Supporting information: Sterically hindered CO_2 reduction catalysts for solar energy conversion

James D. Shipp,* Heather Carson, Steven J. P. Spall, Simon C. Parker, Dimitri Chekulaev, Natalie Jones, Mikhail Ya. Mel'nikov,[a] Craig C. Robertson, Anthony J. H. M. Meijer, Julia A. Weinstein*

Department of Chemistry, University of Sheffield, S3 7HF, U.K.

[a] Department of Chemistry, Moscow Lomonosov State University, Moscow, Russia

Part S1: Additional experimental data

UV-vis spectra

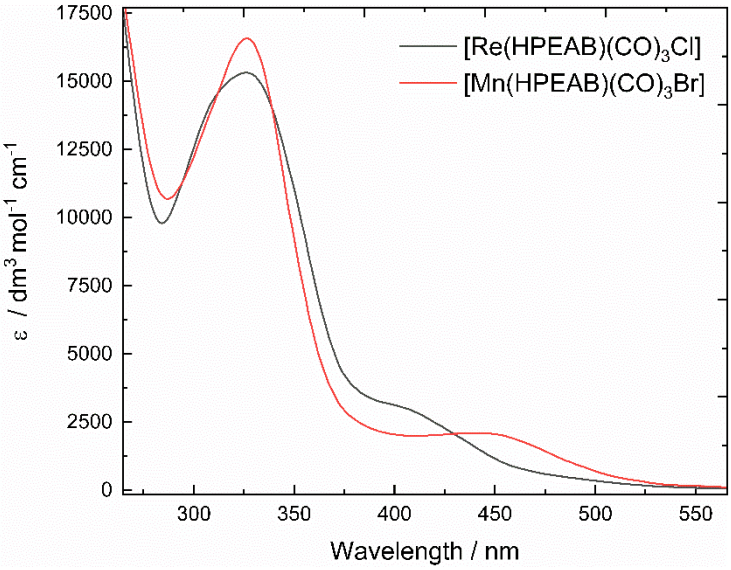


Figure S1. UV-vis absorption spectra of [Re(HPEAB)$(CO)_3$Cl] and [Mn(HPEAB)$(CO)_3$Br] in dichloromethane, as stated on the graph.

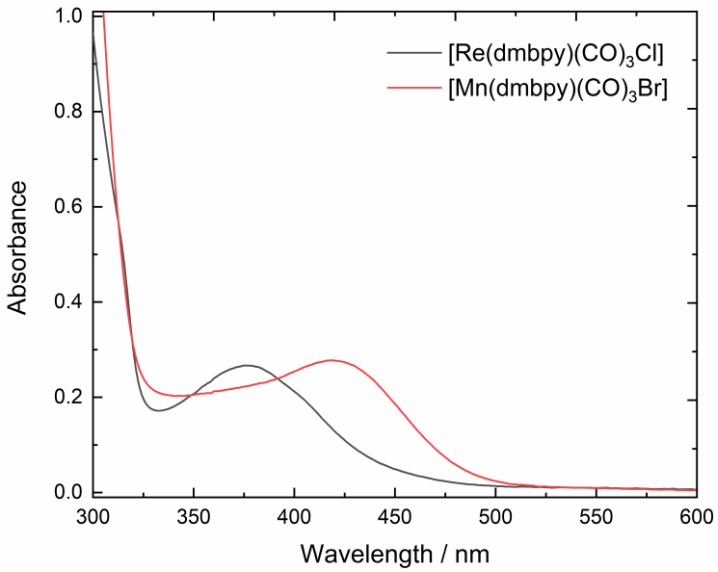


Figure S2. UV-vis absorption spectra of [Re(dmbpy)(CO)$_3$Cl] and [Mn(dmbpy)(CO)$_3$Br] in dichloromethane, as stated on the graph.

FT-IR spectra

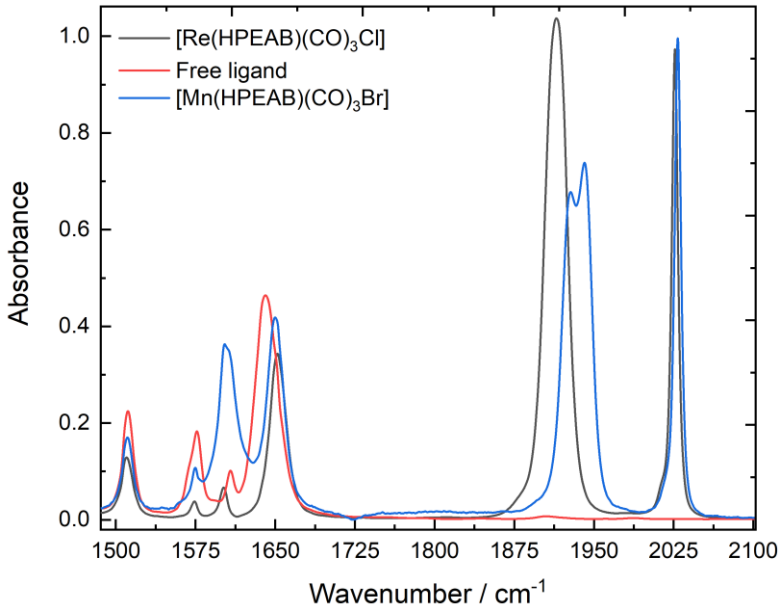


Figure S3. FT-IR absorption spectra of [Re(HPEAB)(CO)$_3$Cl] and [Mn(HPEAB)(CO)$_3$Br] in dichloromethane, as stated on the graph (Free ligand = 6,6′-{N-(4-hexylphenyl)-N(ethyl)-amido}-2,2′-bipyridine)

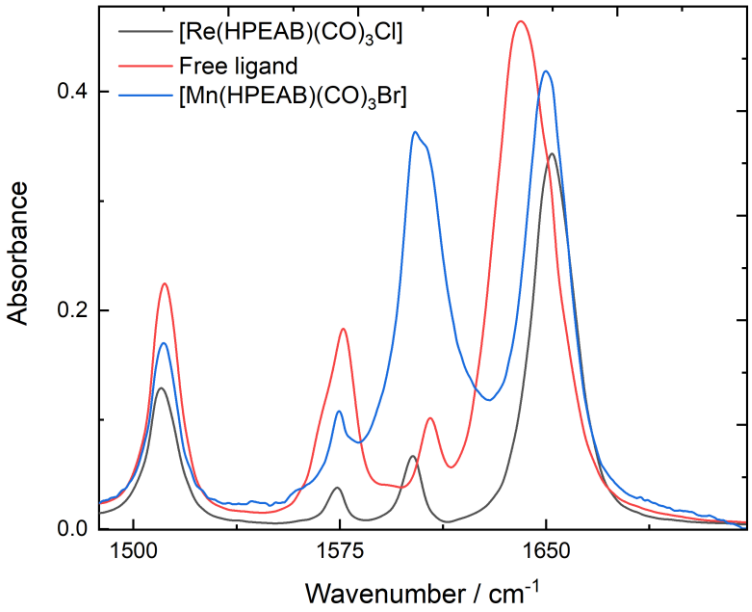


Figure S4. FT-IR absorption spectra of [Re(HPEAB)(CO)$_3$Cl] and [Mn(HPEAB)(CO)$_3$Br] in dichloromethane, as stated on the graph, focussing on the ligand-centred vibrational modes (Free ligand = 6,6'-{N-(4-hexylphenyl)-N(ethyl)-amido}-2,2'-bipyridine).

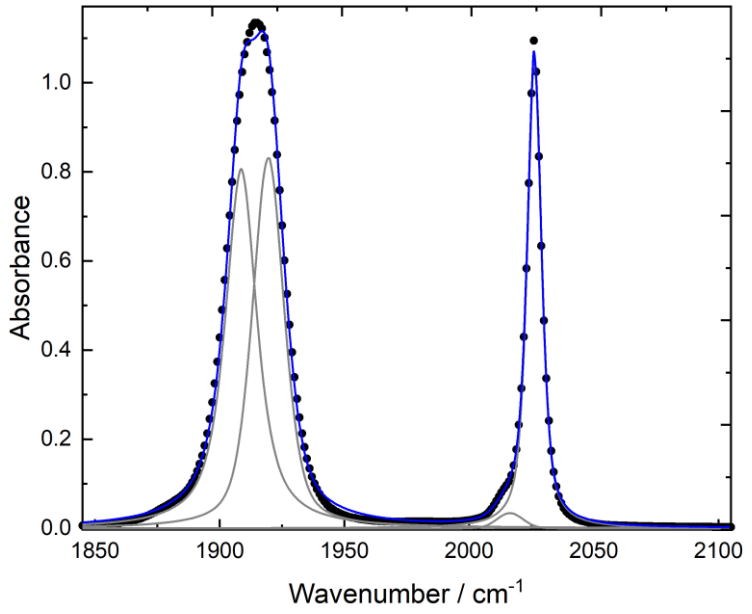


Figure S5. FT-IR spectrum of [Re(HPEAB)(CO)$_3$Cl] in dichloromethane (dots) in the 1850-2100 cm^{-1} region, deconvoluted by fitting of pseudo-Voight profiles (grey), to produce the model spectrum (blue).

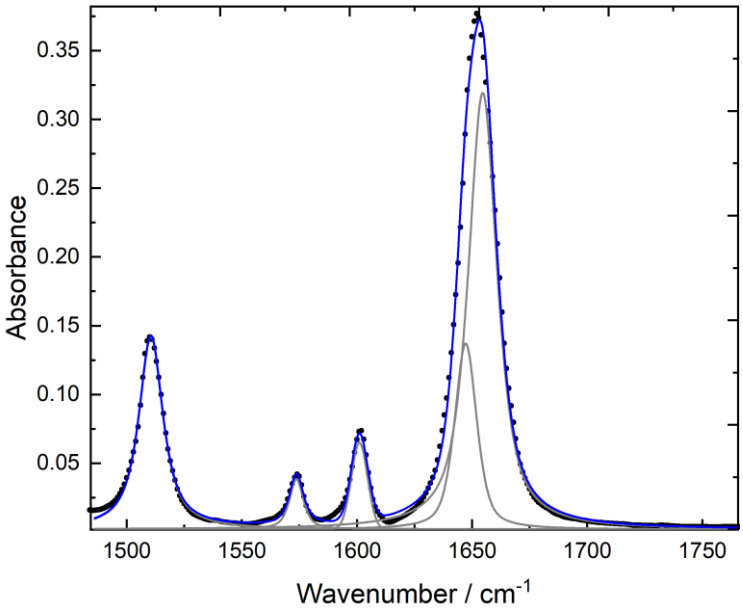


Figure S6. FT-IR spectrum of [Re(HPEAB)$(CO)_3$Cl] in dichloromethane (dots) in the 1475-1780 cm^{-1} region, deconvoluted by fitting of pseudo-Voight profiles (grey), to produce the model spectrum (blue).

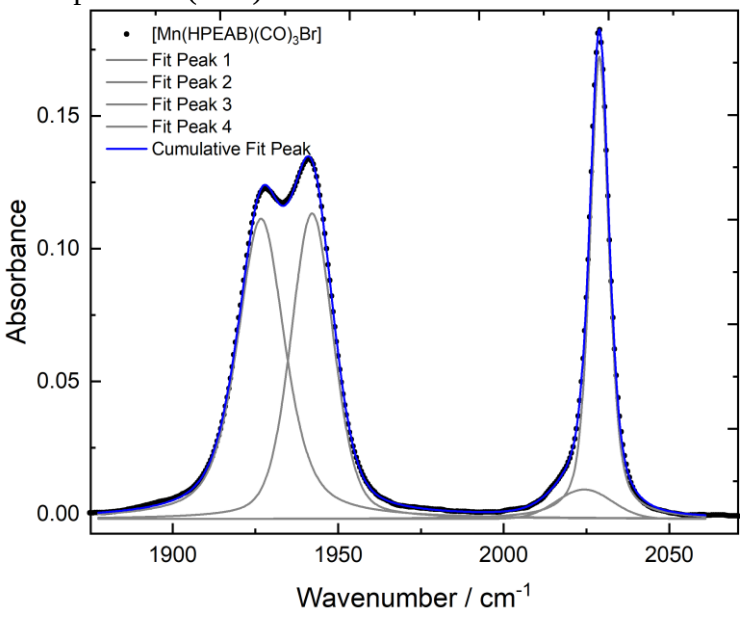


Figure S7. FT-IR spectrum of [Mn(HPEAB)(CO)3Br] in dichloromethane (dots) in the 1875-2075 cm^{-1} region, deconvoluted by fitting of pseudo-Voight profiles (grey), to produce the model spectrum (blue).

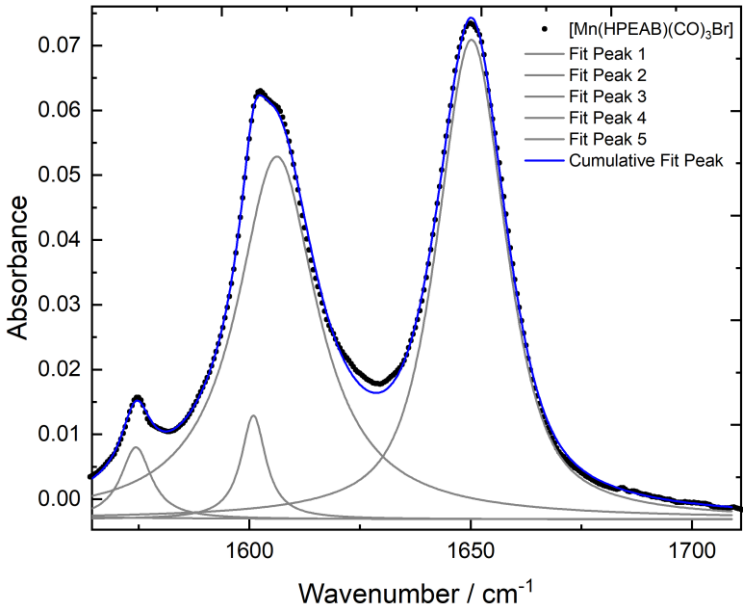


Figure S8. FT-IR spectrum of [Mn(HPEAB)(CO)3Br] in dichloromethane (dots) in the 1525-1725 cm^{-1} region, deconvoluted by fitting of pseudo-Voight profiles (grey), to produce the model spectrum (blue).

NMR spectra

Analysis of NMR spectral data

^{1}H NMR spectra (ESI fig. S9-S15) revealed changes in the proton environments of the ligand following complexation of the diimine to the $[M(CO)_5(X)]$ starting material. For example, in the free ligand the ethyl groups show the expected triplet-quartet for the CH_3CH_2 two-spin system. However, upon complexation the quartet was split into two multiplets of equal intensity. This change to an A_3MX-type spectrum shows that the protons in the methylene group were no longer equivalent. The suggested explanation for this observation is the planar chirality of the complexes, which renders the CH_2 protons diastereotopic because of the limited rotation between the planes of the bipyridyl and phenyl rings. The CH_2 multiplet-multiplet separation in the Re complex was 0.33 ppm, compared to 0.06 ppm in the Mn complex. The smaller coupling constant could indicate faster interconversion between diastereoisomers, a result of reduced steric hindrance with the smaller metal centre.

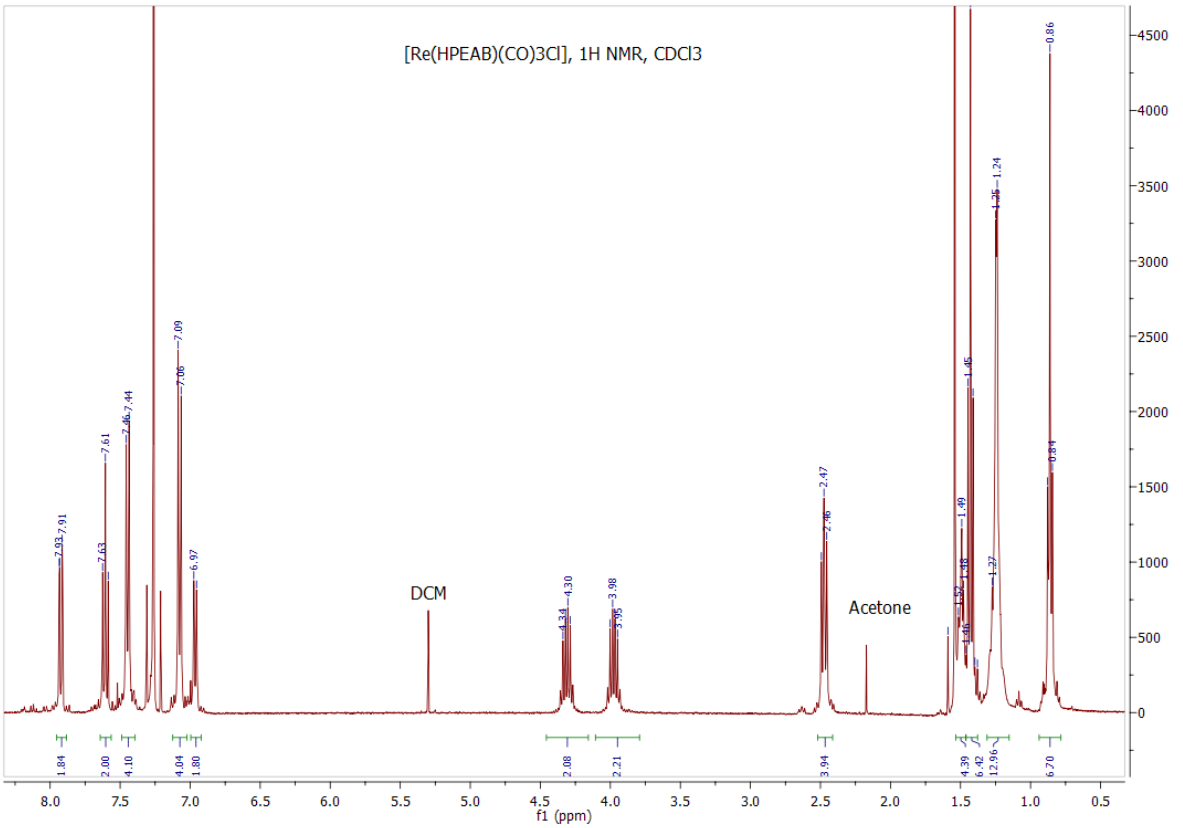


Figure S9. ^{1}H NMR spectrum of [Re(HPEAB)(CO)$_3$Cl] (400 MHz, CDCl$_3$).

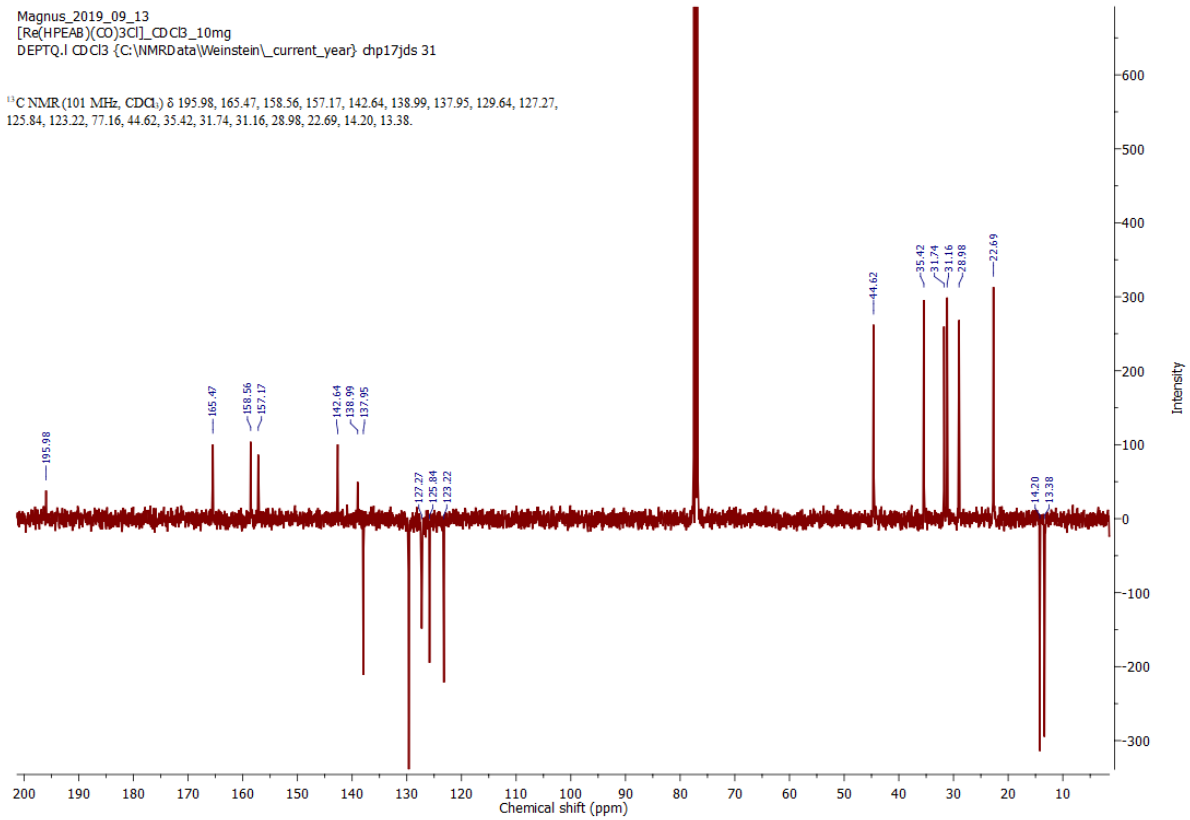


Figure S10. ^{13}C NMR spectrum of [Re(HPEAB)(CO)$_3$Cl] (400 MHz, CDCl$_3$).

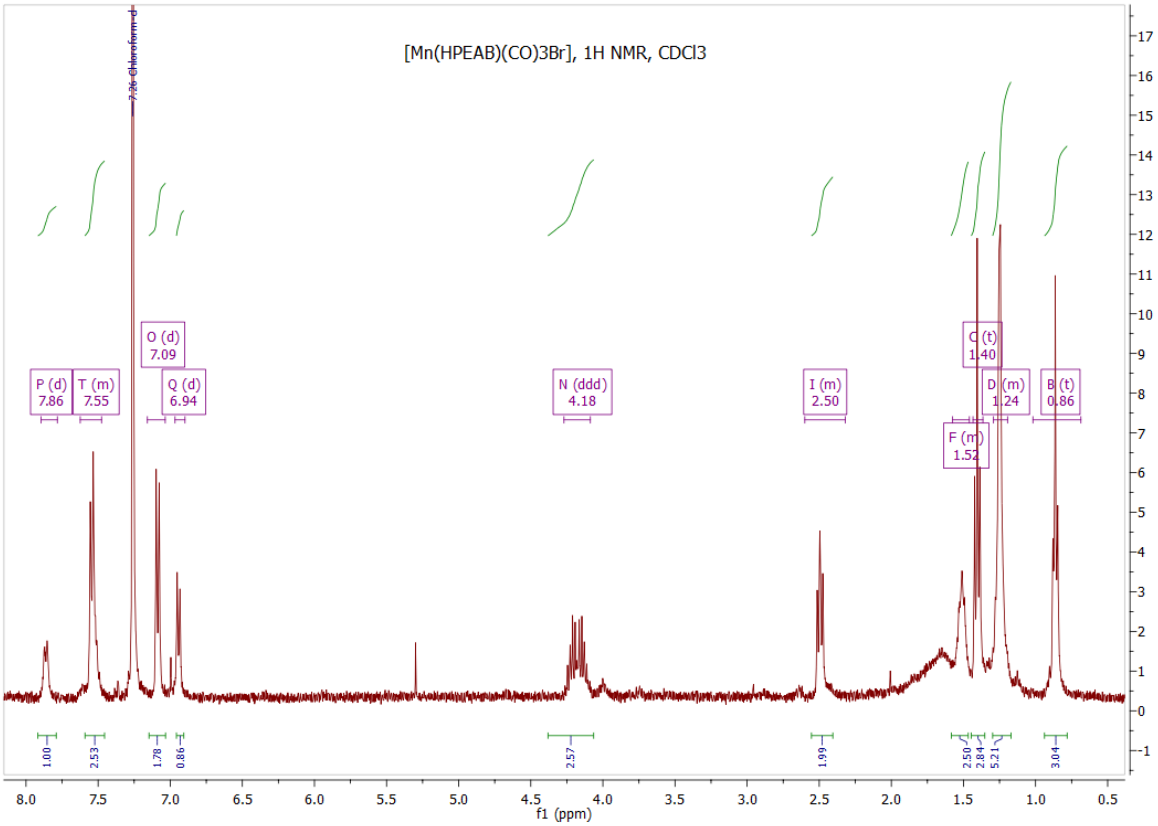


Figure S11. ^{1}H NMR spectrum of [Mn(HPEAB)(CO)$_3$Br] (400 MHz, CDCl$_3$).

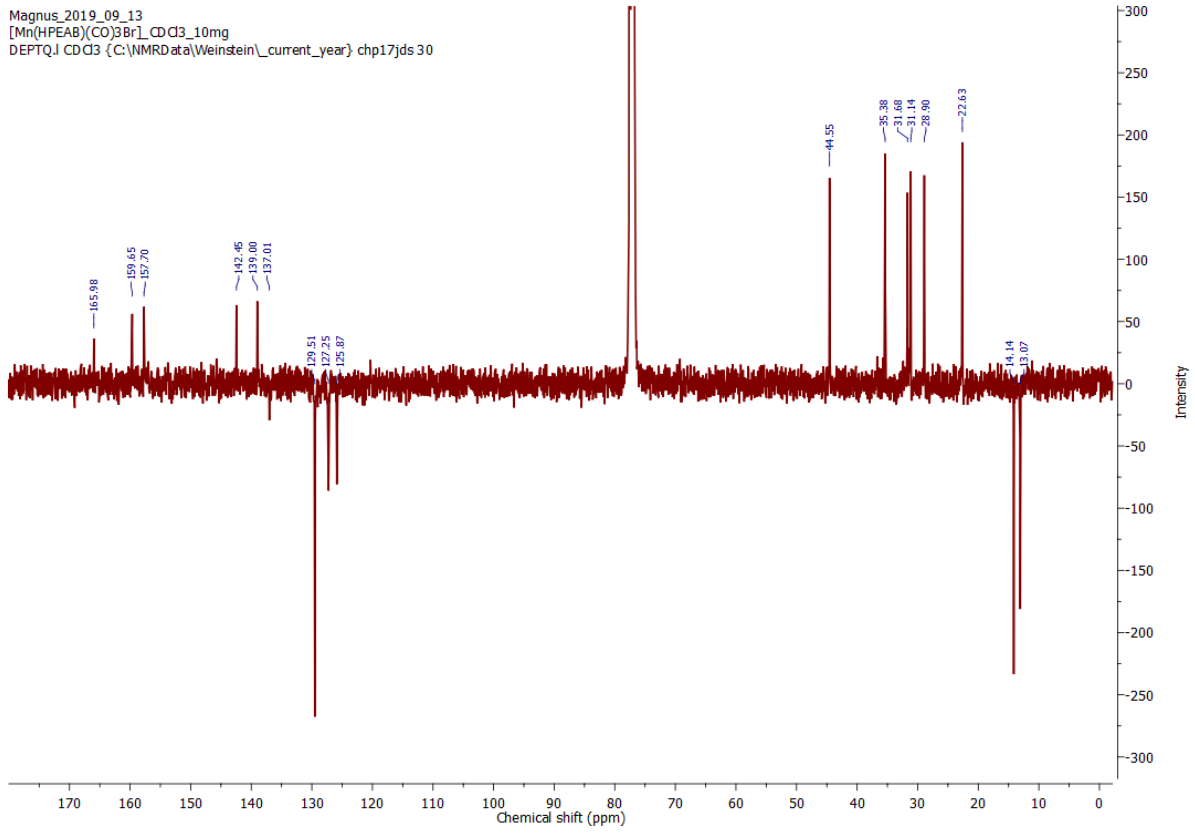


Figure S12: ^{13}C NMR spectrum of [Mn(HPEAB)(CO)$_3$Br] (400 MHz, CDCl$_3$).

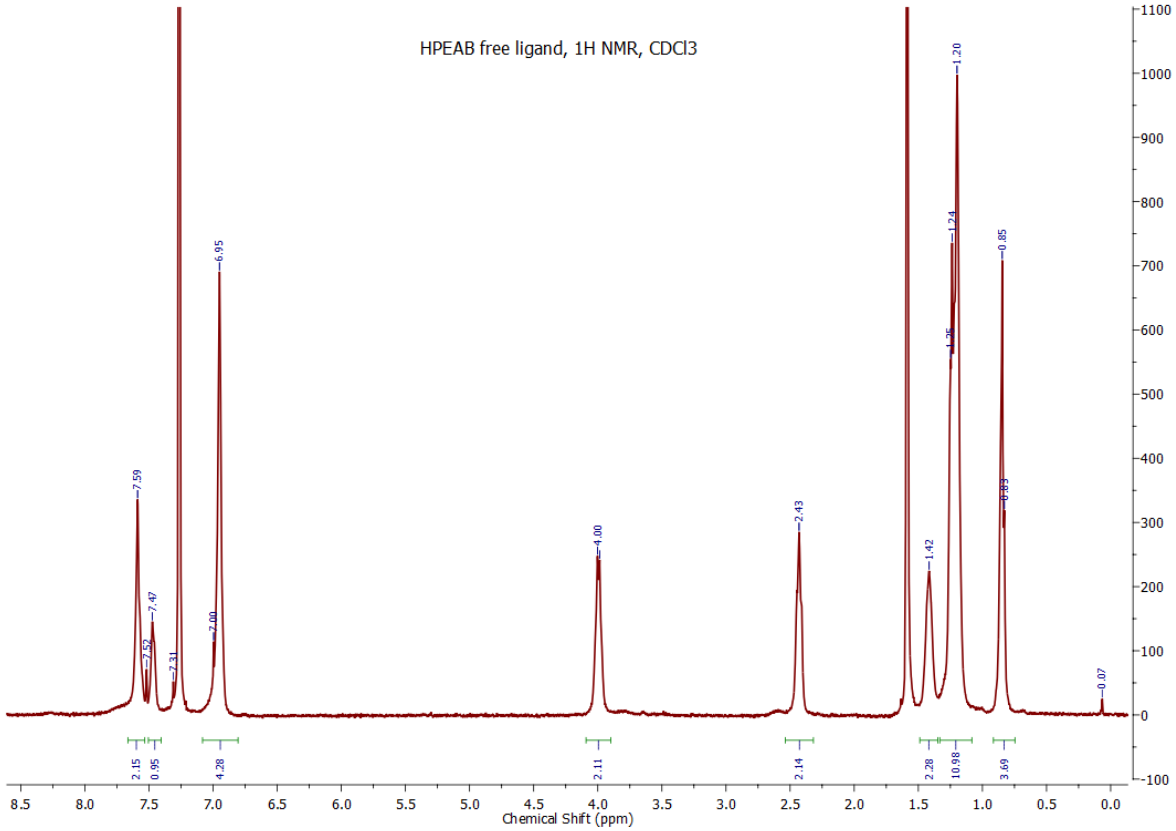


Figure S13. ^{1}H NMR spectrum of 6,6′-{N-(4-hexylphenyl)-N(ethyl)-amido}-2,2′-bipyridine (HPEAB) (400 MHz, $CDCl_3$).

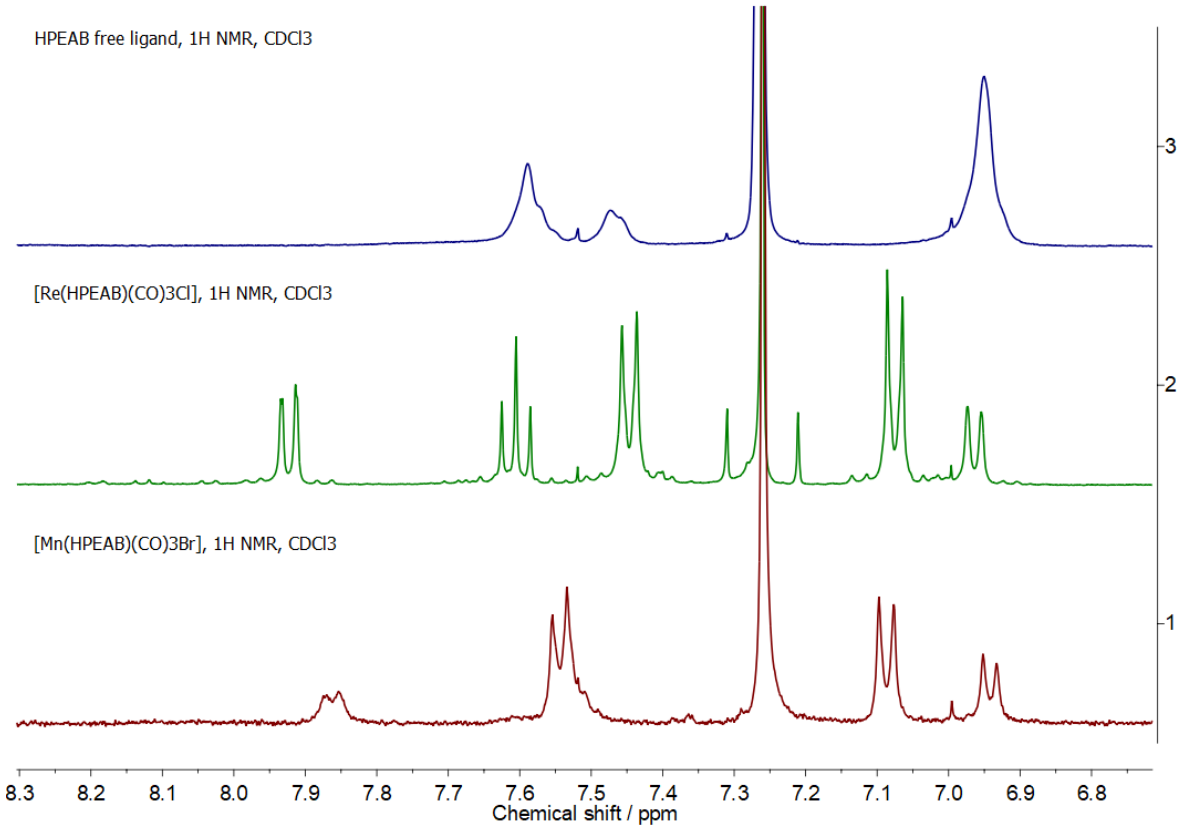


Figure S14. Overlaid ^{1}H NMR spectra of HPEAB, [Re(HPEAB)$(CO)_3$Cl], and [Mn(HPEAB)$(CO)_3$Br] (400 MHz, $CDCl_3$) showing the differences in the aromatic proton environments (6.8-8.3 ppm).

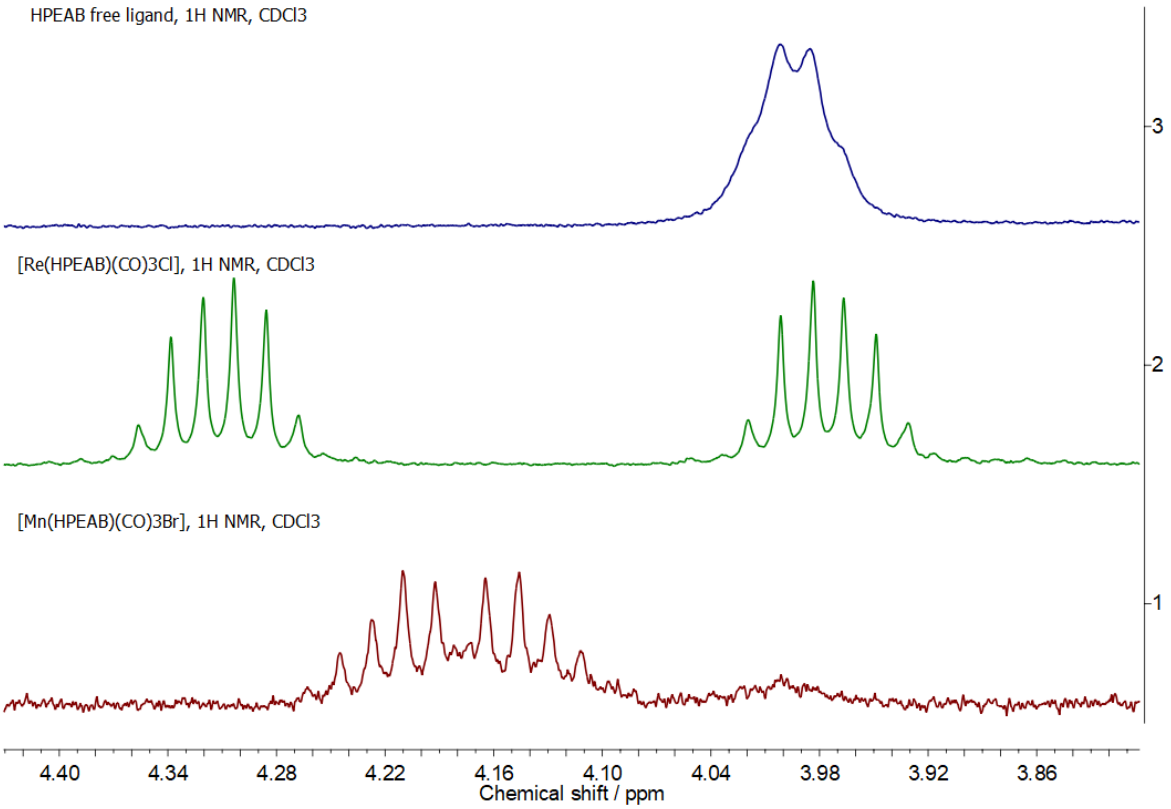


Figure S15. Overlaid ^{1}H NMR spectra of HPEAB, [Re(HPEAB)$(CO)_3$Cl], and [Mn(HPEAB)$(CO)_3$Br] (400 MHz, $CDCl_3$) showing the differences in the ethyl proton environments upon the amide group (3.8-4.4 ppm).

Elemental analysis reports

[Re(HPEAB)(CO)3Cl]

Molecular formula: $C_{43}H_{50}ClN_4O_5Re$
Carbon (Expected value: 55.86%): Found: 55.60%
Hydrogen (Expected value: 5.45%): Found: 5.39%
Nitrogen (Expected value: 6.06%): Found: 6.04%
Chlorine (Expected value: 3.83%): Found: 3.69%

[Mn(HPEAB)$(CO)_3$Br]

Molecular formula: $C_{43}H_{50}BrMnN_4O_5$

Carbon (Expected value: 61.65%): Found: 61.06%

Hydrogen (Expected value: 6.02%): Found: 5.81%

Nitrogen (Expected value: 6.69%): Found: 6.64%

Bromine (Expected value: 9.54%): Found: 10.09%

Photochemical degradation

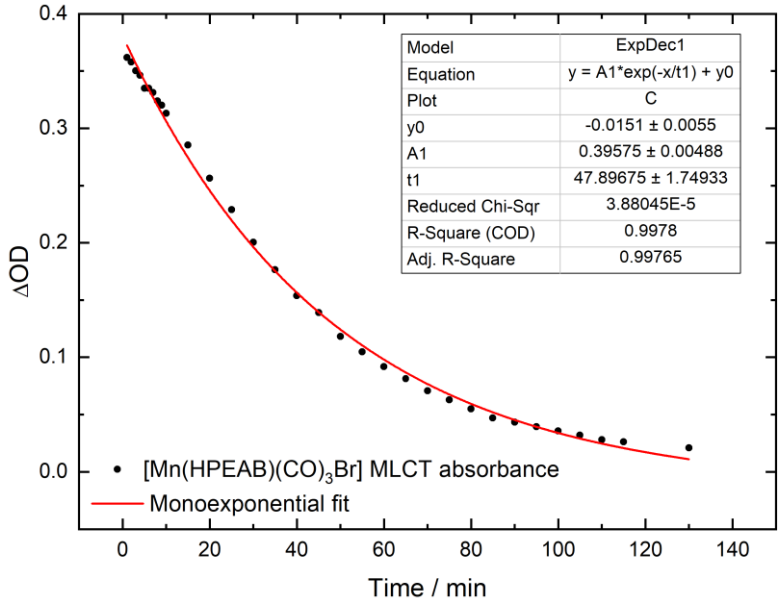


Figure S16. Kinetic trace for the change in optical density at the MLCT maxima of [Mn(HPEAB)(CO)$_3$Br] during irradiation with a xenon arc lamp (dots), and monoexponential fit of the data used to estimate the time constant of photodecomposition (red).

Cyclic voltammetry

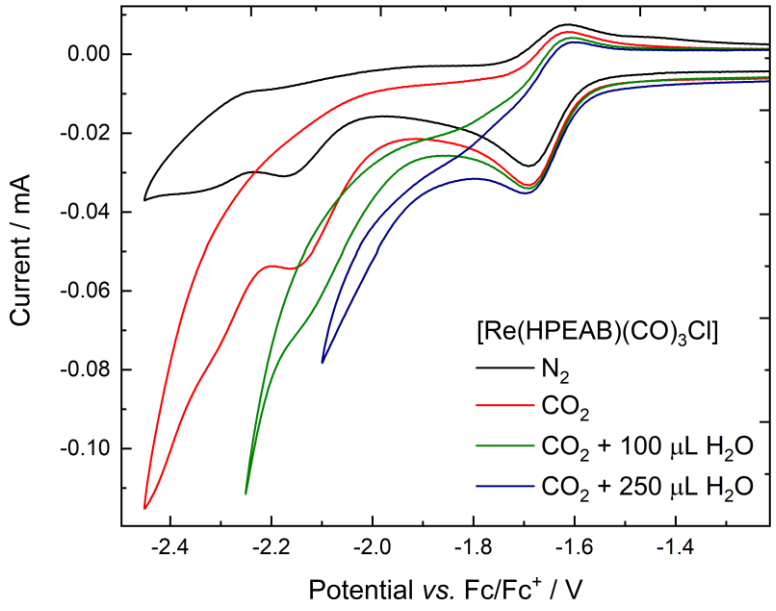


Figure S17. Cyclic voltammograms for [Re(HPEAB)(CO)$_3$Cl] in 0.2 mol dm^{-3} [NBu$_4$][PF$_6$] supporting electrolyte at a scan rate of 100 mV s^{-1} under various conditions, as stated on the graph.

