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Pd/Cu/TsOH-cocatalysed direct synthesis of 1,3-dienyl-2-boronic acid: a new reagent for homoallenylboration

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The homoallenylboration of carbonyls and imines using 1,3-dienyl-2-boron reagents is an appealing strategy for accessing synthetically valuable homoallenyl alcohols and amines. Nevertheless, existing reactive 1,3-dienyl-2-boron reagents generally suffer from drawbacks such as insufficient stability, limited structural diversity, or laborious synthesis and handling, which have significantly impeded the application of this transformation in synthetic chemistry. In this study, we present a novel class of 1,3-dienyl-2-boronic acids that are specifically designed for homoallenylboration. These reagents show sufficient stability and can be efficiently synthesized from structurally diverse and readily available 2,3-allenols *via* a ternary cocatalytic system involving palladium, copper, and TsOH. Moreover, preliminary investigations demonstrate that these 1,3-dienyl-2-boronic acids exhibit high reactivity towards both carbonyls and imines in the homoallenylboration reaction without the need for any additional catalyst, thereby establishing them as promising reagents for such transformations.

Introduction

1,3-Dienyl-2-boron reagents serve as important building blocks in synthetic chemistry, and numerous transformations based on these reagents have been developed.[1] Among them, the Diels–Alder and Suzuki–Miyaura cross-coupling reactions represent the most well-established synthetic applications.[1a–e] In contrast, the use of 1,3-dienyl-2-boron reagents as nucleophiles in homoallenylation reactions[2] with carbonyls and imines remains underdeveloped,[3] even though this transformation offers an attractive route to synthetically valuable homoallenyl alcohols[4] and amines[2a,5] (Fig. 1a). Compared to conventional allylboration, a significant challenge in homoallenylboration stems from the conversion of the conjugated diene motif in the 1,3-dienyl-2-boron reagent into an energetically disfavoured allene moiety[6] in the product through the Zimmerman–Traxler transition state (Z.–T. TS). To effectively reduce the activation energy (E_a) and thereby facilitate the process, previous studies have predominantly concentrated on employing highly Lewis acidic boranes,[3b,d–f] which create robust boron–carbonyl oxygen (B–O=C) or boron–iminyl nitrogen (B–N=C) interactions and force a compact Z.–T. TS. For example, the Soderquist group employed chiral 1,3-dienyl-2-borabicyclo[3.3.2]decanes for the asymmetric synthesis of homoallenyl alcohols and amines through chirality transfer reactions with aldehydes and imines (Fig. 1b).[3d,f] However, these boranes are often unstable, challenging to synthesize, and difficult to handle, which severely limit their synthetic utility in homoallenylboration. Recently, we have utilized Aggarwal's strategy[7] to convert readily available yet chemically inert 1,3-dienyl-2-boronic acid pinacol esters (1,3-dienyl-2-Bpins) into the strongly Lewis acidic 1,3-dienyl-2-borinic species *in situ*, enabling a circuitous homoallenylboration reaction with aldehydes and ketones (Fig. 1c).[3a] Nevertheless, the requirement for harsh reagents (*n*BuLi and TFAA) and demanding reaction conditions not only complicates experimental operation but also reduces the step and atom economy. Therefore, the design and synthesis of novel 1,3-dienyl-2-boron reagents that are readily accessible, structurally diverse, and convenient to use in homoallenylboration reactions are of significant interest to the synthetic community.

Boronic acids are widely used in synthetic chemistry due to their heightened stability and remarkable versatility.[8] A particularly notable characteristic is their ability to undergo reversible trimerization, forming boroxines. Leveraging this behaviour, Szabó and co-workers have demonstrated that

