Electronic Supplementary Information

Tris-(manganese (III)) Corrole-Porphyrin-Corrole Triad: Synthesis, Characterization and Catalytic Epoxidation

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Contents

1. Mass Spectra

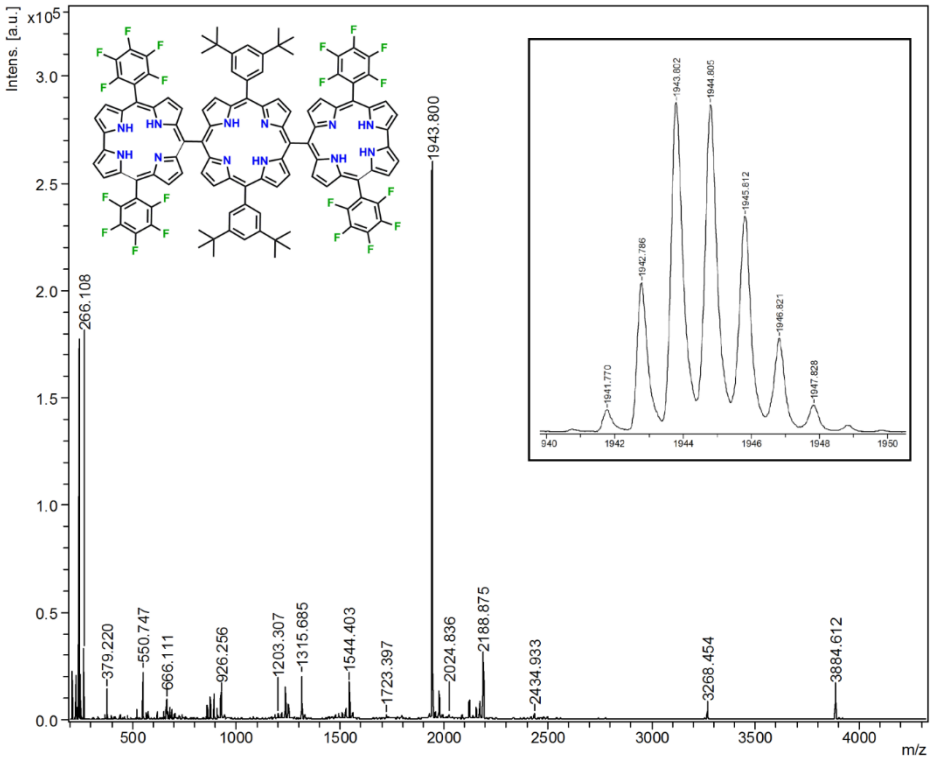

Fig. S1 MALDI-TOF mass spectra of **1**.

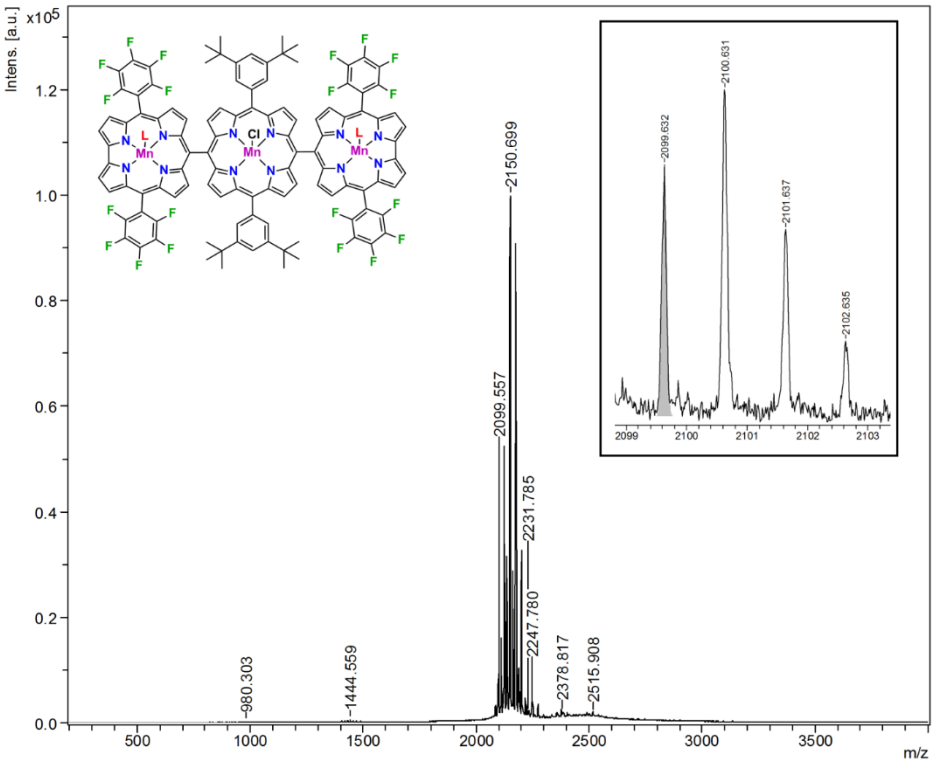

Fig. S2 MALDI-TOF mass spectra of **1-Mn**. (L= Dimethylformamide)

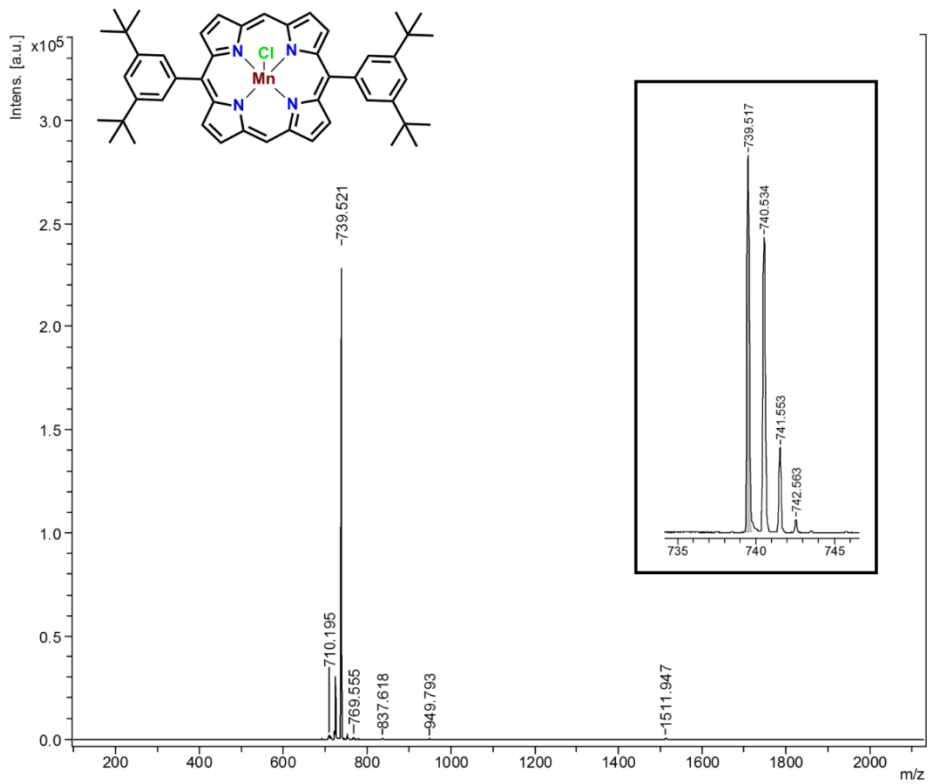

Fig. S3 MALDI-TOF spectra of **2-Mn**.

