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Pd-Catalyzed Decarboxylative Coupling of Propiolic Acids: One-Pot Synthesis of 1,4-Disubstituted 1,3-Diynes via Sonogashira−Homocoupling Sequence

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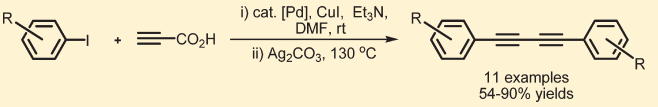
Supporting Information

ABSTRACT: One-pot synthesis of symmetric 1,4-disubstituted 1,3-diynes from iodoarenes and propiolic acid via Sonogashira reaction followed by Pd-catalyzed decarboxylative homocoupling is developed in high yields. Also, this system allows the one-pot synthesis of unsymmetric 1,4-disubstituted 1,3-diynes by cross-coupling of two different 3-substituted propiolic acids.



INTRODUCTION

Conjugated 1,3-diynes are very crucial materials in the fields of chemistry, biology, and material science because they have been used in the preparation of natural products,[1] organic and inorganic composites,[2] pharmaceuticals,[3] and π-conjugated polymers,[4] as well as the molecular recognition process.[5] The traditional method for the construction of symmetric 1,3-diynes is oxidative homocoupling reactions of terminal alkynes, reported by Glaser, via the treatment of Cu(I) salt in the presence of aqueous ammonia followed by air oxidation (Scheme 1, eq 1).[6] Later related modified methods to improve the disadvantage of the original reaction condition were developed by Eglinton[7] and Hay.[8] The method for constructing unsymmetrical 1,3-diynes was described by Chodkiewicz−Cadiot via Cu-catalyzed coupling between haloalkynes and terminal alkynes (Scheme 1, eq 2).[9] Yu and Jiao also reported Cu-catalyzed decarboxylative cross-coupling of propiolic acids and terminal alkynes for the synthesis of unsymmetrical conjugate diynes (Scheme 1, eq 3).[10] Pioneering work for the preparation of symmetrical 1,3-diynes using palladium catalysis was reported by Rossi et al. in 1985 (Scheme 1, eq 4).[11] Recently, Lei et al. demonstrated a new process for the construction of unsymmetrical 1,3-diynes, which includes Ni-catalyzed oxidative coupling of two different terminal alkynes with a high loading of one alkyne partner (Scheme 1, eq 5).[12] However, these methodologies present intrinsic drawbacks, namely the need for prefunctionalization of both coupling partners. For example, in the case of homocoupling of terminal alkynes, the preparation of terminal alkynes was often required, i.e. via Corey−Fuchs reaction with aldehydes,[13] Fritsch−Buttenberg−Wiechell rearrangement of vinyl bromides,[14] Seyferyth−Gilbert homologation with aldehydes,[15] and Sonogashira reaction[16] between haloarenes and metal (Si or Sn)-substituted acetylenes followed by reductive hydrogenation. Moreover, the methods for the synthesis of unsymmetrical 1,3-diynes have required the prefunctionalization to prepare haloalkynes or propiolic acids as well as terminal alkynes. The multistep syntheses required for the preparation of such substrates can pose additional barriers to their use. Therefore, it is highly desirable to develop more efficient methodologies saving synthetic steps and avoiding waste formation for synthesizing conjugate 1,3-diynes.

Transition metal-catalyzed decarboxylative sp^2-sp^2 cross-coupling of aryl carboxylic acids or aryl carboxylates with aryl halides is an established method for the synthesis of biaryl compounds.[17] Lee and co-workers first described palladium-catalyzed $sp-sp^2$ cross-coupling reaction of propiolic acid and aryl halides to afford unsymmetrical diaryl acetylenes.[18] Lee and Kim reported palladium-catalyzed decarboxylative $sp-sp^2$ cross-coupling reactions between alkynyl carboxylic acids and aryl halides or aryl triflates in the presence of Ag_2O and LiX (X = I, Cl).[19] Also, Loh and Feng reported Pd-catalyzed decarboxylative $sp-sp^2$ cross-coupling reactions of alkynyl carboxylic acids with aryl boronic acids.[20] Recently, Li et al. demonstrated palladium-catalyzed $sp-sp^3$ cross-coupling reaction to synthesize internal alkynes using alkynyl carboxylic acids and benzyl halides in the presence of Cs_2CO_3.[21] While there has been considerable research into the preparation of diaryl alkynes through metal-catalyzed decarboxylative cross-coupling reactions, an efficient metal-catalyzed decarboxylative homocoupling and cross-coupling reaction for the construction of 1,4-diaryl 1,3-diynes remains relatively unexplored.[22]

