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SUPPORTING INFORMATION

Title: Preparation and Oxygenation of Cobalt N-Confused Porphyrin Nitrosyl Complexes
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Ref. No.: I200701072

X-ray Analysis of the Structures of [Co(*H*CTPP)] (1), [Co(CTPP*C*$_2$*H*$_2$*Cl*)(NO)] (2) and [Co(CTPP*O*)(NO)] (3). Diffraction measurements were carried out at 150 (1) K on a Bruker SMART 1000 or Apex CCD area-detector diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.7107 Å). Calculations for the structure were performed using SHELXS-97[1] and SHELXL-97[2]. The structures were solved via direct method. Least-squares refinement of the positional and anisotropic thermal parameters for the contribution of all non-hydrogen atoms and fixed hydrogen atoms was based on F^2. A SADABS[3] absorption correction was made.

[Co(*H*CTPP)]: The crystal suitable for structure analysis with the dimensions of 0.16 × 0.11 × 0.10 mm^3 was grown from the CH_2Cl_2 solution of [Co(*H*CTPP)] which was saturated by slowly diffusion of hexane vapor into the solution in an inner atmosphere dry-box. [Co(*H*CTPP)] crystallized in monoclinic unit cell, space group $P2_1/c$, a =12.9892(16) Å, b = 11.4914(15) Å, c = 11.1816(14) Å, β =105.820(2)°, V = 1605.8 (4) Å^3, Z = 2, D_c = 1.389 Mg/m^{-3}, μ= 0.574 mm^{-1}, F(000) = 694. Diffraction data were collected for 1.63 < θ < 27.52°. The structure was solved by direct method and refined by least square against F^2 to R_1 = 0.0497 (wR_2 = 0.0745) and S_{goof} = 0.970. All hydrogen atoms are added with a fixed distance by the SHELX-97 program. The molecule sits on the special position and half of the molecule was generated from symmetry. The atoms of N(2) and C(7) were refined as mutual disorder with 50% occupancy on each site. The coordinates and thermal parameters were defined identical on the carbon and nitrogen sharing the same site.

[Co(CTPP*C*$_2$*H*$_2$*Cl*)(NO)]: The crystal suitable for structure analysis measured 0.30 × 0.20 × 0.12 mm^3 was grown from the toluene solution of [Co(CTPP*C*$_2$*H*$_2$*Cl*)(NO)] and diffused with hexane in an inner atmosphere dry-box. [Co(CTPP*C*$_2$*H*$_2$*Cl*)(NO)] crystallized in triclinic unit cell, space group $P\bar{1}$, a =11.0864(10) Å, b = 13.4384(13) Å, c = 15.3029(15) Å, α = 76.156(2)°, β =85.562(2)°, γ = 68.614(2)° V = 2061.2 (3) Å^3, Z = 2, D_c = 1.376 Mg/m^{-3}, μ= 0.529 mm^{-1}, F(000) = 884. Data were collected for 1.37 < θ < 27.67°. The structure was solved by direct method and refined by least square against F^2 to R_1 = 0.0669 (wR_2 = 0.1247) and S_{goof} = 1.073. All hydrogen atoms are added with a fixed distance by the SHELX-97 program. The atoms of N(4) and C(17) which located at the β-positions of the inverted pyrrole ring were refined as mutually disorder with 50% occupancy on each site. The coordinates and thermal parameters were defined identical on the carbon and nitrogen sharing the same site. The oxygen atom of NO was disorder into two positions with 50% occupancy. The *meso*-phenyl ring on C(15) was also found to disorder into two positions. Two disordered toluenes were located as solvated molecules.

[Co(CTPP*O*)(NO)]: The crystal suitable for structure analysis measured 0.14 × 0.10 × 0.08 mm^3 was grown from the toluene solution of [Co(CTPP*O*)(NO)] and diffused with hexane in an inner atmosphere dry-box. [Co(CTPP*O*)(NO)] crystallized in monoclinic unit cell, space group $C2/c$, a =33.353(2) Å, b = 13.1185(9) Å, c = 17.9949(12) Å, β =94.013(2)°, V = 7854.3 (9) Å^3, Z = 8, D_c = 1.369 Mg/m^{-3}, μ=

0.487 mm^{-1}, $F(000)$ = 3352. Diffraction data were collected for $1.22 < \theta < 27.52°$. The structure was solved by direct method and refined by least square against F^2 to $R_1 = 0.0540$ ($wR_2 = 0.1169$) and $S_{goof} = 1.007$. All hydrogen atoms are added with a fixed distance by the SHELX-97 program. The atoms of N(4) and C(1) which located at the β-positions of the inverted pyrrole ring were refined as mutually disorder with 50% occupancy on each site. The coordinates and thermal parameters were defined identical on the carbon and nitrogen sharing the same site. Two disordered toluenes were located as solvated molecules and were refined isotropically.

