Supporting information

for

Metal-Directed Self-Assembly of Transition Metal Heterometallascorpionates

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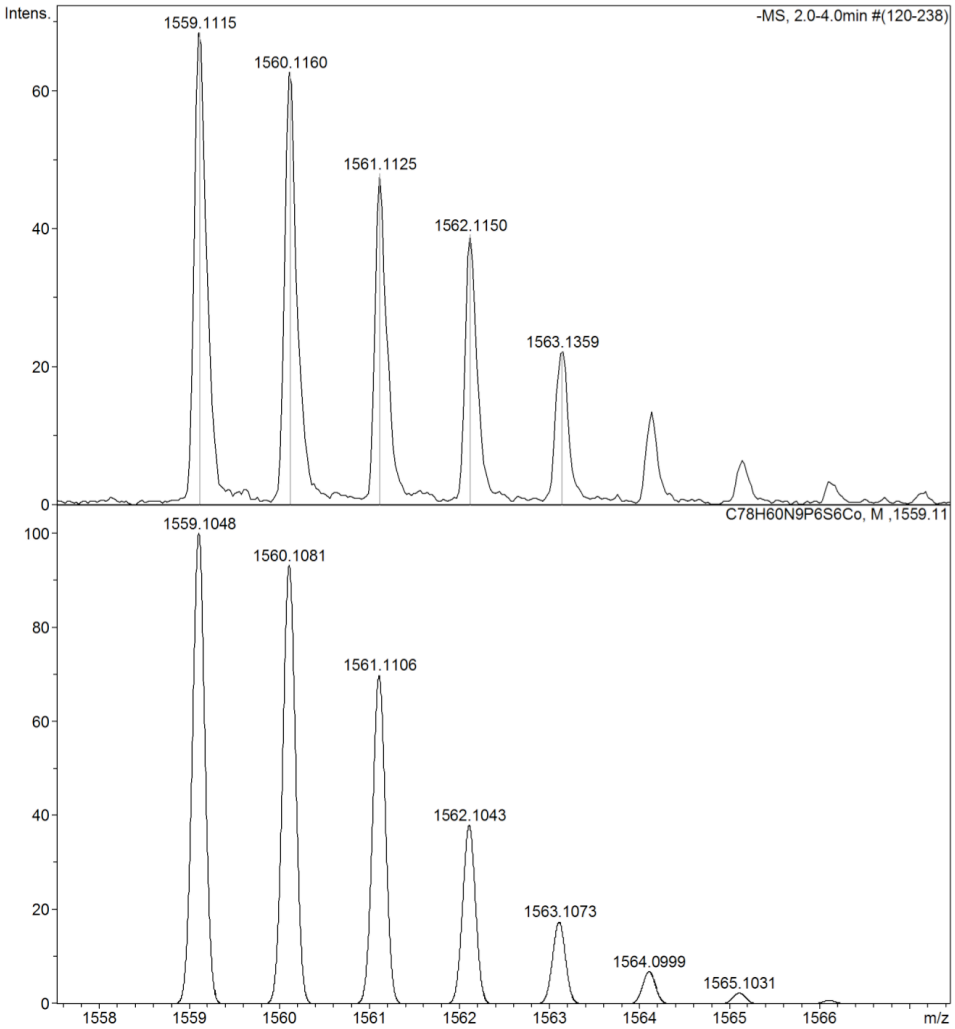

Figure S1. Experimental isotopic pattern for the $[M–K(thf)_2]^-$ peak in the high resolution ESI(⁻) mass spectrum of **3** (top) and the simulated isotopic pattern for the same fragment (bottom).

