Supplementary Information

"Catch and Release" of the Cp^{N3} Ligand Using Cobalt: Dissociation, Protonation, and C-H Bond Thermochemistry

Sanju Luhach, Roger A. Lalancette, and Demyan E. Prokopchuk*

Department of Chemistry, Rutgers University-Newark, 73 Warren Street, Newark, NJ 07102, United States

*Email: demyan.prokopchuk@rutgers.edu

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Experimental

General Comments

All reactions were carried out under an atmosphere of nitrogen or argon using standard glove box or high vacuum line (Schlenk) techniques unless stated otherwise. All reagents and solvents were stored under inert gas unless stated otherwise. Inert atmosphere reactions and workup protocols used HPLC-grade, inhibitor-free solvents, which were dried and degassed over activated alumina using an IT/Inert solvent purification system. Additionally, Acetonitrile (MeCN), dichloromethane (DCM), and toluene were dried over 20% w/v activated 3 Å molecular sieves.[1] Deuterated solvents were subjected to three freeze-pump-thaw cycles and dried over 10% w/v activated 3 Å molecular sieves in a glove box. Elemental analyses were run by CENTC Elemental Analysis Facility (Department of Chemistry, University of Rochester) on a PerkinElmer 2400 Series II Analyzer. Commercially purchased electrolyte [^{n}Bu$_4$N][PF$_6$] (99%) was recrystallized from fluorobenzene/pentane before use. Compound **[Cp^{N3}][BF$_4$]** was prepared using a known literature procedure.[2] Compound **[Cp^{N3}][B(C$_6$F$_5$)$_4$]** was prepared by stirring **[Cp^{N3}][BF$_4$]** and 1.5 equiv KB(C$_6$F$_5$)$_4$ in diethyl ether followed by filtering through a PTFE syringe filter. The liquid was dried under high vacuum, redissolved in a minimum amount of diethyl ether, and crystals suitable for X-ray diffraction grew in ca. 2 weeks inside a glove box freezer (-25 °C) via layering with hexamethyldisiloxane.

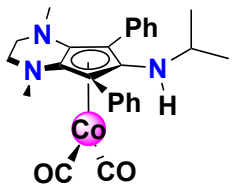
NMR Spectroscopy. Experiments were conducted on a Bruker Avance III HD 500 MHz NMR and Varian Inova 600 MHz NMR spectrometers. Spectra for 1H and 13C were referenced to their respective residual protic solvent signal.[3] NMR signal assignments were made by routine one- and two-dimensional experiments, including 1H-1H COSY, 1H-13C HSQC, 1H-13C HMBC and 1H-31P HMBC spectroscopies. All NMR measurements were carried out at 25 ºC.

X-Ray Crystallography. Single crystals were selected and mounted onto a nylon fiber and cooled to the data collection temperature of 100(2) K with a stream of dry nitrogen gas. X-ray diffraction intensities were collected on a Rigaku XtaLAB Synergy-I diffractometer using CuKα (1.54178 Å) radiation with a HyPIX HPC detector. Structures were refined by full-matrix least squares based on F^2 with all reflections (SHELXTL V5.10; G. Sheldrick, Siemens XRD, Madison, WI). Non-hydrogen atoms were refined with anisotropic displacement coefficients, and hydrogen atoms were treated as idealized contributions. SADABS (Sheldrick, 12 G.M. SADABS (2.01), Bruker/Siemens Area Detector Absorption Correction Program; Bruker AXS: Madison, WI, 1998) absorption correction was applied. Crystallographic data has been deposited with the Cambridge Crystallographic Data Center and is available free of charge through the CCDC online database.

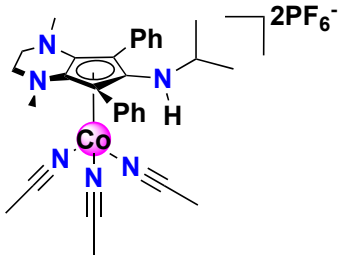
Electrochemistry. Cyclic voltammetry experiments were conducted under N_2 at 295 ± 3 K using a standard three-electrode setup consisting of a 1 mm PEEK-encased glassy carbon working electrode (eDAQ), graphite rod counter electrode, and Ag wire pseudoreference electrode. The working electrode was polished with 0.25 μm diamond polishing paste, lapping oil, and a rayon microcloth pad (Buehler) inside a glove box and thoroughly rinsed with the solvent used in the corresponding experiment. A Gamry Reference 1010B potentiostat and Gamry software were used for data collection and analysis. All CVs are referenced to the $Fc^{+/0}$ redox couple (0 V).

DFT Calculations. Calculations were performed with ORCA Version 5.0.3.[4] As part of the supporting information, a separate .xyz file contains cartesian coordinates for all calculated structures with optimized energies reported in Hartrees. Geometry optimizations and numerical frequency calculations use the meta-GGA TPSS functional with the def2-TZVP[5] basis sets and def2/J[6] auxiliary basis sets (TPSS-D3(BJ)/def2-TZVP). All calculations include D3 dispersion correction with Becke-Johnson damping and three-body correction (D3BJ ABC).[7, 8] All calculations utilize the SMD solvation model in MeCN.[9] Full vibrational and thermochemical analyses were performed on optimized structures to obtain solvent-corrected free energies (G°) and enthalpies (H°) under standard state conditions. Optimized ground states all have zero imaginary frequencies. Redox potentials (E°) were computed relative to ferrocenium/ferrocene ($Fc^{+/0}$, E° = 0.0 V, MeCN), pK_a relative to 2,4,6-trimethylpyridinium (14.77, MeCN)[10] and BDFE(C-H) relative to the homolytic BDFE of 1/2 H_2 (52.0, MeCN).[11]

Syntheses

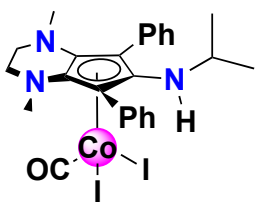


$CpN^3Co(CO)_2$ (1): $[Cp^{N3}]^+$ (500 mg, 1mmol) and 1.14 equiv. $NaCoCO_4$ (246 mg, 1.27mmol) were added to a 25 mL Schlenk flask and suspended in 10 mL toluene in the glovebox. The mixture was refluxed under N_2 for 12 h, after which the solution turned orange. The reaction mixture was cooled to room temperature, dried under a high vacuum, dissolved in 5 mL pentane and passed through a medium pore glass filter frit. Orange-colored crystals were obtained by cooling the filtrate in glovebox freezer, which were also suitable for X-ray diffraction. The solvent was decanted, and the analytically pure product was dried under high vacuum (372 mg, 70%). Anal calcd (%) for $C_{26}H_{28}CoN_3O_2$ C 65.96, H 5.96, N 8.88; found C 65.40, H 5.83, N 8.74. IR (KBr): 1970, 1901 cm^{-1} (ν_{CO}).^{1}H NMR (500 MHz, C_6D_6) δ 7.81 (s, 3H, arom), 7.14 (s, 1H, arom), 7.12 (d, J = 7.6 Hz, 3H, arom), 7.08 – 7.02 (m, 2H, arom), 3.04 – 2.89 (m, 1H, $CHMe_2$), 2.75 – 2.60 (m, 2H, CH_2), 2.28 (d, J = 15.7 Hz, 1H, NH), 2.19 – 2.12 (m, 2H, CH_2), 2.10 (s, 6H, NCH_3), 0.50 (d, J = 13.6 Hz, 6H, $CHMe_2$) ppm.^{13}C NMR (126 MHz, C_6D_6) δ 133.83 (arom), 133.18 (arom), 115.60 (Cp), 112.80 (Cp), 75.33 (Cp), 49.70 (CH_2), 47.71 ($CHMe_2$), 43.86 (N-CH_3) 23.05 ($CHMe_2$) ppm. The ^{13}C signals for CO were not resolved.

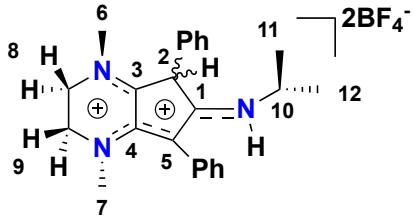


$[CpN^3Co(NCMe)_3][PF_6]_2$ (2): Complex **1** (50mg, 0.1mmol) was dissolved in 2 mL acetonitrile and 2 equiv. $AgPF_6$ (53mg, 0.2mmol) were added. Upon adding $AgPF_6$, the mixture turned violet and was filtered through a medium-pore glass frit after 1 minute, the filtrate was dried under a high vacuum. Longer reaction times led to significant product decomposition. The solids were redissolved in acetonitrile (0.5 mL), layered with diethyl ether (ca. 3 mL) and left to crystallize at -25 °C in a glove box freezer to yield violet-colored crystals. Although crystals were suitable for X-ray diffraction, a whitish precipitate could not be fully separated from the final product (crude yield: 36mg, 40 %). Anal calcd (%) for $C_{26}H_{28}CoF_{12}N_6P_2$ C 43.39, H 4.49, N 10.12; found C 42.02, H 4.38, N 10.05. IR (CH_3CN): 2250 cm^{-1} (ν_{CN}).^{1}H NMR (500 MHz, CD_3CN) δ 7.29 – 9.8 (m, 10H, arom), 4.10 (d, 1H, NH), 3.12-3.26 (m, 4H, $2CH_2$), 2.60-2.73 (m, 1H, $CHMe_2$),

2.10 (s, 6H, 2N-CH_3), 1.96 (s, 9H, MeCN), 0.74 (d, J = 6.4 Hz, 6H, $CHMe_2$) ppm. ^{13}C NMR (126 MHz, CD_3CN) δ 134.7-128.8 (arom), 109.62 (Cp), 69.46 (Cp) 65.61 (Cp), 49.66 (CH_2), 45.58 ($CHMe_2$), 39.90 (N-CH_3), 22.00 ($CHMe_2$) ppm. The ^{13}C signals for CO were not resolved.