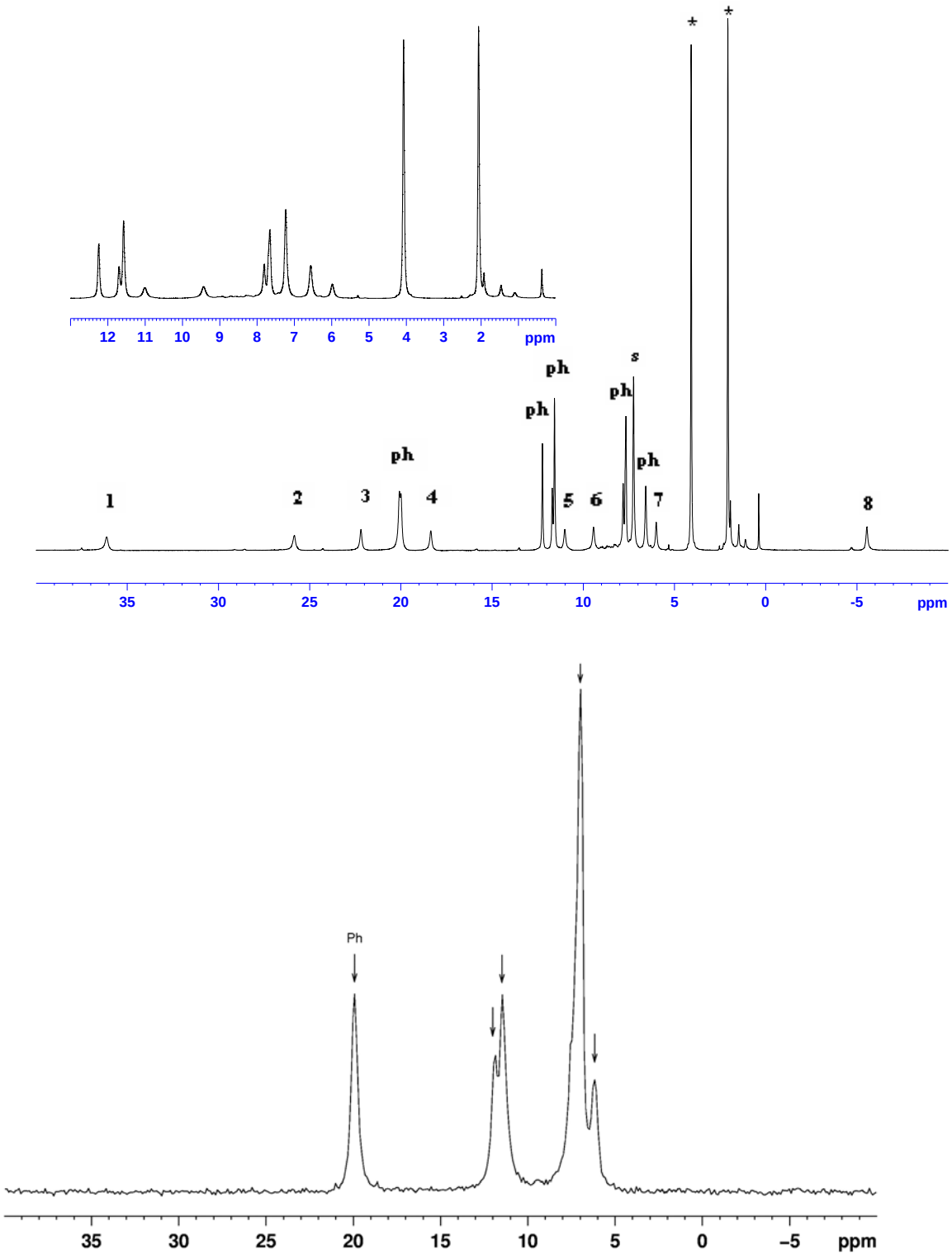

Figure S1. ^{1}H NMR spectrum of [Co(*H*CTPP)] (**1**) in $CDCl_3$ (upper) and ^{2}H NMR spectrum for the *meso*-C_6D_5 substituted [Co(*H*CTPP-d_{20})] in C_6D_6 (lower). The number in the upper panel denoted the peripheral protons of the N-confused porphyrin macrocycle and the asterisk marks denoted resonances from solvated THF

