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## Three-component synthesis of propargylamine derivatives via 1,4-dihydroxyanthraquinone-copper(II) complexes as an efficient catalyst under solvent-free conditions

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### Abstract

Highly active Cu (II) complex with 1,4-dihydroxy anthraquinone as a cheap and accessable ligand could be used as a catalyst for the preparation of structurally different propargylamines from a one-pot, three-component reaction of terminal alkynes, aldehydes, and secondary amines with high yields under solvent-free conditions. The 1,4-dihydroxy anthraquinone is a very efficient Cu(II) scavenger that is able to catalyse the  $A^3$ -coupling reaction without pre synthesis of the catalyst.

Keywords: Propargylamines; anthraquinone; A<sup>3</sup>-coupling; solvent-free

#### 1. Introduction

Activation of a terminal alkyne C–H bond by transition metal catalysts is a reaction of fundamental interest in organic synthesis [1-2]. One of the best examples of such a process is three components coupling of aldehydes, alkynes, and amines (A<sup>3</sup>-coupling).

The resultant propargylamines or  $\beta$ -amino alkenes acquired from A<sup>3</sup>-coupling reactions are important as both synthetic versatile intermediates for the preparation of polyfunctional amino derivatives and as biologically active compounds [3-4].

Numerous synthetic methods and catalysts have developed for the synthesis been of propargylamines due to the significance of this class of compounds. There are several methods and transition metal catalysts, which have carried out these multi-component  $A^3$ -coupling reactions. These include Ag salts [5], Au(I)/Au(III) salts [6], Au(III)-salen complexes [7], CuI salts [8-10], Ir complexes [11-12], Hg<sub>2</sub>Cl<sub>2</sub> [13], Zn(OAc)<sub>2</sub>. 2H<sub>2</sub>O [14], FeCl<sub>3</sub> [15], NiCl<sub>2</sub> [16], Fe<sub>3</sub>O<sub>4</sub> [17], InBr<sub>3</sub> [18], and Cu/Ru dimetallic systems [19]. Also, solid supported metal catalyst has been used to accomplish A<sup>3</sup>-coupling reaction via C-H activation. Some of these catalysts need to attach a ligand on support for complex of metal [20-24].

\*Corresponding author Received: 26 December 2011 / Accepted: 25 January 2012 The 1,4-dihydroxyanthraquinone, "quinizarin" system is an important chemical attribute of all anthracyclines. The capability of anthracyclines and anthraquinones to produce complex metal ions has been recognized for a long time and has been well documented [25-29].

In the continuation of our studies to utilize a catalyst for the synthesis of organic compounds [30-50], in this communication we wish to report a new and stable catalyst for the efficient conversion of aldehydes, alkynes, and amines to corresponding propargylamines under solvent-free conditions.

#### 2. Results and Discussion

Herein, we document a general method for the preparation of propargylamines. The method prescribes the use of piperidine, benzaldhyde and phenylacetylene as a model reaction (Scheme 1).



#### Scheme 1.

A variety of reaction parameters were screened for this reaction. First, we examined the synthesis of corresponding propargylamine by metal complex catalysis. Various metal salts, including Cu(OAc)<sub>2</sub>.H<sub>2</sub>O, NiCl<sub>2</sub>.6H<sub>2</sub>O, Zn(OAc)<sub>2</sub>.2H<sub>2</sub>O, FeCl<sub>3</sub>.6H<sub>2</sub>O, Co(OAc)<sub>2</sub>.4H<sub>2</sub>O (1 eq.) with 1,4-dihydroxyanthraquinone (2 eq.) were tested as cheap and suitable catalysts. The results are presented in Table 1.  
 Table 1. Optimization conditions for synthesis of corresponding propargylamine from benzaldhyde, piperidine and phenylacetylene in a 1:1.1:1.1 molar ratio at 100 °C



