Advanced Synthesis & Catalysis

Accepted Article

Title: One-pot Domino Synthesis of Diarylalkynes/1,4-Diaryl-1,3-diynes by [9,9-Dimethyl-4,5-bis(diphenylphosphino)xanthene]Copper(I) Iodine–Palladium(II) Acetate Catalyzed Double Sonogashira-type Reaction

Authors: Shaozhong Qiu, Caiyang Zhang, Rui Qiu, Guodong Yin, and Jinkun Huang

To be cited as: *Adv. Synth. Catal.* 10.1002/adsc.201701128

Link to VoR: http://dx.doi.org/10.1002/adsc.201701128

10.1002/adsc.201701128

FULL PAPER

DOI: 10.1002/adsc.201((will be filled in by the editorial staff))

One-pot Domino Synthesis of Diarylalkynes/1,4-Diaryl-1,3-diynes by [9,9-Dimethyl-4,5-bis(diphenylphosphino)xanthene]-Copper(I) Iodine–Palladium(II) Acetate Catalyzed Double Sonogashira-type Reaction

Shaozhong Qiu,[a] Caiyang Zhang,[a] Rui Qiu,[a] Guodong Yin[a,*] and Jinkun Huang[b,*]

[a] Hubei Collaborative Innovation Center for Rare Metal Chemistry, Hubei Key Laboratory of Pollutant Analysis and Reuse Technology, Hubei Normal University, Huangshi 435002, People's Republic of China
Tel: (+86)-714-6515602; E-mail: gdyin@hbnu.edu.cn
[b] Xiling Lab, Chengdu 610041, People's Republic of China
E-mail: jinkunh@xilinglab.com

Received: ((will be filled in by the editorial staff))

This paper is dedicated to Professor Elias J. Corey on the occasion of his 90th birthday.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201######. ((Please delete if not appropriate))

Abstract. The low loading combination of complex [9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene]copper(I) iodide and simple ligand-free palladium(II) acetate was found efficient for the domino synthesis of diarylalkynes by the reaction of aryl halides with trimethylsilylethynylene or bis(trimethylsilyl)acetylene in a single-step procedure. The unsymmetrical diarylalkynes can be obtained through a one-pot two-step approach. The reactions of aryl bromides with 1,4-bis(trimethylsilyl)butadiyne also furnished the corresponding 1,4-diaryl-1,3-diynes in a similar fashion. This route to diarylalkynes and 1,4-diaryl-1,3-diynes is complementary to previously reported synthetic procedures.

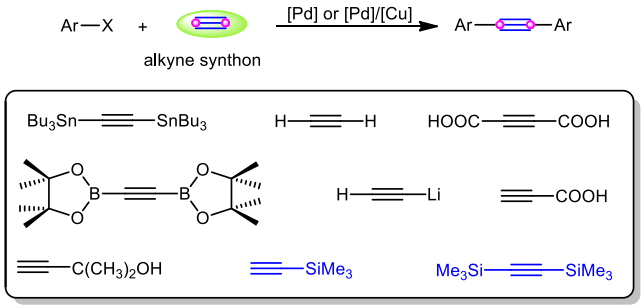
Keywords: diarylalkynes; alkynylation; domino reactions; Sonogashira-type coupling; one-pot synthesis

Introduction

Diarylalkynes are very important precursors in organic synthesis,[1] which can be converted into a variety of functionalized molecules, including biologically active heterocycles via click chemistry[2] and organic materials.[3] The palladium-catalyzed coupling of aryl halides with diborylethyne[4] via Suzuki-Miyaura reaction or with bis(tributylstannyl)acetylene[5] via Stille reaction is practicably useful under certain circumstancese. Nevertheless, these reactions are often limited by the availability of acetylene resources. In general, Sonogashira-type coupling of aryl halides with terminal arylacetylenes is a more powerful strategy.[6] In order to avoid the multi-step protection/deprotection approach to terminal arylacetylenes,[7] the direct reaction of aryl halides with various acetylene synthons in a one-pot domino procedure has been developed in recent years (Scheme 1). The acetylene synthons include gaseous acetylene,[8] lithium acetylide,[9] 2-methylbut-3-yn-2-ol,[10] propiolic acid,[11] 2-butynedioic acid,[12] trimethylsilylacetylene[13] and bis(trimethylsilyl)acetylene.[14] Among them trimethylsilylacetylene is the most frequently used acetylene synthon for the domino synthesis of diarylalkynes due to its availability as well as mild deprotection conditions.[15] The pioneering work of this domino reaction is reported by Brisbios and co-workers through *in situ* deprotection of trimethylsilylethynylene-added intermediates.[16] However, aryl iodides appear more efficient for this reaction, though 4-CN, 4-NMe_2 and phenyl-substituted bromobenzenes are reported inactive even at 80 °C. Apparently, most of these existing one-pot methods have some drawbacks including the limitation in aryl halide substrates, low yield, high reaction temperature or high catalyst loading. Accordingly, a more efficient one-pot approach to symmetrical or unsymmetrical diarylalkynes is still highly desired. Recently, Huang et al. first prepared the Cu(Xantphos)I complex by the simple mixing of 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene (Xantphos) with copper(I) iodide in acetonitrile and found it can effectively catalyze the C–C/C≡C bonding formation in the presence of a palladium source.[17] In a continuation of our efforts to use this copper complex in organic synthesis, herein we

10.1002/adsc.201701128

would like to report the $Pd(OAc)_2$/Cu(Xantphos)I system for efficient synthesis of diarylalkynes in a one-pot domino procedure from aryl halides and trimethylsilylethynylene or bis(trimethylsilyl)acetylene.

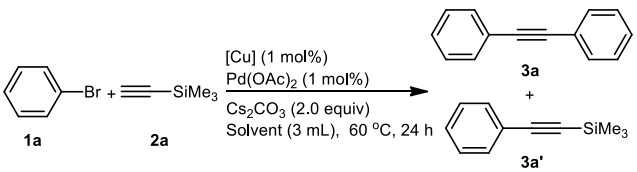


Scheme 1. Synthesis of diarylalkynes from various acetylene synthons

Results and Discussion

Following the previous experimental results conditions,[17b] we investigated the coupling reaction between bromobenzene (1.0 mmol, **1a**) and trimethylsilylacetylene (1.0 mmol, **2a**) in the presence of $Pd(OAc)_2$ (1 mol%) and Cu(Xantphos)I (1 mol%) using Cs_2CO_3 as base in anhydrous DMF at 60 °C for 24 h, and it was found that the expected product trimethyl(phenylethynyl)silane (**3a'**) was not observed. Instead, the reaction afforded the symmetrical 1,2-diphenylethyne (**3a**) in 57% yield with the recovery of unreacted bromobenzene (Table 1, entry 1). The amount of **2a** was reduced to 0.5 equiv, resulting in an obvious improvement of yield to 84%. Best result (93%) was obtained with 1:0.6 ratio of **1a**/**2a** (Table 1, entries 2–5). Notably, the mono-Sonogashira coupling product **3a'** was the major product when the less polar toluene was used as solvent, and **3a** was surprisingly not observed (Table 1, entries 6, 7). In the meantime, **3a'** was afforded in good yield at room temperature by replacing bromobenzene with iodobenzene (Table 1, entry 7). Trace amount of expected product was observed instead of CuI and $Cu(PPh_3)_3I$ with Cu(Xantphos)I (Table 1, entries 8, 10). In addition, the combination of $Pd(Xantphos)_2$[18] with CuI gave **3a** in 61% yield (Table 1, entry 9).

