Supporting Information

Iron Complexes of a Proton-Responsive SCS Pincer Ligand with a Sensitive Electronic Structure

Kazimer L. Skubi,[†,a] *Reagan X. Hooper,*[†,a] *Brandon Q. Mercado,*[a] *Melissa M. Bollmeyer,*[b] *Samantha N. MacMillan,*[b] *Kyle M. Lancaster,*[b] *Patrick L. Holland**[*,a]

[a] Department of Chemistry, Yale University, New Haven, Connecticut 06511.

[b] Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York 14853.

[†] These authors contributed equally, and should be considered co-first authors.

*Corresponding author email: patrick.holland@yale.edu

Contents

Reagent Preparation and Handling

Unless otherwise noted, manipulations were carried out in N_2-filled MBraun or Vigor gloveboxes with < 1 ppm O_2 or on a Schlenk line with an N_2 atmosphere at ambient temperature. Dry protonated and deuterated solvents were stored over 4 Å molecular sieves under N_2. Protonated solvents were dried on Q5 columns maintained under argon. C_6D_6 was degassed and dried over activated alumina prior to storage. THF-d_8 was degassed, dried with potassium benzophenone ketyl, then vacuum transferred. Glassware was either flame-dried or dried overnight in a 150 °C oven.

$Me_3NH{\bullet}BPh_4$,[1] $Fe(PMe_3)_4$,[2] and 2,2",4,4",6,6"-hexamethyl-[1,1':3',1"-terphenyl]-2'-thiol[3] (ArSH) were prepared according to literature procedures. **Caution**: PMe_3 may ignite upon contact with air. ArSH was deprotonated in THF using stoichiometric $KN(TMS)_2$ then concentrated under reduced pressure to a solid and washed with Et_2O to obtain potassium 2,2",4,4",6,6"-hexamethyl-[1,1':3',1"-terphenyl]-2'-thiolate (ArSK). Commercial 18-crown-6 was dissolved in Et_2O and dried over a layer of 4 Å molecular sieves for at least 24 hours, then filtered through a Celite plug and crystallized from Et_2O at −40 °C. KHMDS was crystallized from toluene at −40 °C. Commercial Et_3N was distilled from CaH_2 under N_2. Commercial 2,6-diisopropylaniline was distilled from CaH_2 under reduced pressure. Commercial $SOCl_2$ was distilled under N_2. KC_8 was synthesized by vigorous stirring of a potassium melt with eight equivalents of graphite under argon at 140 °C for 45 minutes. **Caution**: KC_8 may ignite upon contact with air. All other reagents were purchased from commercial sources and used without further purification.

Product Characterization and Spectroscopy

^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were obtained using a DD2 400, 500, 600, or 800 MHz spectrometer at room temperature. ^1H spectra were internally referenced to the residual protio-solvent peak in $CDCl_3$, C_6D_6, or THF-d_8. $^{13}C\{^1H\}$ spectra were internally referenced to $CDCl_3$ (77.16 ppm), DMSO-d_6 (39.52 ppm), or THF-d_8 (67.21 and 25.31 ppm).[4] $^{31}P\{^1H\}$ spectra were absolute referenced to the corresponding ^1H spectra using the method described by Harris, *et al*.[5,6] For diamagnetic compounds, multiplicities are defined using the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), sext (sextet), sept (septet), br. (broad), app. (apparent), virt. (virtual). For paramagnetic compounds, all peaks are singlets due to broadening unless otherwise noted. Paramagnetic broadening, especially in combination with dynamic processes such as rotations, can prevent accurate baseline correction and lead to lower-than-expected peak integral values. In some cases, broadening may be so extreme that the resonance is not observed. Overlapping peaks were deconvoluted using the generalized Lorentzian line fitting function in MestReNova.

Mössbauer spectra were recorded on a SEE Co. MS4 spectrometer at zero field and 80 K. Isomer shifts were referenced to α-^{57}Fe foil at 298 K. Data were fitted using WMoss.

UV-visible spectra were recorded on a Cary 60 spectrophotometer using Kontes-valve sealed cuvettes with 1 mm or 2 mm path lengths.

IR data were collected in an N_2-filled glovebox using a Bruker ALPHA spectrometer with a platinum ATR module.

Continuous-wave X-Band EPR spectra were recorded in perpendicular mode using a Bruker EleXsys EPR Spectrometer equipped with an ER 049X microwave bridge. The spectra were simulated using EasySpin.[7]

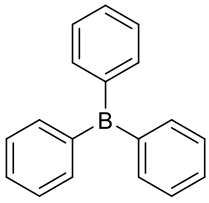
SQUID magnetometry data were collected using a Quantum Design MPMS 3 magnetometer located in the Yale Engineering and Applied Science Center. The samples were prepared by placing crushed solids in a gelatin capsule, secured with eicosane, and placed in a plastic straw sample holder.

Cyclic voltammetry was carried out with a CHI 660E potentiostat inside a nitrogen-filled glovebox using a glassy carbon working electrode, Pt wire counter, and Ag wire pseudo-reference. An electrolytic solution of 0.3 M [N^{n}Bu$_4$][PF$_6$] in THF was used in all measurements, and an internal reference of either ferrocene or decamethylferrocene[8] was included after initial data collection on the reference-free sample.

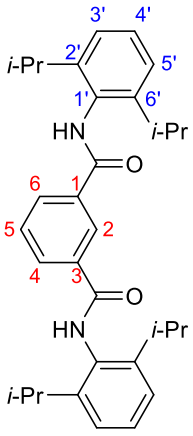
Elemental analysis was performed by the CENTC Elemental Analysis Facility at the University of Rochester on a PerkinElmer 2400 Series II Analyzer, funded by NSF CHE-0650456. Air-sensitive compounds were handled in VAC Atmospheres gloveboxes. Residual solvents in EA samples were identified by ^{1}H NMR spectroscopy.

Density functional theory calculations were carried out using ORCA version 4.2.1 on the Yale high performance computing cluster.

Synthetic Procedures



Triphenylborane (BPh$_3$): Prepared according to a modified literature procedure.[1] In air, a 250 mL round-bottomed flask was charged with trimethylammonium tetraphenylborate[1](15.6 g, 41.1 mmol) and a stir bar. A distillation head was attached to the top of the flask, the receiving vessel was submerged in a dry ice/acetone bath, and the setup was placed under an N_2 atmosphere. The solid powder was stirred vigorously while heating to 200 °C, at which point the solids melted and the byproducts began to distill. A heat gun was used to melt material near the neck of the flask and in the joints. After 15 minutes, no further material appeared to distill, and the solution was cooled to room temperature, during which time it resolidified. The solids were dried under high vacuum. We observed that the crude solid had a residual odor of amine, which could be removed by dissolving the solid in dry toluene (125 mL, added by cannula), then reconcentrating the mixture under vacuum. The solid residue was then brought into an N_2 filled glovebox, dissolved in toluene (5 x 25 mL portions), and filtered through Celite on a frit. The pale yellow filtrate was concentrated until just saturated (ca. 90 mL), then cooled to –40 °C for 5 hours. The resulting crystalline powder was isolated by decanting the supernatant, washing with pentane (2 x 10 mL), and drying under high vacuum. Two additional crops were collected using the same crystallization procedure to yield 8.37 g (84% yield) of the title compound as a white powder. Spectroscopic data were consistent with the literature.[1]



***N*^{1},*N*^{3}-bis(2,6-diisopropylphenyl)isophthalamide (Dipp-OCO)**: Prepared according to a modified literature procedure.[9]

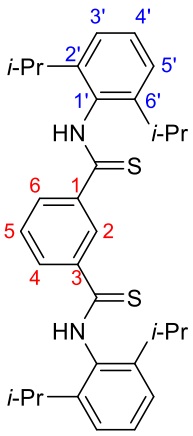
Step 1: A 100 mL round-bottom flask equipped with a reflux condenser was charged with isophthalic acid (24.93 g, 150 mmol), thionyl chloride (33 mL, 452 mmol, 3.0 equiv), and DMF (2 mL), and placed under an N_2 atmosphere. The heterogeneous suspension was heated to 75 °C, and evolved gas was vented through a needle into an aqueous $NaHCO_3$ solution. After 45 min, gas evolution had ceased and the solution had become homogeneous. The mixture was then cooled to room temperature, the reflux condenser was replaced with a short-path distillation head, and all remaining volatile materials were vacuum distilled (40 mTorr, 85 °C) into a liquid nitrogen-cooled receiving flask.

Step 2: A 1 L round-bottomed flask was charged with CH_2Cl_2 (450 mL), 2,6-diisopropyl aniline (67 mL, 355 mmol, 2.4 equiv), and triethylamine (52 mL, 373 mmol, 2.5 equiv), then cooled to 0 °C. While stirring under N_2, a solution of the crude acid chloride in CH_2Cl_2 (50 mL + 2 x 50 mL rinses) was added *slowly* (**Caution**: highly exothermic). The flask headspace was vented with a needle for several minutes, then the mixture was gradually warmed to room temperature and stirred overnight. Following this period, the mixture was concentrated by rotary evaporation to a tan semisolid, then triturated* with room temperature MeCN (3 x 250 mL) to remove the aniline, followed by 1M aq. HCl (3 x 250 mL) to remove Et_3N•HCl. The solids were washed with one additional 250 mL portion of MeCN, then dried under high vacuum to provide **Dipp-OCO** as 64.37 g white powder (89% yield). This powder was carried on to the synthesis of **1** without further purification.

*On smaller-scales, the crude material could be purified by extracting into CH_2Cl_2, followed by washing with 1M HCl, 1M NaOH, and brine. However, on large scale, the poor solubility of **Dipp-OCO** in CH_2Cl_2 necessitated an excessive amount of solvent for the aqueous extraction. Thus, we instead used the trituration procedure described above.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.52 (t, J = 1.8 Hz, 1H, backbone-H2), 8.12 (dd, J = 7.8, 1.8 Hz, 2H, H4/6), 7.63 (t, J = 7.7 Hz, 1H, H5), 7.54 (br. s, 2H, NH), 7.36 (t, J = 7.7 Hz, 2H, H4'), 7.24 (d, J = 7.7 Hz, 4H, H3'/5'), 3.15 (sept, J = 6.9 Hz, 4H, *i*Pr-CH), 1.24 (d, J = 6.9 Hz, 24H, *i*Pr-CH_3) ppm.

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 166.19, 146.48, 135.26, 130.87, 130.49, 129.56, 128.87, 126.22, 123.80, 29.09, 23.86 (br. s) ppm.



***N*^{1},*N*^{3}-bis(2,6-diisopropylphenyl)benzene-1,3-bis(carbothioamide) (1, L =** triply deprotonated **1** in further naming schemes): In air, a 500 mL round-bottomed flask equipped with a reflux condenser was charged with **Dipp-OCO** (5.35 g, 11.0 mmol), toluene (220 mL) and a stir bar. Phosphorus pentasulfide (7.34 g, 33.0 mmol, 3.0 equiv) was added in a single portion and the heterogeneous mixture was heated at 100 °C for 16 hours. The reaction was then cooled to room temperature and concentrated by rotary evaporation to a semisolid. The crude mixture was diluted with H_2O (200 mL) and extracted into EtOAc (4 x 200 mL). The combined organic layers were washed with 1M HCl (200 mL), sat. aq. $NaHCO_3$ (200 mL), dried over Na_2SO_4, filtered, and concentrated to an orange foam. We note that in subsequent preparations of this

compound, we found that washing the organic layer with only water was sufficient. This material was eluted through a short pad of silica gel using EtOAc:hexanes (20:80), concentrated, and reconcentrated several times from Et_2O and hexanes. The resulting product was crystallized by dissolving in boiling Et_2O (100 mL), cooling to room temperature, layering hexanes (100 mL) and cooling at –25 °C overnight. The resulting yellow block-like crystals were isolated by suction filtration on a frit, rinsed with cold hexanes (3 x 10 mL), and dried under high vacuum to afford **1•Et₂O** in 5.09 g (78% yield). Under these conditions, the product appears to co-crystallize with a small amount of unknown aromatic impurity and 1 equiv Et_2O, the latter of which can be removed by subjecting the solid to high vacuum for at least 12 hours. The impurity does not adversely affect purification after the subsequent metalation of **1**.

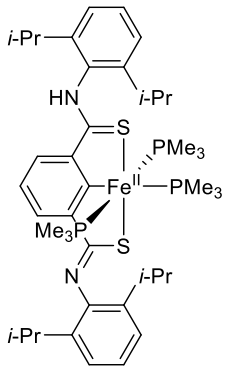
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.84 (s, 2H, NH), 8.47 (t, J = 1.9 Hz, 1H, H2), 8.07 (dd, J = 7.8, 1.9 Hz, 2H, H4/6), 7.55 (t, J = 7.8 Hz, 1H, H5), 7.43 (t, J = 7.8 Hz, 2H, H4'), 7.29 (d, J = 7.8 Hz, 4H, H3'/5'), 3.09 (sept, J = 6.8 Hz, 4H, *i*Pr-CH), 1.30 (d, J = 6.8 Hz, 12H, *i*Pr-CH_3), 1.24 (d, J = 6.9 Hz, 12H, *i*Pr-CH_3) ppm.

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 199.86, 145.88, 142.20, 133.78, 129.66, 129.42, 129.32, 125.02, 124.21, 29.13, 24.69, 23.44 ppm.

UV-vis (THF): 291 nm (ε = 11,900 $cm^{-1}\,M^{-1}$), 415 nm (320 $cm^{-1}\,M^{-1}$).

FT-IR (solid, cm^{-1}): 3199 (m), 3144 (m), 3136 (m), 3069 (m), 3034 (w), 2959 (m), 2926 (m), 2865 (m), 2806 (w), 1493 (m), 1468 (m), 1423 (m), 1382 (m), 1360 (m), 1342 (m), 1329 (m), 1272 (m), 1256 (m), 1201 (m), 1187 (m), 1105 (m), 1085 (w), 1056 (m), 1046 (m), 1024 (m), 991 (m), 936 (m), 924 (w), 909 (m), 891 (m), 826 (w), 797 (m), 769 (m), 744 (m), 730 (m), 714 (m), 683 (m), 634 (m), 587 (m), 569 (m), 563 (m), 557 (m), 536 (m), 504 (m), 465 (w), 449 (w), 432 (w), 412 (m), 402 (m).

Elem. Anal.: We could not obtain satisfactory elemental analysis of this compound due to co-crystallization of impurity.



HLFe^{II}(PMe₃)₃ (2): A 50 mL bomb flask was charged with $Fe(PMe_3)_4$ (107.6 mg, 0.299 mmol, 1.2 equiv) in 4 mL Et_2O. In a separate vial, a slurry of **1** (129.8 mg, 0.251 mmol) was made using 6 mL Et_2O, and this slurry was transferred to the flask of stirring $Fe(PMe_3)_4$. After four hours, the reaction mixture was concentrated under reduced pressure to a dark green powder which was rinsed four times with 2 mL pentane, passed through a Celite plug, and eluted with 25 mL Et_2O. After removal of Et_2O under reduced pressure, 192.3 mg dark green powder remained (96% yield).

^{1}H NMR (400 MHz, THF-d_8): δ 9.84 (s, 1H, NH), 8.09 (d, J = 7.3 Hz, 1H, H4 or H6), 7.97 (d, J = 7.7 Hz, 1H, H4 or H6), 7.34−7.21 (m, 3H, H3'/4'/5' or H3"/4"/5" (inequivalent, second order)), 7.13 (app. t, J = 7.5 Hz, 1H, H5), 6.97 (d, J = 7.6 Hz, 2H, H3'/5' or H3"/5"), 6.79 (t, J = 7.6 Hz, 1H, H4' or H4''), 3.18 – 3.09 (m, 4H, *i*Pr-CH (inequivalent, overlapped)), 1.49 (d, $^2J_{HP}$ = 5.5 Hz, 9H, equatorial PMe_3), 1.20 (d, J = 6.9 Hz, 6H, *i*Pr-CH_3), 1.19

(d, J = 6.9 Hz, 6H, *i*Pr-CH_3), 1.15 (d, J = 7.0 Hz, 6H, *i*Pr-CH_3), 1.08 (d, J = 6.8 Hz, 6H, *i*Pr-CH_3), 0.67 (virt. t, J = 2.7 Hz, 18H, axial PMe_3) ppm.

$^{31}P\{^1H\}$ NMR (162 MHz, THF-d_8): δ 10.99 (A of A_2B, $^2J_{PP}$ = 46.2 Hz, 2P), 9.82 (B of A_2B, $^2J_{PP}$ = 46.2 Hz, 1P) ppm.

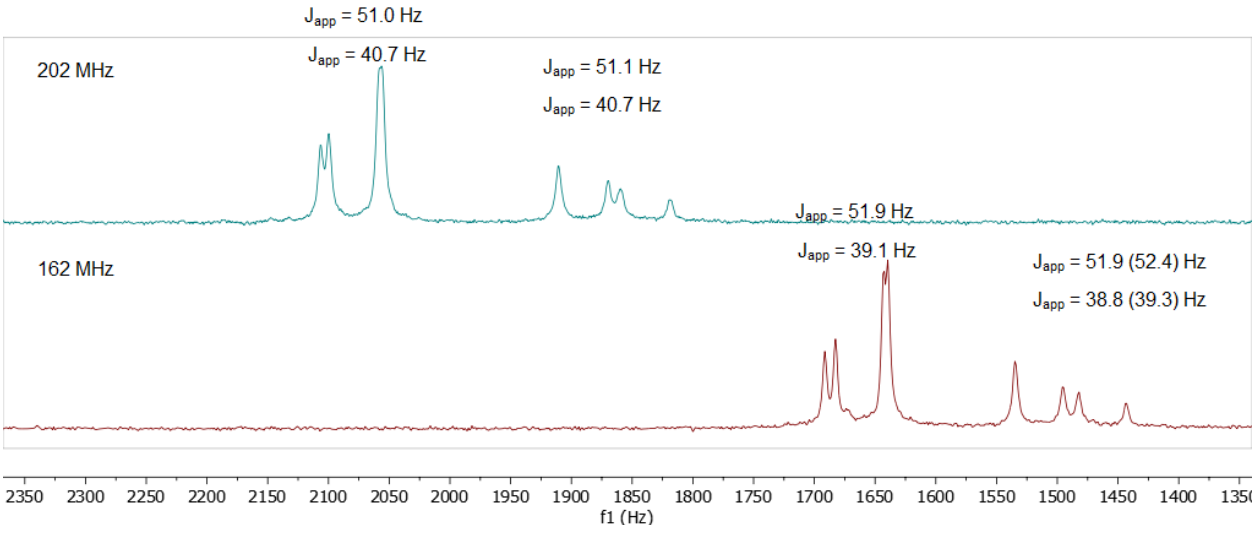
UV-Vis (THF): 286 nm (ε = 10,400 $cm^{-1}\,M^{-1}$), 395 nm (ε = 1,600 $cm^{-1}\,M^{-1}$), 493 nm (ε = 2,100 $cm^{-1}\,M^{-1}$), 633 nm (ε = 2,400 $cm^{-1}\,M^{-1}$).

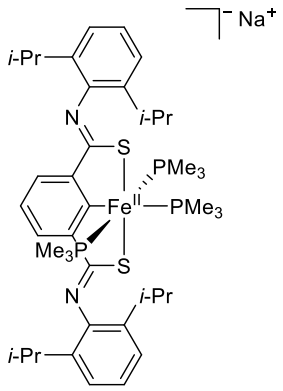
FT-IR (solid, cm^{-1}): 3336 (m), 3052 (w), 2961 (m), 2906 (m), 2861 (m), 2802 (w), 1562 (w), 1507 (m), 1493 (w), 1480 (m), 1462 (m), 1431 (m), 1419 (m), 1378 (m), 1356 (m), 1319 (m), 1295 (m), 1274 (m), 1258 (m), 1225 (m), 1187 (m), 1175 (m), 1099 (w), 938 (m), 926 (m), 865 (m), 846 (m), 834 (m), 799 (m), 756 (m), 734 (m), 703 (m), 675 (m), 659 (m), 640 (m), 630 (m), 610 (m), 589 (m), 557 (m), 536 (m), 498 (m), 453 (m), 434 (m), 418 (m).

Mössbauer (solid, 80 K): δ = 0.21 mm/s, $|\Delta E_Q|$ = 1.25 mm/s, Γ = 0.28 mm/s.

Elem. Anal.: We could not obtain satisfactory elemental analysis of this compound.

Note about the $^{31}P\{^1H\}$ NMR spectrum of 2: It is also possible to interpret the $^{31}P\{^1H\}$ NMR data as three inequivalent signals, which is plausible given the slight inequivalence of the axial phosphines in the crystal structure. A first order analysis of the $^{31}P\{^1H\}$ NMR data in C_6D_6 (below) would give δ 11.01 (d, J = 51.0 Hz), 11.00 (d, J = 40.1 Hz), 9.78 (dd, J = 51.0, 39.9 Hz) ppm, which is almost certainly incorrect because it lacks any trans P–P coupling. However, if the two axial phosphines are truly inequivalent but extremely close in chemical shift, this would produce an ABC spin system with $\nu_{AB} << {}^2J_{AB}$, and thus one would expect a second-order pattern. However, simulations of the ABC and A_2B spin systems in WINDNMR[10] are almost indistinguishable. Furthermore, ^{31}P spectra using higher field strengths did not clearly differentiate these possibilities.





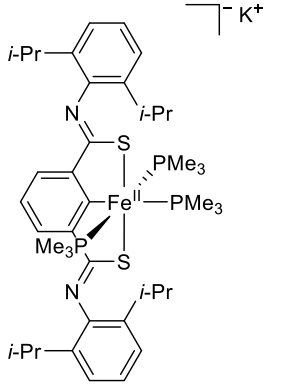
Na[LFe^{II}(PMe$_3$)$_3$] (3-Na): In a 20 mL vial, **2** (80.1 mg, 0.100 mmol) was dissolved in 10 mL Et_2O, giving a dark green solution. $NaN(TMS)_2$ (18.6 mg, 0.101 mmol, 1.01 equiv) in 10 mL THF was added to stirring **2**, resulting in an immediate color change to dark brown/purple. After 30 minutes, solvents were removed under reduced pressure, and the remaining solids were washed three times with 1 mL pentane to remove $HN(TMS)_2$. This afforded 89.6 mg of solid (>100% crude yield). It is possible that sodium-coordinated THF molecules can account for some of the excess mass, as free THF was observed in the NMR spectrum of the solids. The structure of **3-Na** was inferred based on the NMR and IR spectra. Integration relative to a 1,3,5-trimethoxybenzene standard gave an 88% yield of the **3-Na** as drawn. IR and Mössbauer spectra were obtained of the crude solids, and the Mössbauer spectrum showed only one iron species.

^{1}H NMR (400 MHz, THF-d_8): δ 7.80 (d, J = 7.4 Hz, 2H, H4/6), 6.91 (d, J = 7.6 Hz, 4H, H3'/5'), 6.80 (app. s, 1H, H5), 6.70 (t, J = 6.9 Hz, 2H, H4'), 3.19 (sept, J = 6.6 Hz, 4H, *i*Pr CH), 1.41 (s, 9H, equatorial PMe_3), 1.13 (d, J = 7.8 Hz, 12H, *i*Pr CH_3), 1.05 (d, J = 6.8 Hz, 12H, *i*Pr CH_3), 0.76 (s, 18H, axial PMe_3) ppm. Assignments are labeled according to the numbering scheme for the ligand **1**.

^{31}P{^{1}H} NMR (162 MHz, THF-d_8): δ 18.16 (A of A_2B, $^2J_{PP}$ = 43.5 Hz, 2P), 15.79 (B of A_2B, $^2J_{PP}$ = 43.5 Hz, 1P) ppm.

FT-IR (solid, cm^{-1}): 3052 (w), 2955 (m), 2904 (m), 2863 (m), 2800 (w), 1539 (s), 1501 (s), 1464 (m), 1421 (m), 1378 (m), 1366 (m), 1358 (m), 1342 (w), 1319 (m), 1291 (m), 1272 (m), 1256 (m), 1242 (m), 1225 (m), 1185 (m), 1162 (m), 1095 (m), 1046 (m), 1003 (w), 940 (s), 842 (m), 799 (m), 771 (w), 756 (m), 748 (w), 740 (m), 734 (m), 706 (m), 657 (m).

Mössbauer (solid, 80K): δ = 0.24 mm/s, $|\Delta E_Q|$ = 0.94 mm/s, Γ = 0.30 mm/s.

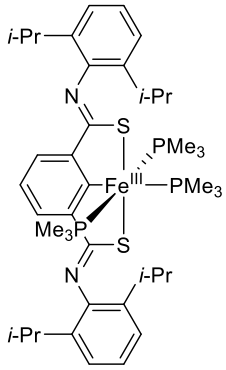


K[LFe^{II}(PMe$_3$)$_3$] (3-K): In a 20 mL vial, **4** (83.5 mg, 0.10 mmol) was dissolved in 8 mL THF and cooled to −78 °C. KC_8 (14.8 mg, 0.11 mmol, 1.1 equiv) was added as a slurry in 2 mL THF cooled to −78 °C. The reaction mixture changed from dark green to dark brown in color and was allowed to warm to room temperature while stirring for 1 hour. The reaction mixture was then filtered through a Celite pad, and removal of THF under reduced pressure left 91.7 mg dark brown powder. The structure of **3-K** was inferred based on the NMR spectrum. Integration relative to a $NiCp_2$ capillary standard gave a 91% yield of **3-K** as drawn. A Mössbauer spectrum of the crude solids was obtained and showed only one iron species.

^{1}H NMR (400 MHz, THF-d_8): δ 7.83 (app. s, 2H, H4/6), 6.91 (d, J = 7.6 Hz, 4H, H3'/5'), 6.80 (app. s, 1H, H5), 6.69 (app. s, 2H, H4'), 3.19 (sept, J = 6.7 Hz, 4H, *i*Pr CH), 1.39 (s, 9H, equatorial PMe_3), 1.13 (d, J = 6.9 Hz, 12H, *i*Pr CH_3), 1.06 (d, J = 6.7 Hz, 12H, *i*Pr CH_3), 0.73 (s, 18H, axial PMe_3) ppm. Assignments are labeled according to the numbering scheme for the ligand **1**.

$^{31}P\{^{1}H\}$ NMR (162 MHz, THF-d_8): δ 18.10 (A of A_2B, $^2J_{PP}$ = 43.0 Hz, 2P), 15.87 (B of A_2B, $^2J_{PP}$ = 43.0 Hz, 1P) ppm.

Mössbauer (solid, 80K): δ = 0.25 mm/s, $|\Delta E_Q|$ = 1.05 mm/s, Γ = 0.29 mm/s.



$LFe^{III}(PMe_3)_3$ (4): $Fe(PMe_3)_4$ (1.57 g, 4.34 mmol, 1.1 equiv) was added to a 250 mL Schlenk flask, along with Et_2O (100 mL) and a stir bar. The yellow-brown solution was stirred vigorously, and ligand **1** (2.04 g, 3.95 mmol) was added quickly as a solid. Additional Et_2O (20 mL) was used to complete the transfer. The dark green mixture was stirred at room temperature for 2.5 hours, then removed from the glovebox. The solution was sparged with N_2 for 5 minutes to remove the bulk of the PMe_3 byproduct (and prevent formation of a large amount of trimethylphosphine oxide in the reaction mixture), then sparged with air for 10 minutes, during which time the color lightened to an olive green. This mixture was then diluted with an additional 50 mL Et_2O and washed with brine (3 x 150 mL) in a separatory funnel to remove any $O{=}PMe_3$. The organic layer was dried over Na_2SO_4, filtered, and concentrated, then dried for several hours at 40 °C and 50 mTorr with a secondary trap of P_2O_5. The solid material was returned to an N_2 glovebox, dissolved in Et_2O and filtered through a pad of activated alumina, eluting all green material (150 mL total). The eluent was concentrated and dried under vacuum to provide 2.87 g of the final olive-green powder (88% yield, accounting for 0.4 equiv Et_2O). Crystallization from Et_2O at −40 °C gave crystals for suitable for X-ray diffraction.

Evans (C_6D_6, 298 K): μ_{eff} = 1.6 μ_B.

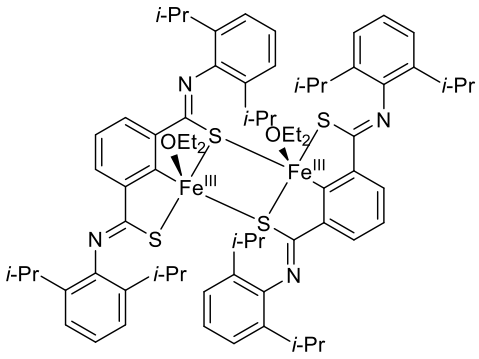
^{1}H NMR (400 MHz, C_6D_6): δ 10.8 (4H, H3'/5' or *i*Pr CH), 7.6 (1H, H5), 7.5 (2H), 4.8 (4H, H3'/5' or *i*Pr CH), 2.9 (12H, *i*Pr CH_3), 2.6 (12H, *i*Pr CH_3), –9.9 (9H, equatorial PMe_3), –13.1 (15H* axial PMe_3) ppm. Assignments are labeled according to the numbering scheme for the ligand **1**. We did not observe a signal integrating to an additional expected 2H. *Integration is lower than theoretical value likely because of broadening.

UV-Vis: 332 nm (ε = 9,800 $cm^{-1}\,M^{-1}$), 389 nm (ε = 5,000 $cm^{-1}\,M^{-1}$), 417 nm (ε = 5,000 $cm^{-1}\,M^{-1}$), 710 nm (ε = 9,000 $cm^{-1}\,M^{-1}$).

FT-IR (solid, cm^{-1}): 3052 (w), 2957 (m), 2908 (m), 2863 (m), 2800 (w), 1593 (m), 1566 (s), 1550 (s), 1462 (m), 1429 (m), 1419 (m), 1387 (m), 1358 (m), 1325 (m), 1299 (m), 1278 (m), 1252 (m), 1232 (m), 1181 (m), 1158 (w), 1099 (m), 1058 (w), 1042 (w), 936 (s), 916 (s), 846 (m), 812 (m), 797 (m), 756 (m), 732 (m), 722 (m), 667 (m), 616 (m), 510 (w).

Mössbauer (solid, 80 K): δ = 0.16 mm/s, $|\Delta E_Q|$ = 3.45 mm/s, Γ_L = 0.57 mm/s, Γ_R = 0.32 mm/s.

Elem. Anal.: Anal. Calcd. for $C_{41}H_{64}FeN_2P_3S_2 \bullet 0.4\ C_4H_{10}O$ (Et_2O): C, 61.84; H, 8.31; N, 3.37. Found: C, 61.94; H, 8.46; N, 3.43.



[LFe^{III}(Et$_2$O)]$_2$ (5-Et$_2$O): A 20 mL vial was charged with a stir bar, LFe^{III}(PMe$_3$)$_3$(Et$_2$O)$_{0.4}$(**4**) (826 mg, 1.00 mmol, 1.0 equiv), and THF (5 mL). While stirring vigorously, BPh$_3$ (800 mg, 3.30 mmol, 3.3 equiv) was added in a single portion, resulting in a rapid color change from green to red. After several minutes, the color gradually lightened to orange and considerable precipitation was observed (Me$_3$P–BPh$_3$). After 2.5 hours, the mixture was filtered through Celite on a frit, rinsing with THF until all orange material eluted. The filtrate was concentrated, dissolved in minimal THF, re-filtered through a Celite plug and concentrated in vacuo. This process was repeated several times until no further precipitate was observed during filtration. The crude product was then reconcentrated several times from Et$_2$O/hexanes (50/50, 3 x 10 mL portions) to exchange the bound solvent with Et$_2$O and remove residual THF. The resulting brown solid was crystallized twice from Et$_2$O (dissolved in 45 mL Et$_2$O, filtered, cooled to –40 °C overnight) to afford 376 mg (58% yield) dark brown needles of **5-Et$_2$O**.

^{1}H NMR (400 MHz, THF-d_8): δ 12.1 (4H, H3'/5'), 6.5 (2H), 3.4 (q, J = 7.0 Hz, 4H, O(C**H**$_2$CH$_3$)$_2$), 2.3 (12H *i*Pr CH$_3$), 1.1 (t, J = Hz, 6H, O(CH$_2$C**H**$_3$)$_2$), 0.2 (12H, *i*Pr CH$_3$), –74.5 (2H), –81.1 (1H, H5). Assignments are labeled according to the numbering scheme for the ligand **1**. We did not observe another signal integrating to 4H (*i*Pr CH), likely because of broadening. There may be an extremely broad peak centered around 3.3 ppm that corresponds to this resonance. Note that upon dissolution in THF, Mössbauer spectroscopy indicates there is a change in the iron coordination environment (Figure S80), which may be consistent with the dimer breaking up into monomers. This could explain why this NMR spectrum suggests a higher symmetry than the dimeric structure.

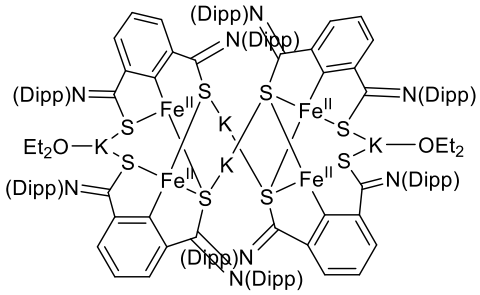
UV-Vis (THF): 304 nm (ε = 7,600 cm^{-1} M^{-1}), 353 nm (6,800 cm^{-1} M^{-1}), 458 nm (4,600 cm^{-1} M^{-1}).

FT-IR (solid, cm^{-1}): 3057 (w), 2957 (m), 2930 (m), 2900 (m), 2865 (m), 1613 (m), 1576 (s), 1458 (m), 1448 (m), 1431 (m), 1382 (m), 1358 (m), 1327 (m), 1274 (m), 1252 (m), 1238 (m), 1179 (m), 1107 (w), 1097 (m), 1085 (m), 1036 (m), 991 (m), 909 (m), 814 (m), 795 (m), 775 (m), 756 (m), 720 (m), 620 (m), 504 (w), 469 (w), 416 (w).

Elem. Anal.: Anal. Calcd. for C$_{64}$H$_{74}$Fe$_2$N$_4$S$_4$ • 2 C$_4$H$_{10}$O (Et$_2$O): C, 67.17; H, 7.36; N, 4.35. Found: C, 67.36; H, 7.46; N, 4.11.

Mössbauer (solid, 80 K): δ = 0.34 mm/s, $|\Delta E_Q|$ = 3.91 mm/s, Γ_L = 0.32 mm/s, Γ_R = 0.27 mm/s.

Mössbauer (frozen THF solution, 80 K): δ = 0.45 mm/s, $|\Delta E_Q|$ = 4.26 mm/s, Γ_L = 0.73 mm/s, Γ_R = 0.49 mm/s.



$K_4[LFe^{II}]_4(Et_2O)_2$ (6): A 20 mL vial was charged with $[LFe^{III}(Et_2O)]_2$ (**5-Et_2O**) (102 mg, 0.079 mmol, 1.0 equiv) was dissolved in 2 mL THF and cooled to −78 °C. While stirring, KC_8 (22.9 mg, 0.169 mmol, 2.1 equiv) was added as a solid. The reaction mixture changed from orange-red to very dark purple upon addition of KC_8. The reaction was slowly warmed to room temperature over an hour, then the mixture was filtered through a Celite plug. THF was removed under reduced pressure, and the dark solids were dissolved in 1 mL Et_2O. After filtering, the Et_2O solution was placed at −40 °C, and dark square crystals formed within several hours. The crystalline material was dried under vacuum to afford 47 mg (46% yield) of **6** as a dark brown solid.

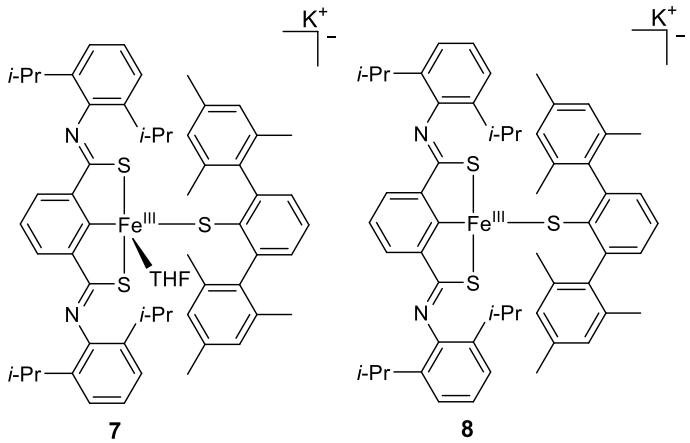
^{1}H NMR (400 MHz, THF-d_8): δ 13.9 (2H), 11.1 (1H), 10.2 (1H), 9.3 (1H), 7.7 (1H), 6.8 (3H, *i*Pr CH_3), 6.2 (1H), 6.1 (1H), 4.8 (3H, *i*Pr CH_3), 1.3 (2H), 0.8 (2H), 0.4 (2H), –0.8 (3H, *i*Pr CH_3), –1.6 (3H, *i*Pr CH_3), –4.3 (3H, *i*Pr CH_3), –7.8 (1H), –26.1 (1H), –26.7 (1H), –41.2 (1H) ppm. Due to the complexity and broadness of the NMR spectrum, we were not able to assign resonances besides the five tentatively-assigned isopropyl CH_3 groups. Assuming all proton environments are chemically inequivalent (except for protons on the same methyl group), there should be 21 signals excluding Et_2O; however, only 19 were found. Additional peaks are probably obscured by overlap or broadening.

UV-Vis (THF): 465 nm (ε = 4,200 $cm^{-1}\,M^{-1}$), 662 nm (ε = 1,300 $cm^{-1}\,M^{-1}$).

FT-IR (solid, cm^{-1}): 3057 (w), 2953 (m), 2924 (m), 2861 (m), 2804 (m), 1605 (m), 1568 (s), 1546 (m), 1458 (m), 1425 (m), 1380 (m), 1358 (m), 1323 (m), 1291 (m), 1262 (m), 1232 (m), 1179 (m), 1158 (m), 1144 (m), 1109 (m), 1097 (m), 1075 (m), 1042 (m), 1011 (m), 958 (w), 932 (m), 907 (m), 797 (m), 756 (m), 730 (m), 718 (m), 693 (w), 653 (w), 610 (m), 555 (m), 506 (w), 473 (w).

Mössbauer (solid, 80 K): δ = 0.34 mm/s, $|\Delta E_Q|$ = 1.87 mm/s, Γ = 0.33 mm/s.

Elem. Anal.: Anal. Calcd. For $K_4C_{128}H_{148}Fe_4N_8S_8 \bullet 2\ C_4H_{10}O$ (Et_2O): C, 63.24; H, 6.56; N, 4.34. Found: C, 62.98; H, 6.18; N, 4.54.



$K[LFe^{III}(SAr)(THF)]$ (7) and $K[LFe^{III}(SAr)]$ (8): A solution of **5-Et_2O** (10.3 mg, 0.0080 mmol, 1.0 equiv) in 2 mL THF was added to solid ArSK (6.4 mg, 0.017 mmol, 2.1 equiv) in a 20 mL vial while stirring. The solution became slightly darker orange. After two hours, THF was removed under reduced pressure, leaving a dark orange solid. Pentane (2 mL) was added, causing the solution to turn dark brown, and evacuation of pentane left dark brown

solids. The solids were redissolved in pentane (2 mL) and passed through a Celite plug, then dried to provide 14.8 mg solid **8** (97% yield). We were unable to crystallize **7** or **8** without 18-crown-6 (see below). Note that upon dissolution in THF, the color of **8** changes from dark brown to red-orange, indicating that THF-adduct **7** is likely formed.

Evans (**7**, THF-d_8, 298 K): $\mu_{eff} = 4.0 \pm 0.1\ \mu_B$.

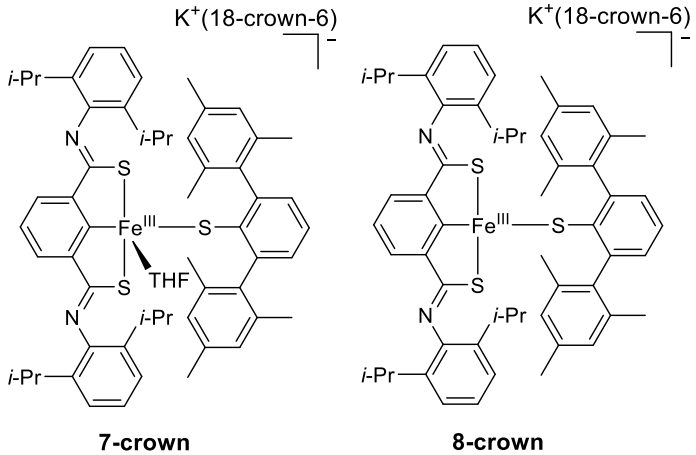
^{1}H NMR (**7**, 400 MHz, THF-d_8): δ 15.0 (2H), 12.8 (4H), 6.9 (4H), 6.6 (6H), 3.0 (12H), 2.6 (12H), 1.3 (12H), –2.1 (2H), –45.5 (2H), –63.2 (1H) ppm. We did not observe additional expected signals integrating to 1H or 4H.

UV-Vis (**7**, THF): 345 nm (ε = 10,400 $cm^{-1}\,M^{-1}$), 465 nm (ε = 6,400 $cm^{-1}\,M^{-1}$).

FT-IR (solid **8**, cm^{-1}): 3050 (w), 2957 (m), 2922 (m), 2865 (m), 1595 (s), 1574 (s), 1450 (m), 1429 (m), 1380 (m), 1358 (m), 1327 (m), 1274 (m), 1252 (m), 1238 (m), 1181 (m), 1160 (m), 1144 (w), 1109 (m), 1097 (m), 1042 (m), 1013 (m), 918 (m), 852 (m), 797 (m), 756 (m), 742 (m), 716 (m), 699 (m), 659 (w), 622 (m), 593 (m), 510 (m), 471 (m), 418 (m).

Mössbauer (solid **8**, 80 K): $\delta = 0.31$ mm/s, $|\Delta E_Q| = 3.88$ mm/s, $\Gamma_L = 0.61$ mm/s, $\Gamma_R = 0.53$ mm/s.

Elem. Anal. (solid **8**): Anal. Calcd. for $KC_{56}H_{62}FeN_2S_3 \bullet C_4H_8O$ (THF): C, 70.21; H, 6.87; N, 2.73. Found: C, 69.84; H, 6.59; N, 2.75. This sample was prepared from crushed material that was dried for several hours under vacuum, giving a dark brown solid that is characteristic of the compound with no THF coordinated to iron. Thus, the single THF molecule per iron in the sample is likely coordinated to K^+ rather than the iron center, as the Fe−THF adduct appears dark orange, not dark brown.



K(18-crown-6)[LFe^{III}(SAr)(THF)] (7-crown) and K(18-crown-6)[LFe^{III}(SAr)] (8-crown): A solution of 18-crown-6 (33.8 mg, 0.128 mmol, 2.1 equiv) was dissolved in 5 mL THF and transferred to solid **5-Et$_2$O** (76.8 mg, 0.060 mmol, 1.0 equiv) while stirring. The resulting solution was added to a solution of ArSK (49.1 mg, 0.128 mmol, 2.1 equiv) in 2 mL THF, resulting in an immediate color change from orange to red-brown. After one hour of stirring, the reaction mixture was concentrated to a sticky brown solid. The solids were washed with hexanes (3 x 3 mL) then extracted into Et_2O, then toluene (each 3 x 3 mL). Combining extractions into toluene and Et_2O followed by solvent removal under reduced pressure gave 136.4 mg (93% yield) of dark green solid **8-crown**. Crystals suitable for diffraction were obtained of **8-crown** by crystallization from toluene at −40 °C. Crystallization from THF at ambient temperature gave the Fe-coordinated THF adduct **7-crown**.

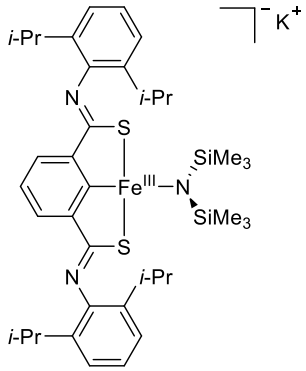
^{1}H NMR (**7-crown**, 400 MHz, THF-d_8): δ 15.7 (2H), 13.0 (4H), 5.0 (12H), 3.3 (24H, 18-crown-6), 2.9 (12H), 2.5 (12H), –0.7 (2H), –46.7 (2H), –49.9 (1H) ppm. We did not observe additional expected signals integrating to 1H, 4H, or 6H, though there may be an extremely broad feature centered around 4 ppm that overlaps with several other more well-defined peaks.

UV-Vis (**7-crown**, THF): 293 nm (ε = 25,200 $cm^{-1}\,M^{-1}$), 360 nm (ε = 12,600 $cm^{-1}\,M^{-1}$), 405 nm (ε = 10,400 $cm^{-1}\,M^{-1}$), 468 nm (ε = 6,500 $cm^{-1}\,M^{-1}$).

FT-IR (solid **8-crown**, cm^{-1}): 3055 (w), 2955 (m), 2910 (m), 2863 (m), 1595 (m), 1576 (s), 1452 (m), 1431 (m), 1382 (m), 1352 (m), 1327 (m), 1297 (m), 1276 (m), 1248 (m), 1181 (m), 1101 (m), 1060 (m), 1044 (m), 1011 (m), 1001 (m), 954 (m), 920 (m), 869 (m), 858 (w), 842 (m), 814 (m), 795 (m), 759 (m), 742 (m), 724 (m), 695 (m), 591 (m), 575 (m), 559 (w), 514 (m), 477 (m), 467 (m).