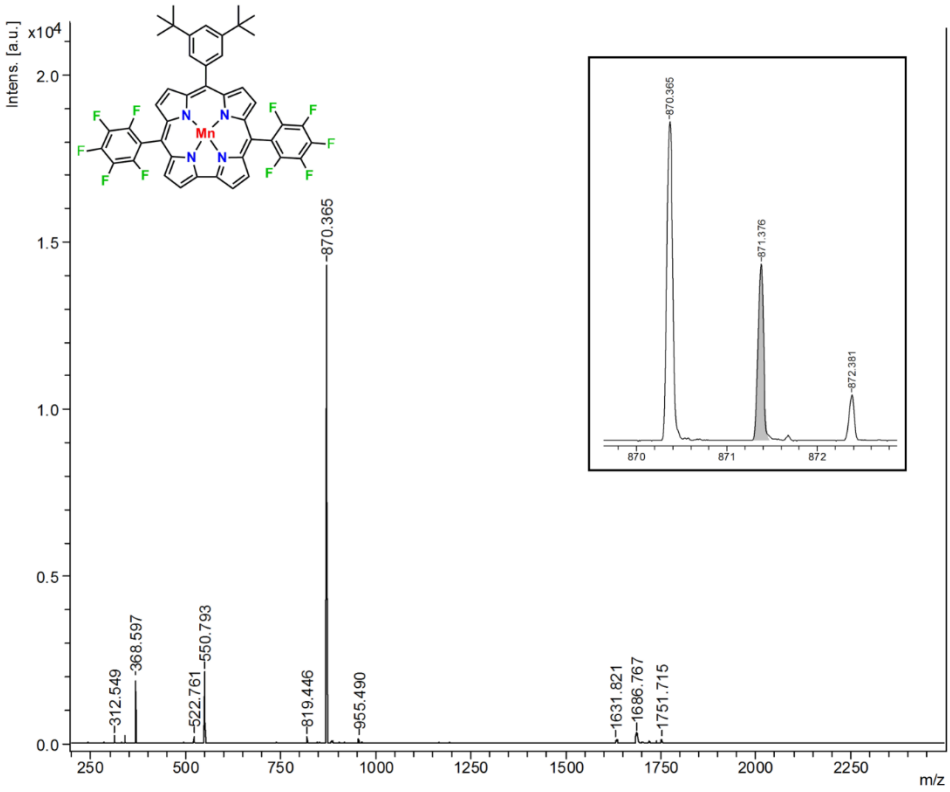

Fig. S4 MALDI-TOF spectra of **3-Mn**.

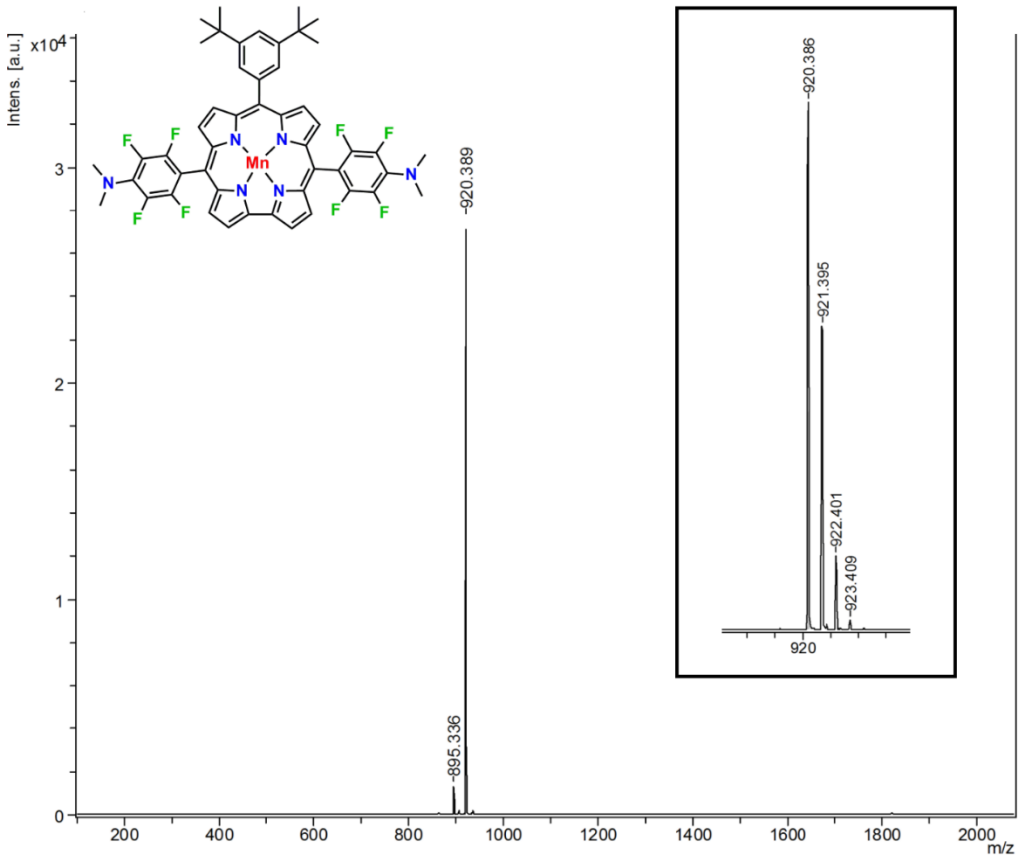

Fig. S5 MALDI-TOF spectra of **3a-Mn**.

