

Supporting information for:

A step beyond the Feltham-Enemark notation:

Spectroscopic and correlated *ab initio* computational support for an antiferromagnetically-coupled M(II)-
(NO)¹⁻ description of Tp*M(NO) (M = Co, Ni)

Neil C. Tomson,^a Mark R. Crimmin,^b Taras Petrenko,^a Lauren E. Rosebrugh,^b Stephen Sproules,^a W. Christopher Boyd,^b Robert G. Bergman,^{b} Serena DeBeer,^{c*} F. Dean Toste,^{b*} and Karl Wieghardt^{a*}*

^a Max-Planck-Institut für Bioanorganische Chemie, Stiftstrasse 34-36, 45470 Mülheim an der Ruhr, Germany.

^b Department of Chemistry, University of California Berkeley, California, 94720, United States

^c Department of Chemistry and Chemical Biology, Cornell University Ithaca, New York 14853, United States

Table of Contents

Experimental and simulated X-band EPR spectra of 1	3-5
SQUID magnetometry data for 1	6
IR/NIR spectrum of 1	7
TD-DFT calculated Vis-NIR data for 1 and 1'	8
React-IR data for the reaction of $[(\text{TMEDA})\text{Co}(\text{NO})_2]\text{BPh}_4$ with KTp^*	9
^1H NMR data for the reaction of 1 with NO	10
NMR data for $[(\text{TMEDA})\text{Co}(\text{NO})_2]\text{BPh}_4$, 1 , and 4	11-14
TD-DFT calculated Co K-edge XAS spectra for $[\text{Co}(\text{NCS})_4]^{2-}$, 1 , and $\text{Tp}^{t\text{Bu},\text{Me}}\text{Co}(\text{NCS})$	15-16
Comparison of calculated pre-K-edge features vs. Co- N_{NO} bond distance for 1	17
Relaxed coordinate scans for 1 with varying Co- N_{NO} bond distance and α -angle	18-19
Spin density profiles for Co, N, O during OLYP geometry optimization	20
Calculated spin density plots for $[\text{Co}(\text{NCS})_4]^{2-}$ and $\text{Tp}^{t\text{Bu},\text{Me}}\text{Co}(\text{NCS})$	21
Additional DFT and CASSCF/MRCI computational results for 1 and 1'	22-24
Additional DFT and CASSCF/MRCI computational results for 5 and 5'	25-26
Additional DFT and CASSCF/MRCI computational results for $\text{Tp}^{t\text{Bu},\text{H}}\text{Cu}(\text{NO})$ and $\text{TpCu}(\text{NO})$	27-28
Input files and optimized coordinates for all complexes	29-59

Figure S1. X-band EPR spectrum of **1** in 1:1 dichloromethane:toluene at 10 K. Conditions: frequency 9.419 GHz, power 0.63 mW, modulation 1.0 mT. Simulation parameters: $g_x = 1.735$, $g_y = 1.810$, $g_z = 3.505$, $A_x\{^{59}\text{Co}\} = 28.0 \times 10^{-4} \text{ cm}^{-1}$, $A_y\{^{59}\text{Co}\} = 28.0 \times 10^{-4} \text{ cm}^{-1}$, $A_z\{^{59}\text{Co}\} = 213.0 \times 10^{-4} \text{ cm}^{-1}$; line-width: $\text{lw}_x = \text{lw}_y = \text{lw}_z = 40.0$; g-strain: $\text{g}_x = \text{g}_y = -0.040$, $\text{g}_z = +0.070$; A-strain: $A_x = 32.0$, $A_y = 25.0$, $A_z = 59.0$.

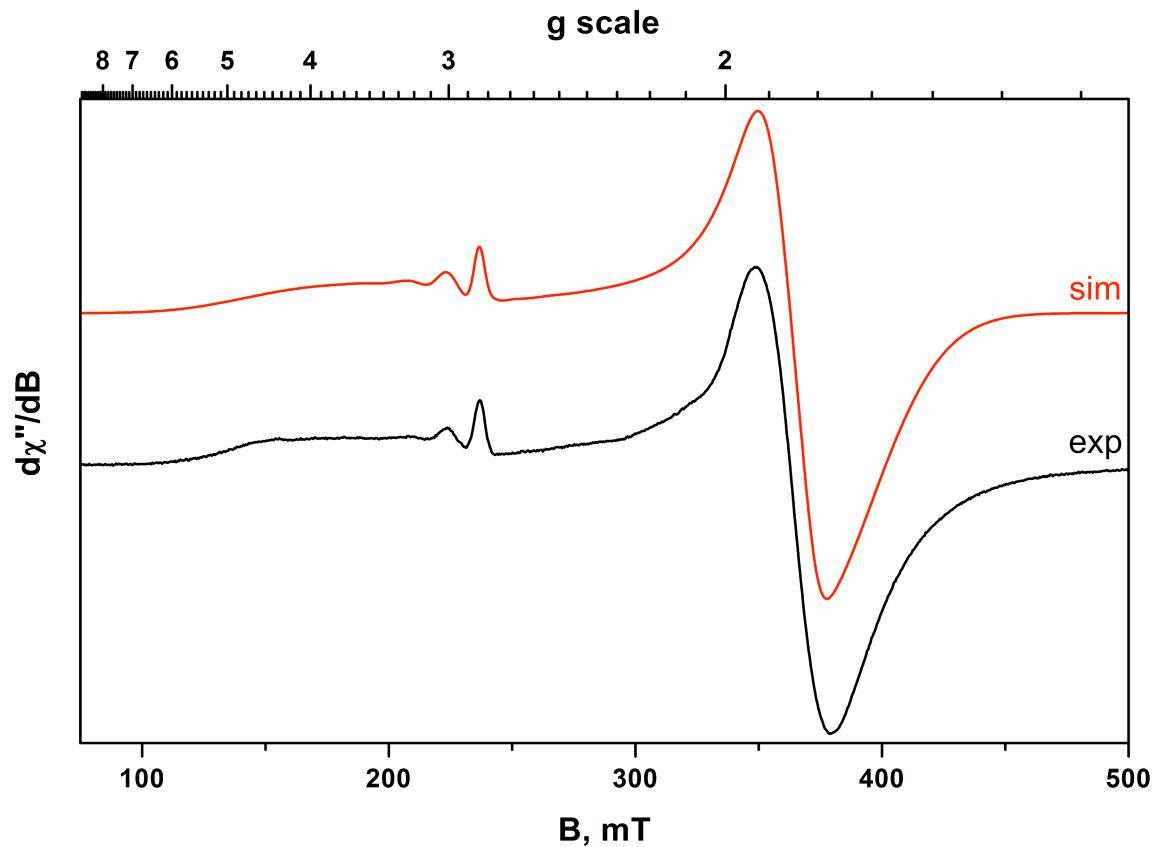


Figure S2. X-band EPR spectrum of **1** in dichloromethane at 20 K. Conditions: frequency 9.621 GHz, power 0.10 mW, modulation 0.7 mT. Simulation parameters: $g_x = 1.8138$, $g_y = 1.9105$, $g_z = 3.32$, $A_x\{^{59}\text{Co}\} = 28.2 \times 10^{-4} \text{ cm}^{-1}$, $A_y\{^{59}\text{Co}\} = 29.0 \times 10^{-4} \text{ cm}^{-1}$, $A_z\{^{59}\text{Co}\} = 110 \times 10^{-4} \text{ cm}^{-1}$; line-width: $lw_x = lw_y = 14.0$, $lw_z = 120.0$; g-strain: $_g_x = _g_y = _g_z = 0.0$; A-strain: $_A_x = 6.669$, $_A_y = 14.663$, $_A_z = 50.000$. Inset: Expanded g_x/g_y region with the same simulation except for the line-width parameters, which are set to $lw_x = lw_y = 5.0$.

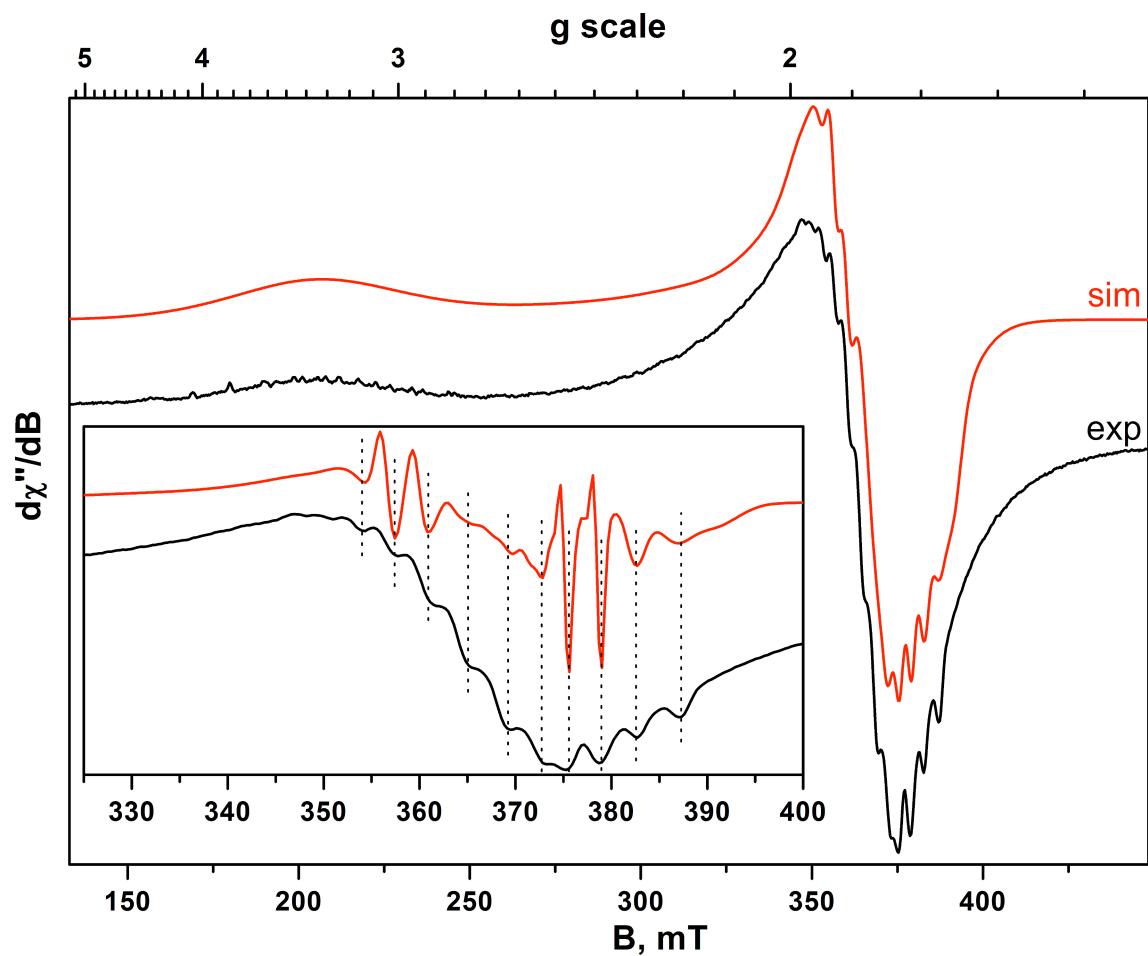


Figure S3. X-band EPR spectrum of a solid sample of **1** at 25 K. Conditions: frequency 9.635 GHz, power 0.6315 mW, modulation 0.746 mT.

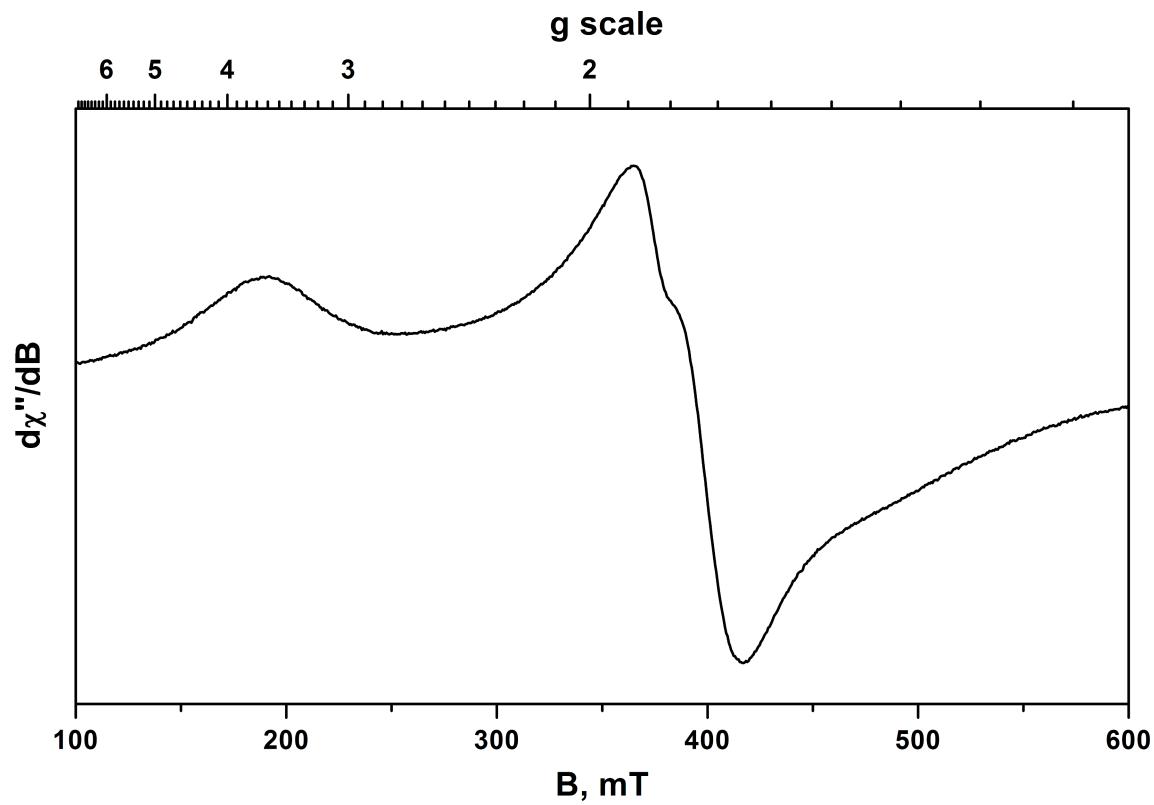


Figure S4. SQUID magnetometry data for **1**. Collected at $B = 1.0$ T. Black dots are data points. Red line represents the fit for a $S = \frac{1}{2}$ system, $g = 2.530$ with a 6.1 % $S = 2.5$ impurity and TIP correction of 0.45×10^{-3} emu .

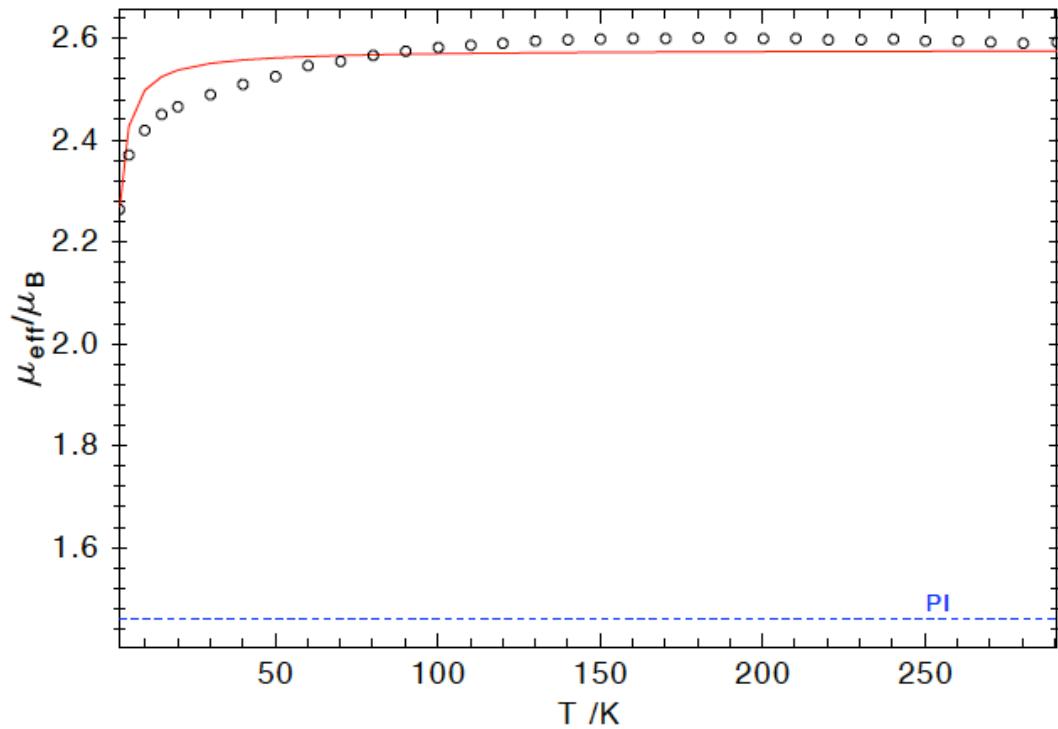


Figure S5. IR/NIR spectrum of **1** in KBr at room temperature. The baseline was manually adjusted, using a blank KBr spectrum as a guide.

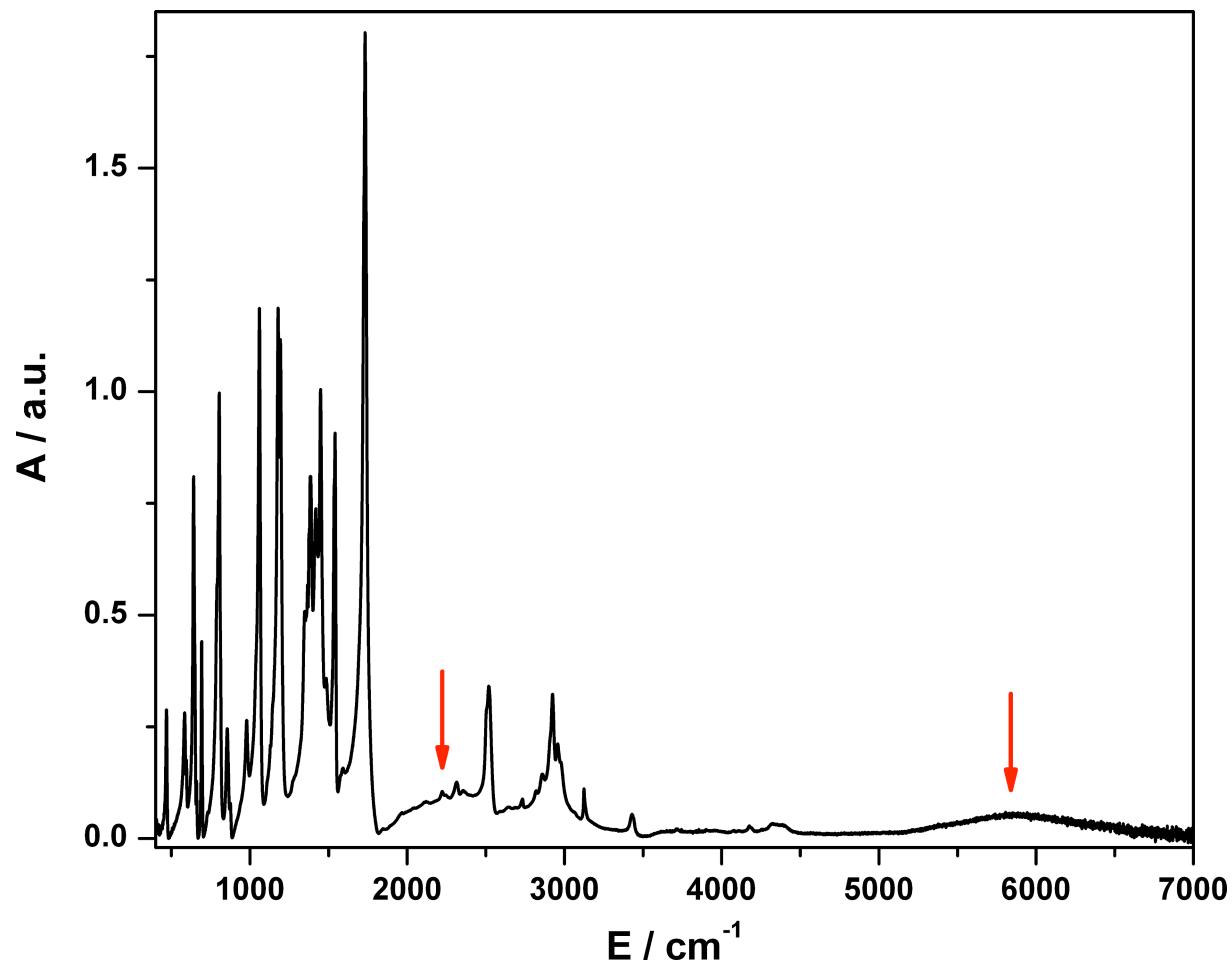


Figure S6. Comparison of the TD-DFT-calculated Vis-NIR spectra for $\text{Tp}^*\text{Co}(\text{NO})$ (top, black line, black sticks) with that for $\text{TpCo}(\text{NO})$ (bottom, red line, red sticks) and the experimental spectrum (blue line).

