Electronic supplementary information for

Syntheses and Characterizations of Iron Complexes of Bulky *o*-Phenylenediamide ligand

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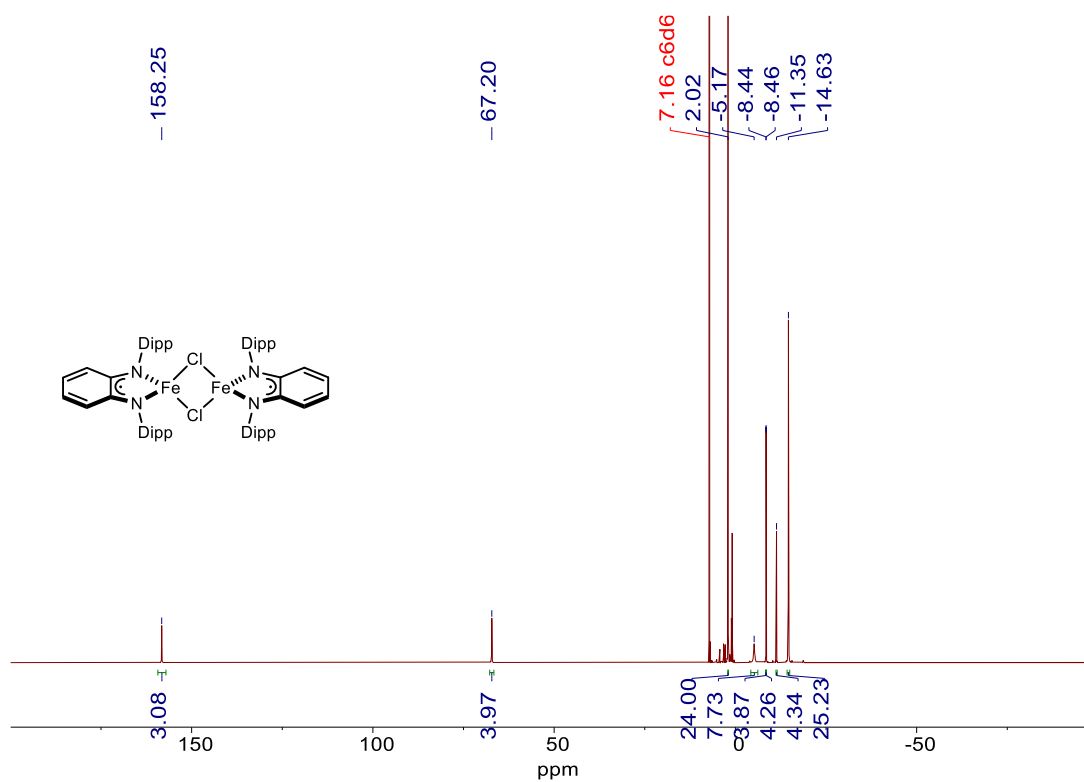
1. NMR spectra

Figure S1. ^{1}H NMR (600 MHz, C$_6$D$_6$, 25 °C) spectrum of **2**.
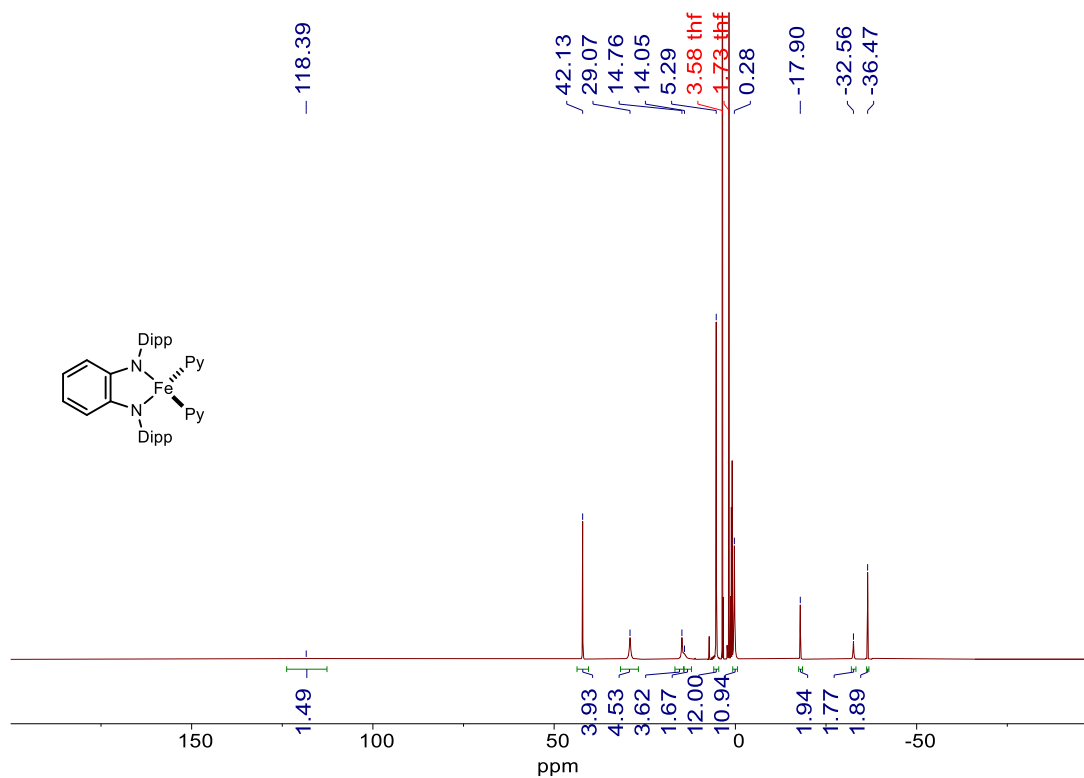

