Supplemental Information

Manganese(I) diamine electrocatalysts: Electrochemical carbon dioxide reduction to carbon monoxide

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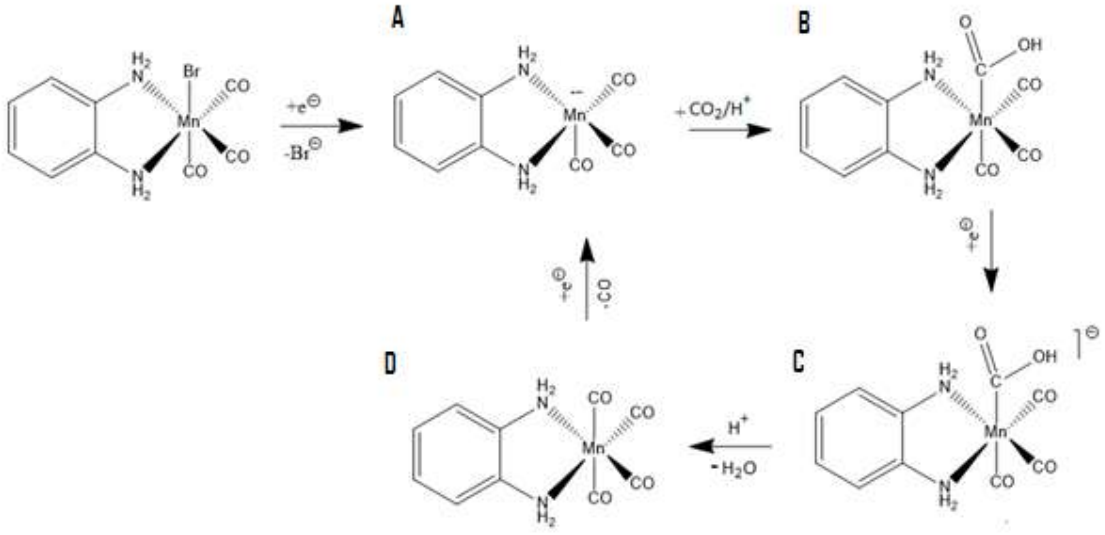


Scheme S1. A proposed mechanism for the electrocatalytic reduction of CO_2 by manganese (I) diamine catalysts. The catalyst is technically a procatalyst, as an active coordination site only becomes available upon initial reduction and subsequent loss of halide to form the catalyst, species A.

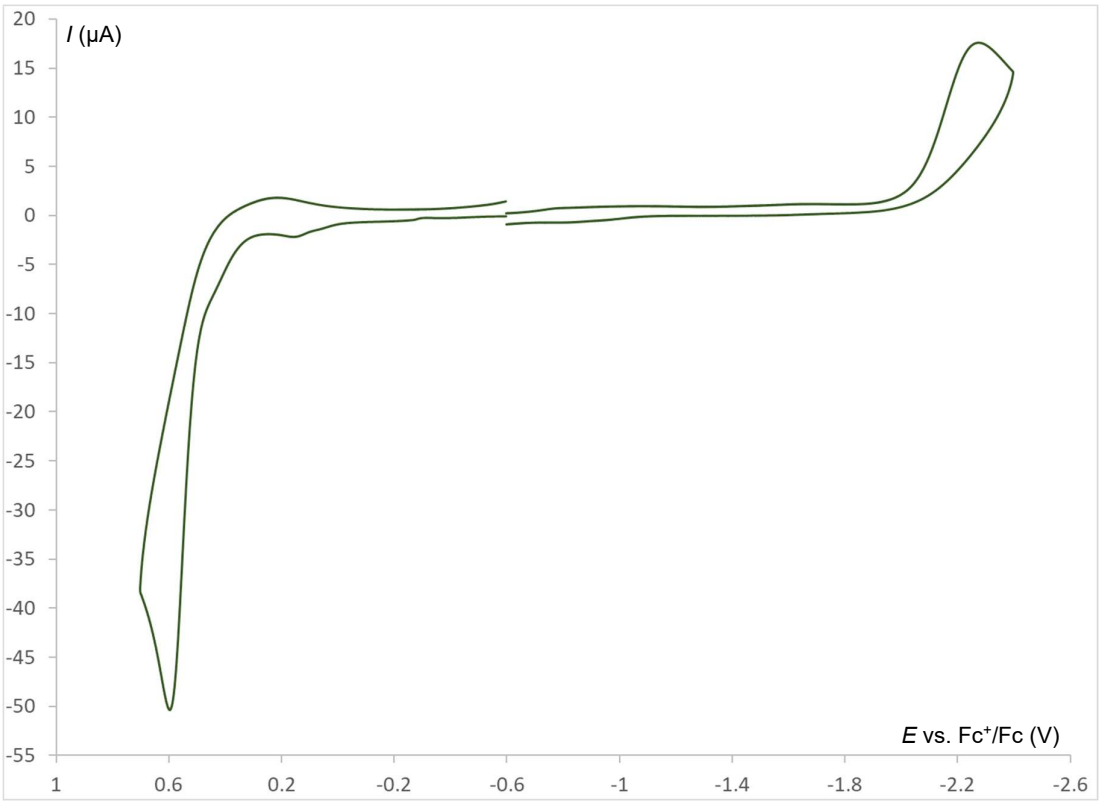


Figure S1. CV of 1.04 mM **Mn-1** recorded in 0.100 M Bu_4NPF_6 in dry Ar-saturated acetonitrile on a 3.00 mm diameter glassy carbon electrode vs. Fc^+/Fc at 0.100 V/s.

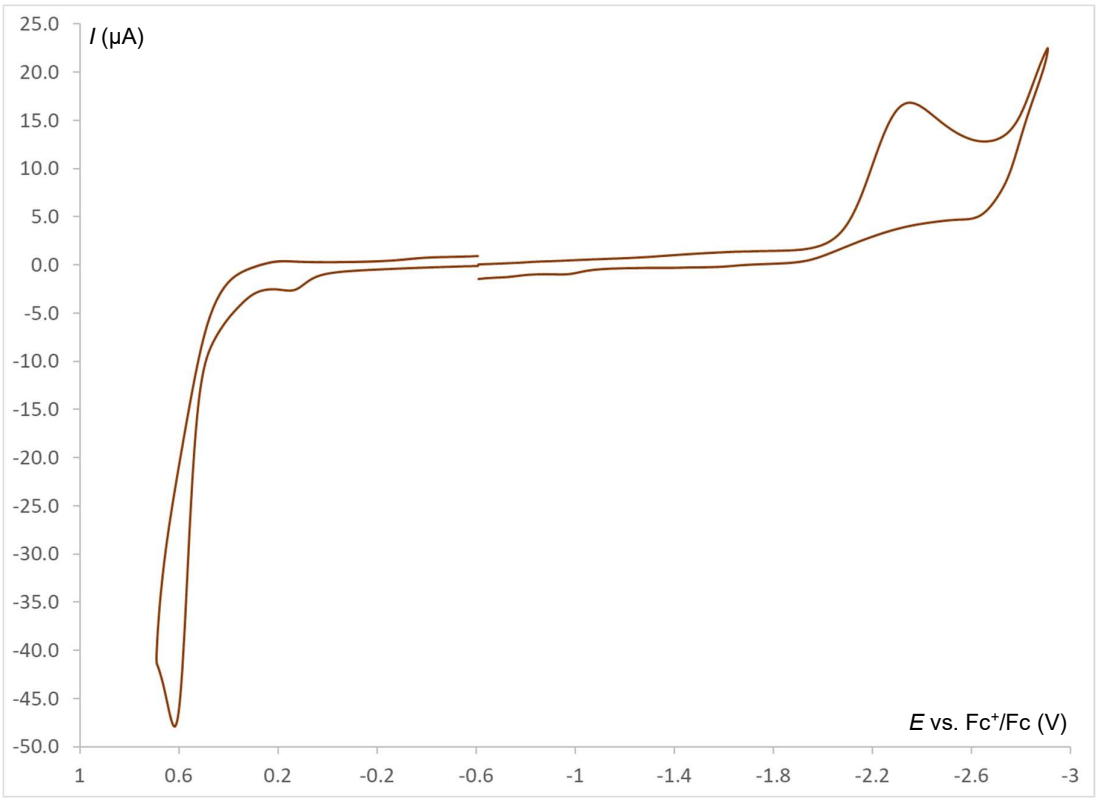


Figure S2. CV of 1.00 mM **Mn-2** recorded in 0.100 M Bu_4NPF_6 in dry Ar-saturated acetonitrile on a 3.00 mm diameter glassy carbon electrode vs. Fc^+/Fc at 0.100 V/s.

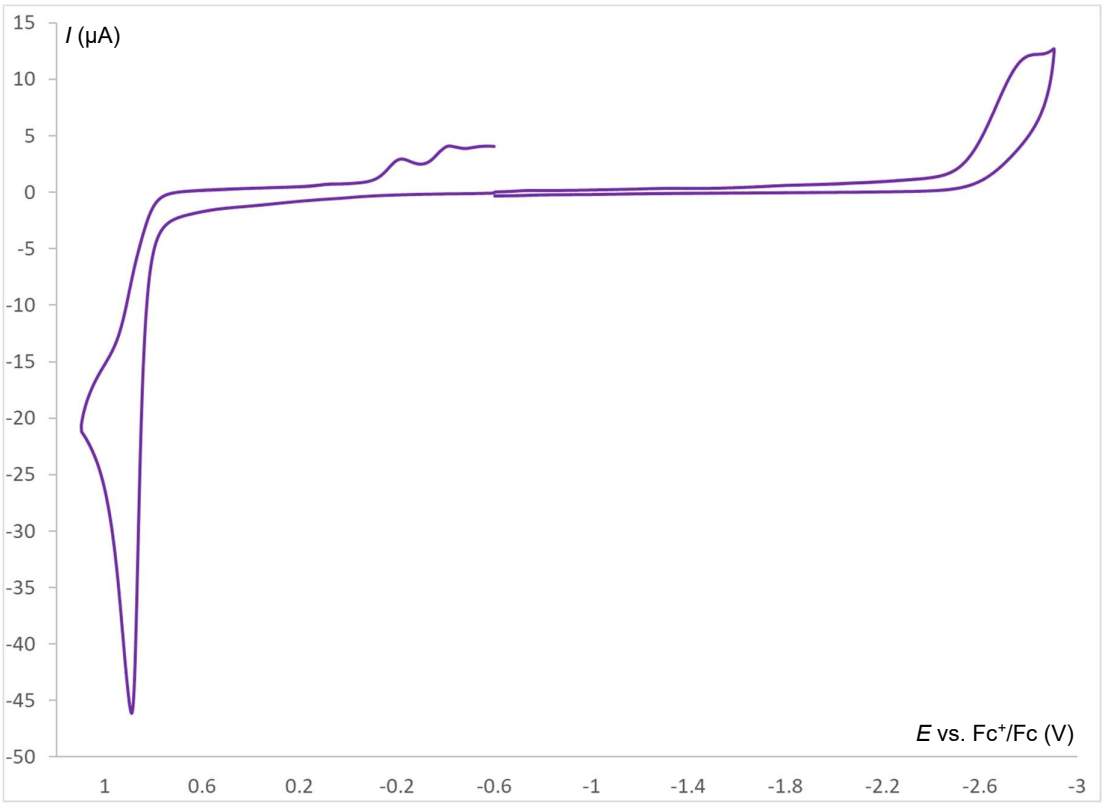


Figure S3. CV of 0.801 mM **Re-1** recorded in 0.100 M Bu_4NPF_6 in dry Ar-saturated acetonitrile on a 3.00 mm diameter glassy carbon electrode vs. Fc^+/Fc at 0.100 V/s.

