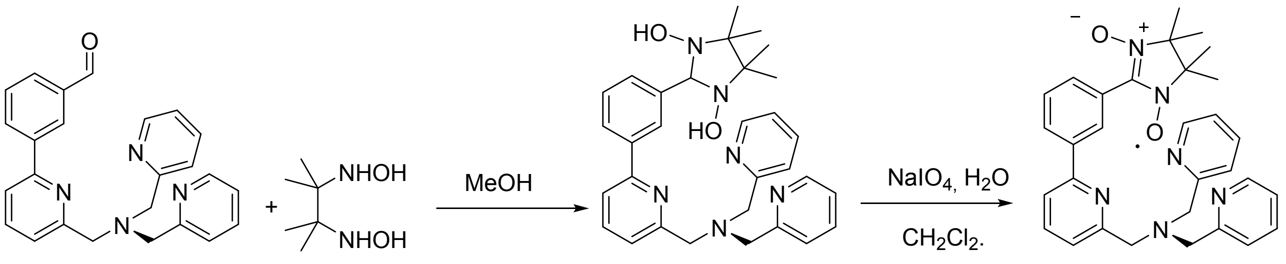
SUPPORTING INFO

1. Experimental Section

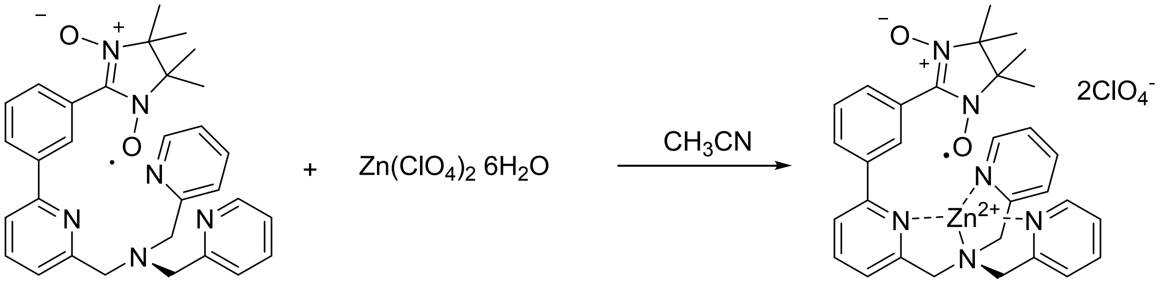
General remarks. Chemicals were purchased from Aldrich and TCI chemicals and used without further purification. ESI-MS experiments were carried out in positive or negative mode with an Agilent Technologies LC/MSD Trap SL AGILENT instrument (mobile phase methanol or acetonitrile). MS peaks are reported as monoisotopic mass. IR spectra were recorded with a Perkin–Elmer FTIR 1650. EPR spectra were obtained with an X-Band Bruker ELEXSYS E500 spectrometer equipped with a TE102 microwave cavity, a Bruker variable temperature unit, a field frequency lock system Bruker ER 033 M and equipped with a NMR Gaussmeter Bruker ER 035 M. The modulation amplitude was kept well below the line width, and the microwave power was well below saturation. All preparations with radicals were performed in dark conditions under inert atmosphere with Schlenk type glassware. Anhydrous solvents were used thoroughly.



1a

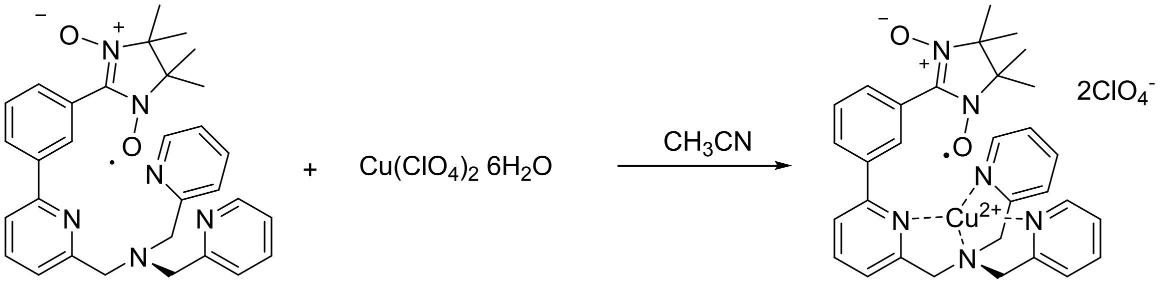
2a

Synthesis of ligand 2a. Ligand **1a** (71 mg, 0.2 mmol) and bis(hydroxylamine) (87 mg, 0.5 mmol) were dissolved in MeOH (2 mL). The mixture was stirred overnight at room temperature. The solvent was evaporated and the residual was dissolved in 40 mL of CH_2Cl_2. The mixture was cooled at 0°C and 51.3 mg of $NaIO_4$ (0.24 mmol) in 2 mL of distilled water were added. The solution was let stirring during 2h, the organic phase was separated, dried with Mg_2SO_4 and filtered. The solvent was evaporated and the solid was crystallized in acetonitrile/diethyl ether to afford the nitronyl nitroxide derivative **2a** (50% yield) as a blue solid. MS (ESI) calcd for $C_{31}H_{33}N_6O_2$ $(M+H)^+$ 522.3, found 522.3. IR (KBr) ν (cm^{-1}): 620,667, 750, 797, 995, 1046, 1087, 1152, 1208, 1362, 1433, 1451, 1473, 1569, 1684, 1755, 2294, 2978, 3060. Anal. Calcd. ($C_{31}H_{33}N_6O_2$): C, 71.38; H, 6.38; N, 16.11. Found: C, 71.44; H, 6.35; N, 16.10.



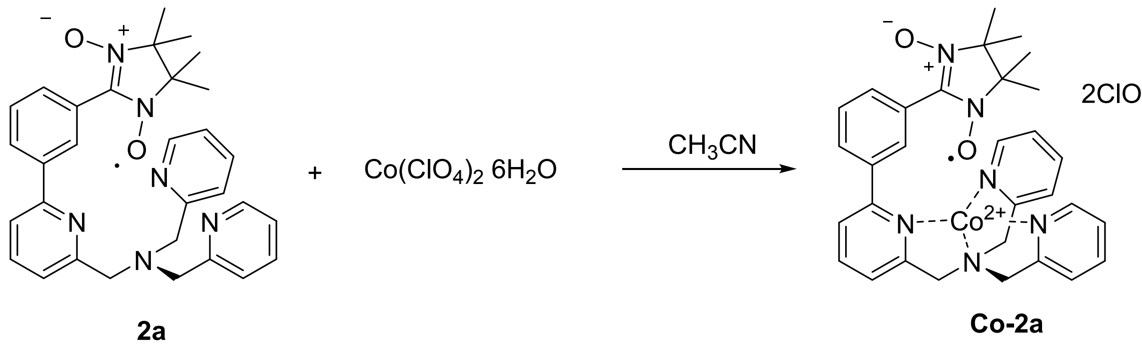
2a **Zn-2a**

Synthesis of compound Zn-2a. Compound **2a** (41 mg, 0.08 mmol) and $Zn(ClO_4)_2$ $6H_2O$ (29 mg, 0.08 mmol) were dissolved in 2 mL of CH_3CN. The mixture was let stirring during 1 hour at room temperature, then diethyl ether was added to the solution until the formation of a blue precipitate. The mixture was stirred for 10 min and filtered. The solid was washed with CH_3CN − diethyl ether (1:10) several times and dried to afford zinc(II) complex **Zn-2a** (90 mg, 85%) as a blue solid. MS (ESI) calcd for $C_{31}H_{33}N_6O_2Zn$ $(M\text{-}2ClO_4+Cl)^+$ 620.2, found 620.2. IR (KBr) ν (cm^{-1}): 696, 770, 1090, 1317, 1358, 1442, 1487, 1575, 1612. Anal. Calcd. ($C_{31}H_{33}Cl_2N_6O_{10}Zn$): C, 47,38 H, 4.23; N, 10.69. Found: C, 47.53; H, 4.44; N, 10.72.

