Supplementary Information (SI) for ChemComm.

iClick reaction of Cu(II) azido complex having Schiff base ligand

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Experimental

Materials and methods:

The experiments were conducted in anhydrous solvents and using oven-dried glassware. Copper acetate monohydrate, sodium azide, N, N-diethylethane-1,2-diamine, 2-cyanopyridine, 2-cyanopyrimidine, pyridine-2,6-dicarbonitrile, dimethyl acetylene-dicarboxylate (DMAD), diethyl acetylene-dicarboxylate (DEAD), 4,4,4-trifluoro-2-butynoic acid ethyl ester, and all other chemicals were purchased from commercial sources and used as received. Infrared spectra in the 4000-400 cm^{-1} region were recorded as KBr pellets using a PerkinElmer FT-IR spectrophotometer. The mass spectra were recorded using a SCIEX Model-X500R QTOF mass spectrometer operated in ESI mode. The magnetism of complexes was recorded using the EZ9 VSM system Microsense at room temperature. Ground-state geometry optimizations for each isomer were conducted using the B3LYP functional[1,2] , LANL2DZ basis set.[3,4] The ground-state optimized structures and corrected energy values of Cu(II) triazolate-bound isomers of complex 2 are given in Figure S16 and Table S2, respectively. Density functional theory (DFT) calculations were carried out on dimer **3** and its corresponding mononuclear derivative. Geometry optimization of both species indicated that the dimer is thermodynamically more stable than the monomer by 17.49 kcal mol^{-1} (Figure S18). Similarly, in the case of dimer **7** and its mononuclear species, the former was found to be more stable by 13.60 kcal mol^{-1} (Figure S19).

Caution! Azides and azido complexes are potentially explosive. Although no problems were encountered with the preparations mentioned below, heating of the solid compounds was avoided.

Single-crystal X-ray diffraction analysis:

Single-crystal X-ray data of crystal **1** were collected using the ‘Xcalibur, Eos’ CCD plate detector. For crystals **2** to **7**, also possessing well-defined morphology, data were collected using the ‘XtaLAB Synergy Dualflex, HyPix-3000’ HPAD detector. In all cases, Cu$K\alpha$ radiation (λ = 1.54184 Å) was employed as the source. Data integration and reductions were processed with the CRYSALISPRO software. The structures were solved using SHELXT and refined by full-matrix least-squares procedures using the SHELX-2019[5,6] software package through the OLEX2 suite.[7] The non-H atoms were refined with anisotropic thermal parameters, and all of the H atoms were placed in their idealized positions and refined riding on their parent atoms. Important crystallographic data and structure solutions are given in Table S1.

Synthesis of [Cu(N_3)(L)] 1:

An ethanol solution (20 mL) of N, N-diethyl-1,2-diaminoethane (0.14 mL, 1 mmol), and 2-hydroxy-1-naphthaldehyde (0.172 g, 1 mmol) was refluxed for ∼1 h to prepare the tridentate Schiff base, HL. The ligand was not isolated and used directly to synthesize the complex. An ethanolic solution (20 mL) of copper(II) acetate monohydrate (0.200 g, 1 mmol) was added to the ethanolic solution of the ligand (1 mmol) and stirred for 30 min. A solution of NaN_3 (0.065 g, 1 mmol) in 1 mL of water was added and refluxed for a further 2 h. A brownish-black precipitate separated immediately and was collected by filtration and washed with ethanol several times. Brown colour diffraction-quality single crystals were obtained after a few days by slow evaporation of the complex's dark green acetonitrile solution in an open atmosphere. Yield: 0.321 g (86%). Elemental Analysis (CHN): Calculated for $C_{17}H_{21}N_5CuO$; C 54.46, H 5.65, N 18.68; Found C 53.93, H 5.66, N 18.12; IR spectrum (KBr, cm^{-1}): 2052 $\nu(N_3)$, 1625 $\nu(CN)$.

Synthesis of [Cu(N1-triazolate^{CF_3,COOMe})(L)] 2:

In a 25 mL round-bottomed flask, complex **1** (94 mg, 0.25 mmol) was dissolved in chloroform (10 mL) at room temperature, to which ethyl 4,4,4-trifluorobut-2-ynoate (107μL, 0.75mmol) was added while stirring at room temperature. The reaction mixture was stirred for 10 min, and the formation of the product was monitored by FT-IR spectroscopy. The solvent evaporated until the solution's volume was reduced to about 5mL. The product was isolated by precipitating it out by adding 25 mL of diethyl ether, and was washed with diethyl ether (3 × 5 mL) and dried under vacuum for 2 h. X-ray-quality dark green crystals were obtained through recrystallization from a chloroform and acetonitrile solution at 4 °C. Yield: 0.120 g (89%). Elemental analysis (CHN): Calculated for $C_{23}H_{26}CuF_3N_5O_3$; C 51.06, H 4.84, N 12.94; Found C 50.92, H 4.46, N 12.52; IR spectrum (KBr, cm^{-1}): 1702 $\nu(CO)$, 1623 $\nu(CN)$. MS spectrum: Calculated for $C_{23}H_{26}CuF_3N_5O_3$ $[M+Na]^+$: 563.118; found: 563.113.

Synthesis of Synthesis of [$Cu_2(L)_2$(N1,N3-triazolate).H_2O] 3:

In a 25 mL round-bottomed flask, complex **1** (94 mg, 0.25 mmol) was dissolved in chloroform (10 mL) at room temperature, to which dimethyl acetylenedicarboxylate (94 μL, 0.75 mmol) was added while stirring at room temperature. The reaction mixture was stirred for 10 min, and the formation of the product was monitored by FT-IR spectroscopy. The solvent evaporated until the solution's volume was reduced to about 5mL. The green solid product was isolated by precipitating it out by adding 25 mL of diethyl ether, and was washed with diethyl ether (3 × 5 mL) and dried under vacuum for 2 h. Yield: 0.088 g (86%).

Before Hydrolysis- Elemental analysis (CHN): Calculated for $C_{46}H_{54}Cu_2N_{10}O_{10}$; C 53.43, H 5.26, N 13.55; Found C 53.12, H 5.04, N 13.17; IR spectrum (KBr, cm^{-1}): 1732 ν(CO), 1623 ν(CN). MS spectrum: Calculated for $C_{46}H_{54}Cu_2N_{10}O_{10}$ $[M+Na]^+$: 1055.251; found: 1055.257, $[M/2+H]^+$ 517.139; found: 517.138.

After Hydrolysis- The complex was dissolved in DMF and allowed to undergo slow crystallization under ambient conditions for three months, resulting in the formation of dark-green single crystals. Elemental analysis (CHN): Calculated for $C_{38}H_{45}Cu_2N_7O_7$; C 54.41, H 5.41, N 11.69; Found C 54.21, H 5.13, N 11.45; IR spectrum (KBr, cm^{-1}): 1660 ν(CO), 1624 ν(CN). MS spectrum: Calculated for $C_{38}H_{45}Cu_2N_7O_7$ $[M-H_2O+H]^+$: 820.195; found: 820.196.

Synthesis of $[Cu(PTZ)_2(H_2O)_2]$ 4:

In a 25 mL round-bottomed flask, complex **1** (94 mg, 0.25 mmol) was dissolved in chloroform (10 mL) at room temperature, to which 2-pyridinecarbonitrile (0.052 g, 0.50 mmol) was added while stirring at room temperature. The reaction mixture was stirred for 4 h, and the formation of the tetrazolato product was monitored by FT-IR spectroscopy. The solvent evaporated until the solution's volume was reduced to about 5mL. The green solid product was isolated by precipitating it out by adding 25 mL of diethyl ether, and was washed with diethyl ether (3 × 5 mL) and dried under vacuum for 3 h. X-ray-quality brown crystals were obtained through recrystallization from a green DMF solution. Yield: 0.044 g (45%). Elemental analysis (CHN): Calculated for $C_{12}H_{12}N_{10}CuO_2$; C 36.78, H 3.09, N 35.75; Found C 36.34, H 2.83, N 35.01; IR spectrum (KBr, cm^{-1}): 1602 ν(CN).

Synthesis of [CuPMTZ(L)] 5:

Complex **5** was synthesized using a similar method to that of Complex **4**, with 2-pyrimidinecarbonitrile replacing 2-pyridinecarbonitrile. X-ray-quality dark green crystals were recrystallized from a DMF solution. Yield: 0.109 g (91%). Elemental analysis (CHN): Calculated for $C_{22}H_{24}N_8CuO$; C 55.05, H 5.04, N 23.34; Found C 54.87, H 4.69, N 23.12; IR spectrum (KBr, cm^{-1}): 1623 ν(CN). MS spectrum: Calculated for $C_{22}H_{24}N_8CuO$ $[M+H]^+$: 480.145; found: 480.142.

Synthesis of [Cu(5-(6-(((2-oxidonaphthalen-1-yl)methylene)carbamoyl)pyridin-2-yl)tetrazol-1-ide)]$_n$ 7:

In a 25 mL round-bottomed flask, complex **1** (94 mg, 0.25 mmol) was dissolved in chloroform (10 mL) at room temperature, to which pyridine-2,6-dicarbonitrile (0.064 g, 0.50 mmol) was added while stirring at room temperature. The reaction mixture was stirred for 4 h, and the formation of the tetrazolato product was monitored by FT-IR spectroscopy. The solvent evaporated until the solution's volume was reduced to about 5mL. The green solid product was isolated by precipitating it out by adding 25 mL of diethyl ether, and was washed with diethyl ether (3 × 5 mL) and dried under vacuum for 2 h. Yield: 0.083 g (82%).

Before Hydrolysis- Elemental analysis (CHN): Calculated for $C_{48}H_{48}Cu_2N_{16}O_2$; C 57.19, H 4.80, N 22.23; Found C 56.95, H 4.52, N 22.01; IR spectrum (KBr, cm^{-1}): 2239 ν(C≡N), 1622 ν(CN). MS spectrum: Calculated for $C_{48}H_{48}Cu_2N_{16}O_2$ $[M+Na]^+$: 1029.2636; found: 1019.2635, $[M/2+H]^+$: 504.145; found: 504.142.

After Hydrolysis- The complex was dissolved in DMF and left for crystallization under ambient conditions. After three months, a crop of dark-green single crystals (**Complex 7)** was formed. Elemental analysis (CHN): Calculated for $C_{18}H_{10}CuN_6O_2$; C 53.27, H 2.48, N 20.71; Found C 53.06, H 2.32, N 20.21; IR spectrum (KBr, cm^{-1}): 1694 ν(CO), 1623 ν(CN). MS spectrum: Calculated for $C_{18}H_{10}CuN_6O_2$ $[M]^+$: 405.016; found: 405.147.

All attempts to crystallize the freshly prepared complex under anhydrous conditions were unsuccessful. However, when the complex was dissolved in DMF (5 mL) with one drop of water and left to crystallize under ambient conditions, a few small crystals appeared at the bottom of the tube after 3 weeks. The dark-green block-shaped single crystals (**Complex 6**) were isolated, and one of them was analysed by single-crystal X-ray diffraction.

