ORGANIC
LETTERS

2004
Vol. 6, No. 22
4093−4096

Rapid Construction of Multisubstituted Olefin Structures Using Vinylboronate Ester Platform Leading to Highly Fluorescent Materials

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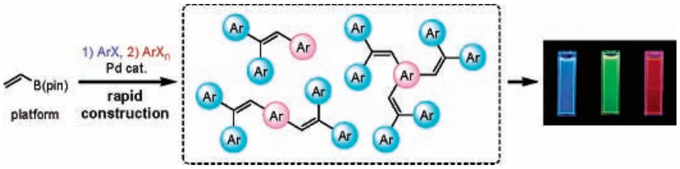
Received September 3, 2004

ABSTRACT



A catalytic one-pot triarylation on the C═C core of vinylboronate pinacol ester (1) produces extended π-systems based on a multisubstituted olefin structure very rapidly. We established an efficient protocol for the Pd-catalyzed double C–H arylation of 1 with aryl halides, which was successfully integrated with C–B arylation with aryl halides (cross-coupling) in one pot. By using this method, several highly fluorescent materials with a wide range of color variations (blue to red) were discovered.

Extended π-systems have received particular attention due to their multiple potential applications as advanced electronic and photonic materials.[1] However, the development of such functional extended π-systems still suffers from time-consuming empirical processes because structure−property relationships are often not predictable in materials science. Although the combinatorial approach is particularly well-suited in this context,[2,3] doing so in a truly meaningful manner requires a powerful and reliable synthetic strategy for structurally well-defined π-systems. Herein we describe an efficient procedure for the rapid construction of multisubstituted olefin structures using vinylboronate pinacol ester (**1**) as a platform. By following this method, we succeeded in rapidly making extended π-systems based on multisubstituted olefin structures, from which several highly fluorescent materials with a wide range of color variations were found.

The carbon−carbon double bond (C═C) is a minimal unit in π-systems. Therefore, an extended π-system based on a C═C core (multisubstituted olefins) would be an interesting target as a functional organic material. However, the paucity of general methods for the synthesis of multisubstituted olefins hampers the rapid construction and property evaluation of such extended π-systems. We envisaged vinylmetals (CH_2═CH-M) to be attractive platforms for such π-systems.

Because vinylmetals could in principle undergo C−H arylation [Mizoroki−Heck reaction (MHR)][4] and C−M

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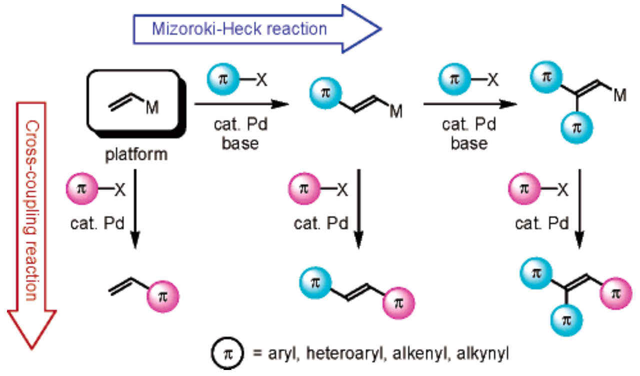
10.1021/ol048217b CCC: $27.50

Scheme 1. Orthogonal and Sequential Integration of Mizoroki−Heck Reaction and Cross-Coupling Reaction of Vinylmetals in the Synthesis of Multisubstituted Olefins



arylation [cross-coupling reaction (CCR)][5] with aryl halides under the catalytic influence of palladium complexes, an orthogonal and sequential integration of these arylation manifolds would produce a multisubstituted olefin structure very rapidly (Scheme 1). However, because of the apparent difficulty in controlling (switching) those two reaction pathways reflecting the similarity in arylating conditions for MHR and CCR, such a sequential integration has not been utilized in the construction of extended π-systems. We recently reported that the use of dimethyl(2-pyridyl)vinylsilane as such a vinylmetal (M = Si) enables the synthesis of multisubstituted olefins through the sequential integration of MHR and Hiyama-type silicon-based CCR.[6−8] Though this can be regarded as a proof-of-principle of our strategy, this silicon-based method suffered severely from limited reaction scope. In addition, the one-pot integration of these π-component-assembling reactions was not possible with the silicon-based method. Toward this end, we embarked on the sequential integration of MHR and CCR of vinylboron compounds (M = B) for the rapid construction of multisubstituted olefin-type extended π-systems.