[$CpN^3Co(CO)(I)_2$] (3): Complex **1** (88 mg, 0.18 mmol) was dissolved in 2 mL diethyl ether and then a solution of 1 equiv. iodine (45 mg, 0.35 mmol) in 1 mL diethyl ether was added. A black solid precipitated immediately and the reaction was stirred for 3 days. The precipitate was isolated on a medium pore glass filter frit, washed with diethyl ether and pentane, and dried under high vacuum to yield the product (107 mg, 83%). The product is insoluble in nonpolar solvents and reacts with polar coordinating solvents such as CD_3CN to release free ligand **[Cp^{N3}]**$^+$ in 72% yield, which was quantified by ^1H NMR by dissolving **3** (8.9 mg, 0.013 mmol) in 0.50 mL CD_3CN and using 1,3,5-trimethoxybenzene as an internal standard (Figure S11). Anal calcd (%) for $C_{25}H_{28}CoI_2N_3O$ C 42.94, H 4.04, N 6.01; found C 41.87, H 4.13, N 5.55. IR (KBr) 2000 cm^{-1} (ν_{CO})



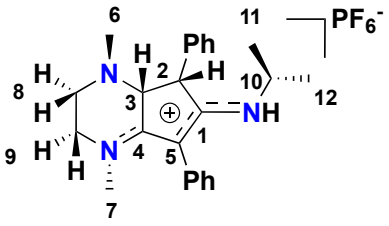
[$Cp^{N3}H$][BF4]$_2$ ([4][BF_4]$_2$): The free ligand **[Cp^{N3}]**$^+$ (100 mg, 0.2 mmol) dissolved in DCM (2 mL), 1 equiv of HBF_4•Et_2O (30 µl, 0.22 mmol) was added while stirring. The color turned yellow and was stirred for 1 h. Diethyl ether (ca. 6 mL) was added to the reaction and the desired product precipitated as a yellow solid. The solid was isolated on a medium pore glass frit, washed with diethyl ether, and dried under vacuum. Crystals were obtained by slow diffusion of diethyl ether in acetonitrile to obtain the product in quantitative yield (133 mg). The product is air stable. The deuterated analogue was prepared by adding two drops of MeOD to a stirring solution of **[4][BF_4]$_2$** in CD_3CN, resulting in 95% deuterium CH/CD exchange on the C1 position and full deuteration of the secondary amine (Figure 5 and Figure S13). **Anal calcd** (%) for $C_{24}H_{29}B_2F_4N_3$ C54.07, H 5.48, N 7.88; found C 53.90, H 5.34, N 7.80.^1H NMR (500 MHz, CD_3CN) δ 8.42 (s, 1H, NH) 7.41–7.61 (m, 10H, arom), 5.73 (s, 1H, H2), 4.17 (ddd, 1H, H8), 3.92(m,1H,H8), 3.983.92-4.01 (m, 1H, H10) 3.84 (ddd, 1H, H9) 3.6 (m, 1H, H9) 3.64 (s, 3H, H6) 2.85 (s, 3H, H7), 1.22, 0.49 (d, J = 6.5 Hz, 3H, H11, H12) ppm. ^{13}C NMR (126 MHz, CD_3CN) δ 173.47 (C1), 171.36 (C3), 151.96 (C4), 127.0-131.0 (arom), 122.4 (C5), 52.73(C10), 52.61(C8), 48.73 (C2), 47.90 (C9), 45.35 (C6) , 41.47 (C7), 21.69 , 20.35 (C11,C12) ppm .

Formation of [4][PF_6]$_2$ from complex 3: Complex **3** (20 mg, 0.02 mmol) and 2 equiv of $AgPF_6$ (14 mg, 0.055 mmol) were mixed in 2 mL DCM and stirred overnight. The reaction color turned from brown to greenish yellow. The reaction was filtered using a PTFE syringe filter and 5 mL of diethyl ether was added. After stirring overnight **[4][PF_6]**$_2$ precipitated as a crystalline solid in 50% yield (7.5 mg).

Reduction of [4][BF_4]$_2$ with chromocene: An NMR scale reaction was done where **[4][BF_4]$_2$** (13mg, 0.024mmol) was dissolved in 0.5 mL CD_3CN and 1 equiv of chromocene (4.4 mg, 0.024

mmol). The reaction turned greenish and was stirred for 20 min. Next, the mixture was filtered through a PTFE syringe filter and ^{1}H NMR spectra were recorded with a known amount of 1,3,5-trimethoxy benzene as an internal standard. Compounds **[Cp^{N3}]$^+$** and **[Cp^{N3}H$_2$][BF$_4$]** were in an approximately 1:1 ratio with a total yield of **93%** for this radical disproportionation reaction.

Reduction of [4][BF$_4$]$_2$ with chromocene and 5 equiv. TEMPO: [4][BF$_4$]$_2$ (12mg, 0.022mmol) was dissolved in 0.50 mL MeCN followed by the addition of 5 equiv. of TEMPO (17 mg, 0.11 mmol) and one equiv. of chromocene (4.1 mg, 0.022 mmol) respectively. The reaction turned bluish and was stirred for 30 min, followed by the addition of 3 mL diethyl ether to precipitate [CrCp$_2$][BF4]. The mixture was filtered over a pad of Celite and the filtrate was dried under vacuum. A ^{1}H NMR spectrum was collected in CD$_3$CN, identifying **[Cp^{N3}]$^+$** as the major product with no detectable amount of **[Cp^{N3}H$_2$][BF$_4$]** (Figure S16).

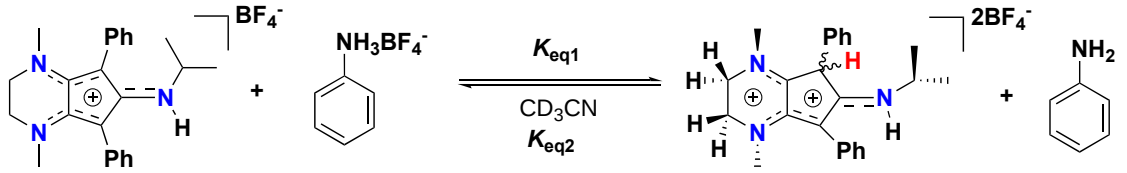


[Cp^{N3}H$_2$][PF$_6$] ([5][PF$_6$]): Two equiv of HBF$_4$•Et$_2$O (61 µl, 0.44 mmol) were added to a solution of **[Cp^{N3}]$^+$** (100 mg, 0.224 mmol) in 2 mL DCM followed by the addition of 2 equiv chromocene (81 mg, 0.44 mmol) to afford a red-orange solution. The reaction was stirred for 30 min, then approx. 7 mL diethyl ether was added, which precipitated [CrCp$_2$][BF$_4$] from the solution. The crude product was filtered through a medium-pore glass frit to obtain a blue solution, which was then dried under high vacuum. Under air, the product was dissolved in methanol (2 mL) and excess ammonium hexafluorophosphate (NH_4PF_6) (150 mg) was added. After stirring for 1 hour, extraction of the product into the organic phase was accomplished by adding the solution to a separatory funnel with a 3:1 DCM:H_2O ratio (ca. 20 mL in total), along with the addition of ca. 500 mg NH_4PF_6 to the separating funnel. The light-green colored organic layer was dried over anhydrous $MgSO_4$, filtered, and then dried via rotary evaporation. The oily liquid was dissolved in a minimum amount of dichloromethane, layered with ca.6 mL hexane and recrystallized in the refrigerator (10 °C). Compound **5** is a pale yellow crystalline solid and colorless single crystals suitable for X-ray diffraction were selected from this crop (33 mg, 32%). Anal calcd (%) for $C_{24}H_{30}PF_6N_3$ C57.03, H 5.98, N 8.31; found C 56.14, H 5.69, N 7.88.^{1}H NMR (500 MHz, CD$_3$CN), δ 7.53 – 7.31 (m, 10H, arom), 6.67 (s, 1H, NH), 4.65 (d, J = 6.3 Hz, 1H, H2), 3.92 – 3.85 (m, 1H, H10), 3.49 (d, J = 6.8Hz, 1H, H3), 3.50 (d, 1H), 3.33 (dd, J = 14.0, 4.9 Hz, 1H) 2.91 (dd, J = 12.4, 5.3Hz, 1H), 2.43 (td, J = 12.2, 4.6Hz, 1H) diastereotopic methylene protons, H8,9), 2.76 (s, 3H, H7),, 2.08 (s, 3H, H6), 1.12, 0.5 (d, J = 6.6Hz, 3H, 3H H11,12) ^{13}C NMR (126 MHz, CD$_3$CN) δ 175.2 (C1), 172.13 (C4), 136.02-129.20 (arom), 106.84 (C5), 70.07 (C3), 52.81, 52.21 (C8,C9), 50.30 (C2), 49.47(C10), 42.81(C7), 41.91(C6), 22.72, 21.94 (C11,12).

Thermochemical measurements of [Cp^{N3}H][BF$_4$]$_2$ in MeCN

In the glovebox, **[Cp^{N3}H][BF$_4$]$_2$** (13 mg, 0.024mmol) was added to a standard 5 mm NMR tube, followed by 0.60 mL CD$_3$CN and aniline (2.2 µl, 2.2 mmol) using a microsyringe. The NMR tube was capped, and the reaction was evaluated after about 10 minutes by ^{1}H NMR. The equilibrium concentration ratio of **[Cp^{N3}H][BF$_4$]$_2$** and **[Cp^{N3}]$^+$** was calculated by integrating the CH$_3$ doublets of the isopropyl groups in the starting material (0.49 ppm) and product (0.84 ppm), respectively (Figure S9). The equilibrium constant (K_{eq2} = 10.5) was calculated for the reaction using equation

S1. The ratio of products remained unchanged after 3 days. The reverse reaction combines **[Cp^{N3}][BF$_4$]** (9.9mg, 0.022 mmol) with 1.0 equiv. of [PhNH$_3$][BF$_4$] (pK_a = 10.62) and was conducted under similar conditions, reaching equilibrium within a minute, with K_{eq1} = 12.7. (Figure S10). The averaged pK_a of **[Cp^{N3}H][BF$_4$]$_2$** is calculated to be 11.7 ± 0.1. Based on this pK_a and the redox potential of **[4]$^{2+/+}$** (-0.72 V vs. Fc$^{+/0}$), the C-H BDFE is calculated to be 51.8 kcal/mol (eq. S3).



pK_a = 10.62 (in MeCN)

^{1}H signal at 0.84ppm for 2-CH$_3$ (isopropyl group) ^{1}H signal at 0.49ppm for -CH$_3$ (isopropyl group)

$$K_{\mathrm{eq}} = \frac{[\mathrm{Cp^{N3}H^{2+}}][\mathrm{PhNH_2}]}{[\mathrm{Cp^{N3+}}][\mathrm{PhNH_3^+}]} = \frac{[\mathrm{Cp^{N3}H^{2+}}]^2}{[\mathrm{Cp^{N3+}}]^2} \quad \text{(S1)}$$

$$pK_a(\mathrm{PhNH_3^+}) = pK_a\left(\mathrm{Cp^{N3}H^{2+}}\right) - logK_{\mathrm{eq}} \quad \text{(S2)}$$

$$BDFE = 23.06E^{\mathrm{o}} + 1.37pK_a + \mathrm{C_G} \ (\mathrm{C_G\ for\ MeCN} = 52.6) \quad \text{(S3)}$$

$$BDFE = 23.06 \times (-0.72) + 1.37 \times 11.7 \pm 0.1 + 52.6 = 51.8 \pm 0.1\mathrm{kcal/mol}$$

