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Supporting information for

Promotion of S-Nitrosation of Cysteine by $\{Co(NO)_2\}^{10}$ Complex

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Materials and Methods

All glassware was oven dried at 110 °C for hours and cooled down under vacuum. All manipulations were carried out by using standard Schlenk techniques. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel. All manipulations were operated under a nitrogen or argon atmosphere using standard Schlenk techniques or in a glovebox. THF, toluene, hexane, and diethyl-ether were purified by Na/benzophenone and distilled prior to use. ArLFc, BocNH-Cys-COOMe, and $Co_2(NO)_4Cl_2$ were synthesized according to the literature methods.[12]-[14] Other chemical reagents were obtained from commercial sources and used as received unless stated otherwise. UV-vis spectra were recorded with Agilent 8454 spectrophotometer. Infrared spectra were recorded with Bruker ALPHA II FTIR. Cyclic voltammetry measurements were performed by means of a three-electrode technique by using a home-built computer-controlled instrument on THF solutions containing 0.1M tetrabutylammonium tetrafluoroborate as electrolyte with Ag wire used as reference electrode and a glassy carbon electrode as the working electrode.

X-ray Data Collection and Structure Determination.

X-ray diffraction data of crystals of 1 was collected on a Bruker Kappa APEX II CCD diffractometer employing Mo Kα radiation (λ = 0.7107 Å) at 200 K and with a θ−2θ scan mode. The space groups for 1 was determined on the basis of systematic absences and intensity statistics. Their structures were solved by direct methods using SIR92 or SIR97, and refined using SHELXL-97 with anisotropic displacement factors for all non-hydrogen atoms. The detailed crystallographic data of 1 was provided in their crystallographic information files.

Synthesis Procedure

*Synthesis of Co(ArLFc)(NO)₂ (**1**):* Co(ArLFc)$(NO)_2$ (**1**) was synthesized by reacting ArLFc (88.4 mg, 0.2 mmol) with nBuLi (0.08 mL, 0.2 mmol) in 15 mL of THF in a 50 mL Schlenk flask. The solution was stirred for 3 h at r.t. and then filtered. The filtrate was then reacted with $Co_2(NO)_4Cl_2$ (30.9 mg, 0.1 m and stirred for 15 h at 100 °C. Eventually, the solution was concentrated under vacuum and recrystallized with hexane at ambient temperature. Deep Brown crystals of 1 were obtained in 68% yield over 6 days. Absorption spectrum (THF) [λ_{max}, nm (ε, M^{-1} cm^{-1})]: 330 (12000), 390 (17500), 450 (4000), 630 (800). Anal. Calcd for $C_{27}H_{33}CoFeN_4O_2$ (F.W. = 560.37): C, 57.87; H, 5.94; N, 10.00. Found: C, 57.814; H, 5.890; N, 9.991.

*Reaction of Co(ArLFc)(NO)$_2$ (**1**) with BocNH-Cys-COOMe:* A dry schlenk tube equipped with a stirring bar was charged with Co(II)(ArLFc)(NO)$_2$ (**1**) (0.2 mmol, 1.0 equiv.) dissolved in THF (5 mL) and was then transferred to the THF solution (5 mL) of BocNH-Cys-COOMe (0.2 mmol, 1.0 equiv.). The reaction was detected by UV-Vis (diluted to 2 x 10^{-5} M), IR spectroscopies, and GC-MS.

Computational Details

Density functional theory (DFT) calculations were carried out using the Gaussian 09 program. Geometries of all stationary points were fully optimized using the dispersion-corrected (U)B3LYP functional. Single-point energy calculations were carried out using a mixed basis set comprised of 6-31g+(d,p) for N and O, 6-31g for C and H, and the pseudopotential (def2-TZVPPD) level for the Co and Fe atoms.

X-ray Data Collection and Structure Determination for Co(ArLFc)$(NO)_2$ (1) and Co(ArLFc)$_2$.

ATOM	X	Y	Z
C	10.61600000	4.95300000	3.28400000
C	11.39900000	5.00500000	4.47600000
C	12.32900000	3.90800000	4.43300000
C	12.15000000	3.20600000	3.23000000
C	11.10100000	3.85500000	2.49700000
C	14.58100000	5.75600000	2.00000000
C	14.31000000	5.03600000	1.69700000
C	13.30600000	5.65300000	0.99100000
C	12.90800000	6.81300000	1.73600000
C	13.72000000	6.87500000	2.91300000
C	8.26800000	4.12300000	1.82400000
C	8.54200000	5.55800000	2.24400000
C	7.57500000	6.49400000	1.82200000
C	7.58400000	7.87800000	2.00000000
C	6.53800000	8.64700000	1.21600000
C	8.38900000	9.93700000	2.92500000
C	9.39300000	10.67200000	2.22900000
C	10.38900000	9.97400000	1.33700000
C	9.84500000	9.77100000	-0.08000000
C	11.73800000	10.67800000	1.30300000
C	9.40300000	12.05100000	2.37600000
C	8.47400000	12.70300000	3.19800000

C	7.53900000	11.96200000	3.87600000
C	7.47300000	10.58000000	3.76600000
C	6.45000000	9.80800000	4.57500000
C	6.73900000	9.98700000	6.08800000
C	5.02600000	10.26100000	4.28400000
Co	9.55700000	7.54800000	4.05600000
Fe	12.64100000	5.12900000	2.82900000
N	8.72100000	7.16500000	5.48800000
N	10.89400000	8.44600000	4.38600000
N	9.58600000	5.88500000	2.99800000
N	8.40900000	8.50000000	2.81600000
O	8.75500000	7.24700000	6.65900000
O	11.78700000	9.21600000	4.42500000
H	11.31700000	5.68300000	5.20700000
H	13.00500000	3.69000000	5.13700000
H	12.65800000	2.39500000	2.94100000
H	10.75300000	3.57600000	1.60300000
H	15.25900000	5.51600000	3.58300000
H	14.76900000	4.19200000	1.42100000
H	12.92700000	5.35300000	0.11600000
H	12.19700000	7.46700000	1.47600000
H	13.67000000	7.56800000	3.63300000
H	7.30100000	3.96200000	1.82300000
H	8.70000000	3.51000000	2.45500000
H	8.62600000	3.97200000	0.92400000

H	6.82500000	6.13900000	1.36000000
H	6.68700000	9.60900000	1.33000000
H	5.64500000	8.41400000	1.54700000
H	6.60500000	8.41600000	0.26700000
H	10.54300000	9.06600000	1.72500000
H	9.76000000	10.64000000	-0.52500000
H	8.96500000	9.34000000	-0.03400000
H	10.46100000	9.20300000	-0.58900000
H	12.38500000	10.12100000	0.82100000
H	12.05100000	10.82600000	2.21900000
H	11.64500000	11.53900000	0.84400000
H	10.05300000	12.56400000	1.91100000
H	8.49100000	13.64900000	3.28500000
H	6.91700000	12.40900000	4.43800000
H	6.52900000	8.83800000	4.34700000
H	7.68300000	9.79300000	6.26400000
H	6.17700000	9.37000000	6.60200000
H	6.53800000	10.90900000	6.35100000
H	4.86100000	10.21800000	3.31900000
H	4.90800000	11.18400000	4.59400000
H	4.39500000	9.67500000	4.75100000

Table S1. Crystal data and structure refinement for $Co(ArLFc)(NO)_2$ (1).

Identification code	d20202a	
Empirical formula	C27 H33 Co Fe N4 O2	
Formula weight	560.35	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 10.2255(12) Å	α= 84.859(3)°.
	b = 11.5646(13) Å	β= 76.424(3)°.
	c = 11.7408(12) Å	γ = 75.669(3)°.
Volume	1306.9(3) $Å^3$	
Z	2	
Density (calculated)	1.424 Mg/m^3	
Absorption coefficient	1.220 mm^{-1}	
F(000)	584	
Crystal size	0.57 x 0.42 x 0.14 mm^3	
Theta range for data collection	2.59 to 25.06°.	
Index ranges	-12<=h<=12, -13<=k<=13, -13<=l<=13	
Reflections collected	27393	
Independent reflections	4549 [R(int) = 0.0477]	
Completeness to theta = 25.06°	98.2 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.8477 and 0.5430	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4549 / 0 / 322	
Goodness-of-fit on F^2	1.176	
Final R indices [I>2sigma(I)]	R1 = 0.0787, wR2 = 0.2294	
R indices (all data)	R1 = 0.0852, wR2 = 0.2331	
Largest diff. peak and hole	1.459 and -0.680 $e.Å^{-3}$	

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for d20202a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	8396(8)	4322(7)	2879(7)	25(2)
C(2)	8877(9)	4333(8)	3924(7)	31(2)
C(3)	10071(10)	3355(8)	3886(8)	40(2)
C(4)	10345(9)	2765(8)	2832(8)	37(2)
C(5)	9324(8)	3366(7)	2189(8)	29(2)
C(6)	12163(10)	5051(11)	2532(10)	53(3)
C(7)	12349(10)	4444(9)	1488(9)	46(2)
C(8)	11374(10)	5016(10)	869(9)	46(2)
C(9)	10525(10)	6029(9)	1522(12)	57(3)
C(10)	11036(11)	6049(10)	2554(12)	62(3)
C(11)	6640(9)	3625(7)	1599(7)	29(2)
C(12)	6454(8)	4893(6)	1967(7)	22(2)
C(13)	5370(8)	5741(7)	1597(7)	24(2)
C(14)	4993(8)	6971(7)	1753(6)	25(2)
C(15)	3956(10)	7681(8)	1066(8)	39(2)
C(16)	5055(8)	8781(6)	2564(7)	23(2)
C(17)	6012(8)	9458(7)	1954(7)	27(2)
C(18)	7363(10)	8862(8)	1172(8)	39(2)
C(19)	7205(15)	8723(12)	-70(10)	69(4)
C(20)	8514(11)	9491(11)	1142(12)	65(3)
C(21)	5643(10)	10684(8)	2083(8)	37(2)
C(22)	4384(10)	11242(7)	2804(8)	37(2)
C(23)	3501(10)	10560(7)	3398(8)	35(2)
C(24)	3806(8)	9330(7)	3302(7)	29(2)
C(25)	2814(9)	8617(8)	4011(8)	35(2)
C(26)	2708(12)	8731(9)	5337(8)	46(2)
C(27)	1375(10)	9030(10)	3756(10)	51(3)
Co(1)	6536(1)	6616(1)	3556(1)	22(1)
Fe(1)	10436(1)	4493(1)	2480(1)	28(1)
N(1)	5488(8)	6231(6)	4811(6)	36(2)
N(2)	7544(8)	7407(6)	3845(7)	34(2)

N(3)	7221(6)	5163(5)	2628(5)	20(1)
N(4)	5458(6)	7502(5)	2469(5)	23(1)
O(1)	5234(9)	6269(7)	5838(6)	57(2)
O(2)	8216(8)	8093(6)	3879(7)	54(2)

Bond lengths [Å] and angles [°] for d20202a.

