

تجانس ألكينات طرفية محفزة بمركبات النحاس من فينانثرولين-1، 10 تحت ظروف الخلو من المذيبات والقاعدة

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الملخص

إن مفهوم الكيمياء الخضراء في الوقت الحاضر يحقق نجاحا سريعا، لأنه يتماشى مع أهداف الأمم المتحدة للتنمية المستدامة. في هذا البحث، تم استخدام إجراء بسيط لكنه فعال في تركيب 1.3-diynes المتماثلة باستخدام أنواع مختلفة من القلويات المحفزة بالنحاس، تحت ظروف خالية من القاعدة والمذيبات.

تم إنتاج 1.3-diynes المتماثلة من مختلف القلويات باستخدام طريقة محسنة بنتائج جيدة تتوافق مع البروتوكول الاصطناعي المحسن ويتماشى مع مبادئ الكيمياء الخضراء، والتي تشمل النظام التحفيزي القابل للتدوير، وتجنب استخدام التفاعل البسيط للقاعدة. يمكن تطبيق البروتوكول المحسن لتصنيع العديد من المركبات التي هي موضع اهتمام الصناعات والأوساط الأكاديمية.

Homocoupling of terminal alkynes catalyzed by copper complexes of 1,10-phenanthroline under base- and solvent-free conditions

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Abstract

Environmentally friendly chemistry growing in popularity as it conforms with the United Nations' Sustainable Development Goals. This research shows a simple yet efficient procedure for the synthesis of symmetrical 1,3-diynes using various alkynes catalyzed by copper under base-free and solvent-less conditions. With the improved protocol, the formation of homocoupled 1,3-diynes from different alkynes were produced in adequate amounts. The improved synthetic protocol is in compliance with the principles of "green" chemistry, which includes recyclable catalytic systems and which avoids the use of base and mild homocoupling reaction conditions. The improved protocol can be applied to the synthesis of different compounds that are necessary in industry.

Keywords: Alkynes; 1,3-diynes; green chemistry; 1,10-phenanthroline; recyclable catalytic systems.

1. Introduction

In recent years, chemists have shown an interest in the utilization of environmentally friendly (green) and recyclable catalytic systems for the preparation of various building blocks in organic synthesis and pharmaceutical important compounds (Liao *et al.*, 2017; Naidu & Reddy, 2017; Sharifi *et al.*, 2014; Yuan *et al.*, 2017). One of the major challenges facing synthetic chemists today is the development of efficient chemical processes that make use of environmentally acceptable reagents and catalysts (Simon & Li, 2012). In this regard, "green chemistry" has been a topic of intense research (Jeon *et al.*, 2005; Pucarevic *et al.*, 2017; Saifuddin & Boyce, 2016; Thilagavathi *et al.*, 2015). Environmentally friendly chemistry is supported by the United Nations' Sustainable Development Goals.

