Transition-Metal-Free C(sp^2)–C(sp^2) Cross-Coupling of Diazo Quinones with Catechol Boronic Esters

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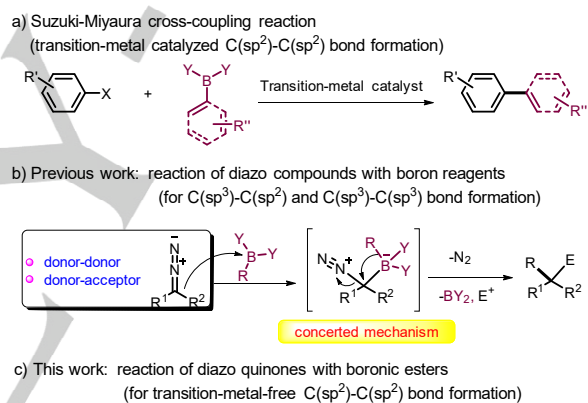
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Abstract: A transition-metal-free C(sp^2)-C(sp^2) bond formation reaction via the cross-coupling of diazo quinones with catechol boronic esters was developed. With this protocol, a variety of biaryls and alkenyl phenols were obtained in good to high yields under mild conditions. The reaction tolerates various functionalities and is applicable to the derivatization of pharmaceuticals and natural products. The synthetic utility of the method was demonstrated by the short synthesis of multi-substituted triphenylenes and three bioactive natural products, honokiol, moracin M and stemofuran A. Mechanistic studies and density functional theory (DFT) calculations revealed that the reaction involves attack of the boronic ester by a singlet quinone carbene followed by a 1,2-rearrangement via a stepwise mechanism.

Scheme 1. Suzuki-Miyaura cross-coupling reaction and the reactions of diazo compounds and boron reagents.

Introduction

Diazo quinones (also called quinone diazides) have attracted increasing attention due to their intriguing electronic and structural properties.[1-5] This class of compounds features a planar six-membered ring system with diazo, carbonyl and alkene groups in conjugation.[1] This feature makes diazo quinones prone to aromatization to phenols,[2-5] which are useful synthetic building blocks prevalent in natural products,[6] and endows them with reactivity similar to acceptor/acceptor diazocarbonyl compounds.[2a,e,4] While diazo quinones are an effective carbene source in a variety of transition-metal-catalyzed organic transformations,[2-5] as exemplified by Baran's work on Rh-catalyzed alkene functionalization with diazo quinones,[4] their application in C-C bond formation under transition-metal-free conditions remains limited.

Over the decades, the construction of C(sp^2)-C(sp^2) bonds has been dominated by transition-metal-catalyzed cross-coupling reactions.[7] Due to the constraints imposed on trace levels of metals in pharmaceuticals, there is growing interest in developing transition-metal-free C(sp^2)-C(sp^2) bond formation reactions, particularly those that take place under mild conditions. Current procedures often require harsh reaction conditions or
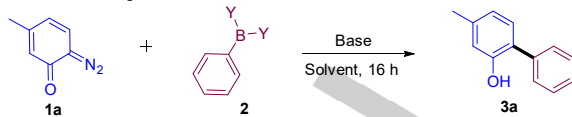
have limited substrate scope.[8] In this context, we turned our attention to transition-metal-free cross-coupling reactions of diazo compounds with organoboranes because of the efficiency, mild conditions and diversity of these reactions as well as the availability of the substrates.[9-11] The reactions usually involve attack of the boron reagents by the diazo compounds accompanied by 1,2-migration of the substituent from boron to the diazo carbon atom with simultaneous release of N_2 (Scheme 1b), and typically require strongly nucleophilic diazo compounds and/or electrophilic organoboranes for the formation of $C(sp^3)$-$C(sp^2)$ and $C(sp^3)$-$C(sp^3)$ bonds (Scheme 1b).[9-11] Because diazo quinones tend to aromatize, we envision that this class of compounds could be used for the construction of $C(sp^2)$-$C(sp^2)$ bonds. Nonetheless, both the nucleophilicity of diazo quinones[4] and the electrophilicity of catecholborane are relatively weak.[11k] Based on thermolysis or photolysis-induced decomposition of diazo quinones to give Wolff rearrangement products via reactive cyclohexadienone carbene **int-A** (Scheme 1c), a boron-trapped carbene might allow the generation of tetra-coordinated boron intermediate (Scheme 1c). In the literature, boron-trapped singlet quinone carbenes remain scarce.[12] Herein, we describe the first transition-metal-free $C(sp^2)$-$C(sp^2)$ cross-coupling reaction of diazo quinones and boronic esters to give biaryls and alkenyl phenols, both of which are useful synthetic building blocks and are prevalent in pharmaceuticals,[6,13] and this reaction proceeds via a stepwise mechanism (Scheme 1c).

