Substituted Cyclopropanols via Sequential Cyclopropanation and Oxidative Hydrolysis of Vinylboronates

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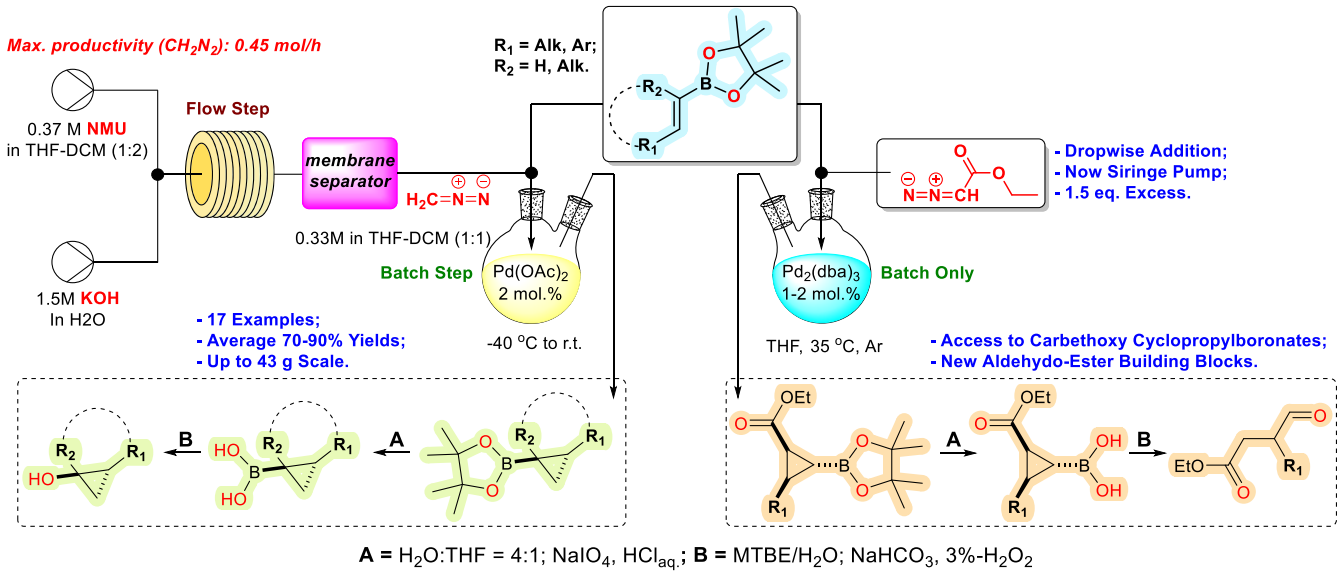

ABSTRACT: *We present a scalable, diastereoselective protocol for synthesizing cyclopropanols, including rare 2-substituted ones, via oxidative hydrolysis of cyclopropyl boron pinacolates. Our previous protocol for Pd-catalyzed cyclopropanation of vinyl boron pinacolates was adapted for flow conditions, allowing safe, scalable utilization of diazomethane and ensuring high yields of target products. The use of ethyldiazoacetate for cyclopropanation allows the formation of boronic acids in the first step; however, decreases the stability of cyclopropanols in the second, yielding esteraldehydes.*

Despite the high attraction to use cyclopropanols as O-nucleophiles, such a strategy is hampered by the numerous ring-opening reactions. This is evidenced by the extensive literature focusing on ring-opening procedures rather than nucleophilic transformations, which indicates that cyclopropanols' instability - not merely community demand - drives this research direction[1]. In particular, seminal works claim the inability to obtain the parent 1-cyclopropanol in pure state[2], and this remains true for today[3]. However, the attention to this class of compounds is growing in every way, yielding 277 publications in peer-reviewed journals over the last five years versus 134 over the previous five, according to the Reaxys database[4].

Classical approaches to cyclopropanols, such as the Kulinkovich[5] and Simmons-Smith[6] reactions, as well as their numerous modifications[5b, 7] offer robust pathways for their synthesis (**Figure 1, I, II**), yet very limited scope of 2-substituted products. Meanwhile, newer approaches, like visible-light-induced organocatalysis[8] and radical-mediated methods,[5b, 7a, 9] (**Figure 1, III, V**) provide more sustainable and efficient but hardly scalable routes with no access to 2-substitution patterns. Oxidative hydrolysis of cyclopropyl boron pinacolates (Cp-BPins)[10] (**Figure 1, IV**) enables a direct and chemoselective synthesis of 2-substituted cyclopropanols with high stereoselectivity potential.[11] However, it may suffer issues with reproducibility, yields, and substrate scope limitations.

