Supporting Information for:

A Cobalt-Nitrosyl Complex with a Hindered Hydrotris(pyrazolyl)borate Coligand: Detailed Electronic Structure, and Reactivity towards Dioxygen

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Table S1. X-ray crystallographic data for **[Co(NO)(L3)]**, **[Co(η²-O₂N)(L3)]**, and **[Co(η²-O₂NO)(L3)]**.

	[Co(NO)(L3)]	**[Co(η²-O₂N)(L3)]**	**[Co(η²-O₂NO)(L3)]**
CCDC deposit num.	1534553	1534554	1534555
Empirical formula	$C_{30}H_{52}BCoN_7O$	$C_{30}H_{52}BCoN_7O_2$	$C_{30}H_{52}BCoN_7O_3$
Formula weight	596.53	612.53	628.53
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/m$ (No. 11)
a /Å	9.5351(9)	9.4573(13)	9.4152(13)
b /Å	17.2416(19)	17.404(2)	17.442(2)
c /Å	20.421(2)	20.336(3)	10.6017(16)
β /°	99.585(3)	100.603(3)	106.857(3)
V /Å^3	3310.4(6)	3290.0(8)	1666.2(4)
Z	4	4	2
Dcalc /gcm^{-3}	1.197	1.237	1.253
R (int)	0.0309	0.0289	0.0315
μ(Mo $K\alpha$) /cm^{-1}	5.517	5.590	5.558
Reflections collected	53745	53446	27761
Unique reflections	7582	7548	3927
No. of variables	361	370	211
Reflections/para. ratio	21.00	20.40	18.61
R ($I > 2\sigma(I)$)	0.0431	0.0303	0.0276
R (All reflections)	0.0592	0.0440	0.0311
R_w (All reflections)	0.1209	0.0752	0.0727
Good. of fit indicator	1.039	1.019	1.054
Max/min peak, /e Å^3	1.92 / –0.49	0.36 / –0.25	0.40 / –0.34

$R = \Sigma \, ||Fo| - |Fc|| \, / \, \Sigma \, |Fo|$; $R_w = [(\Sigma \, w(\, (Fo^2 - Fc^2)^2 \,) / \, \Sigma \, w(\, Fo^2)^2]^{1/2}$

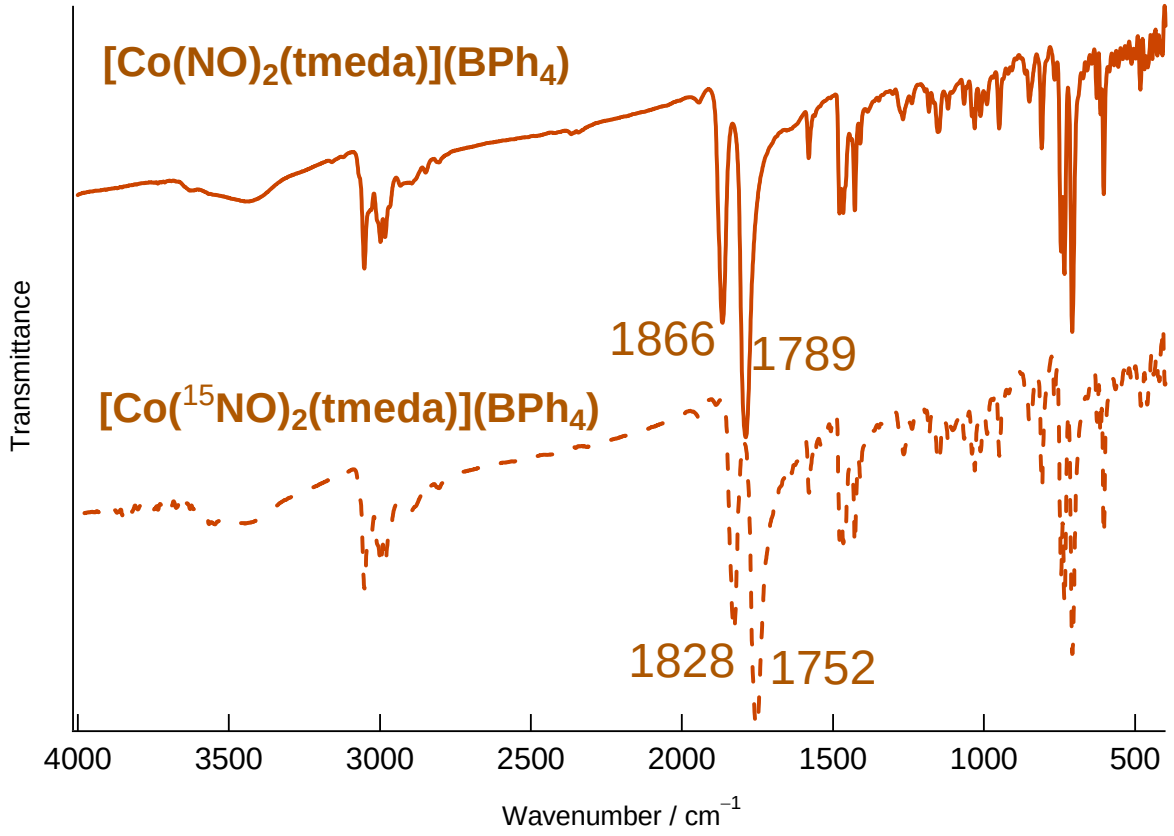

Figure S1. IR spectra of **[Co(NO)$_2$(tmeda)](BPh$_4$)** (solid line) and **[Co(^{15}NO)$_2$(tmeda)](BPh$_4$)** (dotted line).

