Supplemental Information

Inter-ligand intra-molecular through-space anisotropic shielding in a series of manganese carbonyl phosphorous compounds

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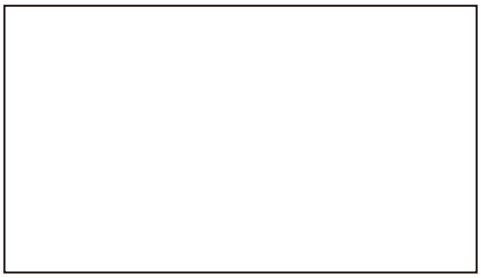
Contents:



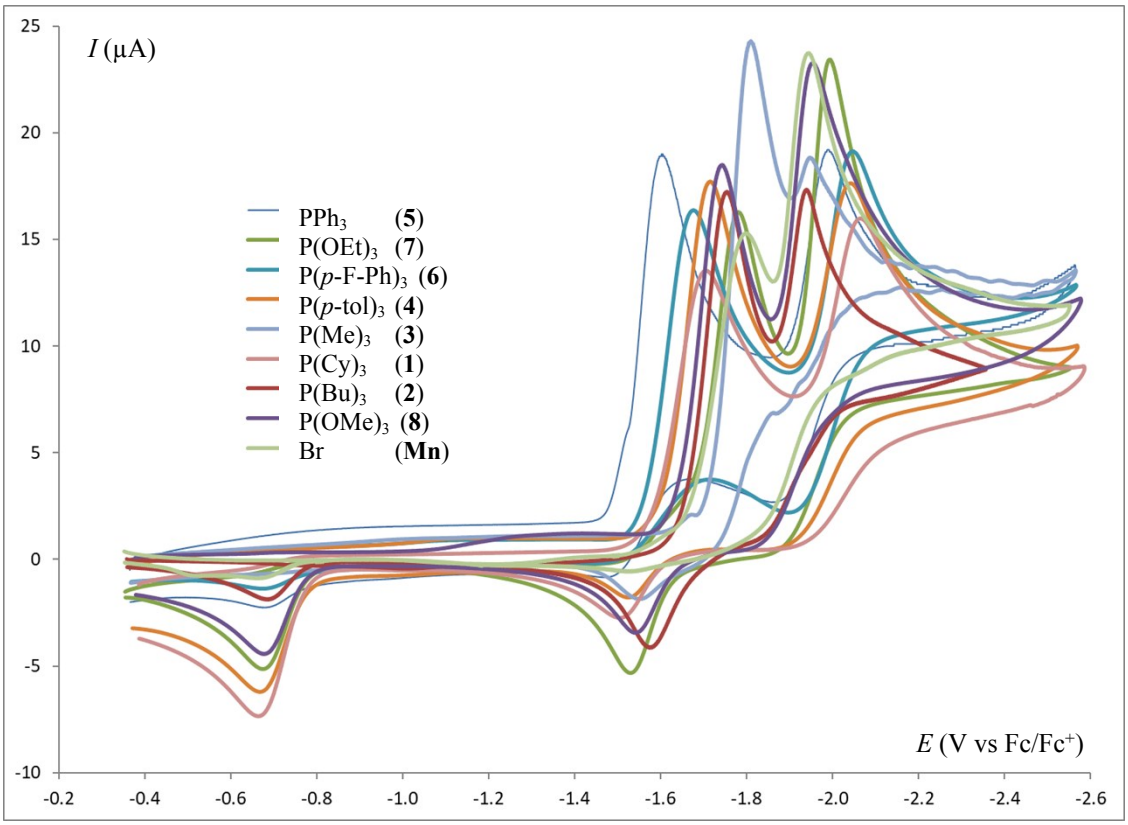


Figure SI-1: Overlaid Cyclic Voltammograms (CV) of 1.00 mM of compounds **Mn, 1 – 8** at 0.100 V/s. All CV collected upon a 3.00 mm glassy carbon electrode, in dry acetonitrile containing 0.100 M Bu_4NPF_6 under an argon atmosphere.

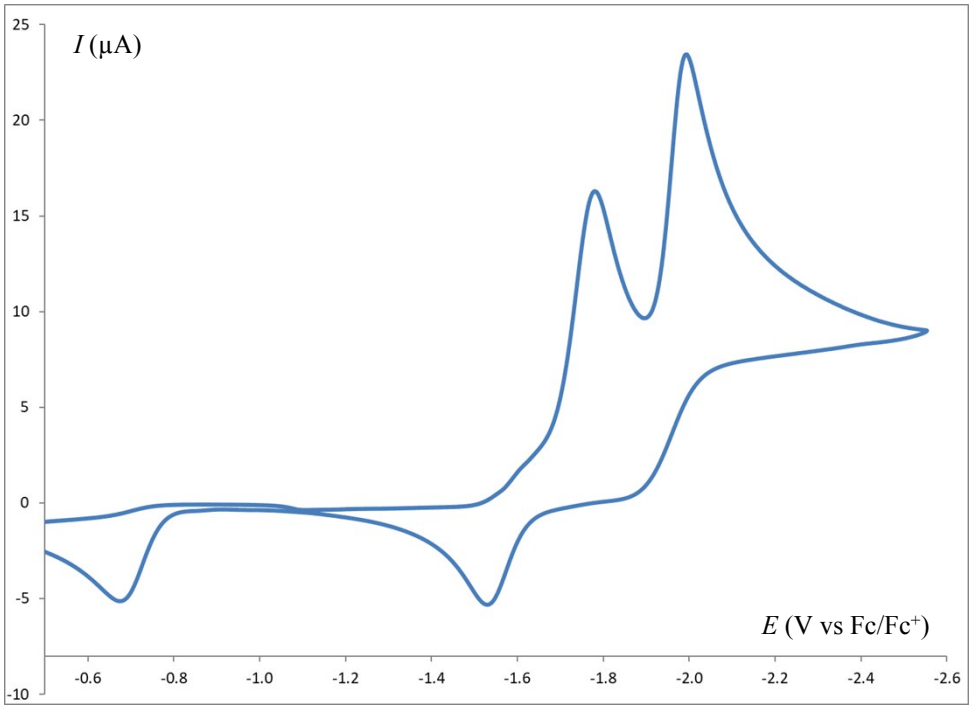


Figure SI-2: CV of 1.00 mM of compound **7** at 0.100 V/s upon a 3.00 mm glassy carbon electrode, in dry acetonitrile containing 0.100 M Bu_4NPF_6 under an argon atmosphere.

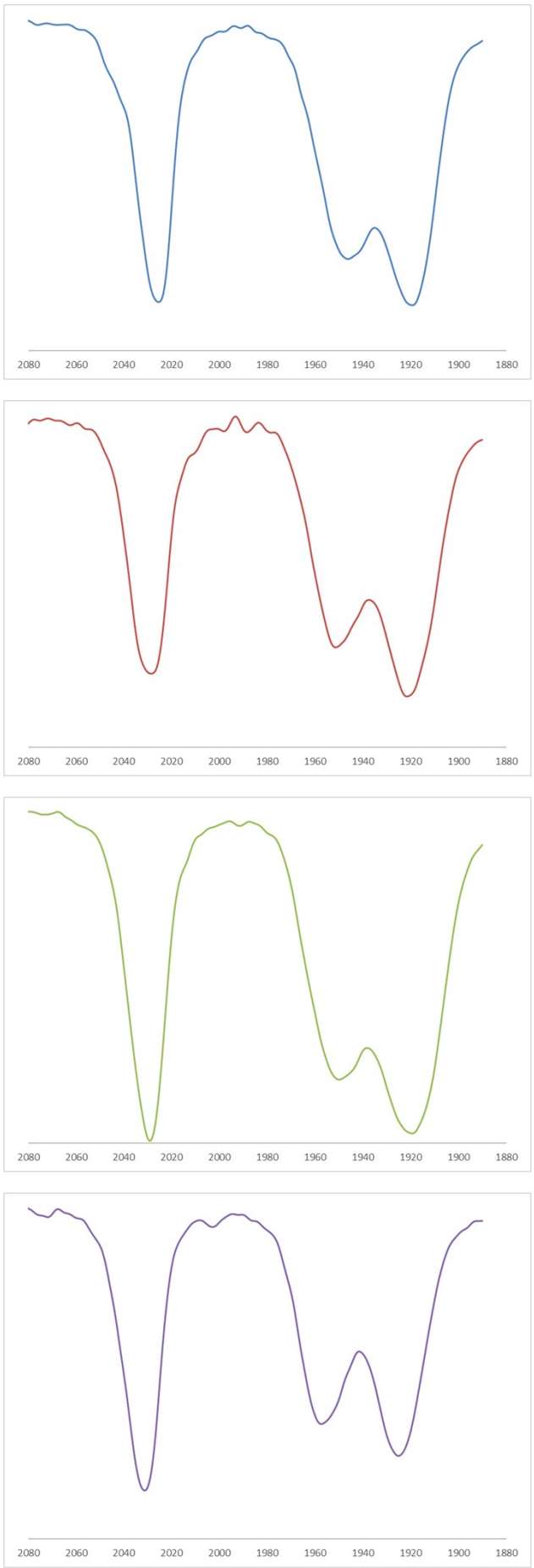


Figure SI-3. Carbonyl region IR spectra (cm^{-1}) of compounds **1** – **4** collected in acetonitrile.

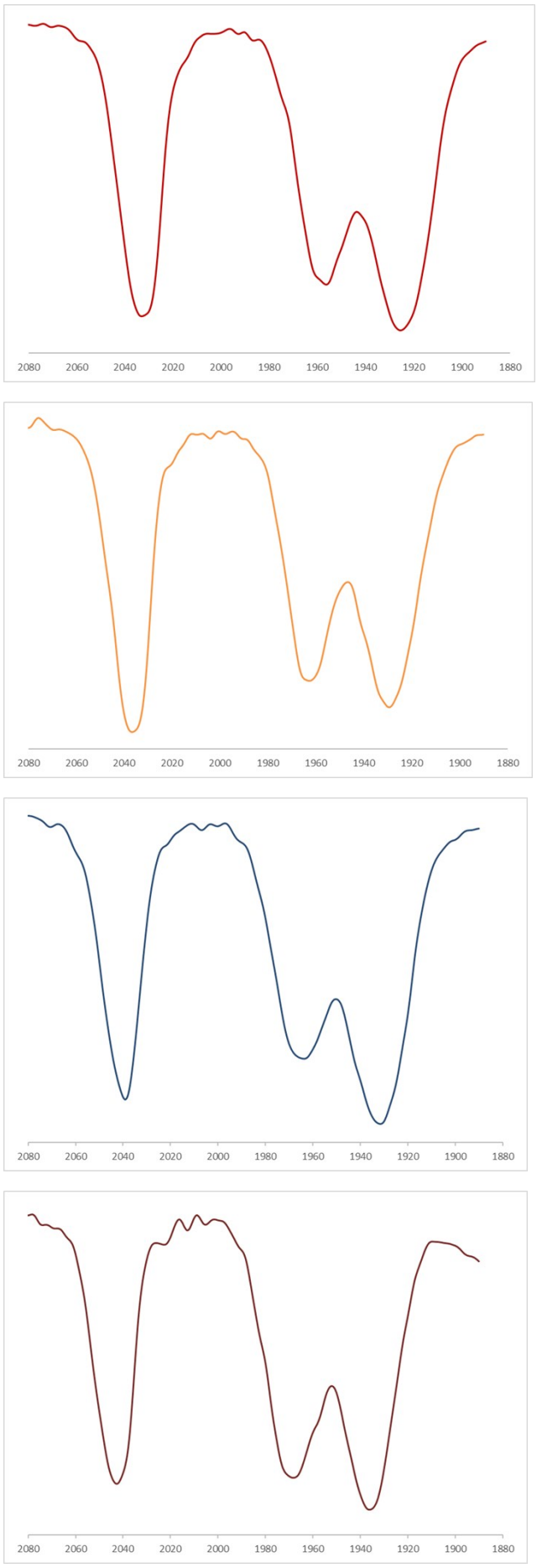


Figure SI-4. Carbonyl region IR spectra (cm^{-1}) of compounds **5** – **8** collected in acetonitrile.

