Electronic Supplementary Material (ESI) for Dalton Transactions.
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Supporting Information for

Heteroleptic Complexes via Solubility Control: Examples of Cu(II), Co(II), Ni(II) and Mn(II) complexes Based on the Derivatives of Terpyridine and Hydroxyquinoline

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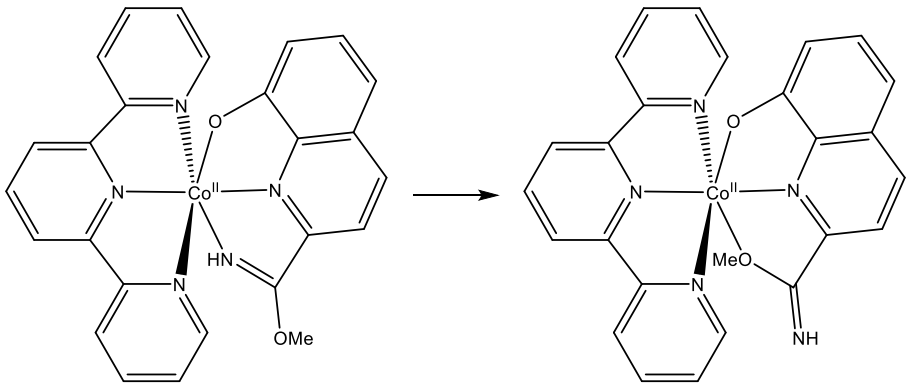
DFT calculations

The intramolecular coordination in the Co complex was studied using static calculations within DFT. The computed isodesmic reactions indicate that **1** is the global minimum with the preferred coordination conformer in which the imine group nitrogen atom is completing the sixths coordination site in the octahedral Co complex. The conformer in which the oxygen is coordinating to the Co atom, **1'**, is 8.70/7.96 kcal/mol higher in enthalpy/free energy than **1**. The five-coordinated Co complex, **2**, is unstable in the presence of methanol. The methanol addition to **2** and the subsequent coordination of the imine group to the Co atom is highly exothermic with **1** being -33.43/19.48 kcal/mol lower in enthalpy/free energy that **2** and methanol.

(1)

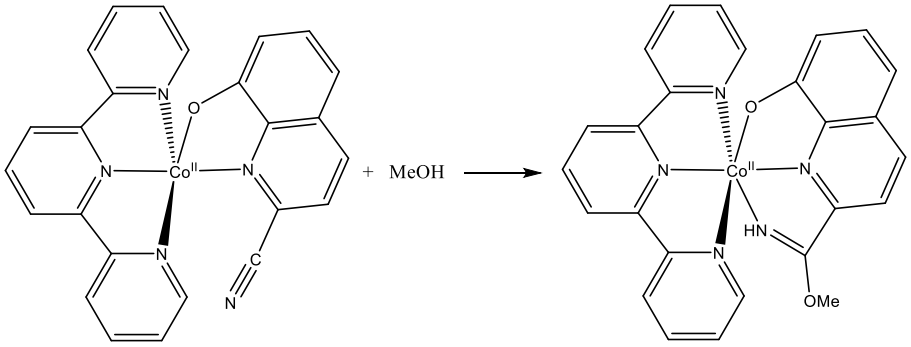


1 **1'**

ΔH/ΔG (kcal/mol)

8.70/7.96

(2)



2 **1**

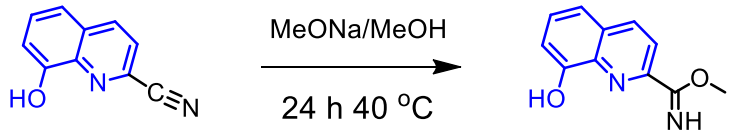
-33.43/-19.48

Computational details:

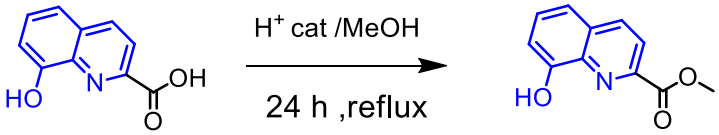
1. The calculations were performed with the Gaussian 09' software, using the PBE1PBE functional with the 6-31+G(d,p) basis set. Stable=opt utility was employed to ensure the conversion of the wavefunction to the lowest state. All geometries were optimized ensuring a local minimum configuration with all positive frequencies.

2. The quartet spin state of **1**, indicating three unpaired electrons, was confirmed with the computed S^2 value of 3.77 being the global minimum while the doublet state, computed S^2 value of 0.76, being 7.15/9.57 kcal/mol higher in enthalpy/free energy.

3. All trials to locate the conformer of **1** in which neither N nor O are completing the sixths coordination site of Co failed, and resulted in either **1** or **1'**.



Scheme 1. Synthesis of methyl 8-hydroxyquinoline-2-carboxyimidate (**HQOMe**)



Scheme 2. Synthesis of methyl 8-hydroxyquinoline-2-carboxylate (**HQO$_2$Me**)

Solubility experiment of HQ_2Cu and Q_2Cu

To a solution of Cu(II) triflate (53 mg, 0.1465mmol, 29 mM) in 5 mL ACN 2 equivalents of the ligands 8-hydroxyquinoline or 8-hydroxy-2-quinolinecarbonitrile (42.65 mg and 50 mg respectively, 0.293 mmol, 58 mM) in 5 mL ACN was added dropwise. After stirring for 2 hours at 50°C the precipitates were separated from the solution by centrifugation, washed twice with water and lyophilized overnight. The final weight of the products HQ_2Cu and $(HQCN)_2Cu$, as verified by UV-Vis (Fig. S2), was 20.7 mg and 1.3 mg, respectively.

Synthesis of TQ'Co complex by the direct approach

To a solution of Co(II) acetate (53.3 mg, 0.215mmol, 43mM) in 5mL MeOH an equimolar amount of the ligands Terpy and methyl 8-hydroxyquinoline-2-carboximidate (HQOMe) (50 mg and 43.5 mg respectively, 0.215 mmol, 43mM each) in 5 mL MeOH was added dropwise. After stirring for 2 hours at 50°C the complex was precipitated by addition of 10 folds excess of NH_4PF_6 in 15 ml of water. The precipitate was separated from the solution by centrifugation, washed twice with water and lyophilized overnight. Final product weight and yield: 111 mg, 82%. The complex was crystalized by slow diffusion of di ethyl ether to a complex dissolved in ACN. The identity of the **TQ'Co** complex was verified by UV-Vis, ESI-MS (Fig. S5&21) and the cell parameters obtained from the X-ray analysis of this product were identical to ones obtained for **TQ'Co** complex.

Attempt to synthesize $Q'_4Q''_2Mn_4$ complex by the direct approach

To a solution of 1 equivalents of Mn(II) acetate (52.5 mg, 0.215mmol, 43mM) in 5mL MeOH mixture of the ligands methyl 8-hydroxyquinoline-2-carboximidate (1 equivalent, 43.1 mg, 0.215mmol) and methyl 8-hydroxyquinoline-2-carboxylate (0.5 equivalents, 21.7 mg, 0.107mmol) in 5 mL MeOH was added dropwise. After stirring for 2 hours at 50°C the complex was precipitated by addition of 10 folds excess of NH_4PF_6 in 12 ml of water. The precipitate was separated from the solution by centrifugation, washed twice with water and lyophilized overnight, to obtain 40 mg of product. The complex was crystalized by slow diffusion of di ethyl ether to a complex dissolved in ACN.

UV-Vis

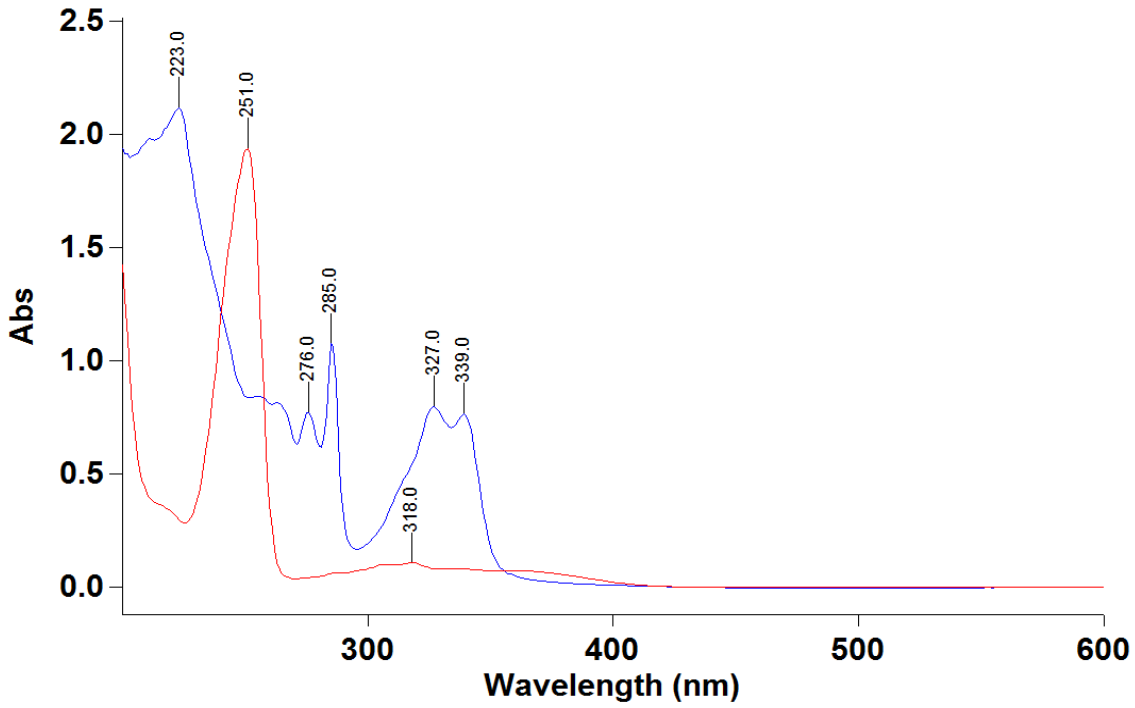


Figure S1. UV-Vis spectrum of green precipitate **HQ_2Cu** (red line) and blue solution with complex **$Terpy_2Cu$** (blue line) measured in MeOH.

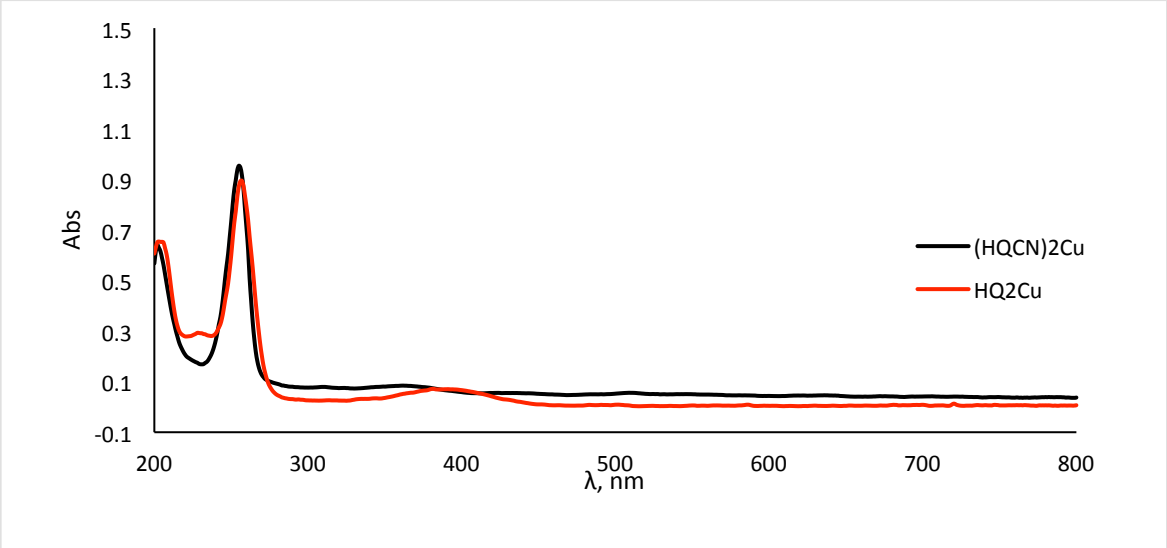


Figure S2. UV-Vis spectrum of **$(HQCN)_2Cu$** (black line) and **HQ_2Cu** (red line) measured in MeOH.

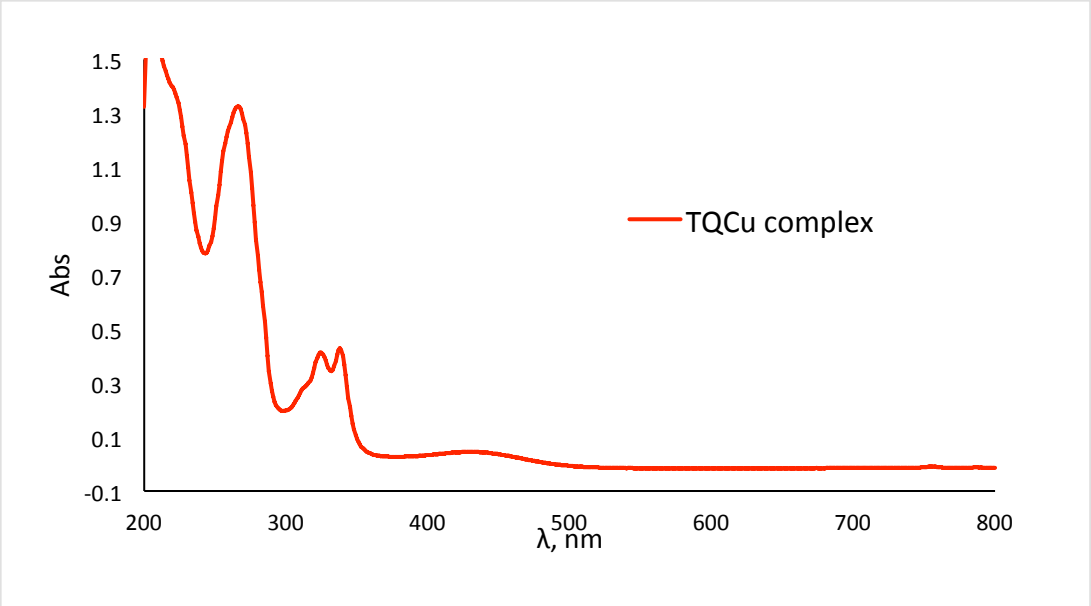


Figure S3. UV-Vis spectrum of **TQCu** complex (36 µM) measured in MeOH.

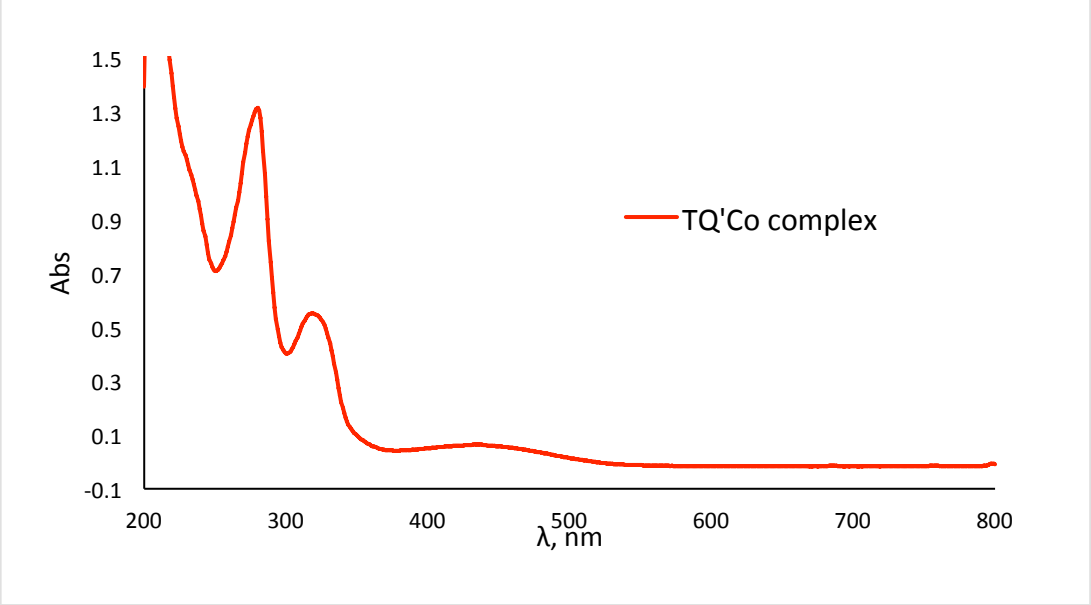


Figure S4. UV-Vis spectrum of **TQ'Co** complex (36 µM) measured in MeOH.

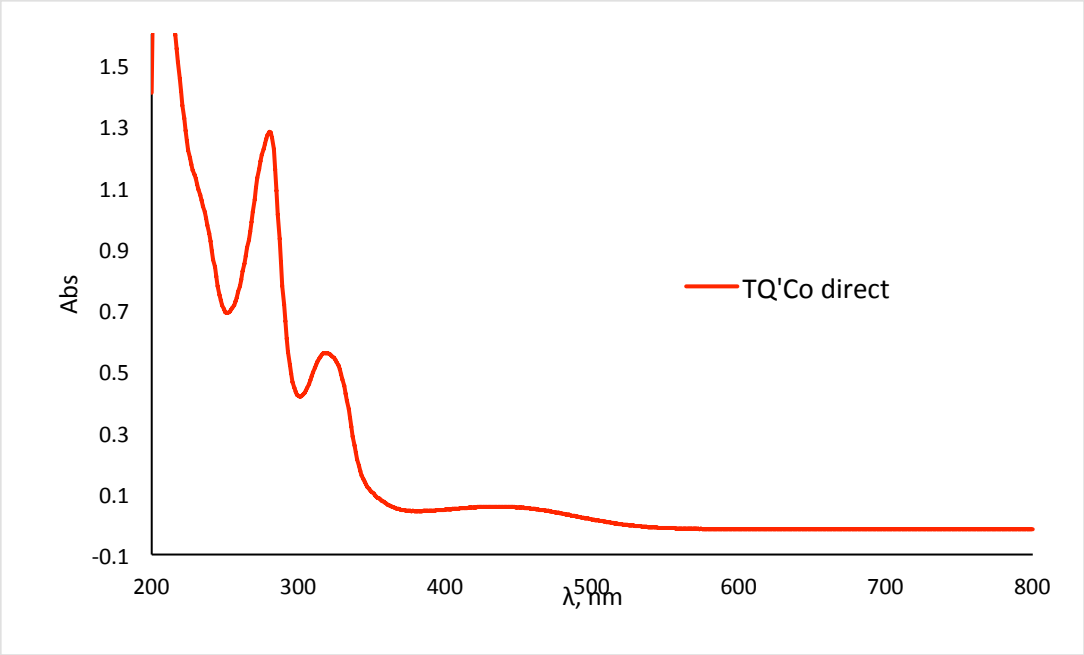


Figure S5. UV-Vis spectrum of **TQ'Co** complex (36 μM) synthesized by direct approach measured in MeOH.

