Supporting Information For

A Chiral Macrocyclic Tetra-N-heterocyclic Carbene Yields an “All Carbene” Iron Alkylidene Complex

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Table of Contents:

Experimental Section:

General Considerations for Synthesis:

All reactions and workups for NHC ligands were conducted under air unless otherwise stated. All reactions, workups and manipulations involving the NHC metal complexes and subsequent reactions were done using standard Schlenk techniques under N_2 or in an MBraun Unilab glovebox under N_2 unless otherwise stated. All glassware for aforementioned reactions were dried at 170 °C overnight before use. For air sensitive reactions, tetrahydrofuran (THF), toluene, hexanes and were dried on an Innovative Technologies Pure Solv MD-7 Solvent Purification System, degassed by three freeze-pump-thaw cycles on a Schlenk line, and subsequently stored under activated 4 Å molecular sieves prior to use. Anhydrous acetonitrile was prepared by distillation over phosphorous pentoxide, followed by degassing by three freeze-pump-thaw cycles and stored over activated 4 Å molecular sieves prior to use. Benzene and pentane were purchased anhydrous from Sigma-Aldrich, degassed by three freeze-pump-thaw cycles and subsequently stored over activated 4 Å molecular sieves prior to use. For anhydrous NMR solvents, benzene-*d6* (C_6D_6), dichloromethane-*d2* (CD_2Cl_2) chloroform-*d3* ($CDCl_3$) and acetonitrile-*d3* (MeCN-*d3*) were degassed by three freeze-pump-thaw cycles and subsequently stored over activated 4 Å molecular sieves prior to use. Celite and silica gel used in the synthesis of metal complexes were dried overnight at 240 °C and subsequently stored in the glovebox prior to use. All reagents were purchased from commercial vendors at highest purity. (1*S*,2*S*)-(+)-1,2-Diaminocyclohexane was purchased from Combi-Blocks at highest available purity (96%). Raney Nickel (2800 mesh) was purchased from Oakwood and used within 2 months of opening. Diphenyldiazomethane[1] and 2-methylallyl 2-diazo-2-phenylacetate (**10**)[2] were synthesized based on previously reported procedures.

General Considerations for Molecule Characterization:

Solution ^1H NMR and $^{13}C\{^1H\}$ NMR were performed on either a Varian Mercury 300 MHz or Varian VNMRS 500 MHz narrow-bore broadband system at 298 K. All ^1H and ^{13}C shifts were referenced to the residual solvent. All solution 2D NMR experiments were performed on Varian VNMRS 600 MHz narrow-bore broadband system at 298 K. All mass spectrometry analyses were conducted at the Biological and Small Molecule Mass Spectrometry Center located in the Department of Chemistry at the University of Tennessee. The DART analyses on neutral organic molecules were performed using a JEOL AccuTOF-D time-of-flight (TOF) mass spectrometer with a DART (direct analysis in real time) ionization source from JEOL USA, Inc. (Peabody, MA) using either dichloromethane or methanol as the solvent. The ESI/MS analyses on charged organic molecules were performed using an Exactive Plus OrbitrapTM Mass Spectrometer (Thermo Scientific, San Jose, CA, USA) with sheath gas set to 25 arbitrary units, auxiliary gas set to 10 arbitrary units, spray voltage to 4kV, capillary temperature set to 350 °C, and resolution of 140,000. Infrared spectra were collected on a Thermo Scientific Nicolet iS10 with a Smart iTR accessory for attenuated total reflectance (ATR) using the neat complexes. UV-vis measurements were taken inside a dry glovebox on an Ocean Optics USB4000 UV-vis system with 1 cm path length quartz crystal cell. Carbon, hydrogen, and nitrogen analyses were obtained from Atlantic Microlab, Norcross, GA, Galbraith Laboratories Inc., Knoxville, TN or Midwest Microlab, Indianapolis, IN.

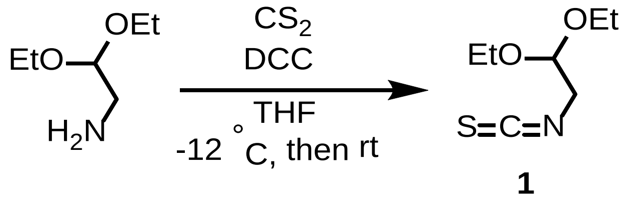
General Considerations for Crystallography:

All X-ray data collections were performed on single crystals coated in Paratone oil on glass slides and mounted on nylon fibers. Crystals for **6**, **8** and **9** were coated in Paratone oil, which had previously been degassed with N_2 and dried with a piece of sodium metal inside the glovebox. X-ray data for complexes **6, 7, 8, and 9** were collected with the use of a Mo microsource and X-ray data for **4** was collected using a Cu microsource on a Bruker D8 Venture diffractometer. Crystals were mounted in a 100 K cold stream provided by an Oxford Cryostream low-temperature apparatus. All data sets were reduced with Bruker SAINT and were corrected for absorption using SADABS. Structures were solved and refined using SHELXT and SHELXLE64, respectively. Compounds **4** and **5** were treated with PLATON SQUEEZE command to remove nonsensical disordered solvent voids and remove heavily disordered toluene molecules, respectively.

General Considerations of Electrochemical Studies

Cyclic voltammetry measurements were made inside a dry glovebox at ambient temperature using a BASi Epsilon electrochemical analyzer with a platinum working electrode, platinum wire counter electrode, and $Ag/AgNO_3$ reference electrode. For all samples, a 0.1M solution tetrabutylammonium hexafluorophosphate ((TBA)(PF_6)) in the appropriate solvent was used as the supporting electrolyte. All peaks were referenced to an external standard of ferrocene. Unless overwise state, all experiments were conducted by first going to more oxidizing potentials, followed by reduction.

Synthesis of 1,1-diethoxy-2-isothiocyanatoethane, 1.



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The synthesis of 1,1-diethoxy-2-isothiocyanatoethane was modified from a previously reported procedure.[3] Dicyclohexyl carbodiimide (DCC) (77.46 g, 375.4 mmol, 1 eq.), THF (375 mL), and carbon disulfide (CS_2) (135 mL) were added to a 2 L round bottom flask. The 2 L flask was then attached to a drop addition funnel and the flask was cooled to -12 °C using an ice-salt cooling bath. Aminoacetaldehyde diethyl acetal (50.01 g, 375.5 mmol, 1 eq.) was added to the drop addition funnel. The amine was then added dropwise to the 2 L flask with vigorous stirring over 30-45 min. A large amount of white precipitate formed towards the end of addition. The funnel was removed, and the flask was covered. The flask was allowed to warm to ambient temperature overnight. The mixture was then filtered over a 350 mL medium porosity frit into another 2 L flask to remove the precipitate. The precipitate was washed with hexanes (500 mL) and then the filtrate concentrated in vacuo. The viscous yellow oil was then diluted with hexanes (800 mL), filtered over a second 350 mL medium porosity frit, and concentrated to a yellow oil. This oil was then stored in a -20 °C freezer overnight. The oil was then carefully transferred into a 250 mL round bottom flask by pipet without transferring any precipitated solid. The yellow oil was then purified by short path distillation and the first fraction was collected at 140 mTorr and 20 °C with an ice bath on the receiving end. The final pure product was a colorless oil (63.2 g, 96.1% yield).

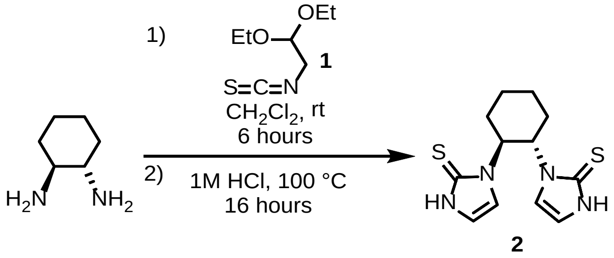
^{1}H NMR ($CDCl_3$, 499.74 MHz): δ 4.68 (t, *J* = 5.5 Hz, 1H), 3.66 (m, 4H), 3.56 (d, *J* = 5.5 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR ($CDCl_3$, 125.66 MHz): δ 133.56, 100.11, 63.12, 47.60, 15.39.

IR: 2977, 2883, 2076, 1442, 1373, 1347, 1299, 1245, 1124, 1056, 934, 906, 816, 702 cm^{-1}.

DART HR MS (*m/z*): $[M+H]^+$: 176.07319 (found), $[C_7H_{14}NO_2S]^+$: 176.07398 (calculated).

Synthesis of 1,1'-((1*S*,2*S*)-1,2-cyclohexanediyl)bis(1,3-dihydro-2*H*-imidazole-2-thione), 2.



(1*S*,2*S*)-1,2-Diaminocyclohexane (13.18 g, 115.4 mmol, 1 eq.) was added to a 1 L round bottom flask with 230 mL of CH_2Cl_2. 1,1-Diethoxy-2-isothiocyanatoethane (**1**) (40.45 g, 230.8 mmol, 2 eq.) was added quickly to the 1 L round bottom while stirring. The resulting solution began self-refluxing immediately. The reaction was allowed to cool to ambient temperature over 6 h. This solution was then concentrated in the round bottom flask under high vacuum, resulting in a sticky light-yellow foam. This foam turned into to a viscous yellow oil quickly on exposure to air. The yellow oil was suspended in a 1M HCl solution (380 mL) and the biphasic mixture was refluxed at 100 °C overnight. [***Caution***: Unreacted **1** or other sulfur containing impurities will hydrolyze, releasing foul-smelling compounds. It is highly advisable to perform this reaction in a well-ventilated fume hood.] After 16 hours, a white precipitate formed. The reaction was then cooled to room temperature and kept in a -20 °C freezer overnight. The white precipitate was then filtered over a 150 mL medium porosity frit and washed with 3 times with 50 mL of ice cold water, which yielded **2** as a white powder (26.15 g, 80.8% yield).

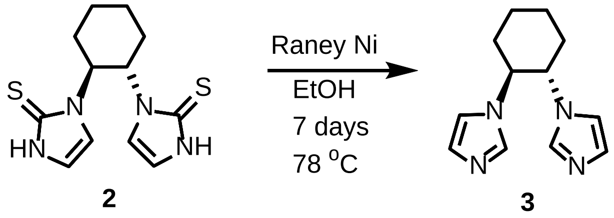
^{1}H NMR (DMSO-d_6, 499.74 MHz): δ 12.00 (s, 2H), 7.10 (t, *J* = 2.4 Hz, 2H), 6.80 (t, *J* = 2.4 Hz, 2H), 5.02 (m, 2H), 1.96 (d, *J* = 12.5 Hz, 2H), 1.79, (d, *J* = 4.8 Hz, 2H), 1.61 (m, 2H), 1.47 (m, 2H).

^{13}C NMR (DMSO-d_6, 125.66 MHz): δ 160.46, 115.23, 114.55, 56.36, 31.81, 24.30.

IR: 3142, 3080, 3017, 2923, 2859, 1577, 1528, 1481, 1447, 1425, 1407, 1390, 1345, 1335, 1307, 1299, 1279, 1261, 1225, 1153, 1138, 1108, 1053, 980, 954, 913, 850, 821, 785, 754, 716, 707, 679, 669 cm^{-1}.

DART HR MS (*m/z*): $[M+H]^+$: 281.08853 (found), $[C_{12}H_{17}N_4S_2]^+$: 281.08891 (calculated).

Synthesis of (1*S*,2*S*)-1,2-di(imidazole)cyclohexane, 3:



Compound **2** (25.25 g, 90.15 mmol) was added to a 500 mL round bottom flask and dissolved in 200 mL of ethanol. 10 mL of activated Raney Nickel in water was added to the flask. The reaction was then heated under an N_2 atmosphere for 5 days at 78 °C with vigorous stirring. After 5 days, another 15 mL of Raney Nickel was added as some **2** remained (based on TLC and DART-MS measurements). After another 2 days, the reaction was cooled to room temperature. The slurry was then filtered over a plug of Celite on a 350 mL coarse filter frit and washed with 600 mL of methanol. [***Caution***: The Raney Nickel collected was not allowed to run fully dry after filtering. The filtration flask was swapped out and the Raney Nickel was washed with 1M HCl followed by water.] The filtrate was then concentrated by rotary evaporation and then fully dried under high vacuum. The resulting black foamy residue was dissolved in 150 mL of CH_2Cl_2 and filtered over Celite to remove black solids. Diethyl ether was added to the solution until solid ceased precipitation. This was filtered and washed with additional diethyl ether resulting in a white powder after drying (14.01 g, 71.8% yield).

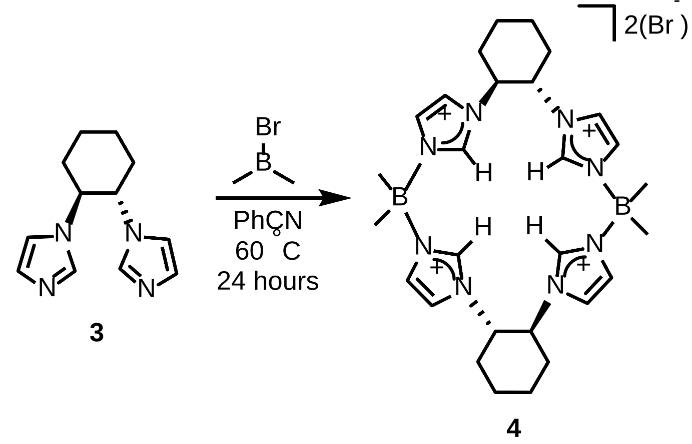
^{1}H NMR ($CDCl_3$, 499.74 MHz): δ 7.13 (s, 2H), 6.94 (s, 2H), 6.65 (s, 2H), 3.95 (m, 2H), 2.28 (d, *J* = 13.6, 2H), 1.98 (m, 4H), 1.53 (m, 2H).

^{13}C NMR ($CDCl_3$, 125.66 MHz): δ 135.67, 129.86, 116.50, 62.16, 32.69, 25.03.

IR: 3128, 3095, 2948, 2867, 1627, 1497, 1449, 1406, 1281, 1236, 1228, 1111, 1102, 1092, 1084, 1030, 973, 955, 914, 877, 847, 826, 813, 766, 751, 734, 662, 643 cm^{-1}.

DART HR MS (*m/z*): $[M+H]^+$: 217.14599 (found), $[C_{12}H_{17}N_4]^+$: 217.14532 (calculated).

Synthesis of ($^{(S,S)\text{-}1,2\text{-Cy,BMe}_2}$TC^{H})(Br)$_2$, 4:



Diimidazole **3** (3.038 g, 13.88 mmol, 2 eq.), was split into two equivalent portions. Half (1.519 g) was put into an oven-dried 250 mL round bottom flask inside the glovebox. To this round bottom flask, 60 mL of benzonitrile (PhCN) was added and the mixture was stirred until full dissolution. Bromodimethylborane (BrBMe$_2$) (1.40 mL, 14.34 mmol, 2.06 eq.) was added slowly by pipette to the round bottom flask. This solution was stirred for 30 minutes. The second portion of **3** (1.519 g) was then added to the flask and stirred for another 5 minutes. The flask was then covered with a septum, removed from the glovebox, and connected to a Schlenk line via a reflux condenser, put under N$_2$, and heated at 60 °C for 24 hours. Over time, the solution become a viscous tan slurry. The slurry was then cooled in an ice bath to 0 °C and filtered over a fine porosity frit to remove the PhCN. The collected solid was washed with CH$_3$CN (3x10 mL) until the tan sludge turned white. This white clumpy solid was triturated with THF (2x50 mL) and diethyl ether (3x50 mL). The solid was completely crushed into a fine powder and dried for at least 24 hours under high vacuum. These successive washings and drying resulted in a pure white solid (3.83 g, 81.8% yield). Single crystals of **4** were grown by dissolving **4** in roughly 0.5 mL of methanol, filtering any off particulates, adding two drops of methanol, followed by careful layering of 4 mL of diethyl ether resulting in colorless plates.

^{1}H NMR (DMSO-d$_6$, 499.74 MHz): δ 8.59 (s, 4H), 7.45 (s, 4H), 7.13 (s, 4H), 4.83 (m, 4H), 2.19 (d, *J* = 12 Hz, 4H), 2.03 (m, 4H), 1.89 (m, 4H), 1.48 (m, 4H), 0.14 (s, 12H).

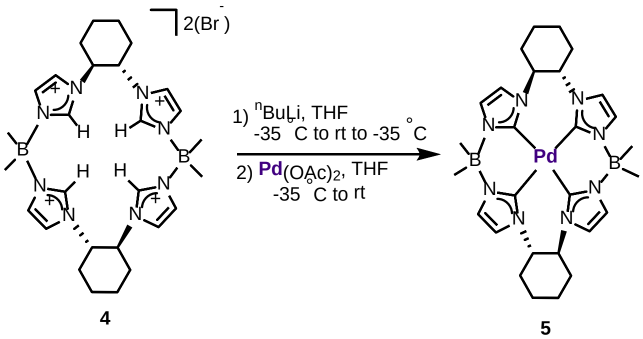
^{13}C NMR (DMSO-d$_6$, 125.66 MHz): δ 135.08, 122.80, 120.96, 61.03, 32.12, 23.98, 7.73.

IR: 3405, 3103, 3050, 2932, 2860, 1621, 1536, 1448, 1355, 1315, 1283, 1261, 1129, 1112, 1086, 1022, 969, 948, 849, 793, 757, 679, 650 cm^{-1}.

ESI HR MS (*m/z*): [M]$^{2+}$: 257.1930 (found), [C$_{28}$H$_{44}$B$_2$N$_8$]$^{2+}$: 257.1932 (calculated)

CHN: Calculated for C$_{28}$H$_{44}$B$_2$Br$_2$N$_8$ • H$_2$O: C: 48.54, H: 6.70, N: 16.18. Found: C: 47.93, H: 6.53, N: 15.82.

Synthesis of [($^{(S,S)\text{-}1,2\text{-}Cy,BMe_2}TC^{H}$)Pd], 5:



($^{(S,S)\text{-}1,2\text{-}Cy,BMe_2}TC^{H}$)(Br)$_2$ (0.2082 g, 0.3088 mmol, 1 eq.), **4**, was added to a 20 mL scintillation vial and 15 mL of THF was added. The vial was then cooled over 30 minutes to -35 °C in a freezer. A 2.5 M ^{n}BuLi solution in hexanes (0.5 mL, 1.250 mmol , 4.1 eq) was then added to the vial, which was subsequently agitated and returned to the freezer. The suspension was manually agitated every 2 to 3 minutes over 5-10 minutes, until the color changed to yellow. The vial was then allowed to warm up to rt while stirring until the suspension became a solution, approximately 45-60 minutes. The vial was then returned to the -35 °C freezer and cooled at least 30 minutes. A second 20 mL vial containing Pd(OAc)$_2$ (0.0697 g, 0.3096 mmol, 1 eq.) in 1 mL of THF was also cooled to -35 °C. The solution of the free NHC of **4** was then quantitatively transferred to the solution of Pd(OAc)$_2$ with stirring. The solution immediately turned brown and precipitated a grey solid shortly thereafter. The mixture was then allowed to stir for 24 hours at rt. The reaction mixture was then filtered through a pad of silica gel on a 15 mL medium porosity frit that was followed by an additional 30 mL of THF. The THF solution was then concentrated and thoroughly dried to leave a white residue. The remaining THF was azeotroped with hexanes (3x10 mL) and the resulting solid residue was extracted with 15 mL of benzene. This benzene solution was concentrated to dryness under reduced pressure. The residue was triturated with 10 mL of hexanes 3 times and dried, which resulted in the pure white solid (0.137 g, 71.9% yield) after drying. Single crystals of **5** were grown by slow evaporation of a concentrated toluene/hexanes mixture in air to form colorless shards.

^{1}H NMR (CDCl$_3$, 499.74 MHz): δ 7.14 (d, J = 1.7 Hz, 2H), 7.06 (d, J = 1.7 Hz, 2H), 6.93 (d, J = 1.7 Hz, 2H), 6.74 (d, J = 1.7 Hz, 2H), 5.61 (dt, J_1 = 12 Hz, J_2 = 1.7 Hz, 2H), 4.16 (dt, $^{3}J_1$ = 11 Hz, $^{2}J_2$ = 4.1 Hz, 2H), 2.27 (t, J = 14 Hz, 4H), 1.99 (m, 4H), 1.87 (m, 2H), 1.61 (dt, $^{3}J_1$ = 13 Hz, $^{2}J_2$ = 3.3 Hz, 2H), 1.50 (m, 4H), 0.26 (s, 6H), 0.01 (s, 6H).

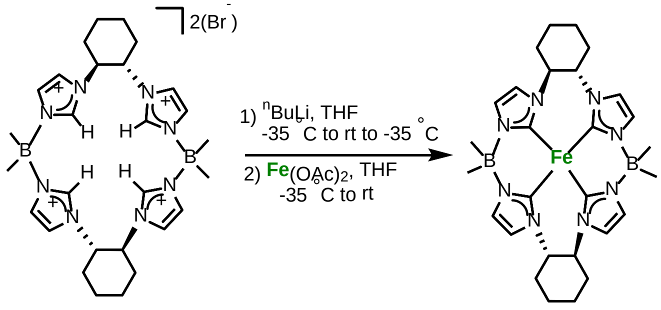
^{13}C NMR (CDCl$_3$, 125.66 MHz): δ 176.86, 165.57, 123.12, 121.90, 119.99, 114.21, 64.58, 58.14, 37.88, 31.75, 25.30, 25.10, 16.14, 9.51.

IR: 2923, 2853, 1679, 1559, 1450, 1430, 1399, 1355, 1337, 1279, 1241, 1207, 1155, 1124, 1113, 1066, 1039, 1015, 953, 943, 917, 874, 855, 823, 793, 754, 730 cm^{-1}.

DART HR MS (*m/z*): [M]$^+$ 616.25973, [$C_{28}H_{40}B_2N_8Pd$]$^+$: 616.25969 (calculated).

CHN: Calculated for $C_{28}H_{40}B_2N_8Pd$: C: 54.53, H: 6.54, N: 18.17. Found: C: 54.93, H: 6.45, N: 18.30.

Synthesis of [($^{(S,S)\text{-1,2-Cy,BMe}_2}$TC^{H})Fe], 6:



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($^{(S,S)\text{-1,2-Cy,BMe}_2}$TC^{H})(Br)$_2$ (0.2082g, 0.3088 mmol, 1 eq.), **4**, was added to a 20 mL scintillation vial and 15 mL of THF is added. The vial was then cooled over 30 minutes to -35 °C in a freezer. A 2.5 M ^{n}BuLi solution in hexanes (0.500 mL, 1.25 mol, 4.1 eq.) was then added to the vial, which was subsequently agitated and returned to the freezer. The suspension was manually agitated every 2 to 3 minutes over 5-10 minsutes, until the color changed to yellow. The vial was then allowed to warm up to rt while stirring until the suspension became a solution, approximately 45-60 min. The vial was then returned to the -35 °C freezer and cooled at least 30 min. A second 20 mL vial containing Fe(OAc)$_2$ (0.0545 g, 0.3133 mmol, 1 eq.) with 1 mL of THF was also cooled to -35 °C. The solution of the free NHC of **4** was then quantitatively transfered to the solution of Fe(OAc)$_2$ with stirring. The solution immediately turned to an intense dark brown/yellow color. The solution was then allowed to stir for 24 hours at rt. Two additional identical reactions were set up in parallel. The combined solutions were washed into a filter flask and the solution was concentrated under vacuum. The brown sludge was treated with pentanes (3 x 10 mL) to azeotrope off remaining THF, which left a brown-yellow powder. This powder was extracted with benzene (60 mL) and the filtrate was filtered over a short Celite plug and washed until no yellow solution was observed. The benzene solution was concentrated to about 20 mL, then frozen at -35 ˚C. The solution was then lyophilized, leaving a powder. The solid was then redissolved in minimal benzene (8 mL) and stirred until full dissolution. This was then filtered over another small Celite plug and was lyophilized again. This was repeated an additional time. The dried powder was triturated with hexanes (3x15 mL) and was dried under vacuum yielding neon yellow powder (0.317 g, 60.5% yield). Single crystals of **6** were obtained taking a precipitated solution of **6** in roughly 2 mL of benzene and 14 mL of hexanes and heating to reflux, decanting off the solution from the leftover solid. Cooling the solution to ambient temperature overnight formed neon yellow block crystals.

Widescan ^{1}H NMR (C_6D_6, 499.74 MHz): δ 78.42 (s, 2H), 35.85 (s, 2H), 30.09 (s, 2H), 29.20 (s, 2H), 27.26 (s, 2H), 15.00 (s, 2H), 9.04 (s, 6H), 8.85 (s, 2H), 6.79 (s, 2H), -5.94 (s, 2H), -13.39 (s, 2H), -17.42 (s, 2H), -19.13 (s, 2H), -23.08 (s, 2H), -74.77 (s, 6H), -90.24 (s, 2H).

Widescan ^{1}H NMR (ACN-d_3, 599.74 MHz): δ 69.68 (s, 2H), 30.62 (s, 2H), 25.30 (s, 2H), 24.30 (s, 2H), 22.68 (s, 2H), 14.80 (s, 2H), 8.32 (s, 2H), 7.11 (s, 2H), 4.66 (s, 6H), -3.57 (s, 2H), -13.19 (s, 2H), -16.37 (s, 2H), -17.18 (s, 2H), -18.52 (s, 2H), -52.09 (s, 2H), -65.75 (s, 2H).

Evans Method: 3.4 μ_B.

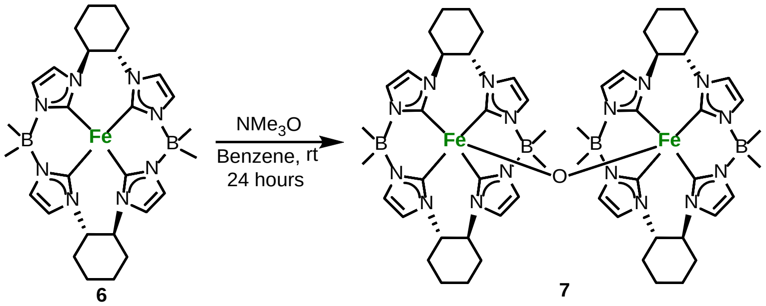
DART HR MS (*m/z*): $[M]^+$: 566.29171 (found), $[C_{28}H_{40}B_2N_8Fe]^+$: 566.29115 (calculated).