Attempted reaction of complex 1 with M-acetylide

In a 25 mL round-bottomed flask, complex **1** (94 mg, 0.25 mmol) was dissolved in chloroform (10 mL) at room temperature, to which (Schiff base)Ni(II) acetylide (0.50 mmol) was added while stirring at room temperature. No new spot in TLC was observed even after 4 days. Refluxing the reaction mixture (overnight) did not show any change.

Reaction of benzyl azide with dimethyl acetylenedicarboxylate

In a 25 mL round-bottomed flask, benzyl azide (0.25 mmol) was dissolved in chloroform (10 mL) at room temperature, to which dimethyl acetylenedicarboxylate (0.75 mmol) was added while stirring at room temperature. The progress of the reaction was monitored by TLC, which showed that 60 % conversion was achieved after 4 h.

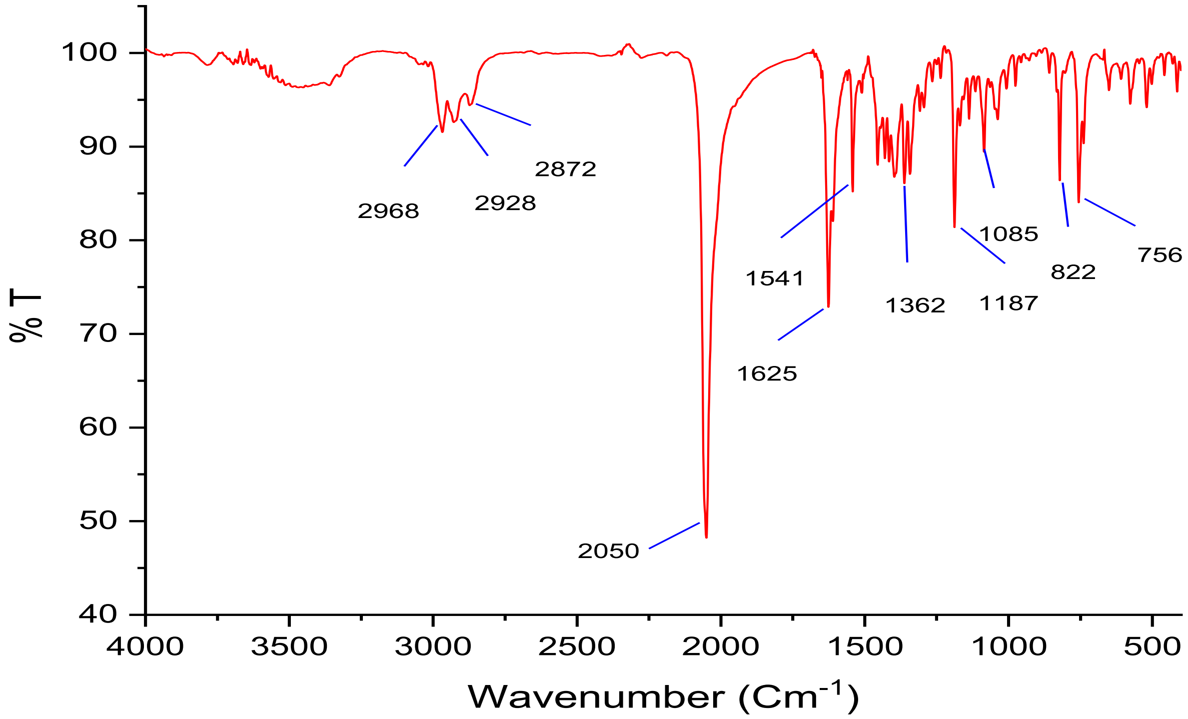


Figure S1: IR spectrum of complex **1**.

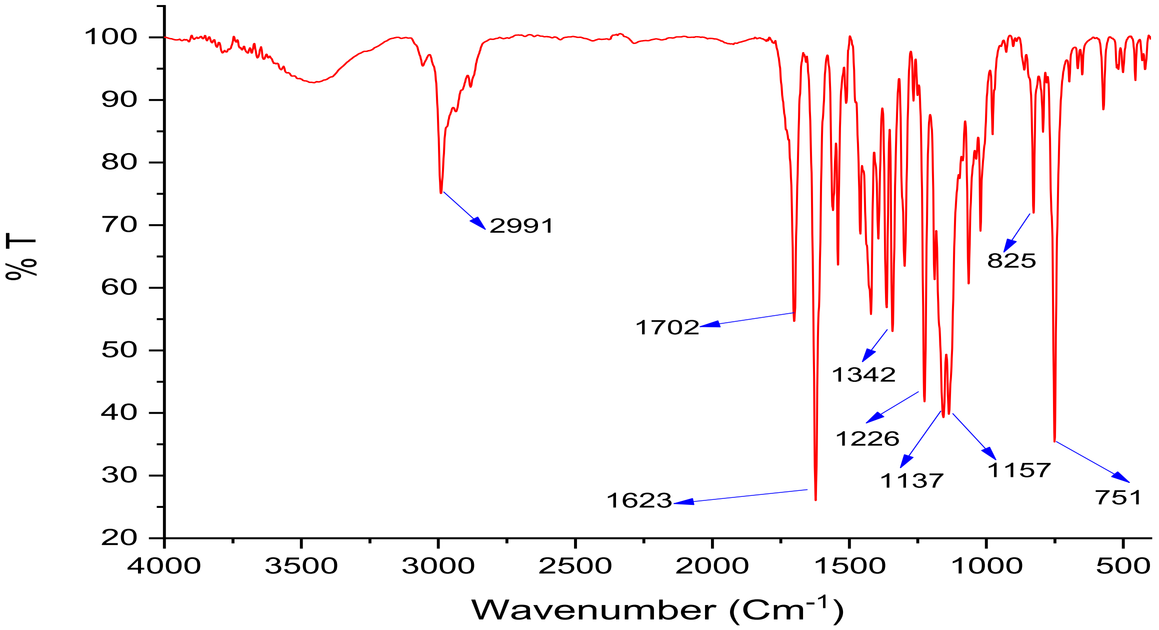


Figure S2: IR spectrum of complex **2**.

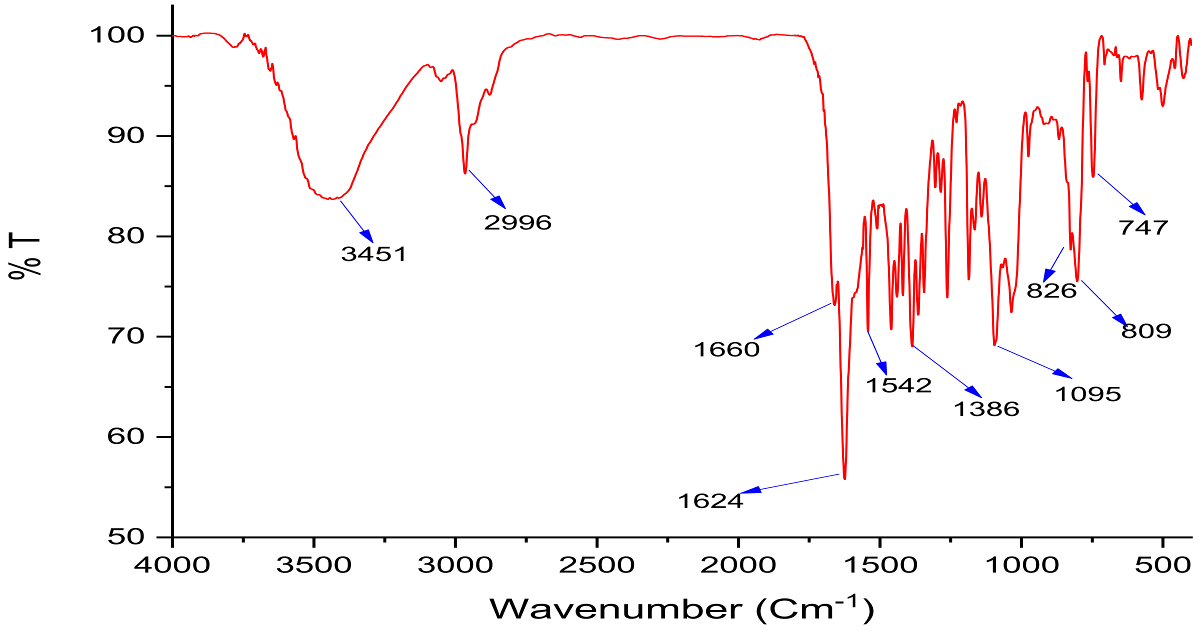


Figure S3: IR spectrum of complex **3** after hydrolysis.

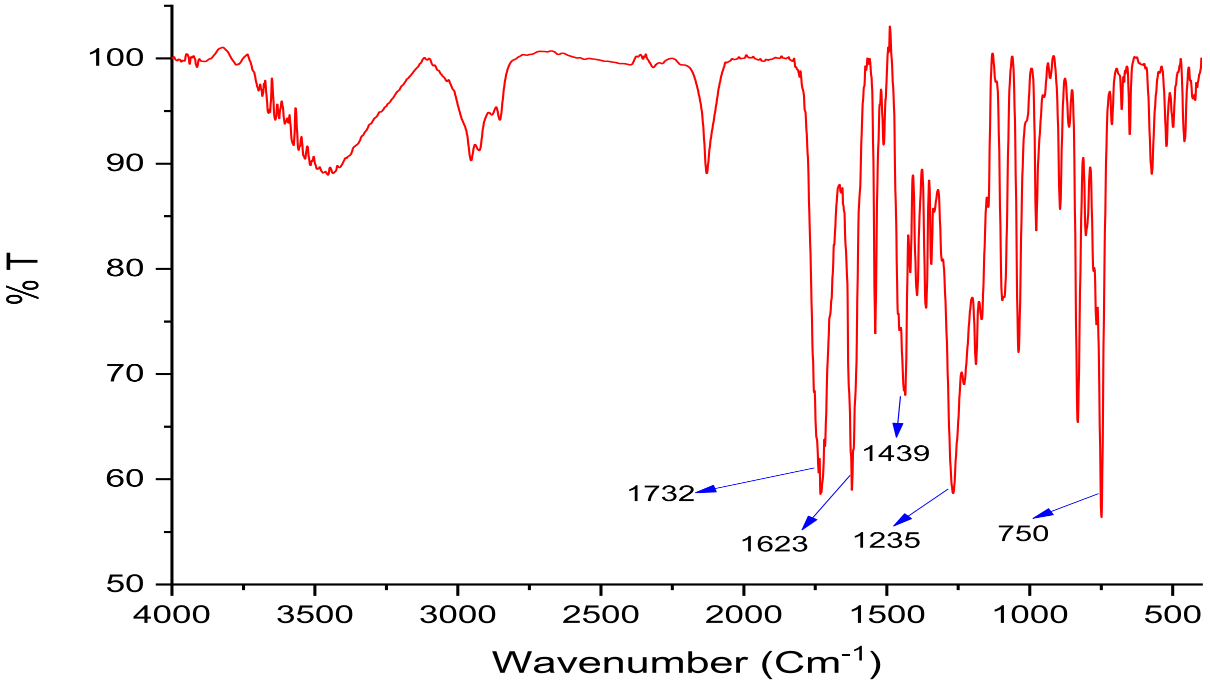


Figure S4: IR spectrum of complex **3** before hydrolysis.