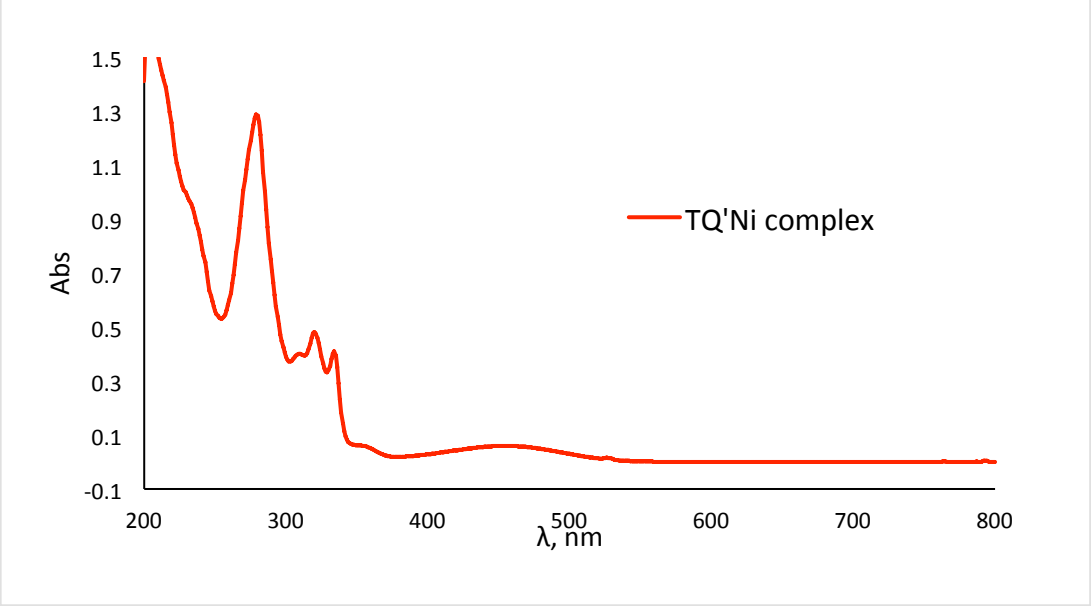


Figure S6. UV-Vis spectrum of **TQ'Ni** complex (36 μM) measured in MeOH.

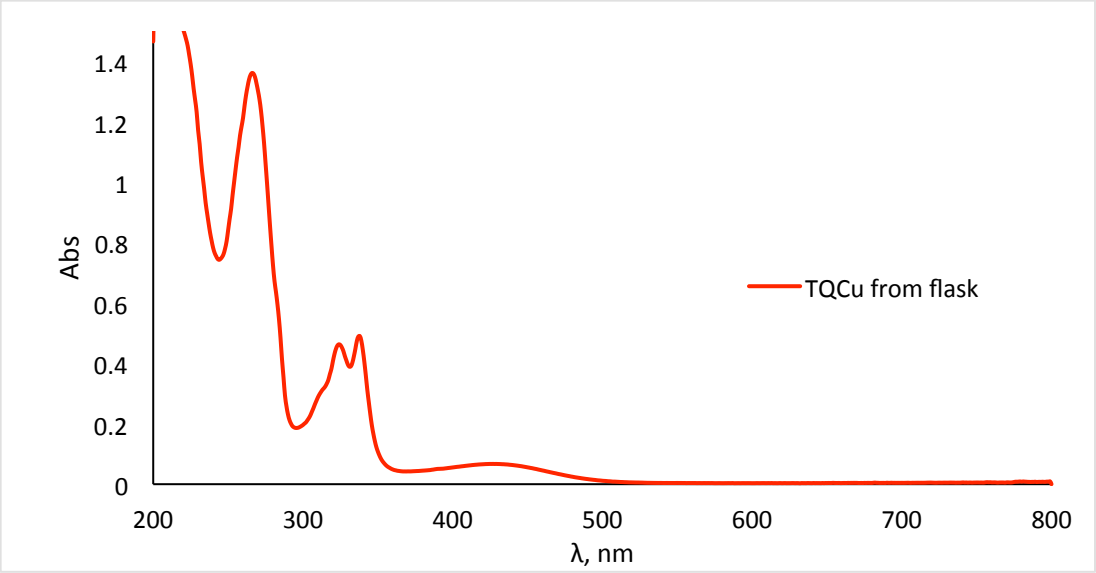


Figure S7. UV-Vis spectrum of **TQCu** complex from the reaction solution measured in MeOH.

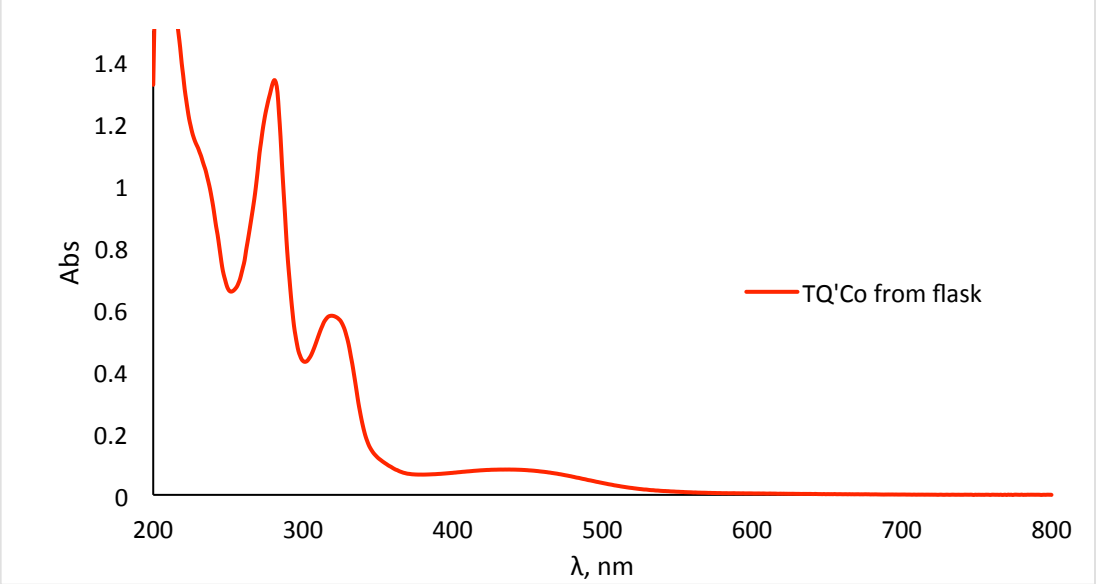


Figure S8. UV-Vis spectrum of **TQ'Co** complex from the reaction solution measured in MeOH.

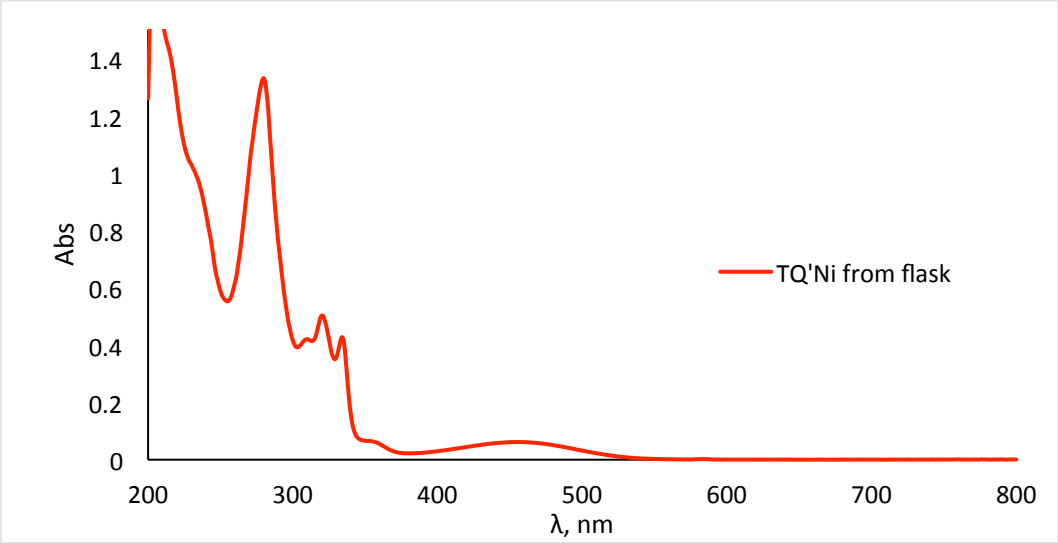


Figure S9. UV-Vis spectrum of **TQ'Ni** complex from the reaction solution measured in MeOH.

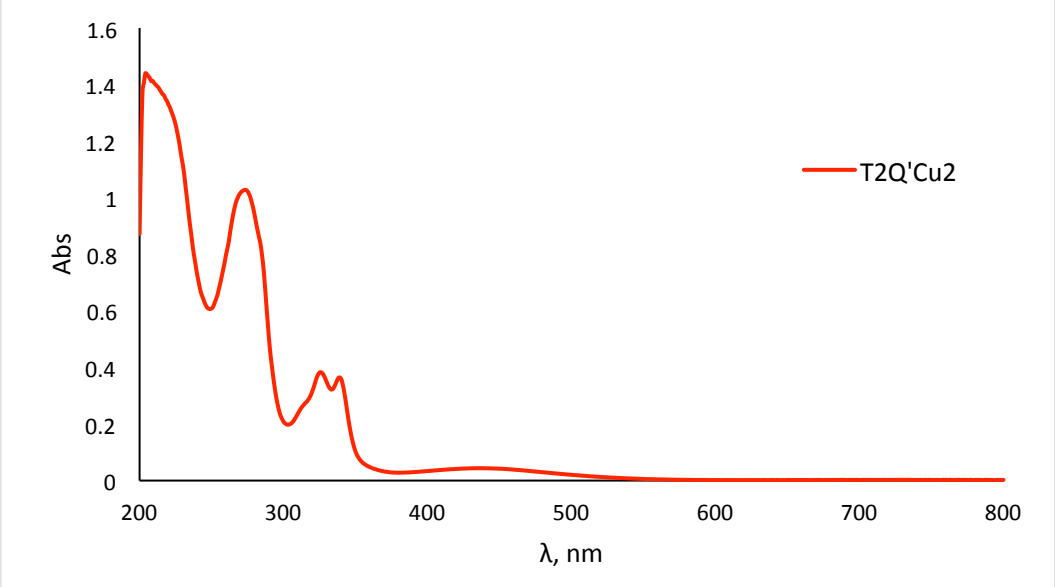


Figure S10. UV-Vis spectrum of of **$T_2Q'Cu_2$** complex measured in MeOH.

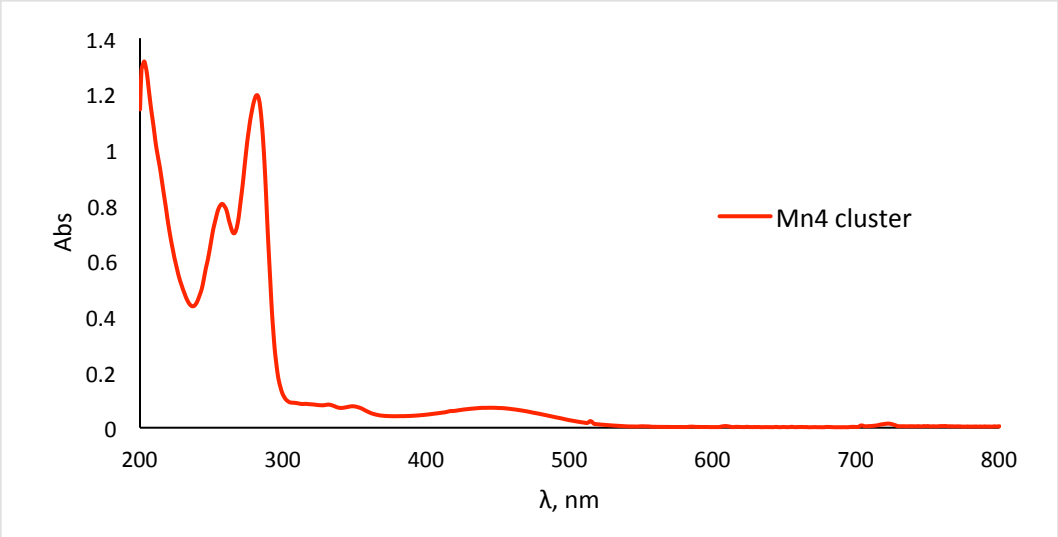


Figure S11. UV-Vis spectrum of **Q'$_4$Q''$_2$Mn4** cluster (8 µM) measured in MeOH.

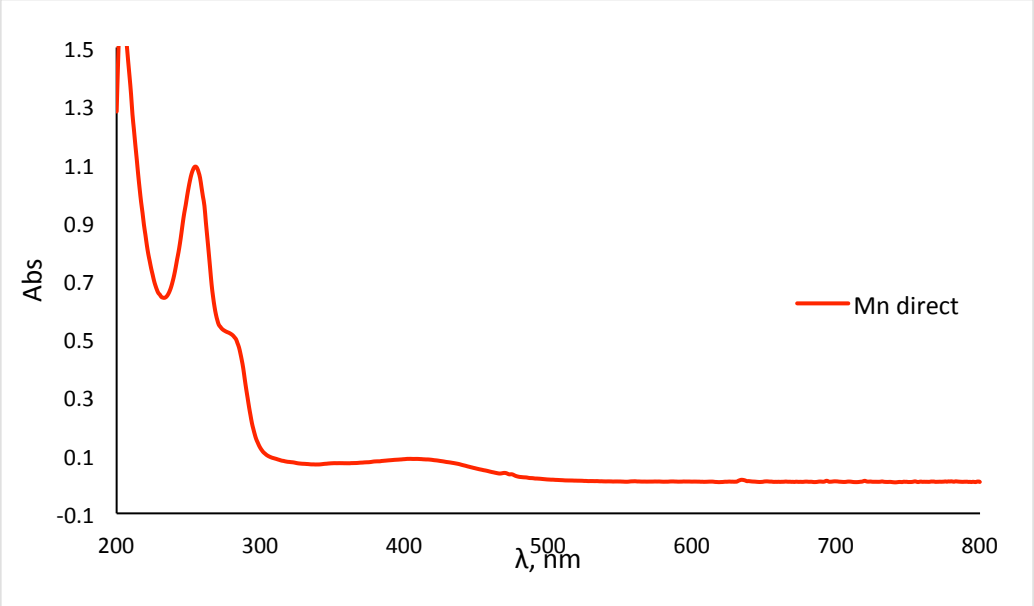


Figure S12. UV-Vis spectrum of an attempt to synthesize **Q'$_4$Q''$_2$Mn4** cluster by direct approach, measured in MeOH.

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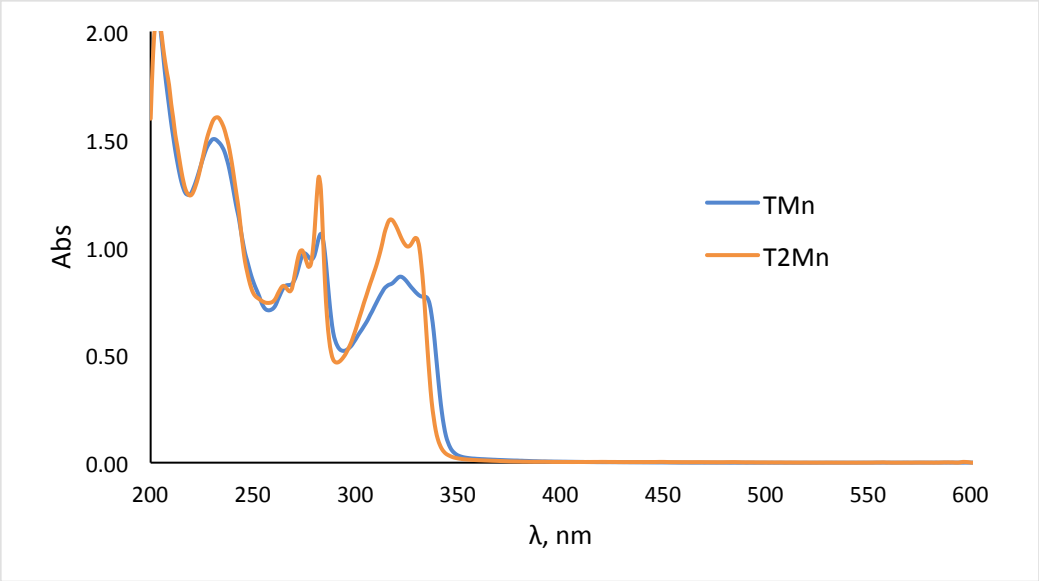


Figure S13. UV-Vis spectrum of **TMn** and **T_2Mn** complexes in MeOH.

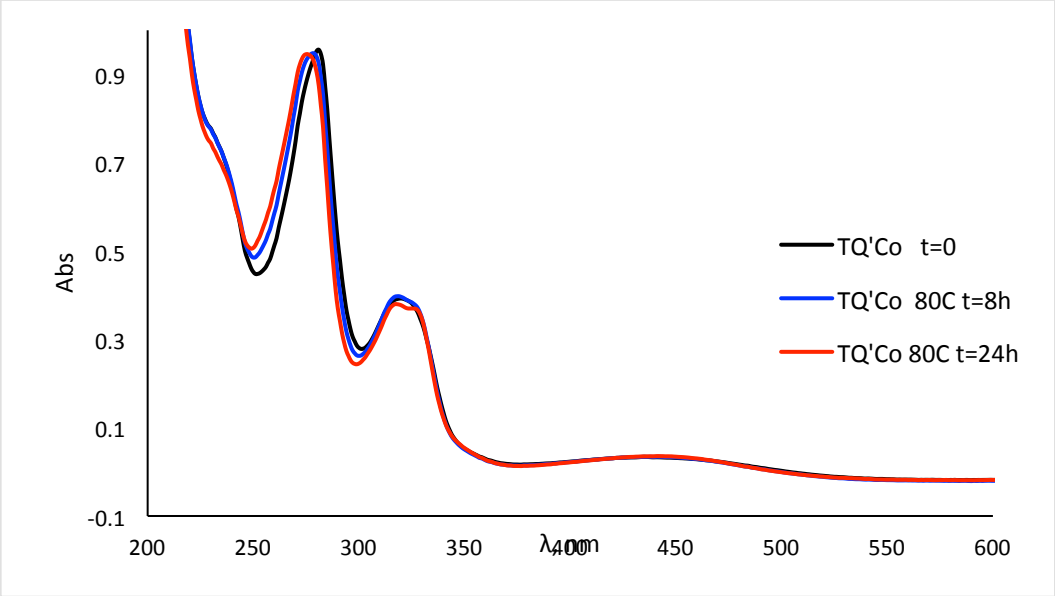


Figure S14. Kinetic stability of the **TQ'Co** complex. UV-Vis spectrum measured in MeOH before and after 8 and 24 hours of heating at 80°C.