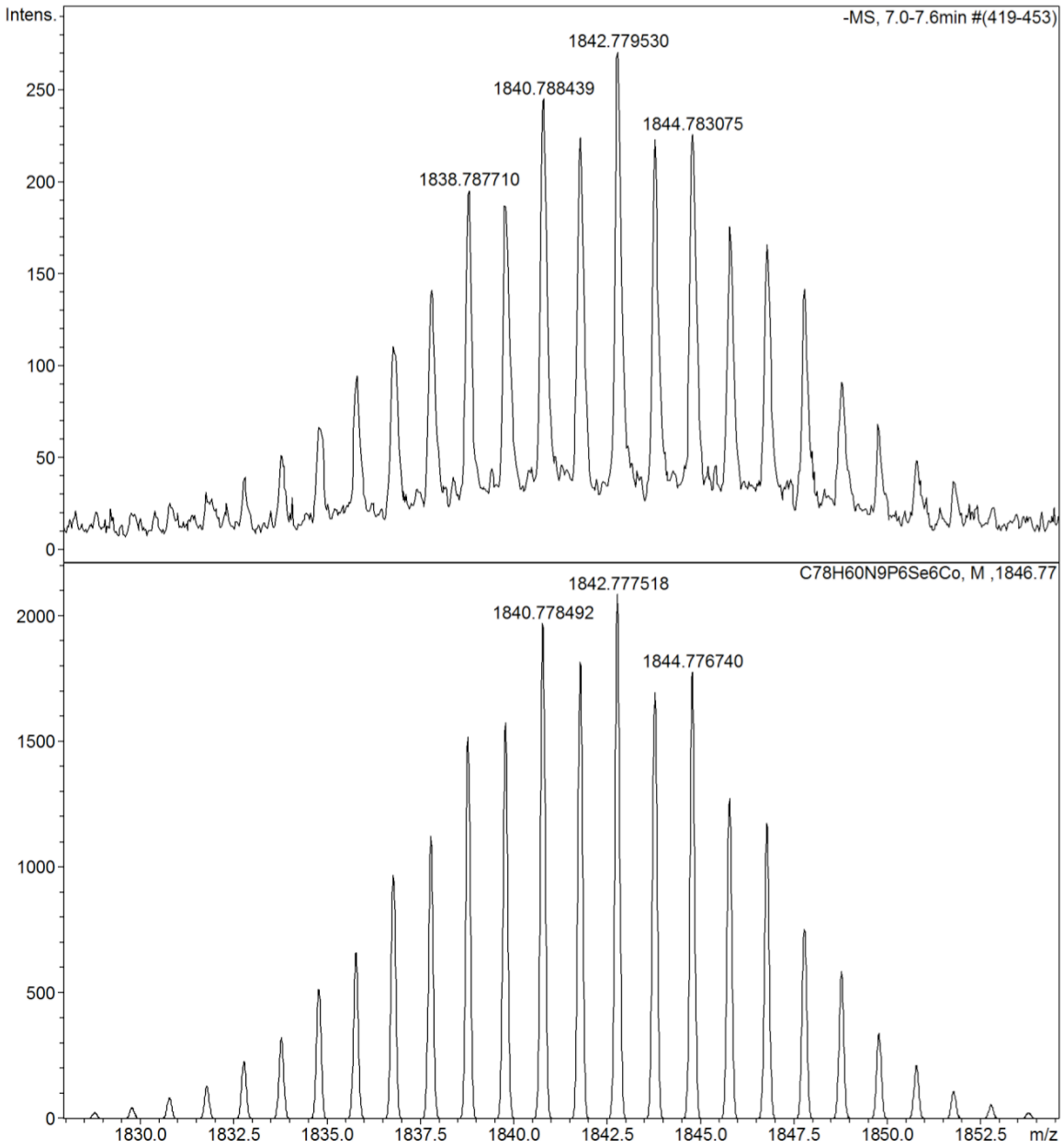

Figure S2. Experimental isotopic pattern for the [*M*–K(thf)$_2$]$^-$ peak in the high resolution ESI($^-$) mass spectrum of **4** (top) and the simulated isotopic pattern for the same fragment (bottom).

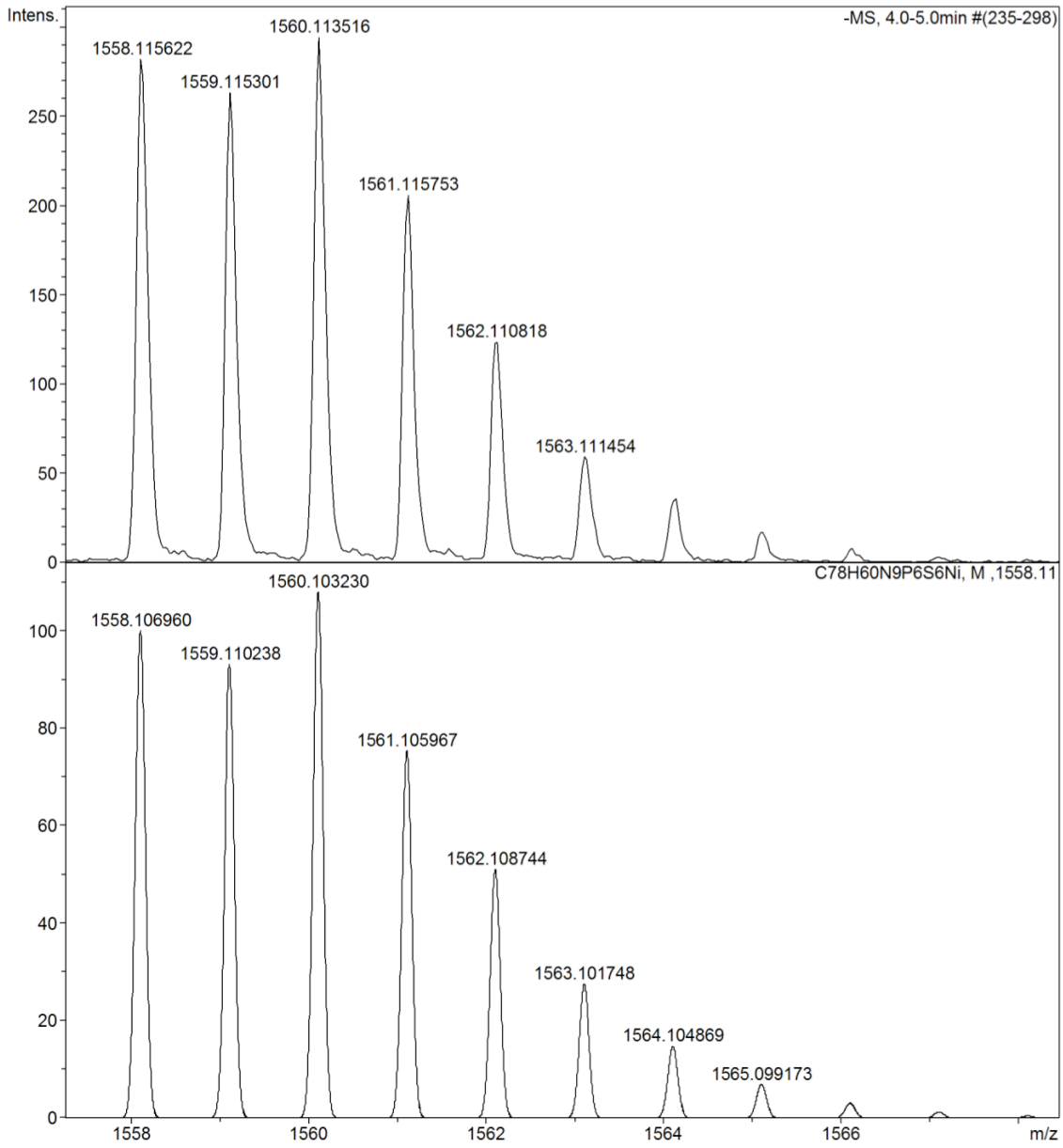

Figure S3. Experimental isotopic pattern for the $[M–K(thf)_2]^-$ peak in the high resolution ESI($^-$) mass spectrum of **5** (top) and the simulated isotopic pattern for the same fragment (bottom).

