



Synthesis of ynones at room temperature catalyzed by copper chloride cryptand complex under solvent free conditions



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ABSTRACT

An air-stable highly efficient reusable CuCl_2 -cryptand-[2.2.Benzo] catalyst is reported first time for coupling reaction of terminal alkynes with different acyl chlorides in the presence of triethylamine acting both as base and solvent at room temperature to give the corresponding ynones. Easy-going, short reaction time, cost-effective, palladium-, phosphorus- and solvent-free, high yield and recyclability up to 5th times make this method green procedure for ynones' synthesis with wide substrate variety.

1. Introduction

In recent years, Ynones (α , β -Acetylenic ketones) have got tremendous importance due to their numerous applications in organic synthesis, click chemistry, pharmaceutical and natural products. Ynones are the constructive building blocks in organic chemistry that are used as synthetic intermediates for the preparation of many biologically-active compounds, heterocyclic derivatives [1] etc. Ynones are also precursors for the synthesis of various valuable organic functional groups like isoxazoles [2a], pyrimidines [2b], quinolones [3], furans [4], pyrazoles [5], flavones [6], oximes [7], polyfunctionalized pyrroles [8], chiral propargylic alcohols [9] and many more. There are various reaction protocols that have been reported for the synthesis of ynones which include oxidation of propargylic alcohols [10], coupling reactions of terminal alkynes with organic halides in the presence of carbon-monoxide gas [11], oxidation of alkynes [12], reaction of terminal alkynes with nitriles [13], and the most important method is the reaction between terminal alkynes and carboxylic acid derivatives in the presence of various strong bases [14] and elements such as silver [15], zinc [16], tin [17], silicon [18], lithium [19], copper [20], magnesium [21], cadmium [22], aluminum [23], thallium [24], gallium [25], stibium [26], indium [27], etc. Recently the synthesis of ynones catalyzed by palladium catalysts like palladacycle complexes [28a], Pd/C [28b], Pd(PPh₃)Cl₂/CuI [28c], PdNPs-PPS [28d], PdCl₂(PPh₃)₂, [28e] Pd(OAc)₂, [28f] palladium (II) acyclicdiaminocarbene complex [28g] Pd(PPh₃)₄/ZnCl₂ [28h] and polystyrene-supported palladium (0) complex [28i] palladium-chloride-cryptand-22 complex [28j] Pd-Ph1-phoxide [28k] gets much

more attention. On the other hand, palladium free methodologies get copious interest because of the high cost of palladium and difficulty to separate from the product. Generally, in industrial practice palladium catalysts are avoided whenever possible in the last step of synthesis of complex molecule [20b].

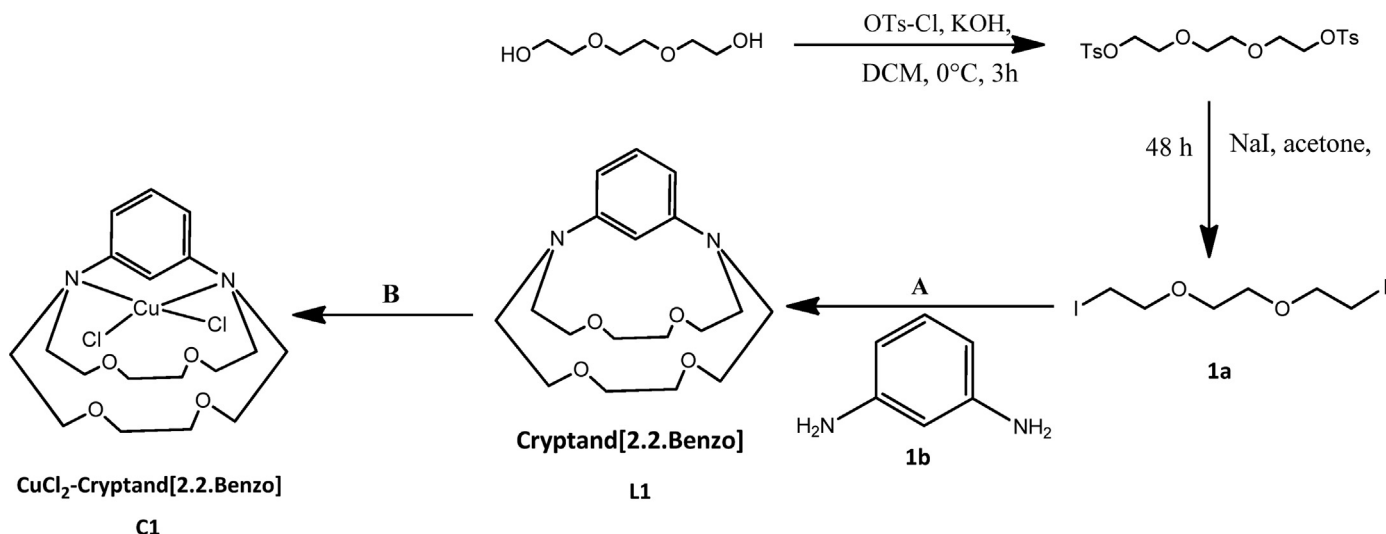
Recently Wang et al. reported synthesis of ynones using copper nanoparticles supported on mesoporous polymer [20e] and a very few copper catalysed methodologies were reported for the synthesis of ynones [20]. The above mentioned reported protocols suffers from various disadvantages such as long reaction time, high temperatures, use of air and moisture sensitive catalysts, phosphorous containing catalysts, necessity of additives, use of hazardous organic solvents, use of toxic carbon-monoxide gas, harsh reaction conditions etc. In practice the best method from environmental and economic point of view is the reaction without solvent and thus solvent-free reactions undeniably have become frequent and specialized over recent years.

