Valorization of natural clay as an ecological catalyst in the regioselective synthesis of some heterocyclic compounds based on 1,2,3-triazoles

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Abstract

Some ecological catalysts were prepared from Tunisian clays; they have been applied in the catalytic coupling reaction of alkynes and azides to prepare bioactive heterocyclic compounds based on 1,2,3-triazoles. Clays used in this work were taken from Jebal Shib (M'dhillia) and Jebal Es Sath (between Gafsa and Metlaoui) in Gafsa at South West of Tunisia. The reaction of terminal alkynes with azides in the presence of studied catalysts was studied for 36 hours at room temperature without solvents and excitements; two isomers (1,4) and (1,5) of 1,2,3-triazoles were obtained. Generally, the (1,4) isomer was obtained with an important proportion if Cu-Pullard clay was used as a catalyst in this synthesis reaction. The studied ecological catalysts were characterized by X-ray diffraction and IR spectroscopy. Heterocyclic triazoles were analyzed by ¹HNMR, ¹³CNMR, Infrared (IR), and Ultraviolet spectroscopy. LC-MS analyses evaluated the molecular masses of synthesized triazoles.

Keywords: Tunisian clays, Catalysts, Regioselective Synthesis, 1,2,3-triazole, 1,4 isomer, 1,5 isomer

1. INTRODUCTION

Nowadays, the chemistry of heterocyclic compounds is considerably developing for their biological activities [1, 2]. The most applied heterocycles in the field of biology are dioxolanes and triazoles. Dioxolanes are heterocyclic acetal compounds with a cycle containing five atoms; two are oxygen. Several types of research report the synthesis of dioxolanes using activated clays as catalysts [3-8]. In contrast, triazoles are heterocyclic compounds with three nitrogen atoms placed in 1,2,3 or 1,2,4 positions of the cycle. This report presents the triazoles compounds with a cycle containing five atoms; three are nitrogen, placed in the 1,2,3 position of the cycle. These triazoles compounds have a several biological activities: Antiproliferative [9], anti-inflammatory [10], antitubercular [11], tyrosinase inhibitory [12], antioxidant [13, 14] and antibacterial [15]. For this reason, the synthesis of triazoles was considerably developed. Several methods are applied in the synthesis of triazoles. The catalysts used in these syntheses are also diverse. Some syntheses of triazoles were carried out with green catalysts prepared from modified clays [16-18], other studies used catalysts prepared from copper (I) fixed on the organic polymers [19-21], CuI-catalyst for organic solvents, and CuI-catalysts for aqueous conditions are developed [18]. Stålsmeden et al. [21] synthesized 1,4 and 1,5-disubstituted-triazoles via Cu and Ru-catalyzed click reactions. Kumar and co-workers reported the synthesis of triazoles using copper-catalyzed azide-alkyne (CuAAC) and Ru-catalyzed azide-alkyne cycloaddition (RuAAC) [22]. Application in the regioselective synthesis of 1,2,3-triazoles using CuI nanoparticles on 3-aminopyridine modified poly(styrene-c-maleic anhydride) as catalyst was reported by Hossiennejad et al. [23]. Khaled et al. [24] applied the copper oxide chitosan nanocomposite for the green regioselective synthesis of 1,2,3-triazoles. In this present work, we applied some modified Tunisian clays as catalysts for testing them in the synthesis of 1,2,3-triazoles with biological activities.

2. EXPERIMENTAL

2.1. Materials

Copper (I) iodide (≥99.5%), methyl propionate (99%), 1,4-benzodioxane-6- amine (≥98%), aniline (≥99.5%), phenyl acetylene (98%), acetonitrile (99.8%), sodium azide (≥99.5%), benzyl bromide (98%), ethyl bromoacetate, N,N'-dicyclohexyl carbodimide DCC (99%) and methylene chloride were purchased from Sigma Aldrich and used without further purification. Azidomethyl phenyl and ethyl azidoacetate were prepared from sodium azide, benzyl bromide, and ethyl bromoacetate following published procedures [25-28]. X-Ray Diffraction (Thermo Scientific ARL 9900 XRF, France) was used to evaluate the Physico-chemical characteristics of washed and purified clays under study. Nuclear magnetic resonance spectroscopy (NMR) was recorded on a Bruker Avance 300 WB spectrometer (Bruker, France) at 300 MHz for the proton spectra (¹H)) and 75.5 MHz for the carbon spectra (¹³C). Chemical shifts (δ) are indicated after calibration on the residual undeuterated solvent peak in part per million (ppm) and as follows: s (singlet),

