Supporting Information File

DNA intercalative trinuclear Cu(II) complex of new *trans* axial nitrato ligation performed as an efficient catalyst for atmospheric CO_2 fixation to epoxides

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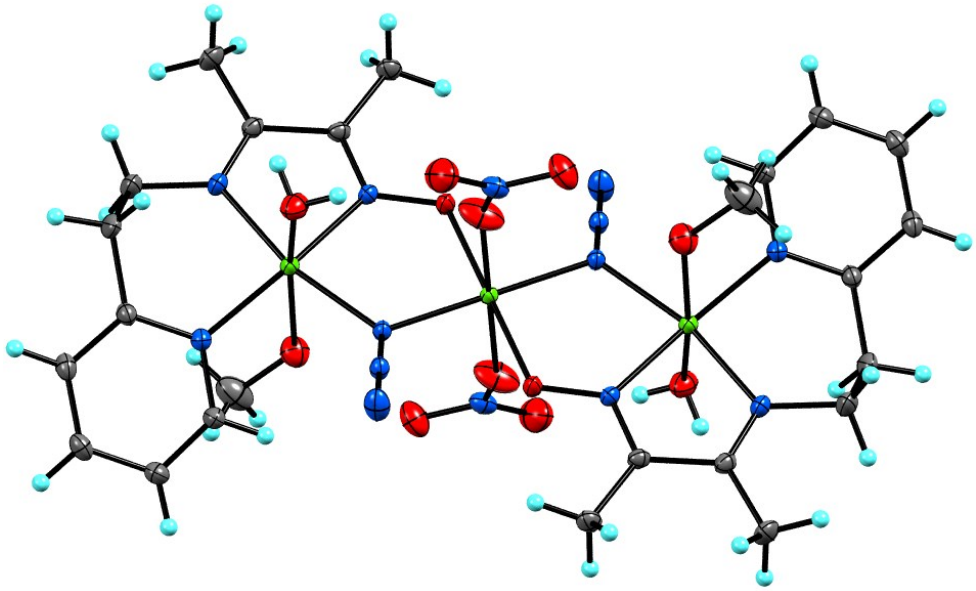


Figure S1. The ORTEP diagram (30% ellipsoid probability) of **1**.

Table S1. Crystal data and structure refinement for **1**.

Empirical formula	C_{24} H_{38} Cu_3 N_{14} O_{12}+2H (CCDC-2000191)
Formula weight	905.33+2
Temperature	273K
Wavelength	0.71073Å
Crystal system	Monoclinic
Space group	P21/c (No. 14)
Unit cell dimensions	a=9.7790(4) Å b=10.1110(4) Å c=18.6534(8) Å α= 90° β= 101.536(2)° γ = 90°
Volume	1807.11(13) $Å^3$
Z	2
Density (calculated)	1.664 g/cm^3
Absorption coefficient	1.827 mm^{-1}
F(000)	926
2Theta range for data collection	2.1 to 27.9 °
Index ranges	-12<=h<=12, -13<=k<=13, -24<=l<=24
Reflections collected	28018
Independent reflections	4328 [R(int) = 0.056]
Completeness to theta = 67.50°	99.7 %
Data / restraints / parameters	4325 / 0 / 252
Goodness-of-fit on F^2	1.00
R, wR2, S	0.0416, 0.1158, 1.00
Max. and Av. Shift/Error	0.01, 0.00

Table 2. Selected bond distances and bond angles of **1**.

Bond type	Bond length(Å)	Bond type	Bond angles(°)
Cu1-O1	1.911(2)	$O1N^a$ -Cu1-$O1N^b$	180.00
Cu1-N1	1.997(3)	$O1^c$ -Cu1 -$O1N^a$	91.85(11)
Cu1-$O1N^a$	2.725(4)	$O1N^a$ -Cu1 -$N1^c$	98.71(11)
Cu1-$O1N^b$	2.725(4)	$O1^c$ -Cu1 -$O1N^b$	88.16(11)
Cu1-$O1^c$	1.911(2)	$O1N^b$ -Cu1-$N1^c$	81.29(11)
Cu1-$N1^c$	1.997(3)	$O1^c$ -Cu1-$N1^c$	91.71(9)
Cu2 -O1W	2.450(4)	O1W -Cu2 -N1	85.59(12)
Cu2 -N1	1.997(2)	O1W -Cu2 -N4	92.09(12)
Cu2 -N4	2.015(3)	O1W -Cu2 -N5	94.44(12)
Cu2 -N5	1.986(3)	O1W -Cu2 -N6	96.92(12)
Cu2 -N6	1.985(3)	$O1M^b$ -Cu2 -O1W	169.42(12)
Cu2 -$O1M^b$	2.591(3)	N1 -Cu2 -N4	99.42(12)
Cu···Cu separation through the azido (EO) and oximato bridges	3.402	N1 -Cu2 -N5	166.50(12)
Bond angles(°)		N1 -Cu2 -N6	86.73(10)
O1 -Cu1 -N1	91.71(9)	$O1M^b$ -Cu2 -N1	85.25(10)
O1 -Cu1 -$O1N^a$	88.16(11)	N4 -Cu2 -N5	94.07(12)
O1-Cu1-$O1N^b$	91.85(11)	N4 -Cu2 -N6	169.47(11)
O1 -Cu1 -$O1^c$	180.00	$O1M^b$ -Cu2 -N4	84.19(10)
O1-Cu1-$N1^c$	88.30(9)	N5 -Cu2 -N6	79.87(11)
$O1N^a$ -Cu1-N1	81.29(11)	$O1M^b$ -Cu2 -N5	95.70(11)
$O1N^b$ -Cu1 -N1	98.71(11)	$O1M^b$ -Cu2 -N6	87.84(10)
$O1^c$ -Cu1 -N1	88.30(9)	Cu2-Cu1-$Cu2^i$	180
N1 -Cu1 -$N1^c$	180.00		

