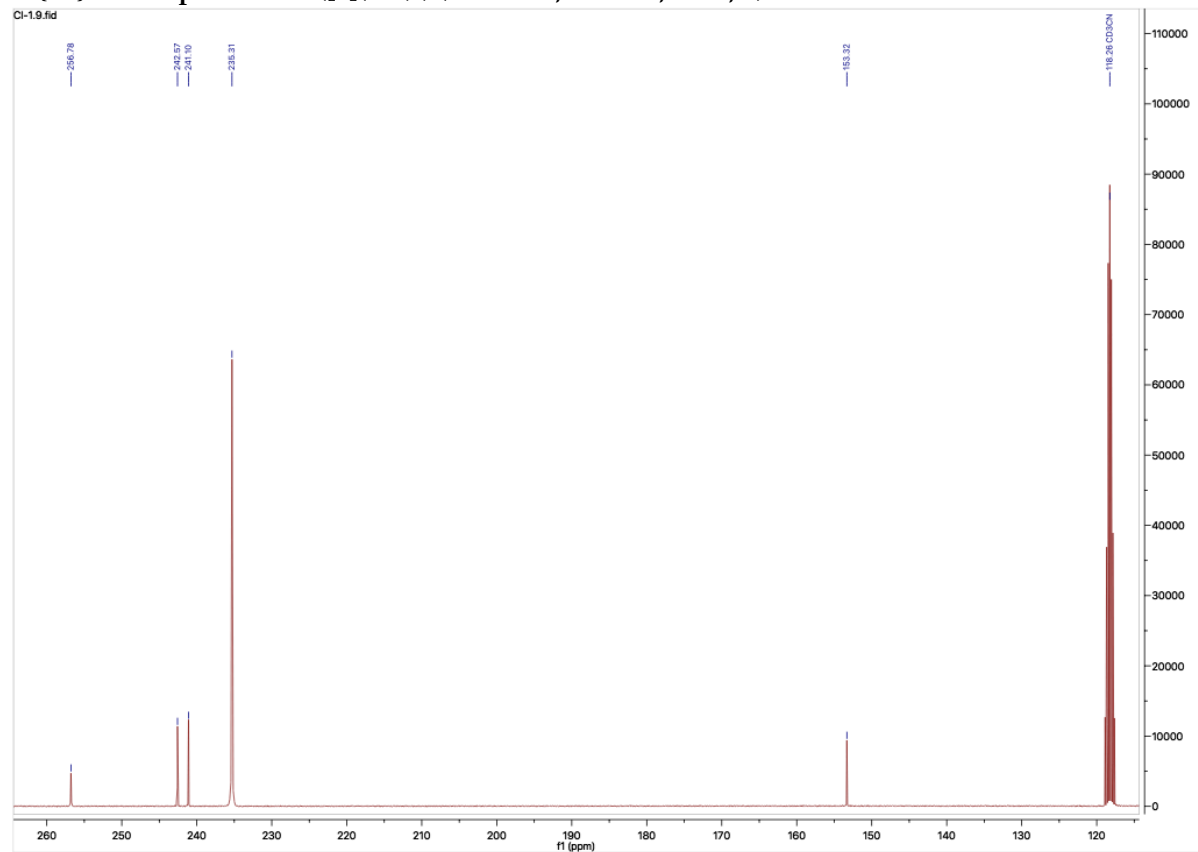
Poly(imidazolyli-den-yl)borato Complexes of Tungsten: Map-ping Steric vs. Electronic Features of Facially Coordinating Ligands

Callum M. Inglis, Richard A. Manzano, Ryan M. Kirk, Manab Sharma, Madeleine D. Stewart, Lachlan J. Watson and Anthony F. Hill *

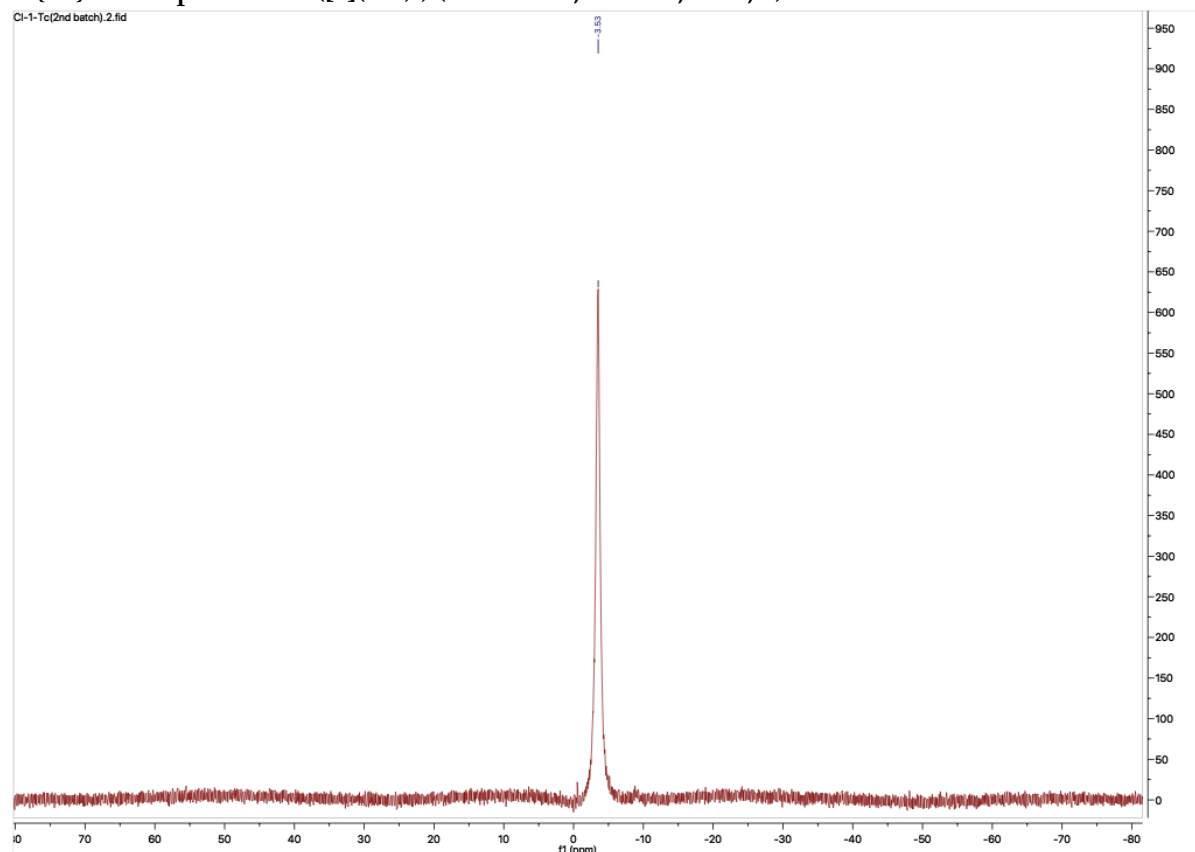
The following supporting information comprise characterisational spectra for new compounds reported in the associated manuscript.

CCDC 2305467 and 2305468 contain the supplementary crystallographic data for this paper and are available free of charge from the Cambridge Crystallographic Data Centre.

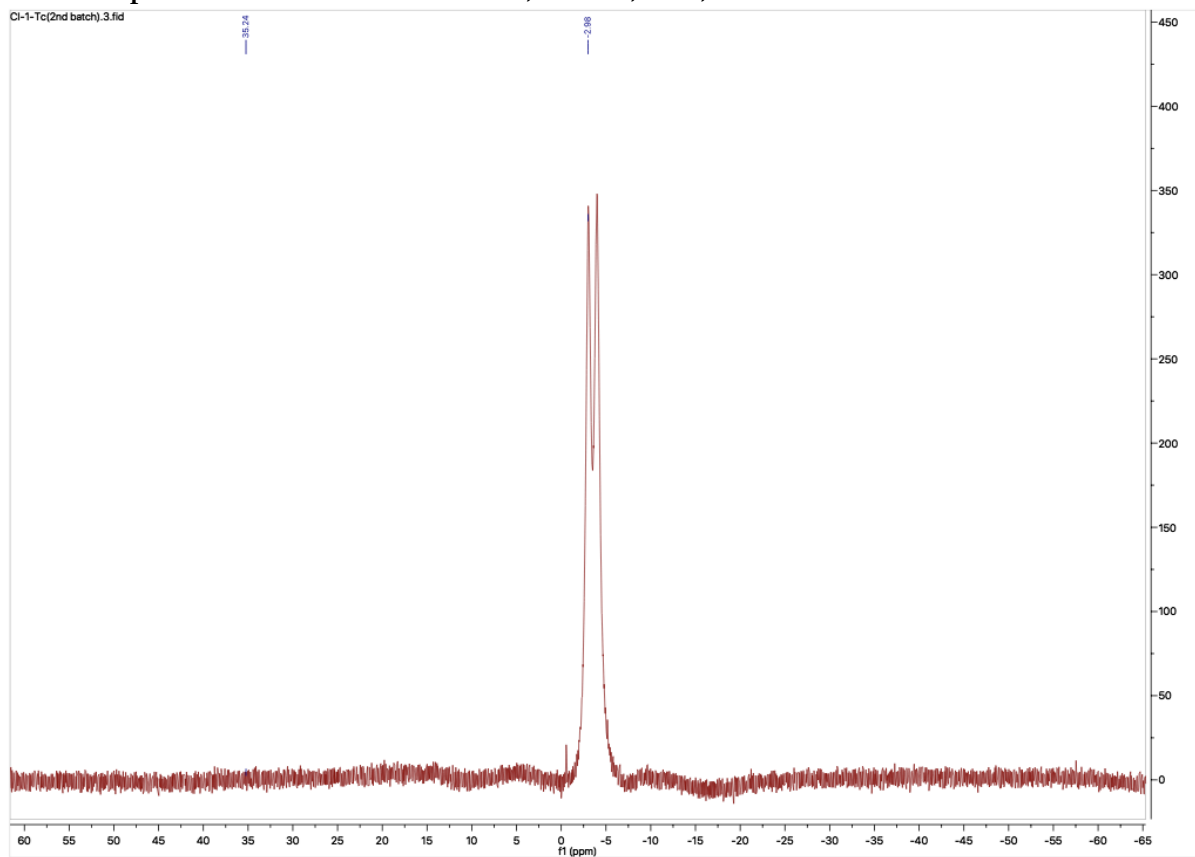
¹H NMR Spectrum of [HB(ImMe)₃](PF₆)₂ ([1](PF₆)₂) (400 MHz, CD₃CN, 25°C, δ)

¹³C{¹H} NMR spectrum of ([1](PF₆)₂) (101 MHz, CD₃CN, 25°C, δ)

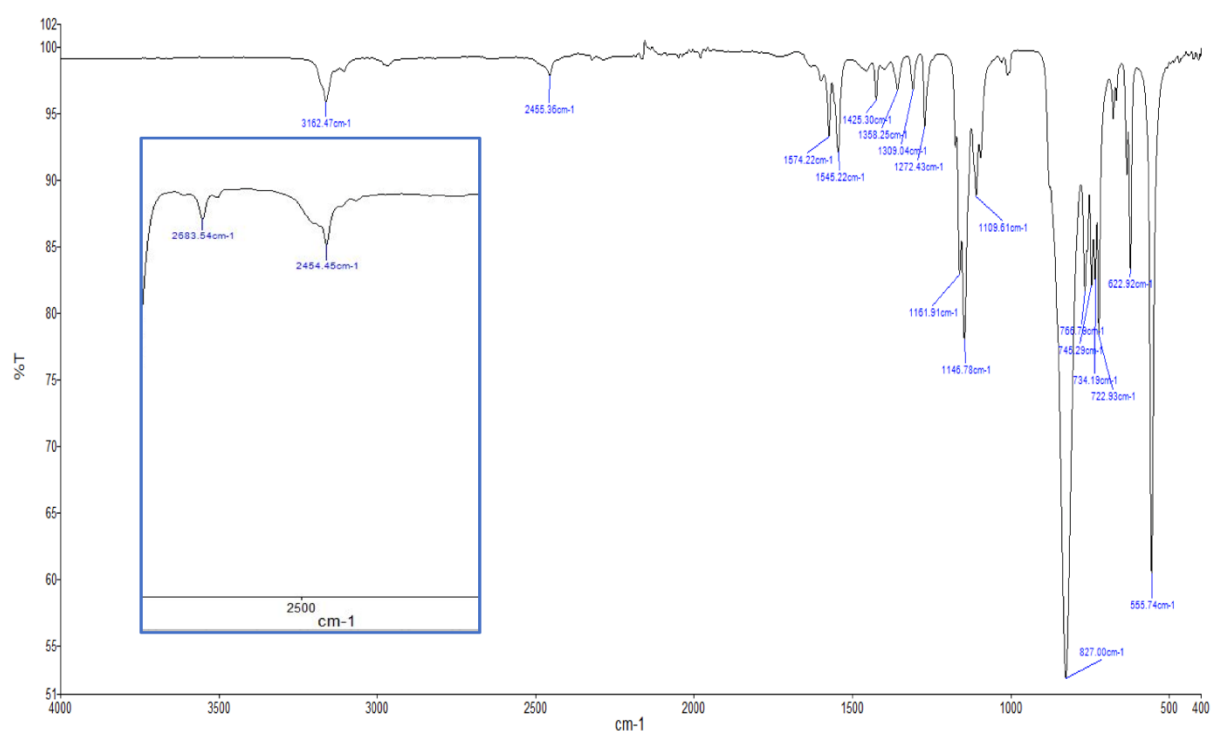
$^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of $([\text{I}](\text{PF}_6)_2)$ (128.4 MHz, CD_3CN , 25°C , δ)



^{11}B NMR spectrum of $([\text{I}](\text{PF}_6)_2)$ (128.4 MHz, CD_3CN , 25°C , δ)