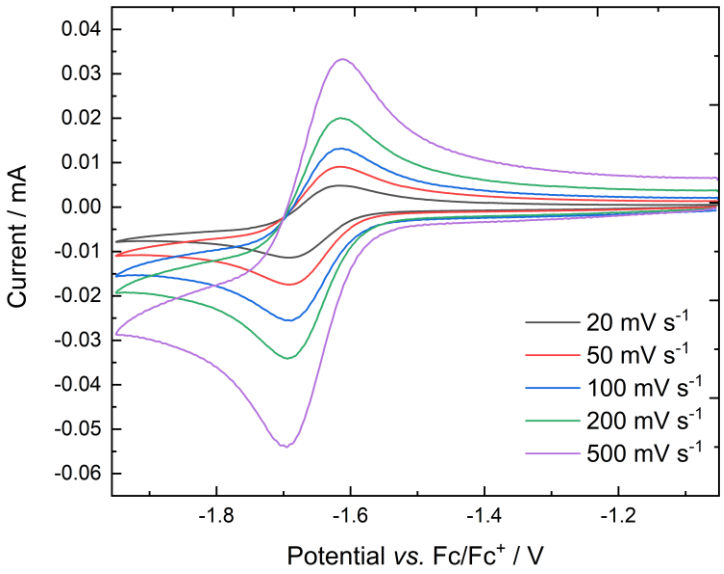


Figure S18. Cyclic voltammograms of the first reduction of [Re(HPEAB)$(CO)_3$Cl] under N_2 atmosphere at multiple scan rates, as stated on the graph.

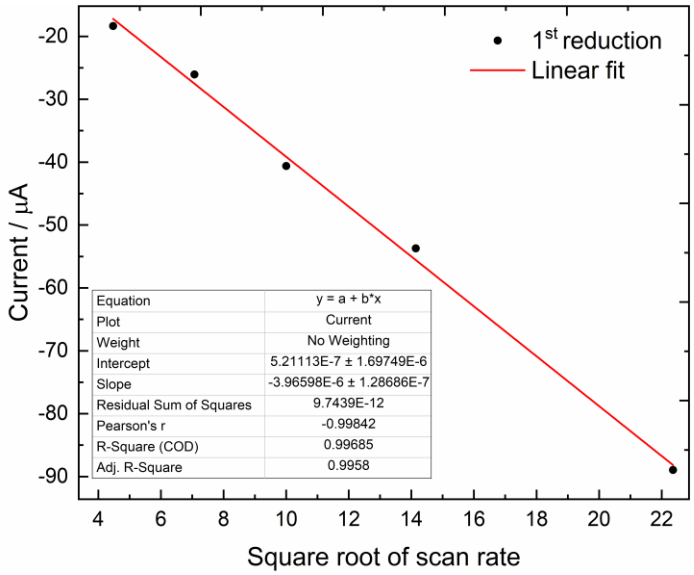


Figure S19. Relationship between the total current of the first reduction couple and the square root of the scan rate for [Re(HPEAB)$(CO)_3$Cl].

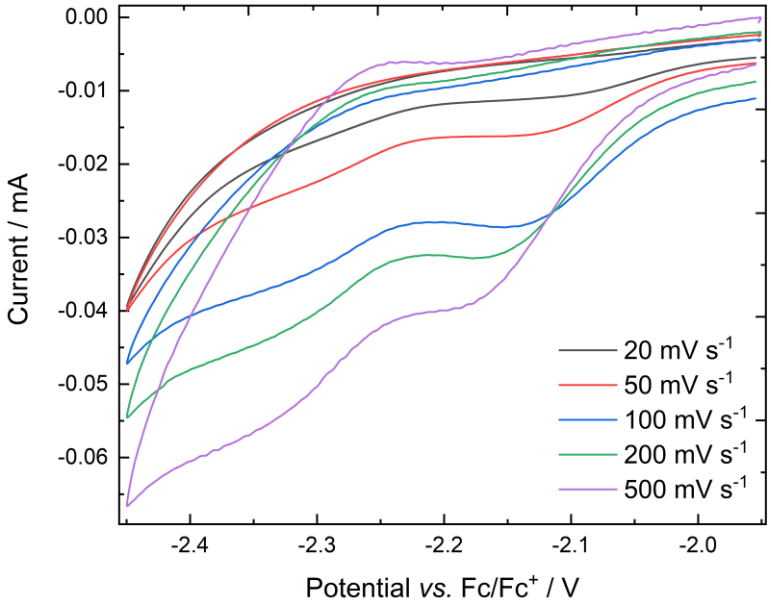


Figure S20. Cyclic voltammograms of the second reduction of [Re(HPEAB)$(CO)_3$Cl] under N_2 atmosphere at multiple scan rates, as stated on the graph.

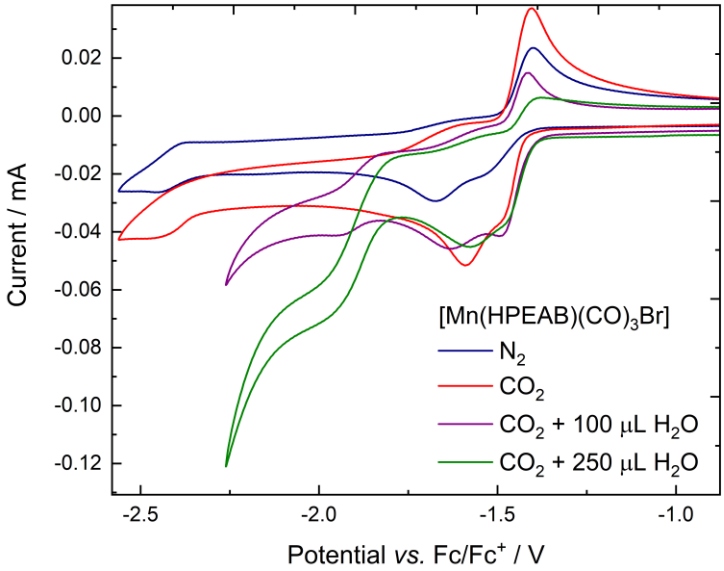


Figure S22. Cyclic voltammograms for [Mn(HPEAB)$(CO)_3$Br] in 0.2 mol dm^{-3} [NBu_4][PF_6] supporting electrolyte at a scan rate of 100 mV s^{-1} under various conditions, as stated on the graph.

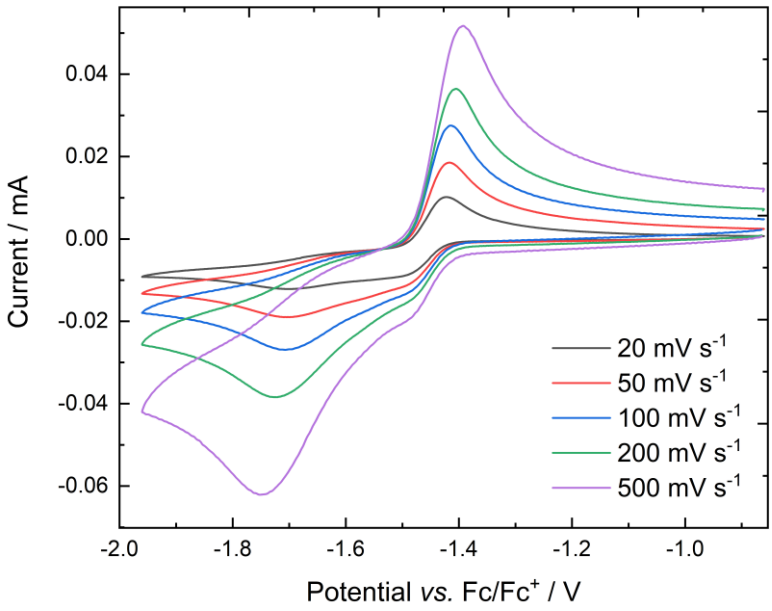


Figure S23. Cyclic voltammograms of the first and second reduction processes of [Mn(HPEAB)(CO)$_3$Br] under N_2 atmosphere at multiple scan rates. Scan rate analysis was not possible due to the significant overlap between redox processes preventing an accurate measure of total current for the redox peak pairs.

Foot of the wave analysis method

As it was not possible to increase the CV scan rate to a point at which substrate diffusion was rate limiting, the electrochemical performance of the catalysts was estimated by foot-of-the-wave analysis. This was done by fit of the onset of catalytic current in four steps:

a) Replotting the cyclic voltammogram with the following equation, where i_p^0 corresponds to the current of the second reduction in inert conditions, F is the Faraday constant, R is the gas constant, T is the temperature, E is the applied voltage, and E_0 is the potential corresponding to the midpoint of the grow-in of the catalytic current.

$$\frac{i}{i_p^0} = \left[1 + e^{\left(\frac{F}{RT}(E-E_0)\right)}\right]^{-1}$$

Equation S1. Relationship between $\frac{i}{i_p^0}$ and $E - E_0$ used for the re-plotting of the cyclic voltammetry data to show the onset of catalytic activity.

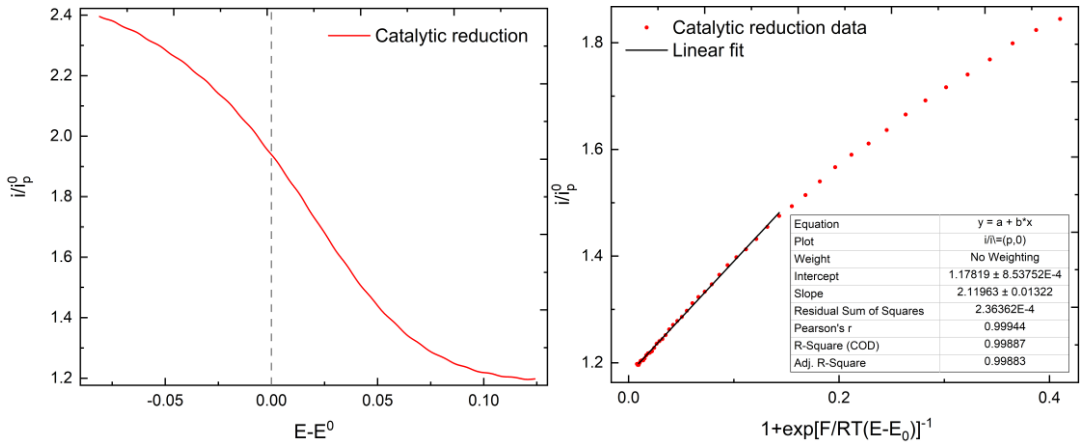


Figure S24. Cyclic voltammogram for the onset of catalytic activity (left) and linear fit of the onset region (right).

b) The resultant plot will contain a linear region, which then deviates from linearity as E-E^0 increases. The gradient of the linear region allows for calculation of the rate constant of catalytic turnover (k_r), where f = F/RT, m is the gradient, n' is the number of electrons involved in the catalytic process, and C is the initial concentration of catalyst.

$$k_r = \frac{fv\left(\frac{m}{2.24}\right)^2}{n'C_{cat}^0}$$

Equation S2. Relationship between the observed rate of reaction for the catalytic process and the gradient of the linear foot-of-the wave plot.

c) The turnover frequency can then be calculated using the observed rate constant. TOF is the turnover frequency, E_r^0 is the standard potential for the catalytic reaction, E_{cat}^0 is the standard potential for the reduction of the catalyst.

$$TOF_0 = k_r C_{cat}^0 e^{\left(-f\left(E_r^0 - E_{cat}^0\right)\right)}$$

Equation S3. Formula for calculation of the observed turnover frequency at zero overpotential.

d) The turnover frequency is a function of the catalytic overpotential (η), and a plot of TOF against overpotential results in a Tafel plot, used for comparing catalytic performance.

$$TOF = \frac{k_r}{1 + e^{\left(f\left(E_r^0 - E_{cat}^0 - \eta\right)\right)}}$$

Equation S4. Relationship between the turnover frequency and the applied overpotential.

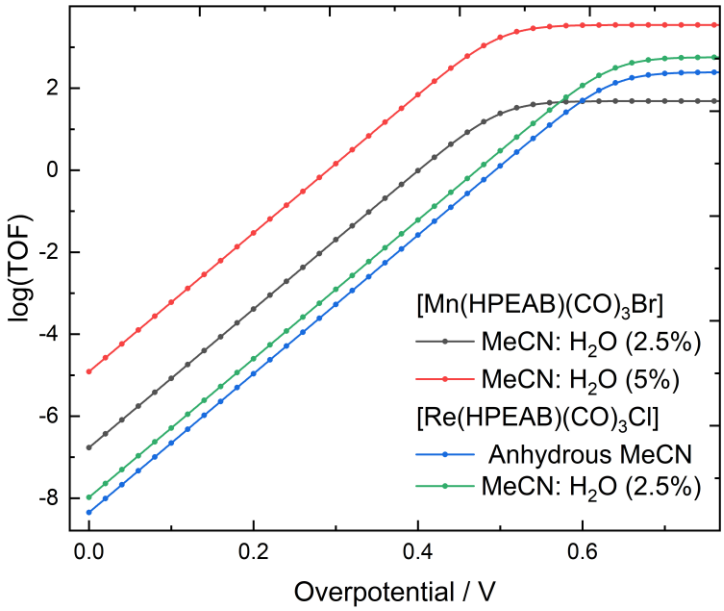


Figure S25. Catalytic Tafel plots for electrochemical CO_2 reduction with [Re(HPEAB)$(CO)_3$Cl] or [Mn(HPEAB)$(CO)_3$Br] under various conditions, as shown on the graph.

Transient absorption spectroscopy

Transient absorption spectra were analysed by global lifetime analysis in Glotaran.[1] A two component sequential model resulted in the most plausible model for the excited state dynamics. The proposed kinetic model involves intersystem crossing from the singlet to the triplet MLCT, after vibrational cooling of the ^{3}MLCT, it then decays to the ground state with a time constant of 3.44 ns. For further elucidation of the dynamics, TRIR spectroscopy is required.

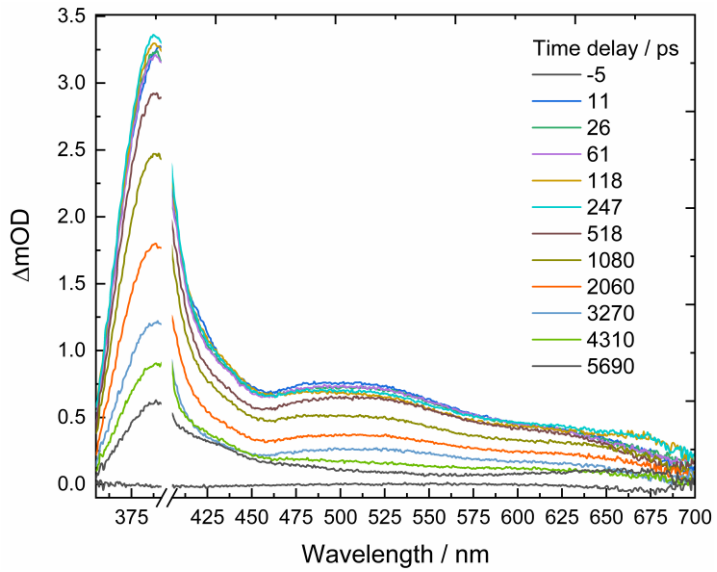


Figure S26. Transient absorption difference spectra of [Re(HPEAB)$(CO)_3$Cl] following 400 nm excitation at various pump – probe time delays (shown in picoseconds), as stated on the graph. The spectral region from 395-405 nm has been removed due to scattered light from the pump pulse.

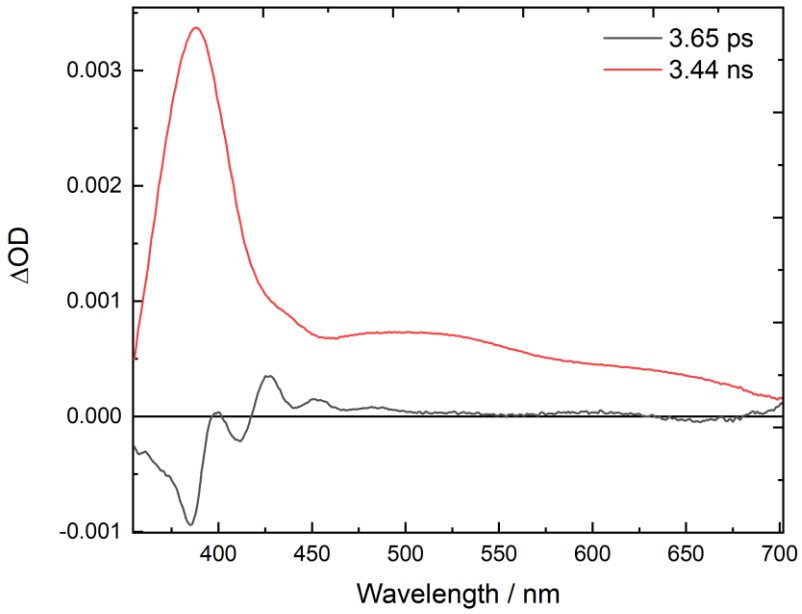


Figure S27. Decay associated spectra resulting from global lifetime analysis of the transient absorption data. A two component sequential kinetic model was used, where the optimised lifetimes were 3.65 ps and 3.44 ns.

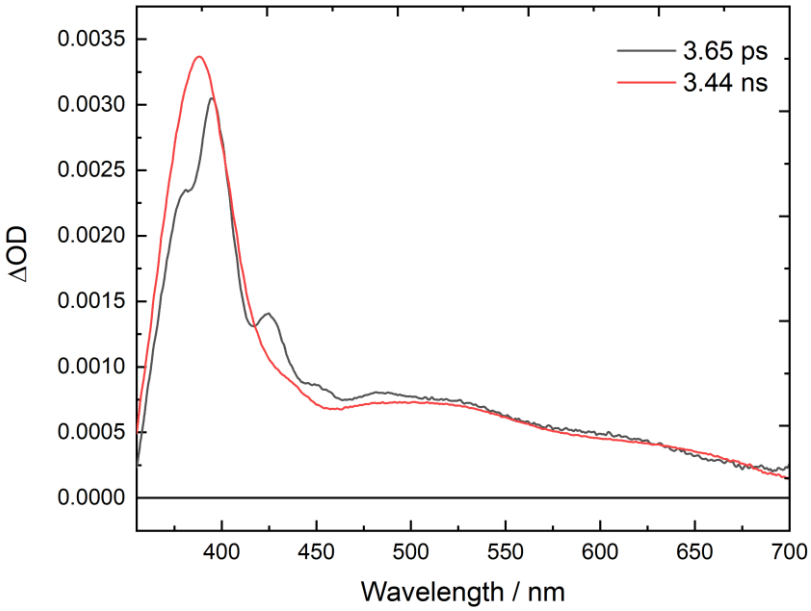


Figure S28. Evolution associated spectra resulting from global lifetime analysis of the transient absorption data. A two component sequential kinetic model was used, where the optimised lifetimes were 3.65 ps and 3.44 ns.

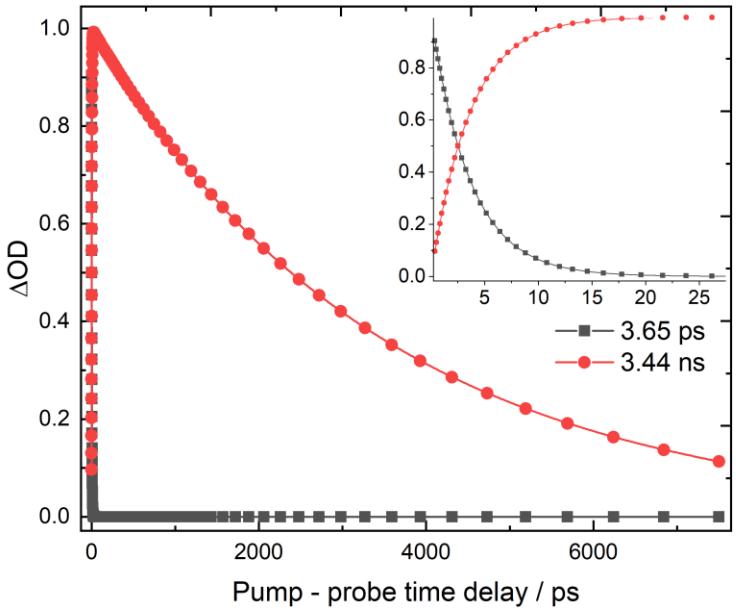


Figure S29. Model kinetic traces representing the decay of the first and second component of the sequential kinetic model. The inset is a magnified graph focussing on the first 25 ps of the data.

Estimation of the Gibbs energy of electron transfer

The thermodynamic favourability of the photosensitisation of [Mn(HPEAB)$(CO)_3$Br] by ZnTPP in the presence of triethylamine sacrificial donor was estimated with the Rehm-Weller equation.

$$\Delta G_{et} = E^{\frac{1}{2}}\left(\frac{D}{D^+}\right) - E^{\frac{1}{2}}\left(\frac{A}{A^-}\right) - E_{00} - \frac{e^2}{\varepsilon d}$$

Equation S5. Rehm-Weller equation for estimation of the Gibbs energy of electron transfer (ΔG_{et}) [D – electron donor, A – electron acceptor, $E^{1/2}$ – electrochemical half-wave potential, E_{00} – Excited/ground state energy difference, $\frac{e^2}{\varepsilon d}$ – coulombic term for electrostatic interaction].

The redox potentials of [Mn(HPEAB)$(CO)_3$Br] were measured by cyclic voltammetry, and the E_{00} value for ZnTPP following 625 nm excitation was estimated by emission spectroscopy as 2.07 eV. Literature values for the redox potential of NEt_3 (+1.07 V vs. Fc/Fc^+) oxidation, ZnTPP oxidation (+0.29 V vs. Fc/Fc^+), and ZnTPP reduction (-1.85 V vs. Fc/Fc^+).[2,3]

Reductive quenching

It was found that the reductive quenching mechanism was not feasible, as the initial reduction of ZnTPP by triethylamine was thermodynamically unfavourable.

i) $ZnTPP + hv \rightarrow [ZnTPP]^*$

ii) $[ZnTPP]^* + NEt_3 \rightarrow [ZnTPP]^- + {NEt_3}^+$

ii) $\Delta G_{et} \; = \; 1.07\,V - -1.85\,V - \; 2.07\,eV \; = \; 0.85\,V$

Equation S6. Estimation of the Gibbs energy of electron transfer for the reduction of the ZnTPP triplet state by triethylamine.

Oxidative quenching

The oxidative quenching of [Mn(HPEAB)$(CO)_3$Br] to form the active catalyst, $[Mn(HPEAB)(CO)_3]^-$ was estimated to be thermodynamically favourable.

i) $ZnTPP + hv \rightarrow [ZnTPP]^*$

ii) $[ZnTPP]^* + [Mn(HPEAB)(CO)_3Br] \rightarrow [ZnTPP]^+ + [Mn(HPEAB)(CO)_3Br]^-$

iii) $[ZnTPP]^* + [Mn(HPEAB)(CO)_3] \rightarrow [ZnTPP]^+ + [Mn(HPEAB)(CO)_3]^-$

ii) $\Delta G_{et} \; = \; 0.29\,V - \; -1.48\,V - \; 2.07\,eV \; = \; -0.30\,V$

iii) $\Delta G_{et} \; = \; 0.29\,V - \; -1.74\,V - \; 2.07\,eV \; = \; -0.04\,V$

Equation S7. Estimation of ΔG_{et} for the photoinduced electron transfer processes required for formation of $[Mn(HPEAB)(CO)_3]^-$ by photosensitisation.

Estimation of the ΔG_{et} required for the two-electron reduction needed for turnover of the catalytic cycle showed that this process was thermodynamically unfavourable. Therefore, turnover of the catalytic cycle was not possible, resulting in a low TON_{CO}.

$$\Delta G_{et} \; = \; 0.29\,V - \; -1.90\,V - \; 2.07\,eV \; = \; 0.12\,V$$

Equation S8. Estimation of ΔG_{et} for the electron transfer required for turnover of the catalytic cycle.

IR-spectroelectrochemical data analysis

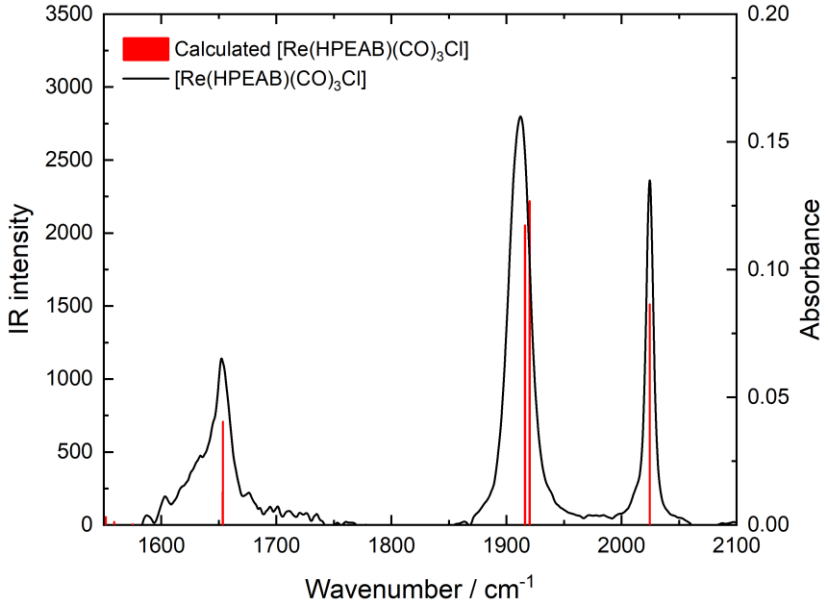


Figure S30. Assignment of absorption bands observed prior to *in situ* electrolysis of [Re(HPEAB)(CO)$_3$Cl] in anhydrous acetonitrile under argon atmosphere. The bars correspond to calculated vibrational frequencies obtained by DFT, black line corresponds to the experimental spectrum.

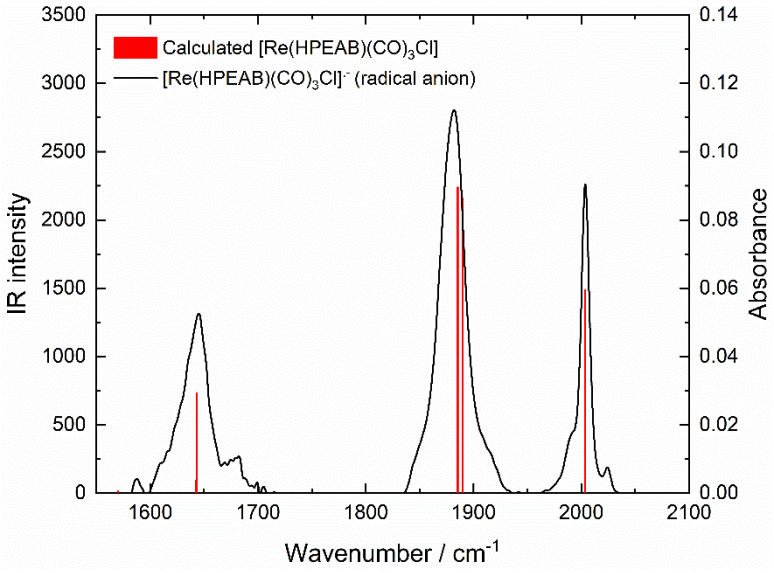


Figure S31. Assignment of absorption bands observed during *in situ* electrolysis of [Re(HPEAB)(CO)$_3$Cl] in anhydrous acetonitrile under argon atmosphere at the first reduction potential. The bars correspond to calculated vibrational frequencies obtained by DFT as shown on the graph, the black line corresponds to the experimental spectrum.

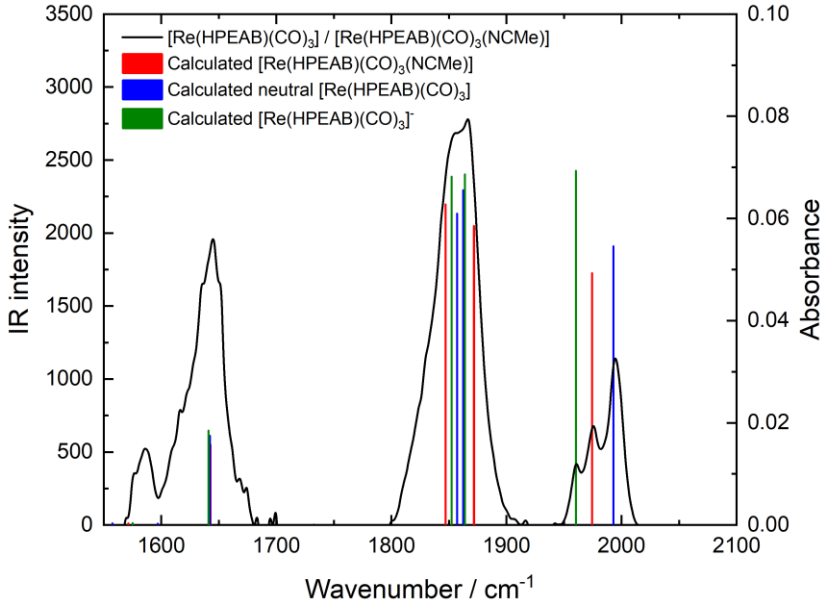


Figure S32. Assignment of absorption bands observed during *in situ* electrolysis of [Re(HPEAB)(CO)$_3$Cl] in anhydrous acetonitrile under argon atmosphere at the second reduction potential. The bars correspond to calculated vibrational frequencies obtained by DFT as shown on the graph, the black line corresponds to the experimental spectrum.

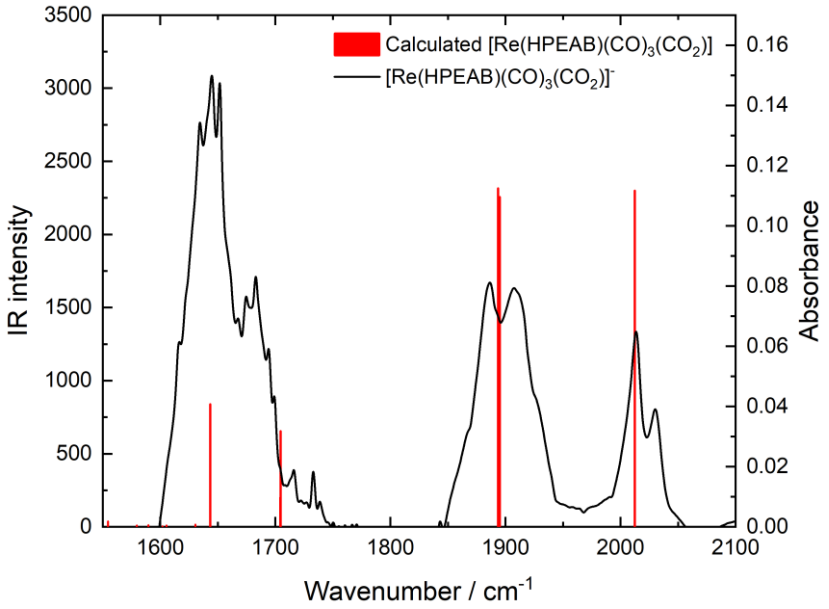


Figure S33. Assignment of absorption bands observed during *in situ* electrolysis of [Re(HPEAB)(CO)$_3$Cl] in anhydrous acetonitrile under CO_2 atmosphere at the second reduction potential. The bars correspond to calculated vibrational frequencies obtained by DFT as shown on the graph, the black line corresponds to the experimental spectrum.

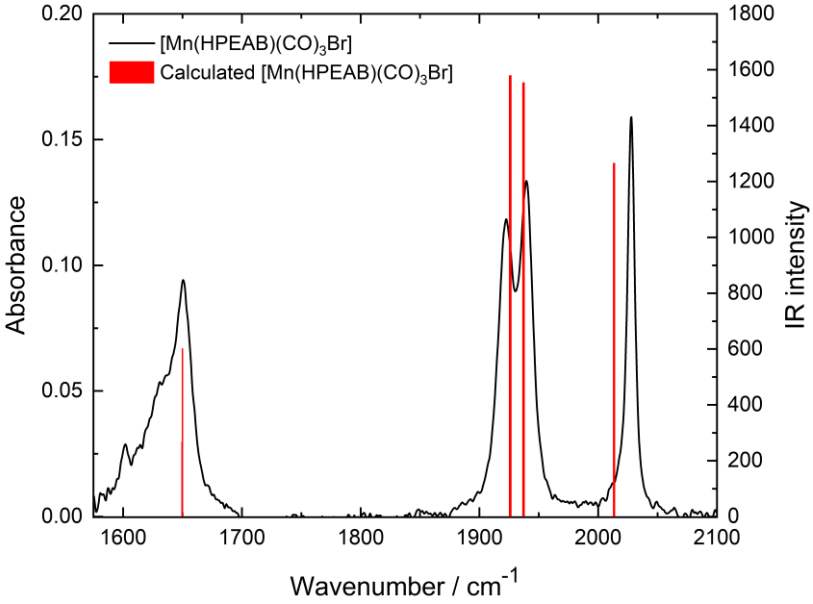
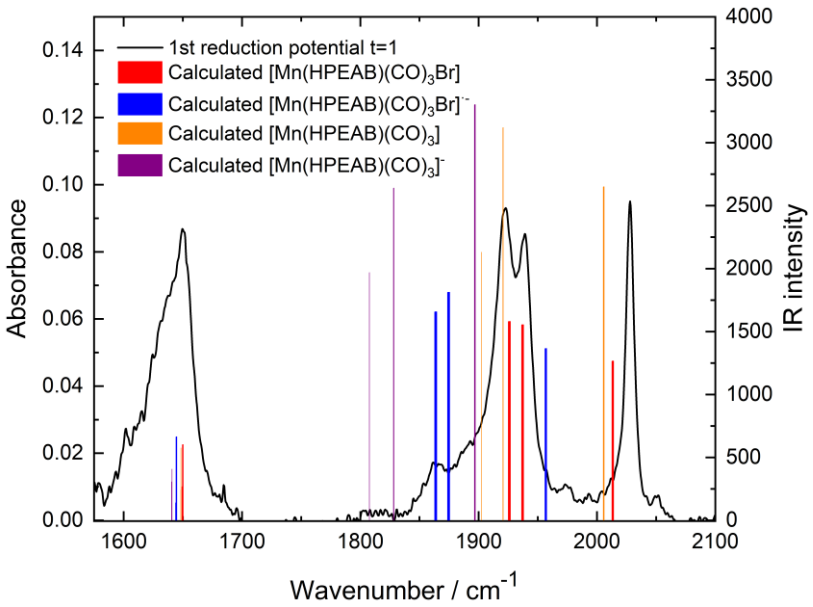


Figure S34. Assignment of absorption bands observed prior to *in situ* electrolysis of [Mn(HPEAB)(CO)$_3$Br] in anhydrous acetonitrile under argon atmosphere. The bars correspond to calculated vibrational frequencies obtained by DFT, the black line corresponds to the experimental spectrum.



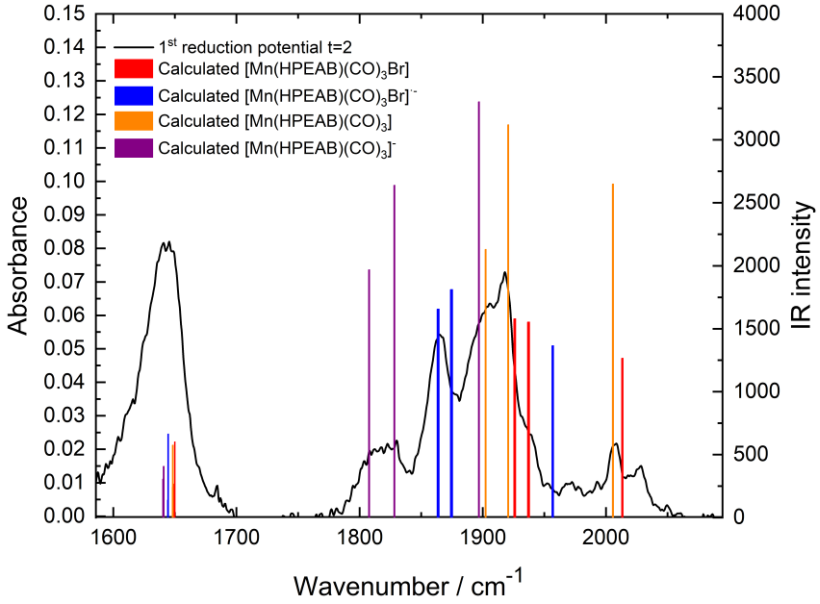


Figure S35. Assignment of absorption bands observed during *in situ* electrolysis of [Mn(HPEAB)(CO)$_3$Br] in anhydrous acetonitrile under argon atmosphere at the first reduction potential. The bars correspond to calculated vibrational frequencies obtained by DFT as shown on the graph, the black line corresponds to the experimental spectrum (t=1 – 2 minutes after electrolysis start; t=2 – 30 minutes after electrolysis start).

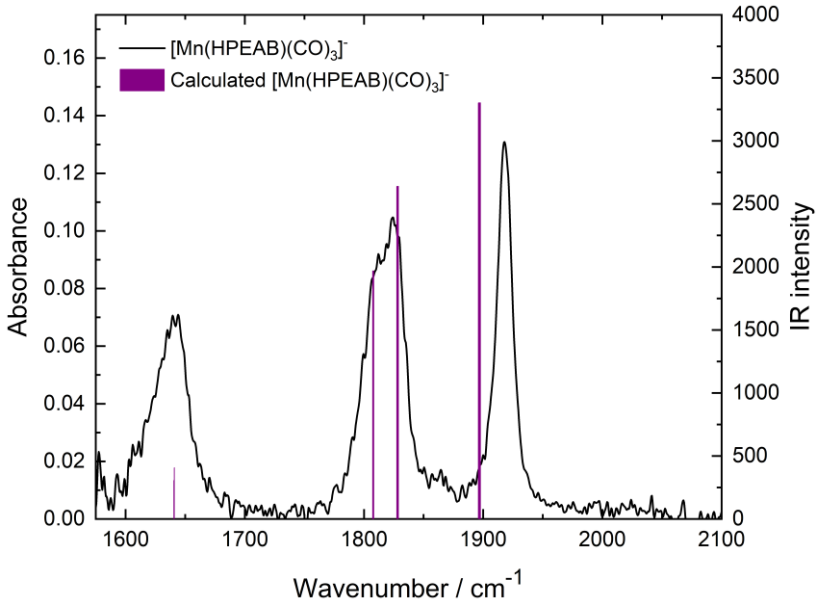


Figure S36. Assignment of absorption bands observed during *in situ* electrolysis of [Mn(HPEAB)(CO)$_3$Br] in anhydrous acetonitrile under argon atmosphere at the second reduction potential. The bars correspond to calculated vibrational frequencies obtained by DFT as shown on the graph, the black line corresponds to the experimental spectrum.

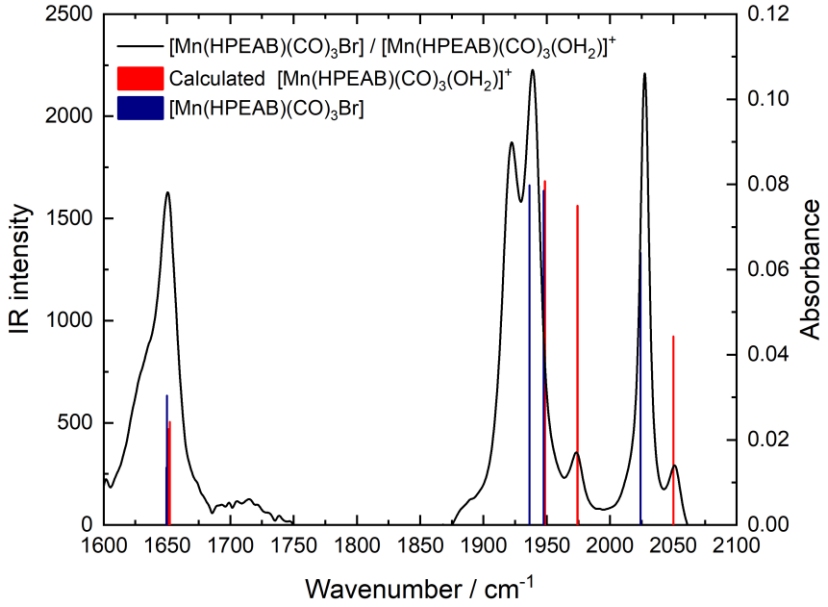


Figure S37. Assignment of absorption bands observed during *in situ* electrolysis of [Mn(HPEAB)(CO)$_3$Br] in acetonitrile under argon atmosphere at the first reduction potential. Hydrolysis of the first reduction product was observed due to trace water present in the solvent. The bars correspond to calculated vibrational frequencies obtained by DFT as shown on the graph, the black line corresponds to the experimental spectrum.

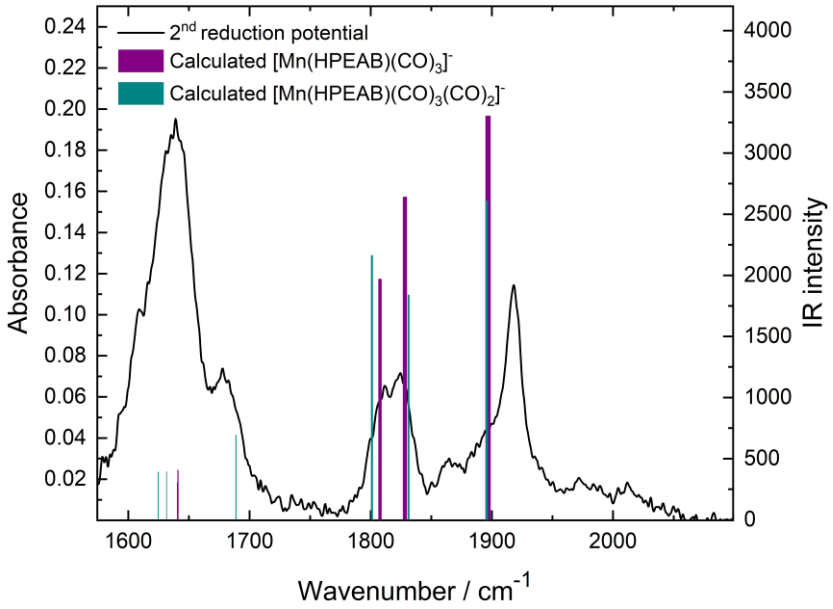


Figure S38. Assignment of absorption bands observed during *in situ* electrolysis of [Mn(HPEAB)(CO)$_3$Br] in anhydrous acetonitrile under CO_2 atmosphere at the second reduction potential. The strong signal observed at 1605 cm^{-1} was due to the presence of water. The bars correspond to calculated vibrational frequencies obtained by DFT as shown on the graph, the black line corresponds to the experimental spectrum.