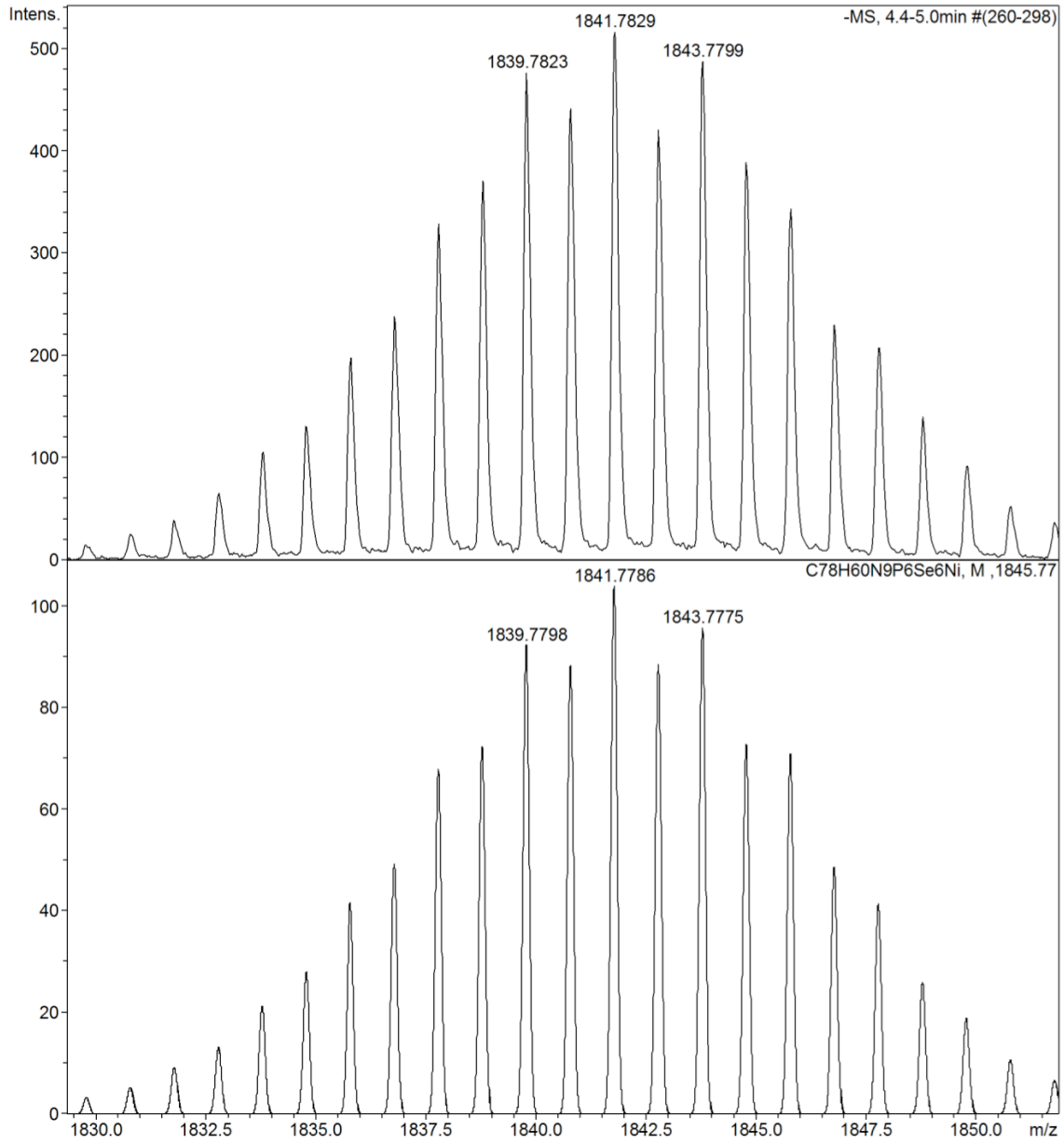

Figure S4. Experimental isotopic pattern for the $[M–K(thf)_2]^-$ peak in the high resolution ESI($^-$) mass spectrum of **6** (top) and the simulated isotopic pattern for the same fragment (bottom).

Table S1. Crystal data and structure refinement details for compounds **3**–**6**

	3·1.696THF·0.304CH_2Cl_2	**4**·2THF	**5**·1.184THF·0.216CH_2Cl_2	**6**·2THF
Empirical formula	$C_{179.09}H_{166.18}Cl_{0.61}Co_2K_2N_{18}O_{5.70}P_{12}S_{12}$	$C_{180}H_{168}Co_2K_2N_{18}O_6P_{12}Se_{12}$	$C_{179.35}H_{166.70}Cl_{0.43}K_2N_{18}Ni_2O_{5.78}P_{12}S_{12}$	$C_{180}H_{168}K_2N_{18}Ni_2O_6P_{12}Se_{12}$
Formula weight	3635.80	4194.54	3633.87	4194.10
Space group	Triclinic	Triclinic	Triclinic	Triclinic
Crystal system	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	16.0136(4)	16.1262(6)	15.9889(6)	16.1143(3)
b/Å	16.3827(4)	16.3809(6)	16.2392(6)	16.3352(3)
c/Å	20.3288(5)	20.5889(7)	20.4481(7)	20.6585(4)
α/°	67.641(1)	67.647(1)	67.523(1)	67.608(1)
β/°	88.941(1)	89.772(1)	89.428(1)	89.713(1)
γ/°	62.375(1)	62.696(1)	62.557(1)	62.413(1)
V/Å^3	4288.04(18)	4372.5(3)	4263.5(3)	4357.72(14)
Temperature/K	100(2)	100(2)	100(2)	100(2)
Wavelength/Å	0.71073	0.71073	0.71073	0.71073
Z	1	1	1	1
$\rho_{(calc.)}$/g cm^{-3}	1.408	1.593	1.415	1.598
μ (mm^{-1})	0.572	2.906	0.599	2.942
Crystal size/mm^3	0.18x0.13 x 0.12	0.15 x 0.14 x 0.09	0.26 x 0.19 x 0.18	0.11 x 0.07 x 0.07
Refl. collected	111939	50814	117974	64282
Unique refl. (R_{int})	16862 (0.0290)	17239 (0.0460)	18120 (0.0445)	19979 (0.0423)
R_1,[a] wR_2[b] (I>2σ(I))	0.0304, 0.0745	0.0399, 0.0817	0.0440, 0.1003	0.0365, 0.0714
R_1,[a] wR_2[b] (all data)	0.0330, 0.0758	0.0588, 0.0880	0.0502, 0.1029	0.0560, 0.0774
GooF	1.045	1.020	1.115	1.018

[a]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b]$wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(F_o^2)^2]^{1/2}$

Table S2. Crystal data and structure refinement details of compounds **3a**, **3b**, **4a** and **4b.**

	3a	**3b**	**4a**	**4b**
Empirical formula	$C_{180}H_{168}Co_2K_2N_{18}O_6P_{12}S_{12}$	$C_{180}H_{168}Co_2K_2N_{18}O_6P_{12}S_{12}$	$C_{180}H_{168}Co_2K_2N_{18}O_6P_{12}Se_{12}$	$C_{180}H_{168}Co_2K_2N_{18}O_6P_{12}Se_{12}$
Formula weight	3631.73	3631.73	4194.53	4194.10
Space group	Triclinic	Triclinic	Triclinic	Triclinic
Crystal system	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	16.0185(15)	16.128(4)	16.1384(8)	16.2092(15)
b/Å	16.1962(16)	16.427(6)	16.3880(8)	16.4743(16)
c/Å	20.537(2)	20.759(5)	20.6000(11)	20.887(2)
α/º	67.0861(16)	67.734(4)	67.7161(8)	67.8293(16)
β/º	89.5626(18)	89.760(5)	89.7051(9)	90.0911(17)
γ/º	63.0038(16)	62.594(4)	62.5180(7)	62.7076(15)
Unit cell volume/Å^3	4279.1(7)	4420.6(17)	4375.7(4)	4485.6(7)
Temperature/K	100(2)	250(2)	100(2)	250(2)
Wavelength/ Å	0.71073	0.71073	0.71073	0.71073
Z	1	2	1	1
$\rho_{(calc.)}$/g cm^{-3}	1.409	1.364	1.592	1.553
μ (mm^{-1})	0.564	0.546	2.904	2.833
Crystal size/mm^3	0.62 x 0.35 x 0.30	0.62 x 0.35 x 0.30	0.31 x 0.27 x 0.21	0.31 x 0.27 x 0.21
Refl. collected	68343	83197	77713	82031
Unique refl. (R_{int})	17435 (0.0351)	18069 (0.0201)	19956 (0.0428)	20461 (0.0261)
R_1,[a] wR_2[b] ($I>2\sigma(I)$)	0.0545, 0.1324	0.0342, 0.0950	0.0704, 0.1417	0.0334, 0.0858
R_1,[a] wR_2[b] (all data)	0.0596, 0.1356	0.0393, 0.1000	0.0796, 0.1454	0.0430, 0.0914
GoF	1.092	1.022	1.186	0.995