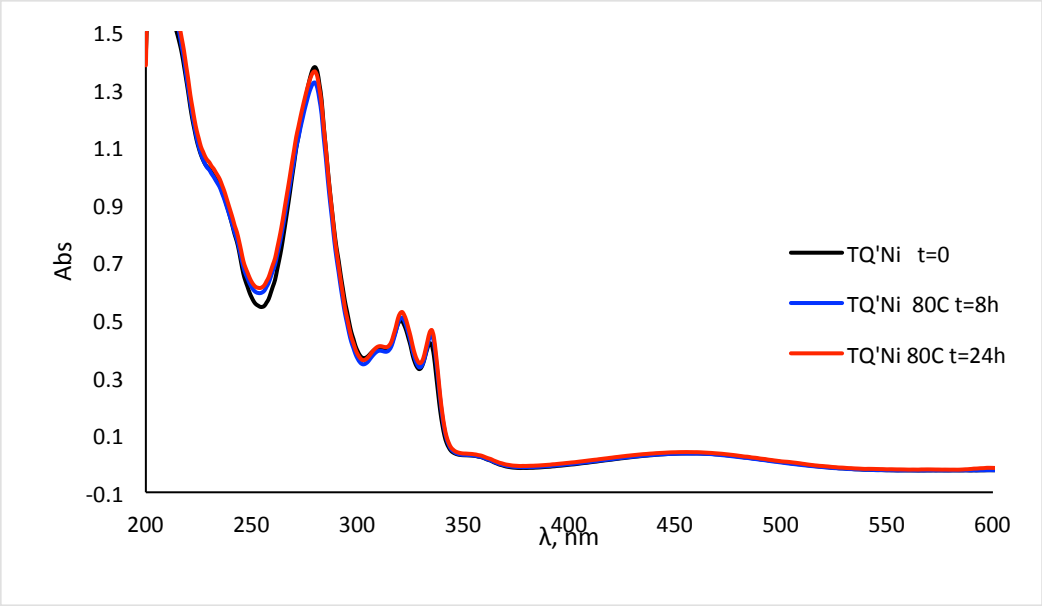


Figure S15. Kinetic stability of the **TQ'Ni** complex. UV-Vis spectrum measured in MeOH before and after 8 and 24 hours of heating at 80°C.

MS analyses:

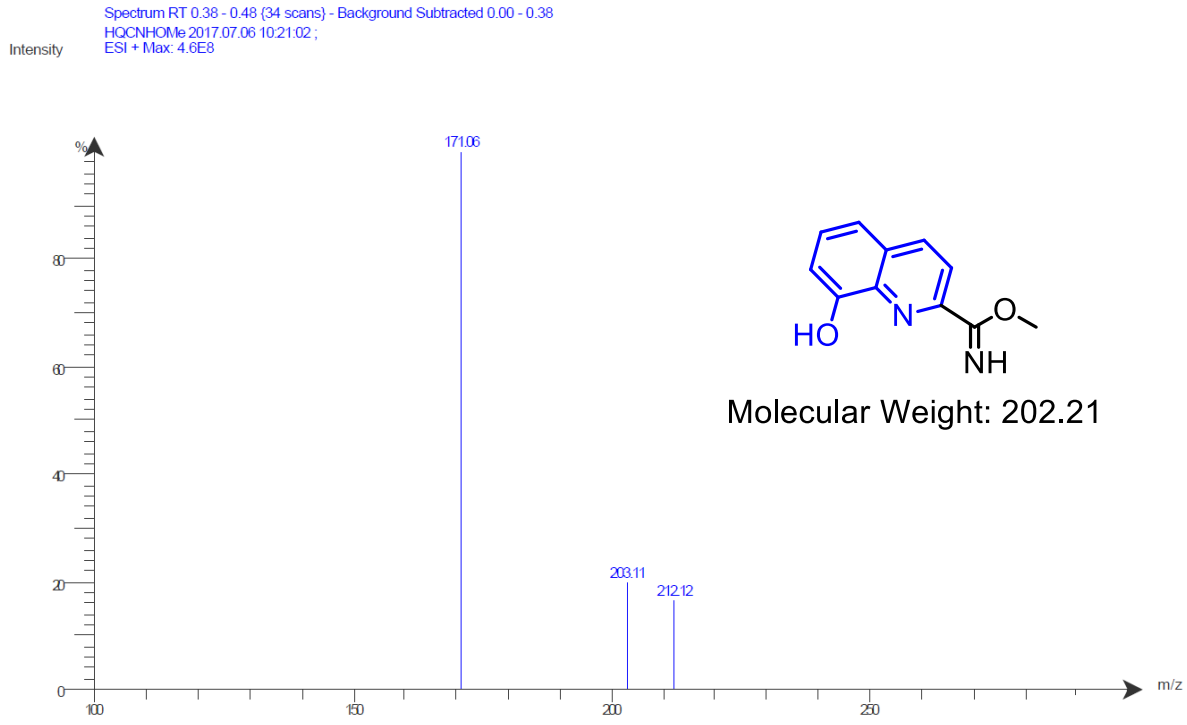


Figure S16. ESI-MS traces of methyl 8-hydroxyquinoline-2-carboxyimidate (HQOMe).

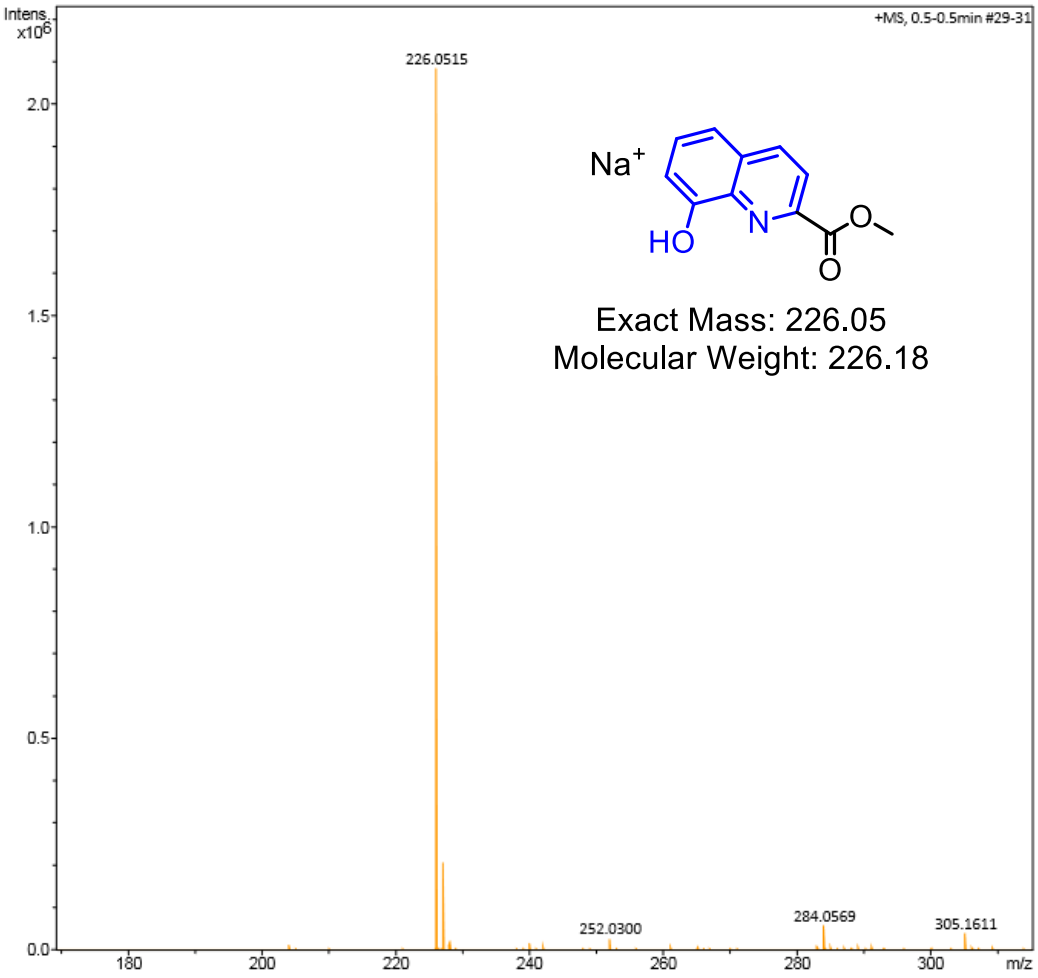


Figure S17. ESI-MS traces of methyl 8-hydroxyquinoline-2-carboxylate (HQO_2Me).

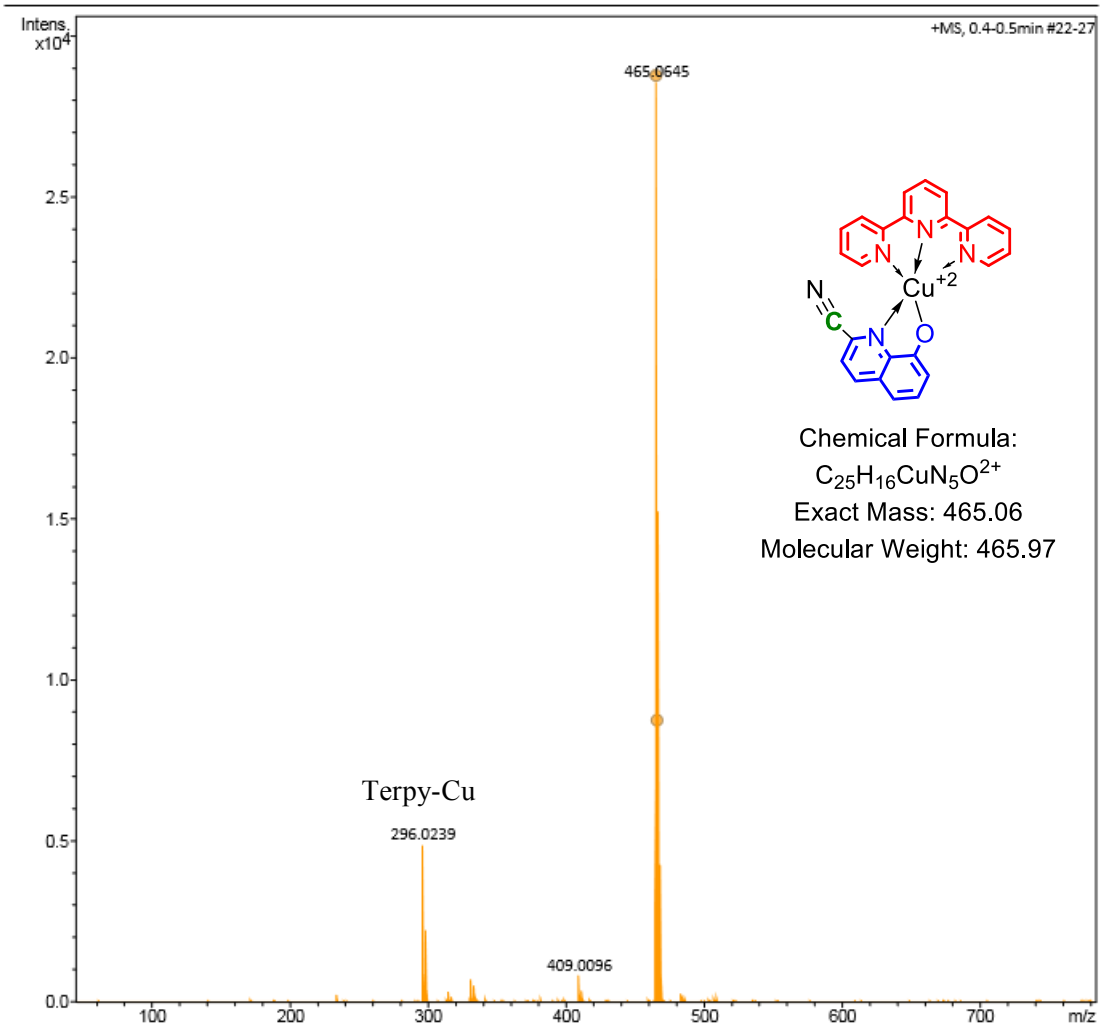


Figure S18. ESI-MS traces of **TQCu** complex.

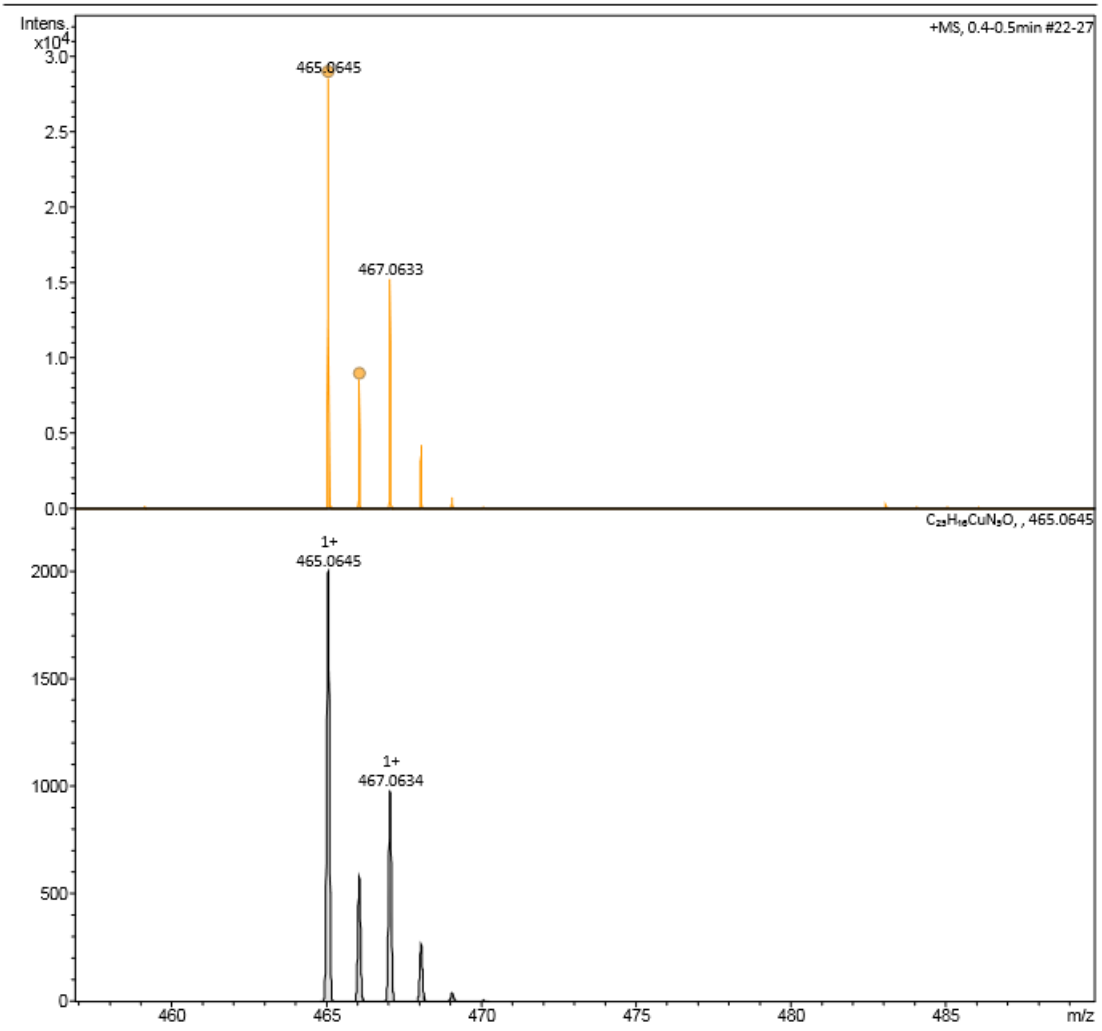


Figure S19. High resolution ESI-MS traces of **TQCu** complex. Experimental isotopic analysis by ESI-MS of **TQCu** complex (top) and calculated ESI-MS spectrum (bottom).

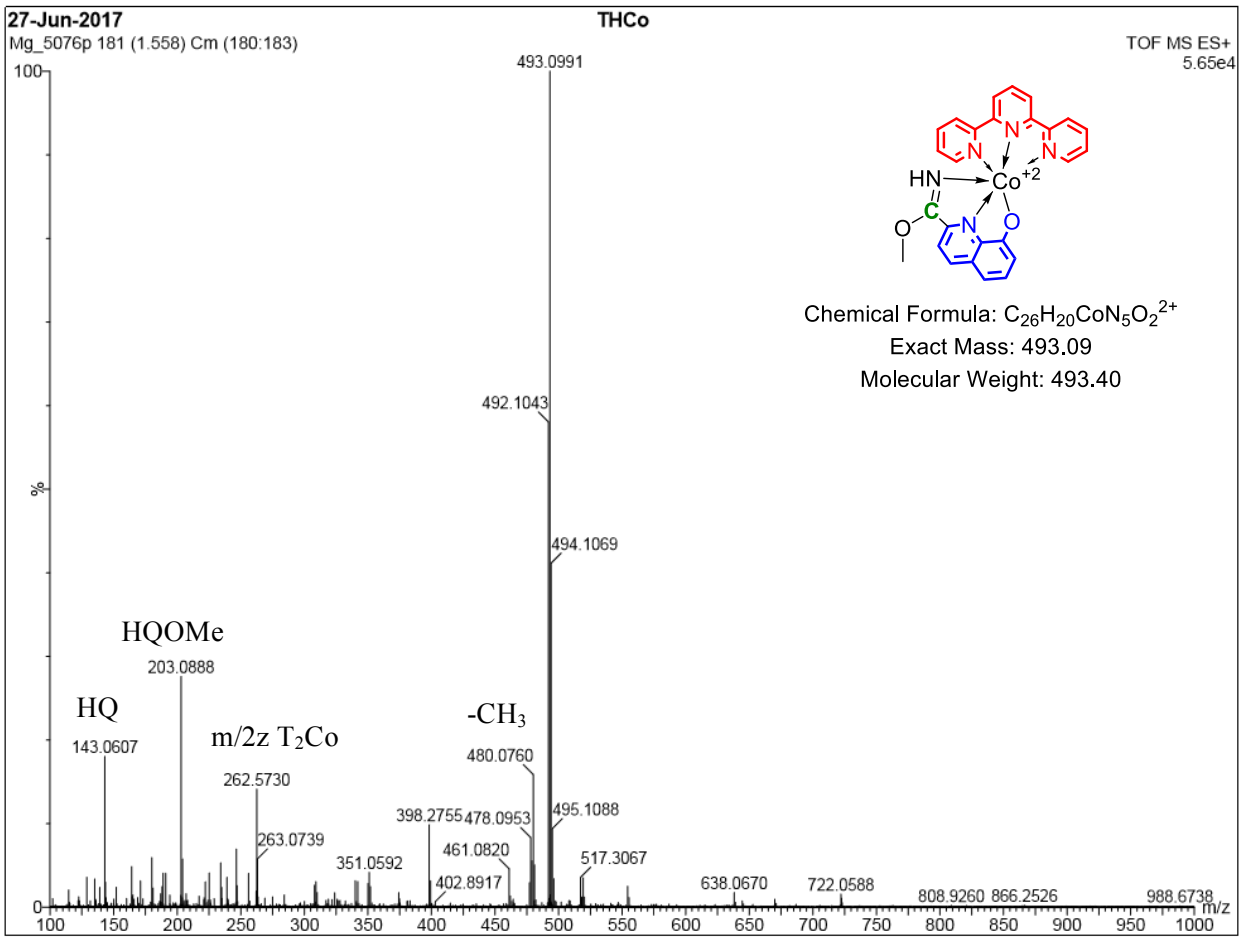


Figure S20. ESI-MS traces of **TQ'Co** complex.