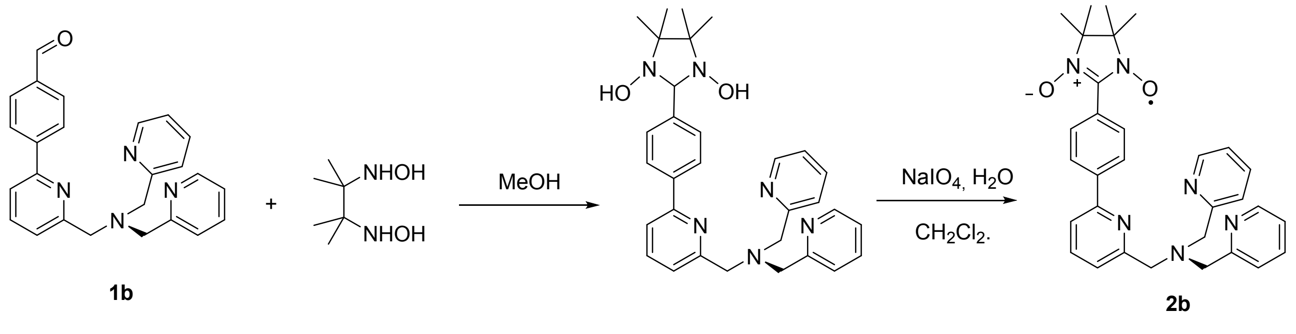


2a **Cu-2a**

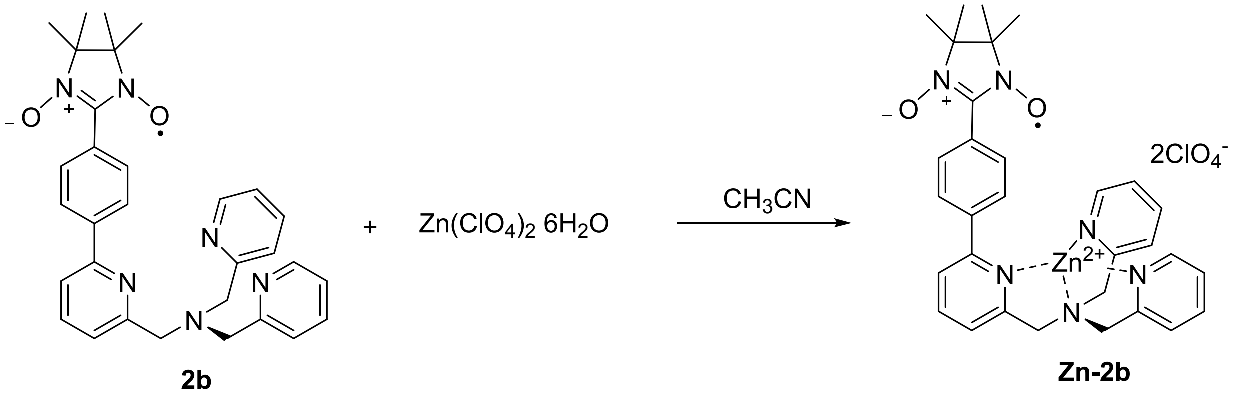
Synthesis of compound Cu-2a. Compound **2a** (71 mg, 0.14 mmol) and $Cu(ClO_4)_2$ $6H_2O$ (50 mg, 0.14 mmol) were dissolved in 2 mL of CH_3CN. The mixture was let stirring during 30 minutes at room temperature, then diethyl ether was added to the solution until the formation of a red precipitate. The mixture was stirred for 10 min and filtered. The solid was washed with CH_3CN − diethyl ether (1:10) several times and dried to afford 90 mg of copper(II) complex **Cu-2a** (86%) as a red solid. MS (ESI) calcd for $C_{31}H_{33}N_6O_2Cu$ $(M+Cl)^+$ 619.2, found 619.2; for $(M+HCOO)^+$ 629.2, found, 629.2; for $(M+ClO_4)^+$ 683.1, found, 683.2. IR (KBr) ν (cm^{-1}): 698, 768, 1123, 1358, 1448, 1569, 1612, 1652. Anal. Calcd. ($C_{31}H_{33}Cl_2N_6O_{10}Cu$): C, 47,49 H, 4.24; N, 10.72. Found: C, 47.55; H, 4.14; N, 10.78.



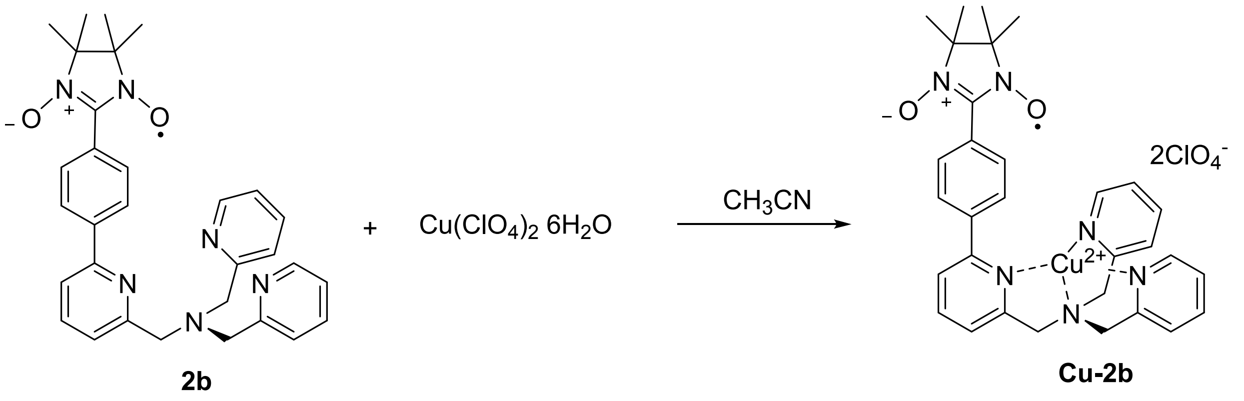
Synthesis of compound Co-2a. Compound **2a** (45 mg, 0.09 mmol) and $Co(ClO_4)_2$ $6H_2O$ (32 mg, 0.09 mmol) were dissolved in 2 mL of CH_3CN. The mixture was let stirring during 1 hour at room temperature, then diethyl ether was added to the solution until the formation of a blue precipitate. The mixture was stirred for 10 min and filtered. The solid was washed with CH_3CN − diethyl ether (1:10) several times and dried to afford 59 mg of cobalt(II) complex **Co-2a** (87%) as a blue solid. MS (ESI) calcd for $C_{31}H_{33}N_6O_2Co$ $(M+Cl)^+$ 615.2, found 615.2; for $(M+HCOO)^+$ 625.2, found, 625.2; for $(M+ClO_4)^+$ 679.2, found, 679.2. IR (KBr) ν (cm^{-1}): 696, 769, 1097, 1214, 1313, 1359, 1485, 1572, 1610, 1612. Anal. Calcd. ($C_{31}H_{33}Cl_2N_6O_{10}Co$): C, 47.77 H, 4.27; N, 10.78. Found: C, 47.65; H, 4.24; N, 10.70.



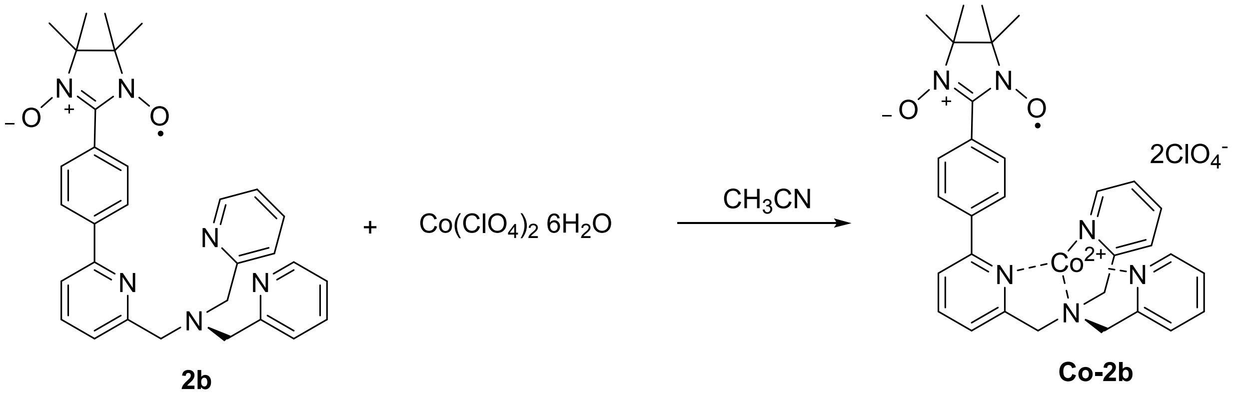
Synthesis of ligand 2b. Ligand **1b** (307 mg, 0.8 mmol) and bis(hydroxylamine) (127 mg, 0.9 mmol) were dissolved in MeOH (1 mL). The mixture was stirred overnight at room temperature. Intermediate compound precipitated as a white solid was filtered, washed with MeOH and dried. The white solid (200 mg, 0.4 mmol) was dissolved in CH_2Cl_2, cooled at 0°C and 100 mg of $NaIO_4$ (0.5 mmol) in 5 mL of distilled water were added. The solution was let stirring during 2h, the organic phase was separated, dried with Mg_2SO_4 and filtered. The solvent was evaporated to afford the nitronyl nitroxide derivative **2b** (78% yield) as a blue solid. MS (ESI) calcd for $C_{31}H_{33}N_6O_2$ $(M+H)^+$ 522.3, found 522.4. IR (KBr) ν (cm^{-1}): 621, 668, 692, 750, 797, 995, 1046, 1087, 1152, 1208, 1362, 1433, 1451, 1473, 1569, 1684, 1755, 2294, 2978, 3060. Anal. Calcd. ($C_{31}H_{33}N_6O_2$): C, 71.38; H, 6.38; N, 16.11. Found: C, 71.49; H, 6.44; N, 16.08.



Synthesis of compound Zn-2b. Compound **2b** (22 mg, 0.04 mmol) and $Zn(ClO_4)_2$ $6H_2O$ (16 mg, 0.04 mmol) were dissolved in 2 mL of CH_3CN. The mixture was let stirring during 1 hour at room temperature, then diethyl ether was added to the solution until the formation of a blue precipitate. The mixture was stirred for 10 min and filtered. The solid was dried to afford 20 mg of zinc(II) complex **Zn-2b** (61%) as a blue solid. MS (ESI) calcd for $C_{31}H_{33}N_6O_2Zn$ $(M+Cl)^+$ 620.2, found 620.2. IR (KBr) ν (cm^{-1}): 694, 772, 1096, 1172, 1362, 1393, 1442, 1460, 1487, 1575, 1635. Anal. Calcd. ($C_{31}H_{33}Cl_2N_6O_{10}Zn$): C, 47,38 H, 4.23; N, 10.69. Found: C, 47.33; H, 4.44; N, 10.61.



Synthesis of compound Cu-2b. Compound **2b** (30 mg, 0.06 mmol) and $Cu(ClO_4)_2$ $6H_2O$ (21 mg, 0.06 mmol) were dissolved in 2 mL of CH_3CN. The mixture was let stirring during 1 hour at room temperature, then diethyl ether was added to the solution until the formation of a red precipitate. The mixture was stirred for 10 min and filtered. The solid was washed with CH_3CN − diethyl ether (1:10) several times and dried to afford 25 mg of copper(II) complex **Cu-2b** (56%) as a red solid. MS (ESI) calcd for $C_{31}H_{33}N_6O_2Cu$ $(M+Cl)^+$ 619.2, found 619.2; for $(M+HCOO)^+$ 629.2, found, 629.2; for $(M+ClO_4)^+$ 683.1, found, 683.2. IR (KBr) ν (cm^{-1}): 768, 1095, 1358, 1448, 1569, 1612. Anal. Calcd. ($C_{31}H_{33}Cl_2N_6O_{10}Cu$): C, 47,49 H, 4.24; N, 10.72. Found: C, 47.33; H, 4.44; N, 10.64.