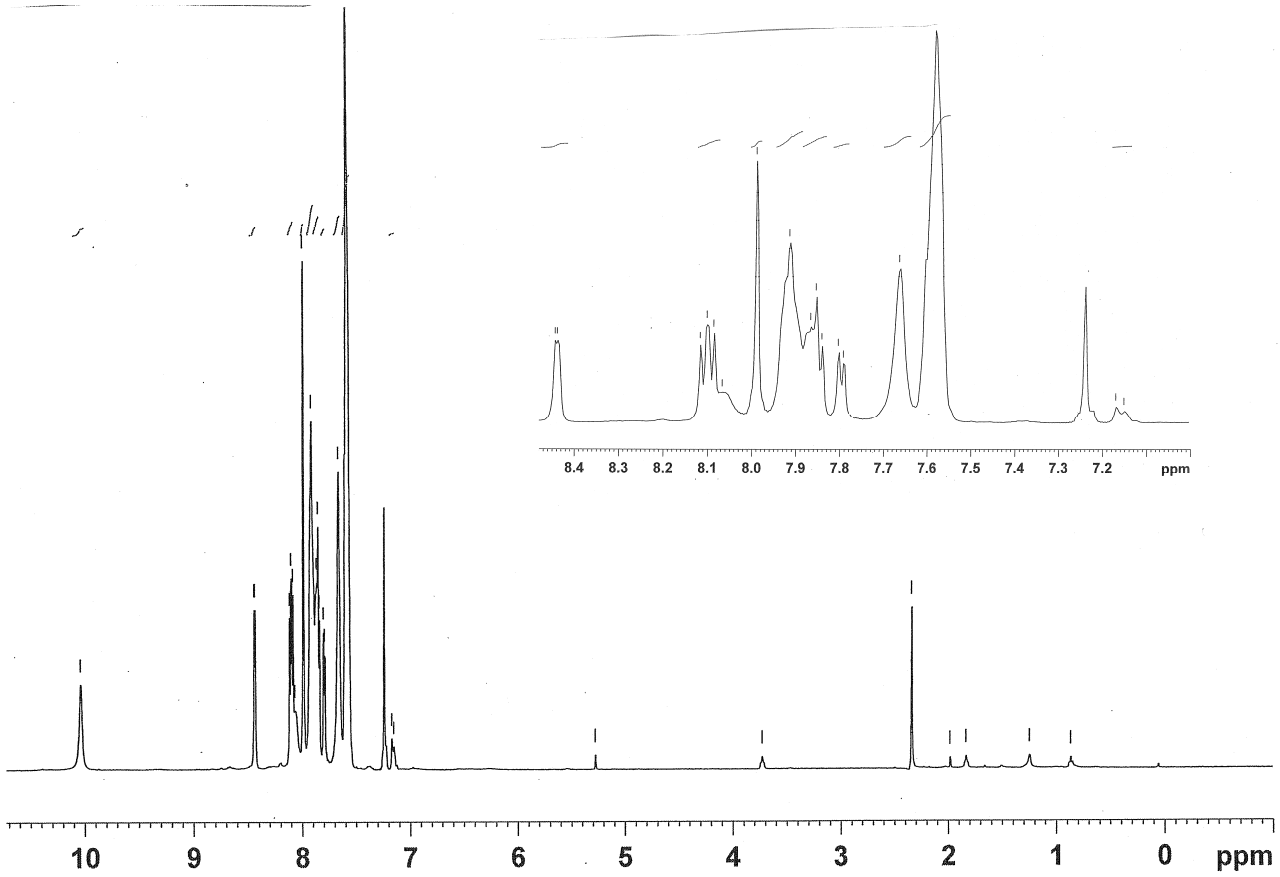

Figure S2. ^{1}H NMR spectrum of [Co(CTPPC_2H_2Cl)(NO)] (**2**) in $CDCl_3$.

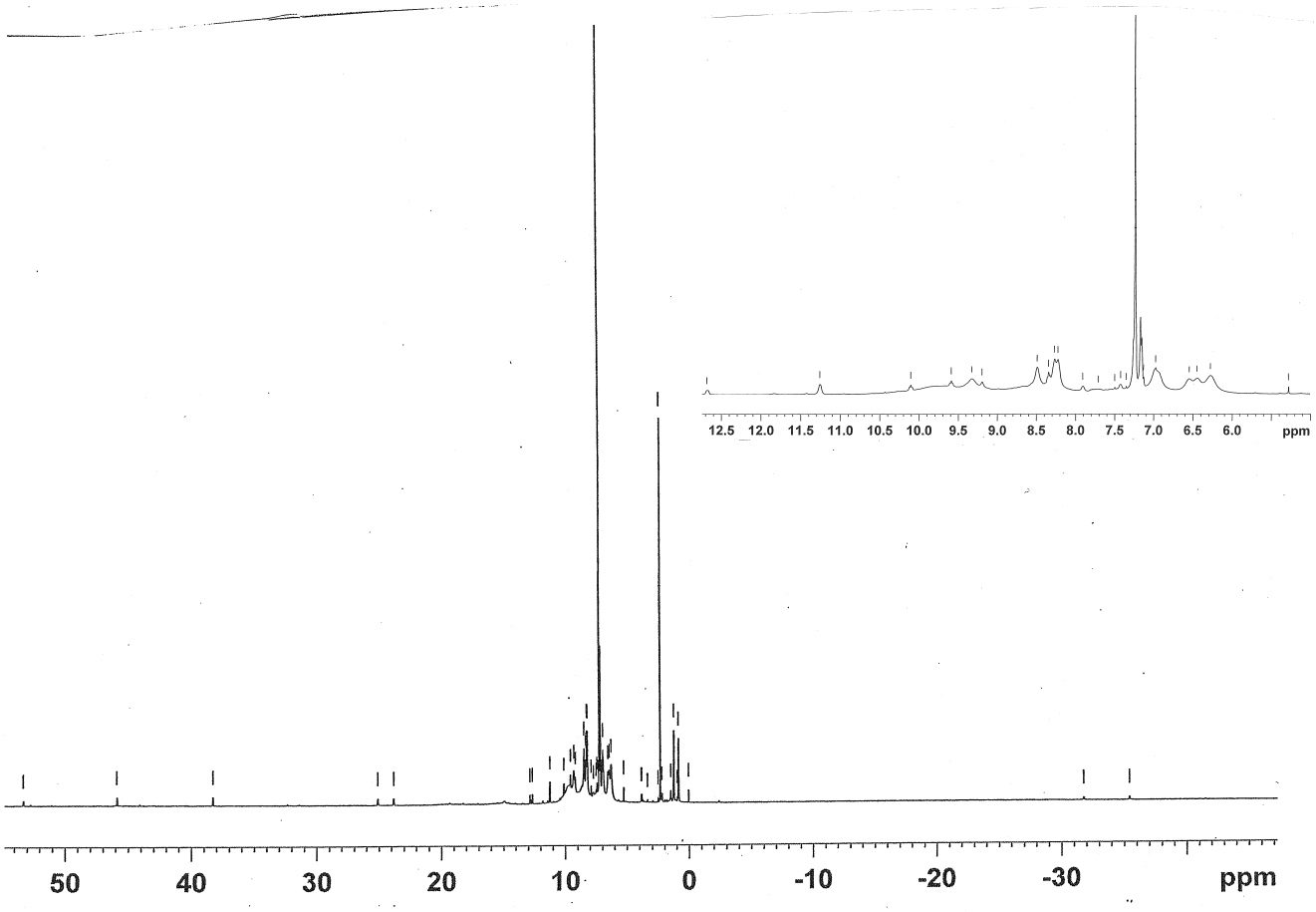

Figure S3. ^{1}H NMR spectrum of [Co(CTPP*O*)(NO)] (**3)** in $CDCl_3$.

