A Highly Selective Synthesis of Diarylethynes and Their Oligomers by a Palladium-Catalyzed Sonogashira Coupling Reaction under Phase Transfer Conditions

Hak-Fun Chow,* Chi-Wai Wan, Kam-Hung Low, and Ying-Yeung Yeung

Department of Chemistry, The Chinese University of Hong Kong, Shatin, NT, Hong Kong, China

hfchow@cuhk.edu.hk

Received October 30, 2000

Introduction

Conjugated oligomers and polymers have received much attention due to their potential uses in optical and electronic applications. Among a large array of conjugated architectures, diarylethynes and their oligomeric, polymeric, and dendritic analogues play a very important role as nonlinear optical materials,[1] photochemical antenna systems,[2] and molecular electronic devices.[3] Of the various synthetic approaches to diarylethynes **1**, the Sonogashira reaction[4] that features the cross-coupling between an arylethyne **2** and an aryl halide **3** in the presence of a Cu(I)/Pd(0) cocatalyst and a base is the most widely used method. This reaction is highly versatile not only for the preparation of diarylethynes but is also extremely useful for the syntheses of oligo- and poly-(aryleneethynylene)s,[5] as well as oligo-(aryleneethynylene) dendrimers.[6]

$$\underset{\mathbf{2}}{Ar^1\text{-}C{\equiv}CH} + \underset{\mathbf{3}}{Ar^2\text{-}X} \xrightarrow[\text{base}]{\text{Pd(0), Cu(I)}} \underset{\mathbf{1}}{Ar^1\text{-}C{\equiv}C\text{-}Ar^2} + \underset{\mathbf{4}}{Ar^1\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}Ar^1}$$

One of the side products formed in the Sonogashira reaction is diarylbutadiyne **4**, a homo-coupling product resulting from the oxidative dimerization[7] of the terminal arylethyne **2**. In instances where the two aryl groups (i.e., Ar^1 and Ar^2) are of very different sizes or chromatographic polarities, this does not pose any problem as one could simply purify the desired diarylethyne by distillation or chromatographic separation. The yield of the cross-coupling product **1** could also be improved by increasing the molar ratio of arylethyne **2** to aryl halide **3** used in the reaction. However, the situation becomes more complicated when the arylethyne **2** is not readily available or when the two aryl groups are of similar nature. This is often encountered in the synthesis of oligo- and poly-(aryleneethynylene)s. In this case, both the diarylethyne **3** and diarylbutadiyne **4** had very similar chromatographic mobility and product purification had been proven to be difficult.[5a,5d] Furthermore, linear[5c] and dendritic oligo-(aryleneethynylene)s[6a] with a terminal ethyne group tended to undergo self-dimerization in preference to cross-coupling with aryl halides under the Sonogashira conditions. As a result, the desired diarylethyne could only be isolated in low yield. The extent of homo-coupling could be reduced, but not totally suppressed, by vigorous exclusion of oxygen.[5a,6a,8] The recent introduction of a copper-free palladium-mediated coupling reaction in the presence of triphenylarsine by Lindsey[8] had proven to be a successful modification which could minimize the amount of diarylbutadiyne **4** formed. Nonetheless, there is still a strong demand for improved procedures which could suppress the formation of Hay homo-coupling product during the Sonogashira reaction. Herein we reported an efficient preparation of diarylethynes by a modified Sonogashira method under phase transfer conditions. This new protocol could effectively reduce the amount of homo-coupling diarylbutadiyne **4** produced and was far superior to the original procedure in terms of coupling efficiency and product homogeneity.

Results and Discussion

Since the Hay homo-coupling product **4** was the result of the intermolecular dimerization of arylethyne **2**, its formation could therefore be suppressed if the terminal arylethyne **2** could be kept at a low concentration during the Sonogashira reaction. Under such circumstances, the arylethyne **2** would have a better chance to couple to the aryl halide **3** than to itself and hence the yield of the cross-coupling product **1** could be increased. This can be achieved by conducting the reaction under conditions in which the arylethyne **2** is slowly generated in situ from a precursor.[9] One such precursor is the acetylenic alcohol **5**, which is readily available via the Sonogashira coupling [$PdCl_2(PPh_3)_2$, CuI, *i*-Pr_2NH] of an aryl halide **6** and 2-methylbut-3-yn-2-ol (Scheme 1).[10] Hence the cross-coupling between the acetylenic alcohol **5** and the aryl

* To whom correspondence should be addressed. Fax: (852)-26035057.

