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Novel [4 + 2]-Benzannulation To Access Substituted Benzenes and Polycyclic Aromatic and Benzene-Fused Heteroaromatic Compounds

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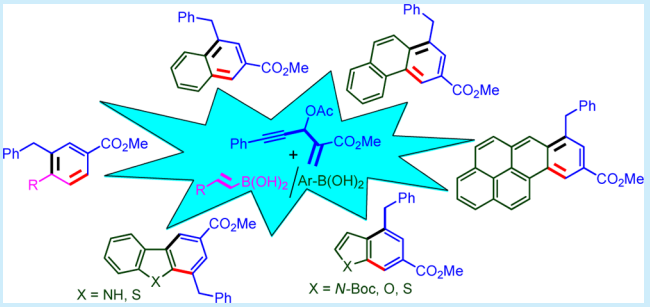
Supporting Information

ABSTRACT: A common [4 + 2]-benzannulation of Morita–Baylis–Hillman acetates of acetylenic aldehydes with boronic acids has been developed for the synthesis of aromatic and heteroaromatic compounds through tandem allylic substitution/hydroarylative cycloisomerization process. This method provides a facile and general route to substituted benzenes, naphthalenes, other polycyclic aromatics, and various benzene-fused heteroaromatic compounds such as benzofuran, benzothiophene, indole, and carbazoles.



The development of new synthetic methods to substituted aromatic, polyaromatic, and heteroaromatic compounds continues to command extensive interest due to their wide range of applications.[1] Benzannulation is one of the important reactions for the construction of substituted benzene ring, and over the years, various benzannulation reactions have been developed for diversely substituted benzene and fused-benzene compounds.[2−9] Among these, [4 + 2]-benzannulation of enynes with alkynes has received substantial attention to construct the functionalized benzenes from acyclic starting materials (Figure 1).[3−5] Danheiser et al. demonstrated the intramolecular [4 + 2]-annulation of conjugated enynes leading to benzene derivatives under thermal or acid-catalysis conditions (eq 1).[3] In 1996, Yamamoto and co-workers first reported the palladium-catalyzed intermolecular [4 + 2]-benzannulation of conjugated enynes with enynophiles (eq 2).[4] Later, this pioneering work was widely explored by Yamamoto, Gevorgyan, and other research groups for the preparation of diversely substituted benzenes using preconstructed conjugated enynes as the four-carbon unit and alkynes with an activating group (alkene or alkyne) as the C2 synthon.[4,5] Herein, we report a novel [4 + 2]-benzannulation using Morita–Baylis–Hillman (MBH) acetates of acetylenic aldehydes as the C4 precursor[10] and aryl or vinyl boronic acids as the C2 synthon (eq 3). This approach offers a significant advantage by giving an access to substituted benzenes as well as to polycyclic aromatic hydrocarbons and benzene-fused heterocyclic compounds from easily accessible substrates.

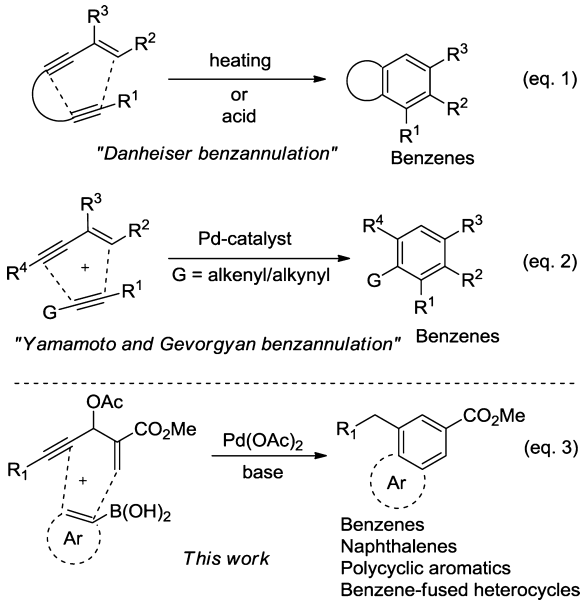


Figure 1. [4 + 2]-Benzannulation reaction of enynes.