Symmetry code to equivalent position: a= x,1+y,z,b= 1-x,1-y,-z,c= 1-x,2-y,-z,i= inversion.

Computational details

The absorbance spectral properties in DMSO medium was calculated by time-dependent density functional theory (TDDFT)[1] associated with the conductor-like polarizable continuum model. We computed the lowest 40 doublet – doublet transitions and results of the TD calculations were qualitatively very similar.

For C, H, N, O, and Cu atoms, we used 6-31+g as basis set for all the calculations. All the calculations were performed with the Gaussian 09W software package.[2] Gauss Sum 2.1 program[3] was used to calculate the molecular orbital contributions from groups or atoms.

DNA binding measurements

DNA was dissolved in 10 mM citrate phosphate (CP) buffer (pH 7.0) and sonicated in a Labsonic sonicator (B. Braun, Germany) to obtain uniform size of (280 ± 50) base pairs and the solution was dialyzed at 5°C in experimental buffer under sterile conditions. The DNA sample exhibited characteristic ultraviolet absorption spectrum with an A_{260}/A_{280} ratio between 1.88 and 1.92 and an A_{260}/A_{230} ratio between 2.12 and 2.22. The concentration of DNA in base pairs was calculated by recording absorbance at 260 nm employing molar absorption coefficient (ε) of 13,200 $M^{-1} \cdot cm^{-1}$. All experiments were performed in filtered 10 mM citrate-phosphate (CP) buffer, pH 7.0 in deionized and triple-distilled water. All experiments were performed at 298.15±0.5 K. Entire bio-physical studies were carried out in 2% DMSO–buffer (v/v) solution of complex **1**.

Absorbance and fluorescence spectral titration

The absorption spectral titrations were performed at on a Jasco V660 unit (Jasco International Co. Ltd., Hachioji, Japan) equipped with a thermoelectrically controlled cell holder and temperature controller in matched quartz cuvettes of 10 mm path length, following generally the methods standardized in our laboratory and reported earlier. [4-6] The electronic spectra of **1** were monitored as a function of the concentration of DNA. In each case a fixed concentration of the **1** (50 μM) was titrated with increasing concentration of DNA over a range of 0–60 μM.

Steady state fluorescence measurements were performed on a Shimadzu RF-5301PC fluorometer in fluorescence free quartz cuvettes of 1.00 cm path length as described previously.[5,6] The excitation wavelength for **1** was 300 nm. All of the measurements were carried out under conditions of stirring and keeping excitation and emission band passes of 5 nm. The sample temperature of the fluorometer was maintained at 298.15±0.5 K using an EyleaUni Cool U55 water bath (Tokyo Rikakikai Co. Ltd., Tokyo, Japan).

Estimation of the binding parameters

The spectral titration data were analyzed by employing the Benesi−Hildebrand plot. The binding affinity of DNA for the **1** was determined using Benesi–Hildebrand equation (1),[7]

$$\frac{1}{\Delta A} = \frac{1}{\Delta A_{max}} + \frac{1}{(\Delta A_{\max}) K_{BH}} \times \frac{1}{[\mathrm{M}]} \qquad (1)$$

where, ΔA is the difference in absorbance or fluorescence and [M] is the DNA concentration. By plotting the reciprocal of the difference in absorbance or fluorescence intensity against the reciprocal of DNA concentration, the

Benesi−Hildebrand association constant (K_{BH}) for the **1**−DNA association was calculated from the ratio of the intercept to the slope.[7]

Hydrodynamic studies

Hydrodynamic studies were carried out to check the binding mode of **1** with DNA. Viscometric measurements[8] were performed using a Cannon–Manning semi micro dilution viscometer immersed vertically in a constant temperature water bath at 298.15±0.5 K. Flow times of DNA alone and DNA with different ratio of the complex **1** were measured in triplicate with an accuracy of ± 0.01 s using a Casio electronic stop watch and the relative specific viscosity was calculated using the equation (2),

$$\frac{\eta_{sp}^{'}}{\eta_{sp}} = \frac{\frac{(t_{complex} - t_o)}{t_0}}{\frac{(t_{control} - t_o)}{t_0}} \qquad (2)$$

Where, $\eta_{sp}^{'}$ and η_{sp} are the specific viscosities of DNA in the presence and absence of the complex **1**, $t_{complex}$ and $t_{control}$ are the average efflux times of complex **1** and DNA respectively and t_0 is the same for the buffer. The relative increase in helix contour length of DNA, L/L_o, can be obtained from a corresponding increase in the relative viscosity using the following equation (3)

$$\frac{L}{L_0} = \left(\frac{\eta}{\eta_0}\right)^{1/3} = 1 + \beta r \qquad (3)$$

where, L and L_o are the contour lengths of DNA in the presence and in the absence of the complex **1**, η and η_0 are the corresponding values of intrinsic viscosity (approximated by the reduced viscosity $\eta = \frac{\eta_{sp}}{C}$) where C is the concentration of DNA and β is the slope of the plot of L/L_o versus r.

