# Double Elimination Protocol for Convenient Synthesis of Dihalodiphenylacetylenes: Versatile Building Blocks for Tailor-Made Phenylene-Ethynylenes

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Dedicated to Dr. Joe P. Richmond on the occasion of his 60th birthday.

Supporting Information for this article is available on the WWW under http://asc.wiley-vch.de or from the author.

**Abstract:** Dihalodiphenylacetylenes are conveniently synthesized by a double elimination reaction of β-substituted sulfones which are readily obtained from halogen-substituted benzyl sulfone and benzaldehyde derivatives. Halogens can be incorporated at any desired positions in the diphenylacetylene skeleton simply by choosing the substitution position of the halogen on the aromatic rings of the starting compounds. The diphenylacetylenes with different halogen substituents thus obtained undergo sequential carbon-carbon bond formations due to the different reactivities of the halogens. Thus, various moieties can be incorporated on the diphenylacetylene skeleton at whichever positions so that a variety of tailor-made phenylene-ethynylenes with regulated structure and composition could be designed.

**Keywords:** acetylene; aldehydes; double elimination; halogen; sulfone;

## Introduction

The phenylene-ethynylene array is an important component for organic materials such as liquid crystals,[1] photo-luminescent compounds[2] and carbon-rich materials.[3] Sonogashira coupling[4] which is commonly employed for arylacetylenes can also be invoked for the synthesis of phenylene-ethynylenes. However, the simple protocol cannot be applied to the fabrication of this framework, for which a variety of kits must be assembled at will, and accordingly, much more elaboration is required. For example, substrates with two terminal acetylenes protected by TMS and TIPS groups are occasionally used. Selective deprotection of the TMS group followed by Sonogashira reaction at the newly generated reaction site incorporates an arylacetylene unit. Next, deprotection of the remaining TIPS-acetylene and another Sonogashira coupling enable incorporation of the other unit to assemble the repeating arene-acetylene kits.[5] Unsymmetrically substituted dihaloarenes are also useful building blocks.[6] Bromoiodo- and chloroiodobenzenes can be converted to structurally diverse phenylene-ethynylenes by making use of the different reactivities of the halogen functions.

Dihalodiphenylacetylenes **1** would be more versatile building blocks for phenylene-ethynylenes (Figure 1). In particular, those with different halogen substituents on the respective phenyl rings (**1**, X≠Y) are expected to serve for designing tailor-made phenylene-ethynylenes with regulated structure and composition because different, and hence selective, carbon-carbon bond formations are feasible on the both sides of the molecules on account of different reactivities of the halogens.

We have been interested in aromatic acetylenes as novel organic materials and have developed a convenient methodology, i.e., a double elimination protocol, for the synthesis of these compounds (Scheme 1).[7] Although this protocol is composed of a number of reactions such as aldol reaction, protection of the aldolate and double elimination of the resulting β-substituted sulfone, all operations could be carried out in one-pot. By taking advantage of this protocol, we have already

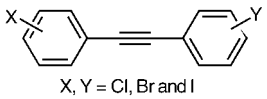


**Figure 1.** Dihalodiphenylacetylenes **1**.

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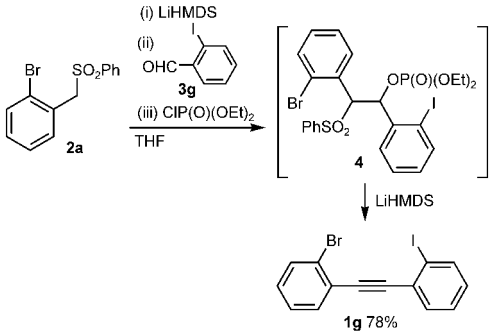
succeeded in the preparation of a highly strained cyclic acetylene,[7c] enantiopure cyclophanes of the phenylene-ethynylene motif[7d] and unsymmetrically substituted di(phenylethynyl)benzenes.[7a, b] We postulated that this methodology could be applied to a convenient synthesis of **1** (Scheme 2). This is indeed the case. We report herein the straightforward synthesis of dihalodiphenylacetylenes. On account of the facile availability of both benzyl sulfones and aldehydes substituted by a halogen at any position of the benzene ring, dihalodiphenylacetylenes with all possible substitution patterns are accessible. In addition, the utilization of these compounds for structurally regulated higher homologues is demonstrated.

## Results and Discussion

The synthesis of the dihalodiphenylacetylenes by the double elimination protocol is straightforward. A procedure for bromoiododiphenylacetylene **1g** is described as an example (Scheme 3). To a THF solution of bromo sulfone **2a** were added consecutively BuLi, iodobenzaldeyde **3g**, diethyl chlorophosphate and LiHMDS (lithium hexamethyldisilazide) in this order. The desired bromoiododiphenylacetylene **1g** was obtained in 78% yield. Although this process is composed of a number of transformations, it was proved by monitoring the reactions that all steps have proceeded smoothly.[8] After addition of $ClP(O)(OEt)_2$, the formation of phosphate **4** was clearly shown on TLC. Addition of LiHMDS gave rise to the formation of the desired acetylene **1g** as the sole product. A single spot due to **1g** was detected on TLC of the crude product.[8] Although rapid lithium-halogen exchange often occurs with aryl bromides and iodides,[9] GC analysis of the crude product indicated no dehalogenation products such as 1-(2-bromophenyl)-2-phenylacetylene (**5**)[10] and diphenylacetylene (**6**).[8] When *t*-BuOK was used instead of LiHMDS, the yield was comparable, but LDA produced an inseparable mixture of **1**, **5** and **6**.




**Scheme 3.** Preparation of **1g** through double elimination of **4** derived from the reaction of **2a** with **3g**.

Next, dihalodiphenylacetylenes with all possible halogen substitution modes were synthesized by use of the corresponding halobenzyl sulfone and halobenzaldehyde partners.

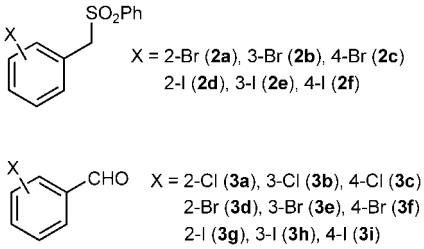
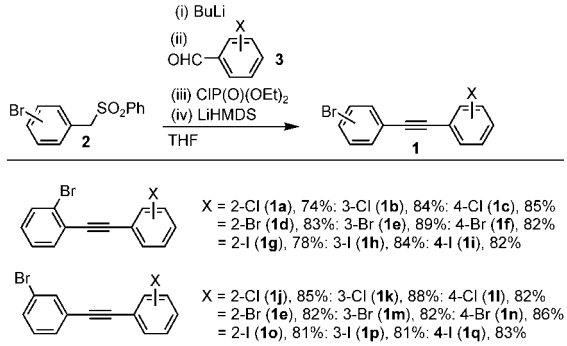
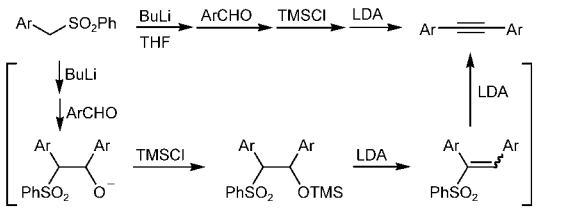