Entry	Catalyst and condition	Solvent/Temperature <sup>o</sup> C Time (h)		Isolated Yield (%)	
1	[AQ <sub>2</sub> Cu(II)] (5.0 mol %)	neat /100	1	90	
2	[AQ <sub>2</sub> Ni] (5.0 mol %)	neat /100	1	72	
3	[AQ <sub>2</sub> Zn] (5.0 mol %)	neat /100	1	77	
4	[AQ <sub>2</sub> Fe(Cl)] (5.0 mol %)	neat /100	1	81	
5	[AQ <sub>2</sub> Co] (5.0 mol %)	neat /100	1	69	
6	-	neat /100	24	-	
7	1,4-dihydroxyanthraquinone (AQ)	neat /100	24	-	
8	Cu(OAC) <sub>2</sub> .H <sub>2</sub> O	neat /100	24	72	
9	[AQ <sub>2</sub> Cu(II)]	neat /150	5	86	
10	[AQ <sub>2</sub> Cu(II)]	neat /50	5	75	
11	[AQ <sub>2</sub> Cu(II)]	neat /25	5	70	
12	[AQ <sub>2</sub> Cu(II)]	EtOH/reflux	5	69	
13	[AQ <sub>2</sub> Cu(II)]	DMSO/reflux	5	59	
14	[AQ <sub>2</sub> Cu(II)]	CH3CN/reflux	5	68	
15	[AQ <sub>2</sub> Cu(II)]	THF/reflux	5	43	
16	[AQ <sub>2</sub> Cu(II)] (1.0 mol %)	neat /100	5	73	
17	[AQ <sub>2</sub> Cu(II)] (10.0 mol %)	neat /100	5	85	
18	[AQ <sub>2</sub> Cu(II)] (20.0 mol %)	neat /100	5	85	

As shown in Table 1, we found that the use of catalyst [AQ<sub>2</sub>Cu(II)] through complexation and stabilization of Cu(II) with the fourth oxygen atom bond in 1,4dihydroxyanthraquinone, providing electron density at copper, should be much more thermodynamically stable and catalytically active than the other metals (Table 1, entry 1). Furthermore, in order to show the importance of the catalyst, we have conducted reactions in the absence of neither the catalyst nor the metal in the 1,4-dihydroxy anthraquinone, no product was found (Table 1, entries 6, 7). Also to determine the most suitable reaction conditions, we focused our attention on the effect of temperature on the model reaction using the optimized amount of catalyst [AQ<sub>2</sub>Cu(II)]. Preliminary investigations showed that the rate of the reaction was significantly affected by the temperature of the reaction and a remarkable increase in yield was observed at 100°C compared to the various temperatures. Further increases in temperature had no influence in the yield and time. (Table 1, entries 9-11). In the next step our attention was focused on investigating the effect of solvents utilizing [AQ<sub>2</sub>Cu(II)] (5.0 mol%) on our model reaction (Table 1, entries 12-15). While the best yield was obtained in solvent-free, much lower yields were observed with organic solvents. The loading levels of the catalyst [AQ<sub>2</sub>Cu(II)] also have an effect on the yield. According to Table 1, entries 16-18, the optimal catalyst loading in the synthesis of corresponding propargylamine is at a

concentration of 5.0 mol%. When the amount of the catalyst was reduced, the yield of the product decreased and the time increased, whereas raising the catalyst concentration did not lead to an appreciable increase in the yield and a shorter reaction time. Finally, we have discovered that the optimized molar ratio of benzaldhyde / piperidine / phenylacetylene /cat. was 1/1.1/1.1/5 mol% and after 1 h, the desired product was isolated in 90% yield at 100 °C under solvent-free condition, without any of the environmental disadvantages of using toxic solvents. The mixture was heated in an oil bath at 100 °C. After completion of the reaction (monitored by TLC), the mixture was diluted and workup was done with ethyl acetate. The crude product was purified by column chromatography on silica gel to afford the pure product. In addition, no other additives were needed for this system, and the experimental process was quite simple and easy. To the best of our knowledge, this is the first report of a copper-catalyzed A<sup>3</sup> coupling reaction with 1.4-dihydroxyanthraguinone as ligand with the optimized conditions in hand and to explore the scope and limitation of the protocol and to establish the generality and applicability of this method, we applied this molar ratio for the reaction of various aldhydes with different substituents, amines and terminal alkynes to furnish the corresponding propargylamines. All the reactions proceeded well and as summarized in Table 2.