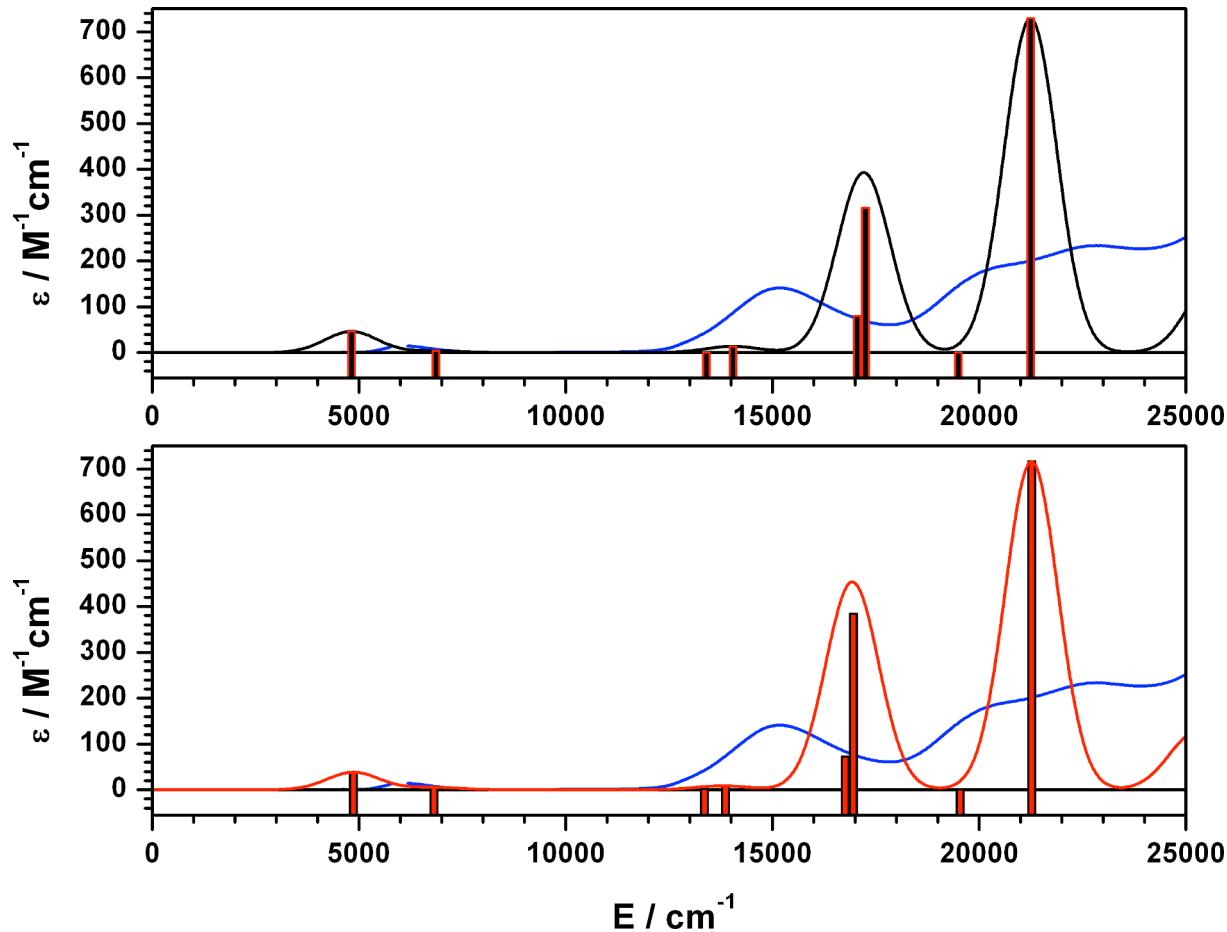


Figure S7. React-IR data for the reaction of $[(\text{TMEDA})\text{Co}(\text{NO})_2]\text{BPh}_4$ (10 mM) with KTp^* (10 mM) in THF solution at room temperature. The dotted line shows the point of addition of KTp^* (the artifact at 1600 cm^{-1} is due to an impurity in THF resulting in a poor baseline subtraction).

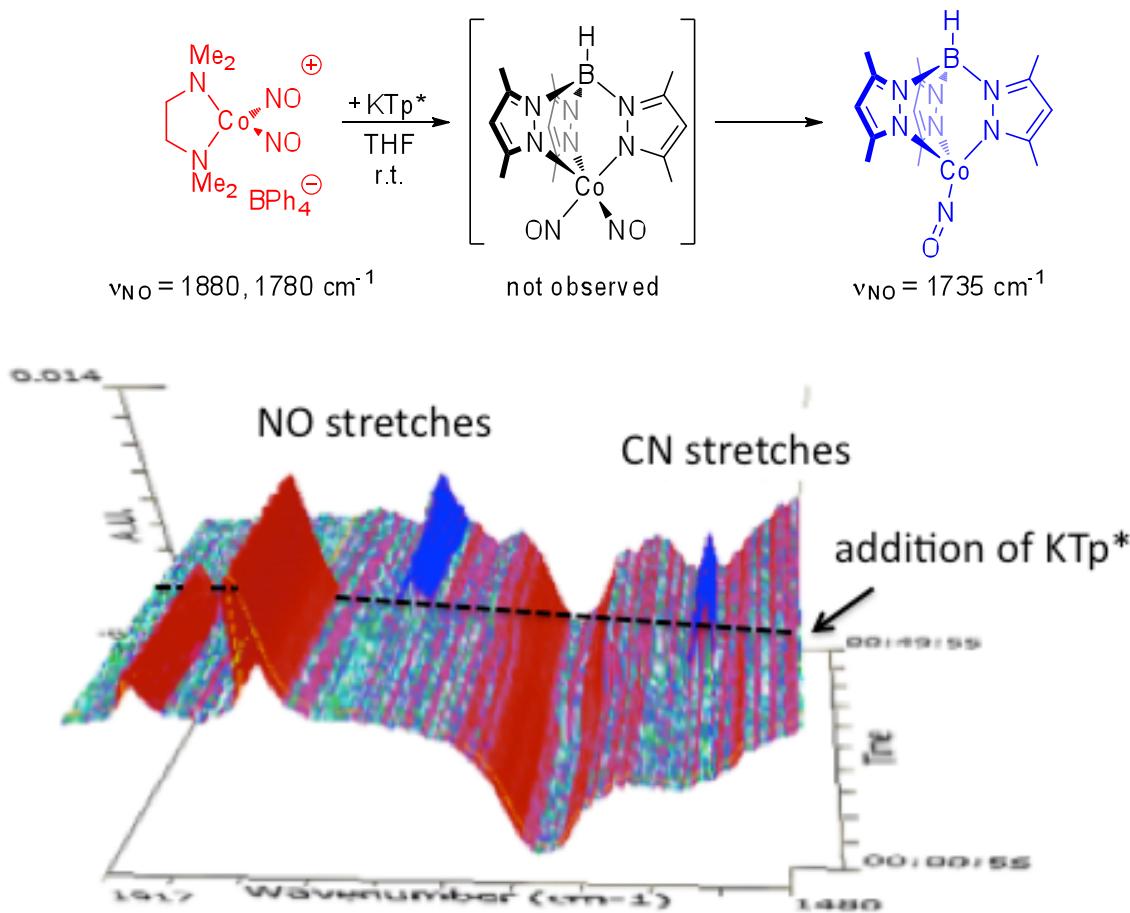
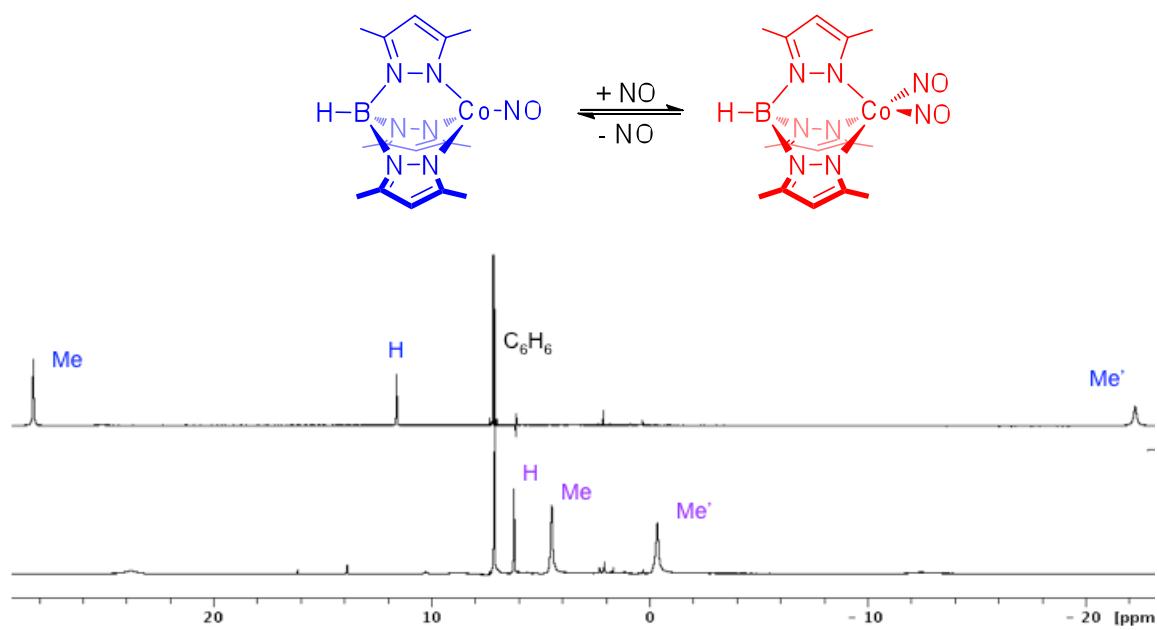
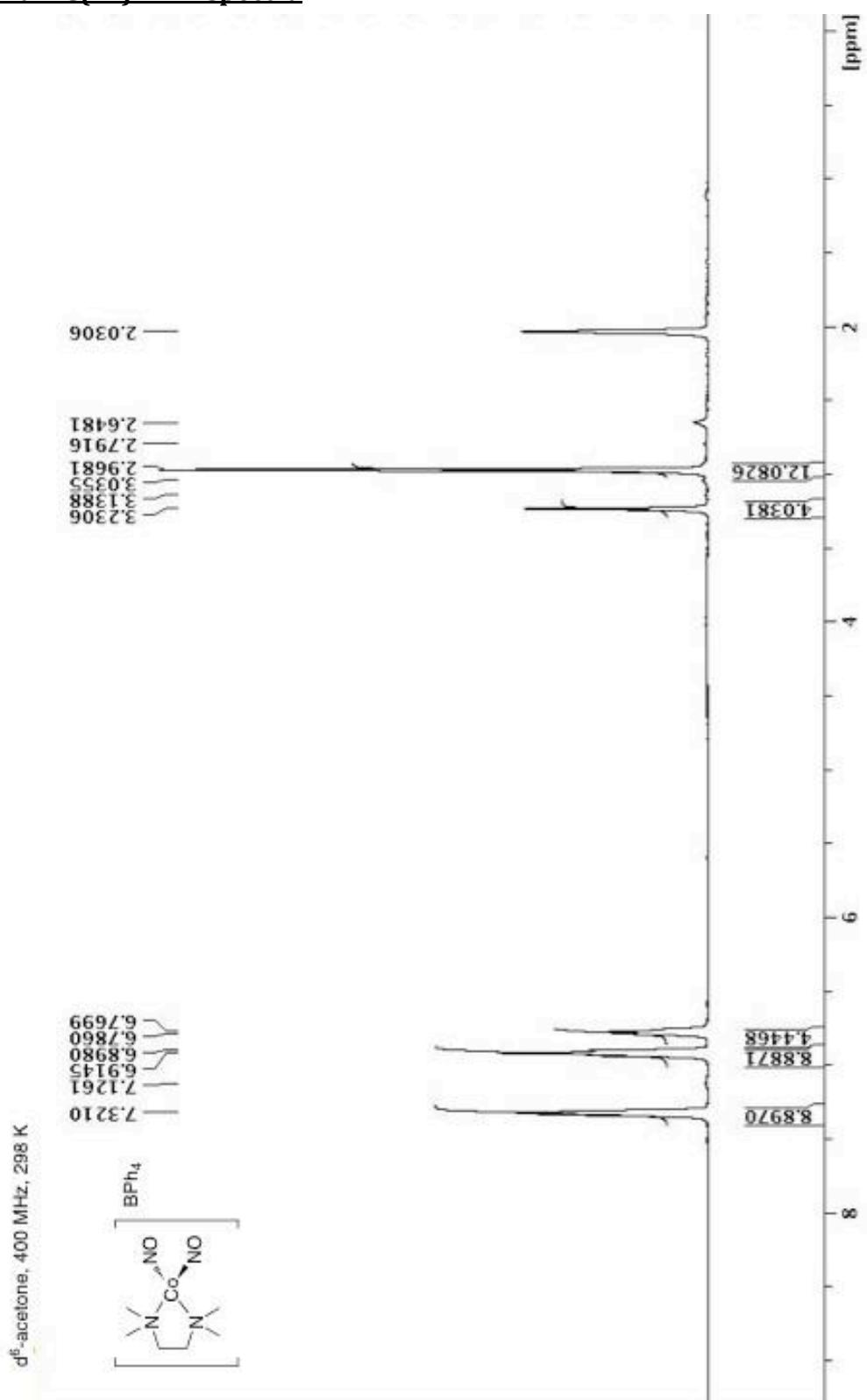
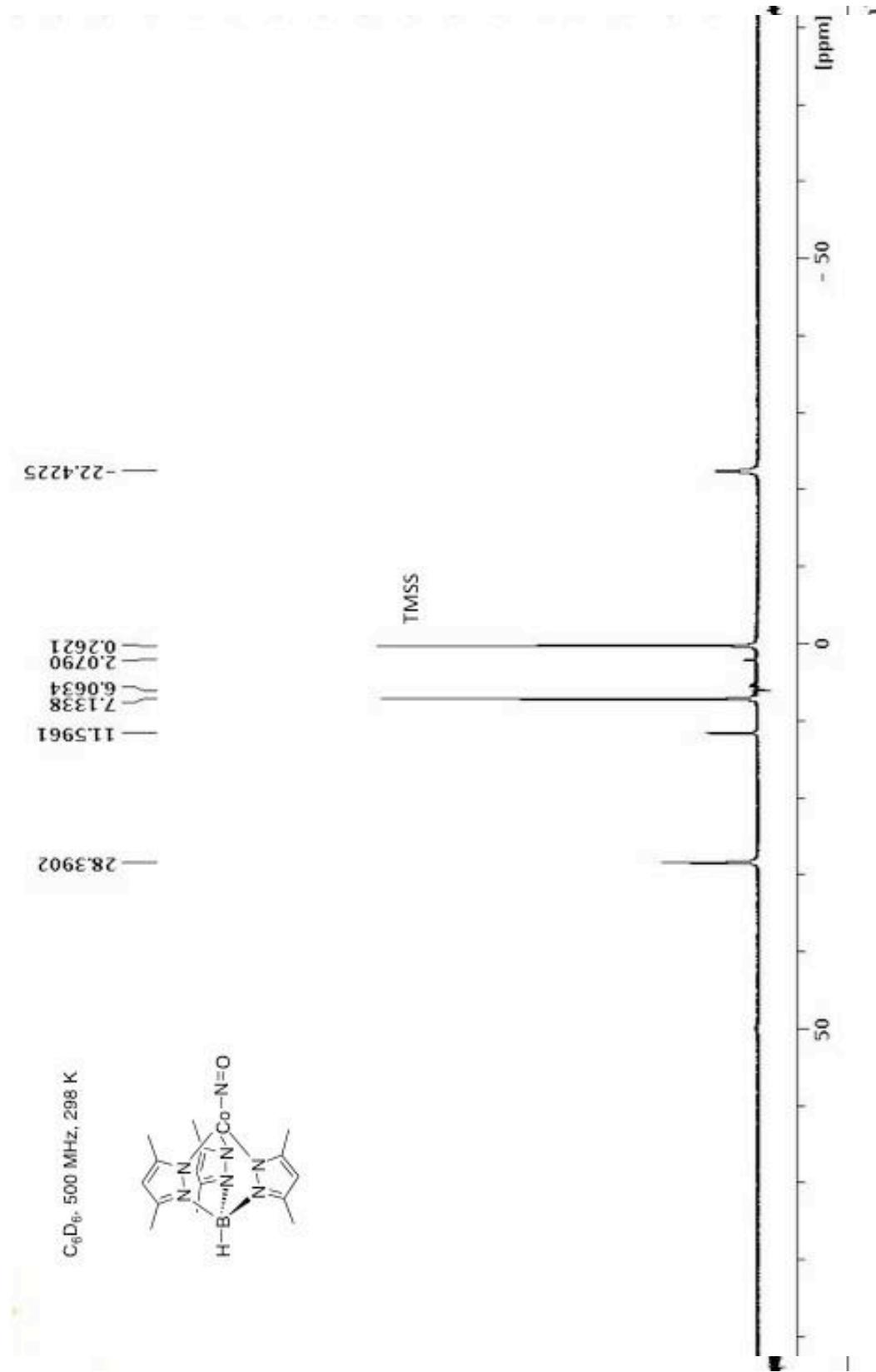


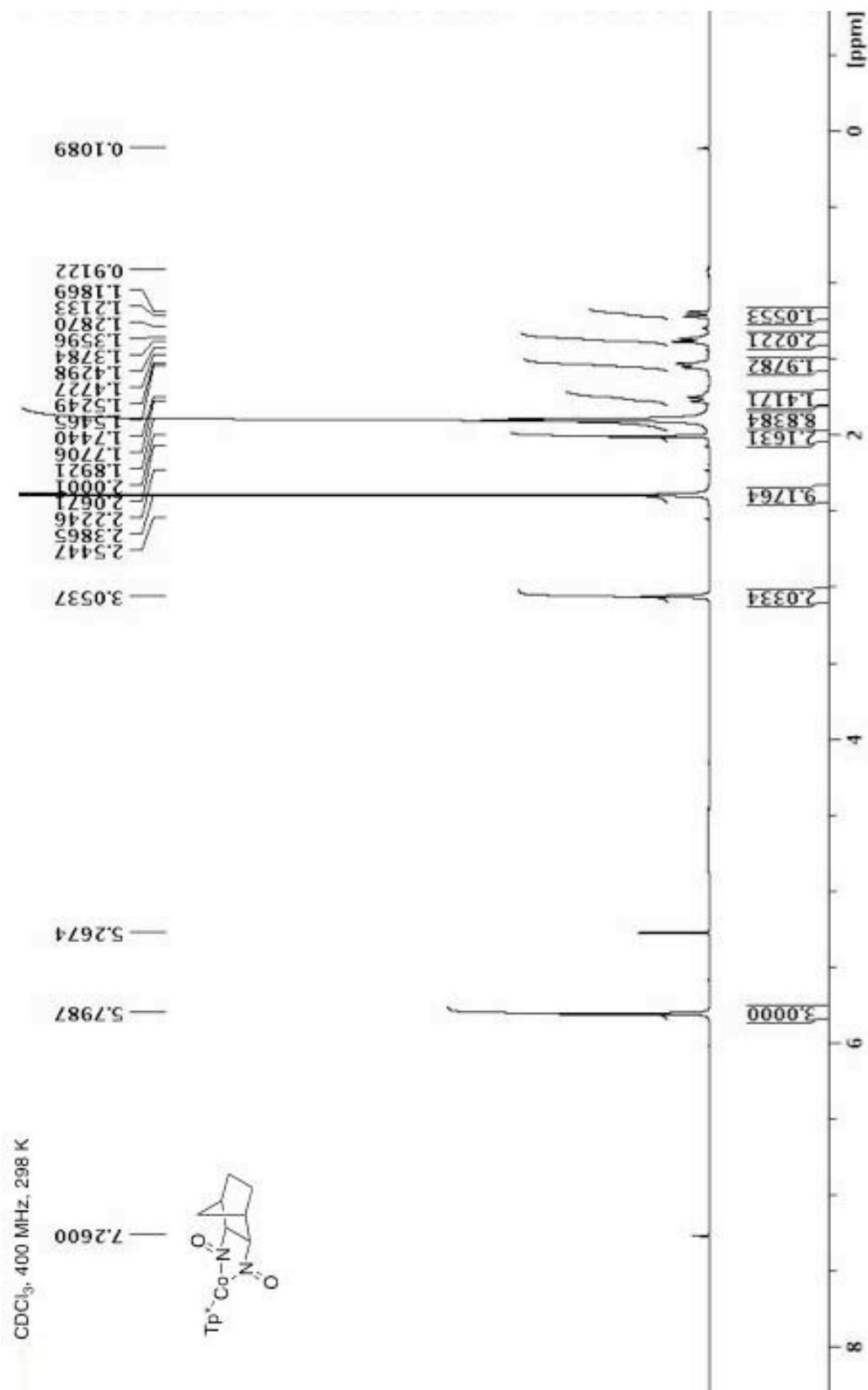
Figure S8. ^1H NMR spectroscopy data for the reaction of **1** (50 mM) with NO (1 atm.) in C_6D_6 solution. Before addition of NO (top spectrum) and 15 minutes after addition of NO (bottom spectrum)