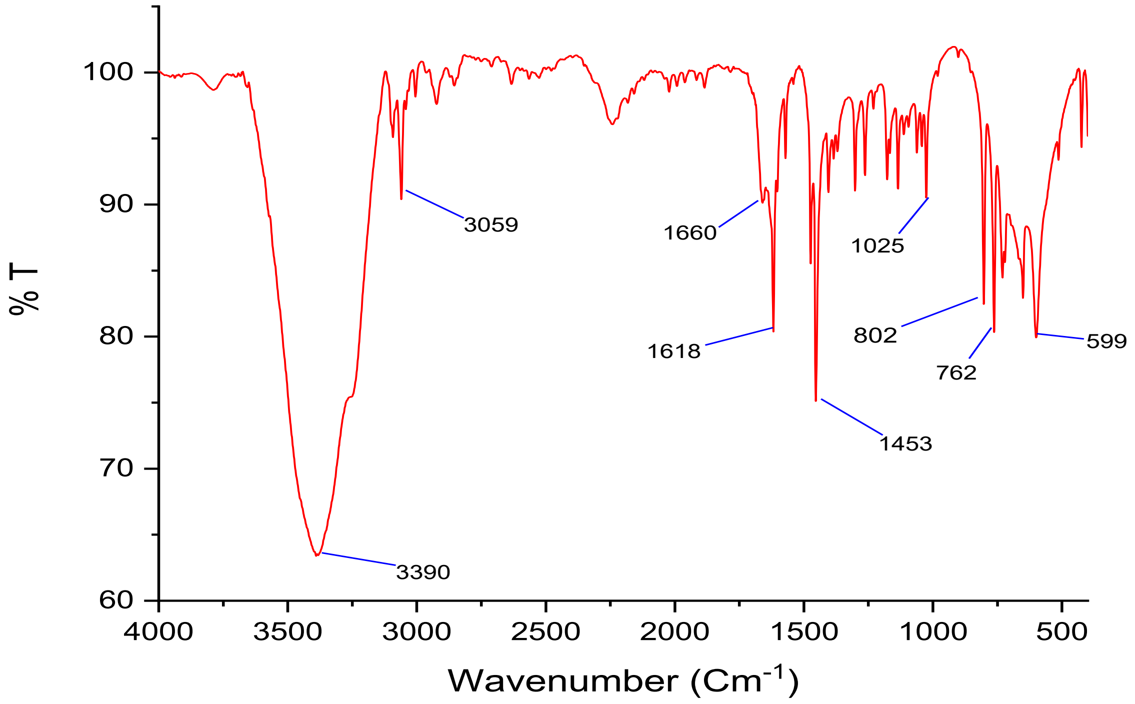


Figure S5: IR spectrum of complex **4**.

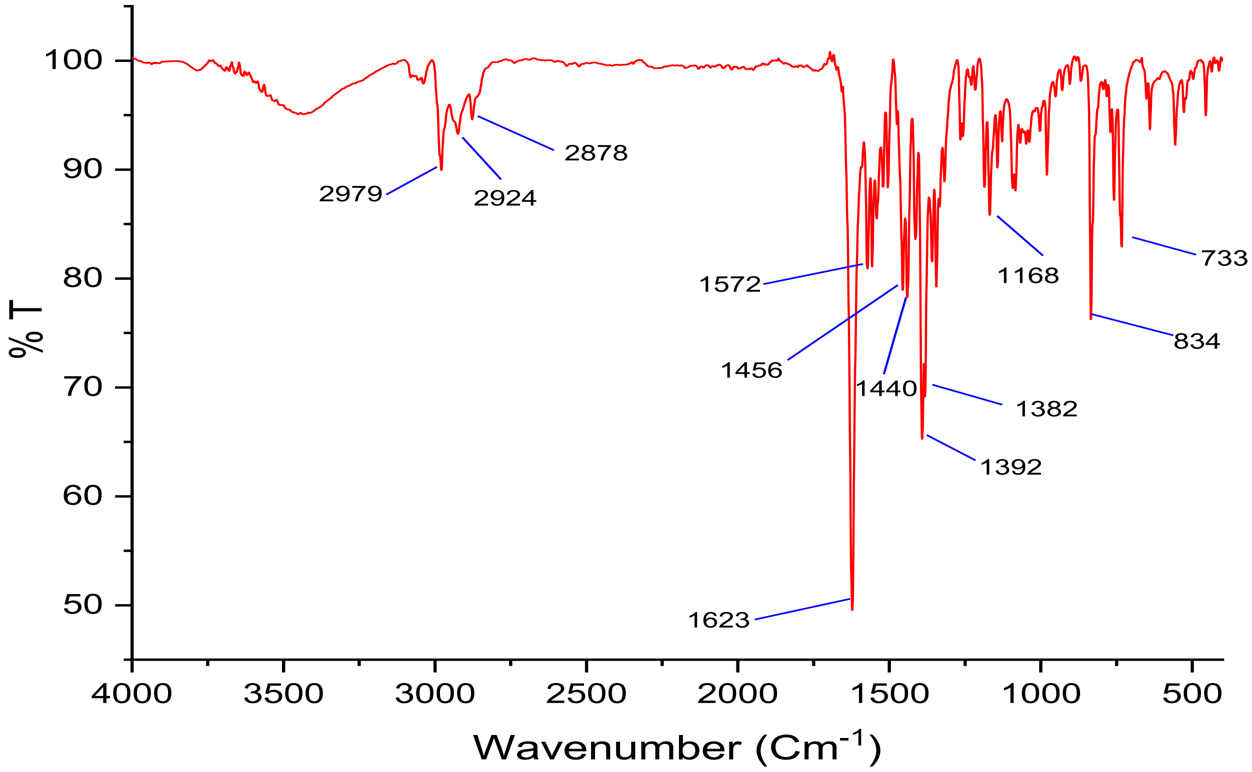


Figure S6: IR spectrum of complex **5**.

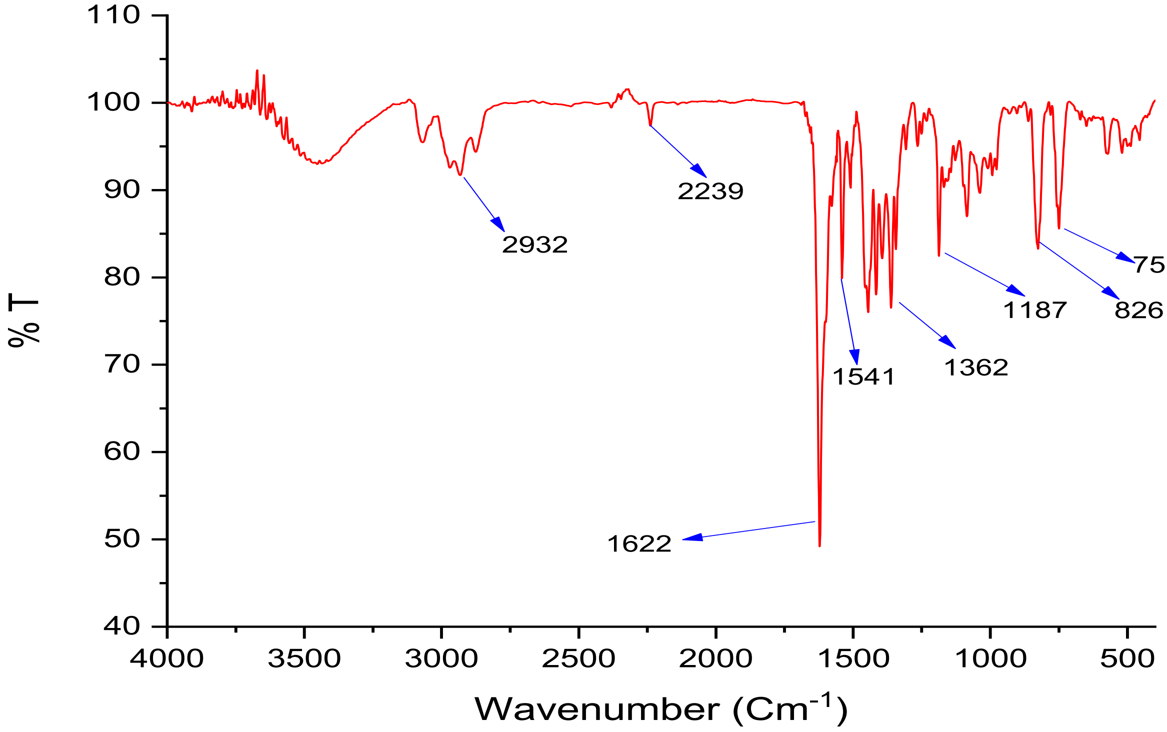


Figure S7: IR spectrum of complex **7** before crystallization.

