doi:10.1246/cl.2011.300

Convenient Synthesis of Dibenzo[*a*,*h*]anthracenes and Picenes via C–H Arylation of Acetophenones with Arenediboronates

Kentaroh Kitazawa,[1] Takuya Kochi,[1] Masashi Nitani,[2] Yutaka Ie,[2] Yoshio Aso,[2] and Fumitoshi Kakiuchi*[1]
[1]*Department of Chemistry, Faculty of Science and Technology, Keio University,*
3-14-1 Hiyoshi, Kohoku-ku, Yokohama, Kanagawa 223-8522
[2]*The Institute of Scientific and Industrial Research (ISIR), Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047*

(Received January 11, 2011; CL-110023; E-mail: kakiuchi@chem.keio.ac.jp)

A new convenient method for the synthesis of dibenzo[*a*,*h*]anthracenes and picenes using ruthenium-catalyzed regioselective C–H arylation of aromatic ketones has been developed. Acetophenone derivatives and 1,4-benzenediboronates were coupled in 2:1 ratios to form *p*-terphenyl derivatives. Conversion of the acetyl group to an ethynyl group, followed by cycloaromatization provided the desired fused aromatic compounds. An organic field-effect transistor fabricated from one of these products gave moderate hole mobility.

Fused aromatic compounds have recently received much attention due to their potential utility for organic optical and electronic materials.[1] For example, linear acenes and their derivatives such as pentacene[2] and rubrene[3] are promising candidates for organic field-effect transistors (OFETs). Development of methods to prepare various derivatives of desired fused aromatic compounds is of great interest because derivatization of the fused aromatic compounds may adjust their optical and electronic properties as well as their solubility and packing structures in the crystals.[4] In this context, our group has initiated efforts toward short syntheses of multisubstituted fused aromatic compounds using our ruthenium-catalyzed C–H arylation[5] of aromatic ketones with arylboronates. This reaction not only provides convenient ways to form a biaryl framework but is also useful for further manipulation because the directing group (the carbonyl group) can be easily transformed into other classes of functional groups. Recently, we succeeded in two- and three-step syntheses of tetra- and hexaarylanthracenes from anthraquinone, taking advantage of the C–H arylation method.[6]

Dibenzo[*a*,*h*]anthracenes[7] and picenes[8] are two classes of fused aromatic compounds which have recently shown some promise as OFET materials. However, only limited strategies have been reported for the syntheses of these compounds,[9–12] and convenient methods for the syntheses of various derivatives are still desired. We envisioned that the use of our ruthenium-catalyzed C–H arylation would lead to a new method for efficient synthesis of these compounds (Figure 1). First, acetophenone derivatives may be coupled with arenediboronates to give teraryl derivatives using our C–H arylation method (step a).[5] The acetyl directing group may then be transformed into an ethynyl group (step b).[13] Finally, cycloaromatization of the 2-ethynylbiphenyl structures would provide the desired fused aromatic compounds (step c).[14] The cyclization of 2-ethynylbiphenyls is a practical way to construct phenanthrene ring systems and has been used in various syntheses of dibenzo[*a*,*h*]anthracenes. For example, Swager and co-workers developed a three-step strategy to construct the dibenzo[*a*,*h*]anthracene cores using a Hagihara–Sonogashira/Suzuki–Miyaura/cyclization sequence, starting from 1,4-dibromo-2,5-diiodobenzene.[9] This method has provided convergent routes to a variety of dibenzo[*a*,*h*]anthracene derivatives,[10] but the position of the substituents at the terminal rings are directed by the substituents themselves in the cyclization step. Therefore, it may be difficult to introduce substituents selectively at the 2-, 4-, 9-, or 11-positions. Introduction of substituents at the central rings may also be difficult using this method.