Elemental Composition Report **Page 1**

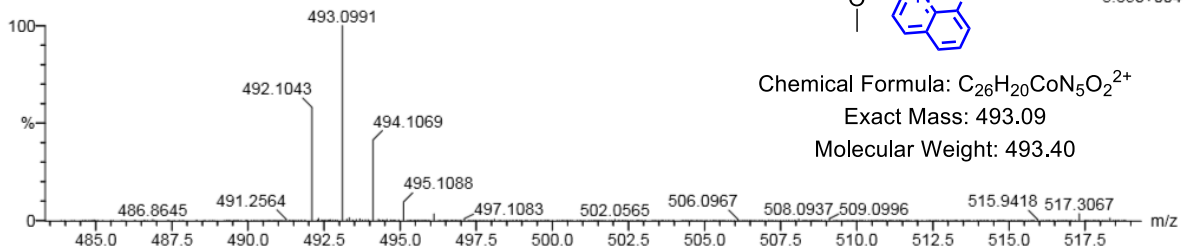
Single Mass Analysis
Tolerance = 40.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

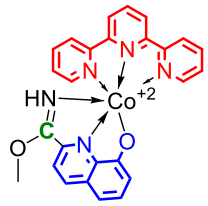
Monoisotopic Mass, Even Electron Ions
96 formula(e) evaluated with 4 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 24-27 H: 19-23 N: 1-10 O: 0-5 Co: 0-2

27-Jun-2017
Mg_5076p 181 (1.558) Cm (180:183)

THCo

TOF MS ES+
5.65e+004





Chemical Formula: $C_{26}H_{20}CoN_5O_2^{2+}$
Exact Mass: 493.09
Molecular Weight: 493.40

Minimum:				-1.5		
Maximum:		40.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
493.0991	493.0949	4.2	8.5	19.5	1050.2	C26 H20 N5 O2 Co
	493.0837	15.4	31.2	19.5	1171.5	C27 H20 N3 O3 Co
	493.1061	-7.0	-14.2	19.5	1181.0	C25 H20 N7 O Co
	493.1174	-18.3	-37.1	19.5	1563.2	C24 H20 N9 Co

Figure S21. High resolution ESI-MS report of **TQ'Co** complex.

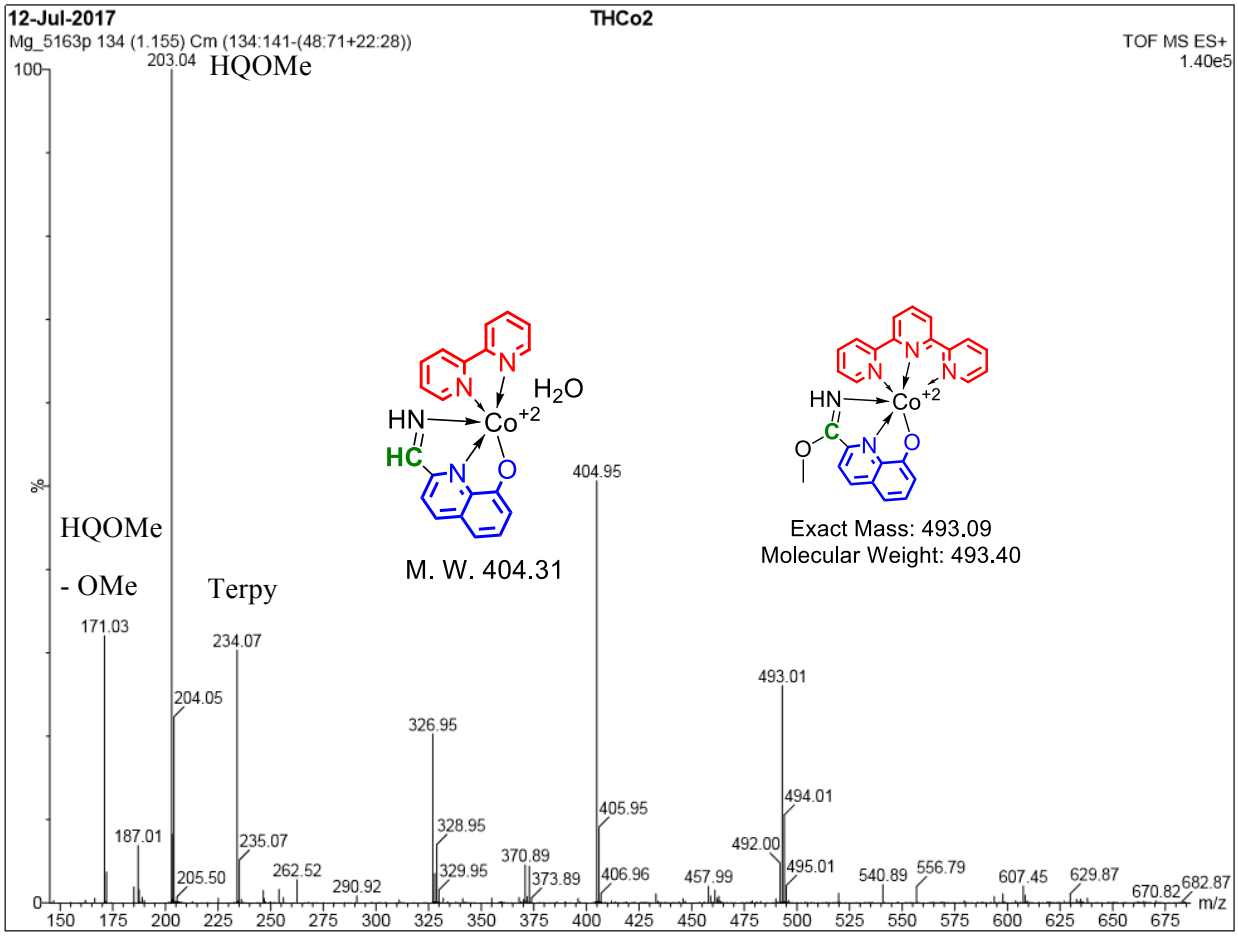


Figure S22. ESI-MS traces of **TQ'Co** complex synthesized by direct approach.

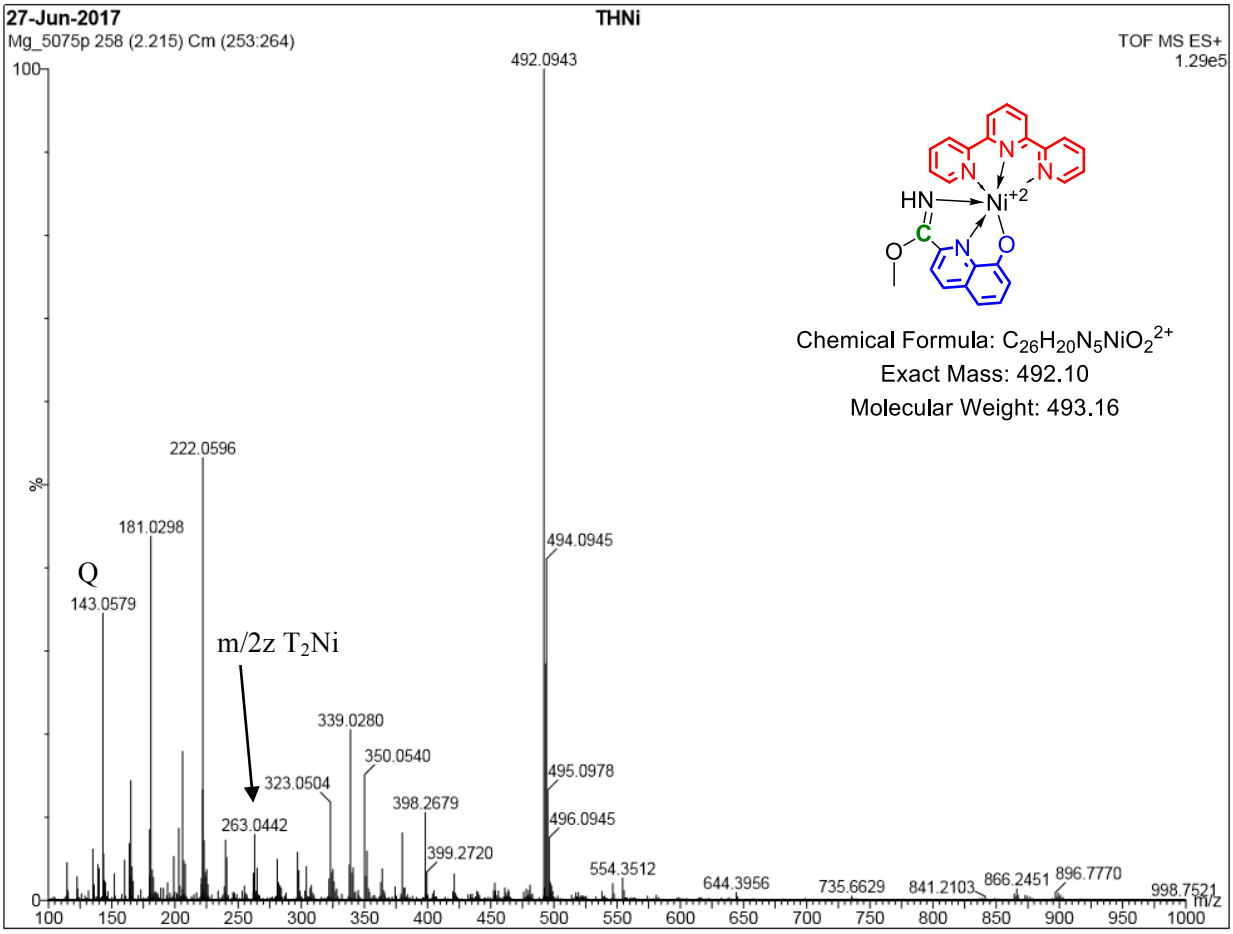
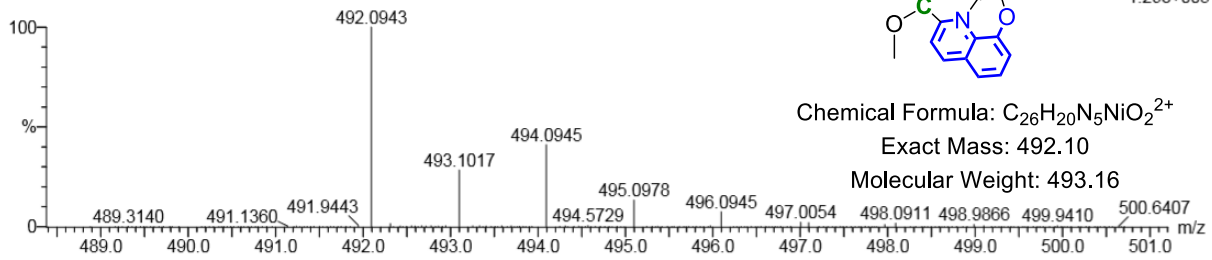
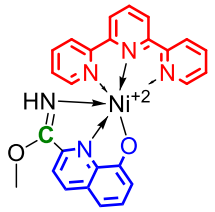


Figure S23. ESI-MS traces of **TQ'Ni** complex.

Single Mass Analysis
Tolerance = 40.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
47 formula(e) evaluated with 7 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 24-27 H: 19-23 N: 1-10 O: 0-5 Ni: 0-1
27-Jun-2017 THNi
Mg_5075p 258 (2.215) Cm (253:264)





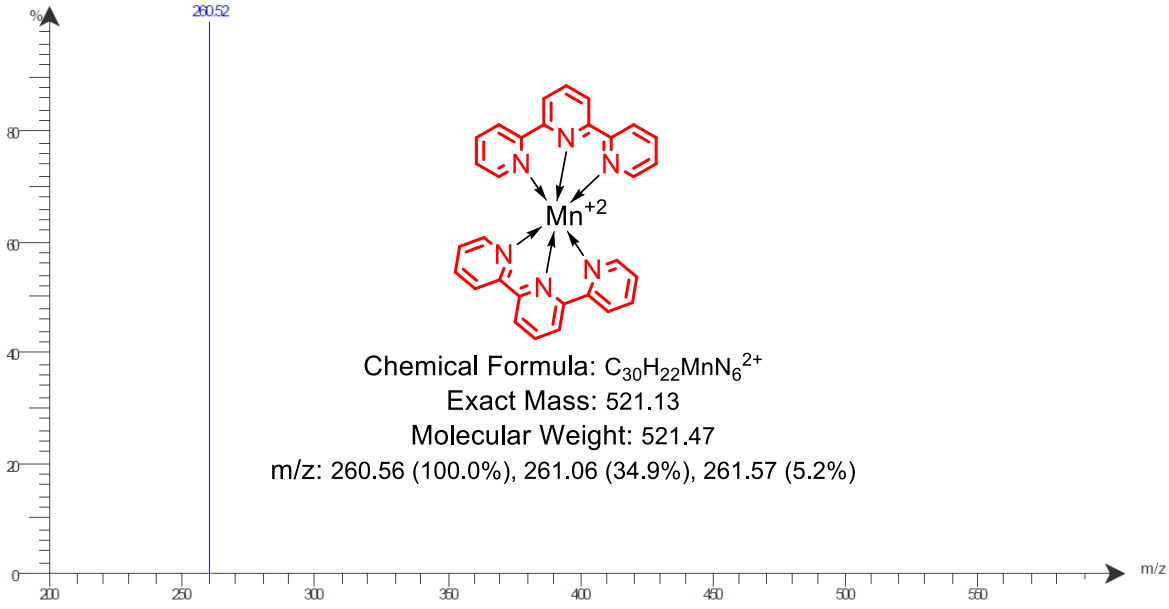
TOF MS ES+
1.29e+005

Chemical Formula: $C_{26}H_{20}N_5NiO_2^{2+}$
Exact Mass: 492.10
Molecular Weight: 493.16

Minimum:				-1.5		
Maximum:		40.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
492.0943	492.0970	-2.7	-5.5	20.0	156.7	C26 H20 N5 O2 Ni
	492.0858	8.5	17.3	20.0	450.2	C27 H20 N3 O3 Ni
	492.1083	-14.0	-28.4	20.0	497.8	C25 H20 N7 O Ni
	492.1096	-15.3	-31.1	19.5	703.4	C27 H22 N4 O2 Ni
	492.1195	-25.2	-51.2	20.0	1464.7	C24 H20 N9 Ni
	492.1209	-26.6	-54.1	19.5	1733.0	C26 H22 N6 O Ni
	492.1321	-37.8	-76.8	19.5	3403.0	C25 H22 N8 Ni

Figure S24. High resolution ESI-MS report of **TQ'Ni** complex.

Spectrum RT 0.38 - 0.93 {91 scans} - Background Subtracted 0.00 - 0.36
Terpy2Mn_full 2017.04.06 16:58:51 ;
ESI + Max: 1.1E9
Intensity



Chemical Formula: $C_{30}H_{22}MnN_6^{2+}$
Exact Mass: 521.13
Molecular Weight: 521.47
m/z: 260.56 (100.0%), 261.06 (34.9%), 261.57 (5.2%)

Figure S25. ESI-MS traces of **T_2Mn** complex.

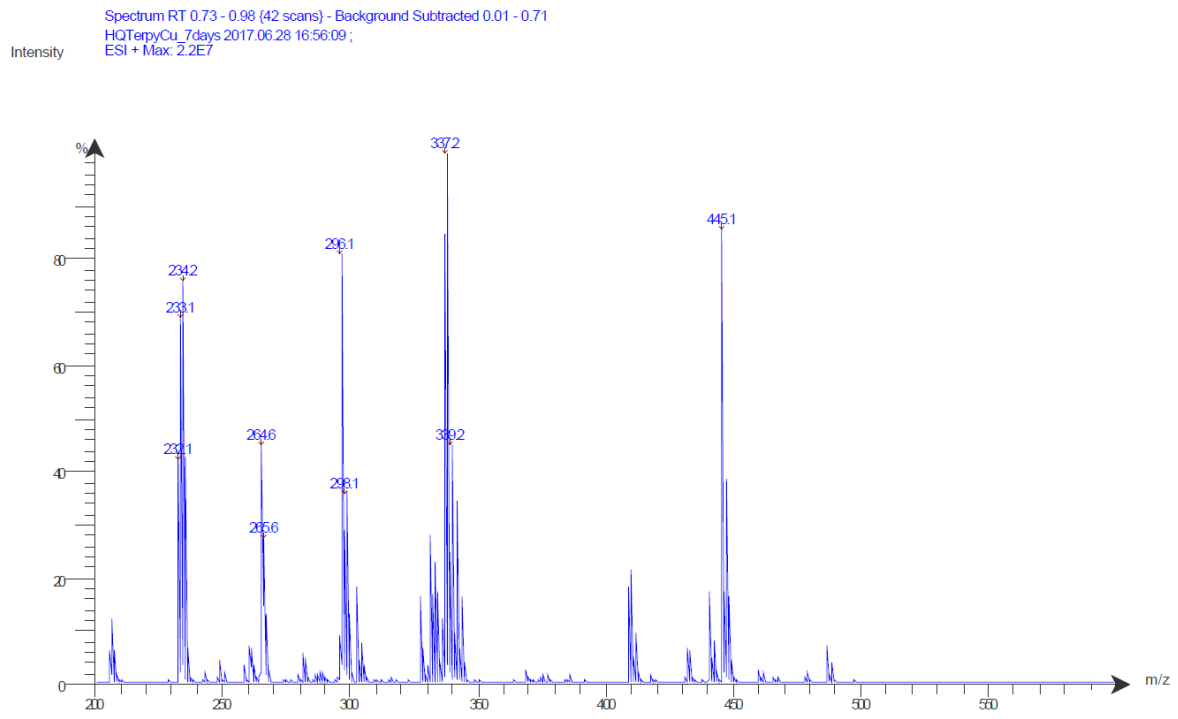


Figure S26. ESI-MS traces of an attempt of synthesis of **TQCu** in ACN after 7 days.