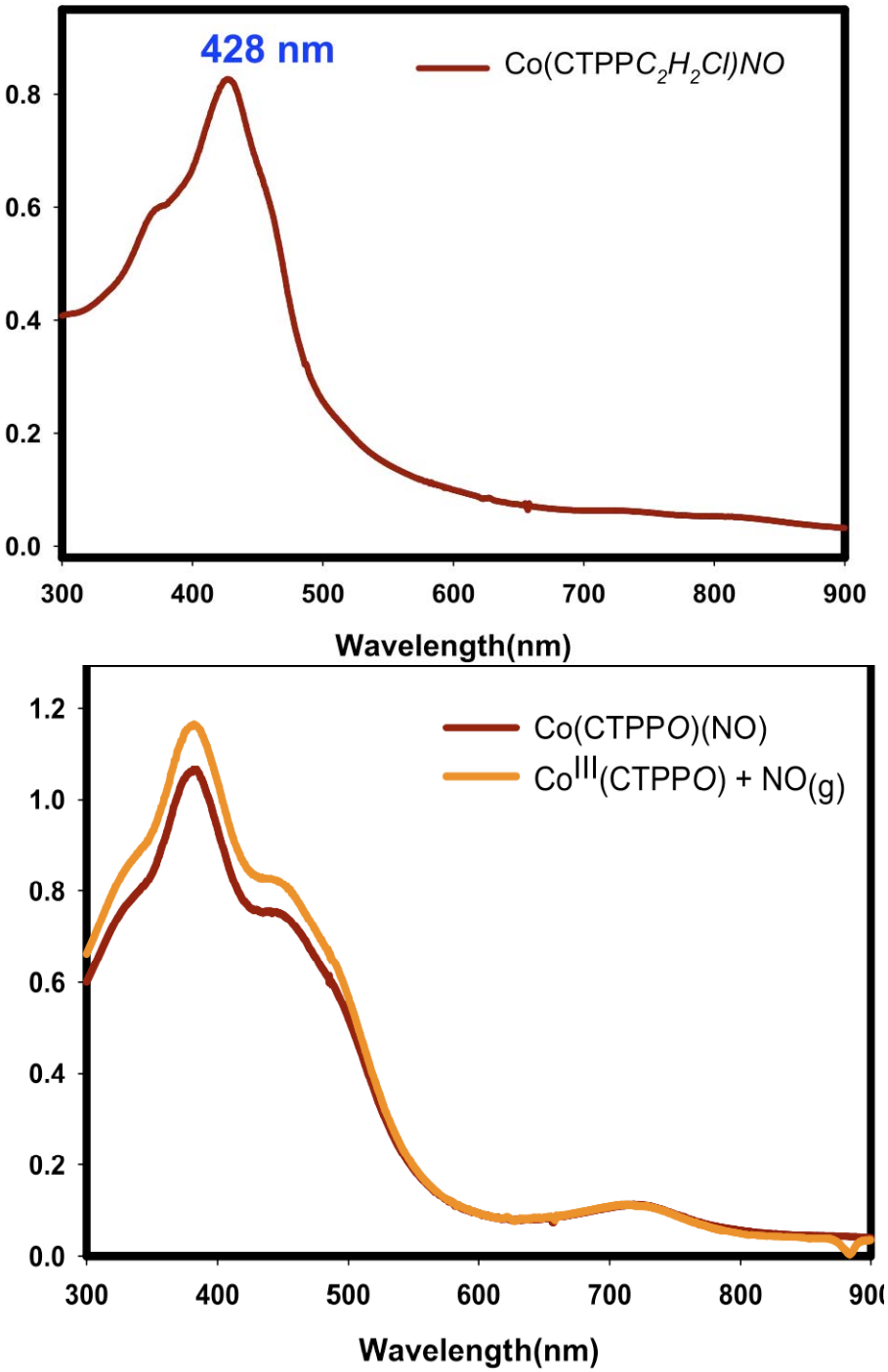

Figure S4. Absorption spectra of [Co(CTPPC_2H_2Cl)(NO)] (**2**) (Top) and [Co(CTPP*O*)(NO)] (**3**) (Bottom).