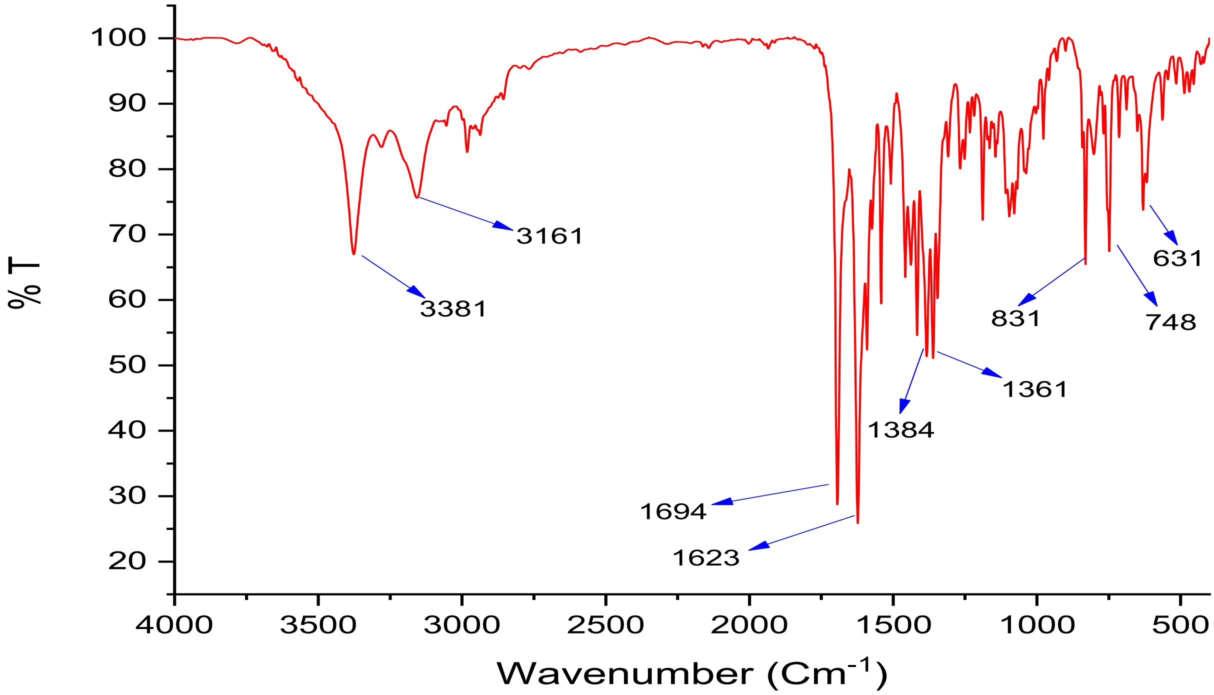
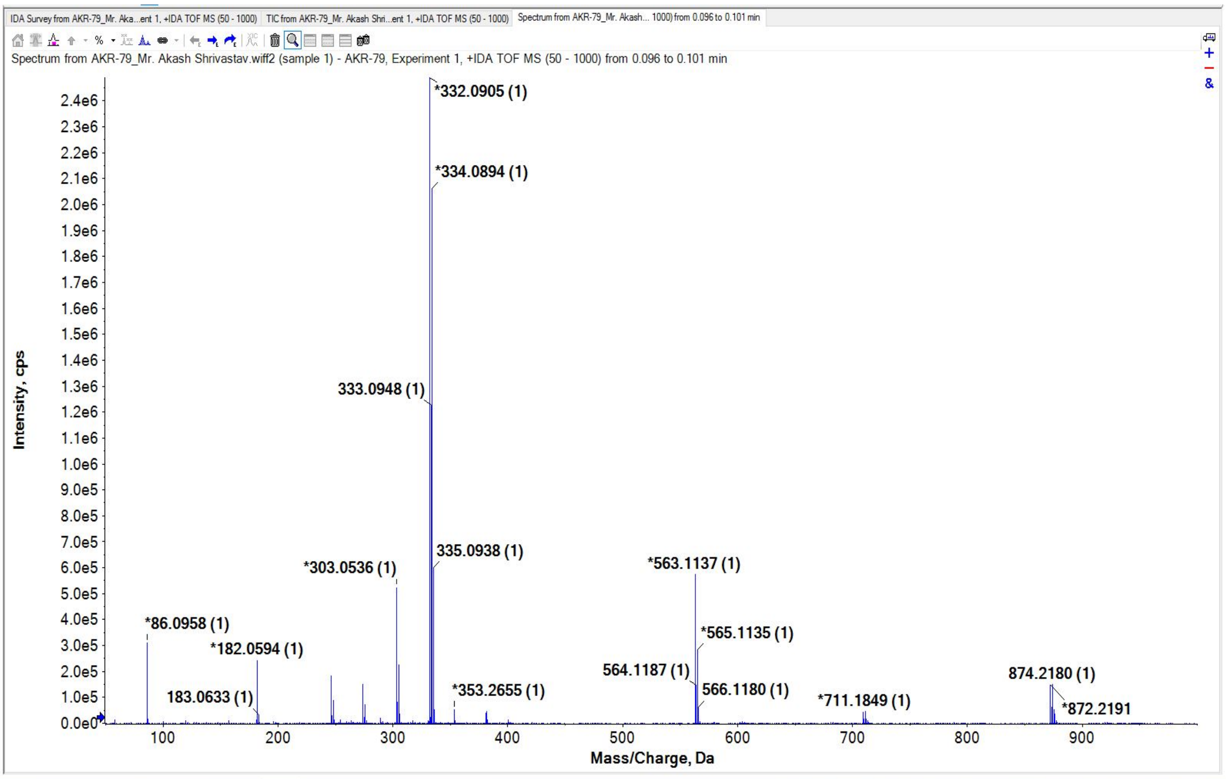
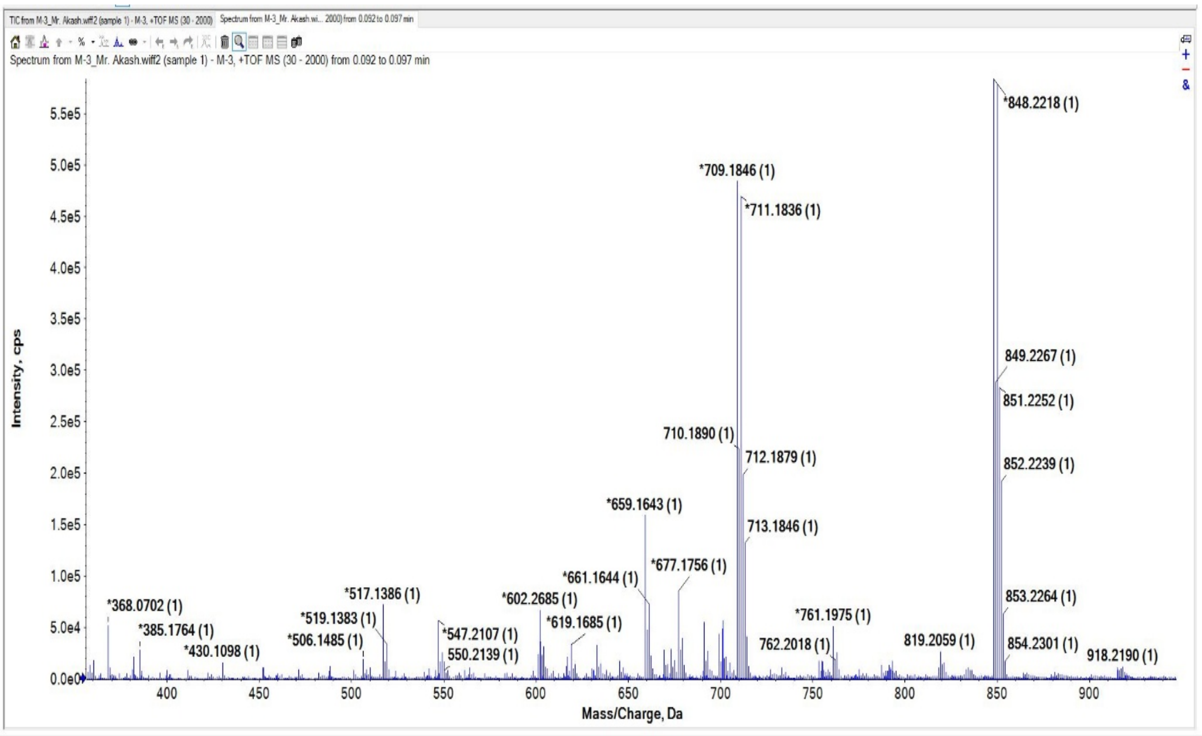


Figure S8: IR spectrum of complex **7** after crystallization.

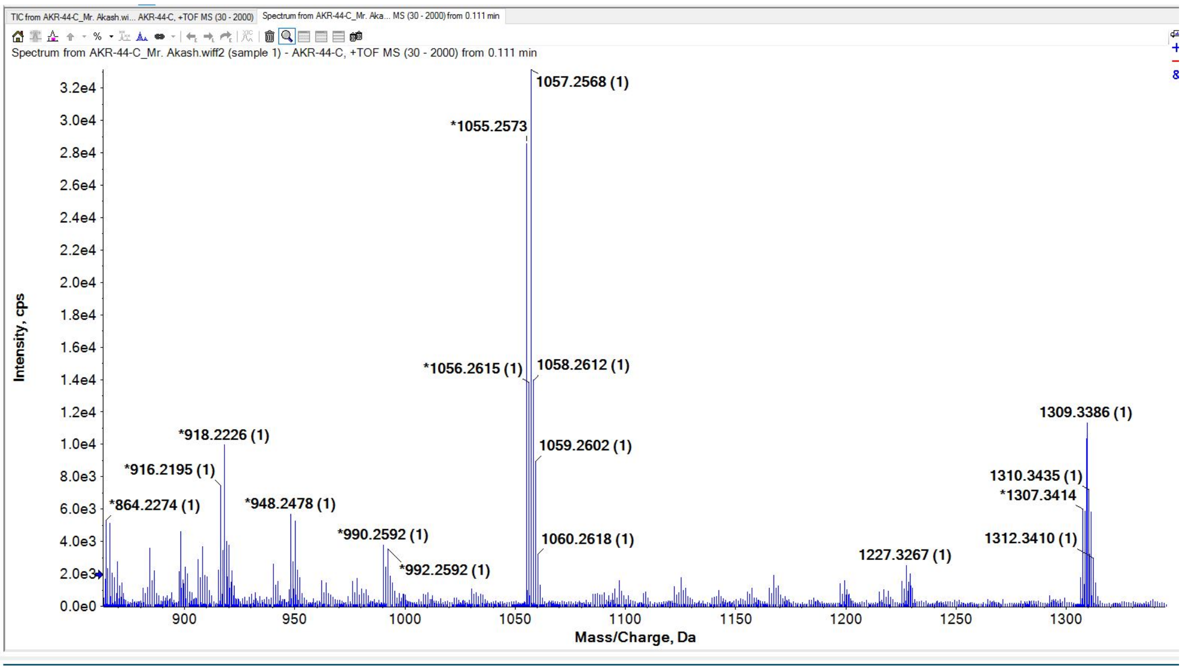


Spectrum from AKR-79_Mr. Akash Shrivastav.wiff2 (sample 1) - AKR-79, Experiment 1, +IDA TOF MS (50 - 1000) from 0.096 to 0.101 min