ATR Infrared Spectrum of [1](PF₆)₂ (Inset = CH₂Cl₂ solution spectrum, ν_{BH} region)



Mass Spectrometry for [1](PF₆)₂

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 3.0 PPM / DBE: min = -1.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions

90 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

C: 0-50 H: 0-50 11B: 0-2 N: 0-6

Cl-100J

67126

2925A 67 (0.149) Cm (43.169)

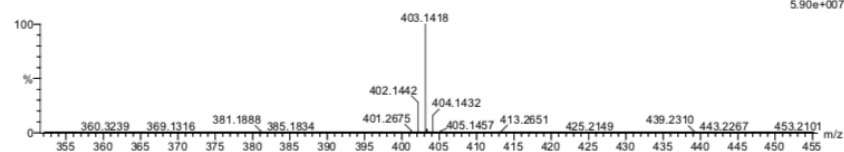
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SYNAPT-G2-Si#NotSet

02-Aug-2022

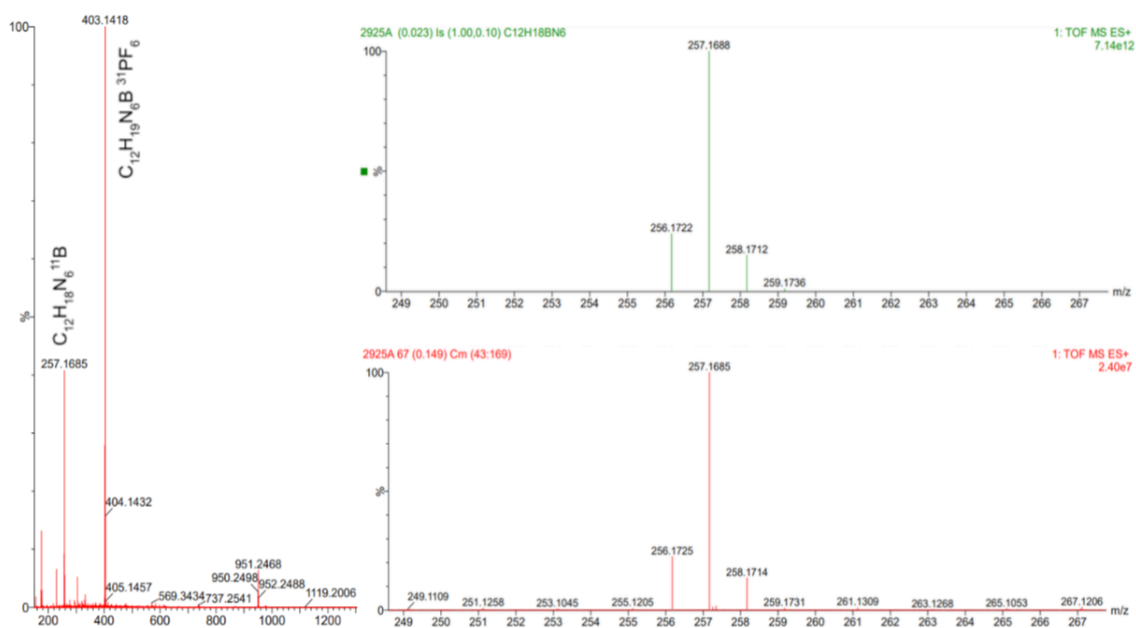
16:00:42

5.90e+007

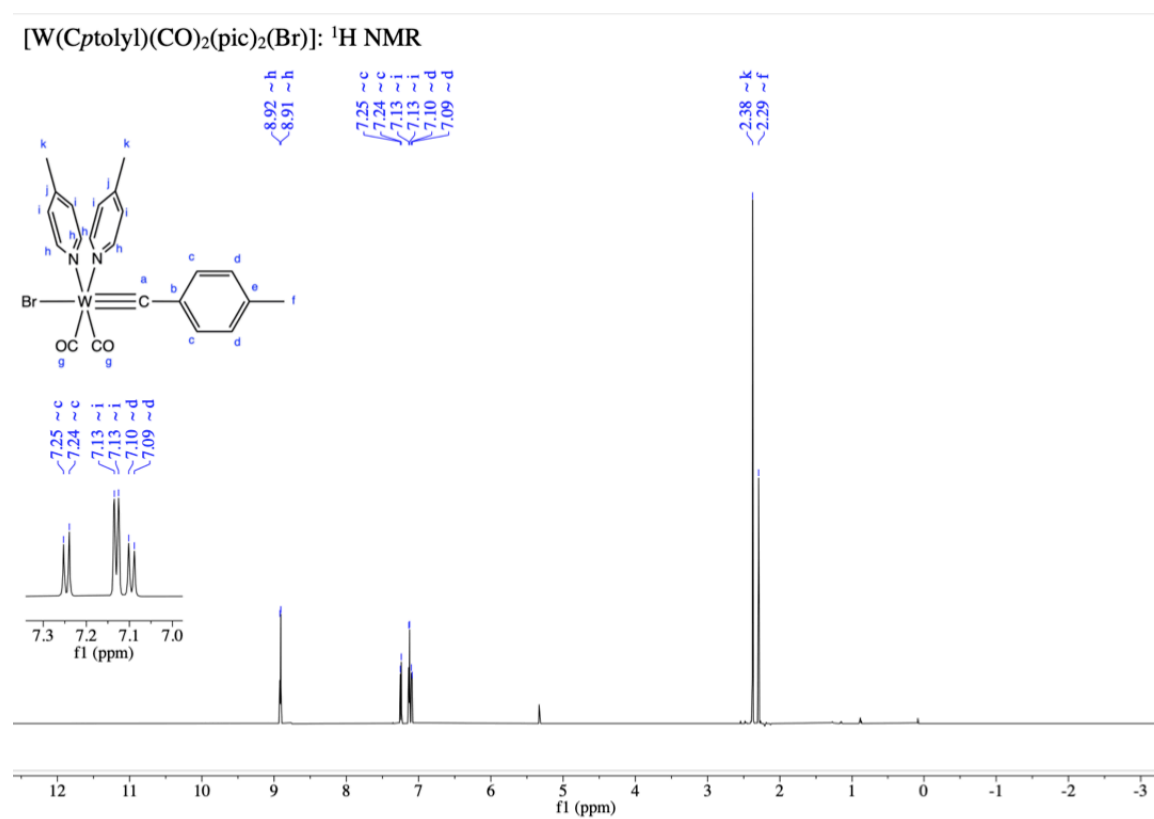


Minimum: -1.5
Maximum: 5.0 3.0 100.0

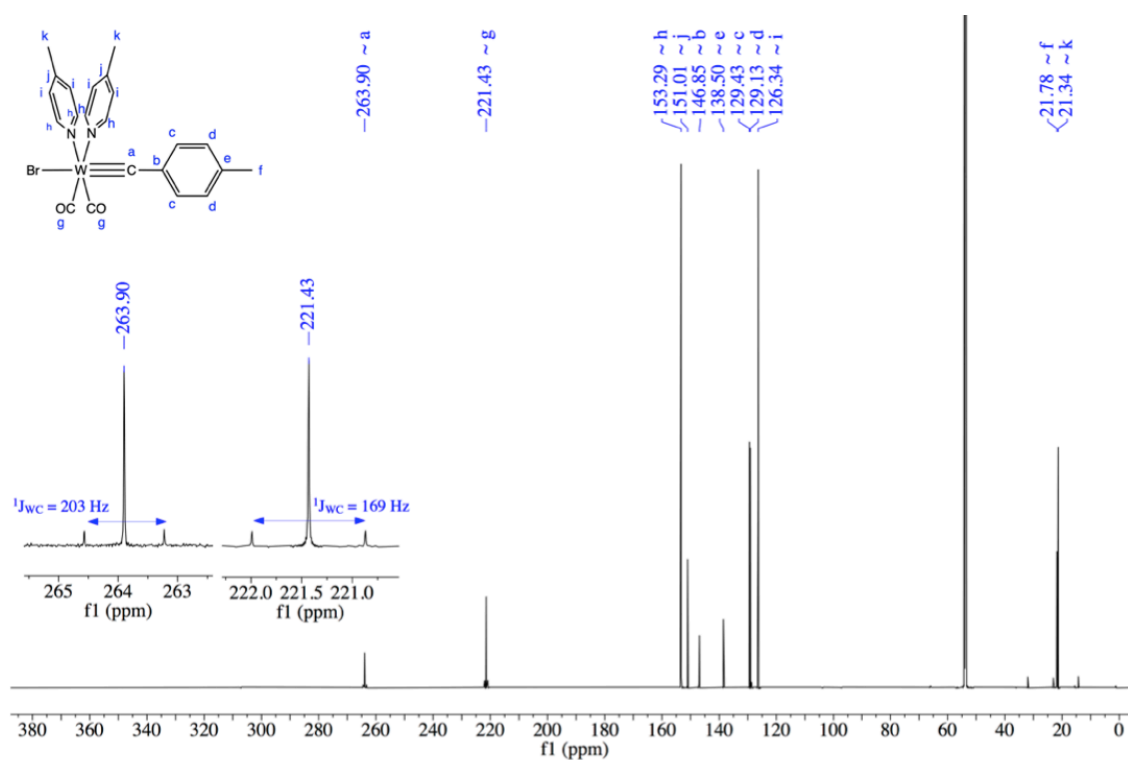
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
403.1418	403.1407	1.1	2.7	23.5	4021.6	C ₂₉ H ₁₆ 11B N ₂



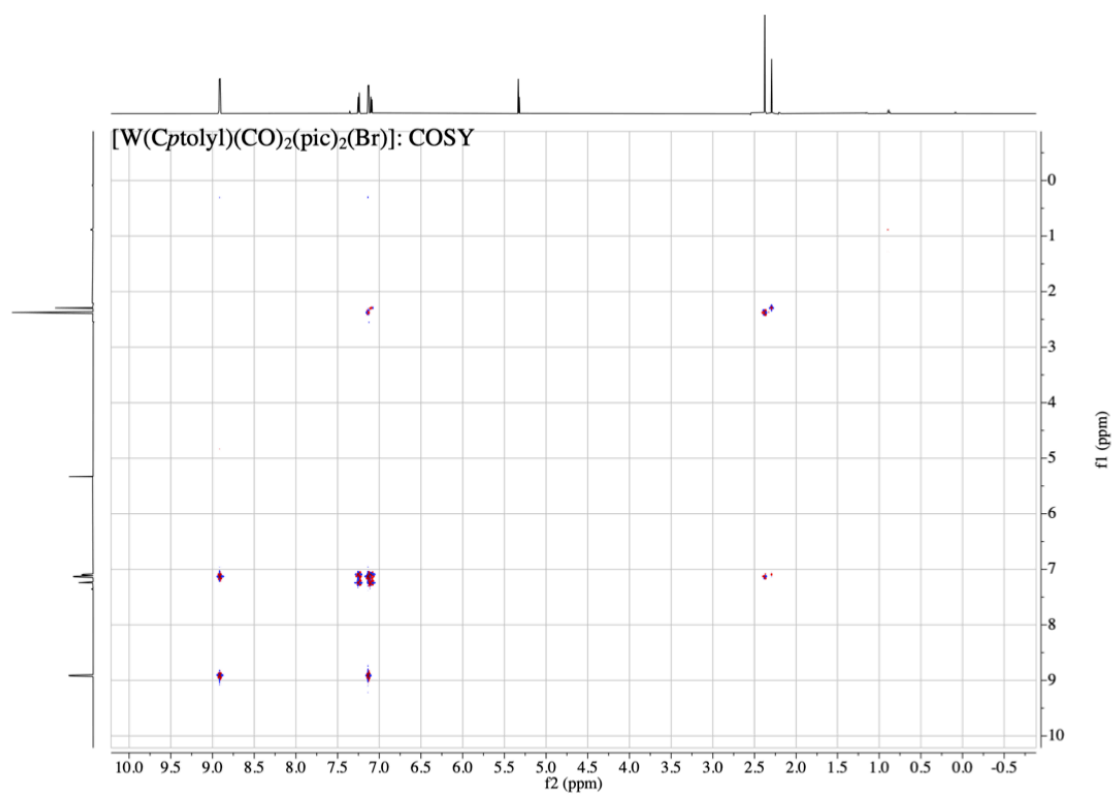
^1H NMR spectrum of $[\text{W}(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\text{pic})_2(\text{Br})]$ (2a) (600 MHz, CD_2Cl_2 , 298 K)



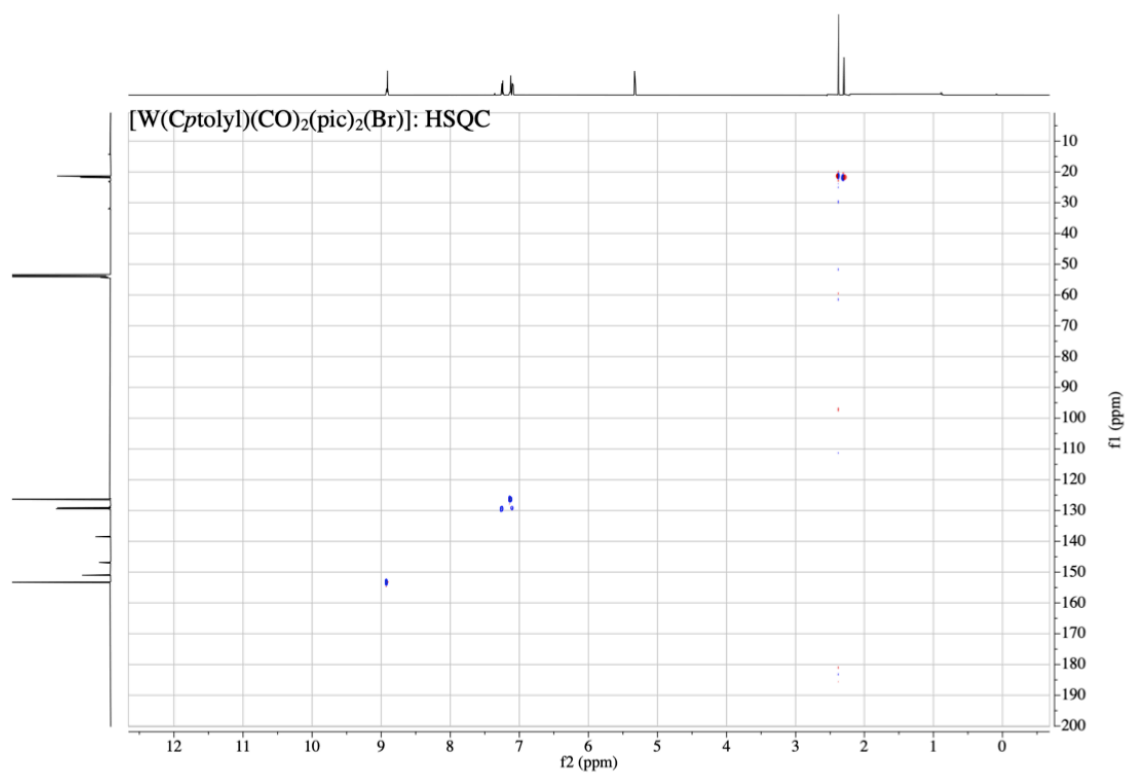
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $[\text{W}(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\text{pic})_2(\text{Br})]$ (2a) (151 MHz, CD_2Cl_2 , 298 K)