Figure S2. ^{1}H NMR (600 MHz, THF-d_8, 25 °C) spectrum of **4**.
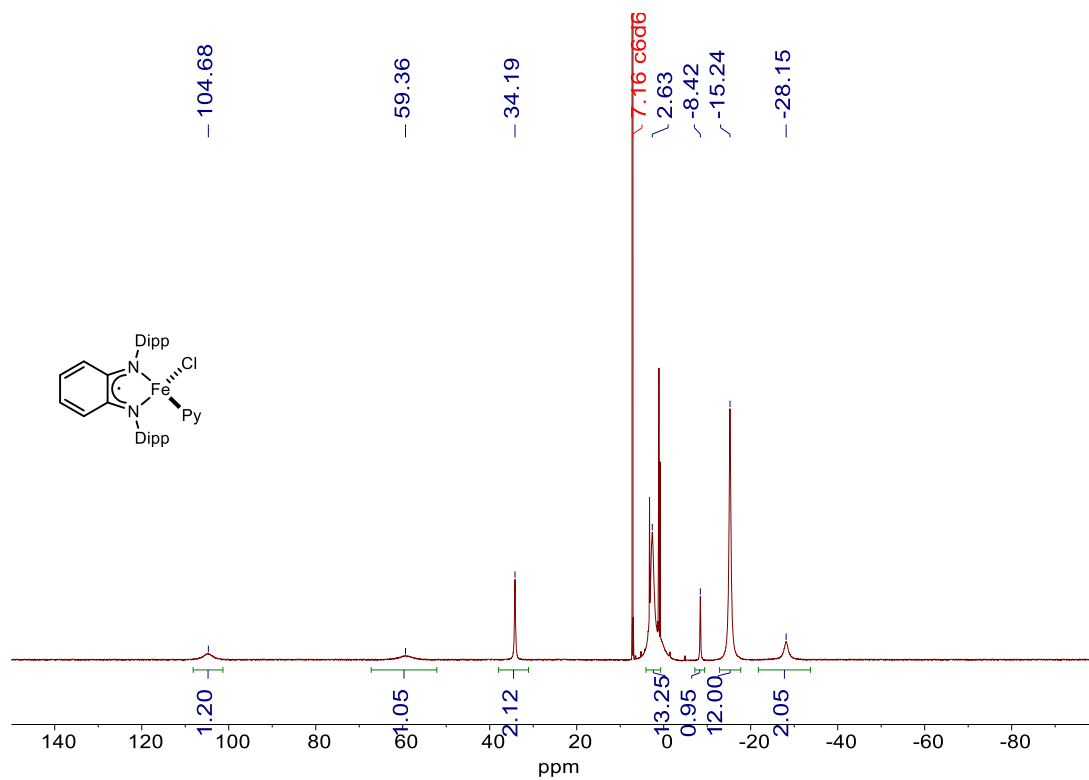
Figure S3. ^{1}H NMR (600 MHz, C_6D_6, 25 °C) spectrum of **5**.
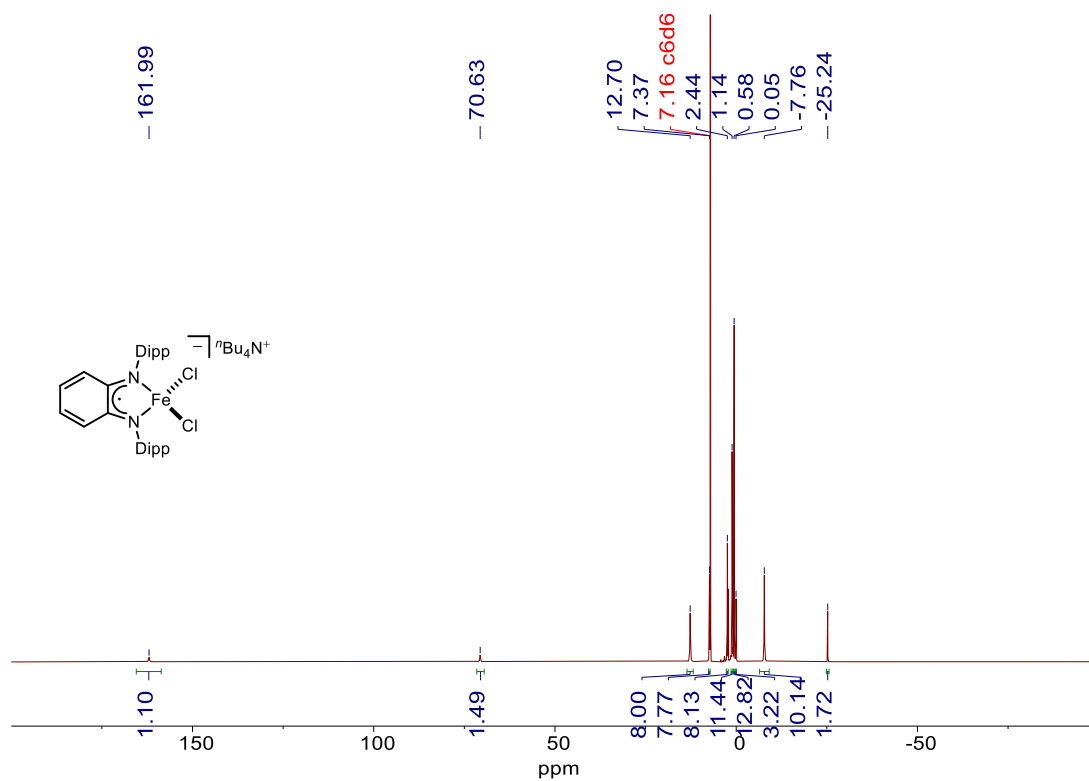
Figure S4. ^{1}H NMR (600 MHz, C_6D_6, 25 °C) spectrum of **6**.
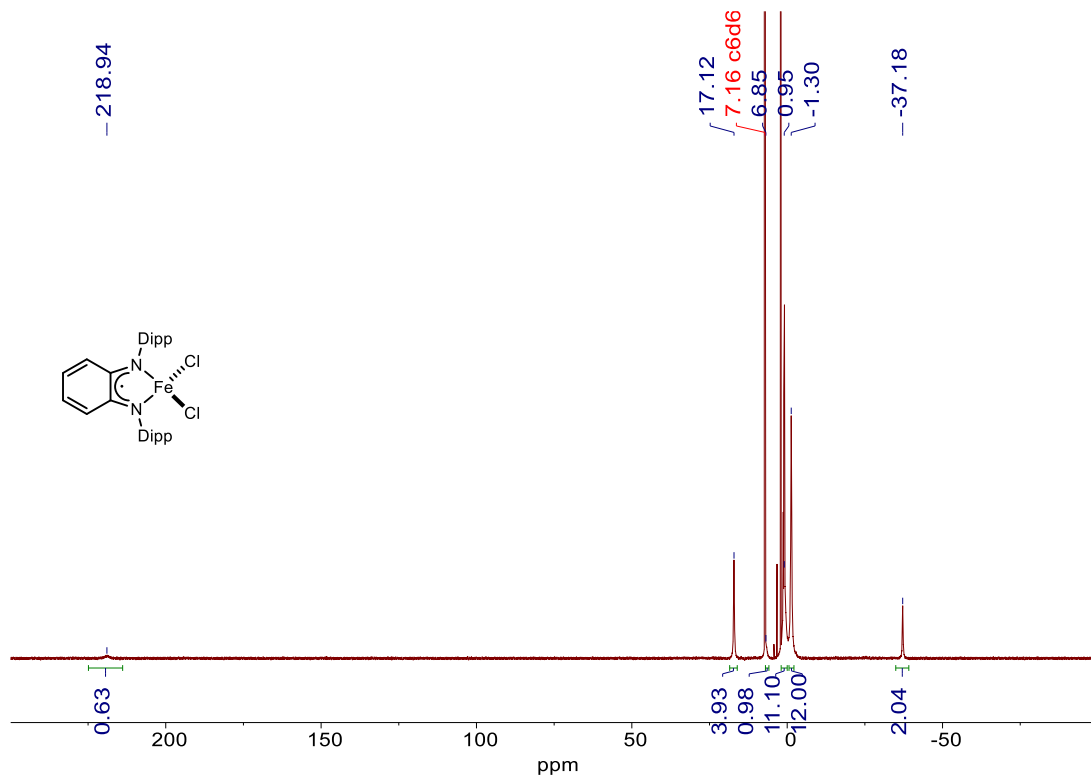
Figure S5. ^{1}H NMR (600 MHz, C$_6$D$_6$, 25 °C) spectrum of **7**.
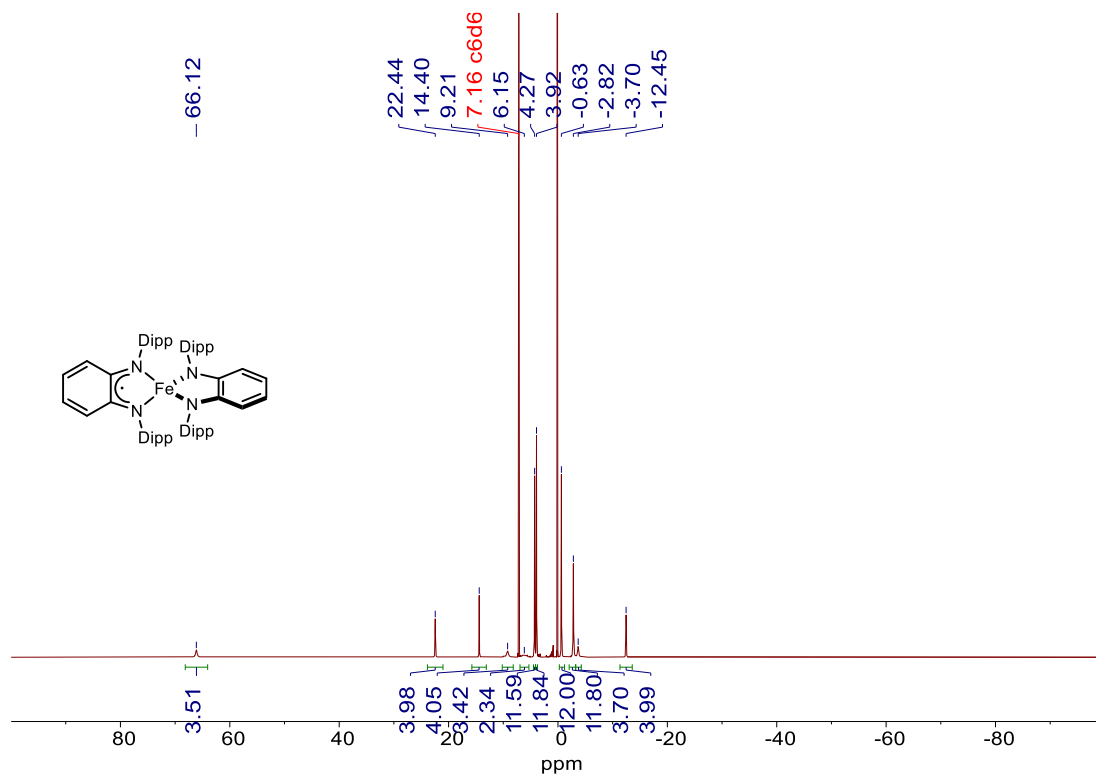
Figure S6. ^{1}H NMR (600 MHz, C$_6$D$_6$, 25 °C) spectrum of **8**.
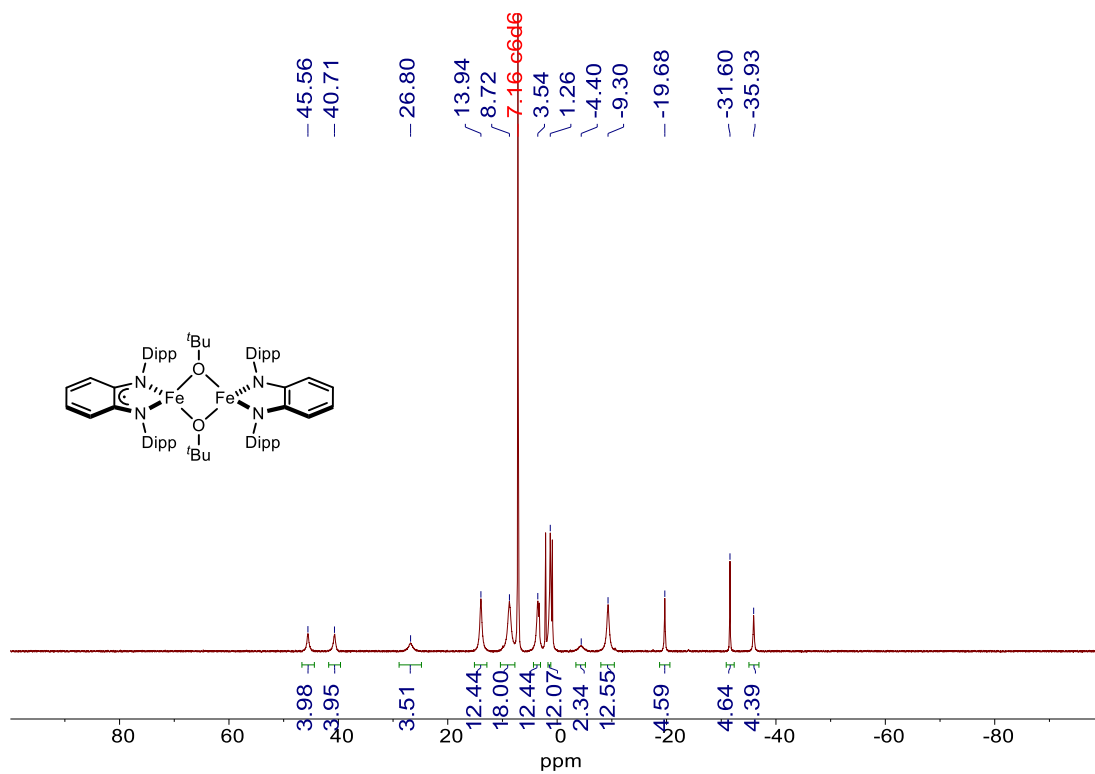
Figure S7. ^{1}H NMR (600 MHz, C$_6$D$_6$, 25 °C) spectrum of **9**.
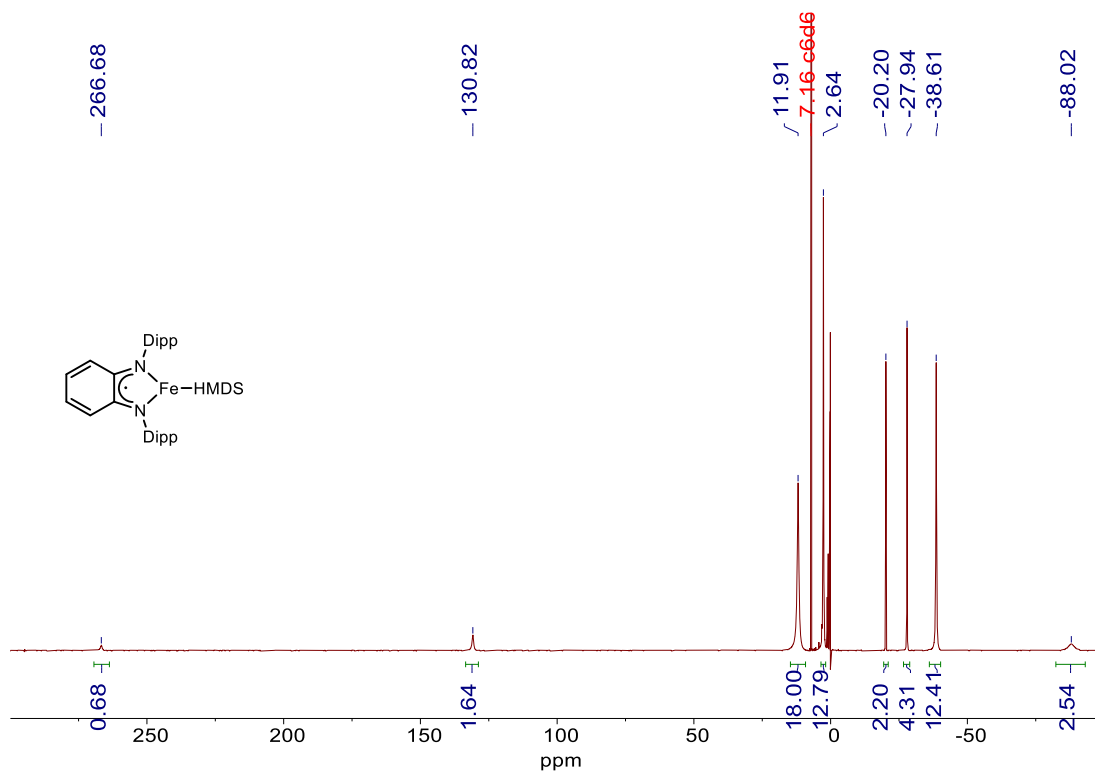
Figure S8. ^{1}H NMR (600 MHz, C$_6$D$_6$, 25 °C) spectrum of **10**.
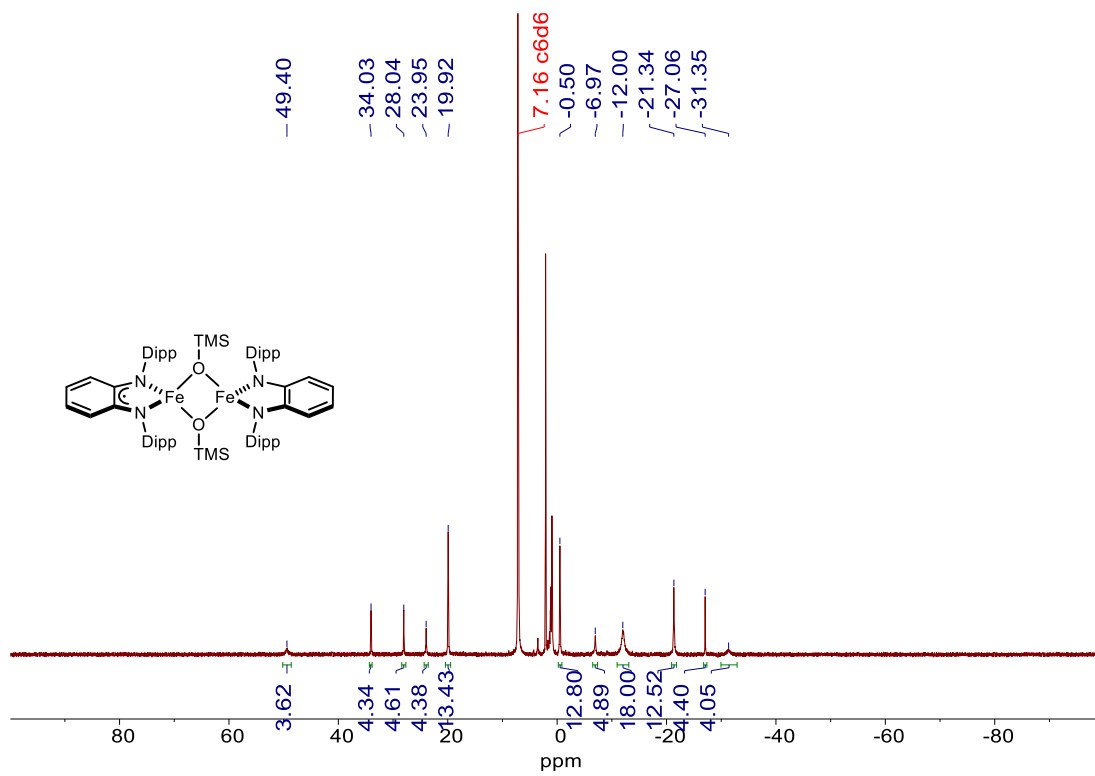
Figure S9. ^{1}H NMR (600 MHz, C$_6$D$_6$, 25 °C) spectrum of **11**.