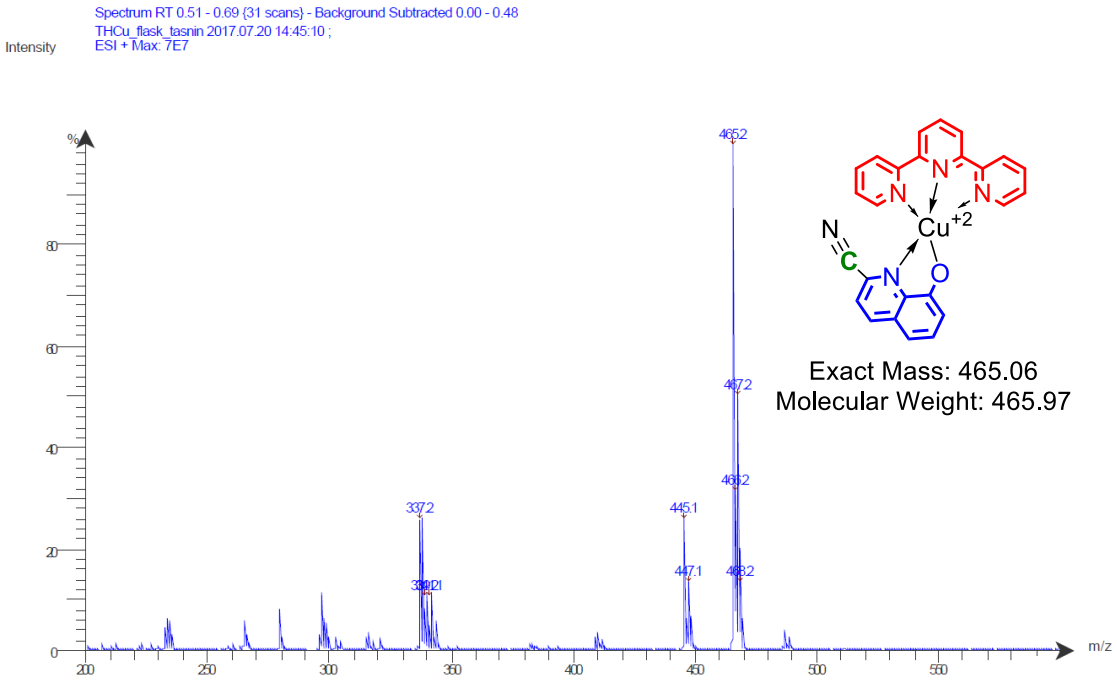


Figure S27. ESI-MS traces of the filtrate solution after precipitation of **TQCu** complex.

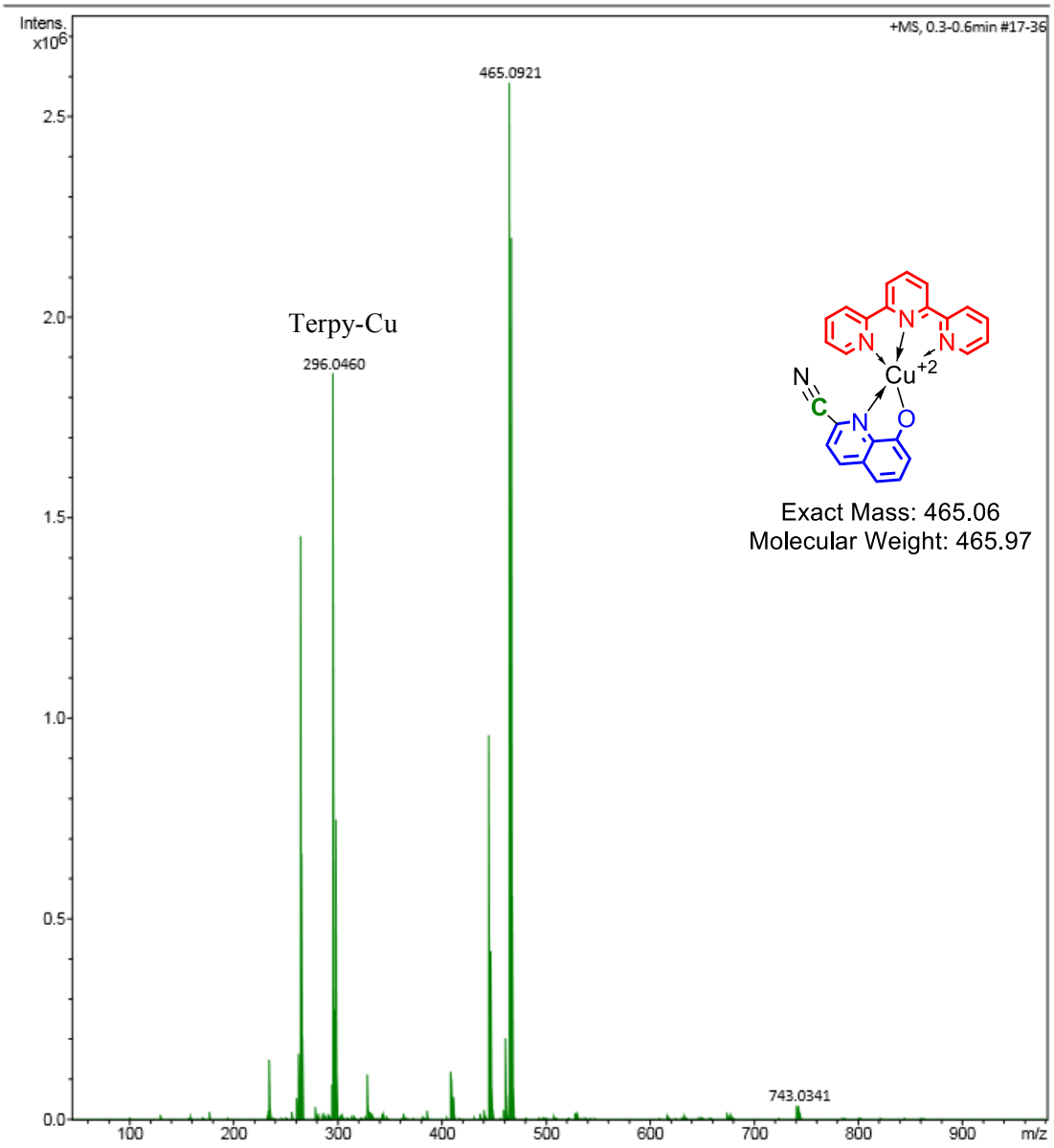


Figure S28. ESI-MS traces from the reaction solution of **TQCu** complex.

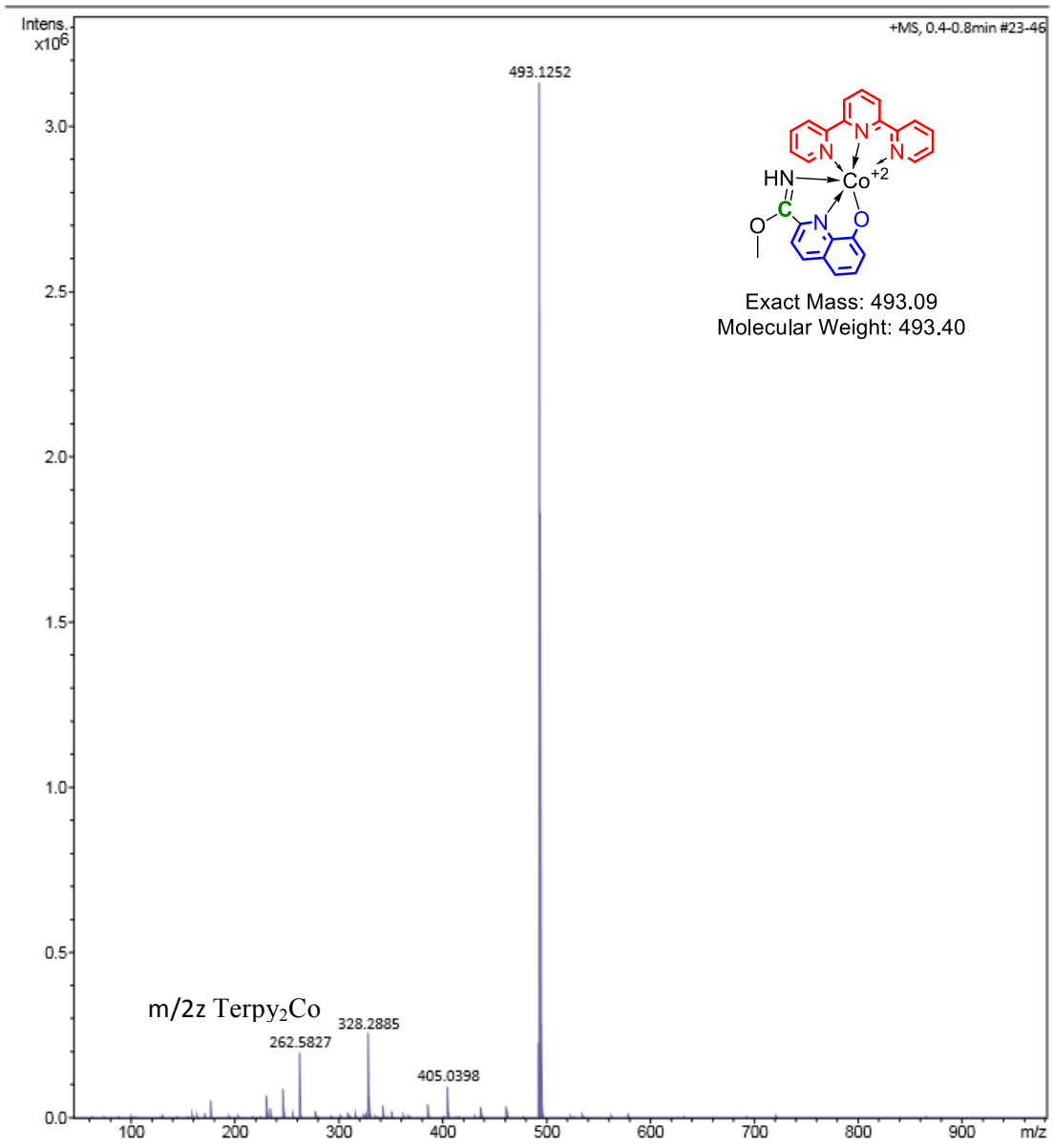


Figure S29. ESI-MS traces from the reaction solution of **TQ'Co** complex.

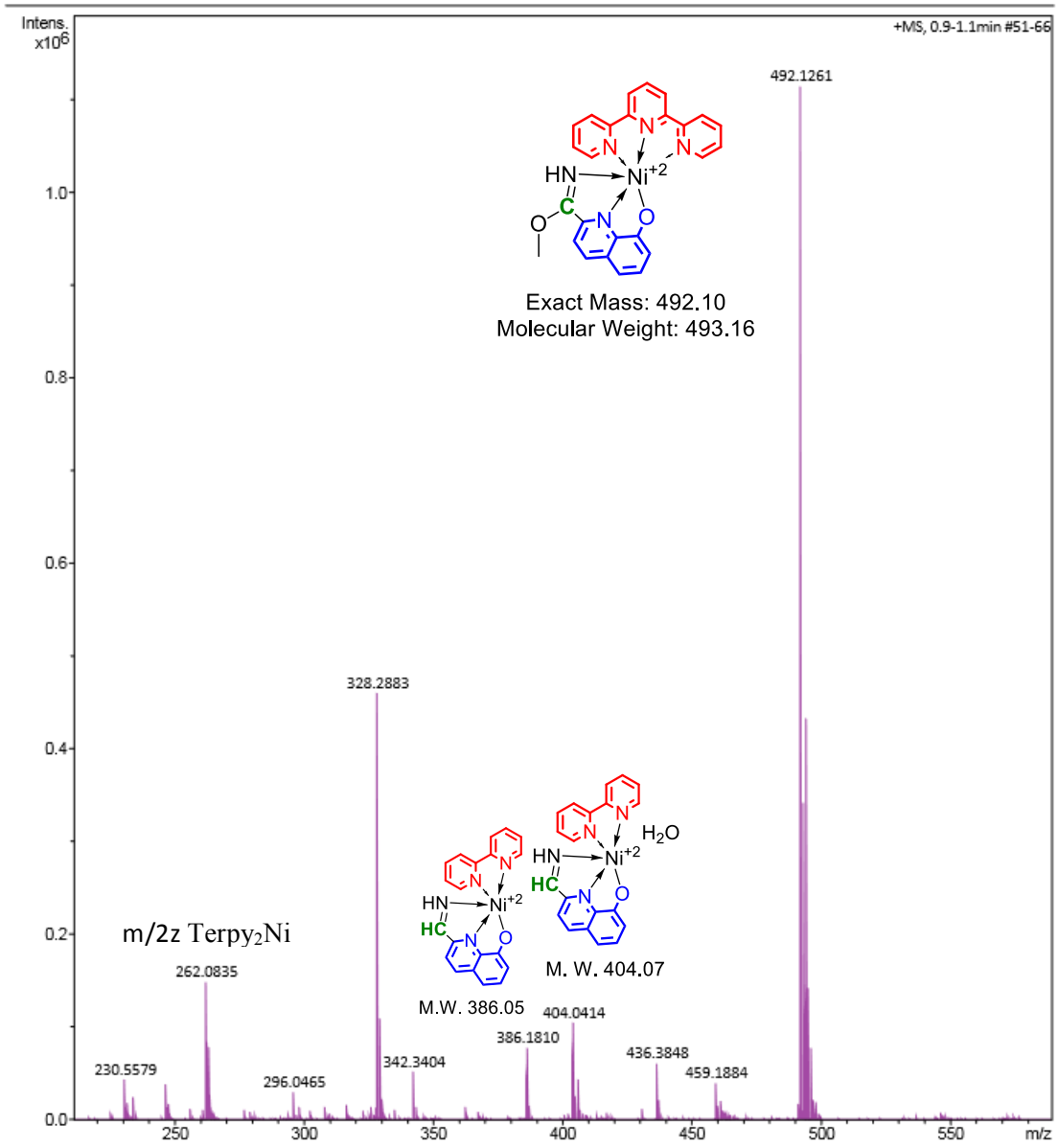


Figure S30. ESI-MS traces from the reaction solution of **TQ'Ni** complex.

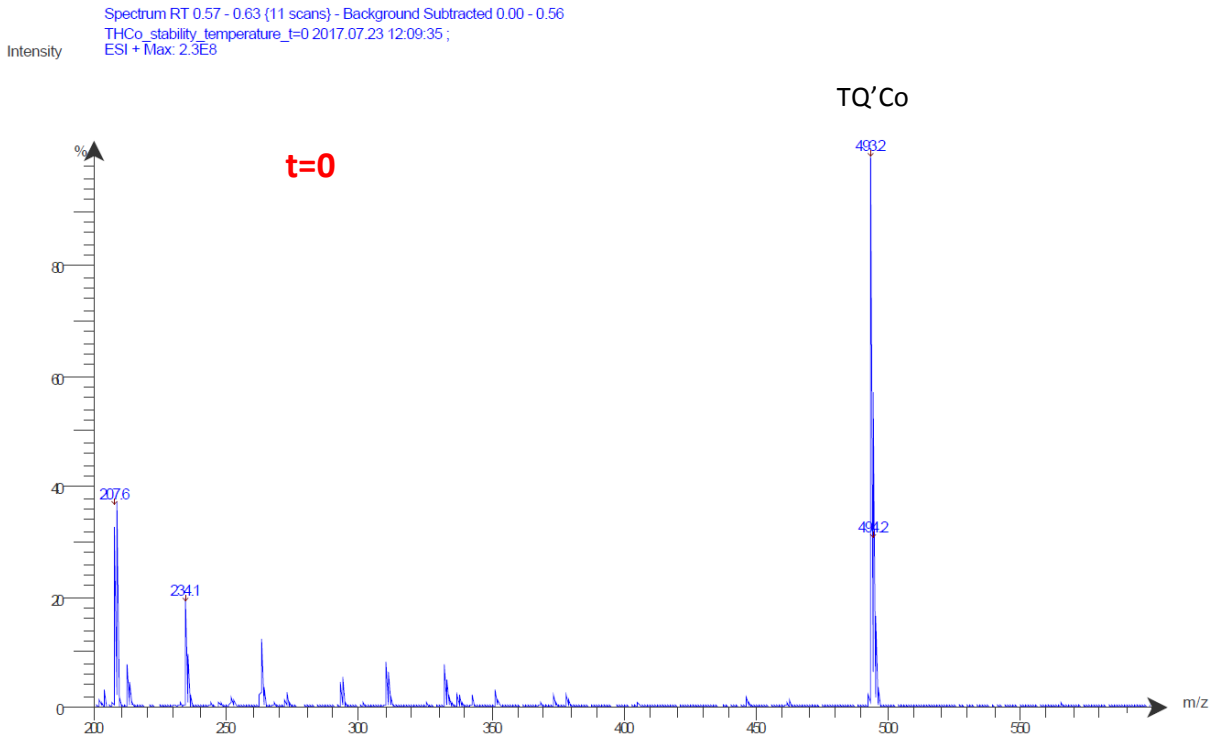


Figure S31. ESI-MS traces of **TQ'Co** complex before heating at 80 °C.

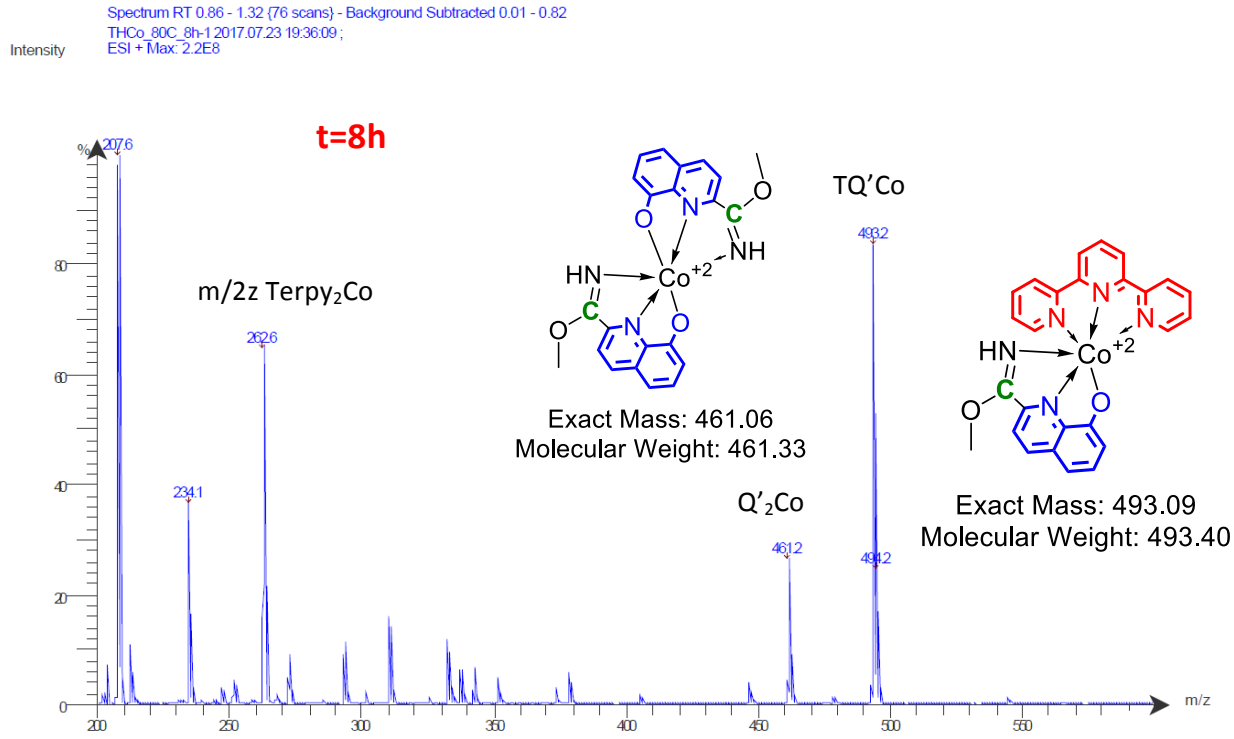


Figure S32. ESI-MS traces of **TQ'Co** complex after 8 hours of heating at 80 °C.