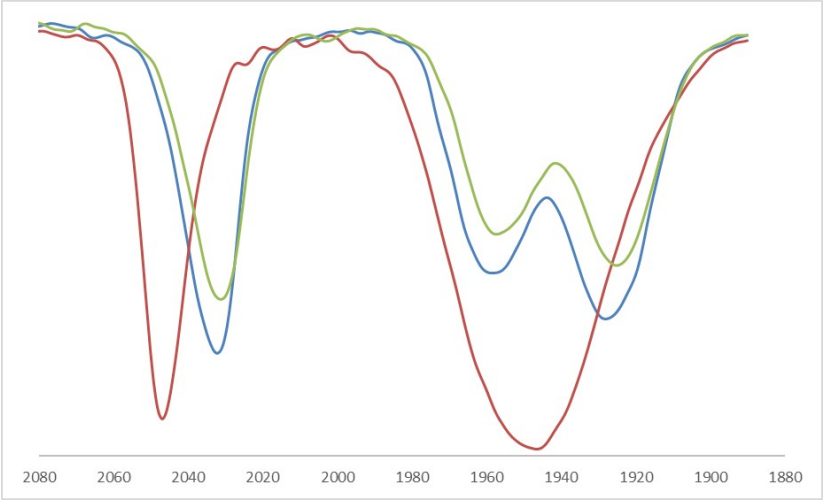
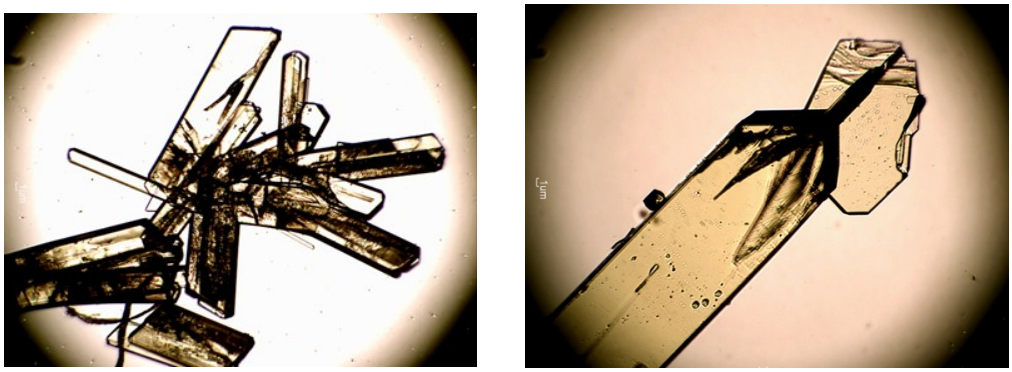


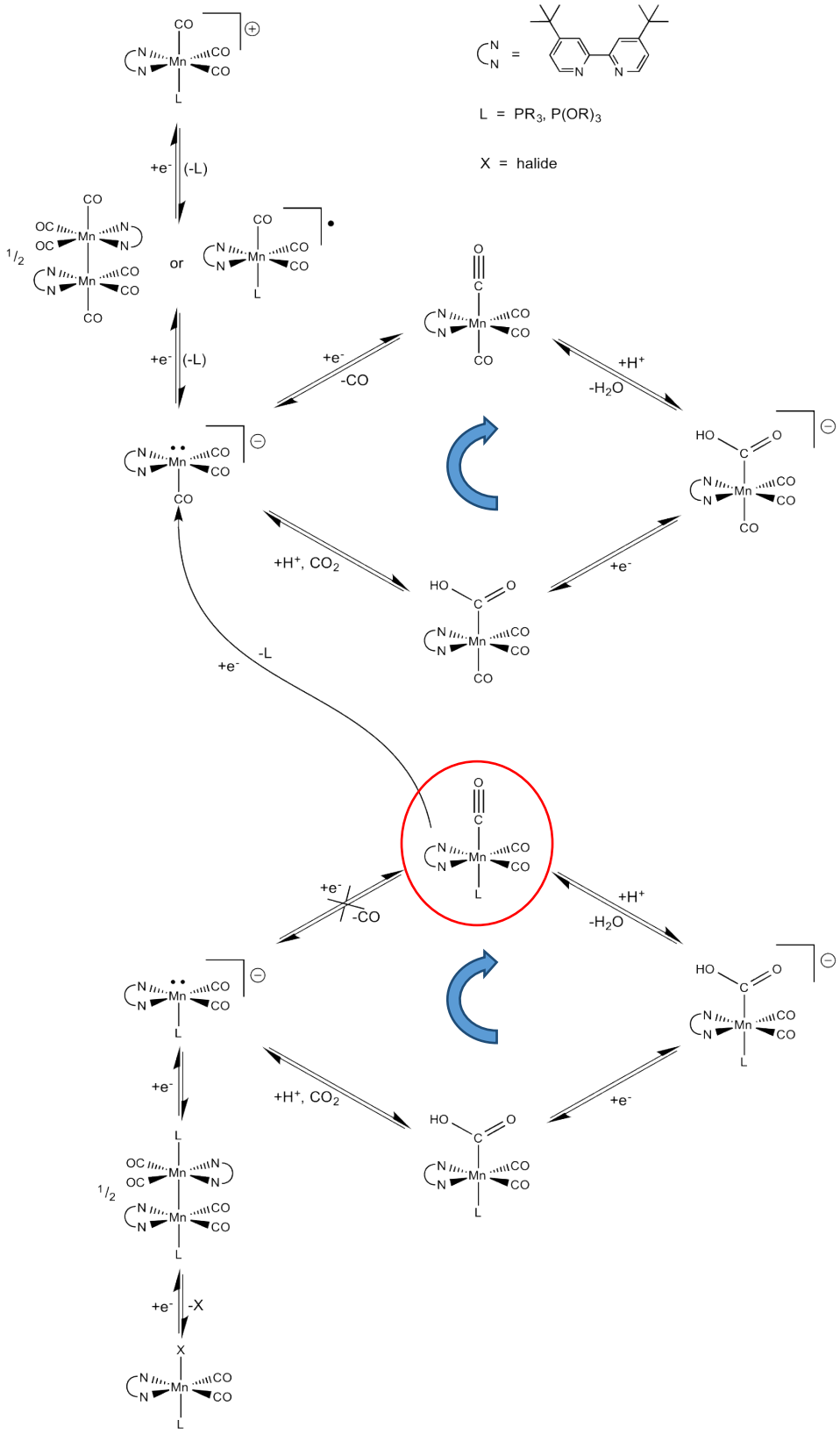
Figure SI-5. Carbonyl region IR spectra (cm^{-1}) of compounds MnOTf(bpy)$(CO)_3$ (red), [Mn(bpy)$(CO)_3$(P(*p*-tol)$_3$)]OTf (blue) and compound **4**, [Mn(*t*Bu-bpy)$(CO)_3$(P(*p*-tol)$_3$)]OTf (green), collected in acetonitrile

Materials/reagents

All the reagents were used as received from the following: tetrabutylammonium hexafluorophosphate ($TBAPF_6$, Sigma-Aldrich), rhenium pentacarbonyl chloride ($ReCl(CO)_5Br$, Acros Organics), manganese pentacarbonyl bromide ($MnBr(CO)_5$, Alfa Aesar), silver trifluromethanesulfonate (AgOTf, Alfa Aesar), 2,2'-bipyridine (bpy, Fluka), 4,4'-di-*tert*-butyl-2,2'-bipyridine (bpy-tBu, Sigma Aldrich), tricyclohexylphosphine (PCy_3, Alfa Aesar), tributylphosphine (PBu_3, City Chemical), trimethylphosphine (PMe_3, Sigma-Aldrich), tri(*para*-tolyl)phosphine (P(*p*-tol)$_3$, Alfa Aesar), triphenylphosphine (PPh_3, Alfa Aesar), tris(*para*-fluoro-phenyl)phosphine (P(*p*-F-Ph)$_3$, Alfa Aesar), triethyl phosphite ($P(OEt)_3$, Alfa Aesar), trimethyl phosphite ($P(OMe)_3$, Alfa Aesar), tetrahydrofuran (THF, Alfa Aesar), dichloromethane (DCM, Alfa Aesar), diethyl ether (EMD), methanol (MeOH, BDH), acetone (BDH), n-pentane (Alfa Aesar), ammonium hexafluorophosphate (NH_4PF_6, Alfa Aesar).
Elemental Analysis carried by Atlantic Microlab, Inc (Norcross, GA)



Crystals of **6**, [Mn(bpy-tBu)$(CO)_3$P(*p*-F-Ph)$_3$]OTf (left), and **3**, [Mn(bpy-tBu)$(CO)_3$(PMe)$_3$]OTf (right) under a microscope. Crystals were grown at room temperature, by vapor diffusion of pentane into a solution of the compound in acetone.



Scheme SI-1. Proposed mechanism for complexes **1** – **8** of the type [Mn(*t*Bu-bpy)(CO)$_3$L]$^+$ studied. Evidence suggests ligand, L, dissociation after first or second reduction produces tricarbonyl anionic active species, identical to electrochemical reductive product (active catalyst) of bromide analog (**Mn**). Bottom cycle is desired mechanism. The carbonyl intermediate in the bottom cycle (in red circle), L dissociates, such that we revert to the top cycle. This is supported by similar electrochemistry and catalytic activity under cyclic voltammetric conditions of compounds **1** – **8** to the parent compound **Mn**.

