Facile access to boryltetralins and borylnaphthalenes *via* a cycloaddition using *o*-quinodimethanes†

Hiroto Yoshida,* Masashi Mukae and Joji Ohshita

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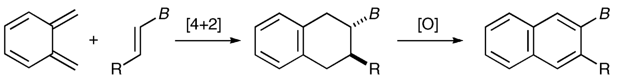
Borylalkenes are found to serve as efficient dienophiles in a cycloaddition reaction with *o*-quinodimethanes, giving diverse boryltetralins, which are convertible into borylnaphthalenes *via* an oxidative aromatization.

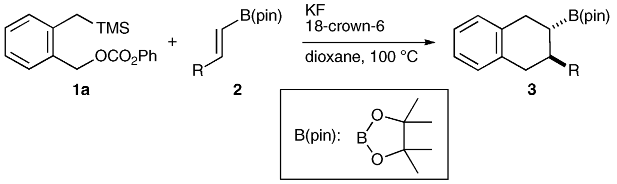
Organoboron compounds constitute one of the most important reagents in synthetic organic chemistry[1] especially for carbon–carbon bond forming processes through Suzuki–Miyaura coupling,[2] Petasis reaction,[3] transition metal-catalysed 1,2- and 1,4-additions,[4] *etc.* Whilst organoboron compounds of multifarious structures are accessible by a reaction of Grignard reagents (or organolithiums) with boron electrophiles, catalytic borylation of C–X (X: halogen or pseudohalogen)[5] or C–H bonds,[6] and cycloaddition of borylalkynes,[7] the search for new synthetic methods which provide access to hitherto unprecedented classes of organoboron compounds is still of great significance.[8]

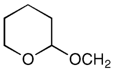
Owing to salient reactivity at an *exo*-diene moiety, *o*-quinodimethanes (*o*-QDMs) have been utilized as a potent four-carbon unit in [4 + 2] cycloaddition reaction (Diels–Alder reaction).[9] Although the cycloaddition enables diverse tetralin derivatives to be synthesized in a straightforward manner, the potential versatility of the reaction remains to be exploited, because most of the dienophiles so far employed have been those having carbonyl or cyano substituents as electron-withdrawing groups. Herein we disclose that introduction of a boryl moiety into alkenes enhances the dienophilicity of the alkenes,[10] leading to facile formation of boryltetralins of structural diversity *via* the [4 + 2] cycloaddition with *o*-QDMs. Furthermore, aromatization of the resulting tetralins provides a convenient approach to borylnaphthalenes (Scheme 1).[11]



Scheme 1 Synthesis of boryltetralins and borylnaphthalenes.

Table 1 [4 + 2] Cycloaddition between *o*-QDM and borylalkenes[a]



Entry	R	Time/h	Yield (%)[b]	3
1	Ph (**2a**)	13	87	**3aa**
2	1-Naphthyl (**2b**)	9	81	**3ab**
3	$4\text{-}PhC_6H_4$ (**2c**)	12	75	**3ac**
4	$4\text{-}n\text{-}BuC_6H_4$ (**2d**)	12.5	65	**3ad**
5	$2,5\text{-}(MeO)_2C_6H_3$ (**2e**)	8	80	**3ae**
6	$4\text{-}CF_3C_6H_4$ (**2f**)	6.5	78	**3af**
7	$4\text{-}BrC_6H_4$ (**2g**)	9	82	**3ag**
8	$4\text{-}(HC{\equiv}C)C_6H_4$ (**2h**)	9	81	**3ah**
9	$4\text{-}(n\text{-}HexC{\equiv}C)C_6H_4$ (**2i**)	12	79	**3ai**
10	2-Thienyl (**2j**)	11	49	**3aj**
11	 (**2k**)	10.5	54	**3ak**
12	*n*-Hexyl (**2l**)	11	32	**3al**
13	Cyclopropyl (**2m**)	13	19	**3am**

[a] The reaction was carried out in dioxane (1 mL) at 100 °C using **1a** (0.3 mmol), **2** (0.2 mmol), KF (0.33 mmol) and 18-crown-6 (0.33 mmol). [b] Isolated yield based on **2**.

