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Efficient and Reusable CuI/1,10-Phenanthroline-Catalyzed Oxidative Decarboxylative Homocoupling of Arylpropiolic Acids in Aqueous DMF

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An efficient method for synthesis of 1,3-diynes through the CuI/1,10-phenanthroline-catalyzed oxidative decarboxylative homocoupling of aryl pioprolic acids in aqueous DMF has been developed. The catalytic system was suitable for a variety of arylpropiolic acids, and the corresponding 1,3-diynes could be prepared in high yields. The catalytic system was recovered from the organic products by filtration and its aqueous DMF filtrate retained good activity even after at least four cycles of use.

Introduction

Conjugated 1,3-diynes are important building blocks that occur widely in natural products,[1] industrial and pharmaceutical intermediates,[2] as well as in electronic and optical materials, and elsewhere.[3] Since Glaser reported the synthesis of 1,3-diynes by Cu^{I}-catalyzed oxidative homocoupling reaction of terminal alkynes in 1869,[4] copper-catalyzed oxidative homocoupling reactions of terminal alkynes or cross-coupling reactions of terminal alkynes with 1-haloalkynes have been one of the most established methodologies for preparing both symmetric and unsymmetrical 1,3-diynes in organic synthesis.[5–7] Usually, terminal alkynes are used as substrates in these methods.[8–13] The alkynyl carboxylic acid, which is common, stable and easy to handle and store, may be an effective alternative. 1,3-Diyne derivatives could also be obtained by the oxidative decarboxylative homocoupling of arylpropiolic acids. For example, Yu, Jiao et al. reported that the CuI/1,10-phenanthroline catalytic system could catalyze decarboxylative cross-coupling of propiolic acids with terminal alkynes to produce 1,3-diynes in moderate yields (Scheme 1, Eq. A) at 120 °C.[14] Lee et al. reported that 1,3-diynes could be obtained by the "one-pot" reaction of aryl iodides with propiolic acid catalyzed by a Pd/Cu system (Scheme 1, Eq. B).[15] Kim et al. reported one-pot synthesis of 1,4-disubstituted 1,3-diynes from iodoarenes and propiolic acid using a Sonogashira reaction followed by Pd-catalyzed decarboxylative homocoupling in the presence of Ag_2CO_3 at 130 °C (Scheme 1, Eq. C).[16] Fu et al. reported that copper-catalyzed decarboxylative coupling of potassium alkynyl carboxylates with 1,1-dibromo-1-alkenes could produce 1,3-diynes (Scheme 1, Eq. D).[17] However, the coupling reactions mentioned above were all carried out in organic solvents, and/or required the addition of the oxidant (e.g. Ag_2CO_3) and high excesses of base. From a sustainable chemistry viewpoint, the use of water or aqueous solvents instead of volatile organic solvents is particularly important. Therefore, the development of simple inorganic copper catalysts[18] that can facilitate the decarboxylative coupling reaction of propiolic acids in aqueous media or aqueous organic solvent mixtures using air as an oxidant agent would be highly desirable.

Although C–C bond formation could be facilitated in aqueous media or in aqueous solvents,[19] homocouplings of terminal alkynes proceed more slowly in an aqueous medium than in organic solvents, which may be due to the fact that most organic alkynes are insoluble in water. To the best of our knowledge, there have been only two reports detailing the synthesis of 1,3-diynes by oxidative homocoupling reactions of terminal alkynes in water. For instance, Tsai et al. reported that $CuSO_4 \cdot 5H_2O$/cationic 2,2-bipridyl system or cationic 2,2-bipridyl/Pd^{II}/CuI systems catalyze the homocoupling of terminal alkynes in water using I_2 or air as the oxidant.[20,21] The alkynyl carboxylic acid, which contains hydrophilic carboxylate group,[22] can dissolve in water or aqueous organic solvents. Could a copper catalyst catalyze decarboxylative homocoupling of alkynyl carboxylic acids to produce 1,3-diynes in aqueous organic solvents or even aqueous media? Very recently, we have developed a ligand-free Cu-catalyzed oxidative decarboxylative homo-