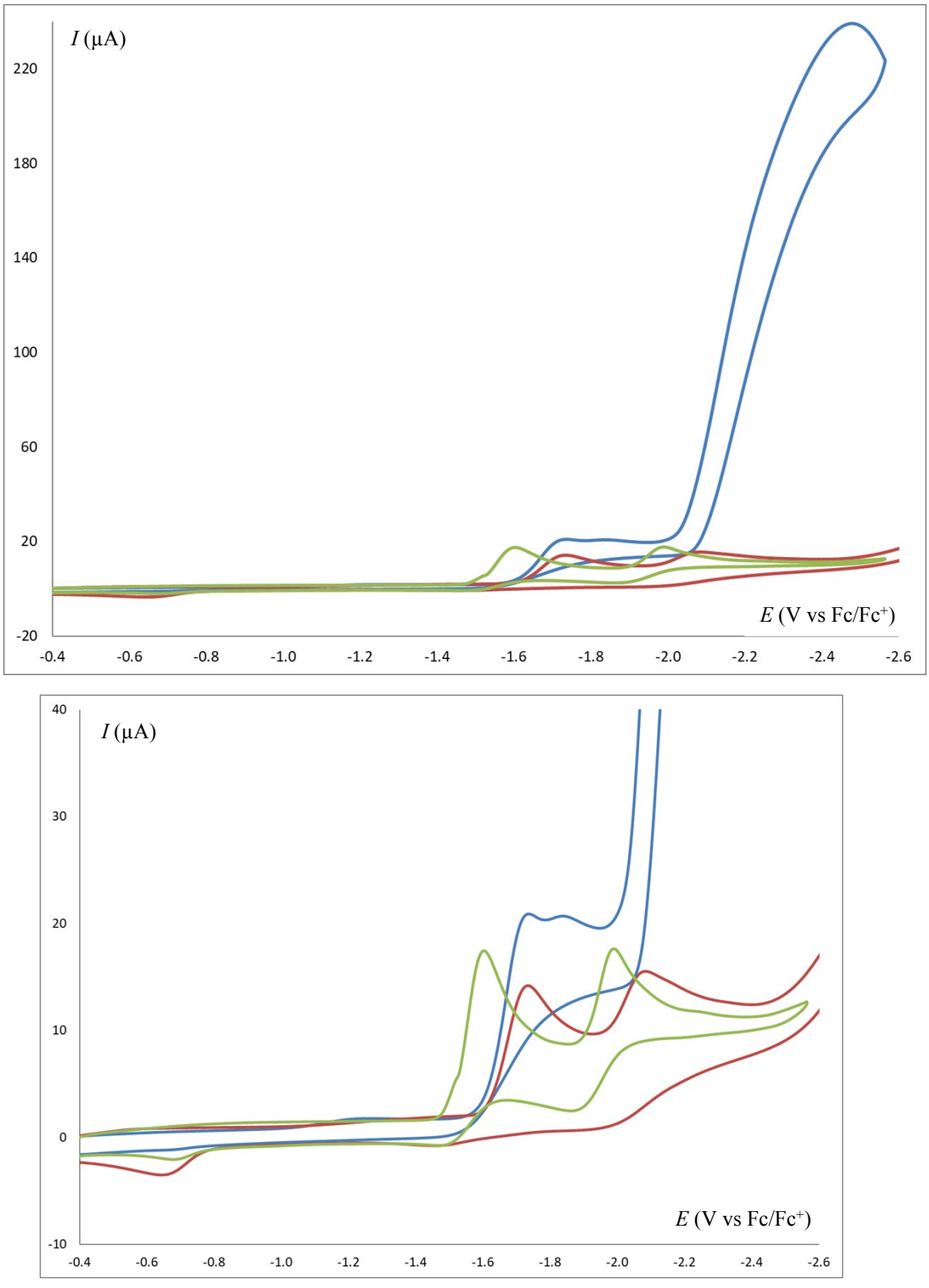


Figure SI-6. CV of Compound **5** under Ar (green), CO_2 (red) and CO_2 /2.47M MeOH. Collected in 0.100 M Bu_4NPF_6 anhydrous acetonitrile at 0.100 V/s on a 3.00 mm diameter glassy carbon working electrode.
Note: Bottom figure is re-scaled to highlight lower portion of bottom figure.

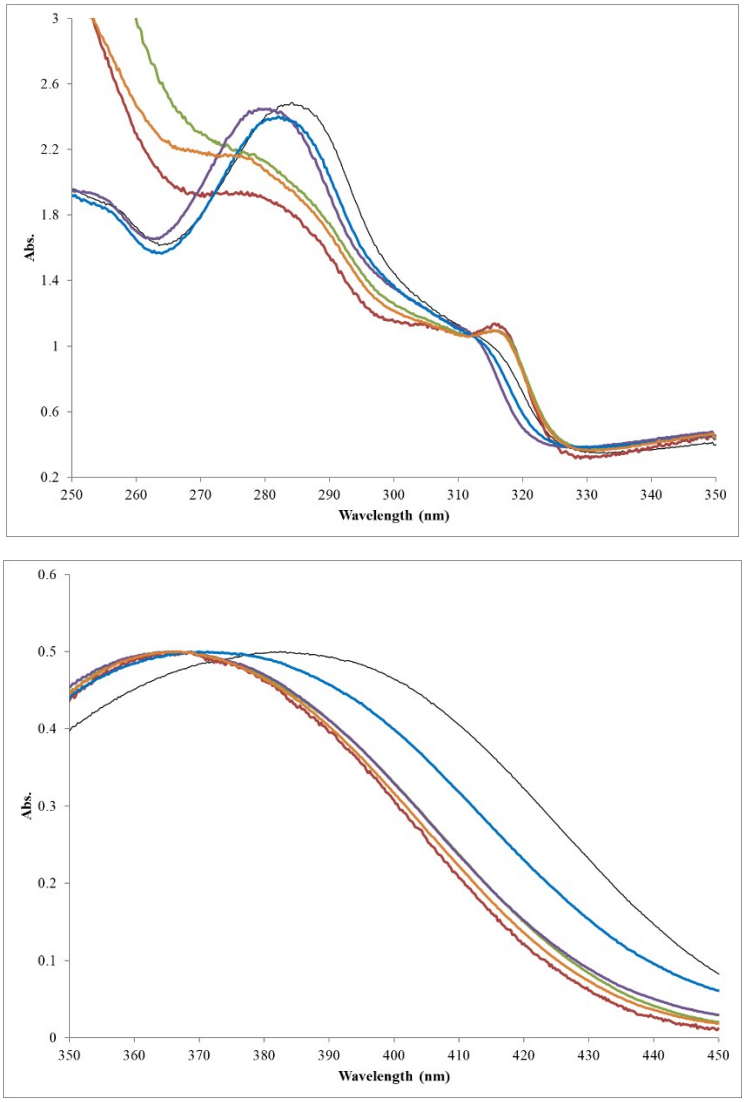


Figure SI-7a: UV/Vis absorption spectra for aliphatic phosphine compounds **1** (black), **2** (blue) and **3** (purple), and aromatic phosphine compounds **4** (green), **5** (orange) and **6** (red), in 0.12 mM in acetonitrile.

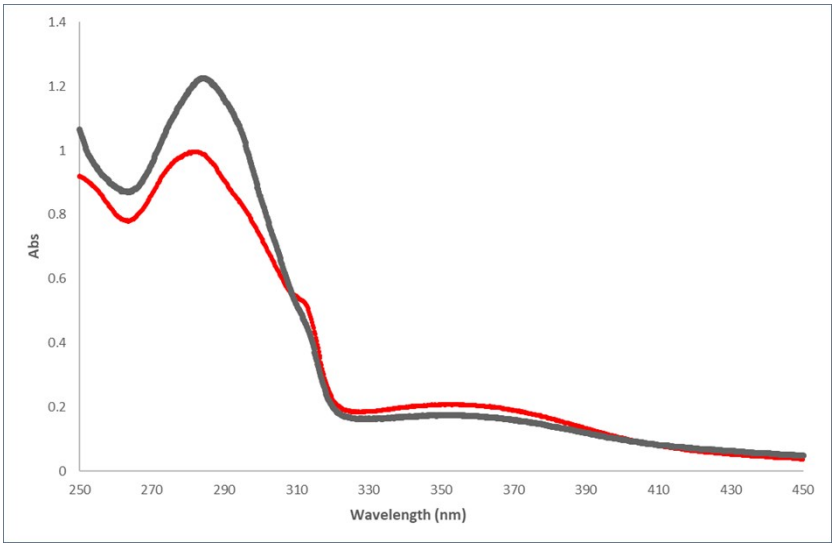


Figure SI-7b: Overlaid UV/Vis absorption spectra for phosphite compounds **7** (grey) and **8** (red), in 0.060 mM in acetonitrile.

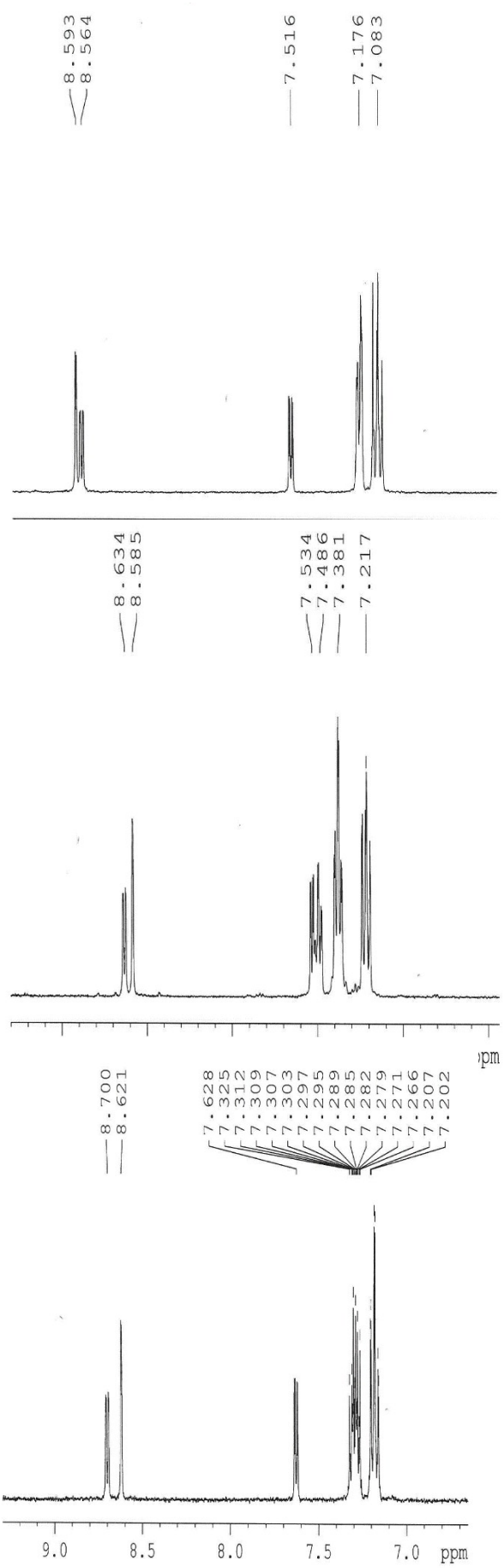


Figure SI-8. ^{1}H-NMR spectra (400 MHz, acetone-*d*6) of aromatic protons in compounds **4** (top), **5** (middle) and **6** (bottom).

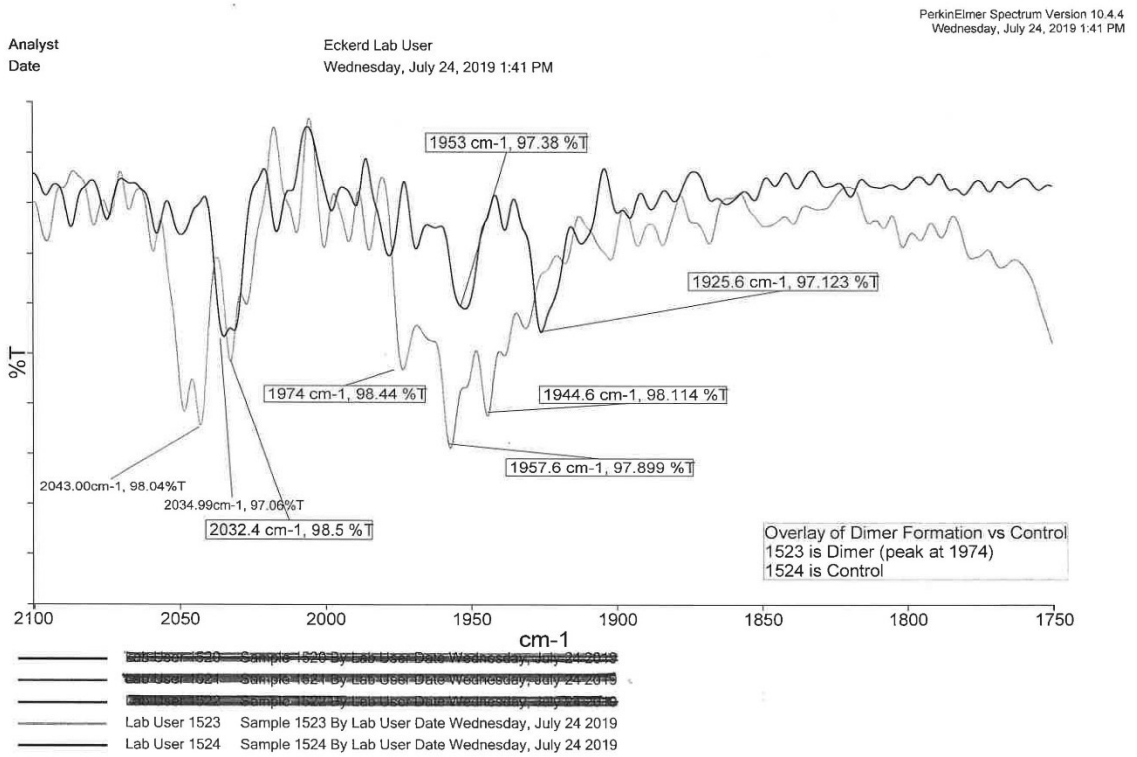
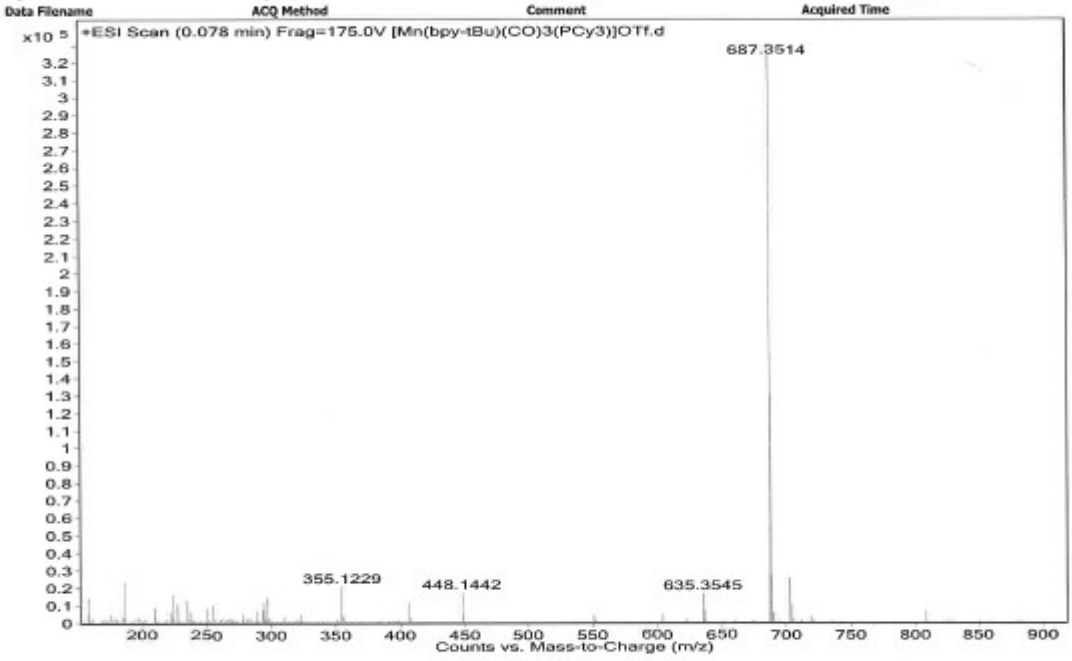