C(1)-N(3)	1.418(10)
C(1)-C(2)	1.426(11)
C(1)-C(5)	1.436(11)
C(1)-Fe(1)	2.082(8)
C(2)-C(3)	1.439(12)
C(2)-Fe(1)	2.066(9)
C(2)-H(2)	1.0000
C(3)-C(4)	1.403(13)
C(3)-Fe(1)	2.039(9)
C(3)-H(3)	1.0000
C(4)-C(5)	1.435(12)
C(4)-Fe(1)	2.025(9)
C(4)-H(4)	1.0000
C(5)-Fe(1)	2.026(8)
C(5)-H(5)	1.0000
C(6)-C(10)	1.412(17)
C(6)-C(7)	1.418(15)
C(6)-Fe(1)	2.040(10)
C(6)-H(6)	1.0000
C(7)-C(8)	1.374(14)
C(7)-Fe(1)	2.019(9)
C(7)-H(7)	1.0000
C(8)-C(9)	1.435(15)
C(8)-Fe(1)	2.024(10)
C(8)-H(8)	1.0000
C(9)-C(10)	1.432(18)
C(9)-Fe(1)	2.026(10)
C(9)-H(9)	1.0000

C(10)-Fe(1)	2.055(11)
C(10)-H(10)	1.0000
C(11)-C(12)	1.519(10)
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-N(3)	1.329(10)
C(12)-C(13)	1.410(11)
C(13)-C(14)	1.395(11)
C(13)-H(13)	0.9500
C(14)-N(4)	1.317(10)
C(14)-C(15)	1.517(11)
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-C(24)	1.401(11)
C(16)-C(17)	1.426(11)
C(16)-N(4)	1.441(9)
C(17)-C(21)	1.387(12)
C(17)-C(18)	1.508(12)
C(18)-C(20)	1.521(14)
C(18)-C(19)	1.531(15)
C(18)-H(18)	1.0000
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-C(22)	1.402(13)
C(21)-H(21)	0.9500
C(22)-C(23)	1.372(13)
C(22)-H(22)	0.9500
C(23)-C(24)	1.387(11)
C(23)-H(23)	0.9500
C(24)-C(25)	1.515(12)

C(25)-C(27)	1.522(13)
C(25)-C(26)	1.550(13)
C(25)-H(25)	1.0000
C(26)-H(26A)	0.9800
C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800
Co(1)-N(2)	1.644(7)
Co(1)-N(1)	1.701(7)
Co(1)-N(4)	1.939(6)
Co(1)-N(3)	1.971(6)
N(1)-O(1)	1.175(9)
N(2)-O(2)	1.180(9)

N(3)-C(1)-C(2)	122.9(7)
N(3)-C(1)-C(5)	129.6(7)
C(2)-C(1)-C(5)	107.5(7)
N(3)-C(1)-Fe(1)	127.3(5)
C(2)-C(1)-Fe(1)	69.3(5)
C(5)-C(1)-Fe(1)	67.5(4)
C(1)-C(2)-C(3)	107.6(8)
C(1)-C(2)-Fe(1)	70.5(5)
C(3)-C(2)-Fe(1)	68.5(5)
C(1)-C(2)-H(2)	126.2
C(3)-C(2)-H(2)	126.2
Fe(1)-C(2)-H(2)	126.2
C(4)-C(3)-C(2)	108.9(8)
C(4)-C(3)-Fe(1)	69.3(5)
C(2)-C(3)-Fe(1)	70.5(5)
C(4)-C(3)-H(3)	125.5
C(2)-C(3)-H(3)	125.5
Fe(1)-C(3)-H(3)	125.5
C(3)-C(4)-C(5)	107.7(8)
C(3)-C(4)-Fe(1)	70.3(5)

C(5)-C(4)-Fe(1)	69.3(5)
C(3)-C(4)-H(4)	126.1
C(5)-C(4)-H(4)	126.1
Fe(1)-C(4)-H(4)	126.1
C(4)-C(5)-C(1)	108.2(8)
C(4)-C(5)-Fe(1)	69.2(5)
C(1)-C(5)-Fe(1)	71.7(5)
C(4)-C(5)-H(5)	125.9
C(1)-C(5)-H(5)	125.9
Fe(1)-C(5)-H(5)	125.9
C(10)-C(6)-C(7)	107.5(11)
C(10)-C(6)-Fe(1)	70.4(6)
C(7)-C(6)-Fe(1)	68.8(6)
C(10)-C(6)-H(6)	126.2
C(7)-C(6)-H(6)	126.2
Fe(1)-C(6)-H(6)	126.2
C(8)-C(7)-C(6)	110.1(10)
C(8)-C(7)-Fe(1)	70.3(6)
C(6)-C(7)-Fe(1)	70.4(5)
C(8)-C(7)-H(7)	124.9
C(6)-C(7)-H(7)	124.9
Fe(1)-C(7)-H(7)	124.9
C(7)-C(8)-C(9)	107.4(10)
C(7)-C(8)-Fe(1)	69.9(6)
C(9)-C(8)-Fe(1)	69.3(6)
C(7)-C(8)-H(8)	126.3
C(9)-C(8)-H(8)	126.3
Fe(1)-C(8)-H(8)	126.3
C(10)-C(9)-C(8)	107.7(9)
C(10)-C(9)-Fe(1)	70.5(6)
C(8)-C(9)-Fe(1)	69.2(6)
C(10)-C(9)-H(9)	126.1
C(8)-C(9)-H(9)	126.1
Fe(1)-C(9)-H(9)	126.1
C(6)-C(10)-C(9)	107.3(10)
C(6)-C(10)-Fe(1)	69.3(6)

C(9)-C(10)-Fe(1)	68.4(6)
C(6)-C(10)-H(10)	126.3
C(9)-C(10)-H(10)	126.3
Fe(1)-C(10)-H(10)	126.3
C(12)-C(11)-H(11A)	109.5
C(12)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(12)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
N(3)-C(12)-C(13)	123.0(7)
N(3)-C(12)-C(11)	122.1(7)
C(13)-C(12)-C(11)	114.9(7)
C(14)-C(13)-C(12)	128.0(7)
C(14)-C(13)-H(13)	116.0
C(12)-C(13)-H(13)	116.0
N(4)-C(14)-C(13)	123.5(7)
N(4)-C(14)-C(15)	120.8(7)
C(13)-C(14)-C(15)	115.7(7)
C(14)-C(15)-H(15A)	109.5
C(14)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(14)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(24)-C(16)-C(17)	121.2(7)
C(24)-C(16)-N(4)	120.8(7)
C(17)-C(16)-N(4)	117.9(7)
C(21)-C(17)-C(16)	117.7(8)
C(21)-C(17)-C(18)	121.2(8)
C(16)-C(17)-C(18)	121.1(7)
C(17)-C(18)-C(20)	112.7(8)
C(17)-C(18)-C(19)	112.0(9)
C(20)-C(18)-C(19)	110.8(9)
C(17)-C(18)-H(18)	107.0
C(20)-C(18)-H(18)	107.0

C(19)-C(18)-H(18)	107.0
C(18)-C(19)-H(19A)	109.5
C(18)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(18)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(18)-C(20)-H(20A)	109.5
C(18)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(18)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(17)-C(21)-C(22)	121.4(8)
C(17)-C(21)-H(21)	119.3
C(22)-C(21)-H(21)	119.3
C(23)-C(22)-C(21)	119.3(8)
C(23)-C(22)-H(22)	120.3
C(21)-C(22)-H(22)	120.3
C(22)-C(23)-C(24)	122.1(8)
C(22)-C(23)-H(23)	118.9
C(24)-C(23)-H(23)	118.9
C(23)-C(24)-C(16)	118.2(8)
C(23)-C(24)-C(25)	119.8(8)
C(16)-C(24)-C(25)	121.9(7)
C(24)-C(25)-C(27)	112.2(8)
C(24)-C(25)-C(26)	109.7(7)
C(27)-C(25)-C(26)	109.1(8)
C(24)-C(25)-H(25)	108.6
C(27)-C(25)-H(25)	108.6
C(26)-C(25)-H(25)	108.6
C(25)-C(26)-H(26A)	109.5
C(25)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
C(25)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5

