

Supporting Information:

Identification of Unknown Metal Acetylacetonate Complexes via Evan's Method

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1 General Considerations

KMnO₄, acetylacetonate, CDCl₃, and CHCl₃ were all sourced from Oakwood Chemicals. A Bruker U500 500 MHz NMR spectrometer was used to obtain all ¹H NMR spectra.

2 Experimental

2.1 Synthesis of Mn(acac)₃^{S1,S2}

To a 250 mL beaker was charged 0.500 g KMnO₄ (3.16 mmol, 1 equiv.), 75 mL DI water, and a stir bar. This solution was heated to 70 °C with stirring until total dissolution. The beaker was cooled in an ice bath, and 2.30 mL acetylacetone (22.4 mmol, 7 equiv.) was slowly poured in over the course of 3 minutes. The solution was brought to a boil for 5 minutes, and was cooled again in an ice bath. The dark brown Mn(acac)₃ crystals were then filtered through a coarse glass frit, washed with 10 mL DI water 3 times, and dried on vacuum for 30 minutes. This reaction resulted in a percent yield of 41% (0.46 g total, 1.11 g exp.).

2.2 Measurement of Magnetic Moments^{S1}

A capillary tube containing 2 mL of 50:1 (v/v) deuterio:proteo chloroform was inserted into a NMR tube. NMR samples were prepared through the addition of 10–15 mg of the species and 600 µL of the same chloroform solution. This procedure was performed for Mn(acac)₃ and the four unknown samples provided. A summary of observations for each of the unknowns is tabulated below. The colors of the unknowns agree well with the colors of their assignments in literature.^{S3–S5}

All spectra were baselined, phase-corrected, and referenced according to the control TMS peak (identified by its lack of peak broadening) prior to analysis. The “p” prefix denotes the paramagnetically shifted peak. The ¹H NMR interpretation (500 MHz, δ, 50:1 d:p chloroform) is as follows. **Mn(acac)₃**: 7.32 ppm (CHCl₃), 4.70 ppm (p-CHCl₃), 2.17 ppm

Table S1: Table of observations recorded for each of the unknowns.

Unk. No.	Color	m_{solid} (g)	m_{solvent} (g)	$\Delta\nu$ (Hz)	T (K)	μ (μ_B)	Assignment
Mn(acac) ₃	Purple	0.0149	0.977	1315	293	4.97	—
1	Green	0.0226	1.240	0	293	0	Low-spin Co(acac) ₃
2	Violet	0.0158	0.625	635	293	2.57	Cr(acac) ₃
3	Crimson	0.0154	0.306	1700	293	2.97	High-spin Fe(acac) ₃
4	Blue-Gray	0.0156	0.885	345	293	1.96	Cu(acac) ₂

(Mn(acac)₃). **Unknown 1:** 7.27 ppm (CHCl₃). **Unknown 2:** 7.26 ppm (CHCl₃), 8.53 ppm (p-CHCl₃). **Unknown 3:** 7.26 ppm (CHCl₃), 10.66 ppm (p-CHCl₃). **Unknown 4:** 7.26 ppm (CHCl₃), 7.96 ppm (p-CHCl₃). The lineshape of paramagnetically shifted peaks were observed to be heavily broadened, in excellent agreement with existing ¹H NMR spectra of paramagnetic compounds.^{S6}

3 ¹H NMR Spectra

In each of the following NMR spectra, there exists instrumental artifact immediately upfield each peak, altering their peak shape. These are not paramagnetic shifts, nor are they impurities. They are labelled with an asterisk “*”.