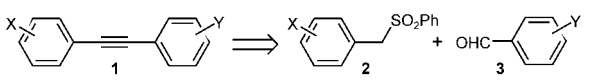

**Figure 2.** Halobenzyl sulfone and halobenzaldehyde partners.



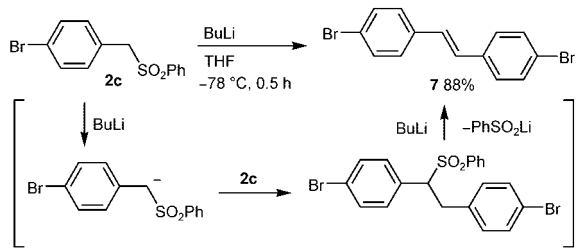

**Scheme 4.** Syntheses of dihalodiphenylacetylenes **1** by use of 2- and 3-bromobenzyl sulfones **2a, b**.




**Scheme 1.** Double elimination of β-substituted sulfones derived from the reaction of a sulfone with an aldehyde.

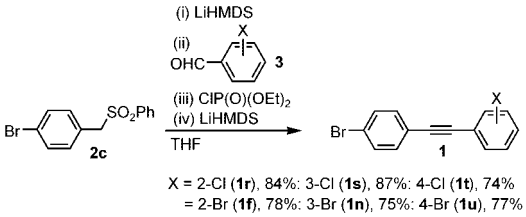



**Scheme 2.** Retrosynthesis for unsymmetrically dihalogen-substituted diphenylacetylenes **1**.

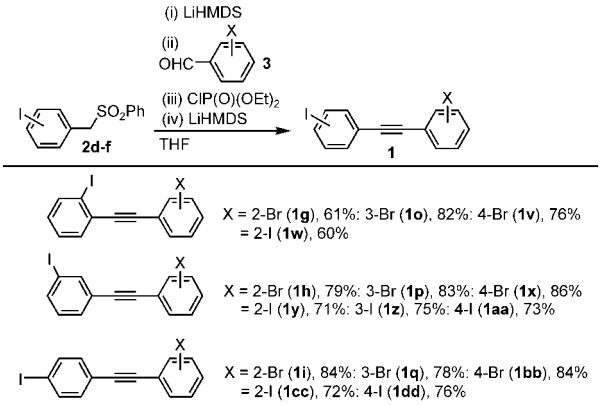



**Scheme 5.** Dimerization of 4-bromobenzyl sulfone **1**.



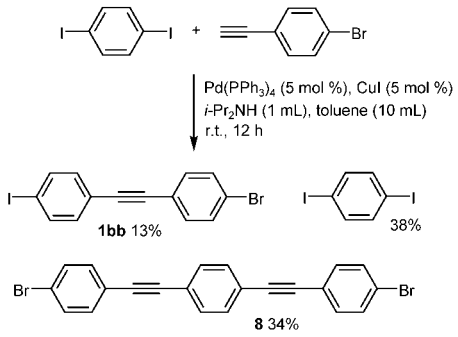

**Scheme 6.** Syntheses of dihalo diphenylacetylenes **1** by use of 4-bromobenzyl sulfone **3c**.




**Scheme 7.** Syntheses of bromo iodo diphenylacetylenes **1** by use of iodobenzyl sulfones **2**.

hyde partners (Figure 2) under similar conditions. Combination of 2- and 3-bromobenzyl sulfones **2a**, **b** and halobenzaldehydes **3** furnished the corresponding products **1a–q** in good yields irrespective of the position of the halogens in **3** (Scheme 4). When 4-bromobenzyl sulfone **2c** was employed, however, dibromostilbene **7** formed in 88% yield (Scheme 5). Fortunately, this reaction was suppressed by use of LiHMDS instead of BuLi as a base to generate the α-sulfonylbenzyl anion, and the desired dihalodiphenylacetylenes **1f, n, r–u** were obtained in good yields (Scheme 6). This modification also allowed us to use iodobenzyl sulfones which are liable to dehalogenation with BuLi, and the desired coupling products were obtained without loss of the halogen (Scheme 7). Note that, when BuLi was employed in place of LiHMDS for the generation α-lithiobenzyl sulfone, deiodination occurred to produce an inseparable mixture of **1** and monobromodiphenylacetylene.

The utility of the double elimination route for the dihalodiphenylacetylenes is apparent from a comparison with the Sonogashira protocol (Scheme 8). When 1,4-diiodobenzene was subjected to Sonogashira coupling with 4-bromophenylacetylene in a 1:1 ratio, the desired coupling product **1bb** was contaminated by double coupling product **8** together with unreacted diiodobenzene. Separation of **1** from these contaminants was difficult on account of their similar polarity and solubility in organic solvents, and repeated column chromatography was



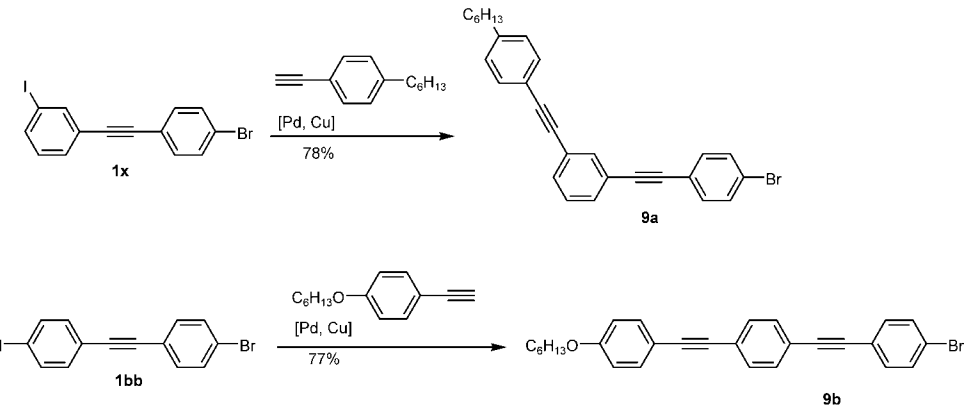

**Scheme 8.** Sonogashira coupling between diiodobenzene and 4-bromophenylethyne.

necessary for isolation of the pure compound. Apparently, it is difficult to differentiate the same halogen functions in the Sonogashira reaction. The other route to arrive at the same target is the combination of 4-bromoiodobenzene and 4-iodophenylacetylene. However, unfavorable self-coupling of the 4-iodophenylacetylene competes with the desired intermolecular reaction under normal conditions.

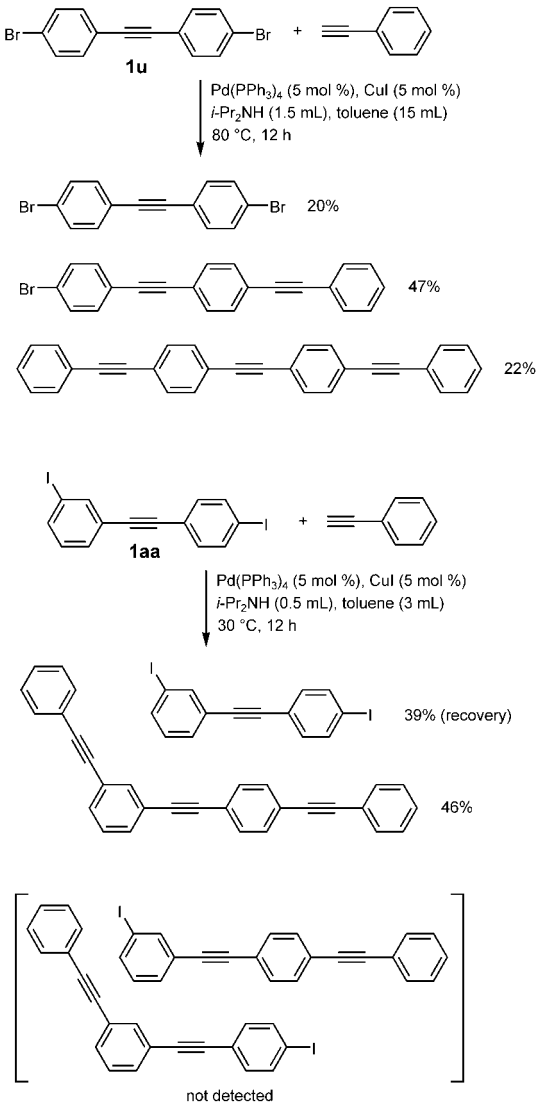
With the above compounds in hand, we turned our attention to demonstrate their synthetic potential as building blocks for a wide spectrum of higher homologues of phenylene-ethynylenes. First, homologation by Sonogashira reaction of bromoiododiphenylacetylenes, **1x** and **1bb**, was carried out (Scheme 9). As expected, treatment of the substrates with one equivalent of arylacetylenes resulted in exclusive reaction on the iodide leaving the bromide intact to afford the desired arylene-ethynylenes **9a** and **9b**, respectively. It should be noted that when a symmetrical dibromodiphenylacetylene **1u** was subjected to a similar reaction, the desired monobromo compound was obtained only in 47% yield (Scheme 10). A considerable amount of the di-coupling product was formed. It is difficult to stop the reaction after the mono-coupling stage. The corresponding diiodide substrate brought about a worse outcome: no monoiodides were detected at all. As soon as the mono-coupling products were formed, they underwent further coupling immediately. Apparently, the bromo iodo derivative is crucial for the selective Sonogashira coupling.