Figure SI-9: Overlaid carbonyl region IR spectra of 1.00 mM Compound **5** after bulk electrolysis at -1.60 V vs Fc/Fc^+ in dry acetonitrile containing 0.050 M Bu_4NPF_6 under an argon atmosphere (grey trace), after solvent removal. Control is compound **5** dry mixed with Bu_4NPF_6 in a 1:50 ratio (black trace). Presence of more peaks, particularly at 1974 cm^{-1}, is evidence of dimer formation (broadly matching Figure 4 of citation 6: *Inorg. Chem.* 52 (2013) 2484-2491). Additionally, the solution turned from yellow to purple-red during bulk electrolysis, with the "dimer" product appearing red upon drying, similar to colors described in citation 5: *Angew. Chem. Int. Ed.* 50 (2011) 9903-9906.

Sample Name	**Position**	**Instrument Name**	**User Name**
Inj Vol	**InjPosition**	**SampleType**	**IRM Calibration Status**
Data Filename	**ACQ Method**	**Comment**	**Acquired Time**



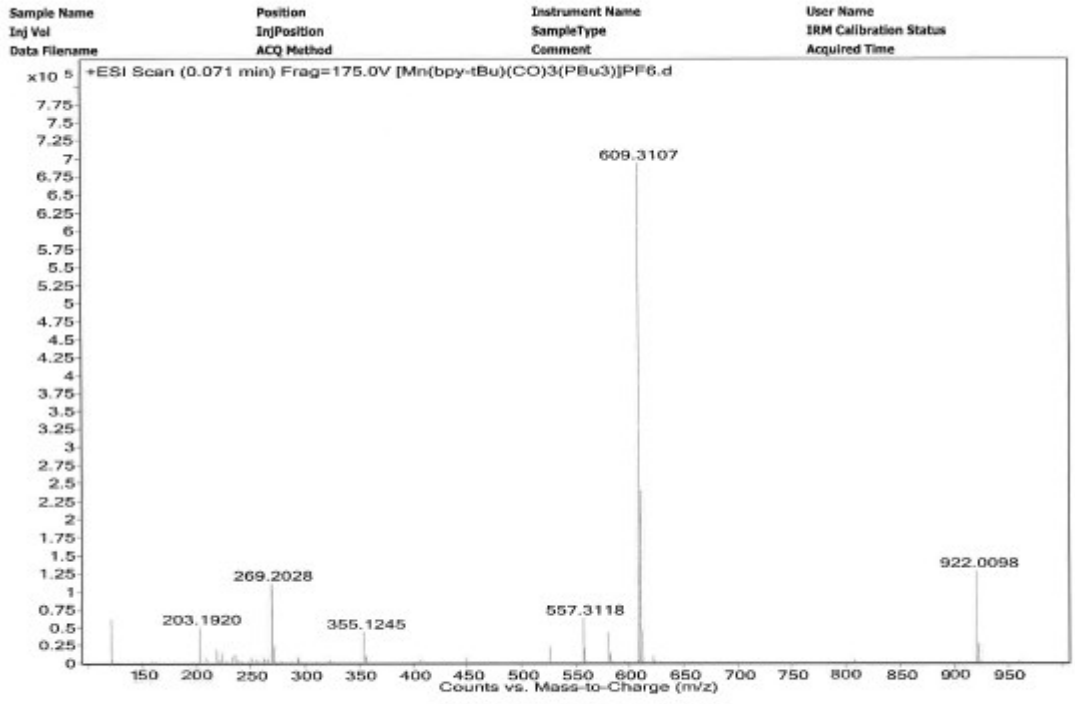
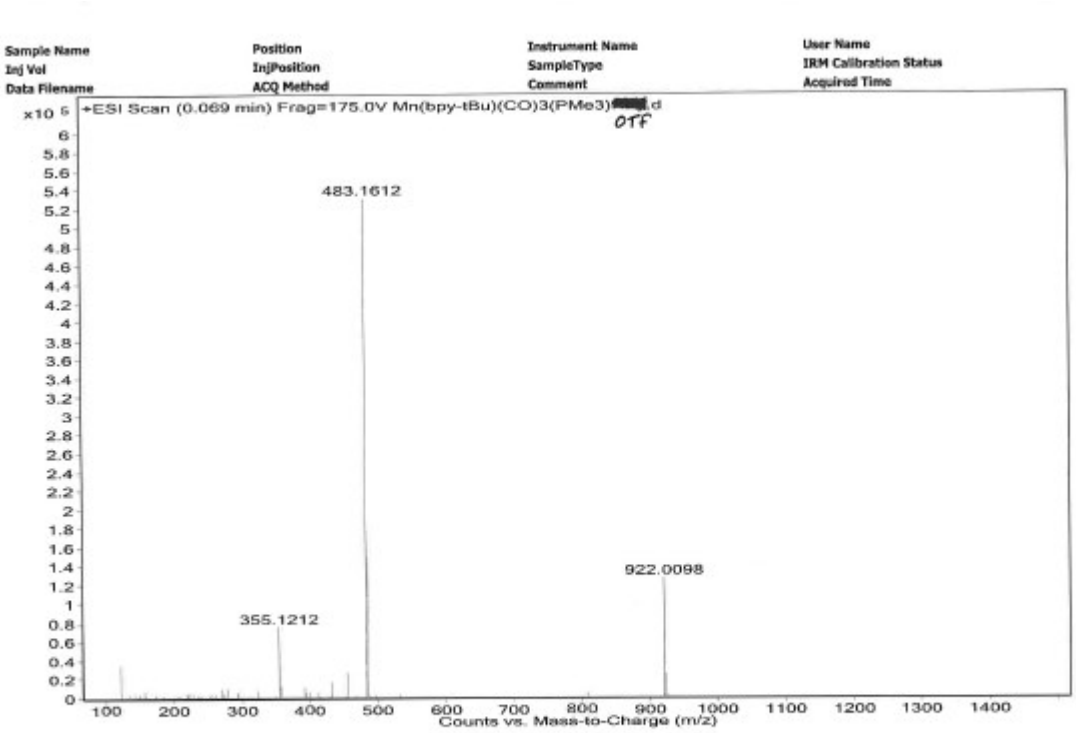


Figure SI-10a: HRMS spectra of compounds **1** and **2**. Note: 922.0098 is a calibrant.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Inj Vol
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Position
InjPosition
ACQ Method
Instrument Name
SampleType
Comment
User Name
IRM Calibration Status
Acquired Time
+ESI Scan (0.069 min) Frag=175.0V Mn(bpy-tBu)(CO)3(PMe3)[redacted].d
OTf
x10 5
483.1612
922.0098
355.1212
Counts vs. Mass-to-Charge (m/z)

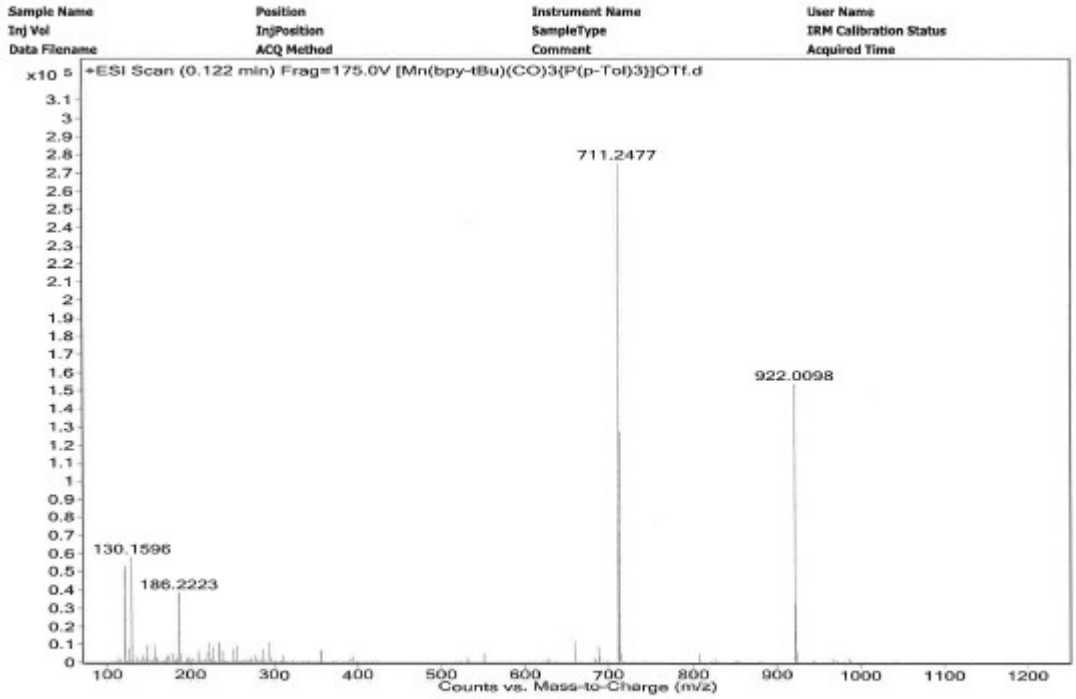

Figure SI-10b: HRMS spectra of compounds **3** and **4**. Note: 922.0098 is a calibrant.