NMR Spectra

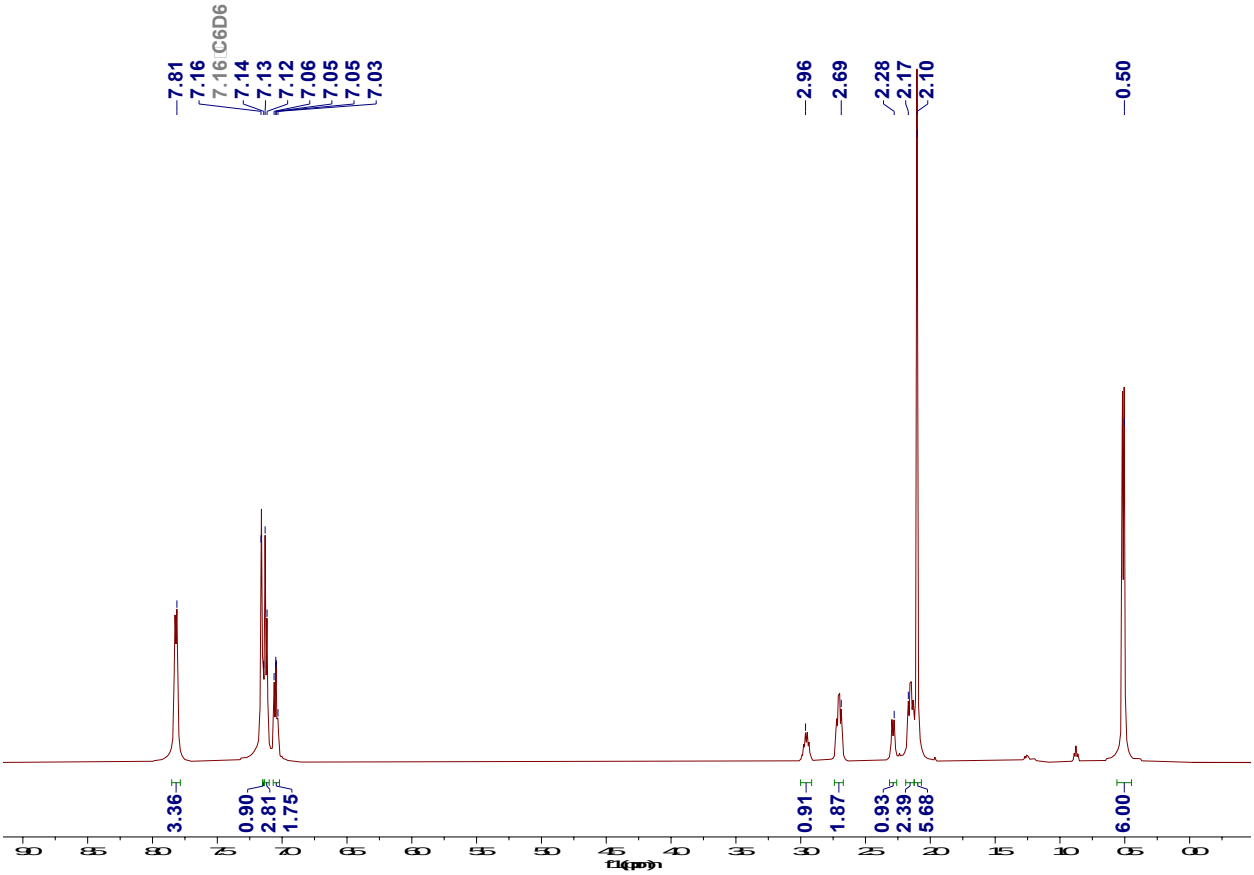


Figure S1: ^{1}H NMR spectrum of **1** (500 MHz, C_6D_6, 25 °C). Residual solvent impurities appear at 0.85 ppm (pentane) and 1.3 ppm (diethyl ether).

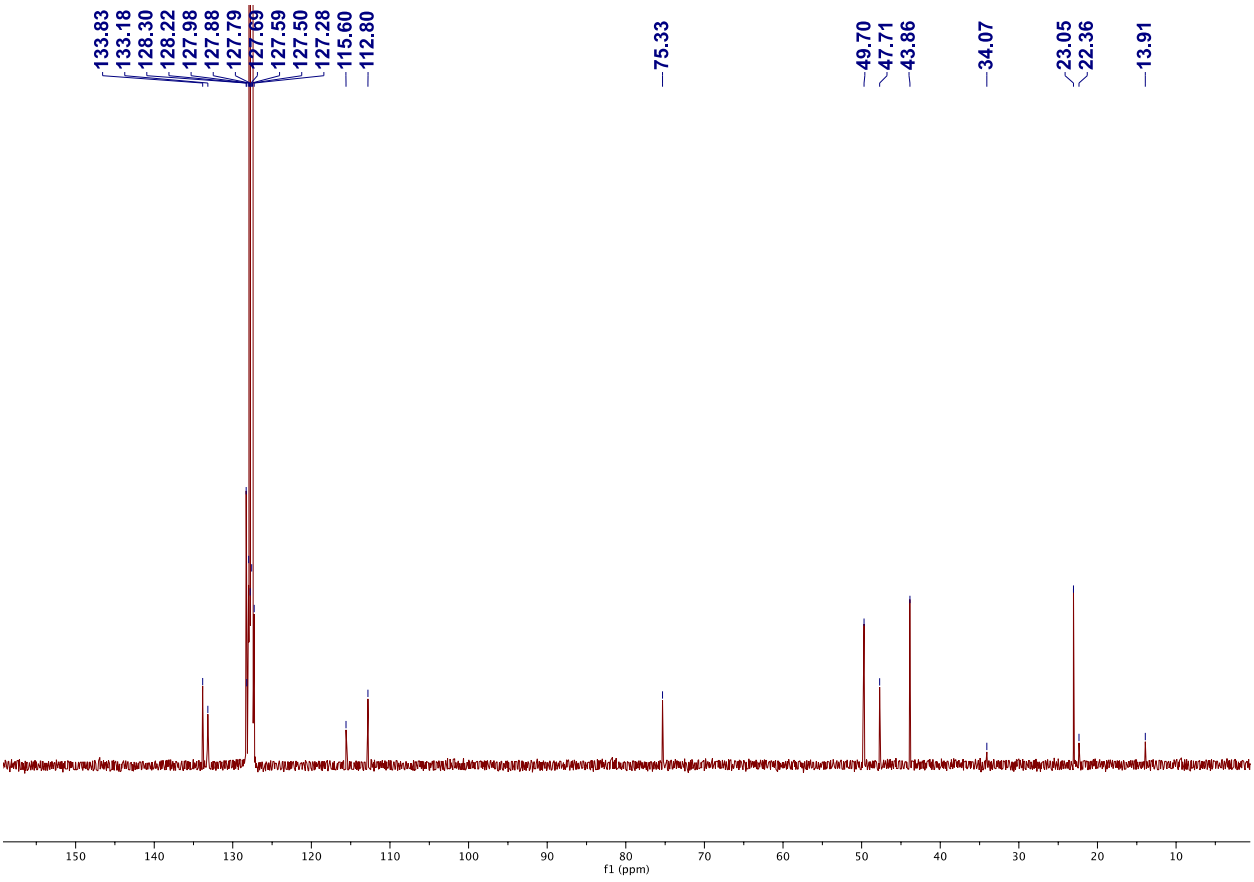


Figure S2: ^{13}C NMR spectrum of **1**. (126 MHz, C_6D_6, 25 °C).

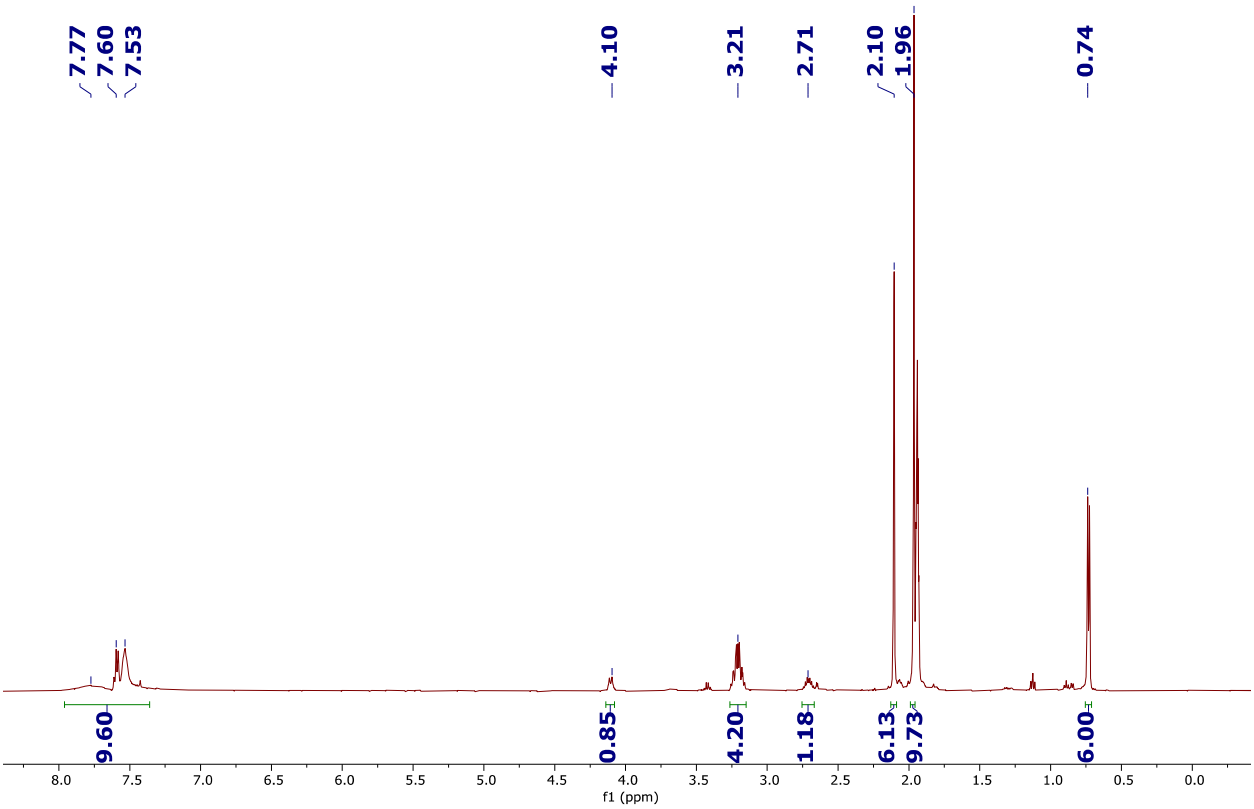


Figure S3: ^{1}H NMR spectrum of **2.** (500 MHz, CD_3CN 25 °C). Residual solvent impurities appear at 0.89 ppm (pentane), 1.13 ppm (diethyl ether), and 3.42 ppm (diethyl ether).

