Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information for:

Synthesis of Pyridine-Alkoxide Ligands for Formation of Polynuclear Complexes

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1. Optimization of ligand synthesis

We investigated the possibility of enhancing the oligomer yield by varying the reaction conditions. Since Grignard reactions are normally carried out at low temperature in part to suppress deprotonation, we studied the effects of running the reaction at elevated temperatures, which could favor aldol coupling, which requires a mixture of protonated and deprotonated acetylpyridine. Doing so increased the relative abundance of starting material and **aD** in the product mixture, decreased the yield of **pyalkH**, but did not increase oligomer yield; in fact, temperatures above 40 ^{o}C resulted in lower yields of all pyridinols. While we suspected that methylation would be favored excessively by classical Grignard conditions (0 ^{o}C), this did not appear to be the case here, with the highest dimer yields (20-25% combined) occurring under these conditions.

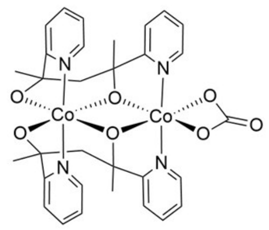
After numerous preparations under the same or differing conditions, we noted that product distribution was poorly reproducible. For example, reactions carried out under the same conditions gave somewhat variable product yields, and merely changing the reaction scale or order of addition resulted in considerable deviations. We suspect that this arises due to several factors: the extremely rapid nature of the reaction (meaning that much of it occurs in the initial contact), its exothermicity, creating uncontrollable localized hot spots at that first contact, and the poor solubility of resulting magnesium adducts, which create a heterogeneous slurry as the reaction progresses. As a result, much of the reaction outcome is likely determined by factors that are difficult to control, such as addition droplet size and velocity, slurry consistency, etc.

Since optimization of the **pyalkH** yield can be accomplished simply by promoting the methylation reaction, which, as the subject of extensive prior reports,[1] is not discussed here. Formation of the oligomers, on the other hand, is much more complicated as it involves three separate reactions (deprotonation, aldol, and methylation) that must occur stepwise implying the presence of the required intermediates. The natural response would be to attempt to perform these steps in a sequential manner: deprotonation and aldol dimerization, followed by methylation.[2] After several attempts with various aldol methods,[3] however, we failed to prepare **aD** in any appreciable yield; in addition, various side products were observed in each case. Attempts to isolate **aD** revealed that it is in fact an unstable compound, readily undergoing retro-aldol to re-form 2-acetylpyridine, presumably due to the unfavorable thermodynamics of diketone coupling. This occurs rapidly in crude mixtures when heated to near 100 ^{o}C, and slowly (approx. 20% over 6 hours) at room temperature in mostly pure samples (crude mixtures appear to be stable at room temperature, however). Indeed, this compound is only known in the literature as a copper-bound adduct.[4] Therefore, the original conditions, where methylation is concurrent, may be successful due to the irreversible trapping of the oligomerized forms.

Even if the sequential strategy had been successful, however, it is unclear that it would have actually been more efficient, due to the additional workup steps required.

Given the low cost of the starting materials and the difficulties presented, we reasoned that the most effective strategy was to simply perform the one-step Grignard reaction on a large scale despite the limited dimer yield.

2. Structures of ligands and complexes 1-12.



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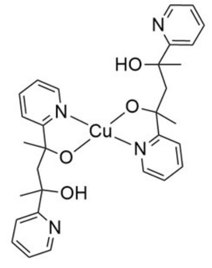

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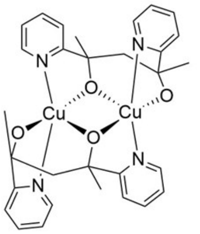

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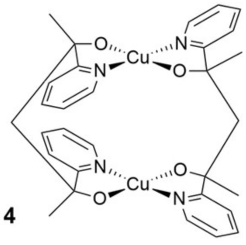

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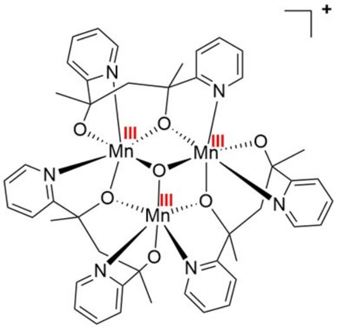

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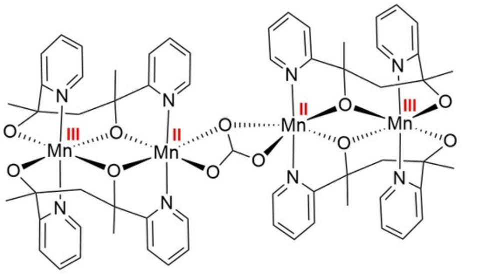

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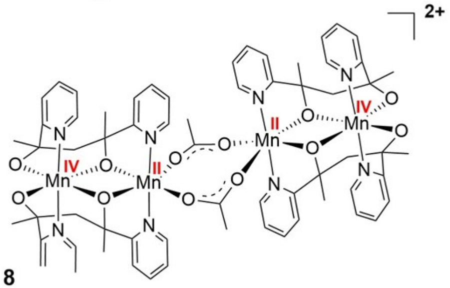

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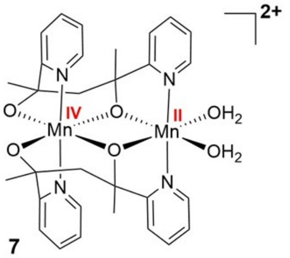

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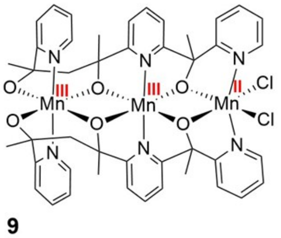

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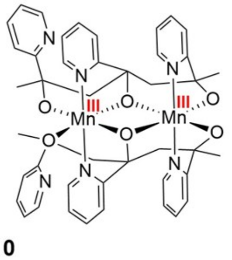

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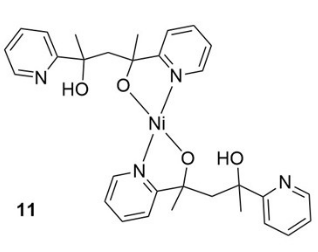

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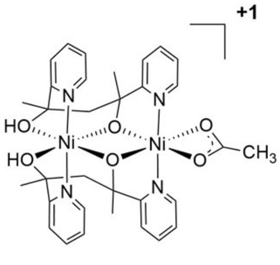

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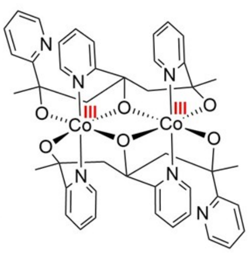
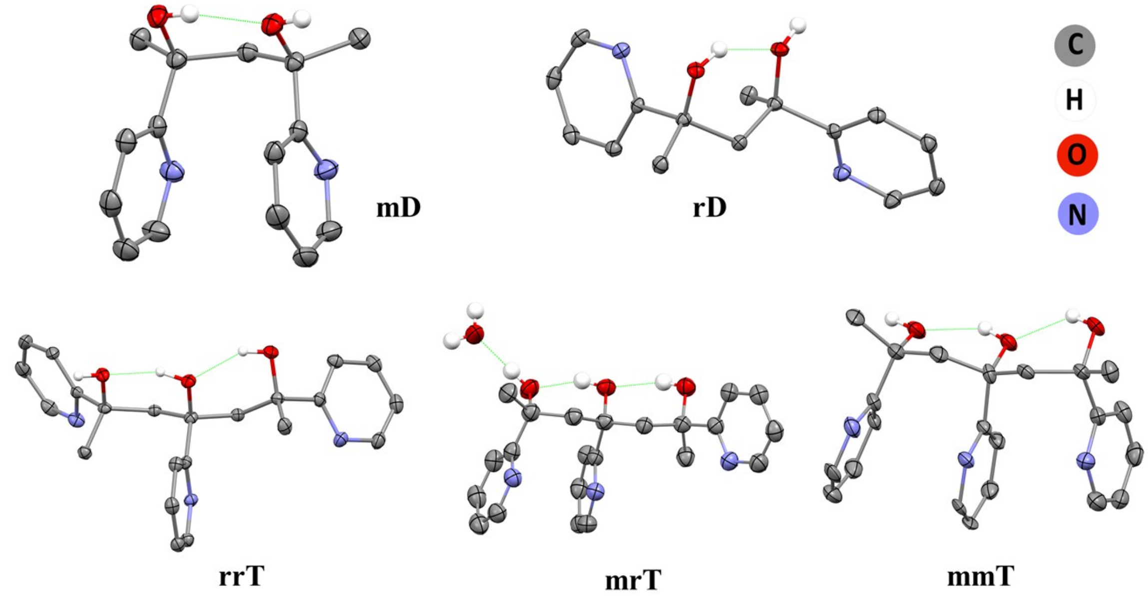


13

Structures of ligands



3. Cyclic voltammetry

Table S1 Redox potentials for selected complexes.

Complex	Redox potential (V vs NHE)
1	None observed
2[b]	0.530[a]
3	1.056, 1.302
4	1.107
6	0.714, 1.270
12[c]	0.870, 1.164[a]

Experiments run in aqueous KNO_3 buffer (0.1M) with BDD working electrode and Ag/AgCl reference electrode unless stated otherwise. [a]Quasi-reversible [b]DMF with 0.1M $TBAPF_6$ and GC working electrode used; potential reported vs. Fc. [c]MeCN with 0.1M $TBAPF_6$ and GC working electrode used; potential reported vs. Fc. In all cases, a Pt counter electrode was used.

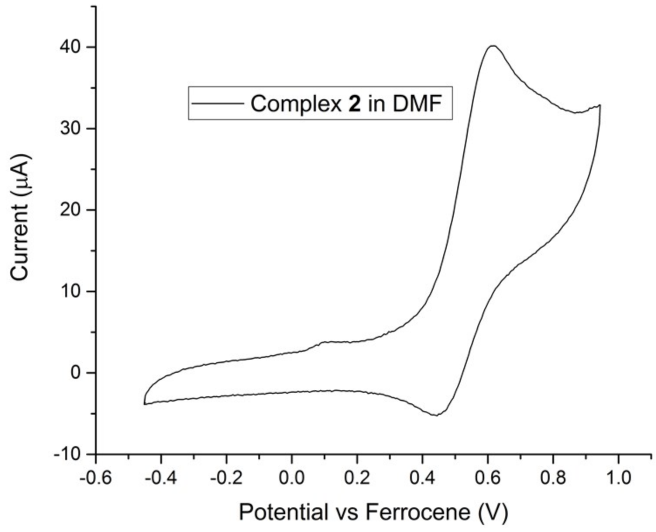


Figure S1. Cyclic voltammogram of complex **2.** Experiment run in DMF with 0.1M $TBAPF_6$ and GC working electrode used; potential reported vs. ferrocene.

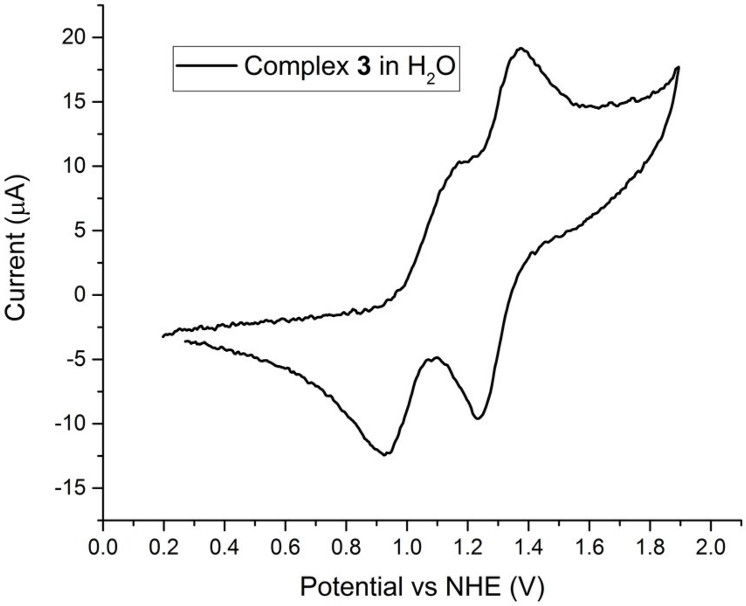


Figure S2. Cyclic voltammogram of complex **2.** Experiment run in aqueous KNO_3 buffer (0.1M) with BDD working electrode and Ag/AgCl reference electrode.

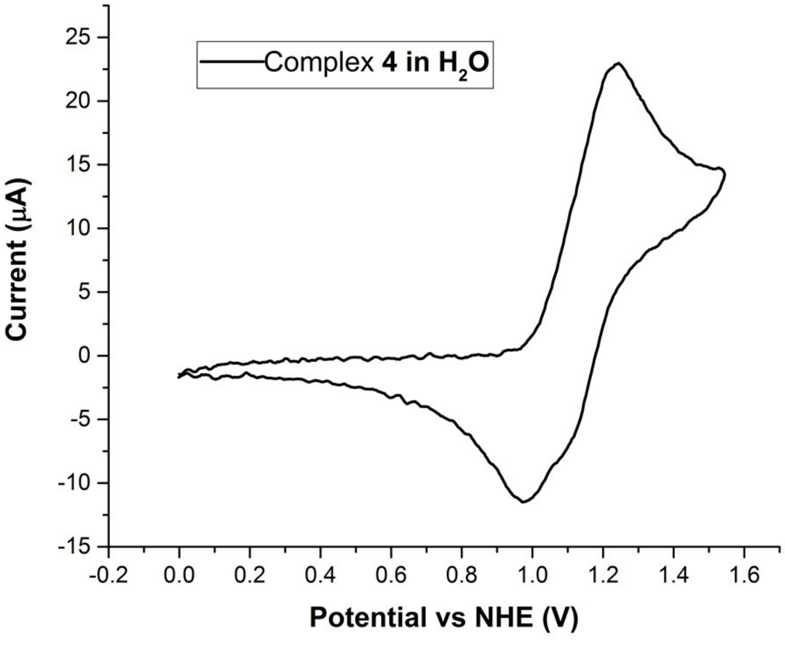


Figure S3. Cyclic voltammogram of complex **4.** Experiment run in aqueous KNO_3 buffer (0.1M) with BDD working electrode and Ag/AgCl reference electrode.

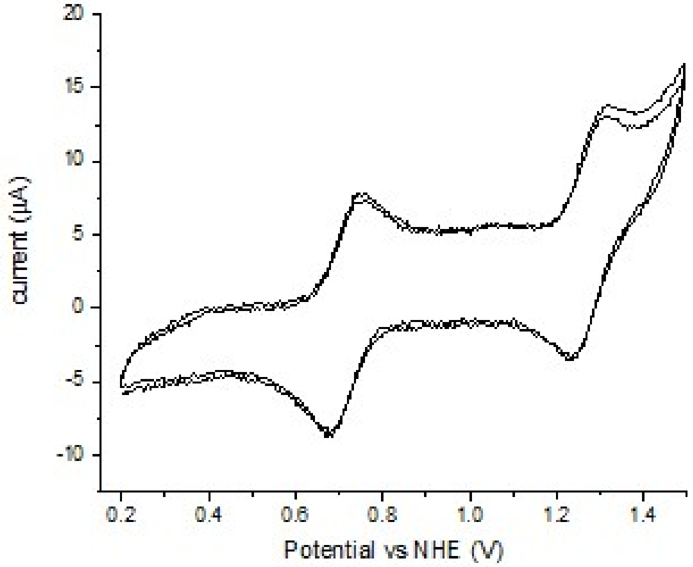


Figure S4. Cyclic voltammogram of complex **6.** Experiment run in aqueous KNO_3 buffer (0.1M) with BDD working electrode and Ag/AgCl reference electrode

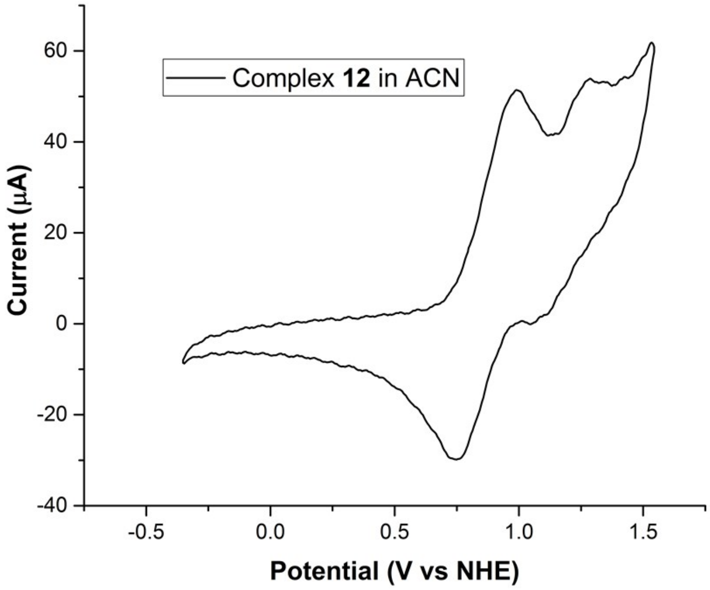


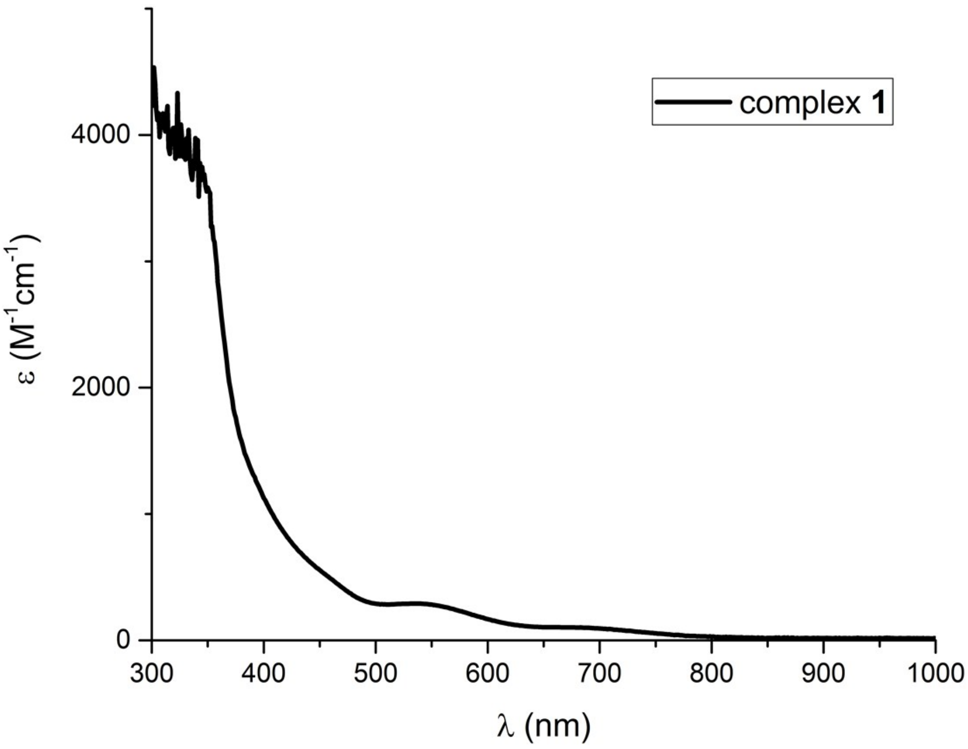
Figure S5. Cyclic voltammogram of complex **12.** Experiment run in ACN with 0.1M $TBAPF_6$ and GC working electrode used; potential reported vs. ferrocene.

4. Uv-visible spectra

Table S2. Uv-visible spectra for selected complexes.

Complex	λ_{max} (nm)	$\varepsilon(M^{-1}cm^{-1})$
1	535	292
2[a]	592	72
3[b]	605	271
4[b]	606	88
6	411, 486	1952, 1918
8	475	2099
12	602	18

DCM used as solvent, unless otherwise noted. [a]Methanol used as solvent. [b]Water used as solvent.



<u>Figure S6.</u> Uv-visible spectrum of complex **1** in DCM.

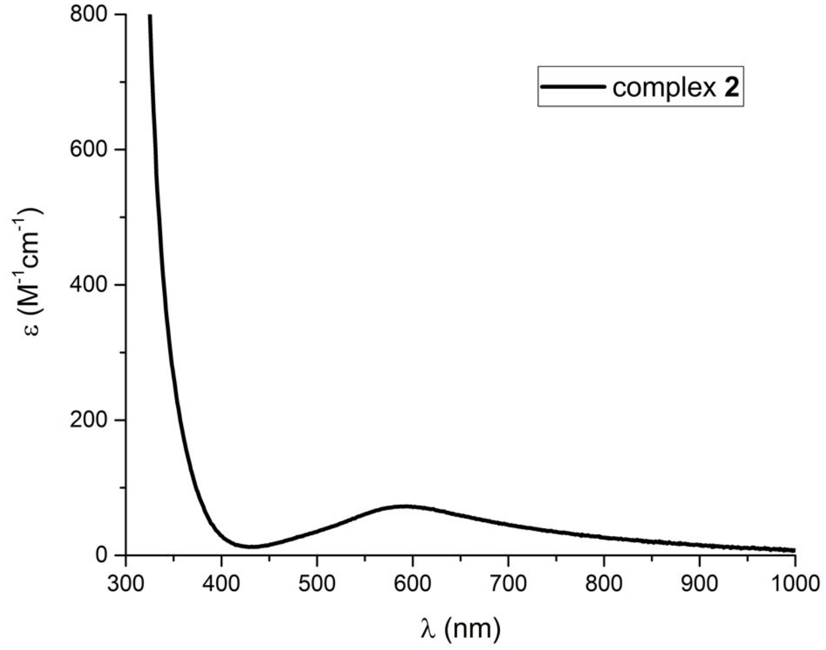


Figure S7. Uv-visible spectrum of complex **2** in methanol.

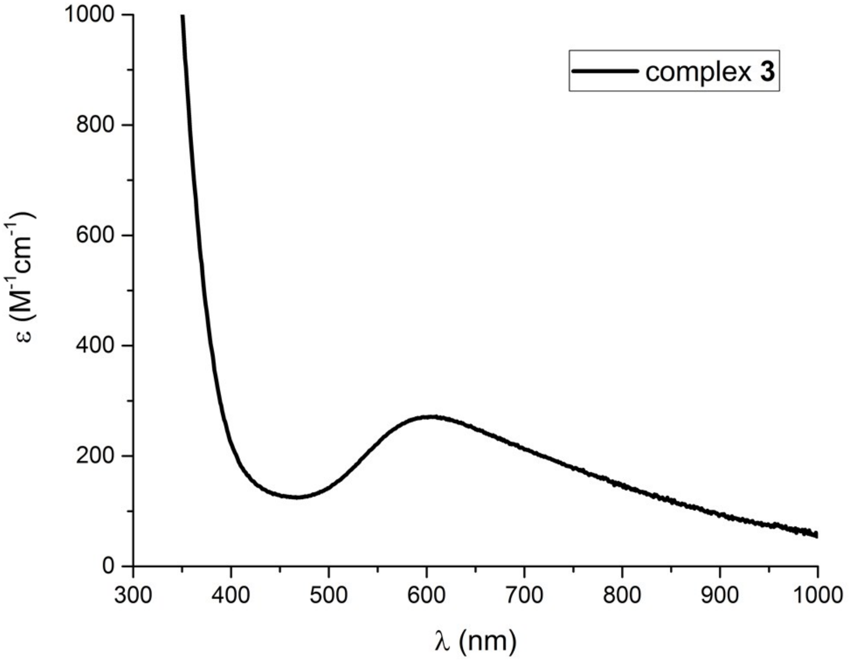


Figure S8. Uv-visible spectrum of complex **3** in water.