Herein, we demonstrate direct synthesis of symmetrical 1,4-disubstituted 1,3-diynes **4** from iodoarenes **1** and propiolic acid (**2**) via Sonogashira reaction followed by Pd-catalyzed decarboxylative homocoupling. Furthermore, one-pot synthesis of

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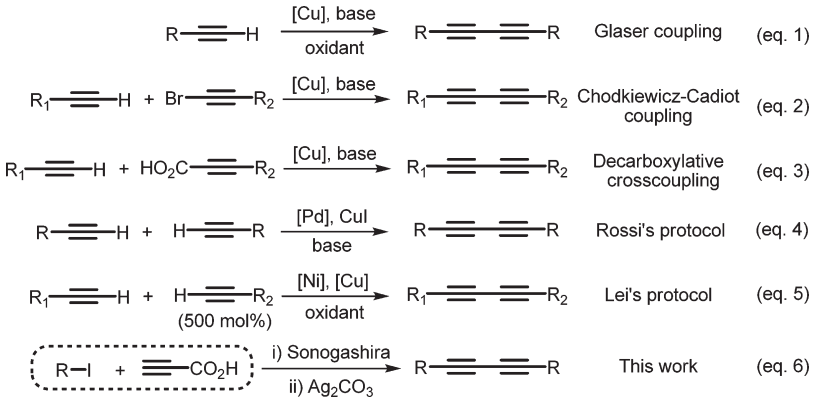
Scheme 1. Strategies for the Construction of 1,3-Diynes



Scheme 2. One-Pot Synthesis of 1,3-Diynes 4 or 5 from Iodoarenes 1 and Propiolic Acid (2)

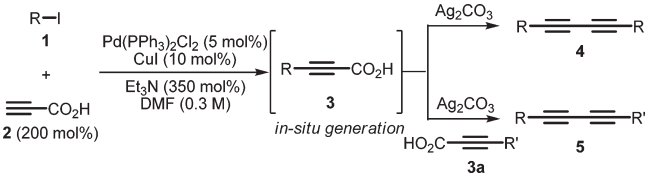
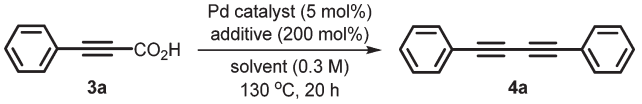


Table 1. Selected Optimization of Decarboxylative Homocoupling of 3-Phenylpropiolic Acid (3a)[a]



entry	catalyst	additive	solvent	yield (%)
1	$Pd(OAc)_2$	Ag_2CO_3	DMSO	56
2	$Pd(PPh_3)_2Cl_2$	Ag_2CO_3	DMSO	78
3	$Pd(TFA)_2$	Ag_2CO_3	DMSO	80
4	$Pd_2(dba)_3$	Ag_2CO_3	DMSO	76
5	$Pd(PPh_3)_4$	Ag_2CO_3	DMSO	82
6	$Pd(PPh_3)_4$		DMSO	0
7		Ag_2CO_3	DMSO	0
8	$Pd(PPh_3)_4$	AgI	DMSO	trace
9	$Pd(PPh_3)_4$	$AgNO_3$	DMSO	trace
10	$Pd(PPh_3)_4$	$CuCO_3$	DMSO	38
11	$Pd(PPh_3)_4$	Ag_2O	DMSO	60
12	$Pd(PPh_3)_4$	Ag_2CO_3	DMF	96

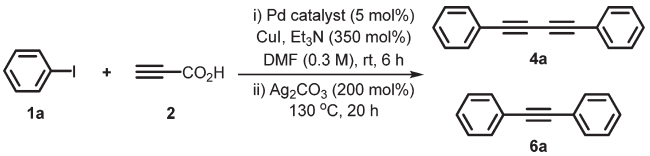
[a] All reactions were performed in 13 mm × 100 mm pressure tubes. The cited yields are of material isolated by column chromatography.

unsymmetrical 1,4-disubstituted 1,3-diynes **5** by cross-coupling of two different 3-substituted propiolic acids **3** and **3a** is described, as depicted in Scheme 2.