Mössbauer (solid **8-crown**, 80 K): δ = 0.30 mm/s, $|\Delta E_Q|$ = 4.03 mm/s, Γ = 0.41 mm/s.

Elem. Anal. (**8-crown**): Anal. Calcd. for $KC_{68}H_{86}FeN_2S_3O_6$: C, 67.02; H, 7.11; N, 2.30. Found: C, 67.06; H, 7.18; N, 2.20.



K[LFe^{III}(N(TMS)$_2$)] (9): A 20 mL vial was charged with **5-Et$_2$O** (128 mg, 0.099 mmol, 1.0 equiv), THF (2 mL), and a stir bar. While stirring, KHMDS (42 mg, 0.21 mmol, 2.1 equiv) was added as a solution in THF (1 mL + 2 x 0.5 mL rinses). The red-orange mixture was stirred at room temperature for 5 minutes, then concentrated under reduced pressure and reconcentrated from Et_2O/hexanes to give an orange solid. The crude product was triturated with 3 x 3 mL portions of hexanes and toluene, discarding these extracts. The remaining orange solid was then collected into a separate flask by dissolving in Et_2O and eluting through a plug of Celite on a frit, followed by concentrating under vacuum to yield 133 mg (87% yield) of bright orange powder. X-ray quality crystals were obtained from vapor diffusion of pentane into an Et_2O solution at −40 °C.

Evans (THF-d_8, 298 K): μ_{eff} = 4.1 ± 0.1 μ_B.

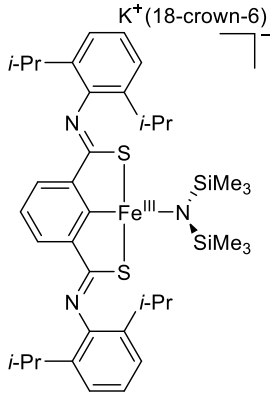
^{1}H NMR (400 MHz, THF-d_8): δ 19.1 (4H, H3'/5' or *i*Pr CH), 13.5 (4H, H3'/5' or *i*Pr CH), 11.0 (2H, H4' or H4/6), 4.9 (12H, *i*Pr CH_3), 4.8 (12H, *i*Pr CH_3), –21.9 (2H, H4' or H4/6), –22.6 (15H*, $Si(CH_3)_3$), –67.9 (1H, H5) ppm. Assignments are labeled according to the numbering scheme for the ligand **1**. *Broadening likely leads to a lower integration than the theoretical value.

FT-IR (solid, cm^{-1}): 3050 (w), 2955 (m), 2924 (m), 2891 (m), 2865 (m), 1593 (m), 1570 (s), 1542 (m), 1460 (m), 1427 (m), 1395 (m), 1382 (m), 1360 (m), 1325 (m), 1301 (m), 1278 (m), 1242 (m), 1225 (m), 1185 (m), 1099 (m), 1058 (m), 958 (s), 934 (m), 856 (m), 830 (m), 799 (s), 769 (s), 740 (m), 712 (s), 669 (m), 626 (m), 618 (m), 518 (m), 479 (m), 469 (m), 428 (m).

UV-Vis (THF): 287 nm (ε = 25,200 $cm^{-1}\,M^{-1}$), 358 nm (ε = 7,600 $cm^{-1}\,M^{-1}$), 417 nm (ε = 6,200 $cm^{-1}\,M^{-1}$).

Mössbauer (solid, 80 K): δ = 0.18 mm/s, $|\Delta E_Q|$ = 0.93 mm/s, Γ_L = 0.30 mm/s, Γ_R = 0.33 mm/s.

Elem. Anal.: We were unable to obtain satisfactory elemental analysis on this compound, likely due to its apparent room-temperature decomposition even as a solid (see Figure S17).



K(18-crown-6)[LFe^{III}(N(TMS)$_2$)] (9-crown): 18-crown-6 (4.8 mg, 0.018 mmol, 2.4 equiv) was dissolved in 0.5 mL THF and transferred to solid **5-Et$_2$O** (9.7 mg, 0075 mmol, 1.0 equiv). This solution was then transferred to solid KN(TMS)$_2$ (3.5 mg, 0.018 mmol, 2.4 equiv), and the resulting reaction mixture stirred vigorously for 10 minutes. The crude mixture was concentrated to an orange semisolid material, which was washed with Et$_2$O over a Celite plug then eluted with THF. Removal of THF under reduced pressure gave 15.5 mg orange powder, which was a yield of 94% when integrated with respect to a NiCp$_2$ capillary standard; some KN(TMS)$_2$ remained. Analytically-pure crystalline material for X-ray diffraction was obtained from vapor diffusion of pentane into an Et$_2$O solution at −40 °C.

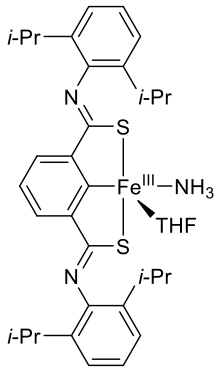
^{1}H NMR (400 MHz, THF-d_8): δ 19.0 (4H, H3'/5' or *i*Pr CH), 13.4 (4H, H3'/5' or *i*Pr CH), 10.9 (2H, H4'), 4.8 (12H, *i*Pr CH$_3$), 4.7 (10H*, *i*Pr CH$_3$), 3.2 (24H, 18-crown-6), –21.9 (2H, H4/6), –22.6 (16H*, Si(CH$_3$)$_3$), –68.0 (1H, H5) ppm. Assignments are labeled according to the numbering scheme for the ligand **1**. *Broadening likely leads to a lower integration than the theoretical value.

UV-Vis: 285 nm (ε = 23,000 cm^{-1} M^{-1}), 408 nm (ε = 7,000 cm^{-1} M^{-1}).

FT-IR (solid, cm^{-1}): 3052 (w), 2953 (m), 2895 (m), 2863 (m), 1564 (m), 1454 (m), 1429 (m), 1352 (m), 1325 (w), 1274 (m), 1248 (m), 1238 (m), 1183 (m), 1101 (m), 1058 (m), 1044 (m), 1005 (w), 960 (m), 932 (m), 832 (m), 810 (m), 797 (m), 754 (m), 722 (m), 697 (w), 626 (m), 477 (w), 459 (m).

Mössbauer (solid, 80 K): δ = 0.17 mm/s, $|\Delta E_Q|$ = 0.88 mm/s, Γ = 0.36 mm/s.

Elem. Anal.: Anal. Calcd. for KC$_{50}$H$_{79}$FeN$_3$S$_2$O$_6$Si$_2$: C, 58.11; H, 7.71; N, 4.07. Found: C, 58.08; H, 7.99; N, 4.04.



[LFe^{III}(NH$_3$)(THF)] (10): A bomb flask was charged with **5-Et$_2$O** (59.4 mg, 0.046 mmol, 1.0 equiv) in 2 mL THF, giving a dark, opaque red-orange solution. On a Schlenk line, the flask contents were frozen in liquid nitrogen and the headspace gas evacuated. The flask was then closed, keeping the contents frozen in LN$_2$. The Schlenk line was then cycled three times with NH$_3$(*g*), then a 12.55 mL bulb was charged with 182 mbar NH$_3$(*g*) (0.0922 mmol at 298 K, 2.0 equiv). The reaction flask was then opened to the bulb containing NH$_3$(*g*), and NH$_3$(*g*) was allowed to condense in the flask for 30 minutes. After the gas transfer, the flask was closed and warmed to room temperature while stirring; the solution became more translucent and orange in color. The reaction was stirred for 1 hour at room temperature, then THF was

removed under reduced pressure, leaving an orange solid. The bomb flask was closed and moved back into an N_2-filled glovebox. The solids were dissolved in 2 mL Et_2O and placed at −40 °C, resulting in crystallization. From this crop, 52.2 mg (86% yield) of bright orange crystals were collected.

Evans (THF-d_8, 298 K): $\mu_{eff} = 4.1 \pm 0.1\ \mu_B$.

^{1}H NMR (400 MHz, THF-d_8): δ 174.9 (1H*, NH_3), 11.7 (4H, H3'/5' or *i*Pr CH), 6.3 (2H, H4' or H4/6), 2.7 (4H, H3'/5' or *i*Pr CH), 2.4 (12H, *i*Pr CH_3), –0.4 (12H, *i*Pr CH_3), –50.1 (2H, H4' or H4/6), –78.1 (1H, H5) ppm. Assignments are labeled according to the numbering scheme for the ligand **1**. Signals for coordinated THF were not observed, presumably because of exchange with THF-d_8. *This signal is assigned to NH_3 because such a downfield signal is only observed in **10**. It likely integrates to less than 3H due to extreme broadening that prevents proper baseline corrections.

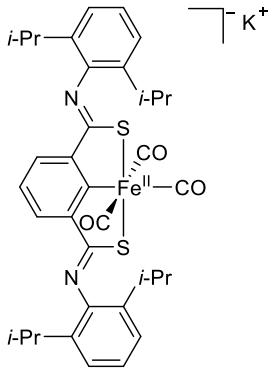
^{1}H NMR (400 MHz, C_6D_6): δ 44.5, 12.7, 9.0, 8.6, 7.1, 5.5, 4.1, 1.8, 0.9, −0.9, −17.3, −47.1, −86.4 ppm. Integrations are not reported due to extreme broadening of many signals.

UV-Vis (THF): 302 nm (ε = 12,100 $cm^{-1}\,M^{-1}$), 350 nm (ε = 8,600 $cm^{-1}\,M^{-1}$), 460 nm (ε = 5,500 $cm^{-1}\,M^{-1}$).

FT-IR (solid, cm^{-1}): 3352 (w), 3299 (w), 3236 (w), 3159 (w), 3055 (w), 2957 (m), 2926 (m), 2885 (m), 2863 (m), 1595 (s), 1578 (s), 1458 (m), 1429 (m), 1380 (w), 1358 (m), 1325 (m), 1254 (m), 1236 (m), 1181 (m), 1107 (w), 1097 (m), 1058 (w), 1042 (w), 1024 (m), 997 (w), 934 (m), 916 (m), 863 (m), 812 (m), 797 (m), 756 (m), 720 (m), 697 (w), 659 (w), 624 (m), 508 (w).

Mössbauer (solid, 80 K): $\delta = 0.35$ mm/s, $|\Delta E_Q| = 4.28$ mm/s, $\Gamma_L = 0.55$ mm/s, $\Gamma_R = 0.43$ mm/s.

Elem. Anal.: Anal. Calcd. for $C_{36}H_{48}FeN_3OS_2$: C, 65.64; H, 7.34; N, 6.38. Found: C, 65.63; H, 7.46; N, 6.11.



K[LFe^{II}(CO)$_3$] (11): A bomb flask was charged with **6** (81.5 mg, 0.032 mmol, 1.0 equiv) in 3 mL THF, giving a dark purple solution. The flask was moved to a Schlenk line which was cycled three times with CO gas. The flask was submerged in liquid nitrogen and the headspace gasses were evacuated, then the flask was opened to 1 atmosphere of CO(*g*) while warming and stirring. Upon melting, the solution changed color to opaque orange, changing to transparent orange within 1 minute. The reaction was stirred for 30 minutes at room temperature, then THF was removed under reduced pressure, leaving an amber-colored oil. Upon addition of 2 mL Et_2O, a light-yellow solid precipitated from the oil. The solids were reconcentrated from Et_2O, then re-suspended in 2 mL Et_2O and collected over a Celite pad, washing with Et_2O until the filtrate was clear. The solids were re-dissolved in THF and eluted through the Celite pad, concentrated to an oil, and precipitated from pentane to give 69.0 mg (79% yield) of **11** as a light-yellow solid.

^{1}H NMR (400 MHz, THF-d_8): δ 8.04 (d, J = 7.4 Hz, 2H, H4/6), 7.12 (t, J = 7.4 Hz, 1H, H5), 6.99 (d, J = 7.6 Hz, 4H, H3'/5'), 6.83 (t, J = 7.6 Hz, 2H, H4'), 3.08 (sept, J = 6.9 Hz, 4H, *i*Pr CH), 1.21 (d, J = 6.9 Hz, 12H, *i*Pr CH_3), 1.09 (d, J = 6.9 Hz, 12H, *i*Pr CH_3) ppm.

^{13}C{^{1}H} NMR (201 MHz, THF-d_8): δ 212.24, 210.45 (CO); 181.88 (C=N); 173.25, 152.34, 150.89, 138.33, 127.07, 123.06, 123.03, 122.44 (Ar); 29.19, 24.26, 24.19 (*i*Pr) ppm.

UV-Vis (THF): 320 nm (ε = 6,300 $cm^{-1}\,M^{-1}$), 400 nm (ε = 1,600 $cm^{-1}\,M^{-1}$).

FT-IR (solid, cm^{-1}): 3254 (w), 2959 (m), 2924 (m), 2865 (m), 2078 (m), 2013 (s), 1988 (s), 1919 (m), 1909 (m), 1588 (m), 1568 (s), 1462 (m), 1429 (m), 1397 (m), 1380 (m), 1360 (m), 1325 (m), 1299 (m), 1274 (m), 1252 (m), 1232 (m), 1187 (m), 1158 (m), 1097 (m), 1058 (m), 1015 (m), 962 (m), 924 (m), 801 (m), 767 (m), 728 (m), 612 (s), 602 (s), 585 (m), 559 (m), 453 (m).

Mössbauer (solid, 80 K): δ = 0.01 mm/s, $|\Delta E_Q|$ = 0.99 mm/s, Γ = 0.30 mm/s.

Elem. Anal.: Anal. Calcd. for $KC_{35}H_{37}FeN_2O_3S_2$: C, 60.68; H, 5.38; N, 4.04. Found: C, 60.59; H, 5.54; N, 3.79.

NMR Spectra

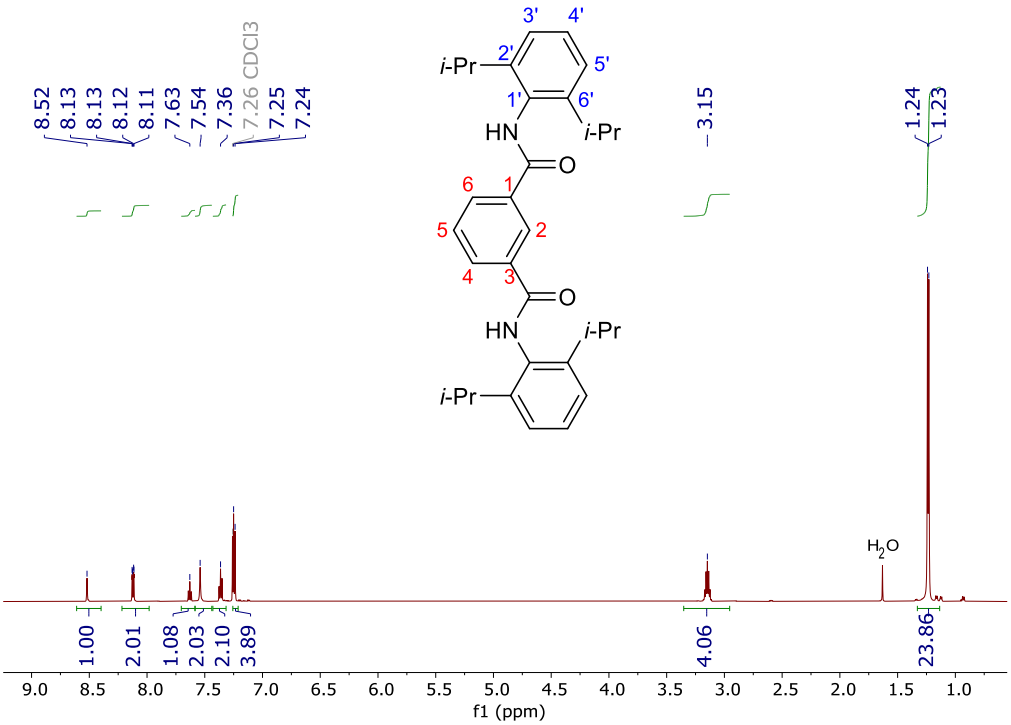


Figure S1. ^{1}H NMR spectrum of **Dipp-OCO** in $CDCl_3$.

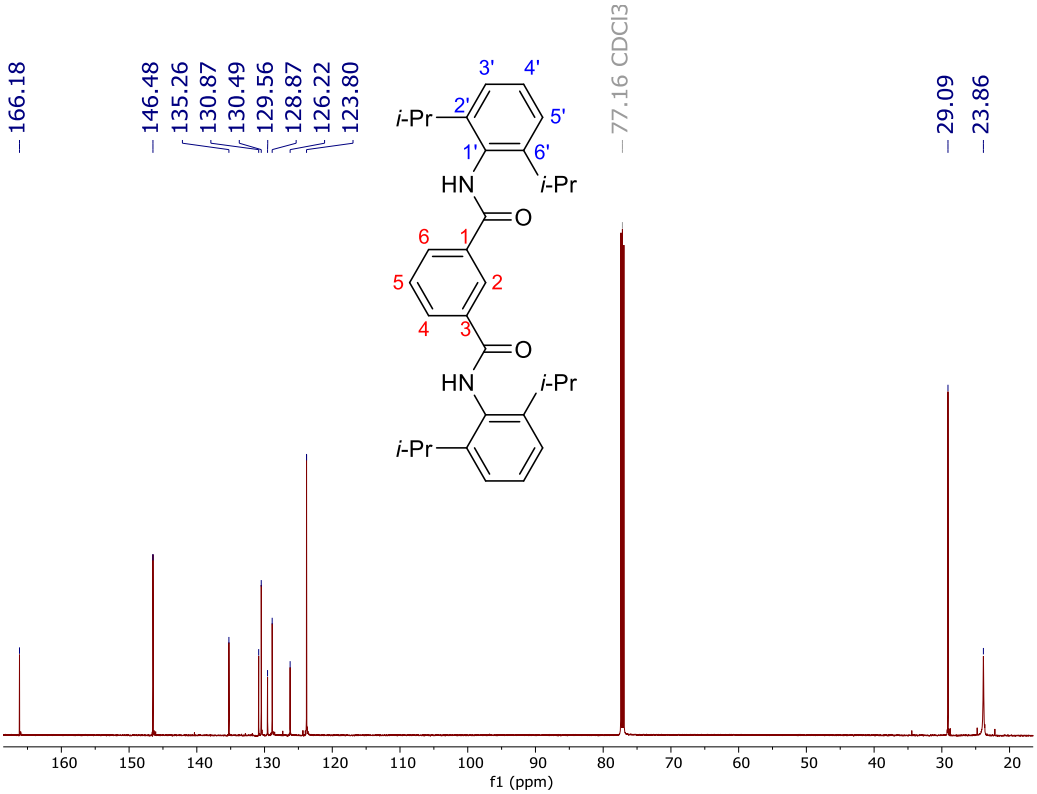


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of **Dipp-OCO** in $CDCl_3$.

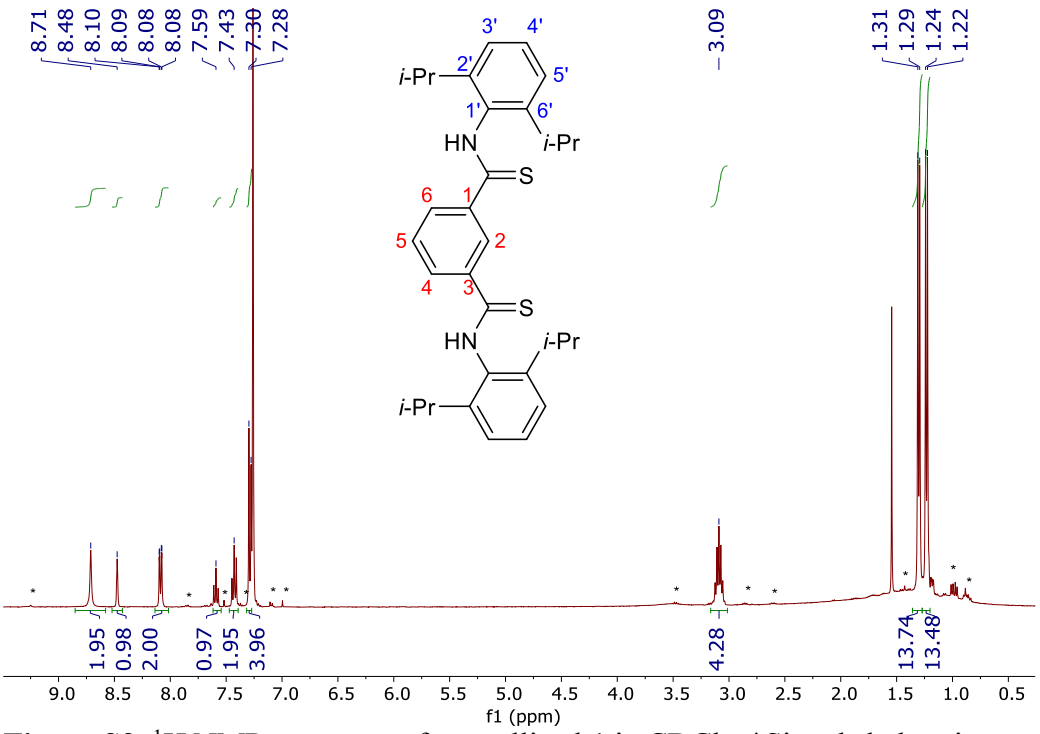


Figure S3. ^{1}H NMR spectrum of crystallized **1** in $CDCl_3$. *Signals belonging to the unidentified co-crystallized impurity.

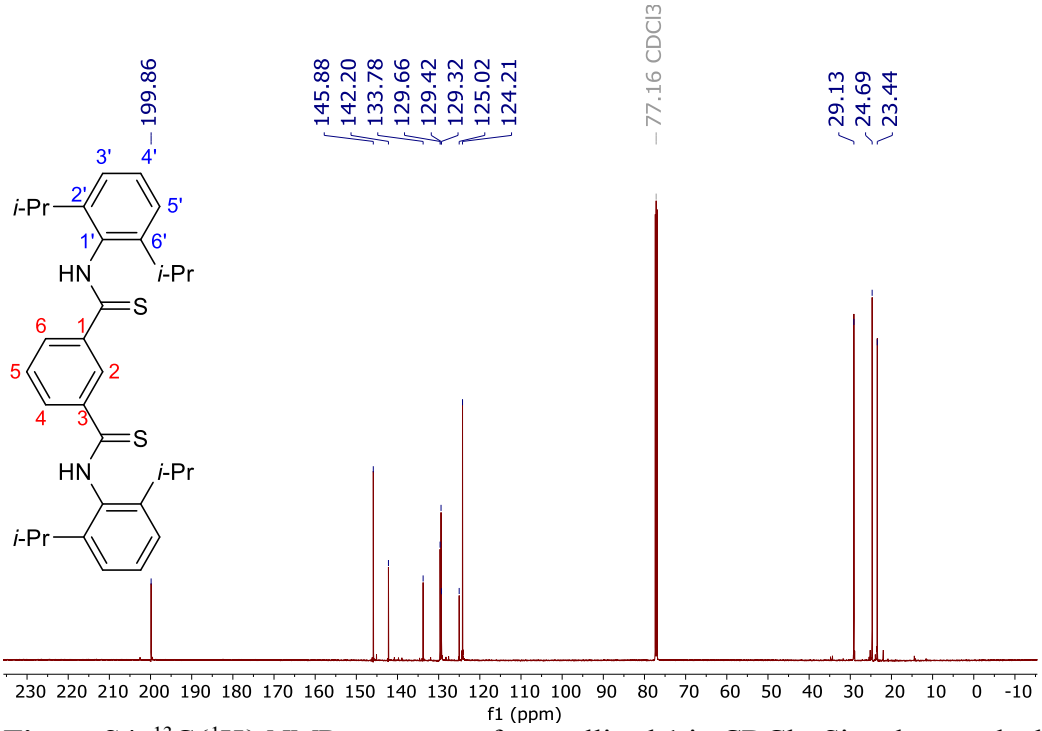


Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of crystallized **1** in $CDCl_3$. Signals near the baseline are assigned to an impurity.

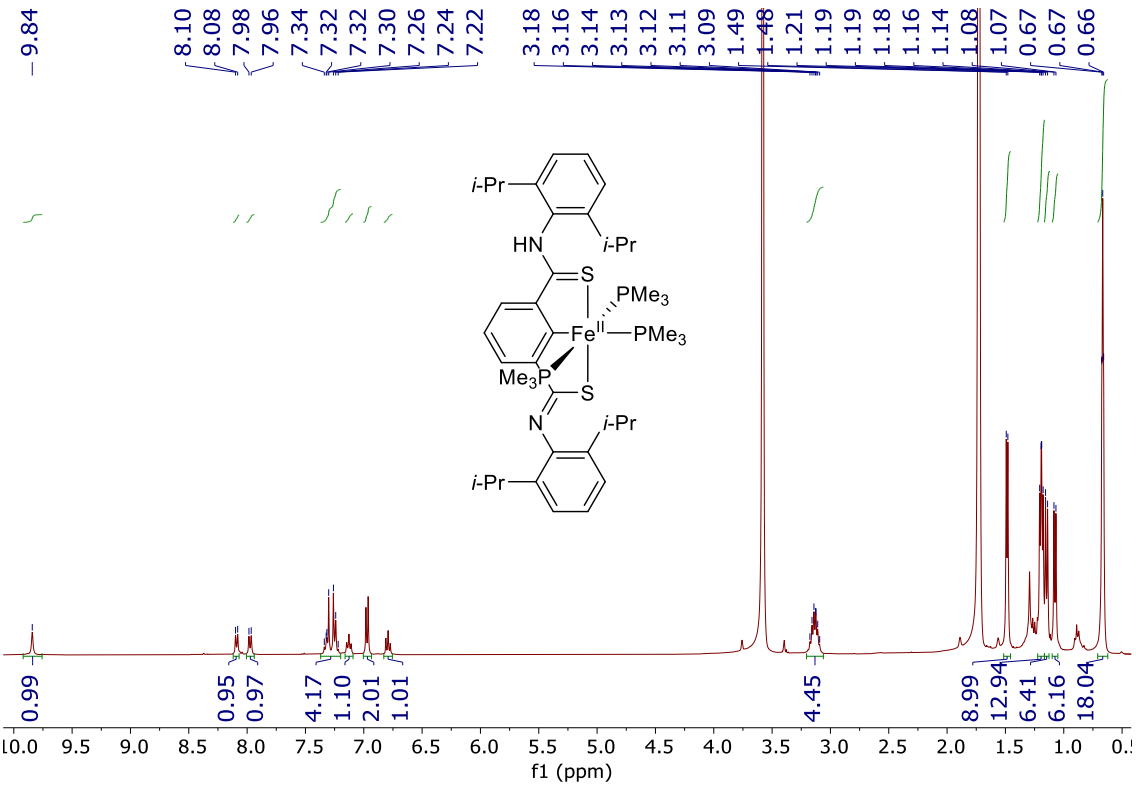


Figure S5. ^{1}H NMR spectrum of **2** in THF-d_8.

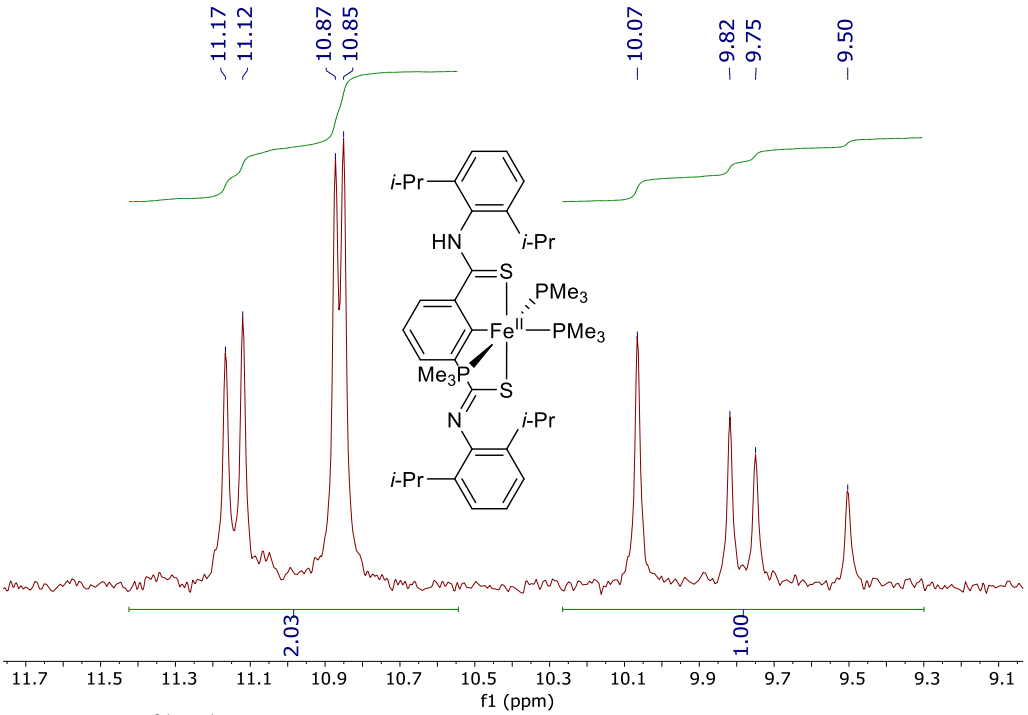


Figure S6. ^{31}P{^{1}H} NMR spectrum of **2** in THF-d_8.

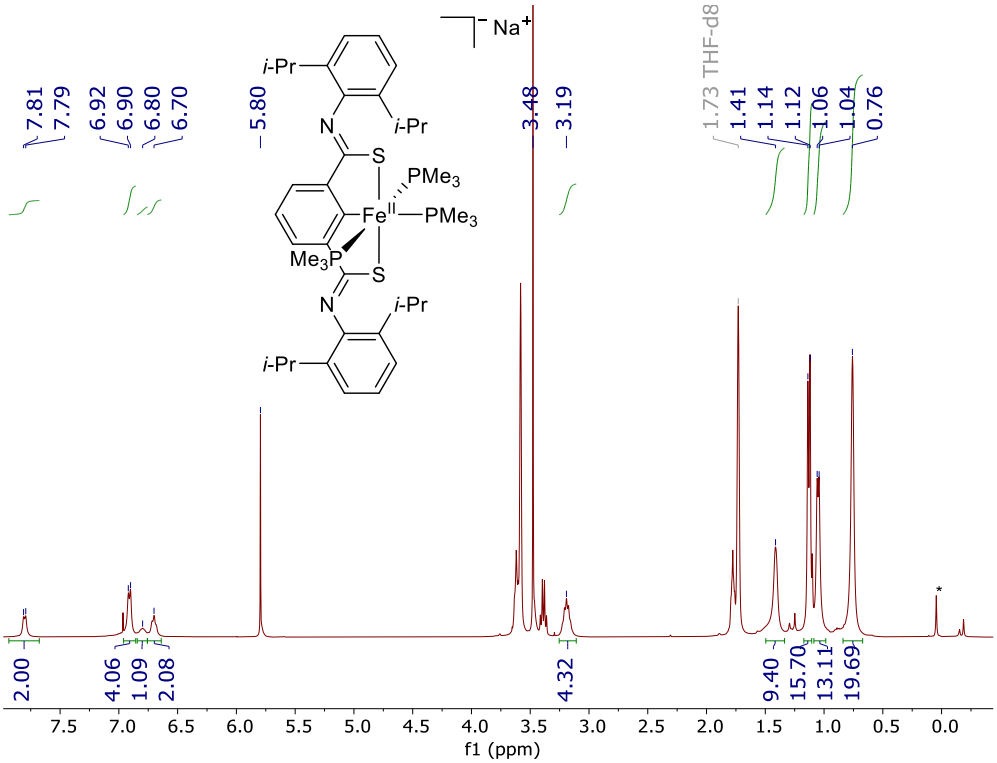


Figure S7. ^{1}H NMR spectrum of **3-Na** in THF-d_8. Signals at 5.80 and 3.48 ppm belong to the 1,3,5-trimethoxybenzene capillary used to determine spectroscopic yield. Residual Et_2O overlaps the doublet at 1.13 ppm, increasing its integration. *Trace $HN(TMS)_2$.

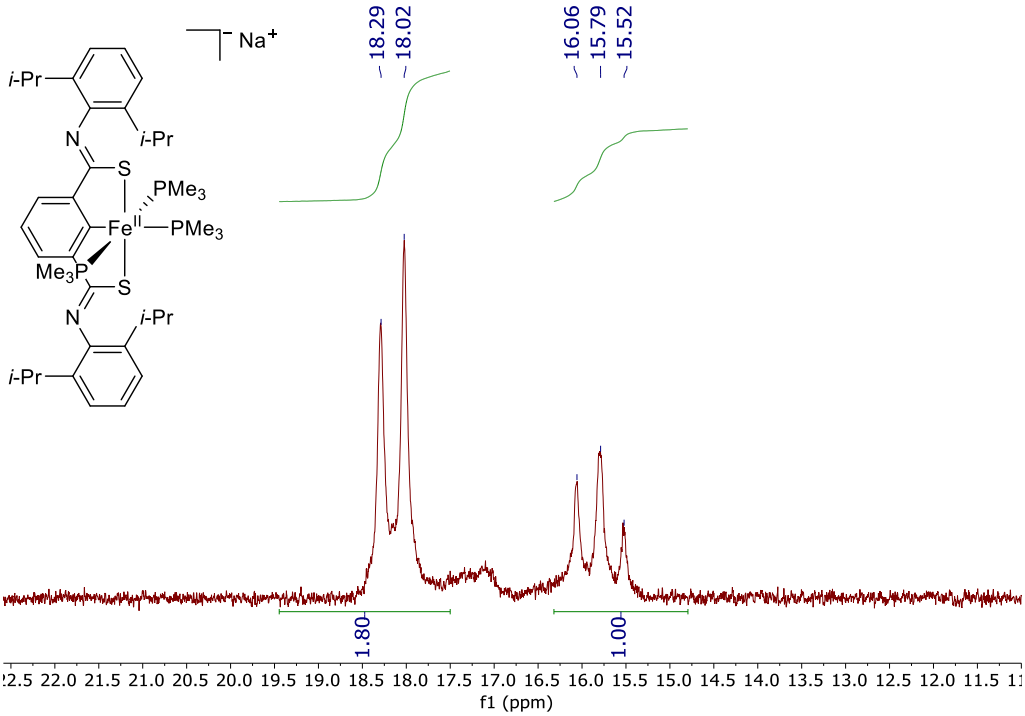


Figure S8. ^{31}P{^{1}H} NMR spectrum of **3-Na** in THF-d_8. There is an unknown impurity at 17 ppm.

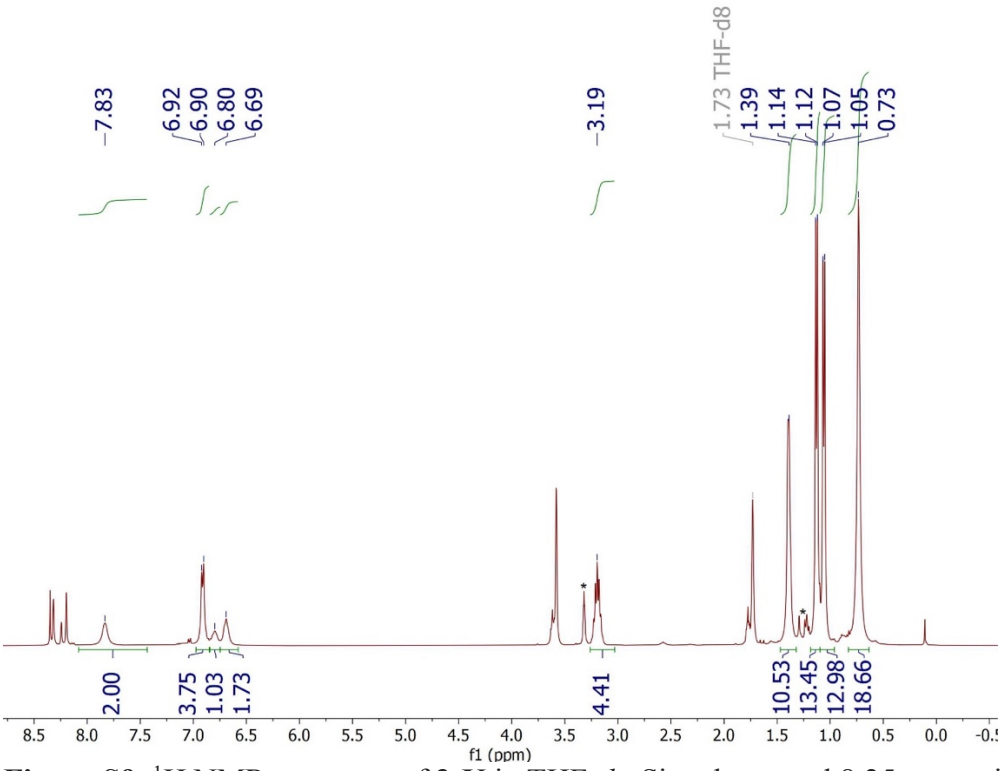


Figure S9. ^{1}H NMR spectrum of **3-K** in THF-d_8. Signals around 8.25 ppm arise from the capillary. *Unknown impurity.

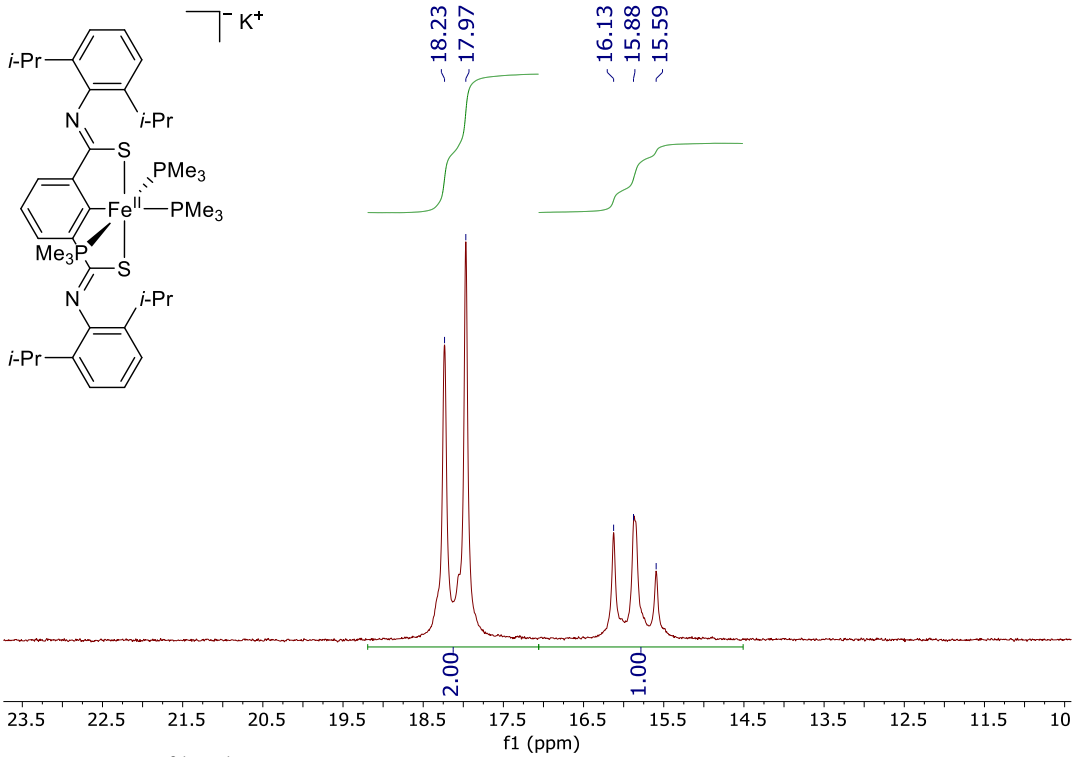


Figure S10. ^{31}P{^{1}H} NMR spectrum of **3-K** in THF-d_8.

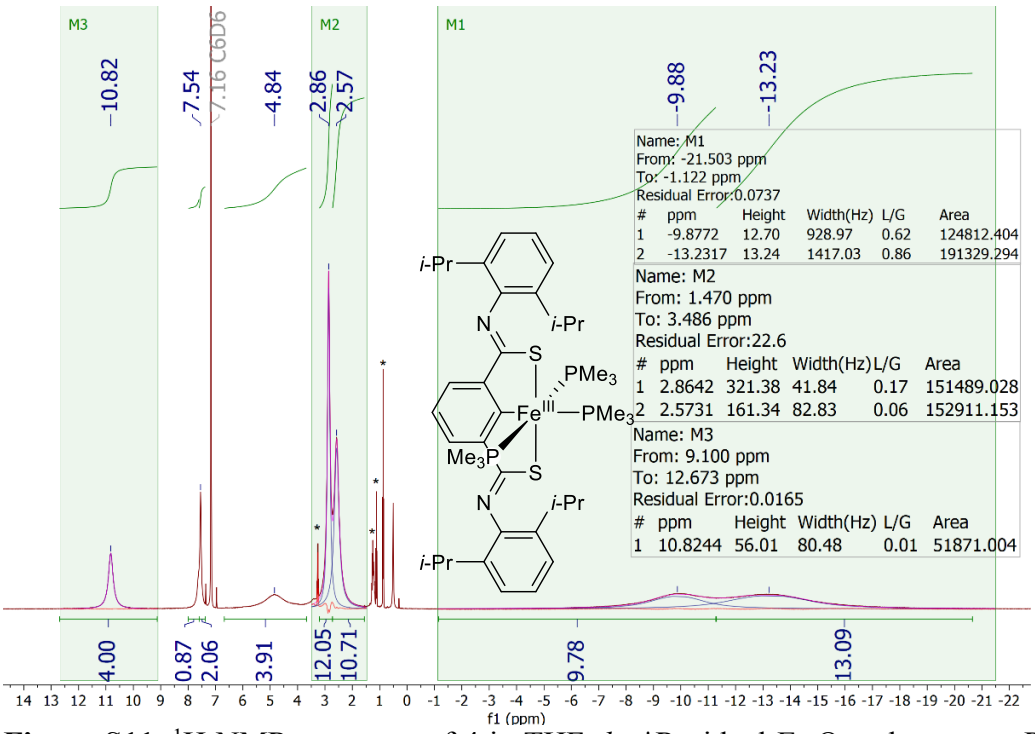


Figure S11. ^{1}H NMR spectrum of **4** in THF-d_8. *Residual Et_2O and pentane. Parameters of the peak-fitted region are shown in the box.

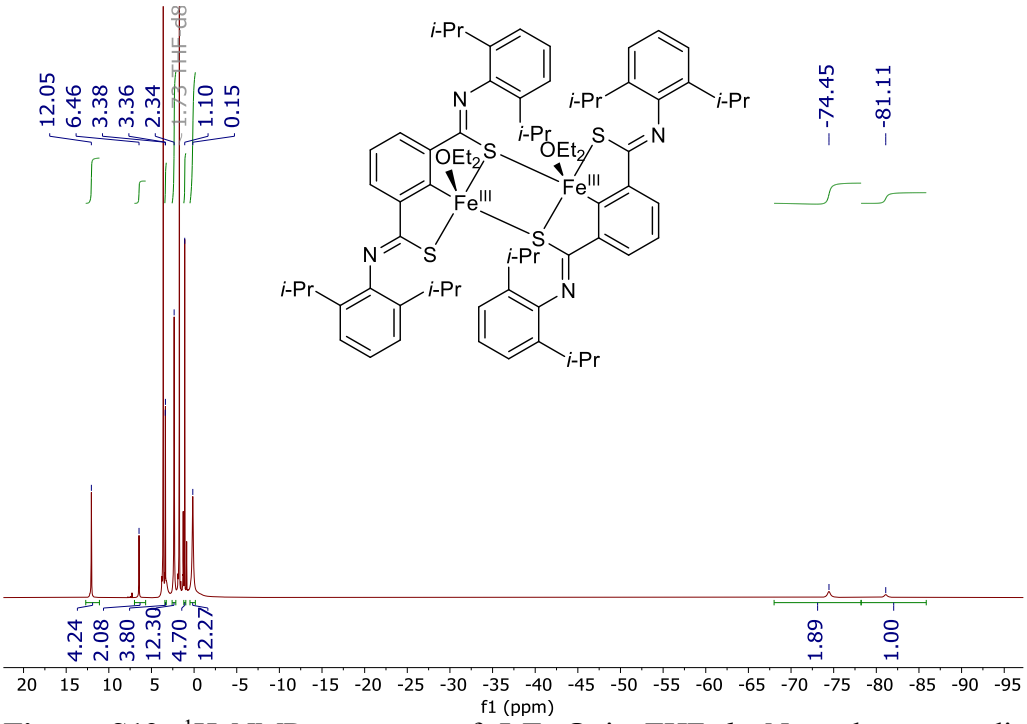


Figure S12. ^{1}H NMR spectrum of **5-Et_2O** in THF-d_8. Note that upon dissolution in THF, Mössbauer spectroscopy indicates there is a change in the iron coordination environment (Figure 87), which may be consistent with the dimer breaking up into monomers. This could explain why this NMR spectrum suggests a higher symmetry than the dimeric structure.