**Table 2.** Synthesis of propargylamines from various aldehydes (1.0 mmol), alkynes (1.1 mmol) and amines (1.1 mmol) in the presence of [AQ<sub>2</sub>Cu(II)]catalyst (5.0 mol%) in solvent-free at 100°C







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A range of functionalized aldhydes that bear methoxy group, methyl, chloride, or isopropyl functionality were successfully used. In all cases, the reactions proceeded smoothly to give the corresponding propargylamines in high yields. As expected, various amines and aldhydes were found to react with phenylacetylene in the presence of a catalytic amount of [AQ<sub>2</sub>Cu(II)] to give the corresponding propargylamines in good to excellent vields. For example, the reaction of N-phenyl piperazine with *P*-chlorobenzaldhyde and phenylacetylene catalyzed by [AQ<sub>2</sub>Cu(II)] under solvent-free condition at 100 °C for 70 min, produced corresponding propargylamine in 98% yield (Table 2, entry 6). After this study, which showed the broad scope of the reaction, we turned

our attention to the sterically hindered amines. For this purpose we chose azacrown ether as a substrate. There are scant, scattered reports that document synthesis of propargylamines containing azacrown ethers. The coupling of azacrown ether, various aldhydes and phenylacetylene proceeded smoothly to afford the corresponding propargylamines in high yields under standard conditions (Table 2, entries 10-17). Encouraged by these good results and realizing the importance of preparation of propargylamines from less reactive terminal alkynes, we decided to studied the reaction of several terminal alkynes and amines with formaline in the presence of catalytic amount of [AQ<sub>2</sub>Cu(II)] under optimized conditions. The results are presented in (Table 2, entry 18-23). In order to assess the feasibility of applying this method on a preparative scale, we carried out the A<sup>3</sup> coupling of piperidine, benzaldhyde and phenylacetylene in a 30-mmol scale in the presence of the [AQ2Cu(II)] catalyst. As expected, the reaction proceeded smoothly, similar to the case in a smaller scale (Table 2, entry 1), and the desired propargylamine was obtained in 89% isolated yield in 1h. In order to show the merit of this catalytic method, we have compared the results of the reaction of piperidine, benzaldhvde and phenylacetylene (Table 3) with some other catalysts used for the same reactions. Most of the listed methodologies suffer from some limitations such as prolonged reaction times, elevated temperatures, or use hazardous materials. For example, preparation of propargylamine carried out in toluene or CH<sub>3</sub>CN as a solvent that is hazardous (Table 3, entries 1, 2, 3, 6, 7). Additionally, the present protocol is effective in causing complete Mannich reaction of piperidine in period time 1 h. The same transformation requires 6-24 h for completion by using other catalysts. It was also observed that, the preparations of those catalysts and their ligands are very difficult (Table 3, entries 4, 8, 9, 12). But the present method shows a new, cheap and easy procedure for preparation of catalyst and introduces a general, simple and efficient synthetic method for preparation of propargylamines. Furthermore, some of the reaction was carried out under argon or nitrogen atmosphere (Table 3, entries 7, 8, 12), or have used expensive metal such as gold or silver (Table 3, entries 10, 11, 12). As evident from the results tabulated in Table 3, [AQ<sub>2</sub>Cu(II)] is a more efficient catalyst than the others.

**Table 3.** Comparison of protocols for synthesis of<br/>propargylamine from benzaldhyde, piperidine and<br/>phenylacetylene

Entry	/ Catalyst	Solvent	Time (h	)Temperature°C	Yield (%	6)Ref.
1	nano CuO	Toluene	6	90	82	[51]
2	CuHAP	CH <sub>3</sub> CN	6	reflux	85	[52]
3	Fe <sub>3</sub> O <sub>4</sub>	Toluene	16	reflux	75	[17]
4	Si(CH <sub>2</sub> ) <sub>3</sub> SO <sub>3</sub> CuC	H <sub>2</sub> O	10	reflux	86	[53]
5	FeCl <sub>3</sub>	-	14	70	34	[15]
6	Zn(OAc) <sub>2</sub> .2H <sub>2</sub> O	Toluene	7	reflux	92	[14]
7	NiCl <sub>2</sub>	Toluene	8	reflux	95	[16]
8	SiO <sub>2</sub> -NHC-Cu(I)	-	24	rt	79	[20]
9	Silica-CHDA-Cu	ı -	12	80	92	[23]
10	AuBr <sub>3</sub>	$\rm H_2O$	12	100	99	[6]
11	AgI	${\rm H}_2{\rm O}$	14	100	70	[54]
12	PS-NHC-Ag(I)	-	24	rt	92	[55]
13	AQ <sub>2</sub> Cu(II)	-	1	100	90	-

