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Electronic Supportion Information (ESI) for:

Small iron–carbonyl clusters bearing imidazolium-2-trithioperoxycarboxylate ligands

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Table S1. Extended selection of bond distances (Å) and angles (°) derived from the molecular structures of clusters **3** and **4**.[a]

Cluster	**3**	**4a**[b]	**4b**[b]
Fe(1)–Fe(2)	2.5013(4)	2.5215(5)	2.5182(4)
Fe(1)–C(1)	1.790(2)	1.795(3)	1.800(2)
Fe(1)–C(2)	1.809(2)	1.799(3)	1.798(2)
Fe(1)–C(3)	1.797(2)	1.794(2)	1.800(2)
Fe(2)–C(8)	1.786(2)	1.804(3)	1.794(3)
Fe(2)–C(9)	1.796(2)	1.797(2)	1.800(2)
Fe(2)–C(10)	1.796(2)	1.797(2)	1.795(2)
Fe(1)–S(1)	2.2450(5)	2.2669(6)	2.2576(6)
Fe(1)–S(3)	2.2522(6)	2.2379(6)	2.2414(6)
Fe(2)–S(1)	2.2584(6)	2.2778(6)	2.2609(6)
Fe(2)–S(3)	2.2502(6)	2.2429(6)	2.2405(6)
C(4)–S(1)	1.725(2)	1.730(2)	1.723(2)
C(4)–S(2)	1.766(2)	1.774(2)	1.772(2)
C(4)–C(5)	1.400(3)	1.393(3)	1.391(3)
C(5)–N(1)	1.371(3)	1.388(2)	1.374(2)
C(5)–N(2)	1.381(2)	1.3843)	1.391(2)
C(6)–C(7)	1.333(3)	1.330(3)	1.329(3)
S(2)–S(3)	2.0633(7)	2.0595(7)	2.0600(7)
C(1)–Fe(1)–C(2)	100.98(9)	97.56(12)	97.05(10)
C(1)–Fe(1)–C(3)	99.05(10)	101.74(11)	101.61(10)
C(1)–Fe(1)–S(1)	103.36(7)	104.00(8)	105.82(7)
C(1)–Fe(1)–S(3)	100.71(7)	101.11(8)	99.28(8)
C(1)–Fe(1)–Fe(2)	149.29(7)	149.67(7)	149.12(7)
C(8)–Fe(2)–C(9)	101.85(9)	97.51(11)	100.75(10)
C(8)–Fe(2)–C(10)	97.97(10)	98.73(10)	99.04(10)
C(8)–Fe(2)–S(1)	100.39(7)	103.20(7)	99.08(7)
C(8)–Fe(2)–S(3)	103.57(7)	103.11(7)	104.39(7)
C(8)–Fe(2)–Fe(1)	148.93(7)	150.20(7)	148.17(7)
S(1)–Fe(1)–S(3)	80.37(2)	80.34(2)	80.30(2)
S(1)–Fe(2)–S(3)	80.13(2)	80.00(2)	80.24(2)
C(4)–S(2)–S(3)	98.65(7)	98.90(7)	98.50(7)
N(1)–C(5)–C(4)–S(1)	169.71(15)	–176.49(16)	–175.80(15)
N(1)–C(5)–C(4)–S(2)	–11.6(3)	–1.2(3)	6.9(3)
S(1)–C(4)–S(2)–S(3)	3.35(11)	4.15(12)	2.32(12)
C(1)–Fe(1)–Fe(2)–C(8)	–9.4(2)	–4.5(3)	–17.6(2)

[a] See Figures 1 and 2 for atom labeling. [b] Compound **4** crystallized with two molecules in the asymmetric unit.

