Supplementary Information (SI) for Dalton Transactions.

Supporting information for the paper entitled:

A mixed isocyanide Mn(I) complex and its reduction to a metallate

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S1. Experimental.

S1.1. General considerations. Unless otherwise stated, reagent-grade starting materials were purchased from commercial sources and either used as received or purified by standard procedures. Solvents were dried and deoxygenated according to standard procedures. CN*p*-FAr$^{\mathrm{DarF2}}$ was prepared as previously described.[1]

S1.2. Physical Measurements.

NMR spectra were recorded with JEOL 600 MHz ECZ or Bruker 300 multinuclear spectrometers. Solid-state IR spectra were collected at 2 cm^{-1} resolution using a Bruker Platinum Alpha ATR-IR or a Thermo Scientific Nicolet iS10 ATR spectrometer. Intensities are classified as vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder.

S1.3. Synthetic procedures.

***mer, trans*-[Mn(CN*p*-FAr$^{\mathrm{DarF2}}$)$_3$(CN$^{\mathrm{t}}$Bu)$_2$Br] (2)**: [Mn(CO)$_5$Br] (55.0 mg, 0.2 mmol) was dissolved in 3 mL of CH_2Cl_2. CN$^{\mathrm{t}}$Bu (45 µL, 0.4 mmol) was added to the solution, which was then stirred for 24 h at room temperature under the exclusion of light as described by Treichel *et al.*[2] CN*p*-FAr$^{\mathrm{DarF2}}$ (327 mg, 0.6 mmol, 3.0 eq) was then added in toluene (2 mL). The resulting pale-yellow solution was heated to 110°C to allow the evaporation of CH_2Cl_2. The heating was then continued under reflux for 5 h. During this time, the reaction mixture turned bright red. ^{19}F NMR spectroscopy was used to monitor the progress of the reaction. Once the starting material was consumed, the reaction mixture was slowly cooled to room temperature. Red-orange crystals formed upon cooling, which were filtered off, washed with a small amount of cold toluene and n-pentane and dried under reduced pressure. Yield: 154 mg, 40%. Elemental analysis: Calcd. for $C_{79}H_{42}BrF_{39}MnN_5$: C, 49.0; H, 2.2; N, 3.6%. Found: C, 49.0; H, 2.2; N, 3.7%. ^{1}H NMR (THF-d$_8$, ppm): 8.00-7.92 (m, 12H), 7.60 (s, 6H), 7.39-7.31 (m, 6H), 1.07 (s, 18H). ^{19}F NMR (THF-d$_8$, ppm) : –62.60 to –63.49 (m, 36F), –113.32 (m$_c$, 2F), –116.23 (m$_c$, 1F). IR (cm^{-1}): 2113 (m, $\nu_{C\equiv N}$), 2024 (s, $\nu_{C\equiv N}$), 1952 (m), 1596 (m), 1362 (s), 1264 (vs), 1161 (s), 1126 (vs), 1064 (sh). ESI+ MS: m/z = 1856.218 $[M - Br]^+$ (calcd. 1856.220), 1884.223 $[M - Br + CO]^+$ (calcd. 1884.215), 1897.243 $[M - Br + CH_3CN]^+$ (calcd. 1897.246).

[K(18-crown-6)][Mn(CN*p*-FAr$^{\mathrm{DarF2}}$)$_3$(CN$^{\mathrm{t}}$Bu)$_2$] (3): [Mn(CN*p*-FAr$^{\mathrm{DarF2}}$)$_3$(CN$^{\mathrm{t}}$Bu)$_2$Br] (130 mg, 0.07 mmol) was dissolved in THF (2 mL). Freshly prepared KC_8 (18 mg, 0.14 mmol) was suspended in another vial in THF (2 mL). Both solutions were then frozen using liquid nitrogen. The solutions were quickly mixed upon thawing and then slowly allowed to warm up to room temperature. The initially bright red mixture became slowly yellow then green and eventually dark blue within 10 minutes. Once the color stopped changing, volatiles were removed under reduced pressure. The obtained brown residue was then dissolved in *n*-pentane and filtered over Celite. A solution of 18-crown-6 (18 mg, 0.07 mmol) in diethyl ether (2 mL) was added resulting in the formation of a precipitate. Volatiles were removed under reduced pressure and the obtained solid was washed with *n*-pentane. It was dissolved in toluene (2 mL) and few drops of benzene were added to the solution which was then cooled to -35°C. Very dark red crystals suitable for X-ray diffraction formed overnight. The obtained crystals were filtered off, washed with little *n*-pentane and then dried under reduced pressure. Yield: 62 mg, 43%. ^{1}H NMR (THF-d$_8$, ppm): 8.19 (s, 12H), 7.69 (6H), 7.21-7.00 (m, 6H), 3.60 (s, 24H), 0.25 (s, 18H). The given integrations were corrected to consider overlapping tetrahydrofuran and toluene signals. ^{19}F NMR (THF-d$_8$, ppm) : –62.95 (s, 36F), –126.68 (s, 3F). IR (ATR, cm^{-1}) : 2919 (br), 1896 (sh), 1807 (s, $\nu_{C\equiv N}$), 1610 (w), 1457 (m), 1396 (s), 1359 (s), 1273 (vs), 1212 (w), 1163 (s), 1122 (vs), 1100 (vs), 998 (w), 959 (s), 993 (m), 867 (w), 843 (m), 792 (w), 732 (w), 703 (m), 681 (m), 631 (w), 583 (s). Mass spectra of reasonable quality and satisfactory elemental analyses could not be obtained due to the sensitivity of the compound. The use of a larger excess of KC_8, which is recommended when using commercial sources or older samples increases the yield slightly, but causes problems during the isolation of a pure product.