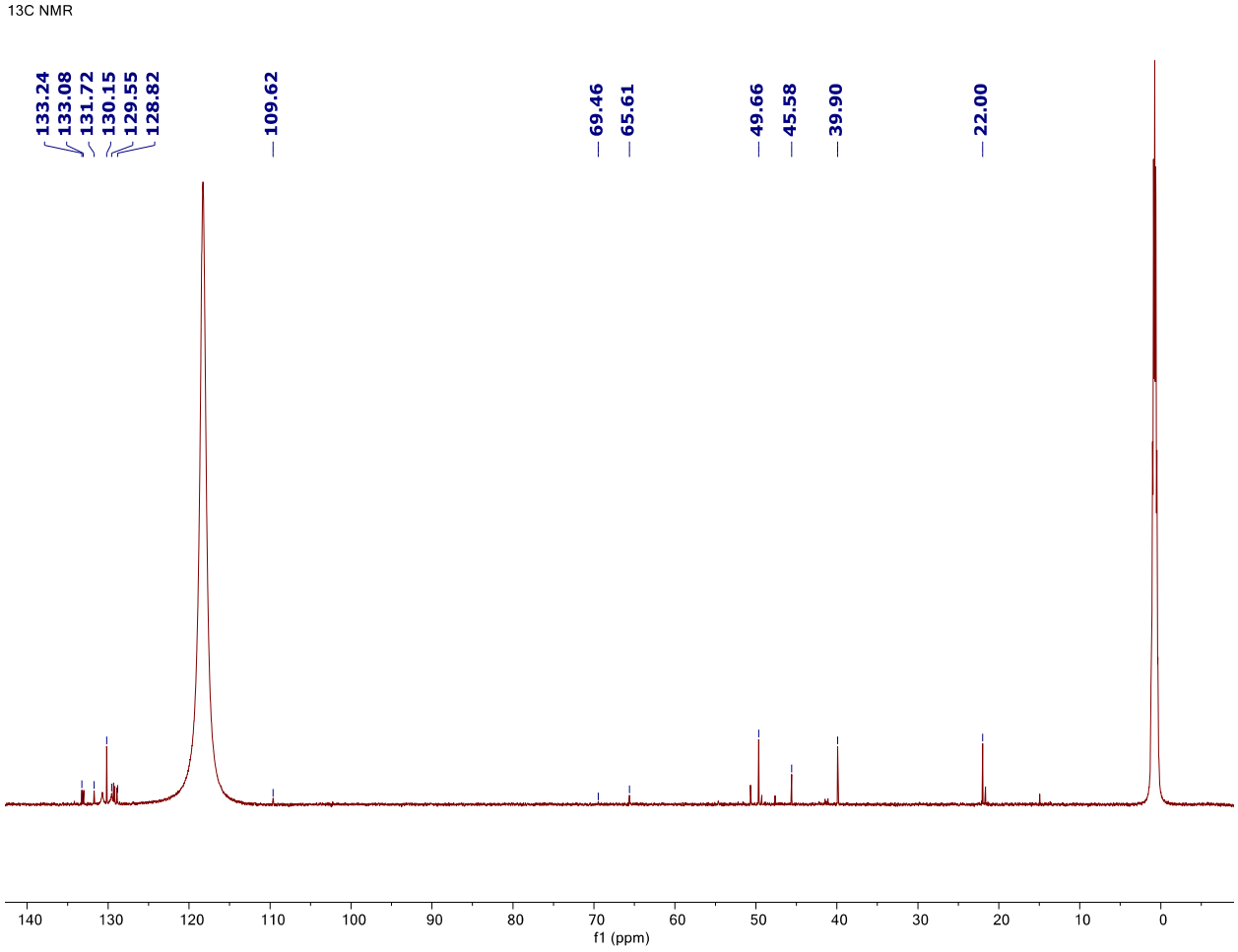


Figure S4: ^{13}C NMR spectrum of **2** (126 MHz, CD_3CN).

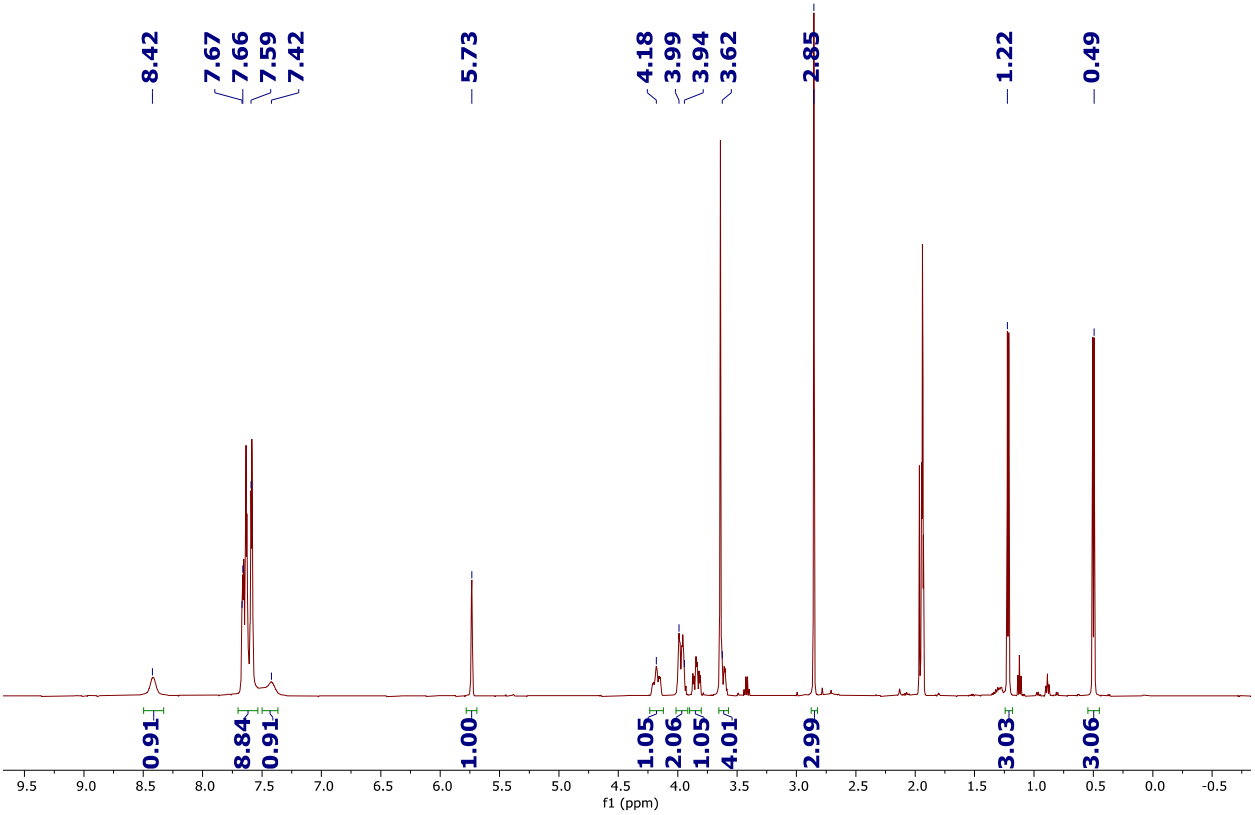


Figure S5: ^{1}H NMR spectrum of **[4][BF$_4$]$_2$** (500MHz, CD_3CN, 25 °C). Residual solvent signals appear at 0.89 ppm (pentane) and 1.13 ppm and 3.42 ppm (diethyl ether).

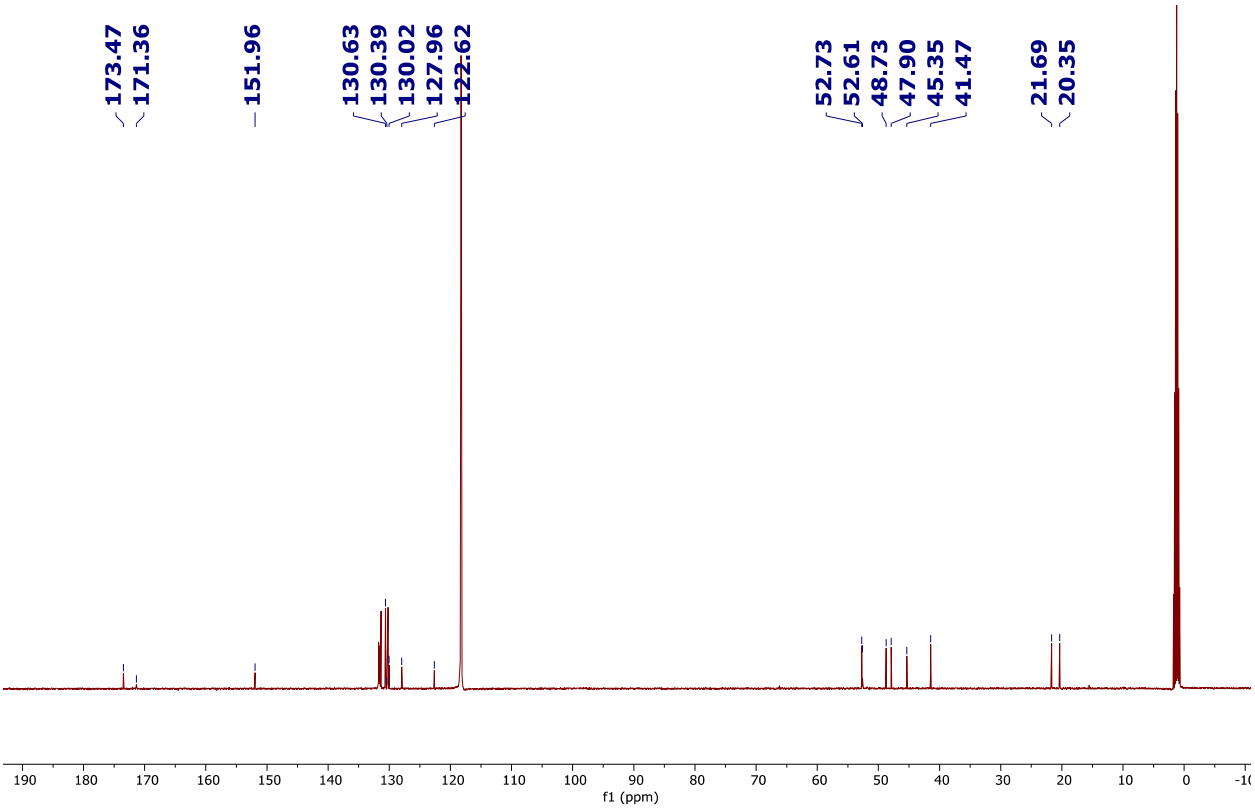


Figure S6: ^{13}C NMR spectrum of **[4][BF_4]$_2$** (126 MHz, CD_3CN)

