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Palladium(II) on 4 Å Molecular Sieves: A Simple and Reusable Catalyst for the Preparation of Ynones

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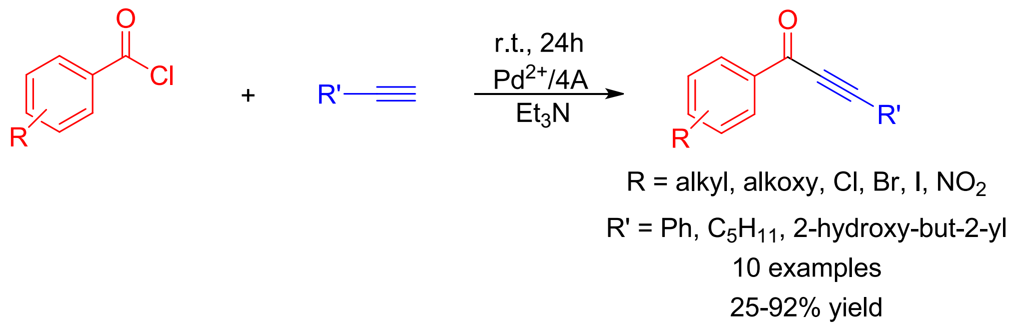
Abstract

Pd^{2+} on 4 Å molecular sieves support has been prepared and investigated. The catalyst has successfully been used in the reaction of acyl chlorides and terminal alkynes yielding ynones. The catalyst can be reused without significant loss of activity.

Graphic Abstract



Keywords Palladium · 4 Å molecular sieves · Ynones · Heterogeneous catalysis

1 Introduction

Ynones are the analogues of benzalacetophenone and form an important group of organic chemical substances, since they are key synthetic intermediates of a variety of biologically active heterogeneous compounds [1–11]. Ynones are widely used as anti-inflammatory and anticarcinogenic [12] agents. They are also important intermediates in the synthesis of dyes for luminescent solar concentrators [13–15].

Due to their importance several synthetic routes were developed for their synthesis, such as the oxidation of alkynes [16–18], propargylic alcohols [19], the reaction of terminal alkynes with nitriles [20], cross-coupling reactions of terminal alkynes with organic halides in the presence of carbon monoxide gas [21–23]. However the most important process is the reaction between terminal alkynes and carboxylic acid derivatives called the acyl Sonogashira reaction. The acyl Sonogashira reaction is usually performed in the presence of a palladium catalyst, a ligand (mostly phosphorous compounds) and CuI [24–26].

Several catalytic methods were developed for this reaction using palladium, copper or bimetallic catalysts. Ynones were synthesized in the presence of copper or palladium nanoparticles [27–34] and different supported metal complexes [35, 36]. The use of tin silicates was also reported [37]. As a copper- and palladium-free method a polystyrene-supported zinc bromide-ethylene diamine complex was described for the reaction [38].

These methods have their advantages and disadvantages, but an efficient heterogeneous catalytic method may be a good alternative.

Our group has been working on the preparation of different supported metal catalysts and the elaboration of

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various heterogeneous catalytic reactions. Methods have been developed for the palladium-catalysed cross-coupling reactions, e.g. Pd^0 on Mg-La mixed oxide in the Heck- [39], Sonogashira- [40] and Suzuki-coupling [41], or palladium-copper bimetallic catalysts in the Suzuki-coupling [42, 43]. In continuation of our interest, in this paper we present our results obtained with Pd^{2+} on 4 Å molecular sieves support in the cross-coupling reaction of different acyl chlorides and terminal alkynes.

2 Experimental

Morphology of the catalyst samples was investigated by a JEOL 6380LVa (JEOL, Tokyo, Japan) type scanning electron microscope and elemental mapping was also accomplished using the energy-dispersive X-ray detector of the equipment. Each specimen was fixed by conductive double-sided carbon adhesive tape and sputtered by gold (using a JEOL 1200 instrument). Applied accelerating voltage and working distance were between 15 and 30 kV and 10 and 12 mm, respectively.