Sample Name	**Position**	**Instrument Name**	**User Name**
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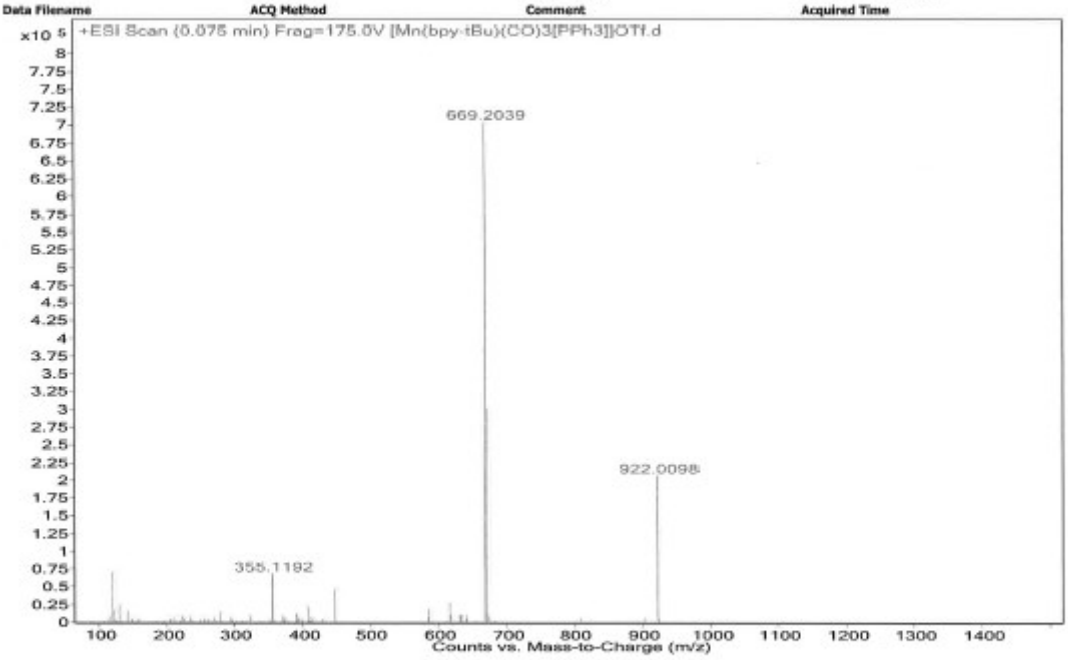
Data Filename	**ACQ Method**	**Comment**	**Acquired Time**



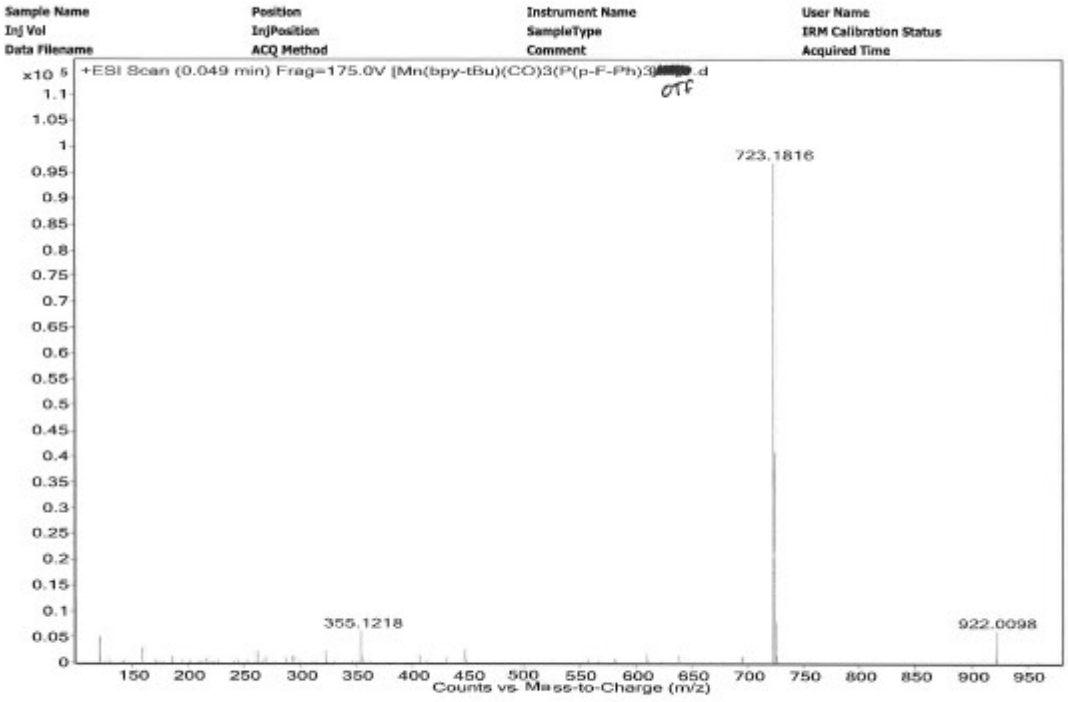
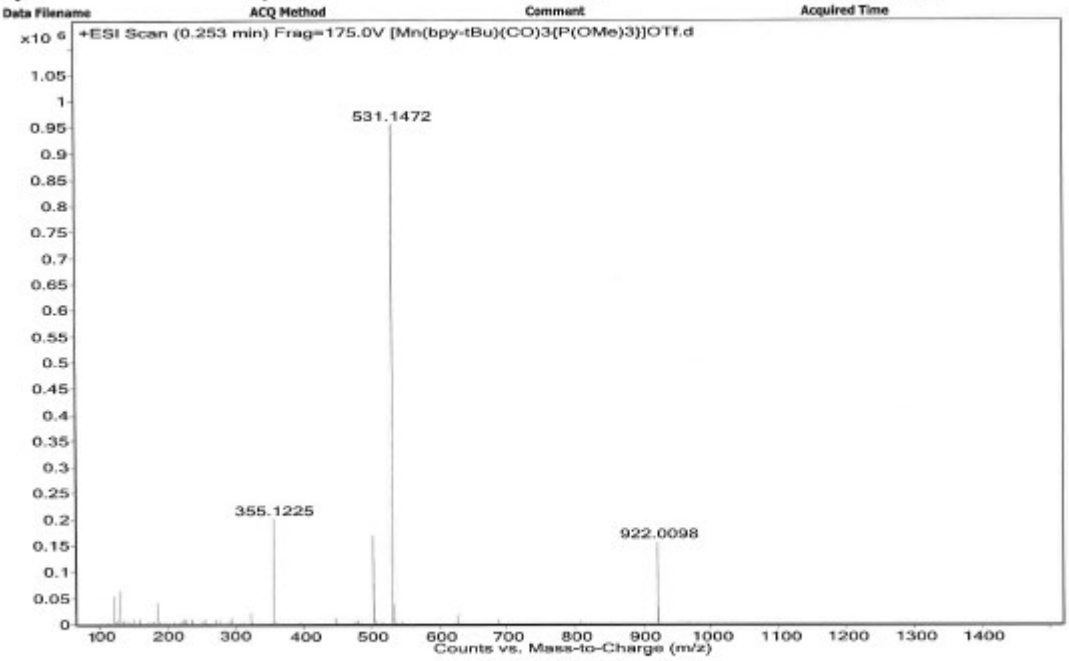


Figure SI-10b: HRMS spectra of compounds **5** and **6**. Note: 922.0098 is a calibrant.

Sample Name	**Position**	**Instrument Name**	**User Name**
Inj Vol	**InjPosition**	**SampleType**	**IRM Calibration Status**
Data Filename	**ACQ Method**	**Comment**	**Acquired Time**



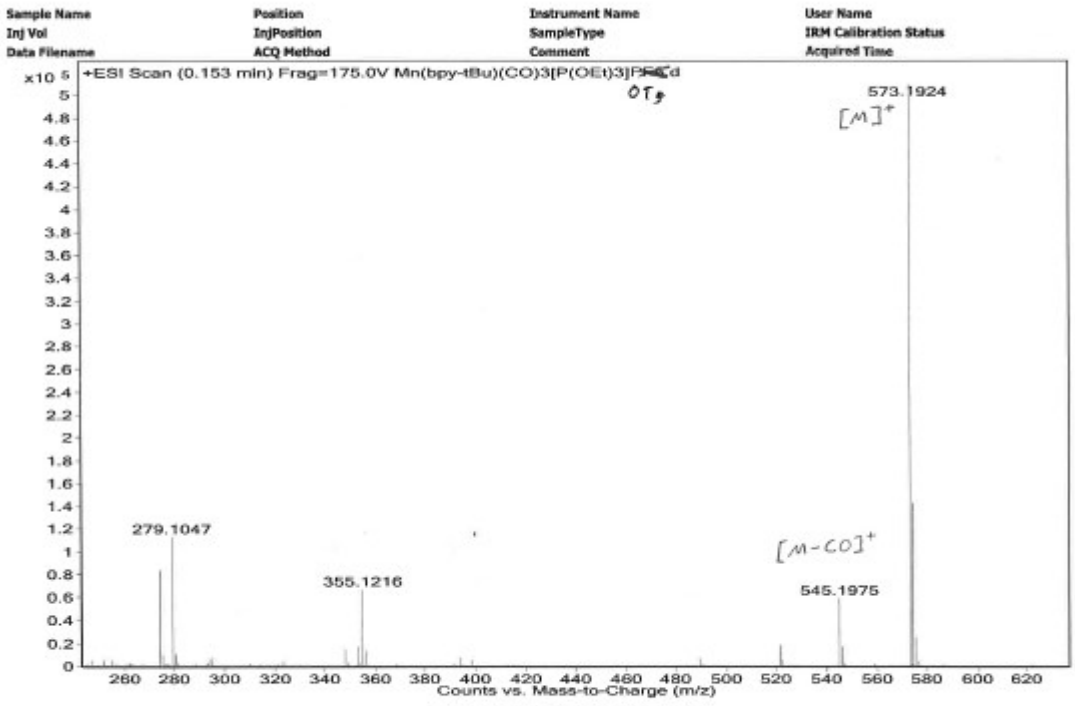


Figure SI-10d: HRMS spectra of compounds **7** and **8**. Note: 922.0098 is a calibrant.

ex4010

Submitted by: **Felton, G.**

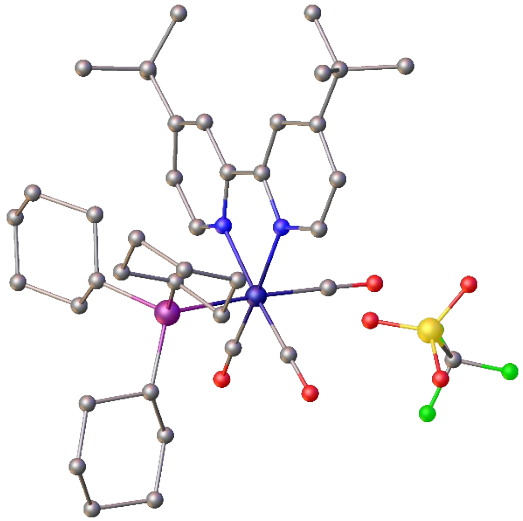
Solved by: **Nichol, G.S.**

Sample ID: **sample 4**

Compound sample 4 was provided as a dried residue on the inside of a small glass vial. Some of

this residue was sufficiently large enough to give reasonable single crystal X-ray diffraction, yielding structure ex4010. The final R_1 for this structure is rather high. This is possibly an effect of the residue nature of the crystals, all of which had cracks and other defects. The TwinRotMat function of PLATON was used to handle some of this twinning, as described below.

Crystal Data and Experimental



Experimental. Single yellow block-shaped crystals of (**ex4010**) were recrystallised from a mixture of pentane and acetone by vapour diffusion. A suitable crystal (0.37 × 0.12 × 0.07 mm^3) was selected and mounted on a MITIGEN holder in Paratone oil. on a SuperNova, Dual, Cu at zero, Atlas diffractometer. The crystal was kept at T = 120.00(10) K during data collection. Using **Olex2** (Dolomanov et al., 2009), the structure was solved with the ShelXT (Sheldrick, 2008) structure solution program, using the Direct Methods solution method. The model was refined with version 2014/6 of **ShelXL** (Sheldrick, 2008) using Least Squares minimisation.

