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Synthesis of Symmetrical and Unsymmetrical Diarylalkynes from Propiolic Acid Using Palladium-Catalyzed Decarboxylative Coupling

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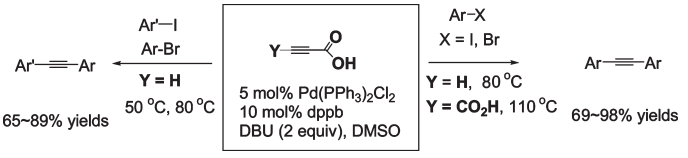

Symmetrical diarylalkynes were obtained from propiolic acid (or 2-butynedioic acid) and aryl halides in good yields. The optimized reaction conditions were 2.0 equiv of aryl halide, 1.0 equiv of propiolic acid, 5.0 mol % $Pd(PPh_3)_2Cl_2$, 10.0 mol % 1,4-bis(diphenylphosphino)butane (dppb), 2.0 equiv of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and dimethyl sulfoxide (DMSO) as the solvent. The coupling reaction of 2-butynedioic acid with aryl halides required 110 °C. The coupling reaction showed tolerance for functional groups such as ester, ketone, and aldehyde and exhibited chemoselectivity. In the coupling reaction of propiolic acid with aryl bromide, the diarylated product was the major one at 80 °C, even though 1 equiv of aryl halides was employed. However, among the monoarylated products that were formed predominantly at 25 and 50 °C in the coupling reaction with aryl iodide, more Sonogashira coupling product was obtained than the decarboxylative coupling product. Unsymmetrical diarylalkynes were also synthesized via this method, in which all reagents, including propiolic acid, aryl iodide, and aryl bromides were added at the beginning of the reaction.

Introduction

The Sonogashira coupling reaction of alkynes and aryl or alkenyl halides is the most straightforward and powerful method for the construction of sp carbon and sp^2 carbon bonds.[1] The structure of arylalkynes and conjugated enynes has received attention due to their important role in bioactive compounds and conjugated functional materials.[2] Since its inception, several new methodologies related to the Sonogashira reaction have been developed and improved to overcome several significant limitations, including the copper-free,[3] ligand-free,[4] microreactor,[5] and aqueous condition[6] reactions. The structure of diarylalkyne was one of the important starting materials for the synthesis of π-conjugated compounds. For the synthesis of symmetrical diarylalkyne derivatives, acetylene has been employed as an alkyne source.[7] However, it is disadvantaged by its cumbersome handling in the gaseous state in the organic laboratory. To overcome this problem, protected acetylenes such as

(1) For original work, see: (a) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *16*, 4467–4470. For reviews on the Sonogashira reactions, see: (b) Tykwinski, R. P. *Angew. Chem., Int. Ed.* **2003**, *42*, 1566–1568. (c) Negishi, E.; Anastasia, L. *Chem. Rev.* **2003**, *103*, 1979–2017. (d) Nicolaou, K. C.; Bulger, P. G.; Sarlah, D. *Angew. Chem., Int. Ed.* **2005**, *44*, 4442–4489. (e) Yin, L.; Liebscher, J. *Chem. Rev.* **2007**, *107*, 133–173. (f) Doucet, H.; Hierso, J.-C. *Angew. Chem., Int. Ed.* **2007**, *46*, 834–871.

(2) For bioactive compounds, see: (a) Boukouvalas, J.; Cote, S.; Ndzi, B. *Tetrahedron Lett.* **2007**, *48*, 105–107. (b) Falcone, D.; Li, J.; Kale, A.; Jones, G. B. *Bioorg. Med. Chem. Lett.* **2008**, *18*, 934–937. For conjugated functional materials, see: (c) Moon, J. H.; McDaniel, W.; MacLean, P.; Hancock, L. F. *Angew. Chem., Int. Ed.* **2007**, *46*, 8223–8225. (d) Liu, J.; Lam, J. W. Y.; Tang, B. Z. *Chem. Rev.* **2009**, *109*, 5799–5867. (e) Heravi, M. M.; Sadjadi, S. *Tetrahedron* **2009**, *65*, 7761–7775. (f) Chinchilla, R.; Nájera, C. *Chem. Rev.* **2007**, *107*, 874–923.

(3) (a) Kawanami, H.; Matsushima, K.; Sato, M.; Ikushima, Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 5129–5132. (b) Bakherad, M.; Keivanloo, A.; Bahramian, B.; MIhanparast, S. *Tetrahedron Lett.* **2009**, *50*, 6418–6420.

(4) Biffis, A.; Scattolin, E.; Ravasio, N.; Zaccheria, F. *Tetrahedron Lett.* **2007**, *48*, 8761–8764.

(5) Sugimoto, A.; Fukuyama, T.; Rahman, M. T.; Ryu, I. *Tetrahedron Lett.* **2009**, *50*, 6364–6367.

(6) Shi, S.; Zhang, Y. *Synlett* **2007**, 1843–1850.

(7) (a) Cassar, L. *J. Organomet. Chem.* **1975**, *93*, 253–257. (b) Rathore, R.; Burns, C. L.; Guzei, I. A. *J. Org. Chem.* **2004**, *69*, 1524–1530.

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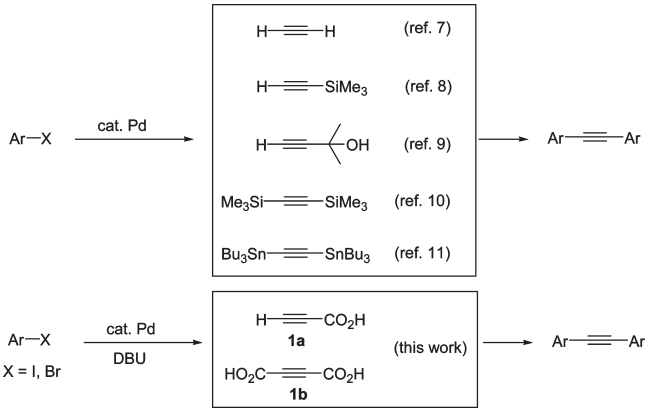
trimethylsilylacetylene[8] and 2-methylbut-3-yn-2-ol[9] have commonly been employed. Nevertheless, further drawbacks include the production of an equivalent of metal or organic waste, with the former being expensive and the latter requiring a strong base in the deprotection step. For example, Grieco and co-workers employed trimethylsilylacetylene in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU); however, their method required a copper cocatalyst and 6 equiv of DBU.[8b] Nishihara and co-workers used bis(trimethylsilyl)acetylene as an alkyne source, but they also experienced some drawbacks.[10] A large amount of copper cocatalyst (50 mol %) was required, and they were only able to apply it to the aryl iodide substrates. In addition, bis(tributylstannyl)acetylene has often been employed in symmetrical diarylalkynes as a functional material, but it is very expensive and produces toxic organometal waste.[11] Recently, research has focused on expanding the pool of viable aryl halide coupling partners by exploring new ligand systems.[12] However, the development of an alkyne source has received less research attention.