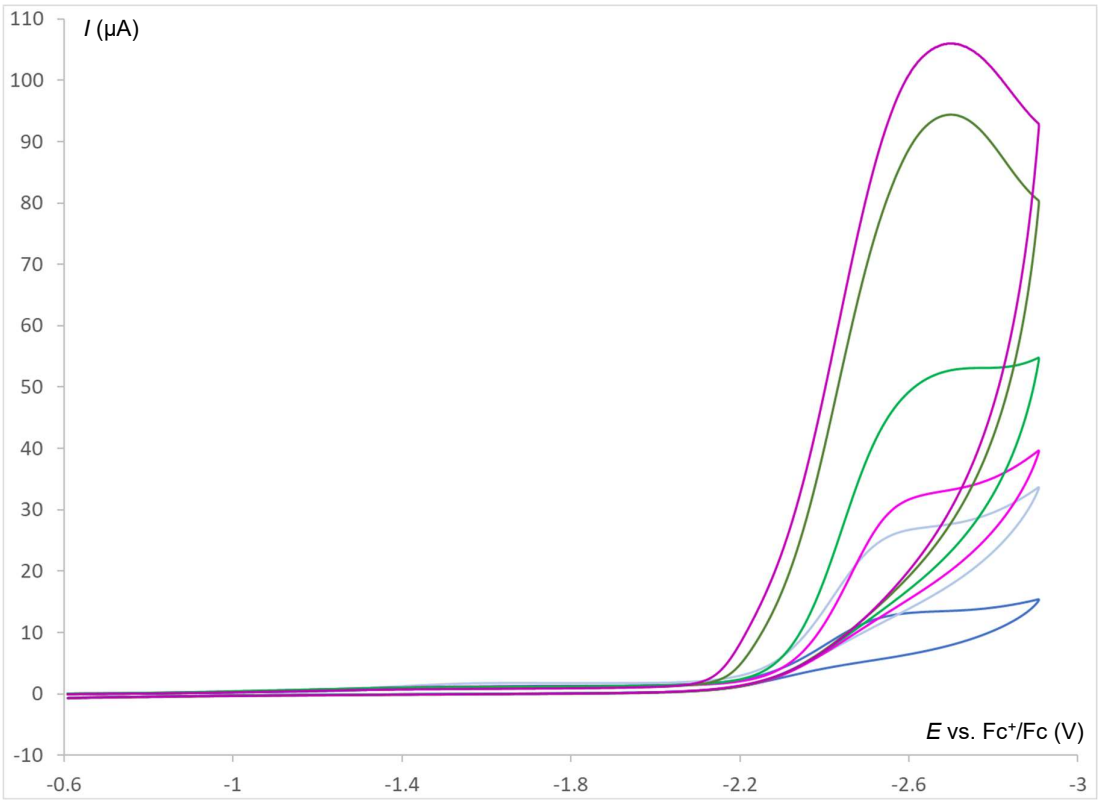


Figure S4. Cyclic voltammetry of 1.002 mM of **Mn-2** (blue) with subsequent additions of trifluoroethanol: 0.20 M, 0.50 M, 1.00 M, 1.50 M, 2.00 M. Recorded in 0.100 M Bu_4NPF_6 in dry CO_2-saturated acetonitrile on a 3.00 mm diameter glassy carbon electrode vs. Fc^+/Fc at 0.100 V/s.

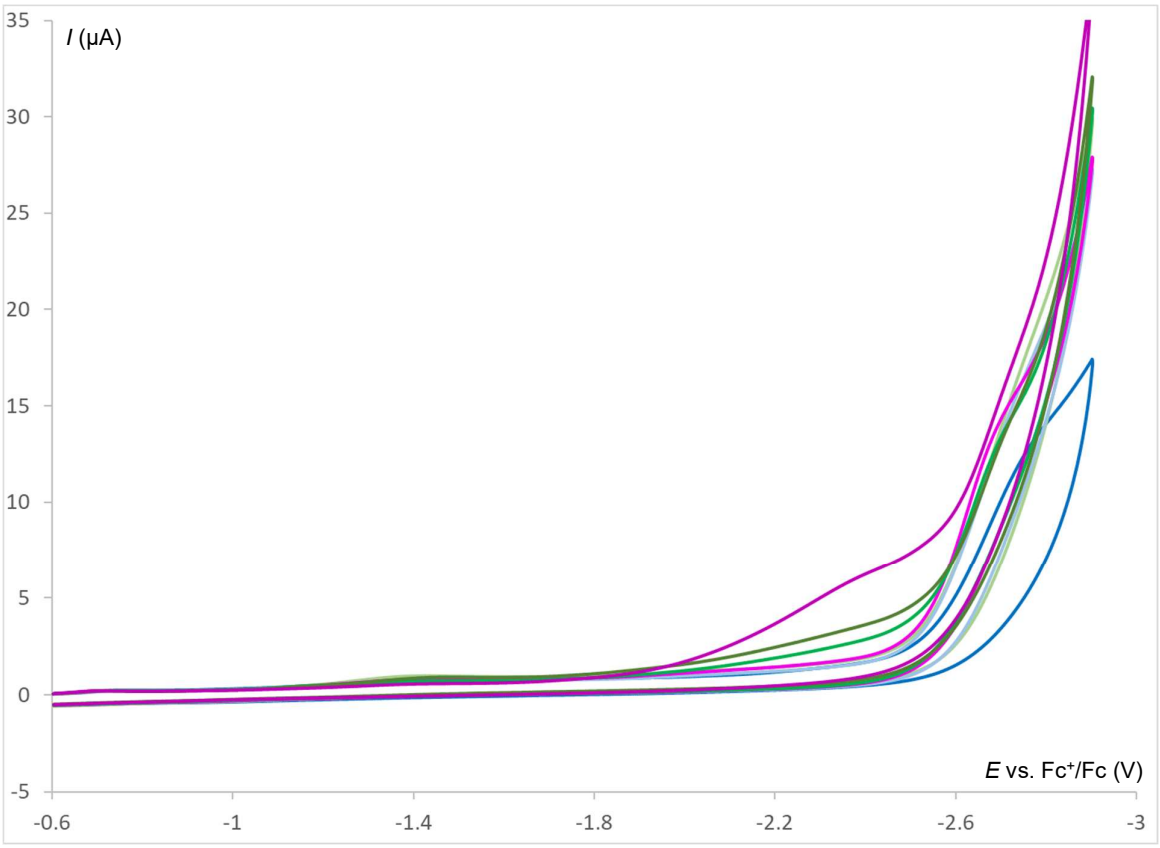


Figure S5. Cyclic voltammetry of 0.992 mM of **Re-1** (blue) with subsequent additions of trifluoroethanol: 0.10 M, 0.20 M, 0.50 M, 1.00 M, 1.50 M, 2.00 M. Recorded in 0.100 M Bu_4NPF_6 in dry CO_2-saturated acetonitrile on a 3.00 mm diameter glassy carbon electrode vs. Fc^+/Fc at 0.100 V/s.

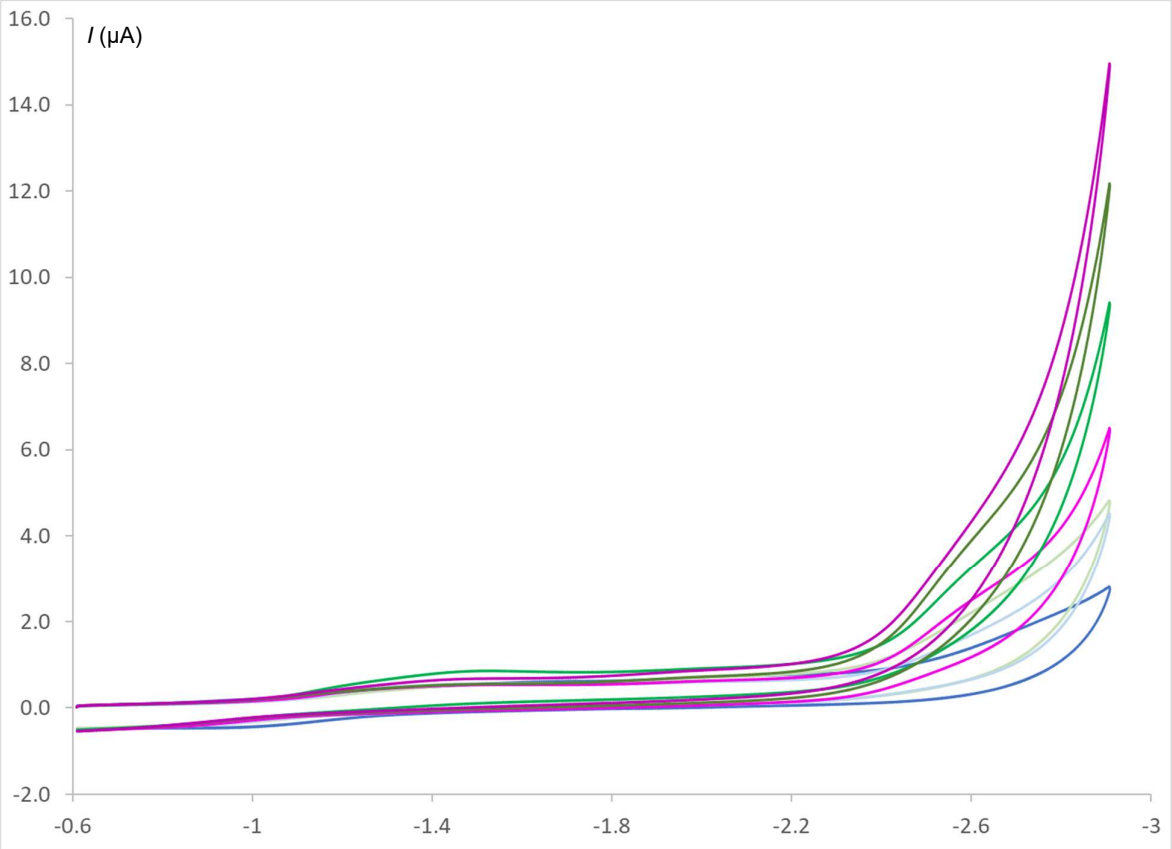


Figure S6. Cyclic voltammetry of electrolyte solution only (blue) with subsequent additions of trifluoroethanol: 0.10 M, 0.20 M, 0.50 M, 1.00 M, 1.50 M, 2.00 M. Recorded in 0.100 M Bu_4NPF_6 in dry CO_2-saturated acetonitrile on a 3.00 mm diameter glassy carbon electrode vs. Fc^+/Fc at 0.100 V/s.

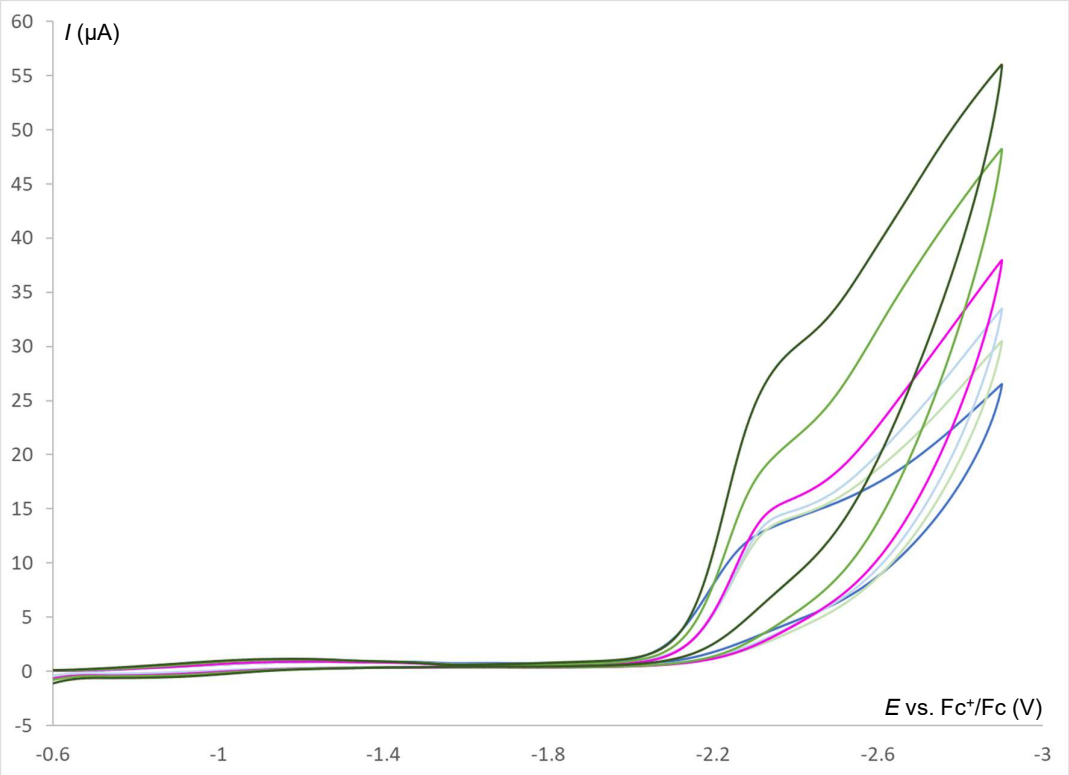


Figure S7. CV of 1.02 mM of **Mn-2** (blue) with subsequent additions of water: 0.05 M, 0.10 M, 0.20 M, 0.50 M and 1.00 M. Recorded in 0.100 M Bu_4NPF_6 in dry CO_2-saturated acetonitrile on a 3.00 mm diameter glassy carbon electrode vs. Fc^+/Fc at 0.100 V/s.