Results and Discussion

As the Lewis acidity of organoboranes has a significant impact on their reaction with diazo compounds,[9,11k] we examined the reactions of a panel of phenylboranes with *ortho*-diazo quinone **1a** (Table 1, entry 1-7). Among the phenylboranes examined, catechol boronic ester **2g-1** gave the best yield of product **3a** (64%, entry 7). Other boron analogues, including boronic acid **2a**, boronic esters **2c** and **2d**, chloroborane **2e**, and trifluoroborate **2f**, were less effective (0-20% yields). Boroxine **2b** displayed similar reactivity, giving **3a** in 63% yield (entry 2). Neither decreasing nor increasing the reaction temperature improved the reaction. With **2g-1** as the coupling partner, a screening of the reaction conditions revealed that the use of a mixed solvent (MeCN/CH_2Cl_2) and K_2CO_3 as the base gave **3a** in the highest yield (84%, entry 8, for details see the Supporting Information). The higher solubility of catechol boronic ester in this mixed solvent system might be the reason for the improvement in the product yield. We next examined the effects of substituents on the catechol moiety. The mildly electron-donating 4,5-dimethyl groups improved the product yield to 94% and shortened the reaction time to 7 h (entry 10, **2g-3**). However, both strong electron-donating groups (OMe) and electron-withdrawing groups (Cl and F) had detrimental effects on the reactivity of catechol boronic ester, giving **3a** in low yields (entry 11-13).

With the optimized conditions in hand, the scope of the transition-metal-free $C(sp^2)$-$C(sp^2)$ cross-coupling reaction was examined. As depicted in Table 2, a broad range of aryl boronic esters reacted with diazo quinone **1a** to give biaryl products in moderate to high yields (50-96%). Electron-rich aryl boronic esters gave higher yields of the desired products than electron-deficient ones (**3b-3c** vs **3d-3i**). The reaction displayed excellent compatibility with halide groups (F, Cl, Br and I, **3d-3g**); the latter can be further manipulated via transition-metal catalysis. Boronic

Table 1. Screening of the reaction conditions [a-c]

| Entry	2	Base	Solvent	Temp [°C]	Yield [%]
1	2a	K_2CO_3	MeCN	55	0
2	2b	K_2CO_3	MeCN	55	63
3	2c	K_2CO_3	MeCN	55	20
4	2d	K_2CO_3	MeCN	55	0
5	2e	K_2CO_3	MeCN	55	0
6	2f	K_2CO_3	MeCN	55	0
7	2g-1	K_2CO_3	MeCN	55	64
8	2g-1	K_2CO_3	MeCN/DCM	55	84
9	2g-2	K_2CO_3	MeCN/DCM	55	70
10	2g-3	K_2CO_3	MeCN/DCM	55	94
11	2g-4	K_2CO_3	MeCN/DCM	55	<10
12	2g-5	K_2CO_3	MeCN/DCM	55	<10
13	2g-6	K_2CO_3	MeCN/DCM	55	49

[a] Conditions: 0.3 mmol **1a**, 0.9 mmol **2** and 0.3 mmol base in 3.0 mL of solvent. [b] Yield was determined by ^1H NMR analysis of the reaction mixture using CH_2Br_2 as an internal standard. [c] DCM = CH_2Cl_2.

esters bearing naphthyl and pyrenyl substituents reacted smoothly to give **3j** and **3k** in 80% and 75% yields, respectively. Heteroaromatics including carbazole, thiophene, pyridine and quinoline were compatible with the coupling reaction, giving the corresponding heterobiaryls in 50-75% yields (**3l-3o**).