UV-VIS (THF): 365 nm (7300 L/mol*cm), 445 nm (4500 L/mol*cm).

Calculated for $C_{28}H_{40}B_2N_8Fe$: C: 59.40, H: 7.12, N: 19.78. Found: C: 57.96, H: 6.96, N: 18.05.

Unsatisfactory CHN analysis is likely due to extreme air sensitivity of **6**. Strong deviation in N value is likely related to uncombustable boron nitride adducts forming during conmbustion.[4]

Synthesis of [((${}^{(S,S)\text{-}1,2\text{-}Cy,BMe_2}TC^{H}$)Fe)$_2$O] 7:



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Trimethylamine *N*-oxide (0.0031 g, 0.0413 mmol, 1 eq.) was added to a 20 mL scintillation vial. To this was added **6** (0.0482 g, 0.0851 mmol, 2 eq.), dissolved in 10 mL of benzene. This solution was stirred at ambient temperature for 24 hours. Following this, the solution was filtered through a short pad of Celite and washed with an additional 5 mL of benzene, until no more color remained. This solution was thoroughly dried, and 3 mL of hexanes were added to the residue, decanted off. This was repeated 3 times and produced **7** as a brown powder (0.0432 g, 88.4% yield). Single crystals were grown by diffusing hexanes into a concentrated benzene solution of **7**, resulting in very dark red crystals.

^{1}H NMR (C_6D_6, 599.74 MHz): δ 7.14 (s, 4H), 6.73 (s, 4H), 6.59 (bs, 4H), 6.07 (s, 4H), 3.40 (d, *J* = 6.8 Hz, 4H), 1.62 (d, *J* = 9.0 Hz, 4H), 1.45 (d, *J* = 10.7 Hz, 4H), 1.35-1.10 (m, 16H), 1.02 (d, *J* = 12.2 Hz, 4H), 0.93 (d, *J* = 9.9 Hz, 4H), 0.66 (s, 12H), -0.15 (s, 12H).

^{1}H NMR (MeCN-d_3, 599.74 MHz): δ 7.19 (s, 4H), 7.07 (s, 4H), 7.05 (s, 4H), 6.81 (s, 4H), 6.54 (bs, 4H), 3.87 (s, 4H), 1.63 (m, 4H), 1.32 (m, 22H), 1.05 (d, *J* = 11.6 Hz, 4H), 0.92 (m, 4H).

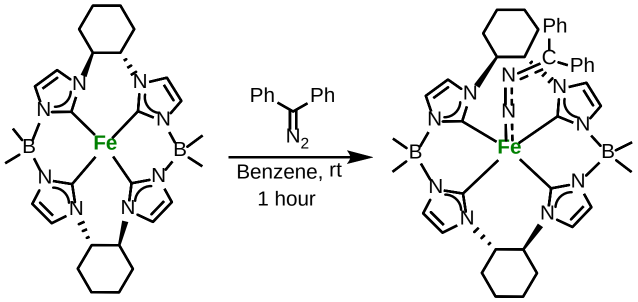
^{13}C NMR (CD_2Cl_2, 149.94 MHz): 123.40, 122.86, 121.86, 117.50, 68.06, 37.65, 30.99, 25.91, 25.65, 17.32, 13.11 (Fe-C signals not observed due metal proximity with anti-ferromagnetic coupling).[5]

IR: 3140, 2931, 2857, 1555, 1448, 1424, 1398, 1348, 1323, 1290, 1273, 1239, 1229, 1208, 1170, 1157, 1135, 1124, 1113, 1045, 1034, 952, 943, 919, 879, 857, 826, 793, 719, 697, 691, 682, 641 cm^{-1}.

CHN: Calculated for $C_{56}H_{80}B_4Fe_2N_{16}O \bullet C_6H_6$: C: 60.72, H: 7.07, N: 18.27. Found: C: 60.50, H: 7.49, N: 16.59.

Unsatisfactory N value for CHN is likely due to uncombustable boron nitride adducts being formed on combustion.[4]

Synthesis of $[(^{(S,S)\text{-}1,2\text{-}Cy,BMe_2}TC^{H})Fe\text{-}N{=}N{=}CPh_2]$, 8:



6

8

In a 20 mL scintillation vial, **6** (0.0746 g, 0.1318 mmol, 1 eq.) was added followed by the addition of 5 mL of benzene. A solution of diphenyldiazomethane (0.0395 g, 0.2034 mmol, 1.54 eq.) in 2 mL of benzene was added, which caused an immediate color change to dark brown. This solution was then stirred at ambient temperature for 1 hour. The solvent was removed under vacuum; hexanes were added to the vial and stirred. The solid was then allowed to settle and the solution was pipetted off. This was repeated 3 times with 10 mL of solvent, until no pink color appeared. The residue was then dissolved in 12 mL of 1:1 benzene:hexanes solution and filtered over a short pad of Celite. This was concentrated in vacuo; the solid was then redissolved in roughly 5 mL of toluene, layered with 15 mL of hexanes, and stored overnight at -35 °C. The mother liquor was decanted off the precipitate. The crystals were washed 3 times with 5 mL of hexanes and dried under vacuum, yielding black crystals (0.0765 g, 76.3% yield). This solid was stored at -35 °C due to slow decomposition to **9**. Single crystals of **8** were grown by dissolving **8** in 0.5 mL of toluene and carefully layering 4 mL of hexanes into the solution at ambient temperature overnight, yielding very dark red plates.

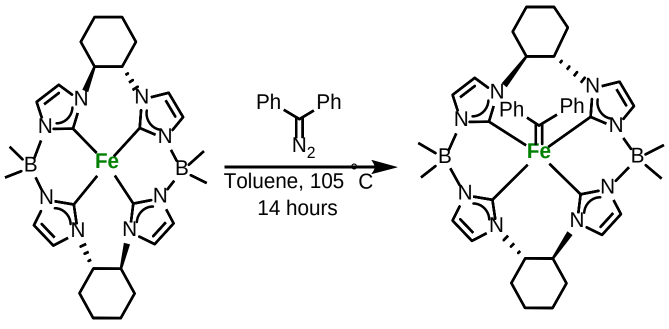
Widescan ^{1}H NMR (C_6D_6, 599.74 MHz): δ 46.95 (s), 22.35 (s), 11.51 (bs), 4.55 (s), 2.97 (s), 2.41 (s), 1.91 (s), 1.12 (s), 0.05 (s), -0.71 (s), -103.45 (s), -104.70 (s).

Evans Method: 2.5 μ_B.

IR: 3132, 2934, 2038, 1657, 1569, 1488, 1448, 1430, 1398, 1335, 1284, 1236, 1208, 1155, 1124, 1067, 1047, 944, 921, 878, 835, 824, 795, 765, 755, 724, 689, 637 cm^{-1}.

UV-Vis (THF): 360 nm (19000 L/cm*mol), 445 (7200 L/cm*mol), 750 nm (1400 L/cm*mol), 785 nm (1500 L/cm*mol).

Synthesis of [[($^{(S,S)\text{-}1,2\text{-Cy,BMe}_2}$TC^{H})Fe=CPh$_2$] 9:



6 **9**

In a 200 mL Schlenk flask, **6** (0.1257 g, 0.2220 mmol, 1 eq.) was dissolved in 45 mL of toluene. To this solution, diphenyldiazomethane (0.0970 g, 0.4884 mmol, 2.2 eq.) was added with 5 mL of toluene. The flask was sealed, removed from the glovebox, and heated in an oil bath at 105 °C for 14 hours. The flask was then cooled and the solvent was removed under high vacuum. Following this, the flask was brought back into the glovebox. The residue was then treated with 20 mL of a 9:1 toluene:hexanes solution and filtered over a Celite plug. This was repeated three times more with 10 mL of the solution, until no green color was observed in the filtrate. The filtrate was concentrated to dryness, then 4 mL of acetonitrile was added. The solution was then cooled to -35 °C and allowed to settle. The acetonitrile was carefully pipetted off; this was repeated four times total. The green solid was dried, redissolved in 3 mL of benzene, and lyophilized to yield **9** as a dark green powder (0.0984 g, 60.5% yield). Single crystals of **9** were grown by layering a concentrated solution of **9** in hexanes (1 mL) into acetonitrile (1 mL) at -35 °C, yielding dark green plates.

^{1}H NMR (C_6D_6, 599.74 MHz): δ 7.59 (bs, 4H), 7.31 (s, 2H), 7.14 (s, 2H), 7.06 (t, J = 8.0 Hz, 2H), 6.73 (t, J = 8.0 Hz, 4H), 6.52 (s, 2H), 6.19 (s, 2H), 4.78 (dt, J_1 = 11.8 Hz, J_2 = 2.8 Hz, 2H), 3.29 (dt, J_1 = 11.8 Hz, J_2 = 3.7 Hz, 2H), 1.52 (s, 2H), 1.28 (d, J = 11.4 Hz, 2H), 1.22 (d, J = 12.7, 2H), 1.14 (d, J = 5.7 Hz, 2H), 1.06 (dq, ${}^3J_1$ = 12.7 Hz, ${}^2J_2$ = 3.0 Hz), 0.83 (s, 6H), 0.86 – 0.70 (m, 6H), 0.26 (s, 6H).

^{13}C NMR (C_6D_6, 149.94 MHz): δ 309.30, 188.82, 172.37, 160.34, 128.34, 126.29, 123.89, 123.85, 123.35, 123.28, 121.65, 114.83, 114.77, 65.66, 53.45, 53.40, 36.13, 30.66, 24.78, 24.37, 18.83, 13.02.

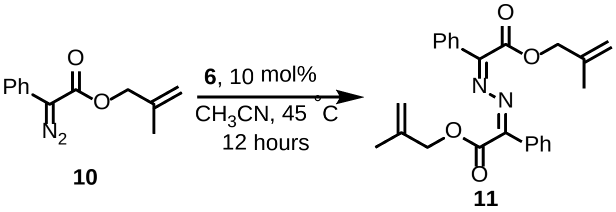
IR: 3136, 2932, 2162, 2036, 1979, 1569, 1438, 1401, 1351, 1286, 1267, 1236, 1208, 1158, 1121, 1069, 1048, 946, 881, 852, 825, 797, 769, 729, 686, 638 cm^{-1}.

DART HRMS: [M+H]$^+$: 733.37506 (found), [$C_{41}H_{51}B_2FeN_8$]: 733.37722 (calculated)

UV-Vis (THF): 420 nm (11000 L/cm*mol), 635 nm (350 L/ cm*mol), 745 nm (120 L/ cm*mol).

CHN: Calculated for $C_{41}H_{50}B_2FeN_8$: C: 67.24, H: 6.88, N: 15.30. Found: C: 66.91, H: 6.90, N: 15.22.

Catalytic Synthesis of 11:



A solution of 2-methylallyl 2-diazo-2-phenylacetate (**10**) (0.1106 g, 0.5115 mmol, 1 eq.) in 4 mL of acetonitrile was added to **6** (0.0281 g, 0.496 mmol, 0.1 eq.) in a 20 mL scintillation vial. The solution immediately turned dark green, then was heated at 45 °C for 12 hours, during which the dark green color turned to yellow-orange. The solution was then concentrated under reduced pressure and the product was purified by silica gel flash chromatography with 9:1 hexanes:ethyl acetate to yield **11** as a tan-yellow solid (0.0837, 81.4%).

Control reaction of **10** without **6** in acetonitrile showed no formation of **11** after 16 hours at 45 °C.

^{1}H NMR ($CDCl_3$, 499.74 MHz): δ 7.80 (dd, J_1 = 8.1 Hz, J_2 = 1.3 Hz, 4H), 7.50 (tt, J_1 = 8.4 Hz, J_2 = 0.8 Hz, 2H), 7.43 (t, J = 7.8 Hz, 4H), 5.13 (s, 2H), 4.99 (s, 2H), 4.86 (s, 4H), 1.79 (s, 6H).

^{13}C NMR ($CDCl_3$, 149.94 MHz): δ 165.14, 162.30, 139.33, 132.17, 131.33, 128.87, 128.24, 128.20, 114.76, 68.87, 19.83.

IR: 2922, 1727, 1656, 1605, 1574, 1495, 1446, 1366, 1325, 1303, 1198, 1178, 1157, 1073, 1033, 1012, 964, 919, 908, 863, 840, 811, 778, 746, 719, 682 cm^{-1}.

DART HRMS: $[M+H]^+$: 405.18192 (found); $[C_{24}H_{25}N_2O_4]^+$: 405.18088 (calculated).

X-ray structure for 4

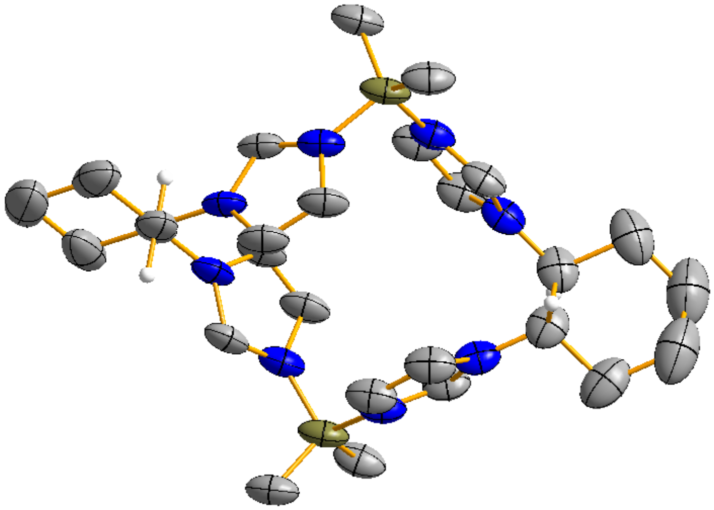


Figure S1A: X-ray crystal structure of $^{(S,S)\text{-1,2-Cy,BMe}_2}$TC^{H})(Br)$_2$, **4**. Blue, gray, and olive ellipsoids (50% probability) represent N, C, and B atoms, respectively. Solvent molecules, counteranions, and H atoms are omitted for clarity (excluding protons off of chiral carbons, which are included as white spheres).

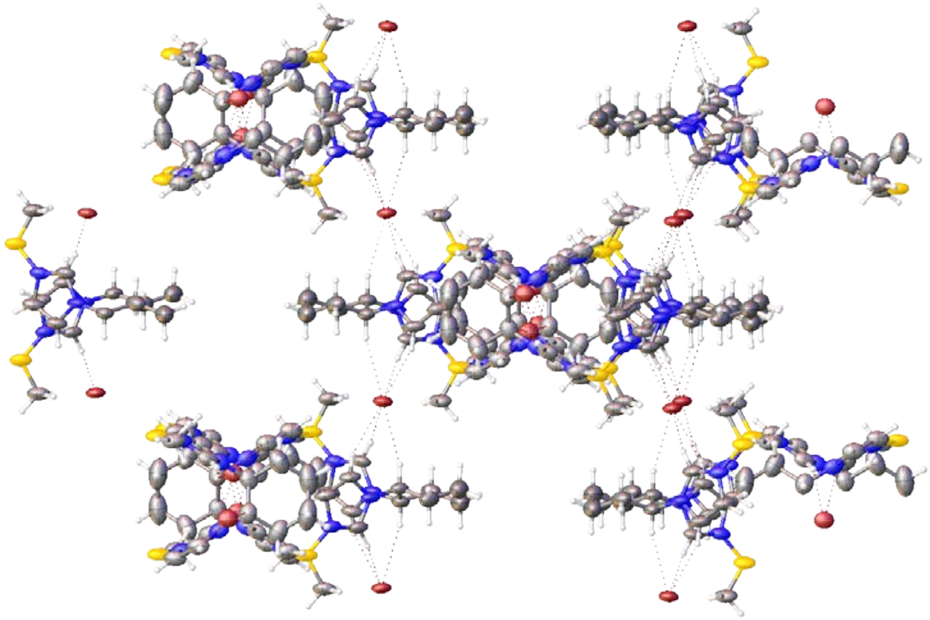


Figure S1B: A packing diagram of macrocycle **4**, showing the interactions of bromide ions (in red) between macrocycles to balance charge.

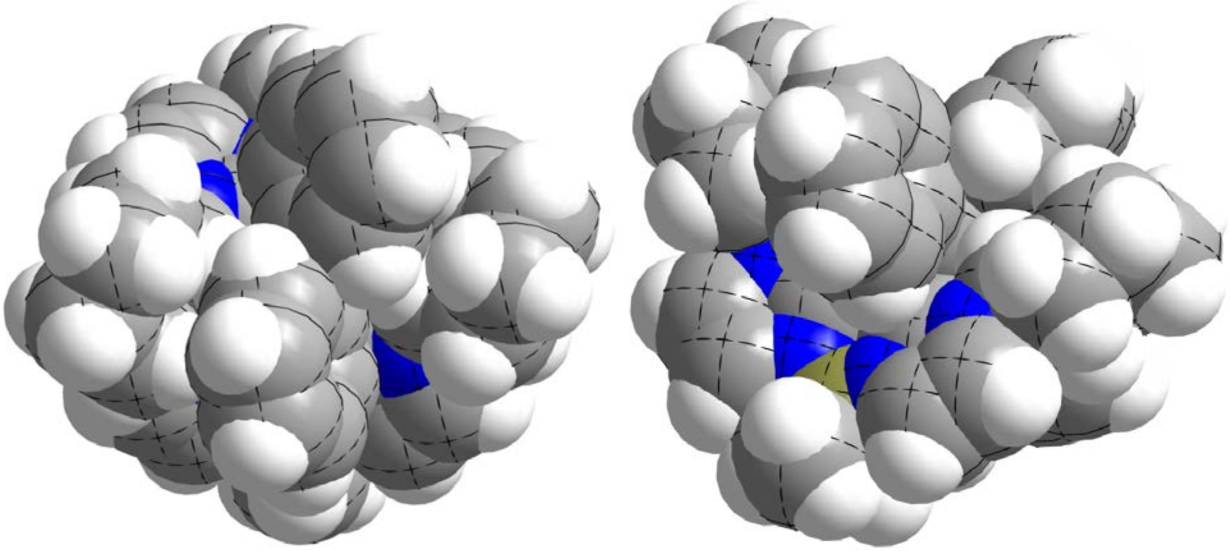


Figure S2: Space filling model of **9** on a top view (left) and side view (right). Green, blue, gray, olive, and white spheres represent Fe, N, C, B, and H atoms, respectively.

Molecule	**4**	**5**	**6**	**7**	**8**	**9**
Empirical formula	$C_{14}H_{22}BBrN_4$	$C_{28}H_{40}B_2N_8Pd$	$C_{28}H_{40}B_2FeN_8$, C_6H_6	$C_{56}H_{80}B_4Fe_2N_{16}O$, C_6H_6	$C_{41}H_{50}B_2FeN_{10}$	$C_{41}H_{50}B_2FeN_8$, C_2H_3N
Color	Colorless	Colorless	Yellow	Red	Red	Green
Formula Weight	337.07	616.7	644.26	1226.4	760.38	773.41
Source, λ (Å)	Cu, 1.54178	Mo, 0.71073	Mo, 0.7103	Mo, 0.71073	Mo, 0.71073	Mo, 0.71073
Crystal System	Tetragonal	Monoclinic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$I4_122$	$P2_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
T(K)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
a (Å)	15.7206(16)	21.2621(10)	13.8984(3)	12.5497(13)	15.5943(14)	11.266(4)
b (Å)	15.7206(16)	18.5788(9)	14.9407(3)	13.4906(13)	17.0596(16)	13.314(4)
c (Å)	24.616(3)	22.9415(11)	15.9817(3)	36.309(4)	29.618(2)	26.872(8)
α (°)	90	90	90	90	90	90
β (°)	90	116.0270(10)	90	90	90	90
γ (°)	90	90	90	90	90	90
V (Å^3)	6083.5(15)	8143.4(7)	3318.63(12)	6147.3(11)	7879.4(12)	4031(2)
Z	8	8	4	4	8	4
d_{calc}(g cm^{-3})	0.736	1.006	1.289	1.325	1.282	1.274
μ (mm^{-1})	1.816	0.479	0.492	0.528	0.427	0.417
R_1/wR_2	0.0324/0.0957	0.0367/0.0853	0.0321/0.0855	0.0534/0.1199	0.0604/0.1172	0.0530/0.1052
Flack Par.	< 0	0.000(12)	< 0	0.009(6)	0.023(10)	0.017(9)
Indep. Refl.	2983	54143	11057	20489	19374	9934

Table S1: Crystallographic data for complexes **4-9**.

	6	**7**	**8_1**	**8_2**	**9**
Bond Lengths (Å)					
$Fe-C_1$	2.0057(15)	2.070(3)	2.023(5)	2.019(5)	2.013(4)
$Fe-C_2$	1.9385(14)	2.017(3)	1.986(5)	1.990(5)	1.977(3)
$Fe-C_3$	2.0049(14)	2.068(3)	2.044(5)	2.032(5)	2.020(3)
$Fe-C_4$	2.0057(15)	2.014(3)	1.980(5)	1.978(5)	1.969(4)
Fe_1-O_1		1.816(2)			
Fe_2-O_1		1.816(2)			
$Fe=N_9$			1.767(4)	1.779(4)	
$N_9=N_{10}$			1.217(5)	1.215(5)	
$N_{10}=C_{29}$			1.345(6)	1.327(6)	
$C_{29}-C_{30}$			1.459(7)	1.477(8)	1.508(5)
$C_{29}-C_{36}$			1.466(7)	1.471(7)	1.490(5)
$Fe-C_{29}$					1.814(4)
Bond Angles (°)					
C_1-Fe-C_2	91.50(6)	84.23(12)	84.9(2)	85.9(2)	86.82(14)
C_1-Fe-C_3	166.64(6)	142.37(13)	143.6(2)	148.5(2)	153.98(15)
C_1-Fe-C_4	87.73(6)	86.29(13)	88.5(2)	87.5(2)	89.00(16)
C_2-Fe-C_3	88.33(6)	86.67(13)	86.7(2)	85.7(2)	88.69(14)
C_2-Fe-C_4	174.87(7)	152.07(14)	156.2(2)	152.6(2)	162.67(16)
C_3-Fe-C_4	91.25(6)	84.96(12)	85.1(2)	86.2(2)	87.71(15)
Fe_1-O-Fe_2		177.33(15)			
$Fe=N_9=N_{10}$			173.8(4)	174.5(4)	
$N_9=N_{10}=C_{29}$			138.1(4)	140.4(5)	
$C_{30}-C_{29}-C_{36}$			124.0(5)	123.8(5)	114.4(3)
$Fe-C_{29}-C_{30}$					123.3(3)
τ_4 or τ_5	0.14	0.13	0.22	0.07	0.14

Table S2: Selected bond lengths and angles for compounds **6** – **9**. Note: **8_1** and **8_2** refer to the different residues in the asymmetric unit for **8**. These molecules are stereoisomers of one another due to free rotation on the bond of N_{10}.

Annotated NMRs, IRs, UV-vis, and HRMS for 1-11.

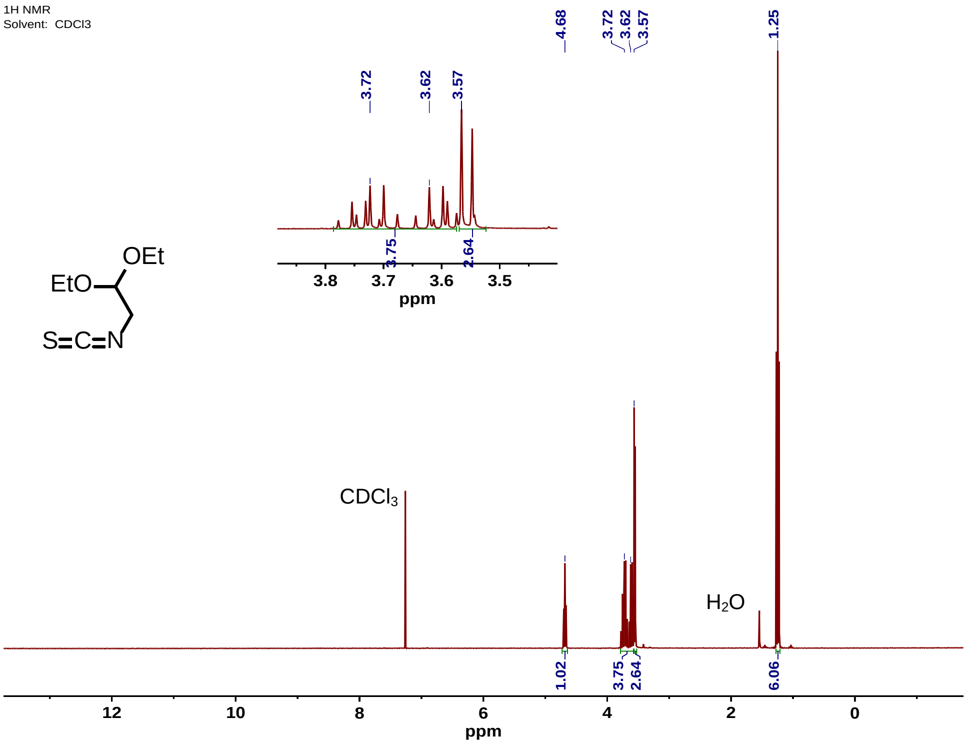


Figure S3: ^{1}H NMR of **1** in CDCl$_3$.