Table 1. Optimization of reaction conditions for the synthesis of 1,2-diphenylethyne[a]



Entry	**1a**/**2a**	[Cu][b]	Solvent	Yield[c](%) **3a**/**3a'**
1	1.0/1.0	Cu(Xantphos)I	DMF	57/0
2	1.0/0.5	Cu(Xantphos)I	DMF	84/0
3	1.0/0.6	Cu(Xantphos)I	DMF	93(83[d])/0
4	1.0/0.7	Cu(Xantphos)I	DMF	74/0
5	1.0/0.8	Cu(Xantphos)I	DMF	68/0
6	1.0/0.5	Cu(Xantphos)I	Toluene	0/81
7	1.0/1.2	Cu(Xantphos)I	Toluene	0/77(0/82[e])
8	1.0/0.6	CuI	DMF	trace/0
9	1.0/0.6	CuI[f]	DMF	61/0
10	1.0/0.6	$Cu(PPh_3)_3I$	DMF	<10/0

[a] All of the reactions were carried out with **1a** (1.0 mmol), **2a** (0.5–1.2 mmol), $Pd(OAc)_2$ (0.01 mmol) and [Cu] (0.01 mmol) and Cs_2CO_3 (2.0 mmol) in anhydrous DMF (3 mL) at 60 °C for 24 h unless otherwise specified.
[b] Xantphos = 9,9-Dimethyl-4,5-bis(diphenylphosphino)-xanthene.
[c] Yield was determined by GC based on the amount of **1a**.
[d] Isolated yield.
[e] Iodobenzene was used at room temperature for 12 h.
[f] $Pd(Xantphos)_2$ (0.01 mmol) was employed.

With the optimized conditions in hand, we examined the reaction scope using a variety of aryl halides, and the results are summarized in Table 2. It was found that the reactions displayed good functional group tolerance. Substrates bearing electron-rich (-Me, -OMe, -SMe, $-NMe_2$) and electron-deficient ($-NO_2$, -COMe, -CN, $-CF_3$, $-SO_2Me$) substitutents on the phenyl ring could be converted to the corresponding symmetrical diarylalkynes **3b**−**3j** in moderate to good yields. The structure of **3j** was confirmed by X-ray crystallographic analysis (Figure 1). The reactions proceeded smoothly at room temperature using aryl iodides as the substrates, affording the corresponding product **3a**, **3c** and **3f** in 77−86% yields. This transformation was also suitable for naphthalene ring (**3k**). The heterocyclic substrates such as pyridine, quinoline, isoquinoline, furan, thiophene, and benzo[*b*]thiophene also furnished **3l**−**3t** in 71−83% yields. Apparently, the substitution position of bromine atom on these heterocycles did not significantly affect the reaction yields. 1,2-Di(thiazol-2-yl)ethyne (**3u**) can be used as an attractive synthon for the preparation of supramolecular ligand, and it was obtained in less than 32% yield from 2-bromothiazole and trimethylsilyl acetylene in three steps protection/deprotection sequence.[19] To our delight, by using our one-pot procedure, a better yield of **3u** was afforded. Similarly, the new fascinating molecule 1,2-di(pyrimidin-2-yl)ethyne **3v** was also obtained in 71% yield. The X-ray crystallographic analysis indicates all the atoms in this struture are nearly in a plane (Figure 2). Next, (*E*)-(2-bromovinyl)benzene and (2-bromoethene-1,1,2-triyl)tribenzene were also suitable for this transformation, delivering the corresponding dienynes **3w** and **3x** in 75% and 68% yields, respectively.

10.1002/adsc.201701128

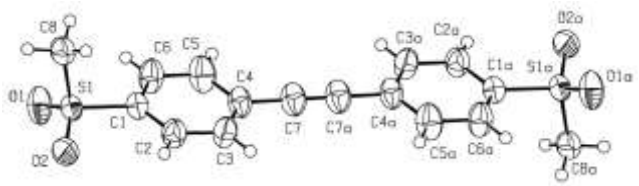


Figure 1. X-ray structures of compounds **3j** (CCDC No. 1570103)

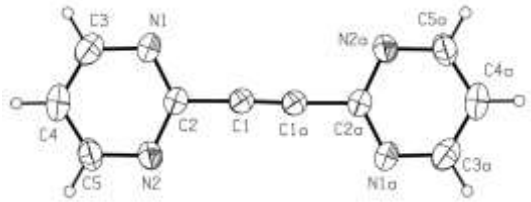
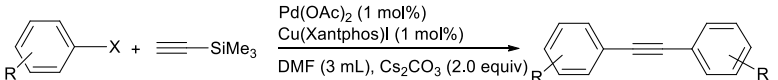
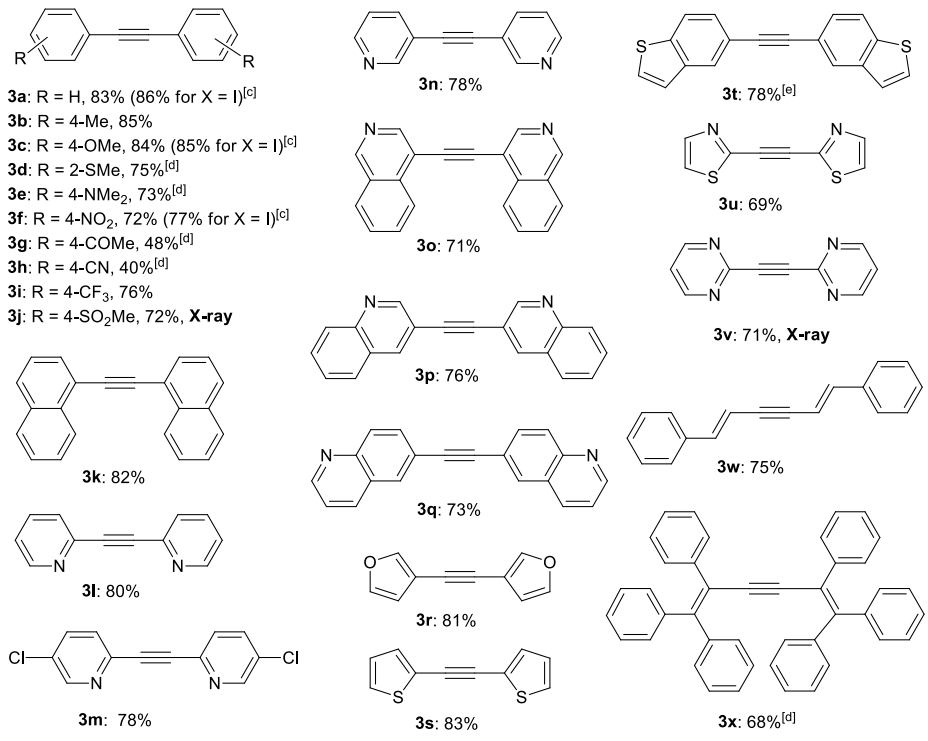


Figure 2. X-ray structures of compounds **3v** (CCDC No. 1570104)

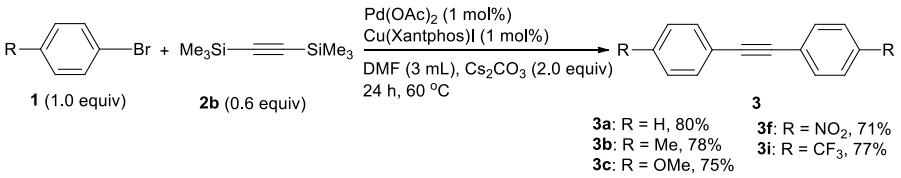
It has been reported that the trimethylsilyl group can be easily removed in the presence of inorganic base.[20] We also found that trimethyl(phenylethynyl)silane (**3a'**) gave phenylacetylene in nearly quantitative yield in the presence of Cs_2CO_3 in DMF within 10 min. Notably, Nishihara and co-workers reported that under non-basic conditions, the sila-Sonogashira coupling reaction of aryl iodides with alkynylsilanes proceeded soomthly *via* the Si-C bond direct activation by using the Pd/Cu co-catalyst system in DMF.[13a, 14c, 21] Accordingly, bis(trimethylsilyl)acetylene (**2b**) was employed to react with several representative aryl bromines, also resulting in the diarylalkynes **3a**−**3c**, **3f** and **3i** in 71−80% yields (Scheme 2).