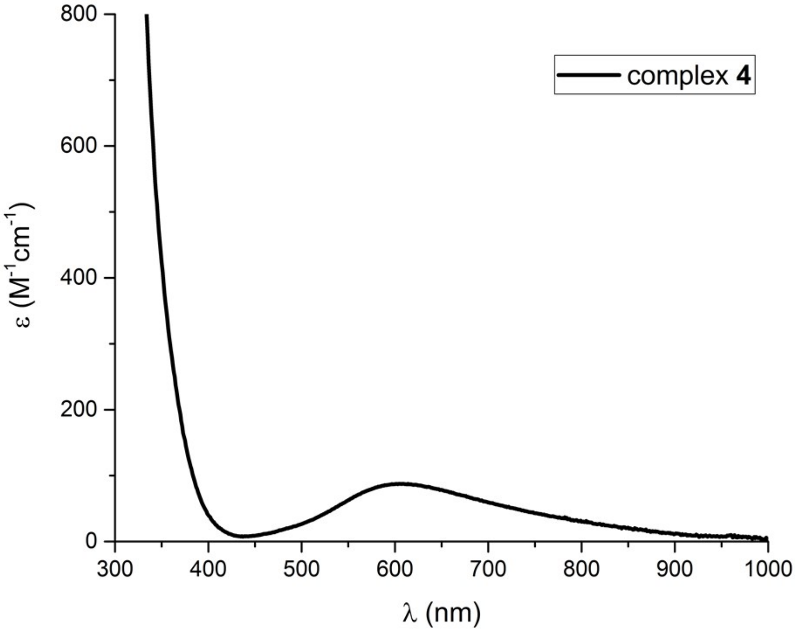


Figure S9. Uv-visible spectrum of complex **4** in water.

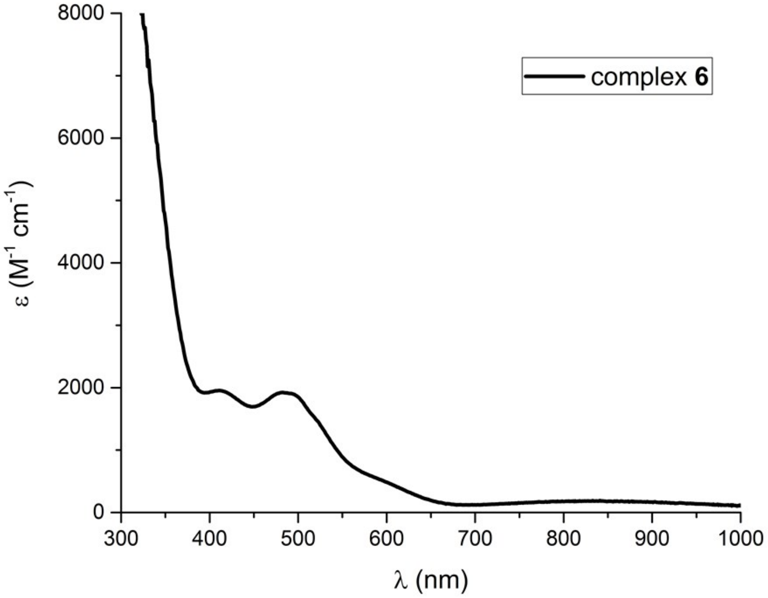
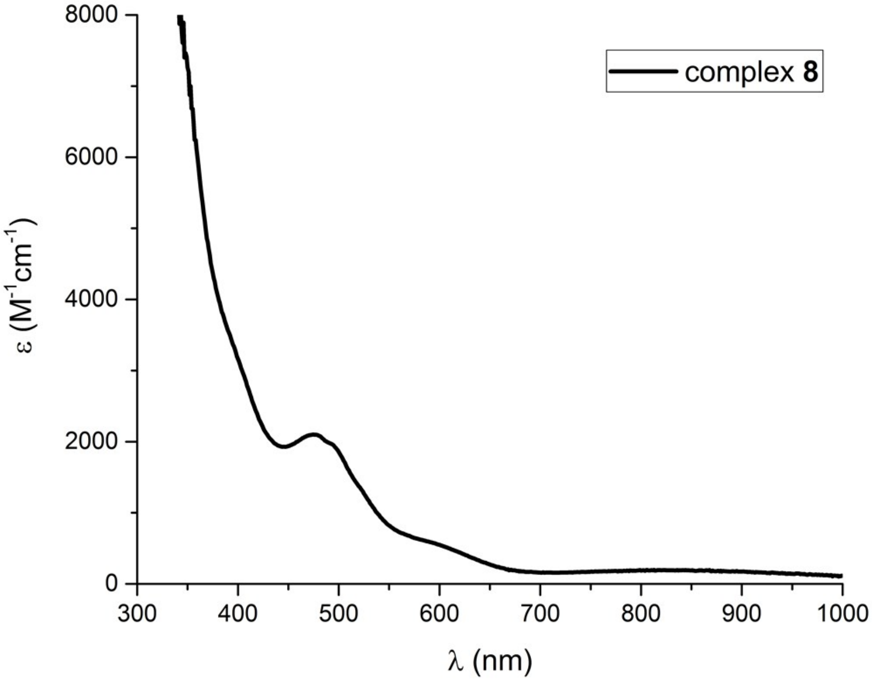
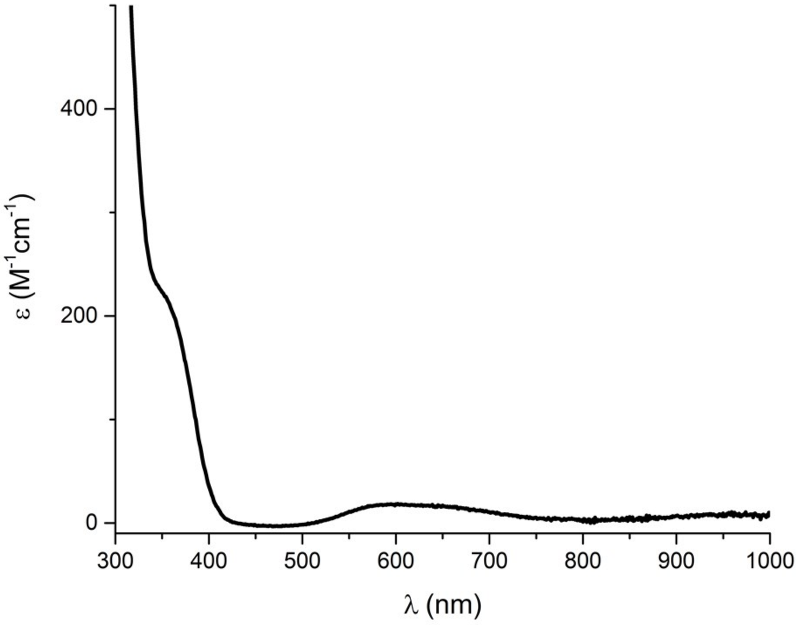


Figure S10. Uv-visible spectrum of complex **6** in DCM.



<u>Figure S11.</u> Uv-visible spectrum of complex **8** in DCM.



<u>Figure S12.</u> Uv-visible spectrum of complex **12** in DCM.

5. FTIR spectra

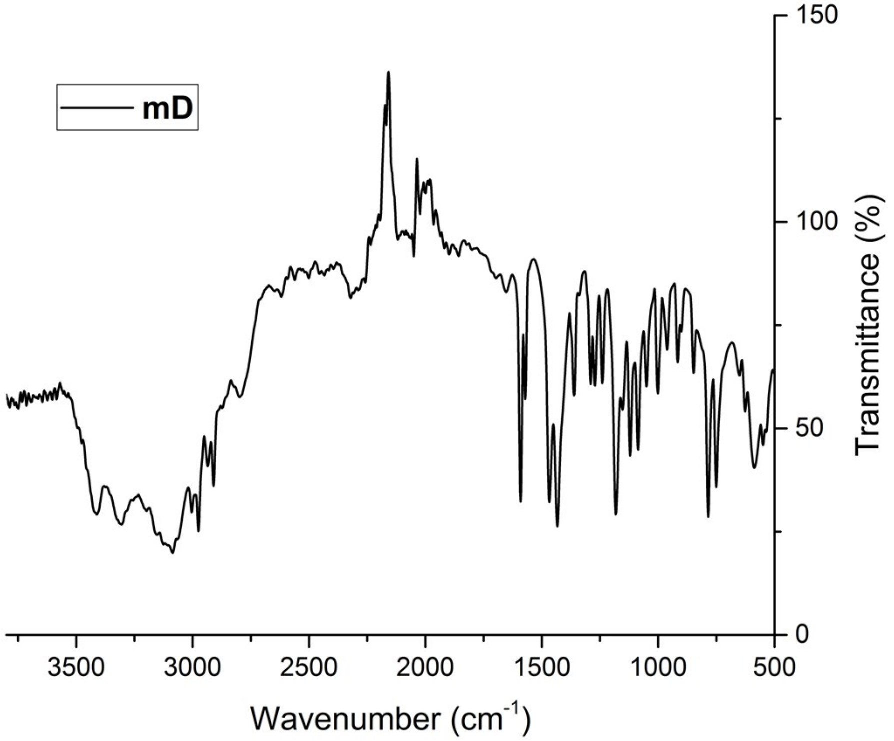


Figure S13. FTIR spectrum of **mD**.

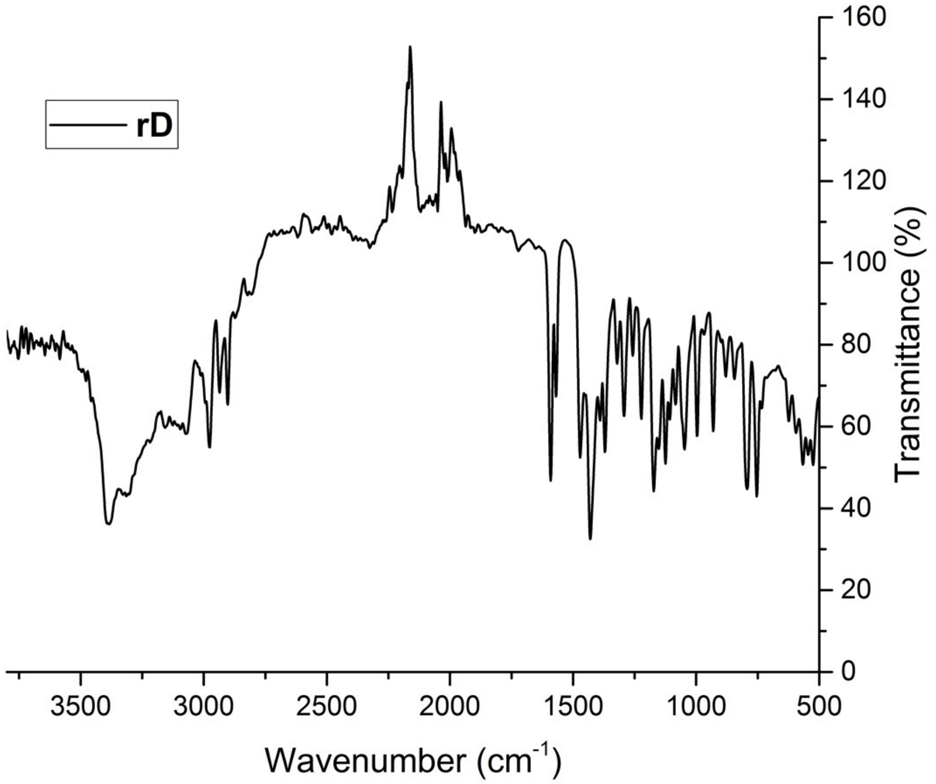


Figure S14. FTIR spectrum of **rD**.

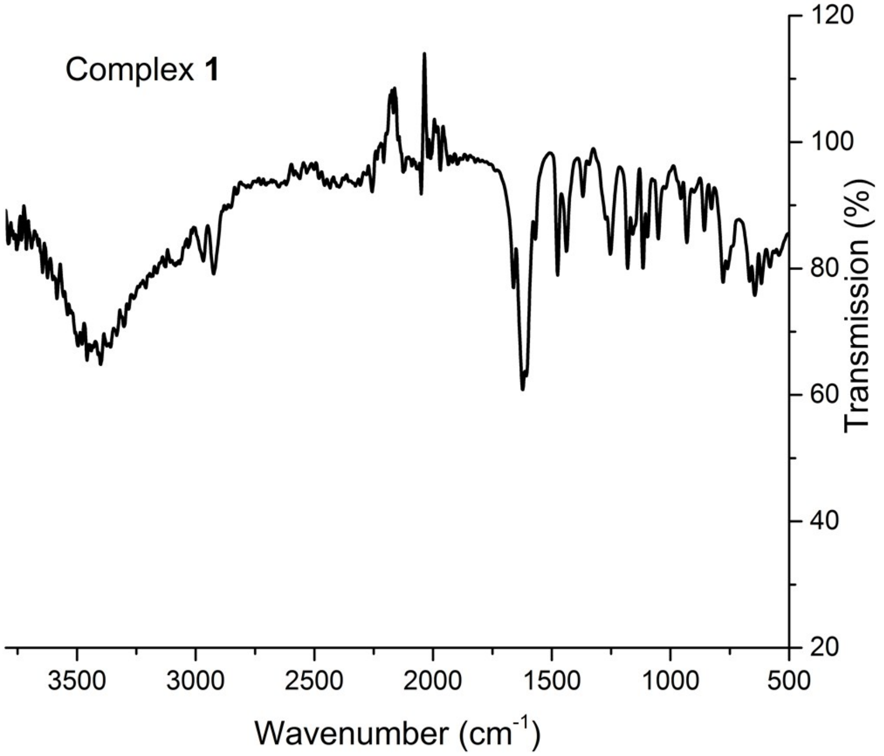


Figure S15. FTIR spectrum of complex **1**.

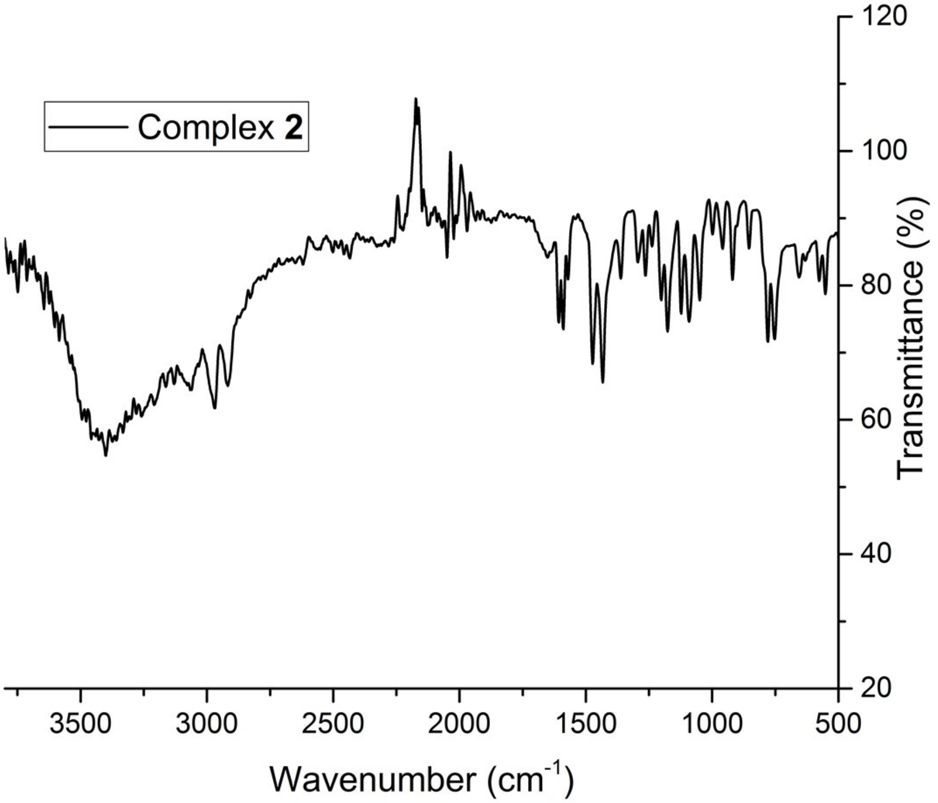
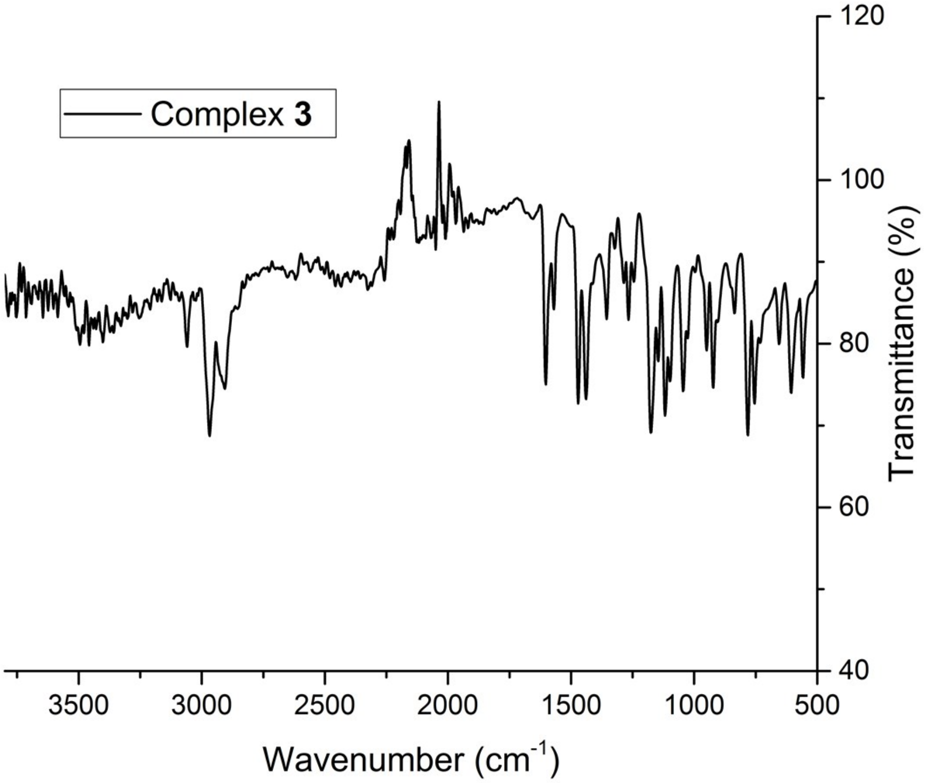


Figure S16. FTIR spectrum of complex **2**.



<u>Figure S17.</u> FTIR spectrum of complex **3**.

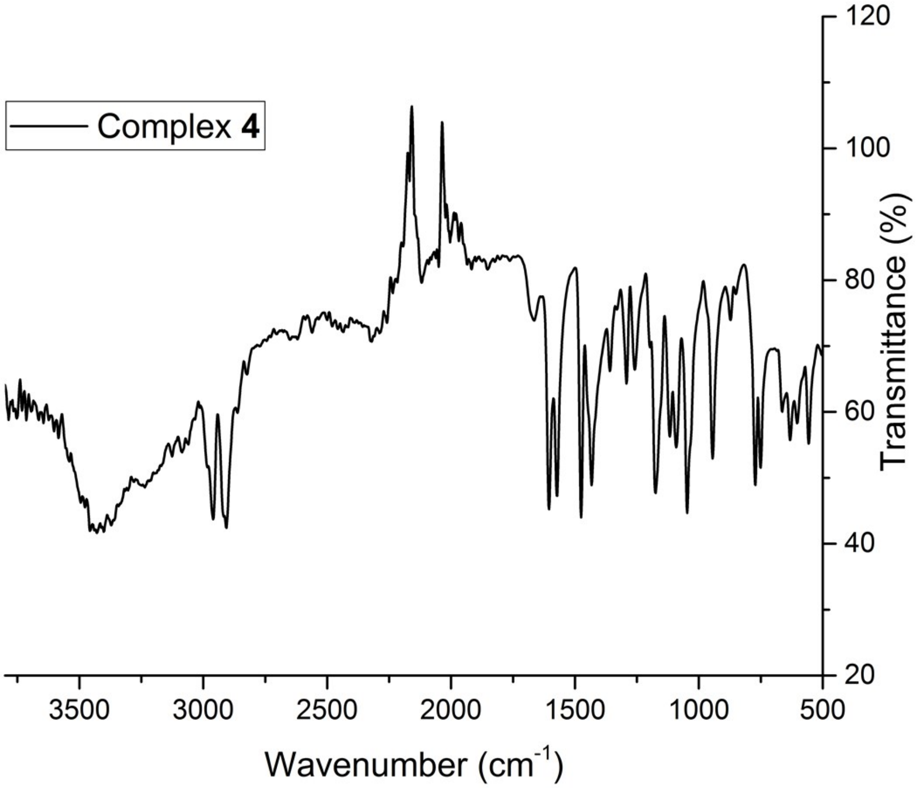


Figure S18. FTIR spectrum of complex **4**.

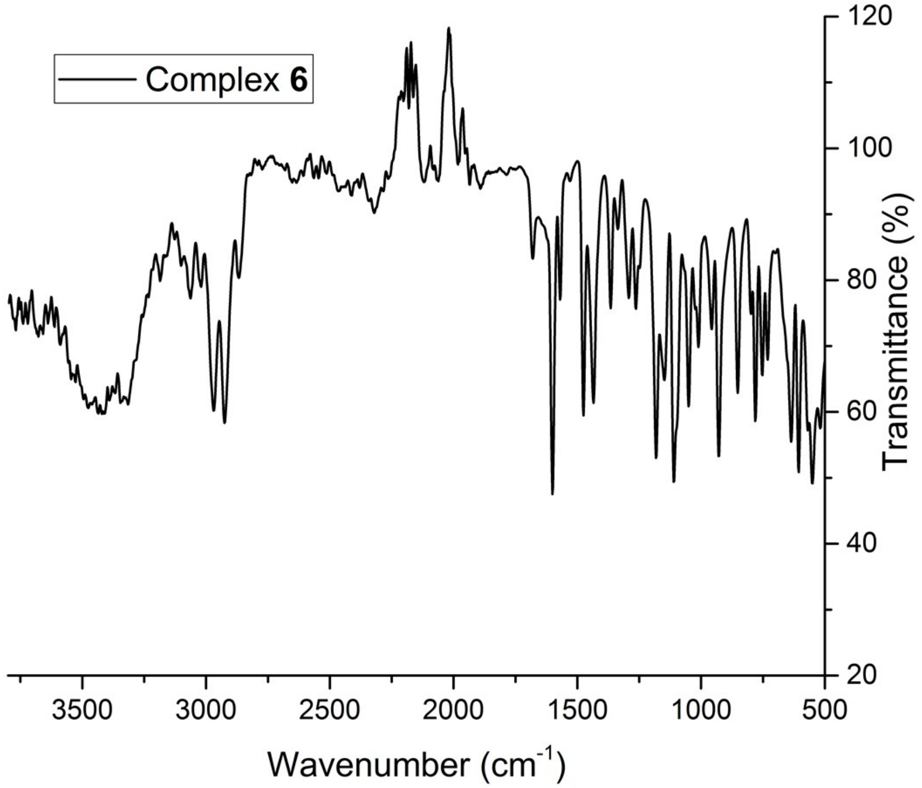


Figure S19. FTIR spectrum of complex **6**.