The initial focal point of our study was to determine the optimal conditions to switch the reaction pathway of vinylboron compounds to the C−H arylation manifold (MHR) from the otherwise favorable C−B arylation manifold (Suzuki−Miyaura-type CCR). In pioneering work on these transformations, Whiting has previously disclosed the realization of MHR of vinylboronate esters.[9] After extensive optimization experiments of our own, we found that the catalyst/base combination of Pd[P(*t*-Bu)$_3$]$_2$/*i*-Pr$_2$NH is particularly effective for MHR of vinylboronate pinacol ester (**1**).[10] More importantly, we found that a "hard-to-achieve" double-MHR[11] also proceeds smoothly when 2.2 equiv of aryl halides are employed, furnishing β,β-diarylated vinylboronate pinacol esters **2**. Thus, under the influence of Pd[P(*t*-Bu)$_3$]$_2$ catalyst (5 mol %) and *i*-Pr$_2$NH (4.0 equiv), the double-MHR of **1** proceeded in good yields with electronically and structurally diverse aryl halides (2.2 equiv) at 80 °C in toluene (Figure 1).[12] Not only aryl iodides but also aryl bromides can be used in this reaction.

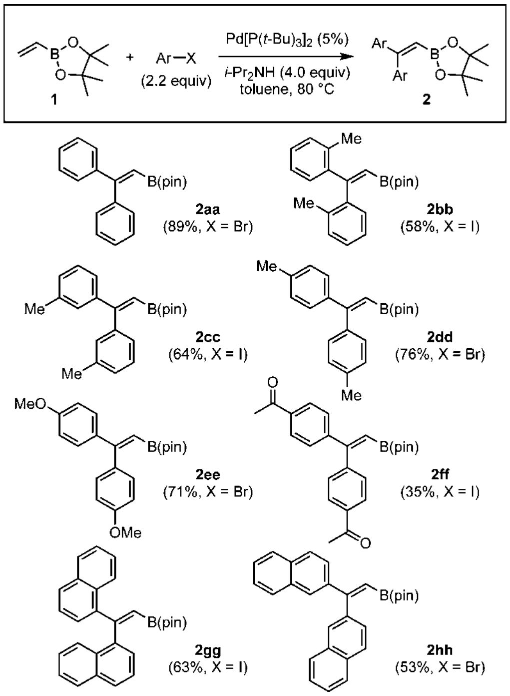


Figure 1. One-pot double Mizoroki−Heck reaction of **1** with ArX.

The resultant β,β-diarylated vinylboronate pinacol esters **2** were found to undergo Suzuki−Miyaura-type CCR under the influence of Pd[P(*t*-Bu)$_3$]$_2$ catalyst and NaOH/H$_2$O.[13] Capitalizing on the ability of Pd[P(*t*-Bu)$_3$]$_2$ to promote both

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[4] Beletskaya, I. P.; Cheprakov, A. V. *Chem. Rev.* **2000**, *100*, 3009.

[5] (a) *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F., Stang, P. J., Eds.; Wiley-VCH: Weinheim, 1998. (b) *Cross-Coupling Reactions*; Miyaura, N., Ed.; Springer: New York, 2002.

