1,2-Diarylethenyl Sulfones: Readily-Prepared Masked Diarylethynes for Access to Aryleneethynylenes

Takashi Doi, Akihiro Orita,* Daisuke Matsuo, Ryosuke Saijo, Junzo Otera*

Department of Applied Chemistry, Okayama University of Science, Ridai-cho, Okayama 700-0005, Japan
Fax +81(86)2564292; E-mail: orita@high.ous.ac.jp; E-mail: otera@high.ous.ac.jp

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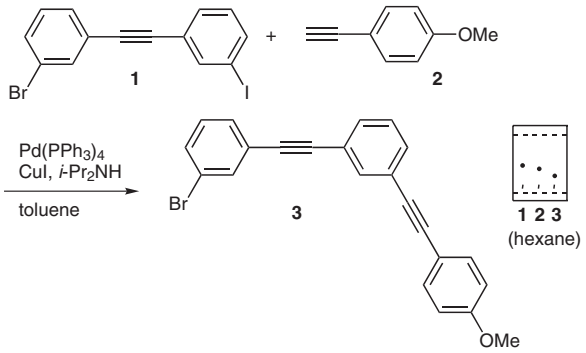
Abstract: 1,2-Di(halophenyl)ethenyl phenyl sulfones were prepared readily by successive treatment of halophenylmethyl sulfones with LiHMDS (lithium hexamethyldisilazide), halobenzaldehydes, diethyl chlorophosphate and LiHMDS. The di(halophenyl)ethenyl sulfones thus obtained were transformed successfully to aryleneethynylenes by Sonogashira coupling with arylethyne followed by LiHMDS-promoted elimination of phenylsulfinic acid.

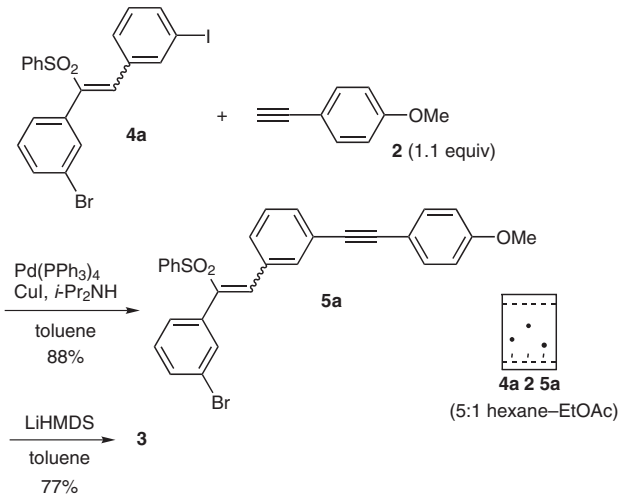
Key words: alkynes, sulfones, aldehydes, eliminations, aryleneethynylenes

Great attention has been focused on aryleneethynylenes as carbon-rich materials.[1] It has been reported that aryleneethynylenes exhibit high fluorescence quantum yields, and the emission λ_{max} can be tuned by introducing electron-donating and/or -withdrawing functional groups on benzenes.[2] Recently we have disclosed that phenyleneethynylene serves as an emission layer showing a high hole carrier ability.[3] For preparation of aryleneethynylenes, Sonogashira coupling between the corresponding aryl halides and terminal acetylenes has been utilized routinely.[4] On the other hand, we have developed a double elimination protocol of β-substituted sulfones for access to acetylenes, and succeeded to prepare aryleneethynylenes bearing a variety of functional groups such as halogen, alkoxy, ester, heteroaromatics and silyl-protected terminal acetylenes.[5] This protocol can be carried out in a one-pot manner; successive addition of base, aldehyde, diethyl chlorophosphate and base to a THF solution of sulfone led to formation of acetylenes. We have already established that unsymmetrically halogen-substituted diphenylethyne **1**, which has been prepared readily by the one-pot double elimination protocol, can be used as a building block for the synthesis of unsymmetrically substituted aryleneethynylenes by use of transition-metal-catalyzed coupling such as Sonogashira, Negishi, Suzuki–Miyaura and Mizoroki–Heck reactions.[5e] Although this process utilizing **1** as a key building block is straightforward for construction of phenyleneethynylene arrays, we found that isolation of the product by column chromatography is somewhat tedious in some cases because of an inherent small difference of polarities between the starting compounds and the coupling products. For instance, in a coupling reaction between **1** and **2**, R_f values of **1**, **2** and **3** were 0.40, 0.33 and 0.22, respectively, upon using hexanes as eluent for TLC (Scheme 1).