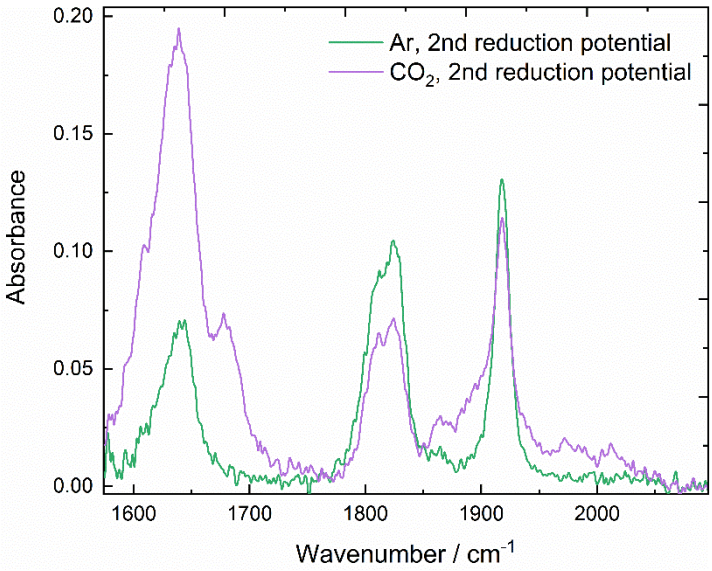


Figure S39. Overlaid experimental IR-SEC spectra for the product formed following two-electron reduction of [Mn(HPEAB)(CO)$_3$Br] under argon or CO_2 atmospheres, as shown on the graph.

Anharmonic scaling factors

Table S1. Correction factors applied to vibrational frequencies obtained through DFT calculations, used to account for the anharmonicity of the vibrational potential energy surface.

Species	Anharmonic scaling factors	
	$\tilde{\nu} < 1700$ cm^{-1}	$\tilde{\nu} > 1700$ cm^{-1}
[Re(HPEAB)(CO)$_3$Cl]	0.927	0.948
[Re(HPEAB)(CO)$_3$Cl]$^-$	0.924	0.948
[Re(HPEAB)(CO)$_3$]	0.925	0.940
[Re(HPEAB)(CO)$_3$(NCMe)]	0.925	0.925
[Re(HPEAB)(CO)$_3$]$^-$	0.960	0.969
[Re(HPEAB)(CO)$_3$(CO_2)]$^-$	0.928	0.951
[Mn(HPEAB)(CO)$_3$Br]	0.925	0.935
[Mn(HPEAB)(CO)$_3$Br]$^-$	0.925	0.918
[Mn(HPEAB)(CO)$_3$Br]	0.925	0.960
[Mn(HPEAB)(CO)$_3$(OH_2)]$^+$	0.928	0.939
[Mn(HPEAB)(CO)$_3$]$^-$	0.925	0.930

$[Mn(HPEAB)(CO)_3(CO_2)]^-$	0.918	0.915

Catalytic studies

Plot of %CO vs time for controlled potential electrolysis of $[Re(HPEAB)(CO)_3Cl]$ compared to $[Re(dmbpy)(CO)_3Cl]$ reference

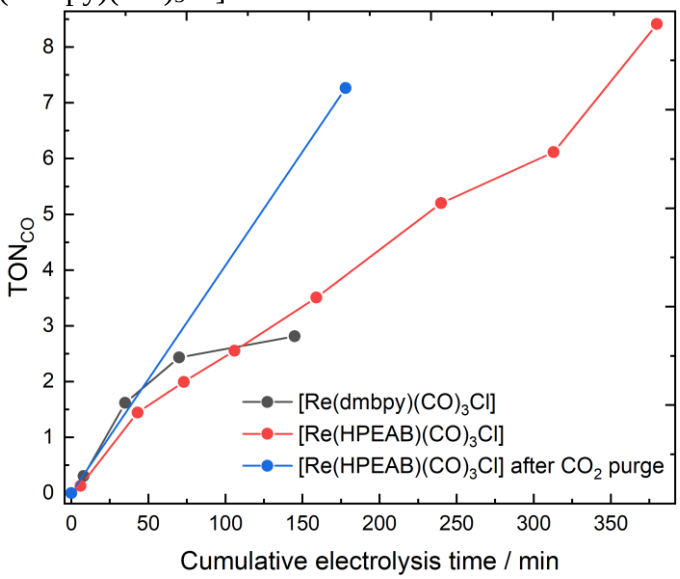


Figure S40. Turnover number-time profile for carbon monoxide produced by $[Re(dmbpy)(CO)_3Cl]$ (grey) and $[Re(HPEAB)(CO)_3Cl]$ (red) during controlled potential electrolysis at -1.9 V vs. an Ag wire pseudoreference electrode. Also shown is the catalytic performance of $[Re(HPEAB)(CO)_3Cl]$ after re-bubbling the solution with CO_2 (blue).

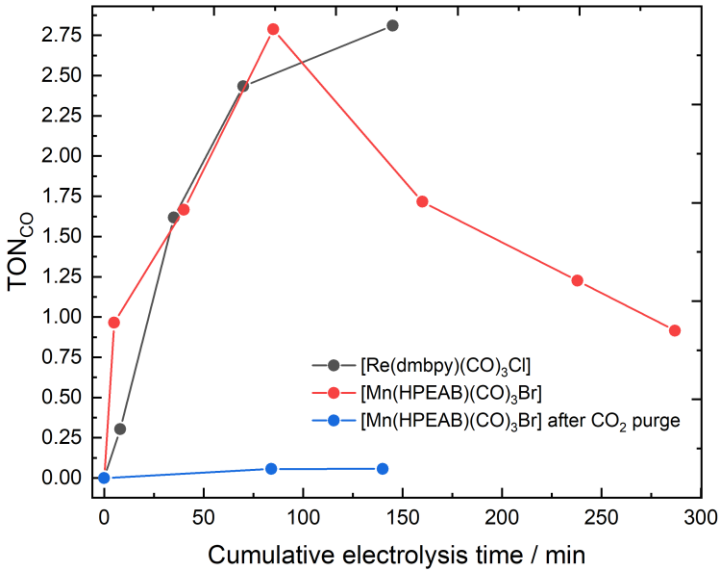


Figure S41. Turnover number-time profile for carbon monoxide produced by $[Re(dmbpy)(CO)_3Cl]$ (grey) and $[Mn(HPEAB)(CO)_3Br]$ (red) during controlled potential electrolysis at -1.9 V vs. an Ag wire pseudoreference electrode. Also shown is the catalytic performance of $[Mn(HPEAB)(CO)_3Br]$ after re-bubbling the solution with CO_2 (blue).

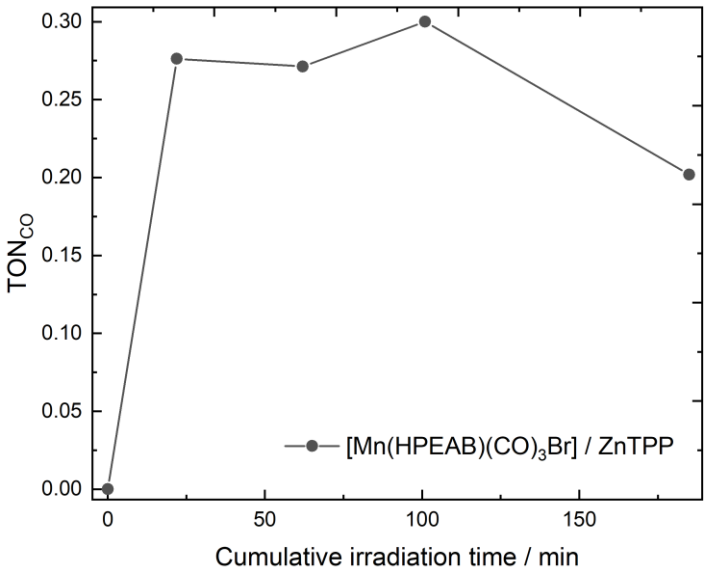


Figure S42. Turnover number-time profile for carbon monoxide produced by [Mn(HPEAB)(CO)$_3$Br] following photosensitisation by tetraphenylporphyrin zinc(II) under 625 nm irradiation in the presence of triethylamine sacrificial donor.

Crystal structure refinement procedure

Data were corrected for absorption using empirical methods (SADABS)[4] based upon symmetry equivalent reflections combined with measurements at different azimuthal angles.[5] The crystal structures were solved and refined against F2 values using ShelXT[6] for solution and ShelXL[7] for refinement accessed via the Olex2 program.[8] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions with idealized geometries and then refined by employing a riding model and isotropic displacement parameters.

Crystallographic information files

[Mn(HPEAB)(CO)$_3$Cl]·$\frac{1}{2}$Et$_2$O – CCSD deposition number 1949135

ch1jw286s_0m

Table 2 Crystal data and structure refinement for ch1jw286s_0m.

Identification code	ch1jw286s_0m
Empirical formula	$C_{45}H_{55}BrMnN_4O_{5.5}$
Formula weight	874.78
Temperature/K	110.01
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	15.8147(12)
b/Å	16.2939(11)

c/Å	17.9380(11)
α/°	90
β/°	106.379(4)
γ/°	90
Volume/Å^3	4434.7(5)
Z	4
ρ_{calc}g/cm^3	1.310
μ/mm^{-1}	1.247
F(000)	1828.0
Crystal size/mm^3	0.37 × 0.187 × 0.083
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.684 to 55.286
Index ranges	-19 ≤ h ≤ 20, -21 ≤ k ≤ 21, -20 ≤ l ≤ 23
Reflections collected	76332
Independent reflections	10219 [R_{int} = 0.1106, R_{sigma} = 0.1125]
Data/restraints/parameters	10219/531/551
Goodness-of-fit on F^2	1.079
Final R indexes [I>=2σ (I)]	R_1 = 0.0947, wR_2 = 0.2175
Final R indexes [all data]	R_1 = 0.1961, wR_2 = 0.2798
Largest diff. peak/hole / e Å^{-3}	1.60/-0.90

Table 3 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for ch1jw286s_0m. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Br01	7086.6(6)	4884.4(4)	6370.0(4)	44.3(3)
Mn1	6554.3(8)	3771.8(6)	7129.1(6)	38.8(3)
O1	6542(4)	1661(3)	6664(3)	47.9(13)
O2	5477(4)	4295(3)	8540(3)	53.4(15)
O3	7571(4)	4549(3)	8592(3)	55.4(15)
O4	8265(4)	2947(3)	7388(3)	54.9(15)
O5	6109(4)	2506(3)	8123(3)	59.5(16)
N1	5874(4)	3285(3)	6054(3)	36.7(13)
N2	5397(4)	4448(3)	6877(3)	36.8(14)
N3	7490(4)	1855(3)	5938(3)	42.0(14)
N4	5916(5)	5629(4)	8567(3)	52.0(17)
C1	6117(5)	2653(4)	5669(4)	38.2(16)
C2	5706(5)	2501(4)	4888(4)	40.7(17)
C3	5033(6)	2990(5)	4484(4)	46.4(19)
C4	4758(6)	3618(4)	4878(4)	43.3(18)
C5	5188(5)	3751(4)	5658(4)	36.1(15)
C6	4914(5)	4401(4)	6126(4)	36.4(15)
C7	4198(5)	4914(4)	5807(4)	40.1(16)
C8	3951(6)	5477(4)	6288(4)	45.2(18)
C9	4423(5)	5511(4)	7067(4)	42.4(17)

C10	5131(5)	4989(4)	7335(4)	39.9(17)
C11	6750(5)	2031(4)	6140(4)	40.3(16)
C12	8052(6)	1171(5)	6351(4)	50(2)
C13	7697(7)	334(5)	6060(5)	64(3)
C14	7792(5)	2322(4)	5389(4)	42.4(17)
C15	7826(6)	3172(5)	5426(4)	51(2)
C16	8135(6)	3618(5)	4897(4)	48.1(19)
C17	8439(6)	3240(5)	4335(4)	50.1(19)
C18	8426(6)	2385(5)	4317(4)	56(2)
C19	8119(6)	1933(5)	4834(4)	54(2)
C20	8767(7)	3736(6)	3762(5)	73(3)
C22	10391(8)	3549(9)	4346(8)	117(3)
C26	5552(6)	4932(5)	8204(4)	43.4(17)
C27	6253(8)	5600(6)	9431(5)	77(3)
C29	6117(6)	6349(5)	8183(5)	51.7(19)
C30	6671(9)	6331(5)	7751(5)	85(4)
C31	6894(9)	7049(6)	7404(6)	92(4)
C32	6545(6)	7786(5)	7508(5)	58(2)
C33	5969(9)	7774(6)	7902(10)	122(6)
C34	5751(9)	7080(6)	8261(11)	132(6)
C35	6797(7)	8566(5)	7160(6)	74(3)
C36	7405(8)	9090(7)	7739(6)	83(3)
C37	8257(11)	8769(13)	8056(15)	203(11)
C38	8978(13)	8912(15)	7872(14)	195(10)
C39	9823(12)	8640(13)	8201(13)	183(8)
C40	9854(13)	7643(14)	8413(13)	205(10)
C41	7138(5)	4276(4)	8015(4)	39.3(17)
C42	7576(6)	3245(5)	7250(4)	43.3(17)
C43	6241(6)	2993(4)	7710(4)	44.6(19)
C21A	9613(9)	3447(12)	3629(10)	71(5)
C23A	11192(17)	3250(20)	4143(17)	117(3)
C24A	12000(30)	3366(19)	4748(19)	117(3)
C25A	11890(20)	2543(17)	5061(17)	117(3)
C28A	5830(20)	6221(15)	9772(10)	84(10)
C21B	9654(10)	4137(12)	4099(11)	100(6)
C23B	11299(12)	3910(16)	4692(14)	117(3)
C24B	12083(18)	3388(17)	5079(14)	117(3)
C25B	12519(18)	2905(16)	4586(14)	117(3)
C28B	5360(20)	5600(20)	9785(13)	105(12)
O1S	9999(19)	4339(18)	8949(17)	200(11)
C1S	11464(17)	3773(18)	10410(20)	158(12)
C2S	10630(20)	4040(30)	9680(20)	180(12)
C3S	9810(30)	5120(20)	8480(20)	181(12)
C4S	9420(20)	5840(30)	7860(20)	221(18)

Table 4 Anisotropic Displacement Parameters ($Å^2×10^3$) for ch1jw286s_0m. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br01	73.6(6)	28.9(4)	32.7(4)	2.1(3)	18.9(4)	-2.0(4)
Mn1	71.3(9)	22.6(5)	23.5(5)	0.9(4)	15.0(5)	-0.7(5)
O1	86(4)	29(3)	32(3)	2(2)	22(3)	-2(3)
O2	94(5)	38(3)	31(3)	4(2)	23(3)	-1(3)
O3	88(4)	34(3)	38(3)	-6(2)	7(3)	3(3)
O4	77(4)	46(3)	38(3)	-5(2)	10(3)	4(3)
O5	121(5)	27(3)	40(3)	-4(2)	39(3)	-9(3)
N1	61(4)	25(3)	25(3)	3(2)	15(3)	-3(2)
N2	67(4)	20(3)	24(2)	3(2)	15(2)	0(3)
N3	73(4)	28(3)	27(3)	2(2)	18(3)	1(3)
N4	86(5)	35(3)	32(3)	-4(2)	11(3)	6(3)
C1	61(5)	30(3)	27(3)	-1(2)	17(3)	-5(3)
C2	64(5)	35(4)	27(3)	-1(3)	20(3)	-6(3)
C3	74(6)	42(4)	22(3)	0(3)	12(3)	-5(4)
C4	71(5)	34(4)	25(3)	5(3)	13(3)	-6(3)
C5	60(5)	29(3)	22(3)	7(2)	16(3)	-4(3)
C6	60(5)	25(3)	27(3)	5(2)	17(3)	-2(3)
C7	60(5)	25(3)	34(3)	6(3)	13(3)	-5(3)
C8	69(5)	30(4)	37(3)	8(3)	15(3)	6(4)
C9	63(5)	29(4)	39(3)	0(3)	19(3)	-4(3)
C10	65(5)	29(4)	28(3)	3(2)	17(3)	-3(3)
C11	67(5)	27(3)	26(3)	-6(3)	11(3)	-4(3)
C12	72(6)	40(4)	33(4)	1(3)	9(4)	7(4)
C13	103(8)	36(4)	53(5)	3(4)	21(5)	5(4)
C14	62(5)	34(3)	28(3)	5(3)	8(3)	0(3)
C15	82(6)	36(4)	37(4)	-1(3)	21(4)	-1(4)
C16	72(6)	33(4)	38(4)	5(3)	13(4)	-2(4)
C17	68(6)	47(4)	34(4)	5(3)	13(4)	0(4)
C18	88(7)	51(4)	33(4)	-6(3)	20(4)	4(4)
C19	96(7)	39(4)	26(3)	2(3)	16(4)	9(4)
C20	120(7)	65(6)	46(5)	5(4)	42(5)	-6(5)
C22	128(7)	132(8)	99(6)	17(6)	48(5)	-19(5)
C26	64(5)	38(4)	32(3)	-4(3)	20(3)	6(3)
C27	125(9)	60(6)	34(4)	-13(4)	4(5)	27(6)
C29	74(6)	29(3)	43(4)	-8(3)	2(4)	0(3)
C30	185(11)	32(4)	59(6)	5(4)	67(7)	29(5)
C31	192(12)	45(5)	58(6)	17(4)	67(7)	32(6)
C32	73(6)	27(3)	67(6)	-4(4)	8(4)	4(4)
C33	122(10)	27(5)	261(17)	-8(7)	126(11)	2(6)

C34	134(11)	33(5)	279(19)	-2(7)	142(13)	4(6)
C35	105(8)	37(4)	82(7)	0(4)	30(5)	3(5)
C36	109(8)	69(7)	78(7)	-1(5)	37(6)	-26(6)
C37	94(9)	174(18)	310(30)	119(18)	2(11)	-37(10)
C38	127(11)	210(20)	250(20)	99(19)	60(15)	56(14)
C39	116(10)	183(15)	220(20)	-48(15)	-2(13)	30(12)
C40	166(18)	206(17)	220(20)	11(17)	14(16)	94(16)
C41	57(5)	27(3)	33(3)	6(3)	11(3)	8(3)
C42	71(5)	34(4)	22(3)	-2(3)	8(3)	-5(3)
C43	82(6)	31(4)	21(3)	-2(3)	16(4)	0(4)
C21A	120(10)	53(12)	61(9)	-2(9)	59(7)	-14(10)
C23A	128(7)	132(8)	99(6)	17(6)	48(5)	-19(5)
C24A	128(7)	132(8)	99(6)	17(6)	48(5)	-19(5)
C25A	128(7)	132(8)	99(6)	17(6)	48(5)	-19(5)
C28A	170(20)	53(13)	29(8)	0(8)	34(11)	21(14)
C21B	122(10)	117(16)	77(13)	22(12)	55(10)	-24(7)
C23B	128(7)	132(8)	99(6)	17(6)	48(5)	-19(5)
C24B	128(7)	132(8)	99(6)	17(6)	48(5)	-19(5)
C25B	128(7)	132(8)	99(6)	17(6)	48(5)	-19(5)
C28B	170(20)	110(30)	47(12)	23(14)	51(14)	70(20)
O1S	200(20)	190(20)	250(30)	-50(20)	131(17)	-80(20)
C1S	89(17)	130(20)	280(30)	-140(20)	86(16)	-74(15)
C2S	93(19)	200(30)	270(30)	-110(20)	101(17)	-30(20)
C3S	200(30)	160(30)	250(30)	-70(20)	160(20)	-70(20)
C4S	72(19)	430(50)	130(30)	-30(30)	-31(19)	0(30)

Table 5 Bond Lengths for ch1jw286s_0m.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br01	Mn1	2.5487(12)	C14	C19	1.396(10)
Mn1	N1	2.082(6)	C15	C16	1.389(10)
Mn1	N2	2.075(6)	C16	C17	1.379(11)
Mn1	C41	1.796(8)	C17	C18	1.392(11)
Mn1	C42	1.788(10)	C17	C20	1.509(11)
Mn1	C43	1.798(7)	C18	C19	1.376(11)
O1	C11	1.238(8)	C20	C21A	1.501(13)
O2	C26	1.223(9)	C20	C21B	1.511(14)
O3	C41	1.156(8)	C22	C21A	1.518(13)
O4	C42	1.154(9)	C22	C23A	1.495(15)
O5	C43	1.143(8)	C22	C21B	1.477(14)
N1	C1	1.355(9)	C22	C23B	1.513(14)
N1	C5	1.351(9)	C27	C28A	1.44(2)
N2	C6	1.350(8)	C27	C28B	1.70(3)
N2	C10	1.350(9)	C29	C30	1.323(13)

N3	C11	1.349(10)	C29	C34	1.348(13)
N3	C12	1.487(9)	C30	C31	1.415(13)
N3	C14	1.429(9)	C31	C32	1.356(12)
N4	C26	1.354(10)	C32	C33	1.300(14)
N4	C27	1.491(10)	C32	C35	1.519(13)
N4	C29	1.441(10)	C33	C34	1.393(16)
C1	C2	1.389(9)	C35	C36	1.473(14)
C1	C11	1.506(10)	C36	C37	1.408(19)
C2	C3	1.364(11)	C37	C38	1.30(2)
C3	C4	1.382(10)	C38	C39	1.37(2)
C4	C5	1.389(9)	C39	C40	1.67(3)
C5	C6	1.490(9)	C23A	C24A	1.44(4)
C6	C7	1.394(10)	C24A	C25A	1.485(16)
C7	C8	1.388(10)	C23B	C24B	1.503(15)
C8	C9	1.388(10)	C24B	C25B	1.491(15)
C9	C10	1.380(11)	O1S	C2S	1.50(3)
C10	C26	1.516(10)	O1S	C3S	1.51(3)
C12	C13	1.509(11)	C1S	C2S	1.63(4)
C14	C15	1.387(10)	C3S	C4S	1.62(4)

Table 6 Bond Angles for ch1jw286s_0m.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	Mn1	Br01	86.47(15)	N3	C12	C13	113.2(7)
N2	Mn1	Br01	84.81(15)	C15	C14	N3	121.0(7)
N2	Mn1	N1	78.9(2)	C15	C14	C19	118.0(7)
C41	Mn1	Br01	89.0(2)	C19	C14	N3	120.8(7)
C41	Mn1	N1	175.0(3)	C14	C15	C16	120.5(7)
C41	Mn1	N2	98.7(3)	C17	C16	C15	121.8(7)
C41	Mn1	C43	88.1(3)	C16	C17	C18	117.3(7)
C42	Mn1	Br01	89.0(2)	C16	C17	C20	121.0(8)
C42	Mn1	N1	98.2(3)	C18	C17	C20	121.7(8)
C42	Mn1	N2	173.3(3)	C19	C18	C17	121.8(8)
C42	Mn1	C41	83.7(3)	C18	C19	C14	120.6(7)
C42	Mn1	C43	88.8(4)	C17	C20	C21B	114.7(10)
C43	Mn1	Br01	176.5(3)	C21A	C20	C17	115.7(10)
C43	Mn1	N1	96.5(3)	C23A	C22	C21A	107.3(16)
C43	Mn1	N2	97.5(3)	C21B	C22	C23B	116.6(16)
C1	N1	Mn1	128.0(5)	O2	C26	N4	124.2(7)
C5	N1	Mn1	113.7(4)	O2	C26	C10	118.9(7)
C5	N1	C1	117.4(6)	N4	C26	C10	116.6(6)
C6	N2	Mn1	113.8(4)	N4	C27	C28B	107.3(11)
C10	N2	Mn1	128.4(5)	C28A	C27	N4	110.3(10)
C10	N2	C6	117.3(6)	C30	C29	N4	122.3(7)

C11	N3	C12	117.9(6)	C30	C29	C34	117.1(9)
C11	N3	C14	123.7(6)	C34	C29	N4	120.6(9)
C14	N3	C12	118.2(6)	C29	C30	C31	121.8(8)
C26	N4	C27	116.9(7)	C32	C31	C30	120.6(10)
C26	N4	C29	125.0(6)	C31	C32	C35	121.4(9)
C29	N4	C27	117.5(7)	C33	C32	C31	115.8(9)
N1	C1	C2	122.0(7)	C33	C32	C35	122.7(8)
N1	C1	C11	117.7(6)	C32	C33	C34	124.5(10)
C2	C1	C11	119.6(6)	C29	C34	C33	119.9(11)
C3	C2	C1	120.4(7)	C36	C35	C32	113.0(8)
C2	C3	C4	118.1(7)	C37	C36	C35	115.5(14)
C3	C4	C5	119.7(7)	C38	C37	C36	129.9(19)
N1	C5	C4	122.3(6)	C37	C38	C39	131(2)
N1	C5	C6	114.9(6)	C38	C39	C40	112.1(19)
C4	C5	C6	122.7(7)	O3	C41	Mn1	173.9(7)
N2	C6	C5	115.5(6)	O4	C42	Mn1	173.9(6)
N2	C6	C7	122.7(6)	O5	C43	Mn1	174.3(8)
C7	C6	C5	121.8(6)	C20	C21A	C22	112.1(12)
C8	C7	C6	118.6(7)	C24A	C23A	C22	114(2)
C9	C8	C7	119.1(7)	C23A	C24A	C25A	89(3)
C10	C9	C8	118.7(7)	C22	C21B	C20	113.9(14)
N2	C10	C9	123.5(6)	C24B	C23B	C22	122(2)
N2	C10	C26	117.7(6)	C25B	C24B	C23B	119(2)
C9	C10	C26	118.3(6)	C2S	O1S	C3S	138(3)
O1	C11	N3	122.5(7)	O1S	C2S	C1S	169(3)
O1	C11	C1	118.5(7)	O1S	C3S	C4S	167(4)
N3	C11	C1	118.8(6)				

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for ch1jw286s_0m.

Atom	*x*	*y*	*z*	U(eq)
H2	5895.54	2054.29	4635.2	49
H3	4760.43	2901.34	3945.96	56
H4	4276.79	3957.13	4617.36	52
H7	3886.04	4879.63	5271.22	48
H8	3465.07	5833.6	6086.01	54
H9	4263.02	5886.33	7408.86	51
H12A	8103.3	1209.39	6912.41	59
H12B	8650.68	1231.15	6286.78	59
H13A	7701.74	269.76	5518.27	96
H13B	7092.43	280.6	6094.95	96
H13C	8067.75	-90.42	6379.36	96
H15	7636.2	3450.43	5815.24	61

H16	8137.34	4200.8	4923.35	58
H18	8633.95	2107.57	3937.69	68
H19	8130.25	1350.21	4813.9	65
H20A	8304.67	3734.9	3257.82	88
H20B	8846.53	4310.79	3947.5	88
H20C	8328.32	4168.6	3541.03	88
H20D	8803.54	3372.05	3330.7	88
H22A	10462.13	4132.95	4503.42	140
H22B	10297.17	3224.77	4782.93	140
H22C	10406.55	3213.64	3889.95	140
H22D	10263.1	3173	4734.34	140
H27C	6628.2	6083.81	9627.31	92
H27D	6608.59	5098.02	9597.86	92
H27A	6134.57	5052.04	9618.67	92
H27B	6898.01	5689.43	9592.66	92
H30	6925.13	5822.07	7670.96	103
H31	7293.09	7013.93	7096.32	111
H33	5677.5	8272.87	7947.03	147
H34	5344.84	7120.98	8561.54	158
H35A	7077	8418.23	6749.58	89
H35B	6255.29	8881.89	6912.38	89
H36A	7457.79	9624.58	7492.79	100
H36B	7140.84	9196.94	8168.47	100
H37A	8401.5	8893.79	8618.39	243
H37B	8180.43	8166.16	8012.99	243
H38A	9029.18	9518.02	7877.71	233
H38B	8843.96	8750.12	7319.03	233
H39A	10089.08	8954.81	8681.63	219
H39B	10179.92	8741.46	7836.5	219
H40A	9750.27	7321.9	7933.53	307
H40B	9396.63	7516.75	8667.27	307
H40C	10433.62	7504.11	8762.53	307
H21A	9725.32	3762.45	3194.35	86
H21B	9555.4	2861.13	3476.79	86
H23A	11119.43	2658.44	4017.03	140
H23B	11234.86	3541.28	3670.22	140
H24A	11984.45	3823.08	5107.05	140
H24B	12530.21	3409.85	4554.6	140
H25A	11300.2	2332.48	4794.46	175
H25B	11951.19	2586.36	5619.28	175
H25C	12336.13	2167.56	4976.61	175
H28A	5778.25	6727.76	9468.2	126
H28B	6184.36	6325.52	10307.02	126
H28C	5242.62	6032	9772.36	126
H21C	9772.26	4511.33	3705.9	120

H21D	9630.57	4472.91	4552.97	120
H23C	11451.58	4213.14	4268.78	140
H23D	11241.49	4325.06	5077.8	140
H24C	12533.97	3751.39	5414.86	140
H24D	11896.75	2997.88	5425.72	140
H25D	12679	3271.09	4214.27	175
H25E	12112.23	2482.17	4302.63	175
H25F	13050.8	2642.69	4915.98	175
H28D	4997.84	6080.72	9591.25	158
H28E	5561.73	5612.94	10354.24	158
H28F	5016.87	5098.92	9614.19	158
H1SA	11785.15	3322.92	10248.62	237
H1SB	11248.89	3593.47	10843.16	237
H1SC	11859.54	4243.9	10570.63	237
H2SB	10359.41	3488.54	9640.65	215
H2SA	10339.47	4341.27	10018.35	215
H3SB	10422.08	5180.26	8446.04	217
H3SA	9813.24	5470.14	8937.25	217
H4SA	8879.46	5655.47	7482.53	332
H4SB	9859.15	5981.56	7579.46	332
H4SC	9299.89	6333.1	8126.13	332

Table 8 Atomic Occupancy for ch1jw286s_0m.

Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
H20A	0.452(10)	H20B	0.452(10)	H20C	0.548(10)
H20D	0.548(10)	H22A	0.452(10)	H22B	0.452(10)
H22C	0.548(10)	H22D	0.548(10)	H27C	0.48(3)
H27D	0.48(3)	H27A	0.52(3)	H27B	0.52(3)
C21A	0.452(10)	H21A	0.452(10)	H21B	0.452(10)
C23A	0.452(10)	H23A	0.452(10)	H23B	0.452(10)
C24A	0.452(10)	H24A	0.452(10)	H24B	0.452(10)
C25A	0.452(10)	H25A	0.452(10)	H25B	0.452(10)
H25C	0.452(10)	C28A	0.52(3)	H28A	0.52(3)
H28B	0.52(3)	H28C	0.52(3)	C21B	0.548(10)
H21C	0.548(10)	H21D	0.548(10)	C23B	0.548(10)
H23C	0.548(10)	H23D	0.548(10)	C24B	0.548(10)
H24C	0.548(10)	H24D	0.548(10)	C25B	0.548(10)
H25D	0.548(10)	H25E	0.548(10)	H25F	0.548(10)
C28B	0.48(3)	H28D	0.48(3)	H28E	0.48(3)
H28F	0.48(3)	O1S	0.5	C1S	0.5
H1SA	0.5	H1SB	0.5	H1SC	0.5
C2S	0.5	H2SB	0.5	H2SA	0.5
C3S	0.5	H3SB	0.5	H3SA	0.5

C4S	0.5	H4SA	0.5	H4SB	0.5
H4SC	0.5				

Crystal structure determination of ch1jw286s_0m

Crystal Data for $C_{45}H_{55}BrMnN_4O_{5.5}$ (M =874.78 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 15.8147(12) Å, b = 16.2939(11) Å, c = 17.9380(11) Å, β = 106.379(4)°, V = 4434.7(5) Å^3, Z = 4, T = 110.01 K, μ(MoKα) = 1.247 mm^{-1}, *Dcalc* = 1.310 g/cm^3, 76332 reflections measured (2.684° ≤ 2Θ ≤ 55.286°), 10219 unique (R_{int} = 0.1106, R_{sigma} = 0.1125) which were used in all calculations. The final R_1 was 0.0947 (I > 2σ(I)) and wR_2 was 0.2798 (all data).

[Re(HPEAB)(CO)$_3$Cl]·Et$_2$O – CCSD deposition number 1953191

spall1_0m

Table 9 Crystal data and structure refinement for spall1_0m.

Identification code	spall1_0m
Empirical formula	$C_{47}H_{60}ClN_4O_6Re$
Formula weight	998.64
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	15.9608(5)
b/Å	16.3375(4)
c/Å	17.8363(5)
α/°	90
β/°	107.5280(10)
γ/°	90
Volume/Å^3	4435.0(2)
Z	4
ρ_{calc}g/cm^3	1.496
μ/mm^{-1}	6.333
F(000)	2040.0
Crystal size/mm^3	0.32 × 0.12 × 0.04
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.502 to 133.708
Index ranges	-19 ≤ h ≤ 19, -19 ≤ k ≤ 19, -21 ≤ l ≤ 21
Reflections collected	68588
Independent reflections	7875 [R_{int} = 0.0690, R_{sigma} = 0.0336]
Data/restraints/parameters	7875/555/580
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0413, wR_2 = 0.1008
Final R indexes [all data]	R_1 = 0.0521, wR_2 = 0.1069
Largest diff. peak/hole / e Å^{-3}	2.69/-0.65

Table 10 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for spall1_0m. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Re1	1620.3(2)	6207.7(2)	7202.9(2)	26.90(9)
Cl1	2000.5(8)	5115.4(7)	6381.6(7)	32.7(3)
O1	1513(2)	8327(2)	6645.6(19)	35.9(8)
O2	433(2)	5674(2)	8552.3(19)	38.3(8)
O3	3374(2)	7096(2)	7481(2)	42.2(9)
O4	2606(2)	5412(2)	8779(2)	42.0(9)
O5	1172(3)	7551(2)	8217(2)	43.1(9)
O6A	4899(10)	5708(10)	9062(10)	116(5)
O6B	4948(17)	5040(20)	8710(20)	319(15)
N1	371(3)	5531(2)	6876(2)	27.1(8)
N2	869(3)	6695(2)	6038(2)	28.3(8)
N3	906(3)	4359(3)	8575(2)	35.4(9)
N4	2494(3)	8095(3)	5977(2)	34.3(9)
C1	93(3)	4997(3)	7330(3)	29.1(10)
C2	-624(3)	4495(3)	7044(3)	33.0(10)
C3	-1086(4)	4539(3)	6251(3)	35.6(11)
C4	-835(3)	5092(3)	5781(3)	34.2(11)
C5	-104(3)	5583(3)	6104(3)	28.1(10)
C6	189(3)	6218(3)	5640(3)	29.6(10)
C7	-242(3)	6352(3)	4846(3)	33.7(11)
C8	32(4)	6970(3)	4457(3)	35.6(11)
C9	711(3)	7469(3)	4866(3)	34.1(11)
C10	1112(3)	7318(3)	5657(3)	29.7(10)
C11	519(3)	5047(3)	8216(3)	33.1(10)
C12	1241(4)	4373(4)	9442(3)	48.8(14)
C13A	500(12)	4247(11)	9832(9)	70(4)
C13B	713(15)	3784(11)	9782(11)	70(4)
C14	1096(3)	3649(3)	8177(3)	35.1(11)
C15	1706(4)	3677(3)	7776(3)	48.7(14)
C16	1911(5)	2979(4)	7426(4)	53.2(16)
C17	1523(4)	2238(3)	7485(3)	38.8(11)
C18	904(5)	2227(4)	7862(5)	64(2)
C19	689(5)	2916(4)	8213(5)	64(2)
C20	1747(4)	1448(4)	7137(4)	47.7(14)
C21	2395(5)	929(4)	7755(5)	67.3(18)
C22A	3286(8)	1374(12)	7831(14)	111(4)
C22B	3293(10)	1244(17)	8268(11)	103(4)
C23A	3997(10)	851(11)	7955(16)	111(4)
C23B	3859(11)	1333(17)	7769(11)	103(4)
C24A	4805(10)	1519(12)	8224(15)	111(4)
C24B	4927(11)	1076(16)	8029(12)	103(4)

C25A	4790(10)	2359(11)	8312(13)	111(4)
C25B	5571(12)	481(14)	8154(11)	103(4)
C26	1749(3)	7943(3)	6150(3)	31.2(10)
C27	3048(4)	8774(3)	6398(3)	39.6(12)
C28	2705(5)	9610(4)	6065(4)	52.5(15)
C29	2821(3)	7603(3)	5454(3)	35.0(11)
C30	2833(3)	6759(3)	5497(3)	36.3(11)
C31	3157(4)	6307(3)	4990(3)	40.2(12)
C32	3485(4)	6679(4)	4430(3)	45.5(13)
C33	3489(4)	7522(4)	4414(3)	49.5(14)
C34	3163(4)	7990(4)	4915(3)	42.4(12)
C35	3812(6)	6171(5)	3872(4)	67.5(19)
C36A	4607(8)	6487(9)	3686(7)	62(3)
C36B	4805(10)	5868(11)	4280(10)	77(4)
C37A	5365(14)	6410(20)	4374(18)	116(11)
C37B	5516(14)	6452(12)	4510(18)	67(6)
C38A	6199(11)	6627(13)	4197(11)	100(6)
C38B	6494(14)	6155(12)	4844(14)	92(6)
C39A	7134(14)	6659(13)	5005(15)	96(5)
C39B	6990(30)	7110(20)	4870(40)	240(30)
C40	7596(10)	7064(10)	4635(10)	171(6)
C41	2713(4)	6777(3)	7358(3)	32.6(10)
C42	2221(3)	5691(3)	8177(3)	33.7(11)
C43	1304(3)	7050(3)	7814(3)	32.5(11)
C44A	5056(18)	4919(16)	8658(16)	116(5)
C44B	4290(20)	4340(30)	8430(30)	319(15)
C45A	4356(14)	4784(15)	7841(13)	116(5)
C45B	4424(19)	3500(30)	8070(30)	319(15)
C46A	5771(14)	5999(16)	9595(14)	116(5)
C46B	5350(20)	5750(30)	9240(30)	319(15)
C47A	6389(14)	6293(15)	10431(14)	116(5)
C47B	5450(20)	6210(30)	10030(30)	319(15)

Table 11 Anisotropic Displacement Parameters ($Å^2×10^3$) for spall1_0m. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Re1	36.25(14)	24.15(13)	20.68(12)	-0.36(8)	9.16(9)	0.36(9)
Cl1	43.1(6)	27.9(6)	30.0(5)	-1.7(5)	15.6(5)	3.1(5)
O1	53(2)	29.5(18)	28.6(17)	-2.1(14)	17.0(16)	-2.5(16)
O2	52(2)	38.0(19)	28.4(17)	-2.2(15)	16.8(16)	3.4(17)
O3	42(2)	45(2)	36.0(19)	9.0(17)	5.5(16)	-7.3(17)
O4	49(2)	38(2)	32.9(18)	9.1(16)	2.2(16)	-4.9(17)

O5	72(3)	30.0(19)	30.8(18)	-4.4(15)	20.6(18)	3.3(18)
O6A	92(6)	128(9)	134(9)	19(7)	43(6)	61(6)
O6B	82(9)	530(40)	310(20)	-200(20)	9(12)	29(14)
N1	33(2)	24.1(19)	25.7(18)	-3.2(15)	10.6(15)	3.9(16)
N2	36(2)	25.3(19)	24.3(18)	-0.9(15)	10.5(16)	5.0(16)
N3	43(2)	37(2)	25.5(19)	6.6(17)	7.9(17)	-3.4(18)
N4	44(2)	33(2)	27(2)	0.9(17)	11.7(18)	-4.0(18)
C1	35(2)	23(2)	31(2)	-1.9(19)	13.7(19)	4.0(19)
C2	42(3)	26(2)	34(2)	0(2)	17(2)	1(2)
C3	44(3)	26(2)	37(2)	-4(2)	12(2)	-1(2)
C4	45(3)	30(3)	28(2)	-4(2)	11(2)	3(2)
C5	37(3)	26(2)	22(2)	-3.8(18)	9.7(18)	3.9(19)
C6	38(3)	25(2)	26(2)	-1.6(18)	12.0(19)	4.9(19)
C7	43(3)	32(3)	25(2)	-2(2)	9(2)	0(2)
C8	48(3)	36(3)	23(2)	0(2)	11(2)	4(2)
C9	47(3)	30(3)	26(2)	1(2)	12(2)	2(2)
C10	38(3)	28(2)	26(2)	1.3(18)	14.8(19)	3.5(19)
C11	38(3)	33(2)	33(2)	3(2)	17(2)	-1(2)
C12	61(4)	50(3)	31(3)	5(2)	7(2)	-12(3)
C13A	108(9)	78(10)	35(4)	0(8)	36(5)	-32(9)
C13B	108(9)	78(10)	35(4)	0(8)	36(5)	-32(9)
C14	38(3)	30(2)	35(3)	11(2)	7(2)	3(2)
C15	73(4)	36(3)	46(3)	-5(2)	31(3)	-20(3)
C16	81(4)	43(3)	45(3)	-9(3)	33(3)	-21(3)
C17	42(3)	31(3)	40(3)	3(2)	6(2)	-2(2)
C18	66(4)	27(3)	118(6)	6(3)	55(4)	-4(3)
C19	61(4)	35(3)	118(6)	4(3)	60(4)	-4(3)
C20	55(4)	38(3)	52(3)	-7(2)	18(3)	-9(3)
C21	70(4)	49(4)	84(5)	-9(3)	26(4)	18(3)
C22A	50(4)	104(7)	167(10)	-40(8)	17(5)	6(4)
C22B	70(6)	170(13)	68(6)	-18(7)	20(4)	0(6)
C23A	50(4)	104(7)	167(10)	-40(8)	17(5)	6(4)
C23B	70(6)	170(13)	68(6)	-18(7)	20(4)	0(6)
C24A	50(4)	104(7)	167(10)	-40(8)	17(5)	6(4)
C24B	70(6)	170(13)	68(6)	-18(7)	20(4)	0(6)
C25A	50(4)	104(7)	167(10)	-40(8)	17(5)	6(4)
C25B	70(6)	170(13)	68(6)	-18(7)	20(4)	0(6)
C26	45(3)	27(2)	21(2)	6.2(18)	9.7(19)	3(2)
C27	47(3)	40(3)	30(3)	-2(2)	9(2)	-10(2)
C28	75(4)	36(3)	45(3)	0(3)	17(3)	-10(3)
C29	38(3)	42(3)	23(2)	2(2)	7(2)	-1(2)
C30	39(3)	41(3)	30(2)	4(2)	11(2)	0(2)
C31	40(3)	43(3)	37(3)	-2(2)	10(2)	-2(2)
C32	52(3)	56(3)	30(3)	-8(2)	13(2)	-7(3)
C33	66(4)	56(3)	33(3)	1(3)	24(3)	-12(3)

