Supporting Information for the Paper Entitled:

Comparison of Nucleophilic- and Radical-Based Routes to the Formation of Manganese-Main Group Element Single Bonds

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S1. Selected ^{1}H NMR, IR and Mass Spectral Data

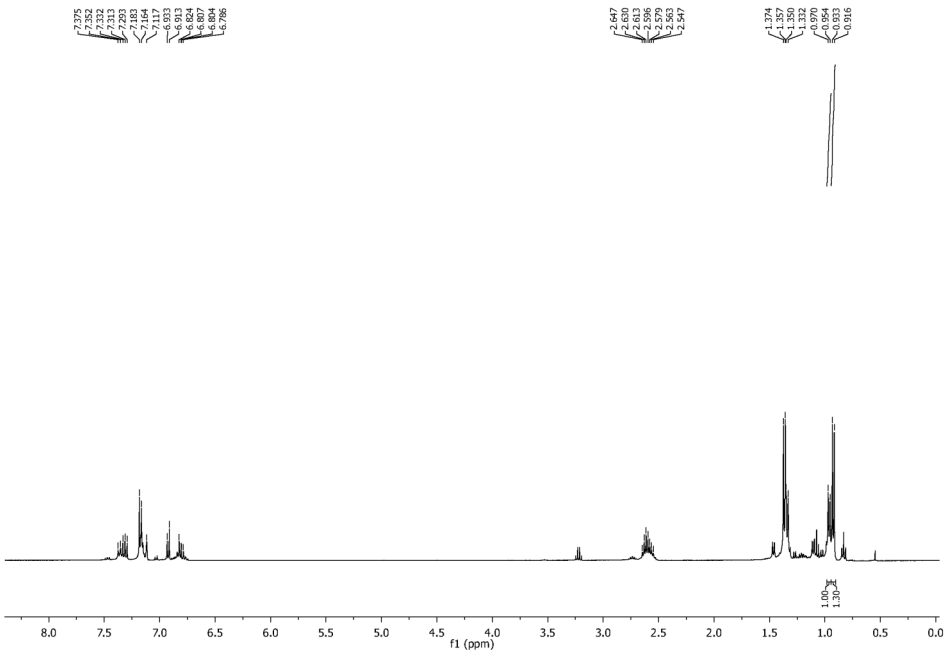

Figure S1.1. ^{1}H NMR (400.1 MHz, C_6D_6, 20 ˚C) of $MnCl(CO)_3(CNAr^{Dipp2})_2$ and $Mn(SnCl)(CO)_3(CNAr^{Dipp2})_2$ resulting from addition of $SnCl_2$ to $Mn(CO)_3(CNAr^{Dipp2})_2$.

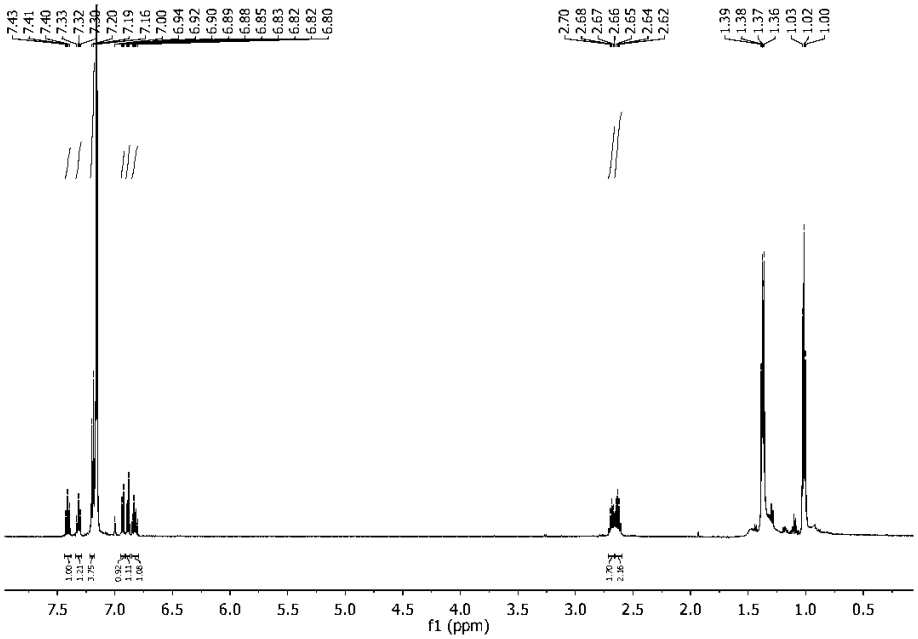

Figure S1.2. ^{1}H NMR (400.1 MHz, C_6D_6, 20 ˚C) of product mixture resulting from addition of SbF_3 to $Mn(CO)_3(CNAr^{Dipp2})_2$.