Scheme 1 Preparation of **3** by use of halogen-substituted diphenylethyne

In order to overcome this drawback, we tried to take advantage of 1,2-diarylethenyl phenyl sulfone (DAES) **4** as a masked diarylethyne. We expected that high polarity of DAES would enable easy isolation of coupling product. This was indeed the case, and a coupling reaction of halogen-substituted DAES **4a** with **2** provided arylethyne-substituted DAES **5a** which could be purified readily by a short column chromatography: DAES **4a** was completely consumed, and R_f values of **2** and **5a** were 0.67 and 0.27, respectively, on TLC using hexanes–EtOAc (5:1) as eluent. The sulfone **5a** could be transformed to **3** in good yield by treatment with a THF solution of LiHMDS (Scheme 2).[6] In this paper, we disclose such an alternative



Scheme 2 Preparation of **3** by use of 1,2-diarylethenyl phenyl sulfone

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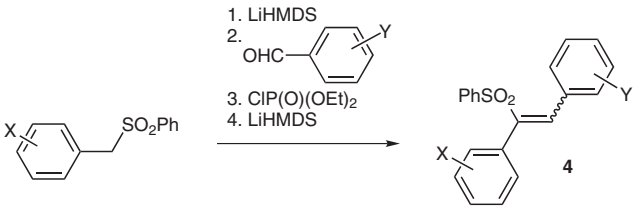
Table 1 Preparation of Halogen-Substituted DAES **4**



	X	Y	Yield[a,b]	R_f[c]
4a	3-Br	3-I	80% (88:12)	0.30
4b	4-Br	3-I	82% (93:7)	0.28
4c	2-Br	3-I	84% (98:2)	0.27
4d	3-Br	4-I	84% (97:3)	0.22
4e	4-I	4-Br	70% (97:3)	0.27
4f	4-I	2-Br	78% (95:5)	0.27
4g	4-I	4-CF_3	84% (93:7)	0.23
4h	4-DMOO[d]	4-I	84% (91:9)	0.33

[a] Isolated yield.
[b] Ratio of geometrical isomers is shown in parentheses; *E*- and *Z*-isomers were not characterized.
[c] Eluted with hexane–EtOAc (5:1).
[d] DMOO = 3,7-dimethyloctyloxy.

two-step double elimination protocol for aryleneethynylenes and ynediynes with recourse to facile isolation of highly polar intermediates, DAESs.

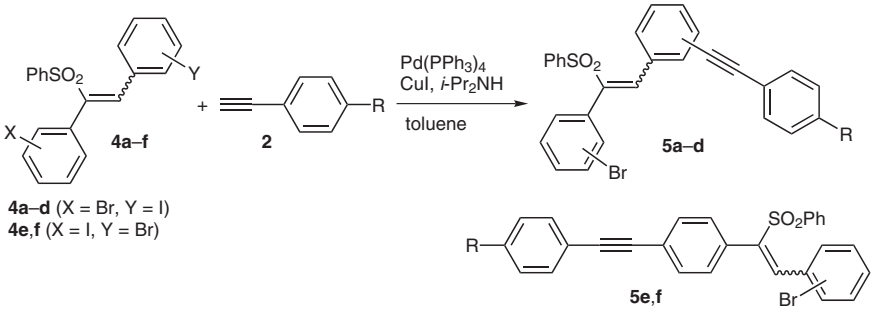
Halogen-substituted DAESs **4** were prepared readily by successive treatment of halophenylmethyl sulfones with LiHMDS, halobenzaldehydes, diethyl chlorophosphate and LiHMDS in THF (Table 1). Bromo- and iodo-substituted diphenylethenyl sulfones **4a–f** were obtained by varying a combination of sulfone and aldehyde. Trifluoromethyl (**4g**) and dimethyloctyloxy (**4h**) derivatives were obtained in good yields as well.

