Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Exploring the Effect of Axial Ligand Substitution (X = Br, NCS, CN) on the Photodecomposition and Electrochemical Activity of $[MnX(N–C)(CO)_3]$ Complexes

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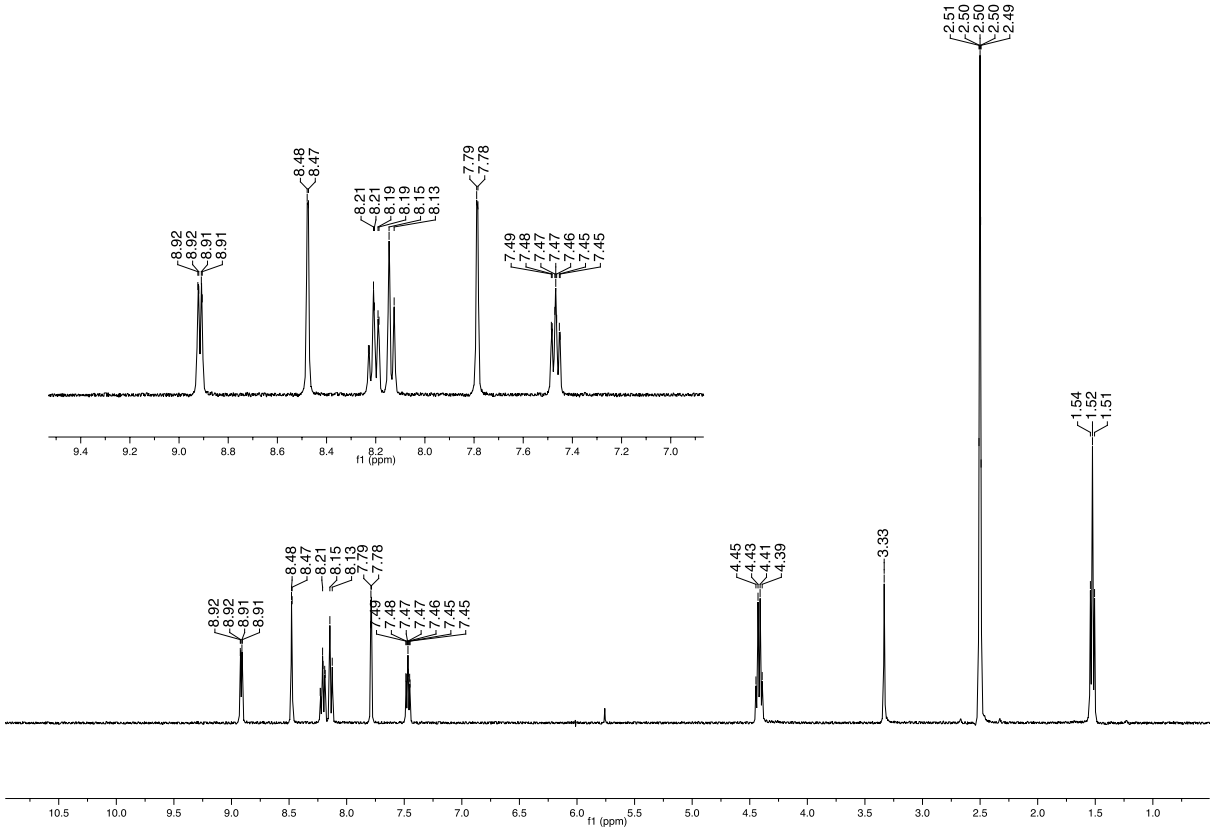
Contents

1 Selected Spectra

1.1 [MnBr(Et-Imid-Py)$(CO)_3$] (1)

1.1.1 ^{1}H NMR

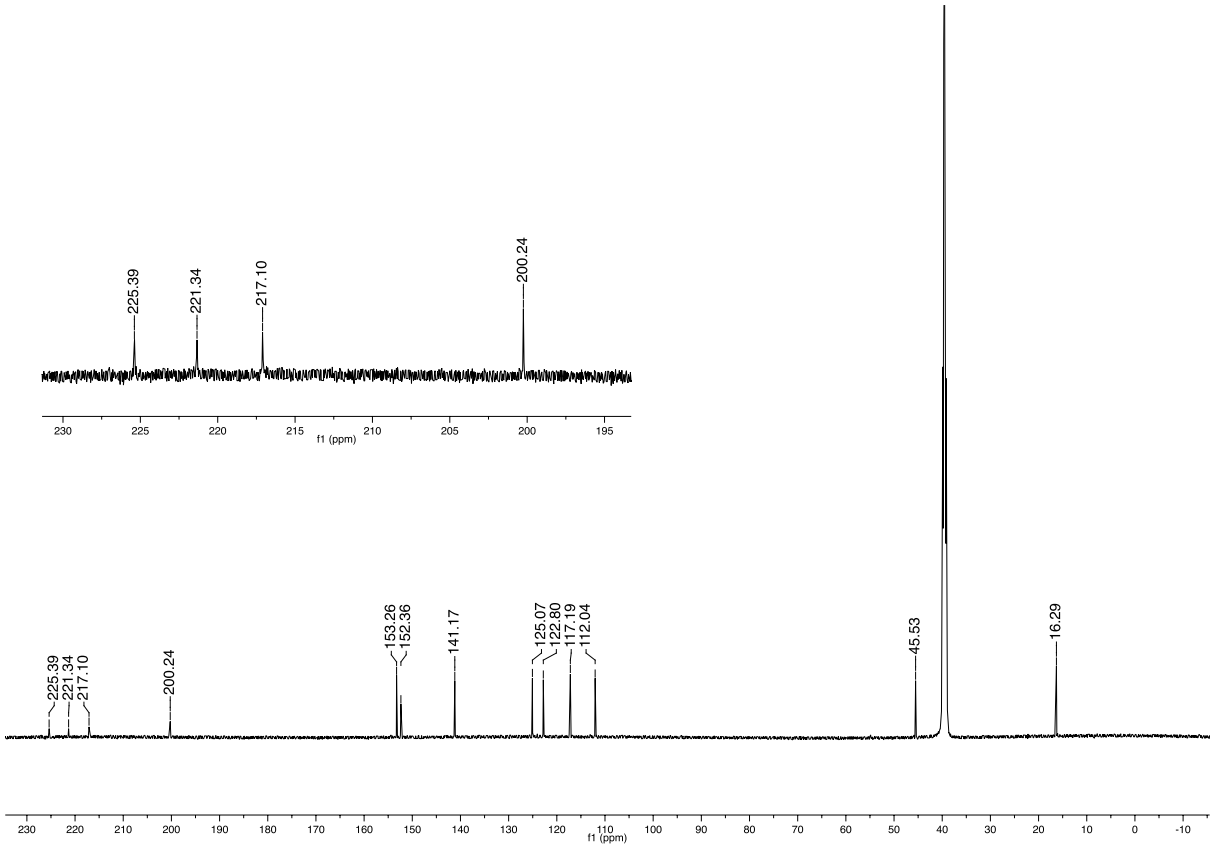
Temperature: 20 °C
Solvent: DMSO-d_6



Note: The peak at roughly 5.7 ppm is assigned to residual dichloromethane, the peak at 3.33 ppm to water, and the peak at 2.50 ppm to dimethyl sulfoxide.

1.1.2 ^{13}C NMR

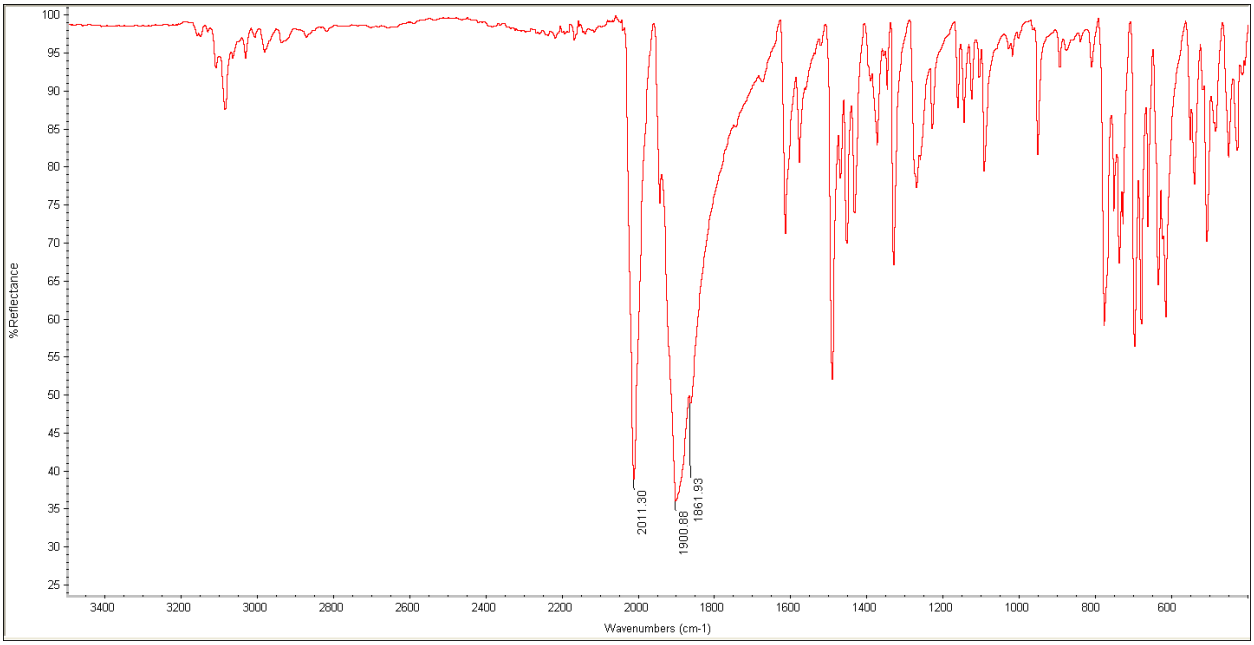
Temperature: 25 °C
Solvent: DMSO-d_6



Note: The peak at 39.52 ppm is assigned to dimethyl sulfoxide.

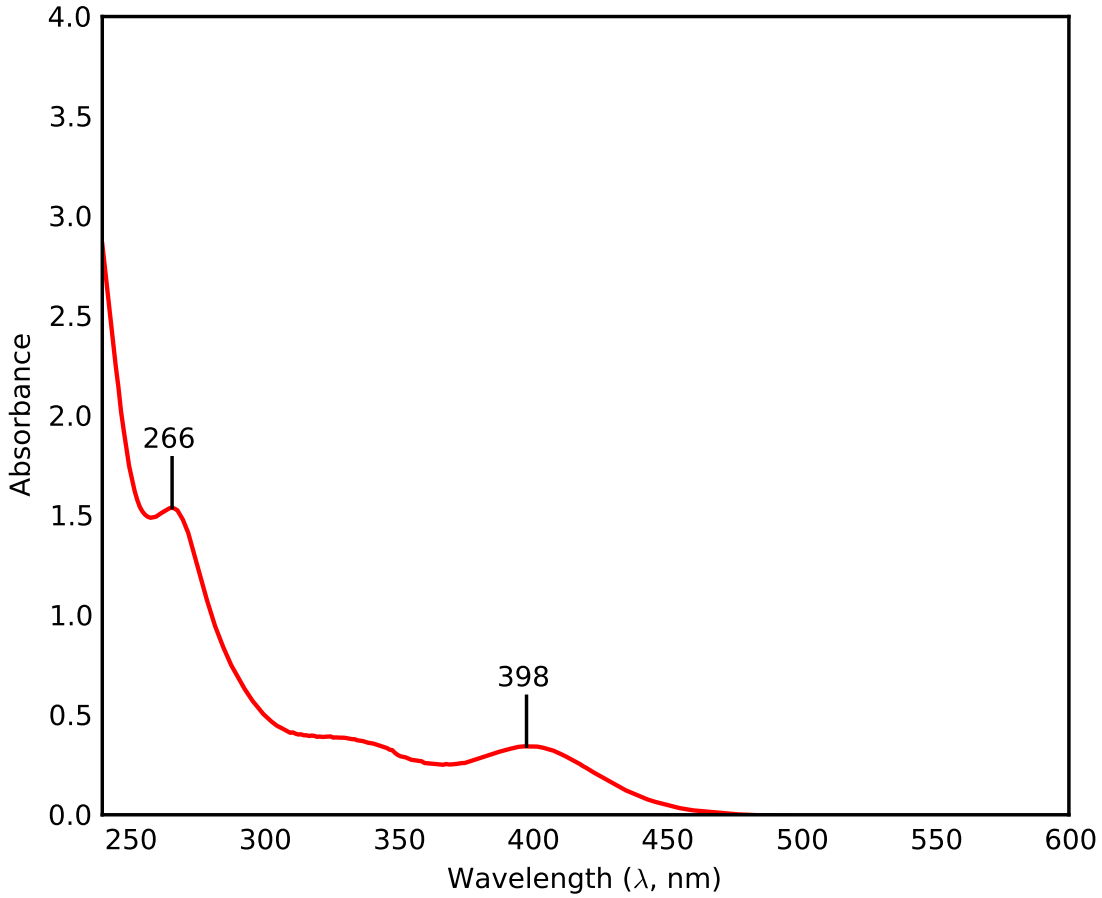
1.1.3 FTIR

Method: ATR



1.1.4 UV-Vis

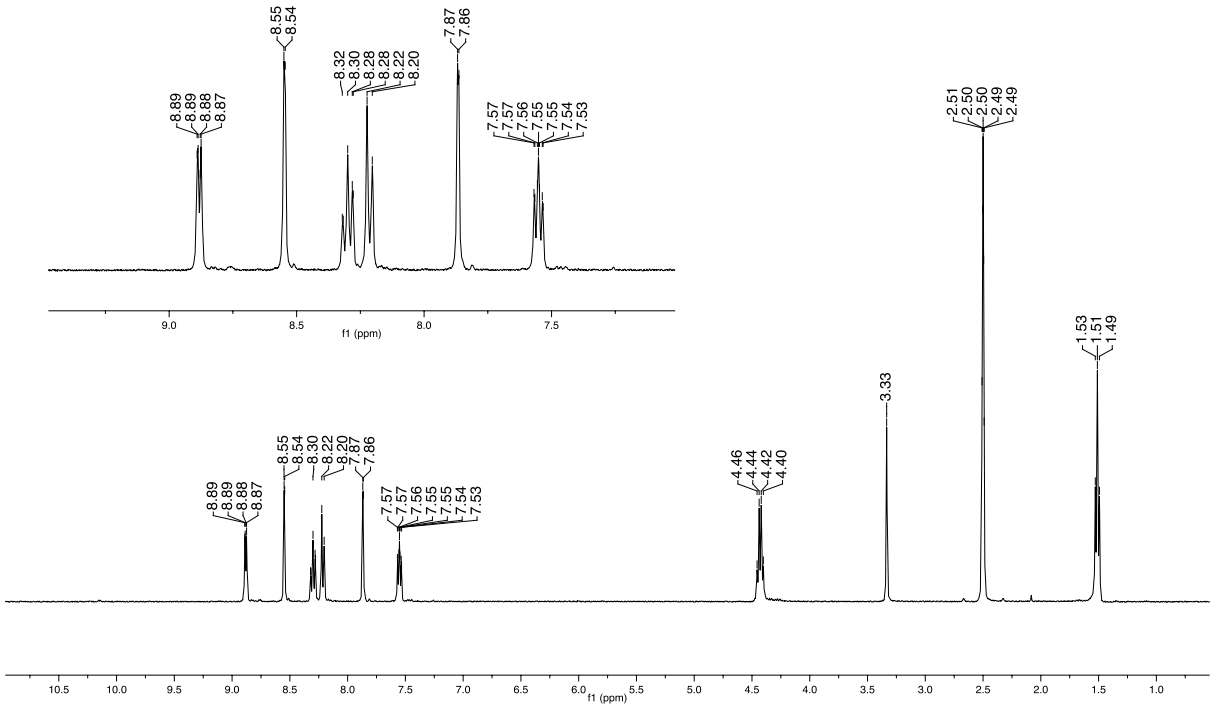
Temperature: 298K
Concentration: 125μM
Solvent: MeCN



1.2 [MnNCS(Et-Imid-Py)$(CO)_3$] (2)

1.2.1 ^{1}H NMR

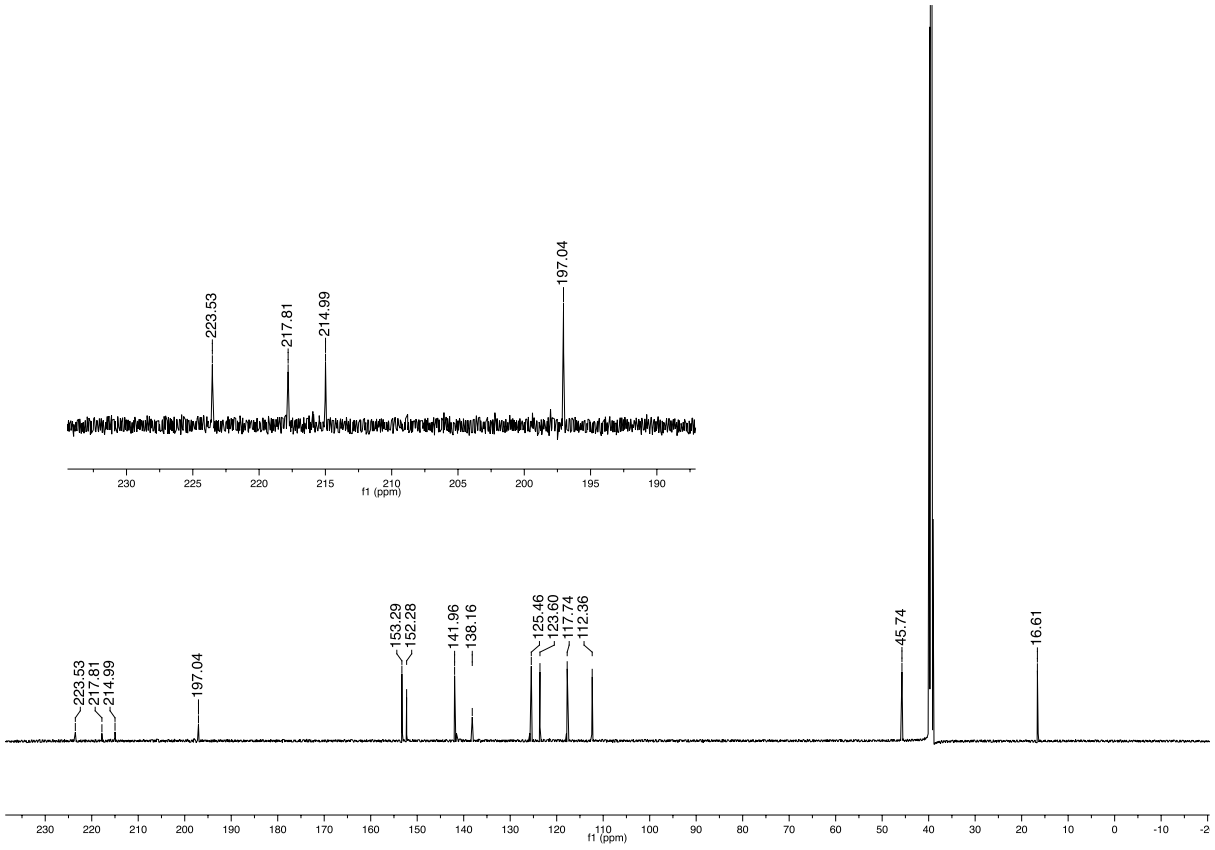
Temperature: 20 °C
Solvent: DMSO-d_6



Note: The peak at 3.33 ppm is assigned to water and the peak at 2.50 ppm to dimethyl sulfoxide.

1.2.2 ^{13}C NMR

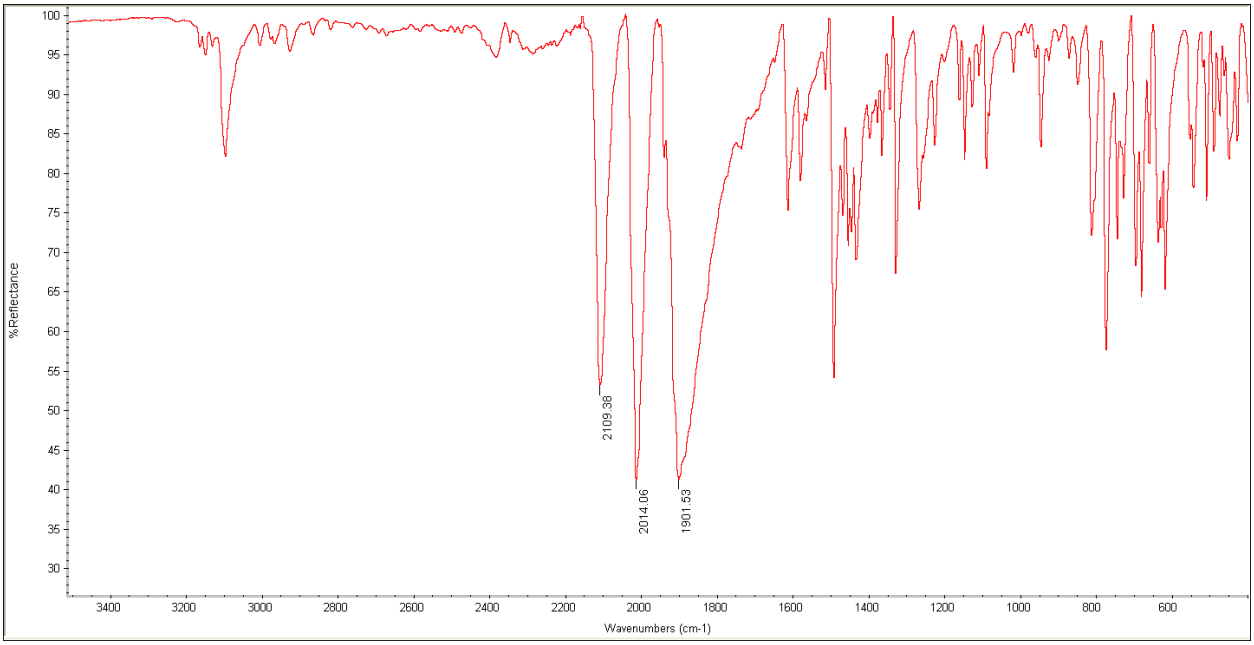
Temperature: 25 °C
Solvent: DMSO-d_6



Note: The peak at 39.52 ppm is assigned to dimethyl sulfoxide.