Furthermore, we investigated the copper scavenger aspect in uncomplexed forms. To demonstrate the 1,4-dihydroxy scavenging abilities of anthraquinone, we set up the reaction of piperidine, benzaldhyde and phenylacetylene, Cu(OAc)2.H2O and of 1,4-dihydroxyanthraquinone as a model reaction. The reaction preceded well and the desired product was obtained in 82% vield after 1.5 h. The filtrate solvent was free of any detectable copper contamination, and had been checked with ICP method. Overall, this result clearly indicated the catalytic benefits and an additional advantage offered by the simplicity of the operational procedure obtained by mixing all starting materials for the reaction (amines, aldehydes, terminal  $Cu(OAc)_2.H_2O$ , alkyne. and 1.4dihydroxyanthraquinone) without the need for any synthesized homogeneous catalyst [AQ<sub>2</sub>Cu(II)].

### 3. Conclusions

In conclusion, we have developed 1,4dihydroxyanthraquinone-copper(II) catalyst in an efficient, one-step and one-pot three-component for the synthesis of propargyl amines from a variety of aldehydes, alkynes, and amines. The reaction was experimentally simple with a high yield and a short reaction time under solvent-free conditions.

### 4. Experimental

General: NMR spectra were recorded on a Bruker Avance DPX-250 (<sup>1</sup>H NMR 250 MHz and <sup>13</sup>C NMR 62.9 MHz) in pure deuterated solvents with tetramethylsilane (TMS) as internal standards. FT-IR spectromnetery (Shimadzu FT-IR 8300 spectrophotometer) were obtained for characterization of Propargylamine derivatives. Metal contents were obtained by ICP analyzer (Varian, vista-pro). Mass spectra were determined on a Shimadzu GCMS-QP 1000 EX instrument at 70 or 20 ev. Melting points were determined in open capillary tubes in a Buchi-535 circulating oil melting point apparatus. The purity determination of the substrates and reaction monitoring were accomplished by TLC on silica gel PolyGram SILG/UV254 plates or by a Shimadzu Gas Chromatograph (GC-10A) instrument with a flameionization detector using a column of 15% carbowax 20 M chromosorb-w acid washed 60-80 mesh. Column chromatography was carried out on short columns of silica gel 60 (70-230 mesh) in glass columns. Chemical materials were either prepared in our laboratories or were purchased from Aldrich, Fluka and Merck Companies.

# General procedure for $A^3$ -coupling reactions in solvent-free catalyzed by $[AQ_2Cu(II)]$ :

To a mixture of a amine (1.1 mmol), alkyne (1.1 mmol), and a aldhyde (1.0 mmol) was added  $[AQ_2Cu(II)]$  (0.05 mmol) and the resulting mixture was stirred at 100 °C for the appropriate time (Table 2). Progress of the reaction was monitored by TLC or GC. After completion, the reaction was extracted by continuous extraction with EtOAc (5 ml). The organic phase was separated and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and after filtration and evaporation of the solvent the crude product was obtained. Purification was performed by column chromatography eluted with n-hexane or a mixture of n-hexane/EtOAc to afford propargyl amines in excellent yields (Table 2).

Spectral data of compounds **4g-h**, **4p** and **4r-w** can be found in our previous reports [31].

#### 1-(1,3-diphenylprop-2-ynyl)piperidine (4a):

m.p. 65-66 °C; IR (KBr) v: 694.3, 725.2, 758.0, 1438.8, 1487.0, 2804.3, 2923.9, 3049.2 cm<sup>-1</sup>; MS (70 eV) m/z (%): 277 (1.6, M<sup>+</sup>+2), 276 (8.7, M<sup>+</sup>+1), 275 (25.5, M<sup>+</sup>), 191 (73.4), 165 (12.8), 115 (18.0), 86 (32.5), 57 (100.0); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz)  $\delta$ : 1.57-1.63 (m, 2H), 1.72-1.83 (m, 4H), 2.71-2.73 (m, 4H), 4.96 (s, 1H), 7.42-7.53 (m, 6H), 7.66-7.69 (m, 2H), 7.82 (*d*, *j*= 7.2 H<sub>Z</sub>, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 62.9 MHz)  $\delta$ : 24.81, 26.54, 50.95, 62.64, 86.33, 88.34, 123.65, 127.72, 128.71, 128.82, 128.91, 129.15, 132.07, 138.98.