The decarboxylative coupling reaction has also been investigated in a variety of coupling reactions.[13] Most recently, we first reported the use of propiolic acid as the alkyne source in the palladium-catalyzed coupling reaction of aryl halides and alkynes.[14] We and another group[15] reported the decarboxylative coupling reaction of aryl or alkyl alkynyl carboxylic acid with aryl halides using palladium catalyst.

SCHEME 1. Synthesis of Diarylalkyne from a Variety of Alkyne Source



This method did not need copper as a cocatalyst and produced CO_2 as a byproduct. Despite its eco-friendliness, however, the method suffered several drawbacks: 6 equiv of tetrabutylammonium fluoride (TBAF) was required for the synthesis of unsymmetrical diarylalkynes from propiolic acid, high catalytic loadings (5 mol % $Pd_2(dba)_3$ and 40 mol % P^tBu_3) were required for the symmetrical diarylalkynes, both TBAF and P^tBu_3 are expensive and sensitive to moisture, and, moreover, the latter is unstable to air. Therefore, the requirement remains for a general protocol that consists of an equal amount of inexpensive base and a more stable ligand system (Scheme 1).

Results and Discussion

Synthesis of Symmetrical Diarylalkynes. First, we attempted to find a less expensive base as a replacement for TBAF and employed propiolic acid as the alkyne. To this end, we screened a variety of bases in the reaction of propiolic acid (**1a**) and phenyl bromide (**2a**) under the following conditions: $Pd(PPh_3)_2Cl_2$ as a palladium source and 1,4-bis(diphenylphosphino)butane (dppb) as a ligand in DMSO solvent. The results are summarized in Table 1.

The bases exerted a significant effect in the reaction. Common organic bases such as 4-*N,N*-dimethylaminopyridine (DMAP), morpholine, 1,8-diaminonaphthalene, and pyridine did not support the coupling reaction and showed no conversion of phenyl bromide (Table 1, entries 1−4). Although Et_3N and DABCO resulted in 30% and 29% conversion, respectively, the desired coupling product was not found in the reaction mixture (entries 5 and 6). Among the organic bases, only DBU and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) exhibited good reactivity. Although all the inorganic bases showed some reactivity, with Cs_2CO_3 affording the best result (entry 9), they were all inferior to DBU. When TBAF was employed as a base, the desired product was formed with 74% yield (entry 13). Evaluation of the palladium sources revealed that $Pd(PPh_3)_2Cl_2$ was superior to all other choices, with low to moderate yields being attained, but not full conversion of phenyl bromide (entries 14−16).

Next, we screened a variety ligands and solvents for the coupling reaction of propiolic acid and phenyl bromide (Table 2). When the reaction was carried out with $Pd(PPh_3)_2Cl_2$ in the absence of dppb as a ligand, the desired product was obtained in 73% yield (entry 1). The yield was slightly improved when the extra PPh_3 ligand was added instead of

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(11) (a) Shi, Y.; Qian, H.; Lucas, N. T.; Xu, W.; Wang, Z. *Tetrahedron Lett.* **2009**, *50*, 4110–4113. (b) Fang, Z.; Teo, T.-L.; Cai, L.; Lai, Y.-H.; Samoc, A.; Samoc, M. *Org. Lett.* **2009**, *11*, 1–4.

(12) (a) Gelman, D.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2003**, *42*, 5993–5996. (b) Feuerstein, M.; Doucet, H.; Santelli, M. *Tetrahedron Lett.* **2005**, *46*, 1717–1720. (c) Yi, C.; Hua, R. *J. Org. Chem.* **2006**, *71*, 2535–2537. (d) Li, J.-H.; Li, J.-L.; Wang, D.-P.; Pi, S.-F.; Xie, Y.-X.; Zhang, M.-B.; Hu, X.-C. *J. Org. Chem.* **2007**, *72*, 2053–2057.

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(14) Moon, J.; Jeong, M.; Nam, H.; Ju, J.; Moon, J. H.; Jung, H. M.; Lee, S. *Org. Lett.* **2008**, *10*, 945–948.

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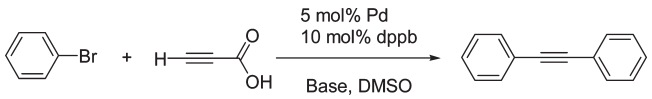
TABLE 1. Screening of Bases and Palladium Sources[a]

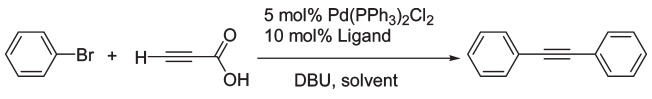


2a **1a** **3a**

entry	Pd source	base	conv (%)[b]	yield (%)[b]
1	$Pd(PPh_3)_2Cl_2$	DMAP	0	0
2	$Pd(PPh_3)_2Cl_2$	morpholine	0	0
3	$Pd(PPh_3)_2Cl_2$	1,8-di(NH_2)Np[c]	0	0
4	$Pd(PPh_3)_2Cl_2$	pyridine	0	0
5	$Pd(PPh_3)_2Cl_2$	Et_3N	30	0
6	$Pd(PPh_3)_2Cl_2$	DABCO	29	0
7	$Pd(PPh_3)_2Cl_2$	DBN	64	61
8	$Pd(PPh_3)_2Cl_2$	DBU	100	99
9	$Pd(PPh_3)_2Cl_2$	Cs_2CO_3	76	64
10	$Pd(PPh_3)_2Cl_2$	K_2CO_3	53	42
11	$Pd(PPh_3)_2Cl_2$	Na_2CO_3	37	34
12	$Pd(PPh_3)_2Cl_2$	K_3PO_4	54	30
13	$Pd(PPh_3)_2Cl_2$	TBAF	82	74
14	$Pd(OAc)_2$	DBU	70	68
15	$Pd_2(dba)_3$	DBU	58	52
16	$Pd(PPh_3)_4$	DBU	90	85

[a]Reaction conditions: **2a** (1.0 mmol), **1a** (0.5 mmol), Pd (0.025 mmol), dppb (0.05 mmol), base (1.0 mmol), and DMSO (3.0 mL) at 80 °C for 3 h. [b]Yield was determined by GC. [c]1,8-Diaminonaphthalene.