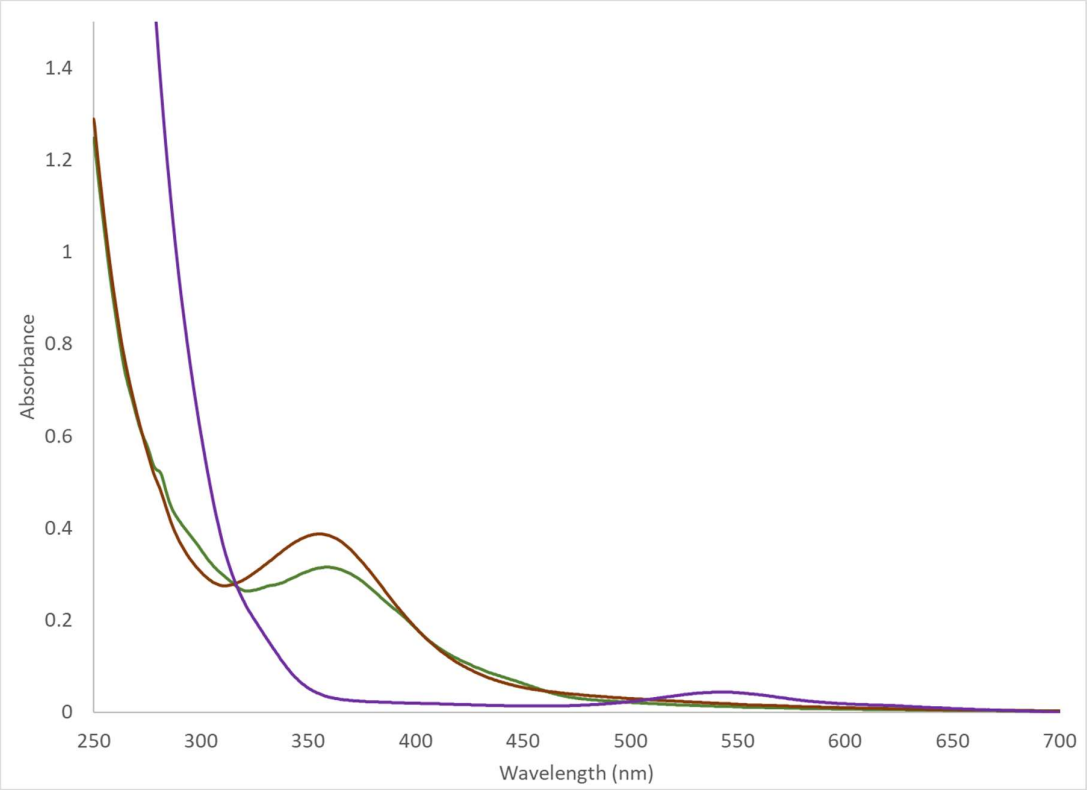


Figure S8. UV/Vis spectra of 0.200 mM **Mn-1** (green), 0.200 mM **Mn-2** (brown) and 0.500 mM **Re-1** (purple) in acetonitrile.

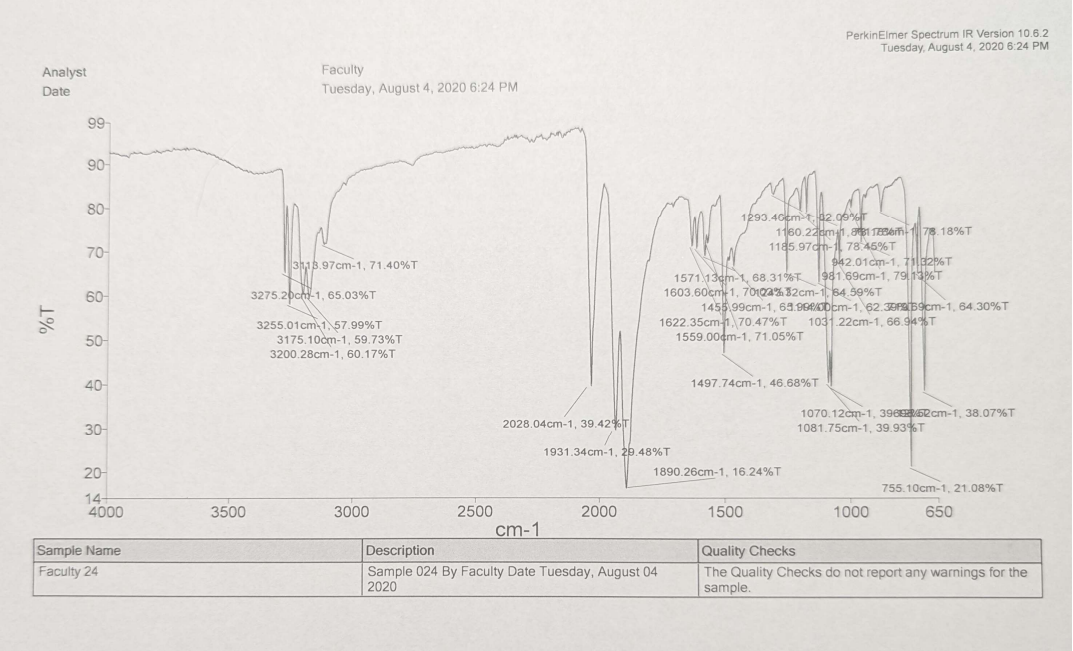


Figure S9. FTIR Spectra of solid **Mn-1**.

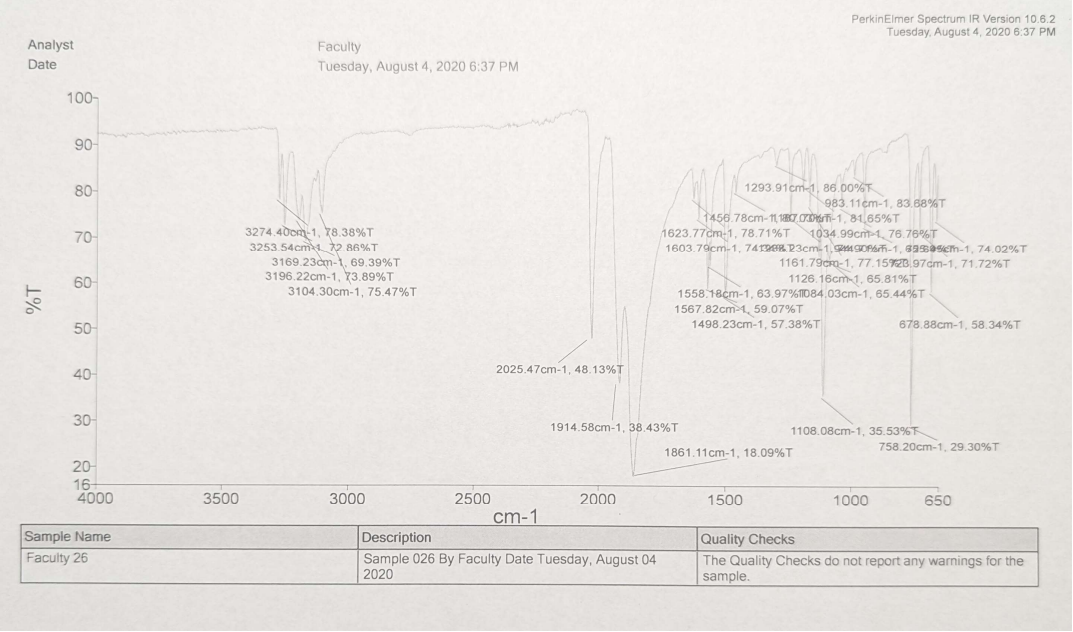
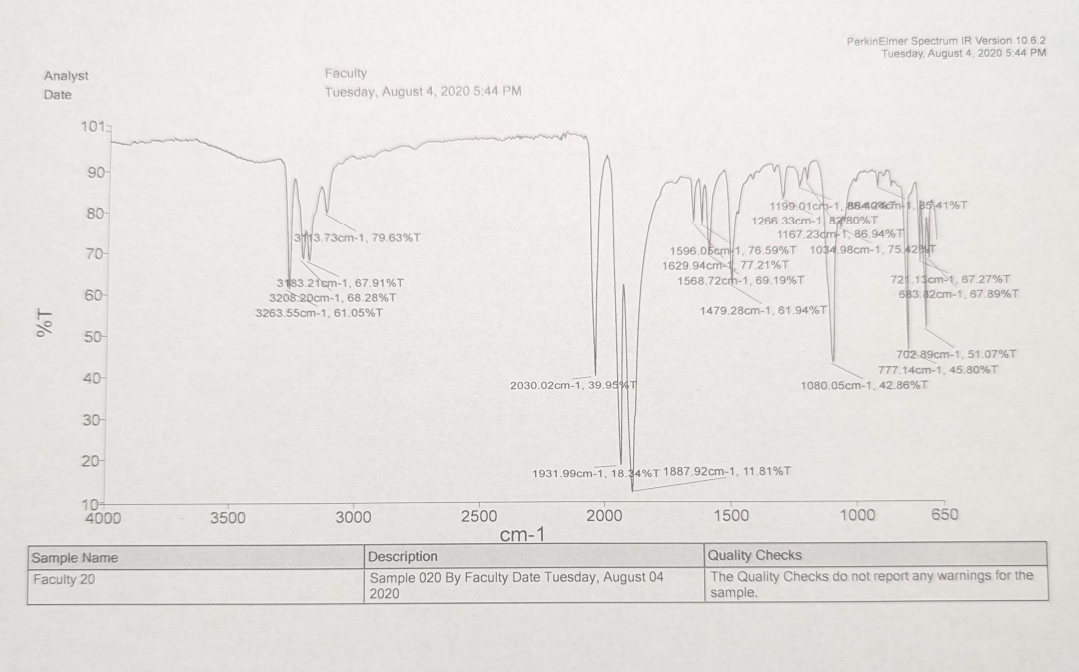
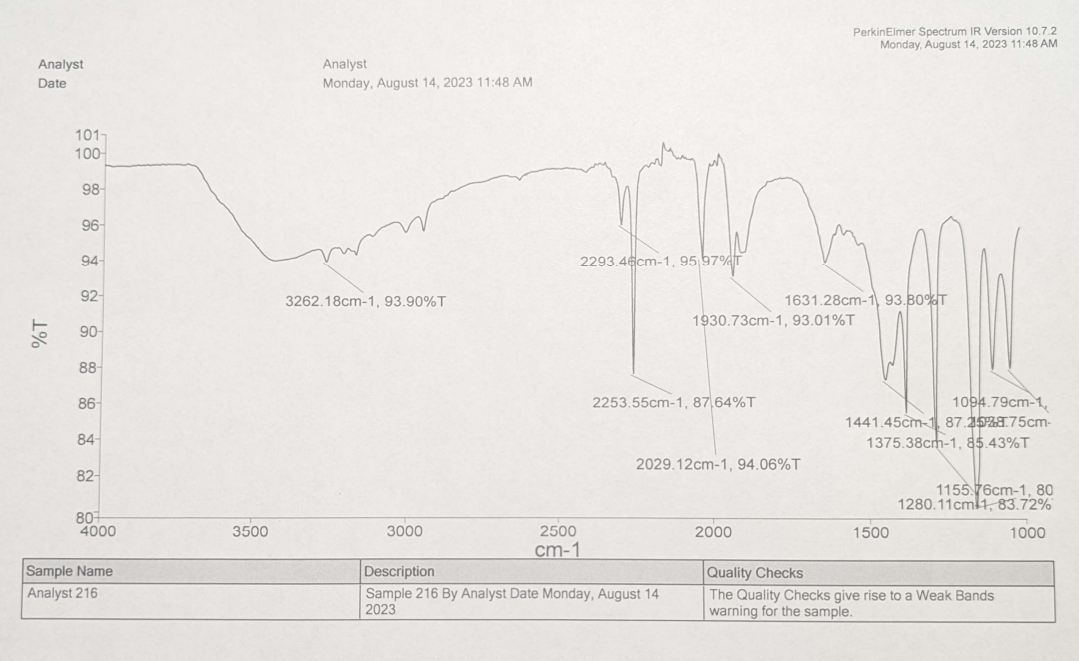


Figure S10. FTIR Spectra of solid **Re-1**.