The nitrogen adsorption/desorption isotherms were measured at − 196 °C with a computer-controlled Nova 200e (Quantachrome) instrument. The apparent surface area (SBET) was calculated using the Brunauer–Emmett–Teller (BET) model. Prior to the adsorption measurement, the samples were evacuated at 110 °C for 24 h. ^{1}H and ^{13}C NMR spectra were made on BRUKER Avance-300 instrument using TMS as an internal standard in $CDCl_3$.

GC–MS measurements were performed on an Agilent 6850-GC-5975C-MS chromatograph using a 15 m × 0.25 mm column with a 0.25 mm HP-5MS layer. The initial temperature of the column was 100 °C and it was heated up to 325 °C with a 5 min run time. The carrier gas was He and the operation mode was split.

All compounds and solvents were purchased from Merck Hungary Ltd.

2.1 Preparation of the Catalysts

2.1.1 Preparation of the Pd^{2+}/4A Catalyst

Four Angstrom molecular sieves (4A) were impregnated with $PdCl_2$ as follows: 1 mmol (0.18 g) of $PdCl_2$ was dissolved in 100 ml of deionised water and stirred with 1 g 4A at room temperature for 24 h. The solid was filtered, washed with deionised water and with acetone, then dried in an oven at 150 °C for 1 h. Samples were heated at 120 °C for 1 h before the reaction.

2.1.2 Preparation of the Cu^{2+}/4A Catalyst

The Cu^{2+}/4A catalyst was prepared according to 2.1.1, where instead of $PdCl_2$ $CuCl_2$ (0.17 g) was used.

2.1.3 Preparation of the Pd^{2+}/Cu^{2+}/4A Catalyst

The bimetallic catalyst was prepared with the co-impregnation method as described earlier [42]. $CuCl_2$ and $PdCl_2$ (5:1 molar ratio) were added simultaneously to the suspension of 4A in deionised water. After the filtration the thermal treatments were the same as described in 2.1.1.

2.2 Typical Reaction Conditions

2.2.1 General Procedure for the Preparation of Ynones

Acyl chloride (1.1 mmol), a terminal alkyne (1 mmol), triethylamine (1.05 mmol) and the catalyst (0.1 g) were stirred in a test tube at room temperature for 24 h. After completion, the reaction mixture was diluted with acetone, the solid was filtered and washed with acetone, then the filtrate was evaporated. The residue was diluted with diethyl ether, extracted with a saturated K_2CO_3 solution. The organic phase was dried over Na_2SO_4 and the solvent was evaporated. The crude product was purified via column chromatography using hexane:ethyl acetate 10:1 as the eluent. The products were subjected to ^{1}H and ^{13}C NMR spectroscopy.

2.2.2 Characterization of the Products

1,3-Diphenyl-2-propyn-1-one (3a) [44, 45] Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.39–7.42 (t, 2H); 7.46–7.47 (d, 1H); 7.49–7.52 (t, 2H); 7.60–7.63 (t, 1H); 7.67–7.68 (d, 2H); 8.21–8.23 (d, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 86.9; 93.1; 120.1; 128.6; 128.7; 129.6; 130.8; 133.1; 134.1; 136.9; 178.

1-(4-Methylphenyl)-3-phenyl-2-propyn-1-one (3b) [46] Yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 2.44 (s, 3H); 7.30–7.31 (d, 2H); 7.40–7.43 (t, 2H); 7.46–7.49 (m, 1H); 7.67–7.69 (d, 2H); 8.11–8.12 (d, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 21.8; 87.0; 92.6; 120.3; 128.7; 129.4; 129.7; 130.7; 133.0; 134.7; 145.2; 177.7.

1-(4-tert-Butylphenyl)-3-phenyl-2-propyn-1-one (3c) [47] Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 1.38 (s, 9H); 7.39–7.42 (t, 2H); 7.45–7.48 (m, 1H); 7.51–7.54 (m, 3H); 7.66–7.68 (d, 2H); 8.15–8.17 (d, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 31.1; 35.3; 87.1; 92.6; 120.3; 125.6; 128.7; 129.6; 130.5; 133.0; 134.6; 158.1; 177.7.