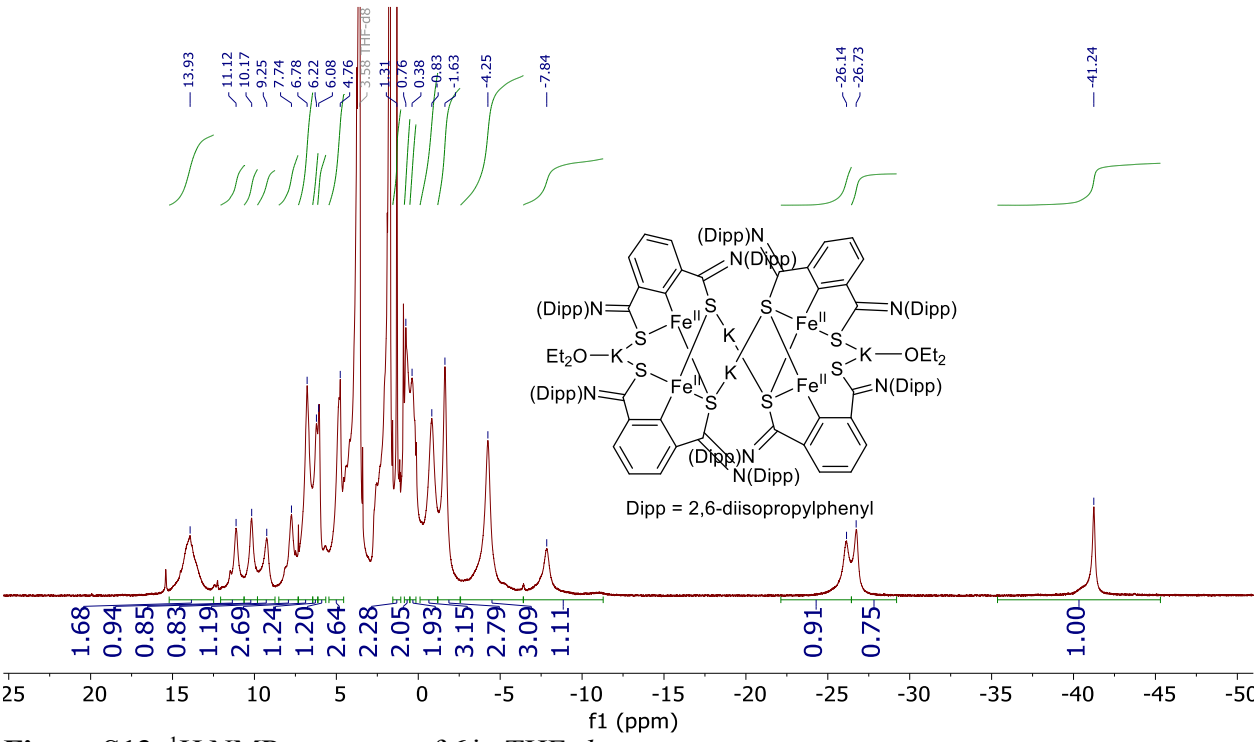


Figure S13. ^{1}H NMR spectrum of **6** in THF-d_8.

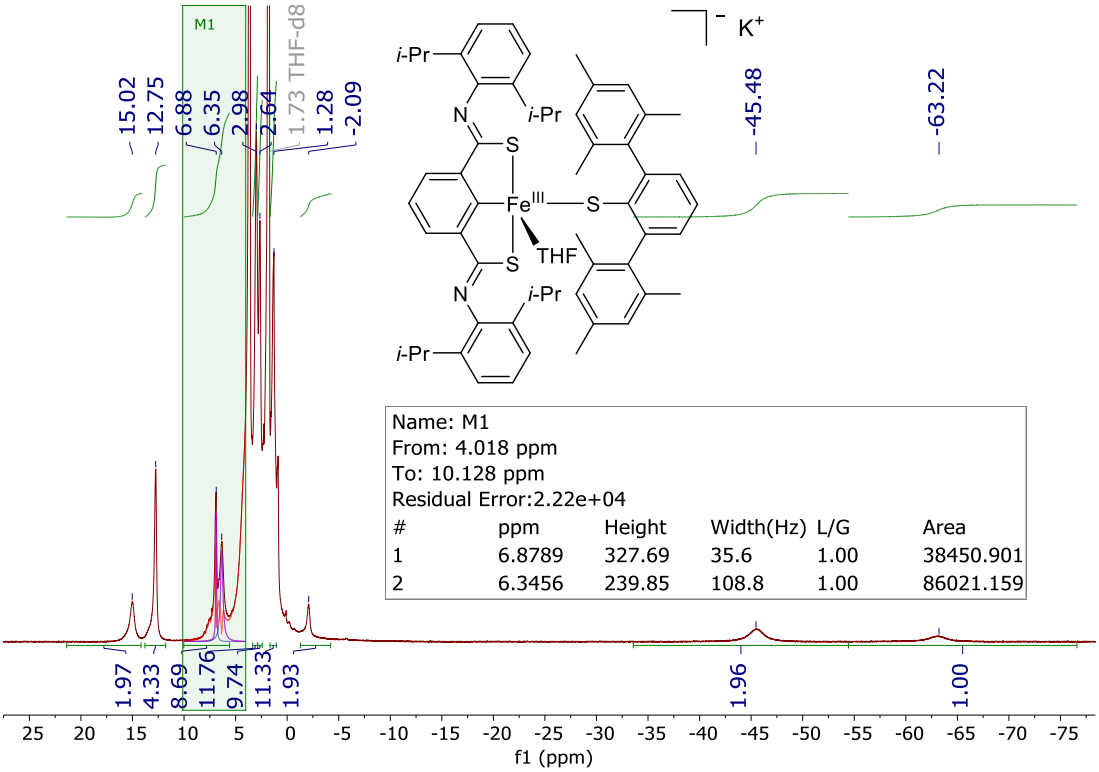


Figure S14. ^{1}H NMR spectrum of **7** in THF-d_8. Parameters of the peak-fitted region are shown in the box.

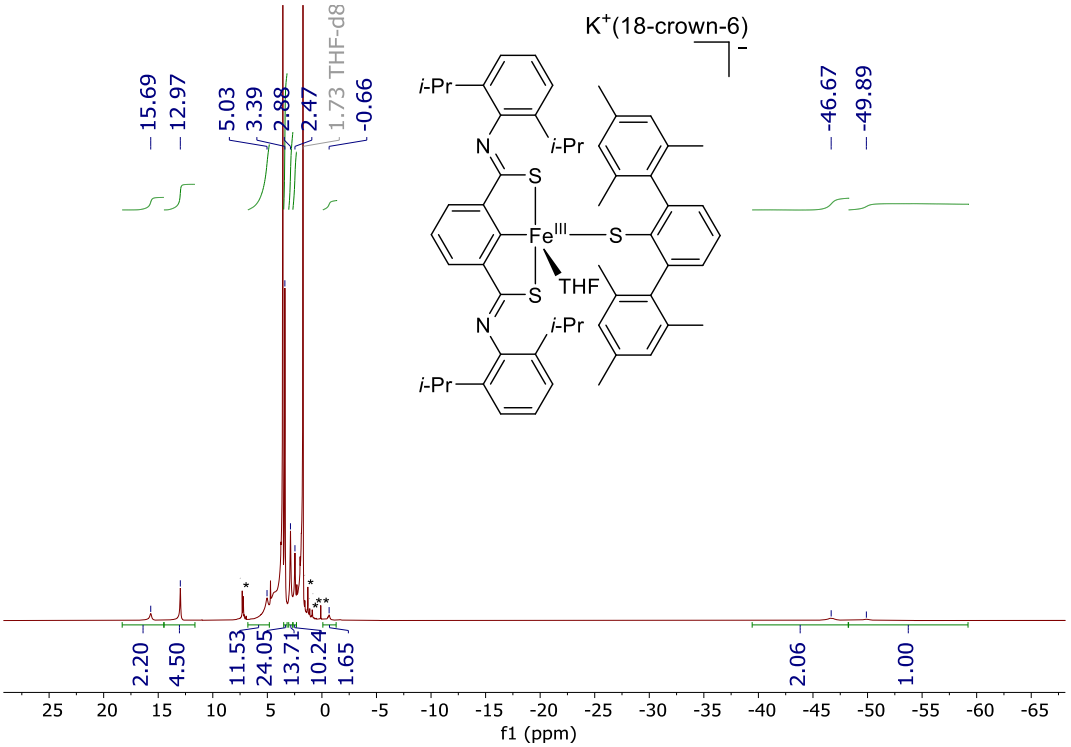


Figure S15. ^{1}H NMR spectrum of **7-crown** in THF-d_8. *Residual solvents (Et_2O, hexanes, toluene). **Silicone grease.

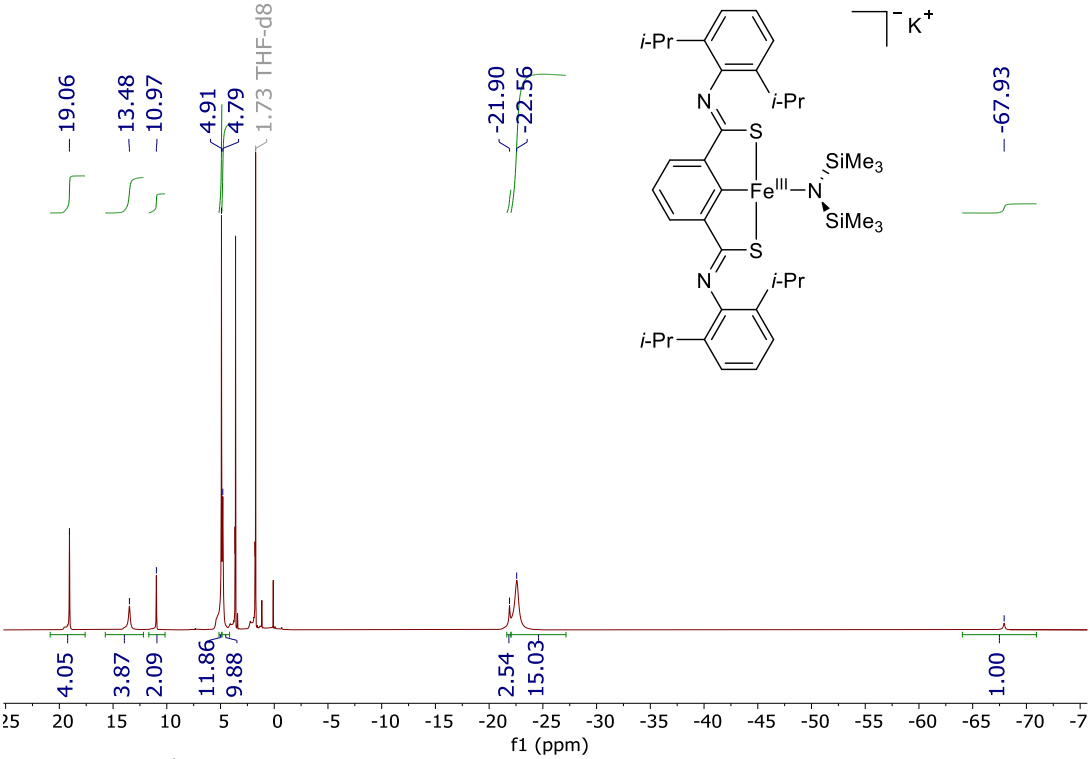


Figure S16. ^{1}H NMR spectrum of **9** in THF-d_8.

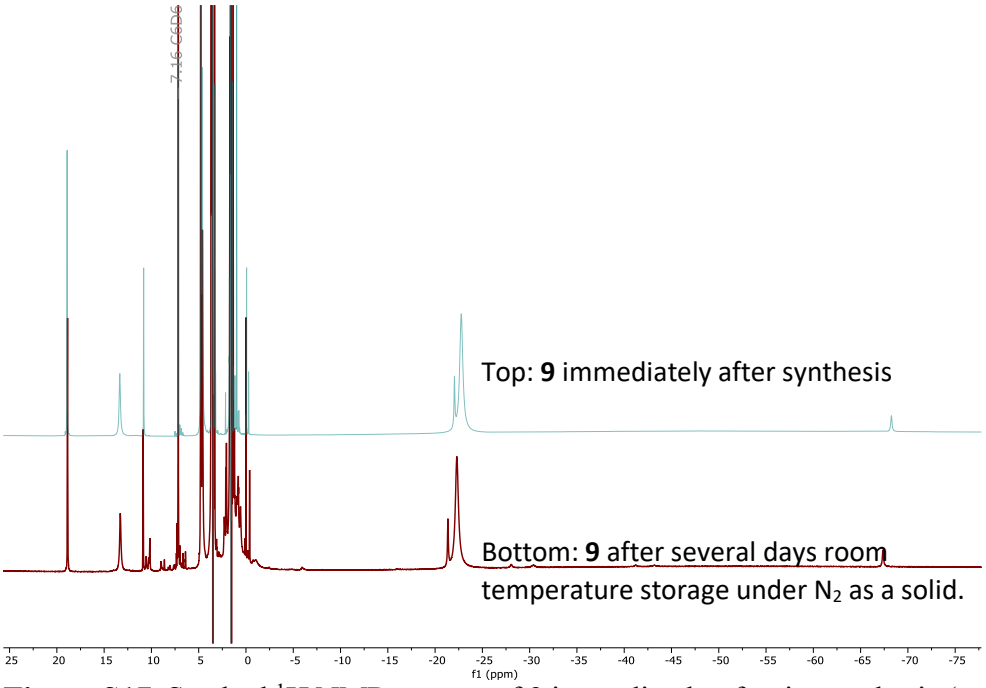


Figure S17. Stacked ^{1}H NMR spectra of **9** immediately after its synthesis (top spectrum) and after several days of room temperature storage under N_2 as a solid (bottom spectrum) in 9:1 THF:C_6D_6. Several new peaks are observed (some outside the region for diamagnetic compounds) and are assigned to an unidentified decomposition product.

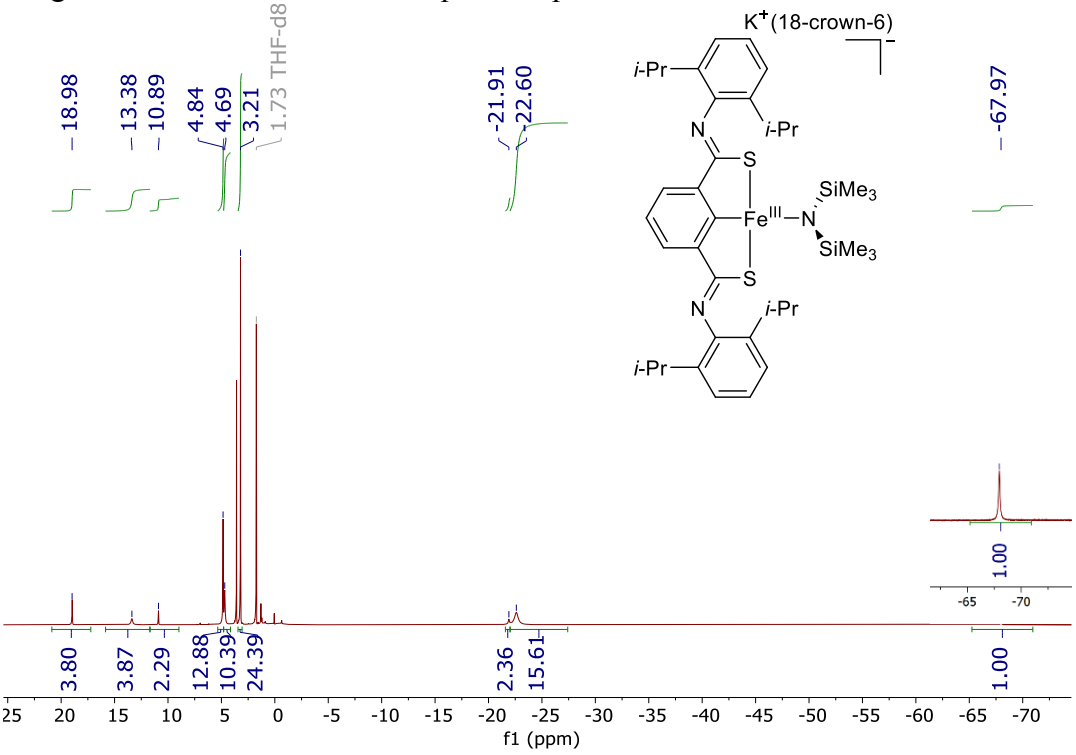


Figure S18. ^{1}H NMR spectrum of **9-crown** in THF-d_8. Inset shows the peak at –67.97 ppm.

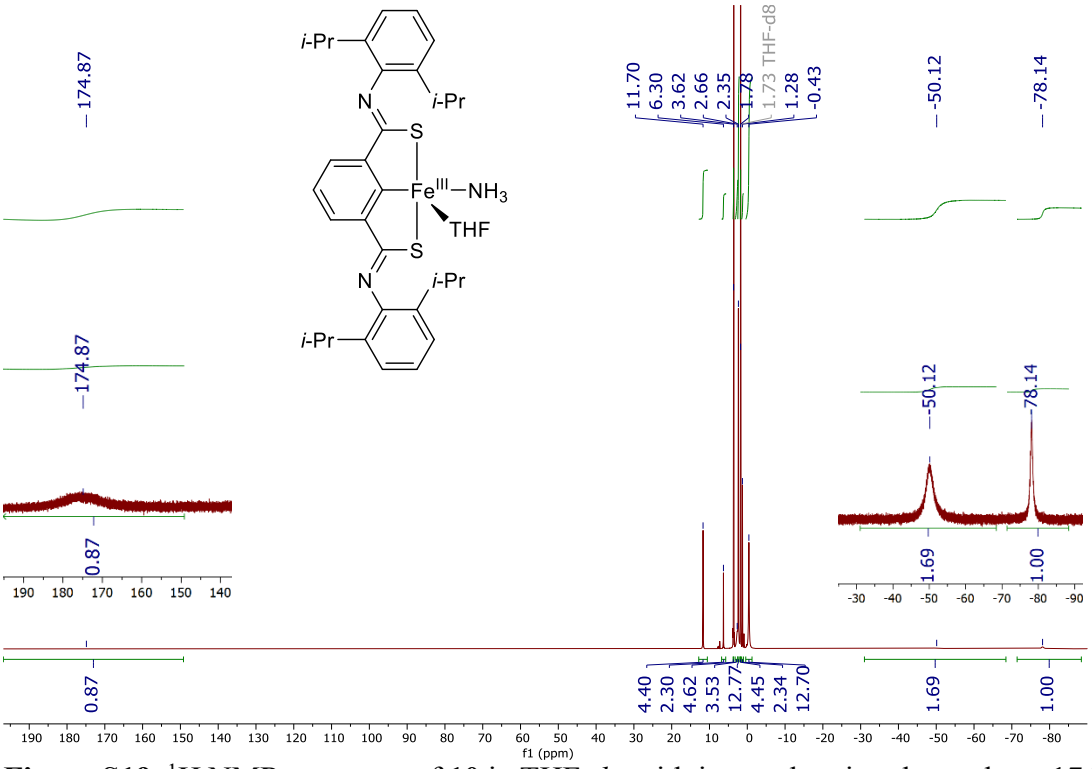


Figure S19. ^{1}H NMR spectrum of **10** in THF-d_8, with insets showing the peaks at 174.87, –50.12, and –78.14 ppm.

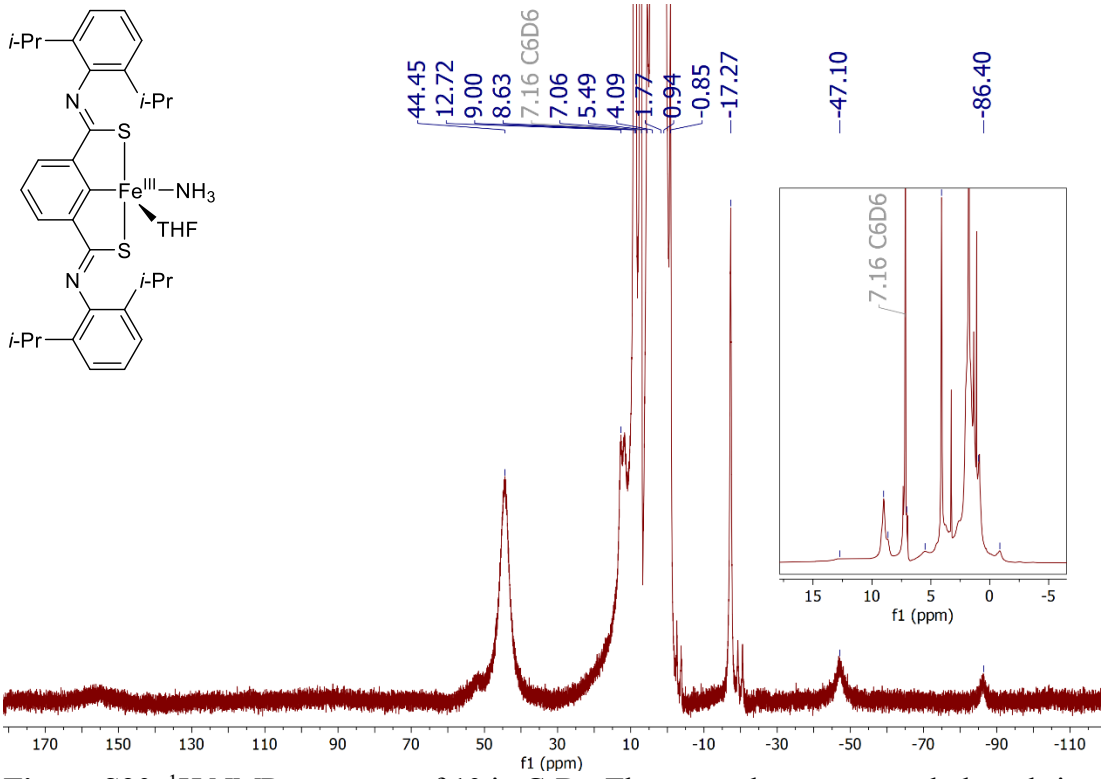


Figure S20. ^{1}H NMR spectrum of **10** in C_6D_6. There may be an extremely broad signal at ca. 155 ppm.

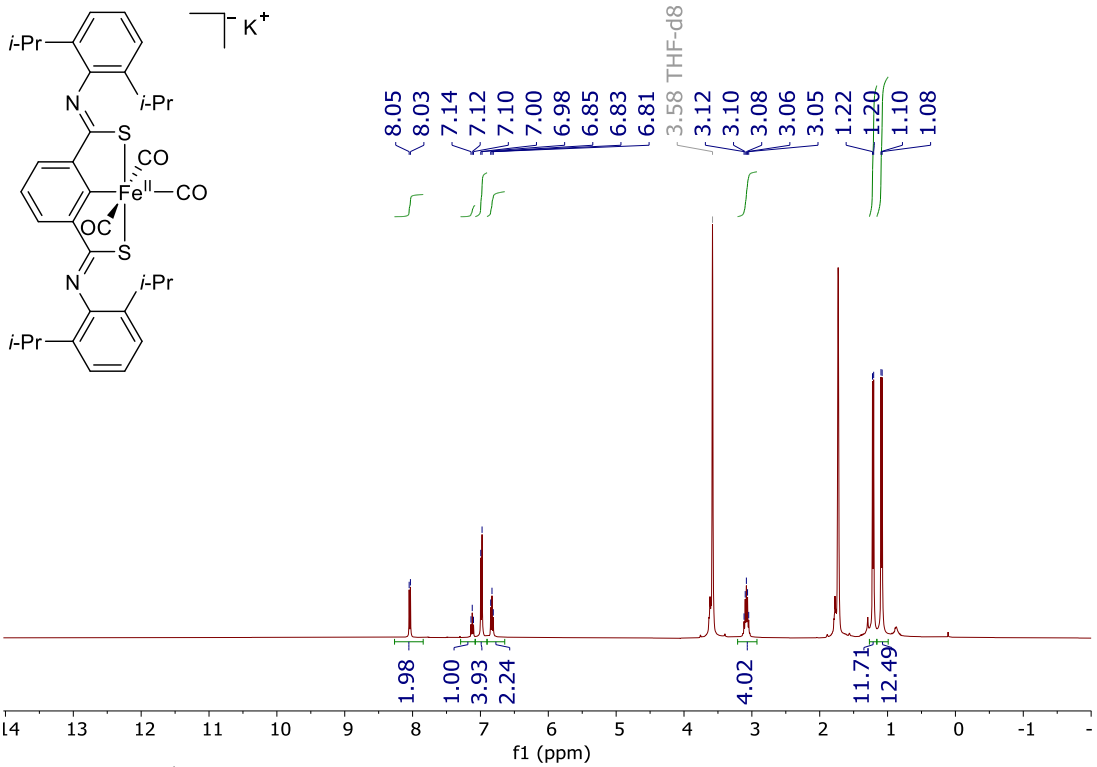


Figure S21. ^{1}H NMR spectrum of **11** in THF-d_8.

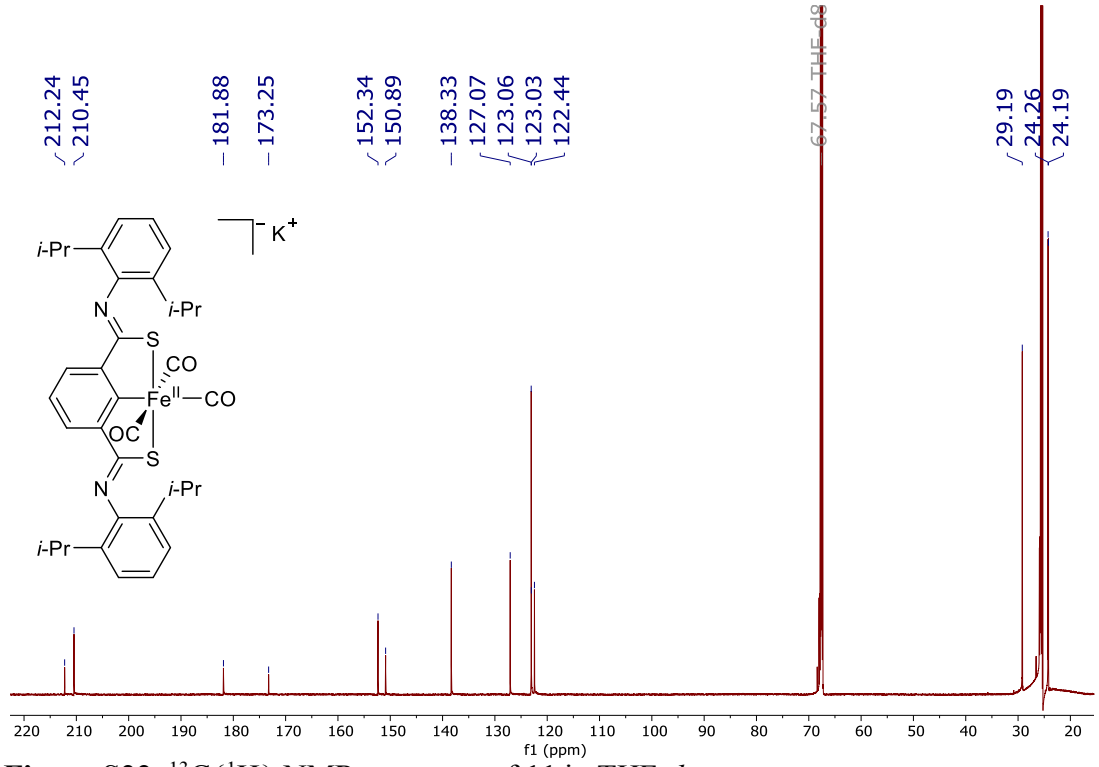


Figure S22. ^{13}C{^{1}H} NMR spectrum of **11** in THF-d_8.

UV-Visible Absorption Spectra

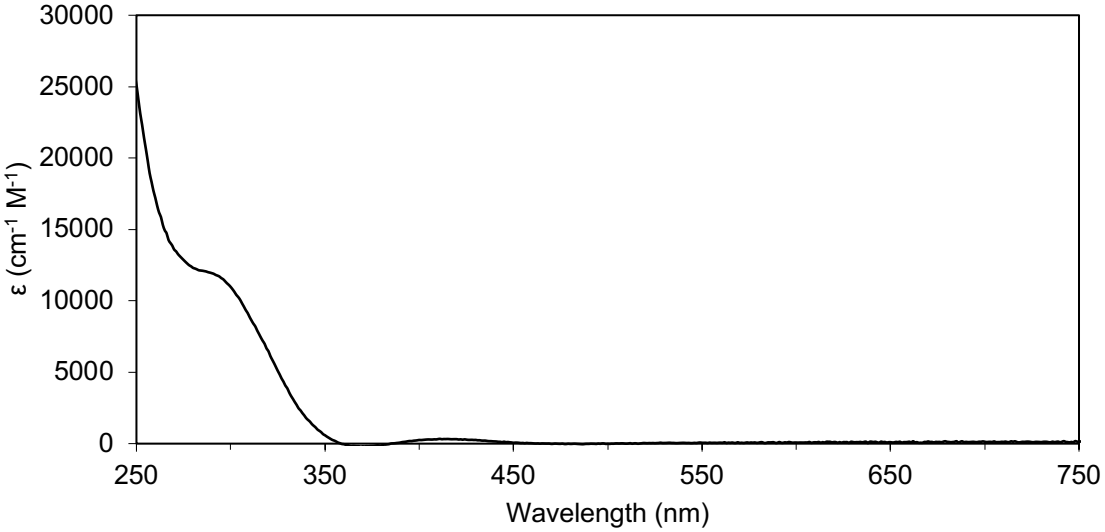


Figure S23. UV-visible spectrum of **1** in THF with absorptions at 291 nm (ε = 11,900 $cm^{-1}\,M^{-1}$) and 415 nm (320 $cm^{-1}\,M^{-1}$).

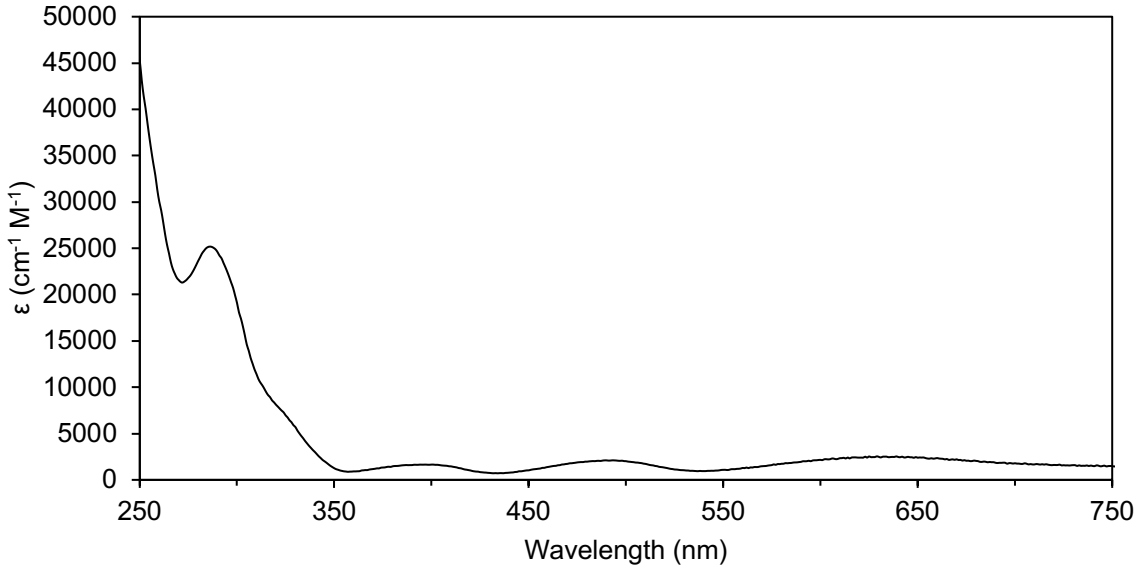


Figure S24. UV-visible spectrum of **2** in THF with absorptions at 286 nm (ε = 10,400 $cm^{-1}\,M^{-1}$), 395 nm (ε = 1,600 $cm^{-1}\,M^{-1}$), 493 nm (ε = 2,100 $cm^{-1}\,M^{-1}$), and 633 nm (ε = 2,400 $cm^{-1}\,M^{-1}$).

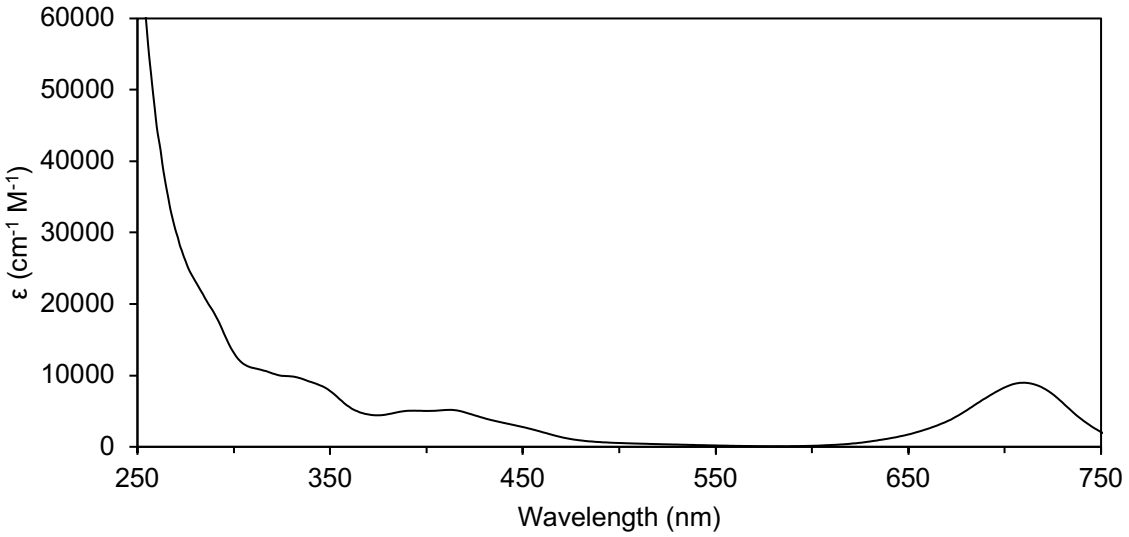


Figure S25. UV-visible spectrum of **4** in THF with absorptions at 332 nm (ε = 9,800 cm^{-1} M^{-1}), 389 nm (ε = 5,000 cm^{-1} M^{-1}), 417 nm (ε = 5,000 cm^{-1} M^{-1}), and 710 nm (ε = 9,000 cm^{-1} M^{-1}).

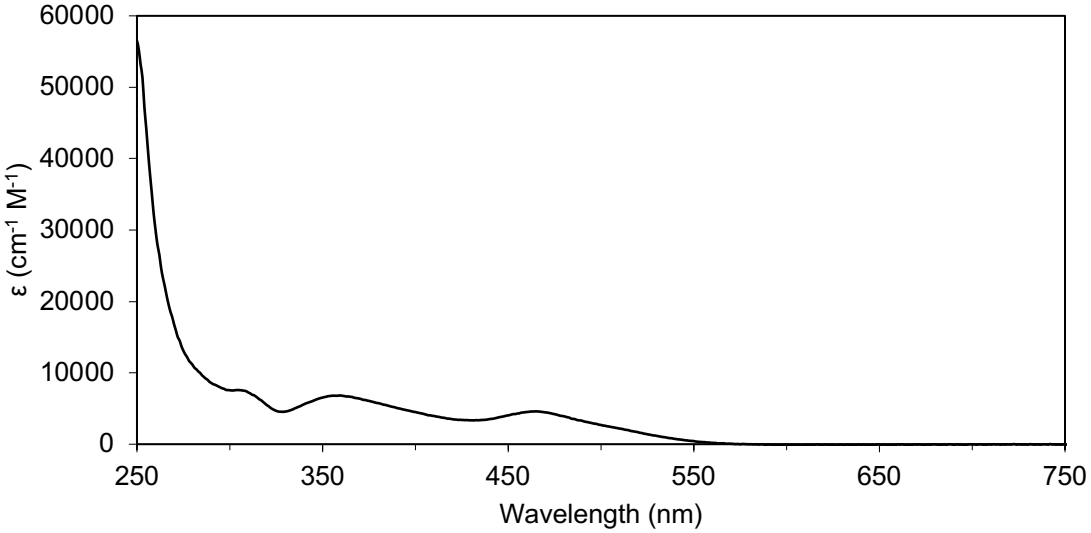


Figure S26. UV-visible spectrum of **5-THF** in THF with absorptions at 304 nm (ε = 7,600 cm^{-1} M^{-1}), 353 nm (6,800 cm^{-1} M^{-1}), and 458 nm (4,600 cm^{-1} M^{-1}).

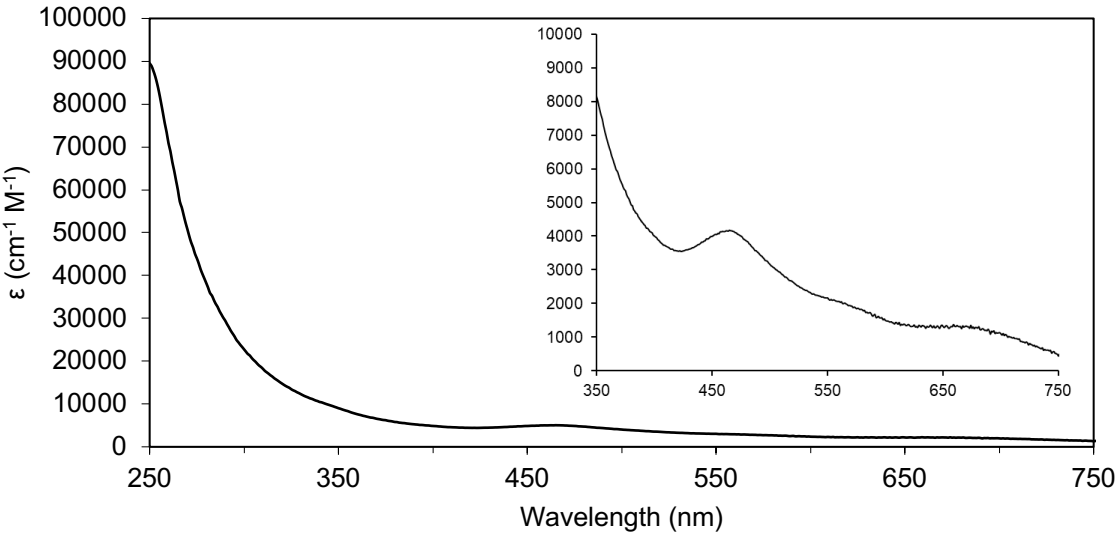


Figure S27. UV-visible spectrum of **6** in THF with absorptions at 465 nm (ε = 4,200 $cm^{-1}\,M^{-1}$) and 662 nm (ε = 1,300 $cm^{-1}\,M^{-1}$).

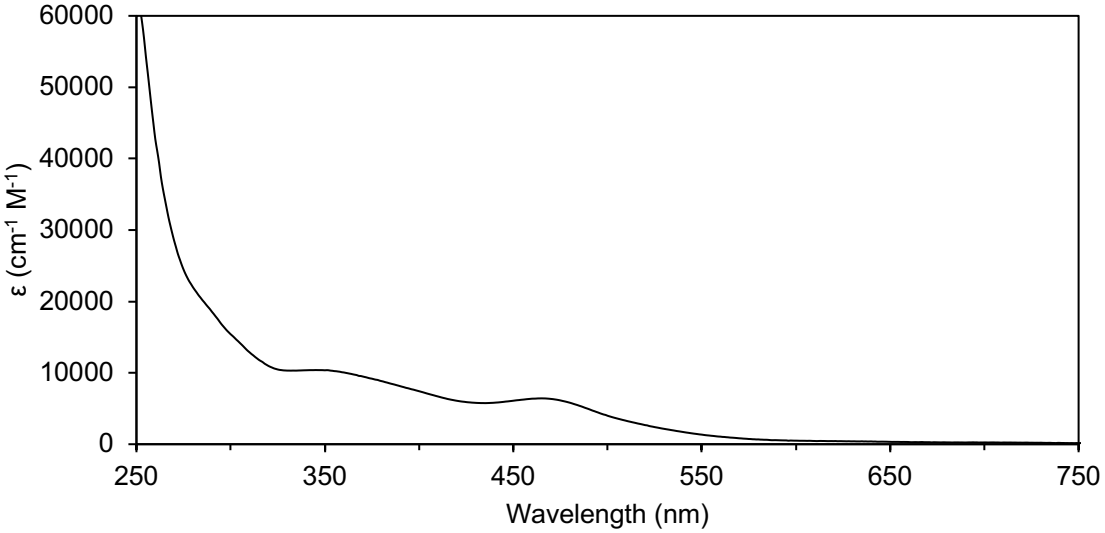


Figure S28. UV-visible spectrum of **7** in THF with absorptions at 345 nm (ε = 10,400 $cm^{-1}\,M^{-1}$) and 465 nm (ε = 6,400 $cm^{-1}\,M^{-1}$)

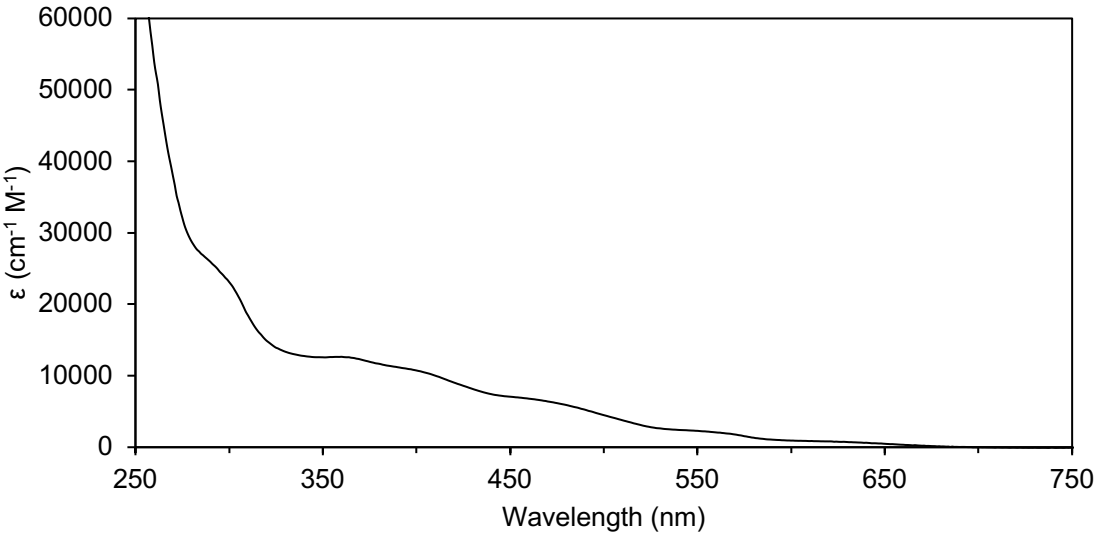


Figure S29. UV-visible spectrum of **7-crown** in THF with absorptions at 293 nm (ε = 25,200 cm^{-1} M^{-1}), 360 nm (ε = 12,600 cm^{-1} M^{-1}), 405 nm (ε = 10,400 cm^{-1} M^{-1}), and 468 nm (ε = 6,500 cm^{-1} M^{-1}).

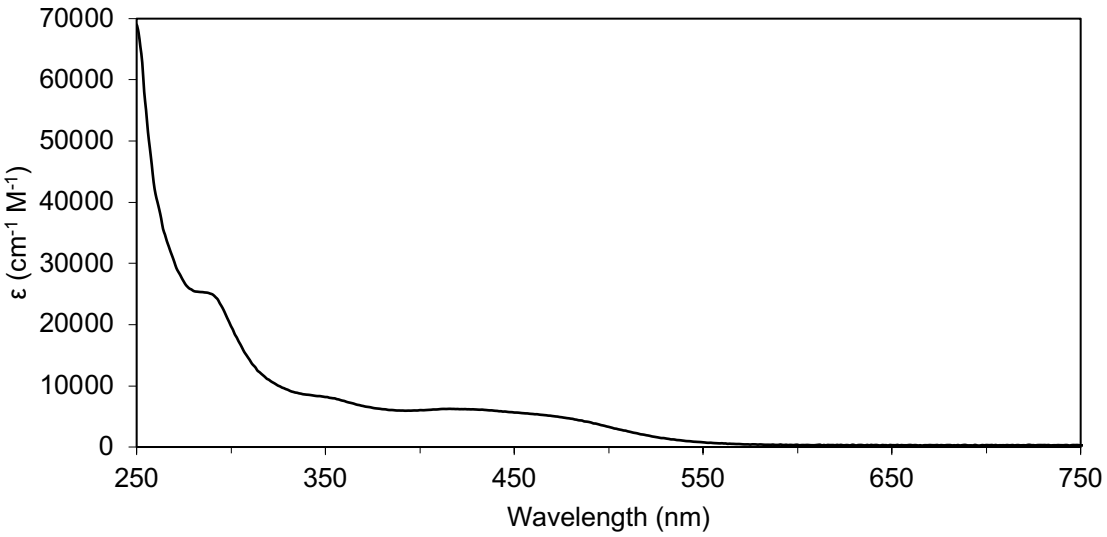


Figure S30. UV-visible spectrum of **9** in THF with absorptions at 287 nm (ε = 25,200 cm^{-1} M^{-1}), 358 nm (ε = 7,600 cm^{-1} M^{-1}), and 417 nm (ε = 6,200 cm^{-1} M^{-1}).

