Electronic Supplementary Material (ESI) for Dalton Transactions.

Iron Complexes Supported by Pyrazolyl-Substituted Cyclopentadienyl Ligands

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Supporting Information

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General Considerations

All air- and moisture-sensitive compounds were manipulated under an inert atmosphere either inside an M. Braun glovebox (nitrogen) or on a Schlenk line (argon).[1] All solvents, with the exception of tetrahydrofuran, were dried over activated molecular sieves in a solvent purification system from LC Technology Solutions Inc. Tetrahydrofuran was distilled from benzophenone ketyl radical prior to use. Potassium *tert*-butoxide (KO^{t}Bu, Oakwood Chemical), silver trifluoromethanesulfonate (AgOTf, Oakwood Chemical), benzylbromide (MilliporeSigma), and iron(II) chloride ($FeCl_2$, Oakwood Chemical) were purchased and used as received. Sodium azide (NaN_3) was purchased from Oakwood Chemical and used as received. *Warning: sodium azide is extremely toxic and has the potential to form explosive compounds when exposed to organic electrophiles or heavy metals. Use caution when handling this reagent.* Butyl lithium (^{n}BuLi, 1.6M in hexanes) was purchased from MilliporeSigma and used as received. *Warning: butyl lithium reacts violently with water and other protic species. Handling and quenching of this reagent should be done with extreme care.* Column chromatography was performed on silica gel (60 Å, 230-400 mesh) from MilliporeSigma. Benzyl potassium,[2] ^{Me}bPzCpLi(THF),[3] 6,6'-diphenylfulvene,[4] 3,5-diisopropyl-1H-pyrazole,[5] sodium 3,5-diisopropylpyrazole,[6] bis(3,5-diisopropylpyrazolyl)methane,[7] and 5-methyl-3-(trifluoromethyl)pyrazole[8] were synthesized according to literature procedures.

Benzene-d_6 was obtained from Cambridge Isotope Laboratories, dried over molecular sieves, and degassed prior to use. Chloroform-*d* was purchased from Cambridge Isotope Laboratories and used as received. ^{1}H and ^{13}C NMR data were recorded using either a Bruker 400 MHz Avance III or a 700 MHz Avance II HDTM spectrometer. ^{19}F and ^{7}Li NMR data were obtained using a Bruker 400 MHz Avance III spectrometer. ^{1}H and ^{13}C NMR shifts are reported in parts per million (ppm) referenced internally to the residual solvent peaks at δ 7.16 ppm for C_6D_5H and δ 7.26 ppm for $CHCl_3$. All ^{19}F NMR shifts are reported in ppm, referenced externally to monofluorobezene (C_6H_5F) at δ -113.15 ppm. All ^{7}Li NMR shifts are reported in ppm, referenced externally to LiCl in D_2O at δ 0 ppm. NMR multiplicities are reported as s (singlet), d (doublet), t (triplet), sep (septet), and m (multiplet). Infrared spectra were recorded on a Shimadzu FTIR-8400S spectrometer using samples prepared in the glovebox as KBr pellets. Elemental analyses were performed by Midwest Microlab (Indianapolis, IN).

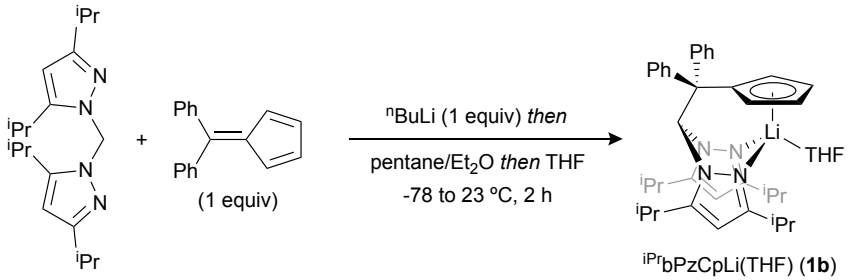
Crystals of compounds **2a**, **2b**, **3**, **4**, **5**, **6**, **10**, and **11** of appropriate dimension were obtained by slow diffusion of pentane into saturated tetrahydrofuran (THF) or diethyl ether solution at -35 ºC or by slow evaporation from saturated diethyl ether or toluene solution at -35 ºC. The crystals were coated with polyisobutylene oil in a drybox and mounted on MiTeGen cryoloops in random orientations for data collection. Preliminary examination and data collection were performed using a Bruker Venture Duo Photon-II single crystal X-ray diffractometer equipped with an Oxford Cryostream LT device. Data sets were collected using an Incoatec IμS micro-focus source (Cu or Mo) with multi-layer mirror optics. Preliminary unit cell constants were determined from a set of 180 degree fast φ scan frames (typically, 1 second exposure, 1º scan). Intensity data collections consist of combinations of ω and φ scan frames with typical scan width of 0.5º and counting time of 1 to 10 seconds/frame at a crystal to detector distance of 3.7 cm. The collected frames were integrated using an orientation matrix determined from the narrow frame scans. Apex II and SAINT software packages[9] were used for data collection and data integration. Analysis of the integrated data did not show any decay. Final cell constants were determined by global refinement

of reflections harvested from the complete data set. Collected data were corrected for systematic errors using SADABS[9] based on the Laue symmetry using equivalent reflections. Crystal data and intensity data collection parameters are listed in Table S1.

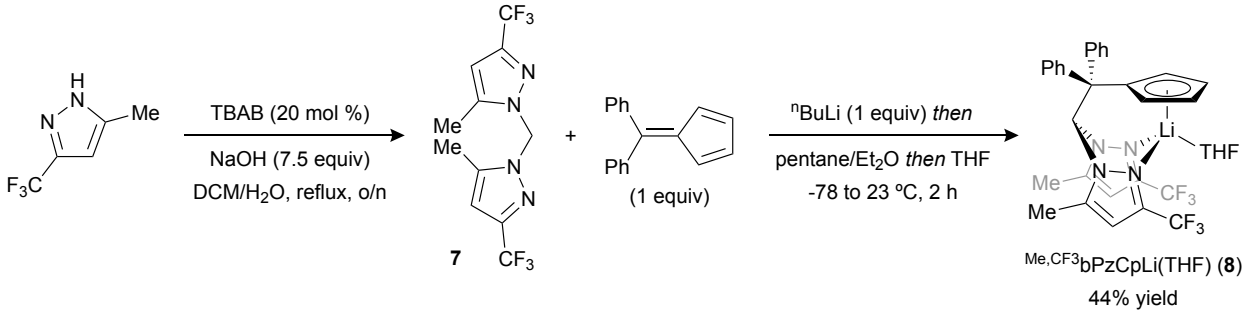
Structure solution and refinement were carried out using the SHELXTL-PLUS software package.[10] The structure of **2a** was solved and refined in the monoclinic space group $P2_1/c$. Complex **2a** crystallizes with a molecule of THF disordered over two sites (75:25%). Disorder in one of the phenyl rings of the ligand was resolved with two orientations with refined occupancies of 52:48%. The disordered atoms were refined with restraints (SADI/SIMU). The structure of **2b** was refined in the space group $P2_1/n$. A molecule of diethyl ether was found in the lattice. Compound **3** crystallizes in the orthorhombic space group Pbca with a molecule of diethyl ether. The solvent is disordered and could not be modeled. Platon/Squeeze was used to remove the solvent contribution. Compound **4** and **5** crystallize in the space group $P2_1/n$. Compound **4** contains a molecule of THF in the lattice. The benzyl ligand and a pyrazolyl isopropyl group are disordered, and this disorder was modeled with partial occupancy atoms and refined with geometrical and displacement parameter restraints (SADI, RIGU, SIMU and ISOR). Compound **5** crystallizes with a molecule of diethyl ether. Disorder in the solvent and CF_3 substituent were modeled using geometrical and displacement parameter restraints (SADI and SIMU). Compound **6** was refined in the monoclinic space group $P2_1/c$. The terminal nitrogen of the azide ligand is disordered and was refined over two positions (68:32%). The disordered atoms were refined with geometrical restraints and displacement parameter constraints. Compounds **10** and **11** crystallize in the triclinic space group P-1. Compound **10** contains a coordinated THF molecule that is disordered over two orientations (68:28%). A partial occupancy water (partial occupancy refines to 0.21) overlaps the position of the THF molecule. The THF and water were refined as PART (1 and 2) and the water was refined as PART 3. Compound **11** crystallizes with a molecule of disordered diethyl ether which sits on a symmetry element. The solvent contribution was removed with Platon/Squeeze. Two isopropyl groups are disordered, and the disorder was resolved with partial occupancies refined to 64:36% and 82:18% and refined with SADI/SIMU restraints.

Tables of calculated and observed structure factors are available in electronic format. Picture representations of molecular structures were rendered using Olex2 software.[10]

Ligand Synthesis



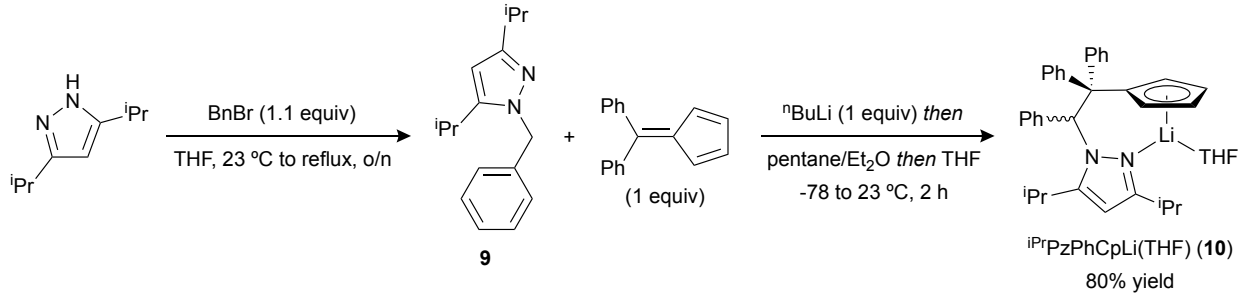
Synthesis of ^{iPr}bPzCpLi(THF) (1b). ^{iPr}bPzCpLi(THF) was prepared following a modified literature procedure.[3] A 100 mL Schlenk flask was charged with bis(3,5-diisopropylpyrazolyl)methane (300 mg, 0.95 mmol), pentane (20 ml), diethyl ether (10 ml), and a stir bar in the glovebox. The flask was brought out of the glovebox, connected to the Schlenk line, and cooled to -78 °C using a dry ice/acetone bath. To this solution, ^{n}BuLi (1.6M in hexanes, 0.6 ml, 0.96 mmol) was added via syringe. The resulting cloudy mixture was stirred at -78 °C for 1 hour and then warmed to 0 °C. 6,6'-Diphenylfulvene (218 mg, 0.95 mmol) in diethyl ether (5 ml) was added via syringe at 0 °C. The mixture was stirred at 0 °C for an additional hour and then the solvent was removed *in vacuo*. The flask was returned to the glovebox and the resulting dark green solid was dissolved in THF, layered with pentane, and placed in the freezer (-35 °C) overnight. The liquid was decanted and the solid residue was washed with pentane (3 x 5 ml) and dried *in vacuo* to yield ^{iPr}bPzCpLi(THF) as colorless crystals (343 mg, 58%). ^{1}H NMR (400 MHz, C_6D_6, 296.8 K): δ 7.63-7.60 (m, 5H, *o*-Ph and -C*H*), 7.04-6.99 (m, 4H, *m*-Ph), 6.94-6.90 (m, 2H, *p*- Ph), 6.56-6.55 (m, 2H, Cp), 5.80-5.79 (m, 2H, Cp), 5.70 (s, 2H, Pz), 3.59-3.55 (m, THF), 2.77 (sep, 2H, C*H*$(CH_3)_2$, $^{3}J_{H\text{-}H}$ = 6.73 Hz), 2.62 (sep, 2H, C*H*$(CH_3)_2$, $^{3}J_{H\text{-}H}$ = 6.78 Hz), 1.43-1.40 (m, THF), 1.12 (d, 6H, CH(C*H*$_3)_2$, $^{3}J_{H\text{-}H}$ = 6.86 Hz), 1.10 (d, 6H, CH(C*H*$_3)_2$, $^{3}J_{H\text{-}H}$ = 6.94 Hz), 0.88 (d, 6H, CH(C*H*$_3)_2$, $^{3}J_{H\text{-}H}$ = 6.86 Hz), 0.85 (d, 6H, CH(C*H*$_3)_2$, $^{3}J_{H\text{-}H}$ = 6.72 Hz). ^{13}C{^{1}H} NMR (C_6D_6, 297.1 K): δ 157.2, 151.8, 148.9, 131.1, 127.7, 126.1, 114.5, 109.5, 102.7, 99.6, 73.8, 67.8, 64.0, 28.0, 26.4, 25.8, 24.3, 23.5, 22.5, 22.4. ^{7}Li{^{1}H} NMR (C_6D_6, 296.9 K): δ -5.84. IR (KBr, cm^{-1}): 3061 (w), 2964 (m), 2870 (w), 1595 (w), 1549 (vs), 1491 (w), 1456 (m), 1385 (m), 1323 (w), 1281 (w), 1233 (w), 1179 (m), 1103 (w), 1070 (s), 1003 (m), 928 (w), 901 (w), 822 (w), 797 (s), 760 (w), 719 (vs). Anal. Calcd for $C_{41}H_{53}LiN_4O$: C, 78.81; H, 8.55; N, 8.97. Found: C, 78.54; H, 8.73; N, 9.04.



Synthesis of bis(5-methyl-3-(trifluoromethyl)pyrazol-1-yl)methane (7). A stirring mixture of 5-methyl-3-(trifluoromethyl)pyrazole (2.44 g, 16.3 mmol), sodium hydroxide (4.88 g, 122 mmol), dichloromethane (20.8 ml, 325 mmol), water (5 ml), and tetrabutylammonium bisulfate (1.10 g,

3.24 mmol) was heated to reflux overnight. The mixture was cooled to room temperature and water (50 ml) was added. The resulting solution was transferred into a separatory funnel and extracted with diethyl ether (3 x 50 ml). The combined organic phase was dried over magnesium sulfate, filtered, and the solvent was removed *in vacuo*. The resulting residue was purified by column chromatography (8:2 hexanes/ethyl acetate) to yield bis(5-methyl-3-(trifluoromethyl)pyrazol-1-yl)methane as a white powder (673 mg, 27%). ^{1}H NMR (400 MHz, C_6D_6, 298.0 K): δ 5.70 (s, 2H, Pz), 5.14 (s, 2H, CH_2), 1.83 (s, 6H, CH_3).^{13}C{^{1}H} NMR (C_6D_6, 298.1 K): δ 141.9, 105.1, 60.6, 10.6. The *C*F_3 and *C*-CF_3 signals could not be located. ^{19}F{^{1}H} (C_6D_6, 298.1 K): δ -62.1.

Synthesis of ^{Me,CF3}bPzCpLi(THF) (8). $^{(Me,CF3)}$bPzCpLi(THF) was prepared in a manner similar to ^{iPr}bPzCpLi(THF) using bis(5-methyl-3-(trifluoromethyl)pyrazol-1-yl)methane (231 mg, 0.74 mmol), 1.6 M ^{n}BuLi (0.46 ml, 0.74 mmol), and 6,6'-diphenylfulvene (170 mg, 1.07 mmol). The product was recrystallized from THF layered with pentane to yield $^{(Me,CF3)}$bPzCpLi(THF) as a light yellow crystalline powder (200 mg, 44%). ^{1}H NMR (400 MHz, C_6D_6, 298.1 K): δ 7.45-7.43 (m, 4H, *o*-Ph), 7.13 (s, 1H, -C*H*), 6.97-6.94 (m, 4H, *m*-Ph), 6.90-6.87 (m, 2H, *p*-Ph), 6.53-6.51 (m, 2H, Cp), 5.80-5.79 (m, 2H, Cp), 5.63 (s, 2H, Pz), 3.58-3.55 (m, THF), 1.43-1.40 (m, THF), 1.32 (s, 6H, CH_3). ^{13}C{^{1}H} NMR (C_6D_6, 298.1 K): δ 147.9, 142.2, 130.5, 127.8, 126.4, 113.1, 104.8, 103.4, 75.3, 67.9, 63.0, 25.6, 10.9. The *C*F_3, *C*-CF_3, and *ipso*-Cp signals could not be located. ^{7}Li{^{1}H} NMR (C_6D_6, 298.1 K): δ -6.38. ^{19}F{^{1}H} NMR (C_6D_6, 298.1 K): δ -62.2. IR (KBr, cm^{-1}): 3063 (w), 2976 (w), 2876 (w), 1491 (s), 1468 (w), 1443 (w), 1381 (w), 1319 (w), 1231 (vs), 1179 (vs), 1134 (vs), 1042 (w), 995 (w), 972 (w), 937 (w), 901 (w), 804 (w), 745 (w), 721 (m), 642 (w), 610 (w). Despite multiple attempts, satisfactory elemental analysis could not be obtained for this compound.

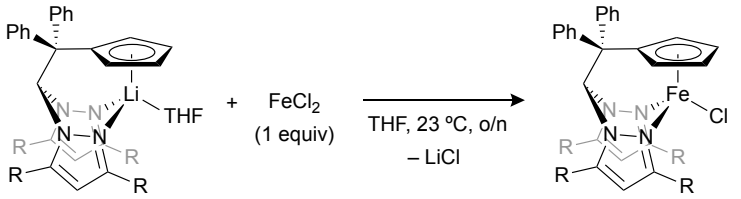


Synthesis of 1-benzyl-3,5-diisopropylpyrazole (9). To a stirring solution of sodium 3,5-diisopropylpyrazole (330 mg, 1.89 mmol) in THF (20 ml), benzyl bromide (0.25 ml, 2.10 mmol) was added via syringe at room temperature. The resulting solution was heated to reflux overnight. After removal of the solvent *in vacuo*, the residue was purified by column chromatography (9:1 hexanes/ethyl acetate) to yield 1-benzyl-3,5-diisopropylpyrazole as a yellow oil (372 mg, 73%). ^{1}H NMR (400 MHz, C_6D_6, 295.5 K): δ 7.07-6.96 (m, 5H, *o*-Ph, *m*-Ph, and *p*-Ph), 5.94 (s, 1H, Pz), 5.02 (s, 2H, -CH_2-), 3.15 (sep, 1H, CH(CH_3)$_2$, $^{3}J_{H\text{-}H}$ = 6.96 Hz), 2.53 (sep, 1H, CH(CH_3)$_2$, $^{3}J_{H\text{-}H}$ = 6.80 Hz), 1.41 (d, 6H, CH(CH_3)$_2$, $^{3}J_{H\text{-}H}$ = 6.92 Hz), 0.95 (d, 6H, CH(CH_3)$_2$, $^{3}J_{H\text{-}H}$ = 6.80 Hz). ^{13}C{^{1}H} NMR (C_6D_6, 295.9 K): δ 158.0, 149.6, 138.9, 128.7, 127.4, 126.9, 99.0, 52.7, 28.6, 25.7, 23.2, 23.0.

Synthesis of ^{iPr}PzPhCpLi(THF)$_x$ (10). A 100 mL Schlenk flask was charged with 1-benzyl-3,5-diisopropylpyrazole (259 mg, 1.07 mmol), pentane (20 ml), diethyl ether (10 ml), and a stir bar in the glovebox. The flask was brought out of the glovebox, connected to the Schlenk line, and cooled to -78 °C using a dry ice/acetone bath. To this solution, ^{n}BuLi (1.6M in hexanes, 0.65 ml, 1.04

mmol) was added via syringe. The resulting cloudy mixture was stirred at -78 °C for 1 hour and then warmed to 0 °C. 6,6'-Diphenylfulvene (246 mg, 1.07 mmol) in diethyl ether (5 ml) was added via syringe at 0 °C. The mixture was stirred at 0 °C for an additional hour and then the solvent was removed *in vacuo*. The flask was returned to the glovebox and the resulting yellow solid was dissolved in THF and transferred into a scintillation vial. The solvent was removed *in vacuo*. The resulting orange solid was dissolved in diethyl ether, layered with pentane, and placed in the freezer (-35 °C) overnight. The liquid was decanted and the solid residue was washed with pentane (3 x 5 ml) and dried *in vacuo* to yield ^{iPr}PzPhCpLi(THF)$_x$ as colorless crystals (458 mg, 80%). The degree of THF association to the product varies depending on the time of solvent removal *in vacuo*. X-ray quality crystals were obtained from toluene solution at -35 °C. ^{1}H NMR (700 MHz, C_6D_6, 298.0 K): δ 7.99 (br s, 2H, Ph-*H*, $v_{1/2}$ = 13.0 Hz), 7.16-7.13 (m, 2H, Ph-*H*), 7.08-7.06 (m, 1H, Ph-*H*), 7.04-7.02 (m, 2H, Ph-*H*), 7.01-6.98 (m, 1H, Ph-*H*), 6.94-6.92 (m, 1H, Ph-*H*), 6.91-6.88 (m, 2H, Ph-*H*), 6.86-6.84 (m, 2H, Ph-*H*), 6.74 (s, 1H, -C*H*-Ph), 6.65-6.63 (m, 2H, Ph-*H*), 6.42-6.41 (m, 1H, Cp), 6.31-6.30 (m, 1H, Cp), 5.88 (s, 1H, Pz), 5.83-5.81 (m, 1H, Cp), 5.59-5.58 (m, 1H, Cp), 3.48-3.47 (m, THF), 2.83 (sep, 1H, C*H*(CH$_3$)$_2$, $^3J_{H\text{-}H}$ = 6.86 Hz), 2.45 (sep, 1H, C*H*(CH$_3$)$_2$, $^3J_{H\text{-}H}$ = 6.93 Hz), 1.36-1.34 (m, THF), 1.14 (d, 3H, CH(C*H*$_3$)$_2$, $^3J_{H\text{-}H}$ = 6.81 Hz), 0.96 (d, 3H, CH(C*H*$_3$)$_2$, $^3J_{H\text{-}H}$ = 6.93 Hz), 0.93 (d, 3H, CH(C*H*$_3$)$_2$, $^3J_{H\text{-}H}$ = 6.93 Hz), 0.67 (d, 3H, CH(C*H*$_3$)$_2$, $^3J_{H\text{-}H}$ = 6.84 Hz). ^{13}C{^{1}H} NMR (C_6D_6, 298.0 K): δ 158.4, 153.2, 150.4, 150.3, 141.4, 132.5, 130.8, 129.7, 127.2, 127.1, 127.1, 126.5, 125.8, 118.7, 110.1, 108.2, 105.3, 102.3, 99.8, 69.1, 68.0, 61.4, 27.6, 26.3, 25.6, 23.3, 22.6, 21.8. ^{7}Li{^{1}H} NMR (C_6D_6, 295.7 K): δ -7.12. IR (KBr, cm^{-1}): 3057 (w), 2965 (m), 2930 (w), 2872 (w), 1545 (m), 1493 (m), 1458 (w), 1319 (w), 1294 (w), 1240 (w), 1182 (w), 1067 (w), 1042 (w), 1005 (w), 903 (m), 874 (w), 816 (w), 793 (w), 748 (m), 708 (vs), 650 (w). Anal. Calcd for $C_{34}H_{35}LiN_2 \cdot (C_4H_8O)_{1.65}$: C, 81.60; H, 8.13; N, 4.69. Found: C, 81.32; H, 8.35; N, 4.96.

