



Cu^(I)/Pd⁽⁰⁾ cooperative catalysis enabled regioselective C(sp²)-carboration of 1,3-diyne[†]

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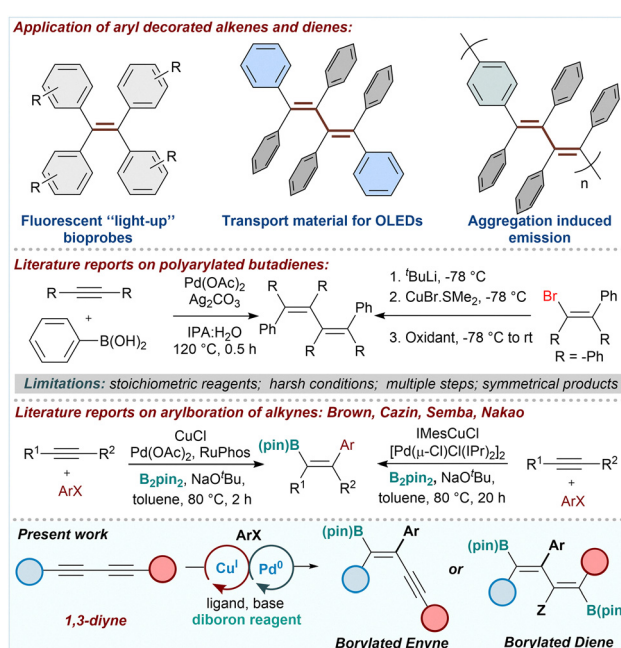
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We present a regioselective C(sp²)-carboration of 1,3-diyne using Cu(I)/Pd(0) cooperative catalysis, enabling access to a diverse range of conjugated aryl-substituted boryl enynes. Furthermore, sequential proto-/carbo-/di-boration strategies afforded highly conjugated multi-boron-substituted dienes. Cross-coupling of the boron end groups facilitated the modular synthesis of highly conjugated enynes and dienes with intriguing properties.

Aryl-decorated enynes and dienes' extended π -conjugation across the backbone imparts interesting photophysical properties, making them desirable candidates for optoelectronics and sensor applications. Multiarylated olefins such as tetraphenylethylene (TPE) and its derivatives show aggregation-induced emission (AIE), enabling their wide application as chemical and biosensing AIEgens (Scheme 1).¹ There is a recent surge of interest in TPE-based soft materials possessing remarkable optical properties.² Multi-arylated-1,3-butadienes (MAB), the higher homologs of TPE, show distinctive AIE with applications in multicolor switching display devices and in sensing toxic metal ions and explosives (Scheme 1). The AIE properties of MABs originate from the restricted intramolecular rotation mechanism.³ However, the perarylation of butadiene enhances its photo-lability to give hydronaphthalene.⁴

Miura pioneered the Pd⁰-catalyzed 2:2 coupling approach to MABs, employing terminal alkynes and boronic acids (Scheme 1).⁵ The Spring and Deng groups disclosed the reductive elimination of densely arylated divinyl metal intermediates mediated by oxidants to access MABs.⁶ The Brown group reported a Cu^I-catalyzed C(sp²)-carboration of internal alkynes using ArI.⁷ Later, the Cazin, Semba, and Nakao group employed cooperative Cu(I)/Pd(0) catalysis for the C(sp²)-carboration of internal alkynes and aryl halides (Scheme 1).⁸ C(sp²)-carboration


 Scheme 1 Prior art and present work on C(sp²)-carboration.