Ethidium bromide (EB) displacement assay

Ethidium bromide (EB) displacement assay was performed in 50 mM Tris-HCl buffer (pH 7) in fluorescence free quartz cuvette having path length 1 cm with an excitation wavelength of 490 nm at 298.15 K. In the experiment, an equilibrated mixture of CT-DNA (30 μM) and EB (7 μM) was prepared (termed as ethidium bromide bound CT-DNA (EB-DNA) solution) and aliquots of compound solutions (**1**) were added to obtain a ratio of [compound]/[EB-DNA] in the range of 0.2 - 2.5. The spectra were recorded in the range of 510-700 nm and were corrected for background fluorescence of free EB in solution.

Isothermal titration calorimetric study

Isothermal titration calorimetry experiments were performed on a VP-ITC microcalorimeter (Malvern Instruments, United Kingdom) to study the binding interaction of **1** with DNA. The data were analysed using Origin 7.0 software to obtain the thermodynamic parameters by following the protocols described in details previously.[9-11] Buffer solutions were degassed extensively to prevent air bubble formation during titration. Titrations were performed by injecting **1** solution (125 μM) from the rotating syringe into the isothermal chamber containing 1.4235 mL of DNA solutions (60 μM) at 298.15 K. The titration was performed in 28 sequential injections and each injection released 10 μL aliquots from the rotating syringe into the calorimeter cell. The corresponding dilution study of each reaction was performed in separate experiment by injecting identical volumes of the same concentration of the **1** into the buffer alone. The heat associated with each injection was observed as a heat spike which is actually the measure of the power needed to maintain the sample and reference cells at same temperatures. The area under each peak was integrated to obtain the heat associated with that injection. The heats of dilution were subtracted from the corresponding heat associated with the binding experiment that afforded the actual heat of **1**-DNA interaction. The corrected injection heats were thereafter plotted

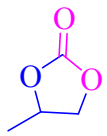
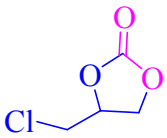
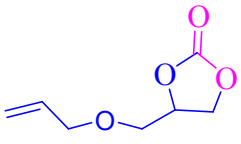
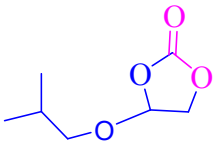
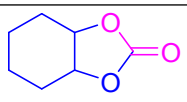
as a function of the molar ratio and this was fitted with a model for one set of binding sites to calculate the equilibrium constant (K), the binding stoichiometry (N) and the standard molar enthalpy change (ΔH^0) of association. The standard molar Gibbs energy change (ΔG^0) was calculated using the standard relationship

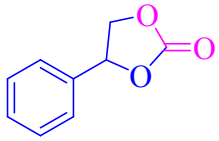
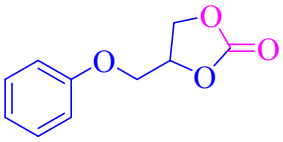
$$\Delta G^0 = -RT \ln K \qquad (4)$$

where R (1.987 cal . K^{-1}. $mole^{-1}$) is the gas constant and T is the temperature in kelvins (K). Analysis of ITC data yielded the values of standard molar Gibbs energy and standard molar enthalpy change that enabled the calculation of $T\Delta S^0$, where ΔS^0 is the calculated standard molar entropy change, using the relationship

$$T\Delta S^0 = \Delta H^0 - \Delta G^0 \qquad (5)$$

^{1}H NMR data of cyclic carbonates

	Yellowish oil, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 3.74-3.85 (m, 2H), 4.044 (t, J = 8.0 Hz, 1H), 4.564 (t, J = 8.4 Hz, 1H), 4.868-4.919 (m, 1H) ppm.
	Yellowish oil, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 3.732-3.846 (m, 2H), 4.406-4.444 (m, 1H), 4.594 (t, J = 8.8 Hz, 1H), 4.998-5.048 (m, 1H) ppm.
	Colourless liquid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 3.499-3.657 (m, 2H), 3.948-4.034 (m, 2H), 4.280-4.349 (m, 1H), 4.395-4.470 (m, 1H), 4.752-4.806 (m, 1H), 5.107-5.242 (m, 2H), 5.756-5.855 (m, 1H) ppm.
	Yellowish oil, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 1.101 (d, J = 6.4 Hz, 6H), 3.515-3.625 (m, 3H), 4.297 (dd, J = 6.0, 8.4 Hz, 1H), 4.412 (t, J = 8.0 Hz, 1H), 4.717-4.774 (m, 1H) ppm.
	Colourless liquid, **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 1.309-1.398 (m, 2H), 1.523-1.593 (m, 2H), 2.088 (t, J = 3.6 Hz, 4H), 4.598-4.623 (m, 2H) ppm.