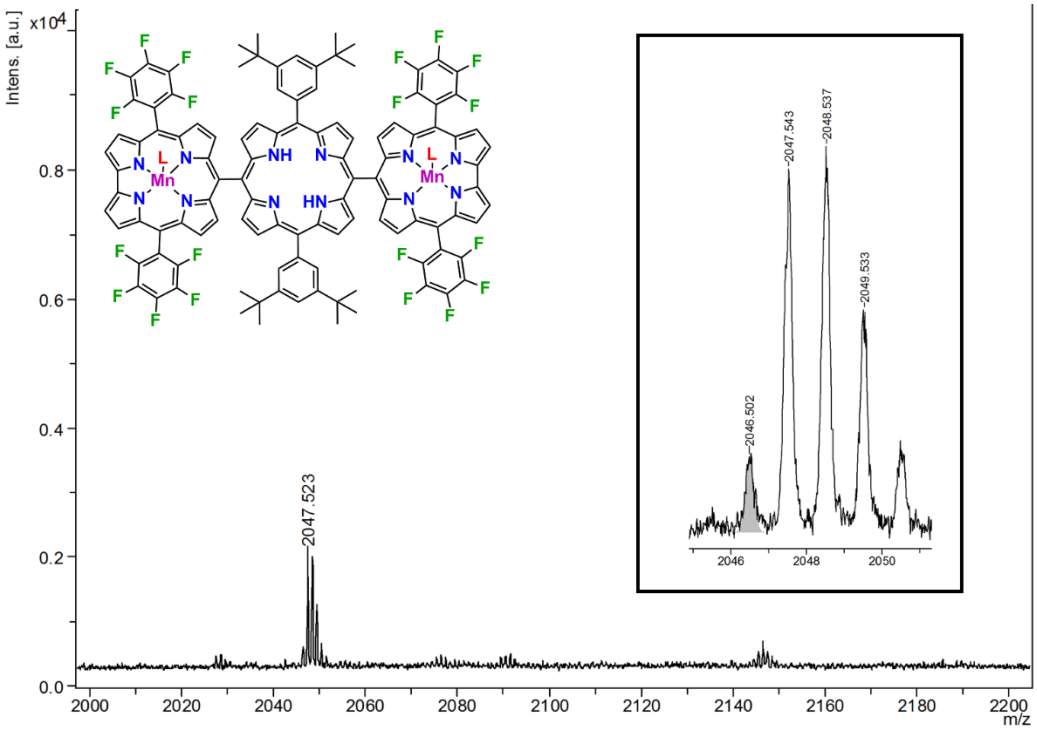

Fig. S6 MALDI-TOF spectra of **4-Mn**. L= Dimethylformamide**.**

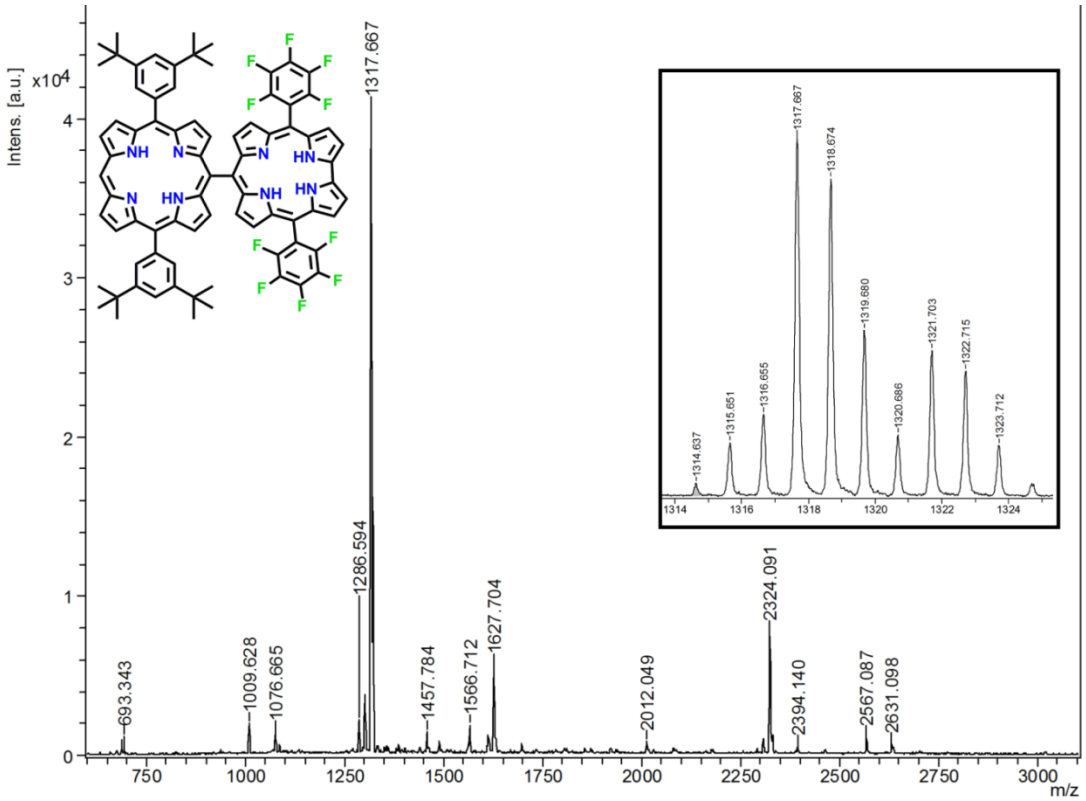

Fig. S7 MALDI-TOF spectra of **5**.

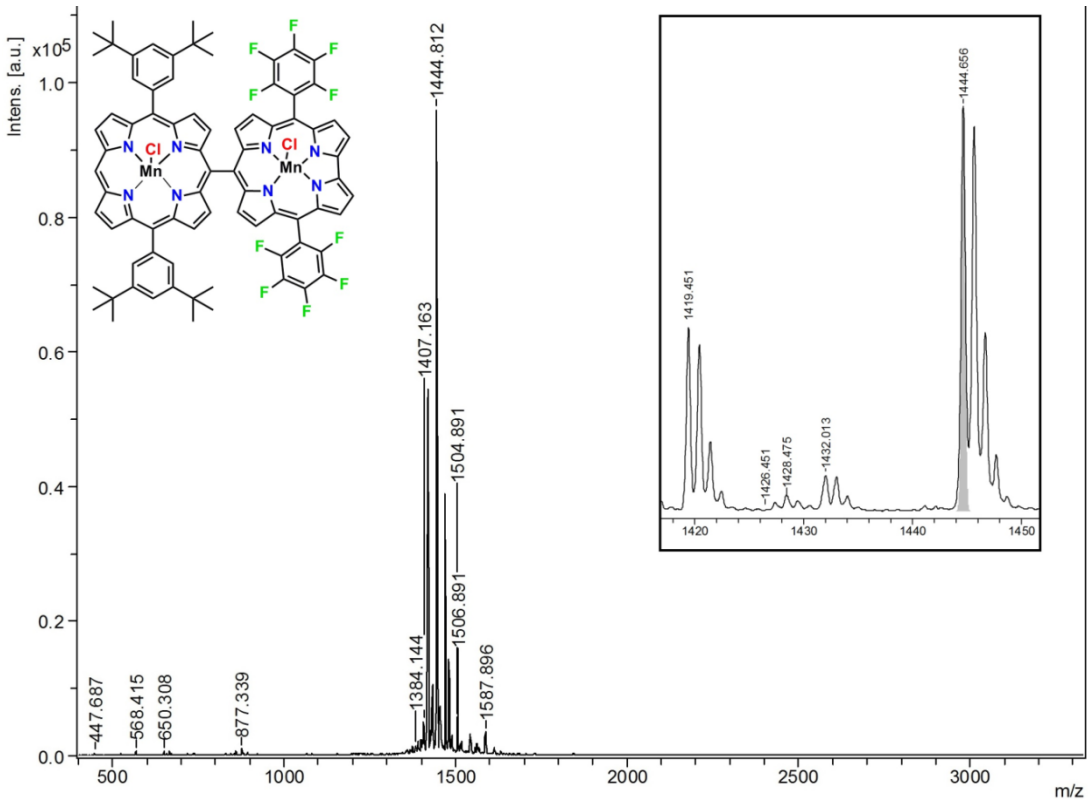

Fig. S8 MALDI-TOF spectra of **5-Mn**.

2. NMR Spectra

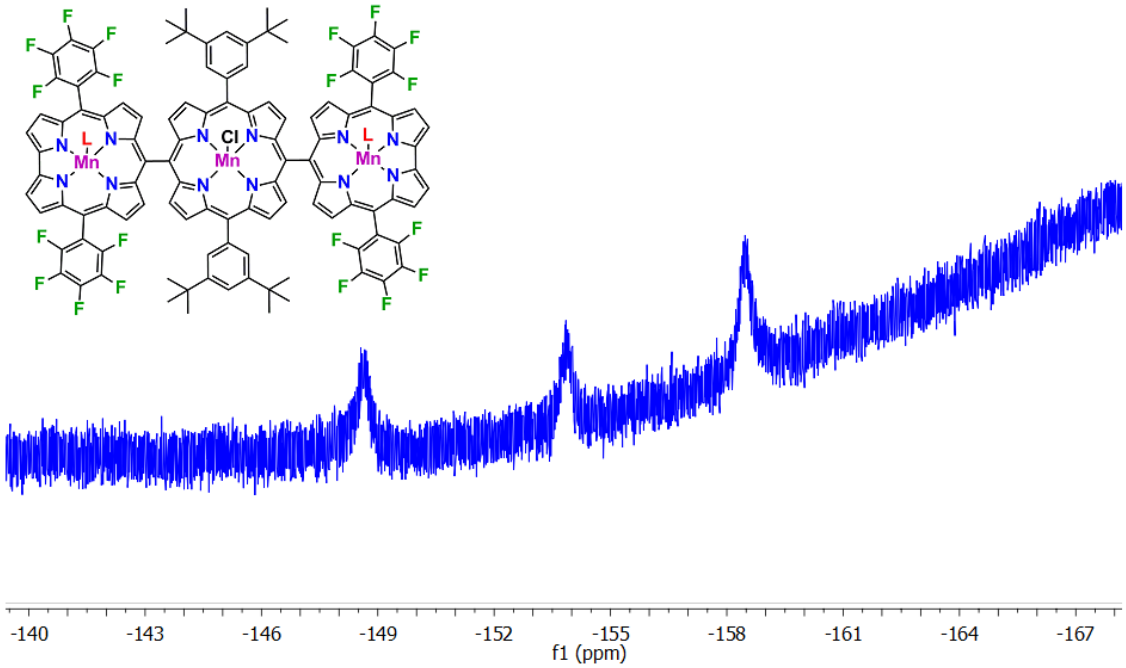

Fig. S9 500 MHz ^{19}F-NMR spectra of 1-Mn triad in $CDCl_3$.

