Supplementary Information

Steric tuning of OH-functionalised *N,N*-manganese(I) complexes for the transfer hydrogenation of carbonyl compounds

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Contents	Page

1. ^{1}H NMR and ^{13}C NMR spectra of starting materials and HL1a – HL1e

All NMR spectra (^{1}H, ^{13}C) of the organic compounds were recorded on a Bruker Avance III 500 MHz spectrometer with a 5 mm BBO probe, Bruker Avance III HD 400 MHz spectrometer with a 5 mm BBO probe and a Bruker Avance NEO 500 MHz spectrometer with either a 5 mm Prodigy BBO cryoprobe or a 5 mm BBFO probe. All deuterated solvents were purchased from Goss Scientific and Sigma-Aldrich.

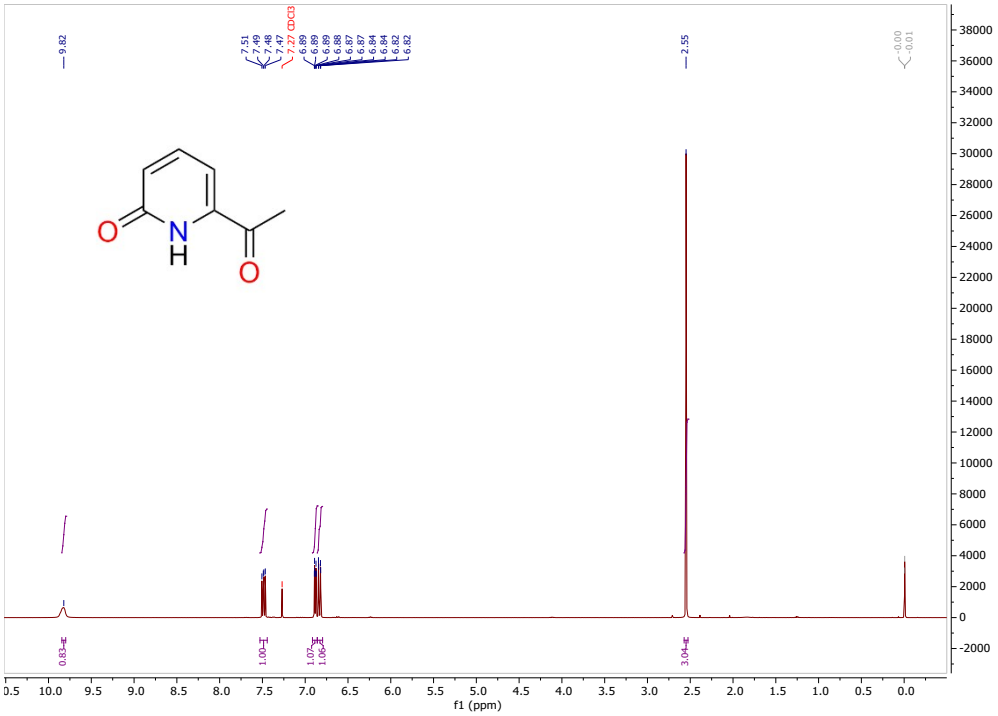


Figure S1 ^{1}H NMR spectrum of 6-acetyl pyrid-2-one; recorded in $CDCl_3$ at ambient temperature

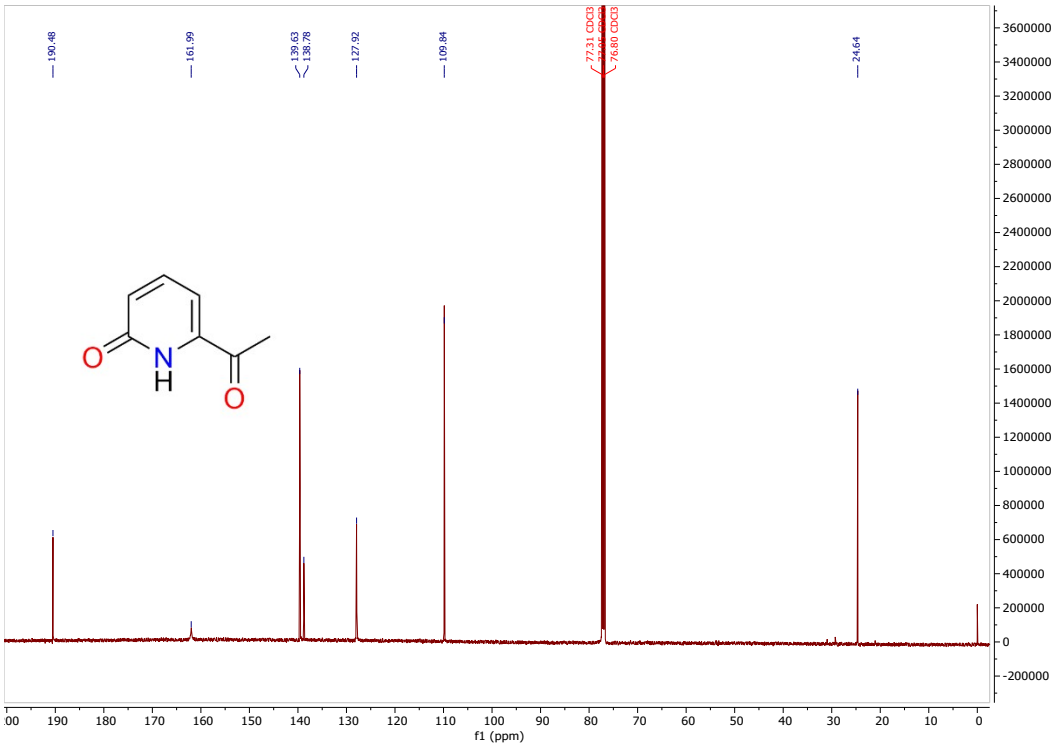


Figure S2 ^{13}C{^{1}H} NMR spectrum of 6-acetyl-pyrid-2-one; recorded in $CDCl_3$ at ambient temperature

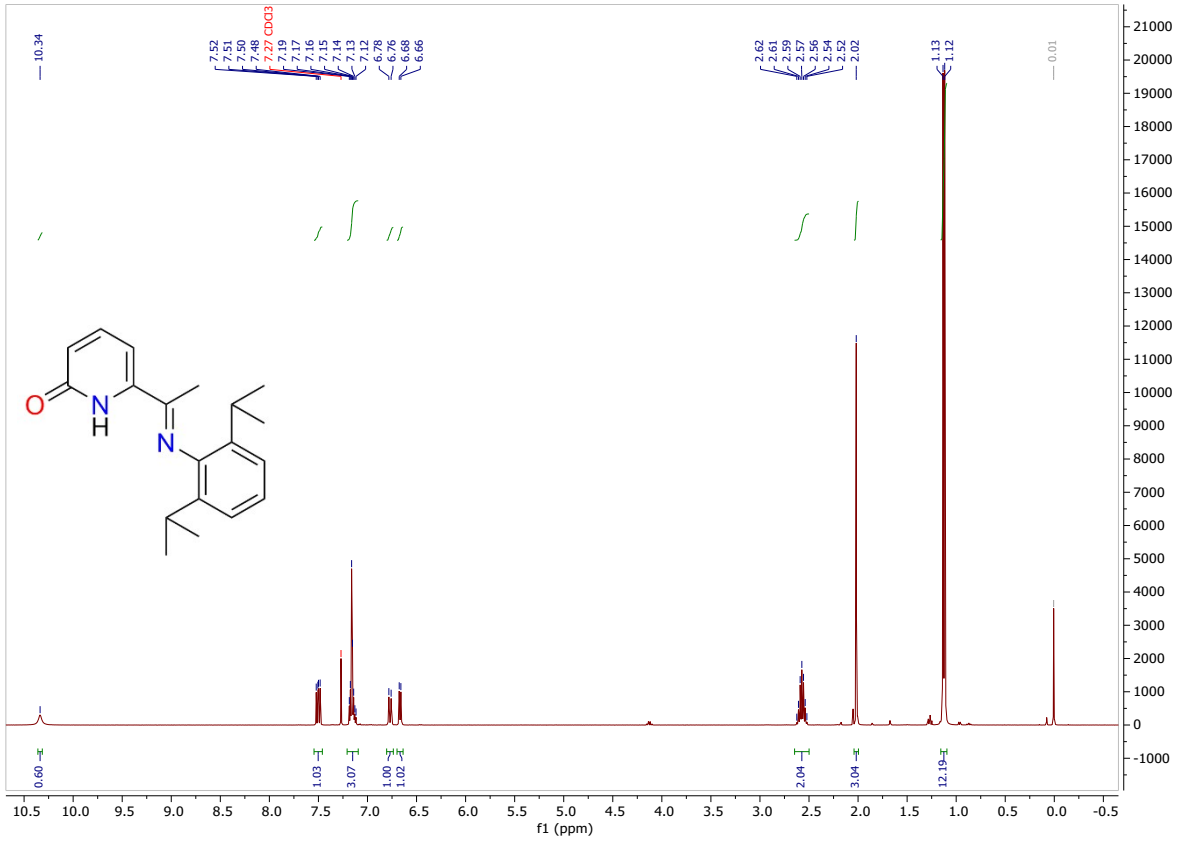


Figure S3 ^{1}H NMR spectrum of H**L1a**; recorded in $CDCl_3$ at ambient temperature

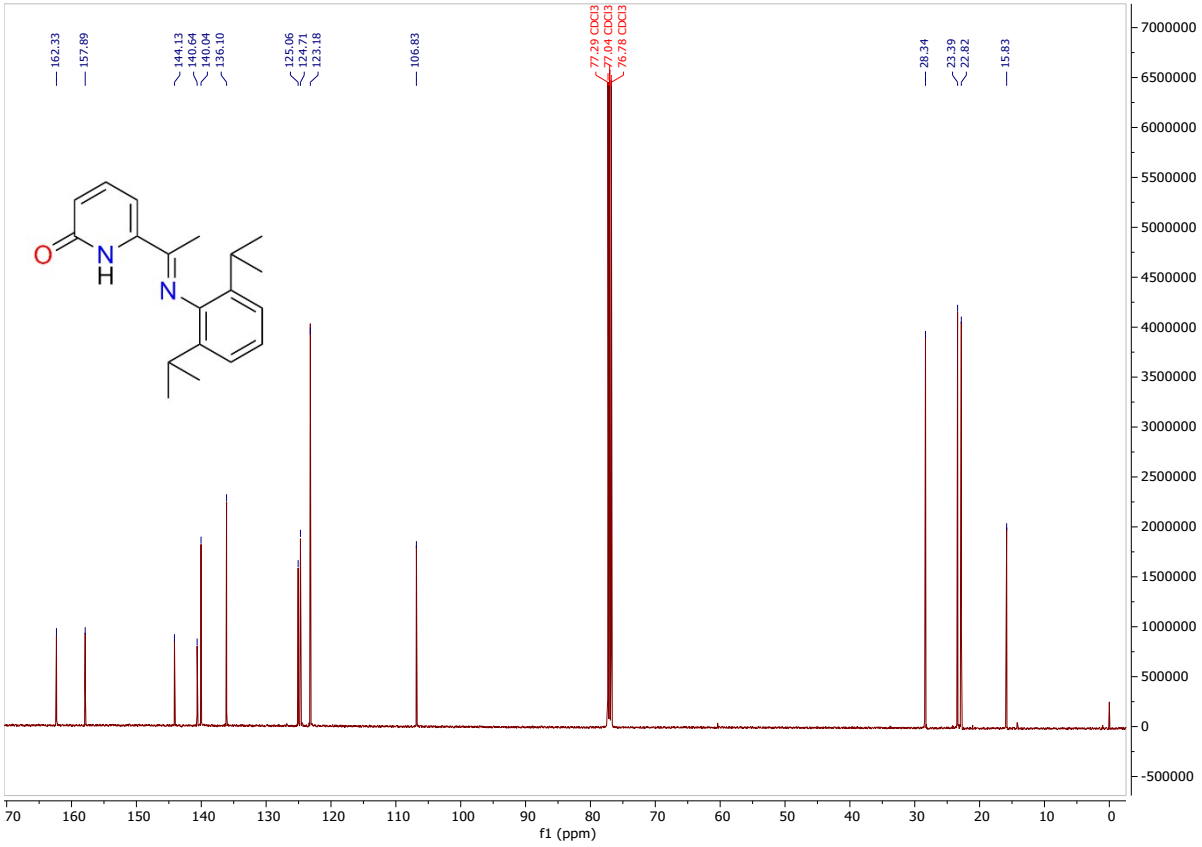


Figure S4 ^{13}C{^{1}H} NMR spectrum of H**L1a**; recorded in $CDCl_3$ at ambient temperature

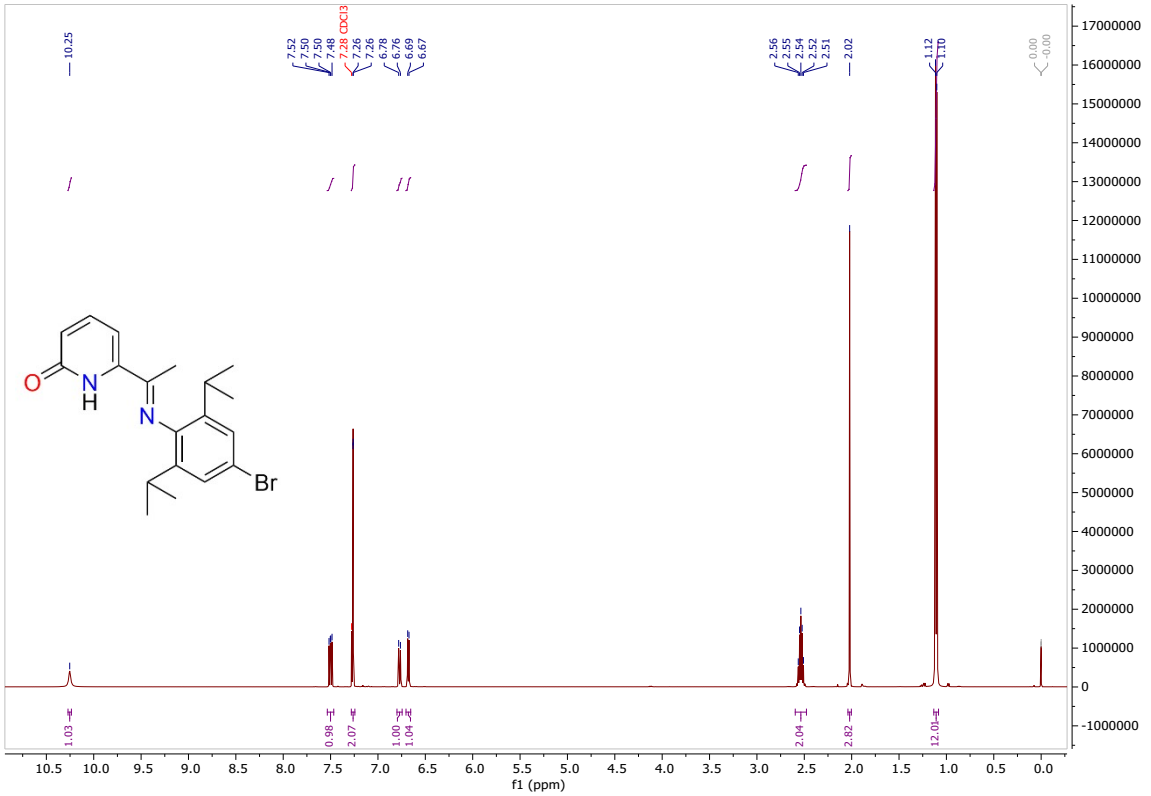


Figure S5 ^{1}H NMR spectrum of H**L1b**; recorded in $CDCl_3$ at ambient temperature

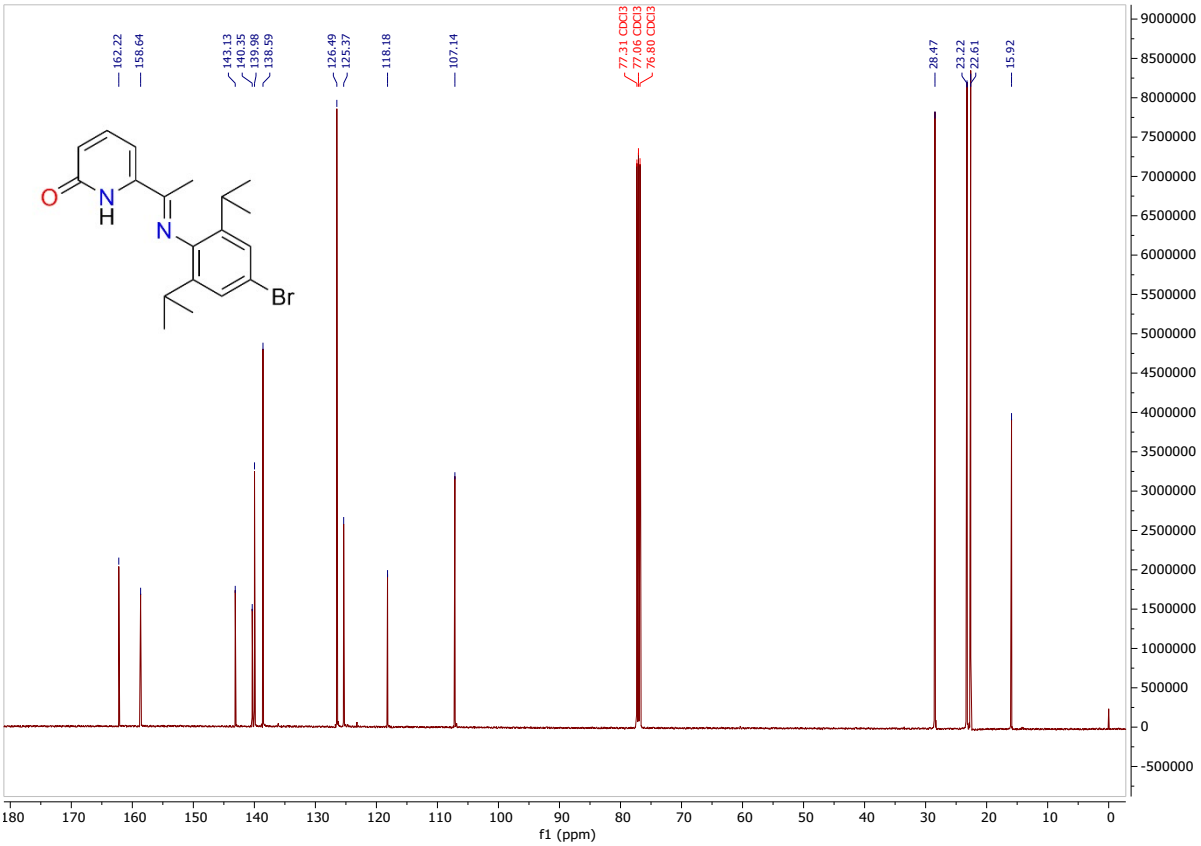


Figure S6 ^{13}C{^{1}H} NMR spectrum of H**L1b**; recorded in $CDCl_3$ at ambient temperature

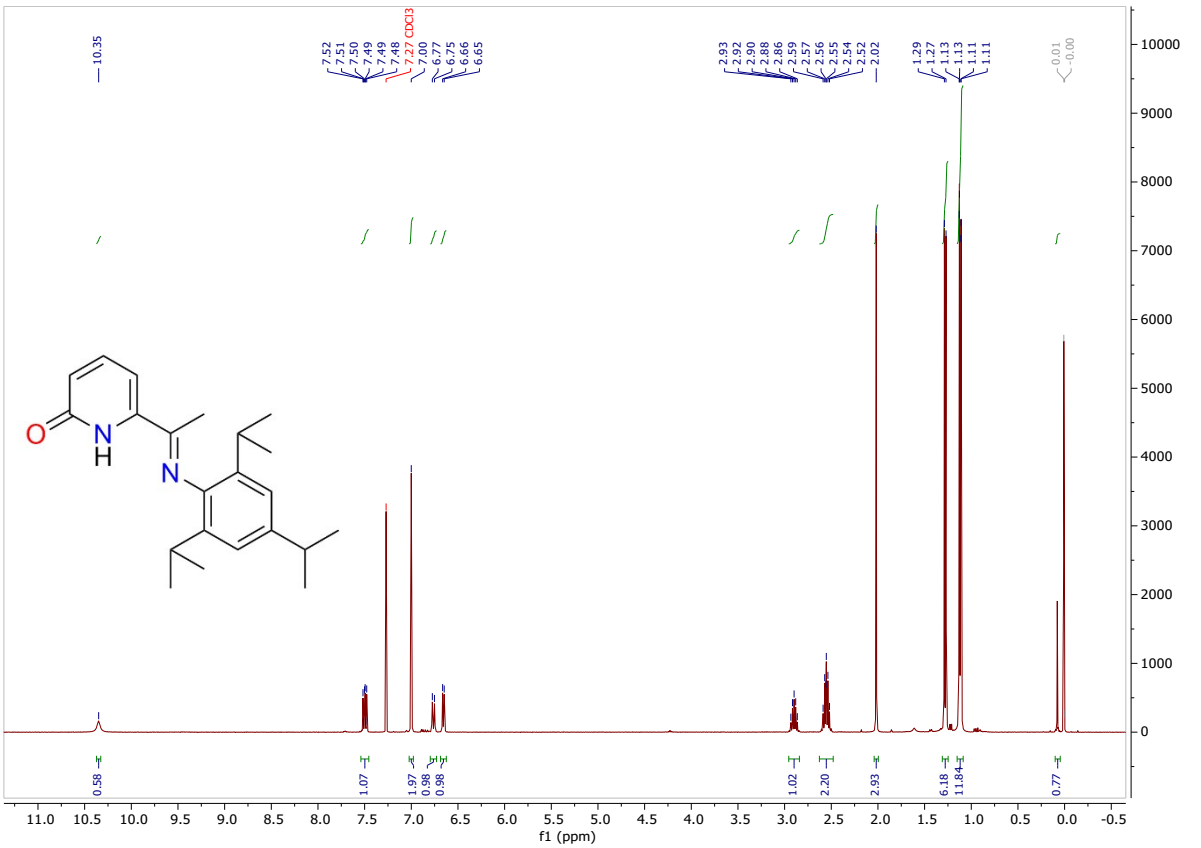


Figure S7 ^{1}H NMR spectrum of H**L1c**; recorded in $CDCl_3$ at ambient temperature

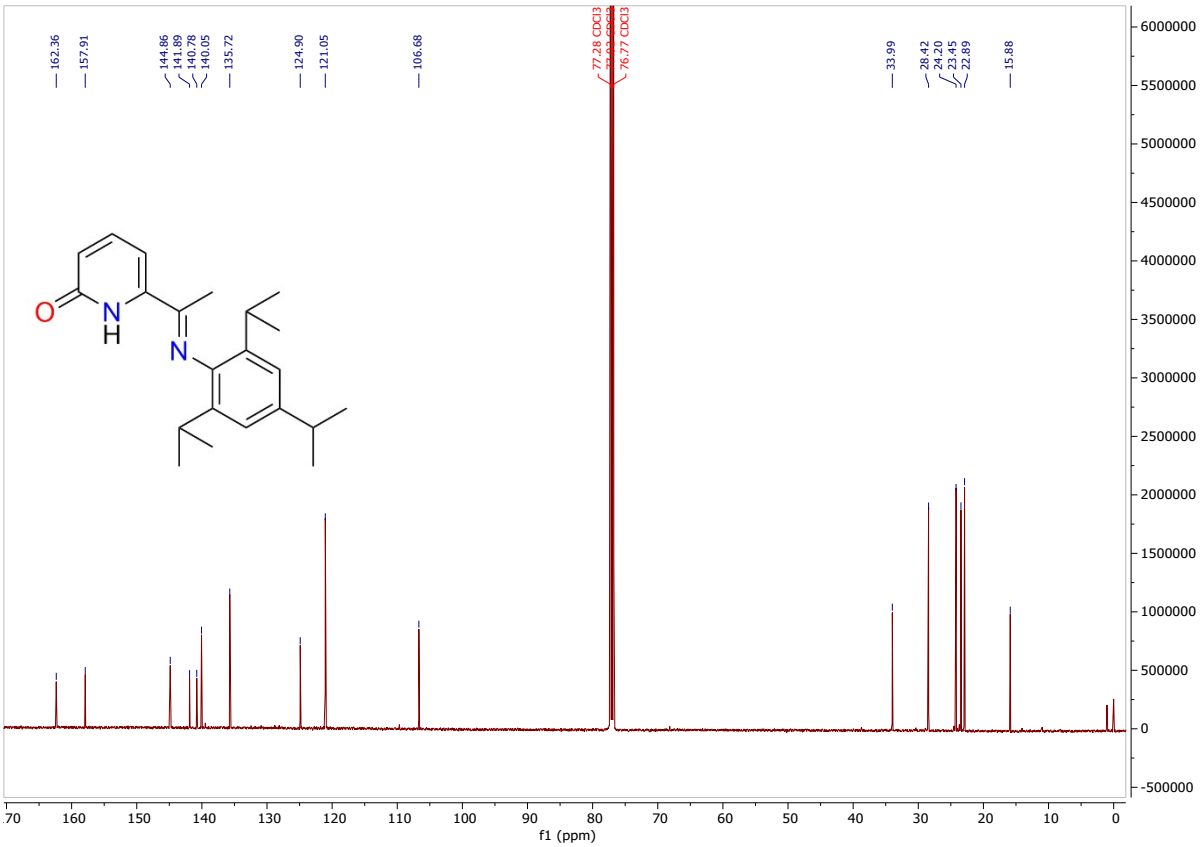


Figure S8 $^{13}C\{^{1}H\}$ NMR spectrum of H**L1c**; recorded in $CDCl_3$ at ambient temperature

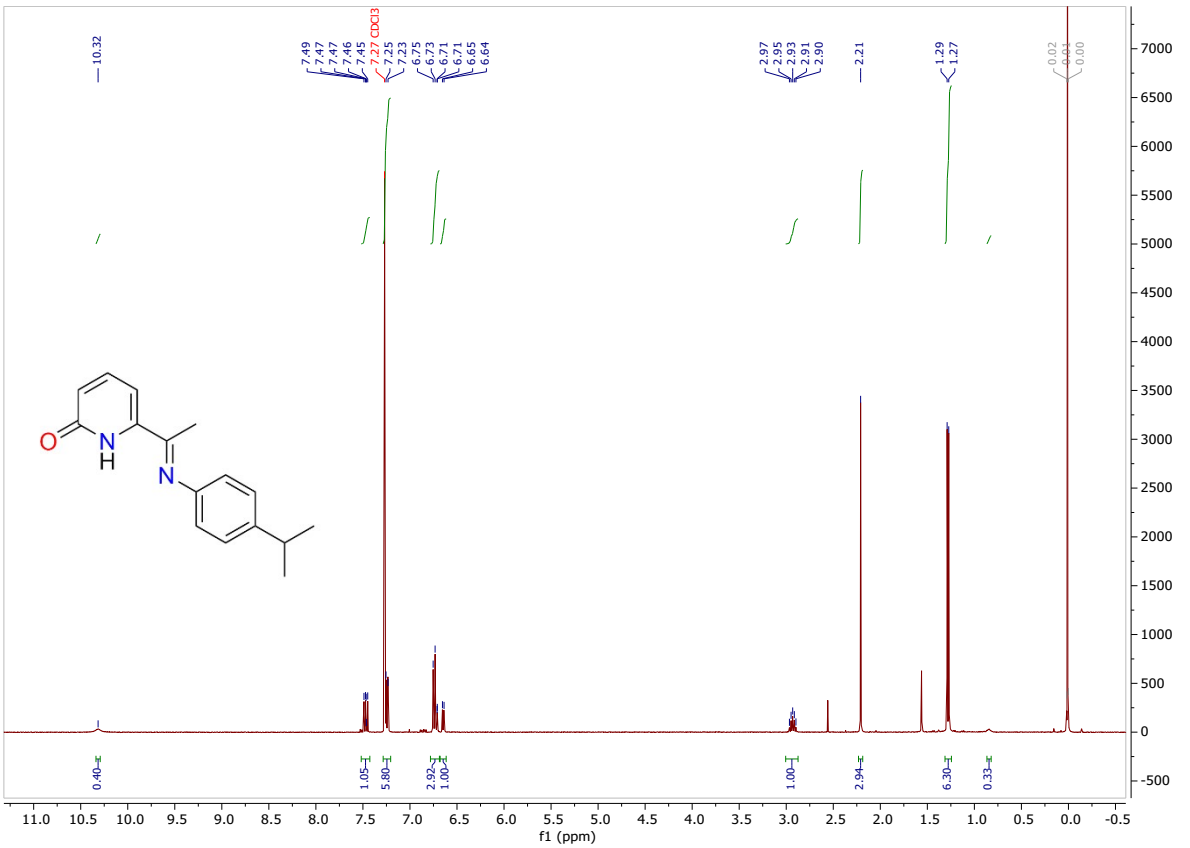


Figure S9 ^{1}H NMR spectrum of H**L1d**; recorded in $CDCl_3$ at ambient temperature

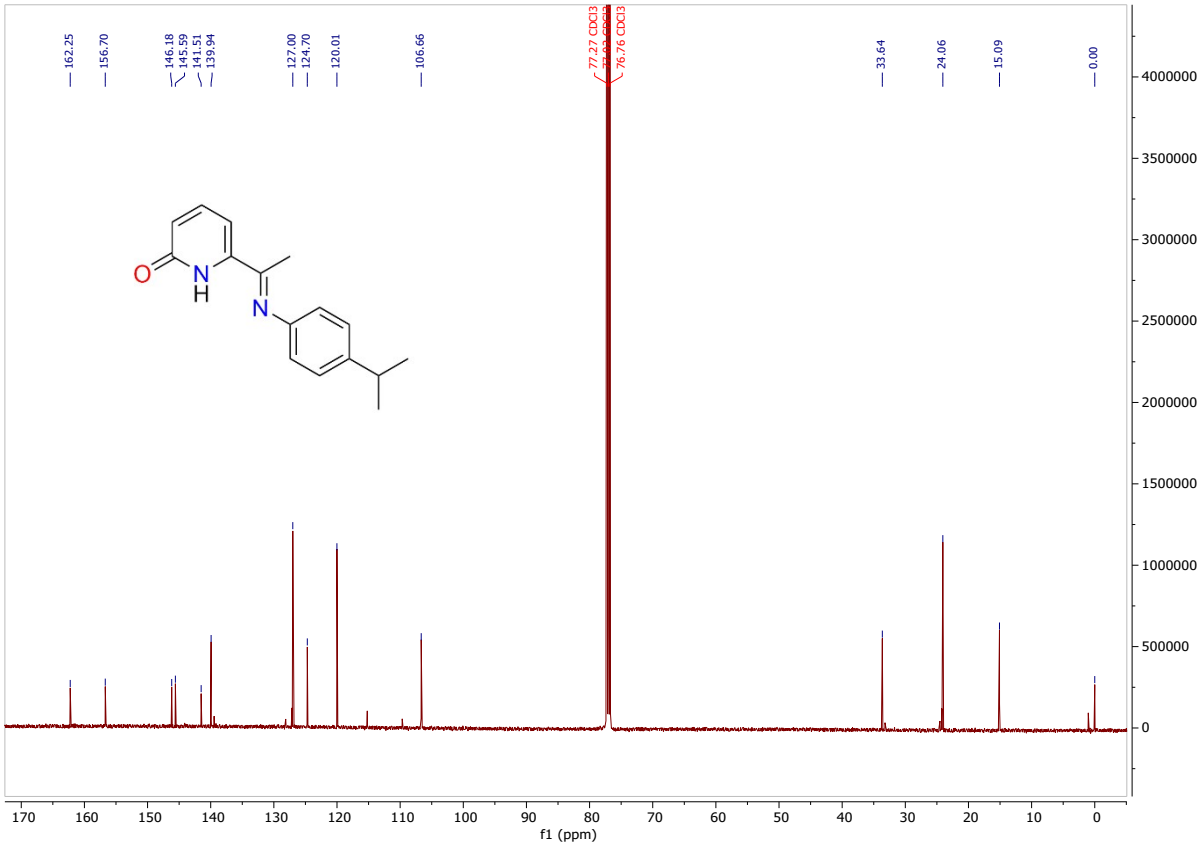


Figure S10 ^{13}C{^{1}H} NMR spectrum of H**L1d**; recorded in $CDCl_3$ at ambient temperature

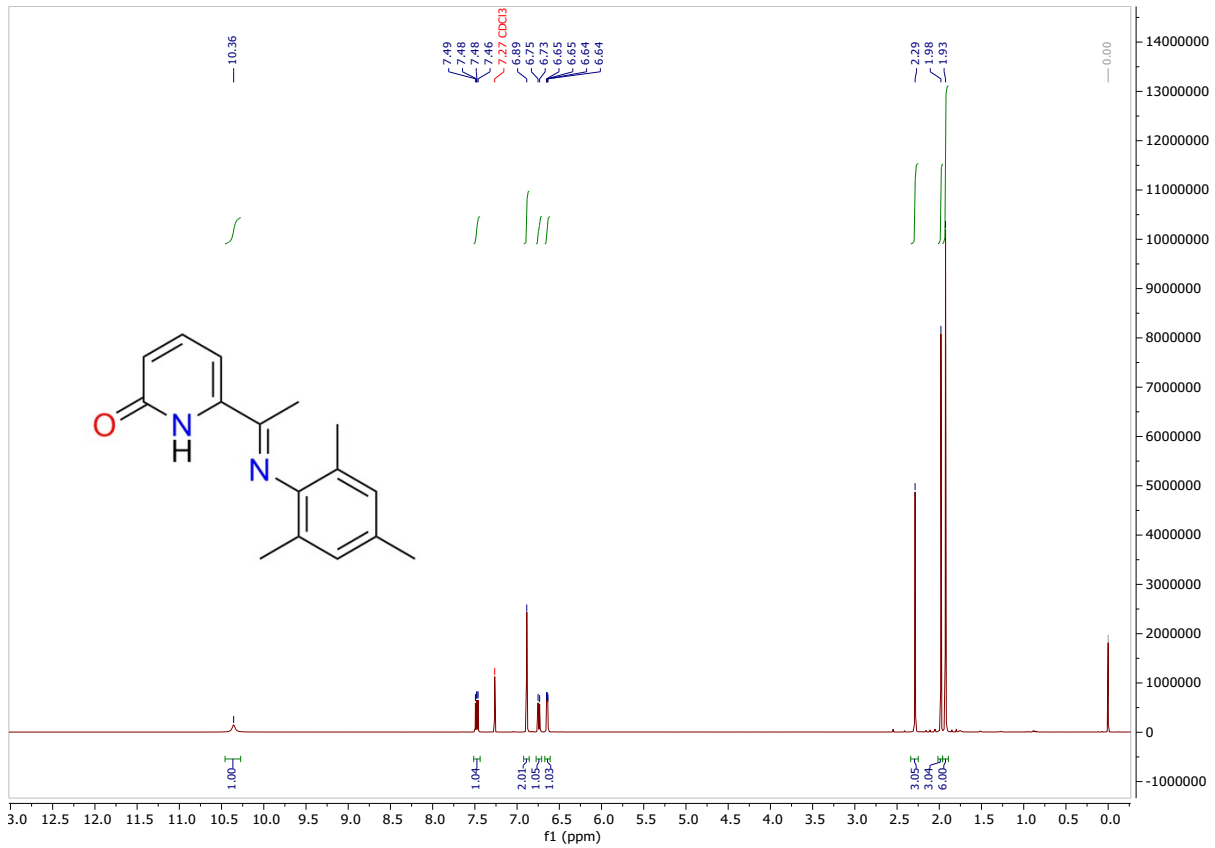


Figure S11 ^{1}H NMR spectrum of H**L1e**; recorded in $CDCl_3$ at ambient temperature

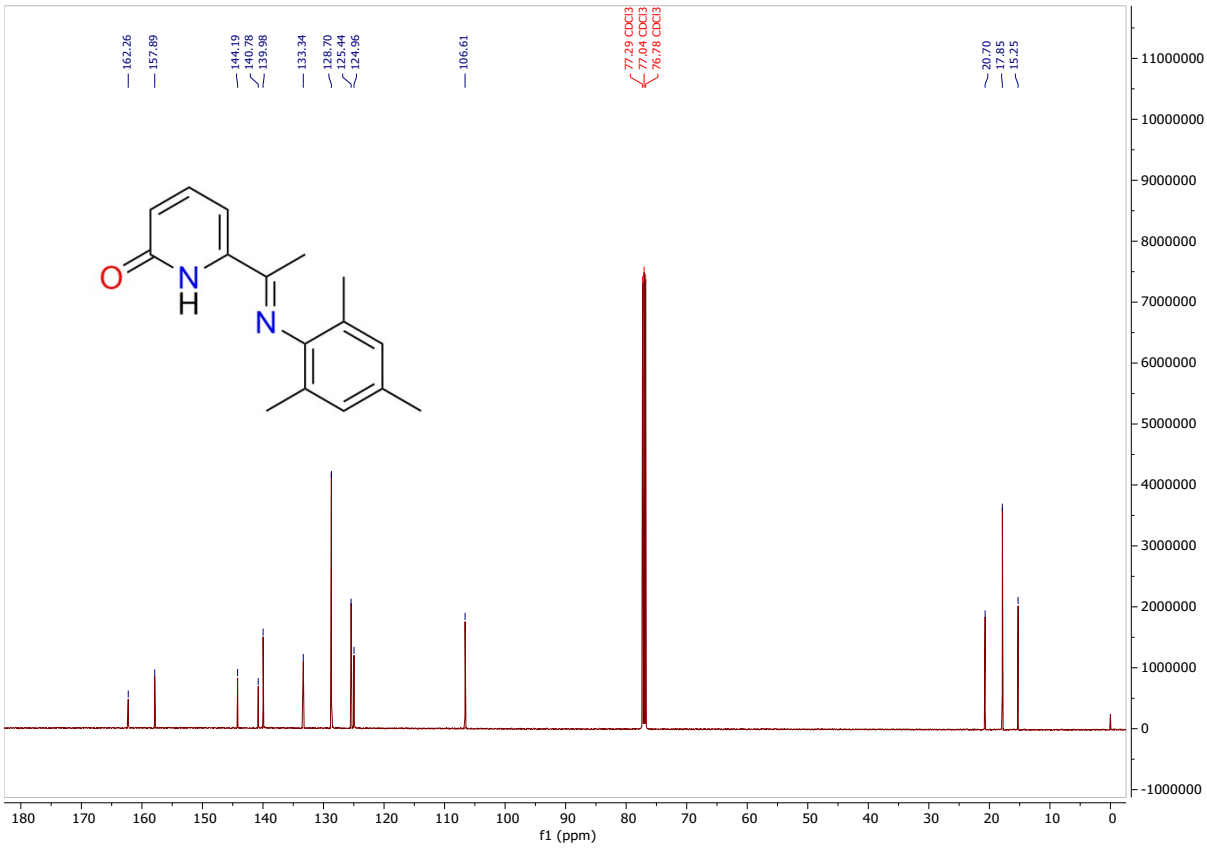


Figure S12 $^{13}C\{^{1}H\}$ NMR spectrum of H**L1e**; recorded in $CDCl_3$ at ambient temperature

2. ^{1}H NMR and ^{13}C NMR spectra of complexes Mn1a – Mn1e and Mn2

All NMR spectra (^{1}H, ^{13}C) of the metal complexes were recorded on a Bruker Avance III 500 MHz spectrometer with a 5 mm BBO probe, Bruker Avance III HD 400 MHz spectrometer with a 5 mm BBO probe and a Bruker Avance NEO 500 MHz spectrometer with either a 5 mm Prodigy BBO cryoprobe or a 5 mm BBFO probe. All deuterated solvents were purchased from Goss Scientific and Sigma-Aldrich.