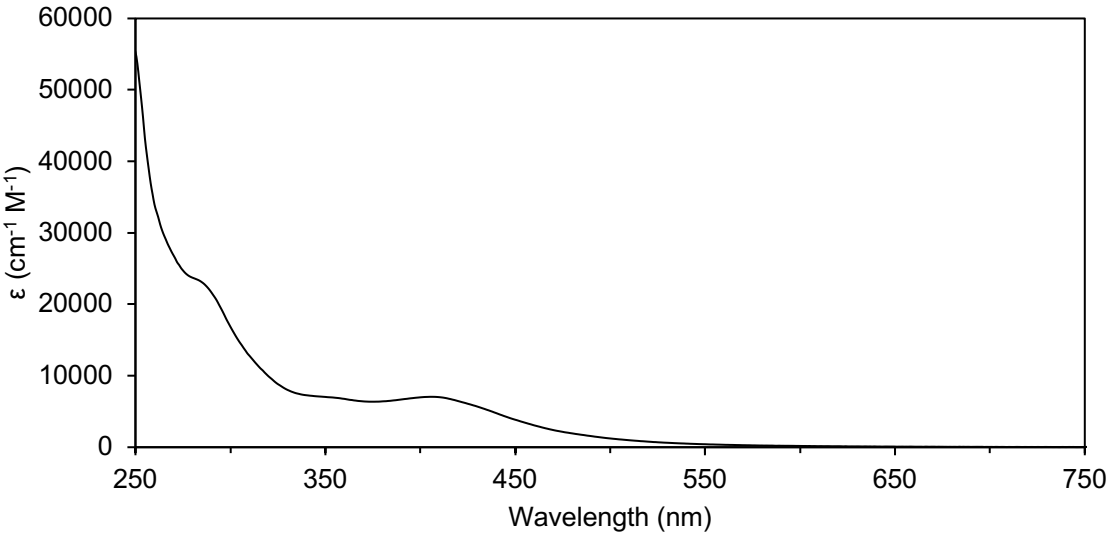


Figure S31. UV-visible spectrum of **9-crown** in THF with absorptions at 285 nm (ε = 23,000 cm^{-1} M^{-1}) and 408 nm (ε = 7,000 cm^{-1} M^{-1}).

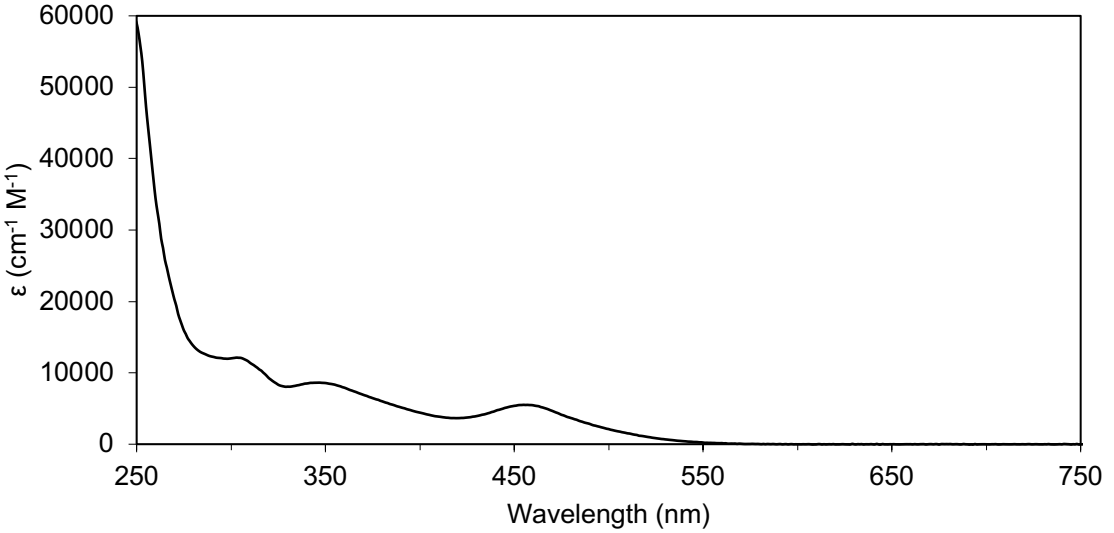


Figure S32. UV-visible spectrum of **10** in THF with absorptions at 302 nm (ε = 12,100 cm^{-1} M^{-1}), 350 nm (ε = 8,600 cm^{-1} M^{-1}), and 460 nm (ε = 5,500 cm^{-1} M^{-1}).

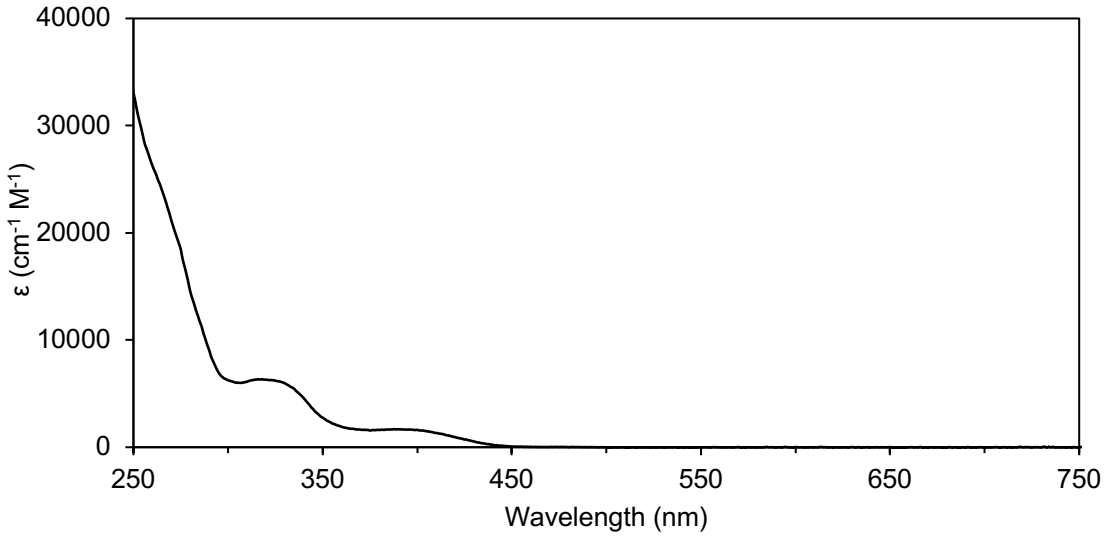


Figure S33. UV-visible spectrum of **11** in THF with absorptions at 320 nm (ε = 6,300 $cm^{-1}\,M^{-1}$) and 400 nm (ε = 1,600 $cm^{-1}\,M^{-1}$).

IR Spectra

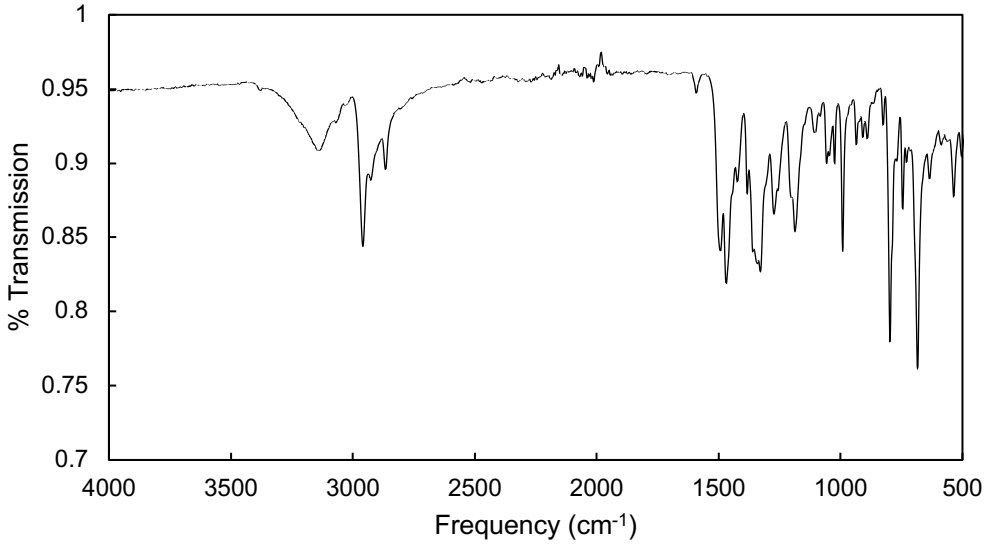


Figure S34. FT-IR spectrum of solid **1**.

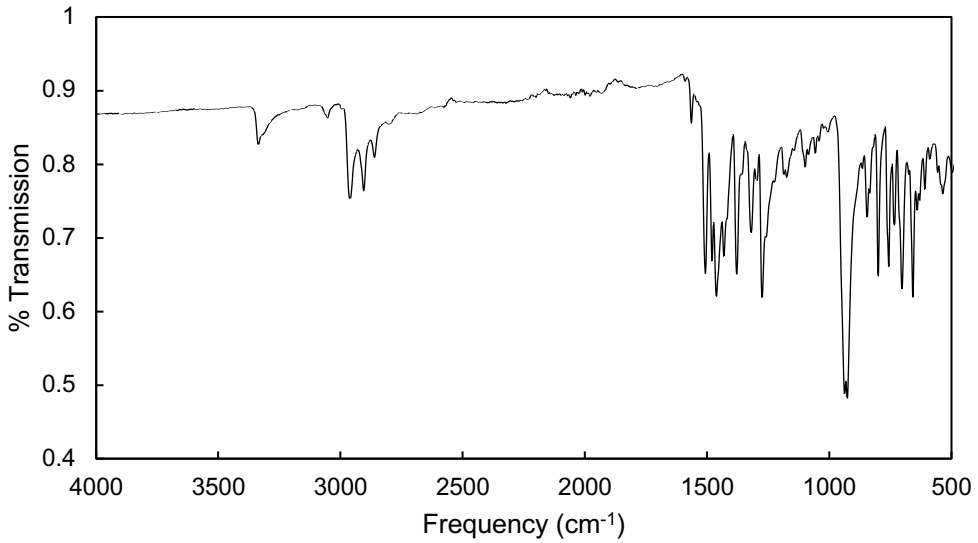


Figure S35. FT-IR spectrum of solid **2**.

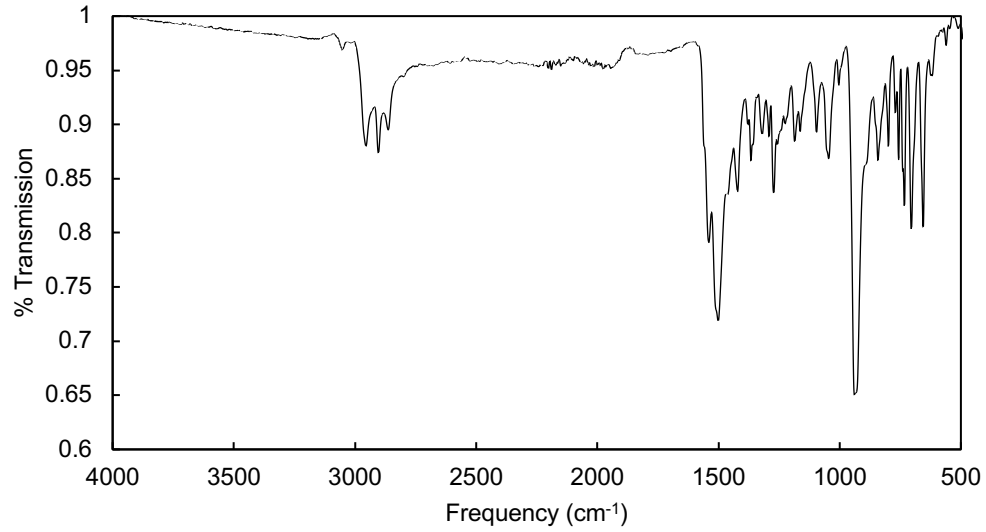


Figure S36. FT-IR spectrum of solid **3-Na**.

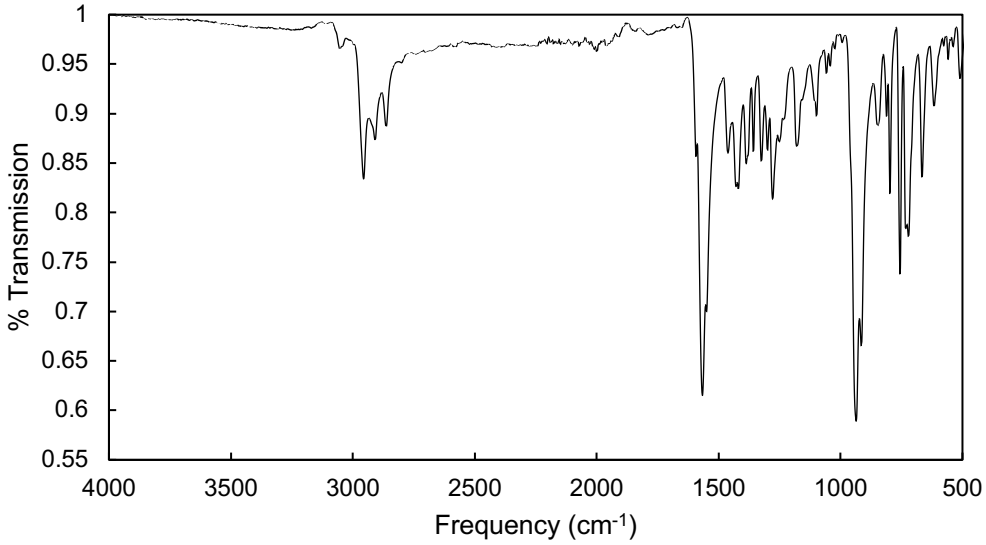


Figure S37. FT-IR spectrum of solid **4**.

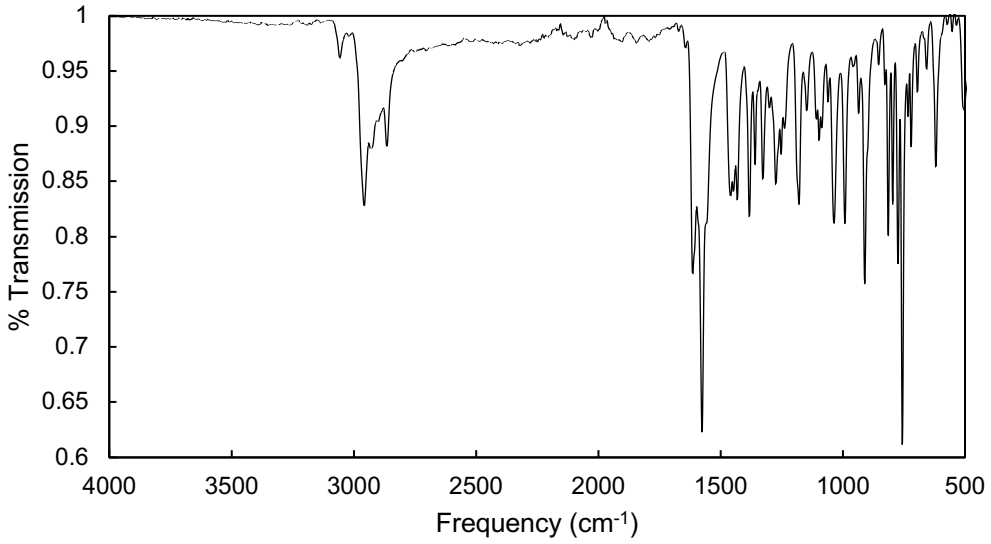


Figure S38. FT-IR spectrum of solid **5**.

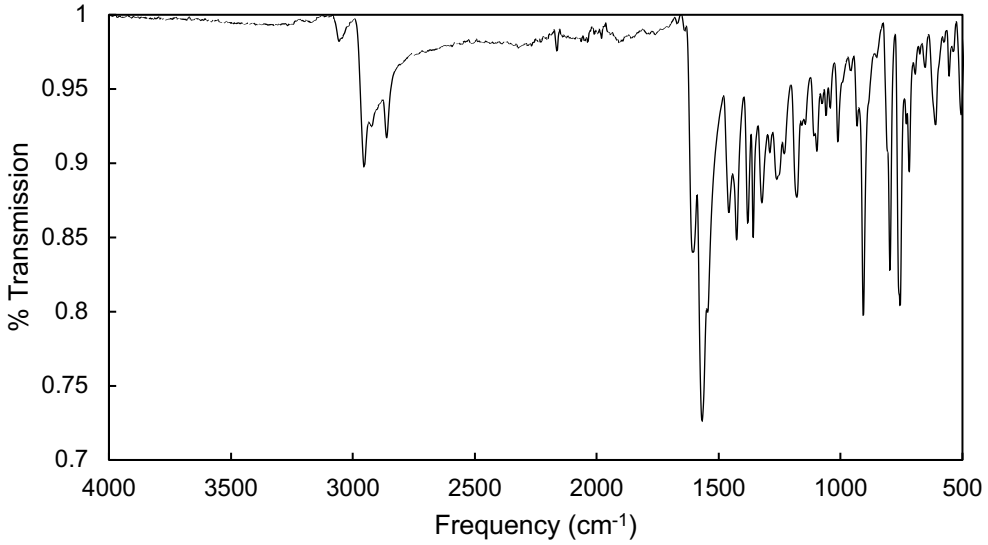


Figure S39. FT-IR spectrum of solid **6**.

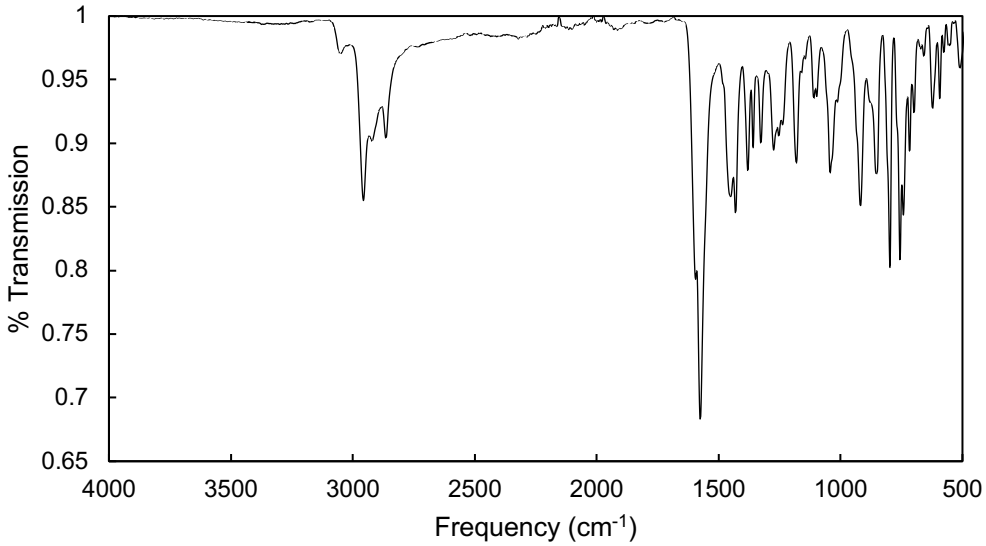


Figure S40. FT-IR spectrum of solid **8**.

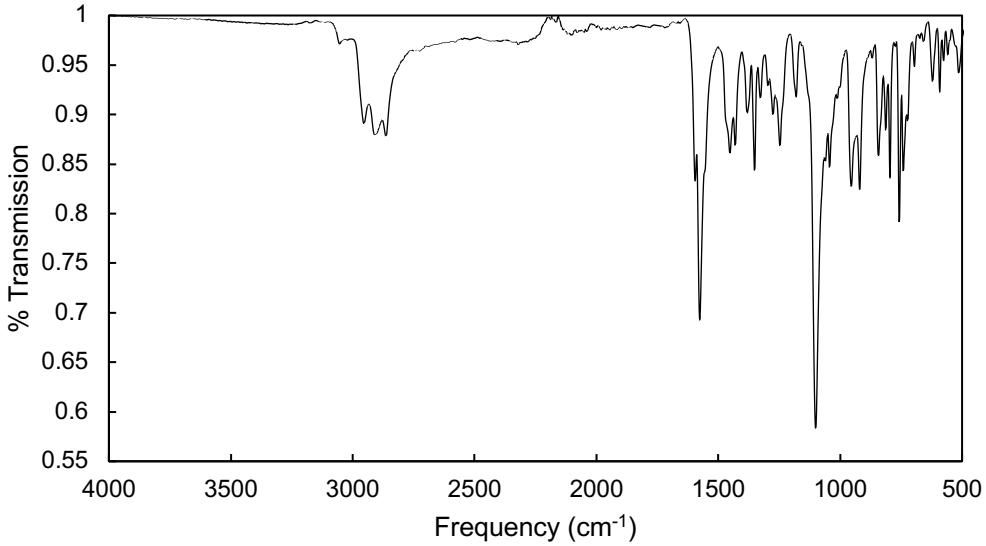


Figure S41. FT-IR spectrum of solid **8-crown**.

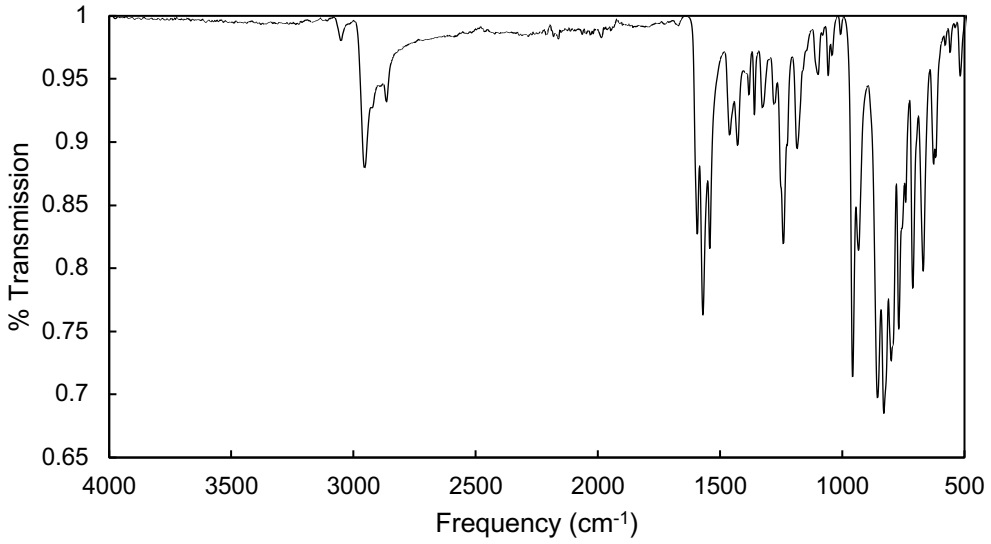


Figure S42. FT-IR spectrum of solid **9**.

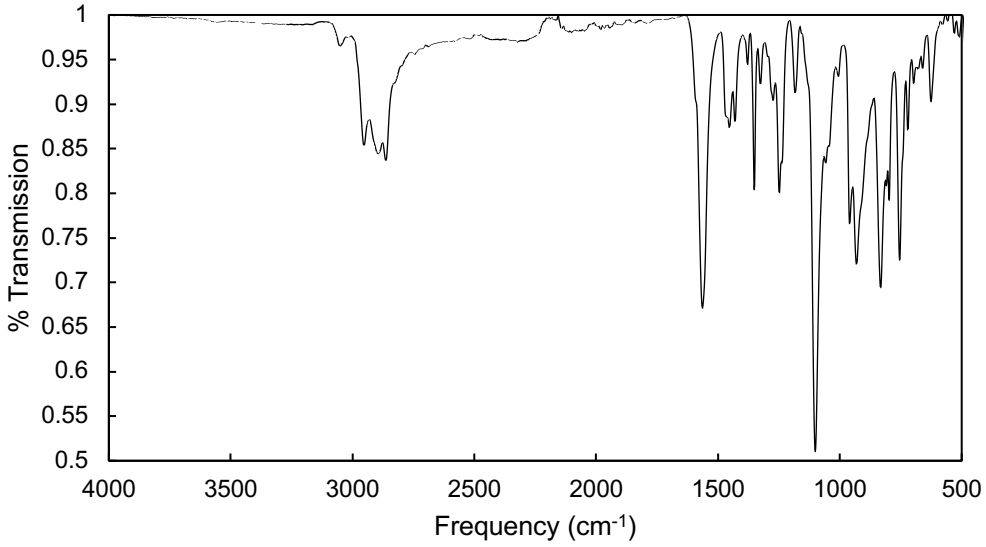


Figure S43. FT-IR spectrum of solid **9-crown**.

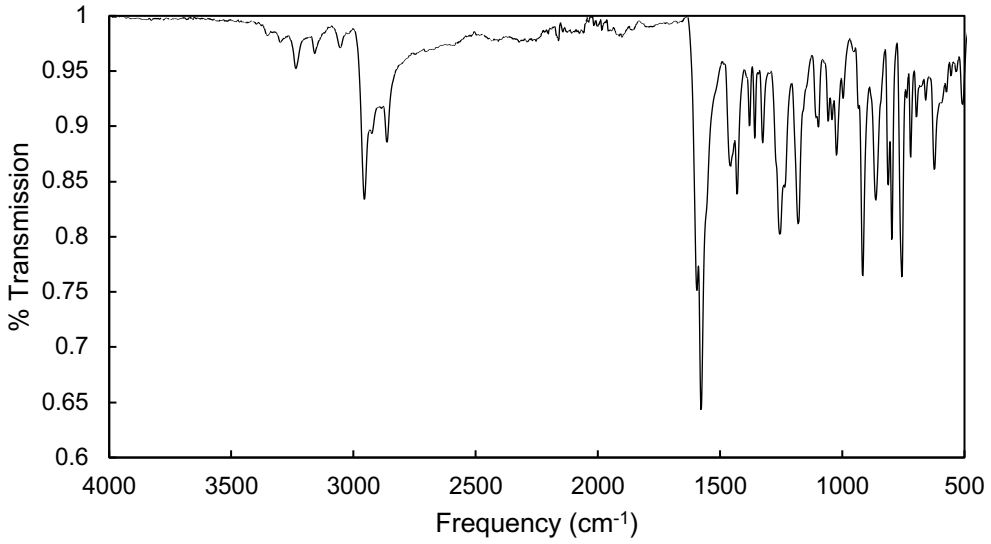


Figure S44. FT-IR spectrum of solid **10**.

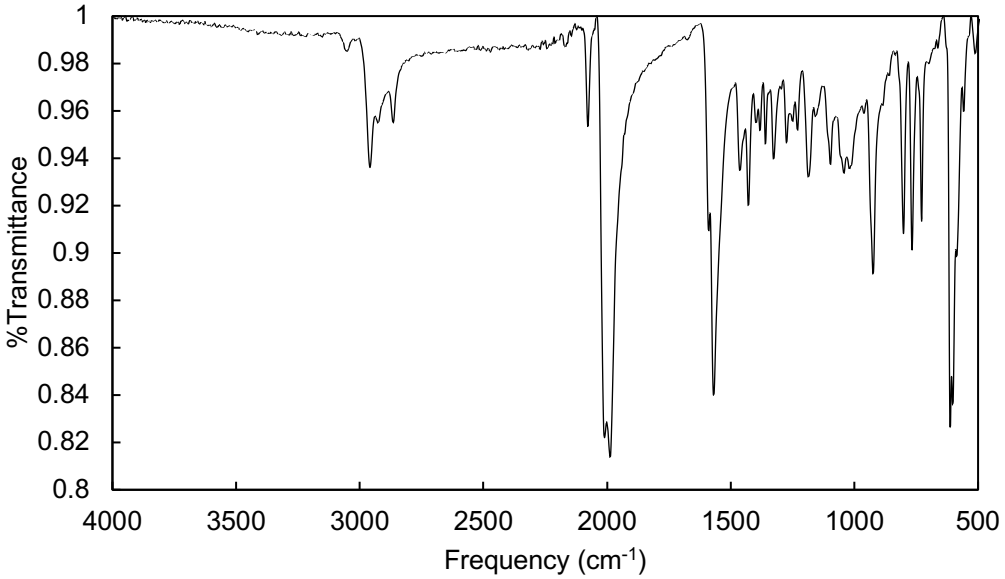


Figure S45. FT-IR spectrum of solid **11** showing bands at 2078, 2013, and 1988 cm^{-1} that are assigned as CO stretches.

Mössbauer Spectra

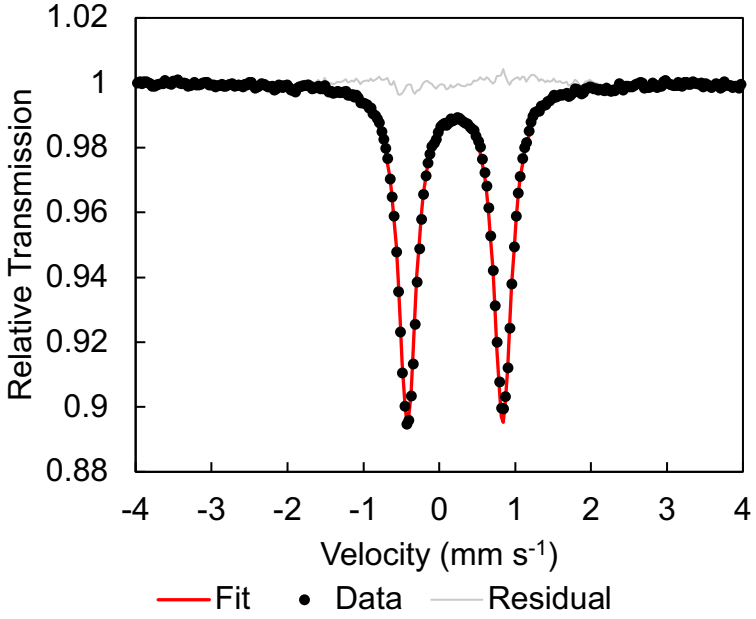


Figure S46. Solid state Mössbauer spectrum of **2**, fit to the following parameters: δ = 0.21 mm/s, $|\Delta E_Q|$ = 1.25 mm/s, Γ = 0.28 mm/s.

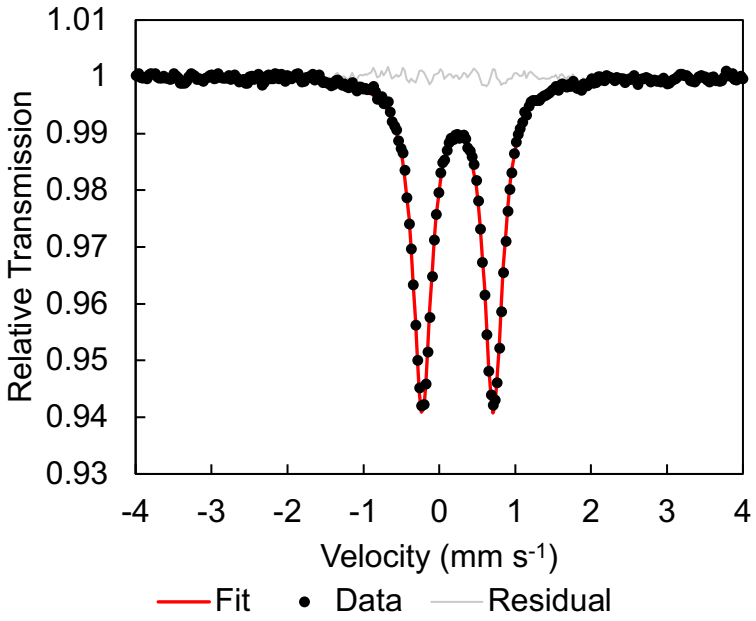


Figure S47. Solid state Mössbauer spectrum of **3-Na**, fit to the following parameters: δ = 0.24 mm/s, $|\Delta E_Q|$ = 0.94 mm/s, Γ = 0.30 mm/s.

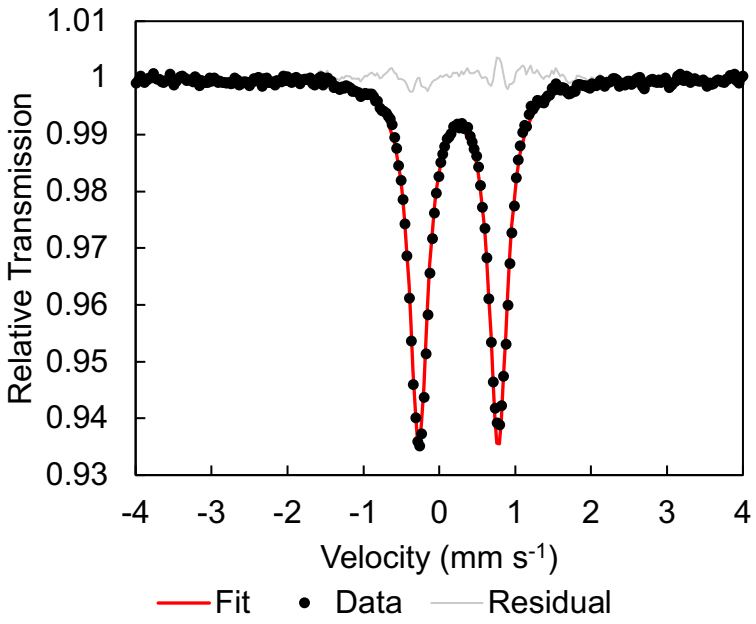


Figure S48. Solid state Mössbauer spectrum of **3-K**, fit to the following parameters: δ = 0.25 mm/s, $|\Delta E_Q|$ = 1.05 mm/s, Γ = 0.29 mm/s.

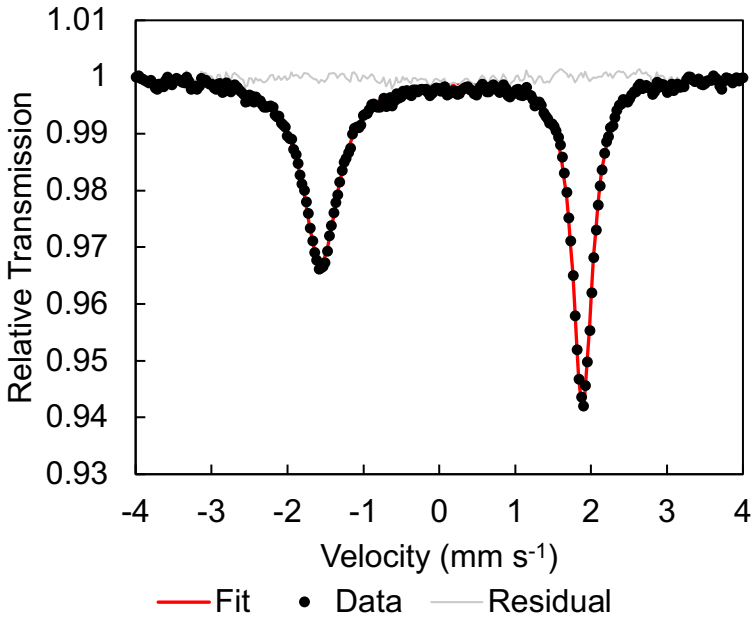


Figure S49. Solid state Mössbauer spectrum of **4**, fit to the following parameters: δ = 0.16 mm/s, $|\Delta E_Q|$ = 3.45 mm/s, Γ_L = 0.57 mm/s, Γ_R = 0.32 mm/s.

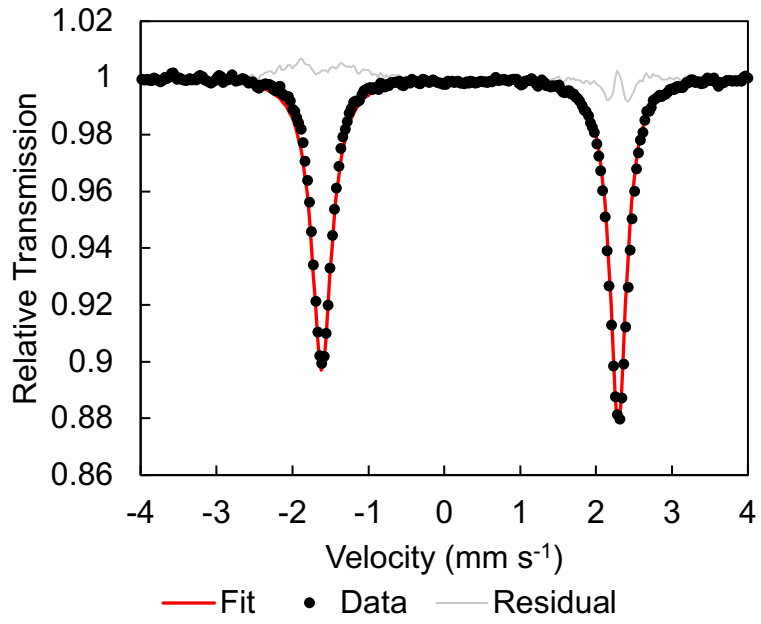


Figure S50. Solid state Mössbauer spectrum of **5-Et$_2$O**, fit to the following parameters: δ = 0.34 mm/s, $|\Delta E_Q|$ = 3.91 mm/s, Γ_L = 0.32 mm/s, Γ_R = 0.27 mm/s.

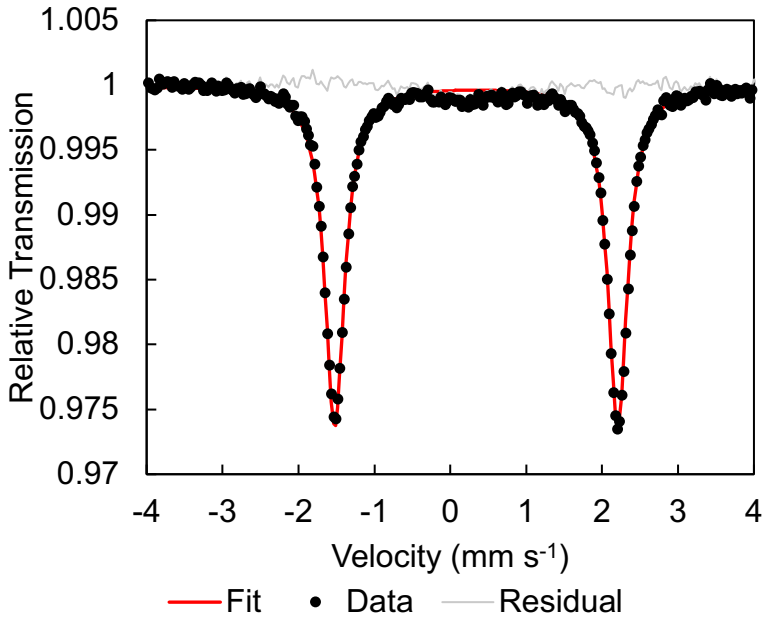


Figure S51. Solid state Mössbauer spectrum of **5-THF**, fit to the following parameters: δ = 0.34 mm/s, $|\Delta E_Q|$ = 3.73 mm/s, Γ = 0.31 mm/s.

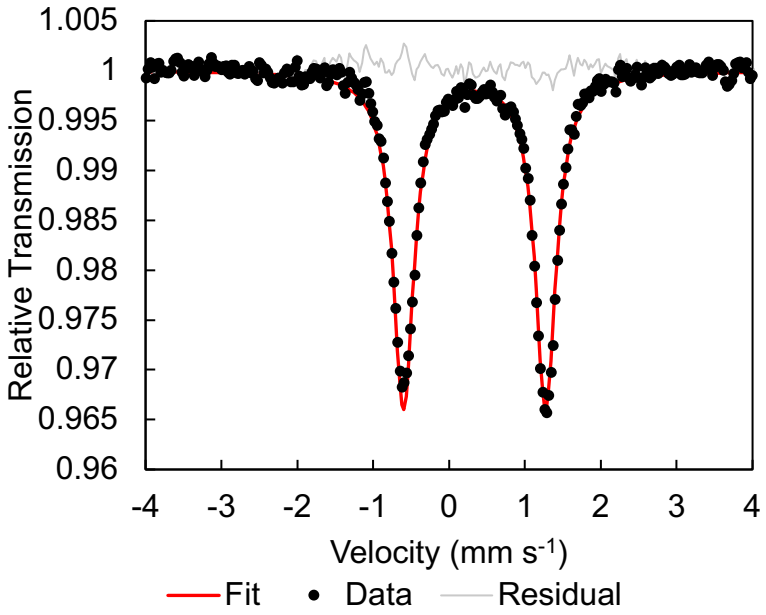


Figure S52. Solid state Mössbauer spectrum of **6**, fit to the following parameters: δ = 0.34 mm/s, $|\Delta E_Q|$ = 1.87 mm/s, Γ = 0.33 mm/s.

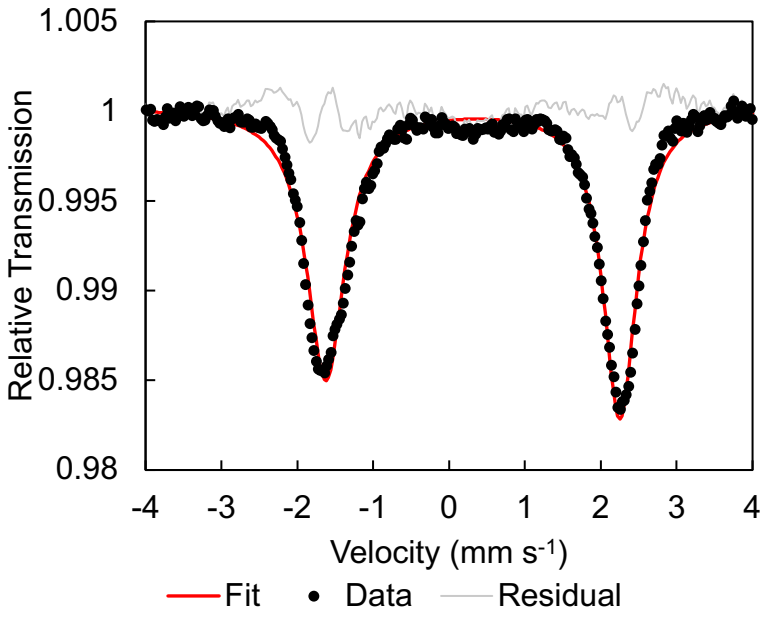


Figure S53. Solid state Mössbauer spectrum of **8**, fit to the following parameters: δ = 0.31 mm/s, $|\Delta E_Q|$ = 3.88 mm/s, Γ_L = 0.61 mm/s, Γ_R = 0.53 mm/s.

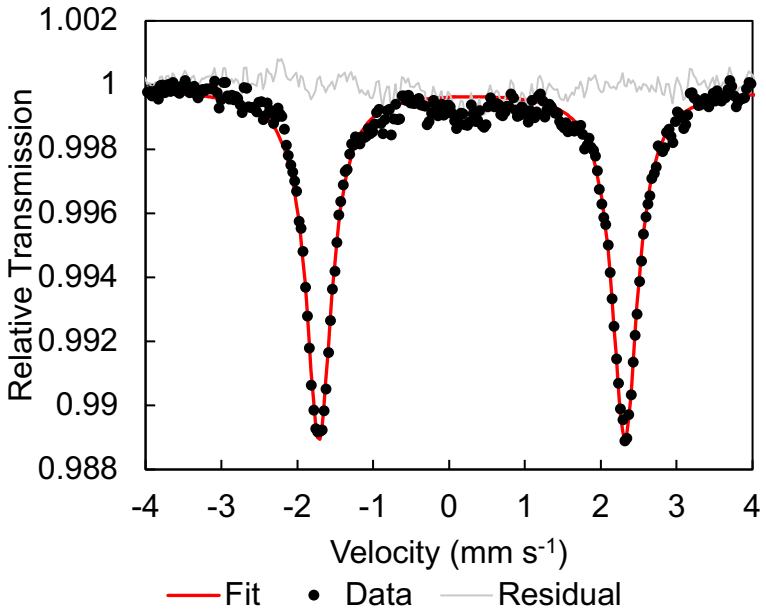


Figure S54. Solid state Mössbauer spectrum of **8-crown**, fit to the following parameters: $\delta = 0.30$ mm/s, $|\Delta E_Q| = 4.03$ mm/s, $\Gamma = 0.41$ mm/s.

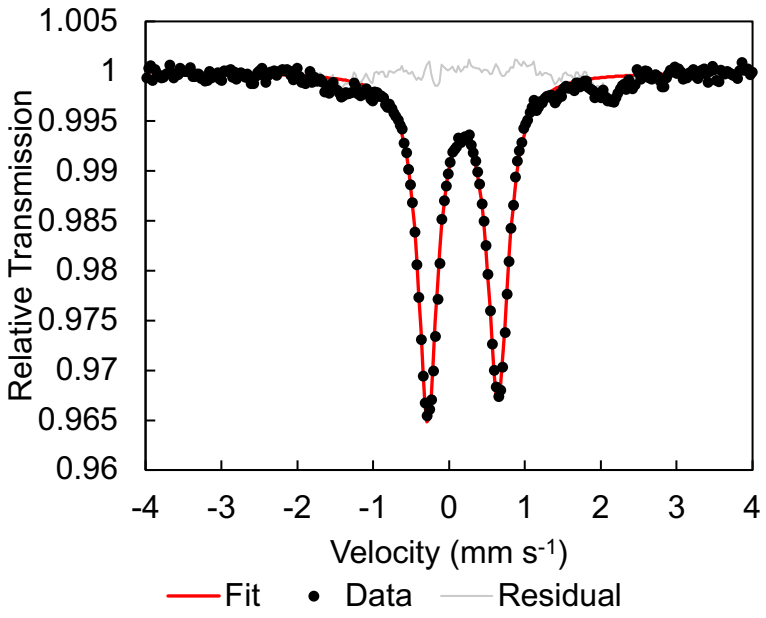


Figure S55. Solid state Mössbauer spectrum of **9**, fit to the following parameters: $\delta = 0.18$ mm/s, $|\Delta E_Q| = 0.93$ mm/s, $\Gamma_L = 0.30$ mm/s, $\Gamma_R = 0.33$ mm/s. There is a 4% impurity with parameter corresponding to the starting material, **5-Et$_2$O**.