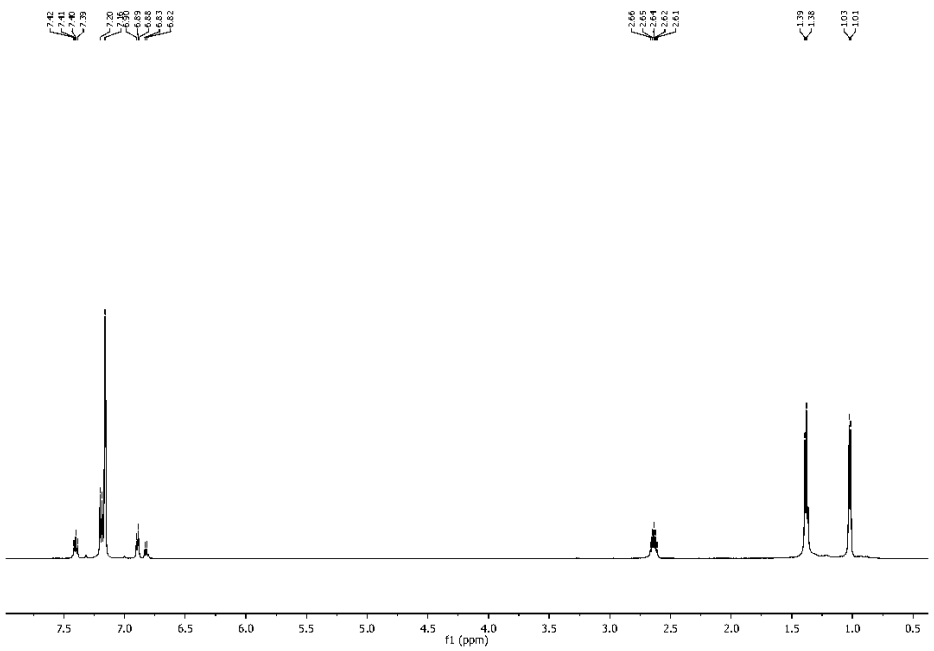

Figure S1.3. ^{1}H NMR (500.1 MHz, C_6D_6, 20 ºC) of $FMn(CO)_3(CNAr^{Dipp2})_2$.

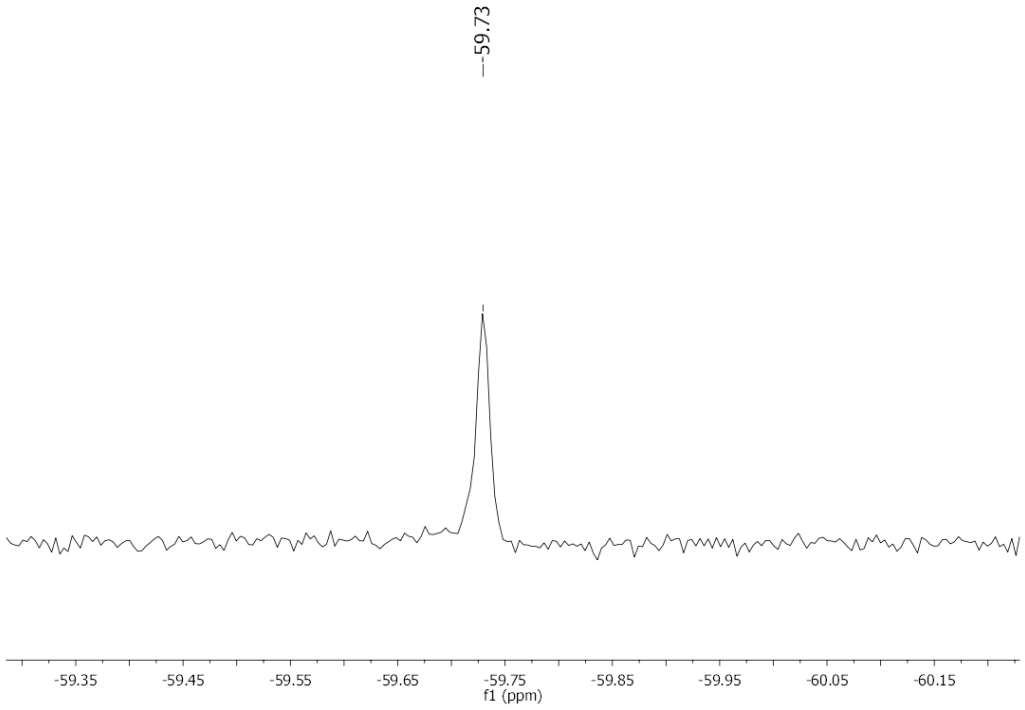

Figure S1.4. ^{19}F NMR (470.6 MHz, C_6D_6, 20 ºC) of $FMn(CO)_3(CNAr^{Dipp2})_2$.