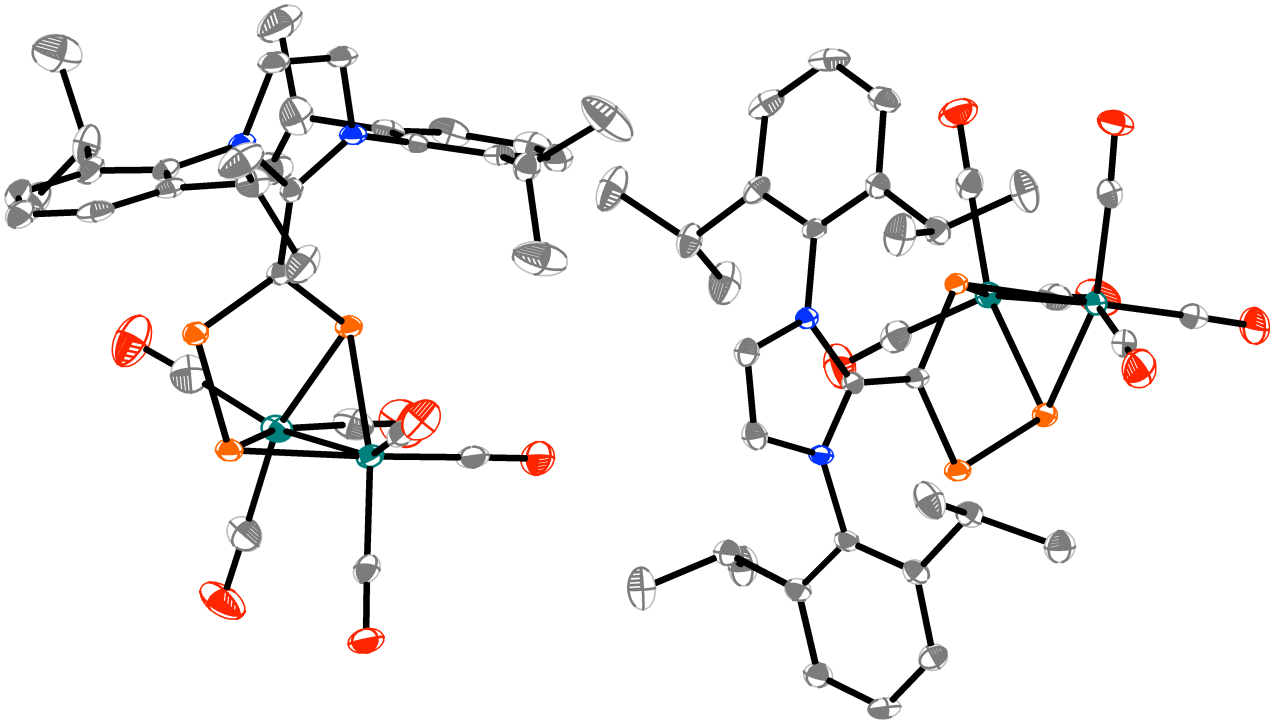

Figure S1. ORTEP representation of $[Fe_2(CO)_6(S_3C{\cdot}IDip)]$ (**4**) showing the presence of two independent molecules in the asymmetric unit with ellipsoids drawn at the 50% probability level. Hydrogen atoms were omitted for clarity.