The synthesis of naphthalenes and polycyclic aromatics from MBH adducts was reported by Kim and others involving multistep reactions.[11] We envisaged that MBH acetate of acetylenic aldehyde will undergo allylic substitution with boronic acid to give conjugated enyne, which would undergo hydroarylative cycloisomerization to lead the benzannulated product. To test the hypothesis, MBH acetate **1a** and phenyl boronic acid (**2a**) were chosen as model substrates. From the optimization studies (see the Supporting Information), we were pleased to find that the [4 + 2]-benzannulation product, naphthalene **3aa**, was accomplished in 89% yield using 5 mol % of $Pd(OAc)_2$, Na_2CO_3 in acetonitrile/H_2O, and DBU reaction conditions (entry 1, Table 1). Encouraged by the above result, we examined the substrate scope of this reaction by using a variety of MBH acetates of acetylenic aldehydes (Table 1). A facile [4 + 2]-benzannulation was observed for the reaction of 1-naphthyl

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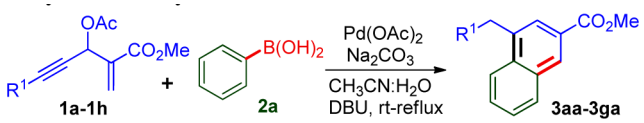
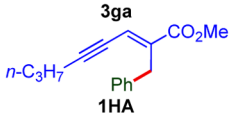
Table 1. [4 + 2]-Benzannulation of MBH Acetates of Acetylenic Aldehydes with 2a[a]



entry	MBH-acetate (**1**)	time (h)	Naphthalene (**3**)	yield (%)[b]
1	R^1 = Ph, **1a**	5	**3aa**	89
2	R^1 = 1-Naphthyl, **1b**	6	**3ba**	88
3	R^1 = 2-Thiophene-yl, **1c**	4	**3ca**	86
4	R^1 = 4-Me-Ph, **1d**	5	**3da**	84
5	R^1 = 4-Cl-Ph, **1e**	6	**3ea**	87
6	R^1 = 3-CF_3-Ph, **1f**	8	**3fa**	75
7	R^1 = Ph-CH=CH-, **1g**	5	**3ga**	60
8	R^1 = *n*-C_3H_7-, **1h**	5	 **1HA**	95

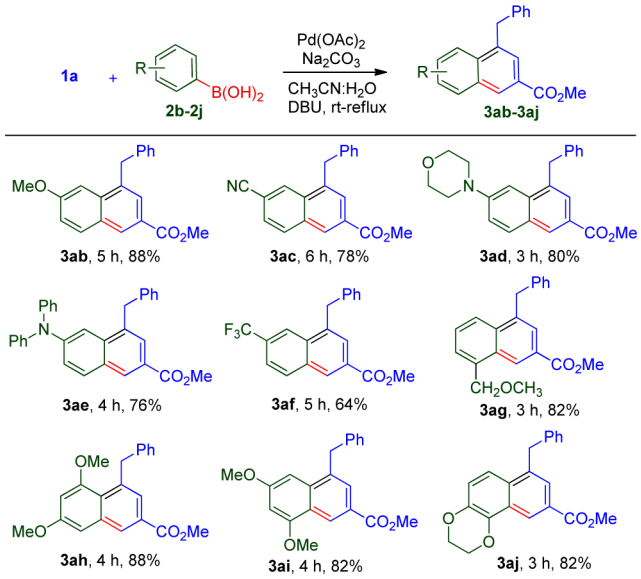
[a]Reaction conditions: MBH acetate **1** (1 equiv), Ph-B(OH)$_2$ **2a** (1.1 equiv), Pd(OAc)$_2$, (5 mol %), Na_2CO_3 (1 equiv), DBU (1 equiv), CH_3CN (5 mL), H_2O (0.1 mL), rt to 85 °C. [b]Isolated yield.

MBH acetate **1b** with **2a** to give the substituted naphthalene **3ba** in 88% yield (entry 2, Table 1). Similarly, 2-thiophene-yl MBH acetate **1c** was also successful in reacting with **2a** to provide the naphthalene **3ca** 86% yield (entry 3, Table 1). The reactions of MBH acetates **1d** (4-Me-Ph), **1e** (4-Cl-Ph), and **1f** (3-CF_3-Ph) with **2a** were studied independently, and it was found that the reactions gave the corresponding naphthalenes **3da**−**fa**, respectively, in good yield (entries 4−6, Table 1). Notably, the reaction of MBH acetate **1g** bearing a styryl group on alkyne with **2a** proceeded very well and led to the expected naphthalene **3ga** in 60% yield (entry 7, Table 1). However, the reaction of MBH acetate **1h** having an *n*-propyl group on the alkyne functionality with **2a** provided the enyne intermediate **1HA** instead of the expected naphthalene (entry 8, Table 1).