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(F_o^2)^2]^{1/2}$

Table S3. Selected bond lengths (Å) and angles (º) for **3a** and **4a** (collected at 100 K).

	3a	**4a**
Co–E	2.507(1), 2.529(1), 2.545(1)	2.653(1), 2.592(1), 2.635(4)
Co–N	2.078(1), 2.085(1), 2.114(3)	2.080(4), 2.092(4), 2.117(4)
P=E	1.953(1), 1.958(1), 1.951(1)	2.123(4), 2.102(1), 2.109(7)
P–E(Co)	1.989(1), 1.984(1), 1.983(1)	2.140(4), 2.131(2), 2.137(2)
Co···K	3.864(1)	3.856(1)
E-Co-E	88.5(1), 87.8(1), 86.2(1)	88.0(2), 86.7(1), 85.3(1)
N-Co-N	94.5(1), 93.8(1), 99.4(1)	101.3(2), 94.5(3), 94.7(2)
E-Co-N$_{(endocyc)}$	86.0(1), 84.8(1), 91.2(1)	87.3(1), 85.4(2), 85.6(1)
E-Co-N$_{(trans)}$	173.2(1), 173.2(1), 171.0(1)	172.0(1), 172.0(2), 170.7(2)
P-E-Co	99.4(1), 100.6(1), 99.0(1)	95.7(1), 95.2(1), 96.3(2)
N-K-N	90.8(1), 80.5(1), 81.1(1)	79.8(2), 80.3(1), 89.6(2)

Table S4. Selected bond lengths (Å) and angles (º) for **3b** and **4b** (collected at 250 K).

	3b	**4b**
Co–E	2.570(1), 2.542(1), 2.500(1)	2.664(1), 2.596(1), 2.634(4)
Co–N	2.083(1), 2.089(1), 2.121(1)	2.088(4), 2.093(2), 2.131(2)
P=E	1.952(1), 1.954(1)	2.114(1), 2.103(1), 2.086(6)
P–E(Co)	1.985(1), 1.984(1), 1.982(1)	2.143(4), 2.134(1), 2.139(1)
Co···K	3.885(1)	3.877(1)
E-Co-E	88.1(1), 88.3(1), 87.1(1)	87.5(2), 86.8(2), 84.8(1)
N-Co-N	94.2(1), 100.0(1), 95.1(1)	101.6(2), 94.7(1), 95.8(3)
E-Co-N$_{(endocyc)}$	86.2(1), 84.7(1), 84.5(1)	87.0(1), 85.2(2), 85.5(1)
E-Co-N$_{(trans)}$	172.7(1), 171.8(1), 172.8(1)	172.0(1), 171.3(1), 170.0(2)
P-E-Co	99.5(1), 100.3(1), 98.9(1)	95.7(1), 95.3(1), 96.8(2)
N-K-N	90.8(1), 79.4(1), 80.9(1)	79.7(1), 79.3(1), 89.5(1)