TABLE 2. Screening of Ligands and Solvents[a]



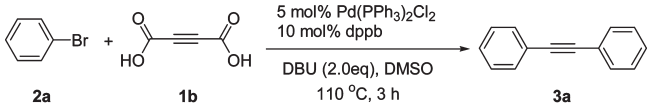
2a **1a** **3a**

entry	ligand	solvent	conv (%)[b]	yield (%)[b]
1		DMSO	80	73
2	PPh_3	DMSO	92	85
3	P^tBu_3	DMSO	97	96
4	PCy_3	DMSO	90	84
5	dppf	DMSO	98	96
6	Xantphos	DMSO	93	90
7	dppb	DMSO/H_2O[c]	100	98
8	dppb	toluene	14	10
9	dppb	diglyme	22	19
10	dppb	*p*-xylene	11	7
11	dppb	NMP	41	23

[a]Reaction conditions: **2a** (1.0 mmol), **1a** (0.5 mmol), $Pd(PPh_3)_2Cl_2$ (0.025 mmol), ligand (0.05 mmol), DBU (1.0 mmol), and solvent (3.0 mL) at 80 °C for 3 h. [b]Yield was determined by GC. [c]DMSO/H_2O (v/v 4:1)

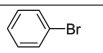
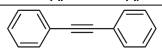
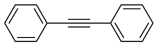
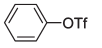
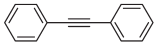
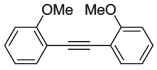
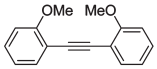
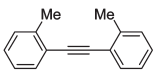
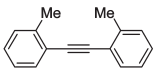
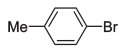
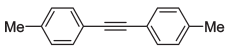
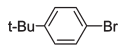
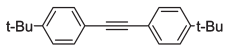
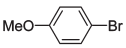
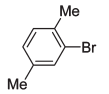
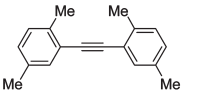
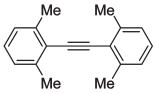
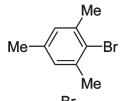
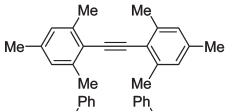
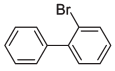
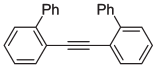
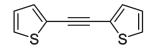
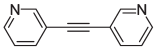
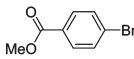
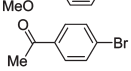
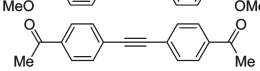
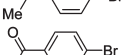
the dppb ligand (entry 2). Other monodentate and chelating phosphine ligands resulted in good yields, but did not show complete conversion (entries 3−6). Among the variety of tested solvents, only DMSO exhibited the full conversion and a high yield of the desired product. Moreover, the desired product was obtained with high yield even in the mixture of H_2O and DMSO, which indicates the insensitivity of this reaction system to moisture (entry 7). The product yields were low in less polar solvents such as toluene, diglyme, and *p*-xylene: 10%, 19%, and 7%, respectively (entries 8−10). Interestingly, *N*-methylpyrrolidone (NMP), which was the best solvent in the presence of TBAF, afforded poor conversion and low yield (entry 11). On the basis of these results, we optimized the reaction conditions as 2.0 equiv of aryl bromide, 1.0 equiv of propiolic acid, 5.0 mol % $Pd(PPh_3)_2Cl_2$, 10.0 mol % dppb, 2.0 equiv of DBU, and

SCHEME 2. Decarboxylative Coupling Reaction of 2-Butynedioic Acid



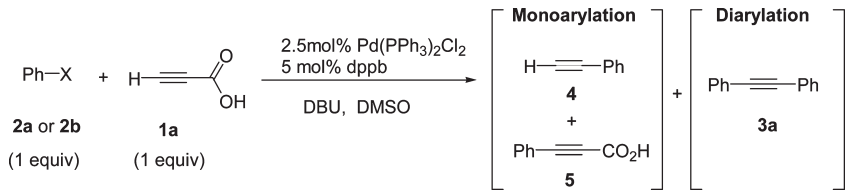
2a **1b** **3a** 97% yield

TABLE 3. Synthesis of Symmetrical Diarylalkynes[a]

Entry	Ar^1X		Products $Ar^1{-}{\equiv}{-}Ar^1$		yield (%) A[b]	yield (%) B[c]
1		**2a**		**3a**	98	97
2		**2b**		**3a**	95	93
3		**2c**		**3a**	92	98
4		**2d**		**3d**	95	91
5		**2e**		**3d**	72	85
6		**2f**		**3f**	95	92
7		**2g**		**3f**	95	92
8		**2h**		**3h**	89	92
9		**2i**		**3i**	86	89
10		**2j**		**3j**	89	91
11		**2k**		**3k**	85	88
12		**2l**		**3l**	86	84
13		**2m**		**3m**	88	84
14		**2n**		**3n**	78	85
15		**2o**		**3o**	72	71
16		**2p**		**3p**	69	78
17[d]		**2q**		**3q**	78	73
18[d]		**2r**		**3r**	81	76
19[d]		**2s**		**3s**	97	83
20		**2t**		**3t**	74	81
21		**2u**		**3u**	91	89

[a]Reaction conditions: Aryl halide (6.0 mmol), propiolic acid or 2-butynedioic acid (3.0 mmol), $Pd(PPh_3)_2Cl_2$ (0.15 mmol), dppb (0.30 mmol), DBU (6.0 mmol), and DMSO (15.0 mL) [b]**A**: Yields from the coupling reaction of propiolic acid at 80 °C for 3 h. [c]**B**: Yields from the coupling reaction of 2-butynedioic acid at 110 °C for 3 h. [d]Reaction time was 1.5 h.