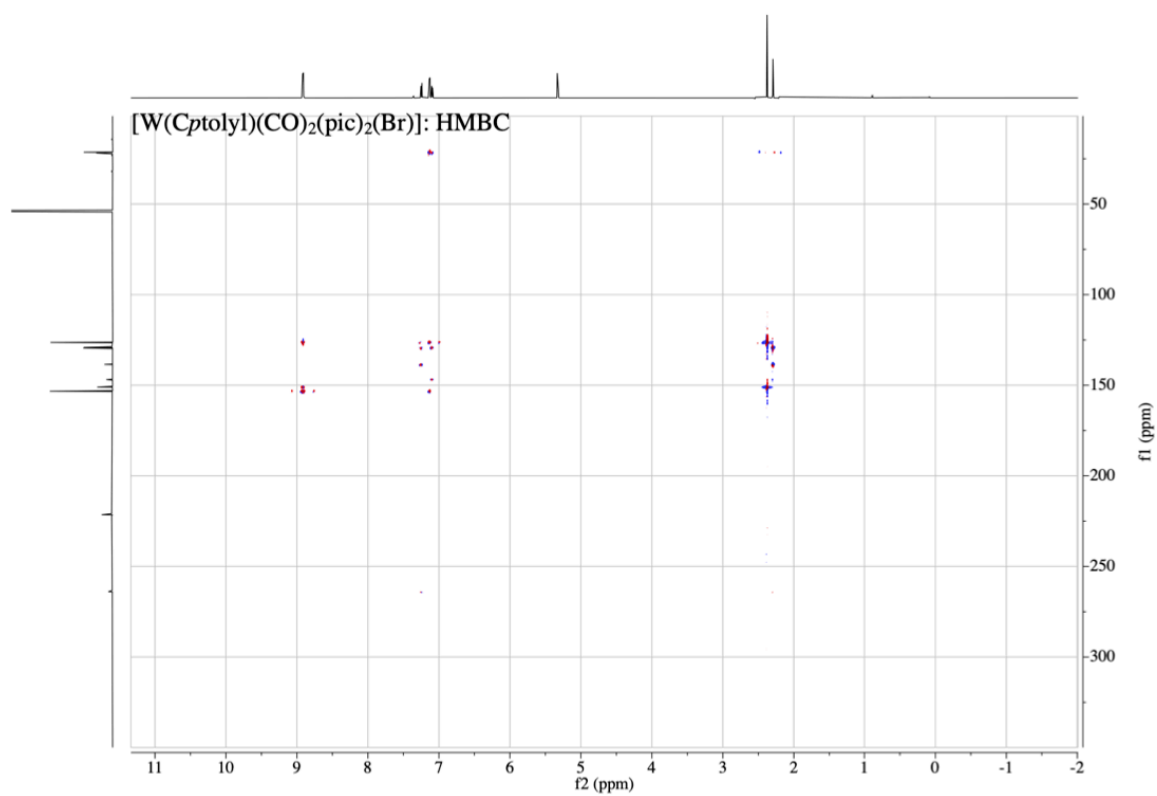
COSY NMR spectrum of $[\text{W}(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\text{pic})_2(\text{Br})]$ (2a) (600 MHz, CD_2Cl_2 , 298 K)



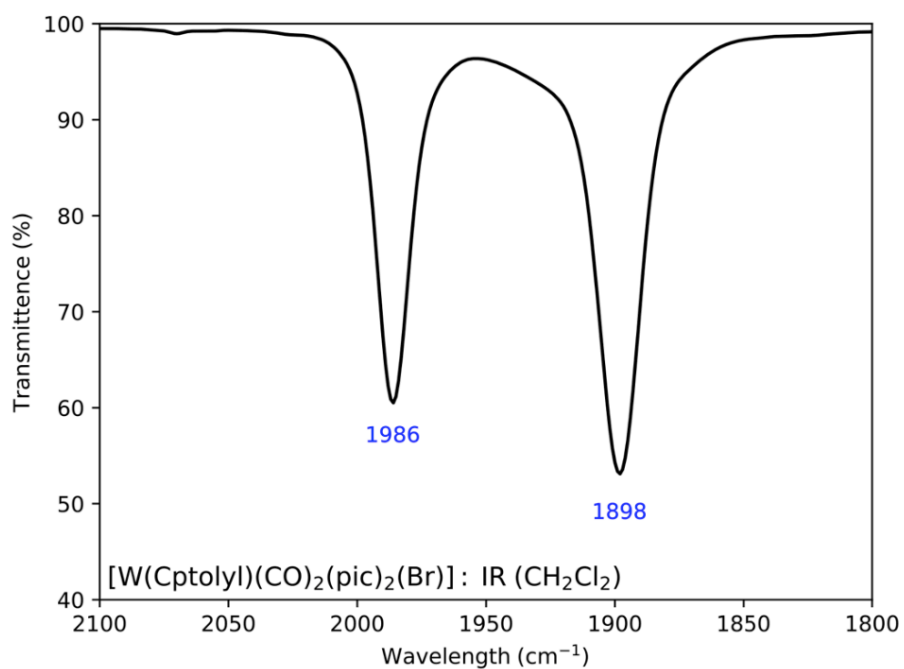
HSQC NMR spectrum of $[W(\equiv CC_6H_4Me-4)(CO)_2(pic)_2(Br)]$ (2a) (600/151 MHz, CD_2Cl_2 , 298 K)



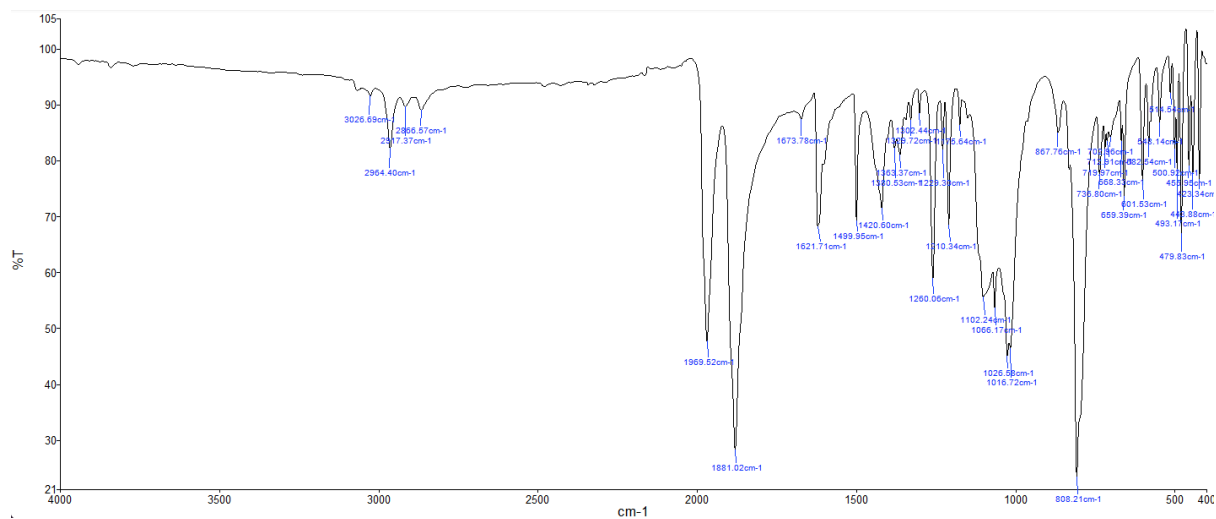
HMBC NMR spectrum of $[W(\equiv CC_6H_4Me-4)(CO)_2(pic)_2(Br)]$ (2a) (600/151 MHz, CD_2Cl_2 , 298 K)



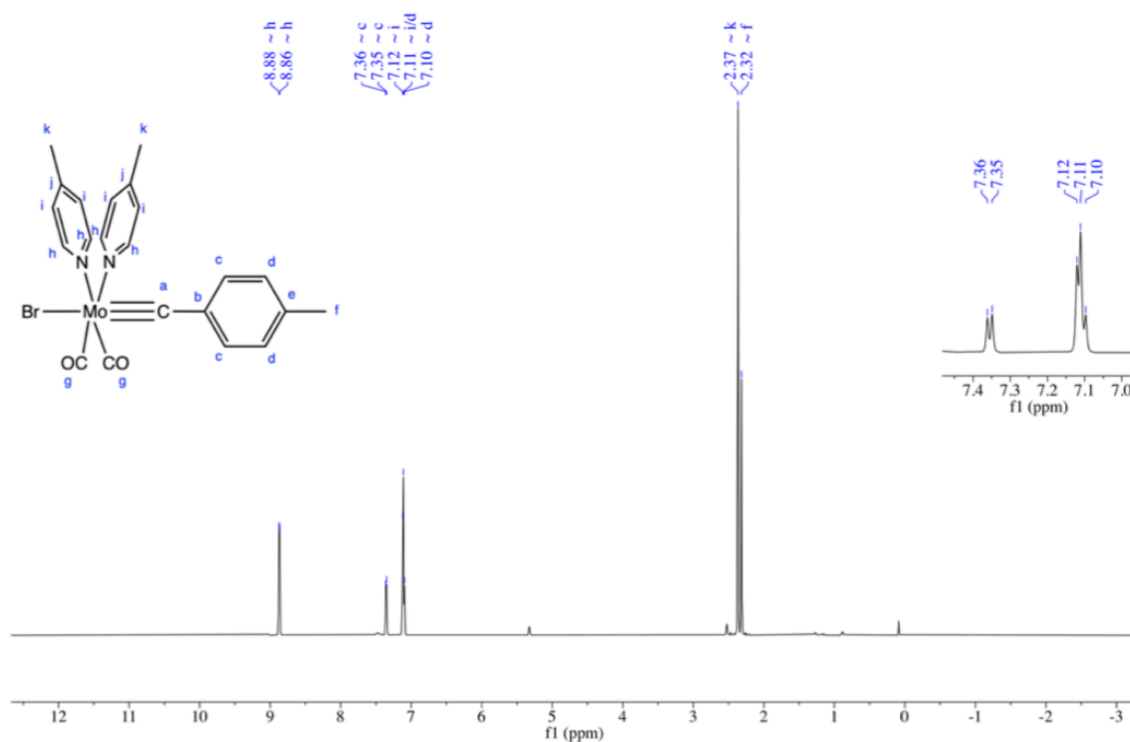
Solution IR spectrum of $[W(\equiv CC_6H_4Me-4)(CO)_2(pic)_2(Br)]$ (2a) (CH_2Cl_2).



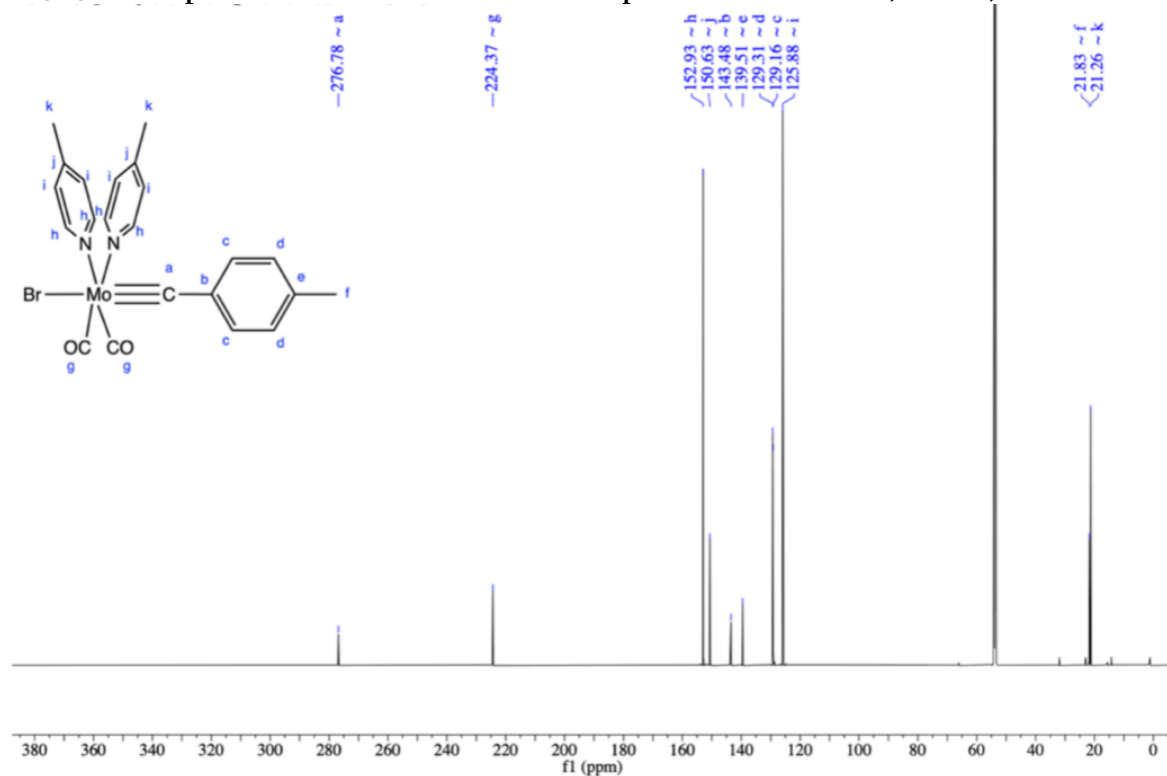
Solid State IR spectrum of $[W(\equiv CC_6H_4Me-4)(CO)_2(pic)_2(Br)]$ (2a) (ATR).