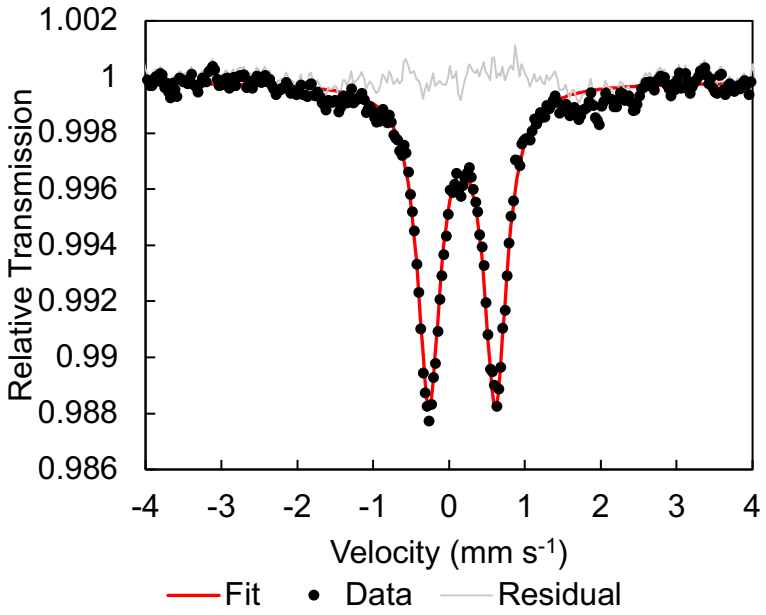


Figure S56. Solid state Mössbauer spectrum of **9-crown**, fit to the following parameters: $\delta = 0.17$ mm/s, $|\Delta E_Q| = 0.88$ mm/s, $\Gamma = 0.36$ mm/s.

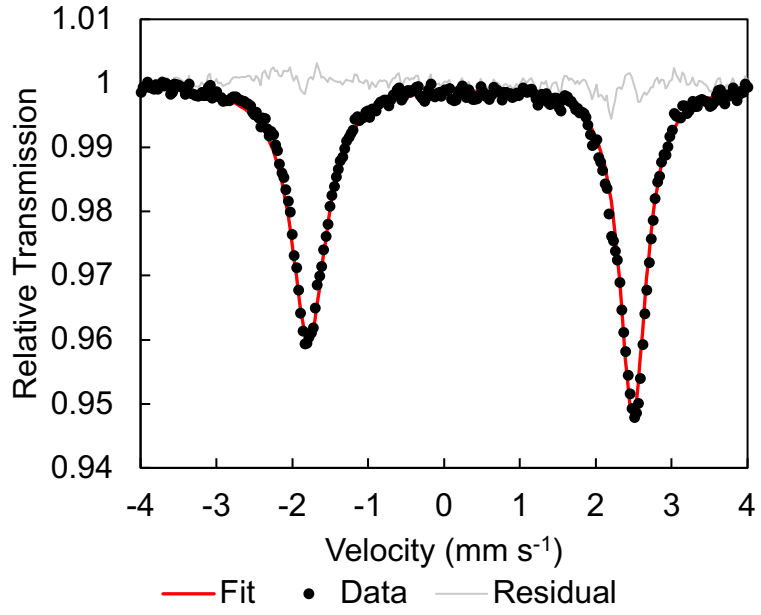


Figure S57. Solid state Mössbauer spectrum of **10**, fit to the following parameters: $\delta = 0.35$ mm/s, $|\Delta E_Q| = 4.28$ mm/s, $\Gamma_L = 0.55$ mm/s, $\Gamma_R = 0.43$ mm/s.

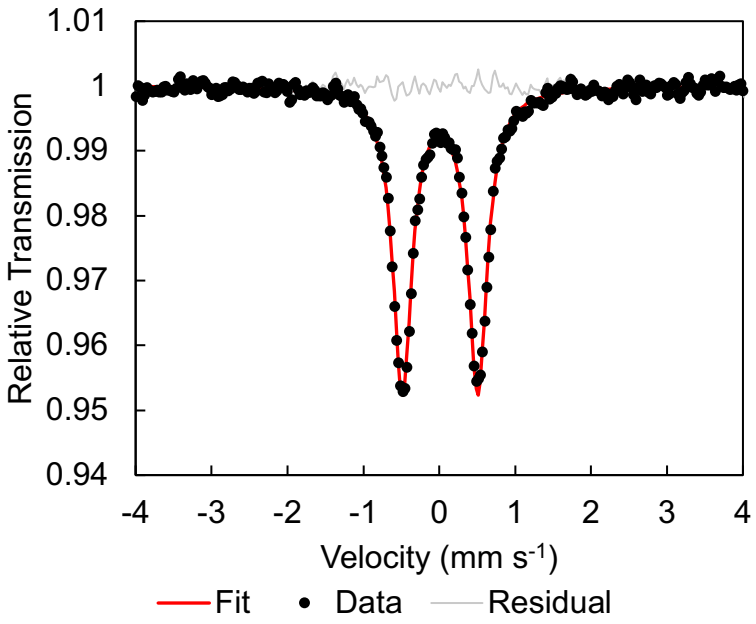


Figure S58. Solid state Mössbauer spectrum of **11**, fit to the following parameters: $\delta = 0.01$ mm/s, $|\Delta E_Q| = 0.99$ mm/s, $\Gamma = 0.30$ mm/s.

Cyclic Voltammograms

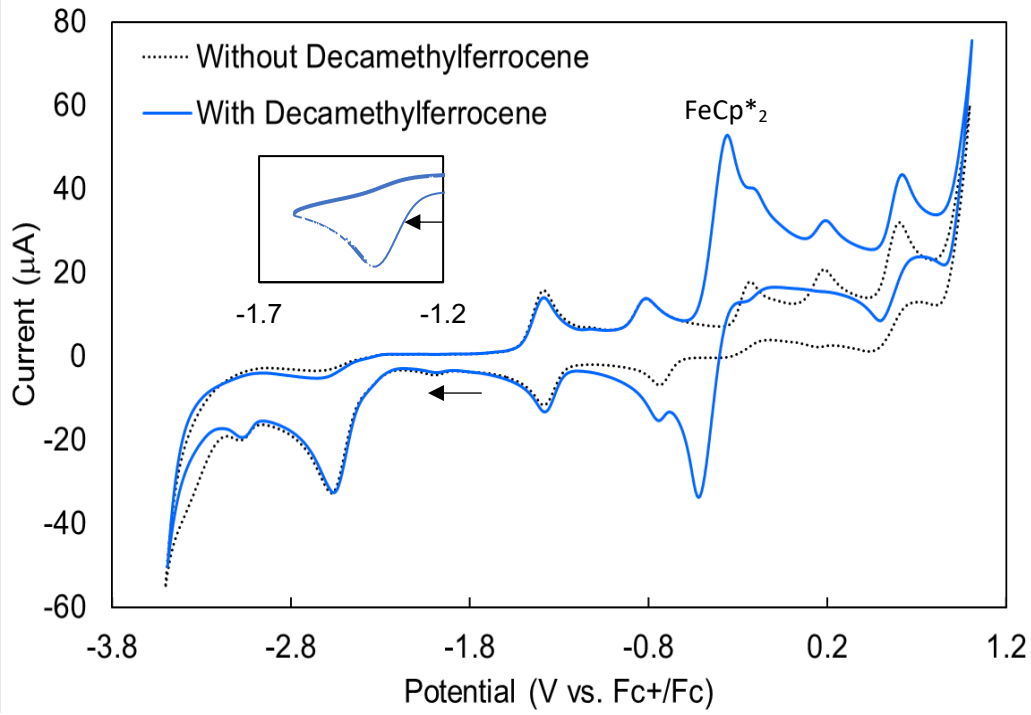


Figure S59. Cyclic voltammogram of **2** in THF with and without decamethylferrocene at a scan rate of 100 mV/s. Inset shows the CV from −1.2 V to −1.7 V when the potential is not swept below −1.6 V, showing that the oxidative feature observed in the full-solvent-window spectrum is not present. The internal reference $FeCp^*_2$ is set to a potential of –0.440 V vs. $FeCp_2$.[8]

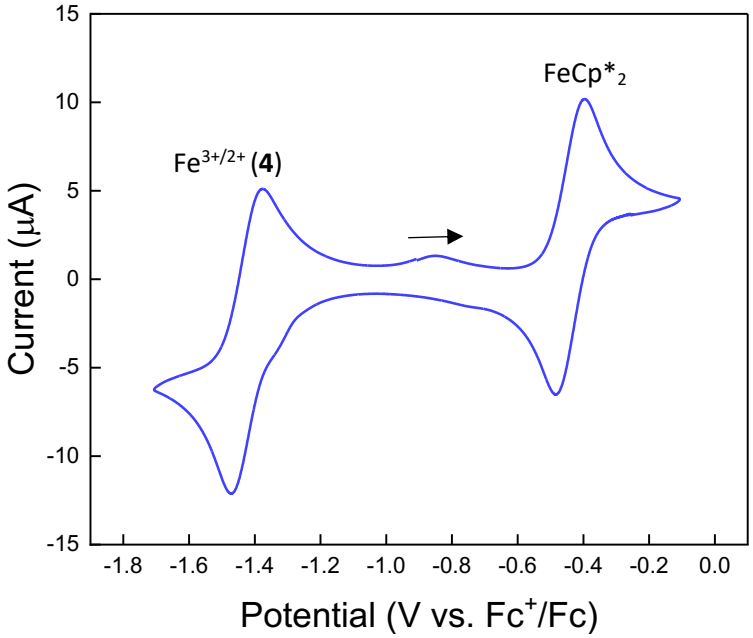


Figure S60. Cyclic voltammogram of **4** in THF showing a redox wave at $E_{1/2}$ = –1.424 V vs. Fc^+/Fc with ΔE_p = 97 mV at a scan rate of 20 mV/s. The internal reference $FeCp^*_2$ is set to a potential of –0.440 V vs. $FeCp_2$.[8]

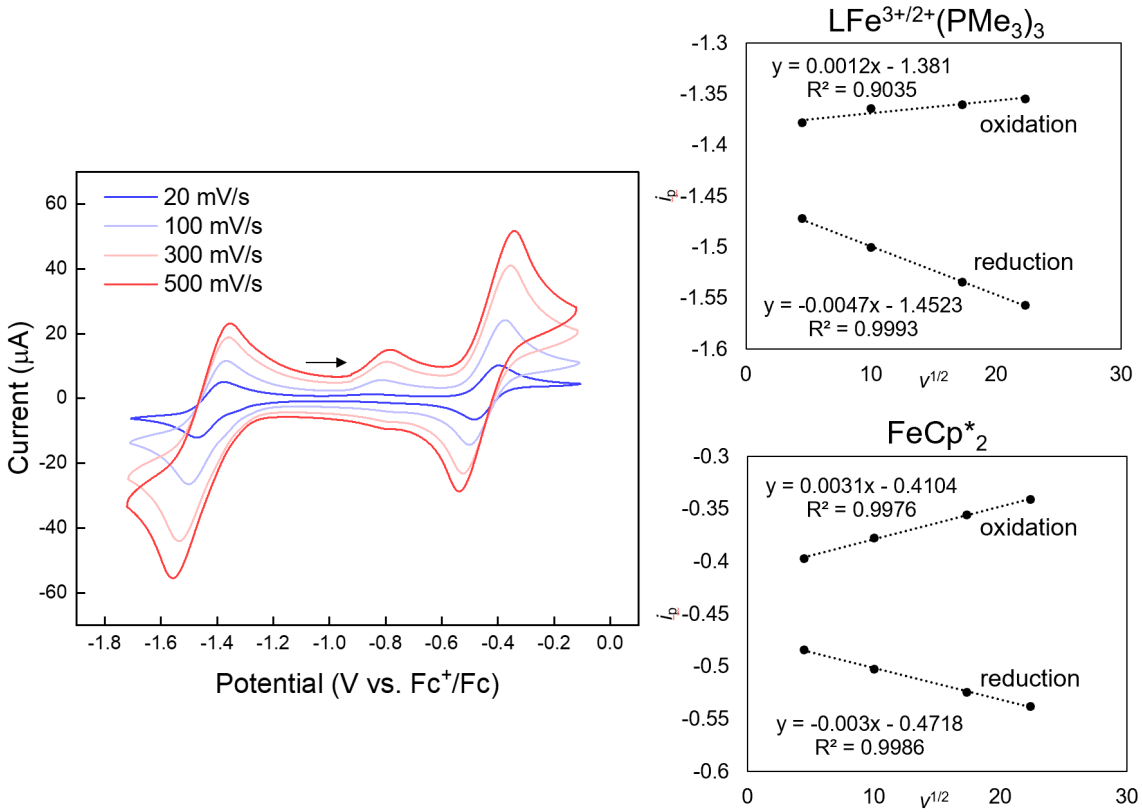


Figure S61. Scan rate dependence for **4** in THF showing linear relationship between $v^{1/2}$ and peak current.

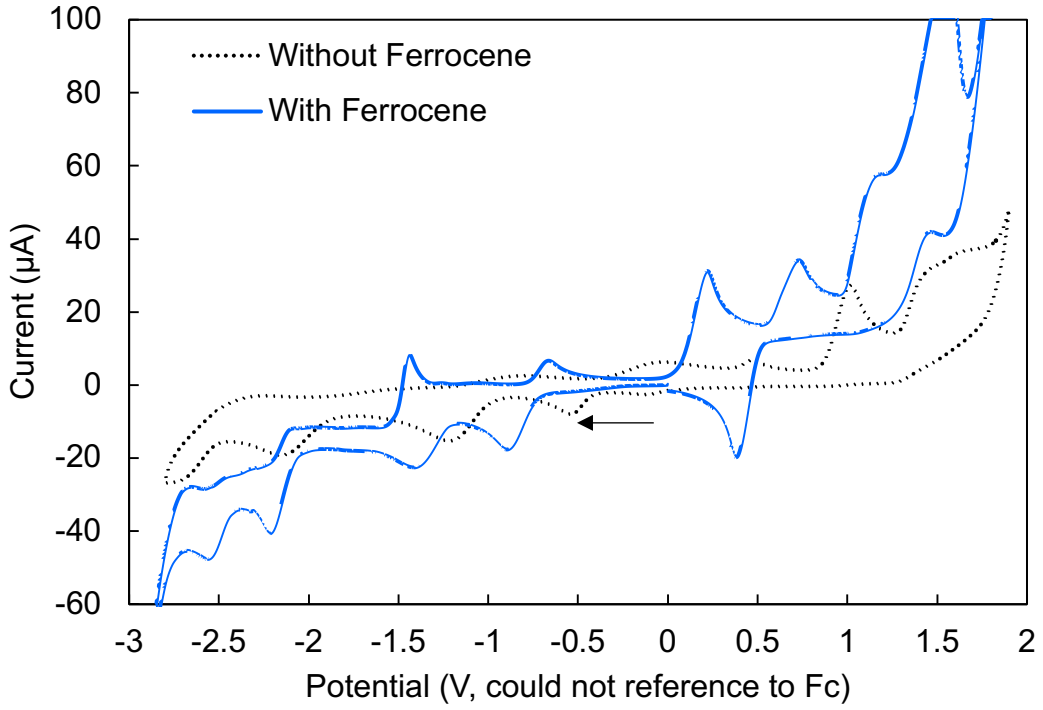


Figure S62. Cyclic voltammogram of **5-Solv** in THF with and without ferrocene at a scan rate of 100 mV/s.

SQUID Magnetometry Data

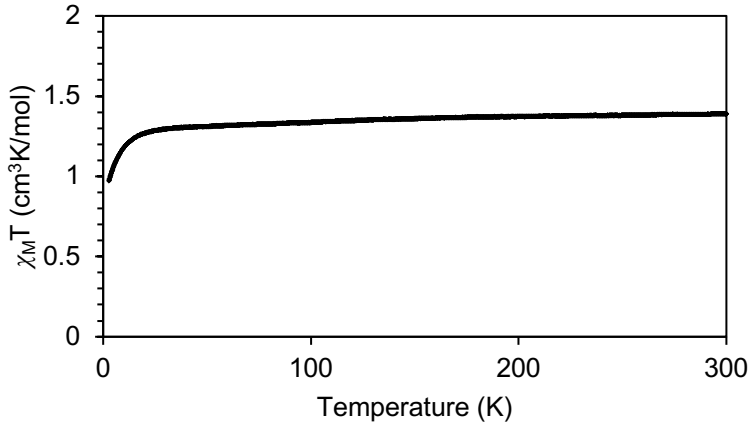


Figure S63. Solid-state temperature-dependent dc magnetic susceptibility of thiolate complex **8** under a 5000 Oe applied field.

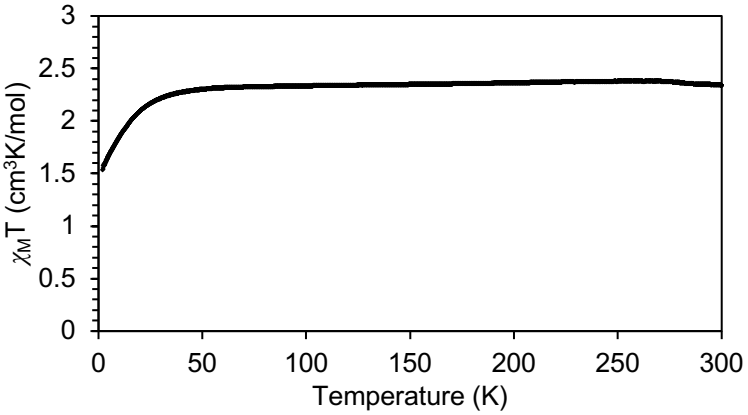


Figure S64. Solid-state temperature-dependent dc magnetic susceptibility of amide complex **9** under a 5000 Oe applied field.

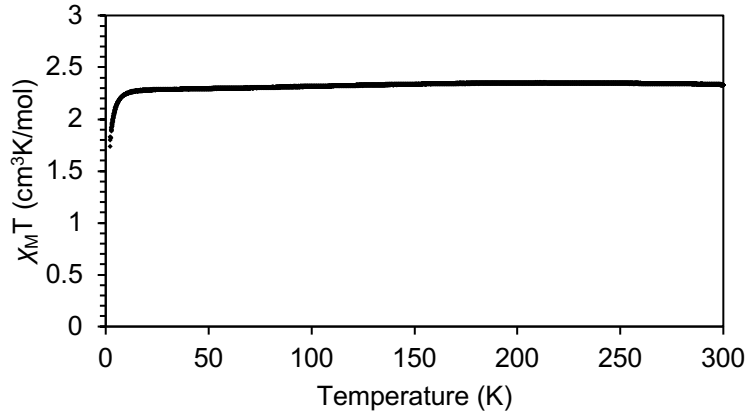


Figure S65. Solid-state temperature-dependent dc magnetic susceptibility of ammonia complex **10** under a 5000 Oe applied field.

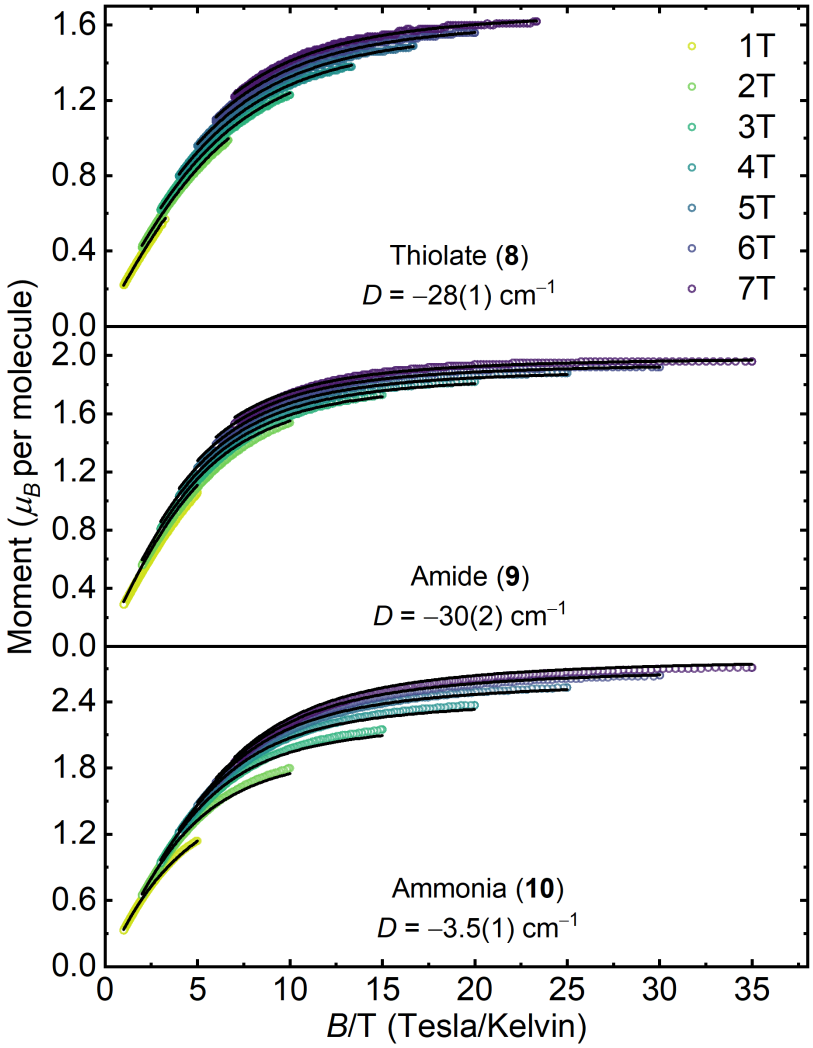


Figure S66. Variable-temperature magnetization data for complexes **8**, **9**, and **10** at fields of 1 T to 7 T. Data are shown as open circles and fits are shown as black traces. Temperature range for **8**: 3 K to 10 K. Temperature range for **9** and **10**: 2 K to 10 K. These temperatures were sufficient to adequately estimate the *D* values.

X-Ray Crystallographic Data

$HLFe^{II}(PMe_3)_3$ (2)

Low-temperature diffraction data (ω-scans) were collected on a Rigaku MicroMax-007HF diffractometer coupled to a Dectris Pilatus3R detector with Mo Kα (λ = 0.71073 Å). The diffraction images were processed and scaled using Rigaku Oxford Diffraction software (CrysAlisPro; Rigaku OD: The Woodlands, TX, 2015). The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL.[11] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). One isopropyl group is disordered over two positions. The site occupancy distribution was freely refined to a converged value near 0.85/0.15. The chemically equivalent 1,2 and 1,3 C-C distances were restrained to be similar. The protons on N12 and N13 were modeled as disordered at 0.50 occupancy. CCDC number 2118692 contains the supplementary crystallographic data for **2**.

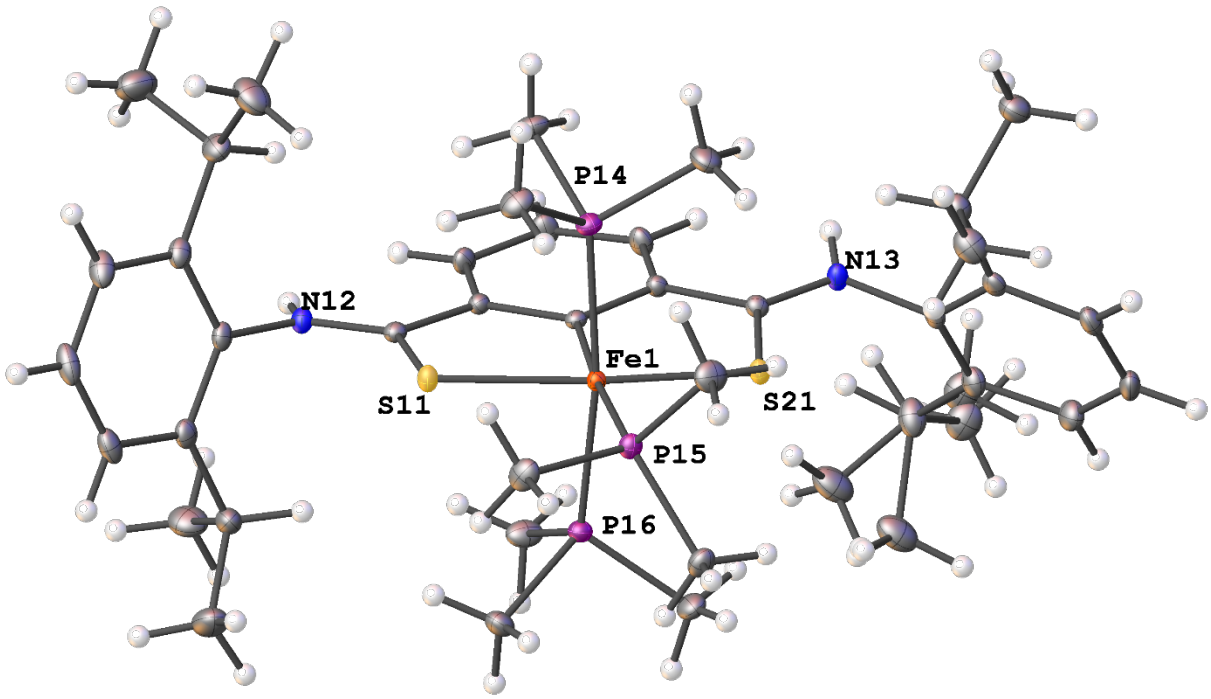


Figure S67. The partial numbering scheme of **2** with 50% thermal ellipsoid probability levels. The hydrogen atoms are shown as circles for clarity.

Table S1. Crystal data and structure refinement for **2**.

Identification code	007c-18063	
CCDC code	2118692	
Empirical formula	C41 H65 Fe N2 P3 S2	
Formula weight	798.83	
Temperature	93(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.4796(3) Å	α= 89.181(2)°.
	b = 13.8527(3) Å	β= 73.053(2)°.
	c = 16.7072(4) Å	γ = 68.946(2)°.
Volume	2154.06(10) $Å^3$	
Z	2	
Density (calculated)	1.232 g/cm^3	
Absorption coefficient	0.588 mm^{-1}	
F(000)	856	
Crystal size	0.100 x 0.100 x 0.040 mm^3	
Crystal color and habit	Black Block	
Diffractometer	Dectris Pilatus 3R	
Theta range for data collection	2.855 to 31.602°.	
Index ranges	-15<=h<=14, -19<=k<=18, -24<=l<=23	
Reflections collected	52714	
Independent reflections	12264 [R(int) = 0.0455]	
Observed reflections (I > 2sigma(I))	10649	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.68850	
Solution method	SHELXT-2014/5 (Sheldrick, 2014)	
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)	
Data / restraints / parameters	12264 / 11 / 468	
Goodness-of-fit on F^2	1.020	
Final R indices [I>2sigma(I)]	R1 = 0.0318, wR2 = 0.0719	
R indices (all data)	R1 = 0.0400, wR2 = 0.0750	
Largest diff. peak and hole	0.440 and -0.550 $e.Å^{-3}$	

$LFe^{III}(PMe_3)_3$ (4)

Low-temperature diffraction data (ω-scans) were collected on a Rigaku SCX Mini diffractometer coupled to a Rigaku Mercury275R CCD with Mo Kα radiation (λ = 0.71073 Å). The diffraction images were processed and scaled using Rigaku Oxford Diffraction software (CrysAlisPro; Rigaku OD: The Woodlands, TX, 2015). The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL.[11] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The methyl on one toluene is disordered over two positions. The site occupancies were freely refined and fixed near their converged values of 0.75/0.25. The hydrogen atoms were generated to reflect the disordered positions. No additional restraints were needed. The program SQUEEZE was used to compensate for the contribution of disordered solvents contained in voids within the crystal lattice from the diffraction intensities. This procedure was applied to the data file and the submitted model is based on the solvent removed data. Based on the total electron density found in the voids (339 e/Å^3), it is likely that ~8 toluene molecules are present in the unit cell. CCDC number 2118693 contains the supplementary crystallographic data for **4**.

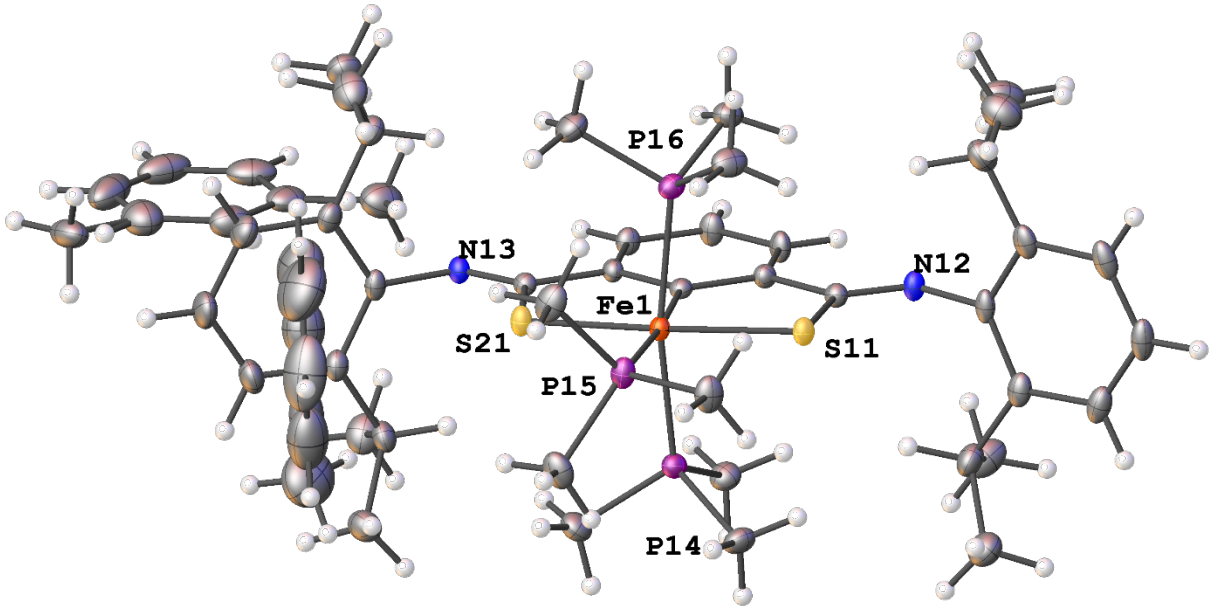


Figure S68. The partial numbering scheme of **4** with 50% thermal ellipsoid probability levels. The hydrogen atoms are shown as circles for clarity.

Table S2. Crystal data and structure refinement for **4**.

Identification code	mini-18057	
CCDC code	2118693	
Empirical formula	C55 H80 Fe N2 P3 S2	
Formula weight	982.09	
Temperature	93(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	I2/a	
Unit cell dimensions	a = 29.971(3) Å	α= 90°.
	b = 13.4638(3) Å	β= 100.515(7)°.
	c = 29.0781(16) Å	γ = 90°.
Volume	11536.8(12) Å^3	
Z	8	
Density (calculated)	1.131 g/cm^3	
Absorption coefficient	0.451 mm^{-1}	
F(000)	4216	
Crystal size	0.300 x 0.200 x 0.200 mm^3	
Crystal color and habit	Red Block	
Diffractometer	Rigaku Mercury275R CCD	
Theta range for data collection	1.663 to 27.485°.	
Index ranges	-38<=h<=38, -17<=k<=17, -37<=l<=37	
Reflections collected	99803	
Independent reflections	13218 [R(int) = 0.0634]	
Observed reflections (I > 2sigma(I))	9553	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.90990	
Solution method	SHELXT-2014/5 (Sheldrick, 2014)	
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)	
Data / restraints / parameters	13218 / 0 / 597	
Goodness-of-fit on F^2	1.045	
Final R indices [I>2sigma(I)]	R1 = 0.0424, wR2 = 0.1034	
R indices (all data)	R1 = 0.0670, wR2 = 0.1167	
Largest diff. peak and hole	0.471 and -0.336 e.Å^{-3}	

[LFe^{III}(THF)]$_2$ (5-THF)

Low-temperature diffraction data (ω-scans) were collected on a Rigaku MicroMax-007HF diffractometer coupled to a Dectris Pilatus3R detector with Mo Kα (λ = 0.71073 Å). The diffraction images were processed and scaled using Rigaku Oxford Diffraction software (CrysAlisPro; Rigaku OD: The Woodlands, TX, 2015). The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL.[11] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). There is likely some disorder in both the isopropyl group and coordinating THF solvent. The chemical model which would account for this density is not obvious, so the density was left unmodeled. Assuming carbon makes up some of the disordered model, free refinement of the disordered sites converged at a site occupancy of ~10% occupancy or less. CCDC number 2118695 contains the supplementary crystallographic data for **5-THF**.

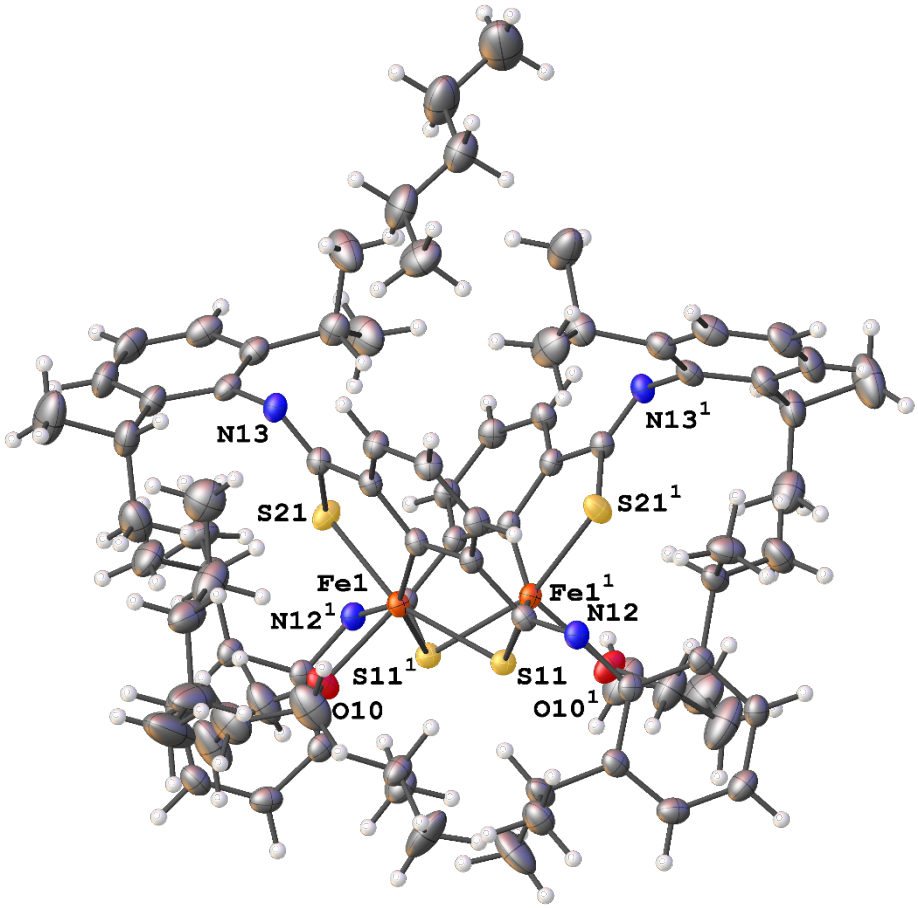


Figure S69. A partial numbering scheme of **5-THF** with 50% thermal ellipsoid probability levels. The hydrogen atoms are shown as circles for clarity. Only the asymmetric unit is labeled, and symmetry equivalent atoms are generated with the operator $\left(1-x, y, \frac{1}{2}-z\right)$.

Table S3. Crystal data and structure refinement for **5-THF**.

Identification code	007c-18076	
CCDC code	2118695	
Empirical formula	C92 H136 Fe2 N4 O2 S4	
Formula weight	1569.98	
Temperature	93(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 20.0317(15) Å	α= 90°.
	b = 19.1179(19) Å	β= 90.551(5)°.
	c = 23.4874(13) Å	γ = 90°.
Volume	8994.4(12) $Å^3$	
Z	4	
Density (calculated)	1.159 g/cm^3	
Absorption coefficient	0.462 mm^{-1}	
F(000)	3392	
Crystal size	0.200 x 0.100 x 0.020 mm^3	
Crystal color and habit	Black Plate	
Diffractometer	Dectris Pilatus 3R	
Theta range for data collection	2.946 to 27.481°.	
Index ranges	-24<=h<=26, -24<=k<=24, -30<=l<=30	
Reflections collected	83677	
Independent reflections	10291 [R(int) = 0.0774]	
Observed reflections (I > 2sigma(I))	8297	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.46063	
Solution method	SHELXT-2014/5 (Sheldrick, 2014)	
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)	
Data / restraints / parameters	10291 / 0 / 486	
Goodness-of-fit on F^2	1.043	
Final R indices [I>2sigma(I)]	R1 = 0.0521, wR2 = 0.1242	
R indices (all data)	R1 = 0.0700, wR2 = 0.1413	
Largest diff. peak and hole	1.541 and -0.492 $e.Å^{-3}$	

[LFe^{III}(Et$_2$O)]$_2$ (5-Et$_2$O)

Low-temperature diffraction data (ω-scans) were collected on a Rigaku MicroMax-007HF diffractometer coupled to a Dectris Pilatus3R detector with Mo Kα (λ = 0.71073 Å). The diffraction images were processed and scaled using Rigaku Oxford Diffraction software (CrysAlisPro; Rigaku OD: The Woodlands, TX, 2015). The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL.[11] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). One ether molecule is disordered over three positions. Their site occupancies were fixed near the values of 0.33, with one carbon shared between two models (site occupancy 0.66). O1A and C1B occupy the same space and were constrained to have the same X, Y, Z and thermal parameters. One Fe coordinated ether is disordered over two positions. Due to the proximity of these atoms, rigid bond restrains and thermal parameter constraints were used. All disordered C-C and C-O bond distances that are chemically similar were restrained to have similar distances. CCDC number 2118694 contains the supplementary crystallographic data for **5-Et$_2$O**.

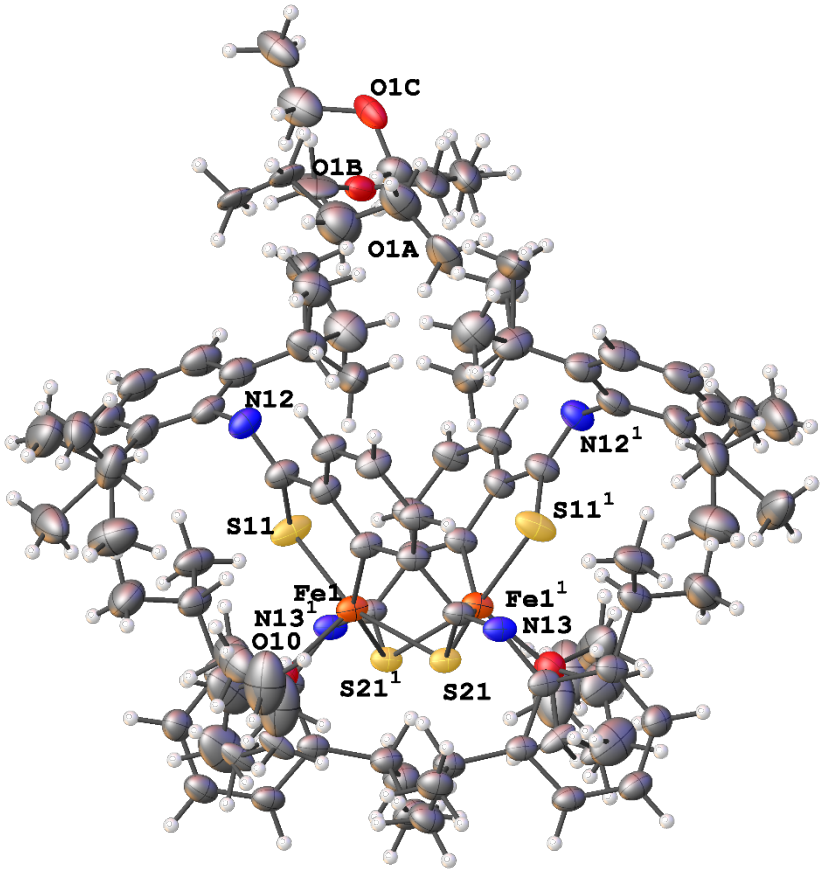


Figure S70. A partial numbering scheme of **5-Et$_2$O** with 50% thermal ellipsoid probability levels. The hydrogen atoms are omitted for clarity. Atoms with superscript 1 are generated by the symmetry operator $\left(1-x,\ y,\frac{3}{2}-z\right)$.

Table S4. Crystal data and structure refinement for **5-Et$_2$O**.

Identification code	007c-19024	
CCDC code	2118694	
Empirical formula	C80.01 H114 Fe2 N4 O4 S4	
Formula weight	1435.78	
Temperature	93(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 18.2490(19) Å	α= 90°.
	b = 19.853(2) Å	β= 95.556(7)°.
	c = 23.4606(17) Å	γ = 90°.
Volume	8459.7(14) Å^3	
Z	4	
Density (calculated)	1.127 g/cm^3	
Absorption coefficient	0.487 mm^{-1}	
F(000)	3080	
Crystal size	0.200 x 0.200 x 0.150 mm^3	
Crystal color and habit	Red Block	
Diffractometer	Dectris Pilatus 3R	
Theta range for data collection	2.931 to 27.482°.	
Index ranges	-17<=h<=23, -25<=k<=22, -30<=l<=26	
Reflections collected	47976	
Independent reflections	9701 [R(int) = 0.0555]	
Observed reflections (I > 2sigma(I))	6818	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.54478	
Solution method	SHELXT-2014/5 (Sheldrick, 2014)	
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)	
Data / restraints / parameters	9701 / 72 / 556	
Goodness-of-fit on F^2	1.051	
Final R indices [I>2sigma(I)]	R1 = 0.0717, wR2 = 0.1917	
R indices (all data)	R1 = 0.1082, wR2 = 0.2353	
Largest diff. peak and hole	1.641 and -0.692 e.Å^{-3}	

$K_4[LFe^{II}]_4(Et_2O)_2$ (6)

Low-temperature diffraction data (ω-scans) were collected on a Rigaku MicroMax-007HF diffractometer coupled to a Saturn994+ CCD detector with Cu Kα (λ = 1.54178 Å). The diffraction images were processed and scaled using Rigaku Oxford Diffraction software (CrysAlisPro; Rigaku OD: The Woodlands, TX, 2015). The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL.[11] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The thermal parameters were restrained with a global application of similarity and rigid bond restraints. The diffraction data was not ideal. The program SQUEEZE (see A.L.Spek, J. Appl. Cryst. 2015, C71, 9-18) was used to compensate for the contribution of disordered solvents contained in voids within the crystal lattice from the diffraction intensities. This procedure was applied to the data file and the submitted model is based on the solvent removed data. Based on the total electron density found in the voids (5094 e/Å^3), it is likely that ~120 ether molecules are present in the unit cell. See "_platon_squeeze_details" in this .cif for more information. CCDC number 2120364 contains the supplementary crystallographic data for **6**.

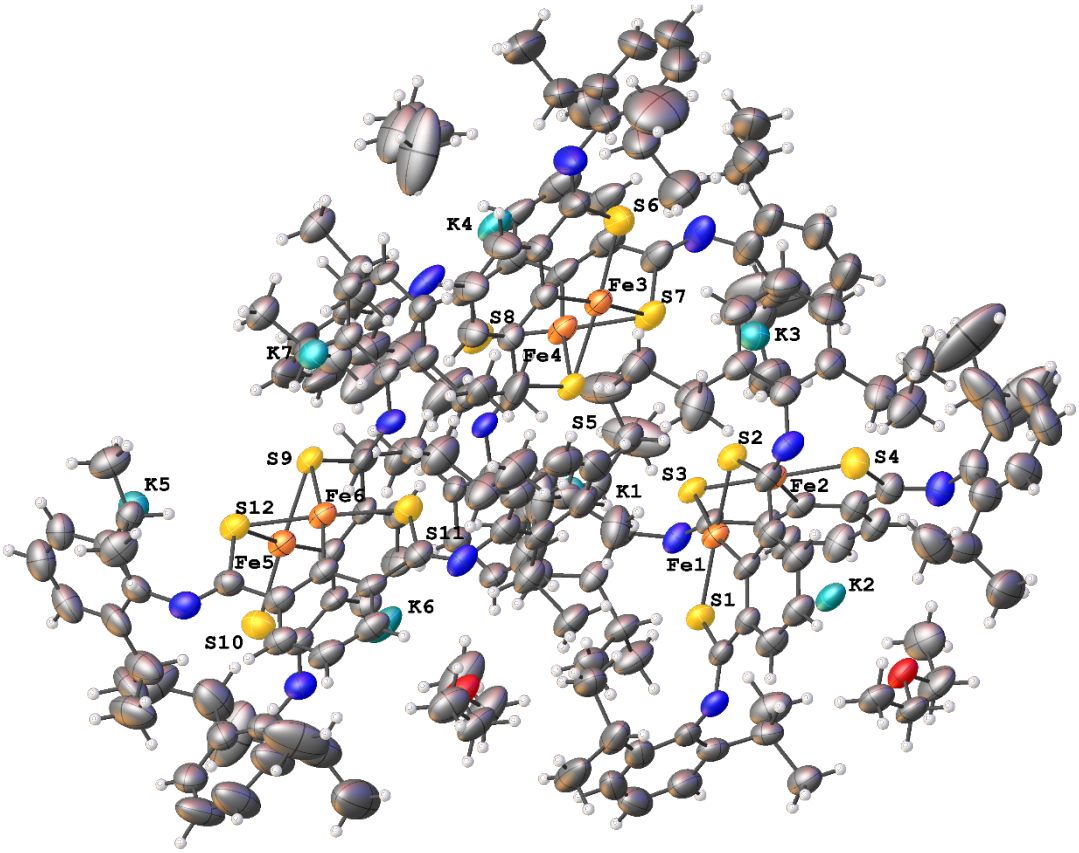


Figure S71. A partial numbering scheme of **6** with 50% thermal ellipsoid probability levels. The hydrogen atoms are omitted for clarity.