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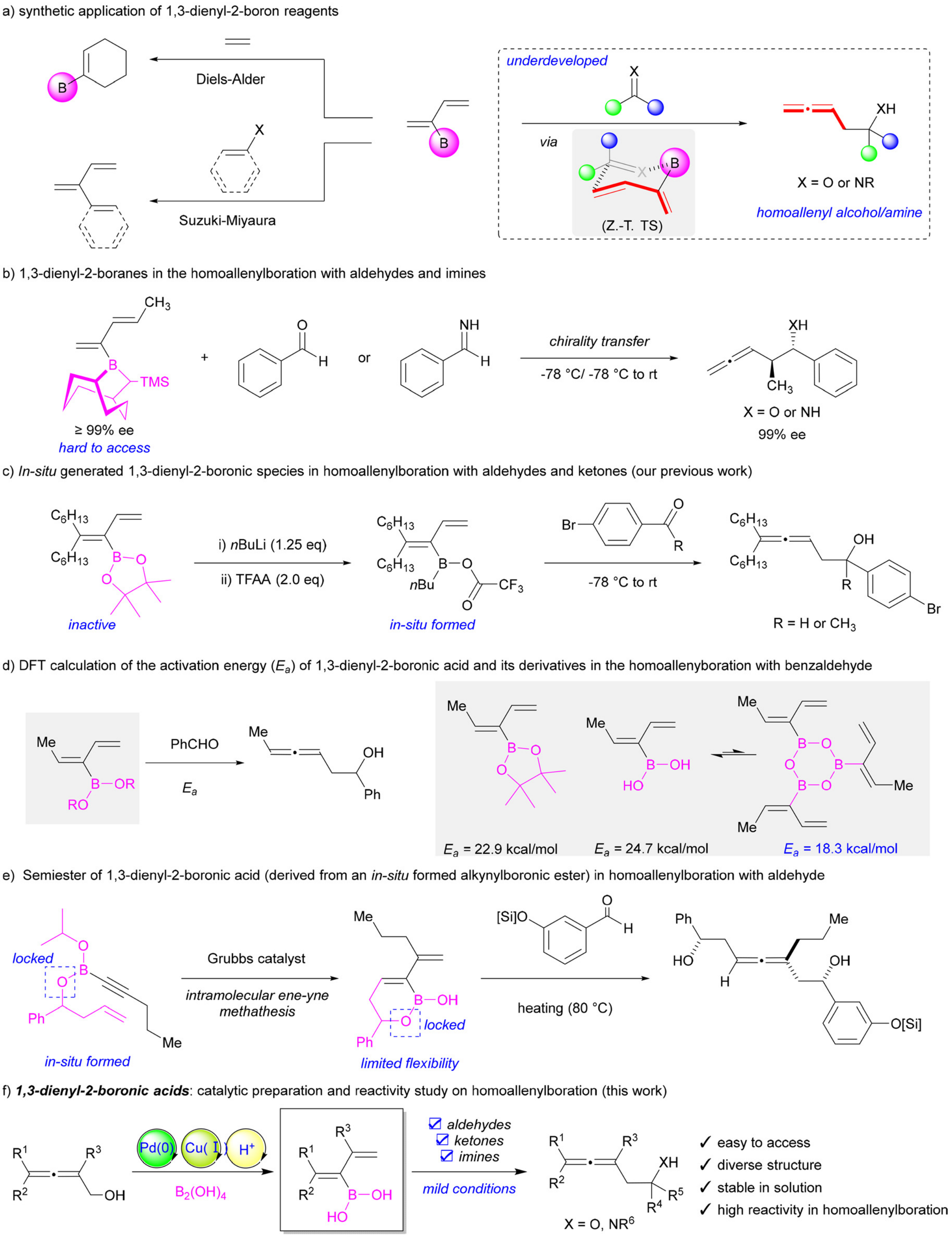


Fig. 1 1,3-Dienyl-2-boron reagents in homoallenylboration.

allylboronic acids exhibit enhanced reactivity toward ketones and imines compared to their pinacol ester analogues in allylboration.[9] DFT calculations further verified that *in situ* formation of allylboroxine in the reaction significantly reduces the activation energy.[9b,10] Inspired by these findings and supported by our preliminary DFT calculations (Fig. 1d, see the SI for more details, Fig. S1–S3), we hypothesized that 1,3-dienyl-2-boronic acid could serve as a promising candidate for homoallenylboration reactions with a wide range of carbonyls and imines, facilitated by a similar trimerization process. Indeed, a structurally specific semiester of 1,3-dienyl-2-boronic acid has shown moderate reactivity toward aldehydes under heating conditions in homoallenylboration (Fig. 1e).[11] However, the structural limitations intrinsically associated with its synthesis *via* intramolecular ene–yne metathesis severely constrain the broad utility. Furthermore, the reactivity of the semiester of boronic acid towards ketones and imines remains unclear. In this paper, we report our achievements in the catalytic preparation of 1,3-dienyl-2-boronic acids from easily accessible 2,3-allenols and $B_2(OH)_4$ (Fig. 1f). Moreover, preliminary studies on homoallenylboration have revealed that 1,3-dienyl-2-boronic acids exhibit high reactivity toward a broad range of aldehydes, ketones, and imines under catalyst-free conditions, establishing them as highly appealing reagents for homoallenylboration.

Results and discussion

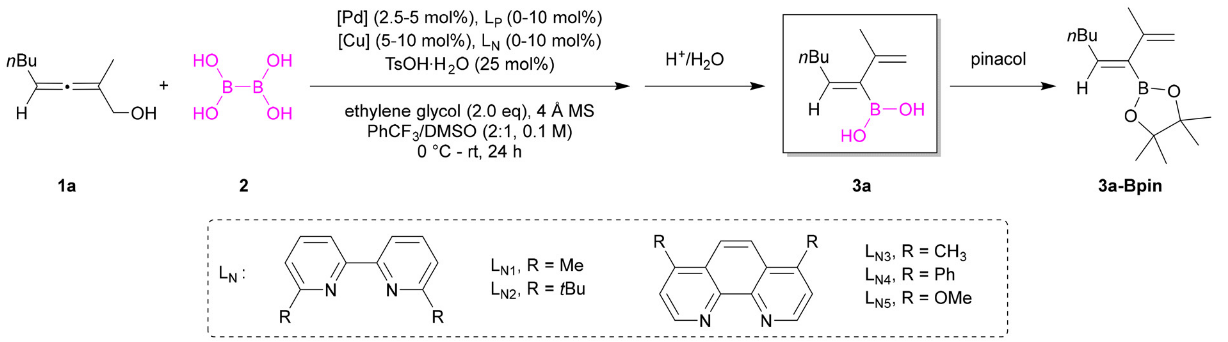
Reaction development for preparation of 1,3-dienyl-2-$B(OH)_2$