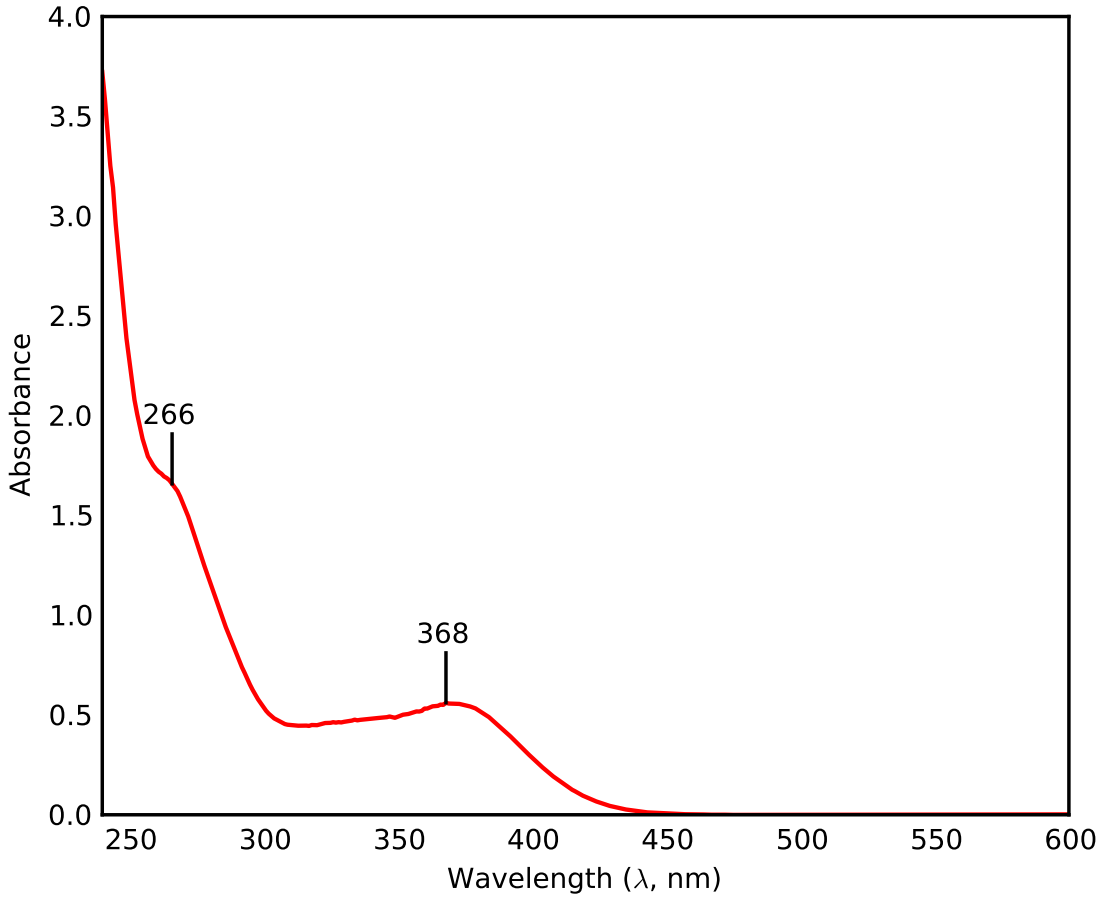
1.2.3 FTIR

Method: ATR



1.2.4 UV-Vis

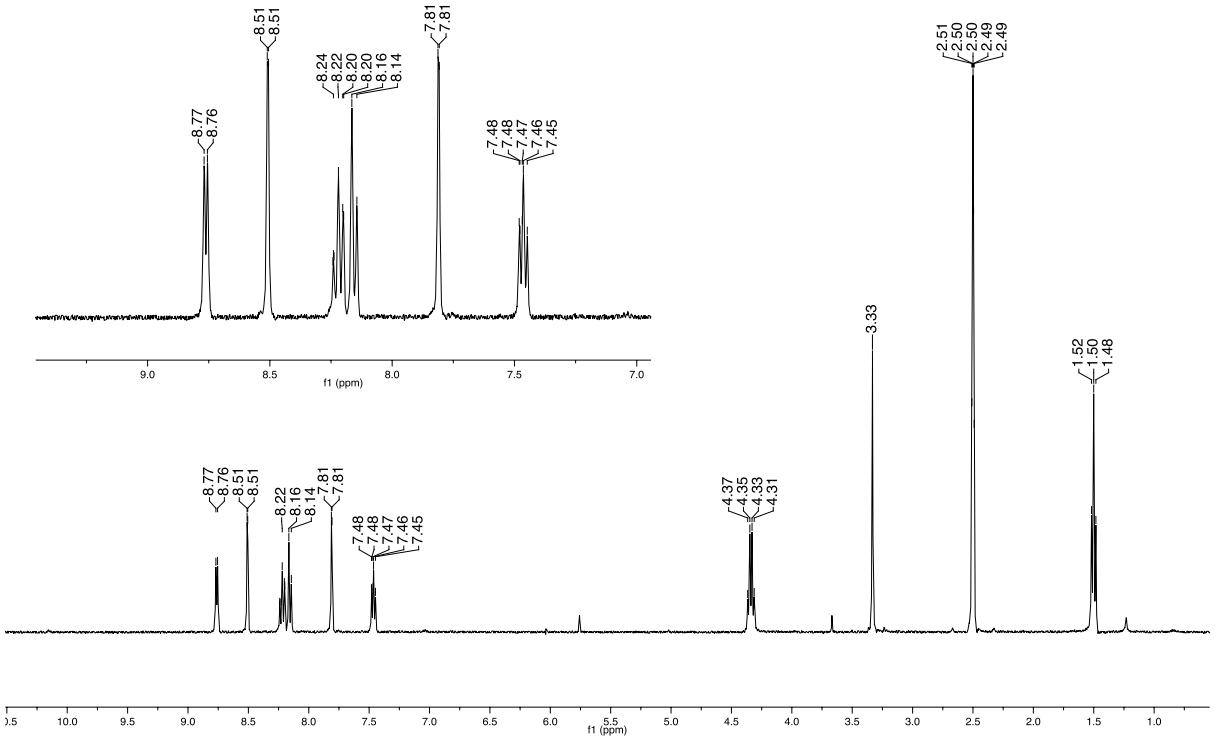
Temperature: 298K
Concentration: 125μM
Solvent: MeCN



1.3 [MnCN(Et-Im-Py)(CO)$_3$] (3)

1.3.1 ^{1}H NMR

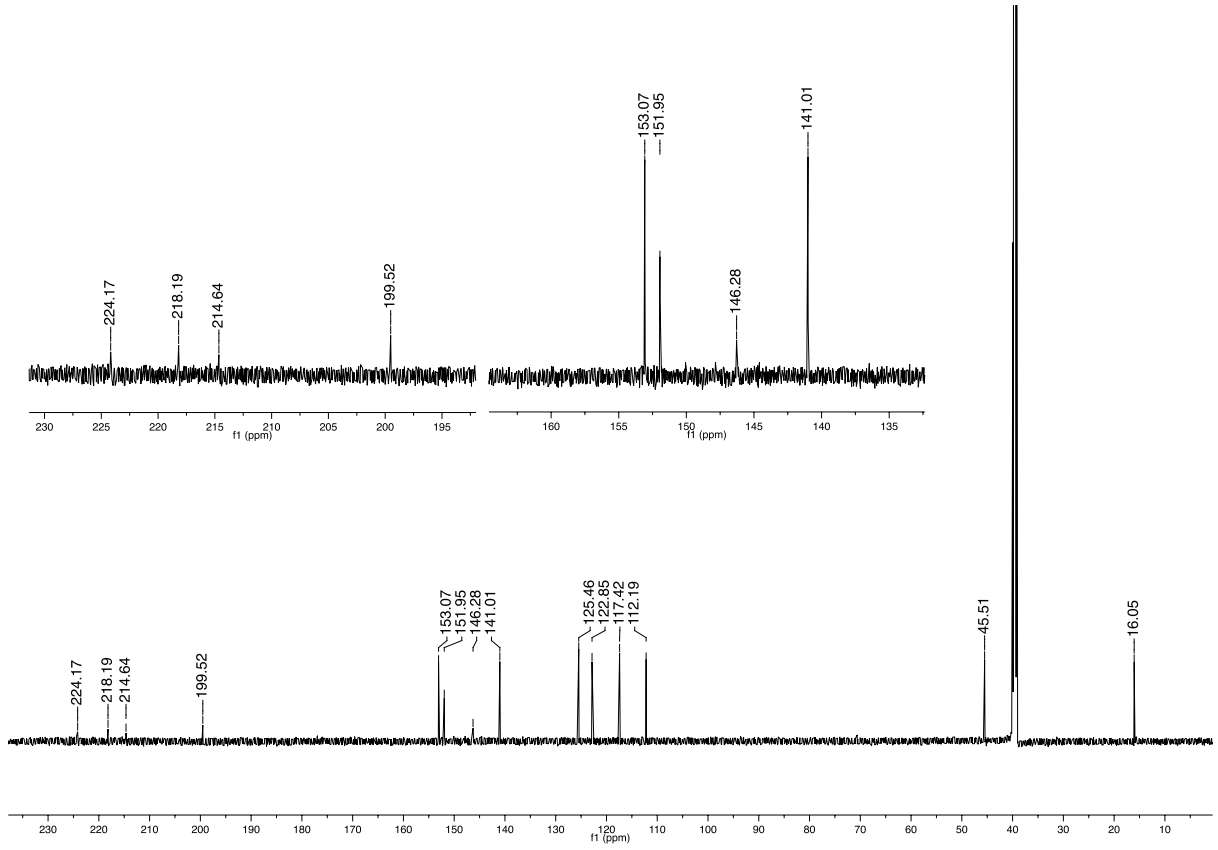
Temperature: 20 °C
Solvent: DMSO-d_6



Note: The peak at 3.33 ppm is assigned to water and the peak at 2.50 ppm to dimethyl sulfoxide.

1.3.2 ^{13}C NMR

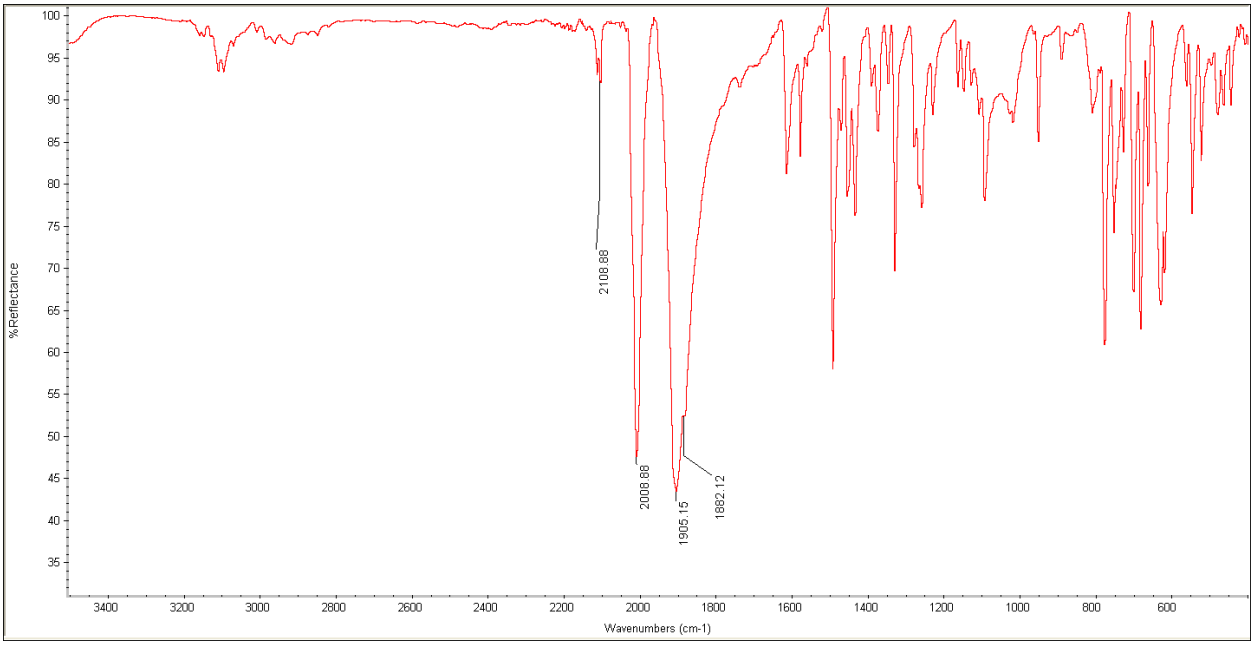
Temperature: 25 °C
Solvent: DMSO-d_6



Note: The peak at 39.52 ppm is assigned to dimethyl sulfoxide.

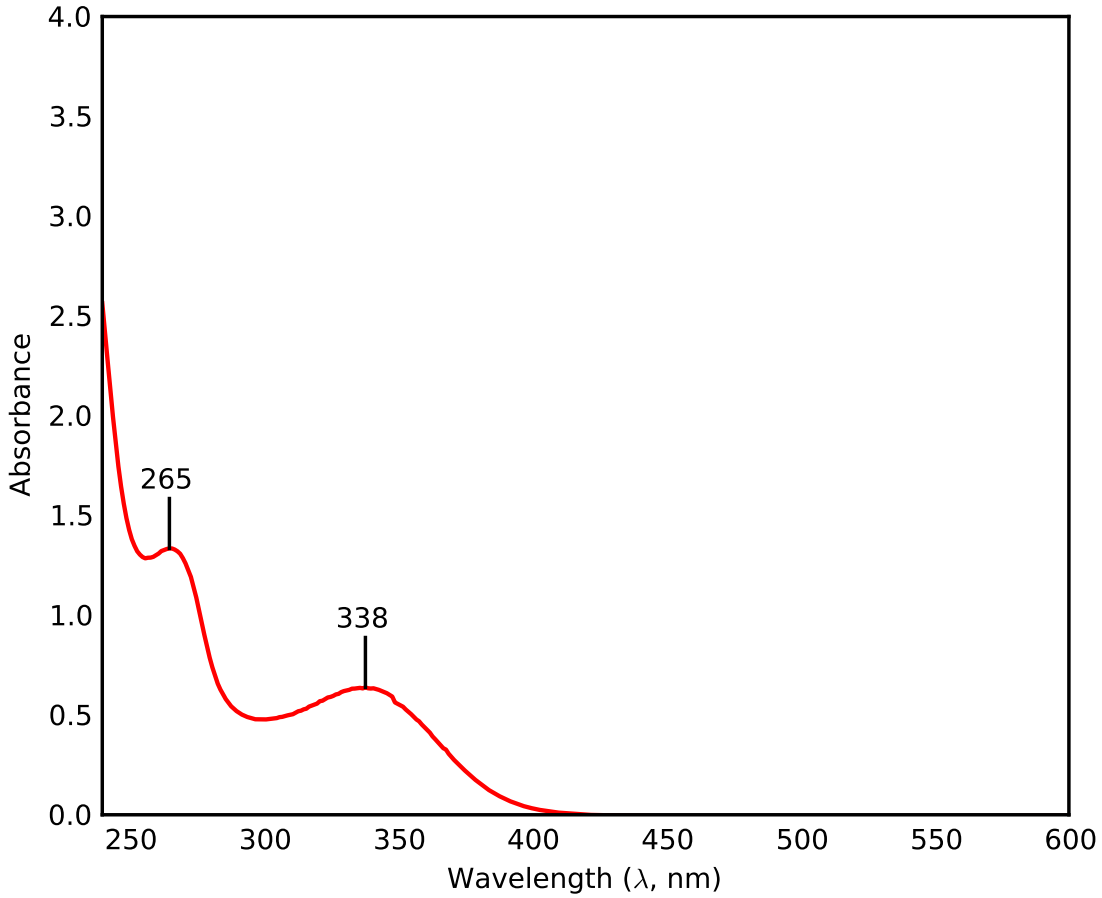
1.3.3 FTIR

Method: ATR



1.3.4 UV-Vis

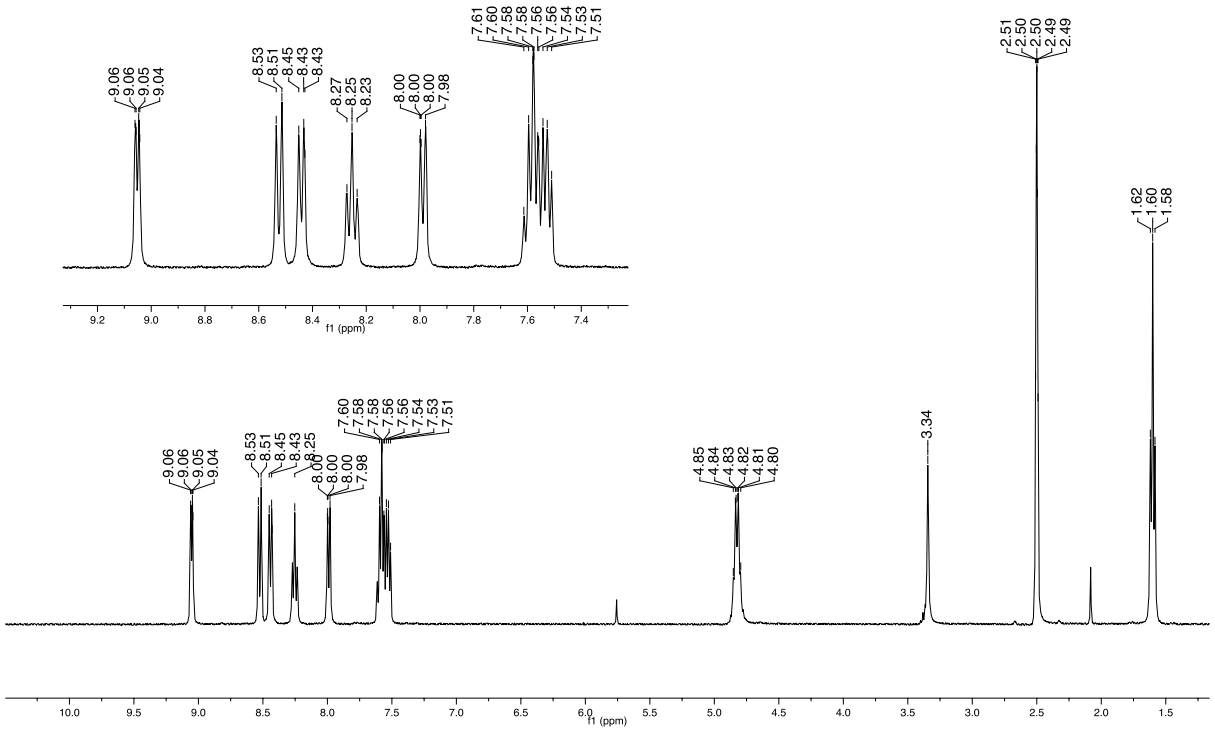
Temperature: 298K
Concentration: 125μM
Solvent: MeCN



1.4 [MnBr(Et-BImid-Py)(CO)$_3$]

1.4.1 ^{1}H NMR

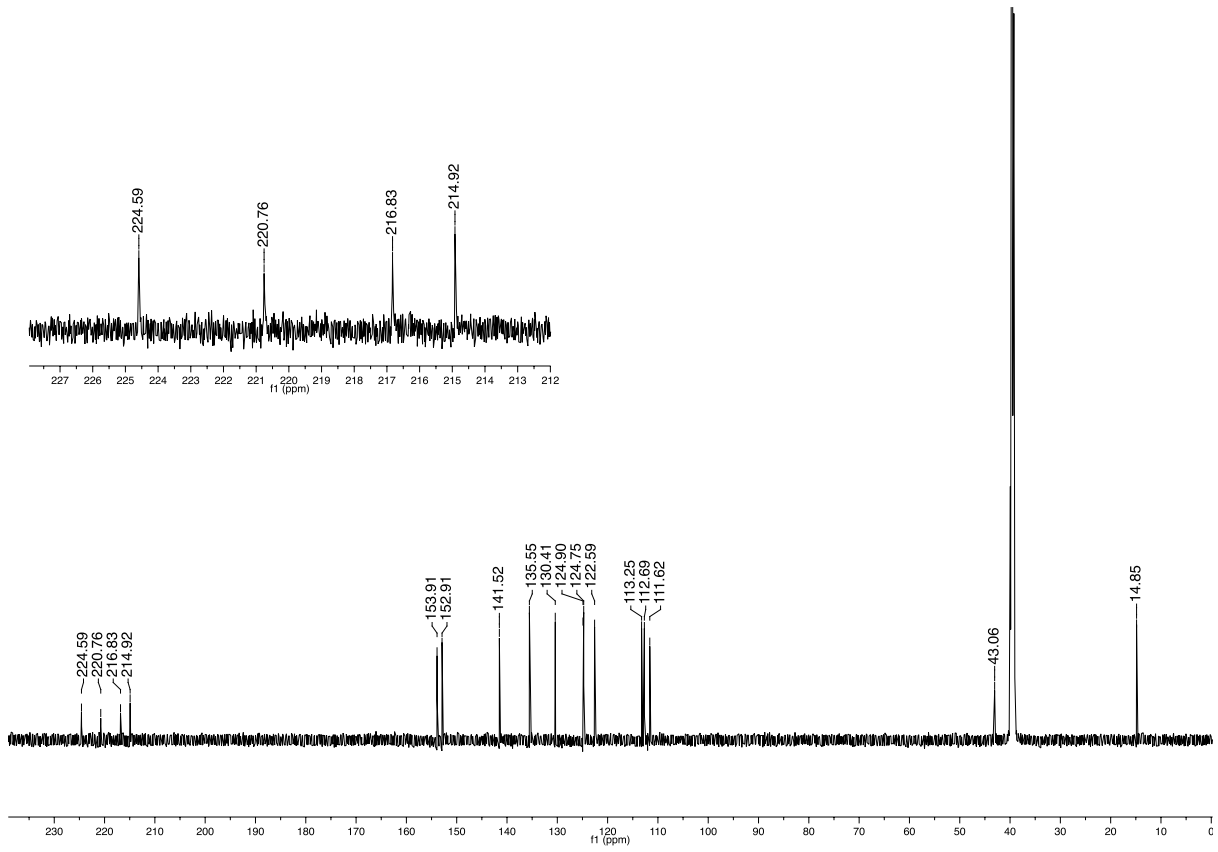
Temperature: 20 °C
Solvent: DMSO-d_6



Note: The peak at roughly 5.7 ppm is assigned to residual dichloromethane, the peak at 3.34 ppm to water, and the peak at 2.50 ppm to dimethyl sulfoxide.