2. ^{57}Fe Mössbauer spectra
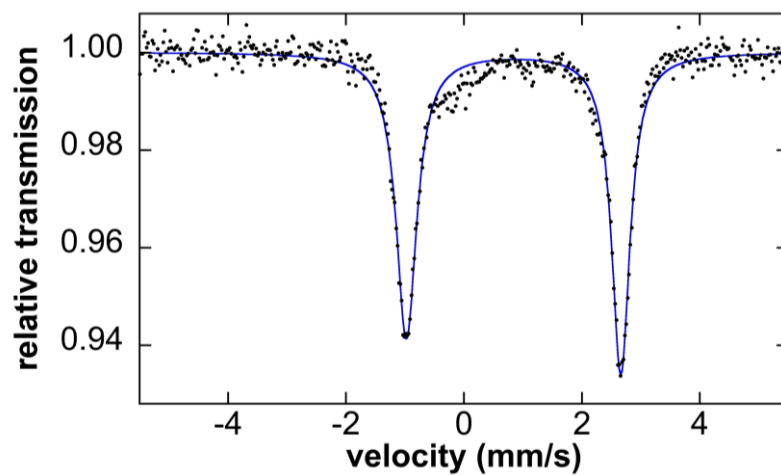
Figure S10. The 80 K ^{57}Fe Mössbauer spectrum of **2**.
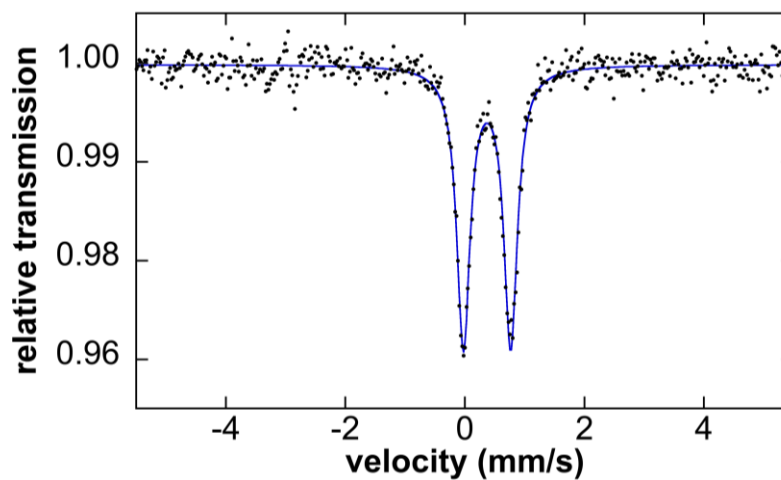
Figure S11. The 80 K ^{57}Fe Mössbauer spectra of **3**.