Table 2. One-pot domino synthesis of diarylalkynes and diaryldienynes from aryl bromides or iodides and trimethylsilylacetylene[a, b]

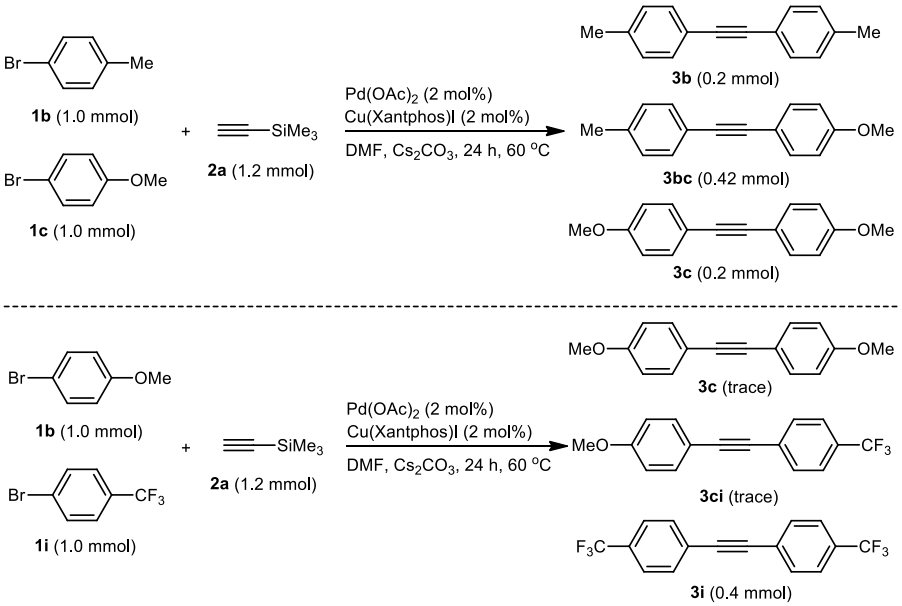




[a] All of the reactions were carried out with **1** (1.0 mmol), **2a** (0.6 mmol), $Pd(OAc)_2$ (0.01 mmol) and Cu(Xantphos)I (0.01 mmol) and Cs_2CO_3 (2.0 mmol) in anhydrous DMF (3 mL) at 60 °C for 24 h unless otherwise specified.
[b] Isolated yields based on the amount of aryl halides (**1**).
[c] Aryl iodides were employed at room temperature for 12 h.
[d] 0.8 mmol of **2a** was employed.
[e] $Pd(OAc)_2$ (0.02 mmol) and Cu(Xantphos)I (0.02 mmol) were employed.



Scheme 2. One-step domino synthesis of diarylalkynes from aryl bromides and bis(trimethylsilyl)acetylene

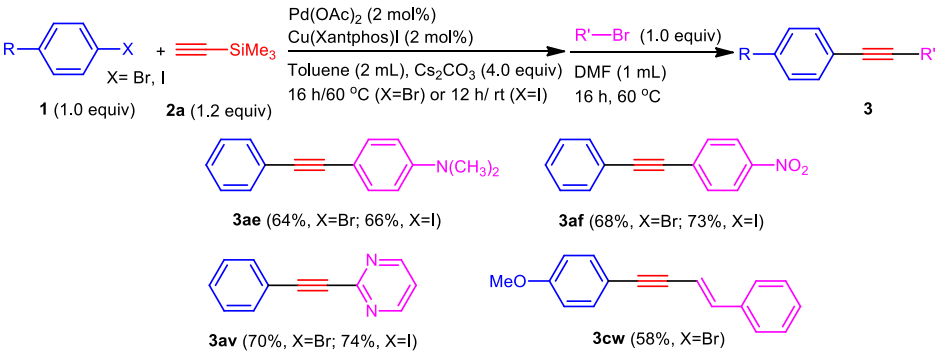


Scheme 3. Competing coupling of aryl bromides with trimethylsilylacetylene

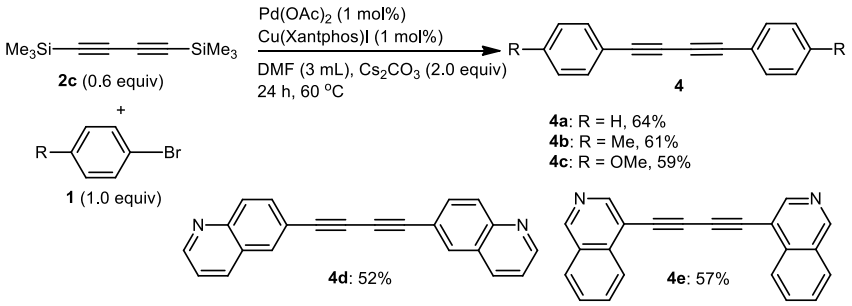
In order to investigate the relative reaction activity, the competing coupling of two different aryl bromines with **2a** was examined (Scheme 3). Two electron-rich (-Me and -OMe) substituted bromobenzenes gave a mixture of homo-coupling products **3b**/**3c** and cross-coupling product **3bc**. When the competing coupling occurred between electron-rich (-OMe) and electron-deficient (-CF_3) substituted bromobenzenes, the reaction gave the homo-coupling **3i** as the major product while small amount of **3c**/**3ci** was observed with the recovery of unreacted starting material **1b**. This may be attributed to the higher reaction activity for the electron-deficient substrate.

Ideally, it is our desire to effectively obtain the unsymmetrical diarylalkynes in a one-pot procedure by using the present catalytic system. It was observed that in the less polar solvent toluene, the resulting trimethylsilyl group was stable (Table 1, entries 6, 7). Accordingly, a one-pot, two-step reaction procedure was examined. The reaction was carried out with the first phenyl halides (**1**) and **2a** in toluene at 60 °C (for X = Br) or room temperature (for X = I), then the solution of the second aryl bromides in DMF was added to the above mixture at 60 °C. The experimental results showed that the corresponding cross-coupling products **3ae**, **3af** and **3av** were obtained in good yields, and the symmetrical products were not observed. In addition, the step-wise reaction of 1-bromo-4-methoxybenzene, **2a** and (*E*)-(2-bromovinyl)benzene also gave the eneyne **3cw** in 58% yield (Scheme 4).

1,3-Diynes are also ubiquitous structural motifs in functional materials and important intermediates in organic synthesis.[22] The copper-catalyzed Glaser oxidative homo-coupling of terminal alkynes is the widely used method.[23] In recent years, some attractive approaches to 1,3-diynes have been developed.[24] Several examples between the reactions of aryl iodides with 1,4-bis(trimethylsilyl)butadiyne (**2c**) gave the corresponding 1,4-diaryl-1,3-diynes.[25] Herein, we also expected to obtain the symmetrical 1,3-diynes directly from the reaction of the more easily available aryl bromides with **2c** in one-pot. We were pleased to find that the desired products **4a**−**4e** were isolated in 52−64% yields, as shown in Scheme 5.