Crystal Data. $C_{40}H_{57}N_2O_6F_3PSMn$, M_r = 836.84, triclinic, P-1 (No. 2), a = 10.7958(5) Å, b = 19.6144(10) Å, c = 20.0400(11) Å, α = 85.551(5)°, β = 89.809(4)°, γ = 76.872(4)°, V = 4119.7(4) Å^3, T = 120.00(10) K, Z = 4, Z' = 2, μ (MoK_α) = 0.471, 15033 reflections measured, 15033 unique (R_{int} = 0.1038) which were used in all calculations. The final wR_2 was 0.2169 (all data) and R_1 was 0.0920 (I > 2(I)).

Compound	**ex4010**
CCDC	1920529
Formula	$C_{40}H_{57}N_2O_6F_3PSMn$
$D_{calc.}$/ g cm^{-3}	1.349
μ/mm^{-1}	0.471
Formula Weight	836.84
Colour	yellow
Shape	block
Max Size/mm	0.37
Mid Size/mm	0.12
Min Size/mm	0.07
T/K	120.00(10)
Crystal System	triclinic
Space Group	P-1
a/Å	10.7958(5)
b/Å	19.6144(10)
c/Å	20.0400(11)
α/°	85.551(5)
β/°	89.809(4)
γ/°	76.872(4)
V/Å^3	4119.7(4)
Z	4
Z'	2
Θ_{min}/°	2.792
Θ_{max}/°	25.394
Measured Refl.	15033
Independent Refl.	15033
Reflections Used	10823
R_{int}	0.1038
Parameters	1105
Restraints	195
Largest Peak	2.083
Deepest Hole	-0.823
GooF	1.075
wR_2 (all data)	0.2169
wR_2	0.1981
R_1 (all data)	0.1283
R_1	0.0920

Experimental Extended. A yellow block-shaped crystal with dimensions 0.37 × 0.12 × 0.07 mm^3 was mounted on on a MITIGEN holder in Paratone oil.. Data were collected using a SuperNova, Dual, Cu at zero, Atlas diffractometer equipped with an Oxford Cryosystems Cryostream 700+ low-temperature apparatus operating at $T = 120.00(10)$ K.

Data were measured using ω scans scans of 1.0° per frame for 30.0 s using MoK_α radiation (SuperNova (Mo) X-ray Source, kV, mA). The total number of runs and images was based on the strategy calculation from the program CrysAlisPro (Agilent, V1.171.37.34k, 2014). The actually achieved resoltion was $\Theta =$ 25.394.

Cell parameters were retrieved using the CrysAlisPro (Agilent, V1.171.37.34k, 2014) software and refined using CrysAlisPro (Agilent, V1.171.37.34k, 2014) on 7413 reflections, 49 of the observed reflections.

Data reduction was performed using the CrysAlisPro (Agilent, V1.171.37.34k, 2014) software which corrects for Lorentz polarisation. The final completeness is 99.80 out to 25.394 in Θ. The absorption coefficient (MU) of this material is 0.471 and the minimum and maximum transmissions are 0.702 and 0.937.

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

The structure was solved in the space group P-1 (# 2). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

One of the cyclohexyl rings (containing C78) was modelled as disordered over two sites with occupancy ratio 0.540:0.460(10). One of the triflate anions (containing S51) was modelled as disorderd over two sites with occupancy ratio 0.704:0.296(7). Geometric and displacement ellipsoid similarity restraints were used on these disordered components. The TwinRotMat function of PLATON was used to handle a small amount of overlooked twinning, with a refined twin scale factor of 0.116(2).

Citations

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

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

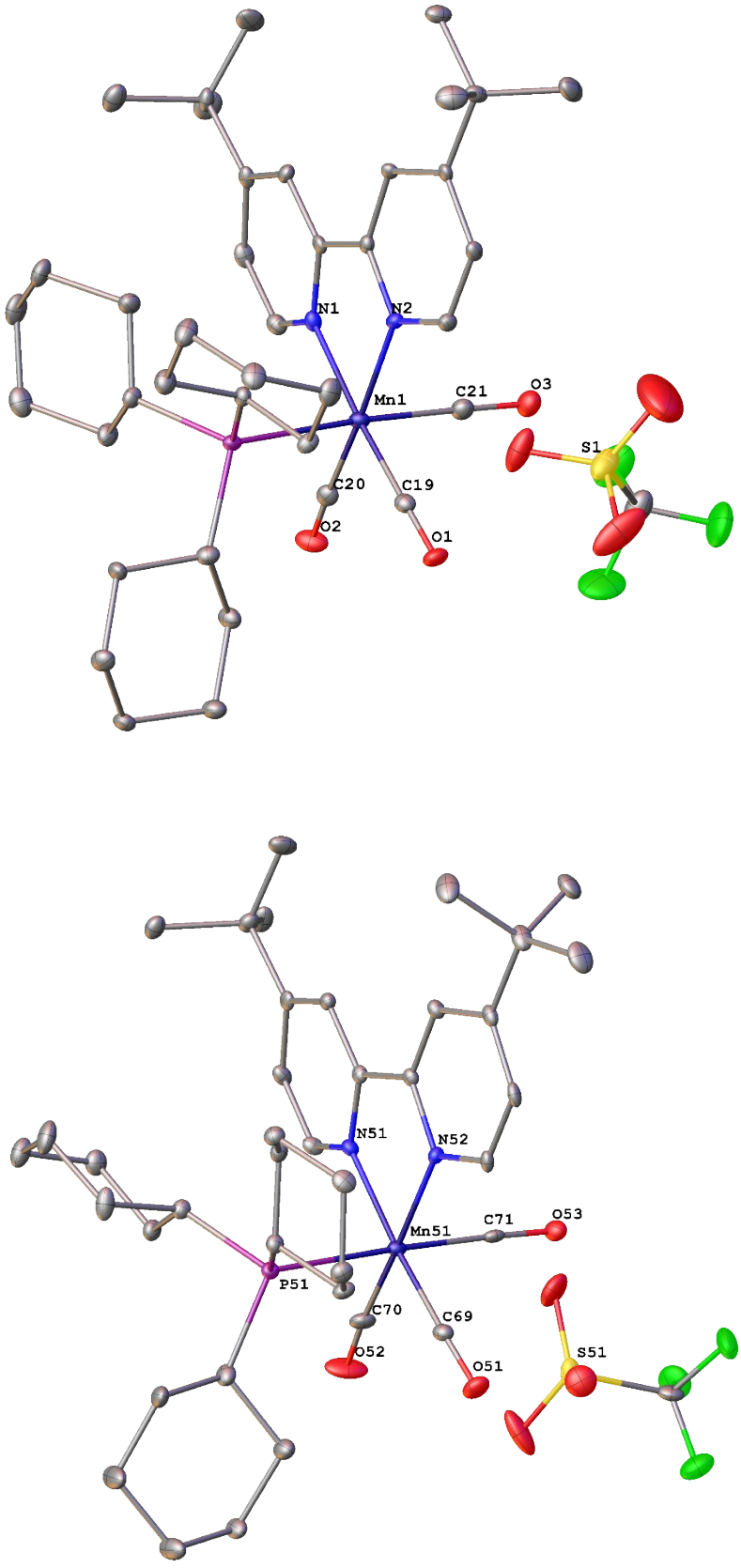


Figure SI-11. X-ray crystallographic structures of **1** (30% probability thermal ellipsoids). CCDC 1920529 formed as a crystal with two conformations of cyclohexyl rings in a 0.540:0.460 ratio.

Table SI-1. Bond lengths in Å for **CCDC 1920529**

Atom	Atom	Length/Å
Mn51	P51	2.4669(17)
Mn51	N51	2.047(5)
Mn51	N52	2.045(5)
Mn51	C69	1.810(6)
Mn51	C70	1.800(7)
Mn51	C71	1.832(6)
P51	C72	1.863(6)
P51	C78	1.848(12)
P51	C78'	1.852(11)
P51	C84	1.856(5)
O51	C69	1.150(7)
O52	C70	1.151(8)
O53	C71	1.139(7)
N51	C51	1.357(7)
N51	C55	1.354(7)
N52	C56	1.378(7)
N52	C60	1.342(7)
C51	C52	1.374(8)
C52	C53	1.388(8)
C53	C54	1.394(8)
C53	C61	1.526(8)
C54	C55	1.389(8)
C55	C56	1.471(8)
C56	C57	1.371(8)
C57	C58	1.395(8)
C58	C59	1.379(8)
C58	C65	1.534(8)
C59	C60	1.371(8)
C61	C62	1.553(8)
C61	C63	1.532(9)
C61	C64	1.519(9)
C65	C66	1.545(9)
C65	C67	1.545(10)
C65	C68	1.519(9)
C72	C73	1.526(8)
C72	C77	1.538(8)
C73	C74	1.518(8)
C74	C75	1.536(8)
C75	C76	1.506(9)
C76	C77	1.528(8)
C78	C79'	1.537(14)
C78	C83	1.538(17)
C78'	C79	1.538(13)
C78'	C83'	1.536(17)
C79	C80	1.507(14)
C79'	C80'	1.517(15)
C80	C81	1.532(15)
C80'	C81'	1.515(15)
C81	C82	1.491(14)
C81'	C82'	1.511(15)
C82	C83'	1.512(13)
C82'	C83	1.535(14)
C84	C85	1.528(8)
C84	C89	1.535(8)
C85	C86	1.527(8)
C86	C87	1.524(8)
C87	C88	1.515(9)
C88	C89	1.529(9)

Atom	Atom	Length/Å
Mn1	P1	2.4445(18)
Mn1	N1	2.055(5)
Mn1	N2	2.047(5)
Mn1	C19	1.809(6)
Mn1	C20	1.811(7)
Mn1	C21	1.834(7)
P1	C22	1.871(6)
P1	C28	1.876(6)
P1	C34	1.867(5)
O1	C19	1.148(7)
O2	C20	1.143(7)
O3	C21	1.147(8)
N1	C1	1.346(7)
N1	C5	1.362(7)
N2	C6	1.366(7)
N2	C10	1.350(7)
C1	C2	1.379(8)
C2	C3	1.392(9)
C3	C4	1.404(8)
C3	C11	1.531(8)
C4	C5	1.373(8)
C5	C6	1.470(8)
C6	C7	1.391(8)
C7	C8	1.399(7)
C8	C9	1.386(8)
C8	C15	1.517(8)
C9	C10	1.384(8)
C11	C12	1.553(9)
C11	C13	1.514(9)
C11	C14	1.520(9)
C15	C16	1.542(8)
C15	C17	1.517(9)
C15	C18	1.537(9)
C22	C23	1.542(7)
C22	C27	1.521(8)
C23	C24	1.547(9)
C24	C25	1.492(9)
C25	C26	1.528(9)
C26	C27	1.531(9)
C28	C29	1.543(8)
C28	C33	1.517(9)
C29	C30	1.513(9)
C30	C31	1.520(9)
C31	C32	1.520(9)
C32	C33	1.546(9)
C34	C35	1.545(8)
C34	C39	1.507(9)
C35	C36	1.537(9)
C36	C37	1.485(10)
C37	C38	1.534(9)
C38	C39	1.542(8)
S51	O54	1.443(9)
S51	O55	1.465(6)
S51	O56	1.401(11)
S51	C91	1.795(10)
F51	C91	1.312(11)
F52	C91	1.331(11)
F53	C91	1.301(10)

Atom	Atom	Length/Å
S51'	O54'	1.418(16)
S51'	O55'	1.471(16)
S51'	O56'	1.360(8)
S51'	C91'	1.837(16)
F51'	C91'	1.319(17)
F52'	C91'	1.331(19)
F53'	C91'	1.310(17)

