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Copper-Catalyzed Decarboxylative Coupling of Alkynyl Carboxylates with 1,1-Dibromo-1-alkenes

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ABSTRACT: A copper-catalyzed decarboxylative coupling reaction of potassium alkynyl carboxylates with 1,1-dibromo-1-alkenes was developed for the synthesis of unsymmetrical 1,3-diyne and 1,3,5-triyne derivatives. Diverse aryl, alkenyl, alkynyl and alkyl substituted 1,1-dibromo-1-alkenes can react smoothly with aryl and alkyl substituted propiolates to produce unsymmetrical 1,3-diynes and 1,3,5-triynes with high selectivity and good functional group compatibility.

1. Introduction

Due to their unique chemical and physical properties, conjugated 1,3-diynes and polyynes occur widely in nature products,[1] pharmaceutical intermediates,[1] and functional materials.[2] Therefore, synthetic methods to construct 1,3-diynes and polyynes have drawn the attention of chemists for decades.[1a] Glaser-Hay coupling, which involves oxidative coupling of two terminal alkynes promoted or catalyzed by copper salts, was the first successful method to construct 1,3-diynes (Figure 1, a).[3] But when considering the synthesis of unsymmetrical 1,3-diynes, the Glaser-Hay

coupling often suffers from low selectivity, giving a mixture of homo and cross coupled products.[1a,4] Cadiot-Chodkiewicz coupling[5] and its modifications[6] which can directly couple a haloalkyne and an alkyne under copper catalysis are the major methods used for unsymmetrical 1,3-diyne synthesis nowadays (Figure 1, b).[1a] Although successful in many circumstances, Cadiot-Chodkiewicz coupling is plagued with considerable amount of undesired homocouplings, especially when the substituents attached to the haloalkynes and the terminal alkynes have similar electronic properties.[1a, 4, 6] Hiyama *et al.* also reported a copper-catalyzed coupling of alkynylsilanes and 1-chloroalkynes to produce unsymmetrical 1,3-diynes (Figure 1, c).[7] Recently, guided by kinetic investigations, Lei *et al.* reported that a palladium- catalytic-system can improve the cross-coupling selectivity of the Cadiot-Chodkiewicz type reaction.[8] However, from an economic point of view, a highly selective copper-catalyzed 1,3-diyne synthesis using readily accessible reactants is more attractive.

Catalytic decarboxylative coupling has already been demonstrated to be powerful in catalytic C-C bond formation.[9] Due to their easy accessibility and stability, alkynyl carboxylic acids have been used as alkynyl nucleophiles instead of alkyne and alkynyl organometallic reagents in transition-metal-catalyzed alkynylation reactions.[10] And 1,1-Dibromo-1-alkenes which can be easily accessed from aldehyde[11], have been used as alkynyl electrophile in copper and palladium catalyzed reactions.[12] In this manuscript, we report a new copper-catalyzed reaction to construct 1,3-diynes and 1,3,5-triynes via decarboxylative coupling of alkynyl carboxylates with 1,1-dibromo-1-alkenes (Figure 1, d). This method is not only a new method for 1,3-diyne synthesis which is complementary with the traditional Glaser-Hay and Cadiot-Chodkiewicz coupling,[13] but also a new type of copper-catalyzed[14] decarboxylative alkynylation reaction.

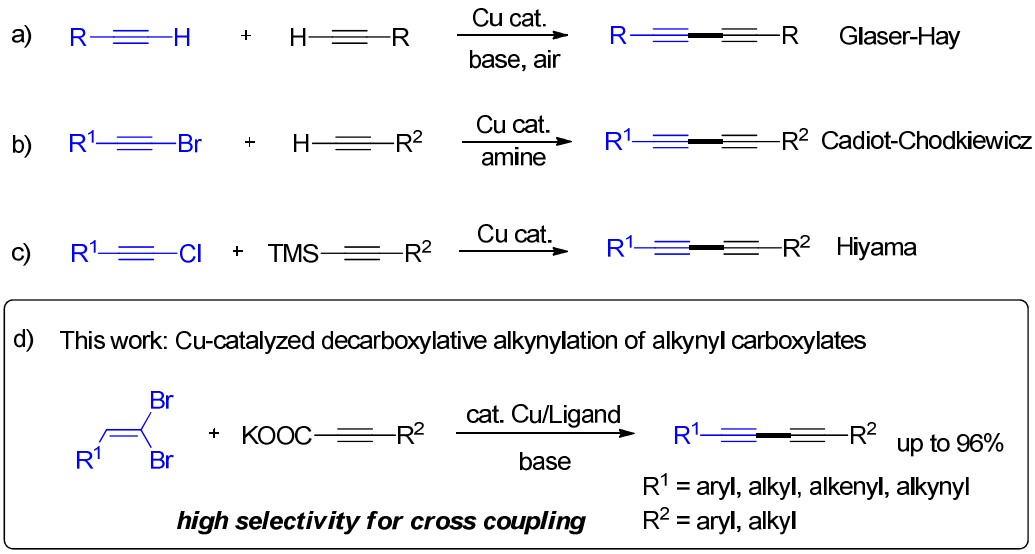


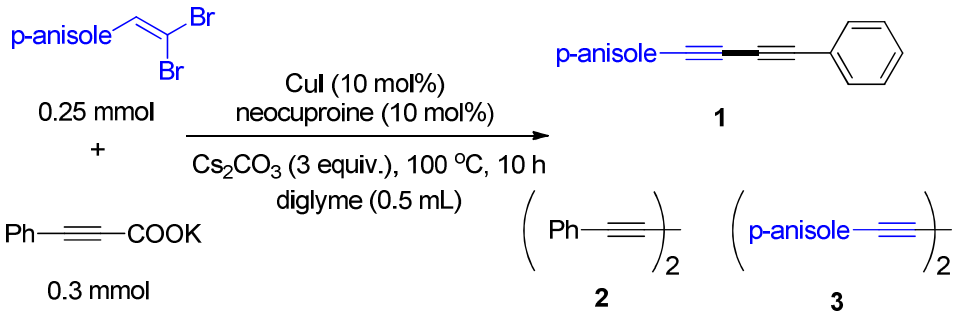
Figure 1. Copper catalyzed synthesis of 1,3-diyne.

2. Results and discussion

Our study began by examining the cross-coupling of 1-(2,2-dibromovinyl)-4-methoxybenzene with potassium 3-phenylpropiolate (Table 1). To our delight, after short optimization, the desired product **1** was obtained in 76% yield when using CuI as catalyst, 1,10-phenanthroline as ligand, and cesium carbonate as base in diglyme solvent. However, we also observed 16% and 7% of the two homocoupling byproducts (Table 1, Entry 1). We subsequently investigated the effect of various ligands on the reaction's yield and selectivity. Monodentate phosphine, bidentate phosphine and NHC-type ligand all gave inferior results (Entry 2-6). When neocuproine (2,9-dimethyl-1,10-phenanthroline) was used, we were delighted to find that the product was produced in 96% yield together with only 2% and 1% of the two homocoupling byproducts (Entry 7). Compared with the results obtained by using 1,10-phenanthroline (Entry 1) and bathophenanthroline (Entry 8), neocuproine was found through this observation that the two methyl substituents on 2- and 9- positions of it play a key role to suppress the homocoupling side

reactions. The use of less rigid bipyridine ligand resulted in a lower yield and poorer selectivity (Entry 9). Both TMEDA and DMEDA ligands gave satisfactory yield, but the amount of homocoupling was relatively higher than that with neocuproine (Entries 10 and 11).