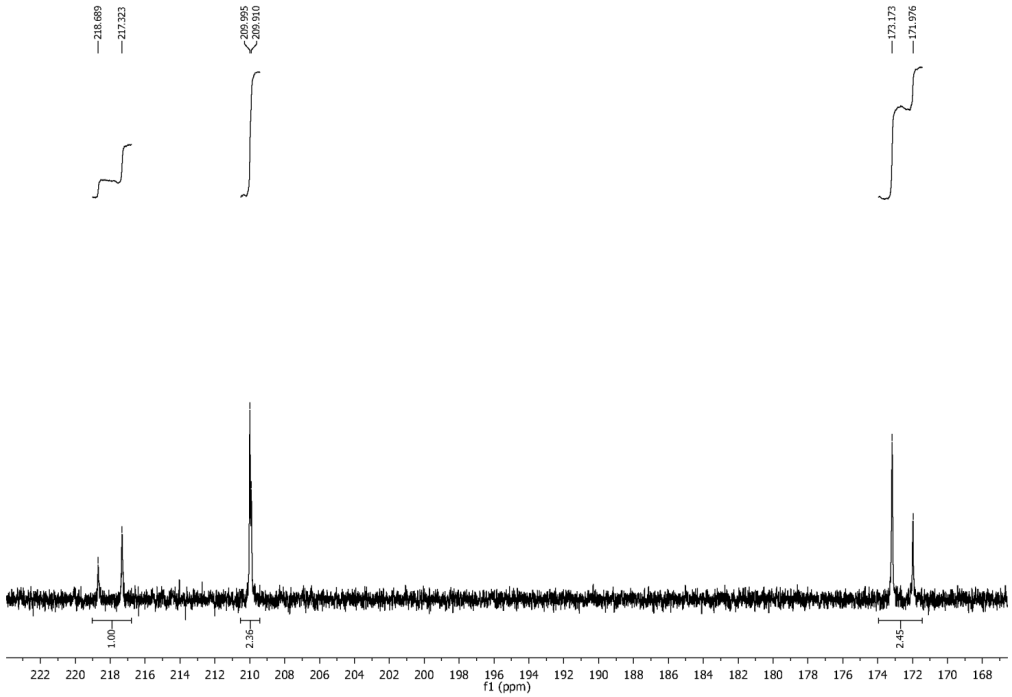

Figure S1.5. Inset view of the isocyanide/CO region of the $^{13}C\{^{1}H\}$ NMR (125.7 MHz, C_6D_6, 20 ˚C) of $FMn(CO)_3(CNAr^{Dipp2})_2$.

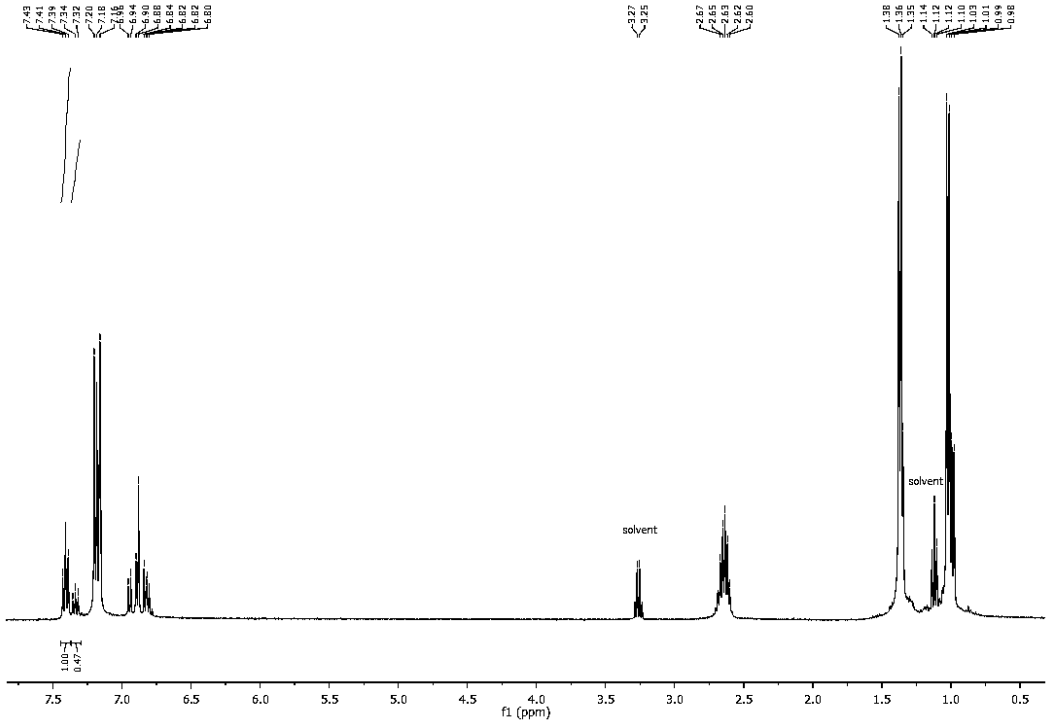

Figure S1.6. ^{1}H NMR (400.1 MHz, C_6D_6, 20 ˚C) of $MnCl(CO)_3(CNAr^{Dipp2})_2$ and $Mn(BiCl_2)(CO)_3(CNAr^{Dipp2})_2$ resulting from addition of $BiCl_3$ to $Mn(CO)_3(CNAr^{Dipp2})_2$.