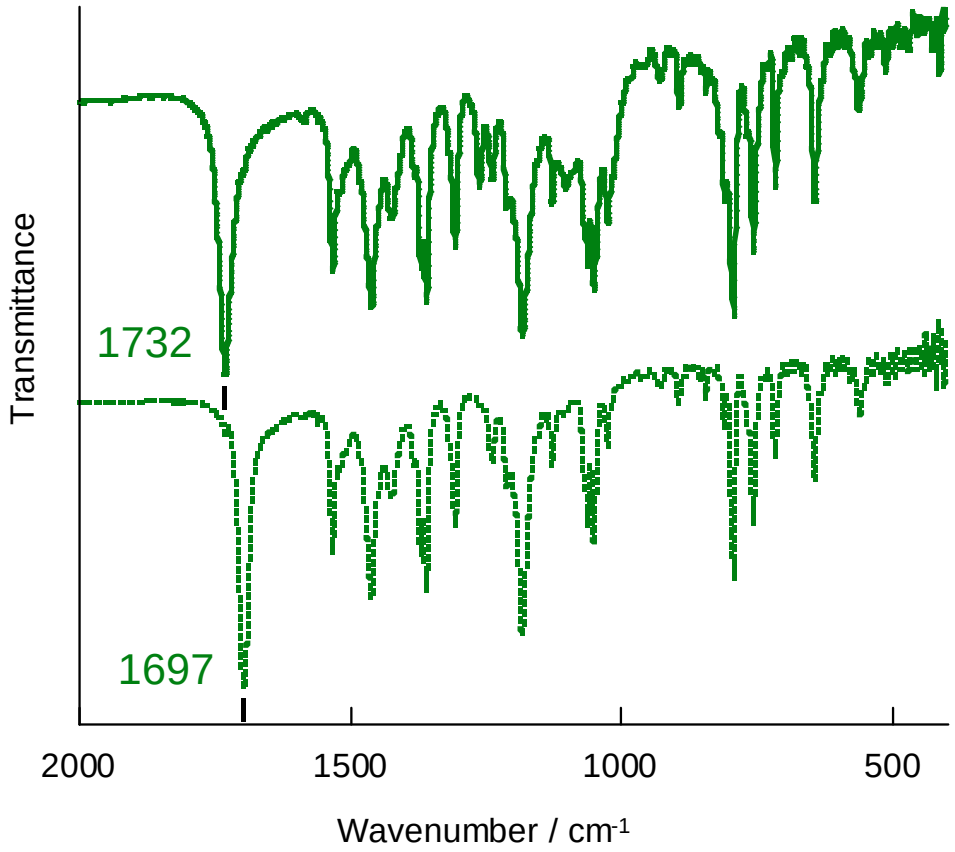

Figure S2. IR spectra of **[Co(NO)(L3)]** (solid line) and **[Co(^{15}NO)(L3)]** (dotted line).

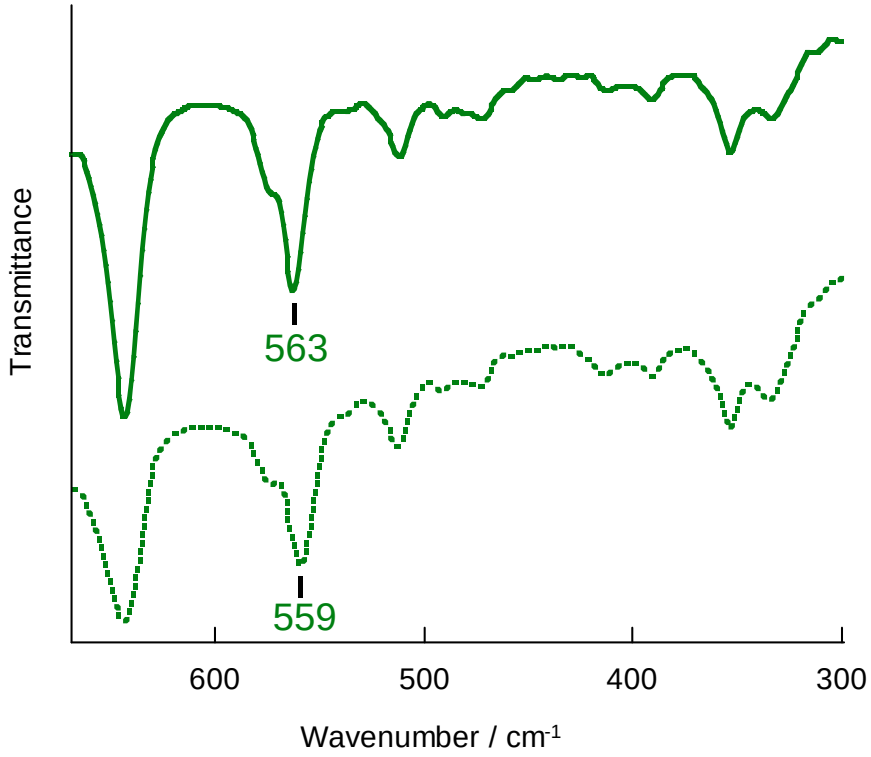

Figure S3. Far-IR spectra of **[Co(NO)(L3)]** (solid line) and **[Co(^{15}NO)(L3)]** (dotted line).