(1) (a) Cheng, L.-T.; Tam, W.; Marder, S. R.; Stiegman, A. E.; Rikken, G.; Spangler, C. W. *J. Phys. Chem.* **1991**, *95*, 10643. (b) Moroni, M.; Le Moigne, J.; Luzzati, S. *Macromolecules* **1994**, *27*, 562.

(2) (a) Xu, Z.; Moore, J. S. *Acta Polym.* **1994**, *45*, 83. (b) Devadoss, C.; Bharathi, P.; Moore, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 9635. (c) Kopelman, R.; Shortreed, M.; Shi, Z.-Y.; Tan, W.; Xu, Z.; Moore, J. S.; Bar-Haim, A.; Klafter, J. *Phys. Rev. Lett.* **1997**, *78*, 1239.

(3) (a) Bumm, L. A.; Arnold, J. J.; Cygan, M. T.; Dunbar, T. D.; Burgin, T. P.; Jones, L., II; Allara, D. L.; Tour, J. M.; Weiss, P. S. *Science* **1996**, *271*, 1705. (b) Schumm, J. S.; Pearson, D. L.; Tour, J. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1360. (c) Tour, J. M.; Jones, L., II; Pearson, D. L.; Lamba, J. J. S.; Burgin, T. P.; Whitesides, G. M.; Allara, D. L.; Parikh, A. N.; Atre, S. V. *J. Am. Chem. Soc.* **1995**, *117*, 9529.

(4) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467.

(5) (a) Ziener, U.; Godt, A. *J. Org. Chem.* **1997**, *62*, 6137. (b) Francke, V.; Mangel, T.; Müllen, K. *Macromolecules* **1998**, *31*, 2447. (c) Yu, C. J.; Chong, Y.; Kayyem, J. F.; Gozin, M. *J. Org. Chem.* **1999**, *64*, 2070. (d) Kukula, H.; Veit, S.; Godt, A. *Eur. J. Org. Chem.* **1999**, *277*, 7. (e) Huang, S.; Tour, J. M. *Tetrahedron Lett.* **1999**, *40*, 3347.

(6) (a) Xu, Z.; Moore, J. S. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 246. (b) Xu, Z.; Moore, J. S. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1354. (c) Bharathi, P.; Patel, U.; Kawaguchi, T.; Pesak, D. J.; Moore, J. S. *J. Am. Chem. Soc.* **1995**, *28*, 5955.

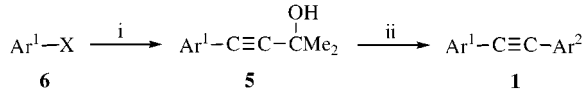
(7) (a) Hay, A. S. *J. Org. Chem.* **1960**, *25*, 1275. (b) Hay, A. S. *J. Org. Chem.* **1962**, *27*, 3320. (c) Siemsen, P.; Livingston, R. C.; Diederich, F. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 2633.

(8) Wagner, R. W.; Johnson, T. E.; Li, F.; Lindsey, J. S. *J. Org. Chem.* **1995**, *60*, 5266.

(9) For earlier examples of Sonogashira coupling reactions using in situ generation of terminal acetylenes, see: (a) Haley, M. M.; Bell, M. L.; English, J. J.; Johnson, C. A.; Weakley, T. J. R. *J. Am. Chem. Soc.* **1997**, *119*, 2956. (b) Schultz, D. A.; Gwaltney, K. P.; Lee, H. *J. Org. Chem.* **1998**, *63*, 4034 and references therein.

10.1021/jo001538q CCC: $20.00
Published on Web 02/02/2001

Scheme 1[a]



[a] Reagents: (i) 2-methylbut-3-yn-2-ol, $PdCl_2(PPh_3)_2$, CuI, *i*-Pr_2NH; (ii) Ar^2-X **3**, $PdCl_2(PPh_3)_2$, CuI, NaOH, H_2O, toluene, Bu_4NI.

halide **3** may be realized in a two-phase heterogeneous system[11] in the presence of a phase transfer agent and an aqueous base, conditions under which the acetylene alcohol **5** is known to transform into the arylethyne **2**.