To date, synthetic approaches for accessing structurally diverse 1,3-dienyl-2-boronic acids have remained underexplored.[12] Building upon our previous study regarding the synthesis of 1,3-dienyl-2-Bpins through Pd/Cu-cocatalysed borylation of allenylic carbonates with B_2Pin_2,[13] our initial objective was to develop a practical and effective method for the direct synthesis of 1,3-dienyl-2-boronic acids by using $B_2(OH)_4$ (Table 1). After several attempts, it was found that when 2,3-allenol **1a** and $B_2(OH)_4$ (**2**) were subjected to a ternary cocatalytic system involving $Pd(PPh_3)_4$, copper(I) thiophene-2-carboxylate (CuTc), and $TsOH{\cdot}H_2O$, along with the incorporation of ethylene glycol and 4 Å molecular sieves as additives, 1,3-dienyl-2-boronic acid **3a** could be formed after quenching the reaction mixture with aqueous HCl (0.5 M) (entry 1). We observed that **3a** remained stable in solution even after being exposed to air for one week at room temperature (see the SI for details, Fig. S4). However, attempts to purify **3a** through general chromatography were unsuccessful owing to its degradation on silica gel. As a result, **3a** was subsequently transformed into its pinacolate form (**3a-Bpin**) through the addition of pinacol for the purpose of purification and data recording. After screening various commonly used mono- and bidentate phosphine ligands (see the SI for details, Tables S1 and S2), we discovered that 1,2-bis(diphenylphosphino)ethane (dppe) exhibited promising potential in this transformation and delivered **3a** despite a low conversion of **1a** (entry 2). Efforts to improve the reaction conversion by prolonging reaction times or conducting reactions at room temperature proved unsuccessful (entries 3 and 4). Taking inspiration from the recent advances in Pd/Cu co-catalysis,[14] a bipyridine ligand such as L_{N1} or L_{N2} was incorporated into the reaction. Gratifyingly, complete conversion of **1a** was achieved, affording **3a-Bpin** in 44–45% yields (entries 5 and 6). Upon further investigation, it was found that substituted 1,10-phenanthroline ligands exhibited superior performance compared to bipyridines (entries 7–9). Specifically, L_{N5} provided **3a-Bpin** in a yield of 56% (entry 9). Ultimately, an increase in isolated yield (69%) was accomplished through the direct utilization of the precoordinated Pd $(dppe)_2$ catalyst (entry 10). A series of control experiments was conducted to assess the individual roles of each catalyst. Omitting either Pd or Cu catalyst led to no discernible reaction occurring (entries 11 and 12). However, under otherwise identical conditions, the reaction proceeded without the use of $TsOH{\cdot}H_2O$ and yielded the desirable product **3a**, albeit with a lower conversion of **1a** (entry 13). This observation indicates that $TsOH{\cdot}H_2O$ can effectively attenuate the allenylic C–OH bond in **1a**, thereby expediting the overall reaction process. Changing the copper catalyst from CuTc to CuOAc in the reaction resulted in the production of **3a** in a diminished yield (entry 14). However, the use of CuI or CuCl significantly inhibited the borylation reaction (entries 15 and 16). These results illustrate the essential role of carboxylate as a weak base in the catalytic system.[15]

Scope and limitation

With the optimized reaction conditions in hand, we next explored the synthetic scope of the above borylation reaction using various 2,3-allenols with $B_2(OH)_4$ (Fig. 2). Again, to ensure the operational convenience of purification and identification, all the 1,3-dienyl-2-boronic acids were further converted into their pinacol (or pinanediol) ester analogues. Similar to **1a**, the β,δ-disubstituted allenols bearing primary or secondary aliphatic groups (**1b–1g**) reacted well with $B_2(OH)_4$ in the presence of catalytic $Pd(dppe)_2$, CuTc and $TsOH{\cdot}H_2O$, affording the corresponding 1,3-dienyl-2-Bpins (**3b-Bpin–3g-Bpin**) in 66–83% yields with high stereoselectivity. We found that the disubstituted 2,3-allenols bearing aryl substituents were also compatible in this transformation. **1h** and **1i** reacted efficiently with $B_2(OH)_4$, delivering the desired products (**3h-Bpin** and **3i-Bpin**) in decent yields. When δ-monosubstituted allenol **1j** was subjected to the reaction, although the reaction proceeded well, it delivered the desirable product **3j-Bpin** with a *Z*/*E* ratio of 3 : 1. Delightfully, the substitution of ethylene glycol with 1,2-propanediol could enhance the *Z*/*E* ratio by up to 5 : 1 while maintaining catalytic efficiency. Under the modified reaction conditions, the other δ-monosubstituted allenols (**2k–2n**) delivered the corresponding products (**3k-Bpin–3n-Bpin**) in good to high yields with good stereoselectivity. When structurally symmetrical 2,3-allenol (**1o**) was used in the reaction, product **3o-Bpin** was obtained efficiently. Other structurally symmetrical 2,3-allenols (**1p–1r**) were also compatible in the transformation, delivering the corresponding 1,3-dienyl-2-boronic acids (**3p–3r**). However, the conversion of these boronic acids with pinacol proceeded at an unexpectedly slow pace, and therefore, the pinanediol esters **3p-B(pinanediol)–3r-B(pinanediol)** were obtained in 70–79% yields. Furthermore, 2,3-allenols bearing a series of functional groups, including protected hydroxyl groups (**1e** and **1f**), Boc-protected amine (**1g**), ether (**1n** and **1p**), and thioether (**1q**), displayed good tolerance towards the borylation reaction con-