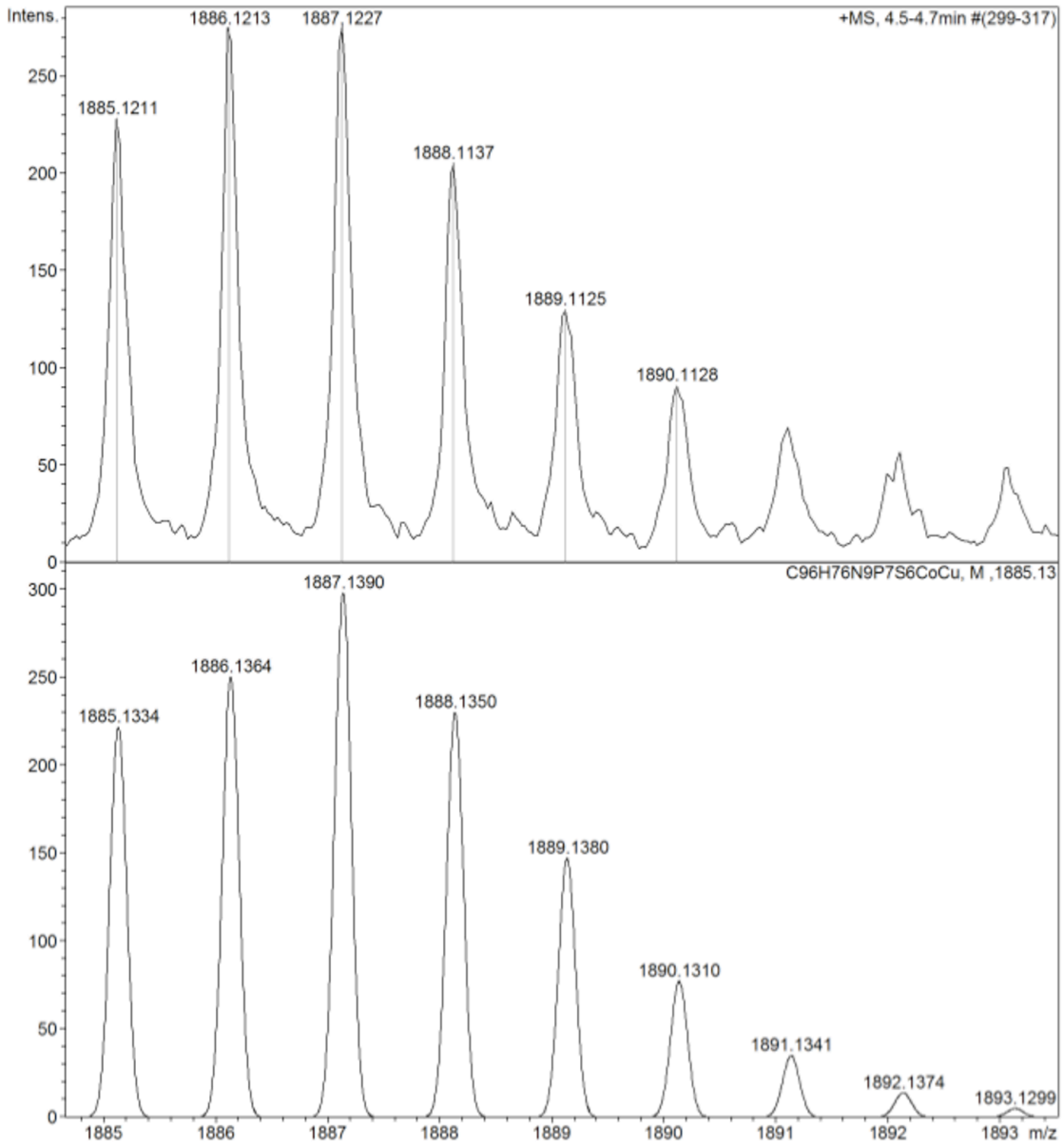

Figure S5. Experimental isotopic pattern for the [*M*+H]$^+$ peak in the high resolution ESI($^+$) mass spectrum of **7** (top) and the simulated isotopic pattern for the same fragment (bottom).

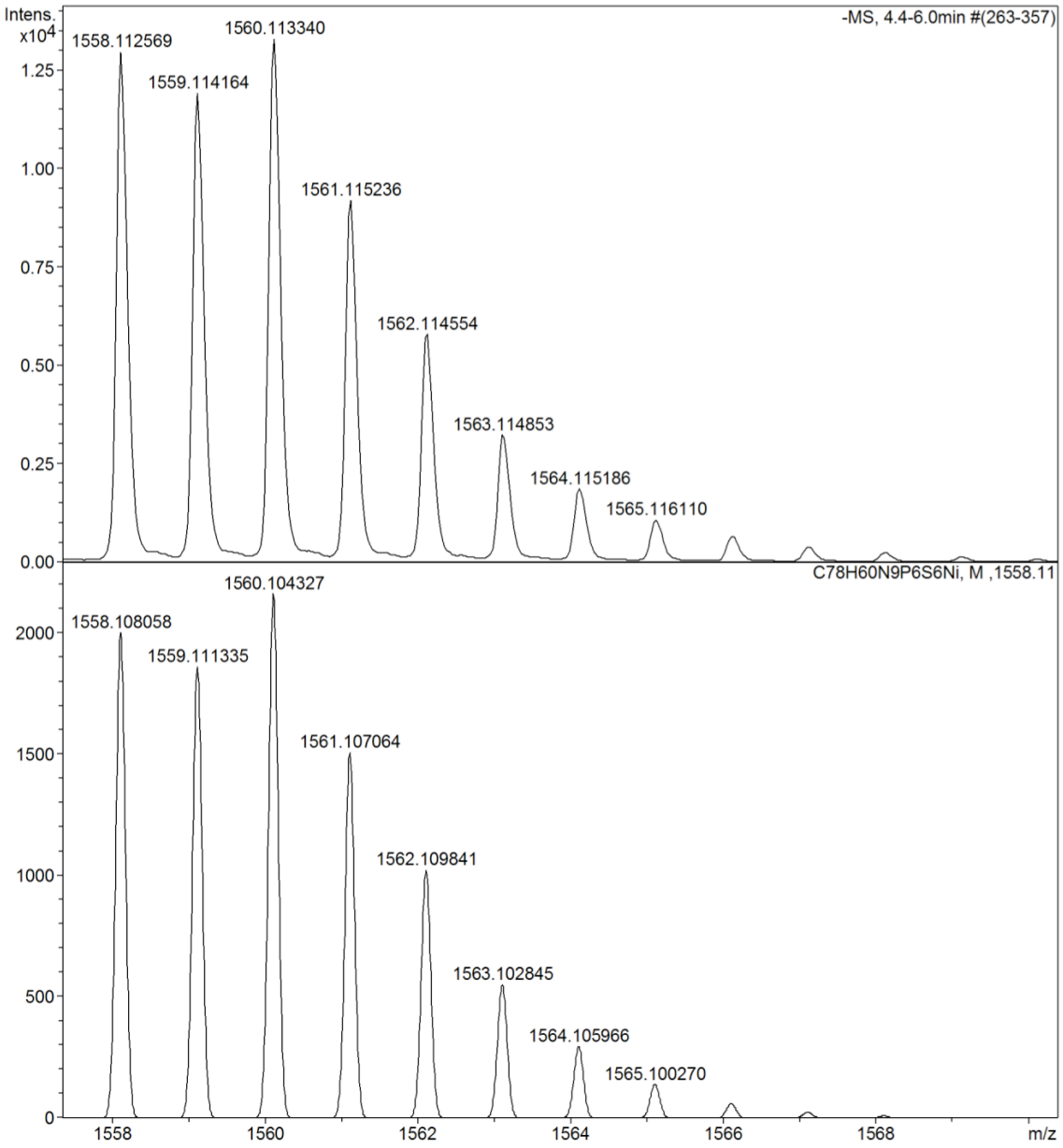

Figure S6. Experimental isotopic pattern for the [*M*–CuPPh$_3$]$^-$ peak in the high resolution ESI($^-$) mass spectrum of **8** (top) and the simulated isotopic pattern for the same fragment (bottom).