S2. Crystallographic Structure Determinations

S2.1. General. The intensities for the X–ray determinations were collected on Bruker D8 Venture and Rigaku MicroMax-007HF instruments with Cu Kα radiation. The space groups were determined by the inspection of systematical absences. Structure solution and refinement were performed with the SHELX program package.[3,4] Hydrogen atoms were placed at calculated positions and treated with the 'riding model' option of SHELXL. The representation of molecular structures was done using the program MERCURY, vers. 2024, 2.0.[5] Additional information on the structure determinations has been deposited with the Cambridge Crystallographic Data Centre under the deposition numbers given in Table S2.1.

Table S2.1 Crystal data and structure determination parameters

	$[Mn(CN\textit{p}\text{-}F\text{-}Ar^{DArF2})_3(CN^tBu)_2Br]$ (**2**) x 0.5 toluene	$[K(18\text{-crown-}6)][Mn(CN\textit{p}\text{-}FAr^{DArF2})_3\text{-}(CN^tBu)_2]$ (**3**) x 0.5 benzene x 0.5 toluene
Formula	$C_{82.5}H_{46}BrF_{39}MnN_5$	$C_{97.5}H_{70}F_{39}KMnN_5O_6$
M_w	1983.09	2242.62
Temperature/K	126	100
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a/Å	12.7013(3))	20.2926(11)
b/Å	13.2387(3)	22.9330(12)
c/Å	24.4356(6)	21.0751(11)
α	87.5900(10)	90
β	88.9030(10)	100.430(3)
γ	83.9410(10)	90
V/ Å^3	4081.80(17)	9645.7(9)
Z	2	4
ρ_{calc} g/cm^{-3}	1.614	1.544
μ/mm^{-1}	3.142	2.69
F(000)	1974.0	4532.0
Crystal size/mm^3	0.22 × 0.14 × 0.09	0.1 × 0.1 × 0.1
Radiation	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)
2Θ range for data collection/°	3.62 to 154.84	5.564 to 129.192
Reflections collected	47210	16142
Independent reflections	16626 [R_{int} = 0.0295, R_{sigma} = 0.0307]	16142 [R_{int} = 0.06, R_{sigma} = 0.0491]
Data/restraints/parameters	16626/282/1420	16142/81/1444
Goodness-of-fit on F^2	1.086	1.089
Final R indexes [I>=2σ (I)]	R_1 = 0.0506, wR_2 = 0.1424	R_1 = 0.0642, wR_2 = 0.1487
Final R indexes [all data]	R_1 = 0.0580, wR_2 = 0.1521	R_1 = 0.0899, wR_2 = 0.1617
Largest diff. peak/hole / e Å^{-3}	0.80/-0.43	0.80/-0.39
Diffractometer	Bruker APEX	Rigaku MicroMax-007HF
Deposit number	CCDC-2410581	CCDC-2410582

S2.2 Disorder and Refinement Specifics. Both structures contain rotational disorder of the trifluoromethyl groups, that of compound 2 additionally disordered CMe_3 groups. They were modeled and refined anisotropically. The solid-state structures of **2** contains 0.5 molecule of disordered toluene, while a disordered mixture of 0.5 equivalents benzene and toluene has been found in the lattice of compound **3**. Ellipsoid plots showing the disordered units are shown in the following Figures.

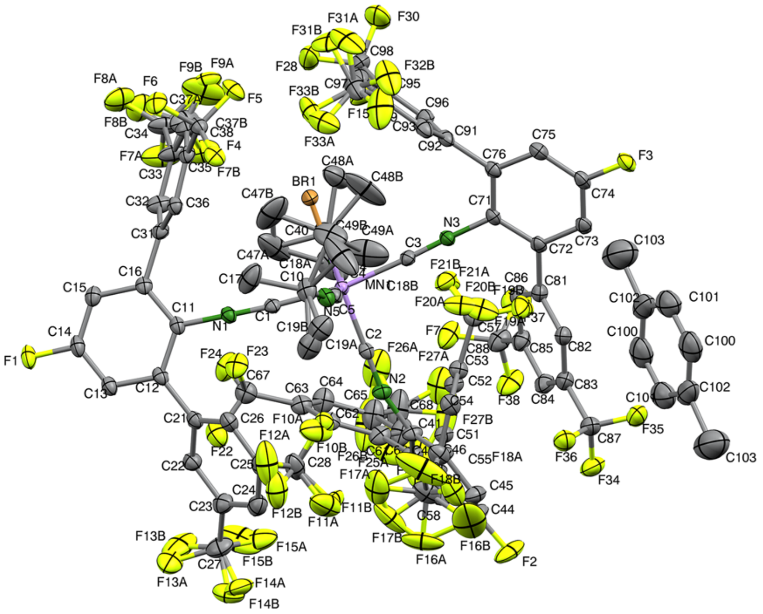

Figure S2.1. Ellipsoid representation of *mer,trans*-[Mn(CN*p*-FAr$^{\mathrm{DarF2}}$)$_3$(CN^{t}Bu)$_2$Br] **(2)** x 0.5 toluene. The thermal ellipsoids are set at a 30% probability level. Hydrogen atoms are omitted for clarity. Some of the CF$_3$ and CMe$_3$ groups as well as the solvent toluene are disordered. The disorders were treated using appropriate distance and thermal ellipsoid restraints.