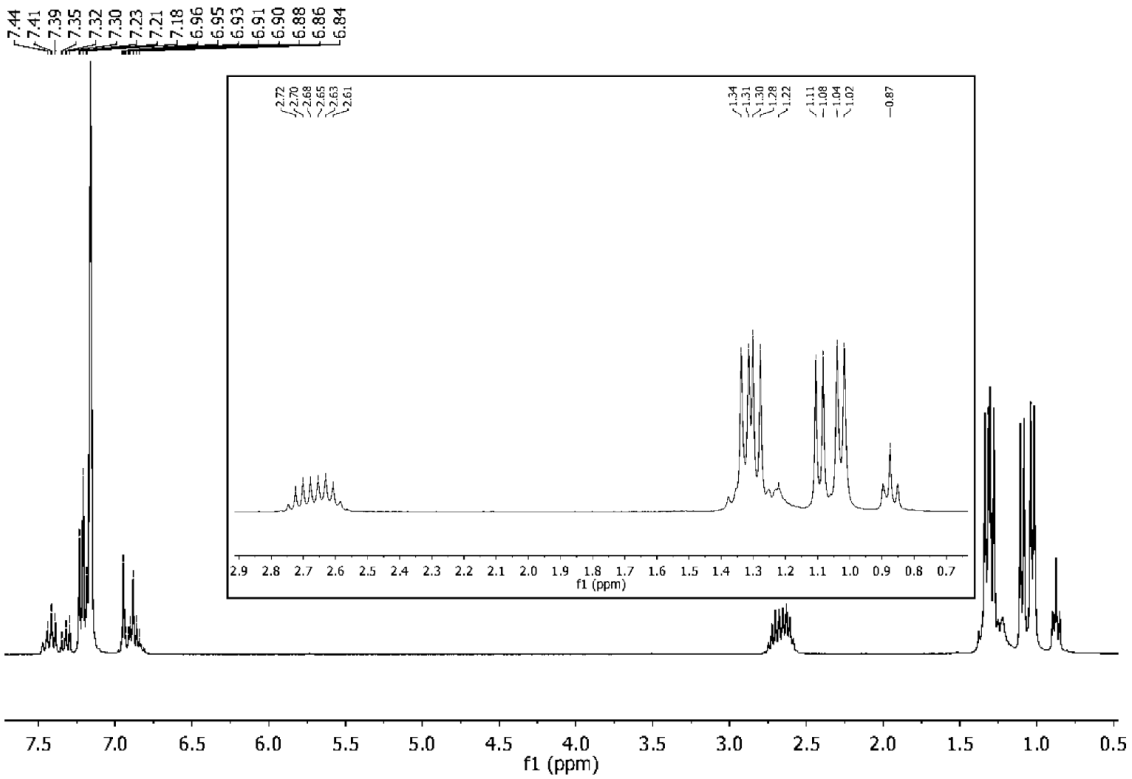

Figure S1.7. ^{1}H NMR (300.1 MHz, C_6D_6, 20 °C) of mixture resulting from decomposition of $MnF(CO)_3(CNAr^{Dipp2})_2$.