Sample Name	Description	Quality Checks
Faculty 20	Sample 020 By Faculty Date Tuesday, August 04 2020	The Quality Checks do not report any warnings for the sample.



Sample Name	Description	Quality Checks
Analyst 216	Sample 216 By Analyst Date Monday, August 14 2023	The Quality Checks give rise to a Weak Bands warning for the sample.

Figure S11. FTIR Spectra of solid **Mn-2** (top).

(bottom) FTIR Spectra of **Mn-2** in acetonitrile (2293 and 2254 cm^{-1}) after bulk electrolysis in 1.50 M TFE, 0.100 M Bu_4NPF_6 in dry CO_2-saturated acetonitrile on a carbon rod electrode (surface area: 5.50 cm^2) at –2.20 V vs Fc/Fc^+ for 90-minutes.

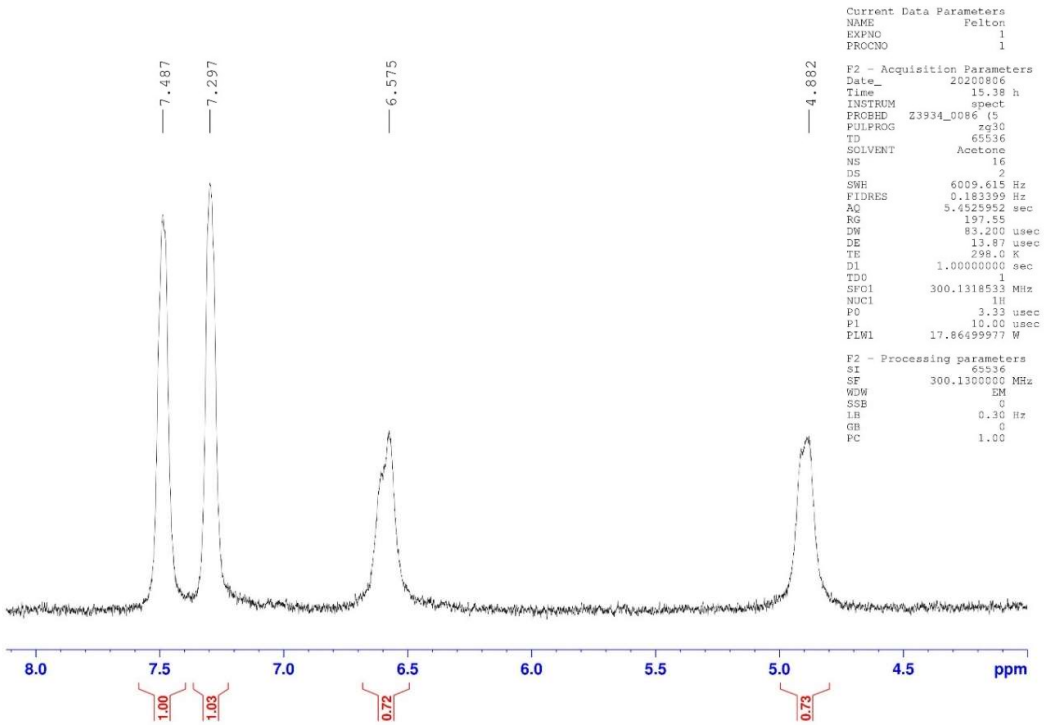


Figure S12. ^{1}H NMR (300 MHz, $(CD_3)_2CO$) spectra of **Mn-1**.

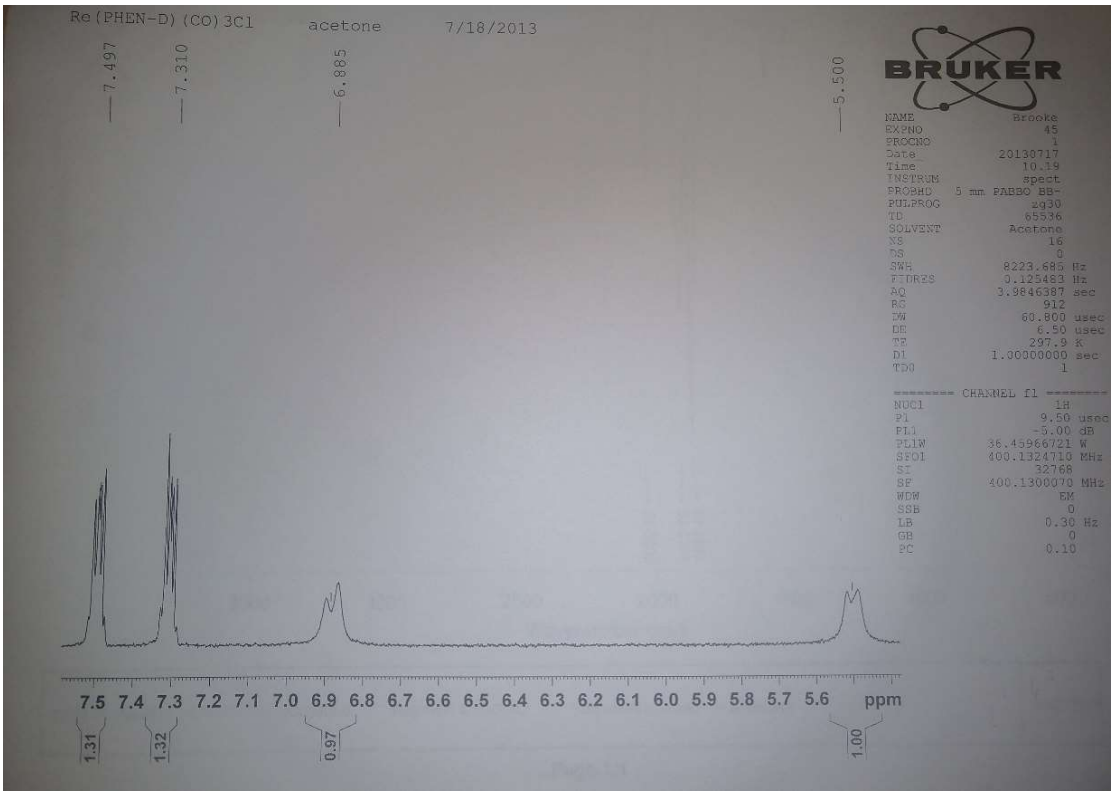


Figure S13. ^{1}H NMR (400 MHz, $(CD_3)_2CO$) spectra of **Re-1**.

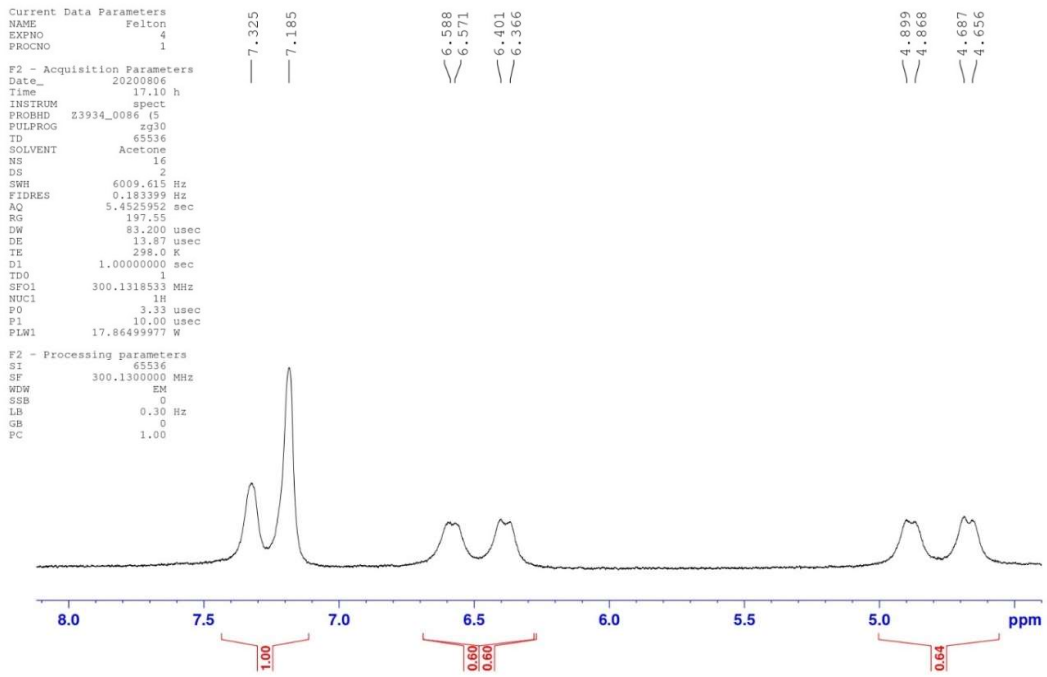


Figure S14. ^{1}H NMR (300 MHz, $(CD_3)_2CO$) spectra of **Mn-2**. Integration of the two peaks at 6.5 was carried out twice over overlapping regions to see if a different value could be obtianed, yet both integrations yielded the same 0.60 value (hence 0.60 is shown above twice).