Table 1. Ligand Optimization.

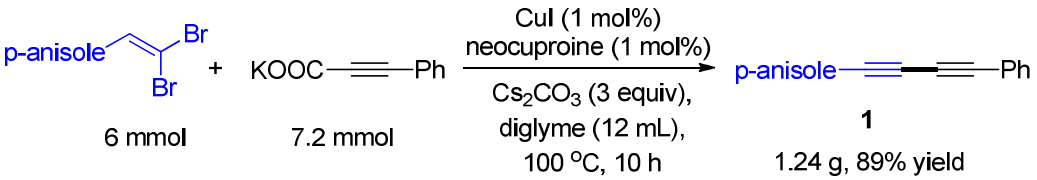


Entry	Ligand	Yield [a] 1	2	3
1[d]	1,10-phen	76%	16%	7%
2	PPh_3[b]	44%	24%	10%
3	dppp	29%	27%	5%
4	dppf	55%	24%	11%
5	S-Phos	52%	25%	11%
6	IMes[c]	41%	11%	3%
7	**neocuproine**	**96%**	**2%**	**1%**
8	bathophen	74%	19%	9%
9	dtbpy	74%	25%	10%
10	TMEDA	83%	6%	3%
11	DMEDA	88%	5%	3%

[a] Yield was detected by GC, average of two runs. [b] 20 mol% of PPh_3 was used. [c] IMes was used as its hydrochloride salt. [d] 6% of **1** was obtained by using K_2CO_3 (3.0 equiv.) as base.

After finding the optimal conditions, we examined the efficiency of this reaction on a gram scale (Scheme 1). With the use of only 1% of the copper-catalyst and the neocuproine ligand, we obtained 1.24 g of **1** (89% yield) without any decrease of selectivity (**2**, 2 % and **3**, 1 %).

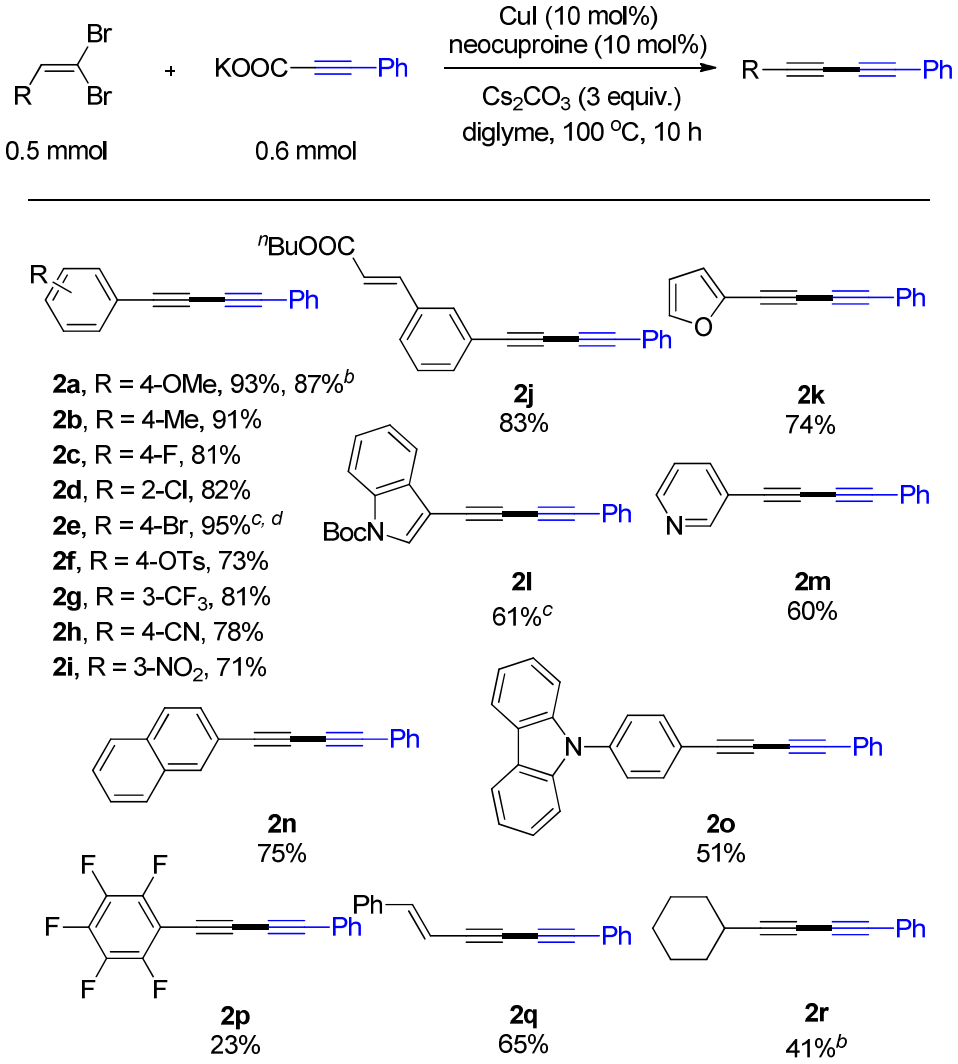
Scheme 1. Gram scale synthesis with 1mol% catalyst loading.



We next examined the scope of this reaction with respect to the 1,1-dibromo-1-alkene coupling partner (Table 2). The results in Table 2 show that substrates possessing both electron rich (**2a** and **2b**) and electron deficient (**2c-j**) aryl substituents on the 2-position of 1,1-dibromo-1-alkenes were transformed well in this reaction. A number of useful functional groups including alkoxy (**2a**), alkyl (**2b**), alkenyl (**2j**), fluoro (**2c**), chloro (**2d**), bromo (**2e**), tosylate (**2f**), trifluoromethyl (**2g**), cyano (**2h**), nitro (**2i**) and ester (**2j**) are all well tolerated. The products containing aryl-Cl, aryl-Br and aryl-OTs bond can easily be further transformed via Pd or Ni catalyzed cross-coupling reactions. It is worth to note that this reaction still gives a high yield and high selectivity even when the electronic properties of the substitution on the alkynyl carboxylate and the dibromoalkene are quite similar (**2b**, 91% yield, homocoupling <3%). 1,1-Dibromo-alkene substrates containing hetero aromatic substituents such as furyl (**2k**), Boc-protected indolyl (**2l**) and pyridyl (**2m**) can all react in good yields of 60-74%. 1,1-Dibromo-1-alkene derived from 2-naphthaldehyde reacted well and the yield was 75% (**2n**). 1,3-Diyne possessing carbazole substituent can be synthesized using this method (**2o**).This type of molecules are often found useful in the synthesis of electroluminescent devices.[15] Pentafluoro 1,4-diphenylbuta-1,3-diyne which is of interest for super-molecular chemistry[16] can also be prepared using this method, but in a relatively low yield (**2p**, 23 %). Besides 2-aryl substituent, 2-alkenyl-substituted 1,1-dibromo-1-alkene was also converted smoothly. Cinnamaldehyde-derived 1,1-dibromo-1-alkene reacted well with potassium 3-phenylpropiolate to produce

(E)-hexa-1-en-3,5-diyne-1,6-diyldibenzene (**2q**). This example demonstrates that this reaction is efficient for the construction of 1-en-3,5-hexadiyne skeleton from the corresponding vinyl aldehyde. In addition, 1-alkyl-4-aryl-1,3-butadiyne can be prepared by this method (**2r**).