RESULTS AND DISCUSSION

Our investigation started with Pd-catalyzed decarboxylative homocoupling of 3-phenylpropiolic acid (**3a**), and the selected results are summarized in Table 1. As shown in entries 1−5, a range of Pd catalysts was screened in the presence of Ag_2CO_3 as an oxidant, and the use of $Pd(PPh_3)_4$ afforded our desirable adduct **4a** in 82% yield (Table 1, entry 5). In the absence of either palladium catalyst or Ag_2CO_3, no homocoupling product **4a** was observed even when using 100 mol % of $Pd(PPh_3)_4$, indicating both metals are required in the reaction (Table 1, entries 6 and 7). Next, our study focused on the use of additives such as AgI, $AgNO_3$, $CuCO_3$, and Ag_2O, but the chemical yield was not improved, as shown in entries 8−11. Solvent screening showed that optimum results could be obtained with DMF solvent, providing the desired product **4a** in 96% yield (Table 1, entry 12), whereas the use of other solvents such as THF, dioxane, DMSO, and AcOH was relatively ineffective.

Table 2. Selected Optimization of One-Pot Synthesis of 1,4-Diphenylbuta-1,3-diyne (4a)[a]



entry	catalyst	2 (mol %)	CuI (mol %)	yield (%)	ratio (**4a**:**6a**)[b]
1	$Pd(PPh_3)_4$	200	10	82	86:14
2	$Pd(PPh_3)_4$	200	20	76	83:17
3	$Pd(PPh_3)_4$	300	10	65	27:73
4	$Pd(PPh_3)_2Cl_2$	200	10	90	95:5

[a] All reactions were performed in 13 mm × 100 mm pressure tubes. The cited yields are of an inseparable mixture of **4a** and **6a** isolated by column chromatography. [b] Ratio was determined by GC-MS analysis.

On the basis of the established reaction conditions for decarboxylative homocoupling, we attempted to expand this transformation to the one-pot synthesis of symmetrical 1,4-diaryl 1,3-diynes from iodoarenes and propiolic acid. Our investigation started to find optimal reaction conditions for the formation of 1,4-diphenylbuta-1,3-diyne (**4a**). As shown in Table 2, the coupling of iodobenzene (**1a**) and propiolic acid (**2**) under standard Sonogashira conditions, such as 5 mol % of $Pd(PPh_3)_4$, 10 mol % of CuI, 350 mol % of Et_3N, and DMF, followed by the treatment of 200 mol % of Ag_2CO_3 afforded an inseparable mixture of the desired product **4a** and diaryl alkyne byproduct **6a** in 82% yield with a moderate chemoselectivity of 86:14 (Table 2, entry 1). Increasing the amount of CuI to 20 mol % provided a slightly reduced yield (76%) and chemoselectivity (83:17)

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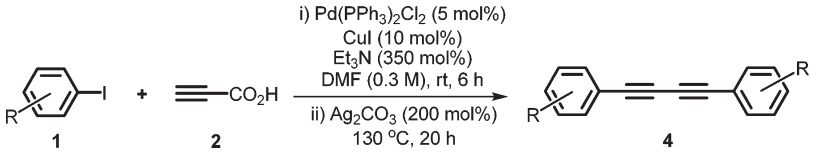
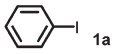
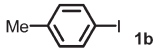
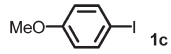
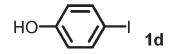
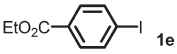
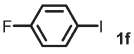
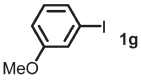
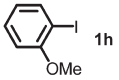
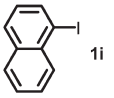
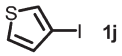
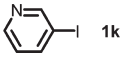
Table 3. Substrate Scope of One-Pot Synthesis of 1,4-Disubstituted-1,3-diynes (4)[a]



entry	iodoarene	product	yield (%)	ratio[b] (4:6)
1	 1a	4a	90	95:5
2	 1b	4b	86	99:1
3	 1c	4c	72	91:9
4	 1d	4d	80	99:1
5	 1e	4e	89	97:3
6	 1f	4f	73	90:10
7	 1g	4g	64	98:2
8	 1h	4h	79	94:6
9	 1i	4i	63	94:6
10	 1j	4j	54	95:5
11	 1k	4k	71	99:1

[a] All reactions were performed in 13 mm × 100 mm pressure tubes. The cited yields are of material isolated by column chromatography. [b] Ratio was determined by GC-MS analysis.