1.4.2 ^{13}C NMR

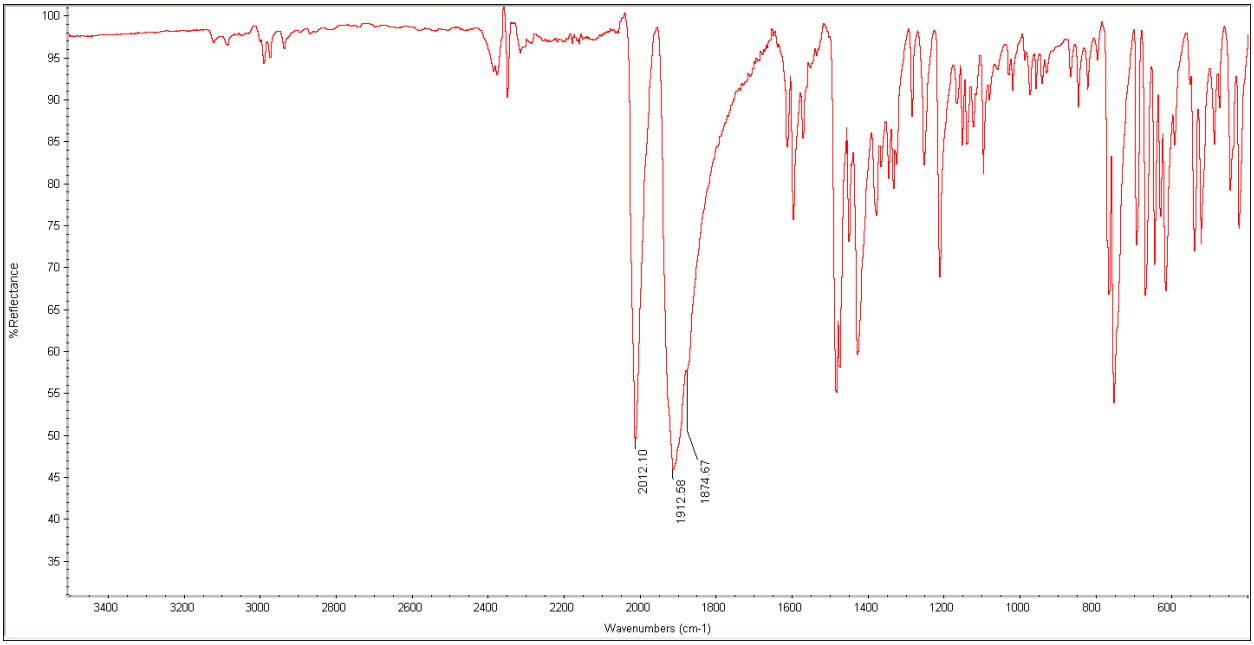
Temperature: 25 °C
Solvent: DMSO-d_6



Note: The peak at 39.52 ppm is assigned to dimethyl sulfoxide.

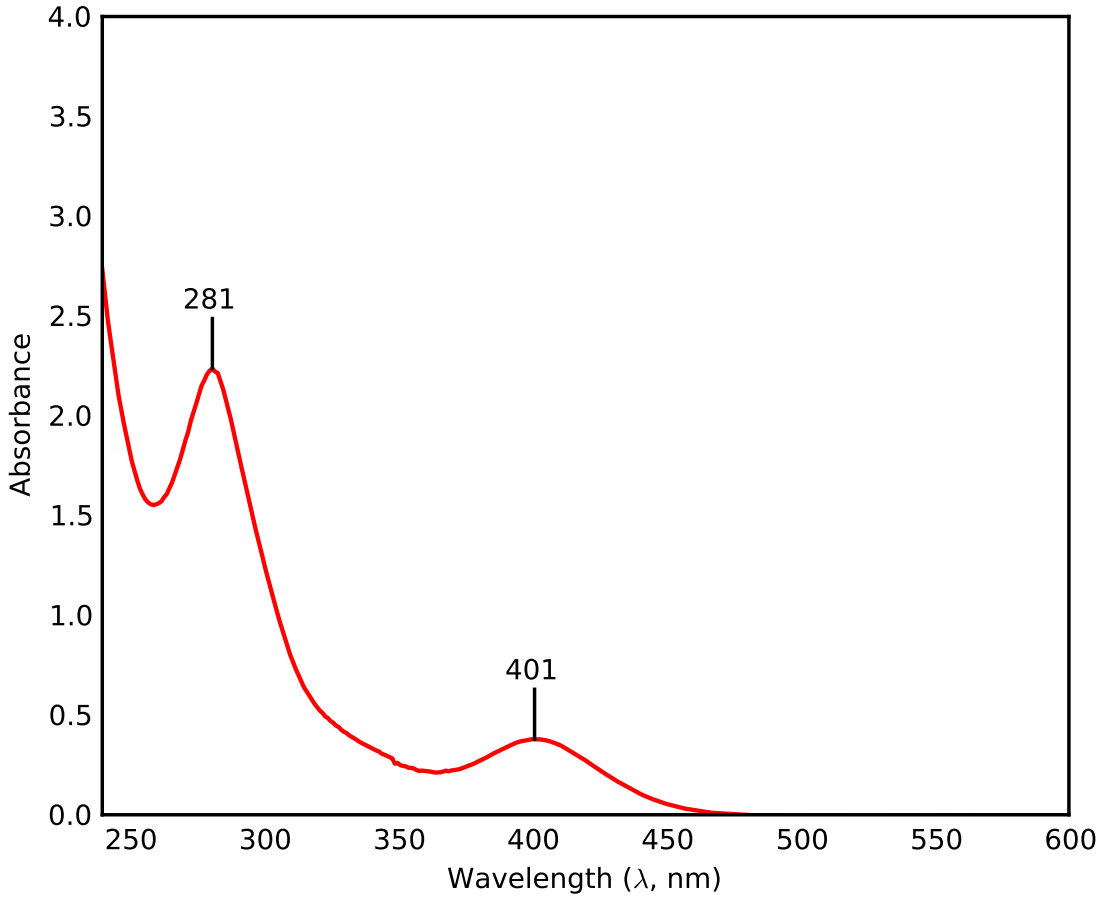
1.4.3 FTIR

Method: ATR



1.4.4 UV-Vis

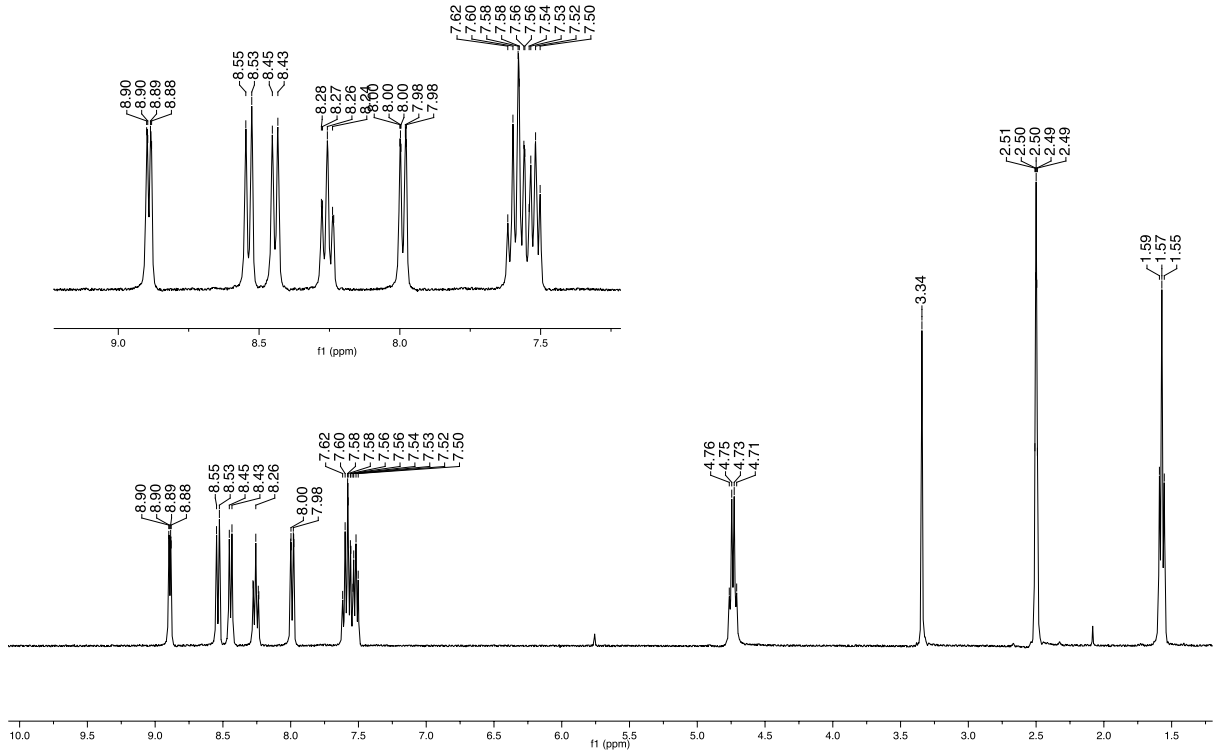
Temperature: 298K
Concentration: 125μM
Solvent: MeCN



1.5 [MnCN(Et-BImid-Py)(CO)$_3$] (4)

1.5.1 ^{1}H NMR

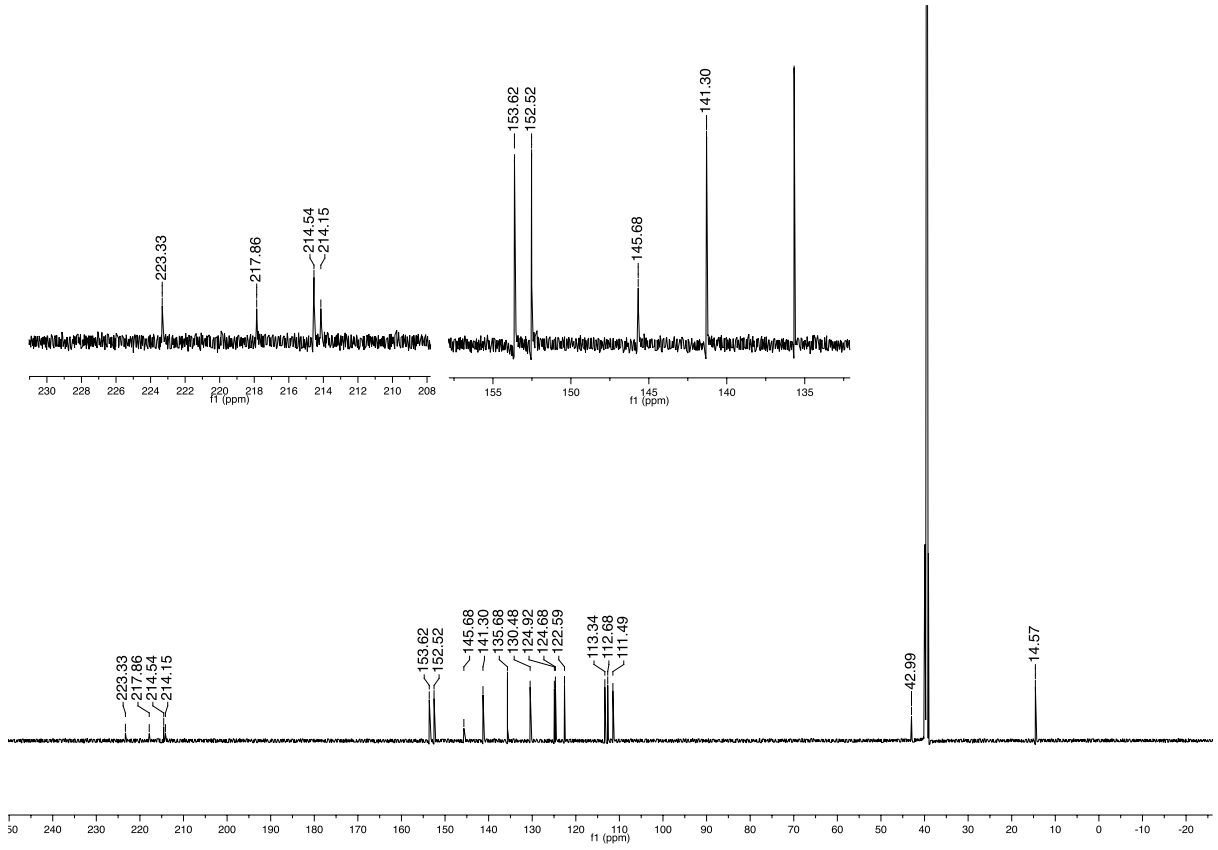
Temperature: 20 °C
Solvent: DMSO-d_6



Note: The peak at roughly 5.7 ppm is assigned to residual dichloromethane, the peak at 3.34 ppm to water, the peak at 2.50 ppm to dimethyl sulfoxide, and the peak at roughly 2.1 ppm to acetone.

1.5.2 ^{13}C NMR

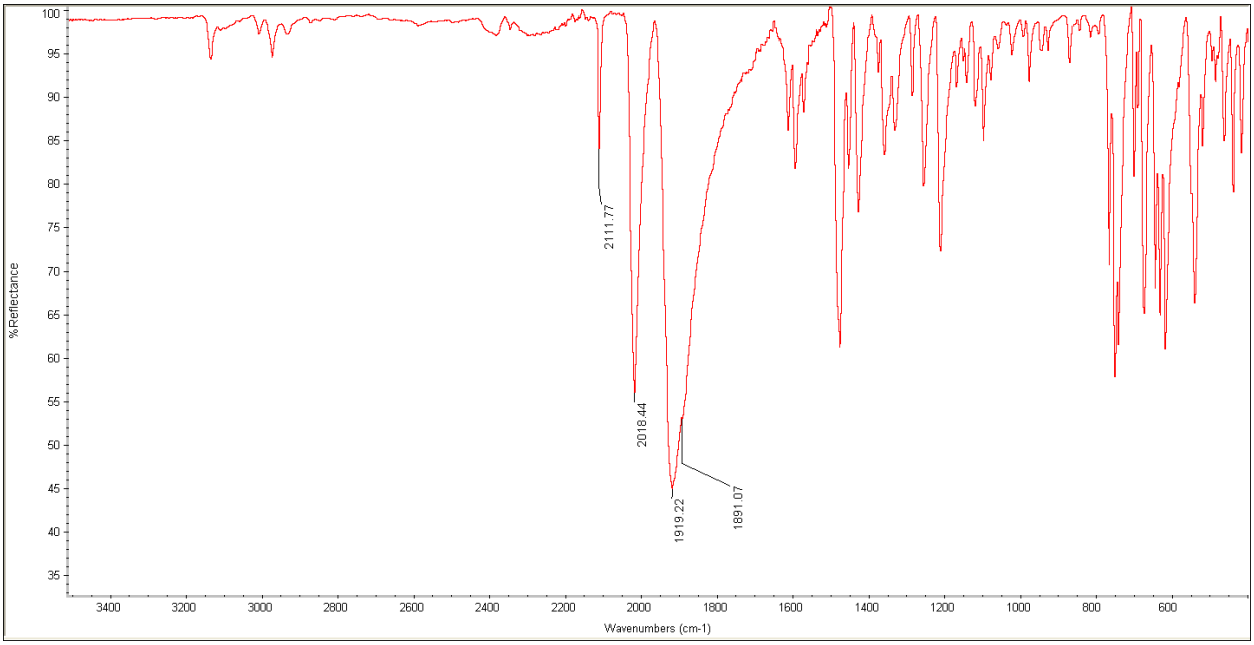
Temperature: 25 °C
Solvent: DMSO-d_6



Note: The peak at 39.52 ppm is assigned to dimethyl sulfoxide.

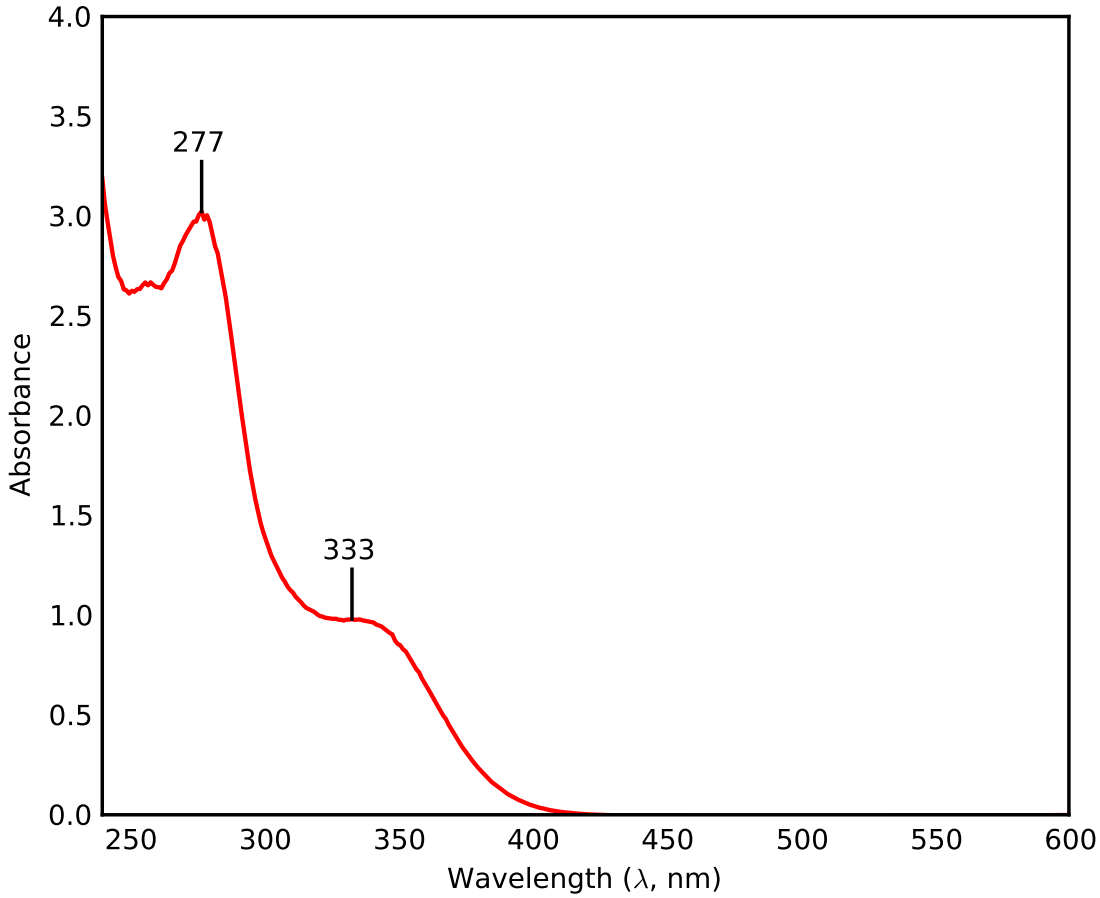
1.5.3 FTIR

Method: ATR



1.5.4 UV-Vis

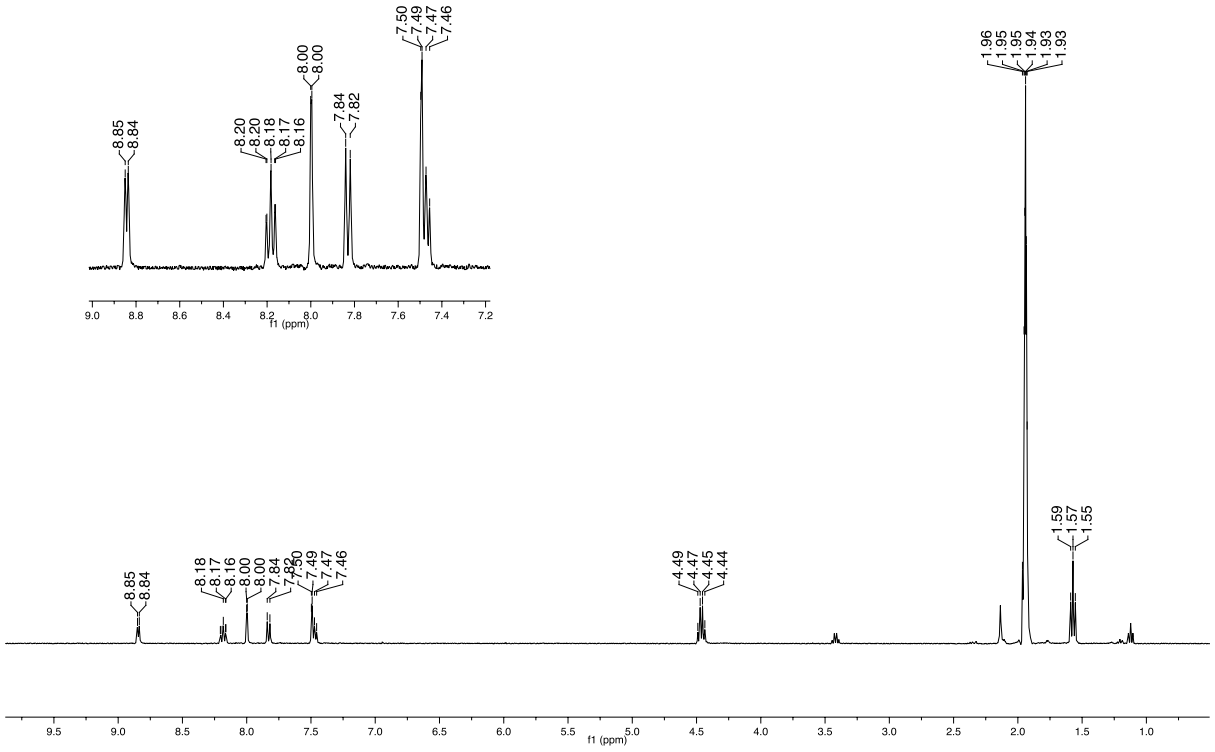
Temperature: 298K
Concentration: 125μM
Solvent: MeCN



