

Supporting Information

Facile N···N Coupling of Manganese(V) Imido Species

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Table S1. Representative data for the formation of the intermediate (**A**) between **2** (2×10^{-4} M) and TFAA in $\text{ClCH}_2\text{CH}_2\text{Cl}$ at 298.0 K and $I = 0.1$ M

TFAA / M	$k_{\text{obs}} / \text{s}^{-1}$
0.002	3.08×10^{-1}
0.004	6.04×10^{-1}
0.008	1.20
0.010	1.79
0.020	3.03
0.040	3.97
0.080	4.79
0.100	4.95

Table S2. Representative data for the decay of the intermediate (**A**) in ClCH₂CH₂Cl at 298.0 K, $I = 0.1$ M, [TFAA] = 0.1 M.

[Mn ^{V(N)}] / M	Initial rate / M s ⁻¹
5.01×10^{-5}	7.86×10^{-5}
7.87×10^{-5}	2.36×10^{-4}
9.66×10^{-5}	4.86×10^{-4}
1.79×10^{-4}	1.32×10^{-3}
2.31×10^{-4}	2.89×10^{-3}
3.48×10^{-4}	7.12×10^{-3}
4.04×10^{-4}	8.34×10^{-3}
5.22×10^{-4}	1.48×10^{-2}

Table S3. Representative data for the temperature dependence of k_2 step in $\text{ClCH}_2\text{CH}_2\text{Cl}$ with $[2] = 5 \times 10^{-5} \text{ M} - 5 \times 10^{-4} \text{ M}$ and $[\text{TFAA}] = 0.1 \text{ M}$

Temperature / K	$k_2 / \text{M}^{-1} \text{ s}^{-1}$
288	$(1.8 \pm 0.1) \times 10^4$
298	$(2.7 \pm 0.2) \times 10^4$
308	$(4.3 \pm 0.4) \times 10^4$
318	$(6.1 \pm 0.1) \times 10^4$

Table S4. Representative data for the decay of the intermediate (**B**) in ClCH₂CH₂Cl at 298.0 K, $I = 0.1$ M, [TFA] = 0.1 M.

Mn ^V (N) / M	Initial rate / M s ⁻¹
7.50×10^{-5}	3.39×10^{-4}
9.30×10^{-5}	8.02×10^{-4}
1.79×10^{-4}	1.21×10^{-3}
3.15×10^{-4}	3.25×10^{-3}
3.90×10^{-4}	4.61×10^{-3}
4.83×10^{-4}	7.05×10^{-3}
5.26×10^{-4}	8.17×10^{-3}

Table S5. Representative data for the temperature dependence of k_2' step in $\text{ClCH}_2\text{CH}_2\text{Cl}$ with $[2] = 5 \times 10^{-5} \text{ M} - 5 \times 10^{-4} \text{ M}$ and $[\text{TFA}] = 0.1 \text{ M}$

Temperature / K	$k_2' / \text{M}^{-1} \text{s}^{-1}$
288	$(8.1 \pm 0.4) \times 10^3$
298	$(1.4 \pm 0.2) \times 10^4$
308	$(2.1 \pm 0.3) \times 10^4$
318	$(4.0 \pm 0.2) \times 10^4$