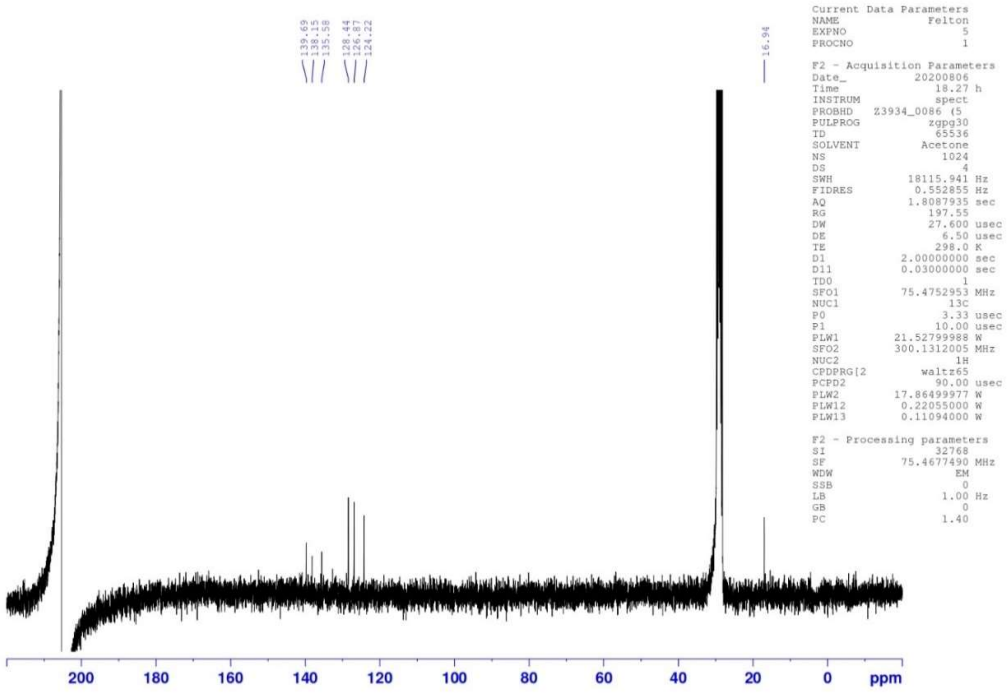
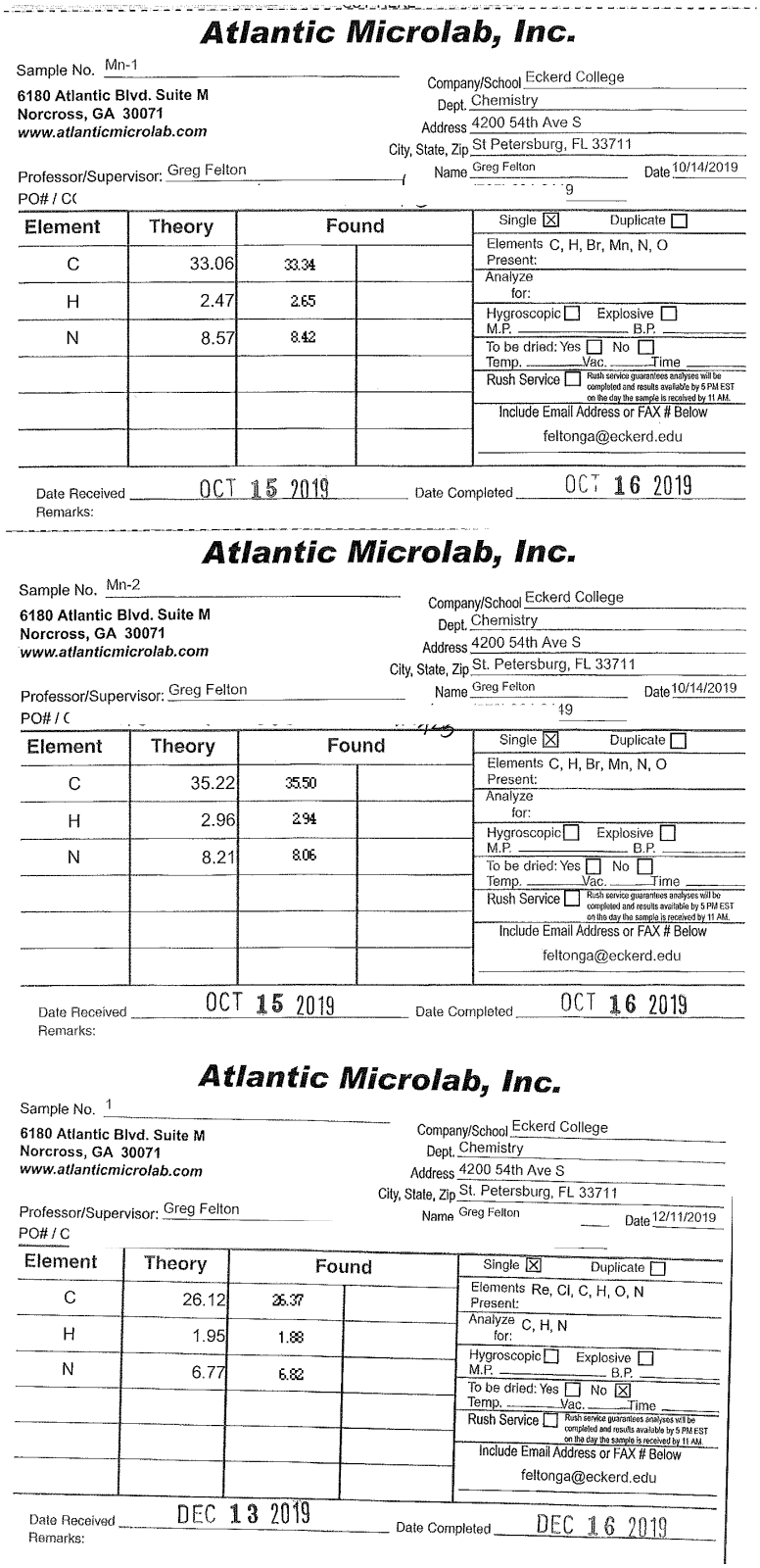


Figure S15. ^{13}C NMR (75 MHz, $(CD_3)_2CO$) spectra of **Mn-2**.



Atlantic Microlab, Inc.

Sample No. Mn-1

6180 Atlantic Blvd. Suite M
Norcross, GA 30071
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Company/School Eckerd College
Dept. Chemistry
Address 4200 54th Ave S
City, State, Zip St Petersburg, FL 33711
Name Greg Felton Date 10/14/2019

Professor/Supervisor: Greg Felton
PO# / C(9

Element	Theory	Found	
C	33.06	33.34	
H	2.47	2.65	
N	8.57	8.42	

Single ☒ Duplicate ☐
Elements Present: C, H, Br, Mn, N, O
Analyze for:
Hygroscopic ☐ Explosive ☐
M.P. ____ B.P. ____
To be dried: Yes ☐ No ☐
Temp. ____ Vac. ____ Time ____
Rush Service ☐ Rush service guarantees analyses will be completed and results available by 5 PM EST on the day the sample is received by 11 AM.
Include Email Address or FAX # Below
feltonga@eckerd.edu

Date Received OCT 15 2019 Date Completed OCT 16 2019
Remarks:

Atlantic Microlab, Inc.

Sample No. Mn-2

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Name Greg Felton Date 10/14/2019

Professor/Supervisor: Greg Felton
PO# / C 19

Element	Theory	Found	
C	35.22	35.50	
H	2.96	2.94	
N	8.21	8.06	

Single ☒ Duplicate ☐
Elements Present: C, H, Br, Mn, N, O
Analyze for:
Hygroscopic ☐ Explosive ☐
M.P. ____ B.P. ____
To be dried: Yes ☐ No ☐
Temp. ____ Vac. ____ Time ____
Rush Service ☐ Rush service guarantees analyses will be completed and results available by 5 PM EST on the day the sample is received by 11 AM.
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Date Received OCT 15 2019 Date Completed OCT 16 2019
Remarks:

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Sample No. 1

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Name Greg Felton Date 12/11/2019

Professor/Supervisor: Greg Felton
PO# / C

Element	Theory	Found	
C	26.12	26.37	
H	1.95	1.88	
N	6.77	6.82	

Single ☒ Duplicate ☐
Elements Present: Re, Cl, C, H, O, N
Analyze for: C, H, N
Hygroscopic ☐ Explosive ☐
M.P. ____ B.P. ____
To be dried: Yes ☐ No ☒
Temp. ____ Vac. ____ Time ____
Rush Service ☐ Rush service guarantees analyses will be completed and results available by 5 PM EST on the day the sample is received by 11 AM.
Include Email Address or FAX # Below
feltonga@eckerd.edu

Date Received DEC 13 2019 Date Completed DEC 16 2019
Remarks:

Figure S16. Elemental analyses for **Mn-1**, **Mn-2**, **Re-1**.

Table S1. Comparison of found elemental analysis values vs theoretical values for proposed "diamine" compounds versus alternative "diimine" compounds.

	Found C H N	Theor. "diamine" C H N	Theor. "diimine" C H N
Mn-1	33.34, **2.65**, 8.42	$C_9H_8BrN_2O_3Mn$ 33.06, **2.47**, 8.57	$C_9H_6BrN_2O_3Mn$ 33.26, **1.86**, 8.62
Mn-2	35.50, **2.94**, 8.06	$C_{10}H_{10}BrMnN_2O_3$ 35.22, **2.96**, 8.21	$C_{10}H_{10}BrMnN_2O_3$ 35.43, **2.38**, 8.26
Re-1	26.37, **1.88**, 6.82	$C_9H_8ClN_2O_3Re$ 26.12, **1.95**, 6.77	$C_9H_6ClN_2O_3Re$ 26.25, **1.47**, 6.80

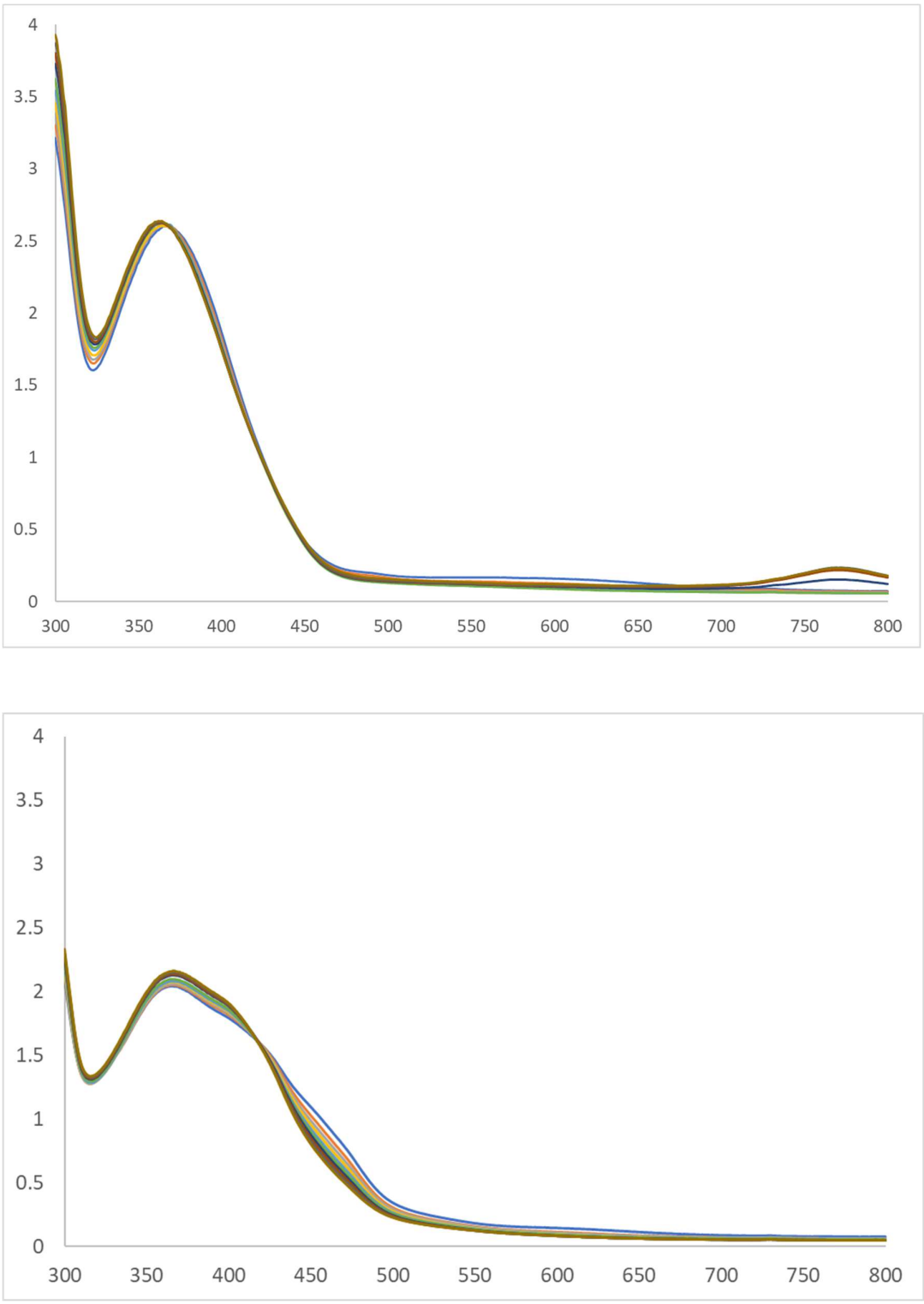
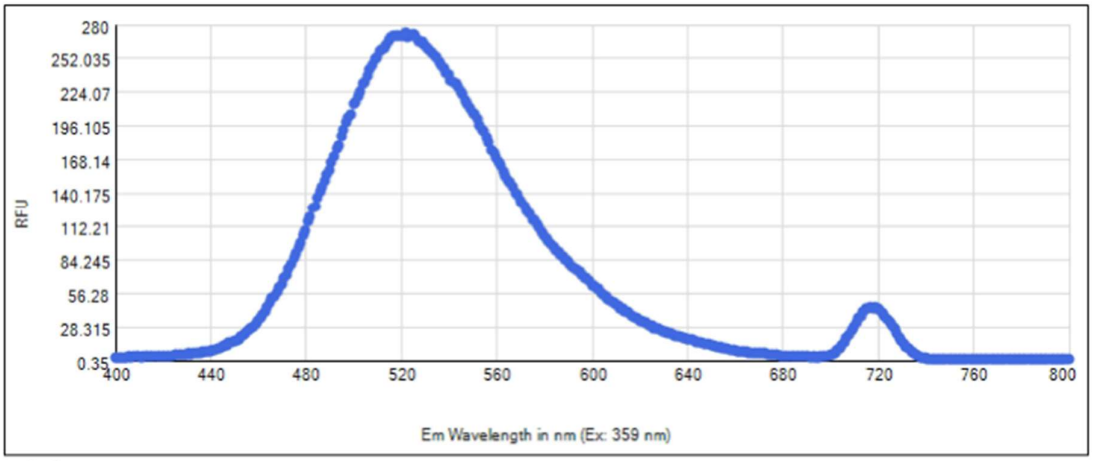