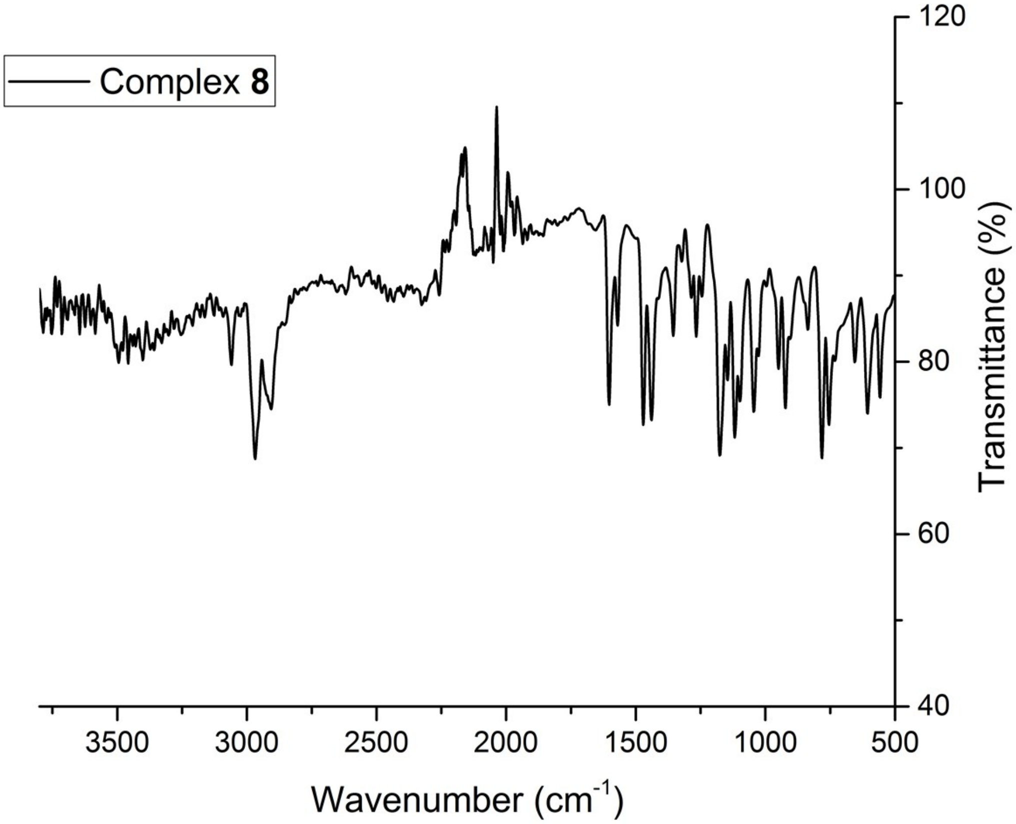


Figure S20. FTIR spectrum of complex **8.**

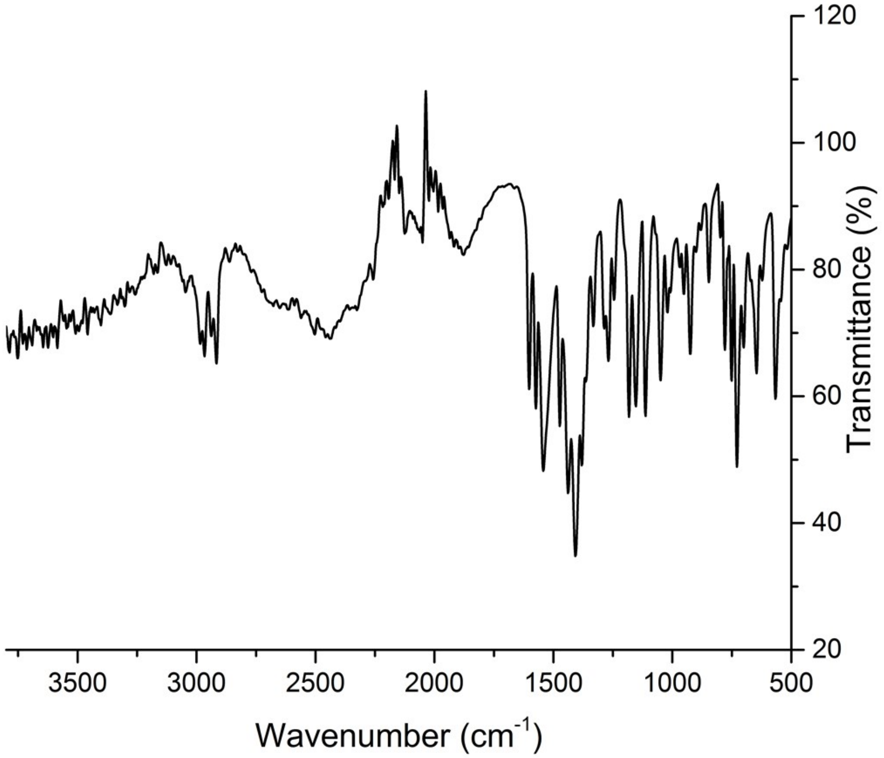
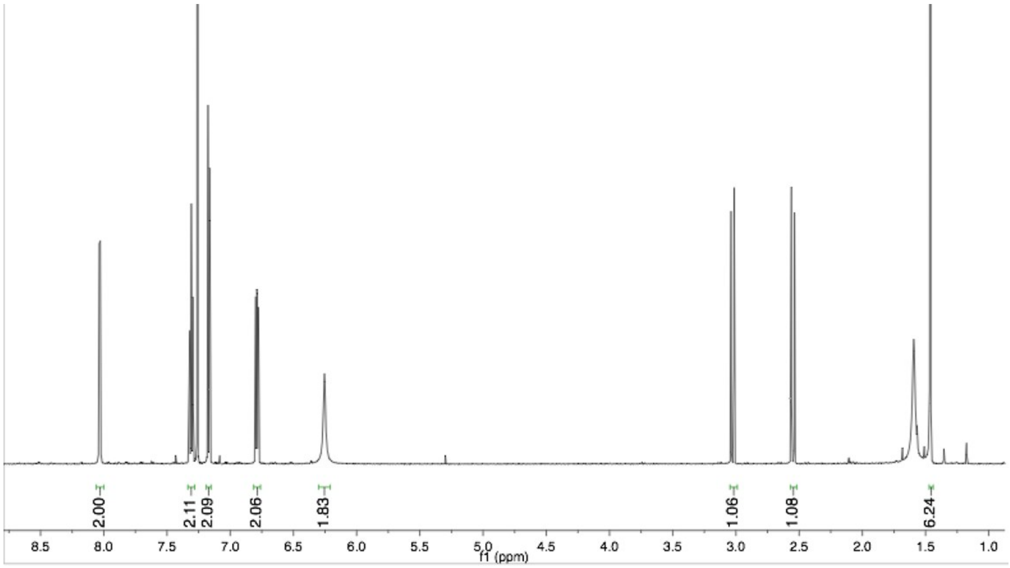


Figure S21. FTIR spectrum of complex **12.**

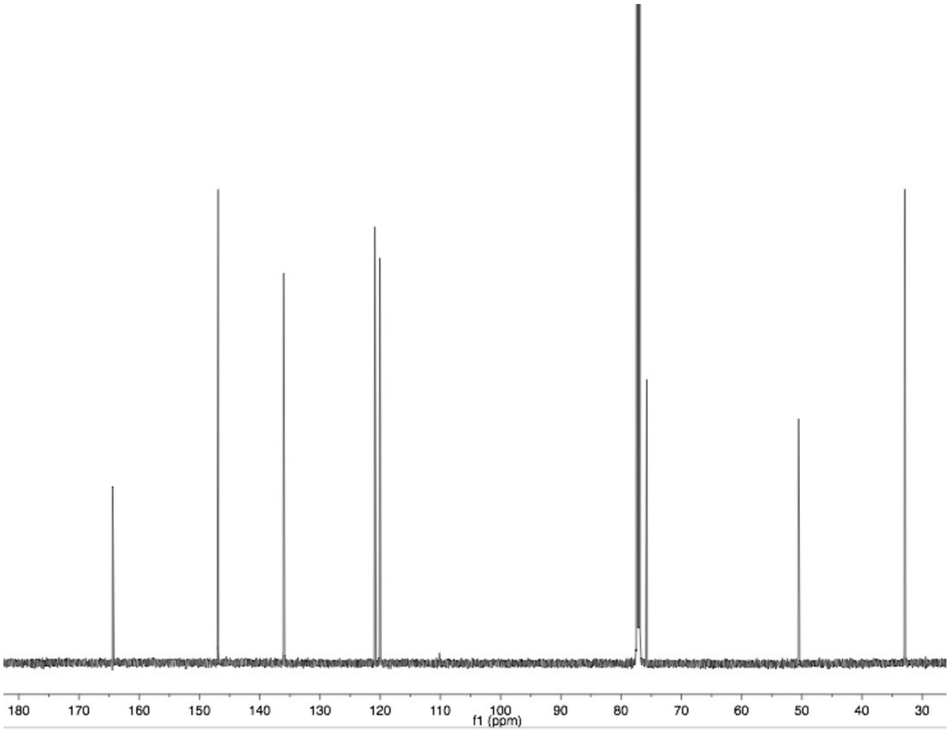
6. NMR and HRMS data

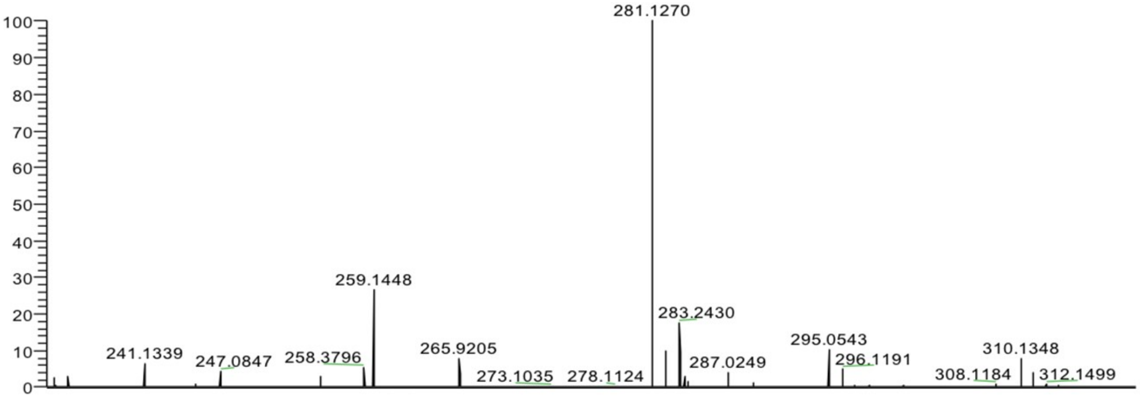
Compound mD

^{1}H NMR



^{13}C NMR

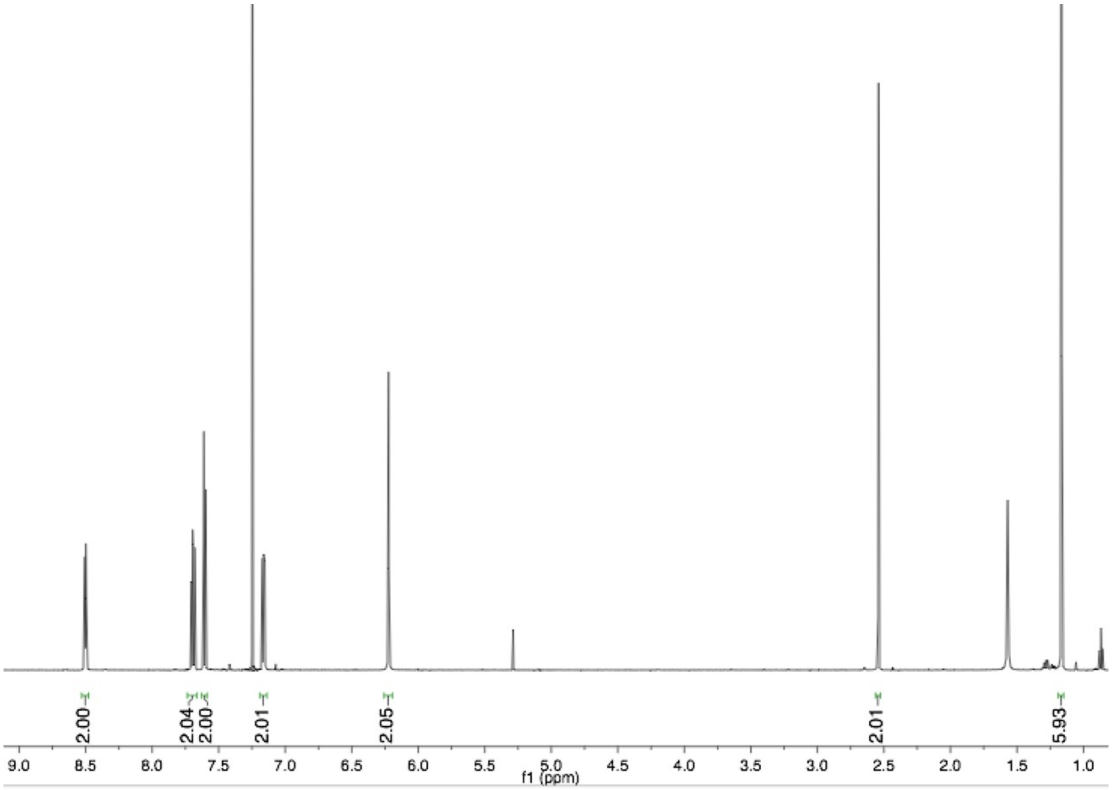




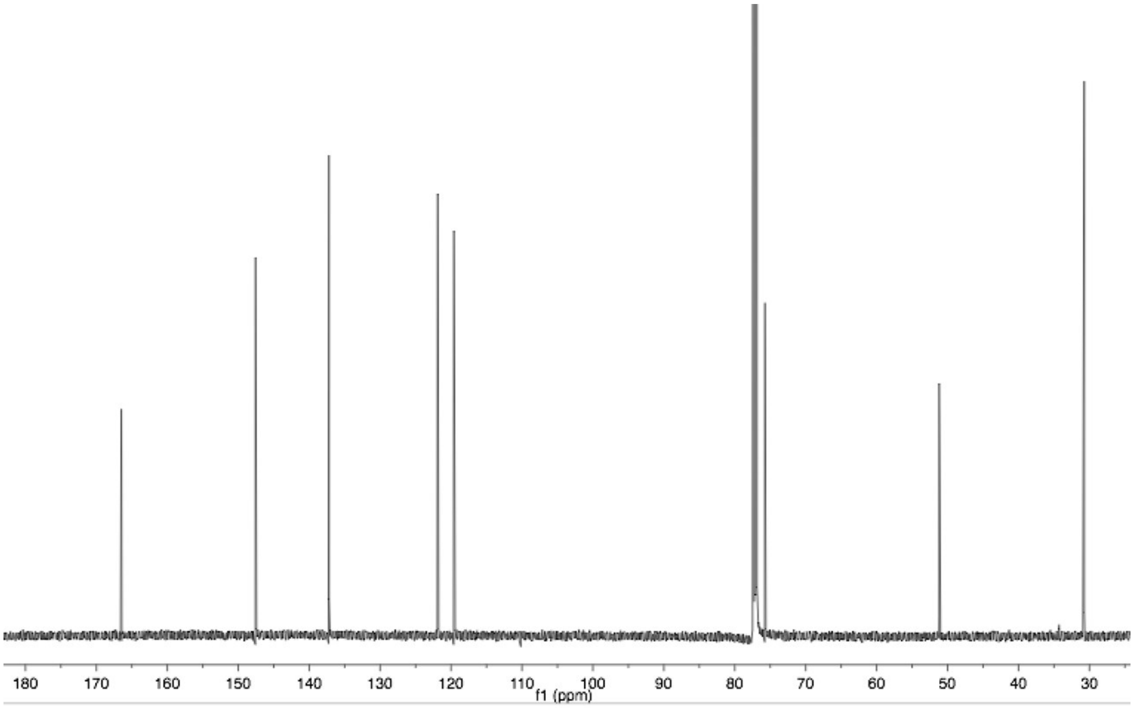
HRMS (FT-ICR): Calculated $[C_{15}H_{18}N_2O_2]Na^+$: 281.1266. Found: 281.1270.

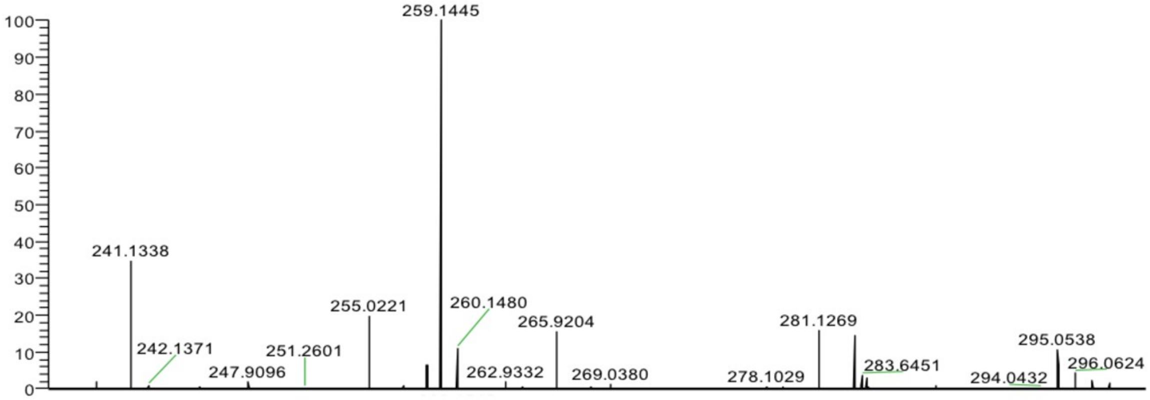
Compound rD

^{1}H NMR



^{13}C NMR





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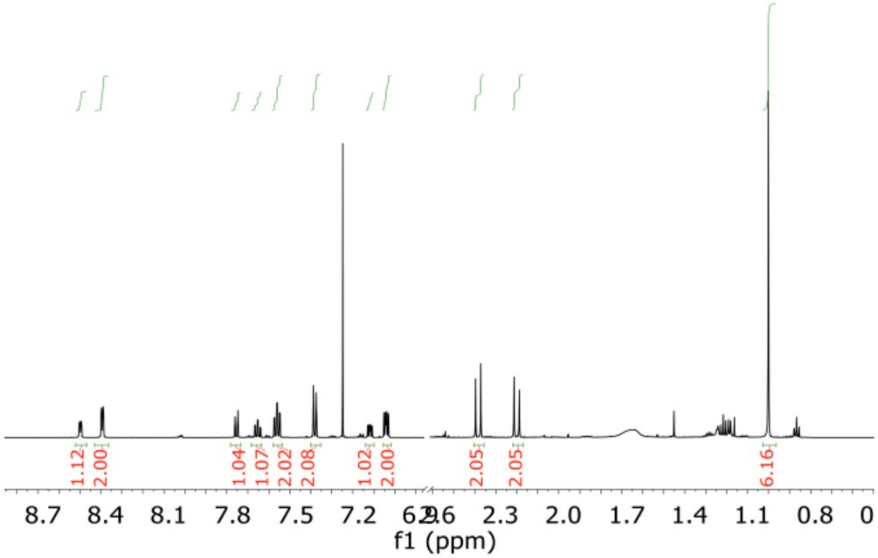
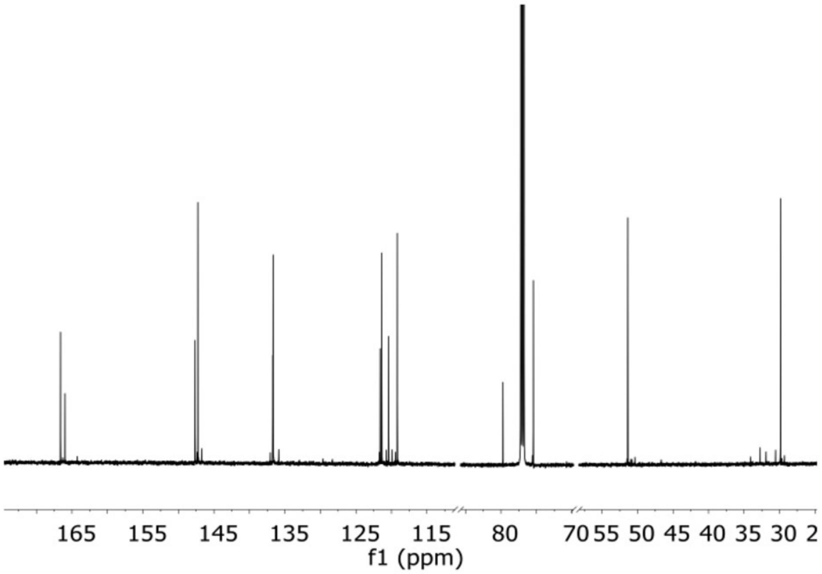
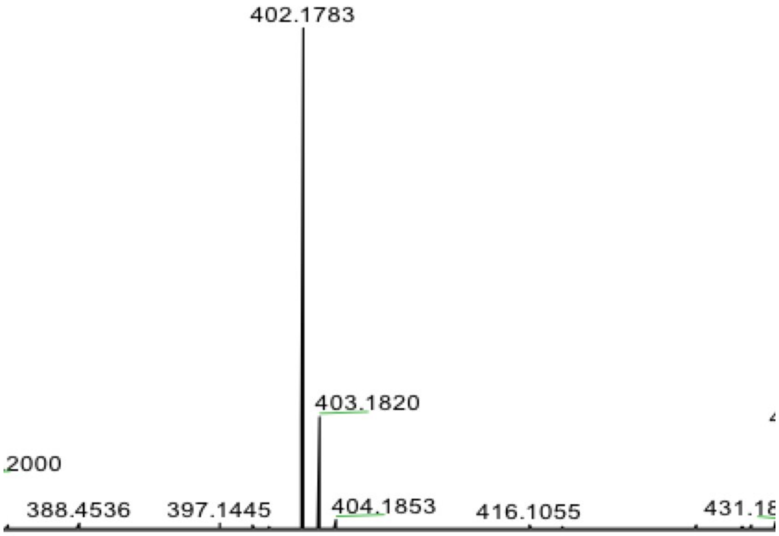
Compound rrT