Atom	Atom	Length/Å
S1	O4	1.394(6)
S1	O5	1.383(10)
S1	O6	1.441(8)
S1	C40	1.768(9)
F1	C40	1.325(9)
F2	C40	1.327(9)
F3	C40	1.376(11)

Table SI-2: Bond Angles in ° for **CCDC 1920529**

Atom	Atom	Atom	Angle/°
N51	Mn51	P51	93.35(13)
N52	Mn51	P51	92.85(13)
N52	Mn51	N51	78.69(18)
C69	Mn51	P51	88.15(19)
C69	Mn51	N51	175.7(2)
C69	Mn51	N52	97.2(2)
C69	Mn51	C71	88.5(3)
C70	Mn51	P51	90.9(2)
C70	Mn51	N51	94.9(2)
C70	Mn51	N52	172.8(2)
C70	Mn51	C69	89.1(3)
C70	Mn51	C71	89.8(3)
C71	Mn51	P51	176.59(18)
C71	Mn51	N51	89.9(2)
C71	Mn51	N52	86.8(2)
C72	P51	Mn51	116.73(19)
C78	P51	Mn51	116.1(6)
C78	P51	C72	105.2(8)
C78	P51	C84	100.4(8)
C78'	P51	Mn51	110.6(5)
C78'	P51	C72	101.9(6)
C78'	P51	C84	110.4(7)
C84	P51	Mn51	113.56(19)
C84	P51	C72	102.7(2)
C51	N51	Mn51	127.2(4)
C55	N51	Mn51	116.5(4)
C55	N51	C51	116.3(5)
C56	N52	Mn51	116.0(4)
C60	N52	Mn51	127.3(4)
C60	N52	C56	116.6(5)
N51	C51	C52	123.4(5)
C51	C52	C53	120.7(5)
C52	C53	C54	116.1(5)
C52	C53	C61	121.6(5)
C54	C53	C61	122.3(5)
C55	C54	C53	120.7(5)
N51	C55	C54	122.6(5)
N51	C55	C56	114.4(5)
C54	C55	C56	122.9(5)
N52	C56	C55	114.1(5)
C57	C56	N52	121.8(5)
C57	C56	C55	124.0(5)
C56	C57	C58	121.2(5)
C57	C58	C65	119.7(6)
C59	C58	C57	116.0(5)
C59	C58	C65	124.2(5)
C60	C59	C58	121.1(5)
N52	C60	C59	123.2(5)
C53	C61	C62	107.1(5)
C53	C61	C63	109.9(5)

Atom	Atom	Atom	Angle/°
C63	C61	C62	108.6(5)
C64	C61	C53	112.2(5)
C64	C61	C62	108.8(5)
C64	C61	C63	110.2(6)
C58	C65	C66	109.1(5)
C58	C65	C67	108.0(5)
C66	C65	C67	110.0(6)
C68	C65	C58	112.0(6)
C68	C65	C66	109.7(6)
C68	C65	C67	108.0(6)
O51	C69	Mn51	174.2(5)
O52	C70	Mn51	175.5(7)
O53	C71	Mn51	177.5(5)
C73	C72	P51	114.6(4)
C73	C72	C77	110.8(5)
C77	C72	P51	112.5(4)
C74	C73	C72	110.8(5)
C73	C74	C75	110.4(5)
C76	C75	C74	111.5(5)
C75	C76	C77	111.7(5)
C76	C77	C72	111.3(5)
C79'	C78	P51	117.4(11)
C79'	C78	C83	108.0(13)
C83	C78	P51	119.0(13)
C79	C78'	P51	120.2(9)
C83'	C78'	P51	116.9(11)
C83'	C78'	C79	106.7(11)
C80	C79	C78'	112.7(11)
C80'	C79'	C78	116.6(13)
C79	C80	C81	112.4(13)
C81'	C80'	C79'	112.4(14)
C82	C81	C80	113.0(12)
C82'	C81'	C80'	111.6(13)
C81	C82	C83'	113.0(11)
C81'	C82'	C83	113.1(13)
C82'	C83	C78	111.3(11)
C82	C83'	C78'	117.3(11)
C85	C84	P51	114.8(4)
C85	C84	C89	107.7(5)
C89	C84	P51	118.1(4)
C86	C85	C84	110.7(5)
C87	C86	C85	110.3(5)
C88	C87	C86	110.6(5)
C87	C88	C89	112.5(6)
C88	C89	C84	109.8(5)
N1	Mn1	P1	95.45(14)
N2	Mn1	P1	92.43(13)
N2	Mn1	N1	78.38(18)
C19	Mn1	P1	86.3(2)
C19	Mn1	N1	176.6(2)

Atom	Atom	Atom	Angle/°
C19	Mn1	N2	98.6(2)
C19	Mn1	C20	90.2(3)
C19	Mn1	C21	86.8(3)
C20	Mn1	P1	92.1(2)
C20	Mn1	N1	92.7(2)
C20	Mn1	N2	170.4(2)
C20	Mn1	C21	91.1(3)
C21	Mn1	P1	172.3(2)
C21	Mn1	N1	91.4(2)
C21	Mn1	N2	85.5(2)
C22	P1	Mn1	110.84(18)
C22	P1	C28	103.2(3)
C28	P1	Mn1	114.4(2)
C34	P1	Mn1	118.3(2)
C34	P1	C22	103.7(3)
C34	P1	C28	105.0(3)
C1	N1	Mn1	126.9(4)
C1	N1	C5	116.5(5)
C5	N1	Mn1	116.6(4)
C6	N2	Mn1	116.0(4)
C10	N2	Mn1	127.0(4)
C10	N2	C6	116.8(5)
N1	C1	C2	123.5(6)
C1	C2	C3	120.5(5)
C2	C3	C4	116.0(5)
C2	C3	C11	122.5(5)
C4	C3	C11	121.5(5)
C5	C4	C3	120.7(6)
N1	C5	C4	122.8(5)
N1	C5	C6	113.6(5)
C4	C5	C6	123.6(5)
N2	C6	C5	114.9(5)
N2	C6	C7	122.3(5)
C7	C6	C5	122.5(5)
C6	C7	C8	120.6(5)
C7	C8	C15	122.3(5)
C9	C8	C7	116.3(5)
C9	C8	C15	121.3(5)
C10	C9	C8	120.8(5)
N2	C10	C9	123.1(5)
C3	C11	C12	106.4(5)
C13	C11	C3	110.8(5)
C13	C11	C12	109.6(5)
C13	C11	C14	109.7(6)
C14	C11	C3	111.3(5)
C14	C11	C12	109.0(6)
C8	C15	C16	112.4(5)
C8	C15	C17	108.7(5)
C8	C15	C18	108.7(5)
C17	C15	C16	108.2(5)
C17	C15	C18	110.1(5)
C18	C15	C16	108.6(5)
O1	C19	Mn1	176.7(5)
O2	C20	Mn1	175.4(6)
O3	C21	Mn1	176.0(6)
C23	C22	P1	112.2(4)
C27	C22	P1	120.1(4)
C27	C22	C23	108.2(5)
C22	C23	C24	110.9(5)
C25	C24	C23	110.7(5)
C24	C25	C26	111.1(6)
C25	C26	C27	111.3(6)

Atom	Atom	Atom	Angle/°
C22	C27	C26	111.6(5)
C29	C28	P1	114.2(4)
C33	C28	P1	117.1(4)
C33	C28	C29	109.1(5)
C30	C29	C28	112.9(5)
C29	C30	C31	111.6(5)
C30	C31	C32	110.1(5)
C31	C32	C33	111.2(5)
C28	C33	C32	112.8(5)
C35	C34	P1	111.8(4)
C39	C34	P1	114.8(4)
C39	C34	C35	110.7(5)
C36	C35	C34	109.5(5)
C37	C36	C35	112.5(6)
C36	C37	C38	111.6(6)
C37	C38	C39	109.4(5)
C34	C39	C38	110.5(5)
O54	S51	O55	114.5(7)
O54	S51	C91	102.9(7)
O55	S51	C91	104.9(4)
O56	S51	O54	114.2(9)
O56	S51	O55	114.2(6)
O56	S51	C91	104.5(7)
F51	C91	S51	113.6(7)
F51	C91	F52	105.6(9)
F52	C91	S51	111.4(7)
F53	C91	S51	112.7(7)
F53	C91	F51	108.9(8)
F53	C91	F52	104.1(8)
O54'	S51'	O55'	115.3(19)
O54'	S51'	C91'	104.2(16)
O55'	S51'	C91'	99.2(13)
O56'	S51'	O54'	121.9(19)
O56'	S51'	O55'	112.2(11)
O56'	S51'	C91'	99.2(8)
F51'	C91'	S51'	115.2(14)
F51'	C91'	F52'	107.0(17)
F52'	C91'	S51'	108.5(15)
F53'	C91'	S51'	114.8(14)
F53'	C91'	F51'	107.8(18)
F53'	C91'	F52'	102.5(19)
O4	S1	O6	112.0(5)
O4	S1	C40	103.4(4)
O5	S1	O4	120.9(7)
O5	S1	O6	114.3(8)
O5	S1	C40	100.6(7)
O6	S1	C40	102.2(4)
F1	C40	S1	114.8(6)
F1	C40	F2	109.6(7)
F1	C40	F3	103.3(7)
F2	C40	S1	116.6(6)
F2	C40	F3	102.7(7)
F3	C40	S1	108.4(6)

EX4012

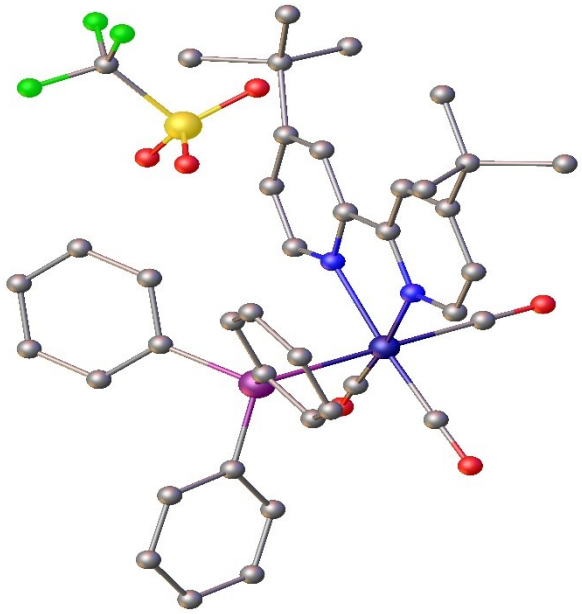
Submitted by: **Felton, G.**

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

Sample ID: **sample 5**

Compound sample 5 was provided as fairly large pale yellow blocks from which a small piece was cut off and found to be suitable for single crystal X-ray diffraction, yielding structure ex4012.

Crystal Data and Experimental



Experimental. Single light yellow block-shaped crystals of (**EX4012**) were recrystallised from a mixture of pentane and acetone by vapour diffusion. A suitable crystal (0.26 × 0.12 × 0.08 mm^3) was selected and mounted on a MITIGEN holder in Paratone oil on a Agilent Technologies SuperNova diffractometer. The crystal was kept at T = 120.0 K during data collection. Using **Olex2** (Dolomanov et al., 2009), the structure was solved with the ShelXT (Sheldrick, 2008) structure solution program, using the Direct Methods solution method. The model was refined with version 2014/6 of **ShelXL** (Sheldrick, 2008) using Least Squares minimisation.

Crystal Data. $C_{40}H_{39}F_3MnN_2O_6PS$, M_r = 818.70, monoclinic, C2/c (No. 15), a = 37.1455(10) Å, b = 10.5546(3) Å, c = 20.3195(5) Å, β = 99.524(3)°, $\alpha = \gamma$ = 90°, V = 7856.6(4) $Å^3$, T = 120.0 K, Z = 8, Z' = 1, μ (MoK_α) = 0.492, 69991 reflections measured, 8027 unique (R_{int} = 0.0666) which were used in all calculations. The final wR_2 was 0.1069 (all data) and R_1 was 0.0437 (I > 2(I)).