Preparation of Iron Complexes

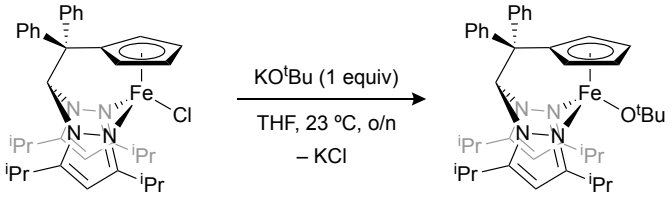


1a (R = Me)
1b (R = ^{i}Pr)

2a (R = Me): 47% yield
2b (R = ^{i}Pr): 57% yield

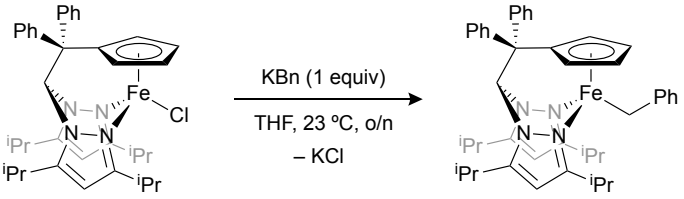
Synthesis of ^{Me}bPzCpFeCl (2a). To a 20 ml scintillation vial charged with $FeCl_2$ (25 mg, 0.20 mmol) and a stir bar, ^{Me}bPzCpLi(THF) (100 mg, 0.20 mmol) in THF (5 ml) was added at room temperature. The resulting mixture was stirred at room temperature overnight to give a slightly darker solution. The solvent was removed *in vacuo*. The resulting solid residue was extracted with toluene (3 x 3 ml) and filtered through Celite. The solvent was removed *in vacuo* to yield ^{Me}bPzCpFeCl as an off-white solid (50 mg, 47%). X-ray quality crystals were obtained from THF solution layered with pentane at -35 °C. ^{1}H NMR (400 MHz, C_6D_6, 295.5 K): δ 54.0 (s, 2H), 7.97 (s, 2H), 5.97 (s, 4H), 4.93 (s, 4H), 1.94 (s, 6H), -3.05 (s, 6H), -28.2 (s, 1H), -115 (bs, $v_{1/2}$ = 1721 Hz), -160 (bs, $v_{1/2}$ = 1608 Hz). μ_{eff} (Evans method, C_6D_6, 298.0 K) = 4.5 μ_B. IR (KBr, cm^{-1}): 3098 (w), 3057 (w), 3028 (w), 2957 (w), 2922 (w), 1558 (w), 1489 (w), 1454 (w), 1418 (w), 1387 (m), 1323 (s), 1238 (w), 1040 (s), 984 (w), 941 (w), 835 (m), 797 (m), 760 (vs), 719 (s), 700 (s), 625 (s). Anal. Calcd for $C_{29}H_{29}ClFeN_4$: C, 66.36; H, 5.57; N, 10.67. Found: C, 65.13; H, 5.68; N, 10.50.

Synthesis of ^{iPr}bPzCpFeCl (2b). ^{iPr}bPzCpFeCl was prepared in a manner similar to ^{Me}bPzCpFeCl using ^{iPr}bPzCpLi(THF) (120 mg, 0.19 mmol), $FeCl_2$ (24 mg, 0.19 mmol), and THF (5ml). After extraction with toluene (3 x 1 ml) and solvent removal, the product was isolated as a white powder (72 mg, 57%). X-ray quality crystals were obtained from diethyl ether solution layered with pentane at -35 °C. ^{1}H NMR (400 MHz, C_6D_6, 295.5 K): δ 55.1 (s, 2H), 7.93 (s, 2H), 6.08 (s, 4H), 3.80-2.47 (m, 18H), -0.96 (s, 6H), -2.27 (s, 2H), -15.2 (s, 6H), -29.2 (s, 1H), -129 (bs, $\nu_{1/2}$ = 3696 Hz), -160 (bs, $\nu_{1/2}$ = 3865 Hz). μ_{eff} (Evans method, C_6D_6, 295.1 K) = 5.1 μ_B. IR (KBr, cm^{-1}): 3094 (w), 2967 (vs), 2930 (m), 2870 (m), 1551 (m), 1491 (m), 1466 (vs), 1391 (vs), 1317 (w), 1298 (m), 1204 (w), 1180 (s), 1159 (w), 1105 (w), 1059 (vs), 1018 (w), 878 (m), 853 (w), 824 (m), 802 (s), 756 (vs), 725 (m), 704 (s), 654 (w). Anal. Calcd for $C_{37}H_{45}ClFeN_4$: C, 69.76; H, 7.12; N, 8.79. Found: C, 69.65; H, 7.09; N, 8.87.



2b **3**, 86% yield

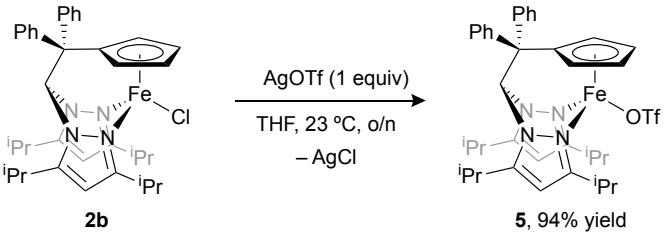
Synthesis of ^{iPr}bPzCpFeO^{t}Bu (3). To a 20 ml scintillation vial charged with ^{iPr}bPzCpFeCl (75 mg, 0.12 mmol) and a stir bar, KO^{t}Bu (13 mg, 0.12 mmol) in THF (5 ml) was added at room temperature. The resulting mixture was stirred at room temperature overnight to yield a yellow solution. The solvent was removed *in vacuo*. The resulting solid residue was extracted with toluene (3 x 1 ml) and filtered through Celite. The solvent was removed *in vacuo* to yield ^{iPr}bPzCpFeO^{t}Bu as a yellow powder (67 mg, 86%). X-ray quality crystals were obtained from diethyl ether solution at -35 °C. ^{1}H NMR (400 MHz, C_6D_6, 297.9 K): δ 48.6 (s, 2H), 8.92 (s, 2H), 7.72 (s, 4H), 5.45 (s, 4H), 3.56 (s, 2H), 1.71 (s, 6H), 1.42 (s, 1H), 0.49 (s, 6H), -0.51– -1.04 (m, 7H), -10.8 – -11.96 (m, 7H), -137.4 – -143.0 (m). One signal could not be located. μ_{eff} (Evans method, C_6D_6, 298.0 K): 4.8 μ_B. IR (KBr, cm^{-1}): 3102 (w), 2965 (m), 2930 (w), 2870 (w), 1703 (w), 1670 (w), 1655 (w), 1639 (w), 1632 (w), 1622 (w), 1602 (w), 1547 (m), 1526 (w), 1493 (w), 1472 (w), 1460 (w), 1443 (w), 1385 (m), 1323 (w), 1300 (w), 1198 (s), 1155 (s), 1113 (vs), 995 (m), 905 (w), 876 (w), 824 (w), 800 (m), 760 (w), 746 (m), 723 (m), 704 (m), 677 (w), 623 (m), 596 (m). Anal. Calcd for $C_{41}H_{54}FeN_4O$: C, 72.98; H, 8.07; N, 8.30. Found: C, 71.25; H, 8.55; N, 7.96.



2b **4**, 82% yield

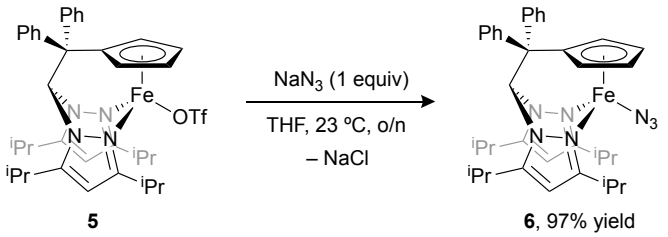
Synthesis of ^{iPr}bPzCpFeBn (4). ^{iPr}bPzCpFeBn was prepared in manner similar to ^{iPr}bPzCpFeO^{t}Bu using ^{iPr}bPzCpFeCl (56 mg, 0.09 mmol), benzyl potassium (12 mg, 0.09 mmol), and THF (5 ml). After extraction with toluene (3 x 1 ml) and removal of solvent, the product was isolated as a yellow solid (50 mg, 82%). X-ray quality crystals were obtained from THF solution layered with pentane at -35 °C. ^{1}H NMR (400 MHz, C_6D_6, 297.9 K): δ 48.3 (s, 2H), 21.7 (s, 2H), 7.78 (s, 2H), 6.42 (s, 4H), 4.5-2.74 (m, 18H), -0.28 (s, 2H), -0.43 (s, 6H), -15.1 (s, 6H), -20.2 (s, 1H), -34.3 (s,

2H), -42.4 (s, 1H), -134 – -139 (m). One signal could not be located. μ_{eff} (Evans method, C_6D_6, 298.1 K): 5.1 μ_B. IR (KBr, cm^{-1}): 3059 (w), 2967 (s), 2928 (m), 2868 (m), 1589 (m), 1547 (m), 1466 (m), 1387 (m), 1300 (m), 1207 (m), 1179 (m), 1058 (s), 959 (m), 902 (w), 876 (w), 800 (m), 752 (m), 721 (w), 700 (m), 625 (w). Despite multiple attempts, satisfactory elemental analysis could not be obtained for this compound.



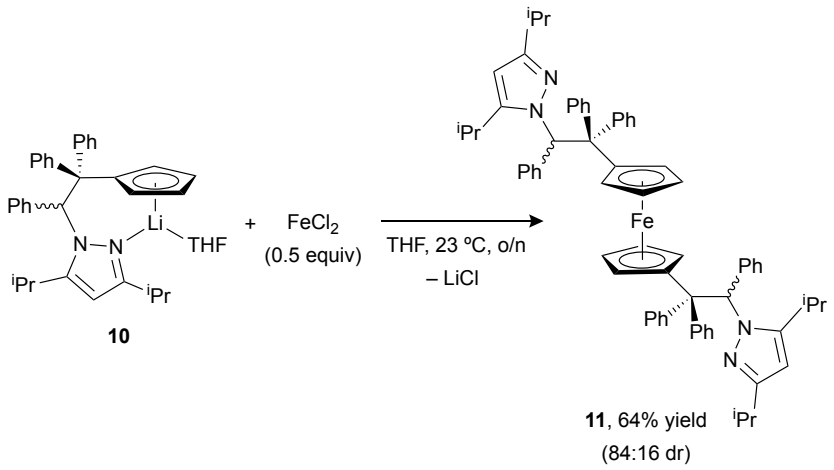
2b **5**, 94% yield

Synthesis of ^{iPr}bPzCpFeOTf (5). To 20 ml scintillation vial charged with ^{iPr}bPzCpFeCl (65 mg, 0.1 mmol) and a stir bar and wrapped in aluminum foil, AgOTf (26 mg, 0.1 mmol) in THF (5 ml) was added at room temperature. The resulting mixture was stirred at room temperature overnight to yield a yellow solution with a gray precipitate. The solvent was removed *in vacuo*. The resulting solid residue was extracted with toluene (3 x 1 ml) and filtered through Celite. The solvent was removed *in vacuo* to yield ^{iPr}bPzCpFeOTf as a yellow powder (72 mg, 94%). X-ray quality crystals were obtained from THF solution layered with pentane at -35 °C. ^{1}H NMR (400 MHz, C_6D_6, 297.9 K): δ 58.8 (s, 2H), 7.79 (s, 2H), 7.03 (s, 4H), 5.70 (s, 4H), 1.88 (s, 6H), -1.45 (s, 6H), -3.50 (s, 2H), -15.1 (s, 6H), -43.2 (s, 1H). Multiple signals could not be located. μ_{eff} (Evans method, C_6D_6, 298.6 K): 4.8 μ_B. ^{19}F NMR (C_6D_6, 294.6 K): δ -14.10. IR (KBr, cm^{-1}): 2967 (m), 2932 (w), 2870 (w), 1641 (m), 1549 (m), 1391 (m), 1331 (m), 1292 (w), 1258 (w), 1234 (m), 1204 (s), 1177 (m), 1059 (m), 1014 (s), 930 (w), 878 (w), 802 (m), 762 (m), 704 (m), 635 (s), 584 (w). Anal. Calcd for $C_{38}H_{45}F_3FeN_4O_3S$: C, 60.80; H, 6.04; N, 7.46. Found: C, 60.49; H, 6.39; N, 7.44.



5 **6**, 97% yield

Synthesis of ^{iPr}bPzCpFeN$_3$ (6). To a 20 ml scintillation vial charged with ^{iPr}bPzCpFeOTf (30 mg, 0.04 mmol) and a stir bar, NaN_3 (3.0 mg, 0.05 mmol) in THF (2 ml) was added at room temperature. The resulting mixture was stirred at room temperature overnight to yield an orange solution. The solvent was removed *in vacuo*. The resulting solid residue was extracted with toluene (3 x 1 ml) and filtered through Celite. The solvent was removed *in vacuo* to yield ^{iPr}bPzCpFeN$_3$ as a yellow powder (25 mg, 97%). X-ray quality crystals were obtained from THF solution layered with pentane at -35 °C. ^{1}H NMR (400 MHz, C_6D_6, 297.9 K): δ 56.5 (s, 2H), 8.01 (s, 2H), 6.24 (s, 4H), 5.02-2.90 (m, 11 H), 2.46 (s, 6H), -0.71 (s, 6H), -1.77 (s, 2H), -13.7 (s, 6H), -29.4 (s, 1H), -127.9 (bs, $\nu_{1/2}$ = 2229 Hz), -159.1 (bs, $\nu_{1/2}$ = 2313 Hz). μ_{eff} (Evans method, C_6D_6, 298.0 K): 5.2 μ_B. IR (KBr, cm^{-1}): 3059 (w), 2970 (m), 2930 (m), 2870 (m), 2062 (vs), 1549 (m), 1491 (w), 1466 (m), 1387(m), 1300 (m), 1182 (w), 1061 (m), 804 (w), 758 (m), 706 (m), 627 (w), 519 (w). Anal. Calcd for $C_{37}H_{45}FeN_7$: C, 69.04; H, 7.05; N, 15.23. Found: C, 68.87; H, 7.21; N, 14.83.



Synthesis of (^{iPr}PzPhCp)$_2$Fe (11). To a 20 ml scintillation vial charged with $FeCl_2$ (20 mg, 0.16 mmol) and a stir bar, ^{iPr}PzPhCpLi(THF) (173 mg, 0.31 mmol) in THF (5 ml) was added at room temperature. The resulting mixture was stirred at room temperature overnight to give an orange solution. The solvent was removed *in vacuo*. The resulting solid residue was extracted with toluene (3 x 1 ml) and filtered through Celite. The solvent was removed *in vacuo* to yield (^{iPr}PzPhCp)$_2$Fe as a yellow powder (100 mg, 64%, 84:16 mixture of diastereomers). X-ray quality crystals were obtained from diethyl ether solution at -35 °C. ^{1}H NMR (400 MHz, C_6D_6, 297.9 K): δ 7.77-7.73 (m, 4H, Ph), 7.67-7.62 (m, 4H, Ph), 7.40-7.34 (m, 4H, Ph), 7.14-7.06 (m, 12H, Ph), 6.96-6.90 (m, 6H, Ph), 6.36 (s, 2H, -C*H*-Ph), 5.67 (s, 2H, Pz), 3.93-3.53 (m, 4H, Cp), 2.93 (sep, 2H, C*H*(CH$_3$)$_2$, $^3J_{H\text{-}H}$ = 6.64 Hz), 2.60 (sep, 2H, C*H*(CH$_3$)$_2$, $^3J_{H\text{-}H}$ = 6.48 Hz), 1.33 (d, 6H, CH(C*H*$_3$)$_2$, $^3J_{H\text{-}H}$ = 6.84 Hz), 1.30 (d, 6H, CH(C*H*$_3$)$_2$, $^3J_{H\text{-}H}$ = 6.88 Hz), 1.00 (d, 6H, CH(C*H*$_3$)$_2$, $^3J_{H\text{-}H}$ = 6.56 Hz), 0.81 (d, 6H, CH(C*H*$_3$)$_2$, $^3J_{H\text{-}H}$ = 6.80 Hz). ^{13}C{^{1}H} NMR (C_6D_6, 298.2 K): δ 156.7, 151.1, 146.2, 139.7, 133.2, 131.9, 131.7, 127.4, 127.2, 126.7, 126.6, 126.5, 126.0, 98.4, 73.6, 71.5, 70.1, 68.4, 60.9, 28.5, 25.9, 23.9, 23.3, 22.8, 22.3. IR (KBr, cm^{-1}): 3055 (w), 2963 (s), 2930 (w), 2868 (m), 1601 (m), 1543 (s), 1493 (s), 1449 (w), 1385 (w), 1292 (m), 1234 (w), 1184 (m), 1069 (m), 1038 (m), 1001 (m), 878 (w), 824 (m), 743 (s), 706 (vs), 617 (w). Anal. Calcd for $C_{68}H_{70}FeN_4$: C, 81.74; H, 7.06; N, 5.61. Found: C, 81.12; H, 7.32; N, 5.27.

NMR Spectra

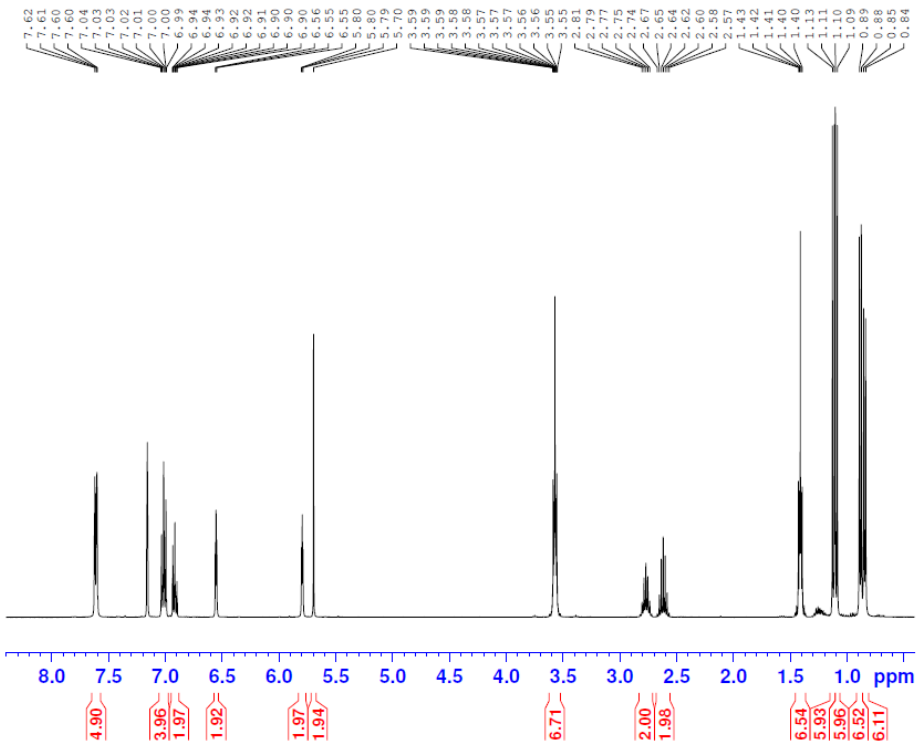


Figure S1. ^{1}H NMR spectrum of ^{iPr}bPzCpLi(THF) (**1b**) in C_6D_6 at 297 K.

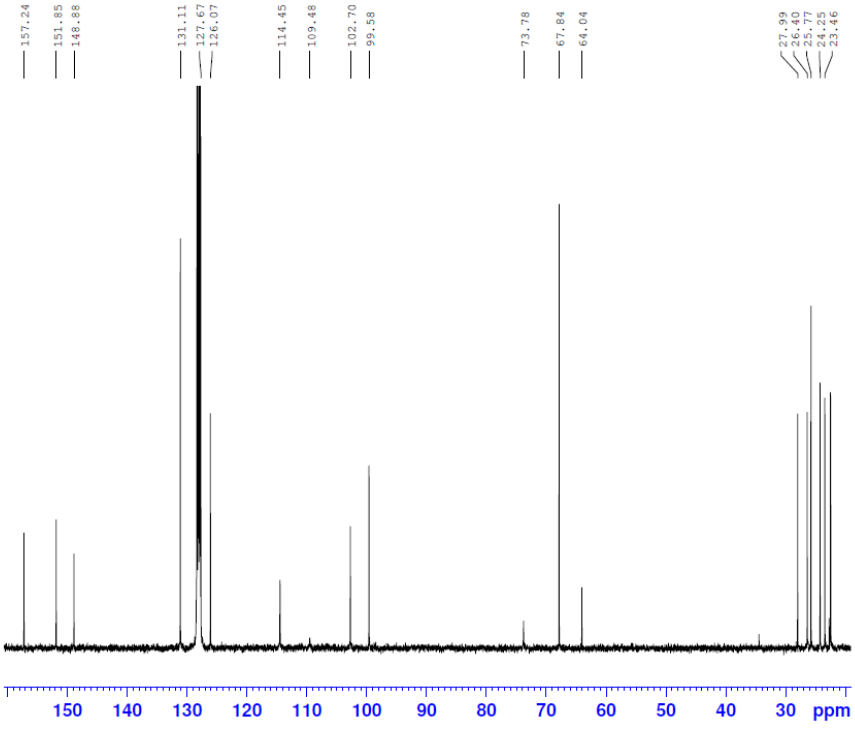


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of ^{iPr}bPzCpLi(THF) (**1b**) in C_6D_6 at 297 K.

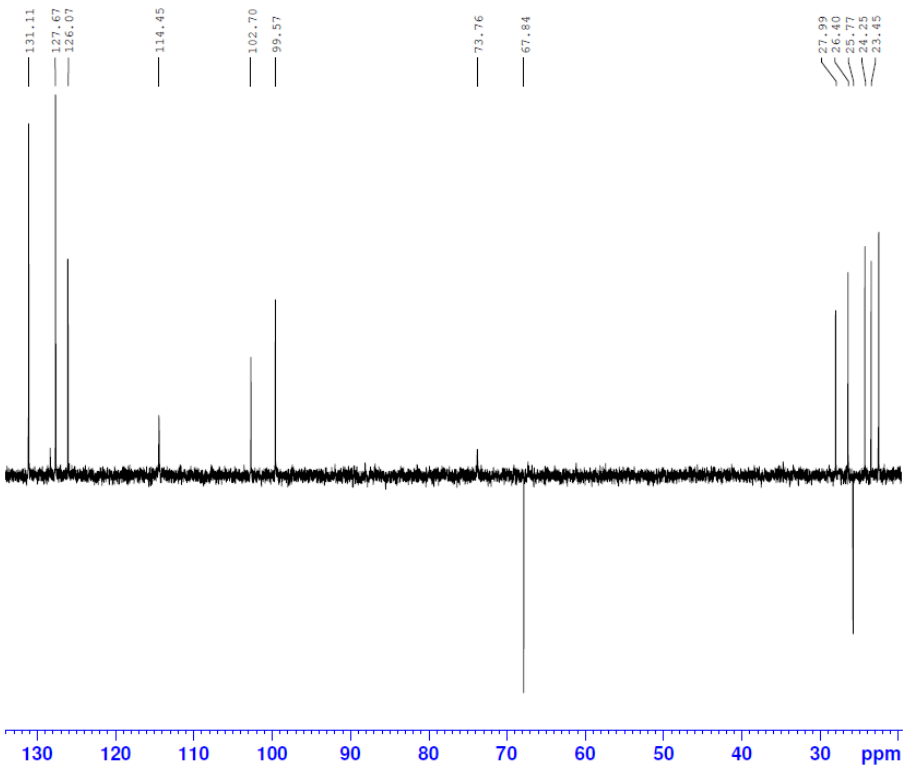


Figure S3. DEPT135 NMR spectrum of ^{iPr}bPzCpLi(THF) (**1b**) in C_6D_6 at 297 K.