Table 1 Optimal reaction conditions for the catalytic synthesis of 1,3-dienyl-2-boronic acid **3a** [a]



Entry	[Pd] source	L_P/(0–10 mol%)	[Cu] source	L_N/(10 mol%)	Yield of **3a-Bpin** [b]/%
1[c,d]	$Pd(PPh_3)_4$ (5 mol%)	—	CuTc (5 mol%)	—	22
2[d]	Pd_2dba_3 (2.5 mol%)	dppe (10 mol%)	CuTc (5 mol%)	—	27
3[e]	Pd_2dba_3 (2.5 mol%)	dppe (10 mol%)	CuTc (5 mol%)	—	31
4[f]	Pd_2dba_3 (2.5 mol%)	dppe (10 mol%)	CuTc (5 mol%)	—	34
5	Pd_2dba_3 (2.5 mol%)	dppe (5 mol%)	CuTc (10 mol%)	L_{N1}	44
6	Pd_2dba_3 (2.5 mol%)	dppe (5 mol%)	CuTc (10 mol%)	L_{N2}	45
7	Pd_2dba_3 (2.5 mol%)	dppe (5 mol%)	CuTc (10 mol%)	L_{N3}	51
8	Pd_2dba_3 (2.5 mol%)	dppe (5 mol%)	CuTc (10 mol%)	L_{N4}	54
9	Pd_2dba_3 (2.5 mol%)	dppe (5 mol%)	CuTc (10 mol%)	L_{N5}	56
10	$Pd(dppe)_2$ (5 mol%)	—	CuTc (10 mol%)	L_{N5}	69[g]
11	—	—	CuTc (10 mol%)	L_{N5}	0
12	$Pd(dppe)_2$ (5 mol%)	—	—	—	0
13[h]	$Pd(dppe)_2$ (5 mol%)	—	CuTc (10 mol%)	L_{N5}	38
14	$Pd(dppe)_2$ (5 mol%)	—	CuOAc (10 mol%)	L_{N5}	50
15	$Pd(dppe)_2$ (5 mol%)	—	CuI (10 mol%)	L_{N5}	7
16	$Pd(dppe)_2$ (5 mol%)	—	CuCl (10 mol%)	L_{N5}	5

[a] Reaction conditions: a mixture of **1a** (0.3 mmol, 1.0 equiv.), **2** (0.45 mmol, 1.5 equiv.), [Pd] source (2.5 or 5 mol%), L_P (0–10 mol%), [Cu] source (5–10 mol%), L_N (0–10 mol%), $TsOH·H_2O$ (25 mol%), ethylene glycol (0.6 mmol, 2.0 equiv.), 4 Å molecular sieves, and anhydrous $PhCF_3$/DMSO (2 : 1, 0.1 M) was initially reacted at 0 °C and gradually warmed to rt for 24 h under Ar. Then, the reaction mixture was quenched with HCl (0.5 M), followed by addition of pinacol (0.9 mmol, 3.0 equiv.) and THF (1.5 mL). The resulting solution was further stirred at rt for 12 h. [b] The yields of **3a-Bpin** (over two steps) were determined using the crude ^1H NMR spectrum with an internal standard. [c] $Pd(PPh_3)_4$ and CuTc were utilized in the reaction without the addition of any extra ligands. [d] Reacted at 0 °C for 12 h. [e] Reacted at 0 °C for 72 h. [f] Reacted at rt for 48 h. [g] Isolated yield after purification. [h] Without the use of $TsOH·H_2O$. dppe = 1,2-Bis(diphenylphosphino)ethane.

ditions, enabling facile synthesis of functionalized 1,3-dienyl-2-boronic acids (**3e**, **3f**, **3g**, **3n**, **3p** and **3q**).

A gram-scale reaction was carried out using **1a** (10 mmol) with a reduced catalyst loading [$Pd(dppe)_2$ (2.5 mol%)/CuTc (5 mol%)/L_{N5} (5 mol%)/$TsOH·H_2O$ (15 mol%)] to further demonstrate the effectiveness of Pd/Cu/$TsOH·H_2O$ catalysis (Fig. 3). The desirable product **3a** was isolated as its MIDA-boronate derivative (**3a-BMIDA**) by column chromatography, affording a 58% yield (over two steps) with no detectable *E* stereoisomer. Subsequent deprotection of **3a-BMIDA** using aqueous NaOH (1 M) enabled selective delivery of the pure boronic acid **3a**, albeit accompanied by a slight loss (94% NMR yield). Additionally, the ^1H NMR spectrum of the crude sample of **3a**, obtained by extraction of the quenched reaction mixture with C_6D_6, closely resembled that of the purified sample (see the SI for details, Fig. S5), confirming the direct formation of the 1,3-dienyl-2-boronic acid under Pd/Cu/$TsOH·H_2O$ catalysis in the borylation reaction. Applying this MIDA-protection strategy to other crude boronic acids **3** similarly afforded pure **3j-BMIDA**, **3k-BMIDA**, and **3m-BMIDA** in 53–60% yields without apparent *E* stereoisomers. Subsequent deprotection of **3-BMIDA** then provided the stereodefined boronic acids **3j**, **3k**, and **3m** in toluene solutions, which were directly used in downstream transformations.