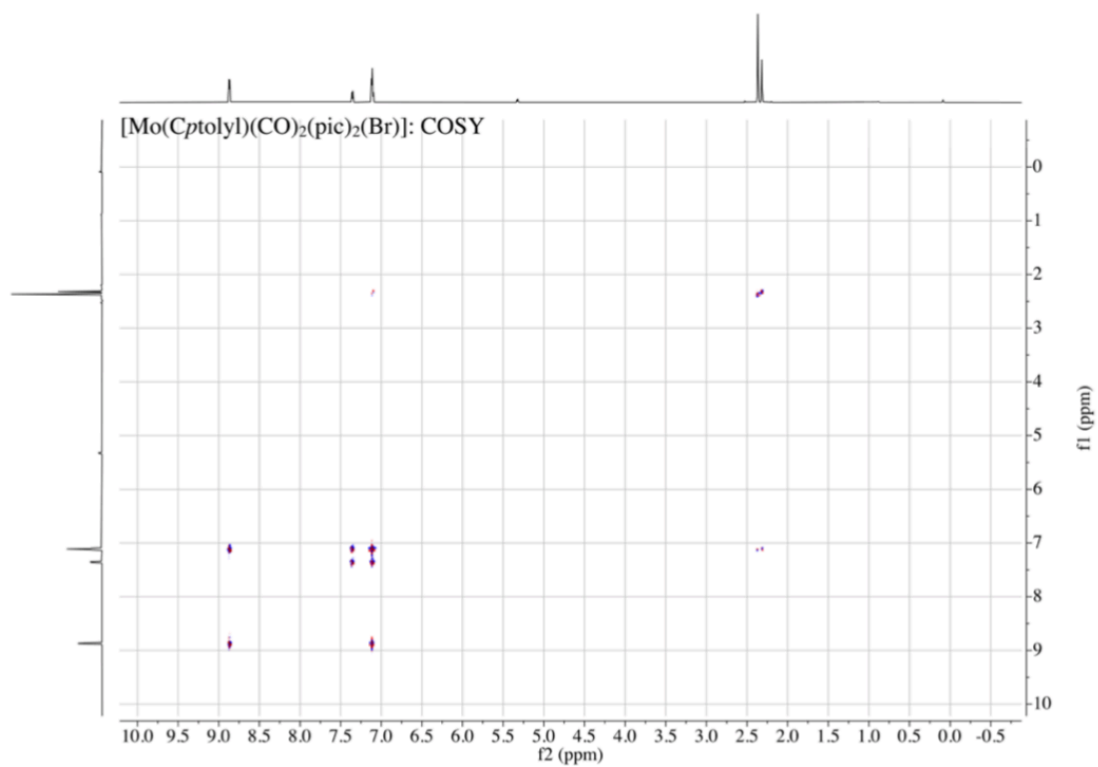
^1H NMR Spectrum of $[\text{Mo}(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\text{pic})_2\text{Br}]$ (2b) (800 MHz, CD_2Cl_2 , 25 °)



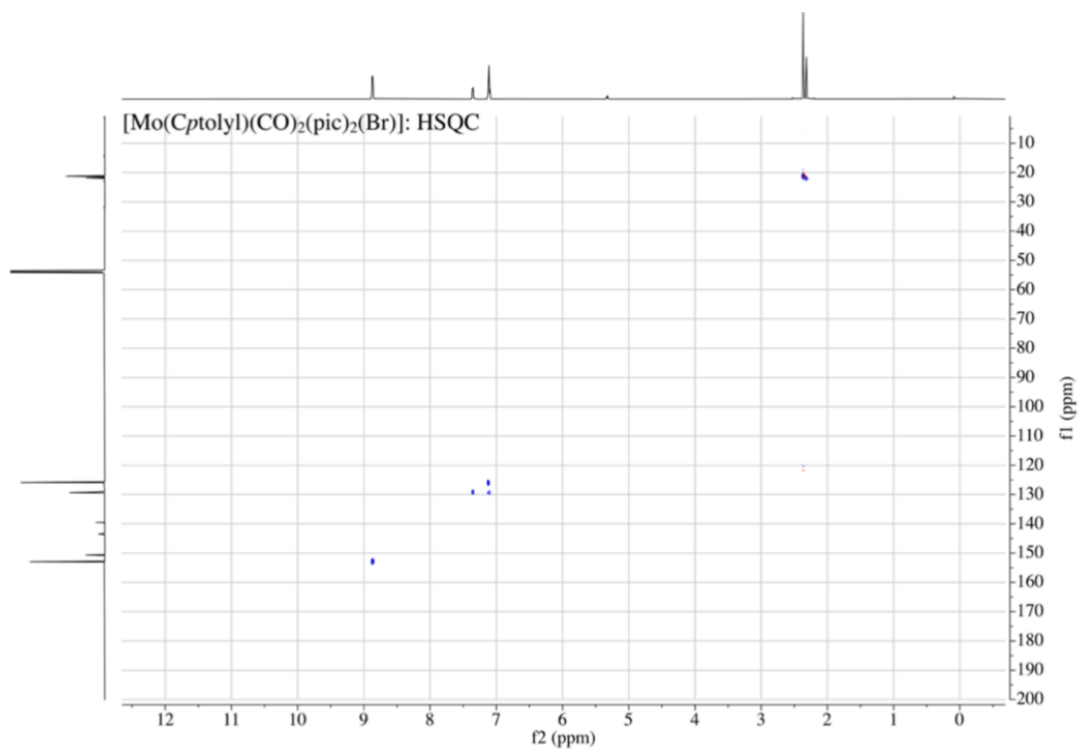
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of $[\text{Mo}(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\text{pic})_2\text{Br}]$ (2b) (151 MHz, CD_2Cl_2 , 25 °)



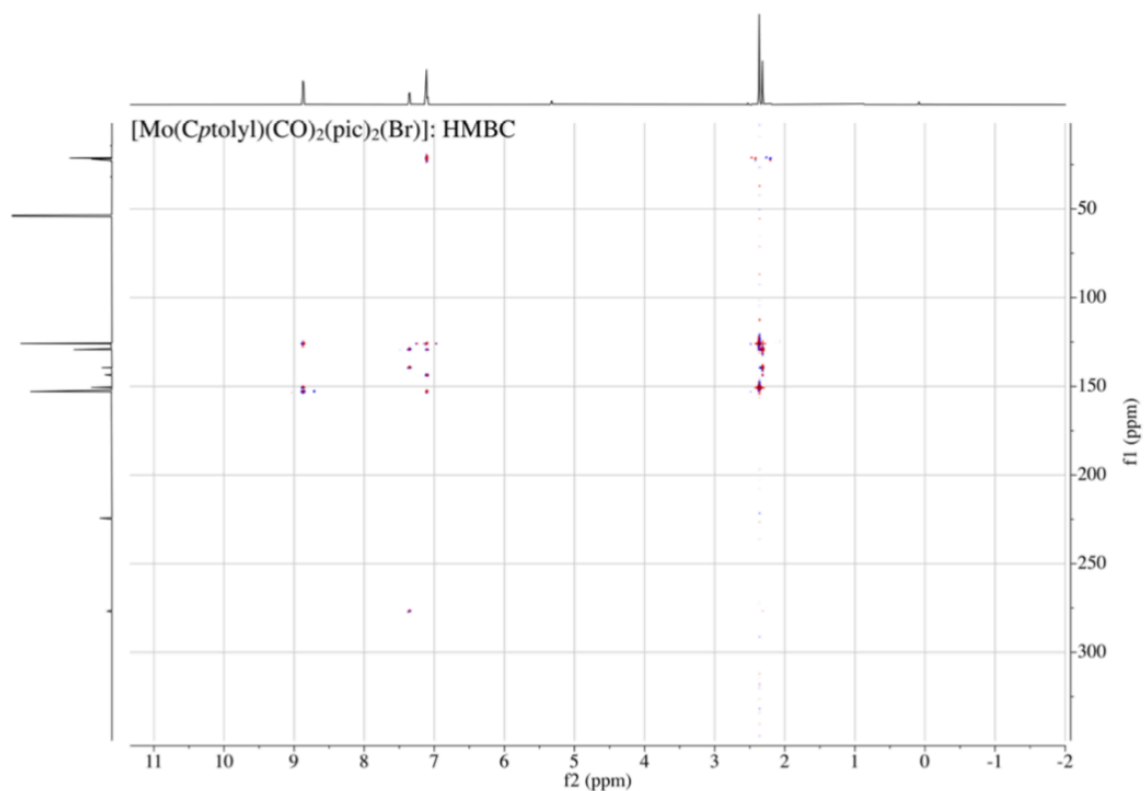
COSY NMR spectrum of $[\text{Mo}(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\text{pic})_2\text{Br}]$ (2b) (600 MHz, CD_2Cl_2 , 298 K).



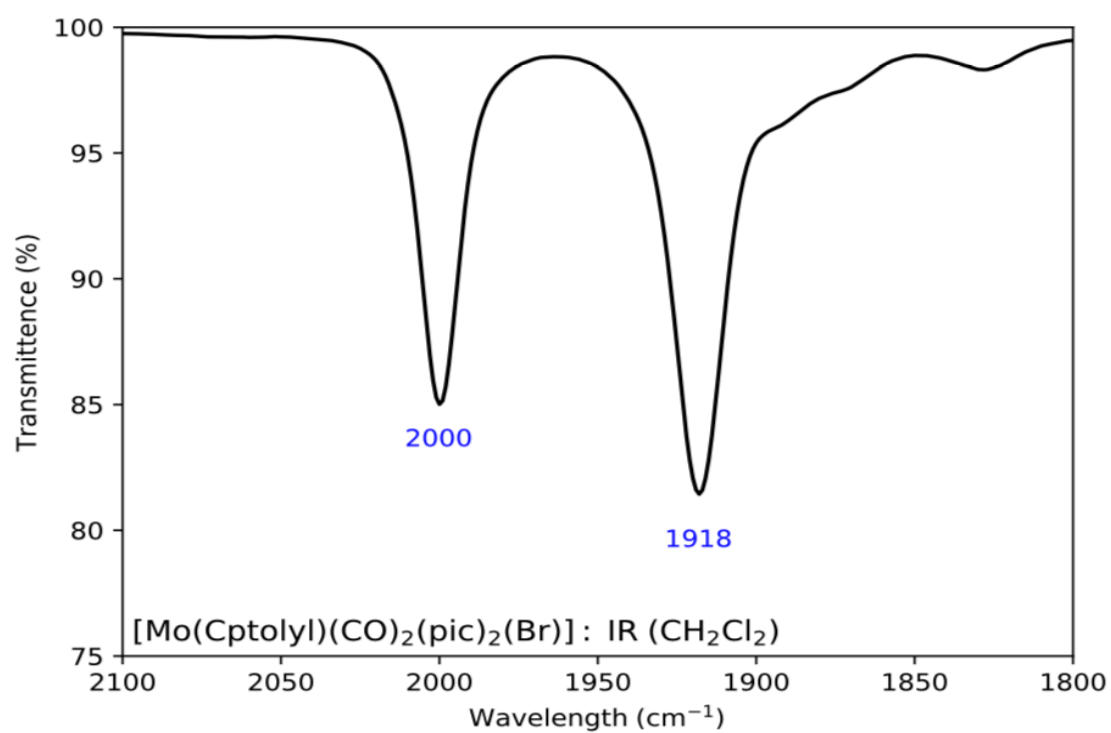
HSQC NMR spectrum of $[\text{Mo}(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\text{pic})_2\text{Br}]$ (2b) (600/151 MHz, CD_2Cl_2 , 298 K)



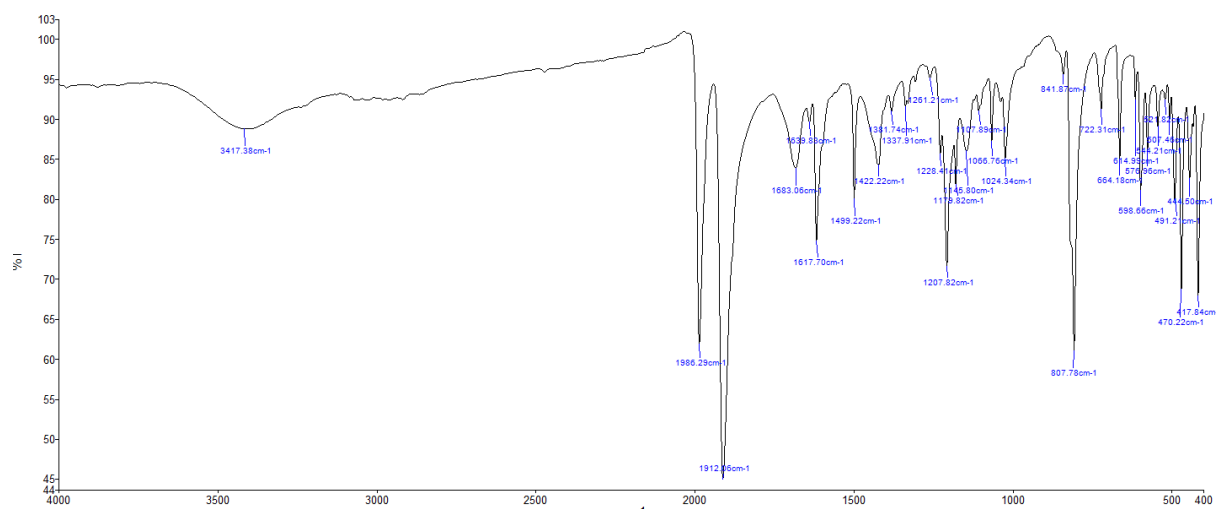
HMBC NMR spectrum of $[\text{Mo}(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\text{pic})_2\text{Br}]$ (2b) (600/151 MHz, CD_2Cl_2 , 298 K)