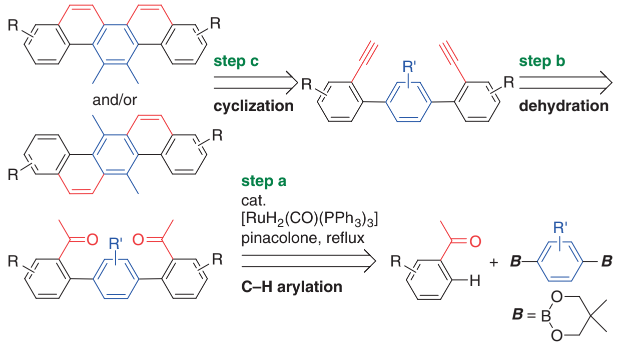


Figure 1. Retrosynthesis of dibenzo[*a*,*h*]anthracene and picene derivatives.

Herein, we report an efficient synthesis of dibenzo[*a*,*h*]anthracene and picene derivatives via our ruthenium-catalyzed C–H arylation method. First, it was found that the C–H arylation can be applied to the 2:1 coupling of acetophenones with arenediboronates to form teraryl structures. The teraryl products were converted to dibenzo[*a*,*h*]anthracenes and picene derivatives in two steps. The OFET properties of the fused aromatic compounds obtained were also studied.

Initially, we examined the synthesis of fused aromatic systems using 2′-methylacetophenone (**1a**) with a 1,4-benzenediboronate, 2,2′-(1,4-phenylene)bis(5,5-dimethyl-1,3,2-dioxaborinane) (**2a**). The ruthenium-catalyzed C–H arylation and dehydration with LDA and (EtO)$_2$P(O)Cl using Negishi's protocol[13] afforded the corresponding diethynylterphenyl derivative in good yield,[15] but step c did not proceed selectively and gave an inseparable mixture of dibenzo[*a*,*h*]anthracene and picene derivatives.

The regioselectivity of the electrophilic intramolecular cycloaromatization was controlled by placing substituents at appropriate positions on arenediboronates or using a thiophene derivative. The arenediboronates used for the selective synthesis of the fused aromatic compounds are listed in Figure 2, as well as acetophenones coupled with the diboronates.

First, we explored the synthesis of dibenzo[*a*,*h*]anthracene derivatives using diboronate **2b** (Table 1). This diboronate

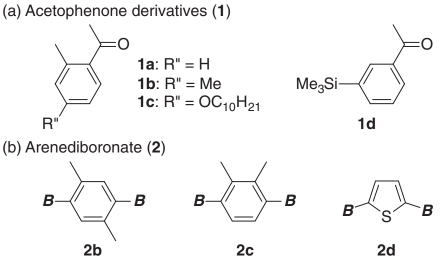
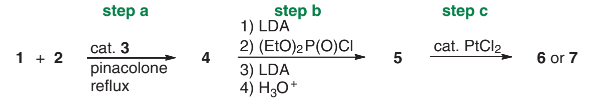
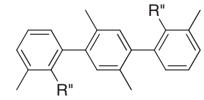
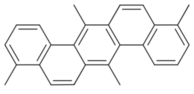
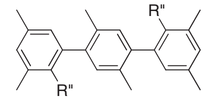
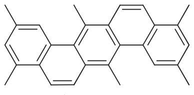
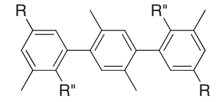
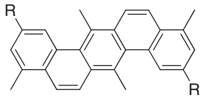
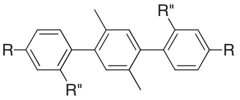
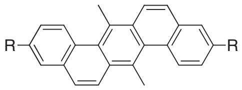
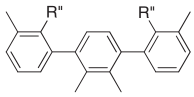
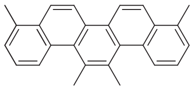
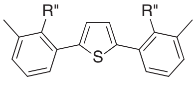
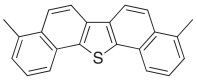
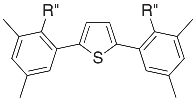
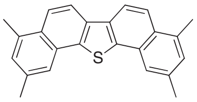
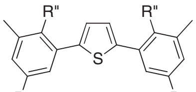
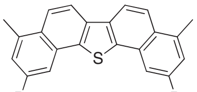


Figure 2. (a) Acetophenones and (b) arenediboronates used for the synthesis of fused aromatic systems.