^{1}H NMR



^{13}C NMR





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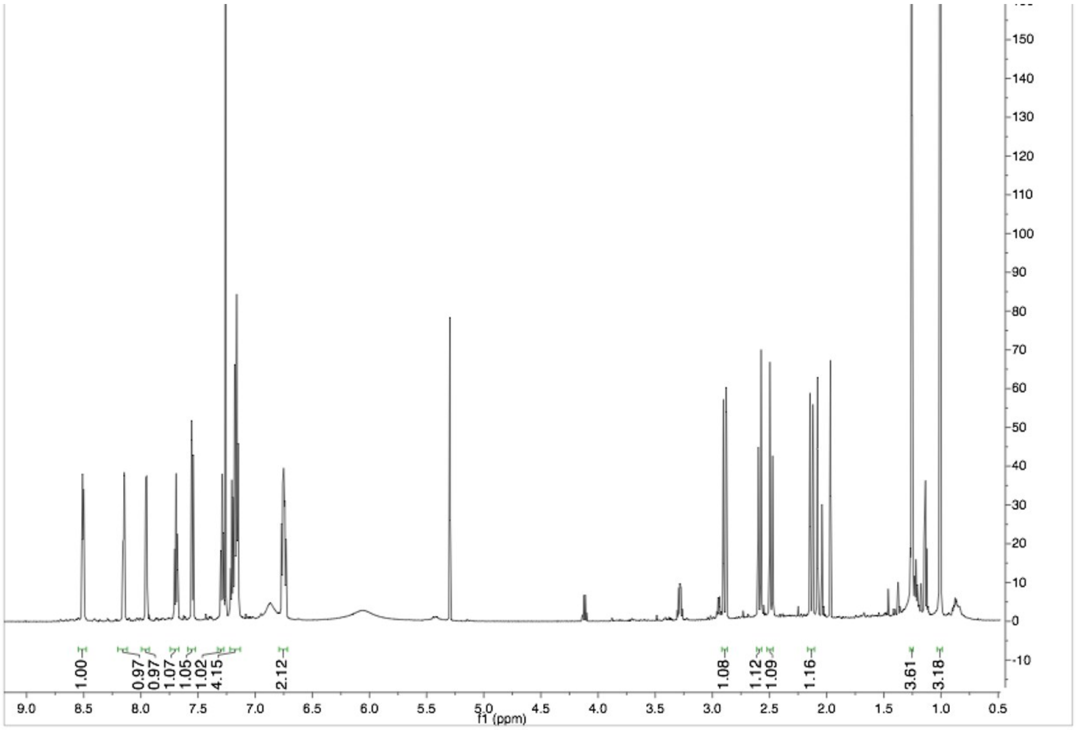
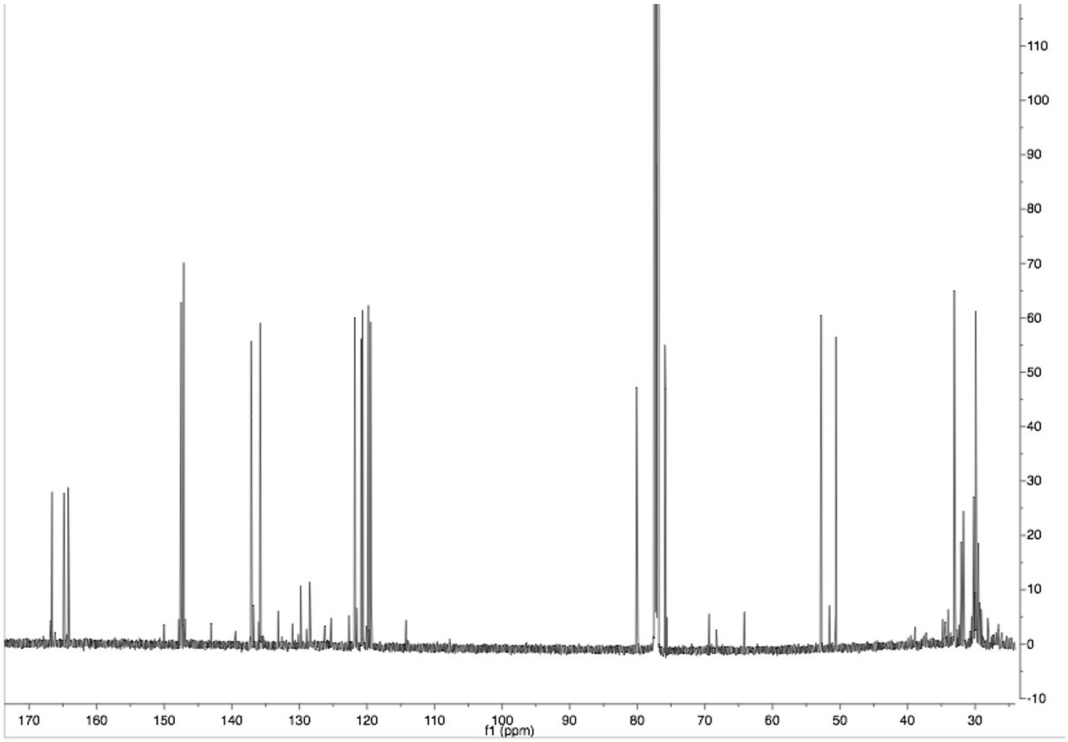
Compound mrT

^{1}H NMR

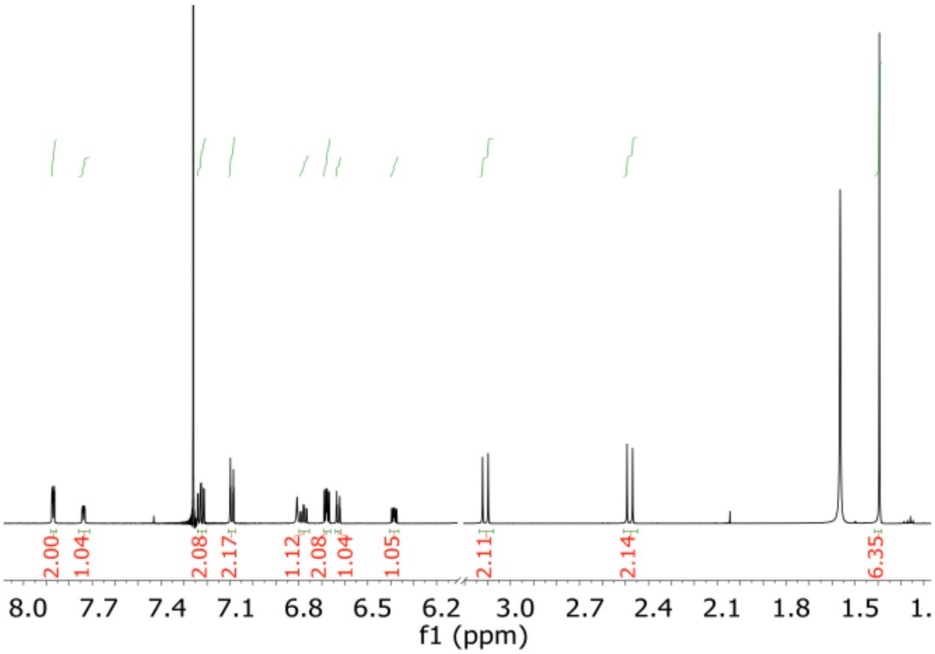


^{13}C NMR

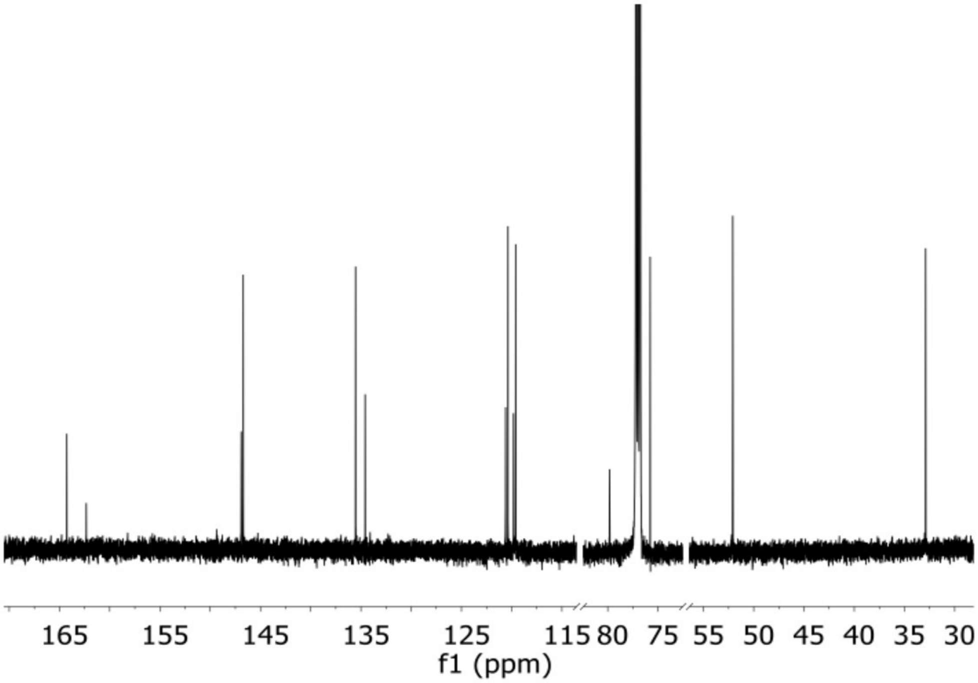


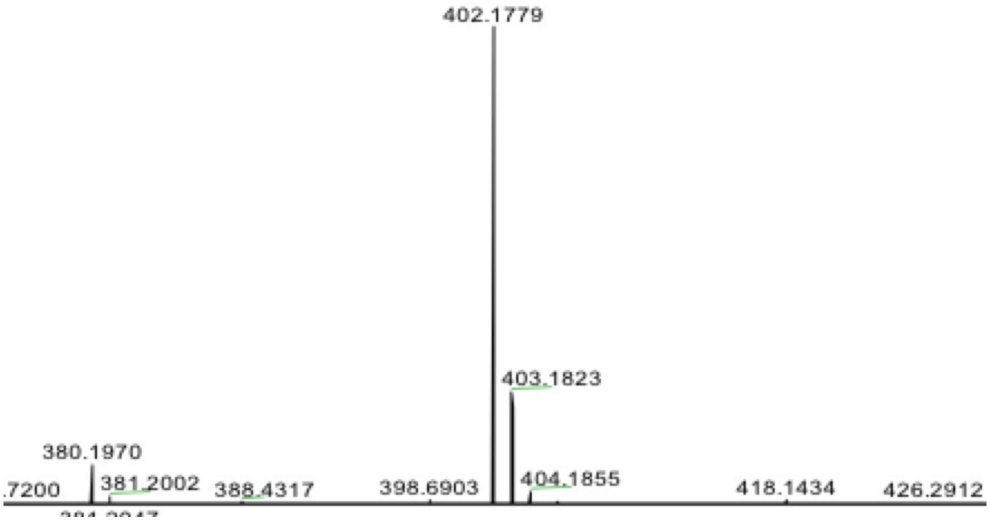
Compound mmT

^{1}H NMR



^{13}C NMR



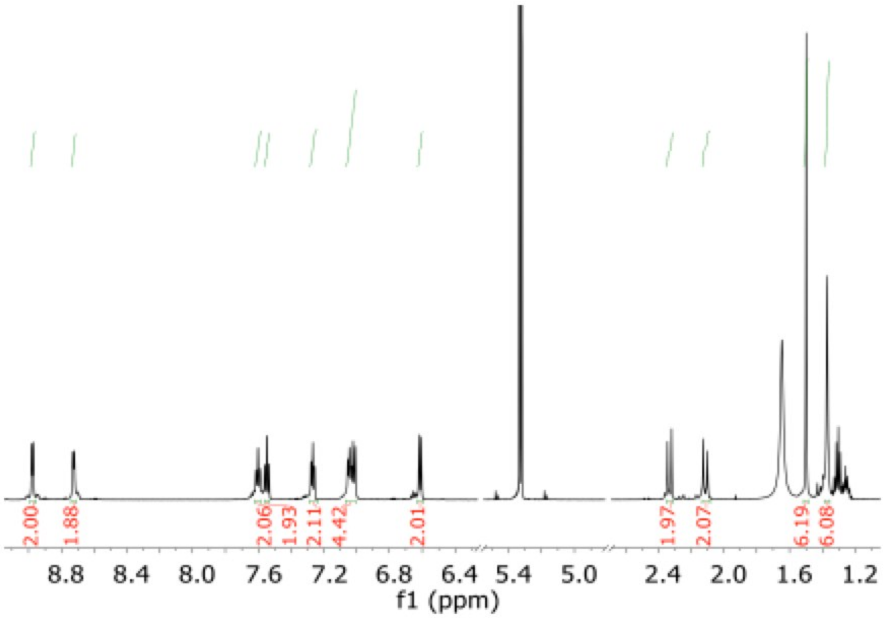


HRMS (FT-ICR): Calculated: $[C_{22}H_{25}N_3O_3]Na^+$: 402.1794. Found: 402.1779.

Complex 1

^{1}H NMR

^{1}H NMR (600 MHz, Methylene Chloride-d_2) δ 8.96 (d, *J* = 5.8, Ar-H, 2H), 8.71 (d, *J* = 5.5 Hz, Ar-H, 2H), 7.59 (m, Ar-H, 2H), 7.53 (m, Ar-H, 2H), 7.25 (m, Ar-H, 2H), 7.04 – 6.99 (m, Ar-H, 4H), 6.60 (d, *J* = 7.9 Hz, Ar-H, 2H), 2.32 (d, *J* = 15.0 Hz, HC-H, 2H), 2.10 (d, *J* = 15.0 Hz, HC-H, 2H), 1.48 (s, CH_3, 7H), 1.36 (s, CH_3, 6H).



Complex 2

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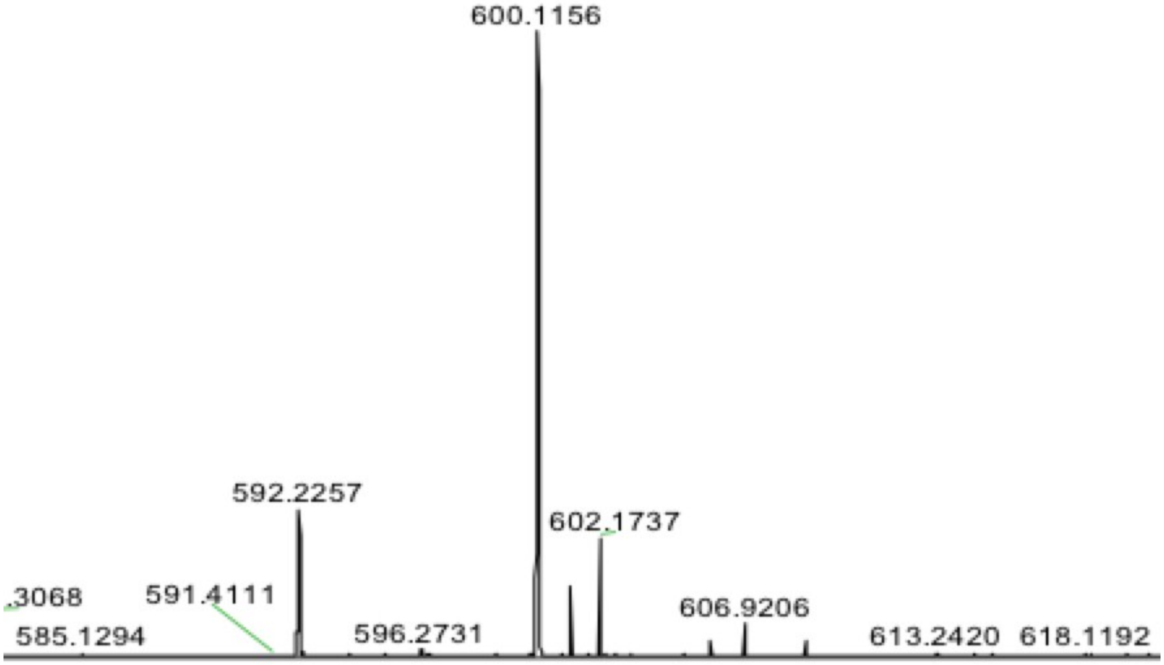
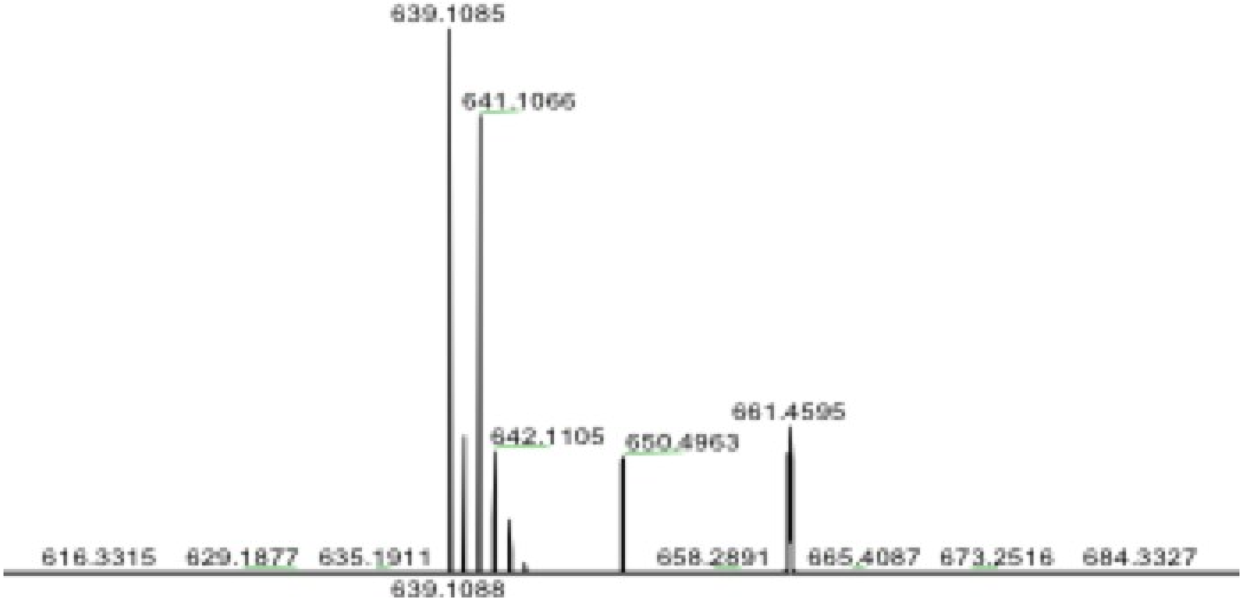


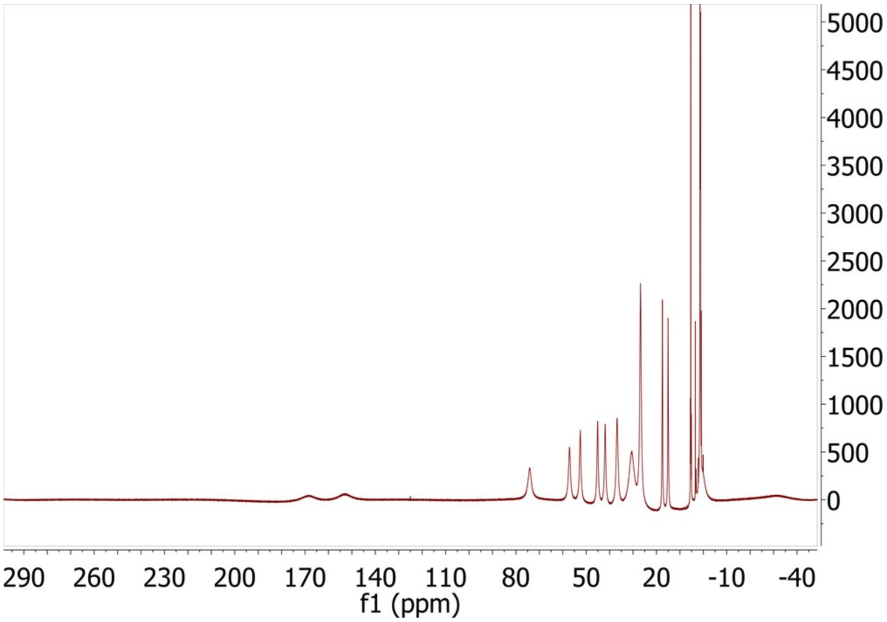
Complex 3

HRMS (FT-ICR): Calculated $[C_{30}H_{32}Cu_2N_4O_4]H^+$: 639.1094. Found: 639.1085.