To evaluate the scope of the phase transfer Sonogashira reaction (hereafter called PT method), we decided to conduct a comparative study between this method and the one reported originally by Sonogashira (original method). Our procedure involved the reaction of the acetylenic alcohol **5** and an aryl bromide **7** in the presence of $PdCl_2(PPh_3)_2$, CuI, and Bu_4NI in a heterogeneous mixture of toluene and aqueous NaOH under nitrogen at 80 °C for 24 h. Similar conditions had previously been applied to the synthesis of 1,3-enynes by reacting 1-alkynes with alkenyl halides.[12] For the original method, the arylethyne **2** and the aryl bromide **7** were directly reacted in the presence of $PdCl_2(PPh_3)_2$, CuI, and triethylamine in toluene at 80 °C for 24 h. To further assess the effectiveness of the coupling reaction, the amount of arylethyne **2** or acetylenic alcohol **5** used was restricted to 1.0 mol equiv per bromine atom with respect to the aryl bromide **7**.

The results of the two coupling methods were tabulated in Table 1. Several interesting findings were noted. First, the yields of the cross-coupling product **1** obtained by the PT method were consistently better than those obtained by the original method (entries A vs B, 1−10). In general, the product yield was at least 23% higher by using the PT method. Second, the Hay reaction leading to the homo-coupling product **4** was a prominent side reaction (>20%) under the original Sonogashira conditions. For example, the ratios of the cross-coupling **1** to homo-coupling product **4** were found to vary from 2.3/1 to 4.6/1 for reactions between phenylethyne and the various aryl monobromides (entries 1A−4A). For the coupling reactions between aryl (4-nitrophenyl)ethyne and the monobromides (entries 5A−6A), the reaction was very dirty and only a complex mixture of unidentifiable compounds was formed. In sharp contrast, the PT reaction protocol smoothly converted a 1:1 molar ratio mixture of the acetylenic alcohol **5** and the aryl bromide **7** to the cross-coupling product **3** in fair to excellent yields (51−92%). More importantly, the ratios of the cross- to homo-coupling product (9/1 to 70/1) were much higher, thus demonstrating the better selectivity of the our method.

An additional feature that was not apparently noticed from the table was that sometimes it was difficult to isolate the cross-coupling product **1** in good purity. This was due to the similar polarities of the homo-coupling byproduct, cross-coupling product, and unreacted aryl bromide, which rendered their separation by column chromatography a difficult task. For example, coupling of phenylethyne and 1-bromonaphthalene (entry 1A) afforded a nearly inseparable mixture of 1-(phenylethynyl)naphthalene **1a** and 1,4-diphenylbutadiyne **4a**, and their product ratio was determined by HPLC analysis. A similar separation problem was also encountered in the coupling reaction between phenylethyne **2a** and 4-bromobenzophenone **7d** (entry 4A). Due to the higher extent of homo-coupling side reaction in the original method, and hence a larger amount of unreacted aryl bromide left in the reaction mixture, product isolation in the original method was particularly difficult. In sharp contrast, because of a better selectivity toward the formation of the cross-coupling product under the PT conditions, the arylethynes **1** obtained were very clean and had little contamination.

To further examine the versatility of the PT coupling conditions, we then compared the two methods toward the preparation of oligomeric and branched (aryleneethynylene)s. 1,4-Dibromobenzene **7f**, 4,4′-dibromobiphenyl **7g**, and bis-(4-bromophenyl)ethyne **7h** were selected as the aryl dibromides and then coupled to phenylethyne (entries 7−9). In principle, a mixture of two cross-coupling products, namely the monoadduct and the bis-adduct, could result. In all three cases studied, the yield of the bis-adduct **1g**−**i** was very poor (<20%) under the original Sonogashira conditions, while the monoadduct as well as the Hay homo-coupling product were formed in significant quantities. On the other hand, the yields of the bis-adduct **1g**−**i** were very high (67−95%) under the PT conditions, and there was no product contamination by 1,4-diphenylbutadiyne. Furthermore, no monoadduct could be detected, and hence this new method was extremely efficient in promoting multiple cross-coupling reactions.

