Supporting Information for:

# Metal- versus Ligand-Centered Reactivity of a Cobalt-Phenylenediamide Complex with Electrophiles

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## Experimental Details

**General Considerations.** All reactions were performed under anaerobic and anhydrous conditions using a Vacuum Atmospheres glovebox or Schlenk techniques unless otherwise specified. All solvents were dried using a Pure Process Technology Solvent Purification System and/or activated 3Å molecular sieves. Acetonitrile (MeCN), tetrahydrofuran (THF), diethyl ether ($Et_2O$), benzene, pentane, and hexanes were also degassed on a high-vacuum Schlenk line with at least three freeze-pump-thaw cycles and stored in a $N_2$-filled glovebox. Deuterated solvents were purchased from Cambridge Isotope Labs or ACROS Organics. $CDCl_3$ and $CD_2Cl_2$ were used as received; $CD_3CN$ and $C_6D_6$ were degassed and stored over 3Å molecular sieves under $N_2$ unless otherwise noted.

5-(Trifluoromethyl)-5H-dibenzo[b,d]thiophen-5-ium trifluoromethanesulfonate ([DBT–$CF_3$]OTf) was purchased from Ambeed, Inc. and used as received. Methyl triflate, ethyl triflate, and potassium bromide (KBr) were purchased from Fisher Scientific, Sigma-Aldrich, or TCI Chemicals and used as received. Bis(pentamethylcyclopentadienyl)iron(II) ($Cp^*_2Fe$), cobaltocene ($Cp_2Co$), and bis(pentamethylcyclopentadienyl)cobalt(II) ($Cp^*_2Co$) were purchased from Sigma-Aldrich and sublimed under vacuum prior to use. Ferrocene (Fc) was purchased from Sigma-Aldrich and recrystallized from hexanes prior to use. Tetra-*n*-butylammonium hexafluorophosphate ([$^n$Bu$_4$N][$PF_6$]) was purchased from Sigma-Aldrich, recrystallized from ethanol, and dried under vacuum for at least 48 h prior to use. [CpCo($^t$BuUreaopda)] **1** was synthesized according to literature procedure.[1]

All NMR spectra were collected at 25°C unless otherwise noted. $^1$H and $^{13}$C{$^1$H} NMR spectra were recorded using Bruker 500 MHz NMR spectrometer. The chemical shifts of $^1$H, $^{13}$C nuclei are reported in ppm and referenced to the residual solvent peaks ($^1$H NMR) or the characteristic resonances of the solvent nuclei ($^{13}$C{$^1$H} NMR) as internal standards. All $^{19}$F NMR spectra were referenced to fluorobenzene ($\delta$ = –113.15 ppm). Electronic absorption spectra were recorded on an Agilent Cary 60 UV-vis spectrophotometer with Cary WinUV software using a 1 cm path length quartz cuvette. Infrared (IR) spectra were recorded on a Bruker Vertex 80 FT-IR spectrometer with a liquid nitrogen cooled MCT detector. High resolution mass spectra (HRMS) were collected using an electrospray ionization (ESI) source on positive ion mode with a Xevo™ G2-XS QTof or SYNAPT G2-SI qTOF mass spectrometer. Continuous wave EPR spectra were recorded at ambient temperature on an X-band Bruker EMXPlus spectrometer equipped with an EMX standard resonator and a Bruker PremiumX microwave bridge. The spectra were simulated using EasySpin for MATLAB.[2]

**Electrochemistry.** Cyclic voltammetry (CV) studies were performed using a BASi Epsilon EClipse potentiostat, and the data were processed using BASi Epsilon-EC software (version 2.13.77). All experiments were performed under $N_2$ in a 20 mL glass vial with a glassy carbon (GC) working electrode (3 mm diameter, BASi), Pt wire counter electrode, and Ag/$AgNO_3$ reference electrode. The GC electrode was polished with alumina (0.05 µm, BASi) prior to use. All potentials are referenced to the $Fc^{+/0}$ couple using ferrocene (Fc) as an internal standard.

**Spectroelectrochemistry (SEC).** Spectroelectrochemistry (SEC) data were recorded on an Agilent Cary 60 UV-vis spectrophotometer using a Specac® Omni Cell with PTFE spacer (ca. 0.2 mm) under $N_2$. Sample solutions were prepared in MeCN with [$^n$Bu$_4$N][$PF_6$] (0.2 M) and cobalt complex (4 mM). The Pt mesh working electrode, Pt mesh counter electrode, and Ag wire pseudo-reference electrode (BioLogic) were placed in the thin-layer solution. The Pt electrodes were cleaned with $HNO_3$ prior to use. SEC was carried out using linear sweep voltammetry at 1 mV/s while acquiring UV-vis spectra from 1000-200 nm at fast scan rate (4800 nm/min).

**X-ray Crystallography.** Single crystal X-ray diffraction (SC-XRD) frames were collected on either a Bruker Smart APEX diffractometer equipped with a CCD area detector using graphite monochromatized Mo/Kα radiation ($\lambda$ = 0.71073 Å) or a Rigaku XTALab Synergy-S single crystal diffractometer equipped with a HyPix-6000HE area detector (hybrid photon counting) using a Kappa 4-circle goniometer with a Cu/Kα radiation ($\lambda$ = 1.54184 Å). Crystals were mounted on a cryo-loop under a mixture of paraffin and Paratone-N oil, and all data were collected at 100 K (or 120 K for **8**) using a Kryoflex low temperature device (Bruker) or an Oxford nitrogen gas 800 Series cryostream system (Rigaku). The X-ray data were corrected for Lorenz effects and polarization. Multi-scan or Gaussian absorption correction was applied in the SADABS[3] or CrysAlisPRO[4] program. The structures were solved by an intrinsic phasing method with SHELXT.[5] All non-hydrogen atoms were refined with SHELXL[6] based on $F_{obs}^2$. All hydrogen atom coordinates were calculated with idealized geometries. Scattering factors ($f_o$, f', f'') are as described in SHELXL. Additional crystallographic data and final R indices are given in Tables S1-S3. All structures have been deposited into the Cambridge Structural Database (CCDC 2294060-2294065 and 2294086).

**Computational Details.** All calculations were performed within the Gaussian 16 Revision A.03 package[7] using the def2-TZVPP basis set for Co, the def2-TZVP or def2-TZVPD basis set for O, and the def2-TZVP basis set for all other atoms.[8] Initial geometry for optimization was obtained from the coordinates of the crystal structures (except **2** where the geometry is largely affected by the presence of triflates). The ground-state structure was optimized in the gas phase on an ultrafine grid with the opt = tight keyword. Harmonic vibrational frequency calculations were performed to ensure no imaginary frequencies were present for the optimized structures. Solvation free energies were computed at the same level of theory with the universal continuum solvation model (SMD) for acetonitrile. Spin density diagrams and MO pictures were visualized on a grid of $80^3$ points within GaussView 6.0.16 at an isovalue of 0.005 and 0.04, respectively. The Cartesian coordinates, electronic energies, and Gibbs free energies in the gas phase and in MeCN solution (in Hartree) for relevant cobalt complexes can be found at the end of the DFT Computational Results.

## Synthesis and Characterization

**[CpCo($^{t\text{BuUrea}}$bqdi)($CF_3$)]OTf (2).** An oven-dried 20 mL vial with a stir bar was charged with **1** (43 mg, 0.10 mmol), [DBT−$CF_3$]OTf (81 mg, 0.20 mmol), and dry MeCN (6 mL). The red mixture was stirred for 2 days, and the solvent was removed under vacuum. The red solid residue was extracted into benzene and filtered through a Celite column. The red filtrate was then added onto a silica gel pipette column, where dibenzothiophene was removed with benzene, and the red fraction was collected using $Et_2O$/MeCN as the eluent. The intense red solid was recrystallized via layering hexanes (ca. 18 mL) upon a red THF/$Et_2O$ solution (1:1, 4 mL) at –35°C. Isolated yield: 60 mg, 92%. Dark red block single crystals suitable for X-ray diffraction were obtained via layering hexanes upon a cobalt solution in THF at –35°C.

$^1$H NMR ($CD_3CN$, 25°C, 500 MHz) $\delta$ (ppm): 6.92 (br s, 6H, N-*H* and Ar-*H* overlapping), 5.81 (br s, 5H, $C_5H_5$), 1.50 (s, 18H, $CH_3$). $^1$H NMR ($C_6D_6$, 25°C, 500 MHz) $\delta$ (ppm): 8.25 (s, 2H, N-*H*), 6.57-6.53 (m, 2H, Ar-*H*), 5.83-5.80 (m, 2H, Ar-*H*), 5.38 (s, 5H, $C_5H_5$), 1.42 (s, 18H, $CH_3$). $^{13}$C{$^1$H} NMR ($C_6D_6$, 25°C, 126 MHz) $\delta$ (ppm): 167.5 (*C*=O), 156.4 ($C_{arom}$N), 134.4 and 119.3 ($C_{arom}$H), 93.8 ($C_5H_5$), 53.4 ($C(CH_3)_3$), 28.4 ($CH_3$). $^{19}$F NMR ($C_6D_6$, 25°C, 471 MHz) $\delta$ (ppm): -11.45 (s, 3F, $CF_3$), -78.26 (s, 3F, $SO_3CF_3$). UV-vis (MeCN, $M^{-1}\cdot cm^{-1}$): 245 nm ($\varepsilon$ = 18,950), 285 nm (sh, $\varepsilon$ = 6,560), 439 nm ($\varepsilon$ = 6,050), 536 nm (sh, $\varepsilon$ = 4,140). FT-IR (KBr pellet, $cm^{-1}$): 3430 (w), 3269 (m), 3118 (w), 3033 (w), 2976 (m), 2939 (w), 1731 (s), 1656 (w), 1610 (w), 1526 (s), 1477 (w), 1461 (m), 1426 (m), 1398 (m), 1370 (m), 1268 (s, br), 1245 (s), 1225 (s), 1167 (s), 1073 (s), 1031 (s, br), 988 (m), 887 (m), 849 (m), 834 (m), 797 (w), 765 (m), 739 (w), 713 (w). HRMS: Calcd for $C_{22}H_{29}CoF_3N_4O_2$ ([**2** – OTf]$^+$): *m/z* 497.1575. Found: *m/z* 497.1529.

**[CpCo($^{t\text{BuUrea}}$s-bqdi)($CF_3$)] (3).** An oven-dried 20 mL vial with a stir bar was charged with **2** (33.5 mg, 52 µmol), bis(pentamethylcyclopentadienyl)iron(II) ($Cp^*_2Fe$, sublimed, 16.5 mg, 51 µmol), and dry MeCN (4 mL). A dark red mixture formed and stirred for 20 min, and the solvent was removed under vacuum. The product was extracted into hexanes (at least 10 × 2 mL). The purple solution was filtered through a Celite column and evaporated under vacuum. Further purification was performed by slow $Et_2O$ evaporation recrystallization at –35°C. Isolated yield: 19 mg, 75%. Dark plate single crystals suitable for X-ray diffraction were obtained via slow evaporation of a concentrated cobalt solution in pentane at –35°C.

UV-vis (MeCN, $M^{-1}\cdot cm^{-1}$): 245 nm (sh, $\varepsilon$ = 18,700), 304 nm ($\varepsilon$ = 7,270), 383 nm ($\varepsilon$ = 5,990), 510 nm (sh, $\varepsilon$ = 2,770), 568 nm ($\varepsilon$ = 3,100), 780 nm (sh, $\varepsilon$ = 750), 864 nm ($\varepsilon$ = 1,040), 978 nm ($\varepsilon$ = 1,000). FT-IR (KBr pellet, $cm^{-1}$): 3442 (s), 3121 (w), 3046 (w), 2967 (s), 2932 (m), 2905 (m), 1672 (s), 1634 (w), 1580 (w), 1532 (m), 1499 (s), 1451 (s), 1395 (m), 1366 (s), 1344 (m), 1335 (m), 1269 (s), 1249 (s), 1225 (m), 1199 (s), 1172 (m), 1145 (s), 1081 (s), 1050 (s), 1011 (s), 968 (s), 891 (w), 871 (m), 838 (m), 827 (m), 773 (w), 755 (s), 743 (m), 701 (w). HRMS: Calcd for $C_{22}H_{29}CoF_3N_4O_2$ ([**3**]$^+$): *m/z* 497.1575. Found: *m/z* 497.1483. Effective Magnetic Moment: $\mu_{eff}$ = 1.75 µB (Evans method).

**[CpCo($^{t}$BuUrea$^{}$opda)(CF$_3$)][Cp$_2$Co] (4).** An oven-dried 20 mL vial with a stir bar was charged with **3** (16 mg, 32 µmol, 1.0 equiv.) and dry benzene (3 mL). Sublimed cobaltocene (Cp$_2$Co, 7 mg, 37 µmol, 1.1 equiv.) was added as a solid. The dark purple mixture turned dark brown quickly and was stirred for another 15 min. Volatile solvent and excess cobaltocene were removed under vacuum. A dark brown powder was washed with hexanes (3 × 2 mL) and dried under vacuum. Isolated yield: 18 mg, 82%. Red-brown plate single crystals suitable for X-ray diffraction were obtained via slow vapor diffusion of pentane into a cobalt solution in THF at –35°C.

$^1$H NMR (C$_6$D$_6$, 25°C, 500 MHz) $\delta$ (ppm): 9.11-9.08 (m, 2H, Ar-*H*), 6.81-6.78 (m, 2H, Ar-*H*), 5.21 (s, 2H, N-*H*), 5.06 (s, 5H, C$_5$*H*$_5$), 4.59 (s, br, 10H, C$_5$*H*$_5$), 1.66 (s, 18H, C*H*$_3$). $^{13}$C{$^1$H} NMR (C$_6$D$_6$, 25°C, 126 MHz) $\delta$ (ppm): 165.4 (*C*=O), 153.9 (*C*$_{arom}$N), 123.1 and 117.3 (*C*$_{arom}$H), 87.3 (*C*$_5$H$_5$), 84.4 (br, *C*$_5$H$_5$, cobaltocenium), 50.2 (*C*(CH$_3$)$_3$), 29.9 (*C*H$_3$). $^{19}$F NMR (C$_6$D$_6$, 25°C, 471 MHz) $\delta$ (ppm): -2.52 (s, 3F, C*F*$_3$). UV-vis (MeCN, M$^{-1}$·cm$^{-1}$): 292 nm ($\varepsilon$ = 17,000), 387 nm ($\varepsilon$ = 1,500), 510 nm ($\varepsilon$ = 760). FT-IR (KBr pellet, cm$^{-1}$): 3936 (w), 3465 (m), 3100 (m), 2961 (m), 2915 (m), 1606 (s), 1560 (m), 1476 (s), 1447 (s), 1416 (m), 1386 (m), 1359 (m), 1331 (m), 1297 (s), 1249 (s), 1192 (s), 1070 (s), 994 (s), 865 (m), 849 (m), 807 (m), 754 (m), 701 (w). HRMS: Calcd for C$_{22}$H$_{29}$CoF$_3$N$_4$O$_2$ ([**4** – Cp$_2$Co]$^+$): *m/z* 497.1575. Found: *m/z* 497.1631.

**[CpCo($^{t}$Bu-NH$^{OMe}$)][OTf]$_2$ (5).** An oven-dried 20 mL vial with a stir bar was charged with **1** (10.0 mg, 23 µmol) and dry Et$_2$O (6 mL). To the dark purple suspension was added dropwise MeOTf (15.5 µL, 142 µmol). The mixture turned deep blue within 30 min and was stirred overnight under N$_2$ atmosphere. Hexanes (6 mL) was added to the resulting light blue suspension to further precipitate the product. The dark blue precipitate was filtered upon a pipette Celite column, washed with hexanes (3 × 2 mL), and recrystallized from CH$_2$Cl$_2$/hexanes (1:10) at –25°C. A dark blue crystalline solid was obtained and stored under N$_2$. Isolated yield: 16.6 mg, 94%. Deep blue block single crystals suitable for X-ray diffraction were obtained via slow vapor diffusion of pentane into a dilute cobalt solution in THF at –35°C under N$_2$.

$^1$H NMR (CD$_2$Cl$_2$, 25°C, 500 MHz) $\delta$ (ppm): 11.61 and 10.77 (*syn-isomer*) (br s, 2H, N-*H*), 7.33-7.31 (m, 2H, Ar-*H*), 6.77-6.75 (m, 2H, Ar-*H*), 5.59 and 5.58 (*syn-isomer*) (s, 5H, C$_5$*H*$_5$), 4.58 (*syn-isomer*) and 4.24 (br s, 6H, OC*H*$_3$), 1.83 (s, 18H, C*H*$_3$). $^{13}$C{$^1$H} NMR (CD$_2$Cl$_2$, 25°C, 126 MHz) $\delta$ (ppm): 174.1 (*C*=NH), 142.7 (*C*$_{arom}$N), 124.4 and 114.6 (CaromH), 120.8 (q, JC,F = 316.0 Hz, SO3CF3), 80.3 (C5H5), 62.0 (OCH3), 58.4 (C(CH3)3), 28.6 (CH3). 1H NMR (CDCl3, –25°C, 500 MHz) δ (ppm): 11.68 and 10.93 (syn-isomer) (s, 2H, N-*H*), 7.28-7.26 (m, 2H, Ar-*H*, *overlapping with CHCl*$_3$), 6.71-6.69 (m, 2H, Ar-*H*), 5.59 and 5.57 (*syn-isomer*) (s, 5H, C$_5$*H*$_5$), 4.59 (*syn-isomer*) and 4.19 (s, 6H, OC*H*$_3$), 1.85 and 1.79 (*syn-isomer*) (s, 18H, C*H*$_3$). $^{13}$C{$^1$H} NMR (CDCl$_3$, –25°C, 126 MHz) $\delta$ (ppm): 173.6 (*C*=NH), 141.8 (*C*$_{arom}$N), 124.4 and 114.3 (*C*$_{arom}$H), 119.9 (q, $J_{C,F}$ = 318.9 Hz, SO$_3$*C*F$_3$), 79.9 (*C*$_5$H$_5$), 61.6 (O*C*H$_3$), 57.9 (*C*(CH$_3$)$_3$), 28.5 (*C*H$_3$). *Syn-isomer*: 173.9 (*C*=NH), 142.4 (*C*$_{arom}$N), 113.9 (*C*$_{arom}$H), 80.2 (*C*$_5$H$_5$), 62.1 (O*C*H$_3$), 57.7 (*C*(CH$_3$)$_3$), 28.3 (*C*H$_3$). HRMS: Calcd for C$_{23}$H$_{34}$CoN$_4$O$_2$ ([**5** – 2OTf – H$^+$]$^+$): *m/z*. 457.2014. Found: *m/z* 457.1989.

**[CpCo($^t$Bu-NH$^{OEt}$)][OTf]$_2$ (6).** The same procedure to prepare complex **5** was followed here, except ethyl triflate was used in place of methyl triflate. A dark blue crystalline solid was obtained and stored under $N_2$. Isolated yield: 18.7 mg, 87%. Dark blue block single crystals suitable for X-ray diffraction were obtained via slow vapor diffusion of pentane into a cobalt solution in THF at –35 °C under $N_2$.

$^1$H NMR ($CDCl_3$, –25°C, 500 MHz) $\delta$ (ppm): 11.50 and 10.71 (*syn-isomer*) (s, 2H, N-*H*), 7.28-7.24 (m, 2H, Ar-*H*, *overlapping with CHCl$_3$*), 6.73-6.70 (m, 2H, Ar-*H*), 5.55 and 5.54 (*syn-isomer*) (s, 5H, $C_5H_5$), 5.43 (*syn-isomer*) and 4.92 (dq, $^3J$ = 7.0 Hz, $^2J$ = 10.7 Hz, 2H, OCH($H_a$)$CH_3$) 4.80 (*syn-isomer*) and 4.14 (dq, $^2J$ = 10.7 Hz, $^3J$ = 7.0 Hz, 2H, OCH($H_b$)$CH_3$), 1.85 and 1.78 (*syn-isomer*) (s, 18H, C($CH_3$)$_3$), 1.66 (*syn-isomer*) and 1.54 (t, $^3J$ = 7.0 Hz, 6H, $OCH_2CH_3$). $^{13}$C{$^1$H} NMR ($CDCl_3$, –25°C, 126 MHz) $\delta$ (ppm): 172.78 (*C*=NH), 142.16 ($C_{arom}$N), 124.20 and 114.20 ($C_{arom}$H), 119.94 (q, $J_{C,F}$ = 319.1 Hz, $SO_3CF_3$), 79.74 ($C_5H_5$), 72.95 ($OCH_2CH_3$), 57.66 ($C(CH_3)_3$), 28.44 (C($CH_3$)$_3$), 14.98 ($OCH_2CH_3$). *Syn-isomer*: 173.18 (*C*=NH), 143.09 ($C_{arom}$N), 124.25 and 113.91 ($C_{arom}$H), 80.02 ($C_5H_5$), 73.57 ($OCH_2CH_3$), 57.44 ($C(CH_3)_3$), 28.28 (C($CH_3$)$_3$), 15.31 ($OCH_2CH_3$). HRMS: Calcd for $C_{25}H_{38}CoN_4O_2$ ([**6** – 2OTf – $H^+$]$^+$): *m/z*. 485.2327. Found: *m/z* 485.2364.