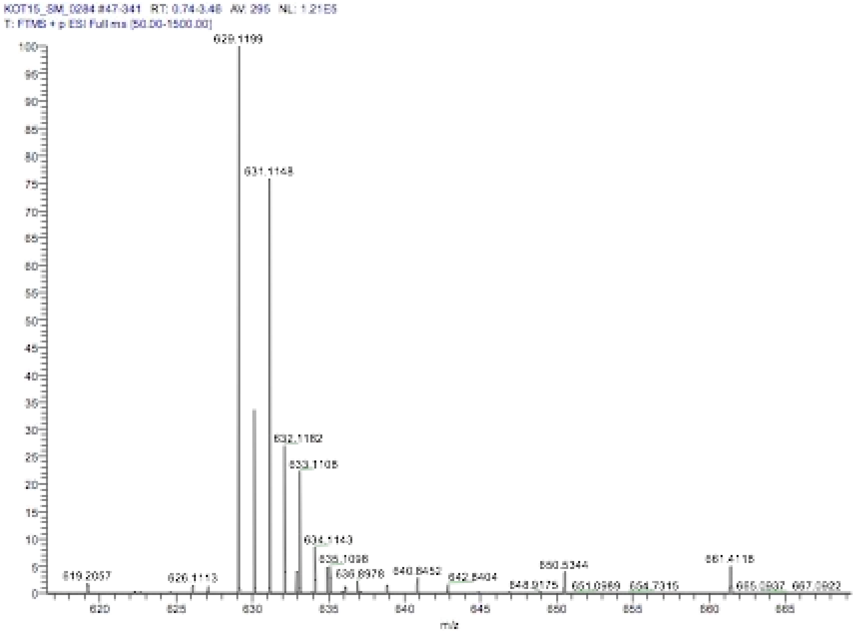


Complex 12

^{1}H NMR

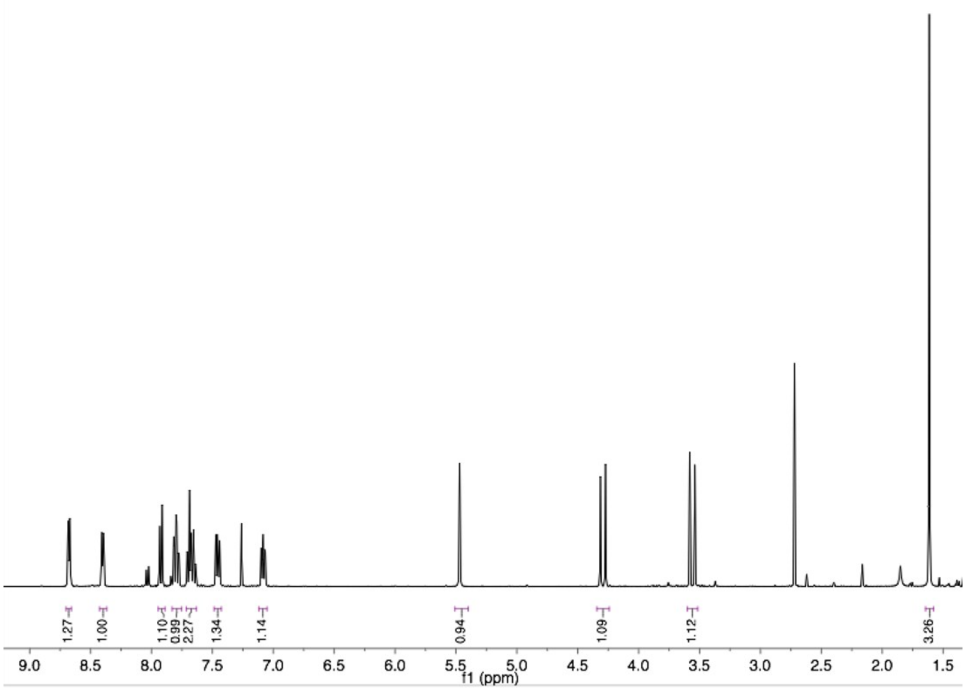


HRMS (FT-ICR): Calc $C_{30}H_{32}N_4Ni_2O_4$: 629.1209. Found: 629.1199

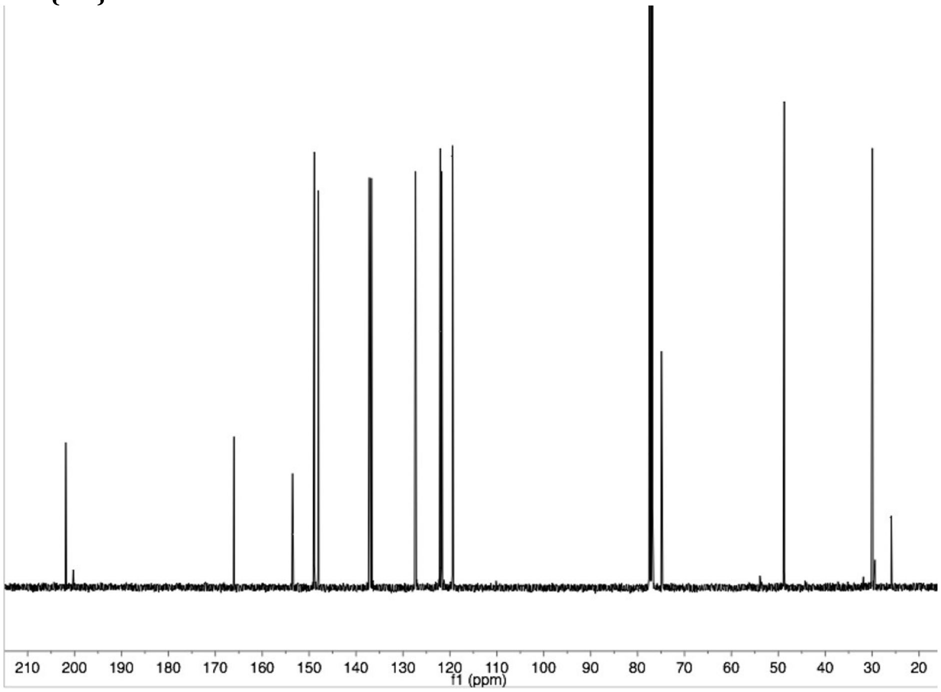


aD

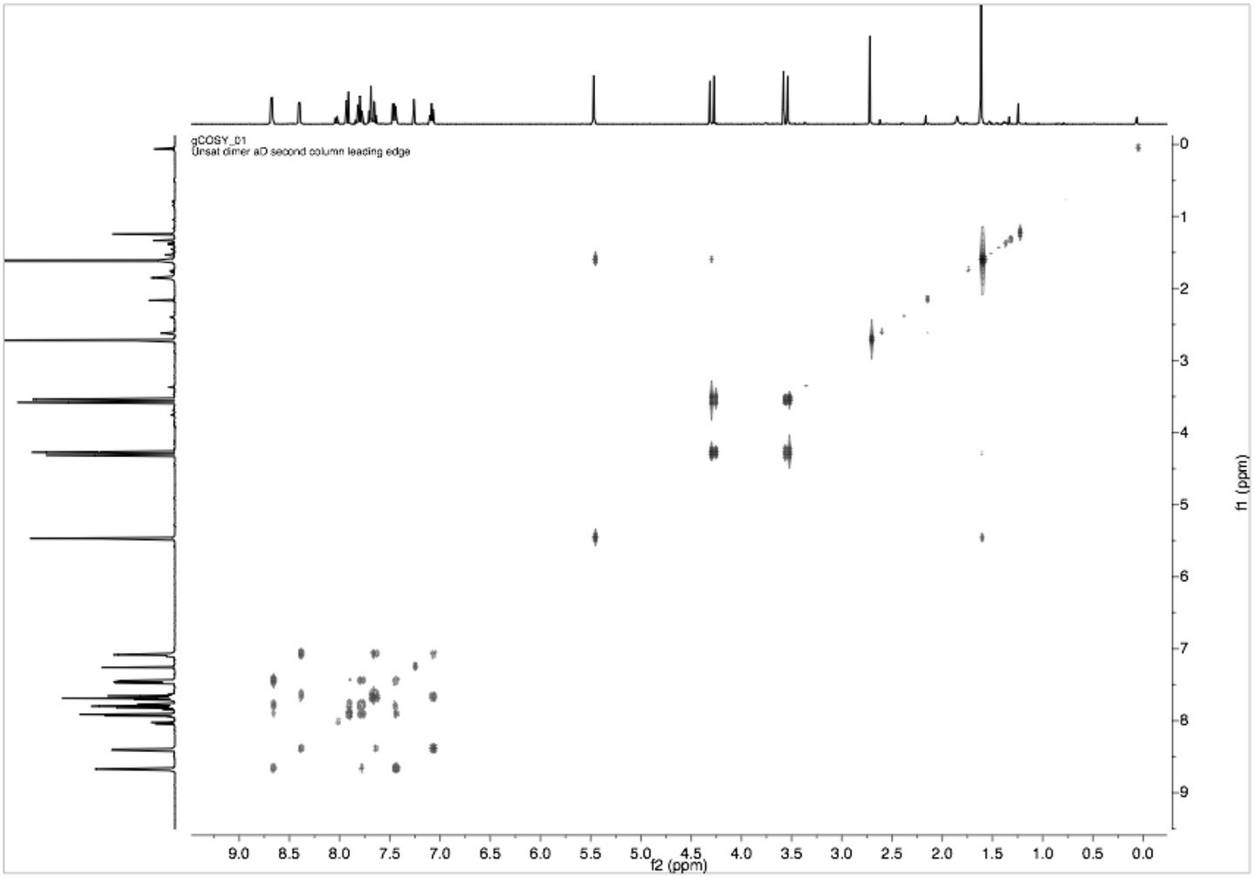
^{1}H NMR



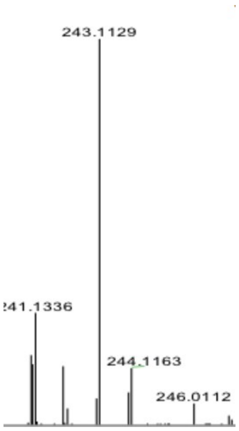
^{13}C{^{1}H} NMR



COSY



HRMS (FT-ICR): Calculated $[C_{14}H_{14}N_2O_2]H^+$: 243.1134 Found: 243.1129.



7. Crystallographic Details

Table S3. Crystal data and structure refinement for mD

Identification code	007-16022-mDL-final	
Empirical formula	C15 H20 N2 O3	
Formula weight	276.33	
Temperature	93(2) K	
Wavelength	1.54187 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 8.32500(10) Å	a= 90°.
	b = 10.87670(10) Å	b= 110.364(8)°.
	c = 8.5879(6) Å	g = 90°.
Volume	729.02(6) Å^3	
Z	2	
Density (calculated)	1.259 Mg/m^3	
Absorption coefficient	0.719 mm^{-1}	
F(000)	296	
Crystal size	0.200 x 0.100 x 0.100 mm^3	
Crystal color and habit	Colorless Block	
Diffractometer	Rigaku Saturn 944+ CCD	
Theta range for data collection	5.495 to 66.582°.	
Index ranges	-9<=h<=9, -12<=k<=12, -10<=l<=10	
Reflections collected	24343	
Independent reflections	2573 [R(int) = 0.0439]	
Observed reflections (I > 2sigma(I))	2485	
Completeness to theta = 66.582°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.853	
Solution method	SHELXT-2014/5 (Sheldrick, 2014)	
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)	
Data / restraints / parameters	2573 / 5 / 199	
Goodness-of-fit on F^2	1.057	
Final R indices [I>2sigma(I)]	R1 = 0.0263, wR2 = 0.0616	
R indices (all data)	R1 = 0.0276, wR2 = 0.0623	
Absolute structure parameter	0.02(8)	

Extinction coefficient	n/a
Largest diff. peak and hole	0.122 and -0.132 e.Å^{-3}

Table S4. Hydrogen bonds for mD [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1)...O(2)	0.86(2)	1.82(3)	2.622(2)	154(3)
O(2)-H(2)...O(3)	0.89(2)	1.78(2)	2.668(2)	174(3)
O(3)-H(3B)...O(1)#1	0.85(2)	1.95(2)	2.783(2)	166(3)
O(3)-H(3A)...N(1)#2	0.89(2)	1.91(2)	2.763(2)	160(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y+1/2,-z+1 #2 x,y,z+1

Refinement Details for mD

Low-temperature diffraction data (ω-scans) were collected on a Rigaku MicroMax-007HF diffractometer coupled to a Saturn994+ CCD detector with Cu Kα (λ = 1.54178 Å) for the structure of **mD**. The diffraction images were processed and scaled using Rigaku CrystalClear software. The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL (Sheldrick, G. M. Acta Cryst. 2008, A64, 112–122). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The only exceptions are H1, H2, H3a and H3b, which were found in the difference map and semi-freely refined with a distance restraint of 0.85(2) Å. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The full numbering scheme of **mD** can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information. CCDC number **1529458** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

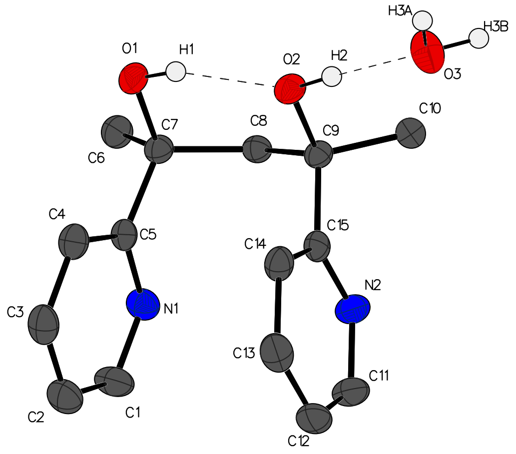


Figure S22. Full numbering scheme of **mD**. Non-heteroatom bound hydrogen atoms have been omitted for clarity.

Table S5. Crystal data and structure refinement for rD.

Identification code	mini-15089-rdl	
Empirical formula	C15 H20 N2 O3	
Formula weight	276.33	
Temperature	93(2) K	
Wavelength	0.71075 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 9.7831(7) Å	a= 90°.
	b = 9.0271(6) Å	b= 103.691(7)°.
	c = 16.4023(12) Å	g = 90°.
Volume	1407.38(18) Å^3	
Z	4	
Density (calculated)	1.304 Mg/m^3	
Absorption coefficient	0.091 mm^{-1}	
F(000)	592	
Crystal size	0.400 x 0.200 x 0.200 mm^3	
Crystal color and habit	Colorless Block	
Diffractometer	Rigaku Mercury275R CCD	
Theta range for data collection	3.112 to 30.505°.	
Index ranges	-13<=h<=11, -12<=k<=12, -23<=l<=23	
Reflections collected	12383	
Independent reflections	4243 [R(int) = 0.0365]	
Observed reflections (I > 2sigma(I))	3275	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.892	
Solution method	SHELXT-2014/5 (Sheldrick, 2014)	
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)	
Data / restraints / parameters	4243 / 3 / 199	
Goodness-of-fit on F^2	1.060	
Final R indices [I>2sigma(I)]	R1 = 0.0540, wR2 = 0.1089	
R indices (all data)	R1 = 0.0774, wR2 = 0.1170	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.426 and -0.241 e.Å^{-3}	

Table S6. Hydrogen bonds for rD [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1)...O(3)#1	0.870(15)	1.797(15)	2.6662(14)	176(2)
O(2)-H(2)...O(1)	0.87(2)	1.87(2)	2.6458(14)	146.3(19)
O(3)-H(3A)...N(1)#2	0.869(15)	2.017(16)	2.8652(15)	165(2)
O(3)-H(3B)...N(2)	0.874(15)	1.980(16)	2.8204(15)	161(2)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y+1/2,-z+1/2 #2 x,y-1,z

Refinement Details for rD

Low-temperature diffraction data (ω-scans) were collected on a Rigaku SCX Mini diffractometer (sealed tube) coupled to a Rigaku Mercury 275R CCD detector with Mo Kα (λ = 0.71075 Å) for the structure of **T3**. The diffraction images were processed and scaled using the Rigaku CrystalClear software (CrystalClear and CrystalStructure; Rigaku/MSC: The Woodlands, TX, 2005). The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL (Sheldrick, G. M. Acta Cryst. 2008, A64, 112–122). All non-hydrogen atoms were refined anisotropically. All carbon-bound hydrogen atoms were first found in the difference map, then generated geometrically and refined as riding atoms with C-H distances = 0.95 - 0.99 angstroms and Uiso(H) = 1.2 times Ueq(C) for CH and CH2 groups and Uiso(H) = 1.5 times Ueq(C) for CH3 groups. H1, H2, H3A and H3B were found in the difference map and semi-freely refined with a distance restraint of 0.85(2) Å for O-H distances. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The full numbering scheme of **mD** can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information. CCDC number **1529459** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

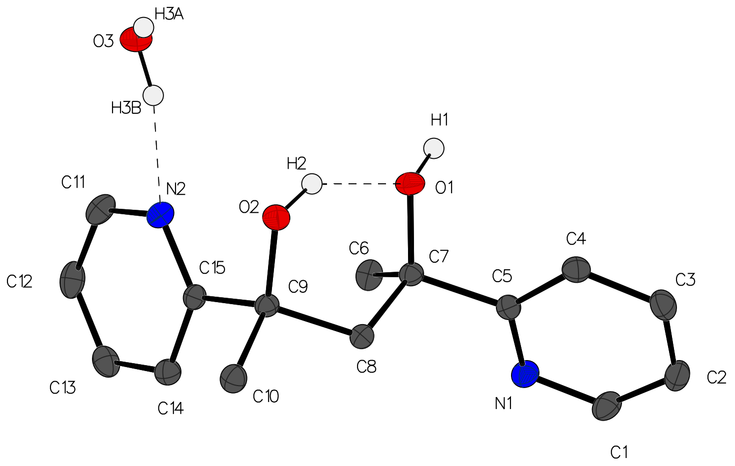


Figure S23. Full numbering scheme of **rD**. Non-heteroatom bound hydrogen atoms have been omitted for clarity.

Table S7. Crystal data and structure refinement for **rrT.**

Identification code	007-16221	
Empirical formula	C22 H25 N3 O3	
Formula weight	379.45	
Temperature	93(2) K	
Wavelength	1.54187 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 13.1202(9) Å	a= 90°.
	b = 13.8904(2) Å	b= 104.628(7)°.
	c = 10.95920(10) Å	g = 90°.
Volume	1932.52(15) Å^3	
Z	4	
Density (calculated)	1.304 Mg/m^3	
Absorption coefficient	0.709 mm^{-1}	
F(000)	808	
Crystal size	0.100 x 0.050 x 0.050 mm^3	
Crystal color and habit	Colorless Plate	
Diffractometer	Rigaku Saturn 944+ CCD	
Theta range for data collection	3.482 to 66.586°.	
Index ranges	-15<=h<=15, -16<=k<=16, -13<=l<=12	
Reflections collected	38183	
Independent reflections	3363 [R(int) = 0.0451]	
Observed reflections (I > 2sigma(I))	2826	
Completeness to theta = 66.586°	98.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.865	
Solution method	SHELXT-2014/5 (Sheldrick, 2014)	
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)	
Data / restraints / parameters	3363 / 3 / 267	
Goodness-of-fit on F^2	1.094	
Final R indices [I>2sigma(I)]	R1 = 0.0422, wR2 = 0.0971	
R indices (all data)	R1 = 0.0514, wR2 = 0.1026	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.251 and -0.245 e.Å^{-3}	

Table S8. Hydrogen bonds for **rrT** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1)...O(2)	0.867(16)	1.852(19)	2.6281(18)	148(2)
O(2)-H(2)...O(3)	0.888(17)	1.802(19)	2.6241(17)	153(2)

Refinement Details for rrT

Low-temperature diffraction data (ω-scans) were collected on a Rigaku MicroMax-007HF diffractometer coupled to a Saturn994+ CCD detector with Cu Kα (λ = 1.54178 Å) for the structure of **rrT**. The diffraction images were processed and scaled using Rigaku CrystalClear software. The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL (Sheldrick, G. M. Acta Cryst. 2008, A64, 112–122). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The only exceptions are H1, H2 and H3, which were found in the difference map and semi-freely refined with a distance restraint of 0.85(2) Å for O-H distances.The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The full numbering scheme of **rrT** can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information. CCDC number **1529460** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

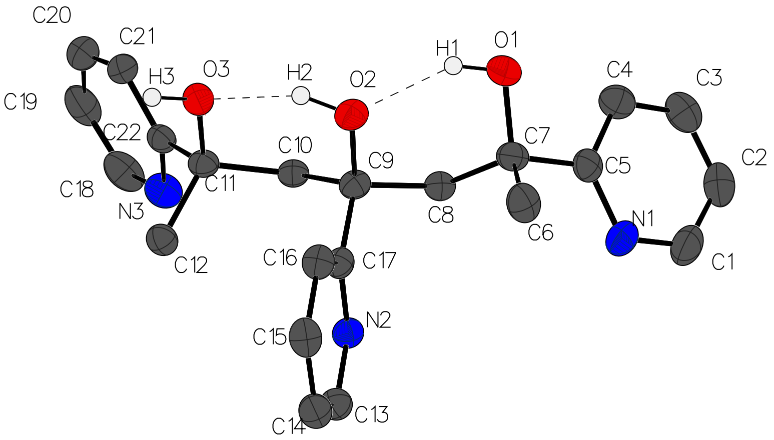


Figure S24. Full numbering scheme of **rrT**. Non-heteroatom bound hydrogen atoms have been omitted for clarity.

Table S9. Crystal data and structure refinement for **mrT.**

Identification code	007-17008-T2	
Empirical formula	C22 H27 N3 O4	
Formula weight	397.46	
Temperature	93(2) K	
Wavelength	1.54187 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 10.84070(10) Å	a= 90°.
	b = 15.3854(2) Å	b= 90°.
	c = 24.0090(16) Å	g = 90°.
Volume	4004.4(3) Å^3	
Z	8	
Density (calculated)	1.319 Mg/m^3	
Absorption coefficient	0.745 mm^{-1}	
F(000)	1696	
Crystal size	0.200 x 0.200 x 0.200 mm^3	
Crystal color and habit	Colorless Prism	
Diffractometer	Rigaku Saturn 944+ CCD	
Theta range for data collection	3.682 to 66.603°.	
Index ranges	-12<=h<=12, -18<=k<=18, -28<=l<=28	
Reflections collected	124474	
Independent reflections	3547 [R(int) = 0.1646]	
Observed reflections (I > 2sigma(I))	2799	
Completeness to theta = 66.603°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.605	
Solution method	SHELXT-2014/5 (Sheldrick, 2014)	
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)	
Data / restraints / parameters	3547 / 6 / 285	
Goodness-of-fit on F^2	1.117	
Final R indices [I>2sigma(I)]	R1 = 0.0673, wR2 = 0.1974	
R indices (all data)	R1 = 0.0771, wR2 = 0.2094	
Extinction coefficient	0.0019(4)	
Largest diff. peak and hole	0.316 and -0.281 e.Å^{-3}	

Table S10. Hydrogen bonds for **mrT** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(4)-H(4B)...N(3)#1	0.854(18)	2.00(2)	2.823(3)	161(4)
O(4)-H(4A)...N(1)#2	0.847(19)	2.06(2)	2.857(3)	157(5)
O(2)-H(2)...O(3)	0.877(19)	1.87(3)	2.654(3)	147(4)
O(1)-H(1)...O(2)	0.866(19)	2.02(3)	2.746(3)	141(4)
O(3)-H(3)...O(4)	0.884(19)	1.78(2)	2.663(3)	177(4)

Symmetry transformations used to generate equivalent atoms:

#1 x-1/2,y,-z+1/2 #2 x-1,y,z

Refinement Details for mrT

Low-temperature diffraction data (ω-scans) were collected on a Rigaku MicroMax-007HF diffractometer coupled to a Saturn994+ CCD detector with Cu Kα (λ = 1.54178 Å) for the structure of **mrT**. The diffraction images were processed and scaled using Rigaku CrystalClear software. The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL (Sheldrick, G. M. Acta Cryst. 2008, A64, 112–122). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The only exceptions are H1-H5, which were found in the difference map and semi-freely refined with a distance restraint of 0.85(2) Å for O-H distances and a distance restraint of 1.388(2) Å between water H atoms H4A and H4B. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The full numbering scheme of **mrT** can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information. CCDC number **1529461** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

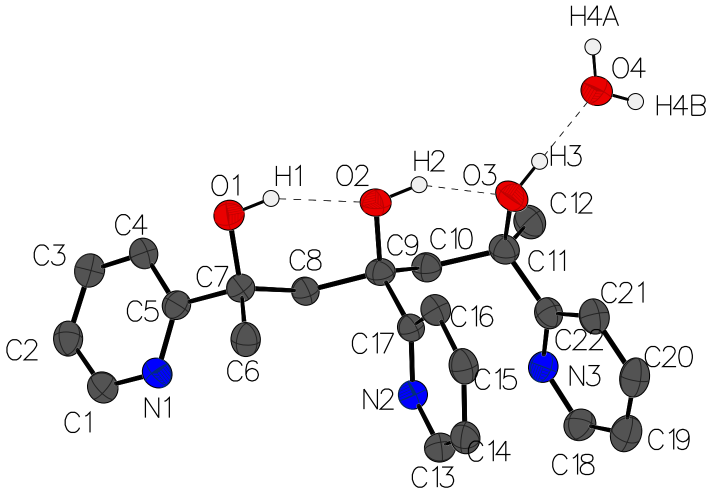


Figure S25. Full numbering scheme of **mrT**. Non-heteroatom bound hydrogen atoms have been omitted for clarity.

<u>Table S11.</u> Crystal data and structure refinement for **mmT**.