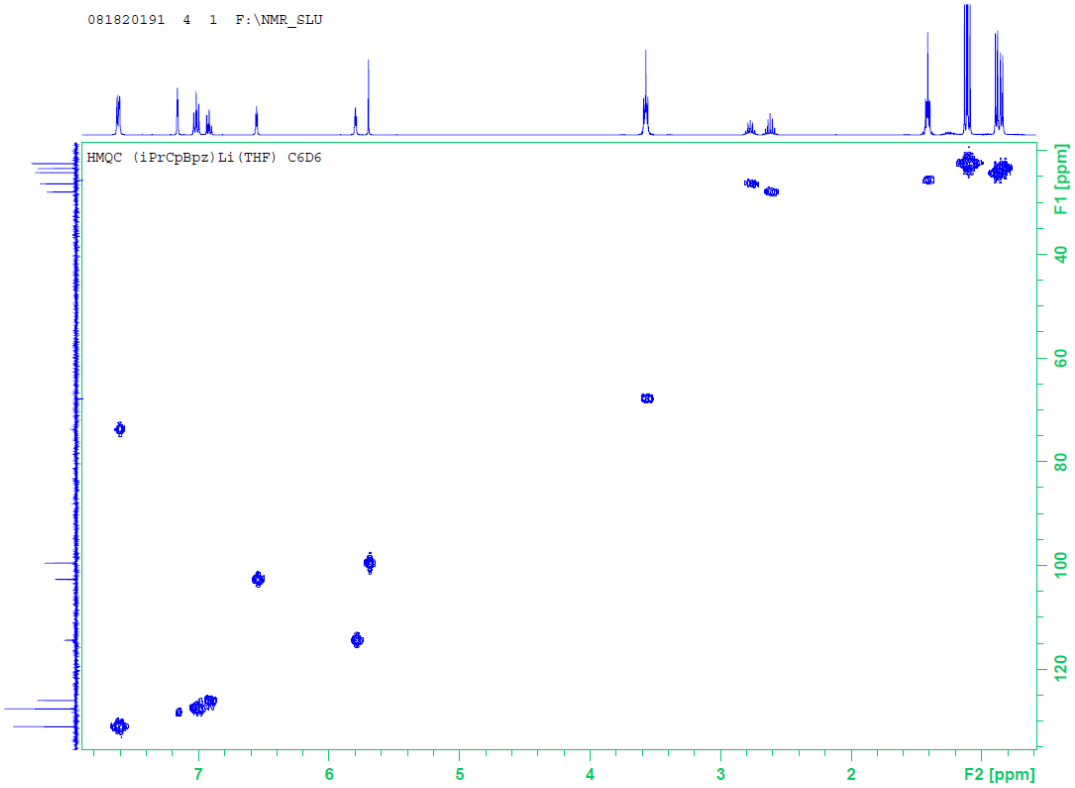


Figure S4. HMQC NMR spectrum of ^{iPr}bPzCpLi(THF) (**1b**) in C_6D_6 at 297 K.

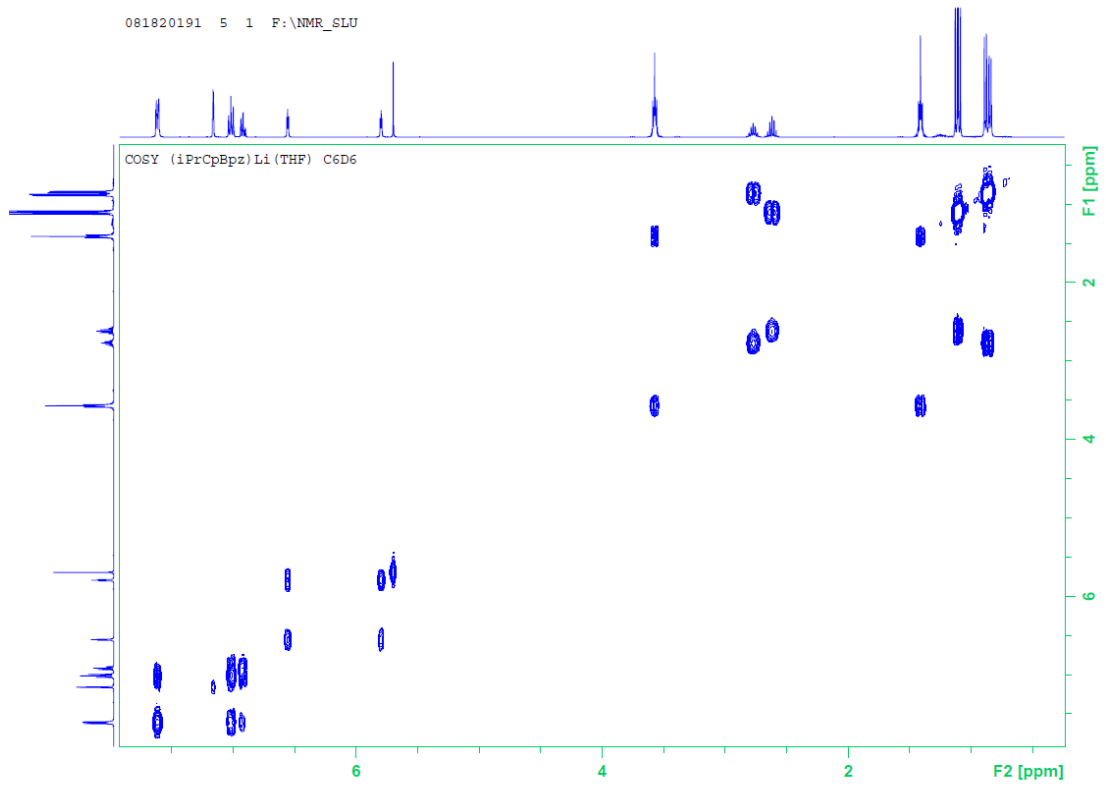


Figure S5. COSY NMR spectrum of ^{iPr}bPzCpLi(THF) (**1b**) in C_6D_6 at 297 K.

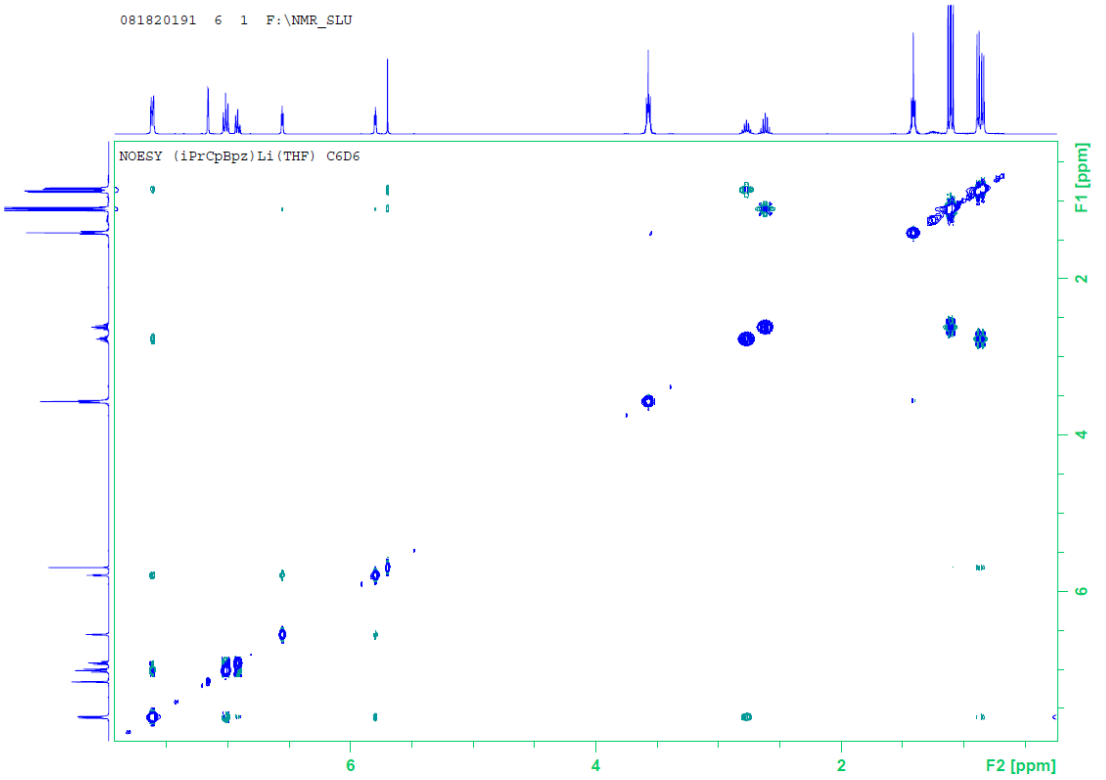


Figure S6. NOESY NMR spectrum of ^{iPr}bPzCpLi(THF) (**1b**) in C_6D_6 at 297 K.

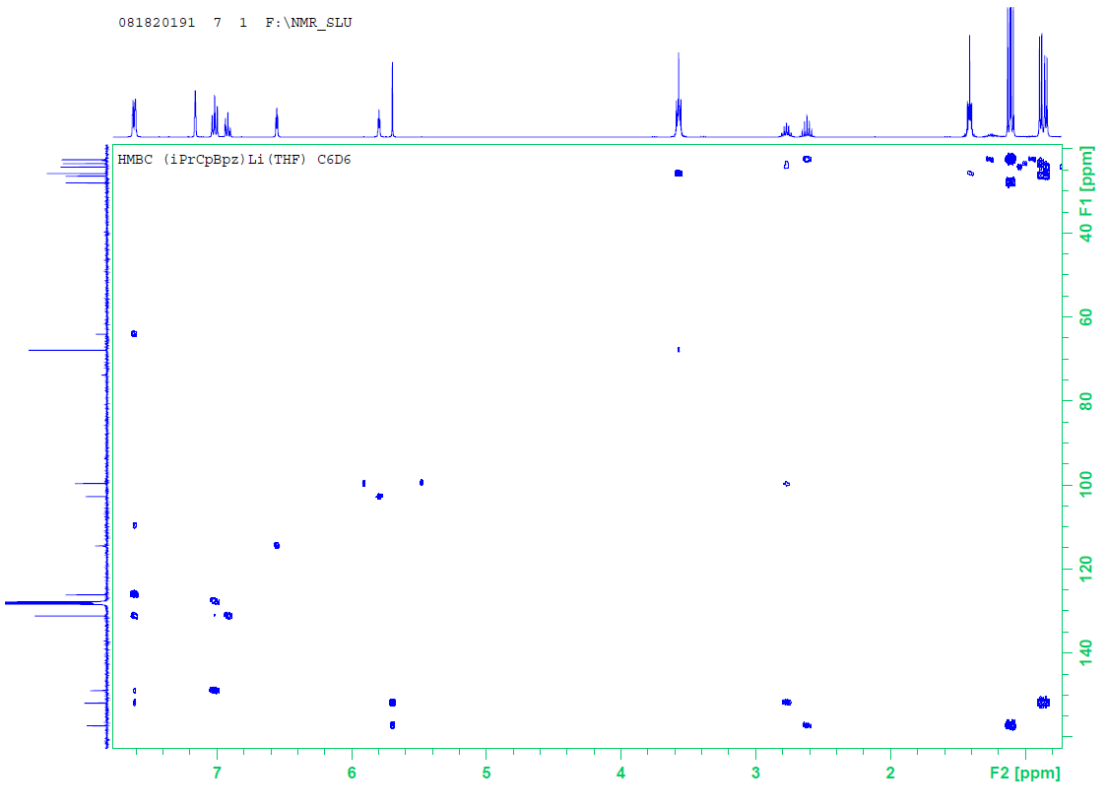


Figure S7. HMBC NMR spectrum of ^{iPr}bPzCpLi(THF) (**1b**) in C_6D_6 at 297 K.

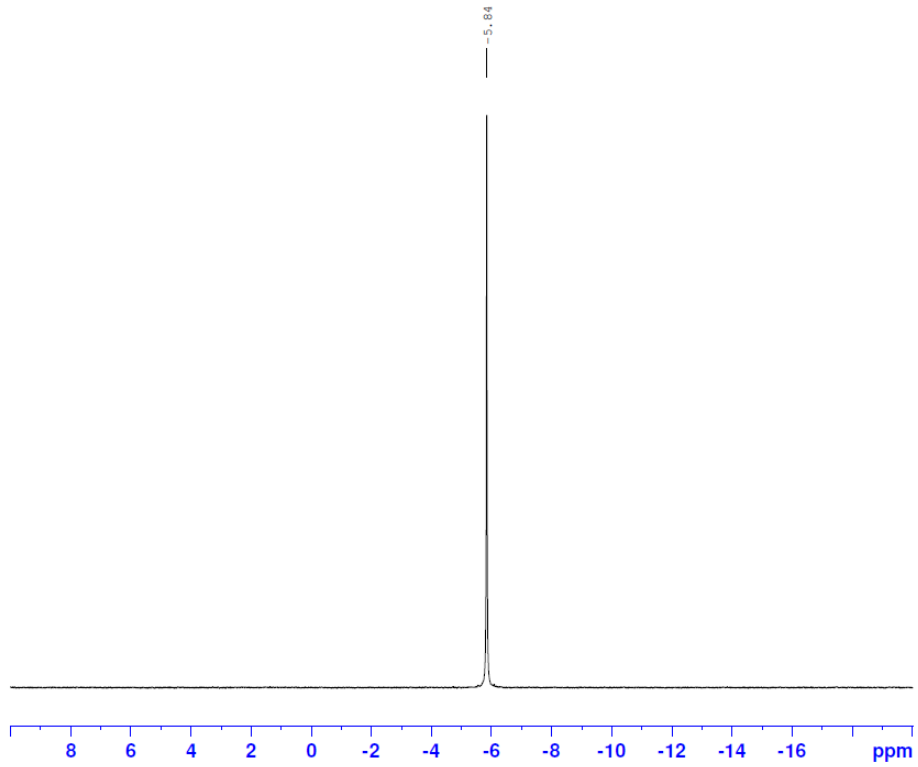


Figure S8. ^{7}Li NMR spectrum of ^{iPr}bPzCpLi(THF) (**1b**) in C_6D_6 at 297 K.

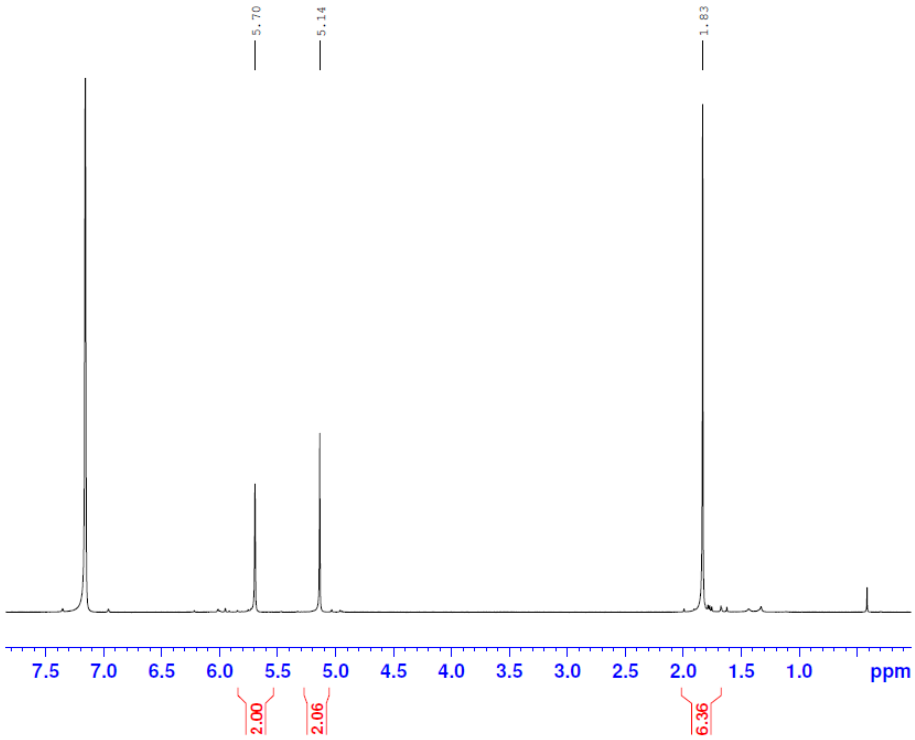


Figure S9. ^{1}H NMR spectrum of bis(5-methyl-3-(trifluoromethyl)pyrazol-1-yl)methane (**7**) in C_6D_6 at 298.0 K.

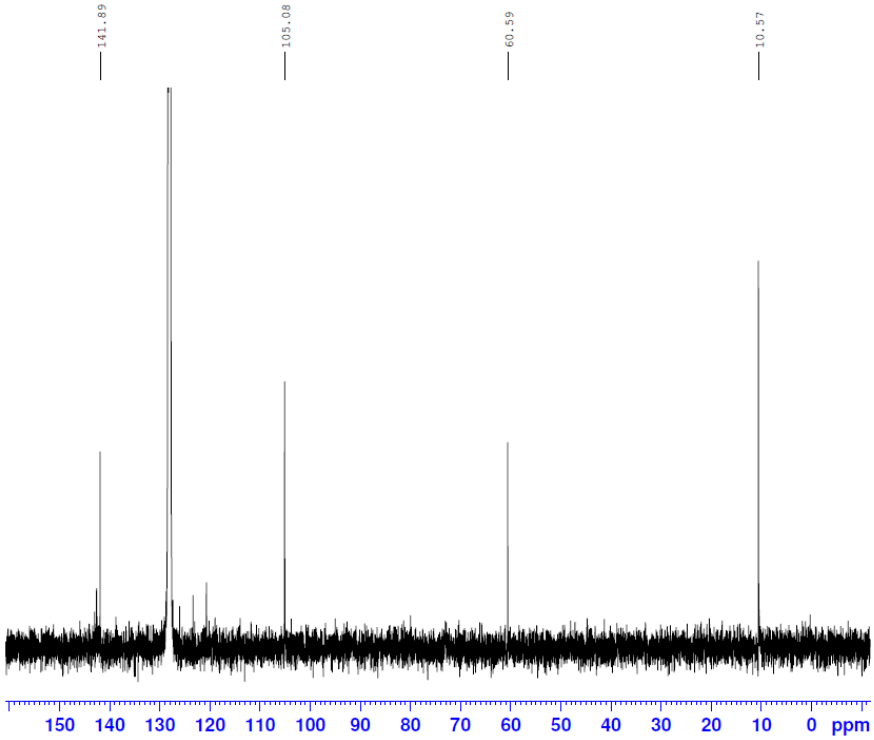


Figure S10. ^{13}C{^{1}H} NMR spectrum of bis(5-methyl-3-(trifluoromethyl)pyrazol-1-yl)methane (**7**) in C_6D_6 at 298.0 K.

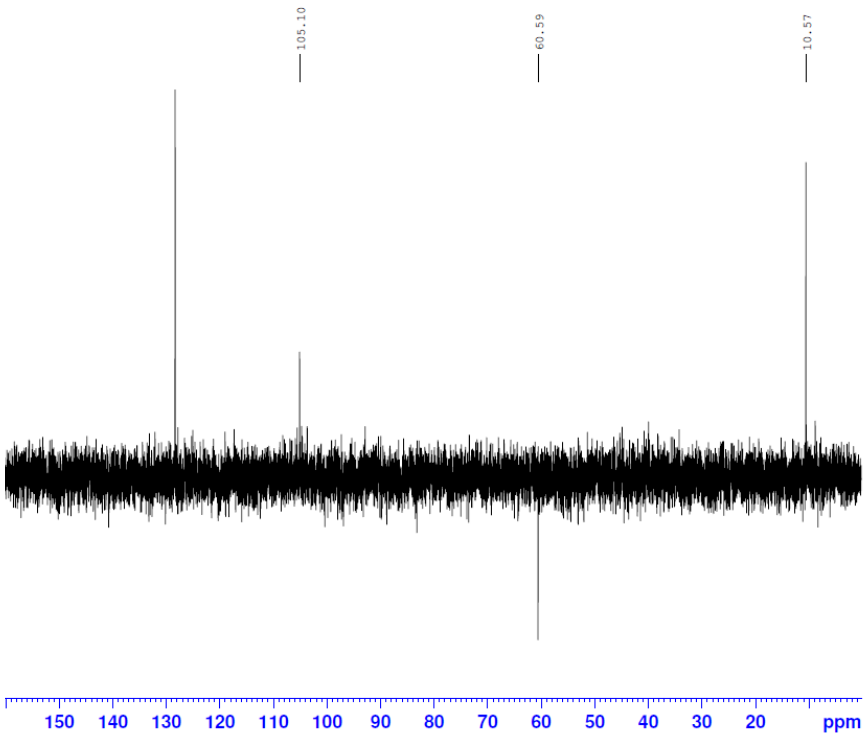


Figure S11. DEPT135 NMR spectrum of bis(5-methyl-3-(trifluoromethyl)pyrazol-1-yl)methane (**7**) in C_6D_6 at 298.1 K.

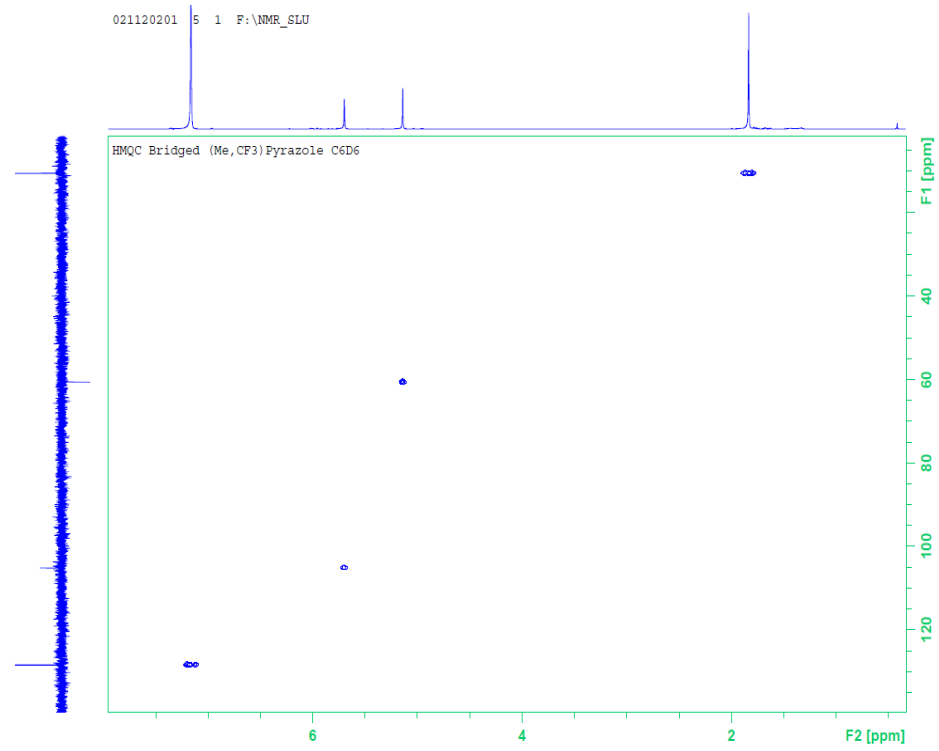


Figure S12. HMQC NMR spectrum of bis(5-methyl-3-(trifluoromethyl)pyrazol-1-yl)methane (**7**) in C_6D_6 at 298.4 K.