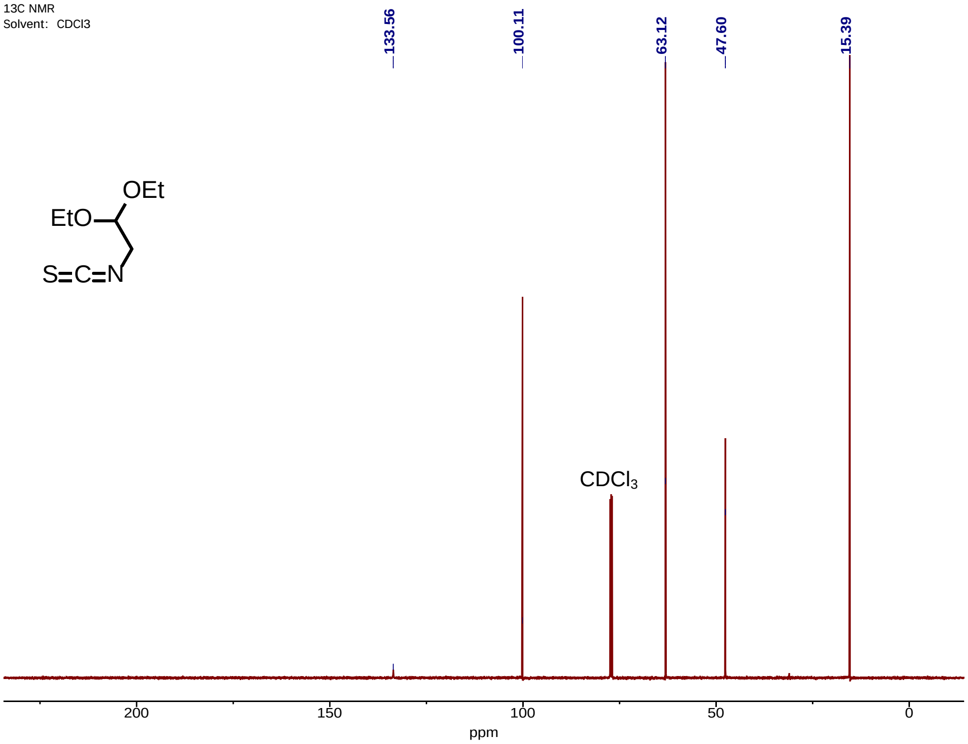


Figure S4: ^{13}C NMR of **1** in CDCl$_3$.

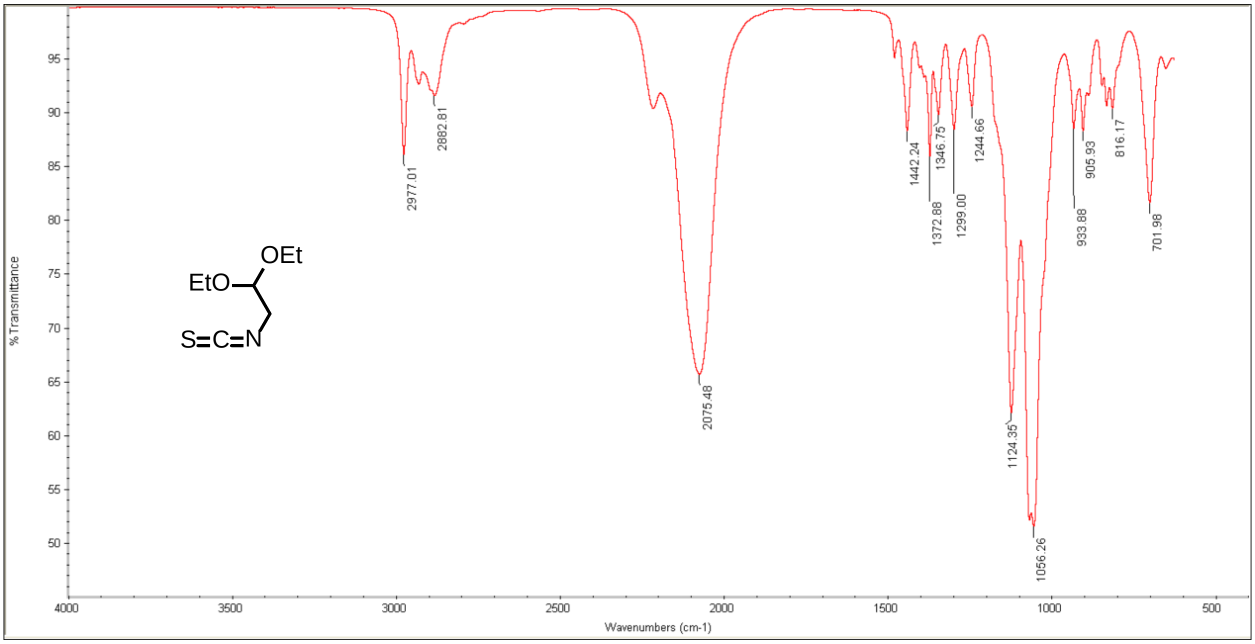


Figure S5: IR of **1**.

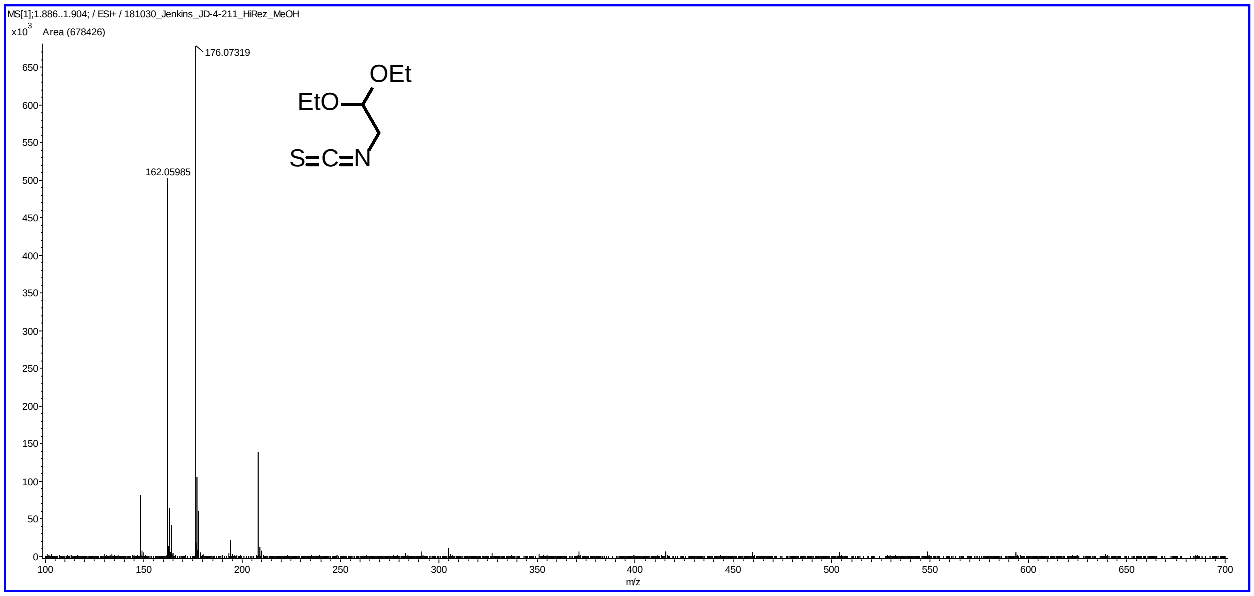


Figure S6: DART HR MS of **1**.

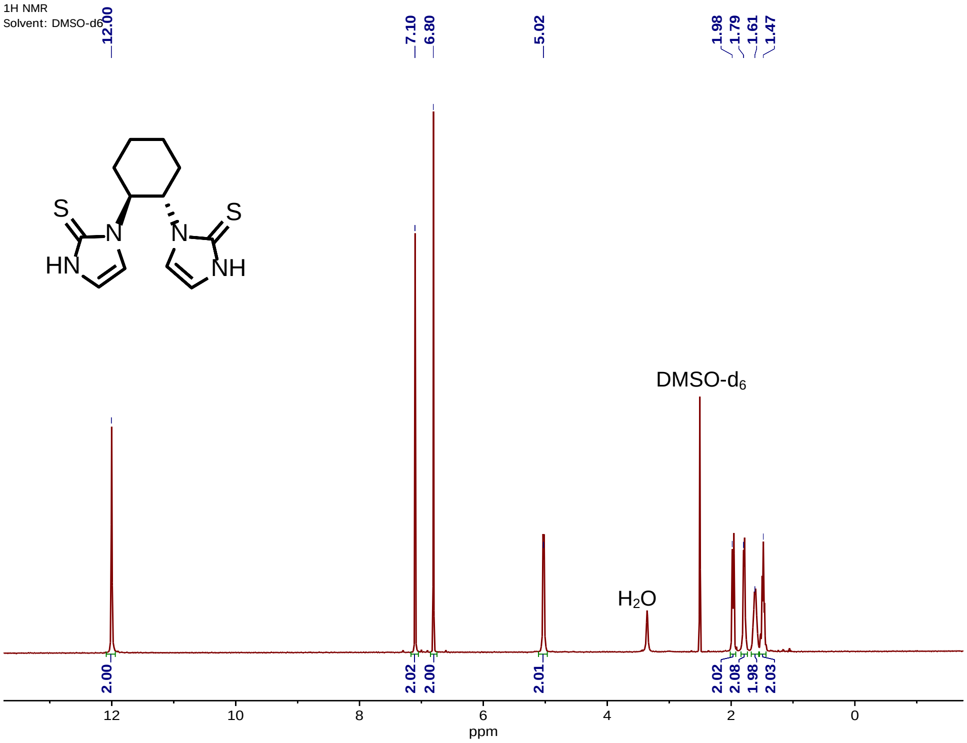


Figure S7: ^{1}H NMR of **2** in DMSO-d$_6$.

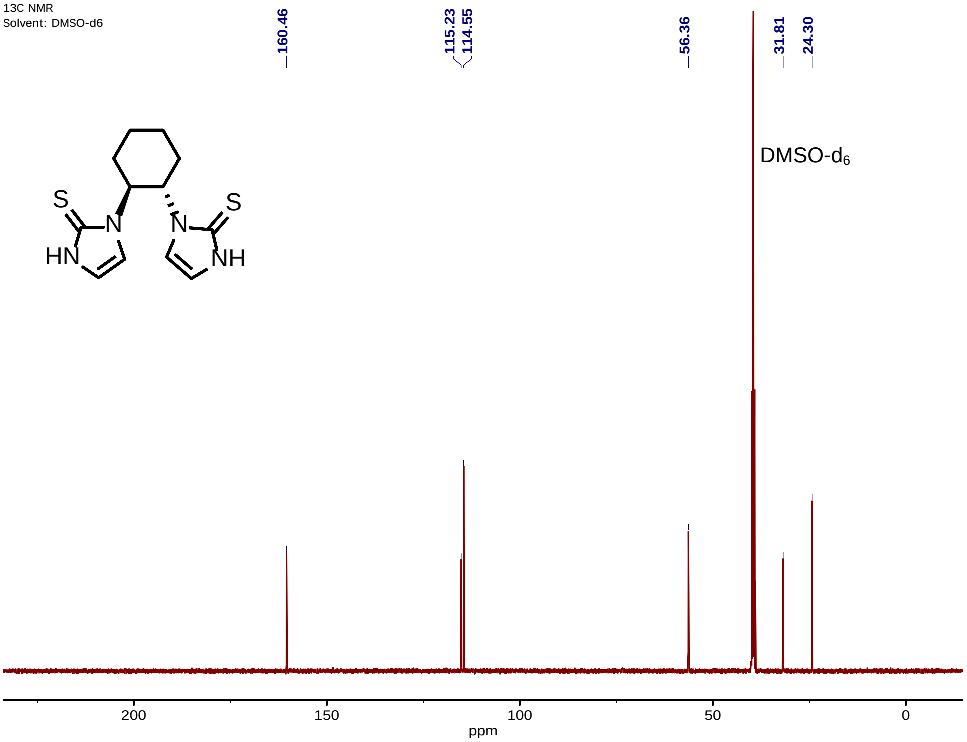


Figure S8: ^{13}C NMR of **2** in DMSO-d$_6$.

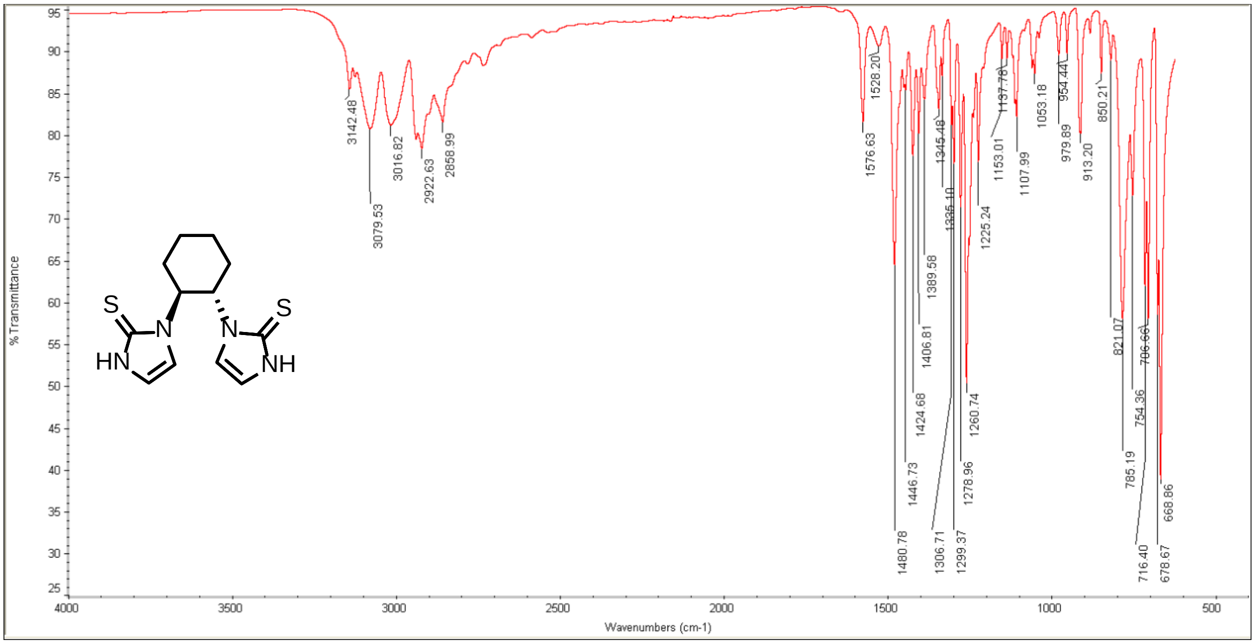


Figure S9: IR of **2**.

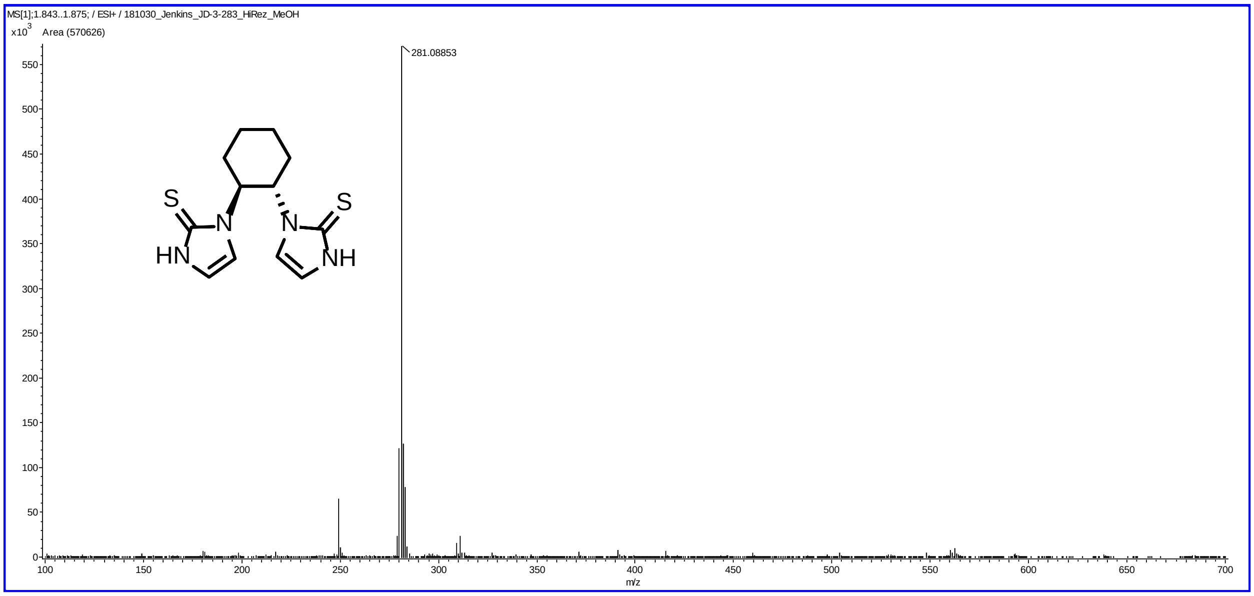


Figure S10: DART HR MS of **2**.

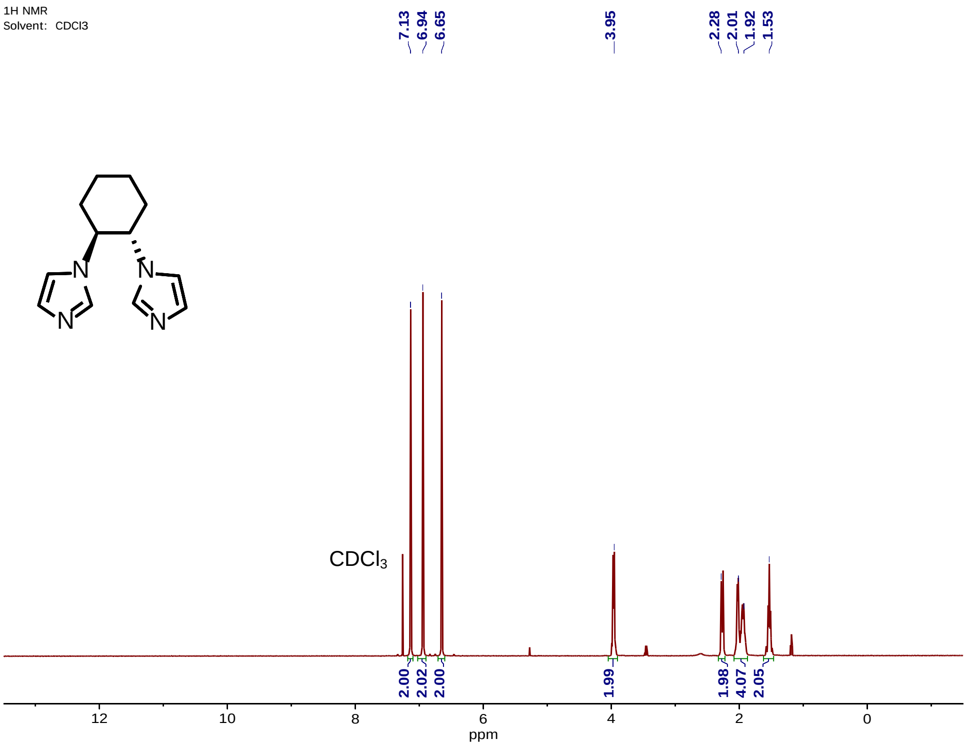


Figure S11: ^{1}H NMR of **3** in $CDCl_3$.

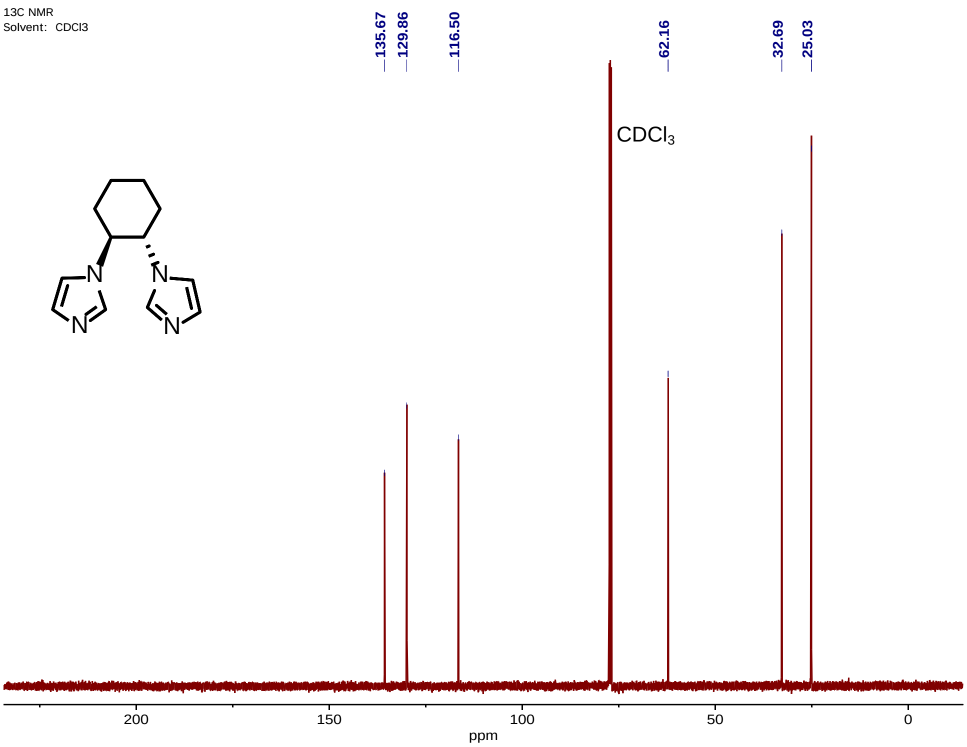


Figure S12: ^{13}C NMR of **3** in $CDCl_3$.

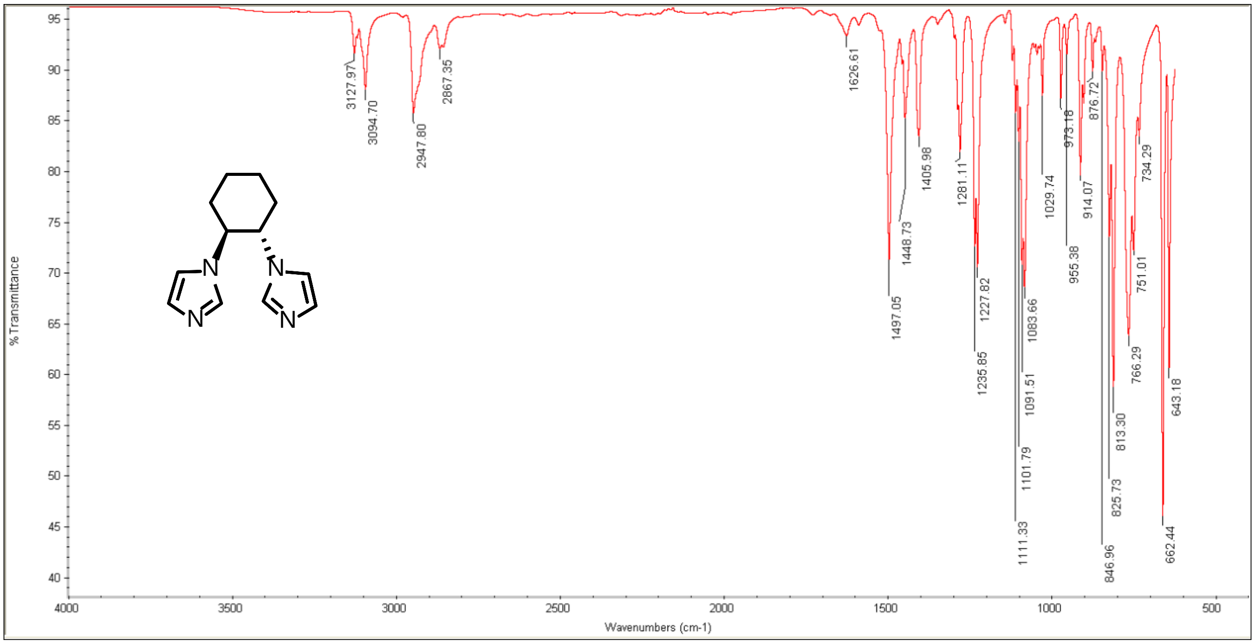


Figure S13: IR of **3**.

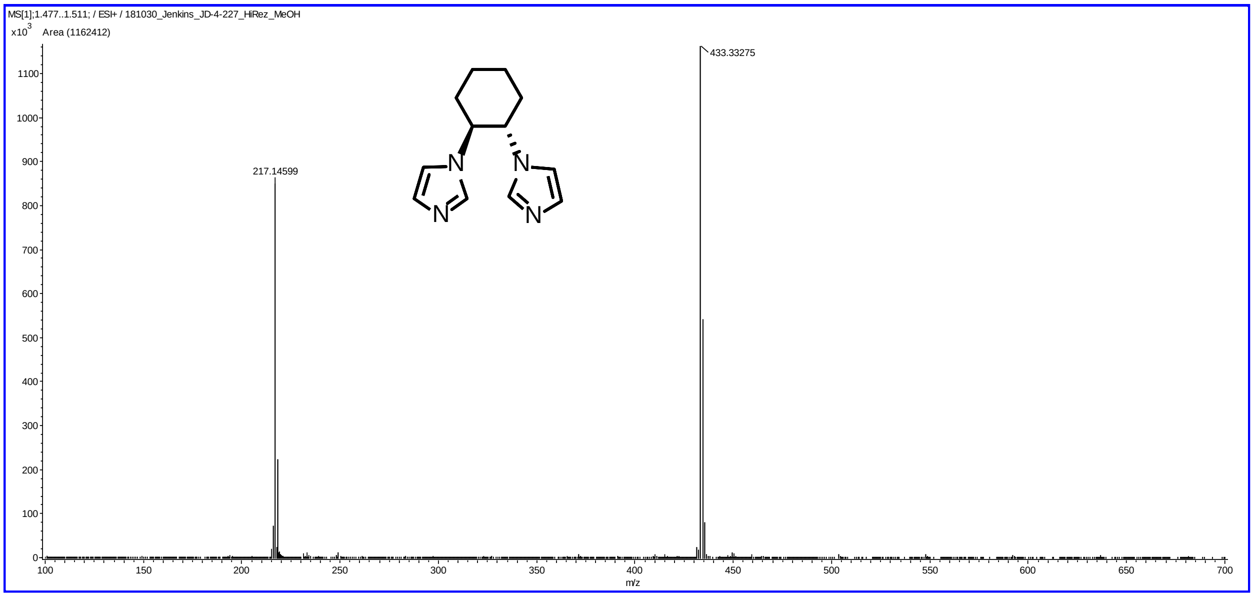


Figure S14: DART HR MS of **3**.