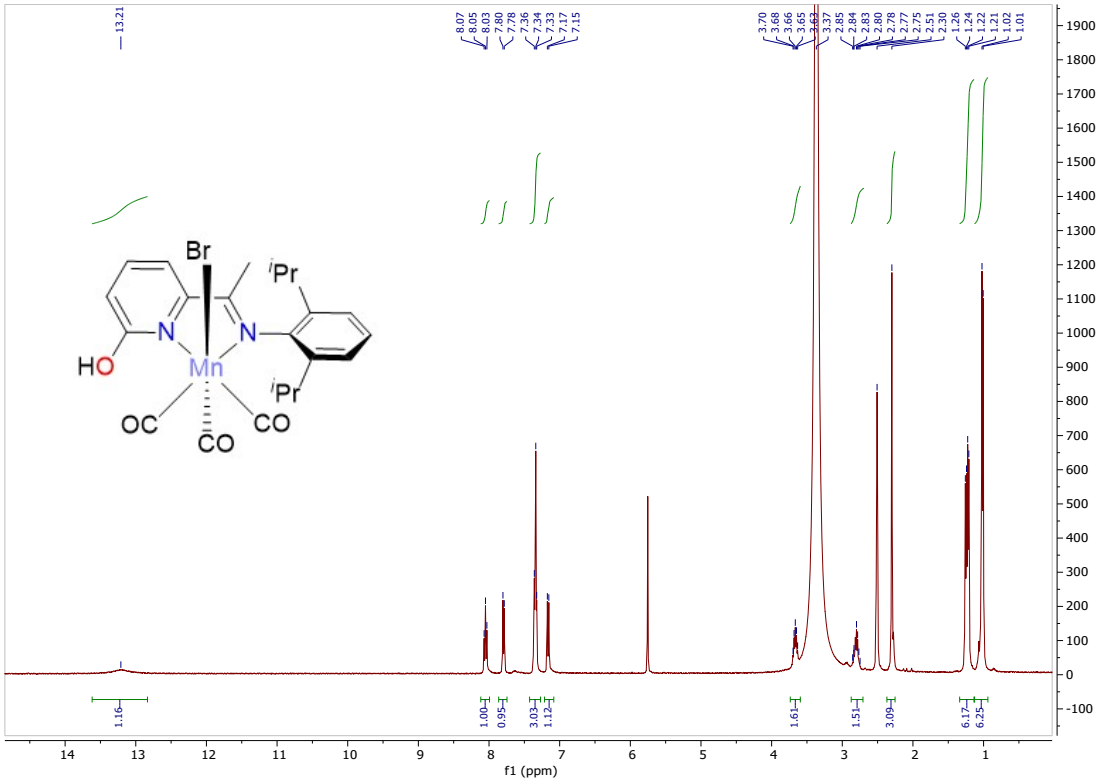


Figure S13 ^{1}H NMR spectrum of **Mn1a**; recorded in DMSO-d_6 at ambient temperature

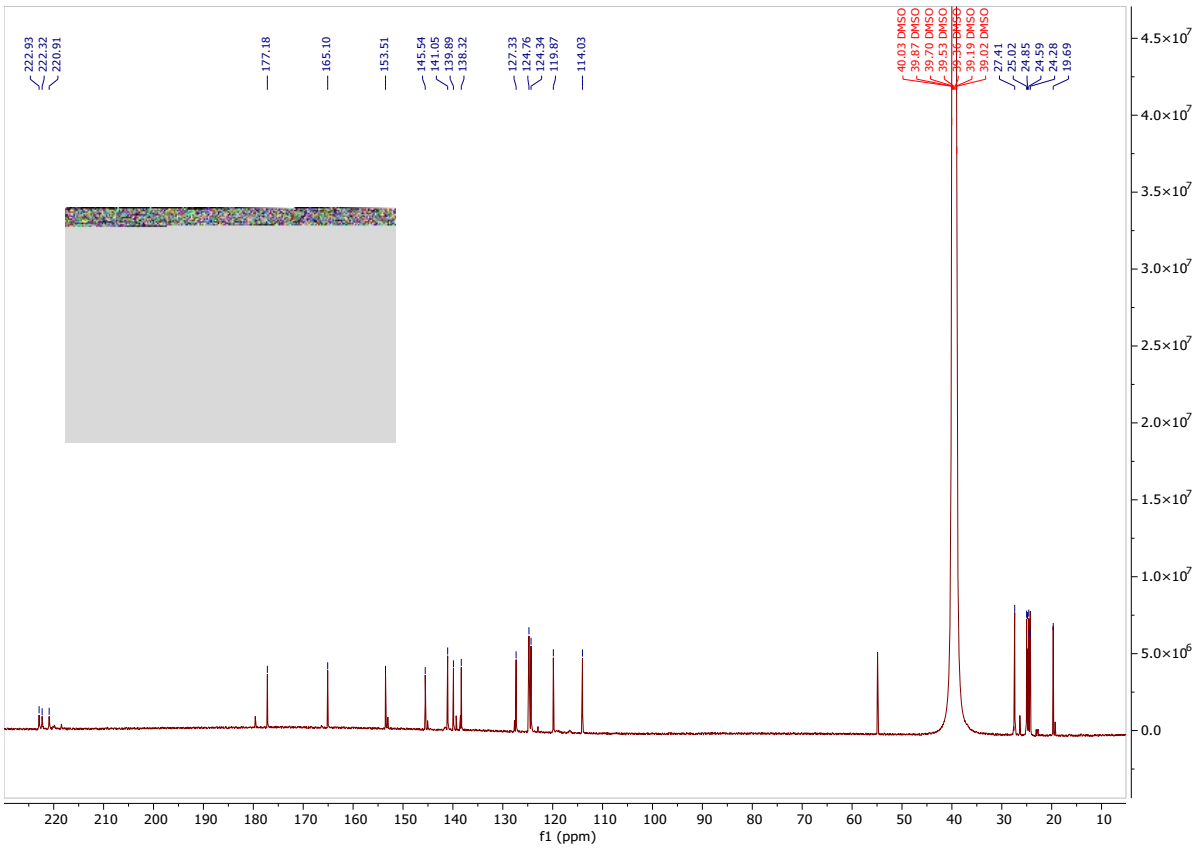


Figure S14 $^{13}C\{^{1}H\}$ NMR spectrum of **Mn1a**; recorded in DMSO-d_6 at ambient temperature

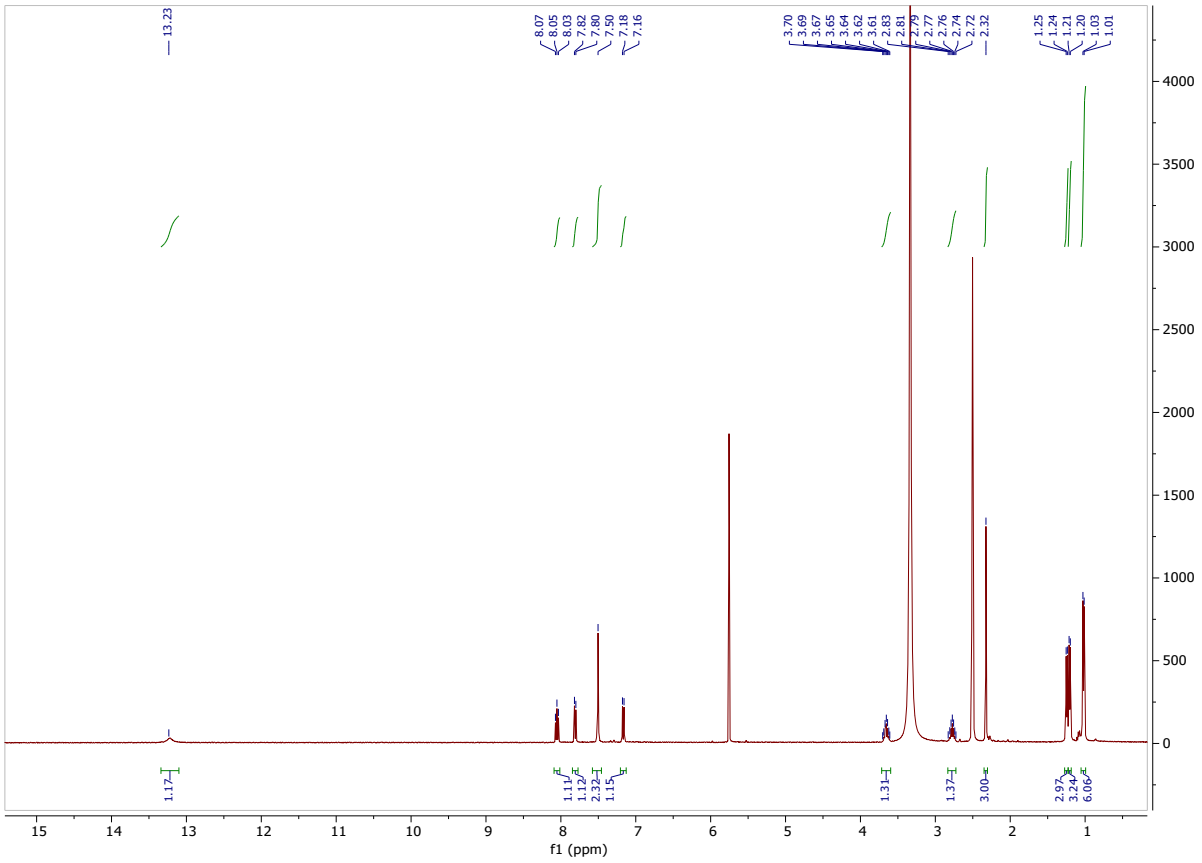


Figure S15 ^{1}H NMR spectrum of **Mn1b**; recorded in DMSO-d_6 at ambient temperature

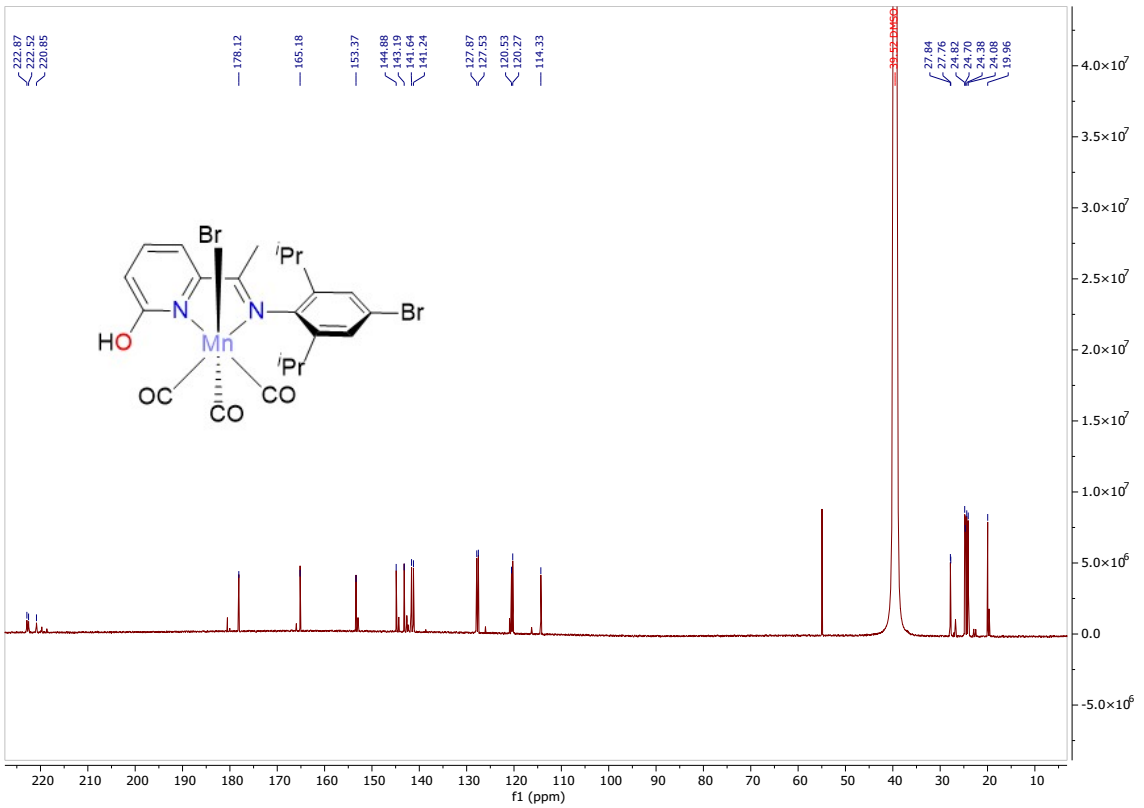


Figure S16 $^{13}C\{^{1}H\}$ NMR spectrum of **Mn1b**; recorded in DMSO-d_6 at ambient temperature

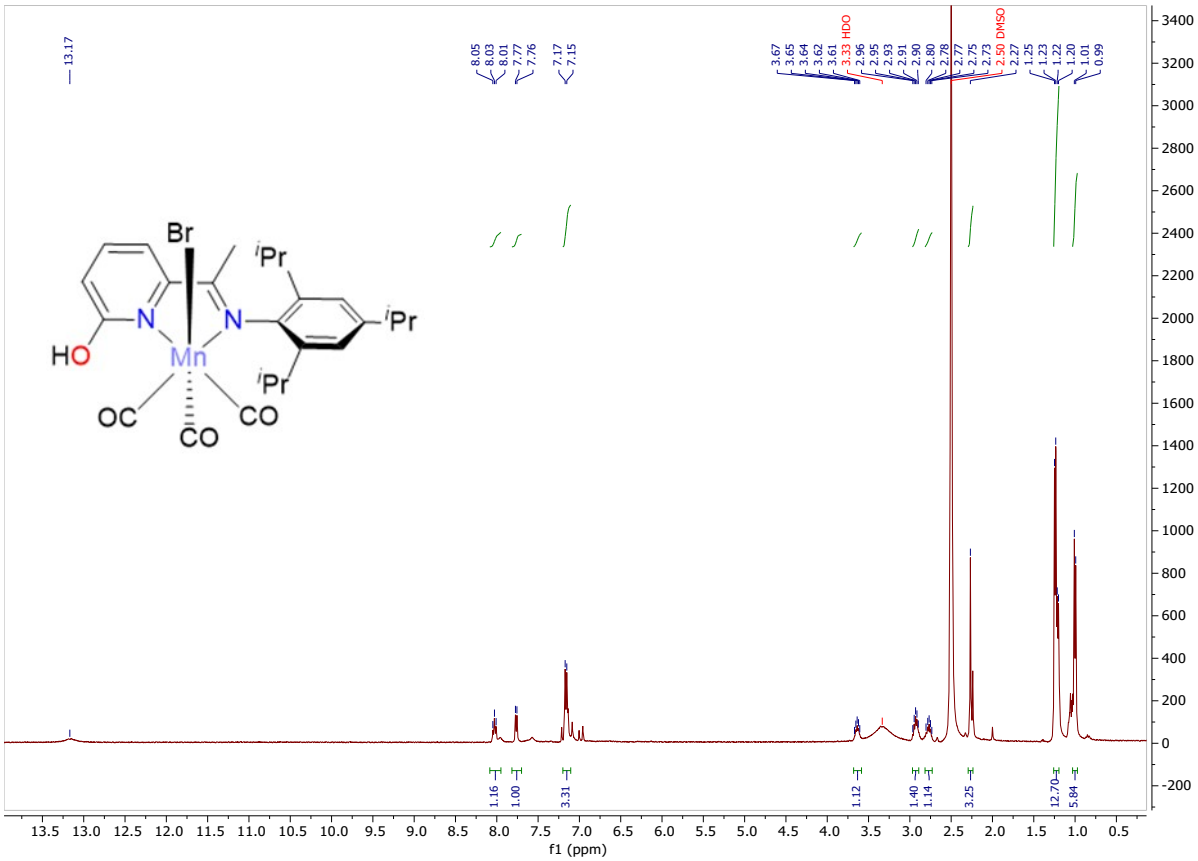


Figure S17 ^{1}H NMR spectrum of **Mn1c**; recorded in DMSO-d_6 at ambient temperature

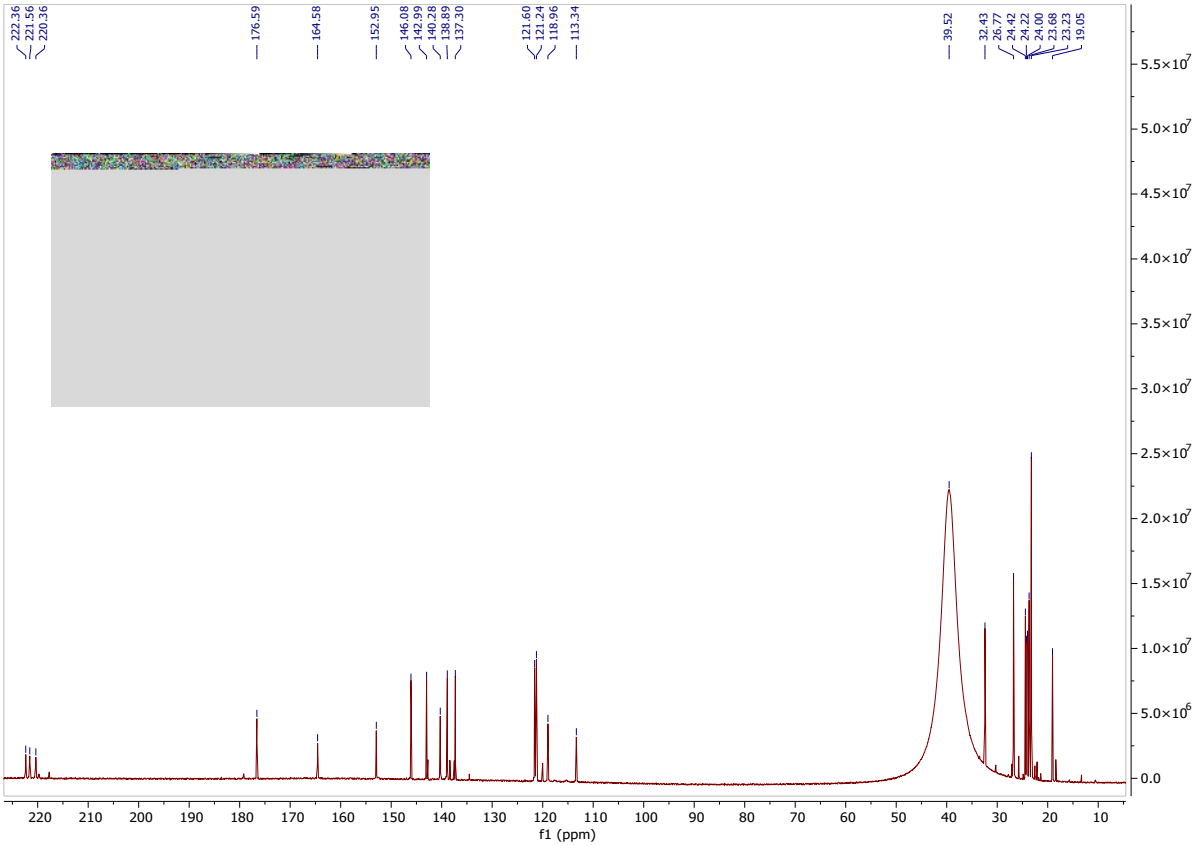


Figure S18 $^{13}C\{^{1}H\}$ NMR spectrum of **Mn1c**; recorded in DMSO-d_6 at ambient temperature

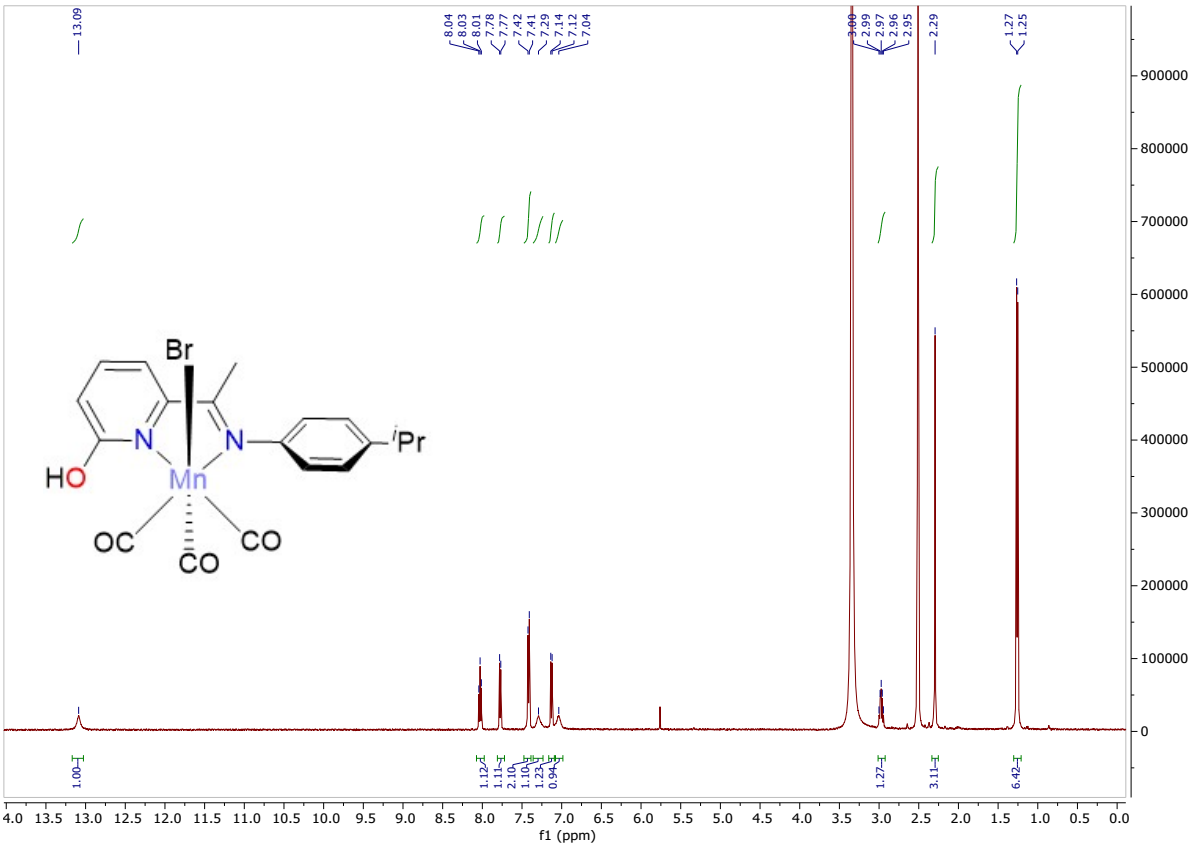


Figure S19 ^{1}H NMR spectrum of **Mn1d**; recorded in DMSO-d_6 at ambient temperature

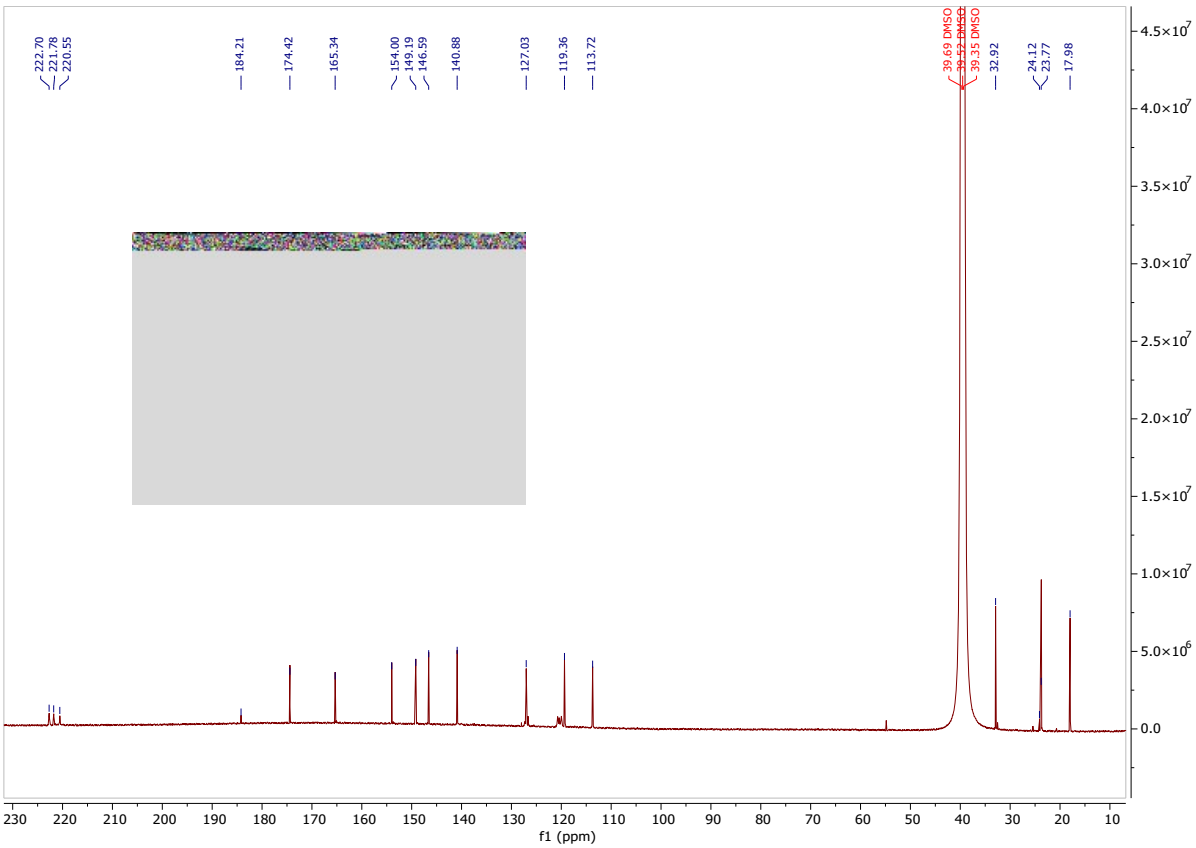


Figure S20 $^{13}C\{^{1}H\}$ NMR spectrum of **Mn1d**; recorded in DMSO-d_6 at ambient temperature

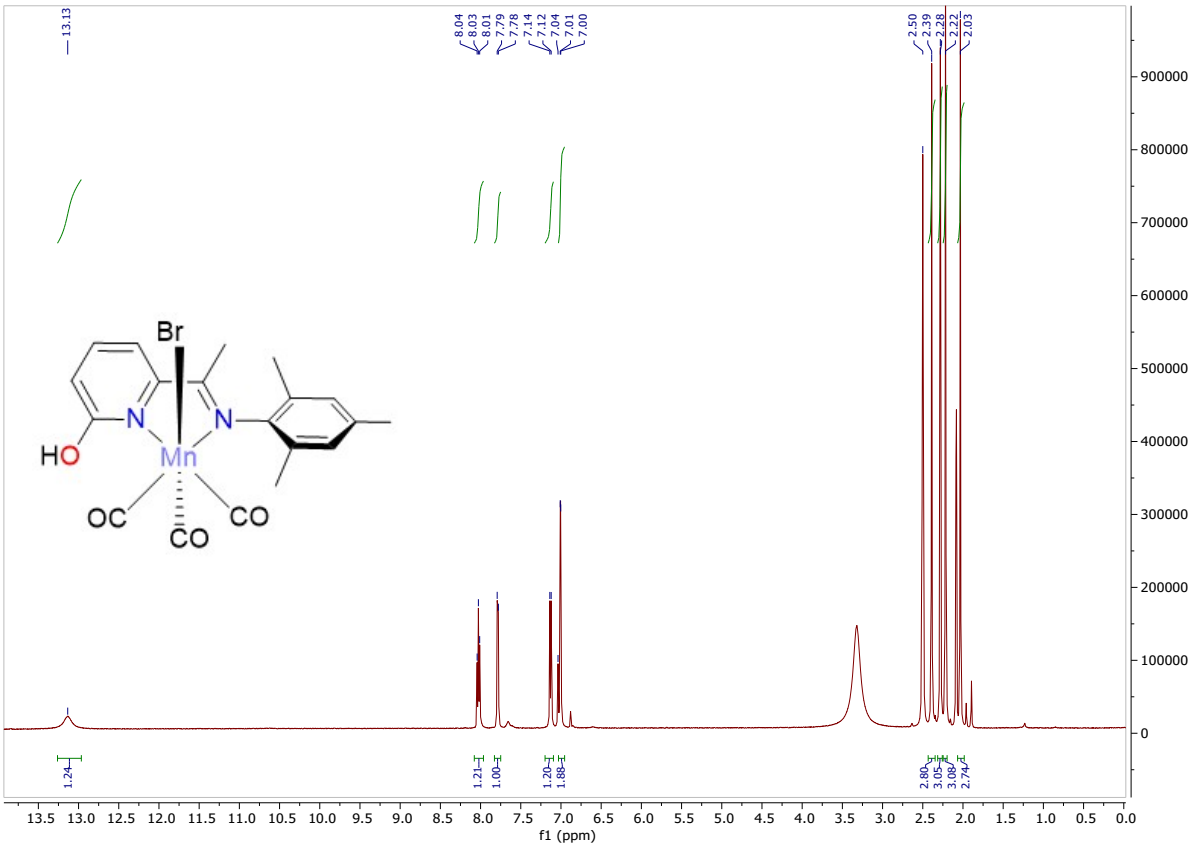


Figure S21 ^{1}H NMR spectrum of **Mn1e**; recorded in DMSO-d_6 at ambient temperature

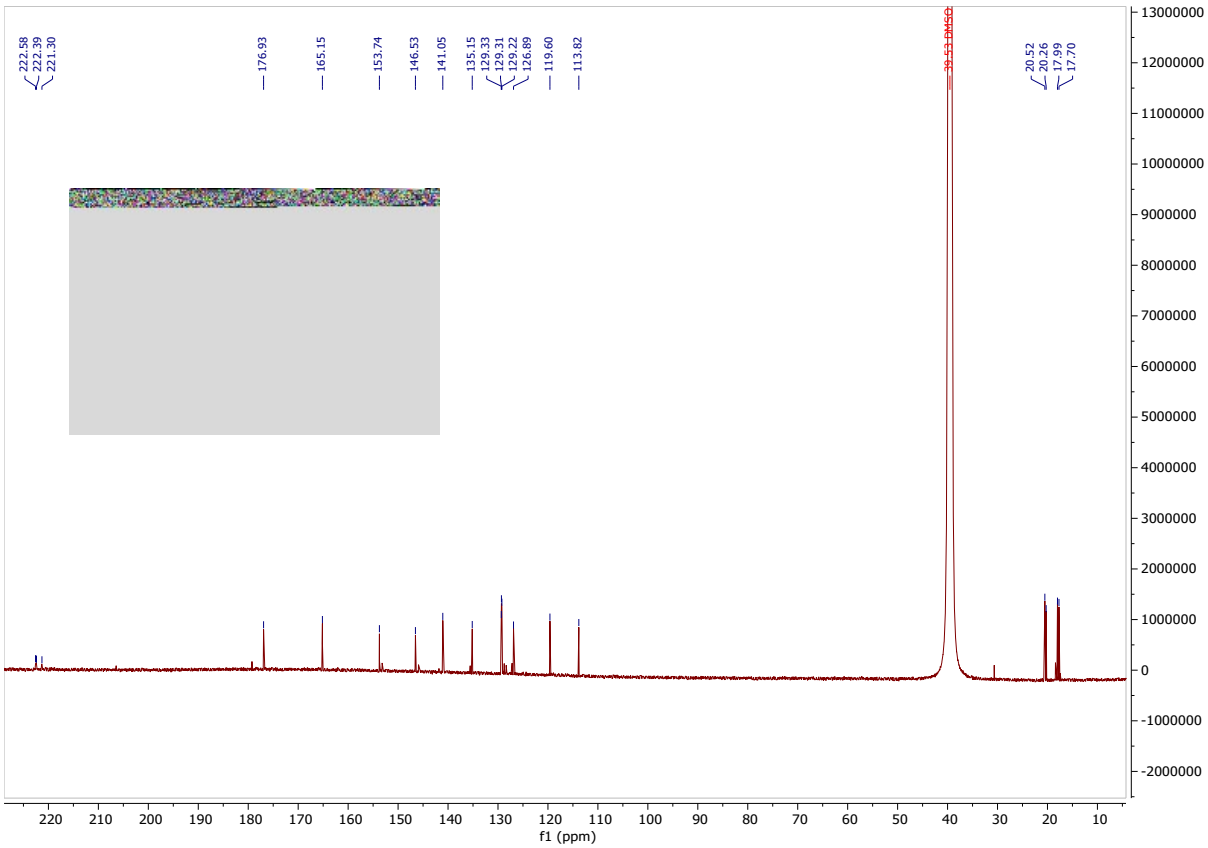


Figure S22 $^{13}C\{^{1}H\}$ NMR spectrum of **Mn1e**; recorded in DMSO-d_6 at ambient temperature

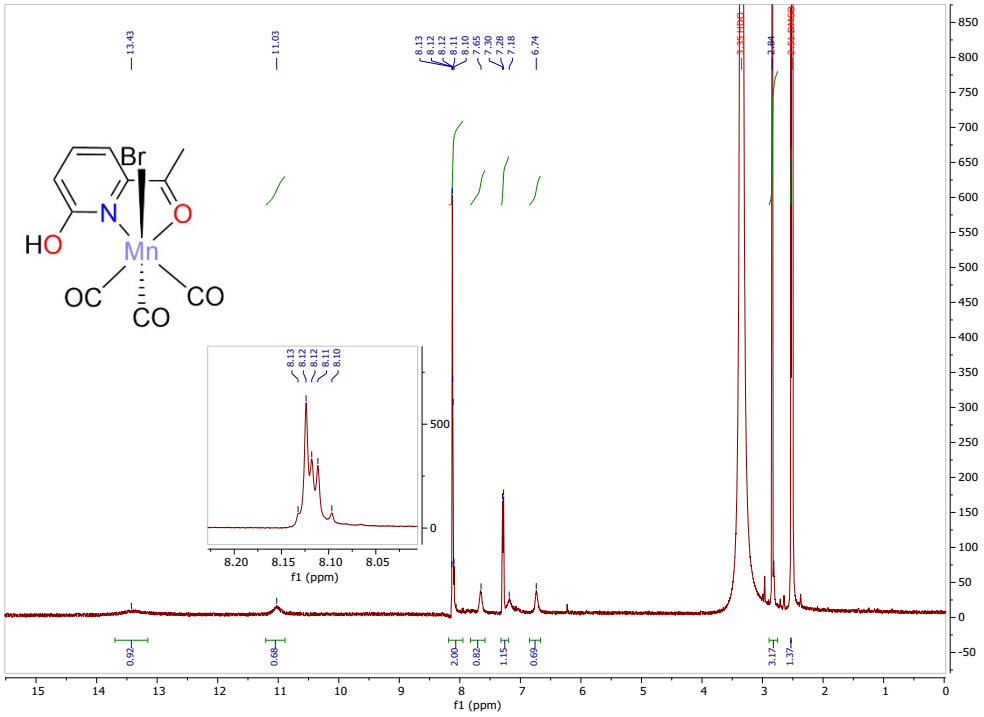


Figure S23 ^{1}H NMR spectrum of **Mn2**; recorded in DMSO-d_6 at ambient temperature. Note: the broad peaks (*ca.* 40%) δ 11.03 7.65, 7.18, 6.74 and 2.52 ppm have been tentatively assigned to [[2-OH-6-(CMe=O)C_5H_3N]Mn(DMSO)$(CO)_3$](Br) (**Mn2**(DMSO)). For related adduct formation see reference 1.[1]

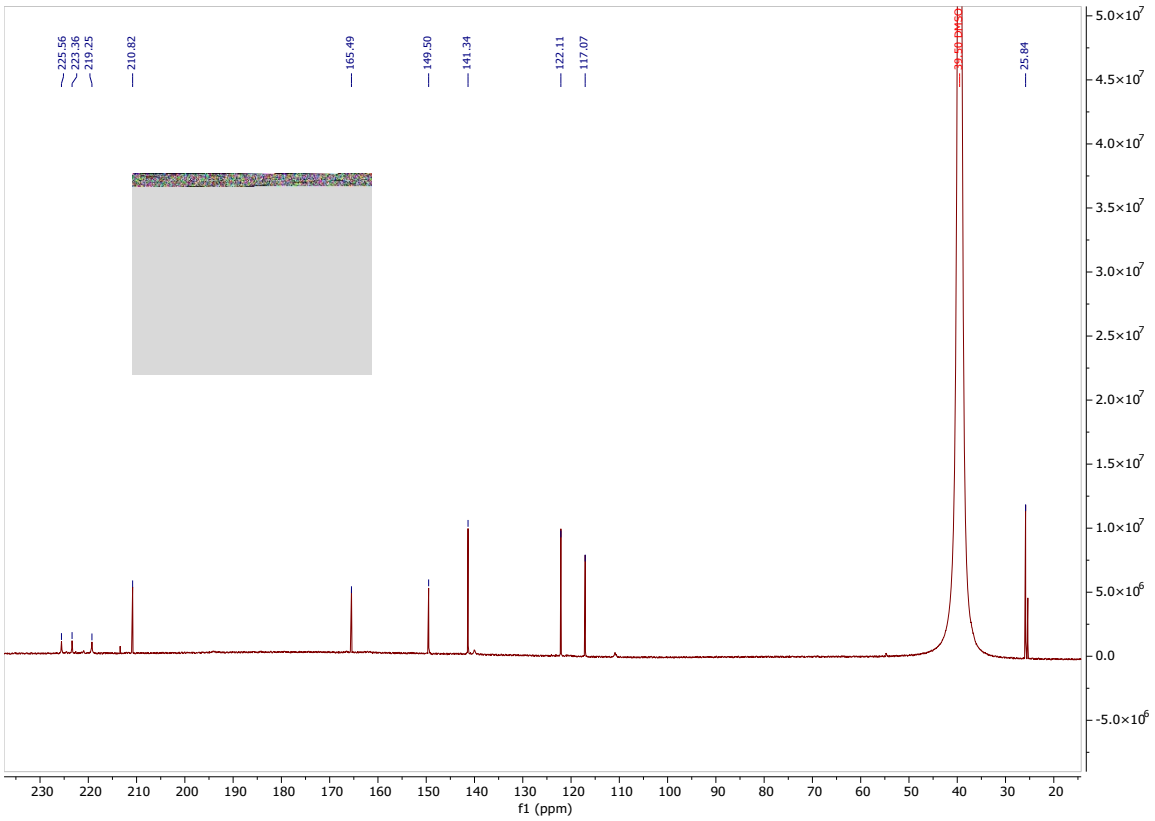


Figure S24 $^{13}C\{^{1}H\}$ NMR spectrum of **Mn2**; recorded in DMSO-d_6 at ambient temperature. The absence of peaks relating to (**Mn2**(DMSO)) is likely due to broadening as noted in the ^{1}H NMR spectrum.