(Table 2, entry 2). Interestingly, the increased use of propiolic acid (**2**) gave the byproduct **6a** as a major compound (Table 2, entry 3). After further optimization, the best results were obtained when 5 mol % of $Pd(PPh_3)_2Cl_2$ was employed as a palladium catalyst, affording selectively the homocoupling product **4a** in 90% yield with a 95:5 ratio (Table 2, entry 4).

With the standard reaction conditions established, the substrate scope and limitations were explored, and the results are summarized in Table 3. As shown in entries 2−5, a variety of substrates with para-substituted electron-donating groups (Me, OMe, and OH) and an electron-withdrawing group (CO_2Et) provided the corresponding products **4b**−**e** in high yield (72−89%) with excellent chemoselectivities (91:9−99:1).

p-Halogen-substituted iodobenzene **1f** was compatible under the optimal reaction condition, and the desired 1,3-diyne product **4f** was produced in 73% yield with a 90:10 ratio (Table 3, entry 6). Electron-rich meta- and ortho-substituted iodobenzenes **1g** and **1h** also can be converted to the corresponding products **4g** and **4h**, respectively, in high yields (Table 3, entries 7 and 8). 1-Iodonaphthalene (**1i**) participated in this reaction to provide the corresponding product **4i** in 63% yield with a ratio of 94:6 (Table 3, entry 9). Finally, the heterocyclic iodides **1j** and **1k** also reacted smoothly in the decarboxylative coupling to furnish **4j** and **4k** in 54% and 71% yields with excellent selectivities, respectively (Table 3, entries 10 and 11).

To further explore the utility of our decarboxylative coupling reaction, the one-pot cross-coupling reaction between two different 3-substituted propiolic acids was examined, as shown in Table 4. Interestingly, the results reveal that the amount of coupling partner **3a** and base controls the reaction outcome. For example, an increase of unsymmetrical 1,3-diyne **5c** was observed with the use of triethylamine (Table 4, entries 1 and 2). However, the use of an excess amount of **3a** provided the reduced chemical yield of both unsymmetrical 1,3-diyne **5c** and symmetrical 1,3-diynes **4c** and **4a** (Table 4, entries 4 and 5). Eventually, the treatment of 200 mol % of phenylpropiolic acid (**3a**) and 200 mol % of Et_3N, under otherwise standard conditions, afforded the desired unsymmetrical 1,3-diyne **5c** in a good yield (55%) (Table 4, entry 3).

To evaluate the electronic effect in the cross-coupling reaction, iodobezene **1e** with the CO_2Et electron-withdrawing group was chosen as a substrate. As was expected, **1e** can accelerate the cross-coupling reaction to give unsymmetrical 1,3-diyne **5e**, compared to the case of electron-donating substrate **1c** (Table 4, entries 2 and 6). In particular, the reaction of **1e** with 200 mol % of phenylpropiolic acid (**3a**) and 200 mol % of Et_3N, under otherwise standard conditions, furnished the desired product **5e** in a remarkably increased yield (73%) (Table 4, entry 7).

A proposed reaction pathway for the formation of 1,4-disubstituted 1,3-diynes is shown in Scheme 3. At the initial stage of

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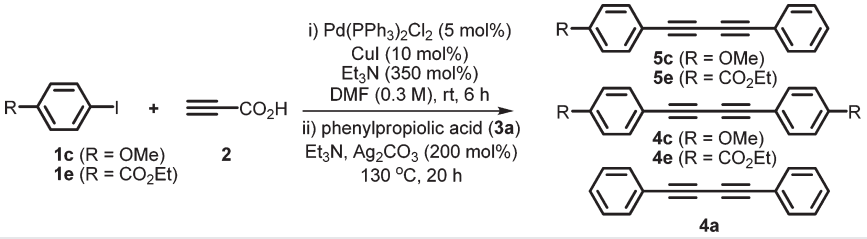
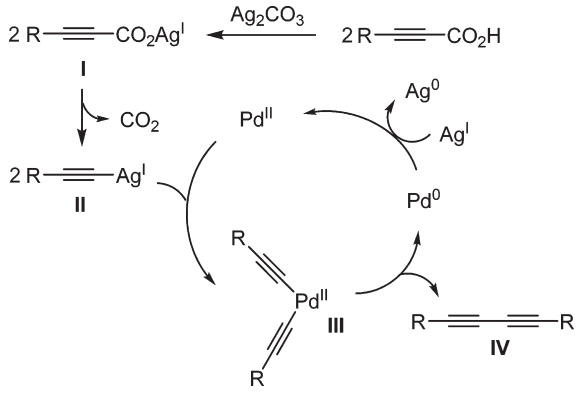
Table 4. One-Pot Cross-Coupling of 3-Substituted Propiolic Acids[a]