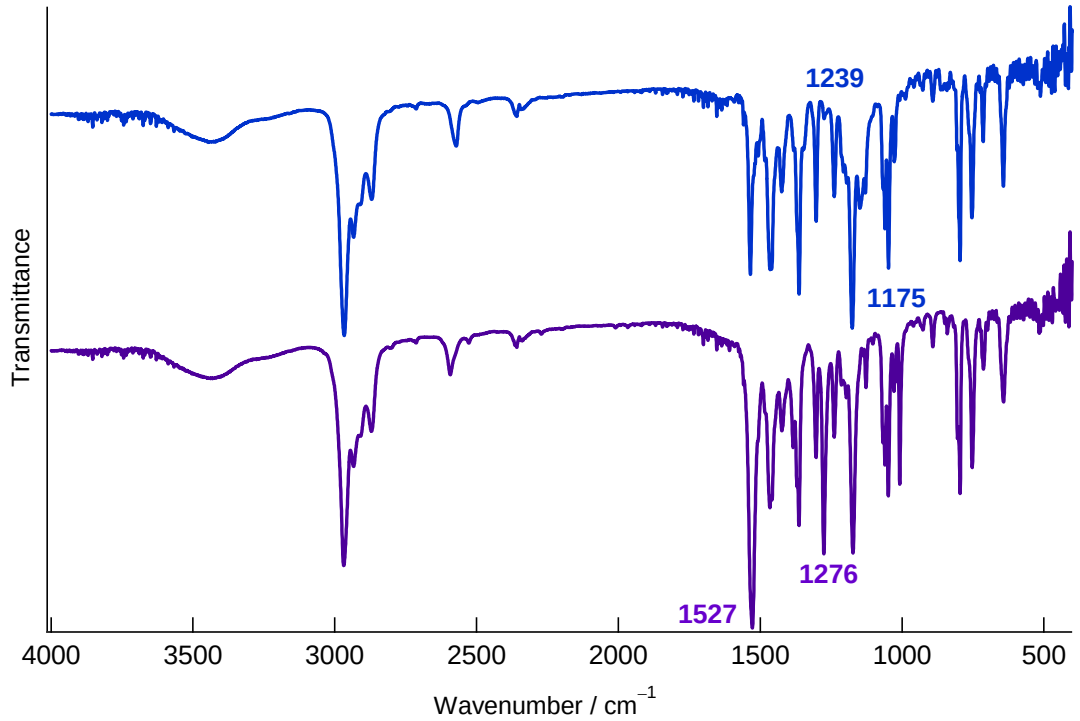

Figure S4. IR spectra of **[Co(η^2-O_2N)(L3)]** (top) and **[Co(η^2-O_2NO)(L3)]** (bottom).

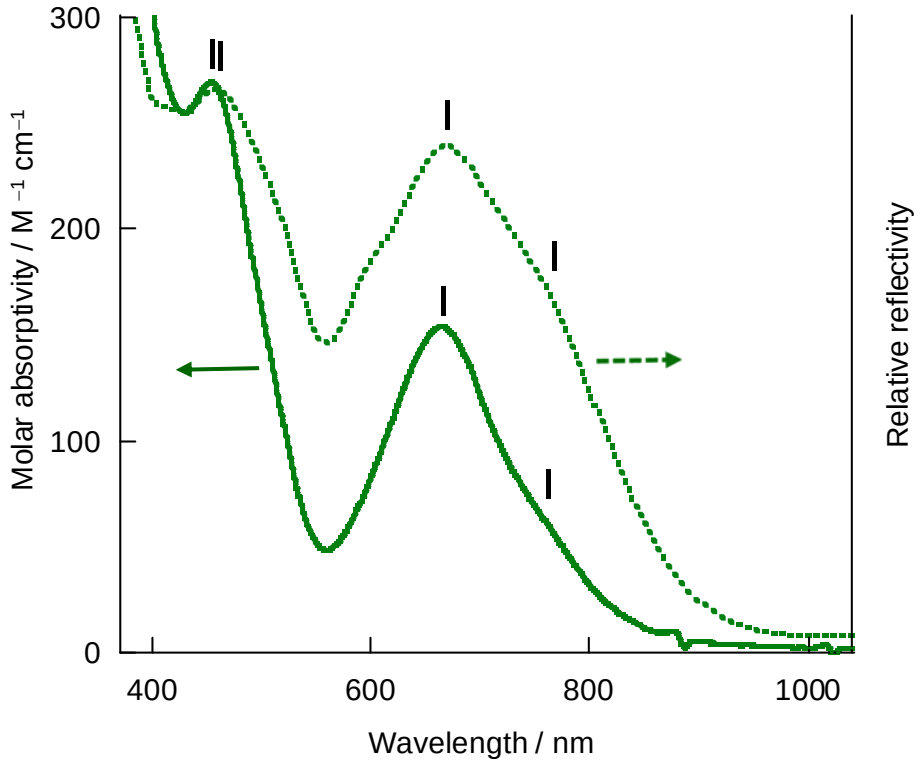

Figure S5. UV-Vis (solid line) and diffuse reflectance (DR, dotted line) spectra of **[Co(NO)(L3)]**.

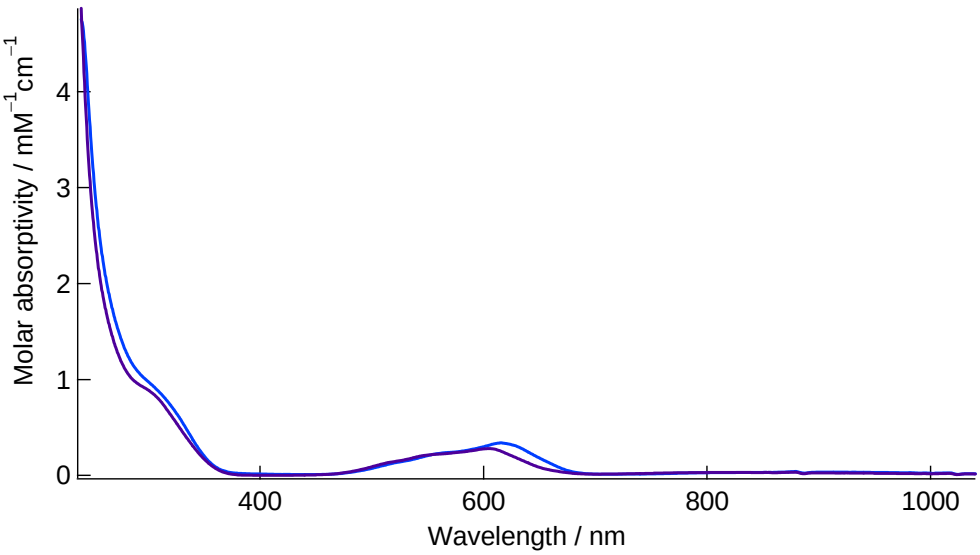

Figure S6. UV-Vis spectra of **[Co(η²-O₂N)(L3)]** (blue) and **[Co(η²-O₂NO)(L3)]** (purple).