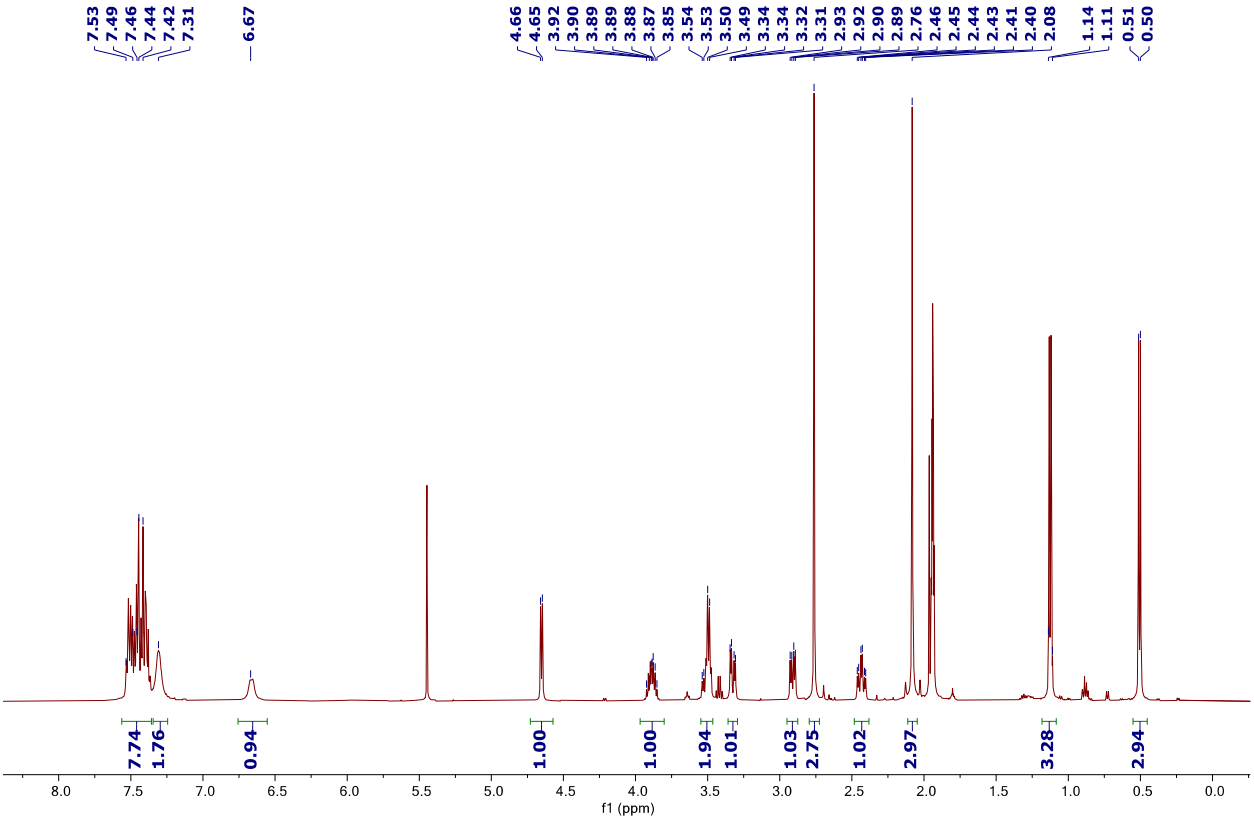


Figure S7: ^{1}H NMR spectrum of **[5][PF$_6$]** (500MHz, CD_3CN, 25 °C). Residual solvent peaks appear at 0.88 ppm (hexane), 3.42 ppm (diethyl ether), 1.96 ppm (MeCN), and 5.45 ppm (DCM).

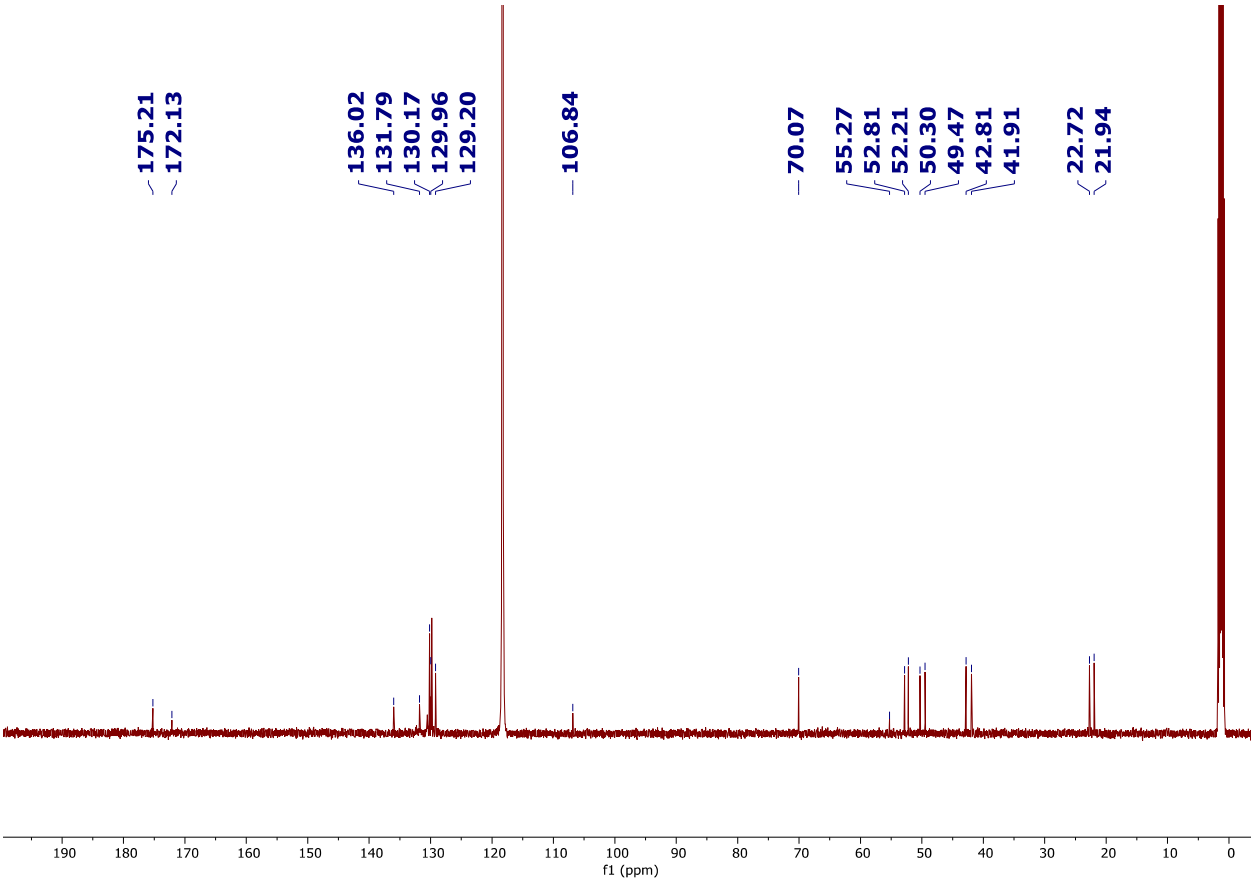


Figure S8: ^{13}C NMR spectrum of **[5][PF_6]** (126 MHz, CD_3CN)

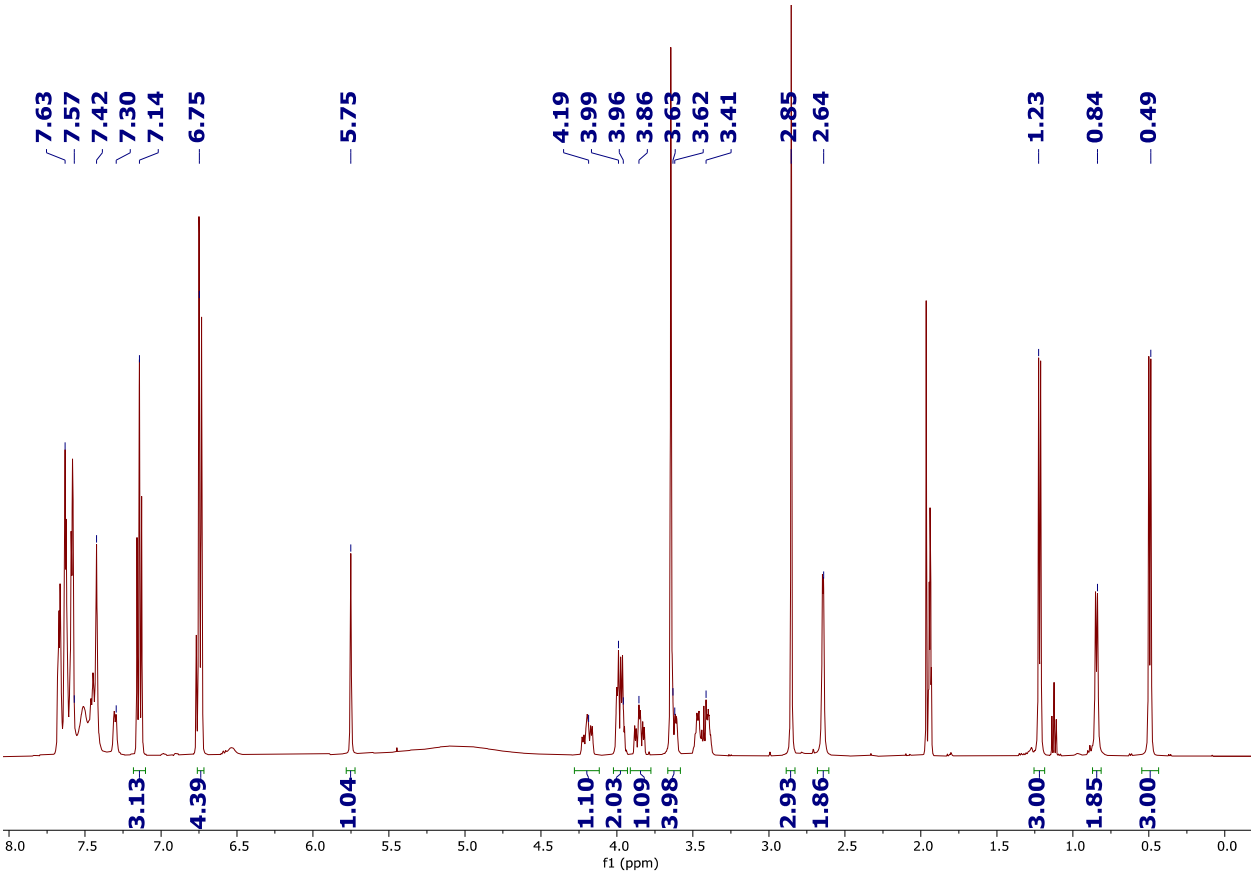


Figure S9: ^{1}H NMR spectrum of reacting **[4][BF$_4$]$_2$** and aniline. (500 MHz, CD_3CN, 25 °C). Residual solvent signals are at 1.13 and 3.42 ppm (diethyl ether). The broad signal at around 5 ppm is for the amine protons of aniline.