The scope of the diazo quinones was also examined with **2g-3** as the coupling partner. As depicted in Table 2, various *ortho*-diazo quinones, including mono-, di- and tri-substituted diazo quinones, reacted efficiently with **2g-3** to give biaryl products in moderate to high yields (57-87%, **3p-3t**). It is worth noting that sterically demanding multi-substituted diazo quinone **1c** displayed good compatibility with the reaction, giving densely substituted arylphenol **3q** in high yield. For the reaction of *o*-diazo-tetrahydronaphthalenone with a naphthyl boronic ester, axially chiral biaryl **3u** was obtained in 65% yield. Thus, this protocol might provide an alternative approach for accessing this class of axially chiral biaryl compounds.[14]

Notably, this transition-metal-free cross-coupling reaction has the following features. 1) Performing the reaction under air affords an efficiency comparable to that of the reaction under N_2 (see examples **3a**, **3q**, and **3t**). 2) The reaction is effective for the derivatization of structurally complex bioactive

Table 2. Cross-coupling of diazo quinones with aryl boronic esters [a,b]
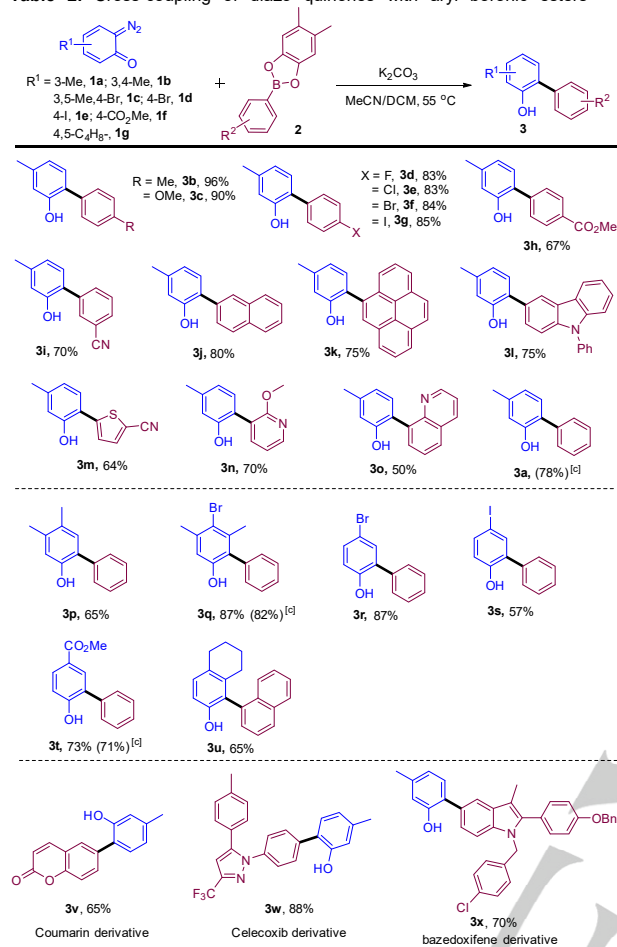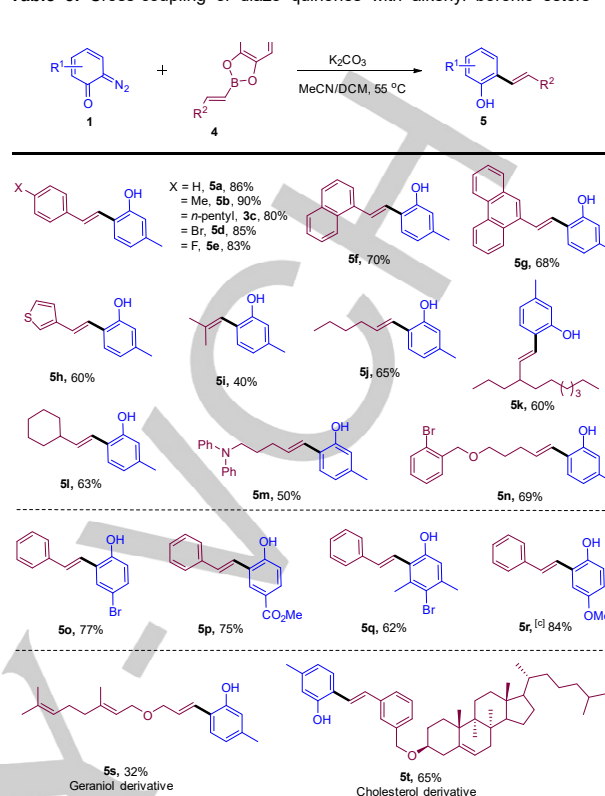

[a] Conditions: 0.3 mmol **1**, 0.9 mmol **2** and 0.3 mmol K$_2$CO$_3$ in 2.0 mL of MeCN and 1.0 mL of DCM. [b] Isolated yield. [c] Isolated yield under air conditions.