Figure S12. The 80 K ^{57}Fe Mössbauer spectra of **4**.

Figure S13. The 80 K ^{57}Fe Mössbauer spectra of **5**. The data (black dots), overall fit (black lines) and individual components are given. Complex **5** exhibits Mössbauer parameters of $\delta = 0.81$ mm/s, $|\Delta E_Q| = 2.05$ mm/s (blue, ~89% of all iron); while a second minor species exhibits Mössbauer parameters of $\delta = 0.92$ mm/s, $|\Delta E_Q| = 3.28$ mm/s (green, ~11% of all iron). The total fit is indicated by the black line.
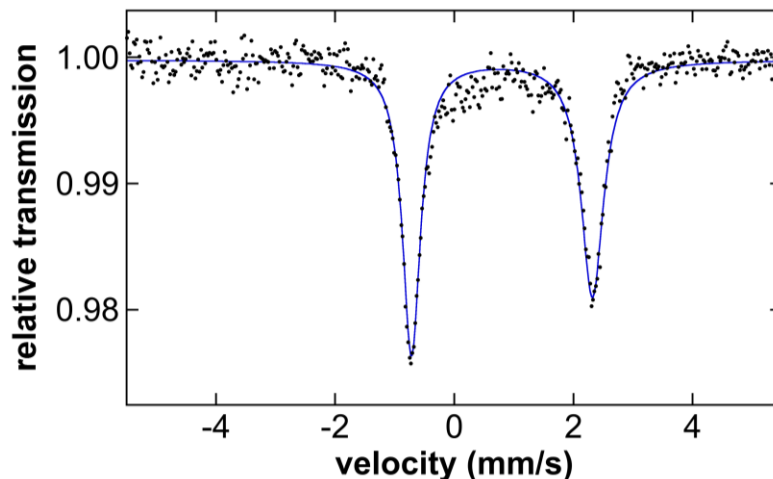
Figure S14. The 80 K ^{57}Fe Mössbauer spectra of **6**.

Figure S15. The 80 K ^{57}Fe Mössbauer spectra of **7**. The data (black dots), overall fit (black lines) and individual components are given. Complex **7** exhibits Mössbauer parameters of $\delta = 0.39$ mm/s, $|\Delta E_Q| = 2.12$ mm/s (blue, ~94% of all iron); while a second minor species exhibits Mössbauer parameters of $\delta = 0.38$ mm/s, $|\Delta E_Q| = 0.71$ mm/s (green, ~6% of all iron). The total fit is indicated by the black line.

Figure S16. The 80 K ^{57}Fe Mössbauer spectra of **8**. The data (black dots), overall fit (black lines) and individual components are given. Complex **8** exhibits Mössbauer parameters of $\delta = 0.42$ mm/s, $|\Delta E_Q| = 2.51$ mm/s (blue, ~78% of all iron); while a second minor species exhibits Mössbauer parameters of $\delta = 0.55$ mm/s, $|\Delta E_Q| = 1.20$ mm/s (green, ~22% of all iron). The total fit is indicated by the black line.
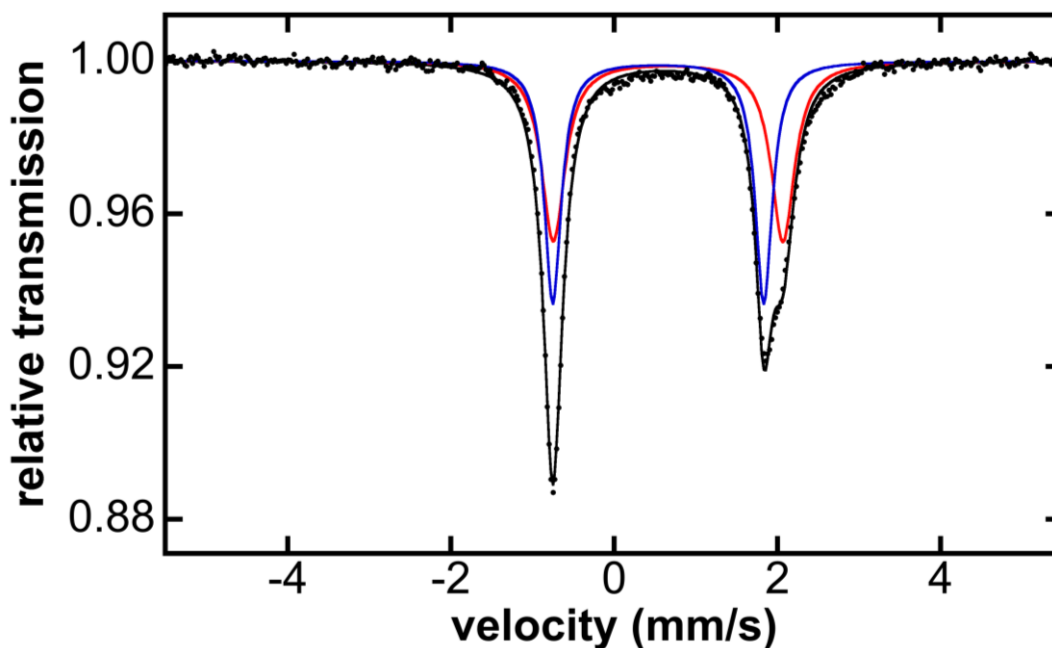
Figure S17. The 80 K ^{57}Fe Mössbauer spectra of **9**. The data (black dots), overall fit (black lines) and individual components are given for each spectrum. The individual components exhibit Mössbauer parameters of $\delta = 0.66$ mm/s, $|\Delta E_Q| = 2.81$ mm/s (red, ~51% of all iron) and $\delta = 0.54$ mm/s, $|\Delta E_Q| = 2.59$ mm/s (blue, ~49% of all iron).
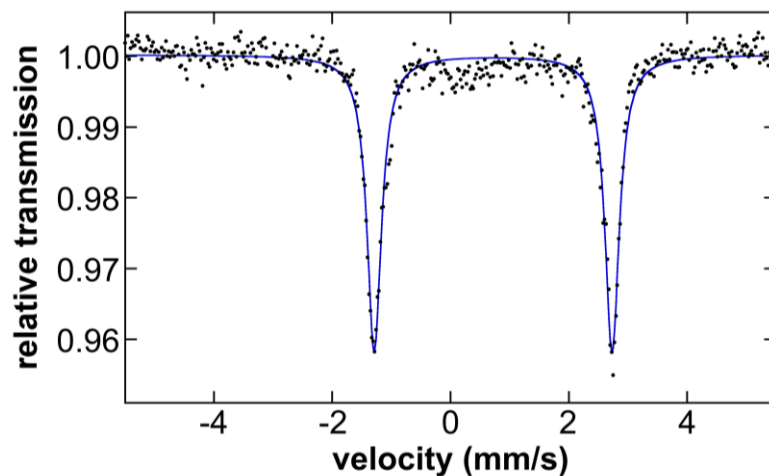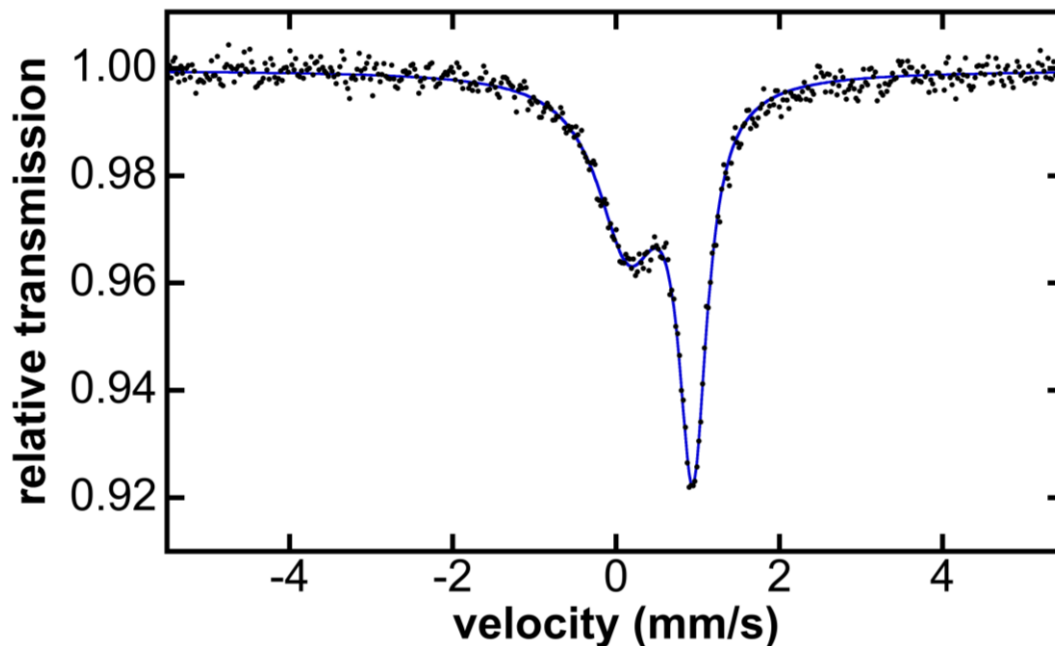
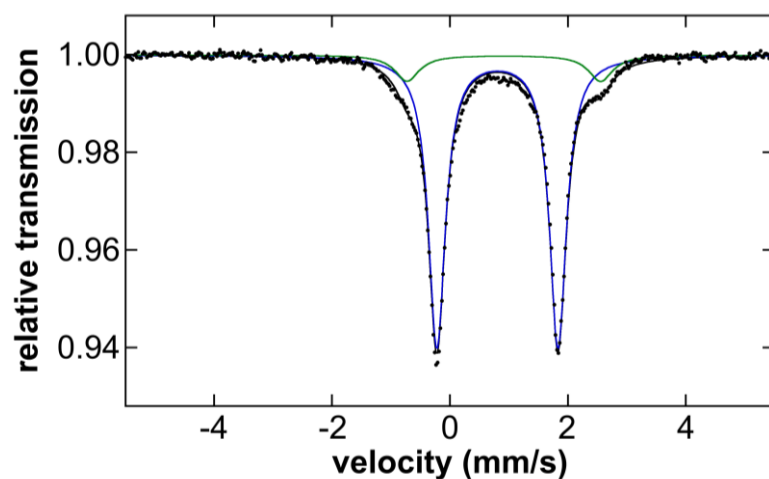**Figure S18.** The 80 K ^{57}Fe Mössbauer spectra of **10**.