^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra







CDCl_3 , 100 MHz, 298 K

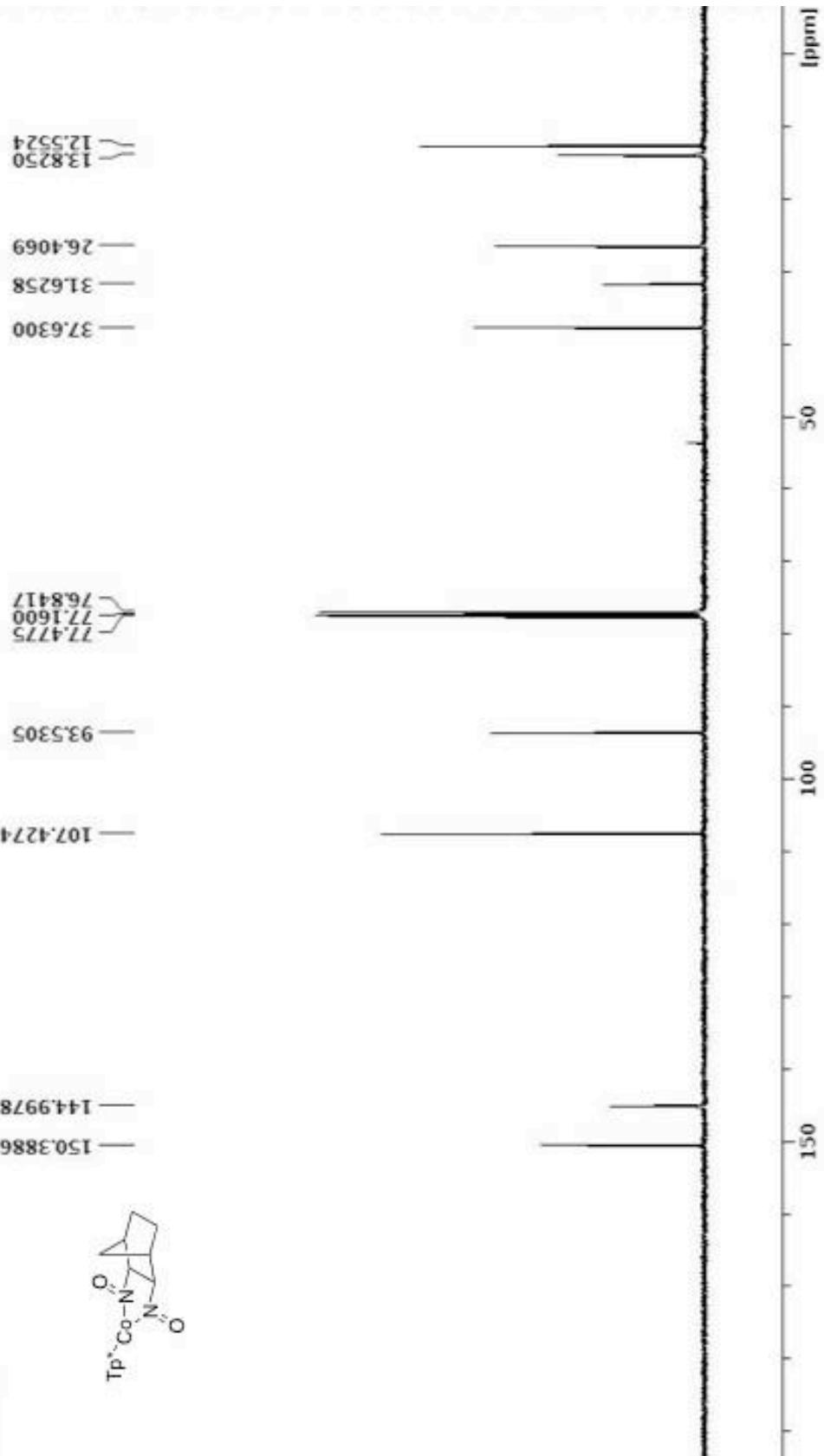
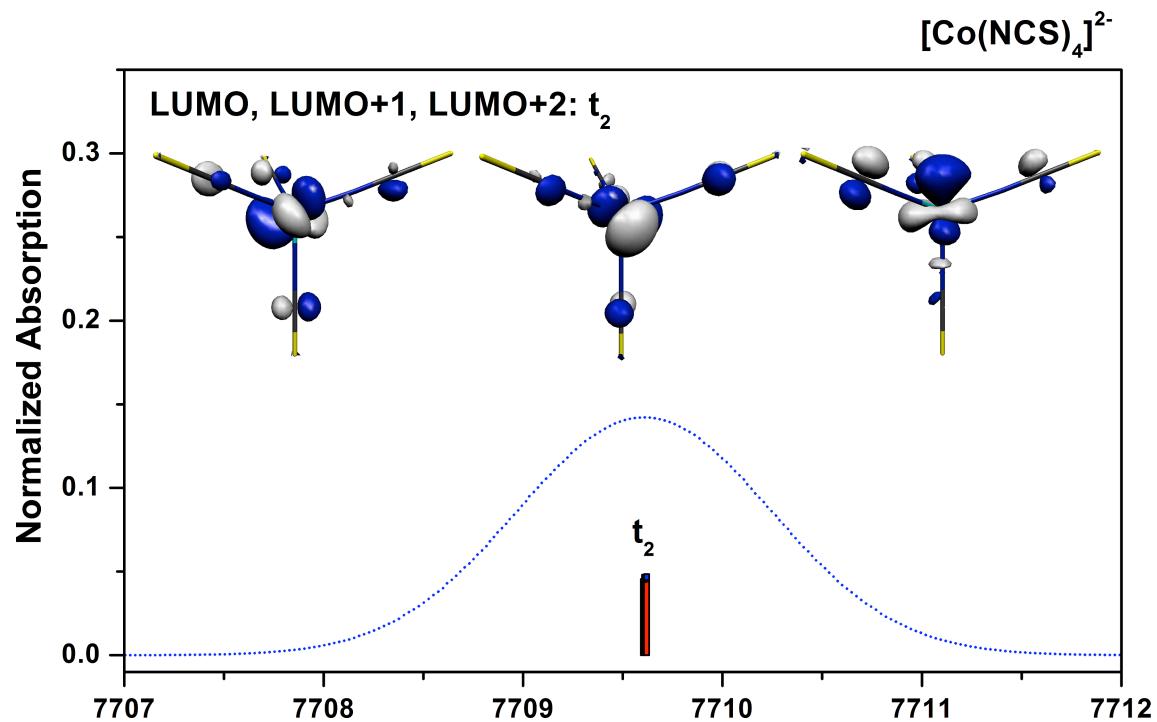


Figure S9. TD-DFT calculated Co pre-K-edge XAS spectra for the indicated compounds with associated unoccupied canonical orbitals. The given orbitals constitute the majority contribution to the 1s->'unoccupied valence orbital' transitions indicated by the stick plots. The given spectrum is based on the intesity of the individual transitions, assuming a fwhm of 1.5 eV.



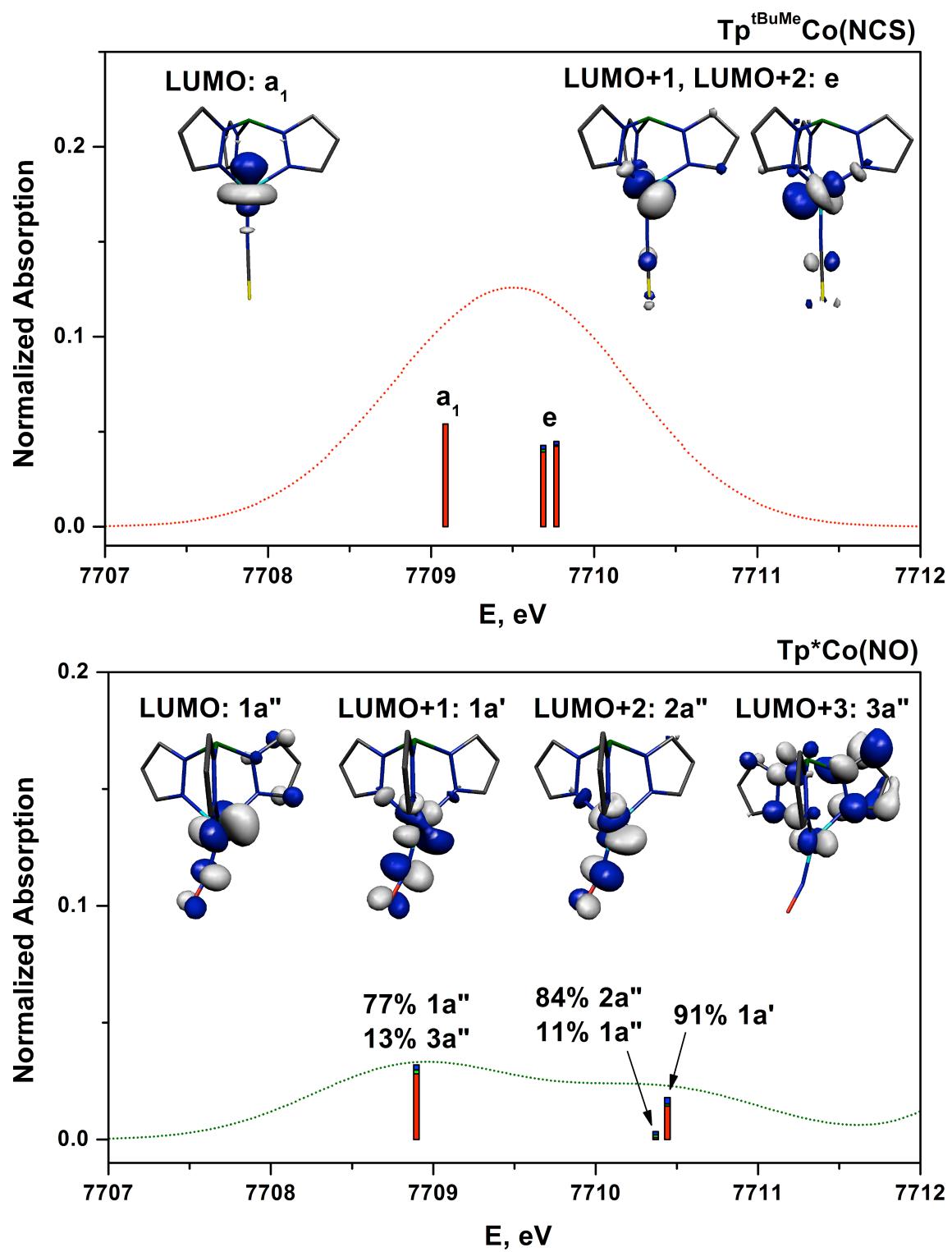


Figure S10. Plot of the difference in energy between the first and third calculated Co K-edge features as a function of changes in the Co-N_{NO} bond distance. At each increment of the Co-N_{NO} bond distance the Co-N_{NO} distance was held constant while the remainder of the structure was optimized. The red horizontal line indicates the experimental difference in energy between the two observable peaks in the pre-edge region of the spectrum. The green and blue vertical lines are for the experimental (with crystallographic averaging) and calculated Co-N_{NO} bond distances.

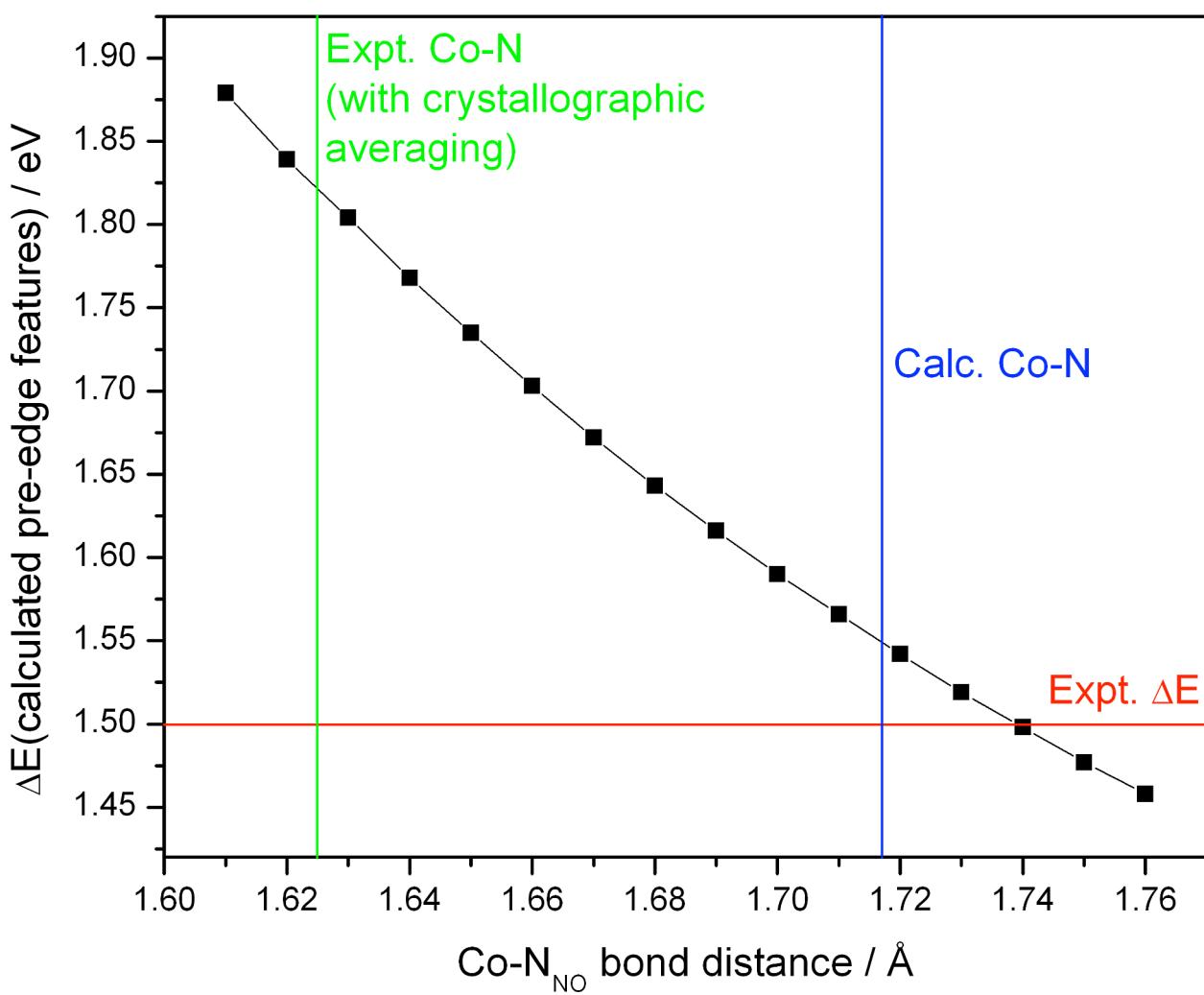


Figure S11. Relaxed coordinate scan along the Co-N_{NO} bond. The Co-N_{NO} distance was varied by 0.1 Å increments, then held constant as the geometry of the structure was optimized.

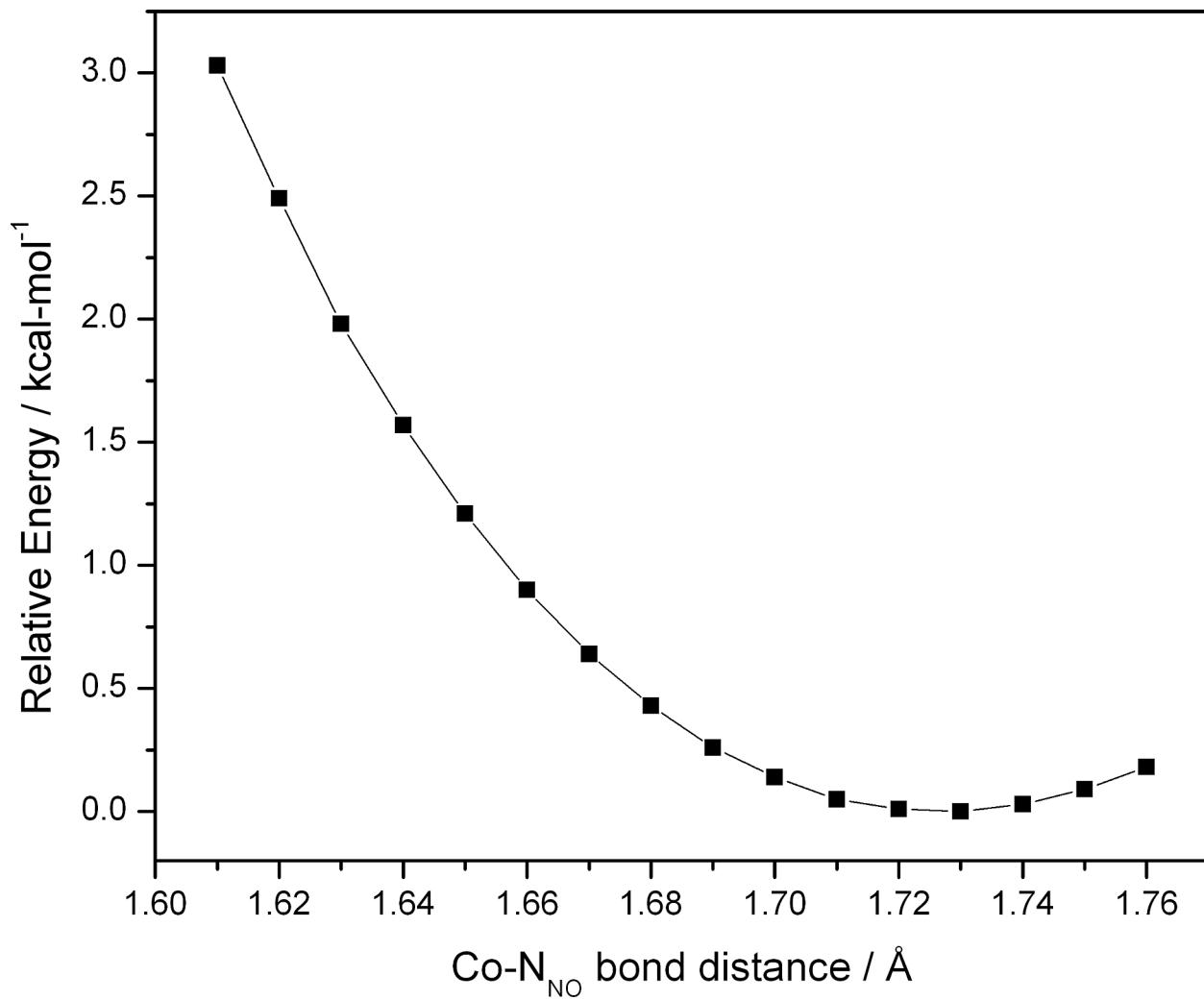


Figure S12. Relaxed coordinate scan along the B-Co-N_{NO} angle. The B-Co-N_{NO} angle was constrained to the indicated value as the geometry of the structure was optimized. The α -angle is defined as $\alpha = 180^\circ - \angle(\text{B-Co-N}_{\text{NO}})$.