Scheme 4. One-pot two-step reaction for the synthesis of unsymmetrical diarylalkynes



Scheme 5. One-pot reaction for the synthesis of symmetrical diaryl-1,3-diynes

Jean-Cyrille Hierso[26] and Manoj Trivedi[27] independently found that the low loading of $[Pd(allyl)Cl]_2$/copper(I) iodide ferrocenyl tetraphosphine complexes and $[Pd(allyl)Cl]_2/[Cu_4(\mu_2\text{-}I)_2(\mu_3\text{-}I)_2(\mu\text{-dtbpf})_2]$ (dtbpf = 1,1′-bis(di-*tert*-butylphosphino)ferrocene) were efficient synergetic system for Sonogashira coupling reaction, which are representative examples for the phosphine ligand complexation to copper instead of commonly used palladium. Moreover, Chin-Fa Lee demonstrated that in the absence of palladium salt, Cu(Xantphos)I can activate the terminal acetylenes and catalyze Sonogashira coupling of aryl/alkenyl iodides and bromides with terminal alkynes under microwave irradiation. But high reaction temperature (135 °C) is required even for aryl iodides. In addition, our further experimental results showed that in the presence of $Pd(OAc)_2$, only trace amount of expected product was observed replacement of Cu(Xantphos)I with CuI and $Cu(PPh_3)_3I$ (Table 1, entries 8, 10). The $Pd(Xantphos)_2$/CuI catalytic system gave **3a** in 61% yield (Table 1, entry 9). Accordingly, the probable reason for this mild and high-efficient $Pd(OAc)_2$/Cu(Xantphos)I catalytic coupling system is that Cu(Xantphos)I could more efficiently activate the terminal acetylenes than copper(I) iodide due to the effect by Xantphos.

Conclusion

In conclusion, we found that the $Pd(OAc)_2$/Cu(Xantphos)I system is effective for the domino synthesis of diarylalkynes from aryl halides and frequently used acetylene synthon trimethylsilylethynylene as well as bis(trimethylsilyl)acetylene in a one-pot procedure. The reactions of aryl bromides with 1,4-bis(trimethylsilyl)butadiyne also furnished the corresponding symmetrical 1,4-diaryl-1,3-diynes. The easy preparation and excellent stability of Cu(Xantphos)I, low loading of ligand-free palladium salt $Pd(OAc)_2$, mild reaction conditions, convenient execution as well as the wide range of substrates make this new system be competitive in currently known methods, which is an efficient route to diarylalkynes and 1,4-diaryl-1,3-diynes.

Experimental Section

General Information: All the chemicals were commercially available and used without further purification. All solvents were dried and distilled according to standard procedures. ^1H and ^{13}C NMR were recorded in $CDCl_3$ using Bruker Avance II 300 MHz spectrometers at 300 and 75 MHz, respectively. Chemical shifts are reported relative to TMS (internal standard). High resolution mass spectra were recorded using a Bruker ultrafleXtreme MALDI-TOF/TOF (HCCA matrix) or Solanx70 FT-MS or Thermo Scientific LTQ Orbitrap XL. IR spectra were obtained as KBr pellet samples using a Nicolet 5700 FTIR spectrometer. Flash column chromatography was performed on silica gel (200–300 mesh). Melting points

were determined using an uncorrected X-4 apparatus. The X-ray crystal structure determination was performed using a Bruker Smart APEX CCD system.

General procedure for one-pot synthesis of symmetry diarylalkynes 3a–3x, 4a–4e (Schemes 1, 2, 5)

The mixture of aryl halides (**1**, 1.0 mmol) and trimethylsilylethynylene (**2a**, 0.6 mmol) or bis(trimethylsilyl)acetylene (**2b**, 0.6 mmol) or 1,4-bis(trimethylsilyl)butadiyne (**2c**, 0.6 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), Cu(Xantphos)I (7.7 mg, 0.01 mmol) and Cs_2CO_3 (652 mg, 2.0 mmol) in anhydrous DMF (3 mL) was heated at 60 ºC for 12–24 h under argon atmosphere. After the reactions were completed, DMF was removed under reduced pressure. The mixture was extracted with ethyl acetate (3×15 mL) three times, and the combined organic layers were dried over anhydrous Na_2SO_4 and filtered. After removal of the solvent, the residue was purified by flash column chromatography on silica gel using petroleum ether or the mixture of ethyl acetate/petroleum ether (v:v, 1/100 to 1/2) as the eluent to afford the target products.

Diphenyl acetylene (**3a**).[8f] White solid; yield 83%, 74 mg; m.p. 60–61 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54–7.50 (m, 4H), 7.32–7.27 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 131.5, 128.3, 128.2, 123.2, 89.4; HRMS *m/z* (ESI) calcd for $C_{14}H_{11}$: 179.0855, found: 179.0861 $[M+H]^+$.

Bis(*p*-tolyl)acetylene (**3b**).[8f] White solid; yield 85%, 88 mg; m.p. 131–133 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.7 Hz, 4H), 7.14 (d, *J* = 7.7 Hz, 4H), 2.36 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.2, 131.4, 129.1, 120.4, 88.9, 21.5; HRMS *m/z* (ESI) calcd for $C_{16}H_{15}$: 207.1168, found: 207.1177 $[M+H]^+$.

1,2-Bis(4-methoxyphenyl)acetylene (**3c**).[8f] Yellow solid; yield 84%, 100 mg; m.p. 140–142 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46–7.43 (m, 4H), 6.88–6.84 (m, 4H), 3.80 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.3, 132.8, 115.6, 113.9, 87.9, 55.2; HRMS *m/z* (ESI) calcd for $C_{16}H_{14}O_2$: 238.0988, found: 238.0986 $[M]^+$.

1,2-Bis(2-(methylthio)phenyl)ethyne (**3d**).[29] Yellow solid; yield 75%, 101 mg; m.p. 123–124 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (dd, J_1 = 7.6 Hz, J_2 = 1.0 Hz, 2H), 7.33–7.27 (m, 2H), 7.18 (d, *J* = 7.8 Hz, 2H), 7.14–7.09 (m, 2H), 2.52 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.6, 132.6, 128.8, 124.22, 124.20, 121.3, 93.1, 15.2; HRMS *m/z* (ESI) calcd for $C_{16}H_{15}S_2$: 271.0610, found: 271.0614 $[M+H]^+$.

4,4'-(Ethyne-1,2-diyl)bis(*N*,*N*-dimethylaniline) (**3e**).[30] Yellow solid; yield 73%, 96 mg; m.p. 232–234 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (dd, J_1 = 6.9 Hz, J_2 = 2.1 Hz, 4H), 6.67–6.64 (m, 4H), 2.97 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.7, 132.4, 111.9, 111.1, 88.1, 40.3; HRMS *m/z* (ESI) calcd for $C_{18}H_{21}N_2$: 265.1699, found: 265.1699 $[M+H]^+$.

1,2-Bis(4-nitrophenyl)ethyne (**3f**).[8f] Yellow solid; yield 72%, 96 mg; m.p. 214–215 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.9 Hz, 4H), 7.71 (d, *J* = 8.8 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.7, 132.6, 128.9, 123.8, 92.0; HRMS *m/z* (ESI) calcd for $C_{14}H_9N_2O_4$: 269.0557, found: 269.0548 $[M+H]^+$.

1,1'-(Ethyne-1,2-diylbis(4,1-phenylene))diethanone (**3g**).[16a] Yellow solid; yield 48%, 63 mg; m.p. 198–200 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.4 Hz, 4H), 7.64 (d, *J* = 8.4 Hz, 4H), 2.63 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.2, 136.6, 131.9, 128.3, 127.5, 91.6, 26.6; HRMS *m/z* (ESI) calcd for $C_{18}H_{14}O_2$: 262.0988, found: 262.0982 $[M]^+$.

4,4'-(Ethyne-1,2-diyl)dibenzonitrile (**3h**).[5c] Yellow solid; yield 40%, 46 mg; m.p. 253–254 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69–7.61 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.3, 132.2, 127.1, 118.2, 112.4, 91.5; HRMS *m/z* (ESI) calcd for $C_{16}H_9N_2$: 229.0760, found: 229.0758 $[M+H]^+$.