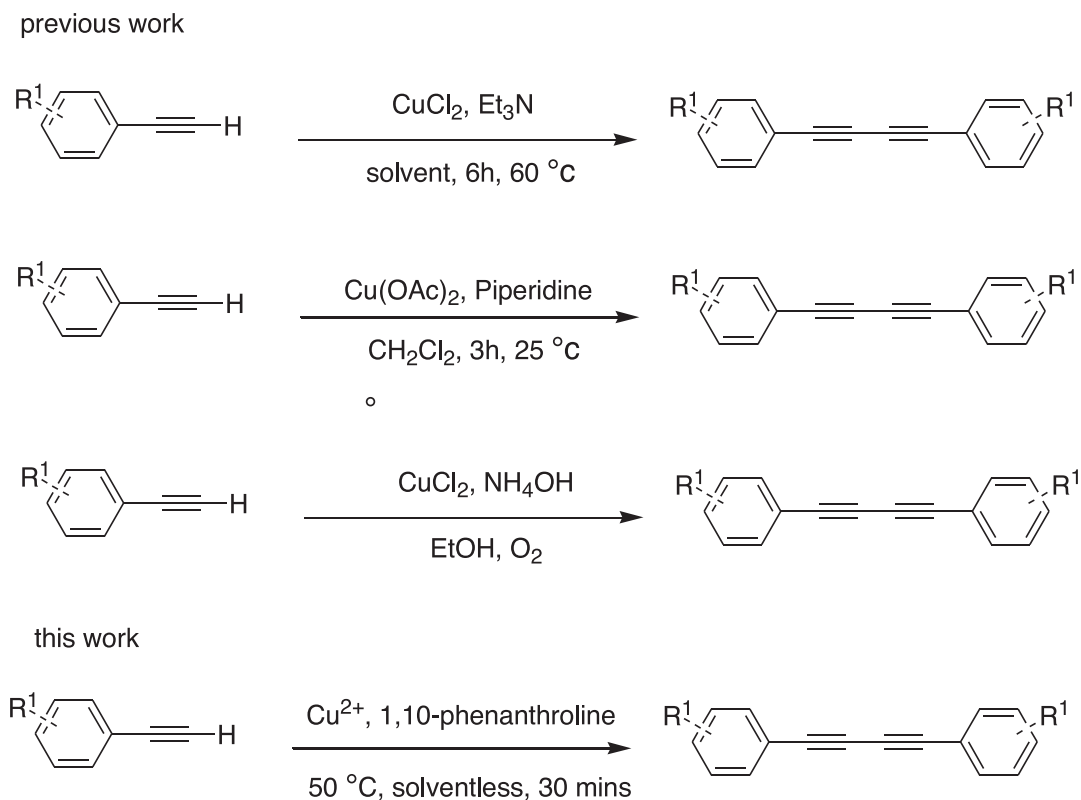
Conjugated 1,3-diynes are important precursors or intermediate in natural products (Shi & Lei, 2014), medicinal compounds (Ma *et al.*, 2017), electronic and optical materials (Eckstein *et al.*, 2017), among others. Traditionally, the synthesis of the 1,3-diynes is achieved by Glaser oxidative dimerization of two terminal alkynes (Hay, 1962). Since then, most studies on the synthesis of 1,3-diynes were based on the modification

on Glaser's original work with the goal of achieving a milder and more efficient reaction using a Pd/Cu catalytic system (Li *et al.*, 2005), gold salt (Peng *et al.*, 2014; Yao, 2013), and palladium pincer complexes (Urigoitia *et al.*, 2017). Unfortunately, the use of these catalytic systems for homocoupling reactions are not economically feasible, as it involve the use of expensive metals. Some previous research involved homocoupling reactions of terminal alkynes. These used supported catalysts, such as mesoporous material, polyacrylonitrile fiber, zeolite, carbon nitride, nitro resin, porphyrin, electrochemical method, etc. These reactions require the use of high temperature, solvents, and need an argon environment and pressurized oxygen (Barot *et al.*, 2016; Jia *et al.*, 2011; Kuhn *et al.*, 2009; Ohmura *et al.*, 1997; Sheng *et al.*, 2016; Shi *et al.*, 2016; Xiao *et al.*, 2012; Xu *et al.*, 2018). There are many catalysts that are efficient for the synthesis of 1,3-diynes. However, an alternative catalytic system, which is simple, less expensive and recyclable catalytic system for synthesizing the 1,3-diynes is still relevant.

This research investigates the "green" synthesis of symmetrical 1,3-diynes. Many synthetic protocols have been reported for this reaction, but most of these

catalytic systems require the use of expensive metals, high temperature, and/or pressurized oxygen. An efficient synthesis of the symmetrical 1,3-diynes by direct

dimerization of alkynes catalyzed by copper complexes of 1,10-phenanthroline under base- and solvent-free conditions is shown in Scheme 1.



Scheme 1. Previous and current methods for preparation of symmetrical 1,3-diynes.