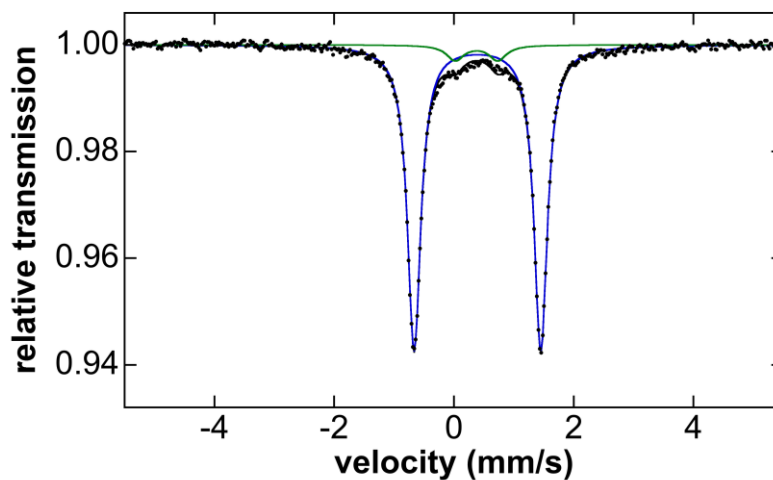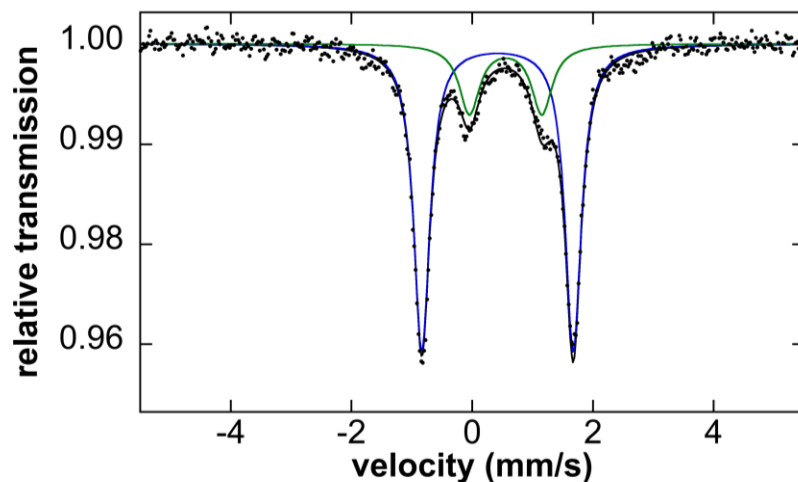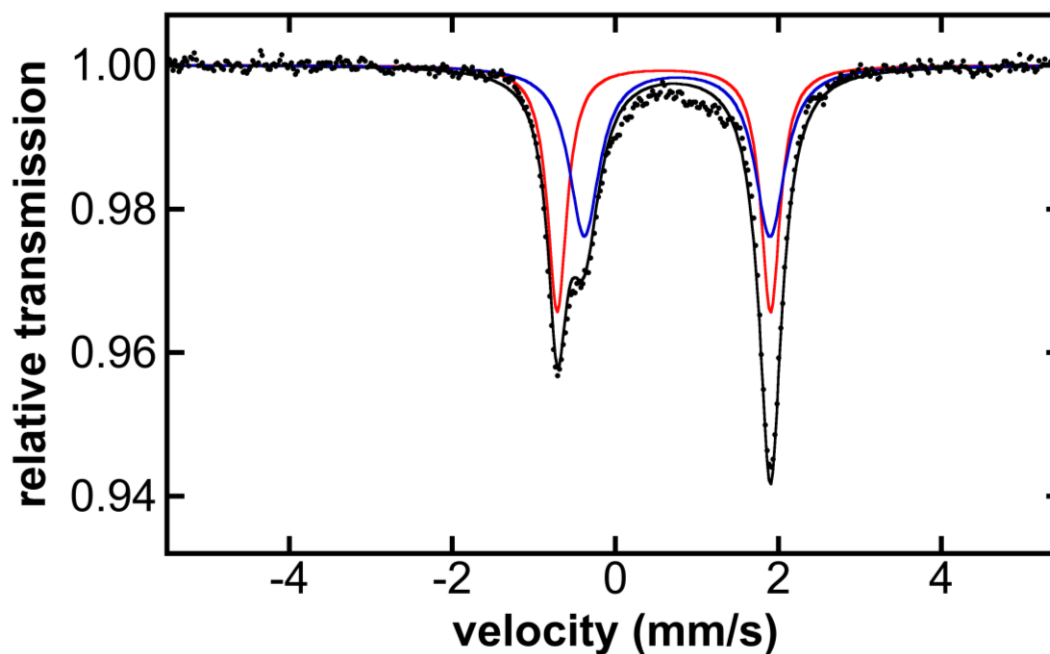**Figure S19.** The 80 K ^{57}Fe Mössbauer spectra of **11**. The data (black dots), overall fit (black lines) and individual components are given for each spectrum. The individual components exhibit Mössbauer parameters of $\delta = 0.76$ mm/s, $|\Delta E_Q| = 2.28$ mm/s (blue, ~52% of all iron) and $\delta = 0.60$ mm/s, $|\Delta E_Q| = 2.62$ mm/s (red, ~48% of all iron).