Cryptands have numerous applications in various fields like sensing [29a], biological activity [29b] etc. Recently it has been shown that cryptand has great catalytic activity in various reactions [30,28j,20e] because of many advantages like owing to their versatile processing capabilities, separation and recycling etc. The chelating effect of nitrogen and oxygen present in macrocycles along with its flexibility give support in stabilizing the complex.

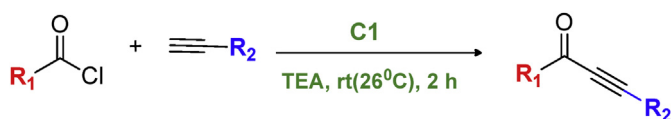
To overcome the drawbacks of the reported protocols we have developed an efficient, environmentally benign and operationally simple CuCl_2 -cryptand [2.2.Benzo] complex catalyst for coupling of acyl chloride and terminal alkynes (Scheme 2) in presence of triethyl amine (TEA)

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Scheme 1. (A) Na₂CO₃ CH₃CN (dry) reflux 48 h. 42% yield. (B) CuCl₂·2H₂O ethanol reflux and 7h.



Scheme 2. Synthesis of ynones by CuCl₂-cryptand [2.2.Benzo] catalyst.

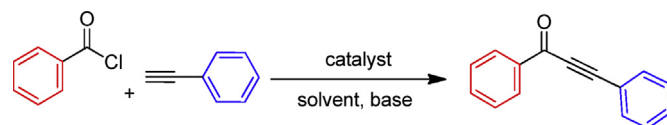


Fig. 1. Reaction picked for optimization.

acting both as a base and solvent. In comparison to the other methods this catalyst catalysed the reaction in a very low amount of catalyst loading without solvent. High yield, solvent-, phosphorus-, palladium free conditions and recyclability up to fifth cycle along with no heat requirement makes this protocol efficient greener and cost effective and may be applied in large scale industrial synthesis. The catalyst is air stable and remains effective for a long period without loss of its catalytic activity. This protocol gives high yield at short reaction time and to the best of our knowledge this is a novel catalyst used for the synthesis of ynones.

2. Experimental

2.1. Synthesis of cryptand and its copper complex

The cryptand derivative L1 was produced by the reaction of 1,2-bis(2-iodoethoxy)ethane (1a) and m-phenylenediamine (1b) as shown in Scheme 1. The CuCl₂-cryptand [2.2.Benzo] (C1) complex was synthesised by adding CuCl₂·2H₂O solution to the cryptand solution in ethanol. The synthetic procedure, characterization data and explanation of complexation were provided supporting information and were found to be coincide with the literature [31].