2. Experimental

2.1 Materials and methods

All chemicals and solvent utilized in this study were of technical grade and used without further purification. The ^1H and ^{13}C -NMR analyses were performed using a Bruker Avance III 400 spectrometer and CDCl_3 as a solvent. The GC-MS spectra were recorded using a Shimadzu QP2010SE furnished with a Supelco fused silica capillary column.

2.2 Typical synthesis protocol for the preparation of symmetrical 1,3-diynes

A mixture of phenylacetylene (1.00 mmol), 1,10-phenanthroline (20 mol %) and Cu(OAc)_2 (10 mol %) was magnetically stirred for about 1 h at room temperature. After that, the reaction mixture was quenched with water (20 mL), and ethyl acetate (3 X 10 mL) was added into the reaction mixture. The organic layer was separated from the aqueous layer and dried using magnesium sulfate before being subjected to concentration under reduced

pressure. The single pure product was separated from the dried crude product by washing with ethyl acetate (5 mL), and the pure product was left overnight to allow for the crystal of the pure compound to form. The synthesized 1,3-diynes products were elucidated and confirmed using NMR spectroscopy (^1H and ^{13}C) and GC-MS analyses.

2.3 Spectral data of 1,3-diynes

1,4-Bisphenylbuta-1,3-diyne (**3a**): White solid, melting point: 84-85 $^\circ\text{C}$ (Liu *et al.*, 2014), isolated yield = 94 %. $^1\text{H-NMR}$ (δ in ppm, CDCl_3) (400 MHz): 7.53-7.51 (m, 4H); 7.38-7.30 (m, 6H); ^{13}C NMR (δ in ppm, CDCl_3) (100 MHz): 132.44, 129.12, 128.41, 121.72, 81.58, 73.89; GC-MS: $\text{C}_{16}\text{H}_{10}$, m/z 202.08. Anal. calcd for $\text{C}_{16}\text{H}_{10}$: C 95.02, H 4.98; found C 94.99, H 4.97.

1,4-Bis(*o*-tolylphenyl)buta-1,3-diyne (**3b**): White solid, melting point: 75-76 $^\circ\text{C}$ (Liu *et al.*, 2014), isolated yield = 76 %. $^1\text{H-NMR}$ (δ in ppm, CDCl_3) (400 MHz): 7.51 (d, $J = 7.9$ Hz, 2H); 7.29-7.24 (m, 2H), 7.24-7.22 (m, 2H), 7.17 (q, 2H), 2.51 (s, 6H); ^{13}C NMR (δ in ppm,

CDCL₃) (100 MHz): 141.7, 132.8, 129.5, 129.0, 125.7, 121.6, 81.0, 76.6, 20.7; GC-MS: C₁₈H₁₄, m/z 230.11. Anal. calcd for C₁₈H₁₄: C 93.87, H 6.13; found C 93.84, H 6.11.

1,4-Bis(*m*-tolylphenyl) buta-1,3-diyne (**3c**): White solid, melting point: 73-74 °C (Liu *et al.*, 2014), isolated yield = 74 %. ¹H-NMR (δ in ppm, CDCL₃) (400 MHz): 7.33-7.31 (m, 1H); 7.23-7.15 (m, 4H); 2.33 (s, 6H); ¹³C NMR (δ in ppm, CDCL₃) (100 MHz): 138.19, 133.10, 129.89, 129.58, 128.31, 121.55, 81.57, 76.65, 73.56, 21.18; GC-MS: C₁₈H₁₄, m/z 230.11. Anal. calcd for C₁₈H₁₄: C 93.87, H 6.13; found C 93.85, H 6.10.