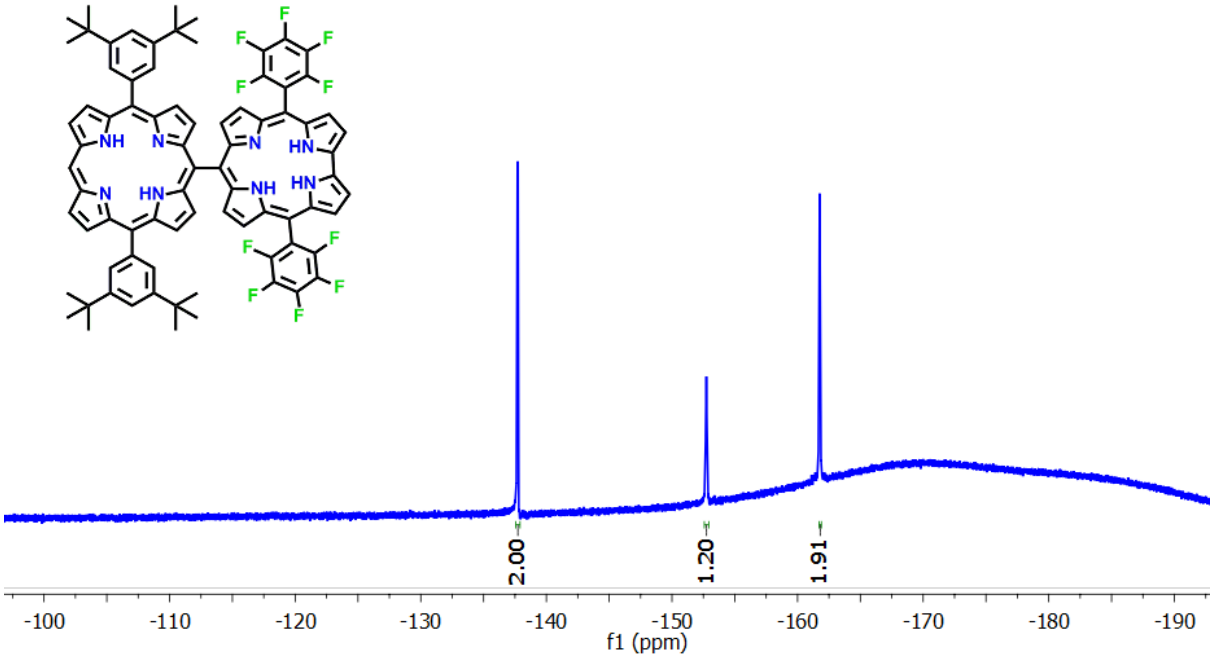

Fig. S10 ^{19}F-NMR spectra of dyad **5** in $CDCl_3$ at room temperature.

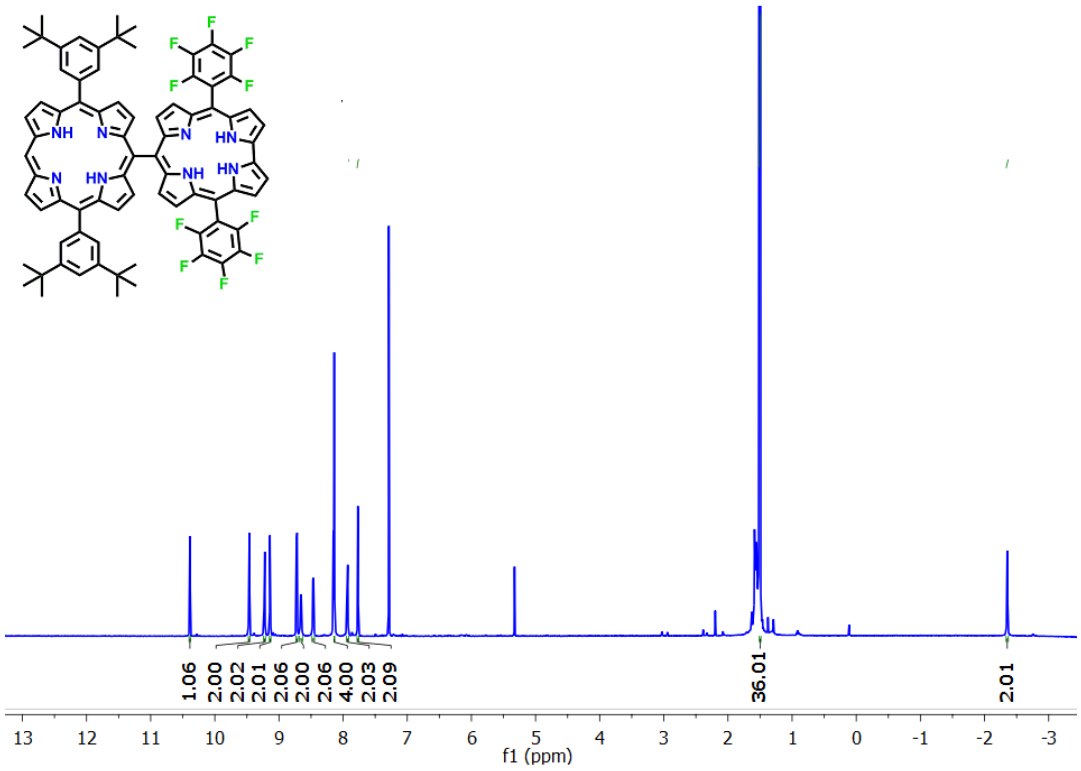

Fig. S11 ^{1}H-NMR spectra of dyad **5** in $CDCl_3$ at room temperature.

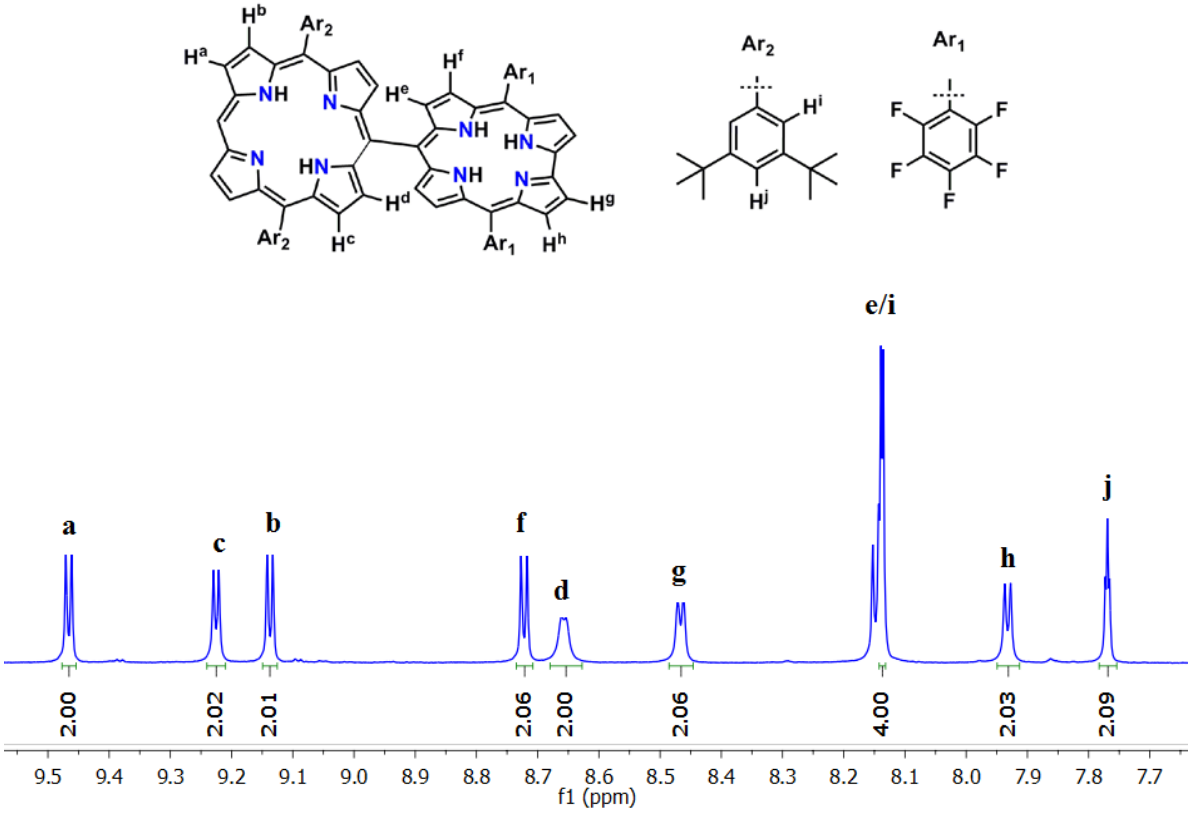

Fig.S12 ^{1}H-NMR spectra showing aromatic region of dyad **5** in $CDCl_3$ at room temperature.