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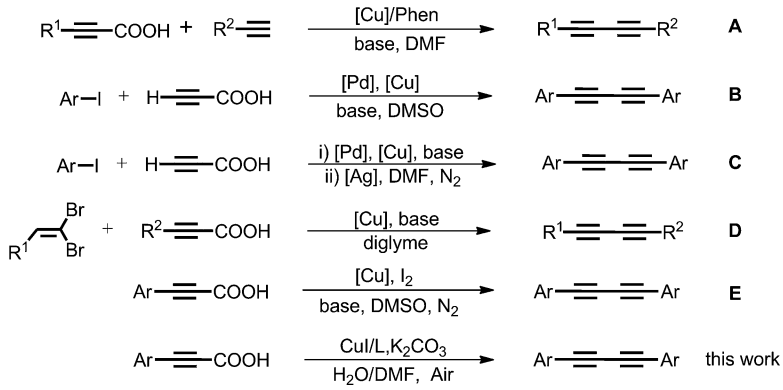


Scheme 1. The synthesis of 1,3-diynes by transition metal-catalyzed decarboxylative coupling reactions.

coupling of arylpropiolic acids (Scheme 1, Eq. E) at lower reaction temperature (50 °C) using DMSO as a solvent and I_2 as an oxidant agent.[23] These limitations prompted us to further investigate new convenient methodologies to generate 1,3-diynes. Herein, we report a new and efficient system for preparing 1,3-diyne derivatives by oxidative decarboxylative homocoupling of arylpropiolic acids using CuI/1,10-phenanthroline as the catalyst system and air as the oxidant in aqueous DMF. The components of this catalytic system could be conveniently and effectively reused for at least four times.

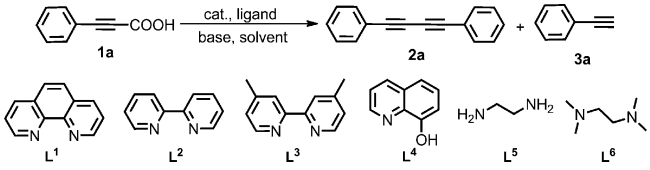
Results and Discussion

We chose phenylpropiolic acid (**1a**) as a model system to optimize reaction conditions (Table 1). Initially, we carried out the reaction of **1a** with CuI (10 mol-%), 1,10-phenanthroline (**L[1]**, 20 mol-%), K_2CO_3 (1.0 equiv.) in 2 mL of H_2O at 100 °C. The mixture gradually turned into a homogeneous blue solution, implying that arylpropiolic acid could be dissolved in water in the presence of base. After 20 h, desired product 1,4-diphenylbuta-1,3-diyne (**2a**) could be obtained in 28% yield coupled with ethynylbenzene (**3a**) (5% yield) (Table 1, Entry 1). This preliminary result implied that CuI/**L[1]** might initiate the oxidative decarboxylative homocoupling of **1a** using air as an oxidant in water to produce **2a**. However, the relatively low yield showed that H_2O may not be the optimal solvent. When the reactions were carried out in different organic solvents such as DMF, DMSO and CH_3CN, the yield of decarboxylation product **3a** increased dramatically but the yield of coupling product **2a** decreased (20% for DMF, 13% for DMSO and 9% for MeCN) (Table 1, Entries 2–4). Considering the structure of the arylpropiolic acid containing the hydrophilic carboxylate group and the hydropholic aryl group, the aqueous organic solvent mixtures may be more suitable for oxidative decarboxylative homocoupling of arylpropiolic acid. When the reactions were performed in H_2O/DMF (v/v = 1:1) mixtures, complete conversion of **1a** into **2a** was achieved within 20 h in air at 100 °C (Table 1, Entry 5). However, the catalyst showed lower activity in aqueous DMSO or MeCN. As shown in Table 1, the optimal ratio of H_2O and DMF was determined to be 1:1 (Table 1, Entries 8 and 9). Other ligands **L[2]**–**L[6]** were also evaluated (Table 1, Entries 10–14) although **L[1]** proved to be the most effective. The controlled reaction showed that the organic ligand was necessary for such an oxidative decarboxylative homocoupling reaction. The catalyst was inactive in the absence of **L[1]** (Table 1, Entry 15). In the absence of CuI, **L[1]** ligand failed to catalyze the oxidative decarboxylative homocoupling reaction even with increased loadings of base (Table 1, Entries 16 and 17). Several other copper salts were evaluated as catalysts for the oxidative decarboxylative homocoupling of phenylpropiolic acid (Table 1, Entries 18–21); CuI was superior to the other salts examined (Table 1, Entry 5). Among a set of bases (e.g., KOH, Na_2CO_3, $NaHCO_3$, $KHCO_3$, K_2CO_3) (Table 1, Entries 22–25), K_2CO_3 was found to be optimal for carrying out the reaction in H_2O/DMF (Table 1, Entry 5).