Successive Sonogashira coupling of **4** with arylethynes **2** proceeded smoothly to provide the desired arylethynyl DAES **5** in good yields (Table 2). In this coupling, the iodide moiety reacted more rapidly than the bromide moiety, and no coupling product of bromide was obtained. The coupling reaction afforded a mixture of the desired product **5** and the remaining phenylethyne **2** and/or the homocoupling product of **2**. In each case, however, isolation of **5** was very easy because the high polarity enabled facile separation of **5** from other byproducts by column chromatography on silica gel.

When the arylethynyl DAES **5** was treated with an excess amount of LiHMDS in THF, the expected elimination of sulfinic acid occurred resulting in formation of the desired aryleneethynylene **3** leaving bromine untouched (Table 3). Since aryleneethynylene **3** was observed as the sole product on TLC, **3** could be purified readily by short column chromatography on silica gel.

Keeping these results in mind, we applied this two-step double elimination protocol to the synthesis of a molecular wire **6** (Scheme 3). In this process, bis(arylethynyl)benzene **7** was successfully obtained in a pure form, and repetition of the two-step double elimination protocol with **7** afforded the target phenyleneethynylene **6**, which has electron-donating and -withdrawing substituents on the terminal benzenes.

Table 2 Sonogashira Coupling of Halogen-Substituted DAES **4** with Phenylethyne **2**



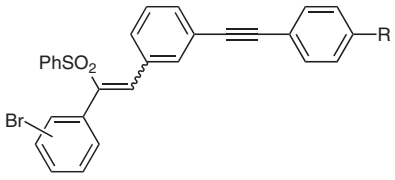
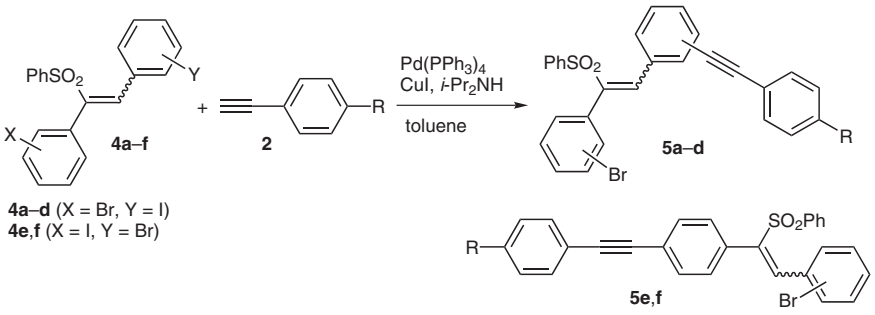
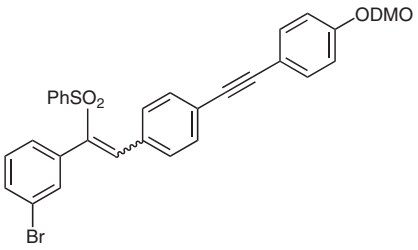
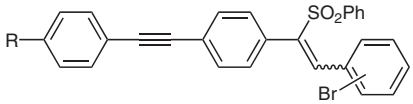
	Br	R	Yield[a,b]	R_f[c]
				
5a	3-	MeO	88% (83:17)	0.27
5b	4-	DMOO	90% (95:5)	0.35
5c	2-	C_6H_{13}	88% (>99:1)	0.28