We first conducted the reaction of simple *o*-QDM, generated *in situ* from 2-[(trimethylsilyl)methyl]benzyl phenyl carbonate (**1a**) and a fluoride ion,[12,13] with (*E*)-β-borylstyrene (**2a**) in 1,4-dioxane at 100 °C, and observed that the cycloaddition product, 3-phenyl-2-boryltetralin (**3aa**), was formed in 87% yield (entry 1, Table 1). The configuration between phenyl and boryl substituents in **3aa** has proven to be *anti*, which verifies that the (*E*)-stereochemistry of the dienophile is retained throughout the reaction. In addition, borylalkenes bearing naphthalene (**2b**) or biphenyl (**2c**) moieties could also participate in the reaction, giving the respective cycloadducts (**3ab** or **3ac**) in high yields (entries 2 and 3). The reaction of electron-rich or electron-deficient borylstyrenes (**2d–2f**) took place smoothly, irrespective of their electronic characters (entries 4–6), and furthermore, a carbon–bromine bond in the dienophile (**2g**) remained intact through the reaction (entry 7). Dienophilicity of a borylalkene moiety was far superior to that of an ethynyl moiety, and thus, the products (**3ah** or **3ai**) were formed solely in the reaction of **2h** or **2i** (entries 8 and 9). A heteroaromatic thienyl group in **2j** and an acetal moiety in **2k** were compatible with the cycloaddition (entries 10 and 11), whereas the reaction of aliphatic borylalkenes (**2l** or **2m**) became sluggish (entries 12 and 13). The reactivity of **2a** toward *o*-QDM has proven to be comparable to that of methyl cinnamate, whereas the reaction of β-bromostyrene did not afford the cycloadduct despite the inductive electron-withdrawing property of the bromine atom, demonstrating that the boryl substituent actually increases the

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Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan.
E-mail: yhiroto@hiroshima-u.ac.jp; Fax: +81-82-424-5494;
Tel: +81-82-424-7724

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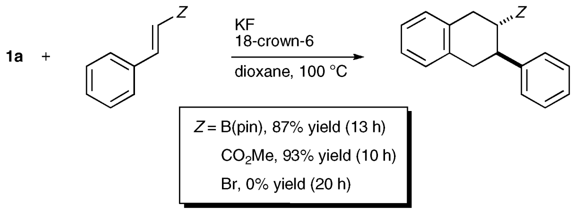
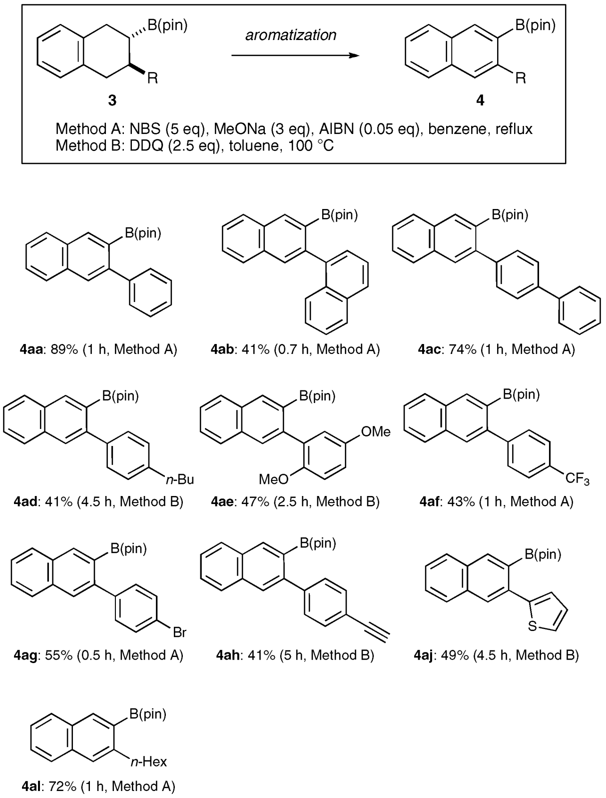


Scheme 2 Comparison of dienophilicity in the reaction with *o*-QDM.