Table 3. Cross-coupling of diazo quinones with alkenyl boronic esters [a,b]

[a] Conditions: 0.3 mmol **1**, 0.9 mmol **4** and 0.3 mmol K$_2$CO$_3$ in 2.0 mL of MeCN and 1.0 mL of DCM. [b] Isolated yield. [c] From **1h** (R^1= 4-OMe).

compounds; for example, substrates containing coumarin, celecoxib and bazedoxifene reacted with **1a** to give new analogues **3v**, **3w** and **3x** in 65%, 88% and 70% yields, respectively (Table 2).

We next investigated the cross-coupling of diazo quinones with alkenyl boronic esters to synthesize alkenyl phenols. As depicted in Table 3, a variety of alkenyl phenols (**5a-5r**) were obtained in moderate to high yields (40-90%). Both electron-rich and electron-deficient styryl boronic esters gave the corresponding products in high yields (**5a-5e**). The reactions of **1a** with naphthyl-, phenanthrenyl- and thiophenyl-substituted alkenyl boronic esters proceeded with good yields (**5f-5h**). Alkyl-substituted alkenyl boronic esters were also reactive (**5i-5n**); various alkyl substituents including acyclic (linear and branched) alkyl, cyclic alkyl as well as amino- and ether-containing alkyl groups were tolerated in the reaction.

Various substituted *ortho*-diazo quinones were also examined in this coupling reaction with styryl boronic ester. As depicted in Table 3, alkenyl phenols were obtained in good to high yields (62-84%, **5o-5r**). The alkenyl boronic esters containing complex natural products such as geraniol and cholesterol underwent this cross-coupling reaction, affording the desired products in yields of 32% and 65%, respectively (**5s-5t**).

Typically, diazo quinones have two resonance structures, **A**

and **B** (Scheme 2).[1a] As a base (K$_2$CO$_3$) is needed for the reaction, form **B** would be responsible for the reaction with catecholboronic ester to give boronate complex **C,** as depicted in Scheme 2. We performed the experiment by adding 3 equiv of **2g-1** and 1 equiv of K$_2$CO$_3$ into a CD$_3$CN solution of **1a** and monitored the reaction by ¹H NMR spectroscopy. Notably, the signals of **H$_1$**, **H$_2$** and **H$_3$** shifted downfield, but those of **H$_4$** and **H$_5$** shifted upfield (Scheme 2), which was attributable to the formation of boronate complex **C**.

We propose that the B-O interaction might facilitate the generation of the quinone carbene. This is because generating a carbene through the direct thermolysis of a diazo quinone commonly requires a high temperature (above 70 °C),[15] and the reaction of donor-type TMS diazomethane (TMSCHN$_2$) with **2g-1** would require heating (60 °C) over an extended time period (15 h),[11k,16] unlike the milder reaction conditions reported in this work. The addition of 3 equiv of **1a** significantly inhibited the reaction, leading to a low product yield (14%) and increased generation of the phenol byproduct (13%) (Scheme 3a). This suggests a significant trapping of **2g-1** by the excess **1a** via B-O bond formation, making **2g-1** less available for trapping free carbenes. When *para*-diazo quinone **1l** was used, no reaction was observed (Scheme 3b). This might be attributable to weaker effect of *para* B-O interaction on C-N bond of diazo quinone due to decreased inductive effect compared to *ortho*-diazo quinone.