3.1 ^1H NMR Spectra of $\text{Mn}(\text{acac})_3$

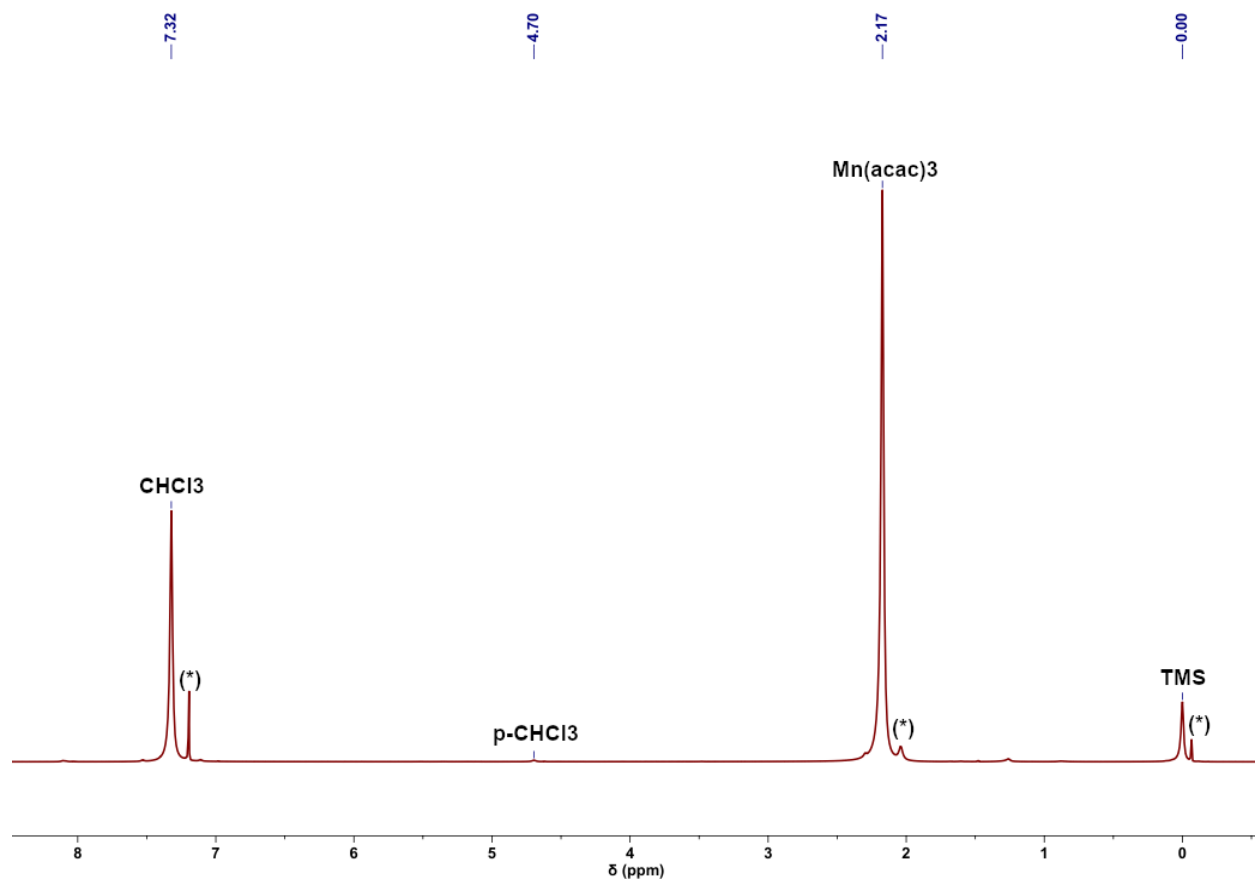


Figure S1: Fully interpreted ^1H NMR spectrum of $\text{Mn}(\text{acac})_3$. Observe the instrument artifact immediately upfield each peak.