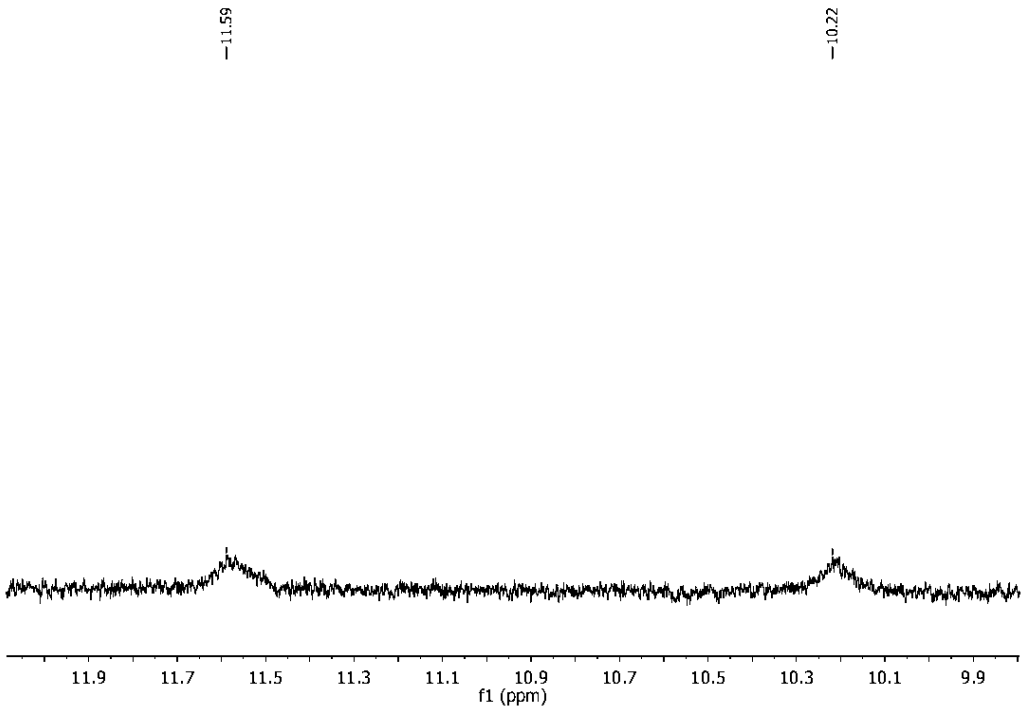

Figure S1.8. Inset view of ^{1}H NMR (300.1 MHz, C_6D_6, 20 °C) of downfield doublet resonance in mixture resulting from decomposition of $MnF(CO)_3(CNAr^{Dipp2})_2$.

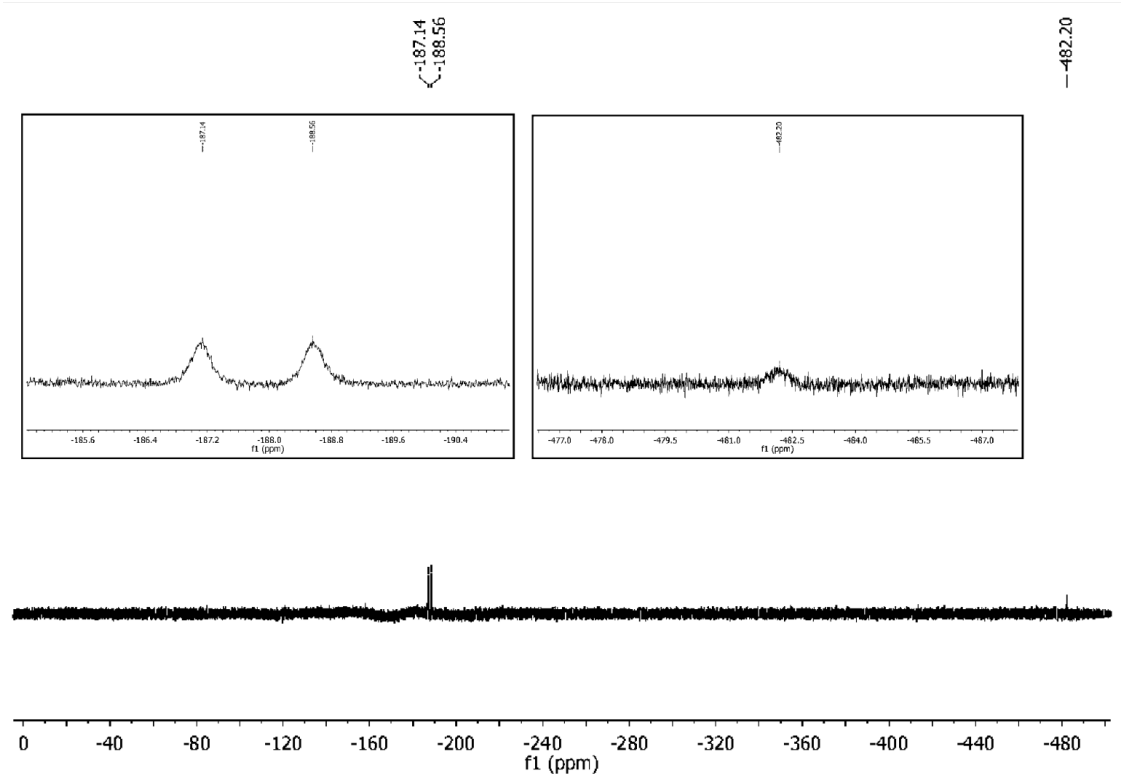

Figure S1.9. ^{19}F NMR (282.2 MHz, C_6D_6, 20 °C) of mixture resulting from decomposition of $MnF(CO)_3(CNAr^{Dipp2})_2$.