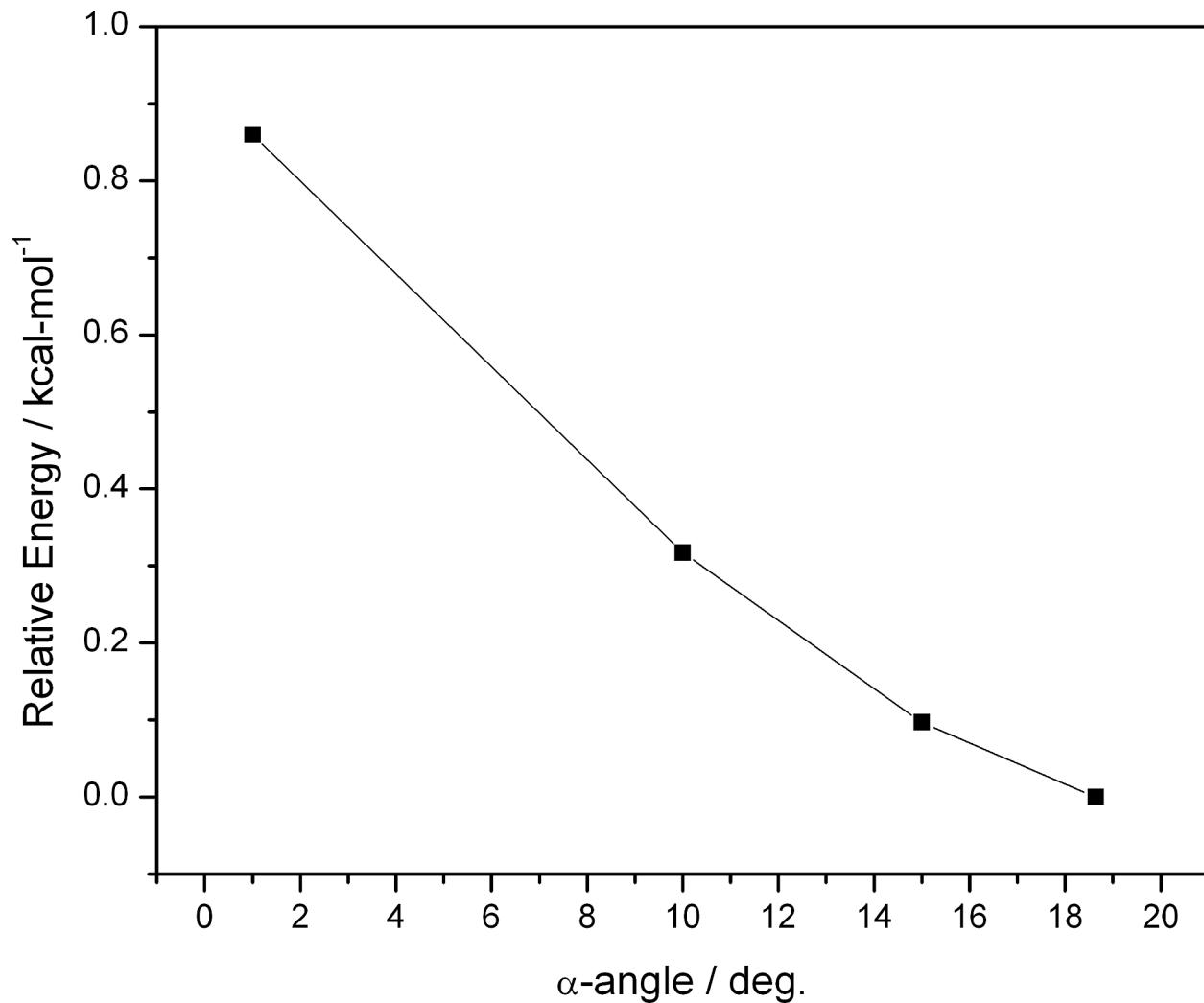


Figure S13. Plot of the spin density distribution on the Co (bottom, black), N (middle, blue), and O (top, red) atoms of $\text{Tp}^*\text{Co}(\text{NO})$ at each step of the unrestricted, $S_{\text{tot}} = \frac{1}{2}$ OLYP geometry optimization procedure.

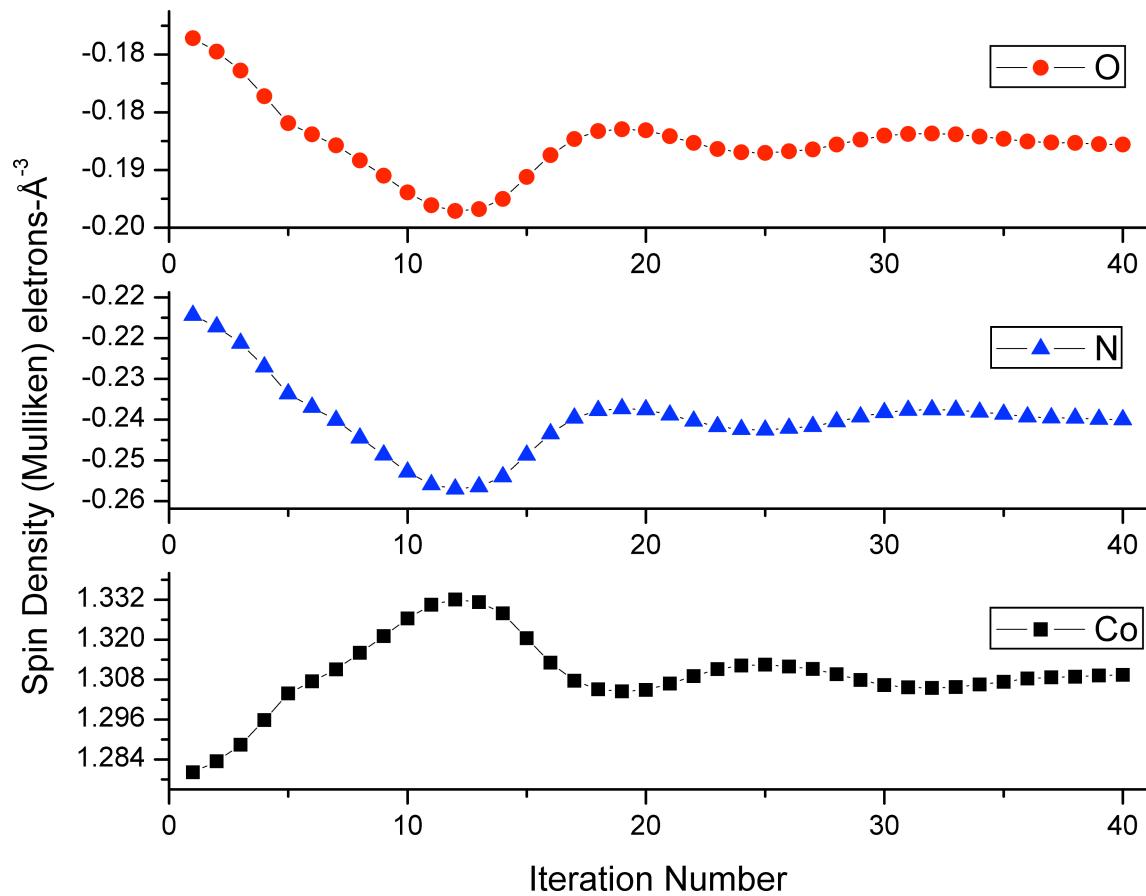


Figure S14. B3LYP-calculated spin density plots with numerically-annotated Mulliken spin densities for $[\text{Co}(\text{NCS})_4]^{2-}$ (left) and $\text{Tp}^{\text{tBuMe}}\text{Co}(\text{NCS})$ (right; ${}^t\text{Bu}$, Me, and H removed for clarity).

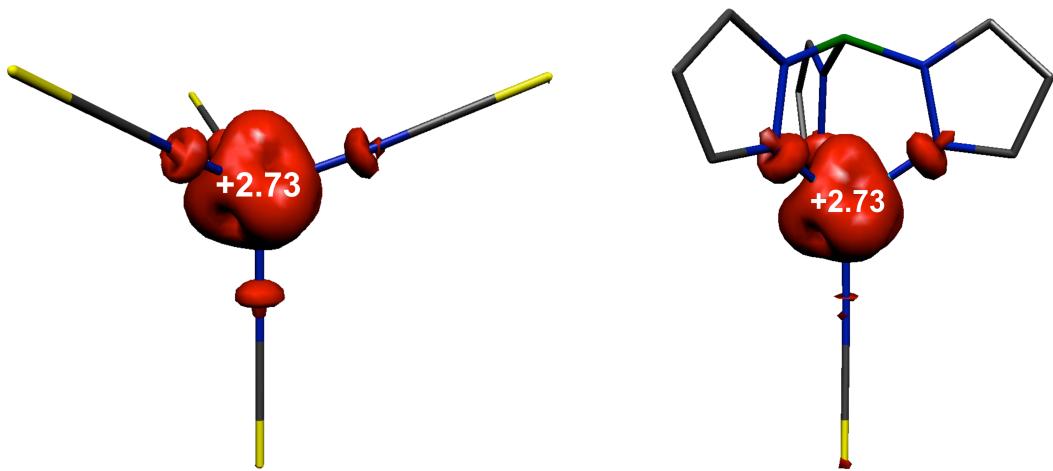


Table S1. Mulliken spin density values for **1** and **1'** from DFT and CASSCF(5,5) calculations as well as spatial overlap components of the HOMO-1 and HOMO orbitals of **1** and **1'** from DFT calculations.

		Mulliken Spin Density		$S_{\alpha\beta}$	
		Co	NO	HOMO-1	HOMO
B3LYP opt (1)	B3LYP SP	2.16	-1.29	0.75	0.71
	OLYP SP	1.51	-0.64	0.95	0.92
OLYP opt (1)	B3LYP SP	1.99	-1.11	0.83	0.78
	OLYP SP	1.31	-0.43	0.98	0.96
OLYP opt (1) ^a	B3LYP SP	2.09	-1.15	0.82	0.78
	OLYP SP	1.44	-0.48	0.97	0.96
B3LYP opt (1')	B3LYP SP	2.16	-1.28	0.76	0.70
	OLYP SP	1.53	-0.65	0.95	0.92
CASSCF(5,5) (1')		1.44	-0.46	-	-
CASSCF(5,5) (1') ^a		1.44	-0.46	-	-

^a Calculation performed using the def2-aug-TZVPP basis functions on Co, N, and O.

Table S2. Natural orbital composition of **1'** from CASSCF(5,5) ground state calculation.

orbital	Co	NO	Tp
<74>	57.3	41.7	1.0
<75>	60.2	39.1	0.7
<76>	97.6	0.2	2.2
<77>	47.2	51.3	1.5
<78>	48.5	49.5	2.0

Table S3. Natural orbital-based wavefunction composition of **1'** as obtained from CASSCF(5,5) ground state calculation.

Configuration weight	Configuration				
	<74>	<75>	<76>	<77>	<78>
0.5601	2	2	1	0	0
0.0855	2	0	1	2	0
0.0846	0	2	1	0	2
0.0699	1	1	1	1	1
0.0613	1	2	1	0	1
0.0600	2	1	1	1	0
0.0423	0	0	1	2	2
0.0167	1	0	1	2	1
0.0158	0	1	1	1	2

Table S4. Natural orbital composition of **1'** from CASSCF(5,5) ground state calculation using the def2-aug-TZVPP basis functions on Co, N, and O.

orbital	Co	NO	Tp
<74>	53.2	44.8	0.6
<75>	56.0	42.4	0.7
<76>	96.1	0.6	2.3
<77>	44.2	53.3	1.2
<78>	45.6	51.1	1.6

Table S5. Natural orbital-based wavefunction composition of **1'** as obtained from CASSCF(5,5) ground state calculation using the def2-auf-TZVPP basis functions on Co, N, and O.

Configuration weight	Configuration				
	<74>	<75>	<76>	<77>	<78>
0.5597	2	2	1	0	0
0.0855	2	0	1	2	0
0.0846	0	2	1	0	2
0.0700	1	1	1	1	1
0.0614	1	2	1	0	1
0.0601	2	1	1	1	0
0.0424	0	0	1	2	2
0.0168	1	0	1	2	1
0.0158	0	1	1	1	2

Table S6. Localized orbital composition of **1'** from CASSCF(5,5) ground state calculation.

orbital	Co	NO	Tp
<74>	97.4	1.2	1.4
<75>	96.2	1.4	2.4
<76>	97.6	0.2	2.2
<77>	10.0	89.3	0.8
<78>	9.5	89.8	0.6

Table S7. Localized orbital-based wavefunction composition of **1'** as obtained from CASSCF(5,5) ground state calculation.

Relative contribution	Configuration					VB description
	<74>	<75>	<76>	<77>	<78>	
0.7526	1	1	1	1	1	Co(II) / NO ¹⁻
0.0881	2	1	1	0	1	Co(I) / NO ⁰
0.0796	1	2	1	1	0	Co(I) / NO ⁰
0.0284	2	0	1	0	2	Co(II) / NO ¹⁻
0.0197	0	2	1	2	0	Co(II) / NO ¹⁻
0.0134	1	0	1	1	2	Co(III) / NO ²⁻
0.0108	0	1	1	2	1	Co(III) / NO ²⁻

Table S8. MR-DDCI3 and SORCI computational results for **1'**.

DDCI3 / m2m4	Tsel = 1*10^-8	Tsel = 1*10^-7	Tsel = 1*10^-6	Tsel = 3*10^-5
E, E _h	-2209.091598539	-2209.089479761	-2209.096479536	-2209.108340147
$\Delta E(^4\Gamma - ^2\Gamma)$, cm ⁻¹	9994.8	9277.9	9120.8	8794.1
² Γ ref weight	0.8940	0.9040	0.9229	0.9716
² Γ E(unsel), E _h	-0.032215737	-0.094765339	-0.208930315	-0.379782269
⁴ Γ ref weight	0.8984	0.9098	0.9301	0.9707
⁴ Γ E(unsel), E _h	-0.037745983	-0.112542561	-0.232638360	-0.381057998
SORCI / m2m4	Tsel = 1*10^-8	Tsel = 1*10^-7	Tsel = 1*10^-6	Tsel = 3*10^-5
E, E _h	-2208.997898972	-2208.979179495	-2208.946243750	-2208.763418361
$\Delta E(^4\Gamma - ^2\Gamma)$, cm ⁻¹	10743.2	10520.7	9948.7	8153.2
² Γ ref weight	0.9001	0.9031	0.9122	0.9642
² Γ E(unsel), E _h	-0.000518376	-0.004243514	-0.020746105	-0.026932011
⁴ Γ ref weight	0.9040	0.9073	0.9154	0.9658
⁴ Γ E(unsel), E _h	-0.000495889	-0.004268022	-0.022844546	-0.029347899
DDCI3 / m2m4m6	Tsel = 1*10^-8	Tsel = 1*10^-7	Tsel = 1*10^-6	Tsel = 3*10^-5
E, E _h	-2209.091917808	-2209.091075989	-2209.099810794	-2209.109134166
$\Delta E(^4\Gamma - ^2\Gamma)$, cm ⁻¹	9770.1	9087.0	9361.8	7902.4
$\Delta E(^6\Gamma - ^2\Gamma)$, cm ⁻¹	24978.0	25056.5	26820.7	26687.2
² Γ ref weight	0.8931	0.9048	0.9253	0.9748
² Γ E(unsel), E _h	-0.039859711	-0.112714796	-0.232021997	-0.392296286
⁴ Γ ref weight	0.8999	0.9129	0.9349	0.9724
⁴ Γ E(unsel), E _h	-0.047437101	-0.131985461	-0.251616182	-0.392055675
⁶ Γ ref weight	0.9090	0.9199	0.9381	0.9686
⁶ Γ E(unsel), E _h	-0.024794541	-0.084784232	-0.189494550	-0.329064189
SORCI / m2m4m6	Tsel = 1*10^-8	Tsel = 1*10^-7	Tsel = 1*10^-6	Tsel = 3*10^-5
E, E _h	-2208.986718019	-2208.975197096	-2208.935309429	-2208.755673124
$\Delta E(^4\Gamma - ^2\Gamma)$, cm ⁻¹	10522.6	10394.3	9516.4	7232.3
$\Delta E(^6\Gamma - ^2\Gamma)$, cm ⁻¹	26136.1	25672.3	24817.6	18489.4
² Γ ref weight	0.8983	0.9016	0.9123	0.9667
² Γ E(unsel), E _h	-0.000549431	-0.004163801	-0.022776371	-0.030214251
⁴ Γ ref weight	0.9047	0.9082	0.9176	0.9677
⁴ Γ E(unsel), E _h	-0.000414237	-0.004087129	-0.025201156	-0.031869265
⁶ Γ ref weight	0.9172	0.9194	0.9267	0.9669
⁶ Γ E(unsel), E _h	-0.000074198	-0.001152822	-0.010476157	-0.015617342

Table S9. Mulliken spin density values for **5** and **5'** from DFT and CASSCF(4,4) calculations as well as spatial overlap components of the HOMO-1 and HOMO orbitals of **5** and **5'** from DFT calculations.

		Mulliken Spin Density		$S_{\alpha\beta}$		J^3 / cm^{-1}	$\langle S^2 \rangle$
		Ni	NO	HOMO-1	HOMO		
B3LYP opt (5)	B3LYP SP	0.93	-1.05	0.82	0.82		
	OLYP SP	0.01	-0.01	1.00	1.00		
OLYP opt (5')	B3LYP SP	0.98	-1.10	0.80	0.80	-4095	0.723
	O3LYP SP	0.51	-0.60	0.95	0.94	-4424	0.215
	OLYP SP	0.01	-0.01	1.00	1.00	-5150	0.000
B3LYP opt (5')	B3LYP SP	0.93	-1.03	0.82	0.82		
	OLYP SP	0.01	-0.01	1.00	1.00		
CASSCF(5,5) (5')		-	-	-	-		

Table S10. Natural orbital composition of **5'** from CASSCF(4,4) ground state calculation.

orbital	Ni	NO	Tp
<75>	60.1	39.0	0.9
<76>	60.1	39.0	0.9
<77>	47.9	50.1	2.0
<78>	47.9	50.1	2.0

Table S11. Natural orbital-based wavefunction composition of **5'** as obtained from CASSCF(4,4) ground state calculation.

Relative contribution	Configuration			
	<75>	<76>	<77>	<78>
0.7123	2	2	0	0
0.0868	2	0	2	0
0.0867	0	2	0	2
0.0694	1	1	1	1
0.0421	0	0	2	2

Table S12. Localized orbital composition of **5'** from CASSCF(4,4) ground state calculation.

orbital	Ni	NO	Tp
<75>	96.5	1.4	2.1
<76>	96.5	1.4	2.1
<77>	11.5	87.7	0.8
<78>	11.5	87.7	0.8

Table S13. Localized orbital-based wavefunction composition of **5'** as obtained from CASSCF(4,4) ground state calculation.

Relative contribution	Configuration				VB description
	<75>	<76>	<77>	<78>	
0.6233	1	1	1	1	Ni(II) / NO ¹⁻
0.0741	2	1	1	0	Ni(I) / NO ⁰
0.0740	1	2	0	1	Ni(I) / NO ⁰
0.0390	1	2	1	0	Ni(I) / NO ⁰
0.0389	2	1	0	1	Ni(I) / NO ⁰
0.0227	1	1	0	2	Ni(II) / NO ¹⁻
0.0226	2	0	1	1	Ni(II) / NO ¹⁻
0.0226	0	2	1	1	Ni(II) / NO ¹⁻
0.0226	1	1	2	0	Ni(II) / NO ¹⁻
0.0123	0	2	0	2	Ni(II) / NO ¹⁻
0.0123	2	0	2	0	Ni(II) / NO ¹⁻

Table S14. MR-DDCI3 and SORCI computational results for 5'.