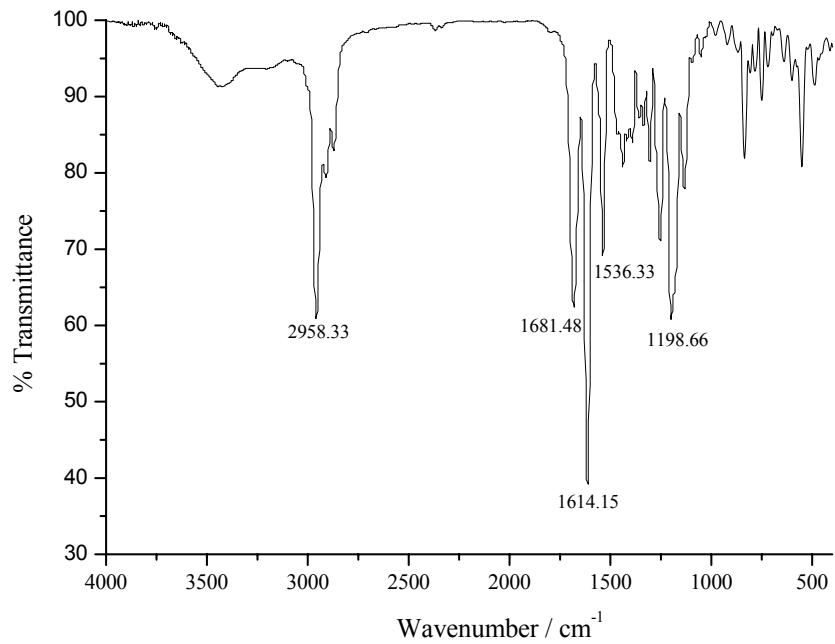


Figure S1. IR Spectrum (KBr) of $[\text{Mn}^{\text{III}}(\text{'Bu}_4\text{salen})(\text{CF}_3\text{CO}_2)]$.

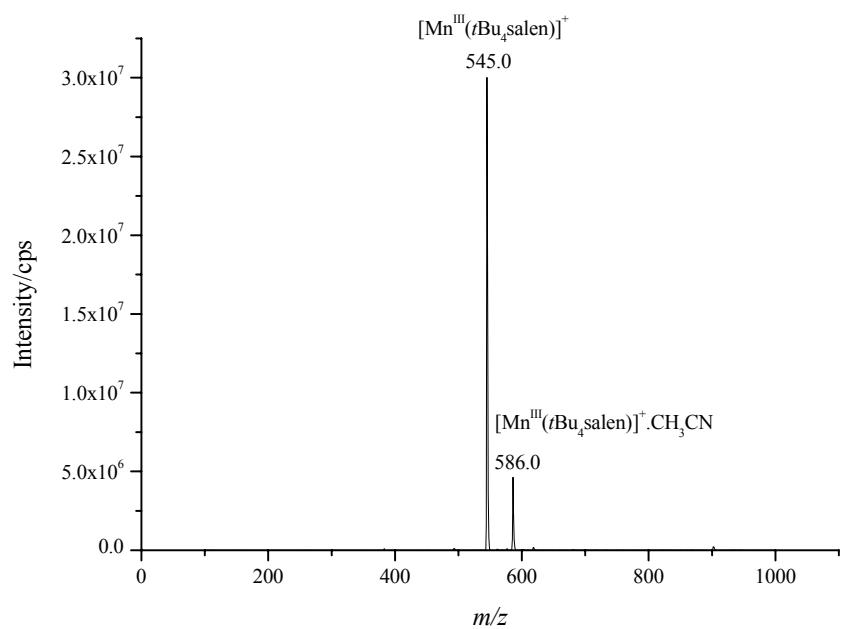


Figure S2. ESI-MS (+ve mode) of $[\text{Mn}^{\text{III}}(\text{tBu}_4\text{salen})(\text{CF}_3\text{CO}_2)]$ in CH_3CN .

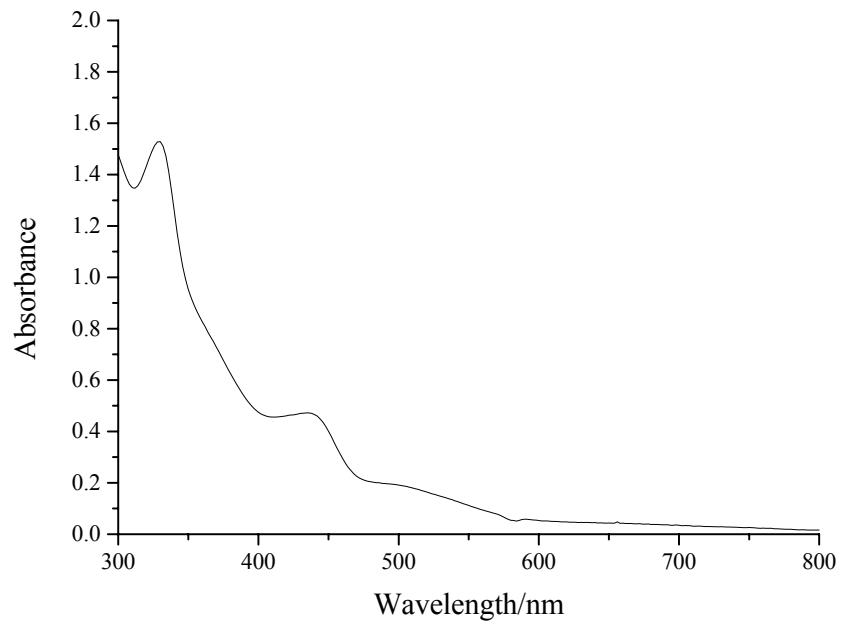


Figure S3. UV-Vis spectrum of $[\text{Mn}^{\text{III}}(\text{tBu}_4\text{salen})(\text{CF}_3\text{CO}_2)]$ (1×10^{-4} M) in $\text{ClCH}_2\text{CH}_2\text{Cl}$.

