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# A new route for the synthesis of symmetric and dissymmetric bis-triazol ligands and the catechol oxidase biomimetic catalytic activity of their copper(II) complexes

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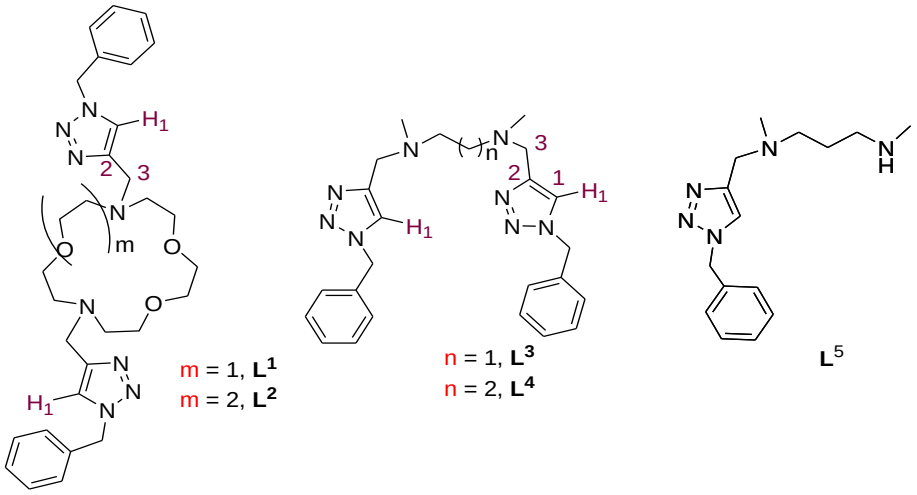
## Absract
An efficient route of synthesis of symmetric and dissymmetric [1,2,3]Triazole-containing ligands via the easily accessible benzyl-protected alkylating synthon benzyl-4-bromomethyl-1H-1,2,3-triazole(**1**) is reported. The structure of $\mathbf{L^2}$ was confirmed by X-ray diffraction. First studies of the catalytic activity of their copper(II) complexes suggest that these complexes could be proposed as catalyst for the oxidation of alcohols in carbonyl compounds or as artificial enzymes.

*Keywords*: Diaza-crown ether; *N*,*N*-diamine; [1,2,3]Triazole; catalytic activity.

## 1. Introduction
Catechol oxidase is a copper enzyme ubiquitous in plants, insects and crustaceans[1], which catalyzes the aerobic oxidation of the *o*-biphenols (catechols) to the highly reactive *o*-quinones [2-4]. This type III copper protein contains a binuclear active site specializing in the two electrons oxidation of many catechols to quinones that auto polymerizes producing the melanin which in turn guards the damages tissues against pathogens and insects [5-6]. Many models that mimic oxidases has been developed with the objective to develop a simple catalytic systems [7-14]. In the previous works, we synthesized neutral transition metals complexes based on ligands bearing IDA (iminodiacetic acid) moiety presenting structural and electronic properties [15-18]. Then, with the aim of obtaining biological models or catalysts for organic reactions, we published a series of macrocyclic and acyclic ligands via the Cu(I)-catalyzed version of the Huisgen reaction between a terminal and an organic azides, with good complexing properties towards copper and other metal ions [19-21]. The metal ions in these complexes can adopt a wide range of geometries, both regular and irregular from 4 to 6, and can go up to 7 coordination with solvent or counter ion as auxiliary ligand which can be exploited to mimic copper metalloenzymes.
We reported herein the extension of our previous works, by studying the catecholase biomimetic catalytic activity of the reported copper(II) complexes synthesized via new route as functional catecholase models. This kinetic investigation would provide good information pertinent to an understanding of the structure versus reactivity correlation of the reported synthetic models.