DDCI3 / m1m3	Tsel = 1*10^-8	Tsel = 1*10^-7	Tsel = 1*10^-6	Tsel = 3*10^-5
E, E _h	-2334.537664672	-2334.534469543	-2334.534469543	-2334.544051840
$\Delta E(^3\Gamma - ^1\Gamma)$, cm ⁻¹	12478.9	11888.9	11888.9	10281.1
¹ Γ ref weight	0.8885	0.9002	0.9002	0.9624
¹ Γ E(unsel), E _h	-0.032806775	-0.094795920	-0.094795920	-0.336092220
³ Γ ref weight	0.8866	0.9009	0.9009	0.9621
³ Γ E(unsel), E _h	-0.049814599	-0.131568352	-0.131568352	-0.364020502
SORCI / m1m3	Tsel = 1*10^-8	Tsel = 1*10^-7	Tsel = 1*10^-6	Tsel = 3*10^-5
E, E _h	-2334.436299173	-2334.426393362	-2334.394639059	-2334.246199116
$\Delta E(^3\Gamma - ^1\Gamma)$, cm ⁻¹	13509.9	13567.3	12667.2	11397.6
¹ Γ ref weight	0.8993	0.9015	0.9096	0.9527
¹ Γ E(unsel), E _h	-0.000191086	-0.001520010	-0.008868286	-0.025601342
³ Γ ref weight	0.8985	0.9028	0.9088	0.9543
³ Γ E(unsel), E _h	-0.000187917	-0.002096482	-0.012690348	-0.034165872
DDCI3 / m1m3m5	Tsel = 1*10^-8	Tsel = 1*10^-7	Tsel = 1*10^-6	Tsel = 3*10^-5
E, E _h	-2334.542669910	-2334.536500849	-2334.535725595	-2334.544080902
$\Delta E(^3\Gamma - ^1\Gamma)$, cm ⁻¹	12721.5	11904.3	11507.9	10612.3
$\Delta E(^5\Gamma - ^1\Gamma)$, cm ⁻¹	31941.9	31014.1	30903.8	31512.0
¹ Γ ref weight	0.8775	0.8866	0.9007	0.9571
¹ Γ E(unsel), E _h	-0.014124289	-0.048806828	-0.130474933	-0.329204215
³ Γ ref weight	0.8814	0.8910	0.9111	0.9632
³ Γ E(unsel), E _h	-0.021921291	-0.071557392	-0.173678381	-0.351899233
⁵ Γ ref weight	0.9059	0.9131	0.9268	0.9564
⁵ Γ E(unsel), E _h	-0.013007984	-0.046880930	-0.127364031	-0.288399706
SORCI / m1m3m5	Tsel = 1*10^-8	Tsel = 1*10^-7	Tsel = 1*10^-6	Tsel = 3*10^-5
E, E _h	-2334.428725731	-2334.420611384	-2334.399673755	-2334.239147171
$\Delta E(^3\Gamma - ^1\Gamma)$, cm ⁻¹	13147.9	13044.4	12453.8	9899.7
$\Delta E(^5\Gamma - ^1\Gamma)$, cm ⁻¹	32156.4	31714.2	30770.5	25353.4
¹ Γ ref weight	0.8937	0.8949	0.9016	0.9496
¹ Γ E(unsel), E _h	-0.000151002	-0.001095113	-0.007072809	-0.020896349
³ Γ ref weight	0.8993	0.9014	0.9075	0.9519
³ Γ E(unsel), E _h	-0.000145680	-0.001542008	-0.010283063	-0.028567946
⁵ Γ ref weight	0.9150	0.9167	0.9211	0.9584
⁵ Γ E(unsel), E _h	-0.000054561	-0.000560950	-0.004476440	-0.014023788

Computational details for $\text{Tp}'\text{Cu}(\text{NO})$ calculations. See the Computational Procedures section for general details. The crystallographically-determined coordinates for $\text{Tp}^{\text{tBu},\text{H}}\text{Cu}(\text{NO})$ were used as a starting point for all geometry optimizations. A truncated form of the molecule was used for the single point CASSCF calculations. For this structure, the BP86-optimized coordinates were truncated to $\text{Tp}\text{Cu}(\text{NO})$ ($\text{Tp} = \text{Tp}^{\text{H},\text{H}}$), then the non-hydrogen atoms were frozen while the positions of the hydrogen atoms were optimized.

Table S15. Mulliken spin densities for $\text{Tp}^{\text{tBu}}\text{Cu}(\text{NO})$ and $\text{Tp}\text{Cu}(\text{NO})$ from DFT and CASSCF calculations, respectively. The spatial overlap components of the HOMO-1 and HOMO orbitals are from DFT calculations.

	Mulliken Spin Density		$S_{\alpha\beta}$
	Cu	NO	HOMO-1
B3LYP opt of $\text{Tp}^{\text{tBu}}\text{Cu}(\text{NO})$	+0.01	+0.99	0.99
OLYP opt of $\text{Tp}^{\text{tBu}}\text{Cu}(\text{NO})$	+0.05	+0.96	1.00
CASSCF(5,4) on $\text{Tp}\text{Cu}(\text{NO})$	-0.04	+1.04	-

Figure S15. Spin density plots with numerically-annotated Mulliken spin densities for $\text{Tp}^{\text{tBu}}\text{Cu}(\text{NO})$ from UKS geometry optimization calculations using the B3LYP (top) and OLYP (middle) functionals. The tBu groups and hydrogens were removed for clarity.

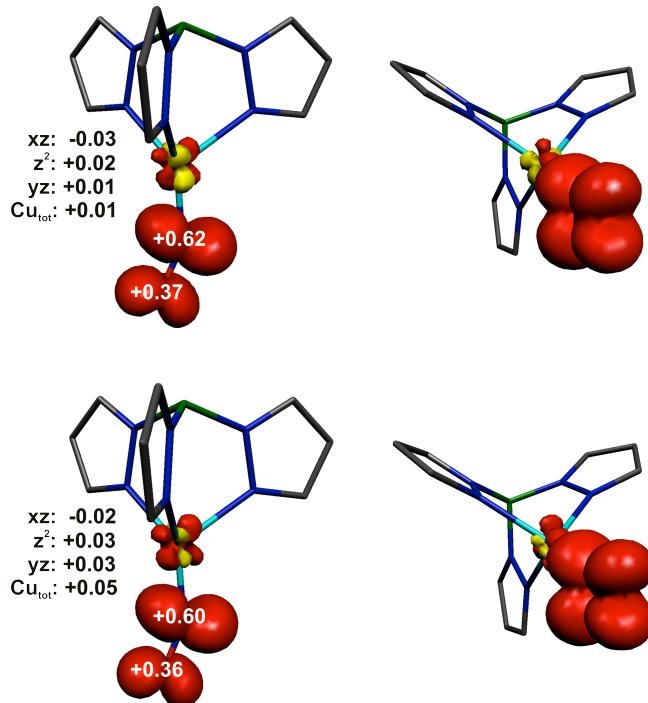


Table S16. Natural orbital composition of TpCu(NO) from CASSCF(5,4) ground state calculation.

orbital	Cu	NO	Tp
<75>	93.4	5.5	1.1
<76>	67.5	30.4	2.1
<77>	8.4	90.3	1.3
<78>	41.5	55.9	2.6

Table S17. Natural orbital-based wavefunction composition of TpCu(NO) as obtained from CASSCF(5,4) ground state calculation.

Relative contribution	Configuration			
	<75>	<76>	<77>	<78>
0.7572	2	2	1	0
0.1670	2	0	1	2
0.0375	2	1	1	1
0.0232	1	1	2	1
0.0103	1	0	2	2

Table S18. Localized orbital composition of TpCu(NO) from CASSCF(5,4) ground state calculation.

orbital	Cu	NO	Tp
<75>	96.1	2.4	1.5
<76>	96.6	0.6	2.8
<77>	5.7	93.4	0.9
<78>	12.6	86.2	1.2

Table S19. Localized orbital-based wavefunction composition of TpCu(NO) as obtained from CASSCF(5,4) ground state calculation.

Relative contribution	Configuration				VB description
	<75>	<76>	<77>	<78>	
0.7980	2	1	1	1	Cu(II) / NO ¹⁻
0.1317	2	2	1	0	Cu(I) / NO ⁰
0.0592	1	2	2	0	Cu(II) / NO ¹⁻

Table S20. MR-DDCI3 computational results for TpCu(NO).

DDCI3 / m2m4	Tsel = 1*10^-8	Tsel = 1*10^-7	Tsel = 1*10^-6	Tsel = 3*10^-5
E, E _h	-2466.632624551	-2466.632987744	-2466.644798048	-2466.649704262
$\Delta E(^4\Gamma - ^2\Gamma)$, cm ⁻¹	16517.6	16859.7	18549.8	17646.0
² Γ ref weight	0.8861	0.8931	0.9061	0.9410
² Γ E(unsel), E _h	-0.018823431	-0.065693865	-0.173128240	-0.316243622
⁴ Γ ref weight	0.9075	0.9169	0.9333	0.9561
⁴ Γ E(unsel), E _h	-0.014872795	-0.056914204	-0.152328194	-0.276973595

[Co(NCS)₄]²⁻ geometry optimization

Input file:

```
! UKS B3LYP RIJCOSX SlowConv TightSCF TightOpt def2-TZVP def2-TZVP/J
! COSMO(water) UCO NORMALPRINT Grid4 NoFinalGrid vdw

%scf directresetfreq 20
  diismaxeq 20
  MaxIter 700
end

%method SpecialGridAtoms 27, 16, 7, 6
  SpecialGridIntAcc 10, 5, 5, 5
end

%geom MaxIter 300
end

%pal nprocs 16 end

*xyz -2 4
  Co    -0.017897    0.068174    0.012702
  N     -0.071450    0.017124    1.938879
  N     1.812296    0.093894   -0.587710
  N    -0.913226    1.655400   -0.613264
  N    -0.895082   -1.492190   -0.700564
  C    -0.086257   -0.015353    3.126292
  C     2.917389    0.106076   -1.023709
  C    -1.454692    2.637843   -1.004261
  C    -1.436116   -2.446851   -1.155875
  S    -0.106061   -0.058256    4.751981
  S     4.431066    0.123652   -1.618227
  S    -2.197842    3.981945   -1.539283
  S    -2.177958   -3.753127   -1.778151
*
```

Optimized coordinates:

Co	-0.025538	0.065203	0.019805
N	-0.062732	0.013846	1.990034
N	1.840963	0.087993	-0.615718
N	-0.939756	1.691785	-0.615167
N	-0.929148	-1.530273	-0.703668
C	-0.088839	-0.016825	3.162631
C	2.931926	0.109430	-1.046689
C	-1.456858	2.667557	-1.010890
C	-1.446636	-2.478204	-1.161711
S	-0.126360	-0.059440	4.786767
S	4.444539	0.139386	-1.641302
S	-2.173602	4.019641	-1.559135
S	-2.163788	-3.791769	-1.796146

Tp^{tBu,Me}Co(NCS) geometry optimization

Input file:

```
! UKS B3LYP RIJCOSX SlowConv TightSCF TightOpt def2-SVP def2-SV/J UCO
! NORMALPRINT Grid4 NoFinalGrid vdw
```

```
%basis NewGTO 27 "def2-TZVP" end
    NewGTO 16 "def2-TZVP" end
    NewGTO 8 "def2-TZVP" end
    NewGTO 7 "def2-TZVP" end
    NewAuxGTO 27 "def2-TZVP/J" end
    NewAuxGTO 16 "def2-TZVP/J" end
    NewAuxGTO 8 "def2-TZVP/J" end
    NewAuxGTO 7 "def2-TZVP/J" end
end

%method SpecialGridAtoms 27, 16, 8, 7, 6, 1
    SpecialGridIntAcc 10, 5, 5, 5, 5
end

%scf MaxIter 700
end

%pal nprocs 24 end

*xyz 0 4
Co      0.000000000  0.000000000  0.000000000
N      -0.731815940 -1.560472288  1.020583036
N      -0.536870594 -1.359819406  2.377625572
N      -1.010435041  1.412272792  1.036859018
N      -0.896663154  1.152370688  2.393536868
N      1.725480417  0.082427052  1.043307499
N      1.443385351  0.210963472  2.395621180
N      0.028634604  0.021384660 -1.915017513
C      0.105349547 -0.029569336 -3.080347676 NewGTO "def2-TZVP" end
S      0.221958336 -0.107784850 -4.681810490
B      0.000000000  0.000000000  2.915810493
C      -1.217580090 -2.807668582  0.870473405
C      -1.328453286 -3.401859476  2.124685921
C      -0.900857485 -2.474047125  3.050283264
C      -1.571652263 -3.367624412 -0.497572068
C      -0.289487552 -3.546105273 -1.327991108
C      -2.540453119 -2.430860579 -1.217573953
C      -2.228453026 -4.744098227 -0.315523022
C      -1.817143709  2.474697622  0.906387906
C      -2.219822735  2.896236895  2.163802731
C      -1.630307921  2.057778890  3.077395967
C      -2.199458697  3.034687675 -0.448118516
C      -2.906335580  1.954931322 -1.276026601
C      -3.169937162  4.207362622 -0.261779736
C      -0.948004080  3.513270160 -1.188054361
C      3.056012822  0.172420416  0.908737551
C      3.625895040  0.385877831  2.167109299
C      2.592039700  0.405658139  3.076137261
C      3.747514398 -0.011165177 -0.420783771
C      5.254996324  0.066918177 -0.226437712
C      3.336089617  1.080296408 -1.417941436
```

C	3.381947587	-1.388303330	-0.983743762
C	-0.849079752	-2.588105480	4.533911441
C	-1.735067512	2.055430103	4.567331783
C	2.645089111	0.609545874	4.557928021
H	-0.003356866	-0.006060193	3.916235082
H	-1.640240579	-4.279922926	2.308023837
H	0.342233002	-4.110914779	-0.835821496
H	0.116199902	-2.669988879	-1.495219527
H	-0.511295033	-3.971272663	-2.182573909
H	-2.804808296	-2.828182310	-2.073040179
H	-2.102389696	-1.569096747	-1.380047090
H	-3.335723149	-2.293607584	-0.662257451
H	-2.469235721	-5.108907544	-1.191902096
H	-3.035321072	-4.650447978	0.231834399
H	-1.599653552	-5.349610736	0.129295011
H	-2.795715533	3.626381921	2.356848758
H	-2.281677591	1.222302939	-1.459368227
H	-3.213949727	2.342031954	-2.122932675
H	-3.675545148	1.610294173	-0.776147611
H	-3.975523472	3.894649804	0.200017383
H	-3.415962619	4.570264264	-1.139149524
H	-2.738480843	4.906257330	0.273003073
H	-0.496440393	4.201231179	-0.655994680
H	-1.205138991	3.888162758	-2.056595197
H	-0.340433257	2.757651467	-1.326930836
H	4.550063580	0.496563400	2.357384066
H	5.490263413	0.938216941	0.154840332
H	5.702569988	-0.041740628	-1.090985926
H	5.543888934	-0.644927638	0.382469975
H	2.359025869	1.100730778	-1.496007161
H	3.729002530	0.886715846	-2.294687855
H	3.657084110	1.949356230	-1.100743184
H	3.638137628	-2.082042605	-0.341771666
H	3.858539351	-1.533067347	-1.827918246
H	2.416035847	-1.430554877	-1.143077499
H	0.057732071	-2.383698339	4.845355258
H	-1.088265480	-3.499941377	4.799998241
H	-1.481870080	-1.953797372	4.932610109
H	-2.048069371	1.177380445	4.871797604
H	-2.371318552	2.744771793	4.850409262
H	-0.855360613	2.241923865	4.956557299
H	2.208154628	1.456340134	4.787665054
H	3.579479397	0.635404131	4.851282680
H	2.181804768	-0.128561015	5.005163299

*

Optimized coordinates:

Co	0.002127	-0.081576	-0.029831
N	-0.725262	-1.633024	1.084928
N	-0.623328	-1.380620	2.423132
N	-0.990230	1.341479	1.052553
N	-0.840530	1.145670	2.395751
N	1.717421	0.081882	1.071756
N	1.455454	0.070543	2.412094
N	0.004643	-0.108063	-1.932748
C	-0.001339	-0.176527	-3.111869

S	-0.008242	-0.270010	-4.709130
B	-0.004311	-0.049232	2.929189
C	-1.285610	-2.838681	0.931019
C	-1.551917	-3.377435	2.205204
C	-1.118787	-2.424420	3.123957
C	-1.543370	-3.440271	-0.441078
C	-0.205124	-3.586918	-1.198933
C	-2.503181	-2.527541	-1.235520
C	-2.186745	-4.829751	-0.284840
C	-1.745924	2.431575	0.873530
C	-2.091451	2.952489	2.135976
C	-1.499640	2.110483	3.074425
C	-2.114145	2.941291	-0.510503
C	-2.909775	1.853631	-1.264999
C	-2.984730	4.204373	-0.382526
C	-0.828322	3.292718	-1.291636
C	3.041784	0.189153	0.908189
C	3.648536	0.248854	2.178072
C	2.611239	0.170472	3.104294
C	3.685530	0.228952	-0.467779
C	5.211619	0.364657	-0.321652
C	3.144425	1.441031	-1.257158
C	3.365836	-1.079059	-1.224101
C	-1.157125	-2.467351	4.618242
C	-1.535476	2.186436	4.567564
C	2.675401	0.188248	4.598332
H	-0.006732	-0.035784	4.132823
H	-2.001290	-4.337850	2.438641
H	0.490409	-4.237413	-0.645214
H	0.280888	-2.613304	-1.350880
H	-0.377636	-4.026339	-2.194110
H	-2.693616	-2.950896	-2.234749
H	-2.078198	-1.524773	-1.380263
H	-3.467612	-2.421768	-0.713430
H	-2.376139	-5.269092	-1.276745
H	-3.150179	-4.769883	0.246011
H	-1.530312	-5.518563	0.270451
H	-2.693892	3.830172	2.348934
H	-2.313391	0.940108	-1.398122
H	-3.191929	2.211777	-2.268043
H	-3.830256	1.588988	-0.719981
H	-3.918996	3.997082	0.163431
H	-3.255149	4.575900	-1.383270
H	-2.449975	5.011191	0.143662
H	-0.243009	4.058839	-0.759135
H	-1.083803	3.680393	-2.290723
H	-0.190740	2.409221	-1.435100
H	4.706419	0.338135	2.405050
H	5.486378	1.290260	0.209153
H	5.680813	0.396779	-1.317372
H	5.643185	-0.488499	0.225923
H	2.058103	1.370962	-1.406807
H	3.610417	1.486731	-2.254360
H	3.361767	2.383796	-0.729998
H	3.738516	-1.955825	-0.670723
H	3.838128	-1.071189	-2.219287
H	2.284392	-1.201614	-1.376873

H	-0.147270	-2.394924	5.052557
H	-1.607434	-3.412336	4.952889
H	-1.749478	-1.636616	5.033721
H	-1.986935	1.284052	5.009803
H	-2.127566	3.057239	4.882461
H	-0.524338	2.287505	4.993316
H	2.113137	1.037241	5.019531
H	3.721124	0.275475	4.924561
H	2.253701	-0.731301	5.034790

Tp*Co(NO) geometry optimization (B3LYP)

Input file:

```
! UKS B3LYP RIJCOSX SlowConv TightSCF TightOpt def2-SVP def2-SV/J UCO
! NORMALPRINT Grid4 NoFinalGrid vdw
```

```
%basis NewGTO 27 "def2-TZVP" end
    NewGTO 8 "def2-TZVP" end
    NewGTO 7 "def2-TZVP" end
    NewAuxGTO 27 "def2-TZVP/J" end
    NewAuxGTO 8 "def2-TZVP/J" end
    NewAuxGTO 7 "def2-TZVP/J" end
end

%scf MaxIter 700
end

%geom MaxIter 300
end

%pal nprocs 24 end

*xyz 0 2
Co      0.141992   -0.050140    0.054331
N       -0.262997   -0.080770   -1.536423
O       -0.845137   -0.079348   -2.569052
N       -0.767117   -1.193263    2.555404
N       -0.820104   -1.379412    1.201317
N       1.490028   -0.060868    2.623043
N       1.735850   -0.114830    1.277777
N       -0.624336   1.317930    2.486640
N       -0.663992   1.431344    1.124282
B       0.008726    0.038503    3.096002
C      -1.438705   -2.193588    3.194292
C      -1.940658   -3.049816    2.205516
C      -1.530633   -2.502780    0.968061
C      2.660668   -0.120949    3.315977
C      3.697411   -0.217504    2.376163
C      3.074391   -0.210351    1.108487
C      -1.182178   2.418853    3.066763
C      -1.595305   3.266401    2.030162
C      -1.252726   2.608903    0.826456
C      2.737781   -0.084050    4.813021
C      -1.288864   2.606573    4.550951
C      -1.562956   -2.284117    4.686280
C      -1.469312   3.053312   -0.589719
C      -1.792918   -3.002183   -0.421735
```