Finally, phenylethyne was coupled to 1,3,5-tribromobenzene **7i** to furnish the G0-dendrimer **1j**. Under the original conditions, a mixture of mono-, bis-, and tris-coupling adducts was formed, and the desired dendrimer **1j** could only be obtained in 22% yield. The homocoupling product **4a** was also found but was not separable from the mono- and bis-coupling products. On the other hand, the dendrimer **1j** could be obtained cleanly in 57% yield under the PT conditions. Again no mono- and bis-adducts were found.

As described earlier, the improved ratio of diarylethyne **1** to butadiyne **4** may be due to the reduced concentration of terminal ethyne **2** under the PT conditions. However, it is also likely that the improvement could be the result of a reduced rate of the oxidative homo-coupling. It has been documented that the rate of Hay coupling depends on the solvent medium and the solubility of the catalyst.[7c] The absence of any tertiary amines in aqueous medium may render the copper species less soluble which resulted in a retardation of the homo-coupling reaction. We are currently looking into this issue.

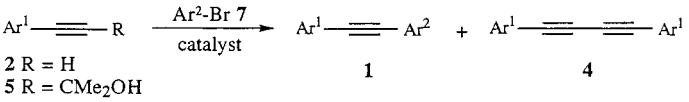
In summary, we disclosed here a highly selective method for the construction of diarylethynes and their oligomeric and branched analogues by a modified Sonogashira reaction under PT conditions. In contrast to the original Sonogashira method, very little Hay homo-coupling product was formed under the new reaction protocol. This method also alleviates the need to use excess arylethyne to promote the cross-coupling efficiency. Furthermore, under the new reaction conditions, the cross-coupling products were less likely contaminated

(10) Nguyen, P.; Todd, S.; van den Biggelaar, D.; Taylor, N. J.; Marder, T. B.; Wittmann, F.; Friend, R. H. *Synlett* **1994**, 299.

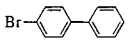
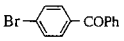
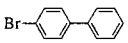
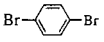
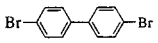
(11) For a review on palladium-catalyzed cross coupling reactions under aqueous conditions, see: Genet, J. P.; Savignac, M. *J. Organomet. Chem*. **1999**, *576*, 305.

(12) Rossi, R.; Carpita, A.; Quirici, M. G.; Gaudenzi, M. L. *Tetrahedron* **1982**, *38*, 631.

Table 1. Cross-Coupling Reactions between Arylethynes and Aryl Bromides



Original method (entries A): $PdCl_2(PPh_3)_2$ (10 mol %), CuI (10 mol %), NEt_3, toluene, 80 °C
PT method (entries B): $PdCl_2(PPh_3)_2$ (10 mol %), CuI (10 mol %), 5 M aq. NaOH (3 eq.), Bu_4NI (10 mol %), toluene, 80 °C

Entry	Arylethyne **2** / acetylenic alcohol **5**	Aryl bromide **7**	Diarylethyne **1** (% yield)	Diarylethyne **1**/ butadiyne **4**
1A	**2a** Ar^1 = Ph	**7a:** 	**1a** (45%)	2.3 / 1
1B	**5a** Ar^1 = Ph	**7a**	**1a** (83%)	9 / 1
2A	**2a** Ar^1 = Ph	**7b:** 	**1b** (50%)	2.3 / 1
2B	**5a** Ar^1 = Ph	**7b**	**1b** (89%)	70 / 1
3A	**2a** Ar^1 = Ph	**7c:** 	**1c** (53%)	2.3 / 1
3B	**5a** Ar^1 = Ph	**7c**	**1c** (84%)	12 / 1
4A	**2a** Ar^1 = Ph	**7d:** 	**1d** (69%)	4.6 / 1
4B	**5a** Ar^1 = Ph	**7d**	**1d** (92%)	28 / 1
5A	**2b** Ar^1 = *p*-$NO_2C_6H_4$	**7c:** 	**1e** (–)[a]	(–)
5B	**5b** Ar^1 = *p*-$NO_2C_6H_4$	**7c**	**1e** (51%)	(–)[b]
6A	**2b** Ar^1 = *p*-$NO_2C_6H_4$	**7e:** 	**1f** (–)[a]	(–)
6B	**5b** Ar^1 = *p*-$NO_2C_6H_4$	**7e**	**1f** (57%)	(–)[b]
7A	**2a** Ar^1 = Ph	**7f:** 	**1g** (6%)[c]	1 / 5.5
7B	**5a** Ar^1 = Ph	**7f**	**1g** (78%)[d]	5.4 / 1
8A	**2a** Ar^1 = Ph	**7g:** 	**1h** (20)[e]	6 / 1
8B	**5a** Ar^1 = Ph	**7g**	**1h** (95%)[d]	30 / 1
9A	**2a** Ar^1 = Ph	**7h:** 	**1i** (–)[a]	(–)
9B	**5a** Ar^1 = Ph	**7h**	**1i** (67%)[d]	4.8 / 1
10A	**2a** Ar^1 = Ph	**7i:** 	**1j** (22%)[f]	(–)[g]
10B	**5a** Ar^1 = Ph	**7i**	**1j** (57%)[f]	4.4 / 1