## 2. Experimental section:
*2.1 Materials:*
Chemicals and solvents (reagent grade or better) were purchased from Sigma-Aldrich. Anhydrous solvents were dried by usual procedures and stored over 4Å molecular sieves under Argon before use. Chromatography was

carried out using basic $Al_2O_3$. $^1H$ & $^{13}C$-NMR spectra were recorded on a Bruker AC250 spectrometer at 250 MHz for 1H and 62.9 MHz for $^{13}C$ in $CDCl_3$ if no other conditions are stated. CHN elemental analyses were performed using a Thermo Finnigan EA 1112 Series Flash Elemental Analyzer. ES+-HRMS spectra were obtained using a Bruker microTOFQ mass spectrometer with capillary tensions between 1200 and 4500 V from diluted MeCN solutions. UV-visible spectra were recorded on a Perkin-Elmer Lambda1050 UV Vis-NIR spectrophotometer using a 1 cm optical path length cell at T = 298 K. X-ray structures were determined using a Bruker Nonius Kappa APEXII or a Agilent SuperNova diffractometer equipped with a low temperature device using liquid N2 to perform XRD intensity measurements near 100 K. X-ray source was a sealed tube giving Mo Ka radiation (l = 0.71073 Å). Diffraction pattern frames were processed with Apex or CrysAlis software. The structure was solved by direct methods using the SIR software package [22a] and refined by full matrix least-squares on F squared using SHELXL software.[22b] In both crystal structure models, non-hydrogen atoms were located in the difference Fourier syntheses and were refined with anisotropic thermal parameters. Observed hydrogen atoms were placed at calculated positions using a riding model.




**Scheme 1**: structures of Ligands $\mathbf{L}^{1\text{-}5}$.

*2.2. Synthesis*

*benzyl-4-bromomethyl-1H-1,2,3-triazole (**1**)*

$^1H$ RMN (250 MHz , $CDCl_3$) : $\delta$ ppm 4.25 (s, 2H, $CH_2$-Br) ; 5.49 (s, 2H, $CH_2$Ph); 7.24-7.38 (m, 5H, Harom) ; 7.45 (s, 1H, $H_{triazol}$), Mass(LCMS) ; $C_9H_9N_3Br$ : $[M+H]^+$ = 252.0.

*General procedure of Synthesis of ligands* $\boldsymbol{L^{1\text{-}4}}$**:**

To a cooled and stirred solution of symmetric sec. N,N'-dimethyldiamine or diaza crown ether (1 equiv., 1.5mmol) and TEA triethylamine (3 equiv., 4.5 mmol) in 20ml of acetonitrile was added dropwise under argon solution of synthon **1** (2 equiv., 3mmol) in acteonitrile (5 mL) in a two-necked round-bottomed flask equipped with a condenser. The solution was heated at reflux overnight. The suspension obtained was cooled to room temperature and quenched with water (15 mL) and extracted with DCM (3x50 mL). The organic phases were combined, washed with water (3 x 20 mL), dried over $MgSO_4$, and finally evaporated under reduced pressure. The crude material was purified by liquid chromatography on silica with mixtures of $CH_2Cl_2$–MeOH as eluents.

*Copper complexes Synthesis:*

Transition metals complexes were synthesized according to *Joly et al* procedures [19-21]:

$M(ClO_4)_2$, $6H_2O$ (M, Cu, Zn) (1.2 equiv.) was dissolved in a solution of the ligand (1.2 equiv.) in 3mL of a mixture of acetonitrile/water/Ethanol (v/v/v, 1/ 1/ 1) at rt. The resulting suspension was stirred for 2 h at 70 °C, allowed to cool to rt, filtered through a small cotton pad, concentrated to half, diluted with two drops of DMF (ca. 30 mg), and finally stored for several days in the dark at 41°C.