Identification code	T3ligand	
Empirical formula	C22 H25 N3 O3	
Formula weight	379.45	
Temperature	93(2) K	
Wavelength	0.71075 Å	
Crystal system	Monoclinic	
Space group	Pn	
Unit cell dimensions	a = 8.7376(14) Å	a= 90°.
	b = 12.3604(19) Å	b= 108.002(8)°.
	c = 9.2476(14) Å	g = 90°.
Volume	949.8(3) Å^3	
Z	2	
Density (calculated)	1.327 Mg/m^3	
Absorption coefficient	0.089 mm^{-1}	
F(000)	404	
Crystal size	0.20 x 0.20 x 0.10 mm^3	
Crystal color and habit	Colorless Block	
Diffractometer	Rigaku Mercury275R CCD	
Theta range for data collection	3.253 to 27.485°.	
Index ranges	-11<=h<=11, -15<=k<=16, -11<=l<=11	
Reflections collected	13819	
Independent reflections	4299 [R(int) = 0.1086]	
Observed reflections (I > 2sigma(I))	3287	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.164	
Solution method	SHELXT-2014/5 (Sheldrick, 2014)	
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)	
Data / restraints / parameters	4299 / 4 / 264	
Goodness-of-fit on F^2	1.074	
Final R indices [I>2sigma(I)]	R1 = 0.1057, wR2 = 0.2481	
R indices (all data)	R1 = 0.1292, wR2 = 0.2641	
Absolute structure parameter	-1.0(10)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.812 and -0.437 e.Å^{-3}	

Table S12. Hydrogen bonds for **mmT** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1)...N(1)#1	0.85(3)	2.01(4)	2.812(8)	158(8)
O(2)-H(2)...O(1)	0.86(3)	1.87(8)	2.597(7)	141(11)
O(3)-H(3)...O(2)	0.82	2.03	2.701(7)	138.3

Symmetry transformations used to generate equivalent atoms:

#1 x+1/2,-y+1,z+1/2

Refinement Details for mmT

Low-temperature diffraction data (ω-scans) were collected on a Rigaku SCX Mini diffractometer (sealed tube) coupled to a Rigaku Mercury 275R CCD detector with Mo Kα (λ = 0.71075 Å) for the structure of **mmT**. The diffraction images were processed and scaled using the Rigaku CrystalClear software (CrystalClear and CrystalStructure; Rigaku/MSC: The Woodlands, TX, 2005). The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL (Sheldrick, G. M. Acta Cryst. 2008, A64, 112–122). All non-hydrogen atoms were refined anisotropically. All carbon-bound hydrogen atoms were first found in the difference map, then generated geometrically and refined as riding atoms with C-H distances = 0.95 - 0.99 angstroms and Uiso(H) = 1.2 times Ueq(C) for CH and CH2 groups and Uiso(H) = 1.5 times Ueq(C) for CH3 groups. H1, H2 and H3 were found in the difference map and semi-freely refined with a distance restraint of 0.85(2) Å for O-H distances. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The full numbering scheme of **mmT** can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information. CCDC number **1529462** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

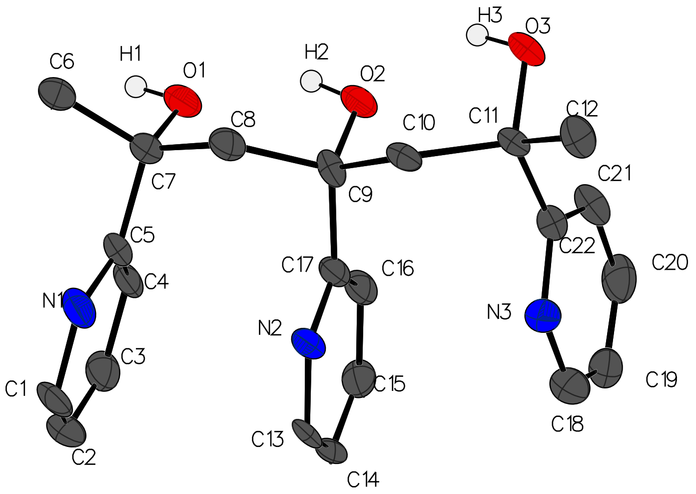


Figure S26. Full numbering scheme of **T3**. Non-heteroatom bound hydrogen atoms have been omitted for clarity.

Table S13. Crystal data and structure refinement for **1**.

Identification code	mini-14056	
Empirical formula	$C_{31}H_{36}Co_2N_4O_9$	
Formula weight	726.50	
Temperature	223(2) K	
Wavelength	0.71075 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 8.267(4) Å	α = 90°
	b = 14.974(8) Å	β = 91.544(12)°
	c = 12.165(6) Å	γ = 90°
Volume	1505.4(14) $Å^3$	
Z	2	
Density (calculated)	1.603 Mg/m^3	
Absorption coefficient	1.165 mm^{-1}	
F(000)	752	
Crystal size	0.400 x 0.400 x 0.400 mm^3	
Θ range for data collection	3.017 to 26.370°.	
Index ranges	$-10 \leq h \leq 10$, $-18 \leq k \leq 18$, $-15 \leq l \leq 15$	
Reflections collected	17486	
Independent reflections	6131 [R(int) = 0.0517]	
Completeness to θ = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.653 and 0.502	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6131 / 1 / 426	
Goodness-of-fit on F^2	1.052	
Final R indices [$I>2\sigma(I)$]	R1 = 0.0450, wR2 = 0.0778	
R indices (all data)	R1 = 0.0554, wR2 = 0.0810	
Absolute structure parameter	0.453(18)	
Largest diff. peak and hole	0.584 and -0.488 e.$Å^{-3}$	

Refinement details for 1

Low-temperature diffraction data (ω-scans) were collected on a Rigaku SCXmini diffractometer coupled to an Mercury2 CCD detector with Mo *K*α radiation (λ = 0.71073 Å) for the structure of **1**. All structures were solved by direct methods using SHELXS and were refined against *F*^{2} on all data by full-matrix least squares with SHELXL (Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112–122). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the *U* value of the atoms to which they are linked (1.5 times for methyl groups). The full numbering scheme of compound **1** can be found in the Supporting Information. Full details of the X-ray structure determination are in the CIF included as Supporting Information. CCDC number **1529487** (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

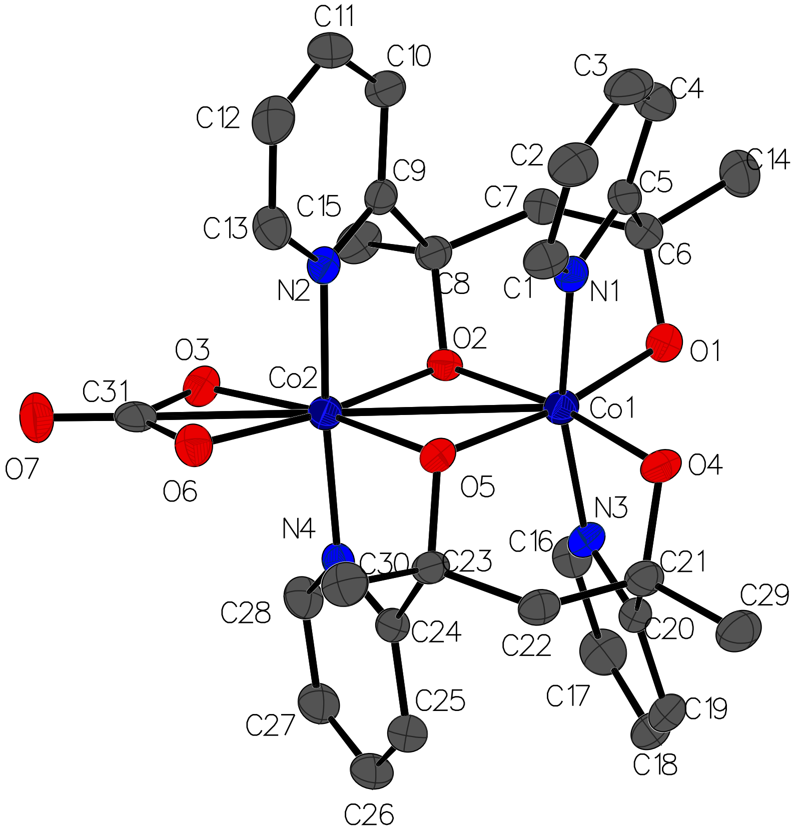


Figure S27. The full numbering scheme of **1**. All atoms shown are depicted with 50% thermal contours. The hydrogen atoms are shown as spheres.

Table S14. Crystal data and structure refinement for **2**.

Identification code	shelx_162B1	
Empirical formula	C30 H34 Cu N4 O4	
Formula weight	578.15	
Temperature	93(2) K	
Wavelength	0.71075 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 8.3252(3) Å	a= 90°.
	b = 14.6827(5) Å	b= 105.716(7)°.
	c = 11.7096(8) Å	g = 90°.
Volume	1377.83(12) Å^3	
Z	2	
Density (calculated)	1.394 Mg/m^3	
Absorption coefficient	0.835 mm^{-1}	
F(000)	606	
Crystal size	.2 x .1 x .1 mm^3	
Crystal color and habit	blue Plate	
Diffractometer	Rigaku Mercury275R CCD	
Theta range for data collection	3.027 to 27.479°.	
Index ranges	-10<=h<=10, -19<=k<=19, -15<=l<=15	
Reflections collected	21525	
Independent reflections	3146 [R(int) = 0.0324]	
Observed reflections (I > 2sigma(I))	2927	
Completeness to theta = 25.242°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Solution method	SHELXT-2014/5 (Sheldrick, 2014)	
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)	
Data / restraints / parameters	3146 / 1 / 184	
Goodness-of-fit on F^2	1.124	
Final R indices [I>2sigma(I)]	R1 = 0.0332, wR2 = 0.1279	
R indices (all data)	R1 = 0.0365, wR2 = 0.1310	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.846 and -0.363 e.Å^{-3}	

<u>Table S15.</u> Hydrogen bonds for **2** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(2)-H(2)...O(1)	0.851(16)	1.795(17)	2.5983(17)	157(2)

<u>Refinement Details for 2</u>

Low-temperature diffraction data (ω-scans) were collected on a Rigaku SCX Mini diffractometer (sealed tube) coupled to a Rigaku Mercury 275R CCD detector with Mo Kα (λ = 0.71075 Å) for the structure of **2**. The diffraction images were processed and scaled using the Rigaku CrystalClear software (CrystalClear and CrystalStructure; Rigaku/MSC: The Woodlands, TX, 2005). The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL (Sheldrick, G. M. Acta Cryst. 2008, A64, 112–122). All non-hydrogen atoms were refined anisotropically. All carbon-bound hydrogen atoms were first found in the difference map, then generated geometrically and refined as riding atoms with C-H distances = 0.95 - 0.99 angstroms and Uiso(H) = 1.2 times Ueq(C) for CH and CH2 groups and Uiso(H) = 1.5 times Ueq(C) for CH3 groups. H2 was found in the difference map and semi-freely refined with a distance restraint of 0.85(2) Å for O-H distance. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The full numbering scheme of **2** can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information. CCDC number **1529488** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

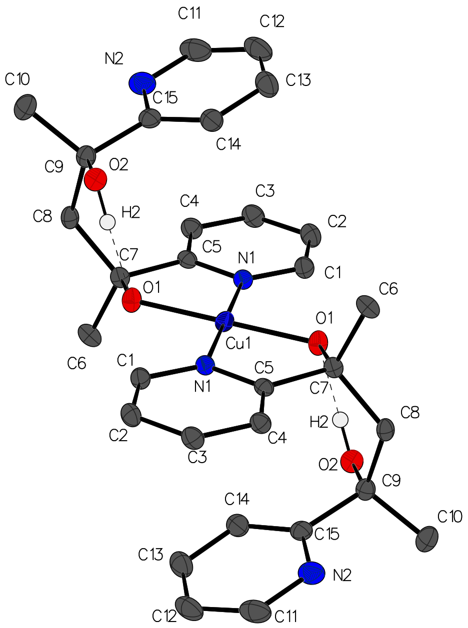


Figure S28. Full numbering scheme of **2**. Non-heteroatom bound hydrogen atoms have been omitted for clarity.

Table S16. Crystal data and structure refinement for **3**.

Identification code	mini_167B1	
Empirical formula	C30 H40 Cu2 N4 O8	
Formula weight	711.74	
Temperature	93(2) K	
Wavelength	0.71075 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 10.1205(6) Å	a= 90°.
	b = 12.7849(8) Å	b= 96.938(7)°.
	c = 11.5863(8) Å	g = 90°.
Volume	1488.17(17) Å^3	
Z	2	
Density (calculated)	1.588 Mg/m^3	
Absorption coefficient	1.488 mm^{-1}	
F(000)	740	
Crystal size	0.200 x 0.100 x 0.100 mm^3	
Crystal color and habit	Blue Block	
Diffractometer	Rigaku Mercury275R CCD	
Theta range for data collection	3.187 to 27.484°.	
Index ranges	-13<=h<=13, -16<=k<=16, -15<=l<=15	
Reflections collected	25325	
Independent reflections	3407 [R(int) = 0.0383]	
Observed reflections (I > 2sigma(I))	3182	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Solution method	SHELXT-2014/5 (Sheldrick, 2014)	
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)	
Data / restraints / parameters	3407 / 0 / 207	
Goodness-of-fit on F^2	1.164	
Final R indices [I>2sigma(I)]	R1 = 0.0352, wR2 = 0.0914	
R indices (all data)	R1 = 0.0389, wR2 = 0.0932	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.534 and -0.753 e.Å^{-3}	

Table S17. Hydrogen bonds for **3** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(3)-H(3B)...O(4)#1	0.85	1.88	2.729(3)	173.3
O(4)-H(4A)...O(1)#2	0.87	1.91	2.763(3)	167.7
O(4)-H(4B)...O(1)#3	0.87	2.01	2.877(3)	176.8
O(3)-H(3A)...O(2)	0.85	1.93	2.774(3)	170.0

Symmetry transformations used to generate equivalent atoms:

#1 -x+3/2,y+1/2,-z+3/2 #2 x+1/2,-y+1/2,z+1/2

#3 -x+3/2,y-1/2,-z+3/2

Refinement Details for 3

Low-temperature diffraction data (ω-scans) were collected on a Rigaku SCX Mini diffractometer (sealed tube) coupled to a Rigaku Mercury 275R CCD detector with Mo Kα (λ = 0.71075 Å) for the structure of **3**. The diffraction images were processed and scaled using the Rigaku CrystalClear software (CrystalClear and CrystalStructure; Rigaku/MSC: The Woodlands, TX, 2005). The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL (Sheldrick, G. M. Acta Cryst. 2008, A64, 112–122). All non-hydrogen atoms were refined anisotropically. All carbon-bound hydrogen atoms were first found in the difference map, then generated geometrically and refined as riding atoms with C-H distances = 0.95 - 0.99 angstroms and Uiso(H) = 1.2 times Ueq(C) for CH and CH2 groups and Uiso(H) = 1.5 times Ueq(C) for CH3 groups. H3A, H3B, H4A and H4B were found in the difference map and semi-freely refined with a distance restraint of 0.85(2) Å for O-H distances. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The full numbering scheme of **3** can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information. CCDC number **1529489** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif

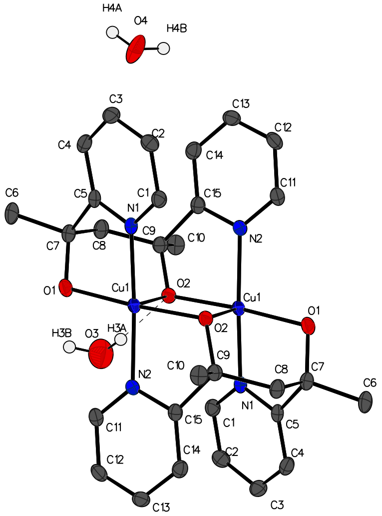


Figure S29. Full numbering scheme of **3**. Non-heteroatom bound hydrogen atoms have been omitted for clarity.

Table S18. Crystal data and structure refinement for **4**.

Identification code	007-16215-curacdl_sq_sq	
Empirical formula	C30 H32 Cu2 N4 O4	
Formula weight	639.67	
Temperature	293(2) K	
Wavelength	1.54187 Å	
Crystal system	Orthorhombic	
Space group	$C222_1$	
Unit cell dimensions	a = 9.73340(10) Å	α= 90°.
	b = 20.3755(3) Å	β= 90°.
	c = 15.4589(10) Å	γ = 90°.
Volume	3065.9(2) Å^3	
Z	4	
Density (calculated)	1.386 Mg/m^3	
Absorption coefficient	2.031 mm^{-1}	
F(000)	1320	
Crystal size	0.20 x 0.20 x 0.20 mm^3	
Crystal color and habit	Colorless Prism	
Diffractometer	Rigaku Saturn 944+ CCD	
Theta range for data collection	4.340 to 66.581°.	
Index ranges	-11<=h<=11, -24<=k<=24, -18<=l<=18	
Reflections collected	47265	
Independent reflections	2731 [R(int) = 0.0427]	
Observed reflections (I > 2sigma(I))	2658	
Completeness to theta = 66.581°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.857	
Solution method	SHELXT 2014/5 (Sheldrick, 2014)	
Refinement method	SHELXL-2016/6 (Sheldrick, 2016)	
Data / restraints / parameters	2731 / 0 / 184	
Goodness-of-fit on F^2	1.079	
Final R indices [I>2sigma(I)]	R1 = 0.0313, wR2 = 0.0806	
R indices (all data)	R1 = 0.0321, wR2 = 0.0813	
Absolute structure parameter	0.386(8)	

Extinction coefficient	n/a
Largest diff. peak and hole	0.260 and -0.656 e.Å^{-3}

Refinement Details for 4

Low-temperature diffraction data (ω-scans) were collected on a Rigaku MicroMax-007HF diffractometer coupled to a Saturn994+ CCD detector with Cu Kα (λ = 1.54178 Å) for the structure of **4**. The diffraction images were processed and scaled using Rigaku Oxford Diffraction software (CrysAlisPro; Rigaku OD: The Woodlands, TX, 2015). The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL (Sheldrick, G. M. Acta Cryst. 2008, A64, 112–122). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The data were refined as a two-component twin. See cif file for details. The program SQUEEZE was used to compensate for the contribution of disordered solvents contained in voids within the crystal lattice from the diffraction intensities. This procedure was applied to the data file and the submitted model is based on the solvent removed data. Based on the total electron density found in the voids (160e/ 531 A3), it is likely that ~8 water molecules are present in the unit cell. The oxygens were visible in the difference map; however, the refinement of the water molecules was a problem, likely due to disorder. See "_platon_squeeze_details" in the .cif for more information. The full numbering scheme of **4** can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information. CCDC number **1529490** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

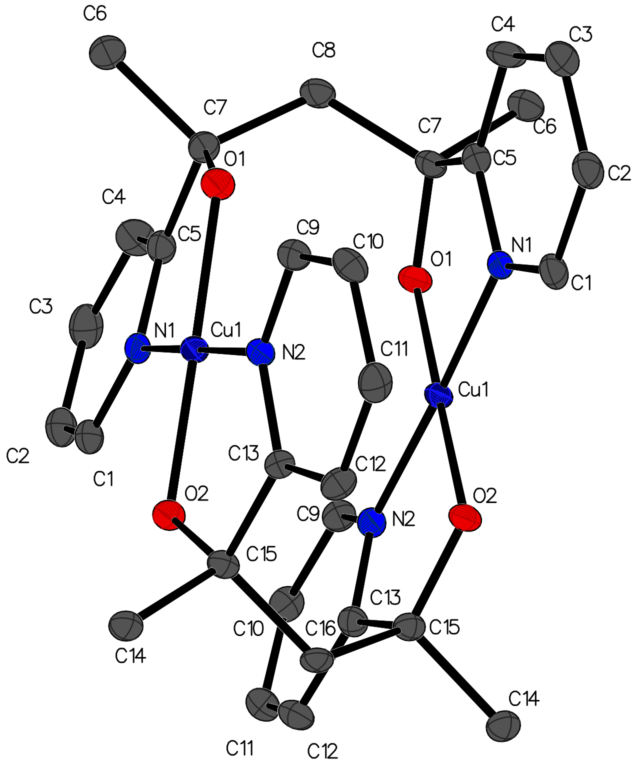


Figure S30. Full numbering scheme of **4**. Non-heteroatom bound hydrogen atoms have been omitted for clarity.

Table S19. Crystal data and structure refinement for **5**.

Identification code	205b1	
Empirical formula	C77 H62 B F24 Mn3 N6 O8	
Formula weight	1830.95	
Temperature	93(2) K	
Wavelength	0.71075 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 32.9393(14) Å	a= 90°.
	b = 32.2445(14) Å	b= 94.087(7)°.
	c = 15.9331(11) Å	g = 90°.
Volume	16879.7(16) Å^3	
Z	8	
Density (calculated)	1.441 Mg/m^3	
Absorption coefficient	0.550 mm^{-1}	
F(000)	7408	
Crystal size	0.050 x 0.050 x 0.040 mm^3	
Crystal color and habit	Red Block	
Diffractometer	Rigaku Mercury275R CCD	
Theta range for data collection	2.989 to 25.025°.	
Index ranges	-39<=h<=39, -38<=k<=38, -18<=l<=18	
Reflections collected	92206	
Independent reflections	14876 [R(int) = 0.1276]	
Observed reflections (I > 2sigma(I))	11347	
Completeness to theta = 25.025°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Solution method	SHELXT-2014/5 (Sheldrick, 2014)	
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)	
Data / restraints / parameters	14876 / 148 / 1195	
Goodness-of-fit on F^2	1.168	
Final R indices [I>2sigma(I)]	R1 = 0.0951, wR2 = 0.1716	
R indices (all data)	R1 = 0.1284, wR2 = 0.1843	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.946 and -0.449 e.Å^{-3}	

Hydrogen bonds for 205b1-3 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(8)-H(8C)...O(4)	0.85(2)	2.05(4)	2.820(6)	150(6)

Symmetry transformations used to generate equivalent atoms:

Refinement Details for 5

Low-temperature diffraction data (ω-scans) were collected on a Rigaku R-AXIS RAPID diffractometer coupled to an R-AXIS RAPID imaging plate detector with Mo Kα radiation (λ = 0.71073 Å) for the structure of **5**. The diffraction images were processed and scaled using the Rigaku CrystalClear software (CrystalClear and CrystalStructure; Rigaku/MSC: The Woodlands, TX, 2005). The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL (Sheldrick, G. M. Acta Cryst. 2008, A64, 112–122). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The full numbering scheme of **5** can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information. CCDC number **1531809** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif. A number of CF3 groups were modeled as disordered. Adding additional parameters for other CF3 groups did not greatly improve the overall refinement metrics. The program SQUEEZE was used to compensate for the contribution of disordered solvents contained in the voids in the crystal lattice from the diffraction intensities (Acta Cryst. 2009, D65, 148-155). This procedure was applied to the data file and the submitted model is based on the solvent removed data. Based on the total electron density found in the voids (449e/ 2192.5 A3), it is likely that ~11 dichloromethane molecules are present in the unit cell. See platon squeeze details in the .cif for more information.