Table S2.2. Selected bond lengths (Å) and angles (°) in *mer,trans*-[Mn(CN*p*-FAr$^{\mathrm{DarF2}}$)$_3$(CN^{t}Bu)$_2$Br] (**2**).

Mn1-C1	1.893(2)	Mn1-C2	1.806(2)	Mn1-C3	1.898(2)
Mn1-C4	1.906(3)	Mn1-C5	1.924(3)	Mn1-Br1	2.5324(4)
C1-N1	1.170(3)	C2-N2	1.180(3)	C3-N3	1.166(3)
C4-N4	1.162(4)	C5-N5	1.161(3)		
Br1-Mn1-C1	85.73(7)	Br1-Mn1-C2	177.66(7)	Br1-Mn1-C3	84.78(7)
Br1-Mn1-C4	85.81(8)	Br1-Mn1-C5	85.86(8)	C1-Mn1-C2	95.62(10)
C1-Mn1-C3	170.51(10)	C1-Mn1-C4	88.80(10)	C1-Mn1-C5	86.92(10)
C2-Mn1-C3	93.85(10)	C2-Mn1-C4	92.31(11)	C2-Mn1-C5	96.10(10)
C3-Mn1-C4	90.33(10)	C3-Mn1-C5	92.57(10)	C4-Mn1-C5	170.90(11)
Mn1-C1-N1	176.8(2)	Mn1-C2-N2	177.4(2)	Mn1-C3-N3	177.2(2)
Mn1-C4-N4	177.0(3)	Mn1-C5-N5	173.2(2)	C1-N1-C11	174.2(2)
C2-N2-C41	165.2(3)	C3-N3-C71	166.6(2)	C4-N4-C40	161.9(3)
C5-N5-C10	165.9(3)				

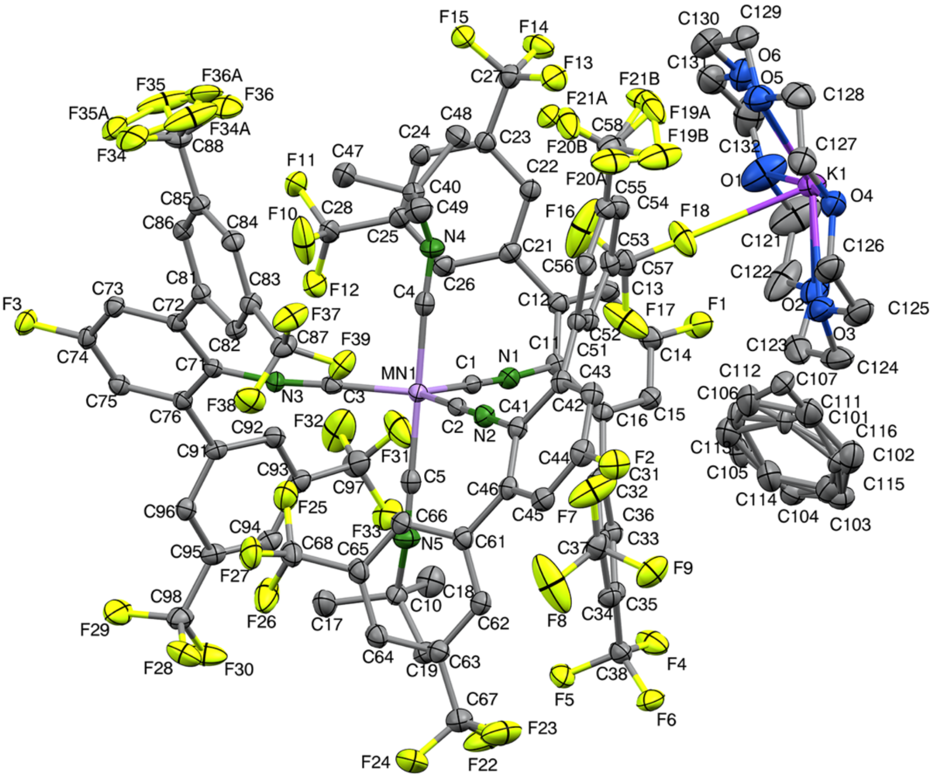

Figure S2.2. Ellipsoid representation of [K(18-crown-6)][Mn(CN*p*-FAr$^{\mathrm{DarF2}}$)$_3$(CN^{t}Bu)$_2$]) (**3**) x 0.5 toluene/benzene . The thermal ellipsoids are set at a 30% probability level. Hydrogen atoms are omitted for clarity. Some of the CF$_3$ groups and the solvent molecules are disordered. The disorder was treated using appropriate distance and thermal ellipsoid restraints.

Table S2.3. Selected bond lengths (Å) and angles (°) in [K(18-crown-6)][Mn(CN*p*-FAr$^{\mathrm{DarF2}}$)$_3$(CN^{t}Bu)$_2$]) (**3**) x toluene/benzene.