			yield (%)		
entry	**3a** (mol %)	Et_3N (mol %)	**5c**	**4c**	**4a**
1	150		44	25	34
2	150	150	50	26	48
3	200	200	55	30	59
4	300	300	46	28	59
5	500	500	35	22	47
			yield (%)		
entry	**3a** (mol %)	Et_3N (mol %)	**5e**	**4e**	**4a**
6	150	150	68	17	22
7	200	200	73	17	35

[a] All reactions were performed in 13 mm × 100 mm pressure tubes. The cited yields are confirmed by GC-MS analysis of combined materials isolated by column chromatography. 1,3-Diphenylacethylene was used as an internal standard.

Scheme 3. Proposed Reaction Mechanism



the reaction, Pd(0) catalyst is oxidized by silver carbonate to Pd(II) catalyst. Also, 3-substituted propiolic acid, generated from the corresponding iodoarene, can be converted into Ag(I)-acetylide intermediate **II** through the decarboxylation of Ag(I)-carboxylate intermediate **I**. Transmetalation of two Ag(I)-acetylides to Pd(II) would directly give dialkynylpalladium intermediate **III**, which can afford the desired 1,3-diyne product **IV** via reductive elimination and regenerate Pd(0) catalyst.

CONCLUSION

In conclusion, an efficient Pd-catalyzed decarboxylative homocoupling reaction of iodoarenes with propiolic acid using silver carbonate has been developed. Furthermore, unsymmetrical 1,3-diynes can be readily prepared by Pd-catalyzed cross-coupling reaction between 3-substituted propiolic acids generated in situ and commercial available 3-phenylpropiolic acid. Efforts are currently underway to extend this protocol to vinyl iodides, and the results will be reported in due course.

EXPERIMENTAL SECTION

Typical Experimental Procedure for the Decarboxylative Homocoupling of 3-Phenylpropiolic Acid (3a) (Table 1). To an oven-dried sealed tube under 1 atm of nitrogen gas charged with 3-phenylpropiolic acid (**3a**) (43.9 mg, 0.3 mmol, 100 mol %) and palladium catalyst (0.015 mmol, 5.0 mol %) in anhydrous DMF (1.0 mL, 0.3 M) was added silver or copper salts (0.6 mmol, 200 mol %). The reaction mixture was allowed to stir at 130 °C for 20 h, at which point the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO_2: *n*-hexanes:ethyl acetate) provided 1,4-diphenylbuta-1,3-diyne (**4a**).

Typical Experimental Procedure for One-Pot Synthesis of 1,3-Diynes from Iodoarenes and Propiolic Acid (Table 3). To an oven-dried sealed tube under 1 atm of nitrogen gas charged with iodoarenes **1a**−**k** (0.3 mmol, 100 mol %), $Pd(PPh_3)_2Cl_2$ (10.5 mg, 0.015 mmol, 5.0 mol %), and CuI (5.7 mg, 0.03 mmol, 10 mol %) in anhydrous DMF (1.0 mL, 0.3 M) was added propiolic acid (**2**) (37.1 μL, 0.6 mmol, 200 mol %) and triethylamine (0.146 mL, 1.05 mmol, 350 mol %). The reaction mixture was allowed to stir at room temperature for 6 h, and then Ag_2CO_3 (165.5 mg, 0.6 mmol, 200 mol %) was added to the reaction mixture. The reaction mixture was allowed to stir at 130 °C for 20 h, at which point the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO_2: *n*-hexanes:ethyl acetate) provided the desired 1,3-diynes **4a**−**k** and diarylalkyne byproducts **6a**−**k**. The ratio between 1,3-diynes and diarylalkynes was confirmed by GC-MS analysis.