d (doublet), t (triplet), m (multiplet). Infrared analysis using the attenuated total reflectance technique (ATR/FTIR) was made on a Nicolet FTIR 200 spectrophotometer (Thermo Scientific, France). The UV-Vis spectra were carried out using

UV-Vis spectrophotometer BKUV 1600 PC in CH_2Cl_2 . The molecular masses of synthesized compounds were evaluated by LC-MS analyses using a Shimadzu LCSM-2010 A instrument equipped with an SPD-M10 A PDA diode array detector (D2, lamp from 190 to 400 nm) and an ELSD-LT light scattering detector on an Altima HP C8 3 μ (Alltech) reversed-phase (L= 53 mm; ID = 7 mm) HPLC column. The LC were ran using a 1mL/min flow using a gradient between acetonitrile and water containing formic acid (0,1%): 0 to 1 min: 30% CH_3CN , 1 to 5 min: from 30% to 100% CH_3CN , 5 to 12 min : 100% CH_3CN , 12 to 14,99 min: from 100% to 30% CH_3CN , 14,99 to 20 min: 30% CH_3CN . MS was recorded between $m/z = 100$ to 500 at the exit of the column using an ESI ionization and positive ion mode (detector = 1.5kV, quadripole = 5 V). Samples of clays from Gafsa were collected from two sites (Jebal Es Sath and Jebal Sehib).

2.2. Preparation of ecological catalysts

2.2.1. Preparation of washed clay

In 200mL of distilled water, we add 100g of raw powder clay. After stirring at 200 tr/mn at room temperature for one hour, centrifugation of obtained mixture was realized at 4000 tr/mn. This same operation was repeated several times until clean water was obtained. The clay was dried at 50°C for 48 hours. The physicochemical characteristics of washed clays were evaluated by X-ray fluorescence (XRF) coupled with diffraction (XRD) on a Thermo Scientific ARL 9900 XRF series workstation and IR spectroscopy. The washed clay was ground and used as such in the catalytic coupling reaction of alkyne-azide.

2.2.2. Preparation of Purified clay

The purified clay was prepared by placing 20g of the obtained washed clay in 400mL of an aqueous sodium chloride solution (1M). The suspension was stirred (100 rpm) for 12 hours before centrifuging (4000 rpm, 10 min). The supernatant substance was removed, and the-process was repeated three other times with fresh molar NaCl solution (1M). The excess of NaCl was removed by stirring in water (400mL, 100 rpm, 5 min) and centrifugation (4000 rpm, 10 min), followed by dialysis. The dialysis was performed on 2g of samples suspended in 200mL of distilled water placed in a dialysis membrane (cellulose, 20cm long, 20.4mm diameter, MWCO 6–8 kD) against 1L of distilled water. The distilled water was changed, and free chloride ions precipitated using the silver nitrate test (AgNO_3 ; 1M). After overnight standing, the suspension was dried at 50°C to obtain the purified clay [29]. The purification of washed clay consists of exchanging minerals ions (Al^{3+} , Fe^{3+} , Ca^{2+} , Mg^{2+} , Cu^{2+} , and K^+) by Na^+ .

2.2.3. Preparation of adsorbed clay by copper (I) iodide

Purified clay exchange minerals ions (Al^{3+} , Fe^{3+} , Ca^{2+} , Mg^{2+} , Cu^{2+} , and K^+) by Na^+ , dried as a thin film at 50°C, and incubated for 3 hours in 45mmol of copper (I) iodide solution in acetonitrile at room temperature. After eliminating acetonitrile, the film was cut into pieces at 3mm of dimensions and used directly in the catalytic reaction [26]. Ecological catalysts prepared in this present work are presented in (Table 1).