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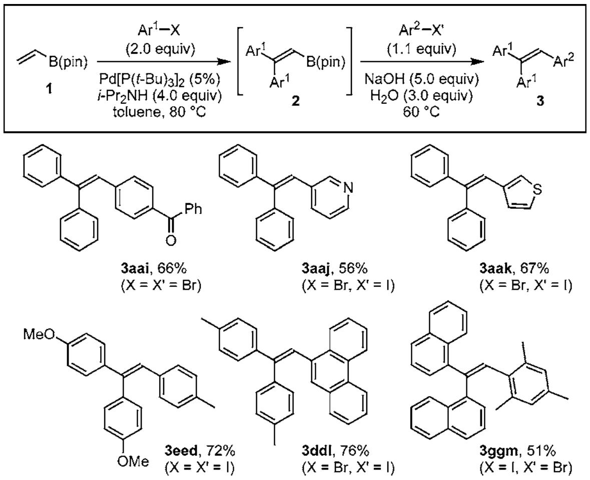
[9] (a) Hunt, A. R.; Stewart, S. K.; Whiting, A. *Tetrahedron Lett.* **1993**, *34*, 3599. (b) Stewart, S. K.; Whiting, A. *J. Organomet. Chem.* **1994**, *482*, 293. (c) Stewart, S. K.; Whiting, A. *Tetrahedron Lett.* **1995**, *36*, 3925. (d) Hénaff, N.; Whiting, A. *Tetrahedron* **2000**, *56*, 5193. (e) Thirsk, C.; Whiting, A. *J. Chem. Soc., Perkin Trans. 1* **2002**, 999. (f) Lightfoot, A. P.; Maw, G.; Thirsk, C.; Twiddle, S. J. R.; Whiting, A. *Tetrahedron Lett.* **2003**, *44*, 7645.

[10] Pd/P(*t*-Bu)$_3$ catalyst for Mizoroki−Heck reaction: (a) Littke, A. F.; Fu, G. C. *J. Am. Chem. Soc.* **2001**, *123*, 6989. Also see: (b) Itami, K.; Mineno, M.; Muraoka, N.; Yoshida, J. *J. Am. Chem. Soc.* **2004**, *126*, 11778.

[11] Multiple Mizoroki−Heck reaction: (a) Bräse, S.; de Meijere, A. In *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E., Ed.; Wiley-Interscience: New York, 2002; p 1179. (b) Nilsson, P.; Larhed, M.; Hallberg, A. *J. Am. Chem. Soc.* **2003**, *125*, 3430. (c) Reference 8. (d) Reference 10b.

[12] The use of *i*-Pr$_2$NH is effective in producing double-MHR products (**2**). For example, when Et$_3$N (2.4 equiv) was used in the reaction of **1** and 4-iodoanisole (2.2 equiv) under the influence of Pd[P(*t*-Bu)$_3$]$_2$ catalyst (5 mol %) in toluene at 90 °C, mono-MHR product (monoarylated vinylboronate pinacol ester) was produced in 34% yield together with **2ee** (50%). The Suzuki−Miyaura coupling products (styrene derivatives) are usually not observed when Pd[P(*t*-Bu)$_3$]$_2$ catalyst are used in combination with amines. As for the low-yielding examples in Figure 1, the mono-MHR products were formed in reasonable yields.

[13] Pd/P(*t*-Bu)$_3$ catalyst for Suzuki−Miyaura coupling: (a) Littke, A. F.; Dai, C.; Fu, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 4020. Also see: (b) Itami, K.; Kamei, T.; Yoshida, J. *J. Am. Chem. Soc.* **2003**, *125*, 14670.