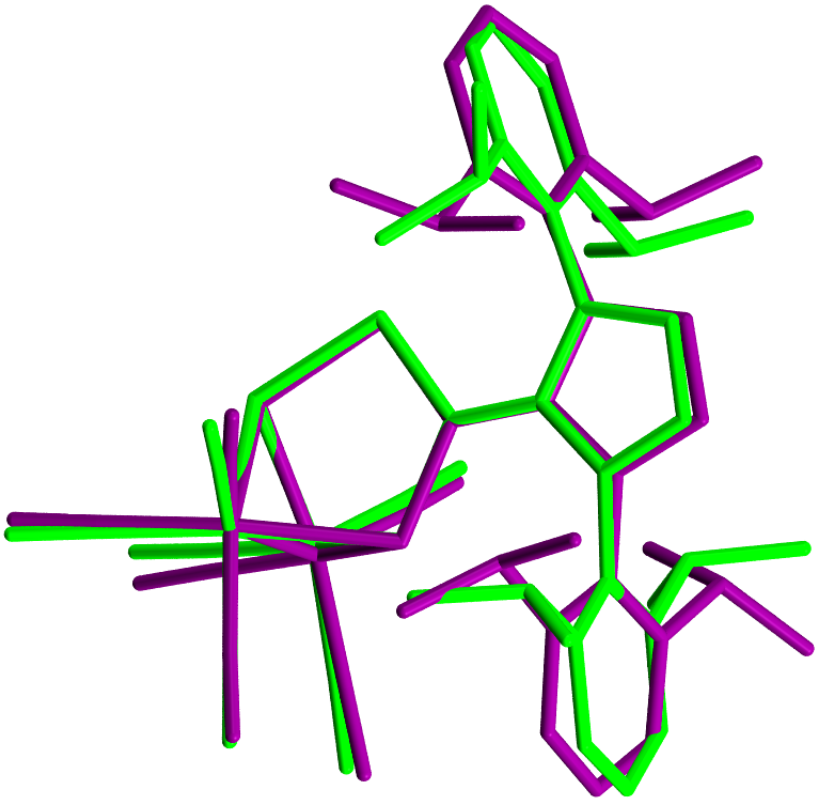

Figure S2. Superimposition of the two molecules present in the asymmetric unit of $[Fe_2(CO)_6(S_3C{\cdot}IDip)]$ (**4**). Hydrogen atoms were omitted for clarity.