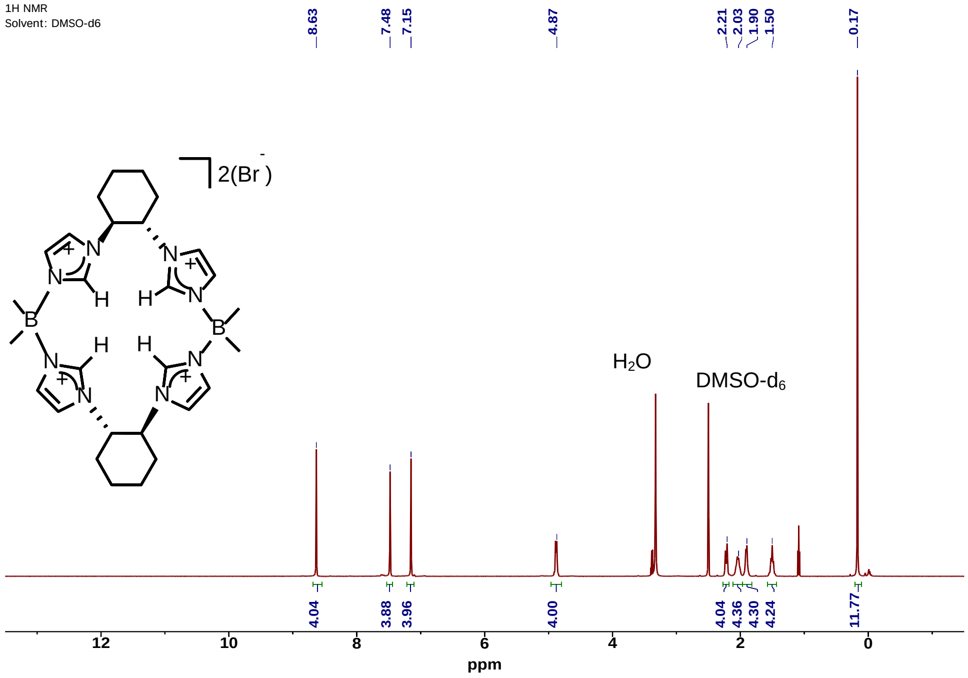


Figure S15: ^{1}H NMR of **4** in DMSO-d$_6$.

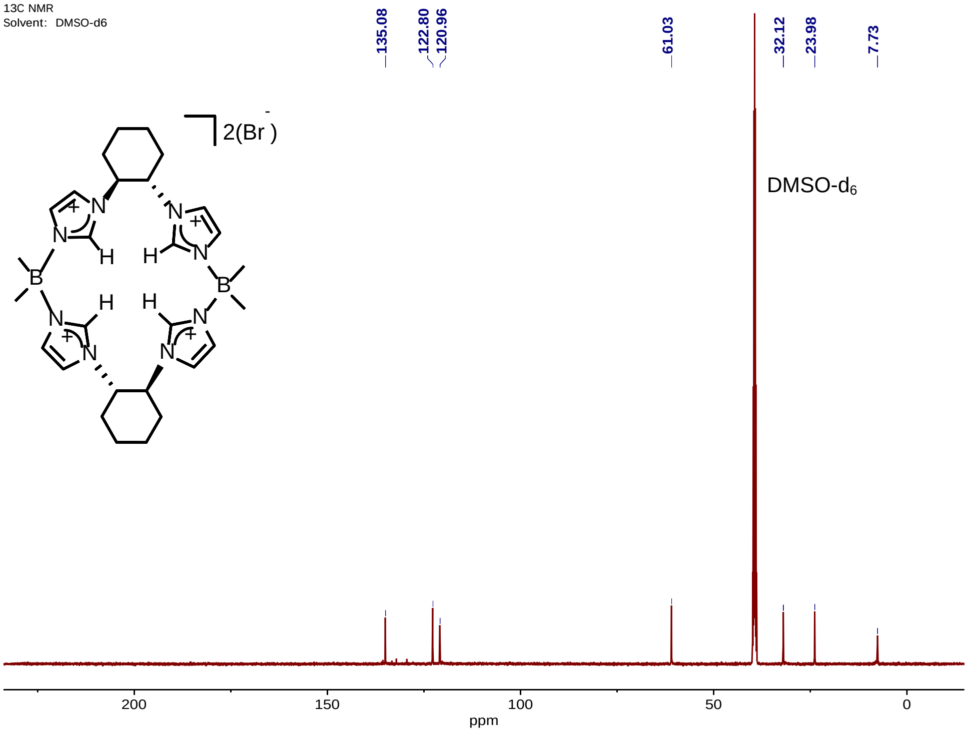


Figure S16: ^{13}C NMR of **4** in DMSO-d$_6$.

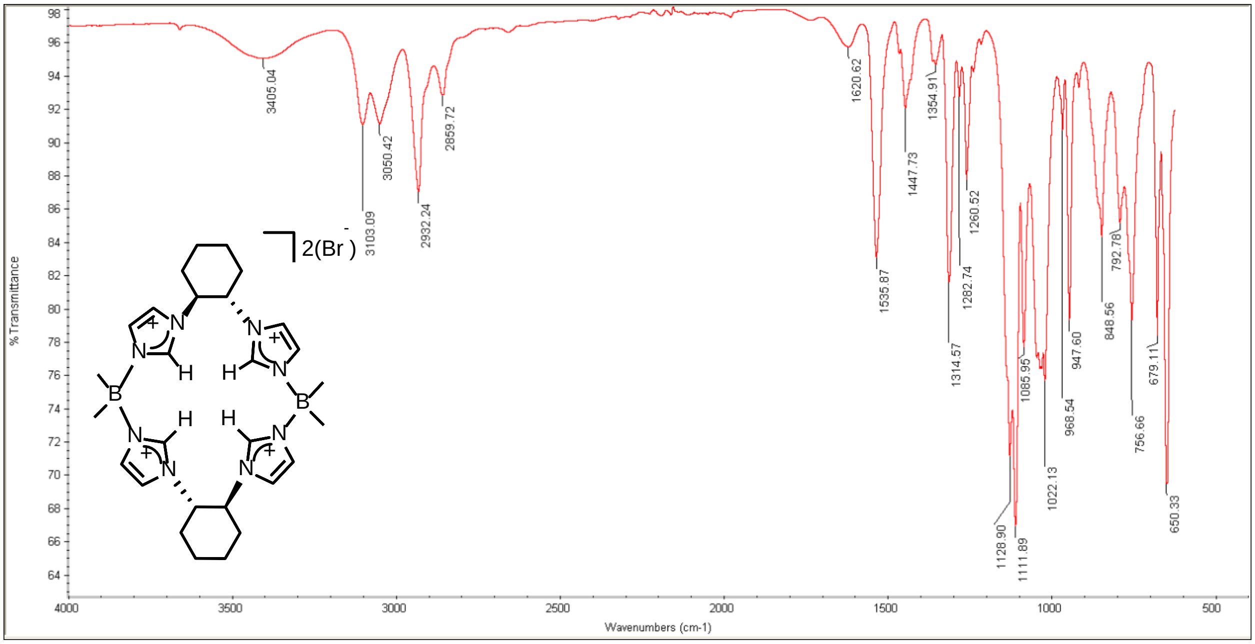


Figure S17: IR of **4**.

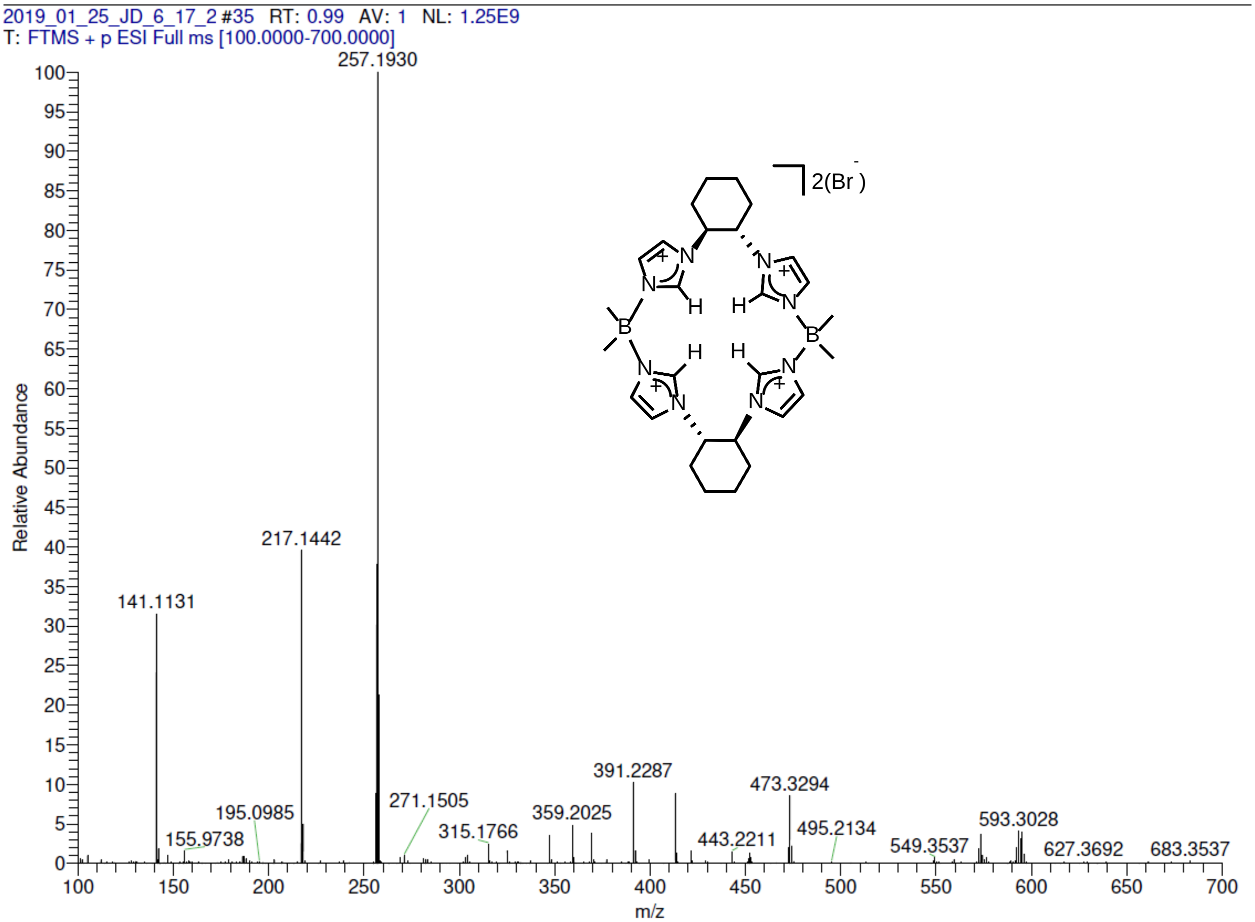


Figure S18: ESI HR MS of **4**.

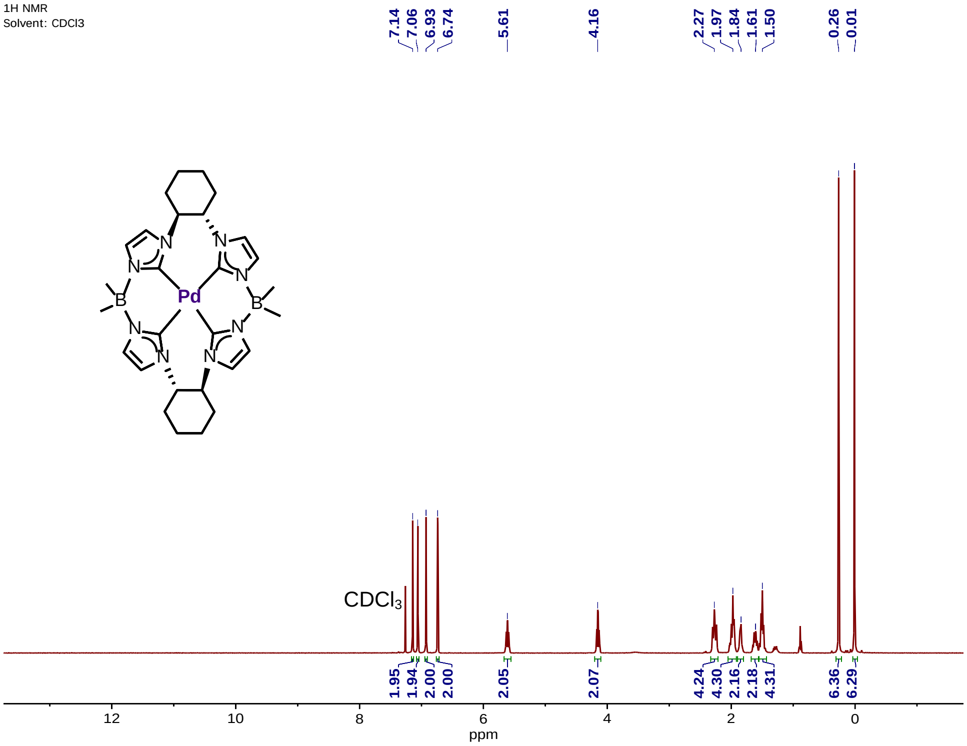


Figure S19: ^{1}H NMR of **5** in $CDCl_3$.

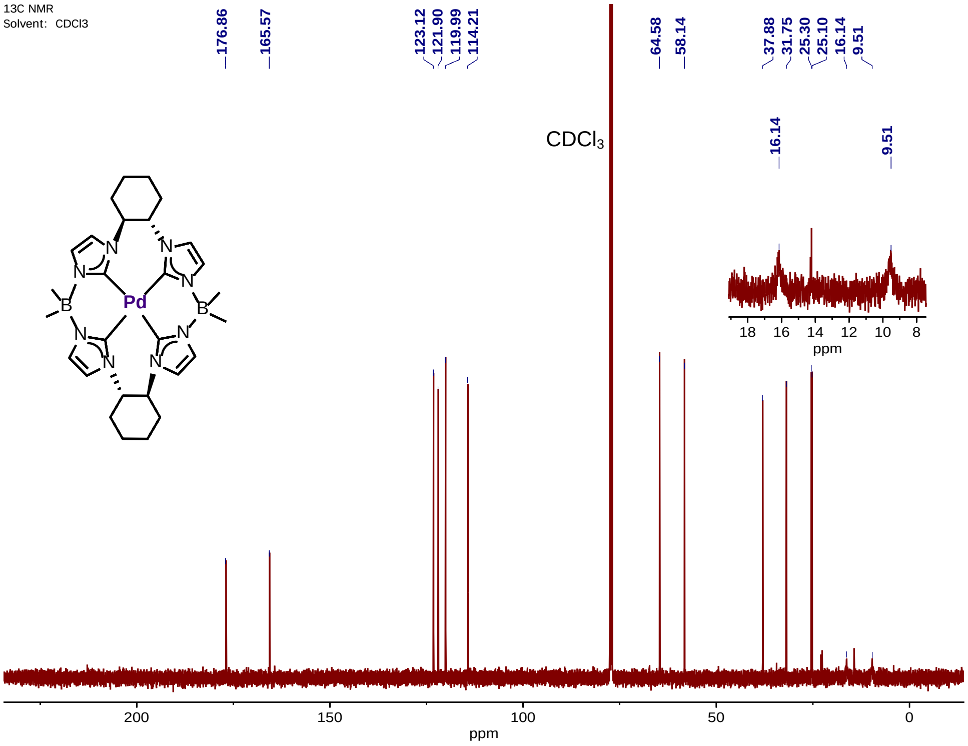


Figure S20: ^{13}C NMR of **5** in $CDCl_3$.

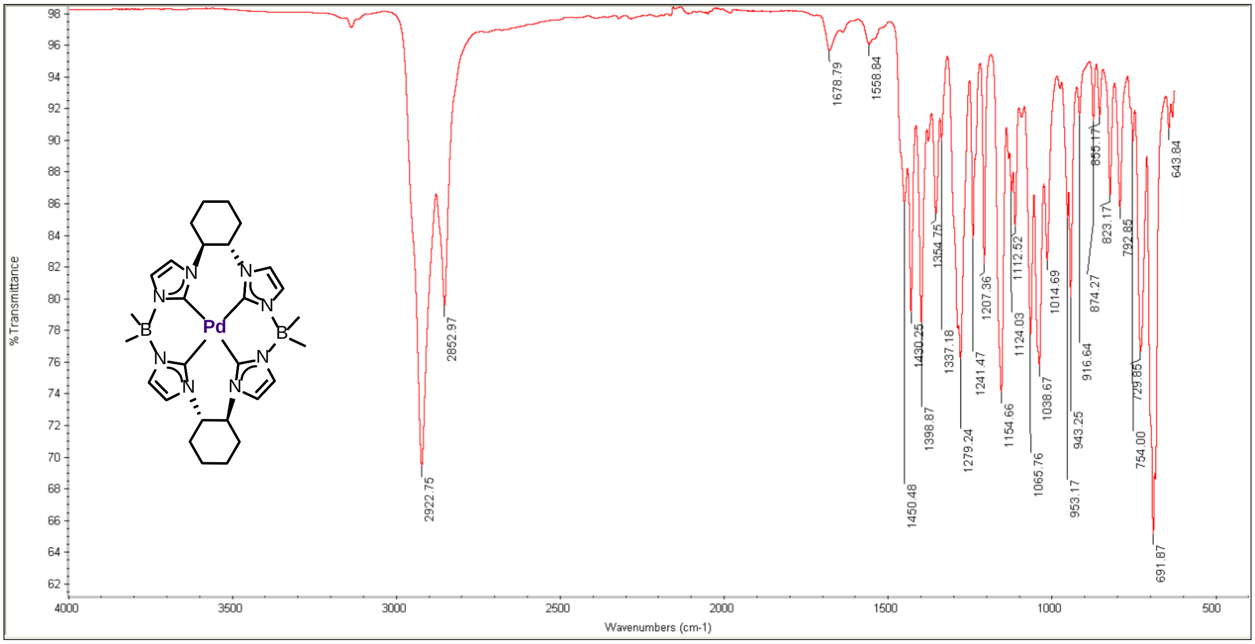


Figure S21: IR of **5**.

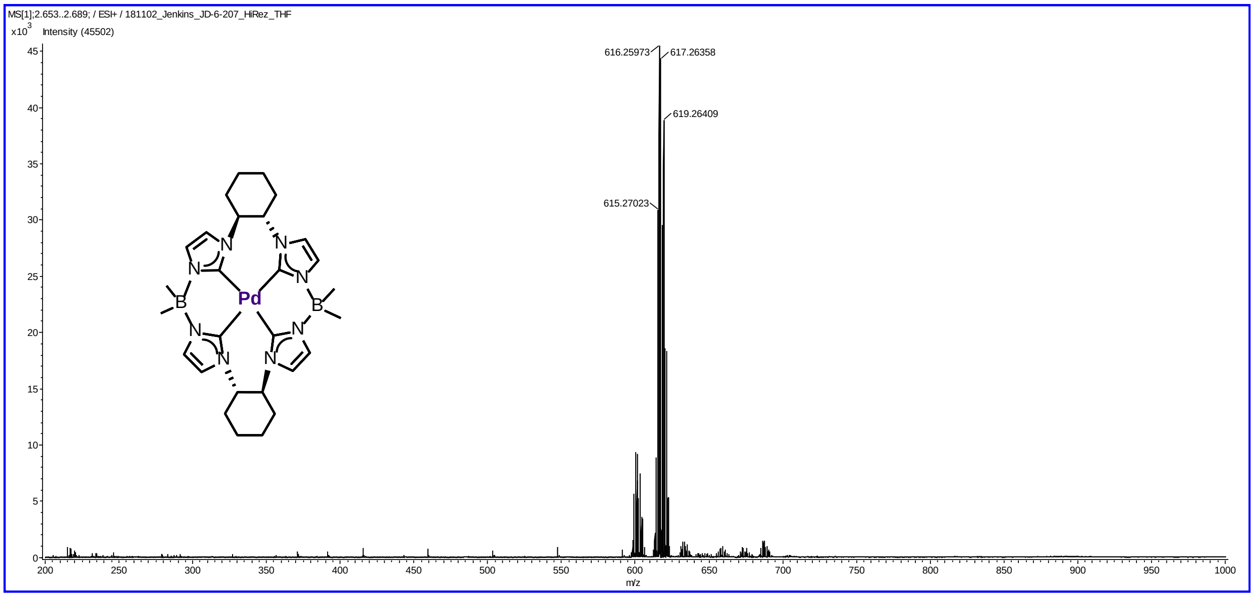


Figure S22: DART HR MS of **5**.

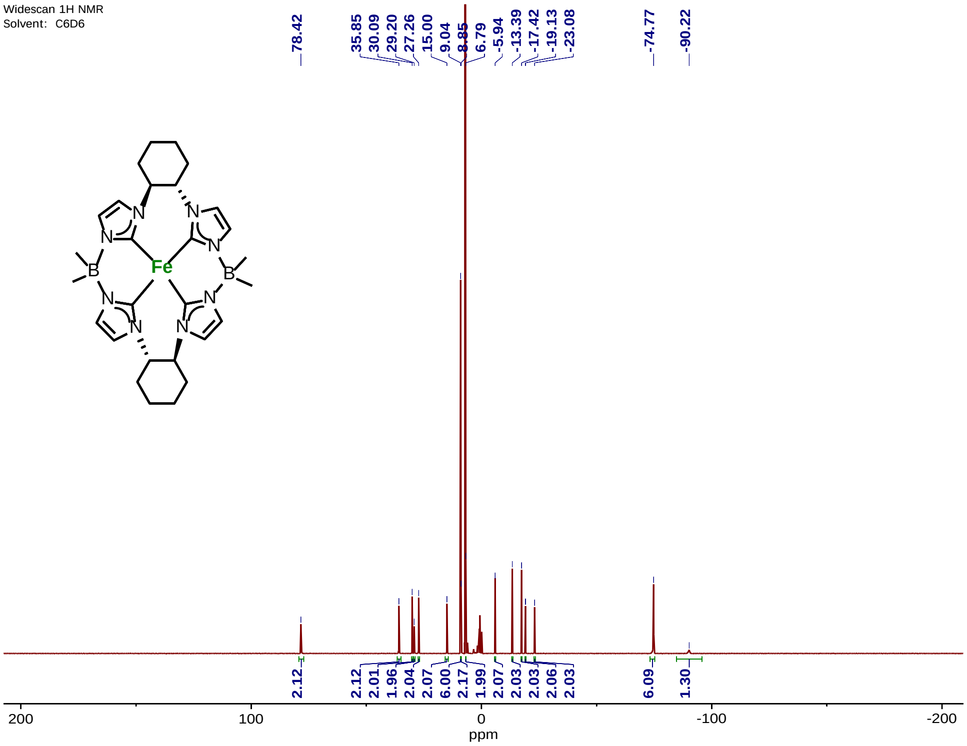


Figure S23: Widescan paramagnetic ^{1}H NMR of **6**.

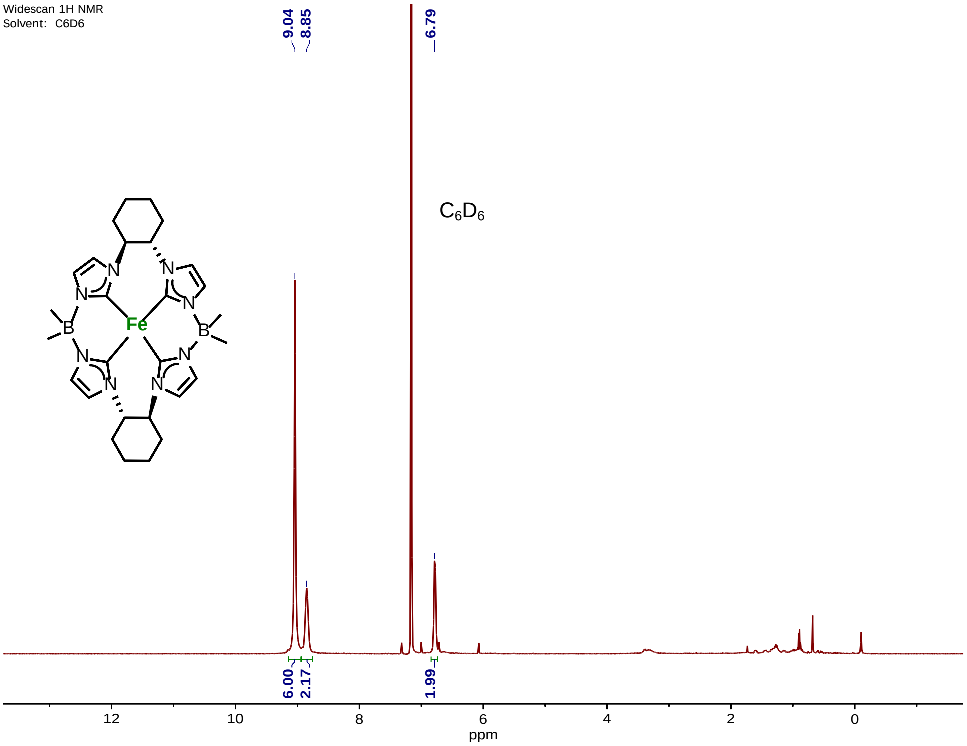


Figure S24: Expansion of diamagnetic region for **6**.