Despite the diversity of the existing synthetic approaches, sizable challenges persist in the preparation of 2-substituted cyclopropanols, particularly on a multigram scale. Few existing methods rely on sensitive metalorganic reagents and expensive catalysts, limiting their scalability and safety. Furthermore, issues related to functional group compatibility restrict the diversity of 2-substituted cyclopropanol-based building blocks[5b]. Although several up-scaled syntheses of cyclopropanols are reported, they typically focus on needs in specific products rather than offering general methods for broad application.[3, 12] With this said, it is safe to conclude that further advancing cyclopropanols synthesis, particularly 2-substituted ones, requires scalable, general methods that also improve substrate scope and diastereoselectivity.

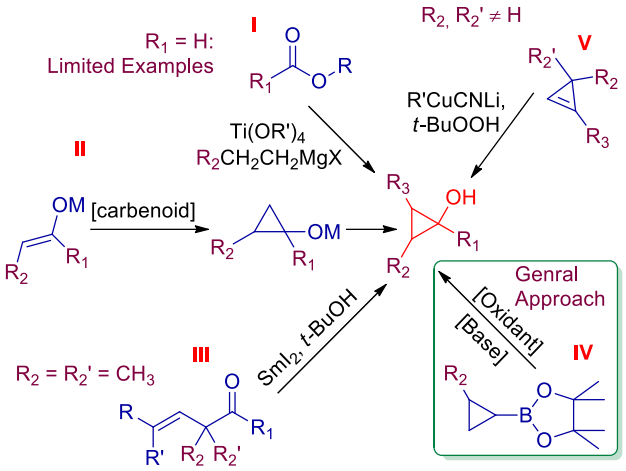

Figure 1. Cyclopropanols synthesis overview: (**I**) Kulinkovich reaction, (**II**) Simmons-Smith reaction, (**III**) visible-light-induced organocatalysis, (**IV**) oxidative hydrolysis of cyclopropylboronates, and (**V**) radical-mediated cyclopropanation.

This work, presents a versatile and scalable (tens of grams) protocol for the diastereoselective synthesis of aliphatic and aromatic-2-substituted cyclopropanols via sequential oxidative hydrolysis of corresponding Cp-BPins. This approach builds on our prior success in synthesizing Cp-BPins from readily available vinyl-BPins[13] through Pd-catalyzed cyclopropanation[14]. While the method requires multiple steps, this is offset by excellent yields at each of them and access to valuable intermediates such as cyclopropylboronic acids and trifluoroborates. Scope and stability studies with electron-donating and electron-withdrawing substrates provide further insights into the chemistry of cyclopropanols.

The starting Cp-BPins (**Figure 2, 1**) were prepared according to our previously reported protocol for Pd-catalyzed cyclopropanation[14] of vinyl-BPins with diazomethane. The method was modified for our previously developed continuous flow conditions of safe and up-scale using the diazomethane.[15] This modification also allowed us to significantly lower the content of the Pd-catalyst and avoid the polymerization of diazomethane. Herein, we focused on substrates with aliphatic (**Figure 2**, compounds **4a-d, 4j**), and aromatic (**Figure 2**, **4e-i**) side chains, as well as spirocyclic derivatives (**Figure 2**, compounds **4k, 4m, 4n, 4q**), which pose a significant challenge for the existing synthetic approaches. We also tested our conditions on the synthesis of well-studied fused core **4l** (**Figure 2**) and previously unavailable fused nitrogen heterocycles **4o-q** (**Figure 2**). The latter proved the tolerance of Boc-protected amines on both steps. Both obtained Boc-derivatives, and amine hydrochlorides (**4o-q, Figure 2**) showed stability on storage. The preservation of *trans*-configuration in the final cyclopropanols was additionally confirmed via XRD analysis of 2-(2,3-dichlorophenyl)cyclopropan-1-ol (**4e, Figure 2**).

We found that previously reported one-step protocols for cyclopropyl boronic ester hydrolysis have significant limitations: the $NaBO_3$-mediated method is efficient only for substrates with an α-hydroxymethylene group,[11a] while the H_2O_2-mediated oxidative hydrolysis with 1M NaOH, as proposed by Bassan et al.,[12] resulting in low and inconsistent yields in our case (discussed in detail below).