Table 1. Three-step syntheses of dibenzo[*a*,*h*]anthracene **6** and picene **7**[a]



Entry	1	2	**4** (R'' = Ac); **5** (R'' = C≡CH),	Fused aromatic compounds **6**, **7**
1	**1a**	**2b**	 **4ab**, 41%;[b] **5ab**, 69%	 **6ab**, 36%
2	**1b**	**2b**	 **4bb**, 43%; **5bb**, 76%	 **6bb**, 38%
3	**1c**	**2b**	 R = $OC_{10}H_{21}$ **4cb**, 69%; **5cb**, 55%	 R = $OC_{10}H_{21}$ **6cb**, 26%
4	**1d**	**2b**	 R = Me_3Si **4db**, 55%;[c] **5db**, 78%	 R = Me_3Si **6db**, 3%
5	**1a**	**2c**	 **4ac**, 14%;[d] **5ac**, 42%	 **7ac**, 51%
6	**1a**	**2d**	 **4ad**, 38%; **5ad**, 61%	 **7ad**, 73%[e]
7	**1b**	**2d**	 **4bd**, 38%; **5bd**, 44%	 **7bd**, 67%
8	**1c**	**2d**	 R = $OC_{10}H_{21}$ **4cd**, 51%; **5cd**, 58%	 R = $OC_{10}H_{21}$ **7cd**, 67%

[a] Conditions: (step a) **1** (4 mmol), **2** (2 mmol), **3** (0.4 mmol), pinacolone (4 mL), reflux, 24 h; (step b) LDA (2.1 equiv), THF, −78 °C to reflux; $(EtO)_2P(O)Cl$ (2.1 equiv), −78 °C to rt; LDA (4.5 equiv), −78 °C to rt; 1 M HCl aq.; (step c) $PtCl_2$ (10 mol %), toluene, 120 °C, 24 h. [b] Performed on a 1.75-fold scale. [c] Performed on a 2.5-fold scale. [d] **1a** (9.0 mmol), **2c** (4.5 mmol), **3** (0.90 mmol), pinacolone (4.5 mL), toluene (4.5 mL), reflux, 65 h. [e] Performed at 80 °C.

possesses C–H bonds para to each other and should give dibenzo[*a*,*h*]anthracenes selectively. The C–H arylation of **1a** with **2b** carried out under pinacolone refluxing conditions gave teraryl product **4ab** in 41% yield and treatment of **4ab** with LDA and $(EtO)_2P(O)Cl$ provided diethynylterphenyl **5ab** in 69% yield (Entry 1). Platinum-catalyzed intramolecular cycloaromatization of **5ab** afforded the desired dibenzo[*a*,*h*]anthracene derivative **6ab** in 36% isolated yield.[14c] Arylation of other acetophenones, such as 2′,4′-dimethyl-, 2′-methyl-4′-*n*-decyloxy-, and 3′-trimethylsilylacetophenones (**1b**, **1c**, and **1d**, respectively) conducted under the same reaction conditions also gave the corresponding coupling products in 43–69% yields (Entries 2–4). Conversion of the acetyl group to ethynyl group in **4bb**–**4db** proceeded smoothly to give 2,2′′-diethynyl-1,1′:4′,1′′-terphenyls **5bb**–**5db** in good yields. The cycloaromatization of terphenyls **5bb** and **5cb** yielded dibenzo[*a*,*h*]anthracenes **6bb** and **6cb** in moderate yields. The yield of the reaction using **6db** is much lower than other substrates (Entry 4) probably due to desilylation and/or related side reactions.