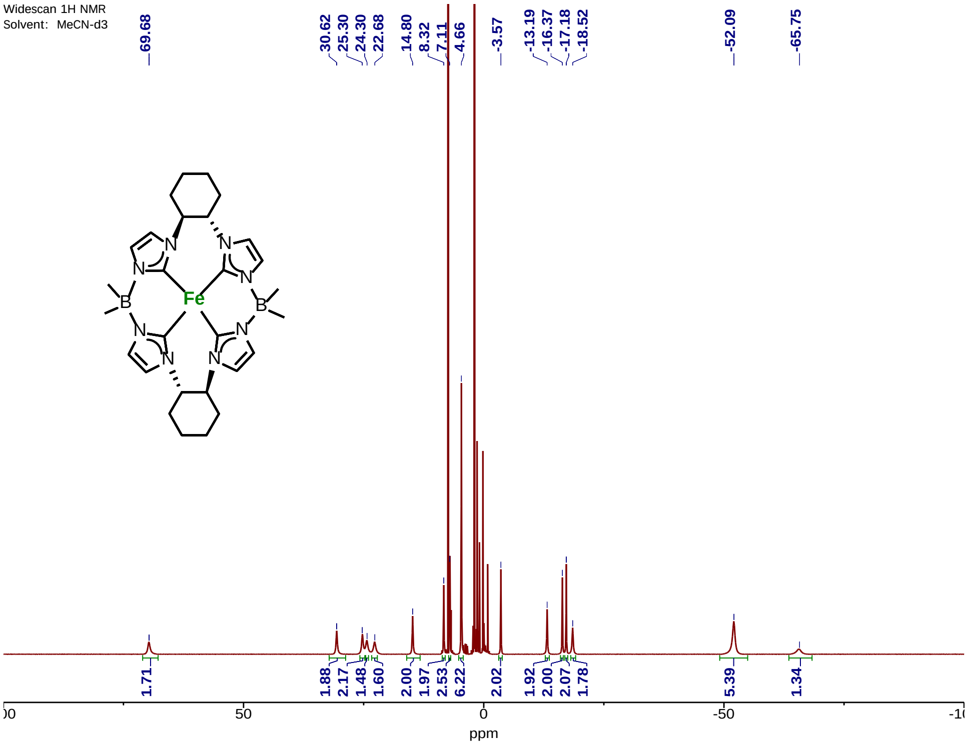


Figure S25: Widescan paramagnetic ^{1}H NMR of **6** in CD_3CN.

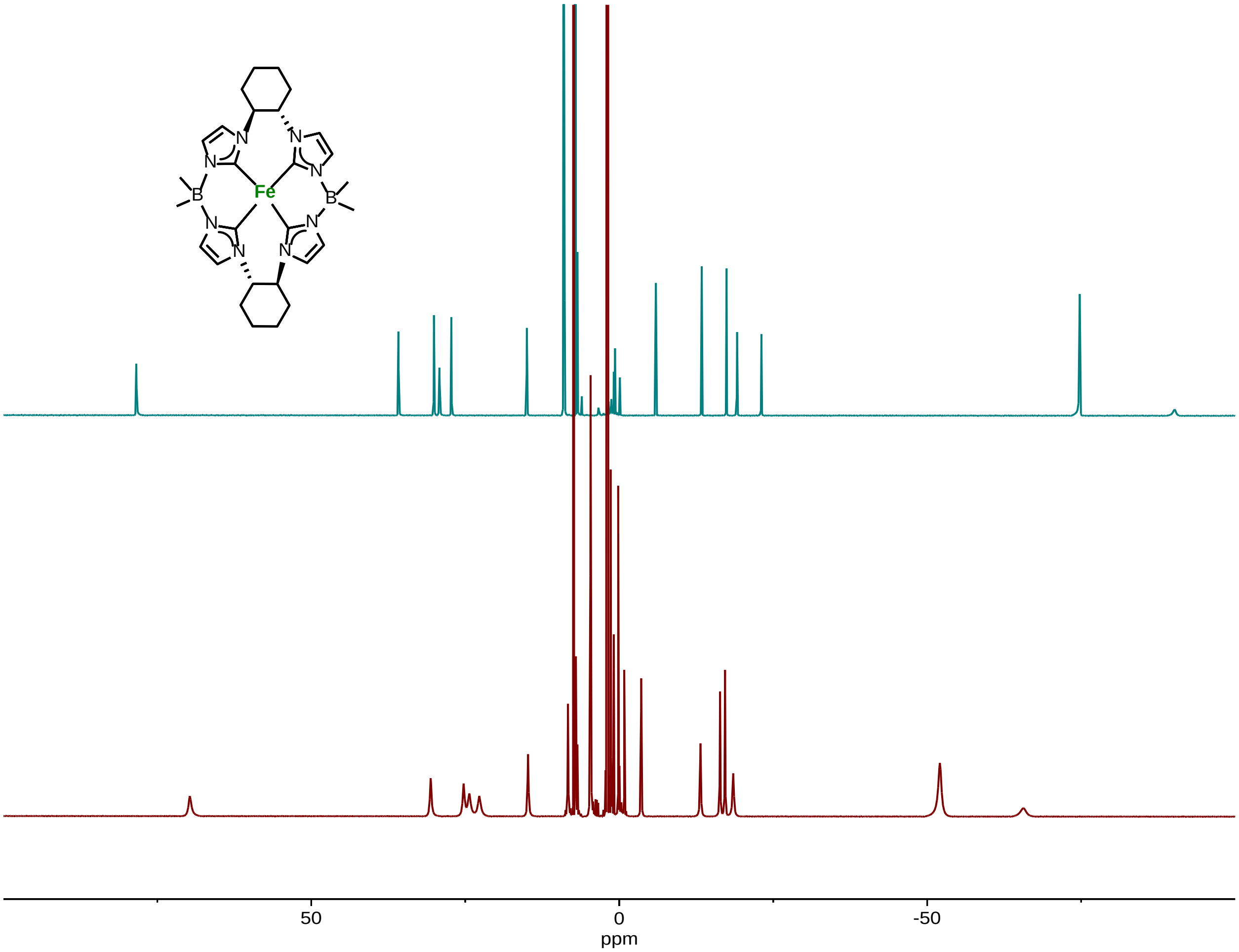


Figure S26: Stacked Widescan ^{1}H NMR Spectra of **6** in C_6D_6 **(top, teal**) and CD_3CN (**bottom, red**).

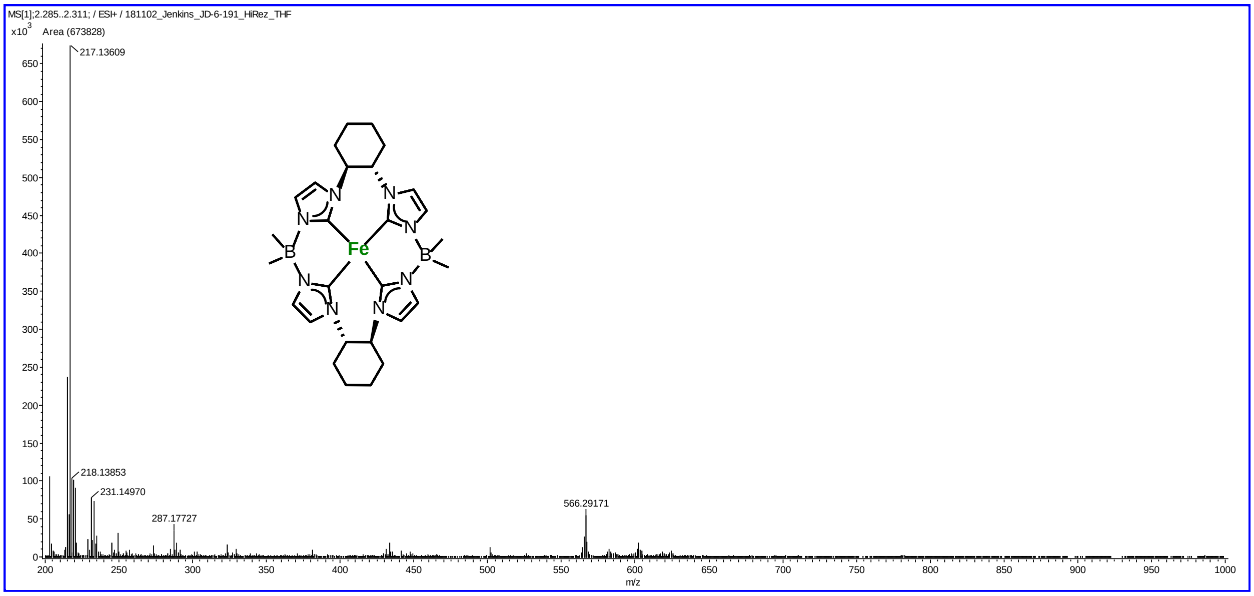


Figure S27: DART HR MS of **6**.

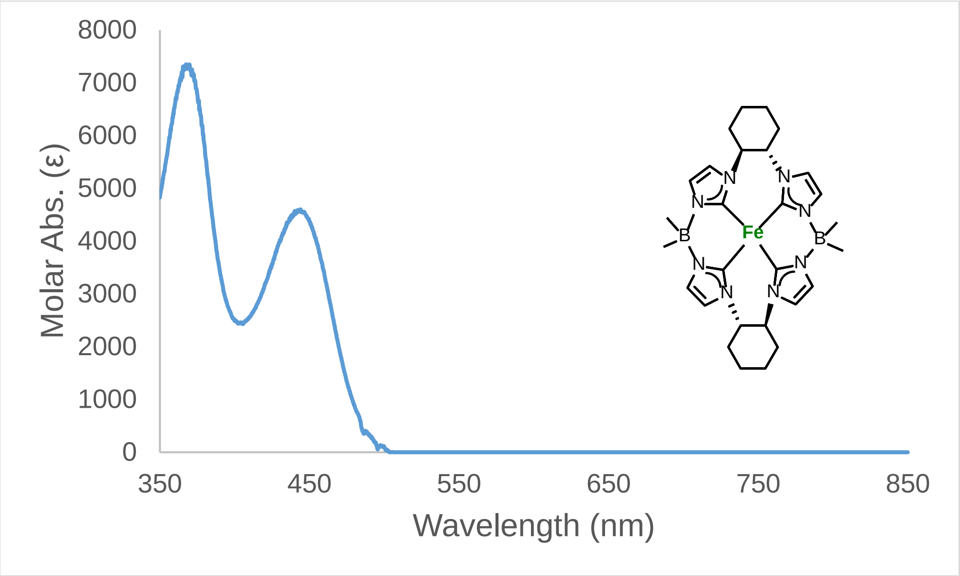


Figure S28: UV-Vis spectrum of **6** in THF.

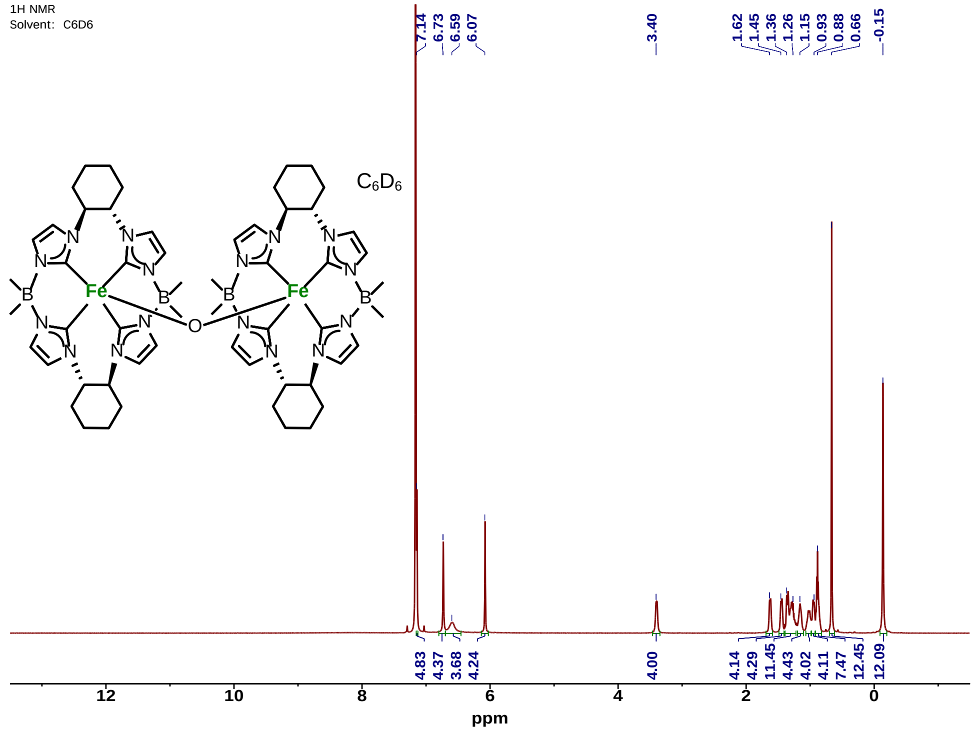


Figure S29: ^{1}H NMR of **7** in C_6D_6.

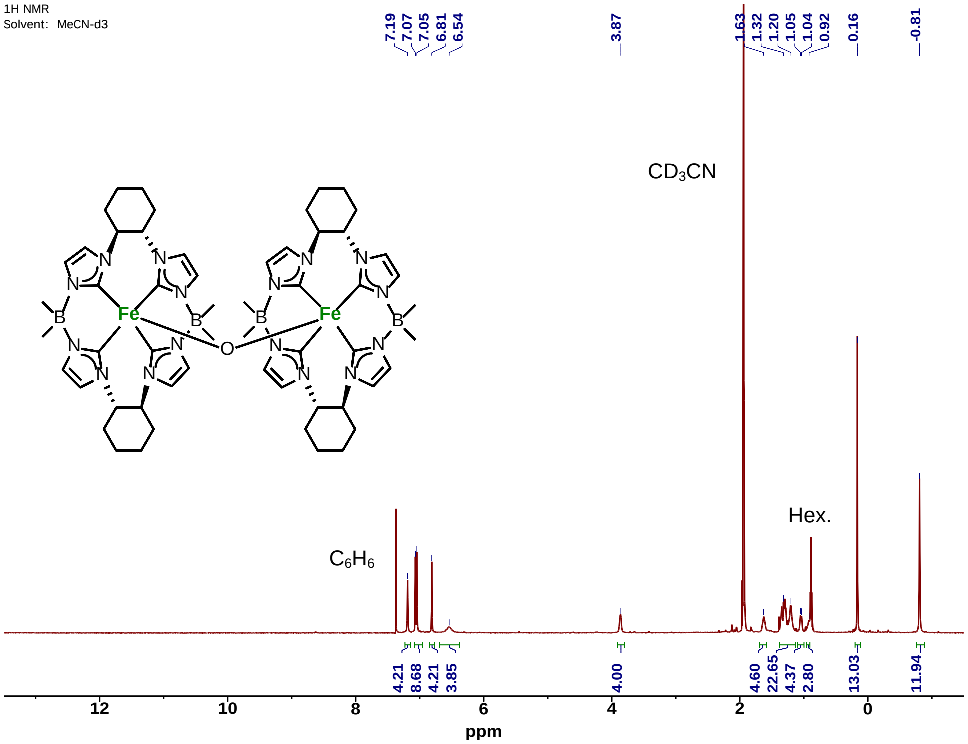


Figure S30: ^{1}H NMR of **7** in CD_3CN.

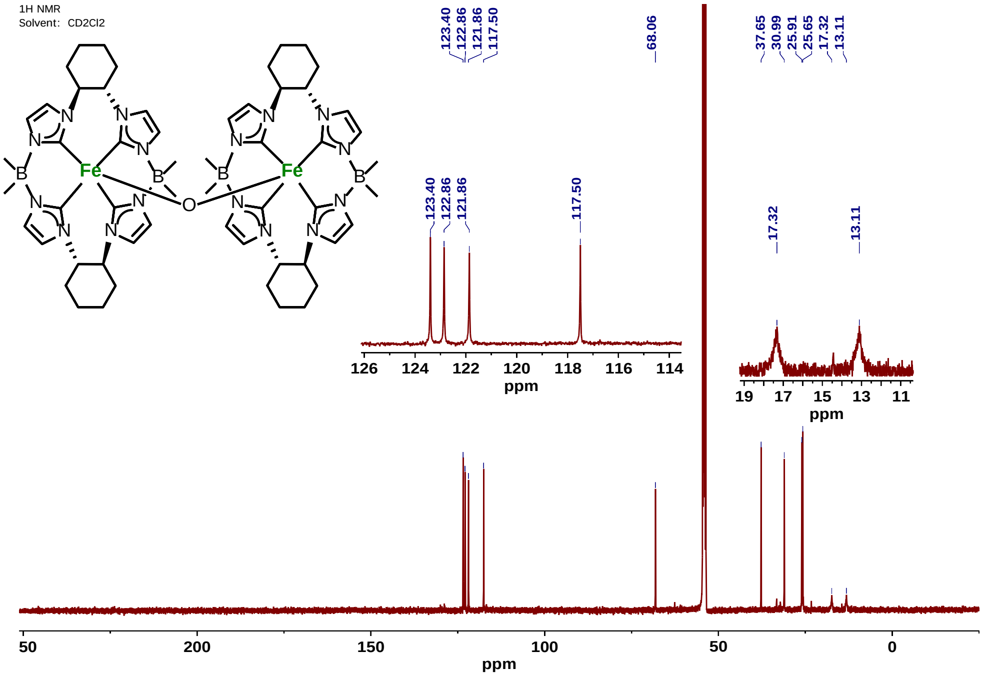


Figure S31: ^{13}C NMR of **7** in CD_2Cl_2.

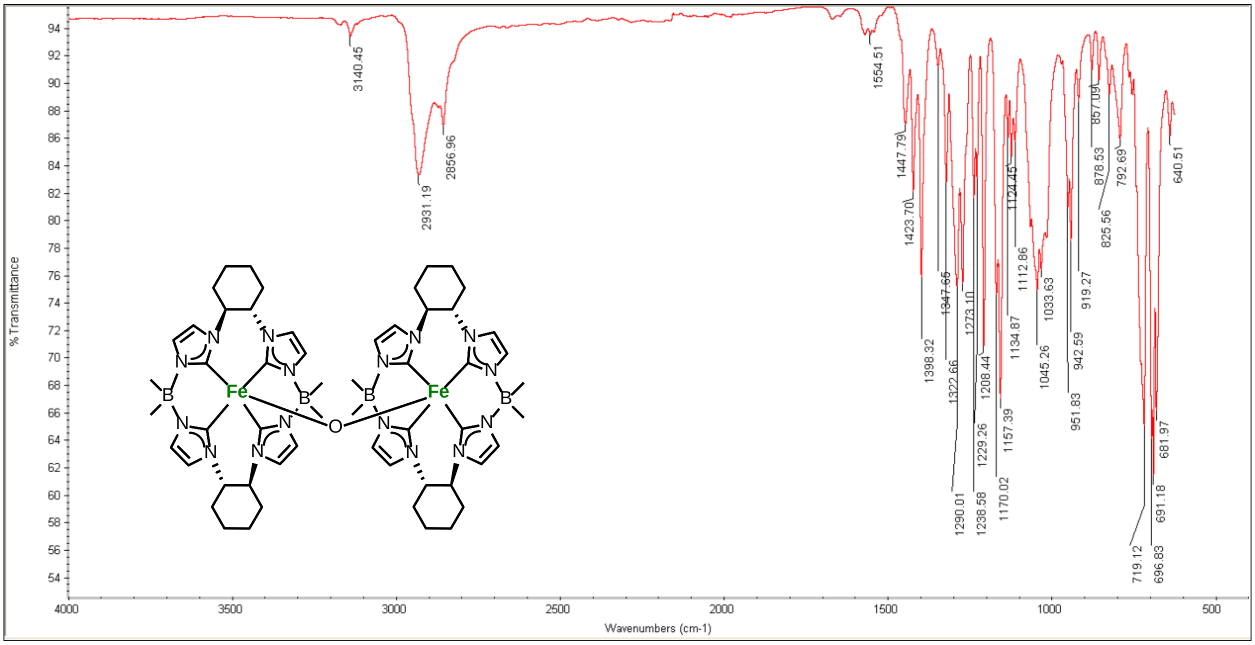


Figure S32: IR of **7**.

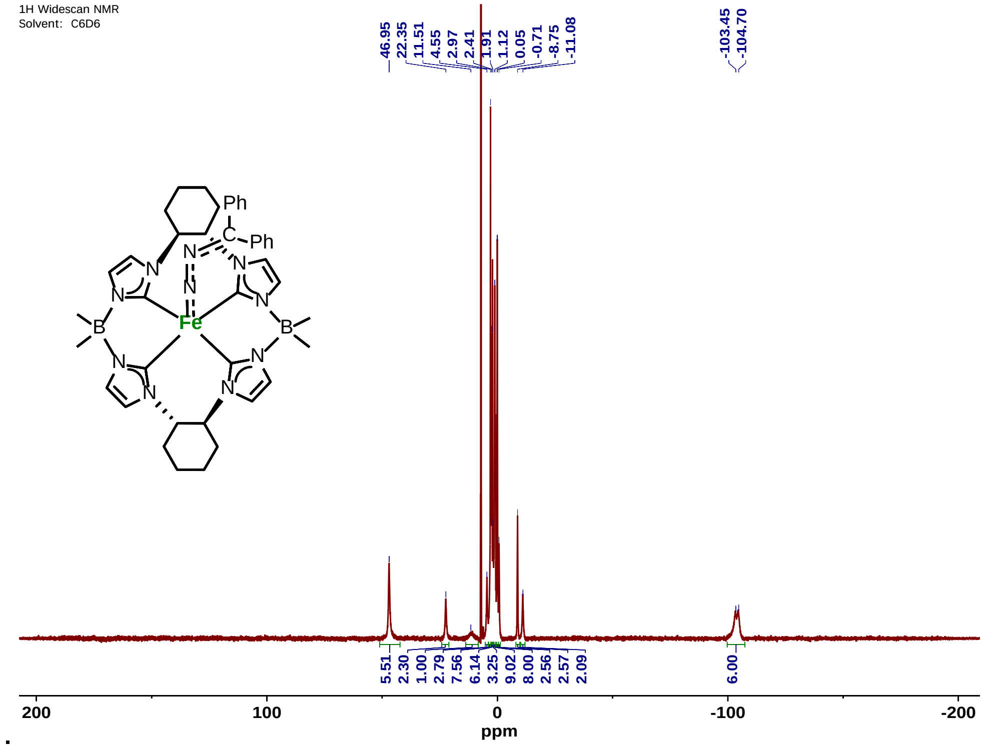


Figure S33: Widescan ^{1}H NMR for **8** in C_6D_6.

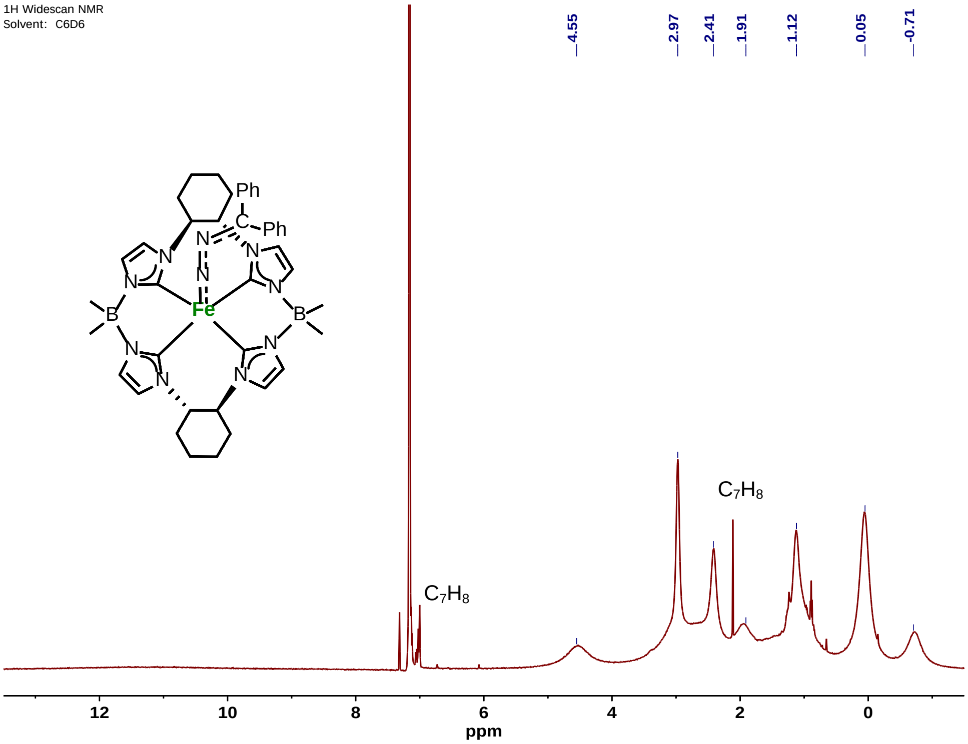


Figure S34: Expansion of Diamagnetic Region for **8** in C_6D_6.

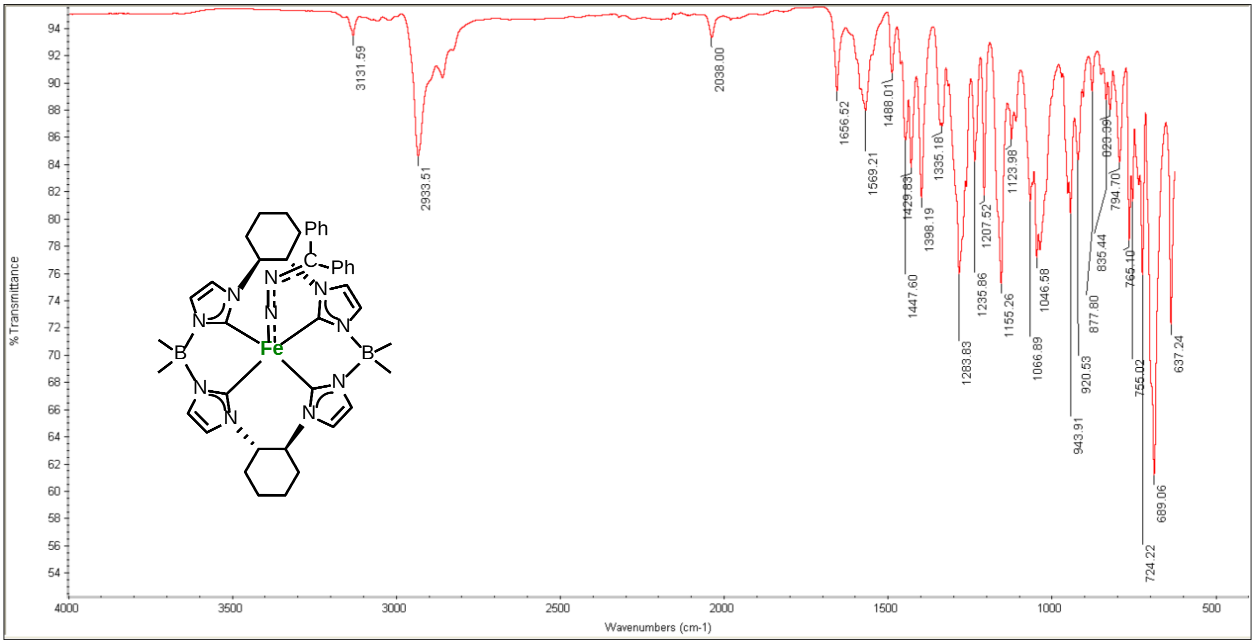


Figure S35: IR of **8**.