1,2-Bis(4-(trifluoromethyl)phenyl)acetylene (**3i**).[8a] White solid; yield 76%, 119 mg; m.p. 107–108 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67–7.61 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.5, 130.6 (q, $J_{C\text{-}F}$ = 32.6 Hz), 126.9, 126.0 (d, $J_{C\text{-}F}$ = 3.6 Hz), 120.7 (d, $J_{C\text{-}F}$ = 270.6 Hz), 90.6; HRMS *m/z* (ESI) calcd for $C_{16}H_9F_6$: 315.0603, found: 315.0600 $[M+H]^+$.

1,2-Bis(4-(methylsulfonyl)phenyl)ethyne (**3j**). Yellow solid; yield 72%, 120 mg; m.p. 292–293 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.4 Hz, 4H), 7.74 (d, *J* = 8.4 Hz, 4H), 3.09 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.5, 132.6, 128.0, 127.6, 91.1, 44.4; IR (KBr) *v*: 770, 843, 967, 1088, 1141, 1304, 1399, 1596, 1631, 2852, 2925, 3432 cm^{-1}; HRMS *m/z* (ESI) calcd for $C_{16}H_{14}O_4S_2Na$: 357.0226, found: 357.0222 $[M+Na]^+$.

1,2-Di(naphthalen-1-yl)ethyne (**3k**).[16a] Yellow solid; yield 82%, 114 mg; m.p. 127–129 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.57 (d, *J* = 8.4 Hz, 2H), 7.91–7.88 (m, 6H), 7.64–7.51 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.3, 130.6, 128.9, 128.4, 126.9, 126.5, 126.3, 125.3, 121.1, 92.4; HRMS *m/z* (ESI) calcd for $C_{22}H_{15}$: 279.1168, found: 279.1161 $[M+H]^+$.

1,2-Di(pyridine-2-yl)ethyne (**3l**).[5c] Brown solid; yield 80%, 72 mg; m.p. 71–73 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.64 (d, *J* = 4.8 Hz, 2H), 7.73–7.68 (m, 2H), 7.62 (d, *J* = 7.8 Hz, 2H), 7.30–7.27 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.1, 142.8, 136.2, 127.7, 123.3, 87.9; HRMS *m/z* (ESI) calcd for $C_{12}H_9N_2$: 181.0760, found: 181.0759 $[M+H]^+$.

1,2-Bis(5-chloropyridin-2-yl)ethyne (**3m**). Yellow solid; yield 78%, 97 mg; m.p. 204–206 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.60 (d, *J* = 2.0 Hz, 2H), 7.70 (dd, J_1 = 8.4 Hz, J_2 = 2.5 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.3, 140.3, 136.2, 132.2, 128.3, 87.8; IR (KBr) *v*: 744, 834, 1007, 1110, 1400, 1596, 1631, 2851, 2922, 3424, 3726 cm^{-1}; HRMS *m/z* (MALDI) calcd for $C_{12}H_7Cl_2N_2$: 248.9981, found: 248.9971 $[M+H]^+$.

1,2-Di(pyridin-3-yl)ethyne (**3n**).[5c] White solid; yield 78%, 70 mg; m.p. 59–60 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.79 (d, *J* = 1.3 Hz, 2H), 8.59 (dd, J_1 = 4.9 Hz, J_2 = 1.6 Hz, 2H), 7.86–7.82 (m, 2H), 7.34–7.30 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.2, 149.0, 138.5, 123.1, 119.7, 89.1;

HRMS *m/z* (ESI) calcd for $C_{12}H_9N_2$: 181.0760, found: 181.0761 $[M+H]^+$.

1,2-Di(isoquinolin-4-yl)ethyne (**3o**).[5c] White solid; yield 71%, 99 mg; m.p. 235–236 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.27 (s, 2H), 8.91 (s, 2H), 8.43 (d, *J* = 8.3 Hz, 2H), 8.06 (d, *J* = 8.2 Hz, 2H), 7.88 (t, *J* = 7.1 Hz, 2H), 7.72 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.5, 146.8, 135.4, 131.4, 128.1 (2C), 127.8, 125.0, 115.6, 91.7; HRMS *m/z* (ESI) calcd for $C_{20}H_{13}N_2$: 281.1073, found: 281.1075 $[M+H]^+$.

1,2-Di(quinolin-3-yl)ethyne (**3p**).[5c] White solid; yield 76%, 106 mg; m.p. 169–171 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.06 (d, *J* = 2.0 Hz, 2H), 8.39 (d, *J* = 1.8 Hz, 2H), 8.13 (d, *J* = 8.5 Hz, 2H), 7.84 (d, *J* = 8.1 Hz, 2H), 7.79–7.74 (m, 2H), 7.60 (t, *J* = 7.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.9, 147.1, 138.7, 130.4, 129.5, 127.7, 127.5, 127.2, 116.8, 89.8; HRMS *m/z* (ESI) calcd for $C_{20}H_{13}N_2$: 281.1073, found: 281.1082 $[M+H]^+$.

1,2-Di(quinolin-6-yl)ethyne (**3q**). Yellow solid; yield 73%, 102 mg; m.p. 162–163 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.94 (dd, J_1 = 4.2 Hz, J_2 = 1.5 Hz, 2H), 8.18–8.10 (m, 3H), 8.09 (d, *J* = 1.6 H z, 3H), 7.87 (dd, J_1 = 8.7 Hz, J_2 =1.8 Hz, 2H), 7.45 (dd, J_1 = 8.3 Hz, J_2 = 4.3 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.1, 147.8, 135.8, 132.1, 131.3, 129.7, 128.0, 121.8, 121.3, 90.2; IR (KBr) *v*: 761, 831, 946, 1115, 1349, 1400, 1589, 1632, 2852, 2923, 3432, 3726 cm^{-1}; HRMS *m/z* (MALDI) calcd for $C_{20}H_{13}N_2$: 281.1073, found: 281.1069 $[M+H]^+$.

1,2-Di(furan-3-yl)ethyne (**3r**).[31] Yellow solid; yield 81%, 64 mg; m.p. 64–65 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, *J* = 0.6 Hz, 2H), 7.39 (t, *J* = 1.6 Hz, 2H), 6.49 (d, *J* = 1.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.4, 142.9, 112.4, 107.5, 82.0; HRMS *m/z* (ESI) calcd for $C_{10}H_6O_2$: 158.0368, found: 158.0377 $[M]^+$.

1,2-Di(thiophen-2-yl)ethyne (**3s**).[16a] White solid; yield 83%, 78 mg; m.p. 98–99 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32–7.27 (m, 4H), 7.03–7.00 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.1, 127.6, 127.1, 122.9, 86.2; HRMS *m/z* (ESI) calcd for $C_{10}H_7S_2$: 190.9984, found: 190.9987 $[M+H]^+$.

1,2-Bis(benzo[*b*]thiophen-5-yl)ethyne (**3t**).[32] Yellow solid; yield 78%, 113 mg; m.p. 218–220 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (s, 2H), 7.86 (d, *J* = 8.3 Hz, 2H), 7.53–7.48 (m, 4H), 7.34 (d, *J* = 5.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.6, 131.5, 127.33, 127.30, 126.9, 123.7, 122.5, 119.3, 89.2; HRMS *m/z* (ESI) calcd for $C_{18}H_{10}S_2$: 290.0224, found: 290.0227 $[M]^+$.

1,2-Bis(2-thiazolyl)ethylene (**3u**).[19] Yellow solid; yield 69%, 66 mg; m.p. 143–144 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, *J* = 3.3 Hz, 2H), 7.49 (d, *J* = 3.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.1, 144.2, 122.1, 86.0; HRMS *m/z* (ESI) calcd for $C_8H_5N_2S_2$: 192.9889, found: 192.9890 $[M+H]^+$.