We next evaluated the reactivity of diversely substituted phenylboronic acids, and the results are summarized in Scheme 1. Remarkably, all the phenylboronic acids investigated efficiently participated in [4 + 2]-benzannulation with **1a** under the optimized conditions to afford the corresponding naphthalenes in good yields. The formation of naphthalenes **3ab**−**ag** revealed that various substitutions such as 4-MeO (**2b**), 4-CN (**2c**), 4-morpholine (**2d**), 4-(Ph)$_2$N (**2e**), 4-CF_3 (**2f**), and 2-MeOCH$_2$ (**2g**) on phenylboronic acid were found to be suitable for the tandem reactions. 3,5-Dimethoxyphenylboronic acid (**2h**) and 2,4-dimethoxyphenylboronic acids (**2i**) readily underwent [4 + 2] benzannulation with **1a** to produce naphthalenes **3ah** (88%) and **3ai** (84%), respectively. Likewise, 2,3-dioxopyranylphenylboronic acid (**2j**) also provided the respective naphthalene **3aj** in good yield (Scheme 1).

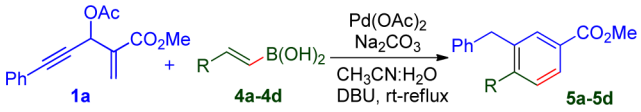
Next, it occurred to us that the use of vinylic boronic acids in the present annulation reaction is also feasible, which allows the synthesis of substituted benzenes. To this end, the [4 + 2]-benzannulation of **1a** with (*E*)-styrylboronic acid (**4a**) was first examined, and to our delight, the formation of 1,3,5-trisubstituted benzene **5a** (81%) was observed (entry 1, Table 2). (*E*)-(4-Fluorostyryl)boronic acid (**4b**) was found to be suitable in providing **5b** in 72% yield (entry 2, Table 2). Notably, aliphatic vinylboronic acids **4c** and **4d** were also effectively

Scheme 1. Synthesis of Substituted Naphthalenes[a]



[a]Reaction schemes along with the structure of boronic acid are shown in Supporting Information.

Table 2. Synthesis of Substituted Benzenes Using Vinyl Boronic Acids[a]



entry	boronic acid (**4**)	time (h)	benzene (**5**)	yield[b] (%)
1	R = Ph, **4a**	5	**5a**	80
2	R = 4-F-C_6H_4−, **4b**	4	**5b**	72
3	R = *n*-C_6H_{13}, **4c**	6	**5c**	80
4	R = *t*-Bu−, **4d**	5	**5d**	78

[a]Reaction conditions: MBH acetate **1a** (0.38 mmol), (*E*)-vinylboronic acid **4** (0.42 mmol), Pd(OAc)$_2$, (5 mol %), Na_2CO_3 (0.38 mmol), DBU (0.38 mmol), CH_3CN (5 mL), H_2O (0.1 mL), rt to 85 °C. [b]Isolated yield.

participated in the [4 + 2]-benzannulation to afford the corresponding trisubstituted benzenes **5c** and **5d**, respectively, in good yield (entries 3 and 4, Table 2).

The reaction scope was further extended to the synthesis of polycyclic aromatic hydrocarbons (Scheme 2). Interestingly, the treatment of **1a** with naphthalene-1-boronic acid (**6a**) under the described reaction conditions smoothly gave the substituted phenanthrene **7a** in 82% yield. In contrast to the reported methods, wherein the middle ring of the phenanthrene was generally constructed,[6d,h,12] in the present method the terminal ring was built. To make further higher numbered rings, phenanthren-4-ylboronic acid (**6b**) and pyren-1-ylboronic acid (**6c**) were independently subjected to the [4 + 2]-benzannulation with **1a**, and gratifyingly, both reactions ensued well to give substituted benzo[*c*]phenanthrene **7b** (83%) and benzo[*pqr*]-tetraphene **7c** (81%), respectively. Thianthren-1-ylboronic acid (**6d**) was well suited for the benzannulation with **1a** to give benzo[*a*]thianthrene **7d** in 71% yield. Additionally, dibenzo-[*b*,*d*]furan-4-ylboronic acid (**6e**) and dibenzo[*b*,*d*]thiophene-4-ylboronic acids (**6f**) were also treated with **1a** under the developed one-pot tandem reaction conditions to obtain the