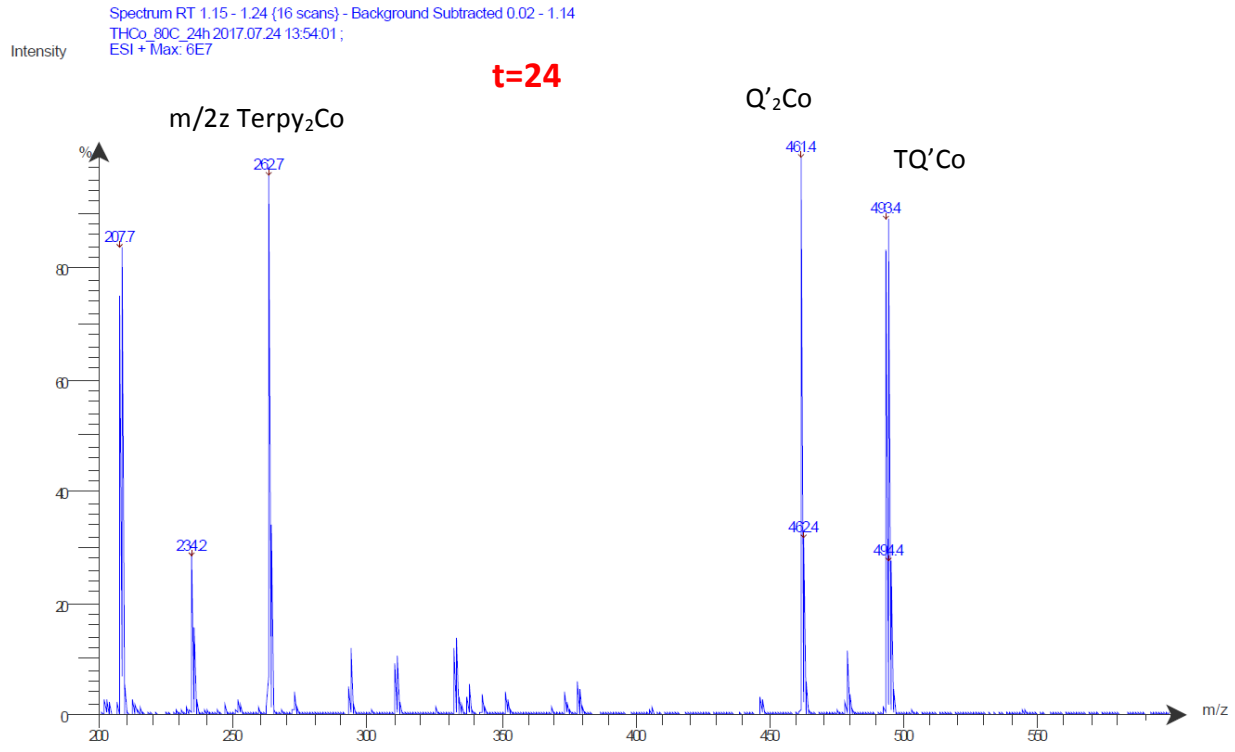


Figure S33. ESI-MS traces of **TQ'Co** complex after 24 hours of heating at 80 °C.

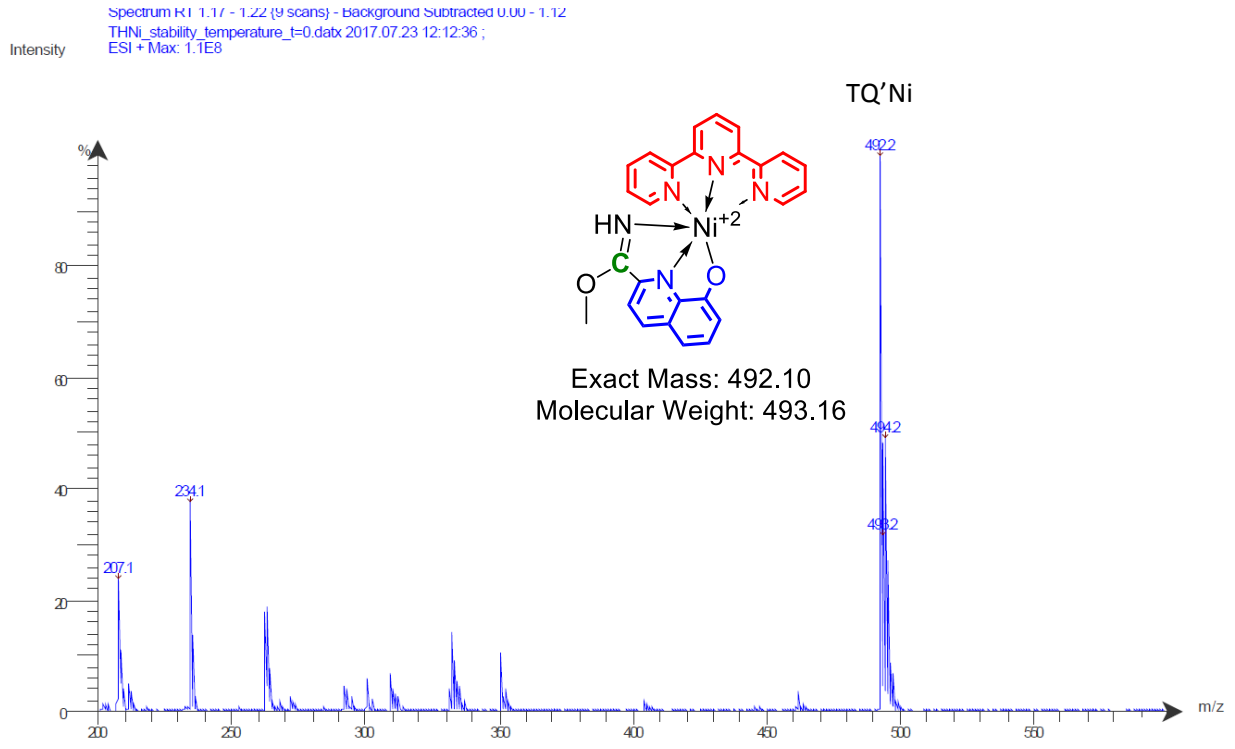


Figure S34. ESI-MS traces of **TQ'Ni** complex before heating at 80 °C.

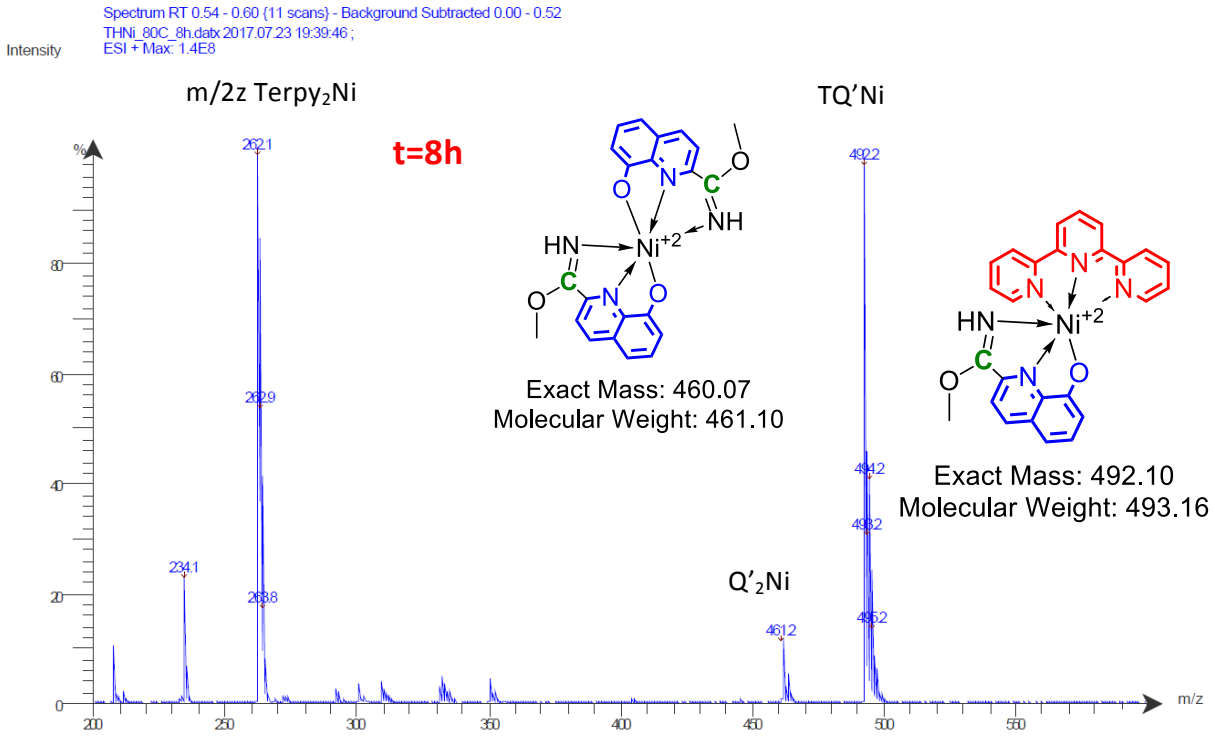


Figure S35. ESI-MS traces of **TQ'Ni** complex after 8 hours of heating at 80 °C.

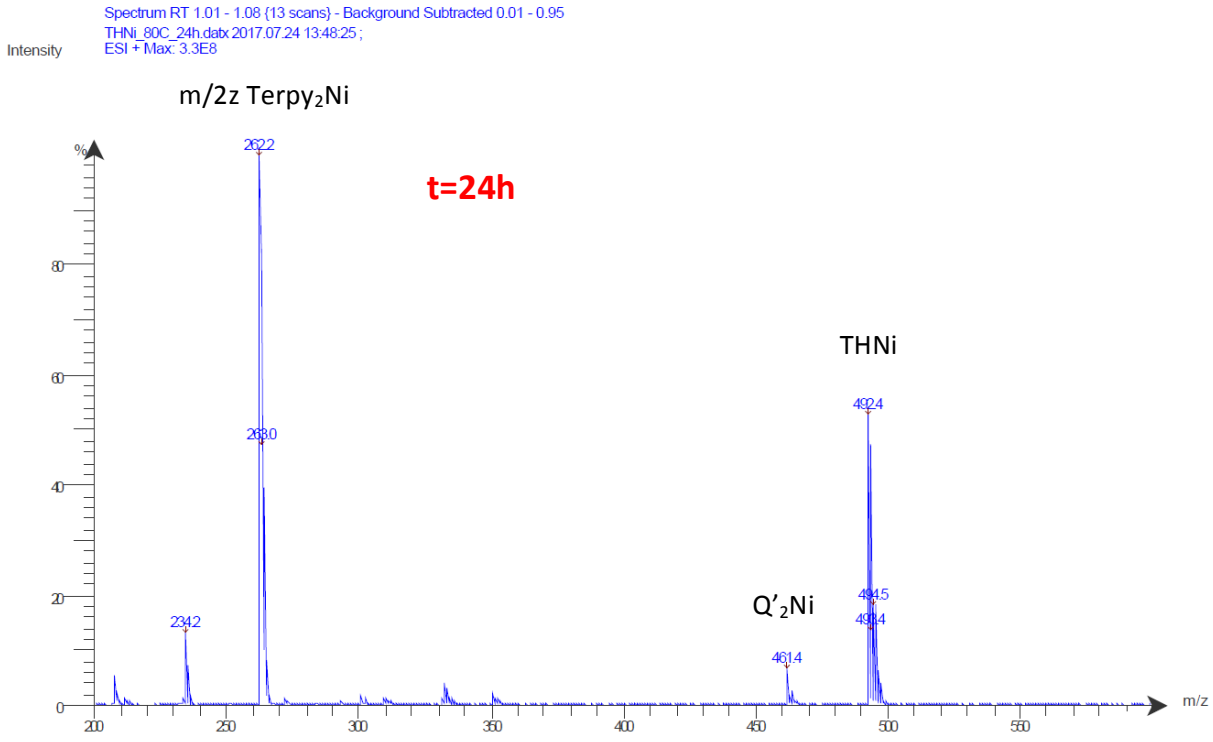


Figure S36. ESI-MS traces of **TQ'Ni** complex after 24 hours of heating at 80 °C.

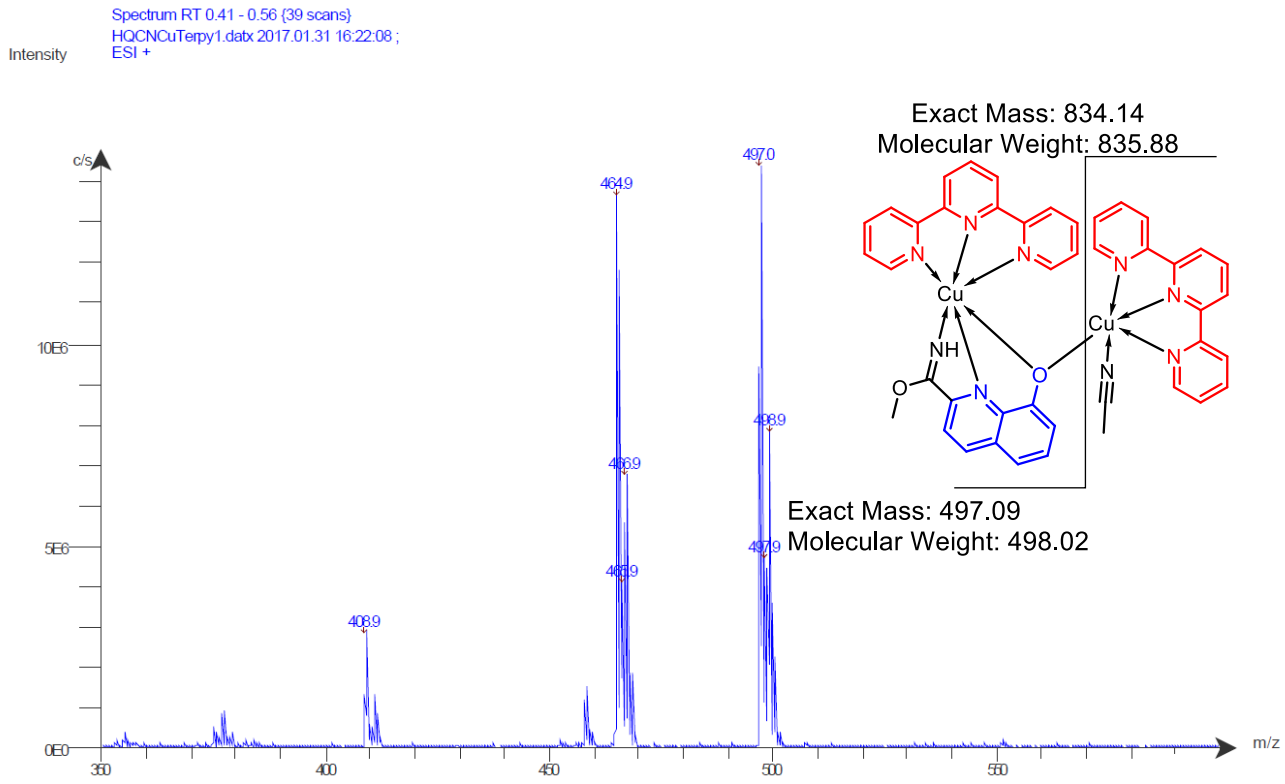


Figure S37. ESI-MS traces of $\mathbf{T_2Q'Cu_2}$ complex.

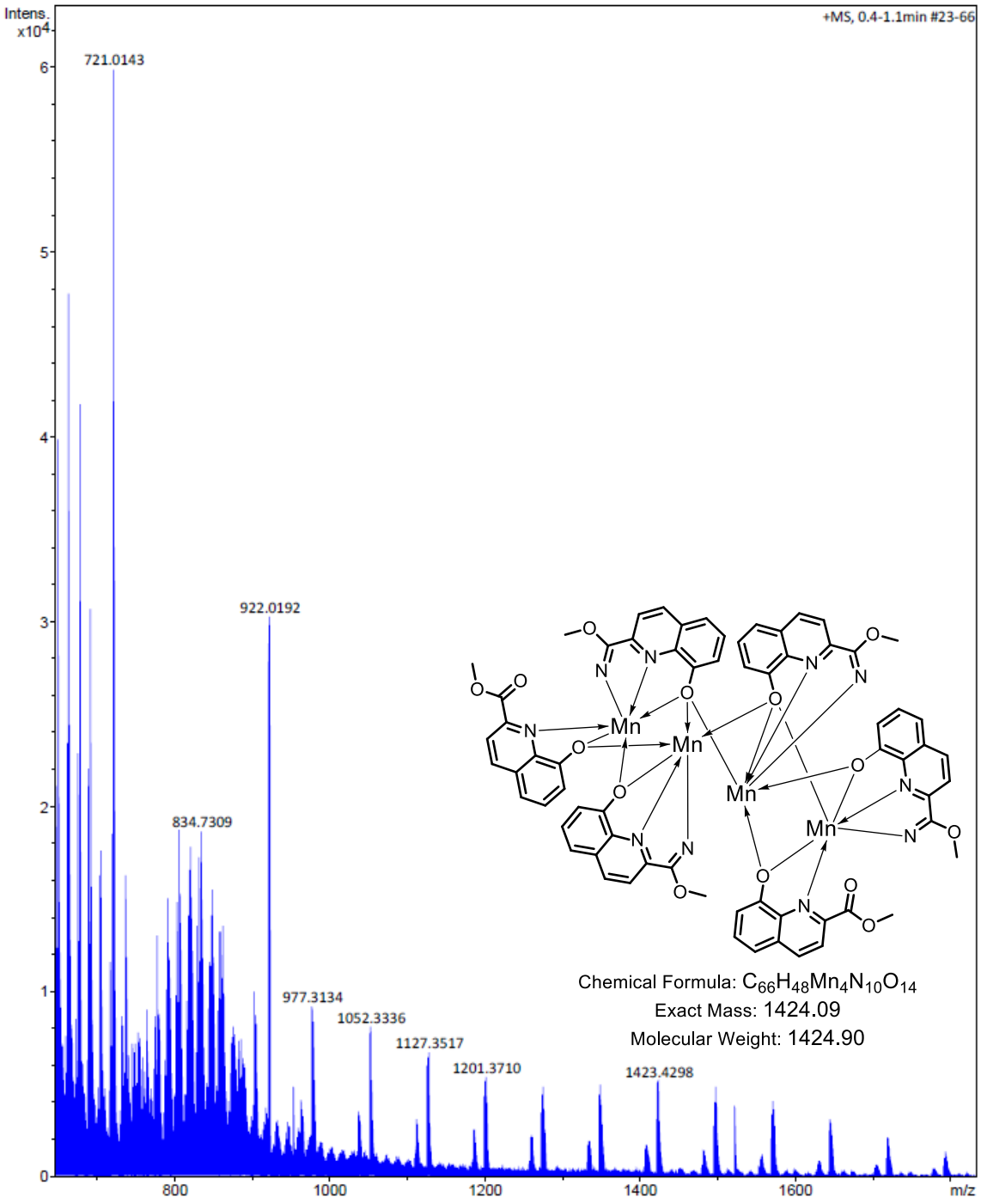


Figure S38. APCI-MS traces of $\mathbf{Q'_4Q''_2Mn_4}$ cluster.