## X-ray Data and Structures

### X-ray Crystallographic Data

**Table S1.** Crystal data and structure refinement for **2**, **3**, and **4**.

| | **2** | **3** | **4** |
|---|---|---|---|
| CCDC Number | 2294060 | 2294061 | 2294062 |
| Empirical formula | $C_{23}H_{29}CoF_6N_4O_5S$ | $C_{22}H_{29}CoF_3N_4O_2$ | $C_{32}H_{39}Co_2F_3N_4O_2$ |
| Formula weight | 646.49 | 497.42 | 686.53 |
| Temperature (K) | 100(2) | 100(2) | 100(2) |
| Wavelength (Å) | 1.54184 | 1.54184 | 1.54184 |
| Crystal shape, color | Block, dark red | Plate, black | Plate, red-brown |
| Crystal size ($mm^3$) | 0.08 × 0.06 × 0.03 | 0.25 × 0.14 × 0.02 | 0.10 × 0.07 × 0.02 |
| Crystal system | Monoclinic | Monoclinic | Orthorhombic |
| Space group | P21/c | P21/n | Pbcn |
| a (Å) | 11.22710(10) | 13.6398(3) | 30.7337(6) |
| b (Å) | 26.3205(4) | 11.7221(2) | 12.0988(2) |
| c (Å) | 19.3546(2) | 14.7206(3) | 17.2692(2) |
| α (deg) | 90 | 90 | 90 |
| β (deg) | 94.8390(10) | 98.940(2) | 90 |
| γ (deg) | 90 | 90 | 90 |
| Volume ($Å^3$) | 5698.95(12) | 2325.04(8) | 6421.40(18) |
| Z | 8 | 4 | 8 |
| Density (calculated) ($Mg/m^3$) | 1.507 | 1.421 | 1.420 |
| Absorption coefficient ($mm^{-1}$) | 6.128 | 6.226 | 8.534 |
| Max. and min transmission | 0.902 and 0.659 | 1.000 and 0.6076 | 1.000 and 0.6773 |
| F(000) | 2656 | 1036 | 2848 |
| Reflections collected | 76340 | 20895 | 31900 |
| Independent reflections | 10817 | 4308 | 5940 |
| Completeness to θ = 67.684° | 100.0% | 100.0% | 99.9% |
| Restraints / parameters | 480 / 733 | 0 / 295 | 0 / 398 |
| R(int) | 0.0691 | 0.0655 | 0.0481 |
| Final R indices [$I > 2\sigma(I)$] | R1 = 0.0462<br>wR2 = 0.1206 | R1 = 0.0459<br>wR2 = 0.1176 | R1 = 0.0438<br>wR2 = 0.1083 |
| Largest diff. peak and hole (e $Å^{-3}$) | 0.701 and -0.571 | 0.630 and -0.557 | 0.687 and -0.391 |
| Goodness-of-fit on $F^2$ | 1.078 | 1.018 | 1.041 |

**Table S2.** Crystal data and structure refinement for the *trans*-isomer of **5** and **6**.

| | **5·THF** | **6·2Pentane** |
|---|---|---|
| CCDC Number | 2294063 | 2294086 |
| Empirical formula | $C_{29}H_{43}CoF_6N_4O_9S_2$ | $C_{37}H_{63}CoF_6N_4O_8S_2$ |
| Formula weight | 828.72 | 928.96 |
| Temperature (K) | 100(2) | 100(2) |
| Wavelength (Å) | 1.54184 | 1.54184 |
| Crystal shape, color | Plate, dark blue | Block, dark blue |
| Crystal size ($mm^3$) | 0.08 × 0.06 × 0.02 | 0.26 × 0.10 × 0.07 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | $P2_1/n$ | P2/c |
| *a* (Å) | 15.1203(3) | 13.3154(7) |
| *b* (Å) | 10.1625(5) | 10.2609(3) |
| *c* (Å) | 24.1368(6) | 15.6925(7) |
| *α* (deg) | 90 | 90 |
| *β* (deg) | 92.2917(19) | 106.217(5) |
| *γ* (deg) | 90 | 90 |
| Volume ($Å^3$) | 3705.9(2) | 2058.73(16) |
| Z | 4 | 2 |
| Density (calculated) ($Mg/m^3$) | 1.485 | 1.499 |
| Absorption coefficient ($mm^{-1}$) | 5.439 | 4.937 |
| Max. and min transmission | 1.000 and 0.885 | 1.000 and 0.530 |
| F(000) | 1720 | 980 |
| Reflections collected | 38802 | 19120 |
| Independent reflections | 6762 | 3783 |
| Data completeness | 99.2% | 97.8% |
| Restraints / parameters | 234 / 504 | 1402 / 466 |
| R(int) | 0.1082 | 0.0755 |
| Final R indices [$I > 2\sigma(I)$] | $R_1$ = 0.0768<br>$wR_2$ = 0.2102 | $R_1$ = 0.0907<br>$wR_2$ = 0.2310 |
| Largest diff. peak and hole (e $Å^{-3}$) | 1.462 and -0.560 | 0.445 and -0.721 |
| Goodness-of-fit on $F^2$ | 1.065 | 1.074 |

**Table S3.** Crystal data and structure refinement for **7** and **8**.

| | **7·THF·Pentane** | **8·Et$_2$O** |
|---|---|---|
| CCDC Number | 2294065 | 2294064 |
| Empirical formula | $C_{51}H_{88}CoF_6N_8O_{11}S_2$ | $C_{76}H_{118}Co_3N_8O_5$ |
| Formula weight | 1226.34 | 1400.57 |
| Temperature (K) | 100(2) | 120(2) |
| Wavelength (Å) | 1.54184 | 0.71073 |
| Crystal shape, color | Block, blue | Block, red |
| Crystal size (mm$^3$) | 0.24 × 0.07 × 0.07 | 0.31 × 0.25 × 0.23 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | P2$_1$/n | P2$_1$/n |
| *a* (Å) | 13.13930(10) | 13.9962(13) |
| *b* (Å) | 18.02370(10) | 24.752(2) |
| *c* (Å) | 27.0667(2) | 21.489(2) |
| *α* (deg) | 90 | 90 |
| *β* (deg) | 99.1800(10) | 92.974(3) |
| *γ* (deg) | 90 | 90 |
| Volume (Å$^3$) | 6327.81(8) | 7434.6(12) |
| Z | 4 | 4 |
| Density (calculated) (Mg/m$^3$) | 1.287 | 1.251 |
| Absorption coefficient (mm$^{-1}$) | 3.394 | 0.715 |
| Max. and min transmission | 1.000 and 0.543 | 0.7459 and 0.6933 |
| F(000) | 2604 | 3004 |
| Reflections collected | 88730 | 65920 |
| Independent reflections | 11792 | 20123 |
| Data completeness | 100.0%<br>(θ = 67.684°) | 100.0%<br>(θ = 25.242°) |
| Restraints / parameters | 2232 / 941 | 1400 / 857 |
| R(int) | 0.0419 | 0.0500 |
| Final R indices [I > 2σ(I)] | $R_1$ = 0.0472<br>$wR_2$ = 0.1339 | $R_1$ = 0.0527<br>$wR_2$ = 0.1214 |
| Largest diff. peak and hole (e Å$^{-3}$) | 0.874 and -0.523 | 0.987 and -0.645 |
| Goodness-of-fit on F$^2$ | 1.002 | 1.040 |

**X-ray Structures**

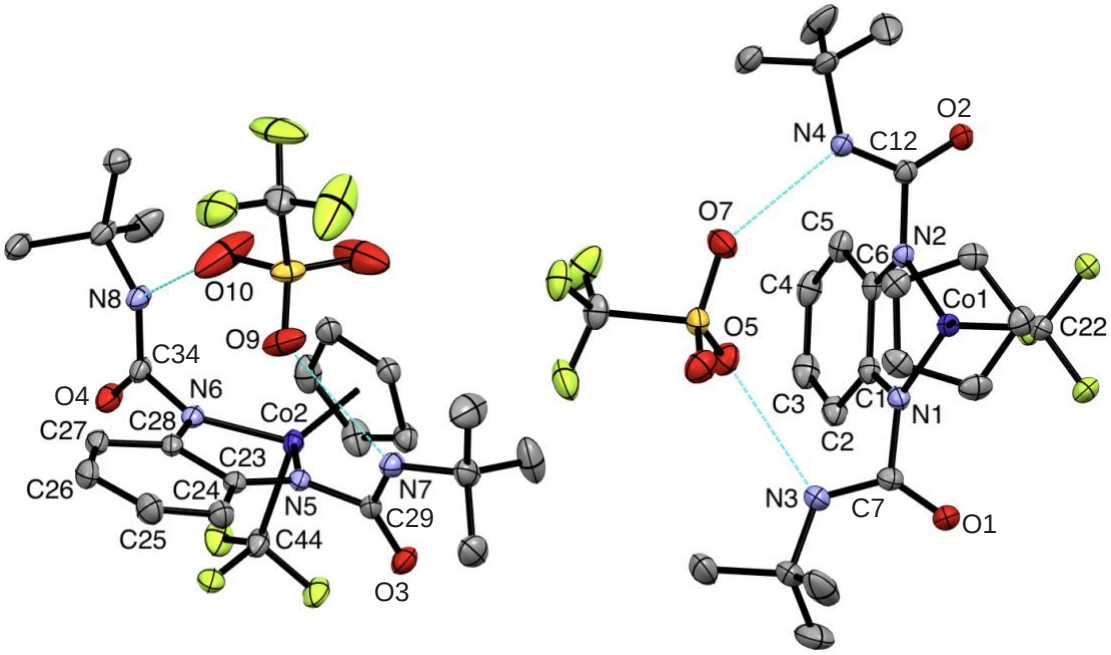



**Figure S1.** Single crystal X-ray structure of **2** shown with 30% probability ellipsoids. Intermolecular hydrogen bonding is shown between O5 and N3, O7 and N4, O9 and N7, O10 and N8 atoms. All hydrogen atoms are omitted for clarity. Selected bond distances (Å): Co1–$Cp_{centroid}$ = 1.686; Co2–$Cp_{centroid}$ = 1.690; Co1–N1 = 1.907(2); Co1–N2 = 1.893(2); Co2–N5 = 1.893(2); Co2–N6 = 1.892(2); Co1–C22 = 1.953(3); Co2–C44 = 1.964(3); N1–C1 = 1.309(4); N2–C6 = 1.313(4); N5–C23 = 1.311(3); N6–C28 = 1.306(4); C1–C2 = 1.438(4); C1–C6 = 1.465(4); C2–C3 = 1.346(5); C3–C4 = 1.439(5); C4–C5 = 1.351(5); C5–C6 = 1.434(4); C23–C24 = 1.429(4); C23–C28 = 1.465(4); C24–C25 = 1.353(4); C25–C26 = 1.450(5); C26–C27 = 1.334(5); C27–C28 = 1.435(4); O1–C7 = 1.208(3); N3–C7 = 1.334(4); O2–C12 = 1.210(3); N4–C12 = 1.331(3); O3–C29 = 1.214(3); N7–C29 = 1.320(3); O4–C34 = 1.212(4); N8–C34 = 1.332(3). Selected angles (°): N1–Co1–N2 = 82.15(10); N5–Co2–N6 = 82.27(9).

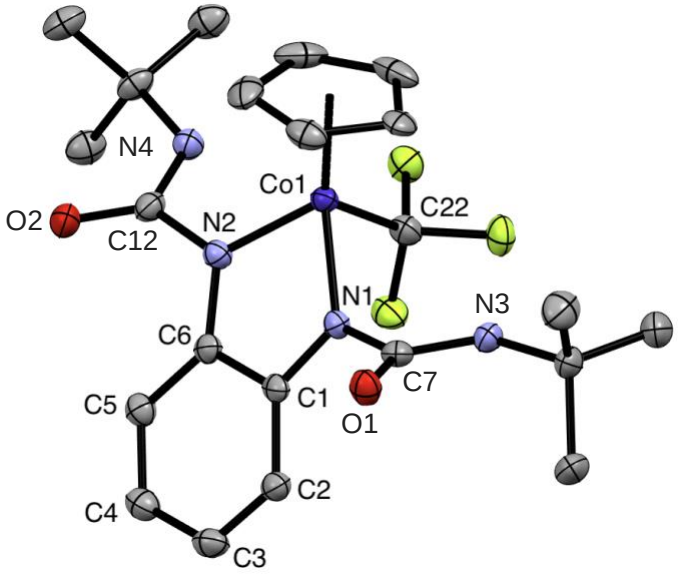



**Figure S2.** Single crystal X-ray structure of **3** shown with 50% probability ellipsoids. All hydrogen atoms are omitted for clarity. Selected bond distances (Å): Co1–$Cp_{centroid}$ = 1.716; Co1–N1 = 1.916(2); Co1–N2 = 1.931(2); Co1–C22 = 1.924(3); N1–C1 = 1.352(3); N2–C6 = 1.357(3); C1–C2 = 1.416(4); C1–C6 = 1.436(4); C2–C3 = 1.363(4); C3–C4 = 1.420(4); C4–C5 = 1.368(4); C5–C6 = 1.427(4); O1–C7 = 1.220(3); N3–C7 = 1.332(3); O2–C12 = 1.225(3); N4–C12 = 1.346(3). Selected angles (°): N1–Co1–N2 = 82.60(9).

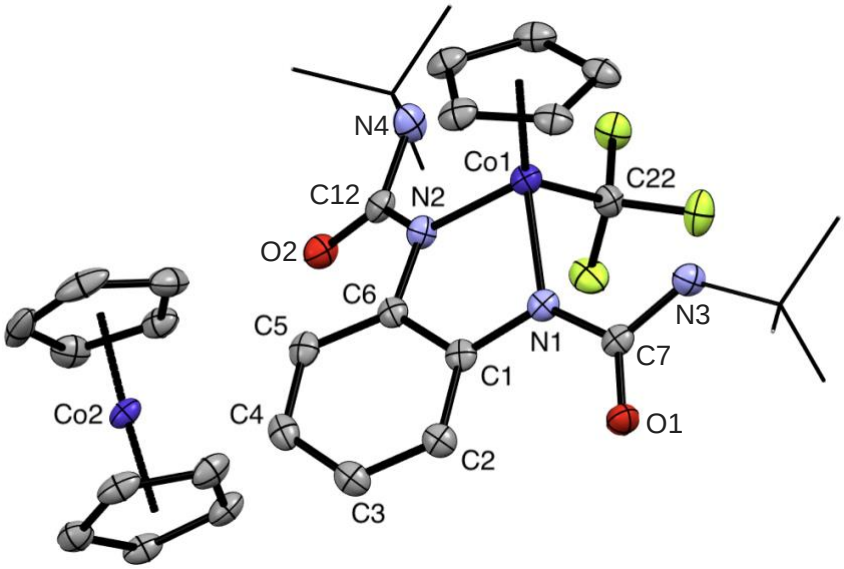



**Figure S3.** Single crystal X-ray structure of **4** shown with 30% probability ellipsoids. All hydrogen atoms are omitted and all *tert*-butyl groups are shown as capped sticks for clarity. Selected bond distances (Å): Co1–$Cp_{centroid}$ = 1.721; Co1–N1 = 1.964(2); Co1–N2 = 1.932(2); Co1–C22 = 1.940(3); N1–C1 = 1.409(4); N2–C6 = 1.405(4); C1–C2 = 1.404(4); C1–C6 = 1.421(4); C2–C3 = 1.392(4); C3–C4 = 1.387(4); C4–C5 = 1.389(4); C5–C6 = 1.400(4); O1–C7 = 1.234(3); N3–C7 = 1.373(4); O2–C12 = 1.236(4); N4–C12 = 1.379(4). Selected angles (°): N1–Co1–N2 = 83.83(10).

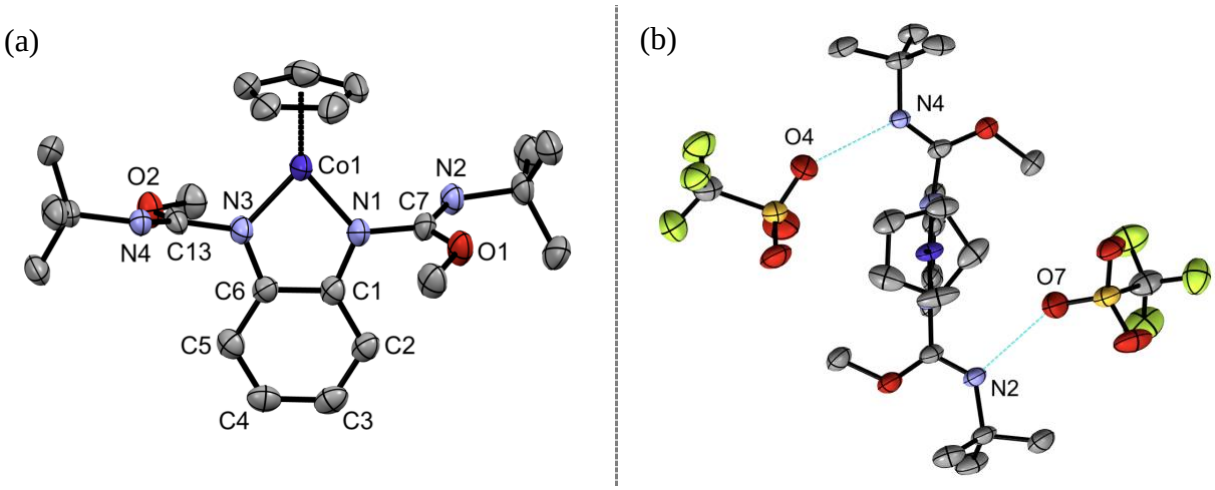



**Figure S4.** Single crystal X-ray structure of **5** shown with 50% probability ellipsoids: (a) *front view*, (b) *top view*. Intermolecular hydrogen bonding was shown between O4 and N4, O7 and N2 atoms. All hydrogen atoms and solvated THF (and triflate counterions in the *front view*) are omitted for clarity. Selected bond distances (Å): Co1–$Cp_{centroid}$ = 1.652; Co1–N1 = 1.868(4); Co1–N3 = 1.860(4); N1–C1 = 1.377(6); N3–C6 = 1.391(5); C1–C2 = 1.410(6); C1–C6 = 1.414(6); C2–C3 = 1.363(7); C3–C4 = 1.407(7); C4–C5 = 1.376(6); C5–C6 = 1.396(6); N1–C7 = 1.389(5); N3–C13 = 1.387(5); C7–N2 = 1.288(6); C13–N4 = 1.295(5); C7–O1 = 1.298(6); C13–O2 = 1.304(6). Selected angles (°): N1–Co1–N3 = 82.47(15); N1–C7–N2 = 119.7(4); N3–C13–N4 = 119.4(4); N1–C7–O1 = 122.2(4); N3–C13–O2 = 121.3(4); N2–C7–O1 = 118.1(4); N4–C13–O2 = 119.3(4).

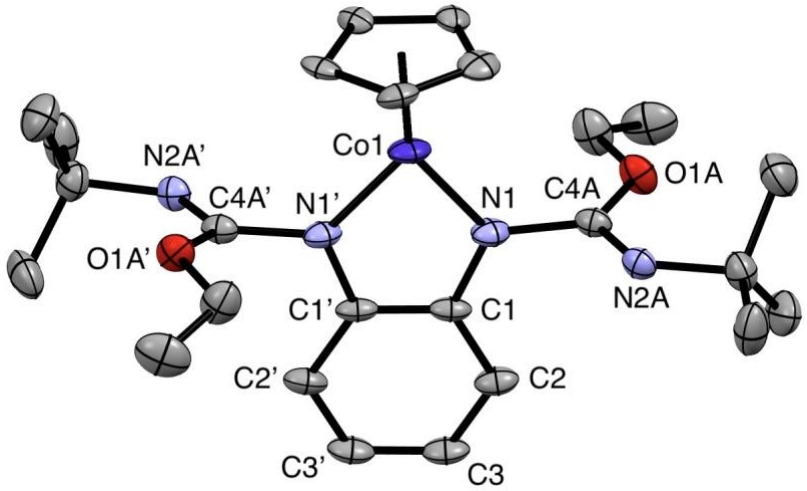



**Figure S5.** Single crystal X-ray structure of **6** shown with 20% probability ellipsoids. All hydrogen atoms, disordered triflate counterions, and solvated pentane are omitted for clarity. Selected bond distances (Å): Co1–$Cp_{centroid}$ = 1.658; Co1–N1 = 1.863(4); N1–C1 = 1.392(6); C1–C2 = 1.403(6); C1–C1' = 1.368(6); C2–C3 = 1.363(7); C3–C3' = 1.388(8); N1–C4A = 1.517(16); C4A–N2A = 1.286(14); C4A–O1A = 1.294(15). Selected angles (°): N1–Co1–N1' = 83.0(3); N1–C4A–N2A = 115.6(12); N1–C4A–O1A = 126.5(13); N2A–C4A–O1A 117.8(14).

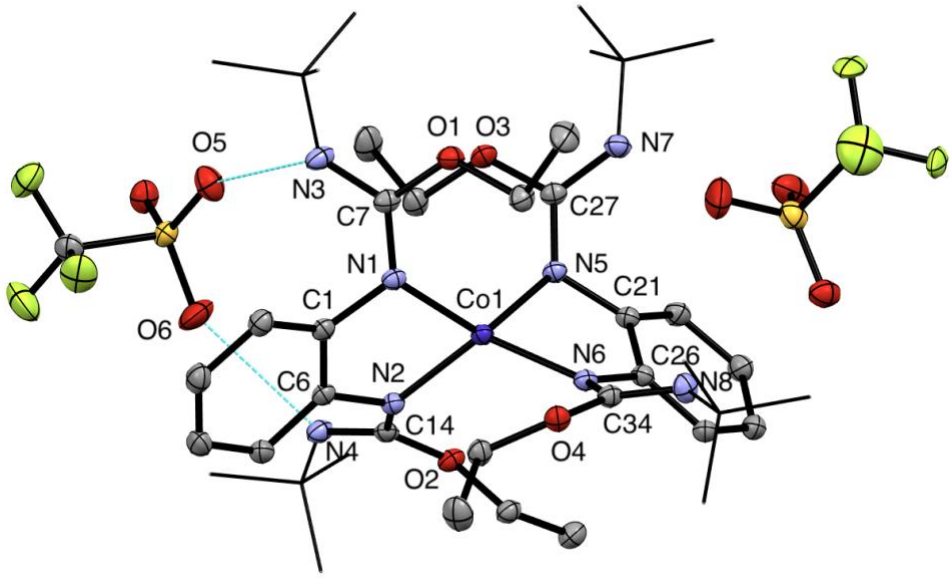



**Figure S6.** Single crystal X-ray structure of **7** shown with 30% probability ellipsoids. Intermolecular hydrogen bonding was shown between O5 and N3, O6 and N4 atoms. All hydrogen atoms, solvated THF and pentane are omitted and all *tert*-butyl groups are shown as capped sticks for clarity. Selected bond distances (Å): Co1–N1 = 2.0184(17); Co1–N2 = 1.9930(17); Co1–N5 = 2.0056(17); Co1–N6 = 1.9931(17); N1–C1 = 1.431(3); N2–C6 = 1.423(3); N5–C21 = 1.428(3); N6–C26 = 1.427(3); N1–C7 = 1.323(3); N2–C14 = 1.320(3); N5–C27 = 1.323(3); N6–C34 = 1.321(3); C7–N3 = 1.326(3); C14–N4 = 1.323(3); C27–N7 = 1.323(3); C34–N8 = 1.326(3); C7–O1 = 1.328(3); C14–O2 = 1.334(3); C27–O3 = 1.330(3); C34–O4 = 1.330(3). Selected angles (°): N1–Co1–N2 = 84.39(7); N5–Co1–N6 = 84.23(7); N1–C7–N3 = 124.98(19); N2–C14–N4 = 125.3(2); N5–C27–N7 = 124.98(19); N6–C34–N8 = 124.63(19); N1–C7–O1 = 120.87(19); N2–C14–O2 = 120.17(19); N5–C27–O3 = 120.22(18); N6–C34–O4 = 120.83(18); N3–C7–O1 = 114.11(18); N4–C14–O2 = 114.44(19); N7–C27–O3 = 114.72(18); N8–C34–O4 = 114.46(18).

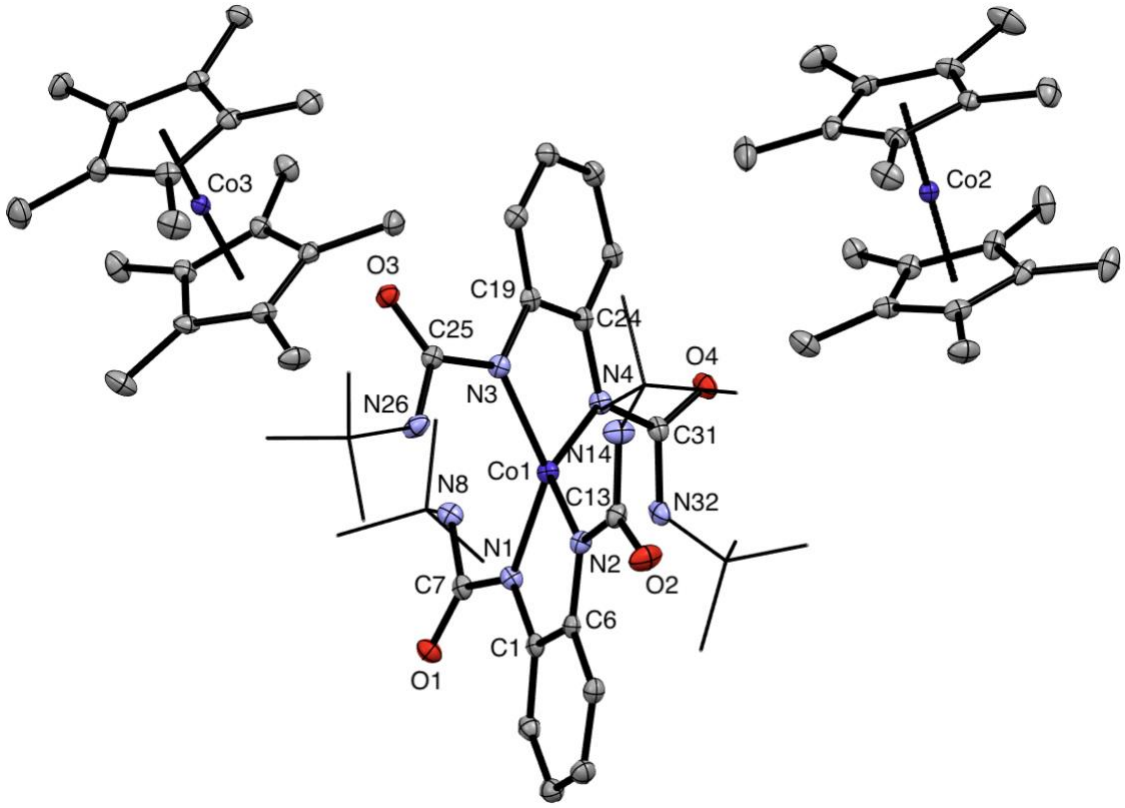



**Figure S7.** Single crystal X-ray structure of **8** shown with 30% probability ellipsoids. All hydrogen atoms and solvated diethyl ether are omitted and all *tert*-butyl groups are shown as capped sticks for clarity. Selected bond distances (Å): Co1–N1 = 1.9970(18); Co1–N2 = 1.9900(18); Co1–N3 = 1.9966(18); Co1–N4 = 1.9972(18); N1–C1 = 1.404(3); N2–C6 = 1.399(3); N3–C19 = 1.406(3); N4–C24 = 1.397(3); N1–C7 = 1.377(3); N2–C13 = 1.380(3); N3–C25 = 1.375(3); N4–C31 = 1.378(3); C7–N8 = 1.379(3); C13–N14 = 1.363(3); C25–N26 = 1.364(3); C31–N32 = 1.372(3); C7–O1 = 1.237(3); C13–O2 = 1.238(3); C25–O3 = 1.241(3); C31–O4 = 1.240(3). Selected angles (°): N1–Co1–N2 = 83.66(7); N3–Co1–N4 = 83.67(7); N1–C7–N8 = 112.38(19); N2–C13–N14 = 112.96(19); N3–C25–N26 = 112.68(19); N4–C31–N32 = 112.71(18); N1–C7–O1 = 127.3(2); N2–C13–O2 = 127.0(2); N3–C25–O3 = 126.9(2); N4–C31–O4 = 127.1(2); N8–C7–O1 = 120.3(2); N14–C13–O2 = 120.0(2); N26–C25–O3 = 120.40(19); N32–C31–O4 = 120.2(2).