Table S5. Crystal data and structure refinement for **6**.

Identification code	007b-21015	
CCDC code	2120364	
Empirical formula	C136 H168 Fe4 K4 N8 O2 S8	
Formula weight	2583.05	
Temperature	93(2) K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	Pbcn	
Unit cell dimensions	a = 26.7161(4) Å	α= 90°.
	b = 38.8484(10) Å	β= 90°.
	c = 51.7223(8) Å	γ = 90°.
Volume	53681.4(18) $Å^3$	
Z	12	
Density (calculated)	0.959 g/cm^3	
Absorption coefficient	4.553 mm^{-1}	
F(000)	16368	
Crystal size	0.200 x 0.080 x 0.020 mm^3	
Crystal color and habit	Red Block	
Diffractometer	Rigaku Saturn 944+ CCD	
Theta range for data collection	1.708 to 66.601°.	
Index ranges	-31<=h<=31, -46<=k<=46, -61<=l<=61	
Reflections collected	1818611	
Independent reflections	47420 [R(int) = 0.4371]	
Observed reflections (I > 2sigma(I))	23538	
Completeness to theta = 66.601°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.37500	
Solution method	SHELXT-2014/5 (Sheldrick, 2014)	
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)	
Data / restraints / parameters	47420 / 2255 / 2189	
Goodness-of-fit on F^2	1.020	
Final R indices [I>2sigma(I)]	R1 = 0.1273, wR2 = 0.3251	
R indices (all data)	R1 = 0.2110, wR2 = 0.3833	
Largest diff. peak and hole	1.000 and -0.490 $e.Å^{-3}$	

K(18-crown-6)[LFe^{III}(SAr)(THF)] (7-crown)

Low-temperature diffraction data (ω-scans) were collected on a Rigaku MicroMax-007HF diffractometer coupled to a Saturn994+ CCD detector with Cu Kα (λ = 1.54178 Å) for the structure of 007a-19041. The diffraction images were processed and scaled using Rigaku Oxford Diffraction software (CrysAlisPro; Rigaku OD: The Woodlands, TX, 2015). The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL.[11] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). CCDC number 2118697 contains the supplementary crystallographic data for **7-crown**.

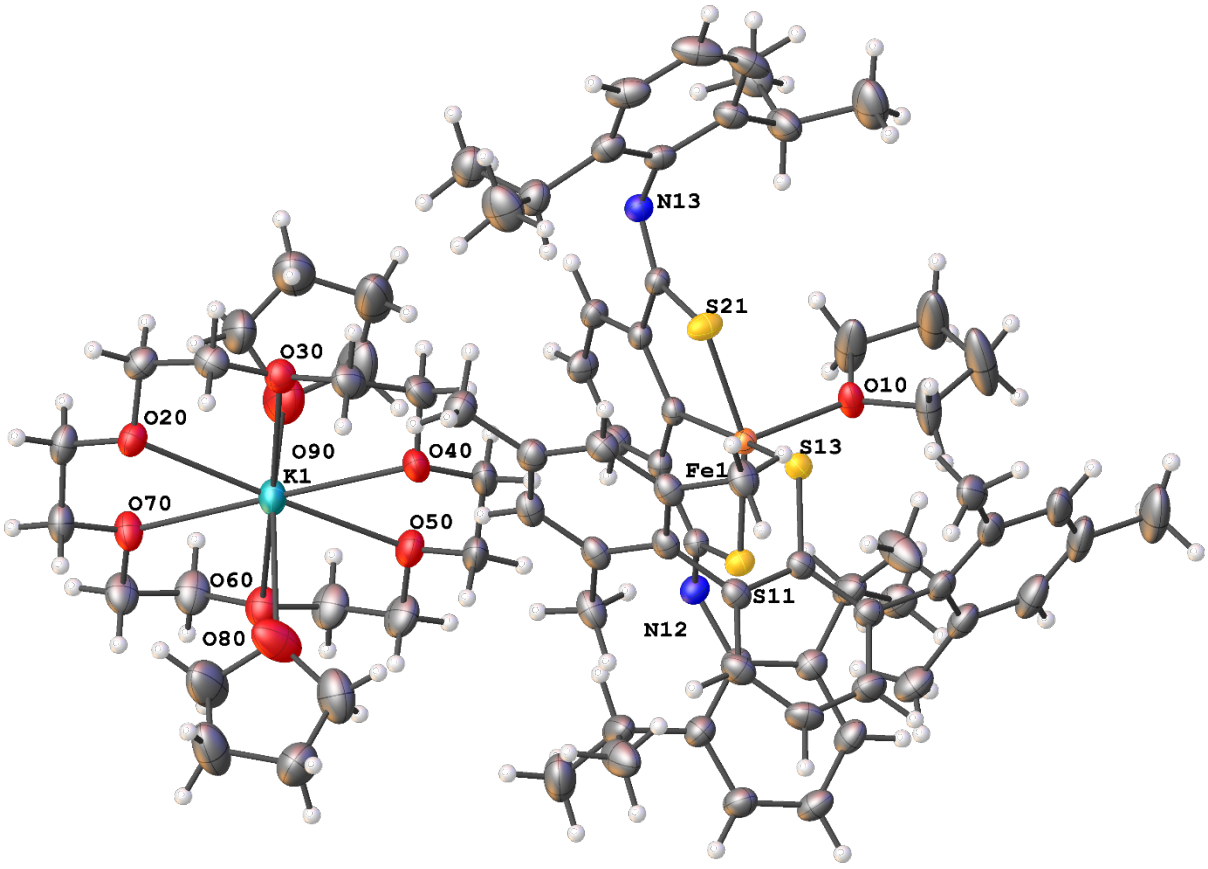


Figure S72. A partial numbering scheme of **7-crown** with 50% thermal ellipsoid probability levels. The hydrogen atoms are shown as circles for clarity.

Table S6. Crystal data and structure refinement for **7-crown**.

Identification code	007a-19041	
CCDC code	2118697	
Empirical formula	C80 H110 Fe K N2 O9 S3	
Formula weight	1434.82	
Temperature	93(2) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 14.6615(2) Å	α= 90°.
	b = 17.3994(2) Å	β= 92.7400(10)°.
	c = 30.6230(4) Å	γ = 90°.
Volume	7803.04(17) $Å^3$	
Z	4	
Density (calculated)	1.221 g/cm^3	
Absorption coefficient	3.212 mm^{-1}	
F(000)	3076	
Crystal size	0.200 x 0.200 x 0.010 mm^3	
Crystal color and habit	Red Plate	
Diffractometer	Rigaku Saturn 944+ CCD	
Theta range for data collection	2.889 to 66.823°.	
Index ranges	-17<=h<=17, -20<=k<=20, -36<=l<=36	
Reflections collected	286932	
Independent reflections	13826 [R(int) = 0.0526]	
Observed reflections (I > 2sigma(I))	13012	
Completeness to theta = 66.823°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.62838	
Solution method	SHELXT-2014/5 (Sheldrick, 2014)	
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)	
Data / restraints / parameters	13826 / 0 / 879	
Goodness-of-fit on F^2	1.015	
Final R indices [I>2sigma(I)]	R1 = 0.0369, wR2 = 0.0967	
R indices (all data)	R1 = 0.0391, wR2 = 0.0985	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.768 and -0.442 $e.Å^{-3}$	

K(18-crown-6)[LFe^{III}(SAr)] (8-crown)

Low-temperature diffraction data (ω-scans) were collected on a Rigaku MicroMax-007HF diffractometer coupled to a Dectris Pilatus3R detector with Mo Kα (λ = 0.71073 Å) for the structure of 007c-19044. The diffraction images were processed and scaled using Rigaku Oxford Diffraction software (CrysAlisPro; Rigaku OD: The Woodlands, TX, 2015). The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL.[11] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). One toluene is disordered across the crystallographic inversion center. The methyl was fixed at half occupancy. The hydrogen atoms were generated and constrained in geometrically expected positions. No additional restraints or constraints were needed. CCDC number 2118696 contains the supplementary crystallographic data for **8-crown**.

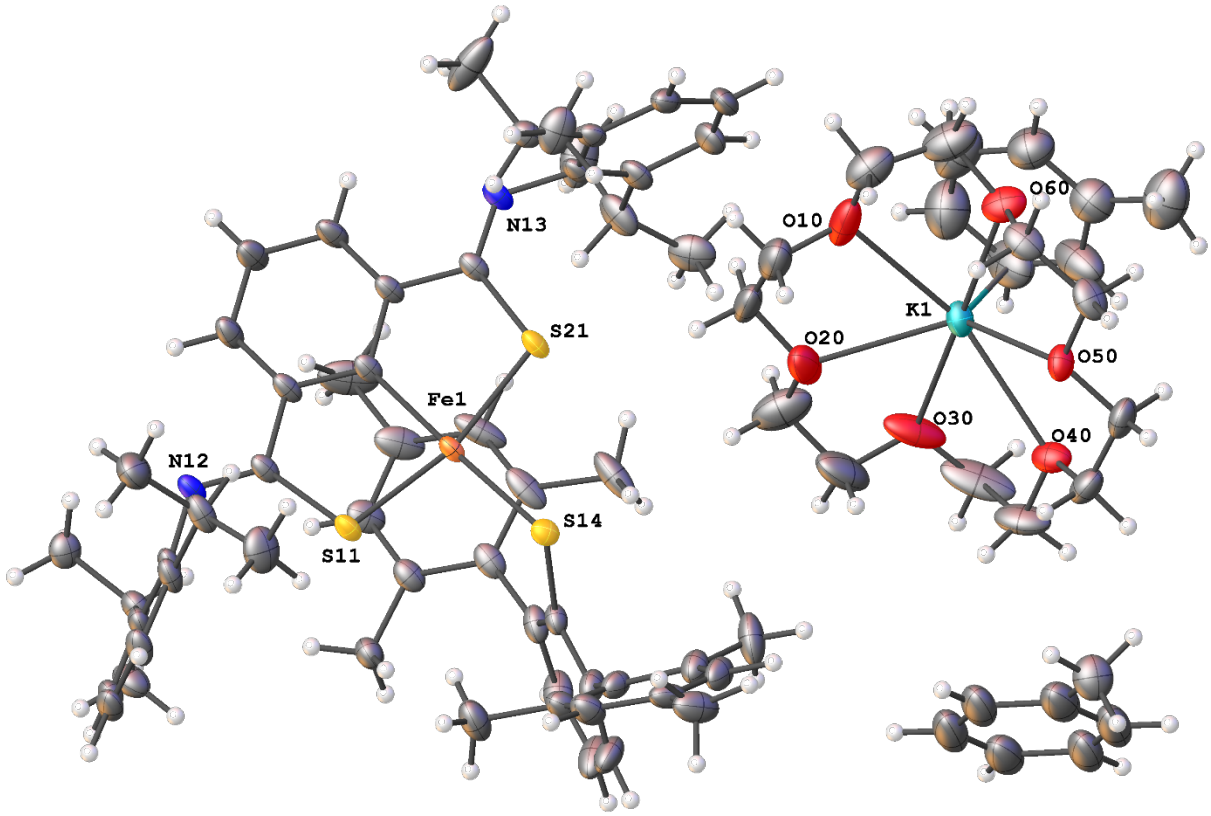


Figure S73. A partial numbering scheme of **8-crown** with 50% thermal ellipsoid probability levels. The hydrogen atoms are shown as circles for clarity.

Table S7. Crystal data and structure refinement for **8-crown.**

Identification code	007c-19044	
CCDC code	2118696	
Empirical formula	C78.50 H98 Fe K N2 O6 S3	
Formula weight	1356.71	
Temperature	93(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 15.5618(6) Å	α= 73.279(4)°.
	b = 16.0210(7) Å	β= 70.720(4)°.
	c = 16.5200(7) Å	γ = 78.134(3)°.
Volume	3695.3(3) $Å^3$	
Z	2	
Density (calculated)	1.219 g/cm^3	
Absorption coefficient	0.397 mm^{-1}	
F(000)	1448	
Crystal size	0.200 x 0.200 x 0.050 mm^3	
Crystal color and habit	Red Plate	
Diffractometer	Dectris Pilatus 3R	
Theta range for data collection	2.947 to 27.793°.	
Index ranges	-20<=h<=20, -20<=k<=20, -21<=l<=20	
Reflections collected	65241	
Independent reflections	16967 [R(int) = 0.0922]	
Observed reflections (I > 2sigma(I))	13858	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.79955	
Solution method	SHELXT-2014/5 (Sheldrick, 2014)	
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)	
Data / restraints / parameters	16967 / 0 / 845	
Goodness-of-fit on F^2	1.077	
Final R indices [I>2sigma(I)]	R1 = 0.0755, wR2 = 0.2068	
R indices (all data)	R1 = 0.0881, wR2 = 0.2190	
Largest diff. peak and hole	1.996 and -1.090 $e.Å^{-3}$	

K[LFe^{III}(N(TMS)$_2$)] (9)

Low-temperature diffraction data (ω-scans) were collected on a Rigaku MicroMax-007HF diffractometer coupled to a Saturn994+ CCD detector with Cu Kα (λ = 1.54178 Å) for the structure of 007b-16092. The diffraction images were processed and scaled using Rigaku Oxford Diffraction software (CrysAlisPro; Rigaku OD: The Woodlands, TX, 2015). The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL.[11] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The program SQUEEZE was used to compensate for the contribution of disordered solvents contained in voids within the crystal lattice from the diffraction intensities. This procedure was applied to the data file and the submitted model is based on the solvent removed data. Based on the total electron density found in the voids (247 e/Å^3), it is likely that ~8 pentane molecules are present in the unit cell. CCDC number 2118698 contains the supplementary crystallographic data for **9**.

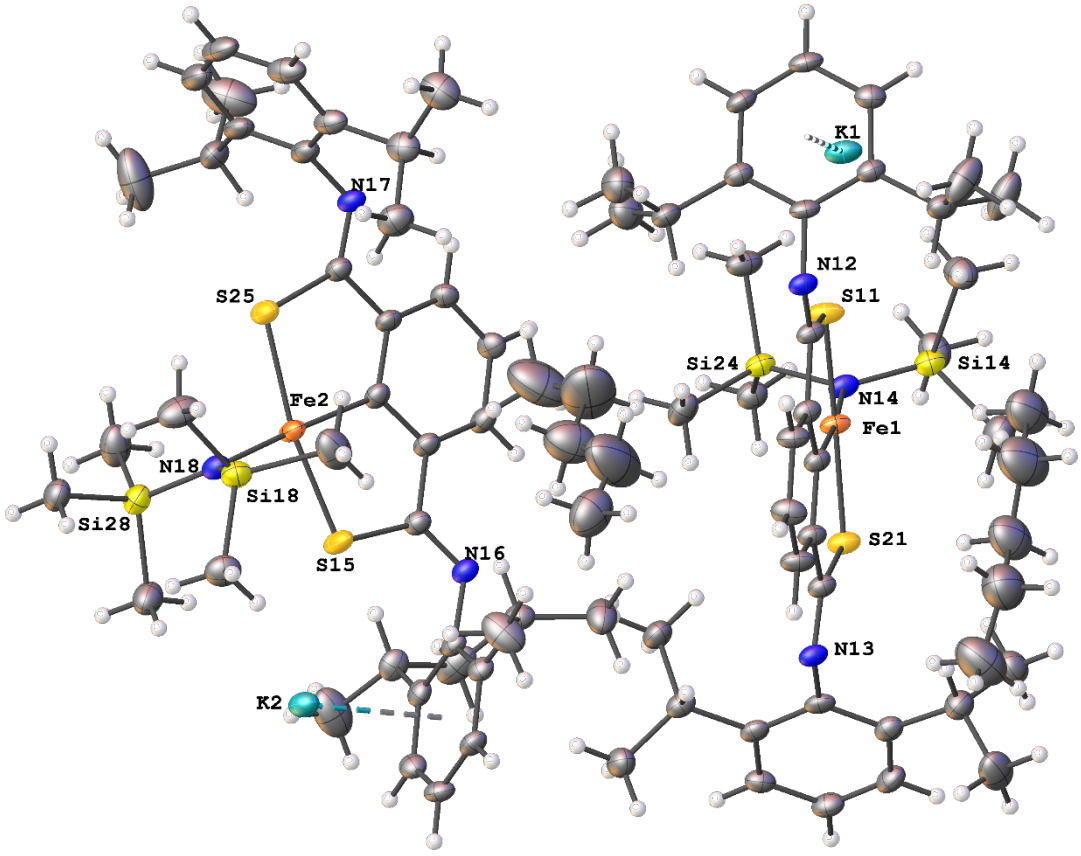


Figure S74. A partial numbering scheme of **9** with 50% thermal ellipsoid probability levels. The hydrogen atoms are omitted for clarity.

Table S8. Crystal data and structure refinement for **9**.

Identification code	007b-19062	
CCDC code	2118698	
Empirical formula	C43 H67 Fe K N3 S2 Si2	
Formula weight	841.24	
Temperature	93(2) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 13.3160(3) Å	α= 90°.
	b = 38.4243(8) Å	β= 102.431(2)°.
	c = 20.3073(4) Å	γ = 90°.
Volume	10146.8(4) $Å^3$	
Z	8	
Density (calculated)	1.101 g/cm^3	
Absorption coefficient	4.550 mm^{-1}	
F(000)	3608	
Crystal size	0.300 x 0.020 x 0.020 mm^3	
Crystal color and habit	Red Needle	
Diffractometer	Rigaku Saturn 944+ CCD	
Theta range for data collection	2.507 to 66.600°.	
Index ranges	-15<=h<=15, -45<=k<=45, -24<=l<=24	
Reflections collected	246866	
Independent reflections	17871 [R(int) = 0.1152]	
Observed reflections (I > 2sigma(I))	13667	
Completeness to theta = 66.600°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.58051	
Solution method	SHELXT-2014/5 (Sheldrick, 2014)	
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)	
Data / restraints / parameters	17871 / 0 / 969	
Goodness-of-fit on F^2	1.013	
Final R indices [I>2sigma(I)]	R1 = 0.0531, wR2 = 0.1202	
R indices (all data)	R1 = 0.0755, wR2 = 0.1310	
Largest diff. peak and hole	0.735 and -0.417 $e.Å^{-3}$	

K(18-crown-6)[LFe^{III}(N(TMS)$_2$)] (9-crown)

Low-temperature diffraction data (ω-scans) were collected on a Rigaku MicroMax-007HF diffractometer coupled to a Saturn994+ CCD detector with Cu Kα (λ = 1.54178 Å) for the structure of 007a-19014. The diffraction images were processed and scaled using Rigaku Oxford Diffraction software (CrysAlisPro; Rigaku OD: The Woodlands, TX, 2015). The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL.[11] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). One THF coordinated to potassium was modeled as disordered. Chemically similar 1,2 and 1,3 distances of the disordered model were restrained to be similar. The site occupancies were freely refined to converged values near 0.65/0.35. The program SQUEEZE was used to compensate for the contribution of disordered solvents contained in voids within the crystal lattice from the diffraction intensities. This procedure was applied to the data file and the submitted model is based on the solvent removed data. Based on the total electron density found in the voids (138 e/Å^3), it is likely that ~3 THF molecules are present in the unit cell. See "_platon_squeeze_details" in this .cif for more information. CCDC number 2118699 contains the supplementary crystallographic data for **9-crown**.

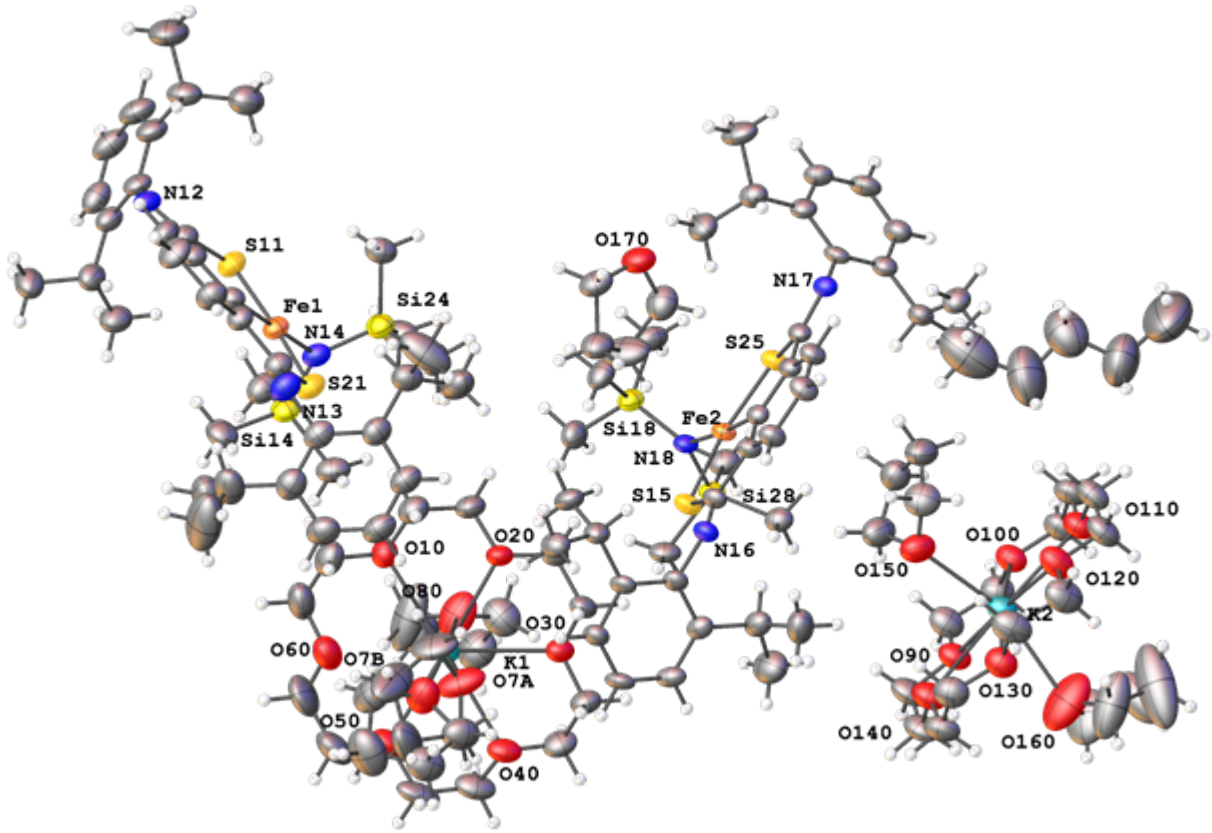


Figure S75. A partial numbering scheme of **9-crown** with 50% thermal ellipsoid probability levels. The hydrogen atoms are shown as circles for clarity.

Table S9. Crystal data and structure refinement for **9-crown**.

Identification code	007a-19014	
CCDC code	2118699	
Empirical formula	C62.50 H105 Fe K N3 O8.50 S2 Si2	
Formula weight	1249.74	
Temperature	93(2) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 22.5668(6) Å	α= 90°.
	b = 13.6389(2) Å	β= 89.938(2)°.
	c = 47.2831(13) Å	γ = 90°.
Volume	14553.1(6) $Å^3$	
Z	8	
Density (calculated)	1.141 g/cm^3	
Absorption coefficient	3.412 mm^{-1}	
F(000)	5392	
Crystal size	0.200 x 0.080 x 0.020 mm^3	
Crystal color and habit	Red Plate	
Diffractometer	Rigaku Saturn 944+ CCD	
Theta range for data collection	1.869 to 66.600°.	
Index ranges	-26<=h<=26, -16<=k<=16, -54<=l<=55	
Reflections collected	512934	
Independent reflections	25521 [R(int) = 0.1838]	
Observed reflections (I > 2sigma(I))	20203	
Completeness to theta = 66.600°	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.34851	
Solution method	SHELXT-2014/5 (Sheldrick, 2014)	
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)	
Data / restraints / parameters	25521 / 22 / 1508	
Goodness-of-fit on F^2	1.134	
Final R indices [I>2sigma(I)]	R1 = 0.0935, wR2 = 0.1944	
R indices (all data)	R1 = 0.1117, wR2 = 0.2023	
Largest diff. peak and hole	1.063 and -0.524 $e.Å^{-3}$	

[LFe^{III}(NH$_3$)(THF)] (10)

Low-temperature diffraction data (ω-scans) were collected on a Rigaku MicroMax-007HF diffractometer coupled to a Dectris Pilatus3R detector with Mo Kα (λ = 0.71073 Å) for the structure of 007c-20076. The diffraction images were processed and scaled using Rigaku Oxford Diffraction software (CrysAlisPro; Rigaku OD: The Woodlands, TX, 2015). The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL.[11] This data was refined as a 2-component inversion twin. The fractional volume contribution of the minor twin component was freely refined to a converged value of 0.087(13). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The only exceptions are the protons in NH_3. Those sites were found in the difference map and freely refined. All N-H distances were restrained to be similar. One isopropyl group is disordered over two positions. The site occupancies were freely refined to converged values of 0.70/0.30. Due to the small amount of electron density, the thermal parameters at the minor site were constrained to be the same as those of the chemically identical major site. A similar approach was used in the disordered ether. All chemically equivalent C-C and C-O distances were restrained to be similar. The program SQUEEZE (see A.L.Spek, J. Appl. Cryst. 2015, C71, 9-18) was used to compensate for the contribution of disordered solvents contained in voids within the crystal lattice from the diffraction intensities. This procedure was applied to the data file and the submitted model is based on the solvent removed data. Based on the total electron density found in the voids (167 e/Å^{3}it is likely that ~4 ether, ~4 THF, or some combination of these two solvent molecules are present in the unit cell. CCDC number 2118700 contains the supplementary crystallographic data for **10**.

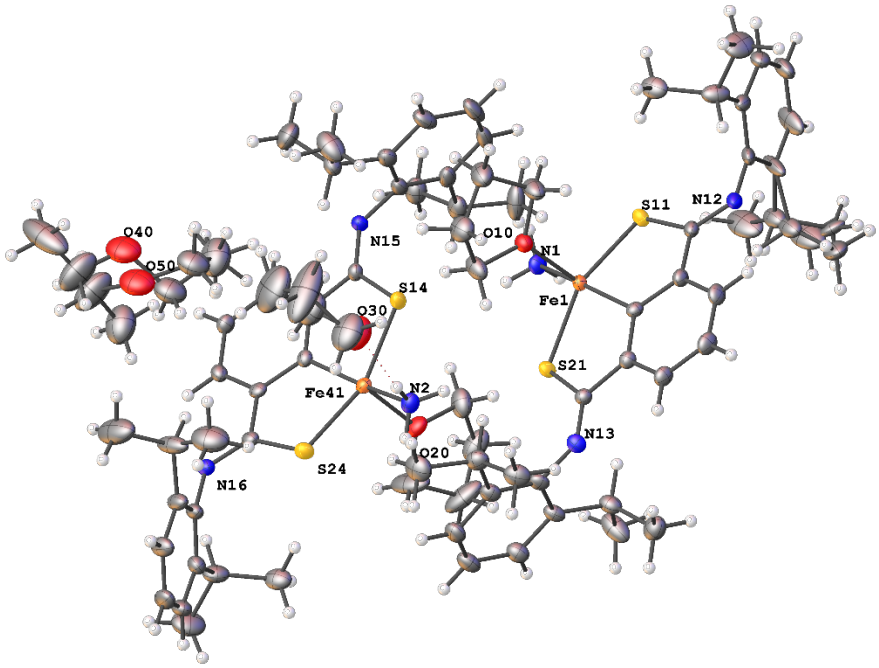


Figure S76. A partial numbering scheme of **10** with 50% thermal ellipsoid probability levels. The hydrogen atoms are shown as circles for clarity.

Table S10. Crystal data and structure refinement for **10**.

Identification code	007c-20076	
CCDC code	2118700	
Empirical formula	C40 H57 Fe N3 O2 S2	
Formula weight	731.85	
Temperature	93(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 17.0373(4) Å	α= 90°.
	b = 15.3942(3) Å	β= 105.434(2)°.
	c = 17.3731(4) Å	γ = 90°.
Volume	4392.22(17) $Å^3$	
Z	4	
Density (calculated)	1.107 g/cm^3	
Absorption coefficient	0.471 mm^{-1}	
F(000)	1568	
Crystal size	0.200 x 0.120 x 0.090 mm^3	
Crystal color and habit	Orange Block	
Diffractometer	Dectris Pilatus 3R	
Theta range for data collection	2.757 to 27.483°.	
Index ranges	-21<=h<=22, -19<=k<=19, -22<=l<=22	
Reflections collected	88042	
Independent reflections	20102 [R(int) = 0.0315]	
Observed reflections (I > 2sigma(I))	18478	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.58906	
Solution method	SHELXT-2014/5 (Sheldrick, 2014)	
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)	
Data / restraints / parameters	20102 / 36 / 933	
Goodness-of-fit on F^2	1.018	
Final R indices [I>2sigma(I)]	R1 = 0.0371, wR2 = 0.0971	
R indices (all data)	R1 = 0.0420, wR2 = 0.1001	
Absolute structure parameter	0.087(13)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.687 and -0.506 $e.Å^{-3}$	

Additional Experiments

To clarify whether the coordinated THF in **10** can be removed, crystals of **10** were crushed, washed with pentane, and dried under vacuum for several hours. A Mössbauer spectrum of the resulting material was identical to the crystalline material, providing evidence against a change in the iron coordination number. There were no free THF signals in the C_6D_6-solvated ^{1}H NMR spectrum of the material before it was subjected to several hours under vacuum. Furthermore, the crystals for X-ray diffraction (which demonstrated iron-coordinated THF) were obtained by pumping down the crude reaction mixture and re-dissolving the solids in neat Et_2O, from which the crystals were grown. All of these indicators are inconsistent with the ability to remove coordinated THF from **10** by simple trituration or vacuum as can be done for **8**.

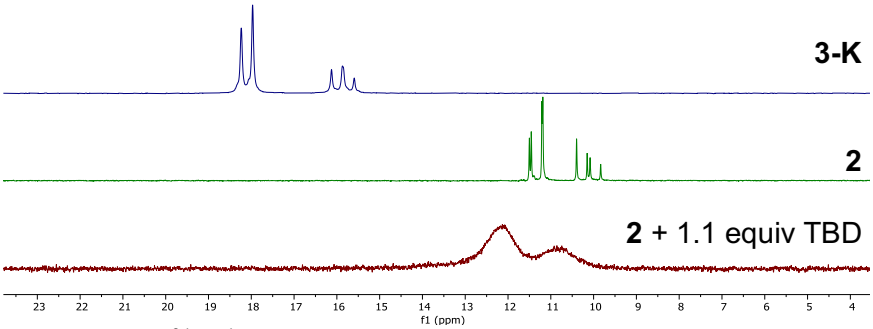


Figure S77. $^{31}P\{^1H\}$ NMR spectra comparison between **3-K**, **2**, and the equilibrium experiment of **2** in the presence of 1.1 equiv triazabicyclodecene (TBD) in THF. We assumed that that the chemical shifts from the ^{31}P NMR spectrum of **3-K** represent the shifts of fully deprotonated **2**. Equilibrium concentrations were determined from the initial concentrations of TBD and **2** and the chemical shifts of the coalesced peaks upon equilibration. Values used to calculate K_{eq}: [**2**] = 22.0 mM, [TBD] = 24.4 mM, [**2**$^-$] = 6.5 mM, [HTBD$^+$] = 7.2 mM. Allowing an error of ±1 ppm in the chemical shift results in a pK_a difference of ±0.9, which we rounded to ±1.

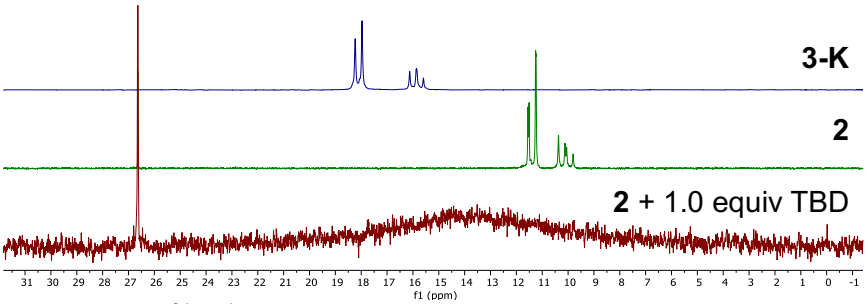


Figure S78. $^{31}P\{^1H\}$ NMR spectra comparison between **3-K**, **2**, and the equilibrium experiment of **2** in the presence of 1.0 equiv triazabicyclodecene (TBD) in a 0.3 M solution of [N^{n}Bu$_4$][PF$_6$] in THF. The signal at ~27 ppm is from a capillary standard of $Me_3P{=}S$. We assumed that that the chemical shifts from the ^{31}P NMR spectrum of **3-K** represent the shifts of fully deprotonated **2**. Equilibrium concentrations were determined from the initial concentrations of TBD and **2** and the chemical shift of the coalesced peak upon equilibration. Values used to calculate K_{eq}: [**2**] = 17.7 mM, [TBD] = 17.4 mM, [**2**$^-$] = 14.3 mM, [HTBD$^+$] = 14.2 mM. Allowing an error of ±1 ppm in the chemical shift results in a pK_a difference of ±0.6, which we rounded to ±1.

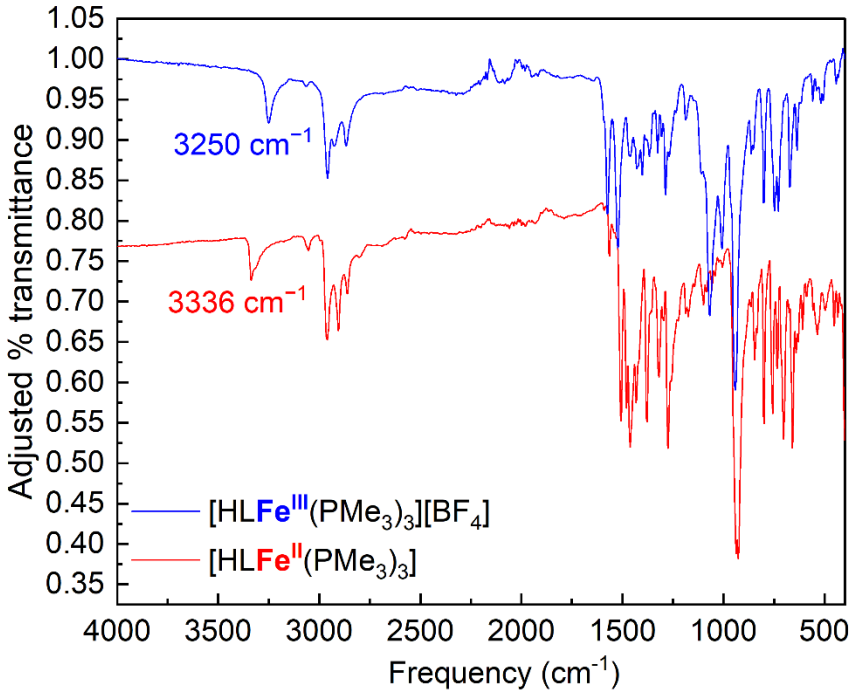


Figure S79. FT-IR spectra of solid $HLFe^{II}(PMe_3)_3$ (**2**, bottom trace) and crude solids (top trace) from the reaction of $LFe^{III}(PMe_3)_3$ (**4**) with stoichiometric $[H(OEt_2)][BF_4]$. The species corresponding to the top trace is tentatively assigned as $[HLFe^{III}(PMe_3)_3][BF_4]$. The top trace shows a peak at 3250 cm^{-1} that is shifted from the peak at 3336 cm^{-1} in the bottom trace, which is assigned to the N−H stretch of the monoprotonated thioamide backbone in **2**.

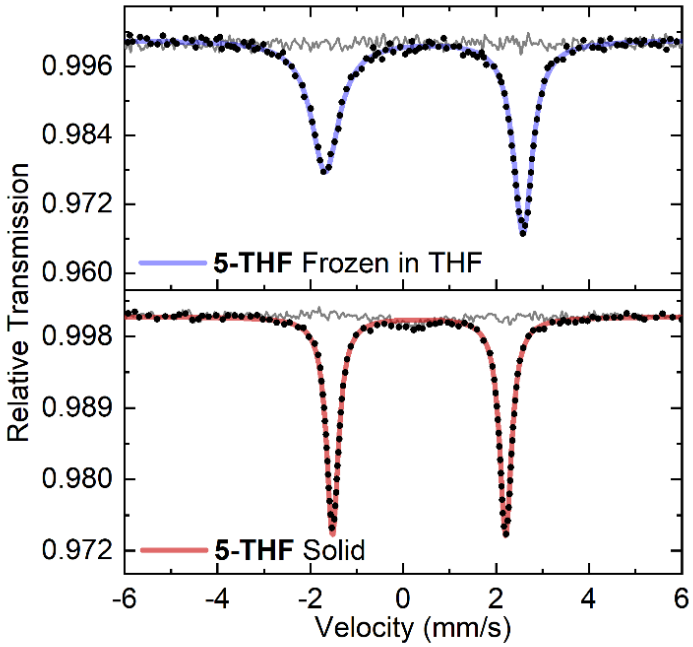


Figure S80. The Mössbauer spectra of **5-THF** as a frozen THF solution (top) and as solid **5-THF** (bottom). Parameters for frozen solution spectrum: δ = 0.45 mm/s, $|\Delta E_Q|$ = 4.26 mm/s, Γ_L = 0.73 mm/s, Γ_R = 0.49 mm/s. Parameters for solid spectrum: δ = 0.34 mm/s, $|\Delta E_Q|$ = 3.73 mm/s, Γ = 0.31 mm/s.

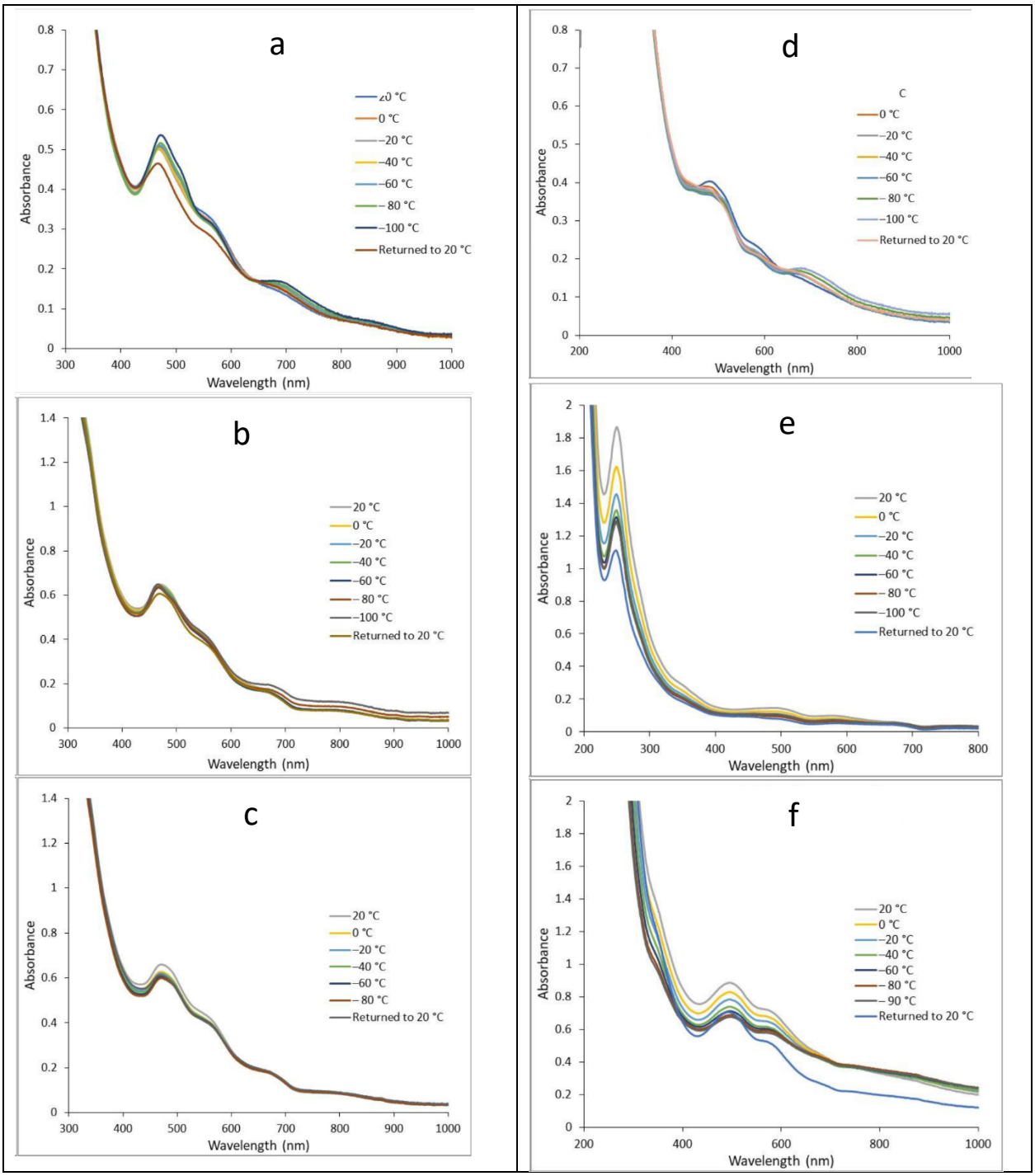


Figure S81. Variable temperature UV-Vis spectra of **6** in THF (a), Et_2O (b), and toluene (c) and analogous spectra after addition of 18-crown-6 (1 equiv per iron) in THF (d), Et_2O (e), and toluene (f). Each spectrum was corrected for changes in solvent density at low temperature.

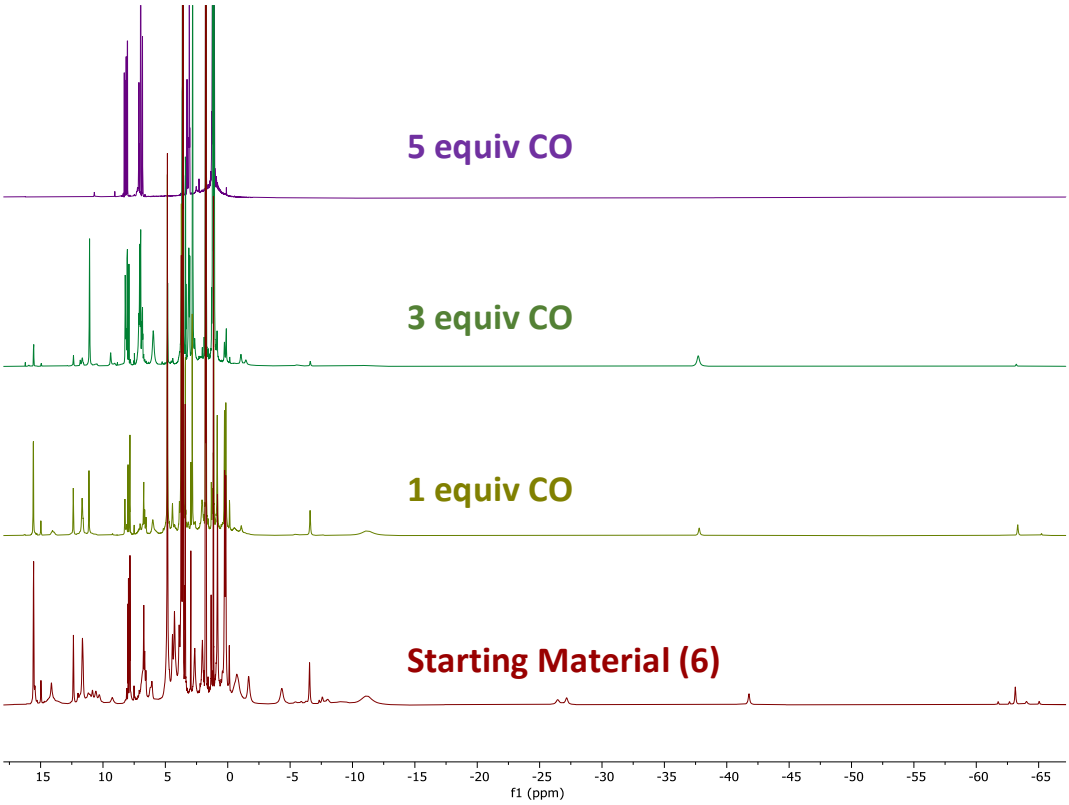
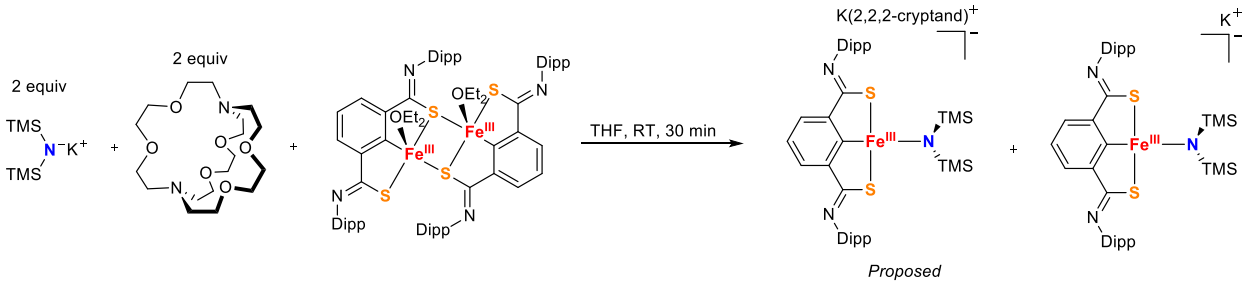


Figure S82. In an effort to produce complexes with fewer CO ligands, we treated 6 with substoichiometric CO. As shown in the figure above, this reaction gave solutions with ^{1}H NMR spectra (400 MHz, THF-d_8) showing a large number of peaks with chemical shifts indicative of multiple paramagnetic species. Though we were unable to isolate any of these species, the mixture converted to diamagnetic **11** upon addition of greater than three equiv of CO.