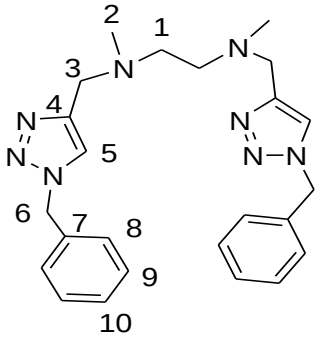
*Ligand* $\boldsymbol{L^1}$ as described in the general procedure I from diaza-15-crown-5 ether (96% yield); $^1H$ NMR (250 MHz, $CD_3CN$): $\delta$ ppm 7.89 (s, 2H, H-triazol), 7.25–7.4 (m, 10H, H-arom), 5.55 (s, 4H, $CH_2$-Ph), 3.83 (s, 4H,

$CH_2$-triazol), 3.59 (s, 4H, H-3), 3.49 (bs, 4H, H-2), 3.35 (bs, 4H, H-2'), 2.6-2.75 (m, 8H, H-1, H-1'); ESI-HRMS$^+$: *m*/*z* calcd. for $C_{30}H_{41}N_8NaO_3$ 583.3116, found 583.3097 $[^{23}NaL^1]^+$.

**$[CuL^1]^{2+}$, $2ClO_4^-$** pale green crystals, Mp: 266-268°C, (92% yield)
ESI-HRMS$^+$: *m*/*z* calcd. for $[C_{30}H_{40}CuN_8O_3]^{2+}$ 311.6254, found 311.6265; calcd. for $[C_{30}H_{40}ClCuN_8O_7]^+$ 722.1999, found 722.2053. Anal. calcd. for $C_{30}H_{42}Cl_2CuN_8O_{12}$, $H_2O$: C, 42.84; H, 5.03; N, 13.32. found: C, 43.05; H, 4.84; N, 13.41.
*Ligand* ***L$^2$*** *a*s described in the general procedure I from diaza-18-crown-6 ether (90%).
white crystals; Mp: 128-130°C; $^1$H NMR ($CDCl_3$, 250 MHz) $\delta$ ppm 7.44 (s, 2H, H triazol), 7.4–7.2 (m, 10H, Ph), 5.5 (s, 4H, C$H_2$Ph), 3.84 (s, 4H, C$H_2$-triazol), 3.68-3.5 (m, 16H, 8 × OC$H_2$), 2.73 (t, 8H, 4 × NC$H_2$).
ESI-HRMS$^+$ (*m*/*z*): calcd for $C_{32}H_{45}N_8O_4$ 605.35, found 605.3542.

**$[CuL^2]^{2+}$, $2ClO_4^-$** green crystals (98 %). Mp : 240-242°C. ESI-HRMS$^+$ (*m*/*z*) calcd. for $[C_{30}H_{40}CuN_8O_3, ClO_4]^+$ 768.20, found 768.20. Anal. calcd. for $[C_{30}H_{42}ClCuN_8O_{12}, 2ClO_4]$, $H_2O$: C, 44.3; H, 5.1; N, 12.9. found: C, 44.0; H, 5.3; N, 12.5.

***L$^3$*** as described in the general procedure I from N,N'dimethylethyldiamine. (96%) Mp 110-112°C, $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ 7.46 (s, 2H, $H_{triazol}$), 7.28–7.4 (m, 10H, $H_{arom}$), 5.50 (s, 4H, $CH_2Ph$), 3.64 (s, 4H, $CH_2$-Triazol), 3.50 (m, 12H, $NCH_2\underline{CH_2}$), 2.20 (s, 6H, $CH_3$). $[M + H]^+$ 444.2358, found 444.2361. HRMS: calcd. for $C_{24}H_{31}N_8$ $[M + H]^+$ 431.26, found 431.27.
**$[CuL^3]^{2+}$, $2ClO_4^-$,** green crystals, Mp: 214-216°C, (98 %).
HRMS: calcd. for $[C_{24}H_{30}ClCuN_8O_4, ClO_4]^+$ 592.13, found 592.14. λmax 621nm, Anal. calcd. for $[C_{24}H_{30}ClCuN_8O_4, 2ClO_4]$, $CH_3CN$: C, 42.5; H, 4.5; N, 17.2. found: C, 42.5; H, 4.4; N, 17.1.
**$[NiL^3]^{2+}$, $2ClO_4^-$,** green powder, 80%
HRMS: calcd. for $[C_{25}H_{32}ClNiN_8O_4, ClO_4]^+$ 601.16, found 601.15 . Anal. calcd. for $[C_{24}H_{30}ClNiN_8O_4, 2ClO_4]$, $CH_3CN$: C, 42.5; H, 4.5; N, 17.2. found: C, 42.5; H, 4.4; N, 17.1.