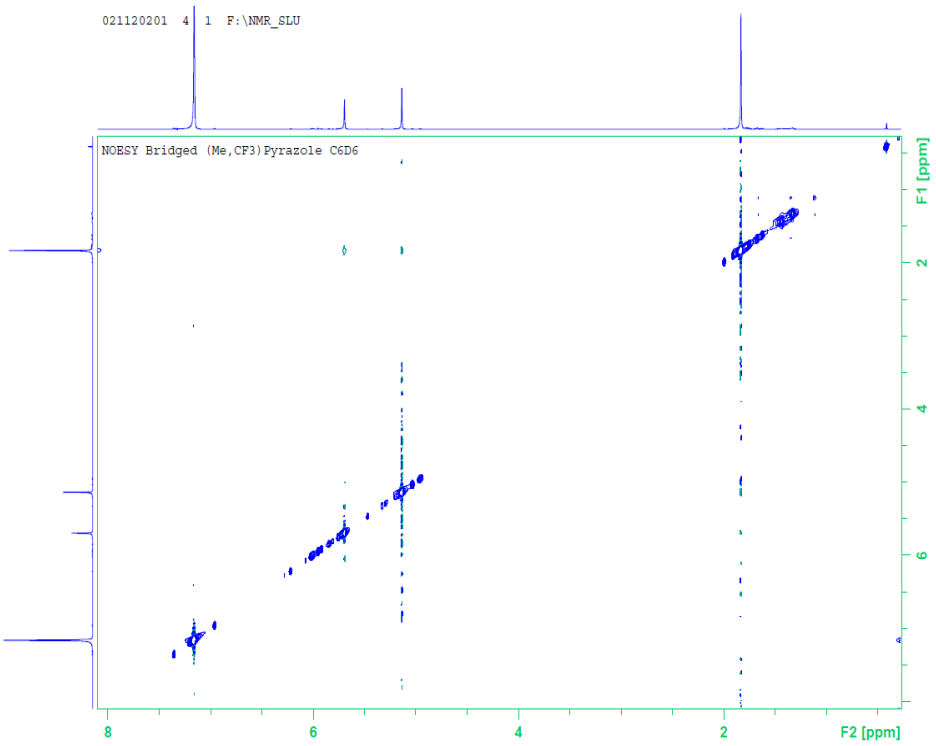


Figure S13. NOESY NMR spectrum of bis(5-methyl-3-(trifluoromethyl)pyrazol-1-yl)methane (**7**) in C_6D_6 at 298.1 K.

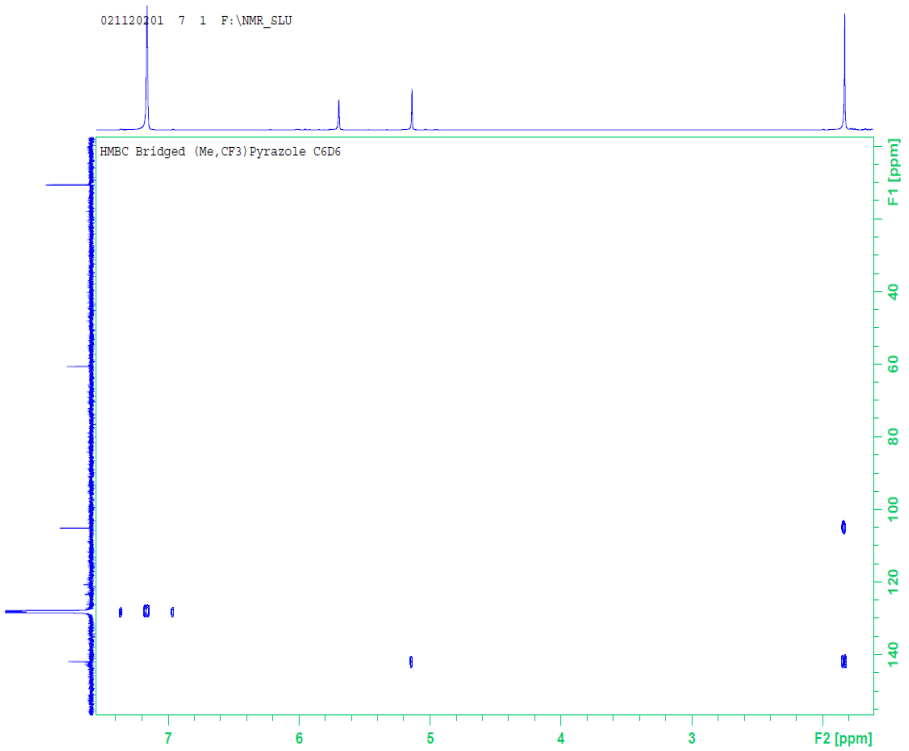


Figure S14. HMBC NMR spectrum of bis(5-methyl-3-(trifluoromethyl)pyrazol-1-yl)methane (**7**) in C_6D_6 at 298.1 K.

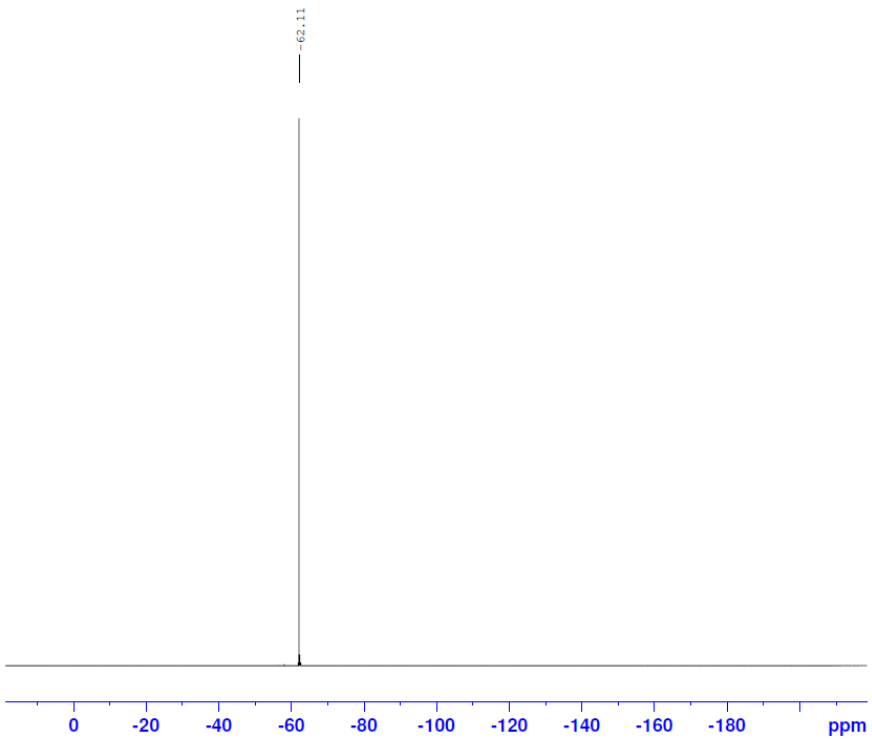


Figure S15. $^{19}F\{^{1}H\}$ NMR spectrum of bis(5-methyl-3-(trifluoromethyl)pyrazol-1-yl)methane (**7**) in C_6D_6 at 298.1 K.

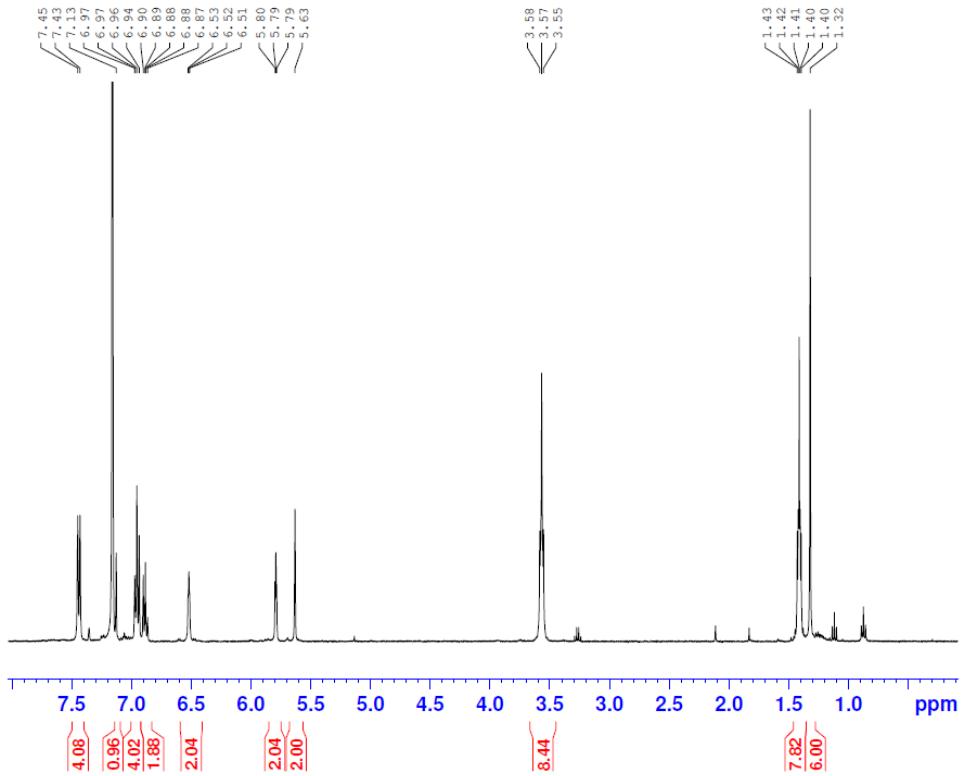


Figure S16. ^{1}H NMR spectrum of ^{Me,CF3}bPzCpLi(THF) (**8**) in C_6D_6 at 298.1 K.

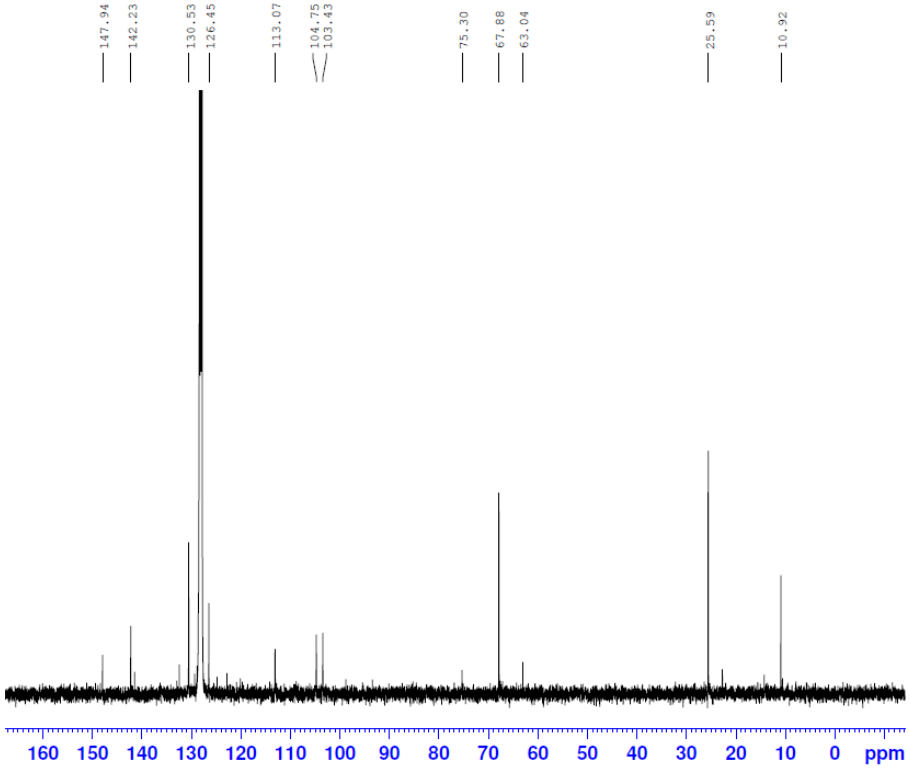


Figure S17. ^{13}C{^{1}H} NMR spectrum of ^{Me,CF3}bPzCpLi(THF) (**8**) in C_6D_6 at 298.1 K.

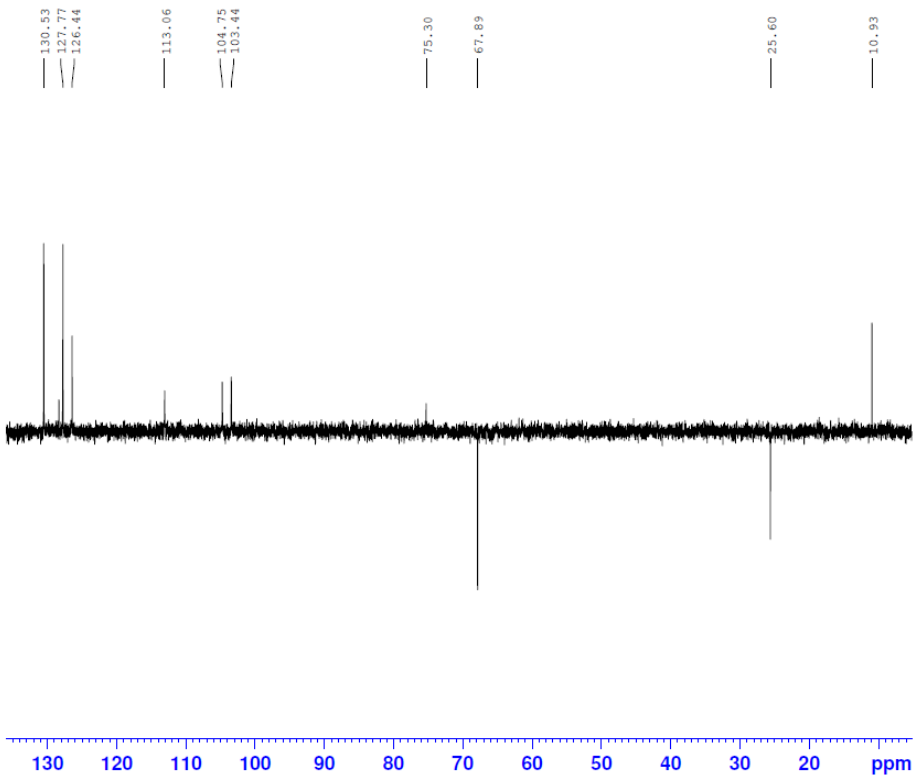


Figure S18. DEPT135 NMR spectrum of ^{Me,CF3}bPzCpLi(THF) (**8**) in C_6D_6 at 298.1 K.

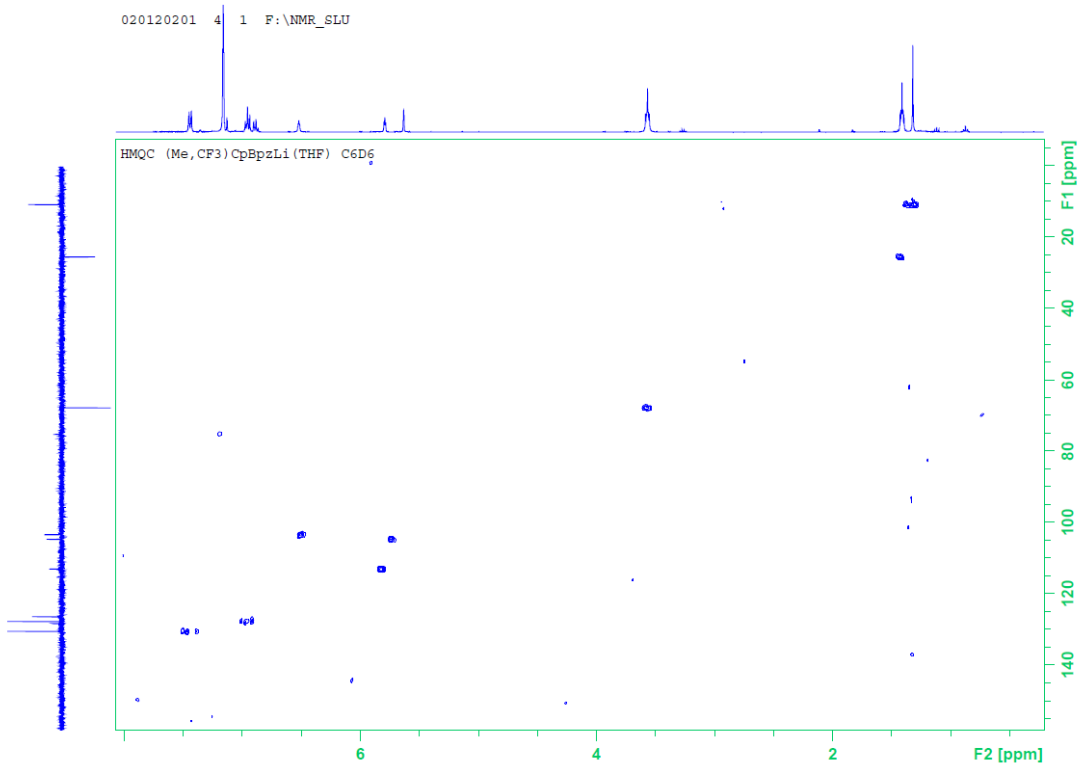


Figure S19. HMQC NMR spectrum of ^{Me,CF3}bPzCpLi(THF) (**8**) in C_6D_6 at 298.1 K.

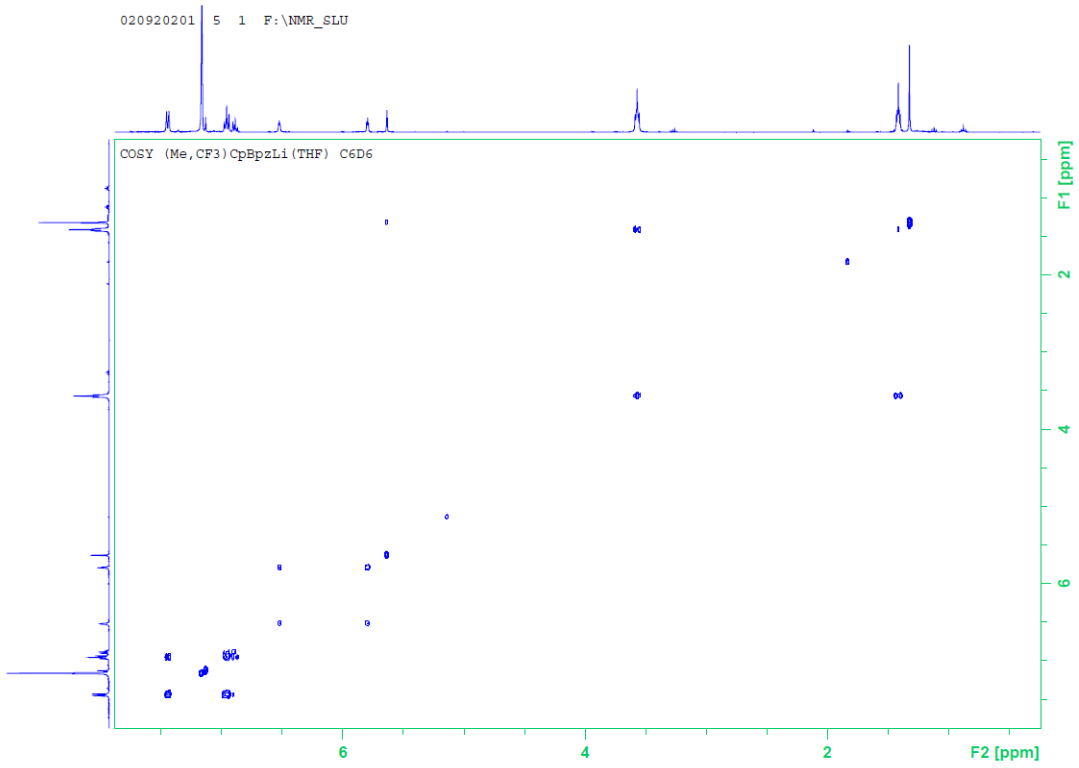


Figure S20. COSY NMR spectrum of ^{Me,CF3}bPzCpLi(THF) (**8**) in C_6D_6 at 298.1 K.

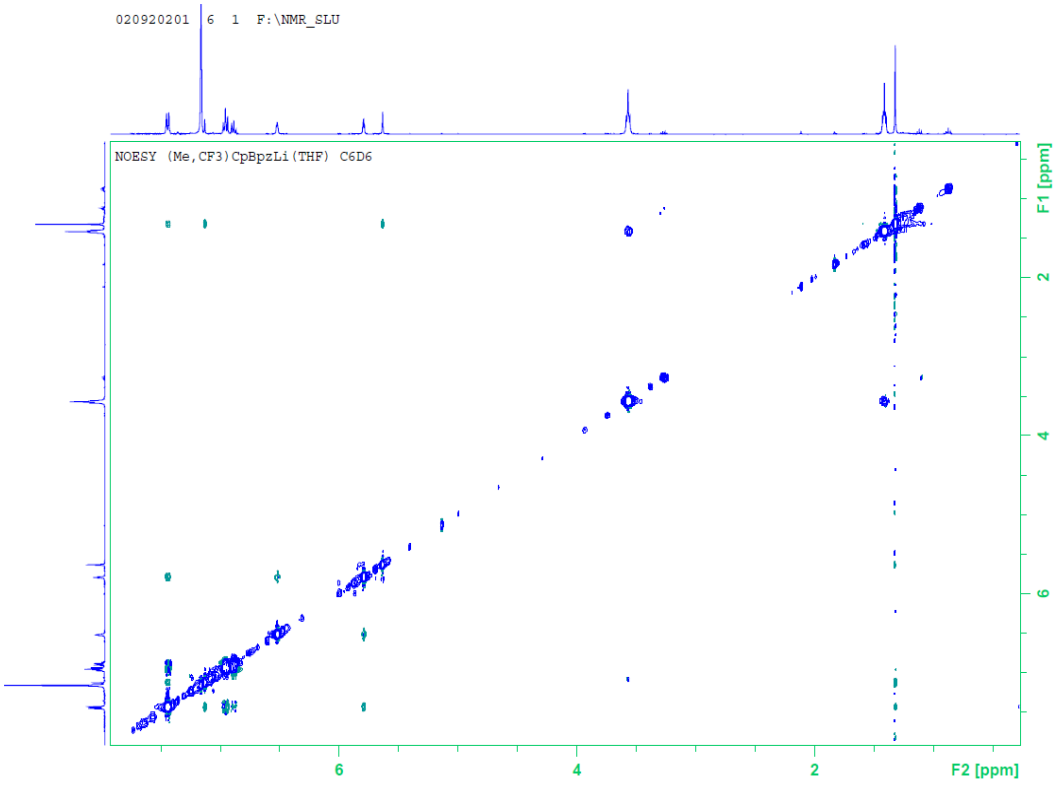


Figure S21. NOESY NMR spectrum of ^{Me,CF3}bPzCpLi(THF) (**8**) in C_6D_6 at 298.1 K.

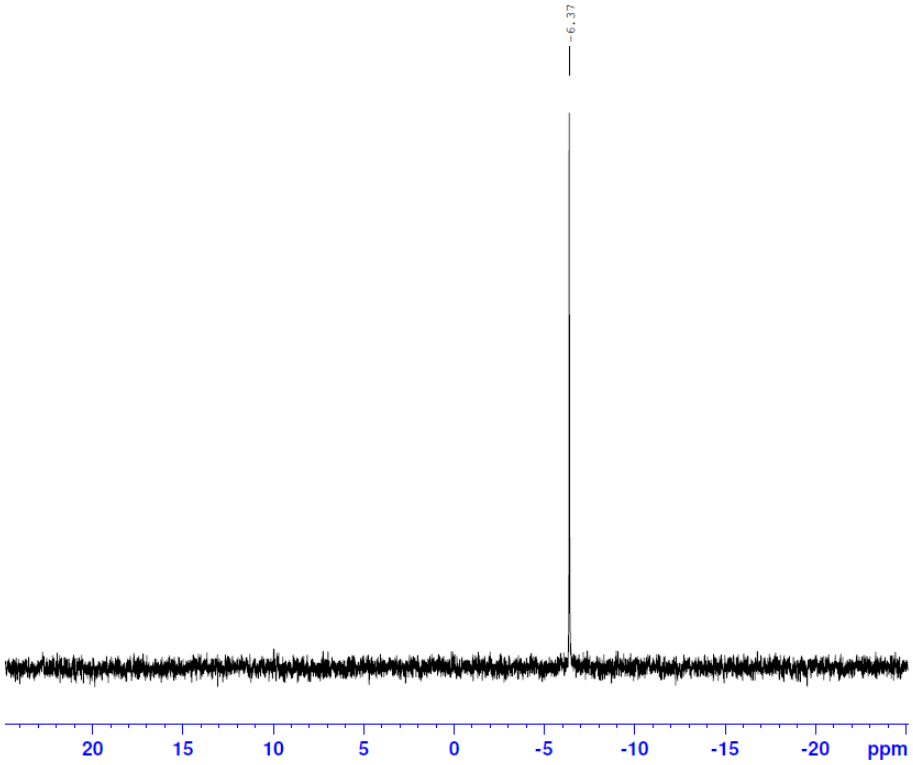


Figure S22. ^{7}Li NMR spectrum of ^{Me,CF3}bPzCpLi(THF) (**8**) in C_6D_6 at 298.1 K.