Mn1-C1	1.811(4)	Mn1-C2	1.828(4)	Mn1-C3	1.838(4)
Mn1-C4	1.877(4)	Mn1-C5	1.873(4)	C1-N1	1.210(5)
C2-N2	1.203(5)	C3-N3	1.209(4)	C4-N4	1.191(5)
C5-N5	1.182(5)	K1-F18	2.909(3)		
C1-Mn1-C2	115.51(15)	C1-Mn1-C3	114.76(15)	C1-Mn1-C4	90.65(16)
C1-Mn1-C5	91.83(15)	C2-Mn1-C3	129.74(15)	C2-Mn1-C4	87.84(15)
C2-Mn1-C5	89.70(15)	C3-Mn1-C4	91.61(15)	C3-Mn1-C5	88.76(15)
C4-Mn1-C5	177.08(17)	Mn1-C1-N1	178.3(3)	Mn1-C2-N2	178.3(3)
Mn1-C3-N3	177.3(3)	Mn1-C4-N4	176.5(3)	Mn1-C5-N5	179.2(4)
C1-N1-C11	170.5(4)	C2-N2-C41	177.3(4)	C3-N3-C71	170.8(3)
C4-N4-C40	146.8(4)	C5-N5-C10	151.7(4)		

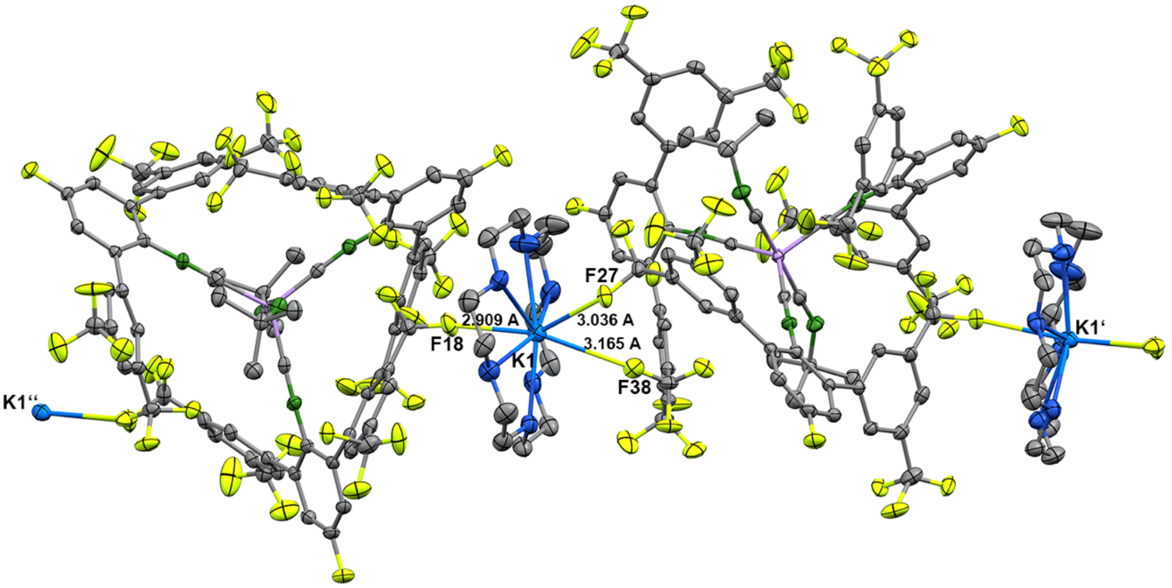

Figure S2.3. Representation of the weak K…F interactions in [K(18-crown-6)][Mn(CN*p*-FAr^{DarF2})$_3$-(CN^{t}Bu)$_2$]) (**3**).

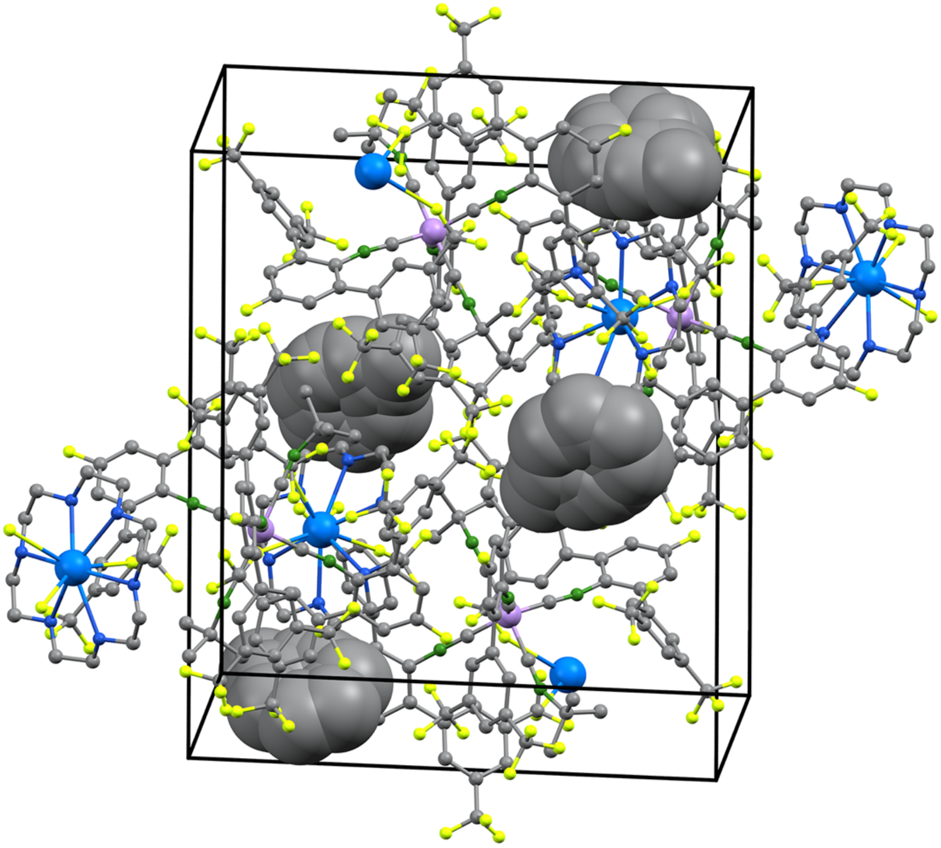

Figure S2.4. Unit cell of [K(18-crown-6)][Mn(CN*p*-FAr^{DarF2})$_3$(CN^{t}Bu)$_2$]) (**3**) x 0.5 toluene/benzene illustrating the solvent-filled voids.