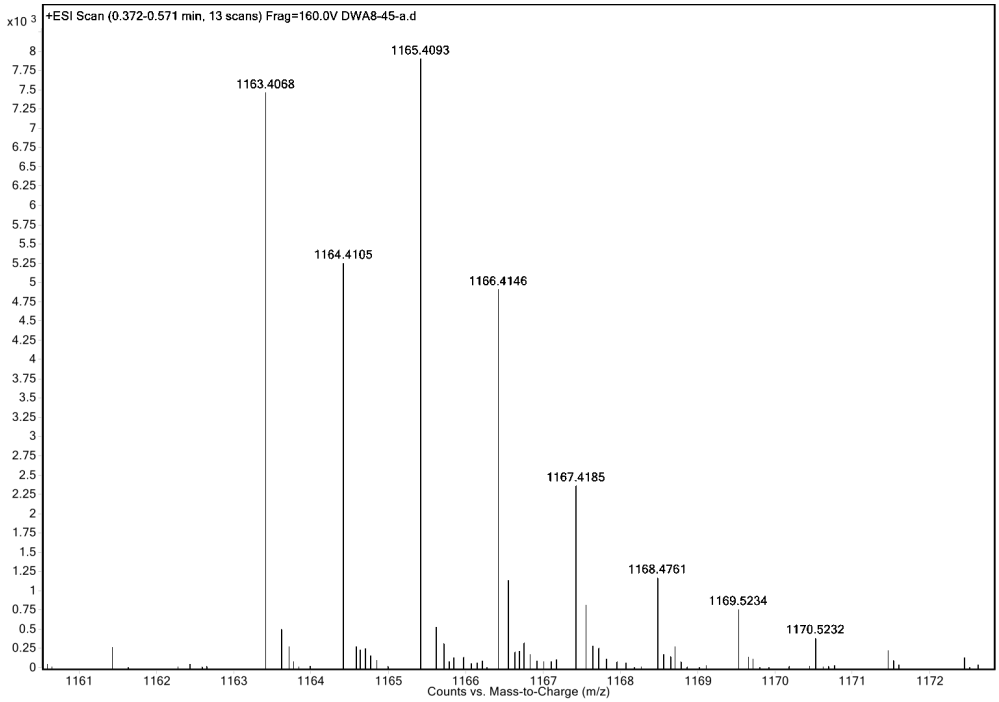

Figure S1.10. Inset view of ESI-MS of $Mn(SbF_2)(CO)_3(CNAr^{Dipp2})_2$.

S2. Crystallographic Structure Determinations

S2.1. General: Single crystal X-ray structure determinations were performed at low temperature on Bruker Kappa Diffractometers equipped with a Mo-Kα or Cu-Kα radiation source and a Bruker APEX or APEX-II area detector. All structures were solved *via* direct methods with SIR 2004 [1] and refined by full-matrix least-squares procedures using SHELXL-2013. [2] Crystallographic data collection and refinement information listed in Table S4.1. $Mn(SbF_2)(CO)_3(CNAr^{Dipp2})_2$ possesses positional disorder of the (SbF_2)-unit and a pyridine solvent molecule, and was modeled and fully refined anisotropically. $Mn(THF{\cdot}AlCl_2)(CO)_3(CNAr^{Dipp2})_2$ possesses positional disorder of one Cl atom, and was modeled and fully refined anisotropically. $Mn(FHF)(CO)_3(CNAr^{Dipp2})_2$ possesses positional disorder of the (FHF)-unit and the *trans*-CO; this was modeled and refined anisotropically. One H atom in the disordered (FHF)-unit could be located in the electron density map and was included in the model.

S2.2. CCDC Deposition: All crystal structures reported herein have been deposited with the Cambridge Crystallographic Data Center (CCDC) and have been assigned the following CCDC deposition numbers:

$Mn(SbF_2)(CO)_3(CNAr^{Dipp2})_2$: **1538898**
$Mn(BiCl_2)(CO)_3(CNAr^{Dipp2})_2$: **1538895**
$Mn(AlCl_2(THF))(CO)_3(CNAr^{Dipp2})_2$: **1538896**
$Mn(FHF)(CO)_3(CNAr^{Dipp2})_2$: **1538897**

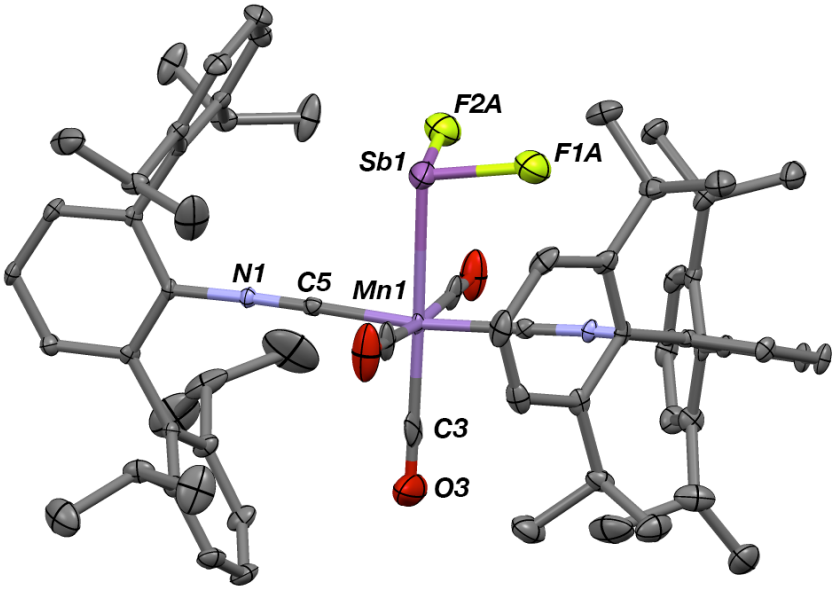

Figure S2.1. Molecular structure of $Mn(SbF_2)(CO)_3(CNAr^{Dipp2})_2$, with pyridine solvent molecule and H atoms omitted for clarity. Selected bond distances (Å) and angles (º): Mn1-Sb1 = 2.6111(6); C5-N1 = 1.157(4); Sb-F2A = 1.900(6); F2A-Sb1-F2A = 92.2(3); Sb1-Mn1-C5 = 86.92(10).