To address this, we developed a two-step protocol: $NaIO_4$ in acidified (HCl) water/tetrahydrofuran system was used for oxidative hydrolysis of boronic esters to corresponding acids in the first step (compounds **2, Figure 2, A**). This was followed by subsequent H_2O_2-mediated oxidative hydrolysis in aqueous methyl-*tert*-butyl ether with a milder base ($NaHCO_3$), which led to respective cyclopropanols **4** (**Figure 2, B**). Our experimentations revealed that regardless of the substituents, in all the cases besides those described below, both oxidative hydrolysis steps resulted in high yields (69-99 %) for gram scales (up to 29.5 g) of cyclopropanols per one run (**Figure 2**). The differences in yields on the first and second hydrolytic steps were noticeable for smaller, more rigid alkyl derivatives **d** (62% vs. 97%) and **j** (64% vs. 78%), as well as spiro-oxygen heterocycles

n (33% vs. 83%) and **m** (9% vs. 72%), as shown in **Figure 2**. Another deviation from the standard case was boronic acid **2m**, which did not yield the cyclopropanol **4m**, so we used the corresponding trifluoroborate salt **3m** to obtain the desired alcohol in similar conditions (**Figure 2**). We assume that such a significant drop in yields in the case of spiro-, oxygen-contained heterocycles **m** and **n**, is connected to the stability of these compounds in given conditions (**Figure 2**). It is also notable that the attempt to hydrolyze the corresponding Cp-BPin **1n** to **2n** in acidic media gave a significantly lower yield (60%), so we used an NH_4OH solution instead of HCl (**Figure 2**). Finally, it is worth underlining that the designed procedure also allows access to cyclopropyl boronic acids and alcohols with a fused carbocyclic compound (**l, Figure 2**) as well as previously unavailable nitrogen-containing heterocyclic ones (**o-q, Figure 2**) with high yields.