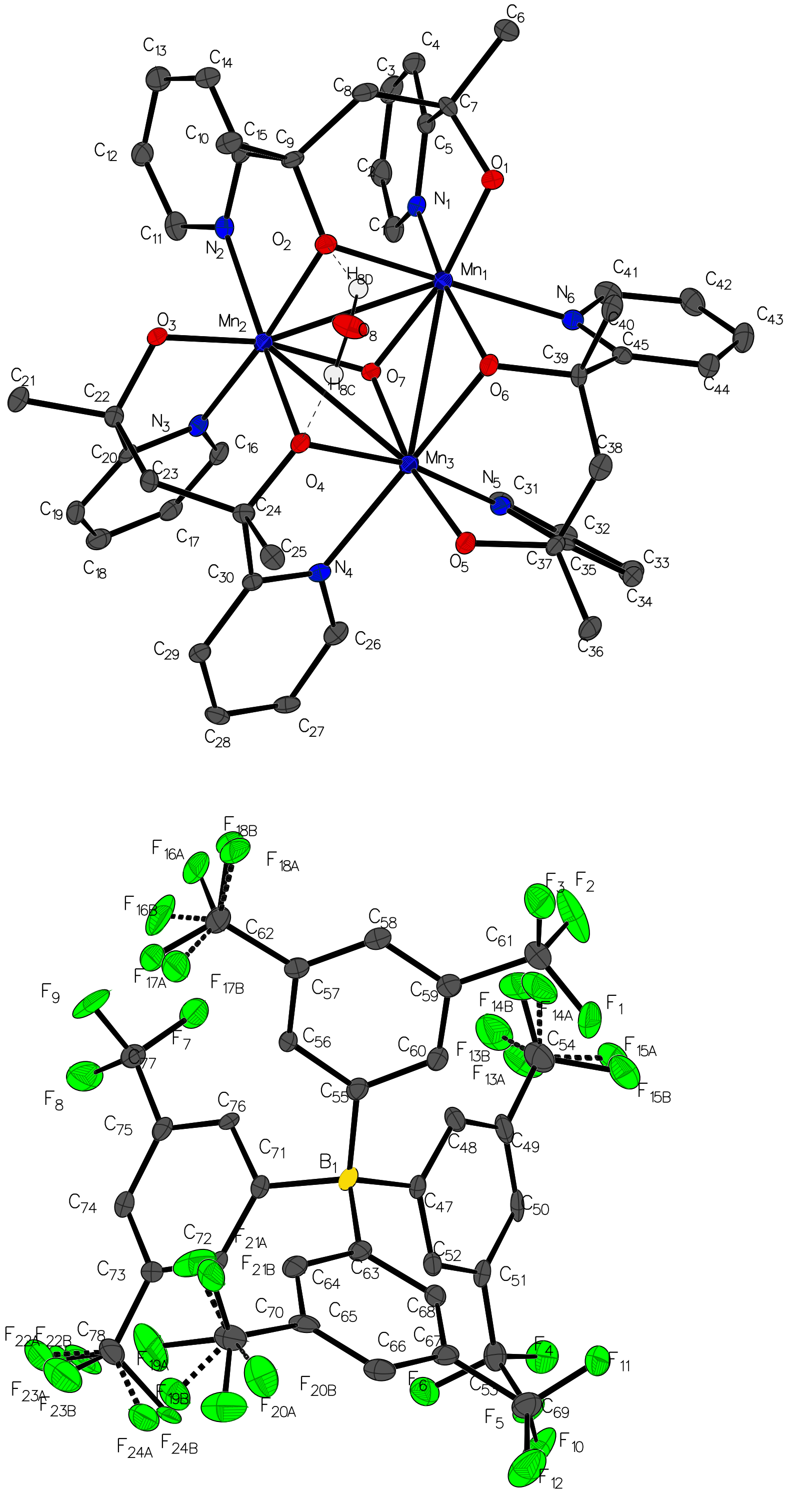


Figure S31. Full numbering scheme of **5**. Non-heteroatom bound hydrogen atoms have been omitted for clarity.

<u>Table S20</u>. Crystal data and structure refinement for **6**.

Identification code	spider-15048	
Empirical formula	C61 H64 Mn4 N8 O11	
Formula weight	1304.96	
Temperature	93(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 16.9929(12) Å	a= 90°.
	b = 13.5907(10) Å	b= 90.478(2)°.
	c = 33.118(2) Å	g = 90°.
Volume	7648.1(9) Å^3	
Z	4	
Density (calculated)	1.133 Mg/m^3	
Absorption coefficient	0.697 mm^{-1}	
F(000)	2696	
Crystal size	0.200 x 0.100 x 0.100 mm^3	
Crystal color and habit	Brown Plate	
Diffractometer	Rigaku R-AXIS RAPID imaging plate	
Theta range for data collection	2.274 to 25.026°.	
Index ranges	-20<=h<=20, -16<=k<=16, -39<=l<=39	
Reflections collected	82104	
Independent reflections	6749 [R(int) = 0.1480]	
Observed reflections (I > 2sigma(I))	4537	
Completeness to theta = 25.026°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.836	
Solution method	SHELXT-2014/5 (Sheldrick, 2014)	
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)	
Data / restraints / parameters	6749 / 0 / 384	
Goodness-of-fit on F^2	0.930	
Final R indices [I>2sigma(I)]	R1 = 0.0461, wR2 = 0.1123	
R indices (all data)	R1 = 0.0756, wR2 = 0.1207	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.521 and -0.348 e.Å^{-3}	

Refinement Details for 6

Low-temperature diffraction data (ω-scans) were collected on a Rigaku R-AXIS RAPID diffractometer coupled to an R-AXIS RAPID imaging plate detector with Mo Kα radiation (λ = 0.71073 Å) for the structure of **6**. The diffraction images were processed and scaled using the Rigaku CrystalClear software (CrystalClear and CrystalStructure; Rigaku/MSC: The Woodlands, TX, 2005). The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL (Sheldrick, G. M. Acta Cryst. 2008, A64, 112–122). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The hydrogen atoms were first found in the difference map, then generated geometrically and refined as riding atoms with C-H distances = 0.95- 0.99 angstroms and Uiso(H) = 1.2 times Ueq(C) for CH and CH2 groups and Uiso(H) = 1.5 times Ueq(C) for CH3 groups. Two low-angle reflections were improperly recorded ordered due to instrument artifacts and omitted from the refinement. The program SQUEEZE was used to compensate for the contribution of disordered solvents contained in the voids in the crystal lattice from the diffraction intensities (Acta Cryst. 2009, D65, 148-155). This procedure was applied to the data file and the submitted model is based on the solvent removed data. Some of this disordered solvent could be modeled as water molecules, but refinement was problematic. Based on the total electron density found in the voids (1086.8 e/2490.6 A3), it is likely that ~109 water molecules are present in the unit cell. See platon squeeze details in the .cif for more information.The full numbering scheme of **6** can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information. CCDC number **1529491** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

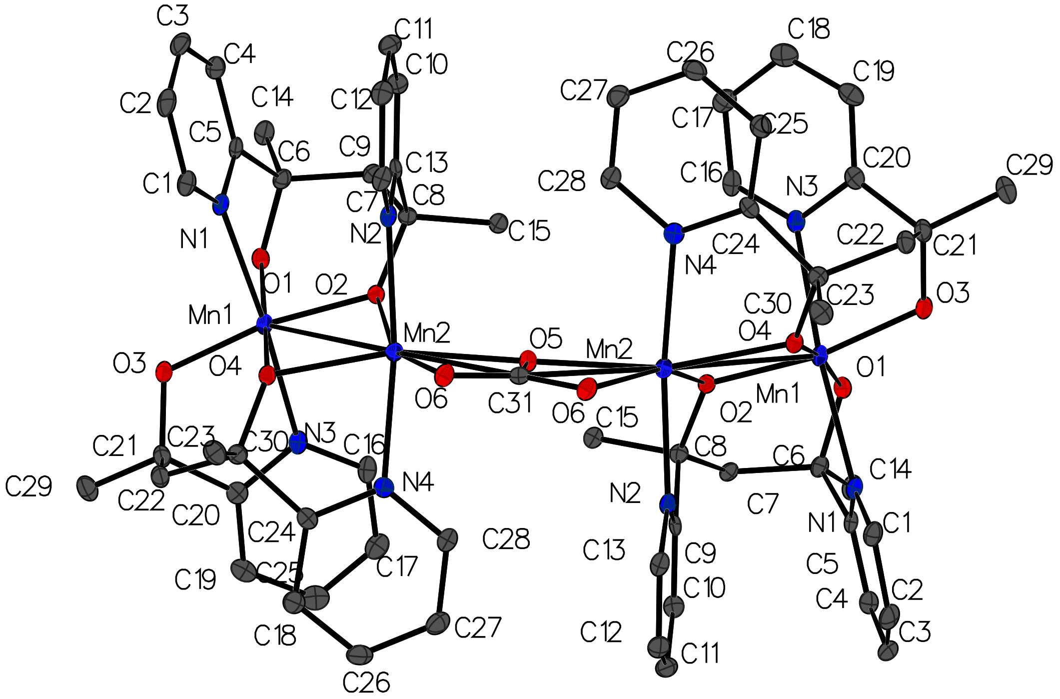


Figure S32. Full numbering scheme of **6**. Non-heteroatom bound hydrogen atoms have been omitted for clarity.

Table S21. Crystal data and structure refinement for **7**.

Identification code	spider-15058	
Empirical formula	C30 H44 Mn2 N6 O16	
Formula weight	854.59	
Temperature	93(2) K	
Wavelength	0.71075 Å	
Crystal system	Monoclinic	
Space group	I2/a	
Unit cell dimensions	a = 19.6402(13) Å	a= 90°.
	b = 8.4523(5) Å	b= 93.816(10)°.
	c = 21.958(3) Å	g = 90°.
Volume	3637.0(6) Å^3	
Z	4	
Density (calculated)	1.561 Mg/m^3	
Absorption coefficient	0.775 mm^{-1}	
F(000)	1776	
Crystal size	0.200 x 0.100 x 0.100 mm^3	
Crystal color and habit	Red Block	
Diffractometer	Rigaku R-AXIS RAPID imaging plate	
Theta range for data collection	3.177 to 25.017°.	
Index ranges	-23<=h<=23, -10<=k<=10, -26<=l<=26	
Reflections collected	24035	
Independent reflections	3198 [R(int) = 0.1417]	
Observed reflections (I > 2sigma(I))	2441	
Completeness to theta = 25.017°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.794	
Solution method	SHELXT-2014/5 (Sheldrick, 2014)	
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)	
Data / restraints / parameters	3198 / 0 / 264	
Goodness-of-fit on F^2	1.069	
Final R indices [I>2sigma(I)]	R1 = 0.0625, wR2 = 0.0844	
R indices (all data)	R1 = 0.0890, wR2 = 0.0916	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.334 and -0.400 e.Å^{-3}	

Table S22. Hydrogen bonds for **7** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(3)-H(3A)...O(4)	0.81(4)	1.89(4)	2.681(4)	166(4)
O(3)-H(3B)...O(1)#1	0.86(4)	1.86(5)	2.711(4)	173(4)
O(4)-H(4A)...O(5)	0.76(6)	2.01(6)	2.769(5)	171(6)
O(4)-H(4B)...O(7)#2	0.92(7)	1.89(7)	2.803(5)	175(6)
O(4)-H(4B)...O(8)#2	0.92(7)	2.54(6)	3.212(6)	130(5)
O(4)-H(4B)...N(3)#2	0.92(7)	2.58(7)	3.442(6)	157(5)
O(5)-H(5A)...O(6)#3	0.85	2.65	3.428(5)	152.0
O(5)-H(5A)...O(7)#3	0.85	2.07	2.865(4)	155.6
O(5)-H(5B)...O(6)	0.85	2.00	2.792(5)	155.1

Symmetry transformations used to generate equivalent atoms:
#1 -x+1/2,y+1,-z+1 #2 x,y+1,z #3 -x+1,y+1/2,-z+3/2

Refinement Details for 7

Low-temperature diffraction data (ω-scans) were collected on a Rigaku R-AXIS RAPID diffractometer coupled to an R-AXIS RAPID imaging plate detector with Mo Kα radiation (λ = 0.71073 Å) for the structure of **7**. The diffraction images were processed and scaled using the Rigaku CrystalClear software (CrystalClear and CrystalStructure; Rigaku/MSC: The Woodlands, TX, 2005). The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL (Sheldrick, G. M. Acta Cryst. 2008, A64, 112–122). All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were first found in the difference map, then generated geometrically and refined as riding atoms with C-H distances = 0.95- 0.99 Å and U-iso-(H) = 1.2 times U~eq~(C) for CH and CH2 groups and U~iso~(H) = 1.5 times U~eq~(C) for CH3 groups. The protons on O3 were found in the difference map and refined as riding atoms. The protons on O4 were freely refined. The protons on O5 were geometrically placed and refined as a rigid group. The full numbering scheme of **7** can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information. CCDC number **1529492** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

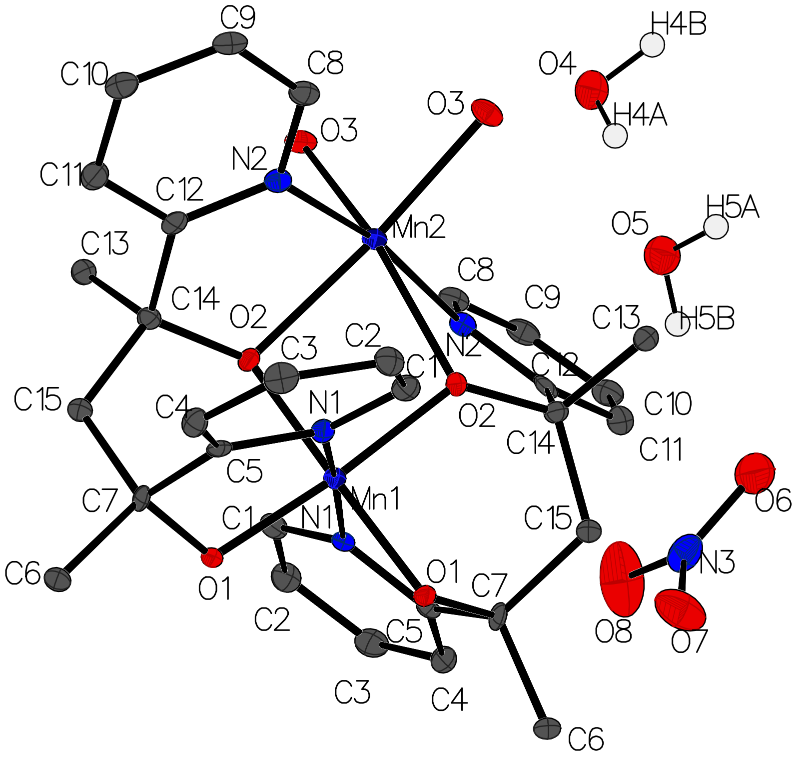


Figure S33. Full numbering scheme of **7.** Non-heteroatom bound hydrogen atoms have been omitted for clarity.

Table S23. Crystal data and structure refinement for **8**.

Identification code	spider-15051	
Empirical formula	C66 H74 Cl4 F12 Mn4 N8 O12 P2	
Formula weight	1822.83	
Temperature	93(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 20.2718(14) Å	a= 90°.
	b = 14.4091(10) Å	b= 90°.
	c = 24.8638(17) Å	g = 90°.
Volume	7262.7(9) Å^3	
Z	4	
Density (calculated)	1.667 Mg/m^3	
Absorption coefficient	0.968 mm^{-1}	
F(000)	3712	
Crystal size	0.200 x 0.200 x 0.050 mm^3	

Crystal color and habit	Orange Plate
Diffractometer	Rigaku R-AXIS RAPID imaging plate
Theta range for data collection	2.009 to 24.407°.
Index ranges	-23<=h<=23, -14<=k<=16, -21<=l<=28
Reflections collected	27738
Independent reflections	5896 [R(int) = 0.1153]
Observed reflections (I > 2sigma(I))	3777
Completeness to theta = 24.407°	98.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.668
Solution method	SHELXT-2014/5 (Sheldrick, 2014)
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)
Data / restraints / parameters	5896 / 0 / 546
Goodness-of-fit on F^2	1.032
Final R indices [I>2sigma(I)]	R1 = 0.0577, wR2 = 0.1252
R indices (all data)	R1 = 0.1098, wR2 = 0.1513
Extinction coefficient	n/a
Largest diff. peak and hole	0.790 and -0.799 e.Å^{-3}

Refinement Details for 8

Low-temperature diffraction data (ω-scans) were collected on a Rigaku R-AXIS RAPID diffractometer coupled to an R-AXIS RAPID imaging plate detector with Mo Kα radiation (λ = 0.71073 Å) for the structure of **8**. The diffraction images were processed and scaled using the Rigaku CrystalClear software (CrystalClear and CrystalStructure; Rigaku/MSC: The Woodlands, TX, 2005). The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL (Sheldrick, G. M. Acta Cryst. 2008, A64, 112–122). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The PF6 group is disordered over two positions. The two groups were found in the difference map and their site occupancies were freely refined to converged values of nearly equal values. The site occupancies were subsequently fixed at 0.50. The thermal parameters of the fluorines were anticipated to be similar, and restrained to reflect this assertion. The PF6 groups were expected to behave as rigid bodies and restrained with rigid bond restraints.The full numbering scheme of **8** can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information. CCDC number **1529493** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

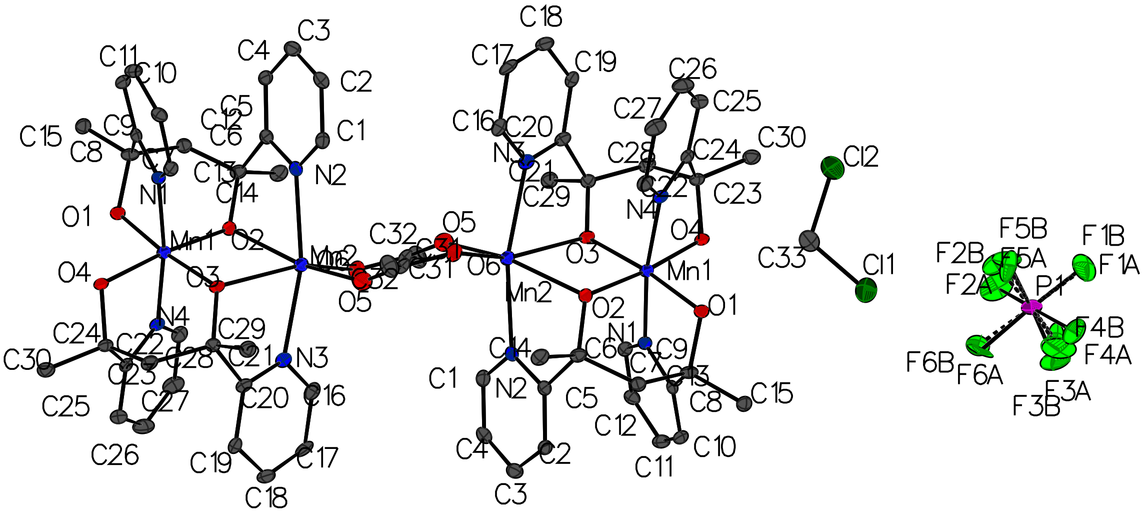


Figure S34. Full numbering scheme of **8.** Non-heteroatom bound hydrogen atoms have been omitted for clarity.

<u>Table S24</u>. Crystal data and structure refinement for **9.**

Identification code	007-15178	
Empirical formula	C45 H46 Cl4 Mn3 N6 O6	
Formula weight	1073.50	
Temperature	93(2) K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	Fdd2	
Unit cell dimensions	a = 22.4234(3) Å	a= 90°.
	b = 33.9852(6) Å	b= 90°.
	c = 25.7898(4) Å	g = 90°.
Volume	19653.5(5) Å^3	
Z	16	
Density (calculated)	1.451 Mg/m^3	
Absorption coefficient	8.605 mm^{-1}	
F(000)	8784	
Crystal size	0.100 x 0.100 x 0.050 mm^3	
Crystal color and habit	Brown Plate	
Diffractometer	Rigaku Saturn 944+ CCD	
Theta range for data collection	2.600 to 66.878°.	
Index ranges	-26<=h<=26, -40<=k<=40, -30<=l<=30	
Reflections collected	174793	
Independent reflections	8723 [R(int) = 0.0554]	
Observed reflections (I > 2sigma(I))	8668	
Completeness to theta = 66.878°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.29659	
Solution method	SHELXT-2014/5 (Sheldrick, 2014)	
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)	
Data / restraints / parameters	8723 / 1 / 582	
Goodness-of-fit on F^2	1.032	
Final R indices [I>2sigma(I)]	R1 = 0.0491, wR2 = 0.1346	
R indices (all data)	R1 = 0.0493, wR2 = 0.1348	
Absolute structure parameter	-0.0016(13)	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.718 and -1.076 e.Å^{-3}	

Refinement Details for 9

Low-temperature diffraction data (ω-scans) were collected on a Rigaku MicroMax-007HF diffractometer coupled to a Saturn994+ CCD detector with Cu Kα (λ = 1.54178 Å) for the structure of **9**. The diffraction images were processed and scaled using Rigaku Oxford Diffraction software (CrysAlisPro; Rigaku OD: The Woodlands, TX, 2015). The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL (Sheldrick, G. M. Acta Cryst. 2008, A64, 112–122). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The program SQUEEZE was used to compensate for the contribution of disordered solvents contained in voids within the crystal lattice from the diffraction intensities. This procedure was applied to the data file and the submitted model is based on the solvent removed data. Based on the total electron density found in the voids (847.4 e/Å^3), it is likely that ~20 dichloromethane molecules are present in the unit cell. See "platon_squeeze_details" in this .cif for more information.The full numbering scheme of **9** can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information. CCDC number **1529494** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

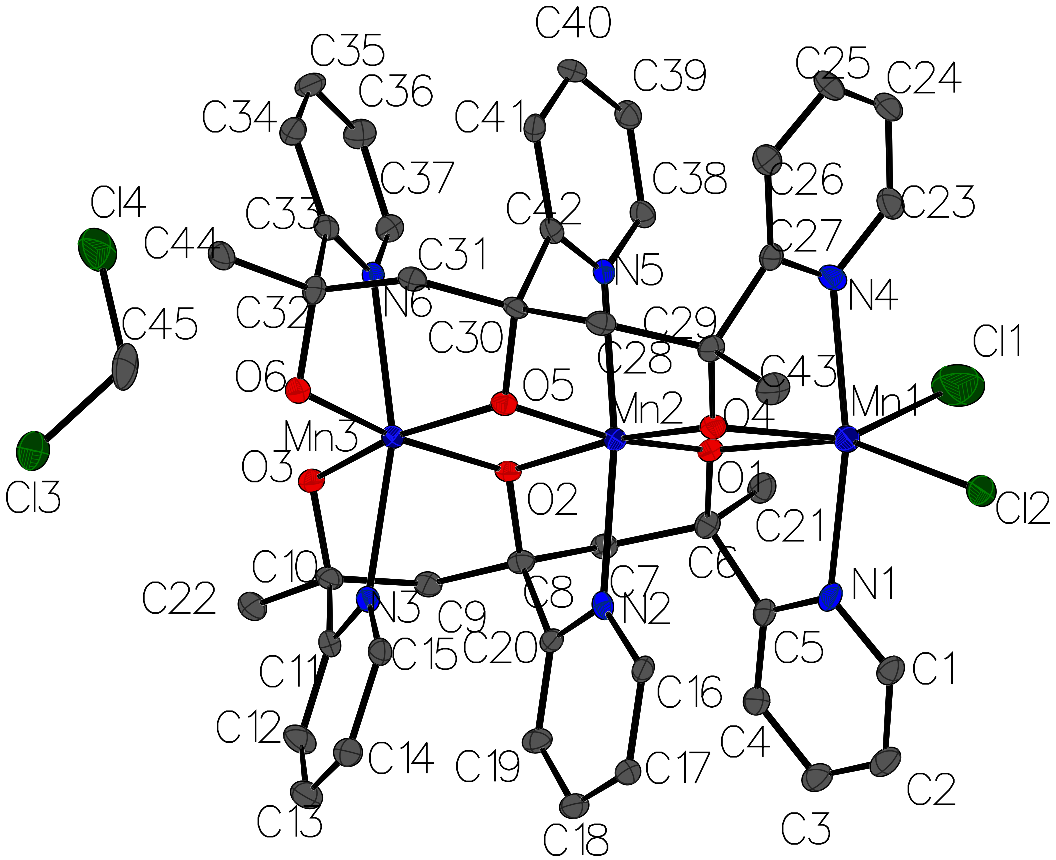


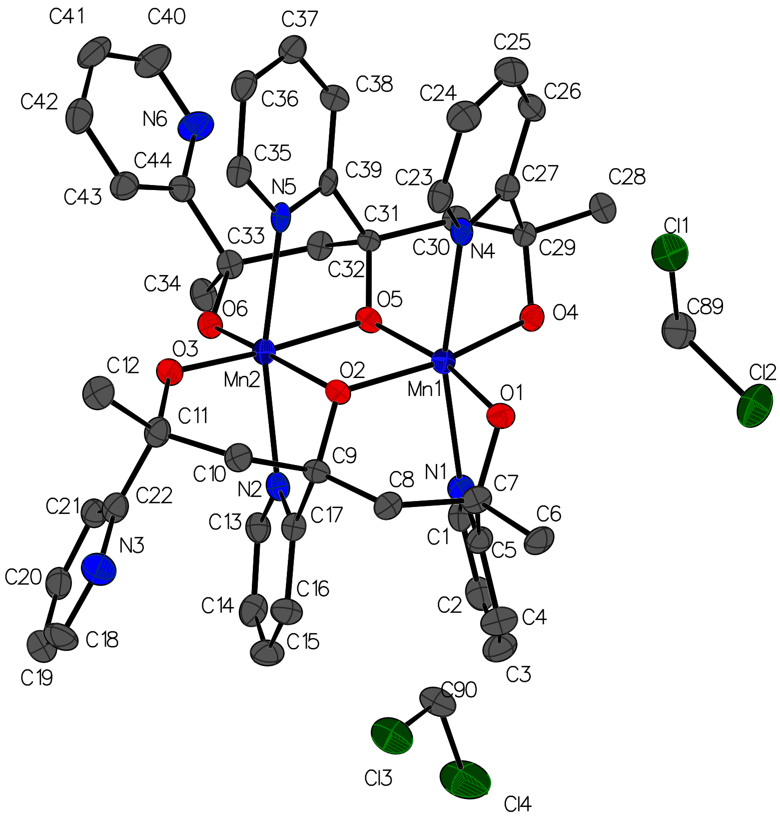
Figure S35. Full numbering scheme of **9**. Non-heteroatom bound hydrogen atoms have been omitted for clarity.