Application of 1,3-dienyl-2-boronic acids in homoallenylboration

After obtaining a substantial quantity of stereodefined boronic acids **3**, we next explored their reactivity and synthetic utility by performing a series of homoallenylboration reactions with a variety of carbonyl compounds and imines (Fig. 4). In the presence of 4 Å molecular sieves, the purified 1,3-dienyl-2-boronic acid **3a** reacted smoothly with 4-bromobenzaldehyde **4a** in toluene solution without any catalyst, producing the desirable product **5aa** in 87% yield with high diastereoselectivity. According to our DFT calculation (Fig. 1d), the remarkably high reactivity of the unprotected 1,3-dienyl-2-boronic acid, compared to the inactive 1,3-dienyl-2-Bpin, is the consequence of its ability to form the highly reactive boroxine (with the aid of molecular sieves). The relative configuration of **5aa** was unambiguously confirmed by means of ^1H/^{13}C NMR and compared with our previous report.[3a] The observed high diastereo-

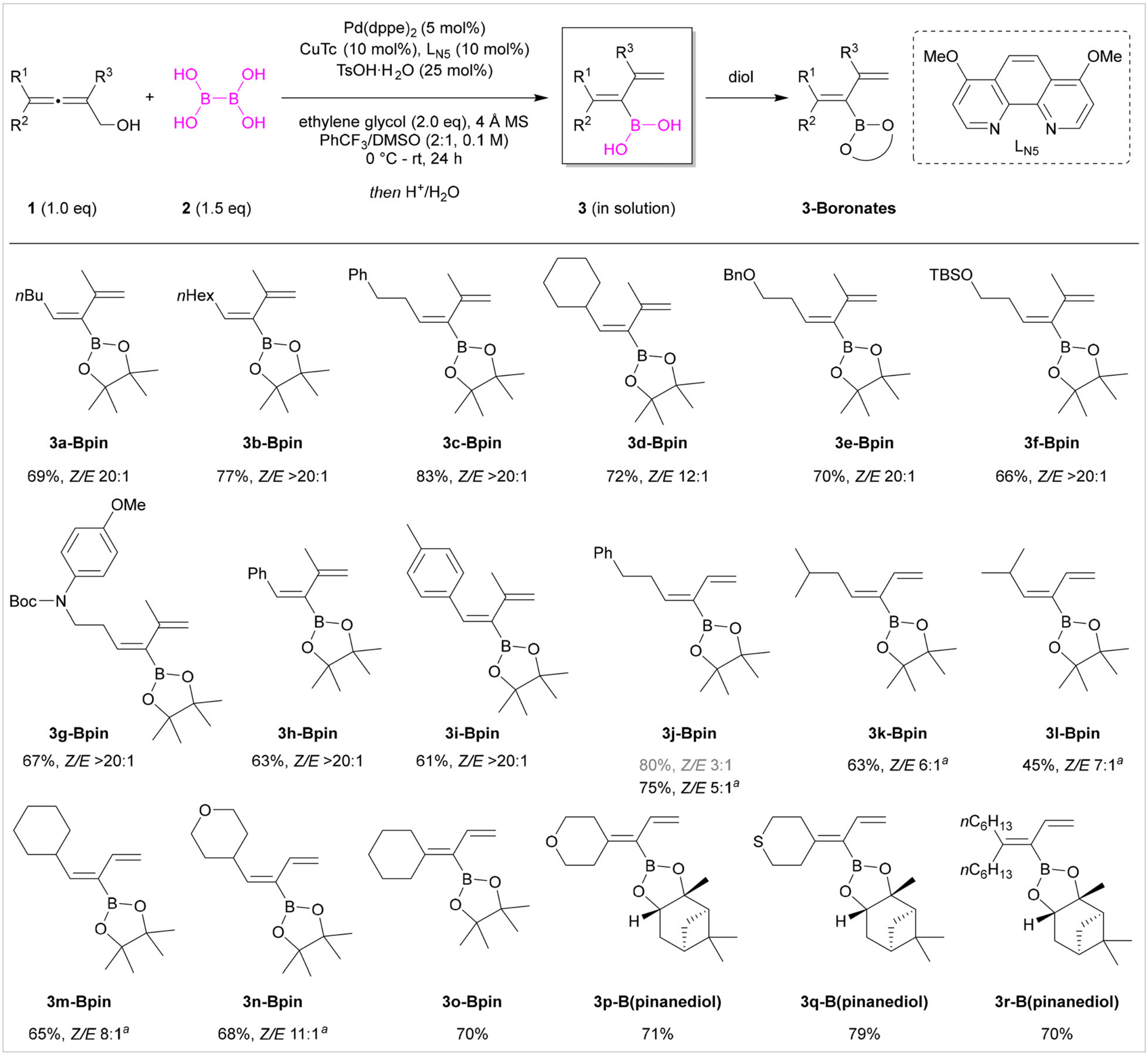


Fig. 2 Pd/Cu/TsOH·H$_2$O-cocatalyzed synthesis of 1,3-dienyl-2-boronic acids with B$_2$(OH)$_4$ using various substituted 2,3-allenols. Unless otherwise stated, all reactions were run on a 0.3 mmol scale. Overall yields (two steps) are of isolated products after purification. ^{a} 1,2-Propanediol (2.0 equiv.) was used in the reaction instead of ethylene glycol.