Figure S17. Decomposition study of **Mn-1** (top) and **Mn-2** (bottom) upon exposure of acetonitrile solution to ambient lab light in ten-minute time increments. **Re-1** showed no change over 90 minutes (data not shown)



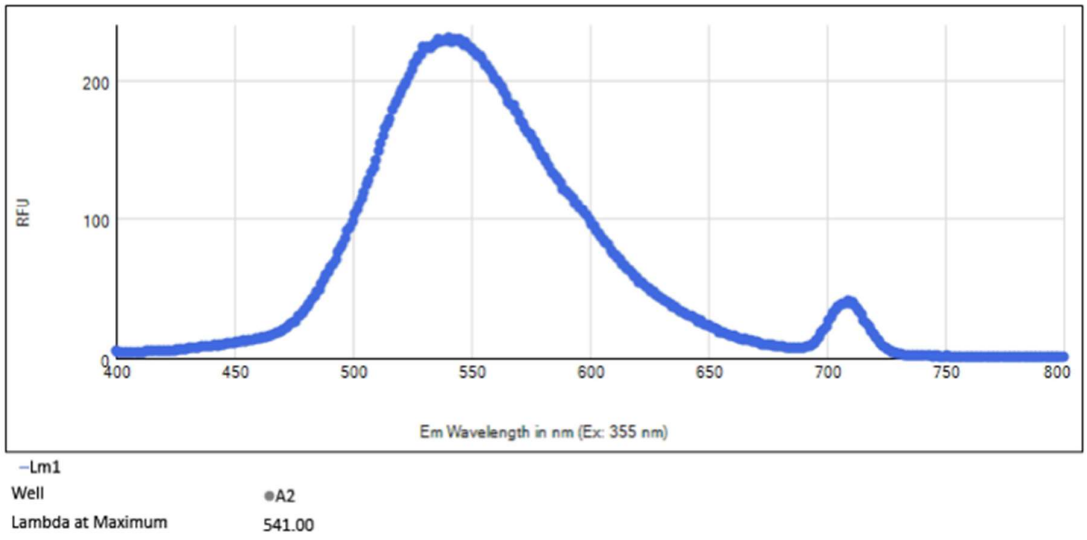


Figure S18. Fluorescence of **Mn-1** (top) and **Mn-2** (bottom) upon excitation at 359 and 355 nm, respectively, of 1.00 mM acetonitrile solution. **Re-1** showed no fluorescence with excitation at 261 or 543 nm (data not shown).

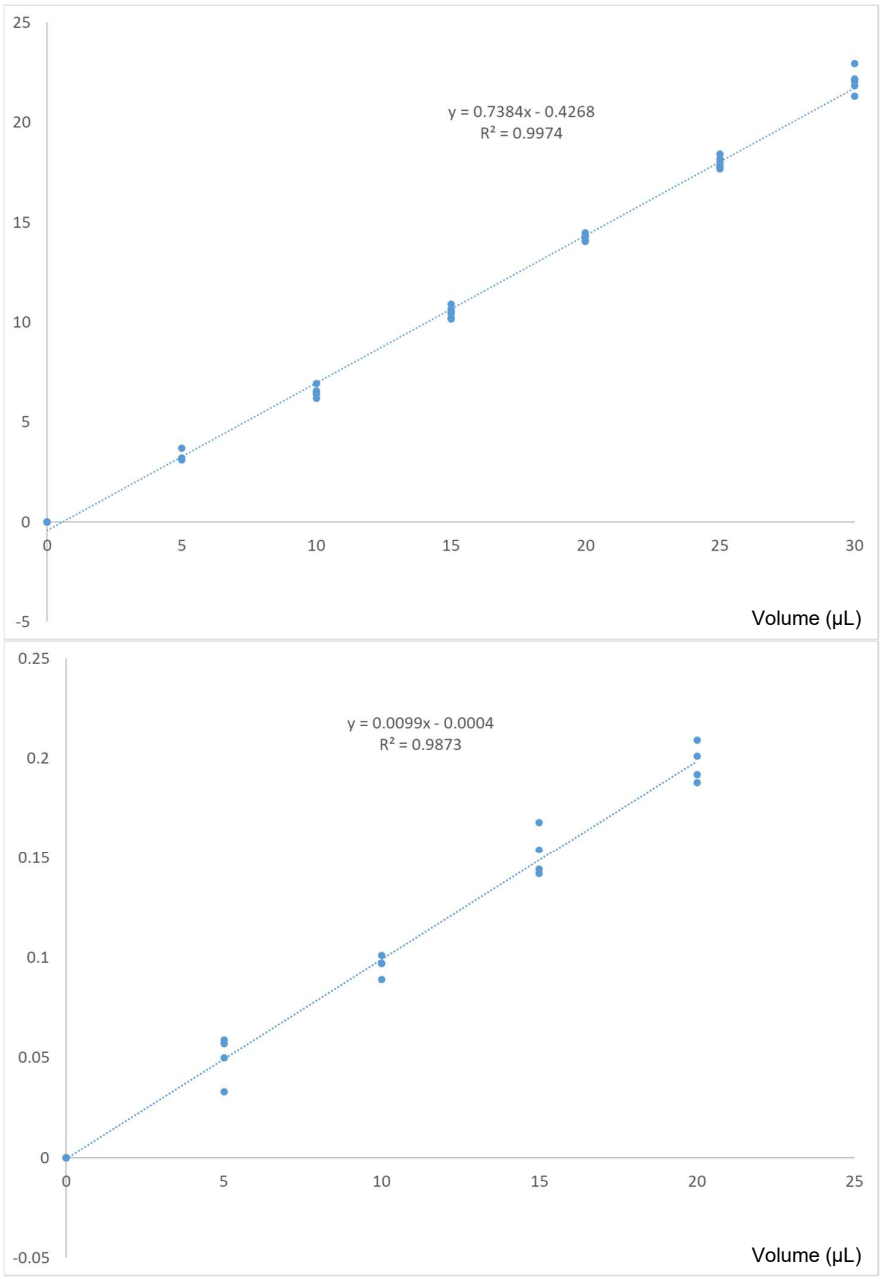


Figure S19. Calibration plot for CO (top) and H_2 (bottom) detection using a gas chromatograph with a thermal conductivity detector and He carrier gas. Neat samples were injected directly into the chromatograph from a gas-tight locking syringe. CO calibration used six injections (over two days) at the six volumes indicated. H_2 calibration used four injections (over two days) at the four volumes indicated. H_2 injections of larger volumes were not linear in response and were not used (beyond 30 µL area integration included negative regions).

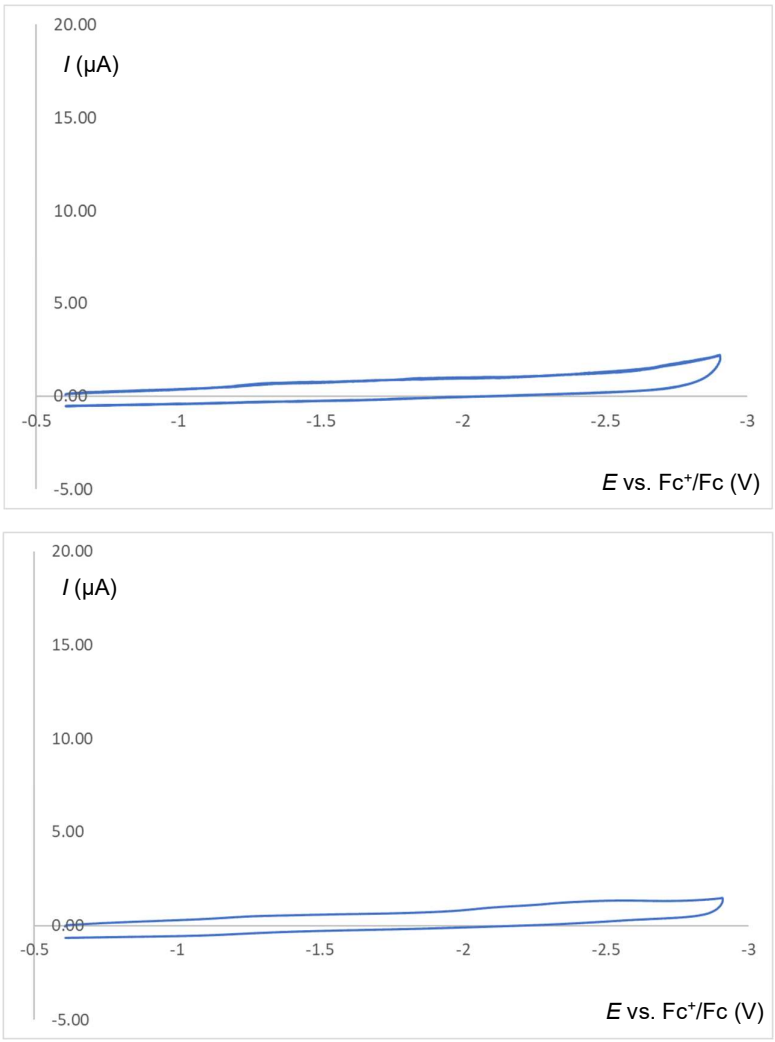


Figure S20. Background Cyclic voltammetry recorded in only 0.100 M Bu_4NPF_6 in argon-saturated acetonitrile (top) and in dry CO_2-saturated acetonitrile (bottom) on a 3.00 mm diameter glassy carbon electrode vs. Fc^+/Fc at 0.100 V/s.

THE UNIVERSITY of EDINBURGH
Crystal Structure Service

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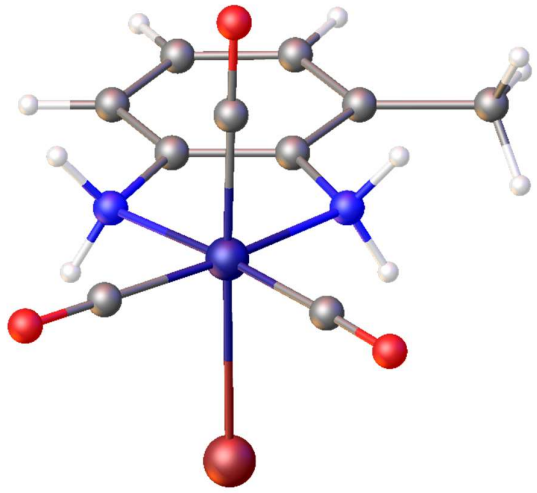
Submitted by: **Felton, G.**

Solved by: **Nichol, G.S.**

Sample ID: **Mn-2**

Compound sample 3 was provided as a dark brown crystalline residue suitable for single crystal X-ray diffraction, yielding structure ex4013.