3. X-ray Crystallography

The X-ray diffraction data were collected on a Bruker Kappa Apex II diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 150 K controlled by an Oxford Cryostream 700 series low-temperature system and processed with the Bruker Apex2 software package.[2] The structures were solved by direct methods and refined using SHELX-2016 software packages.[3,4] All non-hydrogen atoms were refined anisotropically, except for the disordered Et_2O solvent in **4·Et₂O**, Dipp substituent in **5**, isopropyl group in **11**, and Dipp substituents and Me_3Si groups in **12**, which were successfully modeled using two sets of coordinates with the occupancies constrained to a 1:1 ratio. The diffuse residual electron density from solvent molecules in the lattices of **5** (Solvent Accessible Volume = 472 Å^3, # Electrons Found in S.A.V. = 149), **8** (Solvent Accessible Volume = 1693 Å^3, # Electrons Found in S.A.V. = 411), **9** (Solvent Accessible Volume = 201 Å^3, # Electrons Found in S.A.V. = 90), **11** (Solvent Accessible Volume = 210 Å^3, # Electrons Found in S.A.V. = 43) and **12** (Solvent Accessible Volume = 1090 Å^3, # Electrons Found in S.A.V. = 157) was removed with the SQUEEZE function of PLATON[5] and were not included in the formula or the refinement. Selected crystallographic data are summarized in Tables S1−S2.
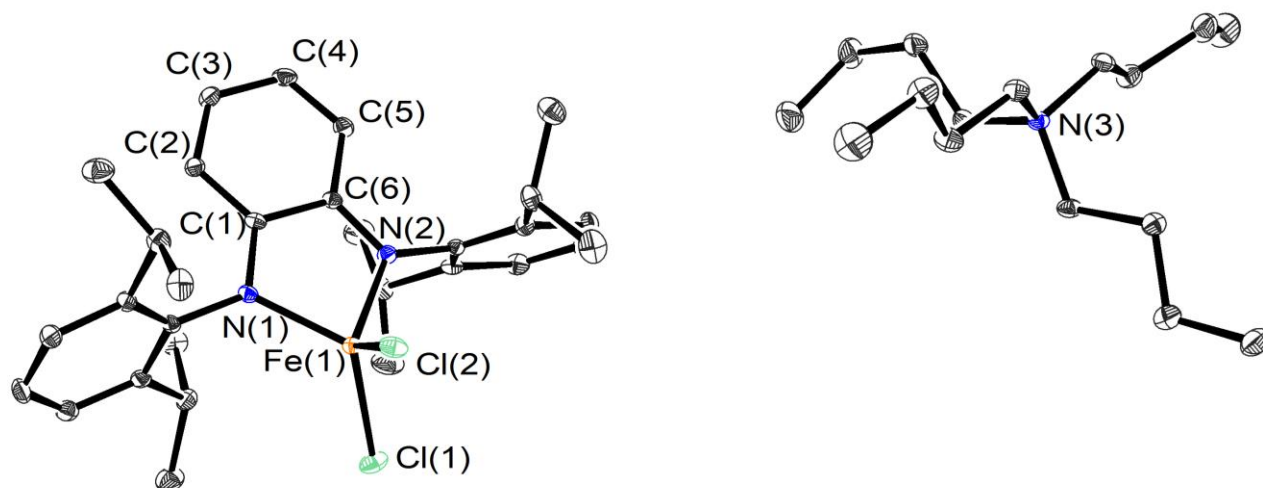
Figure S20. Molecular structure of 6 (30% probability thermal ellipsoids). All hydrogen atoms are omitted for clarity.

Table S1. Selected crystallographic data for compounds **2·Et₂O**, **4·Et₂O**, **5**, **6**, and **7·Et₂O**.

	2·Et₂O	4·Et₂O	5	6	7·Et₂O
Empirical formula	$C_{60}H_{76}Cl_2Fe_2N_4$	$C_{44}H_{58}FeN_4O$	$C_{35}H_{43}ClFeN_3$	$C_{46}H_{74}Cl_2FeN_3$	$C_{34}H_{48}Cl_2FeN_2O$
FW (g·mol⁻¹)	1035.84	714.79	597.02	795.83	627.49
Crystal system	Triclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space Group	P-1	Pbca	I2/a	C2/c	P2₁/m
Z	1	8	8	8	2
a (Å)	10.1107(7)	19.1247(8)	16.794(2)	24.511(3)	10.2114(4)
b (Å)	13.5638(9)	19.4899(10)	12.022(1)	11.903(1)	17.4996(9)
c (Å)	13.8531(10)	21.8687(12)	35.531(5)	32.937(3)	10.2150(6)
α (deg)	61.794(3)	90	90	90	90
β (deg)	68.888(3)	90	91.820(7)	102.358(5)	110.721(2)
γ (deg)	79.987(4)	90	90	90	90
V (Å³)	1561.82(19)	8151.3(7)	7170 (2)	9387(2)	1707.30(15)
D_{calcd}, (g·cm⁻³)	1.180	1.165	1.106	1.126	1.221
μ (mm⁻¹)	0.591	0.407	0.519	0.467	0.625
$F(000)$	592	3072	2536	3448	668
no. of obsd reflns	5131	5432	4227	6424	2945
no. of params refnd	352	450	337	481	213
goodness of fit	1.027	1.007	1.014	1.001	1.021
R₁ (I>2σ)	0.0384	0.0552	0.0675	0.0543	0.0437
wR₂ (All)	0.0902	0.1437	0.1955	0.1050	0.1038

Table S2. Selected crystallographic data for compound **8**, **9**, **10**, **11** and **12**.

	8	9	10	11	12
Empirical formula	$C_{60}H_{76}FeN_4$	$C_{68}H_{94}Fe_2N_4O_2$	$C_{36}H_{56}FeN_3Si_2$	$C_{66}H_{94}Fe_2N_4O_2Si_2$	$C_{67}H_{95}Fe_2N_4O_4Si_2$
FW (g·mol^{-1})	909.09	1111.17	642.86	1143.33	1188.34
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space Group	Ccca	P2$_1$/c	C2/c	P2$_1$/c	P-1
Z	8	4	4	4	2
a (Å)	18.114 (2)	26.0997(6)	13.5549(12)	25.2519(15)	12.9685(12)
b (Å)	20.701 (2)	14.5476(4)	17.0278(19)	14.5116(6)	13.0258(14)
c (Å)	33.700 (4)	18.3090(3)	16.221(2)	19.3032(13)	23.194(2)
α (deg)	90	90	90	90	90.938(5)
β (deg)	90	107.063(1)	98.742(4)	105.013(3)	97.421(5)
γ (deg)	90	90	90	90	90.778(5)
V (Å^3)	12637(2)	6645.7(3)	3700.4(7)	6832.1(7)	3884.3(7)
D_{calcd}, (g·cm^{-3})	0.956	1.111	1.154	1.112	1.016
μ (mm^{-1})	0.273	0.479	0.499	0.501	0.445
$F(000)$	3920	2392	1388	2456	1274
no. of obsd reflns	4591	10024	2778	9312	8471
no. of params refnd	295	707	227	681	607
goodness of fit	1.010	1.035	1.016	1.004	1.027
R$_1$ (I>2σ)	0.0549	0.0517	0.0536	0.0550	0.0747
wR$_2$(All)	0.1553	0.1506	0.1274	0.1365	0.2026

4. Computation

To obtain the spin density distribution, the structure of **8** was optimized in gas phase with broken symmetry calculation using the built-in PBEPBE functionals[6] and TZVP basis set[7] in Gaussian 16, Revision B.01.[8] The atomic coordinates of the optimized structure are given below (E(UPBE-PBE) = −3812.16338584).

Fe	-0.000025000	0.000000000	-0.260674000
N	1.433503000	1.037485000	0.582793000
C	2.596716000	0.858811000	-0.133012000
N	1.439206000	-0.996924000	-1.075213000
C	3.806113000	1.574835000	0.042397000
H	3.867258000	2.321064000	0.834100000
C	4.890853000	1.347168000	-0.795170000
H	5.805981000	1.926729000	-0.659462000
C	4.813347000	0.385963000	-1.821549000
H	5.657764000	0.240060000	-2.497907000
C	3.674520000	-0.396290000	-1.960432000
H	3.622286000	-1.177982000	-2.719715000
C	2.572961000	-0.210239000	-1.095613000
C	1.529103000	1.863420000	1.760913000
C	1.289854000	3.268890000	1.734922000
C	1.408075000	3.981799000	2.938421000
H	1.215875000	5.055086000	2.936172000
C	1.774027000	3.366271000	4.131923000
H	1.853562000	3.950536000	5.051161000
C	2.053227000	2.004710000	4.134897000
H	2.369676000	1.521886000	5.061977000
C	1.950173000	1.235096000	2.968485000
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H	0.723970000	6.107982000	1.191170000
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H	2.103361000	-0.702168000	2.086673000
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H	0.622957000	-1.011270000	4.077166000
H	2.051178000	-2.060256000	4.148161000
H	1.978044000	-0.607708000	5.159696000
C	3.923080000	-0.301145000	3.176289000
H	4.436017000	0.198864000	2.343040000
H	4.250384000	0.177879000	4.112282000
H	4.256729000	-1.349381000	3.204763000
C	1.577110000	-2.334737000	-1.570294000
C	0.800985000	-2.809274000	-2.662213000
C	0.961933000	-4.136012000	-3.088125000
H	0.365865000	-4.494615000	-3.930108000
C	1.877773000	-4.991499000	-2.487924000
H	1.994593000	-6.017631000	-2.842789000
C	2.646382000	-4.518903000	-1.427604000