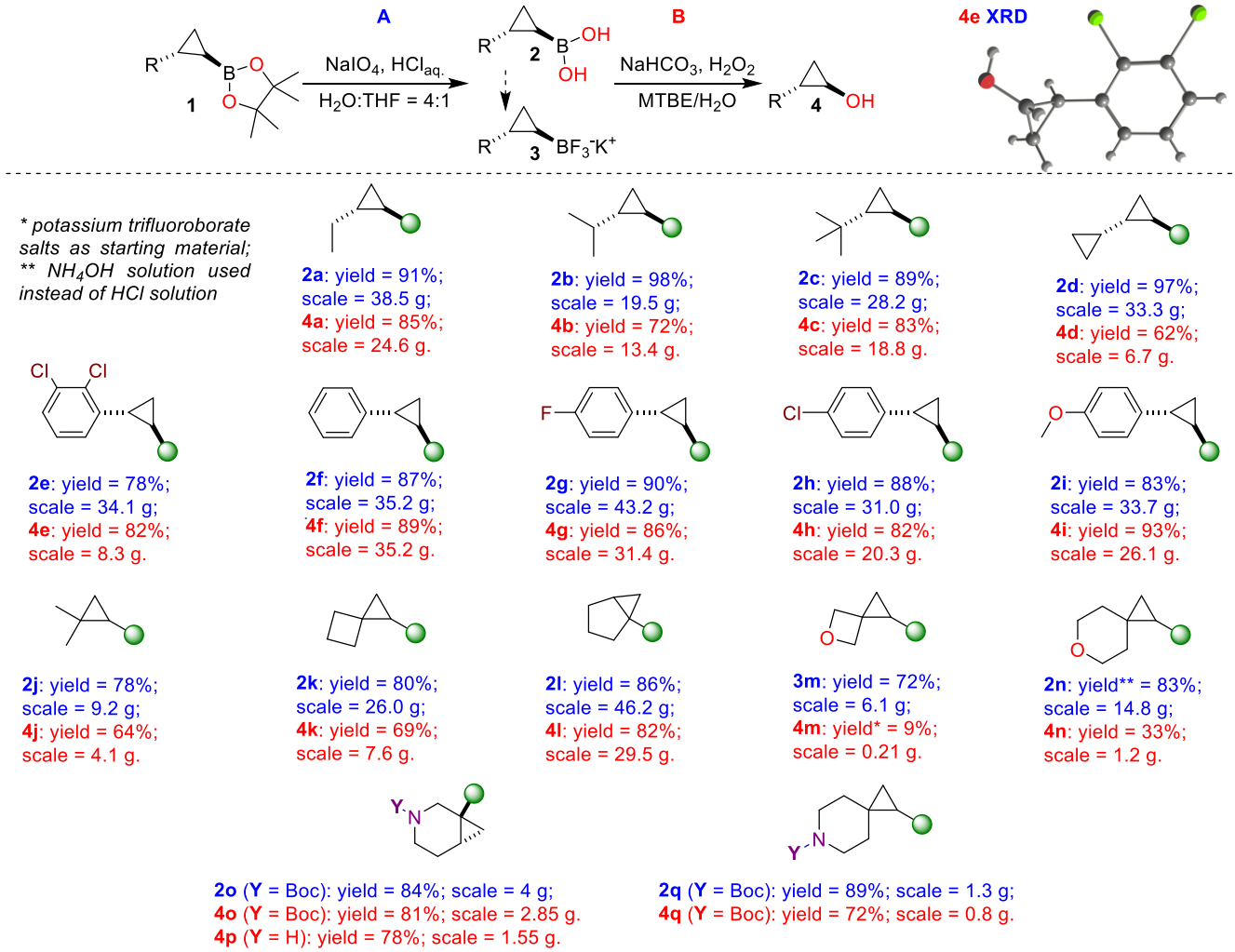

Figure 2. The two-step protocol for cyclopropanols (**4a-q**) and cyclopropylboronic acids (**2a-q**) synthesis via sequential oxidative hydrolysis of cyclopropylboronic esters (**1**).

The limitations of existing literature protocols for cyclopropanol synthesis via Cp-BPins are often attributed to the harshness of H_2O_2 as an oxidant[10]. A few reported attempts to replace H_2O_2 led to no significant improvements and failed to provide practical alternatives for broader, scalable applications[10]. We stepped away from the conclusion that the oxidant was the source of the problem upon observing poor reproducibility in the oxidative hydrolysis of cyclopropylboronic acids to alcohols. The additional argument for us was stability issues during storage of cyclopropanols, as their decomposition occurred even at -80 °C for the examples produced using the literature protocols with 1M NaOH. Considering this, we assumed that the problem was the strong alkali that forced cyclopropanols into decomposition during the reaction and whose traces in the final product promoted further degradation on standing. Based on the above, we replaced the NaOH solution with the weaker base - $NaHCO_3$ solution (**Figure 2**). This led to sustainably higher yields and allowed us to avoid product decomposition during storage, even at room temperature. To support this concept, we performed an NMR-kinetic study, monitoring

substrate concentration diminution over time using *trans*-2-ethylcyclopropan-1-ol (**4a, Figure 2**) as a test case in DMSO-D_6/D_2O with KOH, based on cyclopropanol signal depletion relative to trimethoxybenzene as an internal standard (see SI for details). The results displayed the first-order reaction (R^2 = 0.97) with a half-life of 15.5 minutes (**Figure 3**), which makes it safe to postulate that the instability in the presence of strong bases is an intrinsic property of cyclopropyl alcohols. Notably, we could not identify the exact products from the complex mixture that formed due to the decomposition of **4a** (see SI for details).