	White solid, **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 4.343 (t, *J* = 6.0 Hz, 1H), 4.788 (t, *J* = 8.4 Hz, 1H), 5.669 (t, *J* = 8.0 Hz, 1H), 7.365 (dd, *J* = 2.8, 5.0 Hz, 2H), 7.437 (t, *J* = 4.8 Hz, 3H) ppm.
	White solid. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 4.040-4.179 (m, 2H), 4.468-4.5473 (m, 1H), 4.512-4.554 (m, 1H), 4.923-4.978 (m, 1H), 6.823-6.958 (m, 3H), 7.185-7.253 (m, 2H) ppm.

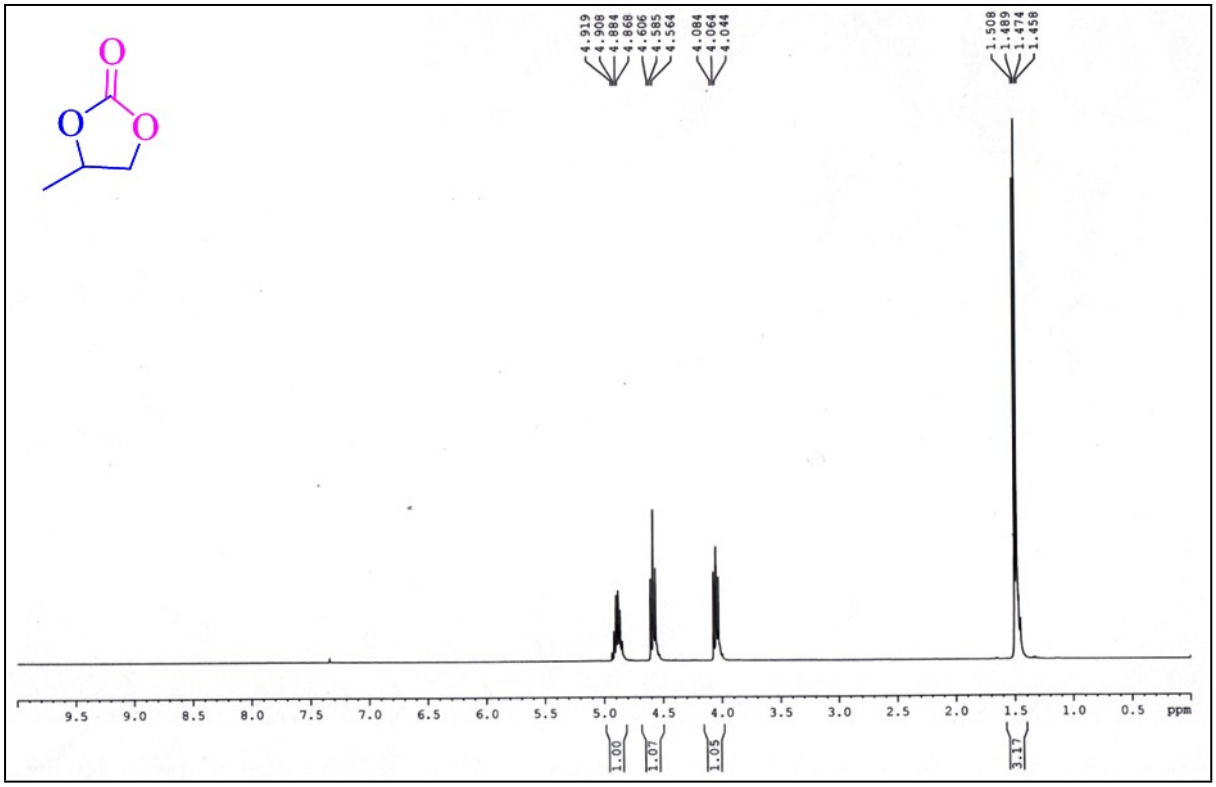


Figure S1. ^{1}HNMR spectra of 4-methyl-1,3-dioxolan-2-one.