TABLE 4. Coupling Reaction of Equimolecular Amounts of Propiolic Acid and Phenyl Halide[a]



						yield (%)		
entry	X	temp (°C)	time (h)	DBU (equiv)	conv (%)[b]	**4**[c]	**5**[d]	**3**[e]
1	I	25	3	2	25	—[f]	25	—[f]
2	I	25	18	2	75	3	70	—[f]
3	I	50	3	2	92	6	84	—[f]
4	Br	50	3	2	0	—[f]	—[f]	—[f]
5	Br	80	3	2	98	—[f]	—[f]	46(92[g])
6	Br	80	3	1	98	—[f]	—[f]	43(86[g])

[a]Reaction conditions: **1a** (1.0 mmol), **2a** or **2b** (1.0 mmol), Pd (0.025 mmol), dppb (0.05 mmol), DBU (1.0 or 2.0 mmol), and DMSO (3.0 mL). [b]Conversion of PhX was determined by GC with internal standard 2-methoxynaphthalene. [c]Yields were determined by NMR with internal standard 2-methoxynaphthalene after acidification of reaction mixture. [d]Yields were determined after the conversion of **5** to methyl phenylpropiolate. [e]Yields were determined by GC and NMR with internal standard 2-methoxynaphthalene. [f]Not detected. [g]Yields were calculated on the basis of the molar amount of phenyl halide.

DMSO as a solvent. We also applied the optimized conditions to 2-butynedioic acid as an alkyne source for obtaining symmetrical diarylalkyne. However, the desired coupled product could be successfully obtained with high yield when the reaction temperature was elevated to 110 °C (Scheme 2).

In an effort to explore the scope of the developed method, we screened the coupling of a variety of aryl compounds and propiolic acid and 2-butynedioic acid (Table 3). In general, the product yield did not exhibit a strong dependence on propiolic acid and 2-butynedioic acid, as shown by **A** and **B** in Table 3. The yields were described on the basis of the coupling reaction of propiolic acid (**A** yields in Table 3). First the coupling of propiolic acid with phenyl bromide (**2a**), iodide (**2b**), and triflate (**2c**) all gave the desired product, diphenylacetylene (**3a**), with high yields of 98%, 95%, and 92% yields, respectively (entries 1−3). The *ortho*-substituted aryl iodides and bromides resulted in good yields (entries 4−7), but 2-bromoanisole (**2e**) gave a slightly lower yield than the others (entry 5). The *para*-substituted aryl bromides all gave the corresponding products with good yields (entries 8−10). This system also proved to be tolerant of sterically hindered aryl halides. Sterically demanding aryl halides such as **2k**, **2l**, and **2m** were coupled with propiolic acid to afford the desired products in good yields (entries 11−13). In addition, 2-bromobiphenyl (**2n**) also exhibited a good yield (entry 14). Various heteroaromatic substrates such as 2-bromothiophene (**2o**) and 3-bromopyridine (**2p**) also afforded the symmetrical arylalkynes in 72% and 69% yield, respectively (entries 15 and 16). The aryl halides with electron-withdrawing groups such as ester, ketone, and aldehyde were completely converted to the desired product faster than the others (entries 17−19). 1-Bromonaphthalene (**2t**) afforded the symmetrical dinaphthylacetylene **3t** with 74% yield (entry 20). 1-Bromochlorobenzene (**2u**) was coupled at the bromo-substituted site, which demonstrated the catalytic system's chemoselectivity (entry 21). As shown in Table 3, all reaction yields from the coupling reactions of 2-butynedioic acid were very similar to those of propiolic acid (**B** in Table 3).

Reactivity of Propiolic Acid in the Coupling Reaction. Propiolic acid has two coupling sites: Sonogashira (C−H) and decarboxylative (C−CO_2H). To determine which reaction site is more reactive under our optimized reaction conditions, we investigated the relative amounts of two reaction intermediates, phenylacetylene (**4**), which is produced from decarboxylative coupling, and phenylpropiolic acid (**5**), which is produced from the Sonogashira coupling in the reaction mixture. We carried out the coupling reaction of equimolecular amounts of propiolic acid and phenyl halide under a variety of reaction conditions.[16] The results are summarized in Table 4. With phenyl iodide, the coupling reaction produced the monoarylated products at 25 and 50 °C, with no diarylated product being formed (entries 1−3). Among the monoarylated products, more Sonogashira coupling product **5** was produced than the decarboxylative coupling product **4**. The Sonogashira coupling reaction was faster than the decarboxylative coupling reaction at 25 and 50 °C. With phenyl bromide, no coupled product was found at 50 °C (entry 4). As the reaction temperature was increased to 80 °C, the conversion of phenyl bromide was increased to 98%, but diphenylacetylene was formed as the major product. We did not detect any monoarylated product in GC and NMR investigations. Interestingly, the major product was diphenylacetylene even though 1 equiv of base was employed.

Synthesis of Unsymmetrical Diarylalkynes. The results indicated that aryl iodide was coupled with propiolic acid at room temperature and at 50 °C without any formation of diarylacetylene. However, at least 80 °C was required for the coupling reaction of aryl bromide with propiolic acid. To investigate the reactivity of aryl iodide and bromide toward propiolic acid in detail, a set of competition experiments were conducted. In the model system, equimolecular amounts of

(16) We could not identify directly the intermediates **4** and **5** in the reaction mixture by GC and NMR because the two intermediates have acidic protons, which are difficult to detect in the basic conditions. Therefore, we treated the reaction mixture of Table 4 with the following procedure. The reaction mixture was reacted with MeI (1.0 mmol) and DBU (1.0 mmol) at room temperature for 3 h for the conversion of phenylpropiolic acid to methyl phenylpropiolate and treated with HCl etherate (1.0 mmol) for the acidification of phenylacetylene. These two compounds were detected in GC and NMR.