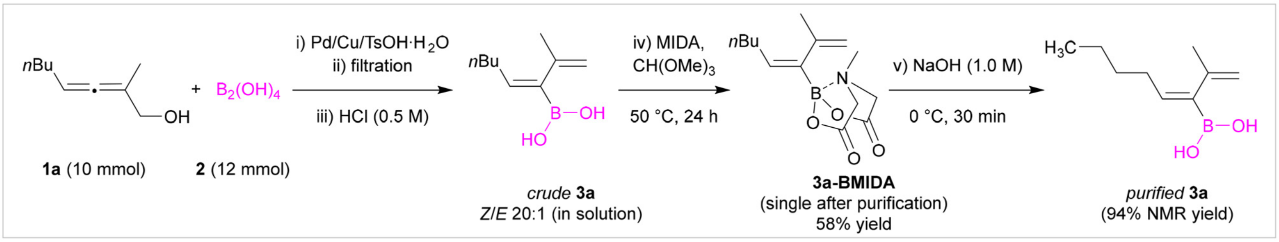


Fig. 3 Gram-scale synthesis and purification of the 1,3-dienyl-2-boronic acid **3a**.

selectivity in the homoallenylboration, along with the configuration outcome of **5aa**, suggests the involvement of a compact Zimmerman–Traxler transition state in the reaction process. Further investigation found that *p*-anisaldehyde (**4b**), α,β-unsaturated aldehydes (**4c** and **4d**), primary and secondary aliphatic aldehydes (**4e** and **4f**) and ethyl glyoxylate (**4g**) all