1,2-Di(pyrimidin-2-yl)ethyne (**3v**). Yellow solid; yield 71%, 64 mg; m.p. 266–267 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.80 (d, *J* = 4.9 Hz, 4H), 7.33 (t, *J* = 4.9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.3, 152.3, 120.6, 84.4; IR (KBr) *v*: 793, 1351, 1400, 1631, 2852, 2923, 3432 cm^{-1}; HRMS *m/z* (MALDI) calcd for $C_{10}H_7N_4$: 183.0665, found: 183.0670 $[M+H]^+$;

(1*E*, 5*E*)-1,6-Diphenylhexa-1,5-dien-3-yne (**3w**).[33] Yellow solid; yield 75%, 86 mg; m.p. 57–59 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43–7.40 (m, 4H), 7.37–7.34 (m, 3H), 7.31–7.28 (m, 3H), 7.01 (s, 1H), 6.96 (s, 1H), 6.37 (s, 1H), 6.32 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.1, 136.3, 128.7, 128.6, 126.3, 108.2, 91.5; HRMS *m/z* (ESI) calcd for $C_{18}H_{14}Na$: 253.0988, found: 253.0993 $[M+Na]^+$.

Hexa-1,5-dien-3-yne-1,1,2,5,6,6-hexaylhexabenzene (**3x**). Yellow solid; yield 68%, 181 mg; m.p. 244–245 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39–7.27 (m, 5H), 7.24–7.19 (m, 5H), 7.09–7.03 (m, 12H), 6.97–6.95 (m, 4H), 6.92–6.89 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.2, 142.6, 141.5, 139.2, 131.1, 130.3, 130.0, 127.8, 127.7, 127.63, 127.57, 127.1, 126.6, 122.0, 95.6; IR (KBr) *v*: 708, 773, 1028, 1074, 1350, 1400, 1440, 1486, 1596, 1631, 3432, 3773 cm^{-1}; HRMS *m/z* (MALDI) calcd for $C_{42}H_{30}$: 534.2342, found: 534.2345 $[M]^+$.

1,4-Diphenylbuta-1,3-diyne (**4a**).[34] White solid; yield 64%, 65 mg; m.p. 85–86 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55–7.52 (m, 4H), 7.38–7.30 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.5, 129.2, 128.4, 121.8, 81.5, 73.9; HRMS *m/z* (ESI) calcd for $C_{16}H_{11}$: 203.0855, found: 203.0865 $[M+H]^+$.

1,4-Di-*p*-tolylbuta-1,3-diyne (**4b**).[34] White solid; yield 61%, 70 mg; m.p. 182–183 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.1 Hz, 4H), 7.14 (d, *J* = 8.0 Hz, 4H), 2.36 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.5, 132.4, 129.2, 118.8, 81.5, 73.4, 21.6; HRMS *m/z* (ESI) calcd for $C_{18}H_{14}$: 230.1096, found: 230.1093 $[M]^+$.

1,4-Bis(4-methoxyphenyl)buta-1,3-diyne (**4c**).[34] Yellow solid; yield 59%, 77 mg; m.p. 139–140 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.7 Hz, 4H), 6.85 (d, *J* = 8.7 Hz, 4H), 3.82 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.3, 134.0, 114.1, 114.0, 81.2, 73.0, 55.3; HRMS *m/z* (ESI) calcd for $C_{18}H_{14}O_2$: 262.0988, found: 262.0979 $[M]^+$.

1,4-Di(quinolin-6-yl)buta-1,3-diyne (**4d**). Yellow solid; yield 52%, 79 mg; m.p. 270–272 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.95–8.93 (m, 2H), 8.16–8.07 (m, 6H), 7.82–7.79 (m, 2H), 7.48–7.43 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.5, 148.0, 135.8, 132.8, 132.2, 129.9, 127.9, 122.0, 119.9, 81.7, 75.0; IR (KBr) *v*: 765, 793, 834, 897, 1115, 1316, 1349, 1400, 1490, 1631, 3430 cm^{-1}; HRMS *m/z* (ESI) calcd for $C_{22}H_{13}N_2$: 305.1073, found: 305.1074 $[M+H]^+$.

1,4-Di(isoquinolin-4-yl)buta-1,3-diyne (**4e**). Yellow solid, yield 57%, 87 mg; m.p. 251–253 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.26 (s, 2H), 8.85 (s, 2H), 8.33 (d, *J* = 8.3 Hz, 2H), 8.04 (d, *J* = 8.2 Hz, 2H), 7.86 (t, *J* = 7.6 Hz, 2H), 7.71 (t, *J* = 7.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.9, 148.2, 136.1, 131.6, 128.3, 128.2, 127.7, 125.0, 114.6, 80.6, 78.8; IR (KBr) *v*: 749, 779, 796, 892, 1020, 1270, 1401, 1617, 1631, 2850, 2919, 3428 cm^{-1}; HRMS *m/z* (ESI) calcd for $C_{22}H_{13}N_2$: 305.1073, found: 305.1065 $[M+H]^+$.

The competing coupling of aryl bromides with trimethylsilylacetylene (Scheme 3)

The mixture of two aryl halides (**1**, 1.0 mmol) and trimethylsilylethynylene (**2a**, 1.2 mmol), $Pd(OAc)_2$ (4.6 mg, 0.02 mmol), Cu(Xantphos)I (15.4 mg, 0.02 mmol) and Cs_2CO_3 (1.3 g, 4.0 mmol) in anhydrous DMF (3 mL) was heated at 60 °C for 24 h under argon atmosphere. After the reactions were completed, DMF was removed under reduced pressure. The mixture was extracted with ethyl acetate (3×15 mL) three times, and the combined organic layers were dried over anhydrous Na_2SO_4 and filtered. After removal of the solvent, the residue was purified by flash column chromatography on silica gel petroleum ether) as the eluent to afford the products. The spectral data for compounds **3bc** and **3ci** are consistent with our published paper.[17b]

General procedure for one-pot synthesis of unsymmetrical diarylalkynes 3ae, 3af, 3av and 3cw (Scheme 4)

The mixture of aryl halides (**1**, 1.0 mmol) and trimethylsilylacetylene (**2a**, 1.2 mmol), $Pd(OAc)_2$ (4.6 mg, 0.02 mmol), Cu(Xantphos)I (15.4 mg, 0.02 mmol) and Cs_2CO_3 (1.3 g, 4.0 mmol) in anhydrous toluene (2 mL) was heated at 60 °C (for X = Br, 16 h) or room temperature (for X = I, 12 h) under argon atmosphere, then the solution of another aryl bromides in DMF (1 mL) was added to the mixture at 60 °C for 16 h. After the reactions were completed, DMF was removed under reduced pressure. The mixture was extracted with ethyl acetate (3×15 mL) three times, and the combined organic layers were dried over anhydrous Na_2SO_4 and filtered. After removal of the solvent, the residue was purified by flash column chromatography on silica gel using the mixture of ethyl acetate and petroleum ether (v:v, 1/6) as the eluent to afford the pure product. The spectral data for compounds **3ae** and **3af** are consistent with our published paper.[17b]

2-(Phenylethynyl)pyrimidine (**3av**).[35] Yellow solid; yield 70%, 126 mg; m.p. 74–75 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.75 (d, *J* = 5.0 Hz, 2H), 7.82–7.66 (m, 2H), 7.42–7.36 (m, 3H), 7.24 (t, *J* =4.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.2, 153.2, 132.5, 129.6, 128.3, 121.2, 119.5, 87.8 (2C) ; HRMS *m/z* (ESI) calcd for $C_{12}H_9N_2$: 181.0760, found: 181.0761 $[M+H]^+$.

(*E*)-1-methoxy-4-(4-phenylbut-3-en-1-yn-1-yl)benzene (**3cw**).[36] Yellow solid; yield 58%, 136 mg; m.p. 49–50 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.7 Hz, 4H), 7.36–7.27 (m, 3H), 7.00 (d, *J* = 16.2 Hz, 1H), 6.87–6.84 (m, 2H), 6.38 (d, *J* = 16.2 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.6, 140.4, 136.5, 133.0, 128.7, 128.4, 126.2, 115.5, 114.0, 108.4, 91.8, 87.6, 55.3; HRMS *m/z* (ESI) calcd for $C_{17}H_{15}O$: 235.1117, found: 235.1109 $[M+H]^+$.