3. IR spectra of starting materials and HL1a – HL1e

All infra-red spectra were obtained using a Bruker ALPHA II compact FT-IR spectrometer using solid samples.

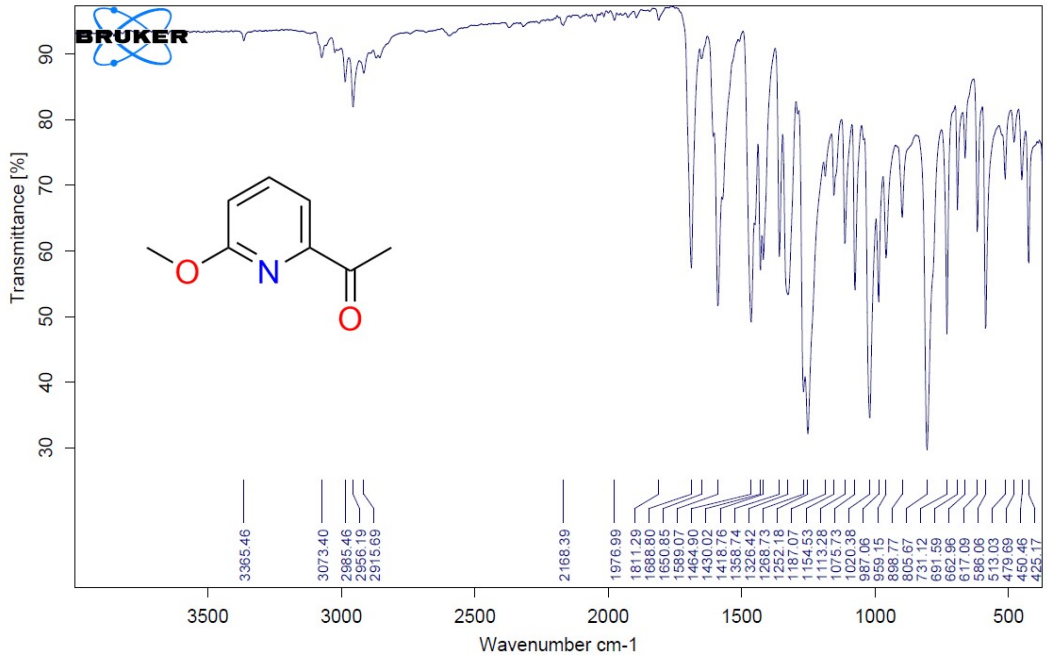


Figure S25 FT-IR spectrum of 6-acetyl-2-methoxy-pyridine

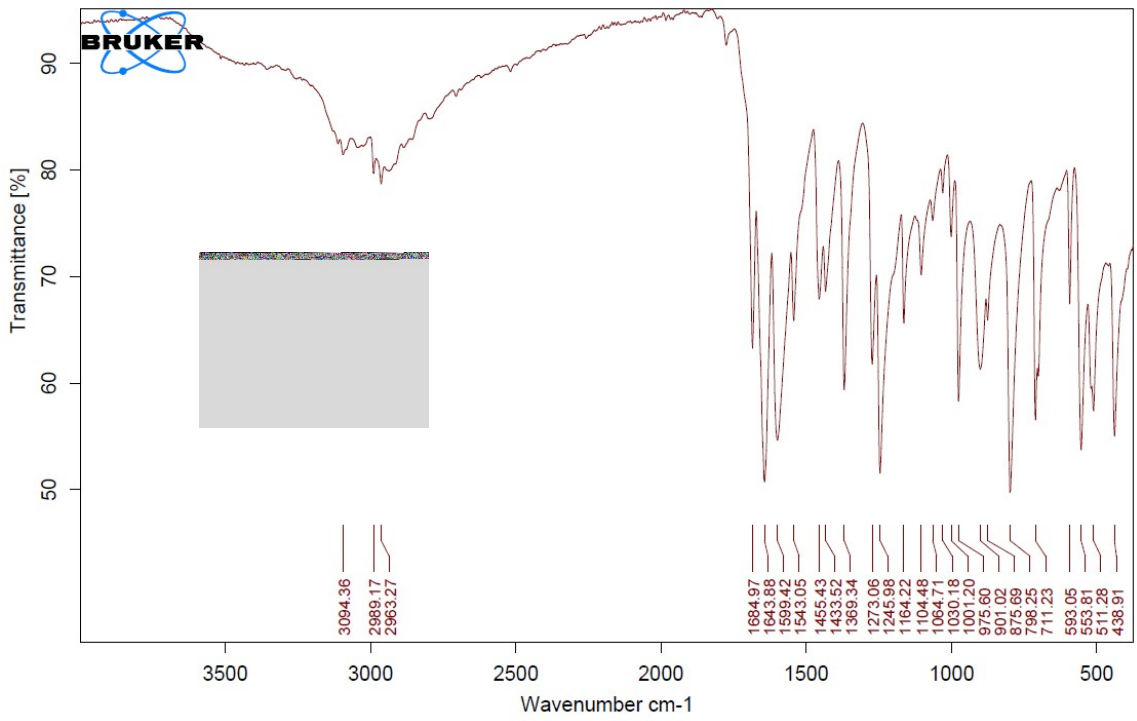


Figure S26 FT-IR spectrum of 6-acetyl-pyridin-2-one

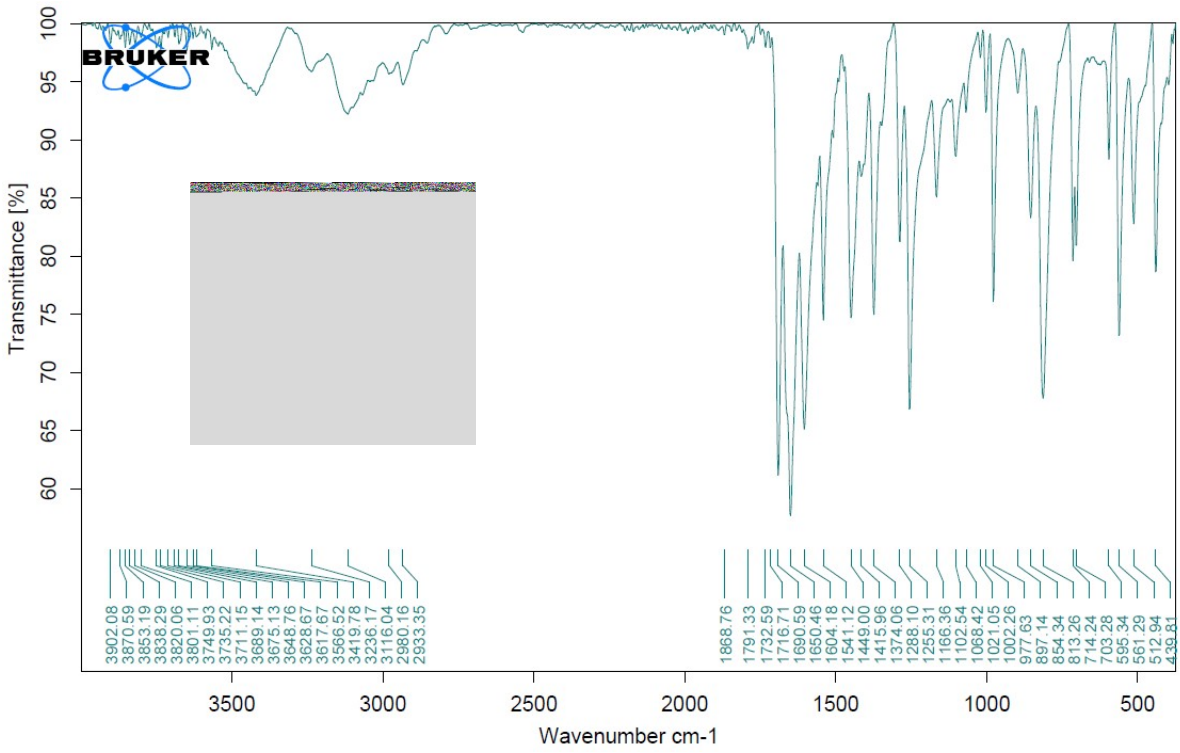


Figure S27 FT-IR spectrum of H**L1a**

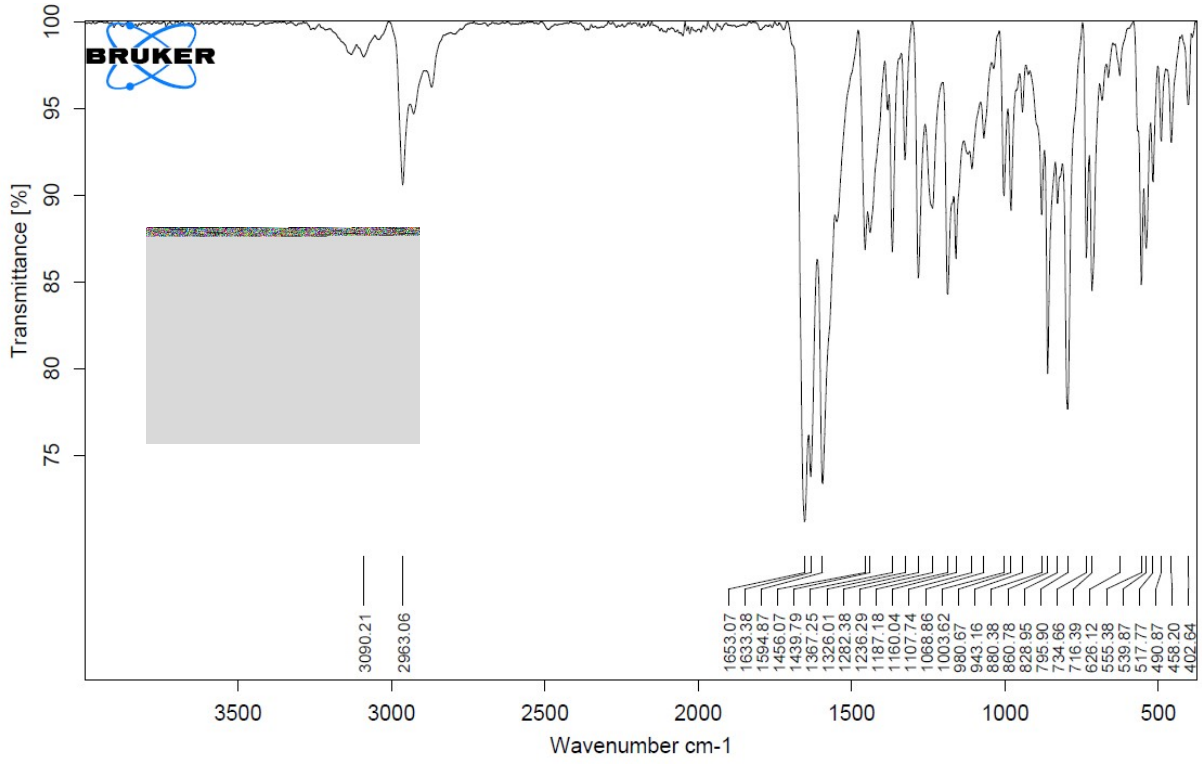


Figure S28 FT-IR spectrum of H**L1b**

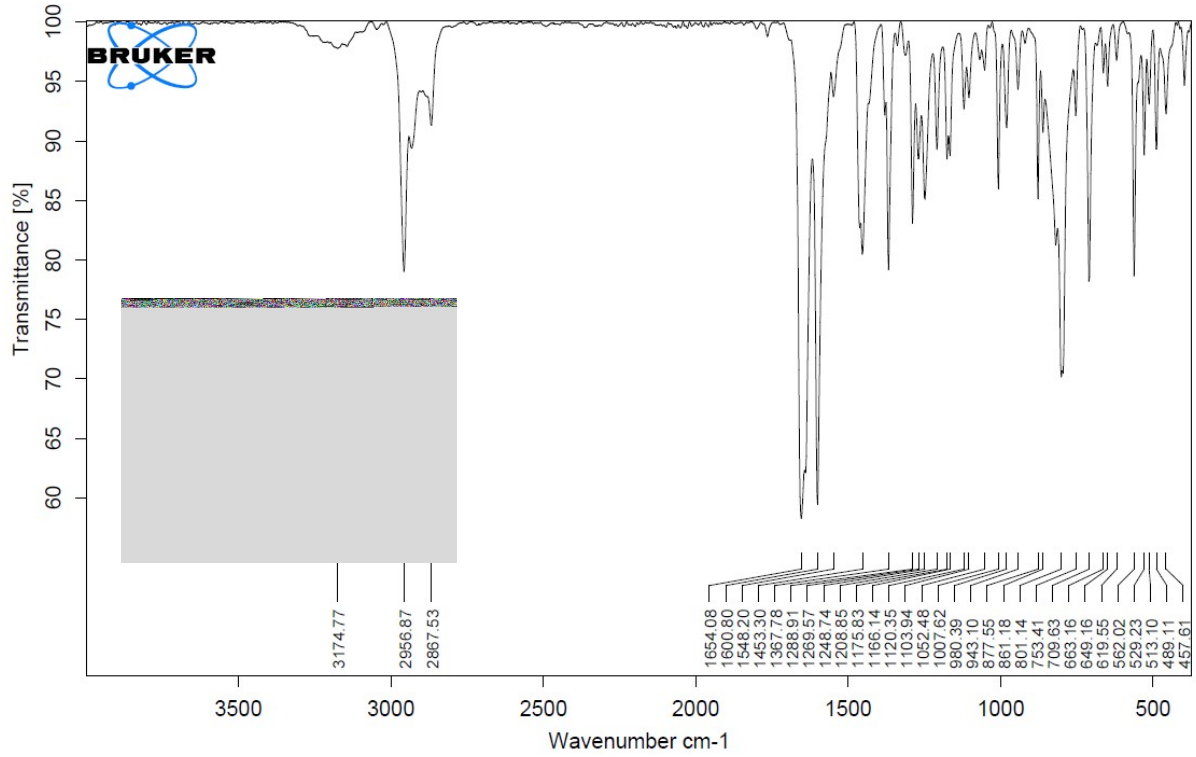


Figure S29 FT-IR spectrum of H**L1c**

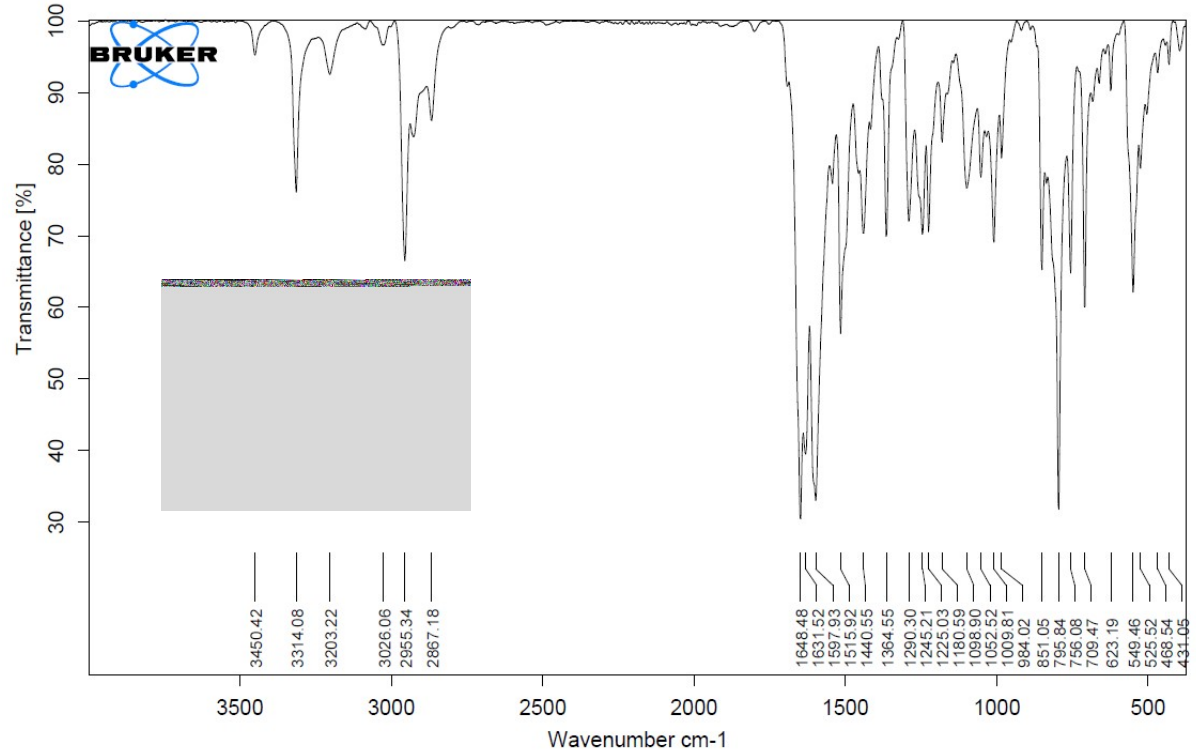


Figure S30 FT-IR spectrum of H**L1d**

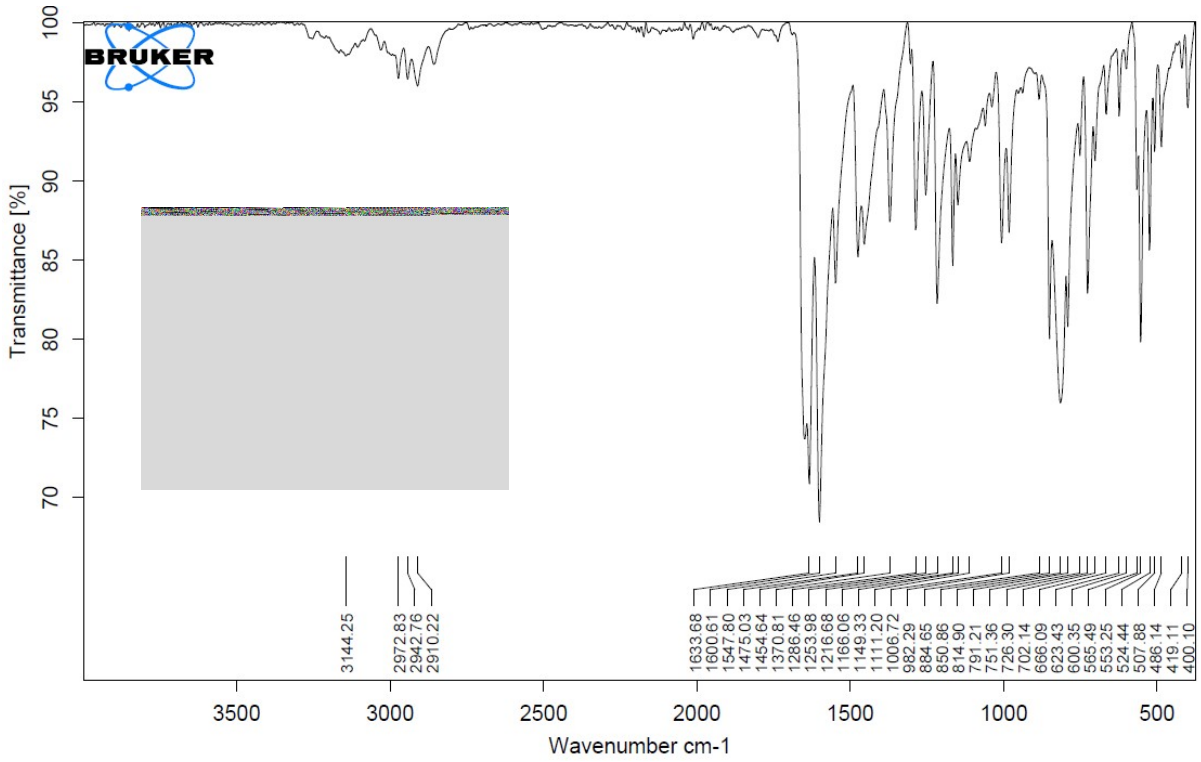


Figure S31 FT-IR spectrum of H**L1e**

4. IR spectra of complexes Mn1a – Mn1e and Mn2

All infra-red spectra of the complexes were recorded using a Bruker ALPHA II compact FT-IR spectrometer using solid samples.

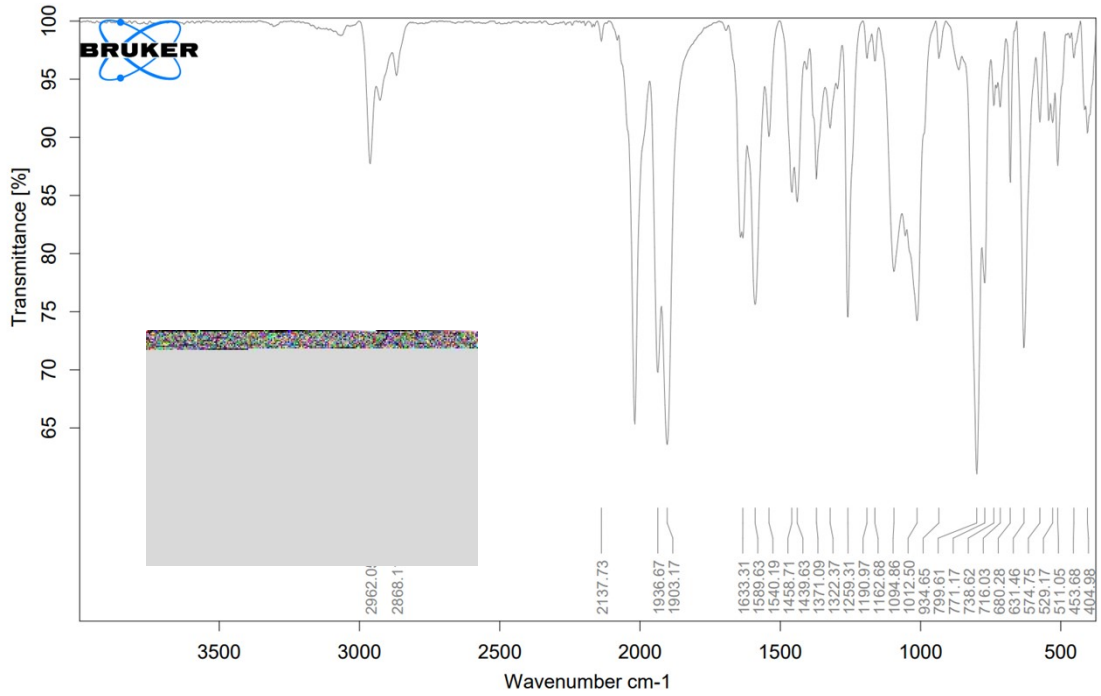


Figure S32 FT-IR spectrum of **Mn1a**

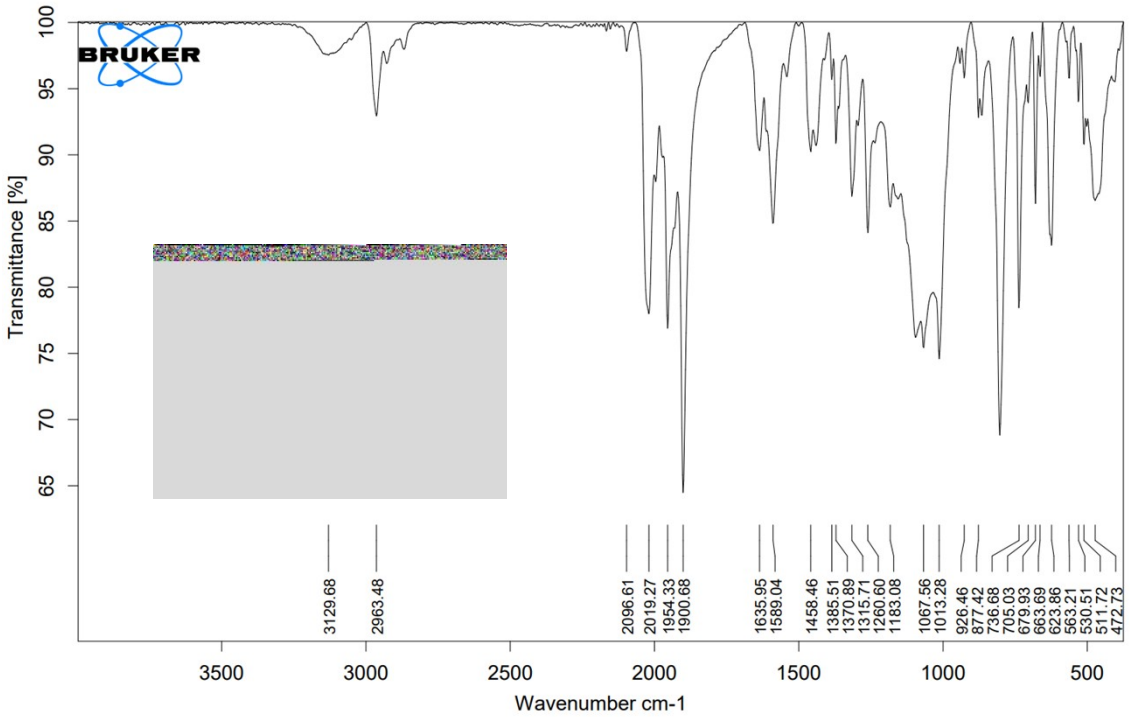


Figure S33 FT-IR spectrum of **Mn1b**

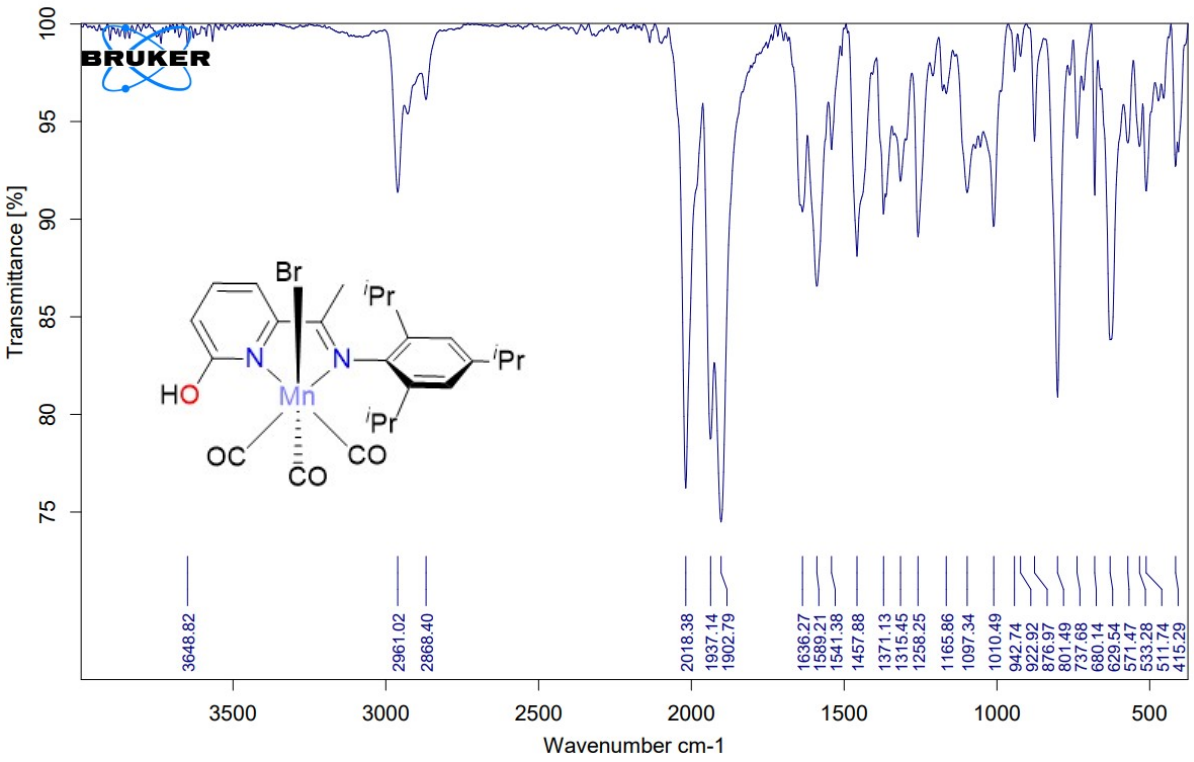


Figure S34 FT-IR spectrum of **Mn1c**

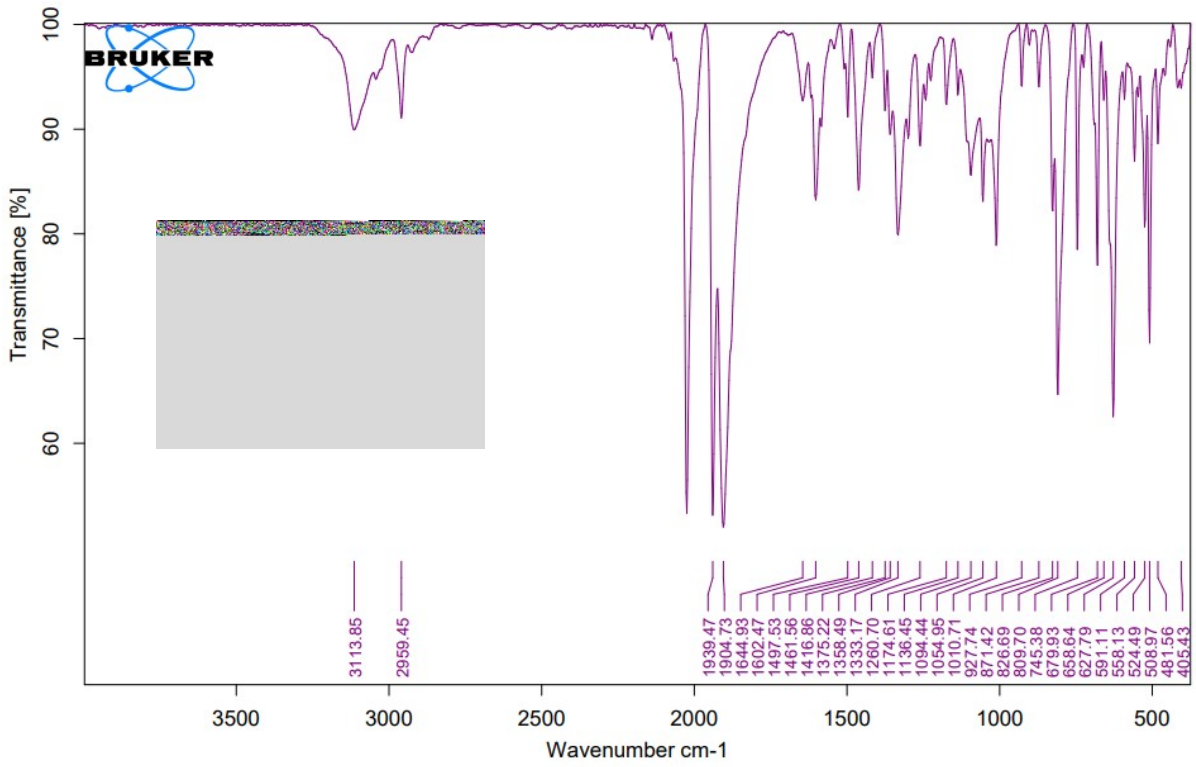


Figure S35 FT-IR Spectrum of **Mn1d**

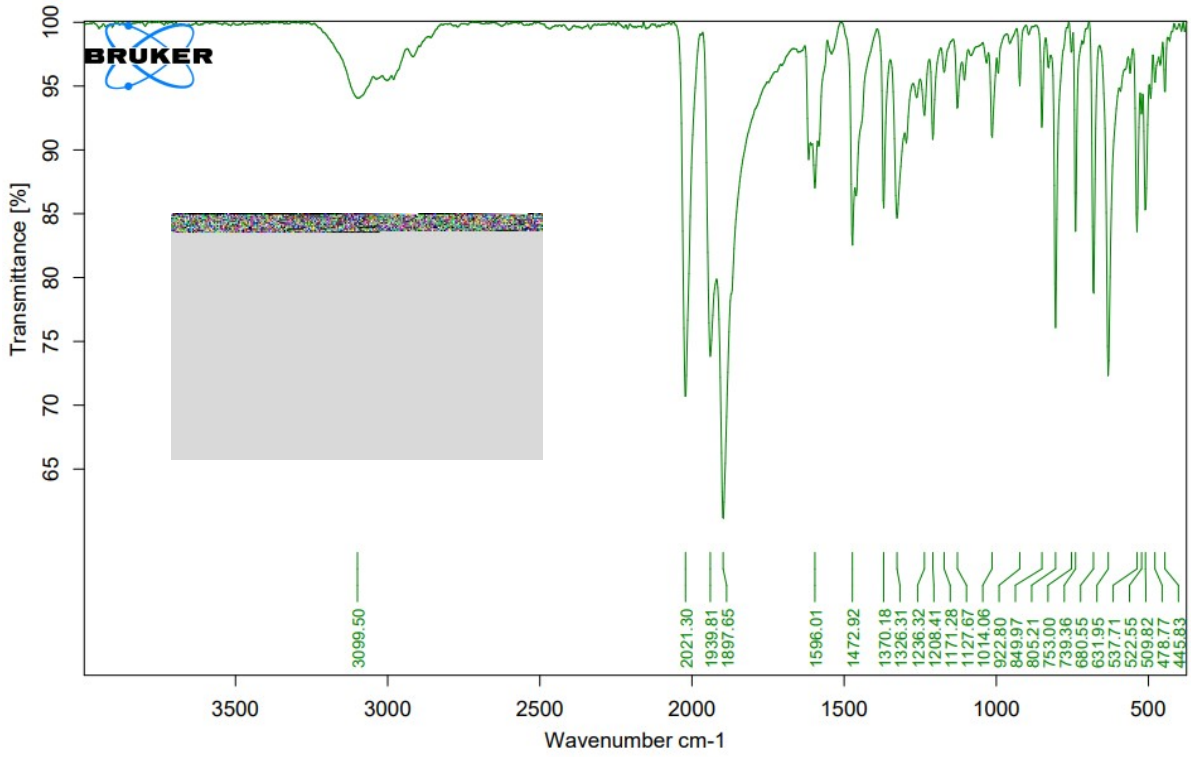


Figure S36 FT-IR spectrum of **Mn1e**

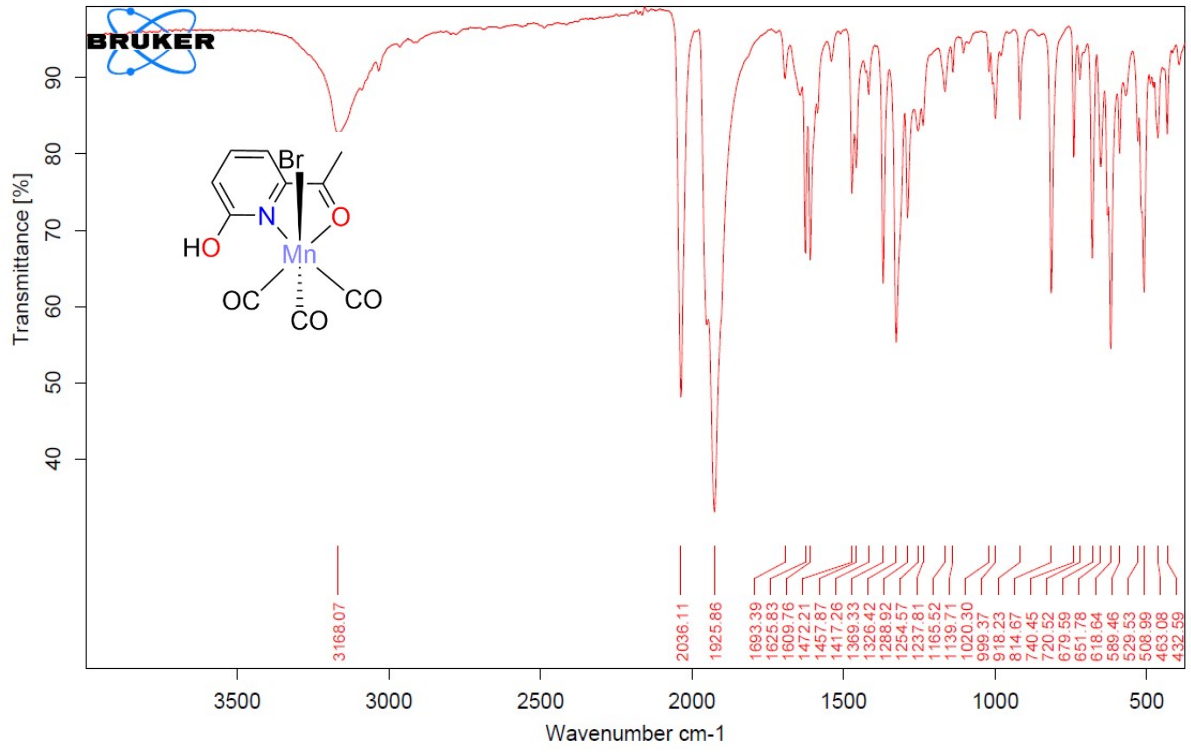


Figure S37 FT-IR spectrum of **Mn2**

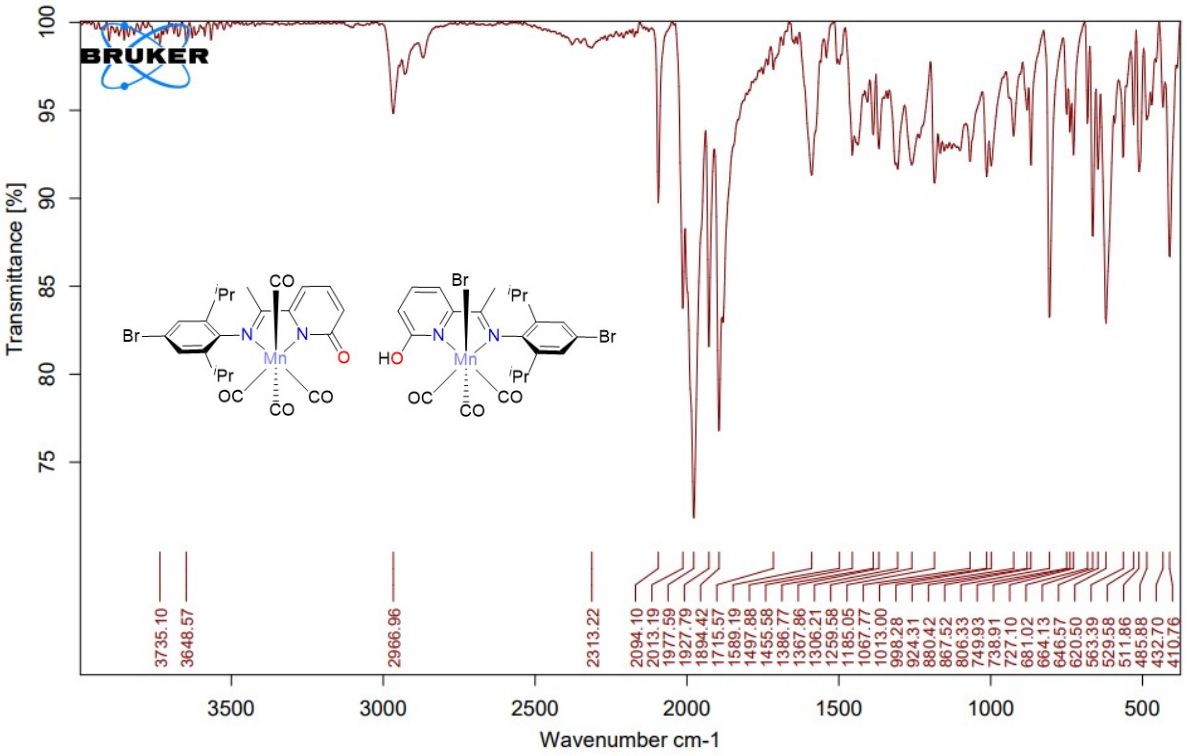


Figure S38 FT-IR spectrum of co-crystallised **Mn1b**···[2-O-6-{CMe=N(2,6-$^{i}Pr_2$-4-BrC_6H_2)}C_5H_3N]$Mn(CO)_4$ (**Mn1b'**)