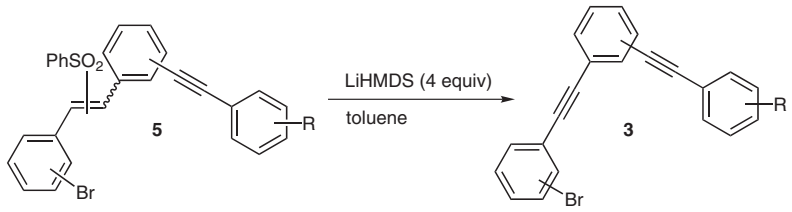
Table 2 Sonogashira Coupling of Halogen-Substituted DAES **4** with Phenylethyne **2** (continued)



	Br	R	Yield[a,b]	R_f[c]
				
5d			93% (91:9)	0.28
				
5e	4-	H	86% (95:5)	0.28
5f	2-	C_6H_{13}	86% (91:9)	0.38

[a] Isolated yield.
[b] Ratio of geometrical isomers is shown in parentheses; *E*- and *Z*-isomers were not characterized.
[c] Eluted with hexane–EtOAc (5:1).

Table 3 Transformation of DAES to **3** by Elimination of Phenylsulfinic Acid



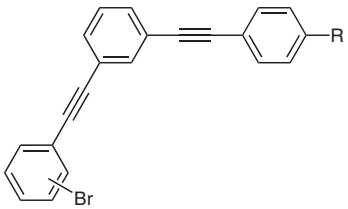
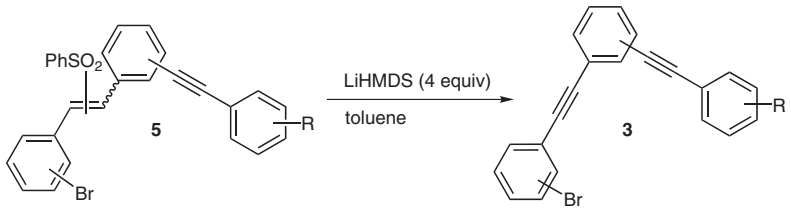
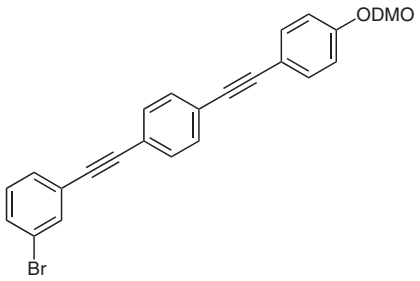
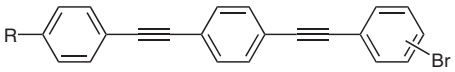
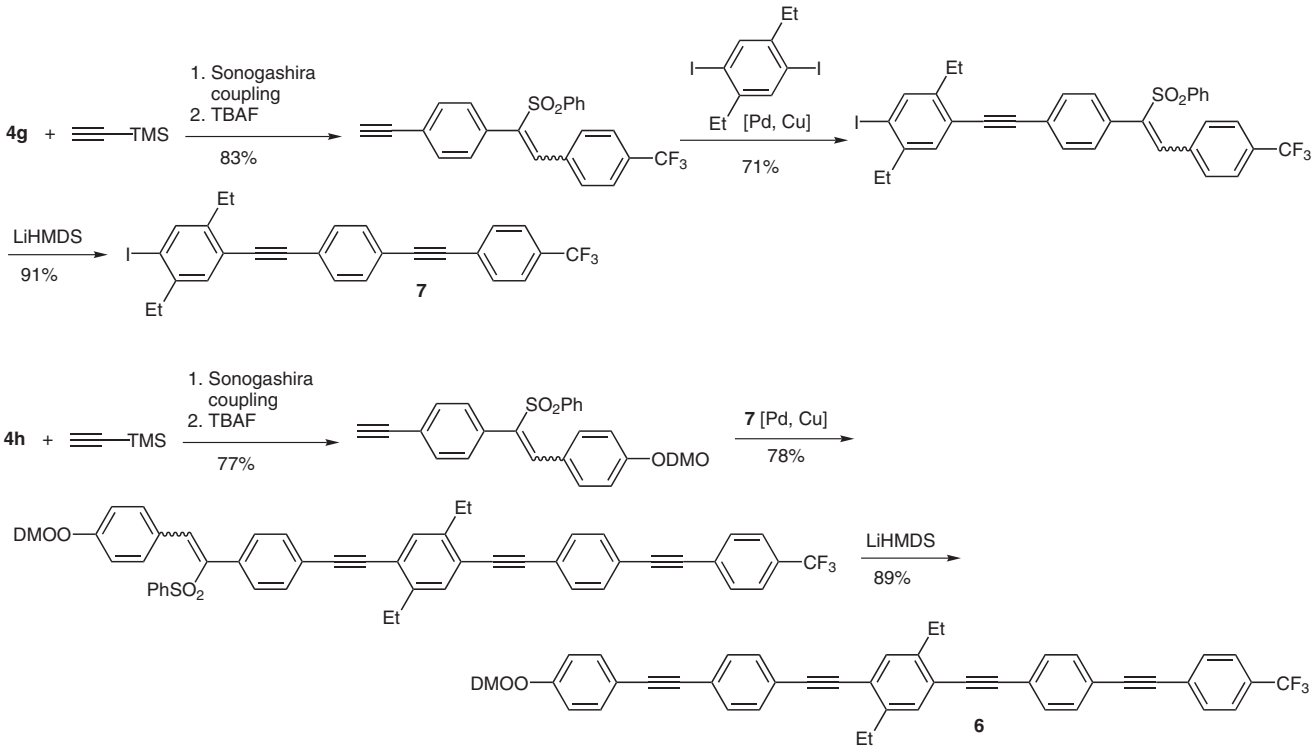
	Br	R	Yield[a]	R_f[b]
				