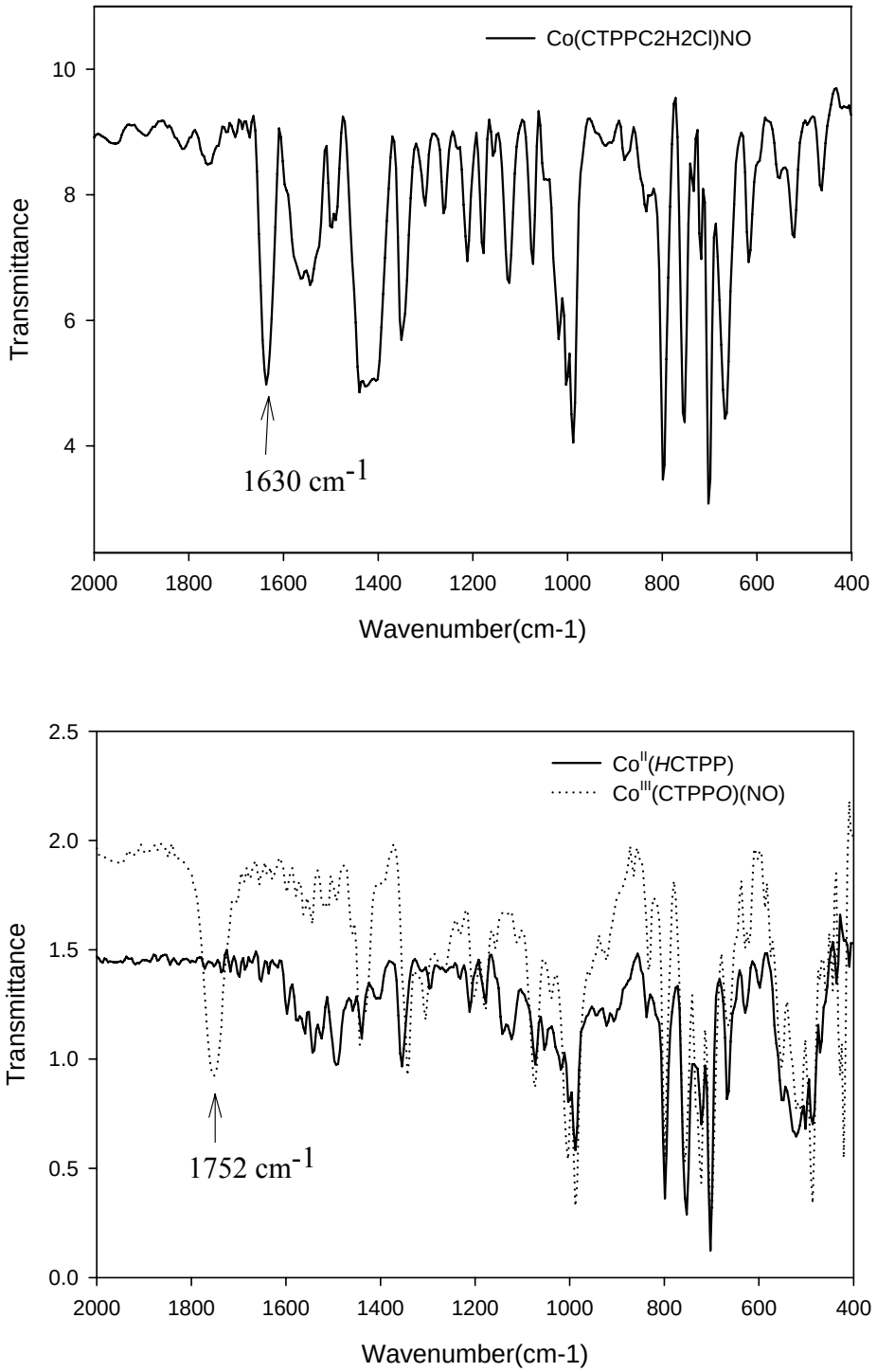

Figure S5. IR spectrum of [Co(CTPPC_2H_2Cl)(NO)] (**2**) (Top) and comparison on IR spectra of [Co(*H*CTPP)] (**1**) and [Co(CTPP*O*)(NO)] (**3**) (Bottom).

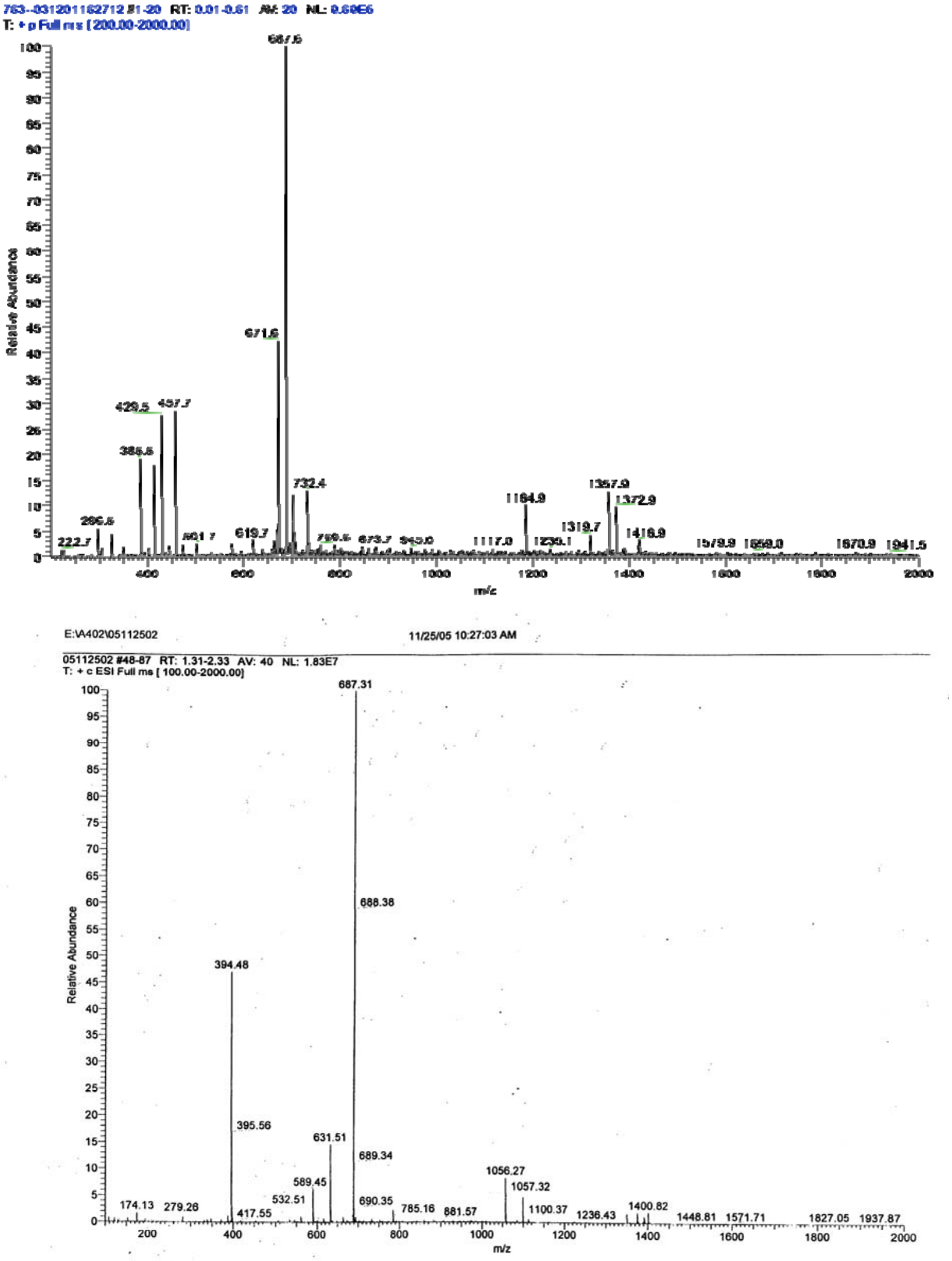

Figure S6. ESI mass spectra of [Co(CTPPC_2H_2Cl)(NO)] (**2**) (Top) and [Co(CTPPO)(NO)] (**3**) (Bottom).