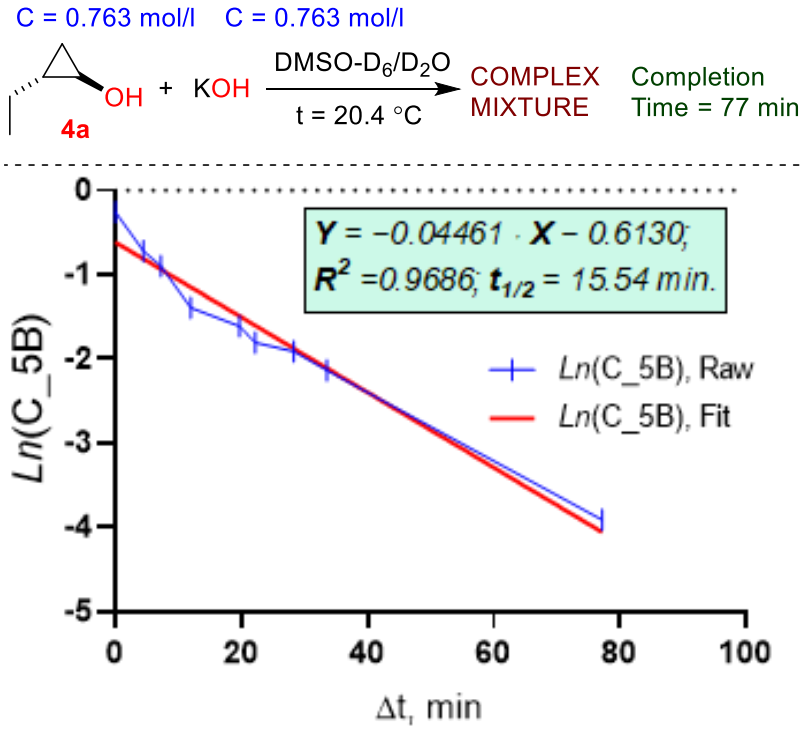

Figure 3. NMR-kinetic study of *trans*-2-ethylcyclopropan-1-ol (**4a**) decomposition in DMSO-D_6/D_2O with KOH at room temperature.

These findings suggest that the choice of base, rather than the oxidant, plays a critical role in the stability and successful synthesis of cyclopropanols.

Cyclopropanes bearing multiple electron-withdrawing groups (EWGs) are readily accessible due to the ring's ability to stabilize electron deficiency through delocalization.[16] On the other hand, cyclopropanols with electron-withdrawing groups (EWGs), for example, carbonyl-containing ones,[17] -CF_3,[8, 18] and others, are generally more challenging to synthesize compared to their electron-donating counterparts discussed above.[10] Cyclopropanols with EWGs positioned on different carbons exhibit significant instability. This is attributed to a destabilizing push-pull electronic effect,[19] which exacerbates ring strain and leads to rapid decomposition or ring-opening reactions.

In our study, we decided to check whether it would be possible to translate our protocol for synthesizing electron-donating cyclopropanols to substrates bearing EWGs. For that, in the first step we used diazoacetic ester instead of diazomethane for cyclopropanation of vinyl-BPins under elaborated conditions. Notably, using $Pd_2(dba)_3$ as a replacement for $Pd(OAc)_2$ or $Rh(OAc)_2$ eliminated the need for excess diazoacetic ester, which was previously required due to its tendency to condense into maleic and fumaric acid esters under such conditions.[20] This adaptation also allowed us to avoid the demand for the slow addition (syringe pump) of diazoacetic ester and simplify previously much-complicated isolation procedures. Unlike diazomethane-based cyclopropanation, which was diastereospecific towards *trans*-isomers (**Figure 2**), the addition of diazoacetic ester, although produced products with high yields, but as diastereomeric mixtures, predominantly trans- (**Figure 4**). The hydrolysis of the obtained Cp-BPins **6+7a-d** (**Figure 4**) resulted in corresponding boronic acids **9a-d** (**Figure 4**) as mixtures of diastereomers in the same proportion as starting materials. We achieved separation of the major *trans*-isomers by washing the residue with hot hexane, yielding preparative amounts close to 50% (**9a-d, Figure 4**), while the *cis*-isomer remained an inseparable mixture with residual *trans*-product. The oxidative hydrolysis of carbethoxy-cyclopropyl boronic acids **9a-d**,

unlike their EDG-counterparts, failed to produce the desired cyclopropanols, instead yielding ester-aldehydes **10a-d** (**Figure 4**) with yields just above 50%. This outcome aligns with our understanding of push-pull instability in EWG-substituted cyclopropanols. Although direct access to these rare molecules was unsuccessful, our findings enable the practical synthesis of valuable bifunctional building blocks with orthogonal groups that are otherwise difficult to obtain.