2.3. Synthesis

2.3.1. synthesis of terminated alkynes (General method)

To a stirred cold solution of aniline derivative (10mmol) at 0°C; added dropwise 0.62mL of propiolic acid (0.62mL, 0.71g, 10mmol, 1 eq.) in 20mL of CH_2Cl_2 , followed by a solution of 2.58g of DCC (12.5mmol, 1.25 eq.) in 20mL of CH_2Cl_2 . The reaction mixture was then stirred at 0°C for 0.5h half an hour and overnight at room temperature. The mixture was then filtered through Celite onto the sintered glass. The Celite was washed with CH_2Cl_2 (20mL). The filtrate was then extracted with HCl (0.1M ; 2 x 10mL) and NaOH (0.1M ; 2 x 10mL). The obtained mixture was washed with distilled water (3 x 20mL) and dried over MgSO_4 . After filtration, the solvent was evaporated under a vacuum. The resulting amides **3a–4a** (Scheme 1) were purified by column chromatography on silica gel using heptanes/ethyl acetate (1:1) [29]. Alkynes **1a** and **2a** were purchased from Sigma Aldrich.

Scheme-1: Structures of organic alkynes used n the synthesis of 1,2,3-triazoles heterocycles.

2.3.2. Synthesis of Azides (General method)

Azides (**1b-2b**) were prepared from sodium azide, benzyl bromide, ethyl bromoacetate as described by [25-28] (Scheme 2).

Scheme-2: Structures of azides used in the synthesis of 1,2,3-triazoles heterocycles.

2.3.3. synthesis of 1,2,3-Triazoles (General method)

Triazoles (**1a1b**), (**2a1b**), (**3a1b**), (**4a1b**), (**1a2b**), (**2a2b**), (**3a2b**) and (**4a2b**) were prepared from 0.5mmol of terminated alkyne, 40mg of the studied catalyst and 0.5mmol of azide [29]. The mixture was maintained at room temperature

without solvents and excitements. After 36 hours of reaction, we add 2mL of CH_2Cl_2 to facilitate the removal of the catalyst by filtration. After evaporation of CH_2Cl_2 under vacuum, the obtained triazole was analyzed by ^1H NMR to evaluate the formation percentages of (1,4) and (1,5) isomers [16,17] (Scheme 3).

Scheme-3: Structures of 1,4-disubstituted-1,2,3-triazoles obtained from coupling reaction between organic alkynes (1a-4a) and azides (1b-2b) using ecological catalysts (Table 1).

3. RESULTS AND DISCUSSION

3.1. Catalysts section

Initially, six catalysts based on Tunisian clays were prepared to test their effects on synthesizing 1,2,3-triazoles (Table 1). Clays were collected from two well-known Tunisian deposits in Gafsa area: Jebal Sehib (JS) located at near M'dhilla, around $34^{\circ}12' \text{ N}/8^{\circ}42' \text{ E}$ and Jebal Es Sath (JES) (located at between Gafsa Metlaoui, around $34^{\circ}23' \text{ N}/8^{\circ}31' \text{ E}$) and of South East Tunisian. Fig.1 summarized the Preparation of ecological catalysts and their application in the synthesis of 1,2,3-triazoles.

Fig-1: Preparation of Tunisian ecological clays used as catalysts.

Elemental compositions of washed clays were presented in (Table 2) while results of XR Diffraction of washed and purified clays were tabulated in (Table 3) and their IR spectroscopies were presented in (Table 4).

Table-1: Catalysts used for the synthesis of 1,2,3-triazoles molecules.