We envisioned that catalyst loading may also have an impact on the catalytic activity. Not surprisingly, the product yield decreased from 99% to 89% when the catalyst loading was further reduced from 10 mol-% to 5 mol-% in H_2O/DMF (Table 1, Entries 5 and 27). The loading of the **L[1]** ligand might also affect catalytic activity. The product yield decreased slightly from 99% to 96% when **L[1]** loading was changed from 20 mol-% to 15 mol-% at 100 °C (Table 1, Entries 5 and 28). In addition, the reaction temperature influenced the coupling reaction. When the reaction temperature was decreased from 100 °C to 90 °C, the yield of **2a** was decreased slightly from 99% to 96% (Table 1, Entry 26).

On the basis of these optimization experiments, the optimized reaction conditions were identified as follows: CuI (10 mol-%) as the catalyst, **L[1]** (20 mol-%) as the labile ligand, K_2CO_3 (1.0 equiv.) as the base, and H_2O/DMF (v/v, 1:1) as the reaction solution. With these conditions in hand, we next began to examine the scope of the reaction. It was found that a variety of functional groups could be tolerated on the arylpropiolic acid including Me, Ph, MeO, MeCO, F, Cl, *t*Bu substituent groups. As shown in Table 2, oxidative decarboxylative homocoupling reactions proceeded well for all substrates examined and desired products were isolated in good to excellent yields. It appears that the *p*-, *m*-substituted groups on the phenyl moiety of arylpropiolic acids do not hamper the coupling reaction. Reactions of 3-(*p*-tolyl)-

Table 1. Optimizing the reaction conditions for the decarboxylative homocoupling reaction of phenylpropiolic acid.[a]