### 4-(1,3-diphenylprop-2-ynyl)morpholine (4b):

IR (neat) v: 686.6, 748.3, 1010.6, 1118.6, 1280.6, 1319.2, 1442.7, 1496.7, 1596.9, 2862.2, 2962.4, 3039.6 cm<sup>-1</sup>; MS (70 eV) m/z (%): 279 (2.5, M<sup>+</sup>+2), 278 (13.1, M<sup>+</sup>+1), 277 (28.9, M<sup>+</sup>), 191 (100.0), 86 (47.0), 56 (80.7); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz)  $\delta$ : 2.67-2.71 (m, 4H), 3.76-3.82 (m, 4H), 4.85 (s, 1H), 7.36-7.46 (m, 5H), 7.57-7.61 (m, 3H), 7.69-7.73 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 62.9 MHz)  $\delta$ : 50.03, 62.10, 67.17, 85.38, 88.77, 123.15, 127.92, 128.40, 128.51, 128.69, 129.68, 131.96, 138.08.

#### 1-(1-(4-isopropylphenyl)-3-phenylprop-2ynyl)piperidine (4c):

IR (neat) v: 694.3, 756.0, 856.3, 1095.5, 1450.4, 1496.7, 2792.7, 2862.2, 2923.9, 3055.0 cm<sup>-1</sup>; MS (70 eV) m/z (%): 320 (0.1, M<sup>+</sup>+3), 319 (6.1, M<sup>+</sup>+2), 318 (15.9, M<sup>+</sup>+1), 317 (39.2, M<sup>+</sup>), 274 (20.9), 233 (100.0), 198 (46.1), 115 (22.5), 84 (24.0), 55 (41.1); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz)  $\delta$ : 1.06 (s, 3H), 1.09 (s, 3H), 1.23-1.29 (m, 2H), 1.40-1.48 (m, 4H), 2.36-2.39 (m, 4H), 2.67-2.87 (s, 1H), 4.58 (s, 1H), 7.03 (*d*, *j*= 8.0 H<sub>Z</sub>, 2H), 7.10-7.13 (m, 3H), 7.30-7.38 (m, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 62.9 MHz)  $\delta$ : 24.13, 24.57, 26.28, 33.87, 50.77, 62.25, 86.48, 87.72, 123.52, 126.19, 128.05, 128.33, 128.57, 131.87, 135.99, 148.10.

# 1-(3-phenyl-1-m-tolylprop-2-ynyl)pyrrolidine (4d):

IR (neat) v: 702.0, 763.8, 1126.3, 1604.7, 1674.1, 2360.7, 2792.7, 2970.2, 3039.6 cm<sup>-1</sup>; MS (70 eV) m/z (%): 277 (0.7, M<sup>+</sup>+2), 276 (12.4, M<sup>+</sup>+1), 275 (27.8, M<sup>+</sup>), 205 (100.0), 184 (98.5), 165 (10.7), 149 (12.4), 115 (32.5), 91 (29.5), 57 (59.1); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz)  $\delta$ : 1.64-1.76 (m, 4H), 2.25 (s, 3H), 2.59-2.65 (m, 4H), 4.77 (s, 1H), 6.98 (*d*, *j* = 8.0 H<sub>Z</sub>, 1H), 7.12 (*d*, *j* = 8.0 H<sub>Z</sub>, 1H), 7.17-7.21 (m, 3H), 7.29-7.32 (m, 2H), 7.36-7.41 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 62.9 MHz)  $\delta$ : 21.56, 23.57, 50.29, 59.23, 86.69, 87.01, 123.23, 125.50, 128.56, 128.20, 128.35, 128.24, 129.11, 131.85, 137.98, 139.09. **4-(3-phenyl-1-p-tolylprop-2-ynyl)morpholine** (4e):

m.p. 79-80 °C; IR (KBr) v: 759.9, 1112.9, 1317.3, 1448.4, 1488.9, 2823.6, 2862.2 cm<sup>-1</sup>; MS (70 eV) m/z (%):293 (5.3, M<sup>+</sup>+2), 292 (15.1, M<sup>+</sup>+1), 291 (24.8, M<sup>+</sup>), 233 (24.5), 205 (100.0), 149 (14.2), 86 (30.5), 56 (48.7); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz)  $\delta$ : 2.40 (s, 3H), 2.65-2.70 (m, 4H), 3.76-3.79 (m, 4H), 4.79 (s, 1H), 7.22 (*d*, *j*= 7.9 Hz, 2H), 7.36 (*dd*, *j*<sub>1</sub>= 6.5 Hz, *j*<sub>2</sub>= 2.3 Hz, 2H), 7.52-7.58 (m, 5H) ; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 62.9 MHz)  $\delta$ : 21.24, 50.02, 61.89, 67.21, 85.56, 88.49, 123.22, 128.33, 128.45, 128.63, 129.06, 131.93, 135.05, 137.41.