Next, analogously prepared monobromides, **9c** and **9d**, were used for exemplifying the effectiveness to control the structure and composition of the higher phenylene-ethynylene homologues (Scheme 11). Subjection of these monobromides to additional Sonogashira reaction led to **10a** and **10b**, respectively. The positions of the ethynyl groups on the aromatic rings can be controlled by choosing appropriate dihalodiphenylacetylenes. Substituents like the hexyl group can also be incorporated at whichever positions depending on the substituents of the starting sulfone and aldehyde. Suzuki–Miyaura coupling[11] was employable for the second reaction as well,




**Scheme 9.** Syntheses of unsymmetrically substituted acetylenes by use of **1** through Sonogashira coupling.




**Scheme 10.** Attempts for selective C–C bond formation of dibromide **1u** and diiodide **1aa**.

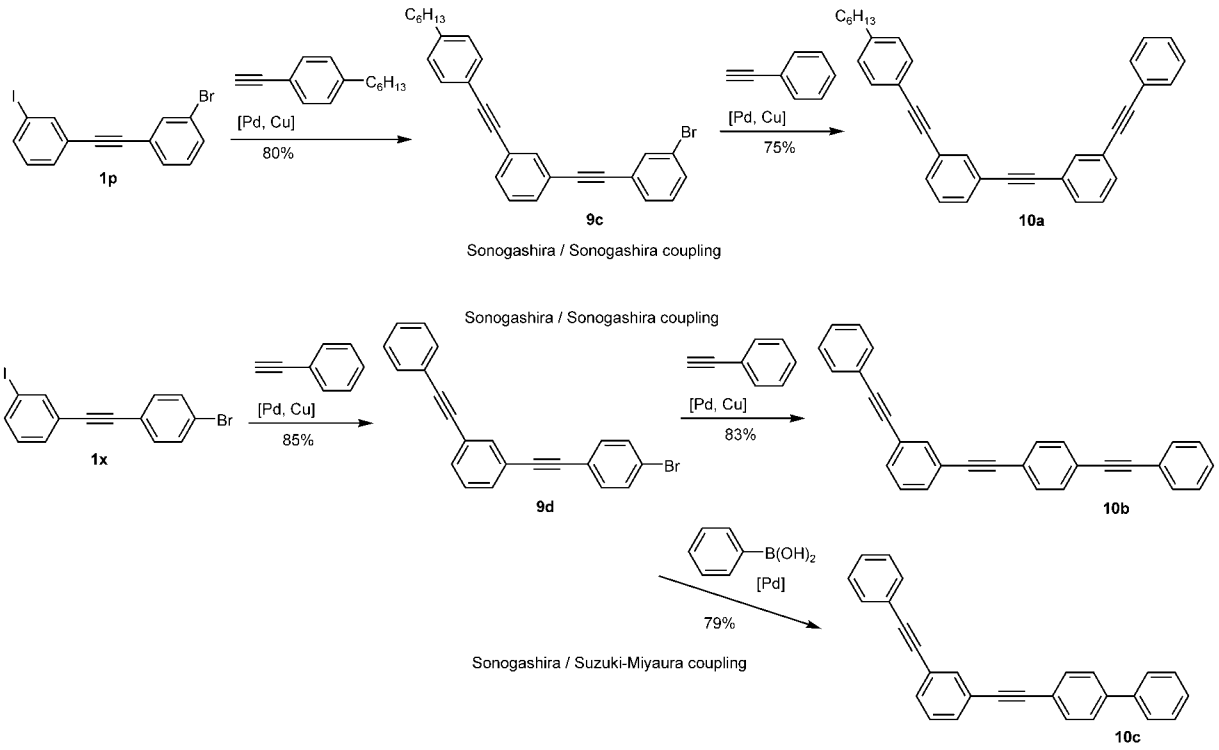
and a biphenylacetylene derivative **10c** was obtained. The Mizoroki–Heck reaction[12] also worked well (Scheme 12). The reaction of the bromo iodo substrate **1x** with methyl acrylate proceeded exclusively on the iodide to afford **9e**. Subjection of this compound to the Sonogashira reaction provided an ene-yne **10d**, while conjunction with Suzuki–Miyaura coupling furnished the corresponding biphenyl derivative **10e**.

The combination of bromo and chloro functions is also useful for selective carbon-carbon bond formations. Subjection of the bromo-chloro substrate **1 l** to a Sonogashira reaction led to monochloride **9f**, which then underwent Negishi coupling[13] to afford the biphenyl derivative **10c** (Scheme 13).

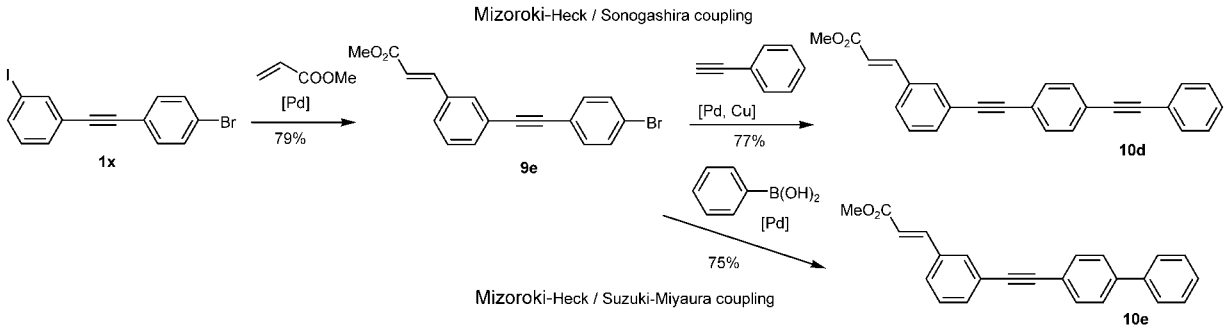
## Conclusion

The double elimination reaction of β-substituted sulfones has proved to be useful for the synthesis of dihalodiphenylacetylenes. In particular, otherwise difficult-to-prepare diphenylacetylenes with different halogen substituents are accessible in a straightforward manner. These compounds are versatile building blocks for higher homologues of phenylene-ethynylenes because various carbon-carbon bond formations like Sonogashira, Mizoroki–Heck, Suzuki–Miyaura, and Negishi couplings can be conducted sequentially on the different halogen functions. The iodo-bromo and bromo-chloro substrates undergo exclusive consumption of the iodo and bromo groups, respectively, in the initial reaction. The remaining halogen functions undergo the other carbon-carbon bond formations. Needless to say, a higher selectivity would be feasible with chloro-iodo substrates. According to this strategy, various moieties can be incorporated at any desired position because all substitution patterns of halogens are accessible for dihalodiphenylacetylenes. Notably, the substitution modes are readily controlled by suitable choice of substituted benzyl sulfones and benzaldehydes. As a consequence,