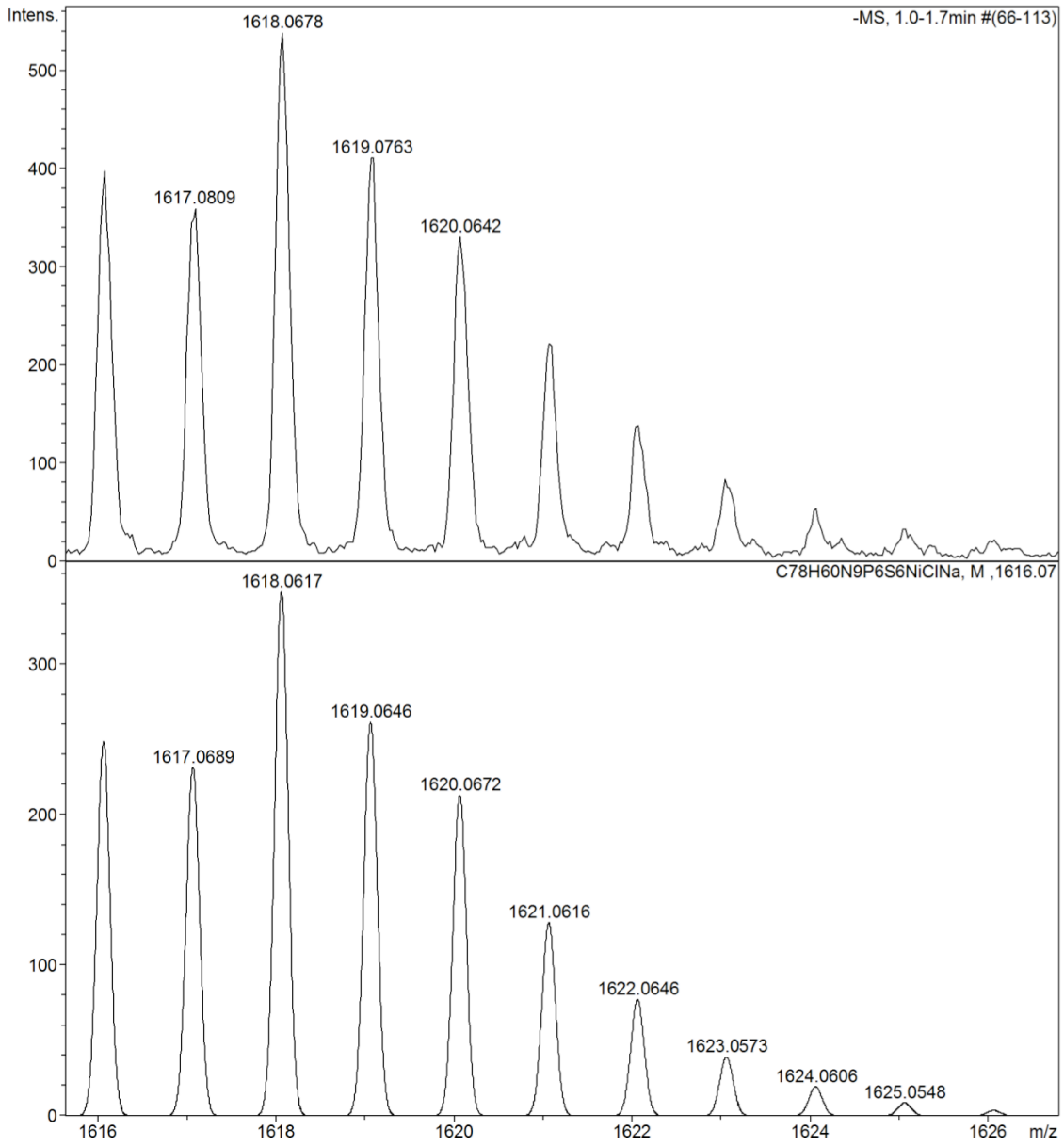

Figure S7. Experimental isotopic pattern for the $[Ni(L^{TzS})_3+NaCl]^-$ peak in the high resolution APCI(⁻) mass spectrum of **9** (top) and the simulated isotopic pattern for the same fragment (bottom).

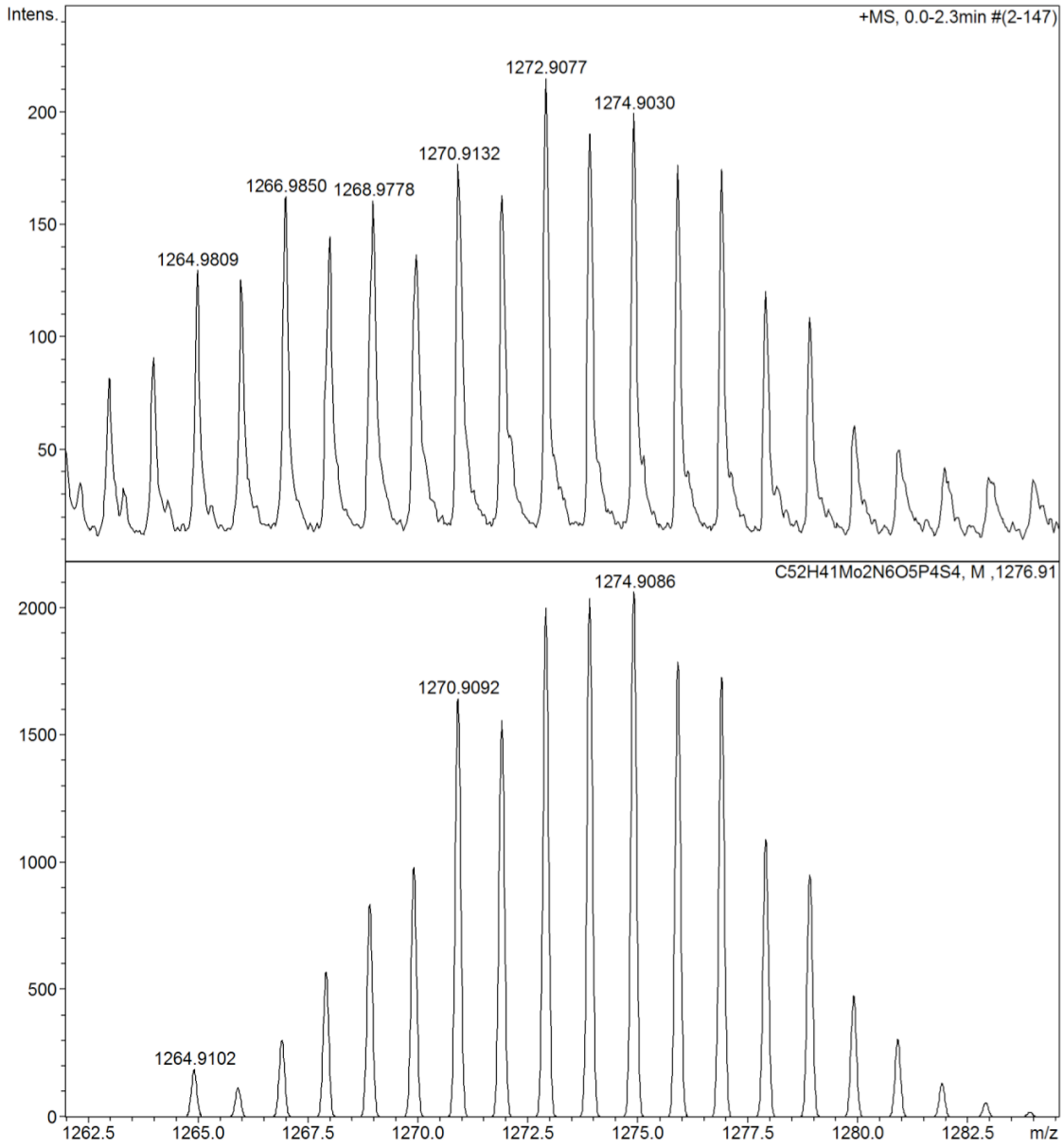

Figure S8. Experimental isotopic pattern for the [*M*+H]$^+$ peak in the high resolution APCI($^+$) mass spectrum of **10** (top) and the simulated isotopic pattern for the same fragment (bottom).