S3. Spectra

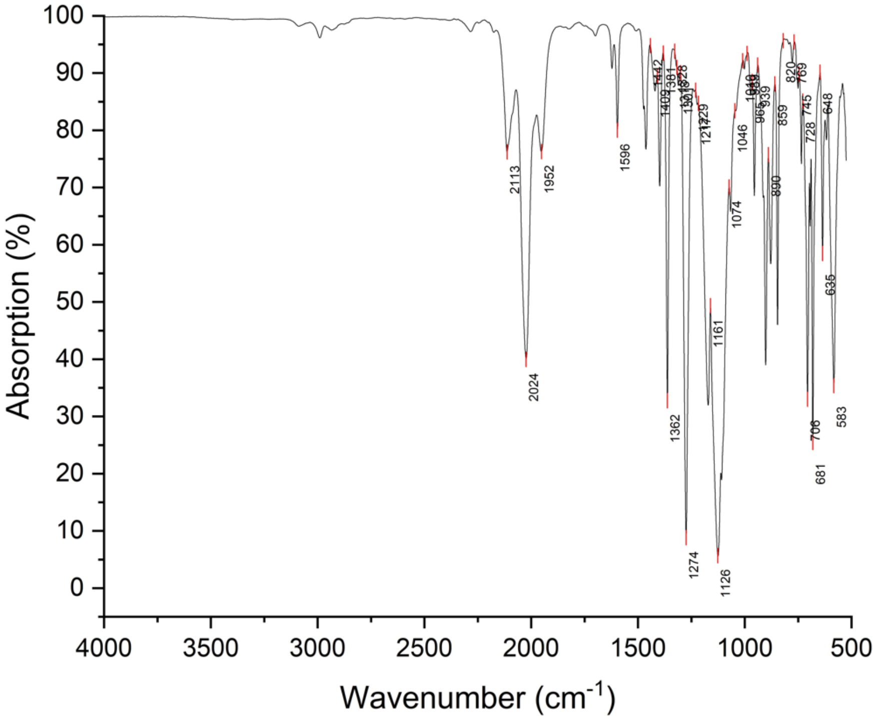

Figure S3.1. IR spectrum of *mer,trans*-[Mn(CN*p*-FAr$^{\mathrm{DarF2}}$)$_3$(CN^{t}Bu)$_2$Br] (**2**).

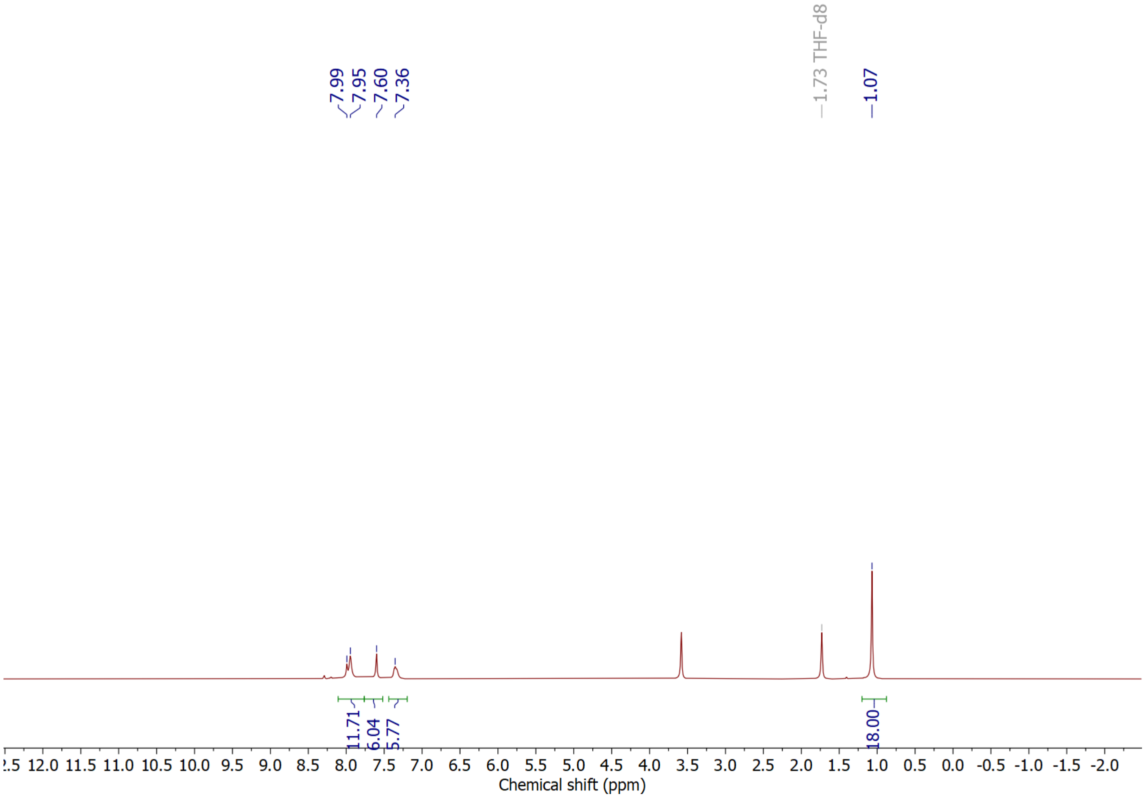

Figure S3.2. ^{1}H NMR spectrum of *mer,trans*-[Mn(CN*p*-FAr$^{\mathrm{DarF2}}$)$_3$(CN^{t}Bu)$_2$Br] (**2**) in THF-d$_8$.