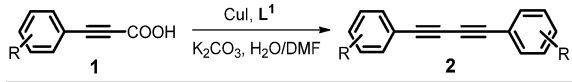


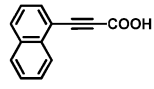
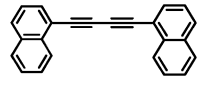
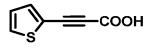
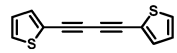
Entry	Cat.	Ligand	Base	Solvent	Yield[b] [%] 2a/3a
1	CuI	L^1	K_2CO_3	H_2O	28:5
2	CuI	L^1	K_2CO_3	DMF	20:86
3	CuI	L^1	K_2CO_3	DMSO	13:94
4	CuI	L^1	K_2CO_3	CH_3CN	9:94
5	CuI	L^1	K_2CO_3	H_2O/DMF[c]	99:0
6	CuI	L^1	K_2CO_3	H_2O/DMSO[c]	96:0
7	CuI	L^1	K_2CO_3	H_2O/MeCN[c]	14:78
8	CuI	L^1	K_2CO_3	H_2O/DMF[d]	97:0
9	CuI	L^1	K_2CO_3	H_2O/DMF[e]	46:0
10	CuI	L^2	K_2CO_3	H_2O/DMF[c]	95:0
11	CuI	L^3	K_2CO_3	H_2O/DMF[c]	98:0
12	CuI	L^4	K_2CO_3	H_2O/DMF[c]	49:12
13	CuI	L^5	K_2CO_3	H_2O/DMF[c]	15:48
14	CuI	L^6	K_2CO_3	H_2O/DMF[c]	trace:8
15	CuI		K_2CO_3	H_2O/DMF[c]	trace/27
16		L^1	K_2CO_3	H_2O/DMF[c]	0:0
17		L^1	K_2CO_3	H_2O/DMF[c,f]	0:0
18	CuBr	L^1	K_2CO_3	H_2O/DMF[c]	97:0
19	CuCl	L^1	K_2CO_3	H_2O/DMF[c]	86:0
20	$CuCl_2$	L^1	K_2CO_3	H_2O/DMF[c]	90:0
21	$Cu(OAc)_2$	L^1	K_2CO_3	H_2O/DMF[c]	94:0
22	CuI	L^1	KOH	H_2O/DMF[c]	97:0
23	CuI	L^1	Na_2CO_3	H_2O/DMF[c]	98:0
24	CuI	L^1	$KHCO_3$	H_2O/DMF[c]	96:0
25	CuI	L^1	$NaHCO_3$	H_2O/DMF[c]	94:0
26[g]	CuI	L^1	K_2CO_3	H_2O/DMF[c]	96:0
27[h]	CuI	L^1	K_2CO_3	H_2O/DMF[c]	89:0
28[i]	CuI	L^1	K_2CO_3	H_2O/DMF[c]	96:0

[a] Reaction conditions: phenylpropiolic acid (0.2 mmol), Cat. (10 mol-%), ligand (20 mol-%), solvent (2 mL), base (0.2 mmol) at 100 °C, for 20 h, in air. [b] GC yields. [c] $V_{water}/V_{organic\ solvent}$ = 1:1. [d] V_{water}/V_{DMF} = 2:1. [e] V_{water}/V_{DMF} = 3:1. [f] K_2CO_3 (0.4 mmol). [g] Reaction temperature: 90 °C. [h] 5 mol-% of CuI. [i] 15 mol-% of **L^1**.

propiolic acid, 3-(*m*-tolyl)propiolic acid or 3-(3,5-dimethylphenyl)propiolic acid produced the corresponding products in high yields (86%–90%). However, this reaction was sensitive to phenyl ring *o*-substitution and good yields were obtained for 3-(*o*-tolyl)propiolic acid (80% yield; entry 2), 3-(2-methoxyphenyl)propiolic acid (72% yield; Table 2, Entry 6) and 2,4,6-trimethyl phenylpropiolic acid (74% yield; Table 2, Entry 13), which may be ascribed to steric hindrance encountered during the course of homocoupling. The electronic nature of substituents on the arylpropiolic acid were also found to have an influence on the oxidative decarboxylative homocoupling reactions. Couplings with electron-deficient *p*-substituted phenylpropiolic acids were found to proceed in higher yields than those with more electron rich propiolic acids. For example, lower yields were obtained using arylpropiolic acids bearing electron-donating groups (Me, MeO, *t*Bu, Ph) (Table 2, Entries 4, 5, 7 and 8) relative to those bearing electron-withdrawing groups such as MeCO, F, and Cl (Table 2, Entries 9–11). In addition, the decarboxylative homocoupling of heteroatom-containing arylpropiolic acid also proceeded efficiently using the described catalytic system. For instance, couplings involving 3-(thiophen-2-yl)propiolic acid afforded anticipated product 1,4-di(thiophen-2-yl)buta-1,3-diyne in 91% yield (Table 2, Entry 15).