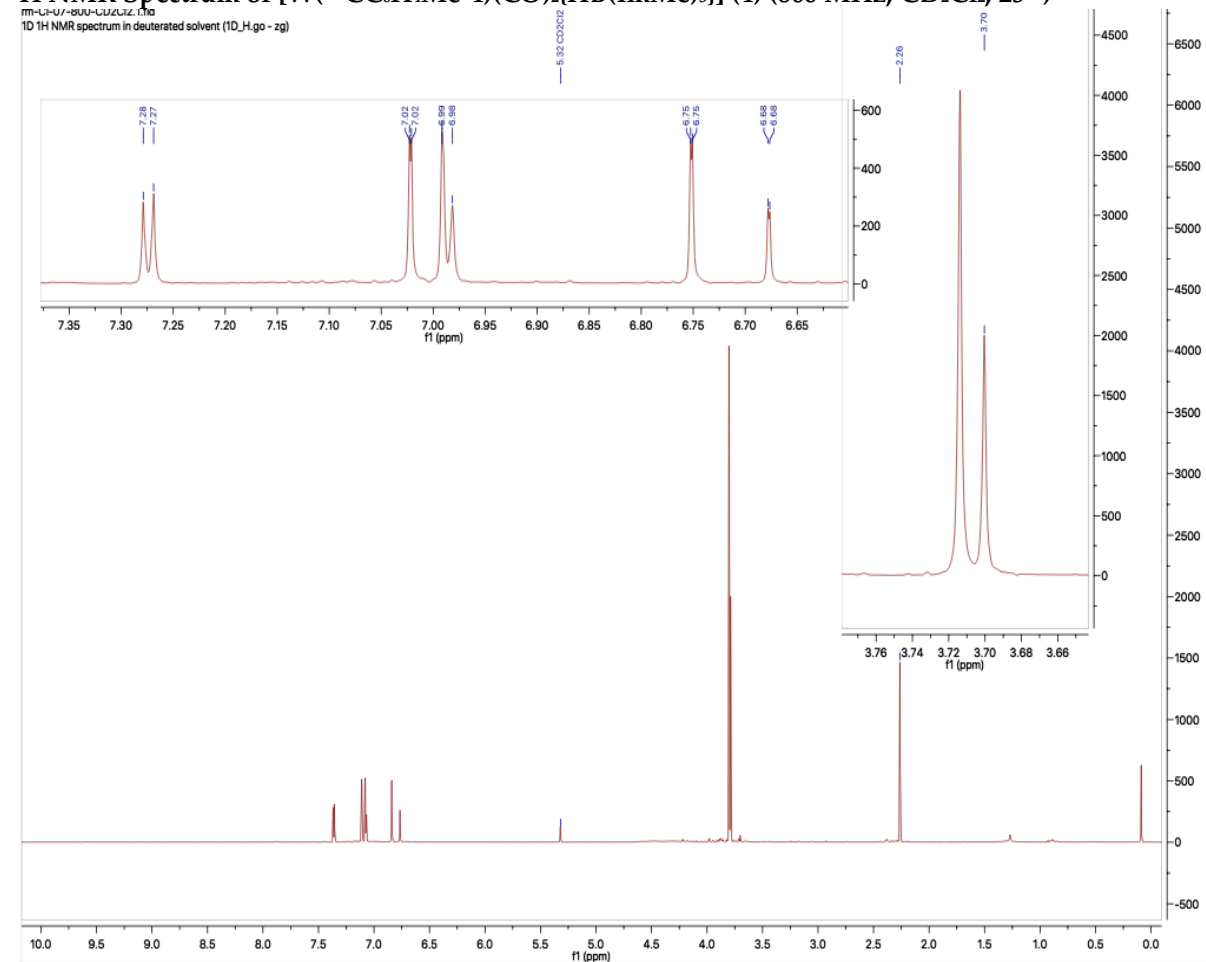
Solution IR spectrum of $[\text{Mo}(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\text{pic})_2\text{Br}]$ (2b) (CH_2Cl_2).



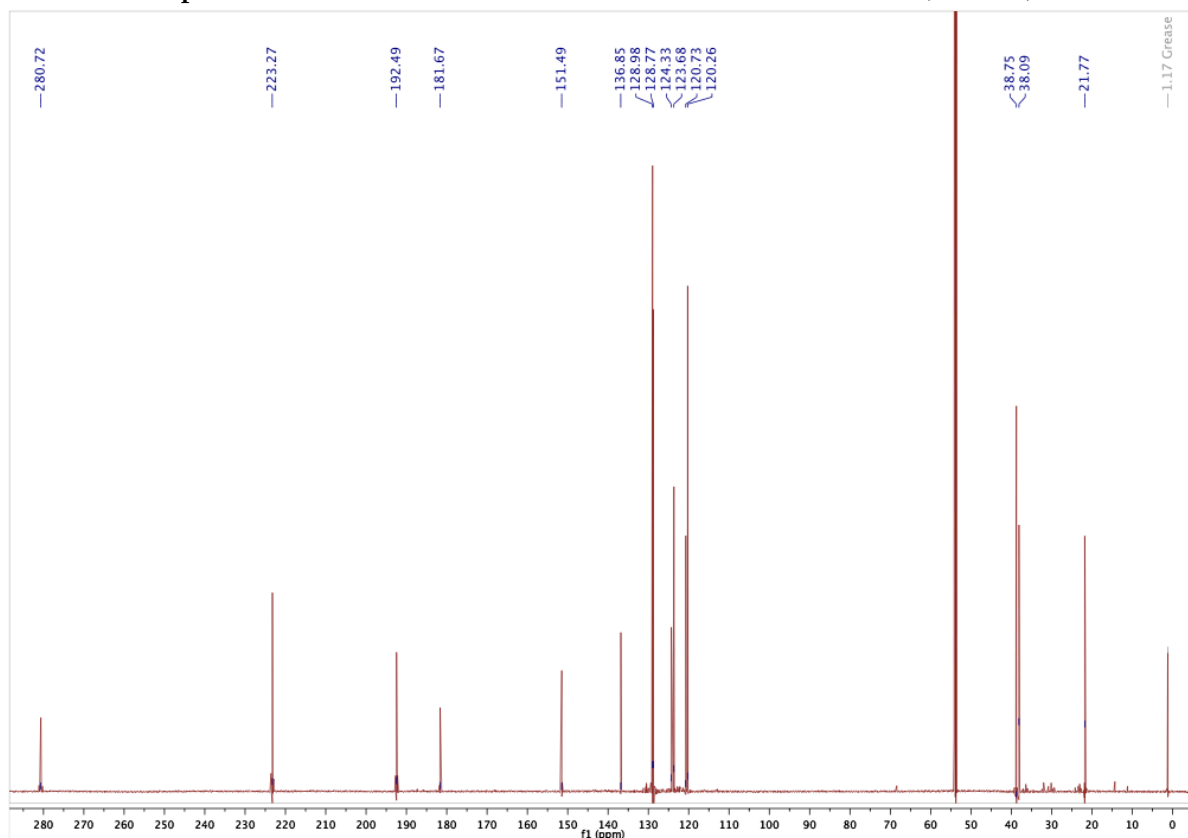
Solid State IR spectrum of [Mo(\equiv CC₆H₄Me-4)(CO)₂(pic)₂Br] (2b) (ATR).



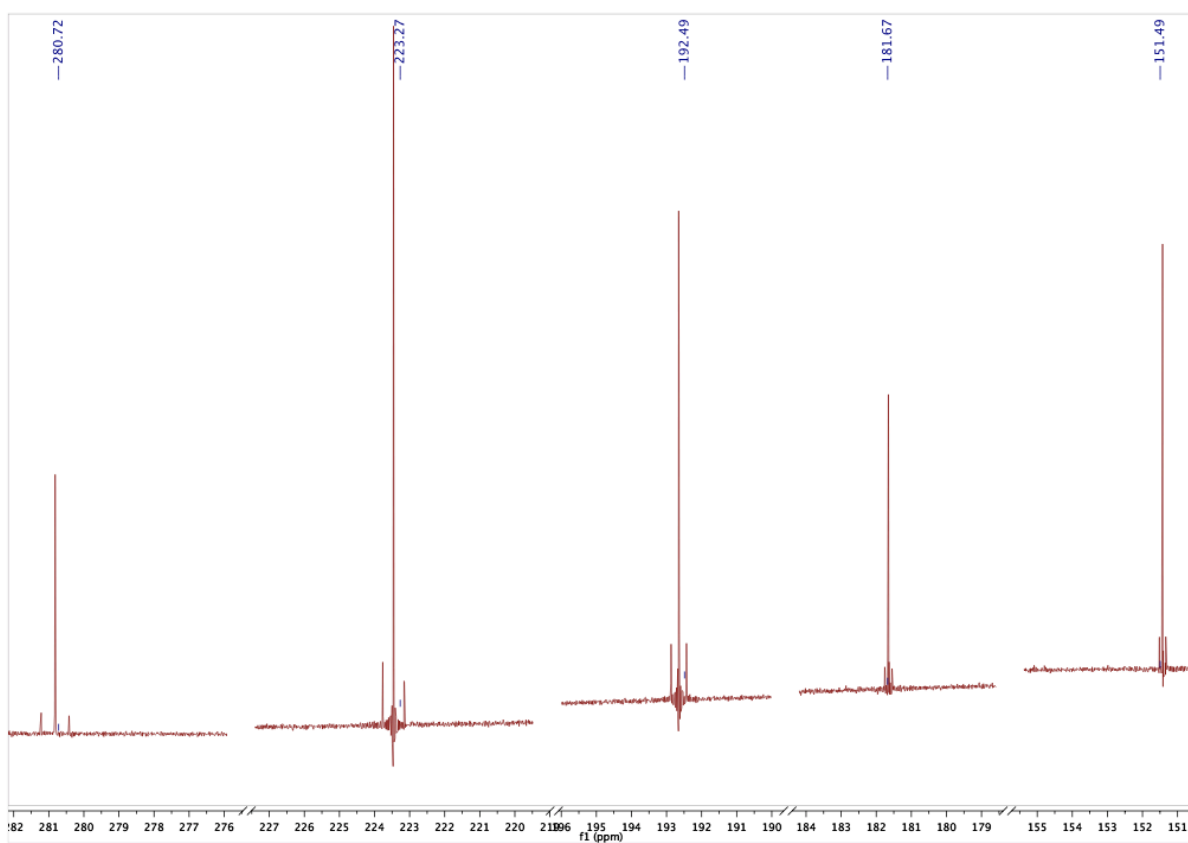
¹H NMR Spectrum of [W(\equiv CC₆H₄Me-4)(CO)₂{HB(ImMe)₃}] (4) (800 MHz, CD₂Cl₂, 25 °)



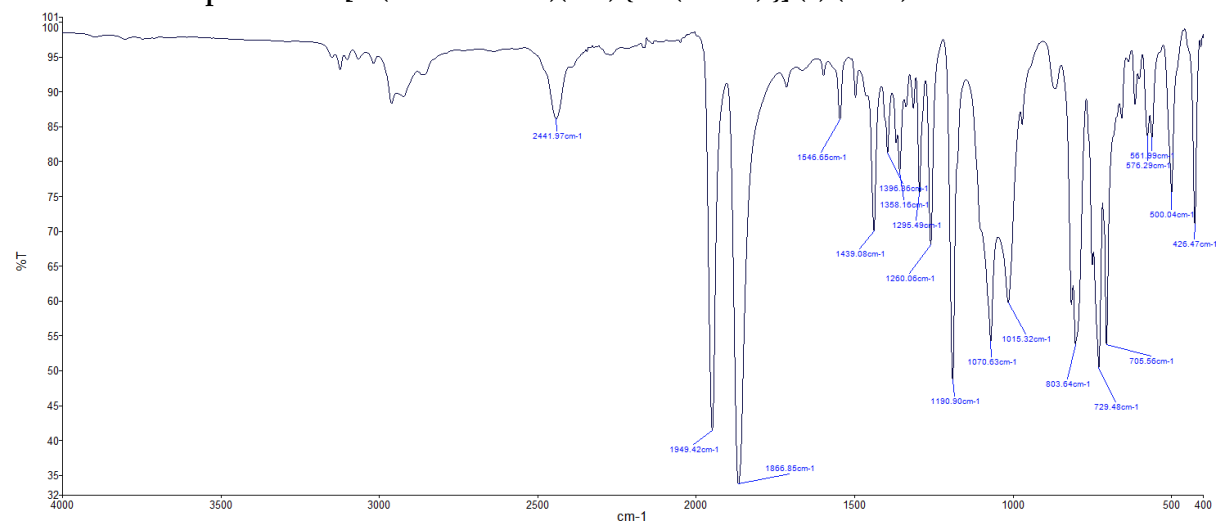
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of $[\text{W}(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2\{\text{HB}(\text{ImMe})_3\}]$ (4) (201 MHz, CD_2Cl_2 , 25 °)