#### 1-(1-(4-chlorophenyl)-3-phenylprop-2-ynyl)-4phenylpiperazine (4f):

IR (neat) v: 694.3, 756.0, 1002.9, 1234.3, 1488.9, 1596.9, 1674.1, 2823.6, 2931.6, 3070.5 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz)  $\delta$ : 2.80 (*t*, *j*= 4.9 Hz, 4H), 3.24 (*q*, *j*= 4.1 Hz, 4H), 4.88 (s, 1H), 6.84-6.95 (m, 3H), 7.25-7.39 (m, 7H), 7.52-7.56 (m, 2H), 7.64 (*d*, *j*= 8.7 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 62.9 MHz)  $\delta$ : 49.45, 49.54, 61.17, 84.70, 89.16, 116.25, 119.89, 122.96, 128.57, 128.59, 129.29, 129.80, 130.05, 132.05, 133.70, 136.96, 151.49.

#### 1-(4-methoxyphenyl)-N,N-dimethyl-3phenylprop-2-yn-1-amine (4i):

IR (neat) v: 756.0, 1033.8, 1172.6, 1242.1, 1458.1, 1512.1, 1612.4, 2785.0, 2823.6, 2939.3 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz)  $\delta$ : 2.33 (s, 6H), 3.80 (s, 3H), 4.79 (s, 1H), 6.92 (*dd*, *j*<sub>1</sub>= 8.8 H<sub>Z</sub>, *j*<sub>2</sub>= 2.8 H<sub>Z</sub>, 2H), 7.30-7.36 (m, 2H), 7.50-7.57 (m, 5H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 62.9 MHz)  $\delta$ : 41.51, 55.20, 61.63, 85.21, 88.29, 113.58, 123.28, 128.20, 128.39, 129.65, 130.53, 131.86, 159.21.

11-[1-(2-Chloro-phenyl)-3-phenyl-prop-2-ynyl]-9,10,11,12,13,14-hexahydro-8H-5,17-dioxa-

# 8,11,14-triaza-benzocyclopentadecene-7,15-dione (4j):

m.p. 215 °C ; IR (KBr) v: 746.4, 1049.2, 1126.4, 1222.8, 1257.5, 1506.3, 1531.4, 1685.7, 2831.3, 2883.4, 3404.1 cm<sup>-1</sup>; MS (70 eV) m/z (%): 520 (0.3, M<sup>+</sup>+3), 519 (3.2, M<sup>+</sup>+2), 518 (2.7, M<sup>+</sup>+1), 517 (7.9, M<sup>+</sup>),406 (5.4), 351 (8.7), 292 (13.7), 225 (63.6), 85 (100.0); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz)  $\delta$ :

11-[1-(2,6-Dichloro-phenyl)-3-phenyl-prop-2ynyl]-9,10,11,12,13,14-hexahydro-8H-5,17-dioxa-8,11,14-triaza-benzocyclopentadecene-7,15-dione (4k):

m.p. 213-214 °C; IR (KBr) v: 748.3, 1249.8, 1504.4, 1527.5, 1681.8, 3070.5, 3409.9 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz)  $\delta$ : 2.77-3.02 (m, 4H), 3.40-3.57 (m, 4H), 4.40 (s, 4H), 5.66 (s, 1H), 6.89-7.04 (m, 4H), 7.18-7.33 (m, 5H), 7.42-7.44 (m, 3H), 7.63 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 62.9 MHz)  $\delta$ : 36.32, 50.93, 55.20, 68.68, 84.16, 88.30, 114.78, 122.84, 128.37, 128.57, 128.69, 129.81, 131.60, 131.73, 133.00, 136.34, 147.44, 167.49.