Table 2. Synthesis of 1,4-disubstituted-1,3-diynes catalyzed in aqueous DMF.[a]



Entry	Arylpropiolic acid	Product	Yield[b] (%)
1	R = H (**1a**)	**2a**	91
2	R = 2-Me (**1b**)	**2b**	80
3	R = 3-Me (**1c**)	**2c**	89
4	R = 4-Me (**1d**)	**2d**	90
5	R = 4-OMe (**1e**)	**2e**	89
6	R =2-OMe (**1f**)	**2f**	72
7	R =4-tBu (**1g**)	**2g**	84
8	R = 4-Ph (**1h**)	**2h**	81
9	R = 4-F (**1i**)	**2i**	95
10	R = 4-Cl (**1j**)	**2j**	93
11	R = 4-COMe (**1k**)	**2k**	92
12	R = 3,5-dimethyl (**1l**)	**2l**	86
13	R = 2,4,6-trimethyl (**1m**)	**2m**	74
14	 **1n**	 **2n**	89
15	 **1o**	 **2o**	91

[a] Reaction conditions: arylpropiolic acid (0.2 mmol), CuI (10 mol-%), **L^1** (20 mol-%), K_2CO_3 (0.2 mmol), H_2O/DMF (1 mL/1 mL), 100 °C, 20 h, in air. [b] Isolated yields.

Being insoluble in aqueous DMF, the desired products could be readily separated by filtration. Consequently, the remaining aqueous DMF solution could be recycled and applied to fresh coupling reactions; this aspect of the current reaction is important from practical and industrial utilization viewpoints. 3-Phenylpropiolic acid (**1a**) was used as a representative coupling partner in experiments to check the amenability of this system to reuse. As shown in Table 3, the oxidative decarboxylative homocoupling reaction of **1a** with 10 mol-% catalyst loading in the presence of **L^1** (20 mol-%) led to the formation of **2a** in 90% yield (by filtration) under the optimized reaction conditions. Following completion of the first cycle, the organic product was isolated by filtration and the remaining aqueous solution was recharged with base and **1a** for a second cycle of

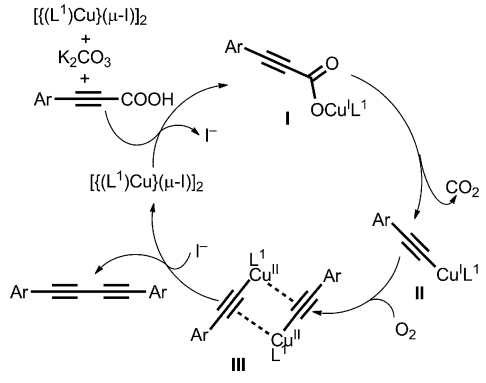
coupling. A third cycle of system application afforded a 59% yield for the desired coupling product indicating that the use of this catalytic system may meet the goal of green chemistry.

Table 3. Reuse of CuI/**L**^{1}-catalyzed oxidative decarboxylative homocoupling of phenylpropiolic acid.[a]

Cycle	Yield [%][b]
Initial run	90
Cycle 1	90
Cycle 2	87
Cycle 3	59
Cycle 4	21
Cycle 5	trace

[a] Reaction conditions: phenylpropiolic acid (0.2 mmol), CuI (10 mol-%), **L**^{1} (20 mol-%), K_2CO_3 (0.2 mmol), H_2O/DMF (1 mL/1 mL), 100 °C, 20 h, under air. [b] Isolated yield.

Although the exact mechanism of the oxidative decarboxylative homocoupling reaction of arylpropiolic acid is unknown at this stage, a plausible mechanism has been proposed based on the reported mechanism for homocoupling reactions of terminal alkynes[5n,6d,24] and decarboxylative reactions.[25] We envision that initially, reaction of [{(**L**^{1})-Cu}(μ-I)]$_2$ with arylpropiolic acid yields carboxylate intermediate **I** in the presence of K_2CO_3. Secondly, intermediate **I** may be converted into [(**L**^{1})Cu^I-acetylide] intermediate **II** through decarboxylation of **I**. Thirdly, intermediate **II** can be converted into intermediate **III** by oxidation of the Cu^I centre of intermediate **II** by O_2 in air. Finally, intermediate **III** may undergo an inner sphere electron transfer breaking the Cu–C bonds and forming the C–C bond to produce C_{sp}–C_{sp} homocoupling product and [{(**L**^{1})Cu}(μ-I)]$_2$, thereby furnishing the completed catalytic cycle (Scheme 2).