[a] No isolable product. [b] No detectable butadiyne. [c] Yield of bis-coupling product. Yield of mono-coupling product was 12%. [d] Yield of bis-coupling product. No mono-coupling product was isolated. [e] Yield of bis-coupling product. Yield of mono-coupling product **8** was 14%. [f] Yield of tris-coupling product. [g] The homo-coupling product could not be separated from the mono- and bis-coupling products.

with residual starting materials and the various side products and could be obtained in good yields and purity. The method was also useful for promoting multiple Sonogashira reactions toward the construction of structurally homogeneous oligo- and branched (aryleneethynylene)s.

Experimental Section

General. All reactions were conducted under a nitrogen atmosphere. Melting points were taken on a hot-plate microscope apparatus and were uncorrected. ^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra (in $CDCl_3$) were acquired on a Brüker Advance DPX NMR spectrometer. Mass spectra were obtained on a Hewlett-Packard 5989B mass spectrometer using electron ionization (EI) technique. Elemental analyses were carried out at MEDAC, Ltd., Brunel Science Center, Surrey, United Kingdom. (4-Nitrophenyl)ethyne **2b**,[10] 2-hydroxy-2-methyl-4-phenylbut-3-yne **5a**,[10] 2-hydroxy-2-methyl-4-(4-nitrophenyl)but-3-yne **5b**,[10] and bis-(4-bromophenyl)ethyne **7h**[13] were prepared according to literature methods. All other aryl bromides, aryl dibromides, and 1,3,5-tribromobenzene were purchased from Aldrich and used without purifications.

General Procedure for the Sonogashira Coupling Between Arylethyne 2 and Aryl Bromide 7 (Original Method). A degassed mixture of aryl bromide **7** (3.0 mmol), arylethyne **2** (3.0 mmol per bromine atom), copper(I) iodide (0.3 mmol), palladium(II) dichlorobistriphenylphosphine (0.3 mmol), and triethylamine (4.0 mL) in dry toluene (5.0 mL) was placed in a sealed tube under nitrogen. The mixture was heated at 80 °C for 24 h and then cooled to room temperature. The solution was filtered through a pad of silica gel, and the filtrate was concentrated under reduced pressure. The residue was chromatographed on silica gel, eluting with the appropriate solvent system (see below for details) to give the homo-coupling products **4** and cross-coupling products **1**. Their ratios were determined either by direct weighting of the products obtained after chro-

(13) Harrison, R. M.; Brotin, T.; Noll, B. C.; Michl, J. *Organometallics* **1997**, *16*, 3401.

matography or by HPLC method. In the case of inseparable product mixtures, product ratios were calculated by ^{1}H NMR method.