C34	55(3)	44(3)	28(2)	1(2)	12(2)	-8(3)
C35	93(5)	75(5)	44(3)	-20(3)	35(3)	-10(4)
C36A	72(7)	69(8)	52(7)	-4(6)	31(5)	21(6)
C36B	91(8)	77(10)	88(11)	-12(9)	63(8)	-5(7)
C37A	81(8)	210(30)	64(10)	-23(14)	30(8)	33(13)
C37B	82(9)	35(8)	93(17)	2(9)	39(10)	21(7)
C38A	77(8)	109(15)	112(13)	7(12)	25(8)	27(9)
C38B	87(9)	96(13)	104(15)	-8(12)	47(10)	41(9)
C39A	94(10)	79(13)	113(14)	14(11)	31(8)	31(10)
C39B	210(30)	210(30)	380(60)	-100(50)	210(40)	-90(30)
C40	165(11)	187(14)	200(15)	-80(11)	114(11)	-65(11)
C41	43(3)	29(2)	26(2)	3(2)	10(2)	3(2)
C42	37(3)	27(2)	36(2)	-3(2)	9(2)	-7(2)
C43	46(3)	28(2)	23(2)	4.0(19)	10(2)	1(2)
C44A	92(6)	128(9)	134(9)	19(7)	43(6)	61(6)
C44B	82(9)	530(40)	310(20)	-200(20)	9(12)	29(14)
C45A	92(6)	128(9)	134(9)	19(7)	43(6)	61(6)
C45B	82(9)	530(40)	310(20)	-200(20)	9(12)	29(14)
C46A	92(6)	128(9)	134(9)	19(7)	43(6)	61(6)
C46B	82(9)	530(40)	310(20)	-200(20)	9(12)	29(14)
C47A	92(6)	128(9)	134(9)	19(7)	43(6)	61(6)
C47B	82(9)	530(40)	310(20)	-200(20)	9(12)	29(14)

Table 12 Bond Lengths for spall1_0m.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Re1	Cl1	2.4968(11)	C14	C15	1.371(8)
Re1	N1	2.199(4)	C14	C19	1.373(8)
Re1	N2	2.211(4)	C15	C16	1.385(8)
Re1	C41	1.921(5)	C16	C17	1.379(8)
Re1	C42	1.911(5)	C17	C18	1.354(8)
Re1	C43	1.915(5)	C17	C20	1.519(8)
O1	C26	1.231(6)	C18	C19	1.380(9)
O2	C11	1.216(6)	C20	C21	1.522(9)
O3	C41	1.138(6)	C21	C22A	1.567(15)
O4	C42	1.157(6)	C21	C22B	1.539(16)
O5	C43	1.149(6)	C22A	C23A	1.383(19)
O6A	C44A	1.53(2)	C22B	C23B	1.45(2)
O6A	C46A	1.51(2)	C23A	C24A	1.647(19)
O6B	C44B	1.52(2)	C23B	C24B	1.68(2)
O6B	C46B	1.52(2)	C24A	C25A	1.38(2)
N1	C1	1.353(6)	C24B	C25B	1.38(2)
N1	C5	1.360(6)	C27	C28	1.524(8)
N2	C6	1.351(6)	C29	C30	1.380(8)

N2	C10	1.344(6)	C29	C34	1.392(7)
N3	C11	1.348(6)	C30	C31	1.382(8)
N3	C12	1.476(6)	C31	C32	1.398(8)
N3	C14	1.440(7)	C32	C33	1.377(9)
N4	C26	1.339(7)	C32	C35	1.505(8)
N4	C27	1.476(6)	C33	C34	1.391(8)
N4	C29	1.442(7)	C35	C36A	1.497(14)
C1	C2	1.374(7)	C35	C36B	1.610(16)
C1	C11	1.522(7)	C36A	C37A	1.45(2)
C2	C3	1.386(7)	C36B	C37B	1.44(2)
C3	C4	1.372(7)	C37A	C38A	1.50(4)
C4	C5	1.391(7)	C37B	C38B	1.57(3)
C5	C6	1.488(7)	C38A	C39A	1.73(2)
C6	C7	1.392(7)	C38B	C39B	1.74(3)
C7	C8	1.370(7)	C39A	C40	1.31(3)
C8	C9	1.377(7)	C39B	C40	1.16(4)
C9	C10	1.384(6)	C44A	C45A	1.56(2)
C10	C26	1.521(7)	C44B	C45B	1.56(3)
C12	C13A	1.556(13)	C46A	C47A	1.59(2)
C12	C13B	1.521(13)	C46B	C47B	1.55(3)

Table 13 Bond Angles for spall1_0m.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	Re1	Cl1	81.16(10)	N3	C12	C13B	109.8(9)
N1	Re1	N2	74.95(14)	C15	C14	N3	121.2(5)
N2	Re1	Cl1	82.21(10)	C15	C14	C19	118.3(5)
C41	Re1	Cl1	93.46(15)	C19	C14	N3	120.5(5)
C41	Re1	N1	172.99(17)	C14	C15	C16	120.5(5)
C41	Re1	N2	99.96(18)	C17	C16	C15	121.1(6)
C42	Re1	Cl1	94.21(15)	C16	C17	C20	123.3(5)
C42	Re1	N1	100.69(18)	C18	C17	C16	117.5(6)
C42	Re1	N2	174.70(17)	C18	C17	C20	119.2(5)
C42	Re1	C41	84.1(2)	C17	C18	C19	122.2(6)
C42	Re1	C43	86.9(2)	C14	C19	C18	120.3(6)
C43	Re1	Cl1	178.68(15)	C17	C20	C21	111.7(5)
C43	Re1	N1	98.00(18)	C20	C21	C22A	101.8(9)
C43	Re1	N2	96.61(17)	C20	C21	C22B	123.5(12)
C43	Re1	C41	87.3(2)	C23A	C22A	C21	114.0(15)
C46A	O6A	C44A	108.1(16)	C23B	C22B	C21	108.0(13)
C46B	O6B	C44B	154(4)	C22A	C23A	C24A	99.8(14)
C1	N1	Re1	126.9(3)	C22B	C23B	C24B	124.9(18)
C1	N1	C5	117.5(4)	C25A	C24A	C23A	130.8(16)
C5	N1	Re1	114.9(3)	C25B	C24B	C23B	150(2)

C6	N2	Re1	114.1(3)	O1	C26	N4	123.9(5)
C10	N2	Re1	126.2(3)	O1	C26	C10	117.5(4)
C10	N2	C6	118.7(4)	N4	C26	C10	118.4(4)
C11	N3	C12	117.1(5)	N4	C27	C28	112.7(5)
C11	N3	C14	124.9(4)	C30	C29	N4	121.5(4)
C14	N3	C12	117.7(4)	C30	C29	C34	119.3(5)
C26	N4	C27	117.3(4)	C34	C29	N4	119.1(5)
C26	N4	C29	124.5(4)	C29	C30	C31	119.9(5)
C29	N4	C27	118.1(4)	C30	C31	C32	121.9(5)
N1	C1	C2	123.3(4)	C31	C32	C35	120.8(6)
N1	C1	C11	117.4(4)	C33	C32	C31	117.1(5)
C2	C1	C11	118.7(4)	C33	C32	C35	122.1(6)
C1	C2	C3	118.4(5)	C32	C33	C34	122.0(5)
C4	C3	C2	119.7(5)	C33	C34	C29	119.7(5)
C3	C4	C5	119.2(5)	C32	C35	C36B	111.2(8)
N1	C5	C4	121.8(4)	C36A	C35	C32	116.3(7)
N1	C5	C6	115.7(4)	C37A	C36A	C35	109.3(16)
C4	C5	C6	122.4(4)	C37B	C36B	C35	120.5(14)
N2	C6	C5	116.6(4)	C36A	C37A	C38A	112(2)
N2	C6	C7	121.1(4)	C36B	C37B	C38B	120.7(16)
C7	C6	C5	122.2(4)	C37A	C38A	C39A	115.4(19)
C8	C7	C6	119.7(5)	C37B	C38B	C39B	97(2)
C7	C8	C9	119.3(5)	C40	C39A	C38A	94.1(17)
C8	C9	C10	118.9(5)	C40	C39B	C38B	111(3)
N2	C10	C9	122.3(5)	O3	C41	Re1	176.9(4)
N2	C10	C26	117.4(4)	O4	C42	Re1	176.7(4)
C9	C10	C26	119.6(4)	O5	C43	Re1	175.2(5)
O2	C11	N3	124.8(5)	O6A	C44A	C45A	112.7(17)
O2	C11	C1	118.5(4)	O6B	C44B	C45B	129(3)
N3	C11	C1	116.5(4)	O6A	C46A	C47A	151(2)
N3	C12	C13A	112.5(8)	O6B	C46B	C47B	147(5)

Table 14 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for spall1_0m.

Atom	*x*	*y*	*z*	U(eq)	
H2	-798.8	4127.83	7381.95		40
H3	-1573.27	4188.41	6034.86		43
H4	-1157.47	5137.84	5239.54		41
H7	-724.59	6015.94	4575.72		40
H8	-243.11	7053.13	3910.85		43
H9	901.77	7909.1	4609.77		41
H12C	1193.27	4933.84	9635.05		59
H12D	1868.13	4212.65	9615.74		59

H12A	1533.06	4904.5	9614.6	59
H12B	1686.19	3936.17	9621.95	59
H13A	-8.91	4583.37	9560.87	106
H13B	715.3	4408.29	10386.47	106
H13C	327.94	3668.79	9795.28	106
H13D	89.57	3932.68	9594.1	106
H13E	919.87	3813.94	10357.53	106
H13F	788.89	3224.62	9614.31	106
H15	1990.35	4179.4	7737.24	58
H16	2326.19	3011.93	7141.23	64
H18	606.94	1728.21	7886.8	77
H19	258.3	2882.8	8480.86	77
H20A	2004.26	1580.95	6711.41	57
H20B	1202.42	1131.01	6905.14	57
H21C	2513.34	436.48	7479.68	81
H21D	2077.48	737.51	8121.62	81
H21A	2403.42	356.3	7575.46	81
H21B	2255.51	932.88	8259.93	81
H22A	3226.2	1690.65	7344.19	133
H22B	3405.53	1767.25	8272.65	133
H22C	3223.54	1777.41	8505.36	123
H22D	3555.09	850.84	8697.68	123
H23A	3994.33	558.1	7468.54	133
H23B	4019.45	449.63	8376.4	133
H23C	3829.71	1917.62	7617.48	123
H23D	3571.97	1023.76	7282.21	123
H24A	5180.59	1317.44	8738.65	133
H24B	5148	1431.65	7851.83	133
H24C	5120.04	1435.54	7665.59	123
H24D	5131.46	1362.35	8540.78	123
H25A	4627.34	2620.11	7793.37	166
H25B	5374.13	2549.05	8622.9	166
H25C	4359.84	2503.69	8582.41	166
H25D	6123.19	730.95	8137.65	154
H25E	5390.58	61.75	7743.98	154
H25F	5655.45	228.27	8670.16	154
H27A	3652.53	8702.46	6367.82	48
H27B	3074.56	8753.65	6959.9	48
H28A	2709.34	9646.77	5517.72	79
H28B	3081.42	10039.81	6376.03	79
H28C	2102.87	9682.45	6086.5	79
H30	2619.34	6489.17	5874.35	44
H31	3157.02	5726.79	5023.19	48
H33	3722.45	7792.33	4049	59
H34	3173.83	8570.53	4890.21	51

H35A	3945.33	5615.54	4097.1	81
H35B	3329.52	6118.24	3372.74	81
H35C	3787.6	6499.76	3399.29	81
H35D	3425.07	5689.59	3701.99	81
H36A	4703.08	6168.81	3246.3	74
H36B	4518.27	7067.55	3522.94	74
H36C	4807.92	5556.62	4756.71	93
H36D	4950.34	5475.63	3915.12	93
H37A	5404.36	5843.66	4573.01	139
H37B	5291.84	6779.49	4791.5	139
H37C	5397.92	6813.42	4912.37	81
H37D	5479.32	6797.66	4045.82	81
H38A	6123.3	7168.64	3936.68	120
H38B	6294.88	6221.5	3818.4	120
H38C	6657.89	5766.16	4485.53	110
H38D	6620.26	5909.86	5373.81	110
H39A	7045.74	6966.97	5452.62	115
H39B	7376.9	6108.96	5177.51	115
H39C	6564.97	7498.37	4539.58	287
H39D	7184.77	7314.79	5412.74	287
H40A	8201.53	7120.62	4977.49	256
H40B	7338.49	7607.6	4492.46	256
H40C	7594.32	6766.18	4157.21	256
H40D	8045.87	6715.95	4986.55	256
H40E	7836.57	7612.48	4615.85	256
H40F	7415.65	6826.28	4105.64	256
H44C	5044.28	4447.17	9002.75	139
H44D	5647.27	4941.68	8586.66	139
H44A	3778.97	4592.23	8040.81	382
H44B	4092.15	4204.42	8891.59	382
H45D	4311.36	5278.37	7520.8	174
H45E	3784.98	4666.48	7916.67	174
H45F	4533.76	4321.01	7573.81	174
H45A	3877.98	3183.56	7952.07	478
H45B	4579.56	3590.99	7586.75	478
H45C	4896.74	3198.24	8448.35	478
H46C	5868.46	6461.73	9272.64	139
H46D	6148.36	5557.6	9493.05	139
H46A	5149.82	6210.66	8866.14	382
H46B	5974.78	5678.99	9273.33	382
H47D	6770.52	6736.59	10359.1	174
H47E	6750.96	5832.92	10699.66	174
H47F	6025.42	6489.36	10749.48	174
H47A	4877.9	6258.14	10112	478
H47B	5698.55	6752.3	10001.83	478

H47C	5849.81	5895.96	10458.67	478

Table 15 Atomic Occupancy for spall1_0m.

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
O6A	0.474(13)	O6B	0.526(13)	H12C	0.470(10)
H12D	0.470(10)	H12A	0.530(10)	H12B	0.530(10)
C13A	0.530(10)	H13A	0.530(10)	H13B	0.530(10)
H13C	0.530(10)	C13B	0.470(10)	H13D	0.470(10)
H13E	0.470(10)	H13F	0.470(10)	H21C	0.470(11)
H21D	0.470(11)	H21A	0.530(11)	H21B	0.530(11)
C22A	0.530(11)	H22A	0.530(11)	H22B	0.530(11)
C22B	0.470(11)	H22C	0.470(11)	H22D	0.470(11)
C23A	0.530(11)	H23A	0.530(11)	H23B	0.530(11)
C23B	0.470(11)	H23C	0.470(11)	H23D	0.470(11)
C24A	0.530(11)	H24A	0.530(11)	H24B	0.530(11)
C24B	0.470(11)	H24C	0.470(11)	H24D	0.470(11)
C25A	0.530(11)	H25A	0.530(11)	H25B	0.530(11)
H25C	0.530(11)	C25B	0.470(11)	H25D	0.470(11)
H25E	0.470(11)	H25F	0.470(11)	H35A	0.530(10)
H35B	0.530(10)	H35C	0.470(10)	H35D	0.470(10)
C36A	0.530(10)	H36A	0.530(10)	H36B	0.530(10)
C36B	0.470(10)	H36C	0.470(10)	H36D	0.470(10)
C37A	0.530(10)	H37A	0.530(10)	H37B	0.530(10)
C37B	0.470(10)	H37C	0.470(10)	H37D	0.470(10)
C38A	0.530(10)	H38A	0.530(10)	H38B	0.530(10)
C38B	0.470(10)	H38C	0.470(10)	H38D	0.470(10)
C39A	0.530(10)	H39A	0.530(10)	H39B	0.530(10)
C39B	0.470(10)	H39C	0.470(10)	H39D	0.470(10)
H40A	0.530(10)	H40B	0.530(10)	H40C	0.530(10)
H40D	0.470(10)	H40E	0.470(10)	H40F	0.470(10)
C44A	0.474(13)	H44C	0.474(13)	H44D	0.474(13)
C44B	0.526(13)	H44A	0.526(13)	H44B	0.526(13)
C45A	0.474(13)	H45D	0.474(13)	H45E	0.474(13)
H45F	0.474(13)	C45B	0.526(13)	H45A	0.526(13)
H45B	0.526(13)	H45C	0.526(13)	C46A	0.474(13)
H46C	0.474(13)	H46D	0.474(13)	C46B	0.526(13)
H46A	0.526(13)	H46B	0.526(13)	C47A	0.474(13)
H47D	0.474(13)	H47E	0.474(13)	H47F	0.474(13)
C47B	0.526(13)	H47A	0.526(13)	H47B	0.526(13)
H47C	0.526(13)				

Crystal structure determination of spall1_0m

Crystal Data for $C_{47}H_{60}ClN_4O_6Re$ (M =998.64 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 15.9608(5) Å, b = 16.3375(4) Å, c = 17.8363(5) Å, β = 107.5280(10)°, V = 4435.0(2) Å^3, Z = 4, T = 100.0 K, μ(CuKα) = 6.333 mm^{-1}, *Dcalc* = 1.496 g/cm^3, 68588 reflections measured (7.502° ≤ 2Θ ≤ 133.708°), 7875 unique

Part S2: Computational Details

Calculations were performed using the SMP version of the Gaussian09 package, revision D.01.[9] Gaussian was compiled using the Gaussian supplied version of BLAS and ATLAS on the EMT64 architecture.[10,11] The solvent, dichloromethane, was simulated using the integral equation formalism polarisable continuum model (IEFPCM) using the parameters as implemented in Gaussian09.[12-14] All calculations utilized the PBE0 functional.[10] The Karlsruhe basis set, def2-SVP,[15,16] was employed for all atoms except Re and Mn. For these, the Dirac-Hartree-Fock basis set, dhf-SVP,[17] was used instead. Frequencies within the harmonic approximation were calculated for all optimized structures. The absence of imaginary frequencies confirmed that energy minima had been found. For all calculations, ultrafine integrals were used and no symmetry constraints were applied. Calculated vibrational frequencies were scaled to account for the anharmonicity of the vibrational modes.[19-23]

1 - [Re(HPEAB)(CO_3)(Cl)]

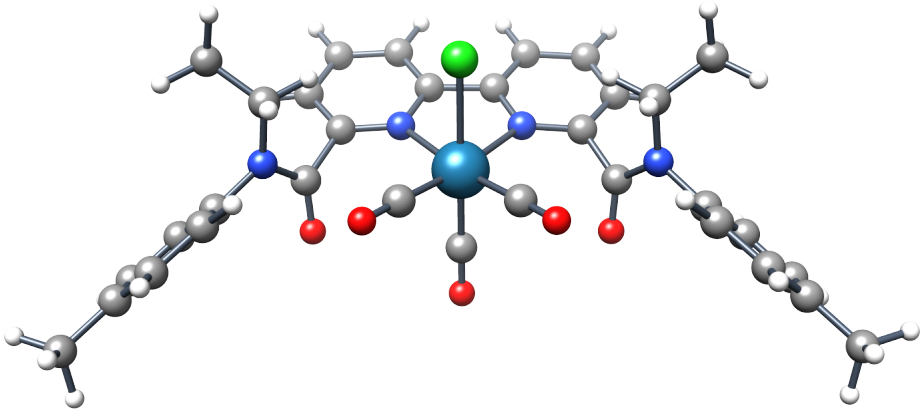


Figure S43: Optimised singlet ground state geometry of [Re(HPEAB)(CO_3)(Cl)]

Route	:	#p opt freq genecp scrf=(cpcm,solvent=dichloromethane)
	:	geom=connectivity int=(acc2e=13,ultrafine) pbe1pbe
SMILES	:	CCN(c1ccc(cc1)C)C(=O)c2cccc-3[n+]2[Re]([n+]
		4c3cccc4C(=O)N(CC)c5ccc(cc5)C)([C][O])([C][O])([C][O])Cl
Formula	:	$C_{33}H_{30}ClN_4O_5Re$
Charge	:	0
Multiplicity	:	1
Dipole	:	32.4609 Debye
Energy	:	-2405.99340823 a.u.
Gibbs Energy	:	-2405.50424600 a.u.
Number of imaginary frequencies	:	0

Cartesian Co-ordinates (XYZ format)

74

C	-0.73677099	2.98297310	-0.49070799

C	-2.68605399	1.72655296	-0.50107598
C	-3.47341490	2.87563610	-0.57459497
C	-2.85492706	4.11765099	-0.59481102
C	-1.46938801	4.16965008	-0.55972803
C	0.73934001	2.98062801	-0.51126599
C	2.68560600	1.71996295	-0.54103601
C	3.47343993	2.86573410	-0.65225202
C	2.85665488	4.10812902	-0.68867201
C	1.47230005	4.16368818	-0.62392801
H	-4.55897999	2.78151608	-0.62638497
H	-3.44282389	5.03577709	-0.64704800
H	-0.96613300	5.13378286	-0.58751702
H	4.55770922	2.76832294	-0.72265500
H	3.44459701	5.02357578	-0.77581602
H	0.96998101	5.12772894	-0.66707999
Re	0.00150900	0.07531100	0.02639200
N	1.34712005	1.77388096	-0.46140301
N	-1.34618795	1.77704895	-0.44564500
C	-0.00580600	-0.64727002	-1.74207795
O	-0.01009600	-1.09498405	-2.80690694
C	-1.26103902	-1.24638104	0.58179700
O	-1.97055697	-2.07868791	0.95373702
C	1.26471996	-1.24901497	0.57433498
O	1.97413695	-2.08300090	0.94247699
C	3.39527297	0.39261600	-0.70221698
O	3.29530406	-0.18560100	-1.77001202
N	4.20898199	0.00820300	0.31878799
C	-3.39786601	0.40271899	-0.68011999
O	-3.29767990	-0.16091600	-1.75567496
N	-4.21350718	0.00494900	0.33424300
C	4.07919312	0.54878902	1.67261195
H	3.86094093	-0.28663400	2.35609794
H	3.17964506	1.18045402	1.70236301
C	5.30257320	1.30922997	2.14635801
H	5.15262890	1.64594197	3.18255997
H	6.20021677	0.67331100	2.12500310
H	5.49568892	2.19575691	1.52428102
C	-4.08261585	0.52150702	1.69725096
H	-3.85943794	-0.32519901	2.36517406
H	-3.18574810	1.15655303	1.73581100
C	-5.30785513	1.26826501	2.18769002
H	-6.20284891	0.62899703	2.15740895
H	-5.15646505	1.58697999	3.22935009
H	-5.50662279	2.16496396	1.58223295
C	5.14953518	-1.04236102	0.09700700
C	6.06224918	-0.94775301	-0.96031398
C	5.20400095	-2.15221596	0.94090003
C	6.99958801	-1.95192802	-1.16927600
H	6.03307009	-0.08049600	-1.62259495
C	6.15737104	-3.14791107	0.72865599
H	4.49201488	-2.25462198	1.76067197
C	7.06948614	-3.07294989	-0.32839301
H	7.70321417	-1.85820997	-2.00137711
H	6.18392801	-4.00863218	1.40251601
C	-5.15397596	-1.04195702	0.09494300
C	-5.20450401	-2.16856408	0.91653103
C	-6.06983280	-0.92711103	-0.95758098
C	-6.15741205	-3.16091299	0.68707502

H	-4.48964119	-2.28642702	1.73170805
C	-7.00667620	-1.92794096	-1.18398297
H	-6.04330683	-0.04661300	-1.60231304
C	-7.07276297	-3.06570601	-0.36555600
H	-6.18097878	-4.03513622	1.34343600
H	-7.71285009	-1.81846595	-2.01198697
C	8.08583927	-4.15149498	-0.56792301
H	7.89092302	-4.67494917	-1.51800704
H	9.10281563	-3.73456311	-0.63586497
H	8.07649994	-4.90038919	0.23610801
C	-8.08849144	-4.14050484	-0.62389898
H	-9.10603046	-3.72343993	-0.68173897
H	-7.89492083	-4.64520788	-1.58435094
H	-8.07673931	-4.90486479	0.16540700
Cl	0.01271100	1.17872095	2.26705098

Frequencies

Mode	IR frequency	IR intensity
1	7.25460000	2.32880000
2	14.05740000	0.50080000
3	16.70060000	0.31820000
4	17.18110000	0.31820000
5	21.17820000	0.33560000
6	24.09110000	2.60340000
7	32.72430000	4.51020000
8	38.38590000	1.24000000
9	43.19980000	2.91510000
10	47.04210000	1.00740000
11	52.42090000	5.37710000
12	58.96530000	2.04670000
13	65.13430000	2.81710000
14	65.85210000	0.27270000
15	70.04450000	1.57070000
16	77.23610000	0.46890000
17	84.70310000	0.34930000
18	92.82540000	1.03080000
19	94.94060000	0.95330000
20	97.33210000	2.14320000
21	101.23780000	2.43530000
22	109.31920000	2.42580000
23	113.42720000	1.17070000
24	121.38110000	0.03100000
25	126.19700000	1.72580000
26	130.49240000	2.94450000
27	146.43600000	2.53730000
28	146.90390000	0.05810000
29	148.55490000	2.31130000
30	176.62670000	0.51110000
31	181.66790000	0.39720000
32	197.35470000	7.20480000
33	210.57940000	0.19050000
34	215.51140000	0.91540000
35	215.98520000	0.76300000
36	233.09920000	12.27330000
37	250.51000000	4.66270000
38	270.30760000	0.01720000
39	282.37770000	33.18060000
40	300.72090000	2.51690000
41	302.83480000	3.02290000
42	310.68960000	14.06470000
43	334.65750000	0.35660000
44	334.97970000	1.97060000
45	351.46240000	1.78640000
46	351.73020000	1.84480000
47	367.62980000	22.33380000
48	384.03910000	13.90300000
49	384.81760000	4.55190000
50	417.71680000	5.19270000
51	420.39180000	2.93010000
52	425.77050000	1.33660000
53	426.07310000	2.57770000
54	457.85900000	2.95030000
55	461.40650000	1.52090000

56	485.71220000	8.98250000
57	489.14060000	24.65470000
58	502.04430000	3.46750000
59	504.25550000	21.31960000
60	507.79330000	4.03210000
61	509.71750000	20.41580000
62	521.85400000	1.89320000
63	525.97530000	5.20230000
64	529.51060000	19.97220000
65	541.15040000	25.32540000
66	542.14720000	6.83410000
67	542.65240000	19.56890000
68	564.66490000	44.06290000
69	619.08770000	3.42500000
70	638.46460000	34.98390000
71	650.27450000	3.81100000
72	651.00670000	0.87540000
73	652.13580000	21.16430000
74	656.21360000	12.00380000
75	657.22000000	10.17390000
76	667.88510000	26.23900000
77	674.44960000	27.23640000
78	683.46980000	26.70570000
79	695.74880000	1.07710000
80	737.87280000	3.91680000
81	737.99730000	2.56880000
82	744.99060000	4.20880000
83	748.48850000	15.26290000
84	764.46890000	2.20840000
85	770.73390000	4.98230000
86	772.51390000	25.10040000
87	777.02150000	2.70880000
88	784.78290000	38.86570000
89	790.61610000	113.68650000
90	815.67430000	6.40570000
91	831.40520000	32.80810000
92	842.92350000	54.30180000
93	843.18890000	6.82100000
94	849.80010000	4.19210000
95	849.89050000	3.39230000
96	855.94420000	73.67800000
97	871.31380000	0.04600000
98	887.10620000	0.15890000
99	923.90480000	2.36380000
100	946.18790000	0.43960000
101	947.90930000	2.05080000
102	972.53570000	11.75450000
103	974.25800000	4.71400000
104	987.27430000	3.63950000
105	993.14920000	13.21410000
106	996.55640000	6.65870000
107	996.77350000	7.14810000
108	1000.19340000	0.66670000
109	1000.43520000	3.80740000
110	1032.73780000	8.72030000
111	1032.87530000	4.35720000
112	1032.97700000	8.30620000
113	1037.19260000	1.97160000

114	1045.66800000	0.11600000
115	1049.24990000	5.39630000
116	1049.53480000	6.81880000
117	1049.58970000	11.31060000
118	1095.38470000	58.80640000
119	1104.63640000	19.43280000
120	1109.52170000	74.35840000
121	1117.41190000	53.75200000
122	1124.12630000	4.44340000
123	1134.57530000	12.56110000
124	1135.09780000	12.80830000
125	1141.16700000	0.59670000
126	1144.07810000	7.71180000
127	1146.80000000	25.61310000
128	1158.94180000	0.43910000
129	1190.97980000	10.61670000
130	1191.85980000	3.52220000
131	1196.15860000	4.75440000
132	1200.21070000	17.50360000
133	1243.12770000	20.41860000
134	1245.68850000	38.52450000
135	1250.55950000	4.33030000
136	1250.56390000	6.90690000
137	1298.66230000	54.57020000
138	1299.55280000	69.54810000
139	1305.26440000	68.54350000
140	1313.30310000	52.67540000
141	1323.67470000	14.63060000
142	1324.60380000	0.10210000
143	1353.37930000	109.97410000
144	1358.97200000	3.55100000
145	1365.97100000	7.23030000
146	1371.15840000	7.46330000
147	1371.36360000	5.65250000
148	1379.28080000	64.10220000
149	1380.76290000	10.74360000
150	1388.89260000	4.54280000
151	1389.01430000	3.63180000
152	1404.33440000	34.70200000
153	1404.50730000	40.98400000
154	1439.58050000	31.56640000
155	1440.13060000	41.81110000
156	1442.95820000	143.15540000
157	1445.06580000	0.37910000
158	1445.18280000	18.46990000
159	1450.30570000	4.62490000
160	1450.44930000	9.93690000
161	1452.97250000	229.08430000
162	1456.19440000	4.58520000
163	1459.06680000	176.72550000
164	1463.48650000	1.01890000
165	1469.66140000	35.04040000
166	1476.34780000	5.94050000
167	1477.11010000	17.88990000
168	1479.23180000	140.66040000
169	1500.96530000	210.00650000
170	1526.16800000	8.97920000
171	1529.27320000	47.18990000

172	1563.65120000	235.12200000
173	1563.82700000	167.37530000
174	1657.40270000	12.38250000
175	1657.52130000	3.30340000
176	1659.50900000	4.59240000
177	1667.05960000	64.99620000
178	1673.89910000	54.92510000
179	1681.83350000	22.18440000
180	1699.03300000	6.25280000
181	1699.07850000	6.32220000
182	1783.47380000	227.69190000
183	1783.79790000	708.62070000
184	2022.24950000	2053.52580000
185	2026.37940000	2219.40550000
186	2136.64990000	1513.10350000
187	3055.73110000	30.89830000
188	3055.74370000	32.12180000
189	3066.10290000	17.93550000
190	3066.34490000	17.43660000
191	3089.80820000	16.82970000
192	3090.47840000	16.18970000
193	3138.10820000	10.23990000
194	3138.12410000	10.11790000
195	3140.97050000	4.23620000
196	3141.76910000	3.79980000
197	3166.54440000	25.63730000
198	3166.66510000	27.87150000
199	3168.56060000	11.01920000
200	3168.58930000	11.92610000
201	3168.72700000	18.52030000
202	3168.88300000	19.40860000
203	3201.34150000	13.56790000
204	3201.40830000	13.38150000
205	3204.76250000	13.01480000
206	3204.78480000	19.23420000
207	3229.73080000	3.86790000
208	3230.07360000	3.76770000
209	3235.76910000	1.20870000
210	3236.27750000	1.02060000
211	3239.86410000	1.99120000
212	3240.15140000	1.87520000
213	3247.42000000	0.02540000
214	3248.04070000	0.08450000
215	3264.61140000	0.08540000
216	3278.99300000	0.07900000

2 - $[Re(HPEAB)(CO_3)(Cl)]^{\bullet-}$

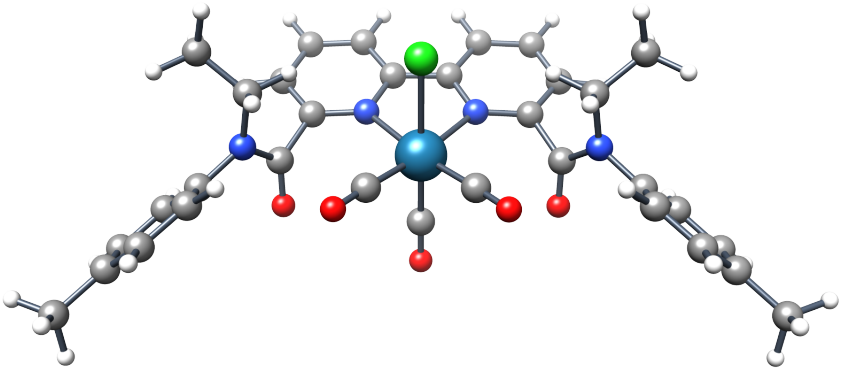


Figure S44: Optimised singlet ground state geometry of $[Re(HPEAB)(CO_3)(Cl)]^{\bullet-}$

Route	:	#p opt freq genecp scrf=(cpcm,solvent=dichloromethane)
	:	geom=connectivity int=(acc2e=13,ultrafine) pbe1pbe
SMILES	:	CCN(c1ccc(cc1)C)C(=O)c2cccc-3[n+]2[Re]([n+]4c3cccc4C(=O)N(CC)c5ccc(cc5)C)([C][O])([C][O])([C][O])Cl
Formula	:	$C_{33}H_{30}ClN_4O_5Re^{1-,2}$
Charge	:	-1
Multiplicity	:	2
Energy	:	-2406.10331305 a.u.
Gibbs Energy	:	-2405.61745600 a.u.
Number of imaginary frequencies	:	0

Cartesian Co-ordinates (XYZ format)

74

C	-0.71202999	2.99200010	-0.47066599
C	-2.69435096	1.73530102	-0.49881500
C	-3.48592210	2.87122512	-0.54538202
C	-2.85191011	4.13512993	-0.55148399
C	-1.48298800	4.18617296	-0.52064800
C	0.71201801	2.99200392	-0.47096500
C	2.69434404	1.73532200	-0.49942800
C	3.48589492	2.87124395	-0.54645598
C	2.85186100	4.13513422	-0.55280697
C	1.48294699	4.18616819	-0.52158701
H	-4.57092714	2.77525210	-0.60001898
H	-3.44173789	5.05359697	-0.58917803
H	-0.97963703	5.15219307	-0.53672701
H	4.57088900	2.77526689	-0.60129702
H	3.44165993	5.05359697	-0.59104401
H	0.97957802	5.15217400	-0.53796297
Re	0.00004700	0.06806900	-0.04112300
N	1.34891796	1.76177204	-0.43779400
N	-1.34890699	1.76175594	-0.43749800
C	-0.00010800	-0.57424998	-1.82810700
O	-0.00008500	-0.98111600	-2.91424799

C	-1.26208794	-1.27887297	0.45194200
O	-1.96557498	-2.13811302	0.78584099
C	1.26228499	-1.27886403	0.45173299
O	1.96572495	-2.13819289	0.78549099
C	3.42165899	0.42439499	-0.69342798
O	3.38593102	-0.12631001	-1.78130305
N	4.20014286	-0.00114800	0.34772199
C	-3.42167497	0.42440701	-0.69300002
O	-3.38582897	-0.12622200	-1.78091502
N	-4.20024014	-0.00124900	0.34802201
C	3.99256206	0.47019401	1.71573901
H	3.76424003	-0.39982599	2.35163593
H	3.07735205	1.07837605	1.72676802
C	5.17115879	1.24025798	2.28017998
H	4.96771717	1.52563798	3.32308197
H	6.08900976	0.63273799	2.27019191
H	5.35904789	2.15852308	1.70415103
C	-3.99289489	0.46992600	1.71612895
H	-3.76475501	-0.40019801	2.35195303
H	-3.07766891	1.07808602	1.72739196
C	-5.17156887	1.23995697	2.28045988
H	-6.08944511	0.63247901	2.27018309
H	-4.96832180	1.52514005	3.32345510
H	-5.35930300	2.15833497	1.70456100
C	5.15879393	-1.02967000	0.12319000
C	6.09857607	-0.89689201	-0.90752798
C	5.21092987	-2.16341591	0.93615103
C	7.05513716	-1.88201404	-1.11994803
H	6.07277012	-0.01312800	-1.54747105
C	6.18373680	-3.14021993	0.72193599
H	4.47830820	-2.29920292	1.73248804
C	7.12118721	-3.02488589	-0.30860999
H	7.77781010	-1.75564098	-1.93144906
H	6.20490599	-4.01900578	1.37265897
C	-5.15887880	-1.02973998	0.12320900
C	-5.21059895	-2.16399193	0.93548501
C	-6.09901905	-0.89639503	-0.90709502
C	-6.18338680	-3.14075398	0.72100103
H	-4.47765493	-2.30016804	1.73146105
C	-7.05556297	-1.88147700	-1.11980402
H	-6.07351208	-0.01220700	-1.54647195
C	-7.12120485	-3.02485991	-0.30915499
H	-6.20425606	-4.01994896	1.37118006
H	-7.77854204	-1.75467002	-1.93096304
C	8.15880680	-4.08283281	-0.55157697
H	7.99769878	-4.58208513	-1.52097595
H	9.17198563	-3.65181088	-0.57930201
H	8.13816547	-4.85479212	0.23036900
C	-8.15872478	-4.08282089	-0.55248803
H	-9.17186260	-3.65177202	-0.58099502
H	-7.99699497	-4.58235216	-1.52164602
H	-8.13859558	-4.85458803	0.22966200
Cl	0.00023100	1.02972102	2.29690504

Frequencies

Mode	IR frequency	IR intensity
1	10.14480000	2.04990000
2	13.71590000	0.32200000
3	17.80960000	0.37860000
4	19.64840000	0.65070000
5	21.83060000	0.22450000
6	27.68920000	0.02790000
7	34.23070000	1.04880000
8	36.37660000	0.78480000
9	42.68670000	7.09880000
10	48.96070000	1.26340000
11	55.47240000	5.37740000
12	56.60390000	0.54570000
13	64.37060000	1.37150000
14	65.06550000	1.88980000
15	69.93570000	0.83780000
16	77.43200000	1.01560000
17	84.74440000	0.52360000
18	93.40710000	0.69260000
19	95.52310000	1.36780000
20	96.77210000	1.21370000
21	97.53040000	2.35530000
22	110.91030000	1.81770000
23	111.88690000	0.96170000
24	119.61930000	0.03570000
25	126.26490000	1.93020000
26	128.34240000	2.51380000
27	147.02850000	2.91850000
28	147.04520000	3.53180000
29	147.37300000	0.04030000
30	175.11370000	0.11010000
31	182.47550000	1.49620000
32	197.44300000	9.94610000
33	204.44290000	0.04580000
34	218.25860000	0.23200000
35	220.26100000	0.80470000
36	237.84840000	9.79880000
37	248.53800000	4.58310000
38	263.21240000	33.10420000
39	267.80440000	0.01650000
40	299.35290000	3.63230000
41	303.03090000	1.75830000
42	311.27880000	12.39250000
43	334.86880000	0.44390000
44	335.05210000	1.17640000
45	352.51180000	3.53710000
46	353.32120000	3.18440000
47	365.58390000	21.22180000
48	374.55260000	31.99180000
49	386.23970000	7.98010000
50	416.06250000	3.61620000
51	418.28760000	3.63720000
52	424.97070000	2.66660000
53	425.12530000	0.27200000
54	431.46670000	0.60620000
55	464.68660000	11.82880000

56	484.61470000	14.70030000
57	488.36640000	8.90070000
58	501.89540000	0.00350000
59	506.30940000	23.74760000
60	510.14460000	2.66270000
61	517.85120000	22.19560000
62	523.91590000	6.34530000
63	525.63400000	40.02640000
64	533.76360000	2.65600000
65	540.93130000	30.22310000
66	541.07730000	2.66340000
67	543.91870000	16.54420000
68	569.52170000	48.47690000
69	610.74310000	0.86840000
70	634.15450000	2.86680000
71	644.00290000	35.62720000
72	649.99310000	6.55630000
73	651.07590000	1.09570000
74	653.90160000	4.93740000
75	657.16930000	12.56840000
76	665.34330000	28.74930000
77	673.14660000	37.54310000
78	674.92480000	31.91880000
79	689.03760000	9.14270000
80	713.04330000	6.67120000
81	732.92280000	3.47970000
82	742.66300000	11.50370000
83	743.92360000	0.00000000
84	745.69530000	19.99450000
85	748.84700000	69.83440000
86	768.03290000	46.46160000
87	768.04800000	79.20160000
88	770.71750000	1.62300000
89	773.86030000	71.57770000
90	807.03430000	49.15950000
91	812.06890000	1.16740000
92	819.54260000	2.44990000
93	834.92650000	3.36300000
94	842.80920000	49.73170000
95	848.41960000	7.08180000
96	848.45980000	5.70090000
97	850.69720000	46.68090000
98	859.21240000	0.80650000
99	863.10850000	14.80210000
100	884.90500000	0.92200000
101	917.47340000	2.61070000
102	970.60940000	6.58790000
103	971.81170000	5.06830000
104	983.01340000	0.16060000
105	985.22110000	0.38760000
106	989.42170000	13.41320000
107	991.87460000	0.14890000
108	995.34620000	5.42100000
109	995.35350000	7.09000000
110	998.06350000	0.24410000
111	998.26380000	4.65830000
112	1007.08890000	329.97570000
113	1032.37780000	9.29530000

114	1032.43210000	5.81930000
115	1038.00280000	17.24960000
116	1048.87140000	1.64490000
117	1048.88110000	17.51000000
118	1085.31800000	80.43590000
119	1092.29190000	41.47310000
120	1099.26810000	33.49180000
121	1108.13220000	14.40810000
122	1109.19330000	7.58210000
123	1118.77220000	17.33950000
124	1132.99180000	0.20460000
125	1134.10280000	14.88200000
126	1139.13130000	56.22550000
127	1146.34930000	19.99070000
128	1153.71590000	3.68250000
129	1174.08670000	218.20260000
130	1190.35050000	4.43930000
131	1191.59360000	0.32310000
132	1193.02530000	3.45190000
133	1228.99990000	34.67400000
134	1237.64120000	8.40550000
135	1250.33540000	3.63530000
136	1250.34100000	5.01680000
137	1297.89900000	109.66970000
138	1298.53560000	299.29170000
139	1305.21330000	74.92050000
140	1307.94060000	115.66120000
141	1321.00430000	0.65150000
142	1325.13270000	26.70520000
143	1325.53940000	5.05900000
144	1357.99950000	128.33210000
145	1368.23750000	5.31990000
146	1368.73600000	6.33310000
147	1376.51010000	14.98790000
148	1377.50930000	107.58490000
149	1388.19900000	7.99970000
150	1388.21050000	4.86550000
151	1399.21110000	15.32790000
152	1403.70590000	15.52260000
153	1406.17320000	272.76550000
154	1421.96660000	222.51830000
155	1438.98410000	245.44270000
156	1440.39720000	0.30360000
157	1442.53170000	14.09110000
158	1444.65040000	45.15720000
159	1444.91040000	15.26430000
160	1445.98120000	298.29530000
161	1450.42680000	57.90990000
162	1450.96380000	22.00410000
163	1452.59180000	30.43620000
164	1454.35890000	63.89890000
165	1461.55190000	249.89820000
166	1472.69210000	2.15640000
167	1475.61490000	35.10720000
168	1476.02920000	30.72060000
169	1482.88970000	195.44790000
170	1490.08570000	350.13640000
171	1554.71040000	25.50880000