## NMR Data

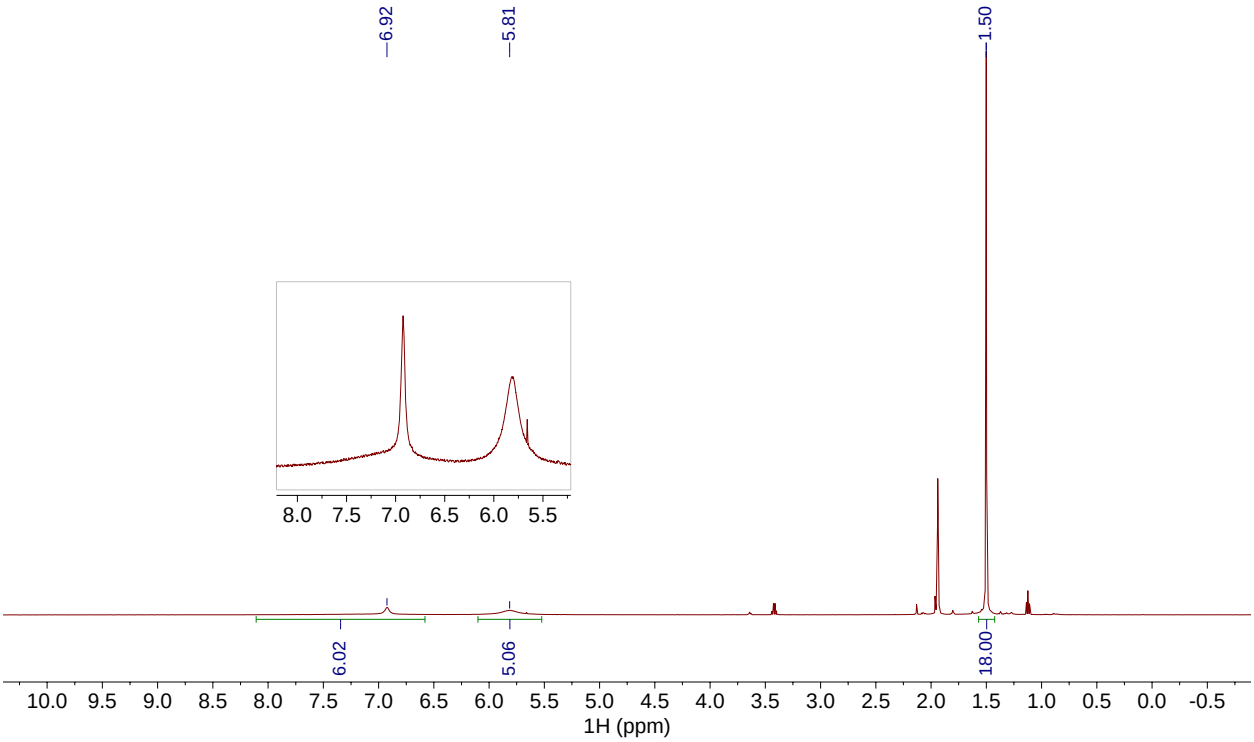



**Figure S8.** $^{1}$H NMR spectrum of **2** in $CD_3CN$.

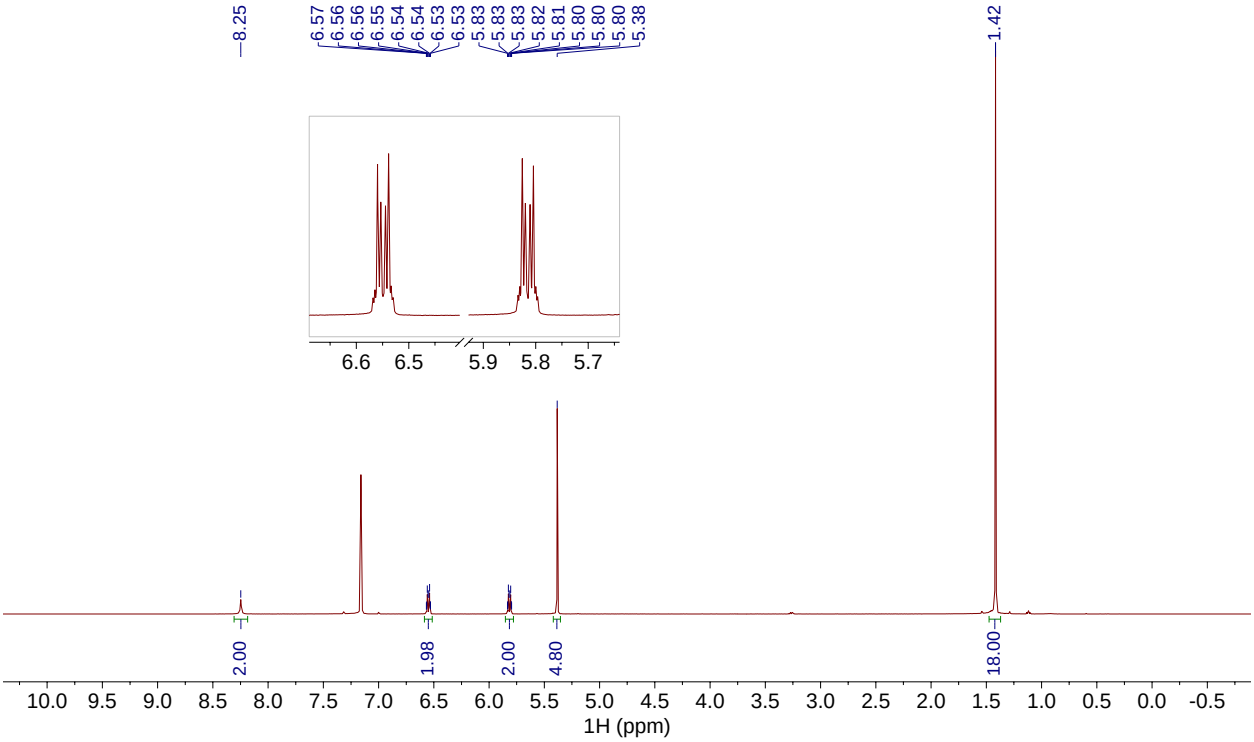



**Figure S9.** $^{1}$H NMR spectrum of **2** in $C_6D_6$.

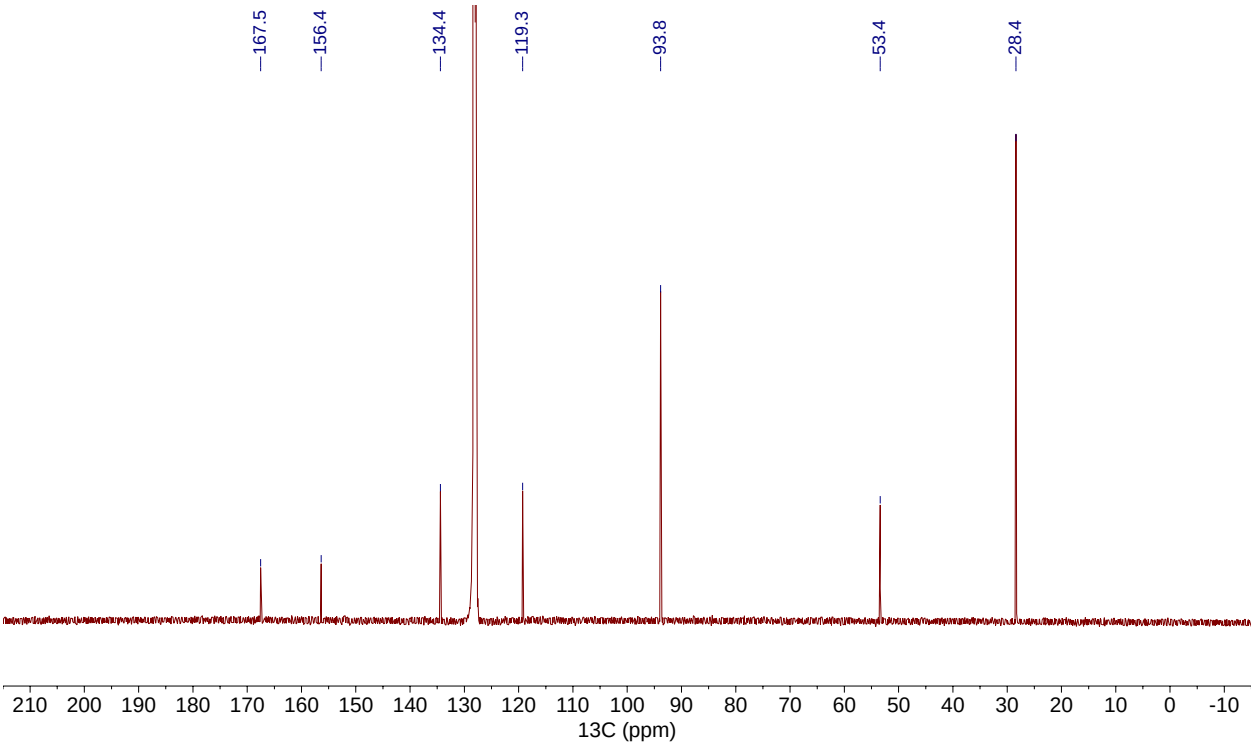



**Figure S10.** $^{13}C\{^{1}H\}$ NMR spectrum of **2** in $C_6D_6$. The signal of the *C*$F_3$ moiety is not visible due to coupling with the quadrupolar $^{59}Co$ nucleus and the $^{19}F$ nuclei.

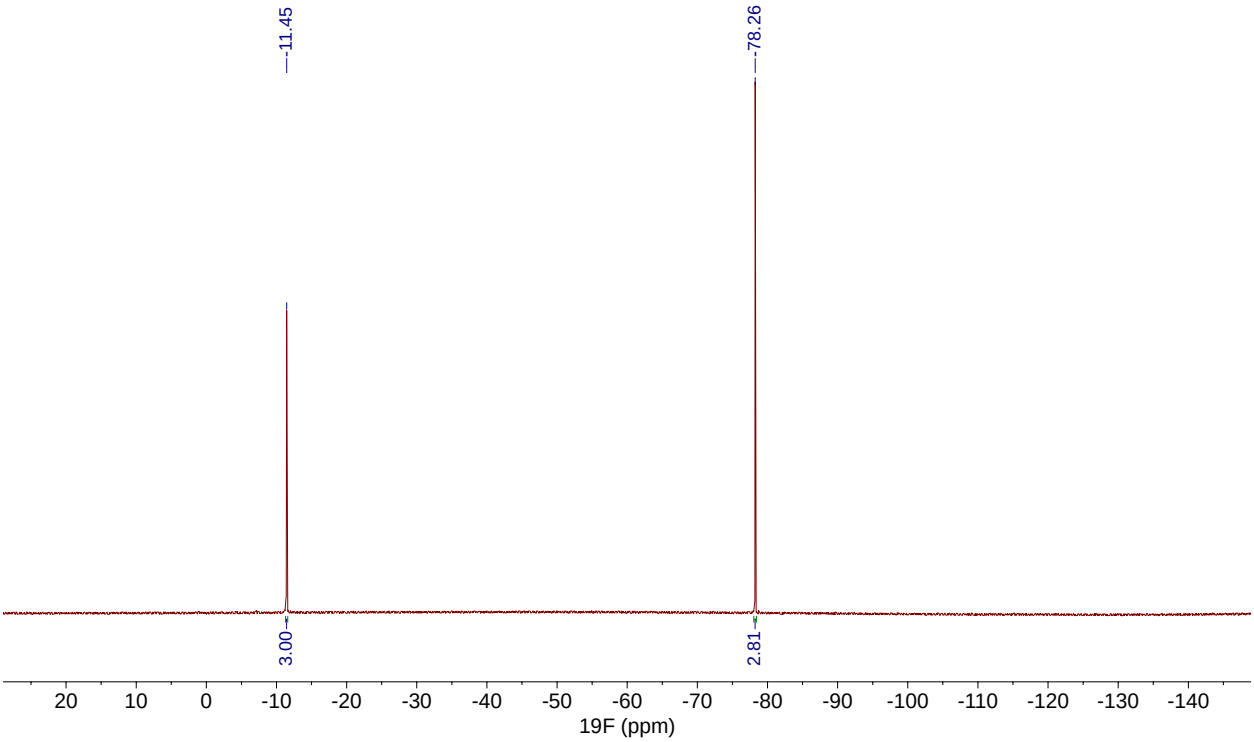



**Figure S11.** $^{19}F$ NMR spectrum of **2** in $C_6D_6$.

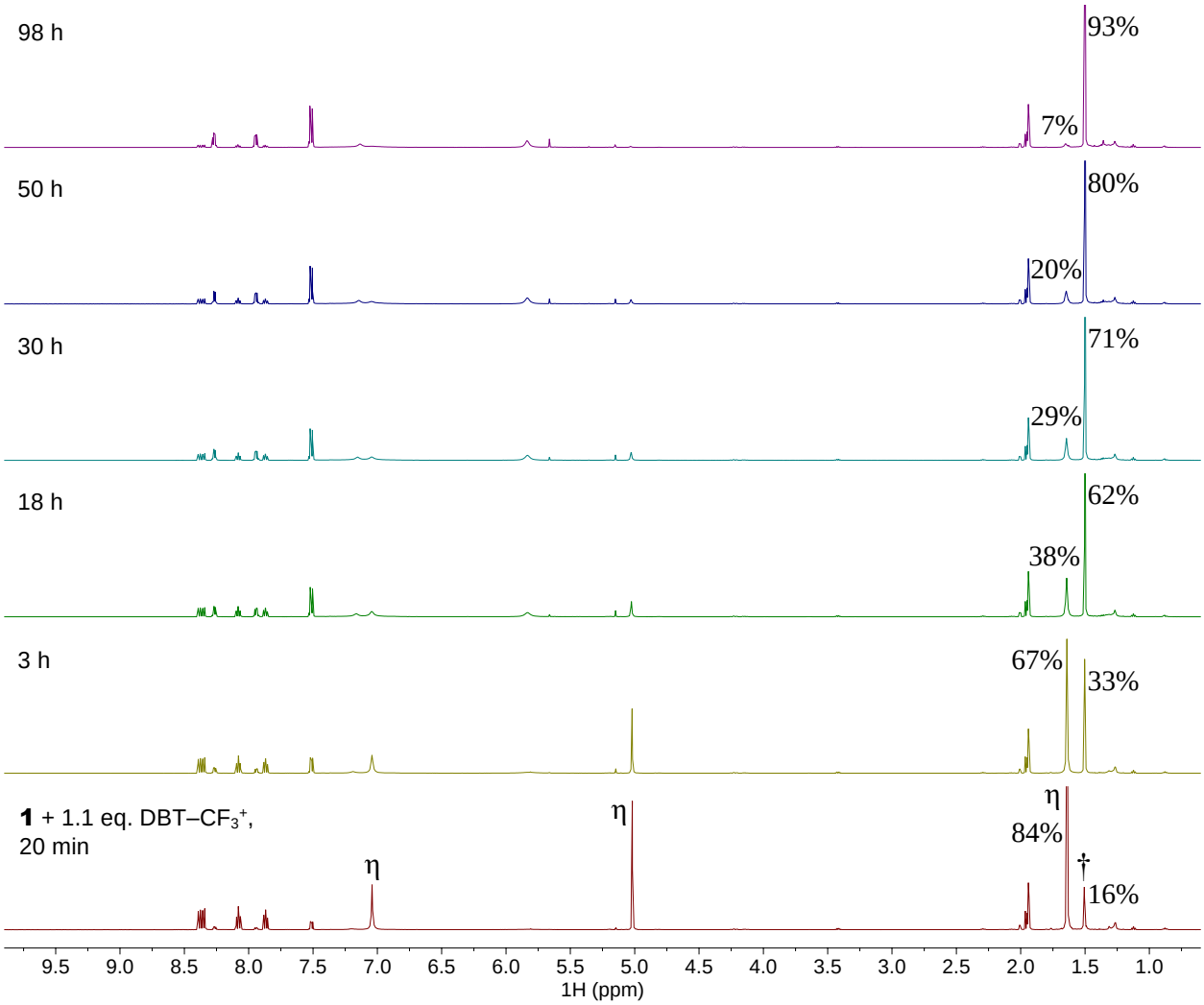



**Figure S12.** Monitoring the reaction of **1** and 1.1 equiv. [DBT–$CF_3$]OTf in $CD_3CN$ by $^1H$ NMR spectroscopy over 98 hours. † = **2**. η = **1**. The percentages of **2** and **1** in $CD_3CN$ are based on integrations of the corresponding *tert*-butyl signal.

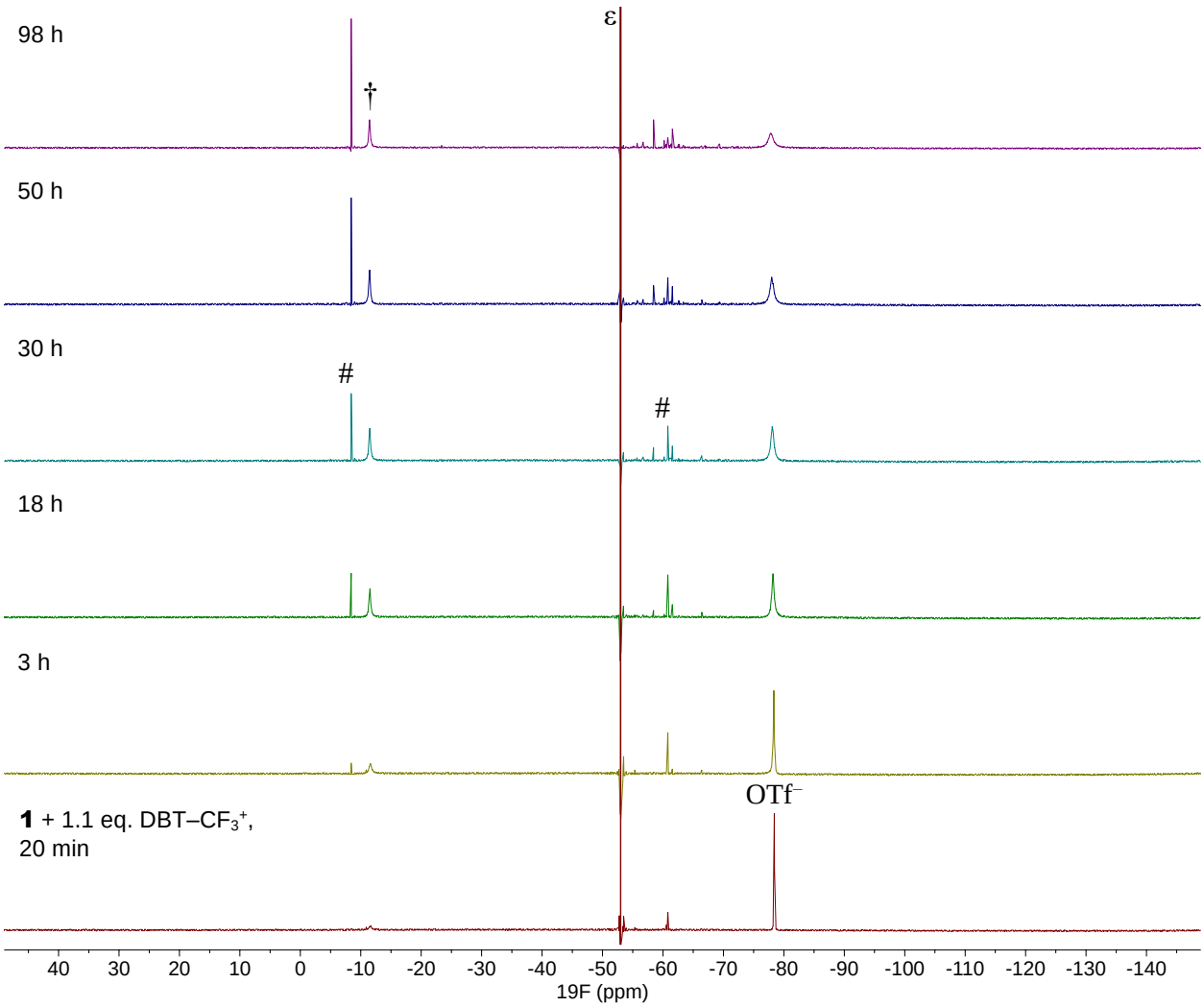



**Figure S13.** Monitoring the reaction of **1** and 1.1 equiv. [DBT–$CF_3$]OTf in $CD_3CN$ by $^{19}F$ NMR spectroscopy over 98 hours. † = **2**. ε = $[DBT–CF_3]^+$. # = unknown.

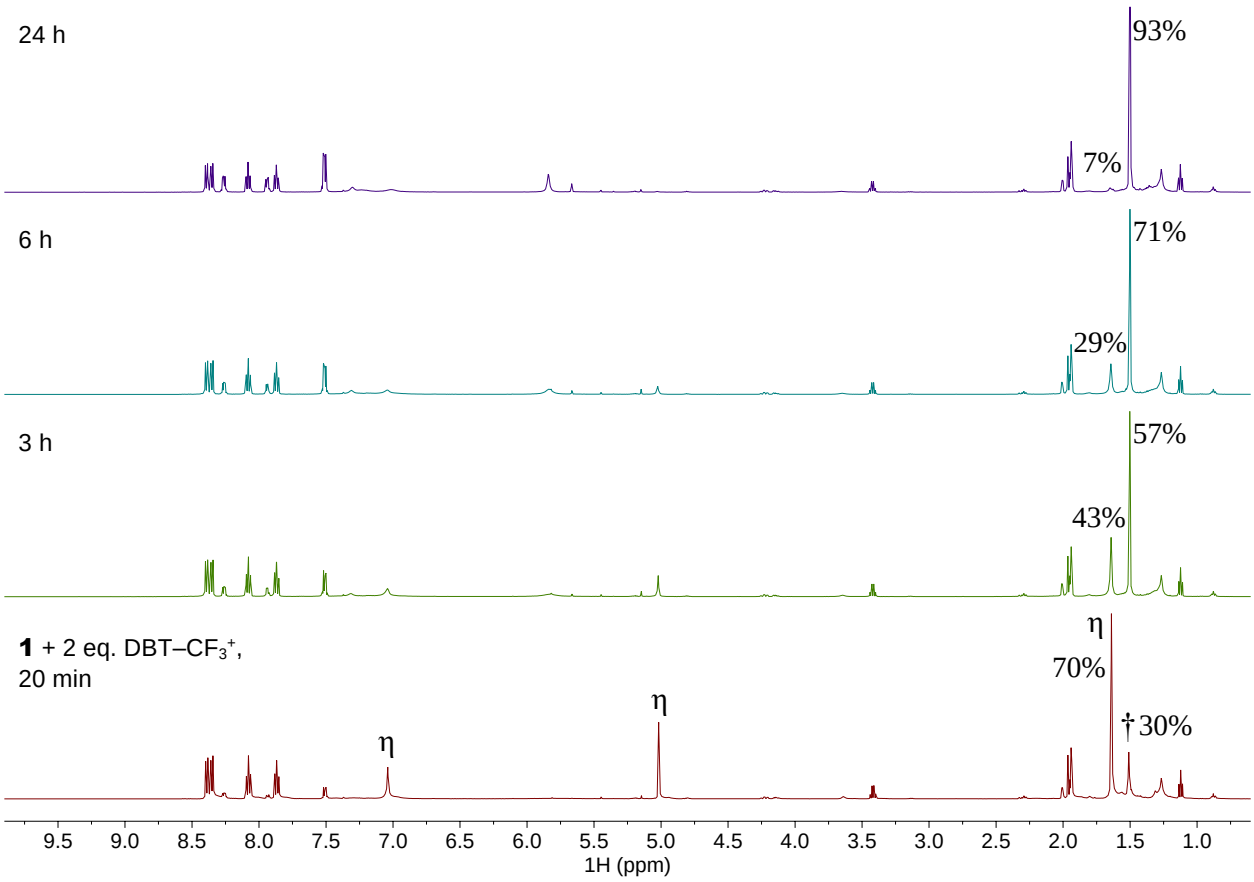



**Figure S14.** Monitoring the reaction of **1** and 2 equiv. [DBT–$CF_3$]OTf in $CD_3CN$ by $^1$H NMR spectroscopy over 24 hours. † = **2**. η = **1**. The percentages of **2** and **1** in $CD_3CN$ are based on integrations of the corresponding *tert*-butyl signal.