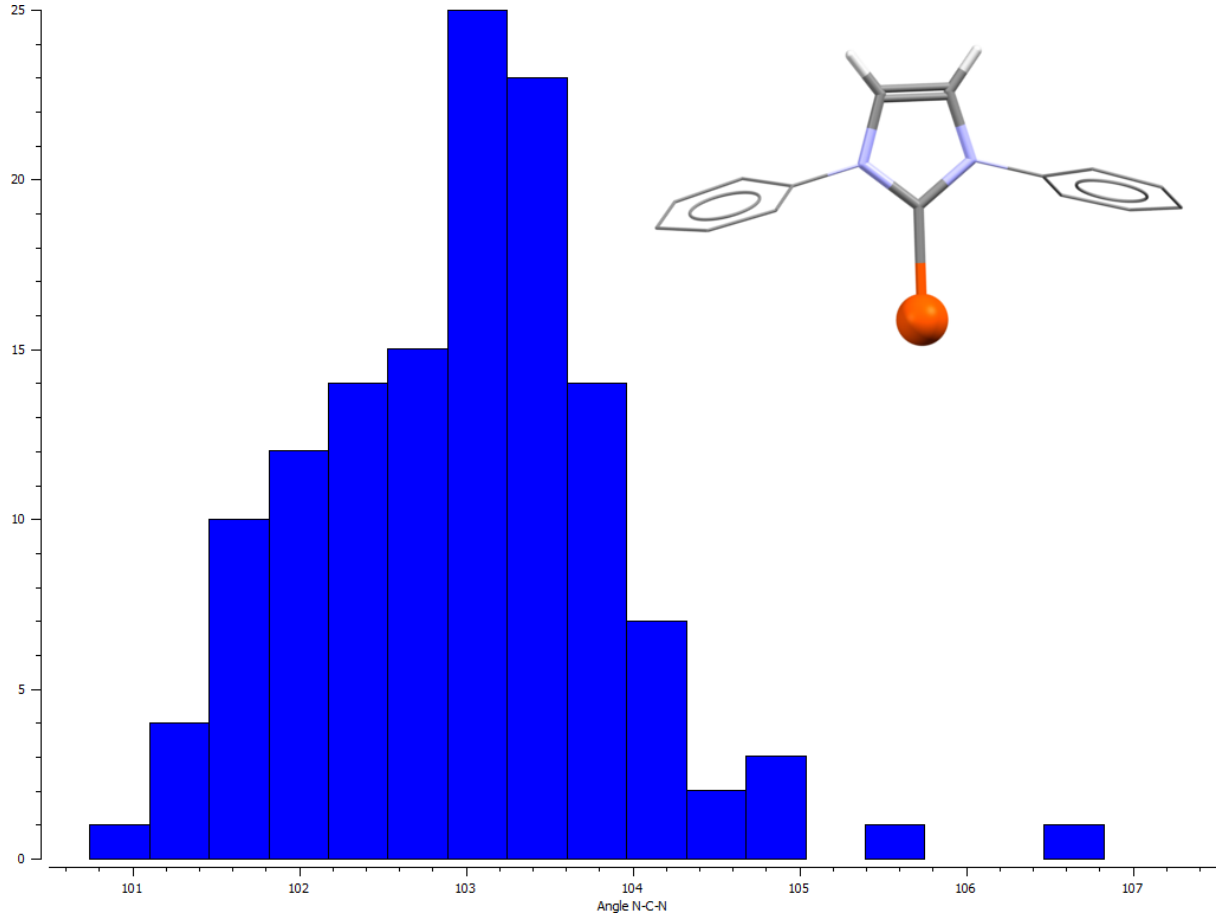

Figure S3. Histogram of N–C–N angle distribution in the structures of Fe–NHC complexes deposited at the Cambridge Crystallographic Data Centre.