Synthesis of compound Co-2b. Compound **2b** (70 mg, 0.13 mmol) and $Co(ClO_4)_2$ $6H_2O$ (54 mg, 0.13 mmol) were dissolved in 3 mL of CH_3CN. The mixture was let stirring during 1 hour at room temperature, then diethyl ether was added to the solution until the formation of a blue precipitate. The mixture was stirred for 10 min and filtered. The solid was washed with CH_3CN − diethyl ether (1:10) several times and dried to afford 61 mg of cobalt(II) complex **Co-2b** (59%) as a blue solid. MS (ESI) calcd for $C_{31}H_{33}N_6O_2Co$ $(M+Cl)^+$ 615.2, found 615.2; for $(M+HCOO)^+$ 625.2, found, 625.2, for $(M+ClO_4)^+$ 679.2, found, 679.2. IR (KBr) ν (cm^{-1}): 696, 769, 797, 1097, 1271, 1359, 1447, 1585, 1610. Anal. Calcd. ($C_{31}H_{33}Cl_2N_6O_{10}Co$): C, 47,77 H, 4.27; N, 10.78. Found: C, 47.85; H, 4.30; N, 10.71.

Additional EPR spectra

- **Ligands 2a and 2b**

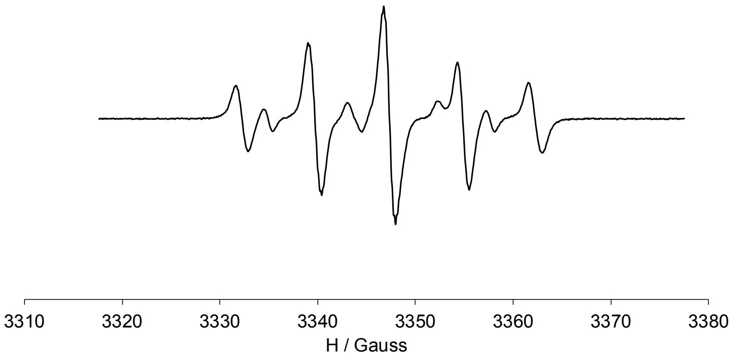


Figure S1. EPR spectrum of **2a** in CH_2Cl_2:TOL (1:1) at 300 K. From simulation: $a_{N\ (2N)}$= 7.52 G, g = 2.00647, L.W.= 1.2 G.

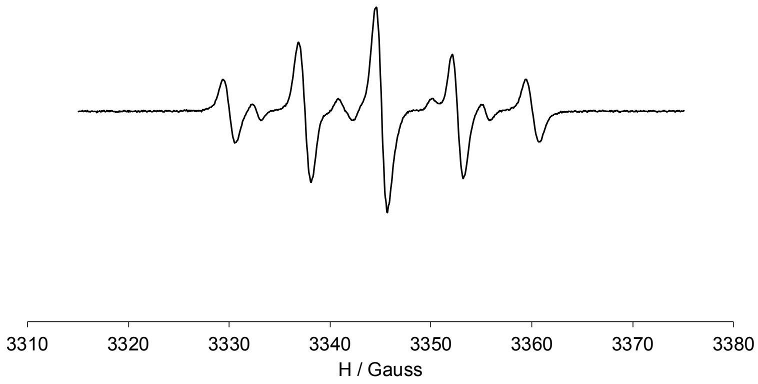


Figure S2. EPR spectrum of **2b** in CH_2Cl_2:TOL (1:1) at 300 K. From simulation: $a_{N\ (2N)}$= 7.53 G, g = 2.00654, L.W.= 1.2 G.

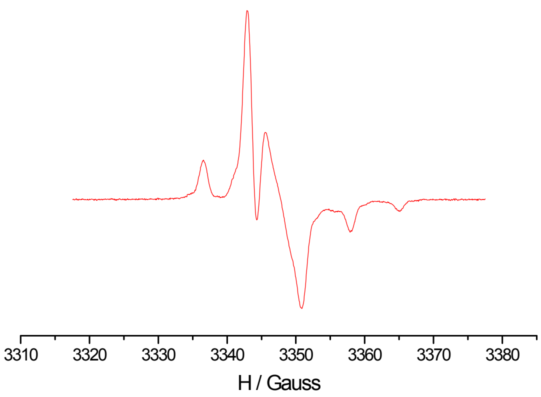


Figure S3. EPR spectrum of **2a** in CH_2Cl_2:TOL (1:1) at 120 K. From simulation data: (A_x=18.7 G, A_y=1.45 G, A_z=1.45G; g_X=2.0018, g_y=2.010, g_z=2.0066; L.W. x =3 G, y =5 G, z =6 G).

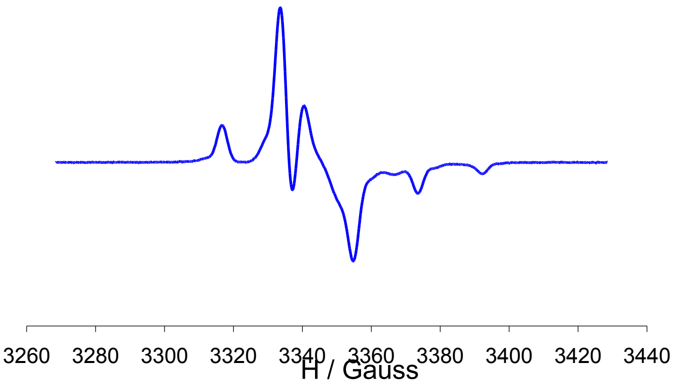


Figure S4. EPR spectrum of **2b** in CH_2Cl_2:TOL (1:1) at 120K. From simulation data: (A_x=18.8 G, A_y=1.45 G, A_z=1.45G; g_X=2.0017, g_y=2.0105, g_z=2.0066; L.W. x =3 G, y =5 G, z =6 G).

- **Compounds Zn-2a and Zn-2b**

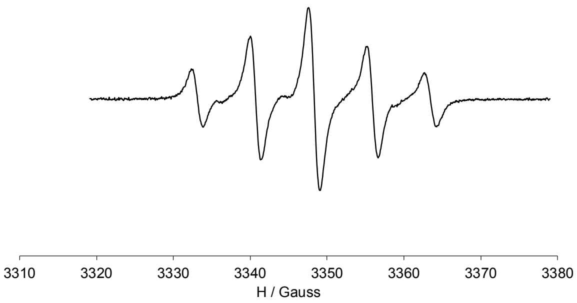


Figure S5. EPR spectrum of **Zn-2a** in CH_3CN + CH_2Cl_2:TOL (1:1) at 300 K. From simulation: $a_{N\ (2N)}$= 7.58 G, g = 2.00699, L.W.= 1.3 G.

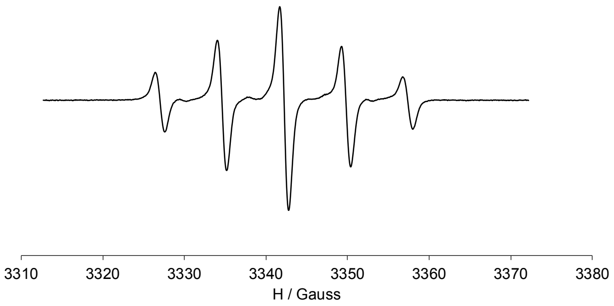


Figure S6. EPR spectrum of **Zn-2b** in CH_3CN + CH_2Cl_2:TOL (1:1) at 300 K. From simulation: $a_{N\ (2N)}$= 7.58 G, g = 2.00705, L.W.= 1.2 G.

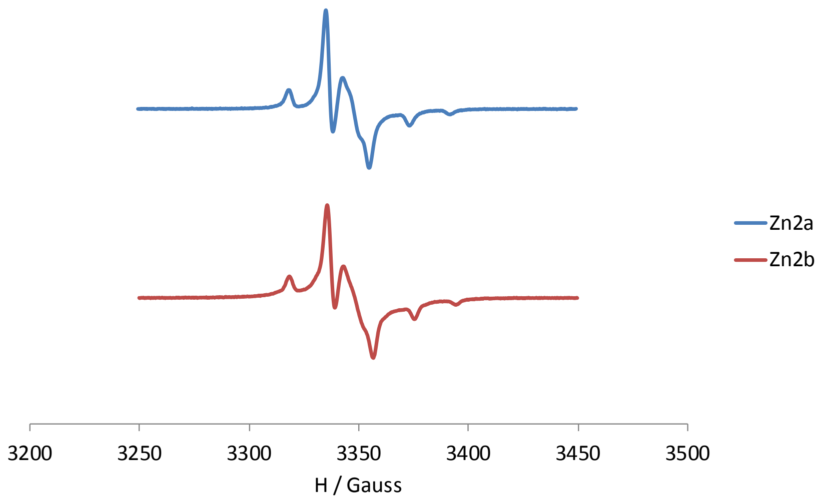


Figure S7. EPR spectrum of **Zn-2a,b** in CH_3CN (80%) + CH_2Cl_2:TOL (1:1) (20%) at 130 K. From simulation data: **Zn-2a** (A_x=18.30 G, A_y=1.45 G, A_z=1.45G; g_X=2.0022, g_y=2.010, g_z=2.007; L.W. x =3 G, y =5 G, z =6 G, Lorentziana/Gaussiana=0.7). **Zn-2b** (A_x=18.75 G, A_y=1.45 G, A_z=1.45G; g_X=2.0012, g_y=2.010, g_z=2.007; L.W. x =3 G, y =5 G, z =6 G, Lorentziana/Gaussiana=0).

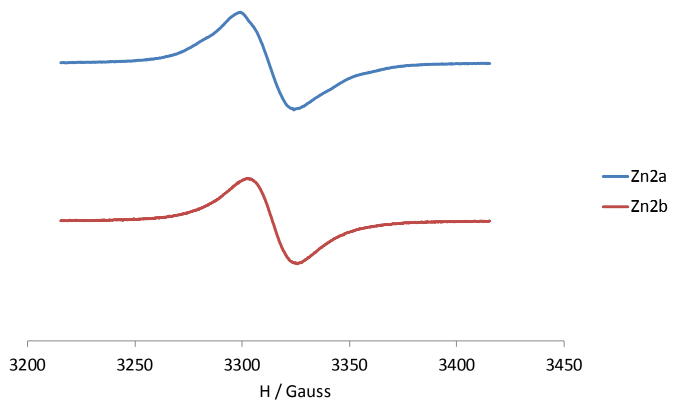


Figure S8. EPR spectrum of **Zn-2a,b** in CH_3CN at 130 K.