1.6 $[Mn(Et\text{-}Imid\text{-}Py)(CO)_3MeCN]^+$

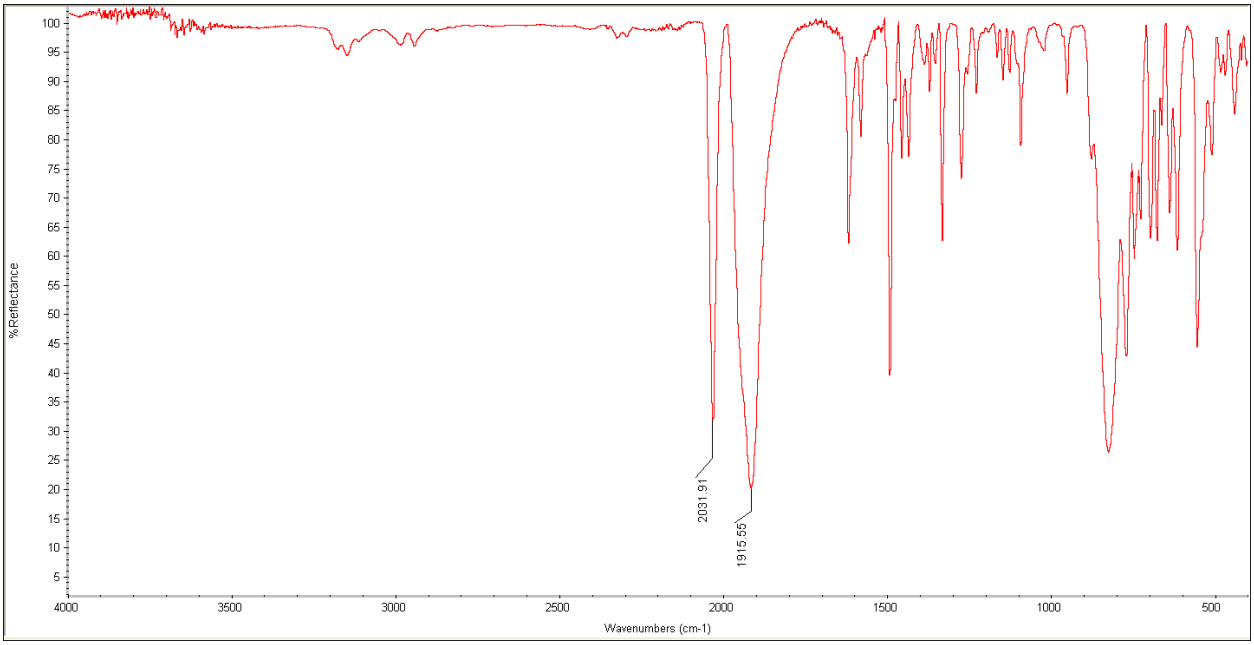
1.6.1 ^1H NMR

Temperature: 20 °C
Solvent: MeCN-d_3



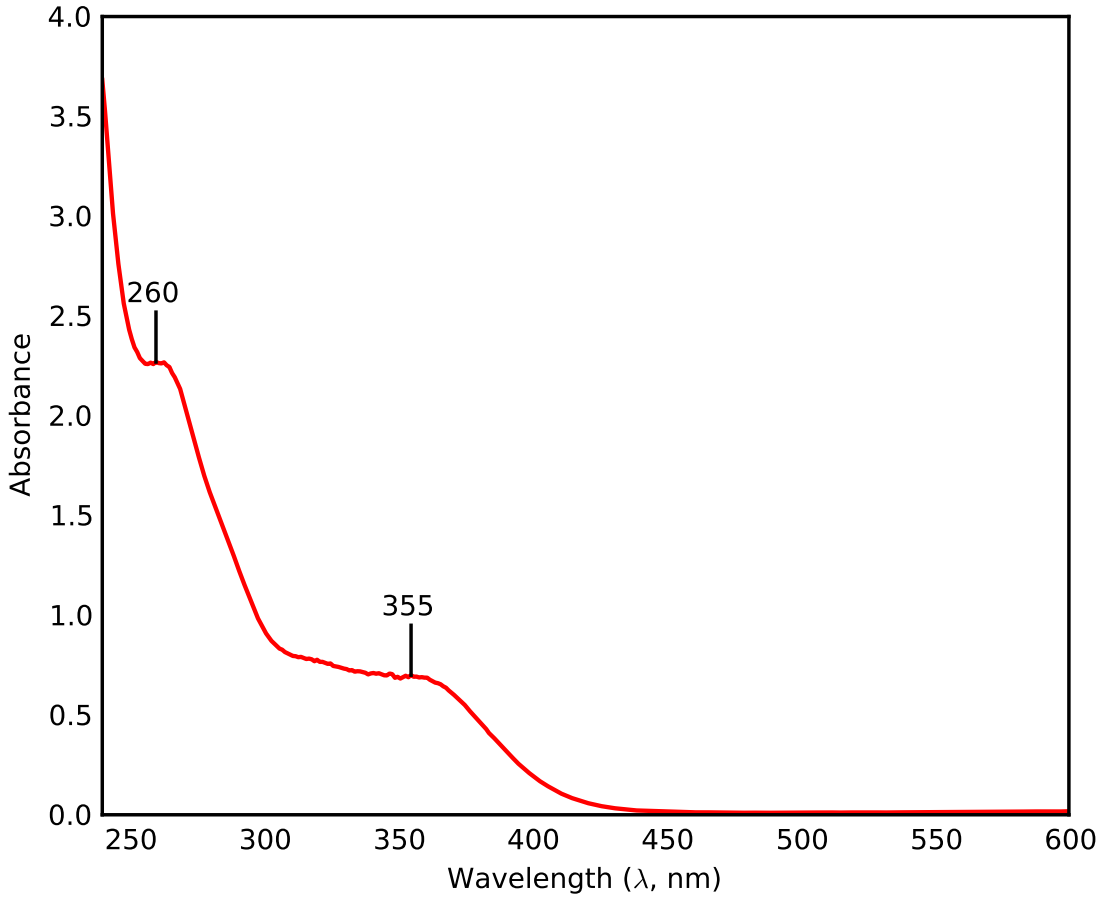
1.6.2 FTIR

Method: ATR



1.6.3 UV-Vis

Temperature: 298K
Concentration: 200μM
Solvent: MeCN

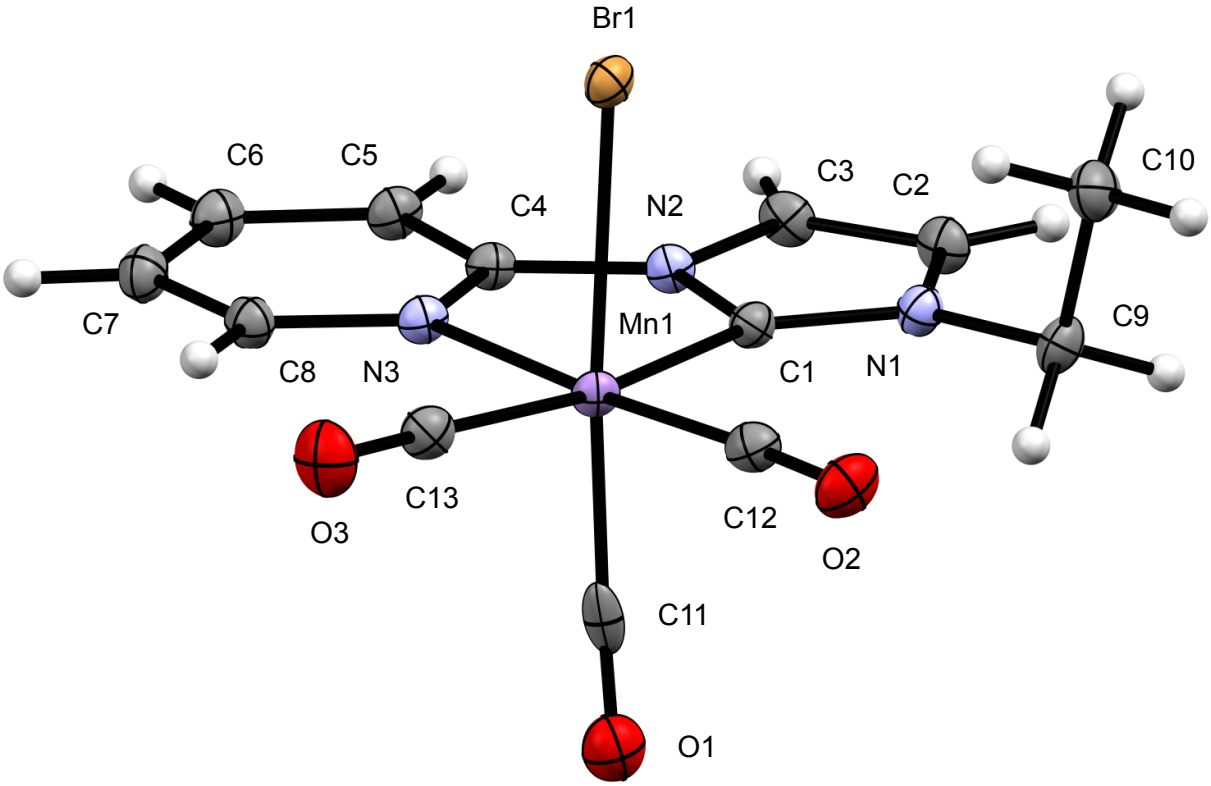


2 X-Ray Crystallography Data

References:

[**1**] Sheldrick, G. M. *SHELXTL-2013, Crystallographic Computinc System*; Siemens Analytical X-Ray Instruments: Madison, WI, 2013 and Sheldrick, G. M. *Acta Cryst.* **2008**, A64, 112.
[**2**] Cromer, D. T. and Waber, J. T. International Tables for X-Ray Crystallography, Vol. IV, Table 2.2B, The Kynoch Press, Birmingham, England, 1974.
[**3**] Cromer, D. T. International Tables for X-Ray Crystallography, Vol. IV, Table 2.3.1, The Kynoch Press, Birmingham, England 1974.

2.1 [MnBr(Et-Imid-Py)$(CO)_3$] (1)



Chemical Formula: C13 H11 Br Mn N3 O3
Formula Weight: 392.10 g mol^{-1}
Crystal System: monoclinic
Space Group: P 21/c
Unit Cell Dimensions: a = 14.3770(9) Å alpha = 90 degrees
b = 10.7747(7) Å beta = 102.8260(10) degrees
c = 14.3770(9) Å gamma = 90 degrees
Cell Volume: 1459.27(16) $Å^3$
Temperature: 100(2) K
Radiation Type: MoKα
Radiation Wavelength: 0.71073 Å
Theta Range for Collection: 2.38 degrees to 32.56 degrees
Reflections Collected (Unique): 23397 (5066)
Goodness-of-Fit on F^2: 1.018

Bond Lengths (Å):

Mn1	C12	1.8055(19)
Mn1	C13	1.8407(19)
Mn1	C11	1.852(2)
Mn1	C1	1.9989(18)
Mn1	N3	2.0795(15)
Mn1	Br1	2.5441(4)
N1	C1	1.347(2)
N1	C2	1.397(2)
N1	C9	1.467(2)
N2	C1	1.374(2)
N2	C4	1.399(2)
N2	C3	1.396(2)
N3	C4	1.341(2)
N3	C8	1.353(2)
C2	C3	1.349(3)
C4	C5	1.392(2)
C5	C6	1.385(3)
C6	C7	1.394(3)
C7	C8	1.382(3)
C9	C10	1.524(3)
C11	O1	1.068(3)
C12	O2	1.148(2)
C13	O3	1.146(2)

Bond Angles (degrees):

C12	Mn1	C13	88.35(8)
C12	Mn1	C11	89.08(8)
C13	Mn1	C11	95.05(8)
C12	Mn1	C1	99.44(8)
C13	Mn1	C1	171.02(8)
C11	Mn1	C1	89.57(7)
C12	Mn1	N3	176.61(8)
C13	Mn1	N3	94.01(7)
C11	Mn1	N3	93.14(7)
C1	Mn1	N3	78.02(7)
C12	Mn1	Br1	89.44(6)
C13	Mn1	Br1	89.39(6)
C11	Mn1	Br1	175.28(6)
C1	Mn1	Br1	86.25(5)
N3	Mn1	Br1	88.14(4)
C1	N1	C2	111.03(16)
C1	N1	C9	124.95(16)
C2	N1	C9	123.83(16)
C1	N2	C4	118.26(15)
C1	N2	C3	111.60(15)
C4	N2	C3	130.13(15)
C4	N3	C8	117.12(15)
C4	N3	Mn1	116.29(12)
C8	N3	Mn1	126.59(12)
N1	C1	N2	104.17(15)
N1	C1	Mn1	141.09(13)
N2	C1	Mn1	114.73(13)
C3	C2	N1	107.74(16)
C2	C3	N2	105.45(15)
N3	C4	C5	123.97(17)
N3	C4	N2	112.70(15)
C5	C4	N2	123.33(16)
C6	C5	C4	117.79(17)
C5	C6	C7	119.44(17)
C8	C7	C6	118.60(18)
N3	C8	C7	123.08(17)
N1	C9	C10	111.18(15)
O1	C11	Mn1	177.64(18)
O2	C12	Mn1	176.42(18)
O3	C13	Mn1	178.37(17)

2.1.1 Data Collection

The orange crystal was mounted on the tip of a glass fiber. The X-ray intensity data were measured at 100K temperature on a Bruker SMART APEX II X-ray diffractometer system with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) using ω-scan technique. The data were collected in 1464 frames with 10 second exposure times. Crystallographic data: C13H11N3O3MnBr: a = 14.3770(9) Å, b = 10.7747(7) Å, c = 9.6613(6) Å, $\alpha = 90^{o}$, $\beta = 102.8260(10)^{o}$, $\gamma = 90^{o}$, V = 1459.27(16) Å^3, Z = 4, F.W. = 392.10, μ = 3.655 mm^{-1}, d = 1.785 g/cm^3, F(000) = 776.

2.1.2 Data Reduction

Of the 5066 unique reflections collected, 4427 were observed (I > 2 $\sigma(I)$). The linear absorption coefficient for Mo Kα radiation is 3.655 mm^{-1}. The data were corrected for Lorentz and polarization effects and integrated with the manufacturer's SAINT software. Absorption corrections were applied with the SADABS.

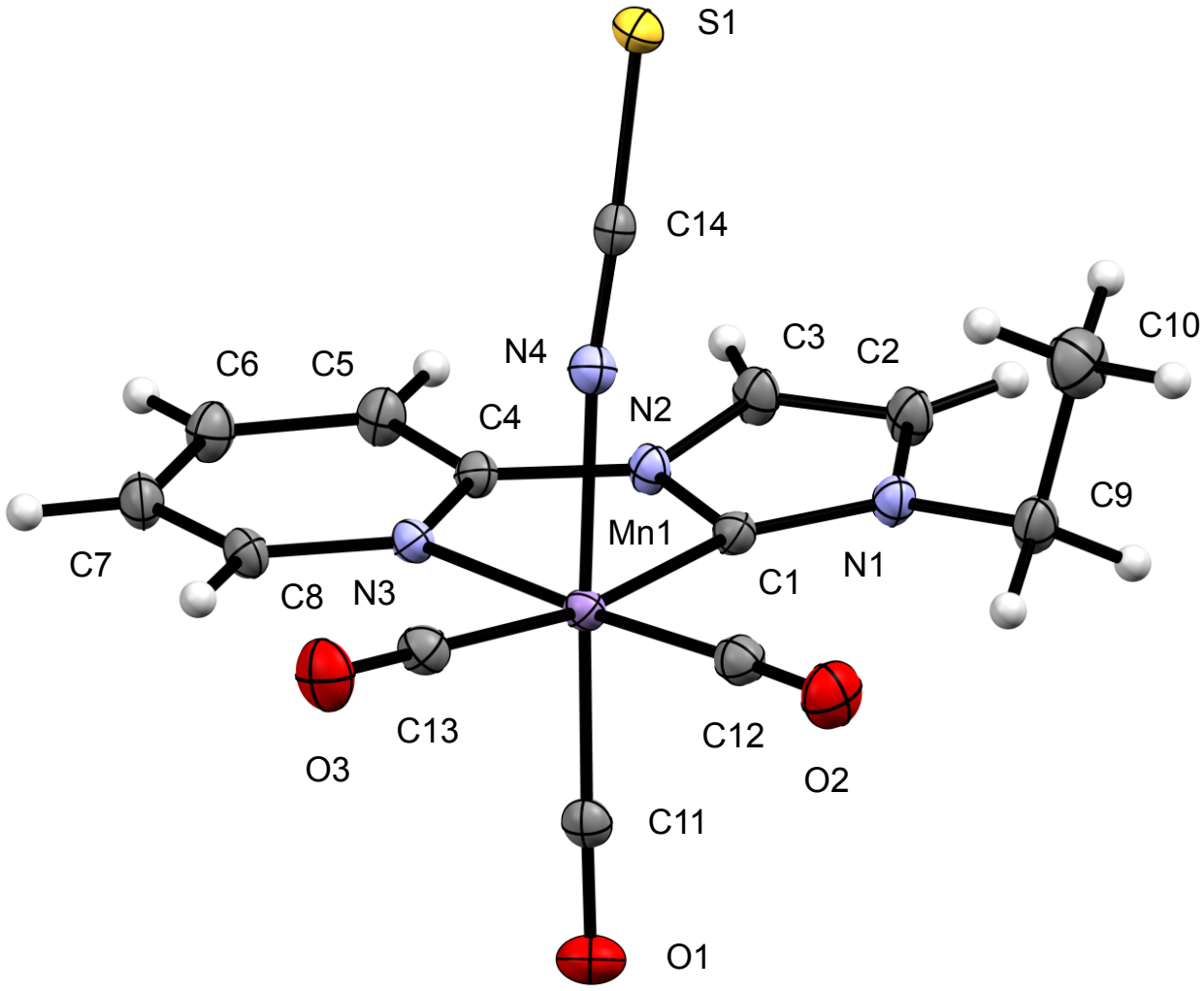
2.1.3 Structure Solution and Refinement

Subsequent solution and refinement was performed using the SHELXTL-2103 [1] solution package operating on a Pentium computer. The structure was solved by direct method using SHELXTL-2103 Software Package. Non-hydrogen atomic scattering factors were taken from the literature tabulations. [2] Non-hydrogen atoms were located from successive difference Fourier map calculations. In the final cycles of each refinement, all the non-hydrogen atoms were refined in anisotropic displacement parameters. All the hydrogen atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a CH bond length of m Å(m =0.99 for CH_2 and 0.98 for CH_3 groups, m = 0.95 for Ph-H groups). Hydrogen atom temperature factors were fixed at n (n = 1.5 for CH_3 groups, n = 1.2 for CH_2 and Ph-H groups) times the isotropic temperature factor of the C-atom to which they are bonded. The crystal system of compound is monoclinic, space group P2(1)/c (No. 14) and the final residual values based on 190 variable parameters and 4427 observed reflections (I > 2 $\sigma(I)$) are R1 = 0.0302, wR2 = 0.0810, and those for all unique reflections are R1 = 0.0371, wR2 = 0.0838. The goodness-of-fit indicator for all data is 1.018. Peaks on the final difference map ranged from 0.857 to -0.532 e/Å^3, which are of no chemical significance. The efforts have been made to resolve as many alerts as possible generated by CheckCIF. The current highest alerts are at level G.

2.1.4 Summary

The compound crystallizes in monoclinic, space group P2(1)/c (No. 14). The asymmetric unit contains one molecule in the form of C13H11N3O3MnBr. Structure solution, refinement and the calculation of derived results were performed using the SHELXTL-2013 [1] package of computer programs. Neutral atom scattering factors were those of Cromer and Waber, [2] and the real and imaginary anomalous dispersion corrections were those of Cromer. [3]

2.2 [MnNCS(Et-Imid-Py)$(CO)_3$] (2)



Chemical Formula: C14 H11 Mn N4 O3 S
Formula Weight: 370.27 g mol^{-1}
Crystal System: monoclinic
Space Group: P 21/c
Unit Cell Dimensions: a = 16.1045(7) Å alpha = 90 degrees
b = 11.0234(5) Å beta = 97.9660(10) degrees
c = 16.1045(7) Å gamma = 90 degrees
Cell Volume: 1556.28(12) $Å^3$
Temperature: 100(2) K
Radiation Type: MoKα
Radiation Wavelength: 0.71073 Å
Theta Range for Collection: 2.55 degrees to 33.05 degrees
Reflections Collected (Unique): 25984 (5165)
Goodness-of-Fit on F^2: 1.024

Bond Lengths (Å):

Mn1	C11	1.8016(10)
Mn1	C12	1.8116(11)
Mn1	C13	1.8342(10)
Mn1	N4	2.0039(9)
Mn1	C1	2.0241(9)
Mn1	N3	2.0883(8)
N1	C1	1.3436(12)
N1	C2	1.3959(13)
N1	C9	1.4683(13)
N2	C1	1.3735(12)
N2	C4	1.3971(12)
N2	C3	1.3953(12)
N3	C4	1.3431(12)
N3	C8	1.3511(12)
C2	C3	1.3464(14)
C4	C5	1.3901(13)
C5	C6	1.3859(14)
C6	C7	1.3906(14)
C7	C8	1.3827(14)
C9	C10	1.5191(17)
C11	O1	1.1520(13)
C12	O2	1.1486(13)
C13	O3	1.1450(13)
N4	C14	1.1621(13)
C14	S1	1.6342(10)

Bond Angles (degrees):

C11	Mn1	C12	89.60(4)
C11	Mn1	C13	93.00(4)
C12	Mn1	C13	88.66(5)
C11	Mn1	N4	175.82(4)
C12	Mn1	N4	91.15(4)
C13	Mn1	N4	91.14(4)
C11	Mn1	C1	93.27(4)
C12	Mn1	C1	99.54(4)
C13	Mn1	C1	169.71(4)
N4	Mn1	C1	82.55(4)
C11	Mn1	N3	92.64(4)
C12	Mn1	N3	176.90(4)
C13	Mn1	N3	93.35(4)
N4	Mn1	N3	86.46(3)
C1	Mn1	N3	78.21(3)
C1	N1	C2	111.41(8)
C1	N1	C9	126.23(9)
C2	N1	C9	121.73(8)
C1	N2	C4	119.16(8)
C1	N2	C3	111.78(8)
C4	N2	C3	128.93(8)
C4	N3	C8	117.09(8)
C4	N3	Mn1	115.79(6)
C8	N3	Mn1	127.11(7)
N1	C1	N2	103.83(8)
N1	C1	Mn1	141.91(7)
N2	C1	Mn1	113.49(6)
C3	C2	N1	107.55(8)
C2	C3	N2	105.43(9)
N3	C4	C5	123.99(9)
N3	C4	N2	113.13(8)
C5	C4	N2	122.88(9)
C4	C5	C6	117.78(9)
C7	C6	C5	119.36(10)
C8	C7	C6	118.79(9)
N3	C8	C7	122.98(9)
N1	C9	C10	110.32(9)
O1	C11	Mn1	178.70(9)
O2	C12	Mn1	176.35(10)
O3	C13	Mn1	179.16(10)
C14	N4	Mn1	171.35(8)
N4	C14	S1	177.40(9)

2.2.1 Data Collection

The orange crystal was mounted on the tip of a glass fiber. The X-ray intensity data were measured at 100K temperature on a Bruker SMART APEX II X-ray diffractometer system with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) using ω-scan technique. The data were collected in 1464 frames with 10 second exposure times. Crystallographic data: C14H11N4O3SMn: a = 16.1045(7) Å, b = 11.0234(5) Å, c = 8.8519(4) Å, $\alpha = 90^{o}$, β = 97.9660(10)^{o}, $\gamma = 90^{o}$, V = 1556.28(12) Å^3, Z = 4, F.W. = 370.27, μ = 1.001 mm^{-1}, d = 1.580 g/cm^3, F(000) = 752.

