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Iterative Approach to Oligo(arylenevinylene)s Containing Tetrasubstituted Vinylene Units

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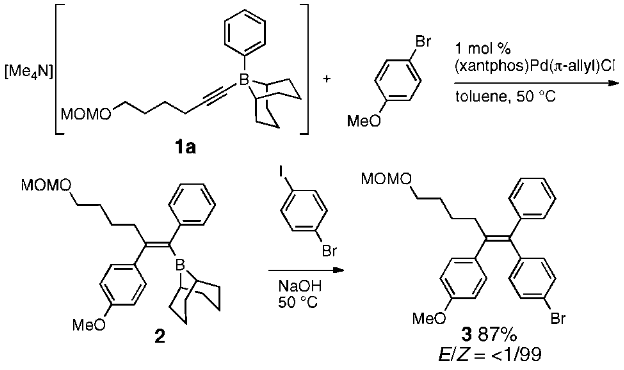
ABSTRACT

Monodispersed oligo(arylenevinylene)s containing tetrasubstituted vinylene units were stereoselectively synthesized in an efficient manner by iteration of two different kinds of palladium-catalyzed reactions.

A current topic in organic synthesis is the preparation of structurally well-defined oligomeric compounds of higher molecular weight. Among various oligomers, oligo(phenylenevinylene)s (OPVs) are of significant interest and have been extensively studied in the field of organic electronics.[1] A wide variety of substituted OPVs have been synthesized and applied to optoelectronic devices such as organic light-emitting diodes[2] and organic solar cells.[3] However, it is still a formidable task to synthesize oligo(arylenevinylene)s containing tetrasubstituted vinylene units due to the difficulty of constructing sterically congested vinylene units in a stereoselective manner.[4] In this paper, we report an efficient and high-yielding method to synthesize such oligo(arylenevinylene)s of single molecular weight.

Initially, 4-bromoanisole was treated with 1.0 equiv of alkynylborate **1a** in the presence of (xantphos)Pd(π-allyl)Cl (1 mol %), and (trisubstituted alkenyl)-9-BBN **2** was formed in a stereoselective manner, as we previously reported (Scheme 1).[5] Although the product **2** contained an alk-

Scheme 1. One-Pot Synthesis of Tetrasubstituted Olefin



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(1) For reviews, see: (a) Tour, J. M. *Chem. Rev.* **1996**, *96*, 537. (b) Martin, R. E.; Diederich, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 1350. (c) Scherf, U. *Top. Curr. Chem.* **1999**, *201*, 163.

(2) (a) Burroughs, J. H.; Bradley, D. D.; Brown, A. R.; Marks, R. N.; Mackey, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539. (b) Grimsdale, A. G.; Chan, K. L.; Martin, R. M.; Jokisz, P. G.; Holmes, A. B. *Chem. Rev.* **2009**, *109*, 897.

(3) (a) Yu, G.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. *Science* **1995**, *270*, 1789. (b) Segura, J. L.; Martin, N.; Guldi, D. M. *Chem. Soc. Rev.* **2005**, *34*, 31. (c) Günes, S.; Neugebauer, H.; Sariciftci, N. S. *Chem. Rev.* **2007**, *107*, 1324. (d) Cheng, Y.-J.; Yang, S.-H.; Hsu, C.-S. *Chem. Rev.* **2009**, *109*, 5868.

(4) Flynn, A. B.; Ogilvie, W. W. *Chem. Rev.* **2007**, *107*, 4698, and references therein.

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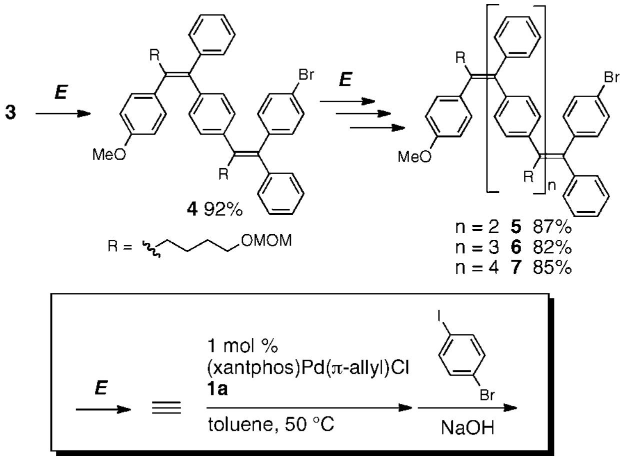
enylborane moiety, it did not couple with 4-bromoanisole in the absence of a base. After completion of the initial reaction with alkynylborate **1a**, 1.0 equiv of 4-bromoiodobenzene and 3 equiv of NaOH were directly added to the reaction mixture. The Suzuki−Miyaura coupling reaction took place chemoselectively at the iodo site to give tetrasubstituted olefin **3** in 87% yield with excellent stereoselectivity (E/Z = <1/99). The bromoaryl moiety was retained in the coupling product **3** due to the reactivity difference between the iodo and bromo groups.[6] Thus, the Pd/XANTPHOS catalyst was proven to be active enough to promote the two different kinds of carbon−carbon bond-forming reactions in one-pot without the need for any additional catalyst or ligand. Through this sequential one-pot procedure, the initial aryl bromide (i.e., 4-bromoanisole) grew into the second-generation aryl bromide **3**, which is expected to be directly used in the reaction with the borate **1a** again without intervention of any activation or deprotection step.