SCHEME 3. Comparison of the Reactivity of Aryl Iodide and Aryl Bromide in the Coupling of Propiolic Acid at 50 °C

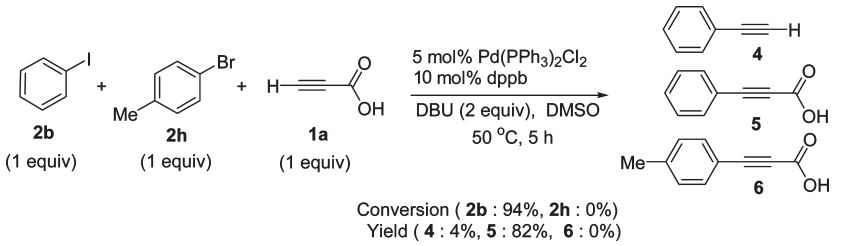
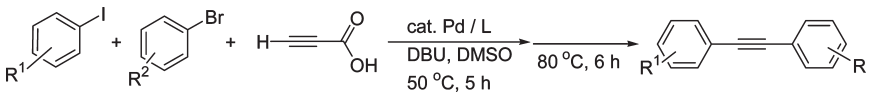
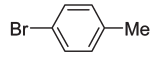
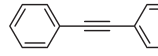
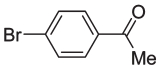
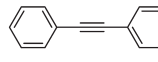
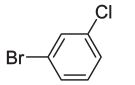
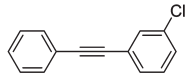
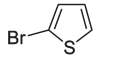
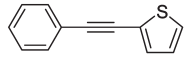
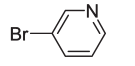
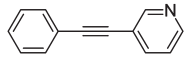
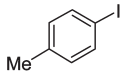
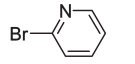
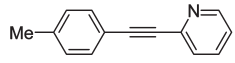
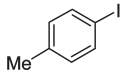
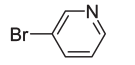
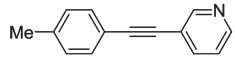
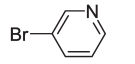
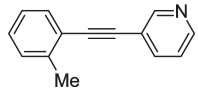


TABLE 5. Synthesis of Unsymmetrical Diarylalkynes[a]



entry	Ar^1I		Ar^2Br		Product		Yield (%)
1		**2b**		**2h**		**7bh**	76([b])
2		**2b**		**2r**		**7br**	68([b])
3		**2b**		**2u**		**7bu**	75([b])
4		**2b**		**2o**		**7bo**	73([b])
5		**2b**		**2p**		**7bp**	65([b])
6		**2v**		**2w**		**7vw**	89([b])
7		**2v**		**2p**		**7vp**	81([b])
8		**2f**		**2p**		**7fp**	74([b])

[a]Reaction conditions: aryl iodide (3.0 mmol), aryl bromide (3.0 mmol), propiolic acid (3.0 mmol), $Pd(PPh_3)_2Cl_2$ (0.15 mmol), dppb (0.30 mmol), DBU (6.0 mmol), and DMSO (15.0 mL) at 50 °C for 5 h and then at 80 °C for 6 h. [b]Yields of symmetrical diarylalkyne from aryl iodide.

phenyl iodide and 4-bromotoluene were allowed to react with propiolic acid in the presence of 2.5 mol % of the catalytic system for 5 h at 50 °C. Only phenyl iodide was coupled with propiolic acid to produce phenylpropiolic acid with 82% yield and phenyl acetylene with 4% yield, without any conversion of 4-bromotoluene.[16,17]

These experimental results suggested that unsymmetrical diarylalkyne could be obtained when all the reagents were added at the beginning of the reaction. This reaction condition did not require the second addition of aryl bromide, as had been the case in our previous report. As expected, the reaction first proceeded at 50 °C for 5 h and then the reaction temperature was raised to 80 °C. When aryl iodides and aryl bromides were employed, the desired unsymmetrical diarylalkynes were obtained in good yields. However, the symmetrical diarylalkyne was produced as a byproduct in 2−8% yield. In the case of phenyl iodide, aryl bromides bearing both an electron-donating group and an electron-withdrawing group worked well (Table 5, entries 1−3). Heteroaromatic bromides such as 2-bromothiophene, 2-bromopyridine, and 3-bromopyridine showed good yields with aryl iodides such as phenyl iodide, 2-iodotoluene, and 4-iodotoluene (Table 5, entries 4−8).

Conclusion

The simple synthesis method presented here offers advantages in requiring neither a copper cocatalyst nor an excess of

(17) We found similar results when 4-iodotoluene and phenyl bromide were employed as aryl halides instead of phenyl iodide and 4-bromotoluene.

expensive TBAF reagents for the decarboxylation step. Moreover, expensive organometallic compounds such as silyl- or tin-protected alkynes are not required and only benign CO_2 is produced as a waste. In summary, a palladium/DBU system was successfully applied to the cross-coupling of aryl halides (and aryl triflate) with propiolic acid and 2-butynedioic acid to provide symmetrical diarylalkyne derivatives. 2-Butynedioic acid required higher reaction temperature than propiolic acid. To the best of our knowledge, 2-butynedioic acid has never been employed as an alkyne source for the decarboxylative coupling reaction, and this is the first example of double decarboxylative coupling. In the coupling reaction of propiolic acid with aryl halides, the diarylated product was the major one at high temperature, whereas the monoarylated products were formed predominantly at 25 and 50 °C when phenyl iodide was employed. Among these monoarylated products, more Sonogashira coupling product was obtained than the decarboxylative coupling product. The competition experimental data revealed the successful synthesis of unsymmetrical diarylalkyne with this palladium/DBU system.

Experimental Section

General Procedure for the Synthesis of Symmetrical Diarylalkynes Using Propiolic Acid or 2-Butynedioic Acid. $Pd(PPh_3)_2Cl_2$ (105 mg, 0.15 mmol), 1,4-bis(diphenylphosphino)butane (128 mg, 0.30 mmol), aryl halides (6.00 mmol), and propiolic acid (**1a**) (212 mg, 3.0 mmol) or 2-butynedioic acid (**1b**) (342 mg, 3.0 mmol) were combined with DBU (913 mg, 6.0 mmol) in a small round-bottomed flask. DMSO (15.0 mL) was added, and the flask was sealed with a septum. The resulting mixture was placed in an oil bath at 80 °C (for propiolic acid) or 110 °C (for 2-butynedioic acid) for 3 h (or 1.5 h). The reaction was poured into 25 mL of saturated aqueous ammonium chloride and extracted with Et_2O (4 × 20 mL). The combined ether extracts were washed with brine (90 mL), dried over $MgSO_4$, and filtered. The solvent was removed under vacuum, and the resulting crude product was purified by flash chromatography on silica gel. The product was eluted with 5% ethyl acetate in hexane.