H(26B)-C(26)-H(26C)	109.5
C(25)-C(27)-H(27A)	109.5
C(25)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
C(25)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
N(2)-Co(1)-N(1)	110.7(4)
N(2)-Co(1)-N(4)	110.0(3)
N(1)-Co(1)-N(4)	111.0(3)
N(2)-Co(1)-N(3)	123.8(3)
N(1)-Co(1)-N(3)	105.6(3)
N(4)-Co(1)-N(3)	94.6(3)
C(7)-Fe(1)-C(8)	39.7(4)
C(7)-Fe(1)-C(4)	105.5(4)
C(8)-Fe(1)-C(4)	120.4(4)
C(7)-Fe(1)-C(9)	68.1(4)
C(8)-Fe(1)-C(9)	41.5(4)
C(4)-Fe(1)-C(9)	158.2(5)
C(7)-Fe(1)-C(5)	120.5(4)
C(8)-Fe(1)-C(5)	105.3(4)
C(4)-Fe(1)-C(5)	41.5(3)
C(9)-Fe(1)-C(5)	122.3(5)
C(7)-Fe(1)-C(3)	122.6(4)
C(8)-Fe(1)-C(3)	156.8(4)
C(4)-Fe(1)-C(3)	40.4(4)
C(9)-Fe(1)-C(3)	160.4(5)
C(5)-Fe(1)-C(3)	68.6(4)
C(7)-Fe(1)-C(6)	40.9(4)
C(8)-Fe(1)-C(6)	68.5(4)
C(4)-Fe(1)-C(6)	121.1(4)
C(9)-Fe(1)-C(6)	68.6(5)
C(5)-Fe(1)-C(6)	157.1(4)
C(3)-Fe(1)-C(6)	107.8(5)
C(7)-Fe(1)-C(10)	68.1(4)
C(8)-Fe(1)-C(10)	69.2(5)

C(4)-Fe(1)-C(10)	157.9(5)
C(9)-Fe(1)-C(10)	41.1(5)
C(5)-Fe(1)-C(10)	160.2(5)
C(3)-Fe(1)-C(10)	123.8(5)
C(6)-Fe(1)-C(10)	40.3(5)
C(7)-Fe(1)-C(2)	160.2(4)
C(8)-Fe(1)-C(2)	159.5(4)
C(4)-Fe(1)-C(2)	68.8(4)
C(9)-Fe(1)-C(2)	124.0(4)
C(5)-Fe(1)-C(2)	68.6(3)
C(3)-Fe(1)-C(2)	41.0(3)
C(6)-Fe(1)-C(2)	124.6(4)
C(10)-Fe(1)-C(2)	109.5(4)
C(7)-Fe(1)-C(1)	157.3(4)
C(8)-Fe(1)-C(1)	122.7(4)
C(4)-Fe(1)-C(1)	68.9(3)
C(9)-Fe(1)-C(1)	108.4(4)
C(5)-Fe(1)-C(1)	40.9(3)
C(3)-Fe(1)-C(1)	68.2(3)
C(6)-Fe(1)-C(1)	160.8(4)
C(10)-Fe(1)-C(1)	125.0(4)
C(2)-Fe(1)-C(1)	40.2(3)
O(1)-N(1)-Co(1)	144.0(7)
O(2)-N(2)-Co(1)	168.1(7)
C(12)-N(3)-C(1)	121.5(6)
C(12)-N(3)-Co(1)	120.1(5)
C(1)-N(3)-Co(1)	117.2(5)
C(14)-N(4)-C(16)	120.6(6)
C(14)-N(4)-Co(1)	122.3(5)
C(16)-N(4)-Co(1)	116.7(5)

Symmetry transformations used to generate equivalent atoms:

Anisotropic displacement parameters ($Å^2 x\ 10^3$)for d20202a. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	26(4)	22(4)	24(4)	1(3)	-2(3)	-7(3)
C(2)	33(5)	36(5)	24(4)	4(3)	-10(3)	-7(4)
C(3)	35(5)	41(5)	35(5)	7(4)	-9(4)	5(4)
C(4)	34(5)	34(5)	37(5)	4(4)	-4(4)	-4(4)
C(5)	25(4)	22(4)	37(5)	-5(3)	-2(3)	-3(3)
C(6)	27(5)	82(8)	54(6)	-9(6)	3(4)	-29(5)
C(7)	25(5)	51(6)	56(6)	-3(5)	-2(4)	-8(4)
C(8)	34(5)	64(7)	39(5)	5(5)	-4(4)	-18(5)
C(9)	26(5)	42(6)	88(9)	21(6)	9(5)	-10(4)
C(10)	42(6)	49(6)	83(9)	-12(6)	25(6)	-19(5)
C(11)	29(4)	23(4)	33(4)	-11(3)	0(3)	-9(3)
C(12)	21(4)	20(4)	24(4)	-6(3)	6(3)	-9(3)
C(13)	26(4)	28(4)	22(4)	-8(3)	-2(3)	-11(3)
C(14)	25(4)	29(4)	19(4)	-5(3)	1(3)	-7(3)
C(15)	50(6)	38(5)	34(5)	-8(4)	-21(4)	-6(4)
C(16)	27(4)	19(4)	27(4)	-3(3)	-11(3)	-6(3)
C(17)	29(4)	27(4)	27(4)	2(3)	-11(3)	-9(3)
C(18)	38(5)	33(5)	40(5)	3(4)	2(4)	-10(4)
C(19)	87(9)	67(8)	38(6)	-15(5)	8(6)	-6(7)
C(20)	40(6)	67(8)	82(9)	-4(6)	15(6)	-30(6)
C(21)	42(5)	28(4)	45(5)	5(4)	-12(4)	-17(4)
C(22)	53(6)	20(4)	42(5)	-2(4)	-13(4)	-12(4)
C(23)	41(5)	23(4)	38(5)	-7(4)	-14(4)	3(4)
C(24)	26(4)	27(4)	33(4)	-7(3)	-9(3)	-3(3)
C(25)	34(5)	31(4)	34(5)	-8(4)	5(4)	-8(4)
C(26)	61(7)	42(5)	33(5)	3(4)	-4(5)	-15(5)
C(27)	30(5)	57(6)	63(7)	-4(5)	-2(5)	-11(5)
Co(1)	25(1)	22(1)	22(1)	-4(1)	-6(1)	-6(1)
Fe(1)	22(1)	32(1)	28(1)	-1(1)	-3(1)	-6(1)
N(1)	44(4)	33(4)	26(4)	-1(3)	-2(3)	-9(3)
N(2)	35(4)	28(4)	43(4)	-8(3)	-16(3)	-7(3)

N(3)	17(3)	20(3)	20(3)	-2(2)	1(2)	-6(2)
N(4)	23(3)	19(3)	25(3)	-3(2)	-2(3)	-6(3)
O(1)	81(6)	56(5)	28(4)	-3(3)	2(4)	-18(4)
O(2)	58(5)	49(4)	69(5)	-6(4)	-21(4)	-30(4)

Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3)
for d20202a.

	x	y	z	U(eq)
H(2)	8461	4916	4565	37
H(3)	10625	3140	4504	48
H(4)	11110	2050	2578	44
H(5)	9257	3144	1405	35
H(6)	12728	4816	3141	64
H(7)	13072	3699	1246	55
H(8)	11278	4774	102	55
H(9)	9726	6620	1294	68
H(10)	10650	6646	3185	75
H(11A)	5735	3482	1598	43
H(11B)	7072	3059	2152	43
H(11C)	7233	3517	810	43
H(13)	4831	5438	1192	29
H(15A)	3836	8536	1166	58
H(15B)	3066	7463	1356	58
H(15C)	4296	7503	234	58
H(18)	7652	8040	1512	46
H(19A)	7006	9512	-460	103
H(19B)	6442	8337	-30	103
H(19C)	8065	8231	-516	103
H(20A)	9396	9008	720	97
H(20B)	8575	9596	1945	97
H(20C)	8313	10273	740	97
H(21)	6257	11156	1675	44

H(22)	4145	12083	2880	45
H(23)	2653	10942	3891	42
H(25)	3186	7758	3811	42
H(26A)	3639	8553	5492	69
H(26B)	2195	8165	5788	69
H(26C)	2221	9546	5568	69
H(27A)	1444	9020	2910	77
H(27B)	958	9844	4028	77
H(27C)	798	8493	4165	77

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d20202a

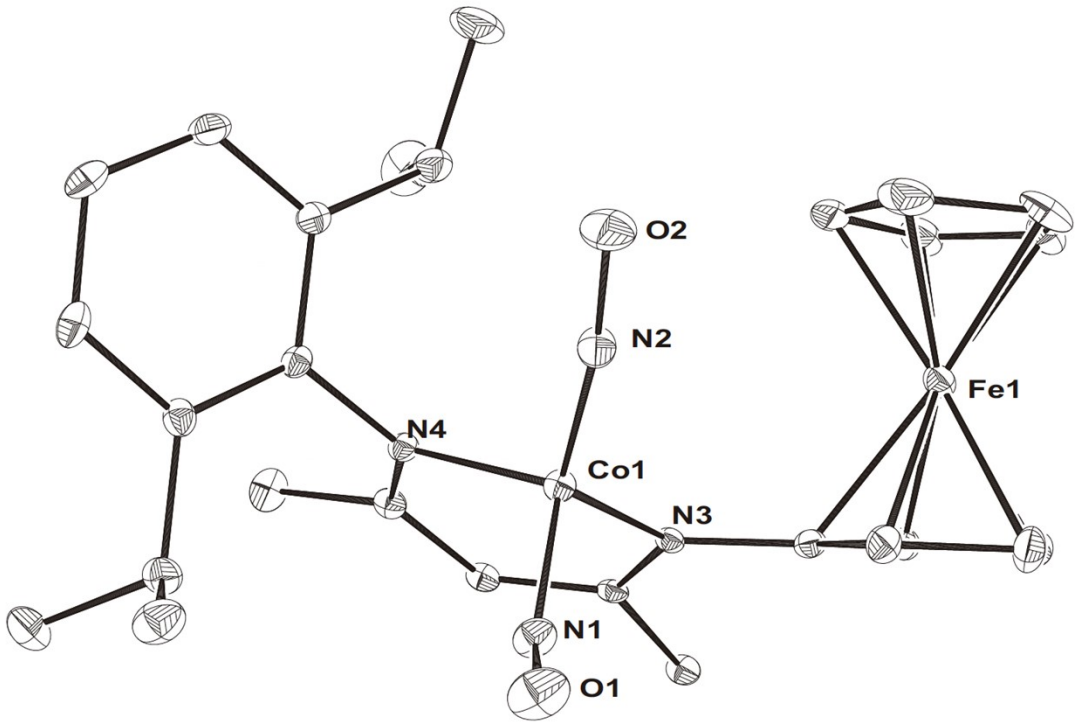


Table S2. Crystal data and structure refinement for $Co(ArLFc)_2$.