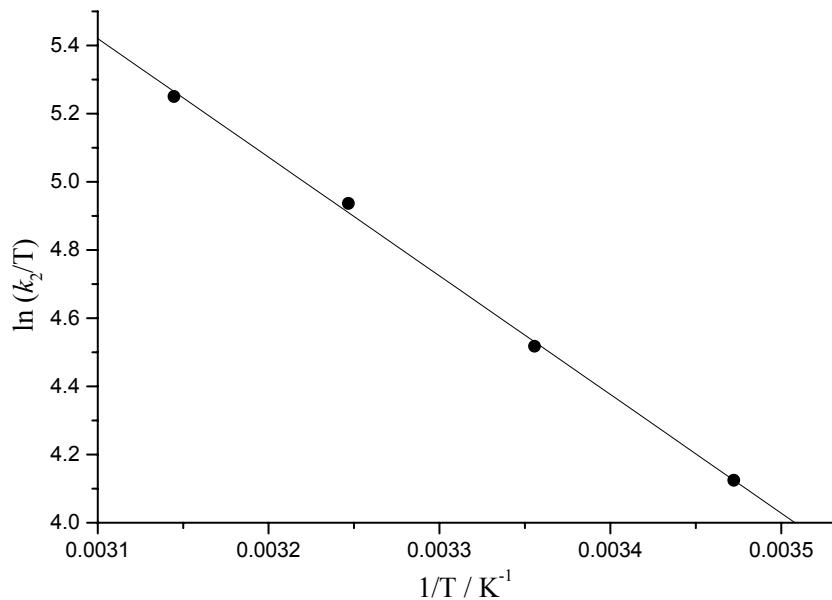


Figure S4. Plot of $\ln(k_2/T)$ vs $1/T$ for the decay of intermediate (A) in $\text{ClCH}_2\text{CH}_2\text{Cl}$.

[slope = $-(3.48 \pm 0.10) \times 10^3$; y-intercept = $(1.62 \pm 0.03) \times 10^1$; $r = -0.999$]

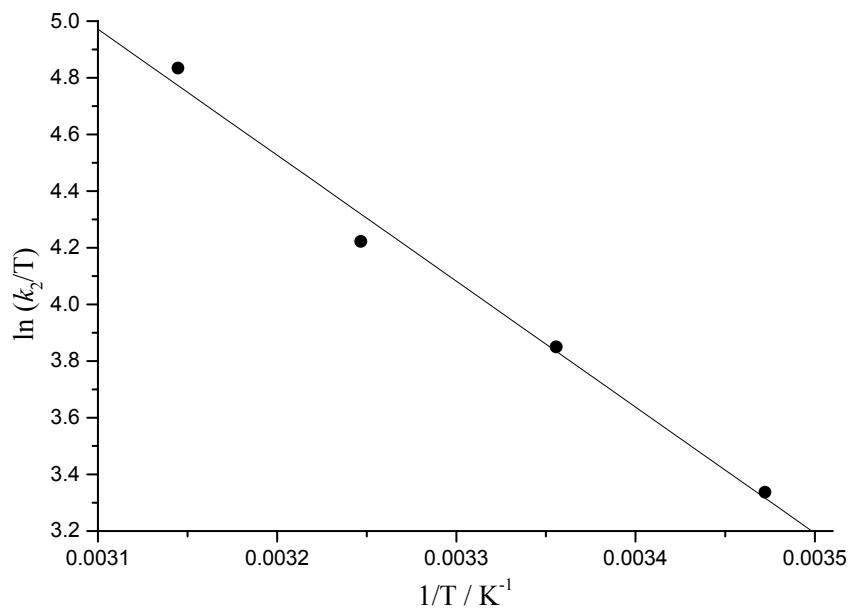


Figure S5. Plot of $\ln(k_2/T)$ vs $1/T$ for the decay of intermediate B in $\text{ClCH}_2\text{CH}_2\text{Cl}$.

[slope = $-(4.45 \pm 0.34) \times 10^3$; y-intercept = $(1.88 \pm 0.11) \times 10^1$; $r = -0.994$]