2.2.2 Data Reduction

Of the 5165 unique reflections collected, 4784 were observed (I > 2 $\sigma(I)$). The linear absorption coefficient for Mo Kα radiation is 1.001 mm^{-1}. The data were corrected for Lorentz and polarization effects and integrated with the manufacturer's SAINT software. Absorption corrections were applied with the SADABS.

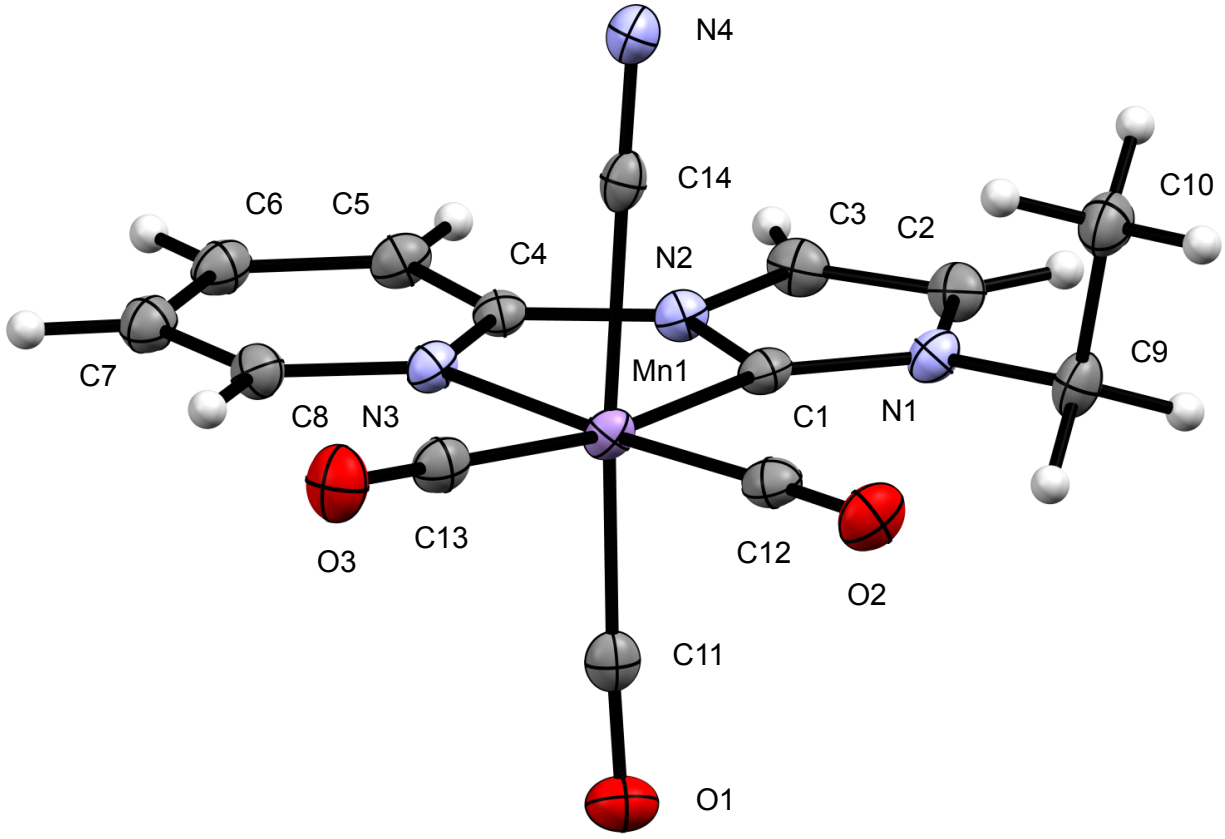
2.2.3 Structure Solution and Refinement

Subsequent solution and refinement was performed using the SHELXTL-2103 [1] solution package operating on a Pentium computer. The structure was solved by direct method using SHELXTL-2103 Software Package. Non-hydrogen atomic scattering factors were taken from the literature tabulations. [2] Non-hydrogen atoms were located from successive difference Fourier map calculations. In the final cycles of each refinement, all the non-hydrogen atoms were refined in anisotropic displacement parameters. All the hydrogen atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a CH bond length of m Å(m =0.99 for CH_2 and 0.98 for CH_3 groups, m = 0.95 for Ph-H groups). Hydrogen atom temperature factors were fixed at n (n = 1.5 for CH_3 groups, n = 1.2 for CH_2 and Ph-H groups) times the isotropic temperature factor of the C-atom to which they are bonded. The crystal system of compound is monoclinic, space group P2(1)/c (No. 14) and the final residual values based on 208 variable parameters and 4784 observed reflections (I > 2 $\sigma(I)$) are R1 = 0.0235, wR2 = 0.0650, and those for all unique reflections are R1 = 0.0260, wR2 = 0.0668. The goodness-of-fit indicator for all data is 1.024. Peaks on the final difference map ranged from 0.492 to -0.393 e/Å^3, which are of no chemical significance. The efforts have been made to resolve as many alerts as possible generated by CheckCIF. The current highest alerts are at level G.

2.2.4 Summary

The compound crystallizes in monoclinic, space group P2(1)/c (No. 14). The asymmetric unit contains one molecule in the form of C14H11N4O3SMn. Structure solution, refinement and the calculation of derived results were performed using the SHELXTL-2013 [1] package of computer programs. Neutral atom scattering factors were those of Cromer and Waber, [2] and the real and imaginary anomalous dispersion corrections were those of Cromer. [3]

2.3 [MnCN(Et-Im-Py)(CO)$_3$] (3)



Chemical Formula: C14 H11 Mn N4 O3
Formula Weight: 338.21 g mol^{-1}
Crystal System: monoclinic
Space Group: P 21/c
Unit Cell Dimensions: a = 14.4018(15) Å alpha = 90 degrees
b = 10.6199(11) Å beta = 100.9552(17) degrees
c = 14.4018(15) Å gamma = 90 degrees
Cell Volume: 1410.0(3) $Å^3$
Temperature: 100(2) K
Radiation Type: MoKα
Radiation Wavelength: 0.71073 Å
Theta Range for Collection: 2.88 degrees to 25.39 degrees
Reflections Collected (Unique): 22382 (4299)
Goodness-of-Fit on F^2: 1.030

Bond Lengths (Å):

Mn1	C12	1.799(2)
Mn1	C11	1.824(3)
Mn1	C13	1.830(2)
Mn1	C1	1.998(2)
Mn1	C14	2.002(3)
Mn1	N3	2.0790(19)
N1	C1	1.344(3)
N1	C2	1.398(3)
N1	C9	1.472(3)
N2	C1	1.371(3)
N2	C4	1.399(3)
N2	C3	1.391(3)
N3	C8	1.347(3)
N3	C4	1.347(3)
C2	C3	1.340(3)
C4	C5	1.387(3)
C5	C6	1.388(3)
C6	C7	1.394(3)
C7	C8	1.376(3)
C9	C10	1.514(3)
C11	O1	1.144(3)
C12	O2	1.153(3)
C13	O3	1.142(3)
C14	N4	1.155(3)

Bond Angles (degrees):

C12	Mn1	C11	89.25(10)
C12	Mn1	C13	89.43(11)
C11	Mn1	C13	94.92(11)
C12	Mn1	C1	98.93(10)
C11	Mn1	C1	90.26(10)
C13	Mn1	C1	170.23(10)
C12	Mn1	C14	90.25(10)
C11	Mn1	C14	174.93(10)
C13	Mn1	C14	90.12(10)
C1	Mn1	C14	84.83(9)
C12	Mn1	N3	176.33(9)
C11	Mn1	N3	92.47(9)
C13	Mn1	N3	93.66(9)
C1	Mn1	N3	77.82(8)
C14	Mn1	N3	87.75(8)
C1	N1	C2	111.4(2)
C1	N1	C9	124.6(2)
C2	N1	C9	123.7(2)
C1	N2	C4	118.00(19)
C1	N2	C3	111.74(19)
C4	N2	C3	130.26(19)
C8	N3	C4	117.12(19)
C8	N3	Mn1	126.60(16)
C4	N3	Mn1	116.28(15)
N1	C1	N2	103.72(19)
N1	C1	Mn1	141.00(18)
N2	C1	Mn1	115.19(16)
C3	C2	N1	107.3(2)
C2	C3	N2	105.9(2)
N3	C4	N2	112.66(19)
N3	C4	C5	123.9(2)
N2	C4	C5	123.5(2)
C6	C5	C4	117.6(2)
C5	C6	C7	119.6(2)
C8	C7	C6	118.4(2)
N3	C8	C7	123.4(2)
N1	C9	C10	110.51(19)
O1	C11	Mn1	177.1(2)
O2	C12	Mn1	177.4(2)
O3	C13	Mn1	179.2(2)
N4	C14	Mn1	177.8(2)

2.3.1 Data Collection

The orange crystal was mounted on the tip of a glass fiber. The X-ray intensity data were measured at 100K temperature on a Bruker SMART APEX II X-ray diffractometer system with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) using ω-scan technique. The data were collected in 1464 frames with 10 second exposure times. Crystallographic data: C14H11N4O3Mn: a = 14.4018(15) Å, b = 10.6199(11) Å, c = 9.3898(10) Å, $\alpha = 90^{o}$, $\beta = 100.9552(17)^{o}$, $\gamma = 90^{o}$, V = 1410.0(3) Å^3, Z = 4, F.W. = 338.21, μ = 0.954 mm^{-1}, d = 1.593 g/cm^3, F(000) = 688.

2.3.2 Data Reduction

Of the 4299 unique reflections collected, 3118 were observed (I > 2 $\sigma(I)$). The linear absorption coefficient for Mo Kα radiation is 0.954 mm^{-1}. The data were corrected for Lorentz and polarization effects and integrated with the manufacturer's SAINT software. Absorption corrections were applied with the SADABS.

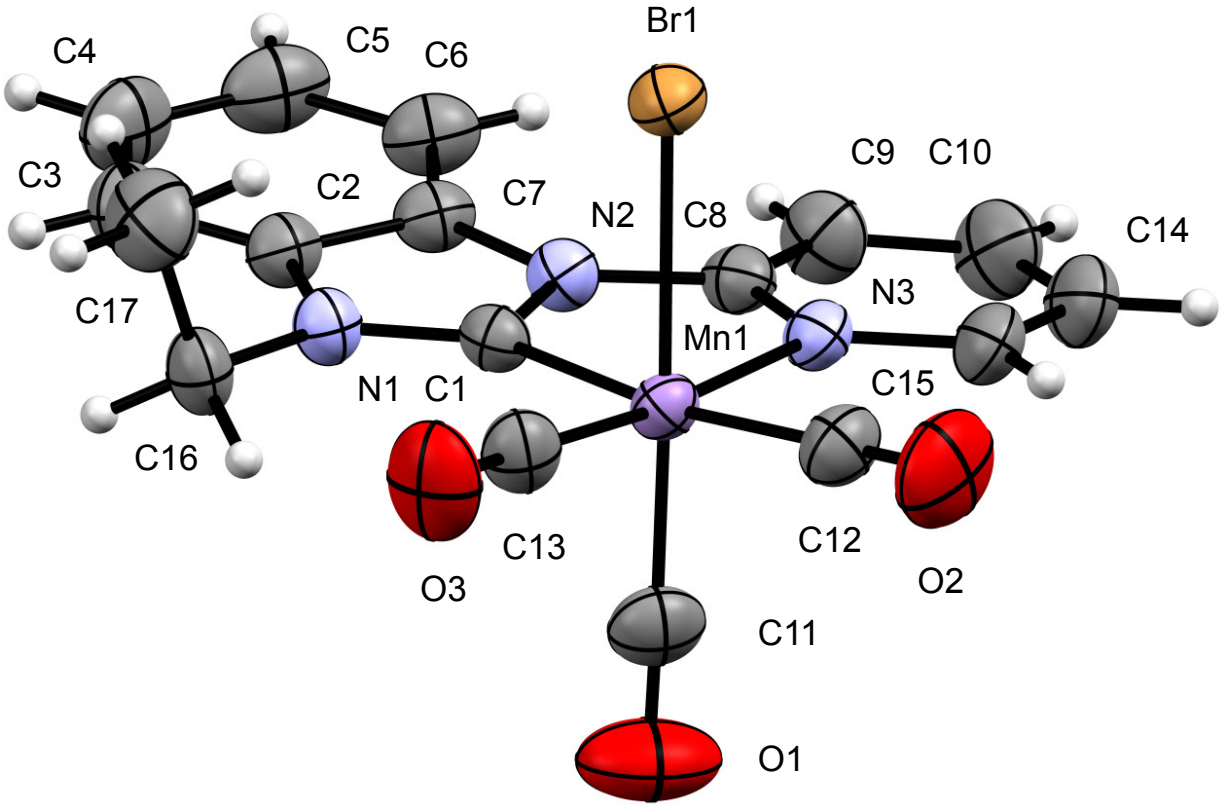
2.3.3 Structure Solution and Refinement

Subsequent solution and refinement was performed using the SHELXTL-2103 [1] solution package operating on a Pentium computer. The structure was solved by direct method using SHELXTL-2103 Software Package. Non-hydrogen atomic scattering factors were taken from the literature tabulations. [2] Non-hydrogen atoms were located from successive difference Fourier map calculations. In the final cycles of each refinement, all the non-hydrogen atoms were refined in anisotropic displacement parameters. All the hydrogen atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a CH bond length of m Å(m =0.99 for CH_2 and 0.98 for CH_3 groups, m = 0.95 for Ph-H groups). Hydrogen atom temperature factors were fixed at n (n = 1.5 for CH_3 groups, n = 1.2 for CH_2 and Ph-H groups) times the isotropic temperature factor of the C-atom to which they are bonded. The crystal system of compound is monoclinic, space group P2(1)/c (No. 14) and the final residual values based on 199 variable parameters and 3118 observed reflections (I > 2 $\sigma(I)$) are R1 = 0.0462, wR2 = 0.1063, and those for all unique reflections are R1 = 0.0741, wR2 = 0.1196. The goodness-of-fit indicator for all data is 1.030. Peaks on the final difference map ranged from 0.727 to -0.557 e/Å^3, which are of no chemical significance. The efforts have been made to resolve as many alerts as possible generated by CheckCIF. The current highest alerts are at level G.

2.3.4 Summary

The compound crystallizes in monoclinic, space group P2(1)/c (No. 14). The asymmetric unit contains one molecule in the form of C14H11N4O3Mn. Structure solution, refinement and the calculation of derived results were performed using the SHELXTL-2013 [1] package of computer programs. Neutral atom scattering factors were those of Cromer and Waber, [2] and the real and imaginary anomalous dispersion corrections were those of Cromer. [3]

2.4 [MnBr(Et-BImid-Py)(CO)$_3$]



Chemical Formula: C17 H13 Br Mn N3 O3
Formula Weight: 442.15 g mol^{-1}
Crystal System: triclinic
Space Group: P -1
Unit Cell Dimensions: a = 7.9754(9) Å alpha = 83.171(2) degrees
b = 8.7199(10) Å beta = 84.768(2) degrees
c = 7.9754(9) Å gamma = 79.192(2) degrees
Cell Volume: 866.26(17) $Å^3$
Temperature: 296(2) K
Radiation Type: MoKα
Radiation Wavelength: 0.71073 Å
Theta Range for Collection: 2.39 degrees to 30.99 degrees
Reflections Collected (Unique): 13441 (5022)
Goodness-of-Fit on F^2: 1.052

Bond Lengths (Å):

Mn1	C13	1.801(2)
Mn1	C11	1.810(2)
Mn1	C12	1.838(2)
Mn1	C1	1.9946(18)
Mn1	N3	2.0673(16)
Mn1	Br1	2.5372(4)
N1	C1	1.336(2)
N1	C2	1.398(2)
N1	C16	1.467(2)
N2	C1	1.384(2)
N2	C8	1.395(2)
N2	C7	1.411(2)
N3	C8	1.345(3)
N3	C15	1.354(3)
C2	C3	1.385(3)
C2	C7	1.394(3)
C3	C4	1.379(3)
C4	C5	1.385(4)
C5	C6	1.376(3)
C6	C7	1.392(3)
C8	C9	1.388(3)
C9	C10	1.380(3)
C10	C14	1.378(4)
C11	O1	1.098(3)
C12	O2	1.137(3)
C13	O3	1.146(3)
C14	C15	1.371(3)
C16	C17	1.502(3)

Bond Angles (degrees):

C13	Mn1	C11	90.72(11)
C13	Mn1	C12	87.74(10)
C11	Mn1	C12	93.24(10)
C13	Mn1	C1	98.58(8)
C11	Mn1	C1	91.82(9)
C12	Mn1	C1	171.85(9)
C13	Mn1	N3	174.77(8)
C11	Mn1	N3	93.25(9)
C12	Mn1	N3	95.42(8)
C1	Mn1	N3	77.91(7)
C13	Mn1	Br1	88.12(7)
C11	Mn1	Br1	178.40(8)
C12	Mn1	Br1	87.81(7)
C1	Mn1	Br1	87.27(5)
N3	Mn1	Br1	87.85(4)
C1	N1	C2	111.52(15)
C1	N1	C16	126.11(15)
C2	N1	C16	122.12(16)
C1	N2	C8	117.52(15)
C1	N2	C7	110.96(15)
C8	N2	C7	131.52(16)
C8	N3	C15	117.31(17)
C8	N3	Mn1	116.73(12)
C15	N3	Mn1	125.93(14)
N1	C1	N2	105.55(15)
N1	C1	Mn1	139.40(13)
N2	C1	Mn1	114.98(12)
C3	C2	C7	122.22(19)
C3	C2	N1	130.53(19)
C7	C2	N1	107.23(16)
C4	C3	C2	116.8(2)
C3	C4	C5	121.3(2)
C6	C5	C4	122.4(2)
C5	C6	C7	117.0(2)
C6	C7	C2	120.39(19)
C6	C7	N2	134.89(19)
C2	C7	N2	104.67(15)
N3	C8	C9	123.29(19)
N3	C8	N2	112.64(15)
C9	C8	N2	124.03(19)

C10	C9	C8	117.8(2)
C14	C10	C9	119.8(2)
O1	C11	Mn1	178.5(3)
O2	C12	Mn1	177.6(2)
O3	C13	Mn1	177.5(2)
C15	C14	C10	119.0(2)
N3	C15	C14	122.7(2)
N1	C16	C17	111.47(18)

2.4.1 Data Collection

The orange crystal was mounted on the tip of a glass fiber. The X-ray intensity data were measured at room temperature on a Bruker SMART APEX II X-ray diffractometer system with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) using ω-scan technique. The data were collected in 1464 frames with 10 second exposure times. Crystallographic data: C17H13N3O3MnBr: a = 7.9754(9) Å, b = 8.7199(10) Å, c = 12.8037(15) Å, α = 83.171(2)^{o}, β = 84.768(2)^{o}, γ = 79.192(2)^{o}, V = 866.26(17) Å^3, Z = 2, F.W. = 442.15, μ = 3.089 mm^{-1}, d = 1.695 g/cm^3, F(000) = 440.

2.4.2 Data Reduction

Of the 5022 unique reflections collected, 4374 were observed (I > 2 $\sigma(I)$). The linear absorption coefficient for Mo Kα radiation is 3.089 mm^{-1}. The data were corrected for Lorentz and polarization effects and integrated with the manufacturer's SAINT software. Absorption corrections were applied with the SADABS.