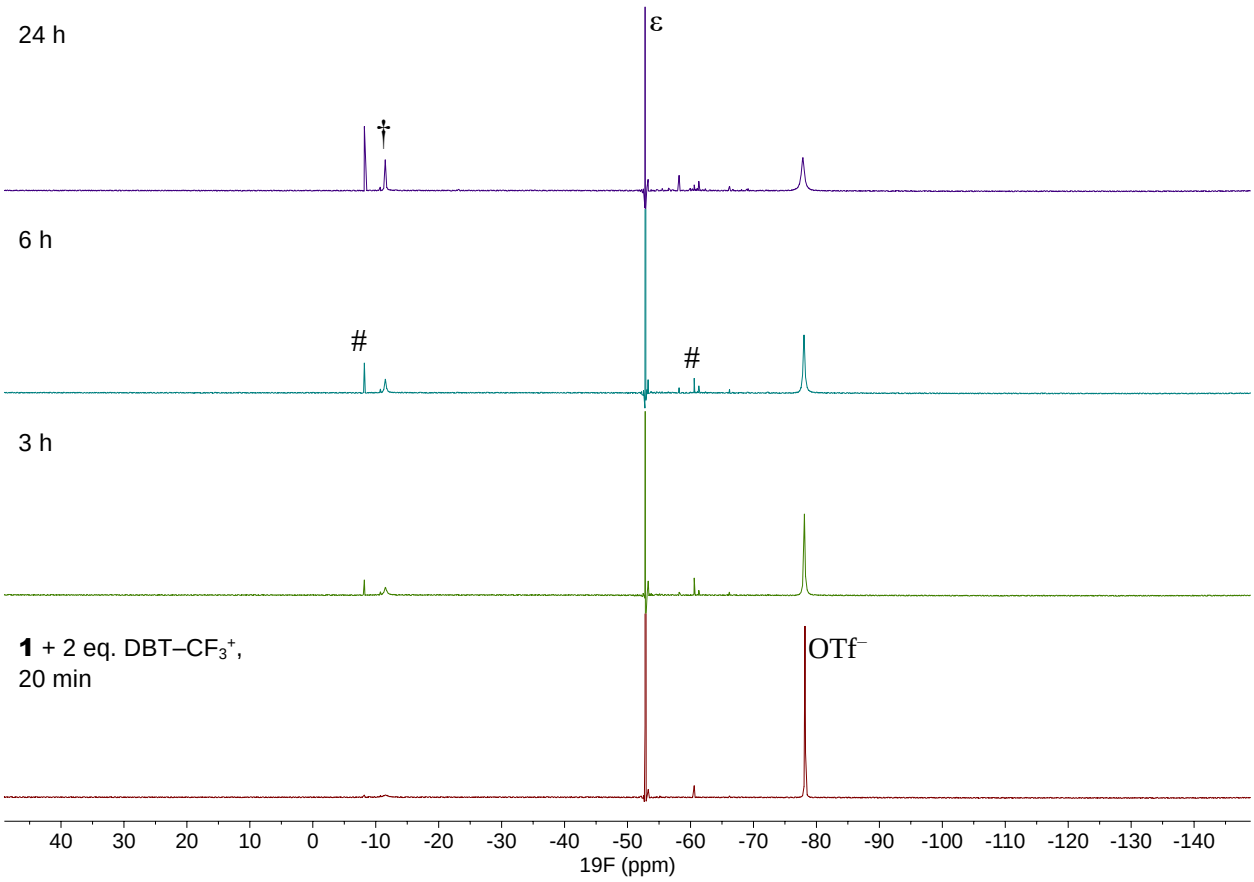



**Figure S15.** Monitoring the reaction of **1** and 2 equiv. [DBT–$CF_3$]OTf in $CD_3CN$ by $^{19}F$ NMR spectroscopy over 24 hours. † = **2**. ε = $[DBT–CF_3]^+$. # = unknown.

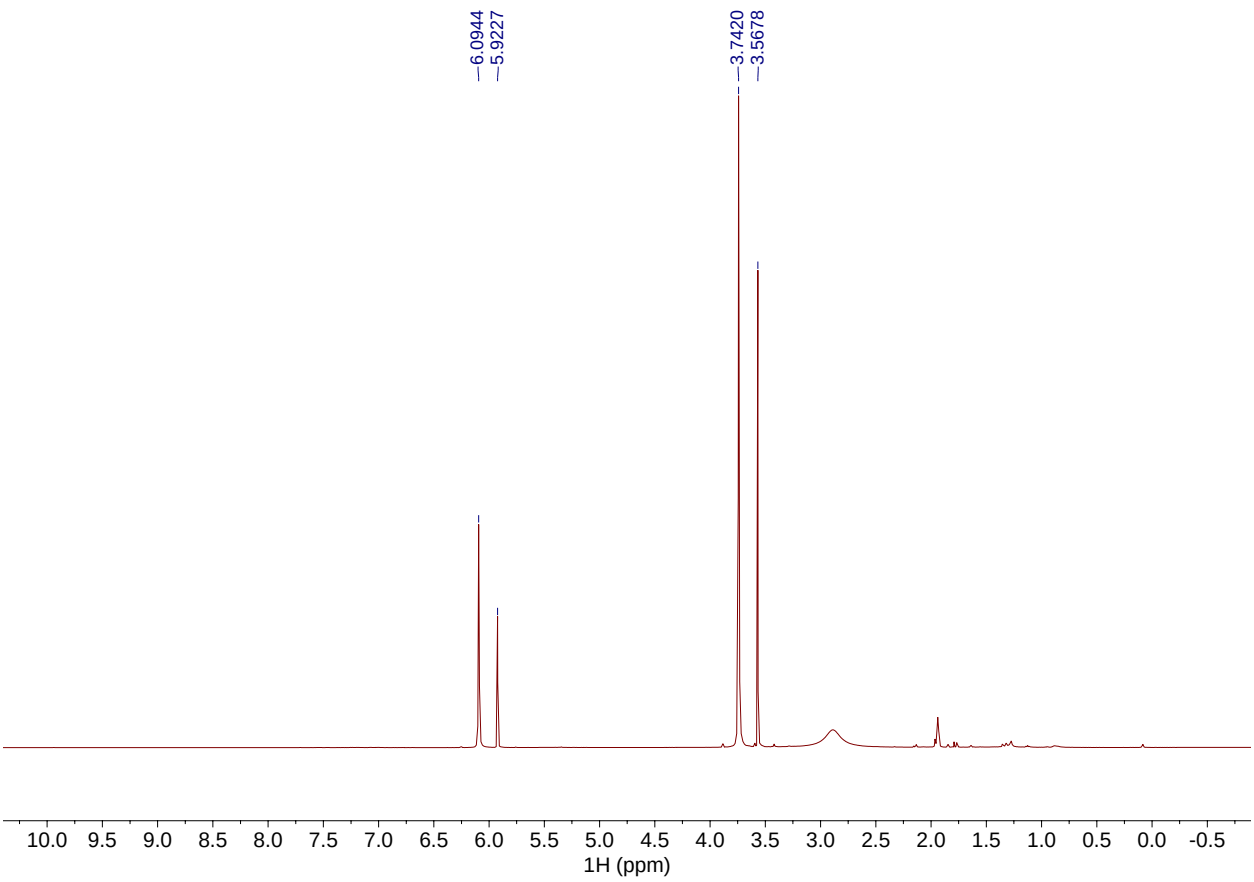



**Figure S16.** Magnetic moment measurement of **3** using Evan's method with 1,3,5-trimethoxybenzene as the internal standard in $CD_3CN$ at 25°C. [Co] = 0.032 M, $\Delta f$ = 86 Hz, f = 500.15 MHz, $\mu_{eff}$ = 1.75 μB.

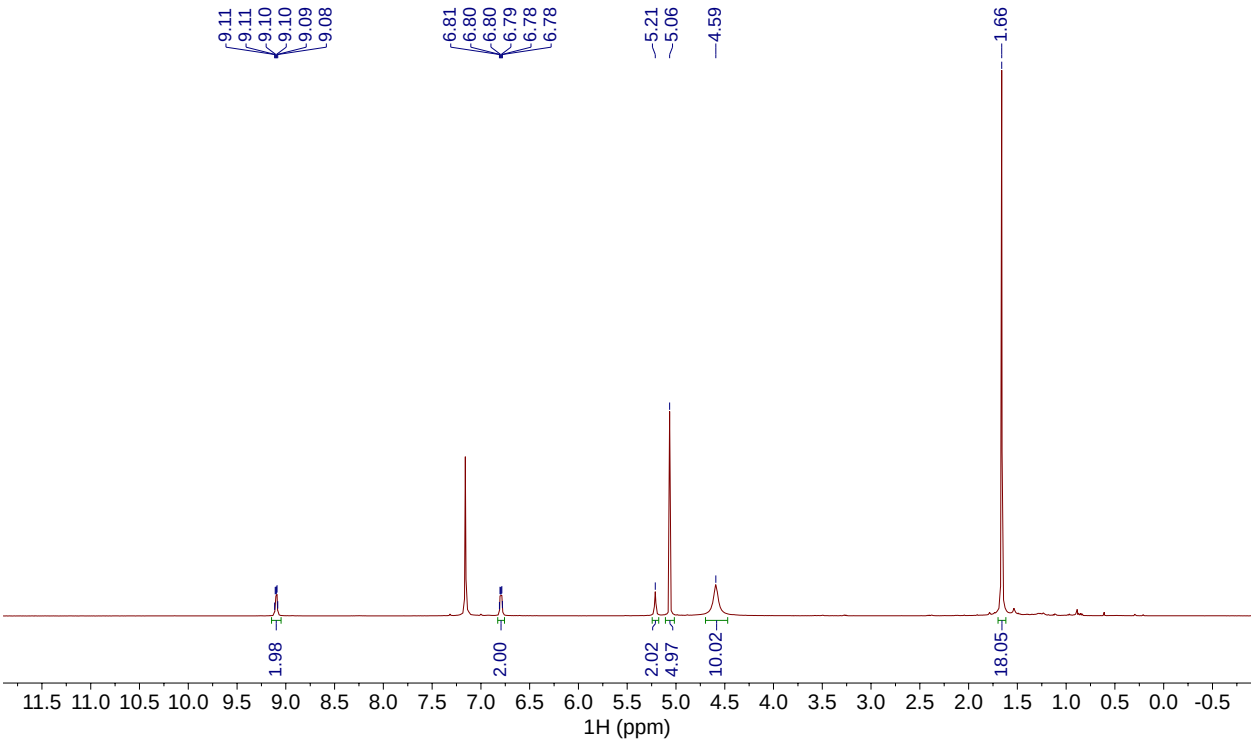



**Figure S17.** $^{1}$H NMR spectrum of **4** in $C_6D_6$.

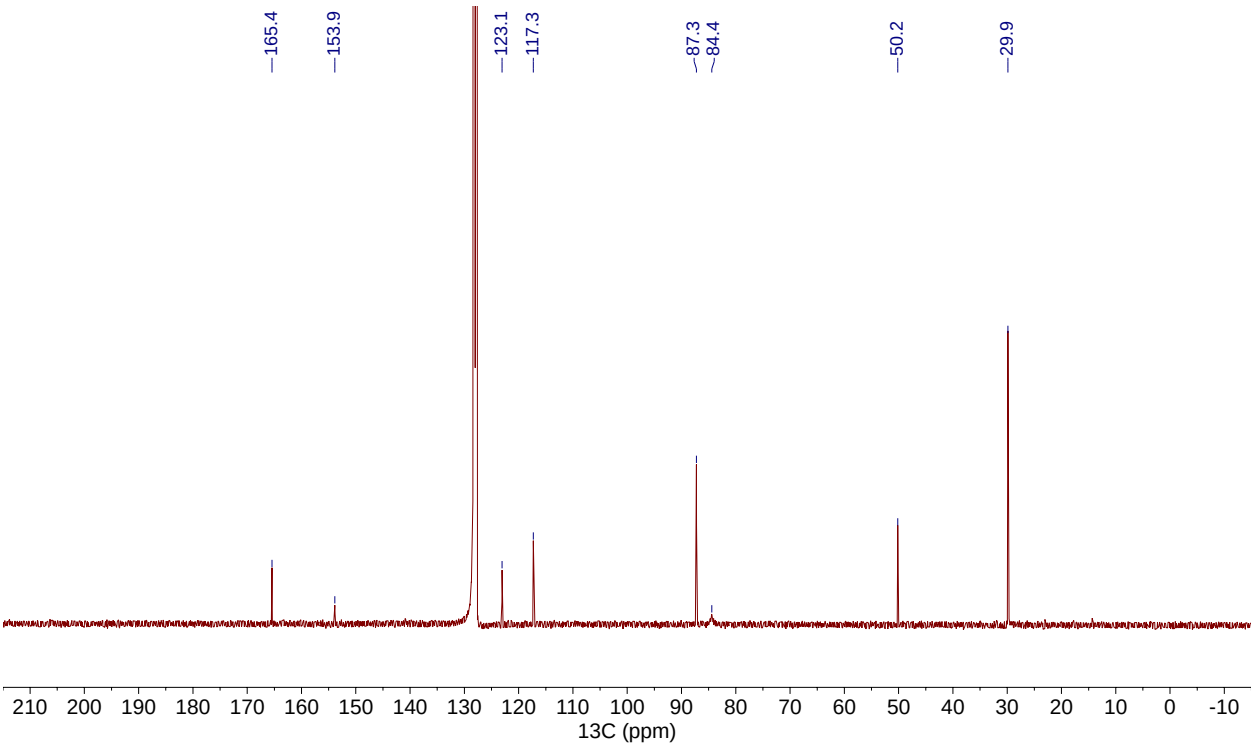



**Figure S18.** $^{13}C\{^{1}H\}$ NMR spectrum of **4** in $C_6D_6$. The signal of the $CF_3$ moiety is not visible due to coupling with the quadrupolar $^{59}$Co nucleus and the $^{19}$F nuclei.