Changing the substituent on the diazo quinone or the phenyl group of the aryl boronic ester from CH$_3$ to an electron-withdrawing CO$_2$Me group facilitated the reaction, but the difference was approximately 2-fold, as depicted in Schemes 4a and 4b. These experiments are consistent with mechanism
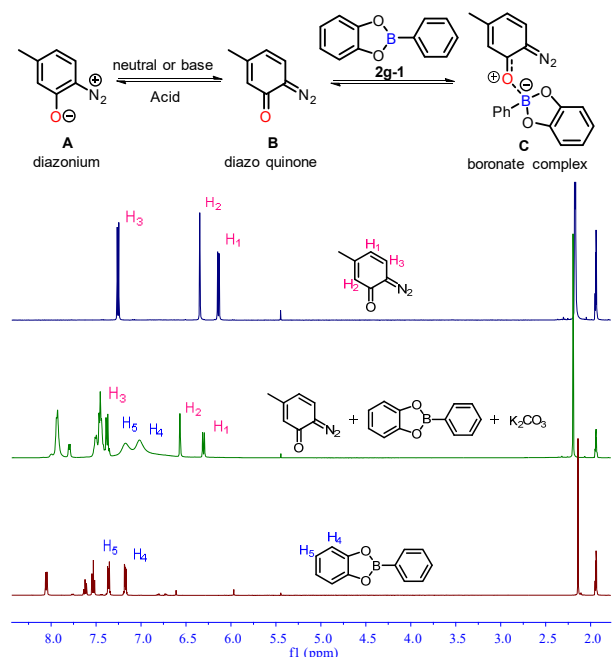
Scheme 2. Reaction performed in CD₃CN at 298 K.
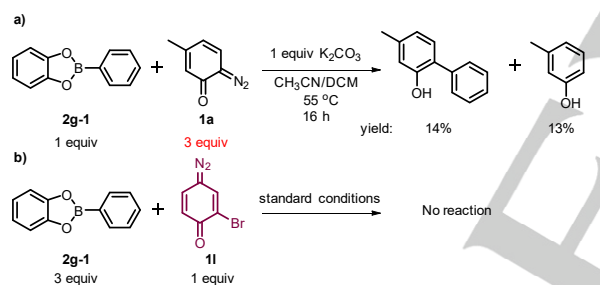
Scheme 3. Mechanistic studies on B–O bonding experiments.
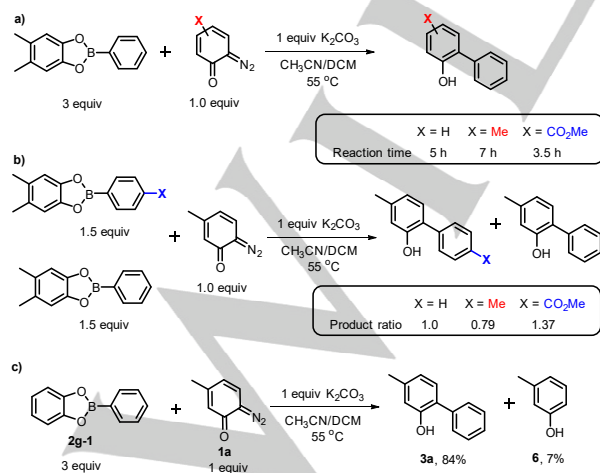
Scheme 4. Control experiments.

shown in Figure 2, in which electron-withdrawing group on diazo quinone or boronic ester will facilitate N_2 extrusion of diazo quinone to form quinone carbene [17] or trapping of singlet carbene intermediate, respectively. For the reaction of diazo quinone **1a** and aryl boronic ester **2g-1**, byproduct phenol **6** was generated in 7% yield (Scheme 4c), indicative of the involvement of the carbene intermediate.[18]