Compound	**EX4012**
CCDC	1920530
Formula	$C_{40}H_{39}F_3MnN_2O_6PS$
$D_{calc.}$/ g cm^{-3}	1.384
μ/mm^{-1}	0.492
Formula Weight	818.70
Colour	light yellow
Shape	block
Max Size/mm	0.26
Mid Size/mm	0.12
Min Size/mm	0.08
T/K	120.0
Crystal System	monoclinic
Space Group	C2/c
a/Å	37.1455(10)
b/Å	10.5546(3)
c/Å	20.3195(5)
α/°	90
β/°	99.524(3)
γ/°	90
V/$Å^3$	7856.6(4)
Z	8
Z'	1
Θ_{min}/°	2.846
Θ_{max}/°	26.371
Measured Refl.	69991
Independent Refl.	8027
Reflections Used	6611
R_{int}	0.0666
Parameters	597
Restraints	48
Largest Peak	0.426
Deepest Hole	-0.348
GooF	1.052
wR_2 (all data)	0.1069
wR_2	0.1004
R_1 (all data)	0.0566
R_1	0.0437

Experimental Extended. A light yellow block-shaped crystal with dimensions 0.26 × 0.12 × 0.08 mm^3 was mounted on on a MITIGEN holder in Paratone oil. Data were collected using a Agilent Technologies SuperNova diffractometer equipped with an Oxford Cryosystems Cryostream 700+ low-temperature apparatus operating at $T = 120.0$ K.

Data were measured using ω scans scans of 1.0° per frame for 15.0 s using MoK_α radiation (SuperNova (Mo) X-ray Source, kV, mA). The total number of runs and images was based on the strategy calculation from the program **CrysAlisPro** (Agilent, V1.171.37.33, 2014). The actually achieved resoltion was $\Theta =$ 26.371.

Cell parameters were retrieved using the **CrysAlisPro** (Agilent, V1.171.37.33, 2014) software and refined using **CrysAlisPro** (Agilent, V1.171.37.33, 2014) on 15745 reflections, 22 of the observed reflections.

Data reduction was performed using the **CrysAlisPro** (Agilent, V1.171.37.33, 2014) software which corrects for Lorentz polarisation. The final completeness is 99.80 out to 26.371 in Θ. The absorption coefficient (MU) of this material is 0.492 and the minimum and maximum transmissions are 0.589 and 0.829.

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

The structure was solved in the space group C2/c (# 15). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

The t-butyl groun containing C11 was modelled over two sites, as indicated by electron density peaks, with occupancy ratio 0.607:0.393(6). The geometry of both disorder componenets was restrained to be similar to that of the ordered t-butyl ground (containing C15). The triflate anion was refined as disordered over two sites, pivoting about the carbon atom, with occupancy ratio 0.518:0.482(2). No geometric restraints were used on the disordered triflate.

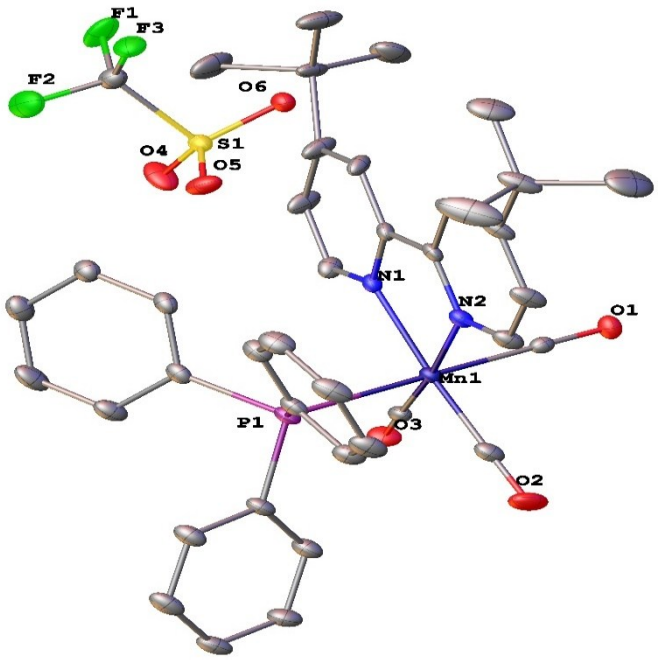


Figure SI-12. Xray crystallographic structures of **5** (30% probability thermal ellipsoids). CCDC 1920530.

Table SI-1: Bond Lengths in Å for **CCDC 1920530.**

Atom	Atom	Length/Å
Mn1	P1	2.3807(6)
Mn1	N1	2.0386(19)
Mn1	N2	2.0475(18)
Mn1	C19	1.836(2)
Mn1	C20	1.805(3)
Mn1	C21	1.807(2)
P1	C22	1.833(2)
P1	C28	1.835(2)
P1	C34	1.835(2)
O1	C19	1.139(3)
O2	C20	1.152(3)
O3	C21	1.148(3)
N1	C1	1.344(3)
N1	C5	1.361(3)
N2	C6	1.352(3)
N2	C10	1.346(3)
C1	C2	1.373(4)
C2	C3	1.391(3)
C3	C4	1.393(3)
C3	C11	1.625(6)
C3	C11'	1.438(8)
C4	C5	1.381(3)
C5	C6	1.470(3)
C6	C7	1.393(3)
C7	C8	1.391(3)
C8	C9	1.395(4)
C8	C15	1.528(3)
C9	C10	1.377(3)
C11	C12	1.546(9)
C11	C13	1.520(7)
C11	C14	1.537(8)
C11'	C13'	1.541(11)
C11'	C14'	1.531(9)
C11'	C15'	1.521(9)
C15	C16	1.522(4)
C15	C17	1.509(4)
C15	C18	1.548(5)
C22	C23	1.399(3)
C22	C27	1.401(3)
C23	C24	1.384(4)
C24	C25	1.380(4)
C25	C26	1.388(3)
C26	C27	1.387(3)
C28	C29	1.387(3)
C28	C33	1.402(4)
C29	C30	1.398(3)
C30	C31	1.381(4)
C31	C32	1.385(4)
C32	C33	1.386(3)
C34	C35	1.390(3)
C34	C39	1.402(3)
C35	C36	1.396(3)
C36	C37	1.381(4)
C37	C38	1.388(4)
C38	C39	1.383(3)
S1	O4	1.438(5)
S1	O5	1.443(4)
S1	O6	1.433(4)
S1	C40	1.824(3)
S004	O4'	1.439(4)
S004	O5'	1.426(5)
S004	O6'	1.445(5)
S004	C40	1.798(3)
F1	C40	1.357(4)
F1'	C40	1.341(4)
F2	C40	1.334(15)
F2'	C40	1.350(13)
F3	C40	1.274(4)
F3'	C40	1.399(5)

Table SI-2: Bond Angles in ° for **CCDC 1920530.**

Atom	Atom	Atom	Angle/°
N1	Mn1	P1	93.08(5)
N1	Mn1	N2	78.71(7)
N2	Mn1	P1	90.75(5)
C19	Mn1	P1	179.20(7)
C19	Mn1	N1	87.54(8)
C19	Mn1	N2	89.87(8)
C20	Mn1	P1	88.63(8)
C20	Mn1	N1	174.95(9)
C20	Mn1	N2	96.53(9)
C20	Mn1	C19	90.80(10)
C20	Mn1	C21	91.18(10)
C21	Mn1	P1	91.25(7)
C21	Mn1	N1	93.53(9)
C21	Mn1	N2	172.08(9)
C21	Mn1	C19	88.20(9)
C22	P1	Mn1	114.67(7)
C22	P1	C28	108.79(11)
C22	P1	C34	103.57(11)
C28	P1	Mn1	110.09(7)
C34	P1	Mn1	117.16(8)
C34	P1	C28	101.49(10)
C1	N1	Mn1	126.26(15)
C1	N1	C5	117.2(2)
C5	N1	Mn1	116.24(14)
C6	N2	Mn1	116.06(14)
C10	N2	Mn1	126.72(16)
C10	N2	C6	117.20(19)
N1	C1	C2	123.0(2)
C1	C2	C3	120.8(2)
C2	C3	C4	116.0(2)
C2	C3	C11	119.9(3)
C2	C3	C11'	124.2(4)

Atom	Atom	Atom	Angle/°
C4	C3	C11	122.7(3)
C4	C3	C11'	117.8(4)
C5	C4	C3	120.9(2)
N1	C5	C4	122.0(2)
N1	C5	C6	114.08(19)
C4	C5	C6	123.88(19)
N2	C6	C5	114.65(18)
N2	C6	C7	122.4(2)
C7	C6	C5	123.0(2)
C8	C7	C6	120.4(2)
C7	C8	C9	116.4(2)
C7	C8	C15	122.7(2)
C9	C8	C15	120.9(2)
C10	C9	C8	120.6(2)
N2	C10	C9	123.1(2)
C12	C11	C3	104.1(7)
C13	C11	C3	110.4(4)
C13	C11	C12	109.7(7)
C13	C11	C14	108.1(5)
C14	C11	C3	112.7(4)
C14	C11	C12	111.8(6)
C3	C11'	C13'	113.4(9)
C3	C11'	C14'	119.1(6)
C3	C11'	C15'	98.3(5)
C14'	C11'	C13'	109.1(9)
C15'	C11'	C13'	104.9(8)
C15'	C11'	C14'	110.6(7)
C8	C15	C18	108.4(2)
C16	C15	C8	107.8(2)
C16	C15	C18	108.3(3)
C17	C15	C8	112.7(2)
C17	C15	C16	111.8(3)
C17	C15	C18	107.7(2)
O1	C19	Mn1	177.73(19)
O2	C20	Mn1	178.3(2)
O3	C21	Mn1	175.83(19)
C23	C22	P1	120.33(19)
C23	C22	C27	118.0(2)
C27	C22	P1	121.37(17)
C24	C23	C22	120.6(2)
C25	C24	C23	120.9(2)
C24	C25	C26	119.4(2)
C27	C26	C25	120.3(2)
C26	C27	C22	120.9(2)
C29	C28	P1	123.41(19)
C29	C28	C33	118.9(2)
C33	C28	P1	117.16(18)
C28	C29	C30	120.0(2)
C31	C30	C29	120.4(3)
C30	C31	C32	120.0(2)
C31	C32	C33	119.7(3)
C32	C33	C28	120.9(2)
C35	C34	P1	122.65(17)
C35	C34	C39	118.6(2)
C39	C34	P1	118.75(18)
C34	C35	C36	120.6(2)
C37	C36	C35	120.2(2)
C36	C37	C38	119.7(2)
C39	C38	C37	120.4(2)
C38	C39	C34	120.6(2)
O4	S1	O5	114.6(3)
O4	S1	C40	105.4(3)
O5	S1	C40	101.81(17)
O6	S1	O4	115.3(3)
O6	S1	O5	115.5(2)
O6	S1	C40	101.7(2)
O4'	S004	O6'	115.4(3)
O4'	S004	C40	100.67(19)
O5'	S004	O4'	115.3(3)
O5'	S004	O6'	114.9(3)
O5'	S004	C40	103.1(3)
O6'	S004	C40	104.7(2)
F1	C40	S1	110.6(2)
F1'	C40	S004	113.0(2)
F1'	C40	F2'	111.9(9)
F1'	C40	F3'	102.5(3)
F2	C40	S1	113.6(9)
F2	C40	F1	106.7(8)
F2'	C40	S004	108.6(10)
F2'	C40	F3'	111.5(9)
F3	C40	S1	115.9(2)
F3	C40	F1	108.7(3)
F3	C40	F2	100.6(10)
F3'	C40	S004	109.2(3)