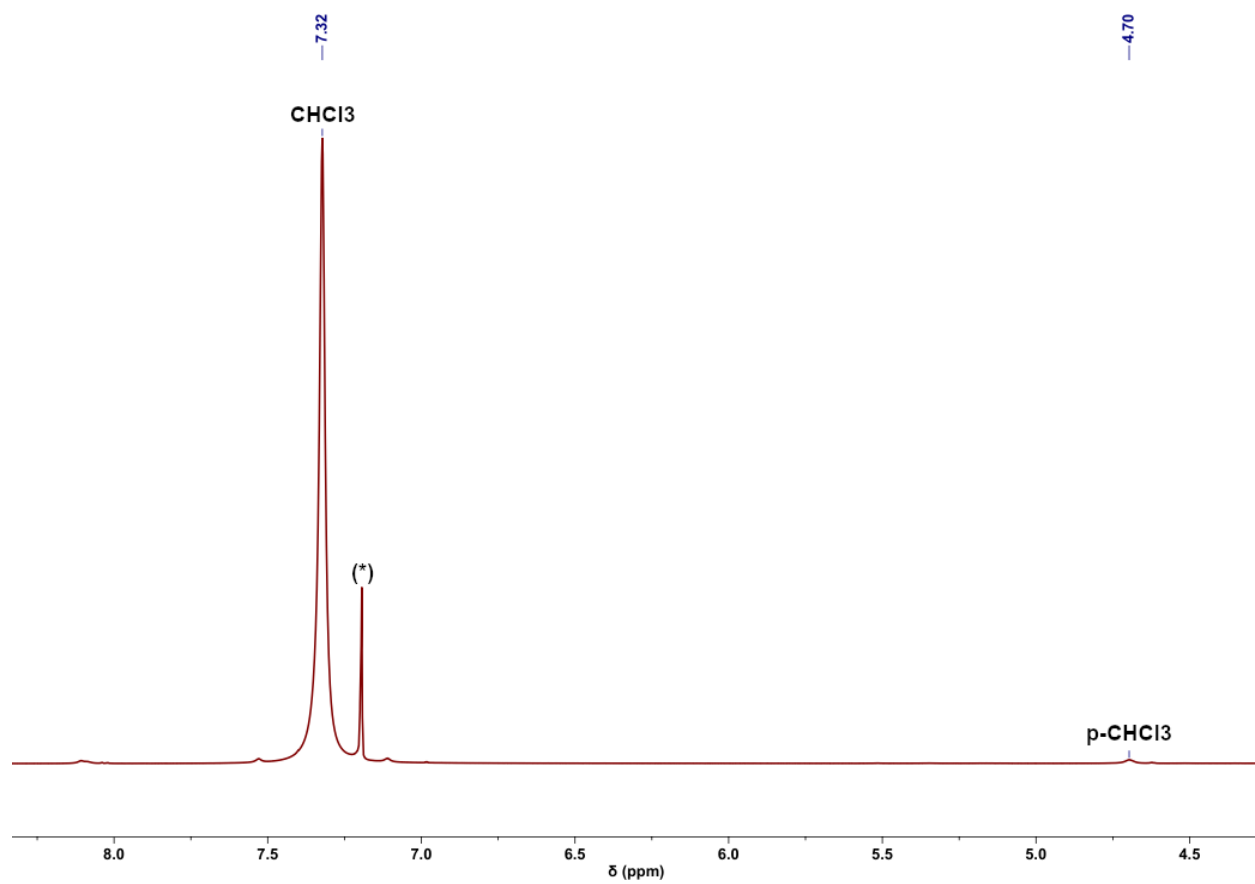


Figure S2: ^1H NMR spectrum of $\text{Mn}(\text{acac})_3$, highlighting the assigned CHCl_3 and p-CHCl_3 peaks.