Figure S9: HRMS spectrum of complex **2.**

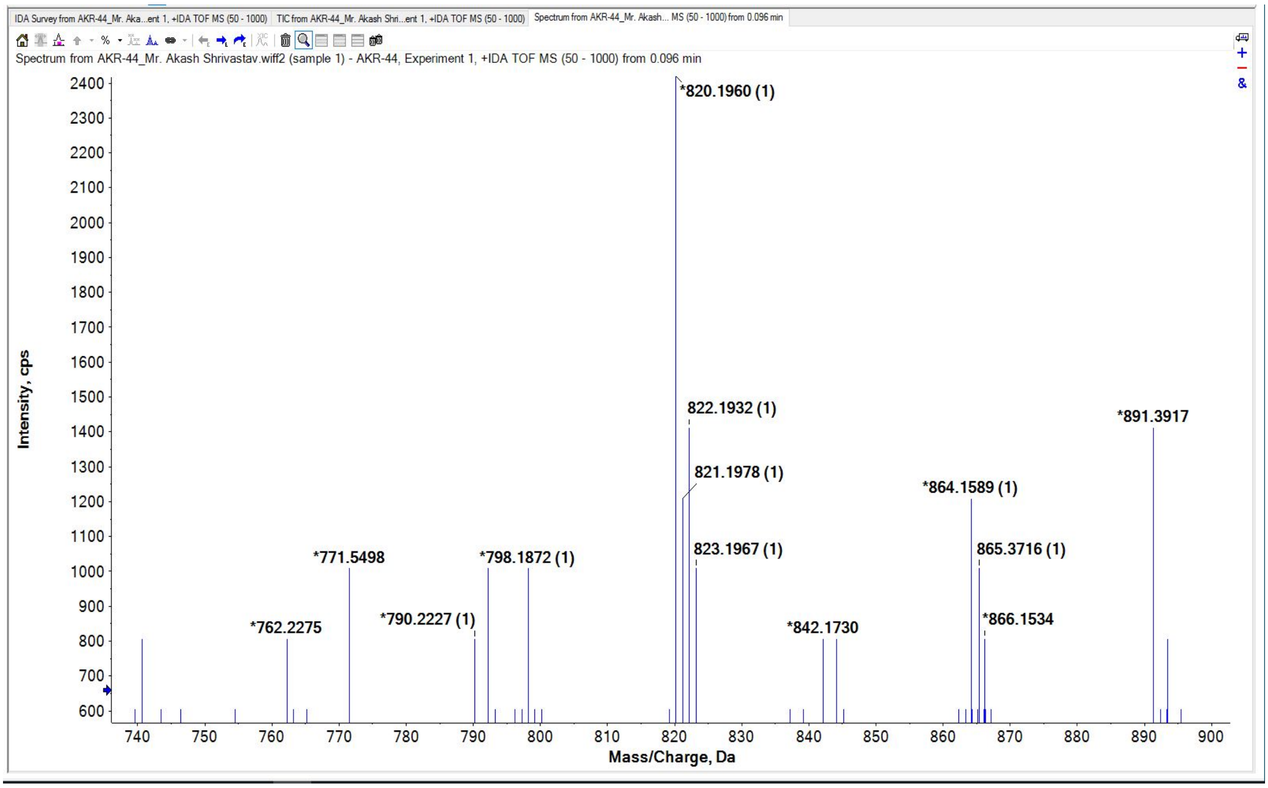


Spectrum from M-3_Mr. Akash.wiff2 (sample 1) - M-3, +TOF MS (30 - 2000) from 0.092 to 0.097 min



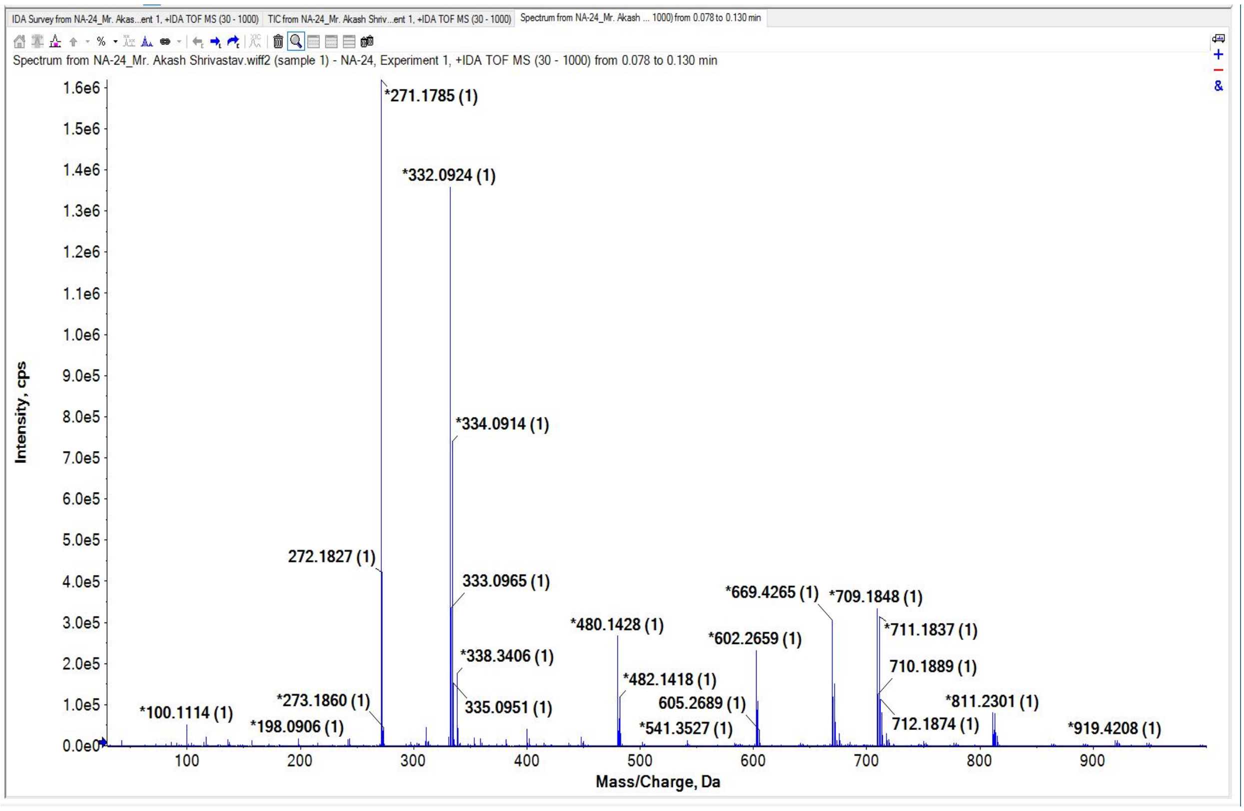
Spectrum from AKR-44-C_Mr. Akash.wiff2 (sample 1) - AKR-44-C, +TOF MS (30 - 2000) from 0.111 min

Figure S10: HRMS spectrum of complex **3** freshly prepared compound (before hydrolysis).



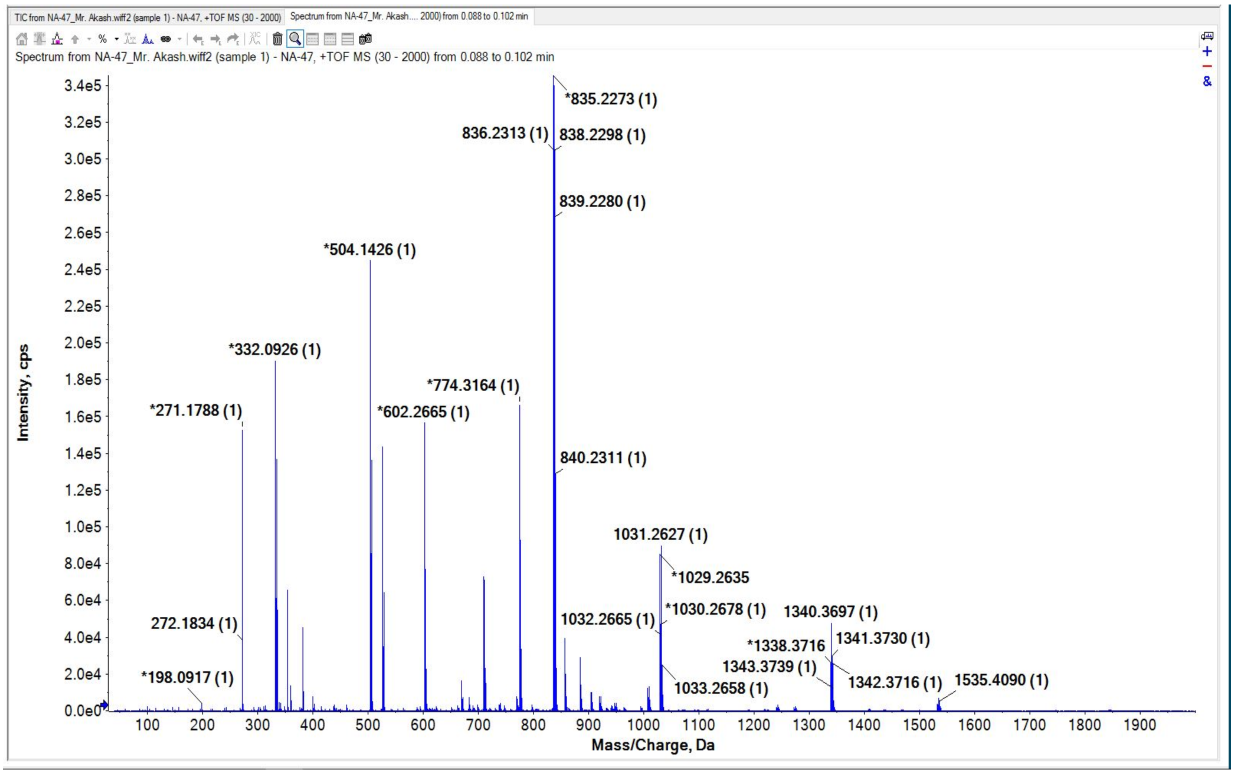
Spectrum from AKR-44_Mr. Akash Shrivastav.wiff2 (sample 1) - AKR-44, Experiment 1, +IDA TOF MS (50 - 1000) from 0.096 min

Figure S11: HRMS spectrum of complex **3** after hydrolysis.



Spectrum from NA-24_Mr. Akash Shrivastav.wiff2 (sample 1) - NA-24, Experiment 1, +IDA TOF MS (30 - 1000) from 0.078 to 0.130 min

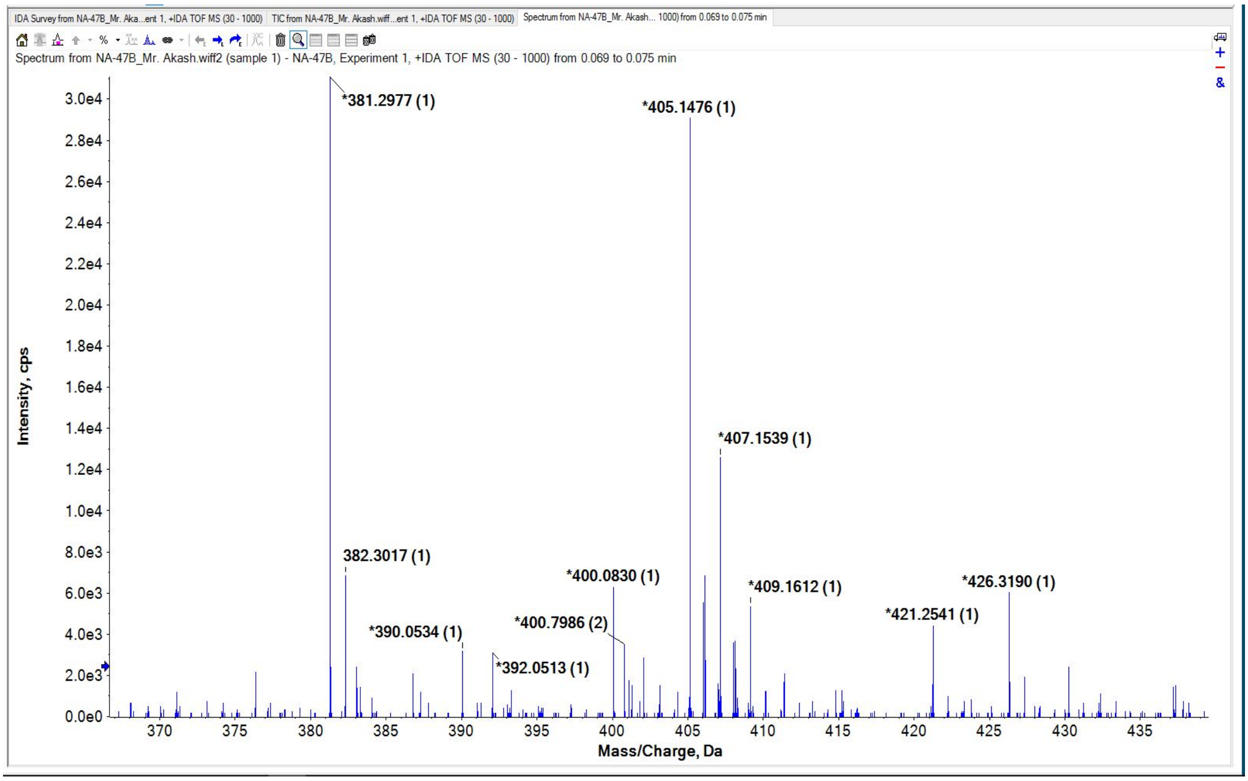
Figure S12: HRMS spectrum of complex **5**.