Identification code	mo_SYC_2_195_0m
Empirical formula	$C_{20}H_{30}CoFeN_4LiClBrO$
Formula weight	579.56
Temperature/K	193.15
Crystal system	triclinic
Space group	P-1
a/Å	10.5731(6)
b/Å	10.7617(6)
c/Å	23.8337(13)
α/°	87.5440(10)
β/°	82.4670(10)
γ/°	80.5960(10)
Volume/Å^3	2651.7(3)
Z	1
ρ_{calc}g/cm^3	0.363
μ/mm^{-1}	0.699
F(000)	294.0
Crystal size/mm^3	0.23 x 0.33 x 0.21 cm^3
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.936 to 55.014
Index ranges	$-13 \leq h \leq 13$, $-13 \leq k \leq 13$, $-30 \leq l \leq 30$
Reflections collected	40740
Independent reflections	12140 [R_{int} = 0.0187, R_{sigma} = 0.0209]
Data/restraints/parameters	12140/0/562
Goodness-of-fit on F^2	1.073
Final R indexes [I>=2σ (I)]	R_1 = 0.0837, wR_2 = 0.2764
Final R indexes [all data]	R_1 = 0.0902, wR_2 = 0.2834
Largest diff. peak/hole / e Å^{-3}	5.23/-0.66

Atom	***x***	***y***	***z***	**U(eq)**
Co1	6799.8(5)	2597.9(5)	2188.0(2)	14.83(17)
Fe1	3134.9(6)	5444.7(6)	3030.2(3)	25.25(19)
Fe2	8119.5(6)	3738.2(7)	3904.4(3)	25.6(2)
N1	7157(4)	713(3)	2248.8(15)	19.8(7)
N2	4999(3)	2813(3)	2611.1(15)	19.6(7)
N3	7006(3)	3417(3)	1421.4(14)	17.7(7)
N4	7900(3)	3620(3)	2548.8(15)	17.7(7)
C0AA	8380(6)	1820(5)	3868(2)	36.6(12)
C1	6481(5)	136(4)	2665.9(19)	23.9(9)
C2	4576(4)	1880(4)	2930.1(18)	21.3(8)

C3	5331(5)	681(4)	2981.6(19)	24.8(9)
C6	3251(5)	2038(5)	3277(2)	30.3(10)
C7	6958(6)	-1225(5)	2831(2)	38.4(13)
C8	4219(4)	3986(4)	2528.5(19)	23.4(9)
C9	4743(5)	5135(5)	2436(2)	31.1(11)
C10	3777(5)	6084(5)	2247(2)	37.0(12)
C11	2650(5)	5545(5)	2230(2)	35.3(11)
C12	2899(5)	4268(5)	2407(2)	27.1(9)
C13	3659(6)	6167(6)	3733(3)	42.8(13)
C14	2704(6)	7028(5)	3506(3)	42.0(13)
C15	1588(5)	6443(6)	3509(3)	39.0(12)
C16	1866(5)	5206(5)	3741(2)	35.4(11)
C17	3156(6)	5027(5)	3878(2)	37.1(11)
C18	8136(4)	-131(4)	1902.3(18)	21.5(8)
C19	9425(5)	-367(4)	2019(2)	25.7(9)
C20	10286(5)	-1318(5)	1728(2)	30.9(10)
C21	9904(5)	-2008(4)	1319(2)	32.9(11)
C22	8651(6)	-1693(4)	1179(2)	33.2(11)
C23	7747(5)	-760(4)	1457(2)	25.8(9)
C24	9912(5)	372(5)	2451(2)	29.1(10)
C25	10853(6)	1187(6)	2154(3)	43.8(13)
C26	10560(8)	-479(7)	2896(3)	53.8(17)
C27	6395(5)	-453(5)	1287(2)	32.6(11)
C28	5433(6)	-1214(6)	1635(3)	44.6(14)
C29	6378(7)	-654(6)	663(3)	46.4(14)
C30	8216(4)	4684(4)	2304.3(18)	18.9(8)
C31	7285(4)	4586(4)	1378.7(18)	20.3(8)
C32	7813(4)	5164(4)	1788.9(18)	20.8(8)
C33	7012(6)	5401(5)	859(2)	31.4(10)
C34	9018(5)	5485(5)	2575(2)	29.5(10)
C35	8338(4)	3133(4)	3065.2(18)	22.4(8)
C36	9563(5)	3074(5)	3271(2)	27.9(10)
C37	9585(6)	2257(5)	3762(2)	36.2(12)
C39	7597(5)	2373(5)	3446(2)	28.6(10)
C40	7323(7)	4121(7)	4721(2)	46.6(14)
C41	8486(7)	4612(7)	4596(3)	51.8(17)
C42	8343(6)	5495(6)	4134(3)	47.7(16)
C43	7115(6)	5534(6)	3975(3)	42.9(13)
C44	6465(6)	4676(6)	4340(3)	44.7(14)
C45	6872(4)	2883(4)	892.5(17)	20.5(8)
C46	5655(5)	2907(5)	708.5(19)	26.0(9)
C47	5624(6)	2477(5)	163(2)	34.8(11)

C48	6736(6)	2039(5)	-188(2)	38.5(13)
C49	7925(6)	1984(5)	8(2)	32.2(11)
C50	8023(5)	2394(4)	547.0(18)	23.8(9)
C51	9357(5)	2354(5)	732(2)	28.9(10)
C52	10236(5)	1115(5)	594(2)	36.1(11)
C53	10025(6)	3440(6)	469(4)	52.2(17)
C54	4410(5)	3417(5)	1065(2)	29.3(10)
C55	3621(6)	2359(6)	1255(3)	44.9(14)
C56	3572(6)	4475(7)	758(3)	50.5(15)

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Co1	16.3(3)	14.7(3)	13.9(3)	0.53(19)	-1.50(19)	-4.1(2)
Fe1	17.7(3)	24.3(3)	31.7(4)	0.7(3)	-0.2(3)	0.2(2)
Fe2	24.8(4)	32.6(4)	20.7(3)	-5.0(3)	-6.1(2)	-4.8(3)
N1	24.1(18)	14.8(15)	19.7(17)	0.4(13)	0.9(14)	-3.6(13)
N2	16.2(16)	22.2(17)	19.8(17)	2.1(13)	-0.1(13)	-3.9(13)
N3	21.2(17)	18.6(16)	14.2(15)	1.4(12)	-3.1(12)	-6.1(13)
N4	19.2(16)	18.7(16)	16.4(16)	-0.5(13)	-4.8(13)	-4.0(13)
C0AA	56(3)	30(2)	26(2)	4.9(19)	-15(2)	-6(2)
C1	31(2)	16.5(19)	24(2)	3.4(16)	-0.5(17)	-4.8(16)
C2	21(2)	25(2)	19.1(19)	0.5(16)	-1.7(15)	-6.7(16)
C3	30(2)	22(2)	22(2)	5.3(16)	2.0(17)	-7.5(17)
C6	25(2)	33(2)	30(2)	4.4(19)	5.9(18)	-6.6(19)
C7	44(3)	23(2)	41(3)	13(2)	11(2)	3(2)
C8	20(2)	25(2)	23(2)	0.7(16)	3.2(16)	-3.4(16)
C9	21(2)	26(2)	43(3)	5(2)	6.7(19)	-1.8(18)
C10	30(3)	31(3)	43(3)	12(2)	8(2)	3(2)
C11	30(3)	39(3)	32(3)	9(2)	-1(2)	5(2)
C12	22(2)	33(2)	24(2)	3.5(18)	-1.9(17)	-2.8(18)
C13	42(3)	41(3)	49(3)	-7(3)	-17(3)	-8(2)
C14	40(3)	29(3)	55(4)	-9(2)	-3(3)	0(2)
C15	23(2)	42(3)	45(3)	-9(2)	5(2)	7(2)
C16	34(3)	38(3)	32(3)	-7(2)	6(2)	-5(2)
C17	41(3)	38(3)	31(3)	-1(2)	-7(2)	-3(2)
C18	28(2)	13.4(18)	22(2)	1.5(15)	2.2(16)	-4.7(15)
C19	31(2)	19(2)	25(2)	0.7(16)	0.7(18)	-2.2(17)
C20	28(2)	24(2)	37(3)	0.1(19)	5.1(19)	0.7(18)
C21	42(3)	19(2)	33(3)	-1.7(18)	10(2)	-0.3(19)
C22	50(3)	21(2)	28(2)	-4.6(18)	9(2)	-16(2)
C23	35(2)	17.7(19)	26(2)	0.0(16)	2.4(18)	-12.8(17)
C24	27(2)	28(2)	31(2)	-4.1(18)	-6.2(18)	3.1(18)