Species	Clay used to prepare catalyst
JS	Washed clay taken from Jebal Shib
JES	Washed clay taken from Jebal Es Sath
JSP	Clay of Jebal Shib purified by Na^+
JESP	Clay of Jebal Es Sath purified by Na^+
JSP-Cu	CuI adsorbed by purified clay of Jebal Shib
JSEP-Cu	CuI adsorbed by purified clay of Jebal Es Sath

Table-2: Elementary compositions of washed clays from Jebal Es Sath and Jebal Sehib [29].

Elements ^a	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	K_2O	P_2O_5	Na	LI ^b
JS	43.34	21.48	7.90	2.96	2.03	0.86	0.36	0.65	9.28
JES	39.52	19.87	15.06	7.87	2.87	0.915	0.23	0.35	9.28

^a: Composition in Wt %

^b: Loss Ignition

Table-3: Results of XR Diffraction of washed and purified studied clays [29].

Species	Rays (Å)
JS	14.65, 7.01, 4.93, 4.39, 4.18, 3.51, 3.30
JES	12.31, 6.81, 3.98, 3.49, 3.11
JSP	12.31, 6.93, 3.53
JESP	11.80, 3.98, 3.12

X-ray diffraction (XRD) of (JES) showed a typical ray of smectite clay-rich with (12.31Å and 3.98Å), probably a Montmorillonite $[(\text{Na},\text{Ca})_{0.3}(\text{Al},\text{Fe},\text{Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}]$, containing kaolinite $(\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4)$; 6.81Å and 3.49Å). After purification (JES), the XRD recorded was quite similar but characterized for sodium smectite (11.80 Å and 3.98 Å). In the case of (JS) clay, the XRD was typical of smectite rich with calcium (Montmorillonite, 14.65Å), with kaolinite (7.01 Å and 3.51Å), quartz (SiO_2 ; 4.18Å and 3.30Å), and other impurities. Once purification was conducted on (JS),

the XRD was the one of a sodium-rich with smectite clay (12.31Å) still containing some kaolinite (6.93Å and 3.53Å). For clays activated by copper iodide (I) (JSP-Cu and JESP-Cu), the results of XRD were similar to those observed for the purified clays (JSP and JESP) [29].

Table-4: IR spectroscopy of washed and purified studied clays [29].

Species	IR observed bands
JS	ν (cm ⁻¹): 3645 (Al-Al-OH), 1642 (H ₂ O), 1442 (calcite), 1034 (SiO)
JES	ν (cm ⁻¹): 3641 (Al-Al-OH), 1644 (H ₂ O), 1442 (calcite), 1034 (SiO)
JSP	ν (cm ⁻¹): 3647 (Al-Al-OH), 1640 (H ₂ O), 1030 (SiO)
JESP	ν (cm ⁻¹): 3644 (Al-Al-OH), 1643 (H ₂ O), 1036 (SiO)

In ATR/FTIR results of studied clays (Table 4), the bands observed at 3641 cm⁻¹ is attributed to the Al–Al–OH vibration and those observed at 1644 cm⁻¹ correspond to OH frequency for the water molecule adsorbed on the clay surface, as well as those for SiO at 1034 cm⁻¹. Washed clays displayed bands relative to calcite (1442cm⁻¹) which are absent from the purified clays. These results and DRX analyses (Table 3) confirmed the purification and sodium exchange of the clays [29]. For clays activated by copper (I) (JSP-Cu and JESP-Cu), the results of IR spectroscopy were similar to those observed for the purified clays (JSP and JESP).

3.2. Synthesis section

In the second step, the coupling reaction between terminal alkynes and azides in the presence of fresh last prepared catalysts (Table 1), without solvents and without enthusiasms at room temperature during 36 hours were carried out. The coupling of alkynes (1a-4a) with azides (1b-2b) in the presence of catalysts (JS, JES, JSP, JESP, JSP-Cu, and JSEP-Cu) at room temperature without solvents and excitements gave two isomers (1,4) and (1,5)-disubstituted-1,2,3-triazoles (Scheme 3). The yields of isomers (1,4) and (1,5) were evaluated by ¹HNMR conversion; results of ¹HNMR conversion were given in Tables (3 & 4).