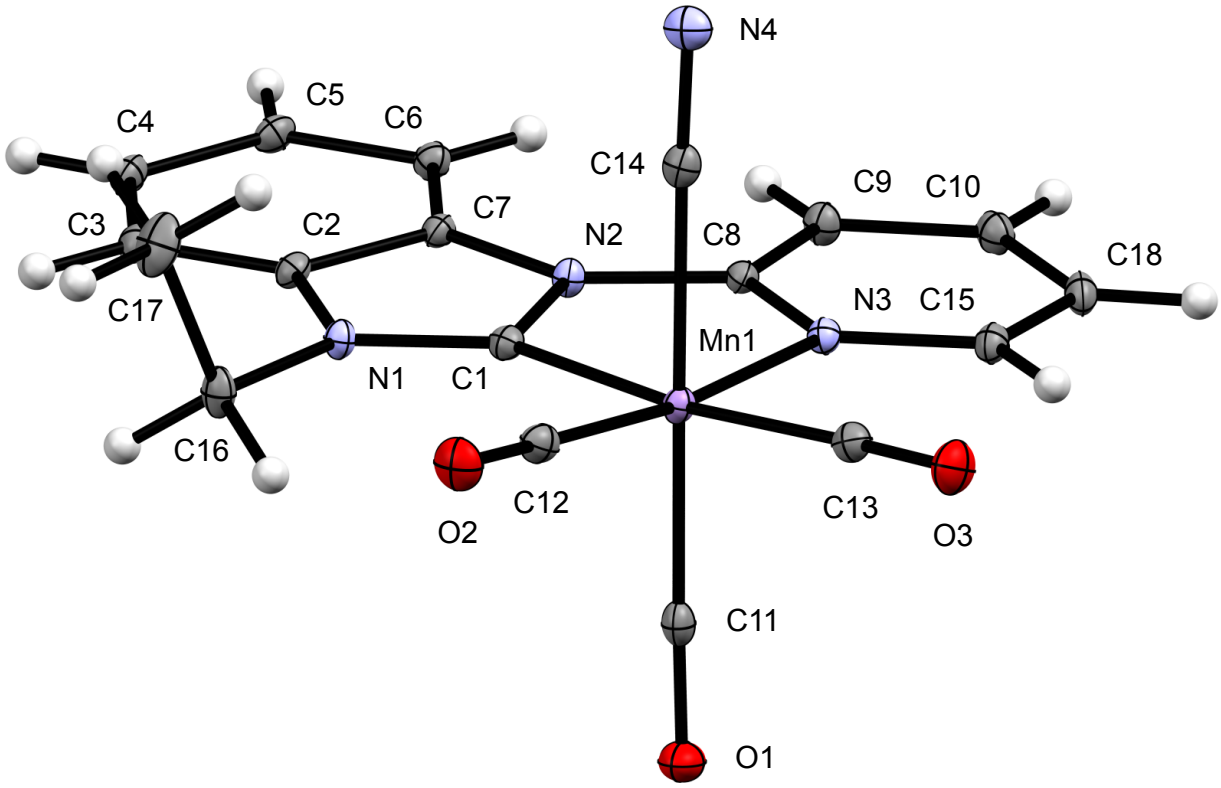
2.4.3 Structure Solution and Refinement

Subsequent solution and refinement was performed using the SHELXTL-2103 [1] solution package operating on a Pentium computer. The structure was solved by direct method using SHELXTL-2103 Software Package. Non-hydrogen atomic scattering factors were taken from the literature tabulations. [2] Non-hydrogen atoms were located from successive difference Fourier map calculations. In the final cycles of each refinement, all the non-hydrogen atoms were refined in anisotropic displacement parameters. All the hydrogen atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a CH bond length of m Å(m =0.99 for CH_2 and 0.98 for CH_3 groups, m = 0.95 for Ph-H groups). Hydrogen atom temperature factors were fixed at n (n = 1.5 for CH_3 groups, n = 1.2 for CH_2 and Ph-H groups) times the isotropic temperature factor of the C-atom to which they are bonded. The crystal system of compound is triclinic, space group P-1 (No. 2) and the final residual values based on 226 variable parameters and 4374 observed reflections (I > 2 $\sigma(I)$) are R1 = 0.0292, wR2 = 0.0723, and those for all unique reflections are R1 = 0.0353, wR2 = 0.0746. The goodness-of-fit indicator for all data is 1.052. Peaks on the final difference map ranged from 0.848 to -0.409 e/Å^3 with the largest peak around the heavy atom of Mn, which are of no chemical significance. The efforts have been made to resolve as many alerts as possible generated by CheckCIF. The current highest alert is at level C that is a false alert.

2.4.4 Summary

The compound crystallizes in triclinic, space group P-1 (No. 2). The asymmetric unit contains one molecule in the form of C17H13N3O3MnBr. Structure solution, refinement and the calculation of derived results were performed using the SHELXTL-2013 [1] package of computer programs. Neutral atom scattering factors were those of Cromer and Waber, [2] and the real and imaginary anomalous dispersion corrections were those of Cromer. [3]

2.5 [MnCN(Et-BImid-Py)$(CO)_3$] (4)



Chemical Formula: C19 H15 Cl2 Mn N4 O3
Formula Weight: 473.19 g mol^{-1}
Crystal System: triclinic
Space Group: P -1
Unit Cell Dimensions: a = 9.2310(9) Å alpha = 85.5287(13) degrees
b = 9.9773(9) Å beta = 74.4239(13) degrees
c = 9.2310(9) Å gamma = 69.7291(13) degrees
Cell Volume: 1001.75(16) $Å^3$
Temperature: 100(2) K
Radiation Type: MoKα
Radiation Wavelength: 0.71073 Å
Theta Range for Collection: 2.43 degrees to 33.00 degrees
Reflections Collected (Unique): 14745 (5311)
Goodness-of-Fit on F^2: 1.040

Bond Lengths (Å):

Mn1	C12	1.8096(16)
Mn1	C11	1.8221(16)
Mn1	C13	1.8299(16)
Mn1	C14	1.9972(16)
Mn1	C1	2.0003(15)
Mn1	N3	2.0745(12)
N1	C1	1.3433(18)
N1	C2	1.3992(18)
N1	C16	1.4666(18)
N2	C1	1.3847(18)
N2	C8	1.4012(18)
N2	C7	1.4089(18)
N3	C8	1.3523(18)
N3	C15	1.3503(19)
C2	C7	1.395(2)
C2	C3	1.392(2)
C3	C4	1.392(2)
C4	C5	1.394(2)
C5	C6	1.394(2)
C6	C7	1.395(2)
C8	C9	1.390(2)
C9	C10	1.387(2)
C10	C18	1.385(2)
C11	O1	1.145(2)
C12	O2	1.1484(19)
C13	O3	1.1485(19)
C14	N4	1.153(2)
C15	C18	1.381(2)
C16	C17	1.515(2)
C19	Cl1	1.767(9)
C19	Cl2	1.762(9)
C19’	Cl2’	1.767(11)
C19’	Cl1’	1.783(10)

Bond Angles (degrees):

C12	Mn1	C11	92.85(7)
C12	Mn1	C13	87.46(7)
C11	Mn1	C13	91.18(7)
C12	Mn1	C14	87.79(6)
C11	Mn1	C14	179.30(7)
C13	Mn1	C14	88.55(6)
C12	Mn1	C1	97.87(6)
C11	Mn1	C1	92.97(6)
C13	Mn1	C1	173.07(6)
C14	Mn1	C1	87.23(6)
C12	Mn1	N3	173.51(6)
C11	Mn1	N3	92.31(6)
C13	Mn1	N3	96.38(6)
C14	Mn1	N3	87.08(5)
C1	Mn1	N3	77.93(5)
C1	N1	C2	111.29(12)
C1	N1	C16	125.88(12)
C2	N1	C16	122.76(12)
C1	N2	C8	117.44(12)
C1	N2	C7	111.15(12)
C8	N2	C7	131.31(12)
C8	N3	C15	117.20(13)
C8	N3	Mn1	116.48(10)
C15	N3	Mn1	126.32(10)
N1	C1	N2	105.44(12)
N1	C1	Mn1	139.43(11)
N2	C1	Mn1	115.10(10)
C7	C2	C3	122.45(13)
C7	C2	N1	107.35(12)
C3	C2	N1	130.18(14)
C2	C3	C4	116.55(14)
C3	C4	C5	121.33(14)
C6	C5	C4	122.04(14)
C5	C6	C7	116.77(14)
C2	C7	C6	120.85(13)
C2	C7	N2	104.75(12)
C6	C7	N2	134.40(13)
N3	C8	C9	123.13(13)
N3	C8	N2	112.75(12)
C9	C8	N2	124.11(13)
C10	C9	C8	118.45(14)
C18	C10	C9	119.11(14)
O1	C11	Mn1	177.96(14)

O2	C12	Mn1	175.83(14)
O3	C13	Mn1	175.64(14)
N4	C14	Mn1	178.01(14)
N3	C15	C18	123.11(14)
N1	C16	C17	110.96(14)
C15	C18	C10	118.99(14)
Cl1	C19	Cl2	114.1(7)
Cl2’	C19’	Cl1’	109.2(8)

2.5.1 Data Collection

The orange crystal was mounted on the tip of a glass fiber. The X-ray intensity data were measured at the temperature of 100 K on a Bruker SMART APEX II X-ray diffractometer system with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) using ω-scan technique. The data were collected in 1464 frames with 10 second exposure times. Crystallographic data: C19H15N4O3MnCl2: a = 9.2310(9) Å, b = 9.9773(9) Å, c = 12.0386(11) Å, α = 85.5287(13)^{o}, β = 74.4239(13)^{o}, γ = 69.7291(13)^{o}, V = 1001.75(16) Å^3, Z = 2, F.W. = 473.19, μ = 0.954 mm^{-1}, d = 1.569 g/cm^3, F(000) = 480.

2.5.2 Data Reduction

Of the 5311 unique reflections collected, 4627 were observed (I > 2 $\sigma(I)$). The linear absorption coefficient for Mo Kα radiation is 0.954 mm^{-1}. The data were corrected for Lorentz and polarization effects and integrated with the manufacturer's SAINT software. Absorption corrections were applied with the SADABS.

2.5.3 Structure Solution and Refinement

Subsequent solution and refinement was performed using the SHELXTL-2103 [1] solution package operating on a Pentium computer. The structure was solved by direct method using SHELXTL-2103 Software Package. Non-hydrogen atomic scattering factors were taken from the literature tabulations. [2] Non-hydrogen atoms were located from successive difference Fourier map calculations. The three non-hydrogen atoms of discrete solvent methylene dichloride (CH2Cl2) were found disordered in two sets labeled as C(19), Cl(1), Cl(2) (one set) and C(19), Cl(1), Cl(2) (another set). Each of these two sets is divided using the PART commands and proper restraints. The set of C(19), Cl(1), Cl(2) has 52.496 % occupancies while the other (C(19), Cl(1), Cl(2)) has 47.504 % occupancies. In the final cycles of each refinement, all the non-hydrogen atoms were refined in anisotropic displacement parameters. All the hydrogen atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a CH bond length of m Å(m =0.99 for CH_2 and 0.98 for CH_3 groups, m = 0.95 for Ph-H groups). Hydrogen atom temperature factors were fixed at n (n = 1.5 for CH_3 groups, n = 1.2 for CH_2 and Ph-H groups) times the isotropic temperature factor of the C-atom to which they are bonded. The crystal system of compound is triclinic, space group P-1 (No. 2) and the final residual values based on 292 variable parameters and 4627 observed reflections (I > 2 $\sigma(I)$) are R1 = 0.0292, wR2 = 0.0741, and those for all unique reflections are R1 = 0.0356, wR2 = 0.0779. The goodness-of-fit indicator for all data is 1.040. Peaks on the final difference map ranged from 0.433 to -0.302 e/Å^3 , which are of no chemical significance. The efforts have been made to resolve as many alerts as possible generated by CheckCIF. The current highest alerts are at level G.

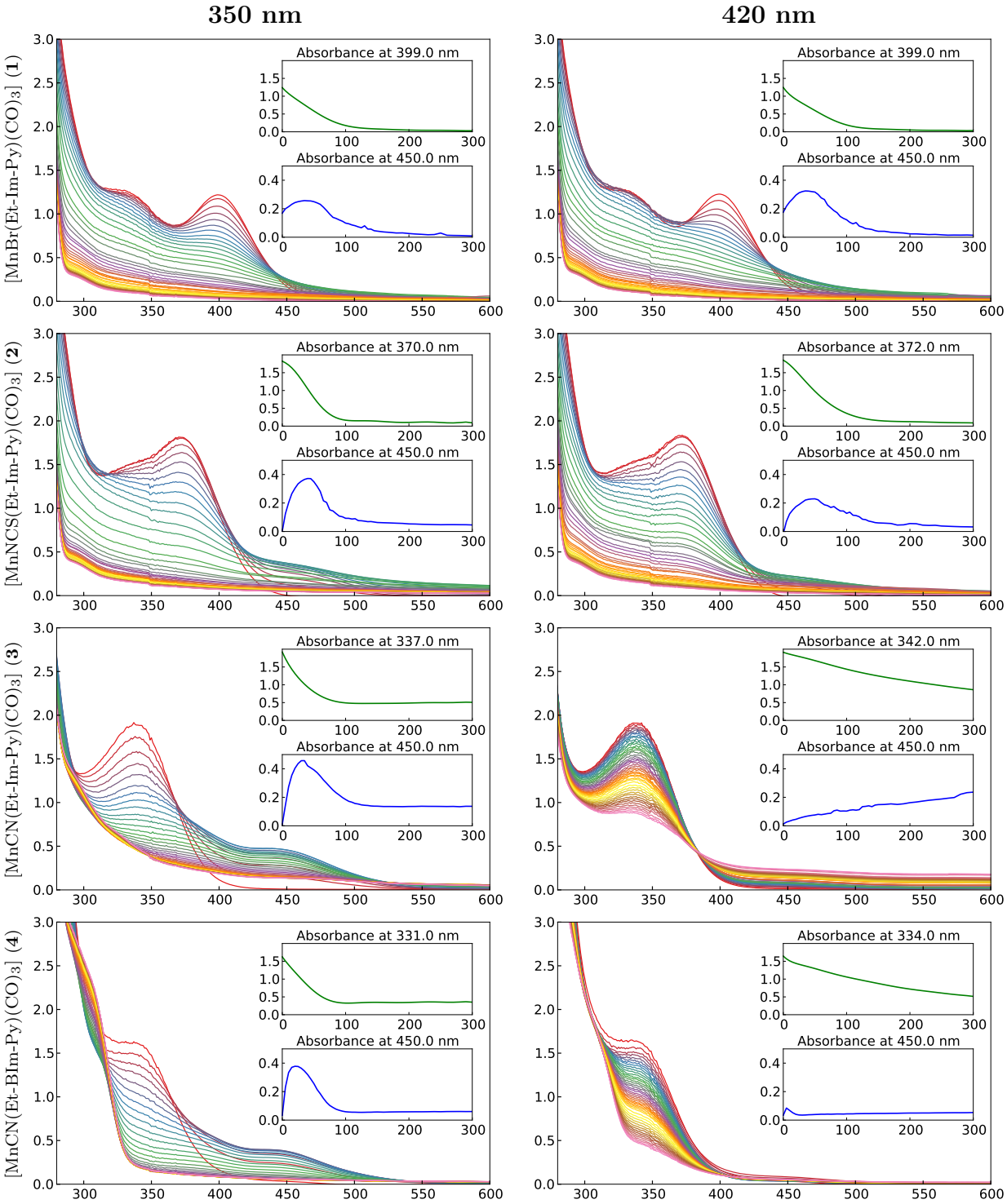
2.5.4 Summary

The compound crystallizes in triclinic, space group P-1 (No. 2). The asymmetric unit contains one molecule in the form of C18H13N4O3Mn plus one solvent methylene dichloride

(CH2Cl2) molecule. The whole formula is in the form of C19H15N4O3MnCl2. Structure solution, refinement and the calculation of derived results were performed using the SHELXTL-2013 [1] package of computer programs. Neutral atom scattering factors were those of Cromer and Waber, [2] and the real and imaginary anomalous dispersion corrections were those of Cromer. [3]

3 UV-Vis Light Study

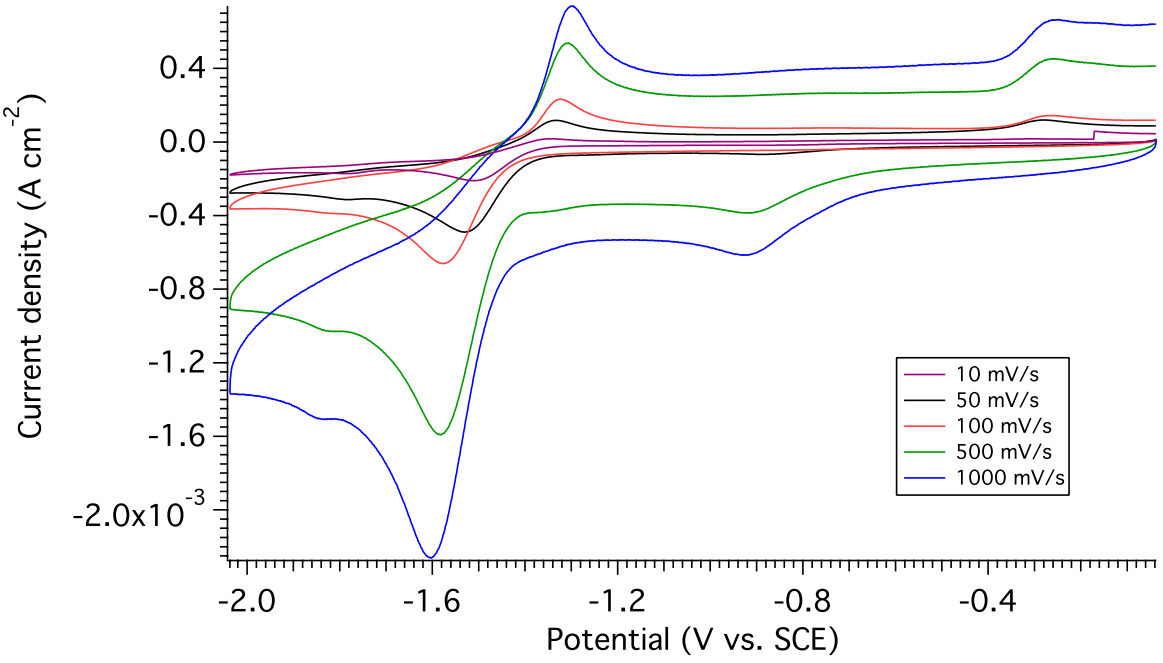
UV-Vis spectra after irradiation with 350 nm or 420 nm light. Each plot shows the absorbance (y-axis) at given wavelengths (x-axis, nm), after irradiation intervals of 5 seconds (0 → 150 s) or 10 seconds (150 → 300 s). The insets show the absorbance (y-axis) versus the total irradiation time (x-axis, seconds) at the wavelength of the MLCT band (top) and at 450 nm (bottom).

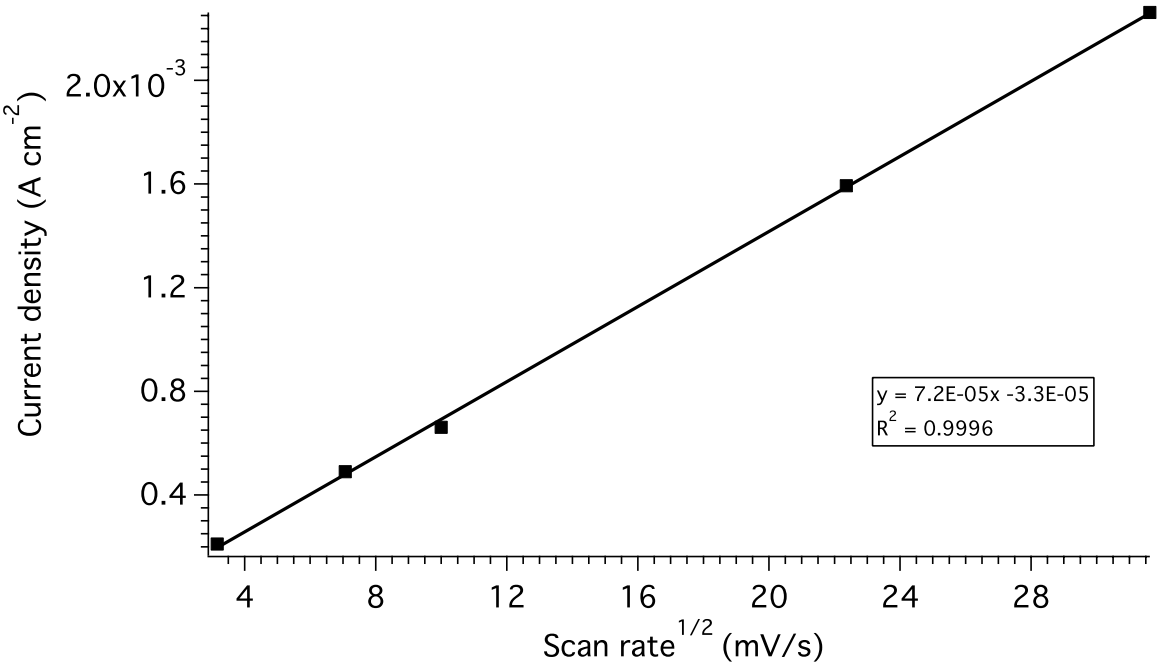


4 Electrochemical Data

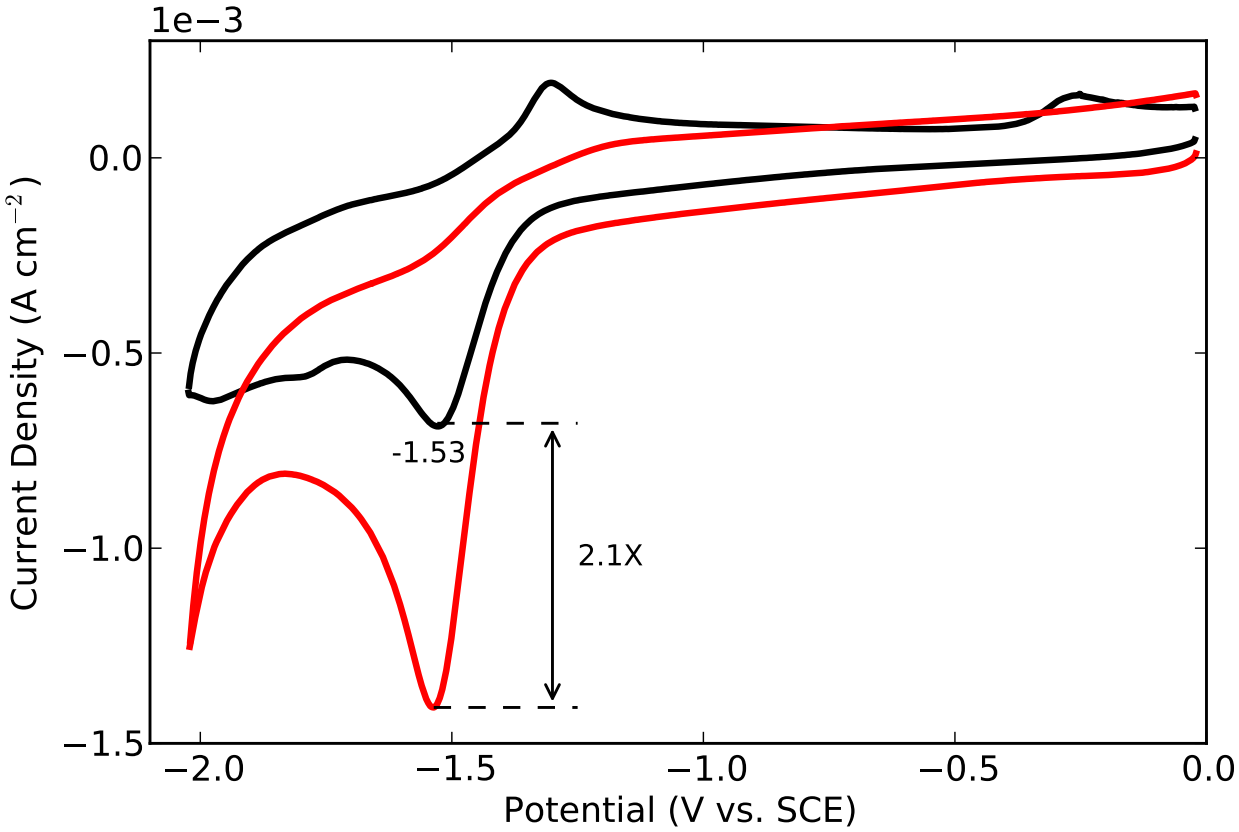
4.1 [MnBr(Et-Imid-Py)(CO)$_3$] (1)