3.2 ^1H NMR Spectrum of Unknown 1

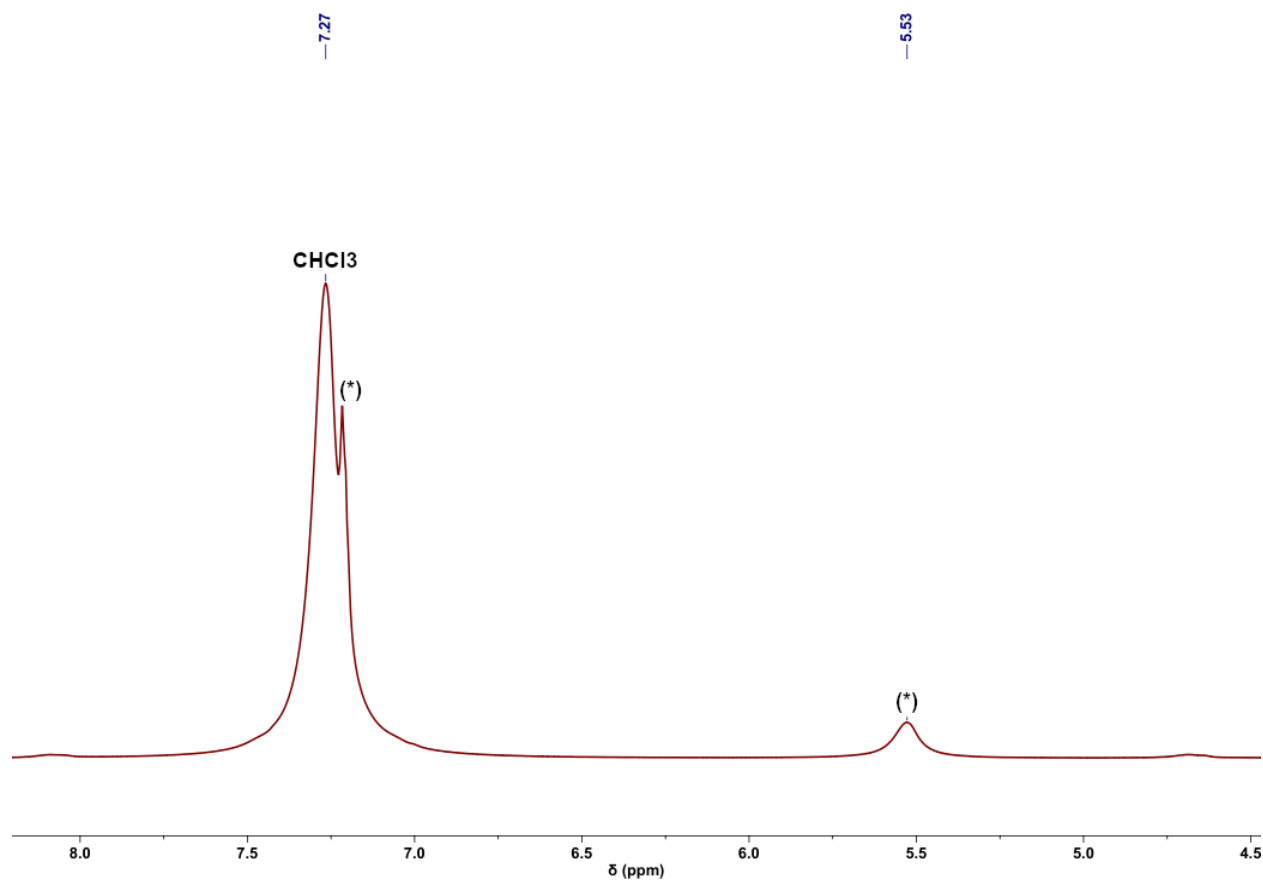


Figure S3: ^1H NMR spectrum of Unknown 1, highlighting the assigned CHCl_3 and $p\text{-CHCl}_3$ peaks. The peak at 5.53 ppm is an instrumental artifact found upfield each peak in the full ^1H NMR spectrum (not shown).