5. Catalytic evaluation for transfer hydrogenation

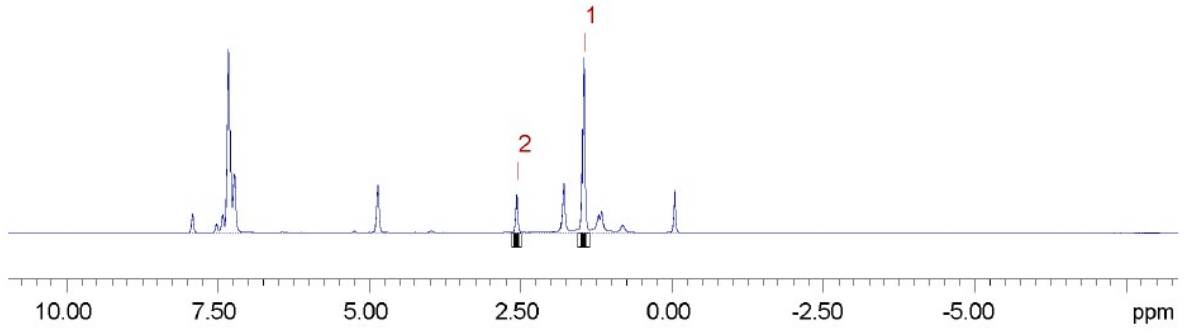
5.1 General Procedure employed in the transfer hydrogenation of aryl ketones 1a – 1n

An oven dry 20 mL Schlenk flask with a micro stir bar was evacuated and backfilled with nitrogen. To this K^{t}BuO was added (7.0 mg, 0.06 mmol, 3 mol%) and the flask re-evacuated. Dry ^{i}PrOH (5 mL) was then added and the contents of the vessel stirred to dissolve/suspend the K^{t}BuO in solution. **Mn1d** (4.7 mg, 0.01 mmol, 0.5 mol%) was the added and stirred to form the active species as a red solution. The substrate was then added (2 mmol) and the reaction surrounded in foil and placed into an oil bath set at 80 ^{o}C for 24 h. After cooling the reaction mixture to room temperature, the mixture was diluted with dichloromethane (5 mL) and passed through a silica plug eluting with dichloromethane. NMR spectra were then recorded in $CDCl_3$.

5.2 NMR method used to measure conversions

All conversions were calculated using the methyl CH_3 protons on the acetophenone derivatives and their corresponding alcohol. Quantitative ^{1}H NMR spectroscopy was used with adjusted T1 values to give accurate integrations of the signals for the conversion calculations. T1 values calculated from a random reaction mixture was used and T1 values shown below. NMR data matched the literature values for alcoholic products [(**2a**, **2b**, **2c, 2d**, **2f**),[2] (**2e**, **2g**, **2n**, **2k**),[3] (**2l**),[4] (**2h**),[5] (**2i**),[6] and (**2j**)[7]].

Fitted function:	f(t) = Io * [1 - a*exp (-t/T1)]
Random error estimation of data:	RMS per spectrum (or trace/plane)
Systematic error estimation of data:	worst case per peak scenario
Fit parameter Error estimation method:	from fit using arbitrary y uncertainties
Confidence level:	95%
Used peaks:	
Used integrals:	area integral
Used Mixing time:	all values (including replicates) used



Peak name	F2 [ppm]	T1 [s]	Error
1	1.451	2.32	0.05072
2	2.557	3.96	0.04634

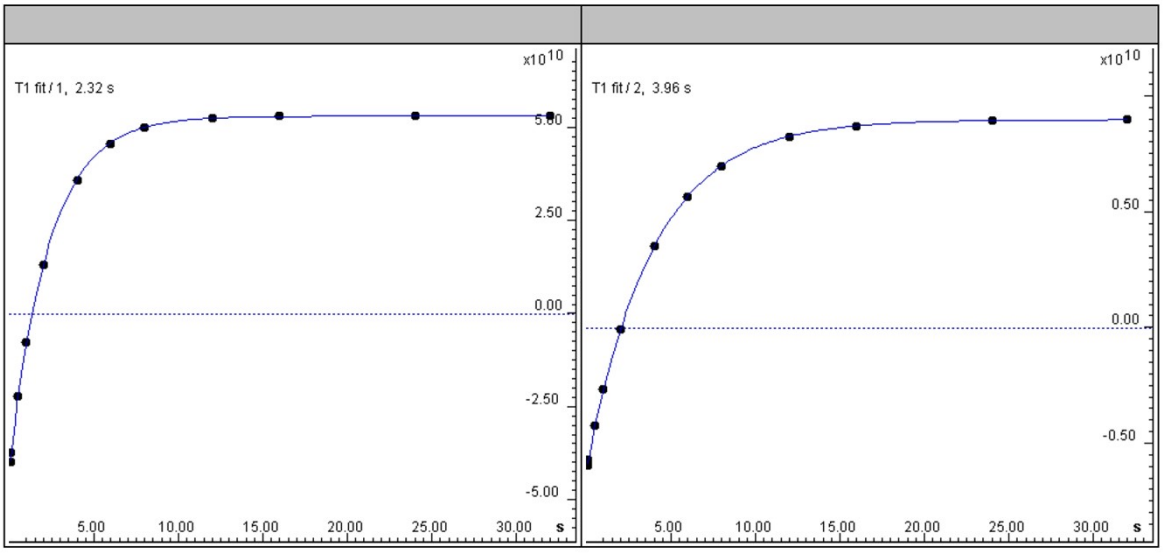


Figure S39 Measured T1 parameters for a typical reaction mixture measured in $CDCl_3$

5.3 ^{1}H (and ^{19}F) NMR spectra used to measure percentage conversions

All NMR spectra (^{1}H, ^{19}F) were recorded on a Bruker Avance III 500 MHz spectrometer with a 5 mm BBO probe, Bruker Avance III HD 400 MHz spectrometer with a 5 mm BBO probe and a Bruker Avance NEO 500 MHz spectrometer with either a 5 mm Prodigy BBO cryoprobe or a 5 mm BBFO probe. All deuterated solvents were purchased from Goss Scientific and Sigma-Aldrich.

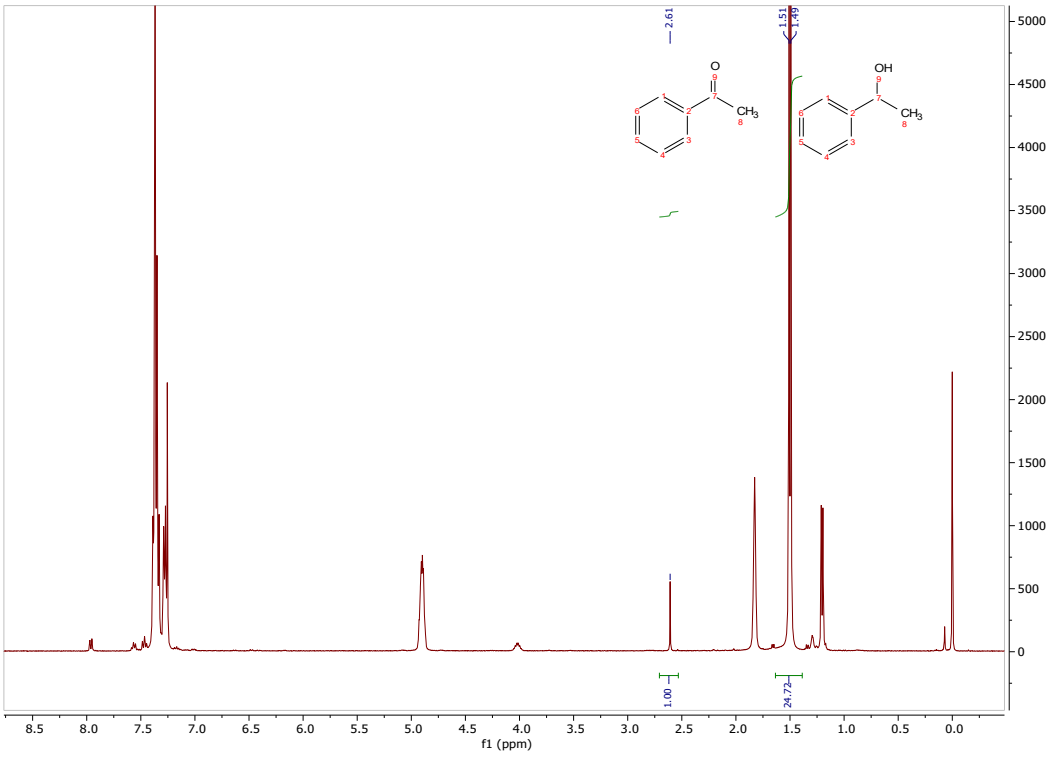


Figure S40 ^{1}H NMR spectrum of reaction mixture following the TH of acetophenone (**1a**) to 1-phenylethan-1-ol (**2a**) using **Mn1d** as (pre)catalyst

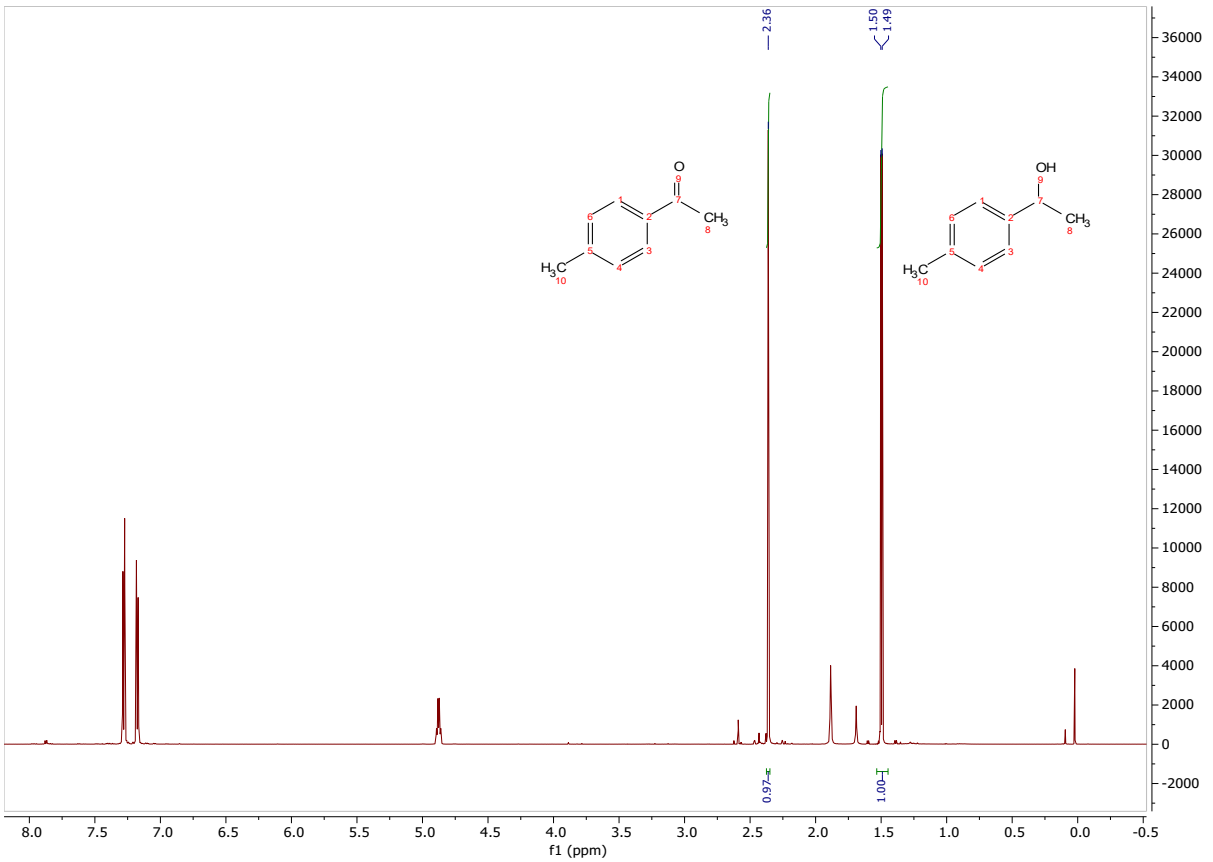


Figure S41 [1]H NMR spectrum of reaction mixture following the TH of 4-methyl-acetophenone (**1b**) to 4 methylphenyl-ethan-(2)-ol (**2b**) using **Mn1d** as (pre)catalyst

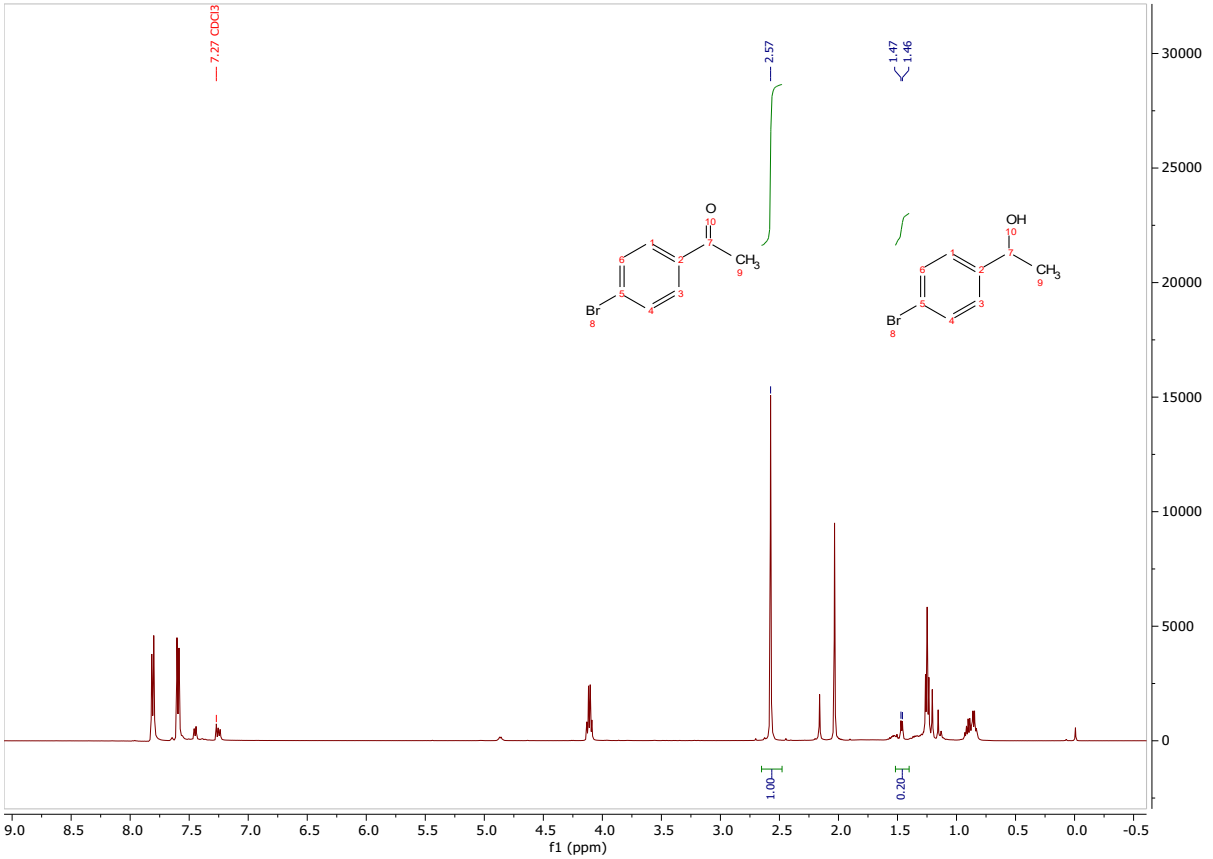


Figure S42 [1]H NMR spectrum of reaction mixture following the TH of 4-bromo-acetophenone (**1c**) to 4-bromo-phenyl-ethan-(2)-ol (**2c**) using **Mn1d** as (pre)catalyst

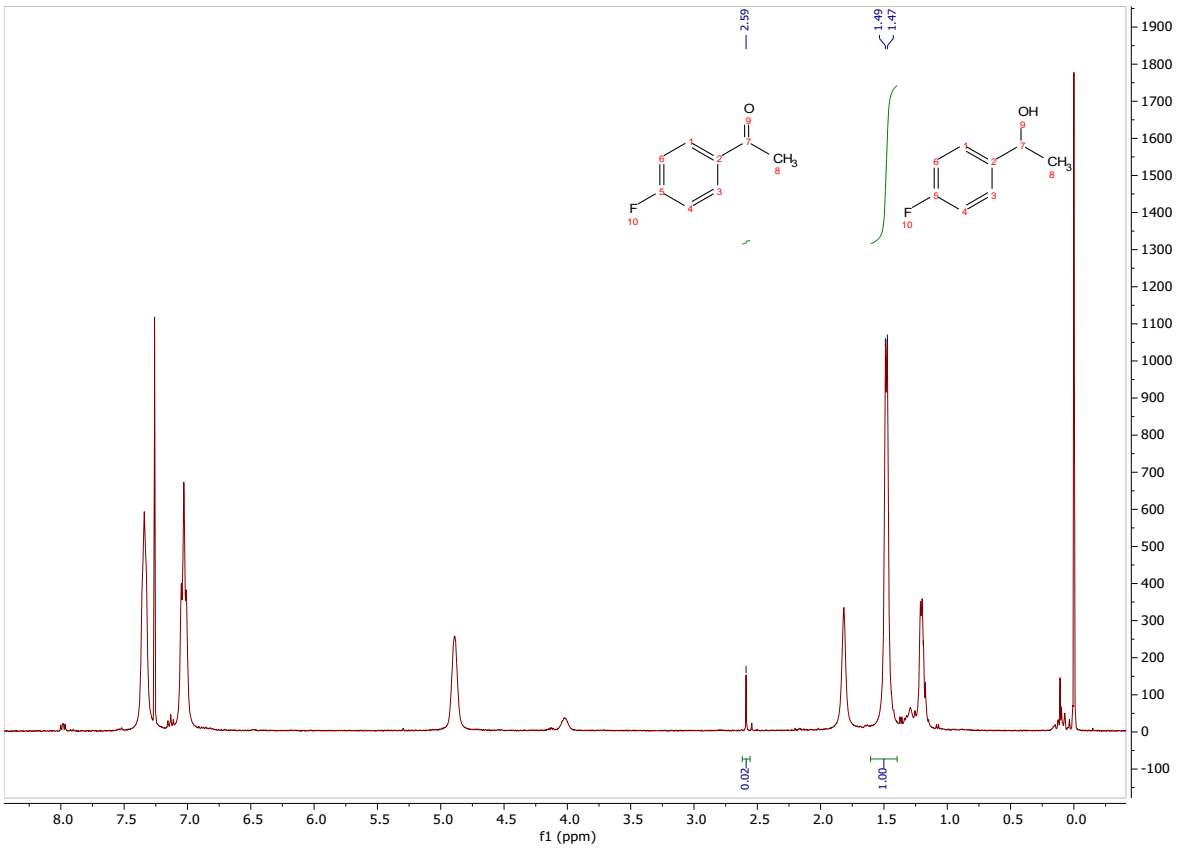


Figure S43 ^{1}H NMR spectrum of reaction mixture following the TH of 4-fluoro-acetophenone (**1d**) to 4-fluoro-phenyl-ethan-(2)-ol (**2d**) using **Mn1d** as (pre)catalyst

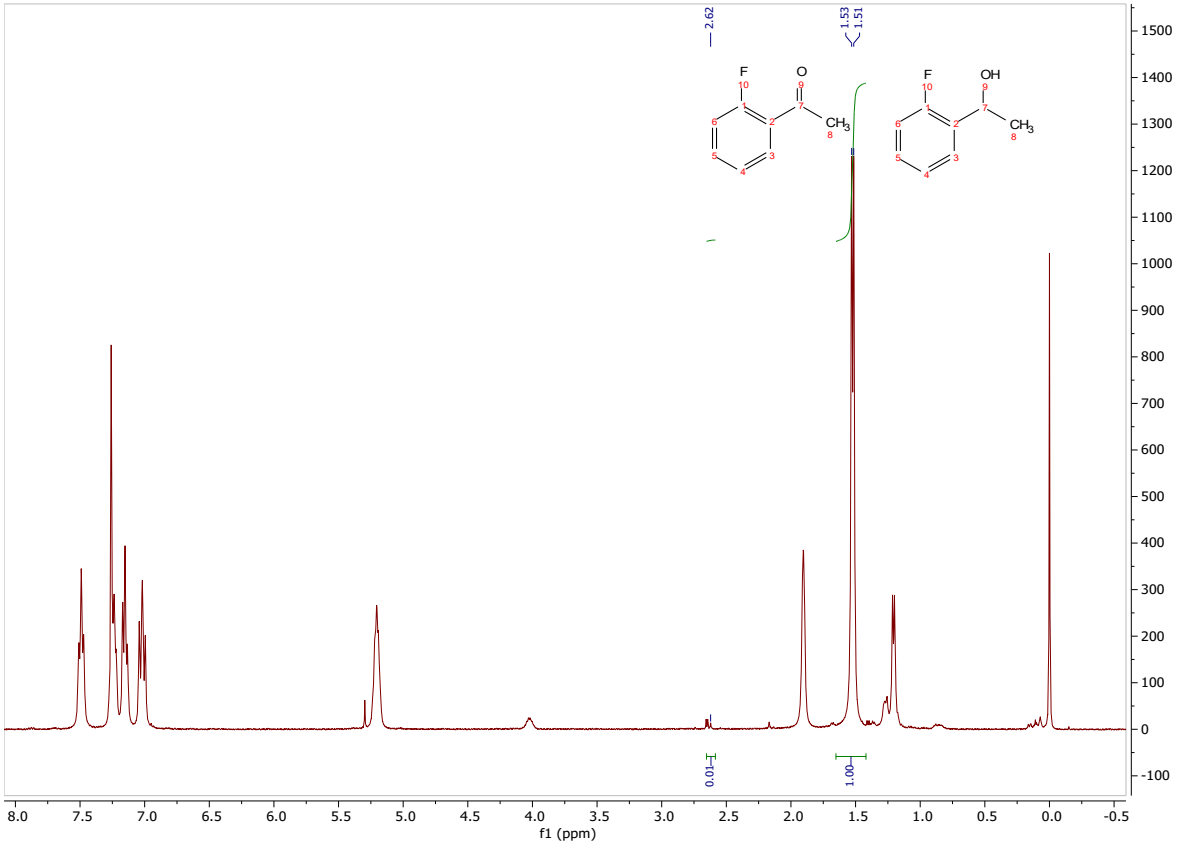


Figure S44 ^{1}H NMR spectrum of reaction mixture following the TH of 2-fluoro-acetophenone (**1e**) to 2-fluoro-phenyl-ethan-(2)-ol (**2e**) using **Mn1d** as (pre)catalyst

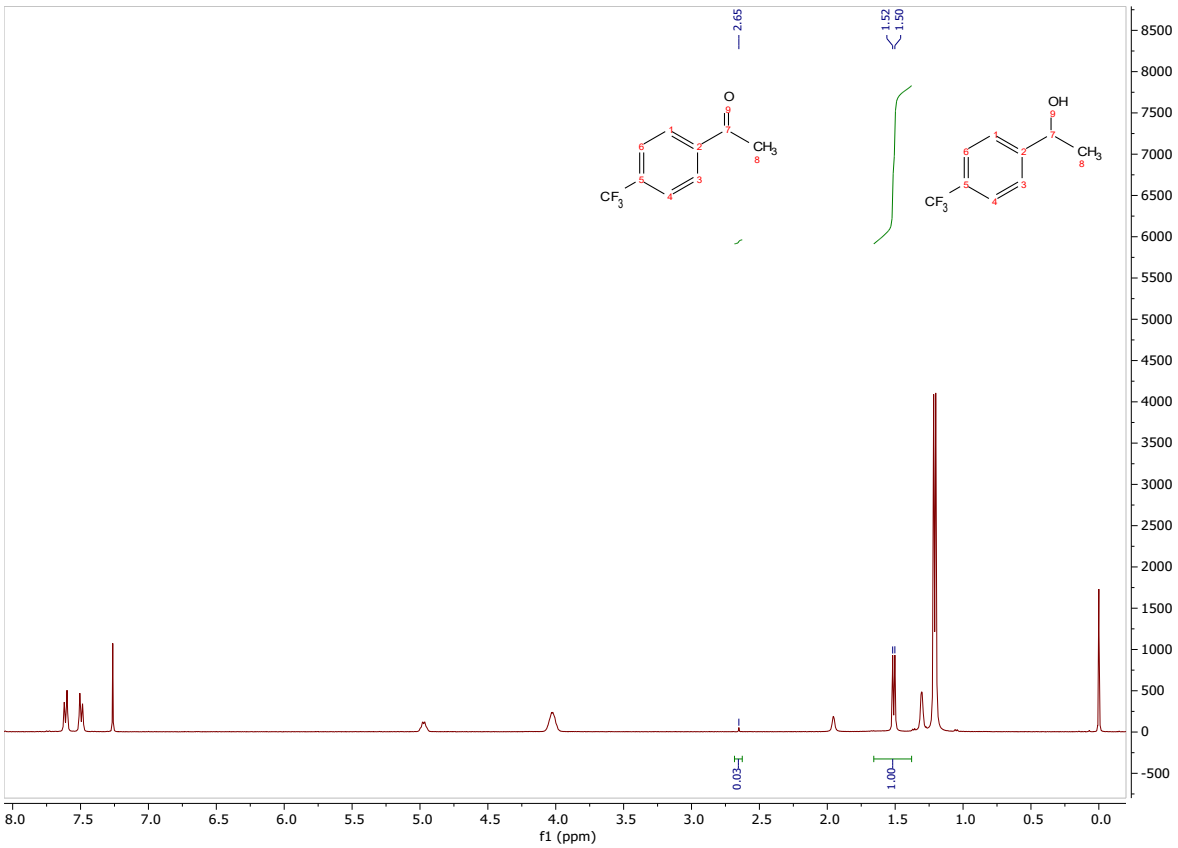


Figure S45 ^{1}H NMR spectrum of reaction mixture following the TH of 4-(trifluoromethyl)-acetophenone (**1f**) to 4-(trifluoromethyl)-phenyl-ethan-(2)-ol (**2f**) using **Mn1d** as (pre)catalyst

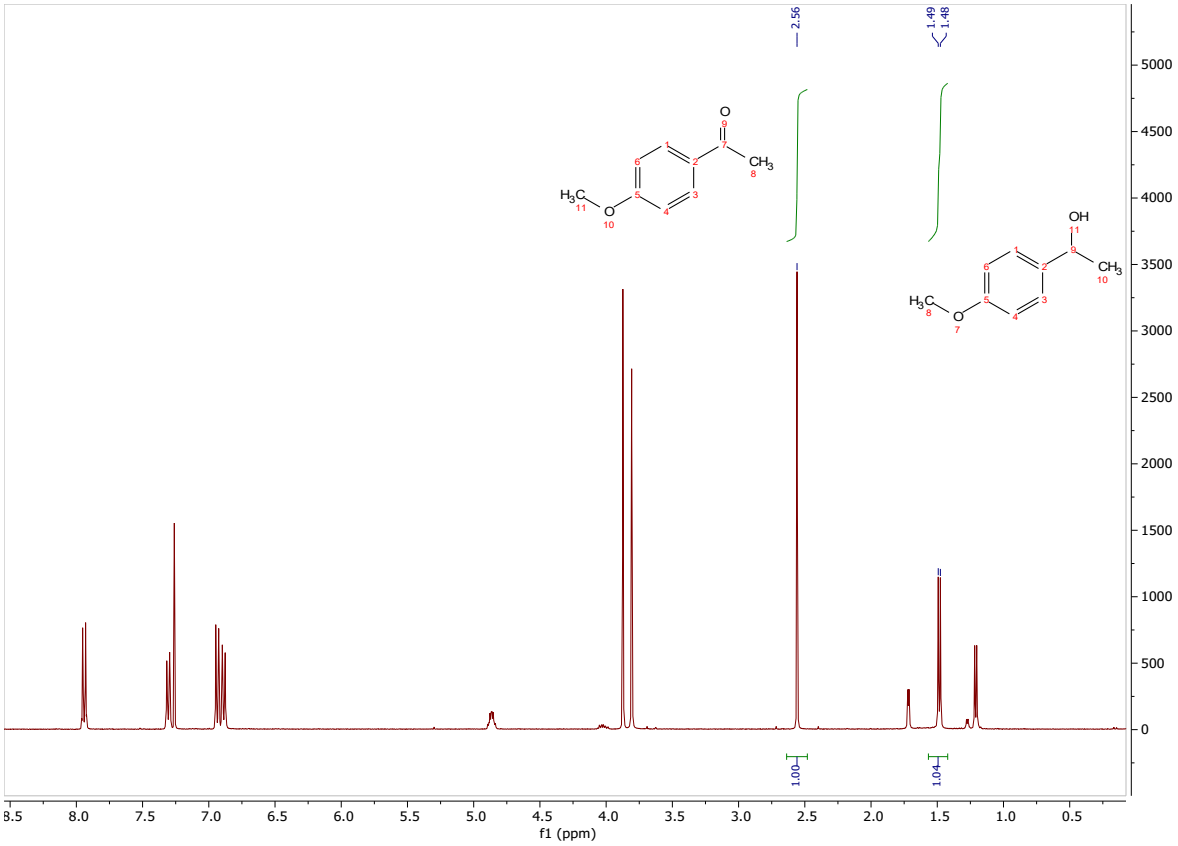


Figure S46 ^{1}H NMR spectrum of reaction mixture following the TH of 4-methoxy-acetophenone (**1g**) to 4-methoxy-phenyl-ethan-(2)-ol (**2g**) using **Mn1d** as (pre)catalyst

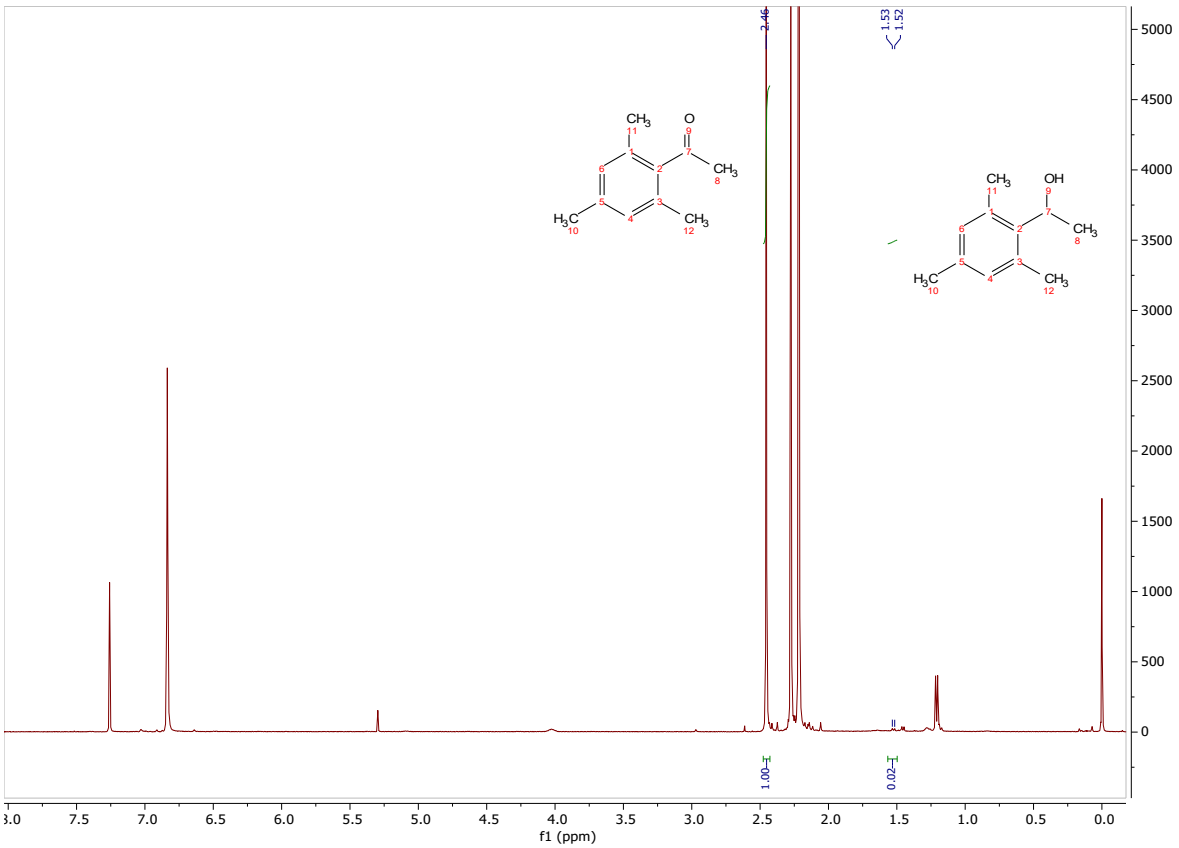


Figure S47 ^{1}H NMR spectrum of reaction mixture following the TH of 2,4,6-trimethyl-acetophenone (**1h**) to 2,4,6-trimethyl-phenyl-ethan-(2)-ol (**2h**) using **Mn1d** as (pre)catalyst