1, 2-Diphenylethyne (3a).[8b] Phenyl bromide (**2a**) (942 mg, 6.00 mmol) was coupled with **1a** to give 524 mg (2.94 mmol, 98%) of **3a** and coupled with **1b** to give 519 mg (2.91 mmol, 97%) of **3a** as a white solid after chromatography: mp 63−64 °C, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55−7.51 (m, 4H), 7.38−7.29 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 131.6, 128.3, 128.2, 123.2, 89.3; MS $C_{14}H_{10}$ 178(100, $[M]^+$), 152(15), 89(10), 76(10).

1,2-Bis(2-methoxyphenyl)ethyne (3d).[18] 2-Bromoanisole (**2e**) (1.12 g, 6.00 mmol) was coupled with **1a** to give 515 mg (2.16 mmol, 72%) of **3d** and coupled with **1b** to give 608 mg (2.55 mmol, 85%) of **3d** as a yellow solid after chromatography: mp 123 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (d, J = 9.6 Hz, 2H), 7.29 (t, J = 7.95 Hz, 2H), 6.96−6.88 (m, J = 7.65 Hz, 4H), 3.92 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.9, 133.5, 129.5, 120.4, 112.8, 110.7, 89.8, 55.9; MS $C_{16}H_{14}O_2$ 238(100, $[M]^+$), 223(25), 165(25), 152(20), 131(40).

1,2-Di-*o*-tolylethyne(3f).[19] 2-Bromotoluene (**2g**) (1.02 g, 6.00 mmol) was coupled with **1a** to give 588 mg (2.85 mmol, 95%) of **3f** and coupled with **1b** to give 569 mg (2.76 mmol, 92%) of **3f** as an oil after chromatography: mp 28−30 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, J = 7.8 Hz, 2H), 7.24−7.13 (m, 6H), 2.52 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.9, 131.8, 129.4, 128.2, 125.6, 123.3, 92.3, 20.9; MS $C_{16}H_{14}$ 206(100, $[M]^+$), 191(25), 101(20), 89(20).

1,2-Di-*p*-tolylethyne (3h).[20] 4-Bromotoluene (**2h**) (1.02 g, 6.00 mmol) was coupled with **1a** to give 551 mg (2.67 mmol, 89%) of **3h** and coupled with **1b** to give 569 mg (2.76 mmol, 92%) of **3h** as a white solid after chromatography: mp 138−140 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (d, J = 7.8 Hz, 4H), 7.15 (d, J = 7.8 Hz, 4H), 2.36 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.1, 131.4, 129.1, 120.4, 88.9, 21.5; MS $C_{16}H_{14}$ 206(100, $[M]^+$), 191(20), 102(10), 89(10).

1,2-Bis(4-*tert*-butylphenyl)ethyne (3i).[21] 1-Bromo-4-*tert*-butylbenzene (**2i**) (1.28 g, 6.00 mmol) was coupled with **1a** to give 773 mg (2.58 mmol, 86%) of **3i** and coupled with **1b** to give 780 mg (2.60 mmol, 89%) of **3i** as a white solid after chromatography: mp 154 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (d, J = 8.7 Hz, 4H), 7.35 (d, J = 8.7 Hz, 4H), 1.32 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.3, 131.2, 125.3, 120.4, 88.8, 34.8, 31.2; MS $C_{22}H_{26}$ 290(47, $[M]^+$), 275(100), 102(21).

1,2-Bis(4-methoxyphenyl)ethyne (3j).[22] 4-Bromoanisole (**2j**) (1.12 g, 6.00 mmol) was coupled with **1a** to give 636 mg (2.67 mmol, 89%) of **3j** and coupled with **1b** to give 651 mg (2.73 mmol, 91%) of **3j** as a pale yellow solid after chromatography: mp 147−148 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 (d, J = 9 Hz, 4H), 6.86 (d, J = 9 Hz, 4H), 3.82 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.4, 132.8, 115.7, 113.9, 87.9, 55.3; MS $C_{16}H_{14}O_2$ 238(100, $[M]^+$), 223(70), 195(20), 152(20), 119(15).

1,2-Bis(2,5-dimethylphenyl)ethyne (3k).[23] 2-Bromo-*p*-xylene (**2k**) (555 mg, 6.00 mmol) was coupled with **1a** to give 598 mg (2.55 mmol, 85%) of **3k** and coupled with **1b** to give 619 mg (2.64 mmol, 88%) of **3k** as a white solid after chromatography: mp 111−113 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (s, 2H), 7.11 (d, J = 7.8 Hz, 2H), 7.03 (d, J = 7.8 Hz, 2H), 2.48 (s, 6H), 2.31(s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.8, 135.0, 132.3, 129.3, 129.0, 123.2, 92.1, 20.7, 20.4; MS $C_{18}H_{18}$ 234(100, $[M]^+$), 219(55), 204(55), 102(15).

1,2-Bis(2,6-dimethylphenyl)ethyne (3l).[19] 2-Bromo-*m*-xylene (**2l**) (555 mg, 6.00 mmol) was coupled with **1a** to give 605 mg (2.58 mmol, 86%) of **3l** and coupled with **1b** to give 591 mg (2.52 mmol, 84%) of **3l** as a yellow solid after chromatography: mp 115−116 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16−7.07 (m, 6H), 2.55 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.1, 127.6, 126.8, 123.6, 95.8, 21.6; MS $C_{18}H_{18}$ 234(100, $[M]^+$), 219(60), 204(60), 105(25).

1,2-Dimesitylethyne (3m).[19] Bromomesitylene (**2m**) (1.19 g, 6.00 mmol) was coupled with **1a** to give 693 mg (2.64 mmol, 88%) of **3m** and coupled with **1b** to give 646 mg (2.46 mmol, 84%) of **3m** as a white solid after chromatography: mp 125 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.91 (s, 4H), 2.50 (s, 12H), 2.30 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.1, 137.7, 127.9, 121.1, 95.5, 21.8, 21.6; MS $C_{20}H_{22}$ 262(100, $[M]^+$), 247(50), 232(70), 119(20).

1,2-Di(biphenyl-2-yl)ethyne (3n).[24] 2-Bromobiphenyl (**2n**) (1.40 g, 6.00 mmol) was coupled with **1a** to give 773 mg (2.34 mmol, 78%) of **3n** and coupled with **1b** to give 843 mg (2.55 mmol, 85%) of **3n** as an oil after chromatography: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (m, 4H), 7.41−7.31(m, 10H), 7.23 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.5, 140.4, 133.0, 129.4, 129.3, 128.3, 127.9, 127.4, 126.9, 121.7, 91.8; MS $C_{26}H_{18}$ 330(15, $[M]^+$), 165(100).