has been applied to alkyne or enynes to give 1,3-dienes.⁹ In alignment with our ongoing exploration of the regio- and stereo-selective functionalization of 1,3-diyne,¹⁰ we envisaged C(sp²)-carboration of 1,3-diyne employing Cu(I)/Pd(0) cooperative catalysis as a streamlined route to diborylated MABs. The two boron end groups provide substantial versatility in incorporating various functional groups, including aryl groups of varying stereoelectronic properties (Scheme 1). The ability to precisely modulate the nature of the aryl groups will enable fine-tuning of the fluorophoric properties and the aggregation modes of MABs. Recently, Wang's group reported a Ni-catalyzed alkyne dimerization strategy to access MABs.¹¹ The Song group reported C(sp)-carboration of 1,3-diyne.¹² However, there are no reports on the C(sp²)-carboration of 1,3-diyne, providing the flexibility of multiple boron handles installed regioselectively. Here, we report

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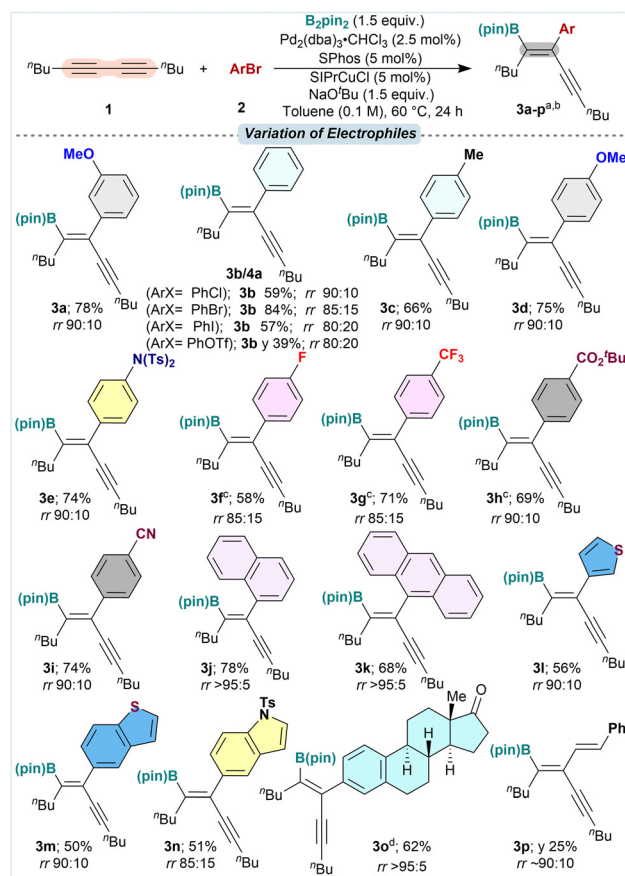
the C(sp²)-carboration of 1,3-diyne employing Cu(I)/Pd(0) cooperative catalysis to achieve boryl enynes and diboryldienes (Scheme 1).

We began our investigation by using dibutyl buta-1,3-diyne (**1a**) as the standard substrate with B₂pin₂ and 3-bromoanisole as the aryl electrophile. Various Pd⁰/phosphine and Cu(I)L_n combinations were studied to facilitate the desired arylboration of **1a** (see ESI,† for details). The best results were obtained with SIPrCuCl/Pd₂(dba)₃·CHCl₃/SPhos catalyst combination, operating cooperatively to deliver the desired product **3a** in 81% NMR yield with rr 90 : 10 (isolated yield: 78%; entry 1, see ESI,† page S6). In the absence of either Pd⁰ or Cu^I catalyst, **1a** remained unreacted, suggesting the cooperative involvement of both metal complexes in the catalytic cycle. Screening other Pd sources showed moderate reactivity (y 59–75%; entry 3). Bases like KO^tBu and Cs₂CO₃ were incompatible for arylboration, delivering poor yields of **3a** (0–30%; entry 4). A variety of phosphines like Johnphos, CyJohnphos, dppf, dppe, PCy₂Ph, and P(*p*-anisyl)₃ were studied; however, the desired product **3a** was obtained only in moderate yields and regioselectivity (y 24–59%; rr up to 80 : 20, entry 5, see ESI,† page S6).