1-(2-Ethoxyphenyl)-3-phenyl-2-propyn-1-one (3d) [48] Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 1.42–1.47 (t, 3H); 4.13–4.19 (q, 2H); 6.96–7.03 (m, 2H); 7.34–7.43 (m, 3H); 7.46–7.52 (m, 1H); 7.58–7.61 (d, 2H); 7.98–8.01

(dd, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 14.7; 64.5; 89.6; 91.5; 113.1; 120.2; 120.8; 127.1; 128.6; 130.3; 131.9; 132.7; 134.9; 159.2; 176.9.

1-(3-Chlorophenyl)-3-phenyl-2-propyn-1-one (3e) [49] Yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.44–7.47 (m, 3H); 7.49–7.52 (m, 1H); 7.59–7.61 (m, 1H); 7.69–7.70 (m, 2H); 8.10–8.12 (m, 1H); 8.17–8.18 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 86.5; 93.9; 119.8; 127.7; 128.8; 129.4; 129.9; 131.1; 133.2; 134.0; 135.0; 138.4; 176.5.

1-(4-Bromophenyl)-3-phenyl-2-propyn-1-one (3f) [50] Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.40–7.45 (m, 5H); 7.63–7.66 (dd, 2H); 7.69–7.71 (dd, 1H); 8.06–8.08 (dd, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 87.9; 94.2; 120.0; 121.2; 127.4; 128.7; 130.9; 131.9; 133.1; 133.5; 134.9; 137.3; 177.5.

1-(4-Nitrophenyl)-3-phenyl-2-propyn-1-one (3 h) Brown solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.45–7.48 (t, 2H); 7.53–7.56 (t, 1H); 7.71–7.73 (d, 2H); 8.23–8.29 (m, 1H); 8.38 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 86.6; 95.4; 119.4; 123.4; 123.9; 128.9; 130.5; 130.9; 131.5; 133.3; 175.9.

1-Phenyl-2-octyn-1-one (3i) [46] Brown solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 0.91–0.95 (t, 3H); 1.31–1.51 (m, 4H); 1.64–1.73 (m, 2H); 2.47–2.52 (t, 2H); 7.45–7.60 (m, 2H); 7.65–7.70 (m, 1H); 8.13–8.17 (t, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 13.9; 19.2; 22.1; 27.5; 31.1; 79.7; 96.9; 128.5; 129.6; 133.8; 136.9; 178.3.

4-Hydroxy-4-methyl-1-phenyl-2-hexyn-1-one (3j) Brown solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 1.1–1.15 (t, 3H); 1.63 (s, 1H); 1.80–1.96 (m, 2H); 7.44–7.49 (m, 2H); 7.58–7.63 (m, 1H); 8.11–8.13 (d, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 8.9; 28.6; 36.1; 68.9; 81.1; 97.5; 120.9; 126.3; 127.2; 128.5; 128.6; 129.6; 130.2; 133.7; 134.2; 177.9.

3 Results and Discussion

During our research on the elaboration of new heterogeneous catalytic methods several different supports were used (e.g. Mg-La mixed oxide, different types of Mg–Al hydrotalcites and 4A molecular sieves). Among them, the 4A molecular sieves has several excellent properties. It is easily accessible from commercial sources and it is not sensitive to the atmospheric carbon dioxide in contrary to the mixed oxides or the different hydrotalcites. The different supported metal catalysts can easily be prepared from 4A and the corresponding metal salt in deionised water (see Experimental). During our research we have successfully applied 4A-supported metal catalysts in different organic syntheses, *e.g.* Cu^{2+}/4A in the A_3-coupling yielding propargylamines [51], as well as in the selective 1,4-additon of Grignard compounds to chalcones [52]. La^{3+}/4A [53, 54] or Ti^{4+}/4A [55] were successfully used in multicomponent reactions yielding heterocycles. In this acyl Sonogashira reaction Pd^{2+}/4A gave good results, thus this was used in the further experiments, no other support has been tested.