Table 2. Scope of 1,1-Dibromoalkenes. [a]



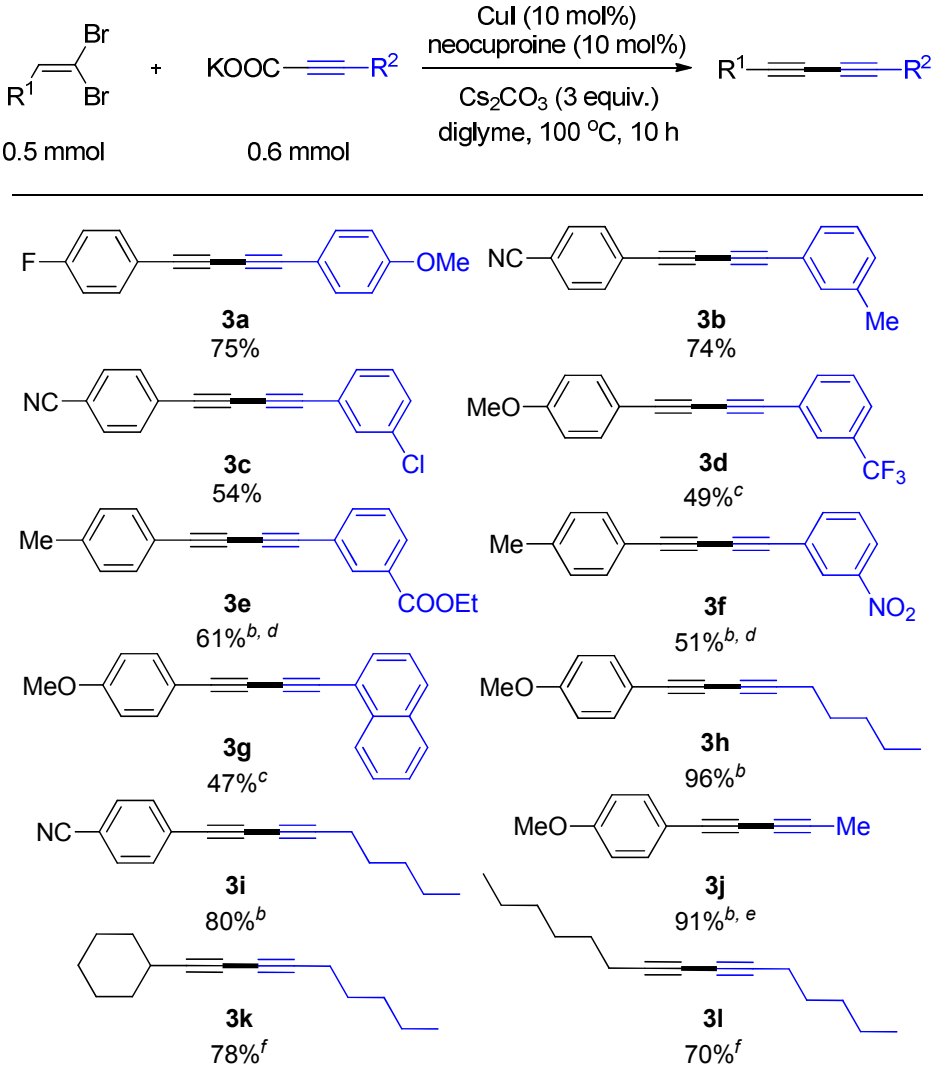
[a] Yields based on 1,1-dibromoalkenes. [b] DMEDA (10 mol%) was used as ligand. [c] The reaction was carried out at 80 °C. [d] $[Cu(MeCN)_4]PF_6$ (10 mol%) was used instead of CuI.

The scope of the alkynyl carboxylate is described in Table 3. Aryl propiolates carrying both electron-donating (**3a** and **3b**) and electron-withdrawing groups (**3c-f**) are amenable substrates. Potassium 3-(naphthalen-2-yl) propiolate can be coupled with 1-(2,2-dibromovinyl)-4-methoxybenzene in a moderate yield (**3g**). A number of functional groups on the aryl propiolates including alkoxy (**3a**), alkyl (**3b**), chloro (**3c**), trifluoromethyl (**3d**), ester (**3e**) and nitro (**3f**) were all tolerated well. Please note that although we only obtained moderate yields in these cases (**3c**, **3d**, **3f**, **3g**), the selectivities for cross coupling were still excellent as in all of these cases we observed only a small amount (<5%) of the homocoupling byproduct.

To our delight, we found that alkyl substituted propiolates can be well coupled with 2-aryl substituted 1,1-dibromo-1-alkenes to produce 1-alkyl-4-aryl-1,3-butadiynes. Potassium oct-2-ynoate reacted with both 1-(2,2-dibromovinyl)-4-methoxybenzene and 4-(2,2-dibromovinyl)benzonitrile to give the corresponding 1,3-diynes in 96% and 80% yields respectively (**3h** and **3i**). Potassium but-2-ynoate reacted with (2,2-dibromovinyl)-4-methoxybenzene to give 1-methoxy-4-(penta-1,3-diyn-1-yl)benzene (**3j**) in a high yield. In this case, potassium but-2-ynoate is a white, crystalized solid, but prop-1-yne is a troublesome gas in laboratory operation (b.p. -23.2 ^{o}C). This case demonstrates the advantage of the decarboxylative coupling methodology of alkynyl carboxylate. Alkyl substituted propiolates also couple well with 2-alkyl-1,1-dibromo-1-alkene to afford 1,4-dialkyl-1,3-butadiyne. Potassium oct-2-ynoate reacts with (2,2-dibromovinyl)cyclohexane and 1,1-dibromooct-1-ene to give the corresponding 1,4-dialkyl-1,3-butadiynes in 78% and 70% yield respectively, combined with only a trace amount of the homocoupling byproduct (**3k** and **3l**). Please note that, in Glaser-Hay and Cadiot-Chodkiewicz couplings, these 1,4-dialkyl-1,3-butadiynes carrying

substituents with similar structural and electronic properties on 1- and 4- positions are sometimes plagued with a significant amount of homocoupling diynes which are difficult to separate from each other.[1a, 17]

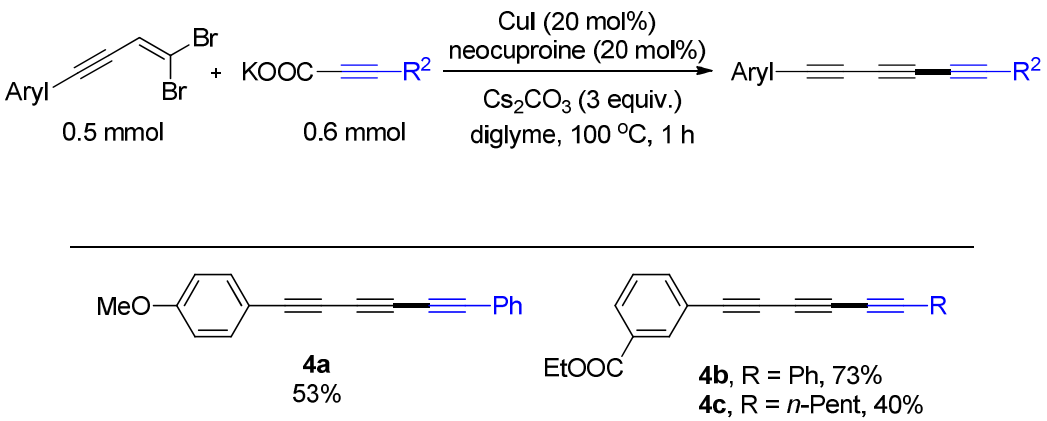
Table 3. Scope of Potassium Alkynyl Carboxylates.[a]



[a] Yields based on 1,1-dibromoalkenes. [b] CuI/neocuproine (20 mol%) was used. [c] *t*-BuOLi (3 equiv.) was used instead of Cs_2CO_3. [d] 1h reaction time. [e] 1.5 equiv. potassium salt was used. [f] homocoupling byproduct <5%.