2.2. General procedure for synthesis of ynones by CuCl₂-Cryptand [2.2.Benzo] complex

For synthesis of ynones by using CuCl₂-Cryptand [2.2.Benzo] catalyst (Scheme 2) mixture of terminal alkyne (1.0 mmol), acid chloride (1.0 mmol), Et₃N (2.5 mmol) and 0.76 mol% CuCl₂-Cryptand [2.2.Benzo] was stirred at room temperature (26 °C) without any solvent under aerobic conditions. The progress of the reaction was monitored by TLC and after completion of the reaction 20 mL diethyl ether was added to the reaction mixture for two times and filtered it off. The residue was separated out and used for further reaction. The filtrated organic layers were washed with 50 mL of water for two times and dried with anhydrous Na₂SO₄, filtered and concentrated in rotary evaporator. The crude product thus obtained was further purified by preparative TLC using hexane and ethyl acetate in 9:1 ratio to obtain the desired product. The residual part

Table 1
Optimization conditions for the synthesis of ynones.^a

Entry	Catalyst (mol %)	Base	Temp (°C)	Solvent	Yield ^b %
Catalyst loading					
1	-	TEA	rt	-	N.R.
2	0.10				60
3	0.21	TEA	rt	-	82
4	0.42	TEA	rt	-	89
5	0.63	TEA	rt	-	91
6	0.76	TEA	rt	-	94
7	1.0	TEA	rt	-	94
Solvent effect					
8	1.0	TEA	rt	Water	Trace
9	1.0	TEA	rt	DMF	Trace
10	1.0	TEA	rt	DCM	29
11	1.0	TEA	rt	CH ₃ CN	40
12	1.0	TEA	rt	Toluene	42
13	1.0	TEA	rt	THF	trace
Test before complexation					
14	CuCl ₂ ·2H ₂ O	TEA	rt	-	Trace ^c
15	Cryptand [2.2.Benzo]	TEA	rt	-	N.R. ^d
Base effect					
16	1.0	-	rt	toluene	N.R.
17	1.0	K ₂ CO ₃	rt	-	N.R.
18	1.0	K ₂ CO ₃	60	-	N.R.
19	1.0	K ₂ CO ₃	60	toluene	12
20	1.0	Cs ₂ CO ₃	rt	-	N.R.
21	1.0	Na ₂ CO ₃	rt	-	N.R.
22	1.0	Na ₂ CO ₃	rt	toluene	Trace
23	1.0	KOH	rt	-	N.R.
24	1.0	KOH	rt	Toluene	10

Bold significance is to point out the amount of catalyst loading for the smooth progress of the reaction.

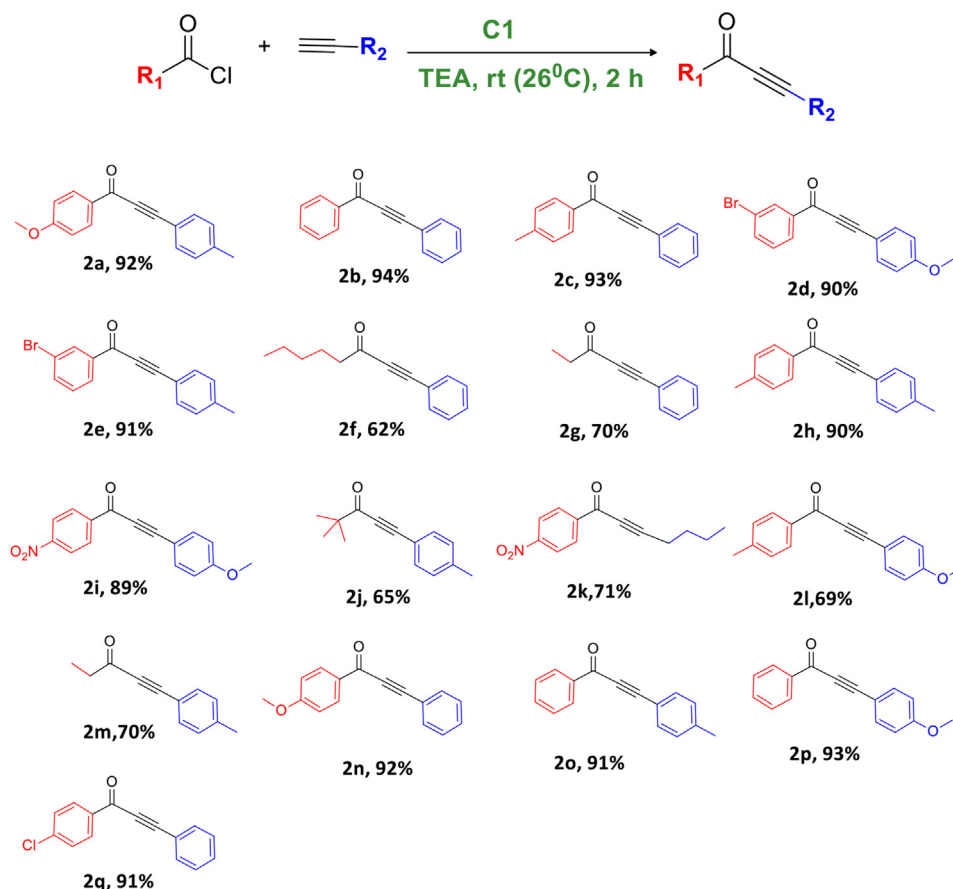
^a Reaction condition: benzoyl chloride 140 mg (1 mmol), phenylacetylene 102 mg (1 mmol), CuCl₂-cryptand [2.2.Benzo] (mol%), Base (2.5 mmol), solvent 2 mL; N.R. = no reaction; All reactions were carried out for 2 h.