3.3 ^1H NMR Spectrum of Unknown 2

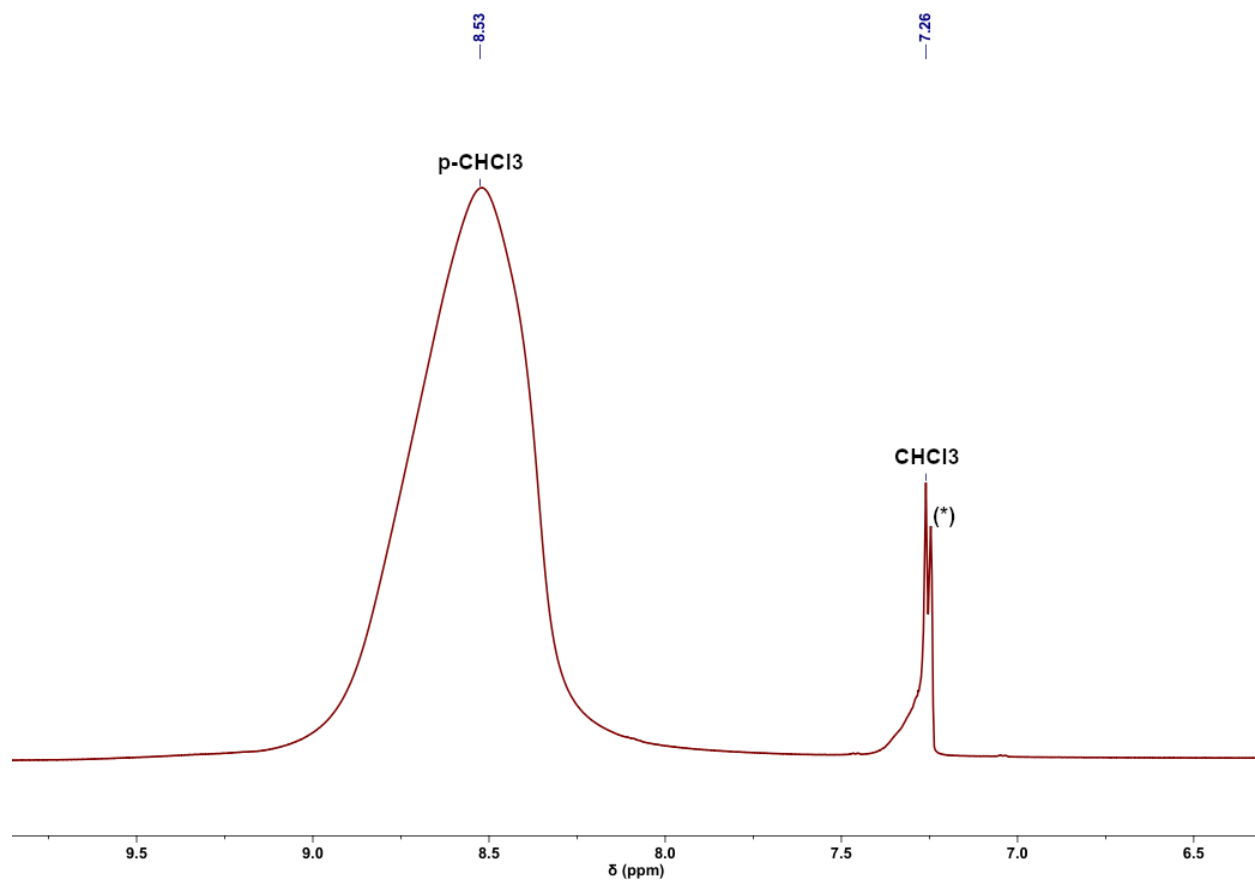


Figure S4: ^1H NMR spectrum of Unknown 2, highlighting the assigned CHCl_3 and p-CHCl_3 peaks.