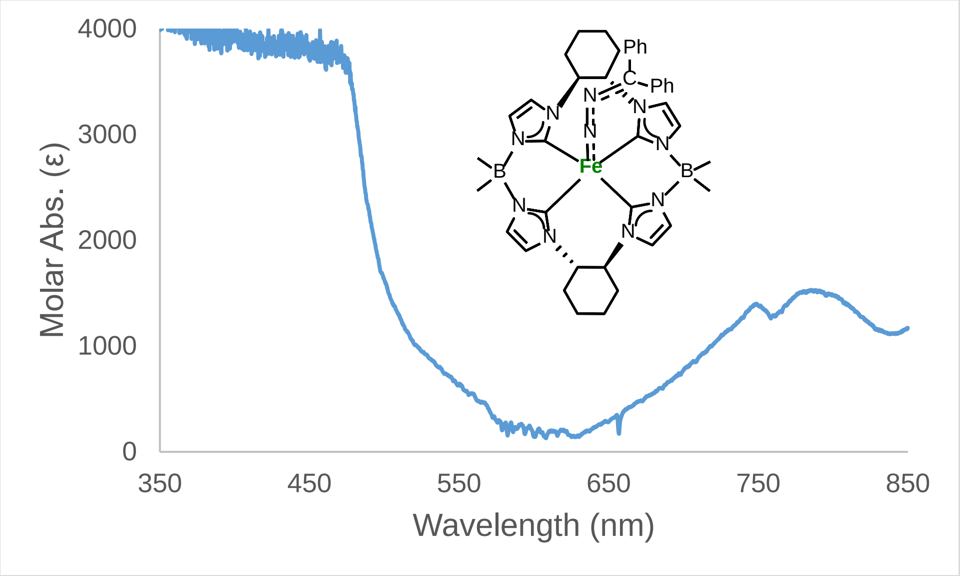


Figure S36: Concentrated (5.92 x 10^{-4} M) UV-Vis Spectrum in THF for **8**.

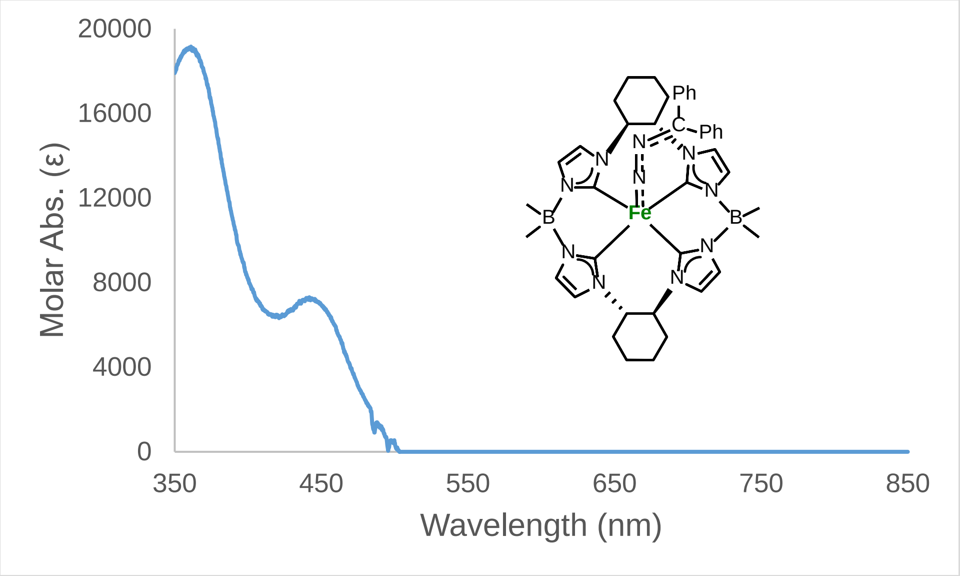


Figure S37: Dilute (4.384 x 10^{-5} M) UV-Vis Spectrum in THF for **8**.

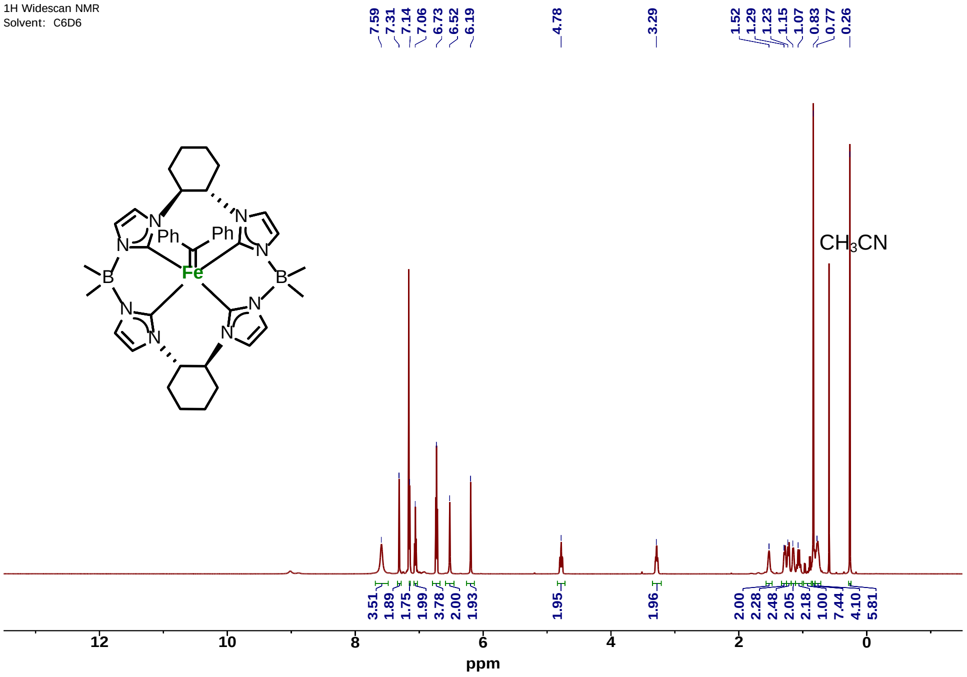


Figure S38: ^{1}H NMR of **9** in C_6D_6.

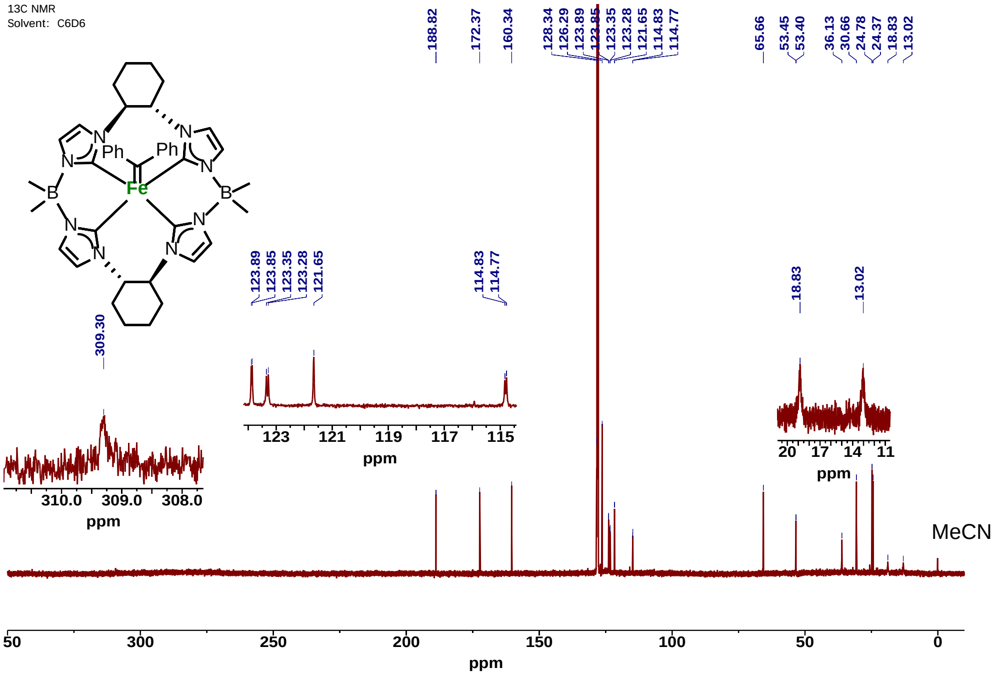


Figure S39: ^{13}C NMR of **9** in C_6D_6. Insert of signal at 309.30 ppm is from ^{13}C spectrum ran at 5 second relaxation delay.

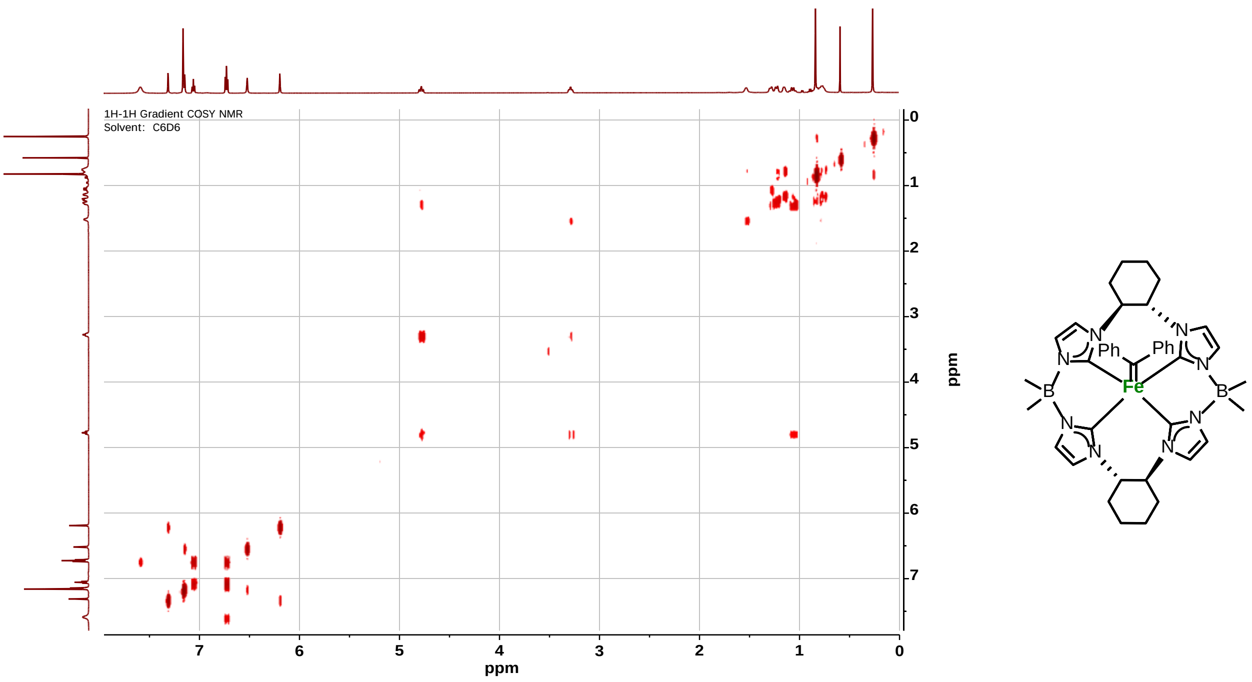


Figure S40: ^{1}H-^{1}H COSY Spectrum of **9** in C_6D_6.

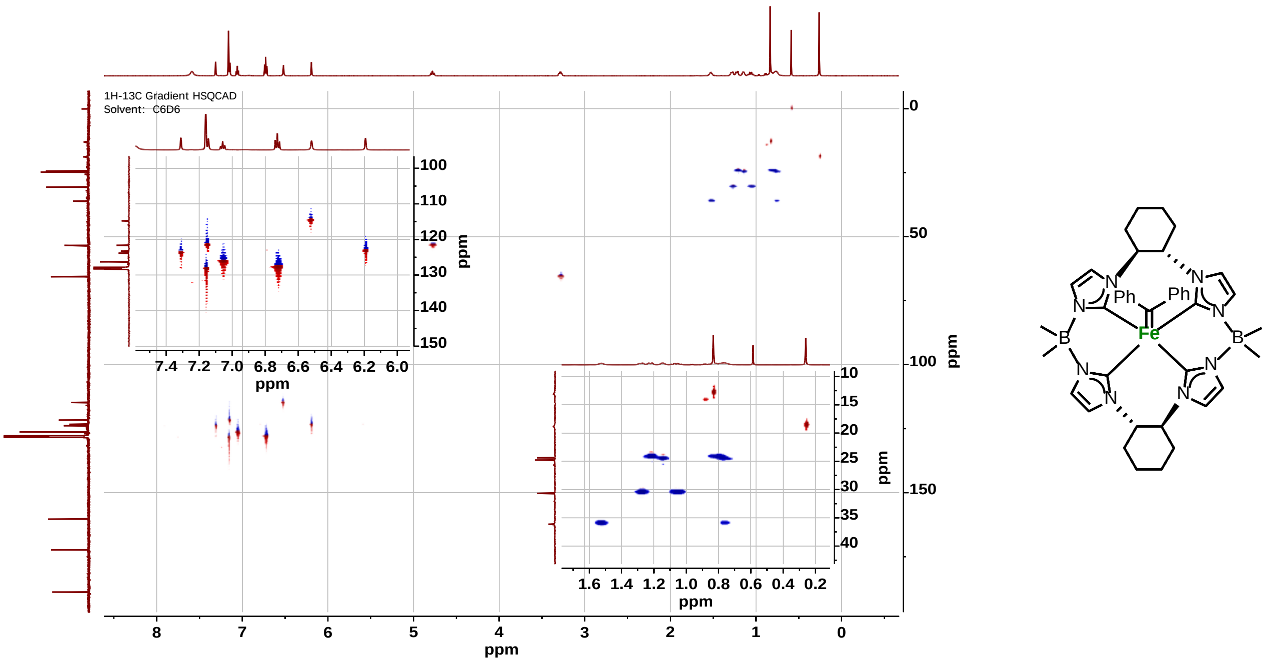


Figure S41: ^{1}H-^{13}C HSQC Spectrum of **9** in C_6D_6.

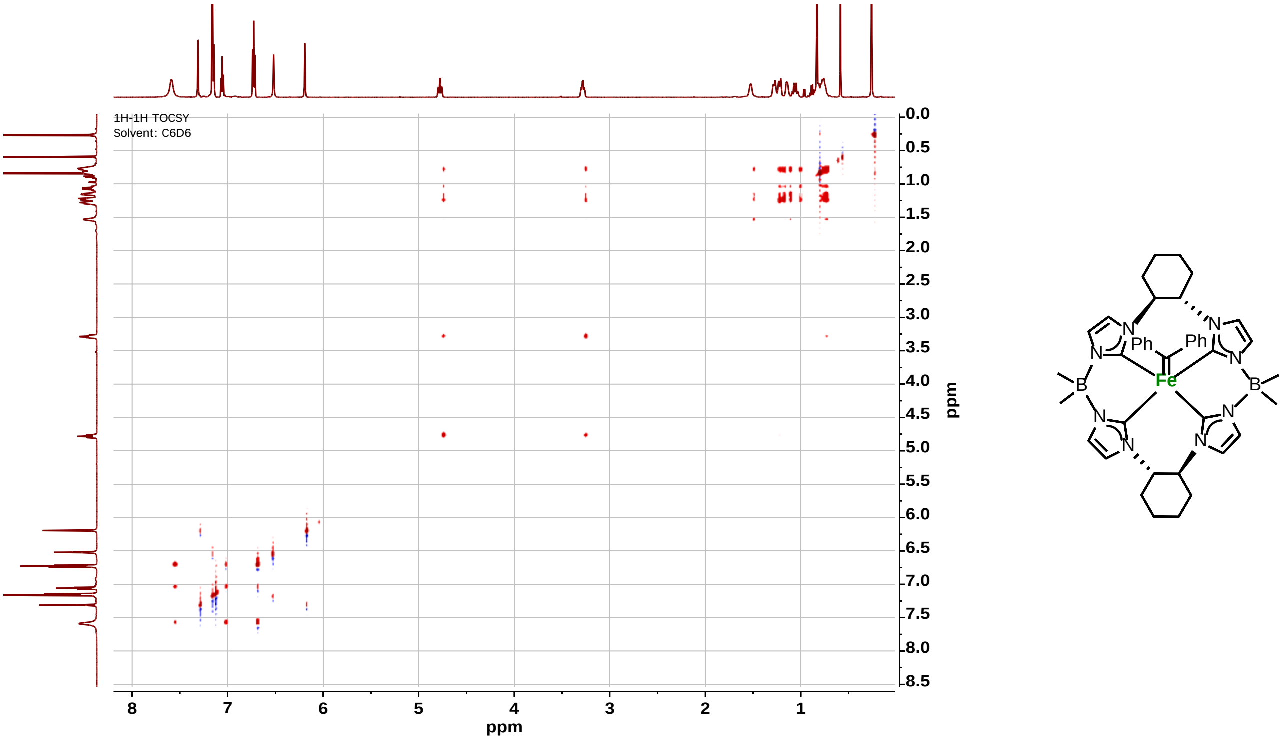


Figure S42: ^{1}H-^{1}H TOCSY Spectrum of **9** in C_6D_6.

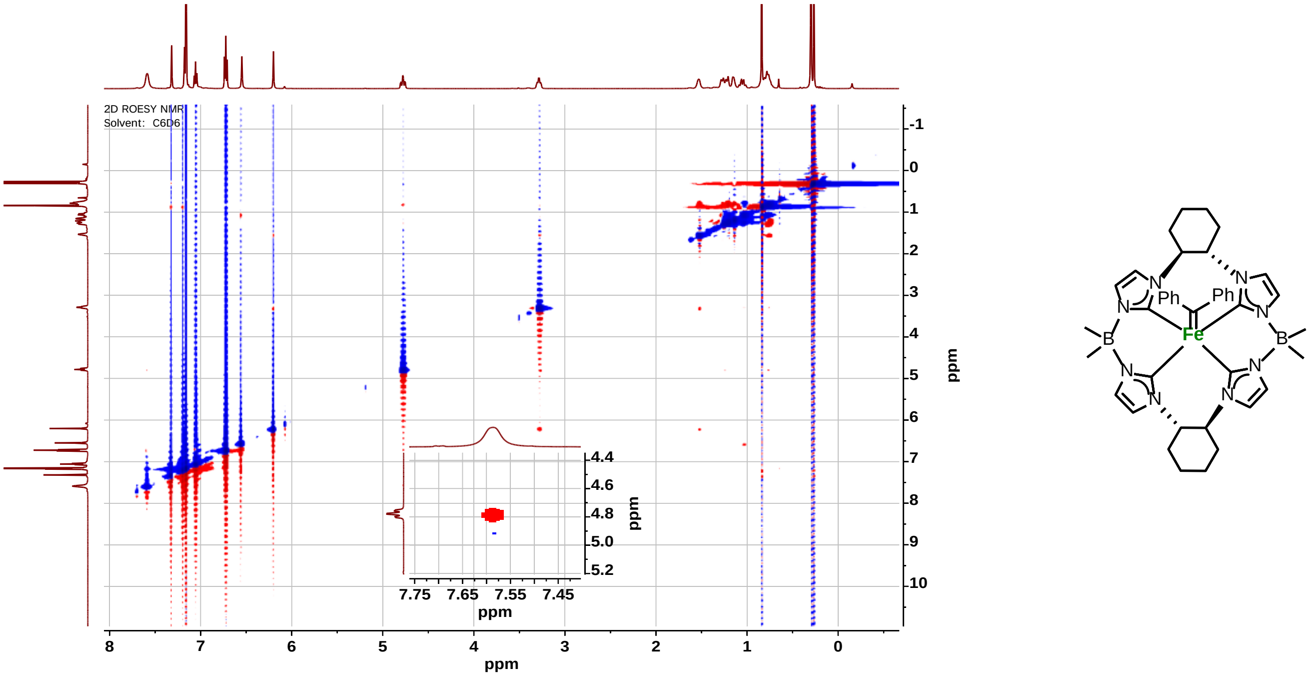


Figure S43: 2D-ROESY NMR Spectrum of **9** in C_6D_6. Expanded region shows the crosspeak of the ortho C-H to the chiral C-H bond over the Fe center.

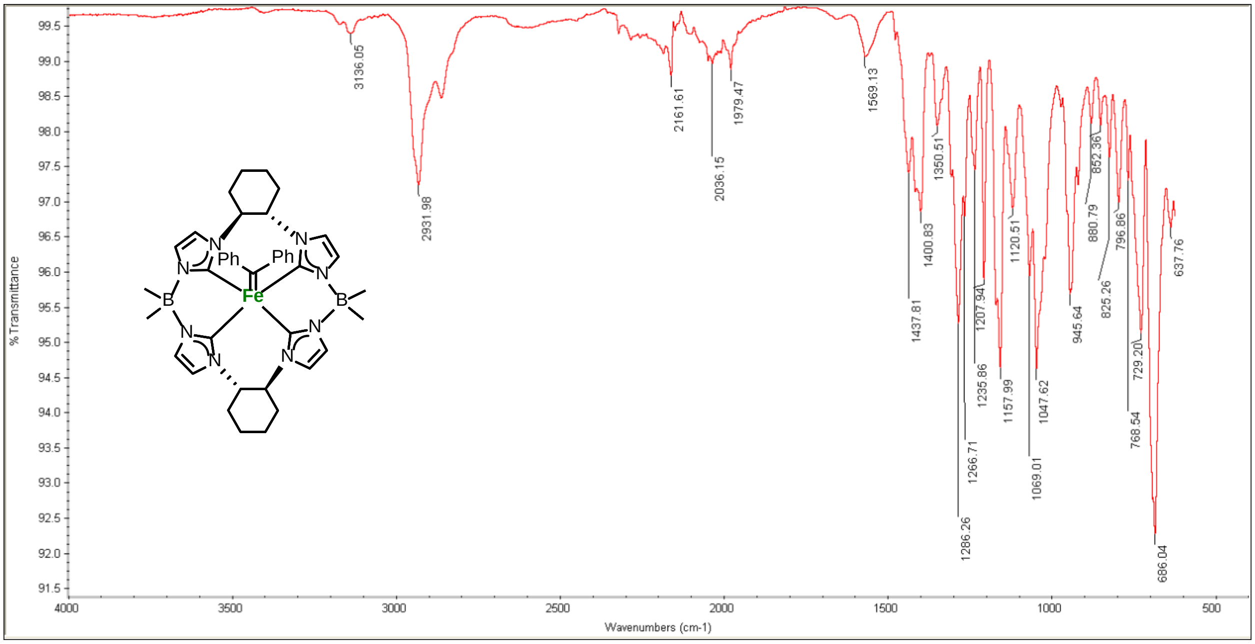


Figure S44: IR of **9**.

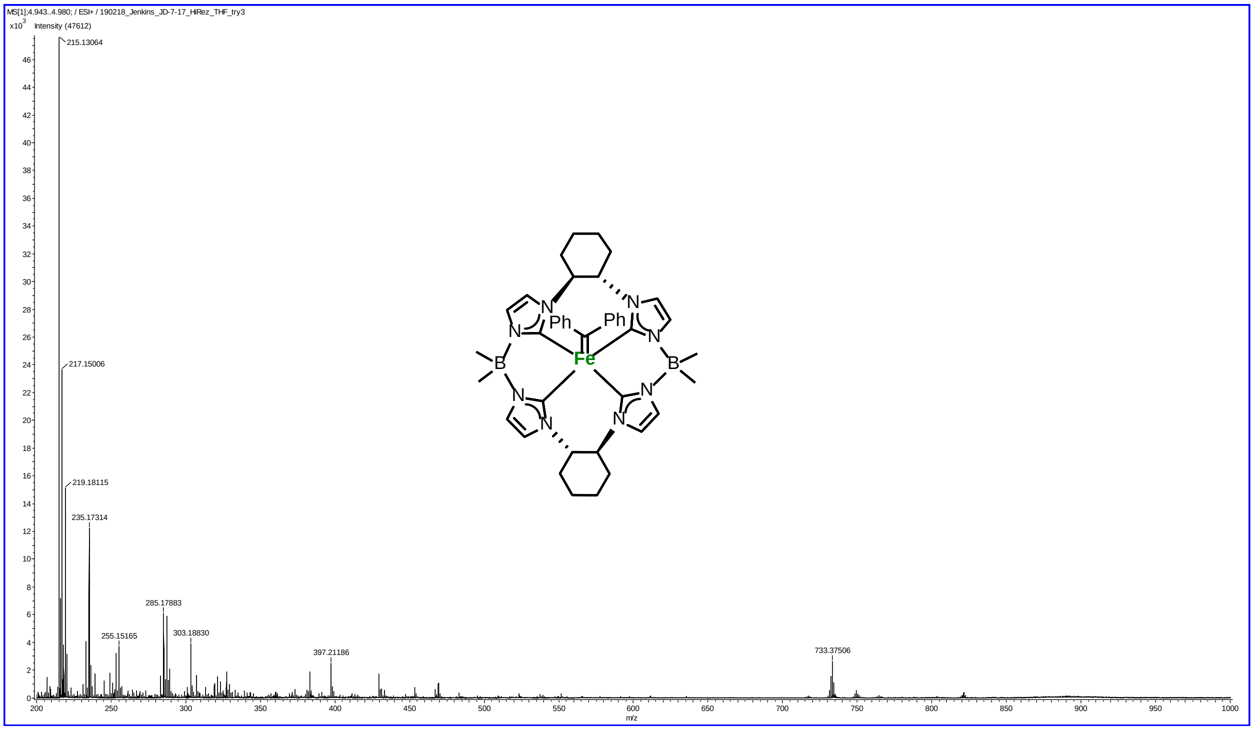


Figure S45: HR DART MS of **9**.