TIC from NA-47_Mr. Akash.wiff2 (sample 1) - NA-47, +TOF MS (30 - 2000) | Spectrum from NA-47_Mr. Akash.... 2000) from 0.088 to 0.102 min

Spectrum from NA-47_Mr. Akash.wiff2 (sample 1) - NA-47, +TOF MS (30 - 2000) from 0.088 to 0.102 min

Figure S13: HRMS spectrum of complex **7** before crystallization.



IDA Survey from NA-47B_Mr. Aka...ent 1, +IDA TOF MS (30 - 1000) | TIC from NA-47B_Mr. Akash.wiff...ent 1, +IDA TOF MS (30 - 1000) | Spectrum from NA-47B_Mr. Akash... 1000) from 0.069 to 0.075 min

Spectrum from NA-47B_Mr. Akash.wiff2 (sample 1) - NA-47B, Experiment 1, +IDA TOF MS (30 - 1000) from 0.069 to 0.075 min

Figure S14: HRMS spectrum of complex **7** after crystallization.

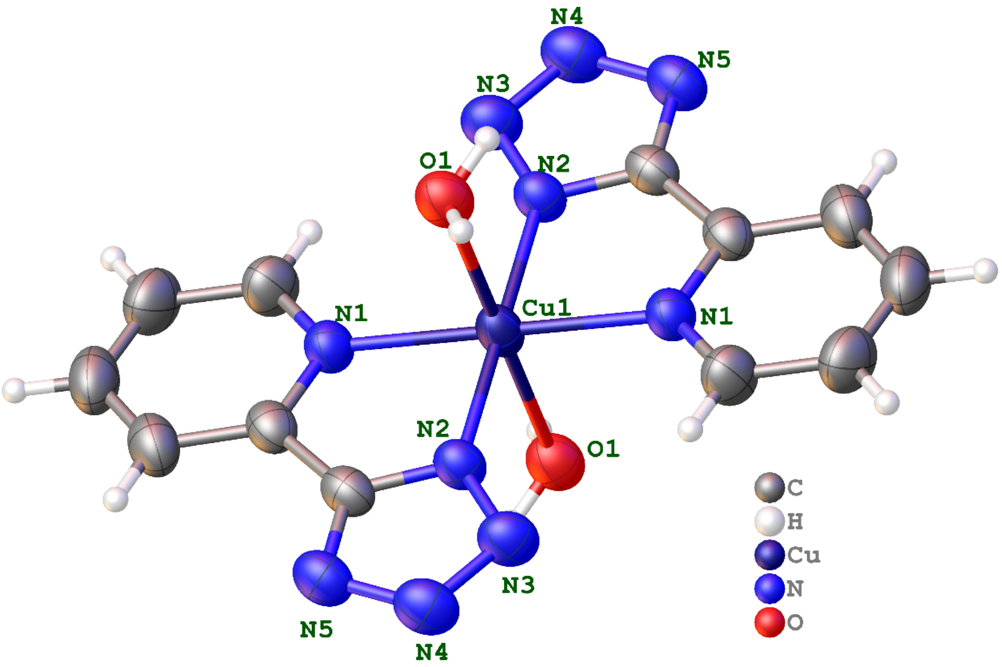
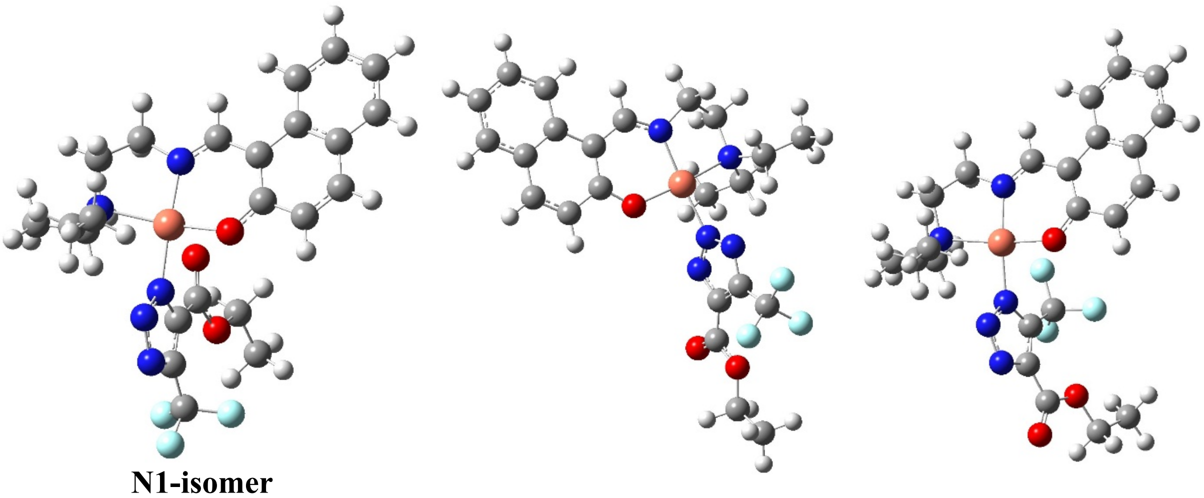


Figure S15. The molecular structure of complex **4**.

Table S1. Selected crystallographic data and structure solution parameters.

	1	2	3	4	5	6	7
CCDC number	2373944	2383064	2524617	2464427	2373943	2533279	2524619
Formula	$C_{17}H_{21}CuN_5O$	$C_{24}H_{27}Cl_3CuF_3N_5O_3$	$C_{38}H_{45}Cu_2N_7O_7$	$C_{12}H_{12}CuN_{10}O_2$	$C_{22}H_{24}CuN_8O$	$C_{24}H_{26}CuN_8O_2$	$C_{18}H_{10}CuN_6O_2$
Fw	374.93	660.39	838.89	391.86	480.03	522.07	405.86
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Orthorhombic	monoclinic	Monoclinic
Space group	$Pbca$	$P2_12_12_1$	$C2/c$	$P21/c$	$Pbca$	$P2_1/c$	$P2_1$
a (Å)	7.2005(2)	9.76640(10)	32.5141(3)	8.0354(2)	14.83030(10)	14.85570(10)	12.1966(6)
b (Å)	13.8992(4)	14.57750(10)	13.80030(10)	12.7317(3)	15.71030(10)	16.8748(2)	8.9640(3)
c (Å)	33.6442(9)	20.2849(2)	19.1607(2)	7.4563(2)	18.46940(10)	9.51710(10)	15.6705(8)
α(°)	90	90	90	90	90	90	90
β (°)	90	90	107.0650(10)	96.782(2)	90	102.3590(10)	97.257(4)
γ(°)	90	90	90	90	90	90	90
V (Å^3)	3367.15(16)	2887.95(5)	8218.96(14)	757.47(3)	4303.16(5)	2330.52(4)	1699.54(13)
Z	8	4	8	4	8	4	4
Measured Reflections	7074	32619	58410	8287	39752	27417	31732
Independent Reflections	3255	5146	7489	1485	4209	4226	5360
θ_{min}/ °	5.259	4.359	2.843	5.544	4.748	3.045	4.338
θ_{max}/ °	72.129	68.093	68.140	71.904	72.047	68.081	68.189
F(000)	1560.0	1348.0	3488.0	398.0	1992.0	1084.0	820.0
μ (mm^{-1})	1.944	4.105	1.725	2.349	1.701	1.654	2.057
ρ (g cm^{-3})	1.479	1.519	1.356	1.718	1.482	1.488	1.586
Final R_1	0.0594	0.0462	0.0488	0.0267	0.0282	0.0398	0.0985
$wR_2(F^2)$	0.1790	0.1366	0.1473	0.0794	0.0834	0.1121	0.2806
GooF	1.016	1.035	1.063	1.084	1.067	1.049	1.016



N1-isomer

N2-isomer N3-isomer

Figure S16. Ground-state optimized structures of N1, N2, and N3 triazolate isomers of complex **2** are obtained at the B3LYP/LANL2DZ level of theory.

Table S2- Corrected energy values of Cu(II) triazolate-bound isomers of complex 2.

	N1	N2	N3
Electronic Energy (EE)	-1887.0886 H	-1887.0845 H	-1887.0826 H
Zero-point Energy Correction	0.475961 H	0.476104 H	0.475847 H
Thermal Correction to Energy	0.510258 H	0.510507 H	0.510153 H
Thermal Correction to Enthalpy	0.511202 H	0.511452 H	0.511097 H
Thermal Correction to Free Energy	0.406122 H	0.403876 H	0.405691 H
EE + Zero-point Energy	-1886.6127 H	-1886.6084 H	-1886.6068 H
EE + Thermal Energy Correction	-1886.5784 H	-1886.574 H	-1886.5724 H
EE + Thermal Enthalpy Correction	-1886.5774 H	-1886.5731 H	-1886.5715 H
EE + Thermal Free Energy Correction	-1886.6825 H	-1886.6806 H	-1886.6769 H