C25	42(3)	52(3)	43(3)	-8(3)	-7(2)	-18(3)
C26	69(5)	46(4)	43(3)	3(3)	-21(3)	12(3)
C27	41(3)	25(2)	35(3)	-1.8(19)	-8(2)	-13(2)
C28	45(3)	47(3)	47(3)	-3(3)	-3(3)	-25(3)
C29	65(4)	42(3)	40(3)	0(2)	-15(3)	-24(3)
C30	17.0(18)	18.3(18)	21.4(19)	-3.8(15)	-1.9(15)	-2.8(14)
C31	25(2)	18.8(19)	17.4(18)	2.0(15)	-1.4(15)	-6.2(15)
C32	24(2)	18.4(19)	21(2)	1.0(15)	-2.5(16)	-8.4(15)
C33	50(3)	23(2)	25(2)	7.9(18)	-14(2)	-13(2)
C34	31(2)	28(2)	34(2)	-2.9(19)	-9.2(19)	-14.3(19)
C35	27(2)	22(2)	19(2)	-3.1(16)	-7.3(16)	-2.2(16)
C36	25(2)	35(2)	23(2)	-6.9(18)	-5.9(17)	1.0(18)
C37	41(3)	40(3)	27(2)	-3(2)	-16(2)	7(2)
C39	40(3)	27(2)	22(2)	1.9(17)	-11.3(19)	-11.0(19)
C40	53(4)	58(4)	26(3)	-11(2)	5(2)	-7(3)
C41	52(4)	71(4)	35(3)	-28(3)	-9(3)	-9(3)
C42	41(3)	51(3)	52(4)	-31(3)	9(3)	-13(3)
C43	35(3)	37(3)	53(3)	-9(3)	7(2)	-1(2)
C44	31(3)	49(3)	50(3)	-6(3)	9(2)	-4(2)
C45	31(2)	19.5(19)	13.6(18)	3.7(14)	-4.6(15)	-10.7(16)
C46	31(2)	30(2)	20(2)	3.6(17)	-7.3(17)	-11.5(18)
C47	44(3)	43(3)	24(2)	-1(2)	-14(2)	-18(2)
C48	61(4)	41(3)	18(2)	-5(2)	-5(2)	-20(3)
C49	45(3)	33(2)	20(2)	-4.0(18)	1.6(19)	-12(2)
C50	32(2)	22(2)	19(2)	0.0(16)	-0.1(17)	-10.2(17)
C51	29(2)	32(2)	25(2)	-7.7(18)	1.7(18)	-8.0(19)
C52	35(3)	36(3)	35(3)	0(2)	4(2)	-4(2)
C53	37(3)	35(3)	86(5)	-7(3)	2(3)	-16(2)
C54	29(2)	38(3)	25(2)	2.8(19)	-10.0(18)	-11(2)
C55	38(3)	54(4)	46(3)	6(3)	-2(2)	-21(3)
C56	40(3)	63(4)	48(4)	11(3)	-13(3)	-4(3)

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Co1	N1	2.004(4)	C11	C12	1.413(7)
Co1	N2	2.017(4)	C13	C14	1.402(9)
Co1	N3	1.996(3)	C13	C17	1.426(9)
Co1	N4	2.016(3)	C14	C15	1.425(9)
Fe1	C8	2.103(4)	C15	C16	1.419(8)
Fe1	C9	2.057(5)	C16	C17	1.425(8)
Fe1	C10	2.032(5)	C18	C19	1.407(7)
Fe1	C11	2.033(6)	C18	C23	1.423(6)

Fe1	C12	2.058(5)	C19	C20	1.395(6)
Fe1	C13	2.052(6)	C19	C24	1.518(7)
Fe1	C14	2.043(6)	C20	C21	1.389(8)
Fe1	C15	2.043(5)	C21	C22	1.393(8)
Fe1	C16	2.054(5)	C22	C23	1.391(7)
Fe1	C17	2.054(6)	C23	C27	1.517(7)
Fe2	C0AA	2.042(5)	C24	C25	1.520(8)
Fe2	C35	2.102(4)	C24	C26	1.527(7)
Fe2	C36	2.061(5)	C27	C28	1.545(7)
Fe2	C37	2.040(5)	C27	C29	1.515(8)
Fe2	C39	2.055(5)	C30	C32	1.403(6)
Fe2	C40	2.048(6)	C30	C34	1.518(6)
Fe2	C41	2.042(6)	C31	C32	1.401(6)
Fe2	C42	2.049(6)	C31	C33	1.519(6)
Fe2	C43	2.050(6)	C35	C36	1.436(6)
Fe2	C44	2.048(6)	C35	C39	1.437(7)
N1	C1	1.338(6)	C36	C37	1.434(7)
N1	C18	1.453(5)	C40	C41	1.409(10)
N2	C2	1.334(5)	C40	C44	1.413(10)
N2	C8	1.412(6)	C41	C42	1.430(11)
N3	C31	1.335(5)	C42	C43	1.393(9)
N3	C45	1.441(5)	C43	C44	1.436(9)
N4	C30	1.335(5)	C45	C46	1.408(6)
N4	C35	1.421(5)	C45	C50	1.415(6)
C0AA	C37	1.418(9)	C46	C47	1.405(6)
C0AA	C39	1.435(7)	C46	C54	1.505(7)
C1	C3	1.398(6)	C47	C48	1.378(9)
C1	C7	1.522(6)	C48	C49	1.390(8)
C2	C3	1.412(6)	C49	C50	1.398(6)
C2	C6	1.519(6)	C50	C51	1.526(7)
C8	C9	1.433(6)	C51	C52	1.517(7)
C8	C12	1.443(6)	C51	C53	1.533(8)
C9	C10	1.425(7)	C54	C55	1.538(7)
C10	C11	1.414(8)	C54	C56	1.544(8)

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
N1	Co1	N2	96.69(15)	N1	C1	C7	120.0(4)
N1	Co1	N4	119.47(15)	C3	C1	C7	114.7(4)
N3	Co1	N1	118.53(15)	N2	C2	C3	122.8(4)
N3	Co1	N2	116.79(15)	N2	C2	C6	122.4(4)
N3	Co1	N4	96.41(14)	C3	C2	C6	114.8(4)

N4	Co1	N2	110.07(15)	C1	C3	C2	130.5(4)
C9	Fe1	C8	40.30(18)	N2	C8	Fe1	137.7(3)
C9	Fe1	C12	68.1(2)	N2	C8	C9	122.3(4)
C10	Fe1	C8	68.17(19)	N2	C8	C12	130.1(4)
C10	Fe1	C9	40.8(2)	C9	C8	Fe1	68.1(3)
C10	Fe1	C11	40.7(2)	C9	C8	C12	106.5(4)
C10	Fe1	C12	68.2(2)	C12	C8	Fe1	68.1(3)
C10	Fe1	C13	119.7(3)	C8	C9	Fe1	71.6(3)
C10	Fe1	C14	104.1(3)	C10	C9	Fe1	68.7(3)
C10	Fe1	C15	120.7(2)	C10	C9	C8	108.4(5)
C10	Fe1	C16	158.4(2)	C9	C10	Fe1	70.5(3)
C10	Fe1	C17	157.1(2)	C11	C10	Fe1	69.7(3)
C11	Fe1	C8	68.1(2)	C11	C10	C9	108.1(5)
C11	Fe1	C9	68.4(2)	C10	C11	Fe1	69.6(3)
C11	Fe1	C12	40.4(2)	C12	C11	Fe1	70.8(3)
C11	Fe1	C13	154.2(2)	C12	C11	C10	108.5(4)
C11	Fe1	C14	118.7(2)	C8	C12	Fe1	71.4(3)
C11	Fe1	C15	105.3(2)	C11	C12	Fe1	68.8(3)
C11	Fe1	C16	123.8(2)	C11	C12	C8	108.4(4)
C11	Fe1	C17	162.1(2)	C14	C13	Fe1	69.6(3)
C12	Fe1	C8	40.57(18)	C14	C13	C17	108.4(5)
C13	Fe1	C8	126.6(2)	C17	C13	Fe1	69.7(3)
C13	Fe1	C9	108.0(3)	C13	C14	Fe1	70.3(3)
C13	Fe1	C12	164.0(2)	C13	C14	C15	108.3(5)
C13	Fe1	C16	68.2(2)	C15	C14	Fe1	69.6(3)
C13	Fe1	C17	40.6(2)	C14	C15	Fe1	69.6(3)
C14	Fe1	C8	160.1(2)	C16	C15	Fe1	70.1(3)
C14	Fe1	C9	122.1(2)	C16	C15	C14	107.9(5)
C14	Fe1	C12	155.4(2)	C15	C16	Fe1	69.3(3)
C14	Fe1	C13	40.0(2)	C15	C16	C17	107.8(5)
C14	Fe1	C16	68.3(2)	C17	C16	Fe1	69.7(3)
C14	Fe1	C17	68.1(2)	C13	C17	Fe1	69.6(3)
C15	Fe1	C8	158.9(2)	C16	C17	Fe1	69.7(3)
C15	Fe1	C9	157.8(2)	C16	C17	C13	107.6(5)
C15	Fe1	C12	121.6(2)	C19	C18	N1	121.1(4)
C15	Fe1	C13	68.0(3)	C19	C18	C23	120.6(4)
C15	Fe1	C14	40.8(2)	C23	C18	N1	118.3(4)
C15	Fe1	C16	40.5(2)	C18	C19	C24	122.3(4)
C15	Fe1	C17	68.3(2)	C20	C19	C18	118.9(4)
C16	Fe1	C8	125.4(2)	C20	C19	C24	118.8(5)
C16	Fe1	C9	160.2(2)	C21	C20	C19	121.4(5)
C16	Fe1	C12	109.9(2)	C20	C21	C22	118.7(4)