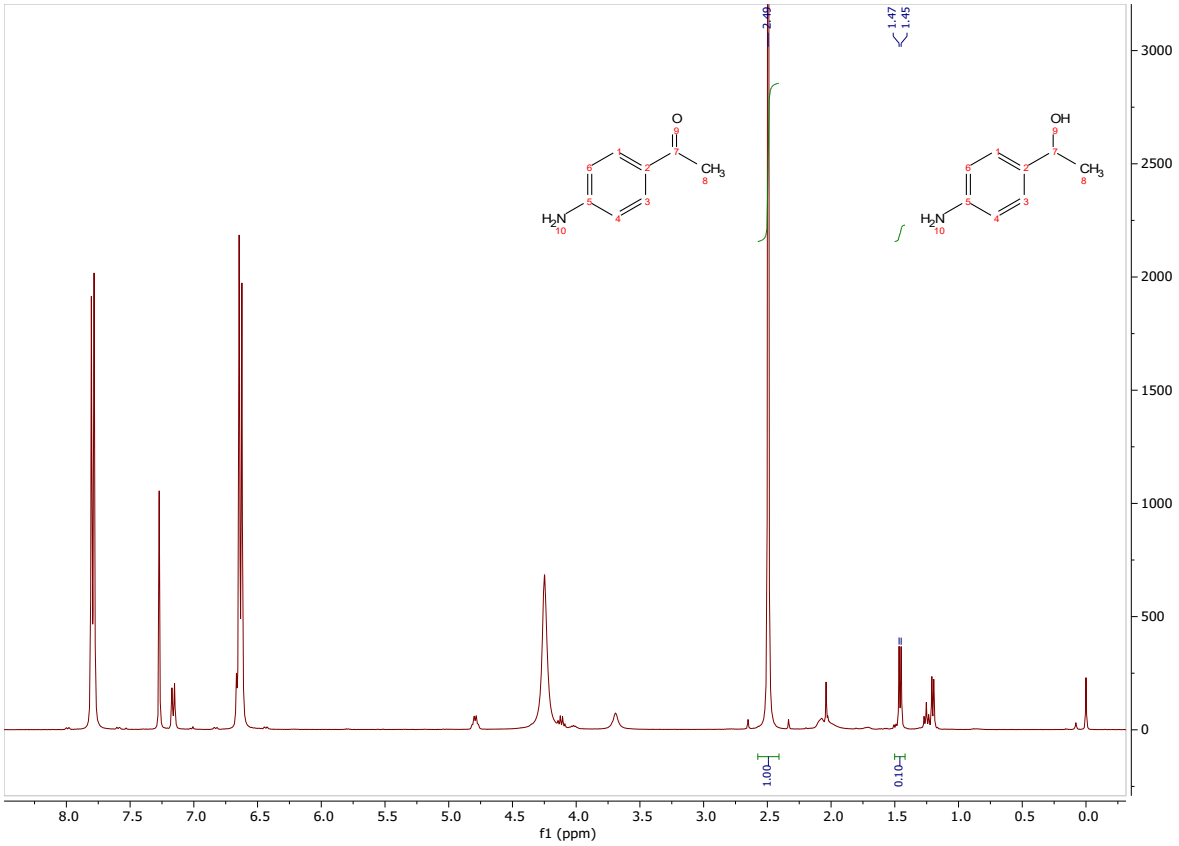


Figure S48 ^{1}H NMR spectrum of reaction mixture following the TH of 4-amino-acetophenone (**1i**) to 4-amino-phenyl-ethan-(2)-ol (**2i**) using **Mn1d** as (pre)catalyst

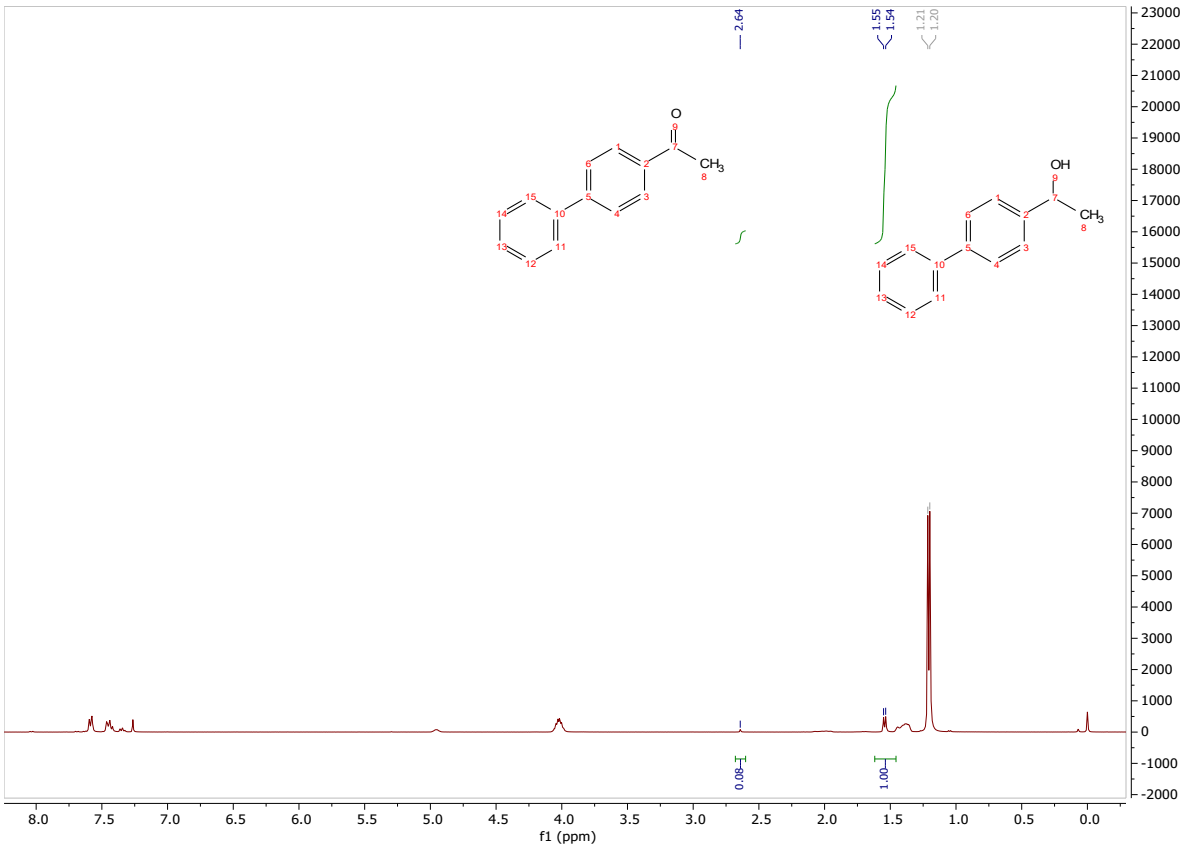


Figure S49 ^{1}H NMR spectrum of reaction mixture following the TH of 4-phenyl-acetophenone (**1j**) to biphenyl-4-ethan-(2)-ol (**2j**) using **Mn1d** as (pre)catalyst

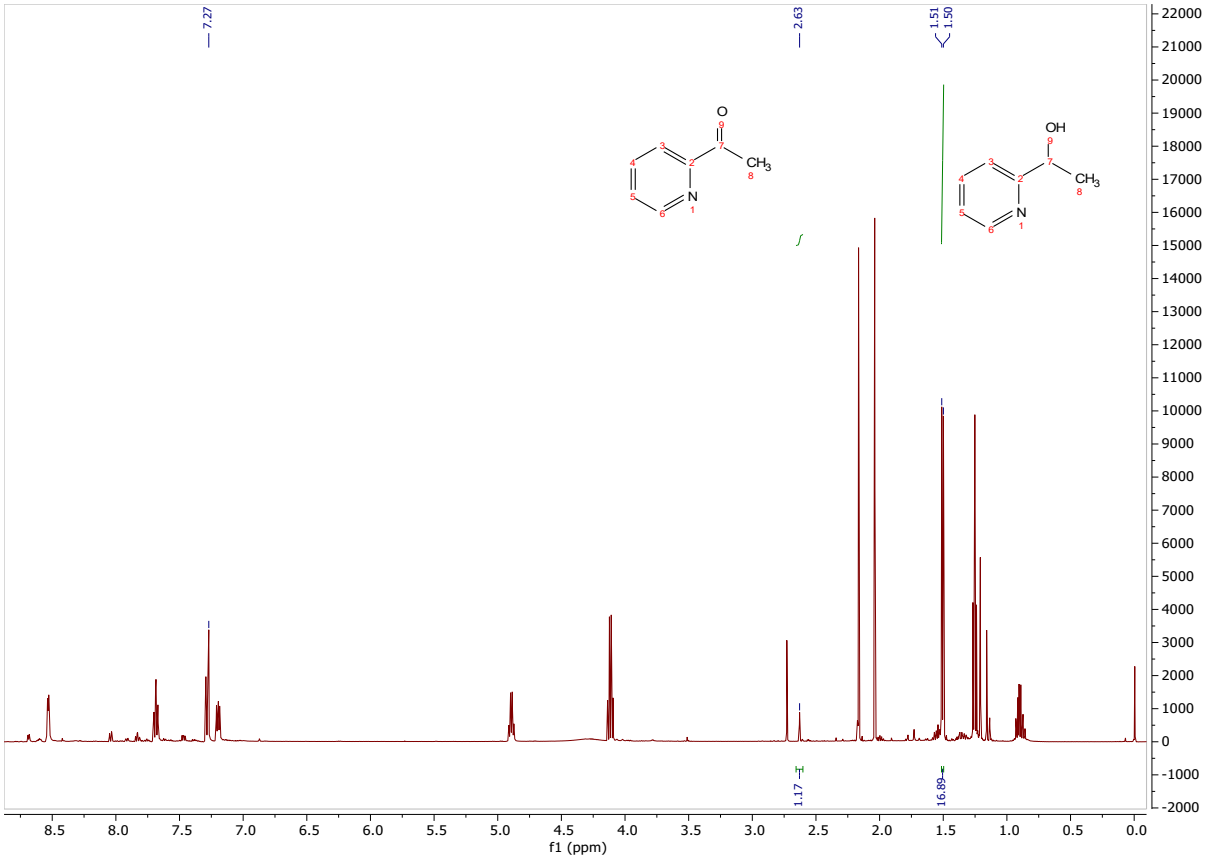


Figure S50 ^{1}H NMR spectrum of reaction mixture following the TH of 2-acetyl-pyridine (**1k**) to pyridine-2-ethan-(2)-ol (**2k**) using **Mn1d** as (pre)catalyst

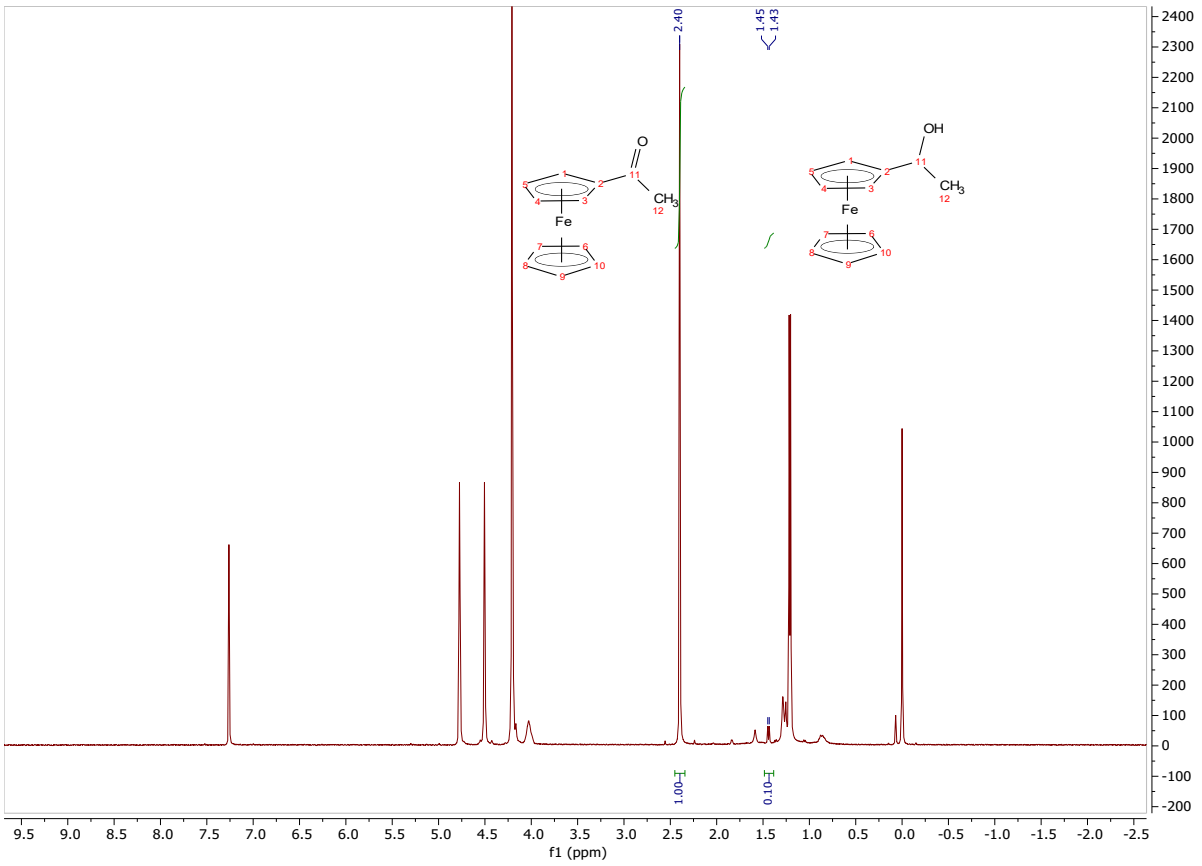


Figure S51 ^{1}H NMR spectrum of reaction mixture following the TH of acetyl ferrocene (**1l**) to 1-ferrocenylethanol (**2l**) using **Mn1d** as (pre)catalyst

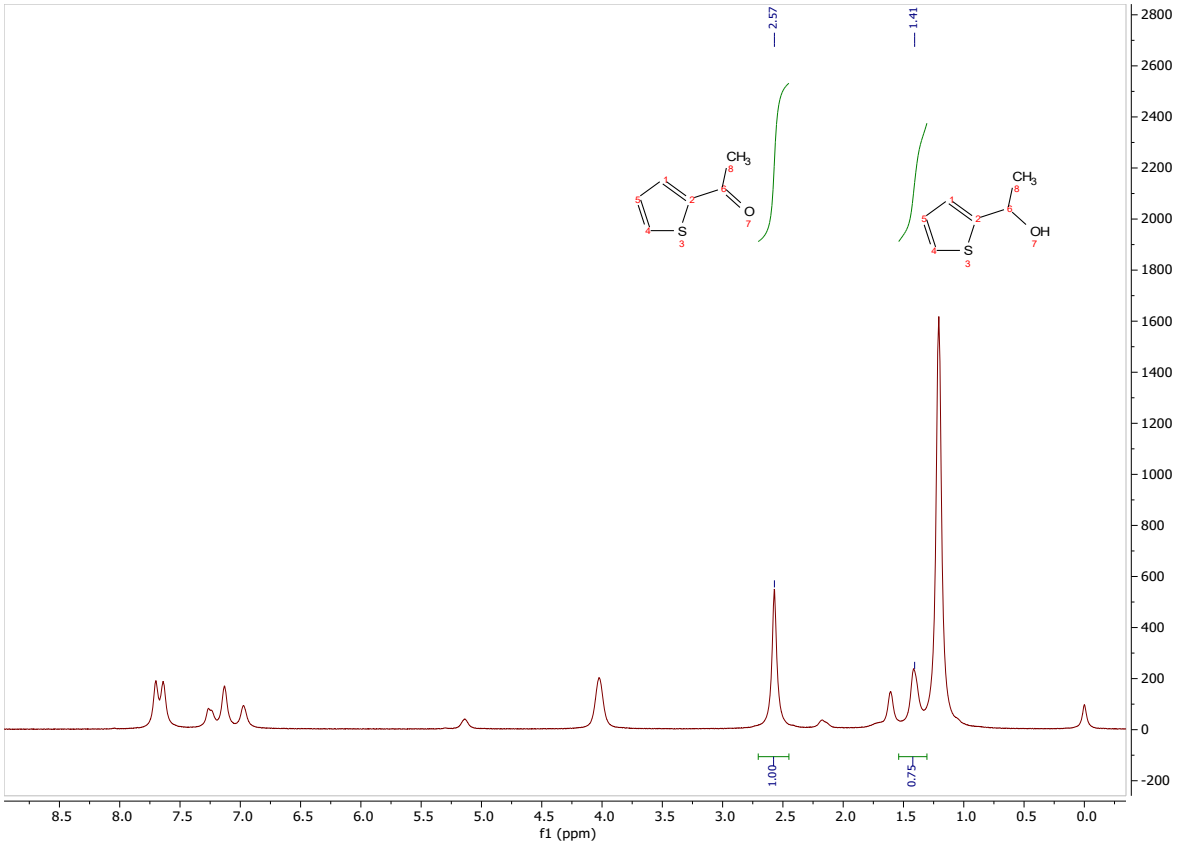


Figure S52 ^{1}H NMR spectrum of reaction mixture following the TH of 2-acetyl-thiophene (**1n**) to thiophene-2-ethan-(2)-ol (**2n**) using **Mn1d** as (pre)catalyst

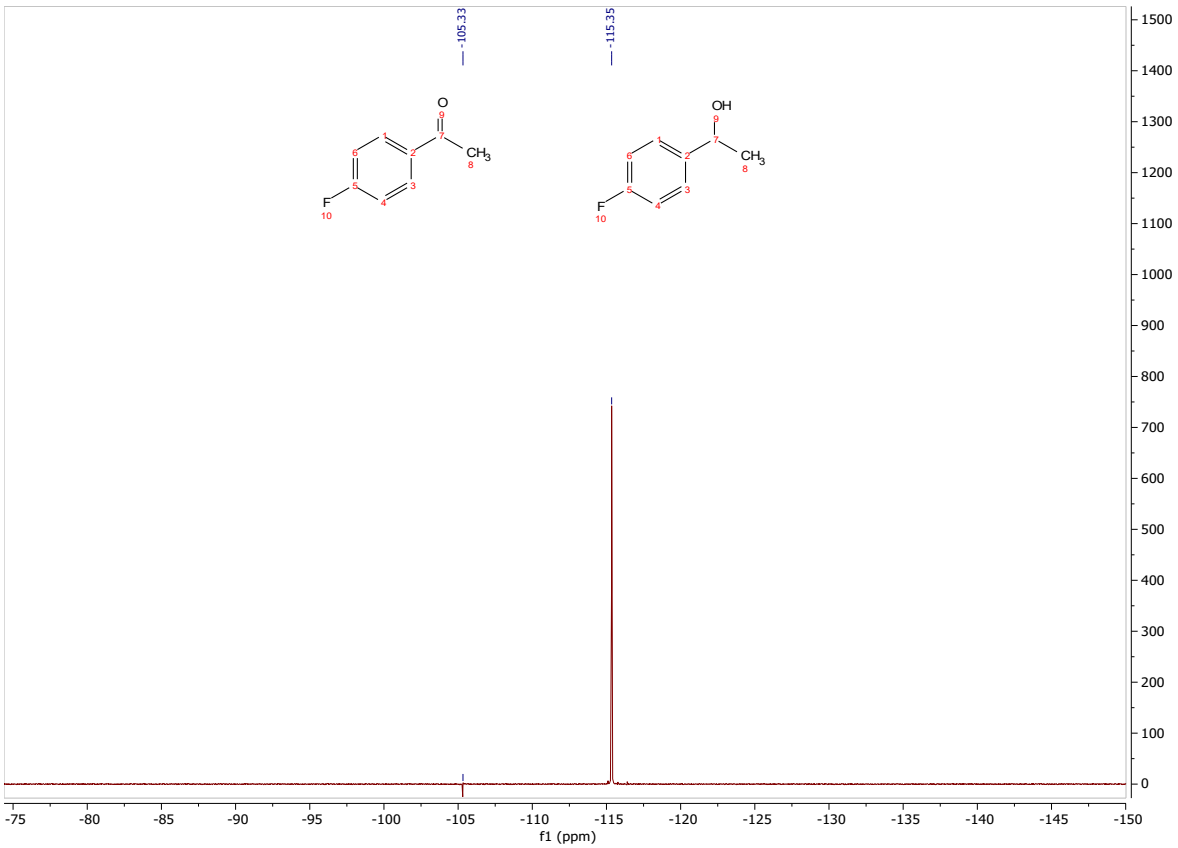


Figure S53 $^{19}F\{^{1}H\}$ NMR spectrum of reaction mixture following the TH 2-fluoro-acetophenone (**1d**) to 2-fluoro-phenyl-ethan-(2)-ol (**2d**) using **Mn1d** as (pre)catalyst

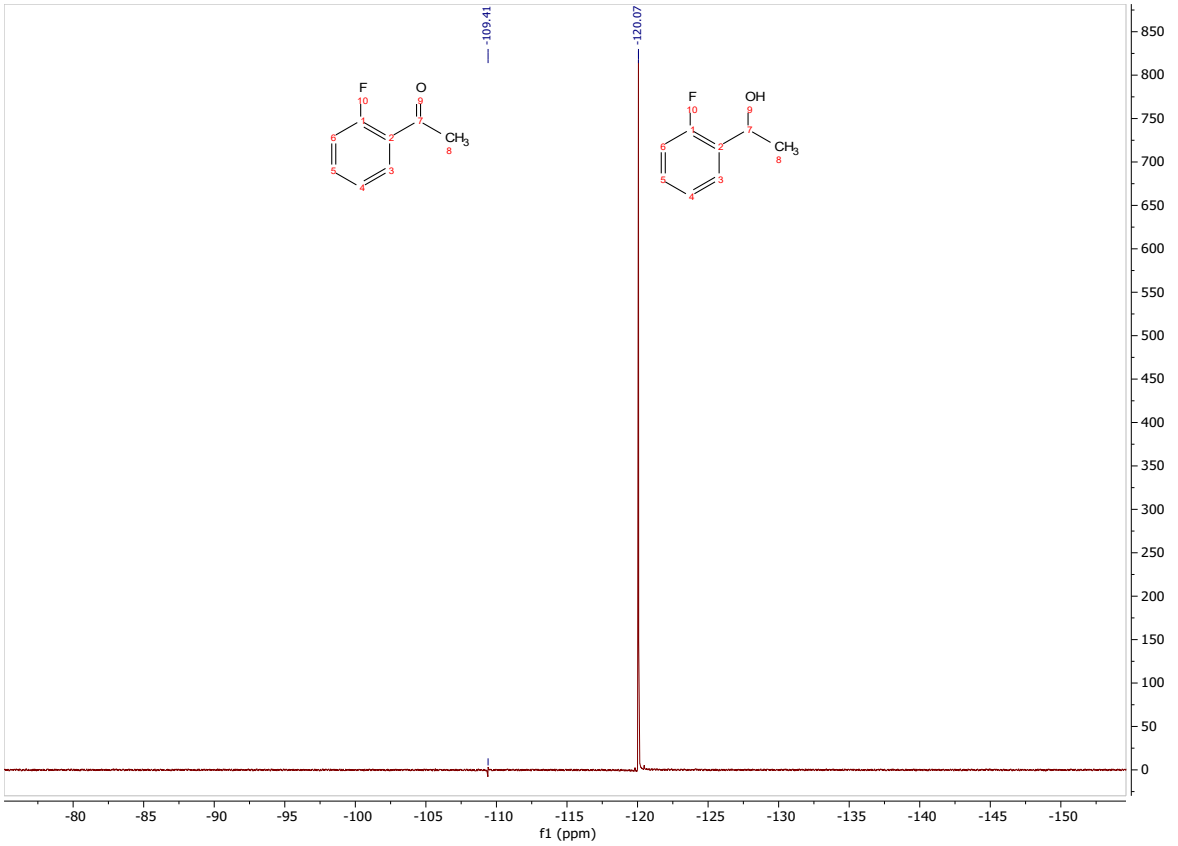


Figure S54 $^{19}F\{^{1}H\}$ NMR spectrum of reaction mixture following the TH conversion of 2-fluoro-acetophenone (**1e**) to 2-fluoro-phenyl-ethan-(2)-ol (**2e**) using **Mn1d** as (pre)catalyst

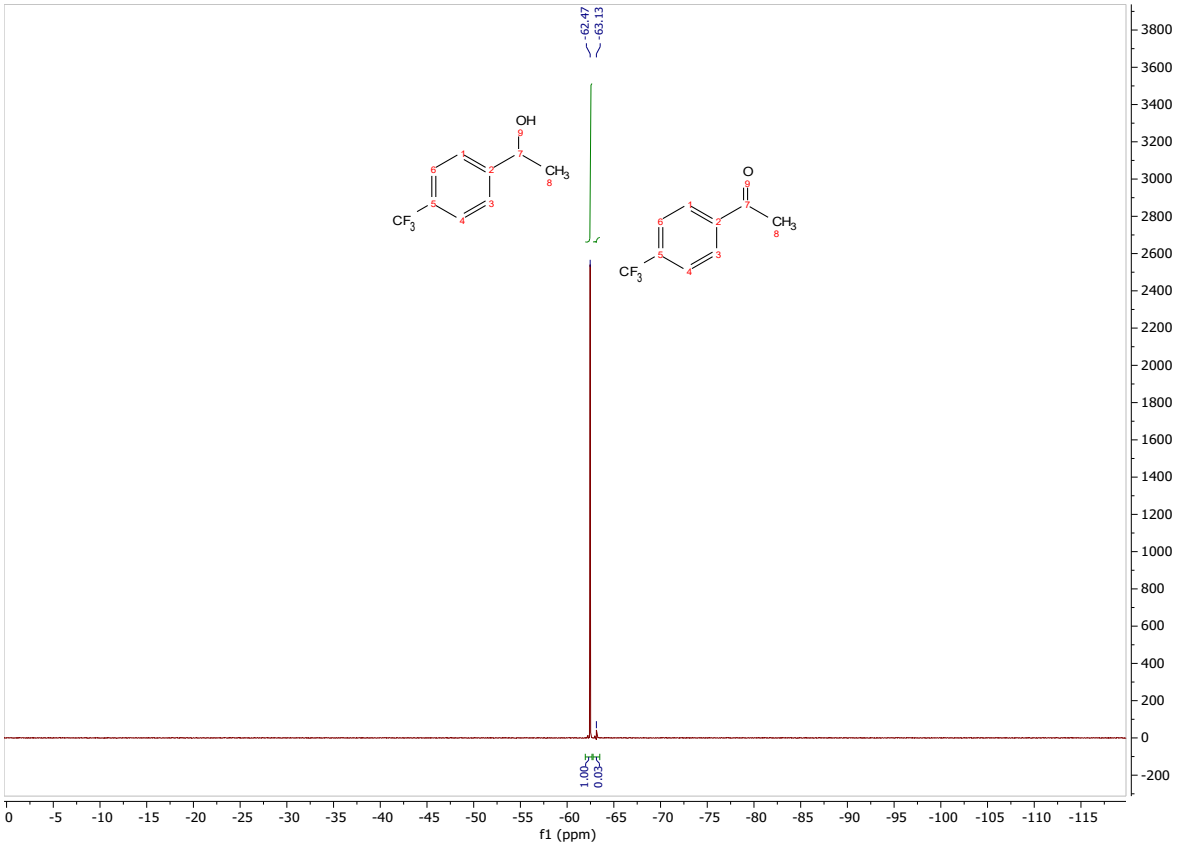


Figure S55 $^{19}F\{^{1}H\}$ NMR spectrum of reaction mixture following the TH of 4-(trifluoromethyl)-acetophenone (**1f**) to 4-(trifluoromethyl)-phenyl-ethan-(2)-ol (**2f**) using **Mn1d** as (pre)catalyst

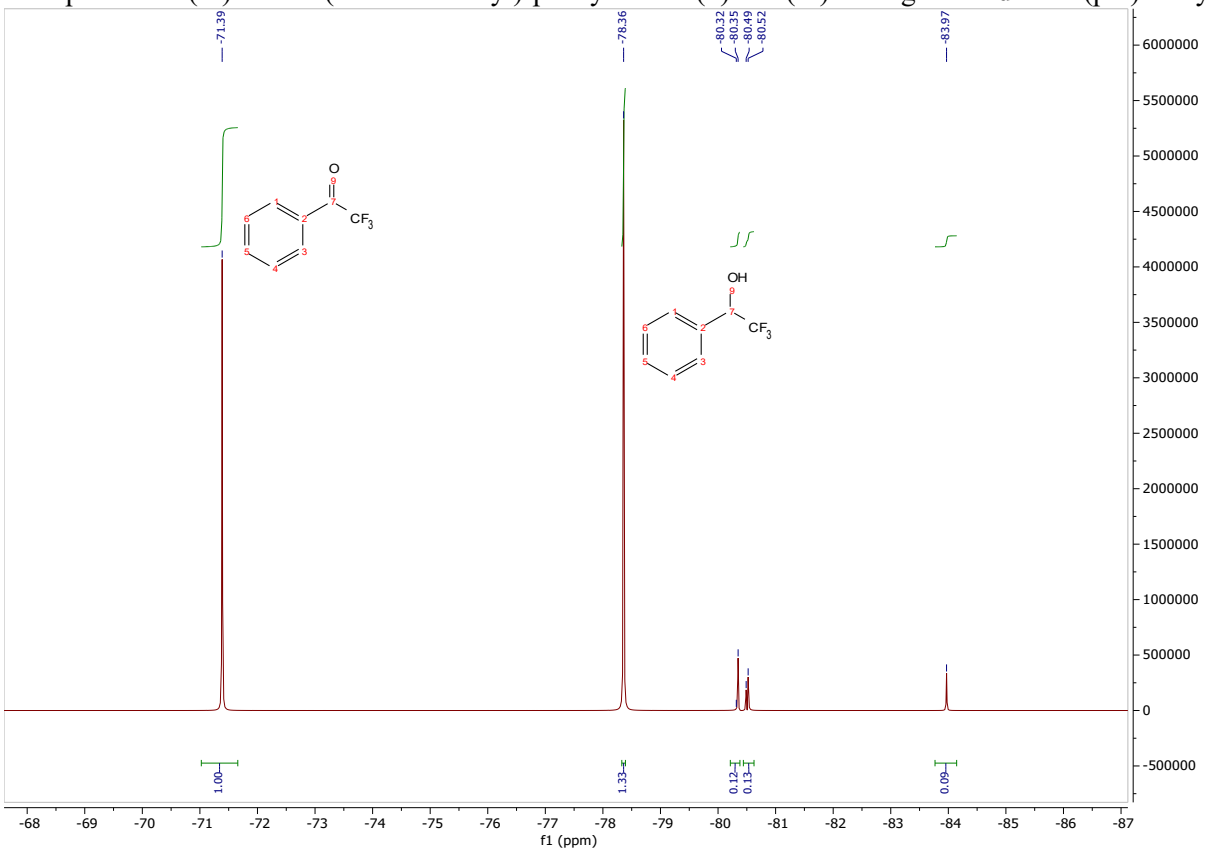
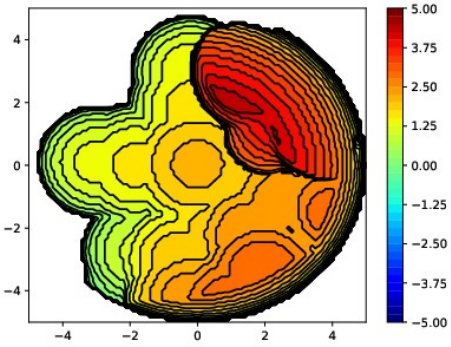


Figure S56 $^{19}F\{^{1}H\}$ NMR spectrum of reaction mixture following the TH of 2,2,2-trifluoro-1-phenylethan-1-one (**1m**) to 2,2,2-trifluoro-1-phenylethan-1-ol (**2m**) using **Mn1d** as (pre)catalyst

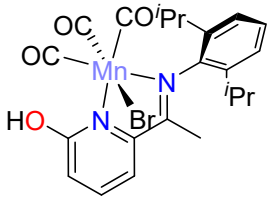
7. SambVca Buried Volume Calculations (%V_{bur})

The topographic steric maps of the (*N,N*)Mn(CO)$_3$ or (*N,O*)Mn(CO)$_3$ fragments in **Mn1a**, **Mn1b**, **Mn1c**, **Mn1d**, **Mn1e** and **Mn2** showing the buried volume (V_{bur}) around the catalytic centre. Map radius set to 5 Å, bromine atom removed with positional representation of molecules orientation. %V_{bur} corresponds to percentage of volume occupied by the molecule in each quadrant [SW (south west), NW (north west), NE (north east) and SE (south east)].[8]



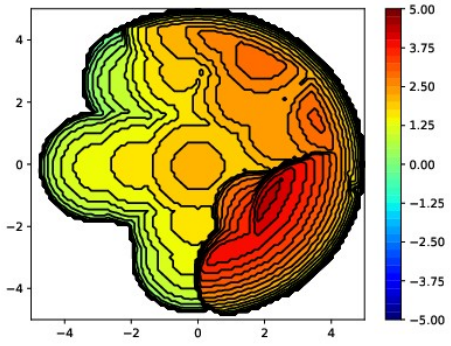
%V_{Bur}

Quadrant	%V_{Bur}
SW	46.5
NW	35.2
NE	79.9
SE	66.4



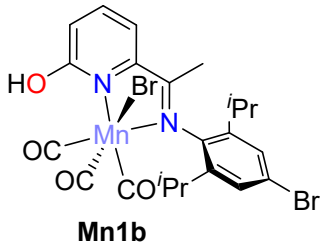
Mn1a

Figure S57 SambVca plot showing the buried volume (V_{bur}) around the manganese centre of **Mn1a**. Map radius set to 5 Å, bromine atom removed with positional representation of molecules orientation.



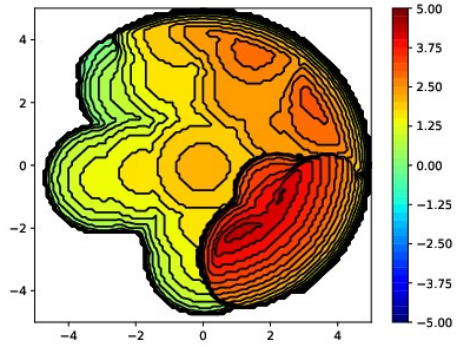
%V_{Bur}

Quadrant	%V_{Bur}
SW	34.9
NW	46.7
NE	67.8
SE	78.2

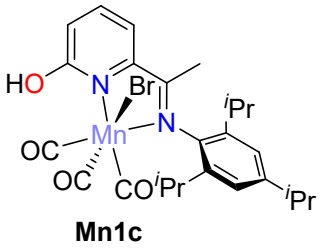


Mn1b

Figure S58 SambVca plot showing the buried volume (V_{bur}) around the manganese centre of **Mn1b**. Map radius set to 5 Å, bromine atom removed with positional representation of molecules orientation.

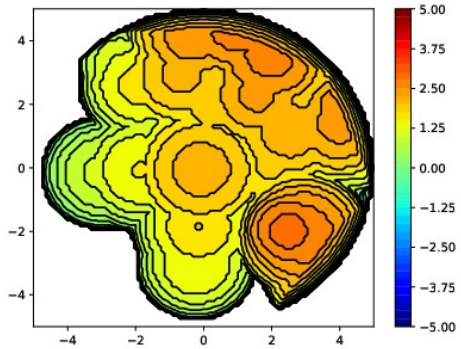


Quadrant	%V_{Bur}
SW	35.1
NW	47.3
NE	69.4
SE	76.1

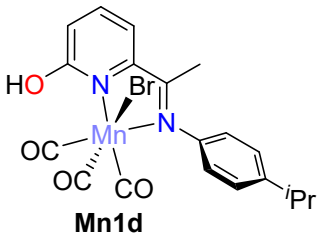


Mn1c

Figure S59 SambVca plot showing the buried volume (V_{bur}) around the manganese centre of **Mn1c**. Map radius set to 5 Å, bromine atom removed with positional representation of molecules orientation.

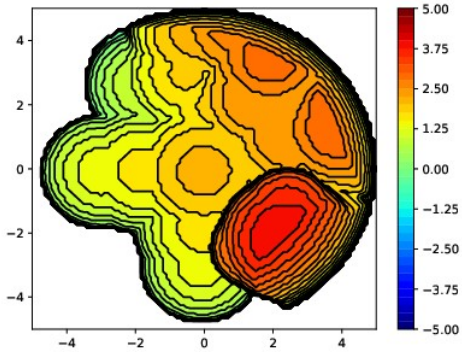


Quadrant	%V_{Bur}
SW	35.3
NW	46.9
NE	58.9
SE	60.0

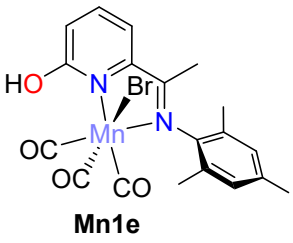


Mn1d

Figure S60 SambVca plot showing the buried volume (V_{bur}) around the manganese centre of **Mn1d**. Map radius set to 5 Å, bromine atom removed with positional representation of molecules orientation.