3aai, 66% (X = X' = Br)

3aaj, 56% (X = Br, X' = I)

3aak, 67% (X = Br, X' = I)

3eed, 72% (X = X' = I)

3ddl, 76% (X = Br, X' = I)

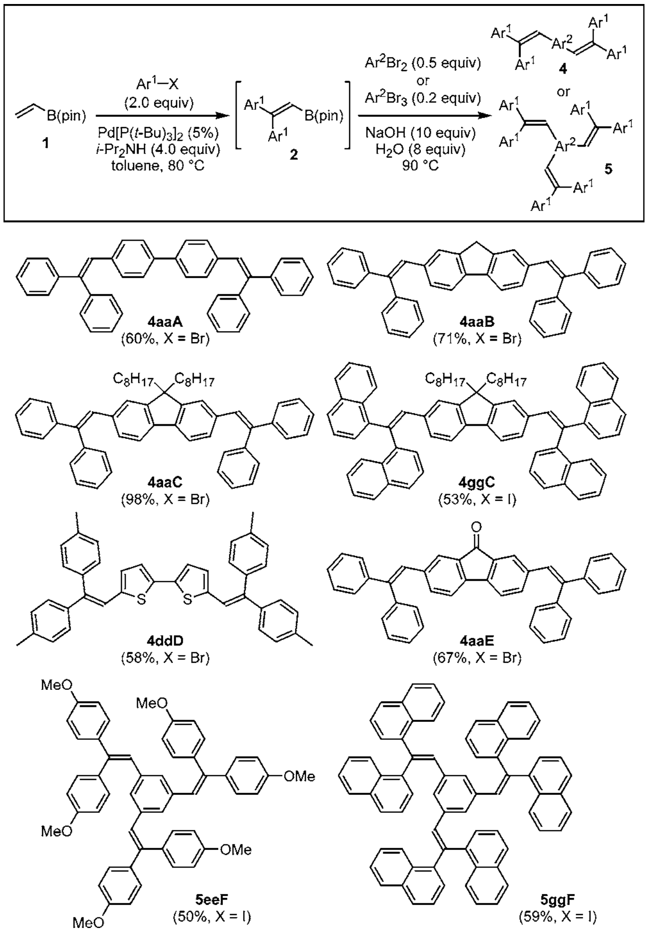
3ggm, 51% (X = I, X' = Br)

Figure 2. One-pot triarylation of **1** with aryl halides.

double-MHR and CCR, we next examined the one-pot synthesis of triarylethenes **3** through the sequential addition of aryl halides and additives into the reaction mixture (Figure 2). Thus, by simply adding second aryl halides Ar^{2}X (1.1 equiv), NaOH (5.0 equiv), and H_2O (3.0 equiv) into the reaction mixture of double-MHR, triarylethenes **3** were obtained in good overall yields (51−76%). Heteroaryl halides as well as sterically hindered aryl halides can also be used. It should be mentioned that our previously reported silicon-based method[8] is incapable of preparing most of **3** described in Figure 2.

The power of this strategy becomes apparent when we utilize aryl dihalides or trihalides in place of monohalides in the cross-coupling step (Figure 3). By applying these reagents, interesting extended π-systems **4** and starburst π-systems **5** were prepared in good to excellent overall yields. The present successful synthesis of **4** and **5**, which includes six or nine C−C bond formations, speaks well for the high productivity and generality of our one-pot method.

Interestingly, many of these extended π-systems were found to be fluorescent. The photophysical properties and the selected pictures of the fluorescence behavior of representative compounds are shown in Table 1 and Figure 4, respectively. It was found that the emission maxima depend heavily on the nature and position of aryl groups in extended π-systems and that fluorescence color variations over a wide range of wavelengths can be realized within this family of π-systems. For example, whereas **3ggm**, **4aaA**, **4aaB**, **4aaC**, and **4ggC** were found to be blue-fluorescent, **4ddD** and **4aaE** were found to emit light of yellow and red, respectively. In particular, **4ggC** was found to possess extremely high fluorescence quantum yield ($\Phi_F = 0.90$) compared to that of the well-known blue-fluorescent **4aaA** ($\Phi_F = 0.06$; DPVBi). Because **4aaA** has been used as a blue-emitting material in organic electroluminescence devices,[14] compounds such as **4ggC** should be highly promising for such purpose.