3.4 ^1H NMR Spectrum of Unknown 3

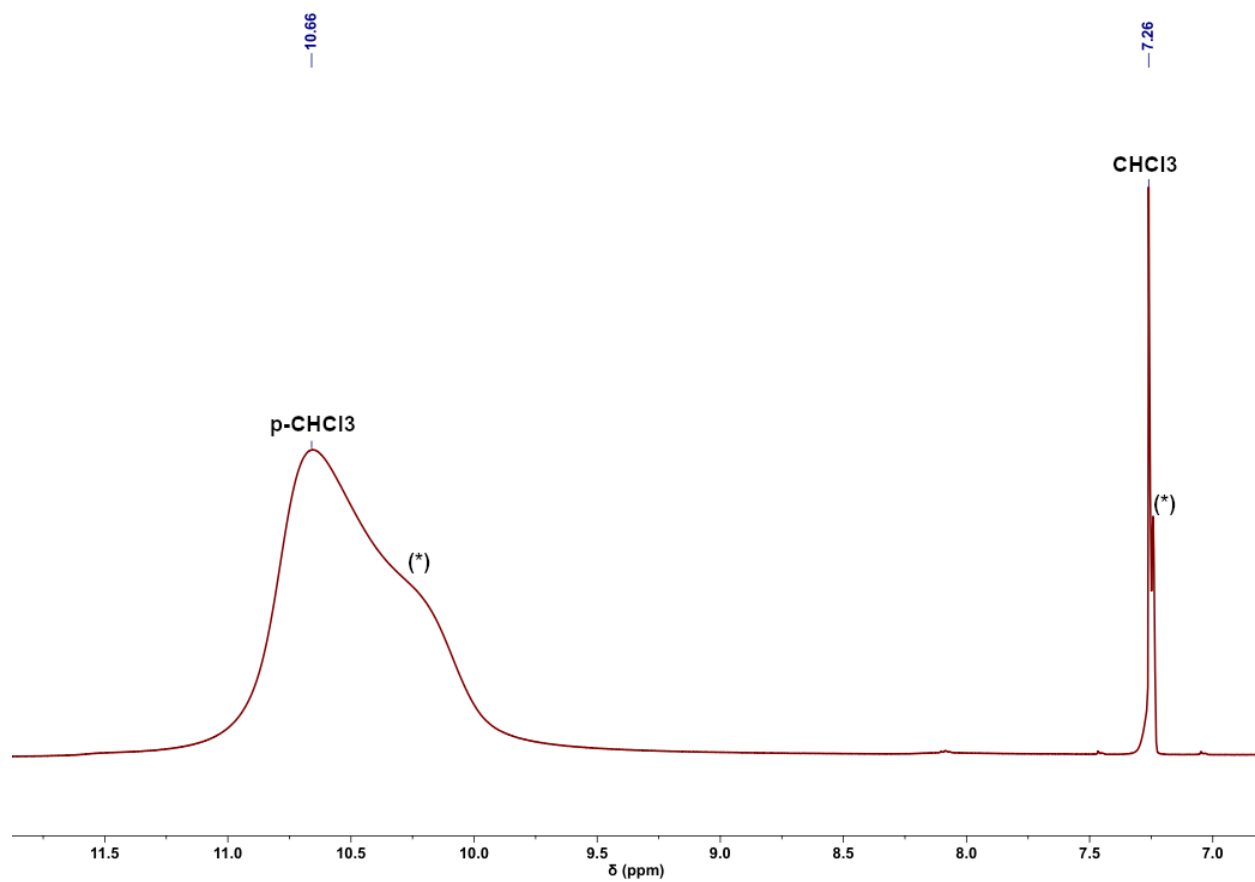


Figure S5: ^1H NMR spectrum of Unknown 3, highlighting the assigned CHCl_3 and p-CHCl_3 peaks.