3a	3-	MeO	77%	0.52
3b	4-	DMOO	81%	0.72
3c	2-	C_6H_{13}	79%	0.68

Table 3 Transformation of DAES to **3** by Elimination of Phenylsulfinic Acid (continued)

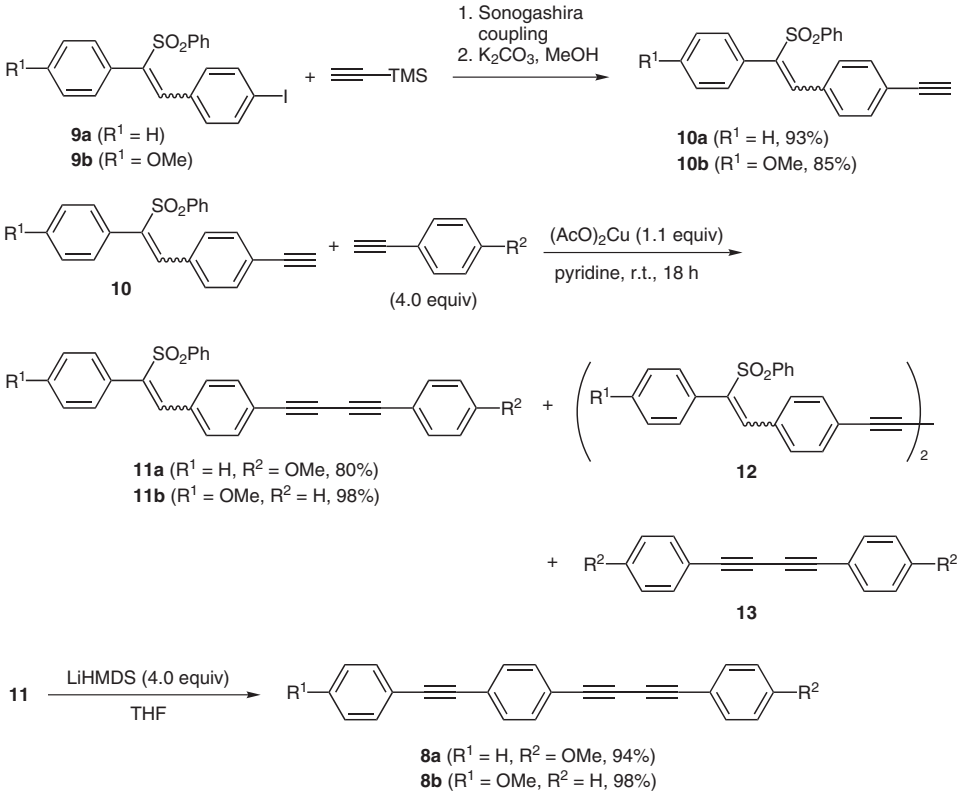


	Br	R	Yield[a]	R_f[b]
				
3d			73%	0.72
				
3e	4-	H	77%	0.67
3f	2-	C_6H_{13}	81%	0.70

[a] Isolated yield.
[b] Eluted with hexane–EtOAc (5:1).



Scheme 3 Synthesis of molecular wire **6**



Scheme 4 Synthesis of ynediyne **8**

The present protocol is indeed useful for preparation of 1-phenylbutadiynyl-4-(phenylethynyl)benzenes **8a**,**b** (Scheme 4). IodoDAESs **9** were prepared from the reaction of the corresponding arylmethyl sulfones with 4-iodobenzaldehyde according to the procedure used in Table 1. The sulfones **9** were transformed to **10** by Sonogashira coupling with TMS-acetylene and base-catalyzed desilylation. Oxidative coupling of **10** with four equivalents of arylethyne gave arylbutadiynyl DAES **11** in good yields. Although, in this coupling, considerable amounts of homocoupling products **12** and **13** were produced as byproducts, high polarity of DAES moiety enabled facile isolation of **11** by column chromatography. Treatment of **11** with LiHMDS afforded the desired ynediyne derivatives **8** in satisfactory yields.

We have succeeded in taking advantage of 1,2-diarylethenyl sulfones (DAESs) as masked diarylethynes. Halogen-substituted DAESs were readily prepared from the reaction of the corresponding halophenylmethyl sulfones with halobenzaldehydes. Sonogashira coupling of the DAES with arylethynes afforded arylethynyl DAESs, which could be isolated easily with recourse to high polarity of the DAES moiety. Successive treatment of the arylethynyl DAESs with LiHMDS provided aryleneethynylenes by elimination of