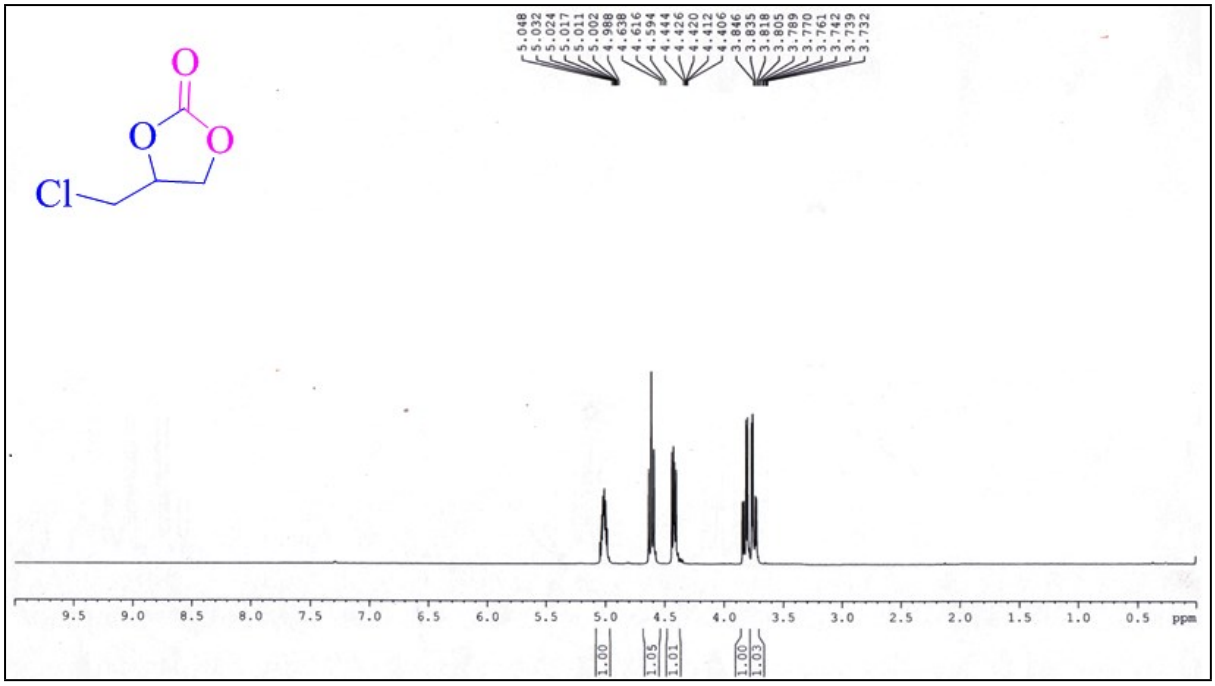


Figure S2. [1]HNMR spectra of 4-(chloromethyl)-1,3-dioxolan-2-one.

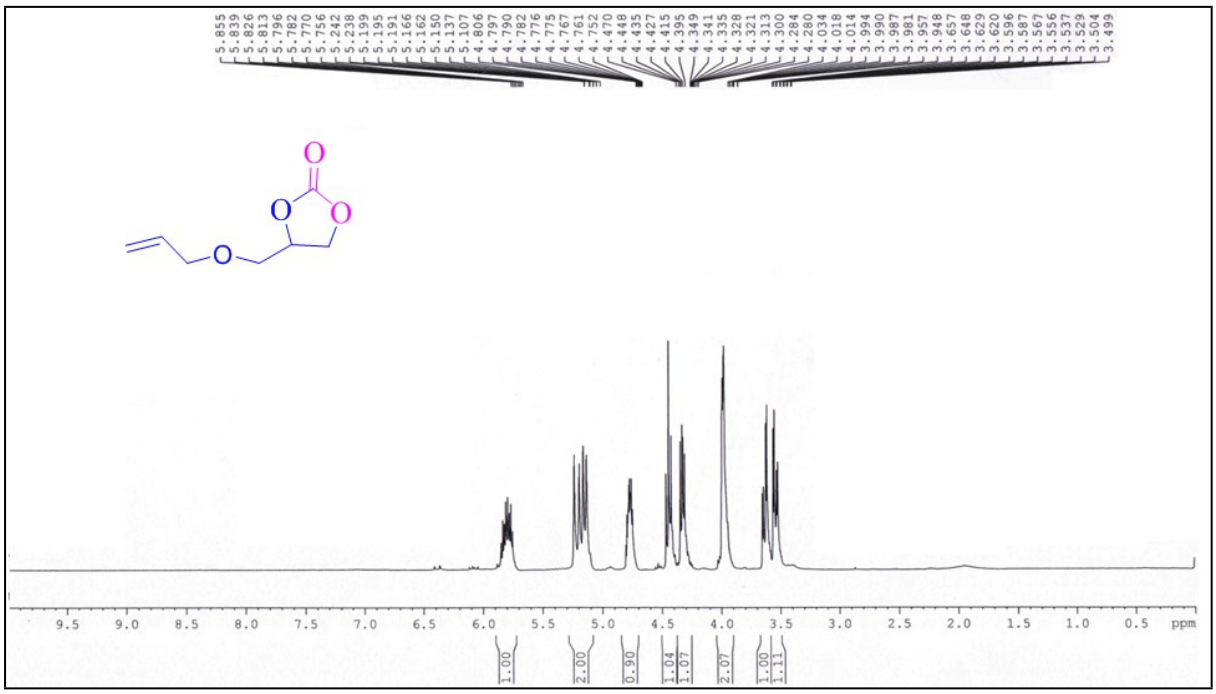


Figure S3. [1]HNMR spectra of 4-((allyloxy)methyl)-1,3-dioxolan-2-one.