Acknowledgements

We gratefully acknowledge support from the National Natural Science Foundation of China (21542009).

References

[1] a) K. Ozaki, K. Murai, W. Matsuoka, K. Kawasumi, H. Ito, K. Itami, *Angew. Chem., Int. Ed*. **2017**, *56*, 1361–1364; b) A. Lerchen, S. Vásquez-Céspedes, F. Glorius, *Angew. Chem., Int. Ed*. **2016**, *55*, 3208–3211; c) E.-C. Liu, M.-K. Chen, J.-Y. Li, Y.-T. Wu, *Chem. Eur. J*. **2015**, *21*, 4755–4761; d) B. Godoi, R. F. Schumacher, G. Zeni, *Chem. Rev.* **2011**, *111*, 2937–2980.

[2] a) F. Alonso, Y. Moglie, G. Radivoy, *Acc. Chem. Res.* **2015**, *48*, 2516−2528; b) P. Thirumurugan, D. Matosiuk, K. Jozwiak, *Chem. Rev*. **2013**, *113*, 4905–4979.

[3] a) Z. Zhuang, F. Bu, W. Luo, H. Peng, S. Chen, R. Hu, A. Qin, Z. Zhao, B. Tang, *J. Mater. Chem. C*, **2017**, *5*, 1836–1842; b) Y. Liu, J. W. Y. Lam, B. Tang, *Natl. Sci. Rev*. **2015**, *2*, 493–509; c) S. Kaur, V. Bhalla, V. Vij, M. Kumar, *J. Mater. Chem. C*, **2014**, *2*, 3936–3941.

[4] a) O. Shynkaruk, Y. Qi, A. Cottrell-Callbeck, W. T. Delgado, R. McDonald, M. J. Ferguson, G. He, E. Rivard, *Organometallics* **2016**, *35*, 2232–2241; b) D. Jung, Y. K. Kang, *Bull. Korean Chem. Soc*. **2016**, *37*, 576–579; c) Y. K. Kang, P. Deria, P. J. Carroll, M. J. Therien, *Org. Lett*. **2008**, *10*, 1341–1344.

[5] a) Q. Yan, K. Cai, D. Zhao, *Phys. Chem. Chem. Phys*. **2016**, *18*, 1905–1910; b) R. Misra, P. Gautam, T. Jadhav, S. M. Mobin, *J. Org. Chem*. **2013**, *78*, 4940–4948; c) A. E. Brown, B. E. Eichler, *Tetrahedron Lett*. **2011**, *52*, 1960–1963; d) D. Türp, M. Wagner, V. Enkelmann, K. Müllen, *Angew Chem., Int. Ed*. **2011**, *50*, 4962–4965; e) Z. Fang, T.-L. Teo, L. Cai, Y.-H. Lai, A. Samoc, M. Samoc, *Org. Lett.* **2009**, *11*, 1–4.

[6] a) R. Chinchilla, C. Nájera, *Chem. Rev*. **2014**, *114*, 1783–1826; b) M. Bakherad, *Appl. Organometal. Chem*. **2013**, *27*, 125–140; c) H. Doucet, J. C. Hierso, *Angew. Chem., Int. Ed*. **2007**, *46*, 834–871; d) R. Chinchilla, C. Nájera, *Chem. Rev.* **2007**, *107*, 874–922; e) E. I. Negishi, L. Anastasia, *Chem. Rev*. **2003**, *103*, 1979–2018; f) A. Nagy, Z. Novák, A. Kotschy, *J. Organomet. Chem.* **2005**, *690*, 4453–4461.

[7] a) L. Patel, J. Chandrasekhar, J. Evarts, A. C. Haran, C. Ip, J. A. Kaplan, M. Kim, D. Koditek, L. Lad, E.-I. Lepist, M. E. McGrath, N. Novikov, S. Perreault, K. D. Puri, J. R. Somoza, B. H. Steiner, K. L. Stevens, J. Therrien, J. Treiberg, A. G. Villaseñor, A. Yeung, G. Phillips, *J. Med. Chem*. **2016**, *59*, 3532–3548; b) B. Desai, K. Dixon, E. Farrant, Q. Feng, K. R. Gibson, W. P. van Hoorn, J. Mills, T. Morgan, D. M. Parry, M. K. Ramjee, C. N. Selway, G. J. Tarver, G. Whitlock, A. G. Wright, *J. Med. Chem.* **2013**, *56*, 3033–3047.

[8] a) C.-J. Li, D.-L. Chen, C. W. Costello, *Org. Process Res. Dev.* **1997**, *1*, 325–327; b) E. K. Yum, J. W. Son, S. K. Kim, S. N. Kim, K. M. Kim, C. W. Lee, *Bull. Korean Chem. Soc.* **2010**, *31*, 2097–2099; c) R.

Rathore, C. L. Burns, I. A. Guzei, *J. Org. Chem.* **2004**, 69, 1524–1530; d) W. Zhang, H. Wu, Z. Liu, P. Zhong, L. Zhang, X. Huang, J. Cheng, *Chem. Commun.* **2006**, 4826–4828; e) R. Matake, Y. Niwa, H. Matsubara, *Org. Lett.* **2015**, *17*, 2354−2357; f) P. Chuentragool, K. Vongnam, P. Rashatasakhon, M. Sukwattanasinitt, S. Wacharasindhu, *Tetrahedron* **2011**, *67*, 8177−8182.

[9] J. Krishna, A. G. K. Reddy, G. Satyanarayana, *Adv. Synth. Catal.* **2015**, *357*, 3597–3610.

[10] a) Y. Zhao, Q. Liu, J. Li, Z. Liu, B. Zhou, *Synlett* **2010**, *12*, 1870–1872; b) C. Yi, R. Hua, H. Zeng, Q. Huang, *Adv. Synth. Catal*. **2007**, *349*, 1738–1742; c) Z. Novák, P. Nemes, A. Kotschy, *Org. Lett*. **2004**, *6*, 4917–4920.

[11] a) X. Li, F. Yang, Y. Wu, *RSC Adv*. **2014**, *4*, 13738–13741; b) J. Park, E. Park, A. Kim, S. A. Park, Y. Lee, K.-W. Chi, Y. H. Jung, I. S. Kim, *J. Org. Chem*. **2011**, *76*, 2214–2219; c) Y. Kim, A. Park, K. Park, S. Lee, *Tetrahedron Lett*. **2011**, *52*, 1766–1769; d) J. Moon, M. Jeong, H. Nam, J. Ju, J. H. Moon, H. M. Jung, S. Lee, *Org. Lett*. **2008**, *10*, 945–948.

[12] a) A. Archambeau, T. Rovis, *Angew. Chem., Int. Ed*. **2015**, *54*, 13337–13340; b) S. Peng, T. Gao, S. Sun, Y. Peng, M. Wu, H. Guo, J. Wang, *Adv. Synth. Catal*. **2014**, *356*, 319–324; c) S. Peng, L. Wang, J. Huang, S. Sun, H. Guo, J. Wang, *Adv. Synth. Catal*. **2013**, *355*, 2550–2557; d) K. Park, G. Bae, J. Moon, J. Choe, K. H. Song, S. Lee, *J. Org. Chem*. **2010**, *75*, 6244–6251.