DFT calculations were employed to further explore the reaction mechanism using diazo quinone **1k** and aryl boronic ester **2g-1** as substrates. We first examined the commonly proposed pathway that involves nucleophilic attack of the boronic ester by the diazo quinone and subsequent 1,2-rearrangement. The concerted N_2 extrusion and 1,2-rearrangement of transition state **TS(C-B)** was calculated to have an activation energy of 42.0 kcal/mol (Figure 1), which is not compatible with the experimental conditions described in this work. We also investigated the coordination of **2g-1** with the carbonyl oxygen and the diazo group of diazo quinone **1k** and subsequent 1,4-rearrangement of transition states **TS(O-B)** and **TS(N-B),** as shown in Figure 1. These two processes require activation energies of 46.4 kcal/mol and 63.6 kcal/mol, respectively. The high energy barriers for the rearrangements of transition states **TS(C-B)**, **TS(O-B)** and **TS(N-B)** indicate that these mechanisms are unfavorable under the present reaction conditions. Interestingly, we found that the energy barrier for the generation of the free carbene from diazo quinone **1k** is 28.0 kcal/mol (Figure S2), which is much lower than those of the concerted processes (**TS-1** in Figure S1). This process can be further facilitated by prior coordination of the boron to the diazo quinone with a $\Delta G^{\ddagger}$ of 24.7 kcal/mol (**TS-2** in Figure 2). The calculation of the complex of **1k** and **2g-1** showed that the C-N bond in **1k** is stretched from 1.33 Å to 1.35 Å. The in situ-generated singlet carbene is highly reactive and is rapidly trapped by another equivalent of boronic ester **2g-1** to form boronate intermediate **Int-2** (Figure 2). It is also possible that the transient carbene **¹Int-2'** undergoes intersystem crossing (ISC) to generate triplet species **³Int-2'** with delocalized spin density on the α-carbon and the catechol moiety (Figure S3), which is a possible resonance structure of a triplet carbene. Although **³Int-2'** may give rise to phenol byproducts, as shown in Scheme 3, ISC is inefficient under the present conditions. The subsequent barrier-less 1,2 migration of the phenyl group and B−O dissociation give cyclohexadienone **Int-3**. The aromatization of **Int-3** to **Int-4** has a moderate barrier of 12.7 kcal/mol, and **Int-4** is then hydrolyzed upon work-up with MeOH/H₂O to give the coupling product. Overall, the stepwise mechanism results in the insertion of the carbene center into the Ar-B bond with the generation of the transient free carbene intermediate as the rate-determining step.