1,4-Bis(*p*-tolylphenyl) buta-1,3-diyne (**3d**): White solid, melting point: 135-136 °C (Liu *et al.*, 2014), isolated yield = 70 %. ¹H-NMR (δ in ppm, CDCL₃) (400 MHz): 7.40 (d, *J* = 8.1 Hz, 4H); 7.13 (d, *J* = 8.1 Hz, 4H), 2.35 (s, 6H); ¹³C NMR (δ in ppm, CDCL₃) (100 MHz): 139.49, 132.41, 129.18, 118.81, 81.52, 73.38, 21.55; GC-MS: C₁₈H₁₄, m/z 230.11. Anal. calcd for C₁₈H₁₄: C 93.87, H 6.13; found C 93.86, H 6.11.

1,4-Bis(4-Chlorophenyl) buta-1,3-diyne (**3e**): White solid, melting point: 254-255 °C (Liu *et al.*, 2014), isolated yield = 88 %. ¹H-NMR (δ in ppm, CDCL₃) (400 MHz): 7.44 (d, *J* = 8.1 Hz, 4H); 7.31 (d, *J* = 8.1 Hz, 4H); ¹³C NMR (δ in ppm, CDCL₃) (400 MHz): 138.39, 133.71, 129.01, 128.17; GC-MS: C₁₆H₈Cl₂, m/z 270.00. Anal. calcd for C₁₆H₈Cl₂: C 70.88, H 2.97, Cl 26.15; found C 70.86, H 2.95, Cl 26.13.

1,4-Bis(4-Bromophenyl) buta-1,3-diyne (**3f**): Brown solid, melting point: 263-264 °C (Lu *et al.*, 2019), isolated yield = 83 %. ¹H-NMR (δ in ppm, CDCL₃) (400 MHz): 7.40 (d, *J* = 8.6 Hz, 4H); 7.55 (d, *J* = 8.6 Hz, 4H); ¹³C NMR (δ in ppm, CDCL₃) (100 MHz): 138.92, 132.13, 128.45, 121.88; GC-MS: C₁₆H₈Br₂, m/z 357.90. Anal. calcd for C₁₆H₈Cl₂: C 70.88, H 2.97, Cl 26.15; found C 70.86, H 2.95, Cl 26.13. Anal. calcd for C₁₆H₈Br₂: C 53.37, H 2.24, Cl 44.39; found C 53.35, H 2.22, Cl 44.36.

1,4-Bis(4-fluorophenyl) buta-1,3-diyne (**3g**): White solid, melting point: 186-187 °C (Liu *et al.*, 2014), isolated yield = 87 %. ¹H-NMR (δ in ppm, CDCL₃) (400 MHz): 7.52-7.48 (m, 4H); 7.03 (q, 4H); ¹³C NMR (δ in ppm, CDCL₃) (100 MHz): 164.29, 161.77, 134.47, 117.78, 116.10, 115.76, 80.36, 73.46; GC-MS: C₁₆H₈F₂, m/z 238.06. Anal. calcd for C₁₆H₈F₂: C 80.67, H 3.38, F 15.95; found C 80.65, H 3.35, F 15.93.

1,4-Bis(2-methoxyphenyl) buta-1,3-diyne (**3h**): White solid, melting point: 138-139 °C (Liu *et al.*, 2014), isolated

yield = 63 %. ¹H-NMR (δ in ppm, CDCL₃) (400 MHz): 7.46 (dd, *J* = 4.0 Hz, *J* = 7.9 Hz, 2H); 6.86 (td, *J* = 7.9 Hz, 2H), 6.94-6.88 (m, 4H), 3.88 (s, 6H); ¹³C NMR (δ in ppm, CDCL₃) (100 MHz): 161.4, 134.5, 130.7, 120.6, 111.4, 110.7, 78.8, 77.8, 55.9; GC-MS: C₁₈H₁₄O₂, m/z 262.10. Anal. calcd for C₁₈H₁₄O₂: C 82.42, H 5.38, O 12.20; found C 82.40, H 5.36, O 12.18.