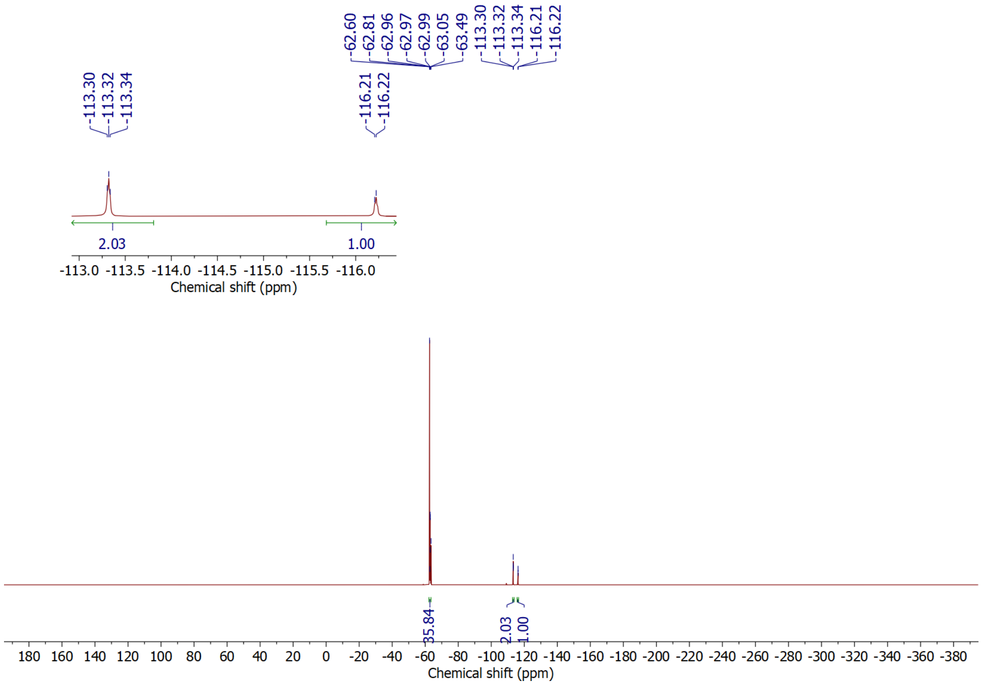

Figure S3.3. ^{19}F NMR spectrum of *mer,trans*-[Mn(CN*p*-FAr$^{\mathrm{DarF2}}$)$_3$(CN^{t}Bu)$_2$Br] **(2)** in THF-d$_8$.