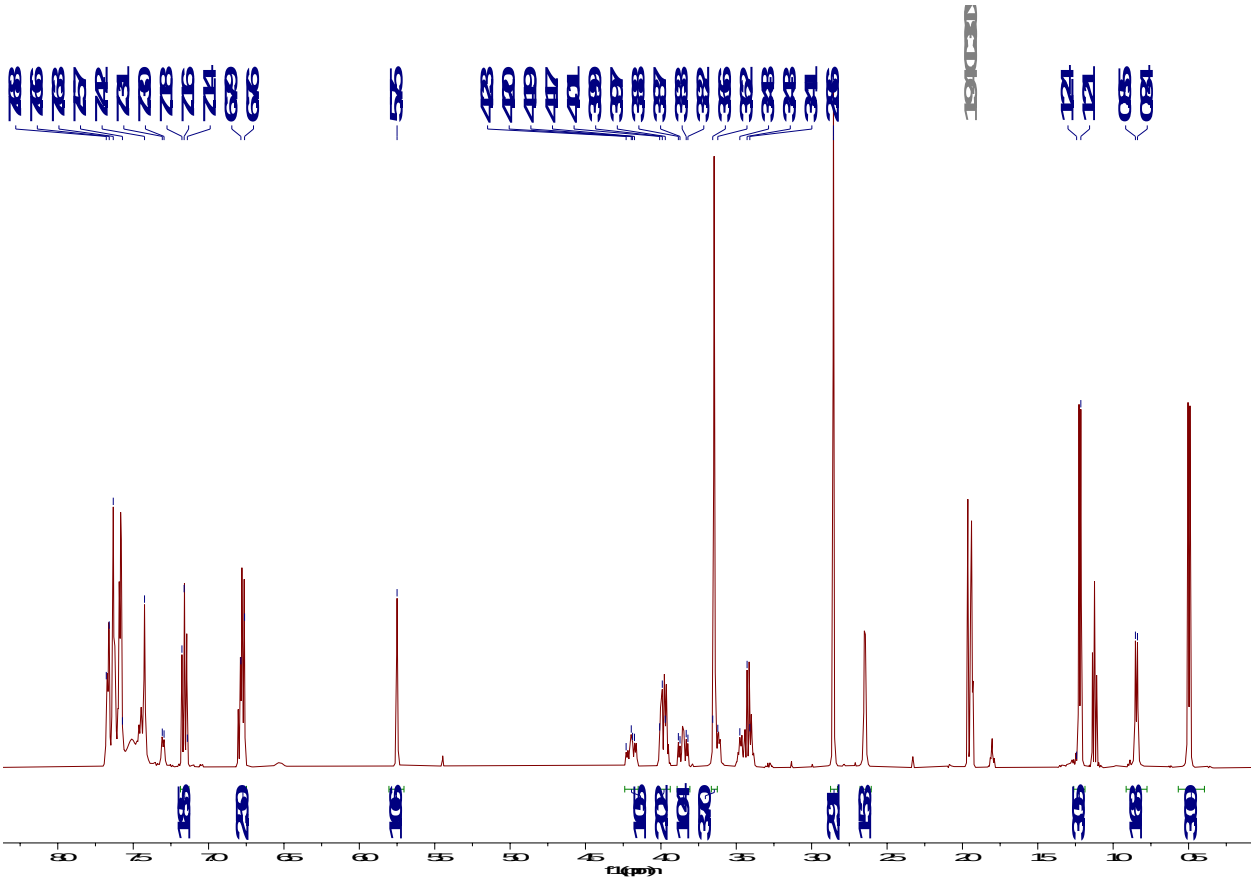


Figure S10. ^{1}H NMR spectrum of **[Cp^{N3}]$^{+}$** and [PhNH$_3$][BF$_4$] (500 MHz, CD$_3$CN, 25 °C). Residual solvents signals appear at 1.13 and 3.42 ppm (diethyl ether) and 5.5 ppm (DCM).

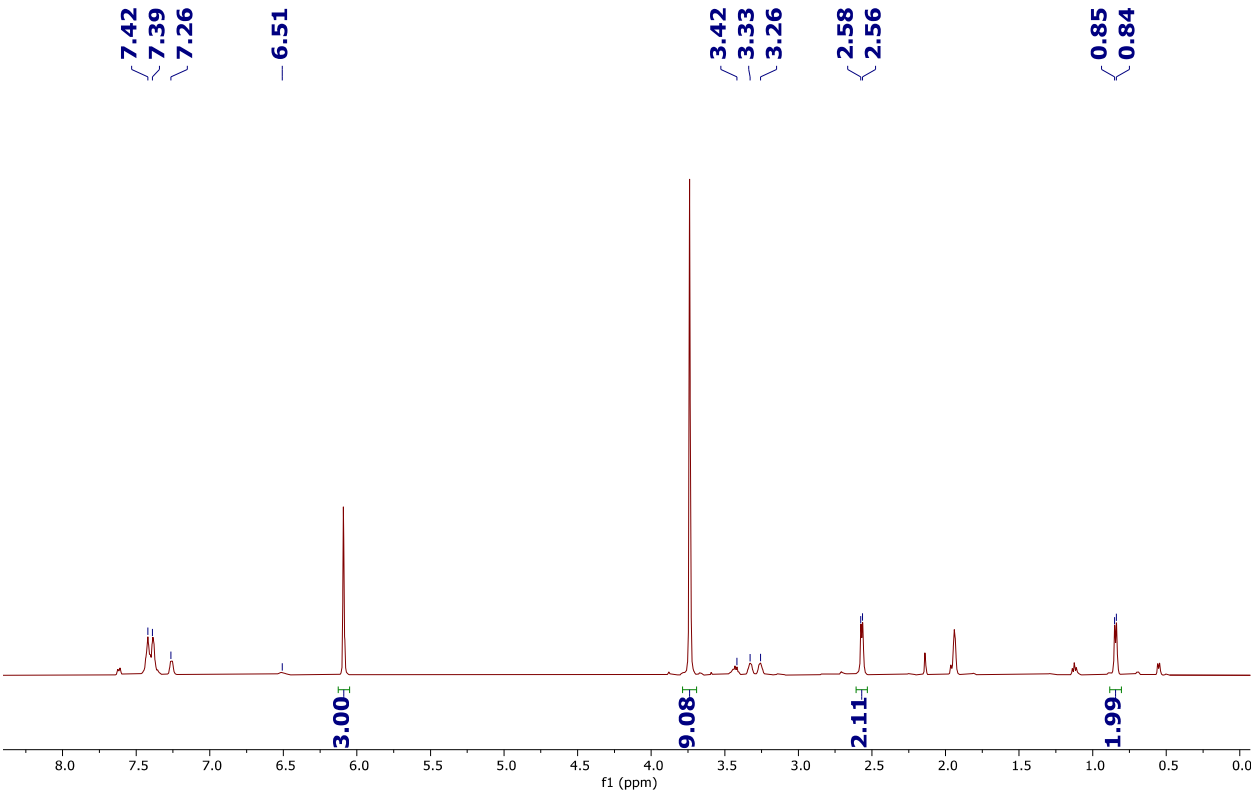


Figure S11. ^{1}H NMR spectrum of complex **3** in MeCN to give **[Cp^{N3}]$^{+}$** back in 72% (NMR Yield) . Peaks at 3.8 ppm and 6.2 ppm are for 2,4,6-trimethoxybenzene, used as reference for yield calculation. Residual solvent signals appear at 3.44 and 1.12 ppm (diethyl ether). Signals at 0.54, 2.13 and 7.62 ppm are for minor impurities.