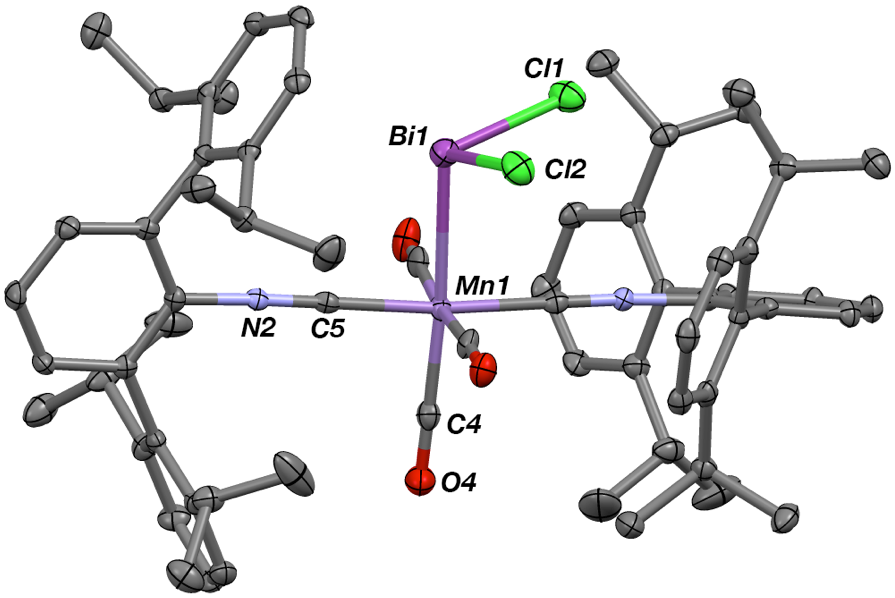

Figure S2.2. Molecular structure of $Mn(Cl_2Bi)(CO)_3(CNAr^{Dipp2})_2$, with THF solvent molecules and H atoms omitted for clarity. Selected bond distances (Å) and angles (º): Mn1-Bi1 = 2.6809(10); C5-N2 = 1.153(8); Bi1-Cl1 = 2.500(2); Cl1-Bi1-Cl2 = 95.06(7); Bi1-Mn1-C5 = 83.81(18).

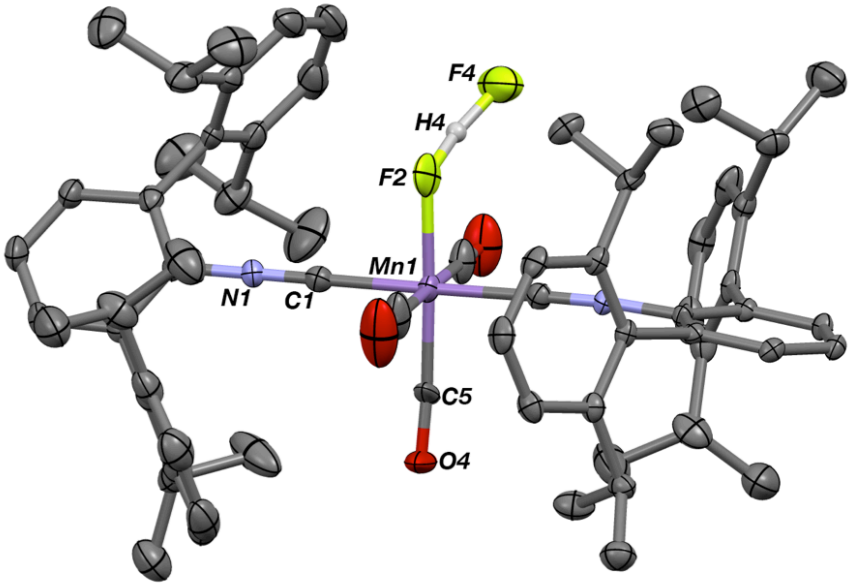

Figure S2.3. Molecular structure of $Mn(FHF)(CO)_3(CNAr^{Dipp2})_2$, with H atoms omitted for clarity. Selected bond distances (Å) and angles (º): F2-H4 = 1.10(5); F4-H4 = 1.20(5); Mn1-F2 = 1.943(11); Mn1-C5 = 1.811(12); Mn1-C1 = 1.927(2); Mn1-F2-H4 = 118(3); F2-Mn1-C1 = 88.7(2); F2-H4-F4 = 164(3).