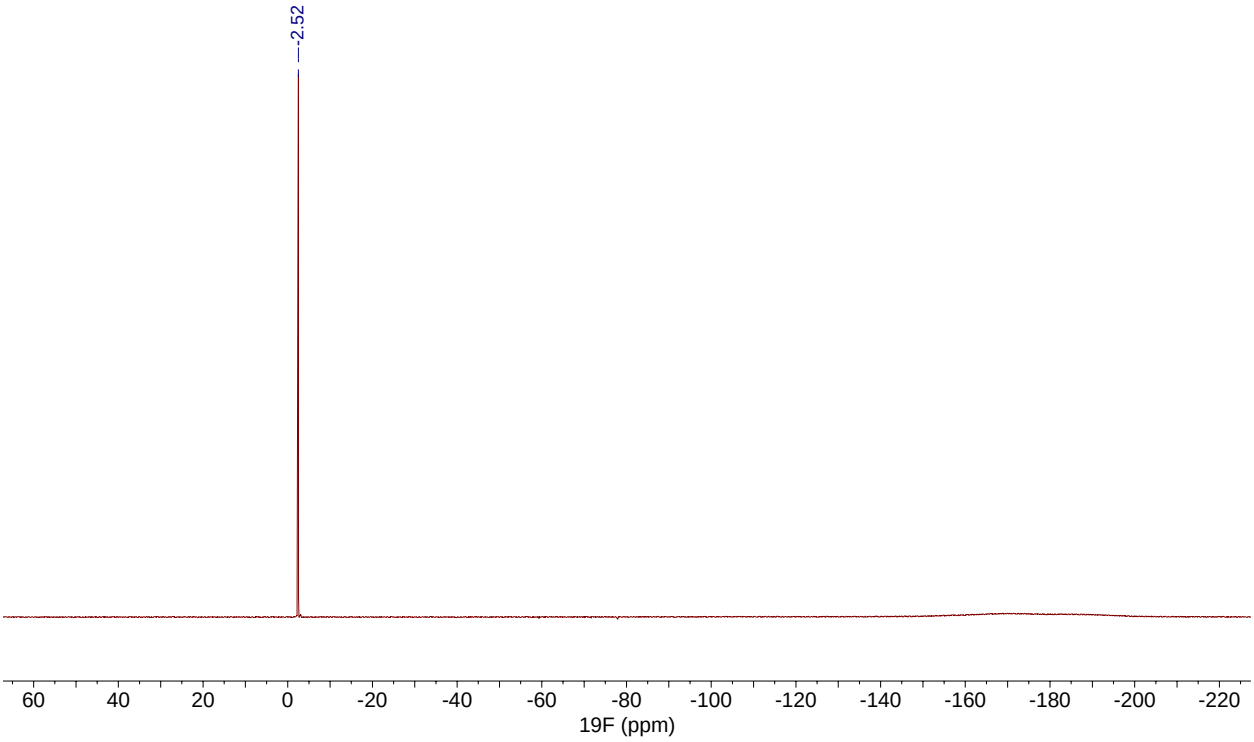



**Figure S19.** $^{19}F$ NMR spectrum of **4** in $C_6D_6$.

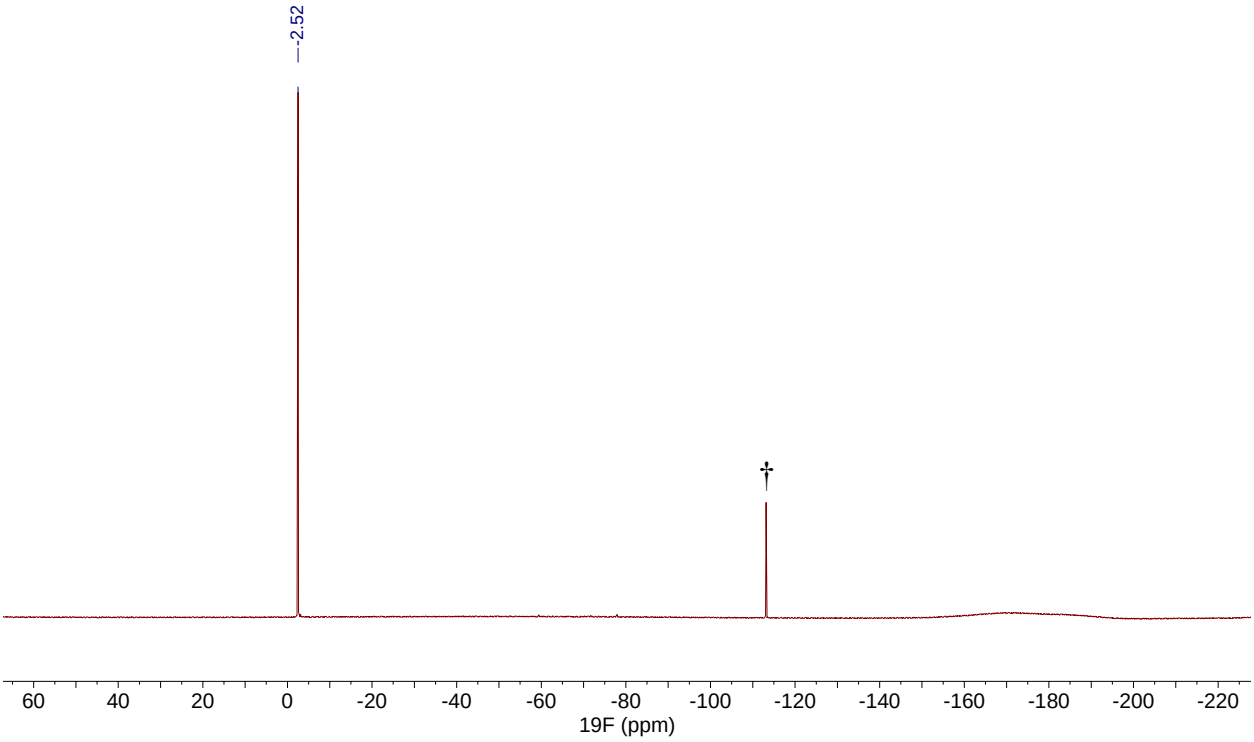



**Figure S20.** $^{19}F$ NMR spectrum of **4** in $C_6D_6$ after storing at 4°C for 24 h. † = fluorobenzene.

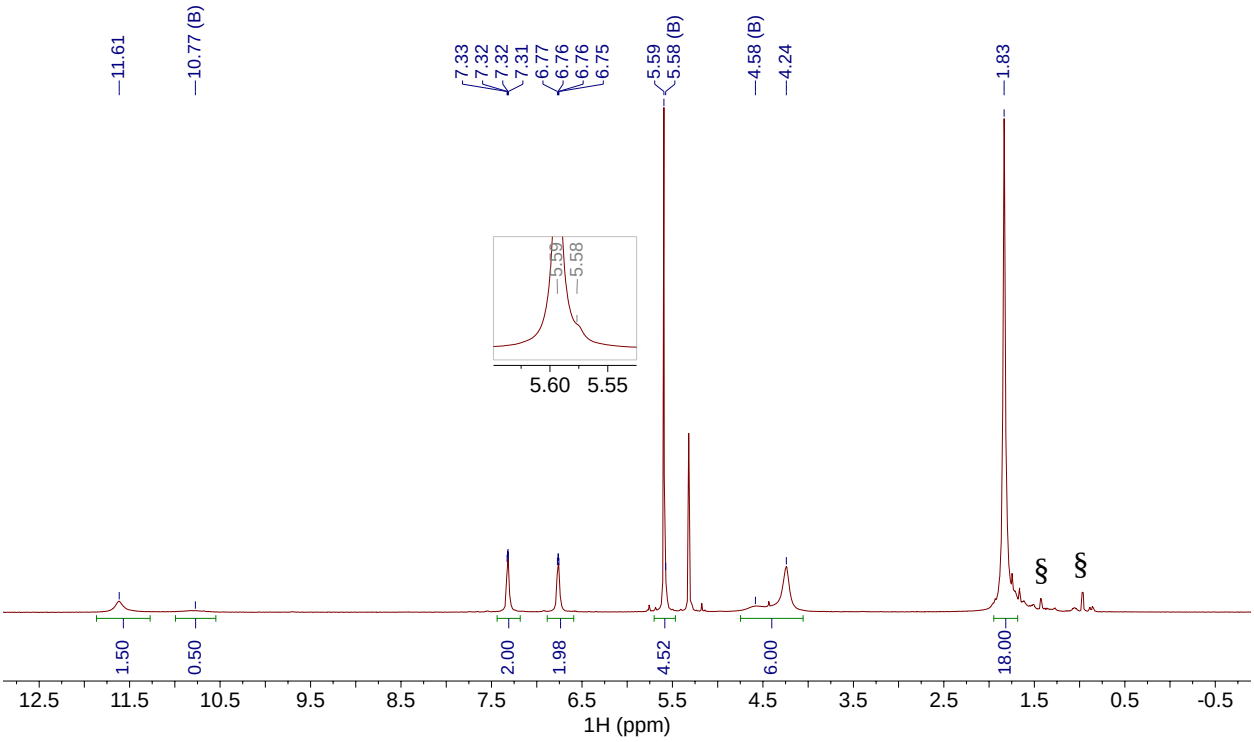



**Figure S21.** $^{1}H$ NMR spectrum of **5** in $CD_2Cl_2$. (B) = Other isomer. § = *n*-Hexane.

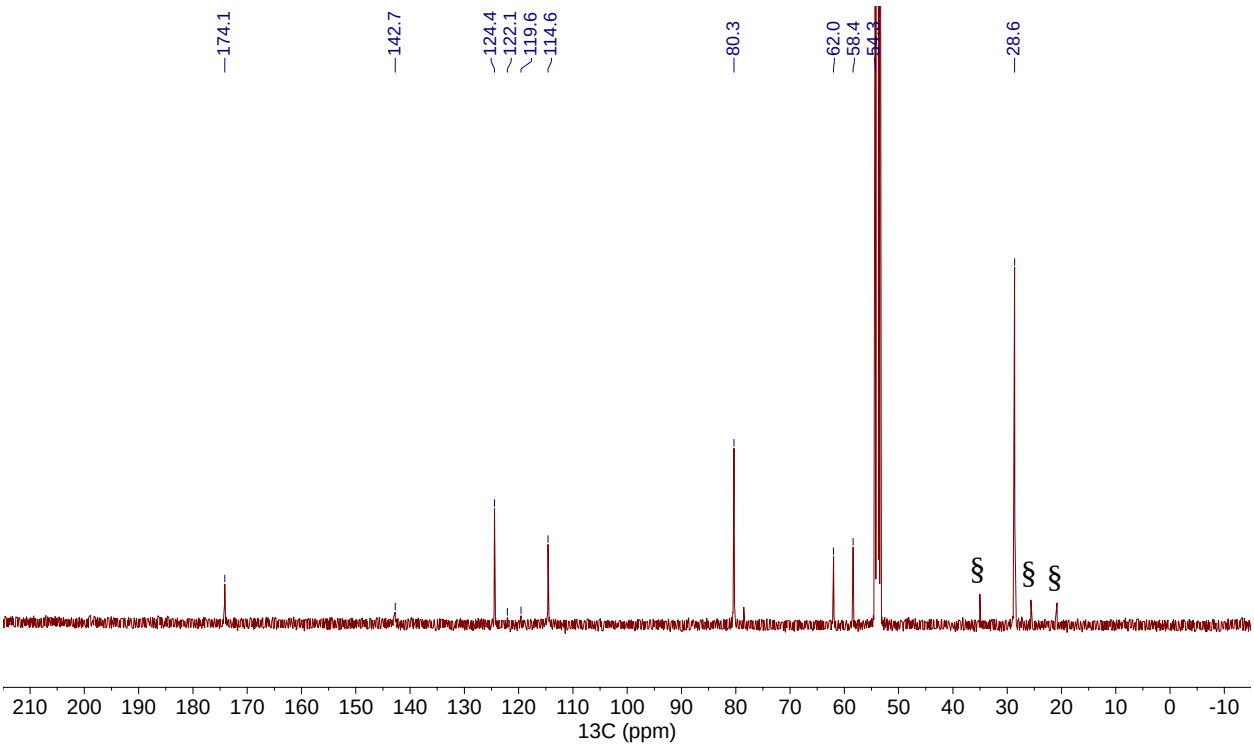



**Figure S22.** $^{13}C\{^{1}H\}$ NMR spectrum of **5** in $CD_2Cl_2$. § = *n*-Hexane.

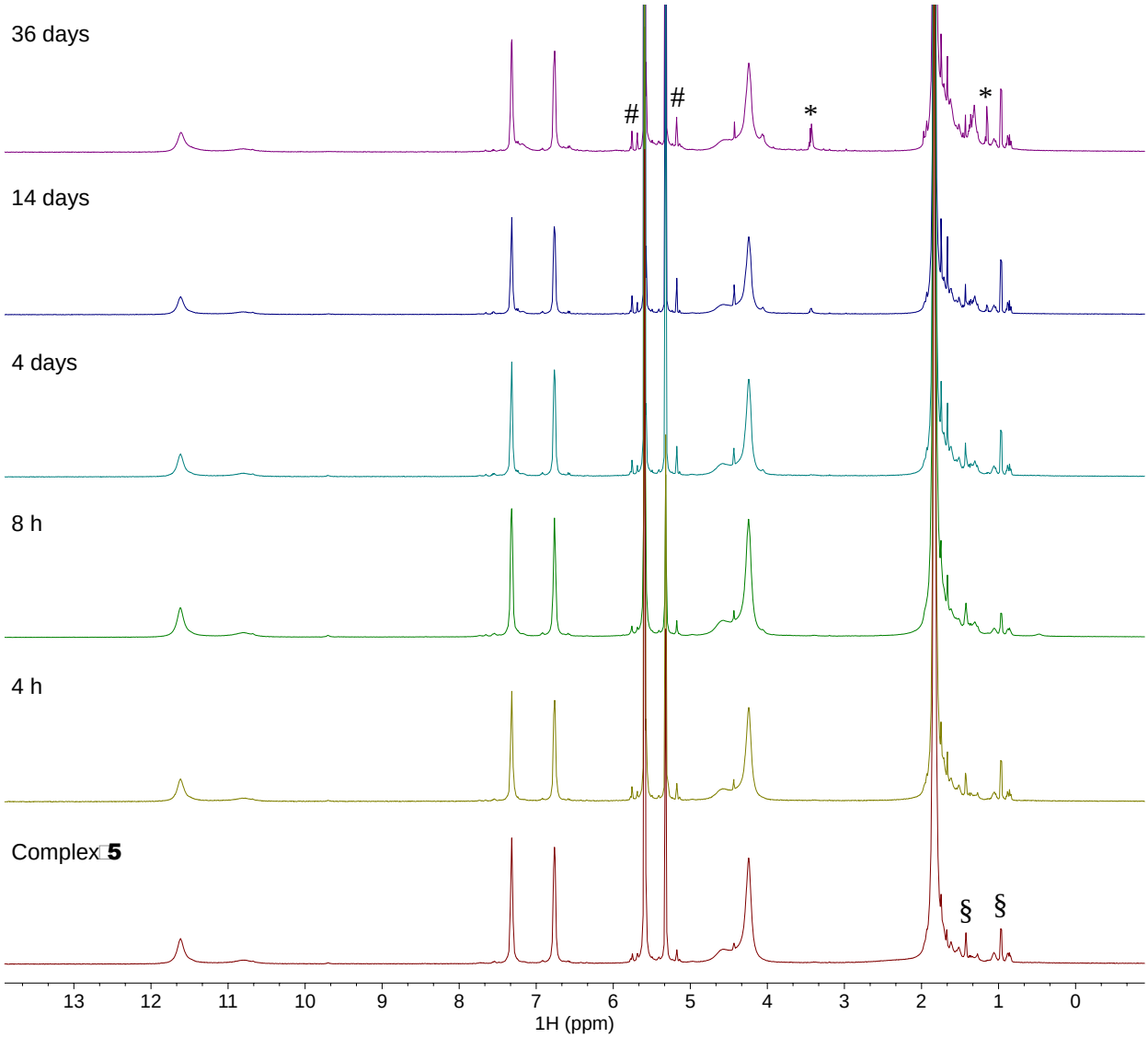



**Figure S23.** Monitoring complex **5** in $CD_2Cl_2$ by $^1H$ NMR spectroscopy over 36 days. The spectra were acquired at 25°C, but the NMR solution was stored at –25°C between data acquisition. * = $Et_2O$. § = *n*-Hexane. # = unknown.

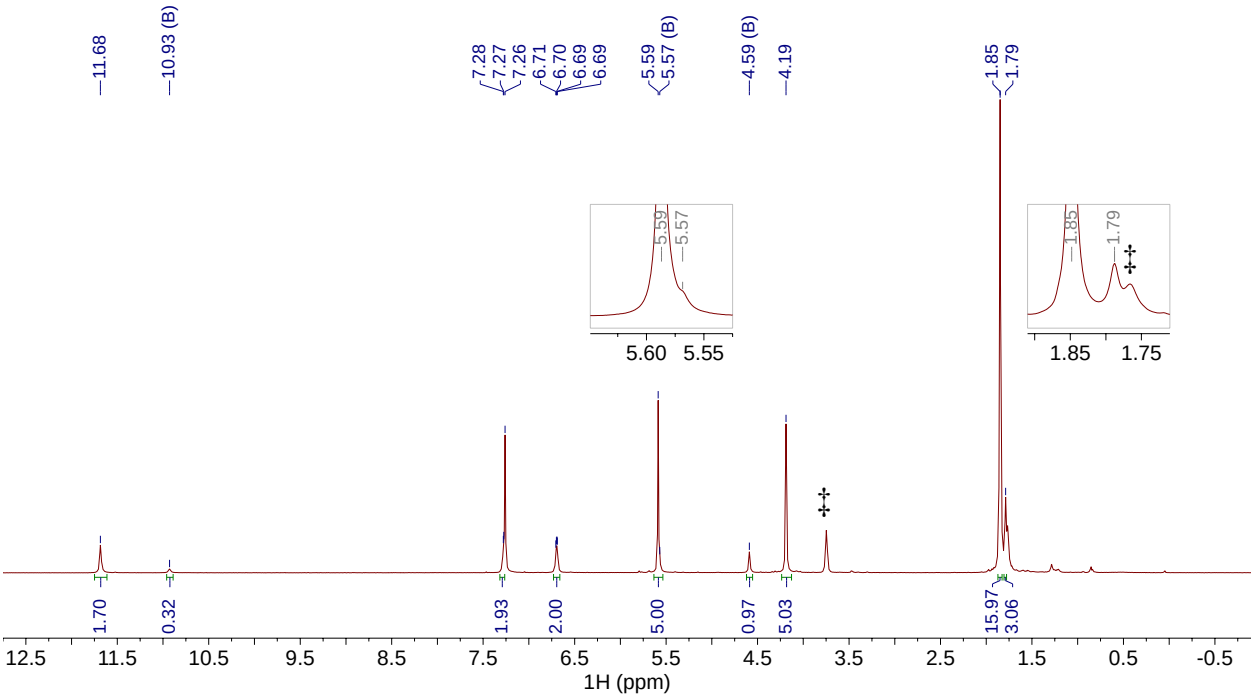



**Figure S24.** $^{1}$H NMR spectrum of **5** in $CDCl_3$ at –25°C. (B) = Other isomer. ‡ = THF.

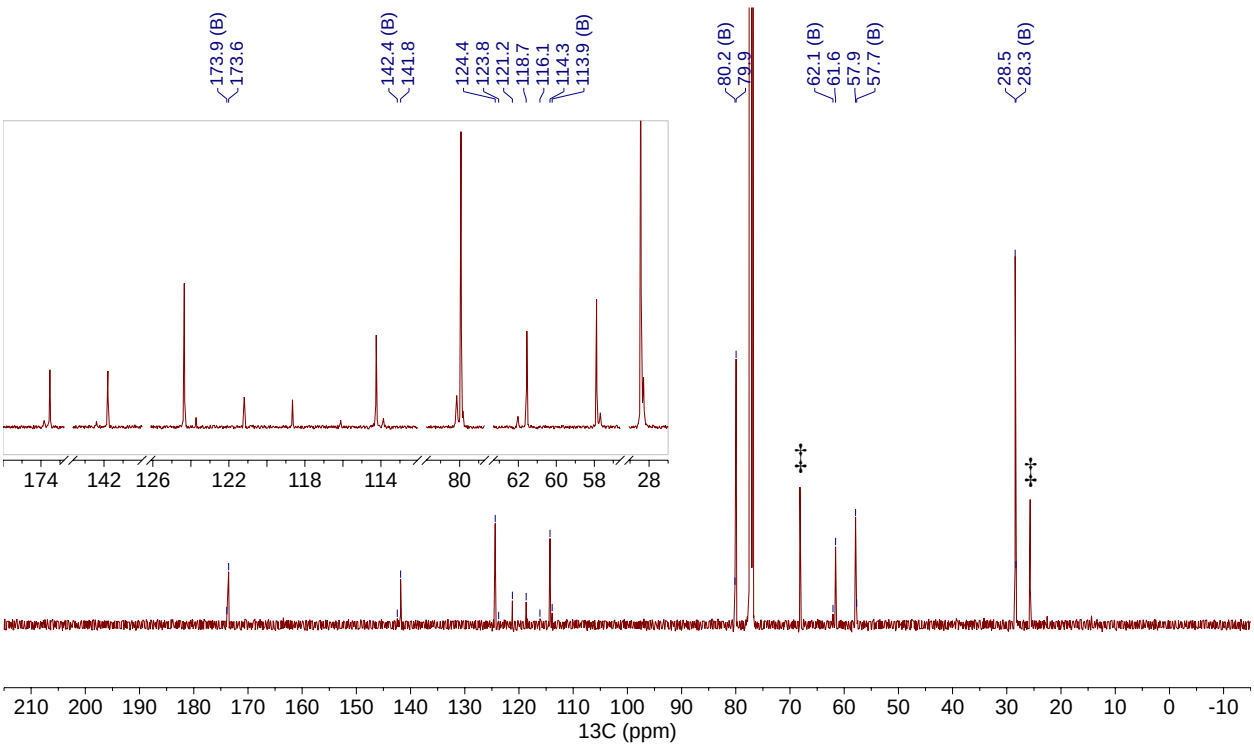



**Figure S25.** $^{13}C\{^{1}H\}$ NMR spectrum of **5** in $CDCl_3$ at –25°C. (B) = Other isomer. The *inset* spectrum was shown for the characteristic peaks of the cobalt complex. ‡ = THF.

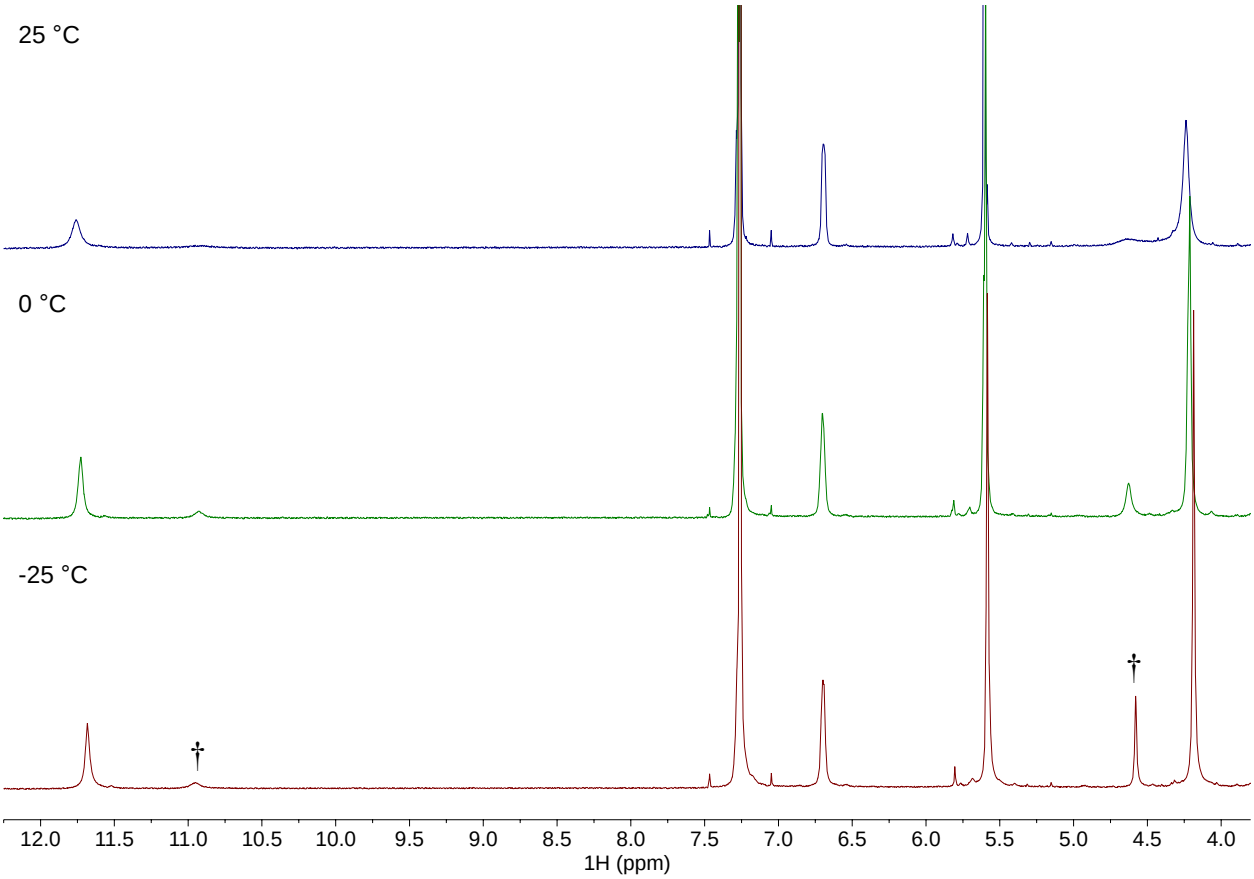



**Figure S26.** $^{1}$H NMR spectra of **5** in $CDCl_3$ at varied temperatures. † = Other isomer.

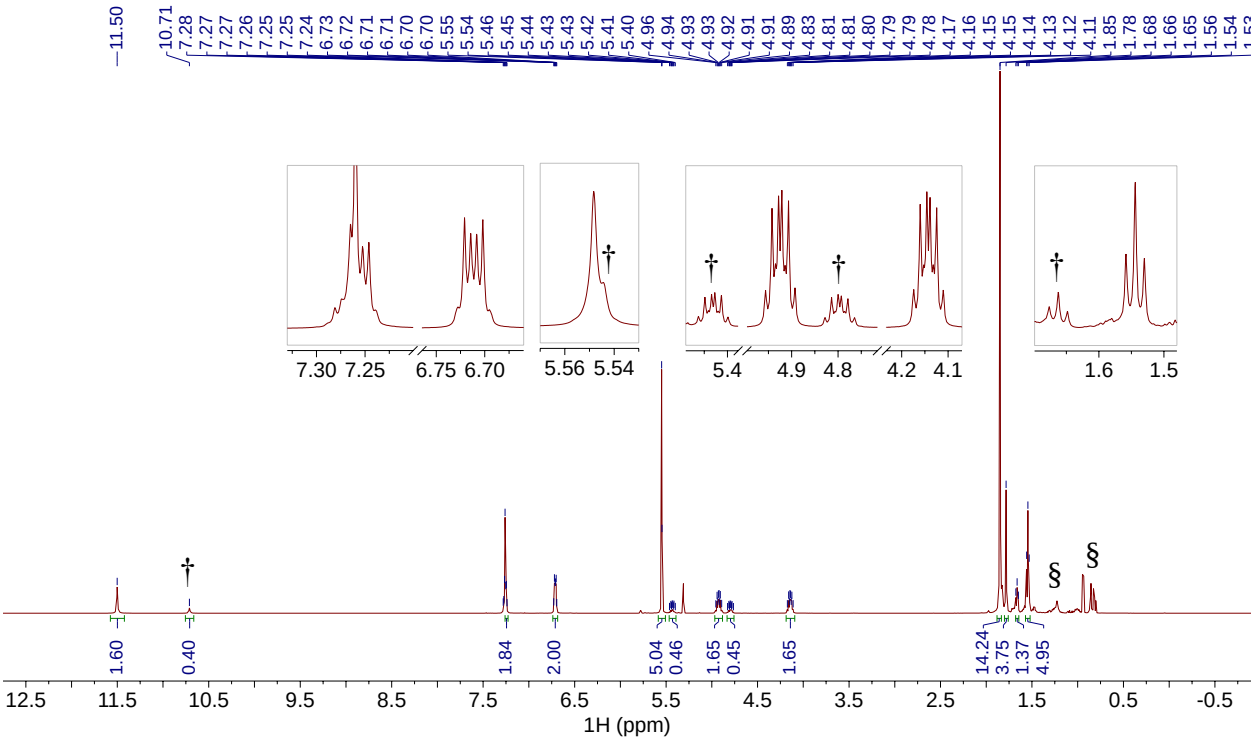



**Figure S27.** $^{1}$H NMR spectrum of **6** in $CDCl_3$ at –25°C. † = Other isomer. § = Hexanes.

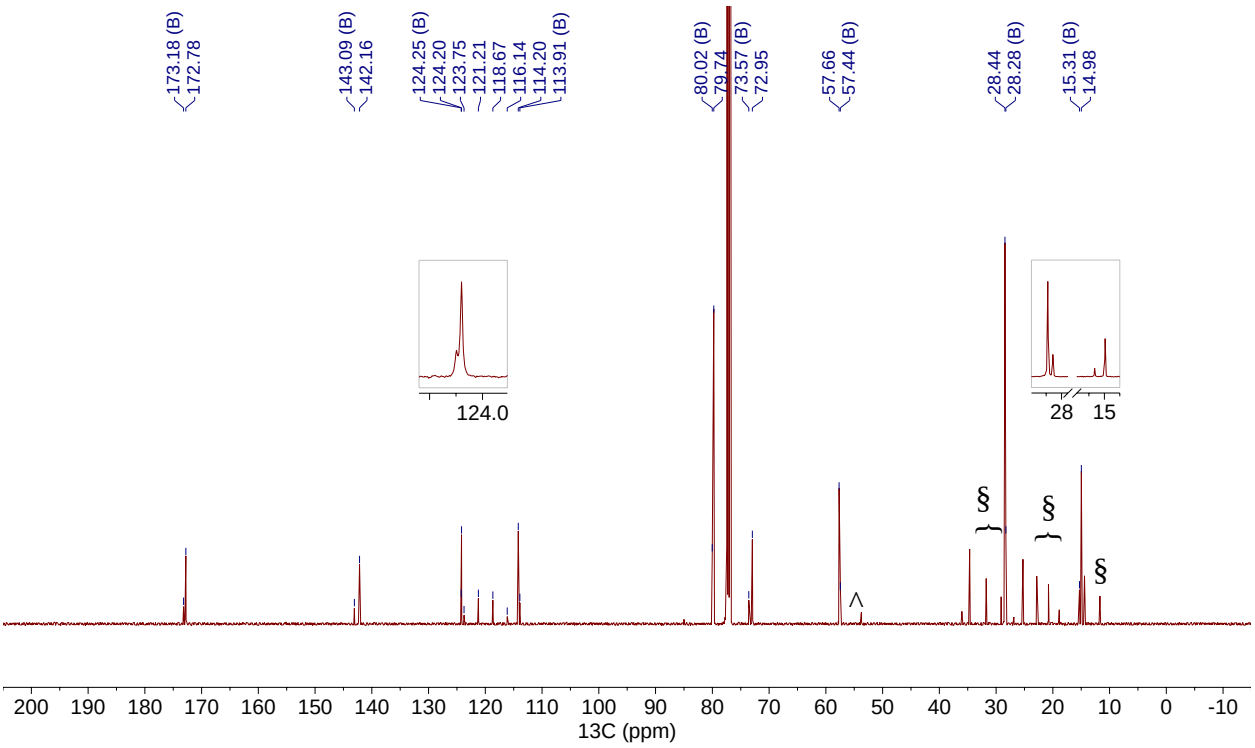



**Figure S28.** $^{13}C\{^{1}H\}$ NMR spectrum of **6** in $CDCl_3$ at –25°C. (B) = Other isomer. ^ = $CH_2Cl_2$. § = Hexanes.

**Mass Spectra**

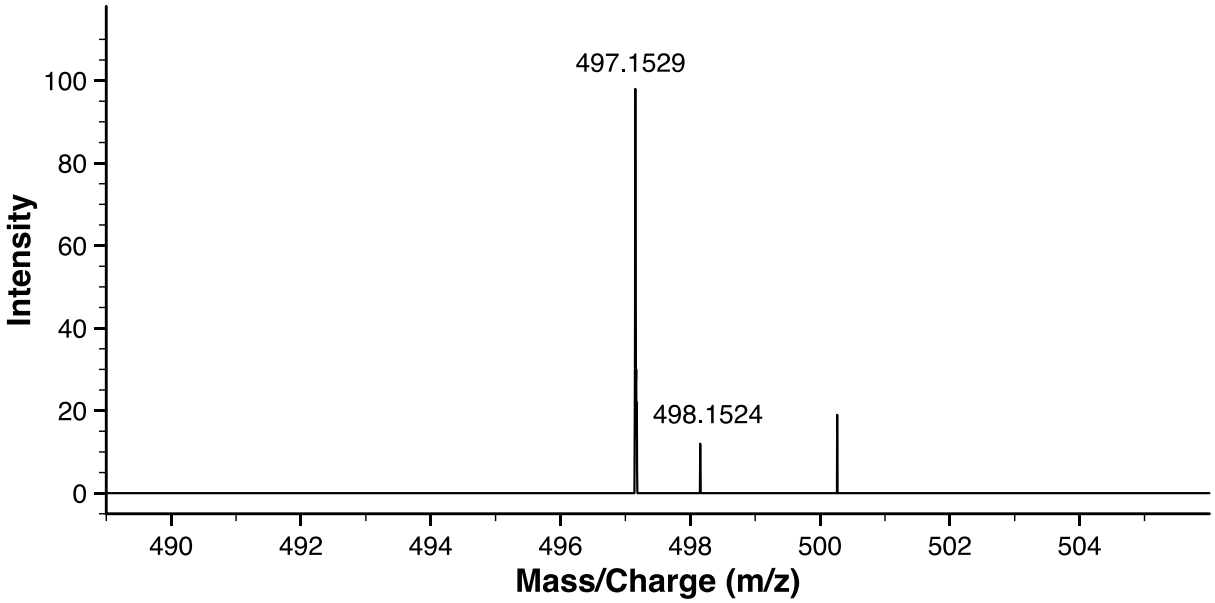



**Figure S29.** Mass spectra of complex **2** collected using an electrospray ionization (ESI) source on position ion mode.