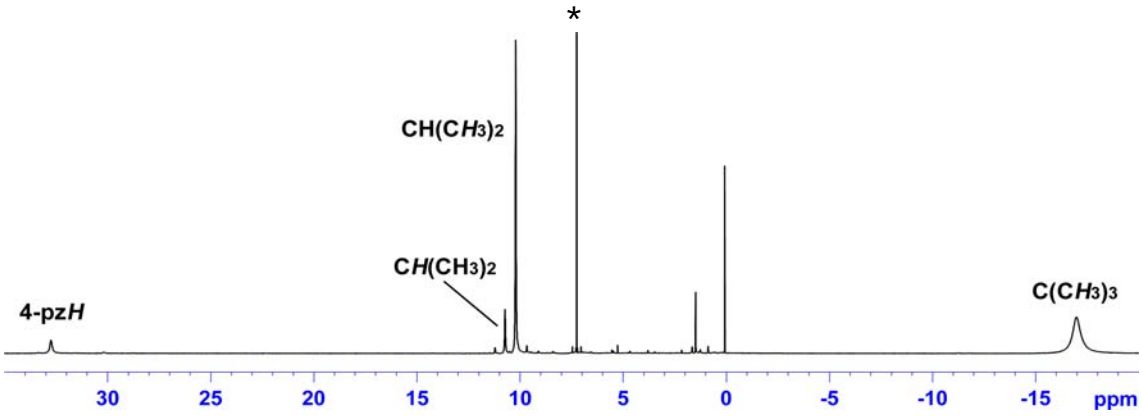

Figure S7. ^{1}H-NMR spectrum of **[Co(NO)(L3)]** in $CDCl_3$ at room temperature (* marks solvents and TMS peaks).

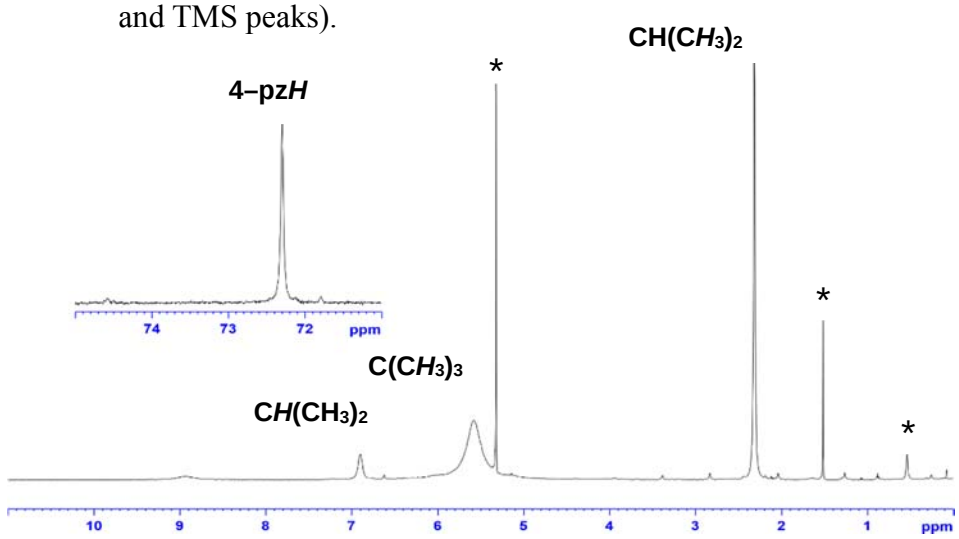

Figure S8. ^{1}H-NMR spectrum of **[Co(η^2-O$_2$N)(L3)]** in CD_2Cl_2 at room temperature (* marks solvents and impurities peaks).

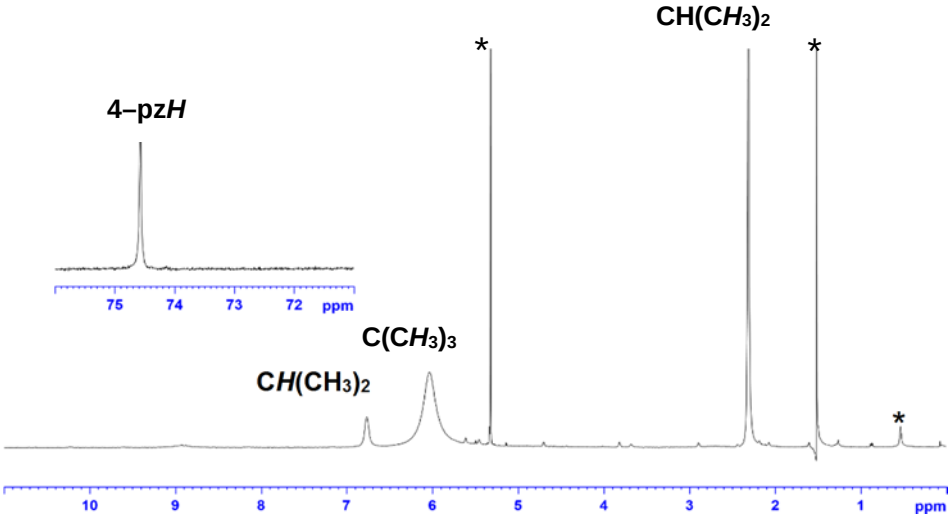

Figure S9. ^{1}H-NMR spectrum of **[Co(η^2-O$_2$NO)(L3)]** in CD_2Cl_2 at room temperature (* marks solvents and impurities peaks).