Using the optimized conditions, the scope of aryl halides was studied for the arylboration using **1a** as the standard substrate. The effect of halides/pseudohalides on the arylboration was investigated by subjecting Ph–Cl, Ph–Br, Ph–I, and Ph–OTf under standard conditions. Among the aryl halides, bromobenzene provided the corresponding product **3b** in 84% isolated yield with rr 85 : 15 (Table 1). Other electrophiles bearing –Cl, –I, and –OTf resulted in inferior yields of the arylboration products (y 39–59%; rr ranging from 80 : 20 to 90 : 10). Then, the substituent effects on bromobenzene were studied using **1a** under standard conditions. Electron-rich aryl bromides containing functional groups like *meta*-OMe (**2a**), –Me (**2c**), *para*-OMe (**2d**), and *para*-(NTs)₂ (**2e**) provided the corresponding products **3a**, **3c–e** in 66–78% yields with 90 : 10 regioselectivity, respectively. Under the standard conditions, aryl bromides bearing electron-withdrawing substituents like –F, –CF₃, –CO₂^tBu, and –CN, all delivered the product **3f–3i** in good yields (58–74%; rr between 85 : 15 and 90 : 10). With polycyclic aryl bromides like 2-naphthyl-**(2j)** and 9-anthracenyl bromide (**2k**) as partners, the reaction showed excellent yields of **3j** and **3k** with improved regioselectivity (78 and 68%; rr > 95 : 5). The present conditions could smoothly accommodate heteroaryl bromides like 3-bromothiophene, 5-bromobenzothiofene, and tosyl-protected 5-bromoindole to result in the corresponding heteroaryl-substituted borylenynes **3l–3n** in 50–56% yield, and rr ranging between 85 : 15 and 90 : 10. Estrone-derived aryl triflate (**2o**), which was easily prepared from triflation of the phenolic moiety of estrone, delivered the corresponding borylenyne **3o** in 62% yield and rr > 95 : 5. Under the standard conditions, with styryl iodide as a C(sp²)-electrophile, the corresponding alkynyl diene boronate **3p** was obtained in moderate yield (25%; Table 1).

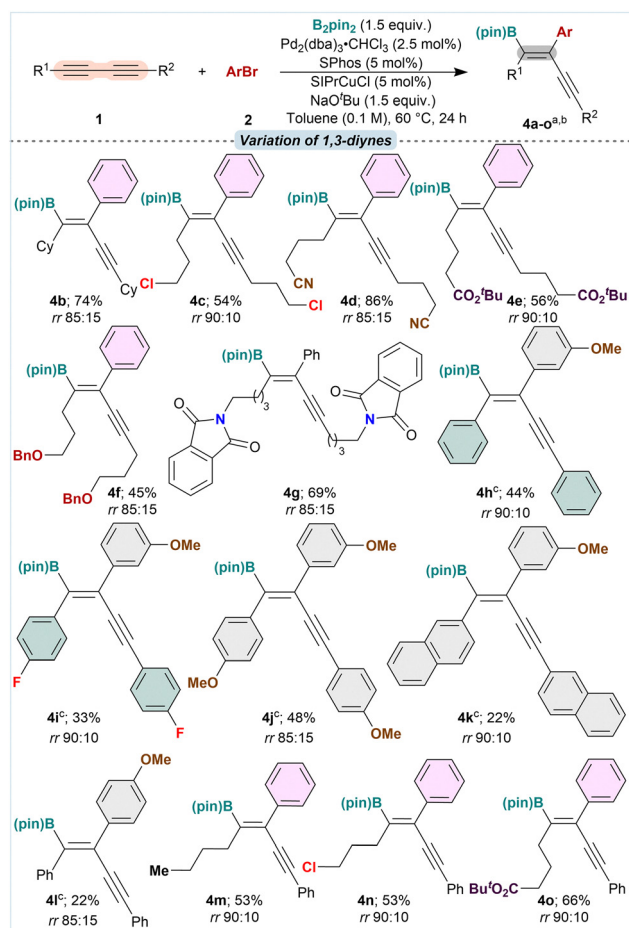
Then, we examined the scope of 1,3-diyne under standard conditions with bromobenzene as the C(sp²)-electrophiles. 1,3-Diyne bearing simple alkyl groups like –ⁿBu (**1a**) and –Cy (**1b**)