Crystal Data and Experimental



Compound	**Mn-2**
CCDC	1893661
Formula	$C_{10}H_{10}BrMnN_2O_3$
$D_{calc.}$/ g cm^{-3}	1.800
μ/mm^{-1}	12.257
Formula Weight	341.05
Colour	dark brown
Shape	plate
Max Size/mm	0.24
Mid Size/mm	0.13
Min Size/mm	0.03
T/K	120.0
Crystal System	orthorhombic
Space Group	Pbca
a/Å	12.5019(5)
b/Å	11.6126(5)
c/Å	17.3371(9)
α/°	90
β/°	90
γ/°	90
V/Å^3	2517.01(19)
Z	8
Z'	1
Θ_{min}/°	5.102
Θ_{max}/°	77.022
Measured Refl.	20449
Independent Refl.	2626
Reflections Used	2314
R_{int}	0.0507
Parameters	229
Restraints	15
Largest Peak	0.779
Deepest Hole	-1.078
GooF	1.132
wR_2 (all data)	0.1185
wR_2	0.1145
R_1 (all data)	0.0494
R_1	0.0439

Experimental. Single dark brown plate-shaped crystals of (**Mn-2**) were recrystallised from a mixture of hexane, acetone and DCM by vapour diffusion. A suitable crystal (0.24 × 0.13 × 0.03 mm^3) was selected and mounted on a MITIGEN holder in Paratone oil on a Agilent Technologies SuperNova diffractometer. The crystal was kept at T = 120.0 K during data collection. Using **Olex2** (Dolomanov et al., 2009), the structure was solved with the **ShelXS** (Sheldrick, 2008) structure solution program, using the Direct Methods solution method. The model was refined with version 2014/6 of **ShelXL** (Sheldrick, 2008) using Least Squares minimisation.

Crystal Data. $C_{10}H_{10}BrMnN_2O_3$, M_r = 341.05, orthorhombic, Pbca (No. 61), a = 12.5019(5) Å, b = 11.6126(5) Å, c = 17.3371(9) Å, α = β = γ = 90 °, V = 2517.01(19) Å^3, T = 120.0 K, Z = 8, Z' = 1, μ (CuK$_\alpha$) = 12.257, 20449 reflections measured, 2626 unique (R_{int} = 0.0507) which were used in all calculations. The final wR_2 was 0.1185 (all data) and R_1 was 0.0439 (I > 2(I)).

Experimental Extended. A dark brown plate-shaped crystal with dimensions 0.24 × 0.13 × 0.03 mm^3 was mounted on on a MITIGEN holder in Paratone oil. Data were collected using a Agilent Technologies SuperNova diffractometer equipped with an Oxford Cryosystems Cryostream 700+ low-temperature apparatus operating at $T = 120.0$ K.

Data were measured using ω scans scans of 1.0° per frame for 1.2 s using CuK_α radiation (sealed X-ray tube). The total number of runs and images was based on the strategy calculation from the program CrysAlisPro (Agilent, V1.171.37.34k, 2014). The actually achieved resoltion was $\Theta = 77.022$.

Cell parameters were retrieved using the CrysAlisPro (Agilent, V1.171.37.34k, 2014) software and refined using CrysAlisPro (Agilent, V1.171.37.34k, 2014) on 6728 reflections, 33 of the observed reflections.

Data reduction was performed using the CrysAlisPro (Agilent, V1.171.37.34k, 2014) software which corrects for Lorentz polarisation. The final completeness is 100.00 out to 77.022 in Θ. The absorption coefficient (MU) of this material is 12.257 and the minimum and maximum transmissions are 0.976 and 0.996.

The structure was solved by Direct Methods using the **ShelXS** (Sheldrick, 2008) structure solution program and refined by Least Squares using version 2014/6 of **ShelXL** (Sheldrick, 2008).

The structure was solved in the space group Pbca (# 61). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

The 3-methylbenzene-1,2-diamine ligand was modelled as disorderd over two sites, as indicated by peaks in a difference electron density map, with occupancy ratio 0.702:0.298(11). The geometry of the minor component, indicated by atoms with a prime suffix, was restrained to be similar to that of the major component, and displacement ellipsoid restraints were used on the nitrogen atoms of the minor component. C4 and C4-prime were constrained to have the same co-ordinates and displacement ellipsoid parameters.

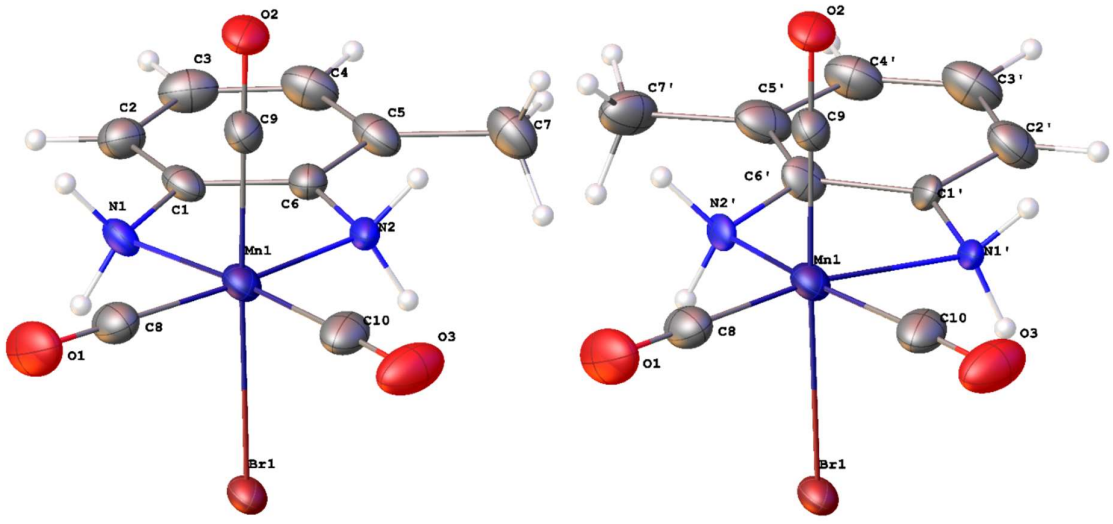


Figure S21. Major and minor component of **Mn-2** (30% ORTEP)

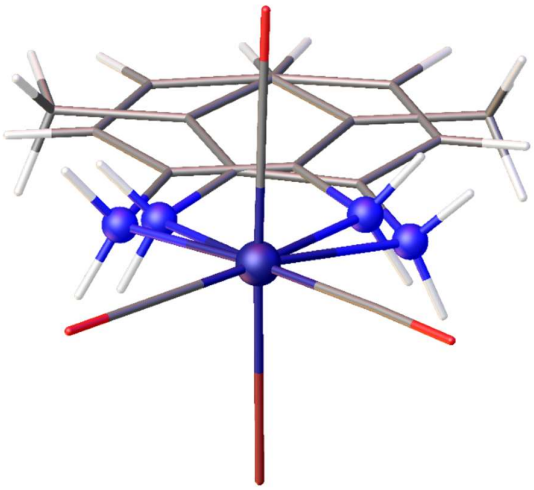


Figure S22. Major and minor component of **Mn-2** overlapped

Reflection Statistics

Total reflections	21994	Unique reflections	2626
Completeness	0.987	Mean I/sigma	21.19
Max hkl collected	(15, 14, 21)	Min hkl collected	(-15, -8, -21)
Max hkl used	(15, 14, 21)	Min hkl used	(0, 0, 0)
Lim d max	100.0	Lim d min	0.77
d max used	12.5	d min used	0.79
Friedel pairs	2241	Friedel pairs merged	1
Inconsistent equivalents	0	R_{int}	0.0507
R_{σ}	0.0235	Intensity transformed	0
Omitted reflections	0	Omitted by user	20
Multiplicity	(6254, 3146, 1459, 924, 239, 30)	ReflectionAPotMax	23
Removed Systmeatic Absences	1525	Filtered Off	0

Table S2. Bond Lengths in Å for **Mn-2**.

Atom	Atom	Length/Å
Br1	Mn1	2.5464(8)
Mn1	N1	2.094(11)
Mn1	N2	2.067(8)
Mn1	C8	1.792(5)
Mn1	C9	1.787(5)
Mn1	C10	1.791(6)
Mn1	N1'	2.179(17)
Mn1	N2'	2.05(2)
O1	C8	1.155(6)
O2	C9	1.151(6)
O3	C10	1.145(7)
N1	C1	1.474(11)
N2	C6	1.453(13)
C1	C2	1.382(14)
C1	C6	1.372(12)
C2	C3	1.389(13)
C3	C4	1.340(10)
C4	C5	1.388(10)
C5	C6	1.409(12)
C5	C7	1.497(12)
N1'	C1'	1.44(2)
N2'	C6'	1.43(2)
C1'	C2'	1.375(19)
C1'	C6'	1.366(19)
C2'	C3'	1.377(19)
C3'	C4'	1.332(16)
C4'	C5'	1.427(17)
C5'	C6'	1.404(17)
C5'	C7'	1.49(3)

Table S3. Bond Angles in ° for **Mn-2**.

Atom	Atom	Atom	Angle/°
N1	Mn1	Br1	86.9(3)
N2	Mn1	Br1	87.01(19)
N2	Mn1	N1	80.5(3)
C8	Mn1	Br1	90.98(16)
C8	Mn1	N1	89.6(3)
C8	Mn1	N2	170.0(3)
C8	Mn1	N1'	171.0(5)
C8	Mn1	N2'	103.7(5)
C9	Mn1	Br1	177.47(16)
C9	Mn1	N1	93.2(3)
C9	Mn1	N2	90.5(2)
C9	Mn1	C8	91.5(2)
C9	Mn1	C10	91.2(2)
C9	Mn1	N1'	95.4(4)
C9	Mn1	N2'	94.3(6)
C10	Mn1	Br1	88.68(16)
C10	Mn1	N1	175.6(3)
C10	Mn1	N2	99.5(3)
C10	Mn1	C8	90.3(3)
C10	Mn1	N1'	83.9(6)
C10	Mn1	N2'	164.8(5)
N1'	Mn1	Br1	82.1(4)
N2'	Mn1	Br1	85.2(6)
N2'	Mn1	N1'	81.5(6)
C1	N1	Mn1	112.1(6)
C6	N2	Mn1	113.3(5)
C2	C1	N1	122.4(8)
C6	C1	N1	116.2(10)
C6	C1	C2	121.4(10)
C1	C2	C3	118.3(9)
C4	C3	C2	119.7(8)
C3	C4	C5	124.3(6)
C4	C5	C6	115.5(7)
C4	C5	C7	122.6(7)
C6	C5	C7	121.9(8)
C1	C6	N2	117.2(10)
C1	C6	C5	120.7(10)
C5	C6	N2	122.0(8)
O1	C8	Mn1	179.9(7)
O2	C9	Mn1	179.7(5)
O3	C10	Mn1	177.9(5)
C1'	N1'	Mn1	105.9(10)
C6'	N2'	Mn1	111.9(13)
C2'	C1'	N1'	117.7(15)
C6'	C1'	N1'	120.8(14)
C6'	C1'	C2'	121.5(17)
C1'	C2'	C3'	118.4(18)
C4'	C3'	C2'	122.7(17)
C3'	C4'	C5'	119.3(11)
C4'	C5'	C7'	123.9(16)
C6'	C5'	C4'	118.2(14)
C6'	C5'	C7'	117.9(17)
C1'	C6'	N2'	117.3(15)
C1'	C6'	C5'	119.5(17)
C5'	C6'	N2'	123.1(17)

Submitted by: **Greg Felton**

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Crystal Structure Service

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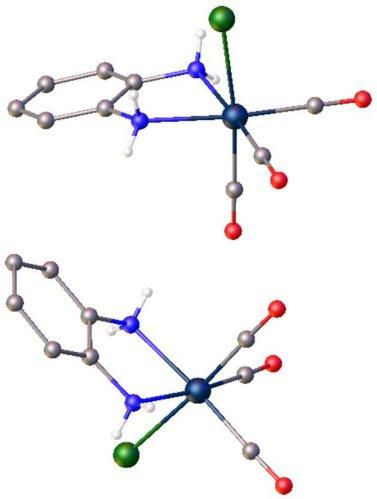
Solved by: **Gary S Nichol**

Sample ID: **Re-1**

Compound Re-diamine was provided as dark red crystals suitable for single crystal X-ray diffraction, yielding structure EX16036.

Crystal Data and Experimental



Experimental. Single dark red block-shaped crystals of (**Re-1**) were recrystallised from diethyl ether by slow evaporation. A suitable crystal (0.17×0.14×0.09) mm^3 was selected and mounted on a MITIGEN holder in Paratone oil on a Rigaku Oxford Diffraction SuperNova diffractometer. The crystal was kept at T = 120.0 K during data collection. Using **Olex2** (Dolomanov et al., 2009), the structure was solved with the **ShelXS** (Sheldrick, 2008) structure solution program, using the Direct Methods solution method. The model was refined with version 2014/7 of **ShelXL** (Sheldrick, 2015) using Least Squares minimisation.