11-(3-Phenyl-1-thiophen-2-yl-prop-2-ynyl)-9,10,11,12,13,14-hexahydro-8H-5,17-dioxa-8,11,14-triaza-benzocyclopentadecene-7,15-dione (4l):

m.p. 194-195 °C; IR (KBr) v: 702.0, 756.0, 1049.2, 1126.3, 1226.6, 1496.7, 1535.2, 1681.8, 3417.6 cm<sup>-1</sup>; MS (70 eV) m/z (%):493 (0.4, M<sup>+</sup>+4), 492 (0.6, M<sup>+</sup>+3), 491 (5.4, M<sup>+</sup>+2), 490 (11.9, M<sup>+</sup>+1), 489 (19.3, M<sup>+</sup>),292 (23.2), 263 (13.3), 238 (12.7), 197 (87.4), 111 (11.0), 85 (100.0), 57 (46.8); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz)  $\delta$ : 2.88-3.04 (m, 4H), 3.44-3.72 (m, 4H), 4.49 (s, 4H), 5.25 (s, 1H), 6.86-7.06 (m, 4H), 7.16 (*d*, *j*=5.0 H<sub>Z</sub>, 1H), 7.25-7.27 (m, 1H), 7.34-7.37 (m, 1H), 7.48-7.56 (m, 7H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 62.9 MHz)  $\delta$ : 34.98, 47.71, 51.40, 67.74, 82.98, 87.68, 113.63, 122.16, 122.39, 126.00, 126.65, 126.86, 128.44, 128.74, 131.89, 142.61, 146.84, 167.46.

### 11-(1,3-Diphenyl-prop-2-ynyl)-9,10,11,12,13,14hexahdro-8H-5,17-dioxa-8,11,14-triazabenzocyclopentadecene-7,15-dione (4m):

m.p. 205-206 °C; IR (KBr) v: 756.0, 1047.3, 1124.4, 1217.0, 1257.5, 1504.4, 1529.4, 1596.9, 1689.5, 2841.0, 2885.3, 3411.8 cm<sup>-1</sup>; MS (70 eV) m/z (%): 486 (0.1, M<sup>+</sup>+3), 485 (1.5, M<sup>+</sup>+2), 484 (3.4, M<sup>+</sup>+1), 483 (3.7, M<sup>+</sup>),412 (1.9), 369 (1.6), 317 (2.6), 292 (4.9), 263 (3.7), 232 (4.3), 206 (3.8), 111 (26.6), 85 (69.8), 57 (100.0); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz)  $\delta$ : 2.85-2.87 (m, 4H), 3.41-3.55 (m, 4H), 4.44 (s, 4H), 5.12 (s, 1H), 6.89-7.06 (m, 4H), 7.14-7.22 (m, 3H), 7.34-7.38 (m, 2H), 7.52-7.55 (m, 3H), 7.60-7.63 (m, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 62.9 MHz)  $\delta$ : 35.00, 47.95, 55.03, 67.54, 82.85, 89.32, 113.32, 122.44, 128.07, 128.36, 128.41, 128.45, 128.64, 131.89, 137.55, 146.68, 167.25.

11-(3-Phenyl-1-m-tolyl-prop-2-ynyl)-9,10,11,12,13,14-hexahydro-8H-5,17-dioxa-

# 8,11,14-triaza-benzocyclopentadecene-7,15-dione (4n):

m.p. 196-197 °C; IR (KBr) v: 1748.3, 1049.2, 1126.3, 1265.2, 1512.1, 1535.2, 1681.8, 3417.6 cm<sup>-1</sup>; MS (70 eV) m/z (%): 499 (3.7, M<sup>+</sup>+2), 498 (9.6, M<sup>+</sup>+1), 497 (14.5, M<sup>+</sup>), 292 (15.1), 246 (13.9), 205 (94.0), 85 (100.0); 1H NMR (CDCl<sub>3</sub>, 250 MHz)  $\delta$ : 2.09 (s, 3H), 2.86-2.90 (m, 4H), 3.44-3.56 (m, 4H), 4.44 (s, 4H), 5.08 (s, 1H), 6.89-7.13 (m, 6H), 7.33-7.39 (m, 3H), 7.44 (*d*, *j*= 7.6 H<sub>z</sub>, 1H), 7.50-7.56 (m, 5H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 62.9 MHz)  $\delta$ : 12.18, 34.95, 47.82, 54.89, 67.53, 83.03, 89.25, 113.29, 122.43, 122.52, 125.45, 128.25, 128.44, 128.59, 128.81, 128.91, 131.89, 137.51, 138.15, 146.67, 167.20.