Next, aryl bromide **3** was subjected to the second-round sequential one-pot procedure. Treatment of **3** with alkynylborate **1a** (1.1 equiv) followed by direct addition of 4-bromoiodobenzene (1.1 equiv) and NaOH to the reaction mixture afforded the third-generation aryl bromide **4** in 92% yield (Scheme 2). Further application of the third-round sequential procedure to **4** furnished the fourth-generation aryl bromide **5** in 87% yield. The sequential procedure was repeated on **5** once to give the fifth-generation **6** in 82% yield and twice to give the sixth-generation **7** in 85% yield. These oligomers were readily soluble in common organic solvents like toluene, THF, AcOEt, and chloroform and, therefore, were isolated with high purity by column chromatography on silica gel and identified by ^{1}H and ^{13}C NMR and mass spectroscopy. Importantly, the yield of each round did not decrease as the molecular size increased, suggesting that further elongation by the iterative method would be possible. Thus, one (tetrasubstituted vinylene)phenylene unit could be added to the chain in a stepwise manner with high efficiency and stereoselectivity by repetition of the sequential one-pot procedure.

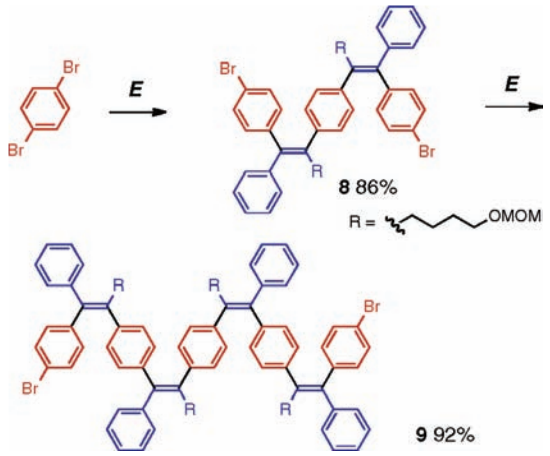
Scheme 2. Repetition of the Sequential Procedure



Monodispersed oligomers can be divergently synthesized by repeating an iterative procedure which generally consists of an extension step and an activation step.[1,7] An extending unit possessing a dormant coupling site is initially added to a main chain (an extension step). The dormant site is then activated to be subsequently coupled with another extending unit (an activation step). On the contrary, the present method to synthesize OPVs dispenses with the need for activation.[8] One cycle that adds a vinylenephenylene unit consists of two different extension steps, one extending a tetrasubstituted vinylene unit and the other extending a phenylene unit. Both extension steps can be executed by the same catalyst system in one-pot. Thus, this simple method makes it practical to synthesize a structurally well-defined oligomer of single molecular weight in an efficient way.

A phenylenevinylene chain could be extended into two directions by using 1,4-dibromobenzene as the starting aryl bromide (Scheme 3). 1,4-Dibromobenzene was reacted with the alkynylborates **1a** (2.1 equiv) under the standard conditions, and the subsequent double cross-coupling reaction with 4-bromoiodobenzene (2.2 equiv) furnished the dibromide **8** in 86% yield. The dibromide **8** was then reacted with the alkynylborate **1a** (3.0 equiv) to afford diborylated phenylenevinylene intermediate, which was treated with 4-bromoiodobenzene (4.0 equiv) and NaOH, resulting in the formation of OPV **9** in 92% yield. Interestingly, OPV **9**

Scheme 3. Extension into Two Directions



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(5) Ishida, N.; Shimamoto, Y.; Murakami, M. *Org. Lett.* **2009**, *11*, 5434.