^b Isolated yield.

^c 10 mg of CuCl₂·2H₂O.

^d 10 mg of cryptand [2.2.Benzo].

obtained after separation of organic layer was used for another reaction. All the synthesized derivatives of ynones were characterized by ¹H and



^aReaction conditions: Acyl chloride (1mmol), terminal Alkyne (1 mmol), CuCl₂-cryptand[2.2.Benzo] (0.76 mol%), TEA (2.5 mmol), All reactions were carried out for 2 hrs.
^bisolated yield.

Fig. 2. CuCl₂-Cryptand[2.2.Benzo] catalysed synthesis of various Ynones.^{ab}

¹³C NMR spectroscopy.

3. Results and discussion

Initially, we selected benzoyl chloride and phenylacetylene as a model substrate for the optimization of reaction conditions (Fig. 1). To evaluate the best condition for synthesis of ynones, we studied the effect of various parameters like catalyst loading, solvent, base and temperature. First, we optimized the reaction for catalyst loading, the reaction was carried out without catalyst (Table no. 1, entry 1) and realized that no conversion of the reaction. Next, we carried out the model reaction with various amount of catalysts loading (Table 1, entry 2–7) and was observed that 0.76 mol % of the catalyst was the best amount to catalyse the reaction and provided 94% yield of 2a. Subsequently we performed solvent optimization (Table 1, entry 8–13) on the model reaction and found that solvent less condition gave the best yield. Among the solvents toluene (Table 1, entry12) gave yield up to 42 %. Next, we carried the reaction only with CuCl₂·2H₂O (Table 1, entry 14) and Cryptand [2.2. Benzo] (Table 1, entry 15) and it was found that the reaction gave trace amount of yield in former but in the later case the reaction did not proceed. Thereafter, we studied the reaction without using any base in toluene solvent and it was observed that the reaction did not proceed (Table 1, entry 16). After that, we studied the effect of various bases like trimethylamine, K₂CO₃, Cs₂CO₃, Na₂CO₃, KOH on the model reaction (Table 1, Entry 17–24) also study the temperature and solvent effect with these bases in Table 1 entry 18–19, observed that these bases did not

	Pd-nps-PPS ^{ref 28d} 50°C, 12hrs, Toluene, TEA
	Nano Cu/Cu ₂ O ^{ref 20d} 90 °C, 24hrs, Toluene,
	Cu-nps/silicagel ^{ref 20a} 40°C, overnight, TEA, neat
	PdCl ₂ (PPh ₃) ₂ /CuI ^{ref 28c} 65°C, 4hrs, K ₂ CO ₃
	Paladacycle catalyst ^{ref 28a} 110°C, 1hrs, Toluene, TEA
	CuI/C22 ^{ref 20b} 60°C, 1hrs, neat, TEA
	CuNPs@MP-3 ^{ref 20c} 40°C, 8hrs, TEA
	NS-MCM-41-Pd/CuI ^{ref 28l} 50°C, 36hrs, N ₂
	TEA, rt, 2 hrs. Our work
	CuCl₂-cryptand[2.2.Benzo]

Fig. 3. Comparison of previous reported works with our work.