Compounds **Zn-2a,b** were not soluble in the good glass CH_2Cl_2:TOL (1:1), and CH_3CN should be added in high proportion. In frozen solution, the samples containing CH_3CN and a little bit of CH_2Cl_2:TOL (1:1) gave the typical spectral pattern part of nytronil nitroxide in frozen conditions (Figure S7), while if only CH_3CN is added, the spectral shape is not resolved anymore (Figure S8), highlighting the importance of the solvent in frozen solution.

- **Compounds Co-2a and Co-2b**

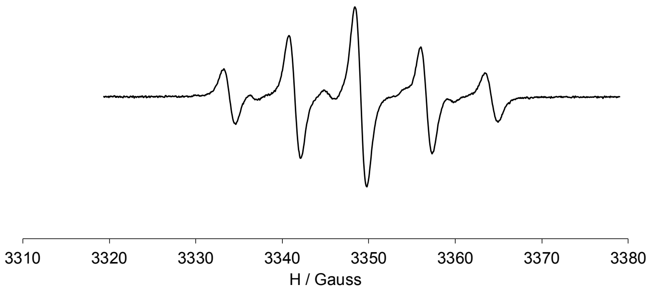


Figure S9. EPR spectrum of **Co-2a** in CH_2Cl_2:TOL (1:1) + CH_3CN at 300 K. From simulation: $a_{N\ (2N)}$= 7.59 G, g = 2.00654, L.W.= 1.3 G.

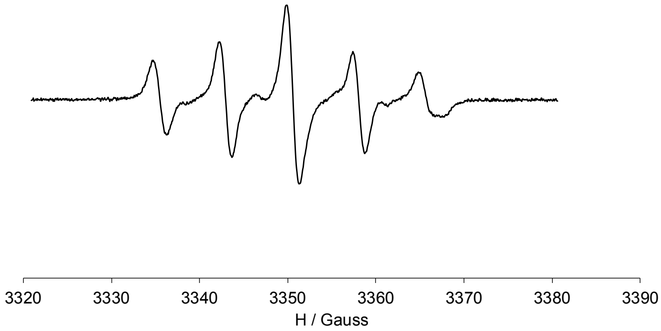


Figure S10. EPR spectrum of **Co-2b** in CH_2Cl_2:TOL (1:1) + CH_3CN at 300 K. From simulation: $a_{N\ (2N)}$= 7.56 G, g = 2.00628, L.W.= 1.3 G.

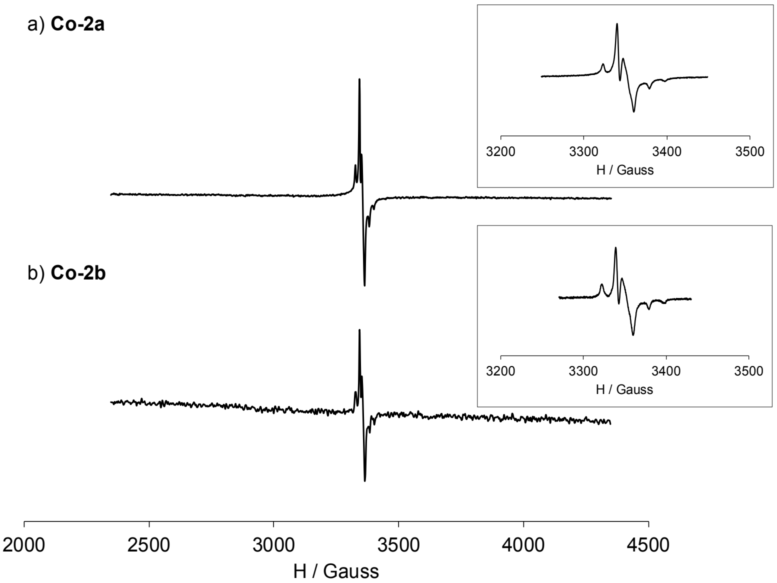


Figure S11. EPR spectra in frozen solution of a) **Co-2a** and b) **Co-2b** in CH_2Cl_2:TOL (1:1) + CH_3CN at 120 K. From simulation data: **Co-2a** (A_x=18.30 G, A_y=1.45 G, A_z=1.45G; g_X=2.0022, g_y=2.011, g_z=2.0066; L.W. x =3 G, y =4.5 G, z =6 G, Lorentziana/Gaussiana=0.8). **Co-2b** (A_x=18.75 G, A_y=1.45 G, A_z=1.45G; g_X=2.0016, g_y=2.011, g_z=2.0066; L.W. x =3 G, y =4 G, z =5 G, Lorentziana/Gaussiana=0).

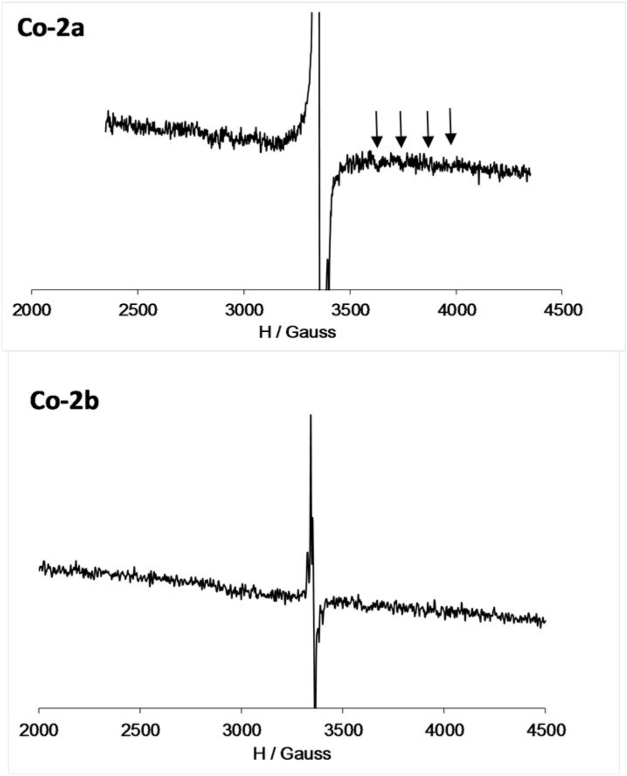


Figure S12. Enlarged EPR spectra of **Co-2a** and **Co-2b** in CH_2Cl_2:TOL (1:1) + CH_3CN at 120 K. We can barely observe the signal of Co(II) metal ion in both EPR spectra, which is only a little bit more intense in the case of **Co-2a**. As Co(II) has a nuclear spin *I* = 7/2, eight peaks should be exhibited. In **Co-2a** spectrum we can barely distinguish four of the eight corresponding peaks, marked with arrows, with a coupling constant of 120 G.

- ## Compound Fe-3a

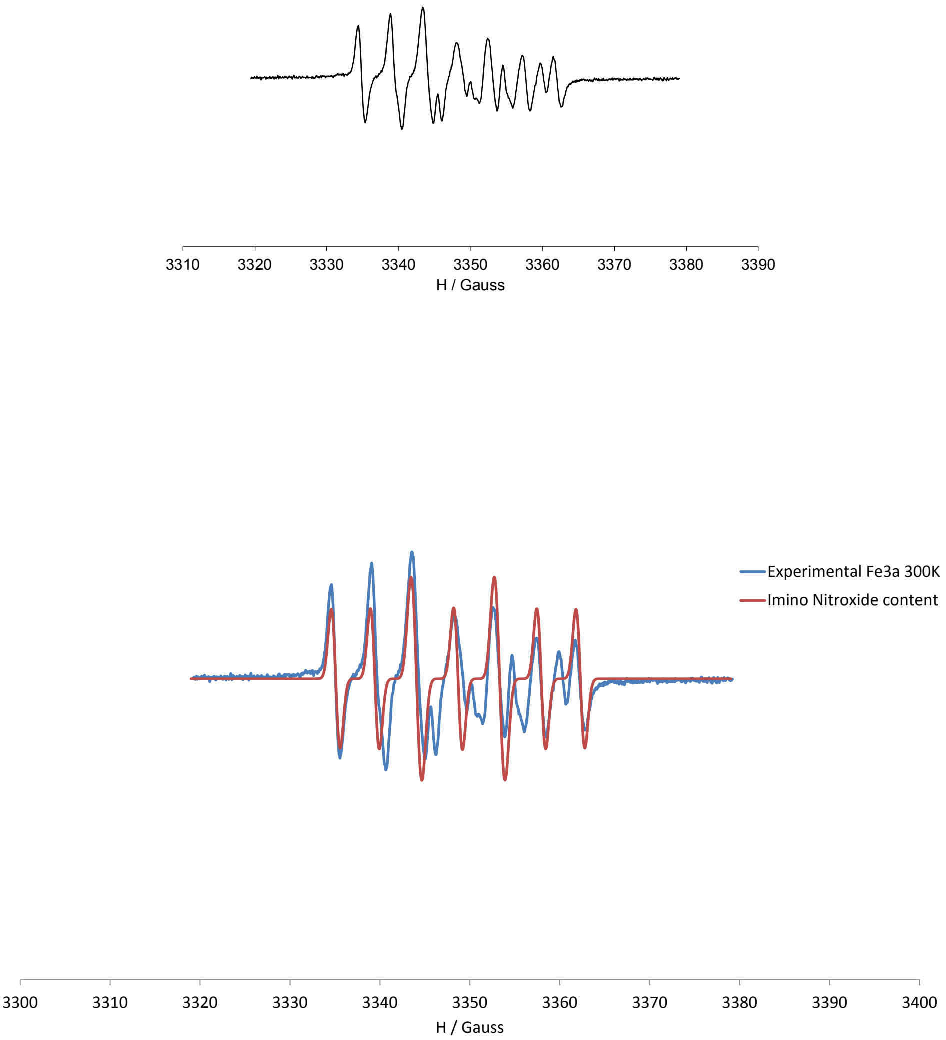


Figure S13. Up) EPR spectrum obtained from the synthesis starting from ligand **2a** and iron(II) perchlorate, in CH_3CN + CH_2Cl_2:TOL (1:1) at 300 K. A mixture of two radical species are formed. Down) The same experimental spectrum with the principal component of the mixture, the imino nitroxide **Fe-3a**.