C16	Fe1	C17	40.6(2)	C23	C22	C21	122.4(5)
C17	Fe1	C8	111.6(2)	C18	C23	C27	122.1(4)
C17	Fe1	C9	123.9(2)	C22	C23	C18	117.6(5)
C17	Fe1	C12	127.6(2)	C22	C23	C27	120.2(4)
C0AA	Fe2	C35	68.39(19)	C19	C24	C25	109.8(4)
C0AA	Fe2	C36	68.5(2)	C19	C24	C26	112.5(5)
C0AA	Fe2	C39	41.0(2)	C25	C24	C26	109.7(5)
C0AA	Fe2	C40	104.5(3)	C23	C27	C28	112.8(5)
C0AA	Fe2	C41	121.2(3)	C29	C27	C23	112.2(5)
C0AA	Fe2	C42	159.5(3)	C29	C27	C28	108.9(5)
C0AA	Fe2	C43	157.1(3)	N4	C30	C32	122.9(4)
C0AA	Fe2	C44	119.5(3)	N4	C30	C34	122.0(4)
C36	Fe2	C35	40.32(18)	C32	C30	C34	115.0(4)
C37	Fe2	C0AA	40.6(2)	N3	C31	C32	125.0(4)
C37	Fe2	C35	68.40(18)	N3	C31	C33	120.0(4)
C37	Fe2	C36	40.9(2)	C32	C31	C33	115.0(4)
C37	Fe2	C39	68.6(2)	C31	C32	C30	130.2(4)
C37	Fe2	C40	118.7(3)	N4	C35	Fe2	136.2(3)
C37	Fe2	C41	105.7(3)	N4	C35	C36	131.3(4)
C37	Fe2	C42	124.7(3)	N4	C35	C39	121.0(4)
C37	Fe2	C43	162.0(3)	C36	C35	Fe2	68.3(2)
C37	Fe2	C44	154.1(3)	C36	C35	C39	106.9(4)
C39	Fe2	C35	40.42(18)	C39	C35	Fe2	68.0(3)
C39	Fe2	C36	68.2(2)	C35	C36	Fe2	71.4(3)
C40	Fe2	C35	160.6(2)	C37	C36	Fe2	68.7(3)
C40	Fe2	C36	155.7(2)	C37	C36	C35	108.5(5)
C40	Fe2	C39	122.6(2)	C0AA	C37	Fe2	69.8(3)
C40	Fe2	C42	68.1(3)	C0AA	C37	C36	108.1(4)
C40	Fe2	C43	68.2(3)	C36	C37	Fe2	70.4(3)
C40	Fe2	C44	40.4(3)	C0AA	C39	Fe2	69.0(3)
C41	Fe2	C35	158.8(3)	C0AA	C39	C35	108.4(5)
C41	Fe2	C36	122.1(2)	C35	C39	Fe2	71.6(3)
C41	Fe2	C39	158.3(3)	C41	C40	Fe2	69.7(3)
C41	Fe2	C40	40.3(3)	C41	C40	C44	108.3(6)
C41	Fe2	C42	40.9(3)	C44	C40	Fe2	69.8(3)
C41	Fe2	C43	68.0(3)	C40	C41	Fe2	70.1(3)
C41	Fe2	C44	68.0(3)	C40	C41	C42	107.7(6)
C42	Fe2	C35	124.6(2)	C42	C41	Fe2	69.8(3)
C42	Fe2	C36	110.1(2)	C41	C42	Fe2	69.3(4)
C42	Fe2	C39	159.0(3)	C43	C42	Fe2	70.1(3)
C42	Fe2	C43	39.7(3)	C43	C42	C41	108.4(6)
C43	Fe2	C35	111.0(2)	C42	C43	Fe2	70.1(4)

C43	Fe2	C36	126.9(2)	C42	C43	C44	108.0(6)
C43	Fe2	C39	123.4(2)	C44	C43	Fe2	69.4(3)
C44	Fe2	C35	126.1(2)	C40	C44	Fe2	69.8(3)
C44	Fe2	C36	163.4(2)	C40	C44	C43	107.5(6)
C44	Fe2	C39	107.4(2)	C43	C44	Fe2	69.6(3)
C44	Fe2	C42	68.0(3)	C46	C45	N3	121.8(4)
C44	Fe2	C43	41.0(2)	C46	C45	C50	121.0(4)
C1	N1	Co1	118.5(3)	C50	C45	N3	117.1(4)
C1	N1	C18	114.3(3)	C45	C46	C54	122.5(4)
C18	N1	Co1	127.2(3)	C47	C46	C45	117.9(5)
C2	N2	Co1	121.3(3)	C47	C46	C54	119.6(4)
C2	N2	C8	123.0(4)	C48	C47	C46	122.1(5)
C8	N2	Co1	115.7(3)	C47	C48	C49	119.1(5)
C31	N3	Co1	118.5(3)	C48	C49	C50	121.6(5)
C31	N3	C45	114.8(3)	C45	C50	C51	122.4(4)
C45	N3	Co1	126.7(3)	C49	C50	C45	118.3(4)
C30	N4	Co1	121.1(3)	C49	C50	C51	119.3(4)
C30	N4	C35	122.3(4)	C50	C51	C53	112.1(5)
C35	N4	Co1	116.6(3)	C52	C51	C50	112.3(4)
C37	C0AA	Fe2	69.6(3)	C52	C51	C53	109.0(4)
C37	C0AA	C39	108.0(5)	C46	C54	C55	110.9(5)
C39	C0AA	Fe2	70.0(3)	C46	C54	C56	112.7(4)
N1	C1	C3	125.4(4)	C55	C54	C56	109.5(5)

Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for mo_SYC_2_195_0m.

Atom	*x*	*y*	*z*	U(eq)
H0AA	8139.48	1270.38	4159.33	44
H3	5011.29	171.04	3273.09	30
H6A	2969.25	2910.8	3362.29	45
H6B	3298.69	1552.81	3623.63	45
H6C	2647.17	1749.08	3065.46	45
H7A	7147.99	-1727.9	2498.39	58
H7B	6301.51	-1540.22	3088.89	58
H7C	7726.19	-1266.16	3010.55	58
H9	5572.76	5243.69	2491.14	37
H10	3871.78	6913.38	2150.82	44
H11	1875.11	5960.93	2121.01	42
H12	2312.51	3704.15	2439.09	32
H13	4480.51	6313.8	3780.7	51
H14	2784.94	7842	3376.31	50
H15	814.14	6806.57	3382.12	47

H16	1305.35	4617.19	3794.23	42
H17	3591.68	4300.01	4034.17	45
H20	11133.61	-1493.54	1810.07	37
H21	10473.95	-2667.03	1141.21	40
H22	8409.98	-2121.07	889.85	40
H24	9170.7	927.61	2645.3	35
H25A	11618.39	658.16	1987.13	66
H25B	11077.93	1725.83	2422.92	66
H25C	10456.28	1692.83	1862.74	66
H26A	9928.14	-897.43	3121.56	81
H26B	10931.39	21.27	3134.55	81
H26C	11226.42	-1094.51	2710.9	81
H27	6082.96	441.7	1358.59	39
H28A	5734.83	-2098.61	1586.25	67
H28B	4599.28	-997.5	1506.37	67
H28C	5365.59	-1019.72	2027.95	67
H29A	7067.63	-298.64	445.6	70
H29B	5565.8	-251.63	552.16	70
H29C	6488.31	-1540.7	594.4	70
H32	7911.86	5997.81	1706.37	25
H33A	7311.77	4917.91	524.37	47
H33B	7452.76	6115.9	848.03	47
H33C	6098.96	5685.36	875.21	47
H34A	8747.84	5516.79	2975.34	44
H34B	8898.93	6322.06	2413.79	44
H34C	9914.45	5120.8	2506.88	44
H36	10230.31	3494.96	3113.15	34
H37	10270.77	2049.1	3974.64	43
H39	6752.25	2259	3422.06	34
H40	7148.67	3531.72	5005.8	56
H41	9216.3	4400.12	4780.74	62
H42	8964.4	5963.59	3967.99	57
H43	6776	6029.1	3684.24	52
H44	5631.22	4514.96	4327.34	54
H47	4828.76	2489.29	34.51	42
H48	6690.68	1782.82	-552.12	46
H49	8674.75	1666.03	-224.92	39
H51	9242.42	2440.41	1144.38	35
H52A	9832.58	431.87	765.93	54
H52B	11043.69	1111.15	737.48	54
H52C	10387.59	1019.28	191.03	54
H53A	10034.18	3451.68	65.59	78

H53B	10896.1	3324.25	558.85	78
H53C	9562.81	4223.61	617.89	78
H54	4628.08	3772.19	1404.75	35
H55A	3541.37	1885.73	932.8	67
H55B	2776.71	2719.45	1428.46	67
H55C	4052.28	1810.44	1523.77	67
H56A	4071.23	5126.35	631.95	76
H56B	2831.28	4819.99	1013.56	76
H56C	3292.29	4136.15	437.58	76

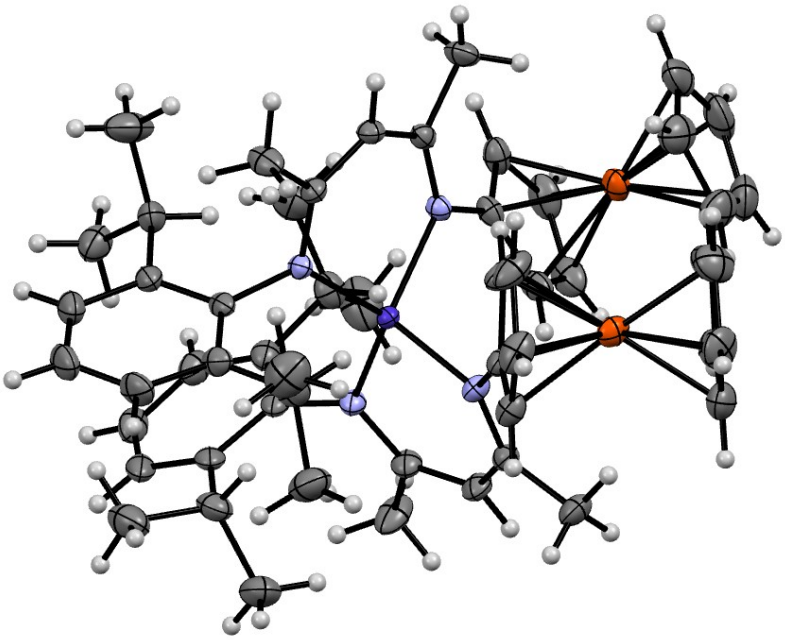


Fig. S1 GC of the resulting solution of Cys-S-S-Cys with ferreocene.