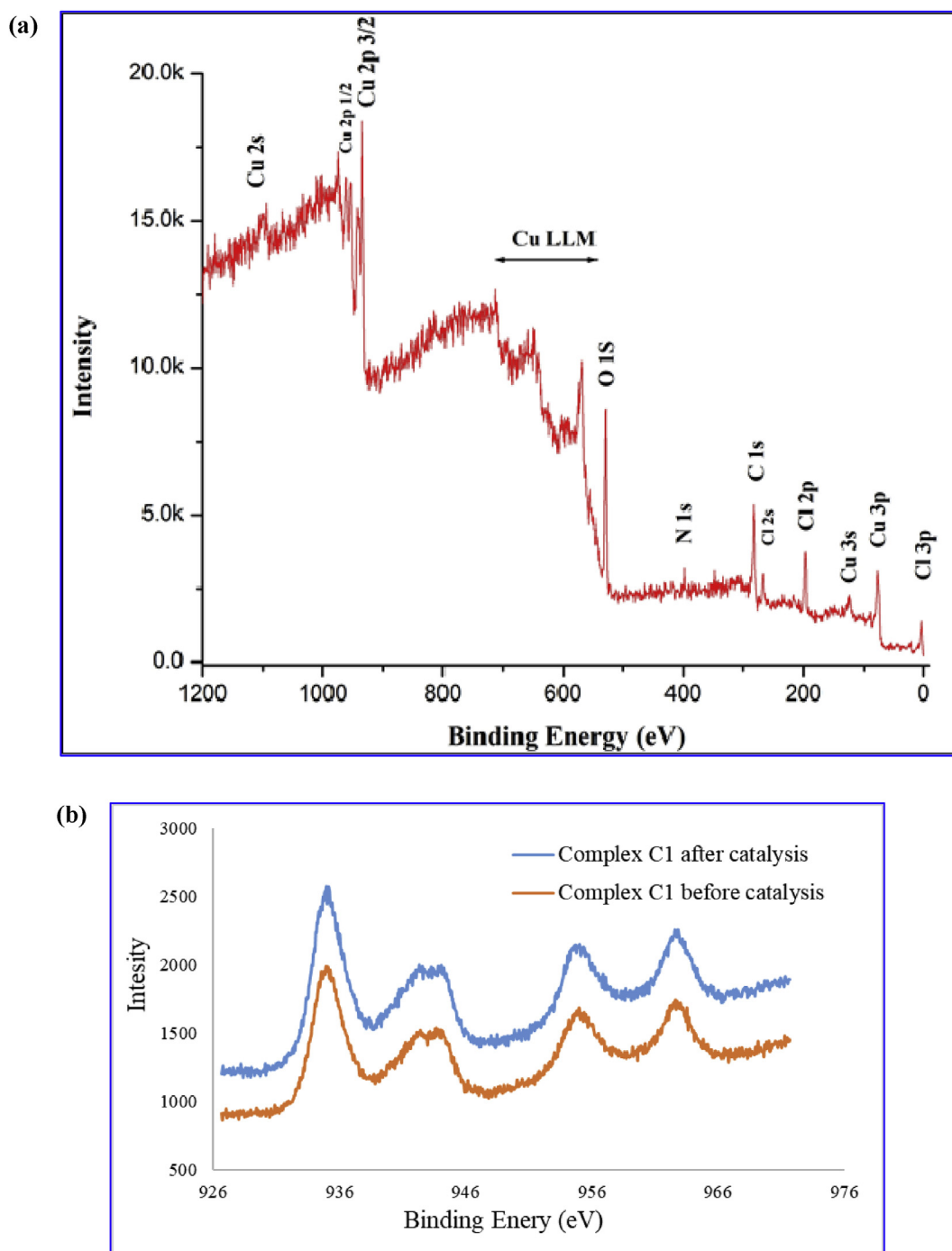


Fig. 4. (a) XPS survey scan of complex C1, (b) High resolution XPS spectra of Complex C1 before and after catalysis.

catalyse the reaction even in presence of solvent while TEA gives excellent yield of the desired product (Table 1 entry 7) without any solvent.

Thus, TEA (2.5 mmol), 0.76 mol % of CuCl_2 -cryptand [2.2.Benzo] catalyst and stirred at room temperature for 2 h are the best conditions for synthesis of ynones. With this optimized conditions of newly adopted efficient protocol we extended our studies to different substrates of acyl chloride and terminal alkyne (Fig. 2). The reaction with various derivatives of arylacetylene with substituents at the para-positions proceeded smoothly (Fig. 2). Moreover, benzoyl chloride substituted with $-\text{Me}$, $-\text{OMe}$, $-\text{Cl}$, $-\text{Br}$ and $-\text{NO}_2$ also provided good yields of the corresponding ynones. Aliphatic acyl chloride derivatives which generally give very low yields, this catalyst pushed these reactions to give good yields. The outcome in Fig. 2 established that the coupling of various

derivatives of acyl chloride and terminal alkyne catalyzed by the cryptand complex gives very good yield in a very short time period.