1,4-Bis(4-methoxyphenyl) buta-1,3-diyne (**3i**): White solid, melting point: 138-139 °C (Liu *et al.*, 2014), isolated yield = 60 %. ¹H-NMR (δ in ppm, CDCL₃) (400 MHz): 7.46 (d, *J* = 8.0 Hz, 4H); 6.84 (d, *J* = 8.0 Hz, 2H), 3.80 (s, 6H); ¹³C NMR (δ in ppm, CDCL₃) (100 MHz): 160.19, 134.01, 114.08, 113.87, 81.18, 72.85, 55.27; GC-MS: C₁₈H₁₄O₂, m/z 262.10. Anal. calcd for C₁₈H₁₄O₂: C 82.42, H 5.38, O 12.20; found C 82.41, H 5.37, O 12.19.

3. Results and discussion

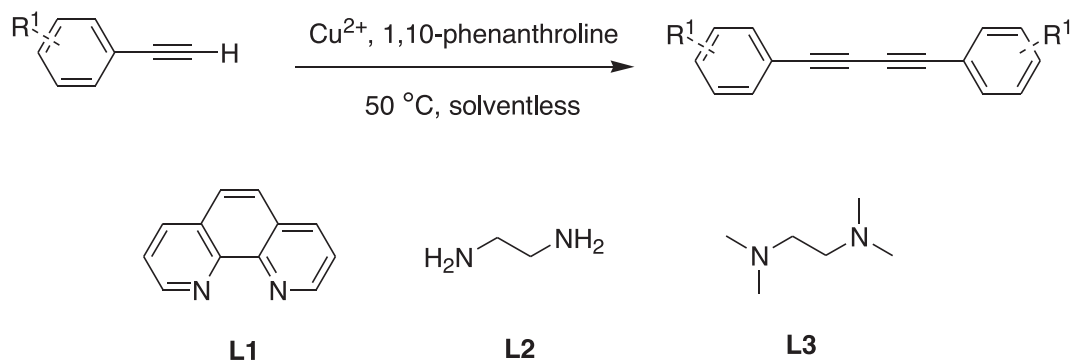
Phenylacetylene was chosen as the model substrate for the study of the optimization reaction condition. At first, the reaction was carried out using phenylacetylene (0.01 mmol), 1,10-phenanthroline (20 mol %), Cu(OAc)₂ (10 mol%) in 3 mL of H₂O, and the crude mixture was stirred at 50 °C for 30 mins. The preliminary result indicated that the Cu/**L1** plays an important part in mediating the homocoupling of phenylacetylene under open air to produce a 30 % yield of **3a** (Table 1, entry 1). In addition, the poor reaction yield indicated in the preliminary reaction showed that the H₂O might not be the optimal solvent for this reaction. Thus, the synthesis of **3a** was performed using various solvents, namely the DMF, DMSO and CH₃CN. The reactions' yields decreased (25 % for DMF, 20 % for DMSO and 8 % for CH₃CN) (Table 1, entries 2-4). However, when a similar reaction was repeated under solventless conditions, **3a** was found to be at a 94 % yield (Table 1, entry 5). The use of other ligands was also evaluated in this study, and **L1** proved to be the most effective ligand, judging from the isolated yield of **3a** (Table 1, entries 5-7). The preliminary reaction shows that the use of **L1** coupled with Cu(OAc)₂ is crucial for initiating the synthesis of **3a**. In contrast, the catalyst is inactive if no ligand was used in this reaction (Table 1, entry 8).