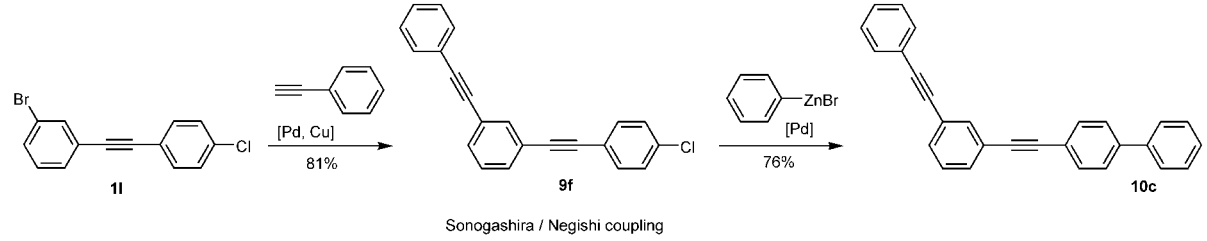
  




**Scheme 11.** Syntheses of unsymmetrically substituted acetylenes by sequential transition metal-catalyzed C–C bond formations.




**Scheme 12.** Syntheses of unsymmetrically substituted acetylenes by sequential Mizoroki–Heck/Sonogashira or Suzuki–Miyaura couplings.




**Scheme 13.** Synthesis of unsymmetrically substituted acetylene by sequential Sonogashira/Negishi couplings.

a variety of aromatic acetylene compounds with regulated structure and composition can be tailored conveniently. We believe that the present protocol will find a wide range of utilization in the synthesis of acetylenic materials.

## Experimental Section

### General Remarks

All reactions were carried out under an atmosphere of nitrogen with freshly distilled solvents, unless otherwise noted. Tetrahydrofuran (THF) was distilled from sodium/benzophenone. Other solvents such as toluene and diisopropylamine were distilled from $CaH_2$. A hexane solution of BuLi was purchased from Aldrich and titrated before use by the Gilman method.[14] A THF solution of LiHMDS was purchased and used without titration. $Pd(PPh_3)_4$ was prepared according to the reported method.[15] Silica gel (Daiso gel IR-60) was used for column chromatography. NMR spectra were recorded at 25 °C on JEOL Lambda 300 and JEOL Lambda 500 instruments and calibrated with tetramethylsilane (TMS) as an internal reference. Elemental analyses were performed with a Perkin Elmer PE 2400.

Starting compounds **3a–f** are commercially available, while sulfones **2a–f** and iodobenzaldehyde **3g–i** were prepared from the corresponding benzyl bromides and benzyl alcohols, respectively. Experimental details are described in the Supporting Information.

### Preparation of 1a through Double Elimination of β-Substituted Sulfone Derived from the Reaction of 2a with 3a; Typical Procedure

To a THF solution (5 mL) of 2-bromobenzyl phenyl sulfone **2a** (372 mg, 1.2 mmol) was added a hexane solution of BuLi (1.60 M, 0.75 mL, 1.2 mmol) at −78 °C, and the mixture was stirred for 0.5 h. A THF solution (3 mL) of 2-chlorobenzaldehyde **3a** (141 mg, 1.0 mmol) was added at −78 °C, and the mixture was stirred for 0.5 h. Diethyl chlorophosphate (0.14 mL, 1.0 mmol) was added at −78 °C, and the mixture was stirred at room temperature for 1 h. A THF solution of LiHMDS (1.0 M, 4.0 mL, 4.0 mmol) was added at −78 °C, and the mixture was stirred at room temperature for 2 h. After usual work-up with ethyl acetate and aqueous $NH_4Cl$, followed by drying over $MgSO_4$ and evaporation, the residue was subjected to a thin pad of silica gel to furnish **1a** in a pure form; yield: 216 mg (74%).

### Preparation of 1r through Double Elimination of β-Substituted Sulfone Derived from the Reaction of 2c with 3a; Typical Procedure

To a THF solution (5 mL) of 4-bromobenzyl phenyl sulfone **2c** (372 mg, 1.2 mmol) was added a THF solution of LiHMDS (1.0 M, 1.2 mL, 1.2 mmol) at −78 °C, and the mixture was stirred for 0.5 h. A THF solution (3 mL) of 2-chlorobenzaldehyde **3a** (141 mg, 1.0 mmol) was added at −78 °C, and the mixture was stirred for 0.5 h. Diethyl chlorophosphate (0.14 mL, 1.0 mmol) was added at −78 °C, and the mixture was stirred at room temperature for 1 h. A THF solution of LiHMDS (1.0 M, 4.0 mL, 4.0 mmol) was added at −78 °C, and the mixture was stirred at room temperature for 2 h. After usual work-up with ethyl acetate and aqueous $NH_4Cl$a, followed by drying over $MgSO_4$ and evaporation, the residue was subjected to a thin pad of silica gel to furnish **1r** in a pure form; yield: 245 mg (84%).

**1-(2-Bromophenyl)-2-(2-chlorophenyl)ethyne (1a):** mp 82–84 °C; $^1$H NMR (300 MHz, $CDCl_3$): δ = 7.16–7.34 (m, 4H), 7.41–7.47 (m, 1H), 7.57–7.67 (m, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 91.2, 93.5, 123.5, 125.7, 126.2, 127.1, 127.7, 130.0, 130.2, 130.4, 133.1, 134.1, 134.2, 136.6; elemental analysis: calcd. for $C_{14}H_8BrCl$ (%): C 57.67, H 2.77; found: C 57.36, H 2.38.

**1-(2-Bromophenyl)-2-(3-chlorophenyl)ethyne (1b):** mp 34–35 °C; $^1$H NMR (300 MHz, $CDCl_3$): δ = 7.16–7.23 (m, 1H), 7.26–7.37 (m, 3H), 7.43–7.49 (m, 1H), 7.54–7.65 (m, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 89.8, 93.0, 125.2, 125.5, 126.4, 127.7, 129.5, 130.2, 130.3, 130.4, 132.1, 133.1, 133.9, 134.8; elemental analysis: calcd. for $C_{14}H_8BrCl$ (%): C 57.67, H 2.77; found: C 57.68, H 2.48.

**1-(2-Bromophenyl)-2-(4-chlorophenyl)ethyne (1c):** mp 71–73 °C; $^1$H NMR (300 MHz, $CDCl_3$): δ = 7.19 (t, $J$ = 7.7 Hz, 1H), 7.26–7.37 (m, 3H), 7.49–7.57 (m, 3H), 7.62 (d, $J$ = 7.7 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 89.5, 93.3, 122.0, 125.7, 126.2, 127.7, 129.3, 130.2, 133.1, 133.5, 133.8, 135.3; elemental analysis: calcd. for $C_{14}H_8BrCl$ (%): C 57.67, H 2.77; found: C 57.56, H 2.37.