1,2-Di(thiophen-2-yl)ethyne (3o).[25] 2-Bromothiophene (**3o**) (984 mg, 6.00 mmol) was coupled with **1a** to give 411 mg (2.16

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mmol, 72%) of **3o** and coupled with **1b** to give 405 mg (2.13 mmol, 71%) of **3o** as a yellow solid after chromatography: mp 99−100 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31−7.25 (m, 4H), 7.01 (dd, J = 3.6 Hz, 1.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.1, 127.6, 127.1, 122.9, 86.2; MS $C_{10}H_6S$ 190(100, $[M]^+$), 158(10), 145(15), 114(15)

1,2-Di(pyridin-3-yl)ethyne (3p).[9b] 3-Bromopyridine (**2p**) (948 mg, 6.00 mmol) was coupled with **1a** to give 373 mg (207 mmol, 69%) of **3p** and coupled with **1b** to give 422 mg (2.34 mmol, 78%) of **3p** as a white solid after chromatography: mp 59−60 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.79 (d, J = 3.2 Hz, 2H), 8.59 (d, J = 7.2 Hz, 2H), 7.83 (dt, J = 8.3 Hz, 1.8 Hz, 2H), 7.34−7.29 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.1, 148.9, 138.4, 122.9, 119.6, 89.0; MS $C_{12}H_8N_2$ 180(100, $[M]^+$), 153(10), 100(10), 74(15).

Dimethyl 4,4′-(Ethyne-1,2-diyl)dibenzoate (3q).[8b] Methyl-4-bromobenzoate (**2q**) (1.29 g, 6.00 mmol) was coupled with **1a** to give 689 mg (2.34 mmol, 78%) of **3q** and coupled with **1b** to give 645 mg (2.19 mmol, 73%) of **3q** as a white solid after chromatography: mp 219−220 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (d, J = 8.7 Hz, 4H), 7.61 (d, J = 8.7 Hz, 4H), 3.94 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.4, 131.6, 129.9, 129.6, 127.3, 91.4, 52.3; MS $C_{18}H_{14}O_4$ 294(100, $[M]^+$), 263(100), 176(25), 116(25).

1,1′-(4,4′-(Ethyne-1,2-diyl)bis(4,1-phenylene))diethanone (3r).[8b] 4-Bromoacetophenone (**2r**) (1.19 g, 6.00 mmol) was coupled with **1a** to give 637 mg (2.43 mmol, 81%) of **3r** and coupled with **1b** to give 598 mg (2.28 mmol, 76%) of **3r** as a white solid after chromatography: mp 198−200 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (d, J = 8.7 Hz, 4H), 7.63 (d, J = 8.7 Hz, 4H), 2.63 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.2, 136.6, 131.8, 128.3, 127.5, 91.6, 26.6; MS $C_{18}H_{14}O$ 262(100, $[M]^+$), 247(50), 232(70), 119(20).

4,4′-(Ethyne-1,2-diyl)dibenzaldehyde (3s).[19] 4-Bromoabenzaldehyde (**2s**) (1.11 g, 6.00 mmol) was coupled with **1a** to give 682 mg (2.91 mmol, 97%) of **3s** and coupled with **1b** to give 583 mg (2.49 mmol, 83%) of **3s** as a white solid after chromatography: mp 213-214 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.0 (s, 2H), 7.90 (d, J = 8.1 Hz, 4H), 7.71 (d, J = 8.1 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.6, 136.1, 132.6, 129.9, 128.9, 92.4; MS $C_{16}H_{10}O$ 234(100, $[M]^+$), 205(15), 176(40), 151(15), 88(10).

1,2-Di(naphthalen-1-yl)ethyne (3t).[19] 1-Bromonaphthalene (**2t**) (1.24 g, 6.00 mmol) was coupled with **1a** to give 618 mg (2.22 mmol, 74%) of **3t** and coupled with **1b** to give 676 mg (2.43 mmol, 81%) of **3t** asa yellow solid after chromatography: mp 127−128 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.56 (d, J = 8.4 Hz, 2H), 7.91−7.87 (m, 6H), 7.66−7.48 (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; MS $C_{22}H_{14}$ 278(100, $[M]^+$), 138(15).

1,2-Bis(3-chlorophenyl)ethyne (3u).[8b] 1-Bromo-3-chlorobenzene (**2u**) (1.15 g, 6.00 mmol) was coupled with **1a** to give 675 mg (2.73 mmol, 91%) of **3u** and coupled with **1b** to give 660 mg (2.67 mmol, 89%) of **3u** as a white solid after chromatography: mp 81−82 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 (m, 2H), 7.40 (m, 2H), 7.34−7.25 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.3, 131.5, 129.8, 129.6, 128.8, 124.5, 89.0; MS $C_{14}H_8Cl$ XXXX(100, $[M]^+$), 176(50), 150(10), 123(10), 88(10).

General Procedure for the Synthesis of Unsymmetrical Diarylalkynes Using Propiolic Acid. $Pd(PPh_3)_2Cl_2$ (105 mg, 0.15 mmol), 1,4-bis(diphenylphosphino)butane (128 mg, 0.30 mmol), aryl iodide (**2b**) (3.0 mmol), aryl bromide (3.0 mmol), and propiolic acid (**1a**) (212 mg, 3.0 mmol) were combined with DBU (913 mg, 6.0 mmol) in a small, round-bottomed flask. DMSO (15.0 mL) was added, and the flask was sealed with a septum. The resulting mixture was placed in an oil bath at 50 °C for 5 h. Then the reaction temperature was increased to 80 °C, and the mixture was stirred for 6 h. The reaction was poured into 25 mL of saturated aqueous ammonium chloride and extracted with Et_2O (4 × 20 mL). The combined ether extracts were washed with brine (90 mL), dried over $MgSO_4$, and filtered. The solvent was removed under vacuum, and the resulting crude product was purified by flash chromatography on silica gel. The product was eluted with 5% ethyl acetate in hexane.

1-(2-(4-Methylphenyl)ethynyl)benzene (7bh).[26] Phenyl iodide (**2b**) (612 mg, 3.00 mmol) and 4-bromotoluene (**2h**) (513 mg, 3.00 mmol) were coupled with **1a** to give 438 mg (2.28 mmol, 76%) of **7ah** as a white solid after chromatography: mp 70−72 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54−7.50 (m, 2H), 7.43 (d, J = 8.1 Hz, 2H), 7.37−7.30 (m, 3H), 7.13 (d, J = 7.8 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.4, 131.5, 131.46, 129.1, 128.3, 128.0, 123.4, 120.1, 89.5, 88.7, 21.5; MS $C_{15}H_{13}$ 192(100, $[M]^+$), 165(15), 95(10).