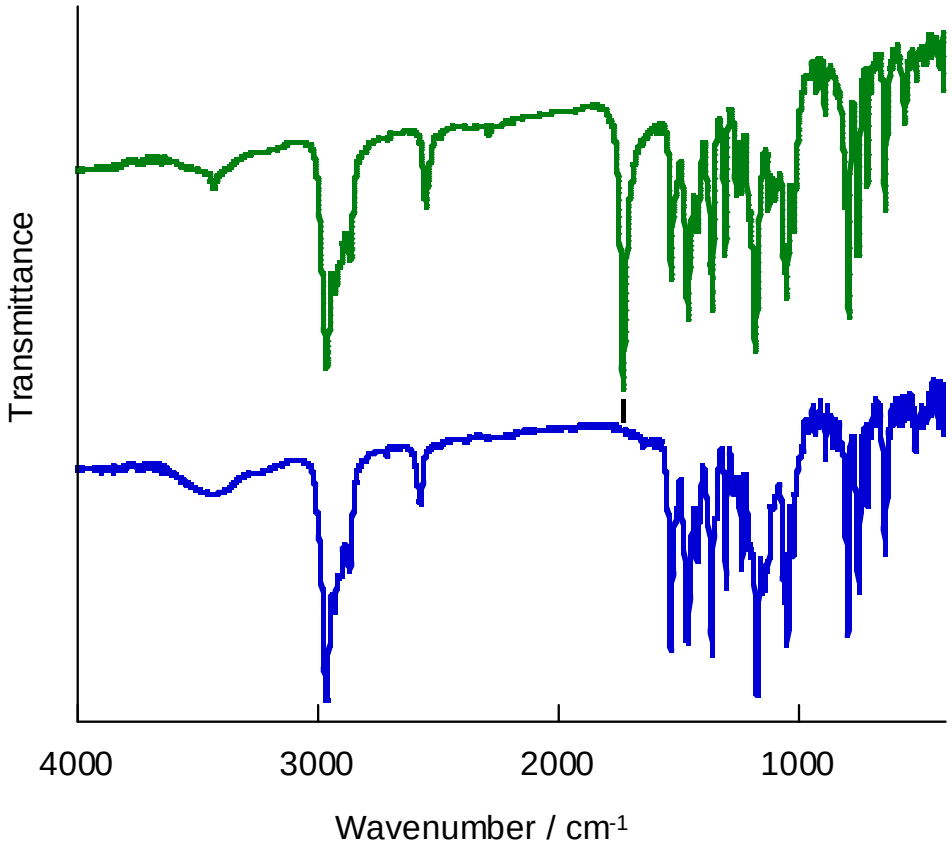

Figure S10. IR spectral changes during the O_2 reaction of [Co(NO)(L3)] in solution: before O_2 addition (green) and after the reaction (blue).

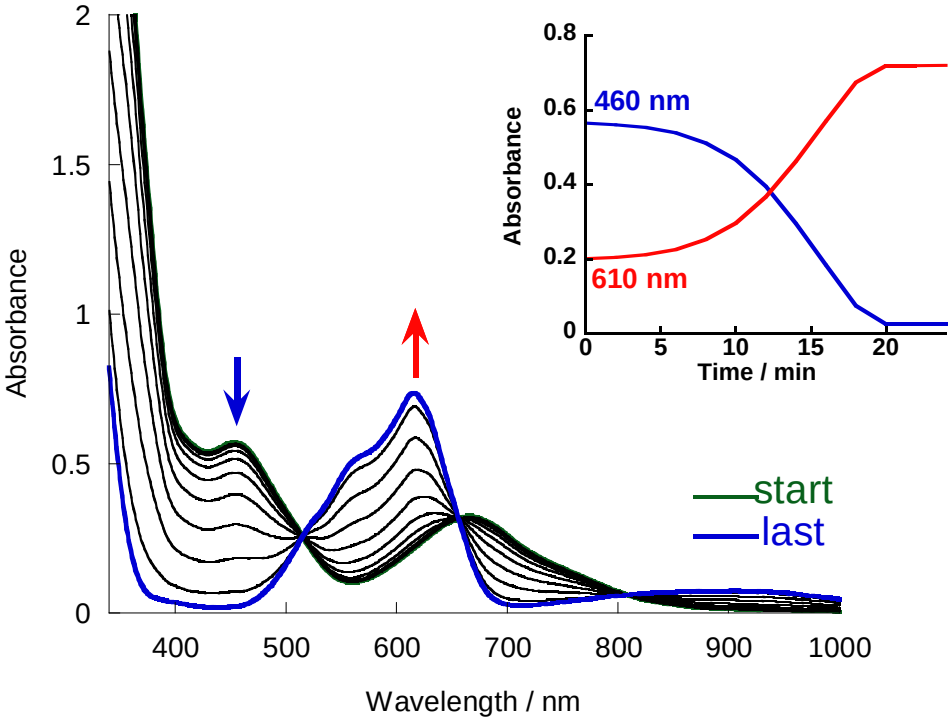

Figure S11. UV-Vis spectral changes during the reaction of [Co(NO)(L3)] with O_2 in the solution state (spectra taken every 2 min): before O_2 addition (green) and after the reaction (blue). Inset: time dependent changes at 460 (blue) and 610 nm (red).