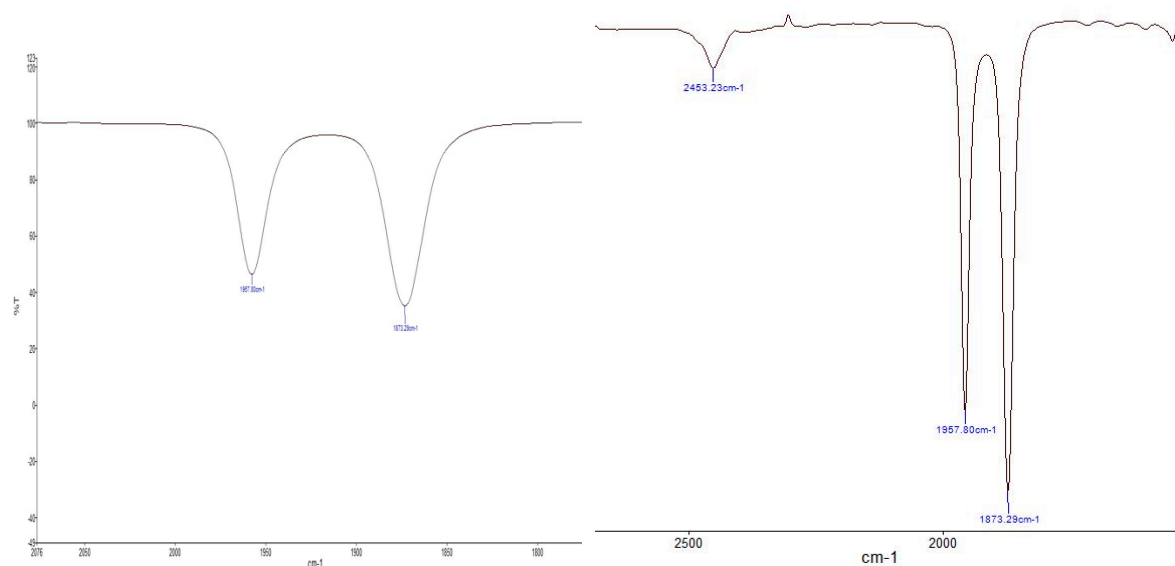
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of $[\text{W}(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2\{\text{HB}(\text{ImMe})_3\}]$ (4) (201 MHz, CD_2Cl_2 , 25 °) – Low field extracts



Solid State IR Spectrum of $[W(\equiv CC_6H_4Me-4)(CO)_2\{HB(ImMe)_3\}]$ (4) (ATR)



Solution IR Spectrum of $[W(\equiv CC_6H_4Me-4)(CO)_2\{HB(ImMe)_3\}]$ (4) (CH_2Cl_2)



High Resolution ESI-MS of [W(≡CC₆H₄Me-4)(CO)₂{HB(ImMe)₃}] (4) (MeOH)

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 3.0 PPM / DBE: min = -1.5, max = 18.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions

364 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

C: 0-50 H: 0-50 11B: 0-1 N: 0-6 O: 0-2 184W: 0-1

CI-7-WCTol/AJ

SYNAPT G2-Si#NotSet

23-Sep-2022

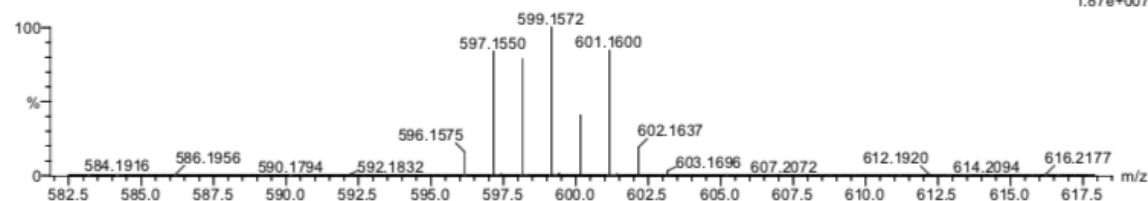
67213

15:10:05

3547.87 (0.192) Cm (80:121)

1: TOF MS ES+

1.87e+007



Minimum:

Maximum:

5.0

3.0

-1.5

18.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
599.1572	599.1563	0.9	1.5	16.0	2745.8	C22 H24 11B N6 O2 184W

CI-7-WCTol/AJ

SYNAPT G2-Si#NotSet

23-Sep-2022

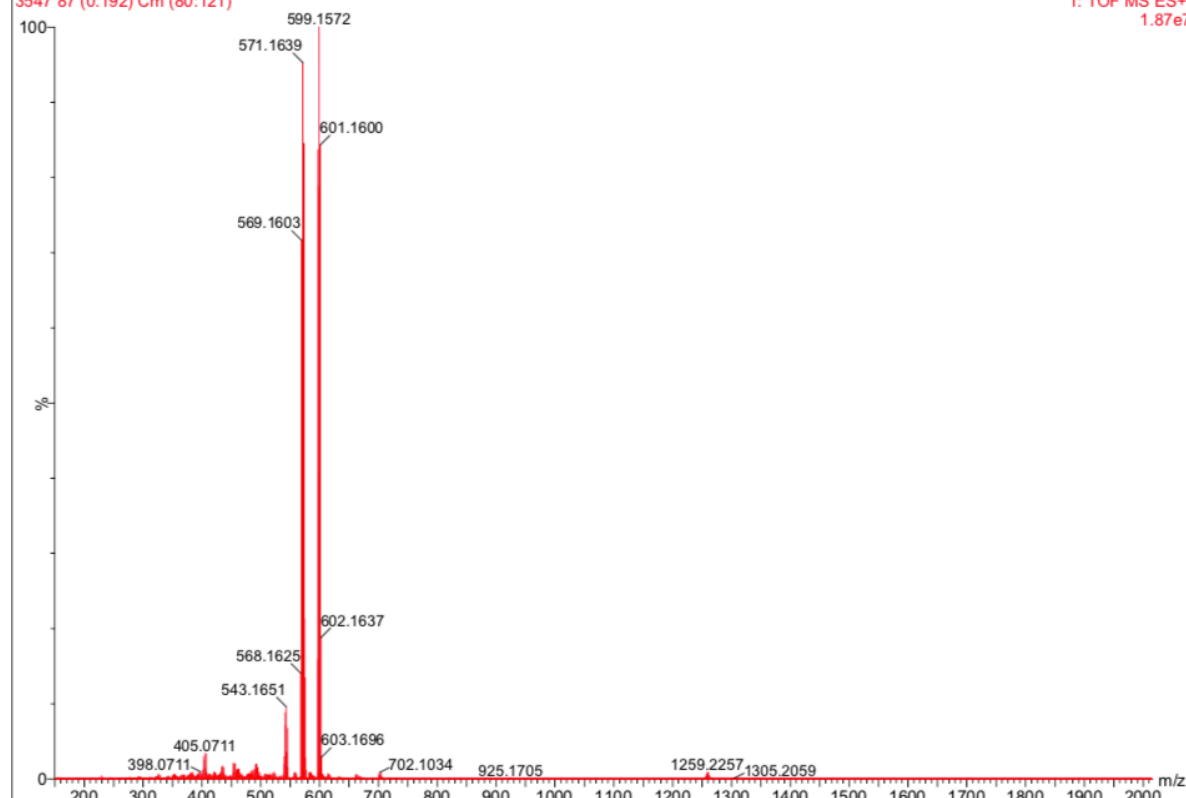
67213

15:10:05

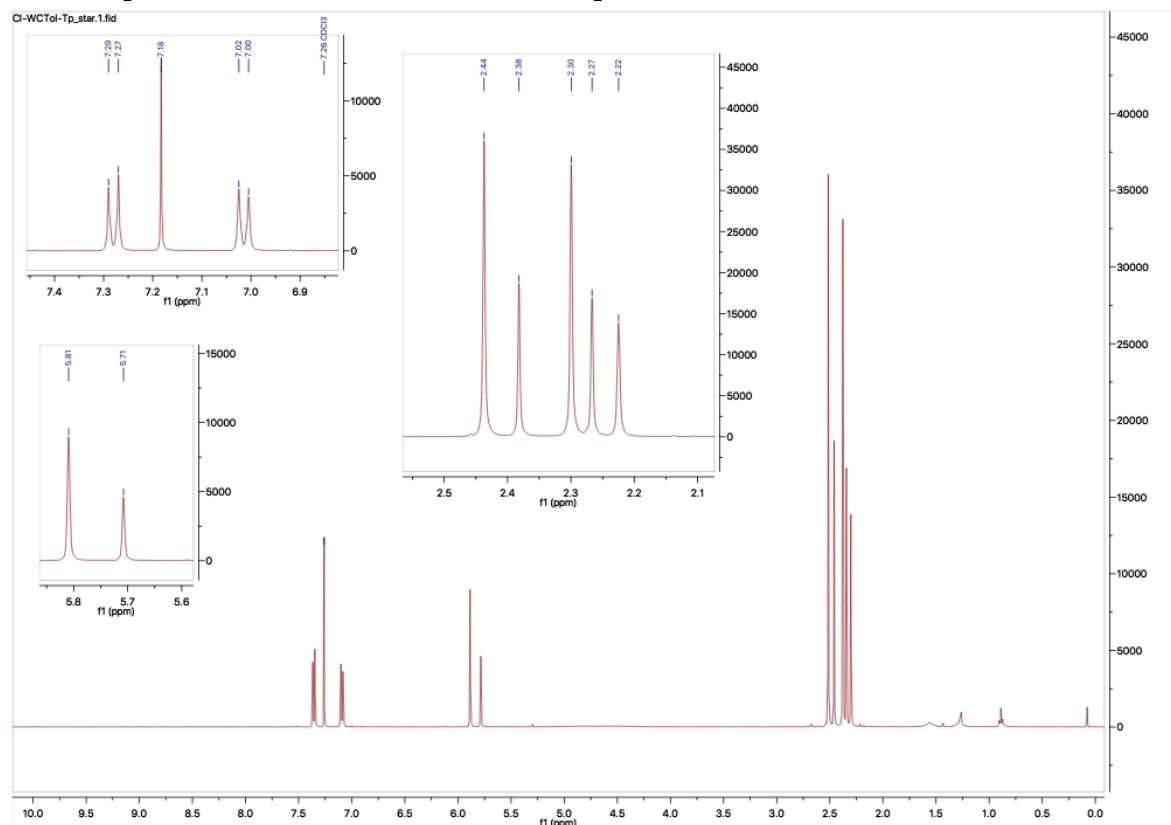
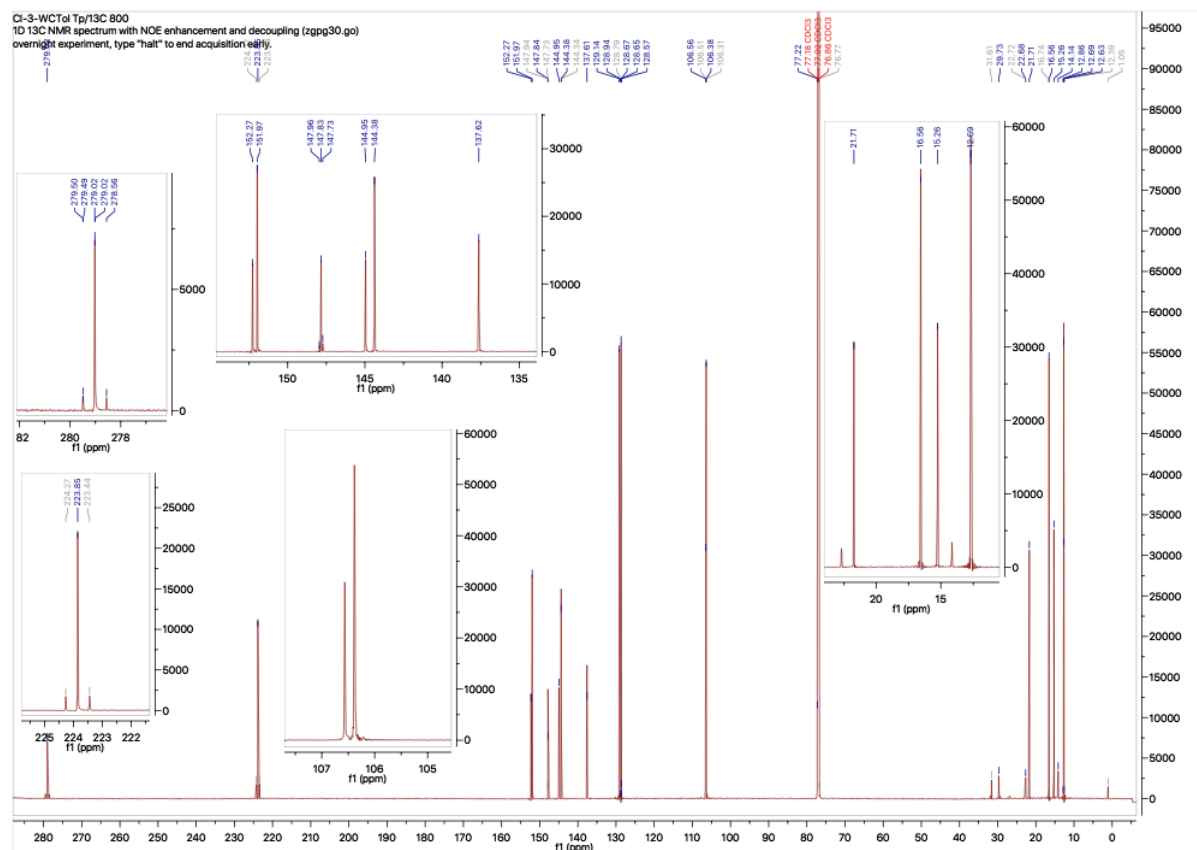
3547.87 (0.192) Cm (80:121)