Scheme 2. Proposed catalytic cycle for the decarboxylative homocoupling.

Conclusions

In summary, we have developed an efficient method of synthesis of 1,3-diynes *via* CuI/1,10-phenanthroline-catalyzed oxidative decarboxylative homocoupling reaction of arylpropiolic acids in aqueous DMF using air as the oxidant. This approach tolerates a variety of functional groups and fails to generate much in the way of by-products. The catalytic system can also be reused several times and has potential for use in industrial applications. The reaction can be carried out under mild conditions and avoids the use of unstable terminal alkynes, haloalkynes and alkynyl metal reagents, thereby offering numerous opportunities for the application of this methodology in the synthesis of other useful compounds. Such studies are currently under way in our laboratory.

Experimental Section

General Procedure for Decarboxylative Homocoupling of Arylpropiolic Acids in Aqueous DMF: A mixture of arylpropiolic acid (0.2 mmol), K_2CO_3 (0.2 mmol) and H_2O (1.0 mL) was stirred at room temperature for 1 min. To this solution were then added DMF (1.0 mL), CuI (10 mol-%), and 1,10-phenanthroline (20 mol-%). The resulting mixture was stirred at 100 °C under air for 20 h. After cooling to ambient temperature, the mixture was extracted with diethyl ether. The extract was then dried with Na_2SO_4. The solvent was removed under reduced pressure. The crude product was purified by flash silica gel column chromatography.

1,4-Diphenylbuta-1,3-diyne (2a):[21] White solid, m.p. 83–84 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54–7.52 (m, 4 H), 7.39–7.31 (m, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 132.5, 129.2, 128.5, 121.8, 81.6, 73.9 ppm.

1,4-Di(*o*-tolyl)-buta-1,3-diyne (2b):[21] White solid, m.p. 74–75 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 (d, J = 8.0 Hz, 2 H), 7.28–7.25 (m, 2 H), 7.23–7.21 (m, 2 H), 7.16 (q, 2 H), 2.50 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.6, 132.9, 129.6, 129.1, 125.7, 121.7, 81.1, 76.7, 20.8 ppm.

1,4-Di(*m*-toly)buta-1,3-diyne (2c):[21] White solid, m.p. 68–69 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.32 (m, 4 H), 7.24–7.16 (m, 4 H), 2.34 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.2, 133.0, 130.1, 129.6, 128.3, 121.6, 81.6, 76.7, 73.6, 21.2 ppm.

1,4-Di(*p*-toly)buta-1,3-diyne (2d):[21] White solid, m.p. 135–137 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, J = 8.0 Hz, 4 H), 7.14 (d, J = 8.0 Hz, 4 H), 2.36 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.5, 132.4, 129.2, 118.8, 81.5, 73.4, 21.6 ppm.

1,4-Bis(4-methoxyphenyl)buta-1,3-diyne (2e):[21] White solid, m.p. 139–140 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 (d, J = 8.0 Hz, 4 H), 6.85 (d, J = 8.0 Hz, 4 H), 3.81 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.2, 134.0, 114.1, 113.9, 81.2, 72.9, 55.3 ppm.

1,4-Bis(2-methoxyphenyl)buta-1,3-diyne (2f):[21] White solid, m.p. 138–139 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 (dd, J = 4.0, J = 8.0 Hz, 2 H), 6.85 (td, J = 8.0 Hz, 2 H), 6.93–6.87 (m, 4 H), 3.89 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.3, 134.4, 130.6, 120.5, 111.3, 110.7, 78.7, 77.9, 55.8 ppm.

1,4-Bis(4-*tert*-butylphenyl)buta-1,3-diyne (2g):[23] White solid, m.p. 210–211 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 (d, J = 8.0 Hz, 4 H), 7.35 (d, J = 8.0 Hz, 4 H), 1.31 (s, 18 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.6, 132.3, 125.5, 118.8, 81.5, 73.5, 34.9, 31.1 ppm.