Crystallization and X-ray analysis

Table S1. Bond distances of geometry center of **TQCu** complex based on X-ray analysis.

Bond	N1-Cu	N2-Cu	N3-Cu	N1'-Cu	O-Cu
Distance (Å)	2.033	1.935	2.048	2.275	1.898

Table S2. Geometry angles of **TQCu** complex based on X-ray analysis.

N1'-Cu-N1	94.48^0	O-Cu-N2	169.53^0
N1'-Cu-N2	109.97^0	O-Cu-N3	99.78^0
N1'-Cu-N3	98.16^0	N3-Cu-N2	79.25^0
O-Cu-N1'	80.50^0	N1-Cu-N3	158.24^0
O-Cu-N1	99.73^0	N1-Cu-N2	79.81^0

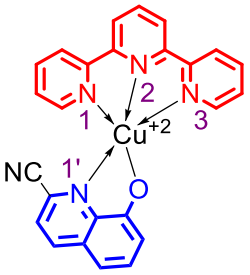


Table S3. Crystal Data for complex **TQCu**.

Moiety formula	$C_{25}H_{16}CuN_5O$, PF_6, C_4H_8O
Crystal system	Monoclinic
Space group	P 21/C
R(reflection)	0.0587 (2810)
T [K]	293
λ [Å]	0.71073
a [Å]	7.67
b [Å]	14.97
c [Å]	26.51
α [deg]	90
β [deg]	101.32
γ [deg]	90
V [$Å^3$]	2982(8)
Z	4
ρ [g/cm^3]	1.520
μ [mm^{-1}]	0.859
F(000)	1388.0

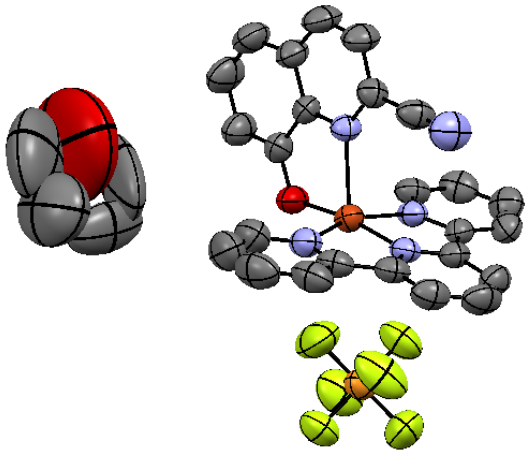
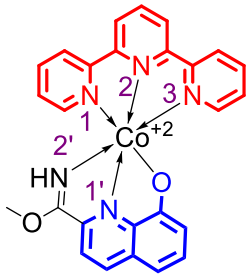


Figure S39. X-ray structure of **TQCu** complex with counter ion PF_6 and THF molecule. Color code: C, gray; N, blue; O, red; Cu, bronze; P, orange; F, yellow. Hydrogen atoms omitted for clarity.

Table S4. Bond distances of geometry center of **TQ'Co** complex based on X-ray analysis.

Bond	N1-Co	N2-Co	N3-Co	N1'-Co	O-Co	N2'-Co
Distance (Å)	2.150	2.059	2.139	2.028	2.145	2.191

Table S5. Geometry angles of **TQ'Co** complex based on X-ray analysis.



N1-Co-N2'	89.75^0	O-Co-N2	97.70^0	N1-Co-N1'	107.02^0
N1'-Co-N2	174.90^0	O-Co-N3	93.28^0	N2'-Co-N2	110.10^0
N1'-Co-N3	101.73^0	N3-Co-N2	75.93^0	N2'-Co-N3	91.63^0
O-Co-N1'	77.82^0	N1-Co-N3	150.48^0	N1'-Co-N2'	74.32^0
O-Co-N1	99.13^0	N1-Co-N2	75.93^0	N2'-Co-O	152.13^0

Table S6. Crystal Data for complex **TQ'Co**.

Moiety formula	$C_{26}H_{20}CoN_5O_2, F_6P, C_4H_{10}O$
Crystal system	Triclinic
Space group	P -1
R(reflection)	0.0385 (3969)
T [K]	200
λ [Å]	0.71073
a [Å]	8.469
b [Å]	12.568
c [Å]	15.238
α [deg]	78.154
β [deg]	76.135
γ [deg]	83.078
V [$Å^3$]	1536.77(8)
Z	2
ρ [g/cm^3]	1.540
μ [mm^{-1}]	0.688
F(000)	730.0

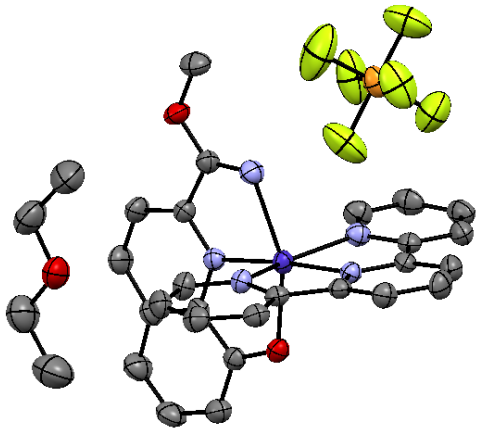
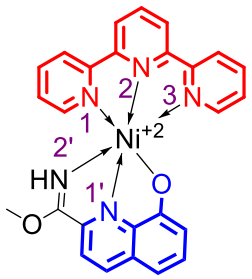


Figure S40. X-ray structure of **TQ'Co** complex with counter ion PF_6 and di ethyl ether molecule. Color code: C, gray; N, blue; O, red; Co, dark blue; P, orange; F, yellow. Hydrogen atoms omitted for clarity.

Table S7. Bond distances of geometry center of **TQ'Ni** complex based on X-ray analysis.

Bond	N1-Ni	N2-Ni	N3-Ni	N1'-Ni	O-Ni	N2'-Ni
Distance (Å)	2.112	2.001	2.098	1.978	2.157	2.153

Table S8. Geometry angles of **TQ'Ni** complex based on X-ray analysis.



N1-Ni-N2'	91.01^0	O-Ni-N2	98.66^0	N1-Ni-N1'	103.99^0
N1'-Ni-N2	176.64^0	O-Ni-N3	89.97^0	N2'-Ni-N2	106.54^0
N1'-Ni-N3	100.43^0	N3-Ni-N2	77.94^0	N2'-Ni-N3	155.54^0
O-Ni-N1'	78.34^0	N1-Ni-N3	77.94^0	N1'-Ni-N2'	76.42^0
O-Ni-N1	96.21^0	N1-Ni-N2	77.74^0	N2'-Ni-O	154.73^0

Table S9. Crystal Data for complex **TQ'Ni**.

Moiety formula	$C_{26}H_{20}CoN_5O_2, PF_6, C_4H_{10}O$
Crystal system	Triclinic
Space group	P -1
R(reflection)	0.0930 (4179)
T [K]	200
λ [Å]	0.71073
a [Å]	8.434
b [Å]	12.608
c [Å]	15.196
α [deg]	77.523
β [deg]	76.595
γ [deg]	82.342
V [$Å^3$]	1528.8(2)
Z	2
ρ [g/cm^3]	1.547
μ [mm^{-1}]	0.765
F(000)	732.0

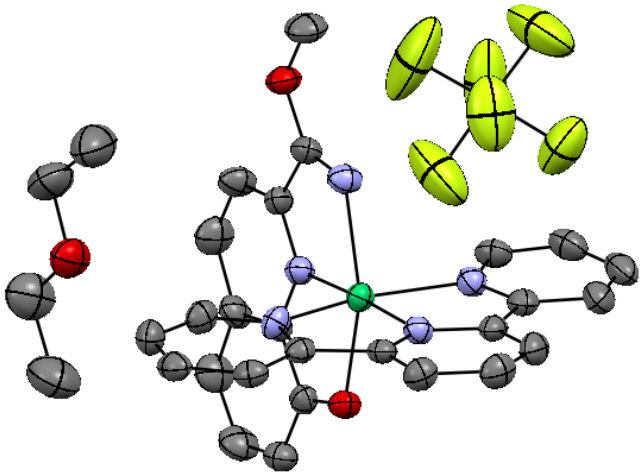


Figure S41. X-ray structure of **TQ'Ni** complex with counter ion PF_6 and di ethyl ether molecule. Color code: C, gray; N, blue; O, red; Ni, turquoise; P, orange; F, yellow. Hydrogen atoms omitted for clarity.

Table S10. Crystal Data for **Q'$_4$Q''$_2$Mn$_4$** cluster.

Moiety formula	$2(C_{66}H_{48}Mn_4N_{10}O_{14}),4(PF_6),3(C_4O)$
Crystal system	Monoclinic
Space group	P 21/C
R(reflection)	0.0720 (7944)
T [K]	200
λ [Å]	0.71073
a [Å]	14.408
b [Å]	20.761
c [Å]	26.866
α [deg]	90
β [deg]	106.036
γ [deg]	90
V [Å^3]	7723.6 (2)
Z	2
ρ [g/cm^3]	1.557
μ [mm^{-1}]	0.715
F(000)	438.0

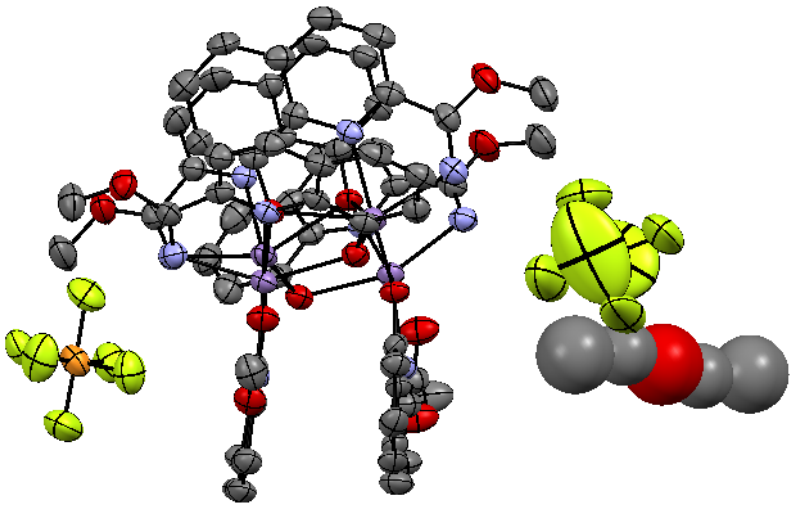


Figure S42. X-ray structure of **Q'$_4$Q''$_2$Mn$_4$** cluster with counter ions PF_6 and di ethyl ether molecule. Color code: C, gray; N, blue; O, red; Mn, purple; P, orange; F, yellow. Hydrogen atoms omitted for clarity.

X-ray data for mono(terpyridine)cobalt(II)bis(acetate) (**TCo**) complex.

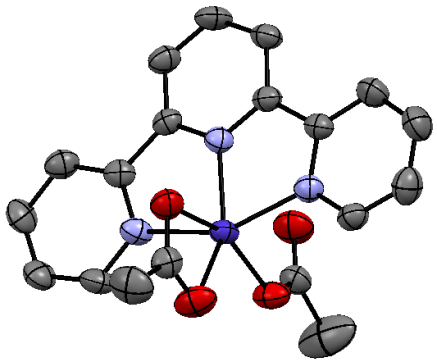


Figure S43. X-ray structure of **TCo** complex. Color code: C, gray; N, blue; O, red; Co, dark blue. Hydrogen atoms omitted for clarity.

Table S11. Crystal Data for **TCo** complex.

Moiety formula	$C_{19}H_{17}CoN_3O_4$
Crystal system	Triclinic
Space group	P -1
R(reflection)	0.0720 (7944)
T [K]	200
λ [Å]	0.71073
a [Å]	8.547
b [Å]	10.983
c [Å]	11.038
α [deg]	73.069
β [deg]	84.894
γ [deg]	68.064
V [$Å^3$]	919.25(14)
Z	2
ρ [g/cm^3]	1.482
μ [mm^{-1}]	0.963
F(000)	422.0

X-ray data for mono(terpyridine)manganese(II)bis(acetate) (**TMn**) complex.

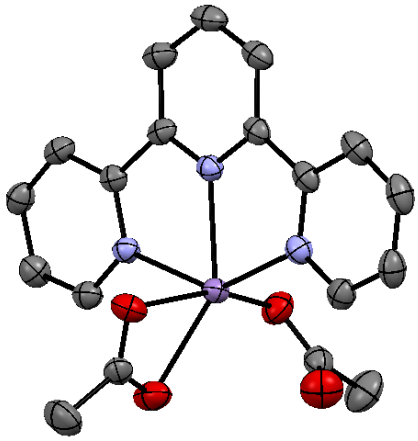


Figure S44. X-ray structure of **TMn** complex. Color code: C, gray; N, blue; O, red; Mn, purple. Hydrogen atoms omitted for clarity.

Table S12. Crystal Data for **TMn** complex.

Moiety formula	$C_{19}H_{17}MnN_3O_4 \cdot H_2O$
Crystal system	Triclinic
Space group	P -1
R(reflection)	0.0506 (2941)
T [K]	200
λ [Å]	0.71073
a [Å]	8.420
b [Å]	10.766
c [Å]	10.903
α [deg]	83.00
β [deg]	83.70
γ [deg]	83.759
V [$Å^3$]	970.5 (5)
Z	2
ρ [g/cm^3]	1.452
μ [mm^{-1}]	0.715
F(000)	438.0

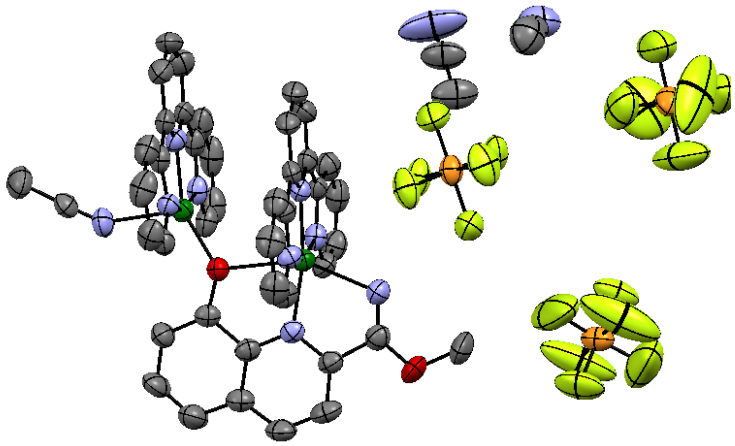


Figure S45. X-ray structure of $\mathbf{T_2Q'Cu_2}$ complex with counter ions PF_6 and acetonitrile molecules. Color code: C, gray; N, blue; O, red; Cu, green; P, orange; F, yellow. Hydrogen atoms omitted for clarity.

Table S13. Crystal Data for $\mathbf{T_2Q'Cu_2}$ complex.

Moiety formula	$C_{43}H_{34}Cu_2N_9O_2$, 0.5(C_8), 3(F_6P),2(C_2H_3N),C_2N
Crystal system	Triclinic
Space group	P -1
R(reflection)	0.0506 (2941)
T [K]	200
λ [Å]	0.71073
a [Å]	10.303
b [Å]	12.525
c [Å]	24.583
α [deg]	91.421
β [deg]	97.104
γ [deg]	104.077
V [$Å^3$]	3048.5 (7)
Z	2
ρ [g/cm^3]	1.568
μ [mm^{-1}]	0.883
F(000)	1446.0

DPV

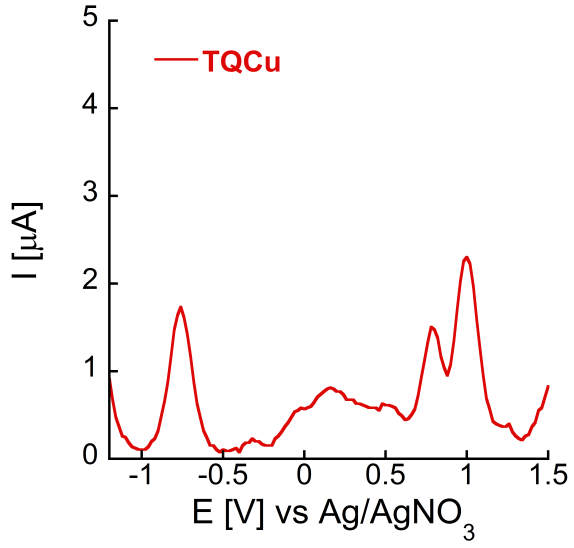


Figure S46. DPV analysis of **TQCu** complex (1mM) recorded in ACN at r.t. with 0.1 M TBA-PF_6 as the supporting electrolyte using glassy carbon working electrode, platinum counter electrode, $Ag/AgNO_3$ reference electrode. Scan rate: 100 mV s^{-1}.

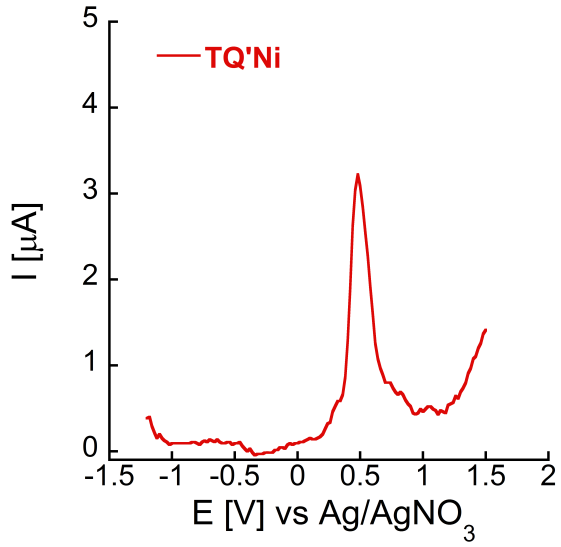


Figure S47. DPV analysis of **TQ'Ni** complex (1mM) recorded in ACN at r.t. with 0.1 M TBA-PF_6 as the supporting electrolyte using glassy carbon working electrode, platinum counter electrode, $Ag/AgNO_3$ reference electrode. Scan rate: 100 mV s^{-1}.