1: TOF MS ES+

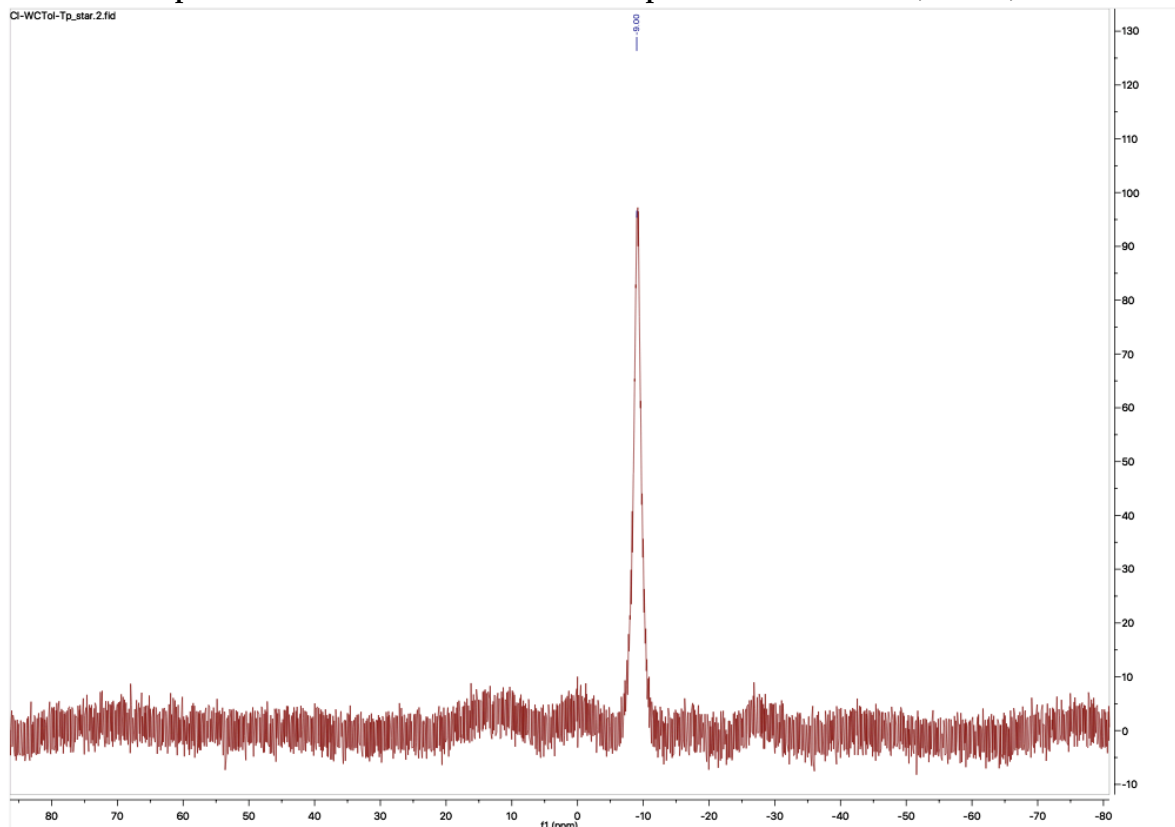
1.87e7



¹H NMR Spectrum of [W(≡CC₆H₄Me-4)(CO)₂{HB(pzMe₂)₃}] (5) (400 MHz, CDCl₃, 25 °)

¹³C{¹H} NMR Spectrum of [W(≡CC₆H₄Me-4)(CO)₂{HB(pzMe₂)₃}] (5) (201 MHz, CDCl₃, 25 °)

$^{11}\text{B}\{^1\text{H}\}$ NMR Spectrum of $[\text{W}(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2\{\text{HB}(\text{pzMe}_2)_3\}]$ (5) (128 MHz, CDCl_3 , 25 °)



High Resolution ESI-MS of $[\text{W}(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2\{\text{HB}(\text{pzMe}_2)_3\}]$ (5) (MeOH)

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 3.0 PPM / DBE: min = -1.5, max = 18.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions

351 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

C: 0-50 H: 0-50 11B: 0-1 N: 0-6 O: 0-2 184W: 0-1

LJW-CI/AJ

SYNAPT G2-Si#NotSet

14-Oct-2022

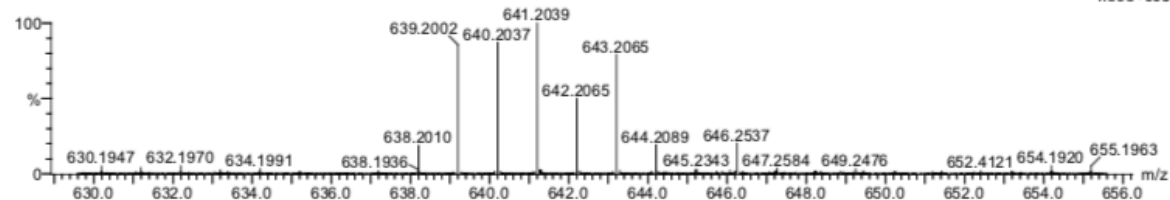
67290

09:53:47

3782.87 (0.192) Cm (87:94)

1: TOF MS ES+

1.89e+005



Minimum: -1.5
Maximum: 5.0 3.0 18.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
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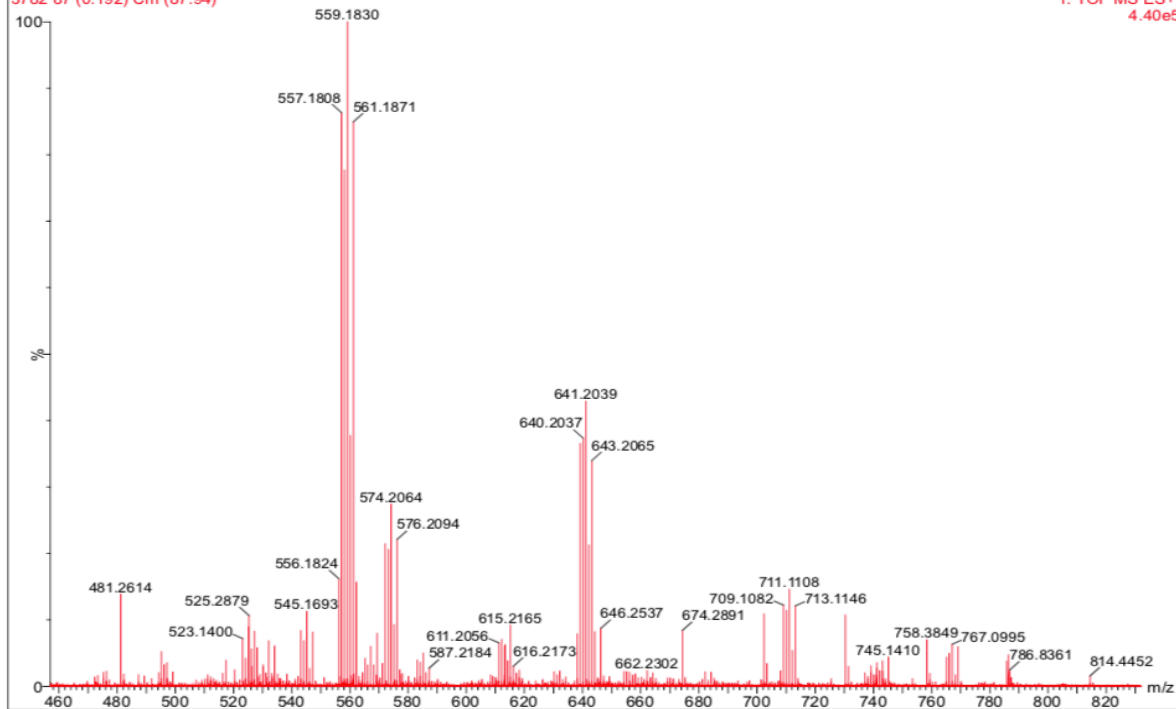
LJW-CI/AJ
67290

SYNAPT G2-Si#NotSet

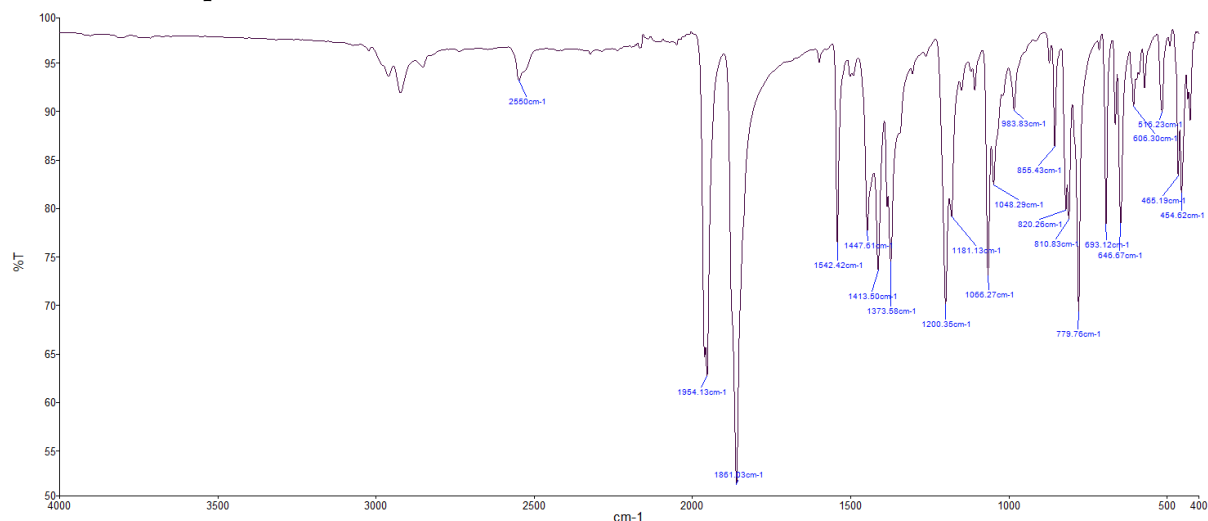
14-Oct-2022
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3782.87 (0.192) Cm (87:94)

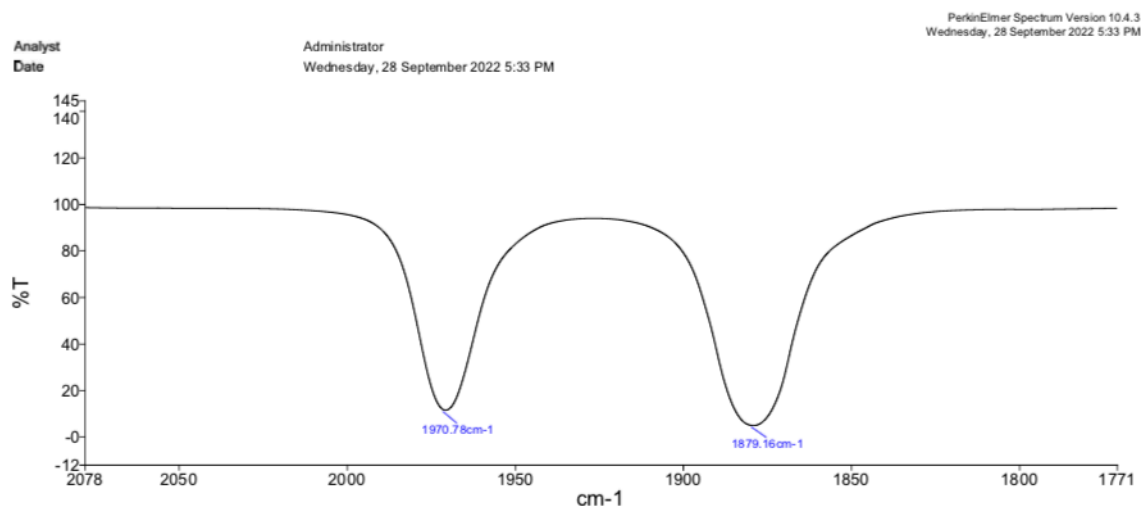
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Solid State IR Spectrum of [W(≡CC₆H₄Me-4)(CO)₂][HB(ImMe)₃] (4) (ATR)

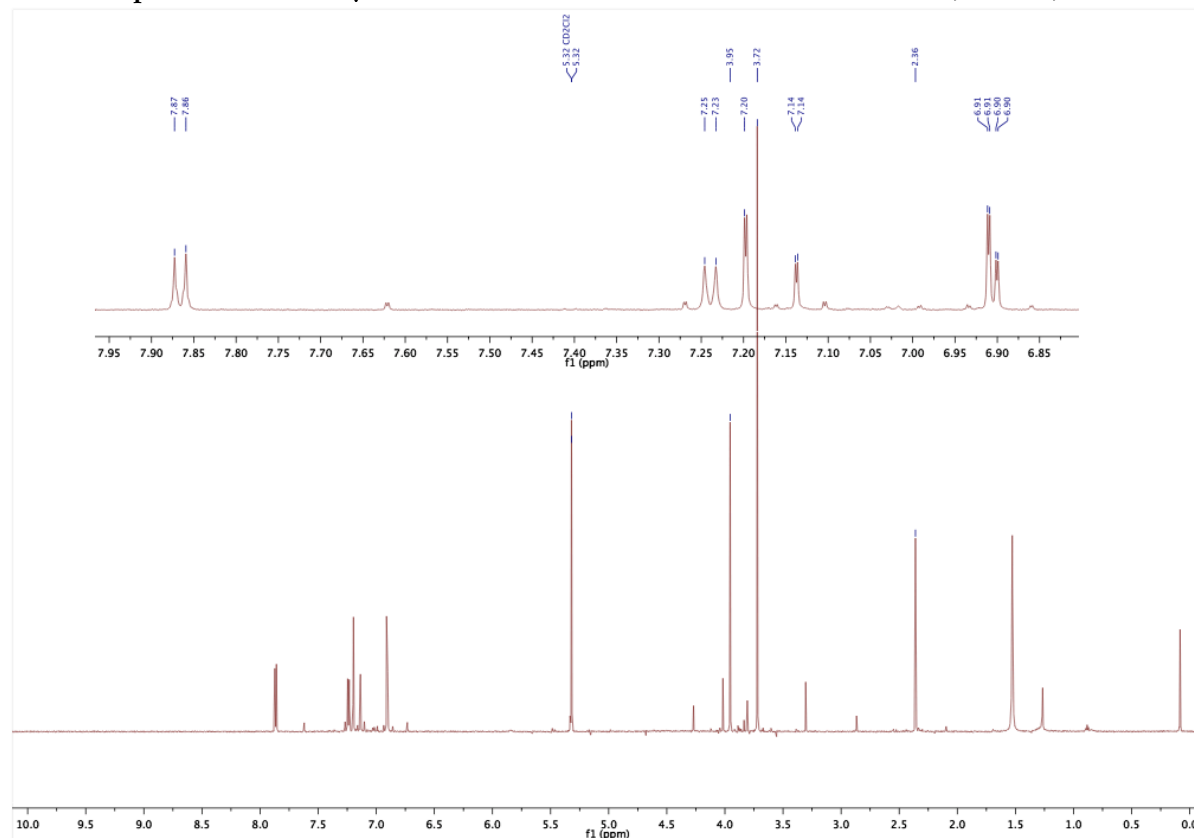


Solution IR Spectrum of [W(≡CC₆H₄Me-4)(CO)₂][HB(ImMe)₃] (4) (CH₂Cl₂)