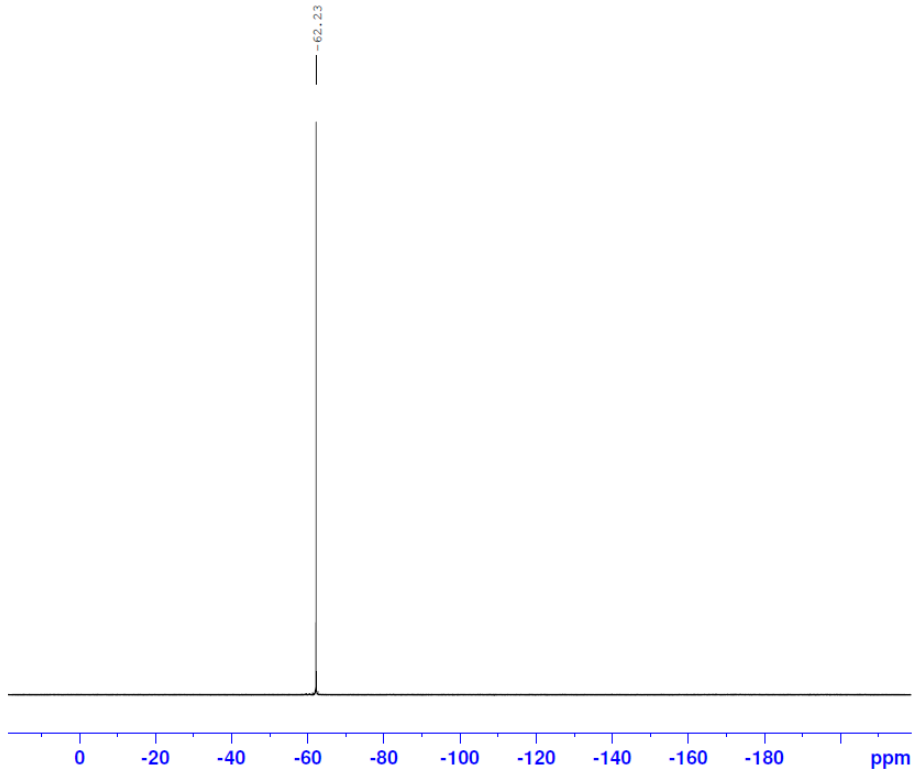


Figure S23. ^{19}F NMR spectrum of ^{Me,CF3}bPzCpLi(THF) (**8**) in C_6D_6 at 298.1 K.

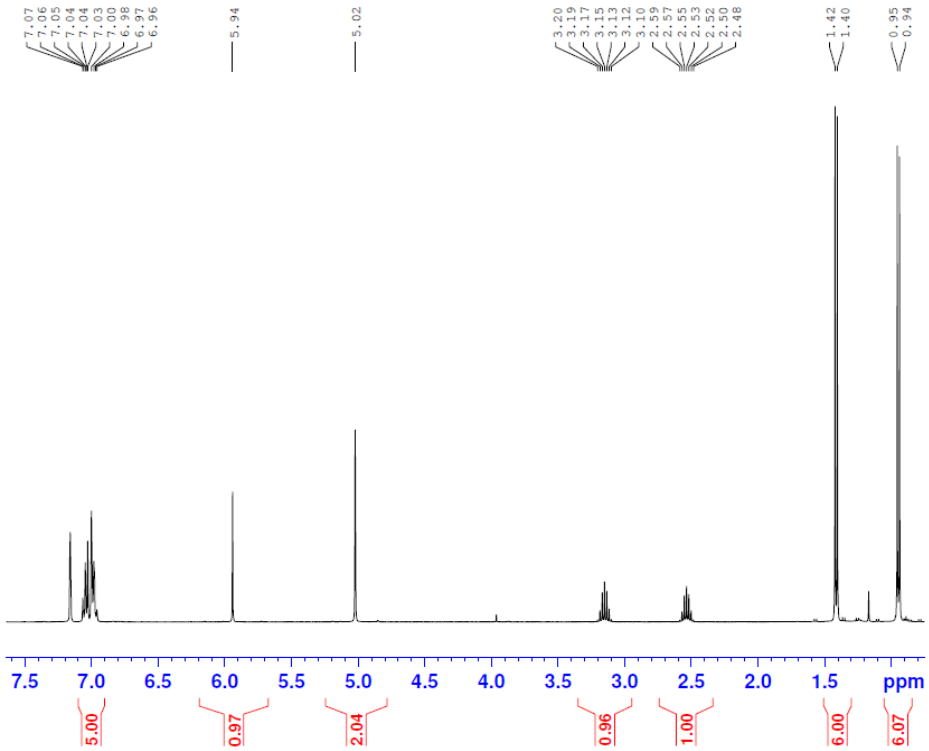


Figure S24. ^{1}H NMR spectrum of 1-benzyl-3,5-diisopropylpyrazole (**9**) in C_6D_6 at 295.5 K.

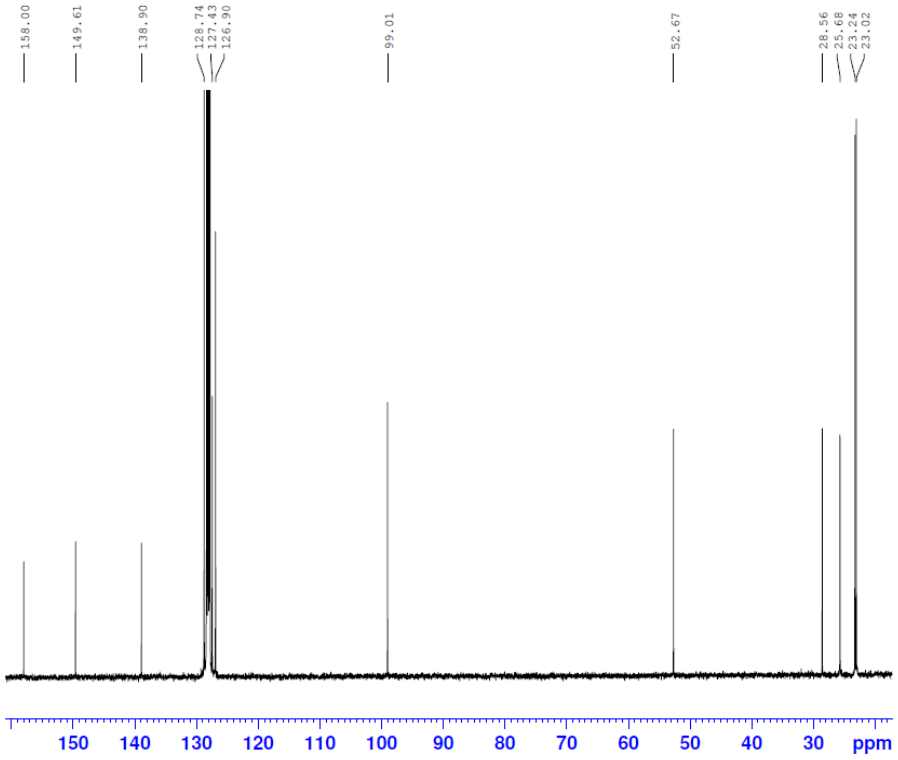


Figure S25. ^{13}C{^{1}H} NMR spectrum of 1-benzyl-3,5-diisopropylpyrazole (**9**) in C_6D_6 at 295.5 K.

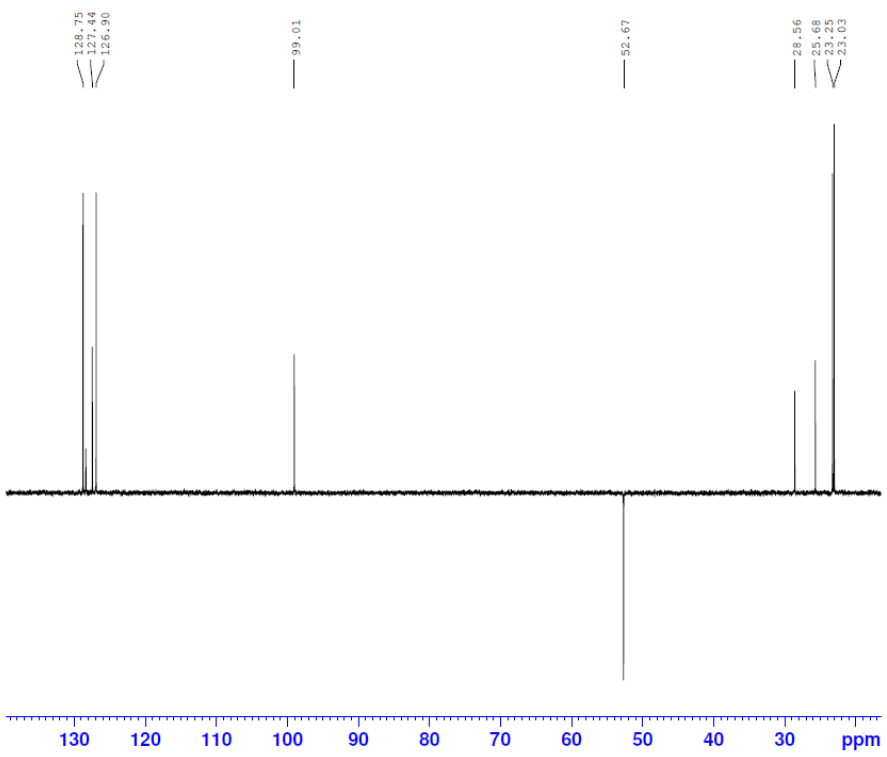


Figure S26. DEPT135 NMR spectrum of 1-benzyl-3,5-diisopropylpyrazole (**9**) in C_6D_6 at 295.5 K.

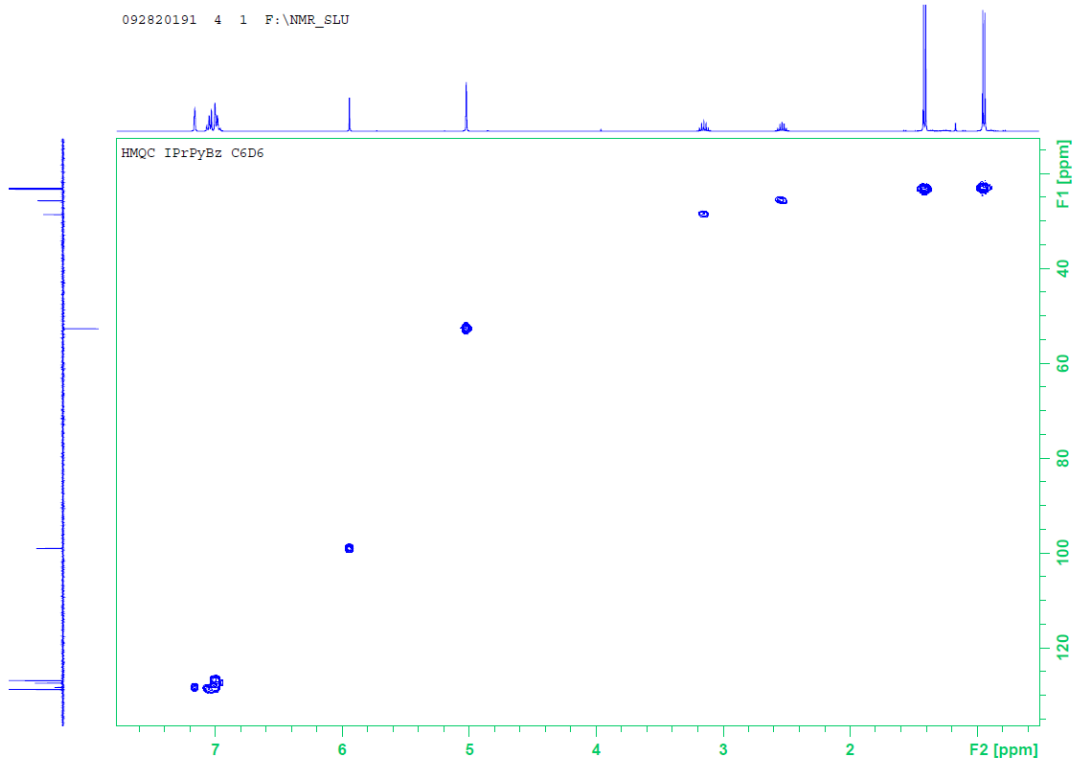


Figure S27. HMQC NMR spectrum of 1-benzyl-3,5-diisopropylpyrazole (**9**) in C_6D_6 at 295.5 K.

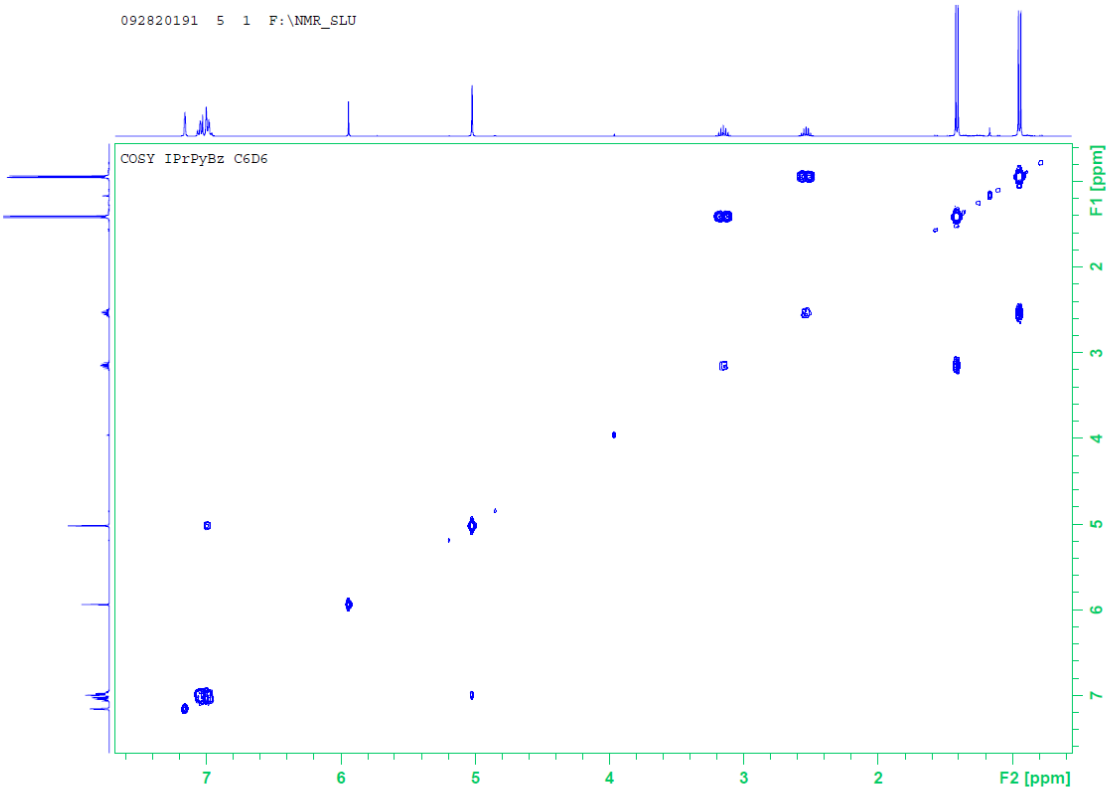


Figure S28. COSY NMR spectrum of 1-benzyl-3,5-diisopropylpyrazole (**9**) in C_6D_6 at 295.5 K.

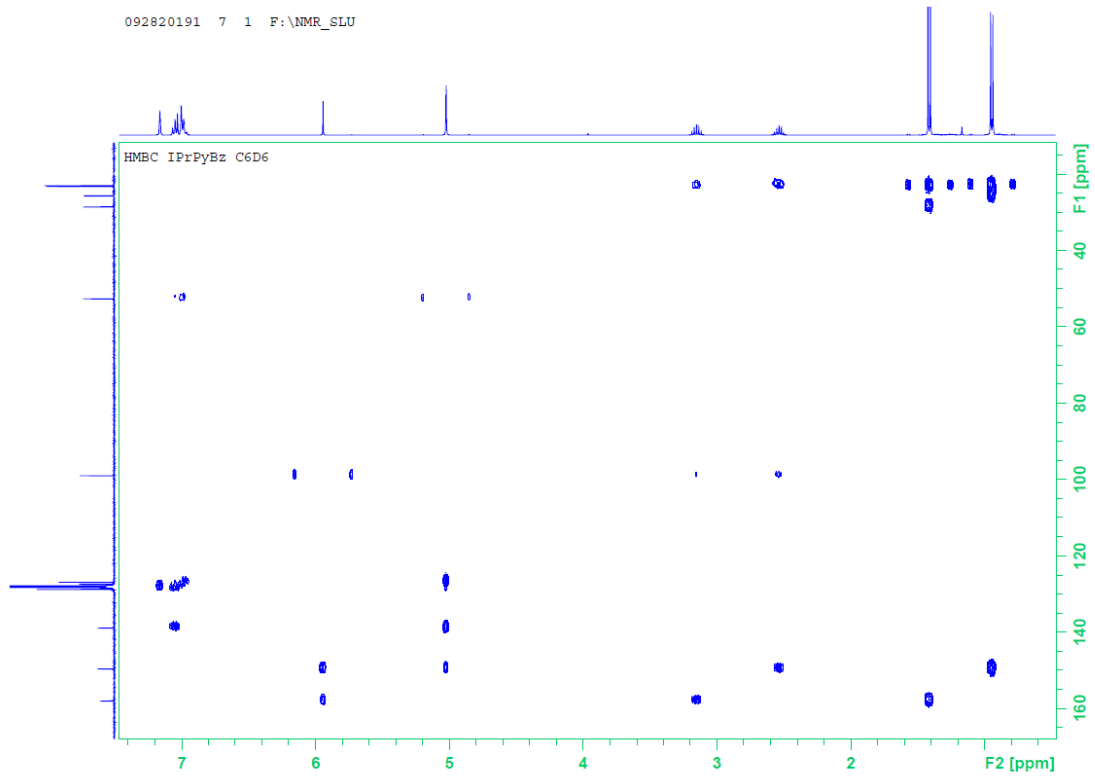


Figure S29. HMBC NMR spectrum of 1-benzyl-3,5-diisopropylpyrazole (**9**) in C_6D_6 at 295.5 K.

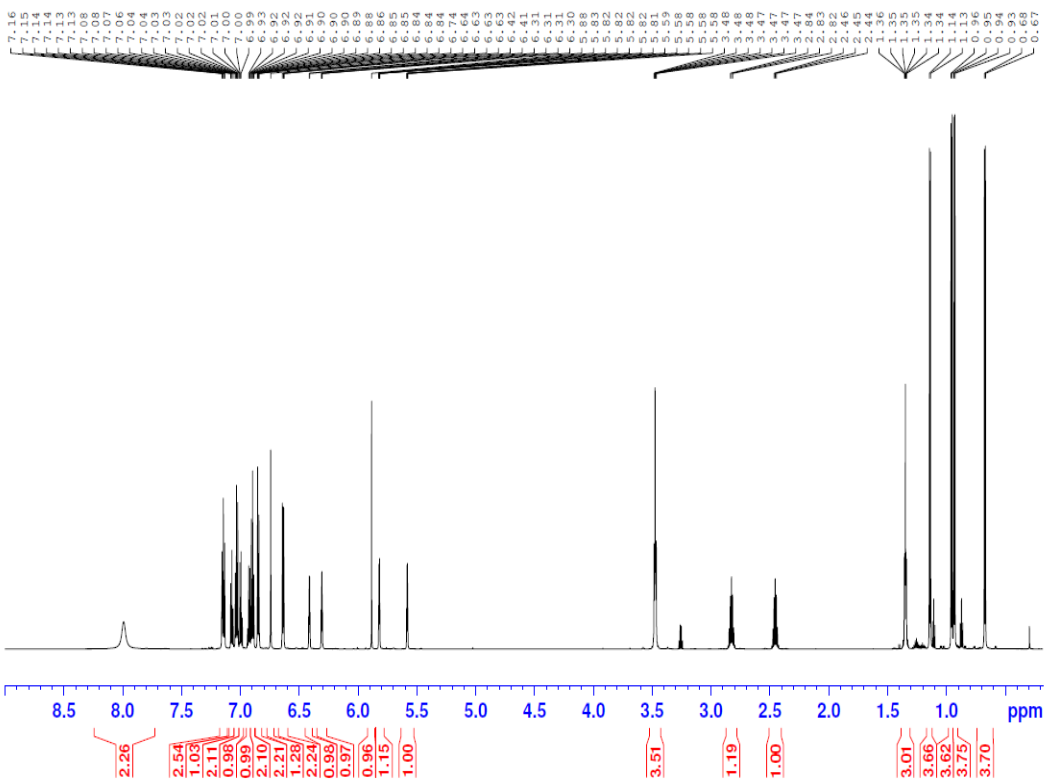


Figure S30. ^{1}H NMR spectrum of ^{iPr}PzPhCpLi(THF)$_x$ (**10**) in C_6D_6 at 298 K.

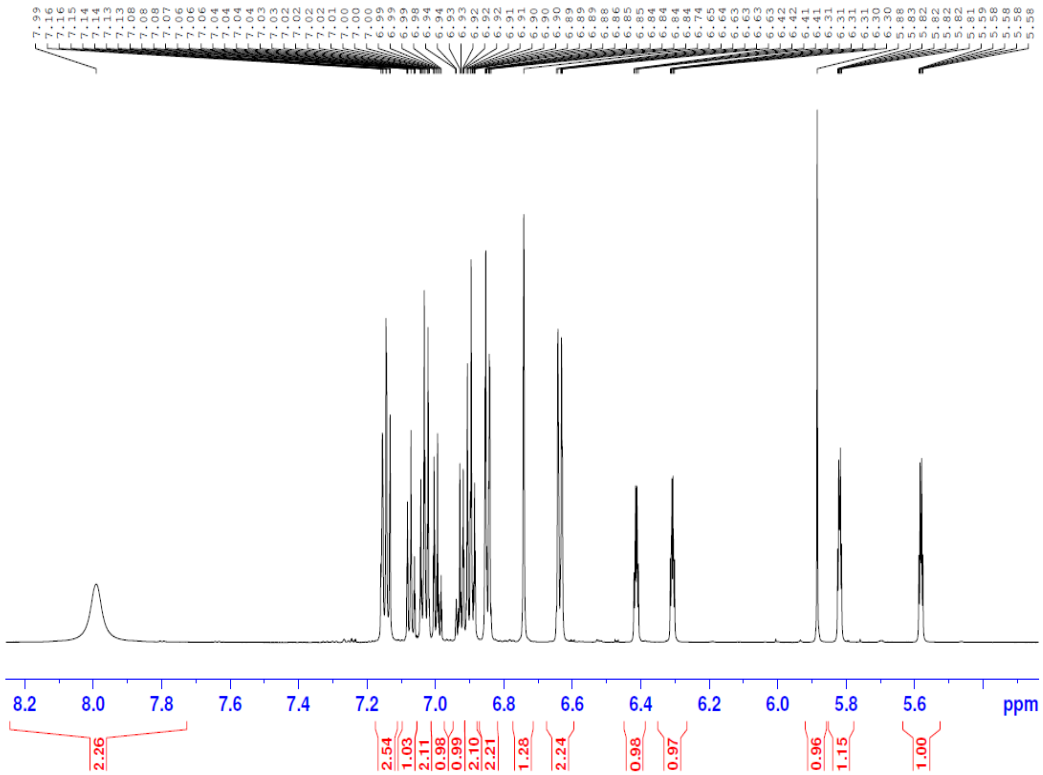


Figure S31. Zoom of ^{1}H NMR spectrum of ^{iPr}PzPhCpLi(THF)$_x$ (**10**) in C_6D_6.