**1,2-Bis(2-bromophenyl)ethyne (1d):**[7e] $^1$H NMR (300 MHz, $CDCl_3$): δ = 7.01 (dt, $J$ = 1.5, 7.6 Hz, 2H), 7.12 (dt, $J$ = 0.9, 7.6 Hz, 2H), 7.45 (dd, $J$ = 1.2, 7.9 Hz, 4H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 92.8, 125.0, 125.4, 126.9, 129.6, 132.4, 133.5.

**1-(2-Bromophenyl)-2-(3-bromophenyl)ethyne (1e):**[16] mp 54–56 °C; $^1$H NMR (300 MHz, $CDCl_3$): δ = 7.16–7.33 (m, 3H), 7.48–7.56 (m, 3H), 7.62 (d, $J$ = 8.0 Hz, 1H), 7.73 (s, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 89.2, 92.2, 122.2, 124.9, 125.7, 127.1, 129.7, 129.8, 130.2, 131.7, 132.5, 133.3, 134.3.

**1-(2-Bromophenyl)-2-(4-bromophenyl)ethyne (1f):**[17] mp 71–73 °C; $^1$H NMR (300 MHz, $CDCl_3$): δ = 7.16 (dt, $J$ = 1.7, 7.6 Hz, 1H), 7.26 (dt, $J$ = 0.9, 7.6 Hz, 1H), 7.39–7.55 (m, 5H), 7.60 (d, $J$ = 8.1 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 89.1, 92.7, 121.8, 122.9, 125.0, 125.6, 127.0, 129.6, 131.6, 132.5, 133.0, 133.2.

**1-(2-Bromophenyl)-2-(2-iodophenyl)ethyne (1g):**[7e] mp 68–70 °C; $^1$H NMR (300 MHz, $CDCl_3$): δ = 7.03 (dt, $J$ = 1.5, 7.8 Hz, 1H), 7.20 (dt, $J$ = 1.5, 7.3 Hz, 1H), 7.28–7.38 (m, 2H), 7.56–7.66 (m, 3H), 7.88 (dd, $J$ = 7.8, 1.0 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 91.4, 95.5, 100.6, 125.1, 125.5, 127.0, 127.8, 129.5, 129.6, 129.7, 132.5, 133.0, 133.6, 138.8.

**1-(2-Bromophenyl)-2-(3-iodophenyl)ethyne (1h):** mp 53–55 °C; $^1$H NMR (300 MHz, $CDCl_3$): δ = 7.10 (t, $J$ = 8.8 Hz, 1H), 7.20 (dt, $J$ = 1.7, 7.5 Hz, 1H), 7.30 (dt, $J$ = 1.2, 7.5 Hz, 1H), 7.50–7.56 (m, 2H), 7.62 (dd, $J$ = 1.2, 8.0 Hz, 1H), 7.69 (d, $J$ = 7.8 Hz, 1H), 7.92–7.94 (m, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 89.2, 92.0, 93.7, 124.9, 125.0, 125.7, 127.1, 129.7, 129.9, 130.8, 132.5, 133.3, 137.6, 140.1; elemental analysis: calcd. for $C_{14}H_8BrI$ (%): C 43.90, H 2.11; found: C 43.87, H 2.30.

**1-(2-Bromophenyl)-2-(4-iodophenyl)ethyne (1i):**[16] mp 63–65 °C; $^1$H NMR (300 MHz, $CDCl_3$): δ = 7.19 (dt, $J$ = 1.8,

7.7 Hz, 1H), 7.25–7.33 (m, 3H), 7.54 (dd, $J=1.8$, 7.7 Hz, 1H), 7.61 (dd, $J=1.3$, 7.9 Hz, 1H), 7.68–7.73 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta=89.4$, 92.9, 94.6, 122.4, 125.0, 125.6, 127.1, 129.6, 132.5, 133.1, 133.2, 137.5.

**1-(3-Bromophenyl)-2-(2-chlorophenyl)ethyne (1j):** mp 57–59 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta=7.20$–7.32 (m, 3H), 7.41–7.58 (m, 4H), 7.71–7.74 (m, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta=88.0$, 93.4, 122.8, 123.3, 125.7, 127.1, 129.9, 130.2, 130.4, 130.9, 132.3, 133.9, 135.0, 136.6; elemental analysis: calcd. for $C_{14}H_8BrCl$ (%): C 57.67, H 2.77; found: C 57.77, H 2.50.

**1-(3-Bromophenyl)-2-(3-chlorophenyl)ethyne (1k):**[18] mp 89–91 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta=7.18$–7.35 (m, 3H), 7.37–7.53 (m, 4H), 7.66–7.70 (m, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta=89.5$, 89.7, 122.8, 125.0, 125.3, 129.5, 130.2, 130.3, 130.4, 130.8, 132.1, 132.3, 134.8, 134.9.

**1-(3-Bromophenyl)-2-(4-chlorophenyl)ethyne (1l):**[18] mp 101–103 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta=7.08$ (t, $J=$ 7.8 Hz, 1H), 7.30–7.36 (m, 2H), 7.41–7.50 (m, 3H), 7.65–7.70 (m, 1H), 7.87–7.89 (m, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta=89.3$, 90.1, 121.8, 122.8, 125.5, 129.4, 130.4, 130.7, 132.2, 133.5, 134.9, 135.3.

**1,2-Bis(3-bromophenyl)ethyne (1m):**[18] mp 99–102 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta=7.23$ (t, $J=7.8$ Hz, 2H), 7.43–7.52 (m, 4H), 7.67–7.69 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta=89.0$, 122.2, 124.7, 129.8, 130.2, 131.8, 134.4.

**1-(3-Bromophenyl)-2-(4-bromophenyl)ethyne (1n):**[18] mp 101–103 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta=7.22$ (t, $J=$ 7.9 Hz, 1H), 7.36–7.51 (m, 6H), 7.66–7.69 (m, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta=88.9$, 89.6, 121.7, 122.2, 122.9, 124.9, 129.8, 130.1, 130.2, 131.6, 131.7, 133.1, 134.3.

**1-(3-Bromophenyl)-2-(2-iodophenyl)ethyne (1o):** mp 58–59 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta=7.04$ (dt, $J=1.7$, 7.5 Hz, 1H), 7.24 (t, $J=8.0$ Hz, 1H), 7.34 (dt, $J=1.0$, 7.7 Hz, 1H), 7.47–7.54 (m, 3H), 7.72–7.75 (m, 1H), 7.88 (dd, $J=1.0$, 8.0 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta=91.3$, 92.8, 101.2, 122.2, 124.9, 127.9, 129.2, 129.7, 129.8, 130.2, 131.8, 132.5, 134.2, 138.8; elemental analysis: calcd. for $C_{14}H_8BrI$ (%): C 43.90, H 2.11; found: C 43.85, H 2.29.

**1-(3-Bromophenyl)-2-(3-iodophenyl)ethyne (1p):** mp 83–84 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta=7.09$ (t, $J=7.9$ Hz, 1H), 7.23 (t, $J=7.9$ Hz, 1H), 7.42–7.50 (m, 3H), 7.67–7.70 (m, 2H), 7.87–7.90 (m, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta=$ 88.8, 89.0, 93.7, 122.2, 124.7, 124.8, 129.8, 129.9, 130.1, 130.7, 131.7, 134.3, 137.6, 140.2; elemental analysis: calcd. for $C_{14}H_8$ BrI (%): C 43.90, H 2.11; found: C 43.83, H 2.27.