We also extended our method to the synthesis of unsymmetrical 1,3,5-triynes (Table 4). 2-Alkynyl substituted 1,1-dibromo-1-alkene can couple with phenyl propiolate in reasonable yields (**4a,** 53% and **4b,** 73%) with high selectivity. 2-Alkynyl substituted 1,1-dibromo-1-alkene can also couple with alkyl substituted potassium propiolate. Potassium oct-2-ynoate can react with ethyl 3-(4,4-dibromobut-3-en-1-yn-1-yl) benzoate to give **4c** in 40% yield. This example demonstrates 1-alkyl-6-aryl-substituted 1,3,5-hexatriyne can also be constructed by this method.

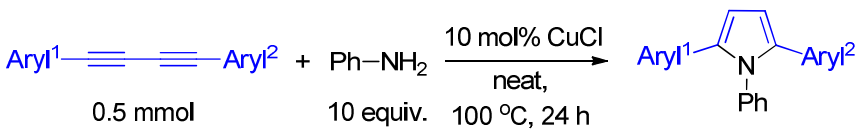
Table 4. Synthesis of unsymmetrical 1,3,5-triynes.[a]



[a] Yields based on 1,1-dibromoalkenes used.

1,3-Diynes are important building blocks in organic synthesis. Here we show that 2,5-diarylpyrroles which possess organic semiconductor behavior[18], can be easily accessed from unsymmetrical 1,4-diaryl-1,3-butadiynes (Scheme 2).[19]

Scheme 2. Synthesis of 2,5-diarylpyrroles from 1,3-diyne.



a. Aryl^1 = p-anisole, Aryl^2 = Ph, 76% yield
b. Aryl^1 = m-trifluoromethylphenyl, Aryl^2 = Ph, 50% yield

3. Conclusions

In summary, we have developed a copper-catalyzed decarboxylative coupling between alkynyl carboxylates and 1,1-dibromo-1-alkenes for highly selective synthesis of unsymmetrical 1,3-diynes and 1,3,5-triynes. This method is not only a new type of copper-catalyzed method for 1,3-diyne construction, but also the first example of transition-metal-catalyzed decarboxylative coupling using 1,1-dibromo-1-alkenes as alkynyl electrophiles. Various aryl, alkenyl, alkynyl and alkyl substituted 1,1-dibromo-1-alkenes can react smoothly with aryl and alkyl substituted propiolate to produce unsymmetrical 1,3-diynes and 1,3,5-triynes with high selectivity and good functional group compatibility.

4. Experimental Section

All chemical and solvents used in this work were purchased from chemical suppliers and used without further purification. ^{1}H-NMR, ^{13}C-NMR spectra were recorded at ambient temperature in $CDCl_3$ unless otherwise noted. Data for ^{1}H-NMR are reported as follows: chemical shift (δ ppm), multiplicity, integration, and coupling constant (Hz). Data for ^{13}C-NMR are reported in terms of chemical shift (δ ppm), multiplicity, and coupling constant (Hz). High-resolution mass spectra were measured on TOF-MS with EI probe. Gas chromatographic (GC) analysis was acquired on a GC System equipped with a flame-ionization detector. Infrared spectra are reported in reciprocal

centimeters (cm^{-1}). Melting points were measured on digital melting point apparatus and are uncorrected. Flash column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (200-300 mesh). 1,1-dibromo-1-alkenes used in this work were prepared according to published literature. [20] Potassium alkynyl carboxylates used in this work were synthesized according to published literature. [21]

General Procedures for the decarboxylative alkynylation of potassium alkynyl carboxylate A 10 mL oven-dried Schlenk tube was charged with copper source (CuI or $Cu[(MeCN)_4PF_6]$, 10 % mol or 20% mol), ligand (neocuproine hemihydrate or DMEDA, 10 % mol or 20% mol, if solid), 1,1-dibromoalkenes (0. 5 mmol, if solid), potassium alkynyl carboxylates (0.6 mmol or 0.75 mmol) and base (3 equiv., Cs_2CO_3 or LiO^tBu). The tube was evacuated and filled with argon (this procedure was repeated for three times). Then ligand (neocuproine hemihydrate or DMEDA, 10 % mol or 20% mol, if liquid), 1,1-dibromoalkenes (0. 5 mmol, if liquid) and diglyme (1 mL) were added with a syringe under a counter flow of argon. The tube was sealed with a screw cap, stirred at room temperature for 1 min, and connected to the Schlenk line which was filled with argon, stirred in a preheated oil bath at 80 ^oC or 100 ^oC for 1 or 10 h. Upon completion of the reaction, the mixture was cooled to room temperature. The mixture was poured into water (10 mL) and extracted three times with ethyl acetate (10 mL each time). The combined organic layer was washed with water (30 mL), brine (30 mL) and dried over $MgSO_4$. It was then filtered and the filtrate was concentrated *in vacuo*. Purification of the residue by column chromatography (silica gel, ethyl acetate/petroleum ether gradient) yielded the corresponding product.

1-methoxy-4-(phenylbuta-1,3-diyn-1-yl)benzene (2a): 108 mg, 93% yield (from neocuproine ligand) and 101 mg, 87% yield (from DMEDA ligand); white solid; ^1H NMR (400 MHz, $CDCl_3$) δ

7.51 (dd, J = 7.2, 1.6 Hz, 2H), 7.46 (dt, J = 8.8, 2.4 Hz, 2H), 7.38 – 7.27 (m, 3H), 6.85 (dt, J = 8.8, 2.4 Hz, 2H), 3.80 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 134.1, 132.4, 129.0, 128.4, 122.1, 114.2, 113.8, 81.9, 81.1, 74.2, 72.8, 55.3. The NMR data meet the literature report [8c].

1-methyl-4-(phenylbuta-1,3-diyn-1-yl)benzene (2b): 98 mg, 91% yield; yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, J = 7.7, 1.7 Hz, 2H), 7.42 (d, J = 8.1 Hz, 2H), 7.36 – 7.29 (m, 3H), 7.13 (d, J = 7.9 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.6, 132.5, 132.4, 129.2, 129.1, 128.4, 122.0, 118.7, 81.9, 81.2, 74.1, 73.3, 21.6. The NMR data meet the literature report [22a].

1-fluoro-4-(phenylbuta-1,3-diyn-1-yl)benzene (2c): 89 mg, 81% yield; pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.46 (m, 4H), 7.38 – 7.29 (m, 3H), 7.03 (tt, J = 8.6, 2.1 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0 (d, J_F = 251.5 Hz), 134.5 (d, J_F = 8.6 Hz), 132.5, 129.3, 128.4, 121.7, 118.0 (d, J_F = 3.6 Hz), 115.9 (d, J_F = 22.2 Hz), 81.6, 80.5, 73.8, 73.8. The NMR data meet the literature report [22b].