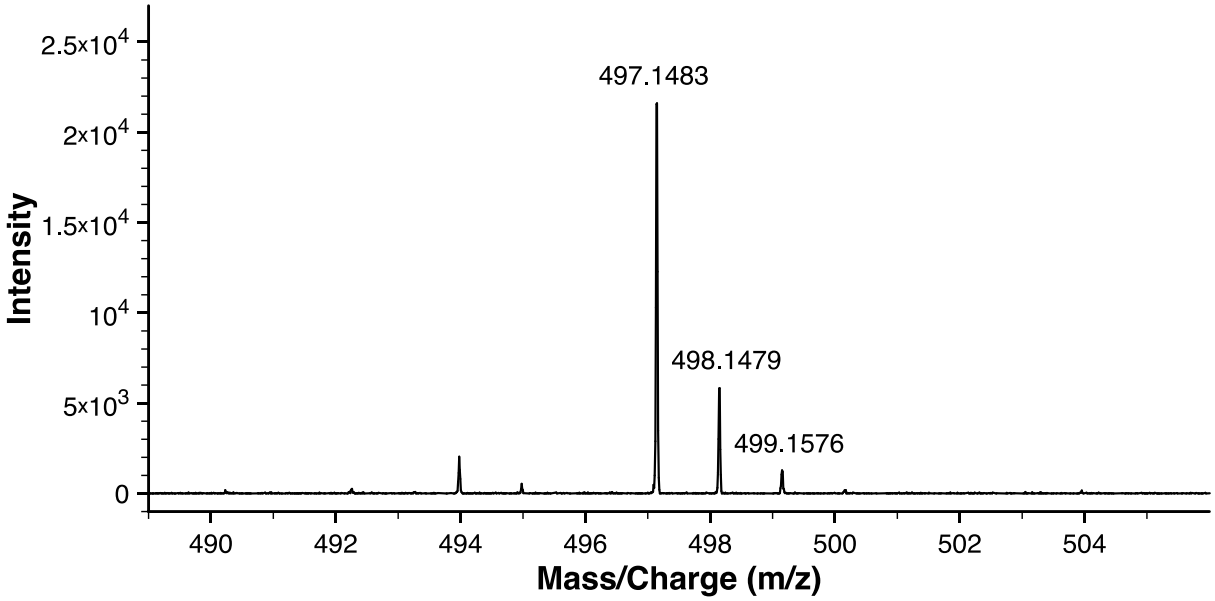



**Figure S30.** Mass spectra of complex **3** collected using an electrospray ionization (ESI) source on position ion mode.

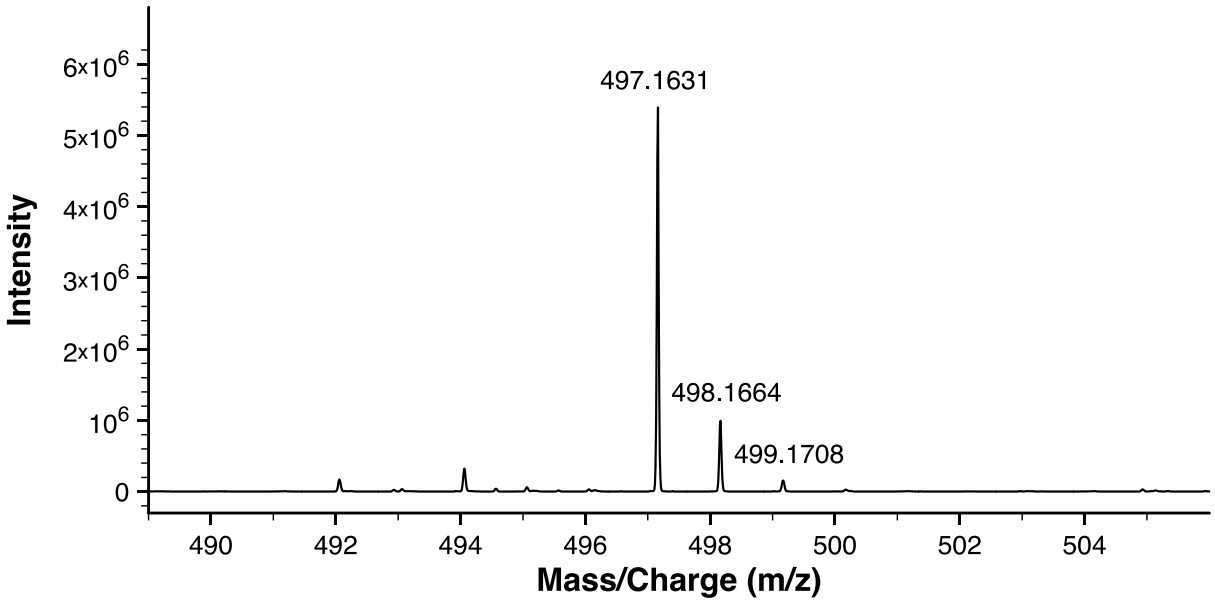



**Figure S31.** Mass spectra of complex **4** collected using an electrospray ionization (ESI) source on position ion mode.

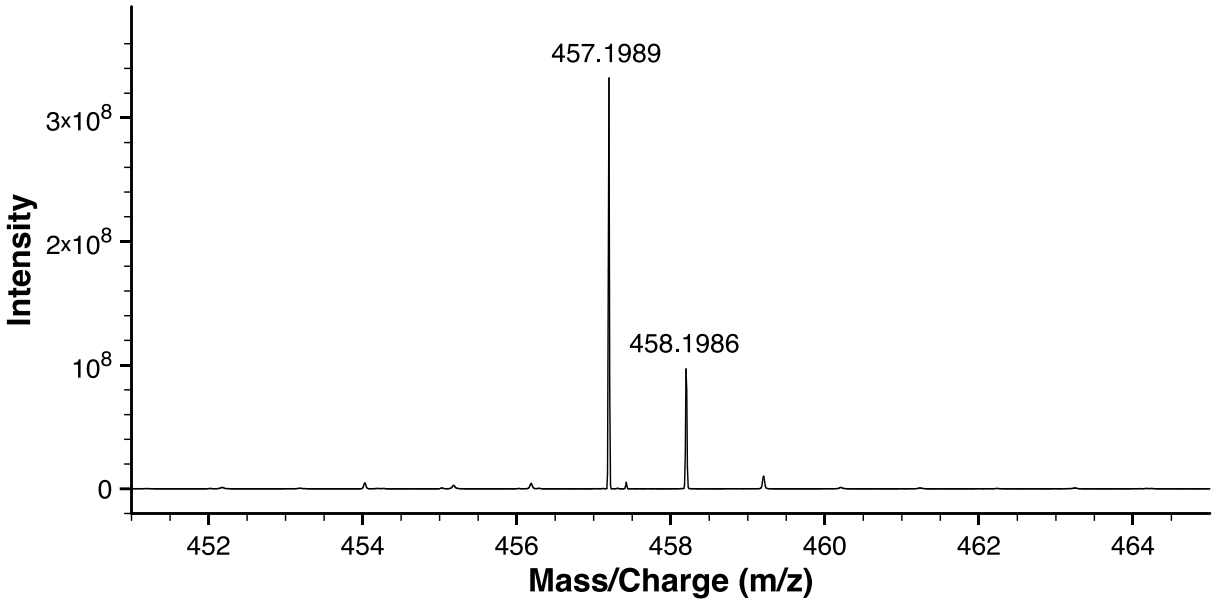



**Figure S32.** Mass spectra of complex **5** collected using an electrospray ionization (ESI) source on position ion mode.

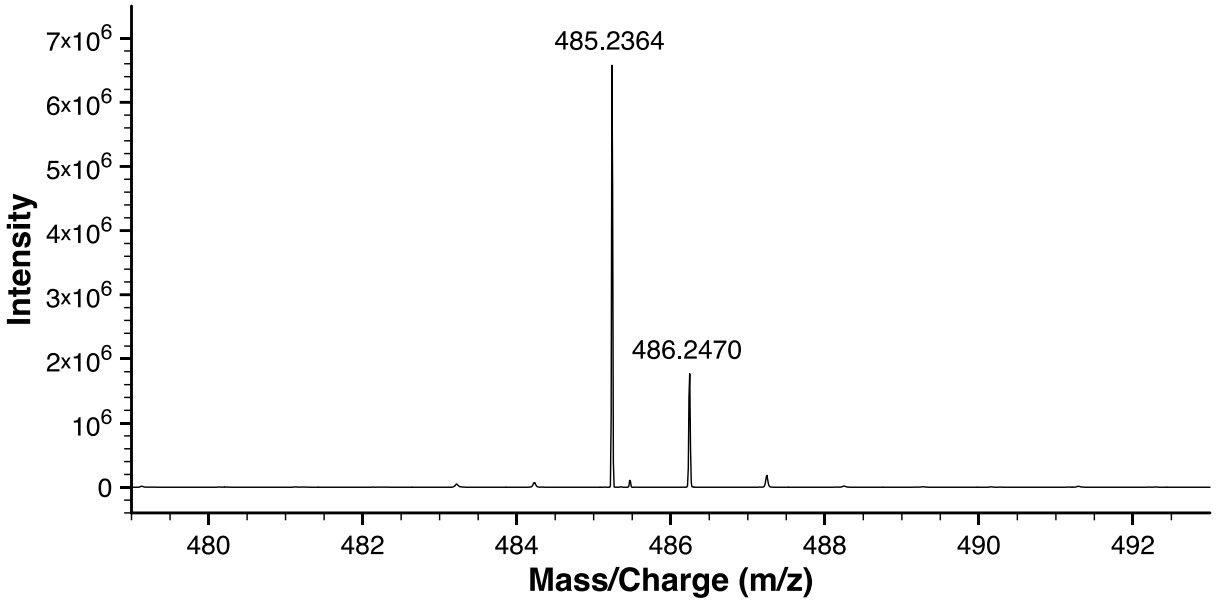



**Figure S33.** Mass spectra of complex **6** collected using an electrospray ionization (ESI) source on position ion mode.

**Electronic Absorption Spectra**

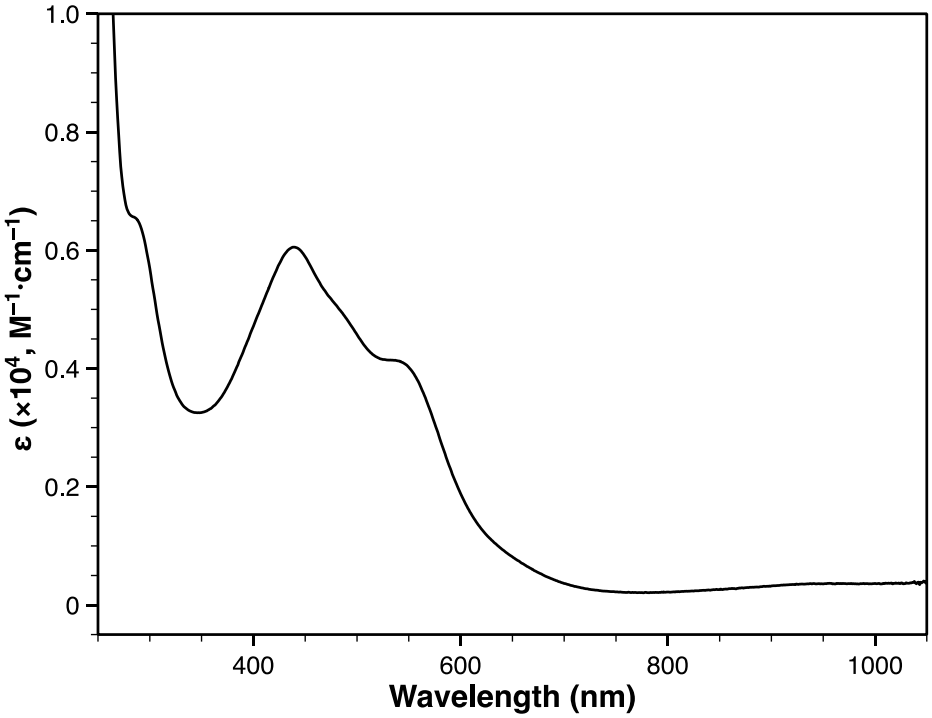



**Figure S34.** Electronic absorption spectrum of **2** in MeCN.

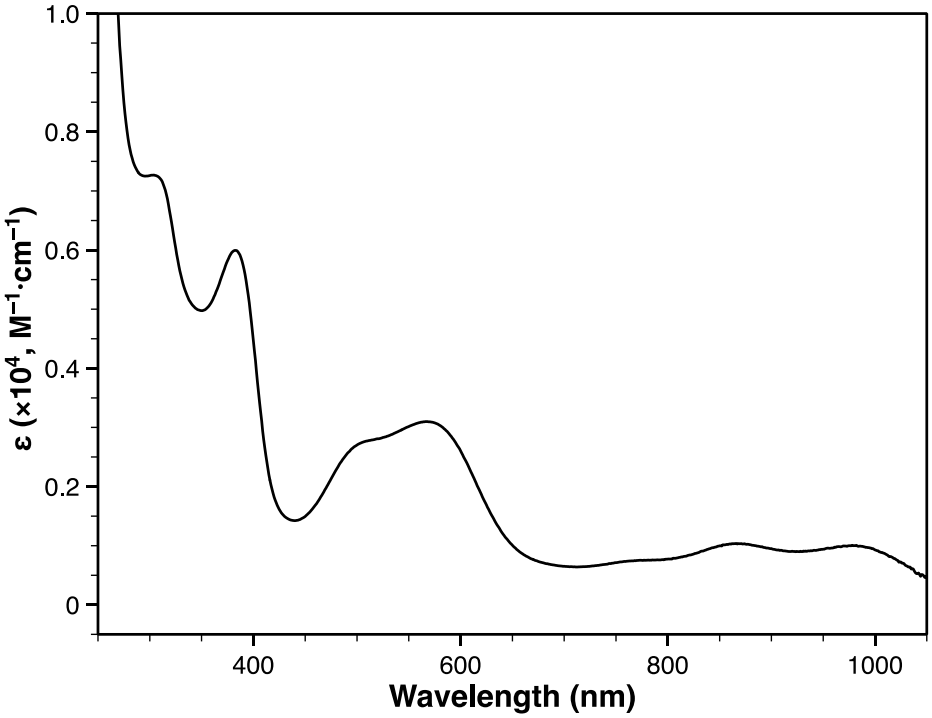



**Figure S35.** Electronic absorption spectrum of **3** in MeCN.

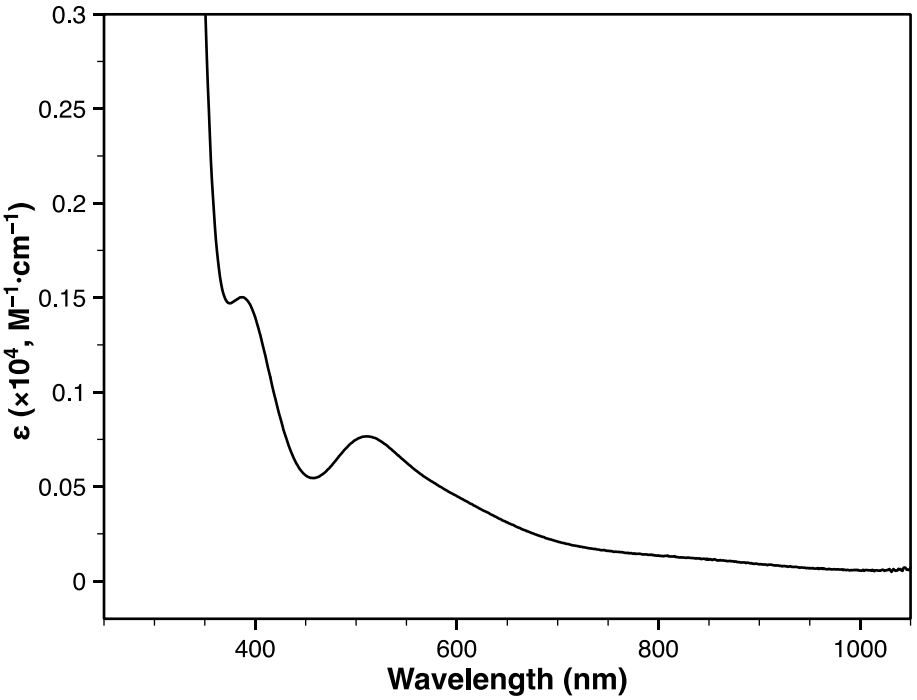



**Figure S36.** Electronic absorption spectrum of **4** in MeCN.

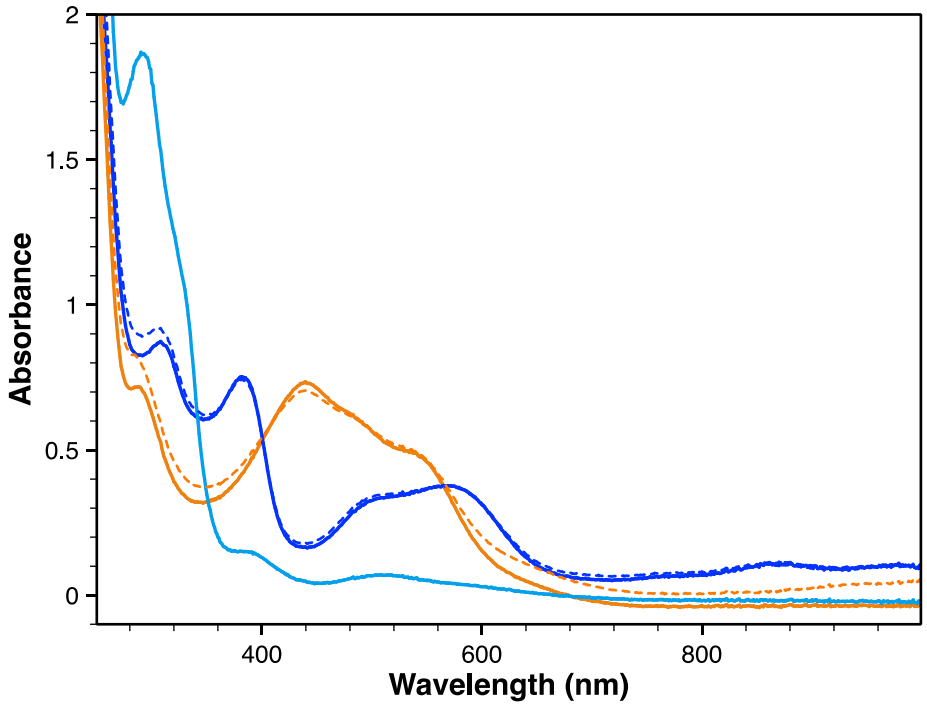



**Figure S37.** UV-vis SEC studies starting with **2** (orange solid trace) and generating **3** (blue solid trace), followed by **4** (cyan trace) in MeCN in 0.2 M [$^{n}$Bu$_4$N][PF$_6$]. The dashed blue and dashed orange traces are from the *in-situ* re-oxidation of **4**.