**1-(3-Bromophenyl)-2-(4-iodophenyl)ethyne (1q):** mp 108–110 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta=7.19$–7.26 (m, 3H), 7.42–7.50 (m, 2H), 7.65–7.72 (m, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta=89.1$, 89.7, 94.6, 122.2, 122.3, 124.9, 129.8, 130.1, 131.6, 133.1, 134.3, 137.6; elemental analysis: calcd. for $C_{14}H_8$ BrI (%): C 43.90, H 2.11; found: C 44.10, H 2.11.

**1-(4-Bromophenyl)-2-(2-chlorophenyl)ethyne (1r):** mp 46–48 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta=7.20$–7.30 (m, 2H), 7.41–7.44 (m, 3H), 7.46–7.56 (m, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta=87.9$, 94.0, 122.4, 123.5, 123.6, 127.1, 130.0, 130.1, 132.3, 133.7, 133.8, 136.5; elemental analysis: calcd. for $C_{14}H_8$ BrCl (%): C 57.67, H 2.77; found: C 57.30, H 2.38.

**1-(4-Bromophenyl)-2-(3-chlorophenyl)ethyne (1s):** mp 104–106 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta=7.24$–7.43 (m, 5H), 7.45–7.55 (m, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta=$ 89.7, 90.1, 122.3, 123.5, 125.2, 129.3, 130.2, 130.3, 132.0, 132.3, 133.7, 134.8; elemental analysis: calcd. for $C_{14}H_8BrCl$ (%): C 57.67, H 2.77; found: C 57.69, H 2.51.

**1-(4-Bromophenyl)-2-(4-chlorophenyl)ethyne (1t):** mp 188–190 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta=7.30$–7.40 (m, 4H), 7.42–7.51 (m, 4H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta=$ 89.8, 89.9, 122.0, 122.4, 123.3, 129.3, 132.2, 133.4, 133.6, 135.1; elemental analysis: calcd. for $C_{14}H_8BrCl$ (%): C 57.67, H 2.77; found: C 57.30, H 2.38.

**1,2-Bis(4-bromophenyl)ethyne (1u):**[19] mp 190–192 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta=7.35$–7.40 (m, 4H), 7.46–7.52 (m, 4H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta=90.0$, 122.4, 123.4, 132.3, 133.6.

**1-(4-Bromophenyl)-2-(2-iodophenyl)ethyne (1v):** mp 93–94 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta=7.03$ (dt, $J=1.7$, 7.7 Hz, 1H), 7.33 (dt, $J=1.0$, 7.7 Hz, 1H), 7.42–7.54 (m, 5H), 7.88 (dd, $J=1.0$, 8.0 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta=91.9$, 92.7, 101.1, 121.8, 122.9, 127.9, 129.4, 129.6, 131.7, 132.4, 133.0, 138.8; elemental analysis: calcd. for $C_{14}H_8BrI$ (%): C 43.90, H 2.11; found: C 43.87, H 2.28.

**1,2-Bis(2-iodophenyl)ethyne (1w):**[20] mp 98–100 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta=7.02$ (dt, $J=1.6$, 7.6 Hz, 2H), 7.33 (dt, $J=0.4$, 7.6 Hz, 2H), 7.57–7.67 (m, 2H), 7.84–7.93 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta=94.7$, 100.5, 127.7, 129.4, 129.6, 132.9, 138.7.

**1-(4-Bromophenyl)-2-(3-iodophenyl)ethyne (1x):** mp 107–110 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta=7.09$ (t, $J=7.9$ Hz, 1H), 7.37 (d, $J=8.4$ Hz, 2H), 7.47–7.51 (m, 3H), 7.65–7.70 (m, 1H), 7.87–7.90 (m, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta=$ 88.7, 89.6, 93.7, 121.7, 122.9, 125.0, 129.9, 130.7, 131.7, 133.0, 137.5, 140.1; elemental analysis: calcd. for $C_{14}H_8BrI$ (%): C 43.90, H 2.11; found: C 44.09, H 2.18.

**1-(2-Iodophenyl)-2-(3-iodophenyl)ethyne (1y):** mp 74–77 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta=7.00$–7.13 (m, 2H), 7.30–7.37 (m, 1H), 7.50–7.57 (m, 2H), 7.66–7.73 (m, 1H), 7.85–7.90 (m, 1H), 7.94 (s, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta=91.1$, 92.8, 93.7, 101.2, 124.9, 127.8, 129.2, 129.7, 129.8, 130.7, 132.5, 137.5, 138.7, 140.0; elemental analysis: calcd. for $C_{14}H_8I_2$ (%): C 39.10, H 1.88; found: C 39.35, H 1.97.

**1,2-Bis(3-iodophenyl)ethyne (1z):**[21] mp 105–106 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta=7.09$ (t, $J=7.9$ Hz, 2H), 7.48 (d, $J=7.9$ Hz, 2H), 7.68 (d, $J=7.9$ Hz, 2H), 7.88 (s, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta=88.9$, 93.7, 124.8, 129.9, 130.7, 137.6, 140.2.

**1-(3-Iodophenyl)-2-(4-iodophenyl)ethyne (1aa):** mp 143–145 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta=7.09$ (t, $J=7.9$ Hz, 1H), 7.24 (dd, $J=1.4$, 7.0 Hz, 2H), 7.48 (d, $J=7.7$ Hz, 1H), 7.66–7.73 (m, 3H), 7.88 (s, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta=89.0$, 89.7, 93.7, 94.6, 122.2, 124.9, 129.9, 130.6, 133.1, 137.5, 137.6, 140.1; elemental analysis: calcd. for $C_{14}H_8I_2$ (%): C 39.10, H 1.88; found: C 39.39, H 1.92.

**1-(4-Bromophenyl)-2-(4-iodophenyl)ethyne (1bb):** mp 210–213 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta=7.24$ (d, $J=$ 8.6 Hz, 2H), 7.38 (d, $J=8.6$ Hz, 2H), 7.49 (d, $J=8.4$ Hz, 2H), 7.69 (d, $J=8.4$ Hz, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta=89.6$, 89.7, 94.4, 121.9, 122.4, 122.8, 131.7, 132.99, 133.04, 137.6; elemental analysis: calcd. for $C_{14}H_8BrI$ (%): C 43.90, H 2.11; found: C 44.23, H 2.01.

**1-(2-Iodophenyl)-2-(4-iodophenyl)ethyne (1cc):** mp 75–77 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta=7.03$ (dt, $J=1.4$, 7.8 Hz, 1H), 7.20 (dt, $J=1.7$, 7.8 Hz, 1H), 7.28–7.38 (m, 2H), 7.57–7.66 (m, 3H), 7.86–7.90 (m, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta=91.4$, 95.5, 100.6, 125.4, 127.0, 127.8, 129.7, 129.8,

132.5, 133.0, 133.6, 138.8; elemental analysis: calcd. for $C_{14}H_8I_2$ (%): C 39.10, H 1.88; found: C 39.29, H 1.97.

**1,2-Bis(4-iodophenyl)ethyne (1dd):**[22] mp 247–250 °C; $^1$H NMR (300 MHz, $CDCl_3$): δ = 7.24 (d, $J$ = 8.6 Hz, 4H), 7.69 (d, $J$ = 8.6 Hz, 4H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 90.0, 94.7, 122.8, 133.4, 138.0.