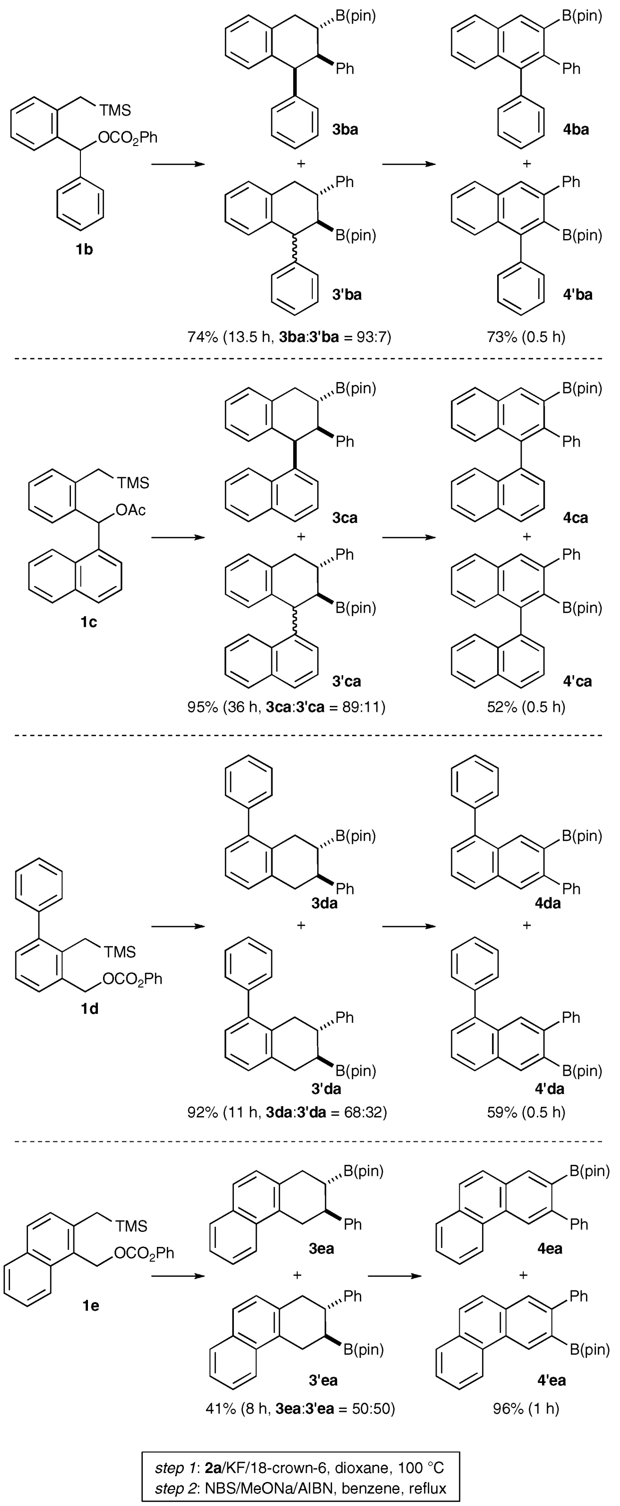
dienophilicity of the carbon–carbon double bond attached with its vacant p-orbital (Scheme 2).

The boryltetralins were found to be convertible into borylnaphthalenes **4** *via* an oxidative aromatization by use of NBS/MeONa/AIBN (Method A) or DDQ (Method B) (Scheme 3). For example, 2-boryl-3-phenylnaphthalene (**4aa**) was synthesised from **3aa** in 89% yield according to Method A. In addition, a variety of substituted borylnaphthalenes, which would be hardly accessible by conventional methods, could be straightforwardly prepared through the cycloaddition/aromatization sequence.