C	3.682098	-0.291992	-0.258848
H	-0.041958	0.074738	4.317718
H	-2.527772	-3.962526	2.363706
H	4.770924	-0.285479	2.591485
H	-2.081917	4.243282	2.135003
H	3.798071	-0.141101	5.136370
H	2.192306	-0.933788	5.281248
H	2.303724	0.851813	5.230654
H	-0.292770	2.614178	5.046646
H	-1.887511	1.801892	5.033254
H	-1.783852	3.576317	4.769416
H	-0.572697	-2.371735	5.186396
H	-2.160592	-3.180047	4.957376
H	-2.069147	-1.392682	5.119713
H	-0.518411	3.058639	-1.166787
H	-1.893106	4.079224	-0.610046
H	-2.171965	2.379282	-1.128681
H	-2.439194	-2.299948	-0.994694
H	-2.302737	-3.987785	-0.387312
H	-0.848893	-3.118788	-0.998250
H	4.386356	0.550574	-0.443504
H	2.885545	-0.257367	-1.033809
H	4.257001	-1.236357	-0.392481

*

Optimized coordinates:

Co	0.189555	-0.065768	-0.016002
N	-0.292436	-0.077732	-1.663523
O	-0.931491	-0.060647	-2.656933
N	-0.734981	-1.194711	2.544815
N	-0.799130	-1.402322	1.204296
N	1.516639	-0.068308	2.594958
N	1.784055	-0.126667	1.262076
N	-0.589700	1.306888	2.473522
N	-0.627963	1.446517	1.123317
B	0.044238	0.031522	3.078309
C	-1.437402	-2.146299	3.196418
C	-1.974319	-3.000725	2.235009
C	-1.543758	-2.487806	0.995545
C	2.666592	-0.114859	3.297385
C	3.716908	-0.207286	2.384573
C	3.109643	-0.211319	1.115415
C	-1.187358	2.362413	3.067122
C	-1.625852	3.216416	2.056636
C	-1.250168	2.593238	0.850292
C	2.701567	-0.069751	4.791703
C	-1.305352	2.491228	4.552473
C	-1.552449	-2.183629	4.687172
C	-1.463533	3.036455	-0.563733
C	-1.818804	-2.978616	-0.391867
C	3.727984	-0.294426	-0.243820
H	0.003118	0.067850	4.284782
H	-2.593150	-3.878354	2.410141
H	4.778545	-0.264047	2.615556
H	-2.147490	4.163352	2.179075
H	3.743260	-0.122141	5.141738
H	2.141846	-0.911952	5.232125

H	2.248700	0.859313	5.176528
H	-0.314931	2.486160	5.037846
H	-1.882483	1.656316	4.984672
H	-1.812377	3.434112	4.807111
H	-0.562188	-2.267274	5.166008
H	-2.160104	-3.048559	4.993374
H	-2.025993	-1.267313	5.078208
H	-0.506893	3.091474	-1.109881
H	-1.939420	4.028473	-0.590550
H	-2.104716	2.324447	-1.110002
H	-2.428901	-2.252657	-0.955536
H	-2.356215	-3.938667	-0.363385
H	-0.880866	-3.115934	-0.955257
H	4.434389	0.536597	-0.411199
H	2.945786	-0.250792	-1.018943
H	4.290005	-1.236012	-0.369003

Tp*Co(NO) geometry optimization (OLYP)

Input file:

```
! UKS OLYP RI SlowConv TightSCF TightOpt def2-SVP def2-SV/J UCO NORMALPRINT
! Grid4 NoFinalGrid vdw
```

```
%basis NewGTO 27 "def2-TZVP" end
    NewGTO 8 "def2-TZVP" end
    NewGTO 7 "def2-TZVP" end
    NewAuxGTO 27 "def2-TZVP/J" end
    NewAuxGTO 8 "def2-TZVP/J" end
    NewAuxGTO 7 "def2-TZVP/J" end
end

%scf MaxIter 700
end

%geom MaxIter 300
end

%pal nprocs 8 end

*xyz 0 2
Co      0.178890   -0.061327    0.027324
N       -0.276615   -0.079692   -1.579259
O       -0.902190   -0.071829   -2.579182
N       -0.744126   -1.192635    2.550494
N       -0.800749   -1.385416    1.206223
N       1.503705   -0.064530    2.611450
N       1.758062   -0.118939    1.275748
N       -0.602141   1.307276    2.479166
N       -0.638454   1.430395    1.126053
B       0.030115   0.033937    3.089390
C      -1.435681   -2.164167    3.192038
C      -1.956336   -3.012663    2.216750
C      -1.532305   -2.484192    0.983514
C      2.662368   -0.116727    3.306556
C      3.701886   -0.208382    2.380829
C      3.087565   -0.206764    1.116987
C      -1.183477   2.382285    3.062546
```

C	-1.608645	3.227492	2.039244
C	-1.245671	2.588509	0.839276
C	2.717849	-0.078041	4.801114
C	-1.297974	2.540309	4.545924
C	-1.556492	-2.228072	4.681950
C	-1.460592	3.020523	-0.577223
C	-1.801184	-2.967775	-0.406867
C	3.692433	-0.286645	-0.247668
H	-0.016337	0.070786	4.292981
H	-2.563222	-3.899827	2.380319
H	4.764786	-0.268357	2.601421
H	-2.115194	4.183035	2.150616
H	3.762822	-0.130417	5.135578
H	2.169456	-0.922885	5.246810
H	2.273370	0.848391	5.197374
H	-0.309138	2.539985	5.031201
H	-1.884633	1.723621	4.995823
H	-1.795626	3.491162	4.780883
H	-0.569996	-2.310272	5.165217
H	-2.153433	-3.104690	4.968808
H	-2.046936	-1.328913	5.087454
H	-0.523100	2.968118	-1.151627
H	-1.837273	4.052063	-0.613227
H	-2.188340	2.367203	-1.084193
H	-2.453198	-2.266103	-0.950852
H	-2.291648	-3.950726	-0.385146
H	-0.866416	-3.053498	-0.981744
H	4.390641	0.547258	-0.422081
H	2.900556	-0.245917	-1.011143
H	4.255028	-1.224754	-0.378281

*

Optimized coordinates:

Co	0.153315	-0.060157	0.021227
N	-0.321178	-0.076931	-1.553233
O	-1.029051	-0.063798	-2.500067
N	-0.755646	-1.199173	2.538203
N	-0.815090	-1.391777	1.193123
N	1.505878	-0.066522	2.614290
N	1.764016	-0.120071	1.279616
N	-0.610378	1.314819	2.466891
N	-0.652514	1.436974	1.112884
B	0.022114	0.033474	3.076998
C	-1.434839	-2.184420	3.184940
C	-1.949405	-3.038070	2.205959
C	-1.538214	-2.504190	0.968302
C	2.666329	-0.117802	3.319817
C	3.709762	-0.207919	2.393398
C	3.099680	-0.206536	1.124189
C	-1.176589	2.402844	3.055125
C	-1.597872	3.251209	2.028148
C	-1.251102	2.607049	0.823700
C	2.730392	-0.080243	4.814203
C	-1.284647	2.581229	4.536731
C	-1.555748	-2.267239	4.673957
C	-1.474605	3.053426	-0.586820
C	-1.812006	-3.002695	-0.415638

C	3.727572	-0.285811	-0.230918
H	-0.034607	0.070944	4.282237
H	-2.546629	-3.934915	2.370964
H	4.775105	-0.266779	2.617188
H	-2.093197	4.215685	2.140691
H	3.778467	-0.133601	5.147874
H	2.183714	-0.924401	5.269883
H	2.289234	0.846485	5.221113
H	-0.294741	2.580752	5.026171
H	-1.877052	1.776359	5.006684
H	-1.775132	3.540664	4.764276
H	-0.569997	-2.354327	5.164149
H	-2.152466	-3.149701	4.953355
H	-2.048826	-1.374720	5.097982
H	-0.537962	3.027940	-1.169296
H	-1.871036	4.080583	-0.611067
H	-2.191069	2.395284	-1.108491
H	-2.447780	-2.297852	-0.979122
H	-2.324025	-3.977153	-0.383344
H	-0.878594	-3.119010	-0.992317
H	4.432517	0.548910	-0.394567
H	2.957242	-0.247058	-1.018292
H	4.299068	-1.223567	-0.352528

Tp*Co(NO) geometry optimization (OLYP) using the def2-aug-TZVPP basis functions on Co, N, and O

Input file:

```
! UKS OLYP RI SlowConv TightSCF TightOpt def2-SVP def2-TZVP/J UCO NORMALPRINT
! Grid5 NoFinalGrid
```

```
%basis NewGTO 27 "def2-aug-TZVPP" end
NewGTO 8 "def2-aug-TZVPP" end
NewGTO 7 "def2-aug-TZVPP" end
End

%scf MaxIter 700
end

%geom MaxIter 300
end

%pal nprocs 16 end

*xyz 0 2
Co    0.178890   -0.061327    0.027324
N     -0.276615   -0.079692   -1.579259
O     -0.902190   -0.071829   -2.579182
N     -0.744126   -1.192635    2.550494
N     -0.800749   -1.385416    1.206223
N     1.503705   -0.064530    2.611450
N     1.758062   -0.118939    1.275748
N     -0.602141   1.307276    2.479166
N     -0.638454   1.430395    1.126053
B      0.030115   0.033937    3.089390
C     -1.435681   -2.164167    3.192038
C     -1.956336   -3.012663    2.216750
```

C	-1.532305	-2.484192	0.983514
C	2.662368	-0.116727	3.306556
C	3.701886	-0.208382	2.380829
C	3.087565	-0.206764	1.116987
C	-1.183477	2.382285	3.062546
C	-1.608645	3.227492	2.039244
C	-1.245671	2.588509	0.839276
C	2.717849	-0.078041	4.801114
C	-1.297974	2.540309	4.545924
C	-1.556492	-2.228072	4.681950
C	-1.460592	3.020523	-0.577223
C	-1.801184	-2.967775	-0.406867
C	3.692433	-0.286645	-0.247668
H	-0.016337	0.070786	4.292981
H	-2.563222	-3.899827	2.380319
H	4.764786	-0.268357	2.601421
H	-2.115194	4.183035	2.150616
H	3.762822	-0.130417	5.135578
H	2.169456	-0.922885	5.246810
H	2.273370	0.848391	5.197374
H	-0.309138	2.539985	5.031201
H	-1.884633	1.723621	4.995823
H	-1.795626	3.491162	4.780883
H	-0.569996	-2.310272	5.165217
H	-2.153433	-3.104690	4.968808
H	-2.046936	-1.328913	5.087454
H	-0.523100	2.968118	-1.151627
H	-1.837273	4.052063	-0.613227
H	-2.188340	2.367203	-1.084193
H	-2.453198	-2.266103	-0.950852
H	-2.291648	-3.950726	-0.385146
H	-0.866416	-3.053498	-0.981744
H	4.390641	0.547258	-0.422081
H	2.900556	-0.245917	-1.011143
H	4.255028	-1.224754	-0.378281

*

Optimized coordinates:

Co	0.138999	-0.064560	0.025112
N	-0.267031	-0.084975	-1.571537
O	-0.886131	-0.077541	-2.578729
N	-0.772085	-1.209294	2.534979
N	-0.836640	-1.406800	1.190116
N	1.498183	-0.069924	2.609399
N	1.757612	-0.122611	1.274530
N	-0.626294	1.316571	2.463946
N	-0.672743	1.443998	1.109947
B	0.008261	0.028776	3.067237
C	-1.441577	-2.199354	3.188136
C	-1.952942	-3.058886	2.213320
C	-1.551911	-2.527145	0.971484
C	2.660709	-0.114976	3.314835
C	3.703163	-0.200143	2.387155
C	3.094668	-0.202268	1.117387
C	-1.174349	2.412733	3.058251
C	-1.586827	3.269109	2.034992
C	-1.254607	2.625321	0.826328

C	2.739976	-0.076208	4.809110
C	-1.279336	2.602520	4.539368
C	-1.563942	-2.291317	4.677204
C	-1.482373	3.097404	-0.576374
C	-1.837013	-3.048121	-0.403154
C	3.737207	-0.277573	-0.232270
H	-0.046788	0.065789	4.268640
H	-2.542440	-3.959506	2.383960
H	4.768594	-0.253549	2.610785
H	-2.067732	4.239984	2.152807
H	3.791797	-0.127213	5.129775
H	2.204217	-0.921482	5.274422
H	2.305950	0.850285	5.222992
H	-0.290540	2.605513	5.030232
H	-1.877501	1.808507	5.019220
H	-1.764365	3.566330	4.758063
H	-0.580899	-2.381437	5.171333
H	-2.157270	-3.178145	4.948305
H	-2.064313	-1.407104	5.108845
H	-0.550341	3.090028	-1.166232
H	-1.878233	4.124819	-0.576452
H	-2.205235	2.456338	-1.110180
H	-2.484026	-2.359728	-0.974078
H	-2.347426	-4.022070	-0.346701
H	-0.912387	-3.180125	-0.989930
H	4.434764	0.564264	-0.390453
H	2.981225	-0.250280	-1.032317
H	4.322380	-1.207764	-0.345243

Tp*Co(NO) B3LYP single point energy calculation on B3LYP/OLYP geometry-optimized coordinates

Input file:

```
! UKS B3LYP RIJCOSX SlowConv TightSCF def2-SVP def2-SV/J UCO UNO NORMALPRINT
! Grid4 NoFinalGrid vdw

%basis NewGTO 27 "def2-TZVP" end
    NewGTO 8 "def2-TZVP" end
    NewGTO 7 "def2-TZVP" end
    NewAuxGTO 27 "def2-TZVP/J" end
    NewAuxGTO 8 "def2-TZVP/J" end
    NewAuxGTO 7 "def2-TZVP/J" end
end

%scf FlipSpin 1,2
    FinalMs 0.5
end

%pal nprocs 16 end

*xyz 0 6
.
.
.
```

Tp*Co(NO) OLYP single point energy calculation on B3LYP/OLYP geometry-optimized coordinates

Input file:

```
! UKS OLYP RI SlowConv TightSCF def2-SVP def2-SV/J UCO UNO NORMALPRINT Grid4
! NoFinalGrid vdw

%basis NewGTO 27 "def2-TZVP" end
    NewGTO 8 "def2-TZVP" end
    NewGTO 7 "def2-TZVP" end
    NewAuxGTO 27 "def2-TZVP/J" end
    NewAuxGTO 8 "def2-TZVP/J" end
    NewAuxGTO 7 "def2-TZVP/J" end
end

%scf FlipSpin 1,2
    FinalMs 0.5
    MaxIter 700
end

%pal nprocs 32 end

*xyz 0 6
.
.
.
*
```

Tp*Co(NO) B3LYP single point energy calculation on OLYP(def2-aug-TZVPP) geometry-optimized coordinates

```
! UKS B3LYP RIJCOSX SlowConv TightSCF def2-SVP def2-TZVP/J UCO NORMALPRINT
! Grid5 NoFinalGrid
```

```
%basis NewGTO 27 "def2-aug-TZVPP" end
    NewGTO 8 "def2-aug-TZVPP" end
    NewGTO 7 "def2-aug-TZVPP" end
end

%scf FlipSpin 1,2
    FinalMs 0.5
End

%pal nprocs 16 end

*xyz 0 6
.
.
.
```

Tp*Co(NO) OLYP single point energy calculation on OLYP(def2-aug-TZVPP) geometry-optimized coordinates

```
! UKS OLYP RI SlowConv TightSCF def2-SVP def2-TZVP/J UCO NORMALPRINT Grid5
! NoFinalGrid
```

```
%basis NewGTO 27 "def2-aug-TZVPP" end
```

```

NewGTO 8 "def2-aug-TZVPP" end
NewGTO 7 "def2-aug-TZVPP" end
end

%scf FlipSpin 1,2
  FinalMs 0.5
End

%pal nprocs 16 end

*xyz 0 6
.
.
.
*
```

TpCo(NO) geometry optimization (B3LYP) for CASSCF input

Input file:

```

! UKS B3LYP RIJCOSX SlowConv TightSCF TightOpt def2-SVP def2-SV/J UCO
! NORMALPRINT Grid4 NoFinalGrid vdw
```

```

%basis NewGTO 27 "def2-TZVP" end
  NewGTO 8 "def2-TZVP" end
  NewGTO 7 "def2-TZVP" end
  NewAuxGTO 27 "def2-TZVP/J" end
  NewAuxGTO 8 "def2-TZVP/J" end
  NewAuxGTO 7 "def2-TZVP/J" end
end

%geom MaxIter 300
end

%pal nprocs 32 end

*xyz 0 2
  Co      0.134900105   -0.050762383    0.134767047
  N      -0.270088919   -0.081392376   -1.455987048
  O      -0.852228954   -0.079970369   -2.488616110
  N      -0.774208892   -1.193885739    2.635840320
  N      -0.827195924   -1.380034787    1.281753239
  N      1.482936250   -0.061490390    2.703479365
  N      1.728758236   -0.115452398    1.358213290
  N      -0.631427873   1.317308011    2.567076306
  N      -0.671083903   1.430722052    1.204718224
  B      0.001634171    0.037880630    3.176438362
  C      -1.445796924   -2.194211043    3.274728350
  C      -1.947749978   -3.050439296    2.285952285
  C      -1.537724977   -2.503403125    1.048497217
  C      2.653576333   -0.121571406    3.396413431
  C      3.690319376   -0.218126425    2.456599396
  C      3.067299312   -0.210973420    1.188923308
  C      -1.189269889    2.418231334    3.147199324
  C      -1.602396931    3.265779590    2.110598249
  C      -1.259817938    2.608281402    0.906892188
  H      -0.049049806    0.074115634    4.398154434
  H      -2.534864015   -3.963149572    2.444142287
```

H	4.763832490	-0.286101451	2.671921314
H	-2.089008953	4.242660878	2.215439240
H	2.710145230	-0.094502794	4.494624550
H	-1.267516045	2.555910098	4.235740179
H	-1.536921122	-2.260604045	4.368935172
H	-1.418649011	2.934184319	-0.131645226
H	-1.730078829	-2.869654074	0.029252277
H	3.513389566	-0.270902364	0.185224109
*			

Optimized coordinates:

Co	0.166518	-0.064581	0.047962
N	-0.280843	-0.082466	-1.608585
O	-0.867783	-0.074789	-2.629897
N	-0.759679	-1.195170	2.612709
N	-0.828863	-1.409810	1.278956
N	1.487102	-0.069076	2.666581
N	1.765902	-0.126321	1.341432
N	-0.613140	1.306488	2.542705
N	-0.659757	1.453703	1.199006
B	0.014437	0.030872	3.152596
C	-1.438648	-2.154373	3.270191
C	-1.973533	-3.032384	2.333186
C	-1.555787	-2.511306	1.095416
C	2.626017	-0.113773	3.376937
C	3.697379	-0.204368	2.490892
C	3.094205	-0.208158	1.223898
C	-1.181094	2.369377	3.143553
C	-1.616766	3.248477	2.157382
C	-1.260857	2.617108	0.952052
H	-0.027354	0.067308	4.364478
H	-2.576492	-3.918403	2.518126
H	4.756742	-0.259558	2.730218
H	-2.118226	4.204289	2.290607
H	2.594905	-0.077952	4.463401
H	-1.233669	2.422444	4.228441
H	-1.491559	-2.141886	4.356248
H	-1.410438	2.942203	-0.076042
H	-1.745087	-2.873857	0.086564
H	3.548079	-0.265589	0.236263

Tp*Ni(NO) geometry optimization (B3LYP)