172	1563.55590000	293.56760000
173	1563.79720000	168.13030000
174	1582.36660000	298.88300000
175	1597.94880000	79.85330000
176	1636.59710000	12.82430000
177	1645.37990000	245.18820000
178	1655.85340000	15.51550000
179	1655.87100000	0.07500000
180	1699.18680000	14.13340000
181	1699.24170000	8.43940000
182	1777.66430000	93.86220000
183	1778.15500000	732.50880000
184	1989.80860000	2238.56830000
185	1994.70310000	2158.93450000
186	2114.70530000	1488.32950000
187	3053.64080000	37.46910000
188	3053.64520000	38.79880000
189	3061.74380000	30.64460000
190	3061.76430000	17.37580000
191	3087.00090000	13.91040000
192	3087.03260000	20.24880000
193	3135.24140000	12.01930000
194	3135.24600000	11.73680000
195	3145.07850000	0.79760000
196	3145.10150000	1.40180000
197	3161.86090000	20.38930000
198	3161.87040000	24.94420000
199	3165.78850000	11.94960000
200	3165.79380000	14.47580000
201	3165.90980000	1.51560000
202	3165.92710000	49.65600000
203	3198.07710000	18.84610000
204	3198.08180000	14.50230000
205	3201.13270000	4.56280000
206	3201.13910000	34.56770000
207	3216.49290000	1.17790000
208	3217.60810000	27.04850000
209	3231.06640000	4.15710000
210	3231.10910000	4.58400000
211	3236.62390000	0.10390000
212	3238.38300000	0.73550000
213	3239.60320000	2.17740000
214	3239.60870000	3.05010000
215	3242.77500000	3.20080000
216	3254.61400000	14.64510000

3 - [Re(HPEAB)(CO_3)]

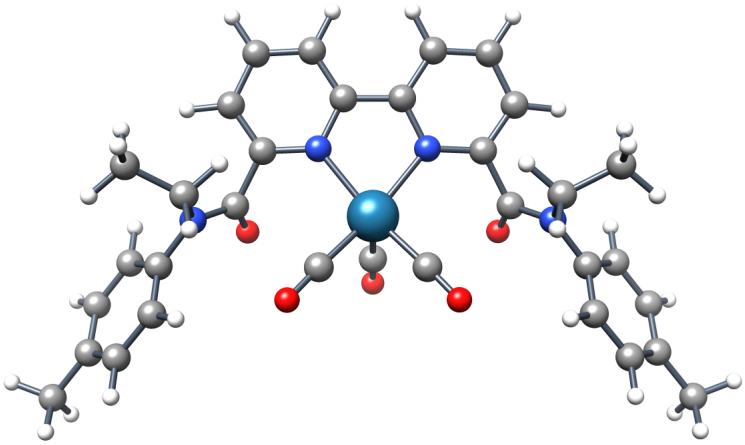


Figure S45: Optimised singlet ground state geometry of [Re(HPEAB)(CO_3)]

Route	:	#p opt freq genecp scrf=(cpcm,solvent=dichloromethane)
	:	geom=connectivity int=(acc2e=13,ultrafine) pbe1pbe
SMILES	:	CCN(c1ccc(cc1)C)C(=O)c2cccc-3[n+]2[Re]([n+] 4c3cccc4C(=O)N(CC)c5ccc(cc5)C)([C][O])([C][O])[C][O]
Formula	:	$C_{33}H_{30}N_4O_5Re^2$
Charge	:	0
Multiplicity	:	2
Dipole	:	30.0392 Debye
Energy	:	-1946.00472467 a.u.
Gibbs Energy	:	-1945.51768400 a.u.
Number of imaginary frequencies	:	0

Cartesian Co-ordinates (XYZ format)

73

C	-0.71754497	3.06635094	-0.38822901
C	-2.68773007	1.78563201	-0.37062001
C	-3.46966600	2.91187596	-0.51682597
C	-2.85531211	4.17915392	-0.58265698
C	-1.48340499	4.24283314	-0.53043902
C	0.71748698	3.06639409	-0.38666299
C	2.68768406	1.78564799	-0.36735401
C	3.46979809	2.91210103	-0.51076001
C	2.85559011	4.17954588	-0.57531399
C	1.48358905	4.24311495	-0.52550298
H	-4.55152893	2.80515003	-0.60711902
H	-3.45347309	5.08490181	-0.69555598
H	-0.98325801	5.20706177	-0.60974801
H	4.55176878	2.80549502	-0.59984601
H	3.45396996	5.08549213	-0.68540901
H	0.98357302	5.20750618	-0.60369003
Re	-0.00026400	0.19719800	0.21682100
N	1.32837796	1.83451903	-0.25905201
N	-1.32862401	1.83460701	-0.26062900

C	-0.00062600	-0.86762100	-1.31810200
O	-0.00079300	-1.51118505	-2.27996612
C	-1.28070796	-1.00961602	0.98137599
O	-2.00622010	-1.75587797	1.48821199
C	1.28002703	-1.00988996	0.98114097
O	2.00568295	-1.75631499	1.48754203
C	3.37245893	0.45103401	-0.55387098
O	3.14330411	-0.19064000	-1.56571805
N	4.30794907	0.09550400	0.37406299
C	-3.37256193	0.45078301	-0.55532998
O	-3.14401507	-0.19193900	-1.56663001
N	-4.30733013	0.09624600	0.37375900
C	4.37463713	0.68220699	1.71127903
H	4.17623186	-0.11168100	2.44942689
H	3.54326510	1.39385498	1.80707705
C	5.69749880	1.36010396	2.01386499
H	5.69269180	1.74396896	3.04465389
H	6.53788996	0.65600300	1.92090201
H	5.88232899	2.20592690	1.33505201
C	-4.37301397	0.68512100	1.71008301
H	-4.17395782	-0.10745900	2.44944310
H	-3.54160190	1.39695501	1.80405402
C	-5.69564486	1.36355996	2.01246595
H	-6.53612280	0.65931702	1.92140102
H	-5.69006205	1.74929595	3.04255295
H	-5.88090897	2.20814610	1.33223104
C	5.17430782	-1.00238395	0.08733700
C	6.01878881	-0.95299101	-1.02737999
C	5.22189617	-2.11767292	0.92447299
C	6.88604212	-2.00502896	-1.29733098
H	5.99173021	-0.08096500	-1.68394494
C	6.10487986	-3.16219211	0.65115798
H	4.55680418	-2.18182492	1.78678501
C	6.95056820	-3.13068199	-0.46213600
H	7.53831911	-1.94677401	-2.17340493
H	6.12895203	-4.02646923	1.32069504
C	-5.17382193	-1.00208700	0.08934400
C	-5.22298384	-2.11477399	0.92986703
C	-6.01704788	-0.95580202	-1.02648997
C	-6.10616112	-3.15971303	0.65880001
H	-4.55899715	-2.17670488	1.79318202
C	-6.88450384	-2.00825310	-1.29412901
H	-5.98887110	-0.08590000	-1.68579698
C	-6.95056105	-3.13129306	-0.45554101
H	-6.13140583	-4.02185917	1.33103502
H	-7.53575611	-1.95236695	-2.17112207
C	7.89133310	-4.26072502	-0.76567101
H	7.60239601	-4.77786493	-1.69509101
H	8.92066383	-3.89681602	-0.90938401
H	7.90174818	-5.00488806	0.04279900
C	-7.89152479	-4.26181889	-0.75662303
H	-8.92048645	-3.89785600	-0.90282398
H	-7.60167408	-4.78212309	-1.68399298
H	-7.90334892	-5.00335789	0.05423700

Frequencies

Mode	IR frequency	IR intensity
1	8.59130000	0.01860000
2	14.00240000	0.77680000
3	18.23410000	0.78390000
4	18.38150000	0.70380000
5	21.58430000	0.00460000
6	23.68060000	1.83360000
7	30.08810000	0.10640000
8	35.11770000	0.28080000
9	44.21360000	0.04590000
10	47.12810000	0.14120000
11	47.28780000	5.90490000
12	56.35980000	1.79330000
13	61.50250000	0.28650000
14	62.87520000	0.88680000
15	70.10220000	0.36960000
16	79.51630000	0.09800000
17	96.52350000	2.84930000
18	99.98910000	0.74990000
19	101.72900000	1.39250000
20	107.46890000	1.46910000
21	115.54700000	2.66170000
22	117.88650000	0.00610000
23	126.96650000	0.88960000
24	129.31310000	2.35520000
25	140.75820000	0.56060000
26	144.36630000	1.39970000
27	149.56620000	0.74650000
28	172.21570000	3.75270000
29	182.25680000	0.69790000
30	195.44180000	8.71220000
31	208.40840000	0.12490000
32	214.80380000	0.49950000
33	214.98310000	1.51330000
34	237.79520000	12.80340000
35	248.78360000	4.30900000
36	257.89420000	10.48080000
37	303.39650000	1.43460000
38	303.64000000	1.13690000
39	308.10530000	6.78400000
40	333.81560000	0.17730000
41	334.16950000	1.85870000
42	351.19420000	4.05990000
43	352.29930000	1.06940000
44	370.67600000	65.37820000
45	376.32000000	27.53910000
46	390.30210000	6.55060000
47	413.40710000	1.27530000
48	418.18240000	3.21180000
49	424.66500000	0.55650000
50	425.02460000	2.11500000
51	435.38660000	10.35950000
52	455.08440000	22.64190000
53	473.52590000	0.33590000
54	490.05840000	36.04270000
55	493.14190000	9.28820000

56	496.23740000	7.47350000
57	503.54120000	1.28770000
58	504.25660000	8.90600000
59	510.21180000	6.84530000
60	523.74750000	17.20350000
61	529.71820000	33.06790000
62	540.31280000	25.39950000
63	542.33640000	9.02240000
64	552.40590000	66.70120000
65	567.48480000	27.52900000
66	612.29090000	0.09330000
67	623.71130000	55.36430000
68	640.50820000	4.72310000
69	644.25900000	77.19770000
70	649.40090000	11.63500000
71	650.88360000	0.71740000
72	654.79180000	10.40460000
73	660.89580000	72.36910000
74	668.22060000	15.42620000
75	676.00920000	48.81150000
76	690.05810000	32.07970000
77	719.66210000	13.71930000
78	736.03030000	1.39650000
79	745.52960000	7.91250000
80	747.85380000	0.85320000
81	749.12460000	19.84070000
82	757.23330000	5.34200000
83	770.78600000	81.77590000
84	772.19530000	15.27360000
85	775.04130000	47.36340000
86	785.27780000	80.80050000
87	811.87100000	50.13200000
88	814.54930000	11.87220000
89	835.48880000	3.99410000
90	836.07380000	3.69650000
91	843.64940000	45.04890000
92	851.83030000	19.69030000
93	852.21860000	7.01210000
94	853.50090000	32.35360000
95	881.16800000	0.27040000
96	912.88770000	4.52310000
97	913.32520000	2.21790000
98	920.73790000	11.76970000
99	972.33060000	9.38820000
100	974.44730000	5.40860000
101	987.85840000	0.12030000
102	989.93680000	0.54760000
103	993.03300000	7.00500000
104	996.30770000	4.91260000
105	996.33350000	8.81330000
106	999.61490000	1.02310000
107	1000.66960000	0.21360000
108	1000.80450000	1.76640000
109	1009.34250000	226.26080000
110	1032.70960000	10.79790000
111	1032.81810000	10.12460000
112	1039.30670000	2.28970000
113	1049.61340000	4.75400000

114	1049.62540000	15.56900000
115	1088.86780000	82.62020000
116	1100.62300000	30.77100000
117	1103.33590000	24.59440000
118	1109.93700000	11.82860000
119	1114.47460000	72.61980000
120	1120.05290000	4.74630000
121	1131.22640000	1.73740000
122	1132.08550000	23.19630000
123	1140.59000000	61.65790000
124	1146.38550000	23.81260000
125	1155.84860000	0.26500000
126	1179.96560000	143.81950000
127	1183.98860000	20.74440000
128	1189.63020000	8.05620000
129	1190.53170000	1.13890000
130	1233.84550000	31.12540000
131	1240.46050000	4.32890000
132	1249.79100000	5.78510000
133	1249.81840000	5.59990000
134	1297.19230000	67.18590000
135	1297.98650000	202.19930000
136	1305.55750000	67.42280000
137	1308.33080000	142.83000000
138	1322.62670000	21.69200000
139	1323.07650000	3.48560000
140	1336.60050000	0.49180000
141	1360.01530000	42.99470000
142	1368.04980000	13.97990000
143	1368.89310000	1.00100000
144	1376.52280000	16.09400000
145	1377.64800000	71.71660000
146	1388.74140000	4.68680000
147	1388.75600000	3.79880000
148	1398.28190000	36.57340000
149	1401.54670000	0.53780000
150	1406.63430000	58.43990000
151	1416.81850000	196.37060000
152	1428.63770000	27.49740000
153	1439.45010000	79.20930000
154	1439.72720000	0.40860000
155	1445.14810000	0.40790000
156	1445.20820000	13.63620000
157	1449.58760000	354.36290000
158	1449.80630000	20.76070000
159	1449.82230000	11.55820000
160	1452.58310000	67.85590000
161	1458.28610000	276.77930000
162	1463.80320000	96.81690000
163	1471.98540000	2.22790000
164	1472.68440000	37.12090000
165	1476.71330000	166.59130000
166	1485.72180000	112.30980000
167	1498.39820000	254.32960000
168	1508.58380000	469.68370000
169	1563.60630000	234.43800000
170	1563.81690000	165.96880000
171	1579.40360000	177.08420000

172	1604.49810000	236.80940000
173	1644.03710000	21.08000000
174	1645.05390000	58.61910000
175	1656.86870000	1.86920000
176	1656.88300000	12.03880000
177	1698.74470000	10.66440000
178	1698.79800000	6.51590000
179	1775.34430000	257.52040000
180	1775.57390000	612.62950000
181	2007.75320000	2134.52850000
182	2013.28980000	2294.38450000
183	2120.21310000	1909.78590000
184	3055.54280000	26.70530000
185	3055.54670000	38.04540000
186	3064.95170000	29.39780000
187	3064.96460000	10.74220000
188	3082.98740000	21.44750000
189	3083.14000000	22.73480000
190	3137.98650000	10.77280000
191	3137.99290000	10.06890000
192	3147.91700000	7.42700000
193	3147.97780000	5.88040000
194	3166.62380000	14.83730000
195	3166.63410000	23.95210000
196	3167.12110000	27.00100000
197	3167.14720000	37.90340000
198	3168.02230000	6.31630000
199	3168.02340000	19.06940000
200	3200.53770000	14.17460000
201	3200.54210000	13.65070000
202	3203.52440000	2.71180000
203	3203.52940000	30.52950000
204	3227.11230000	3.96340000
205	3227.22860000	4.00790000
206	3229.17180000	10.85790000
207	3230.36350000	15.35250000
208	3238.18830000	1.35300000
209	3238.28540000	1.39600000
210	3240.63020000	0.09960000
211	3242.53850000	0.66580000
212	3249.93100000	0.24680000
213	3261.79870000	6.87830000

4 - [Re(HPEAB)(CO_3)(NCMe)]

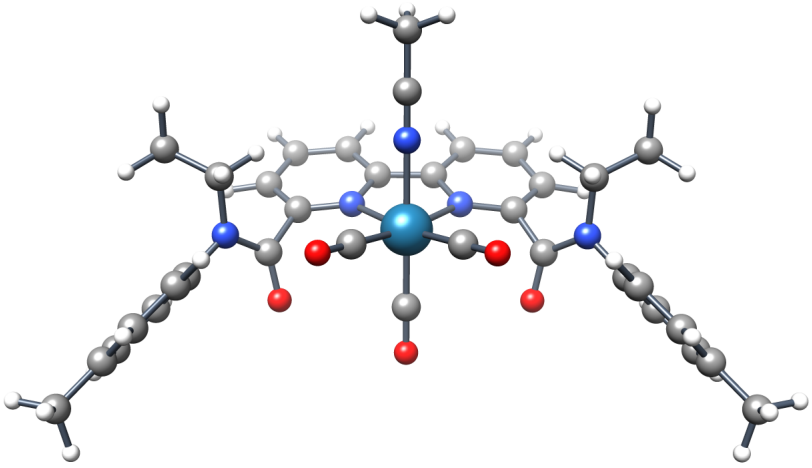


Figure S46: Optimised singlet ground state geometry of [Re(HPEAB)(CO_3)(NCMe)]

Route	:	#p opt freq genecp scrf=(cpcm,solvent=dichloromethane)
	:	geom=connectivity int=(acc2e=13,ultrafine) pbe1pbe
SMILES	:	CCN(c1ccc(cc1)C)C(=O)c2cccc-3[n+]2[Re]([n+] 4c3cccc4C(=O)N(CC)c5ccc(cc5)C)([C][O])([C][O])([C][O])[N]#CC
Formula	:	$C_{35}H_{33}N_5O_5Re^2$
Charge	:	0
Multiplicity	:	2
Dipole	:	43.0343 Debye
Energy	:	-2078.53402596 a.u.
Gibbs Energy	:	-2078.00722600 a.u.
Number of imaginary frequencies	:	0

Cartesian Co-ordinates (XYZ format)

79

C	0.71281803	-2.82206106	-0.99474698
C	2.68631196	-1.55105805	-0.82714999
C	3.47805810	-2.63554096	-1.15850997
C	2.85581899	-3.88415194	-1.39404595
C	1.48963499	-3.96638203	-1.32059503
C	-0.71279198	-2.82204604	-0.99483502
C	-2.68628693	-1.55102801	-0.82735902
C	-3.47801495	-2.63547897	-1.15886796
C	-2.85576606	-3.88407612	-1.39444995
C	-1.48959100	-3.96633005	-1.32085896
H	4.55663204	-2.50939202	-1.25737298
H	3.45229101	-4.76236391	-1.64958799
H	0.99330902	-4.91433907	-1.52607095
H	-4.55658007	-2.50931311	-1.25781000
H	-3.45222092	-4.76225710	-1.65013802
H	-0.99325401	-4.91426897	-1.52638698
Re	-0.00001700	-0.12826900	0.17936400
N	-1.34298897	-1.62364602	-0.69921702
N	1.34300101	-1.62365603	-0.69911897

C	0.00002000	1.05118001	-1.34036899
O	0.00004700	1.77183199	-2.23764300
C	1.28917098	0.99066103	1.05145705
O	2.02610493	1.67871904	1.62000299
C	-1.28925502	0.99065900	1.05139196
O	-2.02621794	1.67871404	1.61990094
C	-3.35602093	-0.19639800	-0.81003797
O	-3.09457898	0.60309798	-1.69384897
N	-4.31710720	0.01620800	0.13738699
C	3.35604906	-0.19642800	-0.80990702
O	3.09464002	0.60299999	-1.69379103
N	4.31711292	0.01625200	0.13752000
C	-4.41803885	-0.76728201	1.36640704
H	-4.23815107	-0.09664000	2.22263002
H	-3.58948207	-1.48850906	1.37064600
C	-5.74820995	-1.47816503	1.52939701
H	-5.77109909	-2.01308799	2.49039412
H	-6.58621120	-0.76502901	1.52155602
H	-5.91334105	-2.21093607	0.72563601
C	4.41802311	-0.76710999	1.36662304
H	4.23815489	-0.09636500	2.22276902
H	3.58944607	-1.48831606	1.37093902
C	5.74817705	-1.47800505	1.52969599
H	6.58619404	-0.76488698	1.52177000
H	5.77105379	-2.01281404	2.49075699
H	5.91329479	-2.21087503	0.72602397
C	-5.17494392	1.14791501	-0.00303300
C	-5.99360609	1.26459205	-1.13222897
C	-5.24099779	2.13072300	0.98509097
C	-6.85278511	2.34845901	-1.26758206
H	-5.95163012	0.49653500	-1.90729594
C	-6.11614513	3.20818400	0.84526098
H	-4.59504318	2.06640196	1.86194694
C	-6.93534517	3.34198403	-0.28011200
H	-7.48394585	2.42081404	-2.15802908
H	-6.15418816	3.96745300	1.63140404
C	5.17497206	1.14793301	-0.00300600
C	5.24080420	2.13099599	0.98487902
C	5.99387789	1.26431298	-1.13205099
C	6.11598015	3.20842099	0.84495801
H	4.59466124	2.06688690	1.86161196
C	6.85308790	2.34814596	-1.26750100
H	5.95207882	0.49604201	-1.90691805
C	6.93542290	3.34192991	-0.28027499
H	6.15385914	3.96789098	1.63091505
H	7.48445415	2.42026305	-2.15782189
C	-7.86841488	4.50756788	-0.43884599
H	-7.57620907	5.13556385	-1.29604304
H	-8.90013885	4.17115021	-0.62676901
H	-7.87515688	5.14378500	0.45708600
C	7.86844778	4.50753117	-0.43914801
H	8.90001965	4.17115593	-0.62795198
H	7.57565308	5.13591909	-1.29586303
H	7.87582588	5.14337397	0.45704499
N	-0.00005600	-1.51797104	1.82387698
C	-0.00007200	-2.26985502	2.69969893
C	-0.00011600	-3.20593905	3.80049992
H	-0.89592201	-3.05264306	4.41871119

H	-0.00046100	-4.23430586	3.41238999
H	0.89603502	-3.05313301	4.41836500

Frequencies

Mode	IR frequency	IR intensity
1	10.55320000	1.38380000
2	10.80590000	0.17270000
3	16.60360000	0.69500000
4	20.39200000	1.37220000
5	20.93590000	0.42110000
6	23.69620000	0.60360000
7	28.67180000	0.96030000
8	32.61660000	0.16120000
9	37.09470000	0.61610000
10	39.42300000	1.21920000
11	46.07710000	11.07500000
12	48.48640000	4.59160000
13	56.48620000	0.96650000
14	59.97370000	0.06840000
15	61.36080000	0.44590000
16	62.69580000	1.85660000
17	66.91840000	0.93850000
18	69.83360000	0.57840000
19	78.43040000	0.21640000
20	94.90850000	0.93090000
21	96.05150000	3.25670000
22	99.02980000	1.53870000
23	110.57680000	2.09520000
24	110.87050000	0.04990000
25	113.80690000	1.43720000
26	120.34050000	2.00690000
27	122.08260000	0.78830000
28	135.05340000	1.57590000
29	139.66830000	1.40120000
30	144.50710000	1.27920000
31	169.86430000	4.20390000
32	179.13820000	0.54800000
33	188.07040000	6.96250000
34	196.55940000	4.49050000
35	208.29430000	0.71280000
36	214.46570000	0.43570000
37	215.89420000	1.15630000
38	225.29400000	5.90240000
39	235.50320000	8.34750000
40	243.13960000	4.40260000
41	252.44630000	0.73080000
42	270.70940000	1.35360000
43	301.02810000	1.35410000
44	303.06180000	4.31550000
45	308.06230000	5.43160000
46	333.17610000	0.01810000
47	333.35150000	1.46290000
48	349.89870000	1.73780000
49	350.65690000	1.35430000
50	372.68970000	27.63780000
51	374.42230000	48.58850000
52	387.78460000	2.00150000
53	413.29150000	3.55140000
54	413.59060000	3.55960000
55	419.26960000	0.86650000

56	425.25730000	0.73610000
57	425.48130000	0.98430000
58	438.69770000	7.08290000
59	450.88930000	0.66640000
60	469.17930000	9.77110000
61	489.56720000	21.50660000
62	492.03460000	11.23820000
63	497.07160000	32.35160000
64	501.33870000	2.50330000
65	504.31240000	14.62770000
66	508.87440000	5.74470000
67	521.10650000	0.02890000
68	526.07210000	33.02890000
69	534.58140000	5.89640000
70	538.98780000	29.97100000
71	540.21100000	8.46220000
72	558.24110000	17.73520000
73	569.07400000	36.86880000
74	608.05810000	1.78390000
75	634.05700000	5.14980000
76	636.52200000	46.12300000
77	648.59090000	11.16680000
78	649.57490000	15.22980000
79	650.90480000	1.63020000
80	653.08060000	1.05360000
81	665.29960000	36.13730000
82	669.03290000	28.72980000
83	674.00050000	53.31850000
84	687.74560000	18.37840000
85	713.83950000	5.02630000
86	733.17080000	3.91050000
87	742.20640000	7.11020000
88	745.96210000	5.73600000
89	747.28630000	23.76650000
90	748.84570000	20.80980000
91	763.57940000	143.36790000
92	768.54850000	14.22440000
93	773.66990000	46.85230000
94	780.87770000	37.83430000
95	807.63960000	61.47400000
96	813.48800000	8.62370000
97	821.47930000	4.30870000
98	835.19470000	3.09150000
99	843.63520000	53.60110000
100	852.00010000	43.67840000
101	852.49030000	4.88610000
102	852.61550000	1.77350000
103	869.77350000	5.15130000
104	874.80180000	8.72790000
105	885.78540000	2.33520000
106	917.24570000	2.34760000
107	972.22620000	9.52160000
108	974.26870000	5.40650000
109	986.60780000	0.09070000
110	987.76960000	0.04610000
111	988.65610000	10.77560000
112	991.94270000	10.35390000
113	995.01940000	0.34620000

114	995.77560000	4.44430000
115	995.79350000	9.61090000
116	1001.00630000	0.04190000
117	1001.14630000	1.71200000
118	1007.40740000	333.72530000
119	1026.26680000	13.11230000
120	1027.97190000	11.75530000
121	1032.71620000	10.55980000
122	1032.77950000	8.23660000
123	1039.07420000	16.97810000
124	1049.51550000	3.88860000
125	1049.52300000	14.93250000
126	1085.45420000	104.13110000
127	1093.04150000	18.95760000
128	1100.55320000	26.18860000
129	1108.62080000	10.07040000
130	1109.53180000	7.61580000
131	1119.13570000	17.82440000
132	1129.40190000	0.54410000
133	1130.34360000	20.22040000
134	1140.26330000	93.60900000
135	1146.72500000	22.21860000
136	1155.66490000	3.04950000
137	1174.68720000	228.91020000
138	1187.51910000	5.16920000
139	1188.81060000	1.21010000
140	1190.04490000	2.66870000
141	1229.29400000	36.86260000
142	1238.54240000	3.62610000
143	1249.37430000	8.97400000
144	1249.38050000	1.92970000
145	1296.34030000	92.86340000
146	1297.08430000	286.72900000
147	1306.34680000	59.86800000
148	1308.09940000	127.38880000
149	1322.66530000	28.28470000
150	1323.07460000	6.01410000
151	1323.41600000	1.68010000
152	1357.83750000	109.64750000
153	1366.72150000	13.73180000
154	1367.41800000	0.15800000
155	1372.74560000	2.08840000
156	1375.96100000	11.17210000
157	1376.91060000	84.87680000
158	1388.49120000	5.78200000
159	1388.50280000	2.57320000
160	1395.13260000	60.15910000
161	1400.98960000	0.03990000
162	1402.07000000	192.89840000
163	1415.87710000	20.45140000
164	1416.29300000	20.48440000
165	1423.13990000	213.95800000
166	1438.19230000	76.83500000
167	1439.71920000	42.14090000
168	1439.79030000	0.86250000
169	1444.79000000	5.78070000
170	1444.90470000	12.74880000
171	1447.46760000	456.06140000

172	1449.90750000	1.47580000
173	1449.93620000	17.09550000
174	1452.06270000	58.99680000
175	1455.99290000	193.72230000
176	1462.94650000	165.91380000
177	1470.93210000	3.05290000
178	1472.21230000	49.50740000
179	1473.95980000	43.99030000
180	1482.75530000	212.70750000
181	1489.41670000	405.60630000
182	1552.78450000	21.91730000
183	1563.54040000	253.20080000
184	1563.78590000	172.17160000
185	1586.01680000	313.92760000
186	1605.70900000	84.04410000
187	1622.95920000	20.19020000
188	1642.87960000	130.54370000
189	1656.60480000	14.09310000
190	1656.60710000	0.81360000
191	1698.70270000	11.73990000
192	1698.75380000	4.83780000
193	1775.42800000	238.01230000
194	1775.93480000	551.12200000
195	2007.66850000	2197.64360000
196	2034.46160000	2048.00190000
197	2134.48320000	1726.67270000
198	2432.18920000	26.67340000
199	3055.18170000	27.69910000
200	3055.18580000	38.89900000
201	3064.00960000	31.99190000
202	3064.02310000	9.91560000
203	3078.72610000	1.59800000
204	3079.36350000	12.30330000
205	3079.38360000	36.04380000
206	3137.43720000	12.39340000
207	3137.43840000	8.56020000
208	3147.41310000	11.44420000
209	3147.43410000	1.87910000
210	3165.07040000	11.68950000
211	3165.07410000	35.50170000
212	3166.76190000	13.36660000
213	3166.78000000	50.80760000
214	3167.40700000	10.74040000
215	3167.41050000	14.81500000
216	3189.97270000	6.88690000
217	3190.98060000	6.90660000
218	3200.15890000	13.45310000
219	3200.16230000	14.04270000
220	3202.86080000	3.01190000
221	3202.86590000	30.97700000
222	3220.82330000	4.12360000
223	3222.24790000	20.74190000
224	3226.38210000	4.29470000
225	3226.39250000	5.08340000
226	3237.27100000	0.19050000
227	3237.27170000	2.82260000
228	3239.05670000	0.81310000
229	3241.87600000	1.02220000

230	3244.56230000	1.34880000
231	3254.10340000	9.96040000

5 - [Re(HPEAB)(CO_3)]$^-$

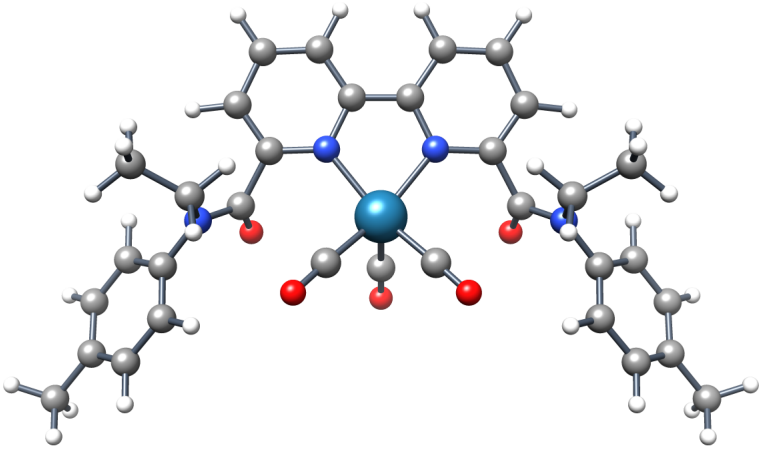


Figure S47: Optimised singlet ground state geometry of [Re(HPEAB)(CO_3)]$^-$

Route	:	#p opt freq genecp scrf=(cpcm,solvent=dichloromethane)
	:	geom=connectivity int=(acc2e=13,ultrafine) pbe1pbe
SMILES	:	CCN(c1ccc(cc1)C)C(=O)c2cccc-3[n+]2[Re]([n+]4c3cccc4C(=O)N(CC)c5ccc(cc5)C)([C][O])([C][O])[C][O]
Formula	:	$C_{33}H_{30}N_4O_5Re^{1-}$
Charge	:	-1
Multiplicity	:	1
Energy	:	-1946.11432331 a.u.
Gibbs Energy	:	-1945.62920400 a.u.
Number of imaginary frequencies	:	0

Cartesian Co-ordinates (XYZ format)

73

C	-0.70217401	3.05631709	-0.46575701
C	-2.68161893	1.76736403	-0.36973399
C	-3.46301603	2.88542008	-0.50494999
C	-2.85737991	4.16995382	-0.60637403
C	-1.49215996	4.22924519	-0.60873002
C	0.70226598	3.05629206	-0.46547100
C	2.68163896	1.76723397	-0.36895400
C	3.46310306	2.88528705	-0.50373799
C	2.85756612	4.16987896	-0.60509199
C	1.49234605	4.22920799	-0.60795099
H	-4.54561520	2.76971602	-0.58386600
H	-3.46542096	5.06977320	-0.71568501
H	-0.99088001	5.19026804	-0.72856301
H	4.54571676	2.76954007	-0.58239597
H	3.46568489	5.06969309	-0.71400601
H	0.99113399	5.19026804	-0.72777402
Re	-0.00007600	0.18917900	0.17920400
N	1.30507600	1.80474997	-0.26315600
N	-1.30511403	1.80483794	-0.26359400
C	-0.00034000	-1.06100595	-1.22695398

O	-0.00045900	-1.84429395	-2.08884311
C	-1.27300799	-0.88165200	1.12285101
O	-2.00083804	-1.54508901	1.74908400
C	1.27269995	-0.88188100	1.12277400
O	2.00045705	-1.54542398	1.74898899
C	3.38723898	0.44800201	-0.56950599
O	3.21260905	-0.19022700	-1.59587395
N	4.31691408	0.09225600	0.37010899
C	-3.38721704	0.44808900	-0.57000798
O	-3.21259809	-0.19028400	-1.59628499
N	-4.31677723	0.09244700	0.36977300
C	4.35919189	0.64671499	1.71956694
H	4.18975401	-0.17386100	2.43569589
H	3.50119805	1.32467306	1.82685995
C	5.65532684	1.36637294	2.04370904
H	5.63965893	1.71582794	3.08696604
H	6.52338982	0.69981700	1.92578995
H	5.80379915	2.24073911	1.39257097
C	-4.35904121	0.64747602	1.71899998
H	-4.18944693	-0.17273800	2.43549395
H	-3.50111699	1.32556999	1.82594204
C	-5.65524817	1.36711597	2.04289293
H	-6.52322006	0.70037198	1.92537200
H	-5.63954306	1.71708000	3.08597898
H	-5.80390120	2.24114394	1.39134598
C	5.19357681	-0.99400699	0.07475200
C	6.16512203	-0.85627002	-0.92225301
C	5.11516809	-2.19283009	0.78441799
C	7.03752613	-1.90222502	-1.20220399
H	6.23081398	0.08163500	-1.47833002
C	6.00271416	-3.23206711	0.50450999
H	4.34167624	-2.31700492	1.54442501
C	6.97708797	-3.11061096	-0.49190700
H	7.79041195	-1.77563703	-1.98571897
H	5.92734385	-4.16452408	1.07119203
C	-5.19340611	-0.99391299	0.07479700
C	-5.11639023	-2.19175792	0.78627598
C	-6.16360378	-0.85727400	-0.92368501
C	-6.00394297	-3.23107791	0.50669003
H	-4.34397316	-2.31518602	1.54749095
C	-7.03599024	-1.90332496	-1.20329499
H	-6.22826719	0.07984900	-1.48118901
C	-6.97692585	-3.11072898	-0.49120900
H	-5.92966700	-4.16272688	1.07484496
H	-7.78780603	-1.77757704	-1.98797095
C	7.92394400	-4.23365402	-0.80486000
H	7.74993610	-4.62864590	-1.81901300
H	8.97164440	-3.89597297	-0.76927102
H	7.80998516	-5.06626177	-0.09668900
C	-7.92361498	-4.23396778	-0.80395401
H	-8.97118092	-3.89548302	-0.77256203
H	-7.74672079	-4.63190508	-1.81646597
H	-7.81238890	-5.06471395	-0.09316400

Frequencies

Mode	IR frequency	IR intensity
1	8.64570000	0.63600000
2	9.26010000	0.57890000
3	13.12770000	0.16850000
4	13.67130000	1.17080000
5	16.57220000	0.00110000
6	20.32760000	0.56790000
7	27.59770000	2.07240000
8	28.67180000	0.43000000
9	49.26910000	0.92860000
10	53.71680000	6.56320000
11	54.82300000	0.50920000
12	56.34030000	0.83740000
13	62.53250000	0.02190000
14	66.83130000	0.36320000
15	72.54840000	0.60950000
16	84.00780000	0.03920000
17	101.14240000	0.22480000
18	101.99480000	0.15800000
19	107.27810000	1.05400000
20	110.12950000	5.13480000
21	118.08930000	4.03030000
22	123.91700000	0.16040000
23	125.89060000	1.23780000
24	130.88480000	0.03940000
25	140.40440000	1.35720000
26	141.92200000	0.68800000
27	148.98740000	0.15450000
28	169.11310000	1.02680000
29	182.13360000	1.22010000
30	196.25100000	7.80830000
31	208.87890000	0.27190000
32	217.97320000	1.80910000
33	219.91560000	0.01350000
34	241.82330000	11.57220000
35	252.80130000	1.49970000
36	268.75930000	11.63710000
37	303.24800000	0.92770000
38	306.38470000	0.00410000
39	315.91150000	9.00110000
40	328.32660000	0.13990000
41	328.69430000	2.69000000
42	351.67830000	2.59510000
43	353.06540000	0.70380000
44	374.24940000	82.61700000
45	376.92900000	27.45140000
46	396.68870000	2.18630000
47	409.48200000	0.01720000
48	414.43780000	6.95620000
49	425.37470000	0.67130000
50	425.43540000	1.02120000
51	433.84650000	12.63580000
52	442.15980000	38.82140000
53	478.96420000	2.23680000
54	490.21740000	112.63840000
55	500.79050000	33.18930000

56	501.20020000	14.10550000
57	506.23160000	6.13540000
58	513.38960000	1.47330000
59	517.05460000	0.07480000
60	533.86240000	27.09870000
61	536.67070000	37.12830000
62	538.78840000	15.60460000
63	540.31350000	187.91730000
64	543.08280000	18.13960000
65	571.57400000	5.73100000
66	597.58870000	118.79990000
67	597.86910000	190.04540000
68	614.78270000	107.48700000
69	634.46330000	0.13080000
70	648.34180000	14.75070000
71	651.41030000	0.76590000
72	654.78640000	3.90970000
73	656.82540000	36.46760000
74	666.34700000	28.69470000
75	673.25620000	44.63360000
76	688.59190000	27.99400000
77	708.91310000	25.74140000
78	732.33400000	3.72050000
79	745.85610000	2.43970000
80	748.26710000	8.46000000
81	750.17470000	18.41550000
82	750.99550000	18.91410000
83	762.22270000	135.37050000
84	767.59710000	12.02180000
85	772.54790000	62.44930000
86	775.51190000	23.98990000
87	799.46460000	65.49260000
88	812.13810000	10.94790000
89	816.02680000	1.63400000
90	834.14750000	18.00450000
91	844.15820000	40.76860000
92	852.52050000	38.48890000
93	858.42820000	12.50510000
94	859.28100000	3.20790000
95	877.47090000	0.17180000
96	889.17750000	17.32040000
97	894.04760000	0.26910000
98	913.84460000	16.32470000
99	966.26310000	0.27510000
100	972.84840000	6.59330000
101	975.87410000	9.16030000
102	976.80850000	0.04050000
103	989.91780000	9.50640000
104	993.63590000	3.28820000
105	995.53210000	5.45390000
106	995.54050000	7.89750000
107	999.68010000	140.11970000
108	1004.24020000	3.83550000
109	1004.33810000	3.41940000
110	1024.71730000	45.08180000
111	1033.67330000	13.62520000
112	1033.82350000	7.74890000
113	1049.46080000	6.97430000

114	1049.48330000	11.91780000
115	1077.59180000	102.58380000
116	1088.62850000	0.86320000
117	1094.12360000	113.97850000
118	1105.47600000	12.00830000
119	1107.25850000	18.75760000
120	1115.31380000	9.98430000
121	1125.91730000	1.14820000
122	1126.36570000	26.69880000
123	1138.68800000	95.93560000
124	1145.09410000	17.54680000
125	1149.72090000	0.02880000
126	1168.17370000	170.32210000
127	1173.01220000	17.08860000
128	1185.36420000	7.14170000
129	1185.94470000	0.87340000
130	1229.18590000	18.77970000
131	1235.39230000	2.15980000
132	1248.26500000	7.17810000
133	1248.29270000	1.14340000
134	1293.95720000	36.15580000
135	1295.40610000	359.99020000
136	1307.79030000	43.79440000
137	1308.71890000	89.17550000
138	1317.61730000	67.36810000
139	1321.81220000	42.42080000
140	1321.85770000	22.63520000
141	1347.55190000	234.27580000
142	1365.42960000	15.84720000
143	1366.72310000	0.00820000
144	1373.33510000	5.36280000
145	1375.47230000	33.91340000
146	1382.80260000	0.10880000
147	1388.24550000	1.73950000
148	1388.26510000	1.34280000
149	1399.48480000	0.67840000
150	1400.75270000	88.44280000
151	1405.56840000	0.00230000
152	1438.53210000	150.01010000
153	1438.89420000	78.83080000
154	1440.24400000	220.29970000
155	1444.04200000	88.81520000
156	1445.08690000	9.33820000
157	1445.16910000	13.84590000
158	1445.53580000	7.75200000
159	1449.71920000	63.38400000
160	1449.92510000	64.57100000
161	1459.24340000	315.75900000
162	1460.83780000	139.34770000
163	1468.84790000	2.79460000
164	1469.06620000	47.57320000
165	1475.88770000	293.54170000
166	1477.42480000	72.29950000
167	1493.15710000	184.22820000
168	1509.81110000	469.37640000
169	1564.16640000	230.92140000
170	1564.36830000	161.22830000
171	1587.99780000	9.73120000