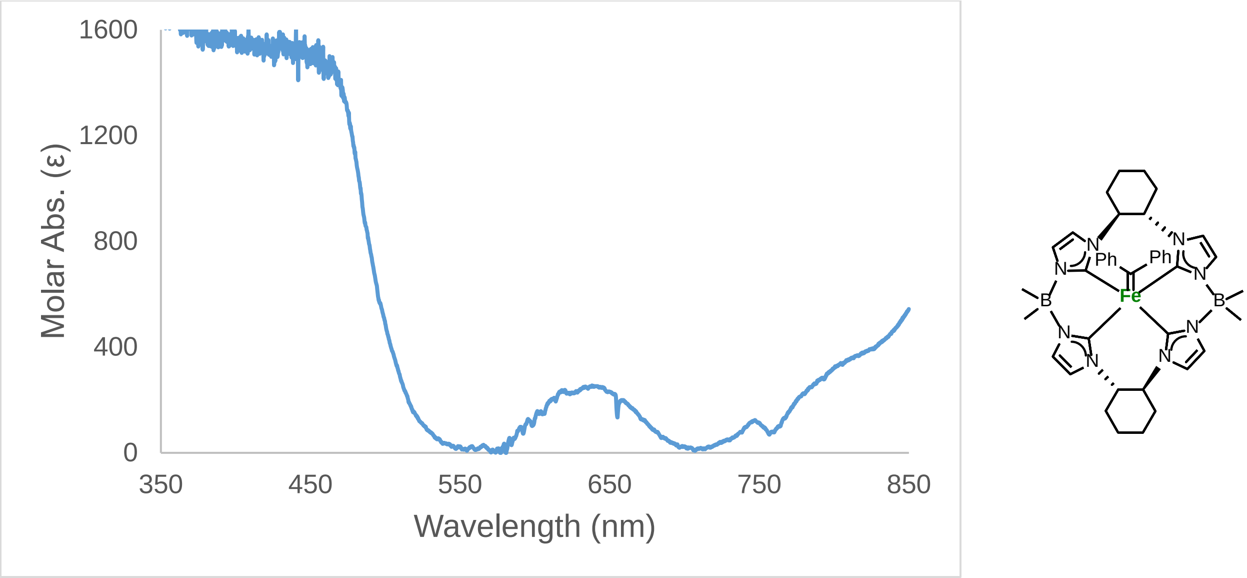


Figure S46: Concentrated (1.412 x 10^{-3} M) UV-Vis Spectrum of **9** in THF.

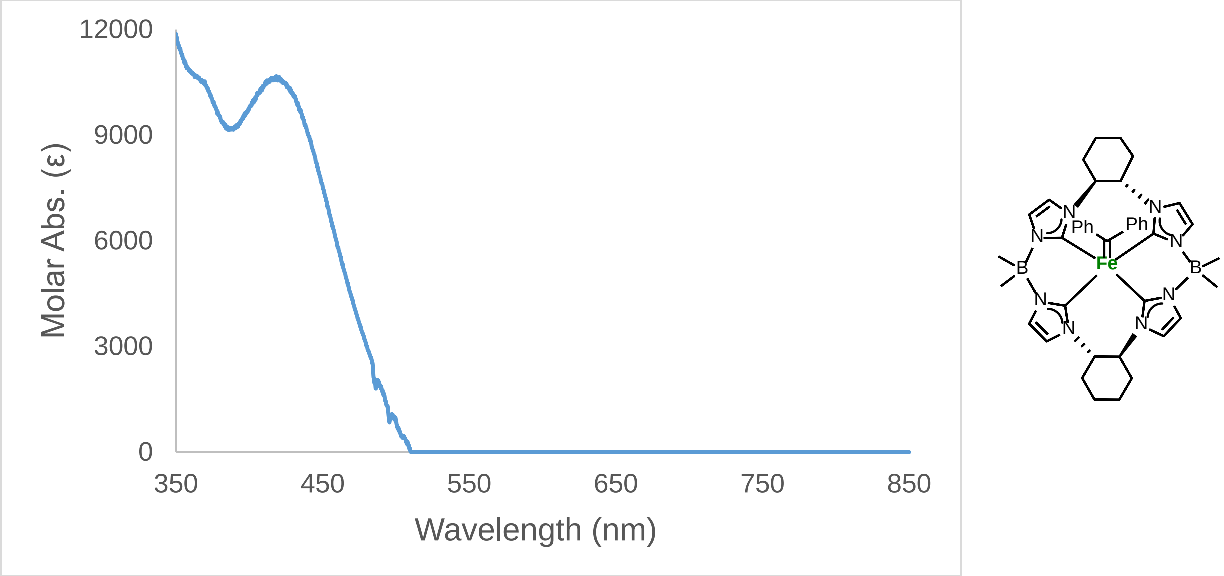


Figure S47: Dilute (7.587 x 10^{-5} M) UV-Vis Spectrum of **9** in THF.

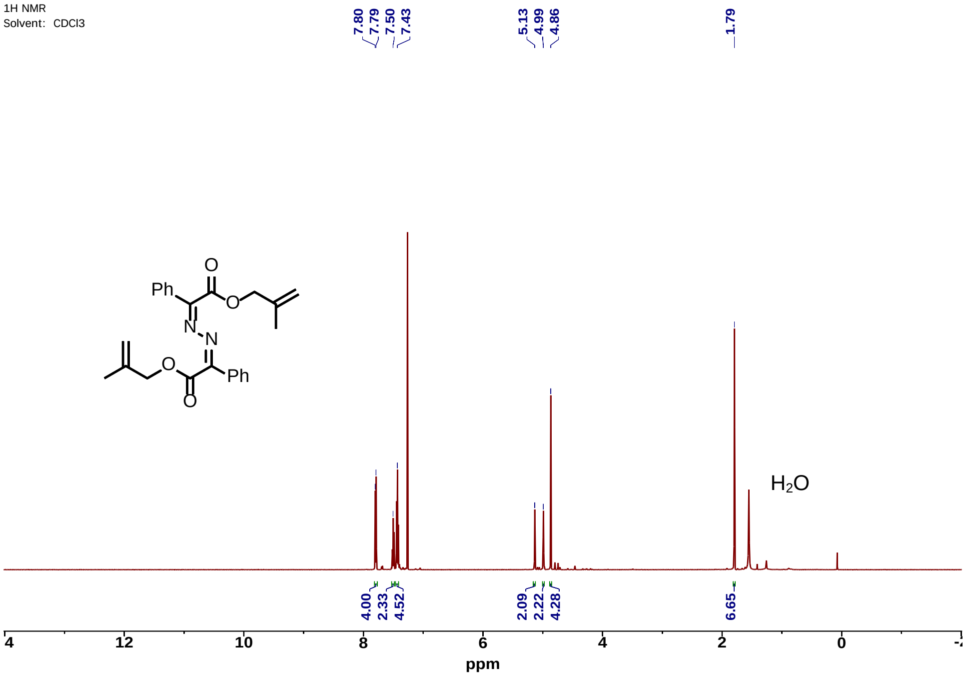


Figure S48: ^{1}H NMR of **11** in CDCl3.

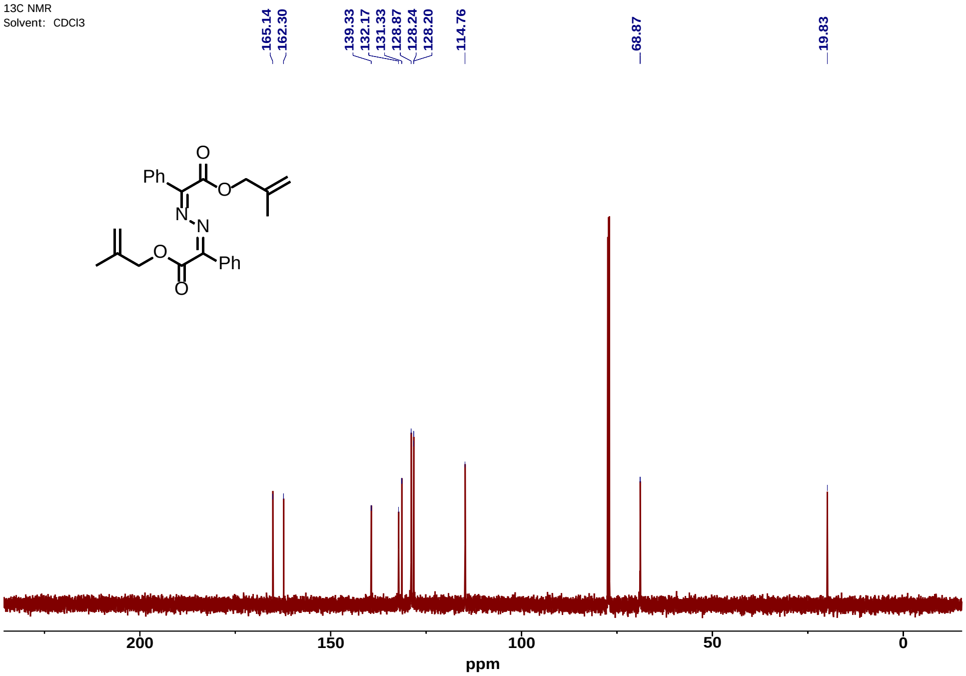


Figure S49: ^{13}C NMR of **11** in CDCl3.

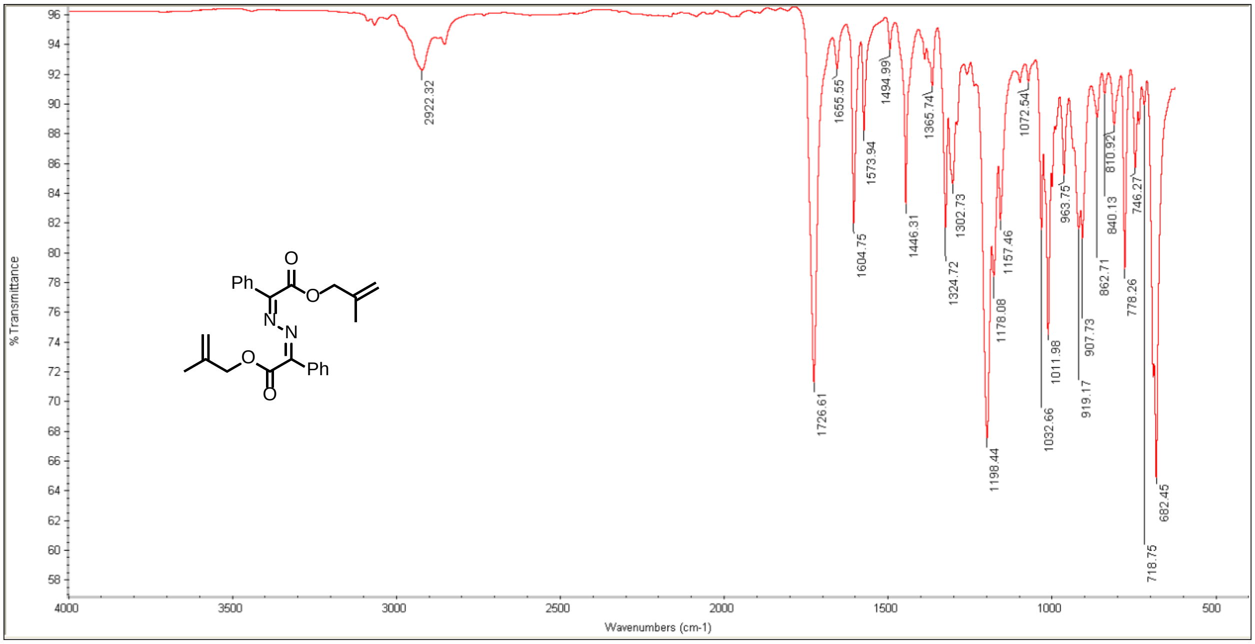


Figure S50: IR of **11**.

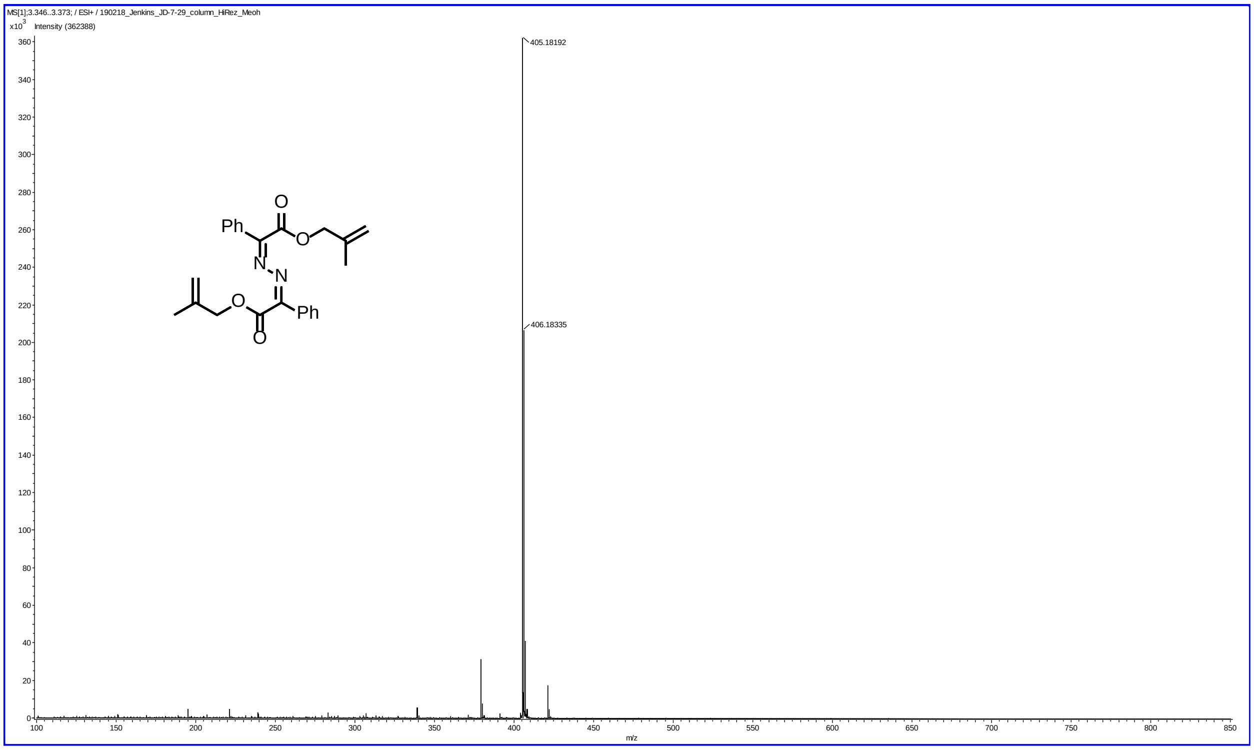


Figure S51: DART HR MS of **11**.

Additional NMRs for reactions

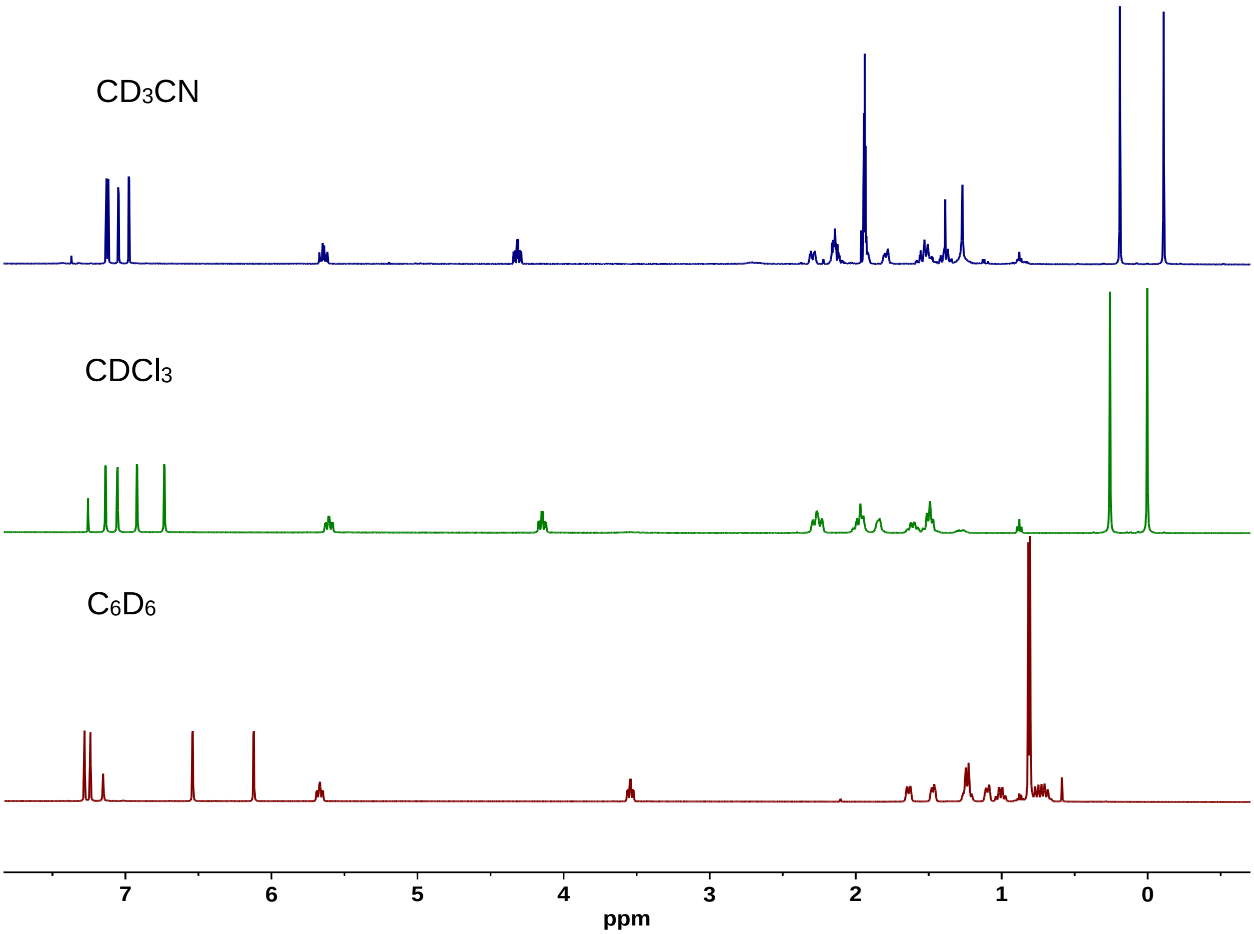


Figure S52: Comparison ^{1}H NMR of **5** in CD_3CN (**top, blue**), $CDCl_3$ (**middle, green**) and C_6D_6 (**bottom, red**).

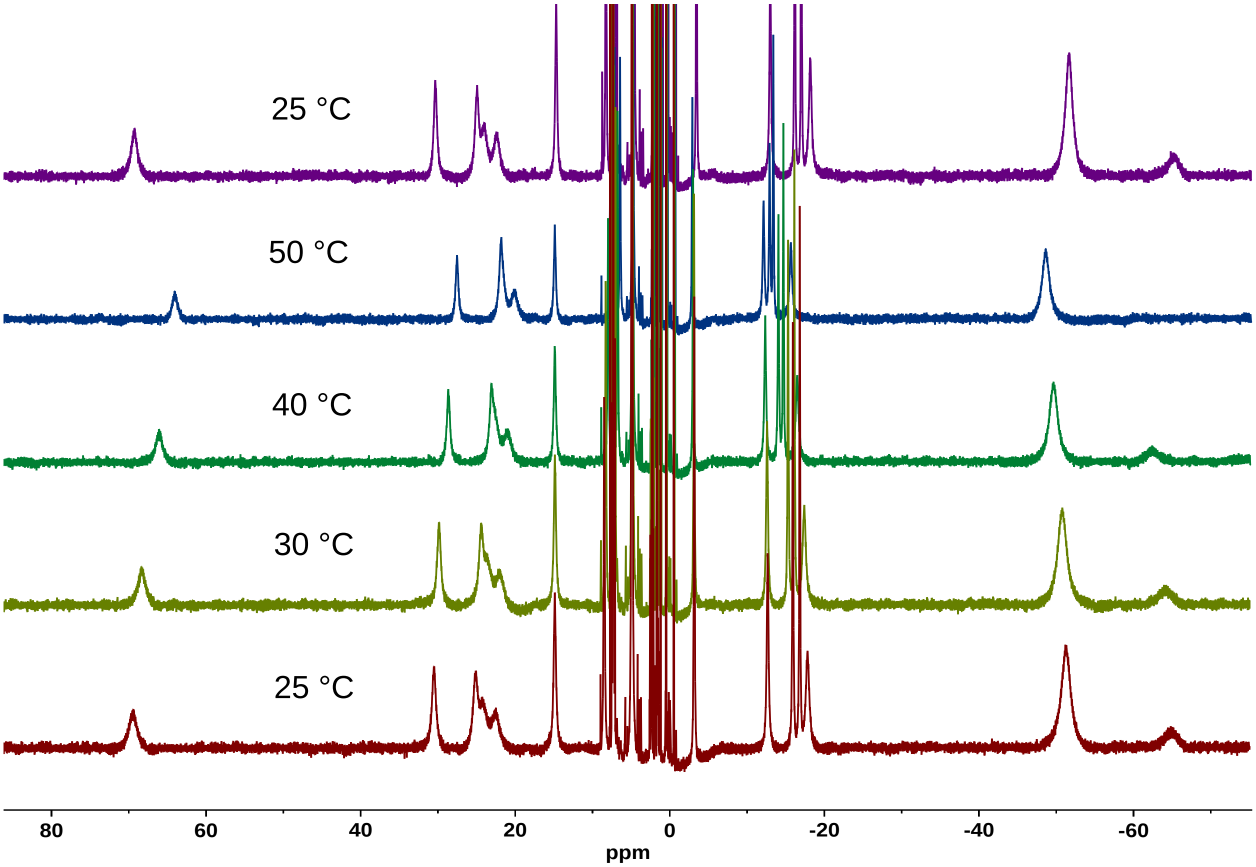


Figure S53: VT NMR of **6** in CD_3CN from 25 °C to 50 °C . **Purple** spectrum is after cooling the 50 °C run back to 25 °C.

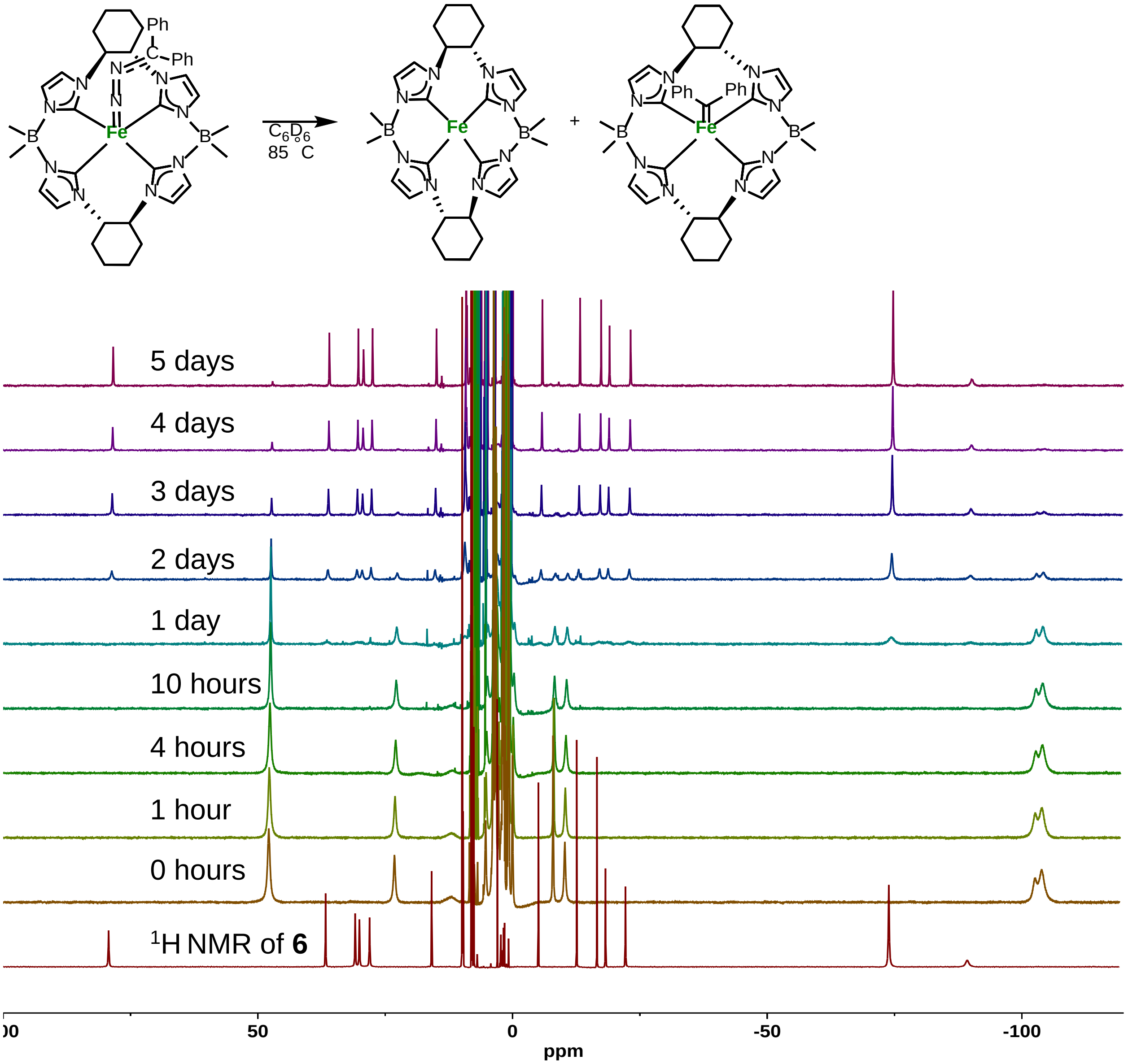


Figure S54: Thermal decomposition of **8** over 5 days in C_6D_6. With time, NMR peaks corresponding to **6** appear in paramagnetic region.