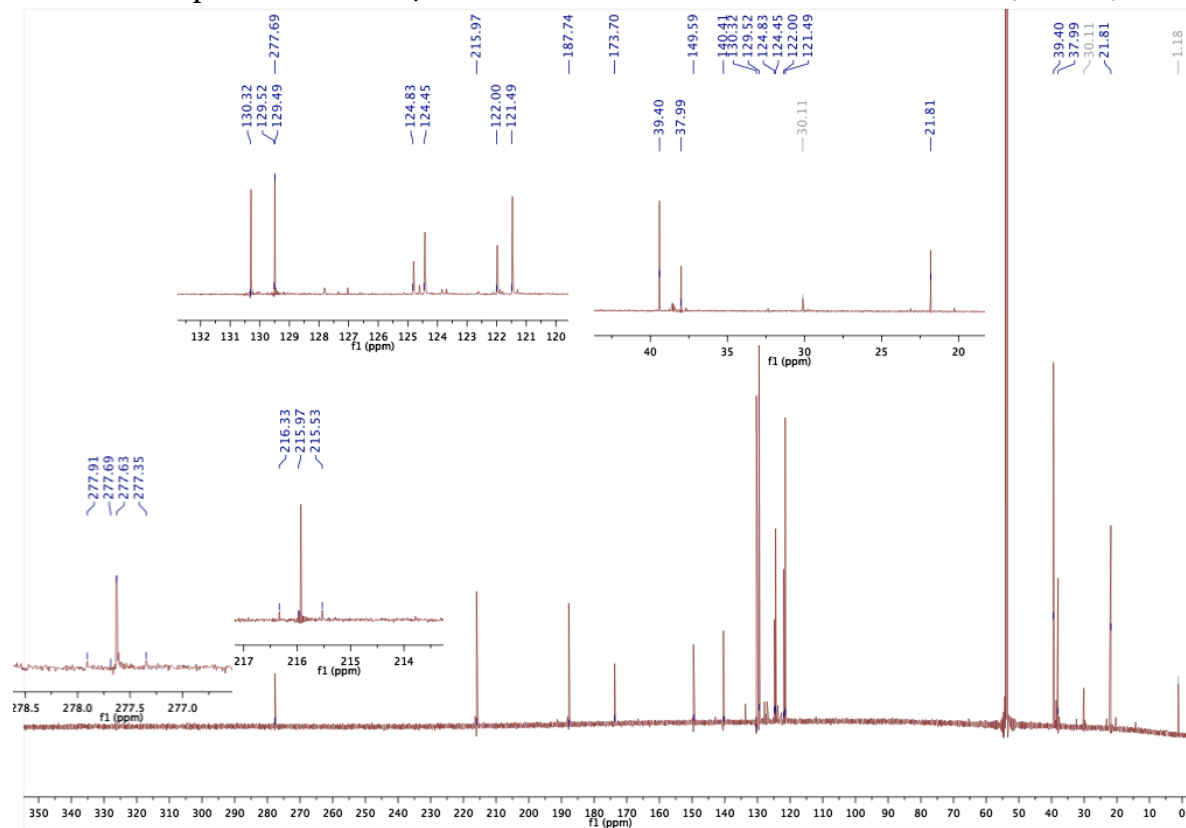


Sample Name	Description	Quality Checks
CI-WCTol-Tp_star	Sample 3669 By Administrator Date Wednesday, September 28 2022	The Quality Checks give rise to multiple warnings for the sample.

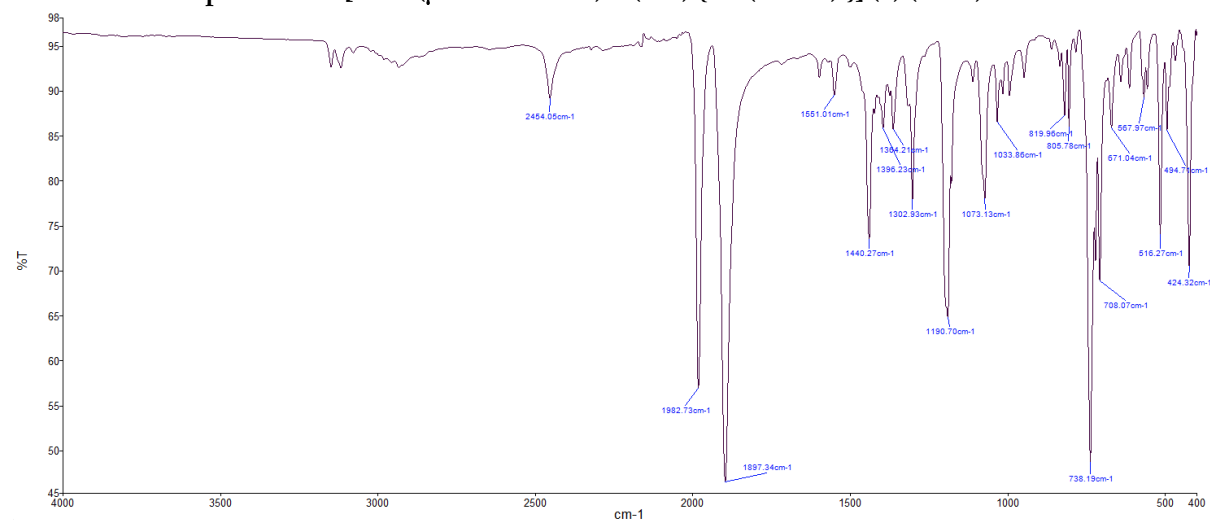
^1H NMR Spectrum of $[\text{WAu}(\mu\text{-CC}_6\text{H}_4\text{Me-4})\text{Cl}(\text{CO})_2\{\text{HB}(\text{ImMe})_3\}]$ (6) (600 MHz, CD_2Cl_2 , 25 °)



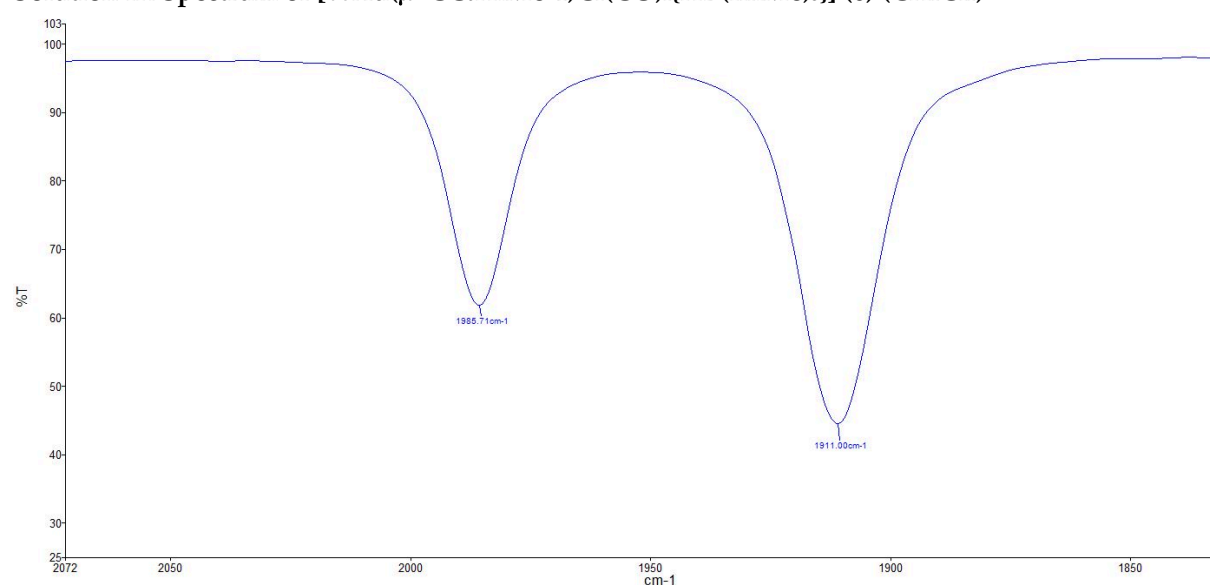
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of $[\text{WAu}(\mu\text{-CC}_6\text{H}_4\text{Me-4})\text{Cl}(\text{CO})_2\{\text{HB}(\text{ImMe})_3\}]$ (6) (151 MHz, CD_2Cl_2 , 25 °)



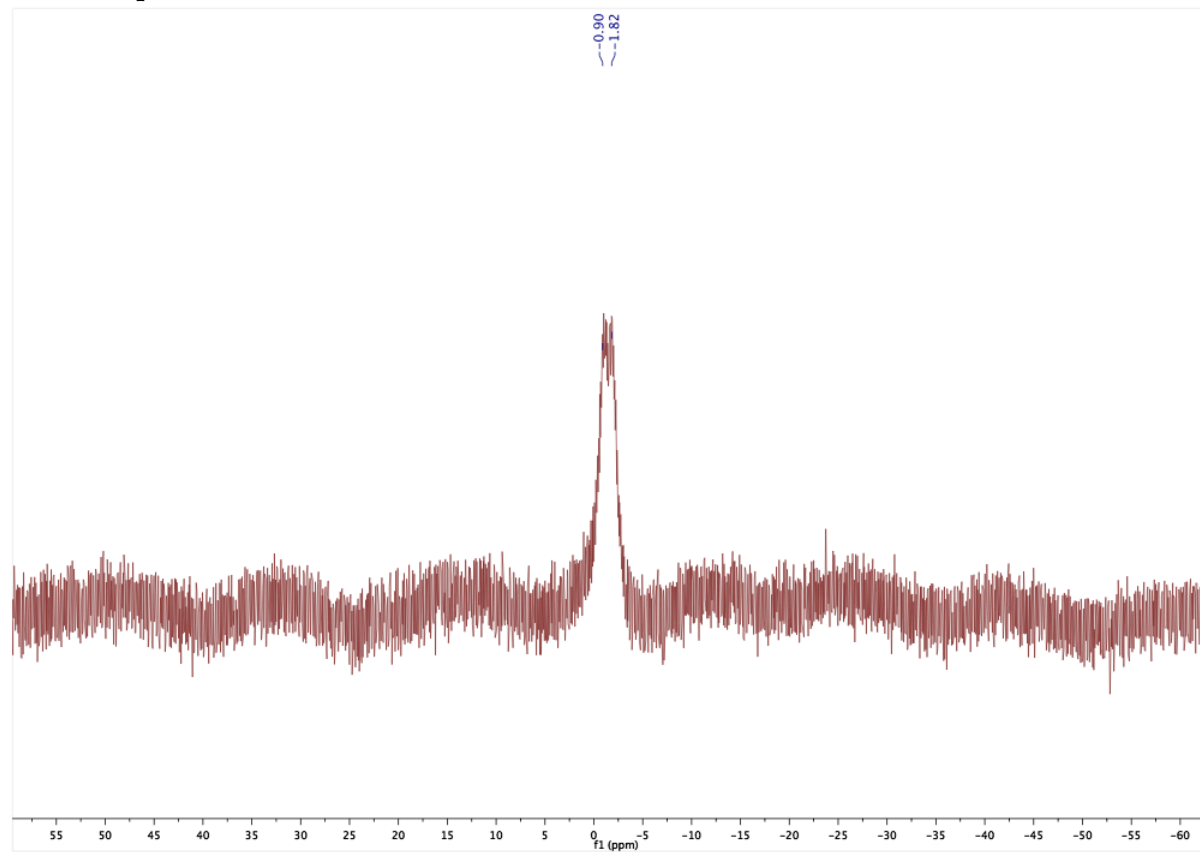
Solid State IR Spectrum of [WAu(μ -CC₆H₄Me-4)Cl(CO)₂{HB(ImMe)₃}] (6) (ATR)



Solution IR Spectrum of [WAu(μ -CC₆H₄Me-4)Cl(CO)₂{HB(ImMe)₃}] (6) (CH₂Cl₂)



^{11}B NMR Spectrum of $[\text{WAu}(\mu\text{-CC}_6\text{H}_4\text{Me-4})\text{Cl}(\text{CO})_2\{\text{HB}(\text{ImMe})_3\}]$ (6) (128 MHz, CD_2Cl_2 , 25 °)



High Resolution ESI-MS of $[\text{WAu}(\mu\text{-CC}_6\text{H}_4\text{Me-4})\text{Cl}(\text{CO})_2\{\text{HB}(\text{ImMe})_3\}]$ (6) (MeOH)