3. Absorption Spectra

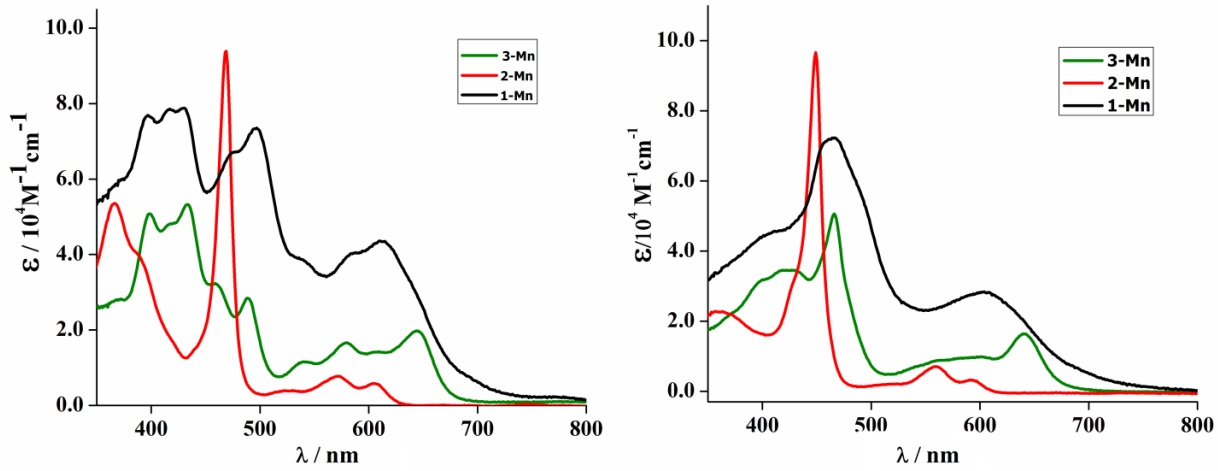

Fig.S13. UV-Vis spectra of **1-Mn**, **2-Mn** and **3-Mn** in THF (left) and DMF (right).

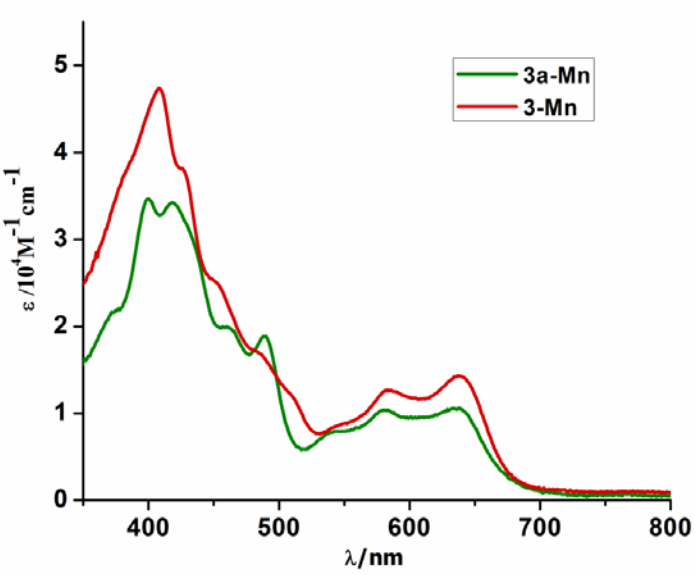

Fig.S14. Comparative absorption spectra of manganese corrole **3-Mn and 3a-Mn** in dichloromethane.

4. Electrochemical Studies

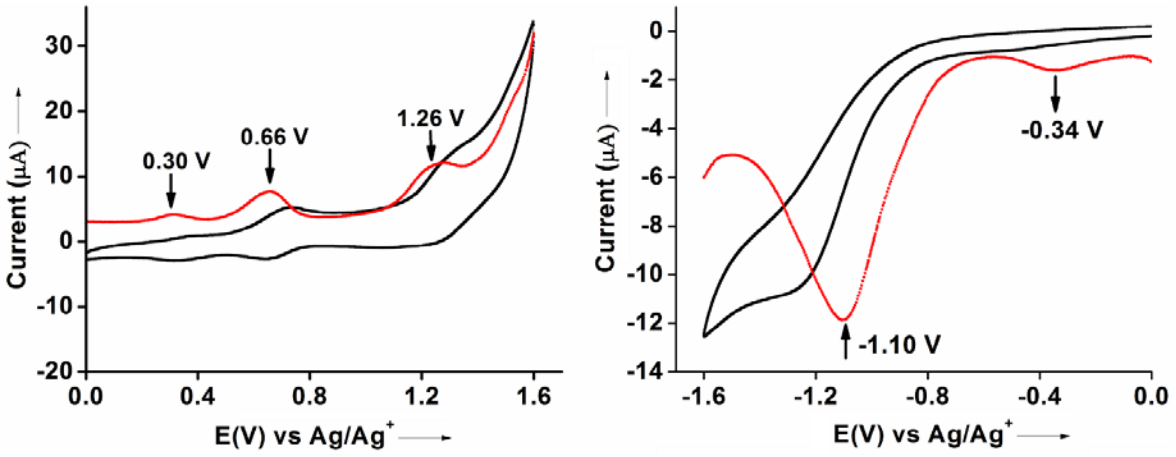

Fig.S15 Cyclic and differential pulse voltammograms of **1-Mn** in CH_2Cl_2. Scan rate 0.1 Vs^{-1}.

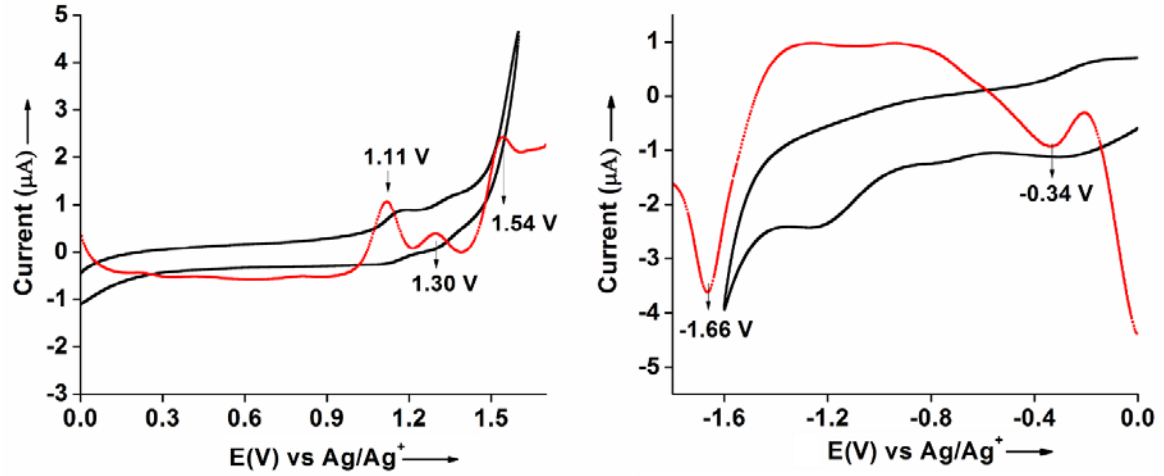

Fig.S16. Cyclic and differential pulse voltammogram of **2-Mn** triad in CH_2Cl_2. Scan rate 0.1 Vs^{-1}**.**