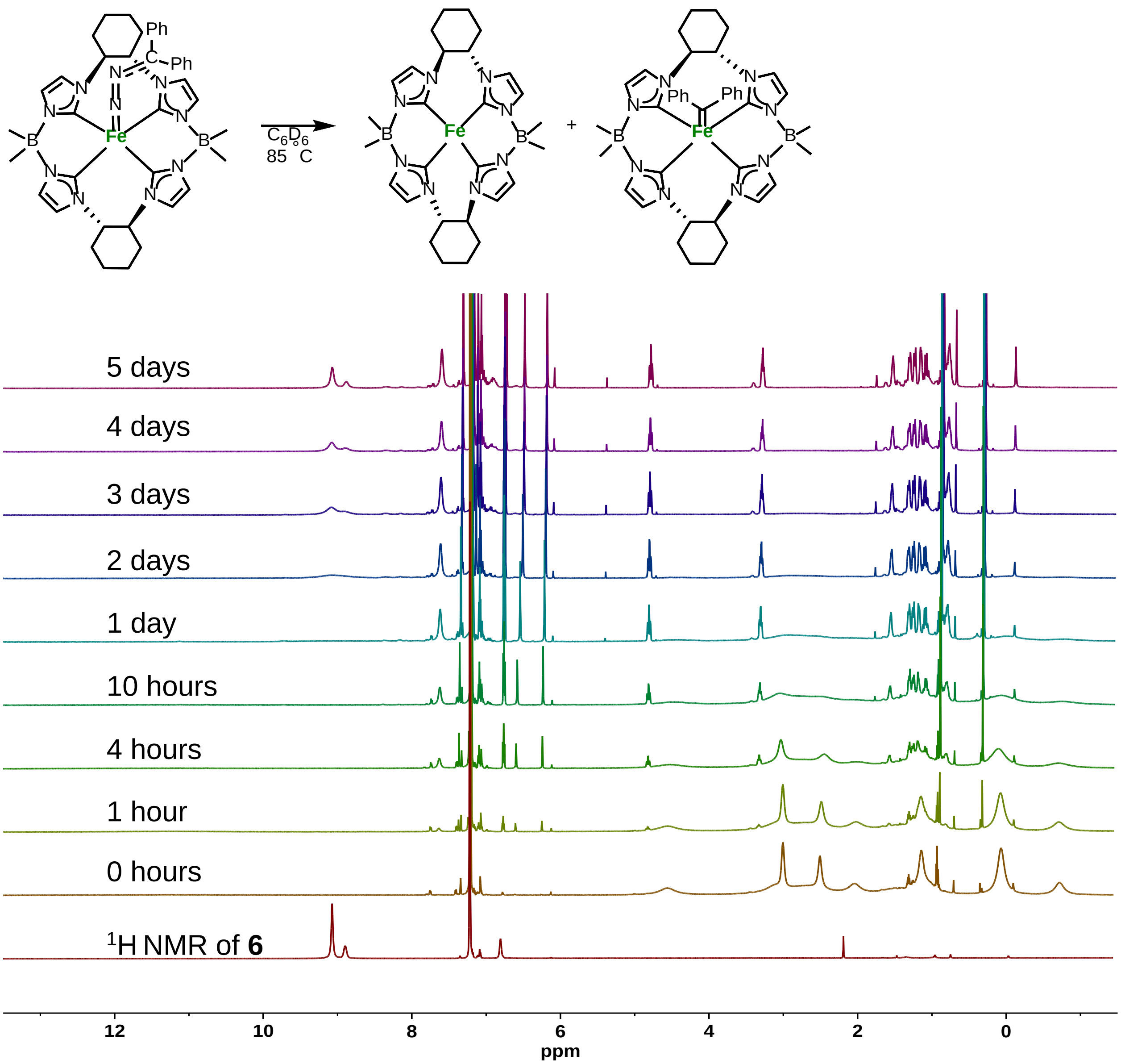
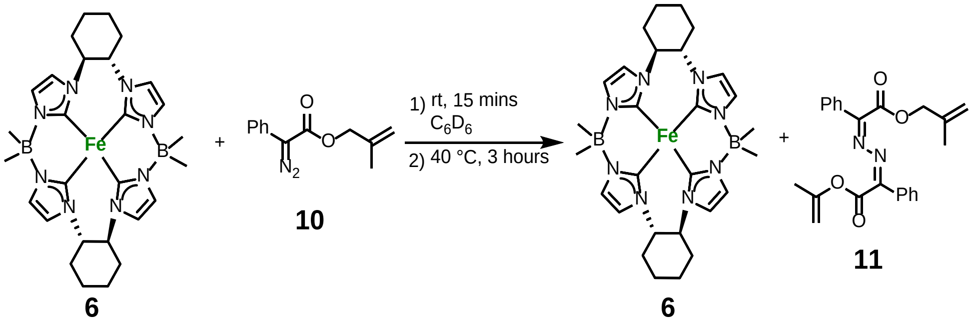


Figure S55: Thermal Decomposition of **8** in C_6D_6 over 5 days. With time, peaks corresponding to **9** appear in the diamagnetic region.



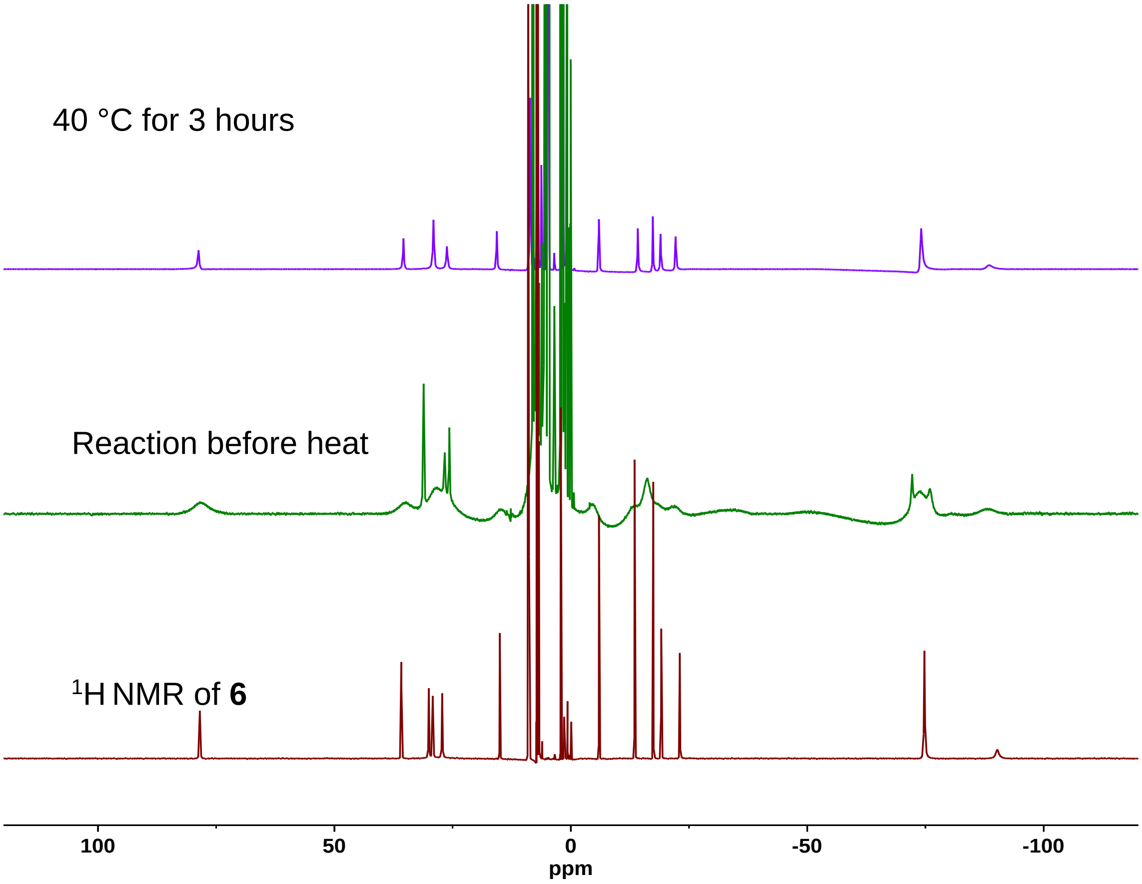


Figure S56: Stoichiometric NMR scale reaction of **6** with **10** in C_6D_6. Widescan shown here. Before heating (**green**) shows a paramagnetic species presumably the diazo adduct. Upon heating at 40 °C for 3 hours (**purple**), the only paramagnetic species is **6**.

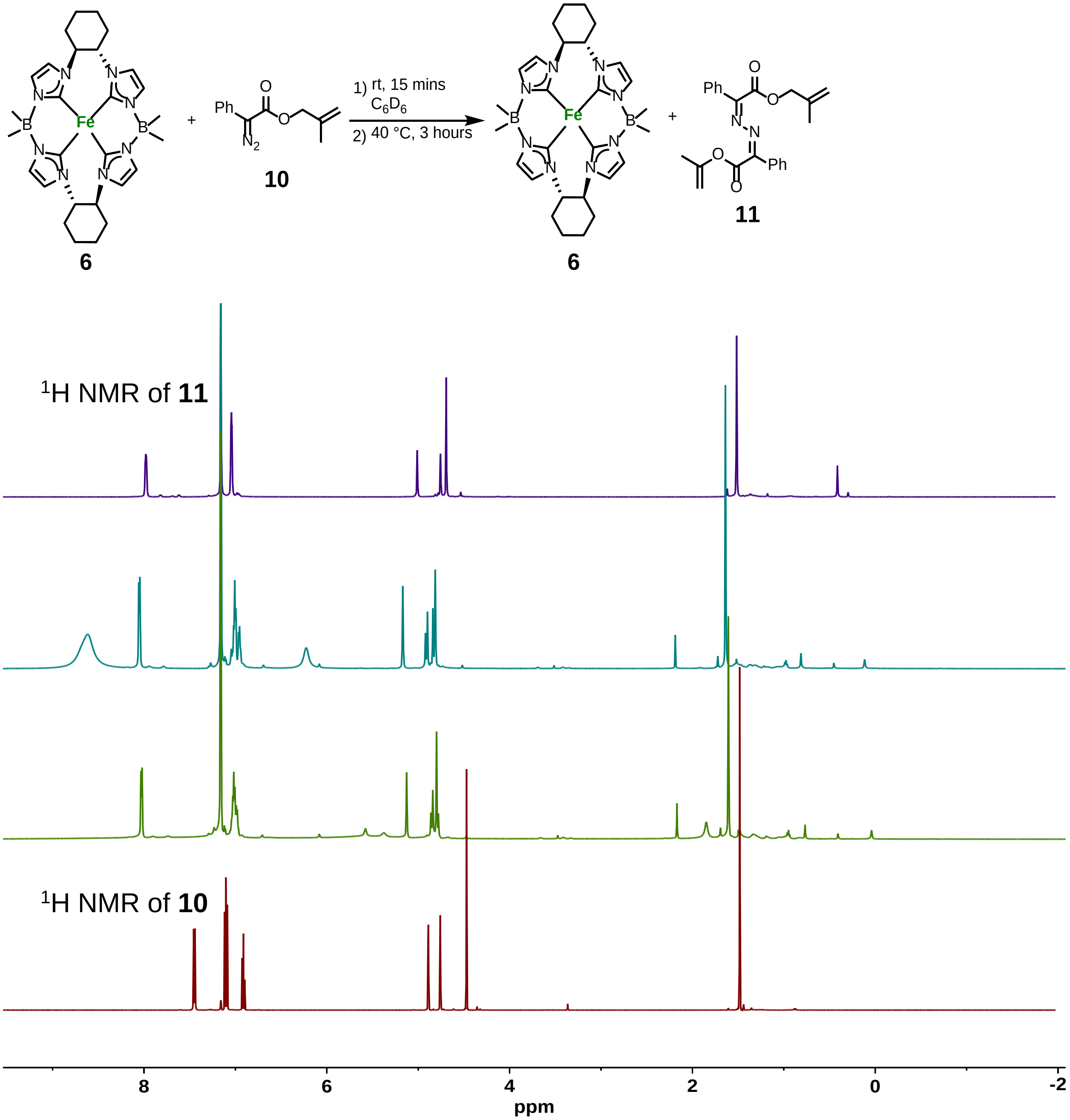


Figure S57: Stoichiometric NMR scale reaction of **6** with **10** in C_6D_6. Diamagnetic regions shown here. Before heat (**green**), shows complete consumption of **10** and formation of **11**. Heating at 40 °C for 3 hours (**blue**) consumes the second paramagnetic species shown in Figure S56 and forms **6** and **11**.

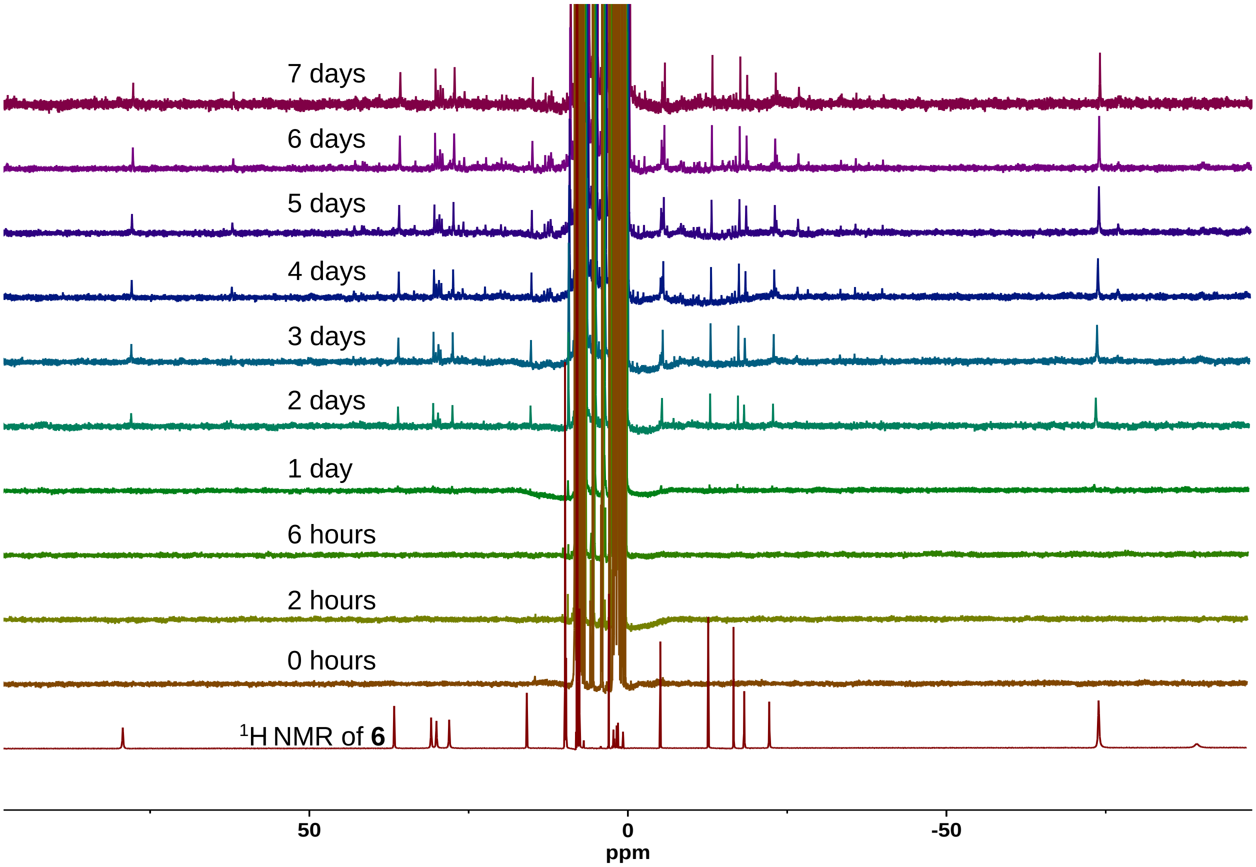


Figure S58: Overtime degradation of **9** in C_7D_8 at 110 °C.

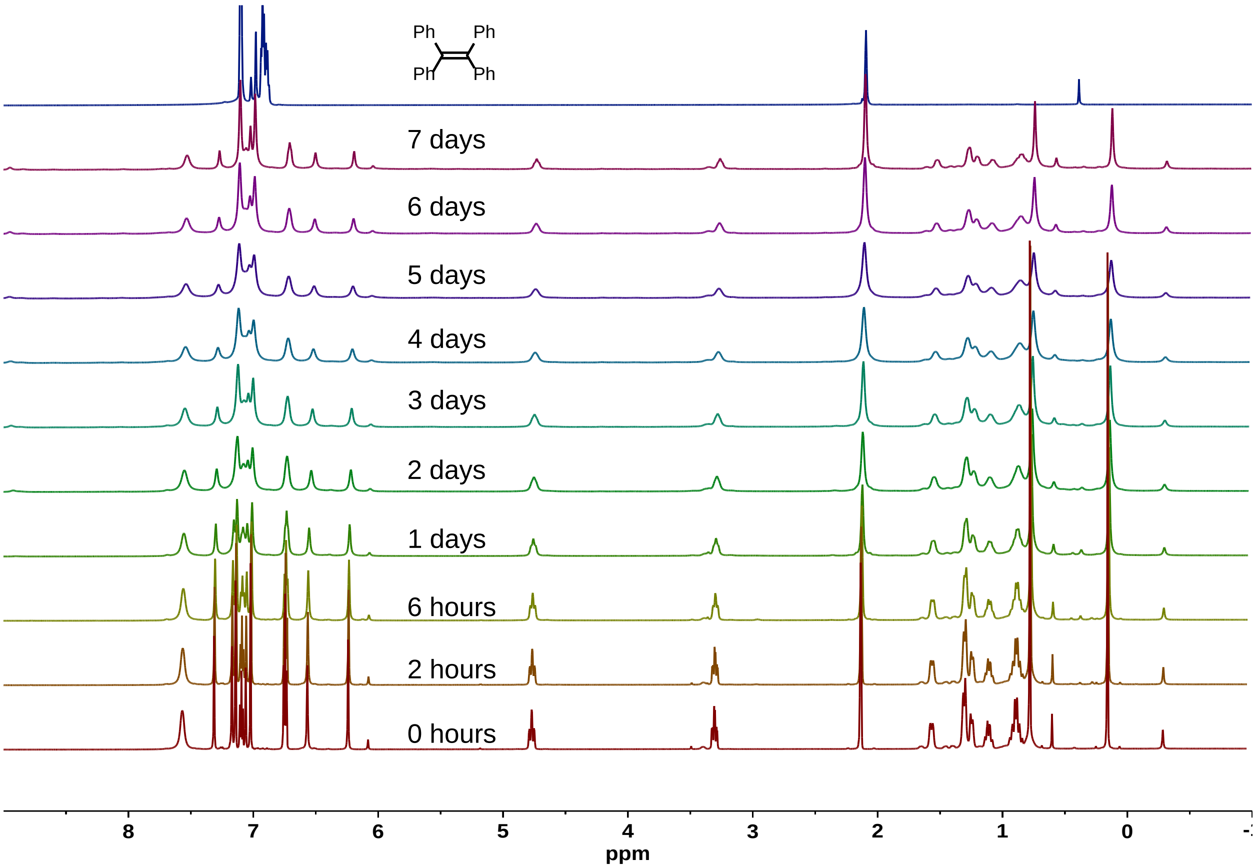


Figure S59: Overtime degradation of **9** in C_7D_8 at 110 °C. **Blue** spectrum is tetraphenylethylene in C_7D_8.

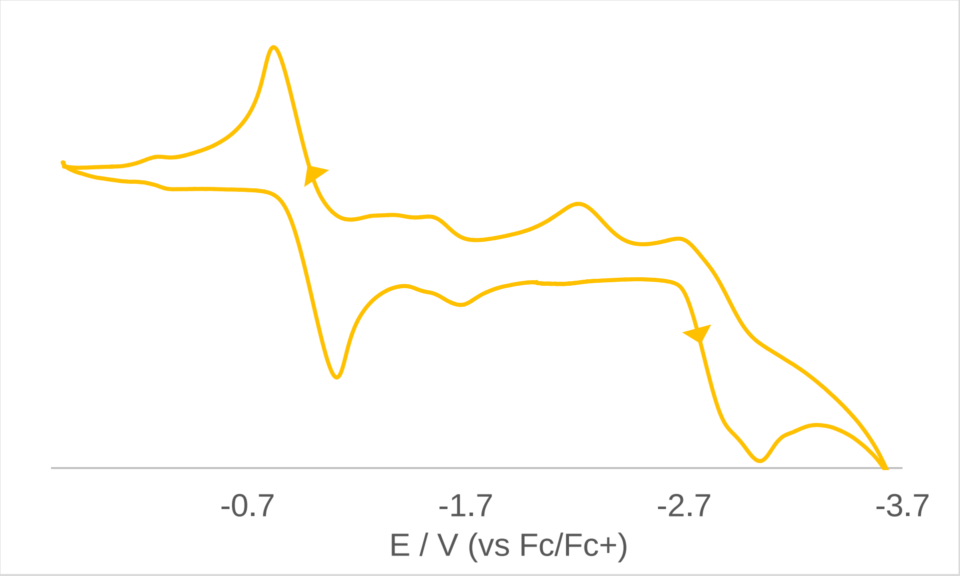


Figure S60: Widescan cyclic voltammogram of **6** in THF at 50 mV/s scan rate.

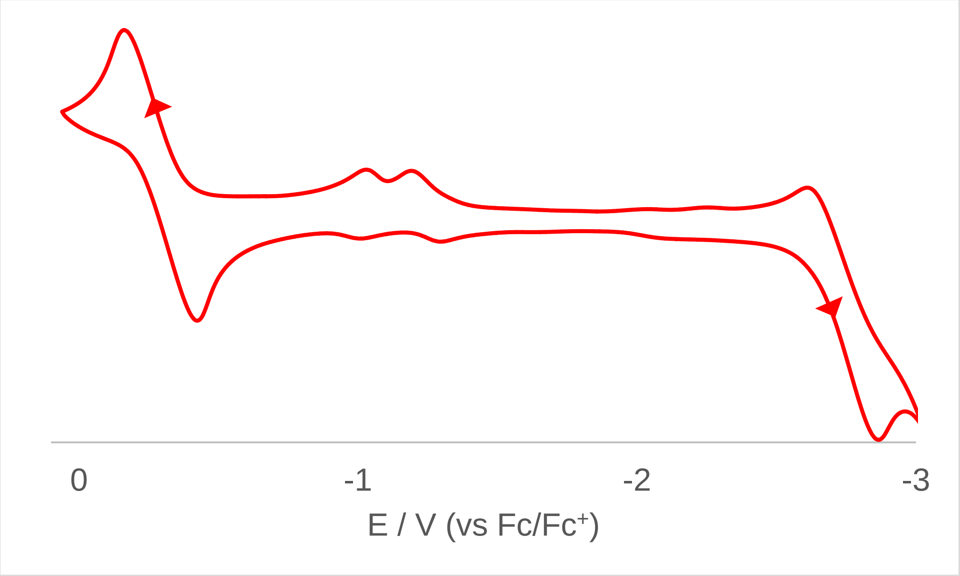


Figure S61: Widescan cyclic voltammogram of **7** in THF at 100 mV/s scan rate.

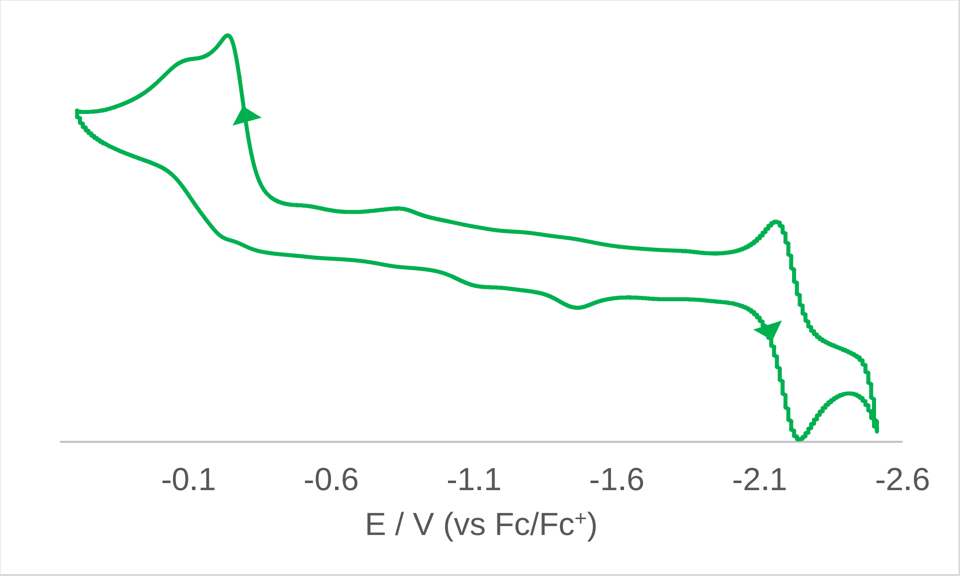


Figure S62: Widescan cyclic voltammogram of **8** in CH_3CN at 100 mV/s scanrate.

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1) Miller, J. B. Preparation of crystalline diphenyldiazomethane. *J. Org. Chem*. **1959**, *24*, 560-561.

2) Keipour, H.; Ollevier, T. Iron-Catalyzed Carbene Insertion Reactions of α-Diazoesters into Si-H Bonds. *Org. Lett.* **2017**, *19*, 5736-5739.

3) Klötzer, W.; Müssner R.; Montavo, M.; Singewald, N. Imidazole Derivatives. U.S. Patent 4,908,363, March 13, 1990.

4) Cao, L. L.; Stephan, D. W. Homolytic Cleavage Reactions of a Neutral Doubly Based Stabilized Diborane(4). *Organometallics*. **2017**, *36*, 3163-3170.

5) Meyer, S.; Klawitter, I.; Demeshko, S.; Bill, E.; Meyer, F. A Tetracarbene–Oxoiron(IV) Complex. *Angew. Chem. Int. Ed.* **2012**, *125*, 935-939.