172	1603.03960000	11.63080000
173	1655.19140000	11.00770000
174	1655.19860000	2.27340000
175	1660.21660000	15.52240000
176	1663.33300000	70.04080000
177	1698.35240000	14.37080000
178	1698.41330000	8.71010000
179	1769.31670000	107.59260000
180	1769.41510000	648.15360000
181	1947.65830000	2388.03520000
182	1959.78600000	2402.99080000
183	2061.29000000	2426.43590000
184	3054.19100000	33.75190000
185	3054.20270000	37.38700000
186	3061.01410000	35.03400000
187	3061.02960000	13.73750000
188	3079.83790000	18.07900000
189	3079.92860000	22.57520000
190	3136.11000000	11.73400000
191	3136.11680000	11.45130000
192	3145.56380000	2.37390000
193	3145.60270000	2.95210000
194	3161.10210000	24.49110000
195	3161.11260000	31.49160000
196	3164.25890000	22.58400000
197	3164.27560000	35.73120000
198	3166.13730000	10.11940000
199	3166.13950000	16.96820000
200	3197.32830000	17.67940000
201	3197.33150000	12.28400000
202	3200.43280000	2.76580000
203	3200.43710000	32.89860000
204	3215.40260000	13.45760000
205	3217.55940000	13.95250000
206	3222.03940000	5.42890000
207	3222.07950000	7.58710000
208	3225.30450000	6.95640000
209	3229.50570000	1.63080000
210	3234.40760000	2.48730000
211	3234.43080000	2.21530000
212	3236.84550000	4.70210000
213	3243.71180000	44.52560000

6 - [Re(HPEAB)(CO_3)(CO_2)]$^-$

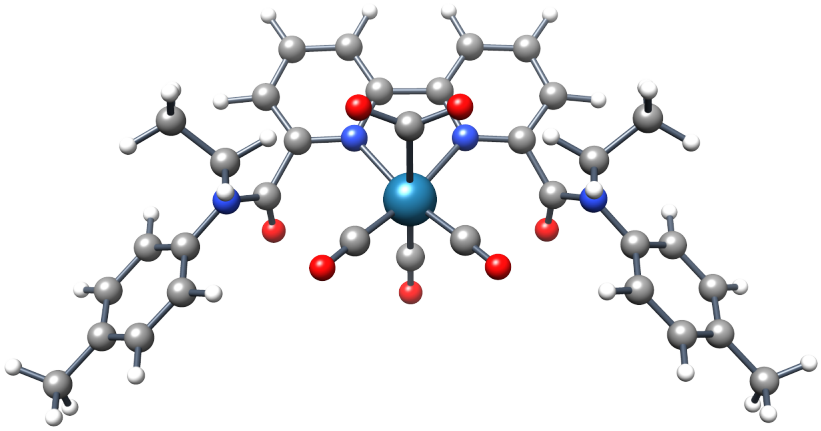


Figure S48: Optimised singlet ground state geometry of [Re(HPEAB)(CO_3)(CO_2)]$^-$

Route	:	#p opt freq genecp scrf=(cpcm,solvent=dichloromethane)
	:	geom=connectivity int=(acc2e=13,ultrafine) pbe1pbe
SMILES	:	CCN(c1ccc(cc1)C)C(=O)c2cccc-3[n+]2[Re]([n+] 4c3cccc4C(=O)N(CC)c5ccc(cc5)C)([C][O])([C][O])([C][O])C(=O)[O]
Formula	:	$C_{34}H_{30}N_4O_7Re^{1-}$
Charge	:	-1
Multiplicity	:	1
Energy	:	-2134.35955615 a.u.
Gibbs Energy	:	-2133.86397000 a.u.
Number of imaginary frequencies	:	0

Cartesian Co-ordinates (XYZ format)

76

C	-0.72982800	2.90846491	-0.72925901
C	-2.67247391	1.64369094	-0.59932297
C	-3.46206903	2.78098297	-0.72936702
C	-2.85757804	4.02886677	-0.86282700
C	-1.47500205	4.08313608	-0.87707102
C	0.73032802	2.90773606	-0.73349297
C	2.67258596	1.64198399	-0.60850102
C	3.46247911	2.77811193	-0.74684799
C	2.85823488	4.02574682	-0.88372099
C	1.47567701	4.08108091	-0.89096600
H	-4.54776621	2.67562389	-0.75168198
H	-3.45493603	4.93604994	-0.96835202
H	-0.97198200	5.04092503	-0.99722600
H	4.54801083	2.67190409	-0.77328402
H	3.45573497	4.93190289	-0.99702901
H	0.97279298	5.03854179	-1.01422501
Re	0.00037500	0.05190100	-0.00085900
N	1.32339203	1.69424295	-0.57418901
N	-1.32303405	1.69495797	-0.57043898
C	0.00122500	-0.97412997	-1.64747000

O	0.00152000	-1.67652297	-2.57175493
C	-1.24759901	-1.11338997	0.84231800
O	-1.94654703	-1.84138799	1.42101300
C	1.24846494	-1.11188495	0.84418303
O	1.94715500	-1.83881795	1.42458105
C	3.39806700	0.32034901	-0.73671597
O	3.31534791	-0.28961101	-1.79048502
N	4.23858976	-0.02245600	0.27701899
C	-3.39859200	0.32287800	-0.73180002
O	-3.31541204	-0.28397900	-1.78734195
N	-4.23983717	-0.02296700	0.28033799
C	4.12712288	0.52864701	1.62802804
H	4.02722883	-0.32066900	2.32215309
H	3.16830802	1.06725097	1.70751798
C	5.30658579	1.39186502	2.03557992
H	5.18961191	1.70939600	3.08262205
H	6.25707722	0.84149098	1.95590198
H	5.38423681	2.29804897	1.41632199
C	-4.12848282	0.52256602	1.63361204
H	-4.02745390	-0.32957801	2.32412696
H	-3.17016006	1.06177902	1.71498096
C	-5.30880213	1.38264406	2.04531407
H	-6.25867414	0.83148098	1.96370995
H	-5.19175816	1.69581103	3.09366107
H	-5.38790321	2.29141092	1.43004203
C	5.19001198	-1.06123900	0.04725500
C	6.20736980	-0.87721401	-0.89557499
C	5.14151096	-2.25422692	0.76907700
C	7.15314007	-1.87315202	-1.11137700
H	6.25181293	0.05630400	-1.46096301
C	6.10183382	-3.24260306	0.55294299
H	4.33662224	-2.41617990	1.48770106
C	7.12224913	-3.07554507	-0.38921100
H	7.94113922	-1.71024203	-1.85242498
H	6.04831886	-4.17133999	1.12800896
C	-5.19095278	-1.06111705	0.04642300
C	-5.14181709	-2.25713897	0.76316398
C	-6.20849800	-0.87353498	-0.89548099
C	-6.10171080	-3.24502397	0.54293901
H	-4.33676386	-2.42175007	1.48100495
C	-7.15385199	-1.86897099	-1.11540997
H	-6.25339079	0.06238400	-1.45685601
C	-7.12230015	-3.07442594	-0.39840099
H	-6.04771280	-4.17617798	1.11403894
H	-7.94201994	-1.70327401	-1.85566103
C	8.14832878	-4.14455414	-0.63338602
H	8.05583954	-4.55820084	-1.65078998
H	9.17102528	-3.74608803	-0.54251099
H	8.04174137	-4.97562695	0.07765200
C	-8.14775467	-4.14297390	-0.64718902
H	-9.17068863	-3.74500990	-0.55693001
H	-8.05345631	-4.55380583	-1.66557801
H	-8.04211235	-4.97601414	0.06168800
C	-0.00065400	1.24122596	2.00920892
O	1.11812699	1.54773200	2.46128607
O	-1.11995304	1.54028296	2.46492100

Frequencies

Mode	IR frequency	IR intensity
1	4.90740000	0.13050000
2	14.06270000	1.05910000
3	14.34470000	0.69610000
4	17.90090000	1.31730000
5	24.57410000	1.95050000
6	25.88520000	0.19100000
7	30.57150000	0.20430000
8	32.93450000	1.07130000
9	41.14870000	0.30560000
10	54.71370000	1.50950000
11	55.45320000	4.32850000
12	57.84330000	3.83080000
13	57.91410000	1.32190000
14	61.62820000	0.29790000
15	62.50600000	10.61160000
16	73.00340000	2.34440000
17	83.20180000	0.25690000
18	88.11410000	0.91800000
19	91.55570000	6.27350000
20	94.83120000	18.39330000
21	97.50840000	0.57260000
22	102.76930000	1.10090000
23	113.34200000	9.93180000
24	122.37100000	3.98190000
25	123.54700000	4.81240000
26	124.93100000	2.70320000
27	131.92660000	0.35410000
28	139.87510000	2.21170000
29	141.26930000	1.61980000
30	149.54080000	0.20550000
31	176.53610000	1.62770000
32	181.02890000	0.10440000
33	197.93620000	3.70440000
34	208.34750000	0.07580000
35	213.51570000	5.07540000
36	215.03240000	0.63280000
37	218.23730000	41.87460000
38	237.05110000	31.44200000
39	243.13430000	0.06300000
40	254.21840000	4.61450000
41	270.46000000	0.62710000
42	302.77630000	2.98350000
43	306.20090000	0.34530000
44	311.00320000	7.68480000
45	328.62540000	0.26010000
46	328.63800000	1.20200000
47	354.28220000	0.59210000
48	354.71640000	4.48130000
49	371.41010000	38.88720000
50	386.16030000	26.81290000
51	386.51570000	20.98000000
52	414.58290000	3.65060000
53	415.63320000	20.68600000
54	427.19660000	1.34770000
55	427.32010000	1.56930000

56	452.11480000	62.85640000
57	469.44830000	256.24250000
58	469.88550000	5.35850000
59	474.94710000	67.05800000
60	493.85500000	8.88550000
61	497.83890000	25.11820000
62	498.27000000	37.76390000
63	510.56400000	17.46030000
64	516.66130000	0.07040000
65	521.38980000	1.77750000
66	534.82060000	20.48670000
67	537.42560000	33.77560000
68	540.73840000	14.28700000
69	544.09000000	14.01820000
70	570.82810000	8.75600000
71	595.34720000	236.07200000
72	595.63490000	144.19410000
73	616.07930000	8.96150000
74	621.59960000	179.05930000
75	647.73390000	3.05620000
76	651.28770000	4.30490000
77	651.66660000	0.03280000
78	657.52320000	10.06570000
79	667.75500000	6.30420000
80	675.45590000	240.20820000
81	681.74380000	33.30330000
82	683.94720000	84.97060000
83	711.66070000	268.14080000
84	735.45170000	20.70550000
85	738.62330000	16.39990000
86	748.31650000	7.25620000
87	754.48190000	2.12740000
88	756.78730000	4.63380000
89	771.93860000	7.99520000
90	773.53170000	0.00560000
91	777.53450000	61.23950000
92	780.80980000	23.11570000
93	793.86410000	100.13210000
94	815.53310000	1.43270000
95	824.85060000	43.41940000
96	839.42150000	5.88800000
97	844.32060000	43.92360000
98	854.81280000	37.61580000
99	857.65890000	14.14510000
100	859.55920000	21.09370000
101	865.37250000	0.02410000
102	885.99200000	0.31450000
103	925.86290000	1.69220000
104	936.54490000	0.30690000
105	939.64120000	2.91570000
106	974.54840000	15.22990000
107	977.36240000	10.69690000
108	991.85250000	1.89200000
109	995.69350000	6.91660000
110	995.84750000	6.58350000
111	996.37860000	14.59090000
112	1004.24960000	2.24940000
113	1004.32120000	1.11630000

114	1007.97980000	0.09180000
115	1014.13210000	0.77910000
116	1032.93030000	79.07520000
117	1033.71670000	21.27690000
118	1034.04180000	22.85970000
119	1036.54940000	25.14410000
120	1049.61530000	3.56690000
121	1049.62350000	15.96110000
122	1093.85880000	18.33030000
123	1101.24430000	13.80520000
124	1107.13890000	82.59950000
125	1118.49350000	69.03060000
126	1119.80720000	2.60120000
127	1128.63120000	7.01880000
128	1128.85980000	15.18610000
129	1139.89570000	14.06730000
130	1140.48790000	0.26390000
131	1146.05470000	10.23170000
132	1154.08230000	1.38540000
133	1186.47610000	9.55600000
134	1186.54340000	14.94680000
135	1191.52180000	39.23560000
136	1193.19110000	6.75600000
137	1240.60160000	532.62230000
138	1247.49450000	15.81860000
139	1248.61180000	531.99560000
140	1248.98080000	106.99930000
141	1249.50930000	2.68370000
142	1305.47560000	50.74540000
143	1305.61250000	35.33380000
144	1309.79650000	74.79930000
145	1314.70550000	107.97930000
146	1320.97780000	20.38060000
147	1323.58020000	26.95340000
148	1351.48220000	25.50760000
149	1361.70020000	8.20770000
150	1374.58630000	3.18650000
151	1375.18170000	2.00250000
152	1376.80390000	6.40210000
153	1378.70340000	76.12830000
154	1384.80990000	1.27070000
155	1388.25680000	2.02550000
156	1388.32330000	1.44070000
157	1414.48950000	267.22710000
158	1417.86180000	61.69550000
159	1431.01870000	114.63130000
160	1439.61330000	23.44170000
161	1439.69770000	1.88610000
162	1445.05220000	7.52660000
163	1445.09290000	9.09940000
164	1451.55900000	2.10550000
165	1451.71470000	20.47050000
166	1453.13340000	65.23270000
167	1454.81530000	129.18810000
168	1456.39480000	3.48800000
169	1463.89050000	111.73470000
170	1466.92530000	59.34320000
171	1478.47350000	167.78080000

172	1484.83320000	55.92540000
173	1485.13670000	3.67990000
174	1488.78360000	51.33000000
175	1519.26150000	153.39070000
176	1519.66940000	116.77560000
177	1564.41260000	290.70210000
178	1564.66610000	155.85750000
179	1619.40420000	38.83160000
180	1645.55260000	10.80460000
181	1655.83640000	1.99590000
182	1655.85110000	12.95320000
183	1668.57630000	4.94450000
184	1672.24760000	10.47350000
185	1698.43690000	16.62880000
186	1698.50400000	10.42580000
187	1711.91390000	839.15800000
188	1775.33240000	202.71830000
189	1775.57120000	655.60290000
190	1972.32190000	2316.29030000
191	1973.91440000	2256.37980000
192	2078.84570000	2299.96570000
193	3054.52210000	34.05960000
194	3054.53180000	35.16770000
195	3058.61260000	55.24320000
196	3058.68980000	15.66220000
197	3069.37630000	18.70290000
198	3069.75090000	32.62610000
199	3120.11920000	41.96260000
200	3120.37820000	16.98140000
201	3136.46090000	11.24680000
202	3136.46290000	11.42360000
203	3154.84450000	14.61990000
204	3154.87650000	19.47940000
205	3161.52750000	21.44100000
206	3161.57220000	28.27250000
207	3166.88530000	10.23870000
208	3166.88750000	16.88860000
209	3198.13370000	15.76380000
210	3198.14530000	13.52490000
211	3201.84170000	3.95020000
212	3201.84660000	31.10510000
213	3222.80170000	5.97290000
214	3222.82910000	6.22160000
215	3230.62560000	0.56390000
216	3231.38470000	1.30320000
217	3239.10690000	1.67650000
218	3239.14800000	1.52250000
219	3242.46250000	1.54750000
220	3243.61200000	0.38560000
221	3254.66370000	0.06840000
222	3268.74270000	3.78480000

7 - [Re(HPEAB)(CO_3)(COOH)]

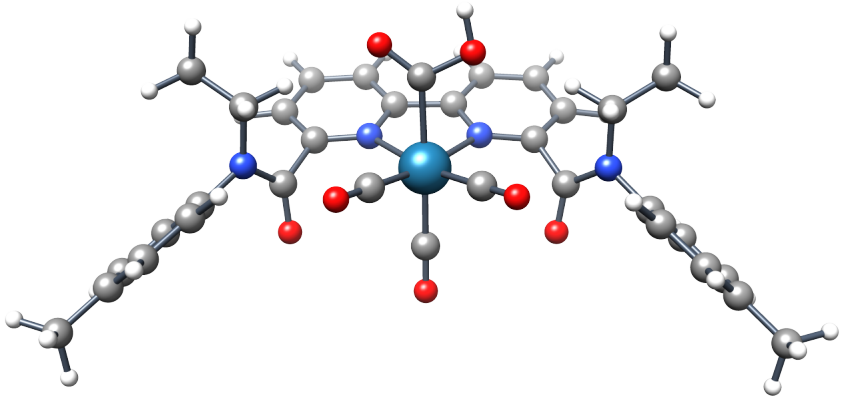


Figure S49: Optimised singlet ground state geometry of [Re(HPEAB)(CO_3)(COOH)]

Route	:	#p opt freq genecp scrf=(cpcm,solvent=dichloromethane)
	:	geom=connectivity int=(acc2e=13,ultrafine) pbe1pbe
SMILES	:	CCN(c1ccc(cc1)C)C(=O)c2cccc-3[n+]2[Re]([n+] 4c3cccc4C(=O)N(CC)c5ccc(cc5)C)([C][O])([C][O])([C][O])C(=O)O
Formula	:	$C_{34}H_{31}N_4O_7Re$
Charge	:	0
Multiplicity	:	1
Dipole	:	34.2781 Debye
Energy	:	-2134.86360191 a.u.
Gibbs Energy	:	-2134.35294700 a.u.
Number of imaginary frequencies	:	0

Cartesian Co-ordinates (XYZ format)

77

C	-0.74366301	2.90575790	-0.74493599
C	-2.68055797	1.63378000	-0.68394899
C	-3.47323489	2.76267195	-0.89347202
C	-2.86506605	4.00293779	-1.02447200
C	-1.48141301	4.07170820	-0.95816398
C	0.73131102	2.91550303	-0.71384501
C	2.67995596	1.66048300	-0.60666299
C	3.46612406	2.79889297	-0.78395802
C	2.85015702	4.03606892	-0.91201502
C	1.46456301	4.09088516	-0.88974202
H	-4.55590296	2.65209603	-0.96766901
H	-3.45830607	4.90441418	-1.18784797
H	-0.98285502	5.03165579	-1.07534206
H	4.55103683	2.69875908	-0.83604598
H	3.43948603	4.94505119	-1.04500997
H	0.96026701	5.04717302	-1.01253700
Re	-0.00865800	0.07451200	0.09784400
N	1.33912694	1.71875501	-0.54342502
N	-1.34332502	1.70267403	-0.59653401

C	0.03574500	-0.88001502	-1.62693501
O	0.05837100	-1.47921503	-2.60908890
C	-1.27759504	-1.15890801	0.81089902
O	-1.99824095	-1.92565501	1.29444098
C	1.26552200	-1.12184405	0.85973501
O	1.99550498	-1.86308801	1.36874497
C	3.38045192	0.32284701	-0.72110599
O	3.19841409	-0.32734200	-1.73597395
N	4.27886915	0.00420500	0.24821401
C	-3.37762403	0.29306400	-0.77424097
O	-3.22330499	-0.36415899	-1.78937101
N	-4.24660683	-0.01613100	0.22477800
C	4.28002310	0.62522000	1.57251799
H	4.10601616	-0.16572100	2.31917691
H	3.39953303	1.27906799	1.64437795
C	5.55912924	1.37452304	1.89319801
H	5.50963402	1.77251995	2.91740298
H	6.43620396	0.71282500	1.83169103
H	5.72069407	2.21990395	1.20783997
C	-4.19059706	0.61502498	1.54422903
H	-4.03392696	-0.17913701	2.29115891
H	-3.27995300	1.23143601	1.59486997
C	-5.43108892	1.41640306	1.89013100
H	-6.33666277	0.79237700	1.84740400
H	-5.34378004	1.81259596	2.91258407
H	-5.57058620	2.26821399	1.20788097
C	5.18268108	-1.07644498	0.01182000
C	6.07599115	-1.01250505	-1.06316197
C	5.21349907	-2.18615508	0.85641599
C	6.97622013	-2.04709291	-1.28814399
H	6.06044483	-0.14397600	-1.72486699
C	6.12942123	-3.21309090	0.62815601
H	4.50869608	-2.25997400	1.68571997
C	7.02420521	-3.16818094	-0.44574699
H	7.66649294	-1.97893798	-2.13382196
H	6.13982582	-4.07488012	1.30114305
C	-5.17354918	-1.08290195	0.02239700
C	-5.22512484	-2.16967010	0.89562899
C	-6.07267904	-1.02774096	-1.04881704
C	-6.16516018	-3.18138409	0.69934899
H	-4.51819611	-2.23910809	1.72334802
C	-6.99701595	-2.04729390	-1.24168599
H	-6.04262018	-0.17778300	-1.73362100
C	-7.06535196	-3.14479589	-0.37013701
H	-6.19061279	-4.02457809	1.39513695
H	-7.69087887	-1.98512602	-2.08491993
C	8.00041866	-4.27965498	-0.70179898
H	7.77737284	-4.79107714	-1.65219402
H	9.03022575	-3.89718699	-0.77903301
H	7.97455883	-5.03183699	0.09877000
C	-8.06918621	-4.23922491	-0.59035701
H	-9.09209347	-3.83609605	-0.65442300
H	-7.87530613	-4.77027321	-1.53631604
H	-8.04434776	-4.97880220	0.22192401
C	-0.11545300	1.22909606	1.95743203
O	1.04582405	1.33739603	2.66161489
O	-1.09170997	1.81082499	2.40523291
H	0.84320998	1.89358902	3.43750191

Frequencies

Mode	IR frequency	IR intensity
1	13.46100000	1.85400000
2	15.07040000	0.48910000
3	15.64320000	0.12840000
4	17.01350000	0.62210000
5	23.18280000	0.81600000
6	31.87640000	0.20560000
7	37.77010000	0.56130000
8	40.61640000	0.38090000
9	41.49000000	1.30880000
10	48.96730000	1.19190000
11	50.49710000	0.99120000
12	55.16590000	10.54400000
13	58.08880000	1.71110000
14	63.73250000	1.58490000
15	64.56380000	3.68930000
16	70.61250000	1.16460000
17	81.59260000	0.41930000
18	84.25640000	0.61080000
19	87.01240000	0.87290000
20	93.15370000	1.83670000
21	97.47020000	0.97930000
22	100.34390000	1.04110000
23	108.25840000	3.83430000
24	116.14670000	3.62670000
25	119.41050000	0.15790000
26	123.61830000	1.37160000
27	129.07370000	0.71290000
28	142.32980000	1.25320000
29	144.22690000	1.43050000
30	146.78370000	0.78340000
31	175.01580000	0.84720000
32	181.62900000	0.14410000
33	194.99070000	5.46320000
34	209.05780000	0.00170000
35	213.43460000	0.36750000
36	214.36940000	0.97080000
37	232.52340000	19.20830000
38	247.24480000	4.81420000
39	262.03480000	1.58920000
40	273.40290000	2.89090000
41	283.65750000	7.29090000
42	300.06180000	1.62430000
43	302.26990000	0.72680000
44	310.21970000	10.65630000
45	332.60980000	0.62290000
46	333.44980000	1.02140000
47	352.25870000	1.12960000
48	352.99160000	2.02080000
49	370.84430000	28.65790000
50	383.95350000	9.23340000
51	387.14750000	13.33460000
52	416.71780000	5.19770000
53	418.92760000	4.10800000
54	426.81930000	1.47290000
55	426.89610000	1.44680000

56	443.73410000	12.68590000
57	451.50430000	39.06140000
58	465.46560000	0.18380000
59	480.80430000	19.59220000
60	487.92420000	6.65570000
61	493.95400000	23.93580000
62	504.31880000	20.65660000
63	510.43060000	1.58930000
64	513.47840000	6.42130000
65	526.02780000	1.71100000
66	529.68170000	9.37820000
67	532.58490000	18.21260000
68	541.17860000	25.82750000
69	543.12580000	10.52250000
70	568.43850000	38.63220000
71	580.67780000	6.96310000
72	614.61830000	43.52290000
73	617.69910000	2.91620000
74	628.29460000	58.86140000
75	650.07620000	4.36120000
76	651.21520000	0.13310000
77	655.02740000	8.91900000
78	657.27480000	12.55160000
79	668.20290000	9.17740000
80	673.50670000	20.46790000
81	675.15240000	92.29240000
82	683.05950000	29.60020000
83	694.27480000	0.21100000
84	732.84870000	192.05640000
85	736.62550000	12.59560000
86	738.61690000	2.18710000
87	746.83020000	5.70020000
88	750.25120000	13.98430000
89	762.28900000	2.67000000
90	770.05990000	7.70420000
91	774.62070000	17.73230000
92	776.67430000	4.87390000
93	783.68310000	66.38220000
94	790.86020000	90.19180000
95	815.34660000	5.61180000
96	831.01990000	30.24680000
97	842.94850000	6.05470000
98	843.86380000	56.97070000
99	852.24190000	6.77750000
100	853.15300000	8.62060000
101	856.66470000	64.27980000
102	873.39360000	0.31330000
103	887.06270000	0.04080000
104	924.10850000	1.48120000
105	944.49260000	0.44670000
106	946.79680000	2.34870000
107	973.31780000	16.35850000
108	975.60670000	5.50590000
109	989.24620000	3.41470000
110	994.69870000	11.83750000
111	996.68080000	6.08410000
112	996.76430000	8.53630000
113	1001.35520000	1.88540000

114	1001.99840000	1.64110000
115	1030.57650000	0.00090000
116	1033.10790000	14.03370000
117	1033.30390000	8.85180000
118	1034.78730000	1.87000000
119	1044.78090000	0.45790000
120	1047.65350000	4.38270000
121	1049.82700000	8.65560000
122	1049.87330000	10.72480000
123	1095.04420000	21.44850000
124	1104.04640000	17.36600000
125	1106.69090000	628.34950000
126	1109.64550000	68.51970000
127	1118.81210000	65.11490000
128	1122.90690000	3.65000000
129	1131.46390000	11.54360000
130	1132.76630000	12.12290000
131	1141.10470000	3.95050000
132	1142.88710000	7.17610000
133	1146.93460000	32.48960000
134	1159.23980000	0.18720000
135	1188.66000000	9.99890000
136	1189.80780000	4.52330000
137	1195.69100000	5.44120000
138	1198.47780000	18.28450000
139	1242.96150000	16.61230000
140	1246.64520000	36.57910000
141	1249.69490000	5.19680000
142	1249.89900000	4.35010000
143	1272.28870000	9.13370000
144	1300.79430000	55.21100000
145	1302.52750000	51.72790000
146	1306.51750000	64.78930000
147	1313.83670000	72.89150000
148	1322.20000000	17.90850000
149	1323.60170000	1.93650000
150	1352.98330000	94.20980000
151	1357.94000000	7.36400000
152	1364.83190000	7.34520000
153	1372.52810000	6.36140000
154	1375.04710000	1.48130000
155	1378.95400000	62.43360000
156	1380.38180000	13.79180000
157	1388.94270000	3.41980000
158	1389.00750000	2.53340000
159	1405.53250000	43.86200000
160	1409.34090000	47.38580000
161	1439.61970000	24.65970000
162	1440.21580000	29.85070000
163	1442.45800000	125.21530000
164	1444.86300000	7.49370000
165	1445.06120000	9.38410000
166	1449.99780000	7.20700000
167	1451.32150000	8.70710000
168	1453.55390000	119.63530000
169	1456.36790000	40.66880000
170	1460.25310000	200.35450000
171	1463.44660000	19.28910000

172	1469.05100000	39.89910000
173	1475.55870000	15.03120000
174	1479.38940000	154.92140000
175	1481.73230000	35.19940000
176	1500.44450000	173.54710000
177	1524.58440000	14.44140000
178	1528.96480000	67.76840000
179	1563.90670000	238.75530000
180	1564.13680000	173.77210000
181	1656.22070000	10.08320000
182	1657.42350000	3.37590000
183	1657.78070000	6.48500000
184	1665.29030000	43.78390000
185	1673.17980000	43.47480000
186	1680.87840000	14.95760000
187	1698.71170000	8.14790000
188	1698.82300000	7.32630000
189	1727.39020000	590.98750000
190	1781.50340000	347.83100000
191	1781.91510000	591.72270000
192	2007.10180000	2366.31220000
193	2028.10170000	2035.92530000
194	2129.37730000	1558.94230000
195	3055.66450000	31.65900000
196	3055.87790000	30.93560000
197	3063.36430000	20.47630000
198	3064.57080000	18.59980000
199	3083.87230000	6.69830000
200	3090.14330000	13.08800000
201	3133.79280000	9.41200000
202	3137.95070000	10.18800000
203	3138.28960000	10.05240000
204	3148.34010000	0.71390000
205	3162.13070000	21.12670000
206	3165.42940000	19.67540000
207	3165.98320000	30.92040000
208	3166.53820000	16.33470000
209	3168.28160000	12.89750000
210	3168.64800000	12.68390000
211	3200.55260000	13.21620000
212	3200.87950000	12.86040000
213	3204.25740000	16.08260000
214	3204.57160000	16.05710000
215	3226.26210000	4.57290000
216	3226.97540000	4.48970000
217	3235.60960000	0.92200000
218	3236.42160000	0.64550000
219	3239.66140000	0.79860000
220	3240.55290000	1.02700000
221	3247.61140000	0.02260000
222	3248.49460000	0.11330000
223	3261.76320000	0.06140000
224	3276.37870000	0.01990000
225	3689.71030000	24.63350000

8 - [Mn(HPEAB)(CO_3)(Br)]

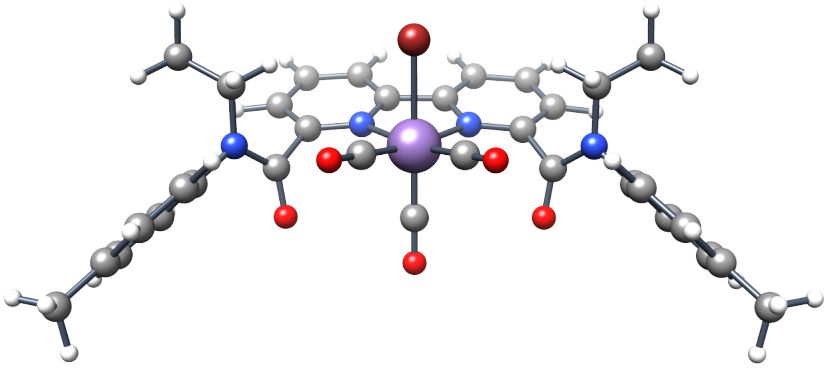


Figure S50: Optimised singlet ground state geometry of [Mn(HPEAB)(CO_3)(Br)]

Route	:	#p opt freq genecp scrf=(cpcm,solvent=dichloromethane)
	:	geom=connectivity int=(acc2e=13,ultrafine) pbe1pbe
SMILES	:	CCN(c1ccc(cc1)C)C(=O)c2cccc-3[n+]2[Mn]([n+]4c3cccc4C(=O)N(CC)c5ccc(cc5)C)([C][O])([C][O])([C][O])Br
Formula	:	$C_{33}H_{30}BrMnN_4O_5$
Charge	:	0
Multiplicity	:	1
Dipole	:	25.7334 Debye
Energy	:	-5591.58903807 a.u.
Gibbs Energy	:	-5591.09799800 a.u.
Number of imaginary frequencies	:	0

Cartesian Co-ordinates (XYZ format)

74

C	-0.73634201	2.86137795	-0.81913602
C	-2.65999293	1.58423197	-0.72041500
C	-3.46185899	2.70738006	-0.93116802
C	-2.86232591	3.95062590	-1.07630396
C	-1.47847295	4.02571583	-1.02897203
C	0.73643500	2.85890198	-0.83069402
C	2.65837598	1.57864594	-0.74059200
C	3.46017098	2.69762897	-0.97296101
C	2.86134791	3.93971300	-1.12993503
C	1.47829795	4.01826620	-1.06717598
H	-4.54484415	2.59109902	-0.99182099
H	-3.46287489	4.84764194	-1.23784196
H	-0.98279703	4.98608303	-1.15796602
H	4.54232883	2.57852697	-1.04269195
H	3.46155405	4.83295107	-1.31233299
H	0.98282099	4.97707701	-1.20777905
N	1.32292497	1.65702498	-0.65341300
N	-1.32356703	1.65934396	-0.64623898
C	-0.00222000	-0.64855099	-1.60710096

O	-0.00417300	-1.18524599	-2.61985397
C	-1.19513297	-0.93643600	0.70987600
O	-1.87126005	-1.69518399	1.24634504
C	1.19636297	-0.93720299	0.70804203
O	1.87247801	-1.69614995	1.24417996
C	3.34179306	0.23009001	-0.79859698
O	3.12908292	-0.48323300	-1.76390600
N	4.25363398	-0.04325100	0.17364500
C	-3.34454489	0.23676100	-0.78866899
O	-3.13289309	-0.46873999	-1.75994098
N	-4.25619316	-0.04436200	0.18167000
C	4.28158188	0.64774698	1.46270204
H	4.08370209	-0.09292700	2.25416899
H	3.42886710	1.34100795	1.49634695
C	5.58586311	1.37107301	1.73758304
H	5.55283308	1.83051395	2.73627996
H	6.43921804	0.67688298	1.71407104
H	5.77239895	2.16739511	1.00177300
C	-4.28194380	0.63334101	1.47782004
H	-4.08031702	-0.11497600	2.26111889
H	-3.43062806	1.32807505	1.51613605
C	-5.58696318	1.35094094	1.76400006
H	-6.43892384	0.65523601	1.73541796
H	-5.55206203	1.79956996	2.76753592
H	-5.77743006	2.15487003	1.03754103
C	5.12421417	-1.16170001	-0.00433500
C	6.02017879	-1.17998898	-1.07852399
C	5.11778688	-2.22824788	0.89469302
C	6.88768005	-2.25246096	-1.24840498
H	6.03327179	-0.34494799	-1.78214395
C	6.00081491	-3.29387593	0.72123498
H	4.41208601	-2.23755097	1.72681606
C	6.89864588	-3.33064389	-0.35058701
H	7.58139086	-2.24867892	-2.09399796
H	5.98327112	-4.12055302	1.43675804
C	-5.12629414	-1.16167605	-0.00573500
C	-5.11745691	-2.23702693	0.88272703
C	-6.02373695	-1.17032695	-1.07878804
C	-5.99958706	-3.30185294	0.69998598
H	-4.41053391	-2.25377798	1.71371102
C	-6.89028883	-2.24203396	-1.25807798
H	-6.03864384	-0.32838199	-1.77410197
C	-6.89880419	-3.32906294	-0.37096000
H	-5.98014593	-4.13554287	1.40727603
H	-7.58513784	-2.23068190	-2.10266995
C	7.83999300	-4.48362303	-0.54636902
H	7.59766388	-5.04044580	-1.46604896
H	8.88041496	-4.13730812	-0.64737701
H	7.79463291	-5.18869877	0.29514799
C	-7.83889818	-4.48126507	-0.57709402
H	-8.87968636	-4.13522816	-0.67514902
H	-7.59582615	-5.02959299	-1.50167894
H	-7.79282379	-5.19381618	0.25806499
Br	0.00473700	1.40719700	2.22110605
Mn	0.00035500	0.18170500	-0.01743800

Frequencies

Mode	IR frequency	IR intensity
1	12.74210000	2.05630000
2	14.24110000	0.03310000
3	20.48850000	0.32980000
4	23.92350000	0.69000000
5	25.97990000	0.44520000
6	31.40100000	1.24140000
7	36.00640000	5.44560000
8	39.52060000	1.27140000
9	43.23550000	3.05490000
10	47.44280000	1.56410000
11	57.50770000	4.68400000
12	58.61790000	2.36410000
13	63.72270000	0.02300000
14	66.76870000	1.99760000
15	74.45600000	4.90770000
16	75.66630000	0.00810000
17	81.45200000	0.38100000
18	82.93740000	0.72950000
19	99.61830000	1.81540000
20	100.29820000	1.29110000
21	108.32760000	2.73610000
22	117.85580000	2.65480000
23	119.02060000	0.39150000
24	127.77330000	0.00690000
25	130.59970000	1.89100000
26	139.80700000	0.18740000
27	149.60670000	0.56680000
28	154.37180000	5.41100000
29	163.06910000	4.05290000
30	174.79290000	0.11010000
31	187.37570000	3.54640000
32	189.81980000	4.01820000
33	209.79770000	0.01540000
34	211.96740000	2.63990000
35	217.51200000	1.10680000
36	229.11930000	16.69080000
37	239.31410000	7.11920000
38	247.74380000	2.61520000
39	270.17050000	0.06900000
40	302.57470000	2.29980000
41	306.17510000	1.43320000
42	309.91770000	13.01430000
43	332.59540000	0.17650000
44	332.96630000	1.59060000
45	352.79050000	0.28810000
46	353.12290000	1.70050000
47	373.93980000	22.27160000
48	385.04310000	16.09330000
49	385.97320000	1.42950000
50	416.09100000	6.38260000
51	417.98140000	3.68340000
52	426.57240000	0.98490000
53	426.63950000	1.03980000
54	453.97470000	5.54830000
55	454.77830000	1.65540000

56	472.24580000	3.95850000
57	481.61160000	0.53960000
58	484.70200000	0.21250000
59	490.26990000	6.93660000
60	496.26480000	17.49720000
61	497.49580000	8.99780000
62	504.66880000	9.89250000
63	509.43770000	0.92500000
64	527.99000000	23.64960000
65	536.32270000	45.44660000
66	540.85520000	24.22120000
67	542.46940000	11.44890000
68	550.05150000	8.10770000
69	616.80730000	3.43220000
70	640.77680000	128.97430000
71	649.64650000	8.96650000
72	650.91490000	6.97580000
73	651.53570000	41.41980000
74	651.87660000	9.85060000
75	658.02700000	7.57410000
76	668.13310000	19.16540000
77	682.01240000	48.98010000
78	690.15260000	20.68570000
79	709.44360000	71.76490000
80	733.66850000	7.65090000
81	738.94580000	2.54430000
82	747.63290000	7.06020000
83	751.62580000	12.11910000
84	761.05870000	2.08820000
85	771.33820000	6.98920000
86	776.85990000	27.69660000
87	780.39240000	1.42250000
88	785.31810000	80.96130000
89	792.39920000	82.05880000
90	815.55740000	7.17890000
91	832.20120000	25.41260000
92	843.97800000	50.78680000
93	844.46020000	5.21800000
94	853.38900000	5.55130000
95	853.54580000	5.46900000
96	858.37510000	66.49970000
97	869.30210000	0.00820000
98	886.79330000	0.00360000
99	925.20180000	1.81840000
100	942.82710000	0.63740000
101	946.47020000	2.42860000
102	973.95180000	12.44250000
103	976.28320000	5.03020000
104	990.30430000	4.02840000
105	996.03870000	8.71160000
106	996.62120000	3.81630000
107	996.91080000	12.91870000
108	1002.10730000	1.20990000
109	1002.19350000	1.51730000
110	1031.40550000	0.00890000
111	1032.85400000	13.33330000
112	1033.01490000	9.76700000
113	1035.91440000	2.08420000

114	1041.26600000	0.00280000
115	1044.91360000	1.44290000
116	1049.96170000	7.60730000
117	1049.97800000	12.86490000
118	1097.42590000	53.56080000
119	1105.50190000	16.83720000
120	1110.66230000	79.45860000
121	1120.07960000	59.19030000
122	1122.15500000	3.13980000
123	1130.32350000	13.03530000
124	1131.20140000	11.36320000
125	1141.51080000	7.65170000
126	1142.25530000	2.15450000
127	1147.34270000	25.46960000
128	1158.96590000	0.46760000
129	1187.61380000	7.92740000
130	1188.19580000	4.05610000
131	1195.49580000	17.94350000
132	1195.61240000	6.16050000
133	1241.70180000	10.91140000
134	1245.97500000	33.88890000
135	1249.44750000	10.01300000
136	1249.50940000	0.41880000
137	1299.39770000	58.79270000
138	1300.89980000	61.56880000
139	1306.27710000	59.32160000
140	1312.85780000	68.69080000
141	1321.57350000	20.63610000
142	1322.76360000	1.68870000
143	1354.51030000	98.88620000
144	1360.76740000	5.22160000
145	1367.38520000	7.83830000
146	1371.11290000	5.89630000
147	1371.27080000	8.34360000
148	1378.31940000	53.06620000
149	1379.67520000	11.13830000
150	1388.74290000	2.71880000
151	1388.80150000	1.94750000
152	1403.76180000	37.48940000
153	1403.92180000	35.23670000
154	1439.32990000	9.84140000
155	1439.54230000	30.17410000
156	1443.33830000	154.91020000
157	1445.43850000	2.11870000
158	1445.50910000	15.52010000
159	1450.37450000	2.96530000
160	1450.57790000	6.96940000
161	1453.00340000	173.81120000
162	1455.91300000	2.86640000
163	1460.39400000	208.98110000
164	1464.26430000	2.32700000
165	1469.17400000	27.39680000
166	1475.38900000	15.33230000
167	1475.62660000	15.63090000
168	1477.83070000	148.83190000
169	1502.58180000	209.25820000
170	1526.93670000	5.76100000
171	1528.25180000	63.01060000

172	1563.89370000	208.97560000
173	1564.07050000	175.15360000
174	1657.46840000	11.43940000
175	1657.51810000	3.05470000
176	1660.32390000	6.61770000
177	1668.03900000	59.20310000
178	1674.96570000	40.31980000
179	1681.06650000	20.59590000
180	1698.60070000	6.07290000
181	1698.64200000	5.83920000
182	1783.22300000	281.93530000
183	1783.80770000	633.00290000
184	2059.94020000	1662.50040000
185	2071.88140000	1635.25150000
186	2153.32460000	1332.30920000
187	3056.03330000	26.72540000
188	3056.03870000	33.92090000
189	3065.46830000	17.48630000
190	3065.59390000	16.42600000
191	3084.91750000	18.08830000
192	3084.92970000	18.25880000
193	3138.64460000	10.11790000
194	3138.65420000	9.74970000
195	3141.58720000	5.31460000
196	3141.63980000	5.39780000
197	3165.79900000	28.02870000
198	3165.90770000	32.99150000
199	3168.15590000	14.83440000
200	3168.18090000	18.08580000
201	3168.74030000	12.22210000
202	3168.75110000	13.69000000
203	3201.31000000	12.24940000
204	3201.39730000	12.18150000
205	3204.95930000	12.95630000
206	3204.98830000	16.65210000
207	3225.87350000	4.12360000
208	3225.88030000	4.77370000
209	3234.33810000	1.32250000
210	3234.93350000	1.32290000
211	3236.63030000	1.40050000
212	3236.67780000	1.45450000
213	3246.17800000	0.06650000
214	3246.91770000	0.16100000
215	3258.28630000	0.08560000
216	3272.17540000	0.01560000