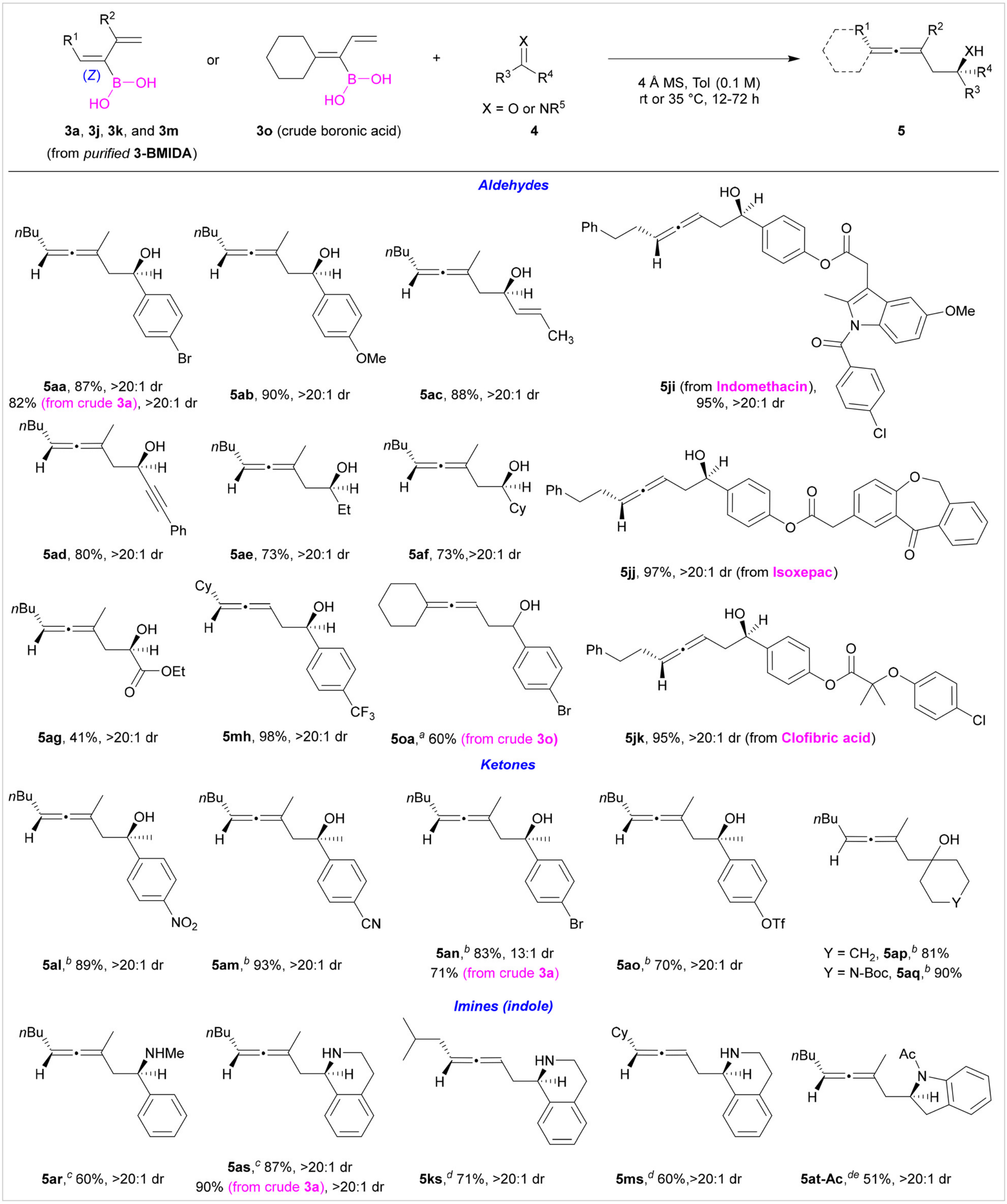


Fig. 4 Catalyst-free homoallenylboration of aldehydes, ketones and imines with 1,3-dienyl-2-boronic acids. Unless otherwise stated, **3** (0.15 mmol) and **4** (0.30 mmol) were reacted in toluene (1.5 mL) in the presence of 4 Å molecular sieves at rt for 12 hours. Yields are of isolated products after purification. dr is determined by ^{1}H NMR. [a] With hexafluoroisopropanol (HFIP, 2.0 equiv.), 60 °C for 48 h. [b] 35 °C for 72 h. [c] rt for 24 h. [d] 35 °C for 48 h. [e] Overall yield for two steps.

reacted well with **3a**, delivering the corresponding products (**5ab–5ag**) in 41–90% yields with high diastereoselectivity. When other 1,3-dienyl-2-boronic acids (**3m** and **3o**) were used in the homoallenylboration with aryl aldehydes, products **5mh** and **5oa** were formed in yields of 98% and 60%, respectively. To our delight, the mild reaction conditions facilitated the application of this homoallenylboration in the late-stage functionalization of complex molecules derived from pharmaceuticals (**5ji–5jk**).

Subsequently, we explored the homoallenylboration of challenging ketone substrates with 1,3-dienyl-2-boronic acids. Delightfully, when aryl ketones (**4l–4o**) bearing a series of functional groups (such as nitro, cyano, bromo and triflate) were reacted with **3a** directly at an elevated temperature (35 °C), the desirable products (**5al–5ao**) were obtained in 70–93% yields with high diastereoselectivity. The aliphatic ketone also showed reactivity in this transformation. When cyclohexanone (**4p**) and *N*-Boc-4-piperidone (**4q**) were subjected to the reaction, the desired products **5ap** and **5aq** were obtained in high yields.

The homoallenylboration of imines with 1,3-dienyl-2-boronic acids (**3a**, **3k** and **3m**) was also feasible. When *N*-benzylidenemethylamine **4r** and 3,4-dihydroisoquinoline **4s** were used in the homoallenylboration, the identified amines (**5ar**, **5as**, **5ks** and **5ms**) were obtained in 60–87% yields with high diastereoselectivity. The reaction of **3a** with indole was slow, likely due to the initial isomerization of indole to its imine tautomer.[16] However, the protected homoallenyl amine **5at-Ac** was obtained with a synthetically useful yield of 51% over two steps. The practicality of 1,3-dienyl-2-boronic acids in homoallenylboration was further substantiated by employing crude boronic acids; **3a** and **3o** were extracted from the reaction mixture and directly engaged in homoallenylboration reactions with selected carbonyls and imines (**4a**, **4n**, and **4s**), affording the corresponding products (**5aa**, **5oa**, **5an**, and **5as**) with comparable yields.

To demonstrate the synthetic utility of homoallenyl alcohols and amines, we performed gold-catalysed cyclization reactions,[4l] which efficiently afforded the corresponding six-membered heterocycles (Fig. 5). The reaction of homoallenyl alcohol **5aa** delivered dihydropyran **6aa** in good yield (79%) with a diastereomeric ratio of 5 : 1. Similarly, homoallenyl amine **5ar** underwent smooth cyclization to furnish tetrahydropyridine **6ar** in 85% yield with high diastereoselectivity (>20 : 1 dr). The relative configurations of **6aa** and **6ar** were further determined by 2D NOESY spectroscopy (see the SI for details, Fig. S7 and S8).

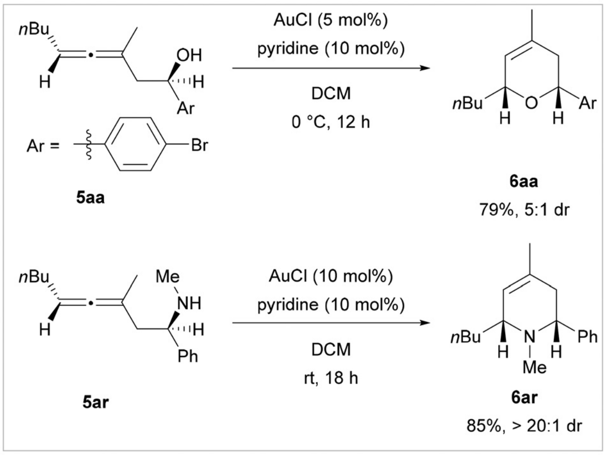


Fig. 5 Gold-catalysed cyclization reactions of homoallenyl alcohol and amine.