Typical Experimental Procedure for One-Pot Cross-Coupling of 3-Substituted Propiolic Acids (Table 4). To an oven-dried sealed tube under 1 atm of nitrogen gas charged with 4-methoxyiodobenzene (**1c**) or ethyl 4-iodobenzoate (**1e**) (0.3 mmol, 100 mol %), $Pd(PPh_3)_2Cl_2$ (10.5 mg, 0.015 mmol, 5.0 mol %), and CuI (5.7 mg,

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0.03 mmol, 10 mol %) in anhydrous DMF (1.0 mL, 0.3 M) were added propiolic acid (**2**) (37.1 μL, 0.6 mmol, 200 mol %) and triethylamine (0.146 mL, 1.05 mmol, 350 mol %). The reaction mixture was allowed to stir at room temperature for 6 h, and then 3-phenylpropiolic acid (**3a**), triethylamine, and Ag_2CO_3 (165.5 mg, 0.6 mmol, 200 mol %) were added to the reaction mixture. The reaction mixture was allowed to stir at 130 °C for 20 h, at which point the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO_2: *n*-hexanes:ethyl acetate) provided the desired unsymmetrical 1,3-diynes (**5c** or **5e**) and unsymmetrical 1,3-diynes, respectively.

1,4-Diphenylbuta-1,3-diyne (4a):[23] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29−7.39 (m, 6H), 7.50−7.54 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 74.1, 81.8, 122.0, 128.6, 129.4, 132.7; GC (HP-5MS capillary column, 0.32 mm × 60 m, Agilent Technologies) carrier gas flow rate = He gas, 1 mL/min, initial column temp = 273 K, final column temp = 573 K, progress rate = 20 deg/min, retention time = 10.3 min; MS (EI) *m*/*z* (%) 202.6 (100%) [M^+].

1,4-Di(*p*-tolyl)buta-1,3-diyne (4b):[23] ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.34 (s, 6H), 7.12 (d, *J* = 8.1 Hz, 4H), 7.39 (d, *J* = 8.1 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.9, 73.6, 81.7, 119.0, 129.4, 132.6, 139.7; GC (HP-5MS capillary column, 0.32 mm × 60 m, Agilent Technologies) carrier gas flow rate = He gas, 1 mL/min, initial column temp = 273 K, final column temp = 573 K, progress rate = 20 deg/min, retention time = 11.7 min; MS (EI) *m*/*z* (%) 230.8 (100%) [M^+].

1,4-Bis(4-methoxyphenyl)buta-1,3-diyne (4c):[23] ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.80 (s, 6H), 6.83 (d, *J* = 8.7 Hz, 4H), 7.43 (d, *J* = 8.7 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.5, 73.1, 81.4, 114.1, 114.3, 134.3, 160.4; GC (HP-5MS capillary column, 0.32 mm × 60 m, Agilent Technologies) carrier gas flow rate = He gas, 1 mL/min, initial column temp = 273 K, final column temp = 573 K, progress rate = 20 deg/min, retention time = 14.1 min; MS (EI) *m*/*z* (%) 262.5 (100%) [M^+].

4,4′-(Buta-1,3-diyne-1,4-diyl)diphenol (4d): ^{1}H NMR (300 MHz, CD_3OD) δ 3.39 (br, 2H), 6.79 (d, *J* = 8.4 Hz, 4H), 7.37 (d, *J* = 8.4 Hz, 4H); ^{13}C NMR (75 MHz, CD_3OD) δ 73.3, 82.1, 113.9, 116.8, 135.2, 160.1; GC (HP-5MS capillary column, 0.32 mm × 60 m, Agilent Technologies) carrier gas flow rate = He gas, 1 mL/min, initial column temp = 273 K, final column temp = 573 K, progress rate = 20 deg/min, retention time = 15.3 min; MS (EI) *m*/*z* (%) 234.8 (100%) [M^+].

4,4′-(Buta-1,3-diyne-1,4-diyl)ethyl benzoate (4e):[23] ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.38 (t, *J* = 6.9 Hz, 6H), 4.36 (q, *J* = 6.9 Hz, 4H), 7.56 (dd, *J* = 6.9, 1.5 Hz, 4H), 8.00 (dd, *J* = 6.6, 1.5 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.5, 61.5, 76.4, 82.1, 126.2, 129.7, 131.1, 132.6, 165.9; GC (HP-5MS capillary column, 0.32 mm × 60 m, Agilent Technologies) carrier gas flow rate = He gas, 1 mL/min, initial column temp = 273 K, final column temp = 573 K, progress rate = 20 deg/min, retention time = 18.8 min; MS (EI) *m*/*z* (%) 346.5 (100%) [M^+].