Crystal Data. $C_9H_8ClN_2O_3Re$, M_r = 413.82, triclinic, P-1 (No. 2), a = 9.3117(3) Å, b = 11.5100(4) Å, c = 12.3513(4) Å, α = 110.072(3)°, β = 101.473(3)°, γ = 107.544(3)°, V = 1115.93(7) Å^3, T = 120.0 K, Z = 4, Z' = 2, μ(MoK$_\alpha$) = 11.120, 30060 reflections measured, 5717 unique (R_{int} = 0.0480) which were used in all calculations. The final wR_2 was 0.0668 (all data) and R_1 was 0.0295 (I > 2(I)).

Compound	**Re-1**
CCDC	1893660
Formula	$C_9H_8ClN_2O_3Re$
$D_{calc.}$/ g cm^{-3}	2.463
μ/mm^{-1}	11.120
Formula Weight	413.82
Colour	dark red
Shape	block
Size/mm^3	0.17×0.14×0.09
T/K	120.0
Crystal System	triclinic
Space Group	P-1
a/Å	9.3117(3)
b/Å	11.5100(4)
c/Å	12.3513(4)
α/°	110.072(3)
β/°	101.473(3)
γ/°	107.544(3)
V/Å^3	1115.93(7)
Z	4
Z'	2
Wavelength/Å	0.71073
Radiation type	MoK$_\alpha$
Θ_{min}/°	3.141
Θ_{max}/°	29.698
Measured Refl.	30060
Independent Refl.	5717
Reflections Used	4872
R_{int}	0.0480
Parameters	313
Restraints	15
Largest Peak	2.578
Deepest Hole	-0.915
GooF	1.063
wR_2 (all data)	0.0668
wR_2	0.0626
R_1 (all data)	0.0390
R_1	0.0295

Structure Quality Indicators

Reflections:	d min 0.72	I/σ 20.2	Rint 4.80%	complete at 2θ=53° 90%
Refinement:	Shift 0.003	Max Peak 2.6	Min Peak -0.9	GooF 1.063

A dark red block-shaped crystal with dimensions 0.17×0.14×0.09 mm^3 was mounted on a MITIGEN holder in Paratone oil.X-ray diffraction data were collected using a Rigaku Oxford Diffraction SuperNova diffractometer equipped with a Oxford Cryosystems Cryostream 700+ low-temperature device, operating at T = 120.0 K.

Data were measured using ω scans scans of 1.0 ° per frame for 2.5 s using MoK_α radiation (micro-focus sealed X-ray tube, 50 kV, 0.8 mA). The total number of runs and images was based on the strategy calculation from the program CrysAlisPro (Agilent).The maximum resolution achieved was Θ = 29.698. °

Cell parameters were retrieved using the CrysAlisPro (Agilent) software and refined using CrysAlisPro (Agilent) on 13691 reflections, 46 % of the observed reflections. Data reduction was performed using the CrysAlisPro (Agilent) software which corrects for Lorentz polarisation. The final completeness is 99.80 out to 29.698 in Θ. The absorption coefficient μ of this material is 11.120 at this wavelength (λ = 0.71073) and the minimum and maximum transmissions are 0.891 and 0.940.

The structure was solved in the space group P-1 (# 2) by Direct Methods using the **ShelXS** (Sheldrick, 2008) structure solution program and refined by Least Squares using version 2014/7 of **ShelXL** (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

_refine_special_details: N-bound H atoms were located in a difference Fourier map and refined with appropriate distance restraints.

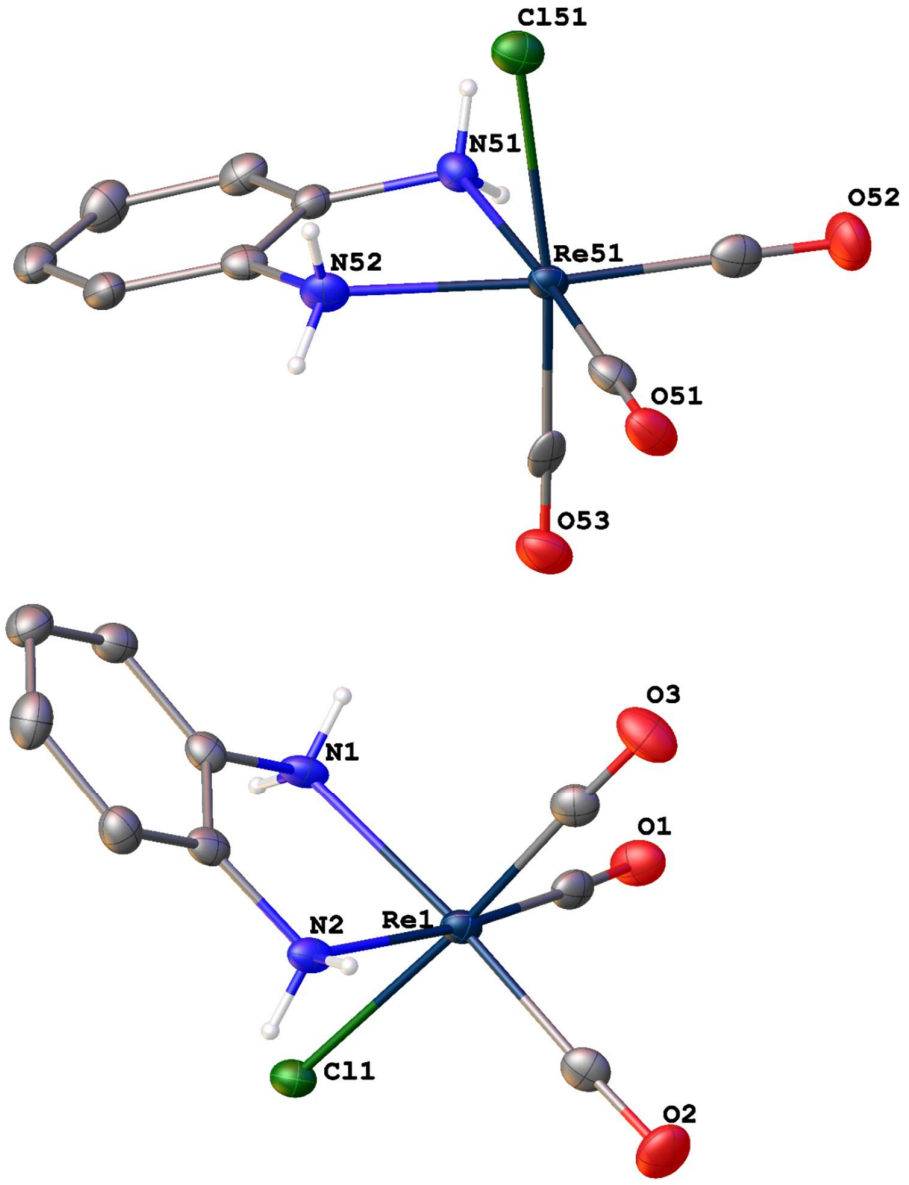


Figure S23: The asymmetric unit of **Re-1**. Displacement ellipsoids are at the 50% probability level.

Reflection Statistics

Total reflections (after filtering)	30060	Unique reflections	5717
Completeness	0.904	Mean I/σ	20.19
hkl_{max} collected	(12, 15, 17)	hkl_{min} collected	(-12, -16, -17)
hkl_{max} used	(12, 14, 17)	hkl_{min} used	(-12, -16, 0)
Lim d_{max} collected	100.0	Lim d_{min} collected	0.36
d_{max} used	6.48	d_{min} used	0.72
Friedel pairs	5033	Friedel pairs merged	1
Inconsistent equivalents	0	R_{int}	0.048
R_{sigma}	0.038	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	0
Multiplicity	(2605, 2945, 2151, 1480, 850, 392, 164, 85, 35, 26, 17)	Maximum multiplicity	16
Removed systematic absences	0	Filtered off (Shel/OMIT)	0

Table S4. Bond Lengths in Å for **Re-1**.

Atom	Atom	Length/Å
Re1	Cl1	2.5103(12)
Re1	N1	2.204(4)
Re1	N2	2.193(4)
Re1	C7	1.911(5)
Re1	C8	1.916(5)
Re1	C9	1.901(5)
O1	C7	1.153(6)
O2	C8	1.149(6)
O3	C9	1.156(6)
N1	C1	1.463(6)
N2	C2	1.448(6)
C1	C2	1.391(7)
C1	C6	1.385(7)
C2	C3	1.387(7)
C3	C4	1.379(7)
C4	C5	1.398(8)
C5	C6	1.376(7)

Atom	Atom	Length/Å
Re51	Cl51	2.4911(13)
Re51	N51	2.197(4)
Re51	N52	2.212(4)
Re51	C57	1.921(5)
Re51	C58	1.916(5)
Re51	C59	1.926(6)
O51	C57	1.149(6)
O52	C58	1.156(6)
O53	C59	1.102(6)
N51	C51	1.454(6)
N52	C52	1.465(6)
C51	C52	1.381(7)
C51	C56	1.383(7)
C52	C53	1.390(7)
C53	C54	1.380(7)
C54	C55	1.387(8)
C55	C56	1.383(7)

Table S5. Bond Angles in ˚ for **Re-1**.

Atom	Atom	Atom	Angle/˚
N1	Re1	Cl1	81.13(12)
N2	Re1	Cl1	81.06(11)
N2	Re1	N1	77.19(15)
C7	Re1	Cl1	95.18(15)
C7	Re1	N1	95.19(18)
C7	Re1	N2	171.90(17)
C7	Re1	C8	90.5(2)
C8	Re1	Cl1	97.19(16)
C8	Re1	N1	174.20(17)
C8	Re1	N2	97.09(17)
C9	Re1	Cl1	174.88(15)
C9	Re1	N1	95.23(19)
C9	Re1	N2	94.66(18)
C9	Re1	C7	88.7(2)
C9	Re1	C8	86.1(2)
C1	N1	Re1	112.3(3)
C2	N2	Re1	113.2(3)
C2	C1	N1	117.5(4)
C6	C1	N1	122.2(4)
C6	C1	C2	120.3(5)
C1	C2	N2	117.8(4)
C3	C2	N2	122.4(4)
C3	C2	C1	119.7(5)
C4	C3	C2	120.1(5)
C3	C4	C5	119.8(5)
C6	C5	C4	120.2(5)
C5	C6	C1	119.8(5)
O1	C7	Re1	178.0(4)
O2	C8	Re1	177.4(5)
O3	C9	Re1	178.1(5)

Atom	Atom	Atom	Angle/˚
N51	Re51	Cl51	81.29(12)
N51	Re51	N52	76.72(15)
N52	Re51	Cl51	81.04(12)
C57	Re51	Cl51	96.13(15)
C57	Re51	N51	174.75(18)
C57	Re51	N52	98.40(18)
C57	Re51	C59	90.0(2)
C58	Re51	Cl51	96.45(16)
C58	Re51	N51	96.10(18)
C58	Re51	N52	172.65(18)
C58	Re51	C57	88.7(2)
C58	Re51	C59	89.2(2)
C59	Re51	Cl51	171.72(14)
C59	Re51	N51	92.12(18)
C59	Re51	N52	92.61(18)
C51	N51	Re51	112.1(3)
C52	N52	Re51	111.4(3)
C52	C51	N51	117.8(4)
C52	C51	C56	120.7(4)
C56	C51	N51	121.4(4)
C51	C52	N52	117.5(4)
C51	C52	C53	119.6(5)
C53	C52	N52	122.8(4)
C54	C53	C52	119.8(5)
C53	C54	C55	120.2(5)
C56	C55	C54	120.1(5)
C51	C56	C55	119.5(5)
O51	C57	Re51	178.9(5)
O52	C58	Re51	177.9(5)
O53	C59	Re51	178.7(4)

Citations

O.V. Dolomanov and L.J. Bourhis and R.J. Gildea and J.A.K. Howard and H. Puschmann, Olex2: A complete structure solution, refinement and analysis program, *J. Appl. Cryst.*, (2009), **42**, 339-341.

Sheldrick, G.M., A short history of ShelX, *Acta Cryst.*, (2008), **A64**, 339-341.

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