To illustrate the synthetic utility of the developed reaction, we used it to synthesize multi-substituted triphenylenes and three natural products, honokiol, stemofuran A and moracin M (Scheme 5-7). Triphenylenes are a class of important polycyclic aromatic hydrocarbons with great potential in optoelectronic materials due to their planar rigidity and superconjugation.[19] In this work, the cross-coupling of diazo quinones and boronic esters was employed as a key step in the synthesis of multi-substituted triphenylenes. The treatment of **1a** with boronic ester **2g-3** under the standard conditions gave biaryl **3a** in 94% yield. The presence of the *ortho*-hydroxy group of **3a** allows the construction of *ortho*-terphenyl **9a** in high yield through a Suzuki-Miyaura cross-
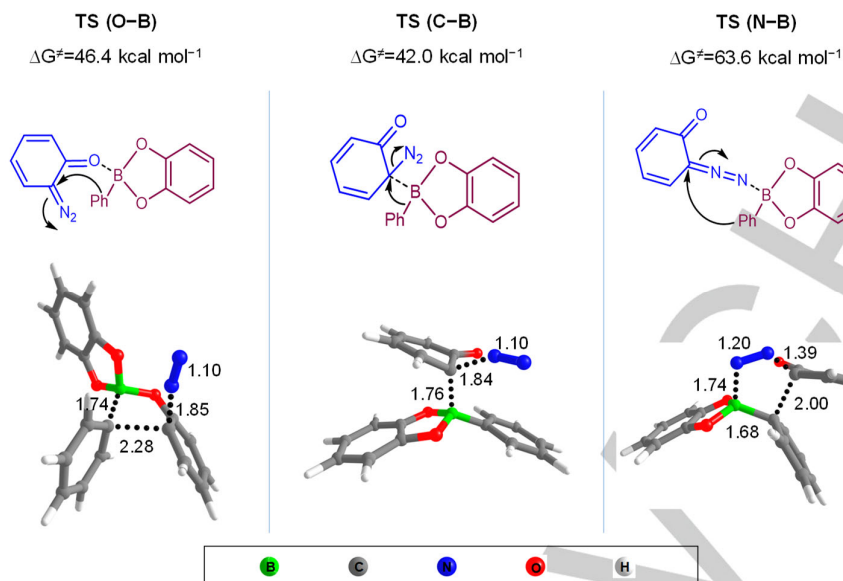
Figure 1. Transition state geometries and associated activation energies for the cross-coupling of **1k** and **2g-1** via a concerted N$_2$ extrusion and benzene transfer process calculated at the M06-2X-D3/6-311++G**/PCM//B3LYP-D3/6-311G*/PCM level of theory. Critical bond lengthens are given in Å.
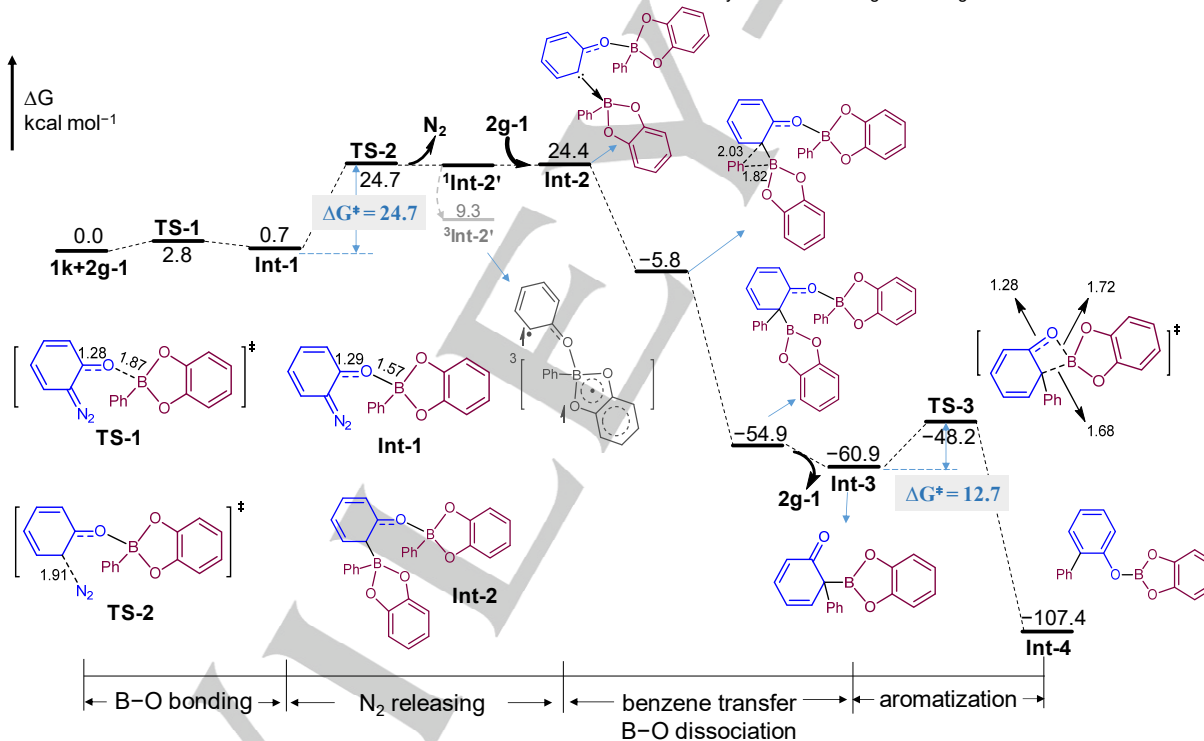

Figure 2. Energy profiles for the cross-coupling of **1k** and **2g-1** via boron-stabilized carbene calculated at the M06-2X-D3/6-311++G**/PCM//B3LYP-D3/6-311G*/PCM level of theory.

coupling reaction, the product of which underwent facile oxidative cyclization at room temperature to give desired triphenylene **10a** in 92% yield, and the overall yield of the four-step synthetic route was 72%. Similarly, multi-substituted triphenylene **10y** was prepared in an overall yield of 53% from **1a**, demonstrating that the method can be used for the rapid and efficient construction of triphenylene analogues. Honokiol, a neolignan isolated from the bark of Magnolia officinalis, displays various biological activities,

including anticancer and antiviral properties.[20] The reaction of diazo quinone **1i** with boronic ester **11** gave biaryl **12** in 73% yield, and **12** underwent a Claisen rearrangement to give honokiol in 90% yield. No metal catalysts were used in this two-step synthesis of honokiol, and the overall yield was 66%.