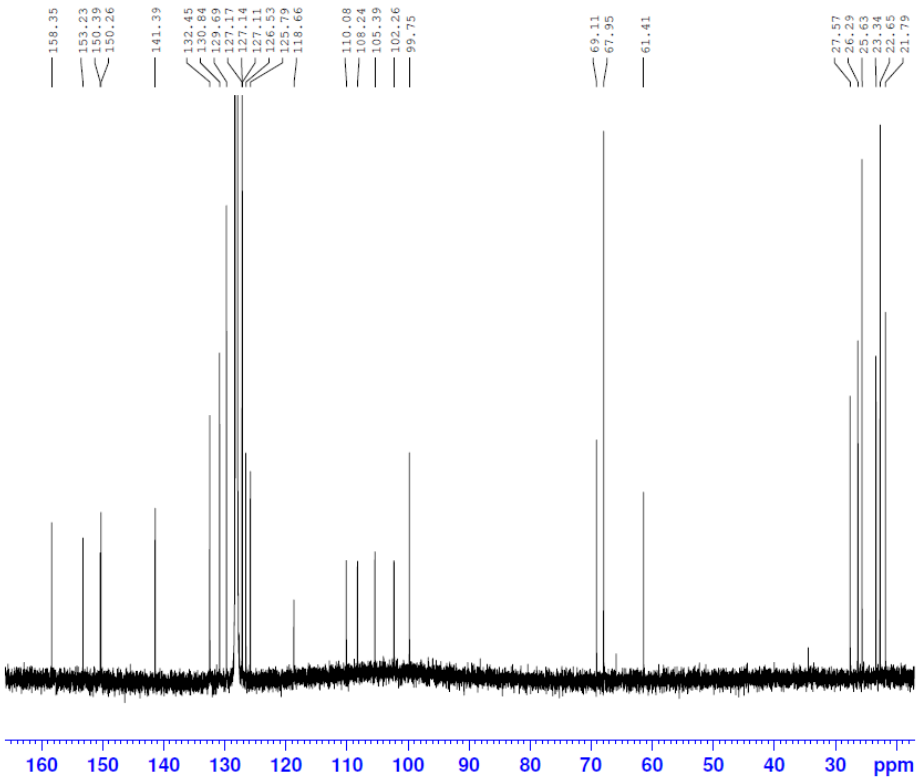


Figure S32. $^{13}C\{^{1}H\}$ NMR spectrum of ^{iPr}PzPhCpLi(THF)$_x$ (**10**) in C_6D_6 at 298 K.

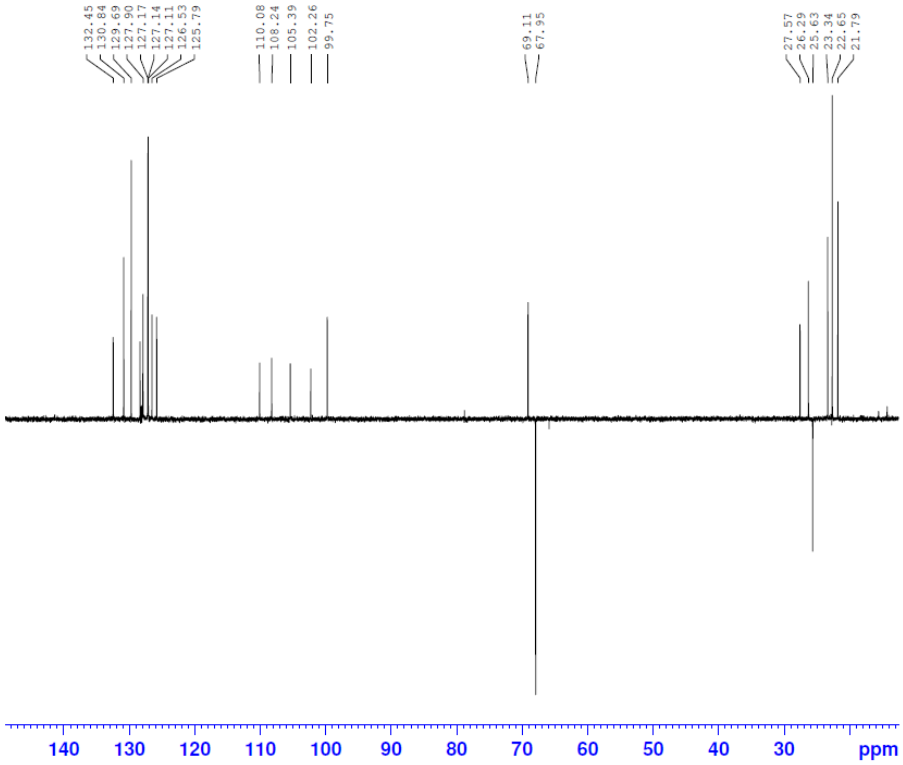


Figure S33. DEPT 135 NMR spectrum of ^{iPr}PzPhCpLi(THF)$_x$ (**10**) in C_6D_6 at 298 K.

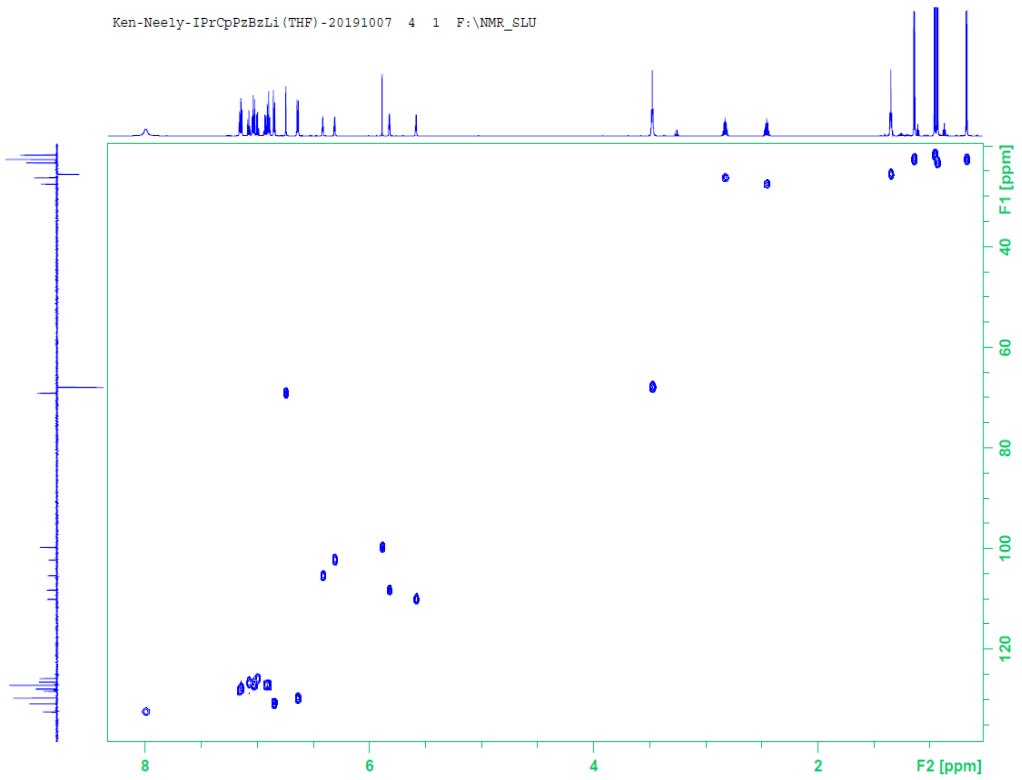


Figure S34. HMQC NMR spectrum of ^{iPr}PzPhCpLi(THF)$_x$ (**10**) in C_6D_6 at 298 K.

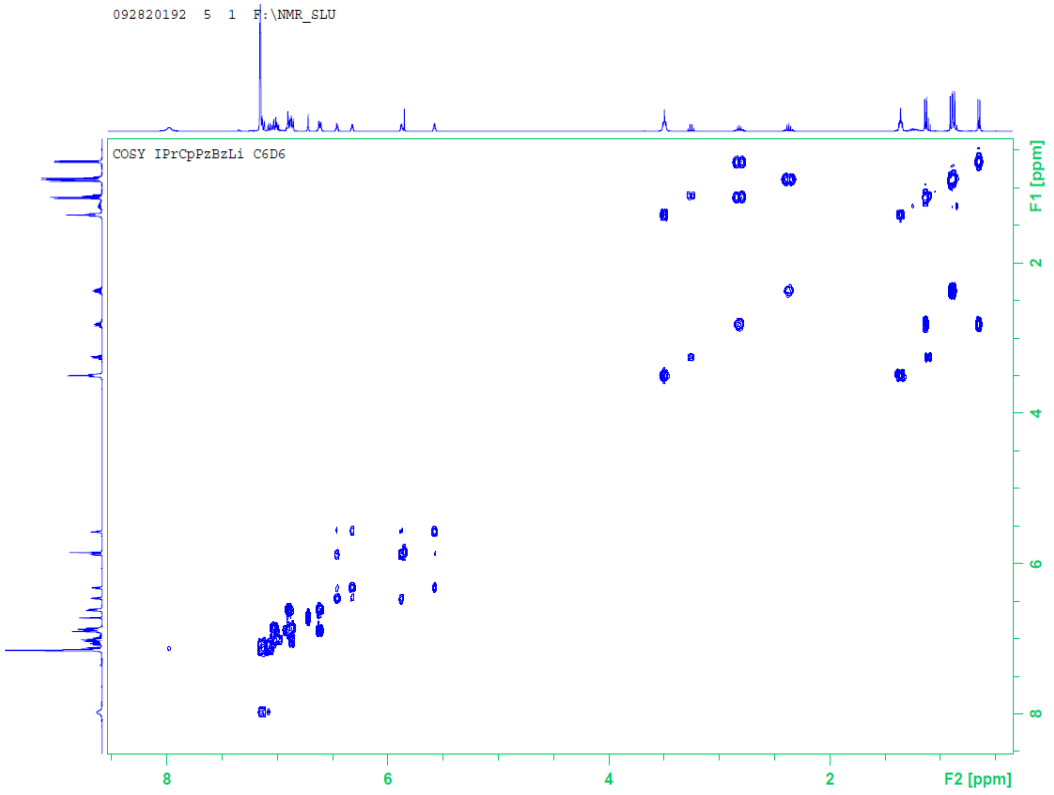


Figure S35. COSY NMR spectrum of ^{iPr}PzPhCpLi(THF)$_x$ (**10**) in C_6D_6 at 296.1 K.

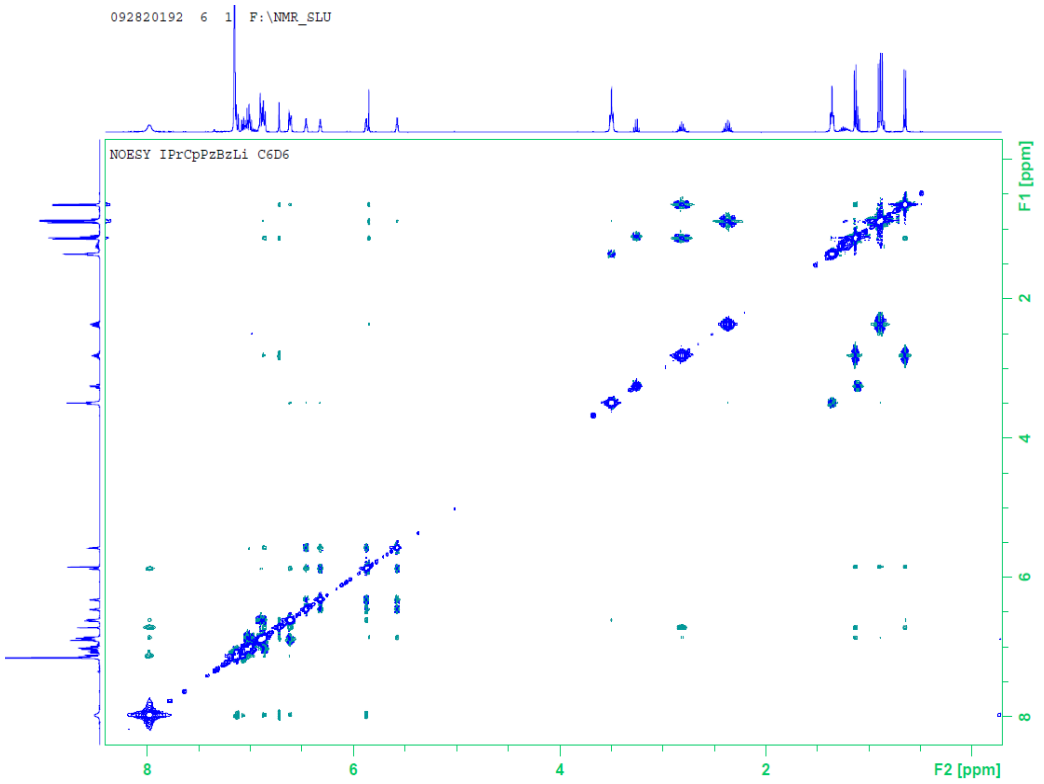


Figure S36. NOESY NMR spectrum of ^{iPr}PzPhCpLi(THF)$_x$ (**10**) in C_6D_6 at 296.1 K.

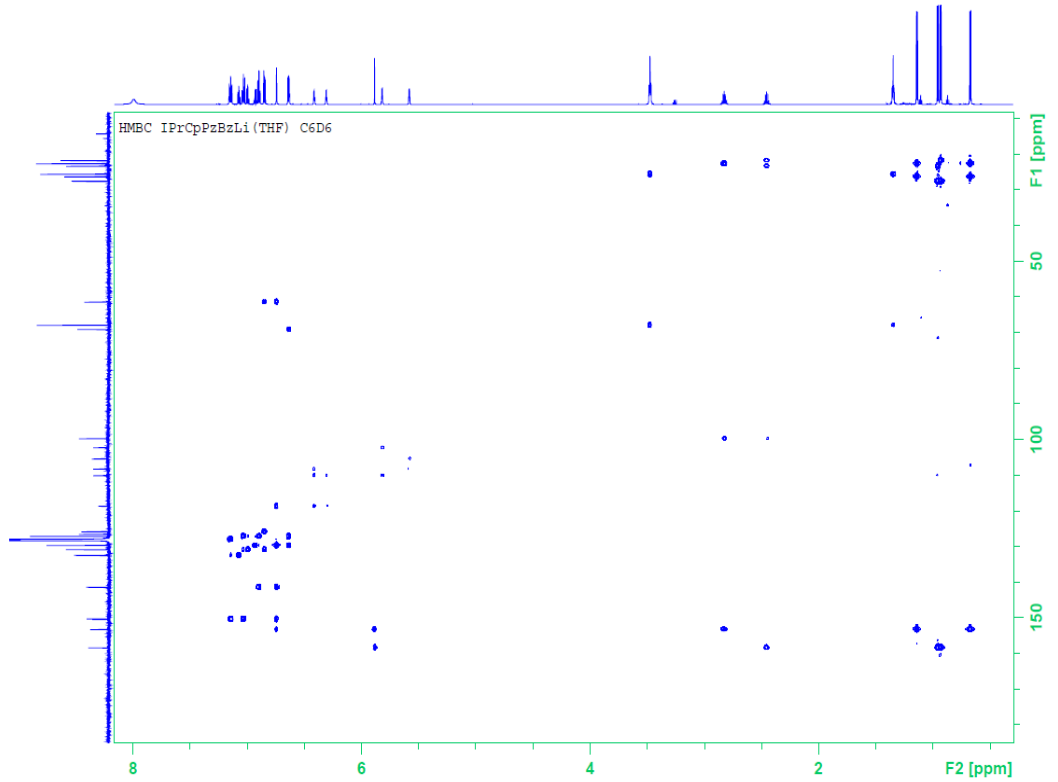


Figure S37. HMBC NMR spectrum of ^{iPr}PzPhCpLi(THF)$_x$ (**10**) in C_6D_6 at 298 K.

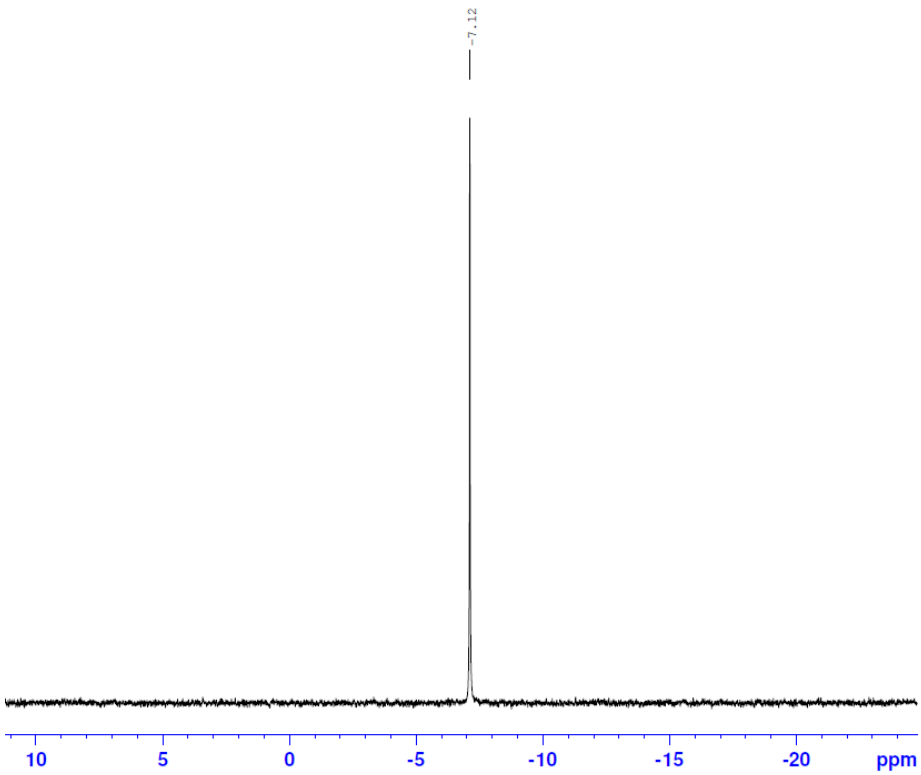


Figure S38. ^{7}Li NMR spectrum of ^{iPr}PzPhCpLi(THF)$_x$ (**10**) in C_6D_6 at 298 K.

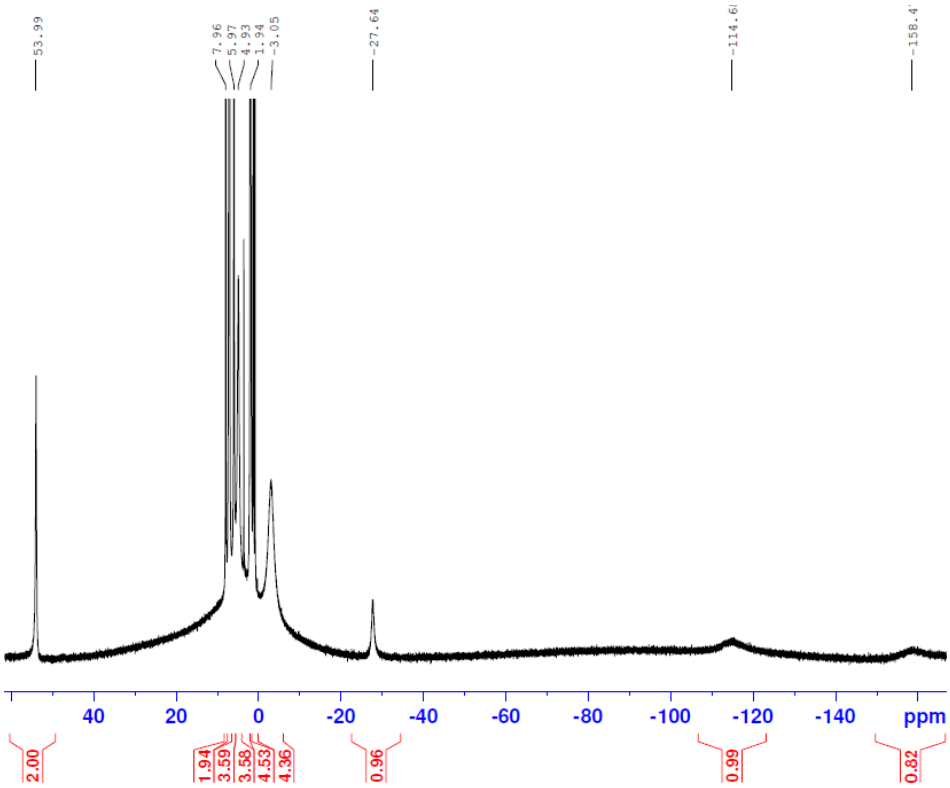


Figure S39. ^{1}H NMR spectrum of ^{Me}bPzCpFeCl (**2a**) in C_6D_6 at 298.1 K.

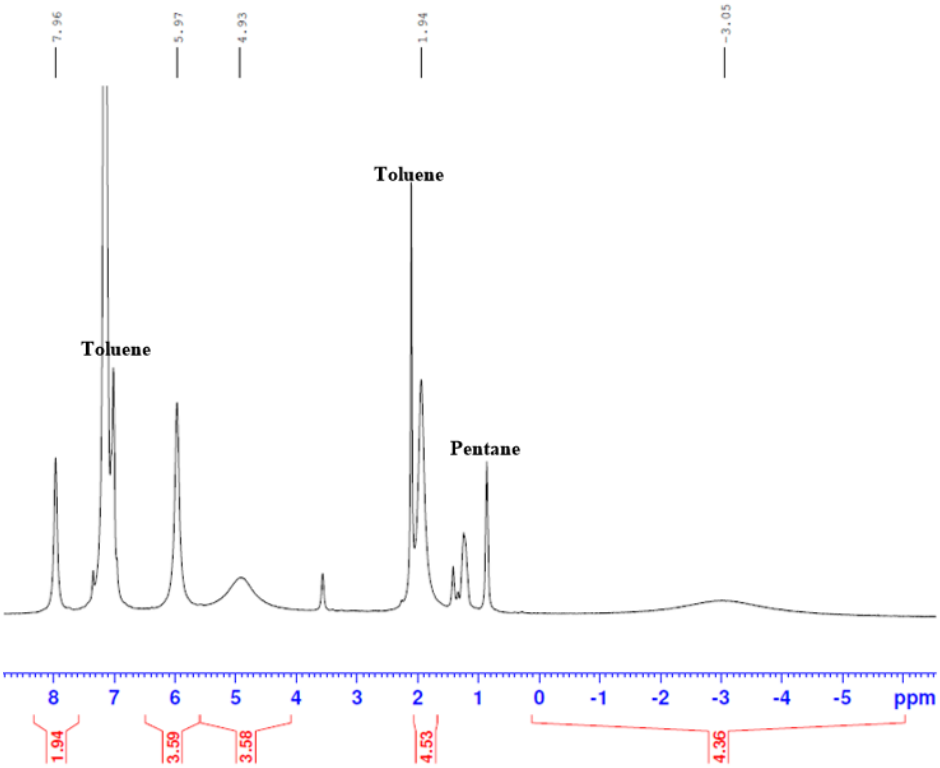


Figure S40. Zoom of ^{1}H NMR spectrum of ^{Me}bPzCpFeCl (**2a**) in C_6D_6 at 298.1 K.