A homogeneous catalytic Sonogashira reaction is generally carried out with Pd(0) catalysts in the presence of different ligands. In heterogeneous catalytic methods Pd(II) compounds may also have good catalytic activity, as shown in our preliminary experiments. A similar effect has already been observed during the arylation of pyrrole with aryl halides in the presence of 4A-supported copper catalysts [56]. A Pd^0/4A catalyst is more sensitive, requires an inert atmosphere and it has pyrophoric properties, thus Pd^{2+}/4A can be used easier.

The structure of the Pd^{2+}/4A catalyst was investigated by scanning electron microscopy (SEM) (Fig. 1). The distribution of the palladium on the surface of the support was also examined. According to the EDS measurement the palladium content is 9.32w/w% and the palladium is evenly distributed on the surface of the support (Fig. 2). The palladium content of the catalyst measured by ICP-OES was 10%, which is in accordance with the theoretical value (9.6%). Comparing the results of the EDS and the ICP-OES measurements, palladium is located on the surface of the catalyst.

The results of the BET measurement showed a significant decrease of the surface from 800 (pure support) to 59 m^2/g. This also verifies the presence of the palladium on the surface.

In the literature the preparation of ynones by the reaction of acyl chlorides and terminal alkynes was described mostly with copper, palladium or bimetallic catalysts. So first, we examined our molecular sieve supported Pd, Cu and Pd/Cu catalysts in a model reaction of benzoyl chloride and phenylacetylene, in 1,4-dioxane, in the presence of triethylamine

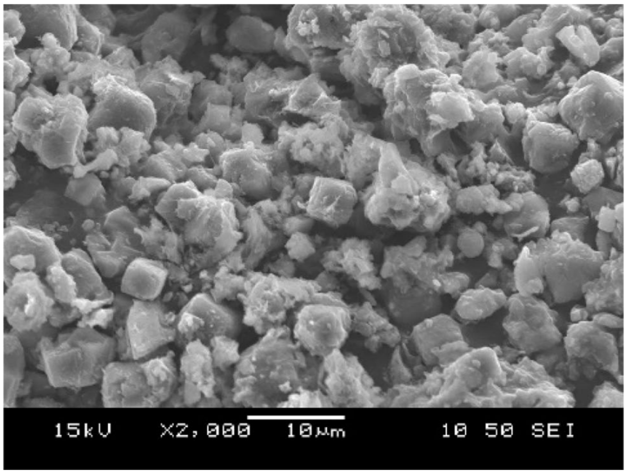


Fig. 1 SEM image of the Pd^{2+}/4A catalyst

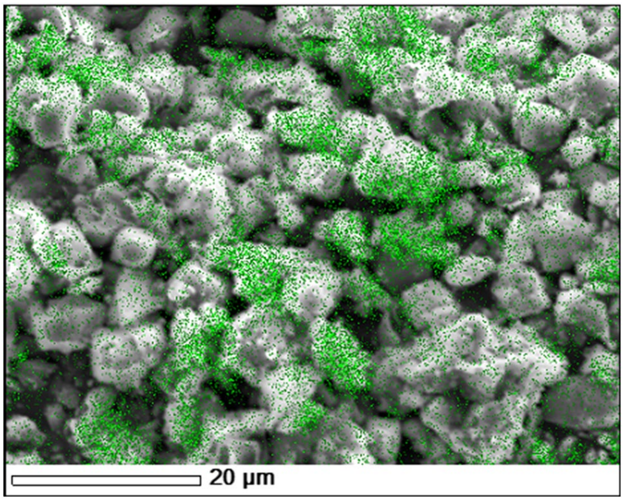


Fig. 2 Palladium on the surface of the support (SEM EDS image of the $Pd^{2+}/4A$ catalyst)