Atmosphere: Argon
Catalyst Concentration: 1 mM
Solvent: CH_3CN
Electrolyte: 0.1 M TBAP





Atmosphere: Argon (black), CO_2 (red)
Catalyst Concentration: 1 mM
Solvent: CH_3CN (5 % H_2O
Electrolyte: 0.1 M TBAP
Scanrate: 100 mV/s



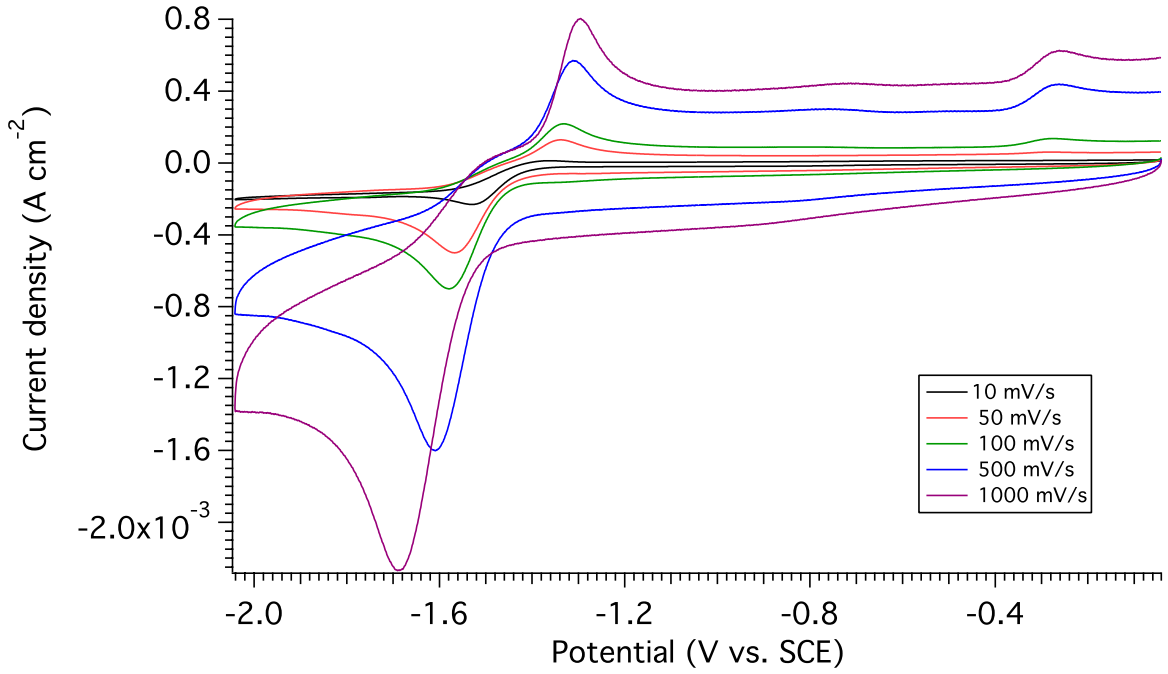
Turnover Frequency Calculation:
$F = 9.6485 \times 10^4$ C mol^{-1} (Faraday's Constant)
$v = 0.10$ V s^{-1} (Scan Rate)
$n_p = 1$ (Number of Electrons for the Uncatalyzed Process)
$R = 8.314$ V C K^{-1} mol^{-1} (Universal Gas Constant)
$T = 298$ K (Temperature)
$n_{cat} = 2$ (Number of Electrons in the Catalytic Process)
$\frac{i_{cat}}{i_p} = 2.1$ (Catalytic Current Enhancement)

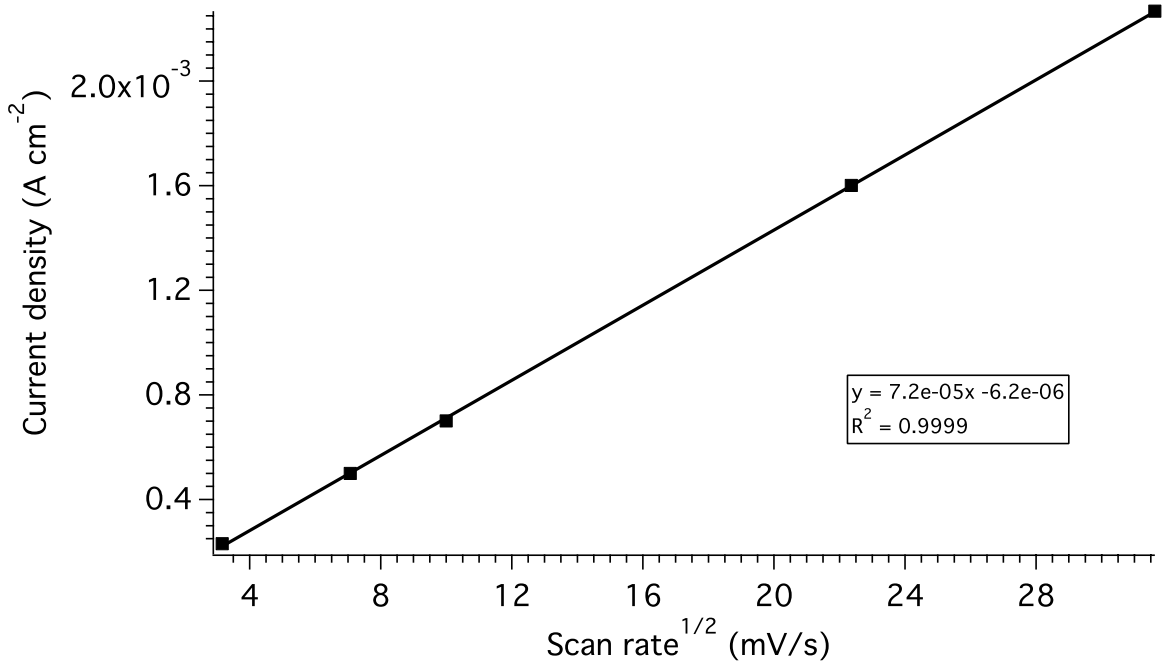
$$\text{TOF} = \frac{Fvn_p^3}{RT}\left(\frac{0.4463}{n_{cat}}\right)^2\left(\frac{i_{cat}}{i_p}\right)^2$$

TOF $= 0.86$ s^{-1}

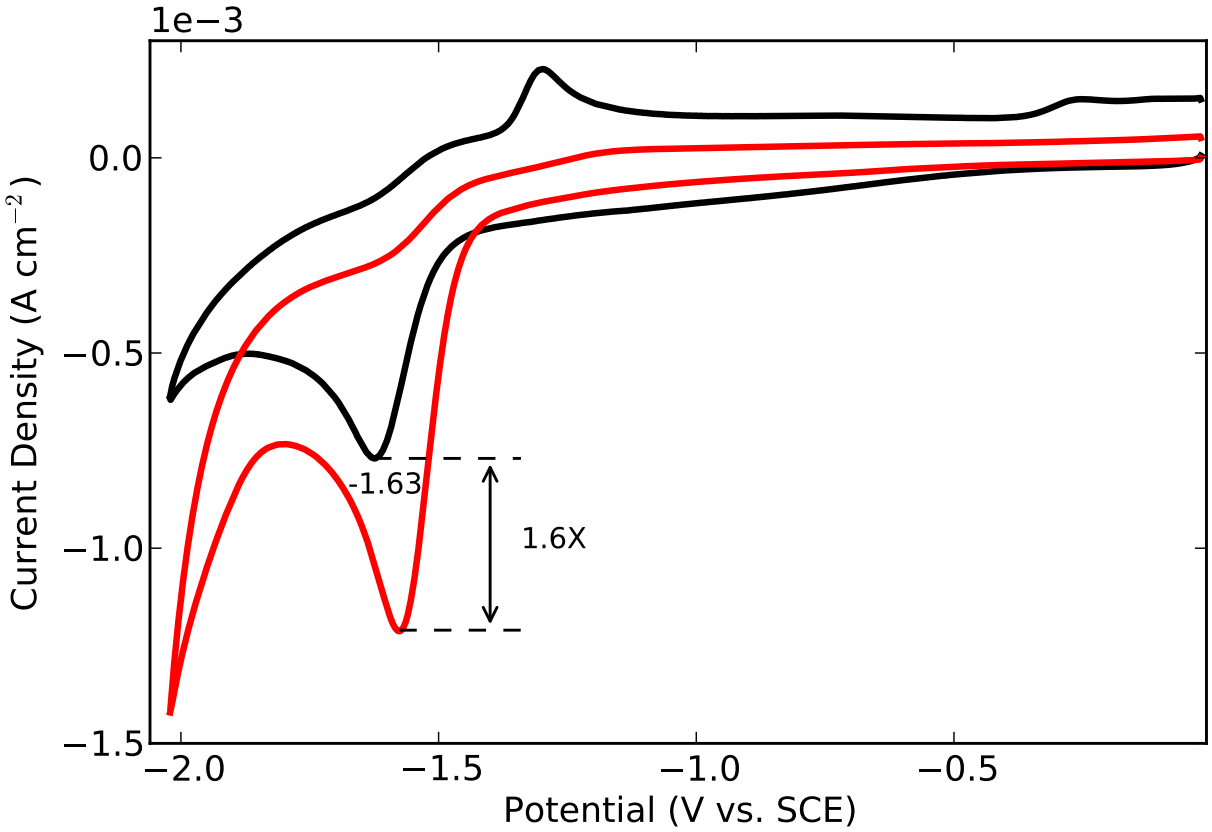
4.2 [MnNCS(Et-Imid-Py)$(CO)_3$] (2)

Atmosphere: Argon
Catalyst Concentration: 1 mM
Solvent: CH_3CN
Electrolyte: 0.1 M TBAP





Atmosphere: Argon (black), CO_2 (red)
Catalyst Concentration: 1 mM
Solvent: CH_3CN (5 % H_2O
Electrolyte: 0.1 M TBAP
Scanrate: 100 mV/s



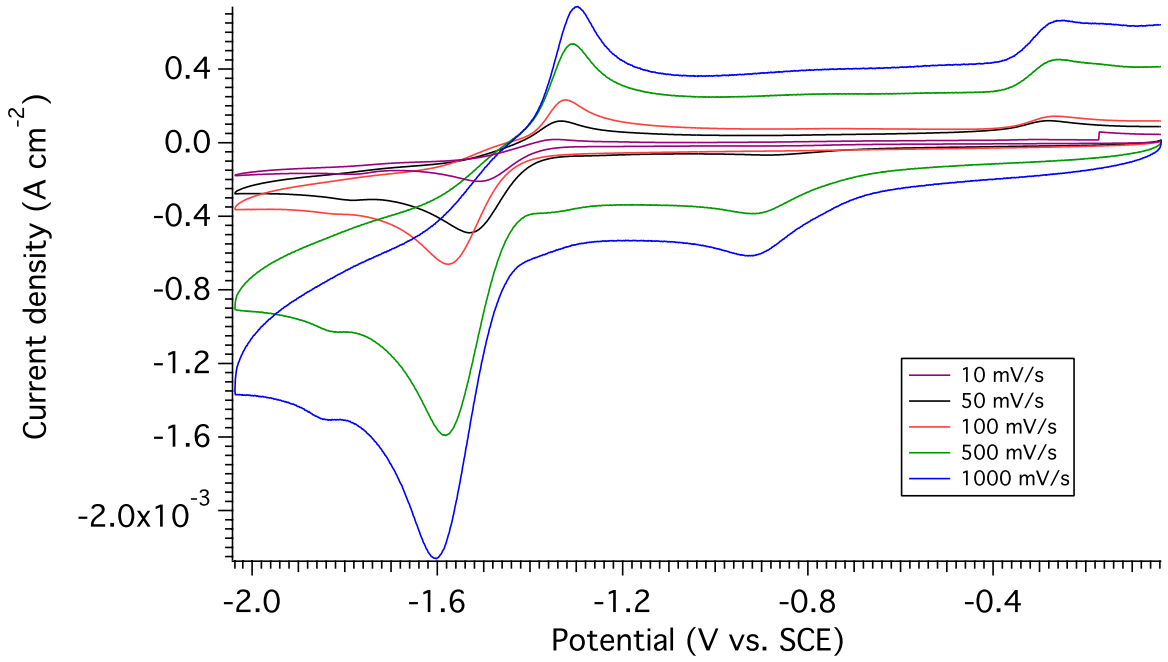
Turnover Frequency Calculation:
$F = 9.6485 \times 10^4$ C mol^{-1} (Faraday's Constant)
$v = 0.10$ V s^{-1} (Scan Rate)
$n_p = 1$ (Number of Electrons for the Uncatalyzed Process)
$R = 8.314$ V C K^{-1} mol^{-1} (Universal Gas Constant)
$T = 298$ K (Temperature)
$n_{cat} = 2$ (Number of Electrons in the Catalytic Process)
$\frac{i_{cat}}{i_p} = 1.6$ (Catalytic Current Enhancement)

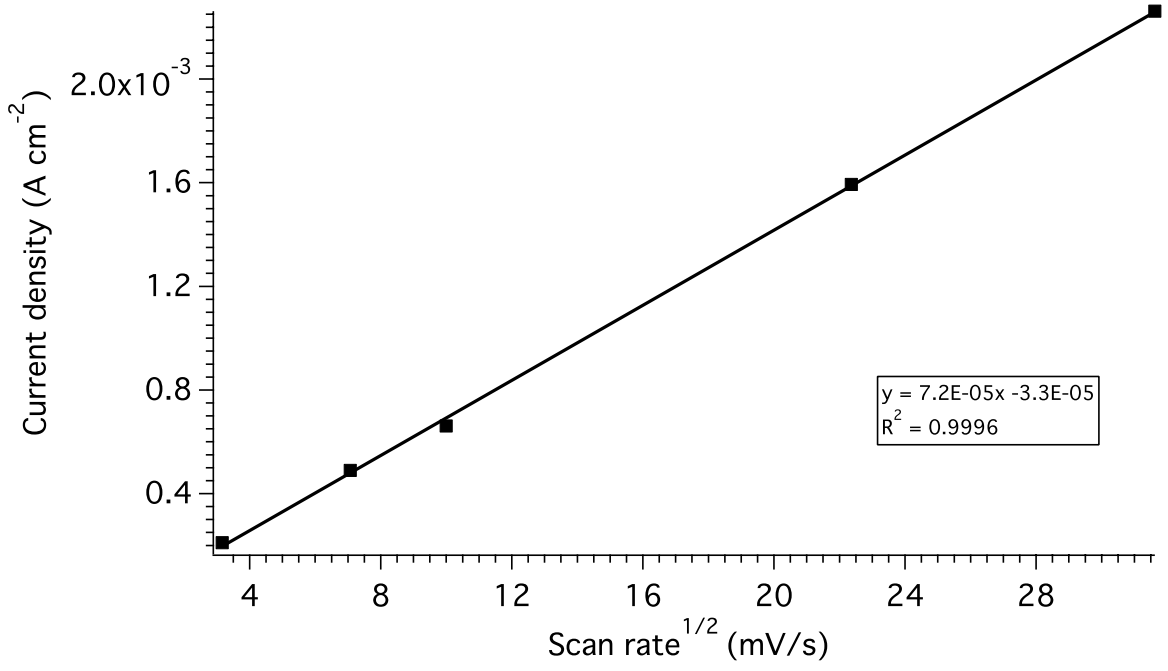
$$\text{TOF} = \frac{Fvn_p^3}{RT}\left(\frac{0.4463}{n_{cat}}\right)^2\left(\frac{i_{cat}}{i_p}\right)^2$$

TOF $= 0.50$ s^{-1}

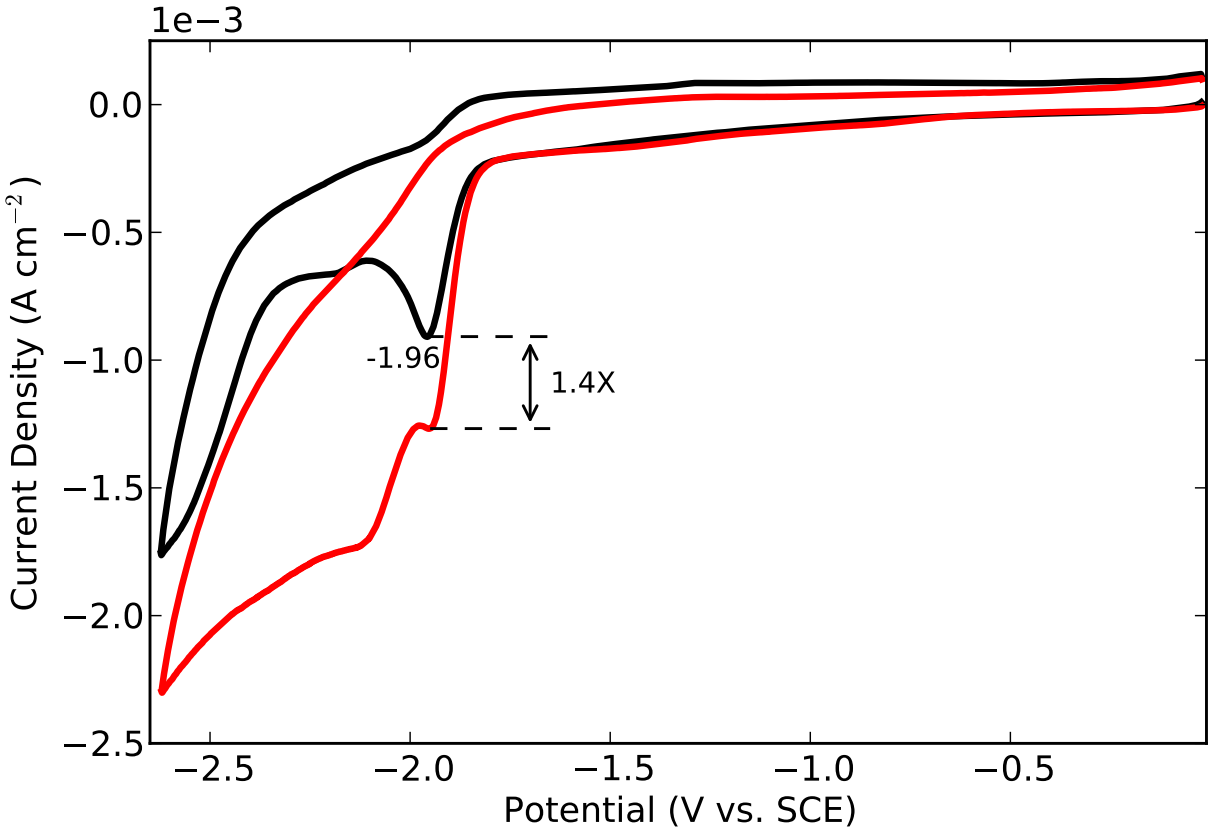
4.3 [MnCN(Et-Im-Py)$(CO)_3$] (3)

Atmosphere: Argon
Catalyst Concentration: 1 mM
Solvent: CH_3CN
Electrolyte: 0.1 M TBAP





Atmosphere: Argon (black), CO_2 (red)
Catalyst Concentration: 1 mM
Solvent: CH_3CN (5 % H_2O
Electrolyte: 0.1 M TBAP
Scanrate: 100 mV/s