**Infrared (IR) Spectra**

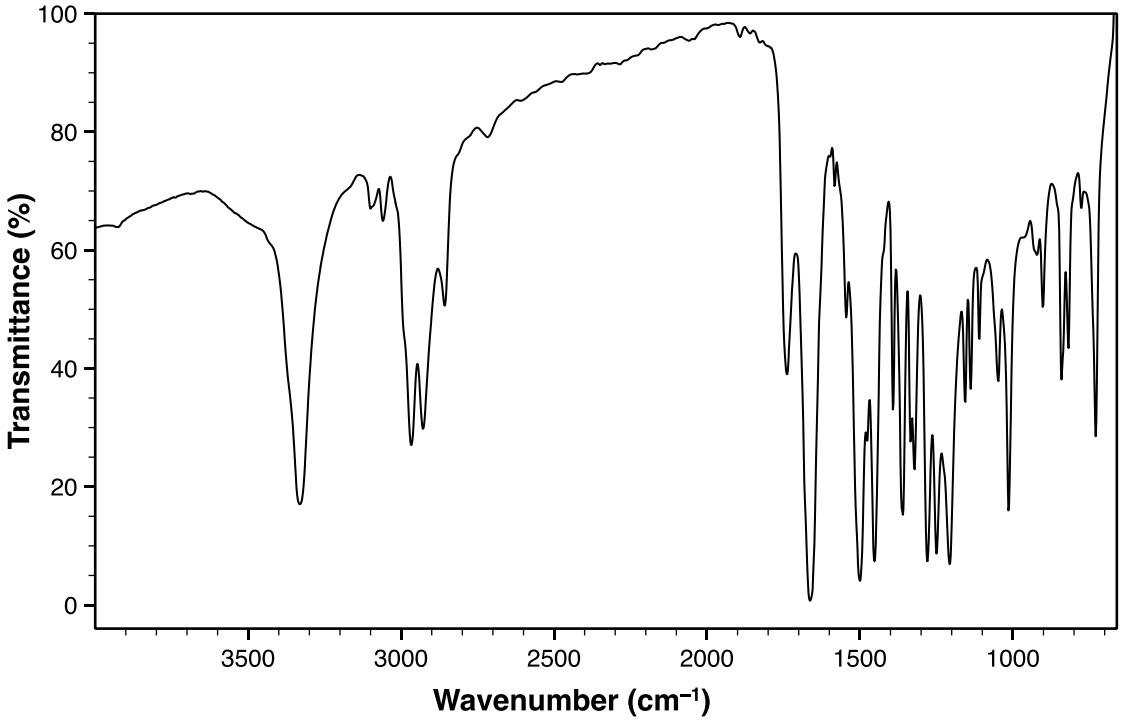



**Figure S38.** IR spectrum of complex **1** (KBr pellet, $cm^{-1}$).

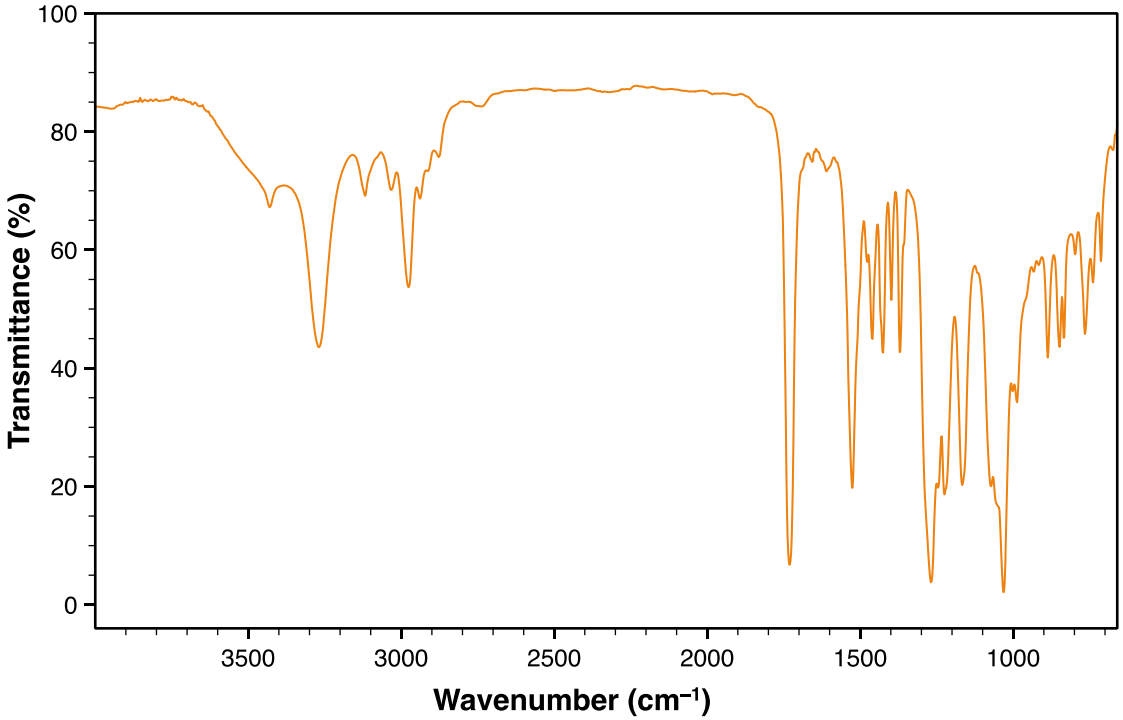



**Figure S39.** IR spectrum of complex **2** (KBr pellet, $cm^{-1}$).

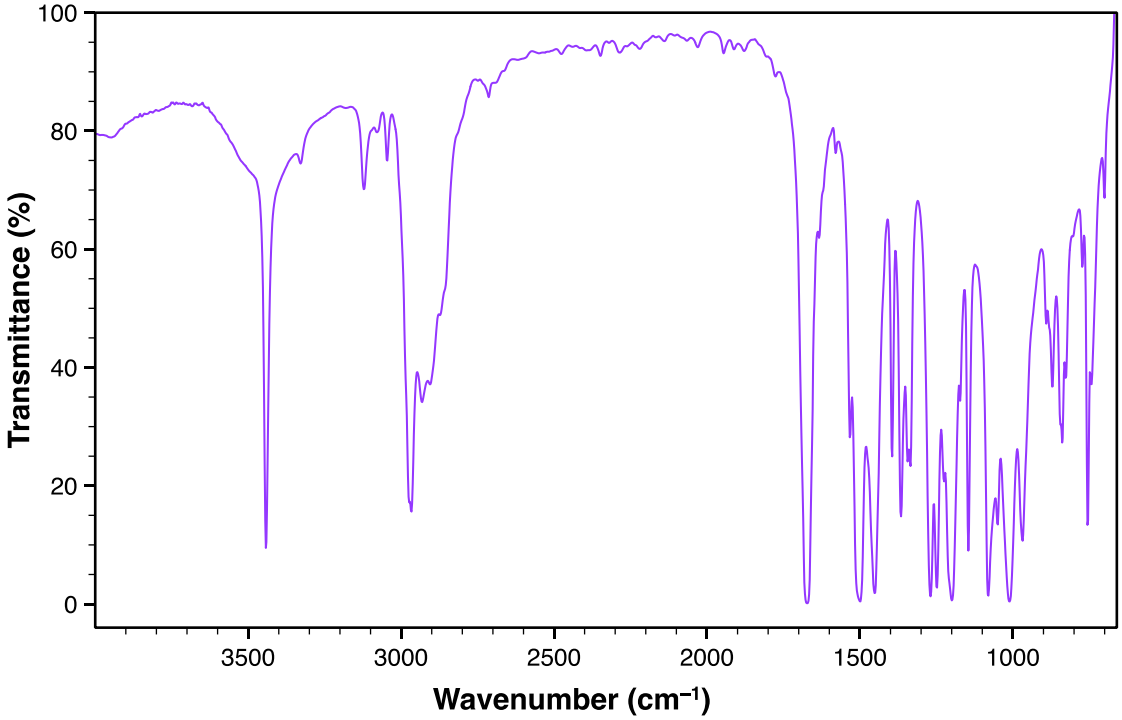



**Figure S40.** IR spectrum of complex **3** (KBr pellet, $cm^{-1}$).

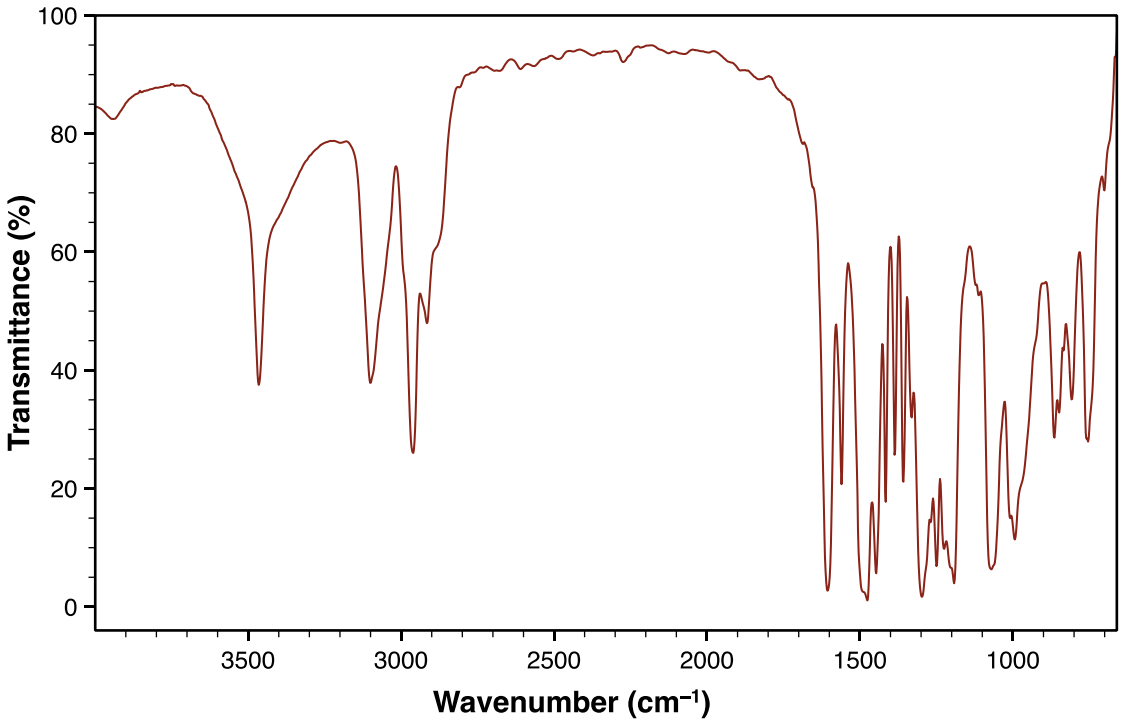



**Figure S41.** IR spectrum of complex **4** (KBr pellet, $cm^{-1}$).

**Table S4.** Characteristic IR stretching frequencies for **1**-**4**.

| Complex | IR Stretch ($cm^{-1}$) | |
|---|---|---|
| | **C=O** | **N−H** |
| **1** | 1663 | 3331 |
| **2** | 1731 | 3269 |
| **3** | 1672 | 3442 |
| **4** | 1606 | 3465 |

## Cyclic Voltammetry Studies

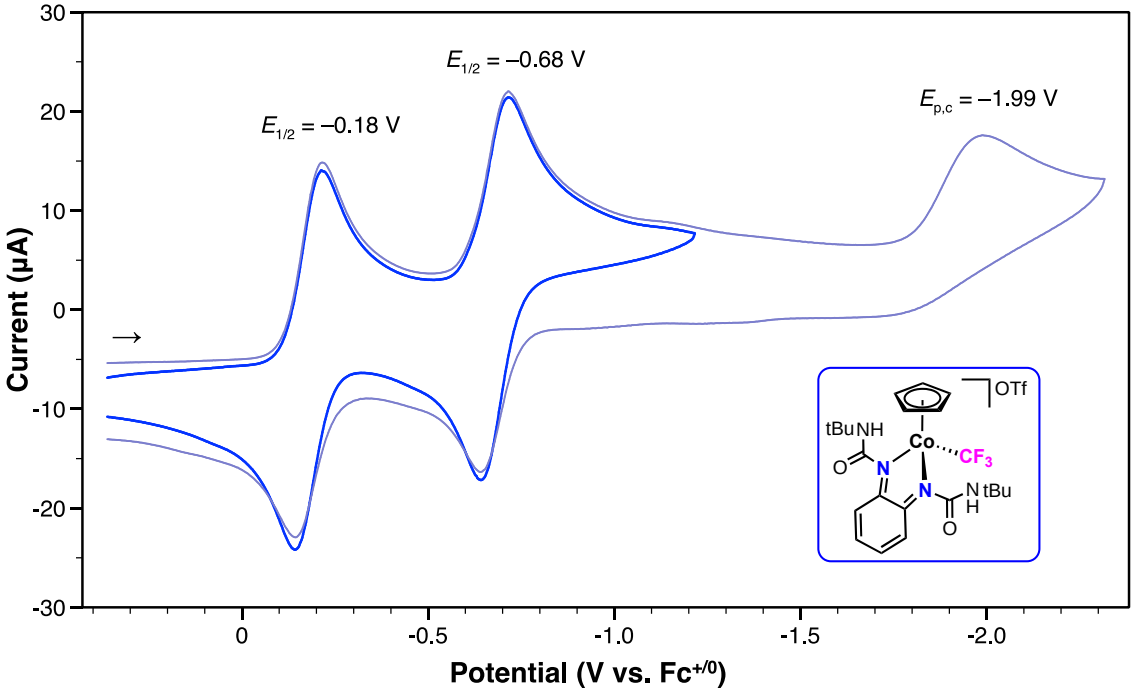



**Figure S42.** CV studies of **2** (1 mM) in MeCN with 0.1 M [$^{n}$Bu$_4$N][PF$_6$] as the supporting electrolyte at 100 mV/s.

**Table S5.** Electrochemical parameters for **2** in MeCN (V versus $Fc^{+/0}$, 0.1 M [$^n$Bu$_4$N][$PF_6$] as the supporting electrolyte).

| $v$ (V/s) | First 1e⁻ Reduction Feature | | | | | Second 1e⁻ Reduction Feature | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $E_{p,a}$ | $E_{p,c}$ | $\Delta E_p$ | $E_{1/2}$ | $i_{p,c}/i_{p,a}$ | $E_{p,a}$ | $E_{p,c}$ | $\Delta E_p$ | $E_{1/2}$ | $i_{p,c}/i_{p,a}$ |
| 0.025 | -0.147 | -0.210 | 0.063 | -0.179 | 1.127 | -0.648 | -0.709 | 0.061 | -0.679 | 0.932 |
| 0.050 | -0.146 | -0.214 | 0.068 | -0.180 | 1.077 | -0.641 | -0.715 | 0.074 | -0.678 | 1.016 |
| 0.100 | -0.142 | -0.213 | 0.071 | -0.178 | 1.056 | -0.641 | -0.716 | 0.075 | -0.679 | 0.988 |
| 0.150 | -0.140 | -0.218 | 0.078 | -0.179 | 1.066 | -0.640 | -0.718 | 0.078 | -0.679 | 1.009 |
| 0.250 | -0.136 | -0.224 | 0.088 | -0.180 | 1.043 | -0.636 | -0.724 | 0.088 | -0.680 | 1.028 |
| 0.400 | -0.128 | -0.228 | 0.100 | -0.178 | 1.027 | -0.632 | -0.731 | 0.099 | -0.682 | 1.029 |
| 0.800 | -0.116 | -0.242 | 0.126 | -0.179 | 0.997 | -0.616 | -0.744 | 0.128 | -0.680 | 1.052 |
| 0.1205 | -0.103 | -0.256 | 0.153 | -0.180 | 0.990 | -0.604 | -0.757 | 0.153 | -0.681 | 1.083 |

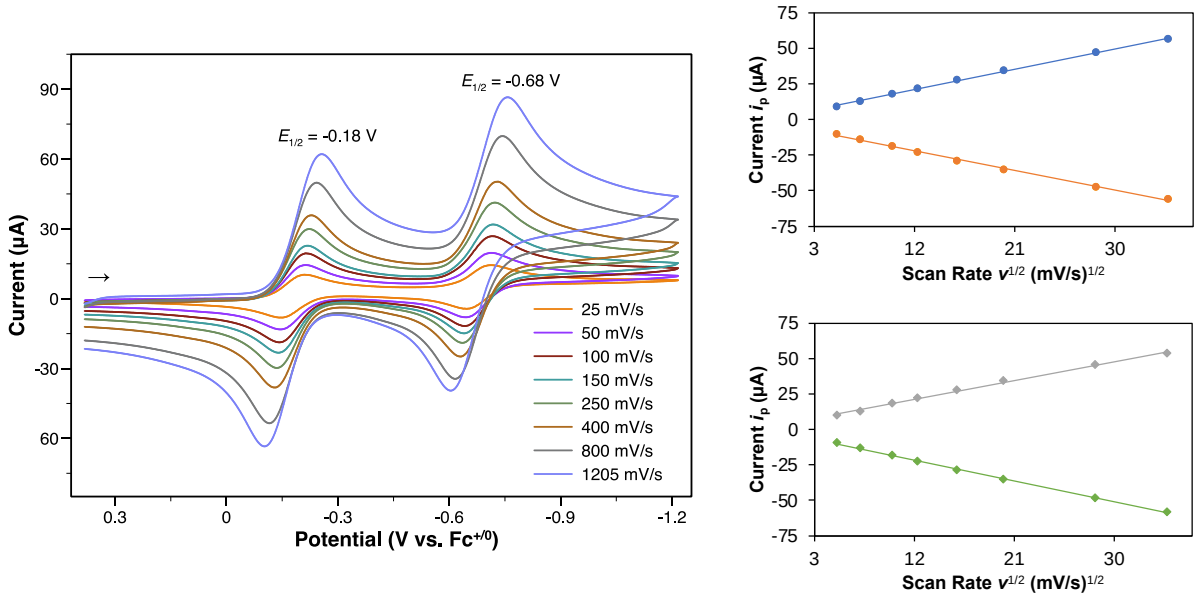



**Figure S43.** *Left*: Cyclic voltammograms for **2** (1 mM) in MeCN with 0.1 M [$^n$Bu$_4$N][$PF_6$] as supporting electrolyte at various scan rates. *Right*: Plots of peak current versus $v^{1/2}$ for the first 1e⁻ reduction (●) and the second 1e⁻ reduction (◆).

## DFT Computational Results

### Calculated Energies of Complexes 5 and 6

**Table S6.** Calculated relative ground-state energies of complex **5**.

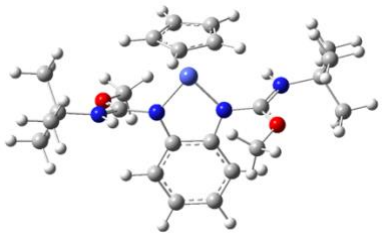
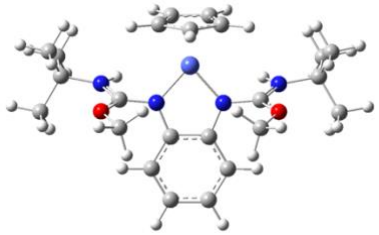
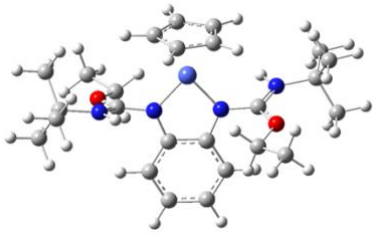
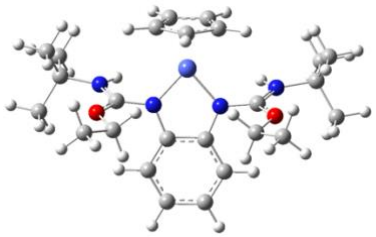
| Complex | Optimized Structure | Relative Energy (kcal/mol) |
|---|---|---|
| **5** (*trans* isomer) |  | –0.241 |
| **5** (*syn* isomer) |  | 0 |

**Table S7.** Calculated relative ground-state energies of complex **6**.

| Complex | Optimized Structure | Relative Energy (kcal/mol) |
|---|---|---|
| **6** (*trans* isomer) |  | –0.011 |
| **6** (*syn* isomer) |  | 0 |

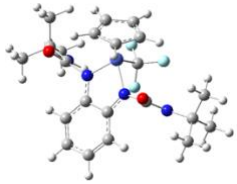
**Optimized Cartesian Coordinates**

For complexes **2**, **3**, and **4**:
*Level of Theory:* BP86 / def2TZVP (C, H, N, O, F) / def2TZVPP (Co) / SMD (MeCN)

For complexes **5** and **6**:
*Level of Theory:* BP86 / def2TZVP (C, H, N) / def2TZVPD (O) / def2TZVPP (Co) / SMD (MeCN)

*Free Energy Calculation in the Solution Phase:* $G_{solv} = G_{gas} + E_{solv} - E_{gas}$

**[CpCo($^{tBuUrea}$bqdi)($CF_3$)]$^+$, 2**

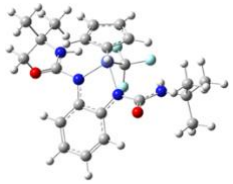


Spin = 0
$E_{gas}$ = -2908.285149 Hartree
$E_{solv}$ = -2908.372153 Hartree
$G_{gas}$ = -2907.878036 Hartree

| | | | |
|---|---|---|---|
| Co | -0.00000100 | -0.94782200 | -0.53246600 |
| F | -1.09749700 | -1.71685300 | 1.93767000 |
| F | 1.09750100 | -1.71685700 | 1.93766500 |
| F | 0.00000600 | 0.16137000 | 2.07664500 |
| O | 3.18387900 | 0.13489300 | -1.75052900 |
| O | -3.18388300 | 0.13491500 | -1.75053000 |
| N | 1.25737900 | 0.47280000 | -0.49782600 |
| N | -1.25738000 | 0.47280300 | -0.49782400 |
| N | 3.36365400 | 0.33853300 | 0.54761300 |
| H | 2.79189200 | 0.43667200 | 1.38439700 |
| N | -3.36365400 | 0.33852700 | 0.54761500 |
| H | -2.79189000 | 0.43665400 | 1.38439900 |
| C | 0.73318000 | 1.69329500 | -0.45984300 |
| C | 1.44055800 | 2.93799900 | -0.45320000 |
| H | 2.53032900 | 2.94385700 | -0.47118000 |
| C | 0.71971600 | 4.10188400 | -0.44942900 |
| H | 1.24208800 | 5.05979100 | -0.45663600 |
| C | -0.71970900 | 4.10188600 | -0.44942900 |
| H | -1.24207900 | 5.05979300 | -0.45663700 |
| C | -1.44055300 | 2.93800200 | -0.45320100 |
| H | -2.53032400 | 2.94386300 | -0.47118100 |
| C | -0.73317800 | 1.69329600 | -0.45984300 |

| | | | |
|---|---|---|---|
| C | 2.71859800 | 0.30227800 | -0.63262600 |
| C | 4.83723700 | 0.13424600 | 0.75097300 |
| C | 5.06808800 | 0.24783300 | 2.26428100 |
| H | 4.77429000 | 1.23960700 | 2.64125200 |
| H | 6.13424300 | 0.10882700 | 2.48689800 |
| H | 4.50782200 | -0.52302200 | 2.81563800 |
| C | 5.61455200 | 1.23149800 | 0.00528000 |
| H | 5.42800800 | 1.18733800 | -1.07555200 |
| H | 6.69227700 | 1.09557300 | 0.17298800 |
| H | 5.33912300 | 2.22959000 | 0.37717400 |
| C | 5.23853500 | -1.26289100 | 0.24936300 |
| H | 4.68986800 | -2.04673500 | 0.79231400 |
| H | 6.31234400 | -1.42097500 | 0.42267100 |
| H | 5.04994300 | -1.36685800 | -0.82735200 |
| C | -2.71860000 | 0.30228500 | -0.63262500 |
| C | -4.83723700 | 0.13424500 | 0.75097400 |
| C | -5.06808600 | 0.24781800 | 2.26428400 |
| H | -4.50782500 | -0.52304700 | 2.81563200 |
| H | -6.13424100 | 0.10881500 | 2.48690100 |
| H | -4.77428200 | 1.23958600 | 2.64126500 |
| C | -5.61454900 | 1.23150800 | 0.00529300 |
| H | -5.33911300 | 2.22959500 | 0.37719600 |
| H | -6.69227400 | 1.09558700 | 0.17300300 |
| H | -5.42800800 | 1.18735600 | -1.07553900 |
| C | -5.23854400 | -1.26288500 | 0.24935100 |
| H | -5.04995300 | -1.36684200 | -0.82736500 |
| H | -6.31235300 | -1.42096500 | 0.42265800 |
| H | -4.68988100 | -2.04673700 | 0.79229300 |
| C | 0.71072700 | -1.81473200 | -2.32135300 |
| H | 1.35867600 | -1.27780100 | -3.00978800 |
| C | -0.71073300 | -1.81473200 | -2.32135200 |
| H | -1.35868200 | -1.27779900 | -3.00978700 |
| C | -1.15722000 | -2.56796500 | -1.17893800 |
| H | -2.19065500 | -2.74189900 | -0.89221300 |
| C | -0.00000300 | -3.05649100 | -0.50125900 |
| H | -0.00000300 | -3.65425800 | 0.40596300 |
| C | 1.15721400 | -2.56796600 | -1.17894000 |
| H | 2.19065000 | -2.74190100 | -0.89221600 |
| C | 0.00000300 | -1.06183000 | 1.45107400 |

**[CpCo($^{tBuUrea}$s-bqdi)($CF_3$)]$^0$, 3**

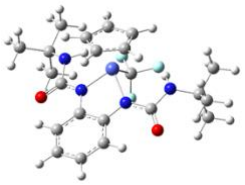


Spin = 1/2
$E_{gas}$ = -2908.503855 Hartree
$E_{solv}$ = -2908.534269 Hartree
$G_{gas}$ = -2908.097646 Hartree

| | | | |
|---|---|---|---|
| Co | 0.00000000 | -0.65657200 | 0.48241100 |
| F | 1.09720700 | -1.83324300 | -1.81672000 |
| F | -1.09720800 | -1.83324300 | -1.81671900 |
| F | -0.00000100 | 0.00018300 | -2.26128900 |
| O | -3.32498400 | 1.38440600 | 1.21324500 |
| O | 3.32498500 | 1.38440700 | 1.21324300 |
| N | -1.28603000 | 0.76468000 | 0.26273400 |
| N | 1.28603000 | 0.76468000 | 0.26273300 |
| N | -3.27998000 | -0.30541900 | -0.34309400 |
| H | -2.67265100 | -0.77635900 | -1.01080900 |
| N | 3.27998000 | -0.30541900 | -0.34309600 |
| H | 2.67265000 | -0.77635900 | -1.01081100 |
| C | -0.72140600 | 1.99786700 | 0.10762700 |
| C | -1.41755200 | 3.21923400 | -0.09387300 |
| H | -2.50533400 | 3.22367300 | -0.07436000 |
| C | -0.70823000 | 4.38987300 | -0.28601300 |
| H | -1.24874000 | 5.32627800 | -0.43652800 |
| C | 0.70822900 | 4.38987300 | -0.28601300 |
| H | 1.24873900 | 5.32627900 | -0.43652900 |
| C | 1.41755100 | 3.21923400 | -0.09387400 |
| H | 2.50533400 | 3.22367300 | -0.07436200 |
| C | 0.72140600 | 1.99786700 | 0.10762700 |
| C | -2.70878000 | 0.66066100 | 0.42885300 |
| C | -4.73445100 | -0.59623000 | -0.41866200 |
| C | -4.88963800 | -1.74590700 | -1.42621700 |
| H | -4.51001200 | -1.45919900 | -2.41918400 |
| H | -5.95126000 | -2.00861700 | -1.53312300 |
| H | -4.34870500 | -2.64519800 | -1.09343900 |
| C | -5.49980900 | 0.64415800 | -0.91925100 |
| H | -5.37686200 | 1.48150200 | -0.22039800 |
| H | -6.57259300 | 0.41513200 | -1.00645100 |

| | | | |
|---|---|---|---|
| H | -5.13161400 | 0.95218400 | -1.90924100 |
| C | -5.26478700 | -1.03200900 | 0.95982000 |
| H | -4.75624800 | -1.94559800 | 1.30430600 |
| H | -6.34147000 | -1.24876100 | 0.89396900 |
| H | -5.11194100 | -0.23927000 | 1.70298000 |
| C | 2.70878000 | 0.66066100 | 0.42885200 |
| C | 4.73445100 | -0.59623000 | -0.41866400 |
| C | 4.88963700 | -1.74590700 | -1.42621900 |
| H | 4.34870400 | -2.64519800 | -1.09344000 |
| H | 5.95125900 | -2.00861700 | -1.53312600 |
| H | 4.51001100 | -1.45920000 | -2.41918600 |
| C | 5.49980900 | 0.64415800 | -0.91925400 |
| H | 5.13161300 | 0.95218300 | -1.90924500 |
| H | 6.57259300 | 0.41513100 | -1.00645500 |
| H | 5.37686200 | 1.48150200 | -0.22040200 |
| C | 5.26478700 | -1.03200800 | 0.95981700 |
| H | 5.11194100 | -0.23926900 | 1.70297800 |
| H | 6.34147000 | -1.24876100 | 0.89396600 |
| H | 4.75624900 | -1.94559700 | 1.30430400 |
| C | -0.70606200 | -1.13549700 | 2.46327400 |
| H | -1.34459200 | -0.46799800 | 3.03658600 |
| C | 0.70606400 | -1.13549700 | 2.46327300 |
| H | 1.34459400 | -0.46799800 | 3.03658500 |
| C | 1.15539300 | -2.09598000 | 1.48813000 |
| H | 2.18867500 | -2.31991300 | 1.24238100 |
| C | 0.00000000 | -2.70672800 | 0.91649300 |
| H | 0.00000000 | -3.46769100 | 0.14123900 |
| C | -1.15539200 | -2.09598000 | 1.48813100 |
| H | -2.18867400 | -2.31991300 | 1.24238200 |
| C | 0.00000000 | -1.06628000 | -1.41618300 |