**$[ZnL^3]^{2+}$, $2ClO_4^-$,** yellowish white powder, (80%)
$^1$H NMR (250 MHz, $CD_3CN$): $\delta$ ppm 8.0 (s, 1H, $H_{triazol}$), 7.99 (s, 1H, $H_{triazol}$), 7.36–7.48 (m, 10H, $H_{arom}$), 5.69 (s, 2H, $CH_2Ph$), 5.68 (s, 2H, $CH_2Ph$), 4.15-3.72 (dd, 2H, *J* =9.8Hz, $H_4$), 4.07-3.82 (dd, 2H, *J* = 9.8Hz, $H_4$), 3.20–3.08 (m, 2H, $H_2$), 2.99–2.87 (m, 2H, $H_2$), 2.46 (s, 3H, $CH_3$), 2.28 (s, 3H, $CH_3$), 1.96 (m, 2H, $NCH_2\underline{CH_2}$). $^{13}$C NMR (62.9 MHz, $CD_3CN$): $\delta$ ppm 143.5(C5), 143.3(C5), 134.8(C8), 129.4(C9), 128.9(C11), 128.6(C10), 124.3(C6), 62.1(C2), 59.9(C2), 55.4(C4), 54.3(C7), 53.0(C4), 45.5(C3), 44.7(C3), 22.0(C1), 21.9(C1). HRMS$^+$: calcd. for $[C_{25}H_{32}ClZnN_8O_4, ClO_4]^+$ 607.16, found 607.15 . Anal. calcd. for $[C_{25}H_{32}ClZnN_8O_4, 2ClO_4]$, $CH_3CN$, $H_2O$: C, 42.3; H, 4.8; N, 16.4. found: C, 42.2; H, 4.6; N, 15.8.
***L$^4$*** *a*s described in the general procedure I from N,N'dimethylpropyldiamine (95%). Mp: 84-86°C, $^1$H NMR (250 MHz, $CD_3CN$); $\delta$ ppm 7.68 (s, 2H, $H_{triazol}$), 7.26–7.45 (m, 10H, $H_{arom}$), 5.53 (s, 4H, $CH_2Ph$), 3.59 (s, 4H, $CH_2$-Triazol), 2.33 (t, *J* = 4.5Hz, 4H, $NCH_2$), 2.15 (s, 6H, $CH_3$), 1.96 (m, 2H, $NCH_2\underline{CH_2}$). HRMS: calcd. for $C_{25}H_{32}N_8$ $[M + H]^+$445.28, found 445.28

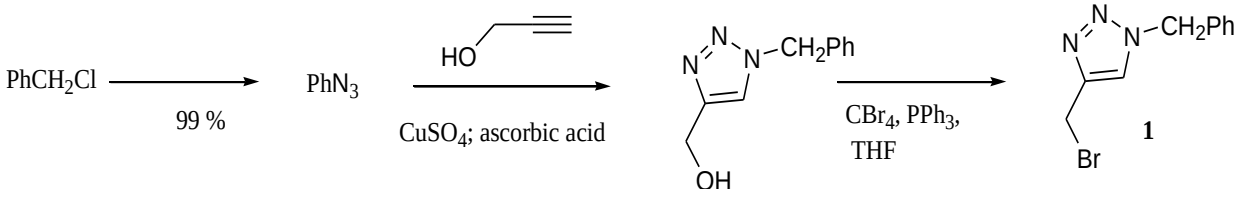
**$[CuL^4]^{2+}$, $2ClO_4^-$** green crystals, (95% yield) Mp: 253-255°C
$HRMS^+$: calcd. for $[C_{25}H_{32}ClCuN_8O_4, ClO_4]^+$ 606.16, found 606.1562 . Anal. calcd. for $[C_{25}H_{32}ClCuN_8O_4, 2ClO_4]$, $CH_3CN$, $H_2O$: C, 42.3; H, 4.8; N, 16.4. found: C, 42.2; H, 4.6; N, 15.8.