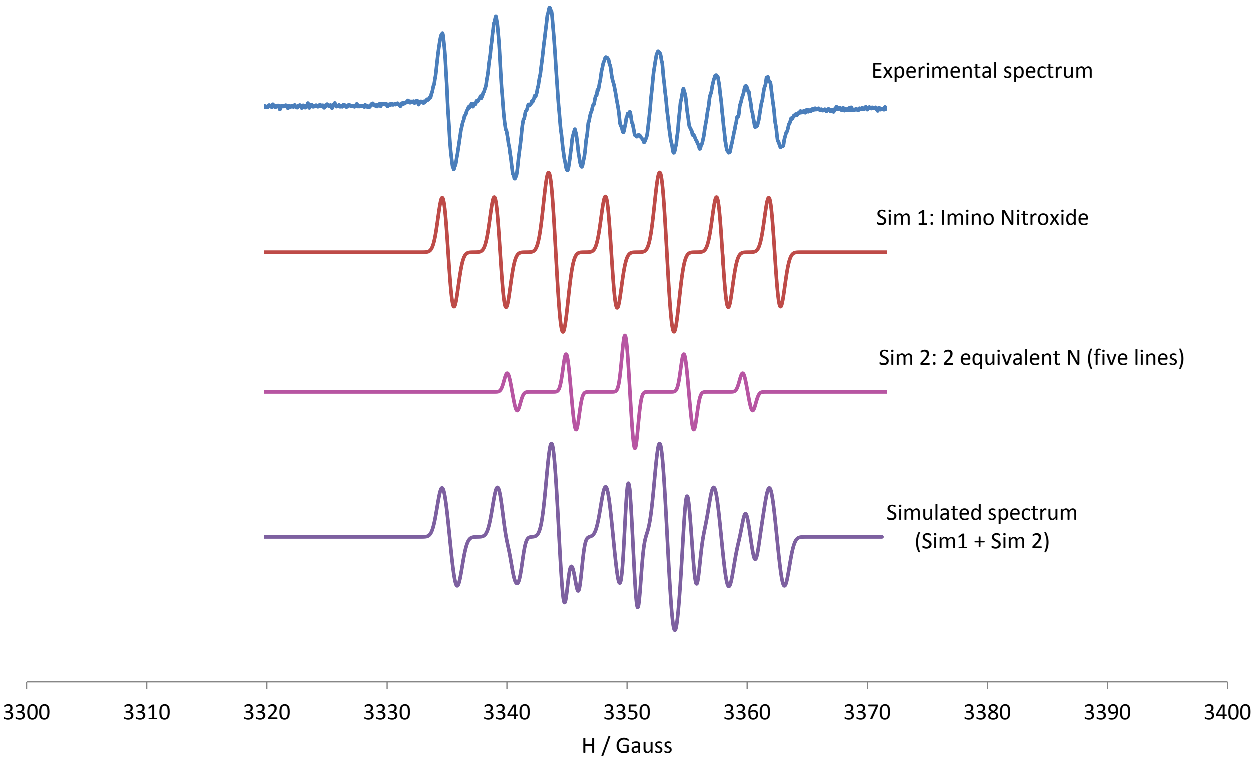
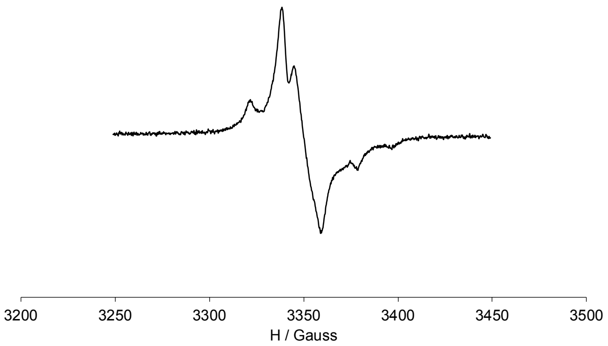


Figure S14. Simulation of the experimental EPR spectrum obtained from the synthesis starting from ligand **2a** and iron(II) perchlorate, in CH_3CN + CH_2Cl_2:TOL (1:1) at 300 K. The simulation is the sum of the imino nitroxide **Fe-3a** (a_{N1} = 4.35 G and a_{N2} = 9.25 G at g-factor = 2.0063) and a second radical species containing 2 equivalent N ($a_{N\ (2N)}$ = 4.9 G at g-factor = 2.0060, in a ratio 2.2:1.



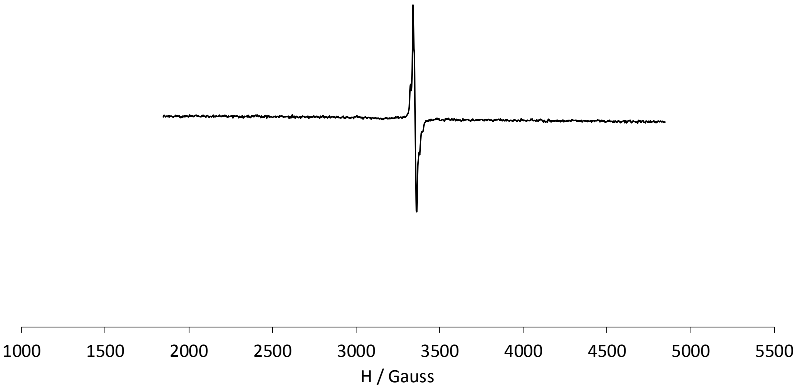


Figure S15. EPR spectrum of the mixture Fe complexes in frozen conditions, in CH_3CN + CH_2Cl_2:TOL (1:1) at 120 K. Magnetic field range from up) 3250 to 3450 G and down) from 1500 to 5000 G. As Fe(II) is not a paramagnetic ion it is not expected any EPR metal signal at frozen solution.

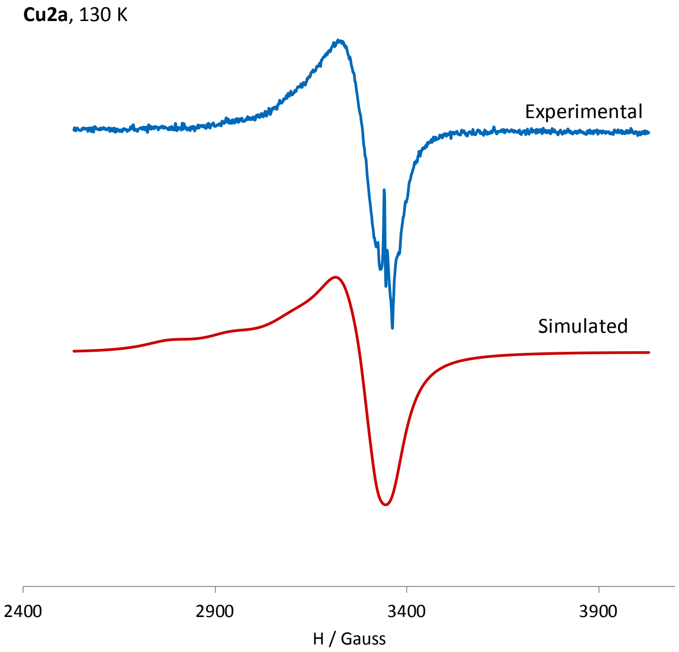


Figure S16. Experimental EPR spectrum of **Cu-2a** at 130 K (up) and the corresponding simulation of the Cu(II) ion. ($A_{(x,x)}$ = 12 G, $A_{(y,y)}$ = 12 G, $A_{(z,z)}$ = 156 G; g_x = 2.032, g_y = 2.075, g_z = 2.23).

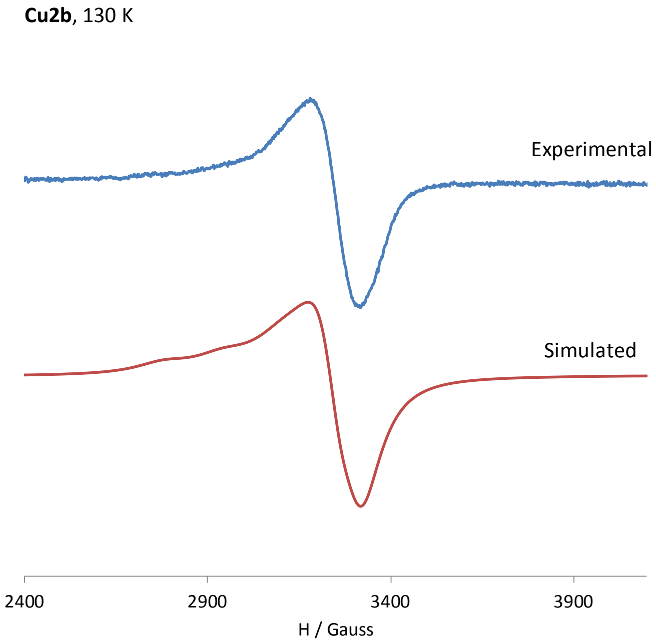


Figure S17. Experimental EPR spectrum of **Cu-2b** at 130 K (up) and the corresponding simulation of the Cu(II) ion. ($A_{(x,x)}$ = 12 G, $A_{(y,y)}$ = 12 G, $A_{(z,z)}$ = 156 G; g_x = 2.075, g_y = 2.075, g_z = 2.23).

Table S1. Crystal data and structure refinement for **Co-2b**.