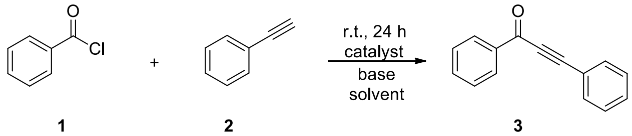
(Table 1, entries 1–3). In our previous experiments (e.g. [43, 53].) generally 0.1 g catalyst/1 mmol substrate was the most efficient ratio in the case of the 4A-supported catalysts, thus we used the same amount in these experiments. This amount is higher than which are used in the homogeneous methods, but the heterogeneous catalyst can be fully recovered from the reaction mixture and it can be reused several times. We found that only the $Pd^{2+}/4A$ catalyst was efficient in the acyl Sonogashira reaction. With the bimetallic $Pd^{2+}/Cu^{2+}/4A$ catalyst no product was formed. This catalyst has been widely investigated earlier [42, 43]. It was found, that during the impregnation a Pd/Cu 1:1 alloy was formed which was responsible for the catalytic activity of this catalyst. The inactivity of this bimetallic catalyst in this reaction might be explained by the lower activity of this alloy. The reaction in the presence of the $Cu^{2+}/4A$ catalyst also gave a very low yield. The weak results obtained with these two catalysts may indicate that copper on 4A support is not active enough in this reaction. Based on these results all further experiments were carried out with $Pd^{2+}/4A$.

Next we examined the effect of the base on the yield of the reaction. According to the literature and the earlier experiences we tried K_2CO_3 and triethylamine. The advantage of the K_2CO_3 would be that it can be easily separated from the reaction mixture by filtration. However, triethylamine was found to be more effective in this reaction (Table 1, entries 3 and 4). In this case, the catalyst needs to be washed with ethanol before it can be reused, to remove the triethylamine hydrochloride salt.

After the suitable base was found, the reaction was carried out in different solvents. The best result could be achieved if no solvent was used (Table 1, entry 7).

Under the optimized reaction conditions a wide range of acyl chlorides and a few terminal alkynes were tested in the reaction (Table 2). The desired products were obtained in 25–92% yields. Benzoyl chloride and derivatives bearing electron-donating or electron-withdrawing groups were tested in the reaction. In case of the alkyl- and nitro-substituents the desired products were isolated in good to excellent yields (Table 2, entries 2, 3 and 8). Using acyl chlorides with halide substituents the yields were significantly lower and in case of the 2-iodobenzoyl chloride no product was formed (Table 2, entries 5–7). In this case the reaction mixture contained mainly 2-iodobenzoic acid. The reason for these low yields can be the reactivity of the halide substituents on the acyl chlorides. The amount of the desired product decreases with the increasing reactivity of the halide substituents. Another influencing factor could be the position

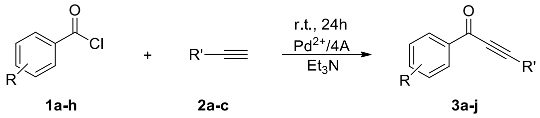
Table 1 Optimization of the reaction conditions in the model reaction of benzoyl chloride and phenylacetylene

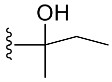


Entry	Catalyst	Base	Solvent	Yield (%)
1	$Pd^{2+}/Cu^{2+}/4A$	Et_3N	1,4-dioxane	0
2	$Cu^{2+}/4A$	Et_3N	1,4-dioxane	5
3	$Pd^{2+}/4A$	Et_3N	1,4-dioxane	70
4	$Pd^{2+}/4A$	K_2CO_3	1,4-dioxane	50
5	$Pd^{2+}/4A$	Et_3N	toluene	43
6	$Pd^{2+}/4A$	Et_3N	acetonitrile	32
7	$Pd^{2+}/4A$	Et_3N	neat	83

Reaction conditions: 1.1 mmol benzoyl chloride, 1 mmol phenylacetylene, 1.05 mmol base, 0.1 g catalyst (10 mol% metal), 3 mL solvent, r.t., 24 h

Table 2 The reaction of acyl chlorides and terminal alkynes in the presence of triethylamine and Pd^{2+}/4A catalyst