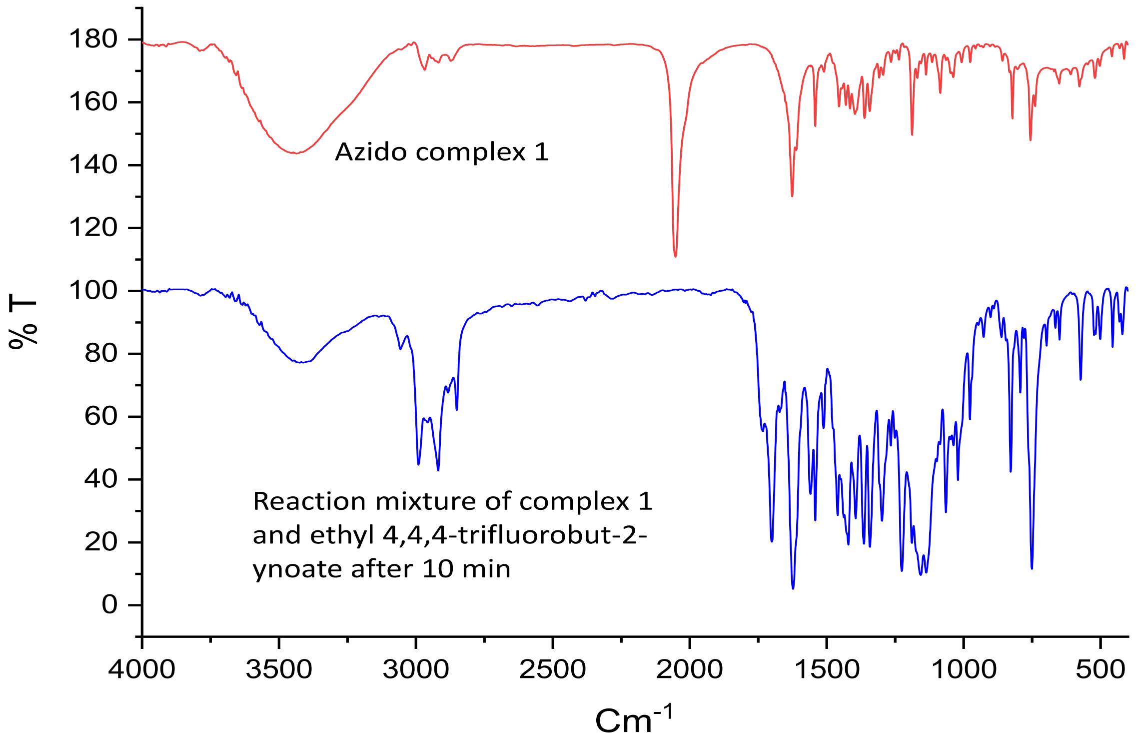
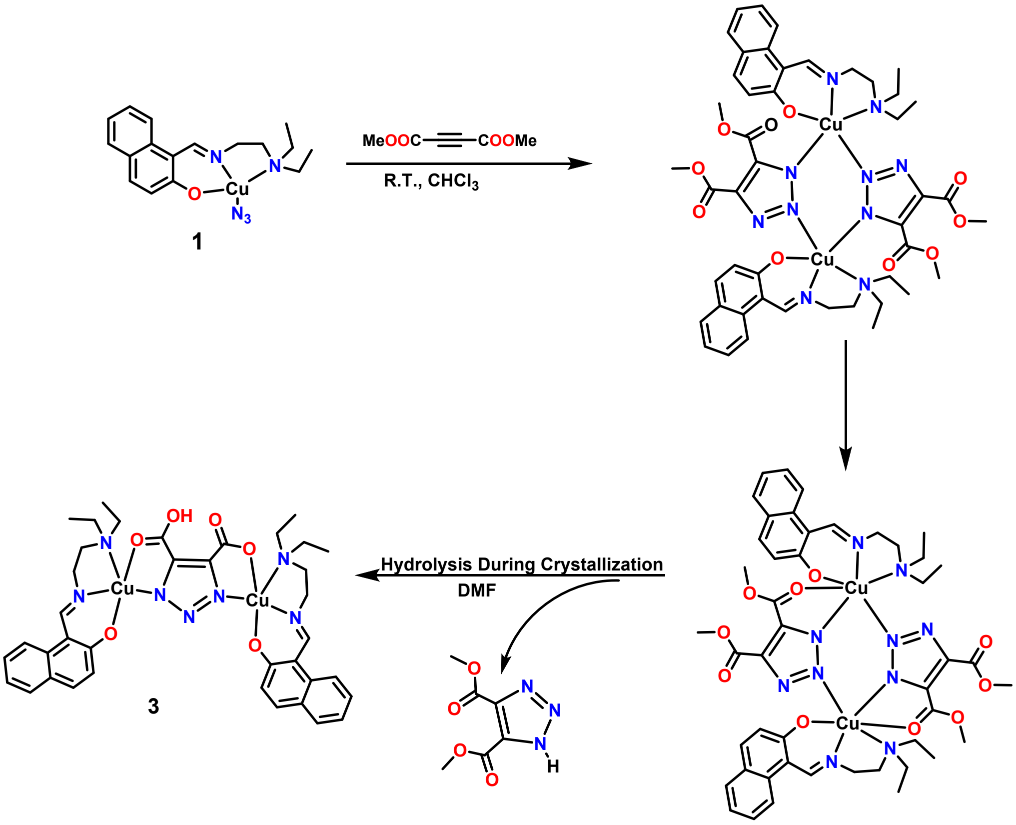


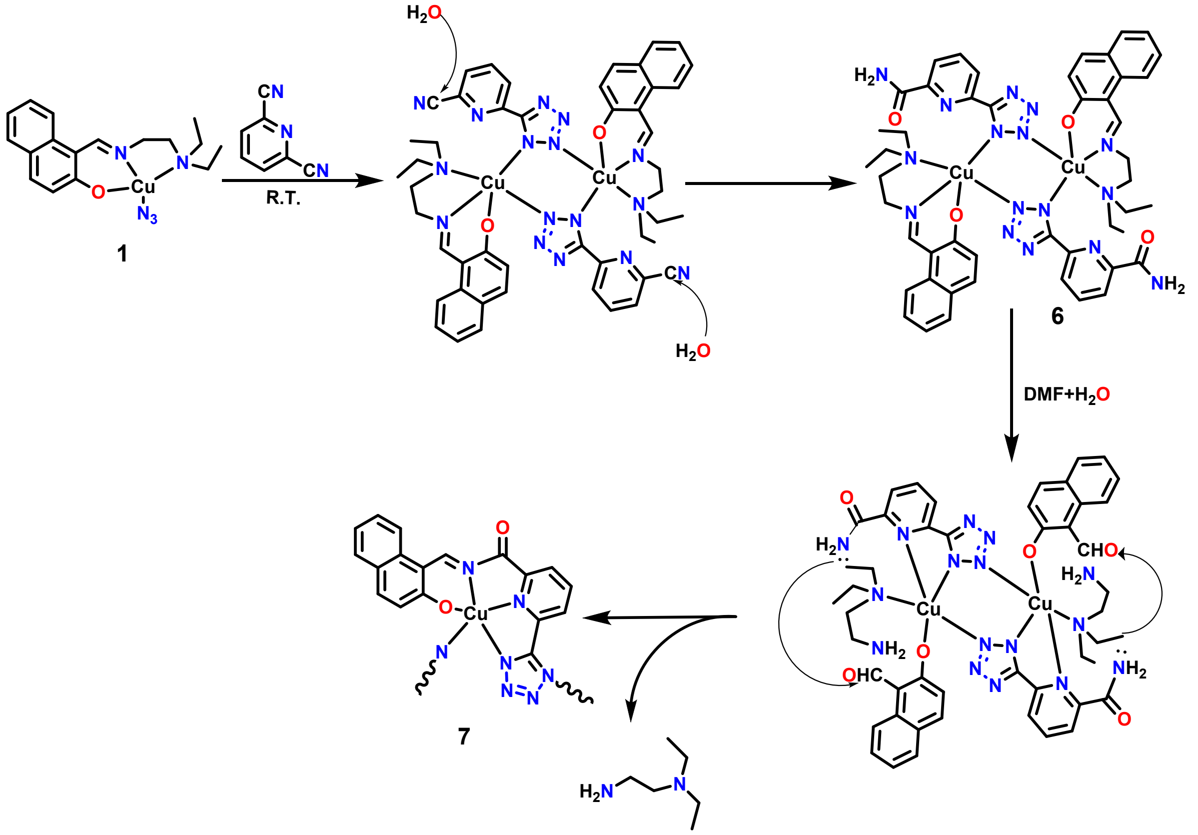
Figure S17. Changes in the IR spectrum of a mixture of Complex **1** [Cu(N_3)(L)] and ethyl 4,4,4-trifluorobut-2-ynoate in chloroform solvent taken after 10 minutes.

Mechanism of Reactions

Formation of Complex 3 took place via hydrolysis of the ester groups of coordinated triazolate ligands, as shown below (Scheme S1). Hydrolysis of the tetrazolate complex formed when 2,6-pyridine dicarbonitrile resulted in an interesting product (Scheme S2). The mechanisms are tentatively proposed on the basis of a few experimental and theoretical studies given below.



Scheme S1: Plausible reaction mechanism for the synthesis of complex **3**.

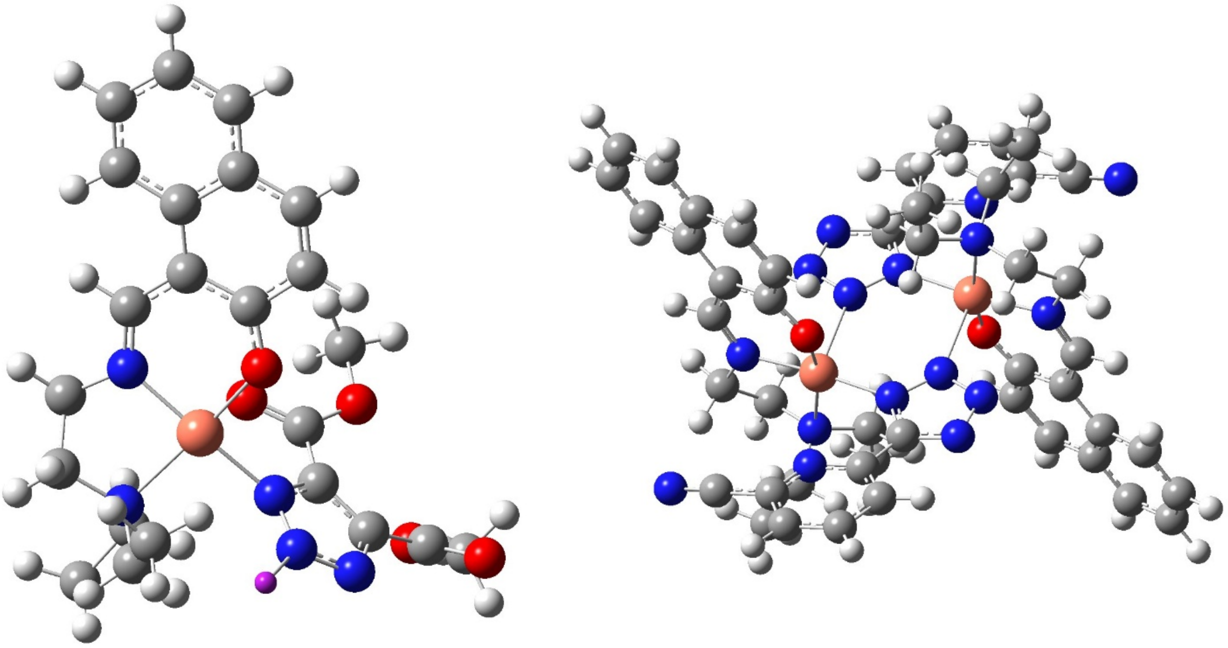


Scheme S2: Plausible reaction mechanism for the synthesis of complex **7**.

Evidences.

1. Peaks corresponding to $[M+Na]^+$ for the dimeric intermediates shown in the Schemes S1 and S2 are observed in the HRMS spectra of the corresponding solutions (Figure S10 and S13).
2. Density functional theory (DFT) calculations were carried out on dimer **3** and its corresponding mononuclear derivative. Geometry optimization of both species indicated that the dimer is thermodynamically more stable than the monomer by 17.49 kcal mol^{-1} (Figure S18). Similarly, in the case of dimer **7** and its mononuclear species, the former was found to be more stable by 13.60 kcal mol^{-1} (Figure S19).
3. Magnetic susceptibility studies showed an S shape of M vs H curves with small hysteresis, indicating weak ferromagnetic coupling due to the presence of two Cu(II) centers in the dimeric structures.
4. A partially hydrolysed species (complex 6) was crystallized and analysed structurally.