Scheme S1. Synthesis of the N(TMS)$_2$ adduct in the presence of [2.2.2]cryptand.

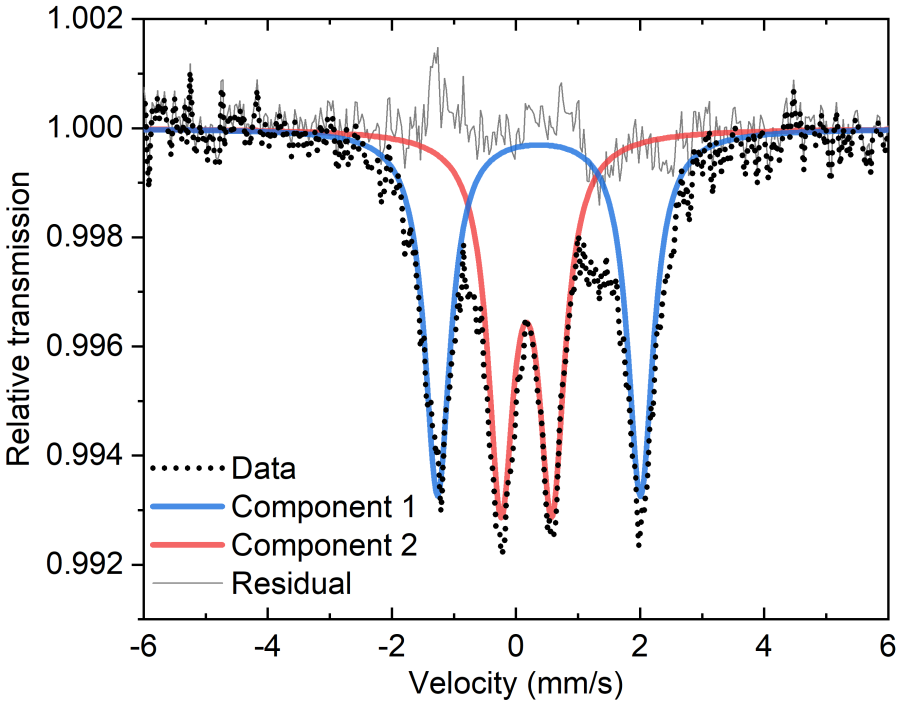


Figure S83. Mössbauer spectrum of crude solids from the reaction in Scheme S1. Component 1 (50%): $\delta = 0.37$ mm/s, $|\Delta E_Q| = 3.27$ mm/s. Component 2 (50%): $\delta = 0.17$ mm/s, $|\Delta E_Q| = 0.82$ mm/s. The 1:1 ratio seems to be coincidental, as repeat reactions of the type in Scheme S1 showed different ratios between Components 1 and 2.

Computations

DFT calculations were performed using ORCA version 4.2.1. Structures were optimized using the BP86 functional and ZORA-def2-TZVP basis set, and minima were confirmed by the presence of all real frequencies. Mössbauer calculations were then performed on the minimized structures. An example input file which generated Mössbuaer parameters and QRO files for plotting is shown below:

```
! UKS B3LYP ZORA ZORA-def2-TZVP SARC/J NORI
! TightSCF SlowConv Grid4 NoFinalGrid
! CPCMC(toluene) UNO UCO MOREAD

%Method SpecialGridAtoms 26
 SpecialGridIntAcc 7 end

%pal nprocs 20 end

%scf maxiter 1800 end

%moinp "KLSC1027B.gbw"

* xyzfile -1 4 L_Dipp_Fe_HMDS_monoanion_BP86_Mult4.xyz

%eprnmr
nuclei = all Fe{fgrad,rho} end
```

When potassium was included in the model, the overall charge was 0 instead of –1. Structures and surfaces generated from calculations were visualized using Chemcraft version 1.8 (Chemcraft - graphical software for visualization of quantum chemistry computations. https://www.chemcraftprog.com). The starting geometry for optimization of models A and B in the main-text Figure 12 was obtained from the crystal structure of **9**, and the molecule in the asymmetric unit containing Fe2 was arbitrarily chosen.

Although the anionic model of thiolate complex **8** was in agreement with experiment, we calculated Mössbauer parameters for optimized **8-crown** with potassium included to evaluate its consistency with experiment. This calculation gave δ = 0.28 mm/s and ΔE_Q = 3.96 mm/s, also in agreement with the spectrum of **8-crown** and essentially unchanged from the potassium-free predictions for **8** that are shown in Table 3. Thus, the experimental and computed Mössbauer spectra for the models described above suggest that the amide donor in **9** leads to an unusual situation in which its electronic structure is dependent on the presence of a nearby cation.

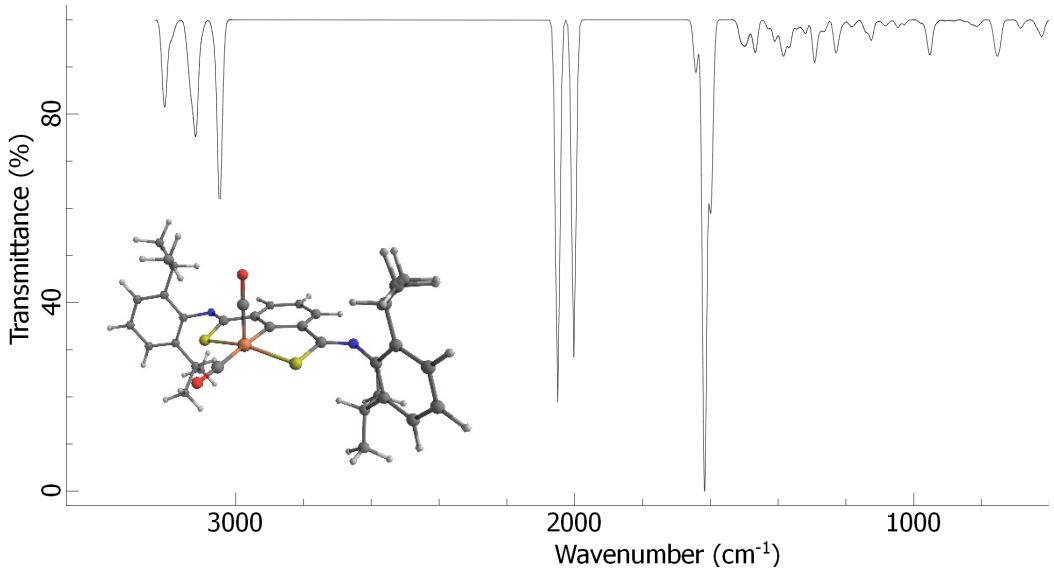


Figure S84. Theoretical IR spectrum and structure of optimized $[LFe(CO)_2]^-$. Optimization and vibrational frequency calculations were carried out using BP86/ZORA-def2-TZVP. CO stretching frequencies occur at 1983 cm^{-1} and 1973 cm^{-1}.

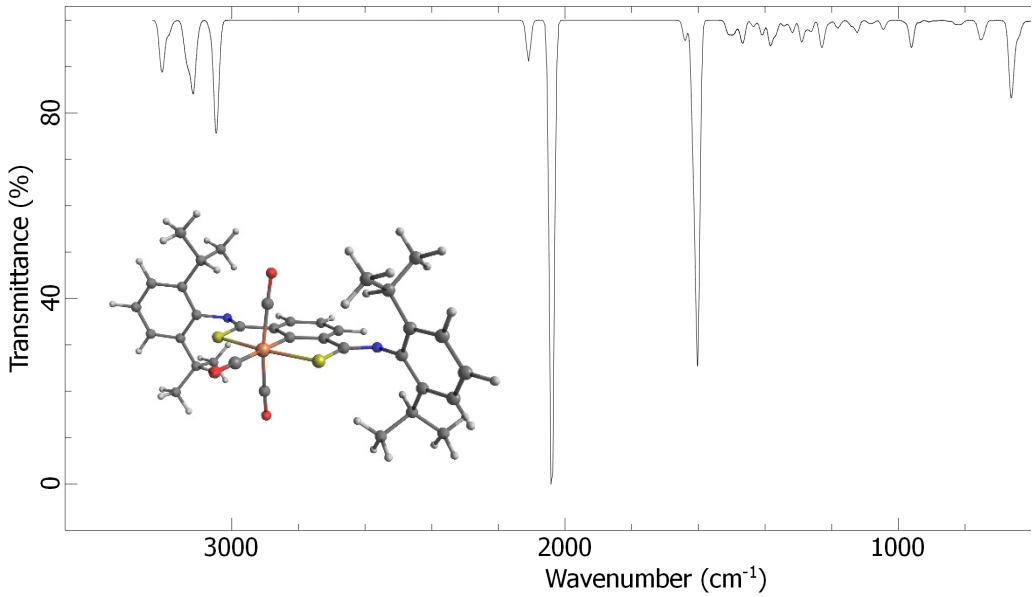


Figure S85. Theoretical IR spectrum and structure of optimized $[LFe(CO)_3]^-$. Optimization and vibrational frequency calculations were carried out using BP86/ZORA-def2-TZVP. CO stretching frequencies occur at 2041 cm^{-1}, 1977 cm^{-1}, and 1970 cm^{-1}.

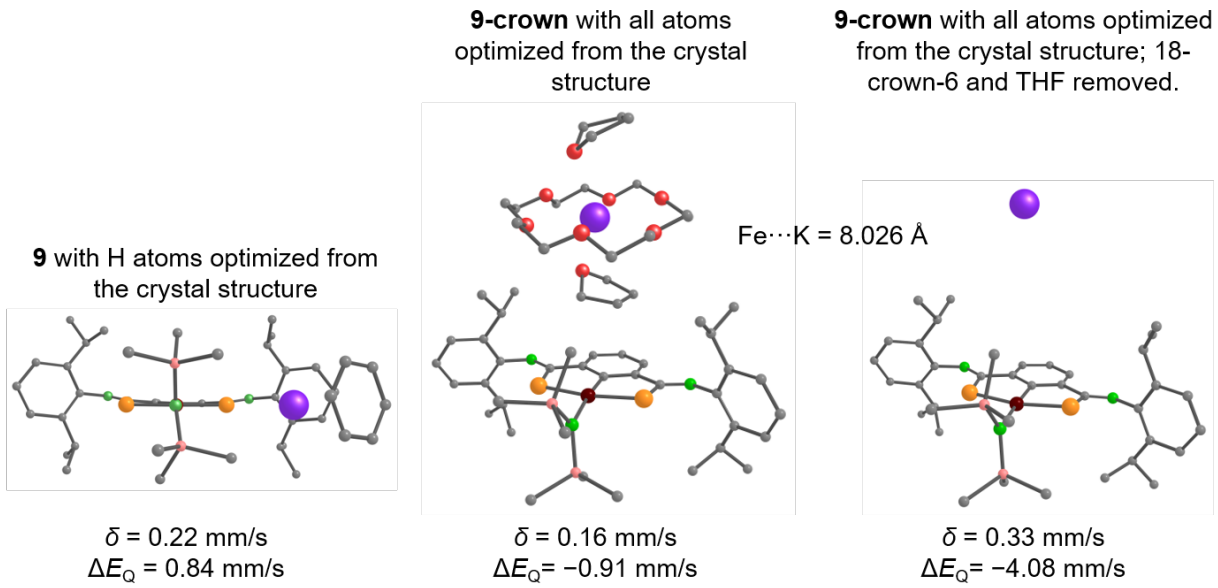


Figure S86. Structures and Mössbauer parameters for BP86/ZORA-def2-TZVP-optimized **9** (H atoms only, left), **9-crown** (all atoms, model C in main text, middle) and the analogous complex after removal of THF and 18-crown-6 but without re-optimization (right).

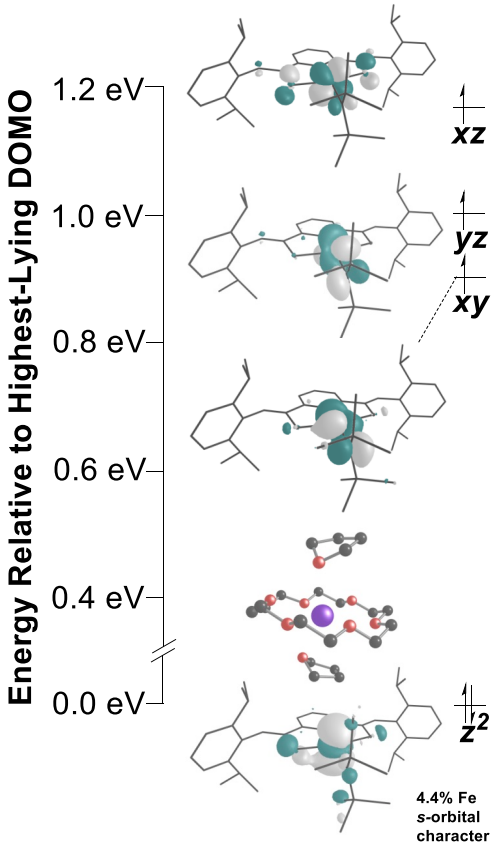


Figure S87. QRO plots at an isovalue of 0.03 au of the d-assigned orbitals for optimized **9-crown** (model C in main text).

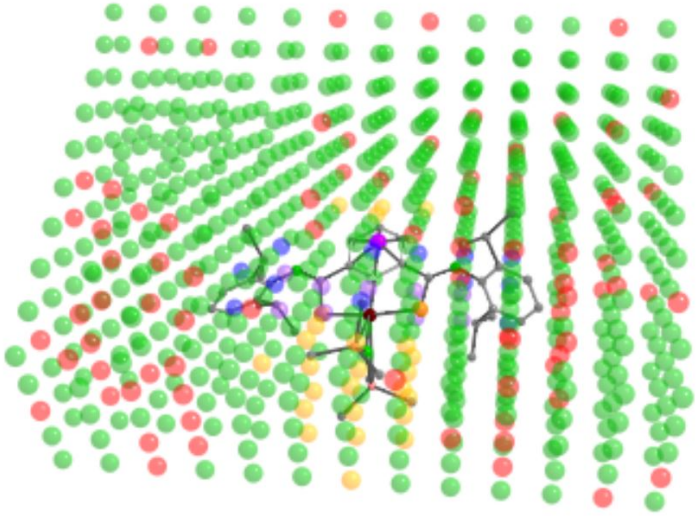


Figure S88. Heatmap showing the distribution of quadrupole splitting values generated by placing a point charge *Q* with +1 charge at intersecting points in a 3-dimensional 2x2 Å grid on the top face of complex **9**. The geometry of **9** was generated by forcing the $N(TMS)_2$ and pincer planes to be 90° to symmetrize the complex so that only one face needed to be sampled. Color key for $|\Delta E_Q|$ (mm/s): **< 0.69, 0.7 – 0.79, 0.8 – 0.89, 0.9 – 0.99, 1 – 1.99, > 4**.

Molecular coordinates used to calculate the Mulliken spin density on the phosphorus atoms of **4** at the BP86/ZORA-def2-TZVP level of theory:

Fe	17.148977944	6.816817752	10.933058047
S	16.917006764	6.829888889	13.148991052
S	17.109884081	6.814247529	8.731085360
C	15.201923271	6.806928868	10.850459209
C	15.140411655	6.824764492	13.310842716
C	14.422609342	6.809619684	12.028065228
C	13.021304949	6.799999176	11.971230892
H	12.458830035	6.802693451	12.906988390
C	12.371607128	6.788733048	10.734060489
H	11.281588531	6.780891430	10.688856964
C	13.121272389	6.791421759	9.554652906
H	12.636278630	6.789834794	8.576454565
C	14.524279863	6.800221659	9.612417176
C	15.349778398	6.827060078	8.396420588
N	14.535783556	6.833068830	14.449424289
C	15.274023540	6.850406418	15.647851835
C	15.618315192	5.626705075	16.268980946
C	16.257829091	5.668660214	17.512644345
H	16.531104871	4.736410401	18.008662886
C	16.565971239	6.885129620	18.124063732
H	17.063964215	6.898799198	19.094990144
C	16.253762687	8.084061124	17.480843909

H	16.524296802	9.030022676	17.951736435
C	15.613685504	8.091378028	16.236853222
C	15.286098380	4.320807503	15.567495039
H	15.484589693	4.487247099	14.495871298
C	16.155395478	3.141232438	16.008546937
H	17.226403554	3.381139479	15.937337623
H	15.955004984	2.269050288	15.369210258
H	15.943446045	2.841234652	17.045864052
C	13.789970995	3.990230122	15.706746737
H	13.530700568	3.830082318	16.764438155
H	13.538019127	3.074959005	15.149200879
H	13.175117437	4.813137855	15.318492471
C	15.275798956	9.377510858	15.502037285
H	15.477358034	9.184891014	14.435492344
C	16.138306372	10.572589500	15.913961642
H	15.924094403	10.897029917	16.943437602
H	15.933385571	11.427457355	15.253041178
H	17.210714073	10.337037714	15.849239621
C	13.777832406	9.703790300	15.630769588
H	13.167853269	8.867584013	15.263877198
H	13.521892781	10.602653316	15.048896009
H	13.516751038	9.890713722	16.683614279
N	14.843043269	6.868680649	7.212417830
C	15.670586648	6.947179558	6.077070646
C	16.153162739	5.764330169	5.469543553
C	16.912681194	5.878385323	4.299832815
H	17.298162896	4.977311747	3.820077613
C	17.194601478	7.126476163	3.741775255
H	17.793041147	7.196769953	2.831822588
C	16.710105293	8.284745277	4.352516898
H	16.937953956	9.257508235	3.914166186
C	15.943671093	8.219559029	5.521120446
C	15.799135538	4.418223701	6.075688260
H	15.750987264	4.569186144	7.164920800
C	16.837263199	3.325998024	5.805526246
H	16.868242674	3.046909294	4.741628582
H	16.586993221	2.416879089	6.372402236
H	17.845413804	3.650079929	6.102758829
C	14.395289992	3.980639734	5.620365806
H	13.651187589	4.750234355	5.868281635
H	14.100307567	3.040997286	6.112618945
H	14.377925030	3.820131153	4.531507208
C	15.359901155	9.459608217	6.176638780
H	15.340992741	9.271388821	7.261981898
C	16.178414990	10.731027279	5.937379647
H	17.228150038	10.595021166	6.236669071

H	15.760308784	11.564629380	6.521069311
H	16.163243291	11.033497395	4.879408828
C	13.895883566	9.645363896	5.737690487
H	13.841170371	9.822176077	4.652666723
H	13.438701089	10.505301031	6.251151343
H	13.307486523	8.747736232	5.973088316
P	16.977926572	9.095591683	11.049506141
C	17.377283595	10.041715131	9.527464782
H	18.366761919	9.775256143	9.145156503
H	17.331734201	11.120822644	9.729870014
H	16.641894679	9.781917255	8.757154515
C	17.966242907	9.949501144	12.344292887
H	19.038493669	9.759749820	12.219796701
H	17.659331709	9.562844683	13.324039286
H	17.786993278	11.032458429	12.302239207
C	15.316410513	9.788160301	11.407340992
H	14.611519587	9.479254721	10.626193255
H	15.382544677	10.884640196	11.436249646
H	14.939785001	9.421988912	12.368910695
P	19.389191555	6.822175839	10.938232553
C	20.273867858	8.193016036	10.075653252
H	19.974725212	8.192740706	9.018768674
H	21.360322364	8.040346743	10.139283232
H	20.029831279	9.168876380	10.508662382
C	20.281096237	5.442523391	10.096964264
H	20.036292427	4.470904351	10.538736333
H	21.366895736	5.598023183	10.165126497
H	19.988343006	5.430725650	9.038308411
C	20.214553665	6.839090749	12.582119438
H	19.892664767	7.725886203	13.142791813
H	21.308871779	6.845281433	12.480783457
H	19.904178109	5.957496430	13.157182737
P	16.995473201	4.539710545	11.084983321
C	17.393351329	3.574224330	9.574731944
H	16.627544978	3.788907902	8.820286696
H	17.392042622	2.498827710	9.800887205
H	18.361205691	3.867588297	9.158463354
C	17.994261403	3.712966205	12.389496512
H	19.064828214	3.908937004	12.261222304
H	17.823297216	2.628201381	12.363272098
H	17.684961526	4.111322455	13.363819270
C	15.341677128	3.836834570	11.458514589
H	14.966812822	4.207903492	12.418836338
H	15.417569049	2.741216030	11.497086254
H	14.631090214	4.132655387	10.677504186

Molecular coordinates used in the Mössbauer calculation of anionic **8**:

Fe	16.05940969739237	6.94938492996654	11.27769740145834
S	16.05633452039649	4.76291607627825	11.62734287824052
S	15.95736731606181	8.77551883681768	10.03741398975629
C	17.80804807739701	6.64252289349321	10.46614474527435
C	17.69142718506889	4.28472048689620	11.10709900205738
C	18.48869090826116	5.41313385582077	10.59680627174721
C	19.81979622000088	5.27927120133649	10.17680085528478
H	20.32067683202515	4.31650258533656	10.29980664038329
C	20.47794541222787	6.36497443472396	9.58905939725453
H	21.51750129226232	6.26534357424203	9.27147730740247
C	19.78834455338035	7.55954429926539	9.35924540399396
H	20.26208171322293	8.39358233103228	8.83739326848216
C	18.45752985155783	7.69185735896299	9.78093678910625
C	17.63220079870992	8.86160609839000	9.43325900395597
N	18.11571844387771	3.06639632783135	11.11029840951498
C	17.24933669970682	2.00688672040660	11.45114002429178
C	16.98275936867108	1.65816787857960	12.79556493170237
C	16.13775733782303	0.57087686129585	13.04981371211853
H	15.91654379002354	0.30191490430934	14.08486855491404
C	15.56816690122580	-0.16564824963391	12.01320477211012
H	14.90464304406592	-1.00399517352834	12.23362603599107
C	15.85928311774921	0.17186043885476	10.68984365395357
H	15.42008450568049	-0.41077151977741	9.87818752819203
C	16.69901807397068	1.24732900378508	10.38624893365996
C	17.62027184400753	2.41042673664749	13.94948502493062
H	18.15126481994973	3.27010702208898	13.52170509278054
C	16.57709670132037	2.94975821378244	14.93803566011020
H	15.85376512181922	3.59749050652333	14.42704855555107
H	17.05818817651938	3.54110169907206	15.73091417171400
H	16.02010598773889	2.13189198873040	15.41999403478683
C	18.66374020332294	1.53469765443348	14.66278414115946
H	18.19014883363655	0.65585998353490	15.12748164758307
H	19.17145680247123	2.10516297986978	15.45604913583913
H	19.42479987272842	1.17358410072420	13.95606315106156
C	16.99441277919808	1.65008559114658	8.95155860762788
H	17.97774024371181	2.14839031405054	8.96700155053836
C	15.96861509203222	2.68334073672655	8.45146080813498
H	14.96078693729048	2.23972130690775	8.42537091873186
H	16.22236367060403	3.02332807547224	7.43549319559712
H	15.92932229842346	3.55996142792766	9.11182380973206
C	17.08035928680411	0.45997177510414	7.98905921158565
H	17.79533529577150	-0.29562822005286	8.34638765442863
H	17.40870846718347	0.80272322695235	6.99641412390073
H	16.10446020503255	-0.03180622432246	7.85684934283343
N	18.08561117692189	9.82636614487268	8.70557902489521

C	17.22043866404180	10.79383047285043	8.16326634438594
C	17.12359879933456	12.07463710593404	8.75159684254948
C	16.33903278584143	13.04803594048099	8.12368902748064
H	16.25203239647161	14.03824578121838	8.57412101030701
C	15.65626886272350	12.76805285883051	6.94012648909902
H	15.04428872095426	13.53618501778725	6.46374015386380
C	15.74849322464348	11.49438901203259	6.37440578103167
H	15.19909294474488	11.27750836829583	5.45737766936828
C	16.51831433121108	10.48853594880266	6.96768971715582
C	17.89444036767700	12.36129673555302	10.02433661446611
H	17.97430276897176	11.40447858006864	10.55949972132380
C	17.19951476907915	13.35245033122717	10.96196912791192
H	17.15562912951818	14.36536608294190	10.53302514956101
H	17.75220289419574	13.42374604703318	11.91125745623066
H	16.17186781696060	13.03221253354405	11.18569134245800
C	19.32078762678648	12.82401006327066	9.68113311872480
H	19.83237062181372	12.07231887333107	9.06415207711467
H	19.91596788423265	12.98418300851270	10.59335912164516
H	19.29208389660372	13.77053996549309	9.11886815002747
C	16.64667578746882	9.10300308852754	6.35493284737920
H	16.61493858865352	8.38036692062409	7.18530514183320
C	15.50580488569477	8.73932523445558	5.40156482663068
H	14.52566671245732	8.85589414156905	5.88599279350951
H	15.60689914996968	7.69140646818541	5.08346436065649
H	15.51549831837157	9.36122418556283	4.49272008471822
C	18.01251729904022	8.94726627365623	5.66214702464706
H	18.09754382231170	9.64949583752165	4.81782334255085
H	18.13749399283108	7.92450110510568	5.27510154389160
H	18.82821589177493	9.15188627699028	6.36844639629000
S	14.05782224420042	7.13220423348060	12.22579054717025
C	14.41863343821321	6.75361691648094	13.91652791820890
C	13.45078657025856	6.06023630015042	14.68187667484392
C	13.72977793672874	5.72463879573671	16.01124296208176
H	12.97928204121840	5.17357230448741	16.58191939588681
C	14.94347333315514	6.08238219306149	16.60013174398042
H	15.15201962299420	5.81826233193602	17.63803810324934
C	15.88774359076094	6.78354916663470	15.85050577011287
H	16.83606777976070	7.07819681391899	16.30357873626558
C	15.65051116055730	7.12606711111897	14.51223092206298
C	12.14039400002784	5.67804797834612	14.08221884672711
C	11.08915847736118	6.61492117609863	14.05122089577939
C	9.86104790261037	6.24278512621627	13.49057735281531
H	9.04904530833617	6.97484863341971	13.46288550122107
C	9.65337016307065	4.96710606318794	12.95554818417869
C	10.71493101511867	4.05494143656888	12.99058927038333
H	10.58053844864093	3.05729772430242	12.56284613142130

C	11.95591886214549	4.38646159676340	13.54632506478327
C	16.71239934159421	7.88498772755995	13.78125823607804
C	16.53177894820053	9.26315512399596	13.47232906585858
C	17.59861080827694	9.99029882777069	12.94180452874752
H	17.44064809012622	11.04483177808744	12.70584769179704
C	18.84995485088864	9.41029866045928	12.69530892624791
C	19.02518916264962	8.07077919051915	13.03375418805711
H	19.98875448596501	7.59191473714186	12.84319686047018
C	17.99431354928245	7.30369428521666	13.58993073997635
C	11.29499303382014	8.01103665519942	14.57834554995114
H	11.68664502922709	8.00147562209746	15.60613053027285
H	10.35597408556290	8.58021456411666	14.56389774633121
H	12.03451028829640	8.54828853027918	13.96364586211479
C	8.31873347473671	4.57657290104869	12.37179406712455
H	7.73798736679126	3.96369542799669	13.08057950587530
H	8.44285545055735	3.98156691407772	11.45533170896514
H	7.71587318269823	5.46235419503744	12.12873179847994
C	13.08610722131813	3.39366746989732	13.53426157090322
H	13.94834411299003	3.78505183115888	12.97237562499607
H	12.78101112977155	2.44717623162167	13.06958498671280
H	13.45060004397180	3.17999454990436	14.54976088456656
C	15.21892089234233	9.95071755898906	13.71095514714835
H	14.49848532361361	9.66759083023163	12.92577259519603
H	15.34185504729507	11.04142327914574	13.69395423113595
H	14.77436161984341	9.65253482680722	14.67109811952738
C	19.96302326583768	10.19193480245469	12.05406064764017
H	19.85770640409142	10.17929639583255	10.95784081082644
H	20.94329451409172	9.75962094886352	12.29683621396176
H	19.95334164826531	11.24409143518710	12.37225509661680
C	18.30829511790979	5.89825262439205	14.01608537983284
H	18.80037927829302	5.88948864496143	15.00246270575048
H	18.99695931872634	5.43007725163290	13.30031654562165
H	17.40721603817661	5.28438386512073	14.08820629086094

Molecular coordinates used in the Mössbauer calculation of **8-crown**:

Fe	16.23261569826193	7.51980305964449	11.46719297922268
S	15.80648230911733	5.37019607698867	11.67414099314939
S	16.37776165141754	9.40272778318890	10.32734328704656
C	17.79130948929521	6.94382453711855	10.43618628378098
C	17.24583993173937	4.61344934399202	10.93642573072721
C	18.20795055298899	5.59740884529247	10.41029889871756
C	19.43087966845594	5.23289212464766	9.82981742419687
H	19.72368597113417	4.18087306055524	9.83776177990845
C	20.23753501881709	6.20782141787847	9.23378274535477
H	21.19509899139656	5.92674103740544	8.79309271307490
C	19.79098088773052	7.52942160535225	9.15042159114576

H	20.36951120680812	8.28833876628090	8.61989890495995
C	18.56863372159572	7.89172647314438	9.73483634760462
C	17.95291255539533	9.20954892792510	9.52687210981245
N	17.39715032550840	3.34317219839722	10.80688736169158
C	16.36063327997297	2.45196647850799	11.15571959081990
C	16.12349368118425	2.05354625801492	12.49079378672071
C	15.09482012796217	1.13679550308459	12.73959552180775
H	14.90146653424880	0.82497548247882	13.76832679531944
C	14.31396325146723	0.62022782368444	11.70894617140177
H	13.51397435939515	-0.08952058501533	11.92780309053673
C	14.57181228264149	1.00655726845497	10.39294786216435
H	13.96562853897394	0.59768452526489	9.58331155930415
C	15.59188664024167	1.91242129197894	10.09314001311414
C	16.97436940788666	2.56465320247308	13.63882078600069
H	17.66401827720764	3.31155619716462	13.22540040962587
C	16.12996374543739	3.25095851773459	14.72114147423131
H	15.56716697350078	4.09641295370184	14.30256237483647
H	16.76779199757596	3.63472740346060	15.53073211309087
H	15.40809481437683	2.55234200242136	15.17140111296013
C	17.82866904680026	1.43260179772788	14.23166970440226
H	17.19476704331951	0.64281770314186	14.66290194828181
H	18.48336674554767	1.81389338768844	15.03088775972706
H	18.46045340757308	0.97090371685410	13.45952469268100
C	15.86389539497549	2.36937956565435	8.67069320138941
H	16.92374422937143	2.67166999099417	8.64240630127524
C	15.02359363955200	3.61197186134430	8.32660992865808
H	13.94990779849402	3.36641691840626	8.34970676019037
H	15.27065210934349	3.98004528611644	7.31856674285195
H	15.19450799242004	4.42487244946531	9.04517869354415
C	15.65514658232723	1.26614493458371	7.62713029360584
H	16.22839265750643	0.36213466195240	7.87656051293601
H	15.98059706007171	1.61675165797836	6.63634541994393
H	14.59579052726753	0.98174801233325	7.53702839727924
N	18.47223226810506	10.12034556247766	8.77446705411804
C	17.70536010085818	11.20644261702024	8.32279090239681
C	17.62004017415627	12.42052975578173	9.03782057544478
C	16.94447356000688	13.50044474763048	8.45320427510035
H	16.89920176794851	14.45294030096017	8.98695641612077
C	16.33818024640334	13.38610205453145	7.20441576731388
H	15.83135646763318	14.24359854563409	6.75789244030550
C	16.39244544256659	12.16704902031723	6.52374184632394
H	15.91483387764892	12.07703087914485	5.54661335065536
C	17.06475681420561	11.06578575361810	7.05984318363632
C	18.25339584088997	12.55800131866510	10.40895327023271
H	18.57563546855746	11.55445096134644	10.71508939574911
C	17.24293418790246	13.05500658223984	11.45049509256620

H	16.86271357735697	14.05721811285966	11.20271279599678
H	17.70895954878166	13.12163123064035	12.44406881233362
H	16.39506344040620	12.35881026533962	11.52064466238283
C	19.49698527961625	13.45856031718571	10.35830099405157
H	20.23173526458548	13.07093211115026	9.63913332585284
H	19.97780556365921	13.51343524313491	11.34698203187853
H	19.23140570867696	14.48295110200611	10.05345083324030
C	17.16178517111906	9.73842047201913	6.32415576268728
H	17.04044293695543	8.94429417173990	7.07840084761379
C	16.08068062963454	9.53106537920116	5.26153657424045
H	15.06918276745020	9.64952877959515	5.67660673439142
H	16.15453774432495	8.51504737658587	4.84831792528612
H	16.19191360817637	10.23334004843795	4.42076044643674
C	18.56098266951964	9.57152278073330	5.70213676113478
H	18.72741365234662	10.33503188651823	4.92676613224320
H	18.66186382563328	8.57899819347734	5.23808609026496
H	19.33868731055342	9.67622557145942	6.46931963317068
S	14.41617405633582	8.03766641239416	12.64807516742026
C	14.82816969560573	7.46920313092408	14.26869545652810
C	13.78823298012180	7.00235235665683	15.10486117291566
C	14.09599906566617	6.48604598911347	16.36765191541383
H	13.28726055517226	6.10380449982547	16.99366894779065
C	15.41526600340197	6.45766946126882	16.82180657282970
H	15.65004920576816	6.04994666175175	17.80543595971783
C	16.43192973431926	6.97227548511591	16.01715148287457
H	17.46148744137568	6.98520310937975	16.38019555140338
C	16.16449865730299	7.48520395667655	14.74135847211185
C	12.37085880654855	7.10116243269605	14.65121486649267
C	11.62130779317460	8.23893050167094	15.00522363462791
C	10.29190701885331	8.34144654807787	14.57666928119341
H	9.70207336468534	9.21013600087707	14.88425046852559
C	9.69447257989766	7.34823993502620	13.79475095324215
C	10.45953826322315	6.22682881050485	13.45386803095281
H	10.01028679652896	5.43337388192273	12.84978230545778
C	11.78652833021256	6.08063212618455	13.87237326519618
C	17.28350065061648	8.08570229150452	13.95098129291277
C	17.34444697906235	9.49885589998218	13.78395960108613
C	18.45321826755151	10.06604907060191	13.15848155402281
H	18.48274339709774	11.14997811567009	13.03703671478093
C	19.51919442609642	9.29419138801808	12.67875182287995
C	19.47594404515516	7.91995129434813	12.89815681864182
H	20.29441916552873	7.29241526887173	12.53790959400286
C	18.39556757123807	7.30262996319056	13.54478469039700
C	12.24474570023711	9.33975948056260	15.82448583696695
H	12.59187882224057	8.97262098919257	16.80084451920075
H	11.52880027822328	10.15511441091257	15.99992512678782

H	13.13245370246959	9.75331267876438	15.32076879209072
C	8.26555516621240	7.47741071028616	13.32997901939090
H	7.70525549981327	6.54441660031127	13.48875249112568
H	8.21190718564458	7.70026215130969	12.25104548208868
H	7.74244371886737	8.28121663316318	13.86646456327148
C	12.58568696147849	4.87243969668383	13.47593973519180
H	13.37663870562276	5.14804497262486	12.76008492439686
H	11.95459733524282	4.10893503261339	13.00368980981365
H	13.09482214061960	4.42252612209205	14.33901339338185
C	16.24412638254665	10.38934955872211	14.28493794903296
H	15.33772554178417	10.25087356914179	13.67203528352700
H	16.54444352894924	11.44375220038321	14.23810050299222
H	15.96996490715585	10.14295633110807	15.32123085916872
C	20.65081090835436	9.92627282735443	11.91625218575783
H	20.40306459497500	9.98501176570661	10.84365517941079
H	21.57515784774363	9.34030061643172	12.00802453001045
H	20.84985824051926	10.95003597704095	12.26463359640268
C	18.48632265983938	5.83307413937933	13.84058112730715
H	19.14577129745931	5.65801917988285	14.70632458740829
H	18.91791729357195	5.29632318701614	12.98594515425213
H	17.50798761734012	5.40594140494128	14.07088497134768
K	10.70057004262527	12.70451913720456	9.60581081114089
O	12.24969136842699	12.36605502117386	7.31907315386488
O	12.76298082145447	10.99093927455277	9.71613461720437
O	11.49666090979303	11.87767083516150	12.12549716688940
O	8.71860393316725	11.70850436888161	11.42688194594287
O	8.07171444474640	12.06073849275509	8.67749979040569
O	9.75373628681736	13.74177011030134	7.07803101496602
C	13.03415405889812	11.16250410486445	7.34736221449641
H	13.79569642686384	11.18935262726186	6.54946872060347
H	12.37495400665788	10.28830756815458	7.18591731924863
C	13.74209275996879	11.06738332463108	8.66956562998034
H	14.39035010246866	11.94861858979028	8.81283914845068
H	14.39202768963325	10.17602594004350	8.68078416328067
C	13.37771383654938	10.90680580085382	11.00985709509226
H	13.95317862757198	11.82804488333343	11.20991295420212
H	14.07850599540159	10.06038744904646	11.04665449410965
C	12.32324933375947	10.69872996330187	12.05863777752153
H	11.72499486316277	9.80185881742631	11.82646005887842
H	12.81201072271860	10.51987816717193	13.03067487765367
C	10.44413875672246	11.76867833497647	13.07854997408040
H	10.13544273210288	12.79863555155325	13.31305213799457
H	10.80729584413859	11.29000233476836	14.00378141624183
C	9.25448443967724	10.99246090260059	12.54868687834161
H	9.54813078037597	9.97146038445257	12.24901553134767
H	8.48682269609077	10.89780470039156	13.33966127540083

C	7.66417736166103	10.99730483926956	10.78615438944362
H	6.86394436125252	10.75411565880494	11.51054476588367
H	8.04260949247964	10.04672170853188	10.36507049663732
C	7.08444920275131	11.86084032373073	9.69181756866188
H	6.19514572671832	11.36054757800136	9.26429500803498
H	6.76644648487868	12.83557986443886	10.10760449131178
C	7.59146654303136	12.88130412395521	7.61287902282260
H	7.32906099773662	13.88669908217745	7.99312706253001
H	6.68326194856758	12.43403869309709	7.16636842408910
C	8.66134783783283	12.98692263861800	6.55357719944854
H	8.98092382840679	11.97223606079431	6.25706942875347
H	8.24397223380524	13.49185414839121	5.66186867578508
C	10.84257305962026	13.88453956850382	6.15632351824293
H	11.45131921534484	14.70739937795778	6.55418153379422
H	10.46470450802451	14.17396931245228	5.15882123225650
C	11.70301756537028	12.63952626860283	6.03975572943441
H	12.50631387007568	12.82845082164499	5.30086716223627
H	11.11851062746003	11.77291018792665	5.67265364249094
C	10.35963951846682	17.02432089120214	10.37529392955837
H	9.77862789837759	16.99906399563814	9.44273361171283
H	10.66103820558789	18.07055089537587	10.54331815400525
H	9.69833273842186	16.73916849811989	11.20523289567969
C	11.56590482626929	16.12416222861218	10.29742640940631
C	12.24476360021194	15.93511659988498	9.08121519851688
H	11.87546006481373	16.43801251382055	8.18440542772875
C	13.38081281020240	15.12442120996695	9.00933580303609
H	13.88989816643608	14.96869264750259	8.05772032634694
C	13.86384168662087	14.48911318743700	10.15648437987392
H	14.74687897230447	13.85206070423578	10.09233469313636
C	13.20053294283879	14.66757662950532	11.37346566974905
H	13.55767273251705	14.15985535786474	12.26960896814803
C	12.06033548331130	15.47488941624203	11.44075052793425
H	11.54568207932195	15.60559078821403	12.39541316992374

Molecular coordinates used in the Mössbauer calculation of anionic **9**:

Fe	-4.62896158122040	3.16058078883923	0.32372846563977
S	-3.82400388122275	4.41813120319837	-1.32417516379727
S	-5.73763199145450	2.10190520049939	1.93420461000402
C	-6.28365709902786	4.24850142839822	0.12672895072335
C	-5.22103008395941	5.42981139124987	-1.75037949363479
C	-6.38581107364316	5.24434577021489	-0.86475744440806
C	-7.55244408660341	6.01024130798168	-1.01041776228274
H	-7.59178099383985	6.76503809447819	-1.79816783319070
C	-8.63530299348868	5.79654166740453	-0.15384625154204
H	-9.54212212966809	6.39480424181162	-0.26151239924655
C	-8.55882521452917	4.81691321702657	0.83933270025562

H	-9.39170598566908	4.63421403110336	1.52113133902386
C	-7.39349244190805	4.04684805977191	0.97151184697205
C	-7.26946023030734	2.99973005660226	2.00242751996754
N	-5.24885792055537	6.25419024648798	-2.74072579112613
C	-4.17398805548073	6.36993674637856	-3.63711279146731
C	-3.95903456609637	5.38689257651214	-4.63501402115763
C	-2.93674287135943	5.59852843933452	-5.56738044145529
H	-2.76402606966708	4.85141441950583	-6.34504951191151
C	-2.13510401275324	6.73895175233824	-5.52351203882387
H	-1.33939167127459	6.88031825176901	-6.25730118452310
C	-2.35926912571971	7.70076934951096	-4.53642192771737
H	-1.73127184381540	8.59276084610128	-4.50461001257690
C	-3.37436796617882	7.53884226314719	-3.58876867288677
C	-4.84826655996010	4.15909204864616	-4.74151809442627
H	-5.43348222237907	4.08805035116264	-3.81572014446085
C	-4.04220677371658	2.86026225430555	-4.86651613083341
H	-3.45719969935214	2.82972197999705	-5.79853702386937
H	-4.71727240951492	1.99147115375039	-4.86814812688126
H	-3.35118352018818	2.75239855588554	-4.02018437734942
C	-5.84080165163875	4.31742640090711	-5.90636664826811
H	-6.44271794824341	5.22945025066184	-5.78606291917473
H	-6.52354755866671	3.45522247869529	-5.95569793095499
H	-5.30703725662807	4.38697211485652	-6.86727304366194
C	-3.61202459936049	8.54582576492920	-2.47856629924315
H	-4.68180546483876	8.47235727365421	-2.22076497684858
C	-2.81260917856458	8.15886337059835	-1.22079362468847
H	-3.04050036239991	7.13230521139778	-0.90271479841785
H	-3.04125329765716	8.84091858335499	-0.38714149603487
H	-1.73167982956880	8.21418255218107	-1.42526988492149
C	-3.31624996081452	9.99326307893184	-2.88673169038497
H	-2.24145297134986	10.15667590313148	-3.06010168496511
H	-3.62408191280399	10.68155081432193	-2.08548162270287
H	-3.85420527324765	10.27128055577308	-3.80485601066128
N	-8.20364685847210	2.78164508365480	2.86379834246517
C	-8.04986831756053	1.82647461288914	3.88297228654147
C	-7.27136816791997	2.11744604829768	5.03007015981843
C	-7.21272406104105	1.16464489924399	6.05369177689930
H	-6.61454671146181	1.37574914296068	6.94291890140300
C	-7.89660332898556	-0.04749205802037	5.95960358279343
H	-7.83099762494172	-0.77953684626141	6.76668057309338
C	-8.66951686234096	-0.31652579653691	4.82820201195481
H	-9.20643625522712	-1.26413121872622	4.75636145539095
C	-8.76392880490232	0.60698447575043	3.78265075615278
C	-6.55825268171274	3.45091801901101	5.18228048668342
H	-6.59243852402448	3.95916731830189	4.21008980084253
C	-5.08017793401499	3.28629215821218	5.55789561867304