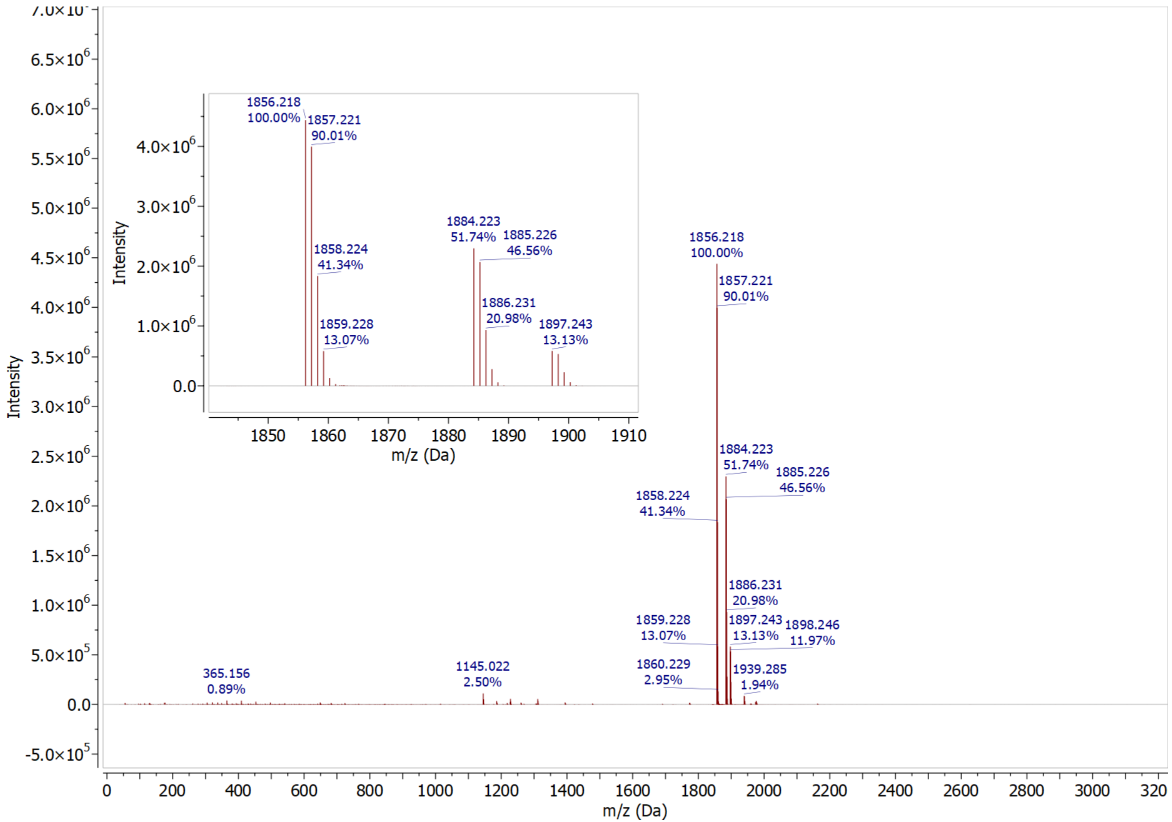

Figure S3.4. ESI+ mass spectrum of *mer,trans*-[Mn(CN*p*-FAr$^{\mathrm{DarF2}}$)$_3$(CN^{t}Bu)$_2$Br] **(2)** in acetonitrile.

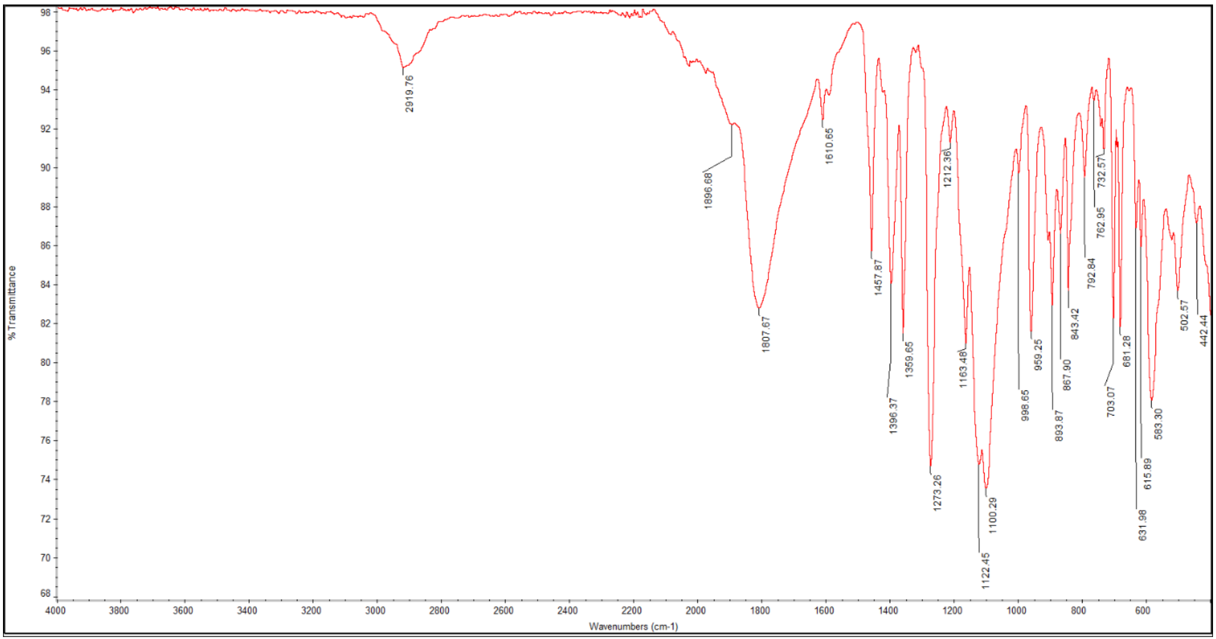

Figure S3.5. IR spectrum of [K(18-crown-6)][Mn(CNp-FAr$^{\mathrm{DarF2}}$)$_3$(CN^{t}Bu)$_2$]) (**3**).