Table 1 Substrate scope of Ar–X for C(sp²)-carboration



^a Standard conditions: diyne **1** (1 equiv.), Pd₂(dba)₃·CHCl₃ (2.5 mol%), SPhos (5 mol%), SIPrCuCl (5 mol%), NaO^tBu (1.5 equiv.), ArBr (1.5 equiv.), toluene (0.1 M), 60 °C, 24 h. ^b rr were determined using ¹H NMR. ^c ArI was used. ^d ArOTf was used.

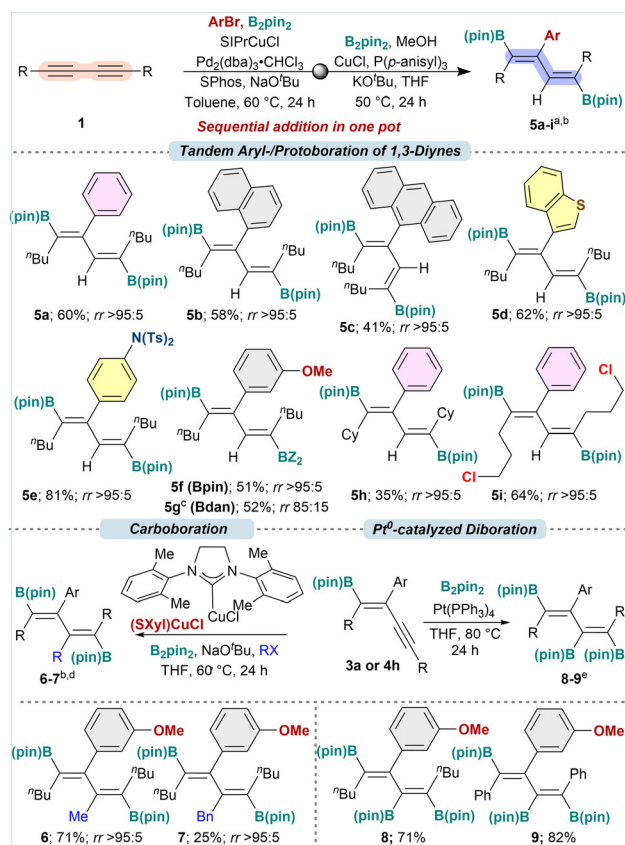
reacted smoothly with bromobenzene and B₂pin₂ under the cooperativity of Cu(I)/Pd(0) catalysts to provide the corresponding arylboration products **4a** and **4b** in 84 and 74% yields, respectively (rr 85 : 15). 1,3-Diyne with alkyl group bearing pendant functionalities like –Cl, –OBn, –CN, –ester, and –phthalimide groups demonstrated excellent functional group tolerance, delivering the arylboration products **4c–g** in 45–86% yields and rr ranging between 85 : 15 to 90 : 10. Diaryl-1,3-diyne under the standard arylboration conditions resulted in a mixture of products due to uncontrolled side reactions with the boron moiety in the desired product. Only a trace amount of the products was observed with these substrates. A quick solvent and base screening, retaining the rest of the optimized conditions, identified DCM as a better choice of solvent for C(sp²)-carboration of diaryl-1,3-diyne substrates. Diphenyl-1,3-diyne with *m*-bromoanisole as the C(sp²)-partner, under the modified conditions in DCM, provided the desired arylboration product **4h** in 44% yield and rr 90 : 10. 1,3-Diyne with aryl groups bearing functionalities with diverse electronic properties like –naphthyl, *p*-fluorophenyl, and *p*-anisyl also provided the desired arylboration products **4i–k**, albeit in low to moderate yields

Table 2 Substrate scope of 1,3-diyne for C(sp²)-carboration

^a Standard conditions from Table 1. ^b rr from ¹H NMR. ^c Using DCM (0.10 M) at 50 °C.