(6) Unrau,; C, M.; Campbell, M. G.; Snieckus, V. *Tetrahedron Lett.* **1992**, *33*, 2773.

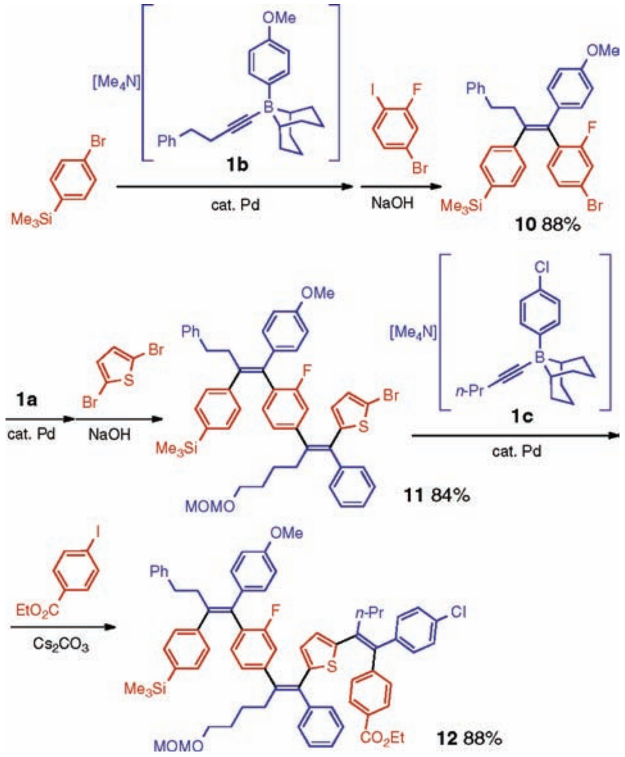
(7) For iterative synthesis of OPVs by an extension/activation sequence, see: (a) Schenk, R.; Gregorius, H.; Meerholz, K.; Heinze, J.; Müllen, K. *J. Am. Chem. Soc.* **1991**, *113*, 2634. (b) Xue, C.; Luo, F.-T. *J. Org. Chem.* **2003**, *68*, 4417. (c) Iwadate, N.; Suginome, M. *Org. Lett.* **2009**, *11*, 1899.

(8) For activation-free iterative synthesis of OPVs by two different extension steps, see: (a) Maddux, T.; Li, W.; Yu, L. *J. Am. Chem. Soc.* **1997**, *119*, 844. (b) Itami, K.; Tonogaki, K.; Nokami, T.; Ohashi, Y.; Yoshida, J. *Angew. Chem., Int. Ed.* **2006**, *45*, 2404.

exhibited visible blue fluorescence in solution, whereas OPVs **4**−**7** did not. Thus, even a small structural change of the OPVs may cause a significant influence on their photophysical properties.

Finally, the functional group compatibility of the palladium-catalyzed sequential procedure was exploited to synthesize the structurally diversified oligo(arylenevinylene) **12** (Scheme 4). 4-Bromotrimethylsilylbenzene was reacted with 1.0 equiv of the alkynylborate **1b** having a 4-methoxyphenyl group on boron, and the reaction mixture was then treated with 1.0 equiv of 4-bromo-2-fluoroiodobenzene to give **10** in 88% yield. The second-round extension was carried out using the alkynylborate **1a** (1.1 equiv) followed by 2,5-dibromothiophene (3.0 equiv) and NaOH. The bi(arylenevinylene) **11** possessing five different aryl groups and two alkyl groups was obtained in 84% yield. Furthermore, **11** was subjected to the third-round extension using 1.1 equiv of the alkynylborate **1c** with a 4-chlorophenyl group on boron and then 1.1 equiv of 4-(ethoxycarbonyl)iodobenzene to give the ter(arylenevinylene) **12** in 88% yield. The structure of **12** is highly diversified, consisting of seven different aryl groups and three alkyl groups. Thus, a wide variety of structural modifications could be installed at the desired positions by changing the arylene and vinylene modules.

Scheme 4. Synthesis of Oligo(arylenevinylene) **12**



In conclusion, we have developed an efficient iterative method for the synthesis of oligo(arylenevinylene)s containing tetrasubstituted vinylene units. Of note is that an aryl bromide grew into the next-generation aryl bromide in one-pot through two different kinds of extending steps. The method dispenses with the need of activation steps and, thus, rapidly increases the molecular complexity. Synthesis of new OPVs and studies on structural features and photophysical properties are now in progress.

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Supporting Information Available: Experimental details and spectral data for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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