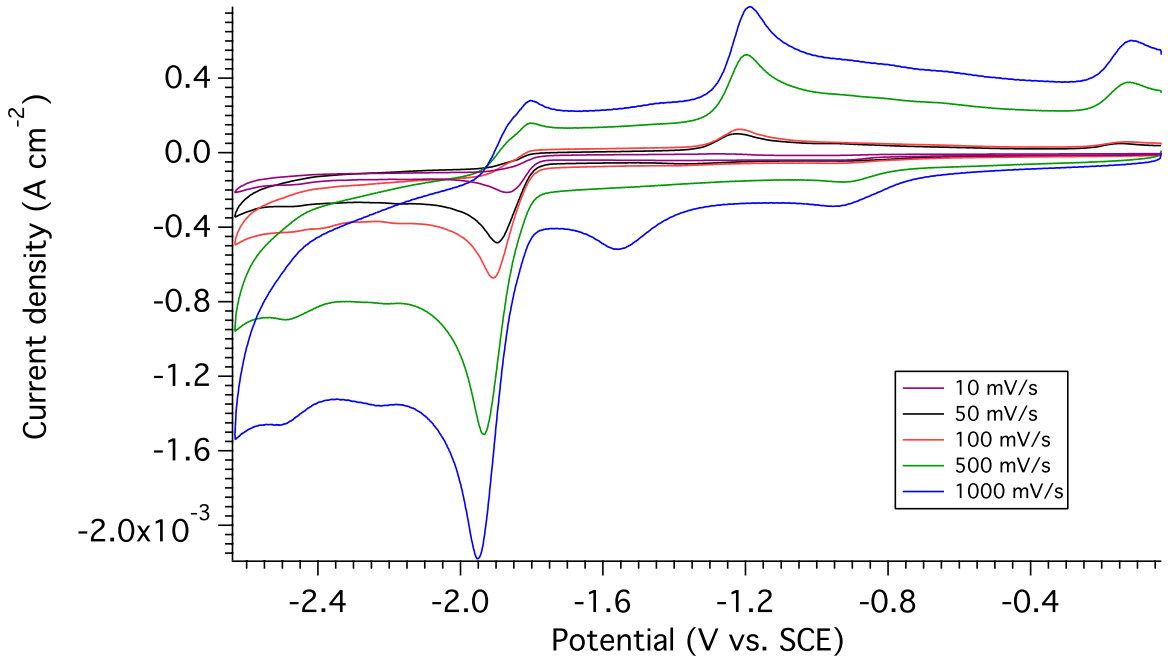
Turnover Frequency Calculation:
$F = 9.6485 \times 10^4$ C mol^{-1} (Faraday's Constant)
$v = 0.10$ V s^{-1} (Scan Rate)
$n_p = 1$ (Number of Electrons for the Uncatalyzed Process)
$R = 8.314$ V C K^{-1} mol^{-1} (Universal Gas Constant)
$T = 298$ K (Temperature)
$n_{cat} = 2$ (Number of Electrons in the Catalytic Process)
$\frac{i_{cat}}{i_p} = 1.4$ (Catalytic Current Enhancement)

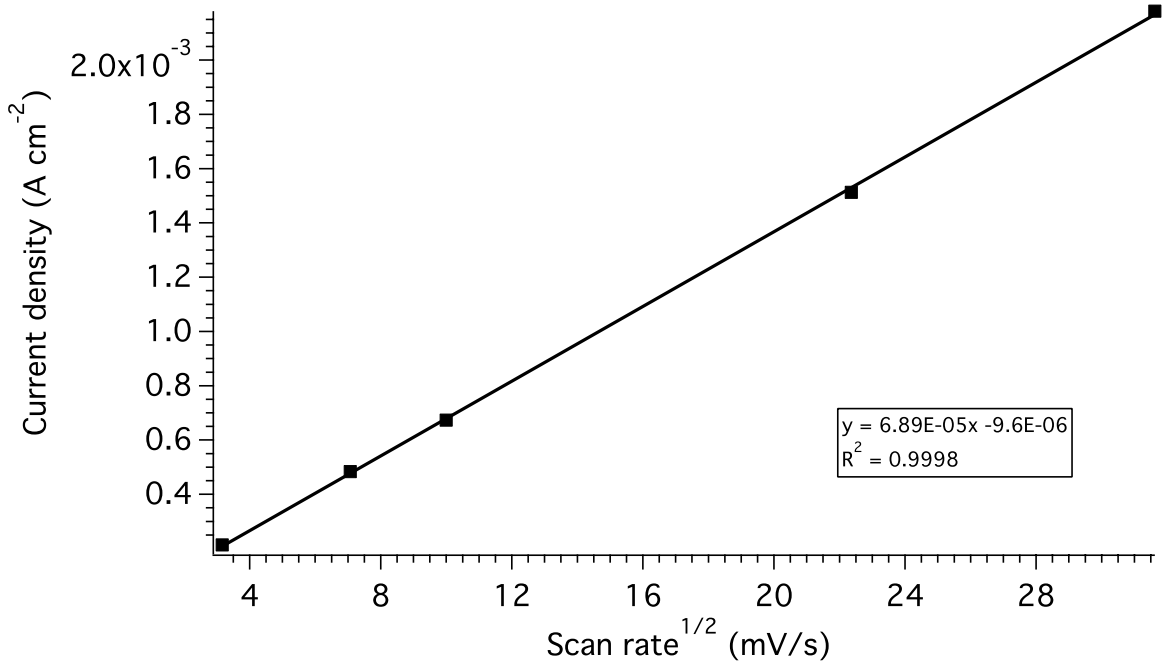
$$\text{TOF} = \frac{Fvn_p^3}{RT}\left(\frac{0.4463}{n_{cat}}\right)^2\left(\frac{i_{cat}}{i_p}\right)^2$$

TOF $= 0.38$ s^{-1}

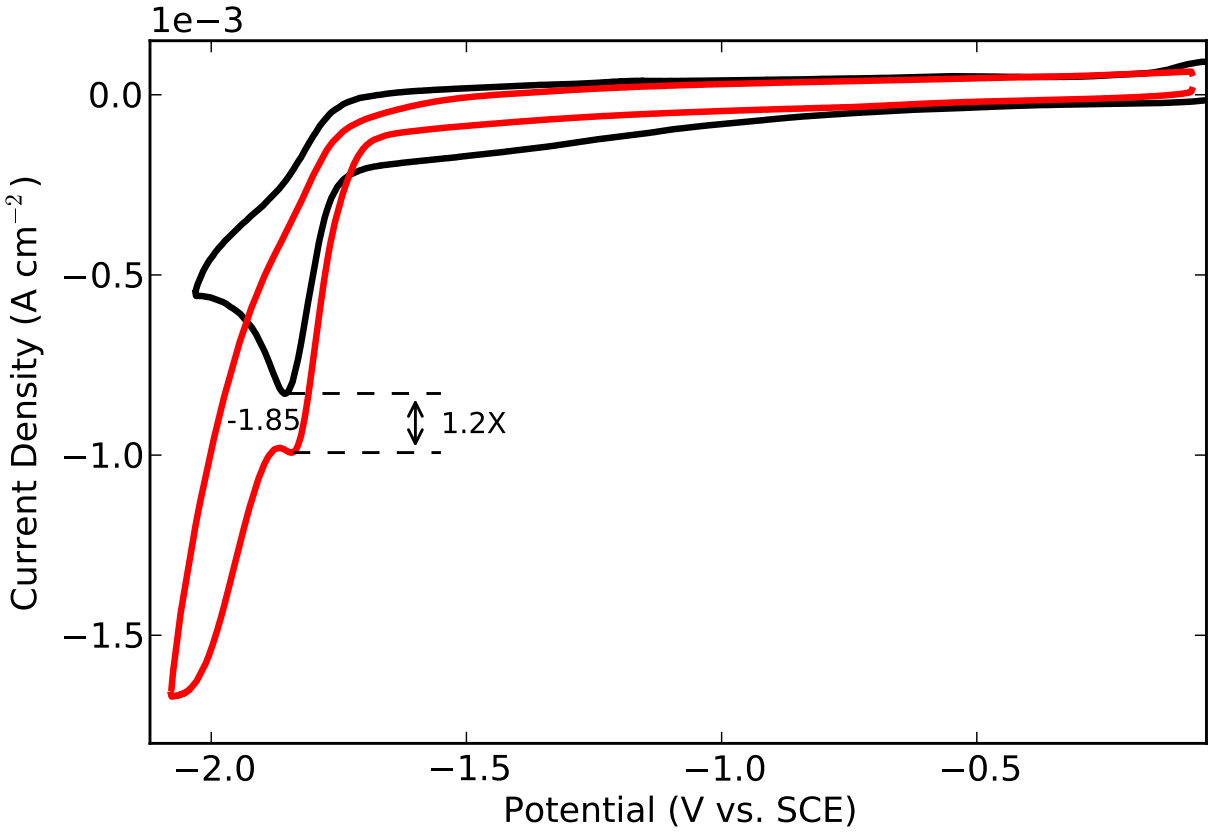
4.4 [MnCN(Et-BImid-Py)$(CO)_3$] (4)

Atmosphere: Argon
Catalyst Concentration: 1 mM
Solvent: CH_3CN
Electrolyte: 0.1 M TBAP





Atmosphere: Argon (black), CO_2 (red)
Catalyst Concentration: 1 mM
Solvent: CH_3CN (5 % H_2O
Electrolyte: 0.1 M TBAP
Scanrate: 100 mV/s

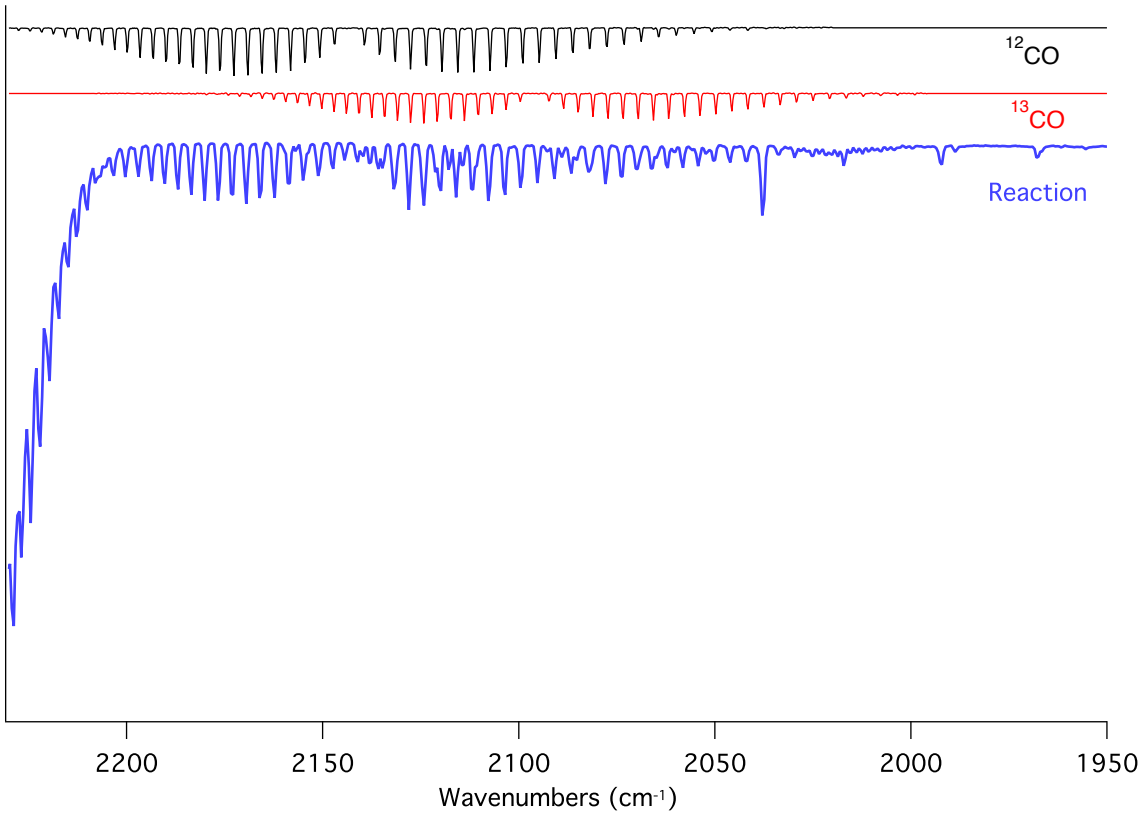


Turnover Frequency Calculation:
$F = 9.6485 \times 10^4$ C mol^{-1} (Faraday's Constant)
$v = 0.10$ V s^{-1} (Scan Rate)
$n_p = 1$ (Number of Electrons for the Uncatalyzed Process)
$R = 8.314$ V C K^{-1} mol^{-1} (Universal Gas Constant)
$T = 298$ K (Temperature)
$n_{cat} = 2$ (Number of Electrons in the Catalytic Process)
$\frac{i_{cat}}{i_p} = 1.2$ (Catalytic Current Enhancement)

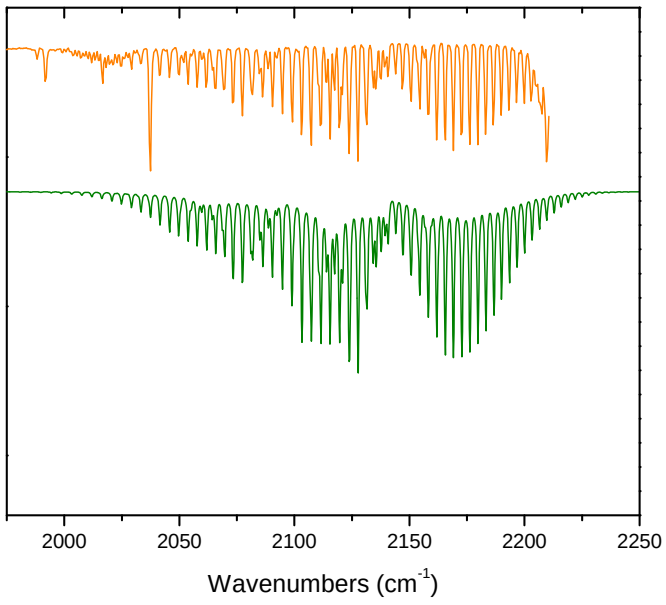
$$\text{TOF} = \frac{Fvn_p^3}{RT}\left(\frac{0.4463}{n_{cat}}\right)^2\left(\frac{i_{cat}}{i_p}\right)^2$$

TOF $= 0.28$ s^{-1}

Analysis of the headspace with FT-IR following the electrolysis of **4** with $^{13}CO_2$. Wet (5 % H_2O) acetonitrile with 0.1 M TBAP was used as the electrolyte. The presence of ^{13}CO in the reaction headspace confirms catalytic conversion.

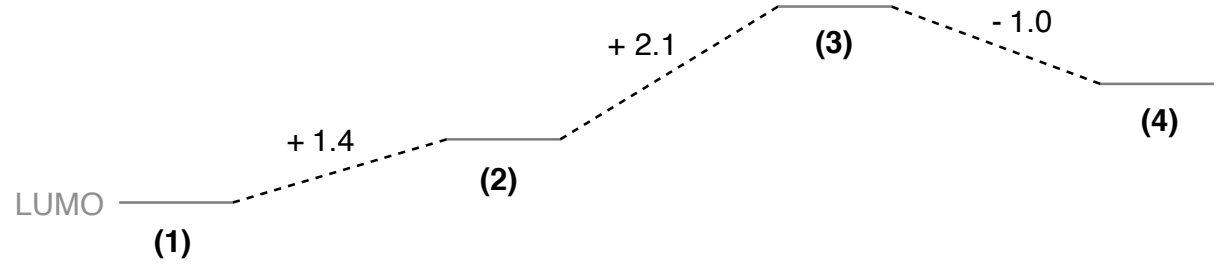


A plot of the headspace (orange) and a predicted spectrum with 30 % ^{13}CO:70 % ^{12}CO (green).



5 Theoretical Data

Relative energy differences between the lowest-unoccupied molecular orbital (LUMO) for the listed compounds. Energies, shown in kcal mol^{-1}, were obtained from computations at the B3LYP/LANL08F (Mn), 6-311++G** (H,C,N,O) level of theory. In the case of **1**, Br was parameterized with LANL2DZ.



5.1 [MnBr(Et-Im-Py)$(CO)_3$] (1)

Theory: B3LYP/LANL08F (Mn), LANL2DZ (Br), 6-311++G** (H, C, N, O)
Program: Orca 3.0.1
Atoms: 32
Charge: 0
Multiplicity: 1
Cartesian Geometry (Angstrom):

C	1.702607	1.049385	0.182012
C	2.816616	0.28762	0.146382
N	0.637997	0.166116	0.017462
C	1.069253	-1.132464	-0.110361
N	2.413452	-1.0382	-0.03329
C	-0.735798	0.44284	-0.015075
C	-1.25593	1.725459	0.133679
C	-2.63671	1.874105	0.089332
C	-3.441258	0.754587	-0.105277
C	-2.832092	-0.482878	-0.242141
N	-1.497535	-0.64967	-0.199316
C	3.376829	-2.146956	-0.143935
H	-4.519724	0.831791	-0.146647
H	-3.426082	-1.373274	-0.391696
H	-3.077408	2.85711	0.204922
H	-0.607824	2.577403	0.285812
H	2.914307	-3.029973	0.290573
H	4.227423	-1.883969	0.486684
C	3.829814	-2.399671	-1.582609
H	1.583967	2.110543	0.313048
H	3.853344	0.563374	0.244215
Mn	-0.450637	-2.483812	-0.299382
C	-1.998284	-3.47198	-0.338594
C	0.537119	-3.99977	-0.157653
O	-2.965532	-4.089958	-0.380729
O	1.136423	-4.975785	-0.043871
C	-0.334119	-2.45407	-2.092093
O	-0.256207	-2.440044	-3.242156
Br	-0.575369	-2.507044	2.357043
H	2.99262	-2.701831	-2.215439
H	4.574594	-3.199688	-1.594953
H	4.288304	-1.505314	-2.012851

5.2 [MnNCS(Et-Im-Py)$(CO)_3$] (2)

```
Theory: B3LYP/LANL08F (Mn), 6-311++G** (H, C, N, O)
Program: Orca 3.0.1
Atoms: 34
Charge: 0
Multiplicity: 1
Cartesian Geometry (Angstrom):
C  1.623327  1.026301  0.292827
C  2.722911  0.242441  0.296163
N  0.551494  0.171038  0.044341
C  0.964787  -1.129088  -0.092193
N  2.302791  -1.069683  0.061857
C  -0.809948  0.485924  -0.093971
C  -1.302403  1.775566  0.075348
C  -2.664957  1.978597  -0.100825
C  -3.48024  0.898337  -0.429156
C  -2.900503  -0.355536  -0.562292
N  -1.58284  -0.570932  -0.398411
C  3.24252  -2.200911  -0.036801
H  -4.545705  1.018234  -0.574983
H  -3.503311  -1.218661  -0.808964
H  -3.083656  2.970664  0.020406
H  -0.646109  2.594751  0.334778
H  2.766106  -3.067382  0.416175
H  4.101783  -1.944484  0.58393
C  3.680597  -2.486927  -1.47358
H  1.519707  2.086427  0.443032
H  3.758216  0.492735  0.456632
Mn  -0.565968  -2.449253  -0.380909
C  -2.097709  -3.452229  -0.599694
C  0.397399  -3.974893  -0.173238
O  -3.024283  -4.108785  -0.761273
O  0.981703  -4.95428  -0.025853
C  -0.259344  -2.415896  -2.171259
O  -0.040263  -2.392521  -3.300442
N  -0.872861  -2.342936  1.649431
C  -1.078891  -2.225392  2.795923
S  -1.374874  -2.057651  4.411822
H  2.835565  -2.787137  -2.096554
H  4.411022  -3.300046  -1.475947
H  4.150329  -1.607935  -1.922469
```

5.3 [MnCN(Et-Im-Py)$(CO)_3$] (3)

Theory: B3LYP/LANL08F (Mn), 6-311++G** (H, C, N, O)
Program: Orca 3.0.1
Atoms: 33
Charge: 0
Multiplicity: 1
Cartesian Geometry (Angstrom):
C 1.700738 1.053435 0.156066
C 2.815063 0.292563 0.124401
N 0.634564 0.165153 0.022888
C 1.067578 -1.134799 -0.085359
N 2.411663 -1.037937 -0.021508
C -0.739120 0.443197 -0.007760
C -1.252895 1.732990 0.110215
C -2.632643 1.887900 0.072424
C -3.441824 0.764070 -0.081350
C -2.839580 -0.479266 -0.191449
N -1.504962 -0.650346 -0.159831
C 3.377076 -2.145415 -0.128715
H -4.520540 0.843588 -0.113372
H -3.438762 -1.370979 -0.309682
H -3.069201 2.875372 0.163077
H -0.598898 2.585182 0.232875
H 2.912860 -3.029791 0.301247
H 4.224562 -1.882249 0.506119
C 3.836057 -2.392685 -1.566443
H 1.581629 2.117059 0.264538
H 3.852444 0.571614 0.204439
Mn -0.453838 -2.497444 -0.253211
C -1.995928 -3.481452 -0.338526
C 0.532809 -4.011140 -0.148541
O -2.961706 -4.100202 -0.414092
O 1.132649 -4.988540 -0.042345
C -0.328406 -2.429574 -2.078307
O -0.243646 -2.408610 -3.224608
C -0.520025 -2.495659 1.766238
N -0.548717 -2.504709 2.932662
H 3.002701 -2.698834 -2.202434
H 4.585843 -3.187945 -1.578052
H 4.290424 -1.494695 -1.993555

5.4 [MnCN(Et-BImid-Py)$(CO)_3$] (4)

Theory: B3LYP/LANL08F (Mn), 6-311++G** (H, C, N, O)
Program: Orca 3.0.1
Atoms: 39
Charge: 0
Multiplicity: 1
Cartesian Geometry (Angstrom):
C 0.899206 0.665896 -0.159851
C 0.948807 2.018439 0.182116
C 2.207479 2.603210 0.323212
C 3.384197 1.867034 0.138551
C 3.338005 0.516600 -0.202706
C 2.083494 -0.062308 -0.357690
N -0.138423 -0.268277 -0.359350
C 0.377472 -1.515708 -0.670322
N 1.714589 -1.380824 -0.658931
C -1.533018 -0.150045 -0.216477
C -2.200979 1.034634 0.085421
C -3.583200 0.996493 0.224797
C -4.262474 -0.204515 0.053608
C -3.524066 -1.329148 -0.272666
N -2.187249 -1.312660 -0.413784
C 2.694637 -2.459878 -0.874113
H -5.336782 -0.276240 0.159901
H -4.016054 -2.278452 -0.427685
H -4.119454 1.906942 0.464302
H -1.674561 1.964394 0.216389
H 0.068616 2.621056 0.341044
H 2.269468 3.653550 0.581952
H 4.345270 2.352103 0.262683
H 4.247836 -0.051752 -0.348282
H 3.553407 -2.236608 -0.239387
C 3.120991 -2.607461 -2.333914
H 2.251633 -3.376070 -0.490908
Mn -1.009553 -2.946802 -1.010967
C -1.147151 -2.429915 -2.766127
C 0.101583 -4.295780 -1.473526
O 0.777053 -5.176226 -1.780976
O -1.219538 -2.122112 -3.870719
O -3.368550 -4.763223 -1.185043
C -2.456863 -4.067297 -1.129125
C -0.843414 -3.447015 0.940905
N -0.755872 -3.745800 2.065389
H 3.860182 -3.408901 -2.414299
H 3.574585 -1.688075 -2.711863
H 2.271982 -2.863711 -2.970350