9 - $[Mn(HPEAB)(CO_3)(Br)]^{\bullet-}$

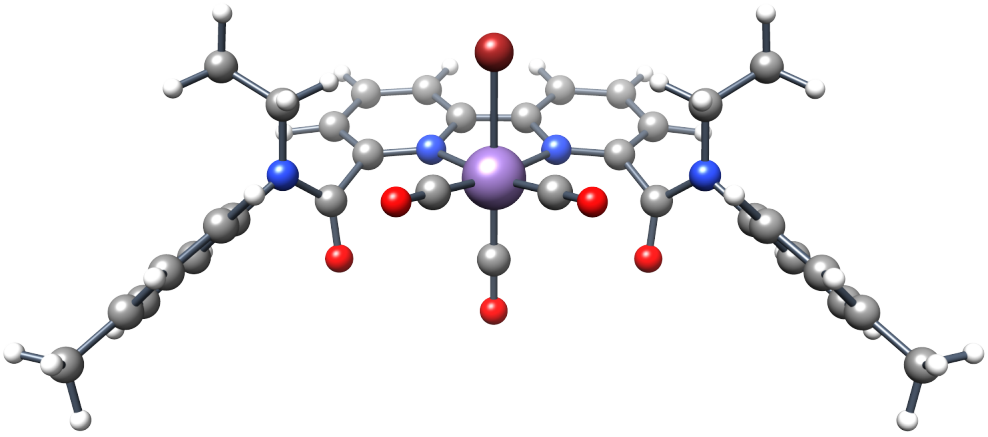


Figure S51: Optimised singlet ground state geometry of $[Mn(HPEAB)(CO_3)(Br)]^{\bullet-}$

Route	:	#p opt freq genecp scrf=(cpcm,solvent=dichloromethane)
	:	geom=connectivity int=(acc2e=13,ultrafine) pbe1pbe
SMILES	:	CCN(c1ccc(cc1)C)C(=O)c2cccc-3[n+]2[Mn]([n+]4c3cccc4C(=O)N(CC)c5ccc(cc5)C)([C][O])([C][O])([C][O])Br
Formula	:	$C_{33}H_{30}BrMnN_4O_5^{1-,2}$
Charge	:	-1
Multiplicity	:	2
Energy	:	-5591.69225333 a.u.
Gibbs Energy	:	-5591.20515100 a.u.
Number of imaginary frequencies	:	0

Cartesian Co-ordinates (XYZ format)

74

C	0.71049201	-2.87782407	-0.80055898
C	2.66573501	-1.59707105	-0.72647101
C	3.47519708	-2.71056509	-0.91073102
C	2.85971498	-3.97713804	-1.03615797
C	1.49201095	-4.05180979	-0.98851299
C	-0.71049500	-2.87782598	-0.80053800
C	-2.66574311	-1.59708595	-0.72637999
C	-3.47519708	-2.71058512	-0.91065502
C	-2.85971093	-3.97715092	-1.03612304
C	-1.49200702	-4.05181313	-0.98850900
H	4.55694914	-2.59078002	-0.97995400
H	3.46188307	-4.87696218	-1.18117702
H	0.99748898	-5.01674604	-1.10010397
H	-4.55694914	-2.59080601	-0.97986799
H	-3.46187592	-4.87697315	-1.18116999
H	-0.99747699	-5.01673889	-1.10015404
N	-1.32705796	-1.65066099	-0.63848102
N	1.32705295	-1.65065300	-0.63854897
C	-0.00002700	0.56632400	-1.69960296

O	-0.00015800	1.03135204	-2.75147510
C	1.19197404	0.98067898	0.59043199
O	1.86340404	1.77506196	1.08827996
C	-1.19188297	0.98069000	0.59051502
O	-1.86321402	1.77515399	1.08836496
C	-3.36429501	-0.26069501	-0.81588000
O	-3.20836496	0.43564701	-1.80589104
N	-4.24757290	0.04222100	0.18388300
C	3.36426497	-0.26066801	-0.81593299
O	3.20822501	0.43575999	-1.80586505
N	4.24761200	0.04217600	0.18378900
C	-4.19877911	-0.59009999	1.50028300
H	-3.98637199	0.18695000	2.25249195
H	-3.32742596	-1.25902700	1.51931596
C	-5.46731281	-1.33836496	1.86345303
H	-5.38169003	-1.74919605	2.88049507
H	-6.34486103	-0.67422098	1.84175003
H	-5.65038013	-2.17368388	1.17132604
C	4.19895983	-0.59032702	1.50010502
H	3.98658609	0.18660700	2.25244188
H	3.32763410	-1.25929296	1.51911902
C	5.46755219	-1.33859897	1.86305594
H	6.34507608	-0.67442101	1.84137297
H	5.38203192	-1.74958205	2.88004494
H	5.65058899	-2.17381096	1.17079103
C	-5.13773012	1.13943994	0.00028200
C	-6.04130507	1.13281798	-1.06918395
C	-5.14983606	2.21809006	0.88590902
C	-6.92930984	2.18700290	-1.24678504
H	-6.04181719	0.29077601	-1.76431894
C	-6.05396700	3.26531601	0.70616299
H	-4.43898106	2.25172710	1.71294105
C	-6.95741415	3.27493310	-0.36105901
H	-7.62662077	2.16069198	-2.08928895
H	-6.04781008	4.09994316	1.41293204
C	5.13770199	1.13945794	0.00024600
C	5.14986181	2.21797991	0.88603300
C	6.04116106	1.13303101	-1.06931603
C	6.05392504	3.26527190	0.70634103
H	4.43910789	2.25145793	1.71315897
C	6.92910099	2.18728304	-1.24686003
H	6.04164886	0.29108301	-1.76456404
C	6.95724487	3.27509189	-0.36098900
H	6.04782200	4.09978294	1.41324699
H	7.62633514	2.16111493	-2.08943200
C	-7.92129993	4.40827608	-0.56491601
H	-7.69682693	4.95839119	-1.49327195
H	-8.95655918	4.04288721	-0.65290099
H	-7.88242292	5.12499905	0.26726899
C	7.92093706	4.40859509	-0.56487298
H	8.95602989	4.04324484	-0.65485799
H	7.69510412	4.95987701	-1.49221396
H	7.88332415	5.12432289	0.26822701
Br	0.00010300	-1.26644599	2.29028702
Mn	0.00001400	-0.16669200	-0.08048800

Frequencies

Mode	IR frequency	IR intensity
1	16.67650000	2.03430000
2	17.94710000	0.48560000
3	21.15170000	0.91530000
4	23.65150000	0.58180000
5	25.32920000	0.26430000
6	30.24520000	1.50650000
7	36.86690000	1.41930000
8	37.34040000	0.89530000
9	40.28390000	6.40280000
10	44.46150000	1.21910000
11	58.82240000	4.54370000
12	59.14480000	1.26830000
13	63.21970000	1.97460000
14	64.57480000	0.00010000
15	73.14700000	2.67760000
16	74.91070000	0.00900000
17	77.94220000	0.63870000
18	80.16030000	0.17820000
19	99.89360000	1.05330000
20	100.92340000	1.65440000
21	108.06910000	2.42250000
22	114.03630000	1.82640000
23	118.13170000	0.30390000
24	125.50520000	0.00070000
25	130.45500000	5.37730000
26	137.33350000	0.42800000
27	149.13420000	7.18450000
28	150.87650000	1.08880000
29	153.94070000	4.04730000
30	170.60590000	0.18970000
31	187.48210000	3.12840000
32	188.69910000	5.60860000
33	206.72160000	0.00800000
34	210.38800000	6.04720000
35	215.95800000	0.59780000
36	224.37520000	10.59360000
37	244.82060000	4.44890000
38	247.30410000	2.00830000
39	265.90250000	0.04670000
40	301.81400000	1.52980000
41	307.69340000	6.73080000
42	308.44020000	11.84400000
43	333.53750000	0.02770000
44	333.80090000	1.20500000
45	351.39900000	1.89350000
46	352.17040000	2.02340000
47	370.53150000	22.31810000
48	376.14070000	35.25180000
49	386.03930000	3.89270000
50	415.54570000	4.54940000
51	415.84560000	5.76490000
52	426.11210000	1.60780000
53	426.67970000	0.10250000
54	428.05140000	0.45420000
55	460.69440000	8.44850000

56	478.85950000	0.01080000
57	480.89430000	2.08990000
58	490.89140000	12.96650000
59	492.99870000	8.23510000
60	496.11050000	0.48340000
61	504.16940000	3.25780000
62	504.34180000	1.65500000
63	510.31830000	4.37360000
64	525.53160000	45.06800000
65	539.79080000	44.46640000
66	540.98520000	20.64590000
67	541.36500000	4.13240000
68	554.22690000	13.70230000
69	608.77180000	0.59660000
70	629.96440000	2.29250000
71	648.76420000	39.51070000
72	649.79150000	64.34880000
73	651.09120000	1.68650000
74	654.60620000	8.67530000
75	657.03770000	38.93550000
76	665.99870000	26.98450000
77	673.45040000	64.77170000
78	681.30750000	38.70900000
79	709.76670000	10.00550000
80	717.65320000	63.81640000
81	734.74360000	8.55900000
82	739.77800000	10.51280000
83	744.40230000	75.93480000
84	746.33750000	5.27230000
85	748.57430000	22.50930000
86	764.32180000	107.02030000
87	766.70550000	29.48850000
88	771.66540000	21.09620000
89	777.31680000	30.24080000
90	808.65840000	54.13510000
91	811.52790000	0.53560000
92	817.68660000	5.68700000
93	835.14560000	3.55000000
94	843.87310000	50.27930000
95	850.84960000	21.34750000
96	851.51050000	2.61020000
97	851.63940000	1.59500000
98	852.02350000	2.38580000
99	858.12650000	39.05280000
100	885.65140000	1.02210000
101	918.82410000	2.46870000
102	972.06570000	6.66890000
103	973.60290000	4.99810000
104	982.01570000	0.10940000
105	987.63590000	0.42080000
106	990.36060000	0.62400000
107	991.73980000	10.80060000
108	995.92380000	4.97710000
109	995.93790000	8.61950000
110	999.98800000	0.00060000
111	1000.13640000	2.30550000
112	1005.53530000	334.06810000
113	1032.31520000	0.96200000

114	1032.71340000	10.20580000
115	1033.54980000	13.54110000
116	1049.45720000	4.10530000
117	1049.46700000	15.17380000
118	1085.72260000	107.54810000
119	1091.26970000	37.91630000
120	1099.31860000	26.75380000
121	1108.25090000	10.50520000
122	1108.86850000	2.58380000
123	1118.04160000	28.98460000
124	1129.57030000	1.69710000
125	1130.46680000	15.14820000
126	1139.64630000	66.58620000
127	1146.62350000	20.15430000
128	1151.89790000	8.84650000
129	1173.02240000	207.11350000
130	1186.98190000	6.27260000
131	1188.62850000	0.84970000
132	1189.50920000	3.89580000
133	1228.15260000	26.14570000
134	1236.75190000	2.42280000
135	1249.30360000	5.52590000
136	1249.30500000	4.32950000
137	1298.39040000	108.05270000
138	1298.93160000	337.50850000
139	1306.09360000	65.05870000
140	1307.82460000	117.49870000
141	1322.62550000	4.75910000
142	1323.73680000	29.26550000
143	1324.06580000	12.04110000
144	1360.85620000	139.41160000
145	1368.27930000	8.63420000
146	1368.80980000	3.37690000
147	1376.11800000	16.12030000
148	1376.93900000	98.60210000
149	1388.32120000	5.80550000
150	1388.33450000	4.34780000
151	1398.61660000	18.88040000
152	1402.89270000	7.83240000
153	1405.60590000	270.55210000
154	1419.75150000	208.47630000
155	1439.09770000	197.45640000
156	1439.96820000	0.24590000
157	1444.42540000	36.86900000
158	1444.54080000	202.75120000
159	1445.26370000	13.54280000
160	1445.66230000	190.21140000
161	1450.03480000	1.22950000
162	1450.14230000	3.14590000
163	1450.97490000	76.63010000
164	1453.65160000	95.28240000
165	1461.68200000	214.26960000
166	1471.01920000	0.73940000
167	1473.12090000	42.34260000
168	1474.05130000	28.85490000
169	1481.25000000	173.93520000
170	1489.10990000	370.18160000
171	1557.82170000	32.21680000

172	1563.89640000	272.71590000
173	1564.15240000	171.71010000
174	1575.91010000	248.89790000
175	1590.62940000	43.44310000
176	1642.47180000	7.38850000
177	1643.02240000	343.88150000
178	1656.21510000	14.84590000
179	1656.23180000	0.01800000
180	1698.94660000	13.15560000
181	1699.00260000	6.44660000
182	1777.28950000	140.26320000
183	1777.96840000	663.48670000
184	2030.32090000	1656.27050000
185	2042.15920000	1811.53290000
186	2131.61170000	1364.78770000
187	3053.99780000	33.25930000
188	3054.00440000	39.84900000
189	3061.61480000	35.27860000
190	3061.63270000	12.68090000
191	3081.33820000	8.05680000
192	3081.35060000	31.67660000
193	3135.84760000	13.91780000
194	3135.84830000	9.18860000
195	3146.36920000	0.35240000
196	3146.38020000	1.30760000
197	3162.22880000	17.08350000
198	3162.23320000	32.31940000
199	3165.23200000	3.12420000
200	3165.25100000	52.64180000
201	3166.06580000	10.85000000
202	3166.06870000	16.68750000
203	3198.12380000	16.96810000
204	3198.12720000	13.79360000
205	3201.47370000	3.01510000
206	3201.47930000	33.63110000
207	3213.07380000	0.45920000
208	3214.41230000	26.85110000
209	3226.73740000	1.13880000
210	3226.73880000	9.03540000
211	3233.84490000	1.17400000
212	3235.75500000	1.51150000
213	3235.75750000	2.75070000
214	3238.12180000	1.66060000
215	3240.04910000	2.65750000
216	3247.57060000	18.06430000

10 - [Mn(HPEAB)(CO_3)]

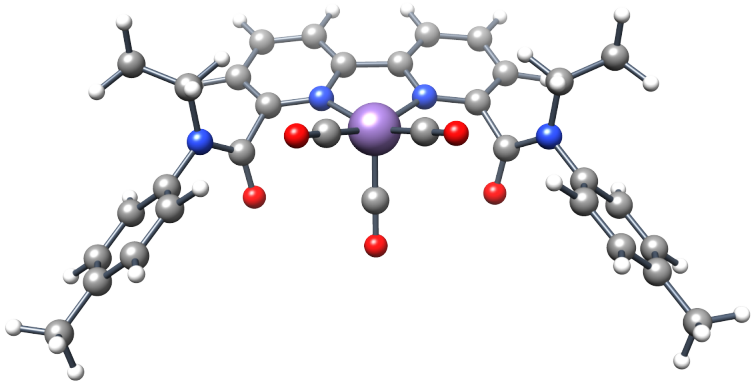


Figure S52: Optimised singlet ground state geometry of [Mn(HPEAB)(CO_3)]

Route	:	#p opt freq genecp scrf=(cpcm,solvent=dichloromethane)
	:	geom=connectivity int=(acc2e=13,ultrafine) pbe1pbe
SMILES	:	CCN(c1ccc(cc1)C)C(=O)c2cccc-3[n+]2[Mn]([n+]4c3cccc4C(=O)N(CC)c5ccc(cc5)C)([C][O])([C][O])[C][O]
Formula	:	$C_{33}H_{30}MnN_4O_5^2$
Charge	:	0
Multiplicity	:	2
Dipole	:	31.5895 Debye
Energy	:	-3017.96398159 a.u.
Gibbs Energy	:	-3017.47609900 a.u.
Number of imaginary frequencies	:	0

Cartesian Co-ordinates (XYZ format)

73

C	-0.73022002	3.13142991	-0.37512600
C	-2.64642191	1.82114899	-0.38833600
C	-3.44972205	2.93848896	-0.58069098
C	-2.86602902	4.20414019	-0.64364201
C	-1.48845398	4.29469299	-0.55416203
C	0.73019701	3.13138795	-0.37542701
C	2.64635110	1.82104397	-0.38891700
C	3.44962692	2.93830705	-0.58182698
C	2.86594510	4.20394802	-0.64504302
C	1.48840296	4.29456615	-0.55512702
H	-4.52732897	2.81055689	-0.69455898
H	-3.47724199	5.09743881	-0.78318602
H	-0.99923599	5.26439905	-0.63389897
H	4.52719879	2.81030989	-0.69595200
H	3.47713089	5.09718180	-0.78512001
H	0.99918002	5.26424885	-0.63511002
N	1.30390799	1.90623200	-0.24716800
N	-1.30393600	1.90627205	-0.24692801
C	-0.00001000	-0.70054799	-1.07858706

O	-0.00004400	-1.45876300	-1.94618404
C	-1.16517305	-0.45748600	1.29068696
O	-1.84361398	-1.08294702	1.99380302
C	1.16524696	-0.45742199	1.29067504
O	1.84372795	-1.08281004	1.99381697
C	3.29299593	0.46373701	-0.56146300
O	3.02043796	-0.18637200	-1.55605495
N	4.24473810	0.09965600	0.34076199
C	-3.29307389	0.46388301	-0.56116599
O	-3.02052689	-0.18599200	-1.55591595
N	-4.24478579	0.09955800	0.34099001
C	4.44226217	0.74245697	1.63770497
H	4.25094891	-0.00599100	2.42350292
H	3.66402888	1.50874400	1.75899899
C	5.82338905	1.34606600	1.81222796
H	5.91600513	1.77896905	2.81917906
H	6.60912418	0.58396399	1.70001805
H	6.01503897	2.14351702	1.07868099
C	-4.44234180	0.74203098	1.63809001
H	-4.25101185	-0.00660900	2.42370105
H	-3.66413593	1.50831294	1.75958300
C	-5.82349300	1.34554303	1.81275904
H	-6.60919809	0.58343601	1.70036495
H	-5.91612482	1.77819800	2.81981492
H	-6.01518202	2.14316392	1.07940698
C	5.00665188	-1.07984602	0.06977700
C	5.97476816	-1.07150900	-0.93807697
C	4.80734587	-2.23960304	0.81861800
C	6.72896624	-2.21230888	-1.19137096
H	6.13297701	-0.16251400	-1.52278101
C	5.57566595	-3.37498093	0.56303698
H	4.03799677	-2.25517201	1.59324503
C	6.54632282	-3.38585901	-0.44493601
H	7.48328018	-2.18992710	-1.98309505
H	5.40941477	-4.27678919	1.15880597
C	-5.00664997	-1.07991505	0.06972300
C	-4.80713415	-2.23990393	0.81815100
C	-5.97491312	-1.07132196	-0.93798500
C	-5.57539082	-3.37526298	0.56230098
H	-4.03767395	-2.25565600	1.59266400
C	-6.72905207	-2.21210194	-1.19154799
H	-6.13328314	-0.16214500	-1.52236295
C	-6.54619503	-3.38588691	-0.44553399
H	-5.40897703	-4.27725697	1.15774298
H	-7.48348379	-2.18952203	-1.98315501
C	7.36008883	-4.61403704	-0.73458302
H	7.07660198	-5.05553007	-1.70404303
H	8.43397045	-4.37869501	-0.79212600
H	7.21813393	-5.38338709	0.03704800
C	-7.35988808	-4.61404181	-0.73548198
H	-8.43379307	-4.37876987	-0.79286200
H	-7.07644796	-5.05521679	-1.70510101
H	-7.21780205	-5.38361597	0.03590100
Mn	0.00000800	0.44289500	0.29988199

Frequencies

Mode	IR frequency	IR intensity
1	5.43660000	0.00270000
2	13.34220000	0.96760000
3	18.59670000	1.08850000
4	19.16910000	0.34050000
5	23.25610000	0.13340000
6	23.69490000	0.13210000
7	26.70770000	2.37280000
8	27.93820000	0.47070000
9	52.11820000	1.63540000
10	53.02880000	4.63760000
11	54.92580000	0.80480000
12	56.01930000	1.04660000
13	58.65010000	1.43050000
14	71.42530000	2.53770000
15	73.10080000	3.14580000
16	80.91590000	0.03050000
17	98.87280000	0.03750000
18	101.72620000	2.83220000
19	108.73940000	1.91010000
20	112.99080000	1.54620000
21	117.96900000	11.05840000
22	124.02570000	7.46580000
23	124.92030000	1.37050000
24	131.22340000	0.05750000
25	141.77990000	6.50130000
26	151.28470000	2.76920000
27	161.32400000	4.58190000
28	178.03910000	3.07300000
29	185.50630000	1.20720000
30	197.96630000	5.03780000
31	210.13490000	0.02180000
32	213.81080000	0.37500000
33	214.57260000	1.08750000
34	240.21090000	18.36400000
35	248.72690000	29.32830000
36	264.26380000	2.88320000
37	299.31670000	7.11240000
38	302.59590000	2.04300000
39	308.86460000	29.53070000
40	326.16140000	1.12310000
41	326.53360000	1.33800000
42	354.44190000	0.45180000
43	355.02370000	3.84520000
44	374.13890000	16.15360000
45	375.67600000	28.64020000
46	390.51300000	51.87420000
47	396.78070000	9.17160000
48	409.26720000	2.16810000
49	410.94270000	10.77260000
50	427.60490000	8.69800000
51	427.93220000	0.68530000
52	428.98180000	16.79570000
53	454.74920000	376.57910000
54	468.12580000	0.00700000
55	475.74380000	16.46400000

56	485.82970000	0.28600000
57	496.63680000	4.18570000
58	505.80600000	29.03510000
59	509.20490000	27.88740000
60	509.47560000	0.39920000
61	529.38420000	0.30780000
62	539.54240000	34.80060000
63	541.08110000	118.29940000
64	542.97350000	1.44880000
65	546.29580000	5.71260000
66	613.69860000	15.31750000
67	615.36070000	107.67080000
68	632.29970000	275.31040000
69	642.74280000	12.73850000
70	649.43310000	16.58460000
71	651.61340000	0.12130000
72	656.68330000	11.03550000
73	666.75350000	14.78800000
74	679.70120000	43.52280000
75	686.56200000	111.30860000
76	689.34620000	58.11350000
77	727.34720000	15.69520000
78	736.84490000	8.14280000
79	750.09250000	11.23840000
80	753.36680000	5.63990000
81	753.84720000	1.88640000
82	766.50050000	3.02250000
83	774.99860000	1.13030000
84	777.62650000	47.28480000
85	777.69660000	78.59920000
86	791.88860000	74.46500000
87	814.63170000	8.38520000
88	826.81320000	40.79210000
89	839.88300000	14.91650000
90	844.46620000	48.35440000
91	856.32590000	37.86530000
92	857.19510000	1.98150000
93	860.58160000	8.63240000
94	861.66540000	7.93100000
95	884.16910000	0.04930000
96	923.58780000	2.17920000
97	934.49710000	1.40600000
98	940.25920000	2.37320000
99	975.54530000	17.95850000
100	979.50570000	14.33850000
101	993.87610000	3.01120000
102	996.26380000	8.49910000
103	996.26690000	3.55730000
104	998.21360000	7.36810000
105	1007.52040000	8.04230000
106	1007.55560000	1.76300000
107	1012.37690000	1.37560000
108	1017.20560000	208.71670000
109	1020.79990000	176.75780000
110	1026.97360000	41.81020000
111	1033.78700000	11.29180000
112	1033.91620000	12.49530000
113	1049.75670000	1.50670000

114	1049.76530000	22.02830000
115	1095.30260000	45.60330000
116	1103.55490000	17.57620000
117	1108.07420000	67.95620000
118	1116.77970000	0.01730000
119	1120.60700000	115.52620000
120	1125.76150000	6.30530000
121	1126.40560000	11.30600000
122	1133.44460000	9.16680000
123	1142.48200000	14.76700000
124	1147.38090000	31.29240000
125	1155.99890000	0.15840000
126	1183.99670000	22.95340000
127	1184.49320000	0.03040000
128	1188.05200000	16.36290000
129	1192.32970000	13.21160000
130	1241.06010000	9.28710000
131	1245.59310000	11.43920000
132	1248.38510000	9.71090000
133	1248.97780000	0.61380000
134	1297.87990000	42.41950000
135	1300.63680000	74.59590000
136	1308.79120000	77.92330000
137	1312.11280000	75.35670000
138	1319.48080000	35.18550000
139	1321.29760000	13.77510000
140	1345.71200000	367.27120000
141	1356.79440000	24.85280000
142	1367.84900000	25.27520000
143	1368.34140000	3.93640000
144	1374.65290000	15.48680000
145	1376.21420000	38.68840000
146	1383.52680000	67.19280000
147	1388.20150000	1.03330000
148	1388.20270000	3.81640000
149	1393.69650000	1004.76680000
150	1400.50660000	2.78610000
151	1401.97750000	87.05600000
152	1437.88280000	26.82760000
153	1437.96140000	0.36520000
154	1446.12450000	2.16080000
155	1446.13730000	12.17790000
156	1448.55320000	14.96120000
157	1448.69640000	9.55420000
158	1449.34520000	32.95850000
159	1451.53790000	150.58140000
160	1452.47530000	19.45610000
161	1461.75200000	215.91030000
162	1463.35540000	14.87320000
163	1472.15650000	18.62250000
164	1472.16000000	14.62140000
165	1474.56800000	171.89690000
166	1476.25830000	33.58630000
167	1516.10780000	295.33240000
168	1516.17570000	161.11350000
169	1564.28850000	196.50100000
170	1564.52550000	191.35700000
171	1613.26540000	177.88730000

172	1642.20110000	29.18570000
173	1656.59370000	0.00260000
174	1656.62680000	10.54680000
175	1662.36520000	5.73970000
176	1667.13130000	13.80050000
177	1697.99210000	8.02010000
178	1698.04750000	7.67700000
179	1781.95910000	242.88200000
180	1782.05630000	576.08430000
181	1981.68930000	2130.96770000
182	2000.71420000	3120.57390000
183	2089.28680000	2649.25120000
184	3055.89940000	17.29480000
185	3055.90260000	42.10330000
186	3064.04630000	29.80460000
187	3064.05790000	8.36270000
188	3085.27560000	18.60440000
189	3085.27970000	21.62420000
190	3138.82790000	13.75680000
191	3138.82880000	7.29180000
192	3146.28840000	12.28300000
193	3146.29770000	1.08360000
194	3165.14710000	7.97000000
195	3165.15500000	48.95170000
196	3166.67220000	12.35120000
197	3166.67570000	35.43470000
198	3168.84590000	6.90340000
199	3168.84730000	18.02090000
200	3200.54020000	13.07790000
201	3200.54240000	10.79680000
202	3203.44910000	0.00690000
203	3203.45190000	27.07510000
204	3223.25740000	3.65390000
205	3223.25930000	6.76220000
206	3230.58850000	2.11680000
207	3230.60230000	2.27610000
208	3231.63350000	0.61020000
209	3232.41120000	0.24480000
210	3242.37310000	0.16640000
211	3243.89400000	0.60210000
212	3252.60500000	0.01060000
213	3264.23330000	2.98160000

11 - [Mn(HPEAB)(CO_3)(NCMe)]

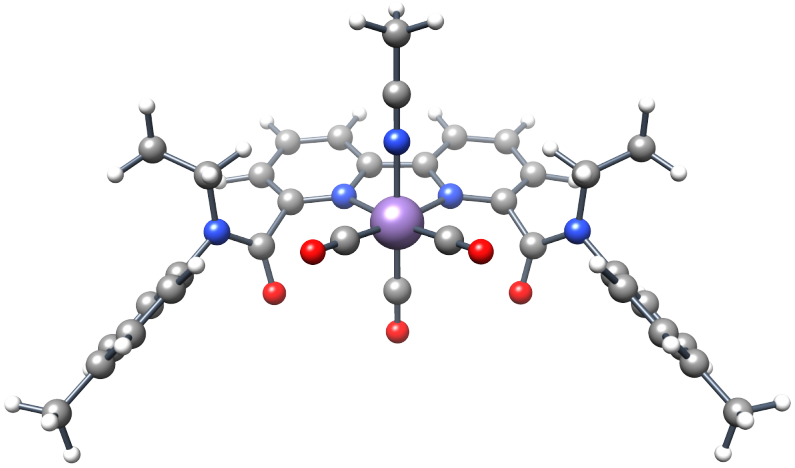


Figure S53: Optimised singlet ground state geometry of [Mn(HPEAB)(CO_3)(NCMe)]

Route	:	#p opt=calcfc freq genecp scrf=(cpcm,solvent=dichloromethane)
	:	geom=connectivity int=(acc2e=13,ultrafine) pbe1pbe
SMILES	:	CCN(c1ccc(cc1)C)C(=O)c2cccc-3[n+]2[Mn]([n+]4c3cccc4C(=O)N(CC)c5ccc(cc5)C)([C][O])([C][O])([C][O])[N]#CC
Formula	:	$C_{35}H_{33}MnN_5O_5^2$
Charge	:	0
Multiplicity	:	2
Dipole	:	38.1233 Debye
Energy	:	-3150.48261346 a.u.
Gibbs Energy	:	-3149.95543200 a.u.
Number of imaginary frequencies	:	0

Cartesian Co-ordinates (XYZ format)

79

C	0.71125901	-2.82950091	-0.92804700
C	2.66680908	-1.54796505	-0.75159597
C	3.47231197	-2.62745905	-1.08306003
C	2.86015105	-3.87941408	-1.32526803
C	1.49456596	-3.97104192	-1.25549901
C	-0.71126503	-2.82948995	-0.92809302
C	-2.66681194	-1.54794204	-0.75170702
C	-3.47230911	-2.62741709	-1.08324397
C	-2.86014605	-3.87936711	-1.32547200
C	-1.49456596	-3.97101092	-1.25563097
H	4.55025911	-2.49243307	-1.17610097
H	3.46389794	-4.75266314	-1.58168602
H	1.00311399	-4.92149401	-1.46331596
H	-4.55025101	-2.49237990	-1.17632306
H	-3.46388698	-4.75259876	-1.58195996
H	-1.00311196	-4.92145681	-1.46346903
N	-1.32895505	-1.62757599	-0.63340801
N	1.32894599	-1.62758696	-0.63335502
C	0.00001100	0.69742298	-1.36859500

O	0.00002400	1.27998900	-2.35177302
C	1.21603703	0.79630703	0.95752698
O	1.91795897	1.50521398	1.53035796
C	-1.21607697	0.79632300	0.95749199
O	-1.91800296	1.50524104	1.53030300
C	-3.33395505	-0.19237900	-0.73236400
O	-3.03864908	0.62813300	-1.58655095
N	-4.32890987	0.00855500	0.18247300
C	3.33395600	-0.19240300	-0.73229200
O	3.03864503	0.62808502	-1.58650005
N	4.32892323	0.00855600	0.18252601
C	-4.47786617	-0.78177297	1.40194297
H	-4.29981613	-0.12315600	2.26856589
H	-3.67184591	-1.52760303	1.41744804
C	-5.83122921	-1.45520794	1.52999401
H	-5.88980484	-1.99836302	2.48485994
H	-6.64831114	-0.71833801	1.51181495
H	-6.00041819	-2.17532706	0.71565801
C	4.47788906	-0.78170800	1.40203500
H	4.29988098	-0.12303400	2.26862502
H	3.67185092	-1.52751803	1.41760504
C	5.83124113	-1.45516396	1.53009295
H	6.64833784	-0.71831203	1.51184297
H	5.88983202	-1.99825799	2.48499298
H	6.00039482	-2.17534089	0.71579897
C	-5.15348387	1.16501200	0.03952500
C	-5.98916292	1.29018199	-1.07553804
C	-5.16262102	2.16764998	1.00947595
C	-6.81154299	2.40200591	-1.21493399
H	-5.98870993	0.50609702	-1.83582199
C	-6.00040007	3.27392292	0.86628598
H	-4.50139284	2.09431505	1.87462103
C	-6.83749104	3.41573906	-0.24512900
H	-7.45712280	2.48189402	-2.09432292
H	-5.99446487	4.04946613	1.63727903
C	5.15349913	1.16500604	0.03952400
C	5.16249800	2.16777492	1.00933599
C	5.98921394	1.29009998	-1.07552302
C	6.00021410	3.27408791	0.86605102
H	4.50113821	2.09455705	1.87439203
C	6.81152010	2.40196204	-1.21502101
H	5.98876715	0.50597101	-1.83576202
C	6.83740091	3.41578388	-0.24530300
H	5.99410677	4.04978609	1.63688600
H	7.45704412	2.48184705	-2.09445000
C	-7.73375607	4.60960913	-0.40628999
H	-7.46953106	5.18566704	-1.30764604
H	-8.78658581	4.30597210	-0.51897597
H	-7.66543484	5.28494215	0.45783201
C	7.73423386	4.60926914	-0.40616801
H	8.78806210	4.30546713	-0.50905401
H	7.47678280	5.18026018	-1.31264400
H	7.65918112	5.28912592	0.45383599
N	-0.00005400	-1.48445594	1.76670694
C	-0.00009000	-2.18635011	2.68220091
C	-0.00014400	-3.07233500	3.82588005
Mn	-0.00001400	-0.25880301	0.16969199
H	0.00095500	-4.11734819	3.48509097

H	0.89467800	-2.89265800	4.43823385
H	-0.89608401	-2.89412689	4.43700981

Frequencies

Mode	IR frequency	IR intensity
1	7.60750000	0.71870000
2	9.07080000	0.52990000
3	11.90970000	0.00710000
4	14.03550000	0.83990000
5	18.58190000	1.11840000
6	23.66070000	0.60650000
7	25.04120000	0.81750000
8	29.96150000	0.11250000
9	37.05430000	0.17510000
10	38.03120000	0.62760000
11	47.05400000	0.00000000
12	50.03730000	13.50010000
13	50.64880000	3.91470000
14	56.77140000	2.06170000
15	60.23100000	0.08310000
16	67.37760000	1.01860000
17	69.17140000	0.60500000
18	71.73530000	1.41790000
19	78.09770000	0.33700000
20	96.20410000	0.37880000
21	98.91470000	2.09020000
22	104.46180000	0.10230000
23	113.50430000	3.52240000
24	119.28280000	0.55480000
25	124.43270000	0.00870000
26	129.96020000	1.82930000
27	131.47950000	0.61400000
28	140.24030000	0.38520000
29	145.50040000	3.14900000
30	152.84410000	1.68230000
31	179.64340000	6.83280000
32	180.65590000	1.05070000
33	189.40360000	5.99010000
34	201.14660000	7.98320000
35	209.21360000	1.35600000
36	213.62130000	0.40850000
37	215.14500000	3.96730000
38	237.62770000	9.32090000
39	249.11680000	0.20700000
40	251.58830000	1.05870000
41	266.21120000	0.01090000
42	271.86040000	0.26550000
43	300.87280000	2.08210000
44	306.92750000	7.26840000
45	311.85730000	6.85320000
46	331.83620000	0.09870000
47	332.20690000	1.15010000
48	349.83840000	0.77940000
49	350.52020000	1.17980000
50	374.21610000	24.04710000
51	376.98560000	44.50500000
52	388.31460000	1.54110000
53	410.48110000	4.09000000
54	412.28610000	4.93050000
55	417.44590000	0.79050000

56	424.45910000	0.48160000
57	424.58550000	0.78720000
58	439.10190000	10.01430000
59	454.16940000	8.32640000
60	470.85040000	0.28650000
61	472.04260000	11.75370000
62	476.78420000	4.52970000
63	487.42860000	4.49400000
64	495.15590000	9.14060000
65	497.12340000	7.61530000
66	500.91960000	3.22090000
67	507.60040000	7.10970000
68	508.72730000	5.98340000
69	530.01220000	30.13140000
70	538.10530000	31.88860000
71	539.37160000	6.91490000
72	548.89250000	27.21900000
73	561.39090000	15.57820000
74	606.79010000	1.12050000
75	629.77670000	0.72390000
76	642.73880000	124.30680000
77	647.18260000	1.24170000
78	650.53580000	2.10240000
79	653.33600000	4.54480000
80	657.97320000	48.75670000
81	666.04260000	29.02450000
82	673.14800000	79.34460000
83	682.11060000	41.75650000
84	710.56940000	7.00550000
85	713.31500000	56.48280000
86	734.49360000	6.65260000
87	740.02840000	9.15470000
88	745.82750000	34.52170000
89	746.70270000	5.78400000
90	748.63700000	33.0702000067
91	761.38620000	135.85250000
92	767.66870000	23.40870000
93	774.59640000	38.59370000
94	782.61560000	22.04930000
95	809.56760000	66.36160000
96	812.50020000	5.09910000
97	818.95470000	11.12520000
98	835.60440000	3.83880000
99	844.03500000	50.05120000
100	852.06430000	32.10390000
101	854.05800000	1.61290000
102	854.20490000	5.03510000
103	859.93660000	5.41780000
104	864.90390000	17.12880000
105	885.30400000	1.15970000
106	917.99870000	2.11810000
107	972.66220000	8.68150000
108	974.73480000	4.91720000
109	984.42730000	8.15150000
110	985.69190000	0.24170000
111	989.02010000	0.670000000372
112	993.15170000	10.88920000
113	993.76100000	0.19450000

114	995.50170000	5.72260000
115	995.51790000	7.96930000
116	1001.89350000	0.07480000
117	1002.02760000	1.42650000
118	1005.50950000	345.89980000
119	1028.56990000	9.89550000
120	1029.02900000	12.58240000
121	1032.63700000	5.38560000
122	1032.77880000	11.05450000
123	1034.32100000	11.01410000
124	1049.66240000	8.51960000
125	1049.68480000	9.55700000
126	1085.89580000	116.05160000
127	1092.36110000	27.25850000
128	1100.49380000	20.70760000
129	1108.41790000	6.71360000
130	1109.24360000	3.15840000
131	1119.41810000	28.68600000
132	1127.82350000	1.53680000
133	1128.72130000	16.62370000
134	1139.86760000	100.53600000
135	1146.59630000	21.69960000
136	1153.77230000	7.02410000
137	1174.06080000	229.63030000
138	1186.12380000	6.44770000
139	1187.62250000	2.60110000
140	1189.45640000	3.19200000
141	1228.58740000	32.84280000
142	1238.12540000	0.78640000
143	1249.00000000	9.59980000
144	1249.02090000	2.52240000
145	1297.48310000	98.87200000
146	1298.05630000	310.00500000
147	1306.85130000	54.93030000
148	1308.18930000	129.44390000
149	1321.52040000	28.36480000
150	1322.28260000	13.71370000
151	1323.84770000	5.82550000
152	1360.16250000	122.98600000
153	1367.32980000	14.21840000
154	1367.98710000	0.75960000
155	1373.57920000	2.99130000
156	1375.29330000	14.57670000
157	1375.99620000	80.51810000
158	1388.48860000	3.48300000
159	1388.50920000	3.12730000
160	1395.94630000	47.48770000
161	1401.39670000	0.39270000
162	1402.79050000	201.25110000
163	1418.09860000	18.27130000
164	1418.85450000	20.30620000
165	1421.75940000	217.82850000
166	1439.25650000	116.04320000
167	1439.81420000	1.58020000
168	1442.81400000	20.64800000
169	1444.16630000	8.00800000
170	1444.21000000	7.11250000
171	1445.77790000	393.04280000

172	1449.03640000	1.88870000
173	1449.40660000	40.68910000
174	1451.12080000	65.39750000
175	1455.07930000	189.97520000
176	1462.96930000	150.68760000
177	1469.60160000	1.05660000
178	1470.94900000	50.88930000
179	1472.34860000	24.15660000
180	1481.31510000	201.97660000
181	1487.31930000	451.16340000
182	1557.26260000	40.01790000
183	1563.70390000	247.12900000
184	1563.97110000	168.98370000
185	1577.88350000	272.37980000
186	1593.51570000	50.03360000
187	1636.73240000	4.06830000
188	1641.49480000	268.04050000
189	1656.46320000	13.57000000
190	1656.47200000	0.11450000
191	1698.53610000	10.81330000
192	1698.59040000	4.99780000
193	1774.08840000	249.18710000
194	1775.03950000	567.09900000
195	2048.90460000	1678.96940000
196	2081.51540000	1677.87020000
197	2162.36580000	1256.22410000
198	2441.34390000	11.48950000
199	3055.49180000	30.70150000
200	3055.50370000	34.60950000
201	3063.69410000	33.44610000
202	3063.70690000	8.84400000
203	3073.08300000	8.28500000
204	3073.10430000	43.76870000
205	3078.77590000	0.53930000
206	3137.72890000	10.39150000
207	3137.73370000	9.96260000
208	3148.72500000	8.95960000
209	3148.74010000	0.97720000
210	3164.94240000	6.17230000
211	3164.94510000	38.37800000
212	3166.49670000	18.26540000
213	3166.51600000	53.05700000
214	3167.55540000	12.04160000
215	3167.56290000	13.63840000
216	3189.50560000	5.09420000
217	3189.69430000	4.87700000
218	3200.06810000	13.50730000
219	3200.08060000	13.61030000
220	3202.65190000	5.86560000
221	3202.65640000	27.42830000
222	3217.16170000	2.10600000
223	3218.67330000	21.71810000
224	3224.79290000	4.55260000
225	3224.79520000	5.74560000
226	3233.09020000	0.71610000
227	3233.09080000	3.53310000
228	3236.37220000	1.79000000
229	3241.36750000	1.79450000

230	3243.00770000	0.82220000
231	3249.27280000	12.32450000

12 - $[Mn(HPEAB)(CO_3)(H_2O)]^+$

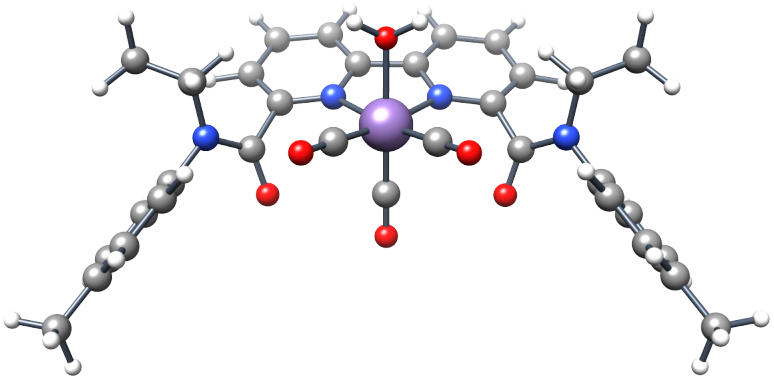


Figure S54: Optimised singlet ground state geometry of $[Mn(HPEAB)(CO_3)(H_2O)]^+$