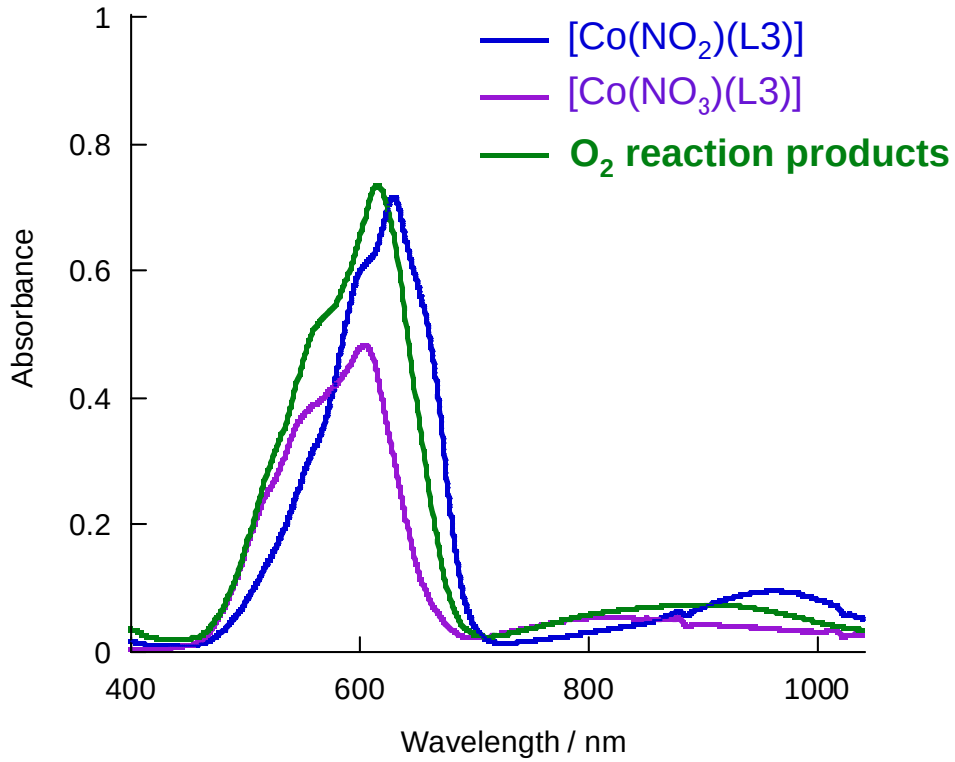

Figure S12. UV-Vis spectral comparison between the cobalt(II) complexes **[Co(η^2-O_2N)(L3)]** (blue) and **[Co(η^2-O_2NO)(L3)]** (purple) and the O_2 reaction products of **[Co(NO)(L3)]** (green; after 20 min reaction time).

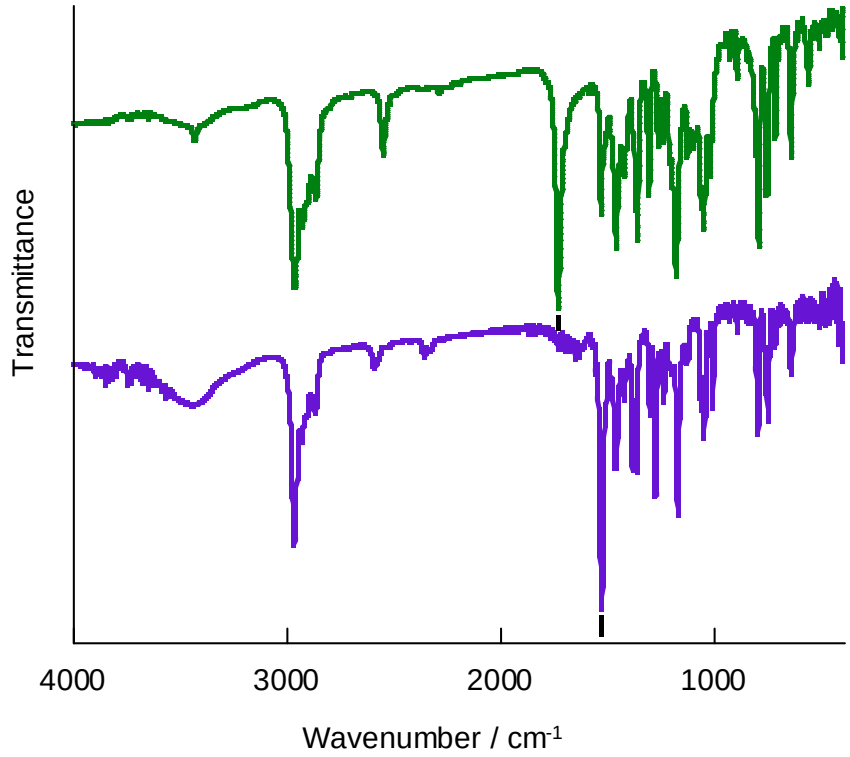

Figure S13. IR spectral changes during the O_2 reaction of **[Co(NO)(L3)]** in the solid state: before O_2 addition (green) and after the reaction (purple).