Syntheses of picene derivatives were also examined. Diboronates **2c** and **2d** were used for this purpose, because they possess two C–H bonds next to each other on the aromatic rings. The C–H arylation of **1a** using 1,2-dimethylphenyl-3,6-diboronate **2c** afforded teraryl product **4ac** in 14% yield (Entry 5), while thiophene derivative **2d** was coupled with **1a** to give the corresponding product **4ad** in 38% yield (Entry 6). The actual cause of the low yield obtained for the coupling with **2c** is unclear at present, but the repulsion between two methyl groups on diboronate **2c** may create more severe steric congestion during the coupling. Transformations of the acetyl group to the ethynyl group of **4ac** and **4ad** were then carried out to form diethynylteraryls **5ac** and **5ad** in 42% and 61% yields, respectively. Subsequent cycloaromatizaion using $PtCl_2$ catalyst provided the desired picene **7ac** and thiophene-containing derivative[16] **7ad** in 51% and 73% yields, respectively. Other thiophene-containing picene derivatives **7bd** and **7cd** were prepared in similar manner using acetophenone derivatives **1b** and **1c** with arenediboronate **2d** (Entries 7 and 8).

Dibenzo[*a*,*h*]anthracenes are expected to exhibit good OFET properties,[7] but there are only a limited number of studies concerning measurements of OFET properties of these types of compounds. Thus, properties and OFET performance of **6db** were preliminarily investigated. The UV–vis absorption spectrum in chloroform shows an absorption maximum at 317 nm and a broad shoulder between 300 and 390 nm (see Figure S1 in the Supporting Information; SI[17]). Cyclic voltammetry (CV) was performed in dichloromethane containing 0.1 M n-Bu_4NPF_6. The half-wave oxidation potentials were found at +0.74 V (Figure 3a). Based on this value, the highest occupied molecular orbital (HOMO) level of **6db** was estimated to be −5.54 eV, which is a suitable level as active materials for p-type OFETs. The performance of OFET of **6db** was evaluated by

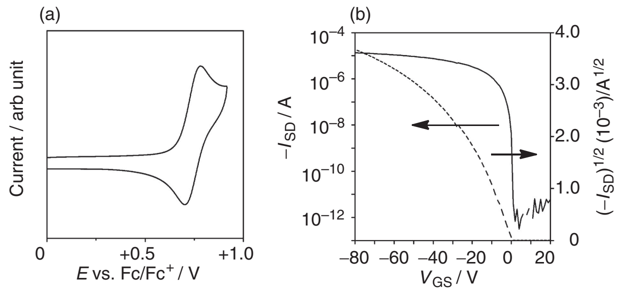


Figure 3. (a) CV curve of **6db** and (b) transfer characteristics of OFET based on **6db** at a drain voltage of −80 V.

employing bottom-contact configuration. The active layer was prepared by spin-coating from 1.0 wt % chloroform solution.

As expected, this compound exhibited typical p-type characteristics, and the hole mobility is found to be $3.0 \times 10^{-4}\,cm^2\,V^{-1}\,s^{-1}$ with the on/off current ratio of 1.3×10^7 and the threshold voltage of 0 V. Its transfer characteristics are shown in Figure 3b.

In summary, we developed a new convenient method for the synthesis of fused aromatic compounds such as dibenzo[*a*,*h*]anthracenes and picenes via our ruthenium-catalyzed C–H arylation method. The arylation of acetophenones using **3** as a catalyst was found to be applicable for the construction of teraryl frameworks using arenediboronates **2**. The C–H arylation, conversion of acetyl group to an ethynyl group, and platinum-catalyzed intramolecular cycloaromatization constitutes a three-step procedure to provide dibenzo[*a*,*h*]anthracenes **6** and picenes **7**. The OFET properties of **6db** fabricated on the OFET devices with a bottom-contact configuration have been measured. This compound exhibited moderate hole mobility ($\mu_{FET} = 3.0 \times 10^{-4}\,cm^2\,V^{-1}\,s^{-1}$).

This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan, by The Science Research Promotion Fund, and by the Cooperative Research Program of "Network Joint Research Center for Materials and Devices." K. K. acknowledges JSPS Research Fellowships for Young Scientists.

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17 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.