The synthesis of **3a** using other copper salts was also evaluated. Cu(OAc)₂ was found to be the most effective catalyst among other copper salts (Table 1, entries 9-11). As temperature could be a variable affecting the synthesis of **3a**, its effect was also investigated. However, an increment of the reaction temperature from 50 °C to

60 °C did not give rise to a better yield of **3a** (Table 1, entry 14). In addition, the reaction's yield of **3a** was found to decrease when the temperature decreased (Table 1, entries 12-13). A controlled experiment was also performed by studying the duration for synthesis of **3a**. The optimum time obtained was 30 mins (Table 1, entries 15-16). The yield of **3a** was also affected by the amount of catalyst loaded. The best yield of **3a** was obtained when 10 mol % of the Cu(OAc)₂ catalyst was used (Table 1,

entries 17-18). The catalytic activity of **3a** might also have been affected by **L1** loading. In this study, the yield of **3a** was found to decrease when the amount of **L1** used decreased from 20 mol % to 10 mol % (Table 1, entry 19). Increments in the **L1** loading did not result in a better yield of **3a** (Table 1, entry 20). As such, the optimum reaction condition for the synthesis of **3a** was identified as: Cu(OAc)₂ (10 mol %), 1,10-phenanthroline (20 mol %) in solventless conditions (Table 1, entry 5).

Table 1. The search for optimum reaction condition for **3a**



Entry	Solvent (mL)	Catalysts	Ligand	Time (mins)	Temperature (°C)	Yield ^a (%)
1	H ₂ O (3.0)	Cu(OAc) ₂	L1	30	50	30
2	DMF (3.0)	Cu(OAc) ₂	L1	30	50	25
3	DMSO (3.0)	Cu(OAc) ₂	L1	30	50	20
4	CH ₃ CN (3.0)	Cu(OAc) ₂	L1	30	50	8
5	Neat	Cu(OAc) ₂	L1	30	50	94
6	Neat	Cu(OAc) ₂	L2	30	50	13
7	Neat	Cu(OAc) ₂	L3	30	50	11
8	Neat	Cu(OAc) ₂		30	50	0
9	Neat	CuBr ₂	L1	30	50	38
10	Neat	CuI ₂	L1	30	50	20
11	Neat	CuO ₂	L1	30	50	35
12	Neat	Cu(OAc) ₂	L1	30	0	20
13	Neat	Cu(OAc) ₂	L1	30	27	67
14	Neat	Cu(OAc) ₂	L1	30	60	89
15	Neat	Cu(OAc) ₂	L1	20	50	77
16	Neat	Cu(OAc) ₂	L1	50	50	88
17 ^b	Neat	Cu(OAc) ₂	L1	30	50	65
18 ^c	Neat	Cu(OAc) ₂	L1	30	50	90
19 ^d	Neat	Cu(OAc) ₂	L1	30	50	72
20 ^e	Neat	Cu(OAc) ₂	L1	30	50	87

^aIsolated yield of product **3a** through recrystallization. ^b5 mol % of Cu(OAc)₂. ^c15 mol % of Cu(OAc)₂. ^d15 mol % of **L1**. ^e5 mol % of **L1**.

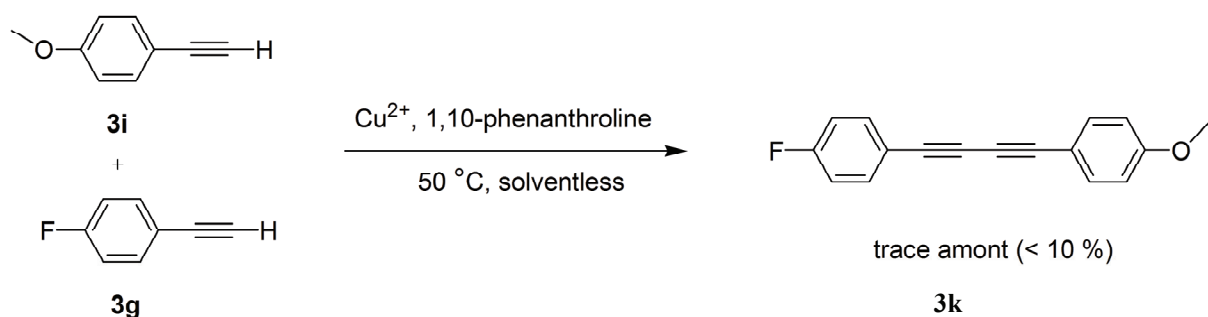
The general applicability of the improved catalytic system using different phenylacetylene derivatives to synthesize a variety of 1,3-diynes was also investigated. The result shows that, under the improved catalytic system, a variety of substituent groups (MeO, Me, F, Br and Cl) could be tolerated on phenylacetylene. In all cases, the 1,3-diynes were obtained in good to excellent yields after silica gel column purification (60-94 % yield). As shown in Table 2, homocoupling with phenylacetylene bearing the electron-withdrawing groups were found to proceed with a higher yields compared to phenylacetylene bearing electron rich groups. For example, the electron withdrawing groups (F, Br and Cl) were found to record a higher yield (Table 2, entries 5-7) relative to the phenylacetylene-bearing electron rich group, such as Me