sulfinic acid. This stepwise double elimination protocol could be applied to the synthesis of other π-conjugated systems such as 1-phenylbutadiynyl-4-(phenylethynyl)benzenes. Further application of this protocol to the synthetic process for functionalized π-system is currently under investigation.

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(6) **Typical Procedures**

1-(3-Bromophenyl)-2-(3-iodophenyl)-1-(phenylsulfonyl)ethene (4a): To a THF solution (30 mL) of 3-bromophenylmethyl phenyl sulfone (2.00 g, 6.4 mmol) was added a THF solution of LiHMDS (1.0 M, 7.0 mL, 7.0 mmol) at –78 °C, and the mixture was stirred for 0.5 h. A THF solution (8 mL) of 3-iodobenzaldehyde (1.24 g, 5.3 mmol) was added at –78 °C, and the mixture was stirred for 1 h. Diethyl chlorophosphate (0.75 mL, 5.4 mmol) was added at –78 °C, and the mixture was stirred at r.t. for 1 h. A THF solution of LiHMDS (1.0 M, 5.4 mL, 5.4 mmol) was added at –78 °C, and the mixture was stirred at r.t. overnight. After usual workup with EtOAc–aq NH_4Cl, the organic layer was evaporated, and the residue was subjected to column chromatography on silica gel (10% EtOAc–hexane) to furnish **4a** (2.24 g, 80%).Compound **4a**: *E*/*Z* = 88:12 (the geometry of *E*- or *Z*-isomers was not determined, several signals overlapped in ^{13}C NMR). ^1H NMR (500 MHz, $CDCl_3$): δ = 6.91 (t, *J* = 7.8 Hz, 1 H), 6.93–7.00, 7.03–7.12 (m, 2 H), 7.13–7.21, 7.32–7.37 (m, 2 H), 7.40–7.68 (m, 8 H), 7.85, 7.88 (s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 94.1 (93.5), 122.7 (122.1), 128.7, 128.9, 129.1, 129.3, 128.1, 128.5, 128.6, 130.1, 130.4, 129.5, 129.7, 132.5, 132.9, 133.3, 133.6, 134.5, 132.1, 132.7, 133.4, 135.3, 136.4, 138.1, 139.0, 139.6, 137.1, 137.3, 137.6, 139.9, 141.6, 141.7.