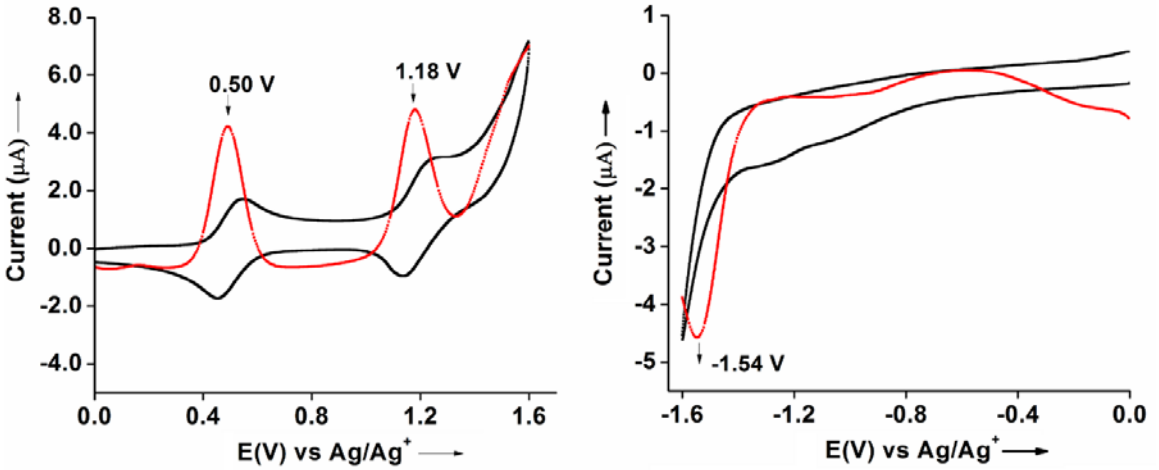

Fig.S17. Cyclic and differential pulse voltammogram of **3-Mn** triad in CH_2Cl_2. Scan rate 0.1 Vs^{-1}**.**

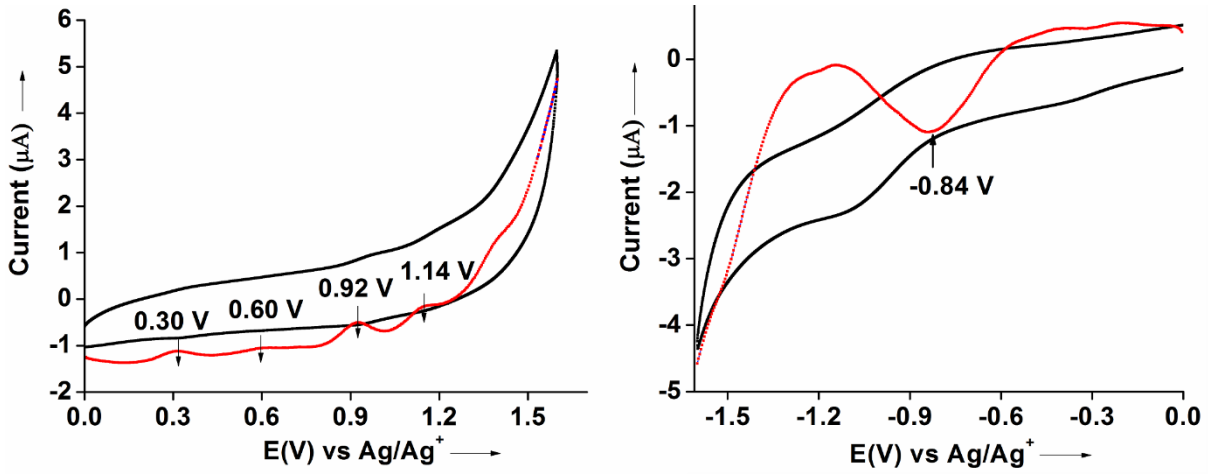

Fig.S18. Cyclic and differential pulse voltammogram of **4-Mn** in CH_2Cl_2. Scan rate 0.1 Vs^{-1}.

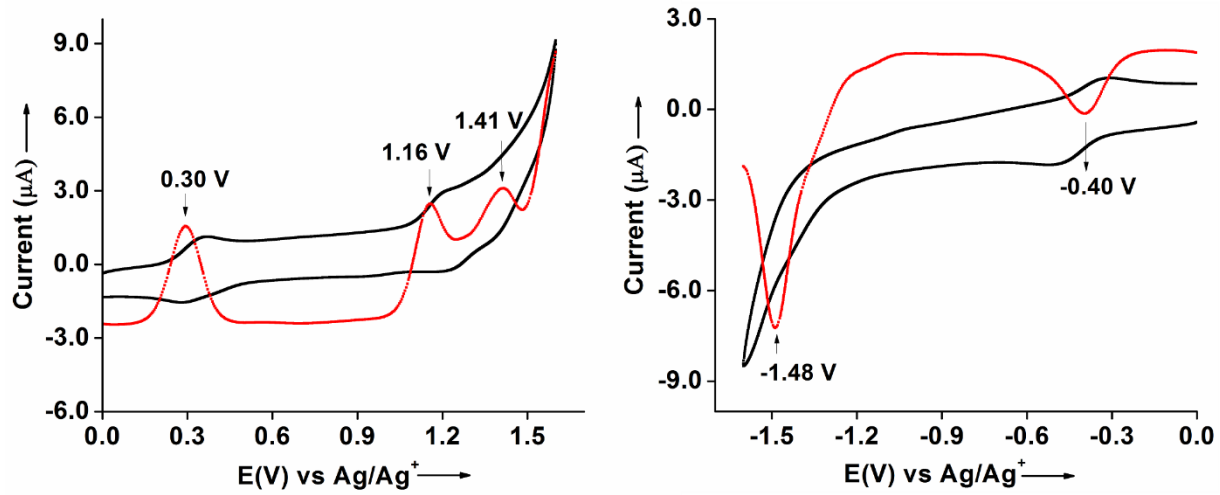

Fig.S19. Cyclic and differential pulse voltammogram of **5-Mn** in CH_2Cl_2. Scan rate 0.1 Vs^{-1}.

5. Catalytic Studies

Table S1: Styrene oxidation with reported catalysts.

Catalyst	Styrene oxide yield (%)
1-Mn	18
2-Mn	3
3-Mn	2
2 parts of **3-Mn**+ 1 part of **2-Mn**	3

Reaction conditions: Alkene (1.2 mmol), oxidant (1.2 mmol), catalyst (1.2 μmol), benzene (1 ml), room temperature, under open atmosphere. Yields are calculated by NMR of the crude reaction mixture after passing through short silica pad with reference to the internal standard added (1.2 mmol) in the reaction mixture after 1 hour of reaction. All reported yields are average of two runs. Other side products formed were negligible.