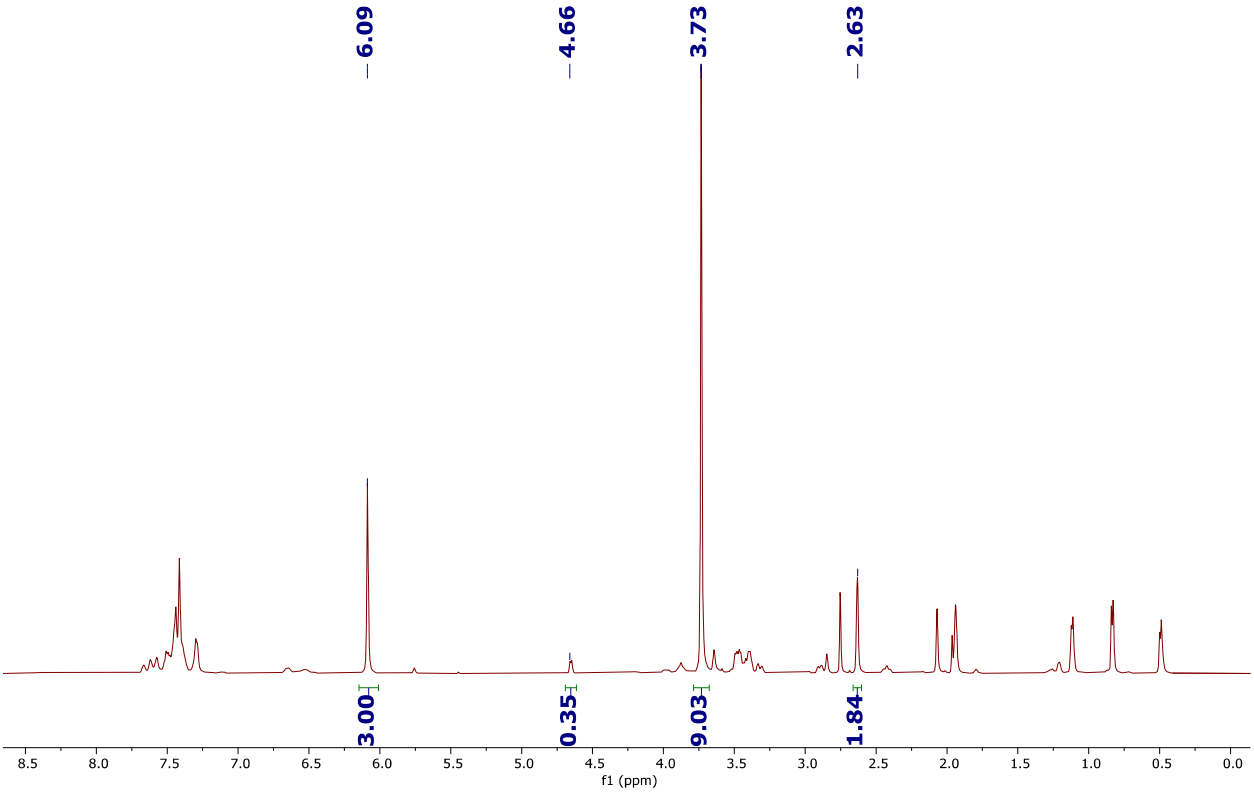


Figure S12. ^{1}H NMR spectrum for the reaction of **[4][BF$_4$]$_2$** with 1 equiv. chromocene where **[4][BF$_4$]$_2$** disproportionates to generate **[5][BF$_4$]** and **[Cp^{N3}]$^+$**in a 10:9 ratio. Peaks at 3.73 ppm and 6.09 ppm are for 2,4,6-trimethoxybenzene, used as reference for calculating reaction yield. Yield is calculated by integrating the N-methyl peaks at 2.63 ppm for **[Cp^{N3}]$^+$** and the peak at 4.66 ppm for **[5][BF$_4$]**.

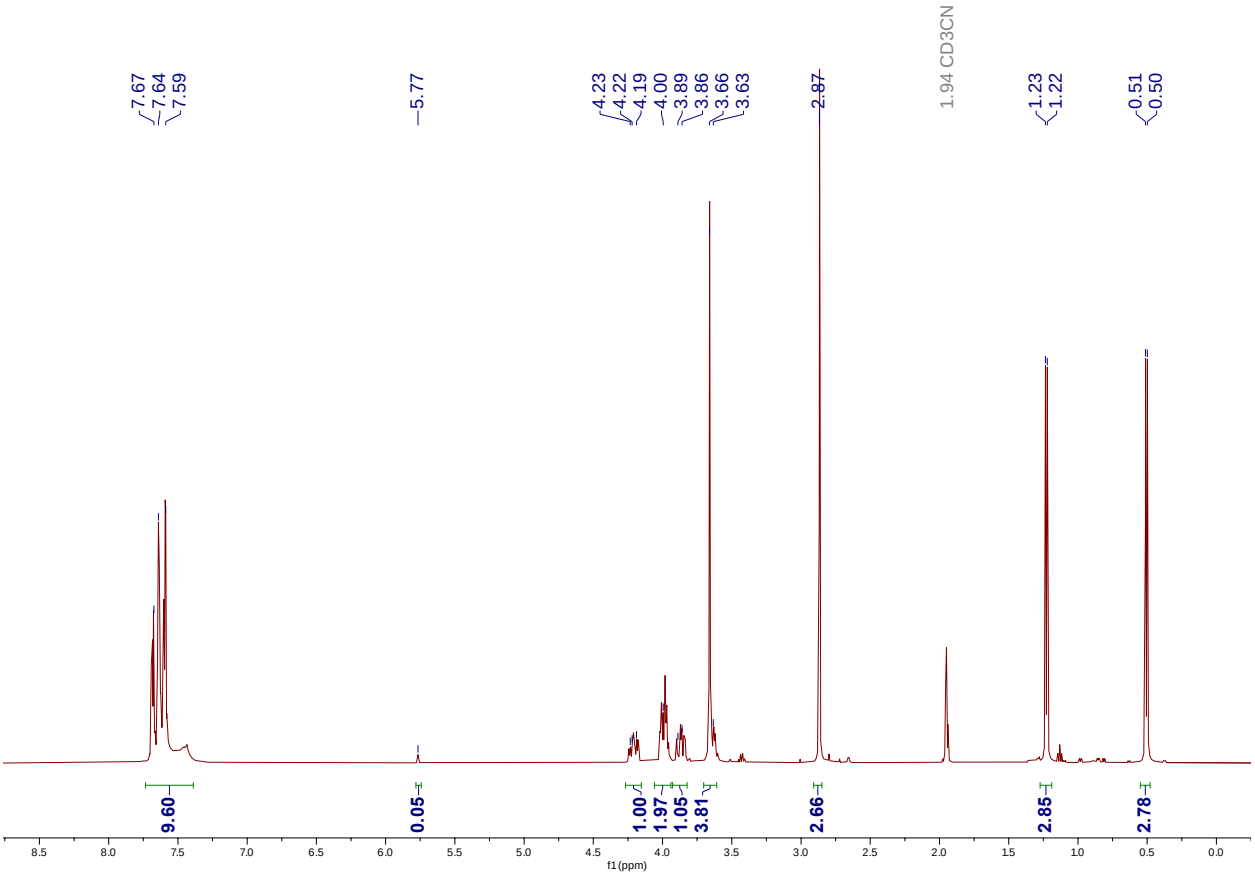


Figure S13: ^{1}H NMR spectrum for the reaction of **[Cp^{N3}D][BF$_4$]$_2$** with ca. 95% H/D exchange at the NH-isopropyl (8.42 ppm) and Cp^{N3}H (5.77 ppm) positions. See Figure S5 for protio spectrum.

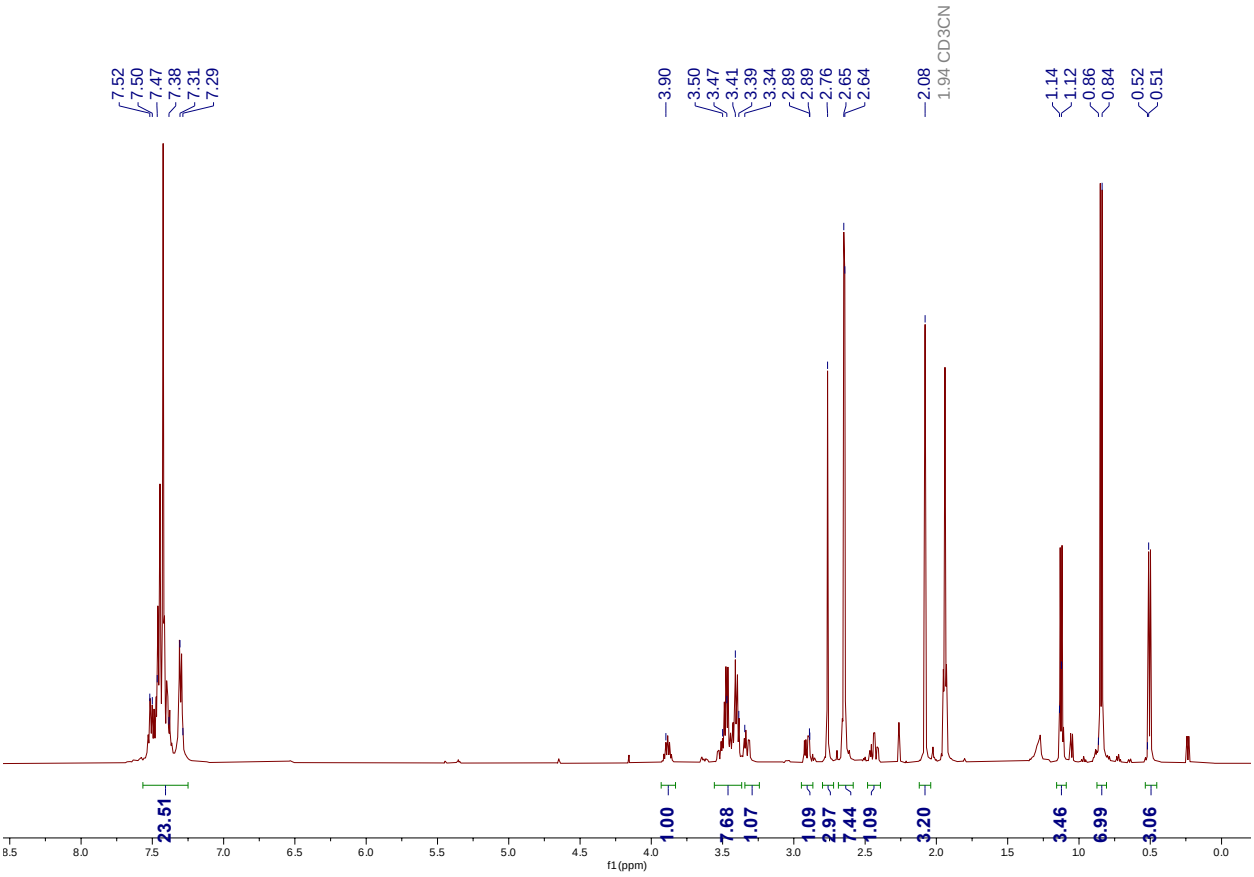


Figure S14: ^{1}H NMR spectrum for the reaction of **[Cp^{N3}D][BF$_4$]$_2$** with 1 equiv. of chromocene to give **[Cp^{N3}D$_2$][BF$_4$]** and **[Cp^{N3}]$^+$** in a roughly 1:1 ratio.