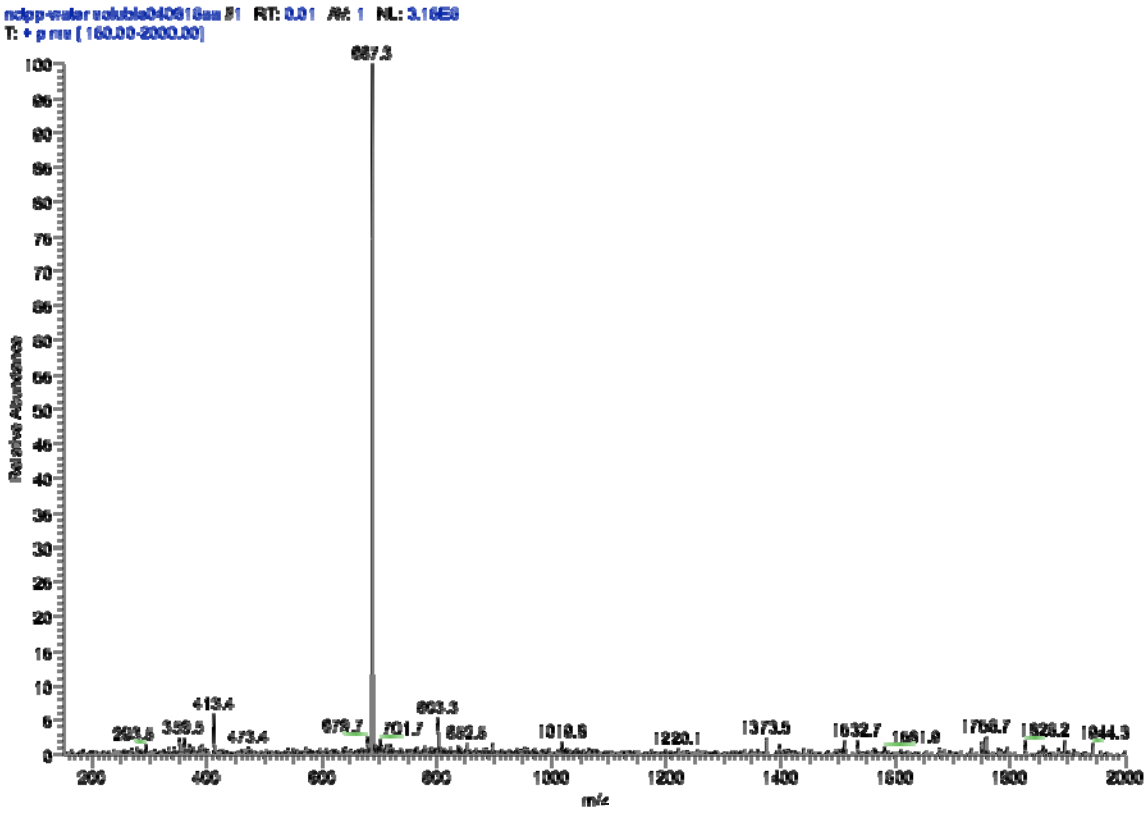

Figure S7. ESI mass spectrum of intermediate [Co(CTPP*O*)].

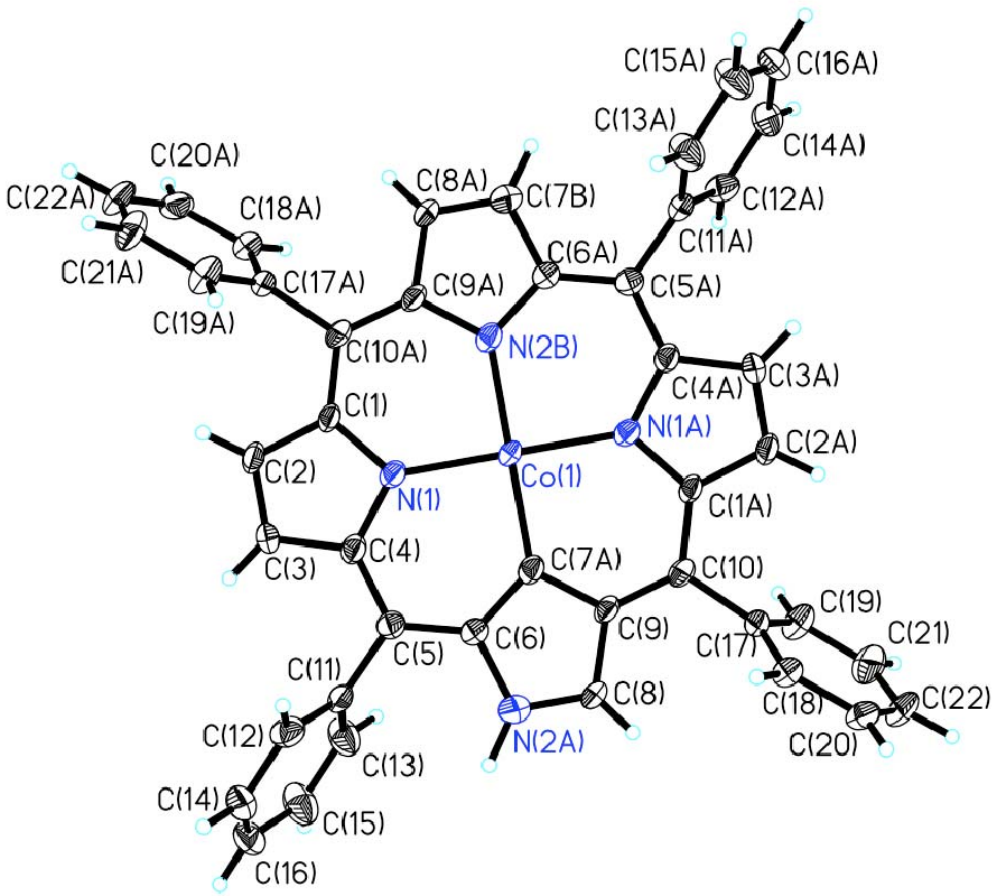

Figure S8. Crystal structure and Atomic labels of [Co(*H*CTPP)] (**1**).