6. Single Crystal X-ray Diffraction Studies

Single crystal growth, data collection, and refinement details:

Single crystals of the compound **1**, **1-Mn** and **5-Mn** were grown from vapour diffusion of pentane in dichloromethane solvent at 4°C. The single crystals of **2-Mn** and **3a-Mn** were obtained from slow evaporation of dichloromethane-hexane mixture at 6°C and room temperature respectively. In all cases (except **2-Mn**), crystals are highly unstable at room temperature and have the tendency to rapidly desolvate (with complete loss of the crystallinity) outside the mother liquid at room temperature. In case of **1-Mn**, single crystal was very small and relatively weak for diffraction even after the high exposure of X-ray. Even after several attempts we could not obtain good quality single crystal for the **1-Mn**. A nearly similar observation was also experienced for **1**, **3a-Mn**, and **5-Mn**. Single crystal data of **1**, **1-Mn** and **5-Mn** were collected on the Bruker Smart APEX II diffractometer equipped with CCD detector using monochromated Mo Kα radiation (λ = 0.71073 Å). The Bruker D8 Venture (equipped with CMOS type PHOTON 100 detector) instrument with above set up was used for data collection of **2-Mn** and **3a-Mn** crystal. Unit cell measurement, data collection, integration, scaling and absorption corrections for the crystal were done using Bruker Apex II software.[1] Data reduction was done by Bruker SAINT suite.[2] The crystal structures were solved by SHELXT 2014[3] and refined by the full matrix least squares method using SHELXL 2018[4] present in the program suite WinGX (version 2014.1).[5] Absorption correction was applied using SADABS.[6] ORTEPs were generated using Mercury 3.5.1 (CCDC) program.[7]

In the crystal structures of **1**, **2-Mn**, **3a-Mn** and **5-Mn**, all non-hydrogen atoms were refined anisotropically and hydrogen atoms were positioned geometrically and refined isotropically using a riding model. For **1-Mn**, all atoms in the core macro-cycles (Corrole-Porphyrin-Corrole) were refined anisotropically and remaining atoms in the satellite phenyl rings attached to the macro-cycles have been treated with the isotropic structural model. For all the structures (Table S2), the refinements have converged to completion with the reasonable GOOF and residual electron densities (peak and hole) of the models.

Comments on individual structures

Structures of **1, 3a-Mn and 5-Mn**:

All of these structures consist a marginal quality of high angle intensity data which was reflected with few B level checkcif alerts. All such alerts have been responded with the valid reasons in their respective CIF (vrf) and can also be found below. The geometrical (SADI) and thermal (SIMU and DELU) restraints along with the rigid-bond restraints (RIGU) were used for the modelling those structures. Furthermore, noticeable void space was found in all structures in which the highly disordered guest solvent molecules (used for crystallization) could not be modelled reliably and for that reason diffuse electron densities corresponding to them were removed by either solvent masking (for **1** only) [8] or PLATON_SQUEEZE program.[9] The crystal structure of **5-Mn** was successfully modelled with the two dichloromethane and one pentane molecule in the asymmetric unit. The details of a SQUEEZE calculations (.fab file) are implemented in individual CIFs.

Structure of **2-Mn:**

The structure consists of very good diffraction data. Two dichloromethane guest solvents were reliably modelled in the asymmetric unit with the restraints on geometrical (SADI) and displacement parameters (SIMU). The remaining smeared electron density was removed using PLATON_SQUEEZE as mentioned in the CIF.

Structure of **1-Mn:**

As mentioned above after the multiple trials we managed to grow poor quality of very small single crystals for this compound, which was weakly diffracting. Few scans were also rejected during integration and scaling due to very weak high angle intensity spots. All alerts (Level A and B) related to them are responded below. Nevertheless, the structure was determined successfully and refined with the SADI, SIMU, DELU and rigid phenyl group restraints as the lack of data-to-parameter ratio for the same. The disordered solvent molecules in the void could not be modelled reasonably and hence the density contribution of the disordered solvent molecules was removed by PLATON_SQUEEZE. The details of SQUEEZE calculations are appended in the CIF.

Table S2: Crystallographic and refinement parameters

Identification code	**1**	**1-Mn**	**2-Mn**	**3a-Mn**	**5-Mn**
Empirical formula	C110 H74 F20 N12 [+Solvent]	C116 H24 Cl F20 Mn3 N14 O2 [+Solvent]	C50 H56 Cl5 Mn N4 [+Solvent]	C52 H48 F8 Mn N7 O [+Solvent]	C165 H134 Cl8 F20 Mn4 N16 [+Solvent]
CCDC No.	1542167	1542168	1542170	1542171	1836584
Formula weight	1943.81	2225.76	945.17	993.91	3224.23
Temperature	100(2) K	100(2) K	100(2) K	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	*P* -1	*P* -1	*P* -1	*P* 2_1/c	*P* -1
Unit cell dimensions (Å, °)	a = 9.1938(13) b = 13.590(2) c = 20.704(3) α= 86.135(8) β= 83.839(9) γ= 89.382(9)	a = 15.367(3) b = 21.799(5) c = 22.853(5) α = 115.178(15) β= 98.215(15) γ = 99.367(15)	a = 10.8862(10) b = 11.5102(11) c = 21.0990(19) α = 99.770(3) β= 104.842(3) γ = 100.808(3)	a = 14.337(5) b = 40.294(14) c = 8.732(3) α = 90 β= 105.150(8) γ = 90	a = 13.9093(6) b = 24.1335(10) c = 27.9860(11) α = 113.583(2) β= 93.214(3) γ = 102.331(3)
Volume ($Å^3$)	2566.0(6)	6640(3)	2443.3(4)	4869(3)	8305.4(6)
Z	1	2	2	4	2
Density (cal.) (Mg/m^3)	1.258	1.113	1.285	1.356	1.289
Absorption coefficient (mm^{-1})	0.100	0.375	0.581	0.347	0.502
F(000)	998	2212	988	2056	3304
Crystal size (mm^3)	0.200 x 0.120 x 0.060	0.240 x 0.140 x 0.060	0.350 x 0.240 x 0.10	0.270 x 0.140 x 0.080	0.360 x 0.190 x 0.120
Theta range for data collection	1.744 to 26.371°.	1.014 to 25.000°.	2.313 to 29.573°.	2.469 to 27.970°.	1.484 to 25.000°.
Index ranges	-10<=h<=11, -16<=k<=14, -24<=l<=25	-17<=h<=18, -25<=k<=20, -19<=l<=27	-15<=h<=15, -15<=k<=15, -29<=l<=29	-18<=h<=18, -47<=k<=53, -11<=l<=11	-16<=h<=14, -28<=k<=28, -30<=l<=33
Reflections collected	19619	45878	82221	52911	108215
Independent reflections	9806 [R(int) = 0.1516]	19304 [R(int) = 0.1991]	13678 [R(int) = 0.0436]	11664 [R(int) = 0.3375]	28361 [R(int) = 0.1087]
Completeness to theta	94.1 %	82.5 %	99.9 %	99.8 %	96.9 %
Data / restraints / parameters	9806 / 24/ 650	19304 / 1584 / 934	13678 / 66 / 575	11664 / 0 / 622	28361 / 3733 / 1822
Goodness-of-fit	0.951	1.094	1.033	1.015	1.159
Final R indices [I>2sigma(I)]	R1 = 0.1099, wR2 = 0.2488	R1 = 0.1928, wR2 = 0.4630	R1 = 0.0396, wR2 = 0.0894	R1 = 0.1353, wR2 = 0.2562	R1 = 0.1355, wR2 = 0.3560
R indices (all data)	R1 = 0.2545, wR2 = 0.3272	R1 = 0.4196, wR2 = 0.5346	R1 = 0.0548, wR2 = 0.0962	R1 = 0.3469, wR2 = 0.3339	R1 = 0.2666, wR2 = 0.4236
Largest diff. peak and hole ($e.Å^{-3}$)	0.476 and -0.346	1.186 and -0.554	0.777 and -0.732	0.423 and -0.612	1.558 and -1.077

Crystallographic Alerts Level A and B from CheckCIF with the Author Responses

Datablock: freebase (1)

Alert level B PLAT026_ALERT_3_B Ratio Observed / Unique Reflections (too) Low .. 34%

Author Response: The crystal data and many others from this class of complexes were poorly diffracting crystals beyond certain resolution limit. Some redundant reflections were omitted from reciprocal lattice before integration.

PLAT029_ALERT_3_B _diffrn_measured_fraction_theta_full value Low . 0.941

Author Response: Incomplete coverage of diffraction patterns and some data was rejected as poor during integration and scaling.

PLAT340_ALERT_3_B Low Bond Precision on C-C Bonds ..... 0.01083 Ang.