1-(4-Phenylethynylphenyl)ethanone (7br).[27] Phenyl iodide (**2b**) (612 mg, 3.00 mmol) and 4-bromoacetophenone (**2r**) (597 mg, 3.00 mmol) were coupled with **1a** to give 449 mg (2.04 mmol, 68%) of **7ar** as a pale yellow solid after chromatography: mp 95−96 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, J = 8.7 Hz, 2H), 7.62 (d, J = 8.7 Hz, 2H), 7.57−7.54 (m, 2H), 7.40−7.35 (m, 3H), 2.62 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.3, 136.2, 131.73, 131.7, 128.8, 128.4, 128.3(2C), 122.6, 92.7, 88.6, 26.6; MS $C_{16}H_{12}O$ 220(70, $[M]^+$), 205(100), 176(50), 176(45), 151(20), 88(20).

1-(2-(3-Chlorophenyl)ethynyl)benzene (7bu).[15a] Phenyl iodide (**2b**) (612 mg, 3.00 mmol) and 1-bromo-3-chlorobenzene (**2u**) (574 mg, 3.00 mmol) were coupled with **1a** to give 479 mg (2.25 mmol, 75%) of **7au** as a colorless oil after chromatography: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55−7.49 (m, 3H), 7.40 (m, 1H), 7.36−7.31 (m, 3H), 7.29−7.23 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.1, 131.6, 131.4, 129.7, 129.5, 128.6, 128.5, 128.4, 125.0, 122.7, 90.5, 87.9; MS $C_{14}H_9Cl$ 212(100, $[M]^+$), 176(26), 151(7), 106(9), 88(12).

2-Phenylethynylthiophene (7bo).[28] Phenyl iodide (**2b**) (612 mg, 3.00 mmol) and 2-bromothiophene (**2o**) (489 mg, 3.00 mmol) were coupled with **1a** to give 404 mg (2.19 mmol, 73%) of **7ao** as a colorless oil after chromatography: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53−7.50 (m, 2H), 7.36−7.31 (m, 3H), 7.28−7.26 (m, 2H), 7.01−6.99 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 131.9, 131.4, 128.4, 128.3, 127.2, 127.1, 123.2, 122.9, 93.0, 82.6; MS $C_{12}H_8S$ 184(100, $[M]^+$), 152(20), 139(20), 92(10).

3-Phenylethynylpyridine (7bp).[29] Phenyl iodide (**2b**) (612 mg, 3.00 mmol) and 3-bromopyridine (**2p**) (474 mg, 3.00 mmol) were coupled with **1a** to give 350 mg (1.95 mmol, 65%) of **7ap** as a yellow oil after chromatography: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.77 (d, J = 2.1 Hz, 1H), 8.54 (dd, J = 1.8 Hz, 3 Hz, 1H), 7.80 (dt, J = 8.1 Hz, 1.8 Hz, 1H), 7.57−7.52 (m, 2H), 7.38−7.34 (m, 3H), 7.27 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.2, 148.5, 138.4, 131.7, 128.8, 128.4, 123.0, 122.5, 120.4, 92.6, 85.9; MS $C_{13}H_8N$ 179(100, $[M]^+$), 151(15), 126(15), 76(15).

2-(*p*-Tolylethynyl)pyridine (7vw).[30] 4-Iodotoluene (**2v**) (654 mg, 3.00 mmol) and 2-bromopyridine (**2w**) (474 mg, 3.00 mmol) were coupled with **1a** to give 516 mg (2.67 mmol, 89%) of **7vw** as a yellow solid after chromatography: mp 63.6 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.59−8.62 (m, 1H), 7.65 (td, J = 7.8, 1.8 Hz, 1H), 7.48−7.52 (m, 3H), 7.15−7.23 (m, 3H), 2.37 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.26, 143.89, 139.48, 136.35, 132.19, 129.41, 127.28, 122.81, 119.42, 89.78, 88.35, 21.82; MS $C_{14}H_{11}N$ 193(100, $[M]^+$), 165(10), 115(10).

3-(*p*-Tolylethynyl)pyridine (7vp).[31] 4-Iodotoluene (**2v**) (654 mg, 3.00 mmol) and 3-bromopyridine (**2p**) (474 mg, 3.00 mmol)

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were coupled with **1a** to give 470 mg (2.43 mmol, 81%) of **7vp** as a colorless oil after chromatography: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.75 (d, J = 1.8 Hz, 1H), 8.52 (dd, J = 4.8, 1.5 Hz, 1H), 7.79 (dt, J = 8.1, 1.8 Hz, 1H), 7.44 (d, J = 7.8 Hz, 2H), 7.26 (dd, J = 8.1, 5.1 Hz, 1H), 7.17 (d, J = 7.8 Hz, 2H), 2.37 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.15, 148.31, 138.97, 138.26, 131.52, 129.15, 122.93, 120.61, 119.38, 92.82, 85.28, 21.49; MS $C_{14}H_{11}N$ 193(100, $[M]^+$), 165(15), 139(10).

3-(*o*-Tolylethynyl)pyridine (7fp).[32] 2-Iodotoluene (**2f**) (654 mg, 3.00 mmol) and 3-bromopyridine (**2p**) (474 mg, 3.00 mmol) were coupled with **1a** to give 429 mg (2.22 mmol, 74%) of **7fp** as a yellow oil after chromatography: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.80 (d, J = 1.5 Hz, 1H), 8.56 (dd, J = 4.8, 1.5 Hz, 1H), 7.82 (m, J = 8.1, 1.8 Hz, 1H), 7.54 (d, J = 7.5 Hz, 1H), 7.71−7.30 (m, 4H), 2.54 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.99, 148.17, 140.17, 138.13, 131.84, 129.45, 128.73, 125.56, 122.90, 122.15, 120.58, 91.51, 89.69, 20.61; MS $C_{14}H_{11}N$ 193(100, $[M]^+$), 165(15), 139(10).

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Supporting Information Available: Copies of spectra. This material is available free of charge via the Internet at http://pubs.acs.org.