In Fig. 3, we demonstrated the comparison of our CuCl_2 -cryptand [2.2.Benzo] complex catalyzed method for the synthesis of ynones over existing protocols. As appeared in Fig. 3, current condition has the extraordinary preferred position over the existing methods.

XPS analysis was also executed to know the oxidation state of the CuCl_2 -cryptand [2.2. Benzo] complex (Fig. 4). In the survey scan Fig. 4 (a), all index peak corresponds to Cu, O, N, C and Cl, which confirms the presence of all these elements in the synthesized complex. The survey scan spectrum shows photoelectron peak of Cu 3s, Cu 2p, Cu 3p, Cu LLM auger for copper, O 1s for oxygen, N 1s for nitrogen, Cl 2s, Cl 3p, Cl 2p for chlorine and C 1s for carbon. High resolution XPS spectra shows characteristic main

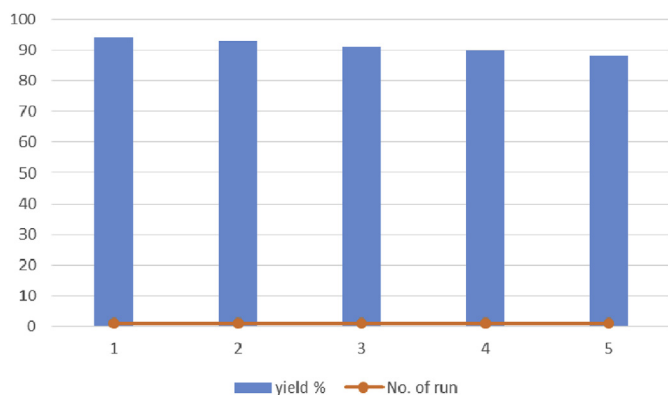


Fig. 5. Recyclability test of the catalyst.

peak at 934.8 eV and two satellite peak at 942.1 eV and 943.5 eV for Cu $2p_{3/2}$, another main peak and satellite peak observed for Cu $2p_{1/2}$ at 954.8 eV and 962.55 eV respectively [32]. From all of these data it is confirmed that copper metal present in the complex **C1** is in +2 oxidation state.

There are several copper catalysed methodologies for the synthesis of ynones²⁰ but the mechanism is not sure till-date. From GC-MS analysis it is evident that no homo-coupling of terminal alkynes were observed in the reaction mixture catalysed by CuCl₂-cryptand [2.2.Benzo] as the same was observed in the reaction of catalyzed by PdCl₂ (for GC-MS spectra see ESI Figs. S9 and 10). For the search role of the catalyst, we performed the XPS analysis of the complex after catalysis [Fig. 4 (b)], comparison with the high-resolution XPS spectra of cryptand complex (**C1**) before catalysis showed that the oxidation state of the complex did not change after catalysis, which remain same as Cu²⁺.

As the catalyst is heterogeneous, the catalyst was separated out from reaction mixture easily by centrifuging at 1200 rpm and washed with water for several times. This catalyst was reused in coupling reaction and established that it could be recycle up to 5th times. A small decrease in each catalytic cycle was observed may be due to loss of catalyst during the process of recovery as it confirmed by weighing the catalyst after each cycle [Fig. 5].

4. Conclusion

In conclusion a mild and efficient palladium-, phosphorus-, solvent-free protocol was developed successfully for synthesis of ynones via coupling of terminal alkyne and acyl chloride catalyzed by a novel CuCl₂-cryptand [2.2.Benzo] complex at room temperature without any additives. The advantages of the current method include, mild reaction conditions, air stable catalyst, short reaction time, broad substrate scope and high yields. A wide-ranging substrate of acyl chlorides and terminal alkynes were converted to their corresponding Ynones with excellent yield. Moreover, the catalyst can be easily separated and can be reused up to five times without any significant loss of its catalytic activity.

Declarations

Author contribution statement

Bolin Chetia: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

Sankar J Bora: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

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