## 11-(3-Phenyl-1-p-tolyl-prop-2-ynyl)-

9,10,11,12,13,14-hexahydro-8H-5,17-dioxa-8,11,14-triaza-benzocyclopentadecene-7,15-dione (40):

m.p. 213 °C; IR (KBr) v: 748.3, 1257.5, 1504.4, 1527.5, 1681.8, 3417.6 cm<sup>-1</sup>; MS (70 eV) m/z (%):499 (1.4, M<sup>+</sup>+2), 498 (8.8, M<sup>+</sup>+1), 497 (17.7, M+), 425 (12.7), 292 (24.5), 246 (14.6), 205 (100.0), 85 (78.2); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz)  $\delta$ : 2.27 (s, 3H), 2.85-2.88 (m, 4H), 3.43-3.55 (m, 4H), 4.44 (s, 4H), 5.08 (s, 1H), 6.89 (m, 2H), 6.98 (*d*, *j*= 8.0 H<sub>Z</sub>, 2H), 7.02-7.09 (m, 2H), 7.34-7.36 (m, 2H), 7.47-7.55 (m, 7H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 62.9 MHz)  $\delta$ : 21.06, 35.01, 47.87, 54.74, 67.56, 83.14, 89.09, 113.31, 122.42, 122.52, 128.20, 128.42, 128.57, 129.10, 131.87, 134.49, 137.75, 146.72, 167.26. **11-[1-(4-Methoxy-phenyl)-3-phenyl-prop-2-**

ynyl]-9,10,11,12,13,14-hexahydro-8H-5,17-dioxa-8,11,14-triaza-benzocyclopentadecene-7,15-dione (4q):

m.p. 173-174 °C; IR (KBr) v: 750.3, 1047.3, 1257.5, 1504.4, 1598.9, 1670.2, 1695.3, 2900.0, 2997.2, 3404.1 cm<sup>-1</sup>; MS (70 eV) m/z (%): 515 (0.5, M<sup>+</sup>+2), 514 (4.9, M<sup>+</sup>+1), 513 (13.6, M<sup>+</sup>), 292 (16.9), 221 (50.3), 97 (41.4), 57 (100.0); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz)  $\delta$ : 2.83-2.87 (m, 4H), 3.41-3.55 (m, 4H), 3.72 (s, 3H), 4.45 (s, 4H), 5.05 (s, 1H), 6.70 (*d*, *j*= 8.6 H<sub>Z</sub>, 2H), 6.90-7.06 (m, 4H), 7.34-7.37 (m, 2H), 7.49-7.54 (m, 7H) ; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 62.9 MHz)  $\delta$ : 34.98, 47.76, 54.37, 55.20, 67.55, 83.24, 89.04, 113.32, 113.68, 122.43, 122.48, 128.43, 128.58, 129.47, 129.49, 131.86, 146.66, 159.26, 167.24.

#### Acknowledgments

We gratefully acknowledge the support of this work by the Shiraz University and Shiraz University of Technology Research Council.

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سنتز سه جزیی مشتقات پروپارژیل آمین به واسطه کمپلکس ۱و۴- دی هیدروکسی آنتراکینون-مس دو ظرفیتی به عنوان یک کاتالیزور موثر تحت شرایط بدون حلال ه شرقی<sup>۱</sup>، ع. خشنود<sup>۱</sup>و ر. خلیفه<sup>۲</sup>

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### چکیدہ:

کمپلکس بسیار فعال ناشی از ترکیب مس دو ظرفیتی و ۱و۴- دی هیدروکسی آنتراکینون به عنوان یک لیگاند ارزان قیمت و فراوان ساخته شده است. از این کمپلکس می توان به عنوان یک کاتالیزور مناسب جهت تهیه ساختارهای متنوع از پروپارژیل آمینها از طریق واکنش سه جزیی و همزمان آلکینهای انتهایی ، آلد هیدها و آمینهای نوع دوم با راندمان بالا، تحت شرایط بدون حلال مورد استفاده قرار داد. ۱ و۴- دی هیدروکسی آنتراکینون به عنوان یک جاذب موثر و قوی می دو ظرفیتی این قابلیت را دارد که واکنش کوپلینگ <sup>3</sup>A را بدون سنتز کاتالیزوز فوق به خوبی انجام دهد.

Keywords: Propargylamines; anthraquinone; A<sup>3</sup>-coupling; solvent-free