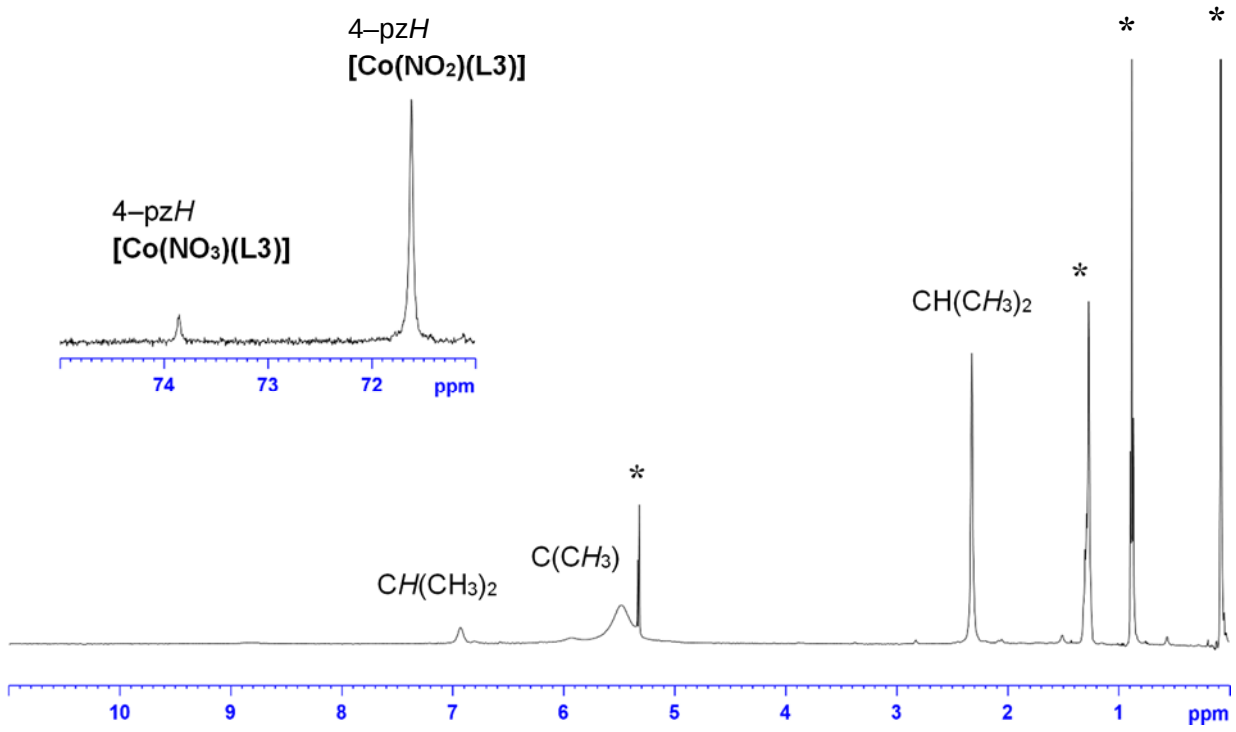

Figure S14. ^{1}H-NMR spectrum of the products of the O_2 reaction of **[Co(NO)(L3)]** in solution. Taken in CD_2Cl_2 at room temperature (* marks solvent, impurities, and TMS peaks).

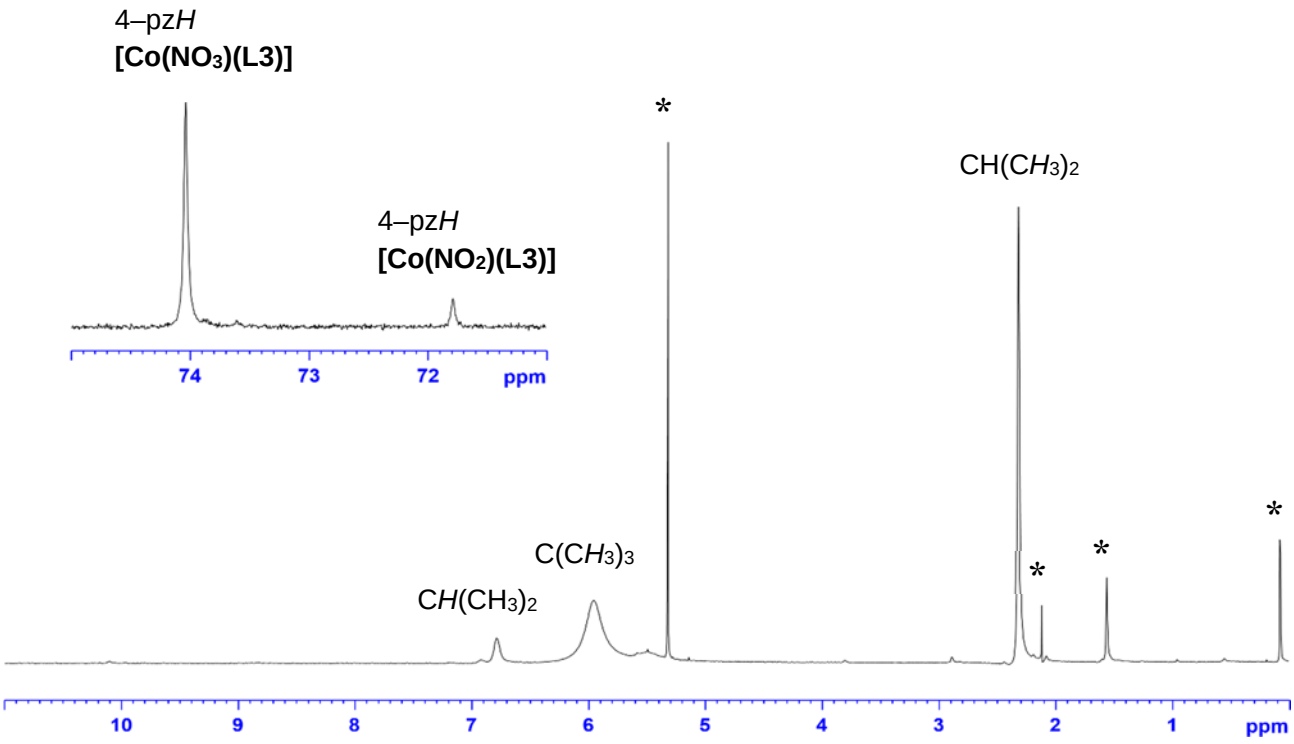

Figure S15. ^{1}H-NMR spectrum of the products of the O_2 reaction of **[Co(NO)(L3)]** in the solid state. Taken in CD_2Cl_2 at room temperature (* marks solvent, impurities, and TMS peaks).

Table S2. Molecular Orbital (MO) decompositions for **[Co(NO)(L0)]** (S = 1/2), calculated with B3LYP/TZVP on the BP86/TZVP-optimized structure.