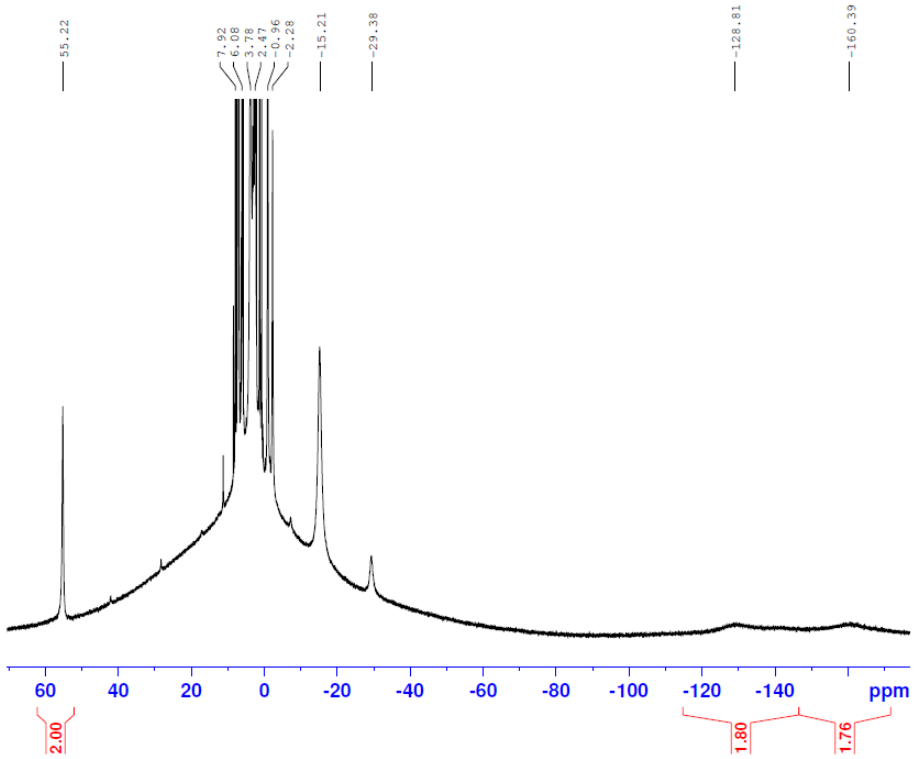


Figure S41. ^{1}H NMR spectrum of ^{iPr}bPzCpFeCl (**2b**) in C_6D_6 at 295.3 K

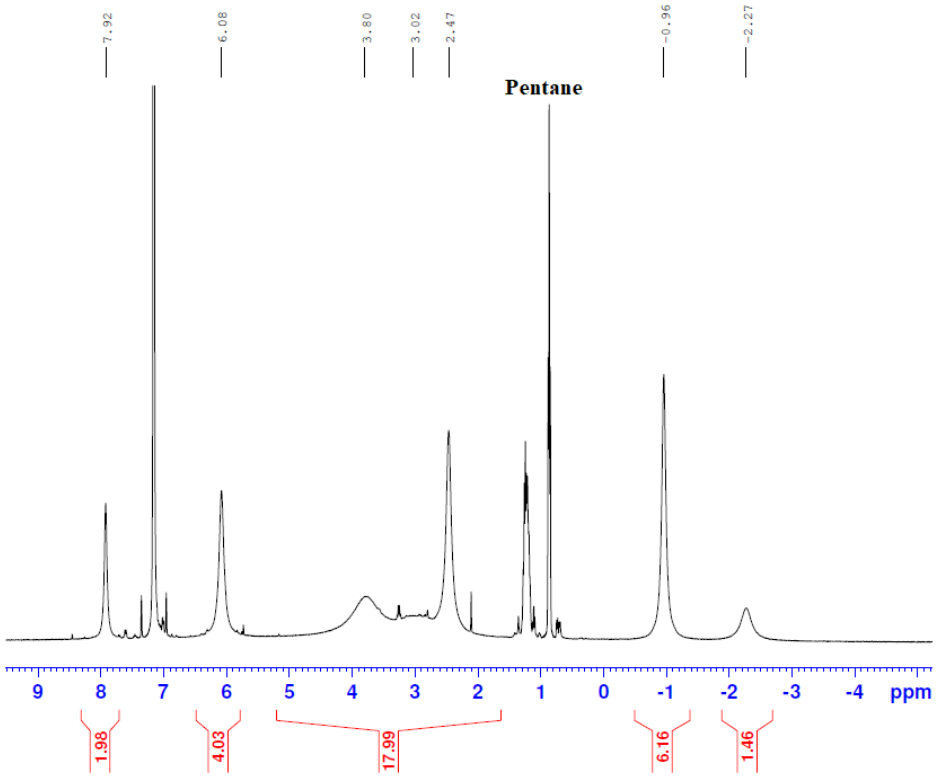


Figure S42. Zoom of ^{1}H spectrum of ^{iPr}bPzCpFeCl (**2b**) in C_6D_6 at 296.1 K.

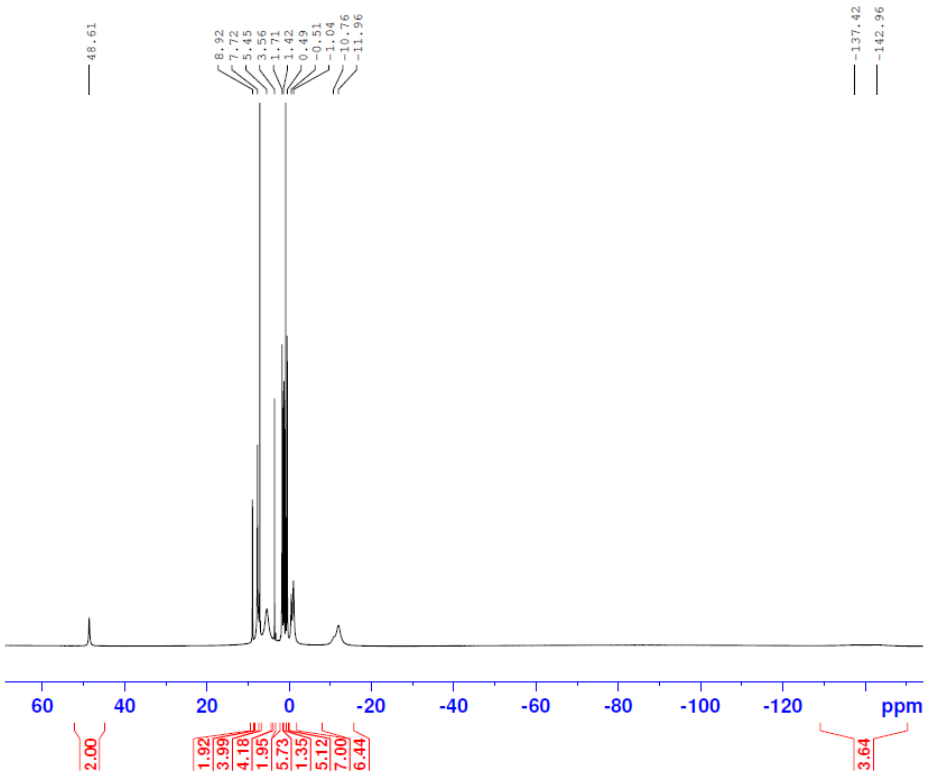


Figure S43. ^{1}H NMR spectrum of ^{iPr}bPzCpFeO^{t}Bu (**3**) in C_6D_6 at 298.1 K.

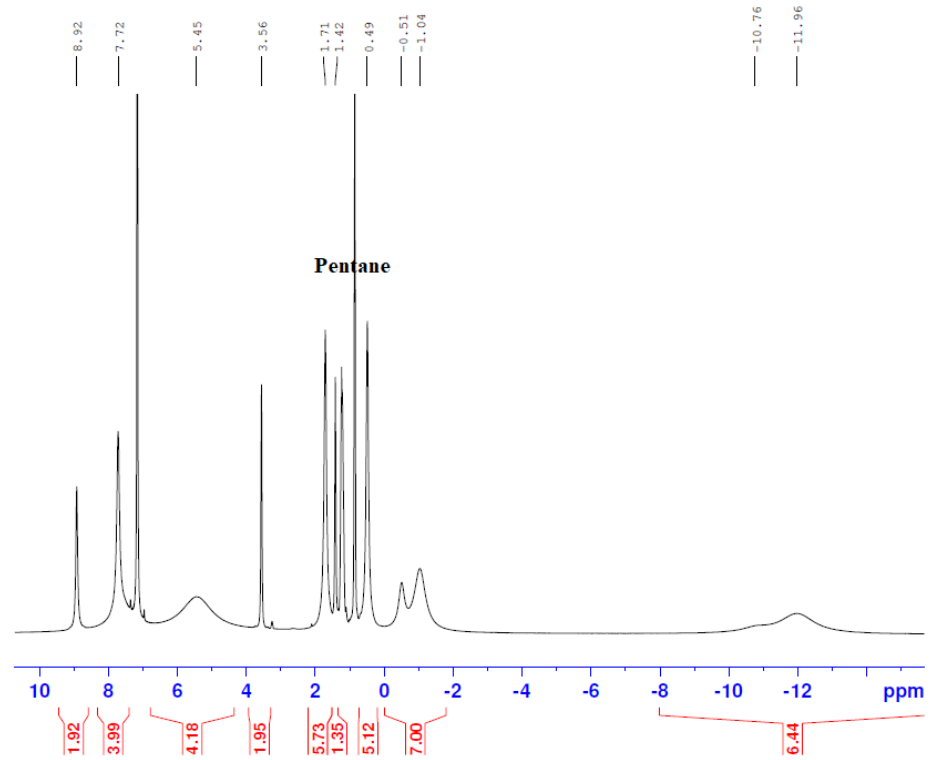


Figure S44. Zoom of ^{1}H spectrum of ^{iPr}bPzCpFeO^{t}Bu (**3**) in C_6D_6 at 298.1 K.

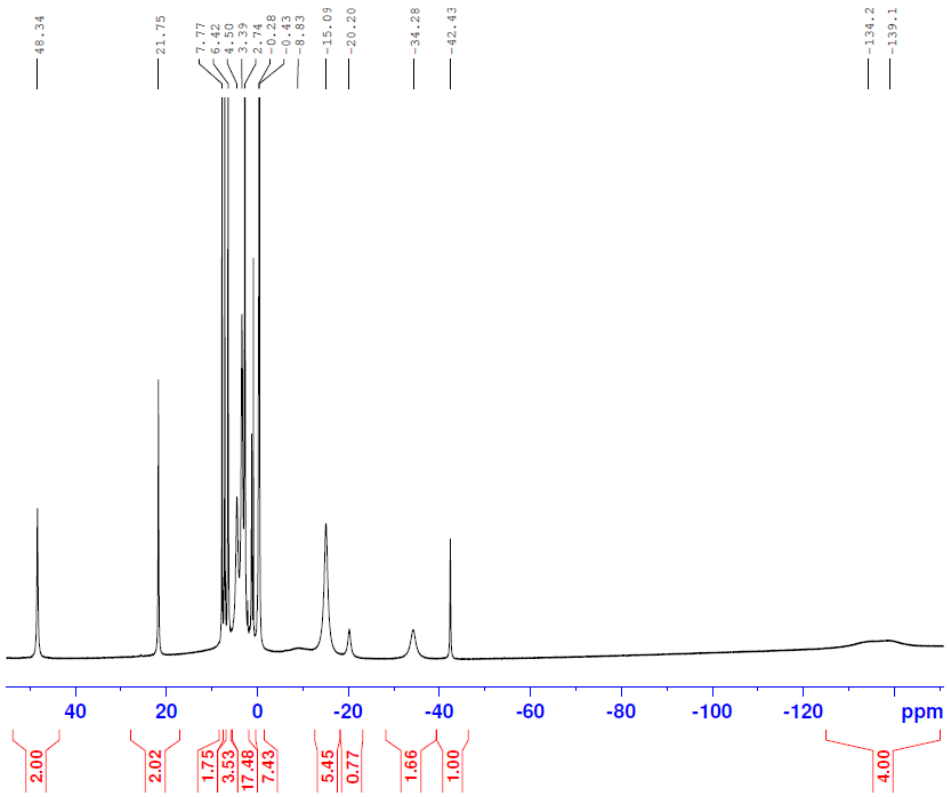


Figure S45. ^{1}H NMR spectrum of ^{iPr}bPzCpFeBn (**4**) in C_6D_6 at 298.1 K.

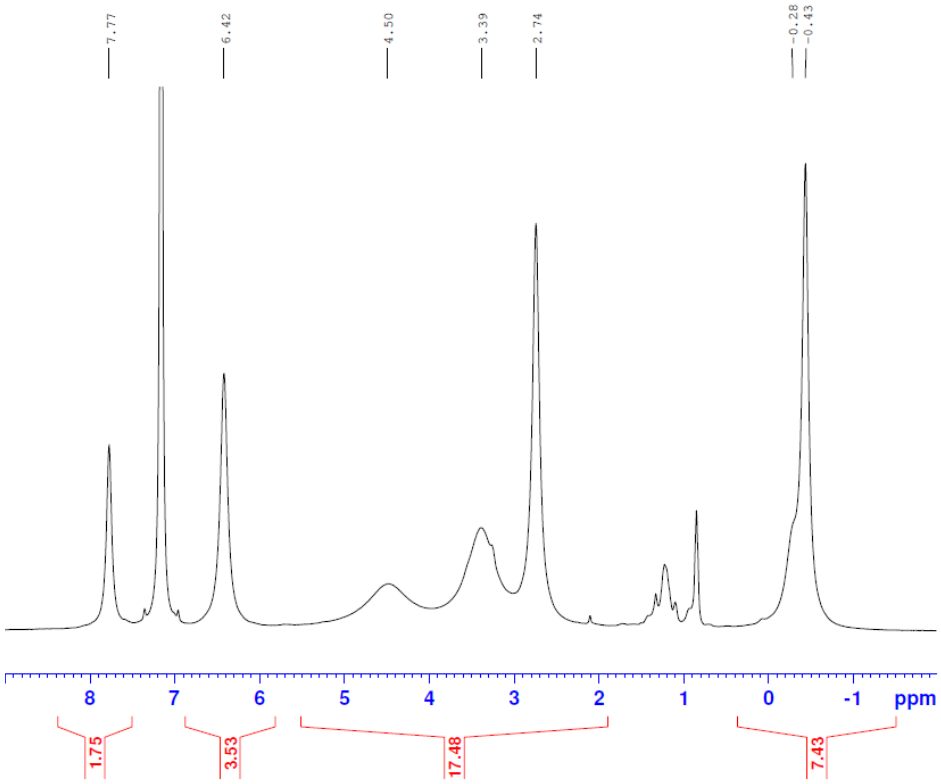


Figure S46. Zoom of ^{1}H NMR spectrum of ^{iPr}bPzCpFeBn (**4**) in C_6D_6 at 298.1 K.

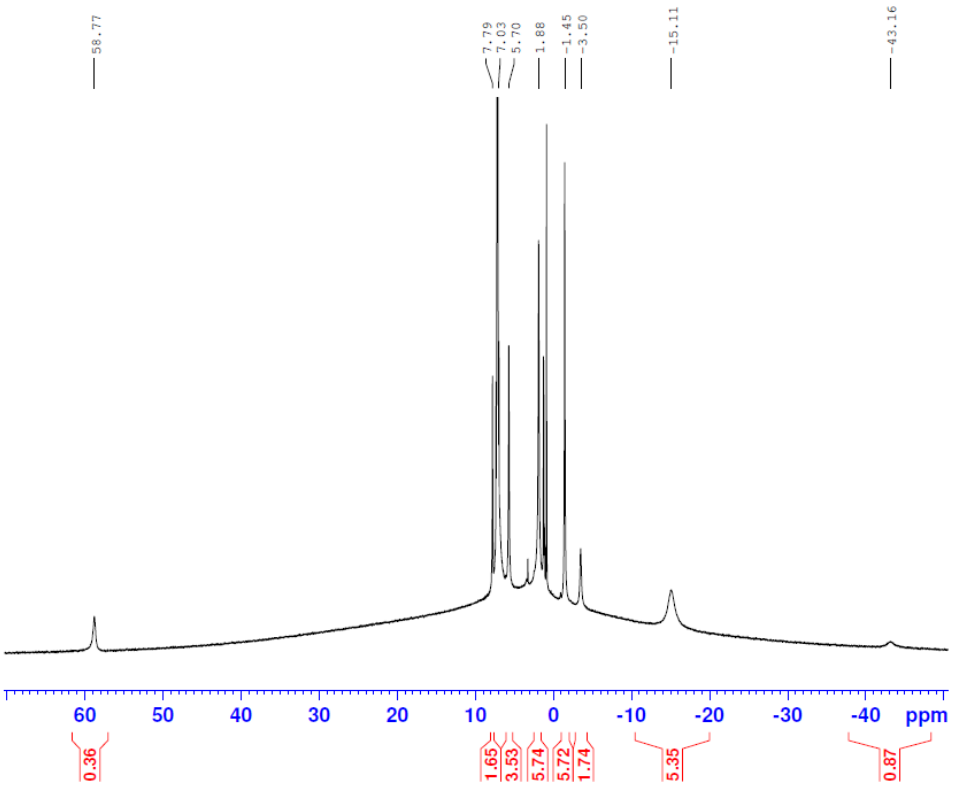


Figure S47. ^{1}H NMR spectrum of ^{iPr}bPzCpFeOTf (**5**) in C_6D_6 at 298.4 K.

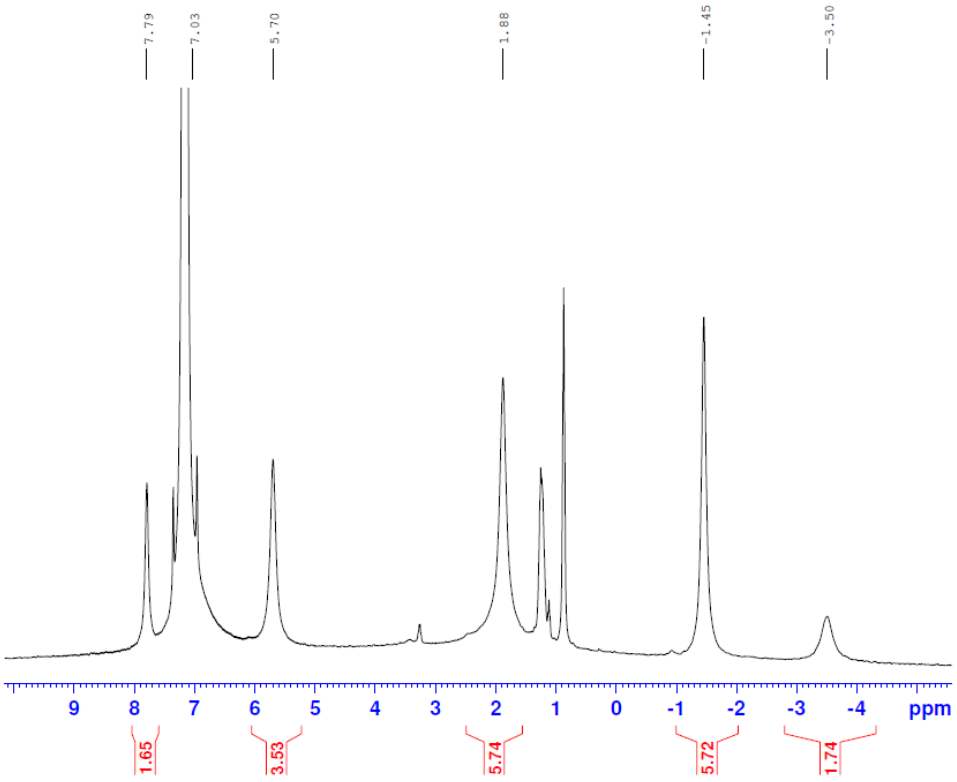


Figure S48. Zoom of ^{1}H NMR spectrum of ^{iPr}bPzCpFeOTf (**5**) in C_6D_6 at 298.4 K.

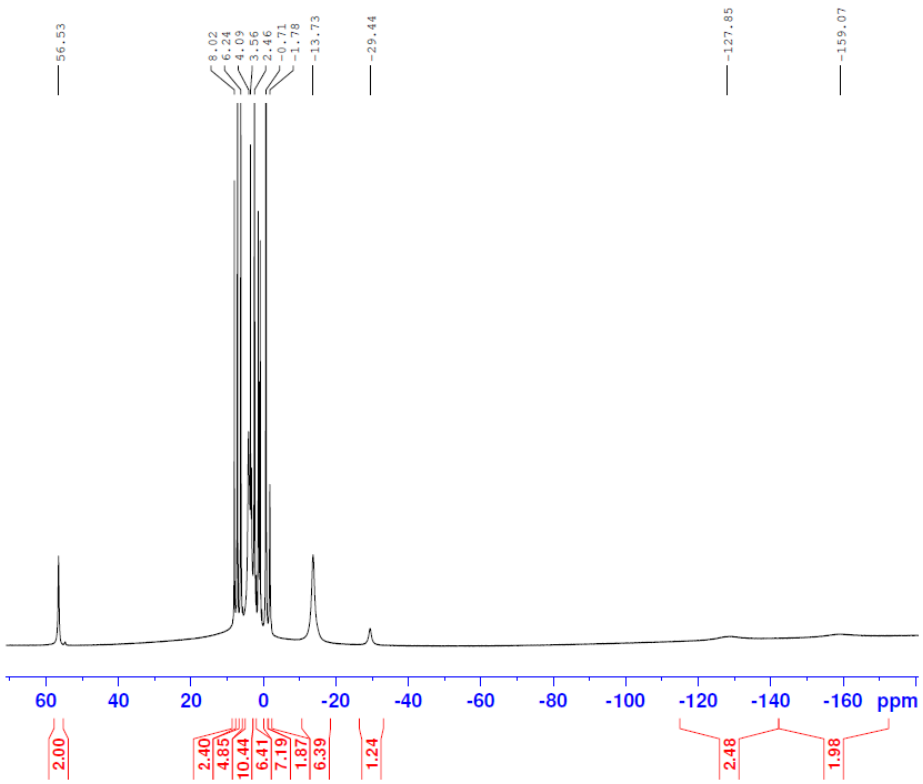


Figure S49. ^{1}H NMR spectrum of ^{iPr}bPzCpFeN$_3$ (**6**) in C_6D_6 at 298.0 K.