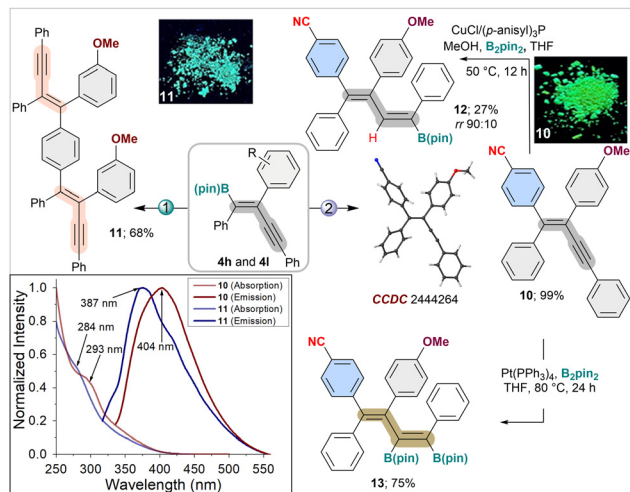
(22–48%) and rr ranging between 85:15–90:10. Using 4-bromoanisole as the C(sp²)-partner, **1h** provided the desired product **4l** in 22% yield and rr 85:15. Surprisingly, with unsymmetrically substituted 1,3-diyne bearing an alkyl group on one side and an aryl group on the other, *viz.*, **1m** smoothly reacted under the standard conditions in toluene to provide the product **4m** in 53% yield and rr 90:10. The boryl moiety was transferred exclusively at the alkyl attached carbon on the alkyne functionality. The reaction showed a similar trend with substrates bearing alkyl groups with pendant –Cl and –ester groups providing the corresponding products **4n** and **4o** in 53 and 66% yields with rr 90:10, respectively (Table 2).

After achieving arylboration of 1,3-diyne to obtain boryl enynes **3** and **4**, we aimed to synthesize aryl-decorated 1,4-diboryl-1,3-dienes directly *via* a second proto-/carboration. Based on our previous studies on Cu(I)-catalyzed proto- and carboration of boryl enynes, we explored a tandem arylboration/protoboration cascade using the developed Cu(I)/Pd(0) cooperative catalysis. The first arylboration would require catalyst cooperativity, whereas the second protoboration step could proceed with the help of Cu(I)-catalyst. Our initial

Table 3 Sequential C(sp²)-carbo/protoboration of 1,3-diyne

^a Standard conditions: (1) standard conditions from Table 1; (2) CuCl (5 mol%), P(*p*-anisyl)₃ (12.5 mol%), B₂pin₂ (2 equiv.), KO^tBu (50 mol%), MeOH (4 equiv.), THF (1 mL for 0.15 mmol of **1**), 50 °C, 18 h. ^b rr was determined using ¹H NMR. ^c KO^tBu (1 equiv.) was used. ^d Enyne **3a** or **4h** (1 equiv.), SXylCuCl (10 mol%), B₂pin₂ (2 equiv.), RX (1.5–6 equiv.), NaO^tBu (1.5 equiv.), THF (0.15 M), 60 °C, 48 h. ^e Enyne **3a** or **4h** (1 equiv.), Pt(PPh₃)₄ (2 mol%), B₂pin₂ (1.2 equiv.), THF (0.1 M), 80 °C, 24 h.