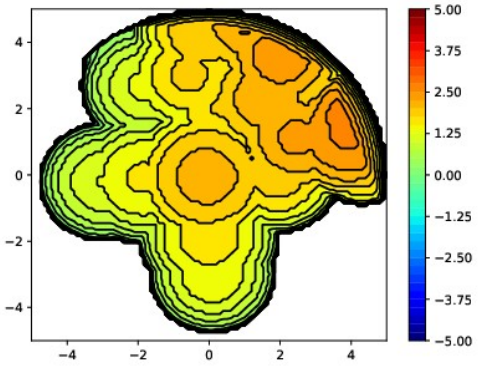


Quadrant	%V_{Bur}
SW	34.0
NW	46.7
NE	66.4
SE	70.6

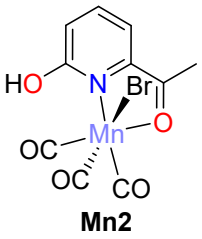


Mn1e

Figure S61 SambVca plot showing the buried volume (V_{bur}) around the manganese centre of **Mn1e**. Map radius set to 5 Å, bromine atom removed with positional representation of molecules orientation.



Quadrant	%V_{Bur}
	%V_{Bur}
SW	33.8
NW	45.8
NE	57.9
SE	30.6



Mn2

Figure S62 SambVca plot showing the buried volume (V_{bur}) around the manganese centre of **Mn2**. Map radius set to 5 Å, bromine atom removed with positional representation of molecules orientation.

7. Crystallographic studies

7.1 Molecular structures of Mn1a, Mn1b, Mn1c, Mn1d, Mn1e and Mn2

Crystals of **Mn1a**, **Mn1b**, **Mn1c**, **Mn1d**, **Mn1e** and **Mn2** suitable for single crystal X-ray diffraction studies were grown through slow evaporation of a concentrated methanol solution.

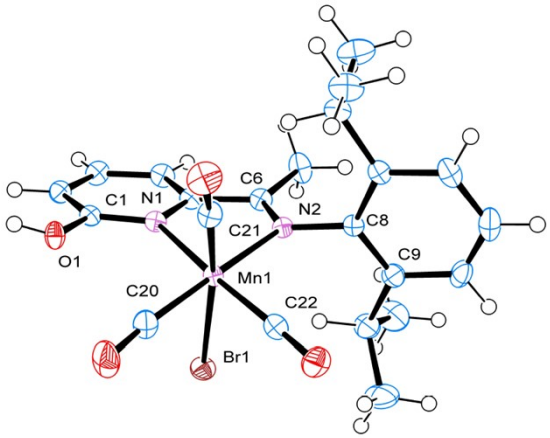


Figure S63a ORTEP representation of **Mn1a** with thermal ellipsoids set to 50% probability. Selected bond distances (Å): Br1 - Mn1 2.5377(4), Mn1 - N1 2.0746(19), Mn1 - N2 2.059(2), Mn1 - C20 1.829(3), Mn1 - C21 1.787(3), Mn1 - C22 1.805(2), O1 - C1 1.337(3), N2 - C6 1.287(3). Selected bond angles (°): N1 - Mn1 - Br1 85.94(5), N2 - Mn1 - Br1 92.40(5), N2 - Mn1 - N1 77.65(8), C21 - Mn1 - Br1 169.76(8). Selected torsion angle (°): M n1 - N2 - C8 - C9: 89.9(2).

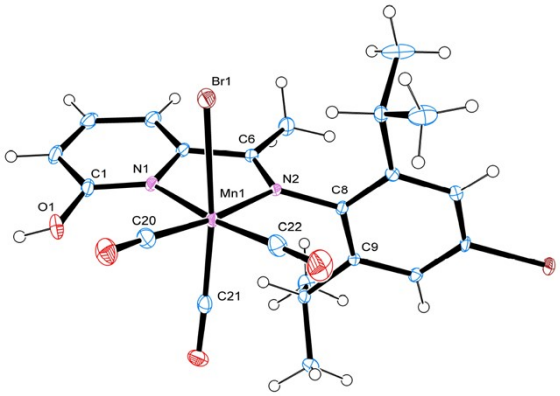


Figure S63b ORTEP representation of **Mn1b** with thermal ellipsoids set to 50% probability Br1 - Mn1 2.5540(4), Mn1 - N1 20555(18), Mn1 - N2 2.0564(17), Mn1 - C20 1.825(2), Mn1 - C21 1.794(2), Mn1 - C22 1.804(3), O1 - C1 1.328(3), N2 - C6 1.295(3). Selected bond angles (°): N1 - Mn1 - Br1 85.48(5), N2 - Mn1 - Br1 91.32(5), N2 - Mn1 - N1 77.77(8), C21 - Mn1 - Br1 170.53(8). Selected torsion angle (°): M n1 - N2 - C8 - C9: 94.9(7).

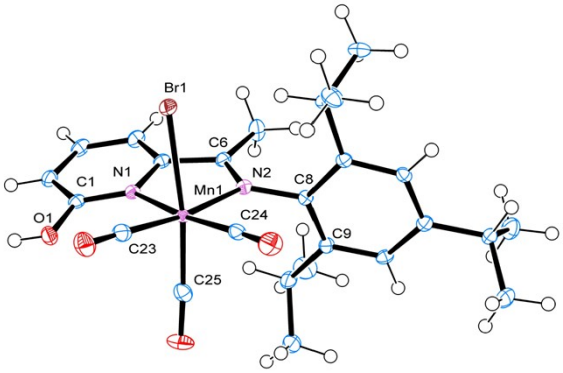


Figure S63c ORTEP representation of **Mn1c** with thermal ellipsoids set to 50% probability. Selected bond distances (Å): Br1 - Mn1 2.5538(6), Mn1 - N1 2.064(3), Mn1 - N2 2.069(3), Mn1 - C23 1.816(4), Mn1 - C24 1.818(4), Mn1 - C25 1.797(4), O1 - C1 1.330(5), N2 - C6 1.285(5). Selected bond angles (°): N1 - Mn1 - Br1 86.10 (8), N2 - Mn1 - Br1 90.05(9), N2 - Mn1 - N1 78.06(8), C25 - Mn1 - Br1 171.40(8). Selected torsion angle (°): M n1 - N2 - C8 - C9: 94.3(3).

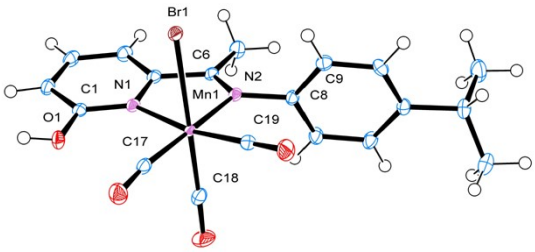


Figure S63d ORTEP representation of **Mn1d** with thermal ellipsoids set to 50% probability. Selected bond distances (Å): Br1 - Mn1 2.5470(3), Mn1 - N1 2.0736(14), Mn1 - N2 2.0300(14), Mn1 – C17 1.8277(18), Mn1 – C18 1.7971(18), Mn1 – C19 1.8094(17), O1 - C1 1.338(2), N2 - C6 1.288(2). Selected bond angles (°): N(1)-Mn(1)-Br(1) 84.57(4), N(2)-Mn(1)-N(1) 77.69(5), C(18)-Mn(1)-Br(1), 179.64(6). Selected torsion angle (°): M n1 - N2 - C8 - C9: 80.83(17).

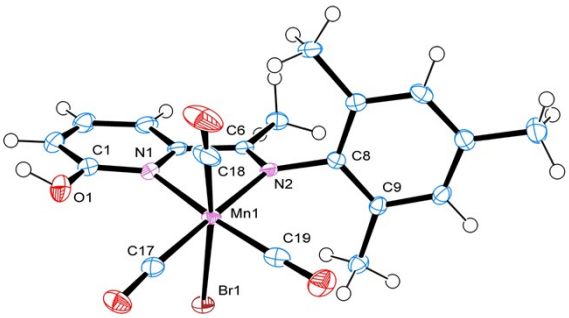


Figure S63e ORTEP representation of **Mn1e** with thermal ellipsoids set to 50% probability. Selected bond distances (Å): Br1 - Mn1 2.5590(6), Mn1 - N1 2.059(3), Mn1 - N2 2.047(3), Mn1 – C17 1.827(4), Mn1 – C18 1.809(4), Mn1 – C19 1.793(4), O1 - C1 1.326(5), N2 - C6 1.291(4) Selected bond angles (°): N1 - Mn1 - Br1 85.30(8), N2 - Mn1 - Br1 90.45(8), N2 - Mn1 - N1 77.73(11), C18 - Mn1 - Br1 171.56(12). Selected torsion angle (°): Mn1 - N2 - C8 - C9: 83.1(3).

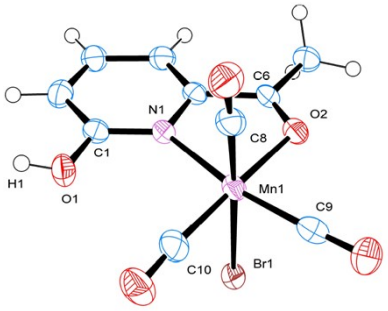


Figure S63f ORTEP representation of **Mn2** with thermal ellipsoids set to 50% probability. Selected bond distances (Å): Br1 - Mn1 2.5477(9), Mn1 - N1 2.091(4), Mn1 - O2 2.033(4), Mn1 – C8 1.805(5), Mn1 – C9 1.806(6), Mn1 – C10 1.808(6), O1 - C1 1.337(6), O2 - C6 1.234(6). Selected bond angles (°): N1 - Mn1 - Br1 88.09(11), O2 - Mn1 - Br1 87.24(10), O2 - Mn1 - N1 77.51(15), C8 - Mn1 - Br1 176.76(18),

7.2 Molecular structures of Mn1b' and Mn1d'

Crystals of **Mn1b'** suitable for single crystal X-ray diffraction were grown by slow diffusion of dichloromethane and hexane, while those for **Mn1d'** were formed through vapour diffusion of diethyl ether into DMF. For **Mn1d'**, there is disorder between CO and Br above and below the *N,N*-coordination plane: this has been modelled for C(18)O(3):Br(1A) as 92:8.

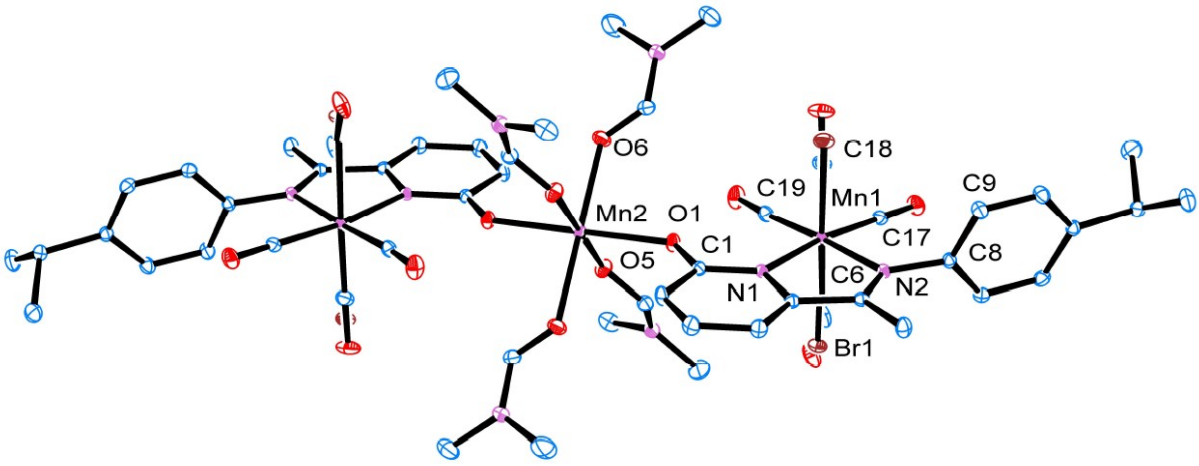


Figure S64a ORTEP representation of **Mn1d'** with thermal ellipsoids set to 50% probability. 'Half' of the molecule has been generated by symmetry, symmetry operation -x, -y+1, -z+1. Selected bond distances (Å): Br(1) - Mn(1) 2.5295(4), Mn(1) - N(1) 2.0535(16), Mn(1) - N(2), 2.0332(16) C(1) - O(1) 1.274(2), O(1) - Mn(2) 2.1485(14). Selected bond angles (°): N(1) - Mn(1) - Br(1) 86.57 (4), N(2)-Mn(1) - N(1) 77.91(6), C(18) - Mn(1) - Br(1), 178.36(11), O(5) - Mn(2) - O(6) 92.31(5).

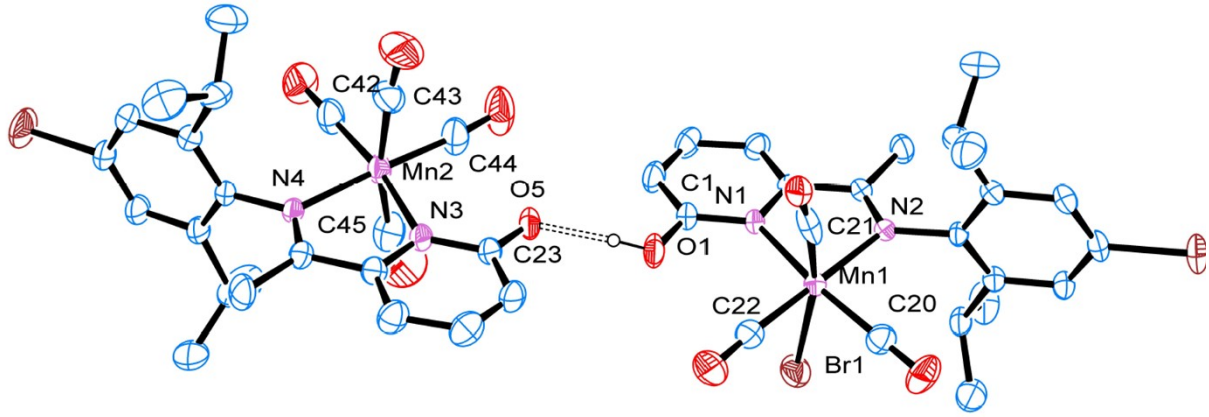


Figure S64b ORTEP representation of **Mn1b'** with the thermal ellipsoids set to 50% probability. All protons except for H1 have been removed for clarity. Selected bond distances (Å): Selected bond distances (Å): Mn(1) – N(1) 2.053(4), Mn(1) – N(2) 2071(4), Mn(1) – Br(1) 2.5343(11), Mn(1) – C(20) 1.815(6), Mn(1) – C(21) 1.813(8), Mn(1) – C(22) 1.805(6), C(1) – O(1) 1.323(7), Mn(2) – N(3) 2.081(4), Mn(2) - N(4)2.078(4), Mn(2) – C(42) 1.805(7), Mn(2) – C(43) 1.859(8), Mn(2) – C(44) 1.799(7), Mn(2) – C(45) 1.854(9), C(23) – O(5) 1.266(7). Selected Bond angles (°): N(2) - Mn(1) - N(1) 77.67(15), C(21) - Mn(1) - Br(1) 166.73(19), N(3) - Mn(2) - N(4) 76.83(17), C(45) - Mn(2) - C(43) 167.2(3).

7.3 Molecular structures of HL1a and HL1b

Crystals of H**L1a** and H**L1e** suitable for single crystal XRD were grown by standing in methanol solutions for 2 days.

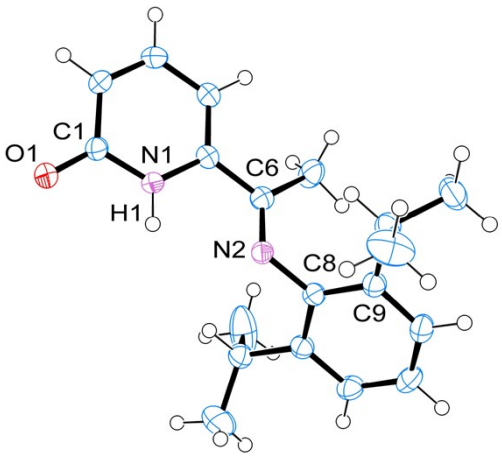


Figure S65a ORTEP representation of H**L1a** with thermal ellipsoids set to 50% probability. Selected bond distances (Å): O1 - C1 1.241(2), N2 - C6 1.276 (2), N2 – C8 1.423(2). Selected bond angles (°): C6 - N2 - C8 120.79(14), O1 - C1 - N1 121.18(10). Selected torsion angle (°): C6 - N2 - C8 - C9 73.1(2).

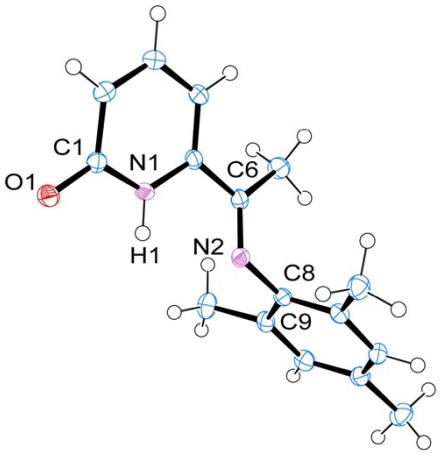


Figure S65b ORTEP representation of H**L1e** with thermal ellipsoids set to 50% probability. Selected bond distances (Å): O1 - C1 1.2450(13), N2 - C6 1.2768(2), N2 – C8 1.4215(14). Selected bond angles (°): C6 - N2 - C8 120.39(9), O1 - C1 - N1 120.49(10). Selected torsion angle (°): C6 - N2 - C8 - C9 - 87.42(13).

7.4 Crystallographic parameters

Data was collected using a using a Bruker D8 Quest diffractometer with a Photon III detector and a microfocus source with Cu-Kα radiation (λ = 1.54178) or a Bruker APEX 2000 CCD diffractometer graphite-monochromated Mo-Kα radiation (λ = 0.71073). Intensities were integrated from data recorded on 1° frames by ω or φ rotation. A multi-scan method absorption correction was applied. The structures were solved using SHELXS or SHELXT the datasets were refined by full-matrix least-squares on reflections with $F^2 \geq 2\sigma(F2)$ values, with anisotropic displacement parameters for all nonhydrogen atoms, and with constrained riding hydrogen geometries; Uiso(H) was set at 1.2 (1.5 for methyl groups) times U_{eq} of the parent atom. SHELX was employed through OLEX2 for structure solution and refinement.[9] The X-ray structure determinations and detailed data are shown in Tables S1 – S4.

Table S1 Crystal data and structure refinement for **Mn1a**, **Mn1b** and **Mn1c**.

	Mn1a	**Mn1b**	**Mn1c**
CCDC deposition number	2540706	2540707	2540708
Identification code	Q24105sp_0m	Q25004sp_0m	Q24087sp_0m
Empirical formula	$C_{23}H_{28}BrMnN_2O_5$	$C_{23}H_{27}Br_2MnN_2O_5$	$C_{26}H_{34}BrMnN_2O_5$
Formula weight	547.32	626.22	589.40
Temperature/K	120.0	120.0	120.0
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/n$	Pbca	$P2_1/n$
a/Å	9.3579(2)	8.6636(3)	8.6029(3)
b/Å	17.8308(4)	15.9084(5)	18.3931(7)
c/Å	14.6057(3)	37.4468(12)	16.9462(6)
α/°	90	90	90
β/°	91.3510(10)	90	93.5070(10)
γ/°	90	90	90
Volume/Å^3	2436.41(9)	5161.1(3)	2676.44(17)
Z	4	8	4
ρcalcg/cm^3	1.492	1.612	1.463
μ/mm^{-1}	6.625	8.084	6.072
F(000)	1120.0	2512.0	1216.0
Crystal size/mm^3	0.179 × 0.105 × 0.068	0.248 × 0.206 × 0.077	0.427 × 0.361 × 0.094
Radiation	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.826 to 144.768	9.446 to 144.382	7.1 to 145.28
Index ranges	-11 ≤ h ≤ 11, -22 ≤ k ≤ 19, -17 ≤ l ≤ 18	-10 ≤ h ≤ 10, -17 ≤ k ≤ 19, -45 ≤ l ≤ 46	-10 ≤ h ≤ 10, -22 ≤ k ≤ 22, -20 ≤ l ≤ 16
Reflections collected	28966	63063	27553
Independent reflections	4780 [R_{int} = 0.0824, R_{sigma} = 0.0463]	5087 [R_{int} = 0.0493, R_{sigma} = 0.0252]	5202 [R_{int} = 0.0494, R_{sigma} = 0.0398]
Data/restraints/parameters	4780/0/297	5087/0/306	5202/0/326
Goodness-of-fit on F^2	1.038	1.066	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0346, wR_2 = 0.0873	R_1 = 0.0300, wR_2 = 0.0784	R_1 = 0.0633, wR_2 = 0.1751
Final R indexes [all data]	R_1 = 0.0434, wR_2 = 0.0911	R_1 = 0.0309, wR_2 = 0.0.0792	R_1 = 0.0648, wR_2 = 0.1780
Largest diff. peak/hole / e Å^{-3}	0.76/-1.18	0.85/-0.56	1.94/-1.55

Table S2 Crystal data and structure refinement for **Mn1d**, **Mn1e** and **Mn2**.

	Mn1d	**Mn1e**	**Mn2**
CCDC deposition number	2540709	2540710	2540711
Identification code	Q24078sp_0m	Q24098sp_0m	Q24092sp_0m
Empirical formula	$C_{19}H_{18}BrMnN_2O_4$	$C_{20}H_{22}BrMnN_2O_5$	$C_{10}H_7BrMnNO_9$
Formula weight	473.20	505.24	356.02
Temperature/K	120.0	120.0	120.0
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/n$	P-1
a/Å	9.6305(3)	13.9705(5)	7.1382(5)
b/Å	16.9692(6)	8.0848(3)	8.0945(6)
c/Å	12.3406(4)	19.7580(7)	10.6095(8)
α/°	90	90	93.792(4)
β/°	108.1300(10)	103.6660(10)	90.167(4)
γ/°	90	90	101.706(4)
Volume/Å^3	1916.60(11)	2168.46(14)	598.87(8)
Z	4	4	2
ρcalcg/cm^3	1.640	1.548	1.974
μ/mm^{-1}	8.282	7.393	13.023
F(000)	952.0	1024.0	348.0
Crystal size/mm^3	0.195 × 0.146 × 0.096	0.33 × 0.216 × 0.132	0.139 × 0.114 × 0.058
Radiation	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)
2Θ range for data collection/°	9.166 to 144.434	7.03 to 146.382	8.354 to 144.782
Index ranges	$-11 \le h \le 11$, $-20 \le k \le 20$, $-15 \le l \le 14$	$-16 \le h \le 17$, $-9 \le k \le 9$, $-24 \le l \le 24$	$-8 \le h \le 8$, $-9 \le k \le 9$, $-13 \le l \le 12$
Reflections collected	21948	18251	11495
Independent reflections	3742 [R_{int} = 0.0369, R_{sigma} = 0.0262]	4236 [R_{int} = 0.0474, R_{sigma} = 0.0427]	2336 [R_{int} = 0.0725, R_{sigma} = 0.0481]
Data/restraints/parameters	3742/0/248	4236/0/279	2336/0/164
Goodness-of-fit on F^2	1.042	1.023	1.066
Final R indexes [I>=2σ (I)]	R_1 = 0.0223, wR_2 = 0.0596	R_1 = 0.0484, wR_2 = 0.1370	R_1 = 0.0454, wR_2 = 0.1062
Final R indexes [all data]	R_1 = 0.0227, wR_2 = 0.0597	R_1 = 0.0510, wR_2 = 0.1409	R_1 = 0.0597, wR_2 = 0.1153
Largest diff. peak/hole / e Å^{-3}	0.75/-0.80	1.46/-1.00	0.99/-0.95

Table S3 Crystal data and structure refinement for **Mn1b'** and **Mn1d'**.

	Mn1b'	**Mn1d'**
CCDC deposition number	2540712	2540713
Identification code	Q23108sp_0m	Q24037sp_0m
Empirical formula	$C_{45}H_{45}Br_3Mn_2N_4O_9$	$C_{50}H_{62}Br_2Mn_3N_8O_{12}$
Formula weight	1135.46	1291.71
Temperature/K	300.0	150
Crystal system	monoclinic	triclinic

Space group	$P2_1/n$	P-1
a/Å	19.7281(5)	9.8003(3)
b/Å	13.7214(4)	11.9289(4)
c/Å	20.1806(5)	13.5920(5)
α/°	90	107.780(2)
β/°	117.4880(10)	105.386(2)
γ/°	90	96.000(2)
Volume/Å^3	4846.1(2)	1428.77(9)
Z	4	1
ρcalcg/cm^3	1.556	1.501
μ/mm^{-1}	7.602	7.487
F(000)	2280.0	659.0
Crystal size/mm^3	0.191 × 0.1 × 0.082	0.182 × 0.117 × 0.099
Radiation	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)
2Θ range for data collection/°	5.182 to 144.688	7.194 to 144.64
Index ranges	-24 ≤ h ≤ 24, -16 ≤ k ≤ 16, -24 ≤ l ≤ 24	-12 ≤ h ≤ 12, -14 ≤ k ≤ 14, -16 ≤ l ≤ 16
Reflections collected	60602	35207
Independent reflections	9528 [R_{int} = 0.0991, R_{sigma} = 0.0536]	5587 [R_{int} = 0.0427, R_{sigma} = 0.0301]
Data/restraints/parameters	9528/1/579	5587/40/375
Goodness-of-fit on F^2	1.027	1.141
Final R indexes [I>=2σ (I)]	R_1 = 0.0600, wR_2 = 0.1501	R_1 = 0.0284, wR_2 = 0.0700
Final R indexes [all data]	R_1 = 0.0929, wR_2 = 0.1687	R_1 = 0.0293, wR_2 = 0.0704
Largest diff. peak/hole / e Å^{-3}	1.25/-1.02	0.45/-0.39

Table S4 Crystal data and structure refinement for H**L1a** and H**L1e**

	H**L1e**	H**L1a**
CCDC deposition number	2540714	2540715
Identification code	Q25011sp_0ma	15126
Empirical formula	$C_{16}H_{18}N_2O$	$C_{19}H_{24}N_2O$
Formula weight	254.32	296.40
Temperature/K	120.0	150(2)
Crystal system	monoclinic	Triclinic
Space group	$P2_1/c$	P-1
a/Å	14.5505(7)	8.866(2)
b/Å	8.3619(4)	12.571(3)
c/Å	12.1374(5)	15.275(3)
α/°	90	91.980(4)
β/°	103.028(2)	100.619(4)
γ/°	90	94.830(4)
Volume/Å^3	1438.74(11)	1665.2(6)
Z	4	4
ρcalcg/cm^3	1.174	1.182
μ/mm^{-1}	0.584	0.073

F(000)	544.0	640
Crystal size/mm^3	0.348 × 0.268 × 0.134	0.36 x 0.15 x 0.10
Radiation	CuKα (λ = 1.54178)	Mo-Kα (λ = 0.71073)
2Θ range for data collection/°	6.234 to 145.002	1.36 to 26.00°
Index ranges	-17 ≤ h ≤ 17, -10 ≤ k ≤ 10, -14 ≤ l ≤ 14	-10<=h<=10, -15<=k<=15, -18<=l<=18
Reflections collected	16057	13003
Independent reflections	2816 [R_{int} = 0.0419, R_{sigma} = 0.0342]	6446 [$R_{(int)}$ = 0.0453]
Data/restraints/parameters	2816/0/176	6446 / 0 / 427
Goodness-of-fit on F^2	1.052	0.932
Final R indexes [I>=2σ (I)]	R1 = 0.0417, wR2 = 0.1097	R1 = 0.0536, wR2 = 0.1234
Final R indexes [all data]	R1 = 0.0434, wR2 = 0.1105	R1 = 0.0801, wR2 = 0.1341
Largest diff. peak/hole / e $Å^{-3}$	0.25/-0.24	0.339/-0.306

8. Computational methods

8.1. Details of calculations

All the calculations were performed at B3LYP-D3(BJ)[10,11] method using ORCA 6.0.1 software package.[12,13] For Mn, the def2-TZVP with the auxiliary def2/J basis sets were used.[14,15] The Br atom was treated with the 6-311+g(d,p) basis set,[16–18] while the remaining atoms (C, H, N, and O) were described using the 6-31+G(d,p) basis set.[17–19] Structures were optimized using the SMD implicit solvation model,[20] with isopropanol as the solvent. Harmonic vibration frequency calculations were used to confirm the stationary points and to obtain thermodynamic data. The 3D representations of the optimized structures were generated by CYLview20.[21]

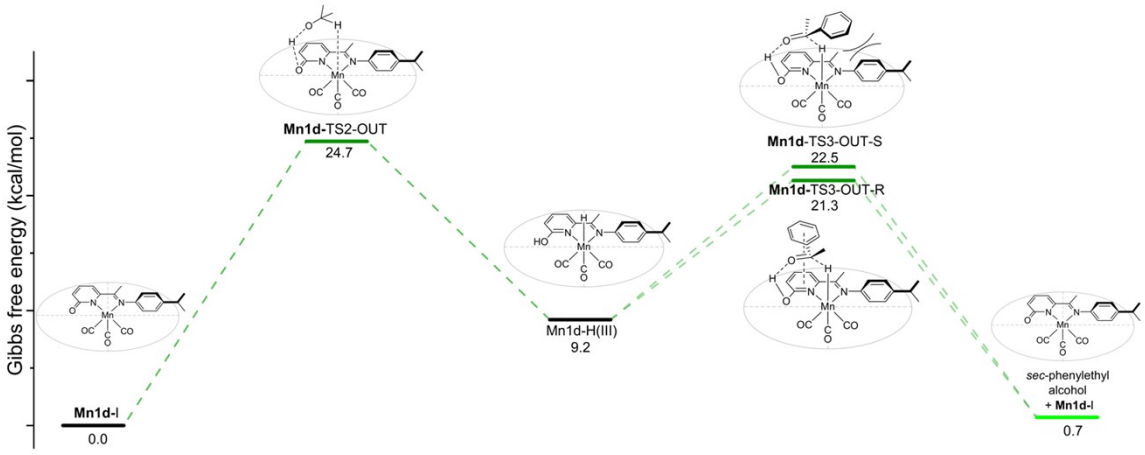


Figure S66 Outer sphere reaction pathway for the TH of **1a** using **Mn1d** and K^{t}BuO in ^{i}PrOH

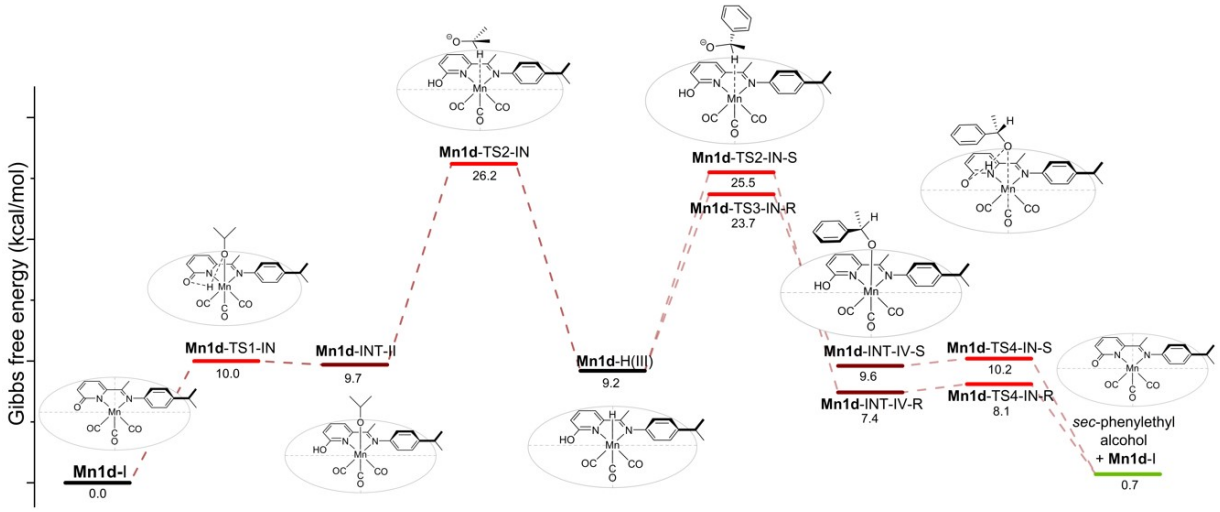


Figure S67 Inner sphere reaction pathway for the TH of **1a** using **Mn1d** and K^{t}BuO in ^{i}PrOH (where multiple transition states and intermediates have been calculated the lowest energy structure has been shown)

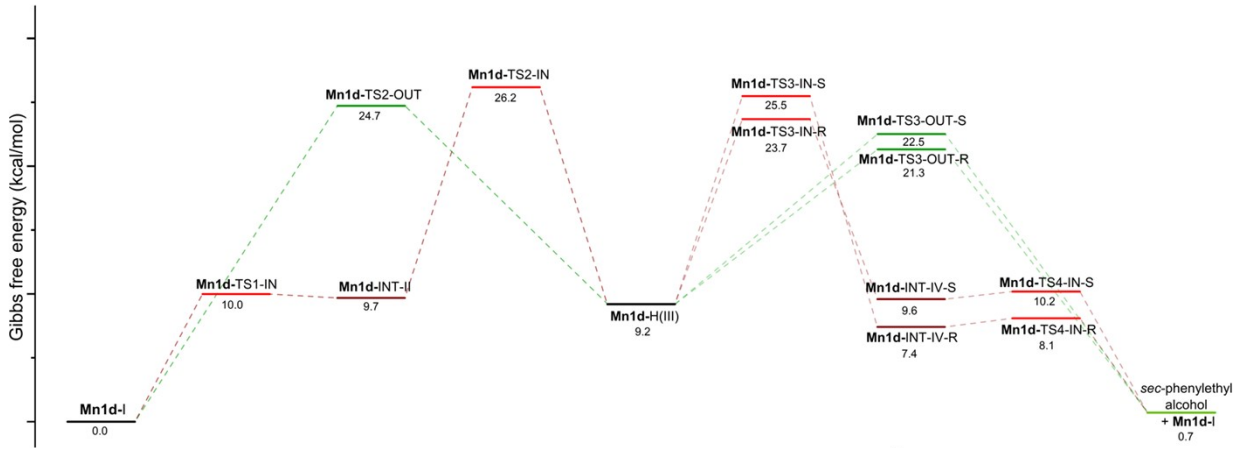


Figure S68 Inner sphere and outer sphere reaction pathways for the TH of **1a** using **Mn1d** and K^{t}BuO in ^{i}PrOH

An alternative inner sphere pathway suggested in the literature follows a more complex stepwise pathway with the initial transfer of the O-H proton of the hydrogen source (^{i}PrOH) to protonate the pyridonate scaffold and subsequently rearomatize it to neutral pyridone form with the newly formed alkoxide now coordinated maintaining the +1 oxidation state of the Mn centre (**Mn1d-**III). β-H elimination then follows (**Mn1d**-TS2-IN) forming the common intermediate (**Mn1d**-III) also found in the inner sphere pathway. Of note in the first half of the reaction pathway, is the difference in energy barrier in the proposed outer sphere pathway (from **Mn1d**-I to **Mn1d**-TS2-IN (ΔG = 24.7 kcal/mol)) compared with the inner sphere pathway **(Mn1d**-I to **Mn1d**-TS2-OUT (ΔG = 26.2 kcal/mol)). Upon approach from an acetophenone molecule to **III**, a 1,2 insertion of the substrate across the Mn-H bond calculations revealed two possible alkoxide coordinated complexes depending on the plane the insertion occurs from with a similar trend to that of outer sphere **Mn1d**-TS3-OUT energy levels the S form of this transition state (**Mn1d-TS3-IN-S**, 25.5 kcal/mol) was calculated to be higher than the corresponding R form (**Mn1d-TS3-IN-R**, 23.7 kcal/mol), these transition states ultimately then form corresponding Intermediates (**INT-IV-R**, 9.6 kcal/mol and **INT-IV-S**, 7.4 kcal/mol) with the between R and S enantiomers reaching greatest difference ($\Delta G_{\text{INT-IV-R to INT-IV-S}}$ = 2.2 kcal/mol). Finally, in similar fashion to **Mn1d-TS1**-IN, transition states **Mn1d-TS4-IN-S** and **Mn1d-TS4-IN-R** show a proton being held between the O^{-} of the alkoxide and the ligand scaffold subsequently leading the deprotonation and dearomatisation of the ligand scaffold along with the dissociation of sec-phenylethyl alcohol and the reformation of **Mn1d**-I. Whilst not conclusive the difference in highest energy transition states (**Mn1d**-TS2-IN and **Mn1d-**TS2-OUT) of 1.5 kcal/mol suggests a preference for an outer sphere pathway to preferable however magnitude of this difference it is plausible that both pathways are possible.