[13] a) P. K. Walia, S. Pramanik, V. Bhalla, M. Kumar, *Chem. Commun*. **2015**, *51*, 17253–17256; b) W. Guo, R. Pleixats, A. Shafir, T. Parella, A*dv. Synth. Catal*. **2015**, *357*, 89–99; c) P. K. Mandali, D. K. Chand, *Catal. Commun*. **2014**, *47*, 40–44; d) N. Sakai, R. Komatsu, N. Uchida, R. Ikeda, T. Konakahara, *Org. Lett*. **2010**, *12*, 1300–1303; e) J. Gil-Moltó, C. Nájera, *Adv. Synth. Catal*. **2006**, *348*, 1874–1882; f) S. U. Son, Y. Jang, J. Park, H. B. Na, H. M. Park, H. J. Yun, J. Lee, T. Hyeon, *J. Am. Chem. Soc*. **2004**, *126*, 5026–5027; g) A. Arques, D. Aunon, P. Molina, *Tetrahedron Lett*. **2004**, *45*, 4337–4340.

[14] a) Y. Nishihara, E. Inoue, D. Ogawa, Y. Okada, S. Noyori, K. Takagi, *Tetrahedron Lett*. **2009**, *50*, 4643–4646; b) J. Gil-Moltó, C. Nájera, *Adv. Synth. Catal*. **2006**, *348*, 1874–1882.

[15] a) A. K. Jaiswal, K. K. Goh, S. Sung, R. D. Young, *Org. Lett.* **2017**, *19*, 1934–1937; b) Á. Sinai, Á. Mészáros, Á. Balogh, M. Zwillinger, Z. Novák, *Synthesis* **2017**, *49*, 2374–2388.

[16] a) M. J. Mio, L. C. Kopel, J. B. Braun, T. L. Gadzikwa, K. L. Hull, R. G. Brisbois, C. J. Markworth, P. A. Grieco, *Org. Lett*. **2002**, *4*, 3199–3202; b) R. Severin, J. Reimer, S. Doye, *J. Org. Chem*. **2010**, *75*, 3518–3521.

[17] a) J. Huang, J. Chan, Y. Chen, C. J. Borths, K. D. Baucom, R. D. Larsen, M. M. Faul, *J. Am. Chem. Soc*. **2010**, *132*, 3674–3675; b) M. Liu, M. Ye, G. Yin, D. Wang, J. Huang, *Tetrahedron Lett*. **2016**, *57*, 3137–3139.

[18] L. M. Klingensmith, E. R. Strieter, T. E. Barder, S. L. Buchwald, *Organometallics* **2006**, *25*, 82−91.

[19] S. Hiraoka, M. Shiro, M. Shionoya, *J. Am. Chem. Soc*. **2004**, *126*, 1214–1218.

[20] a) C. Atienza, C. Mateo, Ó. de Frutos, A. M. Echavarren, *Org. Lett.* **2001**, *3*, 153–155; b) X. You, X. Xie, H. Chen, Y. Li, Y. Liu, *Chem. Eur. J*. **2015**, *21*, 18699–18705; c) F. D. Lewis, M. C. Sajimon, X. Zuo, M. Rubin, V. Gevorgyan, *J. Org. Chem.* **2005**, *70*, 10447–10452.

[21] Y. Nishihara, E. Inoue, S. Noyori, D. Ogawa, Y. Okada, M. Iwasaki, K. Takagi, *Tetrahedron* **2012**, *68*, 4869–4881.

[22] W. Shi, A. Lei, *Tetrahedron Lett*. **2014**, *55*, 2763–2772.

[23] K. S. Sindhu, G. Anilkumar, *RSC Adv*. **2014**, *4*, 27867–27887.

[24] a) B. Vilhanová, J. Václavík, L. Artiglia, M. Ranocchiari, A. Togni, J. A. Bokhoven, J. A. van Bokhoven, *ACS Catal*. **2017**, *7*, 3414–3418; b) X. Li, X. Xie, N. Sun, Y. Liu, *Angew. Chem., Int. Ed*. **2017**, *129*, 7098–7102; c) L. Su, J. Dong, L. Liu, M. Sun, R. Qiu, Y. Zhou, S.-F. Yin, *J. Am. Chem. Soc*. **2016**, *138*, 12348−12351; d) H. Peng, Y. Xi, N. Ronaghi, B. Dong, N. G. Akhmedov, X. Shi, *J. Am. Chem. Soc*. **2014**, *136*, 13174–13177; e) X. Li, X. Liu, H. Chen, W. Wu, C. Qi, H. Jiang, *Angew. Chem., Int. Ed*. **2014**, *53*, 14485–14489; f) D. Liu, F. Li, H. Li, W. Gong, J. Gao, J. Lang, *Eur. J. Org. Chem.* **2014**, *2014*, 4817–4822; g) Z. Huang, R. Shang, Z. Zhang, X. Tan, X. Xiao, Y. Fu, *J. Org. Chem*. **2013**, *78*, 4551–4557.

[25] a) T. M. McCormick, E. I. Carrera, T. B. Schon, D. S. Seferos, *Chem. Commun*. **2013**, *49*, 11182–11184; b) T. M. McCormick, A. A. Jahnke, A. J. Lough, D. S. Seferos, *J. Am. Chem. Soc*. **2012**, *134*, 3542–3548; c) S. Inoue, T. Jigami, H. Nozoe, *Heterocycles* **2000**, *52*, 159–170.

[26] a) M. Beaupérin, A. Job, H. Cattey, S. Royer, P. Meunier, J. C. Hierso, *Organometallics* **2010**, *29*, 2815–2822; b) M. Beaupérin, E. Fayad, R. Amardeil, H. Cattey, P. Richard, S. Brandès, P. Meunier, J. C.Hierso, *Organometallics* **2008**, *27*, 1506−1513.

[27] a) M. Trivedi, G. Singh, A. Kumarb, N. P. Rath, *Dalton Trans*. **2014**, *43*, 13620–13629; b) M. Trivedi, G. Singh, A. Kumarb, N. P. Rath, *Dalton Trans*. **2013**, *42*, 12849–12852.

[28] Y. Y. Lin, Y. J. Wang, J. H. Cheng, C. F. Lee, *Synlett* **2012**, *23*, 930–934.

[29] J. Heppekausen, R. Stade, R. Goddard, A. Fürstner, *J. Am. Chem. Soc*. **2010**, *132*, 11045–11057.

[30] W. Zhang, S. Kraft, J. S. Moore, *J. Am. Chem. Soc.* **2004**, *126*, 329–335.

[31] W. D. Wulff, J. S. McCallum, F. A. Kunng, *J. Am Chem. Soc.* **1988**, *110*, 7419–7434.

[32] M. Gulcur, P. Moreno-García, X. Zhao, M. Baghernejad, A. S. Batsanov, W. Hong, M. R. Bryce, T. Wandlowski, *Chem. Eur. J.* **2014**, *20*, 4653–4660.

[33] M. Huang, Y. Feng, Y. Wu, *Tetrahedron* **2012**, *68*, 376–381.

[34] L. Mahendar, B. V. Ramulu, G. Satyanarayana, *Synth. Commun*. **2017**, *47*, 1151–1158.

[35] B. Tang, F. Wang, J. Li, Y. Xie, M. Zhang, *J. Org. Chem.* **2007**, *72*, 6294–6297.

[36] P. Sun, H. Yan, L. Lu, D. Liu, G. Rong, J. Mao, *Tetrahedron* **2013**, 69, 6969–6974.

10.1002/adsc.201701128

FULL PAPER

One-pot Domino Synthesis of Diarylalkynes/1,4-Diaryl-1,3-diynes by [9,9-Dimethyl-4,5-bis(diphenylphosphino)xanthene]Copper(I) Iodine–Palladium(II) Acetate Catalyzed Double Sonogashira-type Reaction

Adv. Synth. Catal. **Year**, *Volume*, Page – Page

Shaozhong Qiu,[a] Caiyang Zhang,[a] Rui Qiu,[a] Guodong Yin[a,*] and Jinkun Huang[b,*]