General Procedure for the Sonogashira Coupling Between Acetylenic Alcohol 5 and Aryl Bromide 7 Under Phase Transfer Conditions (PT Method). A degassed mixture of aryl bromide (3.0 mmol), acetylenic alcohol **5** (3.0 mmol per bromine atom), copper(I) iodide (0.3 mmol), palladium(II) dichlorobistriphenylphosphine (0.3 mmol), and tetrabutylammonium iodide (0.3 mmol) in a heterogeneous mixture of toluene (5.0 mL) and aqueous sodium hydroxide (5 M, 2.0 mL) was placed in a sealed tube under nitrogen. The mixture was heated at 80 °C for 24 h and then cooled to room temperature. The solution was filtered over a pad of silica gel, and the filtrate was concentrated under reduced pressure. The residue was chromatographed on silica gel, eluting with the appropriate solvent to give the various products.

1,4-Diphenyl-1,3-butadiyne (4a).[14] Eluent, hexane; white solid; mp 85−86 °C (lit.[14] 85−86 °C); ^{1}H NMR δ 7.26−7.35 (m, 6 H), 7.45−7.50 (m, 4 H); ^{13}C NMR δ 73.9, 81.6, 121.8, 128.5, 129.2, 132.5; MS (EI, *m*/*z*) 202 (M^+, 20).

1-(Phenylethynyl)naphthalene (1a).[15] Eluent, hexane; colorless oil; ^{1}H NMR δ 7.35−7.70 (m, 8 H), 7.78 (d, 1 H, J = 8 Hz), 7.89 (t, 2 H, J = 8 Hz), 8.46 (d, 1 H, J = 8 Hz); MS (EI, *m*/*z*) 228 (M^+, 17).

3-Nitro-1-(phenylethynyl)benzene (1b).[16] Eluent, hexane/EtOAc = 20/1; yellow solid; mp 68−70 °C (lit.[16] 56−57 °C); ^{1}H NMR δ 7.24−7.30 (m, 3 H), 7.40 (t, 1 H, J = 8 Hz), 7.40−7.47 (m, 2 H), 7.70 (d, 1 H, J = 8 Hz), 8.05 (d, 1 H, J = 8 Hz), 8.25 (s, 1 H); ^{13}C NMR δ 86.8, 91.9, 122.1, 122.8, 125.1, 126.3, 128.5, 129.0, 129.3, 131.7, 137.2, 148.1; MS (EI, *m*/*z*) 223 (M^+, 100).

4-(Phenylethynyl)-1,1′-biphenyl (1c).[17] Eluent, hexane; white solid; mp 162−163 °C (lit.[17] 165−167 °C); ^{1}H NMR δ 7.31−7.38 (m, 3 H), 7.49 (t, 2 H, J = 7 Hz), 7.54−7.65 (m, 8 H); ^{13}C NMR δ 89.3, 90.0, 122.1, 123.3, 127.0, 127.6, 128.2, 128.3, 128.8, 131.6, 132.0, 140.3, 140.9; MS (EI, *m*/*z*) 254 (M^+, 18).

4-(Phenylethynyl)benzophenone (1d).[18] Eluent, hexane/EtOAc = 10/1; yellow solid; mp 109−111 °C; ^{1}H NMR δ 7.35−7.40 (m, 3 H), 7.45−7.65 (m, 7 H), 7.78−7.84 (m, 4 H); ^{13}C NMR δ 88.7, 92.5, 122.7, 127.6, 128.4, 128.5, 128.8, 130.0, 130.1, 131.4, 131.8, 132.6, 136.7, 137.4, 196.0; MS (EI, *m*/*z*) 282 (M^+, 12).

4-[(4-Nitrophenyl)ethynyl]-1,1′-biphenyl (1e). Eluent, hexane/EtOAc = 4/1; yellow solid; mp 184−185 °C; ^{1}H NMR δ 7.27−7.42 (m, 3 H), 7.50−7.56 (m, 2 H), 7.56 (s, 4 H), 7.61 (t, 2 H, J = 8 Hz), 8.15 (t, 2 H, J = 8 Hz); ^{13}C NMR δ 88.2, 94.7, 120.9, 123.7, 127.0, 127.2, 127.9, 128.9, 130.3, 132.2, 132.3, 140.0, 142.0, 146.9; MS (EI, *m*/*z*) 299 (M^+, 100). Anal. Calcd for $C_{20}H_{13}NO_2$: C, 80.25; H, 4.38; N, 4.68. Found: C, 79.69; H, 4.77; N, 4.54.