### Sonogashira Coupling of 1-(4-Bromophenyl)-2-(3-iodophenyl)ethyne (1x) with Phenylethyne; Typical Procedure for Selective C–C Bond Formation at an Iodide Moiety in 1x

A toluene solution (3 mL) of **1x** (191.5 mg, 0.50 mmol), phenylethyne (51.1 mg, 0.50 mmol), $Pd(PPh_3)_4$ (28.9 mg, 0.025 mmol), CuI (4.8 mg, 0.025 mmol) and diisopropylamine (1.0 mL) was stirred at room temperature for 12 h. After filtration, the filtrate was washed with aqueous $NH_4Cl$, and the aqueous solution extracted with AcOEt. The combined organic layer was washed with aqueous NaCl, dried over $MgSO_4$ and evaporated. The crude products obtained were subjected to column chromatography on silica gel (5% AcOEt/hexanes) to afford 3-[2-(4-bromophenyl)ethynyl]-1-(2-phenylethynyl)-benzene (**9d**); yield: 151.8 mg (85%).

### Sonogashira Coupling of 3-[2-(4-Bromophenyl)ethynyl]-1-(2-phenylethynyl)benzene (9d) with Phenylethyne; Typical Procedure for C–C Bond Formation at a Bromide Moiety

A toluene solution (5 mL) of **9d** (178.6 mg, 0.50 mmol), phenylethyne (51.1 mg, 0.50 mmol), $Pd(PPh_3)_4$ (28.9 mg, 0.025 mmol), CuI (4.8 mg, 0.025 mmol) and diisopropylamine (2.0 mL) was stirred at 70 °C for 12 h. After filtration, the filtrate was washed with aqueous $NH_4Cl$, and the aqueous solution extracted with AcOEt. The combined organic layer was washed with aqueous NaCl, dried over $MgSO_4$ and evaporated. The crude products obtained were subjected to column chromatography on silica gel (hexanes) to afford 1-(2-phenylethynyl)-3-{2-[4-(2-phenylethynyl)phenyl]ethynyl}benzene (**10b**); yield: 157.1 mg (83%).

### Suzuki–Miyaura Coupling of 3-[2-(4-Bromophenyl)ethynyl]-1-(2-phenylethynyl)benzene (9d) with Phenylboronic Acid; Typical Procedure C–C Bond Formation at a Bromide Moiety

A benzene solution (10 mL) of **9d** (357.2 mg, 1.0 mmol), phenylboronic acid (182.9 mg, 1.5 mmol), $Pd(PPh_3)_4$ (23.1 mg, 0.02 mmol), $Ba(OH)_2$ (octahydrate, 473.2 mg, 1.5 mmol) and water (3.0 mL) was heated at reflux for 16 h. After usual work-up with AcOEt/water, the combined organic layer was washed with aqueous NaCl, dried over $MgSO_4$ and evaporated. The crude products obtained were subjected to column chromatography on silica gel (5% AcOEt/hexanes) to afford 1-(2-phenylethynyl)-3-[2-(4-phenylphenyl)ethynyl]benzene (**10c**); yield: 280.0 mg (79%).

### Mizoroki–Heck Reaction of 1-(4-Bromophenyl)-2-(3-iodophenyl)ethyne (1x) with Methyl Acrylate; Typical Procedure for Selective C–C Bond Formation at an Iodide Moiety in 1x

A DMF solution (10 mL) of **1x** (383.0 mg, 1.0 mmol), methyl acrylate (86.1 mg, 1.1 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), $Bu_4NCl$ (277.9 mg, 1.0 mmol) and $NaHCO_3$ (210 mg, 2.5 mmol) was heated at 80 °C for 20 h. After usual work-up with AcOEt/aqueous $NH_4Cl$, the combined organic layer was washed with aqueous NaCl, dried over $MgSO_4$ and evaporated. The crude products obtained were subjected to column chromatography on silica gel (hexanes) to afford methyl (2*E*)-3-{3-[2-(4-bromophenyl)ethynyl]phenyl}prop-2-enoate (**9e**); yield: 269.5 mg (79%).

### Negishi Coupling of 3-[2-(4-Chlorophenyl)ethynyl]-1-(2-phenylethynyl)benzene (9f) with PhZnBr

To a THF solution (2 mL) of iodobenzene (122.4 mg, 0.6 mmol) was added a hexane solution (0.5 mL) of BuLi (1.3 M, 0.65 mmol) at −78 °C. After 10 min, a THF solution (2.0 mL) of $ZnBr_2$ (135.1 mg, 0.6 mmol) was added, and the mixture was stirred at room temperature for 10 min. This mixture was added to a THF solution (3 mL ) of **9f** (156.4 mg, 0.5 mmol) and $PdCl_2$(dppf) (20.4 mg, 0.025 mmol), and the mixture was heated at reflux for 12 h. After usual work-up with AcOEt/aqueous $NH_4Cl$, the combined organic layer was washed with aqueous NaCl, dried over $MgSO_4$ and evaporated. The crude products obtained were subjected to column chromatography on silica gel (hexanes) to afford 1-(2-phenylethynyl)-3-[2-(4-phenylphenyl)ethynyl]benzene (**10c**); yield: 134.7 mg (76%).

### Attempt for Unsymmetrically Substituted Acetylenes by Sonogashira Coupling of Dibromo- and Diiodoarene; Typical Procedure for Coupling of 1,4-Diiodobenzene with 1-Bromo-4-ethynylbenzene)

A toluene solution (10 mL) of 1,4-diiodobenzene (165.0 mg, 0.5 mmol), 1-bromo-4-ethynylbenzene (90.5 mg, 0.50 mmol), $Pd(PPh_3)_4$ (28.9 mg, 0.025 mmol), CuI (4.8 mg, 0.025 mmol) and diisopropylamine (1.0 mL) was stirred at room temperature for 12 h. After filtration, the filtrate was washed with aqueous $NH_4Cl$, and the aqueous solution was extracted with AcOEt. The combined organic layer was washed with aqueous NaCl, dried over $MgSO_4$ and evaporated. The crude products obtained were subjected to column chromatography on silica gel to afford 1-(4-bromophenyl)-2-(4-iodophenyl)ethyne (yield: 24.9 mg, 13%), 1,4-bis[2-(4-bromophenyl)ethynyl]benzene (yield: 74.1 mg, 34%) and 1,4-diiodobenzene (yield: 62.7 mg, 38%).

**3-[2-(4-Bromophenyl)ethynyl]-1-[2-(4-hexylphenyl)ethynyl]benzene (9a):** mp 81–83 °C; $^1$H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, $J$ = 6.6 Hz, 3H), 1.30 ($m_c$, 6H), 1.61 ($m_c$, 2H), 2.62 (t, $J$ = 8.0 Hz, 2H), 7.17 (d, $J$ = 8.0 Hz, 2H), 7.30–7.51 (m, 9H), 7.69 (s, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 14.1, 22.6, 28.9, 31.2, 31.7, 35.9, 87.8, 88.8, 89.7, 90.4, 120.0, 122.0, 122.7, 123.2, 123.9, 128.4, 128.5, 131.0, 131.5, 131.6, 131.7, 133.0,

134.5, 143.7; elemental analysis: calcd. for $C_{28}H_{25}Br$ (%): C 76.19, H 5.71; found: C 76.47, H 5.62.

**1-[2-(4-Bromophenyl)ethynyl]-4-[2-(4-hexyloxyphenyl)ethynyl]benzene (9b):** mp 232–234 °C; $^1$H NMR (300 MHz, $CDCl_3$): δ = 0.91 (t, *J* = 7.3 Hz, 3H), 1.34–1.46 (m, 6H), 1.79 ($m_c$, 2H), 3.97 (t, *J* = 6.4 Hz, 2H), 6.82–6.89 (m, 2H), 7.37–7.51 (m, 10H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 14.0, 22.6, 25.7, 29.1, 31.5, 68.1, 87.7, 89.9, 90.3, 91.7, 113.6, 114.6, 122.0, 122.2, 122.6, 131.4, 131.6, 133.0, 133.1, 134.0, 159.4, 159.8; elemental analysis: calcd. for $C_{28}H_{25}BrO$ (%): C 73.52, H 5.51; found: C 73.90, H 5.67.