4aaA (60%, X = Br)

4aaB (71%, X = Br)

4aaC (98%, X = Br)

4ggC (53%, X = I)

4ddD (58%, X = Br)

4aaE (67%, X = Br)

5eeF (50%, X = I)

5ggF (59%, X = I)

Figure 3. Rapid construction of extended π-systems **4** and **5**.

Along with the discovery of highly fluorescent materials, the rationalization of properties is also important in materials science, though not necessarily easy. We found that the systematic alteration of structure within this family of π-systems (**4aaA** → **4aaB** → **4aaC** → **4ggC**) can provide us a clue for the 15 times increase of fluorescence quantum yields from **4aaA** to **4ggC** (Figure 5). From this structure−property relationship analysis, it may be possible to assume that the significant increase in fluorescence efficiency is attributed to several factors but not any single one. They

Table 1. Photophysical Properties of Representative Compounds

	UV−vis[a]		fluorescence[a]		
compound	λ_{max} (nm)	log ϵ	λ_{max} (nm)	color	Φ_F[b]
3ggm	303	4.19	449	blue	0.05
4aaA	353	4.71	442	blue	0.06
4aaB	370	4.74	449	blue	0.30
4aaC	373	4.70	451	blue	0.59
4ggC	376	4.73	454	blue	0.90
4ddD	429	4.55	523	yellow	0.11
4aaE	465	4.59	599	red	0.01

[a] Measured in CHCl$_3$. [b] Determined with reference to 9,10-diphenylanthracene (excited at 350 nm).

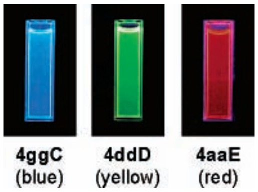


Figure 4. Selected pictures of the emissive behavior of representative compounds (irradiated at 365 nm in $CHCl_3$).

may be (i) planarization of the core π-unit (biphenyl → fluorene), (ii) installation of long alkyl groups on the core π-unit, and (iii) extension of terminal π-units (phenyl → naphthyl). We believe that the highly flexible and diversity-oriented nature of our method made such a rapid analysis possible, though the above-mentioned factors are not entirely novel in the functional π-system chemistry. Yet, these aspects of our synthesis should be advantageous because the accumulation of such structure−property relationships would be extremely important for future property design.

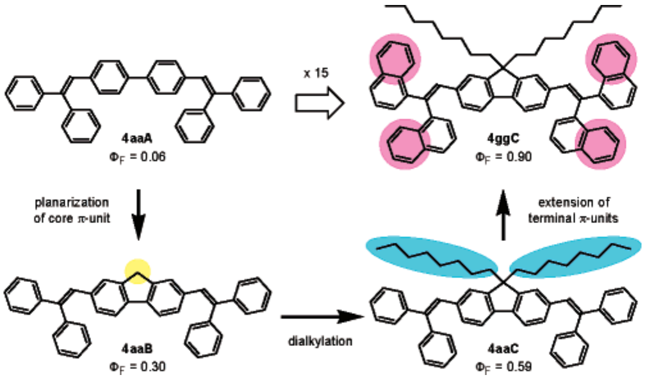


Figure 5. A structure−property relationship analysis with regard to fluorescence efficiency.

In summary, we have developed an efficient procedure for the rapid construction of multisubstituted olefin structures using vinylboronate pinacol ester (**1**) as a platform. By carefully choosing the additives, the potentially possible C−H and C−B arylation manifolds (MHR and CCR) of vinylboron compounds were successfully controlled and integrated in a sequence. Various types of extended π-systems based on multisubstituted olefin structure were prepared very rapidly with this method. The fact that our effort has finally culminated in the finding of highly fluorescent materials with a wide range of color variations speaks well for the potential of the current synthetic strategy in the development of functional organic materials. Investigations along this line are currently ongoing in our laboratory.

Acknowledgment. This work was financially supported by a Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science. K.T. is a recipient of the JSPS Predoctoral Fellowships for Young Scientists.

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

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