1,4-Bis(4-fluorophenyl)buta-1,3-diyne (4f):[23] ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.99−7.05 (m, 4H), 7.47−7.51 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 73.5, 80.4, 115.8, 116.1, 117.78, 117.84, 134.5, 134.6, 161.4, 164.7; GC (HP-5MS capillary column, 0.32 mm × 60 m, Agilent Technologies) carrier gas flow rate = He gas, 1 mL/min, initial column temp = 273 K, final column temp = 573 K, progress rate = 20 deg/min, retention time = 10.0 min; MS (EI) *m*/*z* (%) 238.5 (100%) [M^+].

1,4-Bis(3-methoxyphenyl)buta-1,3-diyne (4g):[24] ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.82 (s, 6H), 6.93−6.97 (m, 2H), 7.06 (br, 2H), 7.13−7.16 (m, 2H), 7.26−7.29 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.5, 73.8, 81.7, 116.3, 117.3, 122.9, 125.3, 129.8, 159.5; GC (HP-5MS capillary column, 0.32 mm × 60 m, Agilent Technologies) carrier gas flow rate = He gas, 1 mL/min, initial column temp = 273 K, final column temp = 573 K, progress rate = 20 deg/min, retention time = 13.5 min; MS (EI) *m*/*z* (%) 262.8 (100%) [M^+].

1,4-Bis(2-methoxyphenyl)buta-1,3-diyne (4h):[24] ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.88 (s, 6H), 6.84−6.92 (m, 4H), 7.30 (dt, *J* = 7.5, 1.8 Hz, 2H), 7.46 (dd, *J* = 7.5, 1.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 56.0, 78.1, 78.8, 110.8, 111.5, 120.7, 130.7, 134.6, 161.5; GC (HP-5MS capillary column, 0.32 mm × 60 m, Agilent Technologies) carrier gas flow rate = He gas, 1 mL/min, initial column temp = 273 K, final column temp = 573 K, progress rate = 20 deg/min, retention time = 13.1 min; MS (EI) *m*/*z* (%) 262.4 (100%) [M^+].

1,4-Di(naphthalen-1-yl)buta-1,3-diyne (4i):[24] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42−7.48 (m, 2H), 7.51−7.57 (m, 2H), 7.59−7.65 (m, 2H), 7.81−7.89 (m, 6H), 8.40−8.46 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 78.9, 81.2, 119.7, 125.5, 126.4, 126.9, 127.5, 128.7, 130.0, 132.3, 133.3, 134.1; GC (HP-5MS capillary column, 0.32 mm × 60 m, Agilent Technologies) carrier gas flow rate = He gas, 1 mL/min, initial column temp = 273 K, final column temp = 573 K, progress rate = 20 deg/min, retention time = 23.6 min; MS (EI) *m*/*z* (%) 302.6 (100%) [M^+].

1,4-Di(thiophen-3-yl)buta-1,3-diyne (4j):[25] ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 7.25 (dd, *J* = 5.1, 1.2 Hz, 2H), 7.57 (dd, *J* = 5.1, 3.0 Hz, 2H), 7.89 (dd, *J* = 3.0, 1.2 Hz, 2H); ^{13}C NMR (75 MHz, $(CD_3)_2CO$) δ 73.9, 77.5, 121.3, 127.5, 130.9, 133.0; GC (HP-5MS capillary column, 0.32 mm × 60 m, Agilent Technologies) carrier gas flow rate = He gas, 1 mL/min, initial column temp = 273 K, final column temp = 573 K, progress rate = 20 deg/min, retention time = 10.7 min; MS (EI) *m*/*z* (%) 214.7 (100%) [M^+].

1,4-Di(pyridin-3-yl)buta-1,3-diyne (4k):[23] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24−7.29 (m, 2H), 7.79 (dt, *J* = 7.8, 1.5 Hz, 2H), 8.56−8.58 (m, 2H), 8.74 (br, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 76.6, 79.2, 118.9, 123.1, 139.4, 149.5, 153.2; GC (HP-5MS capillary column, 0.32 mm × 60 m, Agilent Technologies) carrier gas flow rate = He gas, 1 mL/min, initial column temp = 273 K, final column temp = 573 K, progress rate = 20 deg/min, retention time = 10.8 min; MS (EI) *m*/*z* (%) 204.8 (100%) [M^+].

■ ASSOCIATED CONTENT

Supporting Information. Spectroscopic data for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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