*Synthesis of ligand* ***L*$^5$.**
To a cooled and stirred solution of symmetric sec. N,N'-dimethylpropyldiamine (1 equiv., 1.5mmol) and TEA triethylamine (1 equiv., 1.5mmol) in 20ml of acetonitrile was added dropwise under argon solution of synthon **1** (1 equiv., 1.5 mmol) in 5mL acteonitrile in a two-necked round-bottomed flask equipped with a condenser. The solution was heated at reflux overnight. The suspension obtained was cooled to room temperature and quenched with 15 mL water and extracted with DCM (3x50 mL). The organic phases were combined, washed with water (3 x 20 mL), dried over $MgSO_4$, and finally evaporated under reduced pressure. The crude material was purified by liquid chromatography on silica with mixtures of $CH_2Cl_2$–MeOH as eluents. (90% yield).
$^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ ppm 7.80 (s, 1H, $H_{Triazol}$), 7.3-7.40 (m, *5H*, $H_{arom}$), 5.62 (s, 2H, $CH_2$benzyl), 3.64 (s, 2H, $CH_2$triazol), 2.61 (t, *J* =4.5Hz, 2H, $CH_2$), 2.47 (t, *J* =4.5Hz, 2H, $CH_2$), 2.44 (s, 3H, CH3), 2.36 (s, 3H, CH3), 1.7 (m, 2H, $CH_2\underline{CH_2}CH_2$). $HRMS^+$: calcd. for $C_{15}H_{24}N_5$ $[M + H]^+$ 275.20, found 275.20.

*2.3. Catechol oxidase biomimetic catalytic activity*
A mixture of 3,5-di-*tert*-buty1catechol (3,5-DTBC) solution (30 mM) in water/acetonitrile 50/50 and copper(II) complex solution in water/acetonitrile was placed in a 1 cm path length optical cell containing 1.0 ml of water/acetonitrile in a spectrophotometer. The final concentration of reaction mixture is catechol (20 mM) and complex (0.2 mM). The formation of 3,5-di-*tert*-butyl-catequinone (3,5-DTBQ) was followed by observing the increase of characteristic quinone absorption band at 400 nm.

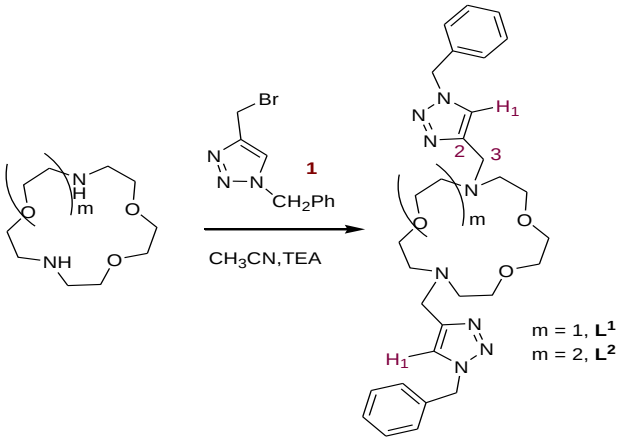
## 3. Results and Discussions

*3.1. Synthesis and characterisation of ligands*
Ligands **L**$^{1,3}$ were prepared following a new procedure in two steps, via the easily accessible benzyl-protected alkylating synthon benzyl-4-bromomethyl-1H-1,2,3-triazole (**1**) by 1,3-Dipolar cycloaddition of benzyl azide obtained from benzyl chloride to propargyl alcohol (Scheme 2). The obtained triazole was then brominated by $CBr_4$ in the presence of triphenylphosphine:

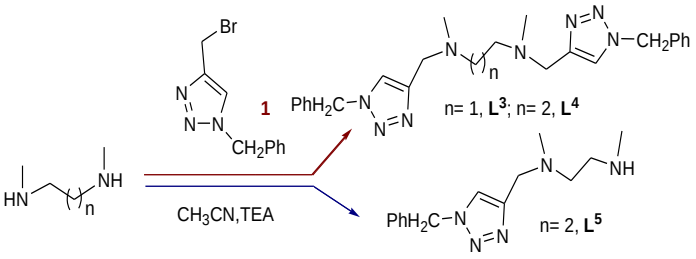



**Scheme 2:** Synthesis of benzyl-4-bromomethyl-1H-1,2,3-triazole **1**

The double N,N'alkylation by this alkylating agent of the diaza crown and commercial secondary bis-N-methyl amines with the use of acetonitrile as solvent and TEA as base (commonly used conditions for alkylation) lead to ligands **L**$^{1-4}$ (Schemes 3 and 4).
All the reactions of substitutions were monitored by LCMS analysis. The synthesized ligands were purified twice by neutral alumina chromatography to give satisfactory yields (90-96%). All ligand structures were unambiguously ascertained by NMR and $ES^+$-HRMS. $^1H$ NMR spectra of all ligands exhibit the expected aromatic singlet between 7.5 and 8.0 ppm for the two isochronous triazol protons at the NMR time scale ($CDCl_3$, 298 K).Further information about the isolation and full characterization of ligands **L**$^{1-5}$ is provided in the experimental section. Single crystals of **L**$^2$ suitable for X-ray structure determination were grown from an EtOH/MeCN mixture at ambient temperature. It crystallized in the *P*-1 triclinic space group. (Figure 1, Table 1).




**Scheme 3**: synthesis route of cyclic ligands $\mathbf{L^{1-2}}$.




**Scheme 4**: synthesis route of acyclic ligands $\mathbf{L^{3-5}}$.

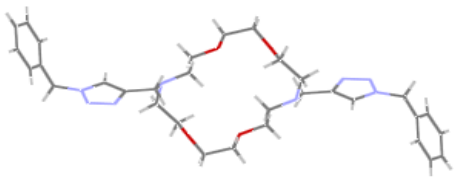


**Figure 1:** RX Structure of $\mathbf{L^2}$ at 110 K.

**Table 1:** Crystal Data and Structure Refinement for Compounds $\mathbf{L^2}$

| | $\mathbf{L^2}$ |
|---|---|
| Formula fw | $C_{16}H_{22}N_4O_2$ |
| Chemical formula weight | 280.20 |
| radiation wavelenght λ | 0.71073 |
| radiation type | MoK\a |
| space group | *P -1* |
| *a* (Å) | 5.5539(5) |
| *b* (Å) | 8.0578(9) |
| *c* (Å) | 17.528(2) |
| α (deg) | 97.614(4) |
| β (deg) | 93.957(3) |
| γ (deg) | 99.070(4) |
| *V* (Å$^3$) | 764.534 |
| *Z, Z'* | 2 , 0 |
| *T* [K] | 100(2) |
| $D_c$ (g cm$^{-3}$) | 1.217 |
| μ (mm$^{-1}$) | 0.086 |
| F000 | 280 |
| h,k,lmax | 5,7,16 |
| Reflns. measd. | 2341 |
| Indep. reflections | 1409 |
| Obsd. reflections | 923(>2sigma(I)) |
| GOF on $F^2$ | 1.192 |
| $R_1[I>2\sigma(I)]$ [a] | 0.0951 |
| w$R_2$ [a] | 0.2206 |

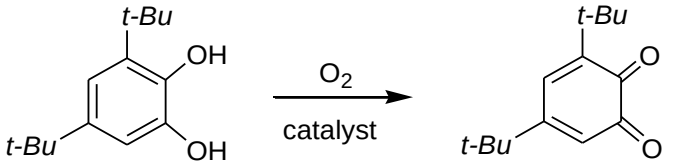
[a] $w = 1/[\sigma^2(F_o^2) + (0.0620P)^2 + 4.4497P]$ in which $P = (F_o^2 + 2F_c^2)/3$.