Empirical formula	C33 H36 Cl2 Co N7 O10 x CH3CN	
Formula weight	861.57	
Temperature	233(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c (no. 15)	
Unit cell dimensions	a = 20.6162(3) Å	α = 90°.
	b = 10.9186(4) Å	β = 93.872(2)°.
	c = 34.6060(10) Å	γ = 90°.
Volume	7772.0(4) Å^3	
Z	8	
Density (calculated)	1.473 g/cm^3	
Absorption coefficient	0.646 mm^{-1}	
F(000)	3568	
Crystal size	0.200 x 0.090 x 0.030 mm^3	
Theta range for data collection	1.980 to 23.997°.	
Index ranges	-23<=h<=19, -10<=k<=12, -39<=l<=39	
Reflections collected	16664	
Independent reflections	6091 [R(int) = 0.0605]	
Completeness to theta = 23.997°	99.4 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6091 / 0 / 578	
Goodness-of-fit on F^2	1.033	
Final R indices [I>2sigma(I)]	R1 = 0.0532, wR2 = 0.1233	
R indices (all data)	R1 = 0.1050, wR2 = 0.1418	
Largest diff. peak and hole	0.397 and -0.323 e.Å^{-3}	

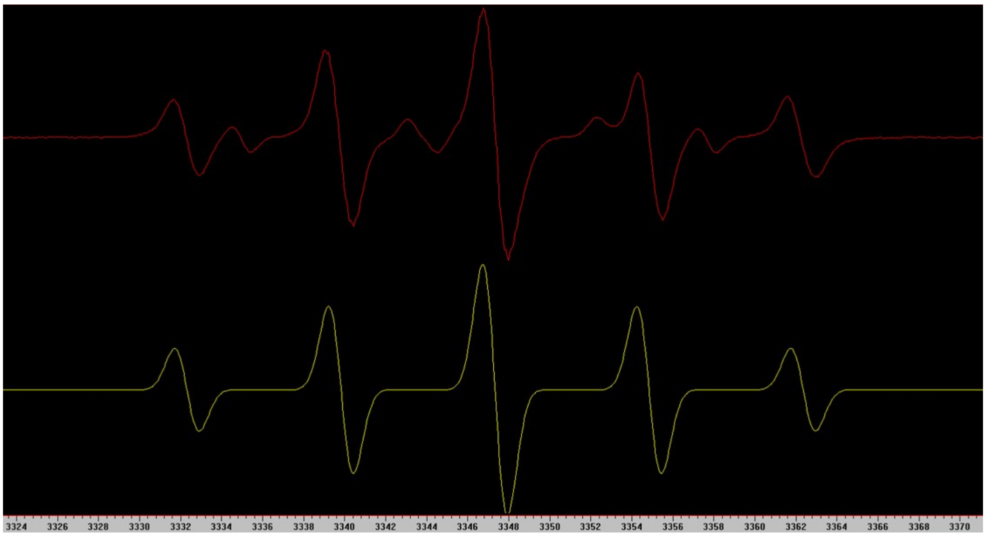
Table S2. Crystal data and structure refinement for **Cu-3a**.

Empirical formula	C33 H37 Cl3 Cu N7 O13 x CH3CN	
Formula weight	950.64	
Temperature	233(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1 (no. 2)	
Unit cell dimensions	a = 11.3545(5) Å	α = 80.651(2)°.
	b = 13.8512(6) Å	β = 72.087(3)°.
	c = 14.6307(7) Å	γ = 86.640(3)°.
Volume	2160.30(17) Å^3	
Z	2	
Density (calculated)	1.461 g/cm^3	
Absorption coefficient	0.761 mm^{-1}	
F(000)	980	
Crystal size	0.250 x 0.250 x 0.030 mm^3	
Theta range for data collection	1.885 to 23.995°.	
Index ranges	-12<=h<=12, -15<=k<=15, -16<=l<=16	
Reflections collected	11860	
Independent reflections	6729 [R(int) = 0.0588]	
Completeness to theta = 23.995°	99.4 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6729 / 1 / 593	
Goodness-of-fit on F^2	1.048	
Final R indices [I>2sigma(I)]	R1 = 0.0767, wR2 = 0.1890	
R indices (all data)	R1 = 0.1038, wR2 = 0.2083	
Largest diff. peak and hole	0.516 and -0.721 e.Å^{-3}	

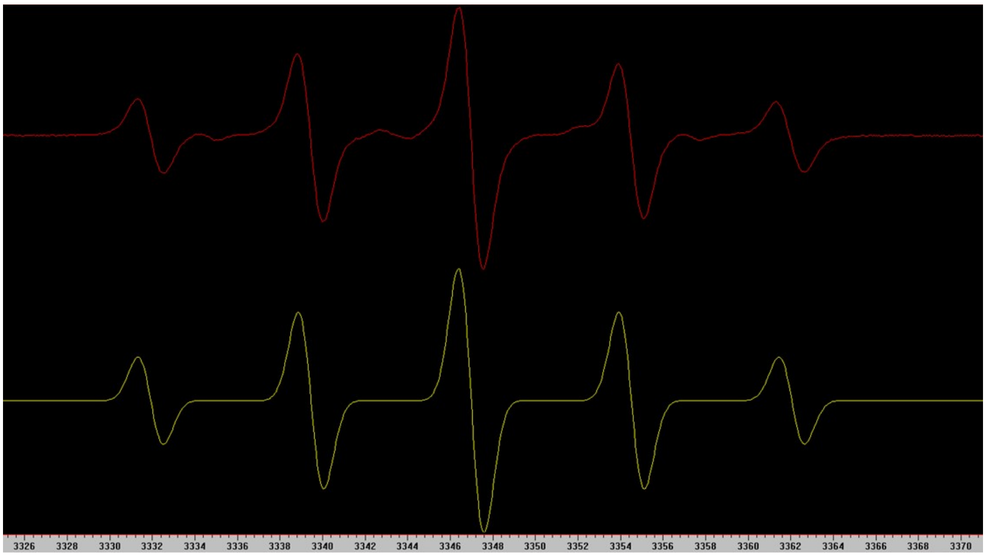
Additional simulation of EPR spectra

At 300 K:

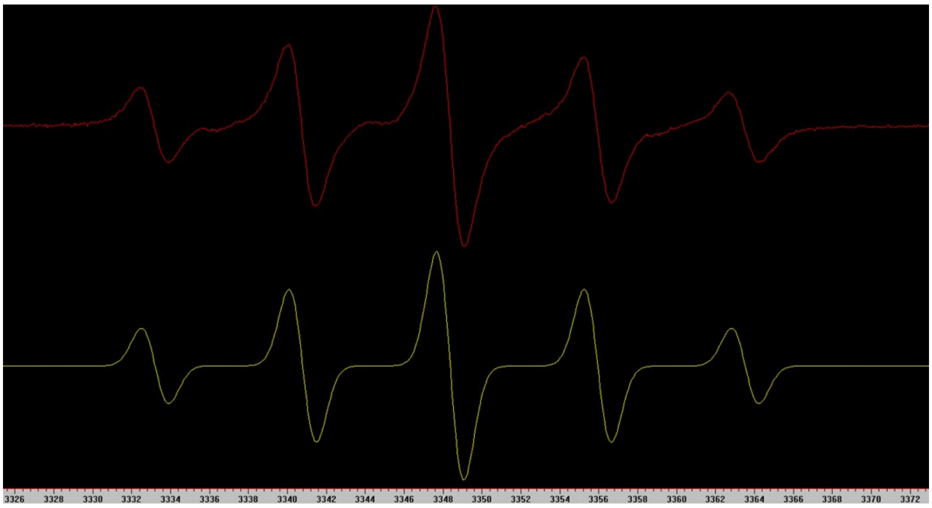
2a



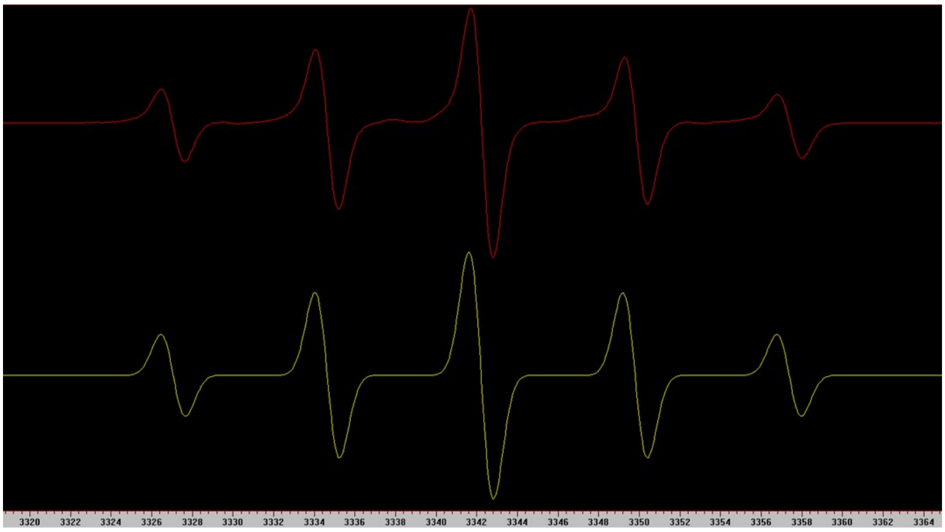
2b



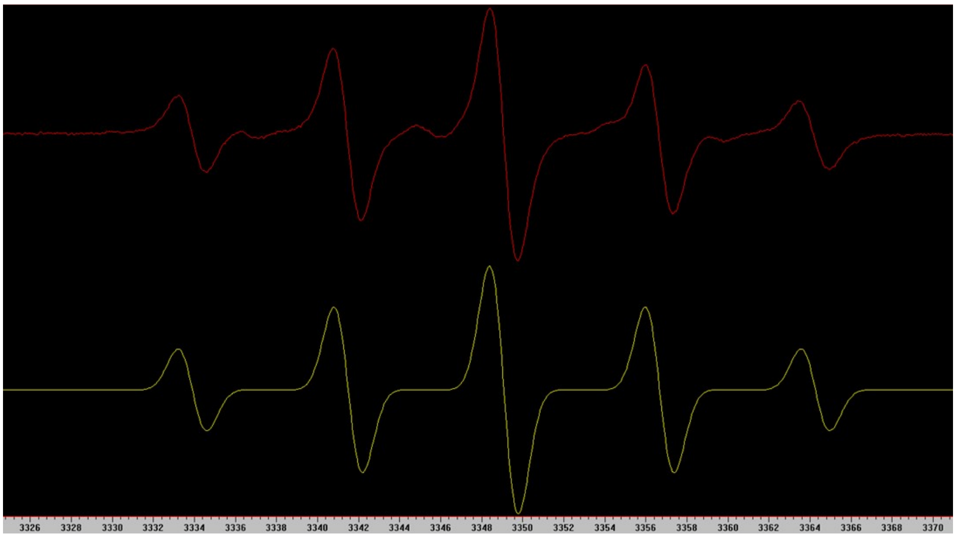
Zn-2a


3326 3328 3330 3332 3334 3336 3338 3340 3342 3344 3346 3348 3350 3352 3354 3356 3358 3360 3362 3364 3366 3368 3370 3372