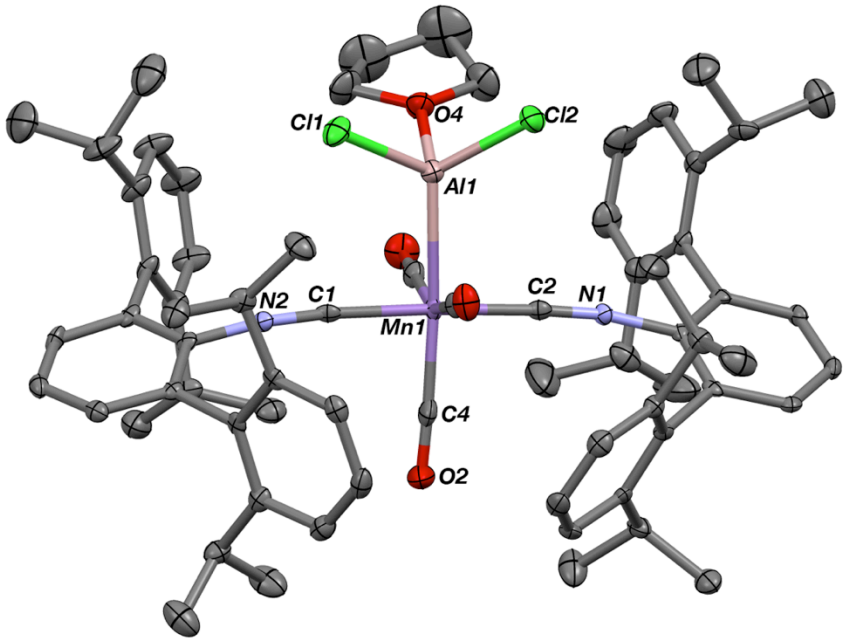

Figure S2.4. Molecular structure of $Mn(AlCl_2(THF))(CO)_3(CNAr^{Dipp2})_2$, with H atoms omitted for clarity. Selected bond distances (Å) and angles (º): Mn1-Al1 = 2.4541(10); Al1-O4 = 1.900(2); Mn1-C4 = 1.829(3); Mn1-C1 = 1.894(3); O4-Al1-Mn1 = 115.92(8); Cl1-Al1-Cl2 = 105.24(10); C1-Mn1-C2 = 177.10(13).

Table S2.1 Crystallographic Data Collection and Refinement Information

Name	$Mn(BiCl_2)(CO)_3(CNAr^{Dipp2})_2$·(THF)	$Mn(SbF_2)(CO)_3(CNAr^{Dipp2})_2$ · 2(Pyridine)	$Mn(THF·AlCl_2)(CO)_3(CNAr^{Dipp2})_2$
Formula	$C_{73}H_{89}BiCl_2MnN_2O_5$	$C_{75}H_{84}F_2MnN_4O_3Sb$	$C_{69}H_{82}AlCl_2MnN_2O_4$
Crystal System	Monoclinic	Monoclinic	Monoclinic
Space Group	P 2 1/c	P 2 1/c	P 1 2/c
a, Å	17.0881(10)	15.9656(4)	13.6958(5)
b, Å	16.5315(9)	17.3952(4)	26.0232(9)
c, Å	24.8358	25.1885(6)	18.4253(6)
α, deg	90	90	90
β, deg	105.3620(10)	101.8090(10)	95.8827(17)
γ, deg	90	90	90
V, Å^3	6765.2(7)	6847.4(3)	6532.4(4)

Z	4	4	4
Radiation (λ, Å)	Mo-K_α, 0.71073	Mo-K_α, 0.71073	Mo-K_α, 0.71073
ρ (calcd.), Mg/m^3	1.384	1.265	1.176
μ (Mo Ka), mm^{-1}	2.913	0.633	0.344
Temp, K	100	100	100
θ max, deg	25.45	26.12	24.141
data/parameters	12473/773	13554/777	10356/742
R_1	0.0612	0.0557	0.0536
wR_2	0.1749	0.1555	0.1073
GOF	1.058	1.041	1.065

Table S2.1 Cont'd.

Name	$Mn(FHF)(CO)_3(CNAr^{Dipp2})_2 \cdot (Et_2O)$
Formula	$C_{67}H_{79}F_{1.2}MnN_2O_{3.47}$
Crystal System	Monoclinic
Space Group	P 2 1/c
a, Å	19.1678(5)
b, Å	16.5149(4)
c, Å	20.6165(5)
α, deg	90
β, deg	114.1020(10)
γ, deg	90
V, $Å^3$	5957.3(3)
Z	4
Radiation (λ, Å)	Cu-K_α, 1.54178
ρ (calcd.), Mg/m^3	1.181
μ (Mo Ka), mm^{-1}	2.217
Temp, K	100
θ max, deg	68.284
data/parameters	10877/749

R_1	0.0462
wR_2	0.1251
GOF	1.034

References

[1] Burla, M.C.; Caliandro, R.; Camalli, M.; Carrozini, B.; Cascarano, G. L.; De Caro, L.; Giacovazzo, C.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **2005**, *38*, 381.

[2] Sheldrick, G. M. *Acta Crystallogr. A*. **2008**, *64*, 112.