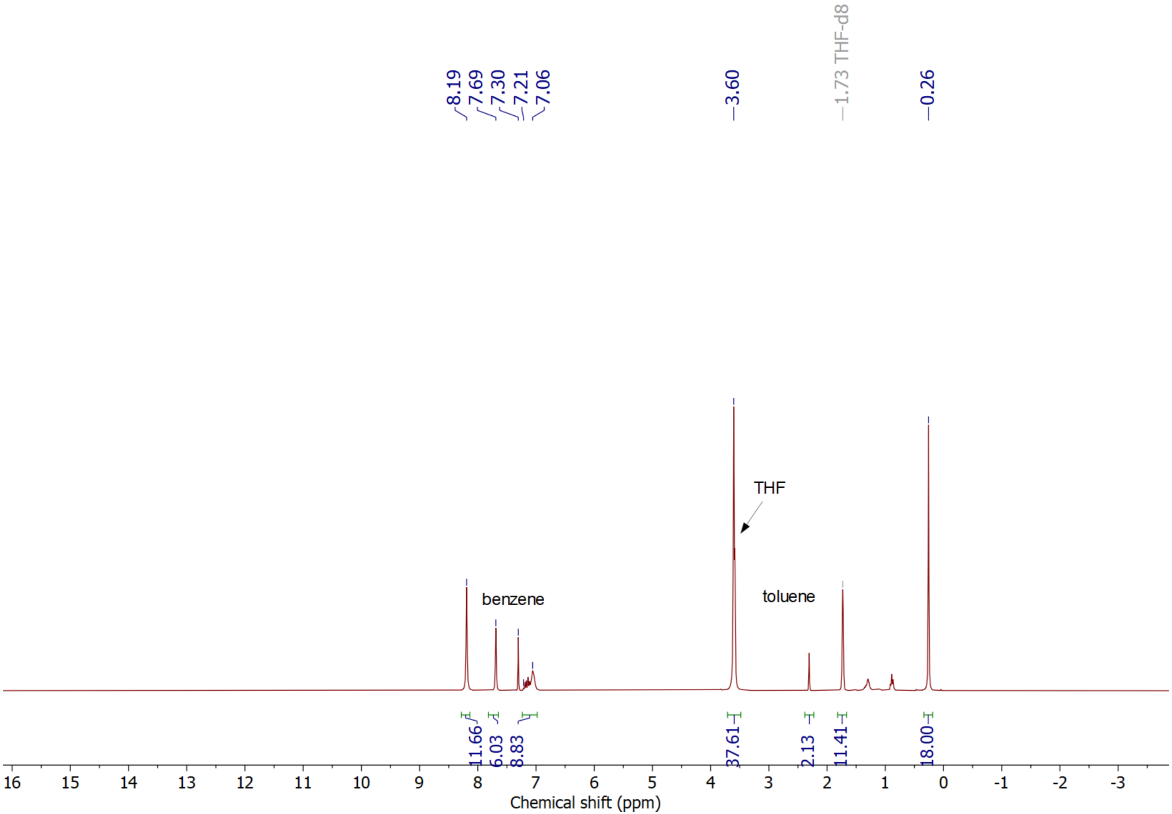

Figure S3.6. ^{1}H NMR spectrum of [K(18-crown-6)][Mn(CNp-FAr$^{\mathrm{DarF2}}$)$_3$(CN^{t}Bu)$_2$]) (**3**) in THF-d$_8$

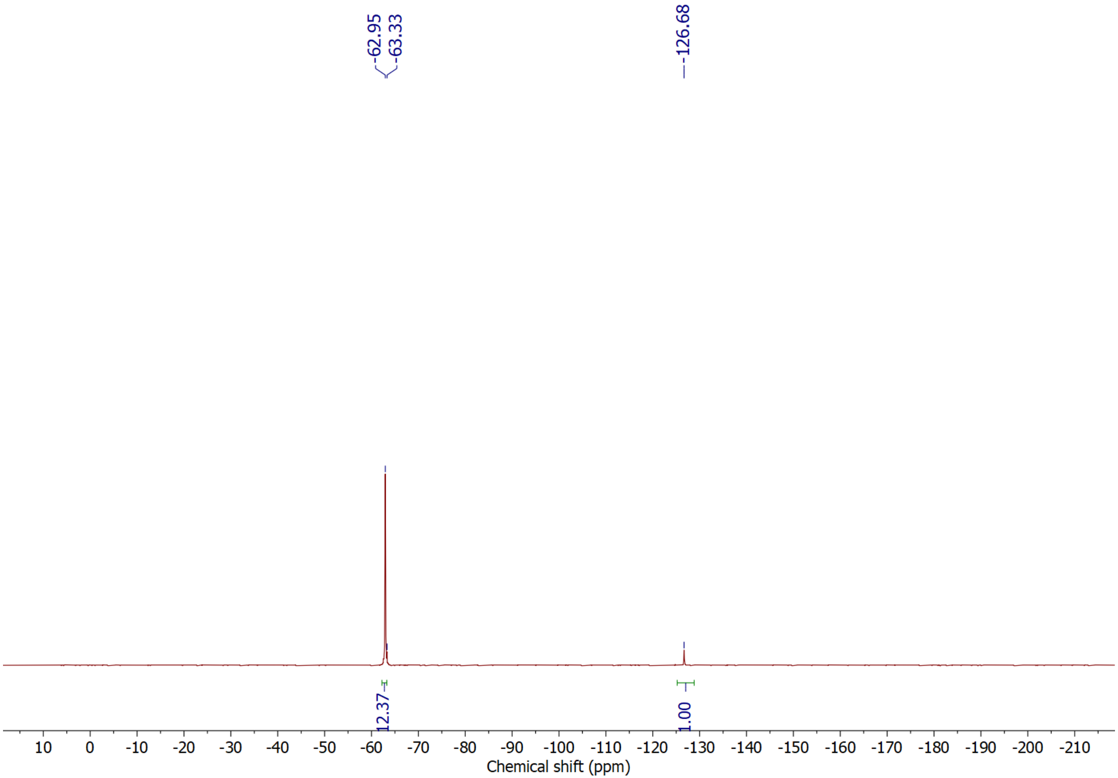

Figure S3.7. ^{19}F NMR spectrum of [K(18-crown-6)][Mn(CN*p*-FAr^{DarF2})$_3$(CN^{t}Bu)$_2$]) (**3**) in THF-d_8.

S4. References

[1] T. B. Ditri, A. E. Carpenter, D. S. Ripatti, C. E. Moore, A. L. Rheingold, J. S. Figueroa, *Inorg. Chem.*, 2013, **52**, 13216-13229.

[2] P. M. Treichel, G. E. Dirreen and H. J. Mueh, *J. Organomet. Chem.*, 1972, **44**, 339-352.

[3] G. M. Sheldrick, *Acta Crystallogr., Sect. A,* 2008, **64**, 112-122.

[4] G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.* 2015, **71**, 3-8.

[5] C. F. Macrae, I. Sovago, S. J. Cottrell, P. T. A. Galek, P. McCabe, E. Pidcock, M. Platings, G. P. Shields, J. S. Stevens, M. Towler, M. Mercury 4.0: From visualization to analysis, design and prediction. *J. Appl. Cryst.* 2020, **53**, 226–235.