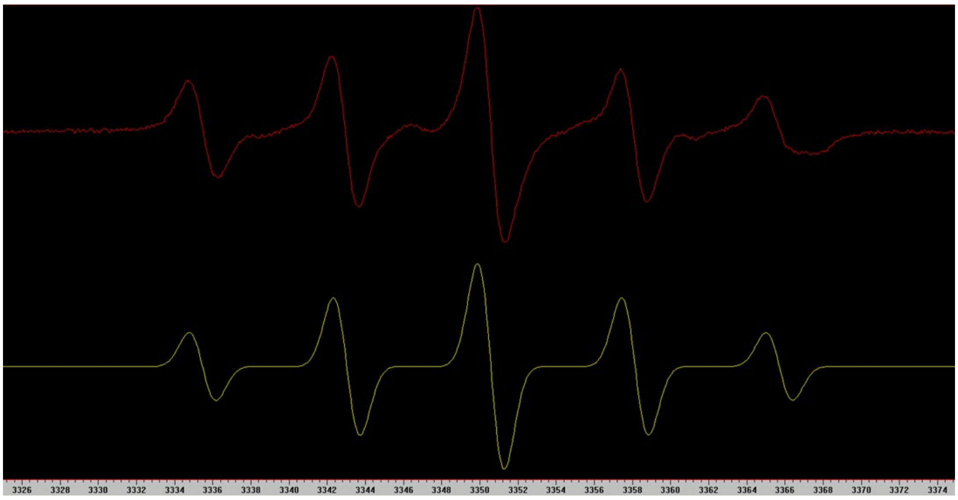
Zn-2b


3320 3322 3324 3326 3328 3330 3332 3334 3336 3338 3340 3342 3344 3346 3348 3350 3352 3354 3356 3358 3360 3362 3364

Co-2a

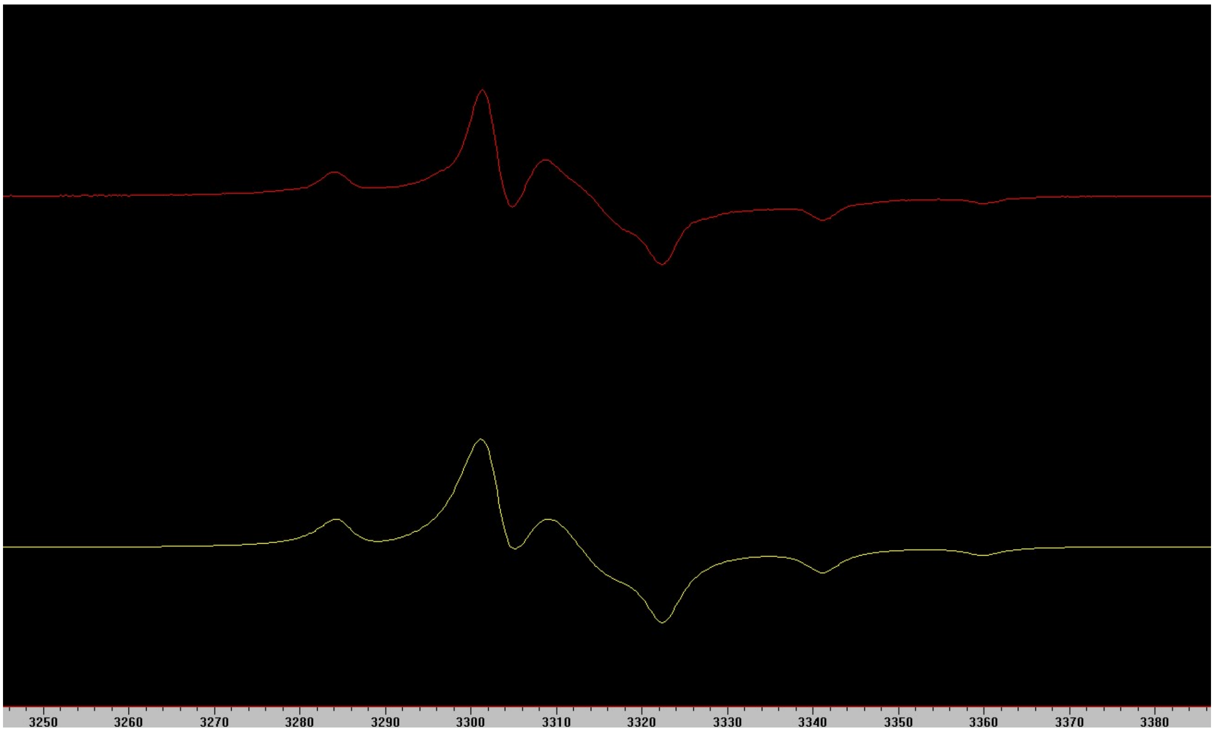

3326
3328
3330
3332
3334
3336
3338
3340
3342
3344
3346
3348
3350
3352
3354
3356
3358
3360
3362
3364
3366
3368
3370

Co-2b


3326
3328
3330
3332
3334
3336
3338
3340
3342
3344
3346
3348
3350
3352
3354
3356
3358
3360
3362
3364
3366
3368
3370
3372
3374

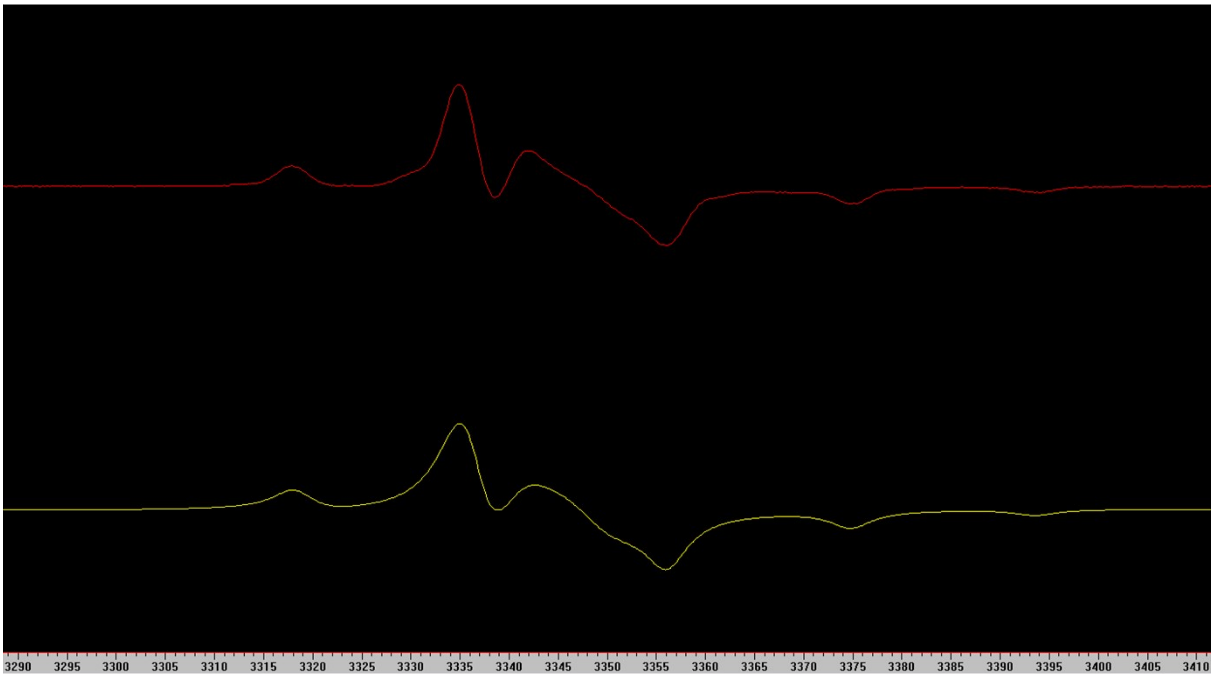
At 120 K:

2a



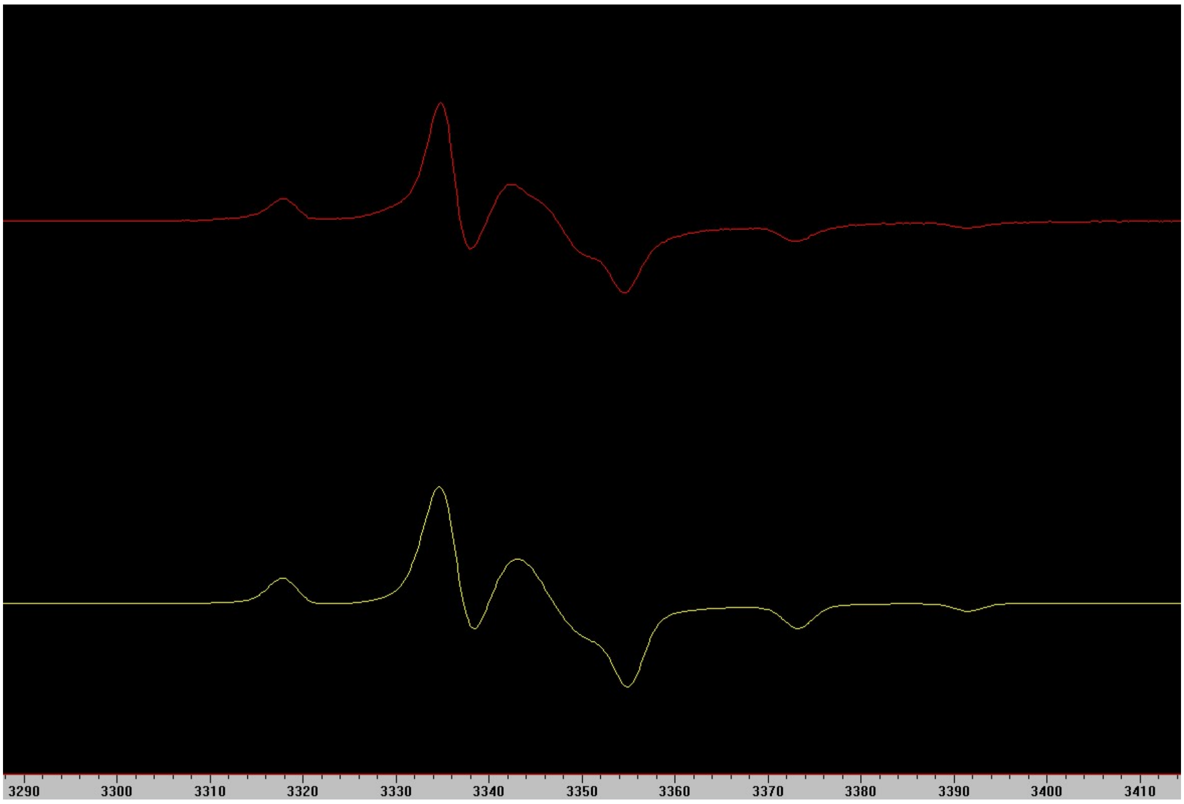
3250
3260
3270
3280
3290
3300
3310
3320
3330
3340
3350
3360
3370
3380