H	-4.96017915872662	2.83640295952161	6.55537754628026
H	-4.57775693595617	4.26507952093468	5.56927812320391
H	-4.56597110754354	2.64991453003353	4.82641988944280
C	-7.29775862478309	4.34027805468665	6.19672982227680
H	-8.34404223496276	4.49333258330289	5.89542014121230
H	-6.81372166900917	5.32586354882563	6.27674428704742
H	-7.29707624058211	3.87665868437828	7.19576001547230
C	-9.56218324670522	0.32113658503408	2.52356383267258
H	-9.86379313376349	1.30254396801408	2.12159701629288
C	-8.67450445670633	-0.35261152237465	1.46142413036627
H	-7.77656277344040	0.24592611664216	1.25597747964559
H	-9.22770477981178	-0.48684951952857	0.51893008393769
H	-8.34500508875757	-1.34360804734648	1.81206788398722
C	-10.82890257420738	-0.50373070209349	2.77810639372470
H	-10.58818723170552	-1.52799860627655	3.10200809708297
H	-11.42056356130601	-0.58477089936912	1.85400607784900
H	-11.45979029003263	-0.04255097958191	3.55195368228132
N	-3.06501305221359	2.14576850102563	0.52431612215886
Si	-2.79083038807731	0.91195775206467	-0.66826729761278
Si	-2.06678303882194	2.53636827132084	1.89232051475541
C	-4.37812223842058	0.51092658294602	-1.59886156977064
H	-5.17379769980190	0.20555759394466	-0.90378328704358
H	-4.20890215248601	-0.30601589003989	-2.31902231084148
H	-4.73328944798820	1.39200941052633	-2.15226101132510
C	-1.49561368838841	1.49468337920394	-1.91146891597603
H	-1.80122075035160	2.46067114012067	-2.33916743230895
H	-1.37651053695120	0.77315062133534	-2.73485897543922
H	-0.51762470382937	1.63445585194535	-1.42902246191717
C	-2.17030517186511	-0.67571870155681	0.15005264195145
H	-1.22222072519322	-0.51105280215019	0.68330198924909
H	-2.00138005531555	-1.46073305966774	-0.60378285963595
H	-2.90544326410670	-1.04987400884551	0.87782090793639
C	-2.50114695570335	4.23699493983780	2.57512655165159
H	-2.39988230567588	5.00859400652165	1.79802745334117
H	-1.83816508072659	4.49725617534156	3.41627545909419
H	-3.54001410902897	4.25505247776728	2.93459431096781
C	-2.31256035064614	1.25948870066352	3.26081786667944
H	-3.38328504464556	1.16715938560185	3.49437611398063
H	-1.78206123471876	1.55443148063924	4.17975749179061
H	-1.94773040253785	0.26862277327445	2.95457768761230
C	-0.23952741900987	2.55224951155966	1.40454412769822
H	0.08538654687600	1.57795587247879	1.01021578526867
H	0.38985558565492	2.78998009002954	2.27670486713859
H	-0.05092973508579	3.30993278372370	0.62959881301949

Molecular coordinates used in the Mössbauer calculation of H-atom-optimized **9** with K^+:

Fe	1.13255015575123	13.11179500069756	4.02417670236894
K	6.13326975351879	13.18947739280974	4.45307774437389
S	3.09252491869167	13.74252086132440	4.92154901014257
S	-0.99542458419372	12.71520543139746	3.44822135231811
C	0.34404698928345	14.25894600211729	5.48129946663226
C	2.61144143204454	14.74529570434458	6.29600002114180
C	1.15487736521336	14.96399693391710	6.39029347243766
C	0.59920712421773	15.80677946470423	7.35366233353631
H	1.26510690900478	16.34011992022345	8.03468239925498
C	-0.77830943552258	15.94751509400592	7.43352982553686
H	-1.21530579872923	16.61453306801726	8.17915468597247
C	-1.60516320783624	15.22747666550157	6.57923240032150
H	-2.69302611005206	15.30061169503920	6.64435527005259
C	-1.05199682298397	14.38629490530882	5.62126152206224
C	-1.89656764046339	13.56052781306532	4.71459380700260
N	3.42090562941109	15.21373626536138	7.17938221286670
C	4.80673041683227	14.91768490149441	7.04667779932390
C	5.64892731196997	15.84466746044266	6.40300575556099
C	7.01609595981980	15.56143972537210	6.35808598771937
H	7.69093116312282	16.26690150452694	5.87074704952090
C	7.53965010607681	14.41341957970658	6.93251406811622
H	8.61576331303933	14.23112465916602	6.90539030245854
C	6.69634337743769	13.51403375278206	7.56897510624317
H	7.11230405222638	12.61701846031277	8.03030578205754
C	5.31519091039521	13.74126244553535	7.63520802313690
C	5.06560074315595	17.13095927581355	5.83329186064329
H	4.06934716259595	16.90235489397519	5.42790459211249
C	5.93922848709813	17.74077745487399	4.71085675221767
H	6.90291824094990	18.09572899322783	5.10192018364279
H	5.42487974174305	18.60679507296862	4.27272408901299
H	6.13761919988861	17.02290659829146	3.90043769654434
C	4.94786125985894	18.17420802072214	6.91733322798959
H	4.31938172088100	17.82443345755156	7.74853940976684
H	4.50205902715947	19.09957514990873	6.52420579366302
H	5.94045063834386	18.42287348528771	7.32325940420365
C	4.39867447986497	12.75967371074385	8.36205855987485
H	3.39634193345449	12.88490918466197	7.92658019685830
C	4.80131995183430	11.30430234870631	8.16523359847062
H	4.87738109968980	11.04688422946905	7.09703607883581
H	4.04599695867544	10.64062751159624	8.60844426614295
H	5.76254977612287	11.06642290303857	8.64663617330629
C	4.30635969804152	13.10798530697382	9.84517569593702
H	5.28952147236423	13.01330251735370	10.33292990943298
H	3.60395190502109	12.43493159848350	10.35793939993993
H	3.95575005439810	14.13941981020399	9.98712811732091
N	-3.15873249412684	13.48276048354550	4.89790876527524

C	-3.96944586636949	12.66743526990139	4.05715630135882
C	-4.37797034480129	13.14015451873925	2.79504706989055
C	-5.22932882275714	12.32553856178066	2.03337136292541
H	-5.54958816158763	12.66920664077017	1.04782078994626
C	-5.67698915197238	11.11319329239982	2.51347393349835
H	-6.33985682197689	10.49695519084860	1.90182316969580
C	-5.29987999294637	10.67355730603816	3.77315295100338
H	-5.67373350927161	9.71987265460841	4.14563420928701
C	-4.44442008894897	11.43889090043189	4.57624952479727
C	-3.97467720575365	14.51806658116268	2.28605711346061
H	-3.14542757420376	14.86133044684082	2.92246259488353
C	-5.10936104969812	15.48815741889425	2.45265023506572
H	-5.97501675622513	15.19752047773341	1.83573430035216
H	-4.81202954322258	16.50475898169724	2.14915588347925
H	-5.45151849383151	15.53428031709607	3.49683602565401
C	-3.46577489190881	14.52998559605782	0.85754031099903
H	-2.62650206864790	13.83098239647260	0.73018044939968
H	-3.11704275872828	15.53772803012900	0.58669463763211
H	-4.25052698280007	14.25124518243922	0.13648331215566
C	-4.00196570942574	10.97323301639711	5.95597533336543
H	-3.90909809279336	11.88471721948306	6.57141622914092
C	-2.61180628113408	10.31221660847278	5.91061056102725
H	-2.64536661599009	9.39710704131729	5.29965189521292
H	-2.28271016731490	10.03781272284353	6.92418364191454
H	-1.85856197157470	10.97683753072048	5.46891880815383
C	-4.99407353752982	10.02348973943703	6.63917106480368
H	-6.01014623856920	10.44332032755403	6.66356891793478
H	-4.67614917010613	9.83270655228564	7.67420244271397
H	-5.04025782287116	9.04989779012028	6.12860212921162
N	1.93415476299925	11.98630889349701	2.72195324683257
Si	2.16431221016405	10.34240530369402	3.20220170819458
Si	2.53372628097050	12.68766255701127	1.26362853466470
C	3.97352331272580	9.88296483307632	3.06279834837563
H	4.36835780464394	10.04360892373420	2.04827190967788
H	4.14365843552303	8.82746373345251	3.32606712596311
H	4.56943358764578	10.49681065012184	3.75749553576561
C	1.14208372620387	9.18689798736133	2.16105739410501
H	0.08539501292457	9.49053108844186	2.21241088023556
H	1.21219495607404	8.15410315215148	2.53700338413394
H	1.43689492921835	9.18165474871244	1.10291598255842
C	1.64944665626912	10.06501429685119	4.97911502826812
H	2.21022406943954	10.70289089136985	5.67745674391156
H	1.81589183366559	9.01279096879511	5.26346745902049
H	0.58099854065634	10.28650554310815	5.11370517603428
C	4.28975935679982	13.34653782300401	1.50247468582896
H	4.28154329245860	14.12157512951351	2.28452171546444

H	4.68472625495106	13.79491178218542	0.57813355057510
H	4.97430003730568	12.53502882045010	1.79852343770184
C	2.59894626960036	11.43996930700740	-0.13396575685686
H	3.23217532580259	10.56934757235386	0.09147524717608
H	3.00382676044893	11.91430227816885	-1.04192824910612
H	1.59416265061608	11.06708038496830	-0.37547494459193
C	1.46050135451132	14.11982382134615	0.73748253003813
H	0.41156006427358	13.80351610990793	0.64755775658416
H	1.78470074236020	14.53011680591554	-0.23159689611171
H	1.48930300024291	14.92975463557712	1.48174245211201
C	9.34655027892362	12.67415104107500	4.06468996433233
C	8.93802582415547	13.14687028430655	2.80258075532333
C	8.08666736914568	12.33225434485893	2.04090500537666
C	7.63900704222550	11.11990905764795	2.52100759703731
C	8.01611620632454	10.68027306387807	3.78068663382623
C	8.87157609725655	11.44560669027829	4.58378319657472
H	7.64254139122897	9.72340150780193	4.14875060225755
H	6.97434584927077	10.50476526064846	1.91324594267628
H	7.76890648724161	12.66821688963312	1.05252236781425
H	9.29801895226303	14.10122815389851	2.42077304237363
H	10.02363234106621	13.28039225555495	4.66900075836079
H	9.18040228007325	11.10343838139625	5.57020907717681

Molecular coordinates used in the Mössbauer calculation of all-atom-optimized **9** with K^+:

Fe	1.28574108301034	13.41200907255977	4.07403069244242
K	4.92995058747031	12.39190139554651	4.22305709168555
S	3.06837520189276	14.68527056111568	4.58337391826944
S	-0.73459758056175	12.68210150947038	3.62091606068901
C	0.43136338357807	14.33765123022162	5.60700817327306
C	2.65679865777388	15.10840627887121	6.27056942455563
C	1.21085542946515	15.06033776988347	6.53206289288332
C	0.63245322305337	15.67258570750650	7.65258242806084
H	1.27366527434955	16.20469318435540	8.35730506353861
C	-0.74989889519877	15.59952250137149	7.84256845662960
H	-1.20785543873216	16.08796998506648	8.70401823057037
C	-1.54615309768919	14.90306792069515	6.93136039355677
H	-2.62855407793626	14.83373622179079	7.05658119622515
C	-0.95484588974723	14.26417242452164	5.83126820297443
C	-1.74007768817030	13.47532902070020	4.87000356604286
N	3.53015730040486	15.38332220182552	7.16978354598105
C	4.90381845207142	15.24936346060828	6.91781053369886
C	5.65329998924846	16.32672349744512	6.39176316644698
C	7.03397566817334	16.16016070307153	6.23292171808786
H	7.62739879317345	16.97971548603910	5.82637774179815
C	7.66559887220376	14.96622257867445	6.58285306430959
H	8.74661463856225	14.86404363127674	6.46814082447983

C	6.91135399245563	13.90629347213210	7.09013418931889
H	7.40820814004161	12.97678466802688	7.36880693620252
C	5.52681597293477	14.02020630351720	7.25962910597063
C	4.94371144505183	17.62367897029388	6.04648188829866
H	3.96967098037298	17.34774181540880	5.61199092148471
C	5.68115893931039	18.47279989762108	5.00881846999147
H	6.62313542418795	18.88098214886631	5.40524430221697
H	5.05816237823243	19.32785985174587	4.71096903202459
H	5.91195339608475	17.89056599181538	4.10501575040736
C	4.66297215390858	18.42810901173259	7.32872022712847
H	4.09076984153366	17.82695686257291	8.04758125534311
H	4.08574357537909	19.33601071278371	7.09973114472685
H	5.60723942230805	18.73155474912519	7.80564883048051
C	4.67624428135578	12.87758257388970	7.79534585789759
H	3.75735428319238	12.84781893331875	7.18145169920946
C	5.34708958975387	11.50200126607906	7.70900885729862
H	5.73412630972555	11.26684354250050	6.70382574662327
H	4.62945827737572	10.71543632660120	7.98034302549542
H	6.20003836344138	11.42463667019474	8.39967538121985
C	4.22928277664741	13.15388579152472	9.24239525216438
H	5.10490301190194	13.19344315143783	9.90747133015168
H	3.55665941852733	12.35957407784698	9.59833832655696
H	3.69830352023759	14.11174715525223	9.30490459868685
N	-3.01110178045192	13.34040615465684	4.95338037046976
C	-3.73793085187740	12.58153079184371	4.01761682575207
C	-4.01412172911432	13.08526365886975	2.72521837193588
C	-4.80687965258083	12.30952081920161	1.87080951805541
H	-5.03542383899748	12.68711531007711	0.87238779090196
C	-5.30860377153545	11.07205950420226	2.26611523292757
H	-5.92027575090084	10.48372988572561	1.58004362726691
C	-5.02943969483678	10.59036789142904	3.54610470021767
H	-5.42532855394842	9.62220569988830	3.85367915304800
C	-4.25344557216466	11.33122309664486	4.44003039667331
C	-3.51732683318901	14.44761412661842	2.26913855770292
H	-2.83211821863407	14.83356745454231	3.03591274976921
C	-4.68546771987775	15.44055038135142	2.15256047766908
H	-5.40649331019133	15.11343786494000	1.38779340585888
H	-4.32124919129184	16.43961665881845	1.86925065000835
H	-5.22304178360138	15.52775076446886	3.10733181530640
C	-2.72658317589035	14.35654203389498	0.95584471428696
H	-1.89657619410640	13.64361532488651	1.05824826417048
H	-2.30923817070886	15.33785497761522	0.68653318115156
H	-3.36369999585845	14.02385024593869	0.12238567540203
C	-3.89487014732923	10.81401451621313	5.82109341810389
H	-3.76127806853271	11.70422268202095	6.45840316482614
C	-2.54524899236485	10.07104487424164	5.78484848343793

H	-2.62015806182010	9.17482383717765	5.15031874585461
H	-2.24754660730827	9.75452359623087	6.79603482888259
H	-1.75063631119753	10.70573146376513	5.37072791249084
C	-4.98041462397377	9.93349170944876	6.44889529688883
H	-5.95757491961013	10.43728139093586	6.44903983801621
H	-4.71704207045873	9.69321421787246	7.48912755136912
H	-5.09064881921616	8.97797019449180	5.91426738380430
N	2.19763845346798	12.13041541438860	2.98699269684894
Si	2.12619666713100	10.49048767379485	3.57097784868752
Si	2.46990758599563	12.65955631778420	1.34767632558938
C	3.72412189311318	9.57239222322562	3.07140124695581
H	4.02320038557644	9.81568800681744	2.04136760865897
H	3.54897154969477	8.48616989135509	3.11118066456099
H	4.59372092688667	9.75568730083139	3.72280785422992
C	0.69188703348700	9.48937835038968	2.89253484446019
H	-0.26366433672234	9.98381982442416	3.11218690480130
H	0.67804483279923	8.49139836377640	3.35636229555246
H	0.76741639272873	9.35816250457514	1.80466078634698
C	2.04175107440722	10.48704797864684	5.45608589715424
H	2.81485677039165	11.10950086907017	5.93408722667308
H	2.15451574931781	9.46290423767182	5.84556956608574
H	1.07282857695717	10.87793416828329	5.79620529236400
C	4.32184465650905	13.00934950365148	1.11140581612737
H	4.65648475424998	13.84611812278725	1.74711706217126
H	4.52761021533132	13.30478980076063	0.07121026437893
H	4.94562925889911	12.12609603439088	1.31945584591459
C	1.96460495419183	11.35250615117887	0.08852603937616
H	2.50662112749851	10.40501751158062	0.21561304652365
H	2.16330867114609	11.71572937154956	-0.93194512881452
H	0.88863874949411	11.14132667314896	0.16473909328526
C	1.56008922334305	14.25302464685475	0.95132210063287
H	0.47191699005646	14.12171597624734	1.02773664969147
H	1.79725106356796	14.57652487402947	-0.07531047970023
H	1.84585982621253	15.06157458104605	1.63980739302383
C	8.34473024785494	11.62927158829927	4.64390853733445
C	8.36872539264289	12.64508571628345	3.68064416618495
C	7.94241742852527	12.37871238334309	2.37445581381720
C	7.48877085270943	11.09820233490363	2.03320497756000
C	7.45785323506963	10.08545296590348	2.99861791685753
C	7.88696623951435	10.35101195010509	4.30506829842843
H	7.10108974519217	9.08994050282052	2.73242789260574
H	7.15926175906922	10.88983314354052	1.01479262433901
H	7.96006883190560	13.16809825302788	1.62171588974811
H	8.71174450932804	13.64349546657833	3.95336782565737
H	8.68490458059412	11.83631071111222	5.65810015113356
H	7.87043916307372	9.55980719689472	5.05629052740270

Molecular coordinates used in the Mössbauer calculation of **9-crown**:

Fe	0.44347289948689	0.46908747892437	10.45963527681639
S	-1.28995009295694	-0.91714177459028	10.45198307880649
S	2.07782052335425	1.93236102234170	10.82943765386246
C	-0.51890753352605	1.41152161010163	11.92114414063293
C	-2.30446643592807	-0.27197459950244	11.76378138893887
C	-1.76051971004648	0.94486771570523	12.39609478375167
C	-2.44782969445531	1.61756120286747	13.41738813247268
H	-3.40599092180353	1.21806908072340	13.75433735590795
C	-1.90713453244892	2.78306194247243	13.96760879245728
H	-2.44836293419711	3.31884752988079	14.74974389521689
C	-0.67770372252955	3.26754100910402	13.51247634115713
H	-0.23128908967112	4.17214745946669	13.92936327674527
C	0.01557691475812	2.57511258585122	12.50749323773146
C	1.35016871318422	3.00318394823831	12.05019571797612
N	-3.42651702567107	-0.78041891021893	12.13677701855735
C	-3.95825949110669	-1.94103666772258	11.54727960992429
C	-5.06614479774529	-1.80660838884604	10.67953358410148
C	-5.64982216000045	-2.96444921746011	10.15525486238499
H	-6.50092613070670	-2.87468986948580	9.47851094755804
C	-5.16306327010446	-4.22893026254907	10.48315482587214
H	-5.63022794621961	-5.12179341629537	10.06515220372987
C	-4.07630336685165	-4.34809509989481	11.35088219575250
H	-3.69796468023121	-5.34023481565362	11.60057122489212
C	-3.45699458775513	-3.22005259243980	11.89514116772736
C	-5.54977045126039	-0.41615849148343	10.31103301070948
H	-5.33260746067422	0.22456673632307	11.18202138714746
C	-4.74288632322474	0.14160484005721	9.12411518168211
H	-3.66430804594090	0.12864368847166	9.33101995615222
H	-5.04209298927268	1.17727360145314	8.90166460747978
H	-4.91713608044771	-0.46844237073139	8.22439057644440
C	-7.05391137254164	-0.34742159914040	10.02929438566361
H	-7.32317698481866	-0.88871057004630	9.10905449093846
H	-7.36620738767975	0.69805851793047	9.89119752864957
H	-7.63933481557385	-0.77358661571973	10.85691619612801
C	-2.29543444930549	-3.31863256728752	12.86697296874357
H	-1.58509625763922	-2.53108530864971	12.57895828447827
C	-1.52578231196891	-4.63949902912422	12.79381908241370
H	-2.12794446554351	-5.48750626610772	13.15940494310192
H	-0.61819952868111	-4.58161646766863	13.41326417071836
H	-1.21685456080409	-4.86268996115817	11.76259784734346
C	-2.76665862992068	-3.02071014120047	14.30075103405878
H	-3.33196729929675	-2.07948261762486	14.33170597953565
H	-1.90335246102161	-2.91387052037949	14.97478075532998
H	-3.41859350498796	-3.82833540378012	14.67082838592448

N	1.91746957066751	4.06336120942609	12.51295016510944
C	3.21270400994080	4.42340593315206	12.10196764599859
C	3.36189595357700	5.50706085445772	11.20279133752177
C	4.65169980905062	5.90370923058350	10.84047765099588
H	4.78123920917511	6.73110543303583	10.14139080981466
C	5.77785801054372	5.26024850594139	11.35521952549704
H	6.77711354857615	5.58360993601851	11.06008150628442
C	5.61721415919240	4.20567909889159	12.25152461224446
H	6.49986589217387	3.70746683537589	12.65873763749986
C	4.34571633557197	3.76738639836052	12.63674628358414
C	2.12114568280329	6.16492006545442	10.62597393940713
H	1.33369705533320	6.05702435312609	11.39053649295316
C	2.30074463954854	7.65833677165395	10.33276605677014
H	2.67338365692053	8.20075389352663	11.21372347238597
H	1.33901071315438	8.10280914204974	10.03746350940964
H	3.00460884244354	7.83084624601982	9.50409425610958
C	1.64245055742762	5.41456740273420	9.36911147476629
H	2.39686905655419	5.48533448546362	8.56995379702767
H	0.70186023852961	5.84491606736977	8.99347306233889
H	1.47832609306132	4.34901078346278	9.57614132892307
C	4.19638594469552	2.65122237868196	13.65597982901998
H	3.13945991036509	2.35763028676802	13.67674782939695
C	4.55737316157740	3.16145357500204	15.06014393271965
H	5.61457978220793	3.46329262529061	15.11054623216560
H	4.38691919511164	2.37996268485295	15.81688102073811
H	3.94543656635237	4.03375435725669	15.32803169902311
C	5.00367785649953	1.40205715817785	13.28493060376273
H	4.71017561970412	1.03981823012847	12.29029063770707
H	4.80994655016775	0.60013817659709	14.01414612358125
H	6.08648698505061	1.60188057895903	13.27474372055252
N	1.18461952364572	-0.19351695237260	8.87704243543340
Si	0.83942746957966	0.77396269411752	7.46414805042162
Si	2.07187636496937	-1.67600835461473	8.93523796316081
C	-0.58142040456038	1.96333693160270	7.78985205739467
H	-1.48141750776625	1.42905664819065	8.12521784411238
H	-0.82999636052007	2.51918109530310	6.87126615951167
H	-0.31437253944510	2.69273470451368	8.56759539962616
C	2.36501287265565	1.77923966893943	7.00016942525255
H	2.67429589797736	2.39746085103505	7.85582345499134
H	2.15463778578458	2.44795297236343	6.15121252759690
H	3.20974800100594	1.13127183193220	6.72642029491066
C	0.35783873175959	-0.35240078475609	6.02649396650768
H	1.15007307538858	-1.07862342294925	5.79272947646216
H	0.16493050918220	0.23652671381879	5.11654003976392
H	-0.55630948667917	-0.91493404045864	6.26691723486619
C	2.71843115562949	-1.98270227226653	10.68496923239384

H	3.22657908634833	-1.08524381491037	11.06753153865906
H	3.43633769310413	-2.81923273948122	10.67420906013657
H	1.89322851147629	-2.22701548595639	11.36837982342979
C	3.58014544034882	-1.62424887175810	7.79863790642976
H	3.29859830573330	-1.47499555830490	6.74659079142209
H	4.14329277387161	-2.56904240236665	7.86118858886889
H	4.25483502336520	-0.80404388384691	8.08522904525081
C	0.98324254110613	-3.13888758399785	8.45939340225386
H	0.09705683506311	-3.17857958690069	9.10932544042216
H	1.52829564011612	-4.09196615053955	8.55313286035593
H	0.63128028755966	-3.05049831644081	7.42211289336650
K	2.45939727132347	-2.87934137056749	16.33517093108631
O	4.09623824016136	-3.83054239425863	14.21228996641636
O	4.77513543206526	-1.45620055874195	15.56622676870299
O	3.67809360373638	-0.96146142487821	18.15505235899966
O	1.07386788029608	-1.97872794183918	18.63256144533220
O	0.35517163707966	-4.45287527565484	17.41600012561222
O	1.56147979087734	-5.03646781602689	14.82659663106234
C	4.83275974096638	-2.78431229558679	13.57509839221071
H	4.14850635318221	-2.08214827396036	13.06795487925867
H	5.51436046664386	-3.20135235241149	12.80963994662410
C	5.65322349037988	-2.07189495184181	14.62145308324701
H	6.32014609466227	-2.78573516348268	15.14298831274236
H	6.27851798747344	-1.30517806441092	14.12911311058285
C	5.48403091083295	-0.74401660171925	16.57638947646435
H	6.15723488204444	0.00332231920385	16.11610394441779
H	6.09872360661212	-1.44524235007082	17.17350548547590
C	4.49884781438109	-0.01984488559071	17.45741022842916
H	5.05543767739610	0.61134113090991	18.17579915344256
H	3.86463593518234	0.64152304807232	16.84025195018723
C	2.72725108879442	-0.29653989386458	18.98863867903571
H	2.12238102157097	0.40476004786133	18.38496622776001
H	3.24742273258942	0.28486431769146	19.77339476021404
C	1.82892335626840	-1.31757432306840	19.64231624349567
H	2.42812549277247	-2.05243392220771	20.21408794587822
H	1.15821195387282	-0.79611018923347	20.35195978853858
C	0.08233167617100	-2.85626420616445	19.16732741973598
H	-0.67030319757970	-2.27738277167357	19.73499520877428
H	0.54996108162334	-3.58449814920475	19.85818272350031
C	-0.59498082386011	-3.58283776736285	18.03194401197595
H	-1.44595913055351	-4.16380413055125	18.43630306409154
H	-0.98416700916643	-2.86388591393179	17.28952052829793
C	-0.24486714352455	-5.24230617115900	16.38323704199270
H	-0.81748469568163	-4.59597305378557	15.69766412140839
H	-0.94024629504050	-5.97900351002251	16.82909044540753
C	0.82976583103933	-5.97395307960029	15.61936115579845

H	1.51825592414927	-6.48915381326236	16.31492765932536
H	0.35120637056952	-6.72827264872664	14.96651252147799
C	2.57590664311811	-5.67071316960001	14.05084941594204
H	2.11919741953178	-6.37606778138829	13.33044028881246
H	3.25715306229389	-6.23763229536592	14.71283725814640
C	3.34073052489461	-4.61855883653464	13.28651521735644
H	4.01964358552337	-5.11206841727210	12.56544730788919
H	2.64650899974202	-3.97749323497309	12.71577875198638
O	0.27376803201027	-1.60628533530588	15.29822649084507
C	0.73741993759546	-1.45125572677772	13.93415492107988
H	-0.11257360432484	-1.21338098061060	13.27456758803145
H	1.16224047120439	-2.41286581234394	13.61943796354816
C	1.72626840391124	-0.28826064061313	13.98861649378945
H	1.77265634448151	0.24466664530422	13.03024221377926
H	2.73848426302609	-0.64358774244332	14.22518043533850
C	1.17764348895847	0.59208100496101	15.13982919419359
H	1.95754640117954	0.79933954585584	15.88699149271708
H	0.80418543353366	1.55380952079123	14.77265359835096
C	0.03593407001989	-0.25109728367508	15.73971347697860
H	0.01136257096884	-0.26934951065570	16.83762410709664
H	-0.94026534036475	0.08764919311393	15.35435809052748
O	3.70822941680608	-5.14575366976803	17.36633816889007
C	5.12773822998220	-5.25133105252602	17.14690138948530
H	5.42052650237918	-6.31665166166260	17.17536520697012
H	5.32539989688688	-4.85600428598511	16.14317697314432
C	5.79873032923296	-4.46482176621867	18.29413959058788
H	6.18754427898612	-3.49902992923334	17.94624790149977
H	6.64317218788116	-5.02538522289082	18.71502062932671
C	4.65826281411397	-4.26222472705458	19.32648835092571
H	4.95771145227773	-4.52920069326889	20.34814943797846
H	4.33260465621090	-3.21309477343580	19.32777429296500
C	3.53979382063798	-5.16389138478970	18.79383529553617
H	3.64358537464209	-6.20002747977705	19.16918382537095
H	2.52142590444489	-4.81357110759879	19.00121430196192

Molecular coordinates used in the Mössbauer calculation of **10**:

Fe	2.59954681324890	6.02258855282492	12.26147240965206
S	1.58002877153884	4.60047011878844	10.91245840581635
S	2.90382448596085	7.87299918533389	13.43097278878009
C	1.30750793953065	5.51326410451047	13.59612956674110
C	0.46148539040145	3.78756553058320	12.05786620740182
C	0.48158999707063	4.38751262991279	13.40420357248672
C	-0.32327693976028	3.91068033602922	14.44944907543352
H	-0.95174366945789	3.03660231672029	14.27082395138335
C	-0.31783651194691	4.56659011142630	15.68387056706732
H	-0.94175881853374	4.19347294044491	16.49759745407513

C	0.45659433751424	5.71447993161067	15.87551374938269
H	0.44719381752949	6.25727191821898	16.82229402075599
N	3.67627378849661	6.83573771747887	10.64951512006920
H	3.37392047655289	6.47929244878168	9.73864766852569
H	4.66091860145515	6.58420433383787	10.77409825499683
H	3.62317799609795	7.85794716424135	10.62505101008891
C	1.25473487077625	6.19607452674931	14.82809556175162
C	2.03876011577478	7.43905316086901	14.94067334102968
N	-0.30381252551336	2.80077706597374	11.76882699709024
C	-0.42634309583419	2.27874968765746	10.47006489170317
C	0.07807052487474	0.97780565618244	10.22724900009758
C	-0.10067514484567	0.41153650943207	8.96367010263425
H	0.29291201043698	-0.58533968780024	8.76106021568447
C	-0.77971809040480	1.10015667535112	7.95779809339973
H	-0.91638250027670	0.64430075591984	6.97603071285274
C	-1.29462930014182	2.36707831622561	8.21962726853365
H	-1.84279471082478	2.89488655012155	7.43648927131658
C	-1.13345741648326	2.98291344572428	9.46637571048730
C	0.84717834967478	0.27146588322593	11.32728471509929
H	0.43130441075386	0.64189317393140	12.27980395565116
C	2.32811190841763	0.68513625137862	11.27947406973033
H	2.79827597957710	0.31479060440151	10.35497220256367
H	2.88376920606861	0.27133171083936	12.13557266452511
H	2.42503777741723	1.77962568372572	11.28619341991018
C	0.70325601280520	-1.25314574099114	11.30303461255438
H	-0.35329849349446	-1.55492354235819	11.30142751420642
H	1.18534785667961	-1.69504917488878	12.18751869163716
H	1.18344649734438	-1.69620709476655	10.41757198608930
C	-1.77639044129116	4.33457249636217	9.72837607630410
H	-1.44961744597858	4.68353919323556	10.71661987685383
C	-3.30802323741415	4.20354276089571	9.77468459364549
H	-3.61578819418437	3.46909617549238	10.53203484271757
H	-3.77317775835057	5.16992277540796	10.02094391871439
H	-3.70771261864675	3.87360193938494	8.80385349353810
C	-1.33557810048188	5.39081984908558	8.70569954090400
H	-0.24158135865957	5.49005075431939	8.70338775026121
H	-1.66131736829606	5.12940772817639	7.68760125392565
H	-1.77190052237035	6.37003854921962	8.95284173902640
N	2.07758034494041	8.12569808978057	16.02317873451619
C	2.81637860934062	9.32267560067720	16.10612908389232
C	4.13473221630970	9.28005969782790	16.61473525064158
C	4.82094447562124	10.48697543787672	16.78154412362904
H	5.83983686632972	10.47631541712344	17.16879836341596
C	4.22458749954508	11.70411753334061	16.45300845788134
H	4.77408691724533	12.63677052126361	16.58890239402258
C	2.92764304348839	11.72641104079314	15.94015562334601

H	2.47538789563204	12.68158790948906	15.67216972781805
C	2.20071093164263	10.54591878832847	15.75409719640572
C	4.74511405959441	7.93888892999860	16.98419341588320
H	4.39127107389276	7.21486008075994	16.23336499588819
C	4.21857553386917	7.46823592821636	18.35188884277281
H	4.54017477740793	8.16143461131822	19.14347368570956
H	4.60219957214385	6.46543796642424	18.59591209604910
H	3.12090434478417	7.43060077100660	18.34968115808984
C	6.27466979046625	7.92119434853698	16.94659890704872
H	6.65938931343866	8.26306980415522	15.97489396823600
H	6.64399706591800	6.89995652022580	17.12483321768445
H	6.71176489407443	8.56084083180499	17.72793597776876
C	0.77703788162285	10.54134097780652	15.22224026735358
H	0.68461114601876	9.66750655207858	14.55806278559129
C	-0.22298706948797	10.35051145369785	16.37593019353996
H	0.00441320141591	9.43977847070311	16.94696283252773
H	-1.25089089807679	10.26971426755248	15.99183528628193
H	-0.18035756543281	11.20775499537277	17.06583982263466
C	0.42517021956107	11.77872425917772	14.39251101875805
H	0.39760220701010	12.68975888512753	15.00891875387059
H	-0.57148352090037	11.65836317690333	13.94411876129684
H	1.14915577702635	11.93728483924030	13.58103638409778
O	4.27117937953545	4.86558884971864	12.94773736422086
C	4.22035527913199	3.41595899307112	12.77140408925892
H	4.26497670461295	3.22427434023818	11.69441193795287
H	3.26050926175273	3.04255755170218	13.16078452383291
C	5.40110825694796	2.91225288409810	13.57985488244661
H	5.31558756640683	1.84477962733947	13.81897260126885
H	6.33794775304392	3.06952329809281	13.02463856869576
C	5.33907539855030	3.81267603666849	14.82498121135729
H	6.31138632172823	3.92469761673793	15.32012163784169
H	4.63275308921677	3.39750277187874	15.55710132344531
C	4.81421115895207	5.14870100260592	14.28727005889622
H	4.01018598587375	5.56730412634069	14.90312656248995
H	5.58950037899744	5.91324795967164	14.15181354254386

Molecular coordinates used in the IR frequency calculation of tricarbonyl complex **11** at the BP86/ZORA-def2-TZVP level of theory:

Fe	2.521309967	6.202905178	12.067408880
S	1.640786804	4.441192943	10.861765949
S	3.155268370	7.856167923	13.554743078
C	1.284141256	5.599140897	13.526639524
C	0.452429791	3.823664480	12.012398111
C	0.435904178	4.499104374	13.325165325
C	-0.423222418	4.074443794	14.351975659
H	-1.072383158	3.218561275	14.158577117

C	-0.433414149	4.744759502	15.576397416
H	-1.096915059	4.409194993	16.375977388
C	0.396541063	5.848936301	15.778247015
H	0.400185222	6.399505453	16.720761543
C	1.253685851	6.280816570	14.753577595
C	2.119921695	7.463236569	14.926382721
N	-0.365209060	2.852877625	11.762750181
C	-0.443614012	2.245346398	10.503356511
C	0.037039886	0.918571038	10.361082221
C	-0.122113769	0.268231014	9.135153366
H	0.249760564	-0.750995055	9.015923205
C	-0.747332804	0.900461365	8.058873122
H	-0.863152529	0.379348968	7.106378350
C	-1.228883662	2.199311412	8.213447214
H	-1.724036235	2.692371982	7.373152546
C	-1.089571890	2.892587099	9.420422342
C	0.745746706	0.270587516	11.535609227
H	0.284745158	0.698760888	12.441878258
C	2.233383395	0.665040343	11.552983099
H	2.745595086	0.258190171	10.666202061
H	2.734764989	0.269014258	12.450153737
H	2.356113028	1.756954064	11.538024410
C	0.585604356	-1.252424524	11.587818800
H	-0.472816407	-1.547331531	11.543723976
H	1.014693554	-1.646923208	12.521412231
H	1.110028421	-1.748979870	10.756465669
C	-1.669125102	4.289618088	9.564960730
H	-1.360350013	4.677994187	10.543683936
C	-1.124874711	5.250917271	8.500290784
H	-0.027947194	5.283544112	8.543225789
H	-1.426162252	4.942014783	7.486654708
H	-1.505536310	6.269238554	8.669054305
N	2.085759577	8.151961548	16.021438535
C	2.860852663	9.310734474	16.178587478
C	4.129283232	9.225880708	16.801146978
C	4.831078301	10.408573105	17.055190172
H	5.813290699	10.360564120	17.527254190
C	4.303933027	11.650258238	16.697839290
H	4.867182639	12.563339042	16.899783754
C	3.063464730	11.718792913	16.061679672
H	2.667451192	12.690461207	15.763375257
C	2.327579921	10.562647176	15.785055242
C	4.668336534	7.856451064	17.179758153
H	4.379012441	7.169681944	16.367922826
C	3.994592416	7.354119917	18.469635783
H	4.258555862	8.006411582	19.316818700

H	4.319796348	6.329291988	18.707714208
H	2.902463678	7.354843071	18.354710547
C	6.192795751	7.804452451	17.300504260
H	6.679613243	8.175422799	16.387290675
H	6.522270031	6.767897086	17.465899917
H	6.557669464	8.403102237	18.150446152
C	0.974268923	10.602064631	15.094795118
H	0.949105576	9.743648636	14.404905213
C	-0.155781228	10.406270587	16.120355428
H	-0.003738378	9.474918603	16.681973357
H	-1.135187700	10.353790031	15.619969071
H	-0.175954614	11.246466130	16.833279293
C	0.743445844	11.862101120	14.257399486
H	0.666197206	12.763545164	14.885652377
H	-0.198413308	11.770869946	13.696766806
H	1.557603252	12.019258612	13.535513679
C	3.611369739	6.743073043	10.773411012
C	1.115096974	7.198968759	11.587208186
C	3.666513589	5.077046630	12.857935808
O	4.364899062	4.340505262	13.407221634
O	4.321075896	7.098682809	9.926708687
O	0.176915211	7.817553749	11.322415616
C	-3.205583320	4.245392300	9.551799109
H	-3.584593021	3.873088114	8.586909605
H	-3.583851925	3.580605274	10.341364621
H	-3.625658133	5.249906728	9.715466004

Molecular coordinates used in the IR frequency calculation of the dicarbonyl analogue of **11** at the BP86/ZORA-def2-TZVP level of theory:

Fe	2.636701533	6.029971459	12.215078703
S	1.541427846	4.620107302	10.902779912
S	3.036586775	7.806683214	13.481138953
C	1.318697383	5.527778837	13.596878990
C	0.414605292	3.855965148	12.046304487
C	0.420602926	4.466217897	13.385709597
C	-0.486143685	4.079458396	14.384913965
H	-1.170119003	3.254214727	14.176392596
C	-0.507908799	4.759517449	15.605355134
H	-1.206992013	4.455518116	16.387214186
C	0.342927190	5.847996544	15.814960898
H	0.314866810	6.423778290	16.742409944
C	1.247001229	6.231319741	14.812923319
C	2.086827665	7.433955020	14.934392777
N	-0.375704329	2.877909376	11.754597853
C	-0.464327599	2.335881040	10.466239243
C	0.083610796	1.046719439	10.243325314

C	-0.076610744	0.453210101	8.989660549
H	0.349009130	-0.534612307	8.804633200
C	-0.770862353	1.102544558	7.966936956
H	-0.886604148	0.625534417	6.991732494
C	-1.318115965	2.361744677	8.202865190
H	-1.866147362	2.867571940	7.404222645
C	-1.178481343	3.000394744	9.440208516
C	0.867284707	0.383643664	11.360176306
H	0.420053793	0.745032725	12.301845977
C	2.333516694	0.850818829	11.342822506
H	2.830241073	0.510334808	10.419953191
H	2.886183446	0.440198763	12.201937549
H	2.406634871	1.946745545	11.374463220
C	0.783012775	-1.146288548	11.345378832
H	-0.260832365	-1.491925035	11.327487159
H	1.268376596	-1.560827363	12.241788135
H	1.297213187	-1.576014283	10.471524385
C	-1.828141463	4.353627167	9.674006550
H	-1.523937818	4.703345395	10.669052288
C	-1.353081491	5.400818790	8.657740364
H	-0.259939712	5.499658461	8.694434195
H	-1.644487323	5.127535002	7.631300476
H	-1.795528143	6.383587308	8.881163782
N	2.071751274	8.164031205	15.999033319
C	2.819873006	9.345847882	16.101640402
C	4.119334742	9.302606961	16.661982730
C	4.794851260	10.508608411	16.872327446
H	5.799783766	10.493232701	17.295548661
C	4.213065739	11.731049054	16.533406223
H	4.757422432	12.662368810	16.700769213
C	2.941615760	11.756966478	15.958901129
H	2.502613307	12.713783920	15.672764829
C	2.228413509	10.576487084	15.728015519
C	4.720463438	7.954496994	17.022267948
H	4.422228112	7.253143969	16.226579488
C	4.120241313	7.436017181	18.341850905
H	4.400207455	8.099601871	19.175098235
H	4.488808554	6.423169517	18.566866991
H	3.024486751	7.400698946	18.276008985
C	6.249494641	7.953794072	17.077451274
H	6.685061309	8.328169528	16.140050703
H	6.617511397	6.929722577	17.238690453
H	6.631374086	8.572914403	17.904928195
C	0.840049604	10.568564659	15.109632772
H	0.800203483	9.699144960	14.434260349
C	-0.230044803	10.360406844	16.195340623

H	-0.028127596	9.442987603	16.764416690
H	-1.232181514	10.276437769	15.747286139
H	-0.234607543	11.211356249	16.895631462
C	0.531408053	11.810331178	14.269490156
H	0.461018258	12.717195221	14.890375329
H	-0.435148704	11.686906850	13.758832695
H	1.303048689	11.979659457	13.505201631
C	-3.360609538	4.229497771	9.679138568
H	-3.736032088	3.894849095	8.699342669
H	-3.691028917	3.500883095	10.432979090
H	-3.829146961	5.199547184	9.906915807
C	3.745735665	6.554891122	10.919905162
C	3.728373684	4.956209396	12.928299467
O	4.465594549	4.211603054	13.441229504
O	4.501077770	6.866345577	10.092988904

References

1. Borger, J. E.; Ehlers, A. W.; Lutz, M.; Slootweg, J. C.; Lammertsma, K. Stabilization and Transfer of the Transient $[Mes^*P_4]^-$ Butterfly Anion Using BPh_3. *Angew. Chem. Int. Ed.* **2016,** *55*, 613-617.
2. Bhattacharya, P.; Krause, J. A.; Guan, H. Iron Hydride Complexes Bearing Phosphinite-Based Pincer Ligands: Synthesis, Reactivity, and Catalytic Application in Hydrosilylation Reactions. *Organometallics* **2011,** *30*, 4720-4729.
3. Mallow, O.; Khanfar, M. A.; Malischewski, M.; Finke, P.; Hesse, M.; Lork, E.; Augenstein, T.; Breher, F.; Harmer, J. R.; Vasilieva, N. V.; Zibarev, A.; Bogomyakov, A. S.; Seppelt, K.; Beckmann, J. Diaryldichalcogenide radical cations. *Chem. Sci.* **2015,** *6*, 497-504.
4. Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist. *Organometallics* **2010,** *29*, 2176-2179.
5. Harris, R. K.; Becker, E. D.; Cabral de Menezes, S. M.; Goodfellow, R.; Granger, P. NMR nomenclature. Nuclear spin properties and conventions for chemical shifts (IUPAC Recommendations 2001). *Pure Appl. Chem.* **2001,** *73*, 1795-1818.
6. Harris, R. K.; Becker, E. D.; Cabral de Menezes, S. M.; Granger, P.; Hoffman, R. E.; Zilm, K. W. Further conventions for NMR shielding and chemical shifts (IUPAC Recommendations 2008). *Pure Appl. Chem.* **2008,** *80*, 59-84.
7. Stoll, S.; Schweiger, A. EasySpin, a comprehensive software package for spectral simulation and analysis in EPR. *J. Magn. Reson.* **2006**, *178*, 42-55.
8. Aranzaes, J. R.; Daniel, M.-C.; Astruc, D. Metallocenes as references for the determination of redox potentials by cyclic voltammetry—Permethylated iron and cobalt sandwich complexes, inhibition by polyamine dendrimers, and the role of hydroxy-containing ferrocenes. *Can. J. Chem.* **2006,** *84*, 288-299.
9. Bisson, A. P.; Hunter, C. A.; Morales, J. C.; Young, K. Cooperative Interactions in a Ternary Mixture. *Chem. Eur. J.* **1998,** *4*, 845-851.
10. Reich, H. J. WinDNMR: Dynamic NMR Spectra for Windows. *J. Chem. Educ.* **1995,** *72*, 1086.
11. Sheldrick, G. A short history of SHELX. *Acta Cryst.* **2008,** *64*, 112-122.