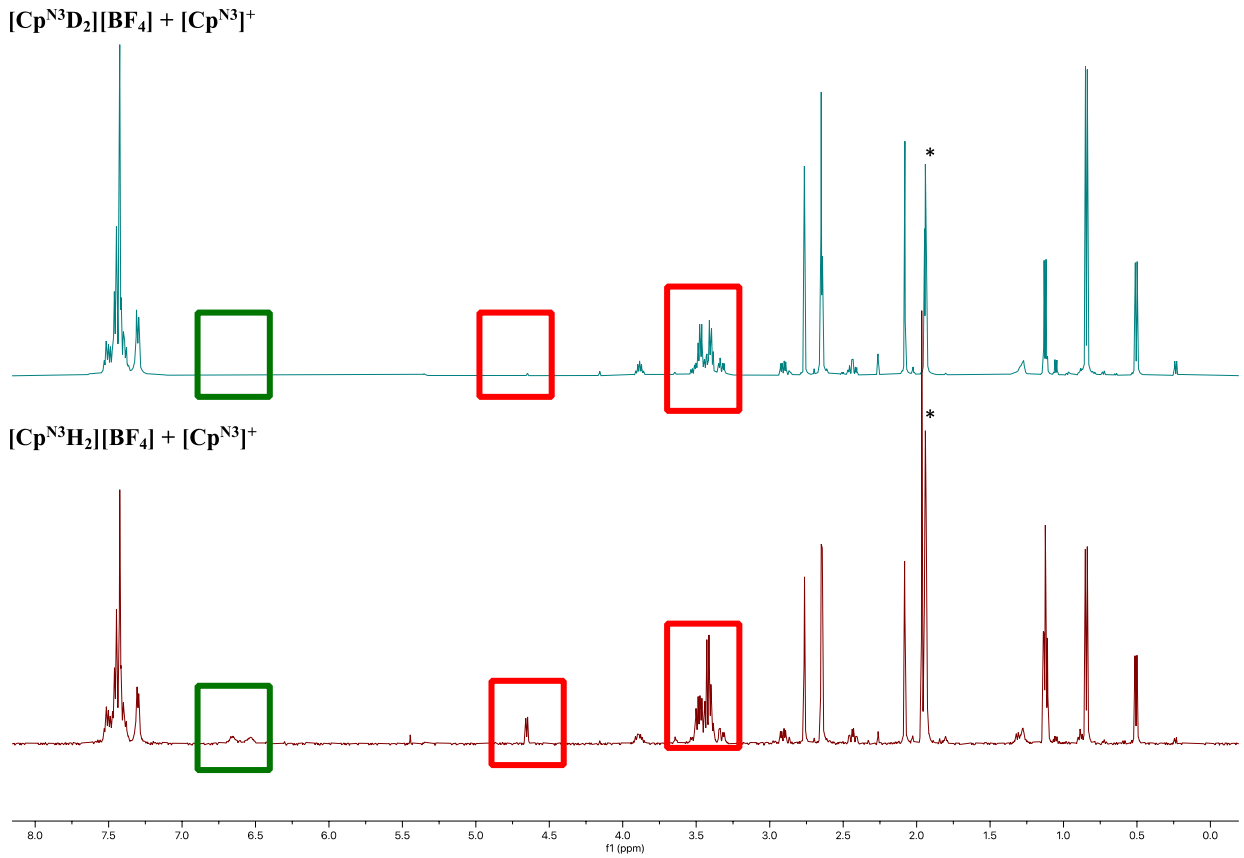


Figure S15: Stacked ^{1}H NMR spectra for reduction **[Cp^{N3}D][BF$_4$]$_2$** (top) and **[Cp^{N3}H][BF$_4$]$_2$** (bottom) with 1 equiv. chromocene. The red boxes highlight the absence of protons on the Cp ring in the reaction with **[Cp^{N3}D][BF$_4$]$_2$**. The NH^{i}Pr proton is also absent at 6.6 ppm in the product spectrum containing **[Cp^{N3}D$_2$][BF$_4$]** and **[Cp^{N3}]$^+$** (green box). The NMR solvent (CD_3CN) is shown with an asterisk.

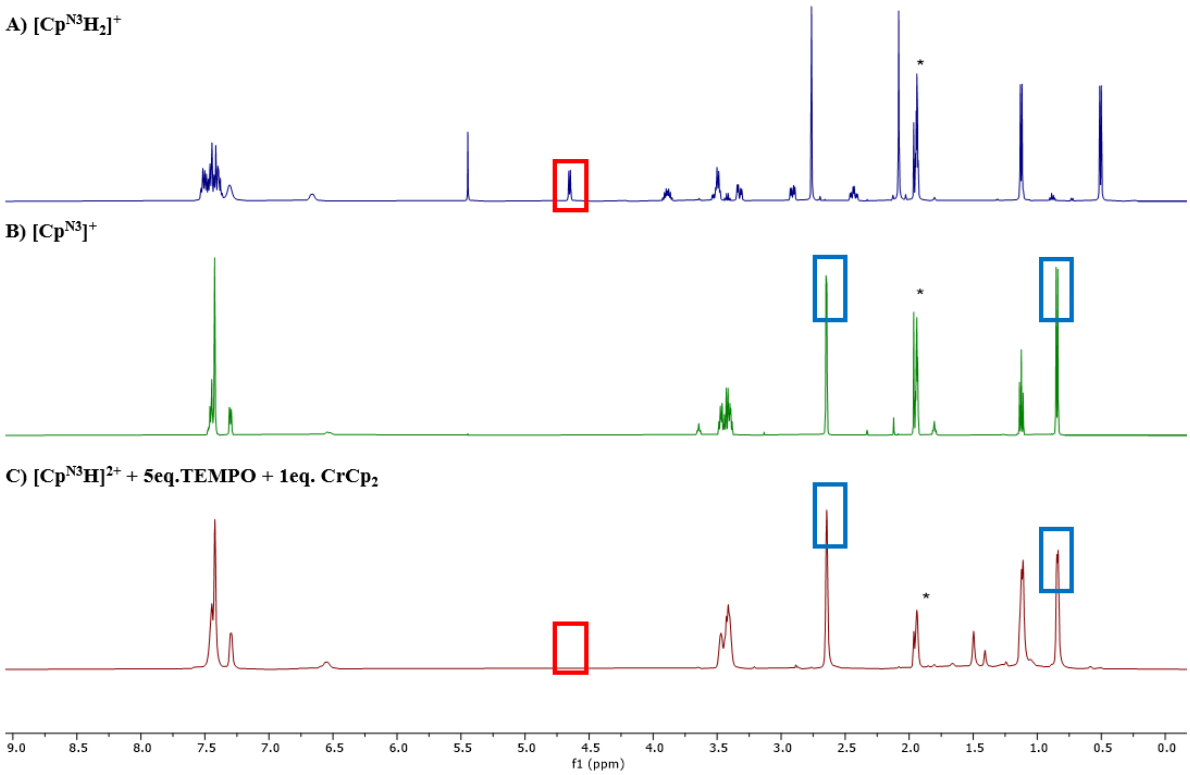


Figure S16. Stacked ^{1}H NMR spectra of A) **[4][BF$_4$]**, B) **[Cp^{N3}]$^+$** and C) **[4][BF$_4$]$_2$** after reacting with 5 equiv. TEMPO and 1 equiv. chromocene. The peaks highlighted in blue boxes show that **[Cp^{N3}]$^+$** is formed in the reaction while the red boxes highlight the absence of a diagnostic C-H resonance for **[5][BF$_4$]$_2$**. The signal at 1.12ppm in all three spectra is for diethyl ether and the signal at 5.5ppm in spectrum A is for residual DCM. The NMR solvent (CD_3CN) is shown with an asterisk.

Electrochemistry

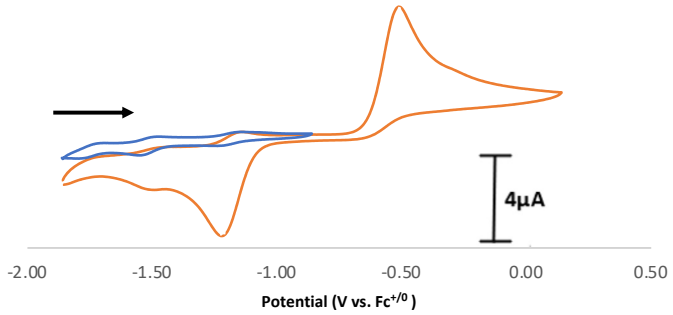


Figure S17**.** Cyclic voltammograms of **1** with scan direction switching after the first oxidation (orange) and scan direction switching before the first oxidation (blue) at 800 mV/s. The small redox waves -1.50 and -1.25 V are likely impurities. Conditions: Ar, MeCN solvent, 0.1 M $[Bu_4N][PF_6]$, 1.0 mM analyte, PEEK-encased glassy carbon working electrode, Type 2 glassy carbon rod counter electrode, Ag/AgCl pseudoreference electrode in a frit-separated (CoralPor) glass compartment containing solvent and electrolyte. Initial scan direction and starting position indicated with arrows.

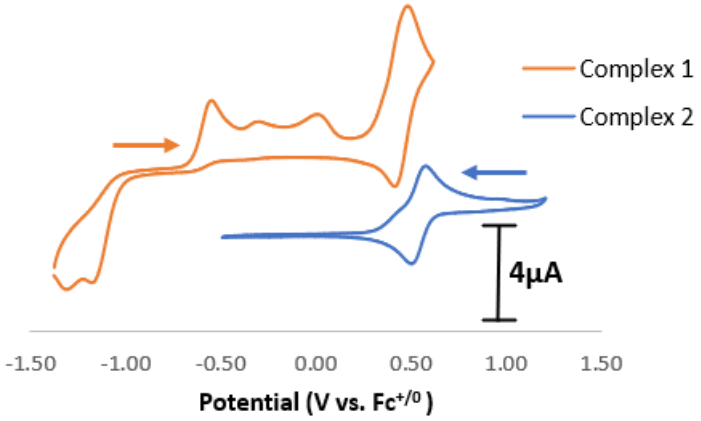


Figure S18**.** Cyclic voltammograms of **1** and **2** at 100 mV/s. Conditions: Ar, MeCN solvent, 0.1 M $[Bu_4N][PF_6]$, 1.0 mM analyte, PEEK-encased glassy carbon working electrode, Type 2 glassy carbon rod counter electrode, Ag/AgCl pseudoreference electrode in a frit-separated (CoralPor) glass compartment containing solvent and electrolyte. Initial scan direction and starting position indicated with arrows.

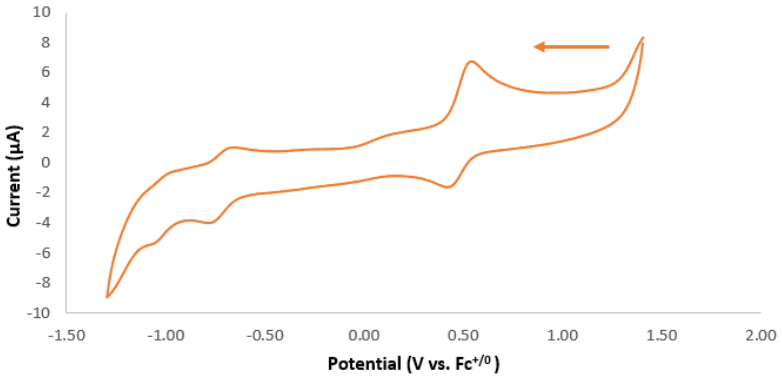


Figure S19. Cyclic voltammograms of **2** at 800 mV/s in the cathodic direction. Conditions: Ar, MeCN solvent, 0.1 M [Bu_4N][PF_6], 1.0 mM analyte, PEEK-encased glassy carbon working electrode, Type 2 glassy carbon rod counter electrode, Ag/AgCl pseudoreference electrode in a frit-separated (CoralPor) glass compartment containing solvent and electrolyte. Initial scan direction and starting position indicated with arrows.

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