α-Spin Molecular Orbitals

MO	%Co(d)	%NO	Character [a]
90	76	7	d_{xy}
91	75	1	d_{x2-y2}
92	57	11	d_{yz}_π^*_h (bonding)
93	21	6	d_{xz}_π^*_v (bonding)
94	7	2	Pyr(π) + d_{xz}
95	8	1	Pyr(π) + d_{z2}
96	46	11	d_{z2} + π^*_h
97	7	1	Pyr(π) + d_{xy}
98	20	2	Pyr(N)_d_{xy}
99	1	0	Pyr(π)
100 (HOMO)	28	3	Pyr(N)_d_{x2-y2}
101 (LUMO)	12	77	π^*_v_d_{xz} (antibonding)
102	14	77	π^*_h_d_{yz} (antibonding)
103	2	3	Pyr(π^*)
104	2	2	Pyr(π^*)
106	0	0	Pyr(π^*)

β-Spin Molecular Orbitals

MO	%Co(d)	%NO	Character [a]
90	38	0	d_{x2-y2}_Pyr(N)
91	4	1	d_{xy}_Pyr(π)
92	1	1	Pyr(π)
93	0	0	Pyr(π)
94	0	1	Pyr(π)
95	0	0	Pyr(π)
96	48	38	π^*_h_d_{yz} (bonding)
97	30	60	π^*_v_d_{xz} (bonding)
98	65	3	d_σ + Pyr(N)
99 (HOMO)	43	36	d_σ + π^*_h (non-bonding)
100 (LUMO)	62	14	d_{xy}/d_{xz} + π^*_v (non-bonding)
101	56	27	d_{yz}_π^*_h (antibonding)
102	55	21	d_{xz}_π^*_v (antibonding)
103	5	1	Pyr(π^*) + d_{x2-y2}
104	27	0	Pyr(π^*) + d_{xy}
106	0	0	Pyr(π^*)

[a] The nomenclature '*a_b*' indicates that orbital *a* interacts with *b* and that *a* has a larger contribution to the resulting MO.

Table S3. Coordinated of the fully optimized structure of **[Co(NO)(L0)]**, obtained with BP86/TZVP.

Co	-1.37068	-0.40828	0.36438
N	-0.56097	1.401	0.65239
N	0.76039	1.5598	0.3126
N	-0.56989	-0.44766	-1.47142
N	0.75117	-0.08906	-1.58762
N	0.26183	-1.29966	1.12994
N	1.48413	-0.82832	0.71557
C	-0.99587	2.57637	1.15134
C	0.06512	3.50368	1.13371
C	1.16437	2.83067	0.598
C	-1.00822	-0.78521	-2.70173
C	0.04986	-0.64283	-3.62168
C	1.15107	-0.20169	-2.88658
C	0.49018	-2.30706	2.0022
C	1.8791	-2.48331	2.14839
C	2.48106	-1.53174	1.32063
B	1.51438	0.34935	-0.30598
H	2.65132	0.64599	-0.56904
H	0.03701	4.53666	1.46862
H	0.01879	-0.83769	-4.68989
H	2.38885	-3.20979	2.77479
C	-2.40303	2.76319	1.62412
H	-2.64814	2.06701	2.44081
H	-2.54748	3.7879	1.99209
H	-3.1257	2.5833	0.81406
C	2.55388	3.3282	0.35247
H	2.62189	4.38563	0.64124
H	3.30055	2.76885	0.93708
H	2.83798	3.24626	-0.70777
C	3.93512	-1.26957	1.08529
H	4.21772	-0.24511	1.37179
H	4.53725	-1.96773	1.68183
H	4.20832	-1.4016	0.02729
C	-0.63889	-3.04364	2.64915
H	-0.58722	-4.12208	2.43365
H	-0.61986	-2.92273	3.74358
H	-1.59973	-2.66072	2.27635
C	-2.4168	-1.22482	-2.94898
H	-3.13274	-0.41091	-2.75732
H	-2.53674	-1.5457	-3.99253
H	-2.69473	-2.06508	-2.29517
C	2.53937	0.10682	-3.35155
H	3.28888	-0.53505	-2.86351
H	2.60816	-0.05669	-4.43538
H	2.81926	1.15179	-3.14746
N	-3.01846	-0.47759	0.4194
O	-4.18032	-0.29496	0.25275

Table S4. Coordinated of the fully optimized structure of **[Co(NO)(L0)]**, obtained with M06L/TZVP.

Co	1.41956	-0.43693	-0.3433
N	0.50249	1.26491	-0.96797
N	-0.80545	1.44484	-0.63329
N	0.58314	-0.14541	1.51345
N	-0.73571	0.19864	1.54341
N	-0.23833	-1.50167	-0.88274
N	-1.45497	-0.98201	-0.55543
C	0.89289	2.35118	-1.64072
C	-0.1777	3.24236	-1.7425
C	-1.2391	2.63926	-1.09043
C	1.00103	-0.2205	2.77904
C	-0.06118	0.07642	3.63799
C	-1.14759	0.33635	2.82384
C	-0.45733	-2.66845	-1.49864
C	-1.83222	-2.90461	-1.56786
C	-2.43504	-1.81882	-0.95762
B	-1.51057	0.36096	0.21431
H	-2.64145	0.66892	0.42607
H	-0.18247	4.20407	-2.2284
H	-0.0424	0.09828	4.7149
H	-2.33055	-3.75442	-2.0039
C	2.28275	2.47888	-2.14283
H	2.55674	1.6386	-2.78248
H	2.4055	3.39365	-2.71886
H	3.00191	2.49901	-1.3219
C	-2.62401	3.12113	-0.87613
H	-2.75115	4.1077	-1.31628
H	-3.36073	2.45435	-1.32751
H	-2.86876	3.19153	0.18517
C	-3.8718	-1.53175	-0.73354
H	-4.17916	-0.60144	-1.2141
H	-4.48347	-2.33616	-1.13622
H	-4.10363	-1.43106	0.32816
C	0.67544	-3.48662	-1.99136
H	0.6263	-4.50816	-1.61323
H	0.68487	-3.54724	-3.08084
H	1.62259	-3.05058	-1.67113
C	2.40691	-0.56286	3.10388
H	3.0874	0.25054	2.84464
H	2.52113	-0.76495	4.16694
H	2.73923	-1.44232	2.55141
C	-2.53866	0.70371	3.18036
H	-3.25967	-0.03034	2.81622
H	-2.64371	0.76917	4.26106
H	-2.82572	1.66714	2.75522
N	3.08716	-0.52301	-0.23419
O	4.22965	-0.28904	-0.07763