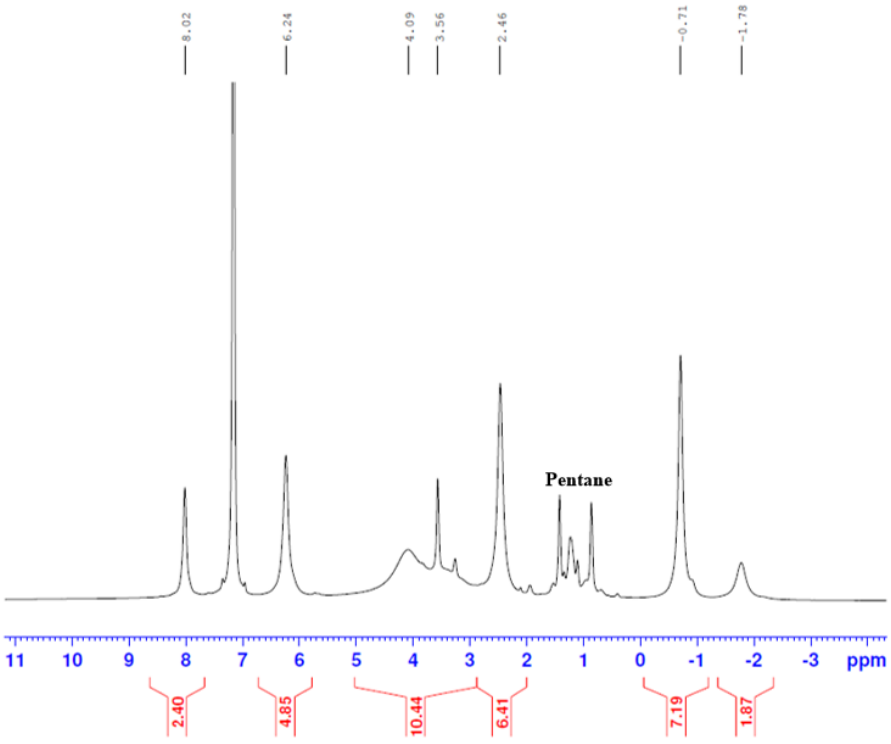


Figure S50. Zoom of ^{1}H NMR spectrum of ^{iPr}bPzCpFeN$_3$ (**6**) in C_6D_6 at 298.0 K.

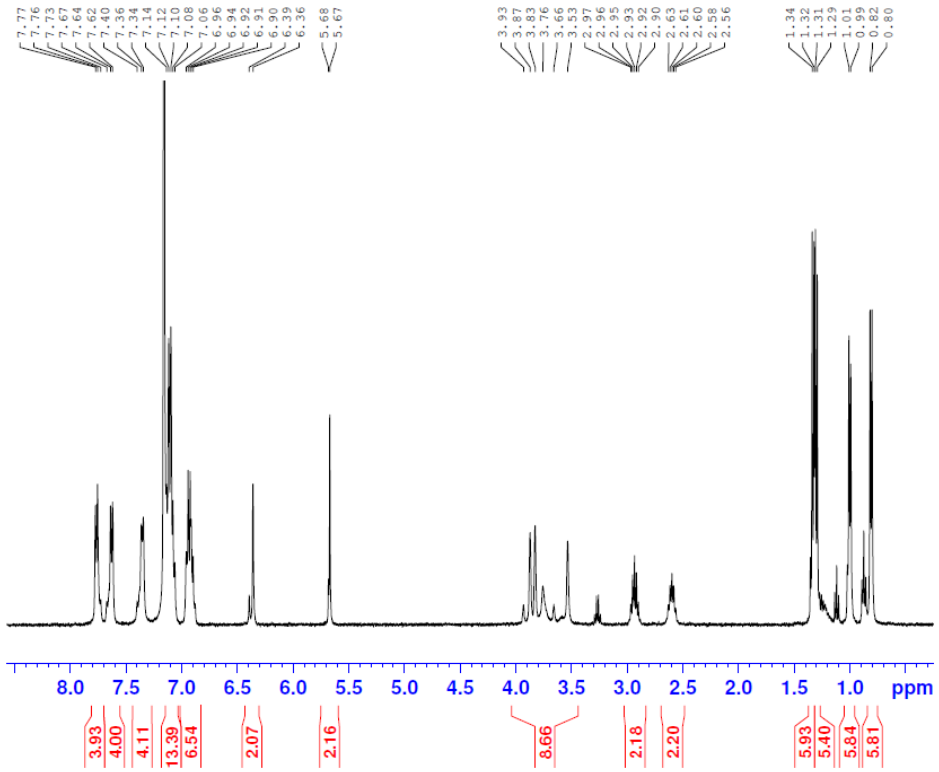


Figure S51. ^{1}H NMR spectrum of (^{iPr}PzPhCp)$_2$Fe (**11**) in C_6D_6 at 297.9 K.

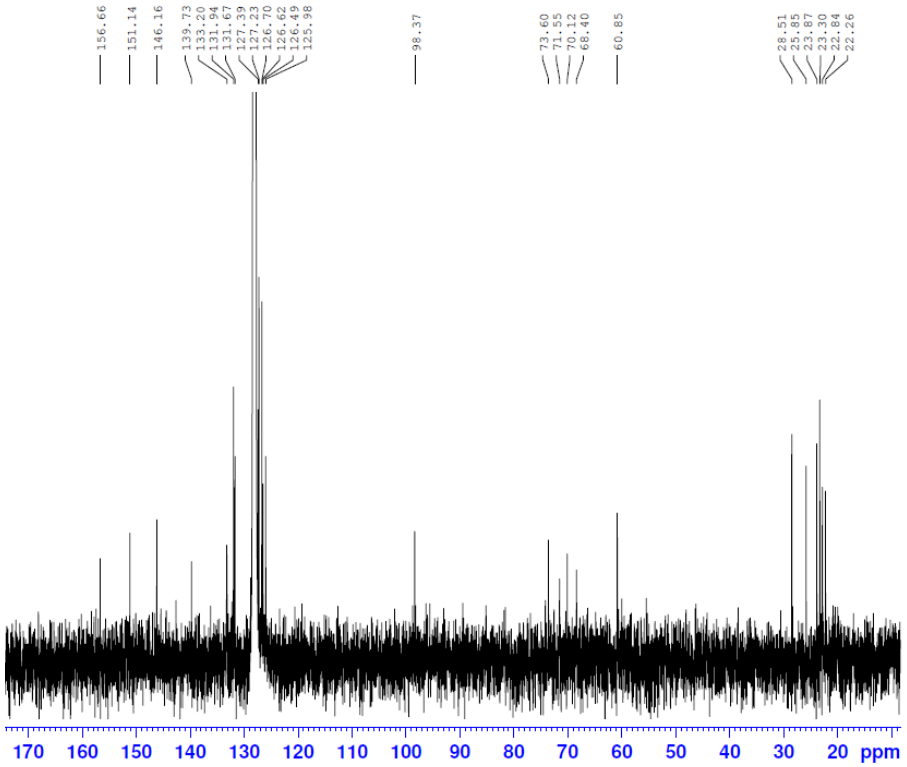


Figure S52. ^{13}C{^{1}H} NMR spectrum of (^{iPr}PzPhCp)$_2$Fe (**11**) in C_6D_6 at 298.2 K.

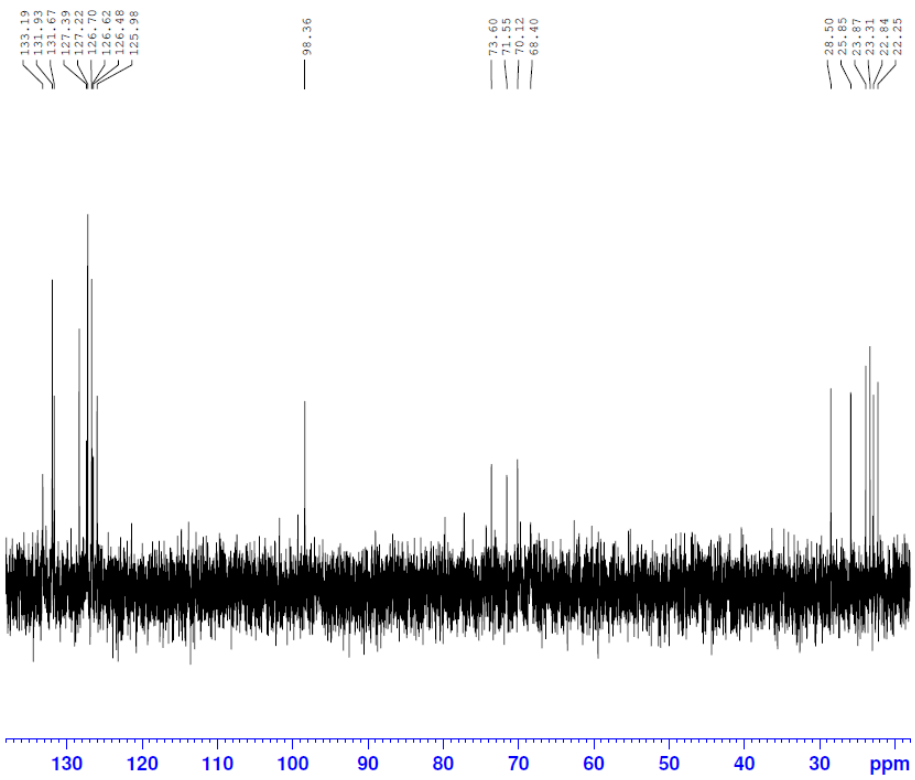


Figure S53. DEPT135 NMR spectrum of (^{iPr}PzPhCp)$_2$Fe (**11**) in C_6D_6 at 298.2 K.

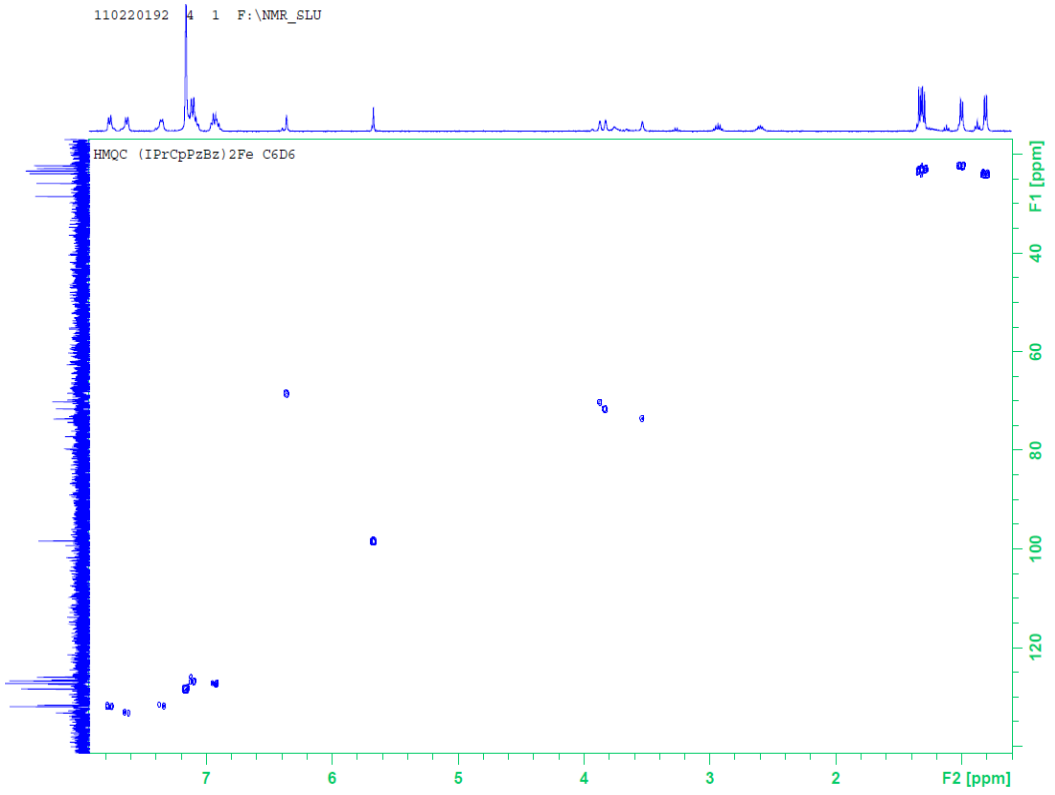


Figure S54. HMQC NMR spectrum of (^{iPr}PzPhCp)$_2$Fe (**11**) in C_6D_6 at 298.2 K.

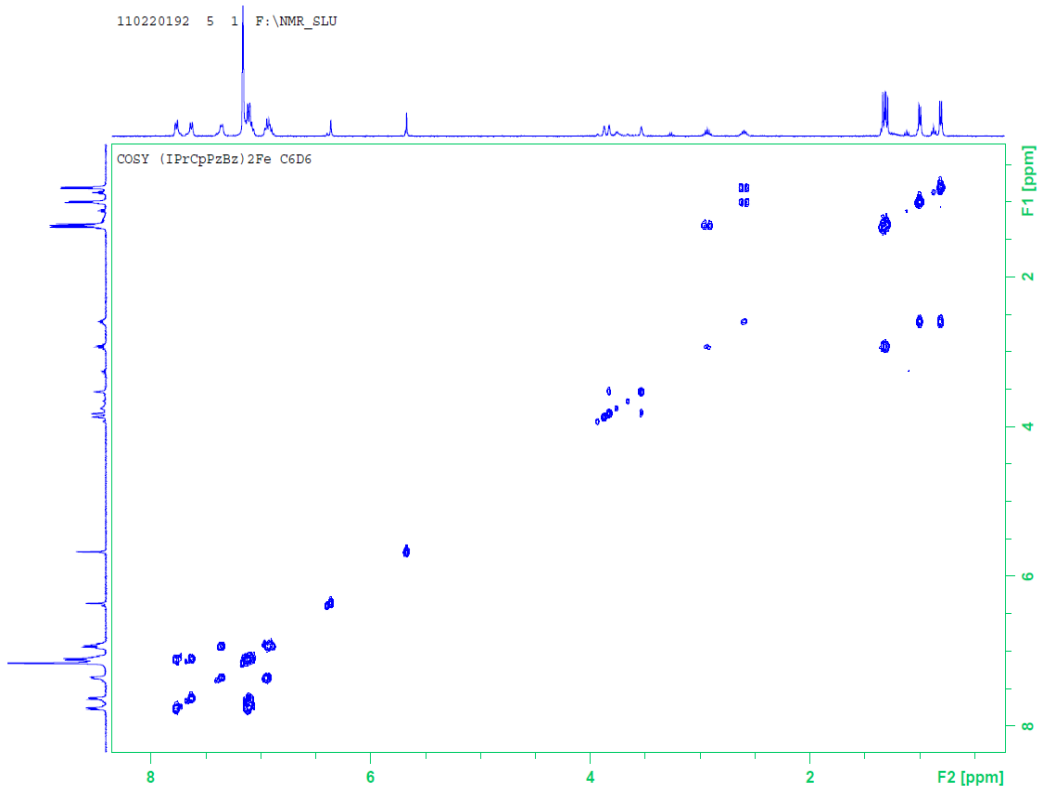


Figure S55.. COSY NMR spectrum of (^{iPr}PzPhCp)$_2$Fe (**11**) in C_6D_6 at 298.2 K.

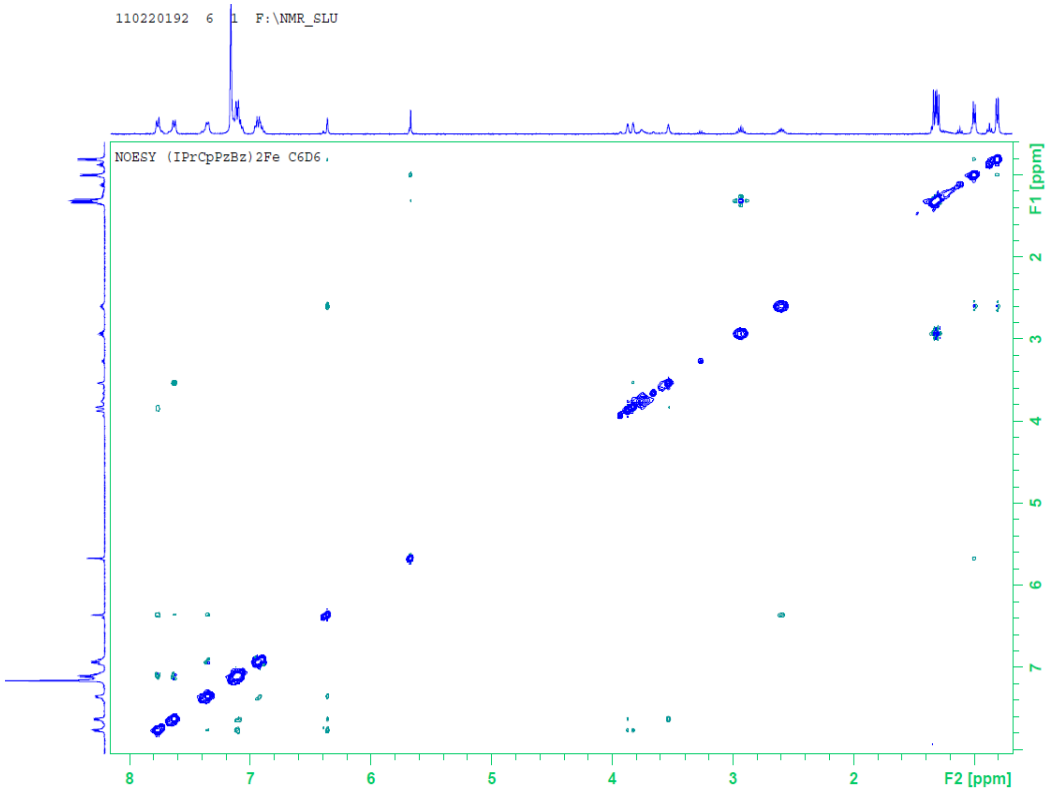


Figure S56. NOESY NMR spectrum of (^{iPr}PzPhCp)$_2$Fe (**11**) in C_6D_6 at 298.2 K.

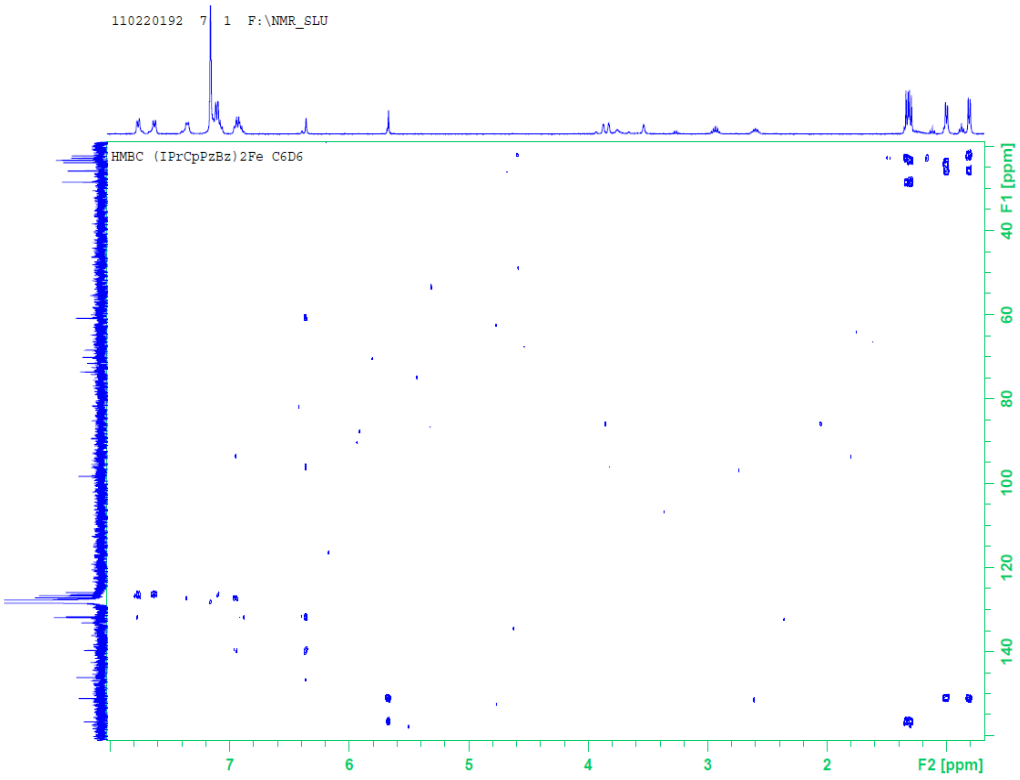


Figure S57. HMBC NMR spectrum of (^{iPr}PzPhCp)$_2$Fe (**11**) in C_6D_6 at 298.2 K.

Crystallographic Data

Table S1. X-ray crystallographic data for complexes **2a**, **2b**, **3**, **4**, **5**, **6**, **10**, and **11**.

Complex	**10**	**2a**	**2b**	**3**
CCDC deposit number	2132880	2132878	2132879	2132883
Empirical formula	C_{38} $H_{43.25}$ Li N_2 $O_{1.12}$	C_{33} H_{37} Cl Fe N_4 O	C_{41} H_{55} Cl Fe N_4 O	C_{45} H_{64} Fe N_4 O_2
Formula weight (g/mol)	552.93	596.96	711.19	748.85
Crystal habit, color	Block, Colorless	Rod, Yellow	Needle, Colorless	Rod, Yellow
Temperature (K)	100(2)	100(2)	100(2)	100(2)
Space group	P-1	$P2_1/c$	$P2_1/n$	Pbca
Crystal system	Triclinic	Monoclinic	Monoclinic	Orthorhombic
Volume (Å3)	1602.03(5)	2909.2(4)	3664.3(7)	8382.0(4)
a (Å)	10.0097(2)	9.3586(8)	9.8833(10)	17.3309(5)
b (Å)	13.3716(2)	19.0408(15)	20.930(2)	20.9805(6)
c (Å)	13.7414(2)	16.5843(14)	18.162(2)	23.0522(7)
α (˚)	69.6737(8)	90	90	90
β (˚)	77.3700(8)	100.123(4)	102.751(4)	90
γ (˚)	69.1267(8)	90	90	90
Z	2	4	4	8
Calculated density (Mg/m3)	1.146	1.363	1.289	1.187
Absorption coefficient (mm-1)	0.068	0.644	0.522	3.187
Final R indices [I > 2σ(I)]	R1 = 0.0523, wR2 = 0.1261	R1 = 0.0515, wR2 = 0.1511	R1 = 0.0631, wR2 = 0.1732	R1 = 0.0526, wR2 = 0.1272

Complex	**4**	**5**	**6**	**11**
CCDC deposit number	2132881	2132885	2132882	2132884
Empirical formula	C_{48} H_{60} Fe N_4 O	C_{38} H_{45} F_3 Fe N_4 O_3 S	C_{37} H_{45} Fe N_7	C_{72} H_{80} Fe N_4 O
Formula weight (g/mol)	764.85	750.69	643.65	1073.25
Crystal habit, color	Block, Yellow	Rod, Colorless	Plate, Yellow	Plate, Yellow
Temperature (K)	157(2)	100(2)	104(2)	100(2)
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	P-1
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Volume (Å3)	4323.0(11)	7369.5(14)	3341.3(2)	2971.89(13)
a (Å)	11.9677(19)	19.996(2)	17.8020(7)	13.4458(3)
b (Å)	11.7643(17)	15.5867(17)	10.9200(4)	13.7445(3)
c (Å)	30.947(4)	24.582(3)	18.9400(7)	19.3806(5)
α (˚)	90	90	90	70.2161(14)
β (˚)	97.162(6)	105.866(5)	114.840(2)	80.4435(18)
γ (˚)	90	90	90	61.8637(13)
Z	4	8	4	2
Calculated density (Mg/m3)	1.175	1.353	1.280	1.199
Absorption coefficient (mm-1)	0.388	4.289	3.899	2.390
Final R indices [I > 2σ(I)]	R1 = 0.0635, wR2 = 0.1711	R1 = 0.0625, wR2 = 0.1514	R1 = 0.0574, wR2 = 0.1520	R1 = 0.0460, wR2 = 0.1141

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