H	3.362833000	-5.189735000	-0.948362000
C	2.519507000	-3.213147000	-0.940522000
C	-0.140003000	-1.927393000	-3.468325000
H	-0.184371000	-0.945806000	-2.975943000
C	-1.572705000	-2.481067000	-3.529099000
H	-2.226988000	-1.783539000	-4.072877000
H	-1.610582000	-3.448656000	-4.053016000
H	-1.995318000	-2.623412000	-2.526242000
C	0.418744000	-1.729860000	-4.890329000
H	-0.259348000	-1.107552000	-5.490840000
H	1.407647000	-1.248065000	-4.872899000
H	0.528080000	-2.696759000	-5.404516000
C	3.397898000	-2.835561000	0.252877000
H	3.244160000	-1.774395000	0.481001000
C	3.019579000	-3.630370000	1.514260000
H	3.693721000	-3.365745000	2.342643000
H	1.990745000	-3.416209000	1.834205000
H	3.110130000	-4.714629000	1.348695000
C	4.894912000	-3.024871000	-0.055802000
H	5.501739000	-2.654276000	0.784159000
H	5.145041000	-4.086898000	-0.202068000
H	5.194379000	-2.475119000	-0.957655000
N	-1.433395000	-1.037587000	0.582900000
C	-2.596677000	-0.858887000	-0.132783000
N	-1.439364000	0.997059000	-1.074875000
C	-3.806035000	-1.574968000	0.042677000
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C	-4.890843000	-1.347308000	-0.794801000
H	-5.805940000	-1.926908000	-0.659051000
C	-4.813446000	-0.386046000	-1.821135000
H	-5.657905000	-0.240160000	-2.497447000
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H	-3.622529000	1.178011000	-2.719284000
C	-2.573057000	0.210262000	-1.095280000
C	-1.528844000	-1.863553000	1.761010000
C	-1.289560000	-3.269023000	1.734961000
C	-1.407646000	-3.981941000	2.938470000
H	-1.215420000	-5.055220000	2.936207000
C	-1.773444000	-3.366431000	4.132029000
H	-1.852858000	-3.950715000	5.051265000
C	-2.052639000	-2.004872000	4.135069000
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H	-0.414845000	-3.392571000	-0.213454000
C	-0.126812000	-5.313323000	0.717022000
H	0.743924000	-5.116472000	1.353045000
H	-0.723981000	-6.108144000	1.191066000
H	0.235547000	-5.708175000	-0.241390000

C	-2.252528000	-4.513492000	-0.274020000	C	-2.519876000	3.213178000	-0.940045000
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H	-2.876471000	-5.130444000	0.392517000	H	0.184241000	0.946205000	-2.975537000
H	-2.863282000	-3.678639000	-0.633990000	C	1.572372000	2.481608000	-3.528751000
C	-2.388676000	0.224076000	3.034930000	H	2.226682000	1.784165000	-4.072605000
H	-2.103149000	0.702020000	2.086870000	H	1.610131000	3.449230000	-4.052617000
C	-1.716023000	1.012313000	4.170033000	H	1.995033000	2.623928000	-2.525913000
H	-0.622582000	1.011218000	4.077228000	C	-0.419035000	1.730187000	-4.889909000
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H	-4.435741000	-0.199176000	2.343488000	C	-3.398200000	2.835499000	0.253379000
H	-4.249876000	-0.178271000	4.112704000	H	-3.244479000	1.774305000	0.481397000
H	-4.256462000	1.349039000	3.205269000	C	-3.019742000	3.630182000	1.514806000
C	-1.577427000	2.334874000	-1.569892000	H	-3.693890000	3.365597000	2.343195000
C	-0.801343000	2.809548000	-2.661783000	H	-1.990925000	3.415860000	1.834699000
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C	-1.878354000	4.991652000	-2.487408000	H	-5.501998000	2.654203000	0.784802000
H	-1.995296000	6.017780000	-2.842242000	H	-5.145342000	4.086955000	-0.201249000
C	-2.646886000	4.518939000	-1.427086000	H	-5.194784000	2.475285000	-0.957063000
H	-3.363387000	5.189686000	-0.947799000				

TD-DFT calculation of **8** was performed using PBEPBE functional[6] and def2svp basis set[9] on the geometry optimized from a broken symmetry calculation using the same functionals and basis set. The first 200 excited states were calculated and the spectrum was visualized using ChemCraft software version 1.8, build 526b. For comparison purpose, the intensity of TD spectrum was normalized to the experimental UV-vis-NIR spectrum using the most intense peaks of both, i.e., ~330 nm (Figure S21). The low energy transitions are listed in Table S3. The frontier orbitals relevant to the low energy transitions are plotted using an iso-value 0.04 (Figure S22 and S23).
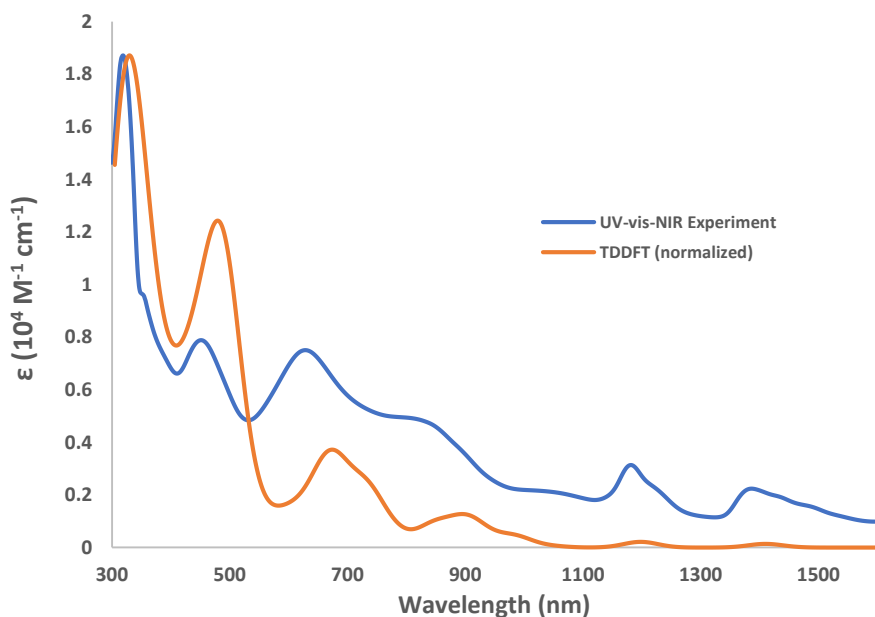

Figure S21. UV-vis-NIR spectrum of **8** (3.5×10^{-4} M in THF, 25 °C) and TDDFT simulated spectra of **8** with intensity of the most intense peak normalized to that of the experimental spectrum.

Table S3. Low energy excited states and the corresponding transitions of **8**.

State	Wavelength (nm)	Transition and Coefficient		Oscillator Strength
1	1433.09	245A -> 247A	-0.10527	0.0002
		246A -> 248A	0.87340	
		242B -> 245B	0.26621	
		243B -> 246B	-0.25577	
		243B -> 247B	0.11419	
		244B -> 248B	0.24631	
2	1408.85	245A -> 248A	0.13159	0.0025
		246A -> 247A	0.71541	
		241B -> 245B	-0.11332	
		242B -> 246B	-0.14908	
		243B -> 245B	0.47326	
		244B -> 246B	-0.13463	
		244B -> 247B	-0.44809	
3	1198.30	246A -> 247A	-0.36046	0.0041
		243B -> 245B	0.86848	
		244B -> 247B	0.24935	
4	1041.36	241A -> 248A	0.10679	0.0011
		242A -> 247A	-0.15055	
		243A -> 247A	0.10370	
		245A -> 247A	0.69842	
		246A -> 248A	0.29638	
		242B -> 245B	-0.39151	
		243B -> 246B	0.40435	
		243B -> 247B	-0.12346	
		244B -> 248B	0.18717	
5	983.88	241A -> 247A	-0.14764	0.0075
		244A -> 247A	0.20672	
		245A -> 248A	0.57354	
		246A -> 247A	0.34026	
		242B -> 247B	0.12004	
		244B -> 247B	0.67766	
6	976.20	241A -> 248A	0.19584	0.0003
		244A -> 248A	-0.34666	
		245A -> 247A	-0.31892	
		246A -> 248A	-0.18437	
		242B -> 245B	0.18781	
		242B -> 248B	0.12796	
		243B -> 246B	0.48041	
		244B -> 248B	0.63600	
7	934.18	241A -> 247A	0.15042	0.0046
		244A -> 247A	-0.21255	
		245A -> 248A	0.20848	
		242B -> 246B	0.91907	
8	920.09	242A -> 247A	-0.12600	0.0013
		244A -> 248A	0.47370	
		245A -> 247A	-0.46234	
		246A -> 248A	0.26723	
		240B -> 245B	0.25033	
		242B -> 245B	-0.18500	