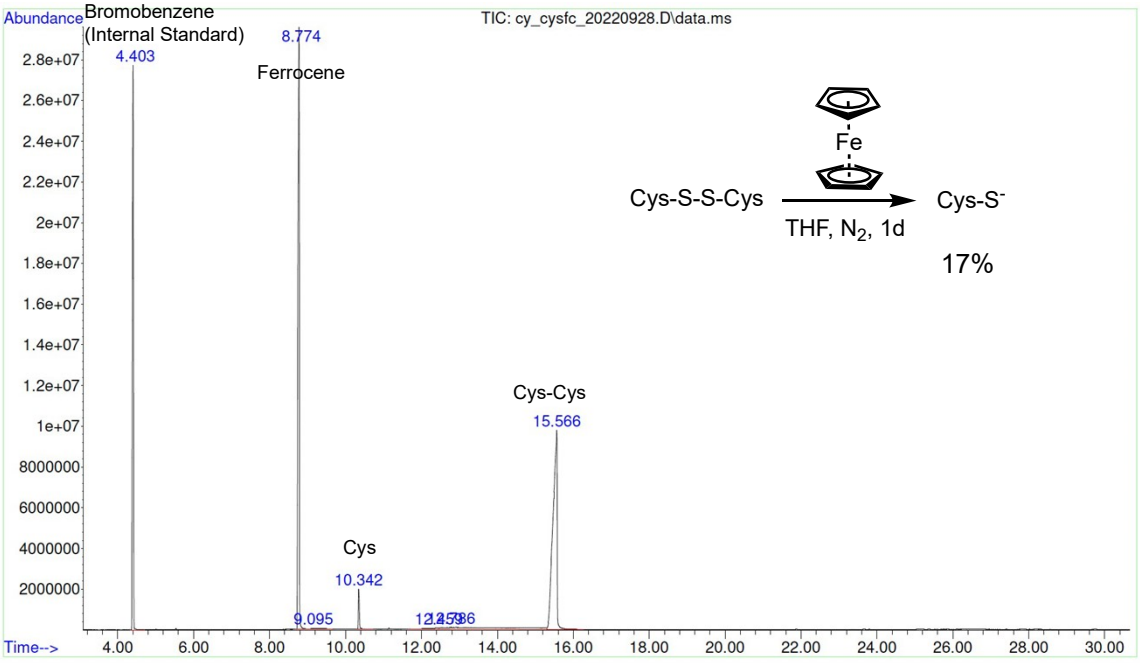


Fig. S2 CV of $Co(ArLFc)(NO)_2$ (**1**) with scan rate at 50 mV

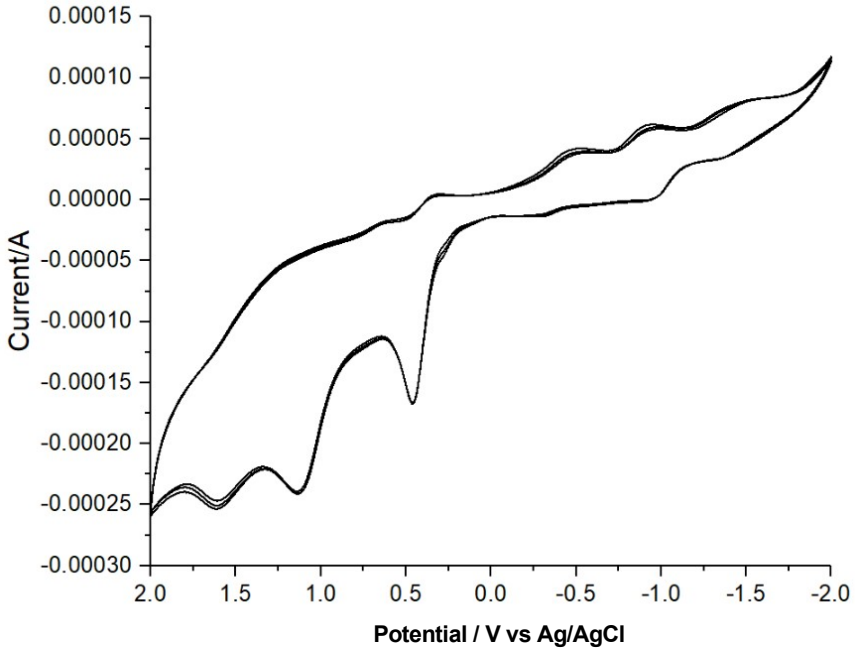


Fig. S3 The time-course analysis of *v*NO(ArLFcCo(NO)$_2$) in the reaction of ArLFcCo(NO)$_2$ with BocNH-Cys-COOMe

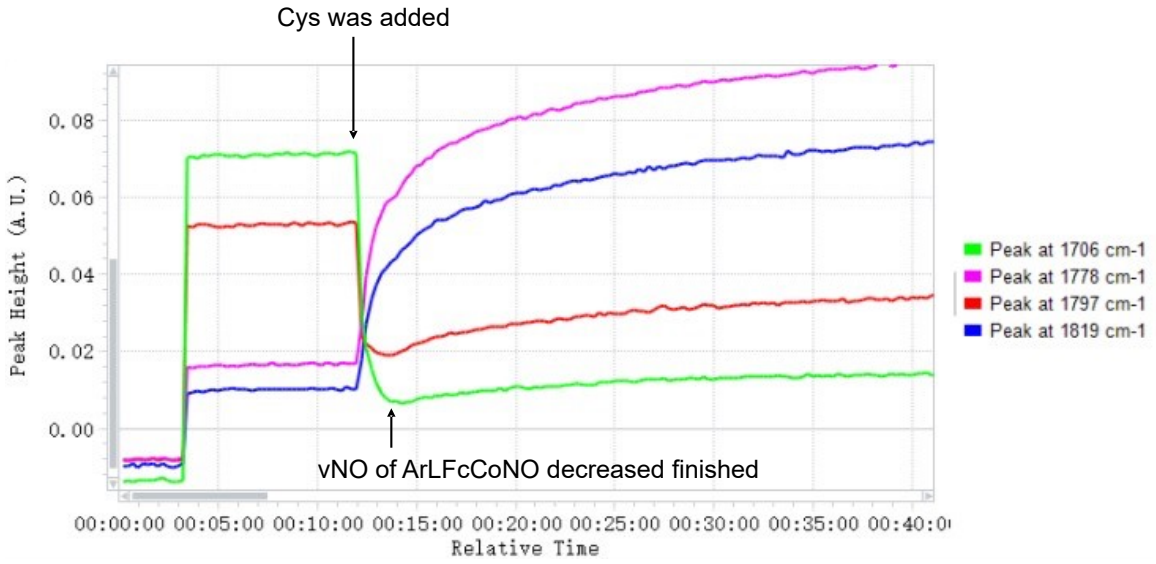
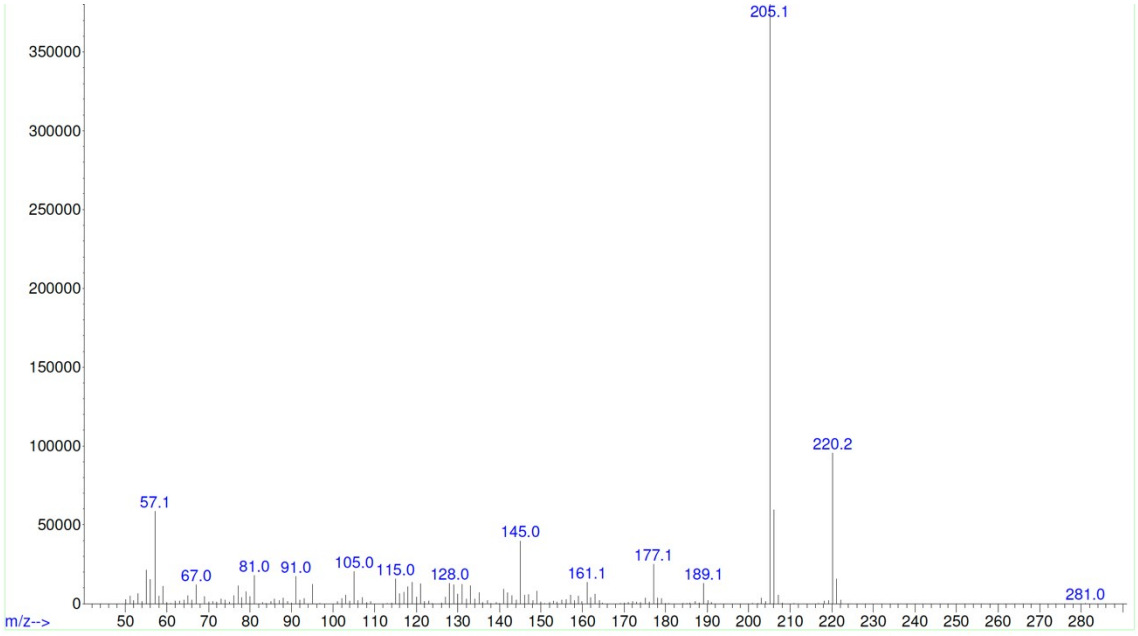