Table-3: Conversion ¹HNMR of 1,4 and 1,5 isomers obtained during coupling reaction between alkynes **1a-4a** and azide **1b** using prepared Tunisian ecological catalysts.

Entry	Triazoles	Catalysts	Conversion (%) of Isomer (1,4)	Conversion (%) of Isomer (1,5)
1	(1a1b)	No one*	0	0
2		JS	0	0
3		JES	0	0
4		JSP	0	0
5		JESP	0	0
6		JSP-Cu	100	0
7		JSEP-Cu	100	0
8	(2a1b)	No one*	87.6	12.4
9		JS	89.9	10.1
10		JES	90.6	9.4
11		JSP	92.2	7.8
12		JESP	92	8
13		JSP-Cu	100	0
14		JSEP-Cu	94.8	5.2
15	(3a1b)	No one*	61.6	38.4
16		JS	55.6	44.4
17		JES	75.8	24.2
18		JSP	76.7	23.3
19		JESP	63	37
20		JSP-Cu	84.2	15.8
21		JSEP-Cu	84.8	15.2
22		No one*	84.4	15.6
23		JS	83.3	16.7

24	(4a1b)	JES	78	22
25		JSP	78.8	21.2
26		JESP	92.1	7.9
27		JSP-Cu	100	0
28		JSEP-Cu	100	0

*Reaction without catalyst

Table-4: Conversion ¹HNMR of 1,4 and 1,5 isomers obtained during coupling reaction between alkynes **1a-4a** and azide **2b** using prepared Tunisian ecological catalysts.

Entry	Triazoles	Catalysts	Conversion (%) of Isomer (1,4)	Conversion (%) of Isomer (1,5)
1	(1a2b)	No one *	0	0
2		JS	0	0
3		JES	0	0
4		JSP	0	0
5		JESP	0	0
6		JSP-Cu	100	0
7		JSEP-Cu	100	0
8	(2a2b)	No one*	88.2	11.8
9		JS	93.6	6.4
10		JES	93.3	6.7
11		JSP	90.3	9.7
12		JESP	86.3	13.7
13		JSP-Cu	98.6	1.4
14		JSEP-Cu	96.7	3.3
15	(3a2b)	No one*	78.5	21.5
16		JS	77.3	22.7
17		JES	79.1	20.9
18		JSP	76.5	23.5
19		JESP	77.7	22.3
20		JSP-Cu	94.5	5.5
21		JSEP-Cu	100	0
22	(4a2b)	No one*	71.9	28.1
23		JS	69.9	30.1
24		JES	61.8	38.1
25		JSP	72.7	27.3
26		JESP	61	39
27		JSP-Cu	100	0
28		JSEP-Cu	100	0

*Reaction without catalyst

Results showed that no reaction took place (Tables 3 & 4, Entries: 1, 2, 3, 4, 5) in the reaction between phenylacetylene (**1a**) and azidomethyl phenyl (**1b**) and/or ethyl azidoacetate (**2b**) without catalyst and/or using the catalysts (JS, JES,