1-(3-Bromophenyl)-2-[3-(4-methoxyphenylethynyl)phenyl]-1-(phenylsulfonyl)ethene (5a): A toluene solution (14 mL) of **4a** (1.20 g, 2.3 mmol), 4-methoxyphenylethyne (341 mg, 2.6 mmol), $Pd(PPh_3)_4$ (132 mg, 0.11 mmol), CuI (23.0 mg, 0.12 mmol) and diisopropylamine (4.6 mL) was stirred at r.t. for 12 h. After filtration, the filtrate was washed with aq NH_4Cl, and the aqueous layer was extracted with EtOAc. The combined organic layer was washed with aq NaCl, dried over $MgSO_4$ and evaporated. The residue was subjected to column chromatography on silica gel (10% EtOAc–hexane) to afford **5a** (1.07 g, 88%). Compound **5a**: only one isomer was obtained. The geometry *E* or *Z* isomer was not determined. ^1H NMR (500 MHz, $CDCl_3$): δ = 3.83 (s, 3 H), 6.87 (d, *J* = 8.9 Hz, 2 H), 6.90 (d, *J* = 8.2 Hz, 1 H), 6.97 (d, *J* = 7.9 Hz, 1 H), 7.12 (t, *J* = 7.8 Hz, 1 H), 7.14–7.18 (m, 2 H), 7.29 (s, 1 H), 7.37–7.46 (m, 5 H), 7.49–7.53 (m, 1 H), 7.57 (t, *J* = 7.5 Hz, 1 H), 7.64 (d, *J* = 7.6 Hz, 2 H), 7.94 (s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 55.3, 86.9, 90.4, 114.1, 114.9, 122.6, 124.4, 128.6, 128.7, 128.9, 129.0, 129.5, 130.3, 132.4, 132.6, 132.9, 133.1, 133.2, 133.4, 133.5, 133.9, 137.5, 138.3, 141.0, 159.9.

1-(3-Bromophenylethynyl)-3-(4-methoxyphenylethynyl)benzene (3a): To a toluene solution (22 mL) of **5a** (285 mg, 0.54 mmol) was added a THF solution of LiHMDS (1.0 M, 2.2 mL, 2.2 mmol) at 0 °C, and the mixture was stirred at r.t. for 2 h. After usual workup with EtOAc–aq NH_4Cl, the organic layer was evaporated, and the residue was subjected to column chromatography on silica gel (2% EtOAc–hexanes) to furnish **3a** (161 mg, 77%). Compound **3a**: ^1H NMR (500 MHz, $CDCl_3$): δ = 3.84 (s, 3 H), 6.89 (d, *J* = 8.9 Hz, 2 H), 7.23 (t, *J* = 7.9 Hz, 1 H), 7.33 (t, *J* = 7.8 Hz, 1 H), 7.43–7.50 (m, 6 H), 7.67–7.70 (m, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 55.2, 87.1, 88.2, 89.9, 90.2, 114.0, 115.0, 122.1, 123.0, 124.0, 125.0, 128.4, 129.7, 130.1, 130.9, 131.4, 131.5, 133.1, 134.3, 134.4, 159.7.