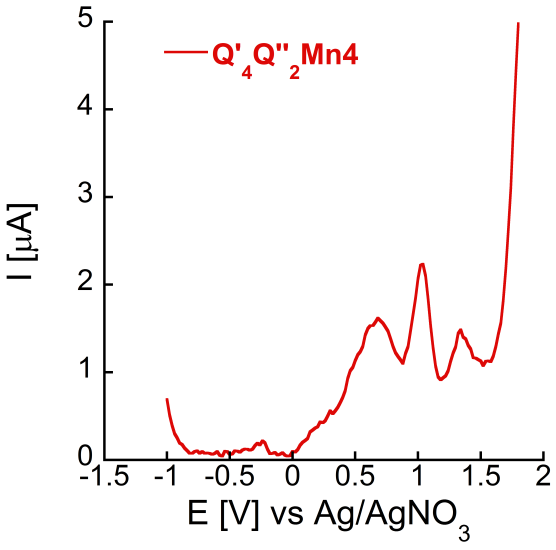


Figure S48. DPV analysis of **Q'$_4$Q''$_2$Mn$_4$** complex (0.5mM) recorded in ACN at r.t. with 0.1 M TBA-PF_6 as the supporting electrolyte using glassy carbon working electrode, platinum counter electrode, $Ag/AgNO_3$ reference electrode. Scan rate: 100 mV s^{-1}.

NMR

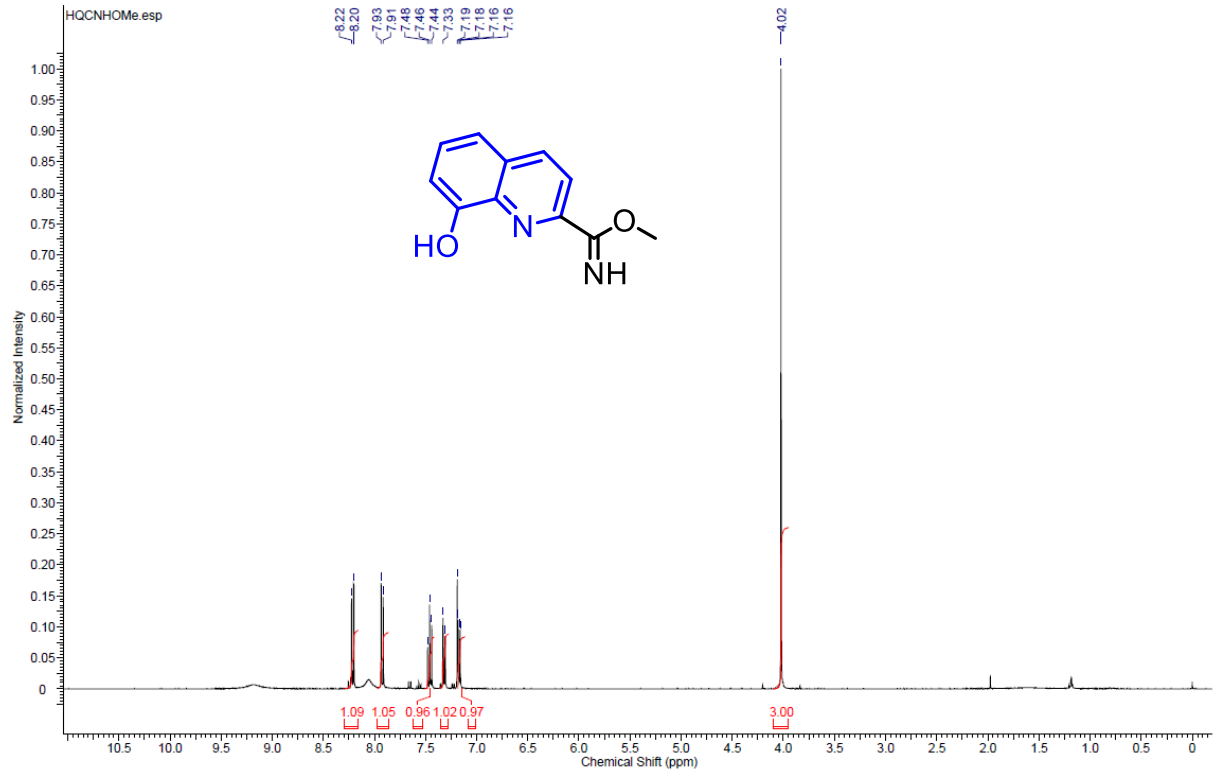


Figure S49. ^{1}H NMR spectra of methyl 8-hydroxyquinoline-2-carboxyimidate.

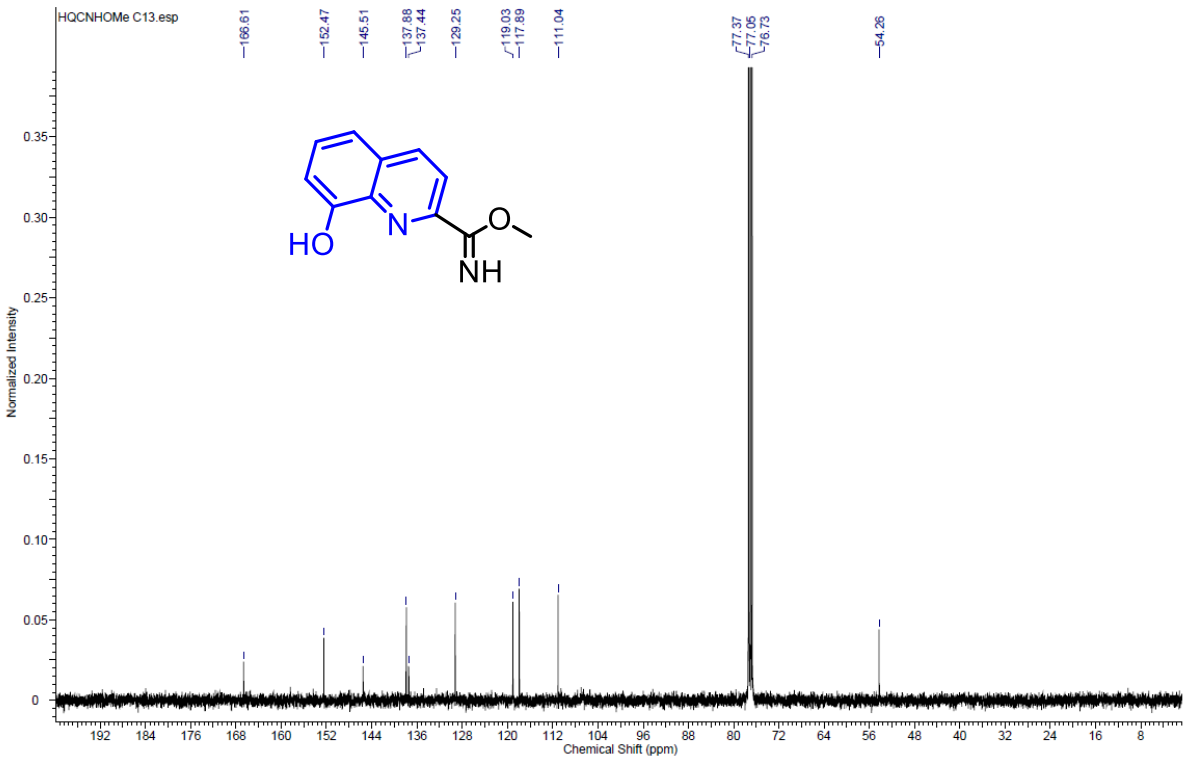


Figure S50. ^{13}C NMR spectra of methyl 8-hydroxyquinoline-2-carboxyimidate.

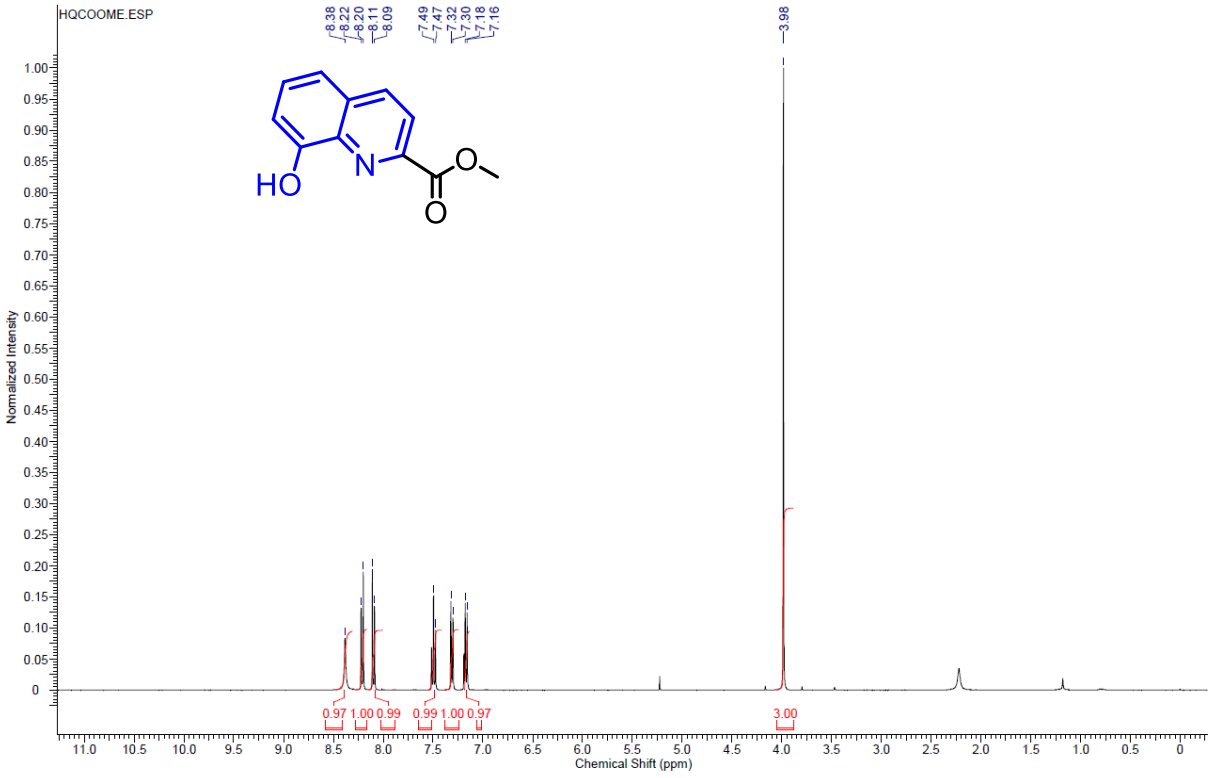


Figure S51. ^{1}H NMR spectra of methyl 8-hydroxyquinoline-2-carboxylate.

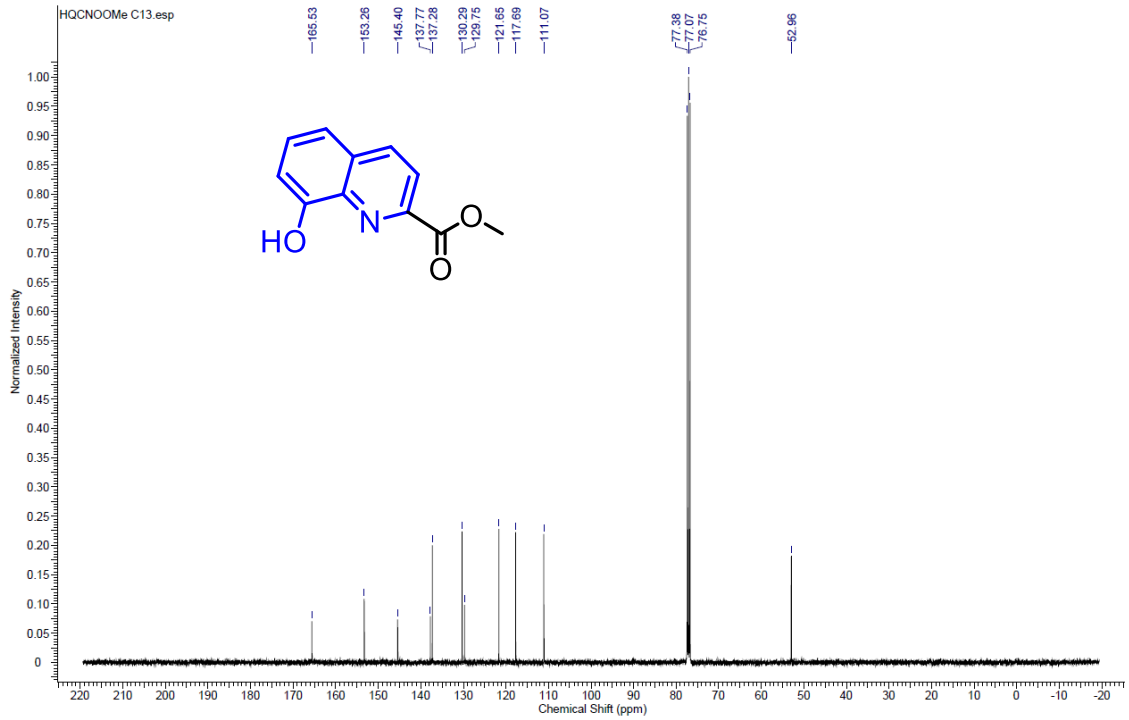


Figure S52. ^{13}C NMR spectra of methyl 8-hydroxyquinoline-2-carboxylate.

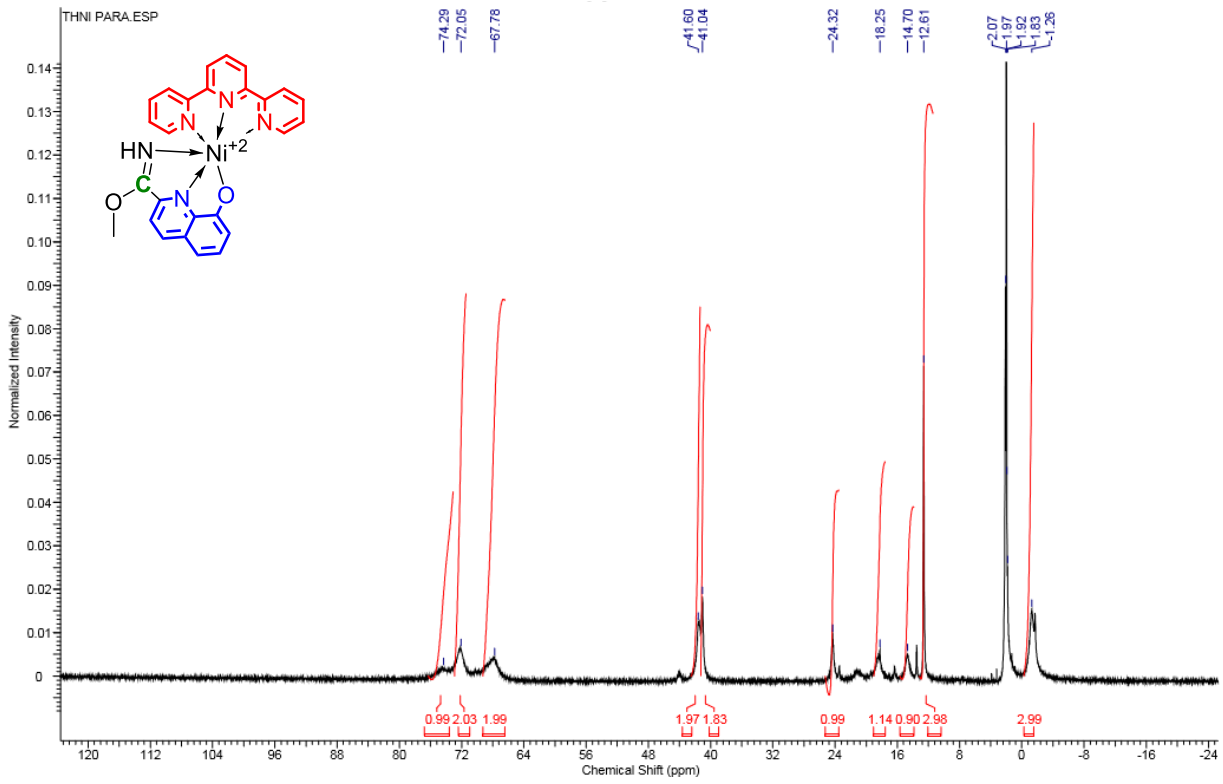


Figure S53. ^{1}H NMR spectra of **TQ'Ni** complex.

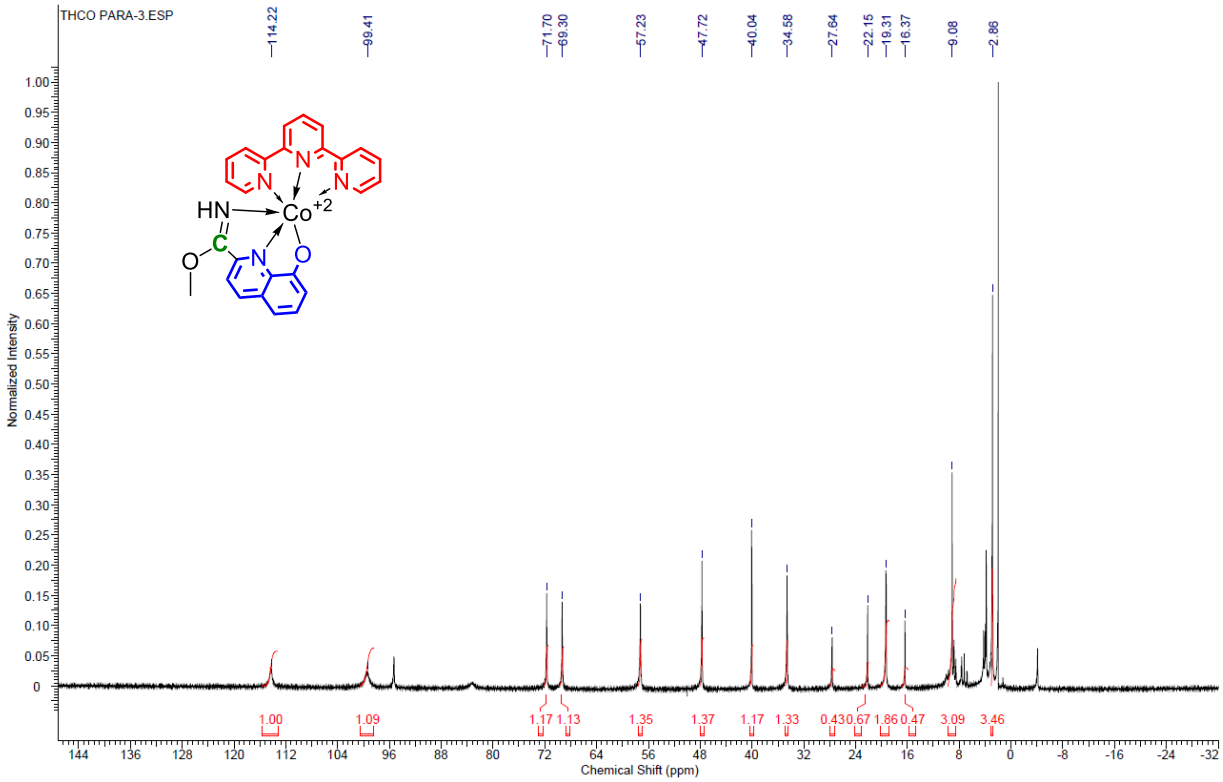


Figure S54. ^{1}H NMR spectra of **TQ'Co** complex.