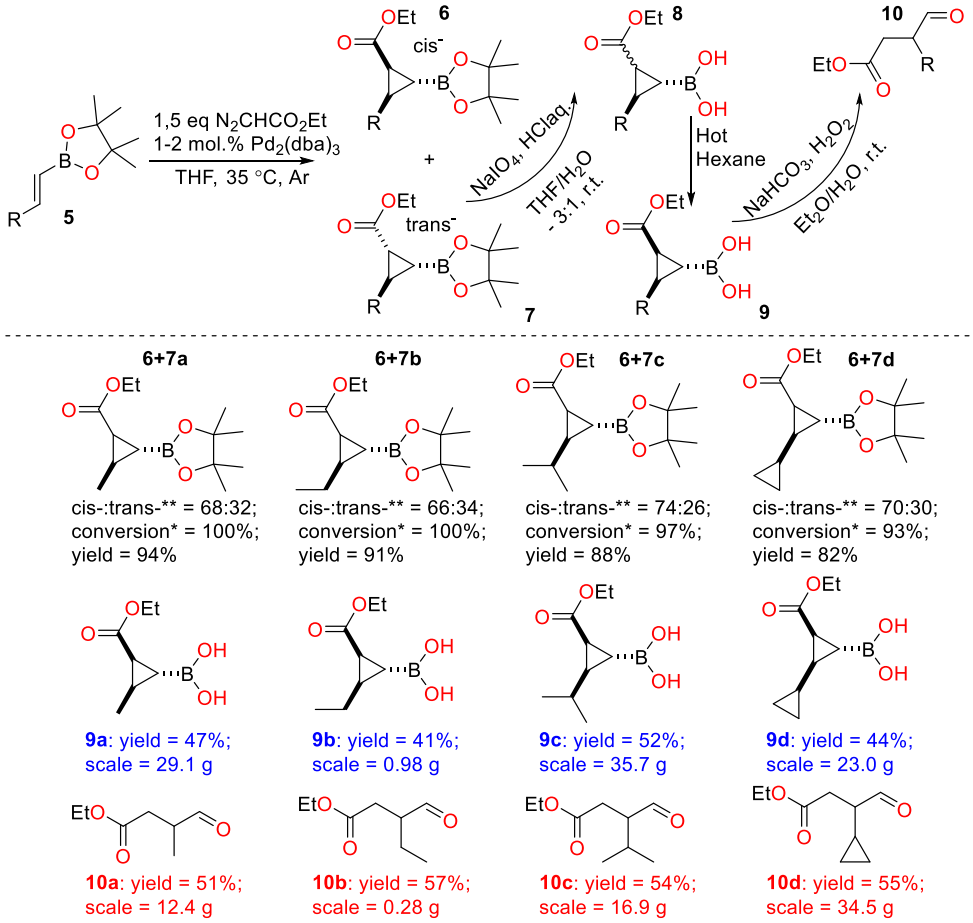

Figure 4. Preparation of *trans*-carbethoxy cyclopropylboronic esters (**6+7a-d**) and their sequential oxidative hydrolysis to cyclopropylboronic acids (**9a-d**) and ester-aldehydes (**10a-d**). **Conversion was determined via ^{1}H NMR analysis of the reaction mixture. **cis:trans ratio was determined by GC/MS analysis of purified products.*

In conclusion, we have developed a scalable, diastereoselective, and safe two-step protocol for synthesizing 2-substituted cyclopropanols via sequential oxidative hydrolysis of Cp-BPins. This method leverages Pd-catalyzed cyclopropanation, allowing efficient, large-scale handling of flow-generated diazomethane. It also achieves high yields without requiring excess ethyl diazoacetate when used instead of diazomethane.

We have shown that in the Cp-BPins oxidative hydrolysis to cyclopropanols, it is not the nature of the oxidant, but the strength of the base determines their yields, synthesis reproducibility, and storage stability. The conducted kinetic studies are in good accord with the first-order equation (R^2 is roughly = 0.97), which indicates that the ability to decompose in the presence of strong bases is the intrinsic property of cyclopropanols. These findings also suggest that cyclopropanols can potentially be used as O-nucleophiles only in mildly basic conditions.

The use of $Pd_2(dba)_3$ as a catalyst enables efficient cyclopropanation of vinyl-BPins with diazoacetic ester, simplifying the process and avoiding unwanted side reactions. Furthermore, our method allows for the synthesis of previously inaccessible ester-aldehydes, expanding the range of valuable intermediates available for further functionalization.

Our new protocols expand the substrate scope, accommodating both electron-donating and electron-withdrawing groups. It provides access to functionalized cyclopropyl boronic acids and previously challenging 2-substituted cyclopropanols, including strained spirocyclic derivatives and nitrogen-containing heterocycles, which were difficult to obtain using existing

methods. These improvements address longstanding issues with scalability, safety, and diastereoselectivity, offering a robust, generalizable pathway for modern cyclopropanols synthesis.

ASSOCIATED CONTENT

• Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

• Supporting Information Statement

The SI contains details of experiments and synthesis; spectral and analytical data for the synthetized compounds; copies of NMR spectra; description of NMR kinetic studies, copies of 2-D NMR spectra for compounds **4d** and **9a**, details on XRD study for compound **4e**.

The Supporting Information is available free of charge on the ACS Publications website.

All information detailed above (SI_Fin.pdf)

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

Notes

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