Input file:

```
! RKS B3LYP RIJCOSX SlowConv TightSCF TightOpt def2-SVP def2-SV/J UCO
! NORMALPRINT Grid4 NoFinalGrid vdw
```

```
%basis NewGTO 28 "def2-TZVP" end
    NewGTO 8 "def2-TZVP" end
    NewGTO 7 "def2-TZVP" end
    NewAuxGTO 28 "def2-TZVP/J" end
    NewAuxGTO 8 "def2-TZVP/J" end
    NewAuxGTO 7 "def2-TZVP/J" end
end

%method SpecialGridAtoms 28, 8, 7, 6, 1
    SpecialGridIntAcc 10, 5, 5, 5
```

```

    end

%geom MaxIter 300
end

%pal nprocs 8 end

*xyz 0 1
Ni      0.00000   0.00000   0.00000
N       0.06295   0.00000  -1.61818
O       0.14032   0.00000  -2.78457
B       0.00000   0.00000   3.05818
N       1.62707   0.00000   1.17091
N       1.43917   0.00000   2.50888
N      -0.82950  -1.38889   1.14086
N      -0.71366  -1.26430   2.50264
C       3.53019   0.00000  -0.40993
C       2.95644   0.00000   0.94186
C       3.59119   0.00000   2.19353
C       2.64458   0.00000   3.13401
C       2.74530   0.00000   4.64752
C      -1.75171  -2.99549  -0.48673
C      -1.45156  -2.56138   0.90934
C      -1.70237  -3.18697   2.12232
C      -1.22466  -2.36465   3.10283
C      -1.20274  -2.56663   4.58838
N      -0.82950   1.38889   1.14086
N      -0.71366   1.26430   2.50264
C      -1.75171   2.99549  -0.48673
C      -1.45156   2.56138   0.90934
C      -1.70237   3.18697   2.12232
C      -1.22466   2.36465   3.10283
C      -1.20274   2.56662   4.58838
H      -0.01717   0.00000   4.06918
H       2.81455   0.00000  -1.06575
H       4.07735  -0.79215  -0.52894
H       4.07735   0.79215  -0.52894
H       4.51874   0.00000   2.34187
H       3.67917   0.00000   4.90963
H       2.31044  -0.79215   5.00062
H       2.31044   0.79215   5.00062
H      -1.44193  -2.32006  -1.10841
H      -2.70819  -3.11615  -0.58900
H      -1.29896  -3.83486  -0.66912
H      -2.12103  -4.01847   2.24595
H      -0.79494  -1.79546   5.01418
H      -0.68813  -3.36140   4.79968
H      -2.11013  -2.67286   4.91332
H      -1.44193  -2.32006  -1.10841
H      -2.70819  -3.11615  -0.58900
H      -1.29896  -3.83486  -0.66912
H      -2.12103  -4.01847   2.24595
H      -0.79494  -1.79546   5.01418
H      -0.68813  -3.36140   4.79968
H      -2.11013  -2.67286   4.91332
*

```

Optimized coordinates:

Ni	0.052302	-0.000004	-0.067786
N	0.044303	-0.000011	-1.685810
O	0.037473	-0.000022	-2.845683
B	0.065038	-0.000003	3.018029
N	1.707649	0.000001	1.125685
N	1.513242	-0.000003	2.470113
N	-0.770382	-1.428407	1.137486
N	-0.663934	-1.255815	2.480031
C	3.580565	0.000015	-0.485970
C	3.022663	0.000007	0.900737
C	3.700561	0.000007	2.137474
C	2.705140	-0.000001	3.110470
C	2.829764	-0.000007	4.601092
C	-1.722529	-3.053149	-0.462372
C	-1.442062	-2.560574	0.921181
C	-1.781157	-3.138899	2.162030
C	-1.268938	-2.277986	3.128565
C	-1.329277	-2.375108	4.619776
N	-0.770378	1.428403	1.137486
N	-0.663932	1.255810	2.480030
C	-1.722526	3.053143	-0.462373
C	-1.442056	2.560571	0.921181
C	-1.781135	3.138905	2.162029
C	-1.268930	2.277984	3.128564
C	-1.329269	2.375106	4.619775
H	0.070733	-0.000002	4.224767
H	2.765878	-0.000017	-1.223927
H	4.209162	-0.888140	-0.663243
H	4.209101	0.888212	-0.663258
H	4.775292	0.000010	2.304968
H	3.890961	-0.000009	4.887358
H	2.352624	-0.886785	5.048873
H	2.352626	0.886769	5.048879
H	-1.455346	-2.285260	-1.202526
H	-2.787986	-3.303551	-0.588213
H	-1.141505	-3.963258	-0.688255
H	-2.328127	-4.063123	2.334791
H	-1.854709	-1.513272	5.061944
H	-0.321977	-2.403412	5.065508
H	-1.860136	-3.291278	4.915165
H	-1.455322	2.285262	-1.202528
H	-2.787989	3.303521	-0.588219
H	-1.141523	3.963267	-0.688250
H	-2.328093	4.063136	2.334790
H	-1.854707	1.513273	5.061943
H	-0.321969	2.403403	5.065508
H	-1.860122	3.291280	4.915165

Tp*Ni(NO) geometry optimization (OLYP)

Input file:

```
! RKS OLYP RI SlowConv TightSCF TightOpt def2-SVP def2-SV/J NORMALPRINT Grid4
! NoFinalGrid vdw
```

```

%basis NewGTO 28 "def2-TZVP" end
NewGTO 8 "def2-TZVP" end
NewGTO 7 "def2-TZVP" end
NewAuxGTO 28 "def2-TZVP/J" end
NewAuxGTO 8 "def2-TZVP/J" end
NewAuxGTO 7 "def2-TZVP/J" end
end

%geom MaxIter 300
end

%pal nprocs 32 end

*xyz 0 1
Ni      0.00000   0.00000   0.00000
N       0.06295   0.00000  -1.61818
O       0.14032   0.00000  -2.78457
B       0.00000   0.00000   3.05818
N       1.62707   0.00000   1.17091
N       1.43917   0.00000   2.50888
N      -0.82950  -1.38889   1.14086
N      -0.71366  -1.26430   2.50264
C       3.53019   0.00000  -0.40993
C       2.95644   0.00000   0.94186
C       3.59119   0.00000   2.19353
C       2.64458   0.00000   3.13401
C       2.74530   0.00000   4.64752
C      -1.75171  -2.99549  -0.48673
C      -1.45156  -2.56138   0.90934
C      -1.70237  -3.18697   2.12232
C      -1.22466  -2.36465   3.10283
C      -1.20274  -2.56663   4.58838
N      -0.82950   1.38889   1.14086
N      -0.71366   1.26430   2.50264
C      -1.75171   2.99549  -0.48673
C      -1.45156   2.56138   0.90934
C      -1.70237   3.18697   2.12232
C      -1.22466   2.36465   3.10283
C      -1.20274   2.56662   4.58838
H      -0.01717   0.00000   4.06918
H       2.81455   0.00000  -1.06575
H       4.07735  -0.79215  -0.52894
H       4.07735   0.79215  -0.52894
H       4.51874   0.00000   2.34187
H       3.67917   0.00000   4.90963
H       2.31044  -0.79215   5.00062
H       2.31044   0.79215   5.00062
H      -1.44193  -2.32006  -1.10841
H      -2.70819  -3.11615  -0.58900
H      -1.29896  -3.83486  -0.66912
H      -2.12103  -4.01847   2.24595
H      -0.79494  -1.79546   5.01418
H      -0.68813  -3.36140   4.79968
H      -2.11013  -2.67286   4.91332
H      -1.44193   2.32006  -1.10841
H      -2.70819   3.11615  -0.58900
H      -1.29896  -3.83486  -0.66912

```

H	-2.12103	4.01847	2.24595
H	-0.79494	1.79546	5.01418
H	-0.68813	3.36140	4.79968
H	-2.11013	2.67286	4.91332

*

Optimized coordinates:

Ni	0.055737	0.000005	-0.053703
N	-0.024971	-0.000045	-1.681812
O	-0.151895	-0.000094	-2.846942
B	0.061228	0.000022	3.035703
N	1.706862	0.000122	1.143906
N	1.515468	0.000039	2.487775
N	-0.752771	-1.423955	1.143362
N	-0.667221	-1.259497	2.487059
C	3.587003	0.000075	-0.470450
C	3.029744	0.000143	0.917824
C	3.708100	0.000068	2.155798
C	2.712317	0.000010	3.133113
C	2.836133	-0.000041	4.624218
C	-1.687719	-3.037633	-0.484180
C	-1.419251	-2.565318	0.910432
C	-1.771958	-3.151146	2.143793
C	-1.276901	-2.291363	3.127255
C	-1.352044	-2.397507	4.617834
N	-0.752881	1.423922	1.143346
N	-0.667277	1.259503	2.487046
C	-1.687909	3.037532	-0.484211
C	-1.419394	2.565262	0.910408
C	-1.772078	3.151113	2.143764
C	-1.276959	2.291373	3.127233
C	-1.352051	2.397560	4.617812
H	0.060232	0.000027	4.244191
H	2.770397	0.002266	-1.210960
H	4.217487	-0.891766	-0.648155
H	4.221124	0.889592	-0.646733
H	4.786110	0.000080	2.322222
H	3.901280	-0.000058	4.909679
H	2.356592	-0.888820	5.074108
H	2.356602	0.888713	5.074169
H	-2.312269	-2.312685	-1.038772
H	-2.212168	-4.007657	-0.470789
H	-0.747089	-3.156638	-1.052863
H	-2.317761	-4.081953	2.302677
H	-1.885530	-1.537281	5.062662
H	-0.346766	-2.427311	5.076932
H	-1.888094	-3.319196	4.899295
H	-2.312414	2.312530	-1.038783
H	-2.212423	4.007521	-0.470836
H	-0.747292	3.156590	-1.052906
H	-2.317905	4.081907	2.302641
H	-1.885498	1.537333	5.062684
H	-0.346756	2.427402	5.076872
H	-1.888113	3.319244	4.899265

Tp*Ni(NO) B3LYP single point energy calculation on B3LYP/OLYP geometry-optimized coordinates

Input file:

```
! UKS B3LYP RIJCOSX SlowConv TightSCF def2-SVP def2-SV/J NORMALPRINT Grid4
! NoFinalGrid vdw

%basis NewGTO 28 "def2-TZVP" end
    NewGTO 8 "def2-TZVP" end
    NewGTO 7 "def2-TZVP" end
    NewAuxGTO 28 "def2-TZVP/J" end
    NewAuxGTO 8 "def2-TZVP/J" end
    NewAuxGTO 7 "def2-TZVP/J" end
end

%scf Flipspin 1,2
    FinalMs 0.0
    MaxIter 500
end

%pal nprocs 32 end

*xyz 0 5
.
.
.
*
```

Tp*Ni(NO) O3LYP single point energy calculation on B3LYP/OLYP geometry-optimized coordinates

Input file:

```
! UKS O3LYP RIJCOSX SlowConv TightSCF def2-SVP def2-SV/J NORMALPRINT Grid4
! NoFinalGrid vdw

%basis NewGTO 28 "def2-TZVP" end
    NewGTO 8 "def2-TZVP" end
    NewGTO 7 "def2-TZVP" end
    NewAuxGTO 28 "def2-TZVP/J" end
    NewAuxGTO 8 "def2-TZVP/J" end
    NewAuxGTO 7 "def2-TZVP/J" end
end

%scf Flipspin 1,2
    FinalMs 0.0
    MaxIter 500
end

%pal nprocs 32 end

*xyz 0 5
.
.
.
```

Tp*Ni(NO) OLYP single point energy calculation on B3LYP/OLYP geometry-optimized coordinates

Input file:

```
! UKS OLYP RI SlowConv TightSCF def2-SVP def2-SV/J NORMALPRINT Grid4
! NoFinalGrid vdw

%basis NewGTO 28 "def2-TZVP" end
    NewGTO 8 "def2-TZVP" end
    NewGTO 7 "def2-TZVP" end
    NewAuxGTO 28 "def2-TZVP/J" end
    NewAuxGTO 8 "def2-TZVP/J" end
    NewAuxGTO 7 "def2-TZVP/J" end
end

%scf Flipspin 1,2
    FinalMs 0.0
    MaxIter 500
end

%pal nprocs 32 end

*xyz 0 5
.
.
.
*
```

TpNi(NO) geometry optimization (B3LYP) for CASSCF input

Input file:

```
! RKS B3LYP RIJCOSX SlowConv TightSCF TightOpt def2-SVP def2-SV/J UCO
! NORMALPRINT Grid4 NoFinalGrid vdw

%basis NewGTO 28 "def2-TZVP" end
    NewGTO 8 "def2-TZVP" end
    NewGTO 7 "def2-TZVP" end
    NewAuxGTO 28 "def2-TZVP/J" end
    NewAuxGTO 8 "def2-TZVP/J" end
    NewAuxGTO 7 "def2-TZVP/J" end
end

%method SpecialGridAtoms 28, 8, 7, 6, 1
    SpecialGridIntAcc 10, 5, 5, 5
end

%geom MaxIter 300
end

%pal nprocs 32 end

*xyz 0 1
Ni      0.072633000     0.000199000    -0.050485000
N       0.066299000     0.000679000    -1.772728000
O       0.049087000     0.001094000    -2.949105000
B       0.060626000     0.000082000     3.026298000
N      1.720436000     0.000120000     1.145693000
```

N	1.512546000	0.000009000	2.487858000
N	-0.755098000	-1.430686000	1.134852000
N	-0.664723000	-1.254261000	2.477844000
C	3.035950000	-0.000328000	0.934157000
C	3.703259000	-0.000768000	2.176895000
C	2.696738000	-0.000527000	3.138439000
C	-1.423507000	-2.562133000	0.914172000
C	-1.775537000	-3.139903000	2.151536000
C	-1.274867000	-2.274385000	3.120357000
N	-0.755319000	1.430693000	1.134977000
N	-0.664605000	1.254540000	2.477962000
C	-1.423235000	2.562411000	0.914255000
C	-1.774478000	3.140709000	2.151560000
C	-1.273896000	2.275164000	3.120454000
H	0.055037000	0.000019000	4.234092002
H	4.776509002	-0.001181000	2.355689000
H	-2.320234000	-4.066521000	2.320657000
H	-2.318621000	4.067669000	2.320578000
H	3.615041249	-0.000392509	-0.001072006
H	2.720084266	-0.000691689	4.238191169
H	-1.613473571	-2.896659141	-0.116364247
H	-1.420079180	-2.499805149	4.187174339
H	-1.613444911	2.896750021	-0.116297079
H	-1.298262203	2.296594931	4.219975248

*

Optimized coordinates:

Ni	0.080912	-0.001525	-0.083622
N	0.085162	0.003084	-1.700519
O	0.076059	0.005874	-2.857102
B	0.051443	-0.010593	3.016194
N	1.721267	-0.005257	1.143913
N	1.503306	-0.009224	2.478160
N	-0.754604	-1.435502	1.115858
N	-0.667122	-1.261279	2.453054
C	3.040895	-0.004833	0.960406
C	3.705097	-0.008657	2.200448
C	2.677171	-0.011350	3.137446
C	-1.416798	-2.573261	0.909619
C	-1.771642	-3.160322	2.137791
C	-1.269816	-2.281872	3.092245
N	-0.754246	1.425553	1.124303
N	-0.666807	1.243548	2.460451
C	-1.415943	2.564771	0.924658
C	-1.770492	3.144861	2.156251
C	-1.269020	2.260675	3.105579
H	0.039207	-0.014207	4.229234
H	4.776575	-0.009355	2.386859
H	-2.313511	-4.088395	2.305037
H	-2.311944	4.072210	2.328797
H	3.448828	-0.001840	-0.048475
H	2.694764	-0.014645	4.224777
H	-1.605975	-2.915428	-0.106162
H	-1.296853	-2.307976	4.179007
H	-1.605057	2.913004	-0.089067
H	-1.295994	2.280434	4.192474

Tp^tBu,MeCu(NO) geometry optimization (B3LYP)

Input file:

```
! UKS B3LYP RIJCOSX SlowConv TightSCF TightOpt def2-SVP def2-SV/J UCO UNO
! NORMALPRINT Grid4 NoFinalGrid vdw
```

```
%basis NewGTO 29 "def2-TZVP" end
    NewGTO 8 "def2-TZVP" end
    NewGTO 7 "def2-TZVP" end
    NewAuxGTO 29 "def2-TZVP/J" end
    NewAuxGTO 8 "def2-TZVP/J" end
    NewAuxGTO 7 "def2-TZVP/J" end
end

%method SpecialGridAtoms 29, 8, 7, 6, 1
    SpecialGridIntAcc 10, 5, 5, 5
end

%geom MaxIter 300
end

%pal nprocs 32 end

*xyz 0 2
Cu      0.000000000      0.000000000      0.000000000
O       0.033330000      0.145150000     -2.840630000
N      -0.032050000     -0.075950000     -1.756830000
N       1.718280000      0.000000000      1.125230000
N       1.443900000      0.007450000      2.449700000
N      -0.874950000     -1.519220000      1.139640000
N      -0.715270000     -1.256390000      2.470590000
N      -0.875110000      1.472650000      1.113170000
N      -0.734590000      1.243080000      2.430370000
C       2.573450000     -0.024240000      3.143090000
C       3.622660000     -0.046800000      2.273900000
C       3.050180000     -0.040380000      1.006830000
C       3.733140000     -0.055800000     -0.349010000
C       5.247990001     -0.034050000     -0.144480000
C       3.364010000     -1.351230000     -1.093790000
C       3.324720000      1.153830000     -1.177820000
C      -1.205770000     -2.281670000      3.168110000
C      -1.699580000     -3.227450000      2.315620000
C      -1.488810000     -2.705970000      1.041530000
C      -1.804940000     -3.328530000     -0.283130000
C      -2.581300000     -4.655450001     -0.062550000
C      -2.693340000     -2.401260000     -1.103290000
C      -0.513880000     -3.618400000     -1.051180000
C      -1.368330000      2.222760000      3.124770000
C      -1.906070000      3.090640000      2.234910000
C      -1.586560000      2.598380000      0.979410000
C      -1.942520000      3.153860000     -0.380780000
C      -0.697660000      3.420220000     -1.182890000
C      -2.873940000      2.143610000     -1.098400000
C      -2.690470000      4.477100001     -0.209820000
B       0.000000000      0.000000000      2.970890000
H       2.688460000     -0.035580000      4.087740000
```

H	4.544840001	-0.018640000	2.530360000
H	5.490040001	0.798050000	0.252870000
H	5.507590001	-0.745210000	0.417230000
H	5.679930001	-0.112160000	-0.990210000
H	3.837480000	-1.413640000	-1.886590000
H	3.632820000	-2.102460000	-0.512990000
H	2.438000000	-1.406020000	-1.216680000
H	3.735270000	1.103630000	-2.012590000
H	2.370860000	1.139580000	-1.275740000
H	3.580320000	1.928330000	-0.707430000
H	-1.236190000	-2.359700000	4.093080000
H	-2.096570000	-4.040710000	2.585000000
H	-2.946280000	-4.939050001	-0.887650000
H	-2.052850000	-5.285530001	0.333230000
H	-3.335740000	-4.433480001	0.526180000
H	-2.270320000	-1.563360000	-1.213660000
H	-2.846050000	-2.787890000	-1.974680000
H	-3.528540000	-2.291660000	-0.672750000
H	-0.052330000	-2.826150000	-1.153760000
H	-0.019330000	-4.256950001	-0.553560000
H	-0.761250000	-3.993090000	-1.891250000
H	-1.397860000	2.262490000	4.088250000
H	-2.435800000	3.847370000	2.451420000
H	-0.212270000	4.105390000	-0.836370000
H	-0.196270000	2.611480000	-1.251650000
H	-0.996720000	3.640560000	-2.091900000
H	-3.078000000	2.541550000	-1.953100000
H	-2.354070000	1.357400000	-1.260060000
H	-3.610820000	1.987980000	-0.605440000
H	-3.000380000	4.794180001	-1.044220000
H	-3.482230000	4.332550001	0.355830000
H	-2.157540000	5.127720001	0.215110000
H	0.012200000	0.045170000	3.945440000

*

Optimized coordinates:

Cu	0.016011	0.006777	-0.013666
O	0.199234	0.237069	-2.899087
N	-0.060216	-0.153575	-1.835120
N	1.693202	-0.027743	1.173697
N	1.439414	-0.015715	2.504000
N	-0.858956	-1.556618	1.218521
N	-0.726180	-1.304978	2.542722
N	-0.887939	1.423966	1.158902
N	-0.761150	1.216374	2.490938
C	2.595095	-0.008180	3.189207
C	3.643901	-0.014563	2.276657
C	3.020037	-0.026318	1.012155
C	3.644253	-0.034105	-0.368457
C	5.175433	-0.019258	-0.250147
C	3.214404	-1.309729	-1.119995
C	3.191611	1.218202	-1.145569
C	-1.273787	-2.301429	3.262588
C	-1.785066	-3.242995	2.378593
C	-1.496530	-2.723387	1.097679
C	-1.805721	-3.310048	-0.265509

C	-2.541635	-4.648604	-0.105804
C	-2.702156	-2.335555	-1.054791
C	-0.488419	-3.550182	-1.030423
C	-1.361526	2.210449	3.166955
C	-1.899605	3.102139	2.246089
C	-1.572403	2.558916	0.986612
C	-1.884534	3.088390	-0.399142
C	-0.569133	3.340855	-1.163663
C	-2.750859	2.065032	-1.160361
C	-2.657355	4.411359	-0.289857
B	-0.015657	-0.027519	3.040237
H	2.586671	0.000299	4.276570
H	4.709104	-0.010554	2.488846
H	5.523295	0.884250	0.277234
H	5.539103	-0.904604	0.296996
H	5.625623	-0.026435	-1.256439
H	3.625864	-1.306412	-2.143514
H	3.580996	-2.208352	-0.596996
H	2.118533	-1.384844	-1.184332
H	3.615290	1.208108	-2.163984
H	2.095649	1.264669	-1.227216
H	3.530968	2.133649	-0.633404
H	-1.258048	-2.266350	4.349407
H	-2.293118	-4.172898	2.617789
H	-2.767110	-5.072221	-1.098511
H	-1.925152	-5.374298	0.449902
H	-3.491901	-4.513759	0.436663
H	-2.221025	-1.351710	-1.154450
H	-2.899186	-2.732874	-2.065450
H	-3.666632	-2.194015	-0.539191
H	0.078781	-2.614425	-1.141095
H	0.145509	-4.271178	-0.488530
H	-0.701533	-3.951839	-2.035776
H	-1.361337	2.210663	4.254344
H	-2.448984	4.016868	2.448704
H	0.041056	4.094885	-0.640157
H	0.029400	2.421789	-1.245836
H	-0.787499	3.706729	-2.181102
H	-2.938136	2.415507	-2.189728
H	-2.256862	1.083205	-1.208933
H	-3.720756	1.927523	-0.654228
H	-2.886033	4.794799	-1.297890
H	-3.607996	4.269468	0.249852
H	-2.064491	5.171696	0.244670
H	-0.006892	0.001724	4.254442

Tp^{tBu,Me}Cu(NO) geometry optimization (OLYP)

Input file:

```
! UKS OLYP RI SlowConv TightSCF TightOpt def2-SVP def2-SV/J UCO UNO
! NORMALPRINT Grid4 NoFinalGrid vdw
```

```
%basis NewGTO 29 "def2-TZVP" end
    NewGTO 8 "def2-TZVP" end
    NewGTO 7 "def2-TZVP" end
    NewAuxGTO 29 "def2-TZVP/J" end
    NewAuxGTO 8 "def2-TZVP/J" end
```

```

NewAuxGTO 7 "def2-TZVP/J" end
end

%method SpecialGridAtoms 29, 8, 7, 6, 1
SpecialGridIntAcc 10, 5, 5, 5, 5
end

%geom MaxIter 300
end

%pal nprocs 32 end

*xyz 0 2
Cu      0.027313    0.008483    0.027192
O       0.161879    0.231673   -2.859058
N      -0.056166   -0.153227   -1.762197
N       1.680650   -0.023294    1.193235
N       1.443565   -0.016448    2.533982
N      -0.846544   -1.541229    1.234521
N      -0.723411   -1.304684    2.570389
N      -0.872275    1.409359    1.177561
N      -0.755536    1.216896    2.520353
C       2.616057   -0.016242    3.208552
C       3.656506   -0.022099    2.275306
C       3.016364   -0.025575    1.013007
C       3.621244   -0.028472   -0.378361
C       5.157068   -0.010372   -0.277968
C       3.180171   -1.307360   -1.125328
C       3.150426    1.228298   -1.144516
C      -1.284698   -2.312332    3.280578
C      -1.795458   -3.245475    2.375953
C      -1.493885   -2.714136    1.097196
C      -1.797276   -3.284478   -0.275805
C      -2.541944   -4.623736   -0.132291
C      -2.685876   -2.291296   -1.057450
C      -0.471757   -3.520077   -1.034047
C      -1.369301    2.222930    3.184440
C      -1.905283    3.104833    2.242004
C      -1.565092    2.549473    0.985391
C      -1.868126    3.059456   -0.411089
C      -0.542172    3.304495   -1.166008
C      -2.727061    2.016894   -1.161903
C      -2.648322    4.383415   -0.323061
B      -0.011892   -0.028005    3.077381
H       2.618033   -0.012599    4.303540
H       4.732594   -0.022311    2.472449
H       5.510266    0.898024    0.253856
H       5.530990   -0.903013    0.266224
H       5.599562   -0.012508   -1.296039
H       3.566835   -1.295805   -2.166522
H       3.569278   -2.210826   -0.610918
H       2.074882   -1.388045   -1.160410
H       3.547608    1.215297   -2.181627
H       2.043750    1.275437   -1.192950
H       3.509154    2.148325   -0.637389
H      -1.275989   -2.285361    4.375388
H      -2.314794   -4.181643    2.601913

```

H	-2.764066	-5.040484	-1.137047
H	-1.927530	-5.362905	0.423740
H	-3.501844	-4.488948	0.409420
H	-2.189145	-1.304062	-1.143801
H	-2.882934	-2.676817	-2.080681
H	-3.656741	-2.146595	-0.538628
H	0.102775	-2.576169	-1.122739
H	0.157965	-4.259509	-0.496080
H	-0.677812	-3.904228	-2.056014
H	-1.376679	2.232072	4.279360
H	-2.465084	4.025836	2.429543
H	0.055762	4.087911	-0.655091
H	0.070391	2.381433	-1.207567
H	-0.749499	3.635856	-2.205585
H	-2.905475	2.348439	-2.206890
H	-2.225043	1.028564	-1.186246
H	-3.707256	1.886137	-0.657500
H	-2.870170	4.757164	-1.344498
H	-3.610349	4.243647	0.213345
H	-2.058288	5.157605	0.211061
H	-0.003397	0.000502	4.299044

*

Optimized coordinates:

Cu	0.048325	0.041164	-0.044885
O	0.165966	0.224027	-2.938498
N	-0.054471	-0.157973	-1.845460
N	1.720801	-0.016209	1.148261
N	1.452539	-0.017851	2.477013
N	-0.863491	-1.574030	1.192588
N	-0.725507	-1.309901	2.515205
N	-0.882413	1.444365	1.132642
N	-0.754552	1.222771	2.463796
C	2.602813	-0.029539	3.181743
C	3.663621	-0.034245	2.280748
C	3.061244	-0.024649	1.003910
C	3.723308	-0.022118	-0.365125
C	5.255953	-0.008562	-0.211827
C	3.314456	-1.296643	-1.137228
C	3.292348	1.239872	-1.145551
C	-1.278950	-2.294958	3.256919
C	-1.801518	-3.244320	2.385779
C	-1.516014	-2.747837	1.092642
C	-1.848775	-3.368078	-0.256316
C	-2.592329	-4.702444	-0.057967
C	-2.756603	-2.408620	-1.057968
C	-0.542479	-3.639210	-1.035781
C	-1.367382	2.204187	3.157541
C	-1.915577	3.102256	2.246530
C	-1.585060	2.584148	0.975478
C	-1.917712	3.141480	-0.399748
C	-0.610679	3.421395	-1.174662
C	-2.790945	2.125517	-1.170169
C	-2.701095	4.460414	-0.260236
B	-0.009439	-0.029336	3.007247
H	2.578598	-0.034210	4.271275

H	4.727013	-0.041891	2.511816
H	5.595298	0.890406	0.331686
H	5.611085	-0.899972	0.333977
H	5.728627	-0.006078	-1.209631
H	3.759106	-1.290305	-2.148722
H	3.664005	-2.199593	-0.606142
H	2.220926	-1.368089	-1.238434
H	3.745492	1.239080	-2.153168
H	2.198583	1.285946	-1.258345
H	3.617938	2.152291	-0.615404
H	-1.257927	-2.244368	4.345551
H	-2.316912	-4.166908	2.646360
H	-2.829860	-5.146127	-1.040856
H	-1.974715	-5.424161	0.504673
H	-3.539199	-4.554715	0.490227
H	-2.264355	-1.436712	-1.212796
H	-2.990833	-2.841814	-2.047487
H	-3.705039	-2.232229	-0.520008
H	0.025535	-2.709260	-1.188920
H	0.099598	-4.347091	-0.481979
H	-0.771264	-4.074777	-2.025532
H	-1.366982	2.188190	4.247221
H	-2.476175	4.008440	2.467425
H	0.000130	4.173474	-0.644718
H	-0.006089	2.508202	-1.281174
H	-0.840660	3.804786	-2.184980
H	-3.008526	2.501470	-2.186163
H	-2.285299	1.152139	-1.260503
H	-3.748171	1.961008	-0.644645
H	-2.938645	4.859080	-1.262039
H	-3.650306	4.306217	0.281817
H	-2.110633	5.220005	0.281156
H	0.000194	0.000584	4.224460

Tp^{tBu,Me}Cu(NO) geometry optimization (BP86)

Input file:

```
! UKS BP86 RI SlowConv TightSCF TightOpt def2-SVP def2-SV/J UCO UNO
! NORMALPRINT Grid4 NoFinalGrid vdw
```

```
%basis NewGTO 29 "def2-TZVP" end
    NewGTO 8 "def2-TZVP" end
    NewGTO 7 "def2-TZVP" end
    NewAuxGTO 29 "def2-TZVP/J" end
    NewAuxGTO 8 "def2-TZVP/J" end
    NewAuxGTO 7 "def2-TZVP/J" end
end

%method SpecialGridAtoms    29, 8,   7,   6,  1
    SpecialGridIntAcc  10, 5,   5,   5,  5
end

%geom MaxIter 300
end

%pal nprocs 32 end
```

*xyz 0 2

Cu	0.000000000	0.000000000	0.000000000
O	0.033330000	0.145150000	-2.840630000
N	-0.032050000	-0.075950000	-1.756830000
N	1.718280000	0.000000000	1.125230000
N	1.443900000	0.007450000	2.449700000
N	-0.874950000	-1.519220000	1.139640000
N	-0.715270000	-1.256390000	2.470590000
N	-0.875110000	1.472650000	1.113170000
N	-0.734590000	1.243080000	2.430370000
C	2.573450000	-0.024240000	3.143090000
C	3.622660000	-0.046800000	2.273900000
C	3.050180000	-0.040380000	1.006830000
C	3.733140000	-0.055800000	-0.349010000
C	5.247990001	-0.034050000	-0.144480000
C	3.364010000	-1.351230000	-1.093790000
C	3.324720000	1.153830000	-1.177820000
C	-1.205770000	-2.281670000	3.168110000
C	-1.699580000	-3.227450000	2.315620000
C	-1.488810000	-2.705970000	1.041530000
C	-1.804940000	-3.328530000	-0.283130000
C	-2.581300000	-4.655450001	-0.062550000
C	-2.693340000	-2.401260000	-1.103290000
C	-0.513880000	-3.618400000	-1.051180000
C	-1.368330000	2.222760000	3.124770000
C	-1.906070000	3.090640000	2.234910000
C	-1.586560000	2.598380000	0.979410000
C	-1.942520000	3.153860000	-0.380780000
C	-0.697660000	3.420220000	-1.182890000
C	-2.873940000	2.143610000	-1.098400000
C	-2.690470000	4.477100001	-0.209820000
B	0.000000000	0.000000000	2.970890000
H	2.688460000	-0.035580000	4.087740000
H	4.5444840001	-0.018640000	2.530360000
H	5.490040001	0.798050000	0.252870000
H	5.507590001	-0.745210000	0.417230000
H	5.679930001	-0.112160000	-0.990210000
H	3.837480000	-1.413640000	-1.886590000
H	3.632820000	-2.102460000	-0.512990000
H	2.438000000	-1.406020000	-1.216680000
H	3.735270000	1.103630000	-2.012590000
H	2.370860000	1.139580000	-1.275740000
H	3.580320000	1.928330000	-0.707430000
H	-1.236190000	-2.359700000	4.093080000
H	-2.096570000	-4.040710000	2.585000000
H	-2.946280000	-4.939050001	-0.887650000
H	-2.052850000	-5.285530001	0.333230000
H	-3.335740000	-4.433480001	0.526180000
H	-2.270320000	-1.563360000	-1.213660000
H	-2.846050000	-2.787890000	-1.974680000
H	-3.528540000	-2.291660000	-0.672750000
H	-0.052330000	-2.826150000	-1.153760000
H	-0.019330000	-4.256950001	-0.553560000
H	-0.761250000	-3.993090000	-1.891250000
H	-1.397860000	2.262490000	4.088250000
H	-2.435800000	3.847370000	2.451420000
H	-0.212270000	4.105390000	-0.836370000

H	-0.196270000	2.611480000	-1.251650000
H	-0.996720000	3.640560000	-2.091900000
H	-3.078000000	2.541550000	-1.953100000
H	-2.354070000	1.357400000	-1.260060000
H	-3.610820000	1.987980000	-0.605440000
H	-3.000380000	4.794180001	-1.044220000
H	-3.482230000	4.332550001	0.355830000
H	-2.157540000	5.127720001	0.215110000
H	0.012200000	0.045170000	3.945440000
*			

Optimized coordinates:

Cu	0.027313	0.008483	0.027192
O	0.161879	0.231673	-2.859058
N	-0.056166	-0.153227	-1.762197
N	1.680650	-0.023294	1.193235
N	1.443565	-0.016448	2.533982
N	-0.846544	-1.541229	1.234521
N	-0.723411	-1.304684	2.570389
N	-0.872275	1.409359	1.177561
N	-0.755536	1.216896	2.520353
C	2.616057	-0.016242	3.208552
C	3.656506	-0.022099	2.275306
C	3.016364	-0.025575	1.013007
C	3.621244	-0.028472	-0.378361
C	5.157068	-0.010372	-0.277968
C	3.180171	-1.307360	-1.125328
C	3.150426	1.228298	-1.144516
C	-1.284698	-2.312332	3.280578
C	-1.795458	-3.245475	2.375953
C	-1.493885	-2.714136	1.097196
C	-1.797276	-3.284478	-0.275805
C	-2.541944	-4.623736	-0.132291
C	-2.685876	-2.291296	-1.057450
C	-0.471757	-3.520077	-1.034047
C	-1.369301	2.222930	3.184440
C	-1.905283	3.104833	2.242004
C	-1.565092	2.549473	0.985391
C	-1.868126	3.059456	-0.411089
C	-0.542172	3.304495	-1.166008
C	-2.727061	2.016894	-1.161903
C	-2.648322	4.383415	-0.323061
B	-0.011892	-0.028005	3.077381
H	2.618033	-0.012599	4.303540
H	4.732594	-0.022311	2.472449
H	5.510266	0.898024	0.253856
H	5.530990	-0.903013	0.266224
H	5.599562	-0.012508	-1.296039
H	3.566835	-1.295805	-2.166522
H	3.569278	-2.210826	-0.610918
H	2.074882	-1.388045	-1.160410
H	3.547608	1.215297	-2.181627
H	2.043750	1.275437	-1.192950
H	3.509154	2.148325	-0.637389
H	-1.275989	-2.285361	4.375388
H	-2.314794	-4.181643	2.601913

H	-2.764066	-5.040484	-1.137047
H	-1.927530	-5.362905	0.423740
H	-3.501844	-4.488948	0.409420
H	-2.189145	-1.304062	-1.143801
H	-2.882934	-2.676817	-2.080681
H	-3.656741	-2.146595	-0.538628
H	0.102775	-2.576169	-1.122739
H	0.157965	-4.259509	-0.496080
H	-0.677812	-3.904228	-2.056014
H	-1.376679	2.232072	4.279360
H	-2.465084	4.025836	2.429543
H	0.055762	4.087911	-0.655091
H	0.070391	2.381433	-1.207567
H	-0.749499	3.635856	-2.205585
H	-2.905475	2.348439	-2.206890
H	-2.225043	1.028564	-1.186246
H	-3.707256	1.886137	-0.657500
H	-2.870170	4.757164	-1.344498
H	-3.610349	4.243647	0.213345
H	-2.058288	5.157605	0.211061
H	-0.003397	0.000502	4.299044

TpCu(NO) geometry optimization (BP86) for CASSCF input

Input file:

```
! UKS BP86 RI SlowConv TightSCF TightOpt def2-SVP def2-SV/J UCO UNO
! NORMALPRINT Grid4 NoFinalGrid vdw
```

```
%basis NewGTO 29 "def2-TZVP" end
    NewGTO 8 "def2-TZVP" end
    NewGTO 7 "def2-TZVP" end
    NewAuxGTO 29 "def2-TZVP/J" end
    NewAuxGTO 8 "def2-TZVP/J" end
    NewAuxGTO 7 "def2-TZVP/J" end
end

%method SpecialGridAtoms 29, 8, 7, 6, 1
    SpecialGridIntAcc 10, 5, 5, 5
end

%geom optimizehydrogens true
end

%pal nprocs 32 end

*xyz 0 2
Cu      0.027313000      0.008483000      0.027192000
O       0.161879000      0.231673000     -2.859058000
N      -0.056166000     -0.153227000     -1.762197000
N       1.680650000     -0.023294000      1.193235000
N       1.443565000     -0.016448000      2.533982000
N      -0.846544000     -1.541229000      1.234521000
N      -0.723411000     -1.304684000      2.570389000
N      -0.872275000      1.409359000      1.177561000
N      -0.755536000      1.216896000      2.520353000
C       2.616057000     -0.016242000      3.208552000
C       3.656506000     -0.022099000      2.275306000
```

C	3.016364000	-0.025575000	1.013007000
C	-1.284698000	-2.312332000	3.280578000
C	-1.795458000	-3.245475000	2.375953000
C	-1.493885000	-2.714136000	1.097196000
C	-1.369301000	2.222930000	3.184440000
C	-1.905283000	3.104833000	2.242004000
C	-1.565092000	2.549473000	0.985391000
B	-0.011892000	-0.028005000	3.077381000
H	2.618033000	-0.012599000	4.303540001
H	4.732594001	-0.022311000	2.472449000
H	-1.275989000	-2.285361000	4.375388001
H	-2.314794000	-4.181643000	2.601913000
H	-1.376679000	2.232072000	4.279360001
H	-2.465084000	4.025836000	2.429543000
H	-0.003397000	0.000502000	4.299044001
H	3.617226976	-0.029447989	0.091622906
H	-1.706770276	-3.110622605	0.093463854
H	-1.871655260	3.056741568	0.058731632

*

Optimized coordinates:

Cu	0.033220	0.018985	0.032674
O	0.172369	0.250334	-2.852716
N	-0.047414	-0.137667	-1.757295
N	1.684703	-0.016076	1.201248
N	1.445488	-0.013022	2.541630
N	-0.842535	-1.534140	1.234228
N	-0.721527	-1.301372	2.570953
N	-0.868211	1.416597	1.185568
N	-0.753603	1.220339	2.527994
C	2.616907	-0.014714	3.218060
C	3.658838	-0.017925	2.286456
C	3.020702	-0.017838	1.023136
C	-1.283930	-2.311028	3.277398
C	-1.793241	-3.241613	2.369328
C	-1.489643	-2.706659	1.092559
C	-1.368434	2.224488	3.193947
C	-1.902929	3.109047	2.253157
C	-1.560735	2.557244	0.995521
B	-0.010830	-0.026126	3.082682
H	2.621038	-0.013981	4.312854
H	4.734658	-0.019027	2.493848
H	-1.278812	-2.290583	4.372178
H	-2.312910	-4.178417	2.599979
H	-1.379668	2.233938	4.288632
H	-2.463656	4.029323	2.450835
H	-0.004306	-0.000944	4.303994
H	3.440275	-0.017977	0.011353
H	-1.700264	-3.097925	0.090633
H	-1.769273	2.910805	-0.019992