*3.2. Copper(II) Complexes synthesis*

Transition metals M(II) complexes were isolated from ligands $\mathbf{L^{1-4}}$ and $M(ClO_4)_2$ hexahydrate (M = Cu, Ni and Zn) in the presence of acetonitrile and dimethylformamide was obtained according to *Joly & al* [20]. The characterization of all the copper (II) complexes was established from the elemental analysis, UV-visible and Mass spectroscopies.

*3.3. Catalytic activity of copper(II) complexes :*

The catechol oxidase biomimetic catalytic activity of the reported copper(II) complexes, as functional models has been determined by the catalytic oxidation of catechols [23-26] (Scheme 5). 3,5-di-*tert*-butylcatechol (3,5-DTBC) is the most widely used substrate for catecholase activity of *tyrosinase*, among the different catechols used in catechol oxidase model studies [27-29].




3,5-DTBC

3,5-DTBQ
λmax = 400nm
ε = 1900M$^{-1}$cm$^{-1}$

**Scheme 5:** Catalytic aerobic oxidation of 3,5-di-*tert*-butylcatechole (3,5-DTBC) to 3,5-di-*tert*-butylquinone (3,5-DTBQ).

Its low redox potential for the, quinone-catechol couple, makes it easy to be oxidized to the corresponding quinone 3,5-DTBQ, and its bulky substituents, make further oxidation reactions such as ring opening remote. The product 3,5-di-*tert*-butyl-*o*-quinone (3,5-DTBQ), is considerably stable and exhibits a strong absorption at $\lambda_{max}$ = 400 nm ($\varepsilon$ = 1900 $M^{-1}$ $cm^{-1}$ in MeOH). [30] Therefore, activities can be determined using electronic spectroscopy by following the appearance of the characteristic absorption of the 3,5-di-*tert*-butyl-*o*-quinone (3,5-DTBQ), for each set of observation, a curve of absorption of 3,5-DTBQ formed *versus* time was plotted. The reactivity studies were performed in water/$CH_3CN$ solution because of the low solubility of the complexes (with benzyl) as well as the substrate. The exceptionally high stability found for *o*-quinone at room temperature suggests that a single reaction pathway is being followed and that the *o*-quinone produced does not undergo further oxidative cleavage.

The kinetic data were determined by the method of initial rates by monitoring the growth of the $\lambda$ at 400 nm band of the product 3,5-DTBQ, formed due to aerobic oxidation of 3,5-DTBC in the presence of metal(II) complexes. For this purpose $2 \times 10^{-4}$ M solutions of $\mathbf{CuL^1}$, $\mathbf{CuL^3}$, $\mathbf{CuL^4}$ in DMF were treated with 100 equivalent of 3,5-DTBC in the presence of air. The absorbance was continually monitored at $\lambda$ = 400 nm each 3 min and the case for complex [Cu$\mathbf{L^1}$] is presented in Figure 2.

Under identical conditions, without the presence of a possible catalyst no significant quinone formation was observed (blue curve). For all complexes, the reactivity order is: [Cu$\mathbf{L^4}$] > [Cu$\mathbf{L^3}$] > [Cu$\mathbf{L^2}$] (Figure 3). The complexes formed with acyclic ligands exhibit high activity than complex with cyclic ligand. The low catechol oxidase activity of cyclic ligand based complex [Cu$\mathbf{L^2}$] may be attributed to the difficult access of the substrate to the metal. Indeed, the coordination sphere of the complex around the copper ion is completely saturated by the ligand so that access of the substrate that require precoordination to metal is blocked, which is not the case for complexes with ligands $\mathbf{L^3}$ and $\mathbf{L^4}$ where the copper ion is easily accessible. The differences in activity between the complexes formed with $\mathbf{L^3}$ and $\mathbf{L^4}$ can be explained by the low tensions of the formed six-ring in Cu$\mathbf{L^4}$ than five-ring in Cu$\mathbf{L^3}$ involved after coordination to copper ions.