1-chloro-2-(phenylbuta-1,3-diyn-1-yl)benzene (2d): 97 mg, 82% yield; white solid; m. p. 62-63 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.49 (m, 3H), 7.45 – 7.26 (m, 5H), 7.23 (td, J = 7.6, 1.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.9, 134.3, 132.6, 130.1, 129.5, 129.4, 128.5, 126.6, 122.0, 121.6, 83.1, 78.8, 78.0, 73.7; IR (KBr) 3062, 2217, 1471, 1435, 1255, 1157, 1127, 1060, 1031, 949, 912, 763, 752, 685 cm $^{-1}$; HRMS (EI-TOF) calcd for $C_{16}H_9Cl$ (M+) 236.0393; found: 236.0398.

1-bromo-4-(phenylbuta-1,3-diyn-1-yl)benzene (2e): 134 mg, 95% yield; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, J = 7.6, 1.4 Hz, 2H), 7.47 (d, J = 8.4 Hz, 2H), 7.41 – 7.29 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.8, 132.5, 131.8, 129.4, 128.5, 123.7, 121.6, 120.8, 82.2, 80.4,

75.1, 73.7. The NMR data meet the literature report [22c].

4-(phenylbuta-1,3-diyn-1-yl)phenyl 4-methylbenzenesulfonate (2f): 136 mg, 73% yield; yellow solid; m. p. 160-164 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.3 Hz, 2H), 7.54 – 7.49 (m, 2H), 7.43 (dt, J = 8.8, 2.2 Hz, 2H), 7.38 – 7.28 (m, 5H), 6.96 (dt, J = 8.8, 2.2 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.9, 144.6, 132.8, 131.5, 131.1, 128.9, 128.4, 127.48, 127.46, 121.6, 120.5, 119.9, 81.2, 79.0, 74.0, 72.6, 20.7; IR (KBr) 2924, 2846, 2217, 2143, 1601, 1566, 1509, 1485, 1461, 1432, 1356, 1320, 1310, 1249, 1159, 1072, 1035, 904, 834, 805, 725, 694, 659 cm $^{-1}$; HRMS (EI-TOF) calcd for $C_{23}H_{16}O_3S$ (M+) 372.0820; found: 372.0812.

1-(phenylbuta-1,3-diyn-1-yl)-3-(trifluoromethyl)benzene (2g): 109 mg, 81% yield; white solid; m. p. 120-121 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.68 (d, J = 7.7 Hz, 1H), 7.60 (d, J = 7.9 Hz, 1H), 7.56 – 7.50 (m, 2H), 7.46 (t, J = 7.8 Hz, 1H), 7.41 – 7.29 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.5, 132.6, 131.2 (q, J_F = 32.8 Hz), 129.5, 129.3 (q, J_F = 3.8 Hz), 129.0, 128.5, 125.7 (q, J_F = 3.7 Hz), 123.6 (q, J_F = 273.51 Hz), 122.9, 121.4, 82.5, 79.7, 75.5, 73.5; IR (KBr) 2962, 2925, 2854, 2219, 1484, 1435, 1353, 1321, 1310, 1278, 1263, 1196, 1156, 1117, 1094, 1072, 896, 802, 755, 687 cm $^{-1}$; HRMS (EI-TOF) calcd for $C_{17}H_9F_3$ (M+) 270.0656; found: 270.0653.

4-(phenylbuta-1,3-diyn-1-yl)benzonitrile (2h): 89 mg, 78% yield; pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.8 Hz, 2H), 7.59 (d, J = 8.8 Hz, 2H), 7.56 – 7.52 (m, 2H), 7.41 (t, J = 7.4 Hz, 1H), 7.38 – 7.32 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.9, 132.6, 132.1, 129.8, 128.6, 126.8, 121.2, 118.2, 112.4, 84.0, 79.3, 78.2, 73.3. The NMR data meet the literature report [8c].

1-nitro-3-(phenylbuta-1,3-diyn-1-yl)benzene (2i): 88 mg, 71% yield; yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 8.21 (dd, J = 8.3, 1.3 Hz, 1H), 7.81 (d, J = 7.7 Hz, 1H), 7.58 –

7.49 (m, 3H), 7.44 – 7.32 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.2, 138.0, 132.7, 129.7, 129.6, 128.6, 127.2, 123.84, 123.76, 121.2, 83.2, 78.6, 76.5, 73.2. The NMR data meet the literature report [22d].

(E)-butyl 3-(3-(phenylbuta-1,3-diyn-1-yl)phenyl)acrylate (2j): 136 mg, 83% yield; yellow solid; m. p. 69-70 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.62 (d, *J* = 16.0 Hz, 1H), 7.56 – 7.47 (m, 4H), 7.40 – 7.29 (m, 4H), 6.44 (d, *J* = 16.0 Hz, 1H), 4.21 (t, *J* = 6.7 Hz, 2H), 1.69 (quint, *J* = 7.1 Hz, 2H), 1.44 (sext, *J* = 7.4 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 143.2, 134.9, 133.8, 132.6, 131.8, 129.4, 129.0, 128.6, 128.5, 122.7, 121.6, 119.6, 82.0, 80.6, 74.7, 73.7, 64.6, 30.8, 19.2, 13.8; IR (KBr) 3059, 2957, 1708, 1643, 1593, 1486, 1419, 1308, 1262, 1222, 1187, 1091, 1065, 1027, 856, 801, 751, 686, 675 cm $^{-1}$; HRMS (EI-TOF) calcd for $C_{23}H_{20}O_2$ (M+) 328.1463; found: 328.1461.

2-(phenylbuta-1,3-diyn-1-yl)furan (2k): 71 mg, 74% yield; brownish solid; m. p. 37-38 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.50 (m, 2H), 7.41 (dd, *J* = 1.8, 0.6 Hz, 1H), 7.38 – 7.30 (m, 3H), 6.74 (dd, *J* = 3.4, 0.6 Hz, 1H), 6.41 (dd, *J* = 3.4, 1.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.6, 136.5, 132.6, 129.5, 128.5, 121.4, 118.1, 111.2, 84.3, 78.7, 73.4, 71.0; IR (KBr) 2925, 2207, 2147, 1492, 1478, 1442, 1327, 1200, 1152, 1076, 1022, 1000, 917, 902, 884, 816, 753, 686 cm $^{-1}$; HRMS (EI-TOF) calcd for $C_{14}H_8O$ (M+) 192.0575; found: 192.0578.

tert-butyl 3-(phenylbuta-1,3-diyn-1-yl)-1H-indole-1-carboxylate (2l): 104 mg, 61% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.1 Hz, 1H), 7.87 (s, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.57 – 7.51 (m, 2H), 7.41 – 7.28 (m, 5H), 1.67 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.8, 134.6, 132.5, 131.1, 130.5, 129.2, 128.4, 125.5, 123.5, 121.9, 120.2, 115.4, 102.1, 84.7, 81.6, 77.2, 74.2, 74.1, 28.1; IR (KBr) 2965, 2930, 2360, 2341, 2212, 2149, 1741, 1555, 1453,

1378, 1336, 1309, 1296, 1261, 1226, 1152, 1098, 1025, 803, 753, 688 cm $^{-1}$; HRMS (EI-TOF) calcd for $C_{23}H_{19}NO_2$ (M+) 341.1416; found: 341.1418.