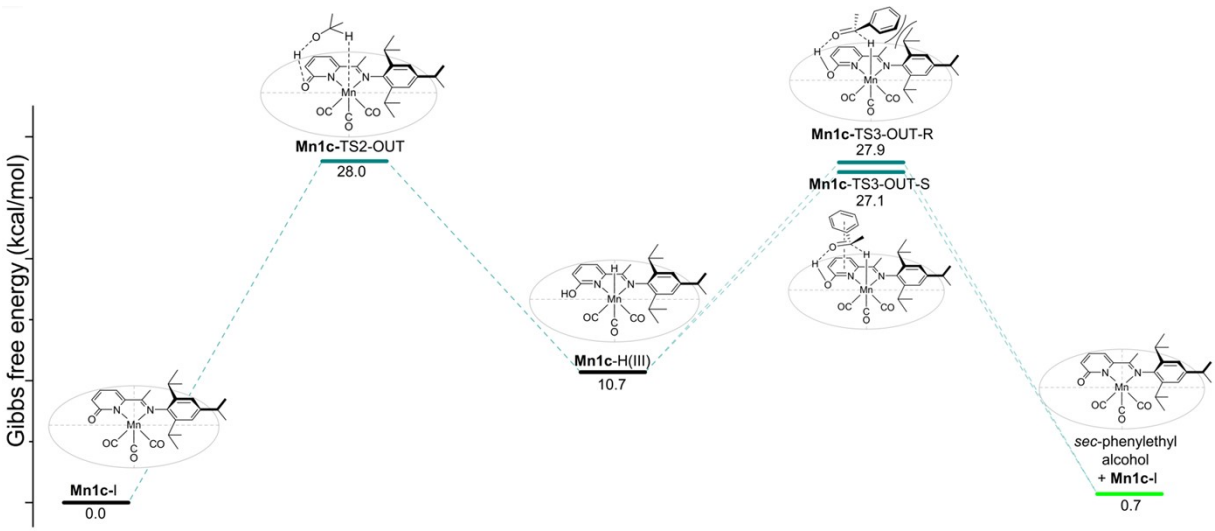
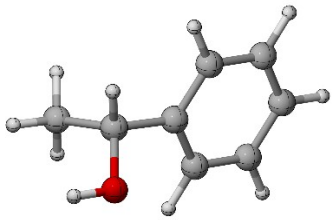


Figure S69 Outer sphere reaction pathway for the TH of **1a** using **Mn1c** and K^{t}BuO in ^{i}PrOH

8.2. Optimised Geometries for common intermediates and substrates

1-Phenylethanol

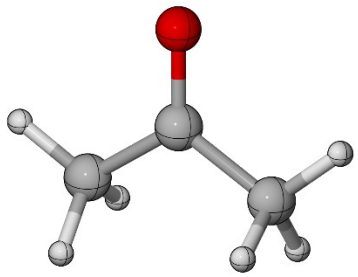
Gibbs free energy: -385.79604933 Eh



C	0.70212	-1.13147	-0.13717
C	0.07472	-2.21844	-0.76495
C	1.95775	-1.32246	0.45374
C	0.69215	-3.47171	-0.79732
H	-0.89970	-2.08466	-1.22588
C	2.58208	-2.57422	0.41564
H	2.44983	-0.48726	0.94677
C	1.94964	-3.65325	-0.20909
H	0.19325	-4.30624	-1.28325
H	3.55648	-2.70583	0.87884
H	2.43003	-4.62769	-0.23613
C	0.06432	0.24187	-0.13950
H	0.58085	0.86560	0.60226
O	-1.31587	0.09259	0.25867
H	-1.73897	0.96254	0.19840
C	0.16070	0.91703	-1.50875
H	1.20971	1.04064	-1.79992
H	-0.34393	0.31444	-2.27227
H	-0.30366	1.91032	-1.47900

Acetone

Gibbs free energy: -193.01955669 Eh

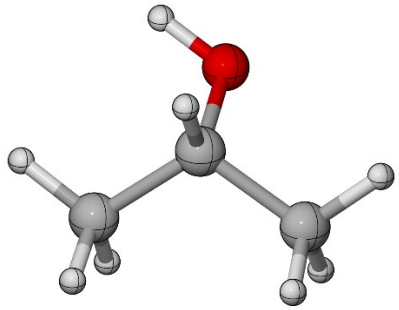


C	-0.20092	0.13892	-0.22842
C	0.50937	-1.17989	-0.39094
H	0.46288	-1.72664	0.56012
H	0.00258	-1.80064	-1.13856

H	1.55466	-1.02885	-0.67013
C	-1.69868	0.09493	-0.07019
H	-2.14717	-0.21932	-1.02181
H	-1.98346	-0.65430	0.67735
H	-2.09115	1.07559	0.20844
O	0.41531	1.20480	-0.22396

Isopropanol

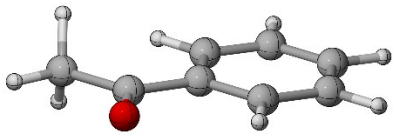
Gibbs free energy: -194.19677155 Eh



C	-0.35059	-0.01546	-0.03135
H	-1.45061	-0.01985	-0.03079
O	0.10236	0.63428	1.18000
H	-0.21612	1.54923	1.16968
C	0.15355	-1.44947	0.02611
H	-0.21365	-1.95688	0.92513
H	-0.19440	-2.00954	-0.84854
H	1.25013	-1.47377	0.03628
C	0.14482	0.73584	-1.26307
H	-0.22310	0.25771	-2.17854
H	-0.21273	1.77273	-1.25875
H	1.24112	0.74698	-1.29466

Acetophenone

Gibbs free energy: -384.62000779 Eh



C	-0.20202	0.09390	-0.28227
C	-1.70950	0.10197	-0.24224
H	-2.06897	1.13218	-0.27637
H	-2.12017	-0.45594	-1.09176
H	-2.07426	-0.38209	0.67106
O	0.42614	1.15528	-0.34666
C	0.52029	-1.21234	-0.24252
C	-0.16903	-2.43571	-0.17115
C	1.92673	-1.21866	-0.27555

C	0.53593	-3.64047	-0.13274
H	-1.25307	-2.45566	-0.14489
C	2.62873	-2.42167	-0.23713
H	2.45860	-0.27440	-0.33064
C	1.93398	-3.63587	-0.16530
H	-0.00541	-4.58061	-0.07740
H	3.71479	-2.41643	-0.26253
H	2.48147	-4.57400	-0.13516

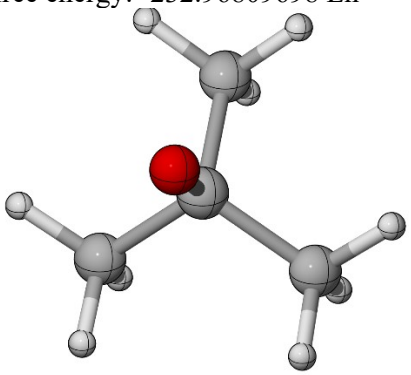
K^+ ion

Gibbs free energy: -599.75799228 Eh

K	0.00000	0.00000	0.00000

^{t}BuO-

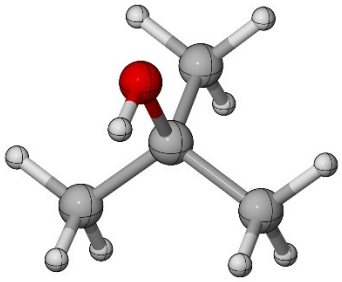
Gibbs free energy: -232.96809698 Eh



C	-3.14634	1.72980	0.00073
C	-1.59744	1.76464	-0.05770
H	-3.54627	2.75258	0.00530
H	-3.54499	1.21808	-0.88533
H	-3.52937	1.21267	0.89221
C	-1.08229	0.30182	-0.03333
C	-1.08229	2.47727	1.21882
H	0.01553	0.28919	-0.05750
H	-1.40839	-0.25181	0.85883
H	-1.44346	-0.23907	-0.91820
H	-1.40920	1.98477	2.14594
H	0.01561	2.50269	1.21823
H	-1.44164	3.51469	1.24192
O	-1.15876	2.42727	-1.20453

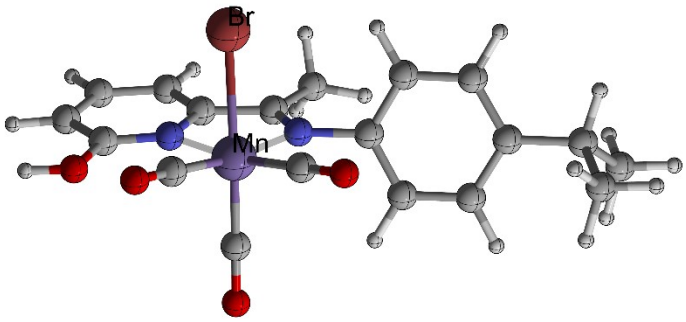
^{t}BuOH

Gibbs free energy: -233.46852378 Eh



C	-3.15613	1.72822	-0.00449
C	-1.62405	1.72421	-0.00096
H	-3.53881	2.75493	0.00199
H	-3.54210	1.22025	-0.89688
H	-3.54895	1.20824	0.87654
C	-1.08070	0.29206	-0.03912
C	-1.07494	2.48825	1.20223
H	0.01484	0.29584	-0.05891
H	-1.40790	-0.27214	0.84148
H	-1.44133	-0.23472	-0.93123
H	-1.39100	2.00961	2.13491
H	0.02051	2.50823	1.18060
H	-1.44115	3.52105	1.20472
O	-1.14262	2.44889	-1.16670
H	-1.46809	1.99507	-1.95927

Mn1d
Gibbs free energy: -4869.60588178 Eh

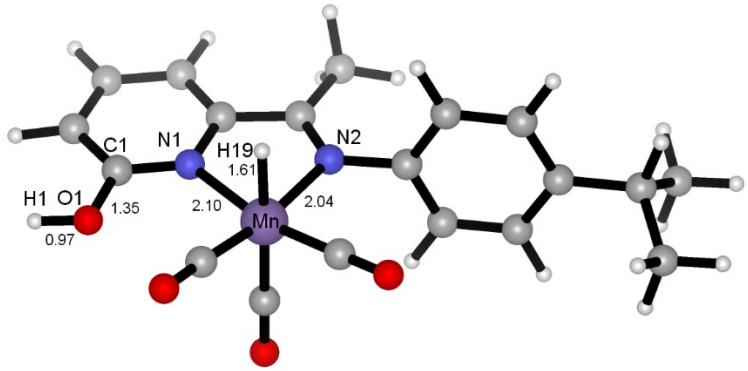


Mn	5.79402	5.17871	6.33172
O	6.02492	3.93273	8.99899
O	5.52553	2.56435	4.95422
N	5.68170	7.10058	7.15371
N	3.77652	5.47888	6.49119
C	5.21824	9.71905	8.00998
H	5.04310	10.73988	8.33438
C	4.14477	8.89442	7.65099
H	3.12729	9.26069	7.69658
C	4.41216	7.59610	7.23649
C	3.35238	6.64082	6.86679
C	1.91303	7.04252	6.95652

H	1.25278	6.19019	6.79938
H	1.70077	7.47872	7.93764
H	1.68728	7.80309	6.19977
C	2.87294	4.44859	6.08651
C	2.28863	4.48259	4.81881
H	2.48991	5.32027	4.15926
C	1.47099	3.42515	4.40984
H	1.02201	3.45568	3.41990
C	1.22141	2.32773	5.24536
C	1.82158	2.31664	6.51607
H	1.64917	1.48120	7.18897
C	2.64778	3.35913	6.93489
H	3.11983	3.33350	7.91252
C	5.92377	4.42268	7.94965
C	5.61719	3.58363	5.49854
C	6.69350	7.88869	7.52688
O	7.91651	7.32934	7.46871
H	8.59644	7.96329	7.75040
C	0.33216	1.18437	4.78552
C	-0.91756	1.04882	5.67295
C	1.10640	-0.14393	4.72406
H	-0.00284	1.42482	3.76855
H	-1.48857	1.98405	5.70126
H	-1.57616	0.25980	5.29073
H	-0.64445	0.78803	6.70247
H	1.98490	-0.06209	4.07377
H	1.45032	-0.44724	5.72014
H	0.46645	-0.94362	4.33251
C	7.58730	5.07379	6.04567
O	8.71209	4.92649	5.81054
C	6.50564	9.21520	7.95718
H	7.36720	9.81217	8.23843
Br	5.65408	6.31725	4.01489

Mn1d-III

Gibbs free energy: -2296.10143046 Eh



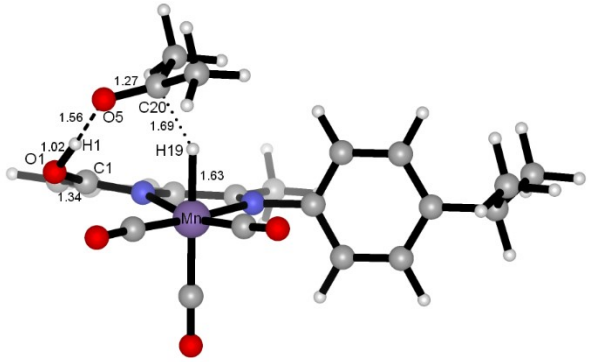
Mn	5.79138	5.18012	6.27982
O	6.12522	3.86113	8.93587
O	5.50284	2.63245	4.81094
N	5.67214	7.11816	7.08367
N	3.78075	5.49493	6.43202
C	5.19114	9.69216	8.07722
H	5.01110	10.69324	8.45608
C	4.12263	8.86470	7.71901

H	3.10026	9.20627	7.81799
C	4.39765	7.58878	7.23699
C	3.34430	6.63467	6.86467
C	1.90043	7.00646	7.01084
H	1.24796	6.16063	6.79667
H	1.70080	7.35613	8.02913
H	1.64835	7.82435	6.32580
C	2.87295	4.46426	6.03296
C	2.30662	4.47840	4.75732
H	2.52126	5.30167	4.08239
C	1.47757	3.42535	4.35947
H	1.04128	3.44222	3.36357
C	1.20036	2.35005	5.21479
C	1.78361	2.35786	6.49328
H	1.58994	1.53981	7.18164
C	2.61884	3.39768	6.90146
H	3.07717	3.38753	7.88597
C	5.96545	4.39967	7.91533
C	5.60393	3.62800	5.40875
C	6.68150	7.91611	7.45208
O	7.91512	7.39093	7.31481
H	8.59016	8.02820	7.60059
C	0.29806	1.21145	4.76828
C	-0.96899	1.12206	5.63688
C	1.04740	-0.13237	4.75353
H	-0.01498	1.43203	3.73984
H	-1.52216	2.06839	5.63127
H	-1.63607	0.33583	5.26373
H	-0.71803	0.88341	6.67739
H	1.93836	-0.08366	4.11699
H	1.36830	-0.41713	5.76269
H	0.39894	-0.92940	4.37060
H	5.68256	5.87994	4.83362
C	7.54911	5.11790	5.90509
O	8.66367	5.01026	5.58369
C	6.48546	9.21538	7.95094
H	7.34618	9.81638	8.22610

Geometries for transition states of the outer sphere reaction pathway using Mn1d

Mn1d-TS2-OUT

Gibbs free energy: -2489.09631521 Eh

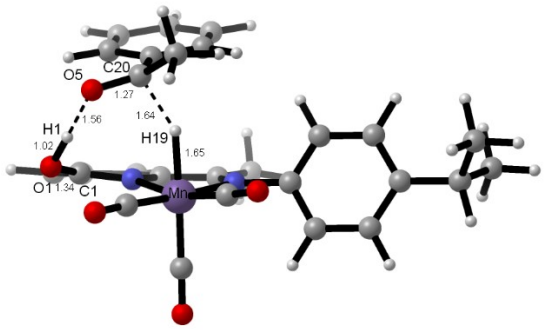


Mn	4.71677	2.88577	2.80274
O	1.87777	2.68882	0.98405
C	4.96113	2.76773	-0.39472
H	5.22883	2.68928	1.27133
O	3.83993	3.33716	-0.55479
H	2.67632	2.92147	0.39535
O	3.82042	3.30216	5.61581
O	7.14709	4.55044	3.01763
N	3.27916	1.42840	2.33911
N	5.65000	1.14161	3.31090
C	1.34282	-0.58488	2.42424
H	0.57930	-1.35472	2.47782
C	2.61718	-0.81159	2.96084
H	2.86655	-1.76068	3.41856
C	3.55583	0.20987	2.89583
C	4.94099	0.06077	3.37317
C	4.15583	3.11436	4.51878
C	6.19026	3.88965	2.97331
C	3.82851	4.36073	2.26546
O	3.31975	5.35913	1.95540
C	2.10400	1.58417	1.70740
C	1.08747	0.61226	1.77801
H	0.14143	0.81336	1.28780
C	6.21632	3.57462	-0.65305
H	6.10123	4.59199	-0.27106
H	7.10248	3.11029	-0.21415
H	6.35684	3.62648	-1.74243
C	5.06358	1.26552	-0.56244
H	4.17730	0.76364	-0.16911
H	5.11799	1.06794	-1.64321
H	5.96217	0.85772	-0.09400
C	5.43867	-1.26913	3.84562
H	4.82361	-1.62588	4.67906
H	5.36236	-2.00892	3.04090
H	6.47574	-1.21182	4.17489
C	7.02895	1.15032	3.68893
C	8.01066	0.90513	2.72429
C	7.39484	1.48699	4.99326

C	9.35881	0.98754	3.07501
H	7.71462	0.65557	1.70975
C	8.74910	1.56485	5.32941
H	6.62566	1.69114	5.73223
C	9.75307	1.32039	4.38161
H	10.11100	0.79274	2.31550
H	9.02812	1.82492	6.34770
C	11.22182	1.41734	4.76058
C	11.94306	2.51254	3.95570
C	11.93570	0.06323	4.60390
H	11.26340	1.69784	5.82070
H	11.45251	3.48487	4.07943
H	12.98317	2.61153	4.28839
H	11.95482	2.27378	2.88552
H	11.44427	-0.71633	5.19739
H	11.94020	-0.26147	3.55648
H	12.97798	0.13758	4.93636

Mn1d-TS3-OUT-R

Gibbs free energy: -2680.70212919 Eh

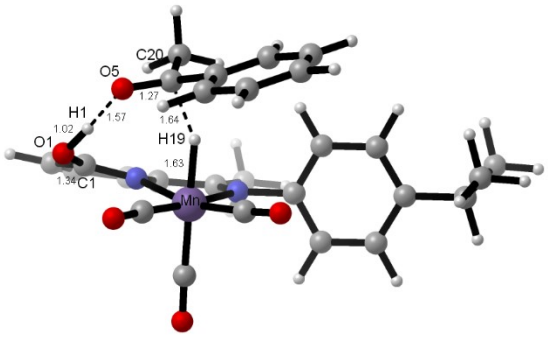


Mn	4.67757	2.86267	2.80748
O	1.79957	2.71551	1.10834
C	4.80705	2.91694	-0.37036
H	5.15107	2.83067	1.23208
O	3.67756	3.49590	-0.47338
H	2.54716	3.04217	0.49512
O	3.76464	3.05383	5.63439
O	7.00896	4.66308	3.03995
N	3.32897	1.37881	2.23132
N	5.73500	1.14018	3.17400
C	1.58121	-0.78845	1.97159
H	0.89511	-1.62524	1.88590
C	2.88013	-0.98414	2.45517
H	3.22168	-1.97292	2.73215
C	3.72159	0.11559	2.57663
C	5.10696	0.01054	3.06134
C	4.12186	2.94830	4.53314
C	6.09668	3.94246	3.00013
C	3.70492	4.32775	2.40263
O	3.15118	5.32798	2.19324
C	2.12979	1.53019	1.64309
C	1.20336	0.47557	1.55469
H	0.23392	0.67272	1.11097
C	6.03962	3.74464	-0.68349

H	5.91535	4.74885	-0.27150
H	6.96381	3.30864	-0.30148
H	6.11921	3.81982	-1.77689
C	5.67990	-1.33436	3.38667
H	6.64943	-1.25064	3.87552
H	5.00040	-1.88226	4.04673
H	5.79962	-1.92406	2.47039
C	7.10170	1.17942	3.59674
C	8.11801	0.67905	2.77449
C	7.43083	1.76826	4.82097
C	9.45053	0.77500	3.17632
H	7.86326	0.21465	1.82890
C	8.76787	1.84587	5.21666
H	6.64746	2.15974	5.46135
C	9.80167	1.35961	4.40372
H	10.22380	0.38390	2.52081
H	9.00984	2.29892	6.17508
C	11.25250	1.46245	4.84329
C	12.07728	2.32796	3.87474
C	11.89010	0.07226	5.01395
H	11.25825	1.95666	5.82302
H	11.64147	3.32769	3.76548
H	13.10401	2.44258	4.24212
H	12.12648	1.86992	2.87966
H	11.32194	-0.54131	5.72261
H	11.93021	-0.46404	4.05830
H	12.91591	0.16430	5.39020
C	4.88059	1.42366	-0.55781
C	6.05735	0.70317	-0.30049
C	3.74134	0.72953	-0.99187
C	6.08911	-0.68230	-0.45336
H	6.94194	1.22164	0.05078
C	3.77080	-0.65852	-1.14311
H	2.83327	1.28141	-1.20907
C	4.94296	-1.36982	-0.87057
H	7.00366	-1.22737	-0.23693
H	2.87707	-1.18321	-1.46934
H	4.96452	-2.45062	-0.98042

Mn1d-TS3-OUT-S

Gibbs free energy: -2680.70017842 Eh



Mn	4.69018	2.91247	2.73097
O	1.92034	2.67324	0.82552
C	5.05368	2.65751	-0.41830

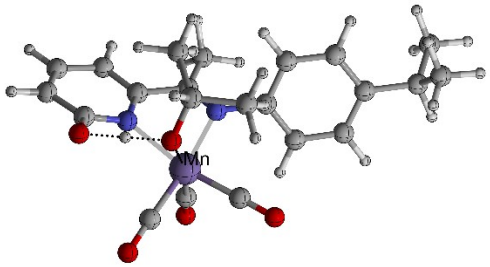
H	5.21164	2.65379	1.21142
O	3.94973	3.23445	-0.67589
H	2.74586	2.87195	0.26202
O	3.80844	3.46276	5.52394
O	7.15618	4.53631	2.85237
N	3.24822	1.46223	2.29480
N	5.59510	1.17896	3.30730
C	1.27714	-0.51056	2.41671
H	0.49784	-1.26320	2.48551
C	2.53165	-0.73418	3.00058
H	2.75131	-1.66546	3.50770
C	3.49040	0.26612	2.91308
C	4.86771	0.11396	3.41350
C	4.13562	3.22261	4.43447
C	6.18435	3.89795	2.85236
C	3.82135	4.37711	2.13315
O	3.32078	5.36794	1.78792
C	2.09918	1.60571	1.61476
C	1.06303	0.65601	1.70266
H	0.13636	0.84634	1.17274
C	5.34126	-1.20279	3.94250
H	4.71593	-1.51432	4.78646
H	5.25683	-1.97441	3.16910
H	6.37759	-1.14739	4.27513
C	6.98080	1.18584	3.65855
C	7.93431	0.89760	2.67742
C	7.38407	1.58173	4.93470
C	9.29157	1.00455	2.98034
H	7.60890	0.60506	1.68445
C	8.74796	1.68009	5.22452
H	6.63686	1.81996	5.68595
C	9.72365	1.40068	4.25686
H	10.02032	0.78378	2.20525
H	9.05686	1.98849	6.22046
C	11.20268	1.53885	4.57804
C	11.85762	2.64498	3.73163
C	11.94972	0.20486	4.40729
H	11.27841	1.83388	5.63230
H	11.34788	3.60538	3.86979
H	12.90927	2.77391	4.01417
H	11.82469	2.39578	2.66420
H	11.50193	-0.58359	5.02318
H	11.92927	-0.12906	3.36303
H	12.99993	0.31262	4.70348
C	6.32368	3.45275	-0.56946
C	7.58913	2.84606	-0.53381
C	6.23892	4.84743	-0.70151
C	8.74707	3.62171	-0.62311
H	7.68087	1.77173	-0.42347
C	7.39588	5.62183	-0.79191
H	5.26131	5.31719	-0.71968
C	8.65509	5.01158	-0.74950
H	9.72028	3.13969	-0.58834
H	7.31677	6.70129	-0.88903
H	9.55678	5.61469	-0.81233
C	5.11723	1.14622	-0.53549
H	5.29424	0.90221	-1.59223

H	5.91127	0.69566	0.06085
H	4.15788	0.71724	-0.24105

9.3. Geometries for transition states and intermediates of the inner sphere reaction pathway using Mn1d

Mn1d-TS1-IN

Gibbs free energy: -2489.11962986 Eh

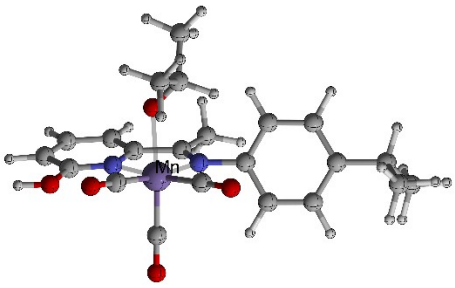


Mn	4.48689	3.42256	3.03285
O	1.64802	3.22519	1.21472
O	4.36541	3.09758	5.97918
O	6.90088	5.14647	3.13462
N	2.92970	1.95238	2.63337
N	5.45729	1.48500	3.10364
C	0.98503	-0.02010	2.67855
H	0.21079	-0.77972	2.73592
C	2.27894	-0.29988	3.16094
H	2.52607	-1.28321	3.54024
C	3.23025	0.70796	3.09919
C	4.67212	0.47965	3.35095
C	4.42939	3.21601	4.82714
C	5.97003	4.45746	3.10730
C	3.43366	4.89149	3.22812
O	2.77422	5.82498	3.41193
C	1.76074	2.15844	1.97618
C	0.72419	1.18996	2.06639
H	-0.23332	1.40567	1.60386
C	5.13757	-0.87390	3.79506
H	5.05670	-1.59842	2.97664
H	6.17415	-0.84588	4.13089
H	4.50847	-1.23141	4.61580
C	6.87617	1.33060	3.14298
C	7.52144	0.59857	2.13751
C	7.63542	1.95441	4.13682
C	8.91211	0.49553	2.13202
H	6.93184	0.12417	1.35949
C	9.02729	1.83443	4.12442
H	7.14584	2.52112	4.92174
C	9.69218	1.11109	3.12444
H	9.39189	-0.07241	1.33964
H	9.60567	2.31737	4.90841
C	11.20772	1.00125	3.11774
C	11.81402	1.63180	1.85191
C	11.66898	-0.45814	3.27714

H	11.57610	1.56614	3.98344
H	11.50922	2.67918	1.74454
H	12.90927	1.59945	1.89384
H	11.49659	1.09302	0.95121
H	11.26102	-0.90651	4.19035
H	11.34532	-1.06951	2.42626
H	12.76285	-0.51142	3.33122
C	6.32172	3.47286	-0.08245
C	4.82443	3.18315	-0.12450
H	6.50553	4.55010	-0.00450
H	6.79164	2.97599	0.77282
H	6.80849	3.10840	-0.99475
C	4.52984	1.68771	-0.24308
H	4.40019	3.68501	-1.00862
H	3.45230	1.49937	-0.29110
H	4.98109	1.29125	-1.16079
H	4.94160	1.13761	0.60578
O	4.19813	3.79222	1.01426
H	2.92207	3.50874	1.11453

Mn1d-INT-II

Gibbs free energy: -2489.12017048 Eh

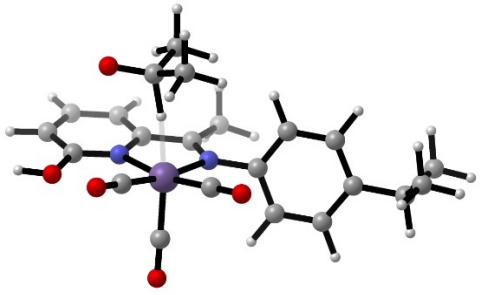


Mn	5.88530	5.37690	6.33340
O	6.25550	3.94100	8.90410
O	5.62930	2.81520	4.87230
N	5.70450	7.28420	7.41800
N	3.79420	5.63040	6.66330
C	5.16940	9.77890	8.53150
H	4.96240	10.75490	8.95920
C	4.11670	8.94910	8.12280
H	3.08990	9.27240	8.23300
C	4.41980	7.70760	7.57530
C	3.37210	6.75220	7.14490
C	1.92890	7.12130	7.31430
H	1.27730	6.26820	7.12800
H	1.74790	7.48880	8.32880

H	1.65900	7.92340	6.61740
C	2.89920	4.63760	6.16940
C	2.18300	4.85050	4.98830
H	2.26480	5.80310	4.47440
C	1.37990	3.82920	4.47350
H	0.83050	4.00200	3.55120
C	1.27010	2.58990	5.11890
C	2.00010	2.39780	6.30460
H	1.93960	1.44830	6.82940
C	2.81660	3.40190	6.82250
H	3.39170	3.23560	7.72850
C	6.10330	4.50180	7.89620
C	5.72010	3.82850	5.43280
C	6.69680	8.07150	7.83000
O	7.93670	7.56670	7.67100
H	8.60460	8.19760	7.98600
C	0.39280	1.48820	4.54810
C	-0.74370	1.11300	5.51540
C	1.21980	0.24750	4.16820
H	-0.06320	1.88130	3.63060
H	-1.35380	1.98730	5.77040
H	-1.40010	0.36000	5.06310
H	-0.34660	0.69440	6.44790
H	2.01720	0.50280	3.46080
H	1.68460	-0.20350	5.05300
H	0.58090	-0.51180	3.70160
C	7.66020	5.37050	5.98290
O	8.78960	5.32520	5.72320
C	6.47490	9.34200	8.39410
H	7.31950	9.94770	8.70620
O	5.54330	6.61960	4.70980
C	6.68970	5.73460	2.73450
C	5.36490	6.13620	3.40080
H	4.71010	5.24270	3.40030
H	7.17660	4.91860	3.27870
H	6.53230	5.39900	1.70080
H	7.37930	6.58920	2.71790
C	4.65000	7.21150	2.57110
H	3.69400	7.48070	3.03600
H	5.26560	8.11900	2.50840
H	4.44820	6.86310	1.54990

Mn1d-TS2-IN

Gibbs free energy: -2489.09391623 Eh

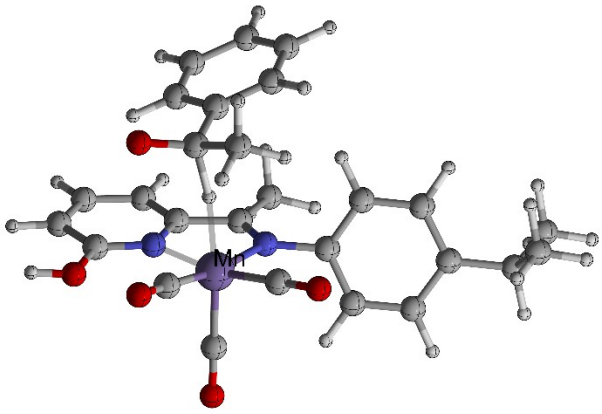


Mn	4.75170	2.95990	2.73140

C	4.96120	2.35320	-0.23150
H	4.94350	2.52570	1.02390
O	3.78770	2.63410	-0.74650
O	4.10740	3.73320	5.51740
O	7.28930	4.49770	2.70350
N	3.19740	1.58940	2.55340
N	5.66450	1.19940	3.21300
C	1.39740	-0.49340	2.07990
H	0.69820	-1.30020	1.88480
C	2.71900	-0.77510	2.45080
H	3.05920	-1.79780	2.54950
C	3.58540	0.28410	2.68160
C	4.99070	0.10040	3.08580
C	4.37160	3.42020	4.43160
C	6.30440	3.88590	2.71940
C	3.92980	4.43330	2.05460
O	3.49770	5.40700	1.60070
C	1.92430	1.84310	2.23300
C	0.98880	0.82360	1.97510
H	-0.02810	1.09030	1.70610
C	6.10840	3.30410	-0.61470
H	5.82170	4.34270	-0.42050
H	7.02810	3.08020	-0.06290
H	6.31010	3.19640	-1.68870
C	5.37490	0.87430	-0.30450
H	4.57140	0.23190	0.06790
H	5.55110	0.62110	-1.35850
H	6.28920	0.66540	0.25740
C	5.53300	-1.27210	3.32900
H	4.85270	-1.84220	3.96850
H	5.62430	-1.81040	2.37780
H	6.51450	-1.23350	3.80030
C	7.03760	1.19030	3.62140
C	8.04770	0.83900	2.72080
C	7.36850	1.62070	4.90850
C	9.38410	0.91730	3.11440
H	7.78780	0.51330	1.71940
C	8.71020	1.68320	5.29190
H	6.58220	1.90360	5.60160
C	9.74080	1.34020	4.40500
H	10.15640	0.64510	2.40040
H	8.95840	2.01200	6.29820
C	11.19700	1.43400	4.82910
C	11.95760	2.48050	3.99570
C	11.89750	0.06600	4.76140
H	11.20760	1.76580	5.87500
H	11.47960	3.46470	4.06160
H	12.98990	2.57910	4.35210
H	11.99340	2.19210	2.93830
H	11.37210	-0.68090	5.36760
H	11.94140	-0.30520	3.73050
H	12.92610	0.14350	5.13310
O	1.58540	3.14330	2.19190
H	0.66270	3.24670	1.90640

Mn1d-TS3-IN-R

Gibbs free energy: -2680.69826142 Eh

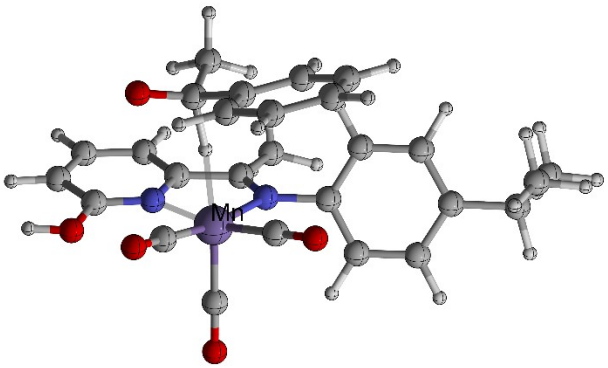


Mn	4.74950	2.92910	2.73040
C	5.04380	2.41970	-0.27130
H	5.01900	2.51890	1.03160
O	3.88400	2.74130	-0.77030
O	4.00980	3.69330	5.49570
O	7.26420	4.50120	2.77580
N	3.21330	1.54090	2.51880
N	5.66820	1.17990	3.23780
C	1.41360	-0.56190	2.13510
H	0.71420	-1.37630	1.97600
C	2.72820	-0.82480	2.53630
H	3.06680	-1.84130	2.68740
C	3.59770	0.24300	2.71100
C	5.00260	0.07410	3.11970
C	4.31170	3.38050	4.41930
C	6.28820	3.87430	2.76460
C	3.93130	4.39780	2.04260
O	3.50260	5.37760	1.59740
C	1.94530	1.77830	2.16430
C	1.01230	0.74880	1.94560
H	0.00110	1.00200	1.64400
C	6.18900	3.40200	-0.56220
H	5.83970	4.41730	-0.35500
H	7.08250	3.21220	0.03870
H	6.45530	3.33720	-1.62480
C	5.55220	-1.29200	3.37890
H	4.87080	-1.86370	4.01550
H	5.65600	-1.83230	2.43020
H	6.52900	-1.24370	3.85920
C	7.03660	1.18410	3.66070
C	8.05290	0.78710	2.78750
C	7.35660	1.66870	4.93130
C	9.38580	0.87680	3.18970
H	7.79610	0.41810	1.80170
C	8.69500	1.74120	5.32470
H	6.56540	1.98620	5.60350
C	9.73250	1.35500	4.46360
H	10.16340	0.56930	2.49590

H	8.93530	2.11270	6.31800
C	11.18490	1.46160	4.89750
C	11.95810	2.46800	4.02700
C	11.88030	0.08920	4.89610
H	11.18700	1.83830	5.92820
H	11.48290	3.45560	4.04450
H	12.98690	2.57890	4.38960
H	12.00380	2.13330	2.98380
H	11.34790	-0.62740	5.53220
H	11.92900	-0.32860	3.88350
H	12.90680	0.17940	5.27090
O	1.60870	3.07520	2.05010
H	0.68950	3.16370	1.74920
C	5.41410	0.93570	-0.36740
C	4.38380	-0.01610	-0.33640
C	6.73490	0.48500	-0.50860
C	4.66160	-1.38040	-0.42970
H	3.35890	0.32520	-0.23660
C	7.01730	-0.88160	-0.61490
H	7.55580	1.19290	-0.54010
C	5.98280	-1.82070	-0.56960
H	3.84840	-2.10040	-0.38760
H	8.04750	-1.20940	-0.72840
H	6.20260	-2.88240	-0.64370

Mn1d-TS3-IN-S

Gibbs free energy: -2680.69542972 Eh

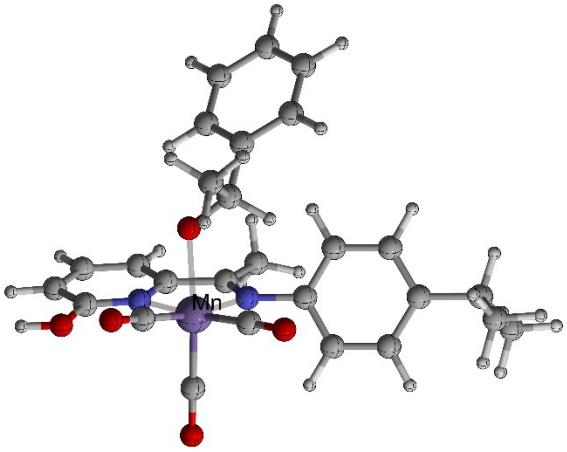


Mn	4.65670	2.95420	2.75140
C	5.04900	2.42010	-0.22670
H	4.94850	2.56520	1.05030
O	3.96390	2.83980	-0.81540
O	3.89850	3.67790	5.52280
O	7.12950	4.59500	2.79470
N	3.15460	1.53210	2.50460
N	5.61610	1.21240	3.24480
C	1.43430	-0.60790	1.98580
H	0.76700	-1.43690	1.77300
C	2.74450	-0.84620	2.42040