Fig. S4 EI-MS of (a) BocNH-Cys-COOMe and (b) BocNH-CysNO-COOMe

(a)



(b)

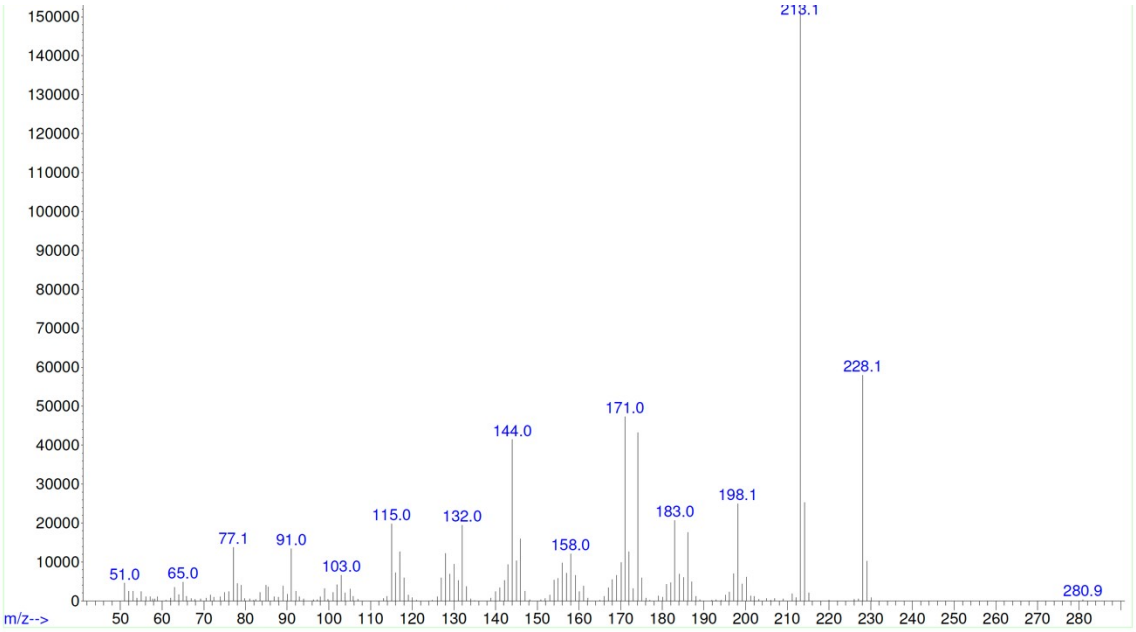


Fig. S5 ESI-MS of (a) BocNH-Cys-COOMe and (b) BocNH-CysNO-COOMe

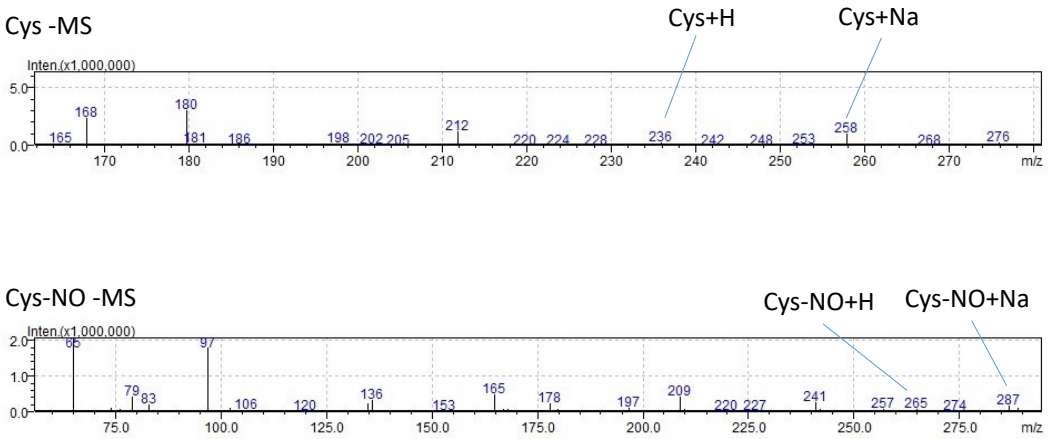


Fig. S6 EPR spectrum of complex 1

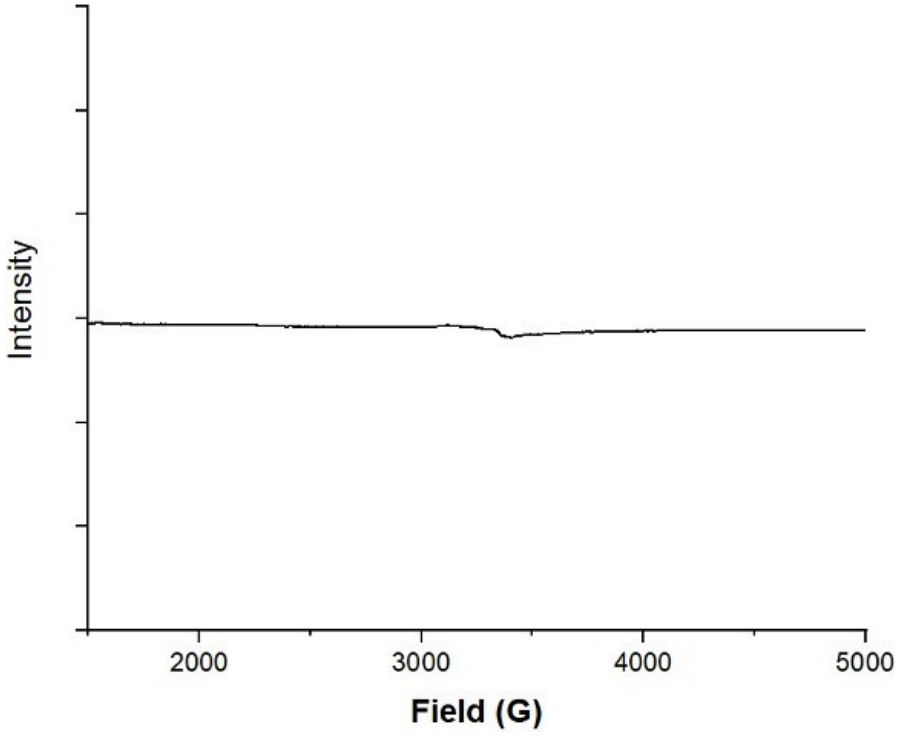


Fig. S7 ^{1}H NMR of the formation of BocNH-CysNO-COOMe

Cys-NO at δ 7.45 (s, 1H), 4.68 (m, 1H), 4.48-4.43 (m, 2H), and 3.80 (s, 3H)

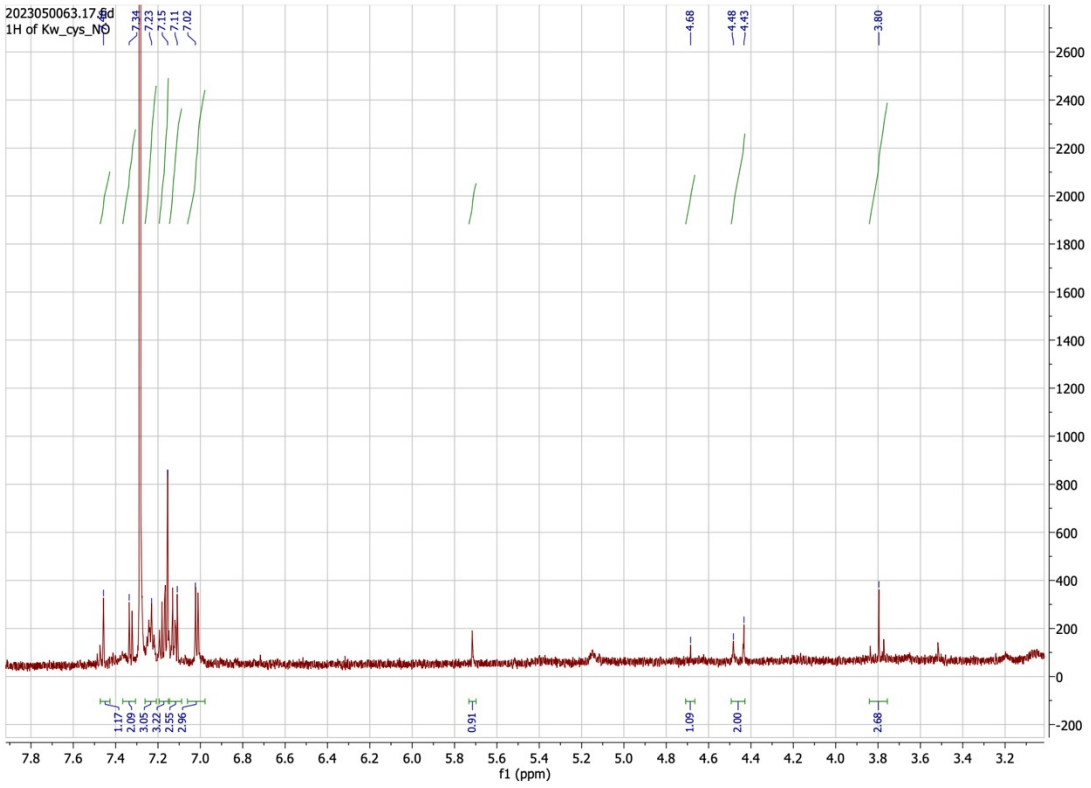


Fig. S8 ^{31}P NMR of the formation of $HNPPh_3$