Route	:	#p opt freq genecp scrf=(cpcm,solvent=dichloromethane)
	:	geom=connectivity int=(acc2e=13,ultrafine) pbe1pbe
SMILES	:	CCN(c1ccc(cc1)C)C(=O)c2cccc-3[n+]2[Mn]([n+] 4c3cccc4C(=O)N(CC)c5ccc(cc5)C)([C][O])([C][O])([C][O])[OH2]
Formula	:	$C_{33}H_{32}MnN_4O_6^+$
Charge	:	1
Multiplicity	:	1
Energy	:	-3094.14117761 a.u.
Gibbs Energy	:	-3093.62404200 a.u.
Number of imaginary frequencies	:	0

Cartesian Co-ordinates (XYZ format)

76

C	0.73911500	-3.02407789	-0.48295701
C	2.66218090	-1.73224604	-0.43131101
C	3.46208596	-2.85107899	-0.66720700
C	2.86512589	-4.09880495	-0.78590202
C	1.48307204	-4.18486691	-0.70292300
C	-0.73637497	-3.02047110	-0.50413197
C	-2.65747595	-1.72457695	-0.47123700
C	-3.45430708	-2.83628201	-0.74771899
C	-2.85703111	-4.08191204	-0.88424897
C	-1.47756505	-4.17335320	-0.77013701
H	4.54156303	-2.73048306	-0.76668102
H	3.46700501	-4.99240303	-0.96080297
H	0.99176198	-5.14912605	-0.81941003
H	-4.53134012	-2.71096897	-0.86639303
H	-3.45612693	-4.96936083	-1.09609103
H	-0.98525000	-5.13493681	-0.90288001
N	-1.32523596	-1.81826901	-0.33312899
N	1.32747197	-1.82123804	-0.31828699
C	0.00611500	0.55050200	-1.15367806

O	0.01048300	1.14217103	-2.12890196
C	1.21394503	0.69247502	1.15178096
O	1.91653001	1.41659904	1.69661701
C	-1.21811700	0.69656301	1.14542902
O	-1.92035699	1.42219305	1.68844104
C	-3.30017805	-0.35663801	-0.55722898
O	-2.92839193	0.38838100	-1.44800794
N	-4.32765818	-0.08257700	0.28894600
C	3.30559611	-0.36607400	-0.53839397
O	2.93897796	0.36166200	-1.44547796
N	4.32851887	-0.07522600	0.30773300
C	-4.59153891	-0.82038403	1.52412105
H	-4.42718792	-0.13907000	2.37515211
H	-3.83055305	-1.60716498	1.62073302
C	-5.98687220	-1.41101301	1.59242594
H	-6.12506390	-1.92533898	2.55453706
H	-6.75525904	-0.62769800	1.51577699
H	-6.16134977	-2.13989711	0.78693801
C	4.58255816	-0.78466702	1.56133997
H	4.41272593	-0.08364900	2.39510107
H	3.81961298	-1.56794906	1.67065895
C	5.97683382	-1.37450695	1.65352798
H	6.74633408	-0.59363598	1.56400597
H	6.10782385	-1.86619401	2.62839603
H	6.15670919	-2.12217093	0.86665702
C	-5.10264492	1.09508395	0.04493700
C	-5.87201977	1.19177794	-1.11848998
C	-5.12112999	2.14173007	0.96618700
C	-6.64187098	2.32473803	-1.35385203
H	-5.86273289	0.37197599	-1.83995402
C	-5.90568590	3.26932311	0.72483402
H	-4.51187420	2.08688211	1.87008500
C	-6.67765093	3.38537788	-0.43585601
H	-7.23682499	2.38479209	-2.26953006
H	-5.90957308	4.08147478	1.45684505
C	5.10412502	1.09761500	0.04318000
C	5.11326981	2.16560507	0.93971401
C	5.88236284	1.16871095	-1.11621594
C	5.89721107	3.28912902	0.67791402
H	4.49703693	2.13054800	1.83988404
C	6.65152597	2.29763508	-1.37224603
H	5.88013506	0.33226299	-1.81838202
C	6.67771387	3.37975001	-0.47929201
H	5.89355898	4.11829710	1.39059198
H	7.25332117	2.33765507	-2.28454494
C	-7.52180910	4.59848785	-0.69826603
H	-7.24313879	5.07802391	-1.64983702
H	-8.58770466	4.33085203	-0.77556801
H	-7.41694498	5.34392500	0.10198000
Mn	-0.00165800	-0.39369601	0.38942900
O	-0.01524500	-1.69899595	2.05895805
H	-0.81251901	-1.70749295	2.60570312
H	0.71905899	-1.63380599	2.68422699
C	7.52064610	4.58857918	-0.76450700
H	8.58758831	4.32190990	-0.82952398
H	7.24635315	5.04539299	-1.72845495
H	7.40937710	5.35206413	0.01765200

Frequencies

Mode	IR frequency	IR intensity
1	15.66790000	0.24430000
2	15.84070000	0.36850000
3	21.36200000	0.57230000
4	22.06590000	1.11490000
5	24.03780000	1.18250000
6	28.73110000	0.02830000
7	33.55340000	0.19300000
8	37.24660000	0.13420000
9	41.83460000	0.09330000
10	48.13880000	7.36450000
11	56.59890000	0.10870000
12	58.10970000	3.14680000
13	63.32850000	0.10290000
14	76.03670000	0.75690000
15	79.21960000	1.43840000
16	85.37060000	2.55810000
17	96.40370000	0.49550000
18	98.86940000	3.07840000
19	105.01860000	1.22650000
20	117.87400000	8.39880000
21	120.28720000	4.47480000
22	124.96640000	15.73890000
23	131.98320000	1.70010000
24	136.13060000	5.42960000
25	138.04960000	0.59100000
26	144.85590000	23.15590000
27	148.13520000	3.79770000
28	153.72310000	22.02020000
29	174.14810000	4.50820000
30	178.58230000	7.72260000
31	186.47270000	4.79750000
32	190.85370000	7.29980000
33	209.35460000	0.22730000
34	210.51530000	0.02350000
35	214.06280000	2.55990000
36	225.91120000	2.78150000
37	242.17040000	5.48120000
38	249.59500000	0.96740000
39	275.82980000	0.10700000
40	301.80540000	2.57570000
41	305.45660000	1.58720000
42	308.65550000	9.61510000
43	332.59660000	0.00360000
44	333.14260000	1.19510000
45	338.86180000	12.42400000
46	351.40770000	0.26360000
47	351.48590000	1.33420000
48	378.04170000	20.75200000
49	387.81210000	21.30270000
50	390.75650000	3.38960000
51	415.29730000	6.11920000
52	416.18990000	2.90100000
53	425.81210000	1.20920000
54	425.93350000	0.69020000
55	454.18720000	3.20500000

56	455.16790000	2.45090000
57	462.69350000	6.27670000
58	466.28450000	2.95360000
59	480.92010000	1.46240000
60	486.94130000	258.28870000
61	487.92340000	24.14310000
62	490.12400000	9.57930000
63	500.29220000	14.09960000
64	502.76280000	10.99780000
65	508.37110000	6.31370000
66	528.10400000	15.71130000
67	531.56770000	25.70200000
68	539.97130000	23.32230000
69	541.94370000	15.42050000
70	553.35390000	11.69170000
71	614.77200000	4.02480000
72	616.31620000	108.46690000
73	649.36660000	7.97940000
74	650.70770000	2.05780000
75	652.04630000	27.04000000
76	653.13150000	17.44160000
77	656.77390000	7.97700000
78	668.39330000	19.19800000
79	673.99420000	14.39750000
80	681.87590000	63.20550000
81	692.05880000	15.99420000
82	711.71560000	32.72010000
83	731.71880000	8.92090000
84	740.06170000	2.73070000
85	747.95010000	7.05350000
86	751.38820000	11.88650000
87	764.29000000	2.14590000
88	769.64410000	18.17040000
89	780.39710000	29.11050000
90	782.63850000	3.57140000
91	786.53890000	93.24530000
92	795.45780000	47.33380000
93	815.00470000	18.10750000
94	833.82210000	20.88890000
95	844.53690000	54.62500000
96	845.79260000	7.65600000
97	854.49710000	1.95810000
98	854.82230000	2.16910000
99	857.76220000	73.24550000
100	872.91100000	1.16100000
101	887.04430000	0.01860000
102	923.67620000	2.42450000
103	947.34130000	0.72780000
104	948.83530000	1.70460000
105	974.22390000	17.65490000
106	976.94750000	4.78300000
107	990.83810000	3.57760000
108	996.63870000	7.40930000
109	996.81140000	5.82830000
110	996.93280000	11.42260000
111	1003.48720000	1.16170000
112	1003.67450000	1.19800000
113	1032.93000000	12.26920000

114	1033.14260000	12.33040000
115	1036.40120000	0.16690000
116	1040.33430000	2.56280000
117	1043.13200000	0.74500000
118	1047.56630000	5.07840000
119	1050.19040000	9.89030000
120	1050.27370000	9.69200000
121	1098.45630000	53.84390000
122	1105.20380000	11.73660000
123	1110.33060000	87.30980000
124	1122.48380000	55.77040000
125	1123.12150000	2.48790000
126	1130.20620000	10.61770000
127	1131.27480000	14.21470000
128	1142.44360000	10.14370000
129	1143.29570000	8.00240000
130	1148.13860000	28.92660000
131	1162.01080000	1.01530000
132	1187.73450000	9.09450000
133	1188.28130000	3.73140000
134	1196.61960000	20.53710000
135	1197.44960000	8.24700000
136	1243.39740000	4.81850000
137	1247.68820000	24.90500000
138	1249.38920000	12.24810000
139	1249.77430000	0.91340000
140	1298.75300000	57.28340000
141	1300.66540000	47.26330000
142	1306.42340000	49.27240000
143	1312.60700000	83.92550000
144	1320.55140000	17.37010000
145	1321.33210000	2.81330000
146	1352.57720000	144.83260000
147	1358.70770000	6.64920000
148	1369.55820000	5.48320000
149	1370.36290000	8.43120000
150	1370.92150000	13.31630000
151	1378.13990000	40.29650000
152	1379.31970000	11.35800000
153	1389.26000000	1.42720000
154	1389.32870000	1.45900000
155	1402.14260000	35.39530000
156	1402.36060000	30.69880000
157	1439.93320000	7.14210000
158	1440.06390000	13.46640000
159	1443.96320000	47.88230000
160	1444.19270000	31.37210000
161	1444.51130000	63.04880000
162	1448.90570000	5.26690000
163	1448.97550000	11.07490000
164	1454.90460000	129.55150000
165	1456.80480000	5.74920000
166	1461.85300000	231.63600000
167	1464.60270000	3.86490000
168	1469.33150000	29.73590000
169	1475.37560000	12.00410000
170	1475.42310000	19.27860000
171	1478.01060000	191.42150000

172	1503.88180000	216.21040000
173	1527.85540000	9.03910000
174	1527.98520000	58.15510000
175	1563.56170000	176.59490000
176	1563.72410000	175.77740000
177	1640.00230000	138.96390000
178	1657.98740000	15.78640000
179	1658.13650000	1.21620000
180	1659.00850000	3.32780000
181	1665.98490000	69.42230000
182	1673.52430000	54.68700000
183	1680.97520000	33.70130000
184	1698.12040000	5.18590000
185	1698.16690000	6.10010000
186	1780.40830000	470.03400000
187	1781.32900000	505.36560000
188	2076.18670000	1681.90980000
189	2103.74480000	1562.53180000
190	2184.34920000	922.80800000
191	3057.49970000	24.75190000
192	3057.50850000	29.99310000
193	3067.07670000	22.24970000
194	3067.08440000	7.29490000
195	3079.59330000	24.46700000
196	3080.25730000	24.74390000
197	3140.36670000	8.72870000
198	3140.40050000	8.63920000
199	3145.22380000	13.91500000
200	3146.52760000	13.37850000
201	3167.36330000	27.53810000
202	3167.52450000	30.38420000
203	3170.20100000	11.91620000
204	3170.22880000	12.56330000
205	3170.95790000	18.76340000
206	3171.09480000	20.29390000
207	3202.91590000	10.75600000
208	3203.10250000	10.75750000
209	3206.02360000	12.51670000
210	3206.11340000	13.53180000
211	3225.77300000	4.04800000
212	3225.96520000	3.98240000
213	3232.23900000	1.84960000
214	3232.84770000	1.87120000
215	3237.19120000	1.47600000
216	3237.78160000	0.42890000
217	3248.66660000	0.43630000
218	3249.49280000	0.13730000
219	3260.32240000	0.18320000
220	3273.29880000	0.46840000
221	3831.00500000	172.32210000
222	3910.82740000	211.72150000

13 - [Mn(HPEAB)(CO_3)]$^-$

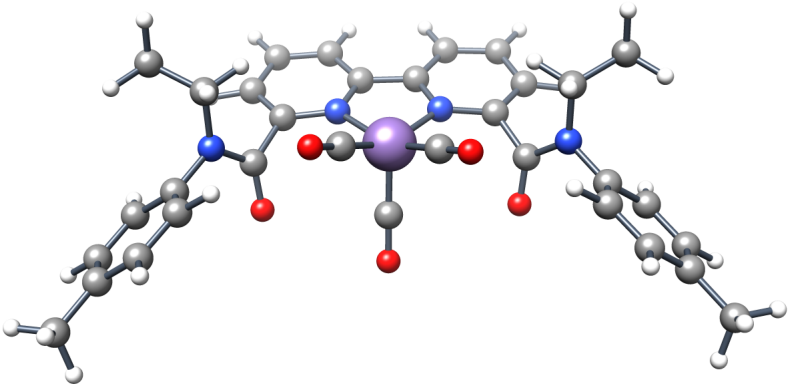


Figure S55: Optimised singlet ground state geometry of [Mn(HPEAB)(CO_3)]$^-$

Route	:	#p opt freq genecp scrf=(cpcm,solvent=dichloromethane)
	:	geom=connectivity int=(acc2e=13,ultrafine) pbe1pbe
SMILES	:	CCN(c1ccc(cc1)C)C(=O)c2cccc-3[n+]2[Mn]([n+] 4c3cccc4C(=O)N(CC)c5ccc(cc5)C)([C][O])([C][O])[C][O]
Formula	:	$C_{33}H_{30}MnN_4O_5^{1-}$
Charge	:	-1
Multiplicity	:	1
Energy	:	-3018.06880918 a.u.
Gibbs Energy	:	-3017.58137800 a.u.
Number of imaginary frequencies	:	0

Cartesian Co-ordinates (XYZ format)

73

C	-0.70992100	3.09618497	-0.40728399
C	-2.64891410	1.78372097	-0.35460800
C	-3.44963789	2.89347696	-0.50417501
C	-2.86697197	4.18200684	-0.59637600
C	-1.49915898	4.26124001	-0.56772298
C	0.70429200	3.09385800	-0.39208800
C	2.64007902	1.77750397	-0.31544200
C	3.44373608	2.88811398	-0.43526500
C	2.86608100	4.17975187	-0.52161002
C	1.49787498	4.25901222	-0.52295500
H	-4.52986383	2.76083708	-0.59070897
H	-3.48638892	5.07237482	-0.71921301
H	-1.00472295	5.22740316	-0.67672300
H	4.52502489	2.75400996	-0.50575101
H	3.48921800	5.07053423	-0.61935300
H	1.00611305	5.22675610	-0.63054103
N	1.26982105	1.83422995	-0.21296300
N	-1.28244901	1.84128404	-0.23354900
C	3.33614492	0.45396599	-0.52468598
O	3.16863608	-0.17229401	-1.55906498

N	4.26108408	0.08504800	0.41491801
C	-3.34002399	0.45468199	-0.54628199
O	-3.16375399	-0.18596099	-1.57025802
N	-4.26593781	0.09378900	0.39455700
C	4.30496120	0.62432700	1.76973796
H	4.11044693	-0.19893099	2.47681808
H	3.46312499	1.32169902	1.87811005
C	5.61555481	1.30981696	2.11030889
H	5.60067081	1.65038395	3.15656304
H	6.46861696	0.62409002	1.99247205
H	5.79000092	2.18611407	1.46808600
C	-4.34244919	0.67079401	1.73233902
H	-4.15487814	-0.13094200	2.46530390
H	-3.50975609	1.37930596	1.83845198
C	-5.66624594	1.35233498	2.02713895
H	-6.51021719	0.65489101	1.91279995
H	-5.67511511	1.72299600	3.06319594
H	-5.83659506	2.20800710	1.35663700
C	5.10241413	-1.03083503	0.12576300
C	6.13579416	-0.90660203	-0.80720901
C	4.92225790	-2.24963903	0.78217399
C	6.97077608	-1.98623800	-1.07845294
H	6.28087187	0.04739300	-1.31933105
C	5.77068806	-3.32251596	0.51211703
H	4.10069990	-2.35702300	1.49318695
C	6.80694485	-3.21492505	-0.42297199
H	7.77533197	-1.87007201	-1.81047595
H	5.61711788	-4.26975012	1.03712296
C	-5.08646917	-1.04282796	0.12463300
C	-4.86832619	-2.25113606	0.78926200
C	-6.13432980	-0.95074397	-0.79516900
C	-5.69377899	-3.34621692	0.53933799
H	-4.03586483	-2.33035302	1.49156201
C	-6.94705915	-2.05257511	-1.04594100
H	-6.30864811	-0.00496600	-1.31339896
C	-6.74465609	-3.27117300	-0.38303700
H	-5.51082420	-4.28494310	1.07018697
H	-7.76395178	-1.96218097	-1.76782799
C	7.69967318	-4.38134480	-0.73662299
H	7.38667822	-4.87714911	-1.67081702
H	8.74388599	-4.06362104	-0.87595898
H	7.67228794	-5.13679790	0.06143700
C	-7.61068106	-4.46283484	-0.67602801
H	-8.65360737	-4.16718292	-0.86352903
H	-7.25849295	-4.99340391	-1.57667601
H	-7.59952307	-5.18395710	0.15372600
Mn	-0.00847300	0.36619699	0.12124600
C	-0.06180800	-0.64576602	-1.31000197
O	-0.08767600	-1.33882999	-2.24028993
C	1.14810300	-0.63167399	1.00478196
O	1.81811094	-1.33593702	1.64949799
C	-1.15424204	-0.56493598	1.08557606
O	-1.82302296	-1.21994495	1.78228104

Frequencies

Mode	IR frequency	IR intensity
1	8.39050000	0.84620000
2	11.00580000	1.54090000
3	14.81150000	0.56600000
4	18.15120000	0.75820000
5	20.92880000	0.23860000
6	23.56400000	1.45520000
7	27.84640000	0.38500000
8	29.05610000	0.13490000
9	49.29630000	8.86270000
10	52.51400000	0.55400000
11	54.28100000	1.41560000
12	57.25260000	0.89360000
13	61.26330000	0.07880000
14	70.20940000	0.85140000
15	70.98020000	2.87100000
16	83.38350000	0.01530000
17	100.66540000	0.17740000
18	101.67080000	1.09630000
19	113.26040000	1.30700000
20	115.22850000	2.39200000
21	119.37890000	6.25960000
22	127.52410000	1.64510000
23	130.92220000	0.36110000
24	138.00100000	0.68380000
25	148.53150000	3.99300000
26	155.48060000	0.27800000
27	166.25950000	4.44750000
28	177.27550000	1.13760000
29	187.99660000	1.08490000
30	203.54220000	2.78580000
31	209.57980000	0.24300000
32	221.04760000	0.56790000
33	221.95330000	1.54370000
34	249.66890000	13.54330000
35	255.95410000	0.82820000
36	266.82180000	18.48120000
37	303.03280000	0.70950000
38	305.05480000	0.30080000
39	324.91870000	2.45160000
40	326.69260000	3.77360000
41	328.79940000	5.79700000
42	354.32080000	2.96460000
43	356.17740000	0.65070000
44	373.25380000	66.87060000
45	378.28280000	27.17320000
46	397.03880000	0.67530000
47	406.37180000	3.70060000
48	414.04090000	13.99360000
49	414.68530000	7.76990000
50	427.26000000	0.54800000
51	427.85940000	0.47130000
52	434.41130000	7.85410000
53	478.01300000	1.96910000
54	490.79060000	60.87860000
55	498.94770000	10.31100000

56	505.05600000	10.41580000
57	507.89190000	19.62420000
58	512.78320000	1.42760000
59	514.74430000	12.20750000
60	527.75930000	144.38350000
61	537.36280000	5.27630000
62	539.40710000	43.36490000
63	544.42410000	15.32390000
64	562.88200000	8.75280000
65	575.26750000	164.86770000
66	609.55220000	10.77570000
67	624.73790000	97.42070000
68	643.77970000	114.55290000
69	648.07770000	15.46470000
70	650.79090000	116.79010000
71	653.07720000	145.50170000
72	655.98670000	1.48090000
73	668.81650000	37.99140000
74	673.92480000	78.65140000
75	687.47240000	144.81130000
76	700.57630000	125.31950000
77	707.77010000	41.36370000
78	733.50650000	5.90850000
79	747.78750000	0.25460000
80	750.49630000	14.03090000
81	754.09100000	8.40910000
82	757.13880000	80.28700000
83	766.56460000	79.15510000
84	767.43290000	10.80270000
85	773.70350000	65.69310000
86	779.03550000	44.68800000
87	804.73450000	49.25570000
88	812.95110000	6.62300000
89	816.11740000	0.39180000
90	834.61020000	23.37130000
91	843.72740000	35.88410000
92	854.80000000	34.18590000
93	860.75880000	8.02380000
94	862.93700000	5.31560000
95	880.25600000	0.63840000
96	898.66370000	13.17640000
97	901.23810000	2.52430000
98	919.06680000	15.01770000
99	967.99940000	0.52660000
100	973.98560000	5.04290000
101	977.43210000	13.06120000
102	978.03230000	1.17680000
103	992.23570000	2.69110000
104	996.02680000	5.96050000
105	996.13840000	1.46110000
106	996.57380000	2.82800000
107	1001.21530000	150.05410000
108	1006.45370000	3.45830000
109	1008.69000000	3.48040000
110	1020.52020000	129.31060000
111	1033.42010000	11.91180000
112	1033.55950000	6.07210000
113	1048.70020000	13.00650000

114	1048.77880000	24.34070000
115	1084.05320000	95.71920000
116	1093.05780000	5.30010000
117	1098.40920000	96.86290000
118	1107.48950000	32.67380000
119	1107.67910000	28.41510000
120	1117.70760000	22.82990000
121	1123.40520000	6.35390000
122	1124.21490000	17.08460000
123	1139.27570000	70.20970000
124	1145.79230000	16.07120000
125	1147.91370000	0.05890000
126	1171.62750000	15.88300000
127	1173.58100000	125.29510000
128	1183.31030000	8.19290000
129	1184.39130000	0.30700000
130	1231.89950000	12.62370000
131	1237.68850000	2.06370000
132	1247.79290000	6.81300000
133	1247.95740000	2.04690000
134	1295.01370000	60.18630000
135	1296.69050000	285.49170000
136	1308.11290000	45.56860000
137	1308.98480000	82.11440000
138	1320.82760000	55.21190000
139	1321.66980000	30.98620000
140	1330.99820000	64.81970000
141	1355.51390000	203.62460000
142	1365.54290000	31.11660000
143	1366.77840000	1.45290000
144	1374.06280000	13.45090000
145	1374.82250000	21.09670000
146	1386.54080000	63.37830000
147	1387.20070000	0.78540000
148	1387.97690000	86.63150000
149	1399.57060000	3.88530000
150	1401.15300000	44.10650000
151	1414.20210000	2.14390000
152	1433.79700000	311.65350000
153	1436.12520000	41.74390000
154	1436.59430000	20.93520000
155	1443.59180000	91.79540000
156	1444.78910000	20.45620000
157	1447.96310000	9.22990000
158	1448.65390000	12.09950000
159	1449.84280000	56.12090000
160	1450.04010000	50.38090000
161	1459.57420000	241.38650000
162	1460.73760000	71.61330000
163	1468.79400000	8.52470000
164	1469.08790000	13.21180000
165	1474.24660000	256.31500000
166	1474.60700000	16.91400000
167	1492.13560000	927.44160000
168	1493.86410000	232.97460000
169	1564.61100000	207.97220000
170	1564.84340000	180.71430000
171	1581.58490000	17.61760000

172	1600.02890000	41.19450000
173	1654.57220000	5.30780000
174	1654.70330000	6.16460000
175	1656.53240000	64.79780000
176	1657.11200000	27.38870000
177	1698.06040000	11.36490000
178	1698.17620000	9.65330000
179	1773.52600000	306.71200000
180	1774.01510000	406.62220000
181	1943.74870000	1968.91700000
182	1965.78740000	2639.88310000
183	2039.69310000	3301.80810000
184	3053.16450000	33.14980000
185	3053.26920000	34.77880000
186	3060.28480000	32.77120000
187	3060.30720000	16.31950000
188	3077.26260000	20.64380000
189	3078.89450000	20.18940000
190	3136.49840000	13.04000000
191	3136.75860000	13.14760000
192	3146.34080000	2.04920000
193	3146.96990000	2.00700000
194	3160.76900000	22.49810000
195	3160.78290000	30.55200000
196	3163.49930000	32.95930000
197	3163.88120000	34.59570000
198	3166.75630000	13.18590000
199	3166.92130000	12.95060000
200	3197.66040000	14.94830000
201	3197.92090000	14.67480000
202	3199.21170000	16.09680000
203	3199.44250000	17.20530000
204	3214.41040000	11.15710000
205	3216.39120000	9.05420000
206	3221.27000000	5.34740000
207	3221.29220000	8.79490000
208	3223.60440000	7.12140000
209	3228.03920000	3.19590000
210	3228.96360000	3.50430000
211	3231.50140000	2.37980000
212	3235.91460000	4.43430000
213	3241.08200000	41.67700000

14 - $[Mn(HPEAB)(CO_3)(CO_2)]^-$

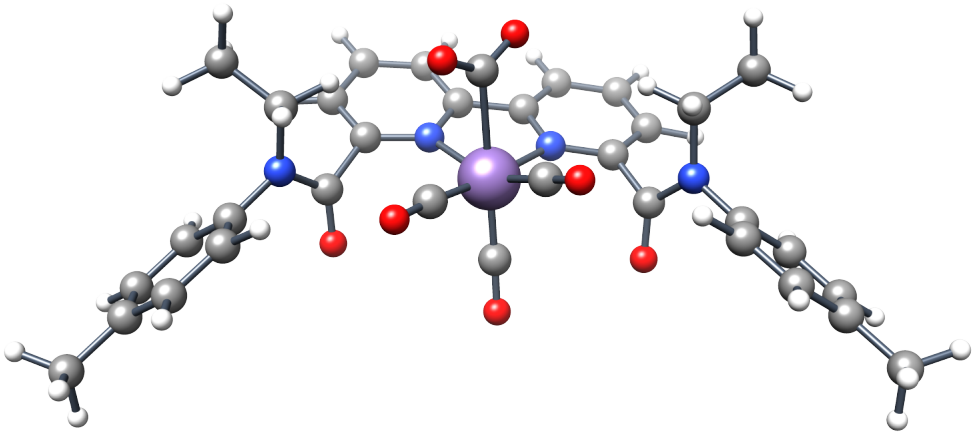


Figure S56: Optimised singlet ground state geometry of $[Mn(HPEAB)(CO_3)(CO_2)]^-$

Route	:	#p opt freq genecp scrf=(cpcm,solvent=dichloromethane)
	:	geom=connectivity int=(acc2e=13,ultrafine) pbe1pbe
SMILES	:	CCN(c1ccc(cc1)C)C(=O)c2cccc-3[n+]2[Mn]([n+]4c3cccc4C(=O)N(CC)c5ccc(cc5)C)([C][O])([C][O])([C][O])C(=O)[O]
Formula	:	$C_{34}H_{30}MnN_4O_7^{1-}$
Charge	:	-1
Multiplicity	:	1
Energy	:	-3206.31631551 a.u.
Gibbs Energy	:	-3205.81941300 a.u.
Number of imaginary frequencies	:	0

Cartesian Co-ordinates (XYZ format)

76

C	-0.67802203	2.94193792	-0.54854798
C	-2.61091995	1.67092896	-0.36780801
C	-3.39871502	2.81236291	-0.34626499
C	-2.80047703	4.07471418	-0.41345900
C	-1.42654395	4.12678719	-0.54591101
C	0.76305002	2.92327189	-0.71083403
C	2.66871405	1.61496699	-0.80002397
C	3.46589398	2.72096205	-1.07075095
C	2.87494707	3.98243189	-1.17416000
C	1.51022696	4.07824421	-0.99400699
H	-4.48454714	2.70726609	-0.31189400
H	-3.40118098	4.98561001	-0.39449000
H	-0.92338097	5.08852482	-0.63986403
H	4.53934193	2.58668494	-1.21435499
H	3.47494102	4.86697197	-1.39668798
H	1.01461804	5.04452276	-1.07781196
N	1.33572602	1.69589806	-0.62257999
N	-1.25325596	1.71334803	-0.40158200
C	0.15749100	-0.60966098	-1.66629195
O	0.20802701	-1.20234203	-2.65868306

C	-1.11620903	-0.99140799	0.49832499
O	-1.76131999	-1.85973203	0.91289800
C	1.16341603	-0.73493999	0.88019198
O	1.79453695	-1.42041504	1.57923603
C	3.36860108	0.27570000	-0.85715699
O	3.28632593	-0.40668401	-1.86449695
N	4.18618202	-0.02075100	0.19251400
C	-3.34365797	0.37146801	-0.60666901
O	-3.25404310	-0.16465500	-1.69933903
N	-4.20034790	-0.04992100	0.36817399
C	4.13451719	0.67615402	1.47665298
H	3.97256088	-0.07829800	2.26227307
H	3.23388600	1.30737698	1.48828006
C	5.37984896	1.48940003	1.77760696
H	5.29969120	1.93994701	2.77817702
H	6.28193903	0.85861403	1.76356006
H	5.51839590	2.30149508	1.04837298
C	-4.08263206	0.35352999	1.76766205
H	-3.91540790	-0.55453801	2.36899400
H	-3.15691996	0.93427402	1.88307595
C	-5.29192400	1.10684299	2.28897190
H	-6.21349382	0.51536101	2.17456388
H	-5.16349888	1.32446301	3.35984898
H	-5.43300915	2.06321907	1.76359105
C	5.07062578	-1.13505101	0.07423100
C	6.13500404	-1.08935595	-0.83218998
C	4.90374613	-2.26786208	0.87133300
C	7.01262999	-2.16280699	-0.93777299
H	6.26917410	-0.20313101	-1.45646501
C	5.79634619	-3.33460307	0.76574302
H	4.05968285	-2.31805801	1.56149006
C	6.86362219	-3.30599904	-0.13832501
H	7.83900404	-2.10971308	-1.65257895
H	5.65147114	-4.21514988	1.39803898
C	-5.12484312	-1.08829904	0.04917000
C	-5.04128790	-2.33945704	0.66108698
C	-6.14805222	-0.85082799	-0.87492800
C	-5.97367811	-3.33158493	0.35773301
H	-4.23083687	-2.54399610	1.36272001
C	-7.06553602	-1.84999001	-1.17962301
H	-6.21861219	0.12794000	-1.35468304
C	-7.00017118	-3.11019993	-0.56646699
H	-5.89273882	-4.30604887	0.84766799
H	-7.85843086	-1.64465404	-1.90478599
C	7.81899786	-4.45820284	-0.26101699
H	7.77017212	-4.90946102	-1.26517701
H	8.85999393	-4.13243484	-0.10772600
H	7.59736919	-5.24538612	0.47300601
C	-7.99830294	-4.18068886	-0.90305400
H	-9.03035736	-3.82837296	-0.74815702
H	-7.91845703	-4.48001909	-1.96067405
H	-7.84948206	-5.07867193	-0.28733000
Mn	0.03816900	0.21584900	-0.09079000
C	-0.11091000	1.21337998	1.98722506
O	-0.87015599	0.64455098	2.76785707
O	0.54925197	2.24384594	2.06116009

Frequencies

Mode	IR frequency	IR intensity
1	4.55640000	0.77770000
2	8.37740000	0.78860000
3	13.06680000	1.77980000
4	18.42260000	0.55460000
5	21.43340000	1.64980000
6	26.67110000	0.14620000
7	28.56850000	0.56590000
8	35.25690000	0.84440000
9	43.69760000	0.76340000
10	51.35200000	6.29010000
11	58.81120000	1.22100000
12	61.66770000	10.90860000
13	63.22240000	1.22630000
14	63.71500000	2.58570000
15	68.53910000	9.49580000
16	74.48640000	5.59450000
17	85.72520000	5.81110000
18	89.22400000	2.48750000
19	97.30300000	1.71800000
20	101.48460000	4.38320000
21	108.47710000	0.45940000
22	119.20890000	5.05890000
23	121.34490000	1.78090000
24	124.33970000	1.00330000
25	129.81040000	1.39140000
26	134.53020000	1.10060000
27	139.93270000	1.93350000
28	150.60080000	6.48760000
29	155.19600000	1.67690000
30	166.16750000	8.84060000
31	180.21860000	55.69910000
32	186.28440000	6.78970000
33	189.04760000	11.41350000
34	208.19000000	3.39480000
35	211.85590000	0.91220000
36	219.59110000	2.71910000
37	226.24920000	4.38850000
38	245.29390000	17.49280000
39	262.37670000	12.59180000
40	273.02400000	2.57980000
41	275.20050000	5.66680000
42	304.13540000	6.22070000
43	310.99890000	6.22080000
44	319.83240000	0.50090000
45	327.12990000	1.22670000
46	330.08630000	1.73230000
47	353.19140000	0.42110000
48	355.00490000	3.65360000
49	373.71170000	45.44620000
50	384.46350000	30.34520000
51	391.37900000	8.37670000
52	413.03120000	1.98590000
53	417.03580000	15.93270000
54	426.27550000	1.26620000
55	427.27320000	0.34880000

56	446.85400000	100.14500000
57	458.97200000	5.62460000
58	476.64910000	100.18420000
59	492.38250000	21.25950000
60	496.85990000	31.85920000
61	501.55750000	8.86870000
62	504.84960000	73.48010000
63	509.74560000	128.44770000
64	514.02890000	27.74970000
65	516.98750000	14.96400000
66	536.08610000	67.85800000
67	539.81810000	2.72960000
68	543.44930000	50.35060000
69	544.08220000	73.29440000
70	558.31020000	219.09930000
71	589.30730000	33.41190000
72	613.56010000	168.06380000
73	625.69270000	369.79530000
74	642.11250000	29.76020000
75	649.67950000	1.05540000
76	651.39520000	3.55840000
77	656.34910000	114.46400000
78	658.88630000	39.33710000
79	669.12920000	52.03310000
80	673.07560000	37.69350000
81	681.08170000	86.01030000
82	699.44060000	96.25570000
83	711.72790000	189.25420000
84	730.30670000	10.69710000
85	738.32600000	9.44410000
86	748.79890000	8.67220000
87	752.81870000	5.95940000
88	759.68090000	2.80820000
89	771.80980000	3.63700000
90	773.11830000	42.22700000
91	774.67630000	17.87910000
92	776.48370000	55.89950000
93	788.93540000	109.05150000
94	813.85680000	1.96570000
95	822.61150000	40.50440000
96	838.92080000	9.56990000
97	844.27200000	33.47280000
98	851.59290000	4.47660000
99	854.87630000	21.62880000
100	856.42450000	26.91570000
101	860.94370000	14.92480000
102	885.31030000	0.26710000
103	923.74380000	0.91900000
104	927.20220000	3.61990000
105	934.25160000	3.86010000
106	973.82380000	12.11180000
107	977.50700000	10.72470000
108	991.63780000	2.53270000
109	995.23190000	7.37330000
110	995.33300000	6.43270000
111	996.56720000	9.95120000
112	997.66910000	0.83620000
113	1002.02760000	1.54530000

114	1006.59930000	2.56260000
115	1010.84010000	1.00060000
116	1027.09490000	117.96480000
117	1031.49180000	54.11390000
118	1033.38010000	8.39250000
119	1034.28910000	10.45840000
120	1049.55790000	9.08760000
121	1049.86960000	9.26110000
122	1092.95540000	33.86510000
123	1102.43670000	21.88010000
124	1107.09720000	62.74970000
125	1115.73290000	5.59930000
126	1116.49210000	73.33960000
127	1125.92970000	10.10730000
128	1127.53020000	11.23740000
129	1133.77080000	9.35080000
130	1140.03380000	6.67250000
131	1146.18570000	11.15940000
132	1151.75420000	2.42510000
133	1184.26740000	20.69160000
134	1184.75590000	6.97050000
135	1189.57800000	24.59640000
136	1191.53100000	17.11870000
137	1238.52980000	198.51070000
138	1245.05190000	57.82520000
139	1248.31100000	66.05530000
140	1248.53500000	58.16680000
141	1250.03190000	557.71070000
142	1301.27500000	63.40680000
143	1302.67400000	112.15530000
144	1308.27650000	65.11950000
145	1312.34740000	86.62730000
146	1321.13380000	27.23520000
147	1323.06780000	17.35870000
148	1350.64450000	24.73780000
149	1363.75530000	8.27470000
150	1370.28600000	13.21130000
151	1372.15770000	2.59440000
152	1375.40910000	21.72600000
153	1376.59000000	53.73330000
154	1388.18970000	1.69590000
155	1388.20600000	1.88400000
156	1394.82340000	57.62430000
157	1404.17700000	40.44990000
158	1407.06740000	89.21740000
159	1421.22600000	239.81750000
160	1439.24290000	26.15010000
161	1439.55600000	11.57820000
162	1444.64230000	9.69250000
163	1444.97170000	7.54030000
164	1447.60810000	69.42000000
165	1449.60620000	13.63810000
166	1450.97380000	7.10810000
167	1451.36080000	67.14850000
168	1453.23120000	45.87200000
169	1460.31530000	202.31490000
170	1465.36330000	54.58670000
171	1473.27610000	8.47750000

172	1473.63070000	33.95710000
173	1475.41510000	118.02460000
174	1484.63950000	55.59320000
175	1512.08530000	193.61370000
176	1521.82290000	205.24940000
177	1564.15900000	227.55500000
178	1564.49700000	185.33060000
179	1608.56280000	87.46310000
180	1644.50350000	50.72700000
181	1655.53640000	5.04330000
182	1655.77010000	7.75660000
183	1664.92120000	34.99000000
184	1669.94760000	30.43690000
185	1698.18940000	8.14500000
186	1698.57370000	10.27090000
187	1775.65540000	392.04040000
188	1783.16750000	394.41560000
189	1845.73450000	693.62290000
190	1968.35820000	2161.86630000
191	2001.40380000	1839.16140000
192	2072.05880000	2608.41580000
193	3054.36460000	35.17490000
194	3054.80540000	34.27900000
195	3060.25860000	24.56130000
196	3061.44410000	21.81870000
197	3086.39110000	13.15090000
198	3087.73650000	11.39160000
199	3136.18860000	11.34760000
200	3136.75400000	11.09980000
201	3140.35830000	0.71780000
202	3146.51710000	7.76230000
203	3160.54590000	22.49950000
204	3161.10730000	15.58770000
205	3163.30280000	25.16260000
206	3164.67890000	24.73420000
207	3166.37760000	13.59730000
208	3166.91350000	13.62540000
209	3197.64310000	14.81470000
210	3198.22390000	13.93820000
211	3201.16330000	18.15320000
212	3201.74240000	16.75710000
213	3222.44930000	6.03310000
214	3222.84560000	5.33460000
215	3224.37030000	3.57700000
216	3226.05720000	3.04560000
217	3235.19160000	0.88870000
218	3235.64710000	3.18020000
219	3236.84870000	3.45830000
220	3238.16930000	0.47880000
221	3249.42610000	0.58990000
222	3258.75130000	9.65840000

References

1 J. J. Snellenburg, S. Laptenok, R. Seger, K. M. Mullen and I. H. M. van Stokkum, *J. Stat. Softw.*, 2012, **49**, 1–22.

2 Y. Pellegrin and F. Odobel, *C. R. Chim.*, 2017, **20**, 283–295.

3 T. T. H. Tran, G. L. Chen, T. K. A. Hoang, M. Y. Kuo and Y. O. Su, *J. Phys. Chem. A*, 2017, **121**, 6925–6931.

4 Bruker, *SADABS*, Bruker Axs Inc., Madison, Wisconsin, USA, 2016.

5 L. Krause, R. Herbst-Irmer, G. M. Sheldrick and D. Stalke, *J. Appl. Crystallogr.*, 2015, **48**, 3–10.

6 G. M. Sheldrick, *Acta Crystallogr. Sect. A Found. Crystallogr.*, 2015, **71**, 3–8.

7 G. M. Sheldrick, *Acta Crystallogr. Sect. C Struct. Chem.*, 2015, **71**, 3–8.

8 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.

9 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, N. R. J. Gao, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, *Gaussian09, Revision D.01, Gaussian, Inc.*, Wallingford CT, 2016.

10 R. C. Whaley and A. Petitet, *Softw. Pract. Exp.*, 2005, **35**, 101–121.

11 R. C. Whaley, A. Petitet and J. J. Dongarra, *Parallel Comput.*, 2001, **27**, 3–35.

12 J. L. Pascual-ahuir, E. Silla and I. Tuñon, *J. Comput. Chem.*, 1994, **15**, 1127–1138.

13 S. Miertuš, E. Scrocco and J. Tomasi, *Chem. Phys.*, 1981, **55**, 117–129.

14 S. Miertuš and J. Tomasi, *Chem. Phys.*, 1982, **65**, 239–245.

15 C. Adamo and V. Barone, *J. Chem. Phys.*, 1999, **110**, 6158–6170.

16 F. Weigend, F. Furche and R. Ahlrichs, *J. Chem. Phys.*, 2003, **119**, 12753–12762.

17 F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297–3305.

18 F. Weigend and A. Baldes, *J. Chem. Phys.*, 2010, **133**, 174102–174110.

19 A. P. Scott and L. Radom, *J. Phys. Chem.*, 1996, **100**, 16502–16513.

20 M. K. Kesharwani, B. Brauer and J. M. L. Martin, *J. Phys. Chem. A*, 2015, **119**, 1701–1714.

21 M. L. Laury, M. J. Carlson and A. K. Wilson, *J. Comput. Chem.*, 2012, **33**, 2380–2387.

22 M. D. Halls, J. Velkovski and H. B. Schlegel, *Theor. Chem. Acc.*, 2001, **105**, 413–421.

23 K. K. Irikura, R. D. Johnson and R. N. Kacker, *J. Phys. Chem. A*, 2005, **109**, 8430–8437.