1,4-Bis(biphenyl-4-yl)buta-1,3-diyne (2h):[6h] Yellow solid, m.p. 91–93 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62–7.58 (m, 12 H), 7.47–7.44 (m, 4 H), 7.39–7.36 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.9, 140.1, 132.9, 128.9, 127.9, 127.1, 127.0, 120.6, 81.8, 74.6 ppm.

1,4-Bis(4-fluorophenyl)buta-1,3-diyne (2i):[21] White solid, m.p. 186–188 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53–7.49 (m, 4 H), 7.04 (q, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.3, 161.8, 134.6, 134.5, 117.8, 117.8, 116.0, 115.8, 80.4, 73.5 ppm.

1,4-Bis(4-chlorophenyl)buta-1,3-diyne (2j):[11b] White solid, m.p. 254–255 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 (d, J = 8.0 Hz, 4 H), 7.32 (d, J = 8.0 Hz, 4 H) ppm. Very insoluble in common organic solvents.[11b]

1,4-Bis(4-acetylphenyl)buta-1,3-diyne (2k):[21] White solid, m.p. 169–170 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (d, J = 8.0 Hz, 4 H), 7.62 (d, J = 8.0 Hz, 4 H), 2.61 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.1, 136.1, 131.7, 127.3, 125.2, 80.9, 75.5, 25.7 ppm.

1,4-Bis(3,5-dimethylphenyl)buta-1,3-diyne (2l):[23] White solid, m.p. 96–97 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.15 (br.s, 4 H), 7.00 (br.s, 2 H), 2.29 (s, 12 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.0, 131.2, 130.1, 121.5, 81.7, 73.4, 21.1 ppm.

1,4-Bis(2,4,6-trimethylphenyl)buta-1,3-diyne (2m):[23] White solid, m.p. 184–185 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.87 (s, 4 H), 2.45 (s, 12 H), 2.29 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.9, 138.8, 127.9, 119.1, 81.2, 80.8, 21.6, 21.2 ppm.

1,4-Di(naphthalen-1-yl)buta-1,3-diyne (2n):[21] Yellow solid, m.p. 174–176 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.43 (d, J = 12.0 Hz, 2 H), 7.89–7.86 (m, 4 H), 7.84–7.82 (m, 2 H), 7.65–7.61 (m, 2 H), 7.57–7.53 (m, 2 H), 7.47–7.43 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.9, 133.1, 132.1, 129.8, 128.5, 127.2, 126.7, 126.1, 125.2, 119.5, 80.9, 78.7 ppm.

1,4-Di(thiophen-2-yl)buta-1,3-diyne (2o):[16] White solid, m.p. 90–91 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.32 (m, 4 H), 7.01–6.99 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.4, 128.9, 127.2, 121.9, 77.8, 76.6 ppm.

Typical Procedure for the Reuse of the Catalytic Aqueous DMF Solution: The reaction was conducted by following the procedure described above under optimized reaction conditions shown in Table 2. After cooling to room temperature, the mixture was filtered, and the remaining aqueous solution was then charged with phenylpropiolic acid (0.2 mmol) and K_2CO_3 (0.2 mmol) for the next cycle of reaction.

Supporting Information (see footnote on the first page of this article): Copies of the ^{1}H and ^{13}C NMR spectra for the isolated products.

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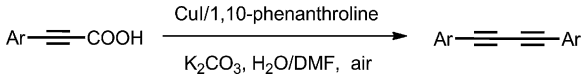
Decarboxylative Homocoupling



A CuI/1,10-phenanthroline system was employed to catalyze the oxidative decarboxylative homocoupling of arylpropiolic acids in aqueous DMF using air as an oxidant, producing 1,3-diynes in good to high yields. Such a catalytic system could be reused several times.

Keywords: Synthetic methods / Oxidation / Alkynes / C–C coupling / Green chemistry