3-(phenylbuta-1,3-diyn-1-yl)pyridine (2m): 61 mg, 60% yield; brownish solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (s, 1H), 8.58 (d, J = 4.1 Hz, 1H), 7.80 (dt, J = 7.9, 1.8 Hz, 1H), 7.57 – 7.50 (m, 2H), 7.43 – 7.31 (m, 3H), 7.28 (dd, J = 7.6, 4.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.1, 149.2, 139.3, 132.6, 129.6, 128.5, 123.1, 121.4, 119.3, 82.8, 78.0, 77.2, 73.4. The NMR data meet the literature report [22e].

2-(phenylbuta-1,3-diyn-1-yl)naphthalene (2n): 95 mg, 75% yield; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.83 – 7.74 (m, 3H), 7.59 – 7.44 (m, 5H), 7.39 – 7.27 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.2, 133.1, 132.9, 132.6, 129.3, 128.5, 128.2, 127.91, 127.87, 127.3, 126.8, 121.9, 119.1, 82.1, 81.8, 74.3, 74.2. The NMR data meet the literature report [19].

9-(4-(phenylbuta-1,3-diyn-1-yl)phenyl)-9H-carbazole (2o): 94 mg, 51% yield; white solid; m. p. 172-174 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 7.7 Hz, 2H), 7.75 (dt, J = 8.4, 2.0 Hz, 2H), 7.59 – 7.53 (m, 4H), 7.46 – 7.40 (m, 4H), 7.40 – 7.34 (m, 3H), 7.34 – 7.26 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.4, 138.5, 134.1, 132.6, 129.4, 128.5, 126.8, 126.2, 123.7, 121.7, 120.6, 120.4, 109.8, 82.2, 80.8, 74.9, 73.9; IR (KBr) 3052, 2355, 1596, 1514, 1480, 1451, 1366, 1335, 1316, 1231, 1181, 1120, 1101, 1016, 914, 835, 749, 723, 686, 624 cm $^{-1}$; HRMS (EI-TOF) calcd for $C_{28}H_{17}N$ (M+) 367.1361; found: 367.1353.

1,2,3,4,5-pentafluoro-6-(phenylbuta-1,3-diyn-1-yl)benzene (2p): 34 mg, 23% yield; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.54 (m, 2H), 7.43 (tt, J = 7.4, 1.9 Hz, 1H), 7.40 – 7.33 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.3 (dm, J_F = 256.0 Hz), 142.1 (dm, J_F = 258.9 Hz), 137.7 (dm, J_F = 259.7 Hz), 132.7, 130.0, 128.6, 120.7, 99.4 (td, J_F = 17.9, 4.3 Hz), 85.4 (q, J_F = 3.4 Hz),

85.2, 72.8, 64.6 (q, J_F = 4.0 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ -134.87 (dd, J_F = 23.1, 9.2 Hz, 2F), -150.63 (t, J_F = 21.9 Hz, 1F), -161.13 (m, 2F). The NMR data meet the literature report [15].

(E)-hexa-1-en-3,5-diyne-1,6-diyldibenzene (2q): 74 mg, 65% yield; pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (dd, J = 7.8, 1.6 Hz, 2H), 7.40 (dd, J = 7.9, 1.4 Hz, 2H), 7.36 – 7.29 (m, 6H), 7.11 (d, J = 16.3 Hz, 1H), 6.26 (d, J = 16.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.6, 135.8, 132.5, 129.3, 129.2, 128.8, 128.5, 126.5, 121.9, 106.8, 82.2, 81.4, 76.1, 74.2. The NMR data meet the literature report [22f].

(cyclohexylbuta-1,3-diyn-1-yl)benzene (2r): 43 mg, 41% yield; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.44 (m, 2H), 7.35 – 7.26 (m, 3H), 2.60 – 2.50 (m, 1H), 1.90 – 1.80 (m, 2H), 1.79 – 1.67 (m, 2H), 1.59 – 1.45 (m, 3H), 1.41 – 1.27 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.5, 128.8, 128.3, 122.2, 88.6, 75.3, 74.4, 65.0, 32.2, 29.8, 25.8, 24.8. The NMR data meet the literature report [22g].

1-fluoro-4-((4-methoxyphenyl)buta-1,3-diyn-1-yl)benzene (3a): 94 mg, 75% yield; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.43 (m, 4H), 7.02 (tt, J = 8.2, 2.2 Hz, 2H), 6.85 (dt, J = 8.8, 2.4 Hz, 2H), 3.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9 (d, J_F = 251.2 Hz), 160.4, 134.4 (d, J_F = 8.5 Hz), 134.2, 118.2 (d, J_F = 3.6 Hz), 115.8 (d, J_F = 22.2 Hz), 114.2, 113.6, 81.8, 79.9, 74.0 (d, J_F = 1.4 Hz), 72.6, 55.4. The NMR data meet the literature report [13b].

4-(m-tolylbuta-1,3-diyn-1-yl)benzonitrile (3b): 89 mg, 74% yield; yellow solid; m. p. 171-173 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.5 Hz, 2H), 7.59 (d, J = 8.7 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H), 7.27 – 7.18 (m, 2H), 2.35 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.4, 133.1, 132.9, 132.1, 130.7, 129.8, 128.4, 126.9, 121.0, 118.2, 112.3, 84.3, 79.2, 78.3, 72.9, 21.2; IR (KBr) 2922, 2225, 1599, 1499, 1483, 1405, 1384, 1272, 1092, 906, 874, 841, 832, 784, 685 cm $^{-1}$; HRMS

(EI-TOF) calcd for $C_{18}H_{11}N$ (M+) 241.0891; found: 241.0883.

4-((3-chlorophenyl)buta-1,3-diyn-1-yl)benzonitrile (3c): 71 mg, 54% yield; yellow solid; m. p. 159-160 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.6 Hz, 2H), 7.60 (d, *J* = 8.6 Hz, 2H), 7.51 (t, *J* = 1.4 Hz, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.40 – 7.35 (m, 1H), 7.29 (t, *J* = 7.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.5, 133.0, 132.3, 132.1, 130.7, 130.0, 129.8, 126.5, 123.0, 118.2, 112.6, 82.2, 80.0, 77.7, 74.3; IR (KBr) 2963, 2228, 1591, 1561, 1472, 1405, 1262, 1095, 1023, 871, 839, 801, 678 cm $^{-1}$; HRMS (EI-TOF) calcd for $C_{17}H_8ClN$ (M+) 261.0345; found: 261.0344.

1-((4-methoxyphenyl)buta-1,3-diyn-1-yl)-3-(trifluoromethyl) benzene (3d): 74 mg, 49% yield; brownish solid; m. p. 119-121 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.52 – 7.43 (m, 3H), 6.87 (dt, *J* = 8.8, 2.4 Hz, 2H), 3.83 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6, 135.4, 134.3, 131.1 (q, J_F = 32.8 Hz), 129.2 (q, J_F = 3.8 Hz), 129.0, 125.5 (q, J_F = 3.7 Hz), 123.6 (q, J_F = 273.5 Hz), 123.2, 114.2, 113.3, 82.8, 79.2, 75.8, 72.4, 55.4; IR (KBr) 3065, 2921, 2216, 2149, 1594, 1497, 1487, 1444, 1402, 1378, 1196, 1180, 1170, 1152, 1091, 1015, 865, 845, 816, 772, 758, 731, 708, 692, 661 cm $^{-1}$; HRMS (EI-TOF) calcd for $C_{18}H_{11}F_3O$ (M+) 300.0762; found: 300.0756.

ethyl 3-(p-tolylbuta-1,3-diyn-1-yl)benzoate (3e): 88 mg, 61% yield; yellow solid; m. p. 113-114 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (t, *J* = 1.5 Hz, 1H), 8.03 (dt, *J* = 7.6, 1.4 Hz, 1H), 7.68 (dt, *J* = 7.6, 1.4 Hz, 1H), 7.47 – 7.37 (m, 3H), 7.15 (d, *J* = 7.9 Hz, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 2.37 (s, 3H), 1.40 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 139.8, 136.3, 133.5, 132.5, 131.0, 130.0, 129.3, 128.6, 122.4, 118.5, 82.4, 80.1, 75.0, 73.1, 61.3, 21.6, 14.3; IR (KBr) 2924, 2214, 1715, 1577, 1469, 1368, 1344, 1304, 1289, 1261, 1194, 1176, 1101, 1077, 1016, 812, 755, 680 cm $^{-1}$; HRMS (EI-TOF) calcd for $C_{20}H_{16}O_2$ (M+) 288.1150; found: 288.1154.