JSP, and JESP). The mineral elements (SiO_2 , Al_2O_3 , Fe_2O_3 , MgO , CaO , SO_3 , P_2O_5 , K_2O , and Na) that constituents of washed clays (Table 2) do not affect the coupling reaction between terminal alkynes and azides. The outcome was 0% for the two isomers (1,4) and (1,5). The coupling reaction between alkynes (**1a-4a**) and azides (**1b-2b**) using adsorbed CuI by purified clays (Cu-pillared clay) was regioselective for 1,4-disubstituted-1,2,3-triazole, the yields of (1,4) isomer were approximately 100% (Table 3, Entries: 6, 7, 13, 27 and 28 & Table 4, Entries: 6, 7, 21, 27 and 28). These results were in agreement with those obtained by Elamari et al. [16]. The yield obtained for the (1,4) isomer using CuI adsorbed by purified Tunisian clays is better than that obtained by Prabakaran et al. [30]. They used synthetic catalysts with copper (II) for coupling phenylacetylene and benzyl azide (yield $\leq 93\%$). The yields of (1,4) and (1,5) isomers obtained from application catalysts (JS, JES, JSP, and JESP) in the coupling alkynes (**1a-4a**) and azides (**1b-2b**) were similar to the reaction realized without catalyst, the maximum yield obtained for the isomer (1,4) was in the order of 93.6% with (JES) catalyst (Table 4, Entry: 10) and it is in the order of 44.4% for (1,5) isomer with (JS) catalyst (Table 3, Entry: 16). In general, the yields of isomer (1,4) and (1,5) obtained by catalysts (JS, JES, JSP, JESP) are in agreement with these obtained from reaction carried without catalyst realized at the same conditions (Tables 3 & 4, Entries: 1). In this context, washed and purified clays have no effect on the coupling alkynes-azides. In general, the (1,4)-disubstituted-1,2,3-triazole was predominantly obtained, these results were comparable to those obtained by Jalia et al. [26], they applied catalysts (Why-Crude) and (Why-Na) for coupling benzylazide and methyl propiolate, They observed the formation of the two isomers (1,4) and (1,5) with a favor for (1,4)-disubstituted-1,2,3-triazole. Practically, the use of copper (I) adsorbed by purified Tunisian clays (Catalysts JSP-Cu & JESP-Cu) in the reaction between alkynes (**1a-4a**) and azides (**1b-2b**) gives complete regioselectivity for the isomer (1,4), which is in agreement with the results found in the literature [16, 17]. A comparison of the effect of the two Cu-pillared clay (JSP-Cu & JESP-Cu) on the coupling alkynes-azides (Fig.2), revealed that the two catalysts are similar, the percentages obtained for the (1,4) isomer by (JSP-Cu & JESP-Cu) were $97.16 \pm 5.57\%$ and $97.03 \pm 5.32\%$, respectively. The maximum percentages obtained for (1,5) isomers using the same catalysts were in the order of 15.8 and 15.2%, respectively. These results explain that the two purified clays (JSP) and (JESP) were adsorbed the same quantity of CuI.

Fig-2. Percentages of (1,4) and (1,5) isomers were obtained during the application of ecological catalysts (JSP-Cu) and (JESP-Cu).

3.3. Analysis section

Benzyl azide (1b): yield 94%, IR ($\nu \text{ cm}^{-1}$): 3042(Car-H), 2986-2869 (CH_2), 2093 (N_3), 1453. ^1H NMR (CDCl_3): δ 4.38 (s, 2H) and 7.35-7.46 (m, 5H). ^{13}C NMR (CDCl_3): δ 55.2, 128.7, 129.1, 129.3, 135.9.

Ethyl azidoacetate (2b): yield 84%, IR ($\nu \text{ cm}^{-1}$): 2992-2866 (CH_2), 2100 (N_3), 1737 (C=O). ^1H NMR (CDCl_3): δ 1.27 (t, 3H, $J=7.1\text{Hz}$), 3.83 (s, 2H) and 4.22 (q, 2H, $J=7.1\text{Hz}$). ^{13}C NMR (CDCl_3): δ 14.2, 50.1, 61.0 and 167.4.

N-phenylpropiolamide (3a): yield 63%, IR ($\nu \text{ cm}^{-1}$): 3342(NH), 2110 ($\text{C}\equiv\text{CH}$), 1746 (C=O). ^1H NMR (CDCl_3): δ 2.96 (s, 1H), 7.17-7.22 (m, 1H), 7.31-7.40 (m, 2H), 7.56-7.59 (m, 2H) and 7.96 (s, 1H). ^{13}C NMR (CDCl_3): δ 74.2, 78, 119.1, 125.6, 128.9, 137.7 and 153. LC-MS calculated for $\text{C}_9\text{H}_7\text{NO}$, m.wt 145.16, m/z: 146 $[\text{M}+\text{H}]^+$.