3.5 ^1H NMR Spectrum of Unknown 4

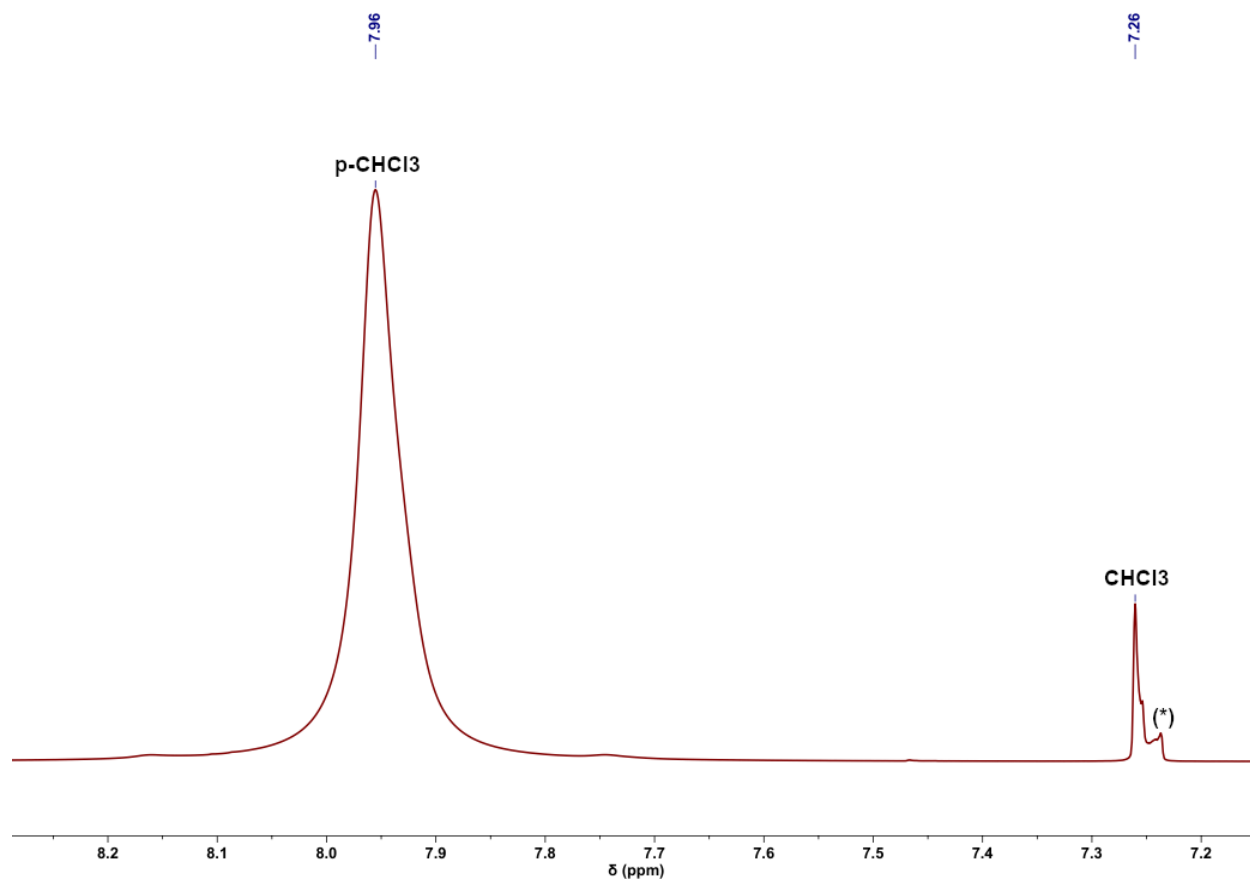


Figure S6: ^1H NMR spectrum of Unknown 4, highlighting the assigned CHCl_3 and p-CHCl_3 peaks.

4 Magnetic Moment Data

Unknowns were determined by computing the absolute difference with respect to the magnetic moments of the low and high-spin complexes of interest. The full set of data is tabulated below. Unknown 1 is excluded from Tables S3 and S4 on the basis of being diamagnetic.

4.1 Tabulated Values of μ

Table S2: μ for each of the samples in units of μ_B , calculated given the molar masses of the elements listed in the columns.

Sample	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Mn(acac) ₃	4.72	4.75	4.75	4.77	4.78	4.80	4.80	4.83
Unknown 1	0	0	0	0	0	0	0	0
Unknown 2	2.55	2.56	2.56	2.57	2.58	2.59	2.59	2.61
Unknown 3	2.96	2.97	2.97	2.99	2.99	3.00	3.00	3.02
Unknown 4	1.90	1.91	1.91	1.92	1.93	1.94	1.94	1.96

4.2 Tabulated Values of $|\Delta\mu|$ for High-Spin Complexes

Table S3: The absolute difference $|\Delta\mu|$ in the calculated (Table S2) and expected magnetic moments of the *high*-spin complexes for each element listed in the columns, in units of μ_B . Smaller differences evidence the identity of a sample being the high-spin complex of the corresponding element. As shown below, this method *almost* correctly identifies the high-spin complex Mn(acac)₃ purely on the basis of $|\Delta\mu|$.

Sample	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Mn(acac) ₃	2.99	1.92	0.88	0.12	1.13	0.09	0.93	2.00
Unknown 2	0.82	0.26	1.30	2.32	3.33	2.30	1.27	0.21
Unknown 3	1.23	0.14	0.89	1.90	2.92	1.89	0.86	0.19
Unknown 4	0.92	1.95	2.98	3.99	2.96	1.92	0.88	0.23

4.3 Tabulated Values of $|\Delta\mu|$ for Low-Spin Complexes

Table S4: The absolute difference $|\Delta\mu|$ in the calculated (Table S2) and expected magnetic moments of the *low*-spin complexes for each element listed in the columns, in units of μ_B . “inf” represents the complex being diamagnetic, and thus $|\Delta\mu|$ does not have a reasonable value for the corresponding entries.

Sample	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Mn(acac) ₃	2.99	1.92	0.88	1.94	3.05	inf	3.07	2.00
Unknown 2	0.82	0.26	1.30	0.25	0.85	inf	0.86	0.21
Unknown 3	1.23	0.14	0.89	0.16	1.26	inf	1.27	0.19
Unknown 4	0.92	1.95	0.91	0.19	inf	0.21	0.88	0.23

4.4 Sample Calculation for Mn(acac)₃

$$c = \frac{m_{\text{solid}}M}{m_{\text{solvent}} * \rho} = \frac{0.0149/352.26}{0.977 * 1.489} \text{ g/mL} = 3.77 * 10^{-5} \text{ g/mL} \quad (1)$$

$$\chi_M = \frac{3\Delta f}{4\pi Fc} = \frac{3 * 1315}{4\pi(500 * 10^6)(3.77 * 10^{-5})} \text{ cm}^3/\text{mol} = 0.0105 \text{ cm}^3/\text{mol} \quad (2)$$

$$\mu = \sqrt{8\chi_M T} = \sqrt{8 * 0.0105 * 293} \mu_B = 4.97 \mu_B \quad (3)$$

References

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