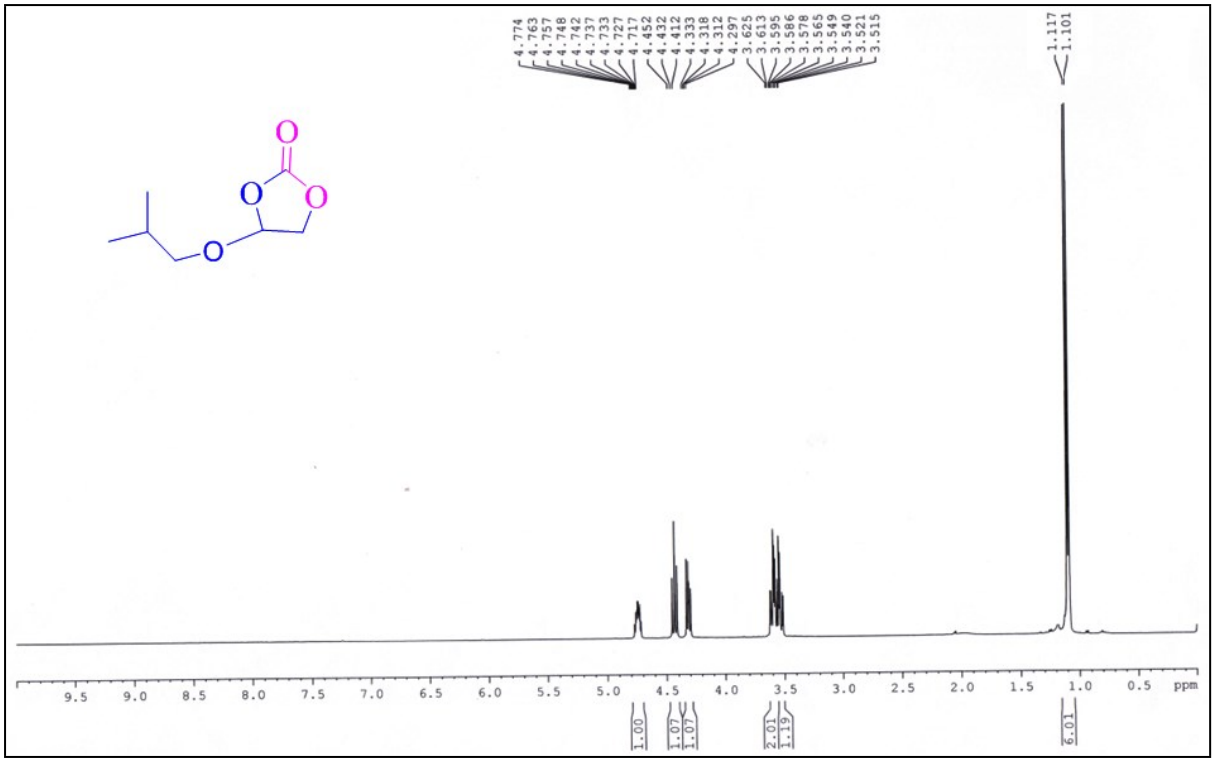


Figure S4. [1]HNMR spectra of 4-isobutoxy-1,3-dioxolan-2-one.