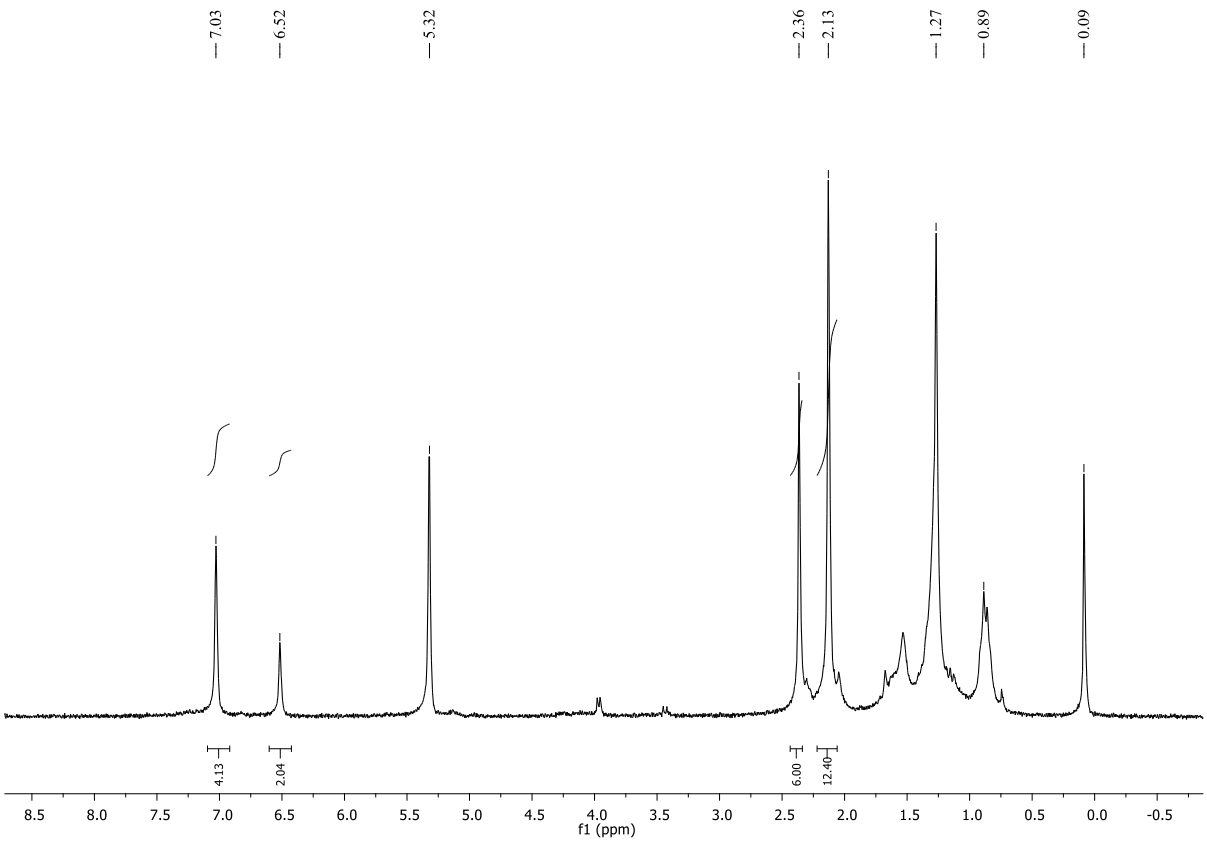

Figure S4. ^{1}H NMR spectrum (250 MHz, CD_2Cl_2, 298 K) of $[Fe_2(CO)_6(S_3C{\cdot}IMes)]$ (**3**).