1-nitro-3-(p-tolylbuta-1,3-diyn-1-yl)benzene (3f): 67 mg, 51% yield; brownish solid; m. p. 141-143 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (t, *J* = 1.8 Hz, 1H), 8.20 (ddd, *J* = 8.3, 2.2, 1.0 Hz, 1H), 7.80 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.52 (t, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.2, 140.2, 137.9, 132.6, 129.5, 129.3, 127.2, 124.0, 123.6, 118.1, 83.5, 78.3, 76.7, 72.6, 21.7; IR (KBr) 3072, 2926, 2353, 2214, 1731, 1601, 1520, 1506, 1472, 1352, 1300, 1273, 893, 882, 814, 806, 760, 735, 667 cm $^{-1}$; HRMS (EI-TOF) calcd for $C_{17}H_{11}NO_2$ (M+) 261.0790; found: 261.0799.

1-((4-methoxyphenyl)buta-1,3-diyn-1-yl)naphthalene (3g): 66 mg, 47% yield; white solid; m. p. 99-100 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.3 Hz, 1H), 7.84 (d, *J* = 8.3 Hz, 2H), 7.76 (dd, *J* = 7.2, 1.0 Hz, 1H), 7.58 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.55 – 7.48 (m, 3H), 7.42 (dd, *J* = 8.2, 7.3 Hz, 1H), 6.87 (dt, *J* = 8.8, 2.4 Hz, 2H), 3.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 134.2, 134.0, 133.1, 131.9, 129.6, 128.4, 127.2, 126.7, 126.2, 125.2, 119.8, 114.2, 113.8, 82.9, 79.4, 78.9, 73.0, 55.4; IR (KBr) 3040, 2920, 2841, 2209, 2137, 1603, 1506, 1397, 1331, 1304, 1291, 1252, 1177, 1168, 1153, 1110, 1025, 864, 825, 792, 766, 693, 619 cm $^{-1}$; HRMS (EI-TOF) calcd for $C_{21}H_{14}O$ (M+) 282.1045; found: 282.1039.

1-methoxy-4-(nona-1,3-diyn-1-yl)benzene (3h): 109 mg, 96% yield; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (dt, *J* = 8.8, 2.4 Hz, 2H), 6.81 (dt, *J* = 8.8, 2.4 Hz, 2H), 3.79 (s, 3H), 2.34 (t, *J* = 7.1 Hz, 2H), 1.57 (quint, *J* = 7.4 Hz, 2H), 1.45 – 1.27 (m, 4H), 0.91 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 134.0, 114.1, 114.1, 84.2, 74.8, 73.2, 65.2, 55.3, 31.0, 28.0, 22.2, 19.6, 13.9. The NMR data meet the literature report [22h].

4-(nona-1,3-diyn-1-yl)benzonitrile (3i): 89 mg, 80% yield; white solid; m. p. 72-73 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.8 Hz, 2H), 7.54 (d, *J* = 8.8 Hz, 2H), 2.38 (t, *J* = 7.1 Hz, 2H),

1.59 (quint, J = 7.3 Hz, 2H), 1.47 – 1.28 (m, 4H), 0.92 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.0, 132.0, 127.3, 118.3, 112.0, 87.7, 78.8, 72.7, 64.6, 31.0, 27.8, 22.2, 19.6, 13.9; IR (KBr) 2961, 2860, 2228, 1601, 1500, 1465, 1407, 1262, 1184, 1099, 1019, 841, 802 cm $^{-1}$; HRMS (EI-TOF) calcd for $C_{16}H_{15}N$ (M+) 221.1204; found: 221.1203.

1-methoxy-4-(penta-1,3-diyn-1-yl)benzene (3j): 77 mg, 91% yield; pale yellow solid; ^{1}H NMR (400 MHz, CDCl3) δ 7.41 (dt, J = 8.8, 2.3 Hz, 2H), 6.82 (dt, J = 8.8, 2.4 Hz, 2H), 3.80 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (101 MHz, CDCl3) δ 160.1, 134.1, 114.1, 114.0, 79.6, 74.3, 73.2, 64.5, 55.3, 4.6. The NMR data meet the literature report [22i].

nona-1,3-diyn-1-ylcyclohexane (3k): 79 mg, 78% yield; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (ddd, J = 12.6, 8.7, 3.6 Hz, 1H), 2.25 (td, J = 7.1, 0.9 Hz, 2H), 1.83 – 1.75 (m, 2H), 1.74 – 1.65 (m, 2H), 1.58 – 1.40 (m, 5H), 1.40 – 1.22 (m, 7H), 0.89 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 81.3, 78.1, 65.2, 65.2, 32.3, 31.0, 29.5, 28.1, 25.8, 24.8, 22.2, 19.2, 13.9; IR (neat) 2931, 2857, 2664, 2359, 2339, 2251, 2230, 2143, 1713, 1673, 1614, 1449, 1378, 1341, 1140, 1046, 965, 934, 890, 860, 842, 815, 766, 730 cm $^{-1}$; HRMS (EI-TOF) calcd for $C_{15}H_{22}$ (M+) 202.1722; found: 202.1724.

pentadeca-6,8-diyne (3l): 72 mg, 70% yield; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.24 (t, J = 7.0 Hz, 4H), 1.58 – 1.46 (m, 4H), 1.43 – 1.21 (m, 10H), 0.90 (t, J = 7.1 Hz, 3H), 0.89 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 77.5, 65.3, 31.3, 31.0, 28.6, 28.4, 28.1, 22.5, 22.2, 19.2, 19.2, 14.0, 13.9; IR (neat) 2932, 2859, 2353, 2257, 2158, 1465, 1427, 1378, 1323, 1108, 1022, 726 cm $^{-1}$; HRMS (EI-TOF) calcd for $C_{15}H_{24}$ (M+) 204.1878; found: 204.1884.