**3-[2-(3-Bromophenyl)ethynyl]-1-[2-(4-hexylphenyl)ethynyl]benzene (9c):** mp 86–88 °C; $^1$H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 6.6 Hz, 3H), 1.30 ($m_c$, 6H), 1.61 ($m_c$, 2H), 2.62 (t, *J* = 7.9 Hz, 2H), 7.17 (d, *J* = 8.2 Hz, 2H), 7.23 (t, *J* = 7.9 Hz, 1H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.43–7.51 (m, 6H), 7.68–7.70 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 14.1, 22.6, 28.9, 31.2, 31.7, 35.9, 87.7, 88.3, 89.9, 90.4, 120.0, 122.2, 123.0, 123.9, 125.0, 128.4, 128.5, 129.8, 130.2, 131.1, 131.4, 131.5, 131.5, 131.7, 134.3, 134.6; elemental analysis: calcd. for $C_{28}H_{25}Br$ (%): C 76.19, H 5.71; found: C 75.92, H 5.66.

**3-[2-(4-Bromophenyl)ethynyl]-1-(2-phenylethynyl)benzene (9d):** mp 135–138 °C; $^1$H NMR (300 MHz, $CDCl_3$): δ = 7.33–7.40 (m, 6H), 7.47–7.55 (m, 6H), 7.71 (s, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 88.4, 88.6, 89.6, 90.1, 121.9, 122.7, 122.9, 123.2, 123.7, 128.4, 128.5, 131.2, 131.5, 131.6, 131.7, 132.5, 133.0, 134.5; elemental analysis: calcd. for $C_{22}H_{13}Br$ (%): C 73.97, H 3.67; found: C 74.25, H 3.72.

**Methyl (2*E*)-3-{3-[2-(4-Bromophenyl)ethynyl]phenyl}prop-2-enoate (9e):** mp 133–135 °C; $^1$H NMR (300 MHz, $CDCl_3$): δ = 3.82 (s, 3H), 6.45 (d, *J* = 16.1 Hz, 1H), 7.36–7.42 (m, 3H), 7.48–7.55 (m, 4H), 7.67 (d, *J* = 16.1 Hz, 1H), 7.68 (s, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 51.8, 89.1, 89.6, 118.8, 121.8, 122.8, 123.7, 128.0, 129.0, 131.0, 131.7, 133.0, 133.1, 143.8, 167.2; elemental analysis: calcd. for $C_{18}H_{13}BrO_2$ (%): C 63.36, H 3.84; found: C 63.48, H 3.63.

**3-[2-(4-Chlorophenyl)ethynyl]-1-(2-phenylethynyl)benzene (9f):** mp 135–136 °C; $^1$H NMR (300 MHz, $CDCl_3$): δ = 7.32–7.37 (m, 6H), 7.44–7.55 (m, 6H), 7.71 (s, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 88.4, 88.8, 89.5, 90.0, 121.5, 122.9, 123.3, 123.7, 128.4, 128.5, 128.6, 128.7, 131.2, 131.5, 131.6, 132.8, 134.5, 134.6; elemental analysis: calcd. for $C_{22}H_{13}Cl$ (%): C 84.48, H 4.19; found: C 84.20, H 4.24.

**1-[2-(4-Hexylphenyl)ethynyl]-3-{2-[3-(2-phenylethynyl)phenyl]ethynyl}benzene (10a):** mp 74–77 °C; $^1$H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 3.8 Hz, 3H), 1.31 ($m_c$, 6H), 1.61 ($m_c$, 2H), 2.62 (t, *J* = 4.8 Hz, 2H), 7.17 (d, *J* = 5.0 Hz, 2H), 7.20–7.24 (m, 1H), 7.30–7.38 (m, 4H), 7.42–7.56 (m, 8H), 7.67–7.73 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 14.1, 22.6, 28.9, 31.2, 31.7, 35.9, 87.7, 88.3, 88.5, 89.0, 89.9, 90.4, 120.0, 122.2, 123.0, 123.3, 123.9, 125.0, 128.4, 128.5, 129.8, 130.2, 131.1, 131.3, 131.4, 131.5, 131.6, 131.7, 132.5, 134.3, 134.56, 134.6; elemental analysis: calcd. for $C_{36}H_{30}$ (%): C 93.46, H 6.54; found: C 93.61, H 6.48.

**1-(2-Phenylethynyl)-3-{2-[4-(2-phenylethynyl)phenyl]ethynyl}benzene (10b):** mp 72–75 °C; $^1$H NMR (300 MHz, $CDCl_3$): δ = 7.32–7.38 (m, 7H), 7.48–7.56 (m, 10H), 7.72 (s, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 88.5, 89.0, 89.7, 90.1, 90.4, 91.3, 122.8, 122.9, 123.0, 123.3, 123.4, 123.7, 128.3, 128.3, 128.4, 128.5, 128.6, 131.3, 131.4, 131.5, 131.5, 131.6, 131.6, 134.6; elemental analysis: calcd. for $C_{30}H_{18}$ (%): C 95.21, H 4.79; found: C 94.88, H 4.44.

**1-(2-Phenylethynyl)-3-[2-(4-phenylphenyl)ethynyl]benzene (10c):** mp 156–158 °C; $^1$H NMR (300 MHz, $CDCl_3$): δ = 7.33–7.40 (m, 5H), 7.44–7.56 (m, 6H), 7.61–7.64 (m, 6H), 7.74 (s, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 88.5, 89.2, 89.9, 90.0, 121.9, 123.0, 123.6, 127.0, 127.1, 127.7, 128.3, 128.4, 128.5, 128.9, 131.3, 131.6, 132.1, 134.6, 140.3, 141.1; elemental analysis: calcd. for $C_{28}H_{18}$ (%): C 94.88, H 5.12; found: C 94.68, H 5.01.

**Methyl (2*E*)-3-(3-{2-[4-(2-Phenylethynyl)phenyl]ethynyl}phenyl)prop-2-enoate (10d):** mp 188–191 °C; $^1$H NMR (300 MHz, $CDCl_3$): δ = 3.82 (s, 3H), 6.49 (d, *J* = 16.1 Hz, 1H), 7.34–7.42 (m, 4H), 7.49–7.56 (m, 8H), 7.67 (d, *J* = 16.1 Hz, 1H), 7.70 (s, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 51.8, 89.0, 89.9, 90.3, 91.4, 118.8, 122.7, 123.0, 123.9, 128.0, 128.5, 129.0, 131.0, 131.5, 131.6, 133.2, 134.7, 143.9, 167.2; elemental analysis: calcd. for $C_{30}H_{20}$ (%): C 86.16, H 5.01; found: C 86.31, H 4.89.

**Methyl (2*E*)-3-{3-[2-(4-Phenylphenyl)ethynyl]phenyl}prop-2-enoate (10e):** mp 174–175 °C; $^1$H NMR (300 MHz, $CDCl_3$): δ = 3.83 (s, 3H), 6.49 (d, *J* = 15.9 Hz, 1H), 7.37–7.51 (m, 5H), 7.55–7.66 (m, 8H), 7.72 (s, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 51.8, 89.2, 90.1, 118.7, 121.7, 124.1, 127.0, 127.1, 127.7, 127.8, 128.9, 129.0, 131.0, 132.1, 133.1, 134.6, 140.2, 141.2, 143.9, 167.2; elemental analysis: calcd. for $C_{24}H_{18}O_2$ (%): C 85.18, H 5.36; found: C 84.89, H 5.30.

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