2-Substituted benzo[b]furans are common structural motifs in natural products and pharmaceuticals.[21] Their synthesis mainly relies on transition-metal-catalyzed cross-coupling/cyclization

reactions of 2-halophenols with terminal alkynes.[22] By employing our diazo quinone and boronic ester coupling reaction as a key step, we developed a transition-metal-free synthetic route to this class of compounds. As shown in Scheme 7, the reaction of diazo quinone **1j** with boronic ester **13** gave coupling product **14a** in 80% yield, which then underwent I₂-catalyzed cyclization and BBr₃-mediated demethylation, giving naturally occurring benzo[b]furan moracin M in an overall yield of 63% for three steps. Likewise, stemofuran A was prepared with a similar efficiency.
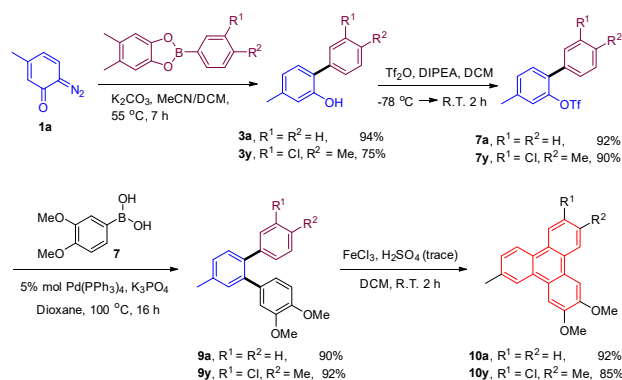
Scheme 5. Synthesis of multi-substituted triphenylenes.
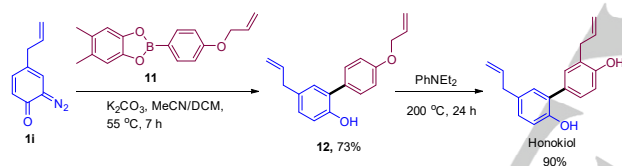
Scheme 6. Synthesis of honokiol.
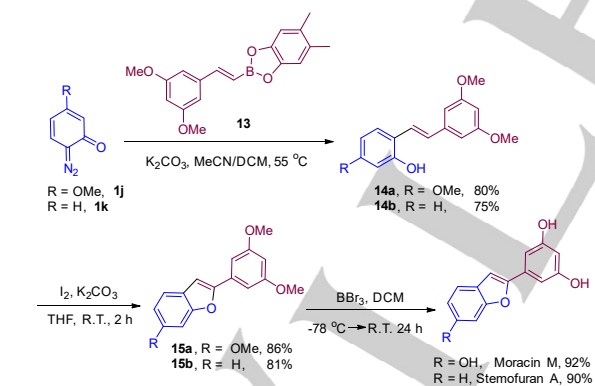
Scheme 7. Synthesis of stemofuran A and moracin M.

Conclusion

In summary, we have developed a transition-metal-free C(sp²)-C(sp²) bond forming reaction via the cross-coupling of diazo quinones with catechol boronic esters. The reaction provides efficient access to a variety of biaryls and alkenyl phenols in good to high yields under mild conditions and is applicable to the derivatization of bioactive organic compounds. The reaction is tolerant of various functional groups, including C(sp²)-halides (F, Cl, Br, and I), esters, alkenes, amines, ethers, cyano groups and heteroaromatics. The cross-coupling reaction has been successfully used in the short synthesis of multi-substituted triphenylenes and three natural products, honokiol, moracin M and stemofuran A. Mechanistic studies and density functional theory (DFT) calculations revealed that the reaction involves attack of a boronic ester by a singlet quinone carbene followed by a 1,2-rearrangement via a stepwise mechanism.

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Entry for the Table of Contents

RESEARCH ARTICLE

Without transition metal catalysts, diazo quinones undergo cross-coupling with catechol boronic esters to give a variety of biaryls and alkenyl phenols in up to 96% yield under mild conditions. The reaction is applicable to the synthesis of multi-substituted triphenylenes and natural products honokiol, moracin M and stemofuran A. DFT calculations revealed a stepwise mechanism involving attack of the boronic ester by a singlet quinone carbene.

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Transition-Metal-Free C(sp^2)–C(sp^2) Cross-Coupling of Diazo Quinones with Catechol Boronic Esters