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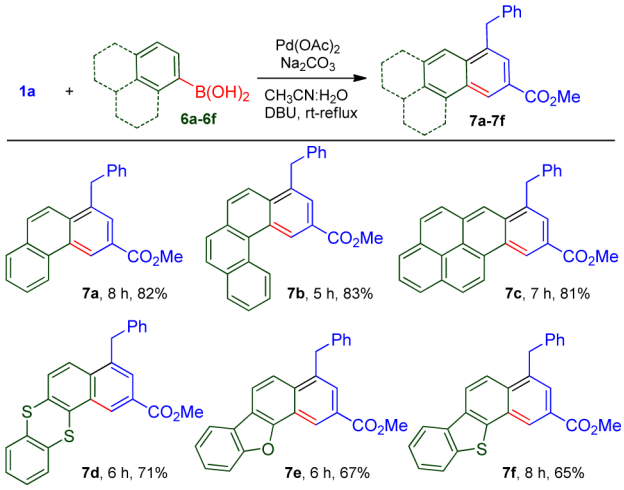
Scheme 2. Synthesis of Polycyclic Aromatic Compounds[a]

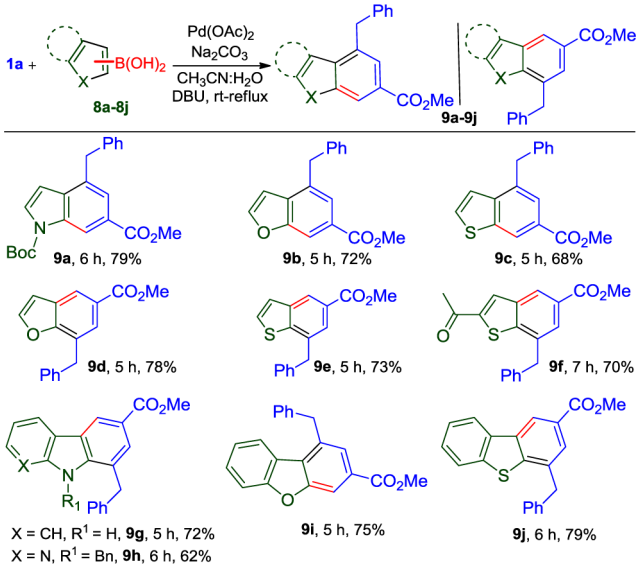


[a]The structure of boronic acid for each product is shown in the Supporting Information.

corresponding naphtho[1,2-*b*]benzofuran **7e** and benzo[*b*]-naphtho[2,1-*d*]thiophene **7f**, respectively.

After achieving the above success, we next embarked on the synthesis of bicyclic or tricyclic benzene-fused heterocycles (Scheme 3). Thus, the reaction of *N*-Boc-pyrrolyl-2-boronic acid

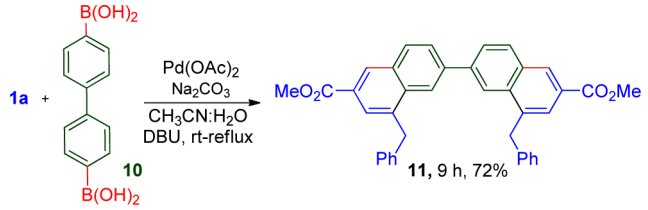
Scheme 3. Synthesis of Benzene-Fused Heteroaromatics[a]



[a]The structure of boronic acid for each product is shown in the Supporting Information.