N-(2,3-dihydrobenzo[1,4]-dioxin-6-yl) propiolamide (4a):

yield 69%, IR ($\nu \text{ cm}^{-1}$): 3262 (NH), 2109 ($\text{C}\equiv\text{CH}$), 1641 (C=O). ^1H NMR ($\text{DMSO}-d_6$): δ 4.23 (s, 4H), 4.37 (s, 1H), 6.82 (d, $J=8.72\text{Hz}$, 1H), 7.04 (d, $J=8.72\text{Hz}$, 1H), 7.22 (s, 1H) and 10.66 (s, 1H). ^{13}C NMR ($\text{DMSO}-d_6$): δ 64.45, 64.66, 77.29, 78.97, 109.35, 113.44, 117.36, 132.32, 140.53, 143.40 and 149.73. LC-MS calculated for $\text{C}_{11}\text{H}_9\text{NO}_3$, m.wt 203.18, m/z: 204 $[\text{M}+\text{H}]^+$.

1-Benzyl-4-phenyl-1H-1,2,3-triazole (1a1b): yield 88%, IR ($\nu \text{ cm}^{-1}$): 3095(Car-H), 2987 (CH_2), 1610-1547 (C=C), 1453 (N=N). LC-MS calculated for $\text{C}_{15}\text{H}_{13}\text{N}_3$, m.wt 235.29, m/z: 236 $[\text{M}+\text{H}]^+$. ^1H NMR (CDCl_3): δ 5.6 s, 2H; 7.32-7.45 (m, 8H); 7.71 (s, 1H) and 7.82-7.85 (m, 2H). UV (MeOH, λ_{max} nm, ϵ_{max} L.mol $^{-1}$.cm $^{-1}$): 338, 3984, $n \rightarrow \pi^*$.

Ethyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl) acetate (1a2b): yield 91%, IR ($\nu \text{ cm}^{-1}$): 3005(Car-H), 2952 (CH_2), 1727 (C=O), 1605-1535 (C=C), 1426 (N=N). LC-MS calculated $\text{C}_{12}\text{H}_{13}\text{N}_3\text{O}_2$, m.wt 231.25, m/z: 232 $[\text{M}+\text{H}]^+$. ^1H NMR

(CDCl₃): δ 1.34 (t, 3H); 4.29 (q, 2H); 5.23 (s, 2H); 7.43-7.89 (m, 5H) and 7.96 (s, 1H). UV (MeOH, $\lambda_{\max}$ nm, $\epsilon_{\max}$ L.mol⁻¹.cm⁻¹): 340, 3872, $n \rightarrow \pi^*$

Methyl-1-benzyl-1H-1,2,3-triazole-4-carboxylate (2a1b): yield 96%, IR (ν cm⁻¹): 3112(Car-H), 2952 (CH₂), 1721 (C=O), 1537 (C=C), 1433 (N=N). LC-MS calculated C₁₁H₁₁N₃O₂, m.wt 217.23, m/z: 218 [M+H]⁺. ¹H NMR (CDCl₃): δ 3.96 (s, 3H); 5.61(s, 2H); 7.30-7.44 (m, 5H) and 8.01 (s, 1H). UV (MeOH, $\lambda_{\max}$ nm, $\epsilon_{\max}$ L.mol⁻¹.cm⁻¹): 337, 3894, $n \rightarrow \pi^*$

Methyl-1-(2-ethoxy-2-oxoethyl)-1H-1,2,3-triazole-4-carboxylate (2a2b): yield 92%, IR (ν cm⁻¹): 3010 (Car-H), 2945 (CH₂), 1730 (C=O), 1546 (C=C), 1425 (N=N). LC-MS calculated C₈H₁₁N₃O₄, m.wt 213.19, m/z: 214 [M+H]⁺. ¹H NMR (CDCl₃): δ 1.27 (t, 3H); 3.92 (s, 3H); 4.26 (q, 2H); 5.25 (s, 2H) and 8.31 (s, 1H). UV (MeOH, $\lambda_{\max}$ nm, $\epsilon_{\max}$ L.mol⁻¹.cm⁻¹): 340, 4000, $n \rightarrow \pi^*$