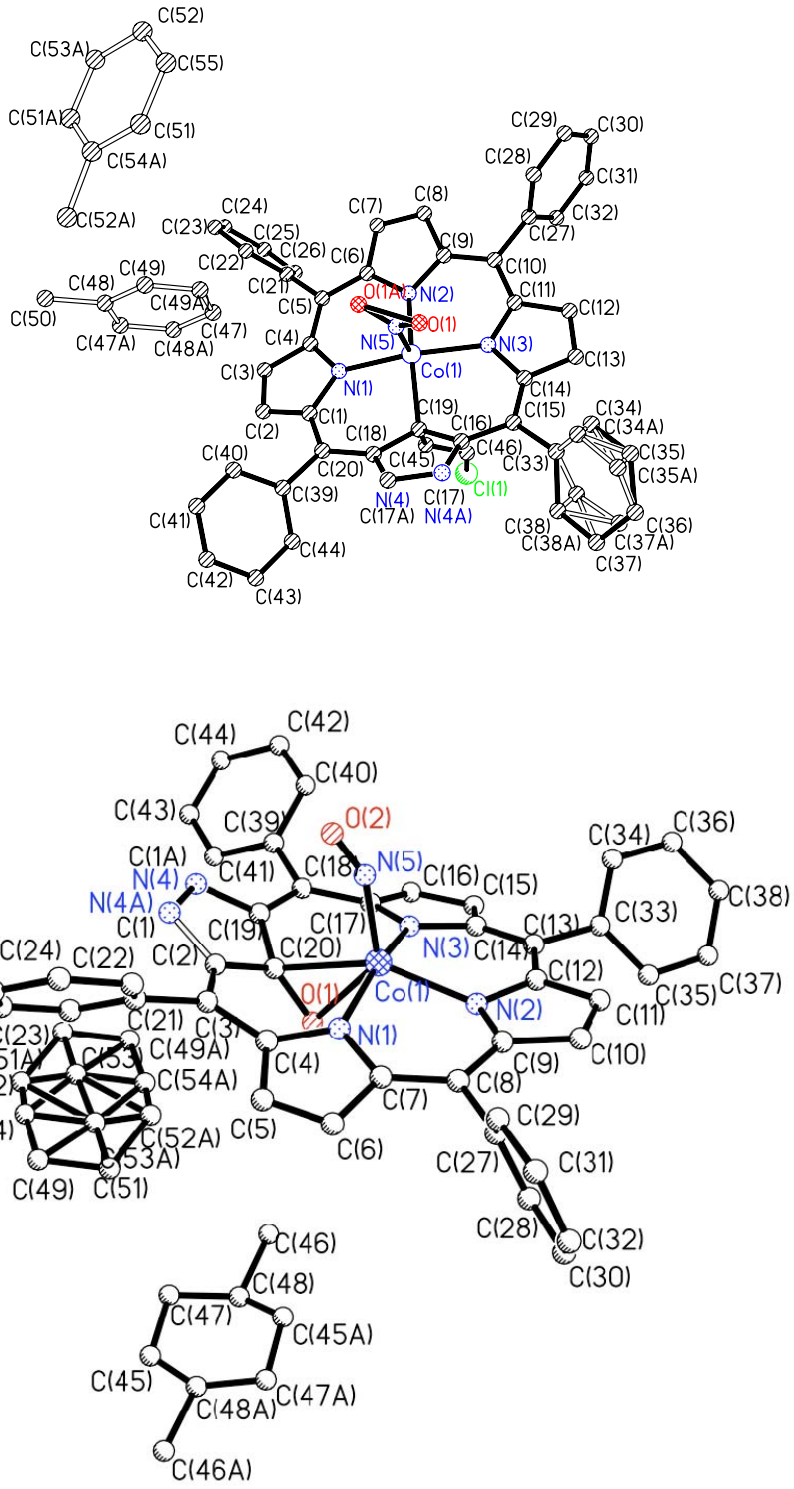

Figure S9. Crystal structures and Atomic labels of [Co(CTPPC_2H_2Cl)(NO)] (**2**) (Top) and [Co(CTPP*O*)(NO)] (**3**) (Bottom).