Reaction pathway for synthesizing 1,3-dienyl-2-B(OH)$_2$

Based on the experimental results and previous studies, a plausible catalytic cycle for the synthesis of 1,3-dienyl-2-boronic acids is proposed using **1a** and $B_2(OH)_4$ as an example in Fig. 6. Initially, protonation of the hydroxyl group in allenol **1a** by TsOH generates the corresponding oxonium salt **TsOH·1a**. This oxonium salt effectively weakens the allenyl C–O bond, thereby facilitating the oxidative addition of the Pd(0) L_P catalyst **7** to generate the methylene-π-allylic palladium(II) complex **8**, with concomitant formation of H_2O (removed by 4 Å MS).[17] Simultaneously, transmetalation between L_NCuTc **10** and the *in situ*-generated bis(glycolato)diboron **9** affords the

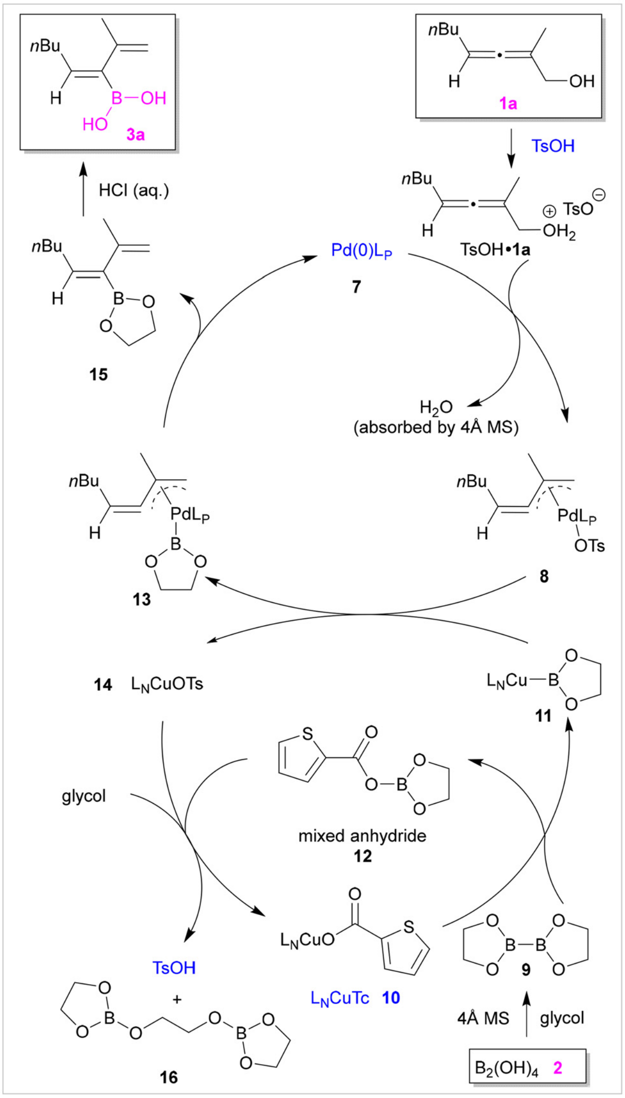


Fig. 6 Proposed reaction pathway for the direct synthesis of 1,3-dienyl-2-boronic acids.

borylcopper species **11** together with the mixed anhydride **12**. Subsequently, a second transmetalation between **8** and **11** generates the intermediate **13** along with L_NCuOTs **14**.[13,18] Next, selective reductive elimination from intermediate **13** affords the glycol-protected product **15**, accompanied by regeneration of the Pd(0)L_P catalyst. Meanwhile, alcoholysis of the mixed anhydride **12** with ethylene glycol in the presence of L_NCuOTs **14** regenerates both the TsOH and L_NCuTc **10** catalysts. The success of the borylation reaction can be attributed to two key factors: the *in situ* protection of the $B(OH)_2$ group by glycol and the careful choice of a mild base (Tc^-), which selectively promotes transmetalation with bis(glycolato)diboron **9**. Together, these factors enhance the stability of product **15** under the reaction conditions. Boronic acid **3a** was finally obtained *via* hydrolysis of **15** with 0.5 M aqueous HCl during work-up.

Conclusions

In summary, we have developed a novel class of stable 1,3-dienyl-2-boronic acid reagents for homoallenylboration reactions. These reagents were efficiently synthesized with good to high yields and high stereoselectivity from readily available 2,3-allenols and $B_2(OH)_4$ *via* a Pd/Cu/TsOH ternary cocatalytic system. The utility of these reagents was demonstrated in their reaction with a range of aldehydes, ketones, and imines. This catalyst-free homoallenylboration provides a straightforward route to synthetically valuable homoallenyl alcohols and amines, which serve as key precursors in the synthesis of natural products and complex molecules. Further investigation on the asymmetric homoallenylboration of carbonyls and imines using 1,3-dienyl-2-boronic acids based on a chiral catalyst is currently underway in our laboratory.

Author contributions

The manuscript was written through the contributions of all authors and all authors have given approval to the final version.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information: DFT calculations, experimental procedures, characterization data of all new compounds, *etc*. See DOI: **https://doi.org/10.1039/d5qo01521a**.

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