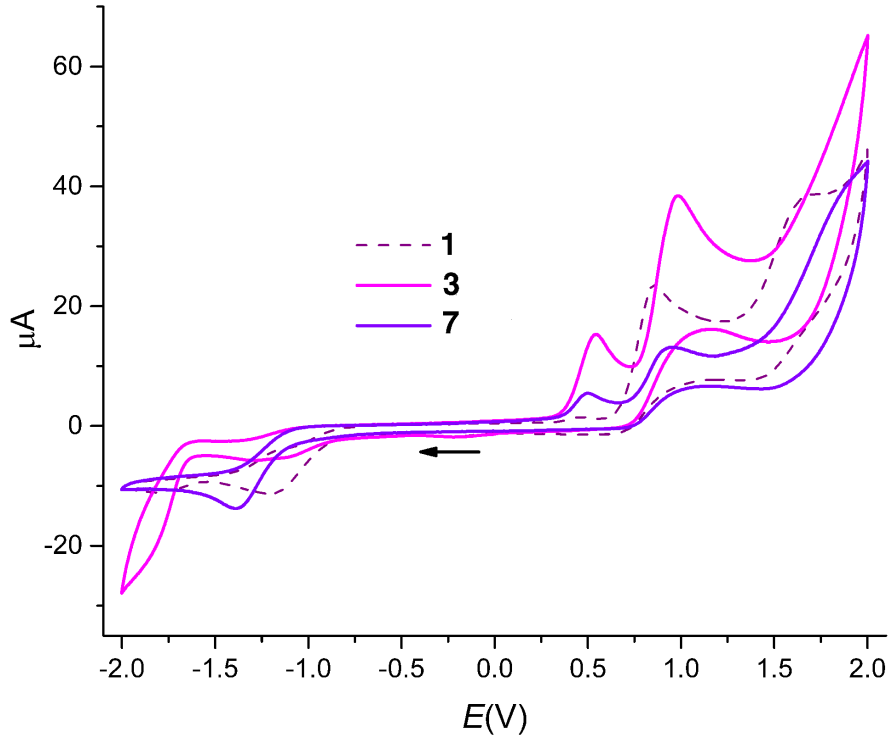

Figure S9. Cyclic voltammogram of compounds **3** and **7** against ligand **1** in CH_2Cl_2 with 0.1 M $[NBu_4][ClO_4]$ at a scan rate of 0.05 V s^{-1}.

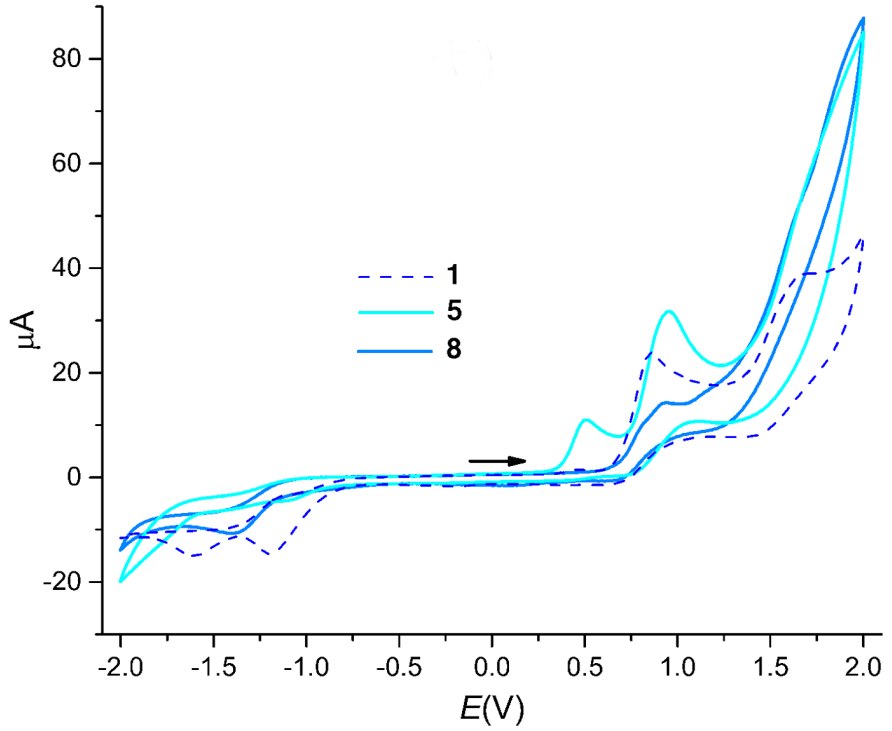

Figure S10. Cyclic voltammogram of compounds **5** and **8** against ligand **1** in CH_2Cl_2 with 0.1 M $[NBu_4][ClO_4]$ at a scan rate of 0.05 V s^{-1}.

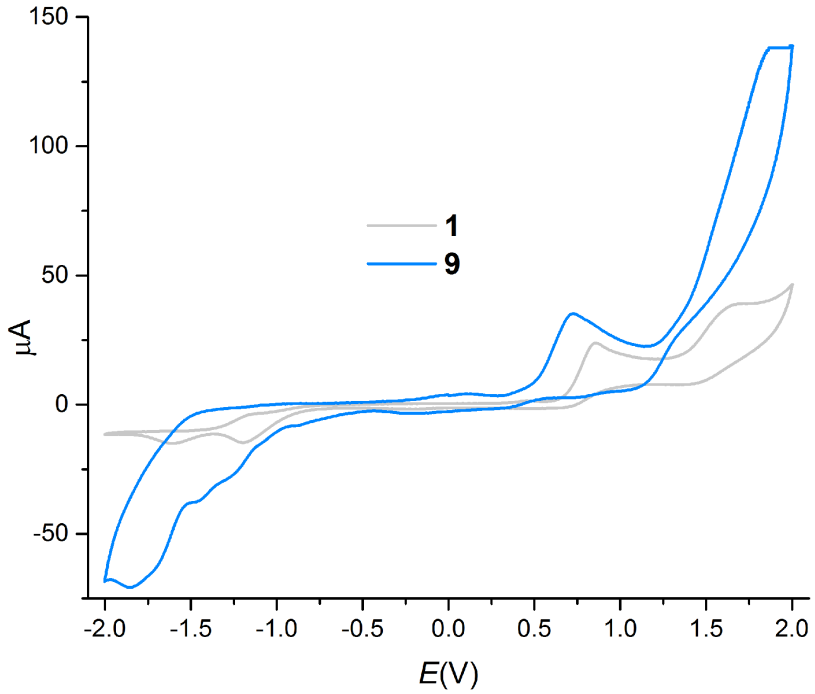

Figure S11. Cyclic voltammogram of compound **9** and ligand **1** in CH_2Cl_2 with 0.1 M $[NBu_4][ClO_4]$ at a scan rate of 0.05 V s^{-1}.