**[CpCo($^{tBuUrea}$opda)($CF_3$)]$^-$, 4**

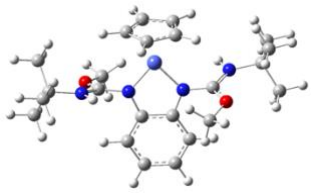


Spin = 0
$E_{gas}$ = -2908.592019 Hartree
$E_{solv}$ = -2908.672541 Hartree
$G_{gas}$ = -2908.185754 Hartree

| | | | |
|---|---|---|---|
| Co | 0.00000100 | -0.38326400 | 0.67022500 |
| F | -0.00000900 | -0.67296800 | -2.14687900 |
| F | -1.08947200 | -2.28333400 | -1.14641100 |
| F | 1.08947200 | -2.28332500 | -1.14641900 |
| O | -3.47677800 | 1.64581500 | -0.49112300 |
| O | 3.47677800 | 1.64581500 | -0.49112700 |
| N | -1.32005600 | 0.91646300 | 0.01662700 |
| N | 1.32005600 | 0.91646300 | 0.01662400 |
| N | -3.14349800 | -0.56563700 | 0.02183700 |
| N | 3.14349900 | -0.56563600 | 0.02184000 |
| H | 2.42385000 | -1.27603700 | -0.09297600 |
| C | -0.71451800 | 2.18975200 | -0.06563500 |
| C | -1.39672700 | 3.42471900 | -0.10732000 |
| H | -2.48154100 | 3.41185000 | -0.11709900 |
| C | -0.69696400 | 4.63419000 | -0.14880500 |
| H | -1.25695400 | 5.57321200 | -0.17972000 |
| C | 0.69696400 | 4.63419000 | -0.14880500 |
| H | 1.25695400 | 5.57321200 | -0.17972000 |
| C | 1.39672600 | 3.42471900 | -0.10732000 |
| H | 2.48154000 | 3.41185000 | -0.11710100 |
| C | 0.71451800 | 2.18975200 | -0.06563500 |
| C | -2.67249200 | 0.74094200 | -0.18460200 |
| C | -4.47441600 | -1.00571200 | -0.45183800 |
| C | -4.54273900 | -2.51997000 | -0.18350000 |
| H | -3.76311100 | -3.05864000 | -0.74459100 |
| H | -5.52142200 | -2.91611500 | -0.49455900 |
| H | -4.40980300 | -2.73228900 | 0.88913100 |
| C | -4.66632000 | -0.74602600 | -1.96267600 |
| H | -4.58866900 | 0.32908800 | -2.16972400 |
| H | -5.65435100 | -1.10521300 | -2.29553100 |
| H | -3.89290200 | -1.27238000 | -2.54263100 |

| | | | |
|---|---|---|---|
| C | -5.58476300 | -0.30500100 | 0.35458300 |
| H | -5.46439500 | -0.51546400 | 1.42897300 |
| H | -6.57414900 | -0.67319400 | 0.03670900 |
| H | -5.53316400 | 0.77983800 | 0.20235500 |
| C | 2.67249200 | 0.74094200 | -0.18460300 |
| C | 4.47441600 | -1.00571200 | -0.45183900 |
| C | 4.54273900 | -2.51997000 | -0.18349800 |
| H | 4.40980600 | -2.73228600 | 0.88913500 |
| H | 5.52142100 | -2.91611600 | -0.49455800 |
| H | 3.76311000 | -3.05864100 | -0.74458500 |
| C | 5.58476500 | -0.30500000 | 0.35457700 |
| H | 5.53316700 | 0.77983900 | 0.20234600 |
| H | 6.57415000 | -0.67319400 | 0.03670100 |
| H | 5.46440100 | -0.51546000 | 1.42896800 |
| C | 4.66631500 | -0.74603000 | -1.96267900 |
| H | 3.89289400 | -1.27238500 | -2.54262900 |
| H | 5.65434400 | -1.10521800 | -2.29553600 |
| H | 4.58866300 | 0.32908400 | -2.16972800 |
| C | -0.00001100 | 0.10965800 | 2.77863200 |
| H | -0.00002300 | 1.13442600 | 3.13870800 |
| C | 1.14908800 | -0.66770400 | 2.44312900 |
| H | 2.18318600 | -0.33876000 | 2.49401700 |
| C | 0.71836100 | -1.92178100 | 1.91960100 |
| H | 1.36021600 | -2.72952500 | 1.57936100 |
| C | -0.71833300 | -1.92179700 | 1.91959700 |
| H | -1.36016800 | -2.72955300 | 1.57935000 |
| C | -1.14909100 | -0.66772900 | 2.44312000 |
| H | -2.18319700 | -0.33880900 | 2.49400300 |
| C | -0.00000200 | -1.39424900 | -0.99536300 |
| H | -2.42385100 | -1.27603900 | -0.09297600 |

**5** (*trans* isomer)

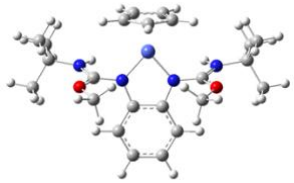


Spin = 0
$E_{gas}$ = -2650.006089 Hartree
$E_{solv}$ = -2650.244576 Hartree
$G_{gas}$ = -2649.534442 Hartree

| | | | |
|---|---|---|---|
| Co | -0.01232000 | -1.03759800 | -0.01391100 |
| N | -3.43862400 | -0.07388600 | -0.52921200 |
| H | -3.01515600 | -0.14383900 | -1.45477600 |
| C | 0.71966500 | 1.66200400 | -0.10577400 |
| C | 1.43288200 | 2.87609100 | -0.17895400 |
| H | 2.51953300 | 2.88043800 | -0.28827100 |
| C | 0.73681100 | 4.07496600 | -0.09721900 |
| H | 1.28067400 | 5.01862200 | -0.15273100 |
| C | -0.66696300 | 4.08775400 | 0.05592400 |
| H | -1.19403200 | 5.04107400 | 0.10808800 |
| C | -1.38399500 | 2.90160300 | 0.14087800 |
| H | -2.47047600 | 2.92465900 | 0.24967100 |
| C | -0.69190800 | 1.67521600 | 0.07078400 |
| N | 1.24185500 | 0.37482200 | -0.15477900 |
| C | 2.59842100 | 0.23709100 | -0.42468300 |
| N | 3.43252000 | -0.09605500 | 0.54114700 |
| H | 2.99271000 | -0.15831900 | 1.45967000 |
| C | 4.93867800 | -0.32449800 | 0.51378700 |
| C | 5.30340600 | -0.69359300 | 1.95885600 |
| H | 4.79783300 | -1.61608300 | 2.28345800 |
| H | 5.05866700 | 0.11999500 | 2.65895500 |
| H | 6.38436800 | -0.87039900 | 2.02752200 |
| C | 5.64200900 | 0.97688200 | 0.09793000 |
| H | 6.72843000 | 0.82452500 | 0.15793200 |
| H | 5.38351200 | 1.80338900 | 0.77523200 |
| H | 5.40428500 | 1.26553600 | -0.93365100 |
| C | 5.27060000 | -1.48197200 | -0.43912300 |
| H | 6.35486900 | -1.65749800 | -0.41316100 |
| H | 4.99709900 | -1.25926500 | -1.47800600 |
| H | 4.78056500 | -2.41522100 | -0.12485300 |
| O | 3.10524400 | 0.41214800 | -1.62562200 |

| | | | |
|---|---|---|---|
| C | 2.25344300 | 0.74391400 | -2.76934100 |
| H | 2.86092200 | 0.49520200 | -3.64411600 |
| H | 2.02638000 | 1.81643400 | -2.74958600 |
| H | 1.33405100 | 0.14800400 | -2.74074700 |
| N | -1.23610900 | 0.39821800 | 0.12320600 |
| C | -2.58838100 | 0.27410700 | 0.41682900 |
| C | -4.94258200 | -0.30748800 | -0.47116200 |
| C | -5.64484800 | 0.99980000 | -0.07220400 |
| H | -6.73140200 | 0.84042700 | -0.10589000 |
| H | -5.40493400 | 1.81138000 | -0.77393800 |
| H | -5.38718200 | 1.31418400 | 0.94700100 |
| C | -5.25146300 | -1.44564000 | 0.51234000 |
| H | -6.33264100 | -1.64011000 | 0.49513500 |
| H | -4.97939800 | -1.18979200 | 1.54403200 |
| H | -4.74390900 | -2.37666700 | 0.22086100 |
| C | -5.33067200 | -0.70967000 | -1.90125000 |
| H | -6.41273900 | -0.88666200 | -1.94857800 |
| H | -4.83186700 | -1.64033500 | -2.21277200 |
| H | -5.09653000 | 0.08698000 | -2.62413200 |
| O | -3.07602400 | 0.47584200 | 1.62215300 |
| C | -2.20173200 | 0.80060200 | 2.75057900 |
| H | -2.81251500 | 0.60035900 | 3.63543000 |
| H | -1.92782900 | 1.86120900 | 2.70278800 |
| H | -1.30975400 | 0.16367200 | 2.73173500 |
| C | 0.33384100 | -2.71871200 | -1.16742000 |
| H | 0.66641500 | -2.73111900 | -2.20269700 |
| C | 1.17568600 | -2.72226500 | -0.00767600 |
| H | 2.26260700 | -2.72915800 | -0.01497600 |
| C | 0.34448800 | -2.70210100 | 1.15663700 |
| H | 0.68193700 | -2.69754700 | 2.19041500 |
| C | -1.01797800 | -2.67727500 | 0.71489000 |
| H | -1.89450800 | -2.65473200 | 1.35843000 |
| C | -1.02357900 | -2.68984700 | -0.71894600 |
| H | -1.90357300 | -2.68161400 | -1.35676800 |

**5** (*syn* isomer)

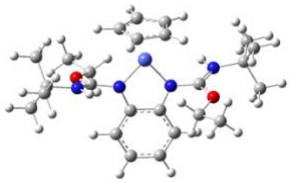


Spin = 0
$E_{gas}$ = -2650.006300 Hartree
$E_{solv}$ = -2650.244632 Hartree
$G_{gas}$ = -2649.534212 Hartree

| | | | |
|---|---|---|---|
| Co | 0.00000000 | -0.98254800 | 0.32648400 |
| C | -0.71151900 | 1.68540200 | -0.12124800 |
| C | -1.41757300 | 2.88217300 | -0.35989700 |
| H | -2.50920100 | 2.89030000 | -0.39253000 |
| C | -0.70604000 | 4.05479700 | -0.57712300 |
| H | -1.24415200 | 4.98471700 | -0.76426600 |
| C | 0.70603500 | 4.05479800 | -0.57712500 |
| H | 1.24414600 | 4.98471900 | -0.76426900 |
| C | 1.41757000 | 2.88217500 | -0.35990000 |
| H | 2.50919800 | 2.89030300 | -0.39253400 |
| C | 0.71151800 | 1.68540300 | -0.12124900 |
| N | -1.24588600 | 0.41741800 | 0.07283500 |
| C | -2.62655100 | 0.29428600 | 0.16724600 |
| N | -3.30639100 | -0.24071300 | -0.82789100 |
| H | -2.73482200 | -0.45219600 | -1.64625100 |
| C | -4.79741300 | -0.51504900 | -0.97401800 |
| C | -4.94112700 | -1.16341300 | -2.35840100 |
| H | -4.38899500 | -2.11363500 | -2.42248300 |
| H | -4.59860100 | -0.48987100 | -3.15900300 |
| H | -5.99899700 | -1.38571100 | -2.54796000 |
| C | -5.56643500 | 0.81428100 | -0.92177100 |
| H | -6.63082400 | 0.61275600 | -1.10506700 |
| H | -5.21888500 | 1.50662100 | -1.70182500 |
| H | -5.48520100 | 1.30185900 | 0.05785800 |
| C | -5.25533200 | -1.48409500 | 0.12570100 |
| H | -6.31898400 | -1.71211900 | -0.02835200 |
| H | -5.15338700 | -1.05352700 | 1.12980800 |
| H | -4.70452700 | -2.43477300 | 0.07717000 |
| O | -3.30800900 | 0.67872300 | 1.22538100 |
| C | -2.63390500 | 1.21630900 | 2.40766400 |
| H | -3.38571600 | 1.15973000 | 3.19994100 |

| | | | |
|---|---|---|---|
| H | -2.34821400 | 2.25831600 | 2.22076800 |
| H | -1.75677600 | 0.60552300 | 2.65054500 |
| N | 1.24588700 | 0.41742000 | 0.07283400 |
| C | 2.62655100 | 0.29428900 | 0.16724500 |
| C | 0.00000300 | -2.39404000 | 1.83994000 |
| H | 0.00000500 | -2.18844100 | 2.90784200 |
| C | -1.15529200 | -2.54523000 | 1.00889000 |
| H | -2.18888000 | -2.47542700 | 1.33993000 |
| C | -0.71526900 | -2.79978100 | -0.33189100 |
| H | -1.35072900 | -2.96670500 | -1.19805500 |
| C | 0.71526700 | -2.79978100 | -0.33189400 |
| H | 1.35072300 | -2.96670600 | -1.19806100 |
| C | 1.15529500 | -2.54523100 | 1.00888500 |
| H | 2.18888400 | -2.47542700 | 1.33992100 |
| O | 3.30801000 | 0.67873000 | 1.22537700 |
| C | 2.63390600 | 1.21631700 | 2.40766000 |
| H | 2.34821300 | 2.25832400 | 2.22076300 |
| H | 1.75677700 | 0.60553100 | 2.65054300 |
| H | 3.38571700 | 1.15974000 | 3.19993700 |
| N | 3.30639100 | -0.24071300 | -0.82789100 |
| H | 2.73482200 | -0.45219900 | -1.64625100 |
| C | 4.79741400 | -0.51504900 | -0.97401700 |
| C | 4.94112700 | -1.16341800 | -2.35839800 |
| H | 5.99899800 | -1.38571700 | -2.54795600 |
| H | 4.38899600 | -2.11364000 | -2.42247700 |
| H | 4.59860100 | -0.48987900 | -3.15900200 |
| C | 5.56643600 | 0.81428000 | -0.92177400 |
| H | 5.21888600 | 1.50661800 | -1.70183000 |
| H | 5.48520100 | 1.30186100 | 0.05785300 |
| H | 6.63082500 | 0.61275400 | -1.10506900 |
| C | 5.25533200 | -1.48409200 | 0.12570500 |
| H | 5.15338700 | -1.05352200 | 1.12981100 |
| H | 4.70452700 | -2.43477000 | 0.07717700 |
| H | 6.31898500 | -1.71211700 | -0.02834600 |

**6** (*trans* isomer)

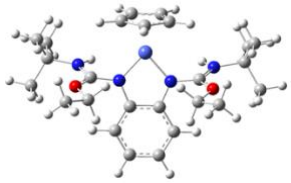


Spin = 0
$E_{gas}$ = -2728.672483 Hartree
$E_{solv}$ = -2728.908468 Hartree
$G_{gas}$ = -2728.150737 Hartree

| | | | |
|---|---|---|---|
| Co | -0.00752400 | -1.07324800 | -0.00154500 |
| N | -3.37081800 | -0.13212400 | -0.85803200 |
| H | -2.85281700 | -0.21403100 | -1.73306300 |
| C | 0.71634500 | 1.62562900 | -0.08757300 |
| C | 1.42774900 | 2.84287600 | -0.12534500 |
| H | 2.51970100 | 2.85113300 | -0.13932100 |
| C | 0.72185700 | 4.03847800 | -0.13428100 |
| H | 1.26412200 | 4.98422100 | -0.16390600 |
| C | -0.69026700 | 4.04549200 | -0.10717700 |
| H | -1.22408000 | 4.99631800 | -0.12505500 |
| C | -1.40668800 | 2.85718500 | -0.05806300 |
| H | -2.49855300 | 2.87531900 | -0.04577200 |
| C | -0.70606600 | 1.63328900 | -0.03718300 |
| N | 1.24460500 | 0.34252800 | -0.06224300 |
| C | 2.62522100 | 0.20335400 | -0.18386200 |
| N | 3.34256700 | -0.09216000 | 0.88467900 |
| H | 2.79743100 | -0.12962700 | 1.74612300 |
| C | 4.84026600 | -0.30934900 | 1.04167100 |
| C | 5.03711900 | -0.61553200 | 2.53339600 |
| H | 4.49929400 | -1.52733600 | 2.83561200 |
| H | 4.71072900 | 0.22455000 | 3.16559000 |
| H | 6.10328300 | -0.78163100 | 2.73386300 |
| C | 5.58492200 | 0.97820000 | 0.65608200 |
| H | 6.65791600 | 0.83547300 | 0.84431400 |
| H | 5.24955400 | 1.82946900 | 1.26564500 |
| H | 5.46343900 | 1.22364800 | -0.40633000 |
| C | 5.28410100 | -1.50332900 | 0.18395900 |
| H | 6.35868900 | -1.66972800 | 0.34117600 |
| H | 5.13041100 | -1.32529400 | -0.88765800 |
| H | 4.76294200 | -2.42557900 | 0.48018800 |
| O | 3.25666500 | 0.33937600 | -1.32465300 |

| | | | |
|---|---|---|---|
| C | 2.52560100 | 0.62808200 | -2.59242400 |
| H | 2.18785300 | 1.67159100 | -2.53240700 |
| H | 1.65198500 | -0.03701200 | -2.62446000 |
| N | -1.24636300 | 0.35559500 | -0.00031700 |
| C | -2.62317800 | 0.23209000 | 0.16758300 |
| C | -4.87102700 | -0.36437800 | -0.95465800 |
| C | -5.60900800 | 0.95029800 | -0.65745200 |
| H | -6.68707600 | 0.79017200 | -0.79633400 |
| H | -5.29785300 | 1.74664900 | -1.34861000 |
| H | -5.45300000 | 1.28638000 | 0.37532300 |
| C | -5.28629700 | -1.48296700 | 0.01199600 |
| H | -6.35962200 | -1.67864600 | -0.11733200 |
| H | -5.12437100 | -1.20592000 | 1.06096200 |
| H | -4.75115700 | -2.41918700 | -0.20364500 |
| C | -5.10809500 | -0.79418400 | -2.40964200 |
| H | -6.17977600 | -0.97015900 | -2.56769100 |
| H | -4.58228100 | -1.73137700 | -2.64885700 |
| H | -4.79555700 | -0.01241400 | -3.11905400 |
| O | -3.22351400 | 0.45002700 | 1.31317200 |
| C | -2.45695800 | 0.79980400 | 2.54328800 |
| H | -2.08954400 | 1.82603300 | 2.40787400 |
| H | -1.60301600 | 0.11106200 | 2.60312700 |
| C | 0.28986000 | -2.77354800 | -1.14288500 |
| H | 0.56309000 | -2.80004000 | -2.19501600 |
| C | 1.19567000 | -2.74454600 | -0.03294100 |
| H | 2.28068900 | -2.74035700 | -0.10146300 |
| C | 0.43060500 | -2.71058000 | 1.17668200 |
| H | 0.82517200 | -2.68571800 | 2.18963800 |
| C | -0.95461000 | -2.70909700 | 0.81354900 |
| H | -1.79460000 | -2.68590500 | 1.50378700 |
| C | -1.03900400 | -2.74920500 | -0.61757200 |
| H | -1.95468100 | -2.75852300 | -1.20261900 |
| C | -3.40326500 | 0.67489500 | 3.71273800 |
| H | -2.86091400 | 0.94996600 | 4.62926500 |
| H | -4.25877700 | 1.35578000 | 3.61324700 |
| H | -3.77192300 | -0.35251300 | 3.83281300 |
| C | 3.49053400 | 0.39726700 | -3.72991500 |
| H | 2.97510200 | 0.62628600 | -4.67424100 |
| H | 4.36463900 | 1.05764800 | -3.65752700 |
| H | 3.82925100 | -0.64644200 | -3.77305400 |

**6** (*syn* isomer)



Spin = 0
$E_{gas}$ = -2728.672719 Hartree
$E_{solv}$ = -2728.908589 Hartree
$G_{gas}$ = -2728.150835 Hartree

| | | | |
|---|---|---|---|
| Co | 0.00000000 | -0.99189300 | 0.39014400 |
| C | -0.71188900 | 1.47752000 | -0.70788900 |
| C | -1.41777900 | 2.57761300 | -1.23752100 |
| H | -2.50941800 | 2.57802300 | -1.26840100 |
| C | -0.70618300 | 3.65809600 | -1.74152900 |
| H | -1.24411700 | 4.51203800 | -2.15475500 |
| C | 0.70618500 | 3.65809600 | -1.74152900 |
| H | 1.24412100 | 4.51203700 | -2.15475400 |
| C | 1.41778100 | 2.57761200 | -1.23751900 |
| H | 2.50942000 | 2.57802200 | -1.26839700 |
| C | 0.71188900 | 1.47751900 | -0.70788800 |
| N | -1.24476800 | 0.30019900 | -0.20227700 |
| C | -2.62924200 | 0.19560600 | -0.09708400 |
| N | -3.28472100 | -0.56083500 | -0.95784300 |
| H | -2.69193700 | -0.95365700 | -1.68947600 |
| C | -4.76979800 | -0.86884300 | -1.07383500 |
| C | -4.88087800 | -1.81485200 | -2.27819300 |
| H | -4.32764100 | -2.75197400 | -2.11193100 |
| H | -4.51808700 | -1.33868800 | -3.20209200 |
| H | -5.93392100 | -2.07965900 | -2.43770200 |
| C | -5.54031000 | 0.43316500 | -1.34301800 |
| H | -6.60078300 | 0.19068000 | -1.49705600 |
| H | -5.17580200 | 0.93031300 | -2.25330800 |
| H | -5.47815900 | 1.13208600 | -0.49952900 |
| C | -5.25551900 | -1.56596200 | 0.20529800 |
| H | -6.31513200 | -1.82894700 | 0.08224300 |
| H | -5.17634800 | -0.91749900 | 1.08675800 |
| H | -4.70285700 | -2.49926700 | 0.38692800 |
| O | -3.32455600 | 0.80686700 | 0.83211100 |
| C | -2.66374000 | 1.62664700 | 1.88701000 |
| H | -2.28561200 | 2.53364100 | 1.39604400 |

| | | | |
|---|---|---|---|
| H | -1.81878700 | 1.04048100 | 2.27358500 |
| N | 1.24476800 | 0.30019900 | -0.20227600 |
| C | 2.62924200 | 0.19560500 | -0.09708300 |
| C | -0.00000200 | -1.98931700 | 2.20341300 |
| H | -0.00000300 | -1.52798900 | 3.18810900 |
| C | -1.15520400 | -2.33933100 | 1.43462200 |
| H | -2.18895600 | -2.19034000 | 1.73767400 |
| C | -0.71513800 | -2.91531900 | 0.19721800 |
| H | -1.35111500 | -3.28915400 | -0.60127000 |
| C | 0.71514100 | -2.91531800 | 0.19722000 |
| H | 1.35112000 | -3.28915200 | -0.60126600 |
| C | 1.15520300 | -2.33932900 | 1.43462500 |
| H | 2.18895400 | -2.19033700 | 1.73768000 |
| O | 3.32455600 | 0.80686300 | 0.83211400 |
| C | 2.66373800 | 1.62664200 | 1.88701500 |
| H | 2.28561400 | 2.53363800 | 1.39604900 |
| H | 1.81878300 | 1.04047700 | 2.27358600 |
| N | 3.28472100 | -0.56083300 | -0.95784300 |
| H | 2.69193700 | -0.95365300 | -1.68947800 |
| C | 4.76979800 | -0.86884100 | -1.07383600 |
| C | 4.88087800 | -1.81484600 | -2.27819700 |
| H | 5.93392100 | -2.07965100 | -2.43770700 |
| H | 4.32764200 | -2.75196900 | -2.11193800 |
| H | 4.51808700 | -1.33868000 | -3.20209500 |
| C | 5.54030900 | 0.43316900 | -1.34301600 |
| H | 5.17580100 | 0.93031900 | -2.25330400 |
| H | 5.47815800 | 1.13208800 | -0.49952500 |
| H | 6.60078300 | 0.19068500 | -1.49705500 |
| C | 5.25552000 | -1.56596200 | 0.20529400 |
| H | 5.17634900 | -0.91750200 | 1.08675600 |
| H | 4.70285800 | -2.49926800 | 0.38692200 |
| H | 6.31513300 | -1.82894700 | 0.08223900 |
| C | 3.70460400 | 1.92964300 | 2.93756400 |
| H | 4.54854400 | 2.49262500 | 2.51777200 |
| H | 3.24135700 | 2.55210200 | 3.71716600 |
| H | 4.08213800 | 1.01524800 | 3.41421000 |
| C | -3.70460700 | 1.92965300 | 2.93755700 |
| H | -3.24136100 | 2.55211300 | 3.71715900 |
| H | -4.54854500 | 2.49263600 | 2.51776100 |
| H | -4.08214400 | 1.01526000 | 3.41420500 |

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