<u>Table S25</u>. Crystal data and structure refinement for **10**.

Identification code	spider-16001	
Empirical formula	C45 H46 Cl2 Mn2 N6 O6	
Formula weight	947.66	
Temperature	93(2) K	
Wavelength	0.71075 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 19.8078(6) Å	a= 90°.
	b = 15.0917(4) Å	b= 96.066(7)°.
	c = 29.829(2) Å	g = 90°.
Volume	8867.0(7) Å^3	
Z	8	
Density (calculated)	1.420 Mg/m^3	
Absorption coefficient	0.745 mm^{-1}	
F(000)	3920	
Crystal size	0.200 x 0.200 x 0.200 mm^3	
Crystal color and habit	Colorless Block	
Diffractometer	Rigaku R-AXIS RAPID imaging plate	
Theta range for data collection	3.029 to 27.485°.	
Index ranges	-25<=h<=25, -19<=k<=19, -38<=l<=38	
Reflections collected	101124	
Independent reflections	19783 [R(int) = 0.0980]	
Observed reflections (I > 2sigma(I))	12603	
Completeness to theta = 25.242°	98.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.844	
Solution method	SHELXT-2014/5 (Sheldrick, 2014)	
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)	
Data / restraints / parameters	19783 / 0 / 1107	
Goodness-of-fit on F^2	1.055	
Final R indices [I>2sigma(I)]	R1 = 0.0520, wR2 = 0.1054	
R indices (all data)	R1 = 0.1011, wR2 = 0.1322	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.792 and -0.736 e.Å^{-3}	

Refinement Details for 10

Low-temperature diffraction data (ω-scans) were collected on a Rigaku R-AXIS RAPID diffractometer coupled to an R-AXIS RAPID imaging plate detector with Mo Kα radiation (λ = 0.71073 Å) for the structure of **10**. The diffraction images were processed and scaled using the Rigaku CrystalClear software (CrystalClear and CrystalStructure; Rigaku/MSC: The Woodlands, TX, 2005). The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL (Sheldrick, G. M. Acta Cryst. 2008, A64, 112–122). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The program SQUEEZE was used to compensate for the contribution of disordered solvents contained in voids within the crystal lattice from the diffraction intensities (A.L.Spek, Acta Cryst. 2009, D65, 148-155). This procedure was applied to the data file and the submitted model is based on the solvent removed data. Based on the total electron density found in the voids (33e/440Å^3), it is likely that ~2 water molecules are present in the unit cell. See "_platon_squeeze_details" in the .cif for more information. Several reflections were improperly recorded due to instrument artifacts. These reflections were omitted. The full numbering scheme of **10** can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information. CCDC number **1529495** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.



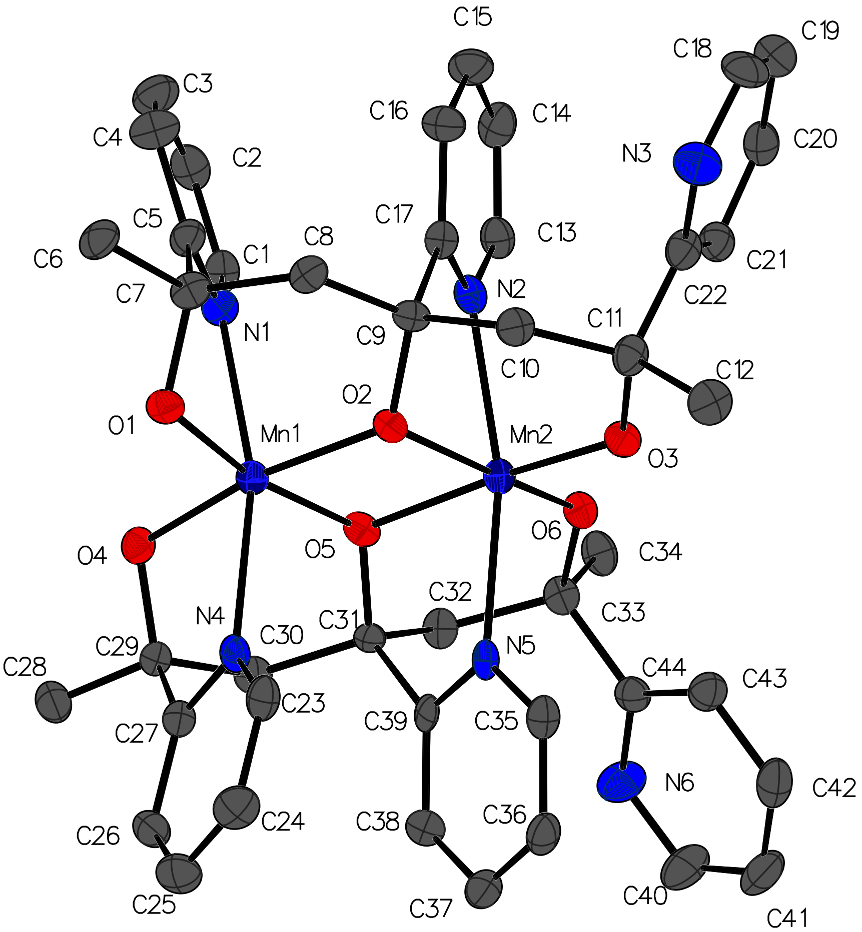


Figure S36. Full numbering scheme of **10**. The two dimers in the asymmetric unit are shown separately, and non-heteroatom bound hydrogen atoms have been omitted for clarity.

Table S26. Crystal data and structure refinement for **11**.

Identification code	shelx_163B1	
Empirical formula	C30 H34 N4 Ni O4	
Formula weight	573.32	
Temperature	93(2) K	
Wavelength	0.71075 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 8.3214(5) Å	a= 90°.
	b = 14.6642(9) Å	b= 105.640(7)°.
	c = 11.6946(8) Å	g = 90°.
Volume	1374.22(16) Å^3	
Z	2	
Density (calculated)	1.386 Mg/m^3	
Absorption coefficient	0.749 mm^{-1}	
F(000)	604	
Crystal size	0.200 x 0.200 x 0.100 mm^3	
Crystal color and habit	Brown Plate	
Diffractometer	Rigaku Mercury275R CCD	
Theta range for data collection	3.031 to 27.485°.	
Index ranges	-10<=h<=10, -19<=k<=19, -15<=l<=15	
Reflections collected	20526	
Independent reflections	3136 [R(int) = 0.0354]	
Observed reflections (I > 2sigma(I))	2892	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Solution method	SHELXT-2014/5 (Sheldrick, 2014)	
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)	
Data / restraints / parameters	3136 / 0 / 184	
Goodness-of-fit on F^2	1.135	
Final R indices [I>2sigma(I)]	R1 = 0.0339, wR2 = 0.0691	
R indices (all data)	R1 = 0.0386, wR2 = 0.0710	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.785 and -0.231 e.Å^{-3}	

<u>Table S27</u>. Hydrogen bonds for **11** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(2)-H(2)...O(1)	0.87(2)	1.77(2)	2.6011(16)	157(2)

<u>Refinement Details for 11</u>

Low-temperature diffraction data (ω-scans) were collected on a Rigaku SCX Mini diffractometer (sealed tube) coupled to a Rigaku Mercury 275R CCD detector with Mo $K\alpha$ (λ = 0.71075 Å) for the structure of **11**. The diffraction images were processed and scaled using the Rigaku CrystalClear software (CrystalClear and CrystalStructure; Rigaku/MSC: The Woodlands, TX, 2005). The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL (Sheldrick, G. M. Acta Cryst. 2008, A64, 112–122). All non-hydrogen atoms were refined anisotropically. All carbon-bound hydrogen atoms were first found in the difference map, then generated geometrically and refined as riding atoms with C-H distances = 0.95 - 0.99 angstroms and Uiso(H) = 1.2 times Ueq(C) for CH and CH2 groups and Uiso(H) = 1.5 times Ueq(C) for CH3 groups. H2 was found in the difference map and semi-freely refined with a distance restraint of 0.85(2) Å for O-H distance. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The full numbering scheme of **11** can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information. CCDC number **1529496** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif

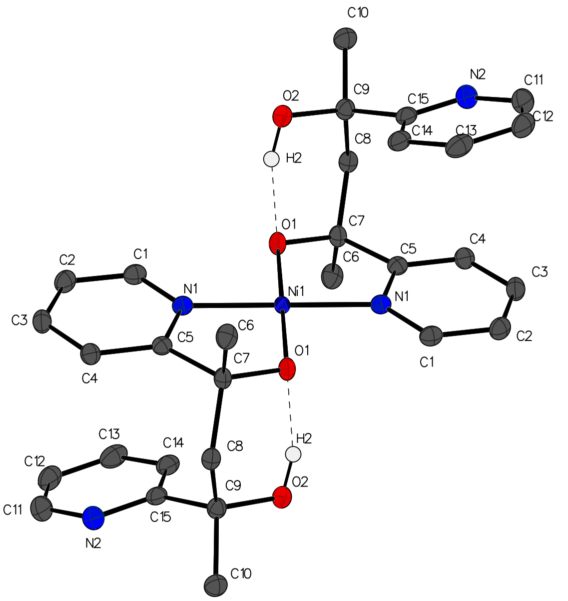


Figure S37. Full numbering scheme of **11**. Non-heteroatom bound hydrogen atoms have been omitted for clarity.

Table S28. Crystal data and structure refinement for **12.**

Identification code	mini-16098	
Empirical formula	C36 H47 Cl4 N4 Ni2 O8	
Formula weight	922.99	
Temperature	93(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 14.8680(4) Å	α= 90°.
	b = 16.1416(4) Å	β= 95.451(3)°.
	c = 16.3814(5) Å	γ = 90°.
Volume	3913.65(19) Å^3	
Z	4	
Density (calculated)	1.566 Mg/m^3	
Absorption coefficient	1.291 mm^{-1}	
F(000)	1916	
Crystal size	0.200 x 0.200 x 0.100 mm^3	
Theta range for data collection	2.498 to 27.484°.	
Index ranges	-19<=h<=19, -20<=k<=20, -21<=l<=21	
Reflections collected	34082	
Independent reflections	4488 [R(int) = 0.0553]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.96425	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4488 / 25 / 298	
Goodness-of-fit on F^2	1.059	
Final R indices [I>2sigma(I)]	R1 = 0.0332, wR2 = 0.0756	
R indices (all data)	R1 = 0.0461, wR2 = 0.0810	
Largest diff. peak and hole	0.351 and -0.492 e.Å^{-3}	

Refinement Details for 12

Low-temperature diffraction data (ω-scans) were collected on a Rigaku SCX Mini diffractometer coupled to a Rigaku Mercury275R CCD with Mo Kα radiation (λ = 0.71073 Å) for the structure of mini-16098. The diffraction images were processed and scaled using Rigaku Oxford Diffraction software (CrysAlisPro; Rigaku OD: The Woodlands, TX, 2015). The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL (Sheldrick, G. M. Acta Cryst. 2008, A64, 112–122). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The only exception was atom H1, which was found in the difference map and semi-freely refined. The O-H distance was restrained to 0.85(2) Å, as suggested by the difference map. Several low angle reflections were obscured by the beam stop and subsequently omitted. The acetate counter ion was modeled as disordered across the crystallographic 2-fold axis. The special position constraints were suppressed and the site occupancies were suppressed. The dichloromethane molecule was positionally disordered. The two models were distinguished with atom label suffixes A and B. The site occupancies of the two models were fixed near their converged values of equal occupancies. The C-Cl bond distances were anticipated to be chemically identical and restrained to reflect this expectation. The two models were also refined with the aid of rigid bond restraints as the thermal displacement of the atoms within the solvent behave as an ensemble. The full numbering scheme of compound **12** can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information. CCDC number **1529497** (mini-16098) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

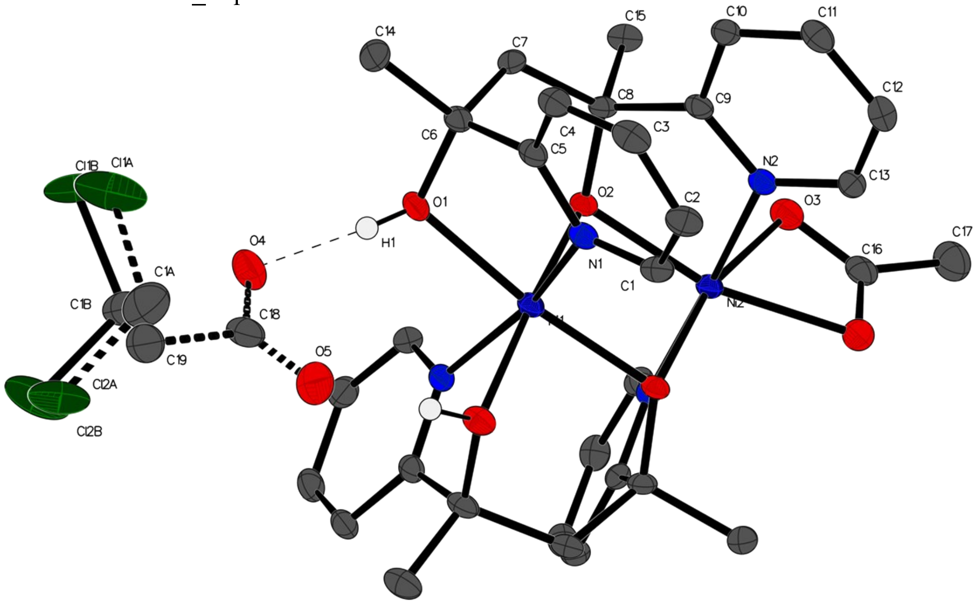


Figure S38. The complete numbering scheme of asymmetric unit of **12** with 50% thermal ellipsoid probability levels. Most of the hydrogen atoms have been omitted for clarity; those shown are arbitrary circles.

Table S29. Crystal data and structure refinement for complex **13**.
Identification code 007-17059-cot3-2_sq
Empirical formula C44 H44 Co2 N6 O6
Formula weight 870.71
Temperature 93(2) K
Wavelength 1.54187 Å
Crystal system Monoclinic
Space group $P2_1/c$
Unit cell dimensions a = 8.4079(2) Å a= 90°.
b = 12.0756(2) Å b= 93.505(7)°.
c = 19.9987(14) Å g = 90°.
Volume 2026.68(15) Å3
Z 2
Density (calculated) 1.427 Mg/m3
Absorption coefficient 6.873 mm-1
F(000) 904
Crystal size 0.200 x 0.200 x 0.100 mm3
Crystal color and habit Brown Plate
Diffractometer
Theta range for data collection 4.279 to 66.599°.
Index ranges -9<=h<=9, -14<=k<=14, -23<=l<=23
Reflections collected 62645
Independent reflections 3562 [R(int) = 0.1705]
Observed reflections (I > 2sigma(I)) 2519
Completeness to theta = 66.599° 99.7 %
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 1.000 and 0.852
Solution method SHELXT-2014/5 (Sheldrick, 2014)
Refinement method SHELXL-2014/7 (Sheldrick, 2014)
Data / restraints / parameters 3562 / 0 / 264
Goodness-of-fit on F2 1.092
Final R indices [I>2sigma(I)] R1 = 0.0793, wR2 = 0.2055
R indices (all data) R1 = 0.1063, wR2 = 0.2592
Extinction coefficient n/a
Largest diff. peak and hole 0.626 and -1.118 e.Å-3

Refinement Details for 13

Low-temperature diffraction data (ω-scans) were collected on a Rigaku MicroMax-007HF diffractometer coupled to a Saturn994+ CCD detector with Cu Kα (λ = 1.54178 Å) for the structure of **9**. The diffraction images were processed and scaled using Rigaku Oxford Diffraction software (CrysAlisPro; Rigaku OD: The Woodlands, TX, 2015). The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL (Sheldrick, G. M. Acta Cryst. 2008, A64, 112–122). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The program SQUEEZE was used to compensate for the contribution of disordered water molecules contained in voids within the crystal lattice from the diffraction intensities. This procedure was applied to the data file and the submitted model is based on the solvent removed data. Based on the total electron density found in the voids (78 e/A3), it is likely that ~8 water molecules are present in the unit cell. See "_platon_squeeze_details" in this .cif for more information. The full numbering scheme of **13** can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information. CCDC number **1552433** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

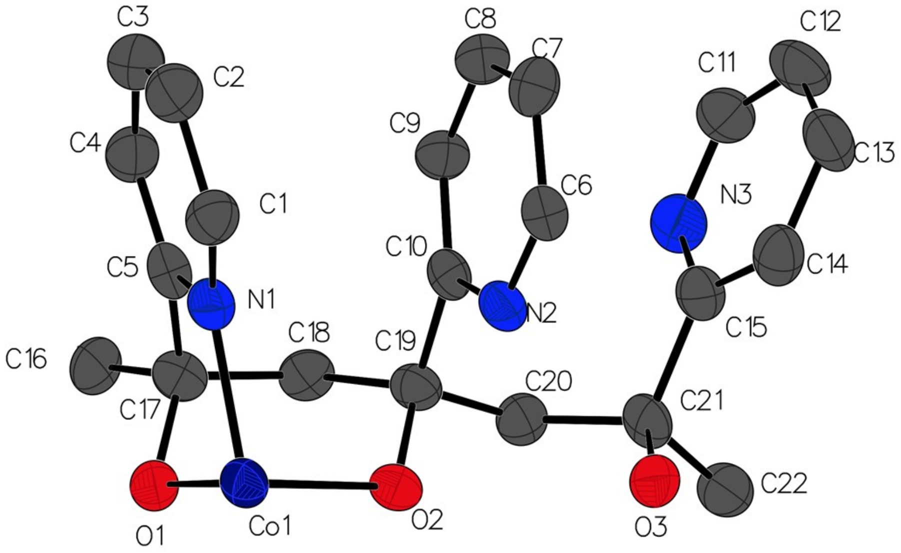


Figure S39. The complete numbering scheme of the asymmetric unit of **13** with 50% thermal ellipsoid probability levels. Hydrogen atoms have been omitted for clarity.

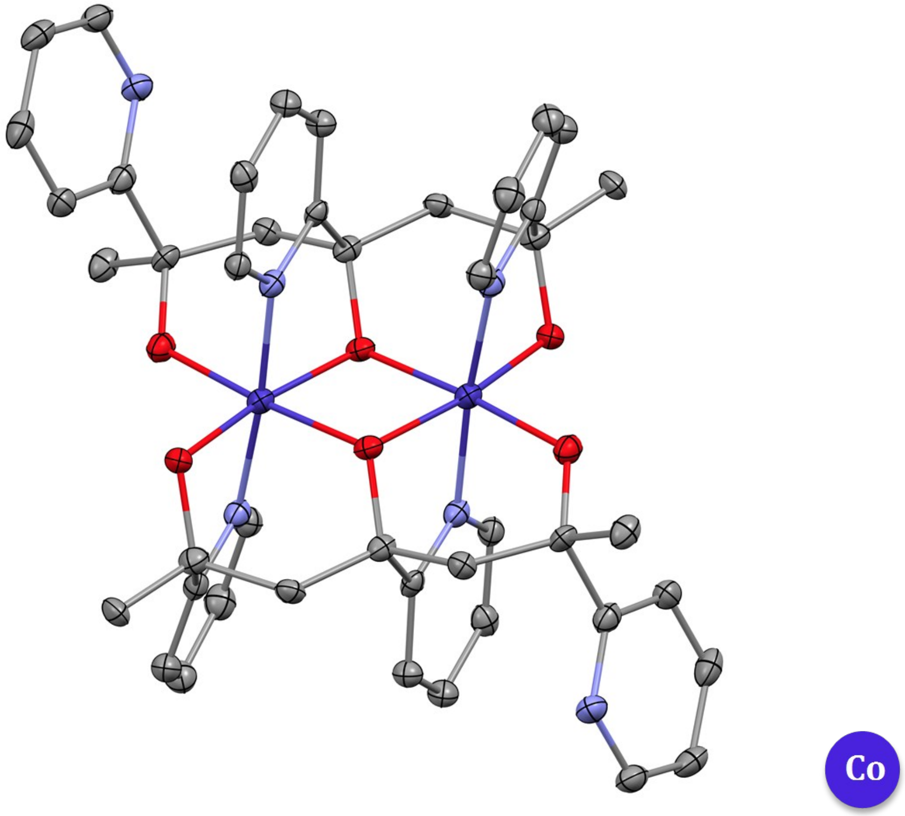


Figure S40. Structure of **13** with 25% thermal ellipsoid probability levels. Hydrogen atoms have been omitted for clarity.

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