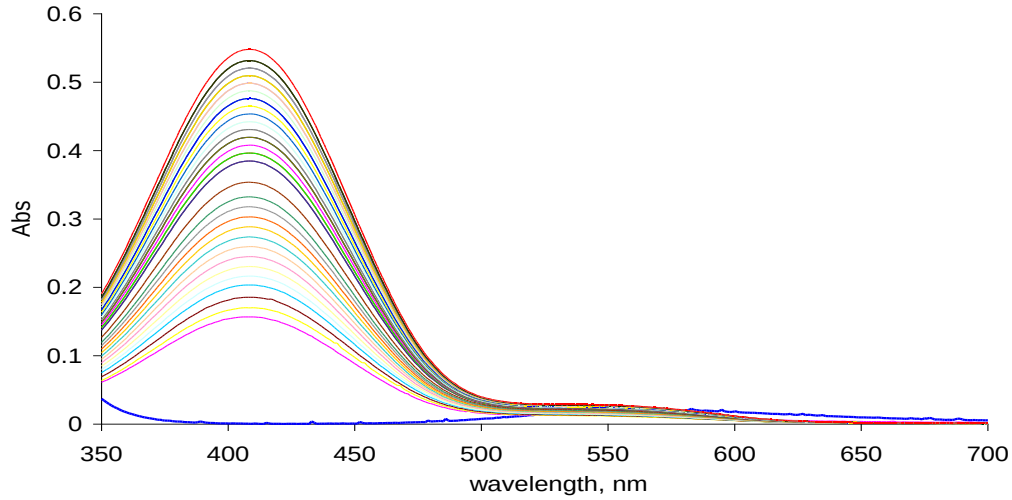



**Figure 3:** Time dependent formation of 3,5-DTBQ catalyzed by $[Cu(L^1)]^{2+}$ in $CH_3CN/H_2O$ (50/50) saturated in $O_2$ at 298 K. The spectra were recorded each 3 min. the blue curve represents autoxidation of 3,5- DTBC.

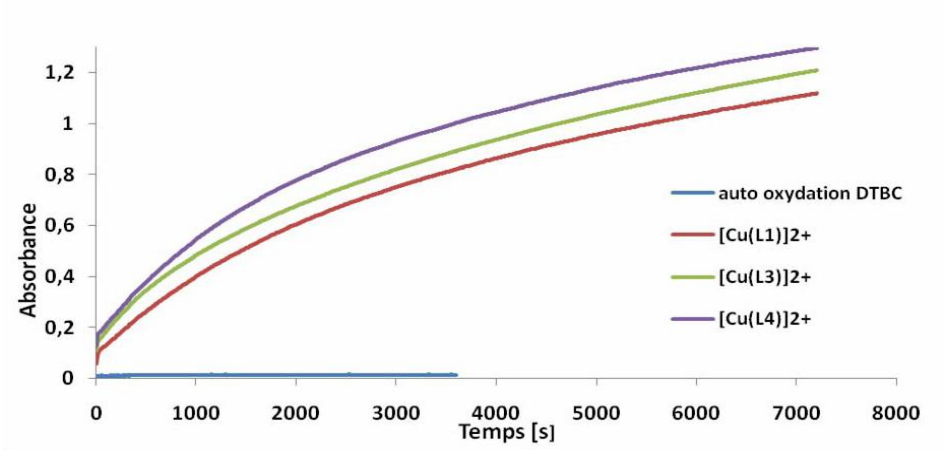



**Figure 3:** A comparison of the reactivity of the complexes for the aerial oxidation of 3,5-DTBC in DMF at 298 K.

## Conclusion

In summary, we reported in this paper a new and efficient method for the synthesis of symmetric cyclic and acyclic ligands containing [1,2,3]Triazoles via the easily accessible benzyl-4-bromomethyl-1H-1,2,3-triazole(**1**). Use of readily available starting materials, high yields and easy purification of products are the advantage of this method. The catechol oxidase activity of their copper(II) complexes were studied and acyclic ligand $L^4$, displays some interesting catalytic properties in the oxidation of this model substrate. We shown that the catalytic activity depends on the coordination environment of the catalyst created by the nature of ligand bound to copper(II) ion in the complex molecule. First studies of cytotoxicity in water of these complexes towards uterine human sarcoma cells are currently underway and showed promising activities.

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