and OMe (Table 2, entries 2-4, 8-9), which is consistent with the result obtained by Liu, *et al.* (2014). The performance of the improved catalytic system is regarded as superior because no solvents or base were involved, and the reaction took place in open air. In addition, the homocoupling reactions had a short reaction time.

The general applicability of the current protocol was extended to aliphatic substrates such as the 1-butyne and 1-pentyne. Unfortunately, the reactions did not give rise to the desired end-products. The possibility was explored of using the current catalytic system in hetero-coupling reaction by reacting **3j** and **3g** compounds (Scheme 2). Yet, the hetero-coupling reaction was unsuccessful as the GCMS analysis only showed a trace amount (<10 %) of the desired compound.

Table 2. Isolated yields of 1,3-diynes

Entry	R ¹	Product	Reaction Time (mins)	Yield (%)
1	H	3a	30	94
2	2-Me	3b	30	76
3	3-Me	3c	30	74
4	4-Me	3d	30	70
5	4-Cl	3e	30	88
6	4-Br	3f	30	83
7	4-F	3g	30	87
8	2-OMe	3h	30	63
9	4-OMe	3i	30	60



Scheme 2. The hetero-coupling reaction study conducted by reacting **3j** and **3g** under the improved protocol.

Furthermore, the recovery and reuse of the catalyst and ligand was also studied (Table 3). After the first run of the synthesis of **3a**, the crude product was extracted using ethyl acetate. The remaining solid, which correspond to the $\text{Cu}(\text{OAc})_2/\text{L1}$, was filtered and recharged with acetic

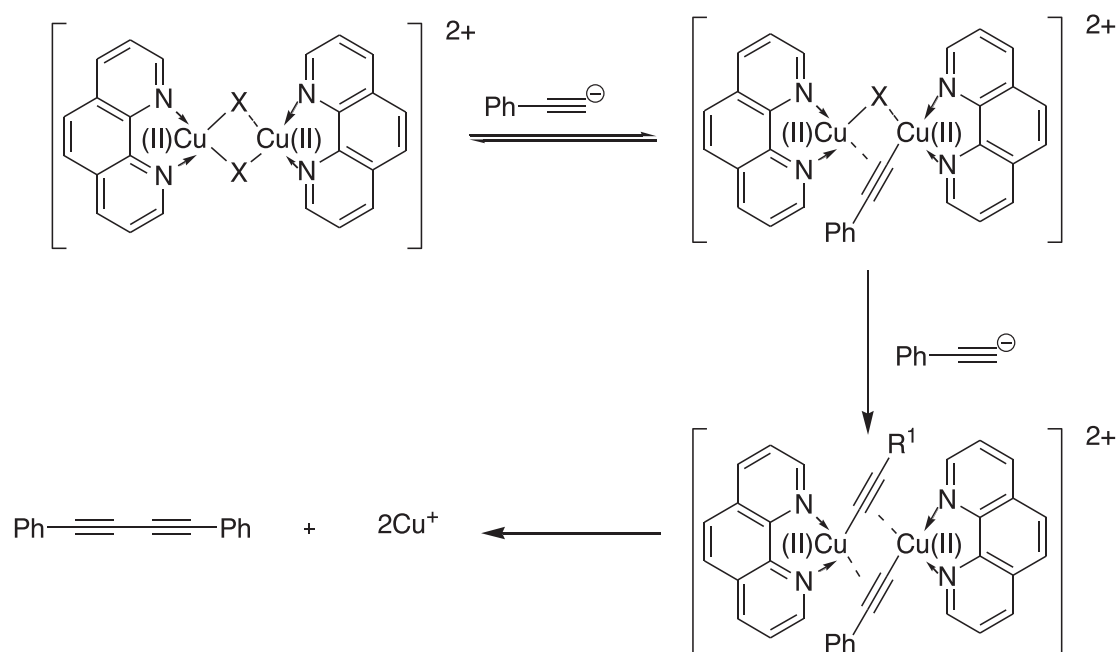
acid and could be reused five more times in subsequent homocoupling reactions of phenylacetylene. Thus, the current catalytic system can be considered a “green” chemical process.