Entry	R	R’	Yield (%)[a]
1	H	Ph	83
2	4-CH_3	Ph	64
3	4-*tert*-C_4H_9	Ph	73
4	2-OC_2H_5	Ph	38
5	3-Cl	Ph	38
6	4-Br	Ph	25
7[c]	2-I	Ph	0
8[c]	4-NO_2	Ph	92
9	H	C_5H_{11}	35[b]
10	H		50[b]

Reaction conditions: 1.1 mmol acyl chloride, 1 mmol terminal alkyne, 1.05 mmol triethylamine, 0.1 g catalyst (10 mol% Pd), r.t., 24 h

[a] Isolated yield

[b] Determined by GC–MS, the product was not isolated

[c] In 0.5 mL 1,4-dioxane

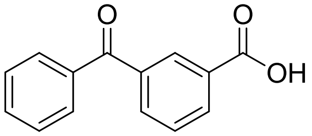


Fig. 3 3-Benzoylbenzoic acid by-product

of the halide substituent. In case of the iodobenzoyl chloride the iodine atom is in *ortho*-position and therefore the reaction can be sterically hindered. In the reaction of 2-ethoxybenzoyl chloride the desired product was obtained only in 38% yield (Table 2, entry 4) proving also a steric hindrance of the *ortho* substituents. In case of 2-iodobenzoyl chloride and 4-nitrobenzoyl chloride 1,4-dioxane had to be added to the reaction mixture to assure the good miscibility.

Besides phenylacetylene, other terminal alkynes were investigated in the reaction. Using heptyne and 3-methyl-1-pentin-3-ol the desired products were formed in only 35% and 50% yield, respectively (calculated from the GC–MS spectra, Table 2, entries 9 and 10). In these cases a by-product in equivalent amount to the product was found. Based on the GC–MS (m/z at 226) and ^{13}C NMR spectra (peak at ca. 172 ppm) this by-product could be identified as 3-benzoyl-benzoic acid (Fig. 3), which can be formed in a Friedel–Crafts type reaction of benzoyl chloride. The two products could not be separated. Although our catalyst is basic in bulk phase, the acid sites on the surface formed by the incorporated metal may catalyse an S_EAr type reaction. This side reaction may become significant, if the reactivity of the alkyne is not high enough.

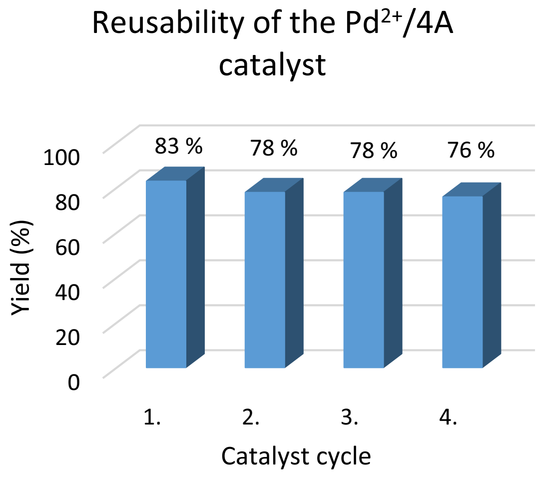


Fig. 4 The reusability of the Pd^{2+}/4A catalyst

The reusability of the catalyst was tested as well. Therefore, the catalyst filtered from the reaction mixture was washed with ethanol and dried at 120 °C for 1 h. Afterwards it was reused in another reaction. It was found, that the catalyst can be simply reused. The experiment was repeated 3 times and the results are shown in Fig. 4. The slight decrease in the yield after the first run can be explained with triethylamine hydrochloride residues precipitated to the surface of the catalyst, which can cover the active metals sites.

4 Conclusion

In conclusion, the Pd^{2+}/4A catalyst proved to be efficient in the reaction of acyl chlorides and terminal alkynes. The desired ynones were formed in all cases, except with 2-iodobenzoyl chloride. However, in some cases a large amount of a by-product was formed. A great advantage of the catalyst is the easy preparation and recovery.

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Compliance with Ethical Standards

Conflict of interest The authors declare that they have no conflict of interest.

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