2b

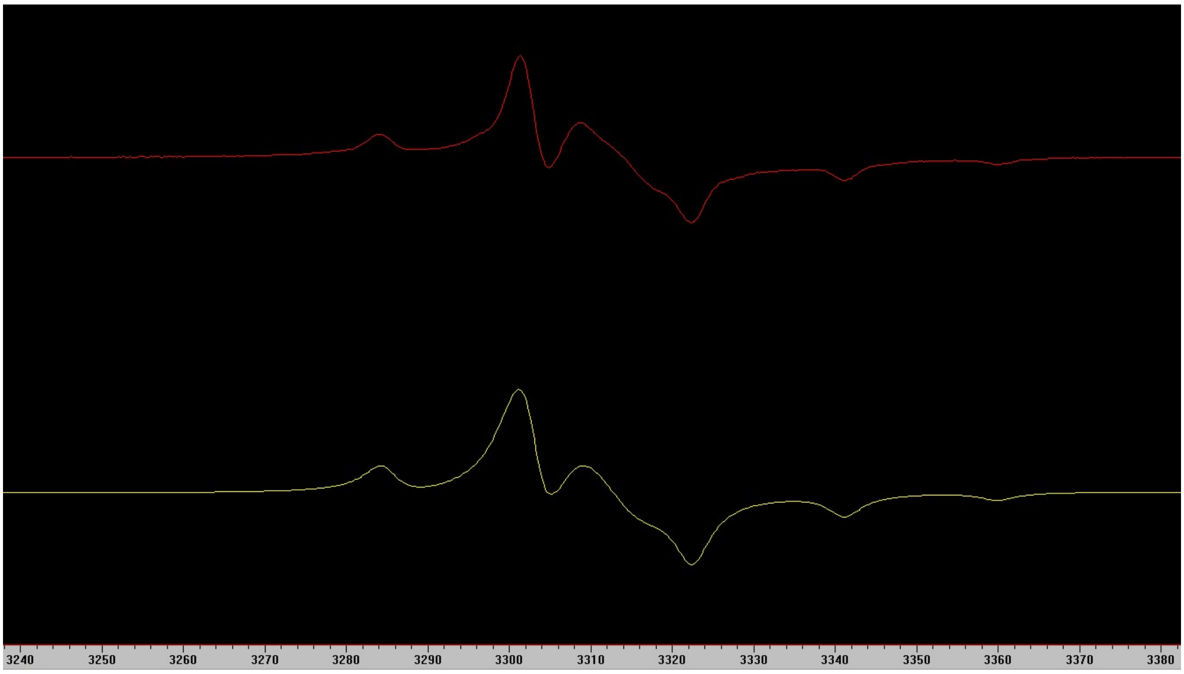


3290
3295
3300
3305
3310
3315
3320
3325
3330
3335
3340
3345
3350
3355
3360
3365
3370
3375
3380
3385
3390
3395
3400
3405
3410

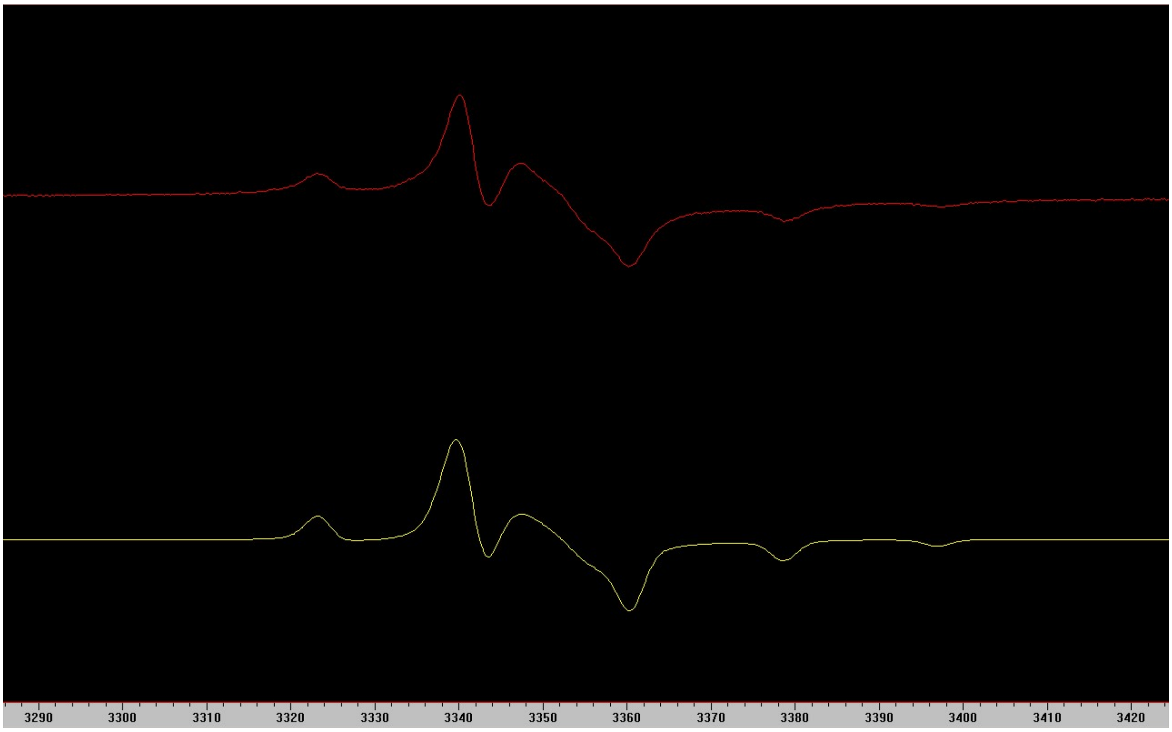
Zn-2a


3290
3300
3310
3320
3330
3340
3350
3360
3370
3380
3390
3400
3410

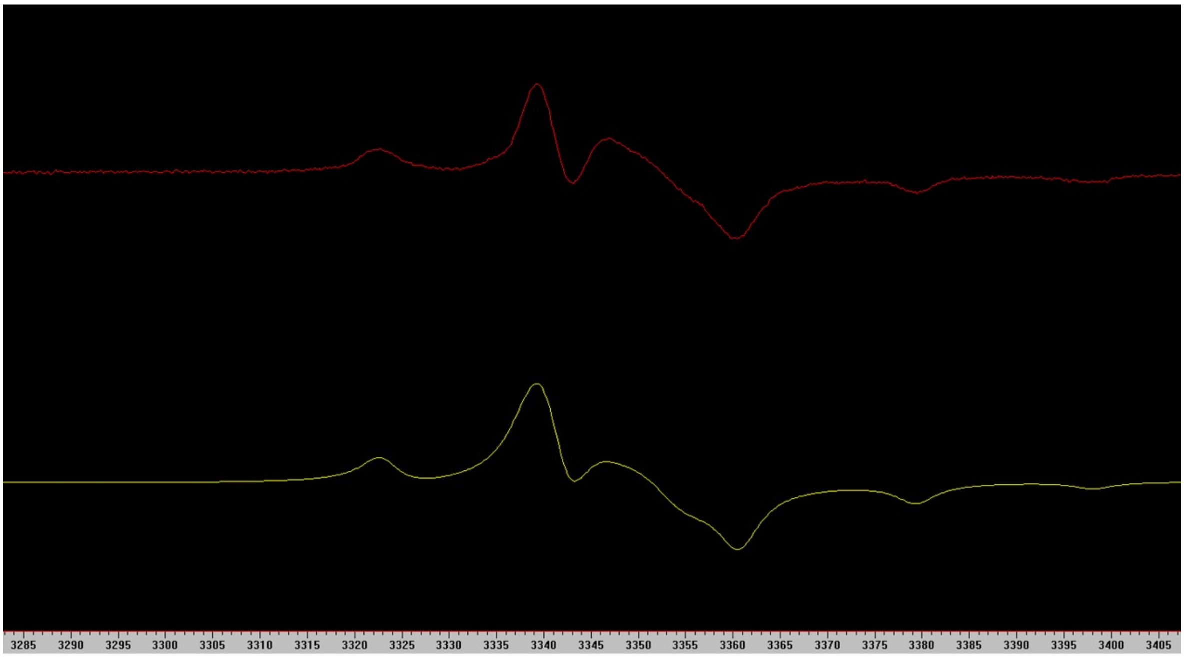
Zn-2b


3240
3250
3260
3270
3280
3290
3300
3310
3320
3330
3340
3350
3360
3370
3380

Co-2a


3290
3300
3310
3320
3330
3340
3350
3360
3370
3380
3390
3400
3410
3420

Co-2b


3285
3290
3295
3300
3305
3310
3315
3320
3325
3330
3335
3340
3345
3350
3355
3360
3365
3370
3375
3380
3385
3390
3395
3400
3405