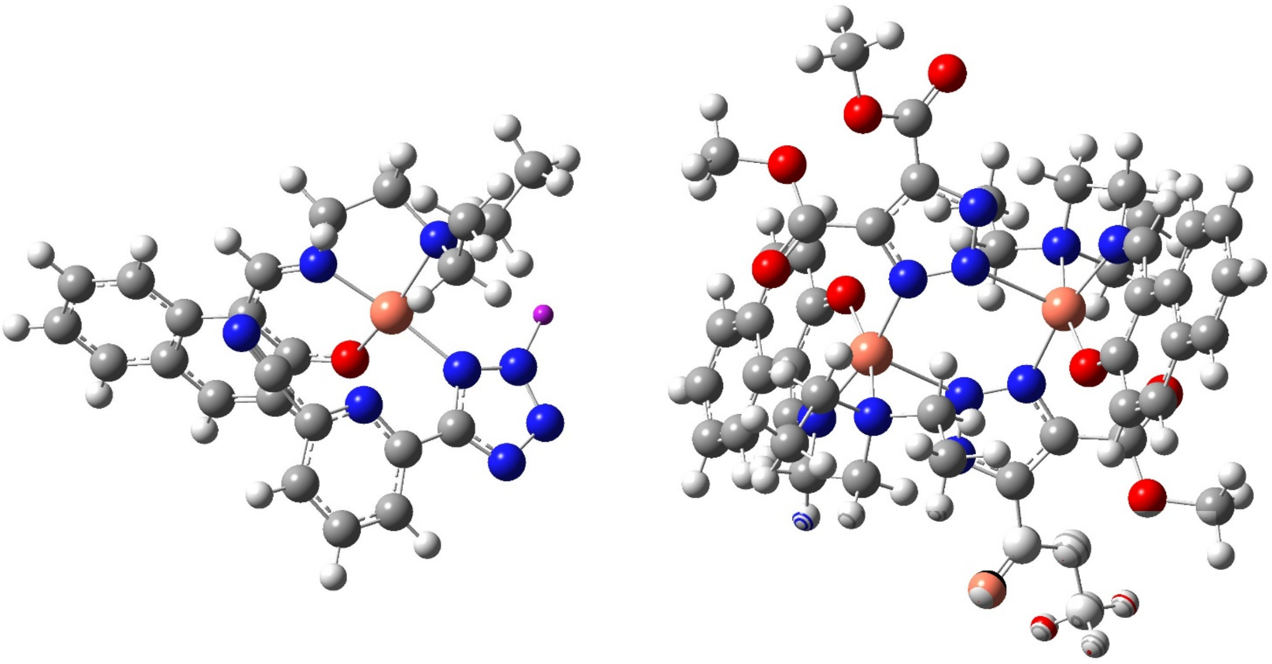
Optimized structures of the proposed dimeric and monomeric intermediates of the hydrolytic reactions and their energies.



Electronic Energy = -1738.536191 H **Electronic Energy = -3477.100265 H**

Electronic Energy × 2 = -3477.072382 H

Figure S18. Ground-state optimized structures of monomeric and dimeric of complex **3** before hydrolysis are obtained at the B3LYP/LANL2DZ level of theory.



Electronic Energy = -1638.148981 H **Electronic Energy = -3276.319639 H**

Electronic Energy × 2 **= -3276.297962 H**

Figure S19. Ground-state optimized structures of monomeric and dimeric of complex **7** before hydrolysis are obtained at the B3LYP/LANL2DZ level of theory.

Magnetic Susceptibility Studies

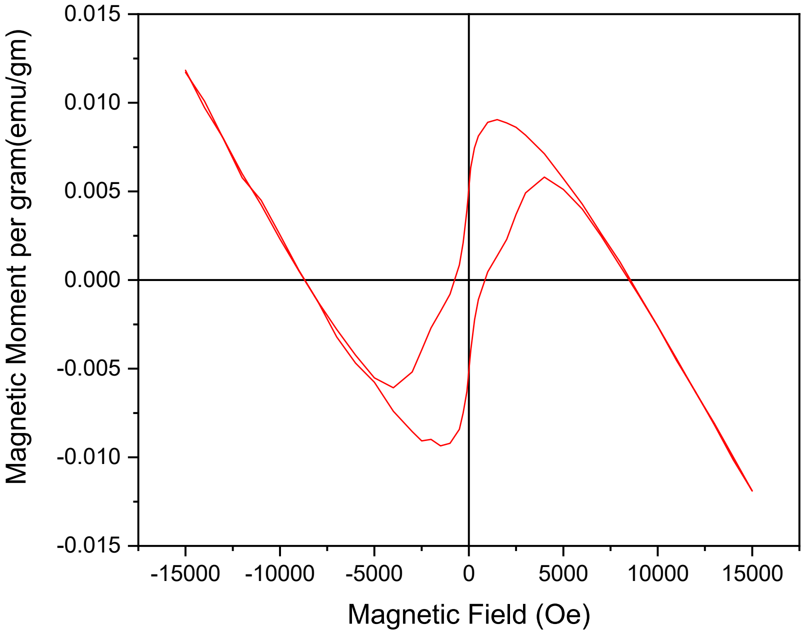


Figure S20. Plot of Magnetic moment (emu/gm) vs magnetic field of freshly prepared Complex **3**.

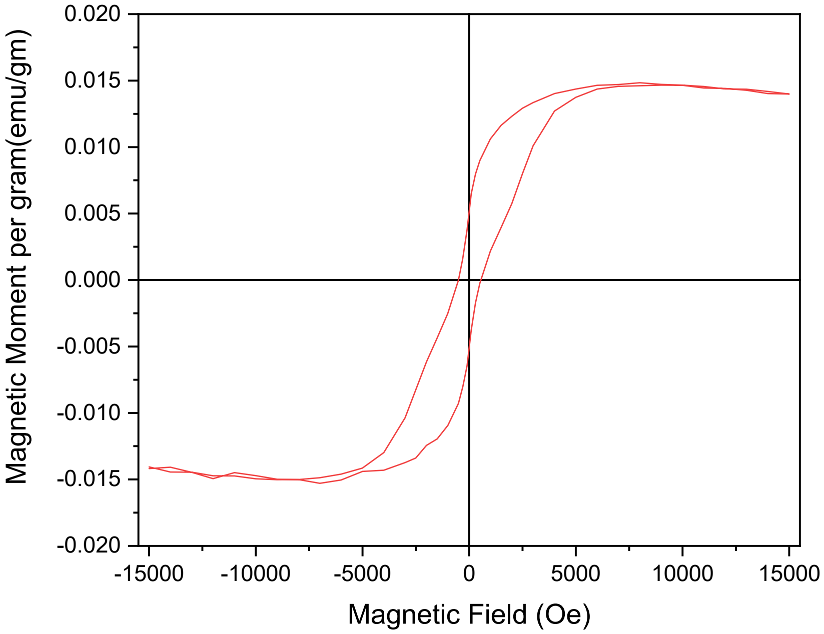


Figure S21. Plot of Magnetic moment (emu/gm) vs magnetic field of freshly prepared Complex **3** after subtracting diamagnetic contribution.

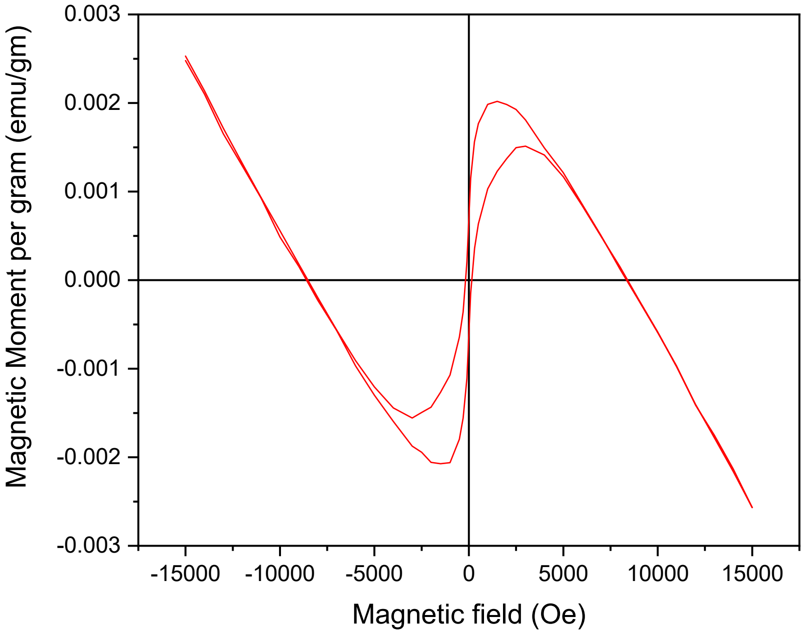


Figure S22. Plot of Magnetic moment (emu/gm) vs magnetic field of freshly prepared Complex **7**.

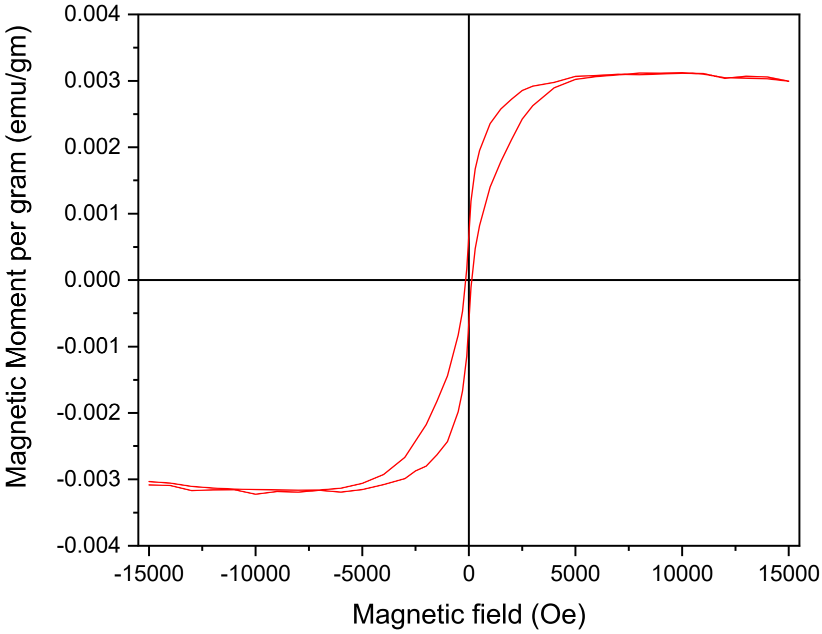


Figure S23. Plot of Magnetic moment (emu/gm) vs magnetic field of freshly prepared Complex **7** after subtracting diamagnetic contribution.

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