		242B -> 248B -0.10169		
		243B -> 246B 0.52790		
		244B -> 248B -0.26049		
9	899.61	244A -> 247A 0.64053	0.0178	
		245A -> 248A -0.55385		
		246A -> 247A 0.21960		
		241B -> 245B -0.36166		
		242B -> 246B 0.24268		
		242B -> 247B 0.11766		
		244B -> 247B 0.11378		
10	845.92	241A -> 247A 0.11399	0.0154	
		244A -> 247A 0.67833		
		245A -> 248A 0.41036		
		246A -> 247A -0.19873		
		241B -> 245B 0.26826		
		242B -> 247B -0.20586		
		243B -> 248B 0.12865		
		244B -> 246B 0.13921		
		244B -> 247B -0.38892		

Alpha 241, Occupied

Alpha 242, Occupied

Alpha 243, Occupied

Alpha 244, Occupied

Alpha 245, Occupied

Alpha 246, Occupied

Alpha 247, Unoccupied
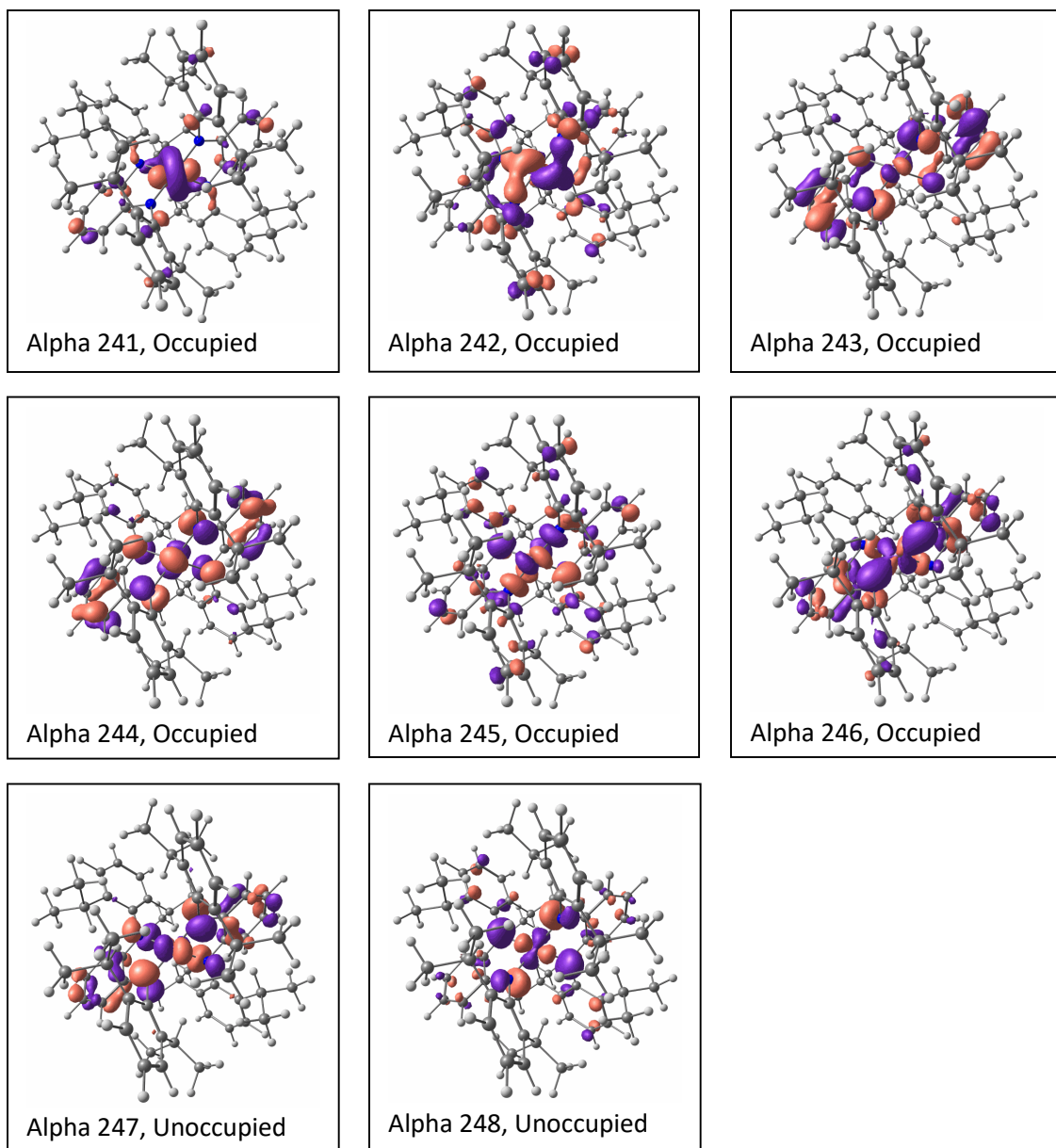
Alpha 248, Unoccupied

Figure S22. Alpha-Spin Frontier Orbitals of **8**.
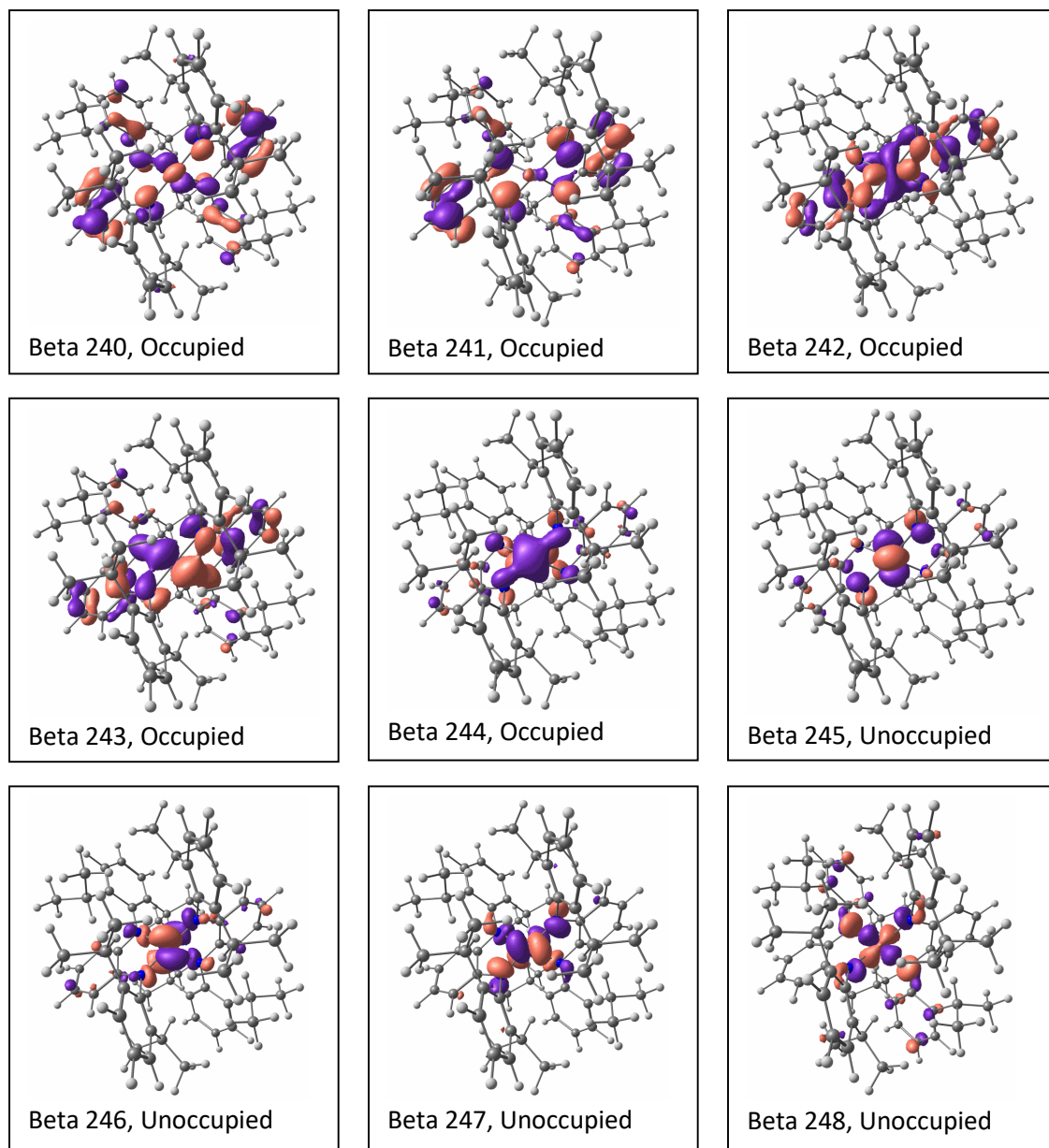
Figure S23. Beta-Spin Frontier Orbitals of **8**.

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