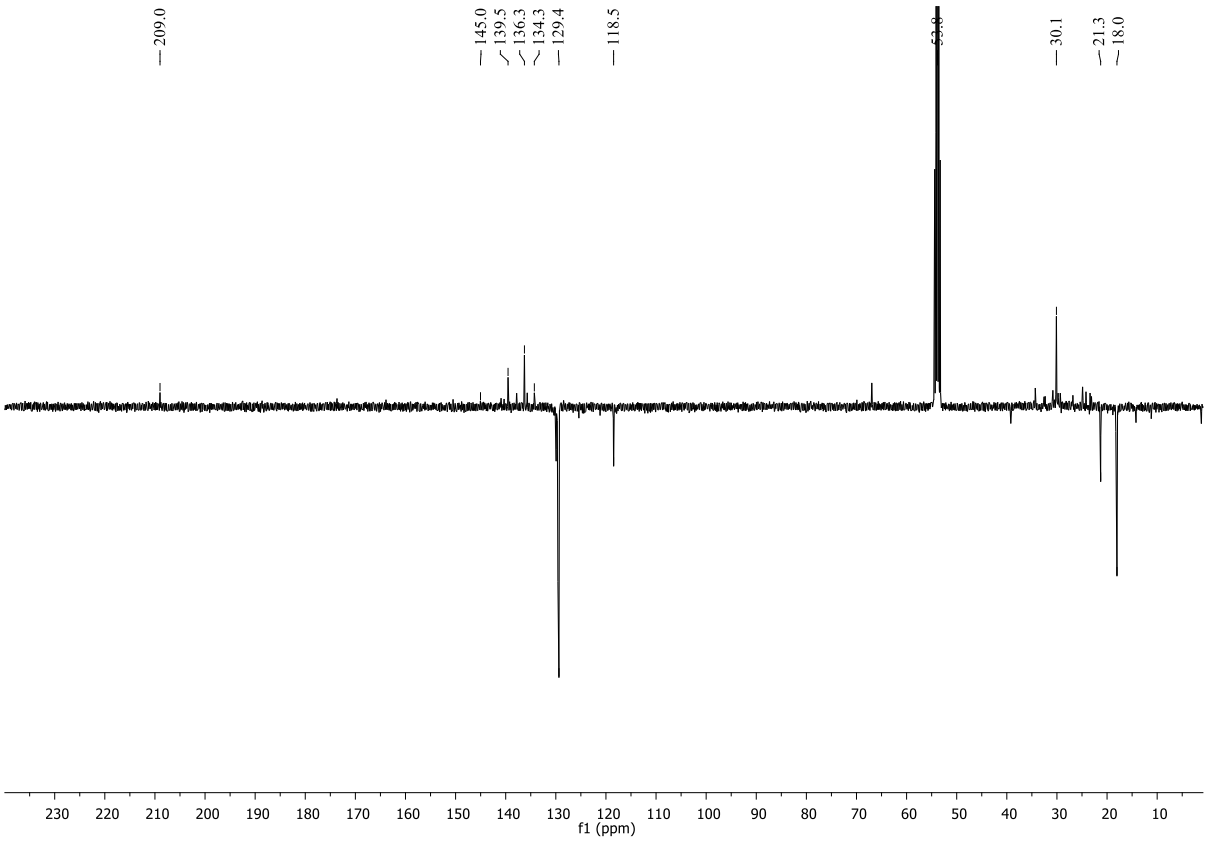

Figure S5. ^{13}C NMR spectrum (100 MHz, CD_2Cl_2, 298 K) of $[Fe_2(CO)_6(S_2C{\cdot}IMes)]$ (**3**).

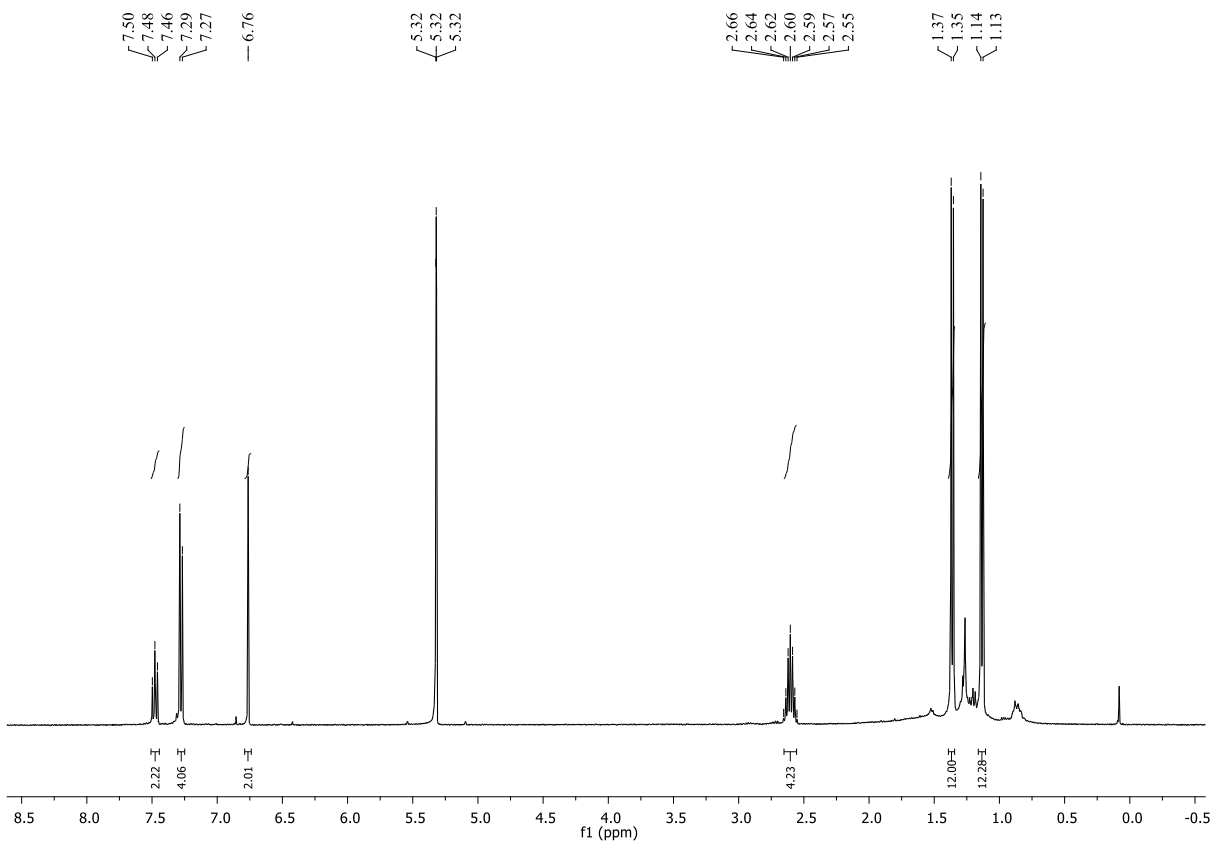

Figure S6. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 298 K) of $[Fe_2(CO)_6(S_3C{\cdot}IDip)]$ (**4**).