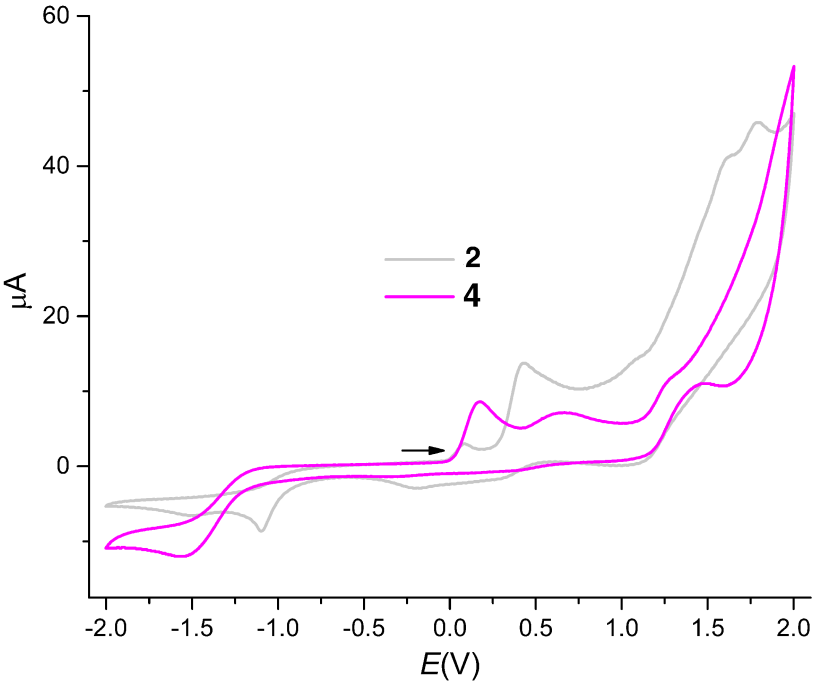

Figure S12. Cyclic voltammogram of compound **4** and ligand **2** in CH_2Cl_2 with 0.1 M $[NBu_4][ClO_4]$ at a scan rate of 0.05 V s^{-1}.

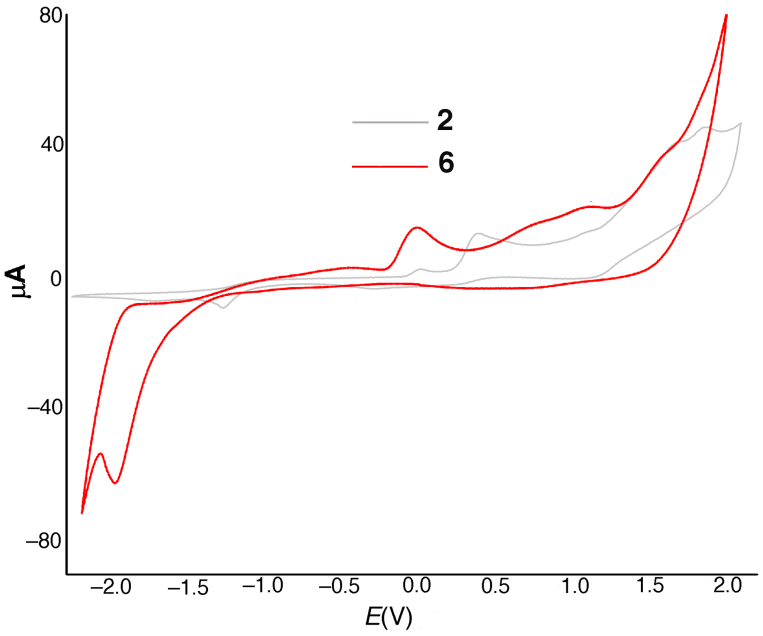

Figure S13. Cyclic voltammogram of compound **6** and ligand **2** in CH_2Cl_2 with 0.1 M $[NBu_4][ClO_4]$ at a scan rate of 0.05 V s^{-1}.

Table S5. Crystal data and structure refinement details for compounds **8**–**10**

	8·2.632THF·2.369CH_2Cl_2	**9**·5.888THF	**10**·2CH_2Cl_2
Empirical formula	$C_{108.90}H_{100.79}Cl_{4.74}CuN_9NiO_{2.63}P_7S_6$	$C_{105.55}H_{115.10}N_{10}Ni_2O_{9.89}P_6S_6$	$C_{54}H_{44}Cl_4Mo_2N_6O_5P_4S_4$
Formula weight	2272.08	2177.61	1442.75
Space group	Triclinic	Triclinic	Monoclinic
Crystal system	$P\bar{1}$	$P\bar{1}$	$C2/c$
a/Å	16.0347(5)	16.0990(10)	27.9452(6)
b/Å	17.7231(6)	16.7130(10)	10.2398(2)
c/Å	19.7522(6)	20.6239(12)	24.6315(9)
α/°	81.0699(6)	84.1575(13)	90
β/°	78.5117(6)	73.4498(12)	122.6709(7)
γ/°	81.7524(6)	79.8242(13)	90
Unit cell volume/Å^3	5397.3(3)	5227.8(5)	5933.2(3)
Temperature/K	100(2)	100(2)	100(2)
Wavelength/Å	0.71073	0.71073	0.71073
Z	2	2	4
$\rho_{(calc.)}$/g cm^{-3}	1.401	1.389	1.615
μ (mm^{-1})	0.763	0.635	0.904
Crystal size/mm^3	0.21 x 0.15 x 0.14	0.27 x 0.16 x 0.10	0.14 x 0.13 x 0.12
Refl. collected	99525	96610	42508
Unique refl. (R_{int})	24639 (0.0470)	23891 (0.0463)	6784 (0.0199)
R_1,[a] wR_2[b] (I>2σ(I))	0.0390, 0.0932	0.0382, 0.0872	0.0220, 0.0564
R_1,[a] wR_2[b] (all data)	0.0533, 0.1007	0.0511, 0.0936	0.0234, 0.0574
GooF	1.023	1.021	1.065

[a]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b]w$R_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(F_o^2)^2]^{1/2}$