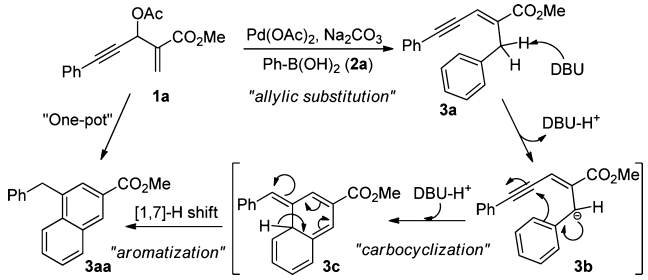
(**8a**) with MBH acetate **1a** under tandem allylic substitution/hydroarylative cycloisomerization conditions yielded the 4,6-disubstituted *N*-Boc-indole **9a** in 79% yield. Equally, furan-2-ylboronic acid (**8b**) and thiophene-2-ylboronic acid (**8c**) underwent smooth benzannulation upon treatment with **1a** to produce the corresponding 4,6-disubstituted benzofuran **9b** and benzo[*b*]thiophene **9c**, respectively, in good yield. It is worth mentioning that furan-3-ylboronic acid (**8d**) and thiophene-3-ylboronic acid (**8e**) can also be employed in [4 + 2]-benzannulation with **1a**, giving an access to 5,7-disubstituted benzofuran **9d** and benzo[*b*]thiophene **9e** in excellent yield. Substituted boronic acid, (5-acetylthiophene-3-yl)boronic acid (**8f**) was also efficient in producing 2, 5, 7-trisubstituted benzo[*b*]thiophene **9f** in 72% yield. Delightfully, the use of (1*H*-indol-3-yl)boronic acid (**8g**) in the [4 + 2]-benzannulation with **1a** provided the corresponding 9*H*-carbazole **9g** in 75% yield. The benzannulation of (1-benzyl-1*H*- pyrrolo[2,3-*b*]-pyridin-3-yl)boronic acid (**8h**) with **1a** was also easily progressed to offer the 9-benzyl-9*H*-pyrido[2,3-*b*]indole (**9h**) in 72% yield. Further, the access to substituted dibenzo[*b*,*d*]furan **9i** and dibenzo[*b*,*d*]thiophene **9j** was fruitful from the reaction of **1a** with respective boronic acids. These results clearly demonstrate the use of MBH acetates of acetylenic aldehydes in [4 + 2]-benzannulation with boronic acids toward the synthesis of a diverse range of heterocyclic frameworks. Interestingly, benzannulation of [1,1′-biphenyl]-4,4′-diyldiboronic acid (**10**) with **1a** gave the resulting 2,2′-binaphthalene **11** in 72% yield (Scheme 4).

Scheme 4. Synthesis of Bis-naphthlene Derivative



A plausible mechanism for the present [4 + 2]-benzannulation is illustrated in Scheme 5. First, the MBH acetate **1a** undergoes a

Scheme 5. Plausible Reaction Pathway



palladium-catalyzed allylic substitution with **2a** to form (*Z*)-alkene[13] **3a** via a π-allyl palladium intermediate. Addition of DBU would facilitate the deprotonation to generate the intermediate **3b**, followed by 6-*exo*-*dig* carbocyclization and subsequent protonation provides **3c**. Finally, a 1,7-hydrogen shift driven aromatization would lead to the formation of benzannulated product **3aa**. The isolation of intermediate **3a** and its treatment with DBU/acetonitrile provided the product **3aa**, which supports that the palladium catalyst has no role in the cycloisomerization reaction.

In summary, a general strategy for the synthesis of substituted benzenes, polycyclic aromatic hydrocarbons, as well as benzene-fused heterocycles has been developed, starting from the reaction of MBH acetates of acetylenic aldehydes with aryl/heteroaryl or vinyl boronic acid. By means of the studied examples, the potential use of MBH acetates of acetylenic aldehydes as a C4-synthon was demonstrated in the construction of benzene ring through a [4 + 2]-annulation involving tandem allylic substitution/hydroarylative cycloisomerization reactions. The use of boronic acids as C2-synthon is an added advantage, due to

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their easy accessibility. Therefore, the disclosed method may find applications in the synthesis of not only aromatics and polyaromatics but also various other benzannulated products from the corresponding (hetero)aryl/vinylboronic acids. To the best of our knowledge, there is no such method described in the literature for the construction of benzene ring on a boronic acid unit.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, characterization details, and ^{1}H and ^{13}C NMR spectra of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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