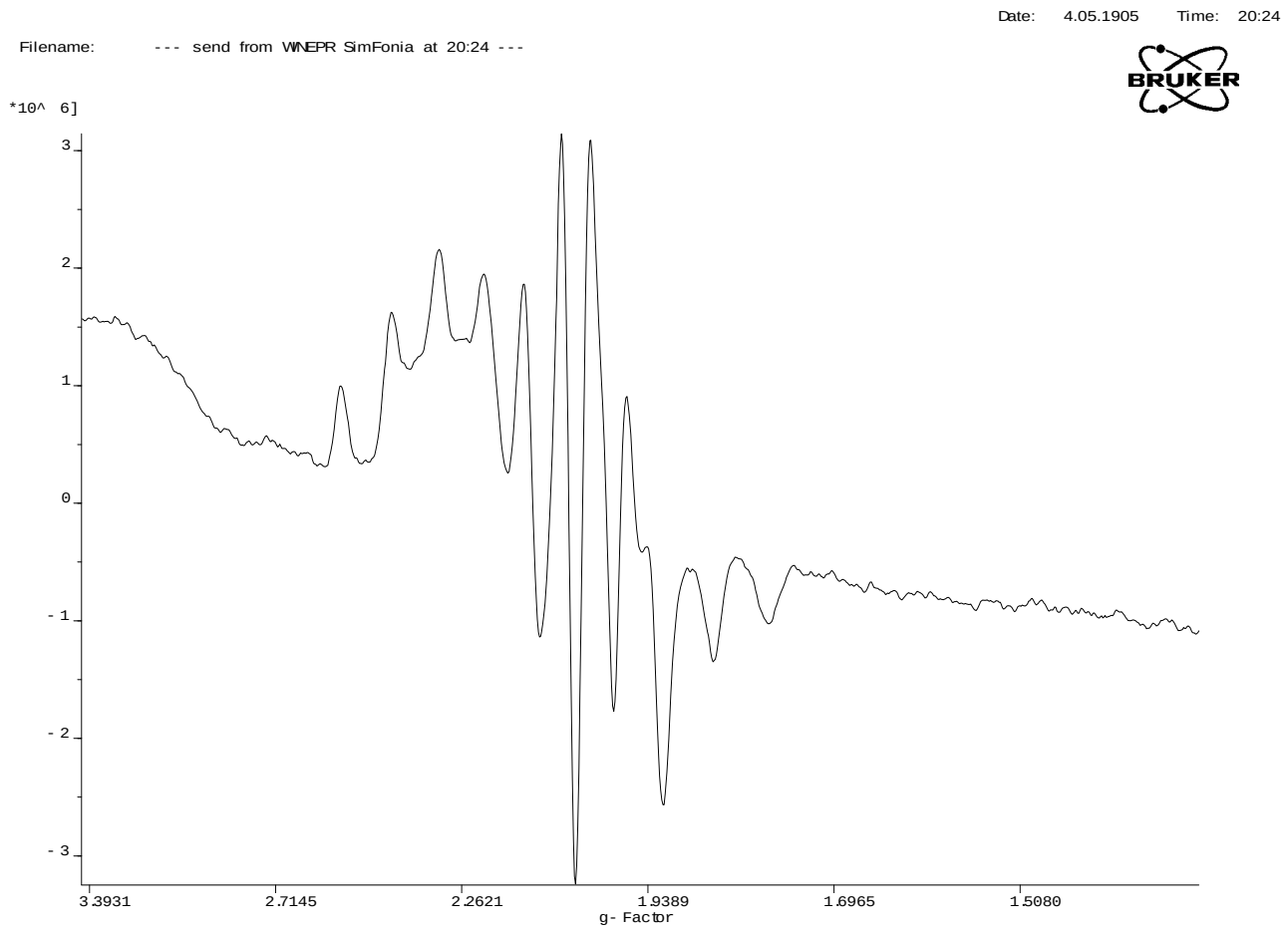

Figure S10. EPR spectrum of [Co(CTPP*O*)(NO)] (**3**) at 77 K.

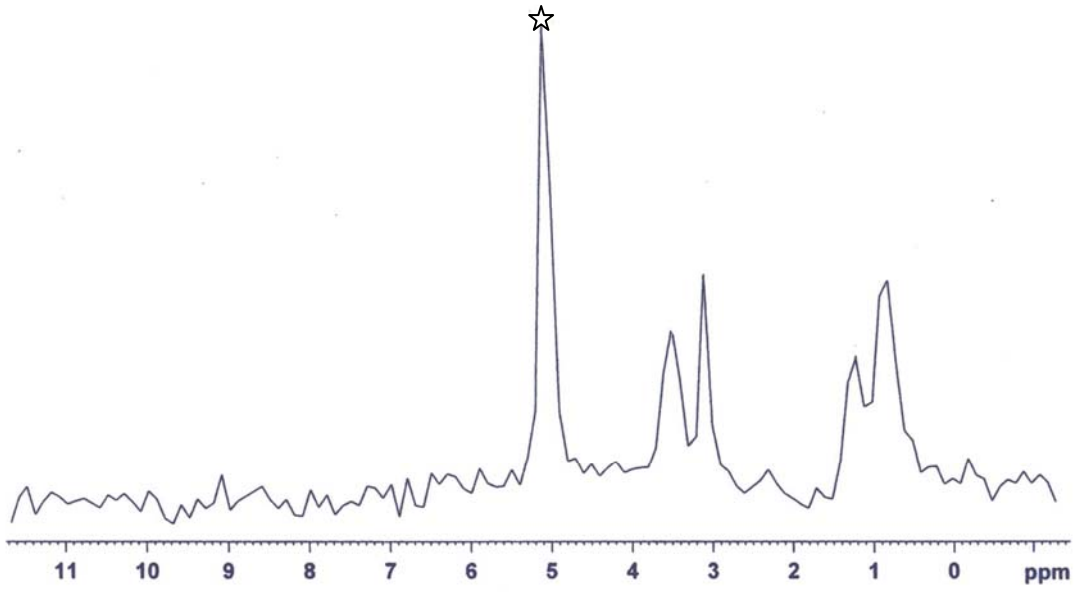

Figure S11. ^{2}H NMR spectrum of deuterated chlorovinyl group substituted [Co(CTPPC_2D_2Cl)(NO)](**2**). (the labeled peak is residual $CDHCl_2$)

References

[1] Sheldrick, G. M. *SHELXS-97—Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1997.

[2] Sheldrick, G. M. *SHELXL-97—Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

[3] Sheldrick**,** G. M. *SADABS, Siemens Area Detector Absorption Correction Program*; University of Göttingen: Germany, 1996.