1-benzyl-N-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-1H-1,2,3-triazole-4-carboxamide (3a1b): yield 90%, IR (ν cm⁻¹): 3005 (Car-H), 2965 (CH₂), 1754 (C=O), 1597-1552 (C=C), 1433 (N=N). LC-MS calculated C₁₆H₁₄N₄O, m.wt 278.31, m/z: 279 [M+H]⁺. ¹H NMR (CDCl₃): δ 6.2 (s, 2H); 7.18-7.23(m, 10H); 7.81 (s, 1H) and 8.98 (s, 1H). UV (MeOH, $\lambda_{\max}$ nm, $\epsilon_{\max}$ L.mol⁻¹.cm⁻¹): 340, 5286, $n \rightarrow \pi^*$

Ethyl-2-[4-(phenylcarbamoyl)-1H-1,2,3-triazol-1-yl]acetate (3a2b): yield 67%, IR (ν cm⁻¹): 3030 (Car-H), 2980 (CH₂), 1750 (C=O), 1651-1559 (C=C), 1430 (N=N). LC-MS calculated C₁₃H₁₄N₄O₃, m.wt 274.28, m/z: 275 [M+H]⁺. ¹H NMR (CDCl₃): δ 1.35 (t, 3H); 4.33(q, 2H); 5.27 (s, 2H); 7.22-7.44 (m, 5H); 8.33 (s, 1H) and 8.98 (s, 1H). UV (MeOH, $\lambda_{\max}$ nm, $\epsilon_{\max}$ L.mol⁻¹.cm⁻¹): 342, 5143, $n \rightarrow \pi^*$

1-benzyl-N-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-1H-1,2,3-triazole-4-carboxamide (4a1b): yield 77%, IR (ν cm⁻¹): 3034 (Car-H), 2942 (CH₂), 1730 (C=O), 1650-1570 (C=C), 1465 (N=N). LC-MS calculated C₁₈H₁₆N₄O₃, m.wt 336.35, m/z: 337 [M+H]⁺. ¹H NMR (CDCl₃): δ 4.39 (s, 4H); 5.61(s, 2H); 6.86-7.36 (m, 8H); 8.07 (s, 1H) and 8.84 (s, 1H). UV (MeOH, $\lambda_{\max}$ nm, $\epsilon_{\max}$ L.mol⁻¹.cm⁻¹): 341, 4758, $n \rightarrow \pi^*$

Ethyl-2-[4-[(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)carbamoyl]-1H-1,2,3-triazol-1-yl]acetate (4a2b): yield 96%, IR (ν cm⁻¹): 3039 (Car-H), 2951 (CH₂), 1722 (C=O), 1610-1570 (C=C), 1452 (N=N). LC-MS calculated C₁₅H₁₆N₄O₅, m.wt 332.31, m/z: 333 [M+H]⁺. ¹H NMR (CDCl₃): δ 1.34 (s, 3H); 4.28-4.40 (m, 6H); 5.25(s, 2H); 6.85-7.37 (m, 3H); 8.33 (s, 1H) and 8.84 (s, 1H). UV (MeOH, $\lambda_{\max}$ nm, $\epsilon_{\max}$ L.mol⁻¹.cm⁻¹): 340, 4714, $n \rightarrow \pi^*$

4. CONCLUSION

For ecological reasons, we have prepared some green catalysts for testing them in the synthesis of 1,2,3-triazoles with biological activities. These catalysts were prepared from Tunisian clays taken from Gafsa region. The reaction of synthesis of 1,2,3-triazoles was studied during 36 hours at room temperature without solvents and excitements. Catalysts prepared from adsorbed CuI by purified clays have given regioselectivity for 1,4-disubstituted-1,2,3-triazole. These prepared catalysts are recyclable for other applications. The characterization techniques used in this work were: X-ray diffraction, IR spectroscopy for ecological catalysts. ¹HNMR, ¹³CNMR, Infrared (IR), and Ultraviolet spectroscopy for triazoles. LC-MS analyses evaluated the molecular masses of synthesized triazoles.

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