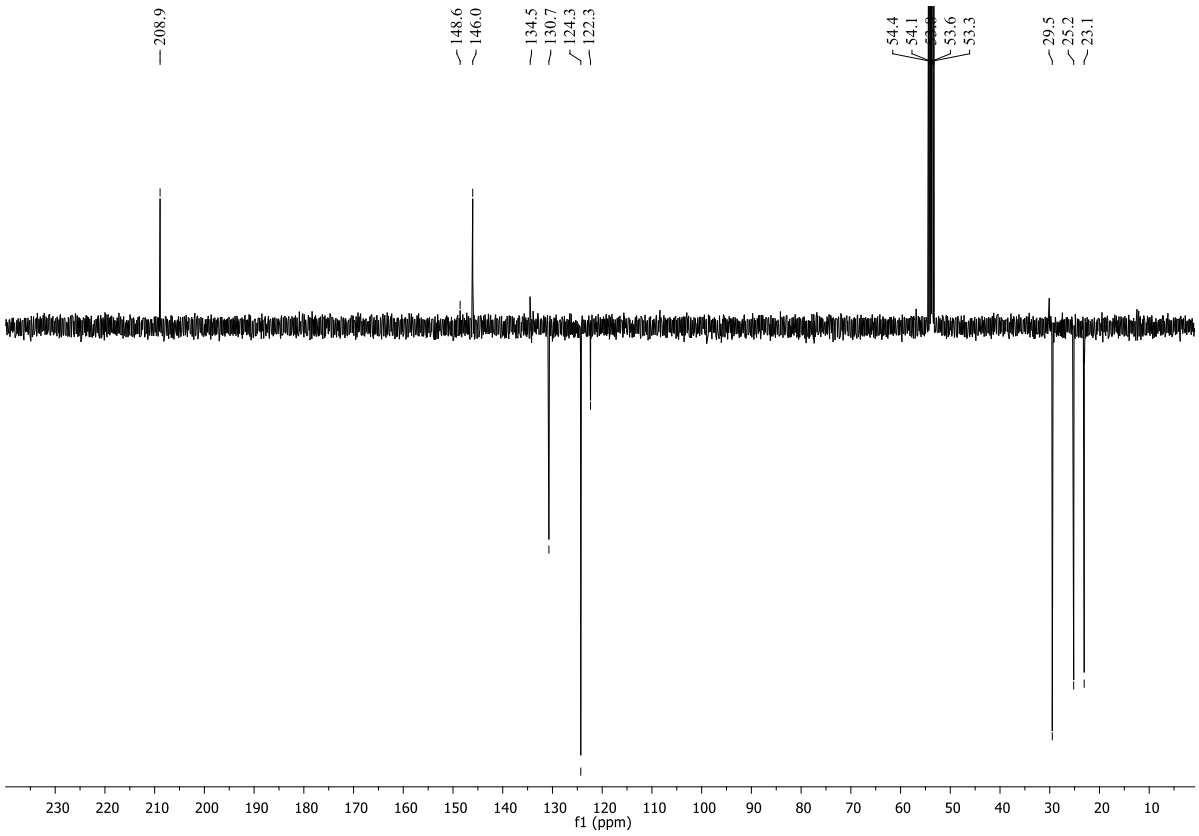

Figure S7. ^{13}C APT NMR spectrum (100 MHz, CD_2Cl_2, 298 K) of $[Fe_2(CO)_6(S_3C{\cdot}IDip)]$ (**4**).