Table 3. Recovery and recyclability of $\text{Cu}(\text{OAc})_2/\text{L1}$ for homocoupling of phenylacetylene^a

Run	Yield [%] ^b
1 st	94
2 nd	91
3 rd	85
4 th	74
5 th	68
6 th	65

^areaction conditions: 1 mmol of phenylacetylene, 20 mol % of L1, 10 mol % of $\text{Cu}(\text{OAc})_2$, solventless, 50 °C, in air. ^bisolated yield.

At this time, the exact mechanism of homocoupling of phenylacetylene is not well understood. However, based on a previous research by Yamaguchi, *et al.* (2008), a plausible mechanism was proposed for the homocoupling of phenylacetylene (Scheme 3). Many studies have investigated the efficient synthesis of the 1,3-dienes (Table 4). In this research, a simple, efficient, inexpensive process has been demonstrated that also has a recyclable catalytic system for the synthesis of 1,3-dienes.

**Scheme 3.** Proposed mechanistic pathway for the synthesis of **3a**.**Table 4.** Synthesis of **3a** catalyzed by various catalysts

Entry	Catalytic systems	Yield (%)	Reference
1	$\text{Cu}(\text{OAc})_2/\text{L1}$	94	This work
2	$\text{CuCl}/\text{Et}_3\text{N}$	95	(Hay, 1962)
3	$\text{CuI}_2/\text{I}_2/\text{NaCO}_3/\text{DMF}$	99	(Li, Yin, Li, & Jia, 2008).
4	$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}/\text{Piperdine}/\text{CH}_2\text{CL}_2$	90	(Balaraman & Kesaven, 2010)
5	$\text{CuCL}_2/\text{NaAOc}/\text{scCO}_2$	100	(Li & Jiang, 1999)
6	$\text{Pd}(\text{OAc})_2/\text{CuI}/\text{DABCO}/\text{MeCN}$	100	(Li, Liang, & Xie, 2005)
7	$\text{AuCL}_3/\text{I}_2/\text{K}_2\text{CO}_3/\text{DMSO}$	94	(Yao, 2013)
8	Resin-CuNPs/ $\text{K}_2\text{CO}_3/\text{DMSO}/\text{O}_2$	96	(Barot, Patel, & Kaur, 2016)
9	MCM-41-2N-CuI/piperdine/ CH_2CL_2	94	(Xiao, Yao, & Cai, 2012)

4. Conclusions

In summary, an efficient synthesis of 1,3-diyne was developed *via* Cu/L1 catalyzed oxidative homocoupling reaction of various phenylacetylene in solventless using air as oxidant. This approach offers several advantages compared to previous methods. First, expensive catalysts are not needed. Second, reactions were conducted in mild condition, making the process simple and inexpensive. Third, a high yield of products was obtained. Finally, the process is a recyclable catalytic system, making it a cost-effective and environmentally friendly laboratory procedure.

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