H	3.10700	-1.85770	2.55050
C	3.57200	0.24000	2.67050
C	4.96810	0.09630	3.11770
C	4.20720	3.38380	4.44310
C	6.17360	3.93970	2.78560
C	3.80900	4.40590	2.06450
O	3.36060	5.36920	1.60390
C	1.89070	1.74400	2.12240
C	0.99610	0.69550	1.83890
H	-0.01350	0.92990	1.51740
C	5.52720	-1.26270	3.40100
H	4.82460	-1.83910	4.00980
H	5.68170	-1.81170	2.46460
H	6.48010	-1.19940	3.92540
C	6.99330	1.23480	3.63380
C	7.98290	0.73830	2.77850
C	7.35680	1.83930	4.84030
C	9.32750	0.85850	3.12810
H	7.69970	0.27240	1.84120
C	8.70630	1.93810	5.18510
H	6.59010	2.23250	5.50030
C	9.71520	1.46220	4.33490
H	10.08180	0.47890	2.44450
H	8.97860	2.40550	6.12830
C	11.18120	1.61210	4.70470
C	11.91310	2.53780	3.71640
C	11.88700	0.24870	4.80360
H	11.21810	2.08250	5.69540
H	11.43140	3.52070	3.66170
H	12.95420	2.68540	4.02720
H	11.92080	2.10870	2.70730
H	11.38260	-0.40960	5.52040
H	11.90530	-0.25950	3.83220
H	12.92480	0.37810	5.13300
O	1.51700	3.03270	2.04080
H	0.60700	3.10310	1.70870
C	6.30410	3.28550	-0.41890
C	7.60200	2.78690	-0.23590
C	6.14530	4.64090	-0.74010
C	8.71440	3.62510	-0.36650
H	7.75890	1.74540	0.01850
C	7.25340	5.48240	-0.86620
H	5.14250	5.02980	-0.88440
C	8.54540	4.97750	-0.67810
H	9.71250	3.21990	-0.22040
H	7.10920	6.53230	-1.10950
H	9.40910	5.63020	-0.77380
C	5.28540	0.90360	-0.29980
H	5.59180	0.64620	-1.32170
H	6.04700	0.54140	0.39310
H	4.34450	0.39070	-0.08380

Mn1d-INT-IV-S

Gibbs free energy: -2680.72077660 Eh

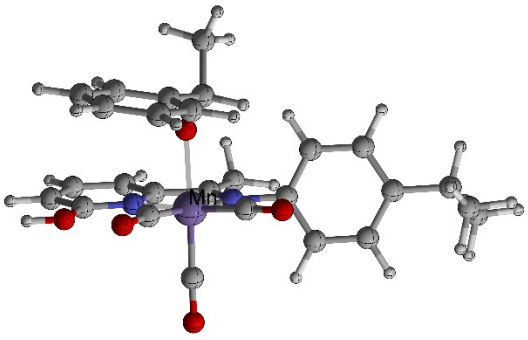


Mn	5.99330	5.33150	6.43750
O	6.17950	3.96600	9.06490
O	5.73990	2.72690	5.05280
N	5.85340	7.27630	7.44140
N	3.89670	5.70300	6.62360
C	5.40260	9.85350	8.38880
H	5.22930	10.86230	8.75000
C	4.33050	9.06910	7.94300
H	3.32210	9.46110	7.95750
C	4.59000	7.78320	7.48250
C	3.51580	6.87230	7.02280
C	2.09180	7.33930	7.07820
H	1.39710	6.51790	6.90690
H	1.87840	7.78340	8.05490
H	1.91440	8.10860	6.31750
C	2.97780	4.74670	6.10350
C	2.28540	4.99300	4.91400
H	2.40760	5.94410	4.40660
C	1.46170	4.00210	4.37480
H	0.93670	4.20080	3.44340
C	1.30390	2.76000	5.00470
C	2.00650	2.53440	6.20120
H	1.90870	1.58190	6.71470
C	2.84510	3.50740	6.74220
H	3.40010	3.31320	7.65500
C	6.10170	4.49920	8.03390
C	5.82390	3.75780	5.58090
C	6.86250	8.02060	7.89070
O	8.07400	7.43030	7.85230
H	8.76020	8.03530	8.17830
C	0.41020	1.68860	4.40280
C	-0.74370	1.31450	5.34920
C	1.21850	0.44060	4.00560
H	-0.02770	2.10970	3.48890
H	-1.33980	2.19450	5.61720
H	-1.40960	0.58530	4.87250
H	-0.36580	0.86700	6.27620
H	2.02760	0.69570	3.31160
H	1.66610	-0.03620	4.88580
H	0.57090	-0.29720	3.51700

C	7.77840	5.25570	6.14300
O	8.90620	5.17110	5.88900
C	6.68330	9.33020	8.37480
H	7.54040	9.89890	8.72070
O	5.81930	6.53650	4.74960
C	6.62340	5.63190	2.64180
C	5.41320	6.00950	3.52010
H	4.81400	5.09130	3.65190
H	7.23700	4.88570	3.16040
H	6.31660	5.21230	1.67570
H	7.24270	6.51830	2.45470
C	4.49550	6.98150	2.77760
C	3.68400	6.51890	1.72890
C	4.42730	8.33640	3.12520
C	2.83050	7.38610	1.04200
H	3.71090	5.46530	1.45840
C	3.57540	9.21110	2.43920
H	5.03700	8.69840	3.94650
C	2.77330	8.74060	1.39500
H	2.20450	7.00550	0.23850
H	3.53510	10.25950	2.72540
H	2.10680	9.41710	0.86620

Mn1d-INT-IV-S

Gibbs free energy: -2680.72423501 Eh

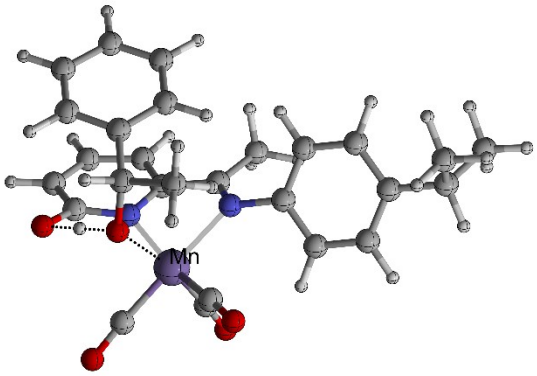


Mn	5.76590	5.15670	6.03690
O	6.25240	3.73330	8.59450
O	5.25260	2.60430	4.63130
N	5.76870	7.10320	7.10350
N	3.73550	5.50400	6.58200
C	5.43180	9.62560	8.23130
H	5.30200	10.61200	8.66560
C	4.31830	8.81500	7.97300
H	3.32000	9.16230	8.20490
C	4.52400	7.56040	7.41080
C	3.40610	6.63410	7.11030
C	2.00240	7.04450	7.43940
H	1.30400	6.22220	7.28700
H	1.93890	7.37300	8.48170
H	1.69510	7.88560	6.80740

C	2.76320	4.54360	6.17880
C	2.00550	4.75440	5.02360
H	2.11290	5.68380	4.47300
C	1.12740	3.76020	4.58350
H	0.54430	3.93060	3.68160
C	0.98490	2.55090	5.27760
C	1.75830	2.36100	6.43570
H	1.67390	1.43440	6.99680
C	2.64780	3.33830	6.88080
H	3.25560	3.17340	7.76540
C	6.05980	4.29130	7.59210
C	5.44760	3.61410	5.17070
C	6.82120	7.87440	7.36850
O	8.02010	7.34240	7.05640
H	8.73590	7.95880	7.28230
C	0.02820	1.47780	4.78490
C	-1.07400	1.18430	5.81760
C	0.77610	0.18880	4.40130
H	-0.45490	1.86710	3.87970
H	-1.62850	2.09370	6.07670
H	-1.78740	0.45260	5.42030
H	-0.65040	0.77200	6.74120
H	1.54660	0.38600	3.64710
H	1.26510	-0.25890	5.27480
H	0.07950	-0.55180	3.99060
C	7.52820	4.99770	5.62300
O	8.65310	4.78960	5.43080
C	6.69920	9.15790	7.93320
H	7.58900	9.75010	8.12130
O	5.24410	6.36250	4.45470
C	5.37900	5.95920	3.11750
H	4.89480	4.97920	2.94590
C	6.84040	5.80270	2.70900
C	7.32400	4.59110	2.20040
C	7.73960	6.86930	2.86940
C	8.67420	4.43990	1.86210
H	6.64000	3.75370	2.08130
C	9.08650	6.72700	2.53130
H	7.38230	7.81100	3.27820
C	9.56070	5.50810	2.02760
H	9.03320	3.48830	1.47750
H	9.77020	7.56190	2.66510
H	10.61050	5.39390	1.77050
C	4.66340	6.97500	2.21280
H	5.10650	7.97200	2.32620
H	4.72970	6.68630	1.15640
H	3.60380	7.03600	2.48810

Mn1d-TS4-IN-R

Gibbs free energy: -2680.71973569 Eh

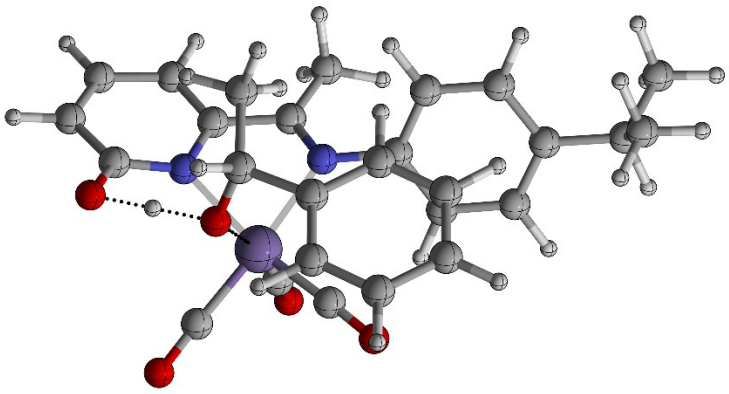


Mn	4.48710	3.42230	3.03310
O	1.64810	3.22530	1.21440
O	4.31882	3.15061	5.98173
O	6.83757	5.23443	3.06603
N	2.95217	1.95128	2.62348
N	5.48389	1.48552	3.19517
C	1.02229	-0.04400	2.63224
H	0.25825	-0.81517	2.66734
C	2.30870	-0.30796	3.13742
H	2.55780	-1.28964	3.51839
C	3.25200	0.70976	3.09858
C	4.67835	0.49082	3.42912
C	4.40735	3.24820	4.82952
C	5.93961	4.50298	3.07790
C	3.40786	4.87404	3.20633
O	2.73464	5.79825	3.38626
C	1.78067	2.15045	1.96178
C	0.75706	1.16838	2.02838
H	-0.19477	1.37810	1.55179
C	5.09613	-0.84084	3.97840
H	4.39844	-1.15149	4.76139
H	5.07733	-1.60696	3.19510
H	6.10055	-0.80211	4.39893
C	6.89539	1.33944	3.36350
C	7.61488	0.40332	2.60504
C	7.59084	2.16092	4.25810
C	9.00084	0.31264	2.72618
H	7.09220	-0.25884	1.92480
C	8.97723	2.04976	4.38142
H	7.05704	2.87254	4.87652
C	9.71157	1.13611	3.61342
H	9.53040	-0.41582	2.11836
H	9.49548	2.69206	5.08929
C	11.22220	1.04260	3.74221
C	11.92295	1.40753	2.42170
C	11.66366	-0.34813	4.23057
H	11.52741	1.77682	4.49844
H	11.63260	2.40803	2.08105
H	13.01197	1.39409	2.54869
H	11.66864	0.69357	1.62922

H	11.18682	-0.60464	5.18358
H	11.40242	-1.12465	3.50179
H	12.75013	-0.37648	4.37552
C	6.32417	3.41478	-0.06058
C	4.81558	3.22469	-0.15707
H	6.55415	4.48038	0.03783
H	6.74220	2.89445	0.80683
H	6.82119	3.03824	-0.96164
H	4.44839	3.81658	-1.00827
O	4.19610	3.79280	1.01260
H	2.92090	3.50950	1.11050
C	4.36561	1.78857	-0.38351
C	3.12750	1.54709	-0.99770
C	5.11888	0.69201	0.04913
C	2.63007	0.24781	-1.12477
H	2.53931	2.38621	-1.35946
C	4.63140	-0.61145	-0.07764
H	6.09036	0.85586	0.49455
C	3.37800	-0.83764	-0.65473
H	1.66087	0.08254	-1.58815
H	5.22834	-1.44813	0.27608
H	2.99098	-1.84916	-0.74562

Mn1d-TS4-IN-R

Gibbs free energy: -2680.72317047 Eh



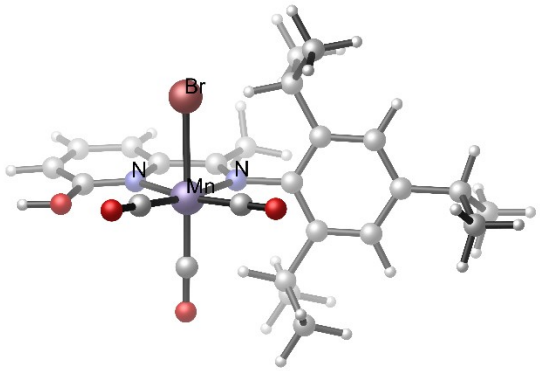
Mn	4.48710	3.42230	3.03310
O	1.64810	3.22530	1.21440
O	4.36018	3.16998	5.98524
O	6.91603	5.13275	3.13497
N	2.91982	1.97066	2.66157
N	5.43773	1.46171	3.18103
C	0.93648	0.03189	2.76159
H	0.14944	-0.71266	2.83849
C	2.22157	-0.25094	3.26343

H	2.44835	-1.22387	3.67988
C	3.19168	0.73725	3.17422
C	4.62137	0.48985	3.46537
C	4.42683	3.25700	4.83042
C	5.98469	4.44683	3.08982
C	3.45514	4.90742	3.20205
O	2.80876	5.85322	3.36896
C	1.75287	2.17491	1.99840
C	0.70059	1.22623	2.11103
H	-0.25073	1.44602	1.63786
C	5.03545	-0.84254	4.01537
H	4.36968	-1.12417	4.83662
H	4.96243	-1.62223	3.24882
H	6.06004	-0.81788	4.38584
C	6.84931	1.26686	3.26190
C	7.47741	0.36108	2.39600
C	7.62577	2.01021	4.15520
C	8.86332	0.21716	2.41595
H	6.87729	-0.21121	1.69548
C	9.01324	1.84862	4.17279
H	7.15454	2.69886	4.84753
C	9.65955	0.96060	3.30221
H	9.32722	-0.47938	1.72311
H	9.60286	2.43038	4.87721
C	11.17243	0.82150	3.31156
C	11.78764	1.32025	1.99175
C	11.61198	-0.62230	3.60931
H	11.54992	1.46100	4.11947
H	11.51144	2.36177	1.79352
H	12.88189	1.26080	2.03241
H	11.44952	0.71170	1.14458
H	11.19338	-0.97803	4.55786
H	11.28619	-1.30748	2.81769
H	12.70468	-0.68371	3.67547
C	4.84951	3.22332	-0.13067
C	4.69636	1.70737	-0.20486
H	4.34880	3.65723	-1.00958
H	3.63378	1.44786	-0.24007
H	5.17069	1.31655	-1.11261
H	5.13943	1.21240	0.66136
O	4.19860	3.79010	1.01540
H	2.92360	3.50630	1.11550
C	6.28155	3.73508	-0.12051
C	6.50144	5.10863	-0.31732
C	7.38288	2.91433	0.14546
C	7.78482	5.64978	-0.23167
H	5.65433	5.75764	-0.52681
C	8.67184	3.45153	0.24061
H	7.24506	1.85082	0.29124
C	8.87717	4.82084	0.05636
H	7.93458	6.71565	-0.38371
H	9.51047	2.79796	0.46309
H	9.87717	5.23983	0.13205

9.4. Geometries for transition states of the outer sphere reaction pathway using Mn1c

Mn1c

Gibbs free energy: -5105.211943 Eh

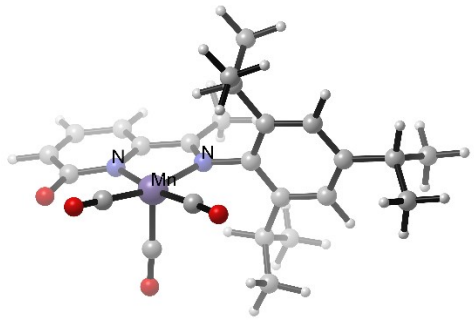


Mn	5.79400	5.17870	6.33170
O	6.02490	3.93270	8.99900
O	5.52550	2.56440	4.95420
N	5.68170	7.10060	7.15370
N	3.77650	5.47890	6.49120
C	5.21820	9.71910	8.01000
H	5.04310	10.73990	8.33440
C	4.14480	8.89440	7.65100
H	3.12730	9.26070	7.69660
C	4.41220	7.59610	7.23650
C	3.35240	6.64080	6.86680
C	1.91300	7.04250	6.95650
H	1.25280	6.19020	6.79940
H	1.70080	7.47870	7.93760
H	1.68730	7.80310	6.19980
C	2.87290	4.44860	6.08650
C	2.28860	4.48260	4.81880
C	1.47100	3.42510	4.40980
H	1.02200	3.45570	3.41990
C	1.22140	2.32770	5.24540
C	1.82160	2.31660	6.51610
H	1.64920	1.48120	7.18900
C	2.64780	3.35910	6.93490
C	5.92380	4.42270	7.94960
C	5.61720	3.58360	5.49850
C	6.69350	7.88870	7.52690
O	7.91650	7.32930	7.46870
H	8.59640	7.96330	7.75040
C	0.33220	1.18440	4.78550
C	-0.91760	1.04880	5.67290
C	1.10640	-0.14390	4.72410
H	-0.00280	1.42480	3.76850

H	-1.48860	1.98410	5.70130
H	-1.57620	0.25980	5.29070
H	-0.64450	0.78800	6.70250
H	1.98490	-0.06210	4.07380
H	1.45030	-0.44720	5.72010
H	0.46640	-0.94360	4.33250
C	7.58730	5.07380	6.04570
O	8.71210	4.92650	5.81050
C	6.50560	9.21520	7.95720
H	7.36720	9.81220	8.23840
Br	5.65410	6.31720	4.01490
C	2.57430	5.67160	3.88270
C	1.43640	6.65680	3.96020
C	2.78280	5.16660	2.47810
H	3.51670	6.15900	4.24880
H	1.30220	7.01570	5.00900
H	1.63610	7.54080	3.30750
H	0.48220	6.18320	3.62440
H	3.62970	4.43960	2.44690
H	1.86370	4.65410	2.10380
H	3.01750	6.01180	1.78680
C	3.31720	3.32280	8.32130
C	3.78980	1.92200	8.61460
C	2.34440	3.81470	9.36210
H	4.20030	4.01410	8.27810
H	4.50820	1.58090	7.83080
H	4.30240	1.87910	9.60590
H	2.92770	1.21220	8.63610
H	2.00960	4.85280	9.12310
H	1.44460	3.15430	9.40300
H	2.81940	3.82100	10.37290

Mn1c-I

Gibbs free energy: -2530.55182730 Eh

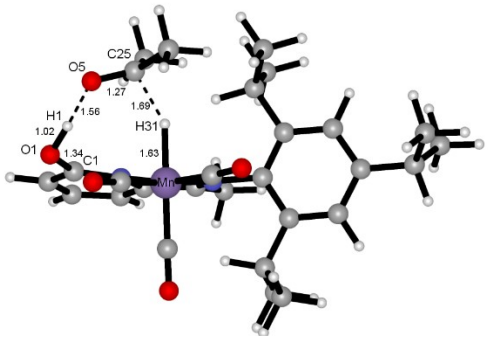


Mn	5.71605	5.34173	6.12180
O	6.79989	4.06530	8.52837
O	5.50179	2.71737	4.72784
N	5.62207	7.15879	6.98550

N	3.74031	5.46467	6.52423
C	5.18269	9.64031	8.20791
H	5.00498	10.60642	8.67236
C	4.09562	8.76641	7.95900
H	3.08531	9.04356	8.23170
C	4.36211	7.55428	7.35861
C	3.31154	6.56972	7.05647
C	1.87673	6.85915	7.35897
H	1.23021	6.04296	7.04066
H	1.75186	7.01205	8.43663
H	1.56284	7.78141	6.85989
C	2.83285	4.42825	6.11398
C	2.34502	4.44293	4.79449
C	1.50237	3.39605	4.39790
H	1.10505	3.39255	3.38613
C	1.15597	2.35209	5.26170
C	1.68440	2.36304	6.55892
H	1.43643	1.55518	7.24140
C	2.52765	3.38529	7.00721
C	6.36419	4.53465	7.56119
C	5.55788	3.74932	5.24991
C	6.71247	7.96353	7.26242
O	7.88516	7.58093	6.99970
C	0.23927	1.23144	4.79758
C	-1.05150	1.17257	5.63294
C	0.96008	-0.12802	4.80879
H	-0.04232	1.45301	3.76017
H	-1.58243	2.13139	5.61217
H	-1.72707	0.40153	5.24358
H	-0.83395	0.92961	6.67988
H	1.86731	-0.10154	4.19416
H	1.25064	-0.41207	5.82731
H	0.30529	-0.91460	4.41498
C	7.40871	5.51817	5.43521
O	8.44116	5.51645	4.91392
C	6.45166	9.25574	7.86593
H	7.30922	9.89496	8.05047
C	2.70340	5.55291	3.81459
C	1.48430	6.44578	3.52241
C	3.30818	5.00016	2.51338
H	3.46597	6.18581	4.27886
H	1.07289	6.86928	4.44479
H	1.76576	7.27523	2.86280
H	0.68998	5.87434	3.02742
H	4.18605	4.37766	2.71694
H	2.58435	4.39517	1.95588
H	3.62200	5.82628	1.86454
C	3.10060	3.34370	8.41627
C	3.96347	2.08668	8.62304
C	1.99309	3.43980	9.47944
H	3.74971	4.21363	8.54405
H	4.74563	2.01386	7.85966
H	4.44746	2.11249	9.60621
H	3.35548	1.17605	8.57153
H	1.39657	4.34941	9.34732
H	1.31554	2.57952	9.42712
H	2.43048	3.46338	10.48463

Mn1c-TS2-OUT

Gibbs free energy: -2724.70400909 Eh

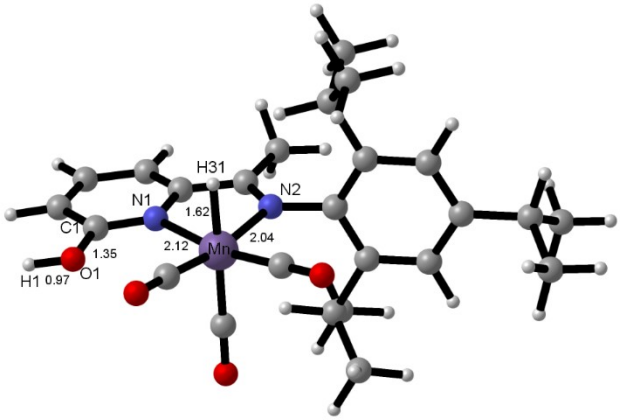


Mn	4.71680	2.88580	2.80270
O	1.87780	2.68880	0.98400
C	4.96110	2.76770	-0.39470
H	5.22880	2.68930	1.27130
O	3.83990	3.33720	-0.55480
H	2.67630	2.92150	0.39530
O	3.82040	3.30220	5.61580
O	7.14710	4.55040	3.01760
N	3.27920	1.42840	2.33910
N	5.65000	1.14160	3.31090
C	1.34280	-0.58490	2.42420
H	0.57930	-1.35470	2.47780
C	2.61720	-0.81160	2.96080
H	2.86650	-1.76070	3.41860
C	3.55580	0.20990	2.89580
C	4.94100	0.06080	3.37320
C	4.15580	3.11440	4.51880
C	6.19030	3.88960	2.97330
C	3.82850	4.36070	2.26550
O	3.31970	5.35910	1.95540
C	2.10400	1.58420	1.70740
C	1.08750	0.61230	1.77800
H	0.14140	0.81340	1.28780
C	6.21630	3.57460	-0.65300
H	6.10120	4.59200	-0.27110
H	7.10250	3.11030	-0.21420
H	6.35680	3.62650	-1.74240
C	5.06360	1.26550	-0.56240
H	4.17730	0.76360	-0.16910
H	5.11800	1.06790	-1.64320
H	5.96220	0.85770	-0.09400
C	5.43870	-1.26910	3.84560
H	4.82360	-1.62590	4.67910
H	5.36240	-2.00890	3.04090
H	6.47570	-1.21180	4.17490
C	7.02890	1.15030	3.68890
C	8.01070	0.90510	2.72430
C	7.39480	1.48700	4.99330
C	9.35880	0.98750	3.07500
C	8.74910	1.56490	5.32940

C	9.75310	1.32040	4.38160
H	10.11100	0.79270	2.31550
H	9.02810	1.82490	6.34770
C	11.22180	1.41730	4.76060
C	11.94310	2.51250	3.95570
C	11.93570	0.06320	4.60390
H	11.26340	1.69780	5.82070
H	11.45250	3.48490	4.07940
H	12.98320	2.61150	4.28840
H	11.95480	2.27380	2.88550
H	11.44430	-0.71630	5.19740
H	11.94020	-0.26150	3.55650
H	12.97800	0.13760	4.93640
C	7.59080	0.55130	1.28550
C	7.83710	-0.91460	1.03640
C	8.34760	1.41920	0.31330
H	6.49220	0.76550	1.20170
H	7.26650	-1.53570	1.76810
H	7.51440	-1.19820	0.00540
H	8.92290	-1.15460	1.14080
H	8.14900	2.49880	0.51800
H	9.44670	1.24020	0.39900
H	8.03820	1.19640	-0.73650
C	6.30410	1.77650	6.04120
C	6.68490	2.99730	6.83870
C	6.12000	0.56750	6.92210
H	5.35370	1.97820	5.47920
H	6.81520	3.87810	6.16480
H	5.89330	3.24050	7.58820
H	7.64340	2.82680	7.38600
H	5.83870	-0.32240	6.30910
H	7.06390	0.33350	7.47150
H	5.31370	0.74740	7.67380

Mn1c-III

Gibbs free energy: -2531.71194594 Eh



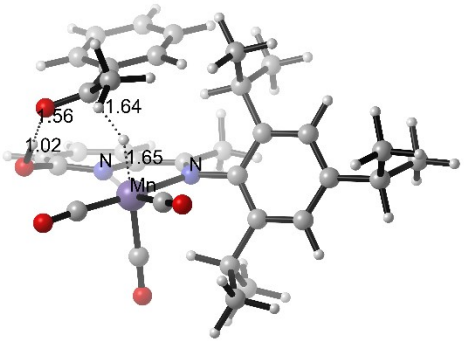
Mn	5.76879	5.19121	6.25495
O	6.10196	3.87482	8.91307
O	5.47999	2.60935	4.84790

N	5.66092	7.14215	7.06931
N	3.76157	5.55310	6.37886
C	5.24615	9.63264	8.27223
H	5.09942	10.60563	8.73250
C	4.14912	8.83598	7.95437
H	3.13954	9.16181	8.14001
C	4.39775	7.60285	7.29654
C	3.33728	6.68337	6.85288
C	1.89770	7.06860	6.99999
H	1.23187	6.28161	6.64741
H	1.66962	7.27417	8.04890
H	1.69485	7.97991	6.43095
C	2.86359	4.50701	5.98454
C	2.33229	4.45639	4.70089
C	1.52673	3.37403	4.32384
H	1.10806	3.35187	3.32074
C	1.24145	2.32487	5.20763
C	1.80338	2.38799	6.49377
H	1.61386	1.58697	7.20341
C	2.61221	3.45468	6.88430
C	5.93420	4.41869	7.89797
C	5.57682	3.62120	5.41605
C	6.69119	7.91146	7.45114
O	7.91215	7.38533	7.24684
H	8.60173	7.99550	7.56029
C	0.34793	1.16433	4.79332
C	-0.92048	1.09185	5.66268
C	1.09521	-0.18127	4.81415
H	0.03284	1.35478	3.75985
H	-1.47581	2.03667	5.63622
H	-1.58578	0.29588	5.30510
H	-0.67083	0.87540	6.70855
H	1.99502	-0.14849	4.19034
H	1.39938	-0.45794	5.83073
H	0.44806	-0.98081	4.43450
H	5.68816	5.86068	4.77831
C	7.53819	5.08498	5.90404
O	8.66081	4.93950	5.60436
C	6.52805	9.18070	8.02764
H	7.40139	9.77215	8.28139
C	2.60879	5.60980	3.71574
C	1.36628	6.47870	3.63156
C	3.00087	5.05623	2.35135
H	3.46410	6.20670	4.14882
H	1.09526	6.87932	4.65239
H	1.54212	7.34083	2.94007
H	0.49159	5.88915	3.23658
H	3.92878	4.42294	2.42495
H	2.17239	4.43068	1.91559
H	3.21171	5.88394	1.62682
C	3.25579	3.45716	8.28390
C	3.74403	2.06892	8.61015
C	2.25897	3.93614	9.30310
H	4.12269	4.16406	8.25127
H	4.46895	1.71436	7.83536
H	4.25183	2.05618	9.60427
H	2.88904	1.35111	8.64640

H	1.92105	4.97382	9.06715
H	1.36351	3.27100	9.31889
H	2.71629	3.93599	10.32249

Mn1c-TS3-OUT-R

Gibbs free energy: -2916.30587083 Eh

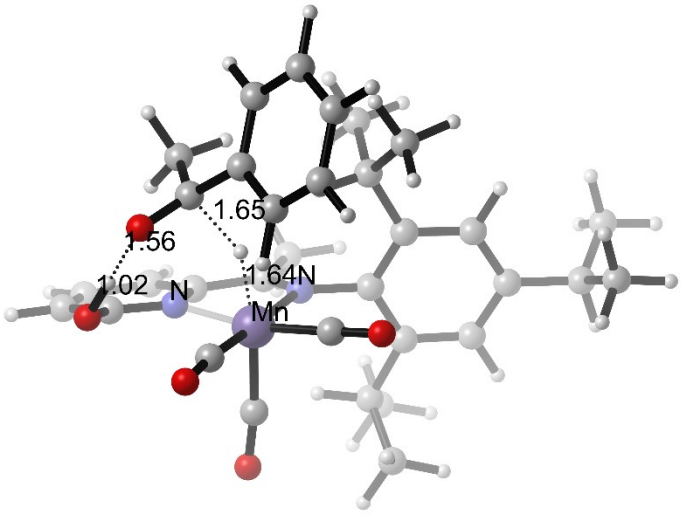


Mn	4.67760	2.86270	2.80750
O	1.79960	2.71550	1.10830
C	4.80700	2.91690	-0.37040
H	5.15110	2.83070	1.23210
O	3.67760	3.49590	-0.47340
H	2.54720	3.04220	0.49510
O	3.76460	3.05380	5.63440
O	7.00900	4.66310	3.04000
N	3.32900	1.37880	2.23130
N	5.73500	1.14020	3.17400
C	1.58120	-0.78840	1.97160
H	0.89510	-1.62520	1.88590
C	2.88010	-0.98410	2.45520
H	3.22170	-1.97290	2.73210
C	3.72160	0.11560	2.57660
C	5.10700	0.01050	3.06130
C	4.12190	2.94830	4.53310
C	6.09670	3.94250	3.00010
C	3.70490	4.32770	2.40260
O	3.15120	5.32800	2.19320
C	2.12980	1.53020	1.64310
C	1.20340	0.47560	1.55470
H	0.23390	0.67270	1.11100
C	6.03960	3.74460	-0.68350
H	5.91530	4.74890	-0.27150
H	6.96380	3.30860	-0.30150
H	6.11920	3.81980	-1.77690
C	5.67990	-1.33440	3.38670
H	6.64940	-1.25060	3.87550
H	5.00040	-1.88230	4.04670
H	5.79960	-1.92410	2.47040
C	7.10170	1.17940	3.59670
C	8.11800	0.67910	2.77450
C	7.43080	1.76830	4.82100

C	9.45050	0.77500	3.17630
C	8.76790	1.84590	5.21670
C	9.80170	1.35960	4.40370
H	10.22380	0.38390	2.52080
H	9.00980	2.29890	6.17510
C	11.25250	1.46240	4.84330
C	12.07730	2.32800	3.87470
C	11.89010	0.07230	5.01400
H	11.25830	1.95670	5.82300
H	11.64150	3.32770	3.76550
H	13.10400	2.44260	4.24210
H	12.12650	1.86990	2.87970
H	11.32190	-0.54130	5.72260
H	11.93020	-0.46400	4.05830
H	12.91590	0.16430	5.39020
C	4.88060	1.42370	-0.55780
C	6.05740	0.70320	-0.30050
C	3.74130	0.72950	-0.99190
C	6.08910	-0.68230	-0.45340
H	6.94190	1.22160	0.05080
C	3.77080	-0.65850	-1.14310
H	2.83330	1.28140	-1.20910
C	4.94300	-1.36980	-0.87060
H	7.00370	-1.22740	-0.23690
H	2.87710	-1.18320	-1.46930
H	4.96450	-2.45060	-0.98040
C	7.75610	0.01920	1.43090
C	8.17370	-1.42870	1.45370
C	8.41630	0.77460	0.30620
H	6.64100	0.08530	1.32220
H	7.67210	-1.96590	2.29430
H	7.89620	-1.93340	0.49670
H	9.27900	-1.51750	1.58760
H	8.09140	1.84290	0.31050
H	9.52790	0.74330	0.41030
H	8.14510	0.32720	-0.68070
C	6.31880	2.32390	5.73010
C	6.76510	3.63440	6.32600
C	5.98590	1.30970	6.79400
H	5.41900	2.49500	5.08150
H	7.00540	4.36780	5.51910
H	5.96150	4.06810	6.96920
H	7.67650	3.49060	6.95530
H	5.65860	0.34910	6.32820
H	6.87720	1.10520	7.43540
H	5.16210	1.68290	7.44940

Mn1c-TS3-OUT-S

Gibbs free energy: -2916.30463883 Eh



Mn	4.69630	2.85850	2.80350
O	1.83290	2.71610	1.09170
C	4.82000	2.90480	-0.37600
H	5.17370	2.82760	1.23220
O	3.71570	3.53240	-0.47230
H	2.57910	3.05380	0.48180
O	3.27146	3.17853	5.39037
O	7.03865	4.56352	3.40517
N	3.34214	1.38307	2.24310
N	5.71559	1.12845	3.28346
C	1.54429	-0.75187	2.06670
H	0.83814	-1.57437	2.01592
C	2.83570	-0.95547	2.56982
H	3.15074	-1.93662	2.90095
C	3.70194	0.12717	2.64657
C	5.06910	0.01114	3.17452
C	3.90153	3.00437	4.42953
C	6.11648	3.89201	3.18332
C	3.78415	4.34133	2.34030
O	3.24756	5.34890	2.12285
C	2.14492	1.54103	1.65257
C	1.19745	0.50205	1.59599
H	0.23227	0.70503	1.14557
C	5.61609	-1.33611	3.53406
H	6.65257	-1.26691	3.85915
H	5.02573	-1.79180	4.33604
H	5.55550	-1.99982	2.66477
C	7.01798	1.15526	3.89810
C	8.16301	1.27780	3.08242
C	7.12352	1.11495	5.30302
C	9.41351	1.33925	3.70634
C	8.40284	1.18722	5.87199
C	9.55779	1.29698	5.09821
H	10.30158	1.42039	3.08872
H	8.49855	1.15964	6.95480
C	10.92945	1.37767	5.74889
C	11.61485	2.72179	5.45142
C	11.82624	0.19923	5.33068
H	10.77643	1.31252	6.83400

H	10.99008	3.56560	5.76612
H	12.57251	2.79229	5.98089
H	11.81502	2.83171	4.37849
H	11.35352	-0.76178	5.56521
H	12.03201	0.22145	4.25373
H	12.78729	0.24160	5.85734
C	8.06614	1.29272	1.56517
C	8.25153	-0.12951	1.00360
C	9.05319	2.27011	0.91476
H	7.05571	1.60861	1.29270
H	7.49968	-0.81598	1.40653
H	8.15502	-0.13106	-0.08920
H	9.24318	-0.52362	1.25847
H	8.91860	3.28825	1.29454
H	10.09466	1.98141	1.08921
H	8.90285	2.28606	-0.16619
C	5.91695	1.01635	6.22419
C	5.82817	2.25044	7.14088
C	5.94067	-0.27534	7.06297
H	5.01391	0.98714	5.61086
H	5.85801	3.18095	6.56645
H	4.89781	2.23301	7.71764
H	6.66227	2.26695	7.85252
H	6.01089	-1.16433	6.42685
H	6.79371	-0.28352	7.75141
H	5.02532	-0.35590	7.66121
C	6.06334	3.67819	-0.75249
C	6.90658	3.20487	-1.76709
C	6.33852	4.91952	-0.16048
C	8.00852	3.96094	-2.18123
H	6.69528	2.25427	-2.24506
C	7.45371	5.65702	-0.55012
H	5.68758	5.29451	0.62164
C	8.29428	5.18096	-1.56515
H	8.64889	3.58829	-2.97595
H	7.67407	6.60127	-0.05953
H	9.16524	5.75610	-1.86607
C	4.84713	1.40878	-0.61894
H	4.71683	1.25128	-1.69777
H	5.80149	0.97164	-0.32180
H	4.02527	0.90670	-0.11255

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