We finally investigated the cycloaddition of substituted *o*-QDMs (Scheme 4). The reaction of α-phenyl-*o*-QDM (from **1b**) with **2a** occurred with high regioselectivity to give **3ba** as the major product (93% selectivity among four possible isomers), in which two phenyl groups are adjoining in *cis* configuration. The observed regio- and stereoselectivities can be rationally explained by the following two factors: *exo* approach of the bulky B(pin) moiety which orients the α-phenyl group to a remote position, and a secondary orbital interaction between C2 of the *o*-QDM and the phenyl group of **2a** (Fig. 1).^{14} α-(1-Naphthyl)-*o*-QDM (from **1c**) reacted with **2a** in a similar manner to afford **3ca** selectively, whereas the reaction of *o*-QDM having a biphenyl (from **1d**) or a naphthalene framework (from **1e**) furnished a mixture of two regioisomers, which shows that a substituent on an aromatic backbone of *o*-QDM exerted a little effect on the regioselectivity. The same



Scheme 3 Synthesis of borylnaphthalenes *via* an oxidative aromatization.



Scheme 4 Reaction using substituted *o*-QDMs.

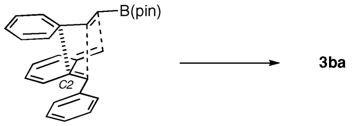
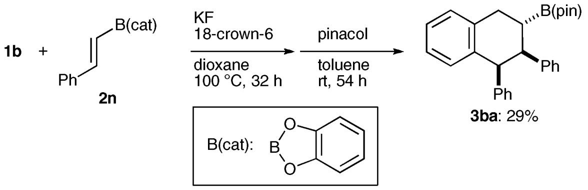
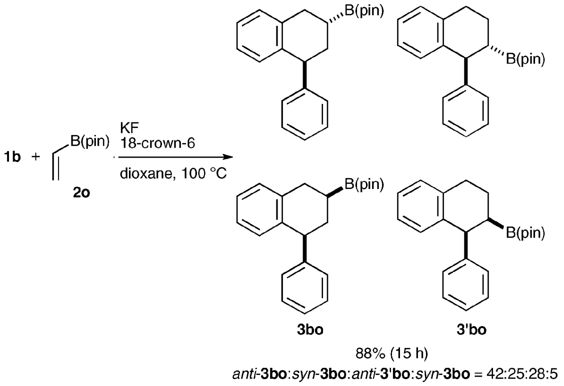


Fig. 1 Secondary orbital interaction in the formation of **3ba**.



Scheme 5 Reaction using a catechol ester.

regio- and stereoselectivities as those with **2a** were observed in the reaction using a catechol ester of (*E*)-styrylboronic acid (**2n**), albeit at the cost of a decreased yield of the cycloadduct (Scheme 5). As depicted in eqn (1), the reaction of borylethene **2o** with α-phenyl-*o*-QDM proceeded with lower regio- and stereoselectivities as compared with those in the reaction of **2a**, which implies that the secondary orbital interaction (Fig. 1) considerably affects the regio- and stereochemical outcome in the present cycloaddition.[14] The multisubstituted boryltetralins thus obtained from substituted *o*-QDMs could be readily aromatized to produce highly π-assembled borylnaphthalenes according to the above procedure.



(1)

In conclusion, we have disclosed that the [4 + 2] cycloaddition between *o*-QDMs and borylalkenes offered facile access to boryltetralins of structural diversity, which were further transformable into variously substituted borylnaphthalenes *via* oxidative aromatization. Moreover, a high level of regio- and stereoselectivities was observed in the cycloaddition of α-arylated *o*-QDMs, which can be attributed to the steric bulkiness of the B(pin) moiety and the secondary orbital interaction. Further studies on synthetic applications of the cycloaddition/aromatization sequence to other substrates are in progress.

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