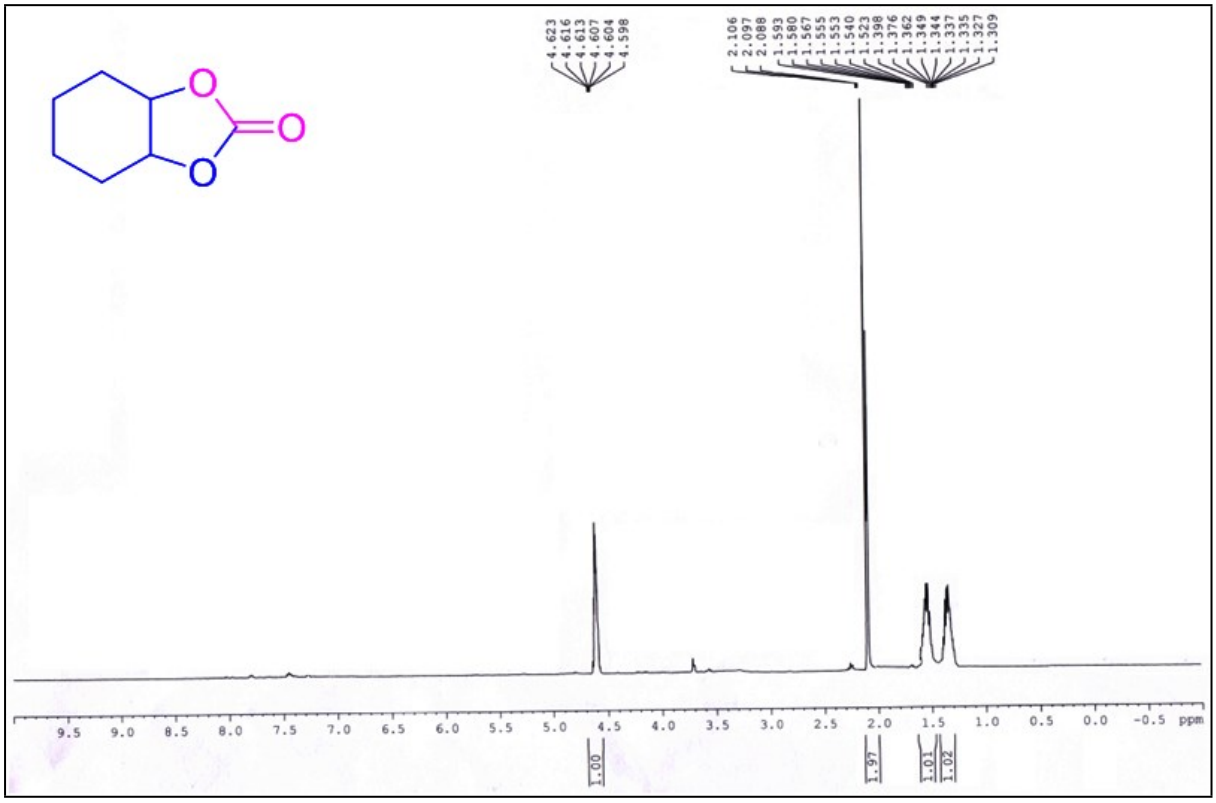


Figure S5. [1]HNMR spectra of hexahydrobenzo[d][1,3]dioxol-2-one.

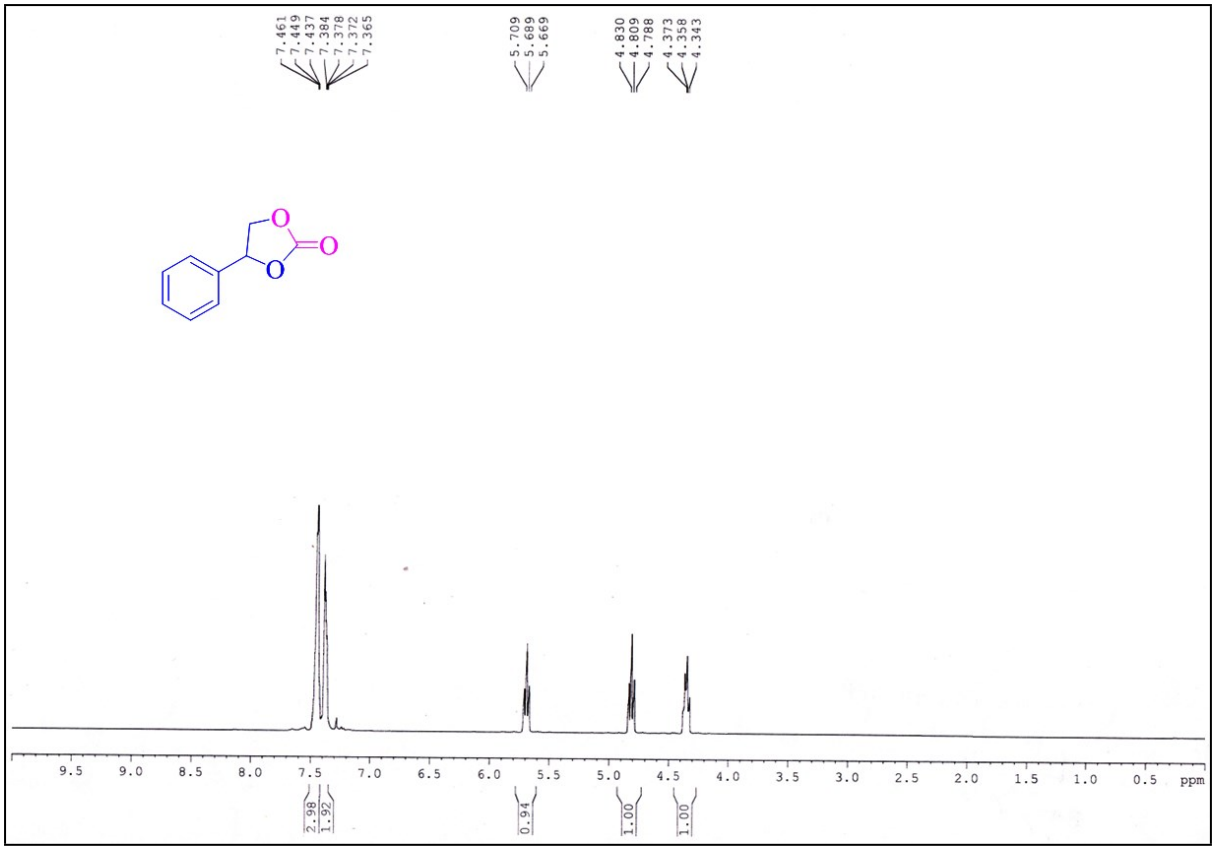


Figure S6. [1]HNMR spectra of 4-phenyl-1,3-dioxolan-2-one.