1-methoxy-4-(phenylhexa-1,3,5-triyn-1-yl)benzene (4a): 68 mg, 53% yield; brownish solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 2H), 7.47 (dt, J = 9.2, 2.3 Hz, 2H), 7.41 – 7.29 (m,

3H), 6.85 (d, *J* = 8.9 Hz, 2H), 3.82 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.8, 134.7, 133.0, 129.6, 128.5, 121.2, 114.3, 112.8, 79.0, 78.4, 74.6, 73.5, 66.9, 66.1, 55.4. The NMR data meet the literature report [22a].

ethyl 3-(phenylhexa-1,3,5-triyn-1-yl)benzoate (4b): 109 mg, 73% yield; white solid; m. p. 69-71 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (t, *J* = 1.5 Hz, 1H), 8.05 (dt, *J* = 8.0, 1.5 Hz, 1H), 7.68 (dt, *J* = 7.6, 1.5 Hz, 1H), 7.56 – 7.50 (m, 2H), 7.45 – 7.28 (m, 4H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 136.8, 134.0, 133.0, 131.1, 130.6, 129.8, 128.7, 128.5, 121.5, 120.9, 78.9, 77.4, 75.2, 74.4, 67.0, 66.2, 61.4, 14.3; IR (KBr) 2974, 2926, 2853, 2192, 1712, 1600, 1489, 1468, 1443, 1432, 1394, 1369, 1282, 1226, 1169, 1118, 1017, 910, 862, 811, 759, 749, 689, 677 cm $^{-1}$; HRMS (EI-TOF) calcd for $C_{21}H_{14}O_2$ (M+) 298.0994; found: 298.0996.

ethyl 3-(undeca-1,3,5-triyn-1-yl)benzoate (4c): 58 mg, 40% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (t, *J* = 1.5 Hz, 1H), 8.03 (dt, *J* = 7.9, 1.3 Hz, 1H), 7.66 (dt, *J* = 7.7, 1.3 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 2.34 (t, *J* = 7.1 Hz, 2H), 1.57 (quint, *J* = 7.1 Hz, 2H), 1.44 – 1.27 (m, 7H), 0.91 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 136.8, 134.0, 131.0, 130.3, 128.6, 121.7, 83.2, 75.5, 74.3, 67.9, 65.6, 61.4, 59.2, 31.0, 27.7, 22.1, 19.6, 14.3, 13.9; IR (neat) 3071, 2959, 2933, 2861, 2352, 2214, 1724, 1599, 1577, 1465, 1431, 1392, 1368, 1281, 1261, 1181, 1104, 1079, 1025, 914, 861, 815, 799, 753, 682 cm $^{-1}$; HRMS (EI-TOF) calcd for $C_{20}H_{20}O_2$ (M+) 292.1463; found: 292.1464.

Procedures for the experiment described in Scheme 1: A 50 mL oven-dried Schlenk flask was charged with CuI (0.06 mmol, 1 % mol), neocuproine hemihydrate (0.06 mmol, 1 % mol), 1-(2,2-dibromovinyl)-4-methoxybenzene (6 mmol), potassium 3-phenylpropiolate (7.2 mmol) and

Cs_2CO_3 (3 equiv.). The tube was evacuated and filled with argon (this procedure was repeated for three times). Then diglyme (12 mL) were added with a syringe under a counter flow of argon. The tube was sealed with a screw cap, stirred at room temperature for 1 min, and connected to the Schlenk line which was filled with argon, stirred in a preheated oil bath at 100 ^{o}C for 10 h. Upon completion of the reaction, the mixture was cooled to room temperature. The mixture was poured into water (100 mL) and extracted three times with ethyl acetate (100 mL each time). The combined organic layer was washed with water (300 mL), brine (300 mL) and dried over $MgSO_4$. It was then filtered and the filtrate was concentrated *in vacuo*. Purification of the residue by column chromatography (silica gel, ethyl acetate/petroleum ether gradient) yielded the 1-methoxy-4-(phenylbuta-1,3-diyn-1-yl)benzene (1.24 g, 5.34 mmol, 89 % yield) as a white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 7.2, 1.6 Hz, 2H), 7.47 (dt, *J* = 8.8, 2.4 Hz, 2H), 7.38 – 7.27 (m, 3H), 6.86 (dt, *J* = 9.2, 2.4 Hz, 2H), 3.82 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 134.1, 132.4, 129.0, 128.4, 122.1, 114.2, 113.8, 81.9, 81.1, 74.2, 72.8, 55.3. The NMR data meet the literature report [8c].

General Procedures for the experiments described in Scheme 2:[18] A mixture of 1,4-diaryl-1,3-butadiyne (0.5 mmol) and CuCl (0.05 mmol) in aniline (5 mmol) was stirred at 100 ^{o}C for 24 h under argon atmosphere. Then the reaction mixture was cooled to room temperature and directly purified by column chromatography on silica gel.

2-(4-methoxyphenyl)-1,5-diphenyl-1H-pyrrole (Scheme 2, a): 124 mg, 76% yield; yellow solid; m. p. 163-164 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.19 (m, 3H), 7.18 – 7.10 (m, 3H), 7.08 – 6.95 (m, 6H), 6.71 (dt, *J* = 8.8, 2.4 Hz, 2H), 6.46 (d, *J* = 3.6 Hz, 1H), 6.40 (d, *J* = 3.6 Hz, 1H), 3.74 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 139.0, 135.7, 135.3, 133.4, 130.0, 128.9, 128.7,

128.6, 127.8, 127.1, 126.1, 125.9, 113.4, 109.8, 109.2, 55.1; IR (KBr) 3049, 2932, 2838, 2360, 1674, 1598, 1574, 1547, 1523, 1491, 1447, 1420, 1387, 1335, 1287, 1245, 1178, 1106, 1070, 1031, 957, 911, 831, 812, 775, 756, 697 cm $^{-1}$; HRMS (EI-TOF) calcd for $C_{23}H_{19}NO$ (M+) 325.1467; found: 325.1469.

1,2-diphenyl-5-(3-(trifluoromethyl)phenyl)-1H-pyrrole (Scheme 2, b): 91 mg, 50% yield; white solid; m. p. 173-174 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 7.6 Hz, 1H), 7.33 – 7.22 (m, 5H), 7.22 – 7.12 (m, 4H), 7.11 – 7.05 (m, 2H), 7.05 – 6.97 (m, 2H), 6.55 (d, J = 3.7 Hz, 1H), 6.49 (d, J = 3.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.6, 136.7, 134.2, 134.0, 133.0, 131.5, 130.4 (q, J_F = 32.1 Hz), 129.0, 128.9, 128.8, 128.3, 128.0, 127.7, 126.5, 125.2 (q, J_F = 3.9 Hz), 124.0 (q, J_F = 273.4 Hz), 122.7 (q, J_F = 3.7 Hz), 110.7, 110.2; IR (KBr) 2925, 1598, 1547, 1497, 1470, 1448, 1425, 1391, 1356, 1344, 1323, 1257, 1177, 1164, 1125, 1099, 1076, 1049, 903, 811, 776, 756, 699 cm $^{-1}$; HRMS (EI-TOF) calcd for $C_{23}H_{16}F_3N$ (M+) 363.1235; found: 363.1234.

ASSOCIATED CONTENT

Supporting Information. Copies of ^{1}H and ^{13}C spectra for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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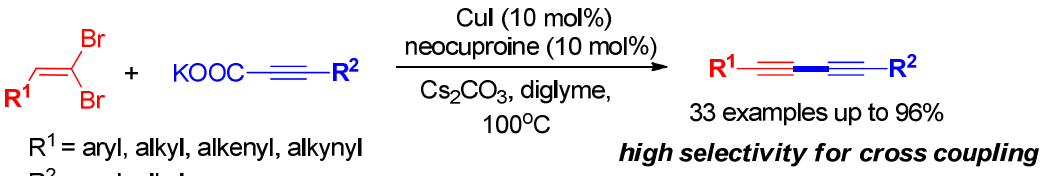
Table of Content



R^1 = aryl, alkyl, alkenyl, alkynyl
R^2 = aryl, alkyl

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