Author Response: Limited resolution and relatively imprecise diffraction data from challenging crystal.

PLAT416_ALERT_2_B Short Intra D-H..H-D H1...H2 . 1.53 Ang. x,y,z = 1_555 Check

Author Response: Not uncommon for free base corrole (triprotic ligand) macrocycle. For that H...H repulsion, one pyrrole ring is distorted from macrocycle plane. Also, the unresolved thermal disorder can affect the H...H distances.

PLAT416_ALERT_2_B Short Intra D-H..H-D H1...H4 . 1.61 Ang. x,y,z = 1_555 Check

Author Response: Not uncommon for free base corrole (triprotic ligand) macrocycle. For that H...H repulsion, one pyrrole ring is distorted from macrocycle plane. Also, the unresolved thermal disorder can affect the H...H distances.

Datablock: JRMNCPC (1-Mn)

Alert level A PLAT026_ALERT_3_A Ratio Observed / Unique Reflections (too) Low .. 22%

Author Response: Crystals were relatively small and weakly-diffracting, hence not all high angle reflections were observed. Few junk reflections were also removed using R-LATT.

PLAT029_ALERT_3_A _diffrn_measured_fraction_theta_full value Low . 0.825

Author Response: Few scans were removed during integration due to very low intensity of diffraction patterns beyond certain resolution limit.

PLAT084_ALERT_3_A High wR2 Value (i.e. > 0.25) 0.53

Author Response: Lack of the crystal quality for this family of compounds. Weakly diffracting crystals. Only core atoms of the macrocycles were treated anisotropically.

PLAT201_ALERT_2_A Isotropic non-H Atoms in Main Residue(s) 82

Author Response: Lack of data quality for challenging sample. Only core atoms of the macrocycles were treated anisotropically.

RINTA01_ALERT_3_B The value of Rint is greater than 0.18 Rint given 0.199

Author Response: Lack of the crystal quality for this class of compounds. Weakly diffracting crystals.

PLAT020_ALERT_3_B The Value of Rint is Greater Than 0.12 ..... 0.199

Author Response: Lack of the crystal quality for this class of compounds. Weakly diffracting crystals.

PLAT082_ALERT_2_B High R1 Value 0.19

Author Response: Lack of the crystal quality for this class of compounds. Weakly diffracting crystals.

PLAT220_ALERT_2_B Non-Solvent Resd 1 C Ueq(max)/Ueq(min) Range 10.0 Ratio Author Response: Unresolvable disorder due to limited resolution of crystals data.

PLAT242_ALERT_2_B Low 'MainMol' Ueq as Compared to Neighbors of C22

Author Response: This is due to the substantial disorder and could not be resolved because of low data quality.

PLAT242_ALERT_2_B Low 'MainMol' Ueq as Compared to Neighbors of C104

Author Response: This is due to the substantial disorder and could not be resolved because of low data quality.

PLAT315_ALERT_2_B Singly Bonded Carbon Detected (H-atoms Missing). C28

PLAT315_ALERT_2_B Singly Bonded Carbon Detected (H-atoms Missing). C29
PLAT315_ALERT_2_B Singly Bonded Carbon Detected (H-atoms Missing). C30
PLAT315_ALERT_2_B Singly Bonded Carbon Detected (H-atoms Missing). C32
PLAT315_ALERT_2_B Singly Bonded Carbon Detected (H-atoms Missing). C33
PLAT315_ALERT_2_B Singly Bonded Carbon Detected (H-atoms Missing). C34
PLAT315_ALERT_2_B Singly Bonded Carbon Detected (H-atoms Missing). C42
PLAT315_ALERT_2_B Singly Bonded Carbon Detected (H-atoms Missing). C43
PLAT315_ALERT_2_B Singly Bonded Carbon Detected (H-atoms Missing). C44
PLAT315_ALERT_2_B Singly Bonded Carbon Detected (H-atoms Missing). C46

PLAT315_ALERT_2_B Singly Bonded Carbon Detected (H-atoms Missing). C47
PLAT315_ALERT_2_B Singly Bonded Carbon Detected (H-atoms Missing). C48
PLAT315_ALERT_2_B Singly Bonded Carbon Detected (H-atoms Missing). C111
PLAT315_ALERT_2_B Singly Bonded Carbon Detected (H-atoms Missing). C112
PLAT315_ALERT_2_B Singly Bonded Carbon Detected (H-atoms Missing). C114
PLAT315_ALERT_2_B Singly Bonded Carbon Detected (H-atoms Missing). C115

Author Response: Few atoms were refined isotropically and hence hydrogen cannot be fixed.

PLAT341_ALERT_3_B Low Bond Precision on C-C Bonds ..... 0.03366 Ang.

Author Response: Limited data quality for challenging crystals.

PLAT369_ALERT_2_B Long C(sp2)-C(sp2) Bond C1 - C21 . 1.62 Ang.

Author Response: A consequence of high thermal disorder.

PLAT911_ALERT_3_B Missing FCF Refl Between Thmin & STh/L= 0.595 4100

Author Response: Incomplete coverage of diffraction pattern for all scans and some data rejected because of poor intensity during integration and scaling. Some reflections can be blocked by the beam stop.

PLAT934_ALERT_3_B Number of (Iobs-Icalc)/SigmaW > 10 Outliers 6

Author Response: A consequence of weak crystallinity of the sample. Different weighting scheme of SHELX and PLATON also can lead to some differences.

PLAT973_ALERT_2_B Check Calcd Positive Resid. Density on Mn1 1.60 eA-3

Author Response: There is no chemically sensible species corresponding to this residual density peak. It can be consequence of thermal restraints in the refinement.

Datablock: mnpor (2-Mn)

ABSMU01_ALERT_1_B The ratio of given/expected absorption coefficient lies outside the range 0.95 <> 1.05 Calculated value of mu = 0.637 Value of mu given = 0.581

Author Response: SQUEEZE was applied to remove density contributions of poorly behaved guest solvents.

Datablock: JRMNCOR (3a-Mn)

RINTA01_ALERT_3_A The value of Rint is greater than 0.25 Rint given 0.338

Author Response: The crystal was very small and weakly diffracting even after prolonged exposure time from challenging sample (crystallinity issue). However, the structure was determined and refined properly.

PLAT020_ALERT_3_A The Value of Rint is Greater Than 0.12 ..... 0.338

Author Response: The crystal was very small and weakly diffracting evenafter prolonged exposure time from challenging sample (crystallinity issue). However, the structure was determined and refined properly.

PLAT026_ALERT_3_B Ratio Observed / Unique Reflections (too) Low .. 33% Check

Author Response: The crystal data and many others from this class of complexes were poorly diffracting crystals beyond certain resolution limit. Few scans were removed from reciprocal lattice before integration.

PLAT230_ALERT_2_B Hirshfeld Test Diff for N7 --C3 . 7.5 s.u.

Author Response: Marginal data quality from very small weakly diffracting crystal.

PLAT413_ALERT_2_B Short Inter XH3 .. XHn H49C ..H51A . 1.93 Ang. -1+x,y,-1+z = 1_454 Check

Author Response: Possibly unresolved thermal disorder.

Datablock: mndiad (5-Mn)

PLAT026_ALERT_3_B Ratio Observed / Unique Reflections (too) Low.. 39%

Author Response: Few scans were removed during data integration because of very low diffraction intensity.

PLAT084_ALERT_3_B High wR2 Value (i.e. > 0.25) 0.42

Author Response: Weakly diffracting crystal leading to relatively poor data of challenging sample.

PLAT341_ALERT_3_B Low Bond Precision on C-C Bonds ..... 0.01719 Ang.

Author Response: Thermal restraints were employed in refinement to treat weak data for a better structural model.

PLAT934_ALERT_3_B Number of (Iobs-Icalc)/SigmaW > 10 Outliers 2

Author Response: A consequence of weak crystallinity of the sample. Different weighting scheme of SHELX and PLATON also can lead to some differences.

7. References

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