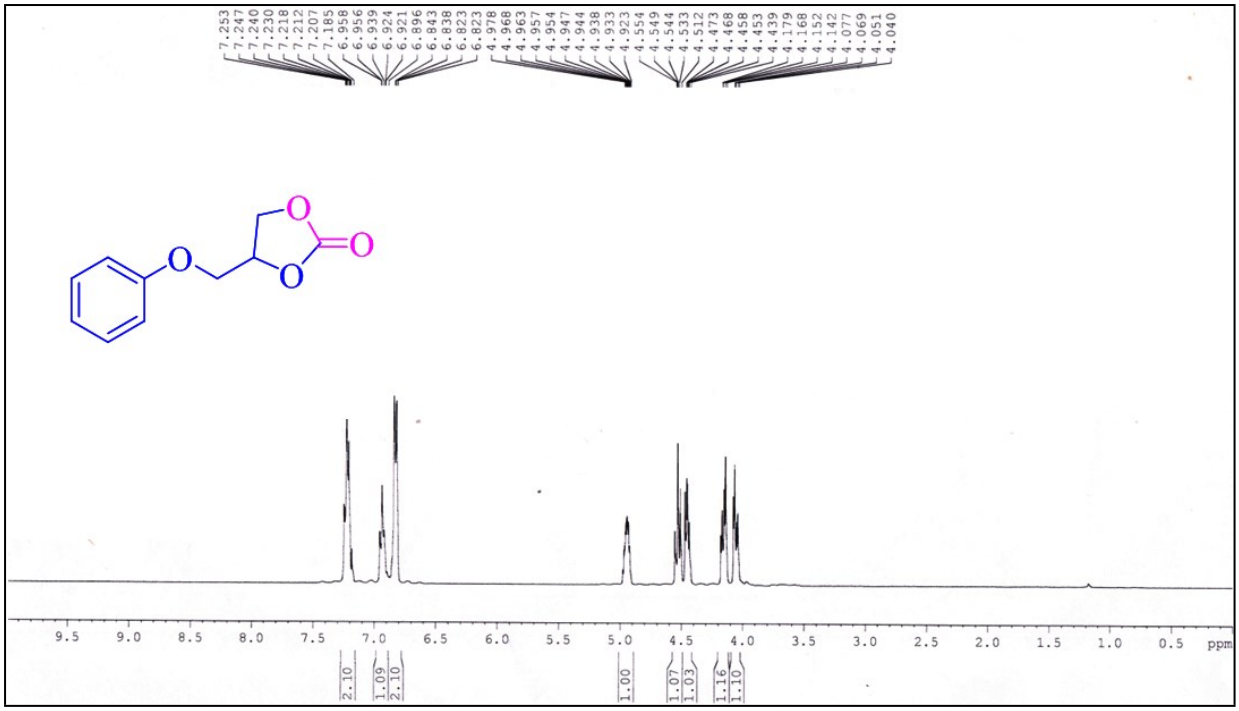


Figure S7. [1]HNMR spectra of 4-(phenoxymethyl)-1,3-dioxolan-2-one.

Stability of 1 in testing media

To investigate the stability of the Cu complex in the testing media, the kinetic study for the decomposition of the complex for 2 h in the 2% DMSO-Buffer (v/v) (testing media) has been performed. The electronic absorption spectra of the complex solution were recorded after 5 s time intervals to see the change in absorbance with respect to time. The absorbance at 658 nm with respect to time was recorded and plotted against respective time and fitted in first order rate equation, from which the dissociation constant (K_d) was obtained. The dissociation constant (K_d) (Figure S8) was found to be $(1.06 \pm 0.04) \times 10^{-5}$ S^{-1} and the $t_{1/2}$ was calculated to be ~18 hours. The dissociation constant value confirms that the complex possess substantial stability in the testing media.

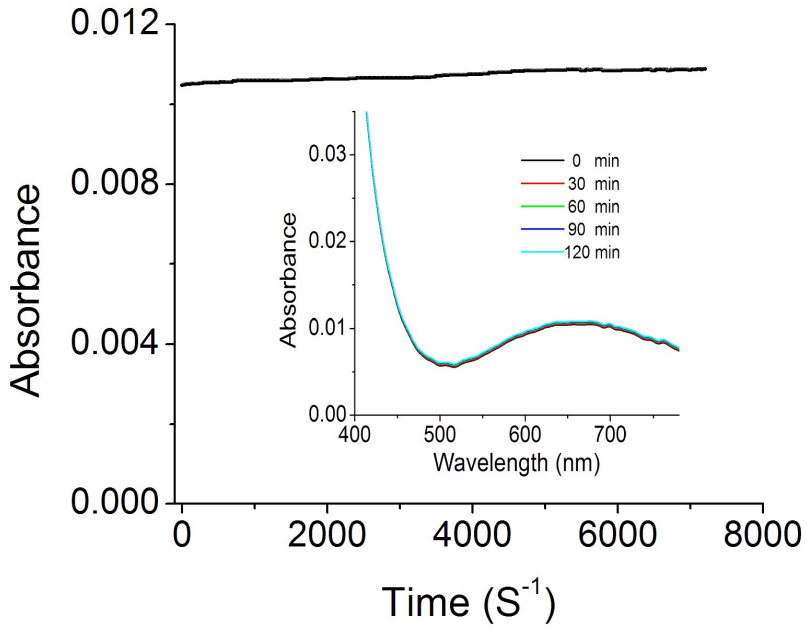


Figure S8. Kinetic trace for the decomposition of **1** in 2% DMSO-buffer (v/v) at 298.15±0.05 K. Inset is the corresponding time resolved spectra. Last spectra were taken at 7200 s.

References

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