attempts with **1a** failed, yielding only arylbored product **3b**. Further investigation showed that SIPrCuCl was ineffective for protoboration, necessitating a Cu(I)/phosphine catalyst system in THF (see ESI[†]). The tandem reactivity was achieved by converting **1a** to **3b** under our arylboration conditions with SIPrCuCl, then adding CuCl/P(*p*-anisyl)₃, B₂pin₂, KO^tBu, MeOH, and THF, yielding **5f** in 51% with rr >95:5 (Table 3). The minor regioisomers were undetectable due to further side reactions generating multi-arylated dienes in the presence of ArX and Pd⁰. These tandem conditions were tested using higher aromatic homologs of ArBr, like naphthyl-, anthracenyl-, and benzothiophenyl bromides. In all cases, the reaction provided the expected penta-substituted 1,4-diboryl-1,3-dienes **5b–d** in 41–62% yields, respectively, with excellent regioselectivity. Other functional groups, such as *para*-N(Ts)₂ and *meta*-OMe on the aryl partner, conveniently transformed to the desired diboryl diene **5e–f** in 81 and 51% yields with rr >95:5. Further, we envisaged the introduction of an orthogonally protected boron moiety by sequentially adding B₂pin₂ for arylboration, followed by a mixed diboron reagent, pinB-Bdan, for the



Scheme 2 Synthetic utility of **4h** and **4l** (1) **4h** (2.2 equiv.), Pd(OAc)₂ (10 mol%), SPhos (20 mol%), 1,4-diiodobenzene (1 equiv.), KOH (6 equiv.), THF, 70 °C, 24 h. (2) **4l** (1 equiv.), Pd(OAc)₂ (5 mol%), SPhos (10 mol%), 4-iodobenzonitrile (1.2 equiv.), KOH (3 equiv.), THF, 70 °C, 24 h.

protoboration. Following the above sequence of addition of the diboron reagent, the desired product **5g** was obtained in 51% yield with rr 85 : 15. **5g** would be a versatile intermediate for the orthogonal functionalization on the 1,3-diene *via* iterative cross-coupling. Other representative diynes substrates like **1b** and **1c** also underwent tandem aryl-/protoboration with B₂pin₂ smoothly to provide **5h** and **5i** in 35 and 64% yields with rr > 95 : 5, respectively.

Then, we attempted a double arylboration and aryl-/alkylboration in one pot by simply doubling the reagent amounts. However, these reactions stopped after the first arylboration, giving the arylbored enynes. Even the stepwise diarylboration failed due to steric strain in achieving hexa-substituted diene. Pleasingly, the arylbored enynes **3a** and **4h** could undergo another round of alkylboration and diboration to provide hexasubstituted dienes. Applying the previously established conditions,^{10d} with Me-I and Bn-Br as C(sp³)-electrophiles, **3a** was converted to the desired hexa-substituted 1,4-diboryl-1,3-diene **6** and **7** in 71 and 25% yields with rr > 95 : 5. Further, a Pt(0)-catalyzed diboration^{10d} of **3a** and **4h** provided 1,3,4-triboryl-1,3-dienes **8** and **9** in 71 and 82% yields.

Having demonstrated the aryl boration of 1,3-diynes, the synthetic utility of the resultant arylated borylenyne **4h** and **4j** was demonstrated. Compound **4l** was successfully coupled with 4-iodobenzonitrile to get the desired donor-acceptor-based tetrasubstituted enyne **10** in 99% yield. Similarly, using 1,4-diiodobenzene as a coupling partner, **4h** delivered a highly conjugated arylated enyne **11** in 68% yield. Compounds **10** and

11 exhibited solid-state fluorescence under UV light (356 nm). The fluorescence emission maxima for **10** and **11** in chloroform appeared at 404 nm and 387 nm. Then, with compound **10**, protoboration and diboration reactions delivered the desired products **12** and **13** in 27 and 75% yields, highlighting the versatility of the enynes and dienes (Scheme 2).

In conclusion, aryl-decorated enynes and dienes hold an illustrious position due to their applications in biological systems and cutting-edge technology. The present approach provides access to aryl-decorated enynes and dienes boronates. These compounds serve as direct synthons for MABs, providing complete control over the selection and introduction of functional groups. The ability to functionalize the enyne backbone with donor-acceptor aryl substituents using our methodology facilitated the solid-state fluorescence properties. The work establishes a modular synthetic platform for the design of functionally diverse boron-containing molecules.

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Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

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