1-Nitro-4-(phenylethynyl)benzene (1f).[15] Eluent, hexane/EtOAc = 8/1; yellow solid; mp 111−113 °C (lit.[15] 118−120 °C); ^{1}H NMR δ 7.35−7.45 (m, 3 H), 7.50−7.58 (m, 2 H), 7.66 (t, 2 H, J = 8 Hz), 8.22 (t, 2 H, J = 8 Hz); ^{13}C NMR δ 87.5, 94.7, 122.0, 123.6, 128.5, 129.2, 130.2, 131.8, 132.2, 146.9; MS (EI, *m*/*z*) 223 (M^+, 100).

1,4-Di(phenylethynyl)benzene (1g).[19] Eluent, hexane; white solid; mp 178−180 °C (lit.[19] 180−181 °C); ^{1}H NMR δ 7.30−7.40 (m, 6 H), 7.45−7.60 (m, 4 H), 7.52 (s, 4 H); ^{13}C NMR δ 89.1, 91.2, 123.0, 123.1, 128.4, 128.45, 131.5, 131.6; MS (EI, *m*/*z*) 278 (M^+, 100).

4(4′-Bromophenyl)tolan (8).[20] (See footnote *e* in Table 1.) Eluent, hexane; pale yellow solid; mp 196−200 °C (dec); ^{1}H NMR δ 7.32−7.40 (m, 4 H), 7.47 (d, 2 H, J = 9 Hz), 7.51−7.63 (m, 8 H); MS (EI, *m*/*z*) 332/334 (M^+, 35).

4,4′-Bis(phenylethynyl)biphenyl (1h).[21] Eluent, hexane; pale yellow solid; mp 250−251 °C (dec) (lit.[21] 252−254 °C); ^{1}H NMR δ 7.33−7.40 (m, 6 H), 7.53−7.59 (m, 4 H), 7.61 (s, 8 H); MS (EI, *m*/*z*) 354 (M^+, 7).

4,4′-Bis(phenylethynyl)diphenylethyne (1i). Eluent, hexane; pale yellow solid; mp 259−260 °C (dec); ^{1}H NMR δ 7.31−7.40 (m, 6 H), 7.48−7.60 (m, 4 H), 7.52 (s, 8 H); MS (EI, *m*/*z*) 378 (M^+, 32); HRMS (EI) 378.1386 ($C_{30}H_{18}$ requires 378.1408).

1,3,5-Tris(phenylethynyl)benzene (1j).[22] Eluent, hexane; white solid; mp 141−142 °C (lit.[22] 144−145 °C); ^{1}H NMR δ 7.32−7.40 (m, 9 H), 7.50−7.58 (m, 6 H), 7.66 (s, 3 H); ^{13}C NMR δ 87.8, 90.5, 122.7, 124.0, 128.4, 128.6, 131.6, 134.0; MS (EI, *m*/*z*) 378 (M^+, 100).

Acknowledgment. We thank the Research Grants Council, HKSAR, for the financial support (CUHK4203/97P).

JO001538Q

(14) Crisp, G. T.; Flynn, B. L. *J. Org. Chem.* **1993**, *58*, 6614.
(15) Okuro, K.; Furuune, M.; Enna, M.; Miura, M.; Nomura, M. *J. Org. Chem.* **1993**, *58*, 4716.
(16) Colvin, E. W.; Hamill, B. J. *J. Chem. Soc., Perkin Trans. 1* **1977**, 869.
(17) Uno, H.; Sakamoto, K.; Suzuki, H. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 218.
(18) Fürstner, A.; Seidel, G. *Tetrahedron* **1995**, *51*, 11165.
(19) Nguyen, P.; Yuan, Z.; Agocs, L.; Lesley, G.; Marder, T. B. *Inorg. Chim. Acta* **1994**, *220*, 289.
(20) Kübel, C.; Chen, S.-L.; Müllen, K. *Macromolecules* **1998**, *31*, 6014.
(21) Aitken, R. A.; Drysdale, M. J.; Hill, L.; Lumbard, K. W.; MacCallum, J. R.; Seth, S. *Tetrahedron* **1999**, *55*, 11039.
(22) Jones, K. M.; Keller, T. M. *Polymer* **1995**, *36*, 187.